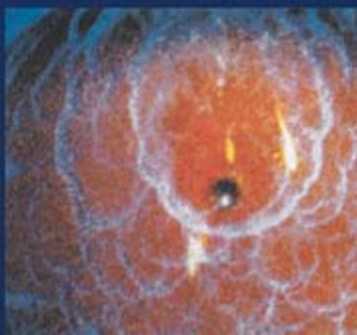
Lees' Loss Prevention in the Process Industries

VOLUME 1

Hazard Identification, Assessment and Control

THIRD EDITION



Edited by

SAM MANNAN

Lee's Loss Prevention in the Process Industries

Volume 1

This book is dedicated to

Herbert Douglas Lees (1860–1944), gas engineer;
Frank Priestman Lees (1890–1916), gas engineer;
Herbert Douglas Lees (1897–1955), gas engineer;
David John Lees (1936–), agricultural engineer;
Frank Lyman MacCallum (1893–1955), mining engineer and missionary;
Vivien Clare Lees (1960–), plastic and hand surgeon;
Harry Douglas Lees (1962–), restaurateur
and their families

'They do not preach that their God will rouse them a little before
the nuts work loose.
They do not teach that His Pity allows them to drop their job when
they dam'-well choose.
As in the thronged and the lighted ways, so in the dark and the
desert they stand,
Wary and watchful all their days that their brethren's days may be
long in the land.'

Rudyard Kipling (The Sons of Martha, 1907)

Wo einer kommt and saget an,
Er hat es allen recht getan,
So bitten wir diesen lieben Herrn,
Er wöll uns solche Kunste auch lehrn

(Whoever is able to say to us
'I have done everything right',
We beg that honest gentleman
To show us how it is done)

Inscription over the 'Zwischenbau' adjoining the Rathaus in Brandenburg-on-the-Haven
(quoted by Prince B.H.M. von Bulow in *Memoirs*, 1932)

If the honeye that the bees gather out of so manye floure of herbes . . . that are growing in other

mennis medowes . . . may justly be called the bees' honeye . . . so maye I call it that I have . . .

gathered of manye good autores . . . my booke.

William Turner (quoted by A. Scott-James in *The Language of the Garden: A Personal Anthology*)

By the same author:

A.W. Cox, F.P. Lees and M.L. Ang (1990): *Classification of Hazardous Locations* (Rugby: Institution of Chemical Engineers)

Elwyn Edwards and Frank P. Lees (1973): *Man and Computer in Process Control* (London: Institution of Chemical Engineers)

Elwyn Edwards and Frank P. Lees (eds) (1974): *The Human Operator in Process Control* (London: Taylor & Francis)

Frank P. Lees and M.L. Ang (1989): *Safety Cases* (London: Butterworths)

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Hazard Identification, Assessment and Control

Volume 1

Third edition

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SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO

Elsevier Butterworth–Heinemann
200 Wheeler Road, Burlington, MA 01803, USA
Linacre House, Jordan Hill, Oxford OX2 8DP, UK

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Library of Congress Cataloging-in-Publication Data
Lee's loss prevention in the process industries. – 3rd ed. / edited by Sam Mannan.
p. cm.
Rev. ed. of: Loss prevention in the process industries / Frank P. Lees. 2nd ed. 1996.
Includes bibliographical references and indexes.
ISBN 0-7506-7555-1 (casebound, set : alk. paper) 1. Petroleum chemicals industry–Great Britain–Safety measures. 2. Petroleum chemicals industry–United States–Safety measures. I. Title: Loss prevention in the process industries. II. Mannan, Sam. III. Lees, Frank P. Loss Prevention in the process industries.
TP690.6.L43 2005
660′.2804–dc22

2004018498

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from British Library

Set ISBN: 0-7506-7555-1
Volume 1 ISBN: 0-7506-7857-7
Volume 2 ISBN: 0-7506-7858-5
Volume 3 ISBN: 0-7506-7589-3

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04 05 06 07 08 09 10 10 9 8 7 6 5 4 3 2 1

Printed in the United States of America

Preface to Third Edition

The first edition of this book appeared in 1980, at the end of a decade of rapid growth and development in loss prevention. In the preface to the second edition, Frank P. Lees wrote,"After another decade and a half the subject is more mature, although development continues apace. In preparing this second edition it has been even more difficult than before to decide what to put in and what to leave out." Frank Lees' statement in 1996 rings even truer today, another eight years later in 2004. Industrial advances and technology changes coupled with recent events have made it essential to focus on new topics while keeping a complete grasp of all of older technologies and learnings as well. Safety programs today must also consider issues such as chemical reactivity hazards, safety instrumented systems, and layer of protection analysis. In the post 9-11 world, process safety and loss prevention must also include consideration of issues related to chemical security and resilient engineering systems.

The history of safety regulations in the United States can be traced back to the year before the beginning of the twentieth century. The River and Harbor Act, the first known federal legislation relevant to safety was promulgated in 1899. Since then, the total number of legislations has steadily increased. In addition to the federal government, local entities such as the state, county, and cities have also promulgated regulations and ordnances, which impose safety requirements on process facilities. Varying degrees of similar legislative action has also occurred in the rest of the world. These legislation were all promulgated in response to some event, demographic changes, as well as changes in the industry. Also, as our understanding of the hazards associated with industrial processes developed, procedures and practices were put in place to limit or eliminate the damage. Government programs and industry initiatives spurred improvements in the science and technology needed for the recognition of hazards and associated risks.

Management systems have been put in place to implement regulations and industry practices. Government regulations will continue to be a significant driver for safety programs. As such, one of the main objectives of these management systems is to ensure compliance. However, it is also quite clear that profitability is directly related to safety and loss prevention. Thus the management systems for safety are intricately tied into the operational management.

The industrial revolution brought prosperity and along with it the use of hazardous processes and complex technologies. Growing economies and global competition has led to more complex processes involving the use of hazardous chemicals, exotic chemistry, and extreme operating conditions. As a result, a fundamental understanding of the hazards and associated risks is essential. Process safety and risk management requires the application of the basic sciences and a systematic approach. Recent advances, such as overpressure protection alternatives and reactive chemistry allow safer design and operation of processes.

In the multiple barriers concept, plants are designed with several layers so that an incident would require the failure of several systems. Another novel approach to process safety and risk management is to consider various actions in a descending hierarchical order. Inherently safer design consideration should be first in the hierarchy followed by prevention systems, mitigation, and response. The success of these systems is dependent on the fundamental understanding of the process and the associated hazards. Chronic as well as catastrophic consequences resulting from toxic and flammable substances can be reduced and/or eliminated through appropriate design and operating practices.

Managing safety is no easy task, but it makes bottomline sense. There is a direct payoff in savings on a company workers' compensation insurance, whose premiums are partly based on the number of claims paid for job injuries. The indirect benefits are far larger, for safe plants tend to be well run in general and more productive. The recipe for safety is remarkably consistent from industry to industry. It starts with sustained support of top management followed by implementation of appropriate programs and practices that institutionalize safety as a culture as compared to add-on procedures. The ingraining of safety as second nature in day-to-day activities requires a paradigm shift and can only be accomplished when safety is viewed as an integral and comprehensive part of any activity as compared to being a stand-alone or add-on activity.

This third edition of ***Loss Prevention in the Process Industries*** represents a combination of appropriate revisions of the essential compilations put together by Frank P. Lees, along with several new chapters and additions on new areas that deserve attention and discussion. The third edition includes five new chapters and three new appendices. The five new chapters address incident investigation, inherently safer design, reactive chemicals, safety instrumented systems, and chemical security. The three new appendices address process safety management regulation in the United States, risk management program regulation in the United States, and incident databases.

The chapter on incident investigation provides a summary of incident investigation procedures that can be used not only to determine causes of incidents but also provides a primer on capturing and integrating lessons learned from incident investigations into design, operations, maintenance, and response programs. Chemical process incidents can be accompanied by significant consequences, both in terms of human life and in financial impact. Many major chemical process incidents are the result of a complex scenario involving simultaneous failures of multiple safeguards. A robust system for incident investigation is usually necessary to determine and understand the causes, as well as implement measures to prevent a repeat event. This chapter is intended to provide an overview of incident investigation by addressing major concepts, principles, and characteristics of effective incident investigations of chemical process events. The focus is on incidents pertaining to chemical processes and their associated hazards, and the associated investigation techniques appropriate for complex systems and scenarios. This chapter is based on

best practices for incident investigation, and those common concepts (i.e., tools, techniques, definitions) included in root cause investigation methodologies currently in the public domain in use in the process industry. It is not the intention to provide a stand-alone investigation methodology/guideline, nor address internal or proprietary investigation methodologies.

The chapter on inherently safer design addresses options and issues that can be considered with regard to the design and operation of plants. Inherently safer design is a philosophy that focuses on elimination of hazards or reduction of the magnitude of hazards rather than the control of hazards. Many of the concepts of inherently safer design have been applied by engineers in a wide variety of technologies for many years, without recognizing the common approach. In the late 1970s, in the wake of many large incidents in the chemical industry, Trevor Kletz recognized the common philosophies of hazard elimination and hazard reduction, gave the philosophy the name "inherently safer design," and developed a specific set of approaches to help engineers in the chemical process industries to design inherently safer processes and plants. Trevor realized that increased expectations for safety, from companies, regulatory bodies, and society in general, combined with the increased potential damage from incidents in the larger plants being built to meet increased demand and global markets, resulted in increased complexity and cost for the safety systems required to satisfy these demands. Furthermore, while hazard control systems can be made highly reliable, they can never be perfect and will always have some failure probability. While this probability can be made very small, there is always some chance that all safety systems will fail simultaneously and the result would be a large incident. Also, the hazard management systems require ongoing maintenance, as well as management and operator training, for the life of the plant. This results in ongoing costs, and the potential for future deterioration of the safety systems. Deteriorated systems will have reduced reliability, increasing the potential for a catastrophic accident. Trevor Kletz suggested that in many cases, a simpler, cheaper, and safer plant could be designed by focusing on the basic technology, eliminating or significantly reducing hazards, and therefore the need to manage them.

The chapter on reactive chemicals provides an overview of this critical issue and provides guidance on management systems as well as experimental and theoretical methods for analyses of chemical reactivity hazards. Serious incidents arising from uncontrolled reactivity have taken place since the inception of the chemical industry. The human toll of such incidents has been staggering. In recent decades, greater recognition and resources have been directed toward preventing and mitigating such occurrences. A number of incidents have been so severe as to prompt regulatory initiatives to force better management of reactivity. It is prudent for any company, organization, or other group to scrutinize the chemicals being handled and implement measures to limit the risk of a major reactive hazards event. A sampling of incidents that have substantially heightened concerns regarding reactive hazards in the general public, in governmental agencies, and in industry includes:

- The 1976 ICMESA incident in Seveso, Italy in which an uncontrolled chemical reaction generated pressure resulting in relief venting of a highly toxic dioxane into the neighboring villages and countryside.
- The 1984 Union Carbide incident in Bhopal, India in which methyl isocyanate was contacted with water, generating highly toxic cyanide gas and leading to thousands of fatalities.
- The 1994 Napp Technology incident in Lodi, New Jersey in which an uncontrolled reaction involving gold ore processing led to the deaths of five firefighters.
- The 1999 Concept Sciences incident in Allentown, Pennsylvania in which an explosion arising from a process concentrating hydroxylamine resulted in five fatalities. Another event involving purified hydroxylamine took place in a Nissin Chemical plant in Gunma Prefecture, Japan in 2000 and led to four fatalities.
- The 2001 TotalFinaElf incident in Toulouse, France in which ammonium nitrate being processed for nitrogen fertilizers exploded leading to 30 fatalities.

These events, as well as numerous others, have influenced the perception and approach to reactive hazards.

The chapter on safety instrumented systems addresses systems and procedures that need to be in place with regard to this area of safety and instrumentation. In many processes, technical or manufacturing issues limit the engineer's capability to design an inherently safer process. Further, there is generally a point where the required capital investment is disproportional to the additional risk reduction provided by the process modification. In other words, the derived safety benefit is too low relative to the economic investment. When this occurs, protection layers or safeguards must be provided to prevent or mitigate the process risk. A Safety Instrumented System (SIS) is a protection layer, which shuts down the plant, or part of it, if a hazardous condition is detected. Throughout the years, SIS have also been known as Emergency Shutdown Systems (ESD, ESS), Safety Shutdown Systems (SSD), Safety Interlock Systems (SIS), Safety Critical Systems (SCS), Safety Protection Systems (SPS), Protective Instrumented Systems (PIS), interlocks, and trip systems. Regardless of what the SIS may be called, the essential characteristic of the SIS is that it is composed of instruments, which detect that process variables are exceeding preset limits, a logic solver, which processes this information and makes decisions, and final control elements, which take necessary action on the process to achieve a safe state.

The chapter on chemical security deals with this new and critical element of the management of a process facility following the events of September 11, 2001. Security management is required for protecting the assets (including employees) of the facility, maintaining the ongoing integrity of the operation, and preserving value of the investment. Process security and process safety have many parallels and make use of many common programs and systems for achieving their ends. Process security requires a management systems approach to develop a comprehensive security program, which shares many common elements to process safety management.

The new appendix on process safety management regulation in the United States provides a summary of this regulatory requirement. The fourteen elements of the OSHA Process Safety Management (PSM) regulation (*29 CFR 1910.119*) were published in the U.S. Federal Register on February 24, 1992. The objective of the regulation is to

prevent or minimize the consequences of catastrophic releases of toxic, reactive, flammable, or explosive chemicals. The regulation requires a comprehensive management program: a holistic approach that integrates technologies, procedures, and management practices. The process safety management regulation applies to processes that involve certain specified chemicals at or above threshold quantities, processes that involve flammable liquids or gases on-site in one location, in quantities of 10,000 pounds or more (subject to few exceptions), and processes that involve the manufacture of explosives and pyrotechnics. Hydrocarbon fuels, which may be excluded if used solely as a fuel, are included if the fuel is part of a process covered by this regulation. In addition, the regulation does not apply to retail facilities, oil or gas well drilling or servicing operations, or normally unoccupied remote facilities.

The new appendix on risk management program regulation in the United States provides a summary of this regulatory requirement administered by the U.S. Environmental Protection Agency. In 1996, EPA promulgated the regulation for ***Risk Management Programs for Chemical Accident Release Prevention*** (40 CFR 68). This federal regulation was mandated by section 112(r) of the Clean Air Act Amendments of 1990. The regulation requires regulated facilities to develop and implement appropriate risk management programs to minimize the frequency and severity of chemical plant accidents. In keeping with regulatory trends, EPA required a performance-based approach towards compliance with the risk management program regulation. The EPA regulation also requires regulated facilities to develop a Risk Management Plan (RMP). The RMP includes a description of the hazard assessment, prevention program, and the emergency response program. Facilities submit the RMP to the EPA and subsequently is made available to governmental agencies, the state emergency response commission, the local emergency planning committees, and communicated to the public.

The new appendix on incident databases addresses compilations of incident databases that can used for improving safety programs, developing trends, performance measures, and metrics. Incident prevention and mitigation of consequences is the focus of a number of industry programs regulatory initiatives. As part of these programs and regulations, accident history data are often collected. There are two basic types of information. One is a database consisting of standardized fields of data usually for a large number of incidents. The second are more detailed reports of individual incidents. Analysis of these incident history databases can provide insight into incident prevention needs. While the analysis and conclusions obtained from the incident database are often limited by the shortcomings of the databases themselves, the fact remains that incident history databases are very useful and can be a powerful tool in focusing risk reduction efforts. The conclusions can be used to identify systematically the greatest risks to allow prioritization of efforts to improve process safety. At the plant level this might entail identifying certain processes, types of equipment, chemicals, operations and other factors most commonly associated with incidents. Databases that cover a very large number of facilities are likely to reveal trends and patterns that no one company or facility could determine from their own experience. Statistical knowledge of the likelihood of the release of certain types of chemicals could help emergency responders, state emergency response commissions, and local emergency planning committees determine the most likely and most serious chemical releases in their areas and plan appropriate chemical accident responses. Incident databases may also help identify technologies and practices to prevent chemical accidents, or the need to develop them. For example, the data could indicate that inspection and preventive maintenance of equipment and instruments should become more thorough or more frequent.

M. Sam Mannan
College Station,
Texas, USA
2004

Preface to Second Edition

The first edition of this book appeared in 1980, at the end of a decade of rapid growth and development in loss prevention. After another decade and a half the subject is more mature, although development continues apace. In preparing this second edition it has been even more difficult than before to decide what to put in and what to leave out.

The importance of loss prevention has been underlined by a number of disasters. Those at San Carlos, Mexico City, Bhopal and Pasadena are perhaps the best known, but there have been several others with death tolls exceeding 100. There have also been major incidents in related areas, such as those on the Piper Alpha oil platform and at the nuclear power stations at Three Mile Island and Chernobyl.

Apart from the human tragedy, it has become clear that a major accident can seriously damage even a large international company and may even threaten its existence, rendering it liable to severe damages and vulnerable to takeover.

Accidents in the process industries have given impetus to the creation of regulatory controls. In the UK the Advisory Committee on Major Hazards made its third and final report in 1983. At the same time the European Community was developing its own controls which appeared as the EC Directive on Major Accident Hazards. The resulting UK legislation is the NIHHS Regulations 1982 and the CIMAH Regulations 1984. Other members of the EC have brought in their own legislation to implement the Directive. There have been corresponding developments in planning controls.

An important tool for decision-making on hazards is hazard assessment. The application of quantitative methods has played a crucial role in the development of loss prevention, but there has been lively debate on the proper application of such assessment, and particularly on the estimation and evaluation of the risk to the public.

Hazard assessment involves the assessment both of the frequency and of the consequences of hazardous events. In frequency estimation progress has been made in the collection of data and creation of data banks and in fault tree synthesis and analysis, including computer aids. In consequence assessment there has been a high level of activity in developing physical models for emission, vaporization and gas dispersion, particularly dense gas dispersion; for pool fires, fireballs, jet flames and engulfing fires; for vapour cloud explosions; and for boiling liquid expanding vapour explosions (BLEVEs). Work has also been done on injury models for thermal radiation, explosion overpressure and toxic concentration, on models of the density and other characteristics of the exposed population, and on shelter and escape.

Some of these topics require experimental work on a large scale and involving international cooperation. Large scale tests have been carried out at several sites on dense gas dispersion and on vapour cloud fires and explosions. Another major cooperative research programme has been that of DIERS on venting of chemical reactors.

The basic approach developed for fixed installations on shore has also been increasingly applied in other fields. For transport in the UK the *Transport Hazards Report* of the Advisory Committee on Dangerous Substances represents an important landmark. Another application is in the offshore oil and gas industry, for which the report on the Piper Alpha disaster, the *Cullen Report*, constitutes a watershed.

As elsewhere in engineering, computers are in widespread use in the design of process plants, where computer aided design (CAD) covers physical properties, flowsheeting, piping and instrument diagrams, unit operations and plant layout. There is increasing use of computers for failure data retrieval and analysis, reliability and availability studies, fault tree synthesis and analysis and consequence modelling, while more elusive safety expertise is being captured by computer-based expert systems.

The subject of this book is the process industries, but the process aspects of related industries, notably nuclear power and oil and gas platforms are briefly touched on. The process industries themselves are continually changing. In the last decade one of the main changes has been increased emphasis on products such as pharmaceuticals and agrochemicals made by batch processes, which have their own particular hazards.

All this knowledge is of little use unless it reaches the right people. The institutions which educate the engineers who will be responsible for the design and operation of plants handling hazardous materials have a duty to make their students aware of the hazards and at least to make a start in gaining competence in handling them.

I would like again to thank for their encouragement the heads of the Department of Chemical Engineering at Loughborough, Professors D.C. Freshwater, B.W. Brooks and M. Streat; our Industrial Professors T.A. Kletz and H.A. Duxbury and Visiting Professor S.M. Richardson; my colleagues, past and present, in the Plant Engineering Group, Mr R.J. Aird, Dr P.K. Andow, Dr M.L. Ang, Dr P.W.H. Chung, Dr D.W. Edwards, Dr P. Rice and Dr A.G. Rushton – I owe a particular debt to the latter; the members of the ACMH, chaired by Professor B.H. Harvey; the sometime directors of Technica Ltd, Dr D.H. Slater, Mr P. Charsley, Dr P.J. Comer, Dr R.A. Cox, Mr T. Gjerstad, Dr M.A.F. Pyman, Mr C.G. Ramsay, Mr M.A. Seaman and Dr R. Whitehouse; the members of the IChemE Loss Prevention Panel; the IChemE's former Loss Prevention Officer, Mr B.M. Hancock; the members of the IChemE Loss Prevention Study Group and of the Register of Safety Professionals; the editorial staff of the IChemE, in particular Mr B. Brammer; numerous members of the Health and Safety Executive, especially Dr A.C. Barrell, Mr J. Barton, Dr D.A. Carter, Mr K. Cassidy, Mr P.J. Crossthwaite, Dr N.W. Hurst, Dr S.F. Jagger, Dr J. McQuaid, Dr K. Moodie, Dr C. Nussey, Dr R.P. Pape, Dr A.F. Roberts and Dr N.F. Scilly; workers at the Safety and Reliability Directorate, particularly Dr A.T.D. Butland, Mr I. Hymes, Dr D.W. Phillips and Dr D.M. Webber; staff at Shell Thornton Research Centre, including Dr D.C. Bull and Dr A.C. Chamberlain; staff at British Gas, including Dr J.D. Andrews, Dr M.J. Harris, Mr H. Hopkins, Dr J.M. Morgan and Dr D.J. Smith; staff at the Ministry of

Defence, Explosives Storage and Transport Committee, including Mr M.A. Gould, Mr J. Henderson and Mr P. Stone; and colleagues who have taught on post-experience courses at Loughborough, in particular Dr C.D. Jones, Dr D.J. Lewis and Mr J. Madden; BP International and Mr R. Malpas for allowing me to spend a period of study leave with the company in 1985–86 and Mr F.D.H. Moysen, Mr G. Hately, Mr M. Hough, Mr R. Fearon and others in the Central Safety Group and in Engineering Department; the Honourable Lord Cullen, my fellow Technical Assessors on the Piper Alpha Inquiry, Mr B. Appleton and Mr G.M. Ford and the Cremer and Warner team at the inquiry, in particular Mr G. Kenney and Mr R. Sylvester-Evans; other professional colleagues Dr L.J. Bellamy, Professor B.A. Buffham, Dr D.A. Crowl, Mr T.J. Gilbert, Mr D.O. Hagon, Dr D.J. Hall, Mr K.M. Hill, Professor T.M. Husband, Mr M. Kneale, Dr V.C. Marshall, Dr M.L. Preston, Dr J. Rasmussen, Dr J.R. Roach, Dr J.R. Taylor, Dr V.M. Trbojevic, Mr H.M. Tweeddale, Dr G.L. Wells and Dr A.J. Wilday; my research colleagues Dr C.P. Murphy, Mrs J.I. Petts, Dr D.J. Sherwin, Mr R.M.J. Withers and Dr H. Zerkani; my research students Mr M. Aldersey, Mr D.C. Arulanantham, Dr A. Bunn, Dr M.A. Cox, Dr P.A. Davies, Dr S.M. Gilbert, Mr P. Heino, Dr A. Hunt, Dr B.E. Kelly, Dr G.P.S. Marrs, Dr J.S. Mullhi, Dr J.C. Parmar, Mr B. Poblete, Dr A. Shafaghi and Dr A.J. Trenchard as well as colleagues' research students Mr E.J. Broomfield, Mr R. Goodwin, Mr M.J. Jefferson, Dr F.D. Larkin, Mr S.A. McCoy, Dr K. Plamping, Mr J. Soutter, Dr P. Thorpe and Mr S.J. Wakeman; the office staff of the Department, Mrs E.M. Barradell, Mr D.M. Blake, Miss H.J. Bryers and Miss Y. Kosar; the staff of the University Library, in particular Miss S.F. Pilkington; and my wife Elizabeth, whose contribution has been many-faceted and in scale with this book.

FRANK P. LEES
Loughborough,
1994

Preface to First Edition

Within the past ten or fifteen years the chemical and petroleum industries have undergone considerable changes. Process conditions such as pressure and temperature have become more severe. The concentration of stored energy has increased. Plants have grown in size and are often single-stream. Storage has been reduced and interlinking with other plants has increased. The response of the process is often faster. The plant contains very large items of equipment. The scale of possible fire, explosion or toxic release has grown and so has the area which might be affected by such events, especially outside the works boundary.

These factors have greatly increased the potential for loss both in human and in economic terms. This is clear both from the increasing concern of the industry and its insurers and from the historical loss statistics.

The industry has always paid much attention to safety and has a relatively good record. But with the growing scale and complexity involved in modern plants the danger of serious large-scale incidents has been a source of increasing concern and the adequacy of existing procedures has been subjected to an increasingly critical examination.

Developments in other related areas have also had an influence. During the period considered there has been growing public concern about the various forms of pollution, including gaseous and liquid effluents and solid wastes and noise.

It is against this background that the loss prevention approach has developed. It is characteristic of this approach that it is primarily concerned with the problems caused by the depth of technology involved in modern processes and that it adopts essentially an engineering approach to them. As far as possible both the hazards and the protection are evaluated quantitatively.

The clear recognition by senior management of the importance of the loss prevention problem has been crucial to these developments. Progress has been made because management has been prepared to assign to this work many senior and capable personnel and to allocate the other resources necessary.

The management system is fundamental to loss prevention. This involves a clear management structure with well defined line and advisory responsibilities staffed by competent people. It requires the use of appropriate procedures, codes of practice and standards in the design and operation of plant. It provides for the identification, evaluation and reduction of hazards through all stages of a project from research to operation. It includes planning for emergencies.

The development of loss prevention can be clearly traced through the literature. In 1960 the Institution of Chemical Engineers held the first of a periodic series of symposia on *Chemical Process Hazards with Special Reference to Plant Design*. The Dow Chemical Company published its *Process Safety Manual* in 1964. The American Institute of Chemical Engineers started in 1967 an annual series of symposia on Loss Prevention. The European Federation of Chemical Engineers' symposium on *Major Loss Prevention in the Process Industries* at Newcastle in 1971 and the Federation's symposium on *Loss Prevention and Safety Promotion in the Process Industries* (Buschmann, 1974) at Delft are further milestones.

Another indicator is the creation in 1973 by the Institution of Chemical Engineers Engineering Practice Committee of a Loss Prevention Panel under the chairmanship of Mr T. A. Kantyka.

In the United Kingdom the Health and Safety at Work etc. Act 1974 has given further impetus to loss prevention. The philosophy of the *Robens Report* (1972), which is embodied in the Act, is that of self-regulation by industry. It is the responsibility of industry to take all reasonable measures to assure safety. This philosophy is particularly appropriate to complex technological systems and the Act provides a flexible framework for the development of the loss prevention approach.

The disaster at Flixborough in 1974 has proved a turning point. This event has led to a much more widespread and intense concern with the loss prevention problem. It has also caused the government to set up in 1975 an Advisory Committee on Major Hazards. This committee has made far-reaching recommendations for the identification and control of major hazard installations.

It will be apparent that loss prevention differs somewhat from safety as traditionally conceived in the process industries. The essential difference is the much greater engineering content in loss prevention.

This is illustrated by the relative effectiveness of inspection in different processes. In fairly simple plants much can be done to improve safety by visual inspection. This approach is not adequate, however, for the more technological aspects of complex processes.

For the reasons given above loss prevention is currently a somewhat fashionable subject. It is as well to emphasize, therefore, that much of it is not new, but has been developed over many years by engineers whose patient work in an often apparently unrewarding but vital field is the mark of true professionalism.

It is appropriate to emphasize, moreover, that accidents arising from relatively mundane situations and activities are still responsible for many more deaths and injuries than those due to advanced technology.

Nevertheless, loss prevention has developed in response to the growth of a new problem, the hazard of high technology processes, and it does have a distinctive approach and some novel techniques. Particularly characteristic are the emphasis on matching the management system to the depth of technology in the installation, the techniques developed for identifying hazards, the principle and methods of quantifying hazards, the application of reliability assessment, the practice of planning for emergencies and the critique of traditional practices or existing codes, standards or regulations where these are outdated by technological change.

There is an enormous, indeed intimidating, literature on safety and loss prevention. In addition to the symposia already referred to, mention may be made of the *Handbook of Safety and Accident Prevention in Chemical Operations* by Fawcett and Wood (1965); the *Handbook of Industrial Loss*

Prevention by the Factory Mutual Engineering Corporation (1967); and the Industrial Safety Handbook by Handley (1969, 1977). These publications, which are by multiple authors, are invaluable source material.

There is a need, however, in the author's view for a balanced and integrated textbook on loss prevention in the process industries which presents the basic elements of the subject, which covers the recent period of intense development and which gives a reasonably comprehensive bibliography. The present book is an attempt to meet this need.

The book is based on lectures given to undergraduate and postgraduate students at Loughborough over a period of years and the author gladly acknowledges their contribution.

Loss prevention is a wide and rapidly developing field and is therefore not an easy subject for a book. Nevertheless, it is precisely for these reasons that the engineer needs the assistance of a textbook and that the attempt has been considered justified.

The structure of the book is as follows. Chapter 1 deals with the background to the historical development of loss prevention, the problem of large, single-stream plants, and the differences between loss prevention and conventional safety, and between loss prevention and total loss control; Chapter 2 with hazard, accident and loss, including historical statistics; Chapter 3 with the legislation and legal background; Chapter 4 with the control of major hazards; Chapter 5 with economic and insurance aspects; Chapter 6 with management systems, including management structure, competent persons, systems and procedures, standards and codes of practice, documentation and auditing arrangements; Chapter 7 with reliability engineering, including its application in the process industries; Chapter 8 with the spectrum of techniques for identifying hazards from research through to operation; Chapter 9 with the assessment of hazards, including the question of acceptable risk; Chapter 10 with the siting and layout of plant; Chapter 11 with process design, including application of principles such as limitation of inventory, consideration of known hazards associated with chemical reactors, unit processes, unit operations and equipments, operating conditions, utilities, particular chemicals and particular processes and plants, and checking of operational deviations; Chapter 12 with pressure system design, including properties of materials, design of pressure vessels and pipework, pressure vessel standards and codes, equipment such as heat exchangers, fired heaters and rotating machinery, pressure relief and blowdown arrangements, and failure in pressure systems; Chapter 13 with design of instrumentation and control systems, including regular instrumentation, process computers and protective systems; Chapter 14 with human factors in process control, process operators, computer aids and human error; Chapter 15 with loss of containment and dispersion of material; Chapter 16 with fire, flammability characteristics, ignition sources, flames and particular types of process fire, effects of fire and fire prevention, protection and control; Chapter 17 with explosion, explosives, explosion energy, particular types of process explosion such as confined explosions, unconfined vapour cloud explosions and dust explosions, effects of explosion and explosion prevention, protection and relief; Chapter 18 with toxicity of chemicals, toxic release and effects of toxic release; Chapter 19 with commissioning and inspection of plant; Chapter 20 with plant operation; Chapter 21 with plant maintenance and modification; Chapter 22 with storage; Chapter 23 with transport, particularly by road, rail and pipeline; Chapter 24 with emergency planning both for works and transport emergencies; Chapter 25 with various aspects of personal safety such as occupational health and industrial hygiene, dust and radiation hazards, machinery and electrical hazards, protective clothing and equipment, and rescue and first aid; Chapter 26 with accident research; Chapter 27 with feedback of information and learning from accidents; Chapter 28 with safety systems, including the roles of safety managers and safety committees and representatives. There are appendices on Flixborough, Seveso, case histories, standards and codes, institutional publications, information sources, laboratories and pilot plants, pollution and noise, failure and event data, Canvey, model licence conditions for certain hazardous plants, and units and unit coversions.

Many of the matters dealt with, such as pressure vessels or process control, are major subject areas in their own right. It is stressed, therefore, that the treatment given is strictly limited to loss prevention aspects. The emphasis is on deviations and faults which may give rise to loss.

In engineering in general and in loss prevention in particular there is a conflict between the demand for a statement of basic principles and that for detailed instructions. In general, the first of these approaches has been adopted, but the latter is extremely important in safety, and a considerable amount of detailed material is given and references are provided to further material.

The book is intended as a contribution to the academic education of professional chemical and other engineers. Both educational and professional institutions have long recognized the importance of education in safety. But until recently the rather qualitative, and indeed often exhortatory, nature of the subject frequently seemed to present difficulties in teaching at degree level. The recent quantitative development of the subject goes far towards removing these objections and to integrating it more closely with other topics such as engineering design.

In other words, loss prevention is capable of development as a subject presenting intellectual challenge. This is all to the good, but a note of caution is appropriate. It remains true that safety and loss prevention depend primarily on the hard and usually unglamorous work of engineers with a strong sense of responsibility, and it is important that this central fact should not be obscured.

For this reason the book does not attempt to select particular topics merely because a quantitative treatment is possible or to give such a treatment as an academic exercise. The subject is too important for such an approach. Rather the aim has been to give a balanced treatment of the different aspects and a lead in to further reading.

It is also hoped that the book will be useful to practising engineers in providing an orientation and entry to unfamiliar areas. It is emphasized, however, that in this subject above all others, the specialized texts should be consulted for detailed design work.

Certain topics which are often associated with loss prevention, for example included in loss prevention symposia, have not been treated in detail. These include, for example, pollution and noise. The book does not attempt to deal in detail with total loss control, but a brief account of this is given.

The treatment of loss prevention given is based mainly on the chemical, petrochemical and petroleum industries,

but much of it is relevant to other process industries, such as electrical power generation (conventional and nuclear), iron and steel, gas, cement, glass, paper and food.

The book is written from the viewpoint of the United Kingdom and, where differences exist within the UK, of England. This point is relevant mainly to legislation.

Reference is made to a large number of procedures and techniques. These do not all have the same status. Some are well established and perhaps incorporated in standards or codes of practice. Others are more tentative. As far as possible the attempt has been made to give some indication of the extent to which particular items are generally accepted.

There are probably also some instances where there is a degree of contradiction between two approaches given. In particular, this may occur where one is based on engineering principles and the other on relatively arbitrary rules-of-thumb.

The book does not attempt to follow standards and codes of practice in drawing a distinction between the words *should, shall* and *must* in recommending particular practices and generally uses only the former. The distinction is important, however, in standards and codes of practice and it is described in Appendix 4[a].

An explanation of some of the terms used is in order at this point. Unfortunately there is at present no accepted terminology in this field. In general, the problems considered are those of loss, either of life or property. The term *hazard* is used to describe the object or situation which constitutes the threat of such loss. The consequences which might occur if the threat is realized are the *hazard potential*. Associated with the hazard there is a risk, which is the probability of the loss occurring. Such a risk is expressed as a *probability* or as a *frequency*. Probability is expressed as a number in the range 0 to 1 and is dimensionless; frequency is expressed in terms of events per unit time, or sometimes in other units such as events per cycle or per occasion. Rate is also used as an alternative to frequency and has the same units.

The analysis of hazards involves qualitative *hazard identification* and quantitative hazard assessment. The latter term is used to describe both the assessment of hazard potential and of risk. The assessment of risk only is described as *risk assessment*.

In accident statistics the term *Fatal Accident Frequency Rate* (FAFR) has some currency. The last two terms are tautologous and the quantity is here referred to as *Fatal Accident Rate* (FAR).

Further treatments of terminology in this field are given by BS 4200: 1967, by Green and Bourne (1962), by the Council for Science and Society (1977) and by Harvey (1979b).

Notation is defined for the particular chapter at the point where the symbols first occur. In general, a consistent notation is used, but well established equations from standards, codes and elsewhere are usually given in the original notation. A consolidated list of the notation is given at the end of chapters in which a large number of symbols is used.

The units used are in principle SI, but the exceptions are fairly numerous. These exceptions are dimensional equations, equations in standards and codes, and other equations and data given by other workers where conversion has seemed undesirable for some reason. In cases of conversion from a round number it is often not clear what degree of rounding off is appropriate. In cases of description of particular situations it appears pedantic to make the conversion where a writer has referred, for example, to a 1 inch pipe.

Notes on some of the units used are given in Appendix 12[a]. For convenience a unit conversion table is included in this appendix. Numerical values given by other authors are generally quoted without change and numerical values arising from conversion of the units of data given by other authors are sometimes quoted with an additional significant figure in order to avoid excessive rounding of values.

Some cost data are quoted in the book. These are given in pounds or US dollars for the year quoted.

A particular feature of the book is a fairly extensive bibliography of some 5000 references. These references are consolidated at the end of the book rather than at the end of chapters, because many items are referred to in a number of chapters. Lists of selected references on particular topics are given in table form in the relevant chapters.

Certain institutions, however, have a rather large number of publications which it is more convenient to treat in a different manner. These are tabulated in Appendices 4[a] and 5[a], which contain some 2000 references. There is a cross-reference to the institution in the main reference list.

In many cases institutions and other organizations are referred to by their initials. In all cases the first reference in the book gives the full title of the organization. The initials may also be looked up in the Author Index, which gives the full title.

A reference is normally given by quoting the author and, in brackets, the date, e.g. Kletz (1971). Publications by the same author in the same year are denoted by letters of the alphabet a, b, c, etc., e.g. Allen (1977a), while publications by authors of the same surname and in the same year are indicated for convenience by an asterisk against the year in the list of references. In addition, the author's initials are given in the main text in cases where there may still be ambiguity. Where a date has not been determined this is indicated as n.d.

In the case of institutional publications listed in Appendices 4[a] and 5[a] the reference is given by quoting the institution and, in brackets, the date, the publication series, e.g. HSE (1965 HSW Bklt 34) or the item number, e.g. IChemE (1971 Item 7). For institutional publications with a named author the reference is generally given by quoting the author and, in brackets, the initials of the institution, the date and the publication series or item number, e.g. Eames (UKAEA 1965 Item 4).

The field of loss prevention is currently subject to very rapid change. In particular, there is a continuous evolution of standards and codes of practice and legislation. It is important, therefore, that the reader should make any necessary checks on changes which may have occurred.

I would like to thank for their encouragement in this project Professor D.C. Freshwater and the publishers, and to acknowledge the work of many authors which I have used directly or indirectly, particularly that of Dr J.H. Burgoyne and of Professor T.A. Kletz. I have learned much from my colleagues on the Loss Prevention Panel of the Institution of Chemical Engineers, in particular Mr T.A. Kantyka and Mr F. Hearfield, and on the Advisory Committee on Major Hazards, especially the chairman Professor B.H. Harvey, the secretary Mr H.E. Lewis, my fellow group chairmen

[a]Appendices 4, 5 and 12 in the first edition correspond to Appendices 27, 28 and 30, respectively, in this second edition.

Professor F.R. Farmer and Professor J.L.M. Morrison and the members of Group 2, Mr K. Briscoe, Dr J.H. Burgoyne, Mr E.J. Challis, Mr S. Hope, Mr M.A. McTaggart, Professor J.F. Richardson, Mr J.R.H. Schenkel, Mr R. Sheath and Mr M.J. Turner, and also from my university colleagues Dr P.K. Andow, Mr R.J. Aird and Dr D.J. Sherwin and students Dr S.N. Anyakora, Dr B. Bellingham, Mr C.A. Marpegan and Dr G.A. Martin-Solis. I am much indebted to Professor T.A. Kletz for his criticisms and suggestions on the text. My thanks are due also to the Institution of Plant Engineers, which has supported plant engineering activities at Loughborough, to the Leverhulme Trust which awarded a Research Fellowship to study *Loss Prevention in the Process Industries* and to the Science Research Council, which has supported some of my own work in this area. I have received invaluable help with the references from Mrs C.M. Lincoln, Mrs W. Davison, Mrs P. Graham, Mr R. Rhodes and Mrs M.A. Rowlatt, with the typing from Mrs E.M. Barradell, Mrs P. Jackson and, in particular, Mrs J. Astley, and with the production from Mr R.L. Pearson and Mr T. Mould. As always in these matters the responsibility for the final text is mine alone.

FRANK P. LEES
Loughborough,
1979

Acknowledgements

Many have helped with the long and tedious production process for this 3rd edition of ***Frank P. Lees Loss Prevention in the Process Industries***. However, I would be seriously remiss if I did not start with Frank P. Lees himself. I have always had great respect and admiration for Frank Lees, the engineer and the educator. After Frank passed away, and late in 2002, our mutual friend, Roy Sanders contacted me with a request from Frank's publisher to take up the job of editing the next version. I had no idea of the enormity of the task and Frank's accomplishment. I must say that this experience has truly humbled me and has given me a new respect and new appreciation for Frank Lees' knowledge, grasp, and mastery of the subject of safety and loss prevention. I am honored and privileged to be the editor of the 3rd edition of ***Frank P. Lees Loss Prevention in the Process Industries***. I have tried to maintain Frank's high standards and appreciate the help that many others have given me, but ultimately any *faux pas* or mistakes in the 3rd edition are all mine.

I want to thank all the people who have helped revise and update the chapters that were carried over from the 2nd edition. In this respect, I would like to mention A.A. Aldeeb, J.A. Alderman, P.C. Berwanger, C.A. Brown, S. Chervin, J. Cowling, W.F. Early, M. Gentile, J.P. Gupta, J.A. Havens, D.C. Hendershot, N. Keren, K. Krishna, S.H. Landis, M.E. Levin, P.N. Lodal, M.E. Livingston, S. Mohindra, D.A. Moore, T.M. O'Connor, S.W. Ostrowski, M. Paradise, J.A. Philley, W.J. Rogers, R.E. Sanders, S.R. Saraf, M.E Sawyer, R.L. Smith, T.O. Spicer, A.E. Summers, Y. Wang, H.H. West, J.L. Woodward, and J. Zanoni. Special thanks go to individuals who helped with the new chapters and appendices: J.A. Philley for the incident investigation chapter; J.P. Gupta and D.C. Hendershot for the inherently safer design chapter; S. Chervin, M.E. Levin, and W.J. Rogers for the reactive chemicals chapter; A.E. Summers for the safety instrumented systems chapter, D.A. Moore for the chemical security chapter and T.M. O'Connor for the new appendix on incident databases.

I also want to thank those who helped with research, literature review, galley proofing, and many other jobs without which such a project is never complete. I would like to specifically mention S. Anand, L.O. Cisneros-Trevino, W. Kowhakul, Y.-S. Liu, Y. Qiao, V. Raghunathan, S. Rajaraman, J. Suardin, M. Vidal, C. Wei, C. Zhang, and Y. Zhou. I would like to make specific mention of K.L. Potucek and L.J. Littlefield who undertook the painful task of converting the pdf files of the 2nd edition to Word format. I would like to thank M.A. Cass and D.K. Startz for administrative support and keeping things going through the long haul.

I would also like to take this opportunity to thank two individuals who have provided more than moral support and encouragement. They are Trevor Kletz and Mike O'Connor. First, I have appreciated Trevor's support for our work at the Mary Kay O'Connor Process Safety Center. I also want to thank him for his pioneering leadership in many areas of process safety. Trevor is really a giant in this field, and as Roy Sanders likes to say, "Trevor does cast a long shadow in the field of process safety." I am proud to have Trevor's friendship and his support. I also want to take this opportunity to thank Mike O'Connor. He has converted his personal tragedy into an opportunity to integrate process safety into education, research, and service activities at universities. He has been a true friend and supporter of the mission and goals of the Center.

I also want to thank Mrs. Elizabeth Lees for being kind, gracious, and helpful throughout this process. I am especially grateful for her hospitality and help during my visit to Loughborough to look through Frank's notes and books.

I am grateful to my mother for her love and everything she has done for me and continues to do. I am indebted to my father for having taught me the desire for learning. He was a humble man who truly believed that, "If you stop learning, you must already be dead." I would also like to thank my wife, Afroza, and our daughters, Joya and Rumki, for their love and support. Quite often a project of this magnitude causes the personal and family life to suffer and my wife and daughters have borne the brunt of it. I appreciate their understanding.

I am sure I have failed to mention everybody who has helped me with the many facets of this project. To them I apologize and want to assure them the oversight is not intended. To everyone who has helped put this 3rd edition together, I extend my heartfelt thanks and warmest gratitude again. I must say that you have helped in a noble cause, spread the word and disseminate information that will, we hope and pray, lead to a safer industry and society.

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2004

Terminology

Attention is drawn to the availability in the literature of a number of glossaries and other aids to terminology. Some British Standard glossaries are given in Appendix 27 and other glossaries are listed in Table 1.1.

Notation

In each chapter a given symbol is defined at the point where it is first introduced. The definition may be repeated if there has been a significant gap since it was last used. The definitions are summarized in the notation given at the end of the chapter. The notation is global to the chapter unless redefined for a section. Similarly, it is global to a section unless redefined for a subsection and global to a subsection unless redefined for a set of equations or a single equation. Where appropriate, the units are given, otherwise a consistent system of units should be used, SI being the preferred system. Generally the units of constants are not given; where this is the case it should not be assumed that a constant is dimensionless.

Use of References

The main list of references is given in the section entitled References, towards the end of the book. There are three other locations where references are to be found. These are Appendix 27 on standards and codes; Appendix 28 on institutional publications; and in the section entitled Loss Prevention Bulletin which follows the References.

The basic method of referencing an author is by surname and date, e.g. Beranek (1960). Where there would otherwise be ambiguity, or where there are numerous references to the same surname, e.g. Jones, the first author's initials are included, e.g. A. Jones (1984). Further guidance on names is given at the head of the section References.

References in Appendices 27 and 28 are by institution or author. Some items in these appendices have a code number assigned by the institution itself, e.g. API (1990 Publ. 421), but where such a code number is lacking, use is generally made of an item number separated from the date by a slash, e.g. IChemE (1971/13). Thus typical entries are

API Std 2000: 1992	a standard, found in Appendix 27 under American Petroleum Institute
API (1990 Publ. 421)	an institutional publication, found in Appendix 28 under American Petroleum Institute
HSE (1990 HS(G) 51)	an institutional publication, found in Appendix 28 under Health and Safety Executive, Guidance Booklets, HS(G) series
Coward and Jones (1952 BM Bull. 503)	an institutional publication, found in Appendix 28 under Bureau of Mines, Bulletins

Institutional acronyms are given in the section Acronyms which precedes the Author Index.

There are several points of detail which require mention concerning Appendix 28. (1) The first part of the appendix contains publications of a number of institutions and the second part those of the Nuclear Regulatory Commission. (2) The Fire Protection Association publications include a number of series which are collected in the *Compendium of Fire Safety Data* (CFSD). A typical reference to this is FPA (1989 CFSD FS 6011). (3) The entries for the Health and Safety Executive are quite extensive and care may be needed in locating the relevant series. (4) The publications of the Safety and Reliability Directorate appear under the UK Atomic Energy Authority, Safety and Reliability Directorate. A typical reference is Ramskill and Hunt (1987 SRD R354). These publications are immediately preceded by the publications of other bodies related to the UKAEA, such as the Health and Safety Branch, the Systems Reliability Service and the National Centre for Systems Reliability.

References to authors in the IChemE *Loss Prevention Bulletin* are in the style Eddershaw (1989 LPB 88), which refers to issue 88 of the bulletin.

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Over the last three decades there has developed in the process industries a distinctive approach to hazards and failures that cause loss of life and property. This approach is commonly called loss prevention. It involves putting much greater emphasis on technological measures to control hazards and on trying to get things right the first time. An understanding of loss prevention requires some appreciation of its historical development against a background of heightened public awareness of safety, and environmental problems, of its relation to traditional safety and also to a number of other developments. Selected references on safety and loss prevention (SLP) are given in Table 1.1.

1.1 Management Leadership

By the mid-1960s, it was becoming increasingly clear that there were considerable differences in the performance of companies in terms of occupational safety. These disparities could be attributed only to differences in management. There appeared at this time a number of reports on safety in chemical plants arising from studies by the British chemical industry of the safety performance in the US industry, where certain US companies appeared to have achieved an impressive record. These reports included *Safety and Management* by the Association of British Chemical Manufacturers (ABCM) (1964, 3), *Safe and Sound* and *Safety Audits* by the British Chemical Industry Safety Council (BCISC) (1969, 9; 1973, 12). The companies concerned attributed their success entirely to good management and this theme was reflected in the reports.

1.2 Industrial Safety and Loss Trends

About 1970, it became increasingly recognized that there was a worldwide trend for losses, due to incidents, to rise more rapidly than gross national product (GNP).

This may be illustrated by the situation in the United Kingdom. The first half of this century saw a falling trend in personal incidents in British factories, but about 1960, this fall bottomed out. Over the next decade, very little progress was made; in fact there was some regression. Figure 1.1 shows the number of fatal incidents and the total number of incidents in factories over the period 1961–74. The Robens Committee on Health and Safety at Work, commenting on these trends in 1972, suggested that part of the reason was perhaps the increasingly complex technology employed by industry (Robens, 1972).

Another important index is that of fire loss. The estimated fire damage loss in factories and elsewhere in the United Kingdom for the period 1964–74 is shown in Figure 1.2.

1.3 Safety and Environment Concerns

There was also at this time growing public awareness and concern regarding the threat to people and to the environment from industrial activities, particularly those in which the process industries are engaged. Taking the United Kingdom as an illustration, the massive vapour cloud explosion at Flixborough in 1974 highlighted the problem of major hazards. This led to the setting up of the Advisory Committee on Major Hazards (ACMH) that sat from 1975 to 1983, and to the introduction of legislation to control major hazard installations. Likewise, there was a continuous flow of legislation to tighten up both on emissions

Table 1.1 *Selected references on safety and loss prevention*

General safety

ABCM (n.d./1, 1964/3); AIChE (see Appendix 28); Creber (n.d.); IChemE (see Appendix 28); IOSHIC (Information Sheet 15); NSC (n.d./2, 4, 6, 7, 1992/11); RoSPA (IS/72, IS/106); Ramazzini (1713); Blake (1943); Rust and Ebert (1947); Plumbe (1953); Gugger *et al.* (1954); Guelich (1956); Harvey and Murray (1958); Armistead (1959); Coates (1960); Thackara *et al.* (1960); ILO (1961, 1972); Meyer and Church (1961); AIA (1962); Devauchelle and Ney (1962); Ducommun (1962); Shearon (1962); Kirk and Othmer (1963–, 1978–, 1991–); Simonds and Grimaldi (1963); Gilbert (1964); Vervalin (1964a, 1973a, 1976c, 1981a,b, 1983); G.T. Austin (1965a); Christian (1965); H.H. Fawcett (1965a, 1981, 1982a, 1985); H.H. Fawcett and Wood (1965, 1982); Gagliardi (1965); Gilmore (1965); Gimbel (1965a); Gordon (1965); Kac and Strizak (1965); Voigtlander (1965); Emerick (1967); FMEC (1967); McPherson (1967); Sands and Bulkley (1967); Tarrants (1967); Badger (1968); J.E. Browning (1968); CBI (1968); Fowler and Spiegelman (1968); Leeah (1968–); Packman (1968); Berry (1969, 1977); Everett (1969); Handley (1969, 1977); Klaassen (1969, 1971, 1979); Maas (1969); Northcott (1969); Freddy (1969); Davidson (1970, 1974); Hearfield (1970, 1974, 1976); D.L. Katz (1970); MCA (1970–/18); Queener (1970); N.T. Freeman and Pickbourne (1971); ILO (1971–72); Kletz (1971, 1975a,c,e, 1976a,c,e,f, 1977f, 1978b, 1979c,e,k, 1980k, 1981c, 1983c,f, 1984b,g,j, 1984 LPB 59, 1985a, 1986g, 1987i, 1988J, 1990d, 1991k, 1994 LPB 120); Rodgers (1971); Tye and Ullyet (1971); Hammer (1972); R.Y. Levine (1972b); SCI (1972); Burns (1973); CAPITB (1973/1, 1975 Information Paper 16); Holder (1973); Kinnersly (1973); Kirven and Handke (1973); Ludwig (1973a,b); Orloff (1973); Society of the Plastics Industry (1973); Widner (1973); C.A.J. Young (1973); Buschmann (1974); Critchfield (1974); Kantyka (1974a,b); Lees (1974a,b, 1980); Malasky (1974); D. Turner (1974); Anon. (1975l); Barber (1975); Boyes (1975); D. Farmer (1975); Gardner and Taylor (1975); HSE (1975 HSW Booklet 35); Institute of Fuel (1975); D. Petersen (1975, 1982a, 1984, 1988a,b, 1989); TUC (1975, 1978, 1986); Bean (1976a,b); D.B. Brown (1976); Koetsier (1976); Marti (1976); V.C. Marshall (1976d, 1990d); Singleton (1976b); Arscott and Armstrong (1977); Atherley (1977b,c, 1978); Barbieri *et al.* (1977); Blohm (1977); IP (1977); J. Jones (1977); Leuchter (1977); Lugenheim (1977); McCrindle (1977, 1981); Nicolaescu (1977); Rogojina (1977); Sisman and Gheorgiu (1977); Wakabayashi (1977); Webster (1977); Allianz Versicherung (1978); M.E. Green (1978, 1979); Napier (1978, 1980); Anon. (1979d); BASF (1979); Birkhahn and Wallis (1979); Hagenkotter (1979); Kerr (LPB 25 1979); R. King and Magid (1979); Menzies and Strong (1979); Peine (1979); Schaeffer (1979); Schierwater (1979); H. Clarke (1980); Heinrich *et al.* (1980); Krishman and Ganesh (1980); Kumar *et al.* (1980); Spiegelman (1980); Srinivasan *et al.* (1980); Wells (1980); Chowdhury (1981); McCrindle (1981); Teja (1981); AGA (1982/7); Laitinen (1982); Ormsby (1982, 1990); Carter (LPB 50 1983); W.B. Howard (1983, 1984, 1985, 1989); Parmeggiani (1983); Preece (1983); Ridley (1983–); Sinnott (1983); Tailby (LPB 50 1983); Warner (LPB 50 1983); Carson and Jones (1984); A.D. Little (1984); Ross (1984); Setters (1984); Zanetti (1984a); Burgoyne (1985b, 1986b); EFCE (LPB 66 1985); Gagliardi (1985); Hildebrand (1985); McKechnie (1985); Munson (1985); Nordic Liaison

Committee (1985 NKA/LIT(85)3); Packer (1985); Pilarski (1985); APCA (1986); T.O. Gibson (1986); Grollier-Baron (1986); Joschek (1986, 1987); Lihou (1986); DnV (1987 RP C201); Romer (1987); Scheid (1987); Hoyos and Zimolong (1988); Kharbanda and Stallworthy (1988); Carson and Mumford (1989); Hoovpr *et al.* (1989); Crawley (1990 LPB 91); Hastings (1990); Jochum (1990); Koh (1990); Krishnaiah *et al.* (1990); H.C.D. Phillips (1990); Renshaw (1990); Dupont, Theodore and Reynolds (1991); Fades (1991); L. Hunt (1991); McQuaid (1991); Rasmussen (1991); Whiston (1991); Pasman *et al.* (1992); Andrews (1993); Fisk and Howes (1993); Cullen (1994); Donald and Canter (1994); M. Richardson (1994)

Total loss control
BSC (n.d./6, 7); Heinrich (1959); Bird (1966, 1974); Bird and Germain (1966, 1985); Gilmore (1970); Goforth (1970); J. Tye (1970); J.A. Fletcher and Douglas (1971); Webster (1974, 1976); Anon. (1975 LPB 4, p. 1); Hearfield (1975); D.G. King (1975); F.E. Davis (1976); Ling (1976, 1979); D.H. Farmer (1978); Planer (1979); Heinrich, Petersen and Roos (1980); Dave (1987)

Safety, health and environment
Berkey, Dowd and Jones (1993); Hawskley (1993b); Walk (1993)

Company policies
Aalbersberg (1991); Auger (1993); Whiston (1993)

Responsible care
CIA (RC51, RC52, 1990 RC23, 1992 RC53); Belanger (1990); Kavasmaneck (1990); Whiston (1991); Jacob (1992)

Product stewardship
Rausch (1990)

Organizational initiatives
IChemE: Hancock (1983); Street, Evans and Hancock (1984)
SRD: Clifton (1983 LPB 52)
CEFIC: Jourdan (1990)
CCPS: CCPS (1985); Carmody (1988, 1989, 1990a,b); R.A. Freeman (1990); K.A. Friedman (1990); Schreiber (1990)
EPSC: Anon. (1992 LPB 103); Anon. (1993 LPB 111); EPSC (1993); Anon. (1994 LPB 115); Hancock (1994 LPB 120)
IPSE: Macoksley (1993a)

Organization guides
NSC (1974); ILO (1989, 1991); OECD (1992)

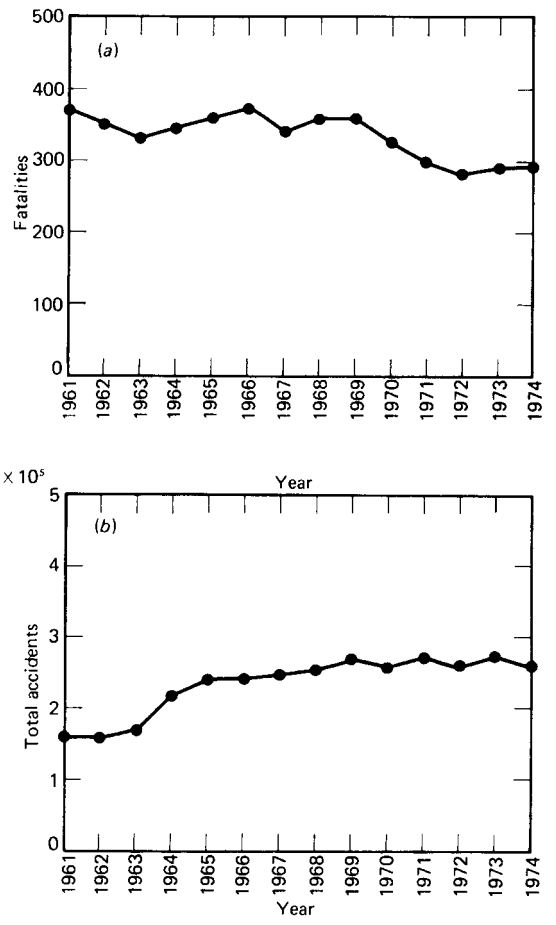
Contractors
Kletz (1991m)

Terminology
IP (Oil Data Sht 3); Harvey (1979b); Burgoyne (1980); Berthold and Loeffler (1981); V.C. Marshall (1981a,b, 1990c); A.E. Green (1982); Kletz (1983c, 1984c); IChemE (1985/78, 1992/98); ACDS (1991) BS (Appendix 27 Glossaries)

Bibliographies
Commonwealth Department of Productivity (1979); Lees (1980); Vervalin (1981a,b); Lees and Ang (1989a)

Critiques
Wallick (1972); Commoner (1973); L.N. Davis (1979, 1984); Hewlett (1982)

Other related fields
Pugsley (1966); Ingles (1980; civil engineering); Thurston (1980; aviation); Garrick and Caplan (1982); V.M. Thomas (1982); Grigoriu (1984; structural engineering)

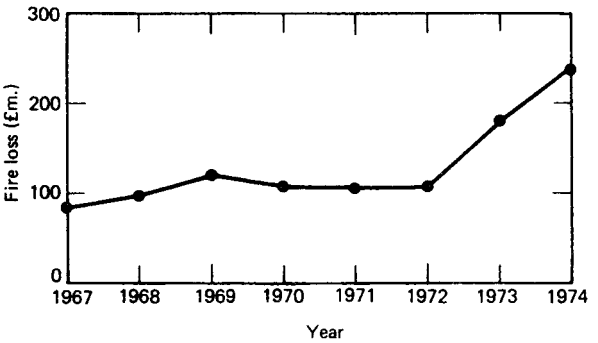


Sources: Robens (1972); HM Chief Inspector of Factories (1974)

Figure 1.1 *(a) Fatalities and (b) total accidents in factories in the UK, 1961–74 (Courtesy of the Health and Safety Executive)*

from industrial installations and on exposure of workers to noxious substances at those installations.

Similarly, in the United States, the Bhopal incident as well as other highly publicized tragedies (Flixborough, 1974; Seveso, 1976; Three Mile Island, 1979; Cubato, February 1984; Mexico City, November 1984; Houston, 1989) caused widespread public concerns about major incidents in US chemical plants that might disastrously affect the public. Not only was the public's confidence in the chemical industry shaken, but also the chemical industry itself questioned whether its provisions for protection against major accidental releases were adequate. The recognition of the chemical industry's need for technical advances led to a number of initiatives. For example, in 1985, the Chemical Manufacturers Association (CMA – now known as the ACC, the American Chemistry Council) published its guidelines on Process Safety Management and the American Institute of Chemical Engineers (AIChE) created the Center for Chemical Process Safety (CCPS) with significant financial support by industry. Over the next several years, many other



Source: British Insurance Association (1975)

Figure 1.2 *Total fire losses in the UK, 1967–74 (Courtesy of the British Insurance Association)*

centers such as the National Institute for Chemical Safety, the National Environmental Law Center and the Mary Kay O'Connor Process Safety Center also came into existence. During this same period, the United States Environmental Protection Agency (USEPA) and the Occupational Safety and Health Administration (OSHA) of the United States Department of Labor started several technical initiatives aimed at gathering information about major accident risks.

It is against this background, therefore, that the particular problems of the process industries should be viewed. The chemical, oil and petrochemical industries handle hazardous substances and have always had to devote considerable effort to safety. This effort is directed both to the safe design and operation of the installations and to the personal safety of the people who work on them. However, there was a growing appreciation in these industries that the technological dimension of safety was becoming more important.

1.4 Loss Prevention-1

The 1960s saw the start of developments that have resulted in great changes in the chemical, oil and petrochemical industries. A number of factors were involved in these changes. Process operating conditions such as pressure and temperature became more severe. The energy stored in the process increased and represented a greater hazard. Problems in areas such as materials of construction and process control became more taxing. At the same time, plants grew in size, typically by a factor of about 10, and were often single stream. As a result they contained huge items of equipment, such as compressors and distillation columns. Storage, both of raw materials and products and of intermediates, was drastically reduced. There was a high degree of interlinking with other plants through the exchange of by-products.

The operation of such plants is relatively difficult. Whereas previously chemical plants were small and could be started up and shut-down with comparative ease, the start-up and shut-down of a large, single-stream plant on an integrated site is a much more complex and expensive matter. These factors resulted in an increased potential for loss – both human and economic. Such loss may occur in various ways. The most obvious is the major incident, usually arising from loss of containment and taking the form of a serious fire, explosion or toxic release. But loss due to such situations as delays in commissioning and downtime in operating is also important.

The chemical and oil industries have always paid much attention to safety and have a relatively good record in this respect. In the United Kingdom, for example, the fatal accident rate for the chemical industry has been about equal to that for industry generally, which in view of the nature of the industry may be regarded as reasonable. These are high technology industries and there has always been a strong technological element in their approach to safety. However, the increasing scale and technology of modern plants caused the chemical industry to re-examine its approach to the problem of safety and loss. If the historical development of this concern in the United Kingdom is considered, there are several problem areas that can be seen, in retrospect, to have given particular impetus to the development of loss prevention.

One of these is the problem of operating a process under extreme conditions and close to the limits of safety. This is usually possible only through the provision of relatively sophisticated instrumentation. About the mid-1960s, several such systems were developed. One of the most sophisticated, influential and well documented was the high integrity protective system developed by R.M. Stewart (1971) for the ethylene oxide process. About the same time many difficulties were being experienced in the commissioning and operation of large, single-stream plants, such as ethylene and ammonia plants, involving quite severe financial loss. On the design side, too, there was a major problem in getting value for money in expenditure aimed at improving safety and reducing loss. It was increasingly apparent that a more cost-effective approach was needed.

These developments did not take place in isolation. The social context was changing also and other themes, notably pollution, including effluent and waste disposal and noise, were becoming of increasing concern to the public and the government. In consequence, the industry was obliged to examine the effects of its operations on the public outside the factory fence and, in particular, to analyse more carefully the possible hazards and to reduce emissions and noise. Another matter of concern was the increasing quantities of chemicals transported around the country by road, rail and pipeline. The industry had to take steps to show that these operations were conducted with due regard to safety. In sum, by the 1970s, these problems became a major preoccupation of senior management. Management's recognition of the problems and its willingness to assign to their solution many senior and capable people as well as other resources has been fundamental in the development of loss prevention.

Table 1.2 *Some milestones in the development of loss prevention*

1960	First UK IChemE symposium on Chemical Process Hazards with Special Reference to Plant Design
1966	Dow Chemical Company's Process Safety Manual
1967	First AIChE symposium on Loss Prevention
1968	First ICI Safety Newsletter; American Insurance Association Hazard Survey of the Chemical and Allied Industries
1971	European Federation of Chemical Engineering symposium on Major Loss Prevention in the Process Industries
1972	UK – Report of Robens Committee on Safety and Health at Work
1973	UK – IChemE Loss Prevention Panel, information exchange scheme and, in 1975, Loss Prevention Bulletin
1974	UK – HSWA 1974; First International Symposium on Loss Prevention and Safety Promotion in the Process Industries; Rasmussen Report; Flixborough disaster
1975	UK – Flixborough Report
1976	First Report of ACMH; Seveso incident
1978	First Canvey Report; San Carlos disaster
1979	Second Report of ACMH; Three Mile Island incident
1981	Norwegian Guidelines for Safety Evaluation of Platform Conceptual Design
1982	EC Directive on Control of Industrial Major Accident Hazards
1984	Third Report of ACMH; Control of Industrial Accident Hazards Regulations 1984; Bhopal disaster; Mexico City disaster
1985	AIChE establishes the CCPS
1986	Russia – Chernobyl disaster; USA, California – Risk Management and Prevention Program; USA, New Jersey – Toxic Catastrophe Prevention Act
1988	Piper Alpha disaster
1990	UK – Piper Alpha Report; USA – •January – API Recommended Practice 750 (Management of Process Hazards); •July – OSHA Process Safety Management Proposed Rule; •October – CMA Responsible Care Code of Management Practices; •November – Clean Air Act Amendments of 1990; Formation of the US Chemical Safety Board
1992	Offshore Safety Act 1992; Offshore Installations (Safety Cases) Regulations 1992
1995	USA – Risk Management Program regulation promulgated by USEPA; Texas A&M University established the Mary Kay O'Connor Process Safety Center

The existence of expertise in related areas has been of great value. In the United Kingdom, the UK Atomic Energy Authority (UKAEA), initially through its Health and Safety Branch and then through its Safety and Reliability Directorate (SRD) was able to advise on reliability assessment. Industry adopted UKAEA techniques in the assessment of major hazards and of protective instrumentation and data on failure rates. Many firms in the industry now have their own reliability engineers.

The historical development of loss prevention is illustrated by some of the milestones listed in Table 1.2. The impact of events has been different in different countries. Within the industry, loss prevention emerged as a theme of technical meetings which indicated an increasingly sophisticated technological approach. The Institution of Chemical Engineers (IChemE) established a Loss Prevention Panel which operates an information exchange scheme and publishes the *Loss Prevention Bulletin*. This growing industrial activity was matched in the regulatory sphere. The Robens Committee (1972) emphasized the need for an approach to industrial safety that is more adapted to modern technology, and recommended self-regulation by industry as opposed to regulation from outside. This philosophy is embodied in the Health and Safety at Work etc. Act 1974 (HSWA), which provides the framework for such an approach. However, the Act does more than this. It lays a definite statutory requirement on industry to assess its hazards and demonstrate the effectiveness of its safety systems. It is enforced by the Health and Safety Executive (HSE). The General Duty Clause requirements under US regulations enforced by OSHA and USEPA have been interpreted similarly.

The disastrous explosion at Flixborough in 1974 has proved a watershed. Taken in conjunction with the Act, it has greatly raised the level of concern for SLP in the industries affected. It also led, as mentioned, to the setting up of the ACMH. The incident at Seveso in 1976 has been equally influential. It had a profound impact in Continental Europe and was the stimulus for the development of the EC Directive on Control of Industrial Major Accident Hazards in 1982. Further disasters such as those at San Carlos, Bhopal and Mexico City have reinforced these developments.

1.5 Large Single-stream Plants

For some decades up to about 1980, there was a strong trend for the size of plants to increase. The problems associated with large, single-stream plants are a major reason for the development of loss prevention. These problems are now considered in more detail in order to illustrate some of the factors underlying its growth. Selected references on large, single-stream plants are given in Table 1.3.

The increase in the size of plant in the period in question for two principal chemicals is shown in Figure 1.3, which gives the size of the largest ethylene and ammonia plants built by a major contractor and the year in which they came on stream. Thus, whereas in 1962 an ethylene plant with a capacity in excess of 100,000 ton/year was exceptional, by 1969 this had become the minimum size ordered, whilst the newest UK plant, the No. 5 Unit of Imperial Chemical Industries (ICI), had a capacity of 450,000 ton/year. Although briefly the largest single-stream naphtha cracker in the world, it was soon overtaken by other plants of 500,000 ton/year capacity or more. Similar trends occurred in ammonia plants.

This increase in plant size took place in a rapidly expanding market. Thus, the growth in world demand for

Table 1.3 *Selected references on large, single-stream plants*

Frank and Lambrix (1966); Quigley (1966); Anon. (1967d); Davidson (1967); Holroyd (1967); R.L. Miller (1967); H.S. Robinson (1967a); Axelrod *et al.* (1968); Deschner *et al.* (1968); Mapstone (1968); Mayo (1968); S.P. Rose (1968); Lofthouse (1969); Chase (1970); Dailey (1970); W.E. Tucker and Cline (1970, 1971); Coulter and Morello (1971, 1972); Flatten (1971); Walley and Robinson (1972); Knight (1973); Ball and Steward (1974); Huettner (1974); Woodhouse *et al.* (1974); Anon. (1975j); Baba and Kennedy (1976); Ball and Pearson (1976); Pilz and van Herck (1976); Ennis and Lesur (1977); Holland and Watson (1977); J.C. Davis (1978); Froment (1979); Hammock (1979); Anon. (1984nn); Remer and Chai (1990); Brennan (1992); Garnett and Patience (1993)

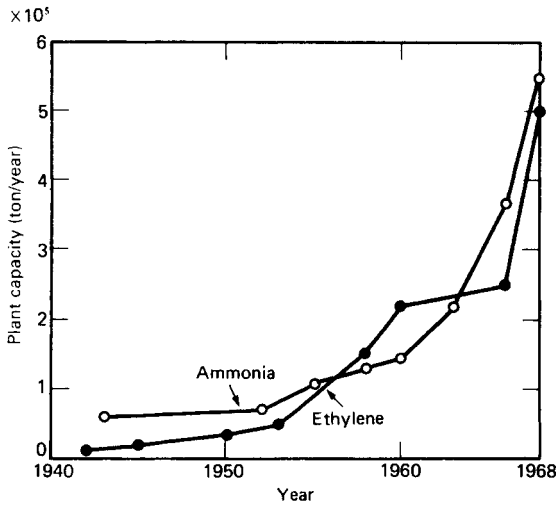


Figure 1.3 *Capacity of ethylene and ammonia plants, 1940–68 (after Axelrod, Daze and Wickham, 1968) (Courtesy of the American Institute of Chemical Engineers)*

ethylene was given as follows (Walley and Robinson, 1972):

1965	8.5 megatonnes/year
1970	20 megatonnes/year
1975 (estimated)	39 megatonnes/year

The basic cause of the increase in size was concern for capital cost. Up to the early 1950s, the chemical industry did not give minimization of capital cost particular priority. But with the move to naphtha feedstocks and the growth of petrochemicals, capital came to represent a much more significant cost than before compared with other costs such as raw materials and labour.

The relationship between size and capital cost is given by the well-known equation:

$$C = kP^n \qquad [1.5.1]$$

where C is the capital cost of the plant, P its design output, k is a constant, and n is the scale-up index. The value of n is often about 0.6–0.7 so that if design output is doubled, the capital cost increases by only 50–60%. There are also some savings on operating costs, particularly in terms of the thermal economy and labour.

Most calculations of the savings obtainable by building big showed the savings to be large; therefore, it was difficult in a competitive industry to avoid doing so, despite the recognized risks. The world price tended to be set by the larger plants, so that smaller plants became obsolete. Although calculations showed savings from large plants, there was considerable variation in the size of these savings, depending on the assumptions made. One figure given was a reduction in the cost of ethylene to about 50% in going from a 150,000 to a 450,000 ton/year plant (Holroyd, 1967); another calculation gave a reduction to about 80% in going from a 200,000 to a 400,000 ton/year plant (Lofthouse, 1969).

The calculation depends on many factors and is complex. This is particularly so for ethylene, which is only one of a number of products from an ethylene plant. The values of the propylene and butadiene produced were each about as great as that of the ethylene. Much therefore depended on whether these and other by-products could be sold at full or only at fuel value. A typical calculation of the effect of plant size and co-product credit on the economics of an ethylene plant at that time is shown in Table 1.4.

Another important factor for an ethylene plant is the acquisition of load. The best situation is where the ethylene is taken away by gas pipeline. The alternative of sea transport, which involves liquefaction, is more expensive and may well cancel the cost advantage of a large plant. However, ethylene pipelines are difficult to justify except where there is a long-term contract, and it is not easy to create an ethylene grid into which other users can tap.

The economics of a large plant are also badly affected if it fails to reach full output immediately, either on account of commissioning difficulties or of lack of demand. A typical calculation of the effect of plant size, lateness and underloading on ammonia plant economics is shown in Table 1.5.

Despite these problems, the general assessment around, say, 1966 was that the building of large plants was justified. However, there continued to be a lively debate as to whether the expected economies of scale were realizable. Several difficulties became apparent. The economies of scale depend very largely on the retention of the single-stream philosophy. This gives economies not only in the cost of the equipment itself but of the associated pipework, heat exchangers, instrumentation, civil engineering etc. These are largely lost if there is resort to duplication. However, in some cases, the equipment appeared to be nearing the limits of size. This had long been so for the furnaces on an ethylene plant, which typically had multiple furnaces with outputs of about 30,000 ton/year. The main compressor was very large – that on ICI's No. 5 plant being 35,000 h.p. The main distillation column was also very big and had to be fabricated on site.

At large sizes, the value of the scale-up index n is subject to some modification. A common value of n for ethylene plants was 0.65 (Lofthouse, 1969). However, as already mentioned, the cracking section of the plant, which accounts for about 30% of the capital cost, offers little scope for scale-up economies. Other items, such as compressors,

distillation columns and heat exchangers, may be near their limits and may have a higher index. Some facilities such as storage and effluent control may even have an index greater than 1.0. Thus, it was suggested (Walley and Robinson, 1972) that a more realistic actual value of n is 0.9.

Storage is a serious problem with large plants. For the size of plant described, storage, whether of raw materials or products, is extremely expensive and has to be kept to a minimum.

The reliability of large plants was often unsatisfactory, there being a number of reasons for this. Compact layout made maintenance more difficult and increased the vulnerability to fire. Arrangements aimed at thermal economy increased the degree of interdependence in the plant. Economies were made in capital cost in areas such as materials of construction and duplication of equipment. As Holroyd (1967) comments:

> Faulty welding has resulted in leaky high pressure piping systems and there has been little improvement as regards jackets, dinners, and footballs left in equipment despite the much more serious effect this sort of thing has in high cost, high capacity single plant units. There have been many examples of faulty equipment – faulty fabrication of interchangers, improper assembly of compressors and high-pressure reactors which have failed under test. Complete shut-down of the plant due to failure of a simple piece of equipment, such as a pump of established design, and of negligible cost in itself, has been a frequent experience. Faulty supervision and human error in operation has shown up in not following the proper sequence of actions in emergencies, inadvertent tripping out of machines, failure to isolate equipment under maintenance and carelessness in checking instruments and with regard to such matters as water treatment.

Table 1.4 *Effects of plant size and co-product credit on ethylene plant economics (after Walley and Robinson, 1972)*

Plant size (ton/year)	200,000	300,000	400,000	500,000
Plant capital (£m.)	25.0	33.0	40.0	47.0
Working capital (£m.)	2.0	2.9	3.8	4.6
Capital charge (£/ton ethylene)	33.5	29.8	27.5	25.9
Fixed costs	9.3	7.7	6.8	6.2
Feedstock	30.5	30.5	30.5	30.5
Fuel, utilities, catalysts	*8.6*	*8.6*	*8.6*	*8.6*
	81.9	76.6	73.4	71.2
Co-product credit (£/ton ethylene)	34.2	34.2	34.2	34.2
Ethylene cost (£/ton)	47.7	42.4	39.2	37.0
Co-product credit (£/ton ethylene)	34.2	29.1	26.6	25.1
Ethylene cost (£/ton)	47.7	47.5	46.8	46.1

As a result of such factors, there were many cases of difficulties and delays in commissioning and operation of such plants throughout the world. A breakdown of the causes of such problems in ammonia plants is given in Table 1.6.

Large plants also have some undesirable features from the safety point of view. Particularly significant is the scale of the inventory. The amount of material in the main distillation column of a large ethylene plant exceeds that formerly contained in the storage vessels of smaller plants.

Problems of pollution and noise, including flares and pressure relief, also appear to increase in severity rather rapidly for large plant sizes. Some more specific faults on ammonia plants have been quoted (Holroyd, 1967). One of these, migration of silica under the more severe operating conditions, is a matter of advanced technology. Most of the others are more mundane.

It is not surprising, therefore, that the trend to large-scale plants was criticized and the economies of scale questioned. The debate was particularly lively over the period 1967–72. Even at the start of the debate, the large, single-stream plant

Table 1.5 *Effects of plant size, lateness and underloading on ammonia plant economics (after Holroyd, 1967)*

Plant	*Output patter* (% design capacity)	*DCF return*		
		No delay (%)	*6-month delay* (%)	*12-month delay* (%)
3 × 333 t/day	Year 1 onwards 100	4	–	–
suitably purchased	Year 1 60			–
	2 80	½	–	
	3 onwards 100			
1 × 1000 t/day	Year 1 onwards 100	26	23	21
	Year 1 60			
	2 80	16	14	13
	3 onwards 100			
	Year 1 30			
	2 80	12	10	9
	3 90			
	4 onwards 100			
	Year 1 30			
	2 70	7	6	5
	3 onwards 90			

Table 1.6 *Causes of commissioning and operating problems in ammonia plants (after Holroyd, 1967)*

Faults	*M.W. Kellogg experience* (%)	*ICI experience* (%)
Design	10	10
Erection	20	16
Equipment	40	61
Operating	30	13

had its defenders (Holroyd, 1967; Lofthouse, 1969). The cost sensitivity and other problems of large plants were admitted. It was also conceded that the economies of scale were not as great as initial estimates suggested. But these factors were not considered sufficient to negate the economies of large plants or to make the return to small ones appear attractive.

It was agreed that part of the problem was that the increase in size of plants had been accompanied by a drive to reduce capital costs which may have been taken too far:

> This drive took many other forms besides increase of scale. It tended to lead to elimination of duplicates of even minor items of plant, to economies which sometimes proved to be false economies in the provision of services such as steam and power, to extreme sophistication in energy recovery which sometimes added so much to the complexity of the plants as to make them difficult to run, and to the concentration of the plant within very much smaller areas which increased their vulnerability to fire and also complicated maintenance. (Lofthouse, 1969)

Moreover, it was reasonable to claim that the industry had already learnt much from the troubles of the first generation of large plants and that it would be able to avoid many of these in the future.

In effect, the argument was that failures in large plants were not primarily due to the size of items of equipment, the single-stream arrangement or the use of high technology. It was conceded, however, and indeed emphasized, that the penalties of failures on large, single-stream plants are very great and that it is essential for their success to put maximum effort into ensuring high reliability and good operation. Particular emphasis was laid on the effectiveness of the operation and maintenance in large plants. Here the main factor is the quality of personnel at all levels: management, process operators and maintenance crews. Close supervision and rigorous inspection have an important part to play, but are no substitute for well-educated and well-trained people.

The large, single-stream plant offers substantial rewards for success, but this does not come easily. It can be achieved only by first class management and engineering in design and operation. The large plant places a premium on these factors and is thus a means by which a firm that possesses them gains a competitive advantage.

The growth in the size of plants has now slowed appreciably. The typical size of a new ethylene plant in 1978 was about 500,000 ton/year. This is still typical for a new plant worldwide. A plant for 700,000 ton/year still ranks among the largest plants (Mahoney, 1990). There is no marked trend to yet larger plants, but equally there is little sign of reversion to smaller ones. However, consequent to widespread interest in inherent safety and security concerns, process intensification and miniaturization are starting to receive some renewed interest. The results of this renewed interest are yet to be seen.

1.6 Loss Prevention-2

The area of concern and the type of approach which goes by the name of loss prevention is a development of safety work. But it is a response to a changing situation and need, and it has certain particular characteristics and emphases. The essential problem which loss prevention addresses is the scale, depth and pace of technology. In fact, control of such hazards is possible only through effective management. The primary emphasis in loss prevention is, therefore, on the management system. This has always been true, of course, with regard to safety. But high technology systems are particularly demanding in terms of formal management organization, competent persons, systems and procedures, and standards and codes of practice. On top of all of this, there is a growing realization that safety performance is quite often influenced by the safety culture of the company. The 2003 Columbia shuttle disaster and the following investigation report brings to light some of NASA's safety culture issues that may have doomed Columbia as well as Challenger.

According to Mannan (2003a), perhaps we should pay more attention to safety culture. One school of thought is that safety culture even though a very important issue is not a specific problem of process safety or loss prevention. However, it seems there is a special set of problems that go along with extreme events and the associated risks. Before the event there is great confidence that such a thing could never happen. Afterward there is denial and no cultural change occurs. This may be true of NASA as well as some process companies as well. What are the attributes of a good safety culture? How do organizations accomplish a good safety culture and maintain it over the life of the organization? How can the safety culture survive through changing leaderships, turnovers, budget pressures, early retirements and other changes? How can we get organizations that do not have a good safety culture make the necessary changes to move towards a good safety culture? These are questions that should be answered.

Mannan (2003a) goes on to describe the investigation of one incident where everyone involved felt that they had done everything they were supposed to do and the incident was just something that was beyond anyone's control. In fact, a few people in the organization even claimed that if the same set of circumstances were to happen again, the same incident would occur again, possibly with the same consequences. Now, that is a safety culture that needs major overhaul.

Mannan (2003b) states that there are a number of attributes of a good safety culture. It is quite difficult to identify objective characteristics of a good safety culture. However, some known characteristics include:

(1) Commitment AND involvement of the highest level personnel.
(2) Open communication at all levels of the organization.
(3) Everyone's responsibilities and accountabilities regarding safety is clearly defined and understood.
(4) Safety is second nature.

(5) Zero tolerance for disregard of management systems, procedures and technology.
(6) Information systems allow all parties access to design, operational and maintenance data.

As part of a multi-layered approach for a good safety culture, organizations use analysis of trends to spot problems. Trend analysis should be focused on leading as well as trailing indicators. A trailing indicator is a downstream measurement of the outcomes of safety and health efforts. These indicators reflect successes or failures of the system to manage hazards. Examples of trailing indicators include fatalities, injuries and incidents. A leading indicator is an upstream measure that characterizes the level of success in managing safety systems; measurement of activities towards risk reduction prior to occurrence of incidents. While every effort should be made to measure and track trailing indicators, relying on the trailing indicators to assess safety performance is self-defeating. Thus, it is very important to measure and track leading indicators, particularly for high-risk activities such as space flight. Leading indicators, however, are more difficult to define and measure and vary according to the activity and the mission of the organization. Examples of leading indicators might include:

(1) the level of near-miss reporting;
(2) effectiveness of incident investigation and corrective action;
(3) management of change;
(4) emphasis on inherently safer design;
(5) effective application of risk assessments;
(6) level of deferred maintenance;
(7) Level of repetitive maintenance;
(8) Number and severity of faults detected by inspection, testing and audits;
(9) Number and nature of unresolved safety issues;
(10) Participation in continuing education and symposia;
(11) Employee morale, level of expertise.

The method of approach is also somewhat different. When systems are small scale and relatively non-hazardous and change slowly over the years, they are able to evolve by trial and error. This is often simply not possible with modern systems, where the pace of change is too fast and the penalties of failure are too great. It becomes necessary to apply forethought to try to ensure that the system is right the first time. In a related area, the widespread application of human factors to large man–machine systems has been motivated by very similar considerations. A major hazard in a modern process plant usually materializes due to loss of containment. The three big major hazards are fire, explosion and toxic release.

Thus, loss prevention is characterized by

(1) an emphasis on management and management systems, particularly for technology;
(2) a concern with hazards arising from technology;
(3) a concern with major hazards;
(4) a concern for integrity of containment;
(5) a systems rather than a trial-and-error approach.

Some other features that are characteristic of loss prevention are the use of

(6) techniques for identification of hazards;
(7) a quantitative approach to hazards;
(8) quantitative assessment of hazards and their evaluation against risk criteria;
(9) techniques of reliability engineering;
(10) the principle of independence in critical assessments and inspections;
(11) planning for emergencies;
(12) incident investigation;

together with

(13) a critique of traditional practices or existing regulations, standards or codes where these appear outdated by technological change.

The identification of hazards is obviously important, since the battle is often half won if the hazard is recognized. A number of new and effective techniques have been developed for identifying hazards at different stages of a project. These include hazard indices, chemicals screening, hazard and operability studies, and plant safety audits.

Basic to loss prevention is a quantitative approach, which seeks to make a quantitative assessment, however elementary. This has many parallels with the early development of operational research. This quantitative approach is embodied in the use of quantitative risk assessment (QRA). The assessment produces numerical values of the risk involved. These risks are then evaluated against risk criteria. However, the production of numerical risk values is not the only, or even the most important, aspect. A QRA necessarily involves a thorough examination of the design and operation of the system. It lays bare the underlying assumptions and the conditions that must be met for success, and usually reveals possible alternative approaches. It is therefore an aid to decision-making on risk, the value of which goes far beyond the risk numbers obtained.

Reliability engineering is now a well-developed discipline. Loss prevention makes extensive use of the techniques of reliability engineering. It also uses other types of probabilistic calculation that are not usually included in conventional treatments of reliability, such as probabilities of weather conditions or effectiveness of evacuation. Certain aspects of a system may be particularly critical and may require an independent check. Examples are independent assessment of the reliability of protective systems, independent audit of plant safety and independent inspection of pressure vessels.

Planning for emergencies is a prominent feature of loss prevention work. This includes both works and transport emergencies.

Investigation of incidents plays an important part in loss prevention. Frequently there is some aspect of technology involved. But the recurring theme is the responsibility of management. While a good safety culture varies according to the mission and activities of the organization, one of the attributes of a good safety culture that is a 'must' is 'learning from incidents'. There is no excuse when 'lessons learned' from incidents are ignored or not implemented, particularly 'lessons learned' from incidents that have occurred in one's own organization or incidents that are widely publicized.

The loss prevention approach takes a critical view of existing regulations, standards, rules or traditional practices where these appear to be outdated by changing technology. Illustrations are criticisms of incident

reporting requirements and of requirements for protection of pressure vessels. These developments taken as a whole do constitute a new approach and it is this which characterizes loss prevention.

It might perhaps be inferred from the foregoing that the problems which have received special emphasis in loss prevention are regarded somehow as more important than the aspects, particularly personal incidents, with which traditionally safety work in the process industries has been largely concerned. Nothing could be further from the truth. It cannot be too strongly emphasized that mundane incidents are responsible for many more injuries than and as many deaths as those arising from high technology.

1.7 Total Loss Control

It is now necessary to consider some other developments that have contributed to the modern approach to SLP. The first of these is total loss control. The basic concept underlying total loss control is that loss due to personal incident and injury is only the tip of the iceberg of the full loss arising from incidents. It follows that attention should be paid, and controls applied, to all losses. Early work in this area is described in *Industrial Accident Prevention* (Heinrich, 1959) and by Bird (1966). Accounts are given in *Total Loss Control* (G.A. Fletcher and Douglas, 1971) and *Practical Loss Control Leadership* (Bird and Germain, 1985).

Total loss control, like loss prevention, is concerned with losses associated with hazards and incidents or other incidents. It is not concerned with losses that do not have a hazard element. It may be seen, therefore, as an extension of the activity of the safety manager. The attraction of such a change of emphasis is that the safety manager becomes involved in a major cost area that is of concern to other managers and thus increases his influence, with consequent benefit to safety.

The ratio between different types of incidents is a key concept in loss control. Early work on this was done by Heinrich (1959), who gave the following ratio for the different types of incidents:

Major or lost time injury/Minor injury/No injury = 1 : 29 : 300

These ratios are frequently shown in the form of the incident pyramid illustrated in Figure 1.4.

The numbers of incidents on which the above ratios were based were evidently fairly limited. Later studies have been done involving much larger numbers. Bird and Germain (1985) report a study of some 1.75 million incidents from 297 cooperating organizations in which the ratio was:

Disabling injury/Minor injury/Property damage/No injury or damage = 1 : 10 : 30 : 600

Tye and Pearson (HSE, 1991b) give the results of an investigation of almost 1 million incidents:

Disabling injury/Minor injury/First-aid injury/Property damage/No injury or damage = 1 : 3 : 50 : 80 : 400

The incident definitions and ratios tend to vary between different studies, but the relationship between the different kinds of event is usually consistent in a given study.

In another study, *The Costs of Accidents at Work* (HSE, 1993a), an investigation was made of incidents at a creamery, a construction site, a transport company, a hospital and an oil platform. For the oil platform, the most relevant here, the ratios obtained were as follows (the values given in parentheses being those for all the studies except the construction site):

Over 3-day injury/Minor injury/Non-injury incident = 1 : 4(7) : 126(189).

Another ratio quoted by Heinrich is the ratio of uninsured to insured costs of incidents, which he gives as about 4 : 1. However, J.A. Fletcher and Douglas (1971) report studies in which this ratio ranges from 2.3 to 101 and suggest that it is necessary to investigate this in any particular work places.

In another recent study in the United States, Mannan *et al.* (2001) reported the statistics on 34,527 incidents for 1998 in all of United States. According to this study, the incidents were distributed in the following ratio:

Fatalities/Serious injury/Minor injury/No injuries = 1 : 7 : 44 : 300.

In the same study mentioned above, Mannan *et al.* (2001) concluded that the underlying causes for incidents are usually the same regardless of which part of the pyramid the incident falls in. In other words, an incident that causes no injury and is classified in the lower part of the pyramid could easily have been classified in the top part of the pyramid. Consider, for example, a gas release that occurs when the wind speed and wind direction are such that the gas disperses before it can encounter an ignition source. The incident would then be classified as a near-miss falling in the lower part of the incident pyramid. But, now consider the same gas release that occurs when the wind speed and wind direction are such that the gas encounters a nearby ignition source. The situation could be more aggravated if nearby workers are knocked down or thrown against concrete walls or equipment. The event could likely lead to injuries or fatalities. Thus, it seems that the same learning could be developed and captured into the procedures and training by analysing and investigating the near-miss. Thus, the broader the incident definition, the more statistically sound the lessons from the incident analysis. In fact, it would seem that as safety programmes mature, the incident definition should be expanded to include not only near-misses but also other leading indicators as well.

An illustration, given by Fletcher and Douglas, of a typical situation in a medium sized factory is shown in Table 1.7 The actual numbers of disabling and minor injury incidents were as indicated, while the number of property damage

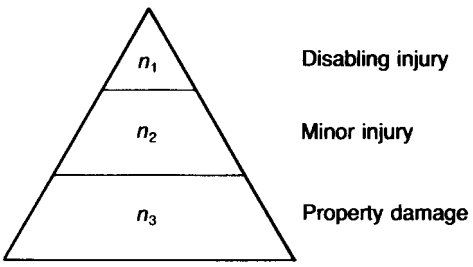


Figure 1.4 *The accident pyramid (after Bird and Germain, 1966)*

Table 1.7 *Losses in a medium sized factory (after J.A. Fletcher and Douglas, 1971) (Courtesy of Associated Business Programmes Ltd)*

Type of incident	*No. of uninsured per year*	*Cost per accident* (US$)	*Total incidents cost* (US$)
Disabling injury	71	52	3,692
Minor injury	10,122	3.86	39,032
Property damage (est.)	35,500	34.67	1,230,794
Total			1,273,518

incidents was computed from the number of disabling incidents using Bird's ratio of 500. In this case, the insured costs were the workmen's compensation costs of US$208,300, while, as shown, the uninsured costs were US$1,273,518, of which the major part was property damage costs. The ratio of uninsured to insured costs was about 6.1.

The relative importance of the damage costs is enough to justify paying attention to damage incidents. But there is the further point that assessment of such costs is straightforward compared with the assessment of injury costs, which frequently involves some rather dubious assumptions. The policy suggested, therefore, is one of monitoring not only injury incidents but also damage incidents. For this it is necessary to have damage control centres that give general information on damage incidents in much the same way as first-aid points and medical centres generate information on injury incidents. The existing maintenance system can normally be adapted for this purpose. As an illustration of the application of such a policy, J.A. Fletcher and Douglas (1971) describe a study on the reporting of damage incidents by crane drivers. In the 3 years prior to the institution of the policy, the number of damage incidents reported was rather less than 25 per year. During the 10 years after its institution, some 1643 incidents per year were reported. Reporting was enforced with an average of nine warnings and three work suspensions per year. Although many incidents were of a minor nature, many others revealed the need for prompt action to avert a more serious incident.

Total loss control areas are listed as: (1) business interruption, (2) injury, (3) property damage, (4) fire, (5) security, (6) health hygiene, (7) pollution and (8) product liability. Each of these areas is treated as follows:

(1) identification – of possible loss producing situations;
(2) measurement – of such losses;
(3) selection – of methods to minimize loss;
(4) implementation – of methods within the capability of the organization.

The application of total loss control in the chemical industry has been described by Webster (1974), Hearfield (1975) and Ling (1976, 1979).

In the company described by Hearfield, incidents reported in 1 year on a particular plant cost about £25,000, including consequential losses. It was estimated that if all the unreported incidents had been included, this figure might have been double. A total loss control programme was instituted, which revealed that the estimated loss in the works was about £350,000. One source of loss on the plant was associated with steam condensate systems. Following an incident involving condensate, a full plant investigation of the use of condensate and demineralized water was undertaken. A 20% deficiency in the demineralized water balance was reported. It was found that the orifice plate was completely missing from one of the water flowmeters. The investigation was extended to the works. Expenditure of £40,000 was incurred on pipework and instrumentation modification. In the first year of operation, savings of £130,000 were made due to reduced consumption of demineralized water, and capital expenditure of £200,000 on new demineralization plant was deferred.

1.8 Quality Assurance

Another development that shapes the modern approach to SLP is quality assurance and total quality management (TQM). Methods of ensuring that a product meets the required quality standards are the province of quality control and quality assurance. The first of these terms in particular tends to be used with different meanings.

Quality control of products has long been standard practice in a range of industries, from those manufacturing cars to those making ice cream. In many cases, the emphasis in such quality control has traditionally been on inspection of the product.

The creation of systems to ensure that the product meets the required standards is the role of *quality assurance*. These systems are applied not only to the intermediate and final products made within the company but also to the inputs, raw materials and products purchased from outside, since unless these meet their specifications, it may be impossible for the company to meet its own quality standards.

The 1980s have seen a strong movement in industry worldwide to adopt quality assurance systems and to seek accreditation to a recognized standard. The international standard is ISO 9000 and the corresponding British Standard is BS 5750:1987:Quality Systems. As just indicated, a move by one firm to seek accreditation creates a chain reaction that obliges its suppliers to do likewise. Adoption of quality assurance involves the creation, and documentation, of a set of systems designed to ensure quality outputs from all the activities of the company.

1.9 Total Quality Management

A related, but not identical, development is TQM. The concept underlying TQM is that the problem of failures and their effects has an influence on company performance that is far greater than is generally appreciated, defining failure in a broad way. TQM has its origins in quality control on production lines. It has spread to industry generally, including the process industries.

Most accounts of TQM highlight the role played by a number of individuals who have been influential in its development. Some principal texts are *Quality is Free* (Crosby, 1979), *Quality Control Handbook* (Juran, 1979), *Quality Planning and Analysis* (Juran and Gryna, 1980),

Quality, Productivity and Competitive Position (Deming, 1982) and *Out of the Crisis* (Deming, 1986). An overview, including an account of the different schools, is given in *Total Quality Management* (Oakland, 1989).

The TQM approach has been pioneered in Japan, particularly in the motor industry. Accounts of the Japanese approach are given by Ishikawa Kaoru (1976, 1985), Taguchi (1979, 1981) and Singo Shigeo (1986).

In many countries, industry is well advanced with the adoption of TQM concepts. Worldwide this typically involves implementation of the requirements of ISO 9000. Guidance on this process is given in ISO 9000 (P.L. Johnson, 1993). In the United Kingdom, the relevant standard to which organizations are accredited is BS 5750 : 1987. Guidance is given in *Implementing BS 5750* (Holmes, 1991). A guide to the associated audit is *Quality Management System Audit* (C.A. Moore, 1992).

As stated earlier, the basic concept of TQM is that failures of various kinds have effects which are much more widespread, damaging and costly than has been generally appreciated. Failures have effects both internal and external to the company. The internal effects experienced by the company include loss of production, waste of materials, damage to equipment and inefficient use of manpower. The external effects experienced by the customer include the same features. Failures undermine the competitiveness of both parties.

The starting point in tackling this problem is to review the product that is required and the system that is to produce it. The requirement for the product is 'fitness for purpose'. In determining fitness for purpose, it is necessary to consider both the effectiveness of the product while it is operating and its reliability of operation. In order to achieve fitness for purpose, it is necessary to ensure that the design of the product is suitable and that the product made conforms to that design. These are two separate aspects and success depends on getting them both right. It is of little use to make a product that conforms well with the design if the design is defective, or to make a product that has a good design but which is produced in such a way that it does not conform to that design.

Given a product that is well designed, it is necessary to consider the system that will deliver conformability to the design. Traditionally, industry has placed much emphasis on an approach to quality control based on inspection. The approach taken in TQM is radically different. The attempt to inspect quality into an inherently defective production process is regarded as ineffective. Instead, the emphasis is on prevention. The basic question asked therefore, is whether the production process is actually capable of producing to the quality required. In many cases it has been concluded that it was not. Attempts were being made to deal with the situation by intensifying the inspection effort, attempts that were largely futile.

The spirit of the TQM approach has been summarized in *Right First Time* (F. Price, 1985) as:

(1) Can we make it OK?
(2) Are we making it OK?
(3) Have we made it OK?
(4) Could we make it better?

The TQM approach seeks to root out failures in all aspects of the company's operation, not just failures of equipment but also in all aspects of the company's operation, including systems, documentation, communications, purchasing and maintenance. TQM is therefore concerned with both products and activities. In assessing the quality of a product or activity, it seeks to identify the 'customers' and to make sure that their requirements are properly defined and met. An important technique for reducing failures is the involvement of the workforce, who are encouraged to not allow failures to persist but to report them and make proposals for their elimination.

The prime responsibility for TQM lies with management, and management leadership is essential to its success. It is management that is responsible for the necessary features such as organization, personnel, systems, design, planning and training. All employees are involved, however, in dealing with failure. An important part of TQM, therefore, is the involvement and motivation of the workforce. The quality circles (QCs) developed in Japan are an example of this. Another aspect of TQM is the 'just-in-time' (JIT) approach developed in Japan, notably in the motor industry. Each section of the production line operates with little or no inventory of input components, but takes them as required from the upstream supplier. This system requires an intolerance of failure, with rapid detection and rectification.

One way of expressing this intolerance is to adopt 'zero defects' as the performance standard, as advocated by Crosby (1979). In the variant of TQM given by Crosby, the overall approach adopted is summarized as:

Definition	Conformance to requirements
System	Prevention
Performance standard	Zero defects
Measurement	Price of non-conformance

It will be apparent that, insofar as the process industries are concerned, this emphasis on, and intolerance of, failures constitutes an approach very close to that of loss prevention.

Accounts of the relationship between quality management and management of safety, health and environment have been given by Berkey, Dowd and Jones (1993), Rooney, Smith and Arendt (1993) and Olsen (1994).

1.10 Risk Management

Another related development is that of risk management. Any industrial project involves risk. But some of the developments described above, such as the increase in the technological dimension and the growth of public concern over safety and pollution, have tended to introduce further dimensions of unpredictability. Risk management addresses these latter risks and provides a means of assessing and managing them along with the normal commercial risks.

Accounts of risk management are given in *Managing Risks* (Grose, 1987), *Risk Management* (Jardine Insurance Brokers Ltd, 1988), *Managing Risk* (Bannister, 1989), *Risk Assessment and Risk Management for the Chemical Process Industry* (Greenberg and Cramer, 1991) and *Reliability, Safety and Risk Management* (S.J. Cox and Tait, 1991), and by Turney (1990a,b) and Frohlich and Rosen (1992b).

The variety of risks and the vulnerability of a business to these risks is now such that they need to be managed explicitly. Individual risks are recognized by line managers, but are frequently not fully addressed by them. There is a

tendency to defer consideration and to take too optimistic a view. In any case, the individual line manager sees only part of the picture. It is for such reasons that risk management has emerged as a discipline in its own right. A systematic review of hazards is now normal practice in the management of projects in the process industries. A complementary system for the review of the totality of risks (commercial, legal and technological) is increasingly common.

1.11 Safety-critical Systems

Another concept that is gaining increasing prominence is that of safety-critical systems. These are the systems critical to the safe operation of some larger system, whether this be a nuclear power station or a vehicle. In a modern aircraft, particularly of the fly-by-wire type, the computer system is safety critical. An account of safety critical systems is given by P.A. Bennett (1991a,b).

1.12 Environment

Another major concern of the process industries is the protection of the environment. Developments in environmental protection (EP) have run in parallel with those in SLP. These two aspects of process plant design and operation have much in common. In recent years, there has been a trend to assign to the same person responsibilities for both. There are also some situations where there is a potential conflict between the two. The environment, and pollution of the environment, are considered in Appendix 11.

1.13 Professional Institutions and Bodies

The professional engineering institutions have responded to the problems described above with a number of initiatives.

1.14 Responsible Care

In a number of countries, the chemical industry has responded to safety, health and environmental concerns with the Responsible Care initiative, which was developed in the early 1980s by the Canadian Chemical Producers Association and was then taken up in 1988 in the United States by the ACC, in 1989 in the United Kingdom by the Chemical Industries Association (CIA), and elsewhere.

Companies participating in Responsible Care commit themselves to achieving certain standards in terms of safety, health and environment. Guidance is given in *Responsible Care* (CIA, 1992 RC53) and *Responsible Care Management Systems* (CIA, 1992 RC51). An account of the development of Responsible Care is given by Jacob (1992). The Canadian perspective is described by Buzzelli (1990) and Creedy (1990).

As stated earlier, in 1973, the IChemE created a Loss Prevention Panel. The Institution itself publishes a range of monographs and books on SLP and the panel publishes the Loss Prevention Bulletin and a range of aids for teaching and training.

In 1985, the AIChE formed the CCPS. The Centre publishes a series of guidelines on SLP issues.

At the European level, the European Process Safety Centre (EPSC) was set up in 1992 to disseminate information on safety matters, including legislation, research and development, and education and training (EPSC, 1993).

The work of these and other bodies is described in Chapter 27. Much of the material referred to in this book derives from these sources.

1.15 Academic and Research Activities

Over the years, academic and research activities aimed at process SLP have ebbed and flowed. However, lately these activities are becoming more formalized. Engineering departments in various universities throughout the world have begun to realize the importance of the subject and the significant role they can play in educating the students and the solution of industry problems through fundamental research. Many universities in the United States, United Kingdom, elsewhere in Europe, Japan, Korea, and other countries now offer specialized courses, certificate programmes, and degree programmes on process SLP. In some universities, for example Texas A&M University and University of South Carolina, process safety courses instead of being optional electives are now part of the required core curriculum. University professors and researchers are also dedicating extensive efforts towards research topics on process SLP. With regard to academic and research activities, the Mary Kay O'Connor Process Safety Center at Texas A&M University is a classic example of a comprehensive academic and research programme dedicated to education, research and service activities on process SLP.

1.16 Overview

The modern approach to the avoidance of injury and loss in the process industries is the outcome of the various developments just described. Central to this approach is leadership by management, starting with senior management, and creation of a safety culture that provides the appropriate environment for reduction of incidents and improvement of safety performance. Such leadership and safety culture are indispensable conditions for success. They are not, however, sufficient conditions. Management must also identify the right objectives. The contribution of total loss control, quality assurance and TQM is to identify as key management objectives the elimination of failures of all kinds and the conduct of activities so that they are satisfactory to those affected by them. These disciplines provide in QCs a tool for meeting these objectives.

As far as the process industries are concerned, it is the contribution of loss prevention to handle the technological dimension and to provide methods by which failure is eliminated. In the modern approach to SLP, these themes come together. The ends are the safety of personnel and the avoidance of loss. The means to achieve both these aims is leadership by management, informed by an understanding of the technology and directed to elimination of failures of all kinds.

2 Hazard, Incident and Loss

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A rational approach to loss prevention must be based on an understanding of the nature of incidents and of the types of loss that actually occur. Therefore, in this chapter, first the nature of the incident process is considered and then the incident and loss statistics are reviewed to give an indication of the problem. Selected references on incident and loss experience are given in Table 2.1. In addition, many other tables of data are given in other chapters. Cross-references to some of these tables are given in Table 2.2.

2.1 The Incident Process

There are certain themes that recur in the investigation of incidents and which reveal much about the incident process. First, although in some reporting schemes the investigator is required to determine the cause of the incident, it frequently appears meaningless to assign a single cause as the incident has arisen from a particular combination of circumstances. Second, it is often found that the incident has been preceded by other incidents that have been 'near-misses'. These are cases where most but not all of the conditions for the incident were met. A third characteristic of incidents is that when the critical event has occurred, there are wide variations in the consequences. In one case there may be no injury or damage, while in another case that is similar in most respects, there is some key circumstance that results in severe loss of life or property. These and other features of incidents are discussed in *Man-Made Disasters* (B.A. Turner, 1978). It is in the nature of disasters that they tend to occur only as the result of the combination of a number of events and to have a long incubation period before such a conjunction occurs.

It is helpful to model the incident process in order to understand more clearly the factors that contribute to incidents and the steps that can be taken to avoid them. One type of model, discussed by Houston (1971), is the classical one developed by lawyers and insurers that focuses attention on the 'proximate cause'. It is recognized that many factors contribute to an incident, but for

Table 2.1 *Selected references on incident and loss experience*

Natural and man-made hazards, disasters
Thygerson (1972, 1977); Walker (1973); G.F. White (1974); Bignell *et al.* (1977); Miinchener Ruck (1978); B.A. Turner (1978); ASCE (1979/9); Ferrara (1979); Whittow (1980); Perry (1981); Rossi *et al.* (1983); Simkim and Fiske (1983); Perrow (1984); Wijkman and Timberlake (1984); McWhirter (1985); Cairns (1986); Sir R. Jackson (1986); E.A. Bryant (1991); Guinness Publishing Co. (1991); K. Smith (1992); R. Smith (1992); Arnold (1993)

Process hazards, incidents
Matheson (1960); Vervalin (1964a, 1973a); BCISC (1968/7); Fowler and Spiegelman (1968); W.H. Doyle (1969); Spiegelman (1969, 1980); Chemical Industries Association (CIA) (1970/3); Cornett and Jones (1970); Rasbash (1970b); Houston (1971); H.D. Taylor and Redpath (1971, 1972); R.L. Browning (1973); Walker (1973); Fire Protection Associa- tion (FPA) (1974b, 1976); AFC (1975); N. McWhirter (1976); J.R. Nash (1976); McIntire (1977); AIA (1979); Harvey (1979); Carson and Mumford (1979); Ferrara (1979); R. King and Magid (1979); Kletz and Turner (1979); Lees (1980); Pastorini *et al.* (1980); Mance (1984); Manuele (1984 LPB 58); Hawkins (1985); D. McWhirter (1985); APCA (1986); Kletz (1986b); V.C. Marshall (1986a, 1988c); Garrison (1988a,b); Instone (1989); Mahoney (1990); Anon. (1991 LPB 99, p. 1); O'Donovan (1991 LPB 99); K.N. Palmer (1991 LPB 99); Guinness Publishing Co. (1991); Marsh and McLennan (1992); Pastorini *et al.* (1992); Bisio (1993); O'Shima (1993); Crooks (1994 LPB 115)

Incident models
Surry (1969b); Houston (1971); Macdonald (1972); Haddon (1973a,b); W.G. Johnson (1973a,b, 1980); de Jong (1980); Rasmussen (1982b, 1983); Haastrup (1983); Benner (1984); A.R. Hale and Glendon (1987); Wells *et al.* (1991); Bond (1994 LPB 120)

Incident ranking
Keller *et al.* (1990); Keller and Wilson (1991)

Annual or periodic reports, statistical summaries
AGA (Appendix 28 Pipeline Incident Reports); American Petroleum Institute (API; Appendix 28 Annual Summaries); BIA (annual report); BRE (annual statistics, Appendix 28 UK Fire and Loss Statistics); FPA (annual report); HM Chief Inspector of Explosives (annual report); HM Chief Inspector of Factories (HMCIF; annual report, annual analysis of accidents); HM Senior Electrical Inspector of Factories (annual report); M&M Protection Consultants (periodic); National Transportation Safety Board (NTSB; Appendix 28); NSC (n.d./l); ABCM (1930–64/2); MCA (1962–/1–4, 1971–/20, 1975-/23); BCISC (1965–/4); Chemical Industry Safety and Health Council (CISHC) (1975–/5); CONCAWE (1977 9/77, 1992 4/92); HSC (1977); Health and Safety Executive (HSE) (1977d, 1986c, 1992b); ILO (1992)

Fire
BRE (annual statistics); FPA (annual report, 1974, 1976, 1991); W.H. Doyle (1969); Spiegelman (1969, 1980); H.D. Taylor and Redpath (1971, 1972); FRS (1972 Fire Research Note 920); P. Nash (1972b); Vervalin (1963a, 1972c, 1973a, 1974a, 1975c, 1976b, 1977, 1978a,b, 1986b); Duff (1975); Redpath (1976); Rutstein (1979a,b); Rutstein and Clarke (1979); Banks and Rardin (1982); Norstrom (1982a); Gebhardt (1984); Uehara and Hasegawa (1986); Mahoney (1990); Home Office (1992)

Explosion
Eggleston (1967); Doyle (1969); Spiegelman (1969, 1980); Duff (1975); Davenport (1977b, 1981b); Norstrom (1982b); Uehara and Hasegawa (1986); Vervalin (1986b); Mahoney (1990); Lenoir and Davenport (1993)

Refineries
Anon. (1970a); McFatter (1972); W.L. Nelson (1974); McIntire (1977); Mahoney (1990)

Ammonia plants
Holroyd (1967); Axelrod *et al.* (1968); Sawyer *et al.* (1972); G.P. Williams and Sawyer (1974); G.P. Williams (1978); G.P. Williams and Hoehing (1983); G.P. Williams *et al.* (1987)

Educational institutions
Bowes (1985)

Table 2.2 *Cross-references to other incident and loss data*

Major fires	Section 16.38
Major condensed phase explosions	Table 17.24; Appendix 1
Major vapour cloud explosions (VCEs)	Section 17.28; Table 17.30
Major boiling liquid expanding vapour explosions (BLEVEs)	Section 17.29; Table 17.37
Major missile incidents	Section 17.34; Table 17.49
Major dust explosions	Section 17.43; Table 17.63
Major toxic releases	Section 18.27; Tables 18.30, 18.31
Case histories	Appendix 1
Failure data	Appendix 14

practical, and particularly for legal, purposes, a principal cause is identified. This approach has a number of defects: there is no objective criterion for distinguishing the principal cause; the relationships between causes are not explained; and there is no way of knowing if the cause list is complete.

There is need for incident models that bring out with greater clarity the common pattern in incidents. Some models of the incident process that may be helpful in incident investigation and prevention are given below, with emphasis on the management and engineering aspects. Further incident models are discussed in Chapters 26–28 and incident investigation procedures are given in Chapter 31. However, irrespective of the incident model used for incident investigation, it is essential that investigations result in the identification of root causes, and recommendations are identified and implemented that target root causes. For example, take the case of a guillotine rupture of a gas pipeline caused by a construction crew. The subsequent gas release accumulates for an extended period of time and ultimately is ignited resulting in an explosion and fire causing multiple fatalities, injuries and extensive loss of property. For the investigation to focus on just how the rupture was caused defeats the purpose of incident investigation completely. In other words, dramatically different answers are obtained when the incident investigation tries to answer any one the following questions:

(1) Why did the rupture occur? OR
(2) Why did the explosion and fire occur? OR
(3) Why did the people die or get hurt?

An investigation trying to answer the first question will quite clearly identify flaws with the construction and digging procedures and may well come up with recommendations aimed at correcting those deficiencies. However, that does not answer the question of why did the explosion and fire occur. An investigation that tries to answer this second question assumes that irrespective of pipeline operating procedures, how should pipeline systems be designed and operated so that the probability of explosions and fires are minimized to the lowest extent possible. Thus, recommendations resulting from such an investigation would identify flaws in the design and operation of the pipeline system. Issues such as engineered systems capable of shutting the flow of gas in a reasonably short period of time would be addressed in answering this second question.

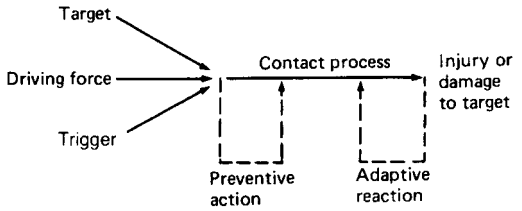

Figure 2.1 *Houston model of the accident process (after Houston, 1977)*

An investigation that tries to answer the third question opens up a lot of additional issues that are also very important. Not only is the design and operation of the pipeline system analysed, but also issues such as emergency response and evacuation of the affected area would be addressed. After all it is a very relevant question to ask that irrespective of the causes of the rupture and accumulation of the gas, was not there any way to evacuate the personnel or respond to their plight in order to reduce or eliminate the casualties.

2.1.1 The Houston model

The model given by Houston (1971, 1977) is shown schematically in Figure 2.1. Three input factors are necessary for the incident to occur: (1) target, (2) driving force and (3) trigger. Principal driving forces are energy and toxins. The target has a threshold intensity θ below which the driving force has no effect. The trigger also has a threshold level θ' below which it does not operate.

The development of the incident is determined by a number of parameters. The contact probability p is the probability that all the necessary input factors are present. The contact efficiency ε defines the fraction of the driving force that actually reaches the target, and the contact effectiveness η is the ratio of damage done to the target under the actual conditions to that done under standard conditions. The contact time t is the duration of the process.

The model indicates a number of ways in which the probability or severity of the incident may be reduced. One of the input factors (target, driving force or trigger) may be removed. The contact probability may be minimized by preventive action. The contact efficiency and contact effectiveness may be reduced by adaptive reaction.

Work by Haddon (1973a,b) emphasizes prevention of incidents by control of the energy. His list of energy control strategies is given in Table 2.3. Failure of one or more of these modes of control is a normal feature of an incident and hence of incident models.

2.1.2 The fault tree model

A simple fault tree model of an incident is given in Figure 2.2. An initiating event occurs which constitutes a potential incident, but often only if some enabling event occurs, or has already occurred. This part of the tree is the 'demand' tree, since it puts a demand on the protective features. The potential incident is realized only if prevention by protec-tive equipment and human action fails. An incident occurs that develops into a more severe incident only if mitigation fails.

A somewhat similar model has been proposed by Wells *et al.* (1992).

Table 2.3 *Some energy control strategies (after Haddon, 1973a)*

(1)	To prevent the initial marshalling of the form of energy
(2)	To reduce the amount of energy marshalled
(3)	To prevent the release of energy
(4)	To modify the rate or spatial distribution of release of energy from its source
(5)	To separate in space or time the energy being released from the susceptible structure
(6)	To separate the energy being released from the susceptible structure by interposition of a material barrier
(7)	To modify the contact surface, subsurface, or basic structure which can be impacted
(8)	To strengthen the living or non-living structure which might be damaged by energy transfer
(9)	To move rapidly in detection and evaluation of damage and to counter its continuation and extension
(10)	All those measures which fall between the emergency period following the damaging energy exchange and the final stabilization of the process (including intermediate and long-term reparative rehabilitative measures)

2.1.3 The MORT model

A more complex fault tree model is that used in the management oversight and risk tree (MORT) developed by W.G. Johnson (1980) and shown in Figure 2.3. This tree is the basis of a complete safety system, which is described further in Chapter 28.

2.1.4 The Rasmussen model

Incident models that show the role of human error have been developed by Rasmussen (1982a,b). Figure 2.4 shows such a model. The role of human error in causing incidents is considered in more detail in Chapter 14.

2.1.5 The ACSNI model

Figure 2.5 shows a model proposed by the Advisory Committee on the Safety of Nuclear Installations (ACSNI, 1991). The model provides a general framework that can be used to identify latent failures that are likely to lead to critical errors.

2.1.6 The Bellamy and Geyer model

A model that emphasizes the broader, socio-technical background to incidents has been developed by Geyer and Bellamy (1991) as shown in Figure 2.6. Figure 2.6(a) gives the generic model and Figure 2.6(b) shows the application of the model to a refinery incident.

2.1.7 The Kletz model

Another approach is that taken by Kletz (1988h), who has developed a model oriented to incident investigation. The model is based essentially on the sequence of decisions and actions that lead up to an incident, and shows against each step the recommendations arising from the investigation. An example is shown in Figure 2.7, which refers to an incident involving a small fire on a pump.

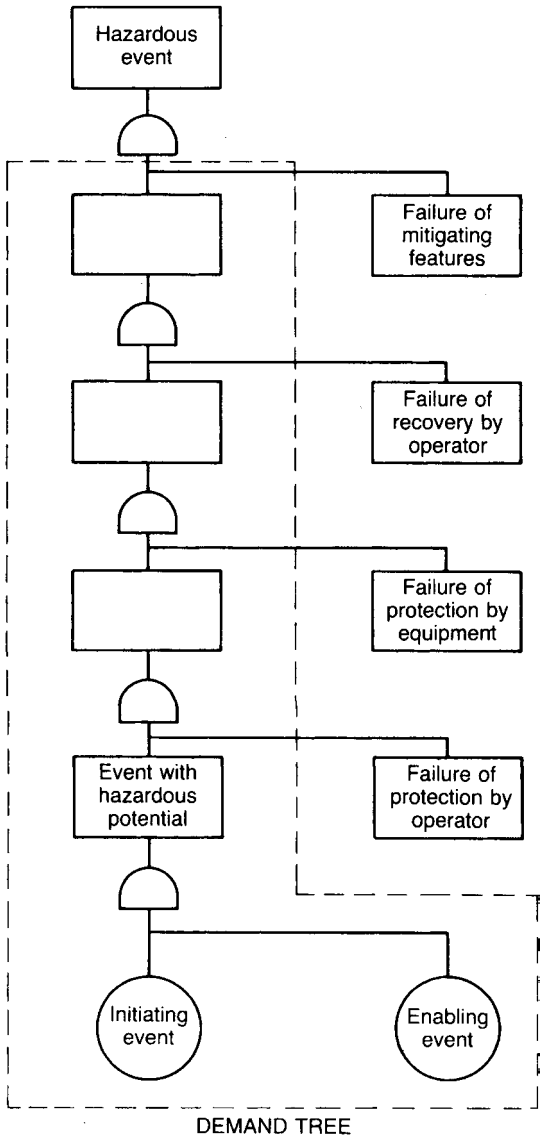

Figure 2.2 *Fault tree model of the accident process*

2.2 Standard Industrial Classification

Statistics of injuries and damage in the United Kingdom are generally classified according to the Standard Industrial Classification 1980 (SIC 80). In this classification, the classes relevant here are: Class 1 Energy and water industries; Class 2 Extraction of minerals and ores other than fuels, manufacture of metals, mineral products and chemicals; Class 3 Metal goods, engineering and vehicles industries; and Class 4 Other manufacturing industries. The mineral oil processing industry falls into Class 1, Subclass 14, and the chemical industry in Class 2, Subclass 25.

In the United States as well, incident and damage statistics are compiled by SIC codes. However, the difference with

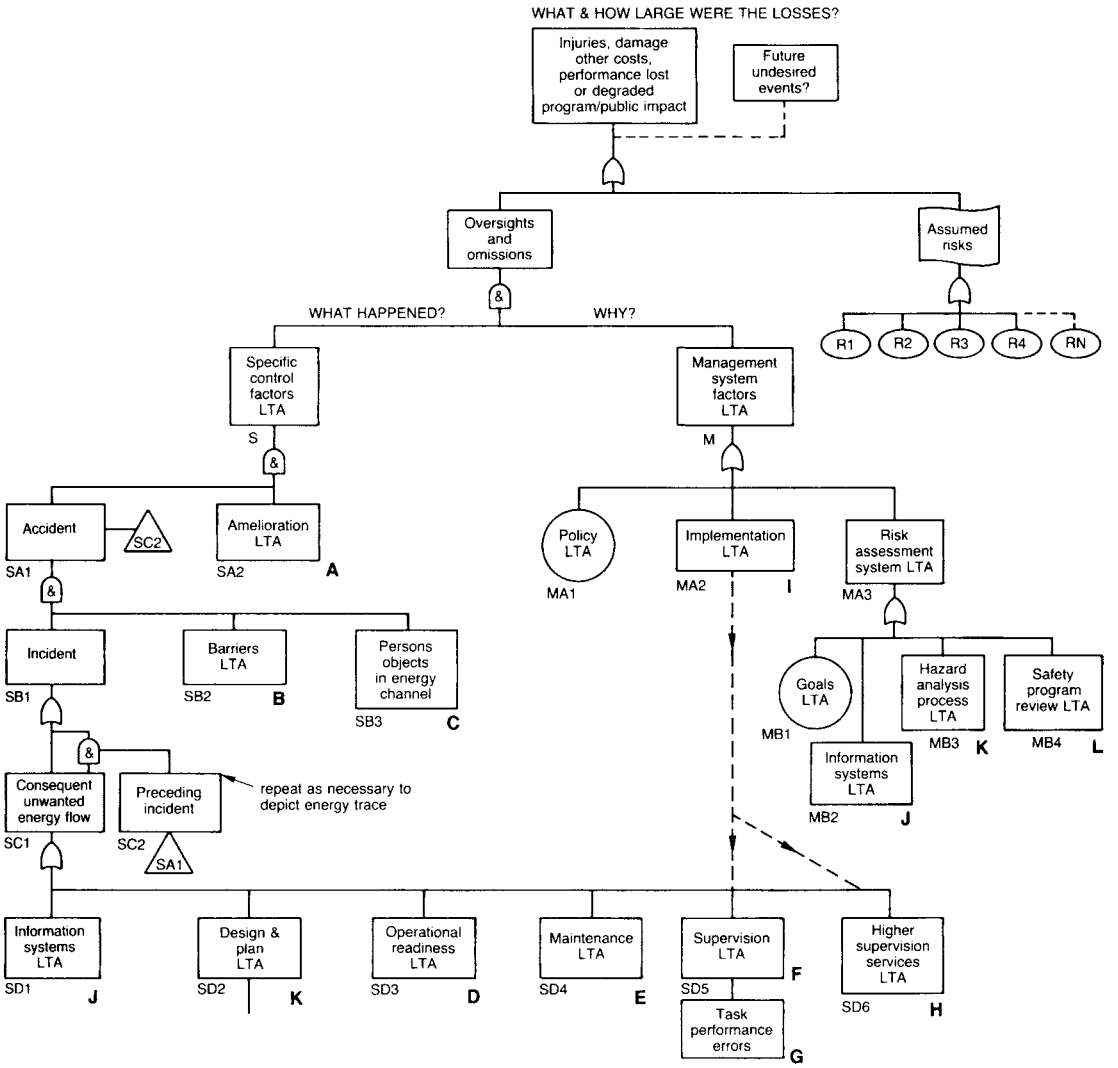

Figure 2.3 *MORT model of the accident process (W.G. Johnson, 1980). The letter A–H refer to further subtrees. LTA, less than adequate (Courtesy of Marcel Dekker)*

United Kingdom is that in the United States, the statistics are compiled by different agencies each of which has different incident definitions and incident taxonomy. A vast amount of data is available in these incident databases and statistics; however, the user must be careful and experienced in dealing with the respective anomalies and inaccuracies of each one of these databases. More details of the advantages and problems associated with these databases are discussed in the next section.

2.3 Injury Statistics

2.3.1 United States of America

In the United States, many federal agencies gather information about the chemical industry. Under statutory mandate, the agencies gather data on releases of chemicals, and on injuries, illnesses and fatalities caused by chemicals. These federal databases, some of which have received information for over three decades, may provide the information needed to develop trends of chemical-related incidents. However, despite the magnitude of data available, chemical industry stakeholders cannot answer the question, 'How do we assess the status of chemical safety in the United States?' In 1995, the US Environmental Protection Agency (EPA) stated in its *Users Guide to Federal Accidental Release Databases*, 'The existence of many different (and often incompatible) federal databases makes it difficult to develop a national picture of the problem of accidental releases'. EPA also determined that federal databases do not provide comparable data sets. This has inhibited data interpretation, comparative analysis and cross agency use of accident data.

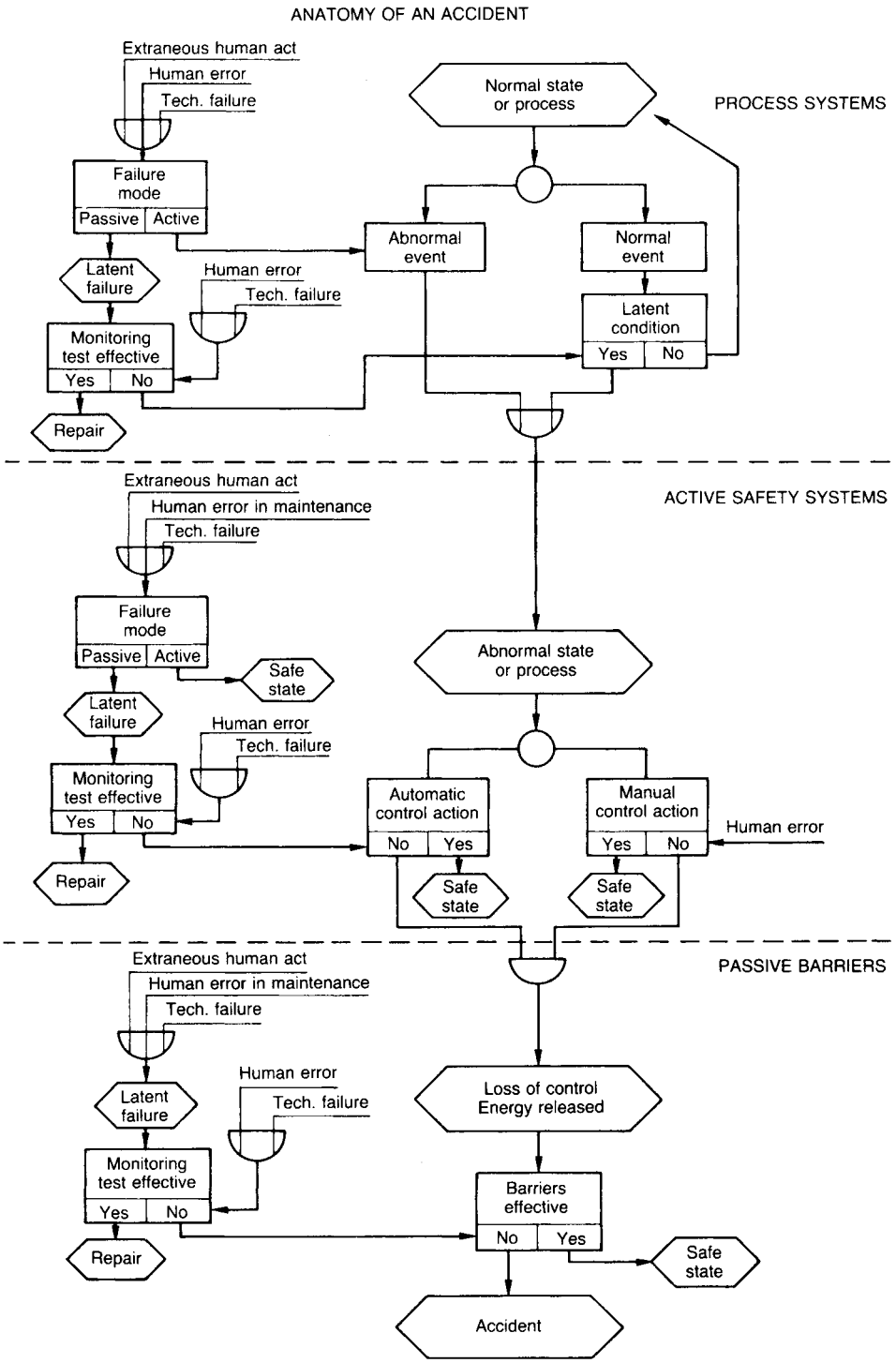

Figure 2.4 *Rasmussen model of the accident process (Rasmussen, 1982b) (Reproduced by permission from High Risk Safety Technology by A.E. Green, copyright John Wiley)*

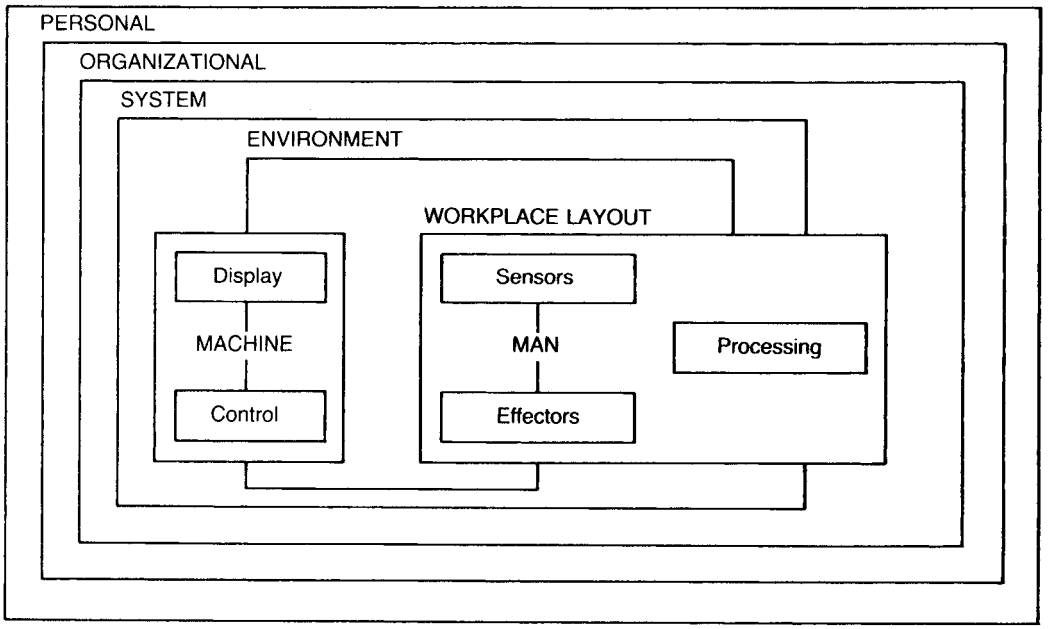

Figure 2.5 *ACSNI model of the accident process (ACSNI, 1991) (Courtesy of HM Stationery Office)*

Six US federal databases provide information about incidents and incident statistics related to chemical safety at fixed facilities. They are:

National Response Center's (NRC) Incident Reporting Information System (IRIS)

Covered Universe IRIS contains data on reported releases from fixed facilities, marine/offshore facilities, pipelines and transportation vehicles. Many federal statutes require reporting of releases to the NRC. Oil spills are reported under:

(1) Section 311(b) of the Federal Water Pollution Control Act of 1973;
(2) Section 306(a) of the Outer Shelf Lands Act Amendments of 1978; and
(3) Section 18(b) of the Deepwater Ports Act of 1974.

Chemical spills are reported under:

(1) Section 302 of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980;
(2) Section 304 of the Emergency Planning and Community Right-to-Know Act of 1986; and
(3) Federal Hazardous Materials Transportations Laws.

Pipeline spills are reported under the Hazardous Liquid Pipeline Safety Act.
Air releases are reported under:

(1) Clean Air Act;
(2) Toxic Substances Control Act;
(3) Federal Hazardous Materials Transportations Law and
(4) Resource Conservation and Recovery Act.

Collection Method This database is primarily used for emergency response notification and is operated 24 h a day, 7 days a week. The initial notification of a release is usually by telephone. These reports are comprised of primarily short answer questions.
Principal Data Elements The database contains data on oil, chemical, biological and etiological discharges into the environment anywhere in the United States or its territories. The NRC collects information nationally on reports of hazardous material releases, as well as releases of hazardous substances and oil from fixed facility and transportation incidents. Two files, INCRPT and MATRPT, compose the IRIS database. The INCRPT file contains information about the location of the release, the company owner of the facility (when it applies), a short description of the incident, and the information related to the consequences (affected medium, fatalities, injuries, evacuations, cost of damages) of the incident. No information regarding the released substance is reported in this file. The MATRPT file contains the information related to the chemical substance(s) involved in the incident (name of the substance, CHRIS code, and quantity and phase of the released chemical).
Strengths NRC handles approximately 300,000 telephone calls each year, of which approximately 25,000 are unique incidents. Coverage of such a large number of incidents provides the potential for statistical analysis to capture meaningful trends.
Weaknesses While reporting to the NRC is required by a number of statutes, it also receives numerous 'complaints' from the public. In addition, practice drills for emergency

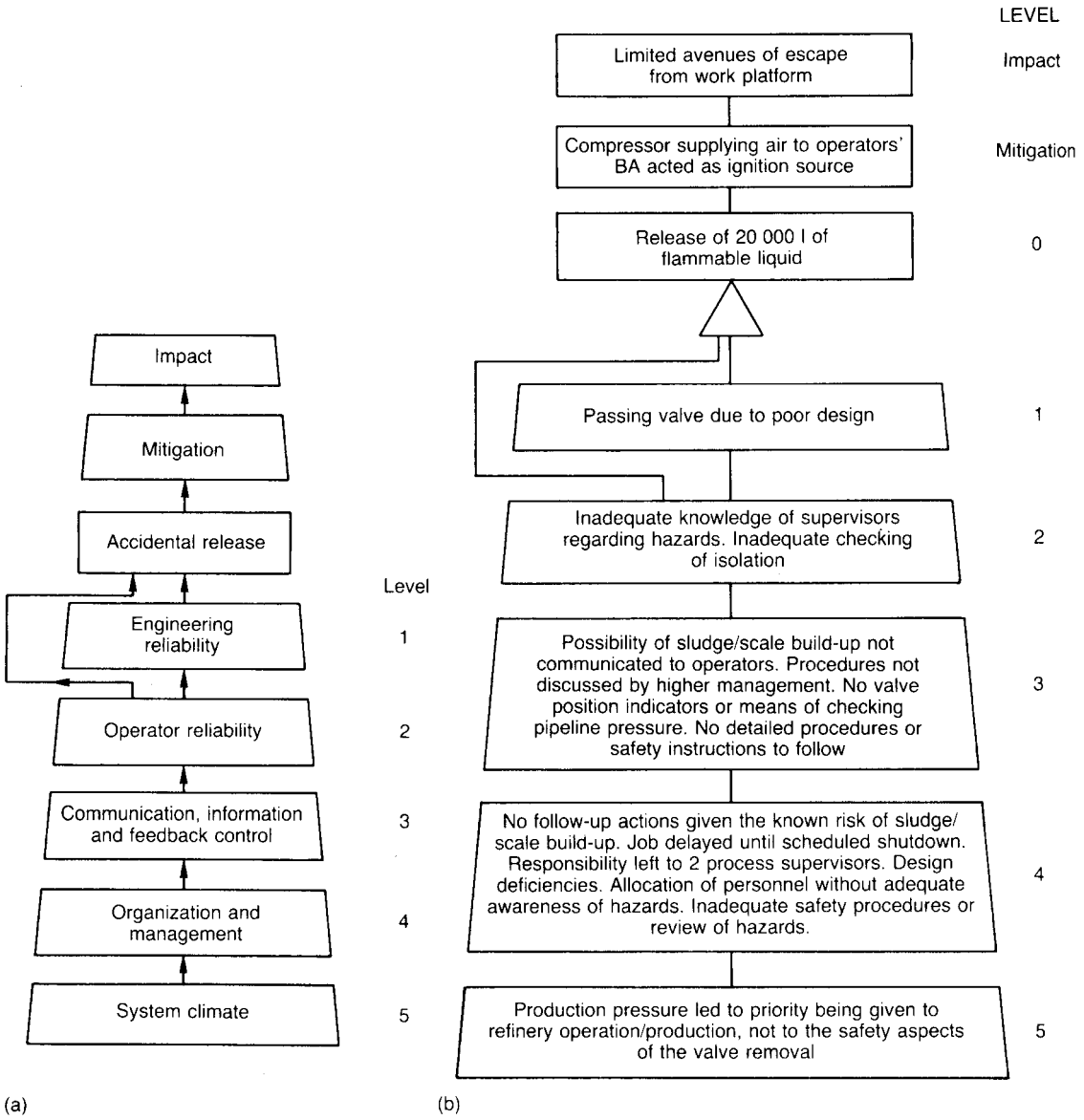

Figure 2.6 *Bellamy and Geyer model of the accident process: (a) generic model; (b) model applied to a refinery incident (Geyer and Bellamy, 1991) (Courtesy of the Health and Safety Executive)*

releases are captured in the database. The NRC also collects in the same database non-chemical-related events such as railroad crossing accidents. Also, both actual and potential releases may be reported to IRIS. Many of the reported incidents are spills of fuel from motor vehicles, small spills of low hazard materials such as lubricating oil and oil sheens on water with unknown sources, quantities and effects. Because this system contains initial reports, the information is preliminary and many times inaccurate or incomplete. There is also duplicate reporting of incidents. The completeness and accuracy of chemical names depend on the knowledge level of the person reporting the incident.

EPA's Risk Management Program (RMP) Rule's 5-year Accident History Database

Covered Universe RMP-covered facilities that have released a listed substance, which is stored above a threshold

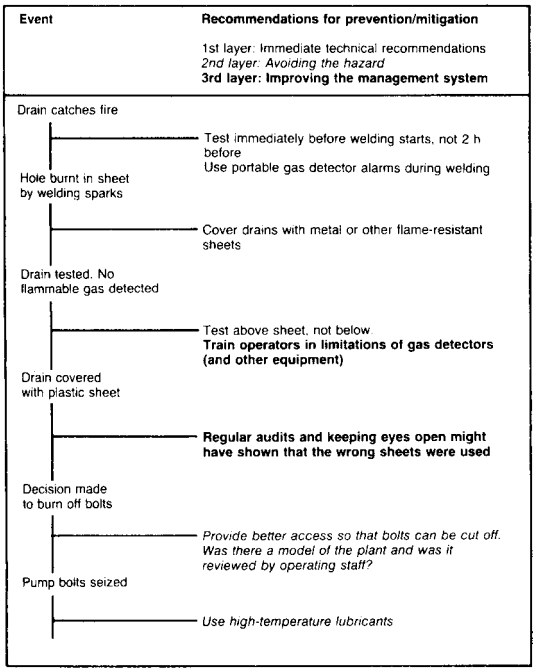

Figure 2.7 *Kletz model of the accident process (Kletz, 1988h) (Courtesy of Butterworths)*

quantity and results in fatalities, injuries, or significant environmental or property damage are required to report 5-year accident histories.
Collection Method 5-year Accident History Report.
Principal Data Elements It contains information on RMP-covered facilities that meet the reporting criteria listed in the 'Covered Universe'. The facility must provide EPA with the following information:

(1) date, time and approximate duration of the release;
(2) chemical(s) released;
(3) estimated quantity released in pounds;
(4) type of release event and its source;
(5) weather conditions, if known;
(6) on-site impacts;
(7) known off-site impacts;
(8) initiating event and contributing factors if known;
(9) whether off-site responders were notified if known; and
(10) operational or process changes that resulted from investigation of the release.

Strengths The reporting is from a well-defined universe of facilities and it allows statistical treatment of the frequency of releases per facility or process unit that is not available from other systems. The reports do address such items as the causes and consequences of the release and steps taken to prevent or mitigate future incidents. Future data from EPA's 5-year Accident History Database may provide more information to be able to determine statistically significant trends and the effects of implementing EPA's RMP Rule and Occupational Safety and Health Administration (OSHA)'s Process Safety Management (PSM) Standard of Highly Hazardous Chemicals, which were promulgated to improve safety in the chemical industry.
Weaknesses The database is limited to RMP-covered facilities that have experienced an incident with a consequence involving a listed chemical stored above its threshold quantity. The reporting criteria excludes a large number of incidents. As a result, only 1900 releases are reported from about 14,500 facilities for the 5-year period. Of the 1900 releases, only 1500 were required to be reported, because 400 of the incidents were without consequences. The RMP data is currently only available in 5-year cycles beginning in 1994. By limiting reporting to cases with consequences, a great deal of information is lost about releases without consequences. Releases without consequences or near misses provide valuable information on how to prevent incidents and the ability to predict possible consequences. There may be corrections and revisions to RMP* Info at any time through submission by a facility of a corrected RMP. It is critical in performing analysis to report the date of last revision and any notable modifications to the data.

EPA's Accidental Release Information Program (ARIP) Database

Covered Universe Facilities were asked by EPA to provide information to the ARIP database if the facility reported an incident to EPA's Emergency Response Notification System and the release event met one or more of the following criteria:

(1) the release resulted in a death or injury;
(2) the release involved 1000 pounds or more of a hazardous substance with a reportable quantity of 1, 10 or 100 pounds, or the release involved 10,000 pounds or more of a hazardous substance with a reportable quantity of 1000 to 5000 pounds;
(3) the release was the fourteenth release in a 12-month period; or
(4) The release involved an extremely hazardous substance from Section 302 of Emergency Planning and Community Right-to-Know Act.

EPA was authorized to gather this information under:

(5) section 3007(a) of the Resource Conservation and Recovery Act;
(6) section104(b)(1) and (e) of CERCLA;
(7) section 308(a) of the Clean Water Act; and
(8) section 114 of the amended Clean Air Act.

Collection Method Facilities were requested to complete a questionnaire with 23 questions.
Principal Data Elements The ARIP database was developed by EPA in 1986 to determine the causes of accidental chemical releases, to identify the steps that could be taken by industrial facilities to prevent releases, and to outline industry prevention practices. The facilities were asked to provide information about the facility, the listed chemical, the circumstances and causes of the incident, the accidental release prevention practices and technologies in place prior to the event, and any additions or changes made to these technologies and practices as a result of the event. The questionnaire focuses on several areas of accident prevention including hazard assessments, training,

emergency response, public notification procedures, mitigation techniques, and prevention equipment and controls.
Strengths ARIP is one of the larger collections of incidents with details concerning causes, consequences, operating mode and corrective actions. ARIP has collected over 4800 release records since its inception. The data are considered accurate because the data are provided directly by facilities several months after the release when most information should be known. This system provides detailed information about causes and prevention practices not available in most other systems.
Weaknesses This programme is discontinued. No trends with time can be gathered. The chemicals reported are the ones reported to EPA under existing statutes and regulations, which tends to exclude gasoline, methane, ethane, propane and other chemicals some of which are included in the EPA 5-year Accident History database. In September 1993, EPA took steps to streamline the database by including only releases with significant off-site consequences, such as casualties, evacuations, sheltering-in-place or any other necessary precautions taken by individuals off-site as a result of a release. In addition, the questionnaire for the database has been revised over time so that some information was added and other information was deleted. Thus, analysis on some data fields cannot be performed on the entire database. In addition, the short description of the accident is not contained in the database and must be analysed in the hard copy of the questionnaire. The collection of ARIP data was dependent on the sometimes uneven collection efforts of the EPA regions; therefore, the data does not truly represent the geographical distribution of releases, nor does it reflect release trends over time.

Bureau of Labor Statistics' (BLS) Databases for the US Occupational Safety and Health Administration (OSHA)

Covered Universe All OSHA-covered facilities.
Collection Method Surveys.
Principal Data Elements The BLS database is a comprehensive statistical system covering work-related deaths, injuries and illnesses in private industry. Work-related fatalities are counted and profiled more accurately in a separate BLS table, Census of Fatal Occupational Injuries. Survey information on non-fatal incidents involving days away from work profiles:

(1) occupation and other demographics (e.g. age and gender) of workers sustaining such injuries and illnesses;
(2) the nature of these disabling conditions and how they occurred; and
(3) the resulting time away from work.

Strengths These statistics are based on an annual sampling of about 250,000 companies in the United States. There is very good detail for chemicals and industries involved in accidents, from a statistical sample, not individual incidents. The data have been collected and reported on in a consistent manner since 1992. Thus, trends from 1992 can be determined and compared with injury rates.
Weaknesses Chemical incidents are only identified for cases with days away from work. Also, the survey was redesigned between 1987 and 1992; thus, statistical analysis is limited for the years prior to 1992.

U.S. Centers for Disease Control and Prevention's (CDC) Wide-ranging On-line Data for Epidemiological Reporting (WONDER)

Covered Universe All fatalities in the United States.
Collection Method Death certificates as recorded by physicians.
Principal Data Elements This database provides the numbers of fatalities and their associated causes.
Strengths The WONDER database is useful for the purpose of determining overall trends in fatalities due to chemicals. The database allows sorting by codes that describe a class of chemicals or a type of event. It also allows sorting by the age of the deceased. This feature was used to eliminate victims under 20 years of age as it is unlikely these were industrial accidents. Unlike most other databases, a physician, who is presumably not biased when determining the cause of death, codes the data. The data is available since 1979 that provides a long and statistically significant trend.
Weaknesses The scope of incidents in WONDER is very broad and contains incidents such as a teenager huffing butane which resulted in a fatal incident, and incidents involving consumer products in residences. The data is not related to specific incidents. Public access to WONDER is limited. Thus, it is not possible to eliminate selected types of incidents. Data can only be gathered by presenting queries by the numbe of fatalities due to a certain cause in a given year by age group.

U.S. Department of Health and Human Services' Agency for Toxic Substances and Disease Registry's (ATSDR) Hazardous Substances Emergency Events Surveillance (HSEES) Database

Covered Universe Sixteen state health departments currently have cooperative agreements with ATSDR to participate in HSEES. The state health departments report an 'event' if it meets the HSEES definition, which is 'any release(s) or threatened release(s) of at least one hazardous substance'. A substance is considered hazardous if it might reasonably be expected to cause adverse human health effects. Releases of petroleum products are excluded from this system.
Collection Method Data are entered by participating state health departments into a web-based application that enables ATSDR to instantly access data for analysis.
Principal Data Elements Data collected on incidents for this database include the following:

(1) time, date and day of the week;
(2) geographical location within the facility where the event occurred;
(3) event type (fixed-facility or transportation-related event);
(4) factors contributing to the release;
(5) environmental sampling and follow-up health activities;
(6) specific information on injured persons: age, sex, type and extent of injuries, distance from spill, population group (employee, general public, responder, student) and type of protective equipment used;
(7) information about decontaminations, evacuation or shelter-in-place;
(8) land use and population information to estimate the number of persons at home or work who were potentially exposed; and
(9) whether a contingency plan was followed and which plan was used.

Strengths ATSDR has a proactive approach to incident collection that facilitates more complete and accurate reporting.
Weaknesses ATSDR's HSEES programme only covers 16 states, which vary, and excludes petroleum products. The public does not have access to the data; ATSDR provides summary reports of the data.
In the United Kingdom, incident statistics are available in the *Annual Report* of HMCIF, or its current equivalent, and the annual *Health and Safety Statistics*. The former also gives occasional detailed studies for particular industrial sectors.

2.3.2 United Kingdom

In the United Kingdom, the definition of a major injury changed with the introduction of the Reporting of Injuries, Diseases and Dangerous Occurrences Regulations 1985 (RIDDOR). The *Health and Safety Statistics 1990–91* (HSE, 1992b) show that in 1990–91 there were 572 fatalities reported under RIDDOR, of which 346 were to employees, 87 to the self-employed and 139 to members of the public. The fatal injury incidence rate for employees was 1.6 per 100,000 workers.

Major injuries to employees in 1990–91 reported under RIDDOR were 19,896 and the incidence rate was 89.9 per 100,000 workers.

For the manufacturing industry (SIC 2–4), fatalities were 88 in 1990–91 and averaged 100 in the 5-year period between 1986–87 and 1990–91 and the fatal injury incidence rate was 1.8 per 100,000 workers.

Fatal and major injuries in the oil and chemical industries in the period 1981–85, inclusive, are shown in Table 2.4. For 1990–91, the Health and Safety Statistics 1990–91 show that in the oil and chemical industries, the incidents to employees were as shown in Table 2.5.

The comparative incidence of fatalities in some principal industries and jobs in the United Kingdom is given in Table 2.6. The table shows that there is a wide variation between industries. It also shows a downward trend. The fatal accident rate of the chemical industry is approximately the same as that for all manufacturing industry. The injury statistics can be dramatically changed, however, by a single major disaster. In the process industries, the worst disaster since 1945 was the VCE at Flixborough in 1974, which killed 28 people. Offshore in the British sector of the North Sea, the Piper Alpha disaster resulted in 167 deaths. The comparative incidence of fatalities in some leading industrial countries, mainly in 1983, is given in Table 2.7.

2.4 Major Disasters

It is appropriate at this point briefly to consider major disasters. A list of the worst disasters in certain principal categories, both for the world as a whole and for the United Kingdom, is given in Table 2.8.

Those that are of primary concern in the present context are fire, explosion and toxic release. Both of the worst fires listed occurred in theatres. The explosion at Halifax which killed 1963 people was that of a ship carrying explosives. The Chilwell explosion, in which 134 people died, was in an explosives factory. The toxic gas release at Bhopal, where the death toll was some 2500, was an escape of methylisocyanate from a storage tank.

There are available a number of accounts of disasters, both natural and man-made, and these are summarized in Table 2.9. *Disasters* (Walker, 1973), *Darkest Hours* (Q.R. Nash, 1976), *Man-Made Disasters* (B.A. Turner, 1978), *The Disaster File: The 1970s* (Ferrara, 1979), *Disasters* (Whittow, 1980) and *Catastrophes and Disasters* (R. Smith, 1992) all contain large numbers of disaster case histories, including those

Table 2.4 *Fatal and major incidents in chemical and petroleum factories in the UK 1981–85 (Cox, Lees and Ang, 1990) (Courtesy of Institution of Chemical Engineers)*

A Period 1981–85: number of fatal (F) and major (M) injuries

	1981		*1982*		*1983*		*1984*		*1985*		*Total*	
	F	*M*	*F*	*M*	*F*	*M*	*F*	*M*	*F*	*M*	*F*	*M*
Chemicals	8	321	6	344	10	374	5	370	5	390	34	1799
Mineral oil processing	3	28	3	36	1	29	1	24	1	24	9	141
Total	11	349	9	380	11	403	6	394	6	414	43	1940

B Period 1981–85: incidence rates of fatal and major injuries

	Incidence per 10^5 employees				
	1981	*1982*	*1983*	*1984*	*1985*
Chemicals	89.4	100.3	115.2	112.7	117.2
Mineral oil processing	108.4	154.2	136.4	130.2	139.7

C 1984

Industry	*No. of employees*	*Fatalities*	*Major injuries*	*Fatal and major injuries per 10^5*
Chemicals	360,000	5	349	98.4
Other chemical processes	38,200	1	38	102.1
Mineral oil processing	18,200	1	14	82.4

Sources: Health and Safety Executive (1986c); HM Chief Inspector of Factories (1986a).

from the process industries. Rail incidents in the British Isles are described in *Red for Danger* (Rolt, 1982) and incidents in the process industries are described in *Chemical Industry Hazards* (V.C. Marshall, 1987).

2.5 Major Process Hazards

The major hazards with which the chemical industry is concerned are fire, explosion and toxic release. Of these three, fire is the most common but, as shown later, explosion is particularly significant in terms of fatalities and loss. As already mentioned, in the United Kingdom, the explosion at Flixborough killed 28 people, while offshore 167 men died in the explosion and fire on the Piper Alpha oil platform. Toxic release has perhaps the greatest potential to kill a large number of people. Large toxic releases are very rare but, as Bhopal indicates, the death toll can be very high. There have been no major toxic release disasters in the United Kingdom.

The problem of avoiding major hazards is essentially that of avoiding loss of containment. This includes not only preventing an escape of materials from leaks, etc., but also avoidance of an explosion inside the plant vessels and pipework. Some factors that determine the scale of the hazard are:

(1) the inventory;
(2) the energy factor;
(3) the time factor;
(4) the intensity–distance relations;
(5) the exposure factor and
(6) the intensity–damage and intensity–injury relationships.

These factors are described below.

Table 2.5 *Fatal and major injuries in the oil and chemical industries in the UK 1981–85 (after HSE, 1992b)*

Industry	*Type of incident*			
	Fatal	*Non-fatal major*	*Over 3 days*	*All reportable*
Mineral oil processing	0	33	147	180
Chemicals	5	503	3427	3935

2.5.1 The inventory

The most fundamental factor that determines the scale of the hazard is the inventory of the hazardous material. The larger the inventory of material, the greater the potential loss. As plants have grown in size and output, so inventory in process and in storage has grown. In the early days of this growth, there was perhaps insufficient appreciation of the increase in the magnitude of the hazard. There is now, however, much wider recognition of the importance of inventory. At the same time, it is important to emphasize that inventory is not the only factor which determines the scale of the hazard.

2.5.2 The energy factor

For an inventory of hazardous material to explode inside the plant or to disperse in the form of a flammable or toxic vapour cloud, there must be energy. In most cases this energy is stored in the material itself as the energy either of chemical reaction or of material state.

In particular, a material which is held as a liquid above its normal boiling point at high pressure and temperature, in other words superheated, contains large quantities of physical energy, which cause a large proportion of it to vaporize by instantaneous flash-off and to disperse if there is loss of containment. On the other hand, a material that is held as a refrigerated liquid at atmospheric pressure contains much less physical energy and does not vaporize to anything like the same extent if containment is lost. In this case, the energy necessary for vaporization has to be supplied by the ground and the air, which is a relatively slow process. Similarly, the hazard presented by an ultratoxic material depends very largely on whether there is energy available for its dispersion. There is a

Table 2.6 *Annual risk and fatal accident rate (FAR) in different industries and jobs in the UK*

Industry or activity	*1974–78*		*1987–90*	
	Annual risk[a,b]	*FAR*[c,d]	*Annual risk*[a,b]	*FAR*[b]
Deep sea fishing	280	140	84	42
Offshore oil and gas	165	82	125	62
Coal mining	21	10.5	14.5	7.3
Railways	18	9	9.6	4.8
Construction	15	7.5	10	5
Agriculture	11	5.5	7.4	3.7
Chemical and allied industries	8.5	4.3	2.4	1.2
Premises covered by Factories Act	–	–	8[e]	4
All manufacturing industry	–	–	2.3[f]	1.2
Vehicle manufacture	1.5	0.75	1.2	0.6
Clothing manufacture	0.5	0.25	0.09	0.05

[a] Annual risk is given as probability of death in 10^5 years.
[b] Health and Safety Executive, quoted in the Royal Society (1992).
[c] Fatal accident rate is defined as probability of death in 10^8 h of exposure.
[d] Some values from Kletz (1992b), evidently obtained from annual risk; remainder obtained in like manner by author.
[e] British Medical Association (1987).
[f] HSE (1988c).

Table 2.7 *Fatal incidents in manufacturing industry in different countries*[a]

	Fatality rate	
	Deaths per 1000 man-years[b,c]	*Deaths per 100,000 workers per year*[d]
Argentina	0.020	
Austria	0.142	
Belgium	0.140 (1979)	
Canada	0.080	14 (1971–74)
Czechoslovakia	0.061	
Eire		9 (1971–75)
France	0.068 (1982)	11 (1971–74)
Germany (FRG)	0.120 (1982)	17 (1971–75)
Germany (GDR)	0.030	
Italy		8 (1971–73)
Japan	0.010	5 (1971–75)
The Netherlands	0.009	4 (1971–73)
Norway	0.050	
Poland	0.066 (1984)	
Spain	0.109	
Switzerland	0.080	
UK	0.020	4 (1971–75)
USA	0.022	7 (1971–74)

[a] The basis of the calculation differs somewhat between countries and the original references should be consulted for further details.
[b] International Labour Office (1985b).
[c] For 1983 unless otherwise stated.
[d] HSE (1977d). Described in *Chemical Industry Hazards* (V.C. Marshall, 1987).

hazard, for example, if an ultratoxic substance is produced as a by-product in a chemical reactor in which a runaway exothermic reaction may occur. But if there is no such source of energy, the hazard is much less.

The energy requirement is thus another fundamental feature. Unless it is taken into account in the calculation, the scenarios considered may be not merely unlikely, but literally physically impossible.

2.5.3 The time factor

Another fundamental factor is the development of the hazard in time. The time factor affects both the rate of release and the warning time.

The nature and scale of the hazard is often determined by the rate of release rather than by the inventory. Thus, it is the rate of release which determines the size of a flammable gas cloud formed from a jet of flashing hydrocarbon liquid, such as occurred at Flixborough. Similarly, the hazard presented by an escape of toxic gas depends on the rate of release. There is a considerable difference in the concentrations attained between an instantaneous and a continuous release of toxic gas.

The warning time available to take emergency countermeasures and reduce the number of people exposed is also very important. An explosion gives a warning time that is usually measured only in seconds and may be zero, whereas a toxic release gives a warning that is often measured in minutes.

2.5.4 The intensity–distance relationship

An important characteristic of the hazard is the distance over which it may cause injury and/or damage. In general, fire has the shortest potential range, then explosion and then toxic release, but this statement needs considerable qualification. The range of a fireball is appreciable and the range of a fire or explosion from a vapour cloud is much extended if the cloud drifts away from its source.

It is possible to derive from the simpler physical models for different hazards analytical expressions that give the variation of the intensity of the physical effect (thermal radiation, overpressure, toxic concentration) with distance. For some models the variation follows approximately the inverse square law. This aspect is discussed in Chapter 9.

With regard to the exposure of the public to process hazards, it is of interest to know the distance at which there might be a significant number of fatalities or injuries and the maximum distance at which any fatality or injury might occur. Estimates of the distance necessary to reduce the risk of fire and explosion to members of the public to a level that is assumed to be not unacceptable, based on criteria such as thermal radiation from fire and overpressure from explosion, are generally of the order of 250–500 m for a major plant handling hydrocarbons, but may be less or more. Estimates of the distance necessary to reduce the risk from toxic release tend to be somewhat greater.

The maximum distance at which there might conceivably be fatalities or injuries cannot be determined with any great accuracy. The explosion effect that can occur at the greatest distance is the shattering of glass – this has happened at distances of up to 20 miles from a very large explosion. But in such cases the energy of the glass fragments is low and very rarely causes injury. Similarly, cases of injury from toxic gas at large distances, say over 10 miles, are rare but are reported to have occurred.

The effects of fire, explosion and toxic release are discussed further in Chapters 16–18. Although a potential effect of a hazard is often expressed as a function of distance, it is the area covered by the effect that determines the number of people at risk.

2.5.5 The exposure factor

A factor that can greatly mitigate the potential effects of an incident is the reduction of exposure of the people who are in the affected area. This reduction of exposure may be due to features that apply before the hazard develops, or to emergency measures that are taken after the hazard is recognized.

The principal mitigating features are shelter and escape. Escape may be by personal initiative or by preplanned evacuation. It should not be assumed that emergency measures are synonymous with evacuation. A combination of evacuation, shelter-in-place as well as other measures may be taken based on the event as well as preplanning evaluations. For releases of flammable substances, evacuation of non-emergency personnel is always beneficial and leads to reduction of casualties. On the other hand, for toxic releases, the emergency instructions may be to evacuate the area but are more likely to be to stay indoors and seal the house. Emergency measures may be of great value in reducing the toll of casualties from a major incident.

For an explosion that gives no advance warning, there is no time for emergency measures such as evacuation. This does not mean, however, that evacuation has no role to play as far as fire and explosion are concerned. On the contrary, although the initial event may be sudden, there are frequently further fire and explosion hazards. Evacuation may then be applicable.

Table 2.8 *Some of the worst non-industrial and industrial disasters worldwide and in the UK (Material from Guinness Book of Records, copyright © reproduced by permission of the publishers)*

Event		*Date*	
A Worst world disasters			
Earthquake	Near East and East Mediterranean	1201	1,100,000
Volcanic eruption	Tambora Sumbawa, Indonesia	1815	92,000
Landslide	Kansu Province, China	1920	180,000
Avalanche	Yungay, Juascaran, Peru	1970	≈18,000
Circular storm	Ganges Delta Islands, Bangladesh	1970	1,000,000
Tornado	Shaturia, Bangladesh	1989	≈1,300
Flood	Hwang-Ho river, China	1887	900,000
Lightning	Hut in Chinamasa Krael nr Umtali, Zimbabwe (single bolt)	1975	21
Smog	London fog, UK (excess deaths)	1951	2,850
Panic	Chungking (Zhong qing), air raid shelter, China	1941	≈4,000
Dam burst	Manchu River Dam, Morvi, Gujarat, India	1979	≈5,000
Fire (single building)	The Theatre, Canton, China	1845	1,670
Explosion	Halifax, Nova Scotia, Canada	1917	1,963
Mining	Hankeiko Colliery, China (coal dust explosion)	1942	1,572
Industrial	Union Carbide methylisocyanate plant, Bhopal, India	1984	≈2,500
Offshore platform	Piper Alpha, North Sea	1988	167
Nuclear reactor	Chernobyl Reactor No. 4	1986	31[a]
Aircraft	KLM-Pan Am, Boeing 747 crash, Tenerife	1977	583
Marine (single ship)	Wilhelm Gustloff, German liner torpedoed off Danzig by Soviet submarine S-13	1945	≈7,700
Rail	Bagmati River, Bihar, India	1981	>800
Road	Petrol tanker explosion inside Salang Tunnel, Afghanistan	1982	≈1,100
Atomic bomb	Hiroshima, Japan	1945	141,000
Conventional bombing	Tokyo, Japan	1945	≈140,000
B UK			
Earthquake	London earthquake, Christ's Hospital, Newgate	1580	2
Landslide	Pantglas coal tip No. 7, Aberfan, Mid-Glamorgan	1966	144
Avalanche	Lewes, East Sussex	1836	8
Circular storm	'The Channel Storm'	1703	≪8,000
Tornado	Tay Bridge collapsed under impact of two tornadic vortices	1879	75
Flood	Severn Estuary	1606	≪2,000
Smog	London fog (excess deaths)	1951	2,850
Panic	Victoria Hall, Sunderland	1883	183
Dam burst	Bradfield Reservoir, Dale Dyke, near Sheffield (embankment burst)	1864	250
Fire (single building)	Theatre Royal, Exeter	1887	188
Explosion	Chilwell, Nottinghamshire (explosives factory)	1918	134
Mining	Universal Colliery, Senghenydd, Mid-Glamorgan	1913	439
Offshore platform	Piper Alpha, North Sea	1988	167
Nuclear reactor	Windscale (now Sellafield), Cumbria (cancer deaths)	1957	[b]
Marine (single ship)	HMS Royal George, off Spithead	1782	≈800
Rail	Triple collision, Quintinshill, Dumfries	1915	227
Road	Coach crash, River Dibb, near Grassington, North Yorkshire	1975	33
Conventional bombing	London, 10–1 May	1941	1,436

[a] The *Guinness Book of Records* states: 'Thirty one was the official Soviet total of immediate deaths. On 25 April 1991 Vladimir Shovkoshitny stated in the Ukrainian Parliament that 7000 "clean-up" workers had already died from radiation. The estimate for the eventual death toll has been put as high as 75,000 by Dr Robert Gale, a US bone transplant specialist'.
[b] The *Guinness Book of Records* states: 'There were no deaths as a direct result of the fire, but the number of cancer deaths which might be attributed to it was estimated by the National Radiological Protection Board in 1989 to be 100'.

Measures that can be taken to mitigate exposure are discussed in Chapter 24.

2.5.6 The intensity–damage and intensity–injury relationships

The range of the hazard depends also on the relationships between the intensity of the physical effect and the proportion of people who suffer injury at that level of the effect. The annular zone within which injury occurs is determined by the spread of the injury distribution. If the spread is small, the injury zone will be relatively narrow, while if it is large, the zone may extend much further out. Similar considerations apply to damage. This aspect is discussed further in Chapter 9.

Table 2.9 *Coverage of some books on disasters*

	Bignell, Peters and Pym (1977)	*Ferrara (1979)*	*R. Smith (1993)*	*Thygerson (1977)*	*Walker (1973)*	*Whittow (1980)*
Natural hazards						
Subterranean stress:						
Earthquakes		X	X	X	X	X
Volcanoes		X	X	X		X
Tsunamis			X	X		X
Surface instability:						
Landslides and avalanches	X		X	X	X	X
Ground surface collapse						X
Weather:						
Wind, storm		X	X			X
Tornadoes		X	X			X
Hurricanes			X	X		X
Floods (river, sea)		X	X	X	X	X
Fires (forest, grass)		X	X	X		
Man-made hazards						
Structures:						
Buildings	X		X		X	
Dams			X		X	
Bridges	X		X		X	
Building fires	X	X		X		X
Gas explosions		X	X		X	
Industrial:						
Mines		X	X		X	
Fire		X	X		X	
Explosion		X	X		X	
Transport:						
Air	X	X	X		X	
Rail	X	X	X		X	
Road		X	X	X	X	
Sea	X	X	X		X	

2.6 Fire Loss Statistics

The loss statistics of interest are primarily those for fire loss. In the United Kingdom, principal sources of statistics on such losses are the Home Office, the FPA, the Loss Prevention Council and the insurance companies. These organizations produce annual statistics for fire losses. Loss due to explosions is generally included in that for fire loss. There are no regular loss statistics on toxic release, since this is a rare event and usually causes minimal damage to property.

Fire loss data are given in *Fire Statistics United Kingdom 1990* (Home Office, 1992), in *FPA Large Fire Analysis for 1989* (FPA, 1991) and in *Insurance Statistics 1987–91* (Association of British Insurers (ABI), 1992).

The Home Office data show that in 1990 fire brigades were called to some 467,000 fires, of which 108,000 were in buildings. The FPA defines a large loss fire as one involving a loss of £50,000 or more. In 1990 there were 739 such fires, with a total cost of £282 million and an average cost of £0.382 million. In the chemical and allied industries, in 1990, there were eight large loss fires, with a total cost of £5.24 million and an average cost of £0.656 million. There were no large loss fires in the coal and petroleum industries class.

A more detailed analysis of fires in the chemical and petroleum industries given by the FPA in 1974 is shown in Tables 2.10 and 2.11, the former giving analysis by number and cost and the latter by number and occupancy, by place of origin, by ignition source, by material first ignited and by time of day. There are a number of significant points in the tables. The chemical industry had the largest number of fires, but the oil industry the most expensive. The origin of the fires is predominantly in storage and in leakages. The sources of ignition are fairly evenly spread. There is only one fire attributed to static electricity and two to arson. But in 35 cases, that is, 44%, the ignition source was unknown. The material phase first ignited also shows a balanced spread, with the solid phase actually being predominant. There is no marked trend in the time of day of the fires, although the number is somewhat higher during the day shift.

Further analyses of fire statistics have been given by H.D. Taylor and Redpath (1971), the FPA (1976) and Redpath (1976). In particular, these sources present additional data of the type given in Tables 2.10 and 2.11. These data are a useful general pointer. They constitute, however, a rather small sample. Moreover, they are not necessarily representative of the type of fire or explosion that constitutes a major disaster.

Work on the occurrence of fires in industrial buildings has been described by Rutstein and Clarke (1979) and Rutstein (1979b). The probability of fire was found to increase with the size of building according to the equation:

$$P = aB^c \qquad [2.6.1]$$

where B is the floorspace (m^2) and P is the probability of fire per year, and a and c are constants. For production buildings

in manufacturing industry generally (SIC Classes 3–19), the values of the constants a and c were 0.0017 and 0.53, and in the chemical and allied industries (SIC 4), they were 0.0069 and 0.60, respectively. (These SIC numbers refer to the Standard Industrial Classification at the time.) The probability of fire in a 1500 m^2 production building was thus 0.083 for manufacturing industry and 0.21 for the chemical industry.

An analysis of some 2000 large loss claims at Cigna Insurance has been given by Instone (1989) and is summarized in Table 2.12.

A study of the contribution of human factors to failures of pipework and in-line equipment by Bellamy, Geyer and Astley (1989) contains a large amount of information characterizing releases, as shown in Table 2.13. As with fatal injuries so with fire losses, a single incident may dominate the process industries' loss for a particular year. In the United, the Flixborough disaster constituted a significant proportion of the fire loss in 1974, whilst the Piper Alpha disaster dominated that for 1988. Fire losses are considered further in Chapter 5.

Table 2.10 *Large fires in the chemical and petroleum industries[a] in Great Britain, 1963–75: number and cost (FPA, 1974; Redpath, 1976)*

Year	*No. of fires*	*Cost* (£m.)
1963	44	2.3
1964	43	2.9
1965	40	3.0
1966	43	2.5
1967	51	4.4
1968	53	3.1
1969	44	3.2
1970	67	6.2
1971	65	6.2
1972	66	3.5
1973	80	12
1974	45	43
1975	46	6.6

[a] The chemical and petroleum industries are taken as Standard Industrial Classification Order 4 (Coal and petroleum products) and 5 (Chemical and allied industries).

2.7 Fire and Explosion

So far no distinction has been made between fire and explosion losses. The latter are normally included in the overall fire statistics. In fact it is explosions that cause the most serious losses. This is illustrated by Table 2.14, which shows losses in the chemical industry insured by the Factory Insurance Association (FIA) of the United States (W.H. Doyle, 1969). Some two-thirds of the loss is attributable to explosions. The nature of these explosions is shown in Table 2.15. Over three-quarters of the explosions involve combustion or explosive materials.

Table 2.11 *Large fires in the chemical and petroleum industries in Great Britain, 1971–73 (Fire Protection Association, 1974b)*

A Number and cost by occupancy

Occupancy	*£10,000–£39,000*	*£40,000–£99,000*	*No. of fires £100,000–£249,000*	*>£250,000*	*Total no.*	*Total cost* (£m.)	*Average cost* (£m.)
Chemicals	1	12	13	7	33	7.215	0.219
Oil and tar	0	1	2	6	9	6.225	0.692
Paint and varnish	1	2	2	1	6	0.738	0.123
Fertilizer	1	1	2	1	5	0.625	0.125
Agricultural products	0	0	3	0	3	0.525	0.175
Plastics	1	1	0	0	2	0.051	0.025
Others	2	7	1	1	11	0.823	0.075
Total	6	24	23	16	69	16.202	0.235

B Place of origin

	No. of fires
Storage:	
Warehouse or open site	21
Tank	12
Leakage:	
From fractured pipe	15
From leaking coupling, flange or seal	6
From electrical equipment	6
Unspecified	2
Reactor or mixer	4
Steam drier	2
Spray booth	1
Cooling tower	1
Unreported	9
Total	79

Table 2.11 *(continued)*

C Ignition source

	No. of fires
Hot surfaces	8
Burner flames	8
Electrical equipment	6
Spontaneous ignition	6
Friction heat and sparks	6
Flame cutting	4
Children with matches	3
Malicious ignition	2
Static electricity	1
Unknown	35
Total	79

D Material first ignited

	No. of fires
Classification by phase	
Gas	10
Vapour	16
Liquid	20
Solid	23
Unknown	10
Total	79
Classification by material	
Hydrocarbons:	
Gas	3
Liquid/vapour	18
Solid	2
Other organics, etc.:	
Liquid/vapour	16
Solid	7
Cellulosic solids (timber, paper, cardboard, fireboard)	6
Hydrogen	7
Steel	2
Sulfur	1
Unknown	17
Total	79

E Time of day

Time of day	*No. of fires*	*Time of day*	*No. of fires*
24.00–1.00 h (midnight)	4	12.00–13.00 h	1
1.00–2.00	0	13.00–14.00	3
2.00–3.00	4	14.00–15.00	2
3.00–4.00	2	15.00–16.00	5
4.00–5.00	3	16.00–17.00	3
5.00–6.00	2	17.00–18.00	6
6.00–7.00	1	18.00–19.00	5
7.00–8.00	4	19.00–20.00	2
8.00–9.00	3	20.00–21.00	5
9.00–10.00	3	21.00–22.00	3
10.00–11.00	3	22.00–23.00	0
1.00–12.00	3	23.00–24.00 (midnight)	2

Table 2.12 *Large losses in the process industries insured by Cigna Insurance (after Instone, 1989) (Courtesy of Cigna Insurance)*

	Proportion (%)
A Operations type	
Refinery complex	48
Petrochemicals	20
General properties	10
Storage terminals	8
Onshore production plants	7
Jetty installations	3
Offshore production plant	2
Coal mines	2
Total	100
B Plant type	
Storage tanks and pipelines	23
Refineries	22
Oil/gas production	13
Off-sites	10
Monomers and polymers	6
Petrochemicals	6
Fertilizers	5
Coal products	3
Gas processing	3
Refinery feedstock and products	3
Acids, glycols, etc.	3
Aromatics	2
Alcohols, ketones, etc.	1
Paraffins	0
Total	100
C Process unit type	
Furnace or heater	10
Pipework	9
Storage tank – unspecified	7
Drilling rig	5
Pump	5
Compressor	5
Boiler	5
Heat exchanger	4
Cone roof tank	4
Distillation column	3
Warehouse	3
Process vessel	3
Floating roof tank	3
Electrical substation	3
Reactor	3
Reformer	2
Conveyor belt	2
Riser pipe	2
Jetty or buoy	2
Gas turbine generator	<2
Control room	<2
Hopper	<2
Transformer	<2
Flare; furnace stack; relief system (2); air cooler; centrifuge; filter; extruder; drier; refrigeration circuit; cooling tower; incinerator; electric motor; meters; instrument analyser; valve; crane; American Petroleum Institute (API) separator (2); hydrogen; loading arm – vessels; loading arm – road vehicles; road tanker; hose; laboratory; office; computer	<1
D Plant status	
Normal operations	50
Plant start-up	15
Plant under maintenance	10
Filling tanks or vessels	6
Well drilling	5
Plant in shut-down state	3
Process upset	2
Emptying tanks or vessels	2
Construction	<2
Well workover	<2
Plant shutting down	<1
Ship berthing/sailing	<1
Plant commissioning	<1
Blending operation	<1
Well logging	<1
E Loss type	
Fire	33
Explosion	12
Explosion and fire	10
Wind, storm and flood	10
Well blowout	5
Mechanical	5
Ship impact	5
Contamination	4
Machinery breakdown	4
Product loss	3
Electric cable fire	3
Construction defect; collapse; subsidence/collapse; earthquake; impact; implosion; floating roof sunk; pool fire; vapour fire; vapour cloud explosion; theft	<1
F Cause of loss	
Operator error	17
Wind, storm and flood	16
Pipe/weld failure	7
Tube failure	7
Machinery breakdown	7
Electrical short-circuit	4
Valve leak	4
Pipe flange leak	4
Instrumentation failure	4
Vehicle/digger impact	3
Corrosion	3
Seal failure	3
Lightning	<2
Anchor/hull damage to jetty	<2
Power failure	<2
Storage tank overflow	<2
Tank vent blocked	<2
Pressure increase	<2
Sabotage	<2
Burst vessel	<2
Compressor leak	<2
Runaway reaction	<2
Lost well circulation fluid	<2
Modification/design error; erosion; feedstock; process vessel overflow; flare carryover; water hammer; insufficient air purge; lubrication failure; instrument air failure; pyrophoric iron sulfide; gauge broken open; corroded electrical contacts; flame impingement; fire water leak; malicious damage	<1

G Material ignited	
Refinery feedstock and products	41
Petrochemicals	31
Gas processing	13
Acids, glycols, additives	6
Monomers and polymers	3
Alcohols, ketones, ethers; aromatics; paraffins; fertilisers; coal products	<1
H Source of ignition	
Material not ignited	35
Furnace	12
Hot surface	12
Autoignition	7
Electrical arcing	3
Operator error3	
Other electrical apparatus	3
Welding	3
Friction	<3
Static electricity	<3
Pyrophoric matter; spontaneous combustion; matches; spark; electric motor; boiler; flare; explosive device; vehicle; lightning; spread of fire; hot embers	<2

Table 2.13 *Characteristics of releases in study of failure of pipework and in-line equipment (Bellamy, Geyer and Astley, 1989) (Courtesy of the Health and Safety Executive)*

	No. of incidents
A Location type	
Chemical plant	278
Refinery	96
Factory	187
Storage depot	47
Tank yard	28
Fuel station	15
Other	38
Unknown	232
Total	921
B Site status	
Normal operations	343
Storage	103
Loading/unloading	33
Maintenance	146
Modification	8
Contractor work	18
Testing	5
Unknown	128
Other	40
Start-up	42
Shut-down	18
Total	884
C Materials released	
Ammonia	54
Hydrocarbons (unspecified)	54
Chlorine	50
Hydrogen	37
Benzene	33
Crude oil	28
Steam	25
Natural gas	24
Propane	20
Butane	18
Fuel oil	18
Hydrochloric acid	16
Sulfuric acid	16
Ethylene	16
Hydrogen sulfide	14
Water	13
Nitrogen	13
Oxygen	13
Vinyl chloride	12
LPG	12
Styrene	11
Naphtha petroleum	10
Total	507
D Material phase	
Liquid	393
Gas	260
Vapour	13
Solid	9
Liquid gas/vapour	120
Solid gas/vapour	3
Total	798
E Unignited material dispersion	
Flammable	127
Toxic1	23
Flammable/toxic	47
Corrosive	97
Irritant	1
Unignited gas	96
Vapour cloud	180
Liquid	212
Spill	186
Jet/spurt	8
Spray	10
Total	1087
F Fire or explosion event	
Fire1	45
Flash fire	11
Pool fire	4
Jet fire	1
Fireball	7
BLEVE	4
Explosion	63
Explosion followed by fire	77
Explosion followed by flash fire	2
Total	314

Note: BLEVE, boiling liquid expanding vapour explosion.

Further analyses of fires and explosions, treated separately, have been made by Norstrom (1982a), as shown in Tables 2.16 and 2.17.

The problem of large fires or explosions in vapour clouds is considered in Chapter 17. The data given in Table 17.33 by V.C. Marshall (1976a), in which the incidents are ranked in terms of the amount of vapour released, suggest that the large releases often result in explosions rather than fires.

Table 2.14 *Large losses in the chemical industry insured by the Factory Insurance Association: fire, explosion and other loss (after W.H. Doyle, 1969) (Courtesy of the American Institute of Chemical Engineers)*

Year	*Fires*		*Explosions*		*Other*		*Total*	
	No.	*Loss* (%)	*No.*	*Loss* (%)	*No.*	*Loss* (%)	*No.*	*Loss* (%)
1964	3	1.6	6	13.4	1	0.4	10	15.4
1965	4	1.9	8	8.7	0	0	12	10.6
1966	7	9.2	6	9.9	1	0.6	14	19.7
1967	8	5.9	12	22.4	2	1.1	22	29.4
1968	13	11.6	12	13.3	0	0	25	24.9
Total	35	30.2	44	67.7	4	2.1	83	100.0

Table 2.15 *Large losses in the chemical industry insured by the Factory Insurance Association: types of explosion (W.H. Doyle, 1969) (Courtesy of the American Institute of Chemical Engineers)*

	No.	*Loss* (%)
Combustion:		
In equipment	13	10.5
Outside equipment, in building	8	24.4
In open	1	3.3
Subtotal	22	38.2
Reaction:		
Explosive liquid or solid	12	16.8
Runaway reaction	4	6.5
Subtotal	16	23.3
Metal failure:		
Corrosion	1	1.4
Overheating	3	4.1
Accidental overpressure	2	1.0
Subtotal	6	6.5
Total	44	68.0

2.8 Causes of Loss

There are almost as many analyses of the causes of loss as there are investigators. Unfortunately, there is no accepted taxonomy, so that it is often difficult to reconcile different analyses. Two typical breakdowns of the causes of loss are given in Table 2.18 (W.H. Doyle, 1969) and in Table 2.19 (American Insurance Association (AIA), 1979), the latter being an up-date of an earlier table (Spiegelman, 1969). Doyle emphasizes the importance of poor maintenance, followed by poor design and layout of equipment and inadequate knowledge of the properties of chemicals. Spiegelman (1969) gives, in addition to the table referred to, a fairly detailed breakdown of the factors considered under each heading. His category of equipment failures evidently has a large element of poor maintenance.

Further information on causes of loss is provided by the data of Norstrom (1982a) given in Tables 2.16 and 2.17.

2.9 Down-time Losses

The losses considered so far are insured losses arising from fire and explosion. Another important, but often uninsured,

Table 2.16 *Large fires in the chemical and allied industries insured by Industrial Risk Insurers (Norstrom, 1982a) (Courtesy of the American Institute of Chemical Engineers)*

	Proportion (%)
A Cause	
Flammable liquid or gas (release, overflow)	17.8
Overheating, hot surfaces, etc.	15.6
Pipe or fitting failure	11.1
Electrical breakdown	11.1
Cutting and welding	11.1
Arson	4.4
Others	28.7
B Location	
Enclosed process or manufacturing buildings	42.2
Outdoor structures	33.3
Warehouses	6.7
Others	17.8
C Occupancy	
Mixing/blending	8.9
Storage	8.9
Distillation	6.7
Control/computer rooms	6.7
Chemical reaction, batch	4.4
Chemical reaction, continuous	4.4
Heating	4.4
Drying	4.4
Others	51.2
D Contributing factors	
Sprinkler or water spray lacking	35.6
Human element	15.6
Presence of flammable liquids	11.1
Rupture of vessel or equipment	8.9
Excessive residue	8.9
Production bottleneck	6.7
Sprinkler or water spray inadequate or impaired	6.7
E Area protection	
Protected building or structure	26.7
Unprotected building or structure	62.2
Outside building or structure	11.1

Table 2.17 *Large explosions in the chemical and allied industries insured by Industrial Risk Insurers (Norstrom, 1982a) (Courtesy of the American Institute of Chemical Engineers)*

	Proportion (%)
A Cause	
Chemical reaction uncontrolled	20.0
Chemical reaction accidental	15.0
Combustion explosion in equipment	13.3
Unconfined vapour cloud	10.0
Overpressure	8.3
Decomposition	5.0
Combustion sparks	5.0
Pressure vessel failure	3.3
Improper operation	3.3
Others	16.8
B Location	
Enclosed process or manufacturing buildings	46.7
Outdoor structures	31.7
Yard	6.7
Tank farm	3.3
Boiler house	3.3
Others	8.3
C Occupancy	
Chemical reaction process, batch	26.7
Storage tank	10.0
Boiler	8.3
Chemical reaction process, continuous	6.7
Compressor	5.0
Evaporation	3.3
Recovery	3.3
Transfer	3.3
Liquefaction	3.3
Others	25.1
D Contributing factors	
Rupture of equipment	26.7
Human element	18.3
Improper procedures	18.3
Faulty design	11.7
Vapour-laden atmosphere	11.7
Congestion	11.7
Flammable liquids	8.3
Long replacement time	6.7
Inadequate venting	6.7
Inadequate combustion controls	5.0
Inadequate explosion relief	5.0
E Area protection	
Protected building or structure	43.3
Unprotected building or structure	36.7
Outside building or structure	20.0

Table 2.18 *Large losses in the chemical industry insured by the Factory Insurance Association: causes of loss (W.H. Doyle, 1969) (Courtesy of the American Institute of Chemical Engineers)*

	No.	*Loss* (%)
Incomplete knowledge of the properties of a specific chemical	6	11.2
Incomplete knowledge of the chemical system or process	6	3.5
Poor design or layout of equipment	13	20.5
Maintenance failure	14	31.0
Operator error	5	6.9
Total	44	73.1

Table 2.19 *Hazard factors for 465 fires and explosions in the chemical industry 1960–77 (American Insurance Association, 1979)*

	No. of times assigned	*Proportion* (%)
Equipment failure	223	29.2
Operational failure	160	20.9
Inadequate material evaluation	120	15.7
Chemical process problems	83	10.9
Material movement problems	69	9.0
Ineffective loss prevention programme	47	6.2
Plant site problems	27	3.5
Inadequate plant layout	18	2.4
Structures not in conformity with use requirements	17	2.2
Total	764	100.0

loss arises from plant shut-down and down-time. Once again there are many different analyses of shut-down and down-time, and its causes on different types of plant. Three sets of statistics on shut-down and down-time are given in Tables 2.20–2.22 for a refinery (McFatter, 1972), in Tables 2.23 and 2.24 for another refinery (Anon., 1970b), and in Tables 2.25–2.28 (G.P. Williams, Hoehing and Byington 1987). In addition, data on down-time causes in ammonia plants were given earlier in Table 1.5.

McFatter's data in Tables 2.20–2.22 are for a single refinery consisting of seven units over a 10-year period. During this time, the overall availability of all the units was 96.4%. In other words, the units were down for scheduled or unscheduled shut-down 3.6% of the time. But in addition there were some 122 failures that were significant in that they resulted in 1313 equivalent days of lost production, although they did not cause shut-down. The large number of unscheduled shut-downs in 1967 was due to a major hydrocarbon line leak and fire, which resulted in complete shut-down of the refinery.

The importance of compressors, furnaces and heat exchangers is clear from Table 2.22. Other data given by McFatter show a rising trend of equivalent days lost due to failures. He comments that this is due to large increases in throughput, reduction in sparage of critical items, for example, compressors and pumps, and lack of opportunity to take items, for example, furnaces, off for maintenance. The data for another refinery given in Tables 2.23 and 2.24 show an essentially similar picture; as do the data given by McIntire (1977a,b). Surveys of ammonia plant shut-downs have been published by Sawyer, Williams and Clegg (1972), G.P. Williams and Sawyer (1974), G.P. Williams (1978),

Table 2.20 *Shut-downs in a refinery[a] (after McFatter, 1972) (Courtesy of the American Institute of Chemical Engineers)*

Year	*Scheduled*	*Unscheduled*
1961	1	1
1962	4	1
1963	3	1
1964	3	1
1965	4	1
1966	1	0
1967	3	10
1968	2	3
1969	4	1
1970	2	5

[a] There are seven units in the refinery.

Table 2.21 *Causes of non-scheduled shut-downs in a refinery (after McFatter, 1972) (Courtesy of the American Institute of Chemical Engineers)*

	%
Line leaks and fires	28
Line leaks	28
Process	12
Utilities	20
Miscellaneous	12
Total	100

Table 2.22 *Causes of significant non-shut-down failures in a refinery (after McFatter, 1972) (Courtesy of the American Institute of Chemical Engineers)*

	%
Compressors	30
Furnaces	18
Exchangers	17
Towers	5
Process	18
Process integration	7
Miscellaneous	5
Total	100

Table 2.23 *Causes of down-time in a refinery (after Anon. 1970b)*

	%
Scheduled maintenance	71.6
Process problems	15.6
Problems in other linked plants	7.6
Utility problems	5.2
Total	100

G.P. Williams and Hoehing (1983) and G.P. Williams, Hoehing and Byington (1987). The 1987 survey covers 136 plants, divided into three groups: (1) large-tonnage, single-stream, centrifugal compressor type plants, worldwide in North America, Europe and the rest of the world; (2) small plants, usually with multiple parallel streams of reciprocating compressors and (3) partial oxidation plants. The general nature of the shut-downs and down-time is shown in Table 2.25. Part of the down-time is due to non-plant problems (gas curtailment and market problems) and part is due to plant problems.

Table 2.24 *Significant equipment failures in a refinery (after Anon., 1970b)*

	All failures	
	No.	*%*
Pumps and compressors	35	33.9
Furnaces	14	13.6
Piping	11	10.7
Towers and reactors	9	8.8
Exchangers	7	6.8
Utilities	23	22.3
Other	4	3.9
Total	103	100

The service factor is the availability net of non-plant problems. The contributions to shut-downs and down-time are given in Table 2.26 in terms of plant area and type of equipment and in Table 2.27 in terms of individual items of equipment. Table 2.28 gives data on fires in the plants.

2.10 Trend of Injuries

The long-term trend of injury rates in the process industry is downwards. The trend in United Kingdom may be seen in Table 2.6, which shows that between 1970–74 and 1987–90, the fatal accident rate for the chemical and allied industries fell from 4.3 to 1.2. However, as Table 2.4 shows, the actual number of fatalities in this industry is small. Consequently, one large incident would have a significant effect on the figures, even if its effect was absorbed over quite a long period such as 10 years.

Evidence is available that the efforts devoted to safety and loss prevention by some companies have borne fruit. Figure 2.8 (Hawksley, 1984) shows the trend of the fatal accident rate in ICI over the period 1960–82. The data represent the 5-year moving average. They show that particular success was achieved in reducing the fatal incidents associated with the process risks, the reduction factor being about 15. The success achieved by certain US companies in reducing the lost time injury rate (LTIR) is illustrated in Figure 2.9 (Brian, 1988). The LTIR is the percentage of workers in the organization who, in a given year, suffer an injury so severe that it causes the worker to lose some work days. In one case the reduction factor is 280.

The trend in multiple fatality incidents has been studied by Keller and Wilson (1991), who obtained the results given in Table 2.29. The table shows a broadly stable situation.

2.11 Trend of Losses

There have been a number of studies addressing the question of whether the number of major incidents in the chemical and oil industries is increasing. Early work on these

Table 2.25 *Shut-down and down-time in ammonia plants (after G.P. Williams, Hoehing and Byington, 1987) (Courtesy of the American Institute of Chemical Engineers)*

	Large tonnage plants				*Reciprocating plants*	*Partial oxidation plants*
	North America	*Europe*	*Rest of world*	*Total*		
A Down-time and availability						
Total down-time (days/plant-year)	71.1	48.6	84.5	70.1	60.2	71.3
Unavoidable down-time (days/plant-year):						
Feedstock curtailment	0.8	0.6	20.0	7.6	11.2	0.5
Inventory control	45.4	8.7	15.2	25.2	20.8	9.7
Other	0.9	2.0	4.2	2.3	3.4	19.1
Total	47.1	11.2	39.4	35.1	35.4	29.3
Net avoidable (days/plant-year)	24.1	37.4	45.2	35.0	24.7	41.9
Service factor (%)	92.4	89.4	87.7	89.4	92.5	87.5
B Turnarounds						
Time between turnarounds (days)	21.7	33.2	33.7	30	30.8	21.2
Actual frequency (months)	24	20.5	13.5	18	17	16
Desired frequency (months)	23.5	25	14.4	20.6	16	12
C Classification of shut-downs						
Avoidable shut-downs (shut-downs/ plant-year):						
Instrument failure	1.2	1.4	1.9	1.5	0.8	1.9
Equipment failure	3.2	3.5	5.5	4.1	10.7	8.0
Turnarounds	0.5	0.4	0.7	0.5	0.5	0.7
Other	0.7	0.4	1.0	0.8	1.1	1.8
Total	5.6	5.8	9.1	6.9	13.1	12.3
Unavoidable shut-downs (shut-downs/ plant-year):						
Feedstock curtailment	0.14	0.08	0.74	0.34	0.31	0.41
Inventory control	0.34	0.07	0.23	0.23	0.29	0.48
Electrical failure	0.36	0.17	1.37	0.67	2.31	2.45
Other	0.27	0.11	0.19	0.20	0.46	3.14
Total	1.11	0.43	2.53	1.44	3.37	6.48
Total shut-downs (shut-downs/plant-year)	6.7	6.3	11.6	8.3	16.5	18.8
D Classification of down-time						
Avoidable shut-downs (days/plant-year):						
Instrument failure	1.1	1.4	1.1	1.2	0.4	2.0
Equipment failure	11.4	20.8	20.3	16.7	9.1	20.0
Turnarounds	10.5	14.6	20.8	15.2	14.0	16.0
Other	1.0	0.7	2.9	1.6	1.4	4.0
Total	24.1	37.4	45.2	35.0	24.7	41.9
Unavoidable shut-downs (days/plant-year):						
Feedstock curtailment	0.8	0.6	20.0	7.6	11.2	0.5
Inventory control	45.4	8.7	15.2	25.2	20.8	9.7
Electrical failure	0.2	0.5	1.7	0.8	2.1	3.1
Other	0.7	1.4	2.5	1.5	1.4	16.0
Total	47.1	11.2	39.4	35.1	35.4	29.3
Total down-time (days/plant-year)	71.1	48.6	84.5	70.1	60.2	71.3

lines was done by V.C. Marshall (1975c) and Kletz and Turner (1979). The insurers Marsh and McLennan (M&M) publish periodically a list of the 100 largest losses in the chemical and oil industries worldwide over a running 30-year period (e.g. Garrison, 1988b; Mahoney, 1990; Marsh and McLennan, 1992). The 1987 edition contains the analysis shown in Table 2.30. This indicates a trend that is rising up to 1986.

Table 2.26 *Major equipment failures causing shut-down and down-time in ammonia plants[a] (after G.P. Williams, Hoehing and Byington, 1987) (Courtesy of the American Institute of Chemical Engineers)*

	Large tonnage plants				*Reciprocating plants*	*Partial oxidation plants*
	North America	*Europe*	*Rest of world*	*Total*		
A Equipment failures causing shut-downs by plant area						
Primary reforming	3.0 (0.70)	3.0 (0.52)	4.8 (0.68)	3.7 (0.65)	1.1 (0.50)	–
Secondary reforming (including waste heat boilers)	1.3 (0.14)	5.4 (0.24)	1.3 (0.13)	2.3 (0.16)	0.8 (0.10)	–
Purification	1.1 (0.44)	1.9 (0.39)	1.9 (0.68)	1.6 (0.51)	1.6 (0.59)	4.3 (1.74)
Synloop	1.3 (0.48)	2.2 (0.34)	1.1 (0.36)	1.5 (0.40)	0.8 (0.52)	3.7 (0.60)
Compression	3.5 (1.20)	3.1 (0.91)	6.1 (2.32)	4.3 (1.52)	1.7 (7.71)	3.3 (1.45)
Miscellaneous	1.3 (0.24)	5.2 (1.10)	5.2 (1.36)	3.7 (0.86)	3.1 (1.23)	8.7 (4.21)
Total	11.4 (3.21)	20.8 (3.51)	20.3 (5.53)	17.0 (4.10)	9.1 (10.65)	19.9 (8.00)
B Equipment failures by type of equipment						
Reformer piping	2.3 (0.48)	1.5 (0.27)	4.1 (0.45)	2.8 (0.42)	0.8 (0.32)	–
Other piping	0.6 (0.22)	2.0 (0.48)	1.1 (0.43)	1.1 (0.36)	0.8 (0.49)	3.3 (0.81)
Valves	0.4 (0.22)	0.2 (0.33)	0.7 (0.53)	0.4 (0.36)	0.4 (0.35)	0.9 (0.57)
Compression:						
Centrifugal	2.6 (1.02)	2.8 (0.60)	5.1 (1.20)	3.5 (0.98)	0.1 (0.17)	1.1 (0.38)
Reciprocating	–	–	–	–	1.7 (7.65)	1.0 (0.02)
Pumps and drives	0.1 (0.10)	0.4 (0.10)	0.3 (0.19)	0.3 (0.13)	0.1 (0.10)	0.3 (0.33)
Exchangers	3.3 (0.66)	5.8 (0.91)	6.1 (1.17)	4.9 (0.91)	2.9 (1.13)	4.0 (1.19)
Vessels	0.7 (0.10)	6.1 (0.24)	1.3 (0.13)	2.3 (0.15)	1.7 (0.23)	5.2 (2.93)
Miscellaneous	1.5 (0.31)	1.8 (0.58)	1.8 (1.40)	1.7 (0.79)	0.6 (0.21)	4.2 (1.8)
Total	11.4 (3.21)	20.8 (3.51)	20.3 (5.50)	17.0 (4.10)	9.1 (10.65)	19.9 (8.00)

[a] Shut-down in shut-downs/plant-year; down-time in days/plant-year, in parentheses.

Table 2.27 *Equipment and other failures in ammonia plants (Courtesy of the American Institute of Chemical Engineers)[a] (after G.P. Williams, Hoehing and Byington, 1987)*

	North America		*Europe*		*Rest of world*		*Total*	
	DT	*SD*	*DT*	*SD*	*DT*	*SD*	*DT*	*SD*
A Equipment failures								
Primary reforming:								
Tube-riser-pig	1.99	0.44	1.25	0.24	2.82	0.35	2.10	0.36
Transfer header	0.32	0.04	0.45	0.04	1.25	0.10	0.68	0.06
Convection section	0.40	0.07	0.38	0.05	0.12	0.03	0.30	0.05
ID–FD fan	0.18	0.12	0.75	0.15	0.45	0.14	0.42	0.13
Miscellaneous	0.12	0.03	0.21	0.04	0.20	0.06	0.17	0.04
Total	3.01	0.70	3.04	0.52	4.84	0.68	3.67	0.65
Secondary reforming:								
Primary waste heat boiler	0.74	0.06	1.76	0.12	0.17	0.01	0.80	0.06
Secondary waste heat boiler	0.35	0.06	0.41	0.05	0.16	0.05	0.30	0.05
Secondary reformer	0.20	0.01	3.05	0.06	0.88	0.13	1.17	0.07
Miscellaneous	0.00	0.01	0.14	0.01	0.04	0.08	0.05	0.03
Total	1.29	0.14	5.36	0.24	1.25	0.27	2.32	0.21
Purification:								
Exchangers	0.41	0.18	0.28	0.07	1.04	0.26	0.60	0.18
Pumps and drives	0.06	0.07	0.25	0.05	0.05	0.05	0.11	0.06
Piping and valves	0.27	0.14	0.08	0.12	0.59	0.29	0.34	0.19
Vessels	0.36	0.04	1.24	0.13	0.18	0.05	0.52	0.07
Miscellaneous	0.01	0.01	0.05	0.02	0.04	0.03	0.03	0.02
Total	1.11	0.44	1.90	0.39	1.90	0.68	1.59	0.51

Table 2.27 *(continued)*

Feed compressor:								
Driver	0.03	0.02	0.00	0.00	0.00	0.00	0.01	0.01
Compressor	0.03	0.01	0.01	0.01	0.02	0.03	0.02	0.02
Miscellaneous	0.00	0.01	0.16	0.02	0.02	0.01	0.05	0.01
Total	0.06	0.04	0.17	0.03	0.04	0.04	0.08	0.04
Air compressor:								
Driver	0.25	0.09	0.14	0.05	0.61	0.02	0.35	0.05
Compressor	0.44	0.15	0.14	0.07	0.69	0.13	0.45	0.12
Miscellaneous	0.11	0.07	0.04	0.09	0.37	0.24	0.18	0.14
Total	0.80	0.31	0.32	0.21	1.67	0.39	0.99	0.31
Syngas compressor:								
Driver	0.50	0.21	0.33	0.07	0.76	0.16	0.55	0.16
Compressor	0.73	0.25	1.38	0.22	2.01	0.58	1.35	0.36
Miscellaneous	0.26	0.19	0.62	0.28	0.93	0.83	0.59	0.44
Total	1.49	0.65	2.33	0.57	3.70	1.57	2.49	0.96
Syngas circulator:								
Driver	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Compressor	0.00	0.01	0.00	0.00	0.01	0.02	0.00	0.01
Miscellaneous	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00
Total	0.01	0.02	0.00	0.00	0.02	0.03	0.01	0.02
Refrigeration compressor:								
Driver	0.14	0.05	0.01	0.02	0.37	0.09	0.19	0.06
Compressor	0.33	0.09	0.07	0.01	0.17	0.04	0.21	0.05
Miscellaneous	0.66	0.04	0.17	0.07	0.09	0.16	0.33	0.09
Total	1.13	0.18	0.25	0.10	0.63	0.29	0.73	0.20
Synloop and refrigeration:								
Exchangers	0.72	0.24	0.26	0.09	0.81	0.15	0.63	0.17
Piping and valves	0.39	0.20	1.51	0.24	0.30	0.19	0.65	0.21
Vessels	0.07	0.03	0.40	0.01	0.01	0.02	0.13	0.02
Miscellaneous	0.10	0.01	0.00	0.00	0.00	0.00	0.04	0.00
Total	1.28	0.48	2.17	0.34	1.12	0.36	1.45	0.40
Miscellaneous equipment:								
Auxiliary boiler	0.48	0.02	0.31	0.03	0.45	0.07	0.43	0.04
Piping and valves	0.27	0.10	0.63	0.44	0.90	0.49	0.59	0.33
Exchangers	0.17	0.02	2.59	0.51	3.31	0.59	1.91	0.35
Vessels	0.06	0.01	1.40	0.04	0.19	0.04	0.45	0.03
Pumps and drives	0.08	0.04	0.17	0.05	0.23	0.14	0.16	0.08
Miscellaneous	0.20	0.05	0.12	0.03	0.08	0.03	0.14	0.04
Total	1.26	0.24	5.22	1.10	5.16	1.36	3.66	0.86
Grand total	11.44	3.20	20.76	3.50	20.33	5.67	16.99	4.16
B Electrical, instrument and other shut-down causes								
Electrical:								
External	0.18	0.36	0.53	0.17	1.70	1.37	0.81	0.67
Internal	0.49	0.22	0.19	0.20	1.70	0.35	0.84	0.26
Total	0.67	0.58	0.72	0.37	3.40	1.72	1.65	0.93
Instruments:								
Feed compressor	0.03	0.04	0.00	0.00	0.02	0.02	0.02	0.02
Air compressor	0.14	0.19	0.08	0.15	0.06	0.20	0.10	0.18
Syngas compressor	0.17	0.33	0.76	0.47	0.37	0.68	0.39	0.49
Refrigeration compressor	0.07	0.09	0.10	0.10	0.06	0.18	0.07	0.12
Miscellaneous	0.64	0.51	0.47	0.70	0.60	0.79	0.58	0.66
Total	1.05	1.16	1.41	1.42	1.11	1.87	1.16	1.48

Table 2.27 *(continued)*

Other:								
Strikes	0.00	0.00	1.35	0.05	0.10	0.01	0.38	0.02
Weather	0.66	0.18	0.04	0.03	1.19	0.05	0.69	0.10
Operator error	0.01	0.18	0.12	0.21	0.08	0.13	0.10	0.17
Catalyst	0.12	0.12	0.23	0.02	0.42	0.08	0.25	0.08
Miscellaneous: avoidable	0.24	0.03	0.16	0.09	0.40	0.38	0.28	0.17
Miscellaneous: unavoidable	0.05	0.34	0.03	0.01	1.24	0.13	0.47	0.18
Total	1.17	0.85	1.93	0.41	3.43	0.78	2.17	0.71
Feedstock/market curtailment								
Feedstock curtailment	0.80	0.14	0.55	0.08	19.97	0.74	7.56	0.34
Inventory control	45.37	0.34	8.69	0.07	15.16	0.23	25.21	0.23
Total	46.17	0.48	9.24	0.15	35.13	0.97	32.77	0.57
Grand total	49.06	3.07	13.30	2.35	43.07	5.34	37.75	3.69

[a] DT, down-time (days/plant-year); ID–FD, induced draft-forced draft; SD, shut-downs (shut-downs/plant-year).

Table 2.28 *Fires in ammonia plants (after G.P. Williams, Hoehing and Byington, 1987) (Courtesy of the American Institute of Chemical Engineers)*

	1973–76	*1977–81*	*1981–85*
A No. of plant fires			
No. of plants having no fires	2	22	41
No. of plants having fires	27	74	95
No. of fires	125	257	520
Frequency of fires (fires/month)	11.1	14.6	12.2
B Classification of fires (%)			
Flange	36	32	31
Valve packing	8	4	8
Oil leaks	20	29	19
Transfer header	7	–	1
Piping	10	9	11
Electrical	2	3	3
Miscellaneous	17	23	27

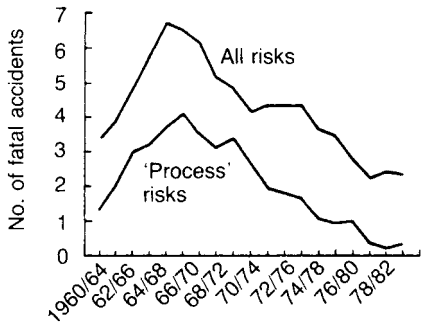

Figure 2.8 *Trend of the fatal accident rate in ICI, 1960–82 (Hawksley, 1984). The number of fatal accidents is given as the number in 10^8 working hours or the number in 1000 men in a working lifetime expressed as a 5-year moving average*

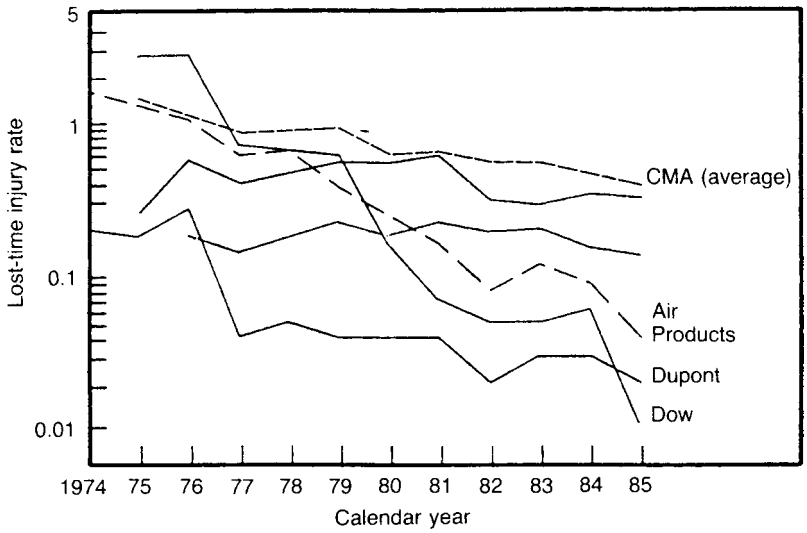

Figure 2.9 *Trend of lost-time injury rate in some US companies, Chemical Manufactures Association 1974–85 (Brain, 1988) (Courtesy of the Institution of Chemical Engineers)*

Table 2.29 *Trend in the number of major incidents in UK, Europe and worldwide (after Keller and Wilson, 1991)*

No. of fatalities	*1970–79*		*1980–87*		*1970–87*		
	Europe	*Worldwide*	*Europe*	*Worldwide*	*UK*	*Europe*	*Worldwide*
A Number of incidents							
5–10	12	53	6	40	3	18	93
10–100	10	45	5	30	2	15	75
$100–10^2$	2	3	0	2	0	2	5
$10^2–10^3$	0	0	0	1	0	0	1
B Frequency of incidents (incidents/year)							
5–10	1.2	5.3	0.75	5.0			
10–100	1.0	4.5	0.63	3.8			
$100–10^2$	0.2	0.3	0	0.25			
$10^2–10^3$	0	0	0	0.13			

Table 2.30 *The 100 largest losses in the chemical and oil industries worldwide (after Marsh and MacLennan, 1987)*

Period	*No. of losses*	*Average loss*
1957–66	15	28.5
1967–76	29	38.2
1977–86	56	36.6

Table 2.31 *Trend in number of vapour cloud explosions worldwide (after Lenoir and Davenport, 1992)*

Period	*No. of VCEs*
1930–34	0
1935–39	1
1940–44	1
1945–49	2
1950–54	5
1955–59	8
1960–64	11
1965–69	12
1970–74	20
1975–79	22
1980–84	8
1985–89	15
1990–July 1991	7

A further review of loss trends is that given by Crook (1994, LPB 115). He comments that the M&M data suggests that until 1989 losses were doubling each decade. He gives further data from a study drawing on the Lloyds Weekly Casualty Reports (LWCRs). The frequency for the incidents that he considers, has risen from some 28/year in 1971 to some 103/year in 1991.

A particular type of incident that has received individual attention is the VCE, formerly generally referred to as unconfined vapour cloud explosion (UVCE). In the United Kingdom, the VCE at Flixborough resulted in a heightened awareness. A study at that time by V.C. Marshall (1975c) showed that the number of VCEs worldwide was indeed on an apparently increasing trend. Similarly, in his book on VCEs, Gugan (1979) stated: 'The trends in frequency, proportion of incidents producing blast and fatalities in UVCEs are all upwards'. This trend appears now to have been arrested. Industrial Risk Insurers (IRI) publish a periodic survey of VCE incidents. The number of VCEs obtained from this survey is given in Table 2.31.

2.12 Case Histories

The generalized statistics may be supplemented by individual case histories. These are treated in Appendix 1, which describes the various sources and gives specific case histories. The sources include: the incident reports of the HSE and the National Transportation Safety Board (NTSB); the collections of the Manufacturing Chemists Association (MCA) and the American Petroleum Institute (API); the periodic reviews of insurers, such as the *100 Large Losses* (Marsh and McLennan); the *NFPA Quarterly* of the National Fire Protection Association (NFPA), the *Chemical Safety Summary* of the Chemical Industry Safety and Health Council (CISHC) and its successor, the Chemical Industries Association (CIA), and the *Loss Prevention Bulletin* of the Institution of Chemical Engineers (IChemE), all of which publish case histories.

Accounts of major incidents are given in: Appendices 2–6 on Flixborough, Seveso, Mexico City, Bhopal and Pasadena, respectively; Appendix 16 on San Carlos; Appendix 19 on Piper Alpha; and Appendices 21 and 22 on Three Mile Island and Chernobyl.

3 Legislation and Law

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It is the object of this chapter to give a brief account of the principal legislation and of the legal background relevant to safety and loss prevention. The account is largely restricted to the situation in the United States. Previous editions of this handbook detailed UK law. The development of legislation on health and safety in the United States may also be followed through the references given in Table A1.4 in Appendix 1. In particular, attention is drawn to the problems of toxic chemicals in the workplace, of pollution and of transport; of litigation; and to the resulting legislation.

In general, it is probably fair to say that legislation has been tougher in the United Kingdom in some areas and in the United States in others, and also that the rate at which controls have been tightened has often been different in the two countries. It is worth emphasizing also that in these areas it is not sufficient merely to pass legislation – it is necessary to enforce it. There has been, in both countries, a considerable tightening of methods of enforcement.

3.1 US Legislation

In the 1970s, there occurred in the United States, a very rapid development of public awareness of problems of health and safety, and of environmental problems, and a corresponding growth in the creation of controls in this area. In the United States, both State and Federal Governments are sources of legislation. In recent years the involvement of the Federal Government in health and safety legislation has greatly increased.

Major categories of safety legislation impacting the process industry can be categorized as follows:

(1) occupational health and safety,
(2) environment,
(3) toxic substances,
(4) accidental releases and
(5) transport

References on major safety issues are detailed below:

Occupational Safety and Health Act 1970
OSHA (2001, 2098, 2253, 2254, 1988); Hodgson (1971); S. Ross (1971, 1972b); Vervalin (1971–, 1972b,d); Nilsen (1972a); L.J. White (1972, 1973b, 1974); Anon. (1973d,e); Ludwig (1973a,b); Anon. (1974h); Peck (1974); Stender (1974); Hopf (1975); D. Petersen (1975); Corn (1976); Anon. (1977m); Demery (1977); Moran (1979); Ladou (1981); ACGIH (1990/50); A. Foster and Burd (1993)

Occupational Safety and Health Administration (OSHA)
J. Shaw (1978, 1979); R.D. Morgan (1979); Cahan (1982b); H. Bradford (1986b); Spiegelman (1987); AGA (1990/14); Burk (1990); Seymour (1992); Donnelly (1994)

Environmental Protection Agency (EPA)
J. Shaw (1978); Porter (1988); K.A. Friedman (1989a,b); Stephan and Atcheson (1989); Matthiessen (1994); Rosenthal and Lewis (1994)

National Standards
van Atta (1982); W.J. Bradford (1985); M.F. Henry (1985); R.K. Johnson (1985)

Process Safety Management
OSHA (1992); Rosenthal and Lewis (1994)

Emergency Planning and Community Right-to-Know Act 1986 (EPCRA)
Makris (1988); Bowman (1989); Bisio (1992b)

New Jersey Toxic Catastrophe Prevention Act 1986 (TCPA)
Florio (1987); Somerville (1990)

Clean Air Act (CAA)
E.B. Harrison (1978b); Siegel *et al.* (1979); G.A. Brown, Cramer and Samela (1988); Zahodiakin (1990); Matthiessen (1992); Kaiser (1993)

Resource Conservation and Recovery Act (RCRA)
Glaubinger (1979); Sobel (1979); Basta (1981c); H.H. Fawcett (1982b); Hoppe (1982)

Superfund
J.S. Shaw (1980b); Resen (1984); Casler (1985); Sidley and Austin (1987); Habicht (1988); Nott (1988); Bowman (1989); Hirschorn and Oldenburg (1989); Melamed (1989); Rhein (1989); Bisio (1992a)

SARA
K.A. Friedman (1989a,b); Anon. (1990k); ACGIH (1990/50); Curran and Kizior (1992); Ffflo and Keyworth (1992); Heinold (1992); Keyworth, smith and Archer (1992)
Chipperfield (1979); Cussell (1979); Malle (1979); Otter (1979); Furlong (1991)

Occupational Safety History
Occupational safety did not begin with the passage of the Occupational Safety and Health Act of 1970. The ill effects of the environment on the worker have been known for thousands of years. Unfortunately, just because the hazards are known does not mean that they have been corrected. Some significant events in occupational safety in the United States include:

(a) 1812, the Embargo of the War of 1812 spurred the development of the New England textile industry and the founding of factory mutual companies. These early insurance companies inspected properties for hazards and suggested loss control and prevention methods in order to secure low rates for their policyholders.
(b) 1864, The Pennsylvania Mine Safety Act (PMSA) was passed into law.
(c) 1864, North America's first accident insurance policy was issued.
(d) 1867, the state of Massachusetts instituted the first government-sponsored factory inspection programme.
(e) 1877, the state of Massachusetts passed a law requiring guarding for dangerous machinery, and took authority for enforcement of factory inspection programmes.
(f) 1878, the first recorded call by a labour organization for a federal occupational safety and health law is heard.
(g) 1896, an association to prevent fires and write codes and standards, the National Fire Protection Association (NFPA), was founded.
(h) 1902, the state of Maryland passed the first workers' compensation law.
(i) 1904, the first attempt by a state government to force employers to compensate their employees for on-the-job injuries was overturned when the Supreme Court declared Maryland's workers' compensation law to be unconstitutional.

(j) 1911, the American Society of Mechanical Engineers (ASME) was founded. A professional, technical organization responsible for developing safety codes for boilers and elevators.
(k) 1911, the American Society of Safety Engineers (ASSE) was founded. The ASSE was dedicated to the development of accident prevention techniques, and to the advancement of safety engineering as a profession.
(l) 1912, a group of engineers representing insurance companies, industry and government met in Milwaukee to exchange data on accident prevention. The organization formed at this meeting was to become the National Safety Council (NSC). (Today, the NSC carries on major safety campaigns for the general public, as well as assists industry in the development of safety promotion programmes.)
(m) 1915, by this time, 30 states passed workers' compensation laws.
(n) 1916, the Supreme Court upheld the constitutionality of state workers' compensation laws.
(o) 1918, the American Standards Association was founded. Responsible for the development of many voluntary safety standards, some of which are referenced into laws, today, it is now called the American National Standards Institute (ANSI).
(p) 1936, Frances Perkins, Secretary of Labor, called for a federal occupational safety and health law. This action came 58 years after organized labor's first recorded request for a law of this nature.
(q) 1936, the Walsh–Healey (Public Contracts) Act passed. This law required that all federal contracts be fulfilled in a healthful and safe working environment.
(r) 1948, all states (48 at the time) now had workers' compensation laws.
(s) 1952, Coal Mine Safety Act (CMSA) was passed into law.
(t) 1960, specific safety standards were promulgated for the Walsh–Healey Act.
(u) 1966, the Metal and Nonmetallic Mines Safety Act (MNMSA) was passed.
(v) 1966, the US Department of Transportation (DOT) and its sections, the National Highway Traffic Safety Administration (NHTSA) and the National Transportation Safety Board (NTSB), were established.
(w) 1968, President Lyndon Johnson called for a federal occupational safety and health law.
(x) 1969, the Construction Safety Act (CSA) was passed.
(y) 1970, President Richard Nixon signed into law the Occupational Safety and Health Act, thus creating the OSHA administration and the National Institute for Occupational Safety and Health (NIOSH).
(z) 1992, The Process Safety Management rule was adopted by OSHA.

3.2 US Regulatory Agencies

The OSHA was created by the Occupational Safety and Health Act of 1970 and has responsibility for enforcing that Act. OSHA comes under the Secretary of Labor and is headed by an Assistant Secretary of Labor. Its activities include the adoption of standards and making of rules, the inspection of workplaces and the investigation of accidents.

The EPA, created by the National Environmental Policy Act (NEPA) 1969, is responsible for environmental legislation, including that on air pollution, water pollution and hazardous wastes. The areas of responsibility between the OSHA and the EPA are not clearcut. Although the OSHA is concerned with the workplace and the EPA with the environment, there are some areas where both agencies are involved. One of these is accidental releases and another is toxic substances, as described below. The relation between the two agencies is discussed by Spiegelman (1987) and Burk (1990).

Mining and mineral processing (such as Alumina refineries and lime processing) are the responsibility of the Mine Safety and Health Administration (MSHA).

Offshore production safety is the responsibility of the Mineral Management Service (MMS), which took over from the original US Coast Guard duties in the mid-1980s. However, the Coast Guard now has responsibility for deep water facilities, in addition to its traditional role of marine safety.

Pharmaceutical safety comes under the watchful eye of the Food and Drug Administration (FDA).

Pipeline safety, rail transport safety, and motor carrier safety issues are the responsibility of the Department of Transportation.

3.3 Codes and Standards

Standards are documented agreements containing technical specifications or other precise criteria to be used as rules, guidelines or definitions of characteristics, to ensure that materials, products, processes and services are fit for their purpose (ISO). Standards may be met on a voluntary basis unless and until they are incorporated into government regulations.

Codes, on the other hand, are legal requirements, which are incorporated in the US Code of Federal Regulations or the equivalent State or local code document. Hence, Code and regulation are synonymous, but standards may or may not be regulations. Laws are passed by government bodies, such as Congress. Then Government agencies (such as OSHA and EPA) are authorized to create regulations, which are eventually codified in the US Code of Federal Regulations. Announcement of new regulations or changes to existing regulations must be published in the US Federal Register.

Many industrial standards are incorporated directly by reference. For example, the OSHA flammable liquid code, 29CFR(106), directly references the ASME standard on pressure vessels. Unfortunately, this direct reference can cause some confusion, specifically on which edition of the ASME standard the government code is actually referencing. Since OSHA originally adopted the NFPA 30 standard flammable liquids in 1972, the ASME section VIII pressure vessel code existing at that specific instance in time was incorporated into law. Even though many updates to the ASME code were made over time, the older edition of the ASME code was a requirement whereas the updates in later editions are voluntary recommendations. OSHA eventually updated their regulations by publishing an announcement in the Federal Register.

There are many examples where older standards are still the referenced edition in regulatory codes. For example,

the OSHA regulation on gas turbine facilities 29CFR 1910.110(b)(20) directly references the 1970 version of NFPA 37 (standard for the installation and use of stationary combustion engines and gas turbines), even though the latest update of this particular NFPA standard is 1998.

Both State and Federal legislation make use of national standards and recommended practices. In particular, standards such as those of the ANSI and the National Fire Codes of the NFPA are widely quoted in legislation. MMS frequently updates its references to American Petroleum Institute standards through announcements in the US Federal Register.

3.4 Occupational Safety and Health Act 1970

The Occupational Safety and Health Act 1970 (OSHA) is the framework Act. It provides that the Secretary of Labor should promulgate safety standards, inspect workplaces and assess penalties. There is a separate commission called the Occupational Safety and Health Commission, which deals with violations of the OSHA. The OSHA has some similarity with the HSWA 1974 in the United Kingdom, in that it is essentially an enabling measure which is superimposed on existing health and safety legislation, lays duties on employers and employees to comply with standards and regulations, and has provisions for inspection and enforcement.

However, there is one most important difference between UK and US regulatory concepts. OSHA regulations do not override any other equivalent federal safety regulation.

Regulations are issued under the Act by OSHA. The initial standards promulgated under the Act were published in the Federal Register 29 May 1971. The OSHA also established the NIOSH to develop and establish recommended occupational safety and health standards.

The Act places the onus for compliance with the law primarily on the employer. This applies even in cases where employees are not working according to instructions that have been issued to them to provide for their safety. An employer has the right to seek a variance from a standard, and may file a petition challenging the validity of a standard.

Accounts of the Act are given by Anon. (1971c), Hodgson (1971), Nilsen (1972a), L.J. White (1973b) and Corn (1976).

3.5 US Environmental Legislation

Of the issues, which have assumed an increasingly high profile in the last two decades, pollution attained an early prominence and has given rise to a large volume of legislation. Legislation of particular importance in this field includes: the Water Quality Act 1965, the NEPA 1969, the CAA 1970, the Federal Environmental Pollution Control Act 1970, the Federal Water Pollution Control Act (FWPCA) 1972, the Safe Drinking Water Act, 1974 and the Noise Control Act 1972.

The NEPA 1969 created the EPA.

The CAA 1970 gives the EPA power to adopt and enforce air pollution standards. The EPA has promulgated air quality standards that set the maximum concentrations for various gaseous pollutants. There have been amendments to the CAA in 1977, 1981 and 1990. Accounts of air pollution legislation are given by Vervalin (1972d), Zarytkiewicz (1975), Halley (1977), Lipton and Lynch (1987), G.A. Brown, Cramer and Samela (1988), Veselind, Peirce and Weiner (1990) and Asante-Duah (1993).

The FWPCA 1972 gives the EPA power to adopt and enforce water pollution standards. The EPA has promulgated effluent quality standards and guidelines that set the maximum concentrations for all liquid pollutants. Accounts of water pollution legislation are given by Weisberg (1973), L.J. White (1974), Veselind, Peirce and Weiner (1990) and Asante-Duah (1993).

Hazardous wastes are regulated by the RCRA 1976. There are rules governing the storage of such wastes in storage tanks, including underground storage tanks. The Act is administered by the EPA.

The Comprehensive Environmental Response, Compensation and Liability Act 1980 (CERCLA, or Superfund) strengthens the regulation of hazardous wastes by the EPA. It creates controls on hazardous waste sites and enforces clean-up of existing and abandoned sites. It seeks to identify potentially responsible persons (PRPs) and, where such parties are not found, it supervises a clean-up paid for from the Superfund. The Act has to be renewed periodically. The Superfund Amendments and Reauthorization Act 1986 (SARA) renews the Superfund. The part of the Act known as SARA Title III extends its application to accidental releases, as described below. Accounts of hazardous waste legislation and of Superfund are given by Caruana (1986), Edelman (1987), Melamed (1989), Veselind, Peirce and Weiner (1990) and Asante-Duah (1993).

The development of legislation on pollution may be followed through the references given in Table A1.4. These references show the evolution of the air and water quality standards and of their application. The NEPA 1969 imposes a duty on Federal agencies to obtain from a developer an environmental impact statement (EIS) before they take any action that affects the environment, such as granting a permit. A number of other Acts also include a requirement for an EIS. A regulation of the President's Commission on Environmental Quality (CEQ) made in 1978 defines requirements for an EIS. Permits may be required from a number of agencies at federal, state and local level. Environmental legislation in the United States is described further in Appendix 11.

3.6 US Toxic Substances Legislation

The Toxic Substances Control Act 1976 (TSCA) is a framework Act, which creates a comprehensive system of controls over toxic substances. It empowers the EPA to regulate the manufacture, processing, distribution, use and disposal of existing and new chemicals in order to avoid unreasonable risk to health or the environment and to delay or ban manufacture or marketing. It provides for the creation of an inventory of existing chemicals and for notification by a manufacturer of a new chemical or of new uses for a chemical. There are requirements for the toxicity testing of chemicals and for Premanufacture Notices (PMNs). The EPA has an Office of Toxic Substances (OTS) dealing with the Act. Accounts of the Act are given by Ricci (1976c), C.W. Smith (1977) and A.S. West (1979, 1982, 1986, 1993b).

Section 313 of SARA Title III also deals with toxic substances, but essentially in relation to high level emissions. It requires the EPA to compile a toxic chemical inventory database, the Toxic Release Inventory (TRI). Section 313 is discussed by Bowman (1989). The control of toxic substances in the workplace and in the atmosphere is also covered by the OSHA 1970 and by pollution legislation.

The development of legislation on toxic substances in the workplace and in the atmosphere may be followed through the references given in Table A1.4. The case of vinyl chloride is of particular interest.

3.7 US Accidental Chemical Release Legislation

The accidents at Flixborough, at Seveso and, above all, at Bhopal, and the development of major hazard controls in Europe led in the second half of the 1980s to US legislation on accidental releases. Accidental releases are covered by the EPCRA 1986. This is Title III of the SARA 1986. It is commonly known as SARA Title III and was signed into law in 1988. It contains four main parts;

(1) emergency planning,
(2) emergency notification,
(3) community right-to-know and
(4) toxic chemicals inventory.

The Act is enforced by the EPA. An account of the EPA's chemical accident release prevention programme is given by Matthiesen (1994).

Controls on accidental releases have also been introduced by the OSHA in the form of a rule for the Process Safety Management of Highly Hazardous Chemicals. This introduces a requirement for a process safety management system to identify, evaluate and control such hazards. An account of OSHA's process safety management rule is given by Donnelly (1994).

Individual states have also brought in their own legislation. The New Jersey TCPA 1985 creates a requirement for a risk management programme for facilities handling certain toxic chemicals above a given inventory. The California Hazardous Materials Planning Program is based on a codification of four laws within the California Health and Safety Program.

Accounts of legislation on hazardous chemicals with potential impact off site are given by Brooks *et al.* (1988) and Horner (1989).

3.8 US Transport Legislation

Another major concern in the United States in recent years has been the problem of the transport of hazardous materials, and this has given rise to a large volume of legislation. Some principal items of legislation (considered further in Chapter 23) in the field include

(1) Rivers and Harbors Act 1899
(2) Explosives Transportation Acts 1908, 1909 and 1921
(3) Tank Vessels Act 1936
(4) Natural Gas Act 1938
(5) Federal Aviation Act 1958
(6) Natural Gas Pipeline Safety Act 1968
(7) Dangerous Cargo Act 1970
(8) Hazardous Materials Transportation Act 1970
(9) Coastal Zone Management Act 1972
(10) Ports and Waterways Safety Act 1972

3.9 Regulatory Support

Legislation that is based on good industrial practice and is developed by consultation with industry is likely to gain greater respect and consent than that which is imposed. Actions by individuals who have little respect for some particular piece of legislation are a common source of ethical dilemmas for others.

The professionalism of the regulators is another important aspect. A prompt, authoritative and constructive response may often avert the adoption of poor practice or a short cut. The regulatory body can contribute further by responding positively when a company is open with it about a violation or other misdemeanor that has occurred.

4 Major Hazard Control

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Foreword by Jerry Havens

I am honored to have the opportunity to update Professor Lees' discussion of Major Hazards. Had the events of 9/11 not occurred, there would be little that I could add, but there is today a new dimension to the problem of major hazards. For fifty years now, we have been wrestling, sometimes not effectively enough, with problems of human error – since 9/11 we are forced to consider malicious acts as well.

I cannot improve on Lees' definition of a major hazard – as being of low probability of realization combined with the likelihood of very great harm if realized. Although this definition may be virtually useless in the eyes of the law, hence most regulatory uses, I think Lees had in mind the public, and the public will ultimately decide the acceptability of activities it considers major hazards. Although benefits accrue to all effective loss prevention activities, major or not, prevention of the realization of major hazards will, I believe, become increasingly important in maintaining industry's reputation as a good, and safe, neighbour.

Lees is primarily interested here in major technological hazards, but he skillfully compares them with natural hazards with which the public is more familiar. He points out that technological hazards can rival natural hazards in severity, as some incidents that have occurred in the twentieth century suggest. Despite significant efforts made to improve public safety, the general public is sadly uninformed about the extent of misery that can accompany major accidental releases of hazardous materials – perhaps best exemplified by the Bhopal and Chernobyl disasters. I have been surprised to find in my teaching experience that few chemical engineering students today know anything about Bhopal – excepting Indian students.

As Lees suggests, the problem of major hazards requires an essential understanding of, and respect for, the most basic desires of our society. If the methods adopted for dealing with these problems do not address the larger desires of society, failure is likely. He hits the nail on the head when he says, 'Policy decisions would be so much easier if a purely quantitative analysis were enough or nearly so.'

The suggestion that 'people select certain risks for attention to defend their preferred lifestyles and as a forensic resource to place blame on other groups' is provocative and sobering. And, his comment that 'While one school of thought argues that the prevention of incidents requires strict discipline and the attribution of blame for error, the other holds that incidents arising from human error are conditioned by the work situation and that the rectification of defects in that situation requires the free flow of information which is inhibited by a blame culture' is all the more sobering in view of the current controversies surrounding the withholding post-9/11 in the United States of Risk Management Plans and other 'sensitive' information from the parties for which it was designed – for fear that it will be used with malice.

Lees' book summarizes the technical/scientific tools that are available for application to the management of major hazards – to define the consequences of scenarios which must be considered, and to define and minimize the likelihood of those scenarios being realized. There remain some areas that are worthy of continued research, to 'sharpen the pencil', and a continued commitment to research and development of loss-prevention management methods is essential. However, it is my belief that the major hazards problems society faces are less a problem of insufficient information about those hazards and more a problem of insufficient application of the tools that we have in hand.

With this foreword, I have decided that Lees' discussion is best left unaltered and unexpanded. To my mind, excepting the growing emergence of a global terrorist threat, there has been little that has occurred since he wrote these words that change the dimensions of the problem of major hazards or the methods that are available for their management.

Some of the installations operated by the chemical industry constitute major hazards. In the early days of the industry, there were some major disasters, particularly ammonium nitrate explosions, involving hundreds of fatalities. The period 1950–80, however, was relatively free of such disasters, but since then there have been several accidents with death tolls of over 100, of which Bhopal was by far the worst.

Process operations are one of a number of activities that are of concern to communities and governments. In particular, high technology, which sometimes brings unforeseen hazards, causes some unease. Inevitably, therefore, the evolution of hazard control policy for the chemical industry must be influenced by developments in public policy for the control of hazards generally.

One area of activity that attracts hazard controls is transport. The evolution of hazard controls on the railways is very instructive and has many lessons for the chemical industry, while air transport illustrates the controls developed for an industry in which high technology is particularly important. Another area of activity closer to the process industries where there has long been a well-developed hazard control policy is the nuclear industry. This has often been suggested, therefore, as a model for the control of hazards in the process industries. Other models include the hazard control systems used in mines, in the explosives industry and in the pharmaceuticals industry.

Selected references on hazard control are given in Table 4.1.

4.1 Superstar Technologies

Within the last two decades, there has been a growing awareness of the problems associated with industrial growth and technological development. This has manifested itself in debate and conflict on such topics as

(1) environment (amenities, countryside, pollution, waste disposal, noise);
(2) resources (oil, metals);
(3) transport (road building, road accidents, aircraft crashes, tanker shipwrecks);
(4) buildings and structures (high rise flats, bridges);
(5) oil and chemical industry (pollution, noxious release, noise);
(6) nuclear power (major accidents, low-level release, waste disposal);
(7) toxic substances (drug and food additive side effects, materials at work).

It is also increasingly recognized that these problems have certain common features and that there is a generic problem in the assessment and control of technological developments. The question is considered in Superstar Technologies (Council for Science and Society, 1976) and the following discussion draws on this work.

Table 4.1 *Selected references on hazard control*

Major projects
Sage (1977); NAE (1986); P.W.G. Morris and Hough (1987)

Catastrophic failures
Bignell *et al.* (1977); B.A. Turner (1978); Michaelis (1986)

Disaster technology
Manning (1976); Cuny (1983); Comfort (1988)

Hazard control policy
Bock (1965); N. Kaplan (1965); NAE (1970); Greenberg (1972); Goldsmith (1973); Bettman (1974); Brodeur (1974); S.S. Epstein and Grudy (1974); Schillmoeller (1974); Chicken (1975); Council for Science and Society (1976, 1977); F. Warner (1976); Hodgkins (1977); IBC (1978/2); Wearne (1979); Collingridge (1980); Gusman *et al.* (1980); Lagadec (1982); Nilsson (1983a); Anon. (1984b); Beveridge and Waite (1985); Weinberg (1985); D. Williams (1985); Kaufman *et al.* (1986); Kharbanda and Stallworthy (1986b); Ostrom (1986); Solomon (1987); Majone (1989); Carnino *et al.* (1990); Funtowicz and Ravetz (1992); The Royal Society (1992)
Safety cases: Mellit (1995) (London Underground)

Interest groups
Stewart (1958); Moodie and Studdert-Kennedy (1970); G.K. Roberts (1970); Wootton (1970); Olson (1971); Wraith and Lamb (1971)

Particular hazards
Aircraft: Wheatcroft (1964); Lowell (1967); Pardoe (1968); W. Tye (1970); Warren (1977)
Drugs: Sjorstrom (1972)
Explosives: L. Allen (1977a)
Motorcars: Nader (1965); Plowden (1971)
Railways: Rolt (1982)
Ships: Cabinet Office (1967)

Hazard assessment
Fussell *et al.* (1974); AEC (1975); Council for Science and Society (1977)
Critiques: Brooks (1972); Weinberg (1972a,b); Mazur (1973); Hafele (1974); The Royal Society (1992)

Warning of disasters
Lees (1982b); The Fellowship of Engineering (1991a,b); J.B. Cook (1991); Cullen (1991); Derrington (1991); Hambly (1991); Sampson (1991); Street (1991)

Planning
Chalk (1973); Dundee Department of Town and Regional Planning (1979); B.D. Clark *et al.* (1981); IBC (1981/17); Petts and Eduljee (1994)
Planning inquiries: Sieghart (1979); Barker (1984); Kemp *et al.* (1984); R.W. King (1984)

Environment
Nicholson (1970); WHO (1972); NAS/NRC (1975); Burton *et al.* (1978); Kates (1978); Conway (1982); Petts and Eduljee (1994)

Cost-benefit, risk-benefit analysis
NAE (1972); Putnam (1980); The Royal Society (1992)

Science and society
von Helmholtz (1895); Steffens (1931); Huff (1954); Cardwell (1957); D. de S. Price (1963); Weinberg (1963, 1967, 1985); Hagstrom (1965); N. Kaplan (1965); Commoner (1966); Greenberg (1967); Nicholson (1967, 1970); Hersch (1968); Crowe (1969); Arendt (1970); Ravetz (1971, 1974a); Rawls (1971); Schrader-Frechette (1984a,b); The Royal Society (1992)

Engineer's, scientist's responsibility (see also Table 3.1):
Gilpin and Wright (1964); Hagstrom (1965); O.K. Price (1965); Ferkiss (1969); Mayo (1970); Nader (1971); Ravetz (1971); Lederberg (1972); Feinberg (1974); Primack and von Hippel (1974); Edsall (1975); Fishbein and Ajzen (1975)

The existence of a problem is due to the combination of a number of factors. Human artefacts are now often large and complex. Society also is complex, interdependent and vulnerable. Technological developments are often rapid and of large scale, and economic pressures militate against extensive testing. Devices are scaled up by extrapolation into untested areas and there is no opportunity for gradual evolution and learning by trial and error.

At the same time, some of the former moderating influences have grown weaker. The complexity of projects involving numerous teams dilutes individual responsibility. There are many new specialisms which tend not to have the same ethos as the older professions. In some of the more important areas the project is so specialized that the organization concerned has a virtual monopoly of the experts available. The combination of the variety and depth of technology increases the difficulty of monitoring by government inspectors.

The degree of acquiescence by the public in technological development has changed considerably in recent years. The increased militancy of interest groups from trade unions to neighbourhood associations shows that people are not prepared to put up with the hazards and nuisances which were tolerated in the past.

Part of the problem is that high technology projects tend to be vulnerable to failures of all kinds. There is only one way in which they can go right, but many in which they can go wrong. In reliability terms, they are series systems in which all the elements must work if the system is to be a success. There is a particular problem in identifying all the ways in which the system may fail. Another aspect of the problem is the question of unforeseen dangerous side effects, of which there have been numerous examples. These include the side effects of drugs and of industrial materials such as asbestos and vinyl chloride.

Occasionally a disaster occurs which is sufficiently dramatic to result in action. Some major technological disasters in the United Kingdom in recent years have been the crashes of the Comet aircraft, the release of radioactive material from Windscale, the side effects of the drug Thalidomide, the defects in the Ronan Point high rise flats, the oil pollution from the Torrey Canyon tanker, the failures of box girder bridges, the collapse of structures built in high alumina cement, the vapour cloud explosion at Flixborough, the sinking of the Herald of Free Enterprise, the fire at the Kings Cross Underground station, the rail crash at Clapham Junction and the explosion and fire on the Piper Alpha oil platform. Some of these have led to improvements of safety procedures (e.g. Windscale), and some to the abandonment of the technology (e.g. Ronan Point). All parties, including the public, the professions and the government tend to react more strongly to such disasters than they do to smaller scale failures, even where these are very frequent.

It is possible to identify a number of factors that allow high technology projects to develop to the point where a disaster can result. At the intellectual level there is the difficulty of trying to foresee the potential problems and of judging where knowledge is inadequate or experiment is required. It is necessary, but not easy, to keep abreast of the technical literature and to maintain contact with experts in other fields. In the moral sphere there are the difficulties of maintaining a conscientious approach to the frequently tedious requirements of safety and of speaking out when doubts arise on safety features. The problem has an organizational aspect in that it tends to require a strong personality to run a major project, but such a person is frequently intolerant of criticism. As a consequence, colleagues are discouraged from dissenting.

Studies of major failures in man-made systems have been described in *Catastrophic Failures* by Bignell, Peters and Pym (1977) and *Man-Made Disasters* by B.A. Turner (1978), and by Wearne (1979).

4.2 Hazard Monitoring

The Council for Science and Society argues for the creation of mechanisms by which the community can monitor and control hazards. Monitoring is likely to be effective only if it is generally accepted as a necessary and constructive activity that not only protects society but also contributes to the project. There is an analogy here with the role of 'Her Majesty's Loyal Opposition' in Parliament.

The project needs to be monitored at all stages: conception, decision and operation. At the conceptual stage, the need is to discover the problems, the hazards and the disbenefits. There should be testing of the basic assumptions, speculative reviews of hazards and study of various scenarios. The debate should involve the public as well as the experts. Argument continues in the decision stage, but now centres on detailed proposals and designs of the project. Here the discussion is mainly between the project team and the other agencies involved. At the operational stage, the emphasis changes to enforcement of operational requirements and monitoring of operating hazards.

Monitoring should be carried out both within the organization itself and through external agencies and fora. Internal monitoring may be conducted by internal but independent functions, such as a pressure vessel inspection section, and by consultants. External monitoring takes place through the activity of interest groups and government agencies. An interest group requires a forum in which to operate; typical fora are courts of law, public inquiries and the news media.

Monitoring by government agencies has a crucial role, but again there are certain difficulties. Despite the resources of government, it is not easy for a government agency to deploy the full range of up-to-date expertise which ideally it should possess. Like any other activity, monitoring may become routine, and complacency may set in. The agency must expect to be subject to the internal politics of the civil service machine. Government itself is not infrequently involved in some way in the projects that require to be monitored.

There are certain relatively detached institutions, such as universities and the professional bodies, which contain expertise and which have a role to play in the monitoring process. It does not follow, however, that they should necessarily themselves be monitors. Their function is rather to provide a source of independent expertise.

An explicit attempt needs to be made to enhance the effectiveness of the individual as a monitor. One important measure is to increase the backing that professional standards can give to the individual. Another is to afford protection to the individual who 'blows the whistle' on a hazard or an abuse.

The process of communal decision-making also places an obligation on those who claim to speak on behalf of the community to be well informed and responsible in their arguments.

4.3 Risk Issues

High technology projects involve risks. These risks raise a number of issues including:

(1) risk perception;
(2) risk criteria;
(3) risk management;
(4) risk estimation.

There is a growing literature on risk issues, which includes *How Safe is Safe?* (Koshland, 1974), *Of Acceptable Risk* (Lowrance, 1976), *The Acceptability of Risks* (Council for Science and Society, 1977), *An Anatomy of Risk* (Rowe, 1977), *Society, Technology and Risk Assessment* (Conrad, 1980), *Societal Risk Assessment* (Schwing and Albers, 1980), *Science, Technology and the Human Prospect* (Starr and Ritterbush, 1980), *Technological Risk* (Dierkes, Edwards and Coppock, 1980), *Acceptable Risk* (Fischhof *et al*., 1981), *The Assessment and Perception of Risk* (F. Warner and Slater, 1981), *Dealing with Risk* (R.F. Griffiths, 1981), *Risk in the Technological Society* (Hohenemser and Kasperson, 1982), *Major Technological Risk* (Lagadec, 1982), *Technological Risk* (Lind, 1982) and *Risk in Society* (Jouhar, 1984).

The Health and Safety Executive (HSE) has published *The Tolerability of Risks from Nuclear Power Stations* (HSE, 1988c), *Risk Criteria for Land Use Planning in the Vicinity of Major Hazard Installations* (HSE, 1989e) and *Quantified Risk Assessment: Its Input to Decision Making* (HSE, 1989c).

A review of risk issues is given in *Risk: Analysis, Perception and Management* (Royal Society, 1992; the RSSG Report) which provides the framework for the following discussion.

The treatment of this topic here is necessarily brief and is limited to an account of some of the principal themes. A further discussion of risk and in particular of risk criteria for hazard control is given in Chapter 9.

4.4 Risk Perception

Work on risk perception shows that people tend not to think in terms of an abstract concept of risk, but rather to evaluate the characteristics of a hazard and to perceive risk in a multi-dimensional way. The idea that risk is an inherent property of the hazard has been criticized by Watson (1981) as the 'phlogiston theory of risk'. Various authors have attempted to define risk. One such attempt is that of Vlek and Keren (1991), who have given 10 different definitions.

4.4.1 Acceptable risk

This question of risk is often treated in the same way as that of 'acceptable risk', although the latter term is itself

contentious, raising as it does the question: Acceptable to whom? Nevertheless, the term 'acceptable risk' has been widely used to describe this generic problem. A discussion of the problem has been given in The *Acceptability of Risks* by the Council for Science and Society (1977). Some of the considerations affecting judgements about risks given by Lowrance (1976) are shown in Table 4.2.

The Council for Science and Society takes up the argument advanced by earlier workers that the distinction between risks that are assumed voluntarily and those that are borne involuntarily is a crucial one. In general, people are prepared to tolerate higher levels of risk for hazards to which they expose themselves voluntarily. The risk to which a member of the public is exposed from an industrial activity is an involuntary one. It is a common view that the risk to which an employee is exposed from this activity is in some degree voluntarily assumed. Thus, the Council's report states:

> Some hazards are accepted voluntarily, even when the risk is high. At one extreme we may say that the risk is 'embraced' when it is an integral part of the challenge in a hazardous sport, such as pot-holing or motor-racing . . . .

The personal attitude is different in emergencies, where the risk may be said to be 'defied' in the course of a response to a call for help. Rescue operations are the prime example of such hazards. In them, the balance of costs and benefits may be very different from that which prevails in ordinary life, as we can see from the lengths to which kind-hearted people will go in retrieving lost or trapped animals . . . .

When a serious hazard is encountered involuntarily, acceptance may extend only to a much lower level of risk than otherwise. When, in addition, the sufferer feels impotent in the face of danger, tolerance is further reduced. Accidents in trains seem peculiarly unacceptable, perhaps more so than accidents in aeroplanes, where rightly or wrongly the passengers are generally considered to have taken the risk on themselves for the sake of the extra benefit of the time saved. In underground tube-trains, only absolute safety seems to be good enough; perhaps the enclosed environment exerts a strong psychological influence. The stark terror of impotence in the face of impending destruction is an important part of the evaluation of such risks. For a strong contrast, we notice how the illusion of control by a driver in a private motor car who is under the influence of alcohol makes very high risk levels acceptable to him.

Table 4.2 *Some considerations affecting judgements on safety (after Lowrance, 1976)*

Risk assumed voluntarily/Risk borne involuntarily
Effect immediate/Effect delayed
No alternative available/Many alternatives available
Risk known with certainty/Risk not known
Exposure is an essential/Exposure is a luxury
Encountered occupationally/Encountered non-occupationally
Common hazard/'Dread' hazard
Affects average people/Affects especially sensitive people
Will be used as intended/Likely to be misused
Consequences reversible/Consequences irreversible

Source: Reproduced with permission from W.W. Lowrance, *Of Acceptable Risk*. Copyright © 1976, William Kaufman Inc., Los Altos, CA 94022. All rights reserved.

Perhaps the most difficult class of hazards for judgements of acceptability are those called 'major hazards'. These are defined by a low probability of realization, combined with the likelihood of very great harm if the hazard is realized. In this case, the intuitions derived from ordinary experience provide little help in conceiving the hazard; and the experts themselves may well disagree even over the probabilities. When harm is liable to be inflicted on people who have neither any conceivable power to avert it, nor any responsibility for its occurrence, the judgement of the 'acceptability' of the risk is at its most difficult.

This variety of perceptions may well be a cause of irritation to the expert on risk assessment. Policy decisions would be so much easier if a purely quantitative analysis were enough or nearly so. The subjective perceptions of risk can have enormous political importance, possibly to the extent of distorting priorities in programmes for coping with the real risks that society encounters. (This problem is most noticeable in medicine.) There is occasionally a temptation on the part of the expert in technological risks to throw in a couple of extra orders of magnitude of restriction of unacceptable hazards and then perhaps be annoyed when even this does not render them acceptable to critics.

In the last analysis, the Council continues, there is only one sort of risk 'that is truly "acceptable" in the ethical sense: the risk that is judged worthwhile (in some estimation of costs and benefits), and is incurred by a deliberate choice made by its potential victims in preference to feasible alternatives'. The important question, therefore, is 'under what conditions, if any, is someone in society entitled to impose a risk on someone else on behalf of a supposed benefit to yet others?'

The Council concludes that it is not practical to give the individual an absolute veto over any development which may be a hazard to him or her. The public interest must also be considered. This does not necessarily mean, however, that it is sufficient to leave the judgement on the acceptability of risk to the organization concerned or to government. The Council cites a number of cases in which it considers that control by government inspection agencies has not achieved the proper balance of risk. It suggests:

> Rather than continuing to demand an answer to the question whether a risk is fair in itself, we should redirect our attention to the ways that risks come about and are controlled. That is, we should focus on the procedures by which the decisions are taken on the creation or persistence of risks, and ask whether these procedures are fair.

The Council advocates that decisions on projects involving hazards should be openly arrived at and that those affected should be able to participate in the decision through the medium of public inquiries and other similar fora.

The report contains a number of appendices that deal with risk in aircraft (D.V. Warren, 1977), in nuclear radiation (Burhop, 1977), with explosives (R.L. Allen, 1977a), at Flixborough (R.L. Allen, 1977b), with asbestos (Woolf, 1977) and with the use of mathematics in risk assessment (Ravetz, 1977b). Many of these are discussed further in later chapters.

4.4.2 Acceptable vs tolerable risk

The account of the acceptability of risk in the RSSG Report describes some of the approaches taken to the problem of

acceptable risk and the distinction between acceptable and tolerable risk.

Fischhoff *et al.* (1981) suggest that there are three main methods used to resolve risk questions. These are professional judgements by experts, formal cost–benefit analyses and methods based on comparisons with the risks accepted from existing hazards. The authors suggest that the relevant factors are whether a method is: comprehensive, logically consistent; practical, open to evaluation, politically acceptable, compatible with existing institutions, conducive to society's learning about risk and whether it improves decision-making in the long run. Fischhoff *et al.* use these seven criteria to evaluate the approaches described.

The concept of acceptable risk came in for criticism from Sir Frank Layfield, chairman of the Sizewell B Inquiry. He argued that the concept understates the seriousness of the problem and that the term 'tolerable risk' is preferable. He expressed the view that the opinions of the public should underlie the evaluation of risk, although he saw no practical way in which they could reliably be so used. The Tolerability of Risk from Nuclear Power Stations, produced following this inquiry (HSE, 1988b) gives the following definition:

> Tolerability does not mean 'acceptability'. It refers to the willingness to live with a risk to secure certain benefits and in the confidence that it is being properly controlled. To tolerate a risk means that we do not regard it as negligible or something we might ignore, but rather as something we need to keep under review and reduce still further if and as we can.

4.4.3 Actual vs perceived risk

One aspect of the risk debate concerns the relationship between objective, or statistical, risk and subjective, or perceived, risk. One line of inquiry draws a distinction between actual and perceived risks, and seeks to investigate the extent to which perceived risks differ from actual ones. The opposing school of thought holds that such a distinction is misconceived.

The attempt to assess the risks arising from a hazard involves a number of areas of considerable difficulty. The RSSG Report highlights two of these: (1) consequences and (2) uncertainty.

Scenarios for the realization of a hazard generally involve a whole range of consequences. There may be injuries, which may be fatal or non-fatal, prompt or delayed. There may be environmental damage where the effects may appear promptly or only after a delay. In other words, the consequences are multi-dimensional.

The assessment of the risk is subject to uncertainty. Traditionally, uncertainty has been discussed in terms of probability, but this does not exhaust the matter. In the taxonomy of ignorance given by Smithson (1989), probability is one aspect along with others such as incompleteness and distortion. Even the concept of probability has different meanings, four conventional interpretations being the classical, frequency, logical and Bayesian.

One type of uncertainty that arises in risk assessments concerns the values to be assigned to the parameters. A more fundamental uncertainty arises over the completeness and correctness of the structure of the analysis. There are both parametric and systemic uncertainties – or as C.H. Green, Tunstall and Fordham (1991) put it 'What you know you don't know' and 'What you don't know you don't know'.

Expert risk assessments do not provide an unambiguous and reproducible measure of risk. The validity of the assessment depends very largely on its pedigree, but this can be mixed, with highly expert and less expert elements, such that the latter may well be the weak link. A study by Lathrop and Linnerooth (1983) found widely differing assumptions underlying three separate studies of the same proposed facility in the United States. Considerations of this kind undermine the assumption that it is possible to determine an objective measure of 'risk' that can then be used as a basis for judging perceptions of risk.

4.4.4 Psychological issues

One of the main fields of study in psychology is sense perception and the methodology for this is one starting point for investigating risk perception. In such a work, an investigation is made of the extent to which the subject's perception of objective stimuli corresponds with reality. The difficulty in applying these methods to risk perception is that risk is not an objective property.

There are, however, several specific topics bearing on risk where progress has been made using the psychological approach. The RSSG Report describes three such areas: (1) estimation of fatality, (2) characterization of hazards and (3) differences between individual and group perceptions.

Lichtenstein *et al.* (1978) investigated the estimation by laymen of the annual number of fatalities in the United States from 40 different hazards. The estimates made by the laymen showed two biases. One was that they overestimated the number of deaths due to infrequent causes such as tornadoes, but underestimated those due to frequent causes such as diabetes. The other was that the infrequent events for which overestimates were highest tended to be those of which laymen have a vivid picture and which are salient in their memory. The authors term this the 'availability heuristic'. The correspondence between the lay estimates and the statistical data were better in respect of rank ordering than in respect of the absolute number of deaths. The conclusion drawn in the Report from this and other work is that individuals are quite capable of making well-founded judgements of the relative magnitude of expected fatalities.

A study of the perception of the qualitative characteristics of hazards was made by Slovic, Fischhoff and Lichtenstein (1980). In this study, respondents were asked to rate 90 hazards in respect of 18 qualitative characteristics. The latter were then reduced to three dominant factors of which the first two were 'dread risk' and 'unknown risk'. Dread has to do with features such as whether the hazard is uncontrollable and exposure to it involuntary, unknowability has to do with features such as whether the hazard is a familiar one and whether its effects are immediate or delayed. The results obtained are shown in Figure 4.1. The third factor was the number of people exposed to the hazard. The findings of this and subsequent studies have also shown that respondents tend not to be satisfied with existing trade-offs between risks and benefits and to desire stricter regulation of hazards.

An individual's perception of risk is likely to be affected by his personality but also by his membership of a group. A number of studies have been done of the effect of membership of groups differentiated by culture, gender or age. Work on groups also includes investigation of the attitudes of individuals within groups with different stances on a

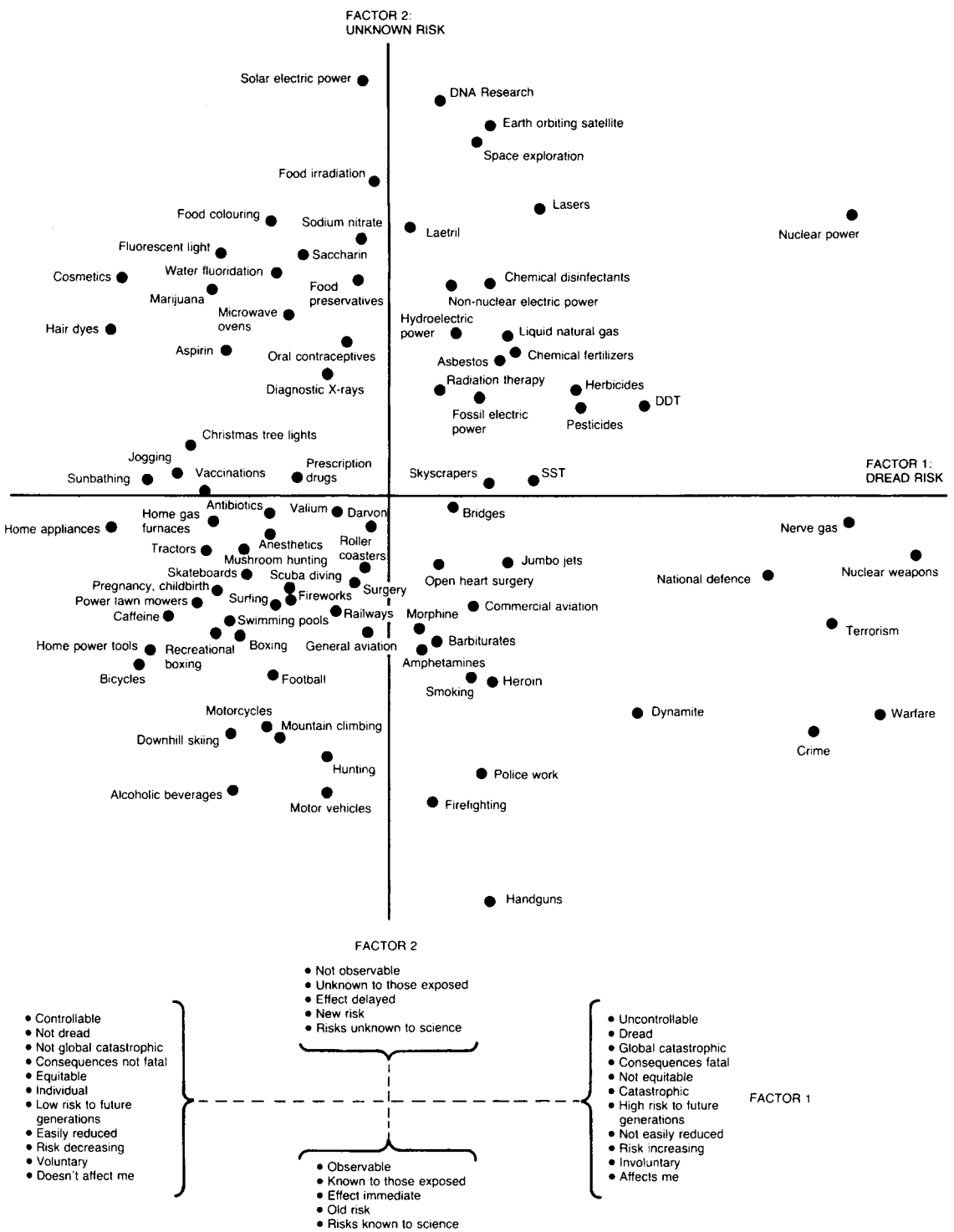

Figure 4.1 *Perception of different hazards: 'dread risk' vs 'unknown risk (Stovic, Fischhoff and Lichtenstein, 1980): locations of 90 hazards on factor 1 (dread risk) and factor 2 (unknown risk) of the three-dimensional space derived from the interrelationships among 18 risk characteristics. Factor 3 (not shown) reflects the number of people exposed to the hazard and the degree of one's personal exposure (Courtesy of Plenum Press)*

particular issue such as pro- and anti-nuclear groups. One finding of this work is that individuals in the two groups had rather similar attitudes to particular undesirable characteristics such as increased centralization of power or imposition of involuntary risk, but differed rather in the extent to which they perceived these characteristics as applying to nuclear power.

Another finding of work in this area is that an attitude which favours a technology is often accompanied by a desire that it be more closely regulated and, therefore, that a call for stricter regulation is not necessarily evidence of hostility.

4.4.5 Social science issues

A starting point for the social sciences is that there is every reason to expect that a person's attitude to hazards is related to his overall system of values and beliefs and that it is affected by broad social factors. Three insights of social science which bear on risk issues described in the RSSG Report are (1) cultural theory, (2) social amplification and (3) social framing.

Cultural theory, developed by Douglas (1966, 1982, 1985, 1990, 1992), holds that attitudes such as that to risks vary systematically with cultural bias. The cultural bias of an individual depends partly on the extent to which he is part of a bounded group ('group') and partly on social interactions which are conducted according to rules rather than negotiated ('grid'). Four principal biases are recognized: hierarchists (high grid/high group), egalitarians (low grid/high group), fatalists (high grid/low group) and individualists (low grid/low group). The Report describes these different types as follows:

> The argument goes that individualists see risk and opportunity as going hand-in-hand; fatalists do not knowingly take risks but accept what is in store for them; hierarchists are willing to set acceptable risks at high levels so long as decisions are made by experts or in other socially approved ways; but egalitarians accentuate the risks of technological development and economic growth so as to defend their own way of life and attribute blame to those who hold to other cosmologies.

It continues:

> The implications of this approach for risk assessment and perception are revolutionary. It implies that people select certain risks for attention to defend their preferred lifestyles and as a forensic resource to place blame on other groups. That is, what societies choose to call risky is largely determined by social and cultural factors. If the cultural theory is accepted, no 'single metric' for risk analysis can be developed on which the different cultural biases can find common ground. Studies point to a divide between egalitarians, who are anti-risk, and others.

The concept of social amplification is that risk perceptions are amplified or attenuated by social processes. This occurs because the knowledge of risk that the individual possesses is largely second-hand. It was suggested by Kasperson *et al.* (1988) that the transformations that occur as the risk signal passes through social 'amplification stations' such as expert groups, mass media, government agencies and politicians may be predictable.

'Social framing' or 'expert framing' is the term used to describe the fact that the risk assessments made by expert groups tend to involve a set of implicit assumptions. These assumptions have been the subject of a series of studies by Wynne (1982, 1989, 1992). One area where the expert group typically makes implicit assumptions is the social and institutional framework within which the risks are to be managed. Another area where implicit assumptions are common relates to operations. Discussing the problem of pesticide safety, Wynne (1992) comments that expert framing involved the assumptions that

> . . . pesticides manufacture process conditions never varied so as to produce dioxin or other toxic contaminants of the main product stream; drums of herbicide always arrived at the point of use with full instructions intact and intelligible; in spite of the inconvenience farmers and other users would comply with the stated conditions, such as correct solvents, proper spray nozzles, pressure valves and other equipment, correct weather conditions, and full protective gear. As a model of the 'real' social world and thus of the typical risk system, this was utterly naive and incredible however good the laboratory science.

4.4.6 Risk communication

Another area of study is that of risk communication. Here the RSSG Report addresses four principal topics: (1) risk communication as a discipline, (2) conceptual approaches, (3) applications and (4) trust.

Risk communication occurs at national and company levels. At the latter level a company needs to communicate about risks both with its employees and with the public. In particular, risk communication is an essential part of emergency planning. More recently, legislative requirements for the provision of information to the public have been introduced. Risk communication at the national level is seen most clearly when opposition arises to developments such as hazardous installations or waste disposal sites.

Risk communication in such a context is now recognized as a discipline, but its study is not well advanced. However, the need for a professional approach is clear. The Report comments that 'One should no more release an untested communication than an untested product.' It distinguishes four conceptual approaches to risk communication. One treats it within a technological framework in which there is one-way communication from the expert to the non-expert. The second emphasizes the need for a two-way dialogue. The third deals with the social and institutional context within which communication occurs and the actions, or inaction, as well as the words of the organizations involved. The fourth views risk communication as an aspect of the general political process.

At the level of applications, some of the attempts made to provide reassurance by comparison of the risks of the activity in question with other, more familiar risks come in for criticism. It is suggested by Covello, Sandman and Slovic (1988) that if such attempts are made, they need to take into account the work described above on the principal qualitative dimensions by which people characterize hazards.

Another aspect of applications is the layman's mental model and the effect which this has on his response to risk communication. Using as a baseline an expert model, the layman's model can be studied, and concepts which are erroneous or entirely absent identified. The attempt can then be made to clear away factual misunderstandings at least.

The credence placed in a communication about risk depends crucially on the trust reposed in the communicator. Wynne (1980, 1982) has argued that differences over technological risk reduce in part to different views of the relationships between the effective risks and the trustworthiness of the risk management institutions. People tend to trust an individual who they feel is open with, and courteous to, them, is willing to admit problems, does not talk above their heads and whom they see as one of their own kind.

Trust in a company depends on many factors and may be put at risk in a number of ways. Its general reputation may be undermined by persistent practice or by particular incidents. Distrust of the political process may rub off on the regulatory body. Risk assessment involves the treatment of uncertainties and mishandling can result in loss of trust.

4.5 Risk Management

'Risk management' is the term generally used to cover the whole process of identifying and assessing risks and setting goals and creating and operating systems for their control. An important input to risk management is risk assessment. Indeed the two terms are sometimes treated as synonymous. Generally, however, risk management is accorded a broader meaning to cover both a wider range of risks and a more complete set of activities.

The hazards with which risk management is concerned include, in general, those from natural events and man-made systems that give rise to a range of physical, financial, legal and social risks. The main concern here is with the risks from technological systems.

Risk management is practised at government as well as company level and, indeed, many of the important issues in risk management have to do with the design of the institutions required for public risk management and with the associated risk evaluation.

4.5.1 Public risk management

Ultimately it is up to the government to decide which activities can be allowed and which must be banned and how any disbenefits from the former are handled. Thus, the government is involved in risk management, but the extent to, and manner in, which it should be is a matter of debate.

Many activities involve external 'costs' that are imposed on other parties. These externalities include danger and environmental pollution. A market solution is to require the party responsible to pay these costs. In the case of pollution, this is the principle of 'polluter pays'. Another market approach is the use of insurance to pool risks. However, there are a number of difficulties in these approaches. The party responsible may not be readily identifiable and may have limited resources. This is illustrated by the difficulties in enforcing clean-up of hazardous waste sites.

Insurance also has it problems. Insurers may be reluctant to provide cover for perils that are poorly defined such as pollution. Even where insurance is available, there are recognized problems. Adverse selection occurs where parties know their own risks better than the insurers and insure only the high risks. Moral hazard occurs where the possession of insurance lessens the incentive to reduce the risk.

Public risk management is subject to two types of error. One is the prohibition of an activity or product that may be harmless; the other is failure to prohibit an activity or product which is harmful. By analogy with the terms applied to hypotheses, these two errors are termed Type I and Type II errors, respectively. A Type II error can lead to public outcry, whereas a Type I error, which may involve foregoing great economic benefit, is unlikely to do so.

Risk management is practised not only at national level but at the supranational and local government levels also.

The RSSG Report identifies nine types of institutional 'player', as shown in Table 4.3. It describes the implications as follows:

> As soon as more than one organization enters the risk management scene, different priorities and preoccupations must be resolved through bargaining. Problems of deadlock, jurisdictional tensions, ordering of preferences and varying levels of preference intensity become more acute. The policy 'packaging' processes involved in trading preferences, particularly in multilevel bargaining situations such as those involved in EC decision-making,

Table 4.3 *Some types of player in institutional risk management (The Royal Society, 1992) (Courtesy of The Royal Society)*

Territorial level	*Institutional type*		
	Core executive bodies	*Independent public bodies*	*Private or independent bodies*
Supranational	Example: EC commission	Example: EC Court of Justice	Example: Greenpeace
National	Example: national Parliaments and ministerial departments	Example: national courts and independent regulatory bodies, like the NRA[a]	Example: National Associations of Insurers
Subnational	Example: state or local governments	Example: independent regional/local statutory bodies	Example: local firms and activists

[a] National Rivers Authority.

may result in outcomes that do not match the preferences of any of the negotiating parties.

Many of the public bodies such as advisory committees concerned with risk management have an advisory rather than an executive role. In this they are analogous to a staff function in a company.

The RSSG Report identifies the following four modes of operation available in public risk management: (1) information, (2) resources, (3) legislation and (4) direct action. Information is of particular importance in relation to emergency warnings of impending natural hazards, although the problem of liability for false alarms is a severe one. Where resources are required and unavailable elsewhere, the state may provide them, as in the clean-up of hazardous waste sites. Direct action, by police or other agencies, is largely limited to emergencies.

The approach taken may rely on prevention or on mitigation. For a major hazard at a fixed installation, this typically means either preventing an incident or providing an adequate distance between the plant and the public offsite. However, the applications of the two approaches are much wider. Mitigation, for example, may include financial compensation.

4.5.2 Risk management rules

Some of the dimensions of risk management systems have been studied by Ostrom (1986), as described in the RSSG Report. Table 4.4 shows six such dimensions and their characteristic trends.

The boundary rules determine the parties allowed to participate in the risk management process. The decision process within the regulatory body typically involves the internal experts, consulting with approved expert groups; it is not readily accessible to other parties and becomes less so at supranational level. The boundaries are a matter of debate. They are challenged, for example, by interest groups seeking to participate.

The scope rules determine the type of decision that the risk management body can take. Typical choices are fact-finding vs blame attribution, national vs international measures in sea and air transport, integrated pollution control vs control of particular vectors.

The position rules determine the hierarchy and relationships of the decision points in the risk management structure, including the power of appointment and dismissal. Thus, in the United Kingdom, many regulatory bodies are independent with direct accountability to Parliament, and Ministers are readily able to dismiss them.

The information rules determine access to information. This has many aspects. The risk management system needs to be able to obtain information, such as the location of major hazard installations or sources of pollution, which it can obtain only by specific legislation. The public needs information on the hazards to which it is exposed and on what to do in an emergency. In this case, the information may be made available on a 'right-to-know' or a 'need-to-know' basis. Again, legislation is required to ensure this information is made available.

The authority and procedural rules determine the mode of decision-making, its timing and the evidence admissible. Typical choices, or emphases, are adversarial vs inquisitorial procedures, anticipatory action vs incident investigation, and qualitative vs quantitative assessments.

The preference-merging rules determine the process by which the individual inputs contribute to the collective decision. Two principal rules are unanimity and majority voting. Both are exemplified in the decision-making processes of the European Community (EC).

Table 4.4 *Some dimensions of, and putative trends in, risk management (Royal Society, 1992; after Ostrom, 1986) (Courtesy of de Gruyter Verlag and The Royal Society)*

Rule type	*Explication*	*Range of key types*	*Characteristic trends*
Boundary	Who is counted as a player?	Technocratic/ participative	More participation
Scope	What is managed and what can be decided?	Broad/narrow	Extension of scope
Position	What is the hierarchy of players?	Single organization/ multi-organization	More multi-organizations
Information	Who is entitled to know what from whom?	Open/closed	More open
Authority and procedure	Under what conditions must decisions be made?	Formal/informal	More formal
Preference merging	How are individual preferences aggregated into collective decisions?	Consensus (integration)/ conflict (aggregation)	More conflict

4.5.3 Risk management issues

The RSSG Report identifies, but does not attempt to resolve, seven areas of debate in risk management. These issues are: (1) anticipation, (2) liability and blame, (3) quantitative risk assessment (QRA), (4) institutional design, (5) risk reduction costs, (6) participation and (7) regulatory goals. They are summarized in Table 4.5. For each issue, the Report presents both sides of the argument, but with caveats that the issues are not usually so starkly posed, that opposing views are not necessarily irreconcilable and that one of the two viewpoints may be much more accepted than the other. The anticipation issue concerns the relative priorities to be given to prevention and to mitigation. The term 'anticipation' has a rather wide meaning and covers different aspects, depending on the context. For accidents, anticipation has to do with the management systems which assure effective hazard control. For pollution, it has to do with caution in not permitting activities or products the effects of which are not fully known. Two complementary arguments are advanced against anticipation. One is that it is not totally effective, so that the alternative (resilience) is necessary anyway; the other is that emphasis on anticipation reduces the motivation and resources needed to promote resilience.

The liability and blame issue concerns the desirability or otherwise of attributing blame where investigation of an incident indicates that someone has made an error. One school of thought argues that the prevention of incidents requires strict discipline and the attribution of blame for error, whilst the other holds that incidents arising from human error are conditioned by the work situation and that the rectification of defects in that situation requires the free flow of information which is inhibited by a blame culture.

Studies are quoted to the effect that such information flow is essential to the efficient functioning of complex

Table 4.5 *Some issues in risk management (Royal Society, 1992) (Courtesy of The Royal Society)*

Doctrine	*Justificatory argument*	*Counter-docirine*	*Justificatory argument*
Anticipationism	Apply causal knowledge of system failure to *ex ante* actions for better risk management	Resilienism	Complex system failures not predictable in advance and anticipation makes things worse
Absolutionism	A 'no-fault' approach to blame avoids distortion of information and helps learning	Blamism	Trageted blame gives strong incentives for taking care on the part of key decision-makers
Quantificationism	Quantification promotes understanding and rationality, exposes special pleading	Qualitativism	Proper weight needs to be given to the inherently unquantifiable factors in risk management
Designism	Apply the accumulated knowledge available for institutional design	Design agnosticism	There is no secure knowledge base or real market for institutional design
Complementarism	Safety and other goals go hand in hand under good management	Trade-offism	Safety must be explicitly traded off against other goals
Narrow participationism	Discussion is most effective when confined to expert participants	Board participationism	Broader discussion, better tests assumptions and avoids errors
Outcome specificationism	The regulatory process should concentrate on specifying structures or products	Process specificationism	The regulatory process should concentrate on specifying institutional processes

organizations (Laporte, 1982; K.H. Roberts, 1989; K.H. Roberts and Gargano, 1989). Mention is made of the explicit adoption of a no-blame policy by Shell International (1988).

The argument concerning blame also extends to the corporate level. In 1990, a suit was brought against P&O Ferries for corporate manslaughter in respect of the sinking of the Herald of Free Enterprise. This case collapsed, but it may well indicate a trend.

The QRA issue concerns the contribution of QRA to decision-making about risks. Supporters of QRA advance it as an aid to, though not the sole determinant of, rational decision-making and argue that it is an effective means of understanding complex technological systems, and also natural hazards, and that there is no real alternative method of ordering priorities. The opponents' critique develops two main themes. One is that QRA contains value judgements that are not made explicit. The other is that QRA is beset by uncertainty, which extends not just to values of the parameters but to the whole structure and completeness of the assessment. The more radical argue that QRA is liable to mislead and is positively harmful.

The institutional design issue concerns the feasibility of designing institutions for risk management and the extent to which good practice in this area can be defined. Changes in risk management systems are typically among the principal recommendations of accident inquiries. Those who believe good practice can be articulated refer to the safety management systems and safety culture in major companies such as those in the oil and chemical industries. Sceptics point to wide differences of practice, or even contradictory practices, which they perceive to yield similar outcomes, such as the blame and no-blame cultures mentioned earlier.

The risk reduction cost issue concerns the cost of risk reduction and trade-offs of risk against other goals. One view is that reduction of risks incurs additional costs and that there has to be a trade-off between risk reduction and other goals. The types of risk cover a wide spectrum, including both safety and environmental risks. The opposing viewpoint is essentially that good practice in respect of risks is generally profitable also, but the arguments that support this appear to differ, depending on the type of risk considered. In safety, the argument is that the good management that ensures high safety also delivers high profits. In terms of the environment, the argument relies rather on examples where the move to more environmentally friendly products appears not to have disadvantaged the company.

The participation issue concerns the extent of participation appropriate in risk management. The general proposal for wider participation embraces a number of different types of participant and does so for different reasons. Thus, it is suggested that human factors experts should participate more in engineering projects to avert the problems which otherwise are liable to arise. Participation by lay groups is held to force consideration of wider issues and to improve the quality of the decision-making in large technological projects. Another argument for the involvement of the latter is to improve public accountability and to broaden the base of those committed to the project. Others are more sceptical and fear that the process is liable to result in less rational decisions and to dispersion of responsibility.

The regulatory goals issue concerns the emphasis to be placed on outputs and on process in respect of risks. The engineering, and regulatory, culture tends to concentrate on outputs in the form of physical products or systems. These are typically designed with safety margins which are implicitly based on doing what is 'practical' and 'reasonable'. Critics argue that the risks of these outputs are subject to such uncertainty that this approach is inadequate, and call for more emphasis on process by the application of quality management concepts.

As stated earlier, whilst it is convenient for purposes of exposition to present these viewpoints as thesis and antithesis, there is on all these issues a spectrum of views, and in many cases a synthesis can be envisioned.

4.5.4 Cost–benefit analysis

The RSSG Report contains an appendix on cost–benefit analysis in relation to risks by Marin (1992), with particular emphasis on risks to people. The application of cost–benefit analysis to such risks is based on the principle of reducing the risks until the marginal cost equals the marginal benefit. In order to do this, costs and benefits have to be expressed in the same units, which means in money terms.

The first requirement is therefore to devise methods of estimating the 'value of a statistical life' or for short, the 'value of a life'. Marin describes both the wide variety of approaches that have been used and the perceived ethical problems. The process of putting a price on life is apt to appear cold-blooded or even unethical. In practice, the allocation of scarce resources demands ordering of priorities. Administrative decisions are constantly being made in which a value is placed on life, if not explicitly then implicitly. Thus, at present, society mainly leaves this problem in the hands of special groups.

There are certain approaches to the determination of the value of a life that have not proved fruitful. One is to base the assessment on the individual's earning power, the 'human capital' approach. This implies that those who cannot work, for whatever reason, are without value and are unethical. It is also incompatible with the normal approach in cost – benefit analysis, which is to ascertain what the course of action proposed is worth to the person(s) affected. On the other hand, it is also not helpful to ask an individual what sum he would be prepared to pay in exchange for his life. This sum may be regarded as infinity.

A more fruitful approach is to consider small increments of risk and then determine what people will pay to eliminate these. Two main methods are available to make this determination. One is to ask people, the other is to observe their behaviour. Typical studies make comparisons of choices such as those between modes of transport or between jobs of different degrees of safety.

Marin quotes two UK studies which both put the value of a life at £3 million at 1990 values, one based on fatal accident rates in different occupations (Marin and Psacharopoulos, 1982) and the other on willingness to pay for improved safety (Qones-Lee, Hammerton and Philips, 1985). For comparison, the estimate given based on the human capital approach is about £235,000.

It is also possible to consider large increments of risk, in particular those that are at the threshold where they are not acceptable to the individual, whatever the financial compensation. This aspect is not well developed, but it is relevant to situations such as those which occur in nuclear accidents where people may be asked to do work in conditions where the levels of radiation are high.

Modes of fatality, non-fatal injury and age pose further problems in determining the value of a life.

4.6 Hazard Control Policy

It is appropriate at this point to consider some of the elements that go to make up a hazard control policy. An account of this has been given in Hazard Control Policy in Britain (Chicken, 1975). The legislation referred to is that current at the time. Chicken considers five fields that illustrate hazard control policy. These are (1) road transport, (2) air transport, (3) factories, (4) nuclear power and (5) air pollution. These fields represent very different hazard control situations.

His argument runs as follows. In road transport, hazard control is mainly by legislation aimed at general improvement. Research is conducted by the Road Research Laboratory (RRL), manufacturers are encouraged to improve design standards, road construction takes account of safety knowledge and compulsory testing of vehicles is required.

Air transport, by contrast, is controlled not only by legislation (Civil Aviation Act 1971) but by a strict system of licensing operated by the Civil Aviation Authority (CAA). Aircraft are technologically much more complex and give rise to hazards that provoke much greater public outcry. The hazards are subjected to quantitative assessment and are reduced to a minimal level by sophisticated technology.

Control of factories is carried out through legislation (Factories Act 1961) which is enforced by a rather thinly spread inspectorate. The level of technology, the degree of hazard and the sophistication in control vary widely.

Nuclear power is again controlled not only by legislation (Nuclear Installations Act 1965) but by a strict licensing system operated by a well-staffed Nuclear Installations Inspectorate. Again, nuclear reactors are technologically complex and constitute major hazards, and full hazard assessment and control is carried out.

Control of air pollution by legislation (Alkali etc. Works Regulation Act 1906, Clean Air Acts 1956 and 1968) is enforced again by a somewhat thinly spread Alkali Inspectorate.

Thus, arrangements for hazard control for factories and for air pollution are rather similar, but they are very different from those for air transport and nuclear power, which are also similar. The situation in road transport does not constitute a hazard control arrangement in the same sense.

It is apparent that there are wide differences in the voluntary component in these policies. In general, this is greatest where a large number of units are involved, where the controls were first applied to an established activity, where other regulatory bodies such as local authorities are involved and where there are strong interest groups.

Thus, the controls are most stringent in air transport and nuclear power, where the number of units or operators is small, the activity is a relatively new technology, there is strong central government involvement and interest groups opposing regulation are absent. It is relevant to note also that these are the two high technology activities considered.

The elements of hazard control policy are (1) identification, (2) legislation and control arrangements, (3) research, (4) consultative arrangements and (5) priorities in resource allocation.

Hazard control policy appears to develop in response to (1) demands for improved control, (2) developments in hazard reduction; (3) defects in existing policies and (4) developments abroad. Study of the way in which hazard control policy evolves indicates that the initiating role of political parties and Parliament is relatively small and that it is most directly influenced by the Civil Service in the departments primarily involved, with the various inspectorates playing a leading role. When major developments are being considered, extensive use is made of independent specialist committees, such as the Edwards Committee on Air Transport or the Robens Committee on Health and Safety at Work. It is largely through these committees that the interest groups are able to influence policy.

Interest groups have an important role to play in the development of hazard control policy. The study of interest groups is a well-established aspect of social science (e.g. Moodie and Studdert-Kennedy, 1970; G.K. Roberts, 1970; Wootton, 1970). Wootton classifies interest groups as economic (e.g. Confederation of British Industry (CBI)), integrative (e.g. Institution of Chemical Engineers) or cultural (e.g. National Trust), and as first, second or third order, depending on whether they operate at local, regional or national level. This role is well illustrated by the proceedings of the Robens Committee, whose report contains much material from such organizations.

It is suggested by Chicken (1975) that the most influential interest groups are the economic (e.g. industrial) and integrative (e.g. professional) groups that operate at national level. While this is no doubt true in terms of detailed positive recommendations, the effect of agitation by local groups and of news media campaigns by groups at all levels on the general spirit in which policy-makers approach their task should not be underestimated.

The broad conclusions of this study remain valid.

4.7 Nuclear Hazard Control

Hazard control is well established in nuclear energy, which is an obvious model for control of chemical industry hazards. It is helpful, therefore, to consider briefly the arrangements in the nuclear industry. A short account of nuclear energy is given in Appendix 20 and the treatment here is confined to hazard control policy for the industry.

One of the principal features of the control of nuclear hazards is the role played by hazard assessment. Many of the hazard assessment techniques used in the process industries were developed in the nuclear industry. Nuclear hazard assessment is one of the topics discussed in Appendix 20.

Selected references on nuclear hazard control are given in Table 4.6.

4.7.1 Nuclear plant licensing

The early work on nuclear energy in the United Kingdom was for military purposes and was controlled by the Ministry of Supply, but in 1954, the UK Atomic Energy Authority (UKAEA) was established and began to operate nuclear power reactors at Calder Hall. Although these were again primarily for defence, they confirmed the feasibility of nuclear power. In 1958, the Central Electricity Generating Board (CEGB) was created and became the main operator of nuclear power reactors. These two operators were later joined by two others, the South of Scotland Electricity Board (SSEB) and British Nuclear Fuels Ltd (BNFL).

The responsibility for the control of nuclear power reactors was shared between the UKAEA and the Nuclear Installations Inspectorate (Nil). The Atomic Energy Act 1954, which established the UKAEA, gave the latter responsibility for the safety of its own reactors. Reasons for this rather unusual arrangement include the facts that the

Table 4.6 *Selected references on nuclear hazard control (see also Table A20.1)*

Nuclear hazard assessment and control
NRC (Appendix 28 Regulation); F.R. Farmer (1967a,b, 1969a,b, 1970, 1971); Dale and Harrison (1971); F.R. Farmer and Gilby (1971); Kirk and Taylor (1971); Weinberg (1972b); Gronow and Gausden (1973); EPA (1974); Karam and Morgan (1974); AEC (1975); Chicken (1975); Freudenthal (1976); Rust and Weaver (1976); Fussell and Burdick (1977); HM Chief Inspector of Nuclear Installations (1977); HSE (1977c, 1992d); NRC (1977a–c); Fremlin (1978, 1983); Higson (1978); R.J. Parker (1978); E.E. Lewis (1979); I.K.G. Williams (1979); Windscale Local Liaison Committee (1979); Bradbury (1980); Fells (1980, 1981); Joksimovic and Vesely (1980); Pentraeth (1980); Strong and Menzies (1980); Charlesworth *et al.* (1981); D. Pearce (1981); Sagan (1981); Schrader-Frechette (1981); Chicken (1982); Openshaw (1982); Amendola (1983a,b); R.F. Griffiths (1984b); C. Tayler (1985f); UKAEA and BNFL (1985); Lester (1986); TUC (1987); Andrews (1988); Solomon and Kastenberg (1988); Ballard (1989); Carnino *et al.* (1990); Wu and Apostolakis (1992)

Debate, critics, public relations
Weil (n.d.); Hedgpath (1965); Bryerton (1970); Novick (1970); R. Lewis (1972); Metzger (1972); Dunster (1973); Gofman and Tamplin (1973); Cochran (1974); Ebbin and Kasper (1974); Kendall and Moglewer (1974); Kendall (1975); Lovins (1975, 1977); Primack (1975); J. Hill (1976, 1979b); Patterson (1976, 1988); Brookles (1977); Hayes (1977); Icerman (1977); Puiseaux (1977); Breach (1978); Foley and van Buren (1978); Grossman (1980); Nickel (1980); Sweet (1980); Dunster (1981); Hewlett (1982); B.L. Cohen (1983, 1989); Cannell and Chudleigh (1984); T. Hall (1986); McGill (1987); V.C. Marshall (1988b); Aubrey (1991); Slovic *et al.* (1991)

initial purpose of the UKAEA was to produce nuclear weapons and that the UKAEA had virtually all the experts. The coincidence of the occurrence in 1957 of the Windscale incident and of the creation in 1958 of the CEGB, which was to operate nuclear power reactors for civil use, led the Fleck Committee, which investigated the former, to recommend a separate nuclear inspectorate. The Nuclear Installations (Licensing and Insurance) Act 1959 created the Nil and also laid down that reactors other than those of the UKAEA must be insured to cover all claims which might arise from the release of radioactivity. The situation that developed was one in which the UKAEA was responsible for the safety of its own reactors, with the Nil controlling other nuclear reactors through a licensing system.

The nuclear licence that the operator of a nuclear power reactor is required to obtain represents a very stringent system of control. The licensee must furnish design and operating documents that effectively cover all aspects of the design and operation of the reactor. A Nuclear Safety Committee must be created to advise the licensee and the names and qualifications of the persons nominated submitted to the Minister for approval. Individuals must also be nominated as Competent Persons to execute particular tasks.

Licensing is not a once-for-all affair but an on-going procedure. The first stage in the granting of a licence is simply the permission, in principle, to use a particular piece of land for a nuclear power reactor. Subsequent stages result in the granting of permission to build and to operate. Inevitably the licensee will wish to make changes in design features, operating procedures and nominated personnel, and these must then be agreed with the licensing authority.

This licensing system has some characteristic features that are important in relation to hazard control. It is flexible and adaptable to change and avoids the disadvantages of general and often irrelevant regulations, but it is highly detailed and involves considerable effort in making changes. And it makes heavy demands on manpower both for the licensee and the controlling authority. It also inevitably tends to shift some of the responsibility from the operator to the inspectorate. It is a highly effective but resource intensive system.

The particular approach taken to the control of nuclear hazards reflects the uncertainties in the early days of nuclear energy, say the mid-1950s, about the hazards of this very high technology industry. It is debatable how applicable this approach is to other hazards.

4.7.2 Nuclear plant siting

In the United Kingdom, the sites that might be used in a power network vary by a factor of 10 at most in population density. Hazard assessments for nuclear plants are accurate only within a similar factor. Thus, reactors cannot be matched to sites with any precision. In effect, the design must be to a standard which, it may be argued, then permits complete freedom of siting.

Hazard assessments have been presented by F.R. Farmer (1967a,b, 1971) to support the relaxation of the historical restrictions requiring remote siting and to permit siting nearer urban areas. However, it is not government policy to allow this degree of freedom in siting nuclear plants. The siting of nuclear reactors in or near large centres of population is not permitted. A major determinant of this policy is the difficulty of devising effective emergency countermeasures to the hazards of a radioactive release.

An account of UK siting policy is given by Gronow and Gausden (1973).

4.7.3 Nuclear safety case

An important feature of the nuclear licensing system is the safety case. The nuclear safety case is broadly similar, *mutatis mutandis*, to the process safety case described below.

The safety issues to be addressed are outlined in *Nuclear Safety. Safety Assessment Principles for Nuclear Reactors* (HSE, 1979d) and, for pressurized water reactors, in PWR (HSE, 1979e).

Quantification of the risks has long been a feature of the nuclear safety case. The evaluation of these risks is addressed in *The Tolerability of Risks from Nuclear Power Stations* (HSE, 1988c).

4.8 Process Hazard Control: Background

The growth of major industrial hazards, especially those associated with the process industries, and the means of controlling them, was one of the main concerns of the Robens Committee. The subsequent Health and Safety at Work etc. Act 1974 (HSWA) provides a much improved framework for control. Even before this, a Department of the Environment (DoE) circular DoE 72/1 had drawn attention to the need to take account of major hazards in planning.

The disaster at Flixborough in 1974 caused a great surge of public concern over such hazards and represents a watershed as far as process industry hazards are concerned. Following Flixborough, the Health and Safety Commission took certain steps to improve control of major hazard installations. A Major Hazards Unit was set up within the HSE and an Advisory Committee on Major Hazards (ACMH) was appointed. Within the Major Hazards Unit, a Risk Appraisal Group (RAG) was formed to give advice to local planning authorities (LPAs) on planning applications for major hazard installations. The supervision of these installations by the Factory Inspectorate was intensified. These arrangements were interim measures taken pending the recommendations of the committee.

Selected references on major hazard control in the process industries are given in Table 4.7.

Table 4.7 *Selected references on major hazard control in the chemical industry*

Harvey (1976, 1979b, 1984); Solomon (1976); Fairley and Mosteller (1977); Lees (1977b, 1980d, 1982c); Locke (1977); Napier (1977b); Schenkel (1977); Wakabayashi (1977); AERA (1978 Harwell Environmental Seminar 1, 1979 Harwell Environmental Seminar 2); Cremer and Warner (1978); Yaroch (1978); Schoch (1979); Beveridge (LPB 31 1980); Levitt (1980); Kunreuther *et al.* (1981); Barrell and Scott (1982); F.R. Farmer (1982); Helsby *et al.* (1982); Kunreuther and Ley (1982); Labour Inspectorate (1982); Lagadec (1982); V.C. Marshall (1982b, 1982 LPB 46, 1985, 1987, 1988c, 1989c, 1990d); Pantony and Smith (1982); Ramsay *et al.* (1982); Pape (LPB 51 1983); Anon. (1984b,m,w); Crossthwaite (1984, 1986); Hawksley (1984); Kunreuther (1984); D.J. Lewis (1984f); Anon. (1985h); Barrel (1985, 1990, 1992); Beveridge and White (1985); K.R. Davies (1985); Dewis (1985a); ILO (1985a, 1989, 1991); R. King (1985); C. Martin (1985); Merriman (1985); Moysen (1985); Otway and Peltu (1985); Wang (1985); Anon. (1986z); Air Pollution Control Association (1986); J.C. Consultancy Ltd (1986); Raman, Stephens and Haddad (1986); Slater *et al.* (1986); Pate-Cornell (1987); Ripple (1987); J.G. Collier (1988); HMCIF (1988b); Withers (1988); Challis (1989); Machida (1990); van Mynen (1990); Renshaw (1990); Shortreed (1990); Zimmerman (1990); Keller and Wilson (1991); Crawley *et al.* (1992); A.J. Williams (1992); Donegani and Jones (1993); Rimington (1993); Rosenthal (1993); CEC (1994)

Natural gas, liquefied natural gas (LNG)
US Congress, OTA (1977); Cofield (1978); DoEn (1978); UN (1978); Sutcliffe (1980); Kunreuther *et al.* (1981)

Community involvement, citizen groups, public relations (*see also* Table 9.1)
Chopey (1967b); F.C. Price (1974b); Sutcliffe (1980); Rodgers (1987); Buzelli (1990); Delbridge (1990); Poje (1990); Grollier-Baron (1992c); Marsili, Volloni and Zaponi (1992); Renn (1992); The Royal Society (1992)

Planning
DoE (1972 Circular 1/72, 1980 Circular 22/80, 1983, 1984a–c, 1984 Circular 22/84); Anon. (1975h); Harvey (1976, 1979b, 1984); Salter and Thomas (1981); Anon. (1984w); Crossthwaite (1984, 1986); IBC (1984/57); Pape (1984); Petts (1984a,c, 1985a,b, 1987, 1988a,b, 1989, 1992); Milburn and Cameron (1992); C. Miller and Flicker (1993)
Planning inquiries: Sieghart (1979); Barker (1984); Wang and Parker (1984); Petts (1985a,b); Petts *et al.* (1986)
Mossmorran: Barrell (1988b); Sellers (1988)

Safety cases
Cassidy (1987, 1988a–c, 1989, 1990); R. Clark (1987); Dyson (1987); Eberlein (1987); Hawksley (1987); Orrell and Cryan (1987); CIA, Chlorine Users Group (1989); R. Clark *et al.* (1989); FMA (1989); Fullam (1989); Lees and Ang (1989b); Pape (1989); Petts (1989); Singleton (1989); IBC (1995/115); Fullam (1995); Myers (1995)
Safety cases and environment: Cassidy (1990)

Offshore (see Table A18.1)

USA
Brooks *et al.* (1988); Keffer (1991)

Germany
Kirsch (1979); Nagel *et al.* (1979); Anon. (1980w); Kremer (1981); Land Nordrhein-Westfalen (1981); Schleifenbaum (1981); Wohlleben and Vahrenholt (1981); Braubach (1982); Pilz (1982, 1987, 1989)

The Netherlands
Meppelder (1977); van de Putte and Meppelder (1980); van de Putte (1981, 1983); Versteeg (1988); Husmann and Ens (1989); Oh and Husmann (1988); Oh and Albers (1989); Ale (1991, 1992); Bottelsburgh (1995)

4.9 Process Hazard Control: Advisory Committee on Major Hazards

The ACMH under the chairmanship of Professor B.H. Harvey, a former Deputy Director-General of the HSE, was set up soon after Flixborough in 1974. The terms of reference of the committee were:

> To identify types of installations (excluding nuclear installations) which have the potential to present major hazards to employees or to the public or the environment, and to advise on measures of control, appropriate to the nature and degree of hazard, over the establishment, siting, layout, design, operation, maintenance and development of such installations, as well as over all development, both industrial and non-industrial, in the vicinity of such installations.

The work of the Committee, which ended in 1983, is described in the three Reports of the ACMH (Harvey, 1976, 1979b, 1984). Some of the main themes of these reports are given in Table 4.8. The first task of the Committee was to define, or rather identify, major hazards. It concluded that, with few exceptions, a major hazard arises only if there is a release from containment. The hazard that then arises is a release that is flammable, toxic or both. A flammable release may give rise to a jet or pool fire or a fireball, or the vapour cloud may burn as a flash fire, or it may give a vapour cloud explosion.

Although there is little in the three reports on numerical risk criteria, the discussion on identification of major hazards in the First Report does contain the following statement:

> Since we cannot achieve or expect to achieve no risk of failure in any of the areas discussed, we feel bound to put

Table 4.8 *Some principal themes in the reports of the Advisory Committee on Major Hazards*

First Report 1976
Identification of major hazards
Notification of major hazard installations
Review of types of regulatory control
Control of major hazards by self-regulation
Monitoring of control by the HSE
Management of major hazards
Prevention of loss of containment
Design and operation of pressure systems
Limitation of hazardous inventory
Limitation of exposure
Planning controls for major hazards

Second Report 1979
Notification of major hazard installations
Comparison of theoretical potential and historical experience
Bounds on consequences of major releases
Unconfined vapour cloud explosions
Limitation of exposure of workforce
Design and location of control rooms
Planning controls for major hazards
Research on major hazards
Model licence conditions

Third Report 1984
Discussion of risk
Role of quantitative assessment
Inherently safer design
High reliability plant
Monitoring of warning events
Separation of major hazards and public
Information to the public
Emergency planning
Planning controls for major hazards
Education of engineers and scientists
Research on major hazards

> forward some quantitative objective. If, for instance, such tentative conclusions indicated with reasonable confidence that in a particular plant a serious accident was unlikely to occur more often than once in 10000 years (or – to put it another way – a 1 in 10000 chance in any one year), this might perhaps be regarded as just on the borderline of acceptability, bearing in mind the known background of risks faced every day by the general public.

The first step in the control of major hazards was clearly that they should be notified, and an outline notification scheme was presented in the First Report. The principle adopted was notification of hazardous substances above a certain level of inventory. It was recognized that inventory is by no means the only factor that determines the hazard, but it was nevertheless adopted as the basis because it is simple to administer. Other characteristics of the materials were to some extent taken into account by the pragmatic approach of specifying different inventories for the principal hazardous materials.

At this basic level of inventory, only notification was proposed, but it was envisaged that for a level of inventory 10 times the notification level, a hazard survey would be required and that the HSE would also have the further power to call for a detailed assessment if it judged this necessary. The Committee held strongly to the view that it should set priorities and should confine its proposals to major hazards. It was appreciated that the various cut-offs were to some degree arbitrary.

The Committee strongly endorsed the principle of self-regulation by industry that it considered particularly appropriate to major hazard plants with their high level of technology. Self-regulation is a constant theme in the reports. The arrangements proposed for the control of major hazards are therefore intended to be part of a continuum of controls for all types of hazard under the HSWA and to avoid introducing a discontinuity specifically for major hazards. On the other hand, it was clear that the community expects not only that such hazards should be under control but also that they should be seen to be so. Consequently, the view was taken that some form of monitoring by the HSE was necessary.

The First Report also began consideration of the measures necessary to prevent major accidents, against the background of Flixborough. Here the factor on which the Committee placed most emphasis was the management. Unless the management is competent to operate a major hazard plant, other measures are likely to be rendered ineffective.

The Flixborough explosion occurred because the plant held a very large inventory of flammable material that on release would undergo partial flashing to form a vapour cloud. The report takes up the theme of the need to limit such hazardous inventories. Given that the plant does contain an inventory of such material, it must be the aim of management to avoid loss of containment.

The design and operation of pressure systems is therefore of particular importance. Here the report places emphasis on pressure systems, including pipes, valves, pumps, etc., as well as pressure vessels and on operation as well as design.

The Committee held strongly to the view that planning powers even for developments involving major hazards should continue to reside with the LPA. There are many factors besides safety which affect the planning decision and which need to be taken into account in arriving at a balanced decision and only the LPA is able to do this.

The Committee also identified the problems in planning control over major hazards. These largely centre around the definition of 'development' in the Town and Country Planning Act 1971 (TCPA). The preferred solution was to amend the Act, but the implications of a change in definition were very far-reaching, and alternative though less satisfactory proposals were also made. A major difficulty in planning identified in the report is that of the compensation due if planning permission already granted is revoked. The sums involved can be very large.

The Second Report gave revised proposals for notification. This revision took into account the problem of ultra-toxic materials, which had been highlighted by the Seveso disaster. Various models of regulatory control were considered, including those for the nuclear industry, mines and pharmaceuticals. The possibility of a licensing scheme similar to that applied to nuclear installations was given particular consideration but, in the event, the Committee decided against licensing.

Much of the work described in the report is concerned with comparison of theoretical estimates of major hazard

scenarios with historical experience and with putting some bounds to the effects to be expected from major releases. The problem is that, for some hazards, taking the most pessimistic scenarios and models yields theoretical estimates of casualties that are very high and barely credible in the light of the historical record. Work on this aspect included collection of incident data and development of a mortality index relating the number of fatalities to the quantity released historically. Work was also done to set some bounds on the range of certain specific hazards which it seemed might have lethal effects at rather far distances, such as vapour cloud explosions and glass breakage. The Flixborough disaster was a vapour cloud explosion, and the report goes into some detail on the technical aspects of such explosions and on methods of estimating their effects.

The influence of Flixborough is also seen in the proposals in the report on the design and location of control rooms for major hazard plants. It became apparent in considering control rooms that this problem is part of the wider question of the limitation of exposure of the workforce. The report gives detailed recommendations for limitation of exposure both by location of the work base and by control of access to the high hazard zone.

The vapour cloud explosion problem highlighted the fact that many major hazard phenomena were imperfectly understood. Another important problem area was that of heavy gas dispersion. The Committee therefore gave encouragement to research on these topics.

Background studies to the reports are described by V.C. Marshall (1976a,c, 1977b, 1978, 1980d, 1982d, 1987).

The Second Report gives as an appendix a set of model licence conditions for a possible licensing scheme for major hazard plants. Although the Committee did not in fact opt for licensing, it retained the model licence conditions and proposed that these be used as a kind of code of practice for such plants. These model licence conditions are given in Appendix 24.

The Third Report opens with a discussion of risk. It does not give any specific numerical criteria, but states certain principles which may assist in deriving such criteria. The report brings together the overall system of hazard control proposed by the Committee. The essential elements are identification, avoidance and mitigation of the hazard and planning for it. In the context of hazard identification, it gives a discussion of the historical development of quantitative hazard assessment in the process industries and of its role in major hazard control.

The report gives support to the avoidance of hazard by inherently safer design, a generalization of the earlier theme of limitation of inventory.

It also discusses the measures necessary to ensure high plant reliability. Another aspect of avoidance is the monitoring of and learning from warnings, specifically the application of hazard warning concepts.

Measures to mitigate consequences which are discussed in the report are separation distances between the hazard and the public and emergency planning. The committee broadly endorsed methods then being devised by the HSE for the control over development at major hazard sites aimed at stabilizing and, where practical, reducing the population at risk.

The Committee took the view that, although a major hazard plant should be designed to high standards, it is nevertheless prudent to seek to have some separation between the plant and the public as a further line of defence. This may be regarded as the extension to the public of the principle of limitation of exposure applied earlier to the workforce.

Both the Second and Third Reports re-echo the basic proposals on planning outlined in the First Report. The Third Report calls again for research on major hazards and also for education on major hazards for the engineers and scientists who are likely to have responsibility for major hazard plants.

4.10 Process Hazard Control: Major Hazards Arrangements

The first legislative initiative in response to the ACMH's recommendations was proposals for the Hazardous Installations (Notification and Survey) Regulations 1978. These draft regulations contained requirements for the notification of installations holding a specified inventory of listed hazardous materials and for a hazard survey for installations containing 10 times the notifiable level.

These legislative proposals were overtaken by the EC Directive on the Major-Accident Hazards of Certain Industrial Activities 1982 (82/501/EEC) (the Major Accident Hazards Directive) and were never implemented. They were replaced by two sets of regulations, the Notification of Installations Handling Hazardous Substances Regulations 1982 (NIHHS) and the Control of Industrial Major Accident Hazards Regulations 1984 (CIMAH).

4.10.1 NIHHS Regulations 1982

The NIHHS Regulations implement a notification scheme based on the ACMH proposals and similar to that of the original Hazardous Installations Regulations proposals. They are confined essentially to notification and do not contain requirements for a hazard survey, which is now covered by the CIMAH Regulations. The NIHHS Regulations provide for the notification of the installations which the authorities in Britain wish to see notified and provide the basis for planning controls over these installations. The schedule of hazardous installations is given in Table 4.9. A critique of inventory levels for substances covered by the NIHHS Regulations is given by D.C. Wilson (1980).

4.10.2 CIMAH Regulations 1984

The CIMAH Regulations are confined to those requirements necessary to implement the EC Directive. The industrial activities covered by the regulations are defined in terms of processes and of storage involving specified hazardous materials.

The EC Major Accident Hazards Directive 1982 has been amended twice, in 1987 (87/216/EEC) and in 1988 (88/610/EEC). The first amendment, prompted by the disastrous toxic release at Bhopal, made a revision of some of the threshold inventories. The second, following the pollution of the Rhine by chemicals from the Sandoz warehouse fire, modified the controls on storage. These amendments of the Directive were implemented by amendments to the CIMAH Regulations in 1988 and 1990.

The regulations apply to defined industrial activities (Regulation 2). There are certain activities to which the regulations do not apply, notably defence, explosives and nuclear installations (Regulation 3). Two levels of activity are defined. For the first level, the requirements are to take the precautions necessary to prevent a major accident and to

Table 4.9 *Notification of Installations Handling Hazardous Substances Regulations 1982: Schedule 1: notifiable inventories*

PART I Named substances

substance	*Notifiable quantity (tonne)*
Liquefied petroleum gas, such as commercial propane and commercial butane, and any mixtures thereof held at a pressure greater than 1.4 bar absolute	25
Liquefied petroleum gas, such as commercial propane and commercial butane, and any mixture thereof held under refrigeration at a pressure of 1.4 bar absolute or less	50
Phosgene	2
Chlorine	10
Hydrogen fluoride	10
Sulfur trioxide	15
Acrylonitrile	20
Hydrogen cyanide	20
Carbon disulfide	20
Sulfur dioxide	20
Bromine	40
Ammonia (anhydrous or as solution containing more than 50% by weight of ammonia)	100
Hydrogen	2
Ethylene oxide	5
Propylene oxide	5
tert-Butyl peroxyacetate	5
tert-Butyl peroxyisobutyrate	5
tert-peroxymaleate	5
tert-Butyl peroxisopropyl carbonate	5
Dibenzylperoxydicarbonate	5
2,2-bis(*tert*-Butylperoxy)butane	5
1,1-bis(*tert*-Butylperoxy)cyclohexane	5
Di-*sec*-butylperoxydicarbonate	5
2,2-Dihydroperoxypropane	5
Di-*n*-propylperoxydicarbonate	5
Methylethyl ketone peroxide	5
Sodium chlorate	25
Cellulose nitrate other than: (a) cellulose nitrate to which the Explosives Act 1875 applies or (b) solutions of cellulose nitrate where the nitrogen content of the cellulose nitrate does not exceed 12.3% by weight and the solution contains not more than 55 parts of cellulose nitrate per 100 parts by weight of solution	50
Ammonium nitrate and mixtures of ammonium nitrate where the nitrogen content derived from the ammonium nitrate exceeds 28% of the mixture by weight other than: (a) mixtures to which the Explosives Act 1875 applies, or (b) ammonium nitrate based products manufactured chemically for use as fertilizer which comply with Council Directive 80/876/EEC	500
Aqueous solutions containing more than 90 parts by weight of ammonium nitrate per 100 parts by weight of solution	500
Liquid oxygen	500

PART II Classes of substance not specifically named in Part I

Class of substance	*Notifiable quantity* (tonnes)
1. Gas or any mixture of gases which is flammable in air and is held in the installation as a gas	15
2. A substance or any mixture of substances which is flammable in air and is normally held in the installation above its boiling point (measured at 1 bar absolute) as a liquid or as a mixture of liquid and gas at a pressure of more than 1.4 bar absolute	25 being the total quantity of substances above the boiling points whether held singly or in mixtures
3. A liquefied gas or any mixture of liquefied gases, which is flammable in air, has a boiling point of less than 0°C (measured at 1 bar absolute) and is normally held in the installation under refrigeration or cooling at a pressure of 1.4 bar absolute or less	50 being the total quantity of substances having boiling points below 0°C whether held singly or in mixtures
4. A liquid or any mixture of liquids not included in items 1 to 3 above, which has a flashpoint of less than 21°C	10,000

limit the consequences and generally to demonstrate safe operation (Regulation 4) and to report any major accident which does occur (Regulation 5). For the higher level of activity (defined in Regulation 6), more extensive requirements apply (Regulations 7–12). These include the requirements to submit a safety report (Regulation 7), to update the safety report (Regulation 8), to provide on request additional information (Regulation 9), to prepare an on-site emergency plan (Regulation 10) and to provide information to the public (Regulation 12). The local authority is required to prepare an off-site emergency plan (Regulation 11).

The initial directive made a distinction between storage associated with a process and isolated storage. In accordance with the directive, the CIMAH Regulations 1984 gave separate lists of inventories for the application of the regulations for isolated storage (Schedule 2) and other storage (Schedule 3). The 1990 revision again gives lists of inventories as Schedules 2 and 3, but the type of storage to which Schedule 2 applies has been broadened to include certain process-associated storage. Schedule 2 gives two sets of inventories. Inventories at either level attract Regulation 4, but only an inventory in the higher level attracts Regulations 7–12.

An outline of the regulations is given in Table 4.10 and details of Regulations 4, 6, 7 and 8 are shown in Table 4.11. Tables 4.12–4.17 give details of Schedules 1–4, 6 and 8, respectively. Schedule 1 gives the indicative criteria for the application of Regulations 2 and 4. Schedule 3 gives the list of substances, with associated inventories, for the application of Regulations 7–12. As just described, Schedule 2 gives two lists of inventories, both attracting Regulation 4, but only the higher level attracting Regulations 7–12. Schedule 4 lists the types of industrial installation other than isolated storage which come within Regulation 2. Schedule 6 gives the information to be included in the safety report (Regulation 7) and Schedule 8 that to be given to the public (Regulation 12).

Guidance on the CIMAH Regulations is given in *A Guide to the Control of Industrial Major Accident Hazards Regulations 1984* (HSE, 1990 HS(R) 21 rev.). A decision tree for the application of the regulations is shown in Figure 4.2.

The requirements for the safety report are discussed below, those for emergency planning, both on-site and off-site, in Chapter 24 and those for provision of information to the public in Section 4.11.

An account of the CIMAH arrangements has been given by Cassidy and Pantony (1988). The sites covered are classified as large inventory top tier sites (LITTSs), holding large inventories of flammable and/or toxic materials, and small inventory top tier sites (SITTSs), holding smaller quantities of more toxic substances.

They state that in the United Kingdom there are over 1700 NIHHS sites and 'several hundred' CIMAH sites.

Table 4.10 *Control of Industrial Major Accident Hazards Regulations 1984: outline of regulations*[a]

Regulation 2	Interpretation
Regulation 3	Application of these Regulations
Regulation 4	Demonstration of safe operation
Regulation 5	Notification of major accidents
Regulation 6	Industrial activities to which Regulations 7–12 apply
Regulation 7	Reports on industrial activities
Regulation 8	Updating of reports under Regulation 7
Regulation 9	Requirement of further information to be sent to the Executive
Regulation 10	Preparation of on-site emergency plan by the manufacturer
Regulation 11	Preparation of off-site emergency plan by the local authority
Regulation 12	Information to the public
Regulation 13	Disclosure of information notified under these Regulations
Regulation 14	Enforcement
Regulation 15	Charge by the local authority for off-site emergency plan
Schedule 1	Indicative criteria
Schedule 2	Storage other than of substances listed in Schedule 3 associated with an installation referred to in Schedule 4
Schedule 3	List of substances for the application of Regulations 7–12
Schedule 4	Industrial installations within the meaning of Regulation 2(1)
Schedule 5	Information to be supplied to the Commission of the European Communities by the Member States pursuant to Regulation 5(2)
Schedule 6	Information to be included in a report under Regulation 7(1)
Schedule 7	Preliminary information to be sent to the Executive under Regulation 7(3)
Schedule 8	Items of information to be communicated to the public in the application of Regulation 12

[a] This table and the following seven tables incorporate the 1990 amendments to the regulations.

4.10.3 CIMAH safety case

A central feature of the regulations is the safety report, commonly called the 'safety case'. Two aspects of particular interest are the requirements concerning the management system and the quantification of the hazards. With regard to the former, Schedule 6 of the original CIMAH Regulations 1984 requires that the report provide information on the management system and specifically on the staffing arrangements, including: for certain responsibilities, the names of the persons assigned; the arrangements for safe operation; and the arrangements for training. The wording of the 1990 Regulations is identical. However, the Guide to the latter (HSE, 1990 HS(R) 21 rev.) is much more explicit on the matters to be covered and is in effect a description of good practice in respect of a safety management system. When the regulations were brought in, it was a matter of some concern to know the extent to which the HSE would require QRA. The guidance to the original regulations (HSE, 1985 HS(R) 21) stated:

> Whilst it may be possible for manufacturers to write a safety case in qualitative terms, HSE may well find it easier to accept conclusions that are supported by quantitative arguments. A quantitative assessment is also a convenient way of limiting the scope of the safety case by demonstrating either that an adverse event has a very

Table 4.11 *Control of Industrial Major Accident Hazards Regulations 1984: Regulations 4, 6, 7 and 8*

Regulation 4 Demonstration of safe operation

(1) This Regulation shall apply to:
  (a) An industrial activity to which subparagraph Regulation 2(1) applies and in which a substance which satisfies any of the criteria laid down in Schedule 1 is involved or is liable to be involved; and
  (b) An industrial activity to which subparagraph (b) of that definition applies and in which there is involved, or liable to be involved –
    (i) For a substance specified in column 1 of Part I of Schedule 2, a quantity of that substance which is equal to or more than the quantity specified in the entry for that substance in column 2 of that Part.
    (ii) For substances and preparations falling within a category or categories specified in an entry in column 1 of part II of Schedule 2, a total quantity of such substances and preparations in the category or categories in that entry which is equal to or more than the quantity for that entry specified in column 2 of the Part.

(2) A manufacturer who has control of an industrial activity to which this Regulation applies shall at any time provide evidence including documents to show that he has:
  (a) Identified the major accident hazards; and
  (b) Taken adequate steps to:
    (i) Prevent such major accidents and to limit their consequences to persons and the environment, and
    (ii) Provide persons working on the site with the information, training and equipment necessary to ensure their safety.

Regulation 6 Industrial activities to which Regulations 7 to 12 apply

(1) Regulations 7 to 12 shall apply to:
  (a) An industrial activity to which subparagraph (a) of the definition of industrial activity in Regulation 2(1) applies and in which there is involved, or liable to be involved, a substance listed in column 1 of Schedule 3 in a quantity which is equal to or more than the quantity specified in the entry for that substance in column 2 of that Schedule; and
  (b) An industrial activity to which subparagraph (b) of that definition applies and in which there is involved, or liable to be involved –
    (i) For a substance specified in column 1 of Part I of Schedule 2, a quantity of that substance which is equal to or more than the quantity specified in the entry for that substance in column 3 of that Part;
    (ii) For substances and preparations falling within a caegory or cateories specified in an entry in column 1 of Part II of Schedule 2, a total quantity of such substances and preparations in the category or categories in that entry which is equal to or more than the quantity for that entry specified in column 3 of that Part.

(2) For the purposes of Regulations 7 to 11:
  (a) A 'new industrial activity' means an industrial activity which –
    (i) Was commended after the date of the coming into operation of this Regulation, or
    (ii) If commenced before that date, is an indusrial activity in which there has been since that date a modification which would be likely to have important implications for major accident hazards, and that activity shall be deemed to have been commenced on the date on which the change was made;
  (b) an 'existing industrial activity' means an indusrial activity which is not a new industrial activity.

Regulation 7 Report on industrial activities

Regulation 7(1) gives the requirement for the submission of a written safety report, 7(2) and 7(3) deal with new activities and existing activities, respectively, and 7(4) wih exemptions granted by the HSE.

Regulation 8 Updating of reports under Regulation 7

(1) Where a manufacturer has made a report in accordance with Regulation 7(1), he shall not make any modification to the industrial activity to which that report relates which could materially affect the particulars in that report, unless he has made a further report to take account of those changes and has sent a copy of that report to the Executive at least 3 months before making those changes or before such shorter time as the Executive may agree in writing.
(2) Where a manufacturer has made a report in accordance with Regulation 7(1), paragraph (1) of this Regulation or this paragraph, and that industrial activity is continuing, the manufacturer shall within three years of the date of the last such report, make a further report which shall have regard in particular to new technical knowledge which materially affects the particulars in the previous report relating to safety and development in this knowledge of hazard assessment, and shall within one month, or in such longer time as the Executive may agree, send a copy of the report to the Executive.
(3) A certificate of exemption issued under Regulation 7(4), shall apply to reports or declarations made under this Regulation as it applies to reports made under Regulation 7(1).

remote probability of occurring or that a particular consequence is relatively minor (p. 34)

The 1990 Guide states that

> The nature and extent of the consequence assessment needed depends upon the magnitude of the hazard, its likelihood of occurrence and, most importantly, the need to describe the adequacy of the prevention, control and mitigatory measures.

It later continues

> In many cases explicit quantification of the consequences of a major accident combined with relatively broad, but justifiable, qualitative predictions about the likelihood of occurrence will be sufficient to enable both

Table 4.12 *Control of Industrial Major Accident Hazards Regulations 1984: Schedule 1: indicative criteria*

Regulations 2(1) and 4(1)

(a) *Very toxic substances:*
- — Substances which correspond to the first line of the table below,
- — Substances which correspond to the second line of the table below and which, owing to their physical and chemical properties, are capable of producing major accident hazards similar to those caused by the substance mentioned in the first line.

	LD_{50} (oral)[1] (mg/kg body weight)	LD_{50} (cutaneous)[2] (mg/kg body weight)	LC_{50}[3] (mg/l inhalation)
1	$LD_{50} \leq 5$	$LD_{50} \leq 10$	$LC_{50} \leq 0.1$
2	$5 < LD_{50} \leq 25$	$10 < LD_{50} \leq 50$	$0.1 < LC_{50} \leq 0.5$

[1] LD_{50} oral in rats.
[2] LD_{50} cutaneous in rats or rabbits.
[3] LC_{50} by inhalation (4 h) in rats.

(b) *Other toxic substances:*
The substances showing the following values of actue toxicity and having physical and chemical properties capable of producing major accident hazards.

LD_{50} (oral)[1] (mg/kg body weight)	LD_{50} (cutaneous)[2] (mg/kg body weight)	LC_{50}[3] (mg/l inhalation)
$25 < LD_{50} \leq 200$	$50 < LD_{50} \leq 400$	$0.5 < LC_{50} \leq 2$

[1] LD_{50} oral in rats.
[2] LD_{50} cutaneous in rats or rabbits.
[3] LC_{50} by inhalation (4 h) in rats.

(c) *Flammable substances:*
- (i) *Flammable gases;* Substances which in the gaseous state at normal pressure and mixed with air become flammable and the boiling point of which at normal pressure is 20°C or below;
- (ii) *Highly flammable liquids;* Substances which have a flash point lower than 21°C and the boiling point of which at normal pressure is above 20°C;
- (iii) *Flammable liquids;* Substances which have a flash point lower than 55°C and which remain liquid under pressure, where particular processing conditions, such as high pressure and high temperature, may create major accident hazards.

(d) *Explosive substances:*
Substances which may explode under the effect of flame or which are more sensitive to shocks or friction than dinitrobenzene.

(e) *Oxidizing substances:*
Substances which give rise to highly exothermic reaction when in contact with other substances, particularly flammable substances.

the manufacturer and HSE to judge whether the precautionary measures are adequate. However, there will be some activities involving highly hazardous and difficult to control processes, e.g. the oxidation of ethylene to produce ethylene oxide, where it may be necessary for the manufacturer to be more precise about the frequency of the various events which could lead to a major accident. . . (p. 65)

4.11 Process Hazard Control: Planning

Some appreciation of the planning system is necessary for the understanding of overall arrangements for the control of major hazards. The treatment given here is limited to providing this essential background. Fuller accounts are given by Petts (1984b,c, 1985a,b, 1988a,b, 1989, 1992). Legislation relevant to planning and major hazards is discussed in Chapter 3.

4.11.1 Planning system

The essential function of planning is the control of land use. This control may be used to prevent incompatible uses of adjacent pieces of land, but such control is much easier to exercise before development has taken place than after it. The control of land use is effected through the structure plans of the counties, which set the overall framework, and through the local plans of the LPAs, which deal in specific developments. New developments are required to relate to these plans. Structure and local plans are essentially instruments for forward planning. Difficulties can arise when the problem is one not of a greenfield development but of an existing installation.

An example of positive forward planning to accommodate hazardous activities is the National Planning Guidelines issued in 1977 by the Scottish Development Department. The guidelines give detailed advice on the incorporation of such activities in local plans.

The main responsibility for planning lies with the LPA. In arriving at a planning decision on an industrial activity, the LPA has to take into account a large number of factors, including employment, safety and amenity. The LPA is publicly accountable both through the elected members on the local planning committee and through the procedures allowing for individual representations which it is required to follow.

Planning control has been exercised through the powers embodied in the TCPA. In general, this allows new development to be controlled by withholding planning permission or by attaching planning conditions. There is provision for a voluntary agreement between the developer and the LPA. There are limited powers to revoke or discontinue planning permission which has been granted.

The TCPA 1971 gives an LPA certain powers to control 'development' but these are circumscribed by the definition of 'development' in the Act and on the subsequent interpretation of this in the courts. The term development is defined as 'the carrying out of building, engineering, mining or other operations, in, on, over or under land or the making of any material change in the use of land'. However, while planning powers exist for the control of the general type of use, they do not extend to the control of particular uses within the general type.

Since the definition of 'development' is so wide, it has been necessary in order not to overload the planning system

Table 4.13 *Control of Industrial Major Accident Hazards Regulations 1984: Schedule 2: storage other than of substances listed in Schedule 3 associated with an installation referred to in Schedule 4*

Regulations 2(1), 4(1) and 6(1)

This Schedule applies to storage of dangerous substances and/or preparations at any place, installation, premises, building, or area of land, isolated or within an establishment, being a site used for the purpose of storage, except where that storage is associated with an installation covered by Schedule 4 and where the substances in question appear in Schedule 3.

The quantities set out below in Parts I and II relate to each store or group of stores belonging to the same manufacturer where the distance between the stores is not sufficient to avoid, in foreseeable circumstances, any aggravation of major accident hazards. These quantities apply in any case to each group of stores belonging to the same manufacturer where the distance between the stores is less than 500 m.

The quantities to be considered are the maximum quantities which are, or are liable to be, in storage at any one time.

Part I Named substances

Where a substance (or a group of substances) listed in Part I also falls within a category of Part II, the quantities set out in Part I shall be used.

Substances or groups of substances (Column 1)	*Quantities* (tonnes)	
	For application of Regulation 4 (Column 2)	*For application of Regulations 7 – 12 (Column 3)*
Acetylene	5	50
Acrolein (2-propenal)	20	200
Acrylonitrile	20	200
Ammonia	50	500
Ammonium nitrate[a]	350	2,500
Ammonium nitrate in the form of fertilizers[b]	1,250	10,000
Bromine	50	500
Carbon disulfide	20	200
Chlorine	10	75
Diphenylmethane di-isocyanate (MDi)	20	200
Ethylene dibromide (1,2-dibromoethane)	5	50
Ethylene oxide	5	50
Formaldehyde (concentration $\geq 90\%$)	5	50
Hydrogen	5	50
Hydrogen chloride (liquefied gas)	25	250
Hydrogen cyanide	5	20
Hydrogen fluoride	5	50
Hydrogen sulfide	5	50
Methyl bromide (Bromomethane)	20	200
Methylisocyanate	0.15 (150 kg)	0.15 (150 kg)
Oxygen	200	2,000
Phosgene (carbonyl chloride)	0.75 (750 kg)	0.75 (750 kg)
Propylene oxide	5	50
Sodium chlorate	25	250
Sulfur dioxide	25	250
Sulfur trioxide	15	100
Tetraethyl lead or tetramethyl lead	5	50
Toluene di-isocyanate (TDI)	10	100

[a] This applies to ammonium nitrate and mixtures of ammonium nitrate where the nitrogen content derived from the ammonium nitrate is $>28\%$ by weight and to aqueous solutions of ammonium nitrate where the concentration of ammonium nitrate is $>90\%$ by weight.

[b] This applies to straight ammonium nitrate fertilizers which comply with Council Directive 8/876/EEC (OJ No. L250, 23.9.80, p. 7) 'on the approximation of laws of the Member States relating to straight ammonium nitrate fertilizers of high nitrogen content' and to compound fertilizers where the nitrogen content derived from the ammonium nitrate is $>28\%$ by weight (a compound fertilizer contains ammonium nitrate together with phosphate and/or potash).

Part II Categories of substances and preparations not specifically named in Part I

The quantities of different substances and preparations of the same category are cumulative. Where there is more than one category specified in the same entry, the quantities of all substances and preparations of the specified categories in that entry shall be summed up.

Categories of substances and preparations (Column 1)	*Quantities* (tonnes)	
	For application of Regulation 4 (Column 2)	*For application of Regulations 7 – 12 (Column 3)*
(1) Substances and preparations that are classified as 'very toxic'	5	20
(2) Substances and preparations that are classified as 'very toxic', 'toxic',[a] 'oxidizing' or 'explosive'	10	200
(3) Gaseous substances and preparations including those in liquefied form, which are gaseous at normal pressure and which are classified as 'highly flammable'[b]	50	20

(4)	Substances and preparations (excluding gaseous substances and preparations covered under item 3 above) which are classified as 'highly flammable' or 'extremely flammable'[c]	5,000	50,000

[a] Where the substances and preparations are in a state which gives them properties capable of producing a major accident hazard.
[b] This includes flammable gases as defiend in paragraph c(i) of Schedule 1.
[c] This includes highly flammable liquids as defined in paragraph (c)(ii) of Schedule 1.

Substances and preparations shall be assigned categories in accordance with the classification provided for by Regulation 5 of the Classification, Packaging and Labelling of Dangerous Substances Regulations 1984 (SI 1984/1244, amended by SI 1986/1922, SI 1988/766, SI 1989/2208 and SI 1990/1255) whether or not the substance or preparation is required to be classified for the purposes of those Regulations, or, in the case of a pesticide approved under the Food and Environment Protection Act 1985 (c.48), in accordance with the classification assigned to it by that approval.

Table 4.14 *Control of Industrial Major Accident Hazards Regulations 1984: Schedule 3: list of substances for the application of Regulations 7–12*

The quantities set out below relate to each installation or group of installations belonging to the same manufacturer where the distance between the installations is not sufficient to avoid, in foreseeable circumstances, any aggravation of major accident hazards. These quantities apply in any case to each group of installations belonging to the same manufacturer where the distance between the installations is less than 500 m.

Substance (Column 1)	*Quantity (for applications of Regulations 7 – 12) (Column 2)*
Group 1 Toxic substances (quantity ≤ 1 tonne)[a]	
	(kg)
Arsine	10
Methyl isocyanate	150[b]
Parathion	100
Phosgene	750[c]
2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin (TCDD)	1
Group 2 Toxic substances (quantity > 1 tonne)[d]	
	(tonne)
Acetone cyanohydrin	200
Acrolein	200
Acrylonitrile	200
Allyl alcohol	200
Allylamine	200
Ammonia	500
Bromine	500
Carbon disulfide	200
Chlorine	25[e]
Ethylene dibromide	50
Ethyleneimine	50
Formaldehyde (concentration ≥ 90%)	50
Hydrogen chloride (liquefied gas)	250
Hydrogn cyanide	20
Hydrogen fluoride	50
Hydrogen sulphide	50
Methyl bromide	200
Nitrogen oxides	50
Propyleneimine	50
Sulfur dioxide	250[f]
Tetraethyl lead	50
Tetramethyl lead	50
Group 3 Highly reactive substances[a]	
	(tonne)
Acetylene	50
Ammonium nitrate[g]	2,500
Ammonium nitrate in the form of fertilizers[h]	5,000
Ethylene oxide	50
Hydrogen	50
Oxygen (liquid)	2,000
Propylene oxide	50
Sodium chlorate	250
Group 4 Explosive substances[a]	
	(tonne)
Cellulose nitrate (containing > 12.6% nitrogen)	100
Lead azide	50
Mercury fulminate	10
Nitroglycerine	10
Pentaerythritol tetranitrate	50
Picric acid	50
2, 4, 6-Trinitrotoluene	50
Group 5 Flammable substances[b]	
	(tonne)
Flammable substances as defined in Schedule 1, paragraph c(i)	200
Flammable substances as defined in Schedule 1, paragraph c(ii)	50,000
Flammable substances as defined in Schedule 1, paragraph c(iii)	200

[a] Selection from complete list for this group.
[b] Reduced from inventory of 1 tonne in original CIMAH Regulations 1984.
[c] Reduced from inventory of 20 tonne in original CIMAH Regulations 1984.
[d] Complete list for this group.
[e] Reduced from inventory of 50 tonne in original CIMAH Regulations 1984.
[f] Reduced from inventory of 1000 tonne in original CIMAH Regulations 1984.
[g] This applies to ammonium nitrate and mixtures of ammonium nitrate where the nitrogen content derived from the ammonium nitrate is > 28% by weight and aqueous solutions of ammonium nitrate where the concentration of ammonium nitrate is > 90%.
[h] This applies to ammonium nitrate fertilizers which comply with Council Directive 80/876/EEC and to compound fertilizers where the nitrogen content derived from the ammonium nitrate is > 28% by weight (a compound fertilizer contains ammonium nitrate together with phosphate and/or potash).

Table 4.15 *Control of Industrial Major Accident Hazards Regulations 1984: Schedule 4: industrial installations within the meaning of Regulation 2(1)*

(1) Installations for the production, processing or treatment of organic or inorganic chemicals using for this purpose, amongst others:
- Alkylation
- Amination by ammonolysis
- Carbonylation
- Condensation
- Dehydrogenation
- Esterification
- Halogenation and manufacture of halogens
- Hydrogenation
- Hydrolysis
- Oxidation
- Polymerization
- Sulfonation
- Desulfurization, manufacture and transformation of sulfur-containing compounds
- Nitration and manufacture of nitrogen-containing compounds
- Manufacture of phosphorus-containing compounds
- Formulation of pesticides and of pharmaceutical products
- Distillation
- Extraction
- Solvation
- Mixing.

(2) Installations for distillation, refining or other processing of petroleum or petroleum products.

(3) Installations for the total or partial disposal of solid or liquid substances by incineration or chemical decomposition.

(4) Installations for the production, processing or treatment of energy gases, for example, LPG, LNG, SNG.

(5) Installations for the dry distillation of coal or lignite.

(6) Installations for the production of metals or non-metals by a wet process or by means of electrical energy.

Table 4.16 *Control of Industrial Major Accident Hazards Regulations 1984: Schedule 6: information to be included in a report under Regulation 7(1)*

(1) The report required under Regulation 7(1) shall contain the following information.

(2) Information relating to every dangerous substance involved in the activity in a relevant quantity as listed in Schedule 2 column 3 or Schedule 3, namely:
- (a) the name of the dangerous substance as given in Schedule 2 or 3 or, for a dangerous substance included in either of those Schedules under a general designation, the name corresponding to the chemical formula of the dangerous substance;
- (b) a general description of the analytical methods available to the manufacturer for determining the presence of the dangerous substance, or references to such methods in the scientific literature;
- (c) a brief description of the hazards which may be created by the dangerous substance;
- (d) the degree of purity of the dangerous substance, and the names of the main impurities and their percentages.

(3) Information relating to the installation, namely:
- (a) a map of the site and its surrounding area to a scale large enough to show any features that may be significant in the assessment of the hazard or risk associated with the site;
- (b) a scale plan of the size showing the locations and quantities of all significant inventories of the dangerous substance;
- (c) a description of the processes or storage involving the dangerous substance and an indication of the conditions under which it is normally held;
- (d) the maximum number of persons likely to be present on site;
- (e) information about the nature of the land use and the size and distribution of the population in the vicinity of the industrial activity to which the report relates.

(4) Information relating to the management system for controlling the industrial activity, namely:
- (a) the staffing arrangements for controlling the industrial activity with the name of the person responsible for safety on the site and the names of those who are authorized to set emergency procedures in motion and to inform outside authorities;
- (b) the arrangements made to ensure that the means provided for the safe operation of the industrial activity are properly designed, constructed, tested, operated, inspected and maintained;
- (c) the arrangements for training of persons working on the site.

(5) Information relating to the potential major accidents, namely:
- (a) a description of the potential sources of a major accident and the conditions or events which could be significant in bringing one about;
- (b) a diagram of any plant in which the industrial activity is carried on, sufficient to show the features which are significant as regards the potential for a major accident or its prevention or control;
- (c) a description of the measures taken to prevent, control or minimize the consequences of any major accident;
- (d) information about the emergency procedures laid down for dealing with a major accident occurring at the site;
- (e) information about prevailing meteorological conditions in the vicinity of the site;
- (f) an estimate of the number of people on site who may be exposed to the hazards considered in the report.

(6) In the case of the storage of substances and preparations to which Part II of Schedule 2 applies, paragraphs 2(a), (b) and (d) and 5(b) of this Schedule shall apply so far as is appropriate.

to grant certain general permissions. Under the Town and Country Planning General Development Order (GDO) 1977, a number of changes of land use are classed as 'permitted' developments, which do not require planning permission.

Table 4.17 *Control of Industrial Major Accident Hazards Regulations 1984: Schedule 8: items of information to be communicated to the public in the application of Regulations 2 and 12*

Regulations 2(1) and 12(1)

(1) Name of manufacturer and address of site.
(2) Identification, by position held, of person giving the information.
(3) Confirmation that the site is subject to these Regulations and that the report referred to in Regulation 7(1) or at least the information required by Regulation 7(3) has been submitted to the Executive.
(4) An explanation in simple terms of the activity undertaken on the site.
(5) The common names, or in the case of storage covered by Part II of Schedule 2 the generic names or the general danger classification, of the substances and preparations involved on site which could give rise to a major accident, with an indication of their principal dangerous characteristics.
(6) General information relating to the nature of the major accident hazards, including their potential effects on the population and the environment.
(7) Adequate information on how the population concerned will be warned and kept informed in the event of an accident.
(8) Adequate information on the actions the population concerned should take and on the behaviour they should adopt in the event of an accident.
(9) Confirmation that the manufacturer is required to make adequate arrangements on site, including liaison with the emergency services, to deal with accidents and to minimize their effects.
(10) A reference to the off-site emergency plan drawn up to cope with any off-site effects from an accident. This shall include advice to cooperate with any instructions or requests from the emergency services at the time of an accident.
(11) Details of where further relevant information can be obtained, subject to the requirements of confidentiality laid down in national legislation.

Further, under the Town and Country Planning (Use Classes) Order (UCO) 1972, changes within a particular Use Class are permitted development. The definition of a Use Class, however, is very broad, for example, light industry. A change of use of a piece of land or a building is not classed as development unless it constitutes both a 'material change' and a change from one Use Class to another.

For large developments it is usual to seek planning permission in two stages: 'outline' permission and then 'detail' permission. This allows the developer to ascertain that it has permission before incurring costs of development. Outline planning permission is full planning permission. Permission is granted subject to 'reserved matters', which cover such aspects as building design, plant design, landscaping and access. These are the only matters which the LPA is subsequently entitled to consider.

In granting outline planning permission, the LPA may stipulate planning conditions. This is an important power, but the conditions must be reasonable and the use of such conditions to deal with matters which are properly the concern of the HSE is discouraged.

A developer which has been refused planning permission or had permission granted subject to planning conditions may appeal to the Secretary of State for the Environment. Alternatively, where the land has become incapable of reasonably beneficial use, it may serve on the LPA a purchase notice.

Planning permission may be revoked before it has been implemented or discontinued for an existing installation or it may be modified, but in such cases the LPA may be liable to pay compensation. The sums involved in such compensation can be very large and are a strong deterrent to revocation.

The Secretary of State has powers to approve all structure and certain local plans, to consider appeals against planning decisions, to call in a planning application for his own consideration and to confirm or reject revocations, modifications and discontinuances of planning permission.

This remains the general framework under the TCPA (1990).

4.11.2 Planning and major hazards

The problem of developments involving major hazards was recognized well before the Flixborough disaster. In 1972, the DoE issued the first of a number of circulars to LPAs on hazardous installations. This circular, DoE 72/1, gave a list of hazardous inventories for which it was recommended that the LPA should seek advice. Some of the DoE circulars are listed in Table 4.18.

Following Flixborough, the HSE experienced an increased number of inquiries from LPAs concerning developments involving hazardous installations and set up a RAG to give advice in response to these queries. In 1974, the ACMH was set up with a membership which included planners. Planning was one of the principal topics considered by the Committee which made a number of recommendations in this area.

Decisions on planning for major hazard installations as for other developments are taken by the LPA. The alternative that the decision might be made by the HSE was considered at some length by the ACMH but rejected. The case for leaving the decision with the LPA was made in the committee's First Report in the following terms:

> It might be argued that the siting of potentially hazardous installations should be controlled by the Health and Safety Executive as part of their application of comprehensive safety controls in general, but we hold very firmly to the view that siting of all industrial developments should remain a matter for planning authorities to determine since the safety implications, however important, cannot be divorced from other planning considerations (paragraph 72)

In its Second and Third Reports, the Committee recognized that this opinion was not universally shared, but reaffirmed its view:

> When a planning application is being considered a balanced view should be taken of all aspects including social and economic factors and not just health and safety. Our view is that the HSE ought to provide a clear assessment of the risks associated with the development and to ensure that plant standards are appropriate for those risks. The decision on whether or not to grant planning permission for an installation which meets

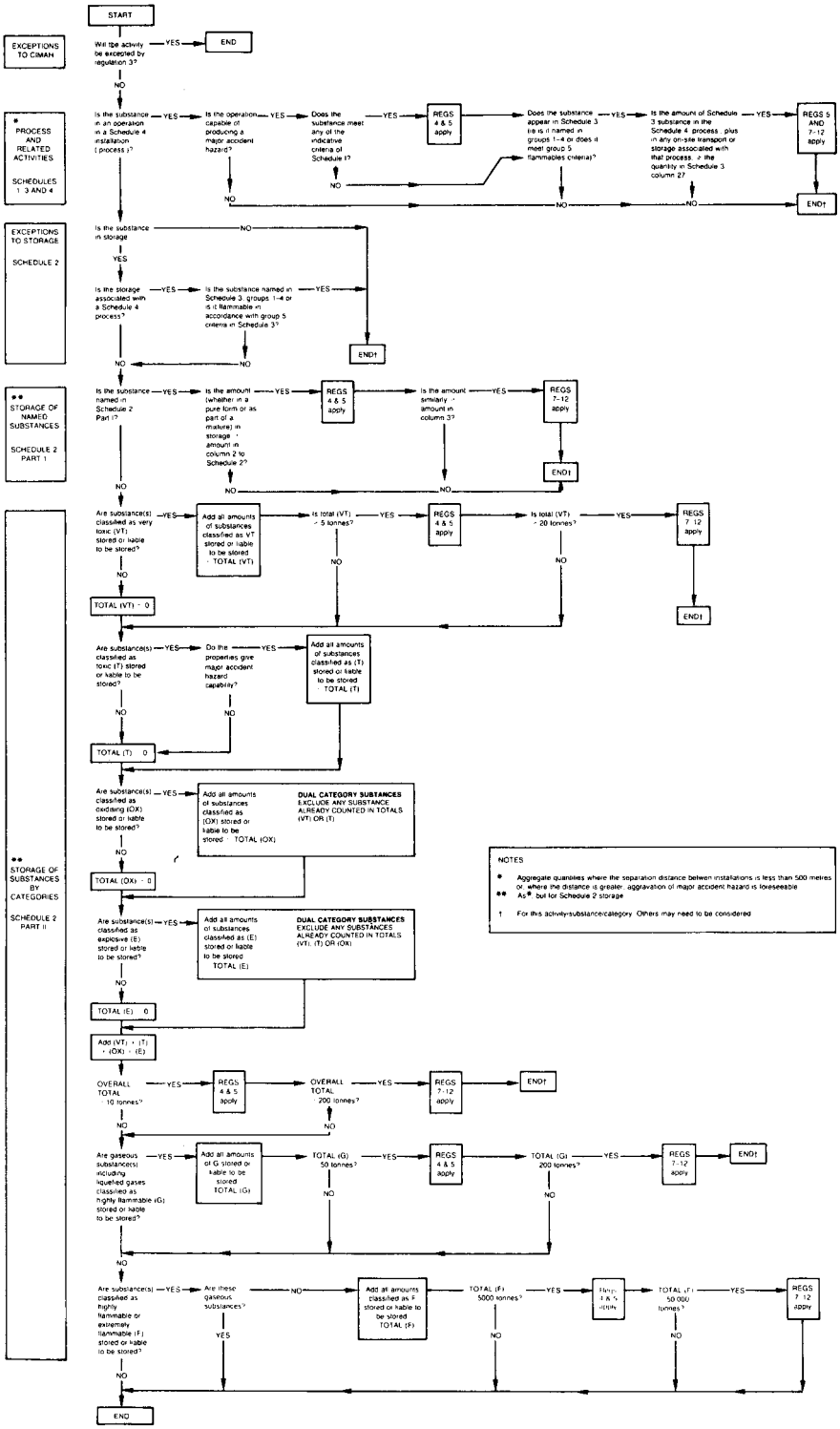

Figure 4.2 *Control of Industrial Major Accident Hazards Regulations 1990: decision tree for application of the regulations (Courtesy of HM Stationery Office)*

Table 4.18 *Department of the Environment Circulars relevant to planning and major hazards*

Circular	
DoE 1/72 (WO 3/72)	Development involving the use or storage in bulk of hazardous materials
DoE 71/73	Publicity for planning applications, appeals and other proposals for development
DoE 4/79	Memorandum on structure and local plans
DoE 22/80 (WO 40/80)	Development control – policy and practice
DoE 26/82	Hazardous substances
DoE 9/84 (WO 17/84)	Planning controls over hazardous development
DoE 22/84	Memorandum on structure and local plans
DoE 1/85	The use of conditions in planning permissions
DoE 2/85	Planning control over oil and gas operations
DoE 15/88	Environmental assessment

> health and safety criteria should however rest with the local authority who, on behalf of the local community, attempts to come to a balanced decision, having taken all the factors into consideration. In some cases where an installation is of wider regional or national significance, the final decision may be taken by central government (Third Report, paragraph 111)

On siting policy, the committee stated:

> The overall objective should always be to reduce the number of people at risk, and in the case of people who unavoidably remain at risk, to reduce the likelihood and the extent of harm if loss of control or containment occurs (Third Report, paragraph 109)

The Committee distinguished between several different development situations involving major hazards:

(1) initial introduction of hazards to 'greenfield' sites;
(2) initial introduction of hazards to existing installations;
(3) intensification of hazards at existing installations;
(4) proposed development in the vicinity of hazardous installations;
(5) existing development in the vicinity of hazardous installations.

In the Committee's view, the existing planning system was well able to handle the initial introduction of hazards to a greenfield site. They recommended that the LPA should impose a standard planning condition prohibiting without specific consent the introduction onto a site of notifiable hazards.

The problems of the initial introduction of a hazard or of intensification of an existing hazard were recognized as more difficult. The ideal solution would have been to amend the definition of 'development' in the TCPA, but this was a fundamental change which in the short term at least the DoE was unable to accept. An alternative approach to the initial introduction of hazard which the Committee recommended in default of amendment of the TCPA was to amend the GDO and UCO, the former to exclude from permitted development modifications which have the effect of creating a notifiable installation, and the latter to omit notifiable activities altogether from the Use Classes. These proposals did not, however, solve the problem of the intensification of an existing hazard.

With regard to development in the vicinity of a hazardous installation, the Committee endorsed the aim of first stabilizing and then reducing the number of people exposed to the hazard. It recommended that, for proposed development, the LPA should consult the HSE. It also drew attention to the power of the LPA to enter into a voluntary agreement with the owners of land to restrict the use to which the land is put.

The Committee recognized that, in a limited number of cases, the LPA might consider it necessary to revoke or discontinue planning permission and recommended that the government review its discretionary powers to make payments to local authorities to meet compensation liabilities.

With regard to existing development, the Committee stated:

> The HSE is also frequently asked to comment on proposals to develop or redevelop land in the neighbourhood of an existing hazardous undertaking where there may be other land users who are closer and possibly incompatible. In these cases the HSE tell us that it takes the view, which we fully endorse, that the existence of intervening development should not in any way affect the advice that it gives about the possible effects of that activity on proposed developments which may appear to be less at risk than the existing ones. In other words the existing situation should never be regarded as providing grounds for failing to draw attention to the implications for development at a greater distance (Second Report, paragraph 108)

The ACMH emphasized the importance of LPAs having available adequate information on which to reach its decision and on the need for the authority to consult the HSE on developments involving hazardous installations and on the necessity for the HSE's advice to be in a form appropriate to a planning authority which is not expert in major hazards.

Following the work of the ACMH, legislative changes have been made to the planning arrangements, as described below. In parallel with these legislative developments have gone administrative changes. The HSE has upgraded its capabilities to provide advice to LPAs. The ability of the HSE to provide advice has been much enhanced by the creation of the Major Hazards Assessment Unit (MHAU), while the local Factory Inspectorate, who have always had the prime responsibility for the control of hazardous installations, has been reorganized so that offices dealing with the process industries have inspectors who specialize in those industries. The problem of major hazards has proved a troublesome one for LPAs. Major hazards involve both high technology and difficult issues of risk. Most local planners have had little training on major hazards matters.

4.11.3 Planning reforms

A number of changes have been made to the planning system to deal with the problem of major hazards. The first step is to ensure that the LPA knows of the existence of hazardous installations in its area. This is effected by the NIHHS

Regulations 1982 and the CIMAH Regulations, originally 1984 and now 1990. Consultation by the LPA with the HSE is now mandatory for any new hazardous development and recommended for other development.

Under the Town and Country Planning General Development (Amendment) Order 1983, development of new hazardous installations and development at an existing notifiable site involving a three-fold increase in inventory is excluded from the general permissions of the GDO, while under the Town and Country Planning Use Classes (Amendment) Order 1983, uses involving notifiable inventories are excluded from the provisions of the UCO. The notification referred to here is that applicable under the NIHHS Regulations 1982.

The Housing and Planning Act 1986 creates a requirement for a written consent from the LPA for a new notifiable inventory. This consent is separate from planning permission. The effect of this written consent procedure is to obviate for such inventories the difficulties of redefining development under planning legislation, to freeze existing hazards at their notified level and to remove liability for compensation.

The Town and Country Planning (Assessment of Environmental Effects) Regulations 1988 require that an environmental impact assessment be submitted to the LPA along with the planning application.

The loophole associated with the concept of development is closed by the provisions of the Planning (Hazardous Substances) Act 1990 and the Planning (Hazardous Substances) Regulations 1992. The Act requires that the presence of a hazardous substance needs the consent of the Hazardous Substance Authority, or LPA.

The Planning and Compensation Act 1991 strengthens the function of the local plan as a means of planning for major hazard installations.

4.11.4 HSE consultation and advice

As stated above, the policy of the HSE is to stabilize and then reduce the number of people at risk from a hazardous installation. The HSE implements this policy primarily through its advice to LPAs. An early account of the HSE's approach was given as an appendix in the Third Report of the ACMH. It is reproduced here in Appendix 25. A later description has been given by Pape (1984).

The vast majority of planning decisions are concerned not with development on industrial sites, but with development in the vicinity of such sites. The HSE issues to LPAs guidelines on the size of 'consultation zones' around these sites and asks to be consulted on developments within these zones. Consultation with the HSE is not appropriate for minor planning applications. Guidance on the type of application for which consultation is required is given in DoE Circular 9/84.

Initially, the HSE set a general consultation distance of 2 km around a hazardous site. This proved to be excessive and the HSE has since refined its assessment methods and now specifies consultation distances which are related to the particular hazard. In particular, it has developed model approaches for two base cases, liquefied petroleum gas and chlorine which have been described by Crossthwaite (1984) and Pape and Nussey (1985), respectively. These model cases are considered in more detail in Chapter 9. Here consideration is limited to the consultation distances and advice which result from them.

The HSE distinguishes three types of development: A, B and S (special). Type A developments are those where control may well be appropriate. They are situations where people would be present most of the time or where large numbers might be present quite often and the people are not highly protected. Examples are housing, markets, large shops, transport termini and sports stadia. Type B developments are those where the risk would not normally be great enough to warrant control. This includes situations where individuals may be present regularly but not full time even though the total number of people is not necessarily small, and situations where people might be readily incorporated into an emergency plan and where they are not particularly vulnerable to the hazard. Examples are relatively low density factories or warehouses, small office buildings, small shops, sport fields and roads. Type S is intended to cover developments which are significantly more vulnerable than type A. Examples are hospitals, old people's homes and schools.

The replies from the HSE following consultation by the LPA are generally in terms of the risk categories given in DoE 9/84: 'negligible', 'marginal' and 'substantial'. Negligible risk means that the HSE assessment of the consequences of realization of the hazard is that it is unlikely, if not inconceivable, that people in the development would be killed, and that if someone was killed, this would be a 'freak' effect. Marginal risk means that the probability of people being affected by a major release is remote, that in such a case they might be seriously affected but that death is unlikely. Safety reasons would not in themselves justify a refusal of planning permission, but might justifiably be among those contributing to it. Substantial risk means that people might be seriously injured by a major release. The risk could in itself justify refusal of planning permission and safety should be a major factor in the decision. If there were other factors strongly favouring granting permission, the HSE would suggest that the LPA should hear a more detailed explanation of its assessment. In quantitative terms, negligible risk means an individual risk of less than the 'trivial' level of 10^{-6}/year, marginal risk an individual risk of about the trivial level and low societal risk, and substantial risk is an individual risk above the trivial level and more substantial societal risk.

Table 4.19 shows the HSE guidelines on consultation zones for LPG storage installations. The table gives guidance not only on the consultation zone but also on zones within this. Section A of Table 4.19 gives the distances to the zone boundaries for different tank sizes and Section B the risk categories for these zones.

The effectiveness of advice from the HSE to the LPAs has been studied by Petts (1987). An account of the use of hazard assessment by the HSE in relation to its advice to planning authorities is described by Pantony and Smith (1982).

4.11.5 Emergency planning

There is a statutory requirement for counties and equivalent authorities to undertake emergency planning for civil defence, and the tendency has been to extend these arrangements to cover process site and transport emergencies. The extent of emergency planning undertaken has been variable. Some authorities whose areas contain major chemical complexes have long had comprehensive emergency plans, while others have not. The CIMAH Regulations 1984 require such authorities to have emergency

Table 4.19 *HSE guidelines on consultation and related zones and risk categories for LPG storage (after Crossthwaite, 1984)*

A Distances to zone boundaries

Zone	*Tank size* (tonnes)						
	6–10	*11–15*	*16–25*	*26–40*	*41–80*	*81–120*	*121–300*
Consultation zone	150	175	250	300	400	500	600
Middle zone	125	150	200	250	300	400	500
Inner zone	50	50	50	75	100	125	150

B Risk categories in zones

Development type	*Zone*		
	Inner	*Middle*	*Consultation*
A	Substantial	Assessment[a]	Negligible
B	Negligible	Negligible	Negligible
S(i)	Assessment	Assessment	Negligible
S(ii)	Substantial	Assessment	Assessment

[a] Individual assessment necessary.

plans for installations notifiable under CIMAH (though not under NIHHS). Off-site emergency plans are considered in Chapter 24.

4.11.6 Information to public

The CIMAH Regulations 1984 contain a requirement that the public be given information about the hazards to which they are exposed and the action which they should take in an emergency. The choice of body to be responsible for informing the public proved a difficult one. The arrangements decided on are as follows. It is intended that the body which informs the public is the local authority. The manufacturer is required to try to reach with the local council an agreement on the information to be provided and then to furnish this to the council, which then issues it to the public. If, however, an agreement cannot be reached, the manufacturer is responsible for informing the public directly.

The information provided must include a statement that the activity is notifiable under the CIMAH Regulations and has been notified to the HSE and information on the nature of the hazard (e.g. fire, explosion or toxic release) and on the safety measures and actions to take in the event of an accident.

4.11.7 Public inquiries

A planning application may become the subject of a public inquiry. This may occur if the developer is refused planning permission and appeals or if the application is called in by the Secretary of State. In some cases, this call-in may be at the behest of the HSE.

It is only relatively rarely that a planning application for a process plant becomes the subject of a formal planning or public inquiry. Nevertheless, there have been a number of public inquiries on such developments. They include

(1) the Mossmorran Inquiry (1977), dealing with proposals by Shell and Esso to build a natural gas liquids plant and ethylene cracker (McGill, 1982);
(2) the Canvey Inquiries (1980 and 1982) into United Refineries' permission for a new refinery and British Gas operation of a methane terminal (Petts, 1985a);
(3) the Pheasant Wood Inquiry (1980) into housing development near an ICI chlorine and phosgene plant (Petts, 1985b).

These inquiries have shown a trend towards the increasing use of hazard assessment. They have also brought out some of the problems in the use of an adversarial forum for the discussion of technical matters.

A discussion of the problems posed by public inquiries with special reference to the use of hazard assessment and to the presentation of expert evidence has been given by Petts, Withers and Lees (1986).

Experience at inquiries indicates that the use of hazard assessments has been fraught with difficulties, but that many of these relate to obscurity, incompleteness and inconsistency in the assessments. Another difficult area is the public perception of risk.

The adversarial approach used in inquiries poses another problem. Many engineers feel it to be a poor way of arriving at the truth in scientific and engineering matters as well as being unfamiliar and intimidating. The Flixborough Inquiry gave rise to some debate on this question (e.g. Mecklenburgh, 1977a; R. King, 1990). It is considered further in relation to accident inquiries in Chapter 27.

The study by Petts, Withers and Lees (1986) suggests that many of the problems of inquiries into hazardous installations can be greatly mitigated if certain practical steps are taken. The adversarial approach is supported as the least imperfect means of arriving at the truth on technical matters and of allowing public participation, but the use is encouraged of informal meetings between parties before and during the inquiry.

The problems experienced over hazard assessment are regarded as capable of mitigation, provided that the deficiencies of hazard assessments in past inquiries are remedied, and provided that the necessary information is available to all the parties and on a suitable schedule. The means proposed is that for any installation to which the NIHHS or CIMAH Regulations apply and which goes to a

planning inquiry, a form of open safety case should be made available by industry.

Although public perception of risk at inquiries remains a continuing problem, there is evidence that much of it is related to deficiencies in the hazard assessments and also to the existence of risks which assessment shows to be rather high. A fuller account of public inquiries is given in Appendix 26.

4.11.8 Planner's viewpoint

The viewpoint of the LPA is given in *Major Hazard Installations: Planning and Assessment* (Petts, 1984b) and *Major Hazard Installations: Planning Implications and Problems* (Petts, 1984c).

Certain LPAs have been conscious from an early date of the need to provide for major hazard installations in their area. Accounts of the measures taken following Flixborough by Halton Borough Council have been given by Brough (1981) and Payne (1981).

4.12 Process Hazard Control: European Community

The arrangements for the control of major hazards in the EC and in certain other European countries are now briefly reviewed. Comparative accounts are given in Risk Assessment for Hazardous Installations Q.C. Consultancy Ltd, 1986), and by Beveridge and Waite (1985) and Milburn and Cameron (1992).

4.12.1 European Community

Controls over major hazards in the EC are established by Directive 82/501/EEC, the Major Accident Hazards Directive, amended by 87/216/EEC and 88/610/EEC, as described in Section 4.10. The Directive contains requirements for notification of installations, for a safety report and for emergency planning.

A critique of the inventory levels set for particular hazardous substances is given by V.C. Marshall (1982b).

A fundamental revision of the major hazard arrangements is in prospect, as outlined in Proposal for a Council Directive on the Control of Major-Accident Hazards Involving Dangerous Substances (COMAH) (Commission of the European Communities, 1994). Features emphasized in the document are land use planning, management and human factors, and the safety report. It proposes requirements on: land use planning, the safety management system, a major accident prevention plan (MAPP) and inspection. It is proposed that the safety report should include management systems, should be harmonized in style and should be available to the public, subject to certain safeguards.

4.12.2 Germany

In Germany, basic safety requirements are embodied in a number of measures which include the Industrial Code 1869–1978, the Imperial Insurance Code 1911, the rules for Prevention of Accidents to Man and the Technical Means of Work Act 1968. Selected legislation relevant to major hazards in Germany is given in Table 4.20.

The Federal Emission Control Act 1974 (FECA) (*Bundesimmissionsschutzgesetz*) is the basic legislation on environmental protection and on major hazards. It creates a system of licensing for installations liable to cause 'harmful effects' to the environment or 'considerable disadvantages' to the public.

These terms are vague and give rise to difficulties of interpretation. More specific requirements are given in the Ordinance on Installations Subject to Licensing 1975 (ISLO), which lists 58 types of installation with a hazard potential sufficient to attract licensing.

Control of major hazards is effected, still under the FECA, through the Hazardous Incident Ordinance 1980 (HIO) (*Stb'rfallverordnung*). The ordinance gives lists of processes and chemicals. The licensing requirements apply to installations which carry out these processes and use these chemicals.

Exemption from the HIO is allowed if the inventory of the hazardous substance is very small. The levels of inventory below which exemption is given are specified in the First General Administrative Regulation 1981 to the ordinance.

The HIO requires the preparation of a safety analysis. The requirements for this are specified in greater detail in the Second General Administrative Regulation 1982. The information supplied must be such as to allow the regulatory authority to assess adequately the compliance by the operator with its safety obligations. Where this involves calculations, the documentation must show that these have been done. There is no stated requirement for QRA.

An account of the legislation is given by Stahl (1988) and an industrial viewpoint is given by Pilz (1982, 1987, 1989).

4.12.3 France

In France, safety legislation is based on the Imperial Decree of 1810, which has been subject to amending Laws in 1917, 1932 and 1961. This legislation was extensively modified in the Law of 19 July 1976 on Registered Works for Environment Protection (Installations Classes) and the associated Decree of 10 September 1977. Under this legislation, a distinction is made between authorized and declared installations. Installations subject to authorization, which is effectively licensing, are defined by inventory of hazardous chemicals.

A safety study is required for an authorized installation. The study must include a justification of the measures taken to reduce the probability of realization of the hazard and its effects. No requirement is stated for a probabilistic risk assessment. The coverage of these arrangements is wide. There are some 50,000 authorized

Table 4.20 *Selected legislation relevant to major hazards in Germany*

Substances at Work Act 1939
Technical Means of Work Act 1968
Explosives Act 1976
Chemicals Act 1980
Federal Emission Control Act (*Bundesimmissionsschutzgesetz*) 1974
Fourth Ordinance for the Implementation of the Federal Emission Control Law: Ordinance on Installations Subject to Licensing 1975
Ordinance on Principles of Licensing Procedure 1977
Twelfth Ordinance for the Implementation of the Federal Emission Control Law: Hazardous Incident Ordinance 1908
First General Administrative Regulation on the Hazardous Incident Ordinance 1981
Second General Administrative Regulation on the Hazardous Incident Ordinance 1982

installations and the number of declared installations is presumably greater still.

4.12.4 The Netherlands

In the Netherlands there are separate systems for the assurance of safety of employees at the workplace and of the public. The first is the responsibility of the Ministry of Social Affairs, and specifically the Labour Inspectorate, and the second that of the Ministry of the Environment. This division is reflected in the requirements for two safety reports, an occupational safety report and an external safety report.

Safety legislation in the workplace is based on the employee safety law of 1934. The Statute of 23 November 1977 creates a requirement for hazardous installations to submit a safety report. This occupational safety report statute is the basic legislation on major hazards at the workplace. Accounts of the safety report have been given by Meppelder (1977), van de Putte and Meppelder (1980), van de Putte (1981, 1983), Husmann and Ens (1989), Oh and Albers (1989) and Bothelsburgh (1995).

The installations for which a safety report is required are defined not by inventory but on a 'threshold value', which is defined as the quantity of material which would present a serious danger to human life at a distance of over 100 m from the point of release. There is a specified method of calculating this value.

The report must contain an assessment of the hazards in the form of a specified fire and explosion index and a toxicity index, derived from the Dow Index method. With regard to QRA, the account given by van de Putte (1981) indicates a view that quantification of probabilities and consequences is desirable, but so is a recognition of the difficulties in the current state of the art. Husmann and Ens (1989) state that a quantitative study involving risk assessment should be performed where novel technology is used.

The external safety report is the concern of the Ministry of the Environment. It deals with the effects of major hazards outside the factory. Accounts are given by Versteeg (1988) and Ale (1991, 1992).

The Ministry of the Environment is deeply involved in QRA. It was one of the sponsors of the Rijnmond Report on hazardous installations in the Rijnmond. It has sponsored the development of the computer-based SAFETI package by Technica (see Ale and Whitehouse, 1986).

4.13 Process Hazard Control: USA

The arrangements for the control of major hazards in the United States are now briefly described. Overviews are given by Brooks *et al.* (1988) and Horner (1989). US legislation on safety has been outlined in Chapter 3. The account given here is confined to accidental releases, which include major hazards.

4.13.1 Plant siting

The development of these controls needs to be seen against the background of the growing problems experienced in the siting of new hazardous installations since the late 1970s.

A case in point at this time was the siting of LNG facilities, as described in the Transportation of Liquefied Natural Gas by the Office of Technology Assessment (OTA) of the US Congress (1977). The Federal Power Commission (FPC) was the lead agency in determining whether an individual LNG project should be allowed. It was the practice of the FPC to make decisions on siting on a case-by-case basis. The OTA identified several problems in this approach. The FPC was a regulatory rather than a policy-making body and there was no national siting policy to which it could refer. The criteria on which the FPC made its decisions on siting were not known to the industry, since no guidelines were issued. There had been pressure from the state legal authorities and from industry for the issue of uniform siting criteria. In some cases the FPA had made its approval contingent on the receipt of state and local approval, so that the criteria that the industry had to satisfy had become even more obscure.

There were several areas of overlapping jurisdiction. The Office of Pipeline Safety Operations (OPSO) was involved through the Natural Gas Pipeline Safety Act 1968, although there appeared to be a statutory provision against OPSO standards prescribing the location of LNG facilities. In the past, the two agencies had clashed directly on the standards required. The FPC required a temporary shut-down on an LNG facility which OPSO had inspected and approved. The US Coast Guard (USCG) was also involved through the Coastal Zone Management Act 1972. This Act required an applicant for a Federal licence or permit for an activity in a coastal zone of a state to certify the project to be consistent with the state's programme.

Siting was also affected by other legislation. The National Environmental Policy Act 1969 required an environmental impact statement.

4.13.2 Accidental releases

The US legislation that covers major hazards is framed in terms of accidental releases. It has been decisively influenced by releases at home and abroad, and particularly by the toxic gas disaster at Bhopal.

The principal Federal legislation is the Emergency Planning and Community Right-to-Know Act 1986 (EPCRA), which is Title III of the Superfund Amendments and Reauthorization Act 1986 (SARA), generally known as SARA Title III, and is enforced by the Environmental Protection Agency (EPA). Other relevant federal legislation is the Occupational Health and Safety Administration (OSHA) rule for Process Safety Management of Highly Hazardous Chemicals 1990. There are also the state laws in New Jersey and California. One focus of concern is the control of high toxic hazard materials (HTHMs).

4.13.3 SARA Title III

SARA Title III is the Federal legislation that creates controls on accidental releases of hazardous substances. The legislation followed soon after Bhopal. Accounts are given by Brooks *et al.* (1988), Bowman (1989), Horner (1989), Burk (1990) and Fillo and Keyworth (1992). SARA Title III has four main parts dealing with emergency planning, emergency notification, community right-to-know and toxic chemicals inventory.

For each state the governor appoints an Emergency Response Commission (ERC) that in turn designates local emergency planning committees charged with the preparation of an emergency plan. The facilities that attract such an emergency plan are those containing certain chemicals above specified inventory levels. These chemicals and inventories are given in the List of Extremely Hazardous Substances and Their Threshold Planning Quantities

(TPQ) developed by the EPA. Management is required to provide any information needed by the local emergency planning committee to implement the emergency plan. The wording has deliberately been left broad enough for the local emergency planning committee to request a QRA (Florio, 1987).

The emergency notification arrangements require the management of the facility to report immediately to the local planning committee any accidental release and the area likely to be affected.

With regard to the right-to-know requirements, for any hazardous chemical that attracts the requirement for a Material Safety Data Sheet (MSDS) under the OSHA 1970, the facility has to submit either the data sheets or a list of the chemicals to the local emergency planning committee, the state ERC and the responsible fire department. The facility must also submit to the same three bodies information on the hazardous inventory.

Section 313 contains the requirement to submit information on the 'toxic chemical release emission inventory', or Toxic Release Inventory (TRI), on the Toxic Chemical Release Form. The data required in this form are concerned primarily with passage of toxic chemicals into the environment. For each chemical, a mass balance and the quantity emitted annually is required.

The subjects of the principal sections of SARA Title III may be summarized as follows: Section 301, state ERC; Section 302, notification requirements; Section 304, accidental release reporting; Section 305, study of safety capabilities; Sections 311 and 312, information for the public; and Section 313, toxic emissions.

4.13.4 Special Emphasis Program

In 1986, OSHA initiated a Special Emphasis Program for installations with large inventories of hazardous chemicals. The purpose of the programme was to ensure that such facilities were subject to a systems safety inspection (Hanson, 1986). The systems safety inspection emphasizes four main areas: risk management, hazard identification and assessment, process design and control, and emergency planning.

4.13.5 Process Safety Management Rule

The OSHA has further extended its controls to prevent accidental releases with the rule for Process Safety Management of Highly Hazardous Chemicals (the Process Safety Management Rule). The governing document (Federal Register 1990 July 17, 29 CFR Part 1901) refers to major accidents such as Flixborough, Seveso and Bhopal, and to EC controls on major hazard installations in the 'Seveso' Directive and to the need to strengthen such controls in the United States, which otherwise largely rely on the OSHA 1970 and on standards. As its name implies, the Process Safety Management rule places particular emphasis on management. The rule covers hazard identification, evaluation and control.

4.13.6 New Jersey Toxic Catastrophe Prevention Act

The New Jersey Toxic Catastrophe Prevention Act 1985 (TCPA) is also addressed to the identification, evaluation and control of hazards for facilities handling extraordinarily hazardous substances (EHSs), there being 11 such chemicals on the initial list. It creates a requirement for a risk management plan (RMP). The RMP covers risk management, safety review, risk assessment and emergency planning.

4.13.7 California Hazardous Materials Planning Program

The California Hazardous Materials Planning Program draws together four complementary laws that are codified in chapter 6.95 of the state Health and Safety Code. It requires a facility handling more than a specified minimum inventory of a hazardous material to establish a 'business plan for emergency response', giving details of the inventory and the emergency plan. The programme requires a business that handles a defined 'acutely hazardous material' to register with the administrative authority. If a business is notified by the authority that a Risk Management and Prevention Program (RMPP) is required, it must then prepare one.

4.13.8 Regulatory agencies

As just described, both the EPA and the OSHA are involved in the regulation of accidental releases, primarily in the case of the former through SARA Title III and of the latter through the OSHA 1970 and, more recently, the Process Safety Management Rule. The division of responsibility between the two agencies is not clear-cut. The Jeffreys Amendment of 1990 defined roles for OSHA and EPA in preventing accidental releases. OSHA was directed to bring in the regulation on Process Safety Management of Highly Hazardous Chemicals and EPA to bring in a regulation on accidental releases that would complement the OSHA requirements and would focus on community issues.

4.13.9 Voluntary initiatives

Mention should also be made of some of the voluntary initiatives that have been taken in the United States in this area. Since 1985, the Chemical Manufacturers Association (CMA) has recommended to its members the Community Awareness and Emergency Response (CAER) programme. This voluntary programme deals particularly with emergency planning. The creation in 1985 of the Center for Chemical Process Safety (CCPS) of the AlChE, described in Chapter 1, is another such initiative.

5 Economics and Insurance

Contents

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5.1 Economics of Loss Prevention

Loss prevention is concerned with the avoidance both of personal injury and of economic loss. In both spheres there is an economic balance to be struck. But there are also quite difficult problems in making the economic assessments. There is no doubt, however, about the economic importance of loss prevention. Some costs arise through failure to take proper loss prevention measures; others are incurred through uninformed and unnecessarily expensive measures. Both types of cost are numerous and can involve major items. The financial viability of a project is often determined by loss prevention factors.

In today's environment, many loss prevention measures that were optional in the past are now mandated by government regulation. Others are voluntarily provided in some countries as they have become 'industry practice'. Still others are provided due to court rulings in liability cases. In the above situations, traditional cost benefit analysis studies may not be relevant.

Selected references on process economics and on economics of loss prevention are given in Table 5.1.

5.2 Cost of Losses

The result of not taking adequate loss prevention measures is to give rise to losses and costs such as those of: (1) accidents, (2) damage, (3) plant design delays, (4) plant commissioning delays, (5) plant downtime, restricted output, (6) equipment repairs, (7) loss of markets, (8) public reaction and (9) insurance. A rational approach to loss prevention requires some understanding of the economic importance of these factors and of the means of estimating them.

Unless otherwise stated, the cost figures given below are those for the year referred to. The cost in real terms may be obtained by correcting the values given using the appropriate inflation index. There may be no single index which is totally applicable, but in some cases the retail price index (RPI) and in others a plant cost index may be the most suitable. There is also the further complication of exchange rate conversion.

5.2.1 National level

It is convenient to consider first the cost of these losses at national level in the United States. Estimates may be based on information on the following: (1) accident statistics, (2) fire loss statistics, (3) insurance statistics, (4) maintenance and downtime statistics and (5) major accidents.

Accident statistics are fairly readily available from the US Department of Labor, Bureau of Labor Statistics and from the National Safety Council in the United States for injuries and from the National Fire Protection Association (NFPA) for fires in the USA (Table 5.2). Accident statistics in the United Kingdom can be obtained from the *Annual Report* of HM Chief Inspector of Factories and the annual *Health and Safety Statistics*. By making certain assumptions, the national resource cost, or cost to the nation, of these accidents may be estimated.

The total number of fatal accidents as listed above for 2001 in the United States is 5270. Of this total, there were 599 fatalities in manufacturing facilities, and, of these, 7.2% or 43 were due to fire or explosion incidents.

In the United Kingdom, statistics for fires are published by the Home Office in the annual *Fire Statistics United*

Table 5.1 *Selected references on process economics and economics of loss prevention*

Peters (1948); Perry (1954); Aries and Newton (1955); Schweyer (1955); Happel (1958); Vilbrandt and Dryden (1959); Baumann (1964); Foord (1967–68); ICI (1968); Peters and Timmerhaus (1968); Raiffa (1968); Rudd and Watson (1968); IChemE (1969/48); IProdE and ICWA (1971); D.H. Allen (1968, 1972 IChemE/52, 1975, 1988, 1990 IChemE/85); H. Gibson and Jackson (1972); Coward (1973 FRS Fire Research Note, 1982); Holland *et al.* (1974); L.M. Rose (1976); Windebank (1976); R. King and Magid (1979); de la Mare (1982); Kurtz (1984); C. Tayler (1984b); T.E. Powell (1985); S.E. Dale (1987); Drangeid (1989); Garrett (1989)

Costs
NRC (Appendix 28 Cost Estimation); *Chemical Engineering* (1958–, 1963, 1978c, 1979a); Anon. (1963); Weinberger (1963); Dow Chemical Co. (1964, 1966 a,b, 1976, 1980, 1987, 1994b); Anon. (1965b); Roth (1965); Dybdal (1966); J.T. Gallagher (1967); Guthrie (1968, 1969, 1970, 1971, 1974); Mendel (1968); Chase (1970); Liptak (1970); Alonso (1971); Frost (1971); S.P. Marshall and Brandt (1971, 1974); Popper (1971); Pitkin (1972); W.L. Nelson (1976); Pikulik and Diaz (1977); Hasselbarth (1977); Baltzell (1978); R. Kern (1978b); Kohn (1978a); Bridgewater (1979); C.A. Miller (1979); Vatavuk and Neveril (1980–); Barrett (1981); Cran (1981); Desai (1981); L.D. Epstein (1981); Mulet *et al.* (1981); Humphreys and Katell (1981); Corripio *et al.* (1982 a,b); S.R. Hall *et al.* (1982); Lonsdale and Mundy (1982); Mcintyre (1982); de la Mare (1982); Matley (1982); Purohit (1983); Vogel and Martin (1983–); K.E. Lunde (1984); T.J. Ward (1984); Anon. (1985j); AIChE (1985/82); F.D. Clark and Lorenzoni (1985); Klumpar and Slavsky (1985 a–c); A. Rose (1985); H.W. Russell (1985); Anon. (1987 f,y); IChemE (1988/82); Kletz (1988g); March (1989); Samid (1990); Kerridge (1992); Lindley and Floyd (1993); Rodriguez and Coronel (1992); Ulrich (1992); Garnett and Patience (1993); Plavsic (1993); Gerrard (1994)

Loss statistics
BIA (periodic); BRE (periodic, see Appendix 28); FRS (periodic, see Appendix 28); HM Chief Inspector of Factories (annual); Ministry of Technology (1969); Munich Re (1991–2001); NFPA (1991–2001)

Costs of accidents
Badger (1968); Beddoe (1969); Calabresi (1970); Mealey (1970); Robens (1972); Sinclair (1972); Munich Re (1991); HSE (1993 HS(G) 96); Anon. (1994 LPB 116); N.V. Davies and Teasdale (1994); Marsh *Large Loss* (1979–2002); Badger (2002) *Large-Loss Fires in 2001*; National Safety Council Facts and Statistics (2001, 2002)

Costs of plant unreliability, downtime
Ministry of Technology (1969); Jenkins *et al.* (1971); Tucker and Cline (1971); C.F. King and Rudd (1972); D.H. Allen (1973); J.A. Richardson and Templeton (1973); de la Mare (1975, 1976); Reynolds (1976); Sancaktar (1983)

Costs of prevention
FRS (1973 Fire Research Note 982); Pratt (1974); Amson (1976); Windebank (1976); C.W. Smith (1977); Amson and Goodier (1978); Ricci (1978c); Anon. (1982b)

Level of loss prevention expenditure
Redington (1965); Sinclair (1972); Melinek (1974 BRE CP 88/74); Kramer (1974); S.B. Gibson (1976d); Kletz (1976d, 1980a, 1980–, 1981f, 1988g); Anon. (1981u); Witter (1982); Berenblut and Whitehouse (1988); Wakeling (1988); Hirano (1990a)

Decision aids: G.H. Mitchell (1972); R.E. Hanna (1979)
Expenditure decisions: Oakland (1982)

Inherently safer plants
Kletz (1984d); D.W. Edwards and Lawrence (1993); Rushton *et al.* (1994); Inherent Safety Workshop (CCPS Annual Meeting, 10 October 2002)

Table 5.2 *Estimated national resource cost of accidents in the United States in 2001 excluding World Trade Center figures*

	Cost ($)
Fatalities and industrial accidents	132,100
Industrial accidents[a]	978
Under-reporting	5,200
Non-reportable accidents	1,500
Total	139,778

[a] Property damage only, from NFPA.

Table 5.3 *Property damage and business interruption losses worldwide, 1985–89 (after Munich Re, 1991)*

No. of losses		*Loss* (US$ million)	
		Unindexed	*Indexed*
Material damage losses			
1985	198	457	571
1986	149	184	204
1987	135	877	947
1988	121	671	698
1989	115	1,336	1,350
Business interruption losses			
1985	53	146	178
1986	22	71	85
1987	31	304	349
1988	31	284	309
1989	56	1,862	1,937

Kingdom and by the Fire Protection Association (FPA). The FPA defines a large fire as one costing £50,000 or more and the Home Office uses this definition. The *Fire Statistics United Kingdom 1990* (Home Office, 1992) gives the annual loss due to large fires over the 4-year period 1986–89 as some £290 million.

The *FPA Large Fire Analysis 1989* (FPA, 1991) gives the number of large loss fires as 739, with an average loss of £0.382 million, making a total loss of £282 million. In the chemical and allied industries there were eight such fires, with an average loss of £0.656 million, making a total loss of £5.2 million, which was 1.9% of the total.

The NFPA report of *Large-Loss Fires* (NFPA, 2002), reports the total number of fires as 1,734,500 with an estimated loss of $44,023 billion. NFPA considers a large loss as one resulting in more than $5 million damage. There were 36 large loss fires in excess of $5 million (measured in 1992 dollars) for 2001 and 20 in excess of $10 million. Total estimated property damage from the 20 largest losses excluding the World Trade Center (WTC) incident was $762 million. Three of the largest 20 losses involved oil refineries.

In previous editions of this guide, the expenditure on insurance was used as a measure of the cost of incidents. With the continued growth of multinational corporations, the globalization of the world economy and the emergence of supermajors in the energy business, insurance costs can no longer be used to effectively estimate the cost of incidents. A large number of events no longer are reported to insurers and the costs of these are absorbed fully by the corporation.

Within the refining industry, Solomon Associates conduct annual surveys of member company facilities that analyse numerous costs and other factors as a means of comparing refineries in geographic market areas. The Solomon ratings provide an indirect measure of the cost of incidents as they impact maintenance costs and on-stream factors.

Data on worldwide fire and explosion losses have been given in *Losses in the Oil, Petrochemical and Chemical Industries* by Munich Re (1991). The property damage and business interruption losses worldwide in the Munich Re data base for the years 1985–89 are given in Table 5.3.

A more recent study, '*The 100 Largest Losses 1972–2001/ Large Property Damage Losses in the Hydrocarbon–Chemical Industries*', 20th Edition, James C. Coco, editor, was published by Marsh Inc., a leading insurance broker. According to this study, the 100 largest losses in the hydrocarbon and chemical process industries during the 30-year period covered cost $10.8 billion in property damage for an average of $108 million per incident. In a separate section covering large losses to offshore facilities, the Marsh study listed 15 incidents that occurred between 1987 and 2001. The total property damage loss for these incidents was $3.81 billion or an average $254 million per incident. All loss amounts in this study were adjusted for inflation to reflect US dollars as of 2002 and include only the cost of direct property damage and debris removal. The greater concentration of assets and the greater likelihood of total loss at offshore installations accounts for the substantially higher average loss compared with the land-based facility losses.

Even at the international level, large losses such as those of the Piper Alpha oil platform in 1988 and of Pasadena in 1989 have a major impact on the cost of losses in a given year. This is even more true at the national level. This needs to be taken into account if annual average figures for periods when no such loss occurs are not to be misleading.

Public reaction to incidents involves the industry in additional costs. A major disaster such as Flixborough may result in legislation or other measures which affect costs throughout the industry. This may occur even if the disaster is in another country. Seveso had a marked influence in Europe and Bhopal worldwide, not least in the United

States, the base of the parent company. In other cases the reaction is at local level. Intermediate cases occur when public reaction causes changes in the practice of a particular branch of the industry. The costs due to public reaction have been discussed in general terms by S.B. Gibson (1976d), but the estimation of such costs is very much a matter of judgement.

Further information relevant to the cost of losses is given in Appendix 1. This appendix lists, in Table A1.4, numerous cases of fires and explosions which resulted in property damage and or business interruption. Also listed in Table A1.4 are numerous instances where, for reasons of hazard and/or pollution, a company has either ceased production at an existing plant or has not proceeded, or has not been allowed to proceed, with a planned development of production. Such cases often involve, of course, heavy financial losses.

5.2.2 Company and works level

If now the methods of determining these costs are considered at the level of the individual company or works, estimates may again be based on the same types of information as before: (1) accident statistics, (2) fire loss statistics, (3) insurance statistics, (4) maintenance and downtime statistics and (5) major accidents. There are some important differences, however, between company and national level. The two principal points are that the company generally has access to higher quality information than is available at national level. The other is that the company is much more vulnerable to a single major incident.

An illustration of the cost of accidents at company level has been given in a Dupont study referred to by McKee of Conoco at the Piper Alpha Inquiry as evidence that safety is good business (1990). Worldwide, in 1985 Conoco had 39 lost work-day cases. On the basis of the industry average, the expected value was 372, so that 333 cases, and their associated costs, were avoided. This was equivalent to a saving of some $6.2 million at the time.

Accident costs for injuries at work was reported by the National Safety Council as costing US economy $132.1 billion in 2001 from 10,700 injuries per day and 15 fatalities. Off the job injuries cost the economy an additional $184 billion. *The Costs of Accidents at Work* by the HSE (1993a) describes a set of five case studies of accident ratios, on the lines described in Chapter 1, and gives corresponding cost estimates.

Company level fire loss statistics may be used, but the effect of a possible single large loss fire needs to be borne in mind.

For companies that purchase insurance with relatively low deductible or self-retention layers, insurance costs may be viewed. The insurance costs incurred by the company are as another measure of the cost of losses. Where relevant, insurance costs need to be considered both in terms of the rates which are currently quoted and of those which might be obtained by the adoption of further loss prevention measures, if any. Actual insurance rates are no longer available, and will need to be obtained from company data and from insurer's quotations. The extent to which reduced rates may be obtained which give credit for loss prevention measures is considered below.

Costs which the company is especially well placed to assess are those of commissioning delays, downtime and maintenance in its own plants. Delays in design or commissioning related to plant safety tend to arise mainly from failure to recognize serious hazards sufficiently early. The influence of plant lateness on profitability is a well-developed topic in process economics and methods are available to estimate it. Estimates of the effect of plant lateness on ammonia plant economics are given in Table 1.5.

Plant unavailability, or downtime, may or may not incur serious cost penalties, depending on whether there is a ready market for the products. Similar considerations apply to partial unavailability or limited output. Moreover, the penalties of unavailability are not necessarily linear. It is quite possible to live permanently with a degree of undesirable downtime, but a single protracted stoppage may be catastrophic in terms of loss of profits and markets. Methods of estimating both the mean and spread of plant availabilities are described in Chapter 7.

The effect of downtime on plant profitability is another standard topic in process economics (e.g. D.H. Allen, 1973). A theoretical study, which considers the effect of downtime, and in particular the point in the plant life when this occurs, has been made by J.A. Richardson and Templeton (1973). A case study of the effect of downtime on the profitability of an actual petrochemical plant has been described by Jenkins, Ottley and Packer (1971).

Data on equipment failures are available as generic failure data given in the literature or as data obtained from the works; similarly for equipment repair times and costs. Often the works accounting system can yield much valuable information in this area (R.P. Reynolds, 1976). It is then a relatively straightforward matter to estimate the direct costs of repairing failures.

If an incident occurs at a works, public reaction must be expected and is likely to give rise to expenditure. The costs outlined are not all mutually exclusive categories. For example, property damage costs as determined by a total loss control programme also appear as equipment repair costs, but the costs have been listed in this way to illustrate the different approaches which may be made to their assessment.

5.3 Cost of Prevention

Some of the areas in which costs tend to be incurred to prevent loss are: (1) management effort, (2) research effort, (3) design effort, (4) process route, (5) operational constraints, (6) plant siting, (7) plant layout and construction, (8) plant equipment (safety margins, materials, duplication), (9) process instrumentation (trip systems), (10) fire protection, (11) inspection effort and (12) emergency planning. Since all aspects of a project have safety implications, any such list is somewhat arbitrary. Others are given in the literature (e.g. Pratt, 1974). The areas listed are those in which additional costs attributable to loss prevention are particularly likely to occur.

Loss prevention requires considerable additional effort in management generally (see Chapters 1, 6, 20 and 21), hazard identification (Chapter 8), process and pressure system design (Chapters 11 and 12), plant inspection (Chapter 19), emergency planning (Chapter 24) and research (Chapter 27).

Considerations of safety may well determine the process route, that is, the basic chemical reactions, and define the operating limits for the process parameters, for example, pressure, temperature, concentration (see Chapter 11). Obviously these factors are of fundamental importance to the economics of the process. Process economics are also greatly

affected by plant siting and layout (see Chapter 10). The site which is otherwise most attractive may be ruled out on safety grounds. A layout which requires large separation distances may be expensive in land and pipework.

The various safety factors which are incorporated in the plant design greatly increase costs. These include design with thicker vessel walls, use of more costly materials of construction, selection of more expensive equipments and duplication of items (see Chapter 12). Additional instrumentation such as trip systems (see Chapter 13) and additional fire protection and fire fighting equipment (Chapters 10 and 16) constitute further costs. While expenditure in all these areas is unavoidable, it is the aim of loss prevention to get value for money in this expenditure.

There are available some global estimates for expenditure attributable to safety and loss prevention, and also to environmental protection. Kletz (1988g) quotes three sets of estimates. One estimate for safety and environmental costs for plant in the United Kingdom given by a Chemical Industries Association (CIA) source is 12–15% of total investment. A second estimate derives from his own survey of 10 ICI plants, which showed that on average 10–15% of the capital cost was spent on safety measures over and above the irreducible minimum necessary for a workable plant; items such as relief valves are regarded as basic equipment and are not included in this figure. Another 5% was spent on pollution control. The proportions spent varied widely between plants; in one case the expenditure on safety was 50% of capital cost. The third estimate is that of a US source to the effect that during the 1990s in the hydrocarbon processing industry (HPI) some 60–75% of capital was spent on safety and environmental compliance issues due to the EPA Clean Air Act, the OSHA 1910.119 PSM Regulation, and other federal and state-related initiatives. A sum equal to 9% of capital is spent on health and safety, though a large part of this is on revenue items.

5.4 Level of Loss Prevention Expenditure

5.4.1 General considerations

The effect of different levels of expenditure on safety is shown in general terms in Figure 5.1 (Kletz, 1986d). The expenditure shown refers to that required over and above that necessary for a workable plant. At the left-hand end of the graph, expenditure on safety is also good business, but as the expenditure is increased the returns diminish and lead eventually to the company going out of business.

The loss prevention approach has altered considerably the terms of the long-standing debate on the optimum level of safety expenditure. An essential element in this approach is the quantitative assessment of hazard. This in turn makes it necessary to take a view of the levels of risk which are unacceptable and which must be removed by expenditure. Moreover, quantification also provides the information on which can be based rational decisions on the cost-effectiveness of additional expenditure in reducing the risk to human life.

The question of safety expenditure then largely revolves around the decisions on these primary and secondary criteria, the levels of unacceptable risk and the expenditure to save a life. Both criteria can be compared with those used explicitly or implicitly in other industries and activities. The question of acceptable risk and risk criteria is considered in more detail in Chapters 4 and 9.

In fact, the area of choice in safety expenditure in the chemical industry is not as wide as sometimes appears from general discussions of optimum levels of expenditure. The standards of safety which are already obligatory are high and have tended to rise. Since in the chemical industry safety is both relatively good and relatively expensive to improve, the high minimum standard may well tend to become the norm. This is not unreasonable provided, but only provided, that additional expenditure is incurred where it is cost-effective in terms of human life.

It can be misleading to assume that increased safety necessarily involves increased expenditure. It is undoubtedly true that safety expenditure which is based on reaction to incidents can be very expensive. But it is general experience that good practice usually costs no more than bad and gives both improvements in safety and reductions in costs. The reason is that high levels of safety require high quality management and management systems, and that

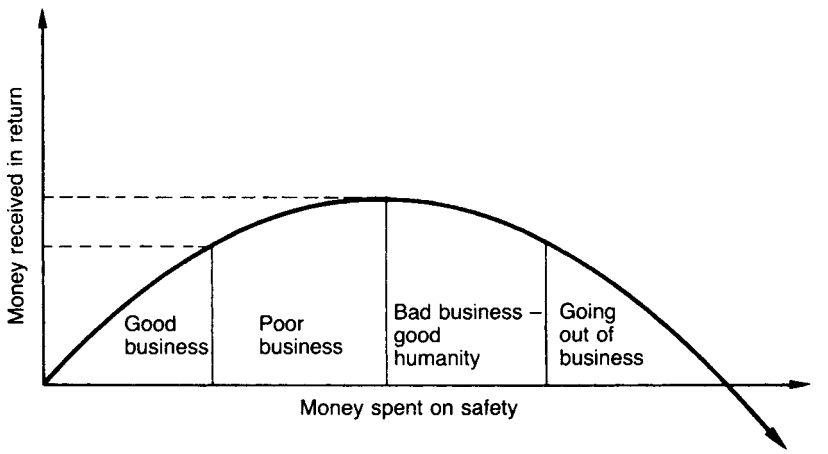

Figure 5.1 *Effects of increasing expenditure on safety and loss prevention (Kletz, 1986d) (Courtesy of the Institution of Chemical Engineers)*

if the company has these, it also has the capability to achieve its other goals.

Thus, given good loss prevention practice, large improvements in safety can be achieved relative to poor practice at no additional cost. That said, there are within the context of good practice some additional costs which are attributable only to safety and which must be borne.

Another aspect of safety expenditure is the estimation of the effect which additional expenditure already incurred has had in improving safety. This is considered in Chapter 27.

5.4.2 Decision aids

The various techniques of economic analysis such as net present value (NPV) and discounted Cash Flow (DCF) may also be used in support of assessment of the economic level of loss prevention expenditure (D.H. Allen, 1973; C.S. Park, 2002). Engineering economic analysis tools are also available on the internet at http://www.eng.auburn.edu/~park/cee2.html; http://www.eng-tips.com; http://www.isr.umd.edu/~austin/ence202.d/economics.html and other sites. The difficulties lie principally in assessing the savings.

Some decisions on the level of loss prevention expenditure are amenable to treatment by other formal decision-making techniques, in particular decision analysis. Current techniques and models for economic decision analysis can be found in Contemporary Engineering Economics by C.S. Park (2002) and Capital Investment Analysis for Engineering and Management by J.R. Canada *et al.* (1995).

Accounts of decision analysis are given by G.H. Mitchell (1972) and Hastings and Mellow (1978). In a typical decision analysis there is a set of possible outcomes, or states of nature, and a set of possible options for action, or decisions. The aim is to choose the decision(s) which maximize the gain, or utility, or minimize the loss, or regret. A common form of the problem is that there is a possibility of obtaining better information, which will improve the decision but will itself involve a cost.

The application of this technique to loss prevention has been illustrated by R.C. Hanna (1979). The problem considered is the appropriate level of fire protection for a process unit handling liquefied petroleum gas (LPG). Three states of nature are considered – S_1 no fire; S_2, a small fire and S_3, a major fire incident – in a given year. There are also three decisions: d_1, no fire protection; d_2, fireproofing and sprinklers; and d_3, fireproofing, sprinklers and surveillance and control instrumentation. There is the option to do a hazard survey which should provide improved information on which to make the decision. The three outcomes of the survey, or indicators, I_1–I_3 correspond to recommendations to implement decisions d_1–d_3, respectively.

The data required for the analysis are shown in Table 5.4. Sections A and B give, respectively, the estimates made of the costs of preventive measures and of probabilities $P(S_j)$ of no fire, a small fire and a major fire, the latter being based on historical data. Section C gives the estimated loss costs, prevention costs and total costs. The loss costs are calculated using the relationship:

$$D(d_i) = \sum_j P(S_j)C(d_i, S_j) \qquad [5.4.1]$$

where C is the loss cost for a particular state of nature and level of protection (US$k/year) and D is the loss cost for a

Table 5.4 *Decision analysis for level of fire prevention expenditure (after R.C. Hanna, 1979)*

A Prevention

	Cost M^* (US$)
d_1	0
d_2	25,000
d_3	100,000

B State of nature probabilities

	States of nature		
	S_1	S_2	S_3
$P(S_j)$	0.93	0.05	0.02

C Loss costs, prevention costs and total costs (without survey)

Loss cost

	Annual				*Present value, D^** (US$k)	*Prevention cost, M^** (US$k)	*Total cost, T^** (US$k)
	C (US$k/year)			*D* (US$k/year)			
	S_1	S_2	S_3	*Total*			
d_1	0	100	1,000	25	156.5	0	156.5
d_2	0	50	200	6.5	40.7	25	65.7
d_3	0	10	50	1.5	9.4	100	109.4

D Probabilities of survey correctness

	States of nature		
	S_1	S_2	S_3
$P(I_1\|S_j)$	0.80	0.05	0.03
$P(I_2\|S_j)$	0.15	0.85	0.07
$P(I_3\|S_j)$	0.05	0.10	0.90
Total	1.00	1.00	1.00

E Branch probabilities

Survey branches

$P(I_1)$	0.747
$P(I_2)$	0.183
$P(I_3)$	0.070

State of nature branches

	States of nature			
	S_1	S_2	S_3	*Total*
$P(S_j\|I_1)$	0.996	0.003	0.001	1.000
$P(S_j\|I_2)$	0.760	0.232	0.008	1.000
$P(S_j\|I_3)$	0.669	0.072	0.259	1.000

F Loss costs, prevention costs and total costs (with survey)

		Loss cost			
		Annual, D	*Present value*	*Prevention*	*Total cost*
I_1	d_1	1.3	8.14	0	8.14
	d_2	0.35	2.19	25	27.19
	d_3	0.08	0.5	100	100.5
I_2	d_1	31.2	195.28	0	195.28
	d_2	13.2	82.62	25	107.62
	d_3	2.72	17.02	100	117.02
I_3	d_1	266.2	1666.15	0	1666.15
	d_2	55.4	346.75	25	371.75
	d_3	13.67	85.56	100	185.56

particular level of protection for all states of nature (US$k/year).

The annual loss cost is converted to a capital sum, the present value, in order to put it on the same basis as the prevention cost. Assuming a 20-year project life and 15% cost of capital the conversion is

$$D^* = 6.259D \qquad [5.4.2]$$

where D^* is the present value of the loss cost (US$k). The total cost is then

$$T^* = M^* + D^* \qquad [5.4.3]$$

where M^* is the prevention cost (US$k) and T^* is the total cost (US$k).

It is possible to make a decision on the basis of the information in Section C. The minimum value in the total cost, or expected cost of the decision, is that which corresponds to decision d_2 and is US$65.7k.

Alternatively, the decision may be deferred until more information has been obtained by conducting the hazard survey. In this case it is necessary to estimate also the probability that the survey will correspond with reality. Section D of Table 5.4 gives the estimates made for the conditional probabilities $P(I_k/S_j)$ of the survey recommendations given the states of nature. The probabilities $P(4)$ of the survey recommendations and the conditional probabilities $P(5,|4)$ of the states of nature given the survey recommendations must also be calculated as shown in Section E. The relationships used are:

$$P(I_k) = \sum_j P(I_k|S_j)P(S_j) \qquad [5.4.4]$$

$$P(S_j|I_k) = \sum_k P(I_k|S_j)P(S_j)/P(I_k) \qquad [5.4.5]$$

Equation 5.5[3] is a form of Bayes' theorem, which is described in Chapter 7.

Then, using the probabilities given in Section E of Table 5.4, the loss cost may be recalculated using the relationship:

$$D(I_k, d_i) = C(d_i, S_j)P(S_j \,|\, I_k) \qquad [5.4.6]$$

The present values of the loss cost and the total cost may then be recalculated using Equations 5.4.2 and 5.4.3. The results are shown in Section F of Table 5.4. The analysis is also illustrated in the decision tree diagram shown in Figure 5.2.

The expected cost of the decision is then given by the relationship:

$$E^* = \sum_k P(I_k)(T_k^*)_{\min} \qquad [5.4.7]$$

where E^* is the loss cost (with survey) (US$k). The value of E^* is US$38.76. This contrasts with the earlier value of US$65.7k. The difference of US$26.94k is a measure of the value of the survey.

5.4.3 Major hazards

While it is generally true in the process industries that good practice costs no more than bad, in the case of major hazards it is often necessary to incur expenditure on safety which is not self-financing. This is illustrated by the following simple calculation given by Lowe (1980). Consider an installation on which an incident causing US$10 million damage is estimated to occur once in 10^4 years so that the average annual loss is US$1000. Expenditure to reduce the frequency of the event to once in 10^5 years would yield a saving of US$900/year. This would justify only about US$2000 capital plus US$200/year operating costs. It is highly unlikely that a 10-fold reduction in incident frequency could be obtained for this expenditure. For major hazards, therefore, some decisions on the level of expenditure are influenced rather by risk criteria for such hazards.

5.5 Insurance of Process Plant

Insurance has always been based on the principle of solidarity, and the more balanced, or homogeneous, the risk structure is within a community of insureds, the better this principle works. When the insurer wants to fit a risk into his portfolio, he checks it against 'his' other risks with regard to quality and homogeneity. An on-site inspection often provides important information for this purpose. Claims analyses and research into the cause of losses show quite clearly that with today's complex production and monitoring processes, risk and safety depend less on technology than on management systems and the risk and safety awareness of the individual employees. In other words, they depend on the way a company deals with risks: on its safety culture.

The insurer cannot be expected to pass judgement on the safety culture of individual companies as such. His only responsibility is to set up communities of insureds. However, this involves evening out recognizable inhomogeneity either through selection, or the pricing and design of cover, or by supporting the insureds' risk management efforts.

Assessing individual industrial risks requires more than experience and technical know-how; it also requires special tools for the systematic appraisal of the factors relevant to safety and risk.

There are a number of ways in which questions of insurance impinge on safety and loss prevention. It is the business of the insurer to carry out assessments of risk in order to set premium rates. The insurer is also increasingly

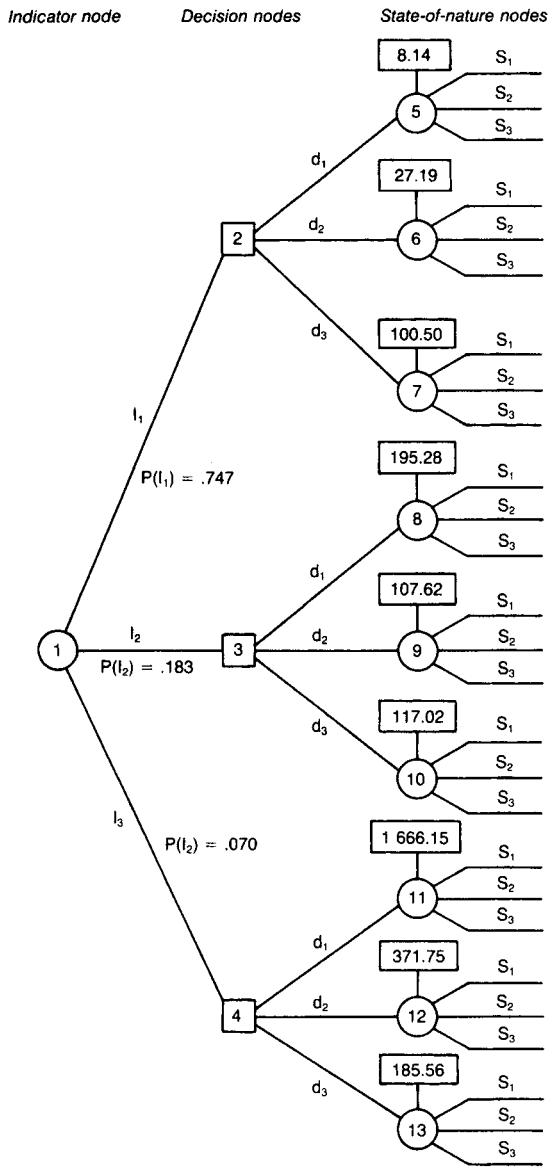

Figure 5.2 *Decision tree for level of fire prevention expenditure (after R.C. Hanna, 1979) (Courtesy of Hydrocarbon Processing)*

concerned with the management of risk and with the effectiveness of loss prevention measures. The economics and the design of the process operated by the insured are affected by insurance factors.

The company operating a hazardous plant must either itself bear the whole financial risk or seek outside insurance for this risk. The decision is an important but difficult one and it needs to be related to the overall approach taken by the company to loss prevention. Insurance practices vary, of course, from country to country and it is essentially the practice in the United Kingdom which is described here.

The insurance scene is constantly changing. There may be some restriction on insurance capabilities where there are novel risks or bad loss experience, but the market is usually able to adapt. The insurance which is of principal interest here is essentially fire insurance, which effectively covers fire and explosion risks.

5.5.1 The insurance process

The basic principle of insurance is to spread the risk so that losses incurred by the few are borne by the many. For industrial fire insurance this is done by a combination of risk sharing called 'quota share' co-insurance and re-insurance. In a quota-share arrangement, co-insurance, the insurers take direct responsibility for providing a specified proportion of the cover. The prime responsibility for assessing the risk is taken by a leading company. In re-insurance the primary insurers and co-insurers lay off their risk with other insurers. For a large risk the re-insurers may themselves re-insure further. The re-insurance business is an international one.

The extent of an individual insurer's participation is usually determined not by the full sum insured but by a loss measure such as the probable maximum loss (PML) or estimated maximum loss (EML), as described below. The underwriter determines his share of the insurance as a proportion of the PML; he usually does this using his company's table of PML limits. He may exercise his discretion to reduce this share, if he has doubts about either the magnitude or the probability of the PML. On this basis the underwriter writes his 'net line.' This net line may then be augmented if re-insurance facilities are brought into play, so that the gross acceptance notified to the buyer may be several times the net line.

The procedure adopted by the insurer in response to an insurance inquiry is to do a breakdown of insurance values by site and by installation, and to obtain a report from the insurance surveyor. Inspection is a normal preliminary to insurance. In general, the industry operates on the principle of 'no insurance without inspection.' Frequently, however, insurers will accept reports or an inspection or survey conducted by an insurance broker or an engineering consultant retained by the insurer or the broker.

5.5.2 Insurance policies

In the past an insurance policy covered a named peril for a specified period. The perils may be standard or special perils. Some of the types of insurance available in a multiline policy in the United States are given by Spiegelman (1987): (1) public liability, (2) product liability, (3) workers' compensation, (4) motor vehicle, (5) business interruption, (6) professional liability, (7) boiler and machinery and (8) property damage.

More recently, insurers have provided policies covering 'all risks of direct physical loss' except for perils or events specifically excluded by the policy language.

The principal peril relevant here is fire. Industrial fire insurance almost invariably includes fire, explosion and lightning, and may include, depending on the geographical location, windstorm, flood and earthquake. The effects of fire include both property damage and business interruption. Insurance may be limited to the first or may cover both.

For property insurance, the sum assured may cover either the current value or the replacement cost.

5.5.3 Loss measures

The insurance policy may provide cover for the full sum at risk, but, as just described, insurers generally find it convenient to work in terms of a more limited sum. There are various measures which are used, notably normal maximum loss (NML), PML and EML, but the definitions of the terms tend to vary. These terms are discussed further below.

5.5.4 Insurance surveyors

It is the function of the insurance surveyor to provide the insurer with a report on the risk to be insured. Insurance surveyors are employees of the insurance companies or insurance brokers, and, in the United Kingdom, are typically experienced people, but are not necessarily qualified engineers. Insurance surveyors have wide experience in risk assessment and there is considerable consensus on the critical features and on good and bad practice in loss prevention.

5.5.5 Insurance surveyor's report

The insurance surveyor's report includes an assessment of the loss measure used such as the PML and serves as a guide to the underwriter in setting the premium. The report involves assessing the fire load and fire risk on a plant and then making allowance for protective features.

5.5.6 Tariff and non-tariff systems

The traditional approach to setting premium rates for industrial fire damage risks has been classification by trade or occupation. Classifications run to as many as 300 trades. For many trades there is a detailed tariff which consists of a basic rate together with increments or decrements for factors which increase or decrease the risk, respectively. However, for some trades there is no tariff.

Investment income potential is a major driver of insurance capacity and pricing. The business of insurance entails a significant time delay between premium collection and payment of losses. Insurance companies invest these funds, which they hold in a fiduciary capacity. When certain economic conditions such as high interest rates or a steadily rising stock market increase investment income, insurers attempt to obtain more money to invest by increasing their business by means of rate reductions or more liberal policy terms. Trade professionals refer to this condition as a 'soft market' for insurance.

The opposite happens when investment-market conditions provide less income on fiduciary funds. The result is a 'hard market' as underwriters raise premiums to offset falling investment income.

In the United States, strict regulation of insurance by individual states prevailed from 1945 through the early 1960s as a consequence of a decision by the US Supreme Court. During the regulated era, insurance associations developed various rating schedules. Among these schedules were the 'Schedule for Petroleum Properties' and the 'Schedule for Rating Petrochemical Plants,' which applied to the process industries. These two schedules were last revised in the early 1960s and gradually fell out of use over the following 10–20 years.

Inherent deficiencies in these schedules lead to their demise. First and most important, the schedules took no account of the potential for investment income. Second, adjustment of rates to reflect recent loss experience was cumbersome and not done often enough to keep schedule-derived rates commensurate with loss payments. Third, as technology changed much about the way process plants were designed, built, operated and protected, many rating criteria used in the schedules no longer reflected the degree of risk. In particular, there has never been a tariff for the chemical industry. Instead, in this industry the premium rates are set according to a scale of relative risk as assessed by the insurance surveyor's report.

5.5.7 Fire insurance in the United Kingdom

Throughout the 1960s there was a history of growing fire loss in many trades in the United Kingdom. Many of these fires were in industries where fire losses have always been high. Insurers dealt with this by applying to each trade appropriate premium weighting factors. This approach was presumably adopted in the belief that the problem was a temporary one. In the event this proved not to be the case so that by the end of the decade the weighing factors in use ranged as high as 7.5. This suggested that the rating structure was no longer an appropriate one.

5.5.8 Business interruption insurance

Business interruption (BI) insurance covers the consequential loss from an insured peril that interrupts or diminishes production. Following a waiting period stated in the policy, BI insurance covers lost profit and continuing or non-avoidable expenses during the time required to restore production. The BI insurance policy may provide for a monetary deductible in lieu of or in addition to the waiting period. Because the coverage related to the time production is impaired, BI insurance is sometimes referred to as 'time-element' insurance.

The advent of large, single-train process plants increased exposure to BI loss and demand for BI insurance. For example, if production depends on the availability of one very large gas compressor that requires an 18-month lead time to replace, a relatively moderate property loss can result in a large BI loss. Today, BI losses frequently exceed the associated property damage (PD) loss. Until about the 1960s much fire insurance was virtually synonymous with PD insurance. There then came into prominence another type of insurance – consequential loss or BI insurance. The need for this is due mainly to the very heavy losses which can occur if a large, single-stream plant is out of action for more than a short period. The costs of losses due to, and of insurance for, BI now tend to exceed several times those of damage.

5.5.9 Large, single-train plants

As described in Chapter 1, the 1960s saw the growth of the large, single-train plant. This has presented many problems to insurers. In considering the problems posed by such plants, it is necessary to distinguish between average and maximum losses and between property and business interruption losses. There does not appear to be much evidence that for property the average losses are any worse than for other plants, but for BI the situation is probably different, although it is difficult to assess, because BI

insurance is largely limited to such plants. The PML is much greater, of course, on such plants for both property and BI insurance.

Large plants pose several problems to insurers. One is the magnitude of the PML for both property and BI. Another is the high premium rates required to provide cover for BI. Another is the difficulty of assessing the adequacy of the management and of the technology.

Insurers have been virtually unanimous in expressing their dislike of large plant risks and in suggesting to the industry that it may have gone too far in putting its eggs in one basket. On the other hand, whilst the early generations of large plants gave rise to many problems, it is arguable that the management and technology of such plants are now better understood, not least due to the development of loss prevention.

Some perspective on this is also provided by the fact that many of the worst losses in the 1960s were on medium-sized, medium-technology plants. Neil (1971) suggests that this may have been due partly to the diversion of management resources to the large plants.

5.5.10 Insurance market

The insurance market is an international one and the insurance of a large plant will normally be spread with insurance companies around the world. Just as business is subject to the business cycle, so the insurance industry is subject to the insurance cycle. This is described by Norstrom (1982b). Expansion of capacity in the insurance industry creates competitive forces which drive premium rates down and reduce profitability, thus causing a contraction of capacity. At some times the business and insurance cycles come together. This was the case, for example, during the period 1977–81 in the United States.

When investment income is high, rates are high and loss experience is good, the insurance industry is more profitable and capacity expands, whilst when investment income falls, rates fall and losses are heavy, profitability and capacity fall. The insurance market is in a continuous state of change and adaptation to new risks. The development of seepage and pollution insurance is an example of the growth of insurance capacity in a new area. The industry has also been able to create capacity to cover very large loss potentials, as described below.

5.5.11 Loss experience

As just indicated, the loss experience of the insurance industry is variable and this has an impact both on capacity and on premium rates.

In the United Kingdom, the late 1960s and the 1970s saw loss on an increasingly serious scale in the chemical industry, which up to this time had had a good record. The experience of the insurance companies was therefore not a happy one. In general, in fire insurance, premium income did not cover losses sustained and administrative costs, so that underwriting was in deficit, although insurance companies benefited from investment income. The insurance market is very competitive and in too many cases business was taken at rates which later experience showed to have been unrealistic.

Likewise in the United States the insurance industry experienced large losses around 1967 with the vapour cloud explosion at Lake Charles in 1967 and other major incidents. The period 1974–76 also saw heavy losses. This trend culminated in the late 1980s with vapour cloud explosion losses at Pampa, Texas (1987), Norco, Louisiana (1988) and Pasadena, Texas (1989).

5.5.12 Insurance capacity

The capacity of the insurance market is usually given in terms of the extent of cover which can be obtained for a single potential loss. As just described, this capacity fluctuates. Although generally the market is able to provide insurance even for very large loss potentials, there is some degree of restriction.

In 1971, the capacity of the worldwide insurance market was described by Neil (1971) as quite limited. He estimated that the theoretical capacity was about £30 million per loss, but also stated that it was difficult to obtain insurance for a PML exceeding £6 million for property damage or £10 million for PD and BI combined. This was certainly not sufficient for complete insurance cover on a large ethylene plant. This limitation of the market was evidently a consequence of the adverse experience in industrial fire insurance in the 1960s and the 1970s.

The vapour cloud explosion at Flixborough had an influence on the insurance market. Some insurers recognized the possibility of such an explosion, either by allowing for it in their assessment of PML or by buying specific re-insurance. A loss of US$100 million from damage and BI due to a major vapour cloud explosion was considered within the realm of possibility.

A later estimate of insurance market capacity by Neil (1978) put the capacity for PML at about £40 million for companies with a good loss record and good reputation for management and design. After 1975 the bulk of oil and petrochemical risks owned by oil companies and to be insured on the London market was directed to International Oil Insurers (IOI), a body set up by the leading British insurers, including Lloyds, to underwrite such business. The capacity of IOI was estimated by Neil (1978) as about US$15 million on a PML basis.

Redmond (1990) describes the capacity available through the Oil Insurance Limited (OIL) mutual together with the London Master Energy Line Slip, which is a facility whereby many insurers commit their capacity automatically. However, disasters such as Piper Alpha, Pasadena and the Exxon Valdez have caused reduction of capacity for periods of time called 'hard markets.' A similar hard market condition developed after the terrorist attacks of 11 September 2001. Market capacity decreased dramatically and has only recently started to improve. Worldwide capacity is now in excess of one billion US dollars for certain risks.

5.5.13 Insurance restrictions

In periods when the capacity of the insurance market is restricted, there may be pressure on the insured to bear part of the risk. There are various ways in which this may be effected. The restrictions may take the form of exclusions, limited coverage for particular activities, or the application of deductibles. If deductibles, or excesses, are applied, the insured company itself is required to meet a fixed degree of loss. Typically, for property damage this is a cash sum, whilst for BI it is typically a waiting period stated in hours or days before insurance coverage applies a number of days of downtime. Alternatively, the operating company may insure itself. Either the company with the risk carries

that risk itself, or it is insured by a subsidiary insurance company.

5.5.14 Self-insurance

A company may often choose not to seek full insurance cover but to bear some or all of the losses itself. Indeed, the demands placed on the world insurance market by the chemical industry have tended to leave companies with little choice but to carry some of the risk themselves. Policy on the purchase of insurance is a complex matter and depends very much on the circumstances of the individual firm, so that only a few general points are made here. Perhaps the most obvious and important is that the scale of potential loss is such that it would be severely damaging to even the largest firm, so that some degree of outside insurance is advisable.

Insurers usually emphasize that it is not reasonable that industry should seek to place only selected risks while withholding from the insurers the 'bread-and-butter' business. A healthy insurance industry cannot tolerate such adverse selection; the former alone cannot sustain a healthy insurance industry. On the other hand, the industry does expect to receive credit for high standards of management and technology and for loss prevention measures, and its decision to purchase insurance may be influenced by its confidence in the assessment made of these by the insurers.

5.5.15 Vapour cloud explosions

A significant proportion of the loss potential on process plants is attributable to vapour cloud explosions. Alexander (1990a) quotes his own estimate made in about 1980 that this proportion was in the range 5–10%. A method for the assessment of the EML due to a vapour cloud explosion has been developed by the IOI (1985 based upon a TNT equivalency calculation). A discussion of insurance with special reference to vapour cloud explosions is given by Davenport (1987). These original vapour cloud loss estimate methodologies have been modified over the years to allow the calculated overpressure diameters to encompass sufficient plant value to match historical loss events. The results have been less than desirable since a point source explosion overpredicts blast loads close to the epicentre and underpredicts blast loads in the far field. Extensive research has been conducted during the past 15 years to analyse vapour cloud explosions of various purity and mixture materials to determine what factors influence the energy released in an explosion. Congestion and confinement and ignition energy and location, are among the more critical variables. The impulse or time element factor of the produced pressure wave is also a critical element that influences damage levels. Insurers are just beginning to incorporate this science into their loss estimating models.

The Marsh study (February, 2003) showed that of the 10 largest on-shore losses in the hydrocarbon–chemical process industries from 1972 to 2001, vapour cloud explosions were the primary damage-causing mechanism in five of the incidents. Each of these losses exceeded $262 million in property damage alone, measured in constant 2002 US dollars.

5.5.16 Major disasters

Disasters such as Piper Alpha in 1988 and Pasadena in 1989 have a significant impact on the insurance world.

The losses incurred in these two accidents have been discussed by Redmond (1990). Piper Alpha was not simply a single oil platform, but the centre of an oilfield, with pipelines coming onto it from other platforms and from satellite fields. The interim estimates of loss given are: for physical damage, US$680 million; BI, US$275 million; fatalities and injuries, US$160 million; removal of wreckage, US$100 million and other items, US$155 million. These items total US$1370 million. The interim estimates for the loss at Pasadena quoted by Redmond are very similar, about US$1400 million, divided almost equally between property damage and BI. The HSE (1993a) has estimated the loss due to Piper Alpha as amounting to some £2 billion, including about £750 million in direct insured losses.

5.6 Property Insurance

There are a variety of factors which are taken into account by insurance surveyors to assess property damage risk for the purpose of premium rating. Some of the features which are frequently mentioned by insurers are: (1) size of plant, (2) novelty of technology, (3) process materials (flammable liquids at high pressures and temperatures), (4) process features and controls, (5) plant layout, (6) building design, (7) fire protection of structures, (8) fire fighting arrangements, (9) management of hazards and (10) natural perils such as earthquakes, floods and hurricanes.

5.6.1 Loss measures

As already mentioned, a number of measures of loss are utilized, but different meanings are attached to the terms used. Alexander (1990a) utilizes the following terms: average loss; NML, or PML; EML, or possible maximum loss and maximum credible loss (MCL), or maximum foreseeable loss. The average loss is self-explanatory. NML is the maximum loss which would be expected if all protective functions work, EML is the maximum loss if one critical item of protection does not work, and MCL is the maximum loss in circumstances where a number of critical items of protection do not work or where a catastrophic event occurs which is just credible. He gives the following approximate frequencies:

$$\text{NML} \geq 10^{-3}/\text{year}$$
$$\text{EML}\ 10^{-4} - 10^{-3}/\text{year}$$
$$\text{MCL}\ 10^{-5} - 10^{-4}/\text{year}$$

5.6.2 Risk profiles

The estimates just given for the frequency of the various levels of loss are general ones. It is also possible, and instructive, to construct the loss profile for a particular plant. The construction and use of such profiles is discussed by Alexander (1990a). The method which he describes is the use of what may be termed a frequency–loss (FL) plot. This plot has similarities with the frequency–number (FN) plot for major accidents described in Chapter 9 but, since the loss levels plotted on it are simply the single values of NML, EML and MCL, the frequency is an absolute rather than a cumulative one.

Figure 5.3 illustrates profiles for two hypothetical plants. For plant (A), a well-protected plant, the frequency of the EML is much less than that of the NML and the frequency for the MCL much less again, but for plant (B),

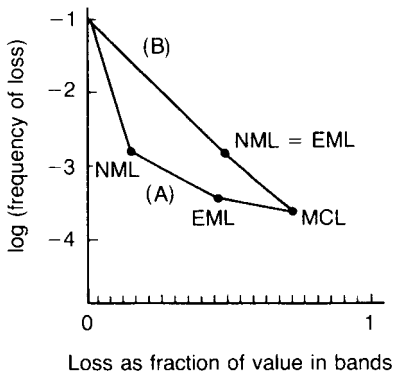

Figure 5.3 *Frequency – loss profiles of two hypothetical process plants (Alexander, 1990a) (Courtesy of the Institution of Chemical Engineers)*

an unprotected plant, the EML has the same frequency as the NML.

It is also possible to construct FL curves for the industry as a whole. In this case the use of a cumulative frequency is more appropriate. Such curves might be constructed from the data published periodically by insurers (e.g. Norstrom, 1982b; Munich Re, 1991; Marsh and McLennan, 1992).

5.6.3 Risk assessment methods

Insurance assessors use a variety of methods to assess the risk and to arrive at a premium rating. These methods include the use of checklists, of various types of hazard index, and of formal premium rating plans. The last two are closely related. Increasingly, such hazard indices and premium rating plans emphasize management aspects. A number of specific management audit methods have been developed.

5.6.4 Checklists

The insurance surveyor tends particularly to use checklists of features to be assessed. A series of such checklists is given by Spiegelman (1969). Later versions of such checklists are given by Norstrom (1982b) and Spiegelman (1987), the latter in the context of gas plants; the two checklists are similar and may be summarized as shown in Table 5.5. The original checklists are much more detailed. Further checklists are given by Ashe (1971) and Ackroyd (1974).

5.6.5 Hazard indices

From such checklists there have evolved a number of hazard indices and premium rating plans. The best known hazard index is probably the Dow Index, given in the so-called Dow Guide, which has gone through a number of versions. The most recent is the *Dow Fire and Explosion Index Hazard Classification Guide* (AIChE, 1994). Another hazard index is the Mond Index, which is an adaptation of the Dow Index (D.J. Lewis, 1979). A third index is the instantaneous fractional annual loss (IFAL). This index was specifically developed for the insurance industry at the Insurance Technical Bureau (Munday *et al.*, 1980). These three indices are described further in Chapter 8.

Table 5.5 *Headings of a checklist for insurance assessment of a chemical plant (after Norstrom, 1982b; Spiegelman, 1987)*

Plant siting
Plant layout
Buildings and structures
Process materials
Chemical process
Materials movement and storage
Operations
Equipment (design, testing and maintenance)
Loss prevention programme

5.6.6 Premium rating plans

Premium rating plans have evolved over the years to incorporate many other risk management factors than previously considered (Tables 5.6 and 5.7). The plans are no longer used to develop a premium rate for insurance, but rather are used to judge the quality of a risk. With this information, the underwriter can determine if he wishes to participate in an insurance programme, at what level he will participate and how much of the risk he is willing to take.

An example of a current risk assessment scheme is provided in Table 5.6.

Another scheme which is relevant to premium rating for damage insurance is the Dow Index (AIChE, 1994). The scheme involves the determination of the Fire and Explosion Index (F&EI) and then of the Maximum Probable Property Damage (MPPD). The Dow F&EI, including determination of the MPPD, is considered in detail in Chapter 8.

5.6.7 Technical services

In the early 1970s, the British insurance industry recognized the need for technological back-up and supported the formation of the Insurance Technical Bureau (ITB) (Chilver, 1973). The IFAL method, mentioned above and described in Chapter 8, was developed by the ITB. The ITB was subsequently dissolved and technical support is now provided by in-house engineers or outside consultancies.

5.6.8 Management audits

The increasing emphasis on management is reflected in the use of audit methods which concentrate particularly on management. Redmond (1984) gives a checklist by which the management may be assessed. A more detailed discussion of the assessment of management for insurance purposes is given by Instone (1990) and in the Swiss Re publication entitled *'Safety Culture – a reflection of risk awareness'* (2003). In this publication, Swiss Re describes additional tools they have developed for assessing management systems as they relate to loss prevention. Their initial effort was a development of an assessment process called Safety Management Audit in the Process Industries (SMAPI). This has since been supplemented by their Safety Awareness Program (SAP) and Change Management Audit Program (ChangeMAP) which are aimed at assessing 'Liveware' systems.

5.6.9 Estimation of EML

Some of the problems of assessing the EML are discussed by Redmond (1984). In general, this assessment is relatively easy for indoor plant with subdivisions each of

Table 5.6 *Outline of a risk assessment scheme for property damage insurance on large capital value plants (Drewitt, 1975)*

Rating factor

L factor	Normal maximum loss
C factor	Inherent hazard classification
HSF factor	Hardware (H), software (S), Fire fighting facilities (F)

L factor

Normal maximum loss (%)	(£m.)	*L factor*
⩾20	⩾2	1
$33\frac{1}{3}$	4	2
50	6	3
$66\frac{2}{3}$	8	4
$>66\frac{2}{3}$	>8	5

If the % and final NMLs give different L values an average may be taken. m. denotes million.

C factor

	C factor
Low risk plants	1–3
Medium risk plants	4–6
Relatively high risk plants	7–9
High risk plants	10–12

C factor parameters:

1.	Nature of raw materials	0 Non-flammables 1 Flammable solids, heavy flammable liquids or vapours, dusts at ambient conditions 2 Light flammable liquids, hydrogen, combustible gases, naphtha, petrol 3 LPG-type materials or other flashing liquids (any substance which is flashing above 5%) materials in use above their ignition point
2.	Nature of products	As (1) above
3.	Process type	Rather difficult to define but must range from the innocuous mixing of solids and liquids under ambient conditions to oxidation reactions, reactions carried out at high temperatures and pressures, reactions involving the use of acetylene above 20 psi, reactions involving the use of explosive materials, special hazards ancillary to the main process, for example, catalyst preparation, catalyst changing or equipment cleaning
4.	Heat content	In considering any plant, cognizance must be taken of the inherent heat content. This involves consideration of heats of combustion of the raw materials and products (hydrocarbons have heats of combustion about 10,000 tcal/t, while most other organic materials are below this value), heat of reaction or heat of polymerization. Associated with these considerations should also be the quantity effect. If we are dealing with large stocks and inventories, then the total heat content potential in the event of an incident must affect the plant hazard rating. The highest of these should be used as the assessment factor. The extent to which inventories of flammable materials within process areas are in excess of actual practical requirements must be taken into account in assessing the hazard in relationship to the minimum unavoidable risk
5.	Reaction temperature	0 Atmospheric temperature 1 Up to 100°C or above flash point of materials involved 2 In range 100–250°C or above boiling point of materials involved 3 Above 250°C or above autoignition point of materials involved
6.	Reaction pressure	0 Atmospheric pressure 1 Vacuum or up to 5 at pressure 2 Up to 100 at pressure 3 Above 100 at pressure
7.	Corrosion and erosion hazards	On a well-designed plant due consideration will have been given to the corrosive and erosive nature of the materials being handled. However, it is accepted that corrosive fluids are difficult to contain and that leakages due to corrosion, particularly at moving parts, do occur. Similarly, the erosive nature of moving fluids and particles is well known

Table 5.6 *(continued)*

8. Domino effect	This factor is included to take account of the hazard that can occur if leakage of a hazardous material can lead to the escalation of the incident, for example, a small leak which fires and damages by flame impingement at larger pipe or vessel with subsequent spillage of a large inventory or hazardous material
HSF factor	
H factor parameters:	
1. Location	Is the plant well sited in relation to dwelling houses, other industries, office blocks, warehouses, other plants, etc.? Is the site well drained? Are soil characteristics suitable for plant requirements?
2. Construction	Is the plant well designed and constructed with adequate safety and contingency factors? Are the materials of construction suitable for the duties involved? Are girders protected with fire resisting cement? Are vessels, particularly up to 20 ft from ground level, protected with fire resisting cement?
3. Separation	Is adequate spacing available between sections of the plant (minimum 20 m) and between items of equipment within the sections of the plant? Are control rooms well sited so that adequate protection is afforded in the event of an incident? Are storage tanks sited away from operating plant? Are storage tanks adequately bunded? Are plants suitably provided with dykes to retain any inadvertent spillage of hazardous material?
4. Ventilation	Is the plant well ventilated? Are machines operating inside buildings or out in the open? Are compressors housed in 'Dutch barn' type structures? Can an inadvertent leak of gas or liquid disperse easily? Are buildings equipped with adequate fire break walls and these fitted with adequate fire doors? Are buildings fitted, where necessary, with explosion relief panels to deal with explosions that may arise from leakage of combustible gases, liquids or dusts?
5. Instrumentation	Is the plant adequately instrumented? Are the instruments kept in Al condition? Are there sufficient trips and alarms to deal with all the eventualities on the plant (see also S factor parameters, item (4), and F factor parameters, item (10))
6. Process valves and lines	Are there sufficient valves and lines to eliminate the possibility of contamination through common-pipe usage? Are there adequate facilities for washing out pipes and valves? Is it possible to divert inventories of hazardous materials to other vessels or to portable containers in the event of an incident? (see also F factor parameters, item (9).) Are there dumping and blowdown facilities available so that inventories of hazardous materials can be safely dispersed in the event of an incident?
7. Cooling	Is there sufficient reserve in the cooling system to deal with happenings outside the normal run of events? Are there adequate facilities to deal with a total cooling water failure?
8. Electrics	Are the electrics well designed and installed to conform with present-day thoughts of area classification? Are there adequate facilities to deal with a complete failure of electricity supply? Are the electric cables adequately protected against fire damage? Are alternative cable runs installed?
9. Emergency supplies	Are there sufficient supplies of nitrogen and inert gases to deal with all blanketing and purging problems? Is there an adequate supply of compressed air and instrument air? Is there an emergency power supply?
10. Flammable waste disposal	Are full facilities available for dealing with the safe disposal of all flammable wastes?
S factor parameters:	
1. Management attitude	What is the management attitude to safety? Are expenditure proposals sympathetically received and treated? Does management take an active interest in the organization and running of safety committees? Does management make a regular inspection of plants to ensure that safety standards are being maintained?
2. Housekeeping	Is the plant clean and truly free from debris, pieces of pipe, paper, plastic bags, wood, etc.?
3. Maintenance	Is the plant well maintained? Is it free from leakage of steam, water and hazardous fluids? Is maintenance conducted in a clean and orderly manner?
4. Plant operating instructions	Are plant operating instructions written in a clear and concise manner? Are they available to all operators? Are they kept up to date and revised at regular intervals? Are they obeyed? Are automatic safety devices tested on a regular schedule and with programmed monitoring on display? Have emergency instructions been written to deal with plant abnormalities?

Table 5.6 *(continued)*

5.	Use of permit-to-work system	Is the permit-to-work system clearly defined and rigidly followed? (Consider competence of issuing authority)
6.	Reporting of accidents	Are all accidents (and near misses) reported accurately and in detail? Are these reports circulated to those in authority? Are they effective in reducing accidents in the future? Are the lessons learned from accidents brought to the attention of new starters on the plants? (Accidents should be considered as abnormal occurrences and it should not be assumed that injury always results)
7.	Labour	What is the quality of plant labour? What is the attitude of plant labour to work, discipline and safety? Is there a high turnover of labour?
8.	Personnel training in plant operation	Are operators well trained in plant operation and tested before given a position of responsibility? Do they have frequent refresher courses?
9.	Personnel training in safety	Is there adequate training in plant safety? Are regular Works Safety Meetings called?
10.	Frequency of technical audits	Are technical audits of plant safety conducted at frequent intervals by an outside body?
F factor parameters:		
1.	Works facilities	Is there a works fire brigade? Is there a full-time Chief Fire Officer? Are adequate fire fighting machines available on site? Are adequate stocks of foam-forming compounds retained on site?
2.	Municipal fire brigade	Is there good liaison with the local municipal fire brigade? How long does it take the municipal brigade to reach the site? Do the works and municipal brigades carry out combined exercises on site?
3.	Water supplies	Is there adequate water supply on site for fire fighting purposes? Is it a separate system or can supplies be tapped off for process use?
4.	First aid extinguishers	Is the plant well provided with first aid extinguishers? Are plant personnel familiar with the use of the extinguishers?
5.	Fixed protection	Is the plant provided with fixed fire protection equipment appropriate to the work, for example, a sprinkler system, a steam fire curtain, a water curtain, fixed monitors?
6.	Automatic fire alarms	Are adequate fire alarms installed throughout the plant? Are adequate gas leak detectors installed throughout the plant?
7.	Communications	Are communications good between the plant and the shift manager and between the plant and the fire services so that incidents can be reported with the minimum of delay?
8.	Training of first aid fire fighters	Are there adequate first aid fire fighters on site? Are they well trained in dealing with the type of incident that might be expected on their plant? Are they familiar with the protective devices installed? Do they have frequent refresher courses?
9.	Remote isolation valves	Is the plant well provided with remote isolation valves so that large inventories of hazardous materials can be isolated in the event of inadvertent leakage, say due to a fractured pipe?
10.	Testing of protective devices	Are the protective devices installed on the plant tested at regular intervals according to an agreed schedule?

If the % and final NMLs give different L values, an average may be taken. m. denotes million.

which is provided with fire protection. It is more difficult to determine for outdoor plant, where there are no such physical barriers. Modes of escalation which must be taken into account include, in particular, running liquid fires and vapour cloud explosions.

Improvements in vapour cloud explosion EML loss estimating techniques have been made during the 1990s, but these have not been adopted by all insurers. This has led to inconsistencies between the various insurers vapour cloud EML assessments for the same plant location. Work is ongoing to develop a consensus methodology which utilizes state of the art vapour cloud analysis techniques.

5.6.10 Risk assessment approaches

There are variations of practice in the methods used to determine the premium rating. As indicated, some insurers have developed formal quantitative methods. Others consider that such quantitative methods offer little advantage over qualitative approaches. This is the view argued by Hallam (1990).

By the 1980s the setting of insurance premiums had become much more market-driven and rating-schedule or similar analytical approaches fell by the wayside. The potential for an insurer to earn investment income on fiduciary funds became the key factor in determining the

Table 5.7 *Illustrative examples for premium rating plans for damage insurance for large capital value plants (Drewitt, 1975)*

	Example 1	*Example 2*
Total insured value	£15 m.	£30 m.
NML	20% and £3 m.	66.67% and £20 m.
L factor	1.5	4.5
C factor	7	8
Basic premium rate R	3.38‰[a]	6.21‰
HSF factor	36	27
HSF discount	18%	−9% (loading)
Discounted premium rate	2.78‰	6.77‰
Discounted annual premium	£41,700 p.a.	£203,100 p.a.

[a] ‰ = rate per £1000 insured.
m. = million.

state of the insurance market. Brokers gradually gained control over large insurance placements, parcelling out small shares of the total sum insured to individual insurers. Insurers continued to consider a prospective insured's loss record and the industry's loss record over the previous 5- or 10-year period as well as the state of the prospective insured's hazard-control efforts and results as documented in survey reports. However, supply and demand forces were paramount. By the mid-1990s no single insurer had so large a share of worldwide insurance capacity that it could enforce pricing by analytical means such as a rating schedule.

5.7 Business Interruption Insurance

The need for BI insurance did not really arise until the mid-1960s, when the first large, single-train plants began to make their appearance. At about the same time, large onshore and offshore oil and gas production fields (North Sea and Alaska North Slope) came on-stream and presented very large cash flow loss potentials for the operators. It then became apparent that consequential losses could be as costly as, or more costly than, property damage losses. The problem of BI insurance is a difficult one. The viability of such insurance depends on the charging of realistic premiums, on the evolution of effective assessment methods and on the progress made in the reduction of loss. Accounts of BI insurance are given by Neil (1971), Cloughton (1981) and di Gesso (1989).

5.7.1 Large, single-train plants

As just indicated, the advent of the large, single-train plant changed the relationship between property damage and BI insurance. The consequential losses which may occur with such plants apply not only to the plant itself, but also to the suppliers of the plant's inputs and the customers for its outputs. The nature and vulnerabilities of such plants have been discussed in Chapter 1.

5.7.2 Minor incidents

Serious BI can be caused by incidents in which the property damage is relatively minor. Typical incidents which may involve only minor damage but which can cause BI for a number of weeks include damage to control rooms, instrument cables, or individual items of equipment, especially large compressors, reactors and fractionation towers. Examples cited are a flash fire resulting from an escape of flashing hydrocarbon liquid and causing damage to instrument cables, and damage to a large gas compressor causing a large section of plant to be shut-down. In oil and gas production operations, the temporary loss of critical pipeline transportation systems, as well as support utility systems, can have significant BI consequences.

5.7.3 BI insurance

The initial approach to BI loss was to assess it as a proportion of damage loss. There is in fact only a weak connection between the two, the BI loss depending rather on the extent to which the loss interrupts a complex business chain. Moreover, the relative magnitude of the two losses has changed dramatically. Whereas BI loss was at first evaluated as a fraction of damage loss, it is now commonly estimated at several times damage loss.

Thus BI insurance merits separate treatment. Basically, the insurance provides cover for a fixed period and against an insured peril, and relates to the margin between expected sales income and variable costs on loss of sales suffered due to the interruption at the insured's plant and, if extended, interruption at suppliers' and customers' plants. It also covers increased working costs incurred in attempts to minimize loss of margin.

BI insurance is for a specified maximum indemnity period. Typical periods are 12 or 18 months. There is a tendency for insurers to require the insured to bear, as an excess, the losses sustained over some initial period such as 5, 10 or 20 days. Insurance may be extended to cover also the contingent liability for losses due to incidents at supplier and customer plants. The cover generally applies provided the losses are due to damage from a peril for which the insured's plant is covered.

5.7.4 BI survey

When BI insurance is to be underwritten, the nature and scope of the insurance survey or inspection is modified accordingly. It is normal to carry out a damage survey as a basis for damage insurance. It is appropriate to conduct an interruption survey for the purposes of BI insurance. This type of survey is, however, rather less well developed.

An interruption survey may extend the assessment of a plant to include features additional to those covered in the damage survey. The factors listed by Neil (1971) are given in Table 5.8 The main object of the interruption survey is normally the assessment of EML/PML on the BI. Survey for BI should not be a one-time exercise, but should be repeated at intervals to ensure that the information is up to date.

Further aspects of BI surveys have been described by Cloughton (1981). Essentially, the problem is that of recovery from the event causing the interruption. People are one of the most significant resources in enabling the recovery to take place. A resourceful purchasing manager is particularly important. Another vital factor is preservation of information on all aspects of the business, from design drawings to customer lists.

In assessing the vulnerability of a single-train operation, Cloughton somewhat discounts in the UK context problems of availability of services and of fuels, but emphasizes weak points in single-train operation. In particular, he highlights vulnerability to loss of particular pieces of

Table 5.8 *Some aspects of an interruption survey (after Neil, 1971) (Courtesy of the Institution of Chemical Engineers)*

1. Whether the process is single- or multi-train, batch or continuous, innovatory or proven
2. Process dependency on a major, unspared equipment item requiring a long lead time to replace
3. The protection of essential services, routing of cables, etc.
4. Dependency on a key unit and the extent to which spares or standby facilities are available, and the time-scale involved in achieving replacement or repair
5. The size of buffer stocks, over and above the minimum necessary to cover shut-down for planned maintenance, and the possibility of alternative sources of supply to keep downstream plants in operation
6. If the plant is a replacement, whether existing plants and production will remain available as insurance against teething troubles and whether there will be an excess of capacity over demand in the short and long term
7. Whether the use of a computer is to control or maximize efficiency of the plant

equipment. Here he draws a distinction between a sole supplier and a unique source. A company may choose to buy from a single supplier, but there may nevertheless be other potential suppliers in the marketplace. In some cases, however, there is a unique source which for some reason may be unable to supply promptly.

Vulnerability to interruption depends not only on features of the production process but also potential loss of stocks in the same incident. Another relevant aspect is the expected profile of the recovery over time. This may be a short total interruption followed by a gradual recovery. Or it may be a partial interruption with production and sales partially maintained but at increased cost.

Generally speaking, the existence or lack of inventory of intermediate or finished products will not significantly affect BI analysis. Inventory costs money to finance and management is not likely to maintain more inventory than that which is necessary to sustain normal operations. If a particular weakness is revealed, such as high exposure to loss of a particular piece of equipment, the solution is not necessarily more insurance. It may make more sense to remedy the exposure.

5.7.5 Estimation of EML

It will be apparent that the assessment of the EML for BI is not straightforward. It involves first determining the downtime of the plant, or sections of it, and then converting this loss of production to loss of financial contribution to fixed costs and profit. This last step may be particularly problematic. The assessment of EML for BI is discussed by di Gesso (1989), who gives an illustrative example.

5.7.6 Property damage and BI

The worldwide data from Munich Re (1991) quoted above show that over the five-year period 1985–89 for property material damage the annual average number of incidents was 144 and the average annual loss US$754 million. The corresponding figures for BI are annual number of incidents 39 and annual loss US$572 million.

At the level of the individual plant, some examples of claims for property damage and BI have been given by

Table 5.9 *Examples of claims for property damage and BI (after di Gesso, 1989)*

Case[a]	*Property damage* (US$m.)	*Downtime* (months)	*Business interruption* (US$m.)
1	–	2	22
2	4	–	32
3	9	10	200

[a] See text.

di Gesso (1989) (Table 5.9). He quotes the following three cases. Case 1, in 1981, involved a tower which failed during a hydrostatic test with water at a temperature of 10°C rather than at 20°C as recommended. In Case 2, also in 1981, a compressor trip led to a furnace tube burst and damage to a common stack. In Case 3, in 1984, a fire in a cable trench damaged a control room. The losses sustained are given in Table 5.9.

5.7.7 BI Insurance Capacity

During the 1960s, it rapidly became apparent, however, that the premiums asked for this class of business had been set at an unrealistically low level. There were some very large claims and some insurers sustained heavy losses. The nature of the problem can be seen from the fact that Neil (1971) estimated the total BI insurance premium income at £35 million. Such a sum could easily be swallowed up by one or two disasters. And in fact, as already mentioned, his estimate of the combined damage and BI insurance obtainable in practice was £10 million per loss.

As already described, since then the market has adapted and has been able, for example, to cover the large BI risks of offshore oil platforms. For Piper Alpha, one estimate of the BI loss, given above, is US$275 million.

Because of the greater uncertainty in assessing BI loss exposure as opposed to PD loss exposure, many insurers will not underwrite BI unless the insured also purchases insurance for PD. Such insurers view an insured's attempt to purchase insurance for BI along as a form of adverse selection.

5.8 Other Insurance Aspects

5.8.1 Insurance credit

The extent to which insurers should encourage and give credit for good practice in general and for loss prevention measures is a long-standing question. Insurers have always been very much involved in measures against fire. The first organized fire brigades in the United Kingdom were run by the insurance companies. In the nineteenth century, the Fire Offices Committee was formed and set standards for fire construction, alarms, sprinklers, etc., which have been widely applied. In 1946, the Joint Fire Research Organization (JFRO) was set up jointly by the Fire Offices Committee and the government and this was followed in 1947 by the formation of the FPA.

Insurers usually emphasize that they prefer to keep both risks and premiums down. Buyers of insurance are equally keen to hold premiums down and seek credit for loss prevention measures. This is well illustrated by the growth of the Factory Mutual Insurance Corporation, which is one of the largest fire insurance groups in the United States and which originated from a group of manufacturers who were dissatisfied with the credit which existing insurers were

prepared to allow for such measures and who therefore formed their own insurance co-operative. The loss prevention measures which constitute the Factory Mutual System are described in the *Handbook of Industrial Loss Prevention* (Factory Mutual Engineering Corporation (FMEC), 1967). There is one particular protective measure on which insurers have placed considerable emphasis and for which they have given generous credit in premium ratings. This is the use of sprinklers. The effectiveness of sprinklers is well proven across a wide range of fire risks, including hotels, schools, offices, factories and warehouses. The premium recognition given to this particular protective measure appears, however, somewhat exaggerated relative to other measures as far as concerns the process industries. These industries have developed a whole range of loss prevention measures and an expectation that they should receive credit for them appears reasonable.

Clearly a precondition for a system of premium rating which allows such credits is the possession by the insurer of a method of risk assessment which it is confident gives a reliable discrimination between risks. In fact, for a period in the 1970s, the trend was rather towards a reduction of differentials. The range of risks in chemical plants is wide. The insurance industry was reluctant, however, to reduce the minimum premium for low risk plants. In consequence, the chemical industry, whose loss experience up to the 1960s had been relatively good, put pressure on insurers to reduce premium rates on the more hazardous plants. The result was an excessive narrowing of the rating scale between the lowest and highest risks. The extent to which the chemical industry does now receive credit for loss prevention measures in the form of reductions in premium rating appears variable. The success of ICI in obtaining reduced insurance premiums for damage cover is illustrated in Figure 5.4 (Hawksley, 1984).

5.8.2 Insurance in design

The degree to which reduction of insurance costs is a design objective is discussed by Alexander (1990a), who suggests that it is not a major aim. The factors governing the safety and loss prevention features of the design, he argues, are, in order: (1) the attitude of the planning and licensing authorities, (2) the policy of the company, (3) the BI assessment, (4) the acceptability as an insurance risk and (5) the cost of insurance.

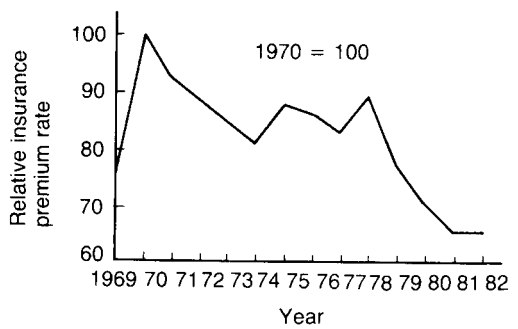

Figure 5.4 *Relative insurance premium rate (1970 = 100) for material damage cover for ICI United Kingdom (Hawksley, 1984)*

He considers the example of the layout of a large petrochemical plant. One design option might be a more generous layout. For this an increase in capital cost of 10% would be a reasonable estimate. Assuming the need for a real return of 15% on this additional capital, the annual cost would be 1.5% of the total replacement cost. Yet the premium rate for the insurance might well be no more than 0.5% of this latter cost. This example suggests that it is not economic to seek to reduce the insurance costs by additional capital expenditure.

5.8.3 Insurers' advice

The experience of the insurer is available to the operating company. There are several forms which advice from the insurer may take. Spiegelman (1987) emphasizes that the primary and only real function of the insurance surveyor is to make a report to the underwriter. Although it is often assumed that he is also there to offer a free consulting service, this is a misconception. However, as described by Redmond (1984), an insurance survey report generally contains recommendations for improvements. Hallam (1990) enumerates some of the recommendations typically made in such reports. In addition an insurer may also offer a separate consulting service. Thus, a large proportion of the major insurers offer inspections in respect of OSHA compliance.

It is constantly emphasized by insurance surveyors that the surveyor should be called in at the design stage, when modifications can be done relatively easily.

5.8.4 Loss adjusters

When an incident involving loss has occurred, it is the job of the loss adjuster to assess the financial value of that loss. The loss adjuster is usually employed by a firm specializing in this business and is independent of the insurer and insured. The report of the loss adjuster is primarily a financial rather than a technical document.

5.8.5 Loss data and analysis

The insurance industry is uniquely placed to provide information on loss and is in fact a prime source of loss data. This is illustrated by the large proportion of the loss data given in Chapter 2 which derives from insurance sources. Data sources include the annual report of bodies such as the Association of British Insurers and the Loss Prevention Council in the United Kingdom, the corresponding bodies in other countries, the periodic reports *Large Property Damage Losses in the Hydrocarbon–Chemical Industries: A Thirty Year Review* (Marsh and McClennan, 1992), earlier versions being those by Garrison (1988b) and Mahoney (1990), as well as occasional publications such as *Losses in the Oil, Petrochemical and Chemical Industries* (Munich Re, 1991). Insurers are also well placed to assess the significant sources of loss in the process industries. This has already been discussed in general terms in Chapter 2, but brief reference may be made here to the features particularly mentioned by insurers. Explosions are identified by W.H. Doyle (1969) as the main type of loss in the chemical industry. Many of his data have already been given in Chapter 2. Weldon (1971) singles out as the predominant initiating factors deviation from standard operating procedures and failure to perform proper maintenance. Almost invariably, insurers emphasize that most losses are caused by common hazards rather than by high technology.

5.9 Notation

C loss cost for a particular state of nature and level of protection (US$k/year)
d decision
D loss cost for a particular level of production for all states of nature (US$k/year)
D^* loss cost (present value) (without survey) (US$k)
E^* loss cost (with survey) (US$k)
i counter for decisions
/ outcome or indicator
j counter for of states of nature
k counter for outcomes
M^* prevention cost (US$k)
P probability
S state of nature
T^* total cost (US$k)

Subscript
min minimum

6 Management and Management Systems

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The preceding chapters have indicated the nature of and the background to the problem of safety and loss prevention (SLP). The starting point for its solution is the management and the management system.

The importance of effective management systems has been stressed in a number of reports on safety in the chemical industry, including *Safety and Management* by the Association of British Chemical Manufacturers (ABCMs) (1964/3), in *Safe and Sound and Safety Audits* by the British Chemical Industry Safety Council (BCISC) (1969/9, 1973/12). It was the main lesson drawn from the Flixborough disaster and is the principal theme of the three reports of the Advisory Committee on Major Hazards (ACMH) (Harvey, 1976, 1976b, 1984). The *Cullen Report* on the Piper Alpha disaster (Cullen, 1990) has a similar emphasis. Accounts of process safety management (PSM) include *Safety Management* (D. Petersen, 1988b) and *Techniques of Safety Management* (D. Petersen, 1989).

Management systems help ensure long-term sustainability of effective safety health and environmental performance. Competent people drive performance. And effective management systems drive sustainability. The importance of having both strong people and well-documented effective management systems cannot be overemphasized.

The importance of management has long been recognized by the Health and Safety Executive (HSE), which has produced a series of publications on safety management and on its regulation, including *Success and Failure in Accident Prevention* (HSE, 1976d), *Managing Safety* (HSE, 1981d), *Monitoring Safety* (HSE, 1985c), *Effective Policies for Health and Safety* (HSE, 1986a), *Successful Health and Safety Management* (HSE, 1991b) and *The Costs of Accidents at Work* (HSE, 1993a).

Other relevant publications include *The Management of Health and Safety* (Industrial Society, 1988), *Developing a Safety Culture* by the Confederation of British Industry (CBI, 1990), *Guidelines for Implementing Process Safety Management Systems* (Center for Chemical Process Safety (CCPS) 1994).

Management is also well represented in the publications of the CCPS, which are described in Section 6.28 of this chapter and Responsible Care Program sponsored by the American Chemistry Council.

The management system is in part specific to the particular process and should be matched to it. This is a point emphasized in the *Code of Practice for Particular Chemicals with Major Hazards: Chlorine* issued by the BCISC (1975/1).

Many treatments of safety and management touch on virtually the whole range of subjects dealt within this book. It is convenient here, however, to limit consideration of the management system to the specific management topics outlined below. The present chapter is structured in the following way. Sections 6.1–6.3 start by laying emphasis on:

(1) management attitude;
(2) management leadership;
(3) management organization.

Sections 6.4–6.11 describe elements of the management system for major hazard installations and in large part reflect the work of the ACMH. These are:

(4) competent people;
(5) systems and procedures;
(6) project safety reviews;
(7) management of change;
(8) standards and codes of practice;
(9) pressure systems;
(10) documentation;
(11) audit systems;
(12) independent checks;
(13) major hazards.

The next part of the chapter describes the management system in more detail and reflects the impact of developments in management generally on the management of SLP. It is introduced by Sections 6.14 and 6.15 on:

(14) quality management;
(15) safety management.

Sections 6.16–6.20 draw on the accounts of management systems in works on safety management such as *Safety Management* (D. Petersen, 1988b) and *Successful Health and Safety Management* (HSE, 1991b). The elements of the management system described are:

(16) policy;
(17) organization;
(18) planning;
(19) measurement;
(20) control;
(21) audit.

Sections 6.22–6.25 deal with four additional topics:

(22) process knowledge;
(23) safety strategies;
(24) human factors;
(25) contractors.

Sections 6.26–6.28 treat:

(26) safety management systems;
(27) process safety management;
(28) CCPS management guidelines.

Section 6.29 covers:

(29) regulatory control;

and Section 6.30 covers the HSE management audit system:

(30) STATAS.

Treatments of the management system typically cover a number of topics, which in this book are dealt with elsewhere. These include hazard identification and assessment (HAZ) (Chapters 8 and 9), process design (Chapter 11), human factors and training (Chapter 14) and the safety system (Chapter 28).

Selected references on management and organization of SLP are given in Table 6.1.

6.1 Management Attitude

Safety and loss prevention in an organization stand or fall by the attitude of senior management. This fact is simply

Table 6.1 *Selected references on management and organization of safety and loss prevention*

ABCM (n.d./l, 1964/3); NRC (Appendix 28 Management and Management Systems); Guelich (1956); Argyris (1957); Black (1958); Christian (1960); Simmonds and Grimaldi (1963); Tver (1964); H.H. Fawcett and Wood (1965, 1982); Pope and Cresswell (1965); BIM (1966, 1990); Herzberg (1966); Likert (1967); CBI (1968, 1974, 1990); Leeah (1968); Porter and Lawler (1968); BCISC (1969/9, 10, 1973/12, 13); Handley (1969, 1977); Gilmore (1970); N.T. Freeman and Pickbourne (1971); Hoffinan (1971); Lloyd and Roberts (1971); R.L. Miller and Howard (1971); D. Petersen (1971, 1980, 1984, 1988a,b, 1989); Sachere (1971); D. Williams (1971); D.J. Smith (1972, 1981, 1985, 1991); Gardner (1973); W.G. Johnson (1973a, 1977, 1980); Kramers and Meijnen (1974); D. Farmer (1975); Harvey (1976, 1979b, 1984); Hope (1976); Arscott and Armstrong (1977); Briscoe and Nertney (1977); Luck (1977); Hawthorne (1978); Nertney (1978); Challis (1979); Kletz (1979l, 1982d, 1984g, 1988c,e); Anon. (1980e); Findlay and Kuhlman (1980); Chissick and Derricott (1981); HSE (1981d, 1981 OP 3, 1991 HS(G) 65, 1985c, 1986a); Laporte (1982); London (1982); Ormsby (1982, 1990); BG (1984 Communication 1233, 1986 Communication 1304); Anthony (1985); Livingston-Booth *et al.* (1985); Tweeddale (1985, 1990); C. Mill (1986); Kharbanda and Stallworthy (1986b); Winkler (1986); Boyen *et al.* (1987); Kemp (1987); Sulzer-Azaroff (1987); ACGIH (1988/17, 1990/45, 47, 1992/81); Brian (1988); Coke (1988); Hawksley (1988); W.B. Howard (1988); ILO (1988, 1991); Industrial Society (1988); Knowlton (1988, 1990); Luck and Howe (1988); Rasmussen (1988); Shell Int. (1988); Tombs (1988); Watson and Oakes (1988); Weise (1988); Whalley and Lihou (1988); Bond (1989a); CONCAWE (1989 4/89); Institute of Materials (1989 PR 1001, 1992 PR 1002); Ognedal (1989); Oh and Albers (1989); K.H. Roberts (1989); K.H. Roberts and Gargano (1989); Schreiber and Sweeny (1989); Verhagen (1989); Belanger (1990); Burk and Smith (1990); P.C. Campbell (1990); Emerson (1990); Frohlich (1990); van Kernel *et al.* (1990); Krause *et al.* (1990); Lihou (1990a, 1992 LPB 103); McKee (1990); Perry (1990); Rowe (1990); Toth (1990); Turney (1990a,b); Wade (1990); Anon. (1991a); Anon. (1991 LPB 98); Hurst (1991); IAEA (1991); B.A Turner (1991); Argent *et al.* (1992); Bird (1992 LPB 103); Bleeze (1992); Burge and Scott (1992); Engineering Council (1992, 1993); HSE, APAU (1992); J. King (1992); McKeever and Lawrenson (1992); NSC (1992/11); A.J. Smith *et al.* (1992); Ball and Proctor (1993 LPB 111); Hoskins and Worm (1993); IMechE (1993/160); Nawar and Samsudin (1993); Pahlow and Dendy (1993); Ramsey *et al.* (1993); Sanders (1993b); Tosic (1993); Walker *et al.* (1993); Ward (1993); Westerberg (1993)

CCPS Guidelines
Schreiber (1991); Sweeney (1992)

IChemE Guide
Cloke (1988)

Total quality management
Ishikawa Kaoru (1976, 1985); Crosby (1979, 1984, 1986); Juran (1979); Taguchi (1979, 1981); Juran and Gryna (1980); Deming (1982, 1986); Laporte (1982); Feigenbaum (1983); F. Price (1985); DTI (1986); Singo Shigeo (1986); Shell Int. (1988); Baguley (1989, 1990); Bond (1989b, 1990a); Hodge and Whiston (1989); Oakland (1989, 1993); K.H. Roberts (1989); K.H. Roberts and Gargano (1989); Taguchi, Elsayed and Hsiang (1989); Whiston and Eddershaw (1989); Cairns and Garrett (1990); Institute of Materials (1990 PR 1004); Knox (1990); Choppin (1991, 1993); Klein (1991a,b); D.J. Smith and Edge (1991); Turney (1991); Zairi (1991); C.A. Moore (1992); Schreurs *et al.* (1992); Abbott (1993); ASME (1993/205); Woodruff (1993) BS (Appendix 27 *Quality Assurance, Total Quality Management*)

Quality assurance, ISO 9000, BS 5750
ASME (Appendix 27); ISO (Appendix 27, 1987 ISO 9000); IMechE (1982/65, 66, 1990/122); ASCE (1985/22); IChemE (1986/124, 1988/133); Allen and Nixon (1987 SRD R455); ICI (1987); Atkinson (1988a); Weismantel (1990); CIA (1991 CE6); Holmes (1991); Fouhy *et al.* (1992); Graham (1992); Hockman and Erdman (1993); P.L. Johnson (1993); Love (1993); Owen and Maidment (1993); Weightman (1993); Mancine (1994) BS (Appendix 27 *Quality Assurance*), BS Handbook 22: 1990, BS PD series

Safety management systems
Cullen (1990); Stricoff (1990); D.J. Griffiths (1993); EPSC (1994)

Process safety management
API (1990 RP 750); Early (1991); Hawks and Merian (1991); Mallett (1992); Barrish (1993); Bisio (1993); Drake and Thurston (1993); Migihon *et al.* (1993); Lohry (1994)

Management of change
Sankaran (1993); Anon. (1994 LPB 119, p. 17)

Risk management
R.N. Hugh (1976); J.Q. Wilson (1980); Wynne (1980, 1982, 1989, 1992); Rica *et al.* (1984); Wildavsky (1985); Ostrom (1986); Pitblado (1986); Caputo (1987); Grose (1987); Kleindorfer and Kunreuther (1987); Jardine Insurance Brokers (1988); Bannister (1989); Hubert and Pages (1989); Weick (1989); O'Riordan (1990); Page (1990); Rowe (1990); Roy (1990); Shortreed (1990); Turney (1990a,b); S.J. Cox and Tait (1991); Greenberg and Cramer (1991); C. Wells (1991); Bergman *et al.* (1992); Frohlich and Rosen (1992b); D.J. Parker and Handmer (1992); Clagett *et al.* (1993); P.L. Johnson (1993); Purdy and Waselewski (1994)

CCPA Code of manufacturing practice
Creedy (1990)

Contractors
Sachere (1971); Cullen (1990); Bisio (1991b); Kletz (1991m); Webb (1993); Whitaker (1993)

Research models
J. Powell and Canter (1984); Dunford (1990 LPB 93); HSE (1992 CRR 33, 34, 38); Hurst *et al.* (1992); J.C. Williams and Hurst (1992); van Steen and Koehorst (1993)

STATAS
Ratcliffe (1993, 1993 LPB 112, LPB 113, LPB 114)

stated, but it is difficult to overemphasize and it has far-reaching implications.

6.1.1 Safety culture

It is the duty of senior management to ensure that this attitude to SLP is realized throughout the company by the

creation of a safety culture in which the company's way of doing things is also the safe way of doing things. It is not easy to create a proper attitude to safety. The most effective approach appears to be to treat safety as a matter of professionalism. This fits particularly well with the development of loss prevention with its more technical and quantitative approach. The discipline required to create and maintain a safety culture brings benefits not only to safety but also to the other aspects of the operation of the company. At this point the culture becomes self-reinforcing.

6.1.2 Will to safety

There is a danger that the emphasis in loss prevention on technological aspects of hazards and their control may obscure a very simple truth that in many cases an accident occurs because the will to avoid it was lacking. This theme has been developed by W.B. Howard (1983, 1984), who has given a number of telling examples of accidents where the essential cause was a conscious decision to take a particular course of action. Among the accidents cited are instances where an operator: was put in charge of equipment for which he had no training; omitted to check trip systems thus allowing them to degrade; chose to bypass trips and alarms to obtain increased production; and failed to provide a necessary trip on a temporary filling system. He also instances the installation of the temporary bypass pipe at Flixborough. Direction of attention to the role of conscious decisions in accidents is a necessary corrective. The specific techniques associated with loss prevention are necessary, but they are not sufficiently alone. It is crucial that there also exists the will to safe design, operation and maintenance.

6.2 Management Commitment and Leadership

The creation and maintenance of a safety culture requires strong commitment and leadership by senior management. This means that the attitude of senior management must be demonstrated in practical ways so that all concerned are convinced of its commitment. Without management commitment and leadership of management, SLP programs are doomed to fail. An account of some of the ways in which management commitment and leadership is demonstrated was given by McKee (1990) of Conoco, part of Dupont, in evidence to the Piper Alpha Inquiry. They include giving safety a high profile, giving managers safety objectives, backing managers who give priority to safety in their decisions, operating an active audit system and responding to deficiencies and incidents.

Safety is given a high profile in a number of ways. This is achieved by the measures just mentioned and also by putting it as the first item on the agenda of the appropriate meetings and making sure that personnel are aware of management's actions both in initiation of, and in response to, safety matters. McKee states:

> I keep the safety priority in front of the organization on a daily basis, mainly through my close interest in safety reporting and my continuous 'drumbeat' about the safety priority.

Managers are given specific safety objectives and are assessed on their performance in achieving them. These objectives cover both personal safety and major hazards. But whereas the former may be monitored in terms of personal accident statistics, the latter are realized so rarely that event statistics are not the appropriate measure and adherence to systems and procedures is a better one. In McKee's words:[6] 'He is accountable not only for what is achieved but also for how it is attempted'.

One of the situations most revealing of senior management's real attitude to safety is its response to a manager's decision in a specific case not to act in a way which he considers unsafe even though there is an immediate financial penalty. As McKee puts it:

> I have to do my part in helping people instinctively feel comfortable about the boundaries within which they make everyday decisions. In Conoco, we all try to let safety be the number one influence on every decision or action.

With regard to audits, McKee states:

> I receive safety audit reports and react to them if required by raising the issues involved directly with the departmental director involved. I conduct my own informal audits on my frequent visits to our installations. I participate in the London safety action committee and I specifically discuss the audit system in general with managers and employees alike.

Another principle is the prompt correction of deficiencies. A deficiency should not be allowed to persist, it should be corrected. But in addition the correction should be prompt and any delay explicitly justified.

Closely related to this is the investigation of, and response to, incidents. An incident should be investigated and the lessons drawn. But, in addition, the involvement of senior management should be explicitly demonstrated. McKee states that he receives a daily report on safety from his safety manager, who is the only manager to report daily to him. If an incident occurs, the manager informs him immediately: 'He interrupts whatever I am doing to do so, and that would apply whether or not I happened to be with the Minister for Energy or the Dupont chairman at the time.' In sum, in McKee's words: The fastest way to fail in our company is to do something unsafe, illegal or environmentally unsound.

The attitude and leadership of senior management, then, are vital, but they are not in themselves sufficient. Appropriate organization, competent people and effective systems are equally necessary.

6.3 Management Organization

The discharge of senior management's duty to exercise due care for the safety of its employees, of other people on the site and of the public requires that it create a rather comprehensive and formal system and that it be active in creating, operating, maintaining, auditing and adapting the system. It is necessary to define clearly the management structure. The distinction between the line, or executive, functions and the staff, or advisory, functions is a crucial one and is a well-established aspect of good management practice, but it is particularly important in SLP. Responsibility needs to be assigned unambiguously. There should be a job description for each of the jobs shown in the management structure. Once a job is defined, it is possible to select a competent person to fill it.

These are essential steps, but they are not sufficient alone. There are other aspects to which it is necessary to pay attention if the organization is to be fully supportive of the efforts of individuals.

One important matter is arrangements to ensure that there is cover available for key jobs. The importance of this point was underlined by the Flixborough disaster. Such cover involves both short-term standby measures and long-term career planning.

A more subtle point concerns discrepancies between function and seniority. This has frequently arisen, for example, in relation to the safety officer, who in many cases has lacked the authority to carry out his functions with full effectiveness. It is necessary to consider the possibility of such problems and to take appropriate steps.

6.4 Competent People

In addition to strong management systems, the design, operation and maintenance of hazardous processes requires competent people. Here it is necessary to try to define carefully what is required. The question is particularly important in respect of the technical executive management which has prime responsibility for the process. The statement of the management structure and the job description is a necessary first step, but does not in itself take the matter very far.

It is generally common ground that academic qualifications, practical training, recent relevant experience and personal qualities are all important. The educational requirement raises questions both of level and content. As far as the former is concerned, the greatest need is for breadth of technological understanding. The person concerned should have his own area of expertise, but should also be able to appreciate what he does not know and where he needs help from others. In the United Kingdom, a first degree or equivalent in engineering or science is commonly held to be some assurance of such a broad technological education, although it may not be the only route.

With regard to the most suitable content, this may depend on the process. Much emphasis was placed following the Flixborough disaster on maintaining the integrity of the plant, which favours chemical or mechanical engineering. In some cases, on the other hand, it may be as important to maintain the integrity of the process, which points to chemistry. Each case should be treated on its merits.

As far as training and experience are concerned, distinctions may be made between design and operation and between different processes. Experience in design does not necessarily fit someone for operation nor does experience in operation of a chlorine cellroom necessarily make him suitable to operate an ethylene cracker. It is necessary that the experience be not only relevant but also recent. This is particularly important in processes with a large content of complex and rapidly changing technology. On the other hand, these requirements should not be interpreted so restrictively that career development is hindered.

Personal qualities are equally important, particularly in relation to operation of major hazard plants. Effectiveness in this job is in large part a question of such qualities as temperament. Particular emphasis is placed on the operation of plants, especially major hazard plants. Here recent relevant experience and personal qualities are particularly important.

6.5 Systems and Procedures

It is fundamental that responsibility for SLP should be shared by all concerned in the project. It cannot be delegated to a separate safety function. This does not mean, however, that reliance should be placed simply on individual competence and conscientiousness. It is essential to support the competent people with appropriate systems of work. Experience indicates that effective systems require quite a high degree of formality.

The purpose of these systems of work is to ensure a personal and collective discipline, to exploit the experience gained by the organization, and to provide checks to minimize problems and errors. The framework of such systems is typically a set of standing orders or instructions which lay down requirements for the conduct of particular activities at the different stages of the project from research and development through to operation.

Some key systems are those which are concerned with (1) Management leadership, commitment and accountability, (2) Risk analysis, assessment and management, (3) Facilities design and construction, (4) Process and facilities information and documentation, (5) Operation of plant (normal, emergency), (6) Control of access to plant, (7) Control of plant maintenance (permits-to-work), (8) Management of change, (9) Inspection and maintenance of plant equipment, (10) Emergency preparedness (9) Third party services and (11) Incident reporting. All these systems are considered in detail in other chapters.

It is important that the various activities be properly phased and matched to the project stages. Thus, for example, hazard identification should be undertaken at a stage early enough to identify any serious hazards which might threaten the viability of the whole project, but such an investigation can be on a relatively coarse scale. As design progresses, other more detailed hazard identification procedures are required.

There is, in principle, no limit to the number of systems which may be devised, but the aim is to have the optimum number which leaves no serious gaps and yet avoids confusion due to overlapping. Inevitably, formal systems sometimes appear tedious or unnecessary. They need to be well thought out so as to minimize this reaction. But experience shows that large proportions of incidents occur due to lack of proper procedures or to non-observance of them.

6.6 Project Safety Reviews

The management system should include a formal system of project safety reviews for the identification of hazards, evaluation of risk and an assessment of the adequacy of controls. The system of reviews should be comprehensive in that it covers all aspects of the project and does so over the whole life cycle.

A typical set of project safety reviews is (1) Inherent safety/health/environment review (2) HAZard and OPerability (HAZOP) Review, (3) Detailed design review, (4) Construction review, (5) Pre-commissioning review and (6) Post-commissioning review. Project safety reviews are considered in Chapter 8.

6.7 Management of Change

A large project is subject throughout its life cycle to numerous changes, or modifications. It is necessary to have systems which will manage these changes satisfactorily. In particular, it is necessary to keep control of modifications, which may occur in design or operation.

These modifications may be to the process or the plant. Either way, modification control systems are required to detect intent to modify, to refer the modification to the appropriate function for checking, to record a modification authorized, to inform others of the modification and to follow up any implications such as a need for training. Modifications may be proposed during the design of a new plant or for existing plant. The latter also embraces major plant extensions. Different modification control systems are required for the design and operation stages. Management of change and control of modifications is discussed in Chapters 11 and 21.

6.8 Standards and Codes of Practice

An important aspect of the procedures is the use of standards and codes of practice, both external and internal. These are referred to extensively throughout this book and it is difficult to overemphasize their importance. They represent a distillation of industry's experience and are not to be disregarded lightly.

Although the majority of standards and codes relate to design, there are also many which are concerned with operation.

6.9 Pressure Systems

Central to SLP is the problem of loss of containment. The management system for the design and operation of pressure systems is therefore of crucial importance. Major failure of a properly designed, fabricated, constructed, tested, inspected and operated pressure vessel is very rare. But failures do occur in pressure systems. They tend to be failures of other pressure system components such as pipework and fittings, pumps and heat exchangers or failures due to maloperation of the system. The management systems for the control and monitoring of a pressure system should be in two parts, covering the two broad areas of design and operation and administered by two separate authorities.

The design authority should be responsible for systems for control of design, fabrication, testing and inspection, and the operating authority for those for control of commissioning, operation, maintenance and modification. The design authority should define the parameters within which the system is to operate, should specify the design codes, should execute the actual design, should identify and assess hazards, should specify standards for fabrication, construction and testing of the systems and should prescribe the documentation required on all these aspects. It should also ensure the inspection of the plant during fabrication and construction. This inspection may be done by the design authority itself or by an external body such as an insurance company or an engineering inspection agency. The inspection should be done to the specified standards and should be recorded in the prescribed way.

The operating authority should prepare written operating instructions based on the method of operation envisaged in the design, the design parameters and the hazard studies, and covering both normal and abnormal conditions. It should also create a system for the control of modifications in order to ensure the integrity both of the plant and of the process. The system should distinguish between proposed modifications that might affect the integrity of the plant and routine maintenance, and should require that the former be referred back to the design authority for checking. Similarly, the system should identify proposed modifications of operating procedures that go beyond established practice and might affect the integrity of the process, and should require that these also be referred back for checking by the design authority.

The operating authority should also provide a code for the regular inspection of the pressure system. There should be documentation on each component giving its unique identification, location, engineering description, operating conditions, inspection interval and maintenance record. Inspection intervals for each class of equipment should be specified and rules stated for the alteration of inspection intervals. The code should ensure that the inspection authority is independent of the operating authority.

6.10 Documentation

A project in the chemical industry involves a large amount of documentation. A list of some principal items is given in Table 6.2.

Some of the material is general documentation on company systems and on standards and codes, but most is specific to the particular process and plant. As the list given indicates, a large project requires a considerable amount of documentation. The table shows essentially the basic elements of the documentation. Selected items may be put together to form manuals for various purposes. Typical manuals are the Design Manual, the Plant Manual and the Operating Manual.

6.11 Audit System

It is essential that there is a mechanism to monitor the system as a whole and to make sure that it is working correctly and is not falling into decay; in other words, an audit system. Audit differs from control. In control, the outputs of a system are measured and corrections made as necessary. Audit examines the control system itself to check that it is still fit for purpose. It takes place over a much longer timescale.

The need for audit may vary. It may be fairly clear without the need for an audit whether certain systems or procedures are working properly. But for others audit is required. Thus, for example, an audit of a permit-to-work system is generally necessary to prevent it from degenerating. The audit system may include a specific instruction that the plant manager should each week examine a sample of the permits issued. The essential point is that the approach adopted is not simply to exhort the plant manager to monitor the permit system but to build the instructions to do an audit into the system.

The audit function is considered further in Section 6.21. The essential point to make at this stage is the need for an audit system.

6.12 Independent Checks

The principle of independent checks is extremely important in ensuring reliability. It is already widely practiced in relation to pressure vessel inspection. Other areas where use is already made of independent checks are audits of management systems, hazard assessment of the plant as a whole and reliability assessment of protective instrumentation.

It is not essential, in order to ensure independence, to go to an outside organization. An independent function can

Table 6.2 *Some principal items of documentation in a large chemical plant project*

Subject area	*Documentation*
Systems	Documents on company systems (e.g., see Section 6.5)
Standards and codes, legal requirements	National standards and codes applicable to the design. In-house standards and codes applicable to the design, including guidance on situations where national standards and codes do not apply Legal requirements, statutory approvals
Organization	Organization chart of personnel Job descriptions and duties of personnel, including: (a) Process operators (b) Maintenance personnel (c) Supervisory staff
Process design	Description and history of process Design basis for plant including economics, output, yield, availability, storage, siting, pollution, loss prevention aspects Design data for process, including: (a) Process reactions and reaction kinetics, including possible reactions under abnormal conditions (b) Physical and chemical properties of materials including flammable, explosive and toxic features (c) Specifications for raw materials, products, by-products and effluents (d) Data relevant to selection of materials of construction (e) Data from pilot plant Process flowsheet giving main items of equipment, quantities of materials and services, inventories and operating conditions Process flow diagram giving all items of equipment, flow rates and other operating conditions Process design data sheets for items of equipment giving design basis, operating conditions, characterizing parameters, safety factors, equipment dimensions Inventories of hazardous materials in process and in storage Safety relief device contingency basis Sources of information (people, literature) Some of this documentation is usually collected together in a Design Manual
Plant layout	Site and plant layout diagrams Site and plant pipework drawings Equipment and pipework identification schemes Documents on hazardous area classification, means of escape, site vehicle routing
Mechanical design	Mechanical job specifications, design data sheets and general arrangement, detail and layout drawings, parts lists for items of equipment Piping job specifications, piping and instrument diagrams, piping plan, elevation and isometric drawings, piping stress and piping support documents, piping parts lists Documentation on pressure relief, blowdown and flare systems
Services design	Job specifications, including arrangements for loss of services covering electricity, steam, cooling water, process water, instrument air, process air, nitrogen and any other service required
Electrical, civil, structural design	Job specifications, general arrangement, detail and layout drawings, and materials or parts lists as appropriate
Plant buildings	Design basis for control room and other buildings Documents on siting, layout, construction and explosion resistance, ventilation, fire limitation, explosion relief as appropriate
Control and instrumentation	Design basis for process control Cause and effect diagrams for all protective systems Instrument job specifications, piping and instrument diagrams, instrument design data sheets Documents on alarm, trip and interlock systems

Table 6.2 *(continued)*

Effluents, waste disposal, noise	Environmental Permits including their basis Effluent, waste disposal and noise specifications and requirements of regulatory agencies Pollution, waste disposal and noise surveys of plant
Fire protection	Design basis for fire protection system Documents on fire protection system, including fire water supply
Plant operation	Works and plant safety rules Chemical data sheets Operating instructions, including instructions on: (a) Normal operation, including all sequential operations (b) Normal start-up and shut-down, including variations dependent on length of shut-down (c) Start-up on new plant (d) Shut-down under abnormal or emergency conditions (e) Trip systems Sampling instructions, including location and identification of sample points, sampling frequency, sampling method, safety precautions Instructions on dealing with leaks and spillages Instructions for reporting incidents Operating documents, including process operator's log, plant manager's log, storage logs, standard calculations of efficiency, costs, etc. Some of this documentation and some documentation from other sections, for example, process design, are usually collected together in a Plant Manual and/or Operating Manual
Training	Documents for process operator training (e.g., see Table 14.10) Documents for safety training (e.g., see Table 28.5)
Safety equipment	Documents on safety equipment covering for installed equipment: (a) Equipment location guide (b) Equipment inspection schedules (c) Equipment use manual (d) Equipment maintenance manual and for equipment in stock (e) Equipment stock control (f) Instructions on equipment issue
Hazard identification and assessment	Records from pilot operation, of work on screening of chemicals or reactions, of hazard and operability studies, of hazard assessments, of safety audits Checklists of all kinds (e.g., see Table 8.4)
Security	Lists of permanent personnel and of temporary personnel, e.g., construction personnel Security passes
Plant maintenance	Documents on plant maintenance, including: (a) Code for maintenance and modifications with supporting documents (permits to work, clearance certificates, modifications forms, etc.) (b) Equipment identification and location guide (c) Equipment inspection and lubrication schedules (d) Equipment maintenance manuals and instructions (e) Instructions on lubricants, gaskets, valve packings, pump seals (f) Maintenance stock requirements (g) Maintenance stock control (h) Standard repair times (i) Equipment turnaround schedules
Plant inspection	Code for inspection of pressure systems Records of equipment, including identification, location, engineering description, operating conditions, inspection intervals and maintenance history Records of non-destructive or condition monitoring tests
Emergency planning	Documents on emergency planning (e.g., see Chapter 24)
Environmental control	Environmental standards (e.g., OESs) Sampling schedules

exist within the organization – but it must be genuinely independent. In fact, many organizations do rely on outside bodies, such as insurers for the inspection of pressure vessels or consultants for hazard assessments of plants.

Another independent check is furnished by the Factory Inspectorate. The most important function which the Inspectorate performs is to provide a further independent audit of the management and management system. It is emphasized, however, in accordance with the principle of self-regulation, that it is the responsibility of management to audit itself and that it should not rely on the Inspectorate to do this.

6.13 Major Hazards

The principles just outlined apply with special force to the management of major hazard installations. But there are also some particular considerations which need to be borne in mind in dealing with major hazards. These have been discussed by Challis (1979). What Challis particularly emphasizes is the combination on major hazard plants of high technology and people. If such plant is to be operated safely, it is necessary that there be strong leadership by management. The level of management which is particularly crucial is the first level of executive technical management.

The people who operate and maintain the plant cannot always be expected to have a full appreciation of all aspects of the complex technology involved. It is the responsibility of the manager on such a plant to address this problem. The workforce needs to have an understanding of the process and the plant, of the hazards involved and of the actions required. It should be well trained. It should be provided with clear instructions, both for normal operation and for emergencies. The manager on such an installation needs to be 'out and about' rather than in the office. There should be a strong executive atmosphere and discipline on the plant.

6.14 Quality Management

Increasingly, SLP is subject to the influence of quality assurance (QA) and total quality management (TQM). An account of these was given in Chapter 1.

6.14.1 Quality assurance

As described in Chapter 1, there is a strong trend for companies to adopt QA throughout their operations and to seek accreditation. In the United Kingdom, this means accreditation to BS 5750: 1987. Since QA covers inputs to the company's activities, this requires that subcontractors and suppliers also address QA.

QA affects all aspects of a company's activities and it will not generally be introduced solely as a means of improving SLP. But given that it is introduced, it will have an impact on the latter. Some SLP activities to which QA has been applied include, in particular, HAZOP (hazard and operability) studies and quantitative risk assessment and the work of consultants.

6.14.2 Total quality management

Essentially similar considerations apply to TQM. This also is unlikely to be introduced for the sole purpose of SLP, but if adopted it will have an impact. It is of interest that the Piper Alpha Inquiry was invited to recommend that TQM be adopted by offshore operators as a means of improving safety, but that the *Cullen Report* (Cullen, 1990) did not do so, considering that although this might be so, the implications of a requirement for TQM went far beyond safety.

The concept underlying loss prevention is that the problem of failures and their effects has an influence on company performance which goes far beyond safety of personnel. Essentially the same concept underlies the TQM approach. Thus TQM and SLP have much in common.

There is some tendency for those involved with TQM to treat SLP as a subset of TQM. Insofar as TQM covers the whole range of a company's activities whereas SLP deals with one aspect, this view might be held to have some force. Against this, SLP has developed within its own field the basic principle of TQM and has evolved a highly successful approach of some depth and sophistication. This evolution may be expected to continue within the context of TQM.

The degree of sophistication of SLP in the process industries is well illustrated by developments in the nuclear power industry. A glance through the publications of the Nuclear Regulatory Commission (NRC) given in Appendix 28 shows clearly the efforts made to foresee and forestall failures. Accounts of the application of TQM in the chemical industry have been given Whiston and Eddershaw (1989) and by Whiston (1991). A description of the application of TQM to HAZOP studies has been given by Turney (1991).

6.15 Safety Management

An account is now given of some principles of a PSM system. Figure 6.1 illustrates the key elements and structure of a safety management system (SMS) as given in *Successful Health and Safety Management* (HSE, 1991b).

The elements described here are similar, except that measurement and control are considered as separate elements, whilst review is treated as an aspect of control. The structure considered here is therefore:

(1) policy;
(2) organization;
(3) planning;
(4) measurement;
(5) control;
(6) audit.

Some of the insets and appendices given in the HSE publication in support of the above topics are listed in Table 6.3.

6.16 Policy

Policy on safety should aim to set appropriate goals and objectives, to organize and plan to achieve these objectives in a cost-effective way, and to ensure by systems of measurement and control and of audit that the plan is implemented. The safety policy should be integrated with the other policies of the business, with the aim of achieving high standards of performance across the whole range of the activities undertaken. It should be the goal of safety policy to ensure that activities take place in a controlled manner and to eliminate deficiencies and failures which result in undesired events, some of which escalate to cause damage and/or injury. Safety policy should take full recognition of the importance of human resources and human factors, in other words of the people, the job they do and the organization within which they work, as shown in Figure 6.2.

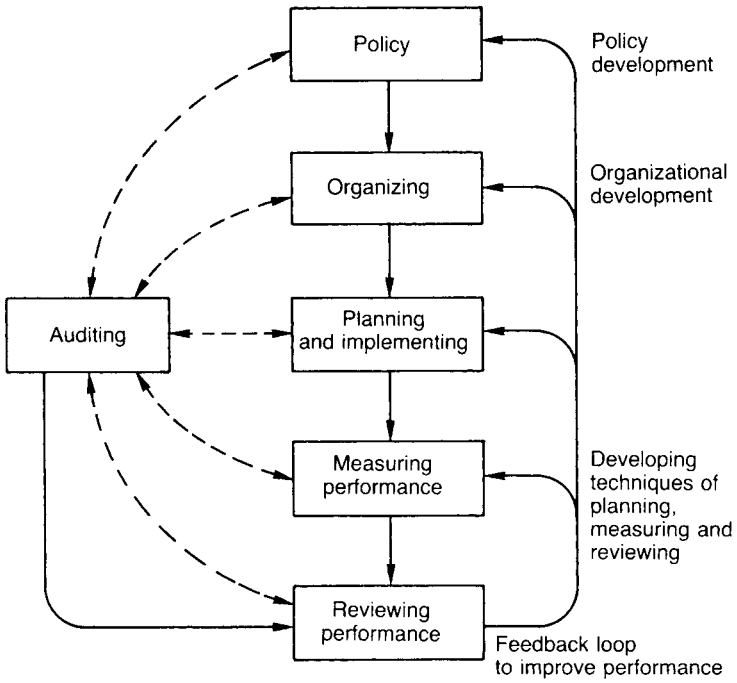

Figure 6.1 *Key elements of health and safety management (HSE, 1991b) (Courtesy of HM Stationery Office)*

Table 6.3 *Insets and appendices given in Successful Health and Safety Management (HSE, 1991b)*

Inset

1. Accident ratio studies
2. Human factors in industrial safety
3. The impact of effective health and safety policies on business thinking
4. Performance standards
5. Supervision
6. Examples of statements of health and safety philosophy
7. An outline for statements of health and safety policy
8. Training for health and safety
9. Role and functions of health and safety advisers
10. A framework for setting performance standards
11. Controlling health risks
12. Assessing the relative importance of health and safety risks
13. 'So far as is reasonably practicable','So far as is practicable' and 'Best practicable means'
14. Inspection
15. Key data to be covered in accident, ill health and incident reports
16. Effective health and safety audits

Appendix

1. Terminology
2. Organizing for health and safety
3. Minimum objectives for performance standards
4. Accident incidence and frequency rates

6.17 Organization

Organization for safety is considered by the HSE under the following headings:

(1) control;
(2) cooperation;
(3) communication;
(4) competence.

6.17.1 Control

The safety goal is to ensure that activities take place in a controlled, and therefore safe, manner. This means putting in place systems of control. Such a control system is analogous to the typical feedback control system used in process control. The variable to be controlled is identified, the variable is measured, the measured value is compared with a desired value, and if necessary control action is taken to effect correction. Furthermore, there may be a system of nested control loops, with the higher loops controlling higher level functions and operating on longer timescales.

Measurement is an essential function in any control system. It is necessary to decide first what specific variables need to be regulated in order to bring the system as a whole under a satisfactory degree of control and then to decide whether for a given variable it is practical to measure it directly or whether it is necessary to infer it from some other measurement. Given that the variable can be measured, it is

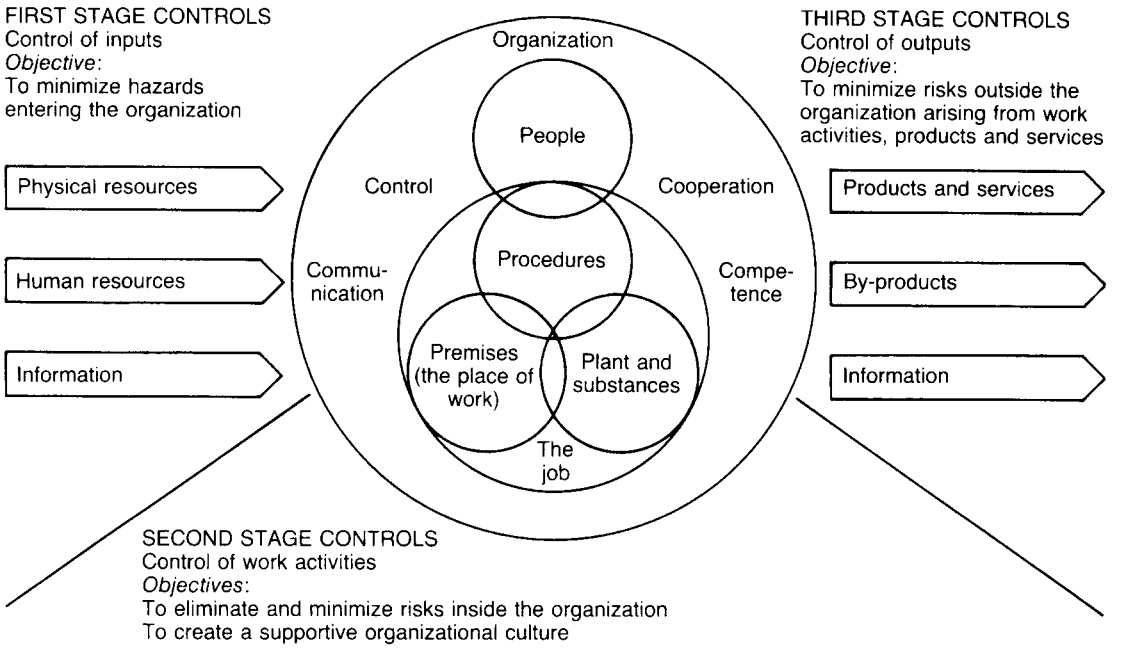

Figure 6.2 *Human factors in industrial safety (HSE, 1991b) (Courtesy of HM Stationery Office)*

necessary to decide what value is acceptable, by establishing a desired value or performance standard.

In the control systems considered here, the control function is exercised by people. It is therefore essential to define responsibilities. There is normally a hierarchy of responsibilities down through the successive levels of line management. It is then necessary to establish accountability for the discharge of responsibility at each level. Accountability may be reinforced by making it part of the job description, using it as an indicator of individual performance, and identifying lapses.

Motivation is crucial to good performance. The most effective motivation is the existence of a safety culture that provides strong reinforcement. Training which enhances understanding and motivation also has an important contribution.

Supervision provides guidance, example and discipline, and furnishes the external element that complements the internal motivation.

6.17.2 Cooperation

A safety culture necessarily involves the cooperation of the whole workforce. Specific measures have to be taken to obtain this. A system of safety committees and safety representatives, such as is required by UK legislation, is one means whereby such involvement can take place. This system alone, however, does not generally yield the degree of cooperation obtained by a TQM culture in which the people at all levels are encouraged to identify and correct deficiencies and failures, by participation in safety circles (analogous to quality circles) and like methods.

6.17.3 Communication

Effective operation of the control systems described involves large flows of information. The forms of communication distinguished by the HSE are: (1) information inputs, (2) internal information flows, (3) visible behaviour, (4) written communications, (5) face-to-face discussion and (6) information outputs. The operation of a SMS actually requires a considerable input of information into the organization.

Good communication within the organization is critical. Effective communication uses three complementary modes: visible behaviour, written communications and face-to-face discussion. Management needs to demonstrate leadership that is visible to all. Written communications are the principal means of transmitting information. The information needs of the recipients differ, however, and such communication is most effective if tailored to those needs. Face-to-face contact provides feedback and allows personal contribution.

6.17.4 Competence

The competence of personnel, particularly those in key positions, is crucial. Some of the relevant factors were discussed in Section 6.4. It is necessary, therefore, to identify those jobs where competence is particularly important and to define what is required for each job. In some cases, the competence needed is a broad managerial one; in others it is a specialism. Competence depends partly on education and training, and partly on experience. Once the competence required is defined, it is possible to try to match the person to the job.

In some cases, the appointment of a 'competent person' is a legislative requirement. A supply of competent people is generally assured by a combination of career progression within the company and external recruitment. For both sources, definition of the relevant competence is required.

Individual competence is not the sole issue, however; there is also an organizational aspect. It is necessary to ensure that for any critical post there is cover if the individual currently filling it is out of action.

6.18 Planning

Planning of the SMS involves:

(1) setting goals and objectives;
(2) defining control systems;
(3) setting performance standards.

6.18.1 Goals and objectives

Broad safety goals need to be translated into specific objectives. The objectives which it is practical to set are essentially determined by the variables which can be measured.

6.18.2 Control systems

In management theory, a distinction is commonly made between the following three stages of an activity to which controls may be applied: (1) input, (2) process and (3) output. Again, on the analogy of process control, the first two may be likened to open loop control in that the required output is obtained if the process gain remains constant and the input is maintained at an appropriate value. Alternatively, the output can be measured, and closed loop (or feedback) control applied. The application of controls to all three stages therefore involves a degree of redundancy. As redundancy enhances reliability, this is a desirable feature.

The systems required for hazards include systems for (1) hazard identification, (2) evaluation of risk and (3) an assessment of the adequacy of hazard controls.

6.18.3 Performance standards

Once objectives have been defined, suitable measurements, or metrics, have been selected and control systems based on those devised, the performance standards which these control systems should meet can be set. The performance standards should cover inputs, process and outputs. Some of the performance standards required are identified by the HSE as follows: (1) For inputs: (a) physical resources, (b) human resources and (c) information. (2) For process, or work activities: (a) control, cooperation, communication and competence; (b) premises, (c) plant and substances, (d) procedures and (e) people. (3) For outputs: (a) products and services, (b) by-products and (c) information.

Performance standards should be set for the systems for hazard identification, hazard assessment and hazard control just mentioned.

6.19 Measurement

The account just given brings out the crucial role played by measurement. Effective systems of control can be devised only if suitable measures, or metrics, can be found. The problem is addressed in the HSE publications mentioned at the start of this chapter.

6.19.1 Accident pyramid

It is helpful to begin by revisiting the accident pyramid described in Chapter 1. What this shows is that for every serious or disabling injury incident there are a number of minor injury incidents; that for every minor injury incident there are a number of damage only incidents; and that for every damage only incident there are a number of incidents with no visible injury or damage. It follows that if incidents at this latter, and lowest, level can be kept under control, the incidence of the former will be much reduced. This is true, although there can be some practical problems. Since such incidents have no visible effect, it is not easy either to define them or to persuade people that they should be reported. The accident pyramid is the centrepiece of the study in *The Costs of Accidents at Work* (HSE, 1993a), which gives five case studies, including one of an offshore oil platform.

6.19.2 Frequent and rare events

There are various definitions of accidents. One of the best known is the lost time accident (LTA). Statistics of such accidents can be compiled and monitored. If the accidents are occurring with a sufficiently high frequency, the accident statistics provide a suitable measure of performance. Some definitions of accidents and the monitoring of accident statistics are discussed in Chapters 26 and 27.

The goal of the SMS, however, is to eliminate accidents. The greater the success achieved, the less useful become the statistics of the more serious types of accident. This is seen most clearly in respect of major hazards, since the realization of a major hazard is a rare event in any company. The fact that there has been no such accident is a poor indicator of the company's performance in the control of major hazards. In dealing with major hazards, the aim is to reduce the already low probability of a realization. Thus, the performance of the system in this regard has to be judged rather in terms of its effectiveness in operating and maintaining safety systems. This points to the need to measure inputs.

It is pertinent to ask, however, whether performance in respect of accidents for which meaningful statistics are available correlates with performance in respect of major hazards. The answer appears to be that it does. Although realizations of major hazards occur too infrequently for their statistics to be a practical measure of the performance of an individual manager, except perhaps at the highest level, over a period statistics of major accidents and near-misses may be compiled for a company and are then a measure of its performance. This point has been discussed by Brian (1988). A correlation does exist between the level of minor accidents and that of major accidents. The common factor is people, their attitude and discipline.

The upshot of this is that for control systems for frequent events there is a need to measure both inputs and outputs, whereas for rare events the only option is to measure inputs.

6.19.3 Proactive monitoring

Turning then to specific measures, some items which may be made the subject of proactive monitoring include (1) achievement of objectives, (2) adherence to systems and procedures, (3) conduct of auditing, (4) state of plant and equipment and (5) state of documentation.

A manager, for example, will be concerned with personal safety and may have responsibility for one or more major hazards. He will have objectives which have been set. There will be various systems and procedures to which he is

required to adhere. He needs to audit the performance of his subordinates in achieving their objectives and adhering to systems and procedures.

The state of plant and equipment is monitored by inspection. This is a feature on which monitoring has traditionally concentrated. The state of the associated documentation can also be very revealing.

If there are noxious substances in the plant environment, reduction of the levels of these should be an objective. In this case, there is something physical to measure and monitor.

6.19.4 Reactive measures

Some items which may be made the subject of reactive monitoring include (1) injuries, (2) damage, (3) other losses, (4) incidents and (5) workplace deteriorations.

6.20 Control

The purpose of the measurement activities just described is to provide the basis for control actions to correct deviations and for review of the performance of the system.

6.20.1 Control and action

If a deviation is detected, control action is required to correct it. In some cases, the corrective action needed is obvious and it can then be taken. In other cases, it is necessary to carry out an investigation. The purpose of the investigation is to discover not a single 'cause' but the total situation which has given rise to the deviation and the corrective action, or actions, required to prevent it.

6.20.2 Review

The other aspect of the control system is the review of performance to ensure that the performance standards are being met. Review is continuous and is performed by line management. These features make it a control rather than an auditing activity.

6.21 Audit

The whole management system just described needs to be examined periodically to ensure that its goals and objectives remain appropriate and that the control systems to achieve these objectives are working. This is the function of the audit system. Continuing the analogy of process control, the audit system constitutes a set of outer, higher level loops around the control systems.

The purpose of an audit is to detect degradations and defects in a management system. This may be the management system of the company as a whole, a subsidiary company, a works or a plant. An audit is performed by competent people who are independent of the organization being audited. It may be carried out by an individual or a team. It is a task requiring its own particular skills.

A full audit of the management system will address the complete set of activities just described: policy, organization, planning, measurement and control. It is more usual to conduct audits with a more limited scope. Two approaches may be taken. One is to examine a specific function such as maintenance or fire protection; this is sometimes termed the vertical approach. The other is to examine a specific level of activity such as planning; this is the horizontal approach.

At plant level, there will typically be a post-commissioning audit followed by audits at a fixed interval. Where the installation is owned by a partnership but operated by a single company, as is typical of many offshore oil platforms, the other partners will usually require audits.

It is not easy to perform an effective audit. That this is so was brought out at the Piper Alpha Inquiry. One of the crucial systems of work on the platform was the permit-to-work system. The installation had been subject to a number of audits, but critical defects in the permit system had not been picked up. Yet, in less than 2 h of evidence from the witness who was describing the system, these defects were laid bare.

Audits are discussed further in Chapters 8 and 28.

6.21.1 Proprietary systems

There exist proprietary audit systems which may be used within a company to promote SLP. One of the best known is the International Safety Rating System (ISRS) (Bird and Germain, 1985). This system is described in Chapter 28.

A critique of packaged audit systems is given by D. Petersen (1989). Essentially the criticism is that in such systems the items on which the rating is based tend to be arbitrary and do not accord well with items identified in other studies as being crucial to safety performance.

6.22 Process Knowledge

Knowledge of its processes and plants is one of the prime assets of a company, but the management of this asset often appears to be relatively neglected.

6.22.1 Organizational memory

In safety, the problem of knowledge management manifests itself most obviously in the repetition of similar incidents, which suggests defects in the collective memory. It is a matter of experience that incidents continue to occur despite the fact that similar, even virtually identical, incidents have occurred before, were fully investigated and reported, and should in principle be known to the profession. The collective memory of the profession is deficient. Likewise, at company level, incidents are repeated even though in the past there has been full knowledge of the problem in the company.

This phenomenon has been discussed and illustrated by Kletz (1980g). One particularly telling case which he quotes is where two similar accidents occurred within a couple of hundred metres, one in 1948 and one in 1968, though in this case in areas which were under separate management.

6.22.2 Awareness

The first requirement in process safety knowledge is simply awareness of hazards. Familiarity with a large number of case histories is one of the most effective ways of acquiring this awareness. Consideration should be given to any additional measures required to promote awareness in personnel entering into new responsibilities or undertaking new tasks.

6.22.3 Understanding

Knowledge is held within the organization in a variety of forms, including systems and procedures, in-house standards and codes, design manuals and other forms of codifications of practice. In sum, these generally represent an enormous store of knowledge. Such traditional forms are now supplemented by computer programs and databases, and in some cases by expert systems.

In almost all cases, these forms constitute abstractions from the original raw data. As necessarily happens when this is performed, some important features of these data disappear. The immediacy of the individual accident case history is lost. The reason why a code contains a particular recommendation is no longer clear. Information is lost in the process of abstraction. The promotion of understanding of the reasons for particular features in codes enhances their effectiveness.

6.22.4 Issues

In the course of a design, there arise a large number of issues, some of which are of considerable importance. Issues may also arise at other stages of the life cycle of the plant. These issues need to be managed. There are two problems. One is to ensure that when the issue first arises it is satisfactorily handled. An important aspect of this is ensuring that the right people participate in its resolution. The other problem is to be able to retrieve information about the issue at a later date, so that the reasons underlying the decisions taken can be understood. It is not uncommon for a plant to have design features, the purposes or limitations of which are not fully understood.

6.22.5 Operating procedures

Design of a plant proceeds on assumptions about the way in which it is to be operated, which may or may not be made fully explicit. Most incidents that occur are related in some way to plant operation or maintenance. Any mismatch between the design and operation of the plant is to be avoided.

6.22.6 Knowledge base

The safe design and operation of process plants requires an effective knowledge base within the company. This knowledge base has some similarities to a living organism. Much attention is devoted to databases. The knowledge base is at least as important. Among other things, it determines the effectiveness of the utilization of the databases.

The knowledge base takes various forms. These include in-house standards, codes and manuals, as already described. But above all it consists of the expertise of individuals.

The maintenance of the knowledge base depends on a certain critical level of activity within the company, and within its individual functions. If this is not sustained, the knowledge base can decay quite rapidly. This is a particular danger if the company goes through a bad patch.

Certain forms of knowledge can be documented, as described. Expertise derived from experience is more difficult to capture, although there is increasing interest in methods of doing so.

6.22.7 Knowledge utilization

There are factors which favour the maintenance, and enhancement, of the knowledge base. The most effective way to maintain it is to utilize it. In effect, it is a case of 'use it or lose it'.

A crucial factor, therefore, is a safety culture in which people are motivated and have occasion to draw on the knowledge base.

A safety culture as such is not enough, however. Specific steps need to be taken to make the necessary knowledge available by an inflow of information into the organization from publications and personal interchange, by converting information to transparent and utilizable forms, by facilitating access and by dissemination. Such arrangements will permit a company of moderate size to maintain a knowledge base which would otherwise be available only to a much larger organization.

6.22.8 Incident investigation

An important aspect of this activity is learning. It is usual in accounts of safety management to assign a prominent place to incident investigation. The point has already been made that incidents tend to repeat themselves. In many cases, investigation of the incident reveals little that is genuinely new. Nevertheless, the emphasis on incident investigation is not misplaced. It has a significant role in educating and motivating people and in keeping alive the knowledge base.

6.23 Safety Strategies

For a given hazard, it is necessary to devise a suitable safety strategy. The strategy should fit the particular hazard, but there are certain principles which can be stated. At the most general level, the basic elements of a hazard control strategy are:

(1) elimination;
(2) control
    (a) reduction of frequency,
    (b) reduction of consequence;
(3) mitigation.

If practical, the hazard should be completely eliminated. Otherwise, it should be controlled by reducing both the frequency and consequence of realization of the immediate event. Other measures to mitigate the effect of this event should be taken as practical. In process plants, the event of particular concern tends to be loss of containment. The strategy will then be built in large part around measures to reduce the frequency of such emission and to reduce the quantity released.

There is frequently a choice of measures which may be taken to ensure safe operation. It is good practice, therefore, to define a 'basis of safety' and then to ensure that the necessary measures are taken. The basis of safety approach has found particular application in relation to the safety of chemical reactors. Another concept is that of the 'design basis accident'. In some cases, it is not practical to have a design which will withstand all eventualities. Instead, a level of accident is defined which the plant is designed to withstand. The safety strategy is particularly important for major hazards.

6.24 Human Factors

The increasing emphasis on management is accompanied by a growing recognition of the importance of human factors. The human element in incidents is illustrated in the numerous case histories described by Kletz in *Learning from Accidents in Industry* (Kletz, 1988h), *What Went Wrong?* (Kletz, 1988n), *Improving Chemical Engineering Practices* (Kletz, 1990d), *An Engineer's View of Human Error* (Kletz, 1991e), and numerous other publications. The essential message is that attribution of such incidents to human error is not an appropriate response and that it is more constructive to treat them as arising from the work situation,

which is the responsibility of management. Human factors is the subject of a number of HSE publications, including *Deadly Maintenance* (HSE, 1985b), *Dangerous Maintenance* (HSE, 1987a) and *Human Factors in Industrial Safety* (HSE, 1989b). Human factors are treated in Chapter 14.

6.25 Contractors

A particular problem is posed by contractors. In some sections of the process industries, contractors constitute a large proportion of the workforce. They carry out not only construction work, but also specialist engineering and, in some cases, serve as process operators or maintenance personnel. These contractors have to conform to the systems and procedures of the company. They must therefore be trained in these and then subject to a discipline that ensures that they comply with them.

Contractors constitute a high proportion, typically some 70%, of the workforce in the UK sector of the North Sea. The problems associated with this surfaced at the inquiry into the Piper Alpha disaster, where the gas release which led to the explosion occurred from the site of a pressure safety valve. The valve had been removed and it was held that the flange assembly had not been made leak-tight. The man leading the two-man specialist team overhauling the valve was on his first tour as a supervisor and was not fully familiar with the permit-to-work system operated on that particular platform.

Good practice requires that a company apply to contractors the same philosophy as it applies to its own personnel. This should cover all aspects, including safety culture, training, discipline and audits. There are certain steps which a company can take to ensure that the work of contractors is satisfactory. One is to specify the standards to be met and to enforce adherence to them as part of a QA system. Another is to be prepared to pay a price which is realistic and not to drive it down below the point at which the contractor is able to deliver the quality required; in some cases this means not accepting the lowest bid.

6.26 Safety Management Systems

The system that delivers the approach to process SLP described above is in effect an SMS. A requirement for a formal SMS has been introduced in UK legislation following the Piper Alpha disaster. The inquiry into the disaster was urged to strengthen the management of safety by requiring offshore operators to adopt TQM, but such a recommendation would have had implications which go far beyond safety. The *Cullen Report* (Cullen, 1990) recommended instead that for offshore installations the safety case should include a formal SMS and this requirement is embodied in the Offshore Installations (Safety Case) Regulations 1992. The corresponding regulations for onshore major hazard plants, the Control of Industrial Major Accident Hazards (CIMAH) Regulations 1984, contained no such requirement. The *Cullen Report* states that *inter alia* the SMS should cover the elements listed in Table 6.4.

Table 6.4 *Elements of the safety management system listed in the Cullen Report (Cullen, 1990)*

Organizational structure
Management personnel
Training for operations and emergencies
Safety assessment
Design procedures
Procedures for operations, maintenance, modifications and emergencies
Management of safety by contractors in respect of their work
The involvement of the workforce (operators and contractors) in safety
Accident and incident reporting, investigation and follow-up
Monitoring and auditing of the operation of the system
Systematic reappraisal of the system in the light of experience of the operator and industry

An account of industrial practice in safety management is given in *Safety Management Systems* by the European Process Safety Centre (EPSC) (1994). The ten components of a typical management system are:

(1) A charter defining the system's purpose, responsible resources and time expectations, (2) The rationale of why the system's purpose is important, its expected outcome, and how the output will be used, (3) The scope, clearly defining boundaries, constraints, specifications of input/output, resources required and excluded areas, (4) An administrator, defined as a single function or individual responsible for ensuring that the system is effective and provides continuity over time, (5) Tools/procedures/resources/schedules, the documentation of what when, how and by whom tasks must be done, including scheduling and measuring or results and periodic assessment of competency of resources, (6) Communications of results and plans to whom, by whom, how often, by what method, (7) Management sponsor to facilitate, monitor, recognize, provide commitment and sustainability, (8) Verification, which includes a measurement process to determine if desired results are being achieved and communicated to customers, sponsor, and members of the system, (9) A continuous improvement mechanism to facilitate improvements over time and (10) A document defining how the system works.

6.27 Process Safety Management

6.27.1 OSHA PSM Rule

In the United States, certain hazardous chemicals attract the statutory requirement for a PSM system, introduced by the Occupational Safety and Health Administration (OSHA) Rule Process Safety Management of Highly Hazardous Chemicals (Federal Register 29 CFR 1910.119). An account is given by Ozog and Stickles (1992).

The PSM system rule specifies national performance standards in 14 elements: (1) employee participation, (2) process safety information, (3) process hazard analysis, (4) operating procedures, (5) training, (6) contractors, (7) pre-start-up safety review, (8) mechanical integrity, (9) hot work permit, (10) management of change, (11) incident investigation, (12) emergency planning and response, (13) compliance audits and (14) trade secrets.

6.27.2 EPA Risk Management Program

In addition to the PSM system given in the OSHA Rule, there are several other American systems. One is the EPA Risk Management Program, the components of which are as follows: (1) hazard assessment, (2) prevention programme, (3) emergency response programme and (4) risk management plan. The prevention programme covers: (1) management system, (2) process hazard analysis, (3) process safety information, (4) standard operating procedures, (5) training,

(6) maintenance of mechanical integrity, (7) pre-start-up review, (8) management of change, (9) safety audits and (10) accident investigation.

6.27.3 API RP 750

Another process safety system is that given in API RP 750: 1990 *Management of Process Hazards*. The elements of the American Petroleum Institute (API) system are (1) process safety information, (2) process hazards analysis, (3) management of change, (4) operating procedures, (5) safe work practices, (6) training, (7) assurance of the quality and mechanical integrity of critical equipment, (8) pre-start-up safety review, (9) emergency response and control, (10) investigation of process-related incidents and (11) audit of process hazards management system.

6.27.4 The ACC system

The process safety system developed by the American Chemistry Council (ACC) has four main parts: (1) management leadership in process safety, (2) process safety management of technology, (3) process safety management of facilities and (4) managing personnel for safety. Detailed elements are given under each of these headings.

6.27.5 CCPS system

Finally, there is the management system of the CCPS, which is described in Section 6.28.

6.28 CCPS Management Guidelines

The CCPS has published several sets of guidance on management. The first of these was *A Challenge to Commitment* (CCPS, 1985) addressed to senior management in the industry. There have since followed a number of guidelines on management systems, as described below.

6.28.1 Guidelines for Technical Management of Chemical Process Safety

The *Guidelines for Technical Management of Chemical Process Safety* (the *Technical Management Guidelines*) by the CCPS (1989/7) give a comprehensive treatment of the management of SLP. An account of these *Guidelines* is given by Schreiber (1991). The main headings of the *Guidelines* may be summarized as follows:

(1) overview;
(2) management and management systems;
(3) goals and objectives;
(4) process knowledge and documentation;
(5) process safety reviews;
(6) process risk management;
(7) management of change;
(8) process and equipment integrity;
(9) human factors;
(10) training and performance;
(11) incident investigation;
(12) company standards, codes and regulations;
(13) audits and corrective action;
(14) enhancement of process safety knowledge.

The *Guidelines* are concerned with PSM. Process safety is defined as 'the operation of facilities that handle, use, process, or store hazardous materials in a manner free from episodic or catastrophic incidents' and PSM as 'the application of management systems to the identification, understanding, and control of process hazards to prevent process-related injuries and accidents'. A distinction is drawn between process and personal safety, the scope of the work being confined to the former. The starting point is the recognition that 'major accidents could not be prevented by technology-oriented solutions alone'.

The *Guidelines* identify 12 key elements of process safety, each of which is broken down into a number of components. These are shown in Table 6.5, together with the location in this book where they are treated. Management leadership is emphasized. Management systems and management of process safety are treated in terms of the functions of (1) planning, (2) organization, (3) implementation and (4) control. Each of these functions operates are three levels: (1) strategic, (2) managerial and (3) task. The format of planning, organization, implementation and control (POIC) is applied to the other elements of the system.

Accountability needs to be: planned so that the general goals are converted into specific objectives owned, or sponsored, by individuals; organized so that roles are defined, lines of authority are established and formal systems specified; implemented by demonstration of compliance to senior management and controlled by performance measurement and audit.

Process knowledge and documentation provides the basis for much of the safety programme. Examples are given of topics on which documentation is required such as chemical data and Material Safety Data Sheets (MSDSs), process definition, process and equipment design, and protective systems.

Process safety review procedures are required for capital projects, whether for new or existing plants, extensions or acquisitions. The review procedure described is a five-stage one: (1) conceptual engineering, (2) basic engineering, (3) detail design, (4) equipment procurement and construction and (5) commissioning. A comparison is given of hazard identification, or review, procedures such as hazard and operability studies, failure modes and effects analysis and fault trees, and of their role in the review process. Examples are given of topics covered in different types of process safety review such as the design stage, review or commissioning review.

Process risk management involves a process of hazard identification, risk analysis, risk reduction, residual risk management and emergency planning. An account is given of the ranking of risks and of risk acceptability. The point is made that the analysis may reveal that the risks of the project may be simply too great to be acceptable.

Management of change requires that mechanisms be in place to recognize and handle changes in the process, the plant or the organization. The features which prompt changes to the process or the plant and the effect of personnel changes on the organization are described.

Process and equipment integrity is assured by measures which include: reliability engineering; materials selection; fabrication and inspection procedures; installation procedures; preventive maintenance; inspection and testing, of process, hardware and software; maintenance procedures; alarm and instrument management; and demolition procedures.

Human factors need to be taken into account in: the operator–process and operator–equipment interfaces; the choice between administrative control (procedures) and hardware controls (interlocks); and the assessment of human error.

Table 6.5 *Elements and components of CCPS Technical Management Guidelines (CCPS, 1989/7)*

		Chapter[a]
1.	*Accountability: Objectives and Goals*	6
	Continuity of operations	
	Continuity of systems (resources and funding)	
	Continuity of organizations	
	Company expectations (vision or master plan)	
	Quality process	
	Control of exceptions	
	Alternative methods (performance vs specification)	
	Management accessibility	
	Communications	
2.	*Process Knowledge and Documentation*	6, 11
	Process definition and design criteria	
	Process and equipment design	
	Company memory	
	Documentation of risk management decisions	
	Protective systems	13
	Normal and upset conditions	11, 20
	Chemical and occupational health hazards	18, 25
3.	*Capital Project Review and Design Procedures*[b]	6, 8, 11
	Appropriation request procedures	
	Risk assessment for investment purposes	
	Hazards review (including worst credible cases)	
	Siting (relative to risk management)	10
	Plot plan	10
	Process design and review procedures	
	Project management procedures	
4.	*Process Risk Management*	5, 6, 8, 9
	Hazard identification	
	Risk assessment of existing operations	
	Reduction of risk	
	Residual risk management (in-plant emergency response and mitigation)	20, 24
	Process management during emergencies	20, 40
	Encouraging client and supplier companies to adopt similar risk management practices	
	Selection of businesses with acceptable risks	
5.	*Management of Change*	6, 11, 21
	Change of technology	
	Change of facility	
	Organizational changes that may have an impact on process safety	
	Variance procedures	
	Temporary changes	
	Permanent changes	
6.	*Process and Equipment Integrity*	11, 12
	Reliability engineering	7
	Materials of construction	12
	Fabrication and inspection procedures	12
	Installation procedures	19
	Preventive maintenance	7, 21
	Process, hardware and systems inspections and testing (pre-start-up safety review)	19
7.	*Human Factors*	14
	Human error assessment	
	Operator-process and operator-equipment interface	
	Administrative controls vs hardware	
8.	*Training and Performance*	14, 20, 21, 28
	Definition of skills and knowledge	
	Training programs (e.g., new employees, contractors, technical employees)	
	Design of operating and maintenance procedures	

Table 6.5 *(continued)*

	Initial qualification assessment Ongoing performance and refresher training Instructor programme Records management	
9.	*Incident Investigation* Major incidents Near-miss reporting Follow-up and resolution Communication Incident reporting Third-party participation, as needed	27
10.	*Standards, Codes and Laws* Internal standards, guidelines, and practices (past history, flexible performance standards, amendments and upgrades) External standards, guidelines and practices	11, 12, App. 27
11.	*Audits and Corrective Actions* Process safety audits and compliance reviews Resolutions and close-out procedures	6, 8
12.	*Enhancement of Process Safety Knowledge* Internal and external research Improved predictive systems Process safety reference library	27

[a] Chapter in this book in which this topic is principally addressed.
[b] For new or existing plants, expansions, and acquisitions.

Training is necessary to provide both knowledge and motivation. Some principal topics requiring training are listed, including operating and maintenance procedures. The approach to training is described, including definition of the knowledge and skills required, assessment before and after training and keeping of training records.

Incident investigation should be approached in terms of failure of the management system rather than of human error. An account is given of the incident investigation process, including: preparation; team selection; recording, reporting and analysis; follow-up and resolution and dissemination of results.

Company standards, codes and regulations provide a framework of requirements and guidance. Use is made of both external and in-house codes. The principal US codes relevant to the process industries are outlined. A plan is given for the repositories of external codes and regulations within a company.

Audits are required to show the company whether its systems and procedures and its practices are adequate and are being adhered to, so that corrective action can be taken if they are not. The reasons for establishing an audit programme are described. They include the raising of safety awareness, acceleration of the development of safety control systems, improvement of safety performance and optimization of safety resources. A particular type of audit is the compliance review, which is carried out to ensure that the company is meeting the legal requirements.

Enhancement of process safety knowledge is an ongoing activity and involves the utilization of a range of resources, some of which are enumerated. The direction in which this work may progress is outlined by Sweeney (1992). The emphasis is on the development of measures of performance.

6.28.2 Plant Guidelines for Technical Management of Chemical Process Safety

The Plant Guidelines for Technical Management of Chemical Process Safety (*the Plant Technical Management Guidelines*) by the CCPS (1992/11) have the same basic structure as the *Technical Guidelines*, but emphasize concrete examples.

These are principally given in the appendices, the titles of which are listed in Table 6.6.

6.28.3 Guidelines for Implementing Process Safety Management Systems

The implementation of a PSM system is covered in *Guidelines for Implementing Process Safety Management Systems* (CCPS 1994/13). The elements of the system are those given in the Technical Management Guidelines and shown in Table 6.5. The treatment of implementation is under the headings: (1) management commitment, (2) definition of goals, (3) evaluation of the present status, (4) development of a plan, (5) development of specific PSM systems, (6) implementation of the system, (7) measurement and monitoring of system installation and (8) expansion beyond the original scope. The guidelines describe a case study.

6.28.4 Guidelines for Auditing Process Safety Management Systems

The auditing of a PSM system is dealt with in *Guidelines for Auditing Process Safety Management Systems* (CCPS 1993/12). These guidelines cover topics closely aligned to, but not identical with, the 12 elements of the CCPS PSM system, the headings being: (1) management of PSM systems audits, (2) audit techniques, (3) accountability and responsibility, (4) process safety knowledge, (5) project safety reviews, (6) management of change, (7) process equipment integrity,

Table 6.6 *Appendices of CCPS Plant Management Guidelines (CCPS, 1992/11)*

2A	Characteristics of a management system
3A	Example of the management of process hazards
4A	Example of typical Material Safety Data Sheet
4B	Lead questions (hazardous conditions)
4C	Example of process definition/design criteria contents
4D	Example of typical protective systems/equipment data
4E	Example of components included in process knowledge and documentation
5A	Plant example of organization of process hazard review for appropriation requests
5B	Plant example of plant procedures: 'Description of hazard review program for appropriation requests'
5C	Example of plant procedures for appropriation request information and approvals
5D	Plant example of 'Standard practice for process reviews'
6A	Plant example of hazard identification
6B	Plant X' risk analysis of operations
6C	Plant Y' risk analysis of operations
6D	Example of process management in emergencies
7A	Management of change policy
7B	Guidelines for review of plant changes or modifications
7C	Control of change – safety management practices
7D	Control of changes
7E	Example of change of process technology
7G	Example of safety assessment form for plant modification work
7H	Safety guidelines variance request
7I	Permanent change considerations
7J	Examples of jumpers/bypass logging
8A	Example of plant management system for materials of construction (MOC)
8B	Example of test and field inspection equipment and procedures
8C	Example of field inspection and testing of process safety systems
8D	Example of a hot work permit
8E	Example of criteria for test and inspection of safety relief devices
8F	Example of management system for critical and unique safety features
8G	Table of contents from Chemical Manufacturers Association Fixed Equipment Inspection Guide
10A	Example of operator process safety training programme
10B	Example of maintenance training program for process safety
10C	Example of operations technical staff training programme
10D	Example of maintenance training implementation
10E	Example of instructional standards
10F	Example of refresher training course frequencies
11A	Example of extraordinary event notification, investigation and reporting
11B	Example of plant follow-up procedures for accident or incident investigation recommendations
11C	Plant example of unplanned incidents causal factors analysis
11D	Example of plant accident or incident reporting procedures
12A	Example of operational safety standards guidelines
12B	Example of critical operating parameters: interpretation guidelines
12C	Example of manufacturing standards
12D	Example of hazardous systems (existing system)
13A	Protocol for estimating progress in implementation of CCPS Guidelines for Technical Management of Chemical Process Safety
13B	'Key questions' for the elements of process hazards management
13C	Example of process safety audit
13D	Example of safety and property protection procedures
14A	Professional industry organizations offering process safety enhancement
14B	Center for Chemical Process Safety Guidelines and conferences
14C	Examples of subjects covered in process safety libraries

(8) process risk management, (9) incident investigation, (10) human factors, (11) training and performance and (12) emergency response planning.

6.29 Regulatory Control

The crucial role of the management and management system in SLP means that it is, or should be, of prime concern to the regulatory body. The organization and activities of that body should reflect this.

6.29.1 Evolution of policy

The HSE has for a long time placed emphasis on the crucial role of management, but its approach has naturally undergone a process of evolution. The process has been described by Bleeze (1992). This evolution is documented in

the series of publications on management already referred to: *Managing Safety* (HSE, 1981d), *Monitoring Safety* (HSE, 1985c), *Effective Policies for Health and Safety* (HSE, 1986a) and *Successful Health and Safety Management* (HSE, 1991b).

6.29.2 Inspection *vs.* audit

In the United Kingdom, as elsewhere, the traditional approach to enforcement has been by inspection. This is reflected in the title of the arm of the HSE which operates at works level, the Factory Inspectorate.

This approach is increasingly being supplanted by the auditing of the management and management systems. The features which are of interest to the regulator are now those such as the arrangements for the identification and assessment of hazards, for the proof testing of protective systems or for the investigation of incidents.

The deficiencies of an approach to regulation based on inspection were highlighted by the *Cullen Report* on the Piper Alpha disaster and the report recommended a change in the regulatory regime away from one based on inspection and towards one based on audit of the SMS (Cullen, 1990).

6.29.3 Accident Prevention Advisory Unit

In order to provide assistance to inspectors in the assessment of management and management systems, the HSE has created the Accident Prevention Advisory Unit (APAU). Much of the HSE work described above derives from this unit.

6.29.4 Management assessment

As described above, the HSE has given guidance on good practice in the management of process safety. It may be assumed to apply much the same criteria in the assessments which it undertakes. It is also active in the evaluation of research models of management effectiveness, including as proprietary systems. An account of one such study has been given by J.C. Williams and Hurst (1992). Against this background, the HSE has been developing a method for auditing a SMS. This is now described.

6.30 STATAS

The HSE is well advanced with the development of a methodology for the audit of SMSs. The method goes by the name of Structured Audit Technique for the Assessment of Safety Management Systems (STATAS) and is described by Ratcliffe (1993, LPB 112, 113, 114) and Hurst and Ratcliffe (1994). The starting point is a field study of failures in vessels and pipework (Bellamy, Geyer and Astley, 1989; Geyer *et al.*, 1990; Geyer and Bellamy, 1991; Hurst *et al.*, 1991). An account of the study and of the pipework failure data is given in Chapter 12, whilst the human error aspects are considered in Chapter 14.

From this study a loss of containment model has been derived. The pipework failures are classified on three dimensions:

(1) origin of failure (basic or underlying cause);
(2) direct (immediate) cause;
(3) recovery (preventive) mechanism.

The origins of failure are divided into nine categories:

(1) design;
(2) manufacture/assembly;
(3) construction/installation;
(4) normal operation;
(5) maintenance;
(6) natural causes;
(7) domino;
(8) sabotage;
(9) unknown.

There are 12 categories of direct cause:

(1) corrosion;
(2) erosion;
(3) external load;
(4) impact;
(5) overpressure;
(6) vibration;
(7) temperature (high, low);
(8) wrong equipment;
(9) defective equipment;
(10) human error;
(11) other;
(12) unknown.

There are four preventive mechanism categories. Two relate to equipment:

(1) hazard identification and assessment (HAZ);
(2) routine checking and testing (ROUT).

and two to people:

(1) human factors review (HF);
(2) task checking (TCHECK).

The influencing factors which bear on the failures are represented by a socio-technical model. The structure of this model is shown in the socio-technical pyramid given in Figure 2.6(a). The model has six levels as follows:

Level
5 System climate
4 Organization and management
3 Communication and feedback
2 Operator reliability
1 Engineering reliability
0 Loss of containment and mitigation

Some influencing factors at Level 5 are background, legislation, regulation and resources; at Level 4, policies, management structure, formal systems, assigned responsibilities, performance criteria and emergency response organization; at Level 3, job descriptions, written procedures, performance evaluation, safety audits, incident reporting and follow-up, and meetings; at Level 2, design, procedures, competence, manning and shifts; at Level 1 plant layout and equipment design.

In STATAS, these models are combined with an audit scheme. The five phases of the plant life cycle are:

(1) design (DBS);
(2) manufacture (MANF);
(3) construction (CON);
(4) operation (OP);
(5) maintenance (MAINT).

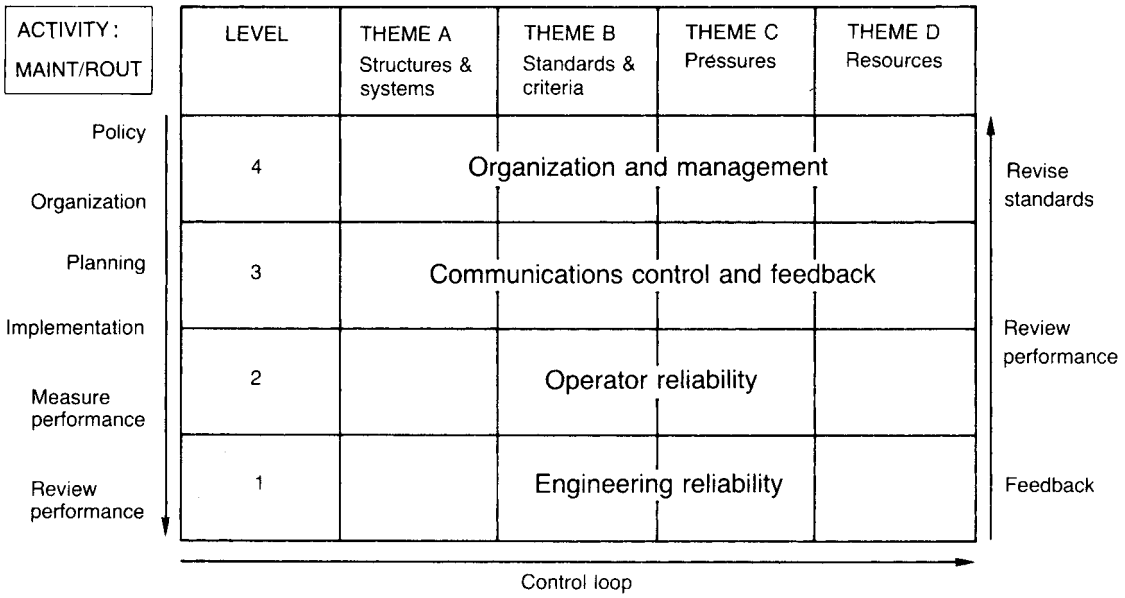

Figure 6.3 *Arrangement of question cell sets for audit of topic MAINT/ROU is STATAS (Ratcliffe, 1993 LPB 114)*

Since there are four recovery, or preventive, categories, there are in principle 20 combinations of plant phase and preventive category. The field study showed, however, that the great majority of failures are associated with just eight combinations. These eight cover 83% of vessel failures, the proportion recoverable being assessed as 87%; the corresponding figures for pipework are 84% and 92%. The eight combinations are

(1) DES/HAZ;
(2) CON/TCHECK;
(3) MAINT/ROUT;
(4) MAINT/HF;
(5) MAINT/TCHECK;
(6) OP/HAZ;
(7) OP/HF;
(8) OP/TCHECK.

Then, for each combination, an audit question set is devised. The themes of the questions are

(1) structures, systems and procedures,
(2) standards and criteria,
(3) mitigation of pressures,
(4) availability and use of resources.

Each question set contains some 40–80 questions. The questions are grouped in cells containing between 2 and 10 questions which explore a particular topic.

The conduct of the audit aims to take samples 'horizontally' and 'vertically' through the system, concentrating mainly on Levels 1–4. The method is illustrated in Figure 6.3, which shows the arrangement of question cell sets for the topic MAINT/ROUT. Work on the question sets links with that of Wells, Hurst and co-workers described in Chapter 8.

7 Reliability Engineering

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7.4 Meanings of Probability 7/7
7.5 Some Probability Relationships 7/7
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Loss prevention is in large part the application of probabilistic methods to the problems of failure in the process industries. The discipline which is concerned with the probabilistic treatment of failure in systems in general is reliability engineering. This chapter gives an account of reliability engineering and of some reliability techniques.

Selected references on reliability engineering are given in Table 7.1. There are numerous books on the subject. These include *Reliability Theory and Practice* (Bazovsky, 1961), *Reliability Principles and Practices* (Calabro, 1962), *Reliability: Management, Methods and Mathematics* (Lloyd and Lipow, 1962), *System Reliability Engineering* (Sandler, 1963), *Reliability Engineering* (von Alven, 1964), *Reliability Engineering*

Table 7.1 *Selected references on reliability engineering*

IEC (Std 1078); NRC (Appendix 28 *Reliability Engineering*); UKAEA (Appendix 28); US Armed Forces (Appendix 27 *MIL Standards, Handbooks*); Fry (1928); Feller (1951); Siegel (1956); Bazovsky (1960, 1961); Chorofas (1960); Hosford (1960); Parzen (1960); Reza (1961); Blackett (1962); Calabro (1962); D.R. Cox (1962); Lloyd and Lipow (1962); Machol and Grey (1962); Savage (1962a,b, 1971); Pieruschka (1963); Sandler (1963); Zelen (1963); von Alven (1964); Myers *et al.* (1964); N.H. Roberts (1964); Barlow and Proschan (1965, 1975); P.L. Meyer (1965); I. Miller and Freund (1965a); A.E. Green and Bourne (1966 UKAEA AHSB(S) R117, 1972); Nathan (1966); Vance (1966); Hahn and Shapiro (1967); Haugen (1968); Hofmann (1968); Ireson (1968); Polovko (1968); Shooman (1968a); Gnedenko *et al.* (1969); A.E. Green (1969–70, 1971 SRS/GR/2, 1972, 1973, 1974a,b, 1976, 1982b, 1983); IEE (1969 Conference Publication 60); C.S. Smith (1969); Thomason (1969); Tribus (1969); Breipohl (1970); Bourne (1970, 1971 UKAEA SRS/GR/4, 1972, 1975 NCSR R7, 1982); Kozlov and Ushakov (1970); R. LeWis (1970); Rau (1970); Truscott (1970); Barnes (1971 SRD R1); Buffham *et al.* (1971); R.A. Howard (1971); Jenkins and Youle (1971); Amstadter (1972); Caplen (1972); A.D.S. Carter (1972, 1973, 1976, 1979, 1980, 1983, 1986); D.R. Cox and Miller (1972); Cunningham and Cox (1972); Ross (1972); D.J. Smith (1972, 1981, 1985a, 1991); Bompas-Smith (1973); Henley and Williams (1973); Kletz (1973b, 19791); Locks (1973); Reinschke (1973); Schneeweiss (1973); D.J. Smith and Babb (1973); Apostolakis (1974); de Finetti (1974); J.R. Taylor (1974b, 1975b, 1976b, 1979); Mann *et al.* (1974); AEC (1975); H.M. Wagner (1975); Henley and Lynn (1976); Moss (1976 NCSR R12); C.O. Smith (1976); Lievens (1976); D.J. Bennett (1977); Dunster (1977); F.R. Farmer (1977a); Kapur and Lamberson (1977); Keller (1977); Mosteller (1977); C. Singh and Billinton (1977); Sorenson and Besuner (1977); Halpern (1978); Hastings and Mellow (1978); Rodin (1978); Richards (1980); Sinha and Kale (1980); Court (1981); Dhillon and Singh (1981); J.W. Foster (1981); Nieuwhof (1981, 1984, 1985a,c, 1986); O'Connor (1981, 1984); Sherif (1981); Durr (1982); S.T. Parkinson (1982); Amendola and Melis (1983); Billinton and Hossain (1983); Hutchinson (1983); MoD (1983); Sayles (1983); Frankel (1984); K.A.P. Brown (1985); Serra and Barlow (1986); Ballard (1987); M.G. Singh *et al.* (1987); Veevers (1989/90); Misra (1992, 1994); F.R. Nash (1993); Andrews and Moss (1993); Sherwin and Bossche (1993); BS 5760: 1981–

Terminology
US Armed Forces (MIL-STD-721B, MIL-STD-781B); IEC (1969); BS 5760: Part 0: 1986

Background mathematics, statistical distributions
Fry (1928); Clopper and Pearson (1934); Kendall (1948, 1970); Arkin and Colton (1950); Hald (1952a,b); Burr (1953); Meehl (1954); K. Pearson and Hartley (1954); Moroney (1956); K. Pearson and Hartley (1956); Siegel (1956); Beers (1957); Kendall and Stewart (1958–); Bowker and Lieberman (1959); Pantony (1961); Raiffa and Schlaifer (1961); Reichman (1961); D.B. Owen (1962); Savage (1962a,b, 1964); Kron (1963); Abromowitz and Stegun (1964); E.L. Grant (1964); N.L Johnson and Leone (1964); Kyburg and Smokier (1964); Lindley and Miller (1964); Lindley (1965); P.L. Meyer (1965); Papoulis (1965); Conway *et al.* (1967); Yamane (1967); Beyer (1968, 1978, 1984); Winkler (1968, 1981); Aitcheson and Brown (1969); N.L. Johnson and Katz (1969); O'Brien (1969); Schmitt (1969); Woodcock and Barnes (1970 AHSB(S) R179); J.R. King (1971); Barks (1972); FRS (1972 Fire Research Note 909); Bolz and Tuve (1973); Lomnicki (1973); Hastings and Peacock (1974); Lehman (1975); Lmstone and Turoff (1975); Patel *et al.* (1976); Worledge (1976 SRD R68); Beck and Arnold (1977); Parry *et al.* (1977 SRD R80, 1979 SRD R129); BRE (1978 CP8/78); Paradine and Rivett (1980); Govil and Agarwala (1982,1983a,b); Nelson and Rasmuson (1982); Patel and Read (1982); Sherif (1982a); Ichikawa (1983, 1984a,b, 1986); Moran (1984); A.T. White (1984); Kececioglu and Dingjun (1985)
Error function approximation: Karlsson and Bjerle (1980); Ernst (1992)

Log–normal distribution, error factor
Chambers *et al.* (n.d.); Finney (1941,1971); Gaddum (1945); Brownlee (1949); Day (1949); Aitcheson and Brown (1969); AEC (1975); Kline (1984); Siu and Apostolakis (1985); Murty and Verma (1986); Savoie (1988)

Weibull distribution
Weibull (1951); Hastings (1967–68); R.A Mitchell (1967); L.S. Nelson (1967); Shooman (1968a); Truscott (1970); Steiger (1971); Hinds *et al.* (1977); Kapur and Lamberson (1977); O'Connor (1977); Sherwin and Lees (1980); Guida (1985); Kekecioglu and Jacks (1985); P.W. Hale (1987); Lihou and Spence (1988)

Extreme value theory, distribution
R.A. Fisher and Tippett (1928); Cramer (1946); Gumbel (1958); B. Epstein (1960); Lloyd and Lipow (1962); Wiesner (1964); Ramachandran (FRS 1972 Fire Research Notes 910, 929, 943; 1973 Fire Research Note 991); Singpurwalla (1972); Bompas-Smith (1973); Mann *et al.* (1974); C.W. Anderson (1976); E.M. Roberts (1979); Perry (1981); Schueller (1982); R.L. Smith (1986); Surman *et al.* (1987)

Bayesian methods
Savage (1962b); Lindley (1965); Schmitt (1968); Weir (1968); Brand (1980); Colombo and Saracco (1983); Kaplan (1983); Puccini (1983); Yuan (1987); Hauptmans and Homke (1989)

Early failure, burn-in
R. Ward (1972); de la Mare and Ball (1981); Jensen (1982); Jensen and Petersen (1982); Mowbray (1991)

Wearout failure
Newby (1986); Mowbray (1991)

Repair times
Sandier (1963); AEC (1975); Kline (1984)

Dependent failure
NRC (Appendix 28 *Common Cause Failure*); Apostolakis (1975, 1976); J.R. Taylor (1976a); Heising and Luciani (1977); Edwards and Watson (1979 SRD R146); P. Martin (1980); A.M. Smith and Watson (1980); Watson (1980); Heising (1983); M.G.K. Evans *et al.* (1984); Plate (1984); Games *et al.* (1985); Crellin *et al.* (1986); Teichman (1986); Yun and Bai (1986); G.T. Edwards (1987a,b); Johnston (1987a,b); Yuan (1987); Ballard (1988); Andrews and Moss (1993)

Markov methods
Kemeny and Snell (1960); Sandier (1963); Shooman (1968); R.A. Howard (1971); Plate (1984); J.N.P. Gray (1985); Andrews and Moss (1993)

Monte Carlo methods
Metropolis and Ulam (1949); NBS (1951); Kahn (1957); Hammersley and Handscomb (1964); Shreider (1964); Tayyabkhan and Richardson (1965); Muth (1967); Rudd and Watson (1968); Shooman (1968a); Schmitt (1969); Ang and Tang (1974–75); Sobol (1974); AEC (1975); Lanore and Kalli (1977); EPRI (1981b); Rubinstein (1981); E.E. Lewis and Tu Zhuguo (1986); Soon Chang *et al.* (1986)

Physics of failure
Kao (1965); Shooman (1968a); Birnbaum and Saunders (1969); Yost and Hall (1976)

Catastrophe theory
Zeeman (1972, 1977); Hilton (1976); Poston and Stewart (1978); Saunders (1980); Gilmore (1981)

Rare events
Selvidge (1972)

Reliability specification, apportionment
US Armed Forces (MIL-S-38130); von Alven (1964); Petkar (1980); Sledge (1982); MoD (1983); EEMUA (1986 Publication 148); Andersen and Neri (1990)

Equipment testing
US Armed Forces (MIL-STD-781A, MIL-STD-810); Kececlioglu and Jacks (1985); P.W. Hale (1986); Irwing (1986); Lydersen and Rausand (1987); BS 5760: Part 10: 1993, BS DD 57: 1978

Reliability growth modelling
US Armed Forces (MIL-HDBK-189, MIL-STD-1635); Madansky and Peisakoff (1960); Duane (1962); Kamins and Gross (1967); Codier (1968); R.C.F. Hill (1977); Sheppard (1983,1985); Catchpole *et al.* (1984); Halliday and Devereux (1984); BS 5760: Part 6: 1991

Proportional hazards modelling
D.R. Cox (1972); Kalbfleisch and Prentice (1980); Prentice *et al.* (1981); Andersen (1982); Lawless (1982); Bendell (1985); C.J. Dale (1985); Wightman and Bendell (1986)

Expert opinion
NRC (Appendix 28 *Expert Judgement*); Thurstone (1927, 1931); Wherry (1938); Kendall (1948, 1955, 1970); Guilford (1954); Khan (1957); B. Brown (1964); C. Peterson and Miller (1964); Pontecorvo (1965); Schmid (1966); C.R. Peterson and Beach (1967); Torgerson (1967); Winkler (1968, 1981, 1986); Alpert and Raiffa (1969); B. Brown *et al.* (1969); Dalkey (1969); Keats (1971); Pill (1971); Klee (1972); L.L. Philipson (1974a); Tversky and Kahneman (1974); Lmstone and Turoff (1975); Spetzler and Stahl von Holstein (1975); Nachmias (1976, 1992); Lichtenstein *et al.* (1977); Saaty (1977, 1980, 1982); Winkler and Murphy (1978); Apostolakis *et al.* (1980); Hunns (1980, 1982); Apostolakis (1982, 1985a,b, 1988, 1990); Mosleh and Apostolakis (1982, 1985, 1986); Uppuluri (1983); Martz (1984); Mosleh *et al.* (1987, 1988); Shields *et al.* (1987); Clarotti and Lindley (1988); Goossens *et al.* (1989); NRC (1989); van Steen *et al.* (1989); Svenson (1989); Wheeler *et al.* (1989); Meyer and Booker (1990); van Steen (1992).
Interviewing: Khan (1957); Oppenheim (1966); Gorden (1969)
Applications: Minarick and Kukielka (1982); Pickard *et al.* (1983); Swain and Guttman (1983); Cottrell *et al.* (1984); Embrey *et al.* (1984); IEEE (1984 Standard 500); Veneziano *et al.* (1984); Minarik *et al.* (1985); NRC, Steam Explosion Review Group (1985); Benjamin *et al.* (1986); EPRI (1986); Hannaman *et al.* (1986); Siu and Apostolakis (1982, 1985, 1986); Mosley, Bier and Apostolakis (1987); Wheeler *et al.* (1989)

Complex systems, large systems
Drenick (1960); Kron (1963); Htun (1965); Shooman (1968a); Nelson *et al.* (1970); Batts (1971); Colombo (1973); C. Singh (1974); NCSR (1975 NCSR R6); Blin *et al.* (1977); Hunns (1977); M.J. Harris and Rowe (1980); Kontoleon (1982); Laviron *et al.* (1982); Windebank (1982); Pickup (1983); Laviron (1985, 1986); Laviron and Heising (1985)

Special topics
J.A. Baker (1963); Buzacott *et al.* (1967); D.B. Brown (1971); Koen and Carnino (1974); Kontoleon and Kontoleon (1974); Bourne (1975 NCSR R7); Buzacott (1976); N.D. Cox (1976); Astolfi and Elbaz (1977); G.O. Davies (1977); Mosteller (1977); Parry and Worledge (1977 SRD R95); Colombo *et al.* (1978); Parry (1979 SRD R143); Kontoleon (1980, 1981); Plate (1980); Hohenbichler and Rackwitz (1981); Moieni *et al.* (1981); Nicolescu and Weber (1981); J.H. Powell (1981); Sharma (1981); Gopalan and Natesan (1982); Govil and Agarwal (1982, 1983a,b); Husseiny *et al.* (1982); Misra and Gadani (1982); Brooks (1983); Hirschman *et al.* (1983); Ichikawa (1983); J.W.H. Price (1983); Sayles (1983); Walker (1983); Bendell and Ansell (1984); Connors (1984); Aven (1985, 1986); Jain and Gopal (1985); Reiser (1985a,b); Witt (1985); Gopalan and Venkateswarlu (1986a,b); Gupta *et al.* (1986); Pickles (1986); Dorre (1987); Knezevich (1987); Limnios (1987); McCormick (1987); D.B. Parkinson (1987); Rushdi (1987); Walls and Bendell (1987)

Stand by systems
Signoret *et al.* (1983); Vaurio (1985)

Quality assurance, control (*see also* Table 6.1)
NRC (Appendix 28 *Quality Assurance*); US Air Force (n.d.); US Armed Forces (Appendix 27); Calabro (1962); C.S. Smith (1969); Thomason (1969); F. Nixon (1971); Schmitt and Wellein (1980); Kolff and Mertens (1984); A. Smith (1991)

Mechanical reliability
ASME (Appendix 28, 1975/129, 1977/17, 1981/18, 1982/161, 1983/9, 1990 PVP 193, 1993 DE 55); NRC (Appendix 28 *Failures*); Haviland (1964); IMechE (1970/3, 1974/10, 1975/16, 1984/79, 1988/105, 1994/172); A.D.S. Carter (1972, 1973, 1976, 1979, 1980, 1983, 1986); API (1973–, *Refinery Inspection Guide*); Bompas-Smith (1973); Barnes (1973 SRSD/GR/12); Fames and Fothergill (1973 (SRS/GR/13);

Hensley (1973 SRS/GR/1); Pronikov (1973); D. Scott and Smith (1975); P. Martin (1976a,b); C.O. Smith (1976); Yost and Hall (1976); Kapur and Lamberson (1977); Venton (1977, 1980); Moss (1980); Sherwin and Lees (1980); Martin *et al.* (1983); ASCE (1985/23); Parkhouse (1987); Davidson (1988)

Failure data analysis
NRC (Appendix 28 *Failure Data Analysis*); Shaw (n.d.); Weibull (1951); Carhart (1953); Karassik (1959); L.G. Johnson (1964); Hastings (1967–68); R.A. Mitchell (1967); L.S. Nelson (1967); Kivenson (1971); Fercho and Ringer (1972); Bompas-Smith (1973); Jardine and Kirkham (1973); Ryerson (1973); Whitaker (1973a,b); J.C. Moore (1974); Nino (1974); de la Mare (1976); Moss (1976 NCSR R12, 1977 NCSR 11); Aird (1977a, 1978); Berg (1977); Blanks (1977); Hinds *et al.* (1977); Kapur and Lamberson (1977); O'Connor (1977); Sherwin (1978, 1983); Hastings and Jardine (1979); Sherwin and Lees (1980); Stokoe *et al.* (1981); Crellin and Smith (1982); Colombo and Jaarsma (1983); Harries *et al.* (1983); Puccini (1983); Bendell and Walls (1985); Nieuwhof (1985b); Lamerse and Bosnian (1985); Walls and Bendell (1985); Coit *et al.* (1986); Crellin *et al.* (1986); Schiffman (1986); Vaurio (1986); Bendell (1987); Andrews and Moss (1993)
Bath tubcurve: Carhart (1953); A.D.S. Carter (1973); Talbot (1977); Aird (1978); Veevers (1989/90); Mowbray (1991)

Availability
H. Smith and Grace (1961); Gibbons (1962); Sandler (1963); R.E. Jackson *et al.* (1965); H.L Gray and Lewis (1967); W.N. Smith (1968); Jenkins (1969); Sherry (1969–70); Buzacott (1970a,b); Dailey (1970); Henley (1971); Jenkins *et al.* (1971); Konoki (1971); Kuist and Fife (1971); Roth and Fiedler (1971); Cason (1972); McFatter (1972); G.H. Mitchell (1972); Ufford (1972); Gaddy and Culbertson (1973); Kardos and Vondran (1973); Locks (1973); Yaro (1973); Inone *et al.* (1974); Kafarov *et al.* (1974); Kardos *et al.* (1974–); Rosen and Henley (1974); Sawyer and Williams (1974); Walsham (1974); Cowan (1975); G.D.M. Pearson (1975, 1977); Vondran and Kardos (1975); NCSR (1976 NCSR R8); Apostolakis and Bansal (1976, 1977); D.H. Allen and Pearson (1976); Caceres and Henley (1976); Cowan *et al.* (1976); Holmes (1976); Platz (1976, 1977); Allen and Coker (1977); Blin *et al.* (1977); Cherry *et al.* (1977); D.H. G.O. Davies (1977); Henley and Hoshino (1977); Siddons (1977); Coker (1978); Parry and Worledge (1978 SRD R113); Ong and Henley (1979); Apostolakis and Chu (1980); Leblanc *et al.* (1980); J.W. Foster (1981); M.J. Phillips (1981); Heising (1983); Nieuwhof (1983b); Piccinnini and Anatra (1983); Sherwin (1984); Brouwers (1986); Brouwers *et al.* (1987); Evans (1987 NCSR/GR/68); Watanabe (1987); Fairclough (1988); Odi and Karimi (1988); E.S. Lee and Reklaitis (1989); Dougan and Reilly (1993); Sherwin and Bossche (1993)

Maintenance
NRC (Appendix 28 *Maintenance, Maintenance Personnel Reliability Model*); US Armed Forces (MIL-HDBK-472, MIL-STD-470, MIL-STD-471); J.C. Moore (1960, 1966, 1974); Bartholemew (1963); Dean (1963); J.E. Miller and Blood (1963); Goldman and Slattery (1964); Nathan (1966); Newborough (1967); Woodman (1967); Blanchard and Lowery (1969); IMechE (1969/2, 1973/6, 1975/ 16, 17, 1994/174); Armitage (1970); Geraerds (1970); Jardine (1970a, 1973a, 1976); Kelly and Harris (1971); D.J. Smith (1972, 1981, 1985a, 1991); Gradon (1973); Hastings (1973); D.J. Smith and Babb (1973); Trotter (1973); Clifton (1974); Priel (1974); Reynolds (1974); Corder (1976); Husband (1976); Andre (1977); Johns and Sadlowski (1977); Kapur and Lamberson (1977); de la Mare (1979 NCSR 21); Sherwin and Lees (1980); J.W. Foster (1981); Barry and Hudson (1983); G.T. Edwards (1983); MoD (1983); Sherwin (1983); van Aken *et al.* (1984); Backert and Rippin (1985); Kelly (1986); L.C. Thomas (1986); Henry (1990, 1993a,b); Factory Mutual Int. (1991a); Rao (1992); Andrews and Moss (1993); Whetton (1993)
Life cycle costing: Sherif (1982b); Lees (1983); Jambulingam and Jardine (1986)
Reliability-centred maintenance: US Armed Forces (MIL-HDBK-472); Nail and Nair (1965); Nowlan and Heap (1978); Jambulingam and Jardine (1986); Anderson and Neri (1990); Moubray (1991); Sandtory (1991)
Spares holdings: G.H. Mitchell (1972); Messinger and Shooman (1976)

Computer system, software reliability (*see also Table 13.3*)
NRC (Appendix 28 *Computer Software Reliability*); Aiken (1958); Anon. (1960b); Naur (1966); Floyd (1967); London (1968); Manna and Pnueli (1969); Bauer (1975a,b); Goos (1975); Poole (1975); Tsichritzis (1975a,b); Fagan (1976); Meyers (1976); Shooman (1976, 1983); J.L. Peterson (1977); R.B. Anderson (1979); Boulton and Kittler (1979); Daniels (1979 NCSR 17, 1983, 1986, 1987); Daniels and Hughes (1979 NCSR 16); Glass (1979); Kopetz (1979); Cho (1980); Longbottom (1980); Dempster *et al.* (1981); Kersken and Ehrenberger (1981); J. Peterson (1981); Dunn and Ullman (1982); McGettrick (1982); Becker (1983); Gubitz (1983); Leveson and Harvey (1983); Leveson and Stolzy (1983); Lord (1983); Bennett (1984, 1991a,b, 1993); Dunn (1984); Goldsack (1985); IEE (1985, 1989); Quirk (1985); Backhouse (1986); CEC (1986); Helps (1986); C.B. Jones (1986); Leveson (1986, 1987); O. Anderson *et al.* (1987); T. Anderson (1987); Baber (1987); Barry (1987); C. Dale (1987); Dale *et al.* (1987 NCSR/GR/65); Ehrenburger (1987); Hennell (1987); Humphreys (1987); IEC (1987/1, 1991 SC65A WG9); Littlewood (1987a,b); Macro and Buxton (1987); MoD (1987, 1989b,c); Musa *et al.* (1987); National Computer Centre (1987, 1989); Nordic Council of Ministers (1987); Pyle (1987, 1991, 1993); Schagen (1987); Schagen and Sallih (1987); Schulmeyer and MacManus (1987); Voges (1987); Heilbrunner (1988); IChemE (1988/132); E. Johnson (1988); Redmill (1988, 1989); Humphrey (1989); Lasher (1989); Littlewood (1989); McDermid (1989a,b, 1991, 1993); Sennett (1989); Somervffle (1989); D.J. Smith and Wood (1989); R. Clarke (1989–90); Bishop (1990); DTI (1990); Frederickson and Beckman (1990); C.B. Jones and Shaw (1990); C. Morgan (1990); Rook (1990, 1991); Schulmeyer (1990); P. Bennett (1991); Facey (1991); Fergus *et al.* (1991); P.A.V. Hall (1991); Hunns and Wainwright (1991); IEE (1991, 1991 Coll. Dig. 91/3, 1992); Ince (1991a,b); L. Jones (1991); Littlewood and Miller (1991); Paula and Roberts (1991); Rook (1991); Shrivastava (1991); A. Smith (1991); J.T. Webb (1991); Woodward (1991); Chudleigh and Catmar (1992); Wichmann (1992); Bologna (1993); Cluley (1993); Danielsen (1993); Drake and Thurston (1993); Ehrenberger (1993); Fink *et al.* (1993); Johnston (1993); Malcolm (1993); Rata (1993); Redmill and Anderson (1993); Rowland (1993); Walton (1993); P. Woods (1993) BS (Appendix 27 *Computers*)

Nuclear systems (see also Tables 9.1 and A20.1)
NRC (Appendix 28); UKAEA (Appendix 28); Siddall (1959); Eames (1966); F.R. Farmer (1967a,b, 1969a,b, 1971, 1977a); Hensley (1968); A.E. Green (1969–70, 1972, 1973, 1974a,b, 1976); Bourne (1970); A.E. Green and Bourne (1972); Ablitt (1975); Carnino (1976); Eames *et al.* (1976); Rudolph (1977); Schmitt and Wellein (1980); Welsh and Lundberg (1980); Bowers *et al.* (1981); Ballard (1989)
Analysis of faults and abnormal occurrences: J.C. Moore (1960, 1966, 1974); R.L. Scott (1971); J.R. Taylor (1974a, 1975c); AEC (1975); NBA (1977)

Electrical power systems
Sherry (1969–70); Billinton (1970); Billinton *et al.* (1973); Wakeman and Laughton (1976); Siddons (1977); C. Singh and Billinton (1977); Sherif (1982c); Snaith (1982); Billinton and Allan (1983); Yip *et al.* (1984); Allan *et al.* (1986); Systems Engineering Comm. (1986)

Process industry systems
Rudd (1962); Rudd and Watson (1968); Weisman (1968); Browning (1969a–c, 1970, 1973); Buffham and Freshwater (1969); Freshwater and Buffham (1969); Bently and Reid (1970); Cornett and Jones (1970); Lenz (1970); Loftus (1970); Pan (1970); H.L Williams and Russell (1970); Buffham *et al.* (1971); Patterson and Clark (1971); C.F. King and Rudd (1972); Low and Noltingk (1972); D.H. Allen (1973); N.D. Cox (1973); Eames (1973 UKAEA SRS/GR/12); Eames and Fothergill (1973 SRS/GR/13); Hensley (1973 UKAEA SRS/GR/1); Whitaker (1973a,b); S.B. Gibson (1974, 1976c); D.R. Wood *et al.* (1974); Henley and Gandhi (1975); Anon. (1976 LPB 11, p. 18; LPB 12, p. 17); Birbara (1976); Campbell and Gaddy (1976); Lees (1976b, 1977a); Sayers (1976); Bennett (1977); Berg (1977); J.H. Bowen (1977); Cannon (1977); Cerda and Napier (1977); Craker and Mobbs (1977); Doering and Gaddy (1977); McLntire (1977); R.W. Nelson (1977); Coltharp *et al.* (1978); Senior (1978); Doig and Reinten (1979); Isaszegi and Timar (1979); Kumamoto and Henley (1979); Mundo (1979); Aird (1980, 1981, 1984); Burton (1980); M.J. Harris and Rowe (1980); Leblanc *et al.* (1980); Sherwin and Lees (1980); Temple (1980); Butterfield (1981); Craker (1981); Dransfield and Lowe (1981); Keller and Stipho (1981); Stokoe *et al.* (1981); Sturrock (1981); Bradbury (1982); Corran and Witt (1982); Piccinnini and Anatra (1983); Sherwin (1983); Bosman (1985); Jebens (1986); Churchley (1987); Keey (1987); Fairclough (1988); Khadke *et al.* (1989); Beckman (1992b)

Other industries and systems
Burgess (1974); F.H. Thomas (1977); Blockley (1980); Kinkead (1982); Tregelles and Worthington (1982); Yao (1985); Harr (1987)

for Electronic Systems (Myers *et al.*, 1964), *Mathematical Theory of Reliability* (Barlow and Proschan, 1965), *Probabilistic Reliability: An Engineering Approach* (Shooman, 1968a), *Probabilistic Systems Analysis* (Breipohl, 1970), *Mechanical Reliability* (A.D.S. Carter, 1972; 2nd edn, 1986), *Reliability Technology* (A.E. Green and Bourne, 1972), *Reliability, Maintainability and Availability Assessment* (Locks, 1973), *Reliability Engineering in Design* (Kapur and Lamberson, 1977), *Engineering Reliability* (Dhillon and Singh, 1981), *Practical Reliability Engineering* (O'Connor, 1981; 2nd edn, 1984), *Reliability and Maintainability in Perspective* (D.J. Smith, 1988) *Reliability, Maintainability and Risk* (D.J. Smith, 1991), *Reliability Analysis and Prediction* (Misra, 1992), *Reliability and Risk* (Andrews and Moss, 1993), *The Reliability Availability and Productiveness of Systems* (Sherwin and Bossche, 1993) *and New Trends in System Reliability Evaluation* (Misra, 1994). It is intended that the material given in this chapter be supplemented by this literature.

7.1 Development of Reliability Engineering

Some of the earliest developments in reliability engineering occurred during the Second World War. The Germans had problems with the reliability of the V-1 missile (Bazovsky, 1961). The project team leader, Lusser, has described how the first approach taken to the problem was based on the argument that a chain is no stronger than its weakest link. This concentrated attention on the small number of low reliability components. But this approach was not successful. It was then pointed out by a mathematician, Pieruschka, that the probability of success p in a system in which all the components must work if the system is to work is the product of the individual probabilities of success p_i:

$$p = \prod_{i=1}^{n} p_i \qquad [7.1.1]$$

This drew attention to the need to improve the reliability of the many medium reliability components. This approach was much more successful in improving missile reliability. Equation 7.1.1 is known as Lusser's product law of reliabilities.

On the other side of the Channel, Blackett (1962) was drawing attention to the significance of Equation 7.1.1 to military operations in general:

> In the simplest case of air attack on a ship, the four main probabilities are (1) the chance of a sighting, (2) the chance the aircraft gets in an attack, (3) the chance of a hit on a ship, and (4) the chance that the hit causes the ship to sink.

This work was the beginning of operational research.

The US armed forces also had serious reliability problems, particularly with vacuum tubes used in electronic equipment. Studies of electronic equipment reliability at the end of the War showed some startling situations (Shooman, 1968a). In the Navy the number of vacuum tubes in a destroyer had risen from 60 in 1937 to 3200 in 1952. A study conducted during manoeuvres revealed that equipment was operational only 30% of the time. An Army study showed that equipment was broken down between two-thirds and three-quarters of the time. The Air Force found that over a 5-year period, maintenance and repair costs of equipment exceeded the initial cost by a factor of 10. It was also discovered that for every vacuum tube in use there was one held as spare and seven in transit, and that one electronics technician was needed for every 250 vacuum tubes. These studies illustrate well the typical problems in reliability engineering, which is concerned not only with reliability but also with availability, maintenance and so on.

From these early beginnings the study of reliability has become a fully developed discipline. It has received particular impetus from the reliability requirements in the fields of defence and aerospace, and electronics and computers. Perhaps the most spectacular example is the moonshots, which depended crucially on reliability technology.

One of the main fields of application of reliability engineering has been in electronic equipment. Such equipment typically has a large number of components. Initially, the reliability of electronic equipment was much less than that of mechanical equipment. But the application of reliability engineering to electronic equipment has now made it generally as reliable.

Another area in which reliability engineering has been widely used is nuclear energy. Methods have had to be developed to assess the hazards of nuclear reactors and to design instrument trip systems to shut them down safely.

In the United Kingdom, work on reliability of nuclear reactors has been done by the UK Atomic Energy Authority (UKAEA), originally through its Health and Safety Branch and subsequently through the Safety and Reliability Directorate (SRD), which runs the National Centre for Systems Reliability (NCSR) and the Systems Reliability Service (SRS). The latter operates a consultancy service on industrial reliability problems and a failure data bank.

The development of reliability engineering and of loss prevention in the chemical and petroleum industries has been described in Chapter 1.

7.2 Reliability Engineering in the Process Industries

7.2.1 Applicability of reliability techniques

It is entirely right that the process industries should seek to apply the techniques and obtain the benefits of reliability engineering. But it is important to recognize that reliability engineering as a discipline has grown up outside these industries. It is to be expected, therefore, that the techniques will need to be adapted to and developed for the problems of the process industries. A similar adaptation was necessary in order to apply control engineering to process problems. The process industries are particularly concerned with mechanical equipment reliability. This is proving a rather more intractable problem.

7.2.2 Reliability assessment and improvement

Reliability engineering involves an iterative process of reliability assessment and improvement, and the relationship between these two aspects is important. Work on the reliability of a system necessarily involves assessment of that reliability. In some cases the assessment shows that the system is sufficiently reliable. In other cases the reliability is found to be inadequate, but the assessment work reveals ways in which the reliability can be improved. It is generally agreed that the value of reliability assessment lies not in the figure obtained for system reliability, but in the discovery of the ways in which reliability can be improved.

The reliability engineer, however, cannot wait until his fellow engineers have solved all their reliability problems. It is his job to identify the areas where improvements are essential for success. But for the rest, he is obliged to accept, as given, the levels of reliability currently being achieved. This is not the case, however, with other engineers. It is they who are in a position to reduce the number of failures. They too should use reliability techniques. But it would be disastrous if they were to take the existing level of reliability as unalterable.

7.2.3 Reliability and other probabilistic methods

Loss prevention makes use of a wide range of probabilistic methods. A large proportion of these are reliability techniques as conventionally defined, but in addition, use is made of other probabilities. In particular, there is considerable emphasis in loss prevention on the assessment of the consequences of failures, taking into account factors such as numbers of people exposed, weather conditions, etc.

7.2.4 Reliability and quality control

There is a close link between reliability and quality control of equipment. But the two are not identical and the distinction between them is important. An equipment is likely to be unreliable unless there is good quality control over its manufacture. In general, quality control is a necessary condition for reliability. It is not, however, a sufficient condition. Deficiencies in specification, design or application are also causes of unreliability. A badly designed equipment may be manufactured with good quality control, but it will remain unreliable. This aspect is discussed in more detail by F. Nixon (1971).

7.2.5 Reliability standards

The principal British Standards dealing with reliability are BS 4778: 1979 Quality Vocabulary, for terminology, and BS 5760: 1981 Reliability of Systems, Equipment and Components. BS 4200: 1967 Guide on the Reliability of Electronic Equipment and Parts Used Therein, which dealt both with terminology and other matters, is now withdrawn.

The constituent parts of BS 5760 are Part 0: 1986 Introductory Guide to Reliability, Part 1: 1985 Guide to Reliability and Maintainability Programme Management, Part 2: 1981 Guide to the Assessment of Reliability, Part 3: 1982 Guide to Reliability Practices: Examples, Part 4: 1986 Guide to Specification Clauses Relating to the Achievement and Development of Reliability in New and Existing Items, Part 5: 1991 Guide to Failure Modes, Effects and Criticality Analysis (FMEA and FMECA), Part 6: 1991 Guide to Programmes for Reliability Growth, Part 7: 1991 Guide to Fault Tree Analysis, Part 9: 1991 Guide to the Block Diagram Technique, and Part 10: 1993 Guide to Reliability Testing.

Another widely quoted set of standards is the US Armed Services MIL standards, and handbooks. Terminology is given in MIL-STD-721B and MIL-STD-781B. Standards dealing with reliability include MIL-STD-756 Reliability Prediction, MIL-STD-781A Reliability Tests: Exponential Distribution, MIL-STD-7810 Reliability Design Qualification and Production Acceptance Tests, MIL-STD-785 Requirements for Reliability Program, and MIL-STD-1635 Reliability Growth Theory, and handbooks MIL-HDBK-189 Reliability Growth Management and MIL-HDBK-217 Reliability Prediction of Electronic Equipment. Maintainability is covered in MIL-STD-470 Maintainability Program Requirements, MIL-STD-471 Maintainability Demonstration and MIL-HDBK-472 Maintainability Prediction.

7.3 Definition of Reliability

Definitions of reliability are given in various British Standards dealing with terminology on quality and reliability. BS 4778: Part 1: 1987 defines reliability as

> The ability of an item to perform a required function under stated conditions for a stated period of time.

This supersedes the definition given in BS 4200: Part 2: 1974, which has now been withdrawn. Further, essentially similar, definitions are given in BS 4778: Section 3.1: 1991 and BS 4778: Section 3.2: 1991. BS 4778: Section 3.1: 1991 states that in definitions relating to reliability, the word

'time' may be replaced by 'distance', 'cycles', or other quantities or units, as appropriate.

An alternative definition of reliability is: 'The probability that an item will perform a required function under stated conditions for a stated period of time'. This definition brings out several important points about reliability: (1) it is a probability, (2) it is a function of time, (3) it is a function of defined conditions and (4) it is a function of the definition of failure.

Some definitions of failure are: (1) failure in operation, (2) failure to operate on demand, (3) operation before demand and (4) operation after demand to cease. The first of these definitions is applicable to an equipment which operates continuously, while the other definitions are applicable to one which operates on demand.

7.4 Meanings of Probability

It may appear intuitively obvious what is meant by probability, but the word, in fact, has several meanings. Moreover, the distinctions are of some practical importance. They are relevant, for example, to the question of the relative weight that should be attached to field data and to other information available to individuals.

7.4.1 Equal likelihood

One definition of probability derives from the principle of equal likelihood. If a situation has n equally likely and mutually exclusive outcomes, and if nA of these outcomes are event A, then the probability $P(A)$ of event A is:

$$P(A) = \frac{n_A}{n} \qquad [7.4.1]$$

This probability can be calculated *a priori* and without doing experiments.

The example usually given is the throw of an unbiased die, which has six equally likely outcomes: the probability of throwing a one is 1/6. Another example is the withdrawal of a ball from a bag containing four white balls and two red ones: the probability of withdrawing a red one is 1/3. The principle of equal likelihood applies to the second case also, because, although the likelihood of withdrawing a red ball and a white one are unequal, the likelihood of withdrawing any individual ball is equal.

This definition of probability is often of limited usefulness in engineering because of the difficulty of defining situations with equally likely and mutually exclusive outcomes.

7.4.2 Relative frequency

The second definition of probability is based on the concept of relative frequency. If an experiment is performed n times and if the event A occurs on nA of these occasions, then the probability $P(A)$ of event A is:

$$P(A) = \lim_{n\to\infty} \frac{n_A}{n} \qquad [7.4.2]$$

This probability can only be determined by experiment. This definition of reliability is the one that is most widely used in engineering. In particular, it is this definition that is implied in the estimation of probability from field failure data.

7.4.3 Personal probability

A third definition of probability is degree of belief. It is the numerical measure of the belief which a person has that the event will occur. Often this corresponds to the relative frequency of the event. But this is not always so, for several reasons. One is that the relative frequency data available to the individual may be limited or nonexistent. Another is that even if he has such data, he may have other information which causes him to think that the data are not the whole truth. There are many possible reasons for this. The individual may doubt the applicability of the data to the case under consideration, or he may have information which suggests that the situation has changed since these data were collected.

It is entirely legitimate to take into account such personal probabilities:

> Personal probability was cast into disrespect during the nineteenth century when science was believed to be absolute truth, because, with this definition the results will depend upon the person solving the problem. However, this objection to subjectivity has recently been countered quite effectively by Savage, Janes and other physical scientists. (Breipohl, 1970, p. 6)

There are several branches of probability theory which attempt to accommodate personal probability. These include ranking techniques (e.g., Siegel, 1956), which give the numerical encoding of judgements on the probability of ranking of items, and Bayesian methods (e.g., Breipohl, 1970), which allow probabilities to be modified in the light of additional information.

Further discussions of personal probability are given by Savage (1962) and by Tribus (1969).

7.5 Some Probability Relationships

It is appropriate to give, at this point, a brief treatment of some basic probability relationships. These are important in the present context not only because they are the basis of reliability expressions, but also because they are needed for work in areas such as fault trees.

7.5.1 Sets and Boolean algebra

Some set theory definitions, operations and laws are given in Table 7.2 and some of these are illustrated by the Venn diagrams given in Figure 7.1.

The union and intersection of sets may be written, respectively, in the notation

$$C = A \cup B \qquad [7.5.1]$$

and

$$C = A \cap B \qquad [7.5.2]$$

or in the notation

$$C = A + B \qquad [7.5.3]$$

and

$$C = A \cdot B = AB \qquad [7.5.4]$$

It is mainly the latter notation that is used here.

Table 7.2 *Some set theory definitions, operations and laws*

Definitions:	
Null set Ø	Ø is a set with no elements
Sample space set S	S is the set containing all the elements in the sample space
Elements	
$a \in A$	a is an element of A
Subsets	
$A \subset B$	A is a subset of B
$B \supset A$	B contains A
$A \subseteq B$	A is a subset of B or is equal to B
Equality	
$A = B$	A has the same elements as B
$A = \emptyset$	A has no elements
Operations:	
Union of sets	
$C = A \cup B$ also writen $C = A + B$	C contains all the elements of A and B
Intersection of sets	
$C = A \cap B$ also written $C = AB$ or $A \cdot B$ $C = A$ and B	C contains only the elements common to A and B
Disjoint sets (mutually exclusive sets)	
$C = A \cap B = \emptyset$	C contains all the elements of A which are not elements of B
Difference of sets	
$C = A - B$	
Complement of a set[a]	
$A' = \mathrm{S} - A$	A' contains all the elements of S which are not elements of A
Laws:	
Commutative laws	
$A + B = B + A$	
$AB = BA$	
Associative laws	
$(A + B) + C = A + (B + C) = A + B + C$	
$(AB)C = A(BC) = ABC$	
Distributive laws	
$A(B + C) = AB + AC$	
$A + BC = (A + B)(A + C)$	
Absorption laws	
$A + A = A$	
$AA = A$	
Dualization (de Morgan's) laws	
$(A + B)' = A'B'$	
$(AB)' = A' + B'$	

[a] Use may also be made of the notation $\bar{A}$ to signify 'not A.'

Attention is drawn in particular to the distributive and absorption laws, which differ somewhat from their apparent analogues in normal algebra. Set theory and Boolean algebra are described in standard texts (e.g., Reza, 1961; Shooman, 1968a; Breipohl, 1970). Probability and set theory are closely related, because the outcomes of a situation constitute, in effect, a set.

7.5.2 Probability of unions

The probability of an event X which occurs if any of the events A_i occur and is thus the union of those events is:

$$P(\mathrm{X}) = P\left(\bigcup_{i=1}^{n} A_i\right) \qquad [7.5.5]$$

If there are two events:

$$P(X) = P(A_1) + P(A_2) - P(A_1A_2) \qquad [7.5.6]$$

If there are three events:

$$P(X) = P(A_1) + P(A_2) + P(A_3) - P(A_1A_2) - P(A_1A_3) - P(A_2A_3) + P(A_1A_2A_3) \qquad [7.5.7]$$

If there are n events:

$$P(X) = P(A_1) + P(A_2) + \cdots + P(A_n) - P(A_1A_2) - P(A_1A_3) - \cdots - P(A_{n-1}A_n) + P(A_1A_2A_3) + P(A_1A_2A_4) + \cdots + P(A_{n-2}A_{n-1}A_n) \cdots (-1)^{n-1} P(A_1A_2 \cdots A_n) \qquad [7.5.8]$$

If the events are mutually exclusive, Equation 7.5.5 simplifies to:

$$P(X) = \sum_{i=1}^{n} P(A_i) \qquad [7.5.9]$$

In general:

$$P\left(\bigcup_{i=1}^{n} A_i\right) \leq P \sum_{i=1}^{n} P(A_i) \qquad [7.5.10]$$

For events not mutually exclusive but of low probability the error in using Equation 7.5.9 instead of Equation 7.5.5 is small. Equation 7.5.9 is sometimes called the low probability, or rare event, approximation. The estimate of probability given by Equation 7.5.9 errs on the high side and hence is conservative in calculating failure probabilities, but is not conservative in calculating success probabilities or reliabilities.

7.5.3 Joint and marginal probability

So far the events considered are the outcomes of a single experiment. Consideration is now given to events which are the outcome of several subexperiments.

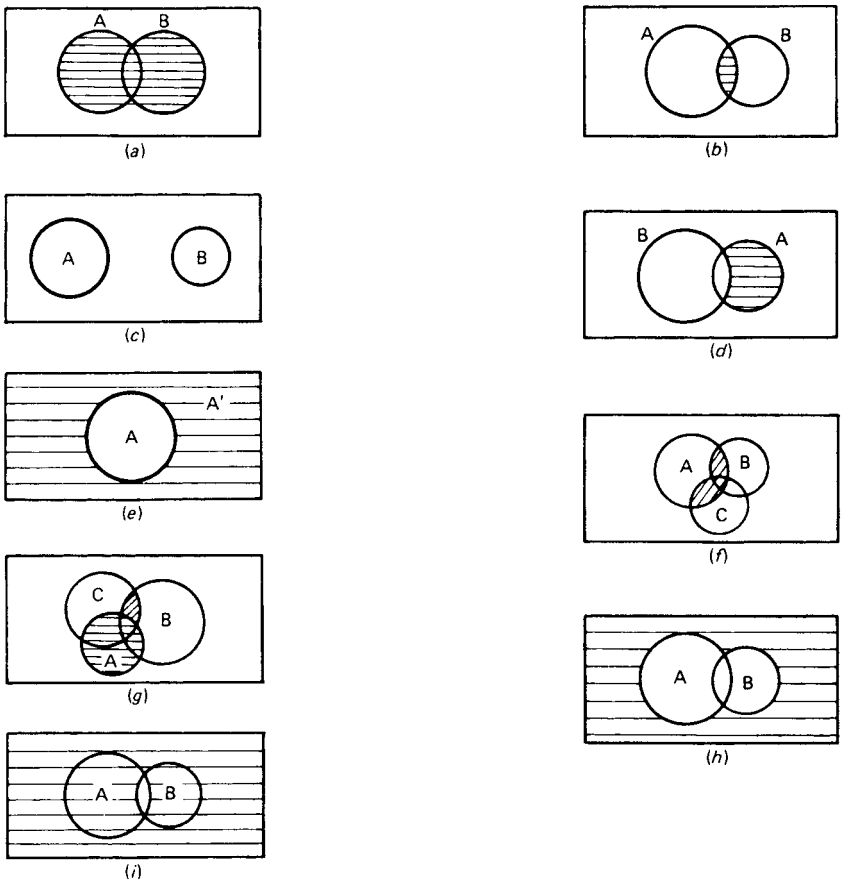


Figure 7.1 *Some set theory definitions, operations and laws: (a) union of sets, A + B: (b) intersection of sets, AB; (c) disjoint sets; (d) difference of sets, A − B; (e) complement of a set; (f) distributive law, A(B + C) = AB + AC; (g) distributive law, (A + B)(A + C) = A + BC; (h) dualization law (A + B) = A′B′; (i) dualization law (AB)′ = A′ + B′*

The probability of an event X which occurs only if all the n events A_i, occur and is thus the intersection of these events is:

$$P(X) = P(A_1 \cdots A_n) = P\left(\bigcap_{i=1}^{n} A_i\right) \quad [7.5.11]$$

$P(A_1 \cdots A_n)$ is the joint probability of the event.

The probability of an event X which occurs if any of the mutually exclusive and exhaustive n events A_i in one subexperiment occurs and the event B in a second subexperiment occurs is:

$$P(X) = P\left(\bigcup_{i=1}^{n} A_i B\right) \quad [7.5.12]$$

$$= \sum_{i=1}^{n} P(A_i)P(B) \quad [7.5.13]$$

$$= P(B) \quad [7.5.14]$$

$P(B)$ is the marginal probability of the event.

7.5.4 Conditional probability

The probability of an event X which occurs if the event A occurs in one subexperiment and the event B occurs in a second subexperiment where the event A depends on the event B is:

$$P(X) = P(AB) = P(A \mid B)P(B) \quad [7.5.15]$$

$P(A \mid B)$ is the conditional probability of A, given B.

The probability obtained in Equation 7.5.15 is a joint probability. Marginal probabilities may also be obtained from conditional probabilities:

$$P(X) = P(B) = \sum_{i=1}^{n} P(B \mid A_i)P(A_i) \quad [7.5.16]$$

7.5.5 Independence and conditional independence

If events A and B are independent:

$$P(AB) = P(A \mid B)P(B) = P(A)P(B) \quad [7.5.17]$$

which is equivalent to

$$P(A \mid B) = P(A) \quad [7.5.18]$$

The probability of an event X, which occurs only if all n events A_i occur is given by Equation 7.5.11. If all n events are independent:

$$P(X) = P(A_1 \cdots A_n) = \prod_{i=1}^{n} P(A_i) \quad [7.5.19]$$

Two events A and B are conditionally dependent if their relationship with a third event C is:

$$P(AB \mid C) = P(A \mid C)P(B \mid C) \quad [7.5.20]$$

Conditional independence does not imply independence.

7.5.6 Bayes' theorem

The relationship given in Equation 7.5.15 is a form of Bayes' theorem. This theorem is extremely important in probability work. It appears in various forms, some of which are:

$$P(AB) = P(A \mid B)P(B) = P(B \mid A)P(A) \quad [7.5.21]$$

$$P(A \mid B) = \frac{P(AB)}{P(B)} = \frac{P(B \mid A)P(A)}{P(B)} \quad [7.5.22]$$

On rewriting the denominator as a marginal probability, and A as A_k

$$P(A_k \mid B) = \frac{P(B \mid A_k)P(A_k)}{\sum_{i=1}^{n} P(B \mid A_i)P(A_i)} \quad [7.5.23]$$

where $P(A_k \mid B)$ is the posterior probability, $P(B \mid A_k)$ is the likelihood, and $P(A_k)$ is the prior probability.

Further treatment of Bayes' theorem is given in Section 7.14.

7.6 Some Reliability Relationships

7.6.1 Reliability function and hazard rate

If n equipments operate without replacement, then after time t the numbers which have survived and failed are $n_s(t)$ and $n_f(t)$, respectively, and the probability of survival, or reliability, $R(t)$ is:

$$R(t) = 1 - \frac{n_f(t)}{n} \quad [7.6.1]$$

The instantaneous failure rate, or failure rate expressed as a function of the number of equipments surviving, $z(t)$ is:

$$z(t) = \frac{1}{n - n_f}\frac{\mathrm{d}n_f(t)}{\mathrm{d}t} = -\frac{1}{R(t)} \cdot \frac{\mathrm{d}r(t)}{\mathrm{d}t} = -\frac{\mathrm{d}[\ln R(t)]}{\mathrm{d}t} \quad [7.6.2]$$

$z(t)$ is also called the 'hazard rate', or just the 'failure rate'.

The cumulative hazard function $H(t)$ is:

$$H(t) = \int_0^t z(t)\,\mathrm{d}t \quad [7.6.3]$$

Then, by integration of Equation 7.6.2 the reliability $R(t)$ is

$$R(t) = \exp\left(-\int_0^t z(t)\,\mathrm{d}t\right) = \exp[-H(t)] \quad [7.6.4]$$

$R(t)$ is also called the 'reliability function'.

7.6.2 Failure density and failure distribution functions

The overall failure rate, or failure rate expressed as a function of the original number of equipments, $f(t)$ is:

$$f(t) = \frac{1}{n}\frac{\mathrm{d}n_f(t)}{\mathrm{d}t} = -\frac{\mathrm{d}R(t)}{\mathrm{d}t} \quad [7.6.5]$$

$f(t)$ is also called the 'failure density function'.

The complement of the reliability, or the unreliability, $Q(t)$ is:

$$Q(t) = 1 - R(t) \quad [7.6.6]$$

$Q(t)$ is also called the 'failure distribution function' and is then commonly written as $F(t)$.

The failure density function and failure distribution function are often referred to, respectively, as the 'failure density' or the 'density function' and the 'failure distribution', the 'distribution function' or the 'cumulative distribution function'.

7.6.3 Relationships between basic functions

The following relationships can readily be derived from Equations 7.6.1–7.6.6 and are particularly useful:

$$z(t) = \frac{f(t)}{R(t)} \quad [7.6.7a]$$

$$= \frac{f(t)}{1 - Q(t)} = \frac{f(t)}{1 - F(t)} \quad [7.6.7b]$$

$$R(t) = \int_t^{\infty} f(t)\,\mathrm{d}t \quad [7.6.8]$$

$$Q(t) = F(t) = \int_0^t f(t)\,\mathrm{d}t \quad [7.6.9]$$

7.6.4 Exponential distribution

An important special case is that in which the hazard rate $z(t)$ is constant:

$$z(t) = \lambda \quad [7.6.10]$$

Then,

$$R(t) = \exp(-\lambda t) \quad [7.6.11]$$

$$f(t) = \lambda \exp(-\lambda t) \quad [7.6.12]$$

$$Q(t) = 1 - \exp(-\lambda t) \quad [7.6.13]$$

These four quantities are shown in Figure 7.2.

In Figure 7.2, the vertical axes for the reliability $R(t)$ and the unreliability $Q(t)$ have the range 0 to 1, but those for the hazard rate $z(t)$ and the failure density function $f(t)$ are proportional to λ. At low values of λt:

$$R(t) = 1 - \lambda t \qquad \lambda t \ll 1 \quad [7.6.14]$$

$$Q(t) = \lambda t \qquad \lambda t \ll 1 \quad [7.6.15]$$

Equation 7.6.14 is useful in obtaining accuracy in numerical computation of high values of the reliability $R(t)$. Equation

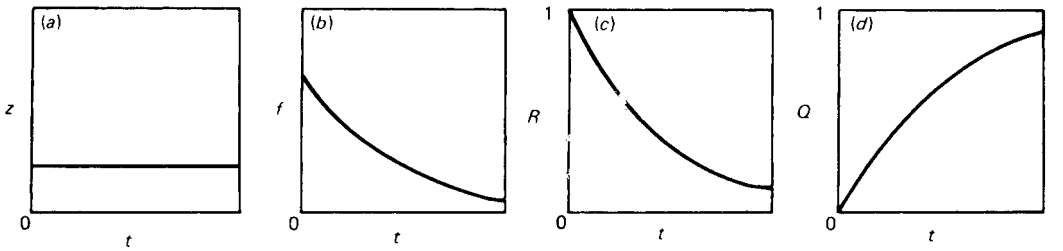


Figure 7.2 *The exponential distribution: (a) hazard-rate; (b) failure density; (c) reliability; (d) unreliability*

7.6.15 is useful in making simple computations of the unreliability $Q(t)$. This latter point is further discussed below.

The assumption of constant hazard rate is that normally made in the absence of other information. This is therefore a special case of particular importance.

The failure distribution with constant hazard rate is called the 'exponential distribution' or, more accurately but less commonly, the 'negative exponential distribution'. It is also referred to as the 'random failure distribution', although in most cases it is a moot point whether the failures are appropriately called random.

7.6.5 Probability and event rate

The relationship between unreliability and hazard rate represented by Equation 7.6.13, or more generally the relationship between the probability $P(t)$ and the event rate ζ

$$P(t) = 1 - \exp(-\zeta t) \qquad [7.6.16]$$

is an important one. It is frequently necessary in reliability work to calculate a probability from a rate, or vice versa, and it is this equation which then applies.

7.6.6 Unreliability and failure rate

There is sometimes confusion between unreliability $Q(t)$ and failure rate λ. This confusion arises because, given certain assumptions, the two are numerically identical. This occurs if in Equation 7.6.15 time t is equal to unity. Then,

$$Q(t) = \lambda \qquad \lambda \ll 1 \qquad [7.6.17]$$

Thus, for example, if a device has a failure rate $A = 0.01$ faults/year, then the unreliability over a year is also numerically 0.01. Error occurs, however, if Equation 7.6.15 is used outside its range of applicability.

7.6.7 Bathtub curve

In general, the failure behaviour of an equipment exhibits three stages: initially during commissioning the rate is high, then it declines during normal operation, and finally it rises again as deterioration sets in. For many equipments, particularly electronic equipments, the rate has been found to form a bathtub curve, as shown in Figure 7.3(a) (e.g., Carhart, 1953). This curve has three regimes: (1) early failure, (2) constant failure and (3) wear-out failure.

Early failure, or infant mortality, is usually due to such factors as defective equipment, incorrect installation, etc. It also tends to reflect the learning curve of the equipment user. Constant failure, or so-called 'random failure', is often caused by random fluctuations of load which exceed the design strength of the equipment. A constant failure

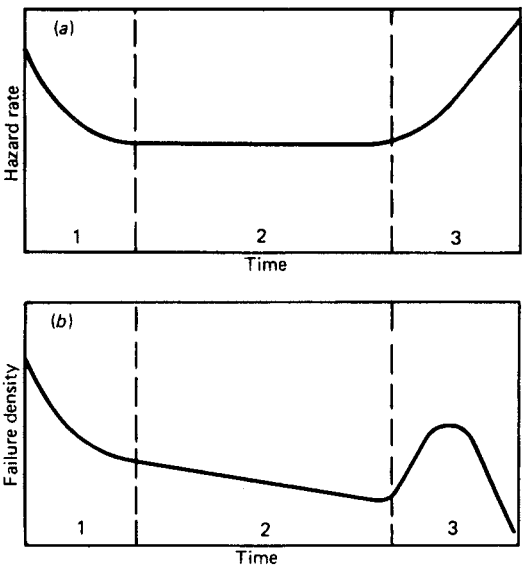


Figure 7.3 *The bathtub curve: (a) hazard rate; (b) failure density*

characteristic is also shown by an equipment which has a number of components that individually exhibit different failure distributions. Wear-out failure is self-explanatory. The corresponding curve for the failure density function is shown in Figure 7.3(b). The bathtub curve is widely quoted in the reliability literature, but it should be emphasized that its applicability to all types of equipment, particularly mechanical equipment, is not established. There are, in fact, good theoretical reasons for treating it with reserve (A.D.S. Carter, 1973). This aspect is considered in more detail below.

It is often said that human mortality follows a bathtub curve. This implies that there are higher death rates in infancy and old age with a lower, nearly constant, death rate in between. However, Aird (1978) has shown that for humans the infant mortality period is followed immediately by the onset of the wear-out period, so that there is effectively no constant failure period.

7.6.8 Mean life

The mean life m is defined as the first moment of the failure density function

$$m = \int_0^\infty tf \, dt \qquad [7.6.18]$$

Alternatively, from Equations 7.6.5 and 7.6.18

$$m = -\int_0^\infty t\frac{dR}{dt}\, dt \qquad [7.6.19a]$$

$$= -[tR]_0^\infty + \int_0^\infty R \, dt \qquad [7.6.19b]$$

Since

$$[tR]_0^\infty = 0$$

provided that

$$\lim_{t\to\infty} (tR) = 0$$

then

$$m = \int_0^\infty R \, dt \qquad [7.6.20]$$

Alternatively, use may be made of the relationships between the moments μ_i and the Laplace transform $\bar{g}(s)$ of a function $g(t)$:

$$\mathcal{L}[g(t)] = \bar{g}(s) = \int_0^\infty g(t)\exp(-st)\, dt \qquad [7.6.21]$$

Hence:

$$\frac{d^i\bar{g}(s)}{ds^i} = (-1)^i \int_0^\infty t^i g(t)\exp(-st)\, dt \qquad [7.6.22]$$

and

$$\left(\frac{d^i\bar{g}(s)}{ds^i}\right)_{s=0} = (-1)^i \int_0^\infty t^i g(t)\, dt \qquad [7.6.23a]$$

$$= (-1)^i \mu_i \qquad [7.6.23b]$$

Applying these relationships to the present case by substituting dR/dt for $g(t)$ in Equation 7.6.23a,

$$m = \left(\frac{d[sR - R(0)]}{ds}\right)_{s=0} = (R)_{s=0} \qquad [7.6.24]$$

For the exponential distribution

$$m = \int_0^\infty t\lambda\exp(-\lambda t)\, dt \qquad [7.6.25a]$$

$$= \frac{1}{\lambda} \qquad [7.6.25b]$$

Other terms used in addition to 'mean life' are the mean time between failures (MTBF), the mean time to failure (MTTF) and the mean time to first failure (MTTFF). These times are sometimes used interchangeably, but they are not identical.

The most widely used is probably MTBF. MTBF has meaning only when applied to a population of components, equipments or systems in which there is repair. It is the total operating time of the items divided by the total number of failures. It is also the mean of the failure distribution, regardless of its form.

MTTF is applied to items without repair and is the mean of the distribution of times to failure. MTTFF is applied to items with repair and is the mean of the distribution of times to first failure.

MTTF and MTTFF are applied particularly to systems. For an n-component parallel system with an exponential failure distribution of the individual components and without repair,

$$\text{MTTF} = \sum_{i=1}^{n} \frac{1}{i\lambda} \qquad [7.6.26]$$

and for an n-component parallel system with repair

$$\text{MTTFF} = \frac{1}{\lambda}\cdot\sum_{i=0}^{n-1} \frac{(1+\mu/\lambda)^i}{i+1} \qquad [7.6.27]$$

where λ is the failure rate of equipment, and μ is the repair rate of equipment Repair rates are discussed in Section 7.10. If the repair rate μ is zero, Equation 7.6.27 reduces to Equation 7.6.26.

Formal definitions of MTBF and MTTF are given in BS 4200: Part 2: 1967. For repairable systems use is also made of mean time to repair (MTTR). A more detailed discussion of these quantities is given by Myers *et al.* (1964).

7.6.9 Expected value

Use is frequently made in reliability engineering of the concept of the expected value. The expected value of a distribution is its mean value. The use of the expected value concept allows convenient manipulation, as the following treatment demonstrates. (A treatment of expected value is given by Breipohl (1970)). For a variable t, the expected value, or mean value, is:

$$m = E[t] \qquad [7.6.28]$$

The variance is:

$$\sigma^2 = E[(t-m)^2] \qquad [7.6.29]$$

The variance may then be expressed in the following alternative forms:

$$\sigma^2 = E[t^2 - 2mt + m^2] \qquad [7.6.30]$$

$$= E[t^2] - 2mE[t] + m^2 \qquad [7.6.31]$$

$$= E[t^2] - 2m^2 + m^2 \qquad [7.6.32]$$

$$= E[t^2] - m^2 \qquad [7.6.33]$$

$$= E[t^2] - E[t]^2 \qquad [7.6.34]$$

7.7 Failure Distributions

There are several statistical distributions which are fundamental in work on reliability. Important discrete distributions are:

(1) binomial distribution;
(2) multinomial distribution;
(3) Poisson distribution.

Important continuous distributions are:

(1) exponential distribution;
(2) normal distribution;

(3) log–normal distribution;
(4) Weibull distribution;
(5) rectangular distribution;
(6) gamma distribution;
(7) Pareto distribution;
(8) extreme value distribution.

Some properties of these distributions are given in Table 7.3 and in Figures 7.4 and 7.5.

The distributions are best regarded as statistical distributions and the independent variable t as a generalized variable, although in the present context the primary interest in many of these distributions is as failure distributions, with time as the independent variable. The distribution function is given as F rather than Q, but the two are identical.

Accounts of the properties of statistical distributions are given in most texts on reliability engineering and in the Center for Chemical Process Safety (CCPS) QRA Guidelines (1989/5). Additional treatments for particular distributions are mentioned below. A rather comprehensive summary of the principal distributions is given by Hastings and Peacock (1974).

7.7.1 Binomial distribution

The binomial distribution is applicable to situations where a series of discrete trials is conducted and each trial can have two outcomes. In reliability work these outcomes are usually success and failure. If the probabilities of success and failure are p and q, respectively, and if there are n trials, then:

$$(p+q)^n = \sum_{k=0}^{n} \binom{n}{k} p^k q^{n-k} = 1 \qquad [7.7.1]$$

with

$$\binom{n}{k} = \frac{n!}{(n-k)!k!} \qquad [7.7.2]$$

The rth term in the expansion in Equation 7.7.1 is the probability $P(r)$ of r events:

$$P(r) = \binom{n}{r} p^r q^{n-r} \qquad [7.7.3]$$

$P(r)$ is the probability density.

A useful expression is the probability $P(0 \le k \le r)$ of r or less than r events:

$$P(0 \le k \le r) = \sum_{k=0}^{r} \binom{n}{k} p^k q^{n-k} \qquad [7.7.4]$$

$P(0 \le k \le r)$ is the probability distribution.

Another useful expression is the probability $P(r \le k \le n)$ of r or more than r events:

$$P(r \le k \le n) = \sum_{k=r}^{n} \binom{n}{k} p^k q^{n-k} \qquad [7.7.5]$$

The coefficients in the expansion in Equation 7.7.3, or terms of $\binom{n}{r}$, may be obtained from Pascal's triangle

n	r	
0	0	1
1	0, 1	1 1
2	0, 1, 2	1 2 1
3	0, 1, 2, 3	1 3 3 1
4	0, 1, 2, 3, 4	1 4 6 4 1

A number in the triangle is obtained by summing the two numbers directly above it to the left and the right.

The mean of the binomial distribution is np and the variance is npq. The binomial distribution approximates to the normal distribution for large values of n and does so most rapidly for $p = q = 0.5$. The approximation holds for $p \le 0.5$ and $np \ge 5$ or for $p > 0.5$ and $nq > 5$. In terms of n and p the mean and variance of the normal distribution are np and $np(1-p)$, respectively. The binomial distribution approximates to the Poisson distribution for $p \le 0.05$ and $n \ge 20$. In terms of n and p, the mean of the Poisson distribution is np.

7.7.2 Multinomial distribution

The multinomial distribution is applicable to situations where a series of trials is conducted and each trial can have more than two outcomes. If the total number of trials is n, the number of outcomes is k, the probabilities of the outcomes are p_i, and the number of times each outcome occurs is n_i, then:

$$f(n_1, n_2, \ldots, n_k) = n! \prod_{i=1}^{k} \frac{p_i^{n_i}}{n_i!} \qquad [7.7.6]$$

$f(n_1, n_2, \ldots, n_k)$ is the probability density.

7.7.3 Poisson distribution

The Poisson distribution is applicable to situations where an event can occur at any point in time. If the mean number of events over a time period is μ so that in terms of the binomial distribution $\mu = np$, then:

$$\exp(-\mu)\exp(\mu) = \exp(-\mu)\sum_{k=0}^{\infty} \frac{\mu^k}{k!} \qquad [7.7.7a]$$

$$= \exp(-\mu)\left(1 + \mu + \frac{\mu^2}{2!} + \frac{\mu^3}{3!} + \cdots\right) \qquad [7.7.7b]$$

$$= 1 \qquad [7.7.7c]$$

The rth term in the expansion in Equation 7.7.7 is the probability $P(r)$ of r events:

$$P(r) = \exp(-\mu)\frac{\mu^r}{r!} \qquad [7.7.8]$$

$P(r)$ is the probability density.

A useful expression is the probability $P(0 \le k \le r)$ of r or less than r events:

$$P(0 \le k \le r) = \exp(-\mu)\sum_{k=0}^{r} \frac{\mu^k}{k!} \qquad [7.7.9]$$

$P(0 \le k \le r)$ is the probability distribution.

Table 7.3 *Some properties of failure distributions*

Distribution	*Failure density function* $f(t)$	*Mean* $m = \int_{-\infty}^{\infty} tf(t)\,\mathrm{d}t$	*Median* $= t$ *where* $\int_{-\infty}^{t} f(r)\,\mathrm{d}r = 0.5$	*Mode* $= t$ *where* $\frac{\mathrm{d}f(t)}{\mathrm{d}t} = 0$	*Variance* $\sigma^2 = \int_{-\infty}^{\infty}(t-m)^2 f(t)\,\mathrm{d}t$
Exponential	$\lambda \exp(-\lambda t)$	$\frac{1}{\lambda}$	$\frac{1}{\lambda}\ln 2$	0	$\frac{1}{\lambda^2}$
Normal	$\frac{1}{\sigma(2\pi)^{1/2}}\exp\left[-\frac{(t-m)^2}{2\sigma^2}\right]$	m	m	m	σ^2
Log–normal	$\frac{1}{\sigma t(2\pi)^{1/2}}\exp\left[-\frac{[\ln(t)-m^*]^2}{2\sigma^2}\right]$	$\exp\left(m^* + \frac{\sigma^2}{2}\right)$	$\exp(m^*)$	$\exp(m^* - \sigma^2)$	$\exp(2m^* + \sigma^2)[\exp(\sigma^2) - 1]$
Welbull (two-parameter)	$\frac{\beta}{\eta}\left(\frac{t}{\eta}\right)^{\beta-1}\exp\left[-\left(\frac{t}{\eta}\right)^{\beta}\right]$	$\eta\Gamma\left(1+\frac{1}{\beta}\right)$	$\eta(\ln 2)^{1/\beta}$	$\begin{matrix}\eta\left(1-\frac{1}{\beta}\right)^{1/\beta}, & \beta > 1 \\ 0, & \beta \le 1\end{matrix}$	$\eta^2\left\{\Gamma\left(1+\frac{2}{\beta}\right) - \left[\Gamma\left(1+\frac{1}{\beta}\right)\right]^2\right\}$
Rectangular	$\frac{1}{b}$	$a + \frac{b}{2}$	$a + \frac{b}{2}$	–	$\frac{b^2}{12}$
Gamma	$\frac{1}{b\Gamma(a)}\left(\frac{t}{b}\right)^{a-1}\exp\left(-\frac{t}{b}\right)$	ba	–[a]	$b(a-1),\ a \ge 1$	$b^2 a$
Pareto	$at^{-(a+1)}$	$\frac{a}{a-1},\ a > 1$	$2^{1/a}$	0	$\frac{a}{a-2} - \left(\frac{a}{a-1}\right)^2,\ a > 2$
Extreme value	$\frac{1}{b}\exp\left(\frac{t-a}{b}\right)\exp\left[-\exp\left(\frac{t-a}{b}\right)\right]$	$a + b\Gamma'(1)$[b]	$a + b\ln\ln 2$	a	$\frac{b^2\pi^2}{6}$

[a] No simple expression is available.
[b] $\Gamma'(1) = -0.57721$ is the first derivative of the gamma function.

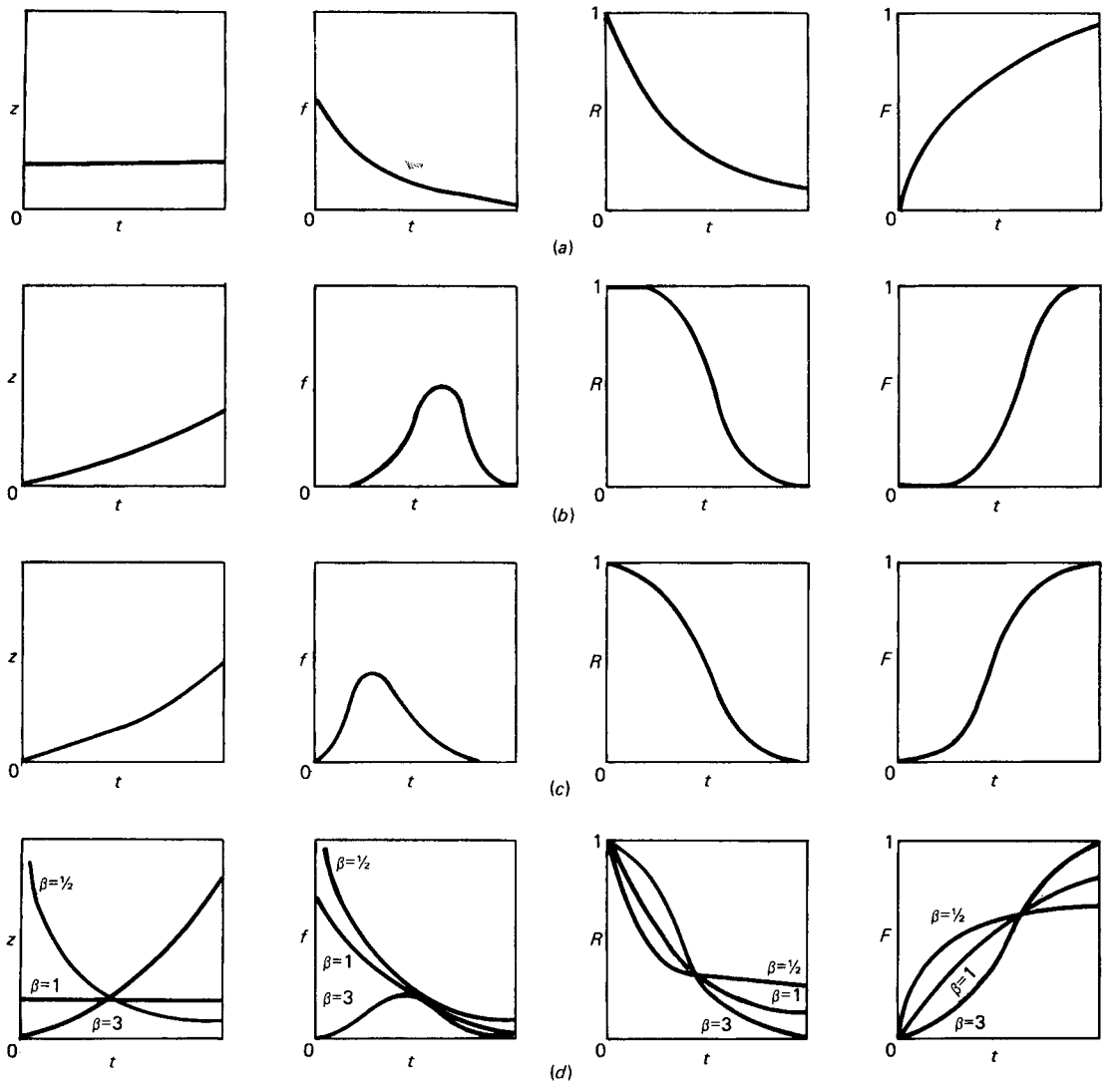


Figure 7.4 *Some failure distributions – 1: (a) exponential distinction; (b) normal distribution; (c) log–normal distribution; (d) Weibull distribution*

The relationship between the binomial and Poisson distributions may be seen by noting that the relation between the mean event rates for the distributions is:

$$\mu = np \qquad [7.7.10]$$

and writing the binomial distribution in the form:

$$\lim_{n\to\infty} \sum_{k=0}^{n} \binom{n}{k} \cdot \left(\frac{\mu}{n}\right)^k \cdot \left(1-\frac{\mu}{n}\right)^{n-k} = \sum_{k=0}^{\infty} \frac{\mu^k}{k!} \exp(-\mu) \qquad [7.7.11]$$

A derivation of the Poisson distribution from Markov models is given below.

7.7.4 Exponential distribution

For the exponential distribution, the characteristics hazard rate z, failure density f, reliability R and failure distribution F have been derived above, and are:

$$z = \lambda \qquad [7.7.12]$$

$$f = \lambda \exp(-\lambda t) \qquad [7.7.13]$$

$$R = \exp(-\lambda t) \qquad [7.7.14]$$

$$F = 1 - \exp(-\lambda t) \qquad [7.7.15]$$

for the range $0 \le t \le \infty$. These quantities are shown in Figure 7.4(a). The distribution is characterized by a single parameter, the hazard rate λ.

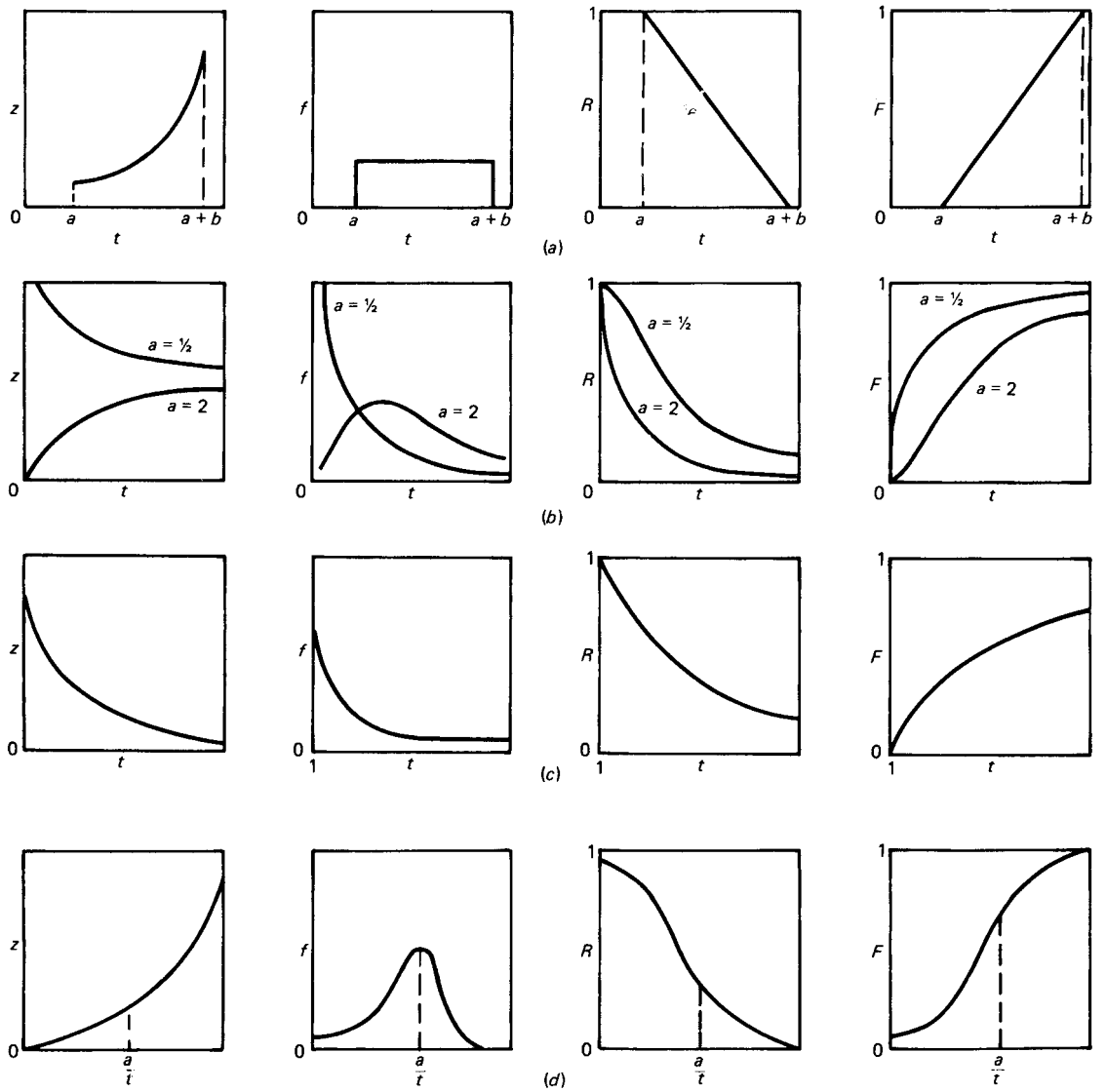


Figure 7.5 *Some failure distributions – 2: (a) rectangular distribution; (b) gamma distribution; (c) Pareto distribution; (d) extreme value distribution*

The exponential distribution, which has a constant hazard rate, is the distribution usually applied to data in the absence of other information and is the most widely used in reliability work.

7.7.5 Normal distribution

For the normal distribution the characteristics are:

$$z = \frac{\exp\left[-(t-m)^2/2\sigma^2\right]}{\int_t^\infty \exp\left[-(t-m)^2/2\sigma^2\right]\mathrm{d}t} \qquad [7.7.16]$$

$$f = \frac{1}{\sigma(2\pi)^{1/2}} \cdot \exp\left[-\frac{(t-m)^2}{2\sigma^2}\right] \qquad [7.7.17]$$

$$R = \frac{1}{\sigma(2\pi)^{1/2}} \cdot \int_t^\infty \exp\left[-\frac{(t-m)^2}{2\sigma^2}\right]\mathrm{d}t \qquad [7.7.18]$$

for the range $-\infty \leq t \leq \infty$. These quantities are shown in Figure 7.4(b).

The failure density f is the quantity most commonly used to define the normal distribution. It may be noted that Equations 7.7.16 and 7.7.18 describing the other quantities

are readily derived from Equations 7.6.7a and 7.6.8, respectively.

The distribution has two parameters, the mean m and the standard deviation σ. It is the natural distribution which is used to characterize data that lie about a mean value and deviate from it by absolute amounts. The normal distribution is widely used in reliability engineering, particularly to fit certain types of failure such as those due to wear out and to fit repair times.

7.7.6 Log–normal distribution

$$z = \frac{1/t \exp\{-[\ln(t) - m^*]^2/2\sigma^2\}}{\int_t^\infty \exp\{-[\ln(t) - m^*]^2/2\sigma^2\}\,\mathrm{d}t} \quad [7.7.19]$$

$$f = \frac{1}{\sigma t(2\pi)^{1/2}} \exp\left\{-\frac{[\ln(t) - m^*]^2}{2\sigma^2}\right\} \quad [7.7.20]$$

$$R = \frac{1}{\sigma(2\pi)^{1/2}} \int_t^\infty \exp\left\{-\frac{[\ln(t) - m^*]^2}{2\sigma^2}\right\} \mathrm{d}t \quad [7.7.21]$$

for the range $0 \le t \le \infty$. These quantities are shown in Figure 7.4(c).

The distribution has two parameters, m^* and σ. It is the natural distribution to use when deviations from the model value are by factors, proportions or percentages rather than by absolute values as in the normal distribution.

The log–normal distribution has a number of uses in reliability work. It is used to fit certain types of failure such as fatigue failures and to fit repair times. It is also used to describe the range of possible hazard rates of equipment where there is uncertainty about these. In this case the independent variable is the hazard rate z ($=\lambda$ for the exponential distribution) rather than time:

$$f(z) = \frac{1}{\sigma_z z(2\pi)^{1/2}} \exp\left\{-\frac{[\ln(z) - m_z^*]^2}{2\sigma_z^2}\right\} \quad [7.7.22]$$

The properties of the log–normal distribution are described in more detail by Aitcheson and Brown (1969).

7.7.7 Weibull distribution

For the Weibull distribution the characteristics are:

$$z = \frac{\beta}{\eta}\left(\frac{t-\gamma}{\eta}\right)^{\beta-1} \quad [7.7.23]$$

$$f = \frac{\beta}{\eta}\left(\frac{t-\gamma}{\eta}\right)^{\beta-1} \exp\left[-\left(\frac{t-\gamma}{\eta}\right)^{\beta}\right] \quad [7.7.24]$$

$$R = \exp\left[-\left(\frac{t-\gamma}{\eta}\right)^{\beta}\right] \quad [7.7.25]$$

for the range $\gamma \le t \le \infty$. These quantities are shown in Figure 7.4(d) for values of the parameter $\beta = 0.5$, 1.0 and 3.0.

The distribution given is the three-parameter one with the characteristic life η, the shape factor β and the location parameter γ. If the latter is set to zero, the two-parameter distribution is obtained.

The significance of the shape factor β is:

$\beta < 1$ hazard rate decreasing;
$\beta = 1$ hazard rate constant;
$\beta > 1$ hazard rate increasing.

By suitable choice of the shape factor β the Weibull distribution may be made to equal or approximate other distributions:

$\beta = 1$ exponential distribution;
$\beta = 2$ Rayleigh distribution.

A value of $\beta \approx 3.4$ corresponds approximately to a normal distribution in which the standard deviation is one-third of the mean.

There are several other versions of the two-parameter Weibull distribution. An alternative form (Truscott, 1970) has the characteristics:

$$z = \frac{\beta}{\alpha} t^{\beta-1} \quad [7.7.26]$$

$$f = \frac{\beta}{\alpha} t^{\beta-1} \exp\left(-\frac{t^\beta}{\alpha}\right) \quad [7.7.27]$$

$$R = \exp\left(-\frac{t^\beta}{\alpha}\right) \quad [7.7.28]$$

This is related to the previous form by:

$$\alpha = \eta^\beta \quad [7.7.29]$$

A third from (Shooman, 1968a) has the characteristics:

$$z = kt^m \quad [7.7.30]$$

$$f = kt^m \exp\left(-\frac{kt^{m+1}}{m+1}\right) \quad [7.7.31]$$

$$R = \exp\left(\frac{-kt^{m+1}}{m+1}\right) \quad [7.7.32]$$

This is related to the first form given by:

$$k = \frac{\beta}{\eta} \quad [7.7.33]$$

$$m = \beta - 1 \quad [7.7.34]$$

The Weibull distribution is frequently used in reliability work to fit failure data, because it is flexible enough to handle decreasing, constant and increasing failure rates. This use of the Weibull distribution is considered in more detail below.

The properties of the Weibull distribution are described in the original paper by Weibull (1951) and in standard texts (e.g., Bompas-Smith, 1973; Kapur and Lamberson, 1977).

7.7.8 Rectangular distribution

For the rectangular distribution the characteristics are:

$$z = \frac{1}{a+b-1} \quad [7.7.35]$$

$$f = \frac{1}{b} \quad [7.7.36]$$

$$R = \frac{a+b-t}{b} \quad [7.7.37]$$

for the range $a \le t \le a+b$. These quantities are shown in Figure 7.5(a).

The distribution is also called the 'uniform distribution' and has two parameters, the location parameter a and the scaling factor b.

The rectangular distribution is used in reliability work mainly to give random variables a uniform distribution across a specified interval. It is used, for example, in Monte Carlo simulation work. Computers generate pseudo-random numbers with a rectangular distribution. Random numbers with other distributions can be obtained from these, using the inverse cumulative distribution, where available, and other techniques.

7.7.9 Gamma distribution

For the gamma distribution the characteristics are:

$$z = \frac{t^{a-1}\exp(-t/b)}{\int_t^\infty t^{a-1}\exp(-t/b)\,\mathrm{d}t} \quad [7.7.38]$$

$$f = \frac{1}{b^a\Gamma(a)}\,t^{a-1}\exp(-t/b) \quad [7.7.39]$$

$$R = \frac{1}{b^a\Gamma(a)}\int_t^\infty t^{a-1}\exp(-t/b)\,\mathrm{d}t \quad [7.7.40]$$

for the range $0 \le t \le \infty$, with

$$\Gamma(a) = \int_0^\infty t^{a-1}\exp(-t)\,\mathrm{d}t \quad [7.7.41]$$

or, if a is an integer,

$$\Gamma(a) = (a-1)! \quad [7.7.42]$$

The quantities given in Equations 7.7.38–7.7.40 are shown in Figure 7.5(b) for values of the parameter $a = 0.5$ and 2.0.

The distribution has two parameters, the shape factor a and the scaling factor b.

The gamma distribution is another distribution used in reliability work to fit failure data, because it is sufficiently flexible to deal with decreasing, constant and increasing failure rates, but the Weibull distribution is more generally used.

7.7.10 Beta distribution

Use is also sometimes made in reliability engineering of the beta distribution. The properties of the beta distribution are given by Hastings and Peacock (1974). Its characteristics are:

$$f = \frac{x^{v-1}(1-x)^{w-1}}{B(v,w)} \quad [7.7.43]$$

$$F = \int_0^x \frac{x^{v-1}(1-x)^{w-1}}{B(v,w)}\,\mathrm{d}x \quad [7.7.44]$$

with

$$B(v,w) = \int_0^1 u^{v-1}(1-u)^{w-1}\,\mathrm{d}u \quad [7.7.45]$$

for the range $0 \ge x \ge 1$. The distribution has two parameters, v (>0) and w (>0). The beta function is related to the gamma function:

$$\Gamma(v)\tau(w) = B(v,w)\Gamma(v+w) \quad [7.7.46]$$

for positive values of v and w.

7.7.11 Pareto distribution

For the Pareto distribution the characteristics are:

$$z = \frac{a}{t} \quad [7.7.47]$$

$$f = at^{-(a+1)} \quad [7.7.48]$$

$$R = t^{-a} \quad [7.7.49]$$

for the range $1 \le t \le \infty$. These quantities are shown in Figure 7.5(c). The distribution has a single parameter, the shape factor a.

The Pareto distribution is commonly used in reliability work in discrete form to describe the distribution of the numbers of failures in different modes. In this case the independent variable is the failure mode.

7.7.12 Extreme value distribution

For the extreme value distribution the characteristics are:

$$z = \frac{1}{b}\exp\left(\frac{t-a}{b}\right) \quad [7.7.50]$$

$$f = \frac{1}{b}\exp\left(\frac{t-a}{b}\right)\exp\left[-\exp\left(\frac{t-a}{b}\right)\right] \quad [7.7.51]$$

$$R = \exp\left[-\exp\left(\frac{t-a}{b}\right)\right] \quad [7.7.52]$$

for the range $-\infty \le t \le \infty$. These quantities are shown in Figure 7.5(d).

Equations 7.7.50–7.7.52 are for the distribution of the smallest extreme. For the distribution of the largest extreme the sign of t should be reversed.

The distribution has two parameters, the location parameter a and the scaling factor b.

The extreme value distribution is used in reliability work to investigate extreme, and therefore very rare, values of phenomena.

7.7.13 Hyperexponential distribution

Another distribution which is sometimes used in reliability engineering is the hyperexponential distribution. This is described by Jardine (1970). Its characteristics are

$$z = \frac{2\lambda\{\sigma^2 + (1-\sigma^2)\exp[-2(1-2\sigma)\lambda t]\}}{\sigma + (1-\sigma)\exp[-2(1-2\sigma)\lambda t]} \quad [7.7.53]$$

$$f = 2\sigma^2\lambda\exp[-2\sigma\lambda t] + 2\lambda(1-\sigma^2)\exp[-2(1-\sigma)\lambda t] \quad [7.7.54]$$

$$F = 1 - \sigma\exp[-2\sigma\lambda t] + (1-\sigma)\exp[-2(1-\sigma)\lambda t] \quad [7.7.55]$$

for $t \ge 0$ and $0 < \sigma \le 0.5$. The distribution has two parameters, λ and σ, the former being the mean arrival rate of failures.

The hyperexponential distribution is suitable for the case where the times to failure are either very short or very long.

7.7.14 Error function

A mathematical function which occurs both in some of the distributions described and also in other topics treated here is the error function. Accounts of the error function are given in standard mathematical texts (e.g., Jensen and Jeffreys, 1963; Paradine and Rivett, 1980).

The error function erf is defined as:

$$\mathrm{erf}(x) = \frac{2}{\pi^{1/2}} \int_0^x \exp(-u^2)\,\mathrm{d}u \qquad [7.7.56]$$

The term $(2/\pi^{1/2})$ is a normalizing factor such as to yield

$$\mathrm{erf}(\infty) = 1 \qquad [7.7.57]$$

The error function complement erfc is defined as

$$\mathrm{erfc}(x) = 1 - \mathrm{erf}(x) \qquad [7.7.58]$$

$$\mathrm{erfc}(x) = \frac{2}{\pi^{1/2}} \int_x^\infty \exp(-u^2)\,\mathrm{d}u \qquad [7.7.59]$$

The integral which constitutes the error function is similar in form to those which occur in the distribution function of the normal distribution and in the log–normal distribution, as comparison of Equation 7.7.56 with Equations 7.7.18 and 7.7.21 shows. A similar integral also occurs in the definition of the probit Y described in Chapter 9.

Furthermore, in passive gas dispersion, the gas concentrations follow a normal, or Gaussian, distribution so that the models used for such dispersion are often referred to as 'Gaussian models'. These models are described in Chapter 15.

7.7.15 Error function approximations

The error function may be looked up in the tables given in standard texts on statistics, but it is convenient for computation to have it in analytical function form. A review of approximations of the error function has been given by Karlsson and Bjerle (1980). Two desirable properties of an expression for the error function are that it should represent the function with acceptable accuracy and should be capable of being inverted.

Karlsson and Bjerle give the following approximate expression of their own for the error function:

$$\mathrm{erf}(x) = \frac{2}{\pi^{1/2}} \sin[\sin(x)] \quad 0 \le x \le 1 \qquad [7.7.60a]$$

$$= \sin(x^{2/3}) \quad 1 \le x \le 2 \qquad [7.7.60b]$$

$$= 1 \quad 2 \le x \le \infty \qquad [7.7.60c]$$

They also give the following approximation for the error function inverse

$$\mathrm{erf}^{-1}(y) = \sin^{-1}\left[\sin^{-1}\left(\frac{y\pi^{1/2}}{2}\right)\right] \quad 0 \le y \le 0.84 \qquad [7.7.61a]$$

$$= [\sin^{-1}(y)]^{3/2} \quad 0.84 \le y \le 0.995 \qquad [7.7.61b]$$

7.8 Reliability of Some Standard Systems

The reliability of some standard systems is now considered. It is assumed that the exponential failure distribution applies, unless otherwise stated.

7.8.1 Series systems

A series system is one which operates only if all its components operate. It is not implied that the components are necessarily laid out physically in series configuration. For a series system the reliability R is the product of the reliabilities R_i of the components:

$$R = \prod_{i=1}^{n} R_i \qquad [7.8.1]$$

This follows directly from Equation 7.5.19.

For the exponential distribution, if the failure rates of the components are constants λ_i,

$$R_i = \exp(-\lambda_i) \qquad [7.8.2]$$

and hence

$$R = \prod_{i=1}^{n} \exp(-\lambda_i t) = \exp\left(-\sum_{i=1}^{n} \lambda_i t\right) \qquad [7.8.3]$$

If the overall failure rate of the system is a constant λ,

$$R = \exp(-\lambda t) \qquad [7.8.4]$$

and hence

$$\lambda = \sum_{i=1}^{n} \lambda_i \qquad [7.8.5]$$

7.8.2 Parallel systems

A parallel system is one which fails to operate only if all its components fail to operate. Again it is not implied that the components are necessarily laid out physically in a parallel configuration. For a parallel system, the unreliability Q is the product of the unreliabilities Q_i of the components:

$$Q = \prod_{i=1}^{n} Q_i \qquad [7.8.6]$$

Again this follows directly from Equation 7.5.19. The reliability R of the system is:

$$R = 1 - \prod_{i=1}^{n} (1 - R_i) \qquad [7.8.7]$$

Since parallel configurations incorporate redundancy, they are also referred to as 'parallel redundant systems'. For the exponential distribution, Equation 7.8.2 applies, and hence:

$$R = 1 - \prod_{i=1}^{n} [1 - \exp(-\lambda_i t)] \qquad [7.8.8]$$

If the overall failure rate of the system is a constant λ, Equation 7.8.4 is applicable. In this case there is no simple general relationship between the system and component failure rates. But, if the component failure rates are all the same,

$$\frac{1}{\lambda} = \sum_{i=1}^{n} \frac{1}{i\lambda_i} \qquad [7.8.9]$$

If the failure rates are different, then for two components

$$\frac{1}{\lambda} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2} - \frac{1}{\lambda_1 + \lambda_2} \qquad [7.8.10]$$

for three components

$$\frac{1}{\lambda}=\frac{1}{\lambda_1}+\frac{1}{\lambda_2}+\frac{1}{\lambda_3}-\frac{1}{\lambda_1+\lambda_2}-\frac{1}{\lambda_1+\lambda_3}-\frac{1}{\lambda_2+\lambda_3}+\frac{1}{\lambda_1+\lambda_2+\lambda_3} \quad [7.8.11]$$

and for n components

$$\frac{1}{\lambda}=\left(\frac{1}{\lambda_1}+\frac{1}{\lambda_2}+\cdots+\frac{1}{\lambda_n}\right)-\left(\frac{1}{\lambda_1+\lambda_2}+\frac{1}{\lambda_1+\lambda_3}+\cdots+\frac{1}{\lambda_{n-1}+\lambda_n}\right)+\left(\frac{1}{\lambda_1+\lambda_2+\lambda_3}+\frac{1}{\lambda_1+\lambda_2+\lambda_4}+\cdots+\frac{1}{\lambda_{n-2}+\lambda_{n-1}+\lambda_n}\right)-\cdots+(-1)^{n-1}\frac{1}{\sum_{i=1}^{n}\lambda_i} \quad [7.8.12]$$

7.8.3 *r*-out-of-*n* parallel systems

For a system which has n components in parallel and operates as long as r components survive, the binomial distribution is applicable. Thus for an r-out-of-n system the reliability R is obtained from the component reliability R_x:

$$R(r\le k\le n)=\sum_{k=r}^{n}\binom{n}{k}R_x^kQ_x^{n-k} \quad [7.8.13]$$

As an illustration, consider the reliability of a 2-out-of-4 system. Expanding

$$(R_x+Q_x)^n=1 \quad [7.8.14]$$

for the terms between n and r to get the individual terms of Equation 7.8.13 gives

$$\textit{Probability of } 0 \textit{ failures}=R_x^4$$
$$\textit{Probability of } 1 \textit{ failure}=4R_x^3Q_x$$
$$\textit{Probability of } 2 \textit{ failures}=6R_x^2Q_x^2$$

The coefficients of the terms may be obtained from Pascal's triangle. The system survives provided no more than two failures occur, and hence

$$R=R_x^4+4R_x^3Q_x+6R_x^2Q_x^2 \quad [7.8.15]$$

An r-out-of-n system reduces in the limiting cases to a series or a parallel system. If all the components must operate for the system to survive, it becomes a series system

$$R=R_x^n \quad [7.8.16]$$

whilst if it is sufficient for one component to operate for the system to survive, it becomes a parallel system

$$Q=Q_x^n \quad [7.8.17]$$

7.8.4 Stand by systems

The simplest stand by system is one in which there is one component operating and one or more on stand by, all components have the same failure rate in the operational mode, the stand by components have zero failure rate in the stand by mode, and there is perfect switchover. For this case, the Poisson distribution can be used. Thus, for such a stand by system, the failure rate is λ, the number of failures which the system can withstand is r, and the system reliability R is

$$R(0\le k\le r)=\exp(-\lambda t)\sum_{k=0}^{r}\frac{(\lambda t)^k}{k!} \quad [7.8.18a]$$

$$=\exp(-\lambda t)\left[1+\lambda t+\frac{(\lambda t)^2}{2!}+\cdots+\frac{(\lambda t)^r}{r!}\right] \quad [7.8.18b]$$

As an illustration, consider the reliability of a stand by system with one component operating and one on stand by, so that the system can survive one failure. Then

$$R=\exp(-\lambda t)(1+\lambda t) \quad [7.8.19]$$

It is relatively easy in this case to take into account imperfect switchover. If the reliability of switchover is R_{SW}, the system reliability R is:

$$R=\exp(-\lambda t)(1+R_{sw}\lambda t) \quad [7.8.20]$$

Stand by systems may be more complex than this simple case in a number of ways. The stand by component may be different from the component normally operating and may have a different failure rate in the operational mode. It may also have a finite failure rate in the stand by mode, and there may be imperfect switchover.

7.8.5 Systems with repair

If it is possible to carry out repair on a system, a much higher reliability can be achieved. The repair time which is used here is the total time from initial failure to final repair, and therefore includes any time required for detection of the failure and organization of the repair. Obviously, the determination of the reliability of systems with repair requires data on repair times as well as failure rates.

Repair times, like failure times, may fit various distributions. It is sometimes assumed that the repair time is a constant τ, but a more common assumption is that the repair times τ_r have an exponential distribution with constant repair rate μ:

$$f_r(t_r)=\mu\exp(-\mu t_r) \quad [7.8.21]$$

For the exponential distribution the mean repair time $m_r$is

$$m_r=\frac{1}{\mu} \quad [7.8.22]$$

Equations 7.8.21 and 7.8.22 are analogous to Equations 7.6.12 and 7.6.25b for failure times and mean life. A more detailed discussion of repair times is given below.

The reliability of some standard systems with repair is now considered. It is assumed that the exponential repair time distribution applies, unless otherwise stated. In particular, this assumption is made in the Markov models described below.

7.8.6 Parallel systems with repair

For a system which has n components in parallel, and which survives provided that at least one component operates, and for which the failure and repair rates are λ and μ, respectively, expressions for the reliability R can be derived using Markov models, as described below. For a parallel system with two components it can be shown that the reliability R is:

$$R = \frac{1}{r_1 - r_2}[(3\lambda + \mu + r_1)\exp(r_1 t) - (3\lambda + \mu + r_2)\exp(r_2 t)] \quad [7.8.23]$$

with

$$r_1, r_2 = \frac{-(3\lambda + \mu) \pm [(3\lambda + \mu)^2 - 8\lambda^2]^{1/2}}{2} \quad [7.8.24]$$

7.8.7 Stand by systems with repair

For a stand by system with two components in which there is one component operating and one is on stand by, both components have the same failure rate in the operational mode, the stand by component has zero failure rate in the stand by mode, the switchover is perfect, and there is repair, it can be shown using Markov models that the reliability R is:

$$R = \frac{1}{r_1 - r_2}[(2\lambda + \mu + r_1)\exp(r_1 t) - (2\lambda + \mu + r_2)\exp(r_2 t)] \quad [7.8.25]$$

with

$$r_1, r_2 = \frac{-(2\lambda + \mu) \pm [(2\lambda + \mu)^2 - 4\lambda^2]^{1/2}}{2} \quad [7.8.26]$$

7.8.8 Constant repair time

As just described, the usual assumption for repair times is a constant repair rate μ, which implies a distribution of repair times. An alternative assumption is a single constant repair time τ.

For a parallel system of n components with repair, the probability of the system being in the 'as new' condition and then suffering an initial failure a given number of times, is given by the Poisson distribution:

$$\exp(-n\lambda t)\left[1 + n\lambda t + \frac{(n\lambda t)^2}{2!} + \frac{(n\lambda t)^3}{3!} + \cdots\right] = 1 \quad [7.8.27]$$

The probability of the system failing completely after an initial failure and before repair to the as-new condition is:

$$Q(\tau) = [1 - \exp(-\lambda t)]^{n-1} \qquad \lambda t \ll 1 \quad [7.8.28]$$

Then the probability of the system suffering one initial failure followed by system failure is:

$$P(t) = \exp(-n\lambda t) n\lambda t Q(\tau) \quad [7.8.29]$$

The probabilities of the system suffering high numbers of initial failures followed by system failure may be obtained in a similar manner. Hence, it can be shown that the reliability of the system is:

$$R = \exp(-\lambda' t) \quad [7.8.30]$$

with

$$\lambda' = n\lambda Q(\tau) \qquad \lambda t \ll 1 \quad [7.8.31]$$

7.8.9 Mean life

Some methods of determining the mean life have been outlined in Section 7.6. The Markov methods described below are a further powerful method for obtaining the mean life and also the variance. The expressions for the mean life of some standard systems, assuming the exponential distribution, are shown in Table 7.4. For systems without repair the expressions allow for different failure rates for each equipment, but for systems with repair they assume the same failure rate. Some expressions for the mean life assuming the Weibull distribution are given by Shooman (1968a).

7.9 Reliability of Complex Systems

7.9.1 System reliability analysis

The reliability analysis of systems is carried out first to obtain an assessment of system reliability and to identify critical features, and then to achieve necessary improvements. A full analysis is likely to require considerable effort. It is important, therefore, to identify those subsystems which particularly affect the overall system reliability. In other words, the direction of effort is assisted by a sensitivity analysis. If the reliability of a particular subsystem does not greatly affect that of the system, it is not necessary to analyse it in great detail.

Reliability calculations require data not only on failure rates but also on repair times. The sensitivity of the system reliability determines the accuracy required in the data in a given case. In some instances it is necessary to obtain a rather accurate estimate from field data. In others an engineering estimate made without any field data may be quite sufficient. The matching of the data to the application is an important element in the art of the reliability engineer.

There are a number of methods which can be used to analyse more complex systems and to decompose them into their subsystems. These techniques may be illustrated by reference to Figure 7.6. Figure 7.6(a) illustrates a system consisting of two intermediate storage tanks and three pumps. Figure 7.6(b) shows the three pumps all in parallel, with complete interchangeability between them. Figure 7.6(c) shows two separate streams, with one tank and one pump in each, and with the third pump available to either stream. The system is defined as successful provided flow is maintained by pumping with at least one pump from one tank.

7.9.2 Reliability graphs

The structure of a system may be represented in terms of simple reliability graphs. Each branch of the graph represents a component. Some examples are given in Figure 7.7. Figure 7.7(a) shows the reliability graph for three components in series, and Figure 7.7(b) shows that for three components in parallel. Figure 7.7(c) shows the reliability graph

Table 7.4 *Mean life for some standard systems assuming exponential failure distribution*

System	*Failure rates*	*Mean life*
Series	Same	$\frac{1}{n\lambda}$
	Different	$\frac{1}{\sum_{i=1}^{n}\lambda_i}$
Parallel	Same	$\frac{1}{\lambda\sum_{i=1}^{n}(1/i)}$
	Different	$\left(\frac{1}{\lambda_1}+\frac{1}{\lambda^2}+\cdots+\frac{1}{\lambda_n}\right)$ $-\left(\frac{1}{\lambda_1+\lambda_2}+\frac{1}{\lambda_1+\lambda_3}+\cdots+\frac{1}{\lambda_{n-1}+\lambda_n}\right)$ $+\left(\frac{1}{\lambda_1+\lambda_2+\lambda_3}+\frac{1}{\lambda_1+\lambda_2+\lambda_4}+\cdots+\frac{1}{\lambda_{n-2}+\lambda_{n-1}+\lambda_n}\right)$ $-\cdots+(-1)^{(n-1)}\frac{1}{\sum_{i=1}^{n}(\lambda_i)}$
Stand by	Same	$\frac{n}{\lambda}$
	Different	$\sum_{i=1}^{n}\left(\frac{1}{\lambda_i}\right)$
r-out-of-*n*	Same	–[a]
Parallel with repair (*n* repairmen)	Same	$\frac{1}{\lambda}\sum_{i=0}^{n-1}\frac{(1+\mu/\lambda)^i}{i+1}$
Stand by with repair (*n* repairmen)	Same	$\frac{1}{\lambda}\sum_{i=0}^{n-1}\frac{n!}{(i+1)(n-(i+1))!}\left(\frac{\mu}{\lambda}\right)^i$

[a] The mean life for this case may be obtained by applying the binomial expansion and using Equation 7.6.20.

for two components in parallel, in series with three components in parallel, which corresponds to the storage tank pump system shown in Figure 7.6(a), assuming the configuration given in Figure 7.6(b). The system reliability may then be determined by computing the reliability of the subsystems and then that of the system itself. Reliability graphs are discussed in more detail by Shooman (1968a).

7.9.3 Logic flow diagrams

The most widely used method of graphical representation is the logic flow diagram, also called the 'logic sequence diagram' or simply the 'logic diagram'. Figure 7.8 shows a logic flow diagram for the storage tank pump system with the configuration shown in Figure 7.6(b). In this case the top event considered is a success, but in other cases it may be a failure. Some typical applications of logic flow diagrams are given in Table 7.5. Logic flow diagrams can be used for systems of considerable complexity. Further examples of logic flow diagrams are given by A.E. Green and Bourne (1972).

One of the most widely used types of logic flow diagram is the fault tree. Fault trees are discussed in Chapter 9. An important development in the area of fault trees is kinetic tree theory, which has been developed by Vesely and co-workers (e.g., Vesely, 1969, 1970b; Vesely and Narum, 1970) and which permits the determination of system characteristics such as reliability and availability in time-varying systems.

7.9.4 Event space method

The event space method involves making a comprehensive list of all the possible states of the system and determining which of these events correspond to success. The events E_i, so listed are mutually exclusive and system reliability R is:

$$R = \sum_{i=1}^{n} P(E_i) \qquad [7.9.1]$$

Table 7.6 gives an event space analysis for a storage tank pump system having the configuration shown in Figure 7.6(b). The events which constitute failure are events 7, 17–19 and 26–32; all other events represent success. Further examples of the event space method are given by Shooman (1968a) and Buffham, Freshwater and Lees (1971).

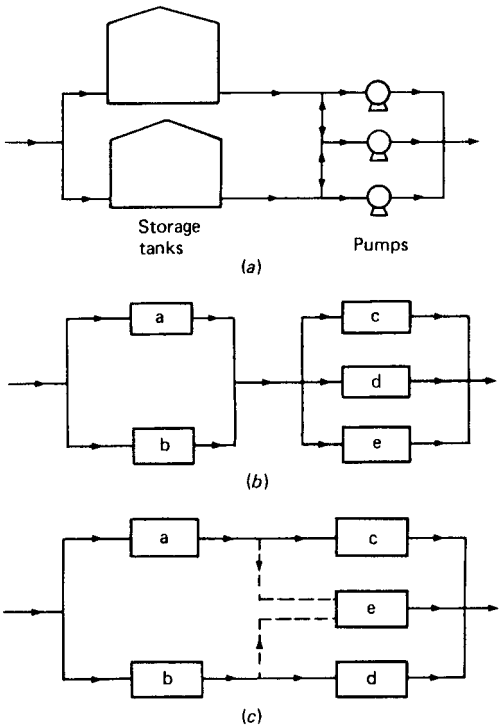


Figure 7.6 *A system to illustrate methods of analysing complex systems: (a) storage tank pump system; (b) system with three pumps in parallel; (c) system with separate streams, but with a common spare pump*

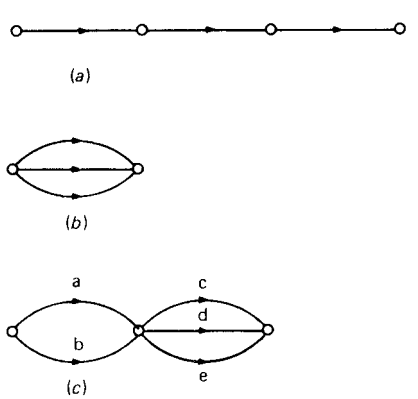


Figure 7.7 *Reliability graphs: (a) for a three-component series system; (b) for a three-component parallel system; (c) for a storage tank pump system (configuration as in Figure 7.6(b))*

7.9.5 Tree diagrams

Another graphical representation is the tree diagram. Figure 7.9 shows such a diagram for a storage tank pump system having the configuration given in Figure 7.6(c). The diagrams can be used for simple cases, but rapidly become rather cumbersome as systems become more complex. Further examples of tree diagrams are given by von Alven (1964) and Breipohl (1970).

7.9.6 Path tracing and tie sets

The path tracing method consists of tracing through the system the paths which constitute success. These paths are known in graph theory as 'tie sets'. System reliability is obtained from the minimum tie sets T_i. These sets of events are not mutually exclusive and the system reliability is given by:

$$R = P\left(\bigcup_{i=1}^{n} T_i\right) \qquad [7.9.2]$$

7.9.7 Path breaks and cut sets

An alternative approach is to determine the sets of events which break all the paths and thus ensure failure. These sets are known in graph theory as 'cut sets'. System unreliability is obtained from the minimum cut sets C_i. Again these sets of events are not mutually exclusive and the system reliability is given by:

$$R = 1 - \left(\bigcup_{i=1}^{n} C_i\right) \qquad [7.9.3]$$

If the event space method is applied to a storage tank pump system having the configuration shown in Figure 7.6(c) rather than that given in Figure 7.6(b), so that paths *ad* and *bc* are not permissible, then the complete cut sets correspond to events 7, 17–19, 22, 24 and 26–32, and are:

$\bar{a}\bar{b}, \bar{a}\bar{b}\bar{c}, \bar{a}\bar{b}\,\bar{d}, \bar{a}\bar{b}\bar{e}, \bar{a}\bar{d}\bar{e}, \bar{b}\bar{c}\,\bar{e}, \bar{c}\bar{d}\bar{e},$

$\bar{b}\bar{c}\bar{d}\bar{e}, \bar{a}\,\bar{c}\bar{d}\bar{e}, \bar{a}\bar{b}\bar{d}\bar{e}, \bar{a}\bar{b}\bar{c}\,\bar{e}, \bar{a}\bar{b}\bar{c}\bar{d}, \bar{a}\bar{b}\bar{c}\bar{d}\bar{e}$

However, a cut set which contains within itself a smaller cut set is not a minimum. The minimum cut sets are:

$\bar{a}\bar{b}, \bar{a}\bar{d}\bar{e}, \bar{b}\bar{c}\,\bar{e}, \bar{c}\bar{d}\bar{e}$

Minimum cut sets are important in fault tree work and are considered further in Chapter 9.

7.9.8 System decomposition

It is often possible to simplify the analysis of a system by selecting a key component which makes it possible to decompose the system into subsystems. In such a case, one approach is the use of Bayes' theorem. This theorem is considered in more detail in Section 7.14. Here it is sufficient to note that the theorem may be written in the form:

$$P(\mathrm{A}) = P(A \mid B)P(B) + P(A \mid \bar{B})P(\bar{B}) \qquad [7.9.4]$$

Thus the reliability $R(\mathrm{S})$ of the system is related to the reliability $R(\mathrm{X})$ of the key component as follows:

$$R(\mathrm{S}) = R(\mathrm{S} \mid \mathrm{X})R(\mathrm{X}) + R(\mathrm{S} \mid \bar{\mathrm{X}})Q(\bar{\mathrm{X}}) \qquad [7.9.5]$$

For a storage tank pump system having the configuration shown in Figure 7.6(c) the system unreliability Q is:

$$Q = Q_a Q_b R_e + Q_{ac} Q_{bd} Q_e \qquad [7.9.6]$$

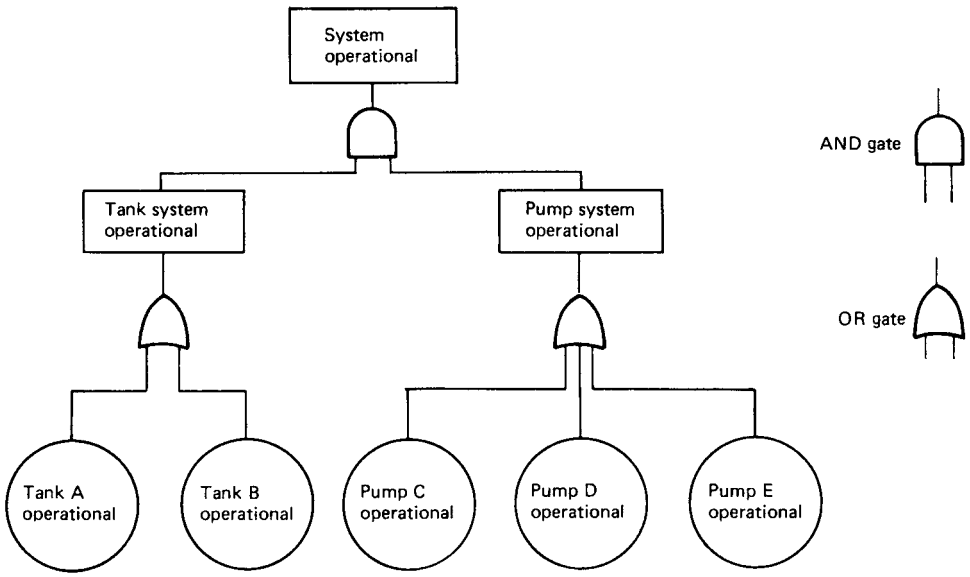


Figure 7.8 *Logic flow diagram for storage tank pump system (configuration as in Figure 7.6(b))*

Table 7.5 *Some typical applications of logic flow diagrams*

Event investigated	*Type of diagram*
Hazardous occurrences	Failure diagram (fault tree)
Trip system operation	Success diagram
Plant availability	Success diagram

with

$$R_{ac} = R_a R_c \qquad [7.9.7a]$$

$$R_{bd} = R_b R_d \qquad [7.9.7b]$$

Further examples of system decomposition using Bayes' theorem are given by Buffham *et al.* (1971).

7.10 Markov Models

A Markov model is a model of the probabilities of different states of a system as a function of time. It therefore has two variables, state and time. There are thus four possible types of model, since each of these variables may be either discrete or continuous. Accounts of Markov models are given by Sandler (1963), Shooman (1968a) and R.A. Howard (1971). In particular, Sandler (1963) gives solutions of numerous standard cases in reliability and availability. It is the discrete-state, continuous-time model which is most widely used in reliability work.

The state of a system can generally be defined in a number of ways. Thus for a two-equipment system with equipments 1 and 2, one set of states is as follows: no equipments failed, one equipment (either 1 or 2) failed, both equipments failed. Another set of states is as follows: no equipments failed, equipment 1 failed, equipment 2 failed, both equipments failed.

The transitions in the system may be in the forward direction only, that is, from state 0 to state 1, then from state 1 to state 2, etc., or they may be in both forward and backward directions, that is, from state 0 to state 1 and from state 1 to state 0, etc. Also, the transitions may be between adjacent states only or between non-adjacent states.

The transition rates are defined by the states chosen. It is generally desirable to choose the states so that the transition rates correspond to quantities which are known, such as failure and repair rates. The transition rate of a Markov model is a constant. The transition rates may include allowance for imperfect switchover. Thus a transition rate may be a function of both a failure rate and a probability of switchover.

Some examples of Markov models are given below.

7.10.1 Discrete-state, continuous-time models

If a system has $n+1$ possible states and transition is between adjacent states in the forward direction only with transition rates $\lambda_{k-1,k}$ between states $k-1$ and k and $\lambda_{k,k+1}$ between states k and $k+1$, the probability $P_k(t+\Delta t)$ of being in state k at time $t+\Delta t$ is:

$$P_k(t+\Delta t) = \lambda_{k-1,k}\Delta t P_{k-1}(t) + P_k(t) - \lambda_{k,k+1}\Delta t P_k(t) \qquad [7.10.1]$$

But

$$\lim_{\Delta t \to 0}\left[\frac{P_k(t+\Delta t) - P_k t)}{\Delta t}\right] = \frac{\mathrm{d}P_k(t)}{\mathrm{d}t} \qquad [7.10.2]$$

Hence

$$\frac{\mathrm{d}P_k(t)}{\mathrm{d}t} = \dot{P}_k(t) = \lambda_{k-1,k}P_{k-1}(t) - \lambda_{k,k+1}P_k(t) \qquad [7.10.3]$$

Table 7.6 *Event space of a storage tank pump system (see Figure 7.6)*

1	abcde	11	$a\bar{b}\bar{c}de$	20	$\bar{a}b\bar{c}\bar{d}e$	27	$a\bar{b}\bar{c}\bar{d}\bar{e}$
2	$\bar{a}bcde$	12	$a\bar{b}cde$	21	$\bar{a}b\bar{c}d\bar{e}$	28	$\bar{a}b\bar{c}\bar{d}\bar{e}$
3	$a\bar{b}cde$	13	$a\bar{b}cd\bar{e}$	22	$\bar{a}bcd\bar{e}$	29	$\bar{a}\bar{b}cd\bar{e}$
4	$ab\bar{c}de$					30	$\bar{a}\bar{b}cd\bar{e}$
5	$abcd\bar{e}$	14	$ab\bar{c}\bar{d}e$	23	$a\bar{b}\bar{c}\bar{d}e$	31	$\bar{a}\bar{b}\bar{c}de$
6	$abcd\bar{e}$	15	$ab\bar{c}d\bar{e}$	24	$a\bar{b}\bar{c}d\bar{e}$		
		16	$abcd\bar{e}$	25	$a\bar{b}cd\bar{e}$	32	$\bar{a}\bar{b}\bar{c}\bar{d}\bar{e}$
7	$\bar{a}\bar{b}cde$						
8	$\bar{a}b\bar{c}de$	17	$\bar{a}\bar{b}\bar{c}de$	26	$ab\bar{c}\bar{d}\bar{e}$		
9	$\bar{a}bcd\bar{e}$	18	$\bar{a}\bar{b}cd\bar{e}$				
10	$\bar{a}bcd\bar{e}$	19	$\bar{a}\bar{b}cd\bar{e}$				

Initial conditions are commonly:

$$P_0(0) = 1; \qquad P_k(0) = 0 \quad 0 < k \leq n \tag{7.10.4}$$

As an illustration, consider a system with three states 0, 1 and 2 and transition rates λ_{01} and λ_{12}. The Markov equations are:

$$\dot{P}_0(t) = \lambda_{01} P_0(t) \tag{7.10.5a}$$

$$\dot{P}_1(t) = \lambda_{01} P_0(t) - \lambda_{12} P_1(t) \tag{7.10.5b}$$

$$\dot{P}_2(t) = \lambda_{12} P_1(t) \tag{7.10.5c}$$

Assume the initial conditions given in Equation 7.10.4. Then, rewriting Equations 7.10.5a–c and 7.10.4 in matrix form:

$$\mathbf{P}(t) = \mathbf{A}\mathbf{P}(t) \tag{7.10.6}$$

where

$$\mathbf{A} = \begin{bmatrix} -\lambda_{01} & 0 & 0 \\ \lambda_{01} & -\lambda_{12} & 0 \\ 0 & \lambda_{12} & 0 \end{bmatrix} \tag{7.10.7}$$

and

$$\mathbf{P}(0) = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \tag{7.10.8}$$

Equations 7.10.6–7.10.8 may be solved analytically by taking Laplace transforms, inverting the matrix, and then inverting the transforms. Thus, taking Laplace transforms of Equation 7.10.6:

$$s\mathbf{P} - \mathbf{P}(0) = \mathbf{A}\mathbf{P} \tag{7.10.9}$$

Hence

$$\mathbf{P} = [s\mathbf{I} - \mathbf{A}]^{-1}\mathbf{P}(0) \tag{7.10.10}$$

But

$$[s\mathbf{I} - \mathbf{A}] = \begin{bmatrix} s + \lambda_{01} & 0 & 0 \\ -\lambda_{01} & s + \lambda_{12} & 0 \\ 0 & -\lambda_{12} & s \end{bmatrix} \tag{7.10.11}$$

The inverse of the matrix, $[s\mathbf{I} - \mathbf{A}]^{-1}$, has as its numerator the matrix of cofactors of $[s\mathbf{I} - \mathbf{A}]$ and as its denominator the determinant of $[s\mathbf{I} - \mathbf{A}]$. Thus:

$$[s\mathbf{I} - \mathbf{A}]^{-1} = \frac{\begin{bmatrix} s(s + \lambda_{12}) & 0 & 0 \\ s\lambda_{01} & s(s + \lambda_{01}) & 0 \\ \lambda_{01}\lambda_{12} & \lambda_{12}(s + \lambda_{01}) & (s + \lambda_{01})(s + \lambda_{12}) \end{bmatrix}}{s(s + \lambda_{01})(s + \lambda_{12})} \tag{7.10.12a}$$

$$= \begin{bmatrix} \dfrac{1}{s + \lambda_{01}} & 0 & 0 \\ \dfrac{\lambda_{01}}{(s + \lambda_{01})(s + \lambda_{12})} & \dfrac{1}{s + \lambda_{12}} & 0 \\ \dfrac{\lambda_{01}\lambda_{12}}{s(s + \lambda_{01})(s + \lambda_{12})} & \dfrac{\lambda_{12}}{s(s + \lambda_{12})} & \dfrac{1}{s} \end{bmatrix} \tag{7.10.12b}$$

Then multiplying out Equation 7.10.10 using Equation 7.10.12b:

$$\bar{P}_0(s) = \frac{1}{s + \lambda_{01}} \tag{7.10.13a}$$

$$\bar{P}_1(s) = \frac{\lambda_{01}}{(s + \lambda_{01})(s + \lambda_{12})} \tag{7.10.13b}$$

$$\bar{P}_2(s) = \frac{\lambda_{01}\lambda_{12}}{s(s + \lambda_{01})(s + \lambda_{12})} \tag{7.10.13c}$$

and inverting these transforms gives

$$P_0(t) = \exp(-\lambda_{01} t) \tag{7.10.14a}$$

$$P_1(t) = \frac{\lambda_{01}}{\lambda_{12} - \lambda_{01}} [\exp(-\lambda_{01} t) - \exp(-\lambda_{12} t)] \tag{7.10.14b}$$

$$P_2(t) = 1 - \frac{1}{\lambda_{12} - \lambda_{01}} [\lambda_{12} \exp(-\lambda_{01} t) - \lambda_{01} \exp(-\lambda_{12} t)] \tag{7.10.14c}$$

This example illustrates a number of practical points about Markov models:

(1) The sum of the terms on the right-hand side of all the original model equations is zero.

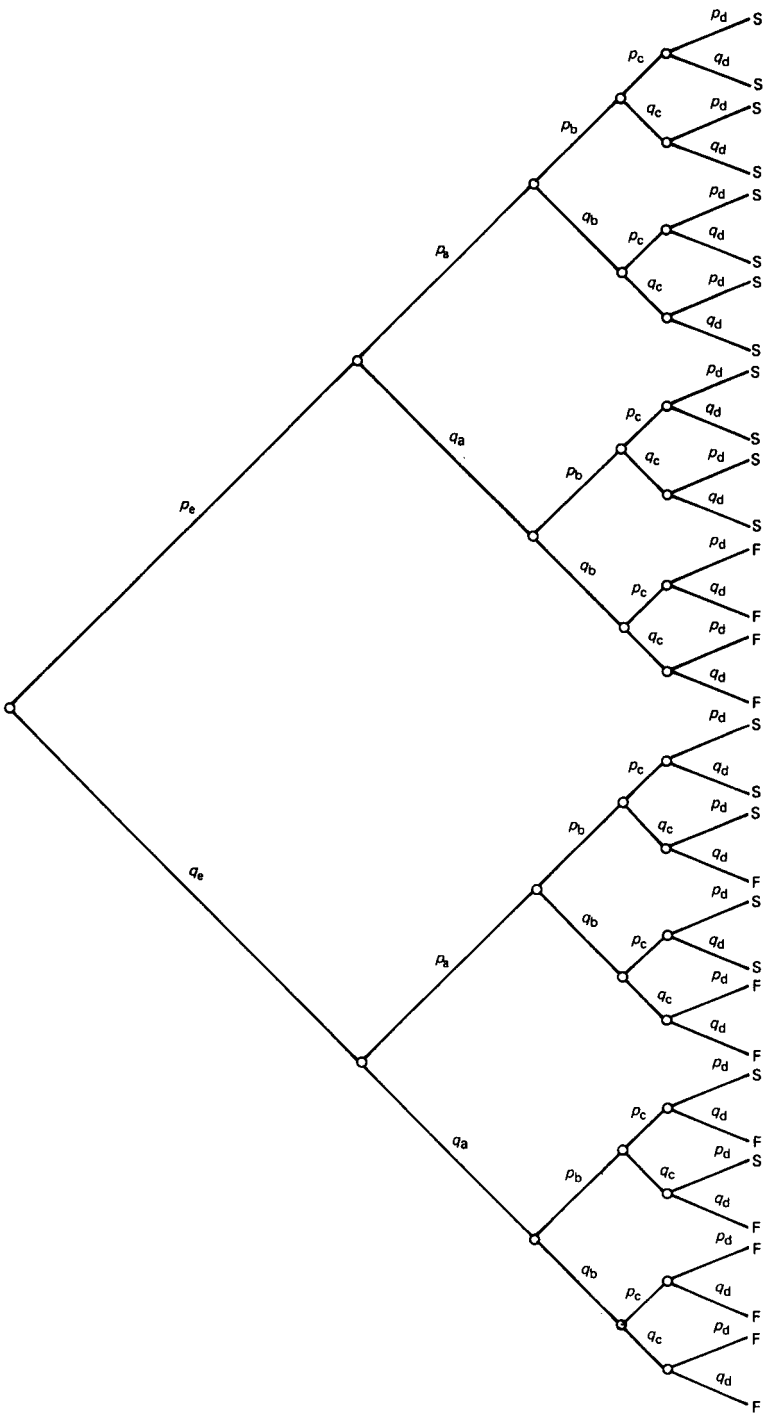


Figure 7.9 *Tree diagram for storage tank pump system (configuration as in Figure 7.6(c)): S, system success; F, system failure*

(2) The sum of the probabilities $P(t)$ is unity and the sum of their transforms $\bar{P}(s)$ is 1/s.
(3) The initial conditions are frequently $P_0(0) = 1$ and $P_k(0) = 0$ $(0 < k \leq n)$, and in this case only the first column of the matrix $[s\mathbf{I} - \mathbf{A}]^{-1}$ is of interest.
(4) If there are no transitions back from the last state, the equation for this may be omitted and the probability calculated at the end from the other probabilities; this is particularly useful in third- and fourth-order models.

7.10.2 Poisson process

If in Equation 7.10.3 the transition rate from one state to the next is a constant λ, the Markov equations are:

$$\dot{P}_0(t) = -\lambda P_0(t) \quad [7.10.15a]$$

$$\dot{P}_1(t) = \lambda P_0(t) - \lambda P_1(t) \quad [7.10.15b]$$

$$\vdots$$

$$\dot{P}_n(t) = \lambda P_{(n-1)}(t) - \lambda P_n(t) \quad [7.8.15c]$$

Assume the initial conditions given in Equation 7.10.4. Then the solution is:

$$P_0(t) = \exp(-\lambda t) \quad [7.10.16a]$$

$$P_1(t) = \exp(-\lambda t)\lambda t \quad [7.10.16b]$$

$$\vdots$$

$$P_n(t) = \exp(-\lambda t)\frac{(\lambda t)^n}{n!} \quad [7.10.16c]$$

This is a Poisson process.

7.10.3 Two-equipment systems

If a system consists of two components then, whatever its configuration, one formulation of the states in which it can be is as follows: no equipments failed, equipment 1 failed, equipment 2 failed and both equipments failed. Let $P_0(t)$, $P_1(t)$, $P_2(t)$ and $P_3(t)$ be, respectively, the probabilities of: no failures, failure of component 1, failure of component 2, and failure of both components. In addition, let λ_1, λ_2, λ_3 and λ_4 be, respectively, the transition rates from: states 0 to 1, 0 to 2, 1 to 3 and 2 to 3. Then the Markov equations are:

$$\dot{P}_0(t) = -(\lambda_1 + \lambda_2)P_0(t) \quad [7.10.17a]$$

$$\dot{P}_1(t) = \lambda_1 P_0(t) - \lambda_3 P_1(t) \quad [7.10.17b]$$

$$\dot{P}_2(t) = \lambda_2 P_0(t) - \lambda_4 P_2(t) \quad [7.10.17c]$$

$$\dot{P}_3(t) = \lambda_3 P_1(t) + \lambda_4 P_2(t) \quad [7.10.17d]$$

Assume the initial conditions given in Equation 7.10.4. Then the solution is:

$$P_0(t) = \exp[-(\lambda_1 + \lambda_2)t] \quad [7.10.18a]$$

$$P_1(t) = \frac{\lambda_1}{\lambda_1 + \lambda_2 - \lambda_3}\{\exp(-\lambda_3 t) - \exp[-(\lambda_1 + \lambda_2)t]\} \quad [7.10.18b]$$

$$P_2(t) = \frac{\lambda_2}{\lambda_1 + \lambda_2 - \lambda_4}\{\exp(-\lambda_4 t) - \exp[-(\lambda_1 + \lambda_2)t]\} \quad [7.10.18c]$$

$$P_3(t) = 1 - [P_0(t) + P_1(t) + P_2(t)] \quad [7.10.18d]$$

Thus far no particular configuration has been assumed. The following cases can be treated to obtain the system reliability $R(t)$:

(1) Series system, failure rates of two equipments identical:

$$\lambda_1 = \lambda_2 = \lambda$$
$$R(t) = P_0(t) = \exp(-2\lambda t) \quad [7.10.19]$$

(2) Series system, failure rates of two equipments different:

$$R(t) = P_0(t) = \exp[-(\lambda_1 + \lambda_2)t] \quad [7.10.20]$$

(3) Parallel system, failure rates of two equipments identical:

$$\lambda_1 = \lambda_2 = \lambda_3 = \lambda_4 = \lambda$$
$$R(t) = P_0(t) + P_1(t) + P_2(t)$$
$$= 2\exp(-\lambda t) - \exp(-2\lambda t) \quad [7.10.21]$$

(4) Parallel system, failure rates of two equipments different:

$$\lambda_1 = \lambda_4 = \lambda; \quad \lambda_2 = \lambda_3 = \lambda'$$
$$R(t) = P_0(t) + P_1(t) + P_2(t)$$
$$= \exp(-\lambda t) + \exp(-\lambda' t) - \exp[-(\lambda + \lambda')t] \quad [7.10.22]$$

(5) Parallel system, failure rates of two equipments operating together identical, but failure rate of one equipment surviving different:

$$\lambda_1 = \lambda_2 = \lambda; \quad \lambda_3 = \lambda_4 = \lambda'$$
$$R(t) = P_0(t) + P_1(t) + P_2(t)$$
$$= \frac{1}{2\lambda - \lambda'}[2\lambda\exp(-\lambda' t) - \lambda'\exp(-2\lambda t)] \quad [7.10.23]$$

(6) Stand by system, failure rates of two equipments identical in operating mode, no failure in stand by mode and no switchover failure:

$$\lambda_1 = \lambda_3 = \lambda; \quad \lambda_2 = \lambda_4 = 0$$
$$R(t) = P_0(t) + P_1(t)$$

In this case the expression for $P_1(t)$ is indeterminate since the denominator is zero, but applying de l'Hopital's rule of differentiating both numerator and denominator by λ_1 gives

$$R(t) = \exp(-\lambda t)(1 + \lambda t) \quad [7.10.24]$$

This example illustrates the versatility of the method.

7.10.4 Single-equipment systems with repair

In the system considered so far the transitions have all been unidirectional towards some failed state. In fact, in most systems there is repair. The transition rate in the reverse direction is the repair rate.

It is normally assumed in Markov models that there is a constant repair rate μ, and hence an exponential distribution of repair times t_r, as given in Equation 7.8.21. If a system comprises a single equipment with repair, there are two possible states it can take. Let $P_0(t)$ and $P_1(t)$ be the probabilities of being operational and failed, respectively, and let λ and μ be the failure and repair rates, respectively. The Markov equations are:

$$\dot{P}_0(t) = -\lambda P_0(t) + \mu P_1(t) \quad [7.10.25a]$$

$$\dot{P}_0(t) = \lambda P_0(t) - \mu P_1(t) \quad [7.10.25b]$$

Assume the initial conditions given in Equation 7.10.4. Then the solution is:

$$P_0(t) = \frac{\mu}{\lambda+\mu} + \frac{\lambda}{\lambda+\mu}\exp[-(\lambda+\mu)t] \quad [7.10.26a]$$

$$P_1(t) = \frac{\lambda}{\lambda+\mu} - \frac{\lambda}{\lambda+\mu}\exp[-(\lambda+\mu)t] \quad [7.10.26b]$$

Since there is now transition in both directions, $P_0(t)$ represents the system availability $A(t)$

$$A(t) = \frac{\mu}{\lambda+\mu} + \frac{\lambda}{\lambda+\mu}\exp[-(\lambda+\mu)t] \quad [7.10.27]$$

Thus the availability is, in general, a function of time. But is it usually the steady state availability $A(\infty)$ which is of most interest:

$$A(\infty) = \frac{\mu}{\lambda+\mu} \quad [7.10.28]$$

7.10.5 Reliability and availability formulations

The availability $A(t)$ introduced in the previous section is the probability that the system will be in the operational state. This is not the same as the reliability $R(t)$, which is the probability that the system will not leave the operational state. The difference lies in the fact that, in determining availability, transition back by repair from the non-operational state is permitted. The availability for a given system is always greater than or equal to the reliability:

$$A(t) \geq R(t) \quad [7.10.29]$$

Different Markov models are required for reliability and availability. For reliability, repair transition from the states constituting failure is not permissible, although repair transition from other states is. For availability, repair transition from all states is permitted.

For an r-out-of-n system, in which the states up to and including the $(n-r)$th state give survival, reliability is obtained from the Markov model as:

$$R(t) = \sum_{i=0}^{n-r} P_i(t) \quad [7.10.30]$$

Availability is obtained as

$$A(t) = \sum_{i=0}^{n-r} P_i(t) \quad [7.10.31]$$

when the states 0 to $n-r$ again constitute survival. But the formulation of the equations for the various states is different in the two types of model. For the reliability formulation, the repair transition rates in equations $n-r+1$ to n are zero.

A state which it is possible to enter but not to leave is an absorbing state. If there is a single absorbing state, the steady state probability of being in that state is unity. The reliability formulations of Markov models have an absorbing state, but availability formulations do not. If the last state of a Markov model is an absorbing state, so that there is no interaction of this state and the preceding states, the last state probability may be omitted in the formulation and determined at the end of the calculation from the other state probabilities. This is particularly useful in the analytical solution or manual calculation of third- and fourth-order models.

7.10.6 Repair rates

The repair rate used in Markov models for systems with more than one equipment needs to be carefully specified. There are two aspects to consider. One is the repair transition rate in systems with n equipments from states in which there is more than one failure. This transition rate will normally lie somewhere in the range μ to $n\mu$. The other aspect is the increase in repair transition rate for a single equipment from μ to $\xi\mu$ which may be obtained by allocating additional effort.

These repair transition rates are often considered in terms of the number of repairmen, it being assumed that the normal case is one repairman for one equipment. Thus for systems with n equipments and with states with multiple failures the repair transition rate in the fully failed state may be $n\mu$. This is often called then 'n repairmen case'. But the number of repairmen may also affect the repair transition rate for a single equipment $\xi\mu$. Thus Sandler (1963) frequently uses $\xi = 1.5$ where two repairmen are available to work on one equipment.

As an illustration, consider a system which consists of two equipments with identical failure rates. Then there are three possible states: no equipments failed, one equipment failed and both equipments failed. Let $P_0(t)$, $P_1(t)$ and $P_2(t)$ be the probabilities of no, one and two failures, respectively, and let λ be the failure rate and μ the basic repair rate. If repair resources allow the repair of only one equipment at a time, that is, the one repairman case, then:

$$\dot{P}_0(t) = -2\lambda P_0(t) + \mu P_1(t) \quad [7.10.32a]$$

$$\dot{P}_1(t) = 2\lambda P_0(t) - (\lambda+\mu)P_1(t) + \mu P_2(t) \quad [7.10.32b]$$

$$\dot{P}_2(t) = \lambda P_1(t) - \mu P_2(t) \quad [7.10.32c]$$

Assume the initial conditions given in Equation 7.10.4. Then the system availability, defined as having both equipments operating, can be shown to be:

$$A(\infty) = P_0(\infty) = \frac{\mu^2}{2\lambda^2 + 2\lambda\mu + \mu^2} \quad [7.10.33]$$

If, on the other hand, the repair resources allow the repair of two equipments simultaneously, that is, the two repairmen case, then:

$$\dot{P}_0(t) = -2\lambda P_0(t) + \mu P_1(t) \quad [7.10.34a]$$

$$\dot{P}_1(t) = 2\lambda P_0(t) - (\lambda+\mu)P_1(t) + 2\mu P_2(t) \quad [7.10.34b]$$

$$\dot{P}_2(t) = \lambda P_1(t) - 2\mu P_2(t) \quad [7.10.34c]$$

and, assuming the same initial conditions and definition of availability,

$$A(\infty) = \frac{\mu^2}{(\lambda+\mu)^2} = \frac{\mu^2}{\lambda^2 + 2\lambda\mu + \mu^2} \quad [7.10.35]$$

It may be noted that there is a difference between the number of repairmen that can usefully be used, depending on whether it is reliability or availability which is being

calculated. In a system with n equipments which fails when $n - r + 1$ equipments have failed, it is possible to use n repairmen to maximize availability, but only $n - r$ repairmen to maximize reliability.

7.10.7 Mean life

Markov models offer a powerful method of obtaining the mean life and the variance of the distribution of complex systems. This is discussed in more detail by Sandler (1963).

7.10.8 Discrete-state, discrete-time models

The discrete-state, discrete-time Markov model is also useful in some applications. If a system has a number of possible states and transition occurs between these states over a given time interval, then the vectors of state probabilities before and after the transition $\mathbf{P}(0)$ and $\mathbf{P}(1)$ are related by the equation:

$$\mathbf{P}(1) = \mathbf{A}\mathbf{P}(0) \qquad [7.10.36]$$

where $\mathbf{A}$ is the matrix of transition probabilities. Then it can be shown that, as the number of transitions tends to infinity:

$$\mathbf{P}(\infty)\mathbf{A} = \mathbf{P}(\infty) \qquad [7.10.37]$$

The final state probabilities are independent of the initial state probabilities. In addition,

$$\sum \mathbf{P}_i = 1 \qquad [7.10.38]$$

The final states of the system may be obtained by solution of Equations 7.10.37 and 7.10.38.

An account of discrete-state, discrete-time Markov models is given by Sandler (1963). An application involving a discrete-state, discrete-time Markov model is given in Section 7.13.

7.11 Joint Density Functions

An alternative to Markov models is the use of the joint density function approach. The joint density function method is convenient where a failure distribution other than the exponential distribution has to be handled. It is also useful where the failure rate changes depending on the failures which have already occurred. The joint density function method is discussed by Lloyd and Lipow (1962) and Shooman (1968a).

If a system consists of two subsystems and if the second subsystem takes over the system function when the first fails at time τ, then the joint density function of the system $\phi(\tau, t)$ is

$$\phi(\tau, t) = f_1(\tau) f_2(t \mid \tau) \qquad [7.11.1]$$

where $f_1(\tau)$ is a density function, and $f_2(t \mid \tau)$ is a conditional density function. The associated marginal density function $f(t)$ is:

$$f(t) = \int_0^\infty \phi(\tau, t)\, \mathrm{d}r \qquad [7.11.2]$$

7.11.1 Parallel systems with variable failure rates

If a system consists of two equipments in parallel and both equipments have the same failure rate λ_1 when both are operating but have a different failure rate λ_2 after the first equipment has failed, then the density functions are:

$$f_1(t) = 2\lambda_1 \exp(-2\lambda_1 t) \qquad [7.11.3]$$

$$f_2(t \mid \tau) = \lambda_2 \exp[-\lambda_2 (t - \tau)] \qquad 0 < \tau < t \qquad [7.11.4a]$$

$$= 0 \qquad \tau > t \qquad [7.11.4b]$$

The joint density function is:

$$\phi(\tau, t) = f_1(\tau) f_2(t \mid \tau) \qquad [7.11.5]$$

and the marginal density function is:

$$f(t) = \int_0^t 2\lambda_1 \exp(-2\lambda_1 \tau) \lambda_2 \exp[-\lambda_2 (t - \tau)]\, \mathrm{d}r \qquad [7.11.6a]$$

$$= \frac{2\lambda_1 \lambda_2}{2\lambda_1 - \lambda_2} [\exp(-\lambda_2 t) - \exp(-2\lambda_1 t)] \qquad [7.11.6b]$$

The reliability is

$$R(t) = 1 - \int_0^t f(t)\, \mathrm{d}t \qquad [7.11.7a]$$

$$= \frac{1}{2\lambda_1 - \lambda_2} [2\lambda_1 \exp(-\lambda_2 t) - \lambda_2 \exp(-2\lambda_1 t)] \qquad [7.11.7b]$$

7.11.2 Stand by systems with variable failure rates

If a system consists of two equipments, one operating and one on stand by, with perfect switchover, and if the failure rates of the operating and the stand by equipments are λ_1 and λ_2, respectively, then the density functions are:

$$f_1(\tau) = \lambda_1 \exp(-\lambda_1 \tau) \qquad [7.11.8]$$

$$f_2(t|\tau) = \lambda_2 \exp[-\lambda_2 (t - \tau)] \qquad 0 < \tau < t \qquad [7.11.9a]$$

$$= 0 \qquad \tau > t \qquad [7.11.9b]$$

and hence

$$f(t) = \frac{\lambda_1 \lambda_2}{\lambda_1 - \lambda_2} [\exp(-\lambda_2 t) - \exp(-\lambda_1 t)] \qquad [7.11.10]$$

$$R(t) = \frac{1}{\lambda_1 - \lambda_2} [\lambda_1 \exp(-\lambda_2 t) - \lambda_2 \exp(-\lambda_1 t)] \qquad [7.11.11]$$

7.12 Monte Carlo Simulation

Many practical problems cannot be solved by any of the analytical methods described and are only soluble by simulation. The principal method used is Monte Carlo simulation. Accounts of Monte Carlo simulation include that given in *Method of Statistical Testing. Monte Carlo Method* (Shreider, 1964) and that by Shooman (1968a).

7.12.1 Simulation method

The application of Monte Carlo simulation to the determination of the reliability and/or availability of complex systems proceeds broadly as follows.

The system configuration, the failure and repair characteristics of the components, and the time period of interest are specified. The time period is divided into small increments. The first trial is then carried out covering the

time period specified. At the first time increment the probability of failure of the first equipment is calculated. This probability is compared with a random number in the range 0 to 1 generated from a uniform distribution: if the random number is less than or equal to the failure probability the equipment fails, otherwise it survives. The state of all the equipments is computed in like manner. The situation is then reviewed to determine the overall state of the system. If failures have occurred, there may be various changes in the system, such as initiation of repair of failed equipments, alteration in failure rates of more highly loaded surviving equipments, etc. The system behaviour at the second time increment is then computed and the process is continued until the specified time period is complete. This whole calculation constitutes only a single trial.

The result of this trial is that the system either has or has not met its reliability/availability objective. It is then necessary to carry out further trials to obtain the full simulation. The ratio of successful trials to total trials asymptotically approaches a constant value and this is the required system reliability/availability result. The equipment characteristics such as failure and repair rates obtained in the series of simulation trials naturally also approach asymptotically the values originally specified.

7.12.2 Illustrative example

As an illustration, consider the determination of the reliability of a single equipment over a specified period of time, assuming the exponential failure distribution. This simple case is chosen for illustration because there is also an analytical solution which is given by Equation 7.6.11. Let the time period to be considered be 10 months and let the failure rate λ be 0.5 faults/year. Then, in Equation 7.6.11,

$\lambda = 0.5$ faults/year

$t = 10$ months $= 0.83$ year

Hence

$R = 0.66$

Now consider the alternative solution using Monte Carlo simulation. The time period is divided into suitable increments, which in this case are shown as 1 month. The probability of failure q in one time increment δt is then calculated as:

$$\begin{aligned} -q &= \lambda \delta t \\ &= 0.5 \times 0.0833 \\ &= 0.0417 \end{aligned}$$

The Monte Carlo simulation is then carried out using a set of random numbers. A suitable series of random numbers, which in this case have been generated by a computer and are therefore strictly pseudo-random numbers, is given in Table 7.7. The first trial is carried out as follows. For the first month the probability of failure q (= 0.0417) is compared with the random number v. The occurrence of survival or failure is determined as follows:

$v > q$ survival;

$v < q$ failure.

Thus, taking the random numbers from the first line of the table, in the first month, since $v = 0.0417$, the equipment survives. The same process is repeated for each of the remaining 9 months. Since in all cases $v > q$, the equipment survives the whole 10-month period. This completes the first trial, in which the equipment has survived.

Further trials are then carried out on the same lines. The second, fourth and sixth lines of the random number table contain values of the random number v which are less than q; these are shown underlined in Table 7.7. In the second, fourth and sixth trials, therefore, the equipment fails, but in all the other trials it survives. The trials which constitute survival and failure may then be tabulated as shown in Table 7.8, assigning 1 to a survival and 0 to a failure.

The reliability of the equipment is then determined as the ratio of the number of trials in which the equipment survives to the total number of trials. In this example the ratio is 0.7. Since only 10 trials have been done, the reliability can be calculated only to one place of decimal. This value of the reliability compares with the value of 0.66 calculated earlier from the analytical relationship.

7.12.3 Applications of the method

As an illustration of the sort of problem to which Monte Carlo methods are applicable consider the olefins plant system shown in Figure 7.10. The system consists of four cracking furnaces in parallel followed by a compressor and then by a separation train. The furnaces have the characteristics shown in Table 7.9. The failure rate of the compressor is 0.3 faults/year and that of the separation train is 3 faults/year. The repair characteristics of the equipment are given in Table 7.10. The furnace repair team is able to work on only one furnace at a time, but there is no other restriction on the repair work. The information required from the simulation might be, say: (1) the probability of achieving full availability, (2) the mean availability

Table 7.7 *A series of random numbers*

Random numbers									
0.7710	0.7818	0.7517	0.4740	0.0782	0.2032	0.5159	0.2664	0.9556	0.3355
0.4129	0.4574	0.0284	0.0538	0.0677	0.9217	0.9214	0.2330	0.1053	0.5345
0.2598	0.7481	0.1507	0.1707	0.6685	0.4742	0.8289	0.7054	0.7725	0.2862
0.7649	0.0135	0.1968	0.0592	0.5838	0.9701	0.5664	0.6681	0.9104	0.4500
0.5064	0.9879	0.3699	0.3285	0.6416	0.8936	0.5872	0.4803	0.5972	0.2603
0.1873	0.7806	0.9981	0.9630	0.7952	0.1043	0.4693	0.8766	0.0359	0.3265
0.6358	0.8761	0.5345	0.3221	0.1226	0.8365	0.9158	0.9662	0.5547	0.6329
0.8050	0.1336	0.5572	0.1402	0.8269	0.7000	0.7549	0.2335	0.6067	0.5389
0.7730	0.7877	0.7693	0.5267	0.2364	0.6778	0.9397	0.5379	0.7701	0.7789
0.7430	0.4476	0.9991	0.9659	0.8040	0.1307	0.5484	0.1139	0.7478	0.4622

Table 7.8 *Monte Carlo simulation example: survival or failure of equipment in trials 1–10*

Trial	*Survival/failure*
1	1
2	0
3	1
4	0
5	1
6	0
7	1
8	1
9	1
10	1

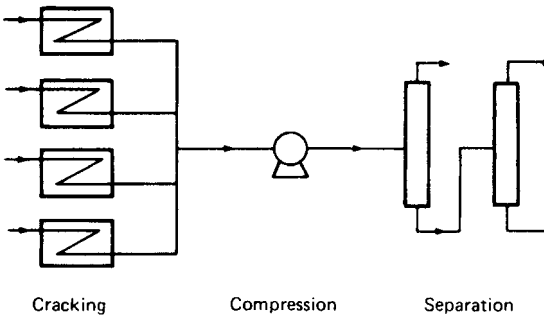


Figure 7.10 *Olefins plant system*

Table 7.9 *Monte Carlo simulation example: characteristics of the furnaces*

Time since start-up (days)	*Proportion of furnaces failing*
0–50	0.08
50–100	0.05
100–200	0.05
200–300	0.10
300–400	0.10

achieved, (3) the range of availabilities and the corresponding probabilities, over a period of 90 days.

7.12.4 Features of the method

It will be apparent from this example that it is necessary to resort to Monte Carlo simulation on account of the complexity not so much of the system configuration, which is in fact rather simple, but rather of that of the failure and repair data and other rules and constraints. A single simulation is capable of giving a number of results. Thus in the example quoted the results required were, in effect, the system reliability, its mean availability and its availability density function.

The failure data are frequently provided in the form of a failure histogram. The quantity which is required in the simulation for comparison with the random number is the probability of failure q. If the fraction failing over one time increment is δF, then

Table 7.10 *Monte Carlo simulation example: repair characteristics of the equipment*

	Repair time (days)	*Proportion of occasions*
Furnace	20	0.7
	30	0.2
	40	0.1
Compressor	10	0.8
	30	0.2
Separation train	10	0.7
	20	0.3

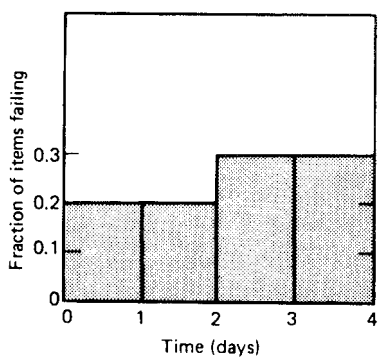


Figure 7.11 *Failure data histogram*

$$q = \frac{\delta F}{1 - F} \qquad [7.12.1]$$

Thus consider the failure histogram shown in Figure 7.11. The probabilities of failure for the 4 days obtained from Equation 7.12.1 are 0.2, 0.25, 0.5 and 1.0.

It is often convenient to perform one set of trials, examine the results and then perform further sets. If this is done, however, it is necessary that the subsequent sets should not start with the same random number as the first set, otherwise the effect is simply to repeat that set continuously.

7.12.5 Number of trials

The Monte Carlo method is extremely powerful, but it does have one serious drawback with regard to the number of trials required to obtain an accurate result, especially where the probability investigated is high. The number of trials required to achieve a given confidence level on the probability cannot, in general, be calculated. An approximate estimate of the number of trials can be obtained, however, if certain simplifying assumptions are made. The following method of estimation has been described by Shooman (1968a).

In determining the value of a single probability, such as a reliability, the simulation may be regarded as a series of n trials which have a binomial distribution with a true probability of success p and of failure q. The binomial distribution approaches the normal distribution for $p > 0.5$ and $nq > 5$. The point estimate of the probability of failure q is

given by n_f/n, where n_f is the number of failures recorded in n trials. Then the fractional error e between the estimated and true probabilities of failure is:

$$e = \frac{n_f/n - q}{q} \quad [7.12.2]$$

If μ and σ are the expected number of failures and the expected standard deviation, then for a $(1-\alpha)$ confidence level:

$$P(-\gamma\sigma < n_f - \mu < \gamma\sigma) = 1 - \alpha \quad [7.12.3]$$

where γ is the number of standard deviations corresponding to that level. In terms of the parameters n, p and q of the binomial distribution:

$$\mu = nq \quad [7.12.4]$$

$$\sigma = (npq)^{1/2} \quad [7.12.5]$$

Then

$$P[-\gamma(npq)^{1/2} < n_f - n_q < \gamma(npq)^{1/2}] = 1 - \alpha \quad [7.12.6]$$

$$P[-\gamma(p/nq)^{1/2} < e < \gamma(p/nq)^{1/2}] = 1 - \alpha \quad [7.12.7]$$

Thus at the 95% confidence level, for which $\gamma = 2$:

$$e > 200(p/nq)^{1/2}\% \quad [7.12.8]$$

The very large number of trials required for a system with very high reliability can be seen by considering the number required to give an error of $\not>5\%$ at a 95% confidence level (see Table 7.11). Thus, despite the undoubted power of the Monte Carlo method, it remains attractive to use and develop analytical techniques wherever possible. A further discussion of the number of trials required in Monte Carlo simulation is given by Shreider (1964).

Monte Carlo simulation also has other applications in reliability work. Its use to generate hazard rates from distributions of hazard rates is described in Chapter 9 in connection with fault tree work.

7.13 Availability

7.13.1 System availability analysis

The availability analysis of systems, like reliability analysis, has as its objectives: (1) to assess system availability and to identify critical aspects; and (2) to effect the required improvements.

It is usually necessary to consider a number of availability characteristics. For process plants these are likely to include: (1) the probability of obtaining nominal output and down-time, (2) the probability of obtaining other outputs and down-times and (3) the probability of infrequent but very long down-times. Long outages are particularly important. It is usually appropriate to deal separately with these. Thus, for example, the frequency of a long outage of 1 year might be about 10^{-4}/year. It is not very meaningful to express this as an additional loss of mean availability of 0.04 days/year.

A full analysis may well involve much effort. Therefore it is important to identify those subsystems which have a particularly strong influence on the overall system availability. Those subsystems which do not greatly affect system availability can be treated in less detail.

There are two main types of availability data which may be used. Sometimes data on the availability of whole subsystems can be obtained. In other cases it is necessary to calculate system availability from failure rate and repair time data. In either case it is important that the accuracy of the data be matched to the sensitivity of the system availability to errors in the data.

As far as possible data on the availability of a process unit should describe the performance of that unit independent of other units. Down-time of the unit due to unavailability of other units or to other extraneous causes should not be included.

Particular attention should be paid to the availability of process raw materials and services. It is also often necessary to consider the availability of other plants which receive from the plant under consideration outputs such as by-products, electricity or steam.

There are a number of methods available for the analysis of more complex systems, and some of these are described below.

Table 7.11 *Monte Carlo simulation: number of trials required in example to give an error of $\not>5\%$ at a 95% confidence level*

Probability of success	*No. of trials required*
0.9	14,400
0.99	158,400
0.999	1,598,400

7.13.2 The availability function

In general, availability $A(t)$ is a function of time. It may be expressed in terms of the up-time $u(t)$ and down-time $d(t)$:

$$A(t) = \frac{u(t)}{u(t) + d(t)} \quad [7.13.1]$$

The unavailability $V(t)$ is

$$V(t) = 1 - A(t) \quad [7.13.2]$$

$$= \frac{d(t)}{u(t) + d(t)} \quad [7.13.3]$$

The point availability $A(t)$ can be integrated over the time period T to give the mean availability over that period:

$$A(T) = \frac{1}{T}\int_0^T A(t)\,\mathrm{d}t \quad [7.13.4]$$

Often, however, it is the long-term, or steady-state, availability $A(\infty)$ which is of most interest:

$$A(\infty) = \frac{u(\infty)}{u(\infty) + d(\infty)} \quad [7.13.5]$$

The long-term availability may also be expressed in terms of the mean up-time m_u and the mean down-time m_d:

$$A(\infty) = \frac{m_u}{m_u + m_d} \quad [7.13.6]$$

For a single equipment or system with exponential failure and repair distributions, failure rate λ and repair rate μ:

$$m_u = \frac{1}{\lambda} \quad [7.13.7]$$

$$m_d = \frac{1}{\mu} \quad [7.13.8]$$

$$= m_r \quad [7.13.9]$$

Then, from Equations 7.13.6–7.13.9:

$$A(\infty) = \frac{\mu}{\lambda + \mu} \quad [7.13.10a]$$

$$= \frac{1}{1 + \lambda m_r} \quad [7.13.10b]$$

$$= 1 - \lambda m_r \qquad \lambda m_r \ll 1 \quad [7.13.10c]$$

This result was given earlier in Equation 7.10.28, and the long-term unavailability is:

$$V(\infty) = \frac{\lambda}{\lambda + \mu} \quad [7.13.11a]$$

$$= \frac{\lambda m_r}{1 + \lambda m_r} \quad [7.13.11b]$$

$$= \lambda m_r \qquad \lambda m_r \ll 1 \quad [7.13.11c]$$

7.13.3 The repair time density function

It is appropriate at this point to consider the distribution of repair times. The mean repair time m_r is defined as the first moment of the repair time density function $f_r(t_r)$:

$$m_r = \int_0^\infty t_r f_r(t_r)\, dt_r \quad [7.13.12]$$

So far, the repair time distribution which has been considered is the exponential. For this distribution the repair time density function $f_r(t_r)$ is

$$f_r(t_r) = \mu \exp(-\mu t_r) \quad [7.13.13]$$

The repair time distribution function $F_r(t_r)$ is:

$$F_r(t_r) = \int_0^{t_r} f_r(t_r)\, dt_r \quad [7.13.14a]$$

$$= 1 - \exp(-\mu t_r) \quad [7.13.14b]$$

The mean repair time is:

$$m_r = \int_0^\infty t_r \mu \exp(-\mu t_r)\, dt_r \quad [7.13.15a]$$

$$= \frac{1}{\mu} \quad [7.13.15b]$$

For the normal distribution:

$$f_r(t_r) = \frac{1}{\sigma_r (2\pi)^{1/2}} \exp\left(-\frac{(t_r - m_r)^2}{2\sigma_r^2} \right) \quad [7.13.16]$$

where the mean repair time is m_r.

For the log-normal distribution:

$$f_r(t_r) = \frac{1}{\sigma_r t_r (2\pi)^{1/2}} \exp\left(-\frac{[\ln(t_r) - m_r^*]^2}{2\sigma_r^2} \right) \quad [7.13.17]$$

Repair time data often fit a log–normal distribution.

7.13.4 The down-time density function

For a single equipment the repair time and the down-time are the same. For a system it is more usual to speak of the down-time.

So far the down-time used in the expressions for availability has been the mean down-time m_d. But, just as there is a repair time distribution, so there is a down-time distribution. It is possible to define a down-time density function $f_d(d)$ and distribution function $F_d(d)$.

Particularly important are long down-times. In the down-time distribution shown in Figure 7.12, the tail in the distribution is due to infrequent, but long, outages.

7.13.5 The throughput density function

So far it has been assumed that either an item is available or it is not. In fact, however, in the process industries many items may exhibit a range of throughputs. This partial availability can be expressed by a throughput density function $f_w(w)$.

Typical throughput data from a process unit given by G.D.M. Pearson (1975) are shown in Table 7.12 and plotted in Figure 7.13. These data constitute a throughput density function. Similarly, the throughput of a whole plant can be expressed as a throughput density function.

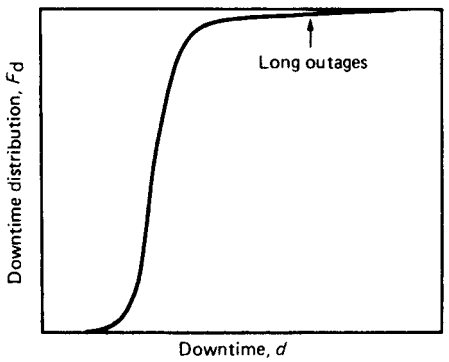


Figure 7.12 *Down-time distribution showing a tail corresponding to infrequent, but long, outages*

Table 7.12 *Throughput capabilities of a process unit (G.D.M. Pearson, 1975) (Courtesy of the University of Nottingham)*

Throughput capability (fraction of normal throughput)	*Probability*
0	0.035
0.025	0.015
0.050	0.005
0.800	0.001
0.850	0.002
0.900	0.005
0.925	0.007
0.950	0.010
0.975	0.020
1.000	0.900

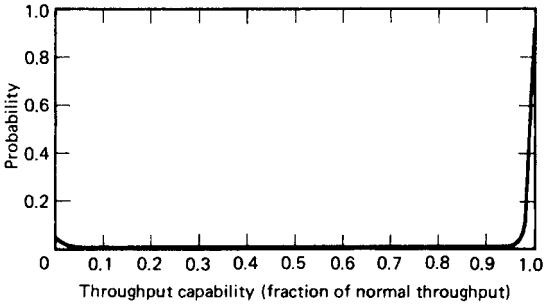


Figure 7.13 *Throughput density for a process unit (G.D.M. Pearson, 1975) (Reproduced by permission of the University of Nottingham)*

7.13.6 Markov models

The derivation of expressions for availability from Markov models has been described briefly above. This method is now considered in more detail.

It is normally assumed in such models that the repair time distribution is exponential with constant repair rate μ. Usually it is the long-term availability which is of interest. In this case the Markov equations become steady-state equations. Thus, for example, Equation 7.10.25 becomes

$$0 = -\lambda P_0 + \mu P_1 \qquad [7.13.18a]$$

but Equation 7.10.25b becomes

$$1 = P_0 + P_1 \qquad [7.13.18b]$$

Equations 7.13.18a,b then yield equation [7.10.28] directly.

The definition of availability used depends on the configuration of the system. Considering systems with n equipments, for a series system only the first state P_0 constitutes survival:

$$A(\infty) = P_0 \qquad [7.13.19]$$

For a parallel system only the last state represents failure:

$$A(\infty) = 1 - P_n \qquad [7.13.20]$$

For an r-out-of-n system the states up to and including the $(n-r)$th state give survival:

$$A(\infty) = \sum_{i=0}^{n-r} P_i \qquad [7.13.21]$$

Long-term availabilities for some standard systems assuming exponential failure and repair time distributions are given in Table 7.13. The availabilities are defined by Equations 7.13.19–7.13.21. The repairman assumption is that each repairman repairs one equipment, so that the repair transition rates between states are limited by the number of repairmen.

Another important and general case is that in which there are n equipments but only m repairmen. If there are k equipments down then, at steady state:

$$0 = (n-k+1)\lambda P_{k-1} - [(n-k)\lambda + k\mu]P_k + (k+1)\mu P_{k+1} \qquad k < m \qquad [7.13.22a]$$

Table 7.13 *Long-term availabilities for some standard systems assuming exponential failure and repair time distributions*

System	*No. of components*	*No. of repairmen*	*Availability*
–	1	1	$\dfrac{\mu}{\lambda+\mu}$
Series	2	1	$\dfrac{\mu^2}{2\lambda^2+2\lambda\mu+\mu^2}$
Series	2	2	$\dfrac{\mu^2}{(\lambda+\mu)^2}$
Series	n	1	$\dfrac{(\mu/\lambda)^n}{n!\sum_{i=0}^{n}(1/i!)(\mu/\lambda)^i}$
Series	n	n	$\dfrac{\mu^n}{(\lambda+\mu)^n}$
Parallel	2	1	$\dfrac{\mu^2+2\lambda\mu}{2\lambda^2+2\lambda\mu+\mu^2}$
Parallel	2	2	$\dfrac{\mu^2+2\lambda\mu}{\lambda^2+2\lambda\mu+\mu^2}$
Parallel	n	1	$1-\dfrac{1}{\sum_{i=0}^{n}(1/i!)(\mu/\lambda)^i}$
r-out-of-n	n	n	$\sum_{i=r}^{n}\binom{n}{i}\left(\dfrac{\mu}{\lambda+\mu}\right)^i\left(\dfrac{\lambda}{\lambda+\mu}\right)^{n-i}$
Stand by	2	1	$\dfrac{\mu^2+\lambda\mu}{\lambda^2+\lambda\mu+\mu^2}$
Stand by	2	2	$\dfrac{2\mu^2+2\lambda\mu}{\lambda^2+2\lambda\mu+2\mu^2}$
Stand by	n	1	$1-\dfrac{1}{\sum_{i=0}^{n}(\mu/\lambda)^i}$
Stand by	n	n	$1-\dfrac{1}{\sum_{i=0}^{n}(n/i!)(\mu/\lambda)^{n-i}}$

$$0 = (n-k+1)\lambda P_{k-1} - [(n-k)\lambda + m\mu]P_k + m\mu P_{k+1} \qquad k \geq m \qquad [7.13.22b]$$

$$1 = \sum_{i=0}^{n} P_i \qquad [7.13.22c]$$

Equations 7.13.22a–c have the solution:

$$P_0 = \left[\sum_{k=0}^{m-1}\frac{n!}{(n-k)!k!}\rho^k + \sum_{k=m}^{n}\frac{n!}{(n-k)!m!}\rho^m\left(\frac{\rho}{m}\right)^{k-1}\right]^{-1} \qquad [7.13.23a]$$

$$P_k = \frac{n!}{(n-k)!k!}\rho^k P_0 \quad k<m \qquad [7.13.23b]$$

$$= \frac{n!}{(n-k)!m!}\rho^m\left(\frac{\rho}{m}\right)^{k-m} P_0 \quad k \geq m \qquad [7.13.23c]$$

with

$$\rho = \frac{\lambda}{\mu} \qquad [7.13.24]$$

The long-term availability of an r-out-of-n system with m repairmen is given by:

$$A(\infty) = \sum_{i=0}^{n-r} P_i \qquad [7.13.25]$$

using Equations 7.13.23a–c.

These and numerous other cases are treated in more detail by Sandler (1963).

7.13.7 Logic flow diagrams

Logic flow diagrams are often used to represent system availability. Thus the logic flow diagram shown in Figure 7.8 for the storage tank pump system with the configuration given in Figure 7.6(b) is in fact an availability diagram. In order to use the logic flow diagram method it is necessary to represent the plant flow diagram in logical form. It is necessary, therefore, to convert the plant flow diagram into a network of relatively simple blocks such as series or parallel units.

The plant availability determined using a logic flow diagram may be the mean availability or the availability density function. Usually the calculation is limited to the former. There are two main methods of determining the mean availability of the plant. In many cases the availability data are the mean availabilities of the units which constitute the plant. Typical units might be a tank-pump system, a complete distillation column or a set of centrifuges. The mean unavailability of a unit is effectively a fractional dead time or probability of being unavailable. Then the mean availability of the plant may be calculated from the mean unavailabilities of these units.

In other cases the availability data obtainable are the failure rates and repair times of the equipments which constitute the units. Typical equipments are a pump, a heat exchanger or a drier. The mean unavailability, or fractional dead time, of an equipment may be calculated from the failure rate and repair time data using Equation 7.13.10. The fractional dead time of the unit may be calculated from those of the constituent equipments. Then the mean unavailability of the plant may again be calculated from the unavailabilities of the units. The mean repair time of the plant may be determined by calculating the failure rate and the mean unavailability.

It is also possible, however, to express the unit availabilities as throughput density functions, and in this case the plant availability is also a throughput density function. This may be obtained from the logic flow diagram by Monte Carlo simulation in a manner similar to that used in fault tree evaluation, as described in Chapter 9.

7.13.8 Throughput capability method

There is an alternative method, which allows the system availabilities to be expressed as throughput densities and still avoid the use of simulation (G.D.M. Pearson, 1975). The method involves converting the system into a series system and determining successively the limiting throughputs.

As an illustration, consider the distillation plant system flow diagram given by Pearson and shown in Figure 7.14(a). The corresponding availability block diagram is given in Figure 7.14(b). The path (11) affects the operation of paths (2, 6, 7, 9) and (1, 5) and therefore takes the position shown, while side paths (13) and (14) affect the operation of the main forward path and are therefore shown there. The main forward path is also affected by the single supplies of electricity, high pressure steam and cooling water. The units (1–2) can be reduced to an equivalent but simplified block diagram, as shown in Figure 7.14(c). This is a complex subsystem, which cannot be resolved into simple series or parallel systems.

The throughput capability of the system is evaluated by series and parallel state enumeration techniques. The series enumeration technique is as follows. All the stages of the system, that is, the units or the subsystems, are treated together as a series system. The throughput levels of the system are considered in turn, starting at zero throughput and rising to full throughput. At each level there is a stage which has the lowest throughput capability and limits the system throughput capability; this is the 'bottleneck' stage. The probability that the system has this throughput is determined by the probability that this bottleneck stage is in this state. The throughput capability of the bottleneck stage is then increased to its next discrete level. A new bottleneck stage is then identified and the procedure is repeated. Table 7.14 shows the throughput capabilities for a system of 10 identical process units with throughput capabilities as given in Table 7.13. The corresponding plot of system throughput capabilities is illustrated in Figure 7.15. This is the throughput density function of the system. The mean throughput capability of a single unit is 0.943 and that of the system is 0.557.

The parallel path enumeration technique is as follows. Only two stages of the system are considered at a time. The throughput density function of this subsystem is obtained by summing the discrete throughput capabilities of the two stages and multiplying the corresponding probabilities. If in the original system there are more than two stages in parallel, this subsystem and the next parallel stage are then considered and the procedure repeated.

Further details of the throughput capability method, including the application of the state enumeration technique to complex subsystems, are given by G.D.M. Pearson (1975).

7.13.9 Flowsheeting and simulation methods

Flowsheeting methods and, in particular, computer flowsheeting programs, may also be used to determine plant availability. The use of this approach has been described by Holmes (1976).

7.13.10 Storage

Plant availability is affected by storage, which introduces flexibility, and may allow units upstream or downstream of a failed unit to continue in operation for a time. Methods of determining the effect of storage on plant availability have been discussed by Holmes (1976) and by Henley and Hoshino (1977).

There are two main classes of storage tank: (1) raw material and product storage tanks, and (2) intermediate storage tanks. Storage tanks are provided for various reasons, some of which have nothing to do with plant availability. Raw material and product storage tanks are used to smooth deliveries and collections and to blend materials. Intermediate storage tanks are also used to smooth fluctuations and to blend intermediates.

As an illustration, consider the simplest system with intermediate storage capacity of an upstream unit, an intermediate storage tank and a downstream unit. This system and its operating policies have been investigated by Henley and Hoshino (1977).

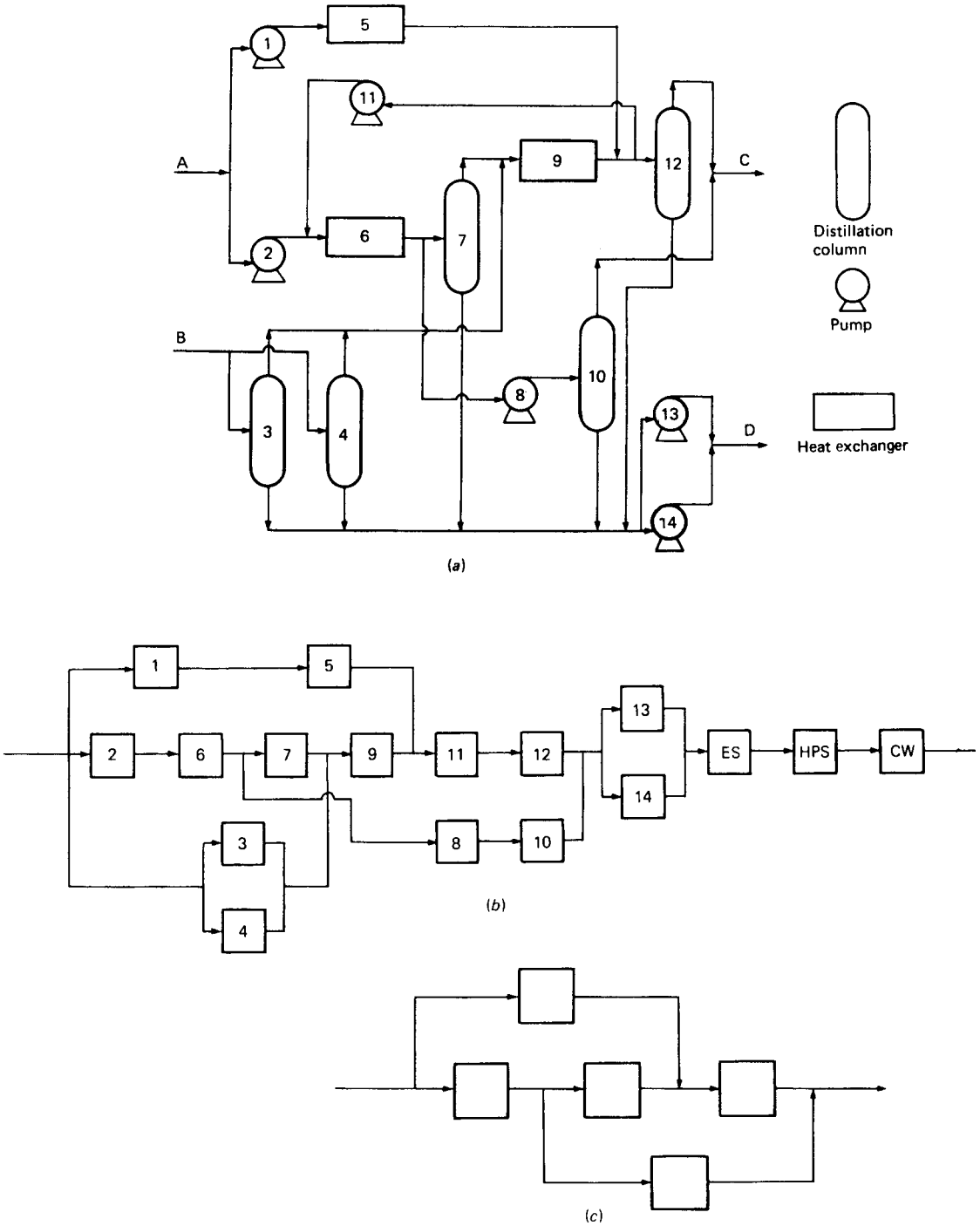


Figure 7.14 *Distillation plant system (G.D.M. Pearson, 1975): (a) flow diagram of system; (b) availability block diagram of system; (c) equivalent block diagram of units 1–2. ES, electricty supply; HPS, high pressure steam; CW, cooling water (Reproduced by permission of the University of Nottingham)*

Table 7.14 *Throughput capabilities of a process system (G.D.M. Pearson, 1975) (Courtesy of the University of Nottingham)*

Throughput capability (fraction of normal throughput)	*Probability*
0	0.300
0.025	0.102
0.050	0.031
0.800	0.006
0.850	0.012
0.900	0.029
0.925	0.038
0.950	0.050
0.975	0.086
1.000	0.349

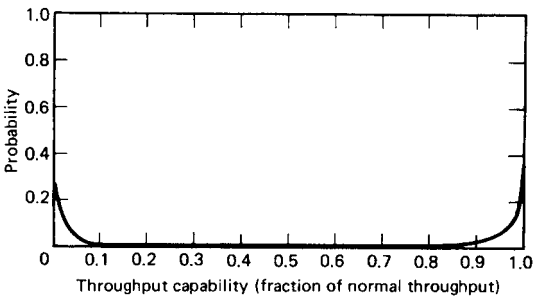


Figure 7.15 *Throughput density for a process system (G.D.M. Pearson, 1975) (Reproduced by permission of the University of Nottingham)*

Some basic operating policies are: (1) to keep the tank filled if possible, (2) to keep the tank empty if possible, (3) to keep the tank half full if possible and (4) to allow the tank level to fluctuate. The appropriate operating policy depends on the objectives to be achieved by the use of the storage. It is convenient to consider initially only the improvement of plant availability.

The policy necessary to maximize plant availability depends on the relative maximum capacities and failure rates of the upstream and downstream units. If the capacities and failure rates are equal, the appropriate policy is to run with the tank half full, emptying and filling during unit failures. If the capacity of the upstream unit is higher but its failure rate is also higher, the appropriate policy is to run with the tank full, filling during normal operation or downstream unit failure. If the capacity of the downstream unit is higher, but its failure rate is also higher, the appropriate policy is to run with the tank empty, emptying during normal operation or upstream unit failure. A general principle underlying these policies is that unit production is not interrupted merely in order to fill or empty the tank.

It may be necessary, however, to adopt other policies which have objectives other than improvement of plant availability. Thus, if the shut-down of the downstream unit is relatively hazardous or difficult or if the output of the upstream unit needs to be blended, the policy adopted may be to run with the tank full. On the other hand, if the shut-down of the upstream unit is relatively hazardous or difficult, the policy adopted may be to run with the tank empty.

Table 7.15 *Plant availability example: unit throughput capabilities*

	Throughput capability (m^3/h)	*Probability*
Upstream unit	0	0.02
	95	0.03
	100	0.95
Downstream unit	0	0.04
	90	0.06
	100	0.90

For certain defined cases, a relatively simple treatment is possible. One such case, described by Henley and Hoshino (1977), is that of an upstream unit with excess capacity. It is assumed that the time required to fill the tank using this excess capacity is much less than the mean time to failure of the upstream unit and that the operating policy is to keep the tank full. Then it can be shown that the following relationships apply:

$$V_s = \frac{\lambda_u m_{ru}}{1 + \lambda_u m_{ru}} \qquad [7.13.26]$$

$$V_{st} = k V_s \qquad [7.13.27]$$

$$k = \exp(-T_e/m_{ru}) \qquad [7.13.28]$$

$$\lambda_{st} = \frac{k[\lambda_u/(1 + \lambda_u m_{ru})]}{1 - k[\lambda_u m_{ru}/(1 + \lambda_u m_{ru})]} \qquad [7.13.29]$$

where m_{ru} is the mean repair time of the upstream unit, T_e is the time required to empty the tank, V_s is the unavailability of the upstream unit, V_{st} is the unavailability of the upstream unit + the tank, λ_{st} is the failure rate of the upstream unit + the tank, and λ_u is the failure rate of the upstream unit.

A fuller treatment of this and other cases is given by Henley and Hoshino (1977).

The problem of the effect of storage has also been treated by Coker (1978), who has extended the throughput capability method of Pearson to take account of storage. The system considered is an upstream unit, an intermediate storage tank and a downstream unit. The states of the storage are defined as discrete levels of storage, or hold-ups. These states are then determined using a discrete-state, discrete-time steady-state Markov model, as described in Section 7.10.

As an illustration of the method, consider the system given by Coker in which the throughput capabilities of the upstream and downstream units are as shown in Table 7.15 and in which the tank capacity is 15 m^3. Then the probability of a net inflow of 100 m^3 into the tank is $0.95 \times 0.04 = 0.038$. The probabilities of the other net inflows may be calculated in a similar manner. It should be noted that a zero net inflow is obtained both for a flow of 0 m^3/h in both units and for one of 100 m^3/h in both units. The probability distribution of net inflow is then as shown in Table 7.16.

Now assume that the states of the tank are defined as hold-ups of 0, 5, 10 and 15 m^3. The transition probabilities, which are the elements of the matrix A in Equation 7.10.37, are determined by considering the possible changes in tank

Table 7.16 *Plant availability example: probability of net inflow*

Net inflow into tank (m^3/h)	*Probability*
100	0.0380
95	0.0012
10	0.0570
5	0.0018
0	0.8558
−5	0.0270
−90	0.0012
−100	0.0180

hold-up and the net flow differences which can produce such changes, and then summing the probabilities of these net flows. Thus for a hold-up 'change' of 0 to 0 m^3 the net flows which can cause this change are 0, −5, −90 and −100 m^3/h. Then the transition probability between an initial hold-up state of 0 m^3 and a final state of 0 m^3 is:

$$0.8558 + 0.027 + 0.0012 + 0.018 = 0.902$$

The other transition probabilities may be calculated in a similar manner. The transition matrix is then:

$$\mathbf{A} = \begin{bmatrix} 0.9020 & 0.0018 & 0.0570 & 0.0392 \\ 0.0462 & 0.8558 & 0.0018 & 0.0962 \\ 0.0192 & 0.0270 & 0.8558 & 0.0980 \\ 0.0192 & 0 & 0.0270 & 0.9538 \end{bmatrix}$$

Then application of Equation 7.10.37 gives the probabilities of tank hold-up listed in Table 7.17.

The throughput capability of the system is now calculated. A throughput capability of 10 m^3/h occurs when the throughput capabilities of the upstream and downstream units are 0 m^3 and 90 or 100 m^3, respectively. The probability of a system throughput capability of 10 m^3/h is:

$$0.02 \times 0.1826 \times (0.06 + 0.90) = 0.0035$$

The other throughput capabilities may be calculated in a similar manner. The result obtained is given in Table 7.18.

Table 7.17 *Plant availability example: probabilities of tank holdup*

Tank holdup (m^3)	*Probability*
0	0.1722
5	0.0363
10	0.1826
15	0.6089

Table 7.18 *Plant availability example: system throughput capabilities calculated in the example*

Throughput capability of system (m^3/h)	*Probability*
0	0.0433
5	0.0007
10	0.0035
15	0.0167
90	0.0588
95	0.0046
100	0.8774

7.14 Bayes' Theorem

It frequently occurs in reliability engineering that there is a need to test a hypothesis or to revise an estimate in the light of additional information. A powerful tool for handling such problems is Bayes' theorem. Accounts of Bayes' theorem include those given in *Introduction to Probability and Statistics from a Bayesian Viewpoint* (Lindley, 1965), and those by Savage (1962a), Brand (1980) and Kaplan (1983). Its use in expert systems is discussed by Michie (1979).

7.14.1 Basic formulation

A basic formulation of Bayes' theorem is as follows. Consider the probability of the joint event AB. If the event A has two outcomes A and $\bar{A}$:

$$P(AB) = P(A \mid B)P(B) \quad [7.14.1]$$

$$= P(B \mid A)P(A) \quad [7.14.2]$$

Then:

$$P(\mathrm{A} \mid \mathrm{B}) = \frac{P(B \mid A)P(A)}{P(B \mid A)P(A) + P(B \mid \bar{A})P(\bar{A})} \quad [7.14.3]$$

In this equation the term $P(A)$ is known as the prior probability, $P(A \mid B)$ as the posterior probability and $P(B \mid A)$ as the likelihood.

Equation 7.14.3 may also be reformulated to accommodate multiple outcomes. If the event A has n outcomes

$$P(A_j \mid B) = \frac{P(B \mid A_j)P(A_j)}{\sum_{i-1}^{n} P(B \mid A_j)P(A_i)} \quad [7.14.4]$$

7.14.2 Hypothesis formulation

Equation 7.14.3 may also be written in terms of a hypothesis H and an event E, which serves to confirm or deny the hypothesis:

$$P(H \mid E) = \frac{P(E \mid H)P(H)}{P(E \mid H)P(H) + P(E \mid \bar{H})P(\bar{H})} \quad [7.14.5]$$

7.14.3 Continuous formulation

There is also a continuous formulation of Bayes' theorem in terms of distributions. If X is a random variable, its density function may be written as $f_X(x)$. Then a formulation of Bayes' theorem in terms of such distributions is:

$$f_{Y|X}(y \mid x) = \frac{f_{X|Y}(x \mid y)f_Y(y)}{f_X(x)} \quad [7.14.6]$$

But

$$f_X(x) = \int_{-\infty}^{\infty} f_{X|Y}(x \mid y)f_Y(y)\,\mathrm{d}y \quad [7.14.7]$$

Hence

$$f_{Y|X}(y \mid x) = \frac{f_{X|Y}(x \mid y)f_Y(y)}{\int_{-\infty}^{\infty} f_{X|Y}(x \mid y)f_Y(y)\,\mathrm{d}y} \quad [7.14.8]$$

7.14.4 Failure rate estimation

A common problem in reliability work is the estimation of a failure rate and the revision of this estimate as more information becomes available. A typical situation might be that the initial estimate is one obtained from the literature which it is desired to revise in the light of works data.

If the failure rate is considered as a random variable, its density function may be written as $f_\Lambda(\lambda)$. The field data are assumed to be available as times to failure $t_1, \ldots, t_n$. Then from Equation 7.14.8, for the first time to failure t_1.

$$f_{\Lambda|T1}(\lambda \mid t_1) = \frac{f_{T1|\Lambda}(t_1|\lambda) f_\Lambda(\lambda)}{\int_{-\infty}^{\infty} f_{T1|\Lambda}(t_1|\lambda) f_\Lambda(\lambda)\, \mathrm{d}\lambda} \qquad [7.14.9]$$

At this stage the formulation is a general one. Its application may be illustrated by considering the common case of the revision of an initial estimate of the failure rate in the exponential distribution. In the terminology used here the exponential distribution itself may be written in terms of the random variable T:

$$f_T(t) = \Lambda \exp(-\Lambda t) \quad t \geq 0 \qquad [7.14.10a]$$

$$= 0 \qquad t < 0 \qquad [7.14.10b]$$

If Λ is now considered to be a random variable, to be estimated on the basis of observed values of T, the exponential distribution just given may be rewritten as

$$f_{T|\Lambda}(t \mid \lambda) = \lambda \exp(-\lambda t) \qquad t \geq 0 \qquad [7.14.11a]$$

$$= 0 \qquad t < 0 \qquad [7.14.11b]$$

Since the failure rate is to be treated as a random variable, it is necessary to specify the form of the distribution which it follows. The distribution assumed is again the exponential distribution, so that

$$f_\Lambda(\lambda) = \mu \exp(-\mu\lambda) \qquad [7.14.12]$$

where μ is the parameter of this distribution. Its dimensions are time, or lifetime, being the inverse of those of λ.

Then, from Equations 7.14.9, 7.14.11 and 7.14.12

$$f_{\Lambda|T1}(\lambda \mid t_1) = \frac{\lambda \exp(-\lambda t_1) \mu \exp(-\mu\lambda)}{\int_0^{\infty} (\lambda \exp(-\lambda t_1) \mu \exp(-\mu\lambda)\, \mathrm{d}\lambda} \qquad [7.14.13]$$

which yields

$$f_{\Lambda|T1}(\lambda \mid t_1) = \lambda(\mu + t_1)^2 \exp[-(\mu + t_1)\lambda] \quad \lambda \geq 0 \qquad [7.14.14a]$$

$$= 0 \qquad \lambda < 0 \qquad [7.14.14b]$$

By extension to further times to failure $t_2, \ldots, t_n$, it can be shown that

$$f_{\Lambda|T1,\ldots,T_n}(\lambda \mid t_1, \ldots, t_n) = \frac{\lambda^n}{n!} \left(\mu + \sum_{i=1}^{n} t_i\right)^{n+1} \exp\left[-\left(\mu + \sum_{i=1}^{n} t_i\right)\lambda\right] \qquad [7.14.15]$$

From this density function the mean value is determined in the usual way, the quantity obtained being the estimate $\hat{\Lambda}$ of the mean:

$$\hat{\Lambda} = \int_0^{\infty} f_{\Lambda|T1,\ldots,T_n}(\lambda \mid t_1, \ldots, t_n)\, \mathrm{d}\lambda \qquad [7.14.16]$$

The required result is thus:

$$\hat{\Lambda} = \frac{n+1}{\mu + \sum_{i=1}^{n} t_i} \qquad [7.14.17]$$

The estimate $\hat{t}$ of the mean life, or MTBF, is obtained as the inverse of that of the failure rate:

$$\hat{t} = \frac{\mu + \sum_{i=1}^{n} t_i}{n+1} \qquad [7.14.18]$$

This equation shows that for the case of the exponential distribution the estimate of the mean life is the average of the prior estimate and of the observed values times to failure.

As an illustration, consider the case where there is for an equipment a prior estimate μ of the time to failure of 8 months which is to be revised in the light of four further measurements ($n = 4$) of the times to failure of 17, 13, 18 and 12 (t_1 to t_4). Then from Equation 7.14.18 the estimated values are:

$$\hat{t} = \frac{8 + (17 + 13 + 18 + 12)}{4 + 1}$$

$$= 13.6 \text{ months}$$

$$\hat{\Lambda} = 0.074 \text{ failures/month}$$

7.15 Renewal Theory

Another technique for the analysis of repairable systems is renewal theory. Accounts of renewal theory are given in *Renewal Theory* (D.R. Cox, 1962) and by Shooman (1968a) and G.H. Mitchell (1972).

Renewal theory is illustrated here by considering the case of a single component system with instantaneous replacement of the component when it fails by another component. The theory is developed initially for the case where each replacement may be by a component with different failure characteristics.

Let system failures occur at time intervals t_1, $t_2, \ldots$, t_n. Then the system operating time τ_n to n renewals is:

$$\tau_n = t_1 + t_2 + \cdots + t_n \qquad [7.15.1]$$

The density function $f_{\tau n}(t)$ of τ_n is obtained by convolution of the individual density functions $f_1(t), f_2(t), \ldots, f_n(t)$. This is handled most easily in the Laplace domain. Then taking Laplace transforms, the convolution becomes:

$$f_{\tau n}(s) = f_1(s) \cdot f_2(s) \cdots f_n(s) \qquad [7.15.2]$$

For simplicity, consideration is now limited to the case where replacement is by identical components. Then Equation 7.15.2 becomes:

$$f_{\tau n}(s) = [f(s)]^n \qquad [7.15.3]$$

The probability that the nth renewal occurs before or at time t is given by the distribution function:

$$F_{\tau n}(t) = \int_0^t f_{\tau n}(t)\, \mathrm{d}t \qquad [7.15.4]$$

The mean, or expected, value of the time for n renewals is:

$$E[\tau_n] = \int_0^\infty t f_{rn}(t)\,\mathrm{d}t \qquad [7.15.5]$$

The probability of the number N of renewals occurring exactly at time t is:

$$P(N = n) = F_{\tau n}(t) - F_{\tau n+1}(t) \qquad [7.15.6]$$

The mean, or expected, value of N renewals in time t is:

$$E[N] = \sum_{n=0}^{\infty} nP(N = n) \qquad [7.15.7]$$

From Equations 7.15.6 and 7.15.7

$$E[N] = \sum_{n=0}^{\infty} n[F_{\tau n}(t) - F_{\tau n+1}(t)] \qquad [7.15.8]$$

Expanding the terms in Equation 7.15.8, it can be shown that:

$$E[N] = \sum_{n=1}^{\infty} F_{\tau n}(t) \qquad [7.15.9]$$

The application of these relationships may be illustrated by considering the case where the components have an exponential failure distribution with constant failure rate λ, so that the density function is:

$$f(t) = \lambda \exp(-\lambda t) \qquad [7.15.10]$$

Taking Laplace transforms

$$f(s) = \frac{\lambda}{s + \lambda} \qquad [7.15.11]$$

and then substituting Equation 7.15.11 into Equation 7.15.3 yields

$$f_{\tau n}(s) = \left(\frac{\lambda}{s + \lambda}\right)^n \qquad [7.15.12]$$

Inverting back into the time domain gives:

$$f_{\tau n}(t) = \lambda \frac{(\lambda t)^{n-1}}{(n-1)!} \exp(-\lambda t) \qquad [7.15.13]$$

This equation is the Erlangian operating time density function.

The distribution function of Equation 7.15.4 may be integrated using the expression for the density function given in Equation 7.15.13. For example, for the first renewal ($n = 1$)

$$f_{\tau 1}(t) = \lambda \exp(-\lambda t) \qquad [7.15.14]$$

Hence the distribution function is:

$$F_{\tau 1}(t) = \int_0^t \lambda \exp[-(\lambda t)]\mathrm{d}t \qquad [7.15.15]$$

$$= 1 - \exp(-\lambda t) \qquad [7.15.16]$$

and from Equation 7.15.5 the mean value

$$E[\tau 1] = \int_0^\infty t\lambda \exp(-\lambda t)\,\mathrm{d}t \qquad [7.15.17]$$

$$= 1/\lambda \qquad [7.15.18]$$

Furthermore, the probability given in Equation 7.15.6 may be written, by using Equation 7.15.4, as:

$$P(N = n) = \int_0^t f_{\tau n}(t)\,\mathrm{d}t - \int_0^t f_{\tau n+1}(t)\,\mathrm{d}t \qquad [7.15.19]$$

Substituting Equation 7.15.13 in this equation yields

$$P(N = n) = \int_0^t \lambda \frac{(\lambda t)^{n-1}}{(n-1)!} \exp(-\lambda t)\,\mathrm{d}t - \int_0^t \lambda \frac{(\lambda t)^n}{n!} \exp(-\lambda t)\,\mathrm{d}t \qquad [7.15.20]$$

which can be shown to reduce to

$$P(N = n) = \frac{(\lambda t)^n}{n!} \exp(-\lambda t) \qquad [7.15.21]$$

Again, for the case of the first renewal ($n = 1$)

$$P(N = 1) = \lambda t \exp(-\lambda t) \qquad [7.15.22]$$

and

$$E[N] = \sum_{n=1}^{\infty} F_{\tau n}(t) \qquad [7.15.23]$$

But, using Equation 7.15.4 and then taking Laplace transforms:

$$F_{\tau n}(s) = \frac{f_{\tau n}(s)}{s} \qquad [7.15.24]$$

From Equation 7.15.3

$$F_{\tau n}(s) = \frac{[f(s)]^n}{s} \qquad [7.15.25]$$

Then

$$E[N(s)] = \frac{1}{s} \sum_{n=1}^{\infty} [f(s)]^n \qquad [7.15.26]$$

$$= \frac{1}{s} [f(s) + f(s)^2 + \cdots] \qquad [7.15.27]$$

$$= \frac{1}{s} \frac{f(s)}{1 - f(s)} \qquad [7.15.28]$$

Substituting from Equation 7.15.11:

$$E[N(s)] = \frac{1}{s} \frac{\lambda/(s + \lambda)}{\lambda/(s + \lambda)} \qquad [7.15.29]$$

$$= \lambda/s^2 \qquad [7.15.30]$$

Inverting into the time domain:

$$E[N] = \lambda t \qquad [7.15.31]$$

7.16 Replacement Models

One of the principal decisions in the maintenance of plant is whether to replace an equipment. Support for such decisions is provided by replacement theory. Treatments of replacement are given by Dean (1963), Hastings (1970), Jardine (1970a,b) and Mitchell (1972).

Some reasons for replacing an equipment are that: (1) it has failed, (2) it is about to fail, (3) it has deteriorated and (4) an improved version has become available.

In most replacement models the quantity sought is the overall economic optimum. Some models treat the problem solely in terms of the equipment, whilst others take into account the effects on the process either of outright failure or of deterioration of the equipment. Another distinction is between models which allow for the time to effect the replacement and those which do not.

A somewhat different model is required where the case considered is that exemplified by the lightbulb replacement problem. Here the cost of the actual replacement actions is high and has a significant influence on the result. This type is known as a 'group replacement model'. Treatments are given by Bartholemew (1963) and Naik and Nair (1965).

Other cases to be considered include replacement as opportunity arises, possibly during a major shut-down, and replacement of an equipment which cannot be repaired to the 'as new' condition.

In general, for simple items which are used in large numbers, what is required is straightforward rules, while for more complex individual equipment a more detailed analysis may be justified.

If the time-scale over which replacement occurs extends over a number of years, it may be necessary to allow for the change in the value of money using a technique such as net present value.

A common type of replacement model is that which considers only the equipment and determines the optimum trade-off between capital cost and operating cost. It is necessarily assumed that the latter increases with time, since if it does not, the best policy is to run the equipment until it fails. A replacement model of this type has been given by G.H. Mitchell (1972) and is as follows:

$$C = \frac{C_c - S}{n} + \frac{1}{n}\int_0^n f(t)\,\mathrm{d}t \qquad [7.16.1]$$

where C is the average annual cost of operation, C_c is the capital cost of the equipment, $f(t)$ is the rate of expenditure on maintenance, t is time, and S is the scrap value of the equipment. As just stated, $f(t)$ is taken to increase with time t. Then it can be shown by differentiating Equation 7.16.1 that the average annual cost is a minimum when

$$f(n) = \frac{C_c - S}{n} + \frac{1}{n}\int_0^n f(t)\,\mathrm{d}t = C \qquad [7.16.2]$$

Thus the equipment should be replaced when the current maintenance cost becomes equal to the average annual cost to date.

Further replacement models are given by Jardine (1970a) who treats the cases of failure replacement + preventive replacement, where the latter is (1) fixed-term and (2) based on equipment age.

7.17 Models of Failure: Strength–load Interaction

7.17.1 Strength and load

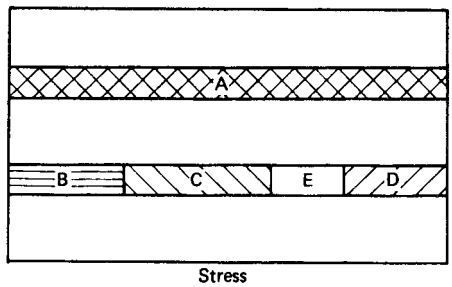
Failure occurs when the load on a component exceeds the strength or, more generally, when the duty exceeds the capability. There are various factors which may cause the load to be higher, or the strength lower, than expected. Factors which increase stress include: internal residual stresses and stress raisers; reductions of cross-sectional area due to size variations in manufacture, wear and corrosion; and applications of the component different from that for which it was designed. Factors which reduce strength include quality variations in manufacture, defects, fatigue and creep.

7.17.2 Safety factor and safety margin

The traditional method of allowing for factors which increase stress or reduce strength is the use of a safety factor. The approach has been to define the safety factor as the ratio of the mean of the strength to that of the load, both mean values being assumed constant. This is a deterministic approach, and increasingly it is being superseded by a probabilistic approach which allows for the variability of both strength and load. This does not mean, however, that concepts of the safety factor, and the associated safety margin, are abandoned, but merely that they are redefined, as described below.

7.17.3 Deterministic approach: mean of strength and load

Traditional safety factors are shown in Figure 7.16. The design safety margin (the difference between the design strength and the design stress) and the design safety factor (the ratio of the design strength and the design stress) are normally substantial. However, by the time account is taken of the margin of ignorance, which is the sum of the increases in stress and the decreases in strength, the actual safety margin and safety factor are greatly reduced.



A Assumed static strength
B Design working stress
C Factors increasing stress: internal residual stresses, stress raisers, size variations in manufacture, wear, corrosion
D Factors reducing strength: quality variations in manufacture, defects, fatigue, creep

Design safety margin = A − B
Margin of ignorance = C + D
Actual safety margin = A − (B + C + D) = E
Design safety factor = A/B
Actual safety factor = A/(B + C + D)

Figure 7.16 *Design and actual safety factors and margins*

This reduction in the design safety factor is important. The actual safety factor is often much less than might be supposed and the potential causes of reduction in the safety factor need to be given close attention. As stated earlier, this approach is based essentially on the means of the strength and of the load.

7.17.4 Probabilistic approach: variability of strength and load

The weakness of the approach just described is that it does not take into account the variability of the strength and of the load. A more realistic representation of failure is shown in Figure 7.17. Both the strength and the load can be expressed as density functions characterized by a mean and a spread. Failure occurs when the tails of the distributions overlap and create an area where the load exceeds the strength.

7.17.5 Interference theory

The effect of this interaction between load and strength can be quantified using interference theory. Accounts of interference theory are given by Lloyd and Lipow (1962) and von Alven (1964). In this subsection an account is given of the basic theory. A failure model based on the interference approach is given in Section 7.17.

The basic approach may be illustrated by considering the case where the variabilities of the load and the strength can each be represented by a normal distribution. Then the joint density function $g(z)$ for the load to exceed the strength is:

$$g(z) = \int_b^a f(x)f(x-z)\,\mathrm{d}x\,\mathrm{d}z \qquad [7.17.1]$$

with

$$z = x - y \qquad [7.17.2]$$

where $f(x)$ is the density function of the load x, $f(y)$ is the density function of the strength y $(= x - z)$, and z is the difference between x and y.

A safety parameter may be defined as:

$$\phi = S/L \qquad [7.17.3]$$

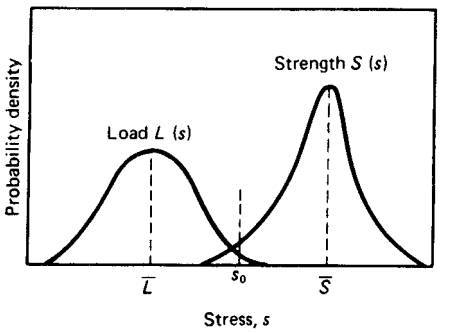


Figure 7.17 *Effect of variability of strength and load on failure (A.D.S. Carter, 1973) (Reproduced by permission of the Institution of Mechanical Engineers)*

where L is the load, S is the strength, and ϕ is the safety parameter. The variability of the load and the strength may be written as:

$$L = m_x + n_x\sigma_x \qquad [7.17.4]$$

$$S = m_y - n_y\sigma_y \qquad [7.17.5]$$

Since the load has a normal distribution, its density function is:

$$f(x) = \frac{1}{\sigma_x(2\pi)^{1/2}}\exp\left[-\frac{(x-m_x)^2}{2\sigma_x^2}\right] \qquad [7.17.6]$$

Similarly, the density function of strength is:

$$f(y) = \frac{1}{\sigma_y(2\pi)^{1/2}}\exp\left[-\frac{(y-m_y)^2}{2\sigma_y^2}\right] \qquad [7.17.7]$$

From Equations 7.17.1, 7.17.6 and 7.17.7, it can be shown that:

$$g(z) = \frac{1}{[2\pi(\sigma_x^2+\sigma_y^2]^{1/2}}\exp\left[-\frac{(z+m_y-m_x)^2}{2(\sigma_x^2+\sigma_y^2)}\right] \qquad [7.17.8]$$

which itself is the density function of a normal distribution with a mean value

$$m_z = m_x - m_y \qquad [7.17.9]$$

and standard deviation

$$\sigma_z = (\sigma_x^2+\sigma_y^2)^{1/2} \qquad [7.17.10]$$

Then the probability that the load exceeds the strength is given by the distribution function

$$G(z) = \int_0^\infty g(z)\,\mathrm{d}z \qquad [7.17.11]$$

which may be integrated to give

$$G(z) = \frac{1}{(2\pi)^{1/2}}\int_u^\infty \exp(-v^2/2)\,\mathrm{d}v \qquad [7.17.12]$$

with

$$u = \frac{m_y - m_x}{(\sigma_x^2+\sigma_y^2)^{1/2}} \qquad [7.17.13]$$

$$v = \frac{z+m_y-m_x}{(\sigma_x^2+\sigma_y^2)^{1/2}} \qquad [7.17.14]$$

As an illustration, consider the example given by von Alven (1964):

$m_x = 1;\ \ \sigma_x = \sigma_y = 0.4;\ \ n_x = n_y = 2;\ \ \phi = 1.25$

From Equations 7.17.3–7.17.5,

$m_y = 3.05$

and from Equation 7.17.13

$u = 3.6$

Then evaluating the distribution function in Equation 7.17.12 using statistical tables for the integral of the distribution function of the normal distribution between 3.6 and ∞, the value is found to be of the order of 0.0001, indicating that the load may be expected to exceed the strength once in every 10,000 loadings.

7.17.6 Carter's rough loading model

A theory of failure based on the overlap of the strength and load distributions has been developed by A.D.S. Carter (1973). The approach is illustrated in Figure 7.17 and is broadly as follows.

Initially, a component has a strength s_0 but this gradually deteriorates so that by the ith application of load the strength is reduced to $s_0 - \Delta s_i$. The probability (P_1) of obtaining a component with initial strength lying between s_0 and $s_0 + \mathrm{d}s$ is:

$$P_1 = S(s_0)\,\mathrm{d}s \qquad [7.17.15]$$

The probability (P_2) of encountering a load which is less than $s_0 - \Delta s_i$ is:

$$P_2 = \int_0^{s_0 - \Delta s_i} L(s)\,\mathrm{d}s \qquad [7.17.16]$$

Then the probability (P_3) of encountering a load which is less than the current strength of the component the initial strength of which is s_0 in any of the n applications of load is:

$$P_3 = \prod_{i=1}^{n} \int_0^{s_0 - \Delta s_i} L(s)\,\mathrm{d}s \qquad [7.17.17]$$

And the probability (P_4) of obtaining a component of initial strength s_0 and of encountering a load which over n applications is always less than its strength:

$$P_4 = S(s_0)\,\mathrm{d}s \prod_{i=1}^{n} \int_0^{s_0 - \Delta s_i} L(s)\,\mathrm{d}s \qquad [7.17.18]$$

Then the reliability of the component is:

$$R(n) = \int_0^{\infty} S(s) \prod_{i=1}^{n} \left[\int_0^{s_0 - \Delta s_i} L(s)\,\mathrm{d}s \right] \mathrm{d}s \qquad [7.17.19]$$

The decrements of strength Δs_i may be expressed in terms of a constant scaling factor σ and a shaping factor $f(i)$:

$$\Delta s_i = \sigma f(i) \qquad [7.17.20]$$

with

$$f(i) = (i-1)p \qquad [7.17.21]$$

where $p < 1$ gives a fatigue-type curve; $p = 1$ gives a corrosion deterioration-type curve; and $p > 1$ gives an erosion/wear-type curve.

The hazard rate z is then obtained from the relationship:

$$z(n) = -\frac{1}{R(n)} \frac{\mathrm{d}R(n)}{\mathrm{d}t} \qquad [7.17.22]$$

If preferred, n may be replaced by kt to give the reliability as a function of time.

The quantities in Equation 7.17.19 are not normally known, but the theory can be used to explore the implications of making various assumptions. In Carter's work this was done by expressing $S(s)$ and $L(s)$ as Weibull distributions with the shape factor β given a value of 3.44 to approximate normal distributions. Various values of the means $\bar{S}$ and $\bar{L}$ and standard deviations σ_s and σ_L of the strength and load distributions were investigated. Three regimes were distinguished

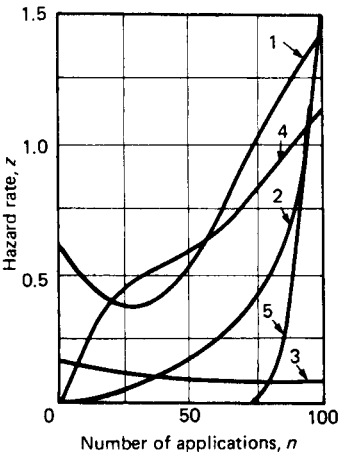
$\sigma_L \ll \Delta_s$	smooth loading
$\sigma_L = \sigma_s$	medium loading
$\sigma_L \gg \sigma_s$	rough loading

The following quantities were defined:

$\bar{S}/\bar{L}$	safety factor
σ_L/σ_s	roughness of loading
$\dfrac{\bar{S} - \bar{L}}{(\sigma_s^2 + \sigma_L^2)^{1/2}}$	safety margin

This definition of safety margin is different from that conventionally used, as described above.

Some examples of hazard rate curves obtained by Carter are shown in Figure 7.18. The values of σ_s and σ_L were chosen to give a safety margin of six standard deviations and the scaling factor σ was chosen to give $\Delta s_{100} = 2.333$. These results throw considerable doubt on the applicability of the bathtub curve to mechanical components.



curve 1	$\bar{S} - \bar{L} = 1.0$	$p = 0.2$	medium loading
curve 2	$\bar{S} - \bar{L} = 1.0$	$p = 1.0$	medium loading
curve 3	$\bar{S} - \bar{L} = 1.333$	$p = 0.2$	smooth loading
curve 4	$\bar{S} - \bar{L} = 1.666$	$p = 0.2$	rough loading
curve 5	$\bar{S} - \bar{L} = 1.666$	$p = 3.0$	rough loading

Figure 7.18 *Effect of mean and spread of strength and load on hazard rate (A.D.S. Carter, 1973) (Reproduced by permission of the Institution of Mechanical Engineers)*

7.18 Models of Failure: Some Other Models

7.18.1 Bathtub curve revisited

As already indicated, the original bathtub curve concept has come in for a good deal of criticism. Frequently it appears that it is honoured more in the breach than the observance. The rough loading theory of Carter gives one indication why this should be so.

A modern critique of the concept is that by Moubray (1991), who gives instead the failure patterns shown in Figure 7.19. Moubray states that studies on civil aircraft have shown the following distribution of patterns of failure in terms of the curves in Figure 7.19:

A	4%	*D*	7%
B	2%	*E*	14%
C	5%	F	68%

Discussion of these features is taken up again in Section 7.19.

7.18.2 Lightbulb curve

Systems with large numbers of components often tend to exhibit a constant hazard rate. This is readily understood intuitively in terms of a smoothing out of particular hazard rate characteristics of individual components.

The phenomenon is well illustrated by the so-called 'lightbulb curve' shown in Figure 7.20. If a building is provided with new lightbulbs throughout, then assuming that these fail by wearout with a normal distribution and that the failed bulbs are replaced each day, the number of failures recorded per day will be as shown in the figure. The dotted curves (a)–(e) show the numbers actually failing, and the horizontal full line shows the constant number of failures per day to which the system is tending. Each successive curve has a smaller modal value and higher spread than the previous one. Eventually the number of failures recorded per day will become constant. If the lighting system of the building taken as a whole is considered as a series system, then when the number of bulb failures has become constant, the system hazard rate is also constant, so that the system itself appears to have an exponential failure distribution, although its components have a normal failure distribution.

7.18.3 Drenick's theorem

A theoretical demonstration that systems with many components tend to have a constant hazard rate is given by Drenick's theorem (Drenick, 1960). A modified version of this theorem has been given by Shooman (1968a). For an n-component series system, from Equation (7.6.4):

$$\ln R(t) = -\sum_{i=1}^{n} H_i(t) = -\sum_{i=1}^{n} \int_0^t z_i(t)\,\mathrm{d}t \qquad [7.18.1]$$

Assume that the hazard rates for small values of t can be expressed as

$$z_i = a_i + b_i t^m \qquad [7.18.2]$$

the value of m being the highest found for the n components. Then

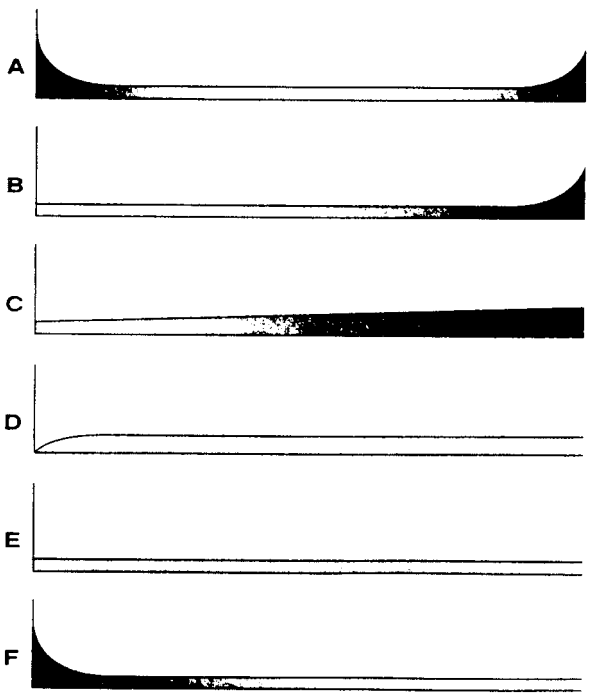


Figure 7.19 *Some patterns of equipment hazard rate, including and additional to the bathtub curve (Moubray, 1991) (Courtesy of Butterworth-Heinemann)*

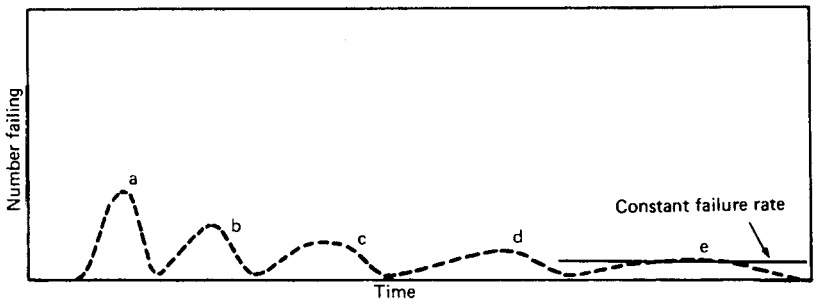


Figure 7.20 *The lightbulb curve*

$$\ln R(\tau) = -\tau - k\frac{\tau^{m+1}}{\bar{\lambda}^m} \quad [7.18.3]$$

with

$$\bar{\lambda} = \sum_{i=1}^{n} a_i \quad [7.18.4]$$

$$k = \frac{1}{(m+1)\bar{\lambda}} \sum_{i=1}^{n} b_i \quad [7.18.5]$$

$$\tau = \bar{\lambda}t \quad [7.18.6]$$

Assuming that as $n \to \infty$, $\bar{\lambda} \to \infty$, and that k is bounded, then as $n \to \infty$

$$\ln R(\tau) = -\tau \quad [7.18.7]$$

and hence

$$R(t) = \exp(-\bar{\lambda}t) \quad [7.18.8]$$

The theorem assumes that the system has a series structure. If the system contains parallel paths, the treatment is pessimistic. In practice, there are many systems which are well fitted by the theorem, but also many which are not.

The equation

$$k = \sum_{i=1}^{n} b_i/(m+1)\bar{\lambda}$$

is bounded, provided at least one $z_i(0) \neq 0$. Its rate of convergence depends, however, on the number of components for which $z_i(0) = 0$. If these are numerous, the convergence is slow.

The implications of this theorem are considered in more detail by Shooman (1968a).

7.19 Failure Behaviour and Regimes

7.19.1 Failure regimes

The measures which can be taken to reduce failure depend very largely on the failure regime of the equipment. The three regimes are: (1) decreasing hazard rate (2) constant hazard rate and (3) increasing hazard rate. The bathtub curve illustrates these three regimes but, as indicated, this model is honoured as much in the breach as in the observance. However, this does not alter the fact that the failure regime must be one or other of those just listed.

The failure regime of an equipment may be identified using the methods described in Section 7.20. In particular, the failure data may be fitted to the Weibull distribution. The relationship between the failure regime and the Weibull shape factor β is:

$\beta < 1$ decreasing hazard rate (early failure);
$\beta = 1$ constant hazard rate (constant failure);
$\beta > 1$ increasing hazard rate (wearout failure).

7.19.2 Catastrophic failure vs tolerance failure

Some failures occur suddenly, whilst others develop much more gradually. In early work the two types were often called 'catastrophic failure' and 'tolerance failure'. These terms were not well chosen. There is no implication that a catastrophic failure has any consequences wider than the failure itself. Nor is there any implication that catastrophic failures occur early in life or tolerance failures late in life.

Tolerance failures are associated with the interaction between the component and the system. Catastrophic failures have a greater tendency to occur independently of the system.

7.19.3 Bimodal failure distributions

Analysis of failure data not infrequently yields a failure density function with two distinct peaks, indicating a bimodal distribution. Such a density function may be written as

$$f(t) = pf_1(t) + (1-p)f_2(t) \quad [7.19.1]$$

where p is a weighting factor. As described below, early failure can give rise to a bimodal failure distribution.

7.19.4 Wearout failure

Two principal types of failure are wearout failure and early failure. These are now considered in more detail. The discussion here is limited to failure itself and discussion of the determination of the type of failure by data analysis and of maintenance policies appropriate to the types of failure is deferred to later sections.

Failure by wearout is one of the principal failure regimes of industrial equipment. Some of the causes of wearout are: (1) fatigue, (2) wear, (3) corrosion and (4) erosion. It is often associated with contact with process materials.

Wearout failure is a common experience with everyday objects such as clothes and tools. It is natural, therefore, that there should be carried over from this a preconception that it is the dominant mode in industrial equipment but, as just indicated, this can be misleading.

In the results quoted in Section 7.18 for failures in civil aircraft, only some 6% are classified as in some way involving wearout (patterns A and B). In the process industries the overall operating environment is probably conducive to a higher proportion of wearout failures, but how much higher is uncertain.

7.19.5 Early failure

Another of the principal failure regimes of industrial equipment is early failure. Although initially perceived as failure due essentially to premature failure of weak components, there is now better understanding that there is more to early failure than this, and that it can be the dominant mode. In particular, it is now appreciated that early failure in the sense of a decreasing hazard rate is a phenomenon which is not confined to new equipment but is often exhibited by old equipment. The proportion of early failure in the results for civil aircraft quoted in Section 7.18 is 68% (pattern F).

Causes of early failure may be grouped under three headings: (1) those which result in failure of newly commissioned equipment, (2) those which result in failure of equipment which has been operating for some time and (3) those associated with start-up and shut-down stresses, whether on new or old equipment. Among the former causes, in design and commissioning, are: (1) incorrect design specification, (2) incorrect design, (3) incorrect user specification and selection, (4) incorrect manufacture, (5) incorrect installation and (6) incorrect commissioning and initial operation.

Causes of early failure in equipment with a longer operating history, centre on the quality of the maintenance and include: (1) incorrect fault identification, (2) incorrect repair technique, (3) incorrect replacement parts, (4) incorrect reassembly and alignment, (5) dirty working conditions and (6) disturbance to other parts of the equipment. The effect of such failings is that the equipment is not fully restored to the 'as new' condition after repair or overhaul. Underlying these causes of early failure due to maintenance are two more fundamental causes. One is the conduct of unnecessary preventive maintenance (PM). The other is inadequate training and/or discipline of maintenance personnel.

The third group of causes of early failure is the mechanical and thermal stresses associated with plant start-up and shut-down.

Evidence of early failure in process equipment was found in a study by Berg (1977) who investigated some 600 centrifugal and air vacuum pumps and some 200 bottom run-off valves and found values of the shape parameter β ranging from 0.735 to 1.072. Aird (1977b) obtained values of β as low as 0.5 for some mechanical equipment in process plants.

In a further study Sherwin and Lees (1980) found early failure to be prevalent in both process plant equipment and hospital autoclaves. The process plant investigation was done in two stages. In the first stage failure data were collected and analysed and the maintenance tasks were observed. Recommendations were then made for improvement to the conduct of maintenance. In the second stage, 2 years later, further data collection and analysis was carried out. The items of plant equipment studied were: (1) acid pumps, (2) water pumps, (3) vacuum pumps, (4) agitators, (5) screw conveyers, (6) filters, (7) fans, (8) heat exchangers, (9) evaporator flash vessels, (10) other tanks and vessels, (11) pipes and ducts and (12) other items. The failure modes were classified as: (1) blockages, (2) leaks, (3) drives, (4) electrical, (5) holes and breaks, (6) instruments, (7) valves and (8) other faults. The authors found that with few exceptions the failures could be characterized as early failures with β values less than unity. In the first stage, values of β obtained on six types of equipment ranged from 0.61 to 1.07, whilst β values for five failure modes of the acid pumps ranged from 0.48 to 0.76 with the overall value for the eight failure modes being 0.63. As stated, the maintenance work was also observed. The research revealed many of the problems of maintenance work listed above, such as incorrect use of consumables, use of incorrect parts, failure to realign correctly and failure to adjust clearances correctly, as well as working in dirty conditions. Above all, it pointed to a lack of training. Recommendations were made to rectify these shortcomings, in particular proposals on training, and these were acted on. Analysis of the failure data from the second stage found that of the 12 types of equipment, 8 showed improvements in MTBF and 3 deteriorations in MTBF, with one type classed as N/A (not applicable). The MTBFs of the acid, water and vacuum pumps, for example, were increased from 47.5 to 108 days, from 75.8 to 382 and from 57.3 to 117, respectively, and that of the agitators from 910 to 4641 days.

The hospital study was on autoclaves used for sterilization, which were breaking down at an unacceptable frequency. The study yielded results remarkably similar to those on the process plant. Again early failure ($\beta < 1$) was the dominant regime. Recommendations were made and acted on, particularly with respect to training, and the overall failure rate was reduced from 0.065 to 0.014 failures/cycle.

These studies indicate that as a result of early failure the overall failure rate of the equipment is higher than it need be and often never settles down to the lower constant failure rate which might be regarded as the more 'normal' condition. The concept of 'maintenance induced' failure has long been familiar to plant engineers. The investigations described give it statistical support.

7.19.6 Burn-in

In the foregoing discussion wearout and early failure have been viewed as failure regimes. It is also of interest to develop models of failure in these regimes. An account of such modelling is given in *Burn-In* (Jensen and Petersen, 1982).

The starting point is the observation that analysis of failure data for components often gives a bimodal distribution, such that the failure density function exhibits two distinct peaks: the first for 'freak' failures and the second for the main failures. An example is the work of Herr, Baker and Fox (1968) on the failure of electronic components.

Jensen and Petersen have developed a model for the freak failures which is based on two assumptions: (1) the strength of all components deteriorates with time and (2) the strength of weak components deteriorates faster. The more rapid deterioration of the weaker components results in a

sharper separation between the peaks of the two failure distributions.

The foregoing refers to components in isolation. Another concept developed by Jensen and Petersen is that once incorporated in a system, the susceptibility to failure of some of the components may be drastically increased. They term this phenomenon 'infant mortality' and treat it as distinct from freak failures. In their terminology, the early failures are made up of the two separate sets of failures (freak and infant mortality). It follows that there is potential for a failure distribution which is not just bimodal but trimodal.

The implications of such concepts of early failure for burn-in policies are discussed in Section 7.25.

7.20 Failure Data Analysis

Guidance on current performance in equipment reliability and on measures which may be taken to improve it can be obtained from the analysis of failure data.

7.20.1 Need for failure data

The application of reliability techniques creates a demand for data on equipment failure and repair time, on other failure-related events and on human error. These data may be obtained from the literature, from data banks or within the works. Usually it is possible to obtain approximate data fairly readily, but the determination of accurate data tends to involve much more effort. It is wasteful, therefore, to seek for greater accuracy in the data than the problem warrants.

The accuracy required in the data varies considerably between different types of reliability calculation and even between different parts of the same calculation. In general, where the reliability problem has a structure, as in a comparison of a simple equipment with a parallel or stand by system or in a fault tree analysis, less accurate data may often be used, at least in some parts of the calculation. Thus in a fault tree study, for example, some branches of the tree may be sensitive to the failure rates used, whilst others may not be. On the other hand, where the problem is a straight comparison, as between the failure rates of two instruments, the accuracy required is clearly greater.

Often, for the solution of the reliability problem to be clear it is sufficient to know that the failure rate lies between certain broad limits. In such cases it may be sufficient to rely on expert judgement or on relatively crude failure data rather than on accurate data.

7.20.2 Types of failure data

The failure information required for reliability work includes not only data on (1) overall failure rates, but also data on (2) failure rates in individual modes, (3) variation of failure rates with time and (4) repair times.

Failure modes can be classified in several ways. Some important categories of failure mode are (1) condition, (2) performance, (3) safety and (4) detection. In the failure classification based on condition, a failure mode is exemplified by a faulty seal on a pump or by a defective gearbox on an agitator. It is the failure classification which is normally used in maintenance. In the classification by performance, illustrations of failure are inability of a heat exchanger to achieve the required heat transfer or of a pump to give the specified head. The safety classification divides failure into fail-safe and fail-to-danger in the context of the process. The detection classification makes a distinction between revealed and unrevealed failure. These different categories of failure mode are particularly important in instruments and are discussed further in Chapter 13.

Generally, information on the variation of failure rate with time is not available and therefore is not used much in ordinary reliability work, but it is important in relation to maintenance problems. It is also necessary to have information on human error rates. This aspect is discussed in Chapter 14.

Other information required relates to other events which have a bearing on failure. Typical examples are the probability of a worker being nearby when an explosion occurs in an equipment, the distance travelled by a vapour cloud before it finds a source of ignition and the time taken for the fire services to reach the scene of a tanker crash.

For availability studies the type of data used varies. In some cases the availability is determined from the failure rates and repair times of the basic equipment. In other cases data on the availability of blocks of plant are used.

Failure rates may be expressed in terms of several parameters. The parameter most commonly used is time, but it may be appropriate to distinguish between operating time and non-operating time, and other measures such as the number of cycles or the number of demands are appropriate in some cases. In this connection it should be emphasized that it is often not known which is the important measure in a particular case. Thus misleading results may be obtained if a particular failure is expressed as failures/year when failures/cycle would be more appropriate.

7.20.3 Failure data sources, data collection and data banks

The sources of failure data are essentially external sources such as the literature and data banks. Alternatively, data may be collected within the works. Often it is the works which is the most dependable source of applicable data, and in this case it is necessary to have some form of data collection system. In other cases, particularly for rare events, it will be necessary to make use of the external sources.

The acquisition of data from these various sources is not straightforward. The data are of use only if they are of the right type, originate from a dependable source and apply to the case in hand. These and other issues related to failure data are discussed in Appendix 14.

7.20.4 Fundamentals of failure data analysis

Analysis of failure data should begin with consideration of the fundamental qualitative factors. One of these factors is the appropriateness of lumping together, as a homogenous set, equipments which may differ in design, manufacture, system function and process environment. Another factor is the parameter by which the failure rate is to be measured. As mentioned, this is usually time, but in some cases another measure such as the number of cycles is more suitable.

The qualitative analysis which can be done depends on the information available. Some items which can be calculated are:

(1) overall failure rates;
(2) failure rates in individual modes;
(3) confidence limits and bounds on failure rates;
(4) failure distributions;
(5) repair time distributions.

Frequently, the only information available is the total number of failures and the total operating time of

the equipments, and the analysis is restricted to calculation of the overall failure rate and corresponding mean life.

7.20.5 Failure rates in individual modes

If the failure modes and their relative frequency are available, they are often analysed in the form of a histogram, as shown in Figure 7.21. In many cases there are a few failure modes which have a high relative frequency followed by a larger number of low frequency modes. This is generally referred to as a 'Pareto-type distribution' of failure modes.

It is the failure rates in the individual modes which are the data primarily required for fault tree analysis and for improvement of equipment performance by design and by maintenance.

7.20.6 Confidence limits on failure frequency and mean life

The confidence which can be placed in the estimate of the mean life depends on the number of failures recorded. If this number is small, it may be useful to determine the confidence limits. For the estimate of the mean life in the exponential distribution, the confidence limit may be determined using the χ^2 distribution.

It is necessary to distinguish between the case where the end of the test period T coincides with the final failure n and that where it does not. In the latter case it is conservative to assume that a further failure was just due to occur when the test was terminated.

For the failure-terminated test with replacement, the estimate of the mean life is

$$\hat{m}_1 = \frac{T}{n} \qquad [7.20.1]$$

and the degrees of freedom f are

$$f_1 = 2n \qquad [7.20.2]$$

whilst for the time-terminated test

$$\hat{m}_2 = \frac{T}{n+1} \qquad [7.20.3]$$

and

$$f_2 = 2(n+1) \qquad [7.20.4]$$

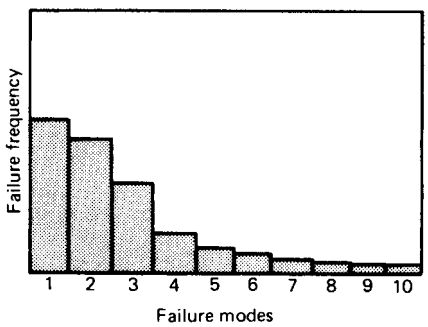


Figure 7.21 *Failure modes of an equipment*

Then for the failure-terminated test it can be shown that the ratio $f_1\hat{m}_1/m$ has a χ^2 distribution. For a two-sided confidence interval at a confidence level $(1-\alpha)$

$$P\left(\chi^2_{1-(\alpha/2):f1} \leq \frac{f_1\hat{m}_1}{m} \leq \chi^2_{\alpha/2;f1}\right) = 1-\alpha \qquad [7.20.5]$$

Then the lower limit L and the upper limit U of the ratio $m/\hat{m}$ are:

$$L\left(\frac{m}{\hat{m}}\right) = \frac{f_1}{\chi^2_{\alpha/2;f1}} \qquad [7.20.6]$$

and

$$U\left(\frac{m}{\hat{m}}\right) = \frac{f_1}{\chi^2_{1-\alpha/2;f1}} \qquad [7.20.7]$$

with

$$\hat{m} = \hat{m}_1 = \frac{T}{n} \qquad [7.20.8]$$

For the time-terminated test it can be shown that:

$$L\left(\frac{m}{\hat{m}}\right) = \frac{f_1}{\chi^2_{\alpha/2;f2}} \qquad [7.20.9]$$

and

$$U\left(\frac{m}{\hat{m}}\right) = \frac{f_1}{\chi^2_{1-(\alpha/2):f1}} \qquad [7.20.10]$$

again with $\hat{m}$ defined by Equation 7.20.8.

Values of the percentage points of the χ^2 distribution may be obtained from standard tables (e.g., Yamane, 1967, p. 879). It should be noted that some tables give the α percentage points and others the $(1-\alpha)$ percentage points. A graph showing the confidence limits on $m/\hat{m}$ according to Equations 7.20.9 and 7.20.10 is given in Figure 7.22.

As an illustration, consider the situation in which 5 failures have been recorded on 10 pumps over a period of half a year, with the final failure occurring before the end of the observation period, and in which it is required to estimate the confidence limits within which the ratio $m/\hat{m}$ lies at a 90% confidence level. Then

$n = 5$ failures

From Equation 7.20.8

$$\hat{m} = \frac{0.5 \times 10}{5} = 1 \text{ year}$$

From Equations 7.20.2 and 7.20.4

$f_1 = 10$

$f_2 = 12$

For a 90% confidence level, $\alpha = 0.1$. From tables of percentage points of the χ^2 distribution

$\chi^2_{\alpha/2;f2} = \chi^2_{0.05:12} = 21.0$

$\chi^2_{1-(\alpha/2);f1} = \chi^2_{0.95:10} = 3.94$

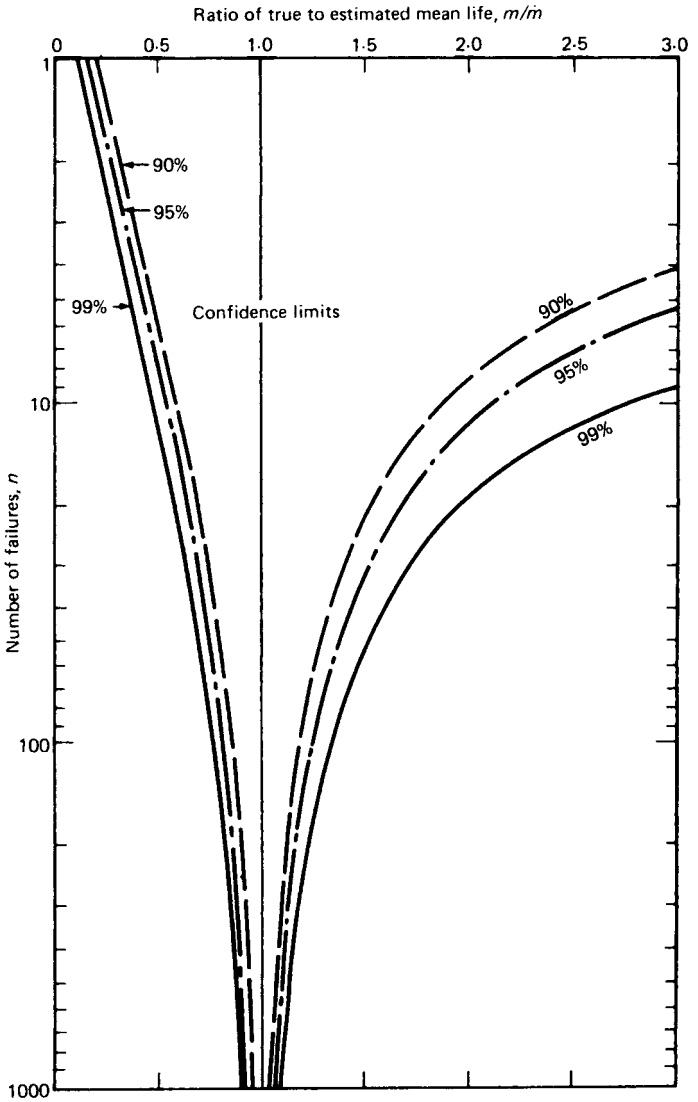


Figure 7.22 *Two-sided confidence limits for the ratio of true to estimated mean life m/m̂ vs number of failure n in a time-terminated test with an exponential failure distribution (Buffham, Freshwater and Lees, 1971) (Reproduced by permission of the Institution of Chemical Engineers)*

Then from Equations 7.20.9 and 7.20.10, the lower and upper confidence limits on the ratio $m/\hat{m}$ are:

$$L\left(\frac{m}{\hat{m}}\right) = \frac{10}{21.0} = 0.476$$

and

$$U\left(\frac{m}{\hat{m}}\right) = \frac{10}{3.94} = 2.54$$

Alternatively, the confidence limits may be obtained from Figure 7.22. Then

$$L(m) = 0.476 \text{ year}$$
$$U(m) = 2.54 \text{ year}$$

In some cases no failures are observed. Nevertheless, it is still possible to make an estimate of the lower limit of the ratio $m/\hat{m}$. For a one-sided confidence limit at a confidence level $(1-\alpha)$:

$$L\left(\frac{m}{\hat{m}}\right) = \frac{f_2}{\chi^2_{\alpha:f2}} \qquad [7.20.11]$$

with

$$\hat{m} = \hat{m}_2 = \frac{T}{n+1} \qquad [7.20.12]$$

$$f_2 = 2 \qquad [7.20.13]$$

$$\chi^2_{x:2} = 4.61$$

Then from Equation 7.20.11 the lower confidence limit on the ratio $m/\hat{m}$ is

$$L\left(\frac{m}{\hat{m}}\right) = \frac{2}{4.61} = 0.434$$

and that on the mean life is $L(m) = 4.34$ years.

Further accounts of confidence limits on failure data are given by Bazovsky (1961) and A.E. Green and Bourne (1972).

There is often a quite wide spread in failure rates reported by various sources. The variability of failure rates may be described by a log–normal distribution. Since this distribution has two parameters, it is determined by the end-points of a suitably defined range. This method of describing failure data was extensively used in the *Rasmussen Report* (AEC, 1975). The use of these log–normal distributions in fault trees in this study is discussed in Chapter 9.

7.20.7 Confidence limits on failure probability

The treatment just given refers to failure frequencies. It may also be necessary to determine the confidence limits on failure probabilities. A treatment of this problem is given by von Alven (1964). The approach taken in this case is the use of the binomial theorem. Use may be made of the binomial theorem itself or of charts constructed from it.

Such a plot is given in Figure 7.23, which shows, for the case where there are S successes in N trials, the 95% confidence limits as a function of the ratio S/N, or success probability. As an illustration, consider the case where there are 16 successes in 20 trials. Then the estimated value of the probability of success is 0.8 and the upper and lower confidence limit values are 0.98 and 0.6. The failure probabilities are the complements of these values.

7.20.8 Fitting of failure distributions: graphical methods

Information on the variation of a failure rate with time, that is, the failure distribution, can lead to its reduction through improvement in design and maintenance. The data required for the determination of the failure distribution are the individual times to failure of the equipment.

The procedure is to convert the data to a set of values of the failure distribution $F(t)$ vs times to failure t, and to plot the latter against that function of $F(t)$ on a scale which corresponds to the distribution to be fitted.

For the exponential distribution:

$$F(t) = 1 - \exp(-\lambda t) \qquad [7.20.14]$$

and hence

$$t = \frac{1}{\lambda} \ln \left[\frac{1}{1 - F(t)}\right] \qquad [7.20.15]$$

Thus a plot of $1/[1 - F(t)]$ on a log scale vs t on a linear scale gives a straight line.

For the Weibull distribution:

$$\ln(t - \gamma) = \frac{1}{\beta} \ln \left\{ \ln \left[\frac{1}{1 - F(t)}\right] \right\} + \ln \eta \qquad [7.20.16]$$

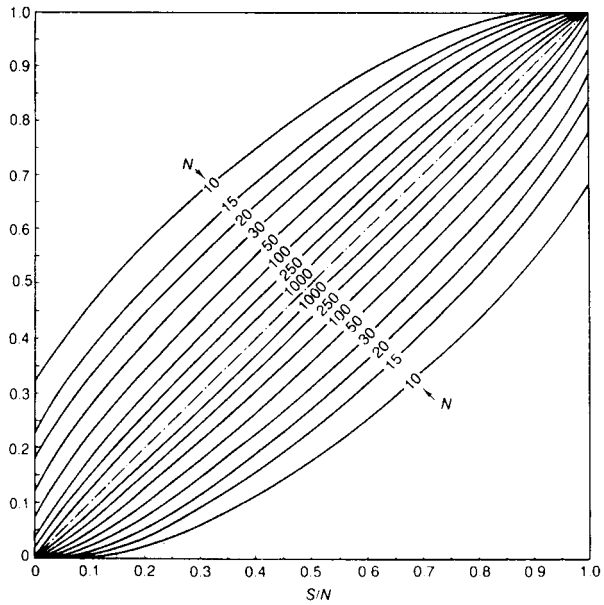


Figure 7.23 *Two-sided 95% confidence limits for the success probability S/N vs number of trials N (Clopper and Pearson, 1934)*

For these common distributions special graph papers are available which allow $F(t)$ vs t to be plotted directly. Figures 7.24–7.27 illustrate such graphs for the exponential, the normal and the Weibull distributions (two cases), respectively.

The determination of the failure distribution $F(t)$ from the experimental data is not entirely straightforward, however, and requires further discussion.

7.20.9 Fitting of failure distributions: ranking

If a test is considered in which n equipments operate without replacement and all fail during the test and if $n_f(t)$ equipments have failed at time t, then intuitively the failure distribution is simply the proportion which have failed:

$$F(t) = \frac{n_f(t)}{n} \qquad [7.20.17]$$

But the matter is not quite so simple. While Equation 7.20.17 holds for the n items tested, it is not the best estimate if these items tested are a sample from a large population. In this case a better estimate is the expected value:

$$F(t) = \frac{n_f(t)}{n+1} \qquad [7.20.18]$$

An alternative approach is the use of ranking. This involves calculating the order number m_j of the jth failure. The following ranking expressions are used:

$$F_{\text{mean}} = \frac{m_j}{n+1} \quad \text{mean rank} \qquad [7.20.19]$$

$$F_{\text{med}} = \frac{m_j - 0.3}{n+0.4} \quad \text{median rank} \qquad [7.20.20]$$

It is usual to calculate the failure distribution $F(t)$ as either the mean rank F_{mean} or the median rank F_{med}. The use of ranking is essential when the number of items n under test is small. The mean is commonly taken as a representative descriptor of a sample from a distribution. In the case of a highly skewed distribution, however, a better description may be the median. A discussion of the difference between mean rank and median rank and of the choice between them is given by Kapur and Lamberson (1977). Illustrative examples involving the use of the mean rank and median rank of a set of failure data are given in Tables 7.19–7.22.

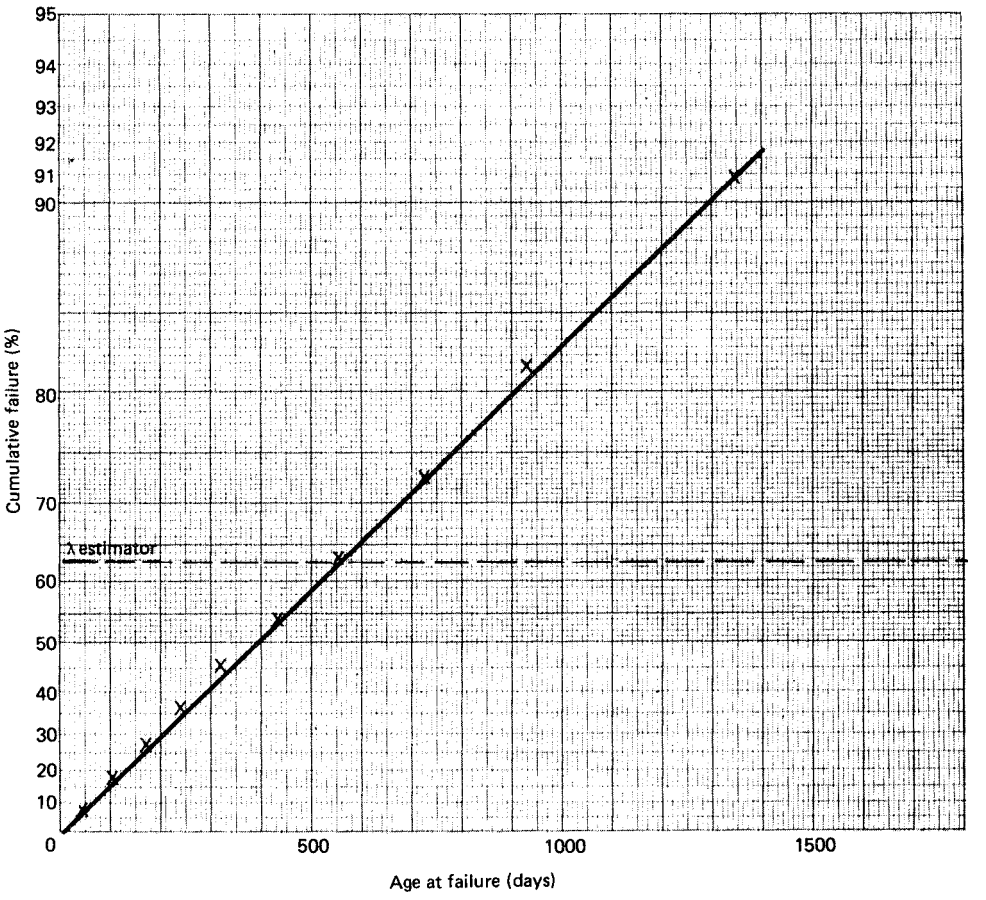


Figure 7.24 *Fitting of failure distributions using special graph paper: exponential distribution (data from Table 7.19)*

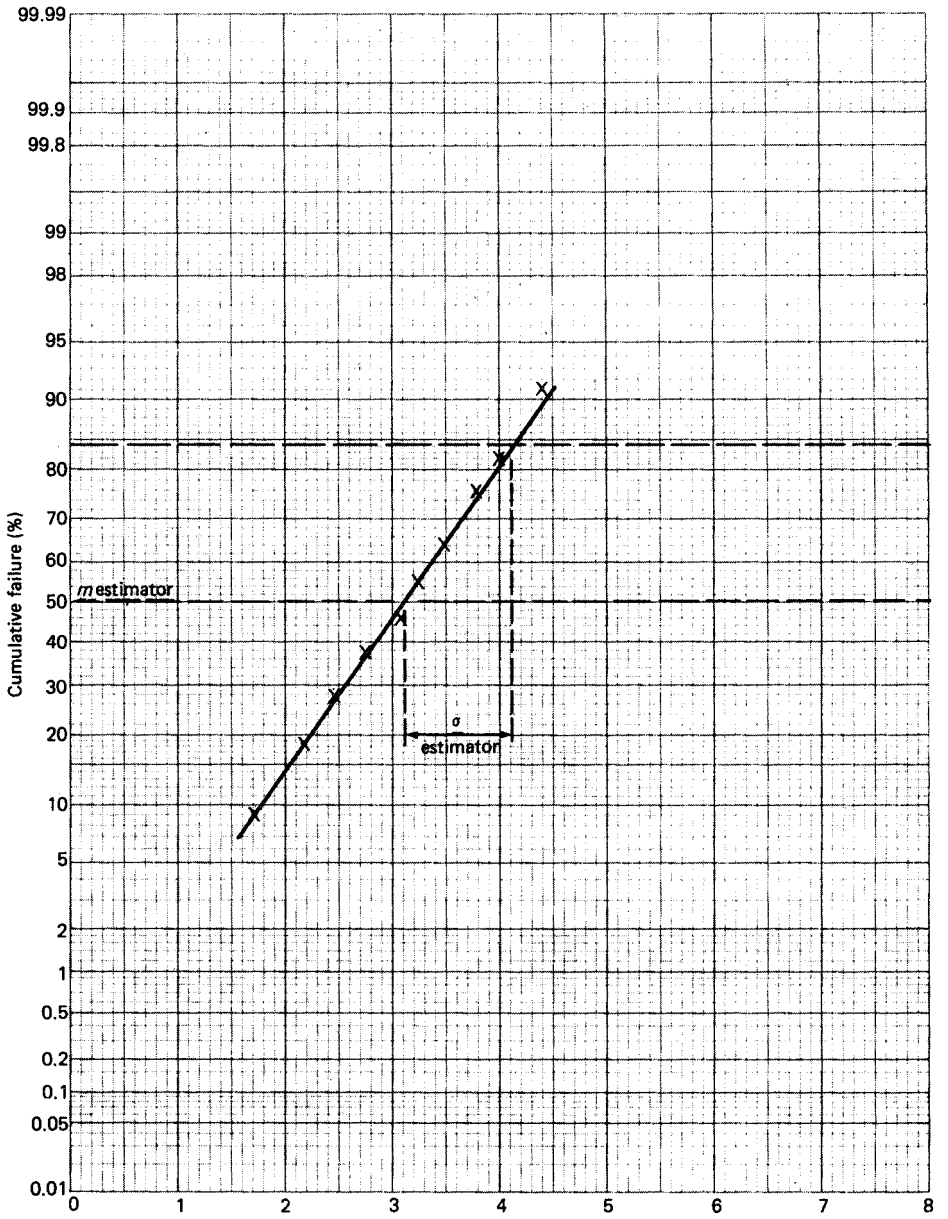


Figure 7.25 *Fitting of failure distribution using special graph paper: normal distribution (data from Table 7.20)*

7.20.10 Fitting of failure distributions: exponential distribution

The data in Table 7.19 correspond to an exponential failure distribution and are plotted in Figure 7.24. The estimator for the parameter failure rate λ in this distribution is given by the point at which the cumulative percentage failure has the value 63.2; the value of λ is then read off as the age at failure at this point, which in this case is 550 days.

7.20.11 Fitting of failure distributions: normal distribution

The data in Table 7.20 correspond to a normal failure distribution and are plotted in Figure 7.25. The estimator for the parameter mean life m is given by the point at which the cumulative percentage failure has a value of 50; the value of m is read off as the age at failure at this point. The estimator for the standard deviation σ is given by the interval between the cumulative percentage failures of 50 and 84;

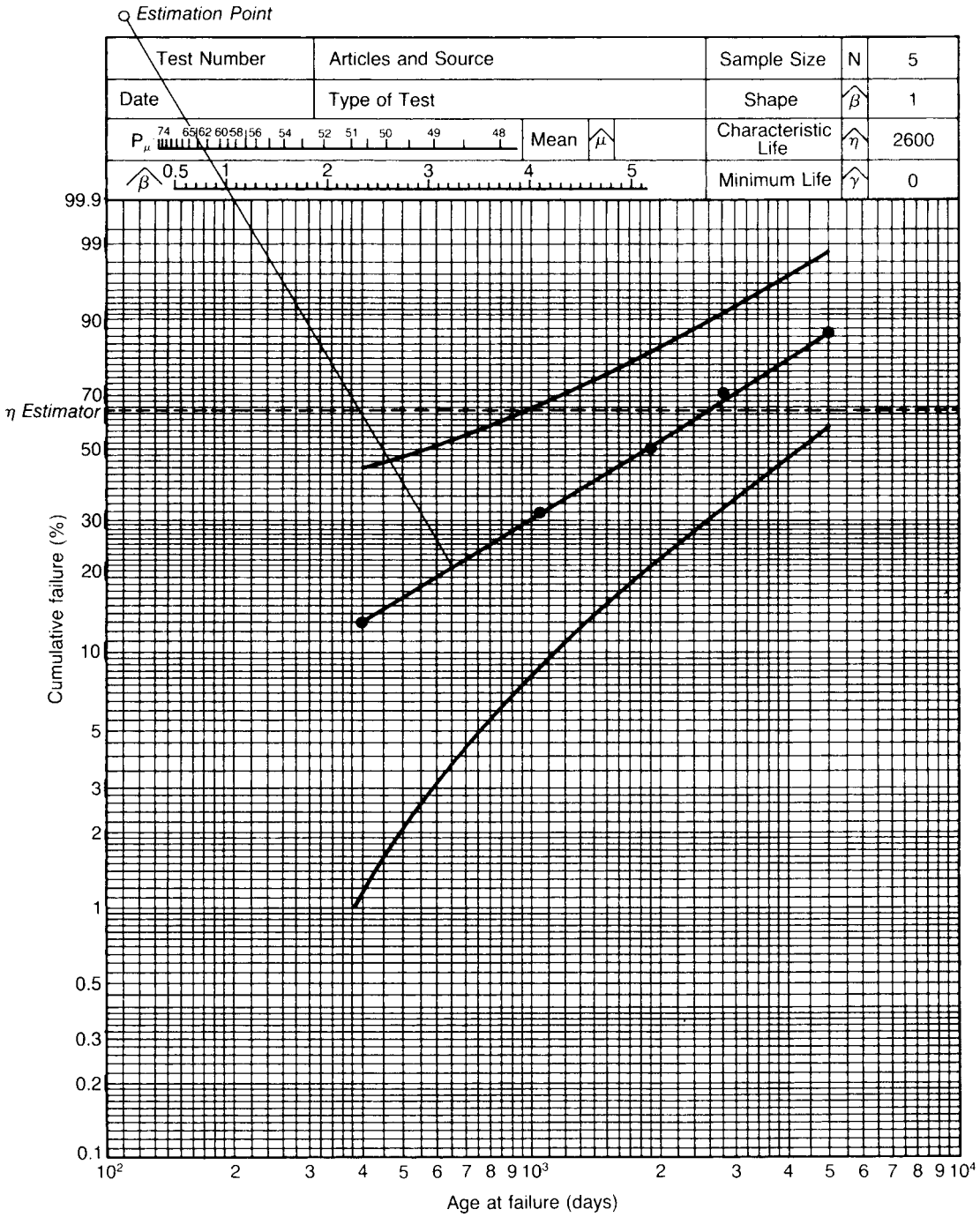


Figure 7.26 *Fitting of failure distributions using special graph paper: Weibull distributions (data from Table 7.21)*

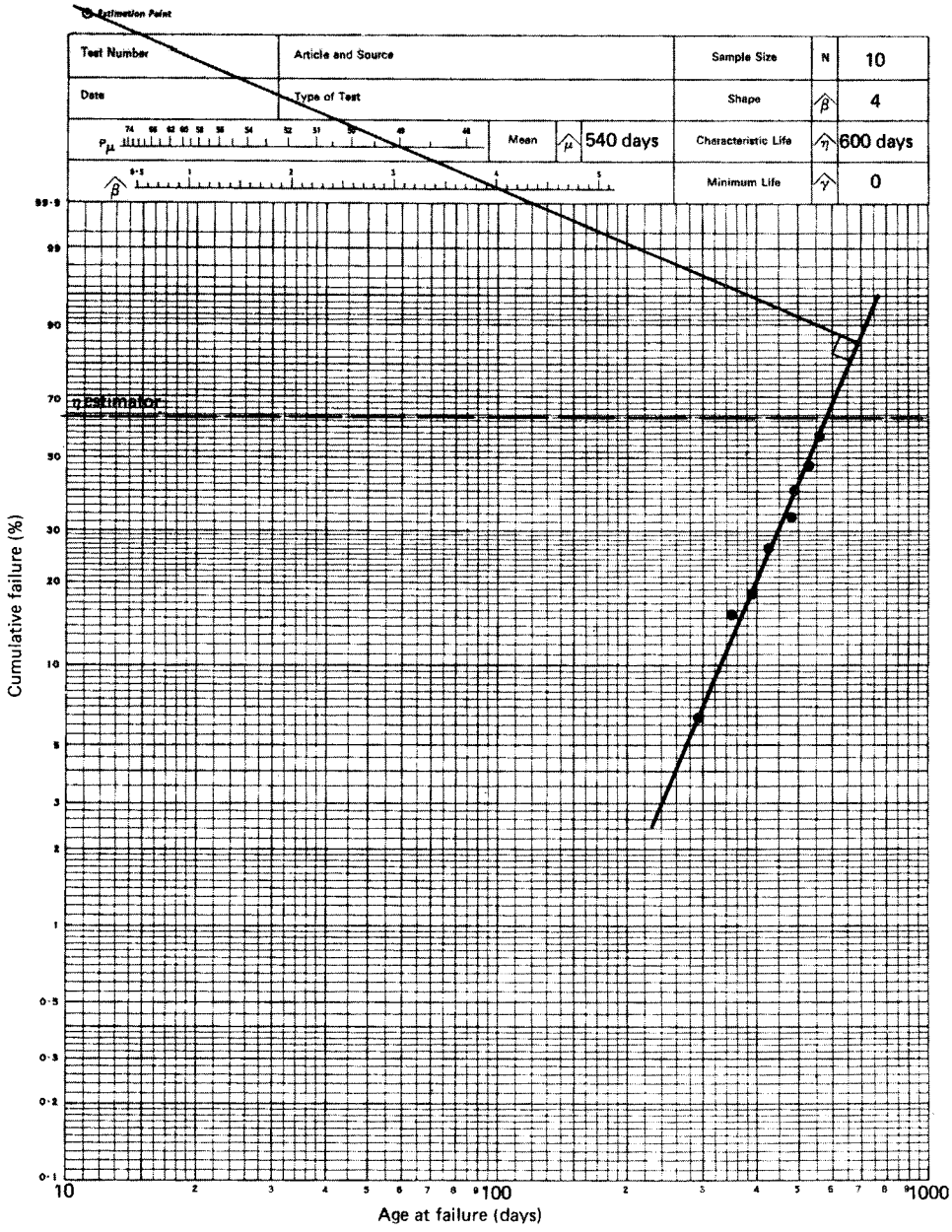


Figure 7.27 *Fitting of failure distribution using special graph paper: Weibull distributions (data from Table 7.23)*

the value of σ is read off as the interval between the ages at failure at these two points.

7.20.12 Fitting of failure distributions: Weibull distribution

The data in Table 7.21 correspond to a Weibull distribution with $\beta = 1$ and are plotted in Figure 7.26. The estimator for the characteristic life η is given by the point at which the cumulative percentage failure is 63.2; the value of η is read off as the age at failure at this point. The shape parameter β is obtained by constructing a line through the 'estimation rsquo; point and perpendicular to the line through the experimental points and reading off the value of β on the special scale.

The mean of the distribution may be obtained as follows. The value of the cumulative probability P_μ is read off from the construction line just described. Then the mean of the distribution is obtained by entering the vertical scale at this

Table 7.19 *Failure data from a failure-terminated test and derived ranked cumulative failure distribution – 1*

Failure No.[a]	*Operating time* (days)	*Cumulative failure distribution (mean rank,* F_{mean}*)*
1	40	0.091
2	98	0.182
3	165	0.273
4	235	0.364
5	312	0.455
6	428	0.545
7	547	0.636
8	720	0.727
9	925	0.818
10	340	0.909

[a] Original no. = 10.

Table 7.20 *Failure data from a failure-terminated test and derived ranked cumulative failure distribution – 2*

Failure No.[a]	*Operating time* (years)	*Cumulative failure distribution (mean rank,* F_{mean}*)*
1	1.69	0.091
2	2.11	0.182
3	2.42	0.273
4	2.73	0.364
5	3.05	0.455
6	3.20	0.545
7	3.44	0.636
8	3.76	0.727
9	4.02	0.818
10	4.37	0.909

[a] Original no. = 10.

Table 7.21 *Failure data from a failure-terminated test and derived ranked cumulative failure distribution – 3*

Failure No.[a]	*Operating time* (days)	*Cumulative failure distribution (median rank,* F_{med}*)*
1	400	0.130
2	1050	0.314
3	1900	0.500
4	2800	0.686
5	5000	0.871

[a] Original no. = 10.

Table 7.22 *The median rank, 5% rank and 95% rank for sample size n = 5 used to plot the confidence limits in Figure 7.26*

Failure No.	*Median rank*	*5% rank*	*95% rank*
1	12.95	1.02	45.07
2	31.38	7.64	65.74
3	50.00	18.93	81.08
4	68.62	34.26	92.36
5	87.06	54.93	98.98

value of P_μ, going to the data line and reading off on the horizontal scale.

Also shown in Figure 7.26 are the 90% confidence limits, which are obtained in the following manner. Use is made of the appropriate percentage ranks for the particular sample size. A table of such ranks is given in Appendix VIII of Kapur and Lamberson (1977). The values of the median rank, the 5% rank and the 95% rank for a sample size of $n = 5$ are given in Table 7.22. These values have been used to plot the confidence limits shown.

7.20.13 Fitting of failure distributions: censored data

It frequently happens that items are withdrawn from test before they have failed. The test is then a censored one. Such a test has both failures and survivals. The mean order number m_j is calculated as

$$m_j = m_{j-1} + \Delta m \qquad [7.20.21]$$

$m_0 = 0$ and $m_1 = 1$ if the sequence begins with a failure. The mean order number increment Δm, which is only recalculated for a failure following a survival, is

$$\Delta m = \frac{n + 1 - m_{j-1}}{n + 1 - x} \qquad [7.20.22]$$

where x is the number of items before the jth failure.

An illustrative example of the determination of mean and median ranks of a set of censored failure data is given in Table 7.23. The data in Table 7.23 can be fitted by a Weibull distribution and are plotted in Figure 7.27. The characteristic life η and the shape parameter β are obtained in the same way as in the previous example.

Further discussions of ranking are given by L.G. Johnson (1964) and Bompas-Smith (1973).

7.20.14 Fitting of failure distributions: observation window

These methods are appropriate for test situations, such as the testing of new equipments by the manufacturer. In this case, the equipments are known to be in the new condition at the start of the test.

In the process industries the position is often rather different. Frequently the test situation is that working equipments are observed through a test 'window', as shown in Figure 7.28 (Aird, 1977b). In this case the equipments are not in the 'as new' condition when the test is started. There appears to be no entirely satisfactory method of dealing with this case at present. The difficulty arises in the handling of the period before the first failure of such equipment. It is possible either to neglect this period or to treat it as a time to failure, but neither approach is accurate. The error in the parameters thus estimated increases as the ratio of the observation window to mean life decreases.

7.20.15 Fitting of failure distributions: parameter estimation

Failure data in the form of times to failure or hazard rates may also be fitted to failure distributions by parameter estimation methods. Three principal methods are (1) least squares, (2) moments and (3) maximum likelihood. These methods are considered for the exponential distribution

$$z(t) = \lambda \qquad [7.20.23]$$

Table 7.23 *Failure data from a time-terminated censored test and derived ranked cumulative failure distribution*

Event No.[a]	*Operating time* (days)	*No. left*	*Increment*	*Mean order No.*	*Cumulative failure distribution (mean rank, F_{mean})*	*Cumulative failure distribution (median rank, F_{med})*
1F	300	14	1	1	0.063	0.045
2F	360	13	1	2	0.125	0.110
3F	400	12	1	3	0.188	0.175
4W	420	11	–	–	–	–
5F	440	10	1.083	4.083	0.255	0.246
6F	480	9	1.083	5.166	0.323	0.316
7W	490	8	–	–	–	–
8F	500	7	1.204	6.370	0.398	0.394
9F	540	6	1.204	7.574	0.473	0.472
10F	570	5	1.204	8.778	0.549	0.551

[a] F, failure; W, withdrawal; original no. 15.

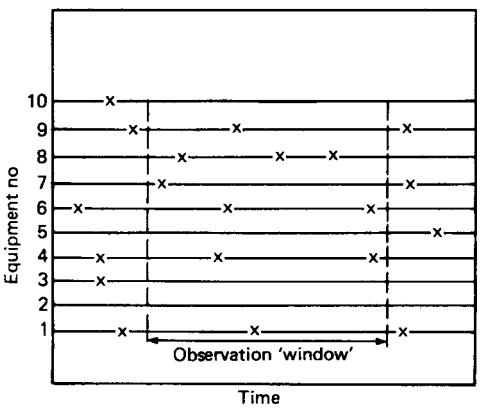


Figure 7.28 *Observation of failures in an operational system (after Arid, 1977b): x, failure*

Table 7.24 *Failure data from a failure-terminated test and derived hazard rates and failure densities*

Failure No.[a]	*Operating time* (days)	*Time interval, Δt* (days)	*Hazard rate, z* ($\times 10^2$)	*Failure density, f* ($\times 10^2$)
1	40	40	0.250	0.25
2	98	58	0.192	0.172
3	165	67	0.187	0.149
4	235	70	0.204	0.143
5	312	77	0.216	0.130
6	428	116	0.172	0.086
7	547	119	0.210	0.084
8	720	173	0.193	0.058
9	925	205	0.244	0.049
10	1340	415	0.241	0.024

[a] Original no. = 10.

and the Weibull distribution

$$z(t) = kt^m \qquad [7.20.24]$$

The least squares method may be applied in various ways. It is often used to fit data in the form of hazard rates. The hazard rate $z(t)$ and the failure density $f(t)$ over each time interval Δt between failures are:

$$z(t) = \frac{1}{n_s \Delta t} \qquad [7.20.25]$$

$$z(t) = \frac{1}{n \Delta t} \qquad [7.20.26]$$

where n and $n_s(t)$ are, respectively, the initial number of equipments and the number of equipments surviving. An illustrative example of the determination of hazard rate and failure density of a set of failure data is given in Table 7.24.

In the least squares method the error e is defined as:

$$e = \sum (z - z_c)^2 \qquad [7.20.27]$$

where z and z_c are the observed and calculated hazard rates. Then if

$$z = f(a_1, \cdots, a_p) \qquad [7.20.28]$$

the parameters a_i are given by the equations:

$$\frac{\partial e}{\partial a_1} = 0 \qquad [7.20.29a]$$

$$\vdots$$

$$\frac{\partial e}{\partial a_p} = 0 \qquad [7.20.29b]$$

A simple relationship for the hazard rate is:

$$z = a + b(t - \bar{t}) \qquad [7.20.30]$$

where $\bar{t}$ is the mean time to failure. From Equation 7.20.27

$$e = \sum_{i=1}^{n} \{z_i - [a + b(t_i - \bar{t})]\}^2 \qquad [7.20.31]$$

Then from Equation 7.20.28

$$a = \frac{1}{n}\sum_{i=1}^{n} z_i \qquad [7.20.32]$$

$$b = \left[\sum_{i=1}^{n}(t_i - \bar{t})z_i\right] \Big/ \left[\sum_{i=1}^{n}(t_i - \bar{t})^2\right] \qquad [7.20.33]$$

For the exponential distribution the parameters in Equation 7.20.30 are

$$a = \lambda$$
$$b = 0$$

For the Weibull distribution, from Equation 7.20.27

$$e = \sum_{i=1}^{n}(z_i - kt_i^m)^2 \qquad [7.20.34]$$

$$k = \left(\sum_{i=1}^{n} z_i t_i^m\right) \Big/ \left(\sum_{i=1}^{n} t_i^{2m}\right) \qquad [7.20.35]$$

m is obtained from the implicit equation:

$$\sum_{i=1}^{n} z_i t_i^m \ln t_i - \sum_{i=1}^{n} k t_i^{2m} \ln t_i = 0 \qquad [7.20.36]$$

The moments method is used to fit data in the form of times to failure. The moments of the data m_k are:

$$m_k = \frac{1}{n}\sum_{i=1}^{n} t_i^k \qquad [7.20.37]$$

The moments of the distribution μ_k are:

$$\mu_k = \int_0^\infty t_k f(t)\,\mathrm{d}t \qquad [7.20.38]$$

The method is to equate the moments of the data and those of the distribution:

$$\mu_k = m_k \qquad [7.20.39]$$

For the exponential distribution:

$$\mu_1 = \int_0^\infty t\lambda \exp(-\lambda t)\,\mathrm{d}t = \frac{1}{\lambda} = m_1 \qquad [7.20.40]$$

For the Weibull distribution:

$$\mu_k = \int_0^\infty t^k k t^m \exp\left(-\frac{kt^{(m+1)}}{m+1}\right)\mathrm{d}t \qquad [7.20.41a]$$

$$= \left(\frac{k}{m+1}\right)^{-k/(m+1)} \Gamma\left(\frac{k+m+1}{m+1}\right) \qquad [7.20.41b]$$

m and k are obtained from the implicit equations

$$\mu_1 = \left(\frac{k}{m+1}\right)^{-1/(m+1)} \Gamma\left(\frac{m+2}{m+1}\right) = m_1 \qquad [7.20.42a]$$

$$\mu_2 = \left(\frac{k}{m+1}\right)^{-2/(m+1)} \Gamma\left(\frac{m+3}{m+1}\right) = m_2 \qquad [7.20.42b]$$

The maximum likelihood method is also used to fit data in the form of times to failure. The likelihood function L is defined as:

$$L(t_1, \ldots, t_n; a_1, \ldots, a_p) = f(t_1; a_1, \ldots, a_p) \cdot f(t_2; a_1, \ldots, a_p) \cdots f(t_n; a_1, \ldots, a_p) \qquad [7.20.43]$$

where f is the density function. Then the maximum likelihood estimate is obtained by maximizing L or $\mathcal{L} = \ln L$ with respect to the parameters a_i

$$\frac{\partial L}{\partial a_i} = 0 \qquad [7.20.44a]$$

or

$$\frac{\partial \mathcal{L}}{\partial a_1} = 0 \qquad [7.20.44b]$$

$$\vdots$$

$$\frac{\partial L}{\partial a_p} = 0 \qquad [7.20.44c]$$

or

$$\frac{\partial \mathcal{L}}{\partial a_p} = 0 \qquad [7.20.44d]$$

For the exponential distribution:

$$L = \prod_{i=1}^{n} \lambda \exp(-\lambda t_i) \qquad [7.20.45]$$

or

$$\mathcal{L} = \ln L = n \ln \lambda - \lambda \sum_{i=1}^{n} t_i \qquad [7.20.46]$$

Then from Equations 7.20.44 and 7.20.46:

$$\frac{\partial \mathcal{L}}{\partial \lambda} = \frac{n}{\lambda} - \sum_{i=1}^{n} t_i = 0 \qquad [7.20.47]$$

$$\lambda = \frac{1}{\frac{1}{n}\sum_{i=1}^{n} t_i} = \frac{n}{\sum_{i=1}^{n} t_i} \qquad [7.20.48]$$

For the Weibull distribution:

$$L = \prod_{i=1}^{n} k t_i^m \exp\left(-\frac{kt_i^{m+1}}{m+1}\right) \qquad [7.20.49]$$

or

$$\mathcal{L} = n \ln\ k + m \sum_{i=1}^{n} \ln\ t_i - \frac{k}{m+1} \sum_{i=1}^{n} t_i^{m+1} \qquad [7.20.50]$$

Then from Equations 7.20.44 and 7.20.50:

$$k = \frac{n(m+1)}{\sum_{i=1}^{n} t_i^{m+1}} \qquad [7.20.51a]$$

$$\left[\left(\sum_{i=1}^{n} t_i^{m+1} \ln t_i\right) \Big/ \left(\sum_{i=1}^{n} t_i^{m+1}\right)\right] - \left(\frac{1}{m+1}\right) - \left[\left(\sum_{i=1}^{n} \ln t_i\right) \Big/ n\right] = 0 \qquad [7.20.51b]$$

Once the parameters of the distribution have been estimated by one of the methods described, an assessment can be made of the goodness of fit. A common approach is to use the χ^2 distribution.

7.20.16 Generation of failure distributions

It is sometimes necessary for purposes such as the testing of failure analysis schemes to generate sets of times to failure obtained from particular distributions. This is normally done by rearranging the equation of the failure distribution $F(t)$ to give the time to failure t as a function of the probability, and then generating the set of times to failure by replacing the probability by a set of random numbers v in the range 0 to 1 from the uniform distribution.

For the exponential distribution, from Equation 7.7.14

$$t = -\frac{1}{\lambda} \ln(1 - v) \qquad [7.20.52a]$$

or, since v and $(1 - v)$ are both uniform distributions with the same range,

$$t = -\frac{1}{\lambda} \ln v \qquad [7.20.52b]$$

For the normal distribution, with zero mean and unit variance from Equation 7.7.18, the following approximation may be used:

$$t = \lim_{n \to \infty} \left[\left(\frac{12}{n}\right)^{1/2} - \left(\sum_{i=1}^{n} v_i\right) - \frac{n}{2}\right] \qquad [7.20.53]$$

It is normally sufficient to take $n = 12$, in which case

$$t = \sum_{i=1}^{12} v_i - 6 \qquad [7.20.54]$$

For the Weibull distribution, from Equation 7.7.25

$$t = \eta(-\ln v)^{1/\beta} + \gamma \qquad [7.20.55]$$

The generation of failure distributions is described in more detail by Hastings and Peacock (1974).

7.20.17 Proportional hazards modelling

Another technique useful in failure data analysis is proportional hazards modelling. This is a method of determining the relative effects of influencing factors on the failure rate. Proportional hazards modelling was proposed by D.R. Cox (1972), who suggested that it might have application to data in the fields of medicine and reliability engineering. Its initial development was in the latter. Accounts are given in *The Statistical Analysis of Failure Time Data* (Kalbfleisch and Prentice, 1980) and *Statistical Models and Methods for Lifetime Data* (Lawless, 1982). The application of the method to reliability engineering is described by Bendell (1985) and Dale (1985).

The basic relationship in proportional hazards modelling is:

$$z(t) = z_0(t) \exp\left(\sum_{i=1}^{n} \beta_i z_i\right) \qquad [7.20.56]$$

where $z(t)$ is the hazard rate, z_i the ith influencing variable, or explanatory factor, $z_0(t)$ the baseline hazard function, and β_i the coefficient of z_i.

Thus the action of the explanatory factors on the hazard rate is, in this model, assumed to be multiplicative, in contrast to the more common correlation models, in which it is taken to be additive. A multiplicative effect appears more realistic. The baseline hazard rate $z_0(f)$ is, in principle, distribution free.

Examples of the application of proportional hazards modelling are given by Dale (1985).

7.20.18 Time-varying failure data

The foregoing treatment is based on the assumption that the failure distribution and its parameters do not vary with time. Some guidance on the effect of variation of the failure rate with time is available from work by Blanks (1977). He shows that significant error occurs where failure rates are estimated from exposure periods which are very much less than the representative life, which for the log-normal distribution is the median life and for the Weibull distribution the characteristic life.

This is illustrated in Figure 7.29, which shows that for the Weibull distribution the product (Failure rate ×

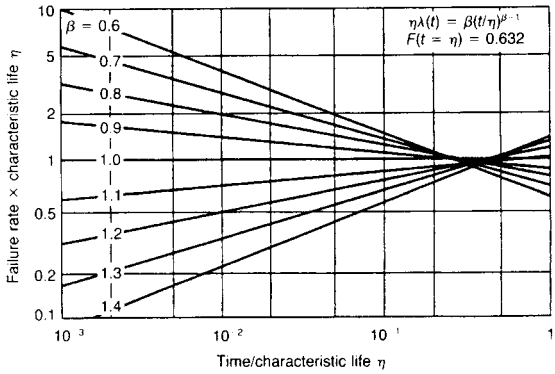


Figure 7.29 *Variation of failure rate with observation time, in terms of the Weibull distribution (Blanks, 1977)*

Characteristic life) diverges significantly from unity for low values of the time/characteristic life ratio.

7.20.19 Combination of failure data

A common situation is that some failure data are available, typically from the literature, whilst further data have been obtained within the company. A method is needed for combining these two sets of data to produce a single value for the failure rate. In this case use may be made of Bayes' theorem, as described in Section 7.14. The problem is also discussed by the Center for Chemical Process Safety (CCPS, 1989/1).

7.20.20 Role of failure data analysis

Failure data analysis can be a powerful tool for improvement in reliability and in maintenance. It is most effective if used as one prong of an integrated approach. It also has certain limitations. For work on reliability, as opposed to maintenance, the acquisition of data is clearly essential.

For maintenance, at the most elementary level collection and analysis of failure data can highlight which equipments have high failure rates and the most frequent failure modes of such equipment. At a more sophisticated level, determination of failure distributions can identify the failure regime and can point to particular types of remedial action or maintenance policy.

Such an analysis is more effective if it is combined with other methods. In the study by Sherwin and Lees (1980) described above, the authors emphasize the value of combining failure data analysis and observation of the maintenance task. They state that this combination is more powerful than either method on its own.

Failure data analysis has it limitations, however. A works commonly contains a large number of equipments, each with a number, often a large number, of failure modes. The collection and analysis of failure data for these is a serious undertaking. Furthermore, failure data analysis is effectively a form of epidemiology, and is thus subject to criticisms which are directed at the latter, namely that it is a method which comes into play only after failures, and possibly harm, have occurred.

An alternative approach which seeks to get things right first time is that of reliability-centred maintenance (RCM). This is described below. Here it is sufficient to note its critique of failure data analysis. Failure data analysis appears to be of most value in application to significant items of equipment with a few dominant failure modes and perhaps also to lesser items present in large numbers.

7.20.21 Repair times

Information on repair times is also required in reliability work. Repair time data are sometimes difficult to obtain accurately as there is a tendency for nominal repair times to be recorded, particularly when tasks are of short duration. It is frequently found that repair times fit a log–normal distribution.

7.21 Reliability in Design

An outline is now given of the design and development of an equipment which is to have high reliability. It draws largely on accounts of the practice of suppliers and users in high technology industries such as defence and aerospace where the users have stringent reliability requirements.

7.21.1 Design process

An overview of the design process for mechanical systems with specific reference to reliability has been given by A.D.S. Carter (1986). He distinguishes three broad stages: (1) the formulation of objectives, (2) the conventional design process and (3) the development process.

7.21.2 Manufacturer ± user relationship

Before considering the three stages of the design process, it is relevant to recognize that the relationship between the manufacturer and the user can have a strong influence on the reliability requirements. In some cases, such as defence, there may be a single manufacturer and single user who work closely together to define the requirements. At the other extreme there is a market in which there are several manufacturers and numerous users. The users may be imprecise about their requirements so that the manufacturers must take their own view about what is needed.

In principle, a user should be seeking to minimize the life cycle costs. In practice, he may well not do this, but may concentrate on some less global objective such as minimization of the combined capital and operating costs of the equipment, or even of the capital cost alone.

The interests of the manufacturer and user do not necessarily coincide. However, in principle, both parties have an interest in the formulation of the reliability goals and specification.

7.21.3 Reliability targets

The reliability requirement is formulated in the first instance as a set of broad targets. In addition to the normal design considerations targets for reliability, these will include availability and maintainability. The priority accorded to reliability proper, the minimization of outright failure, will depend on the consequences of failure, and in particular on the extent to which the item is safety critical. The targets should ideally include the minimization of life cycle cost, but the extent to which the manufacturer does this will depend on the information about use available to him and on commercial judgement.

7.21.4 Reliability prediction

System design and development need to be supported by a continuous process of reliability prediction. This can be significant activity in its own right, and consideration of this is deferred to the next section.

7.21.5 Reliability feasibility study

Before embarking on detailed specification and design, it is usual to carry out a feasibility study. The purpose of this is to confirm that the proposed design is capable of meeting the reliability goals.

7.21.6 Reliability specification

Once established, the reliability targets need to be converted into reliability specifications. There will be a reliability specification for the system as a whole and further specifications for its component parts. The specification process involves sharper definition of features, such as the precise performance requirements for the system, the limits of the conditions and loads which it is required to withstand and the maintenance requirements and the criteria for success in meeting these various requirements. An

account of the practicalities of reliability specification is given by Calabro (1962).

7.21.7 Conventional design

Within his overall account of reliability in design, Carter (1986) gives a detailed description of the conventional design process. The potential system failures should be identified and evaluated. For safety-critical features, techniques such as fail-safe behaviour or redundancy may be appropriate.

In most cases it is possible to make use of an existing design, either unchanged or with relatively minor modification. In this case information should be sought on its reliability in the field under the conditions of interest.

If a new design is indicated, care should be taken to avoid known generic causes of unreliability. These include features which constitute stress raisers, promote corrosion, result in poor connections, allow rupture of pipes, hoses and wires, and so on. The design should be suitable for the environment in which it is to be used. The components should be compatible with each other. A.D.S. Carter gives checklists covering this aspect. Efforts should be made to obtain information on the field reliability of similar designs.

The design should adhere to some basic principles. It should be kept simple. And it should be adequately conservative.

Care should be taken that 'improvements' to an existing or proposed design, whether arising from activities such as value engineering or otherwise, do not in fact result in an unwarranted decrease in reliability.

The maintainability of the system should be considered as well as its reliability.

The components and subsystems used in the design should be fully specified, and there should be inspection and test procedures for them.

Prior to entry into service the system may be subject to handling, packing, transport and storage, which may cause damage or deterioration, and attention should be paid to this aspect.

A quantitative evaluation should be made of the reliability of the system, as much for the sake of stimulating a critical review as for the determination of a numerical value.

7.21.8 Mechanical design

Traditional mechanical design of equipment is based on deterministic methods. It is also possible, however, to take a probabilistic approach using concepts such as those of interference theory. A.D.S. Carter (1986) gives illustrations of the application of this latter approach to problems of stress-rupture phenomena and of fatigue.

7.21.9 Design reviews

The design function should have a formal procedure for the review of the reliability of the systems and equipment under design. This procedure should cover not just the design stage proper but also the testing and development stages, and follow-up at each stage.

7.21.10 Problem identification

The design reviews should make use of the various techniques for problem identification, such as critical examination, checklists, failure modes and effects analysis (FMEA), fault tree analysis, and so on. These methods are described in Chapter 8 and are therefore not discussed further here.

7.22 Reliability Prediction

As just indicated, design for reliability requires the supporting activity of reliability prediction. Reliability prediction is not simply the estimation of numerical values of reliability using suitable models. The term is used to cover the various and much wider range of activities running through the design and development stages, and possibly beyond. Reliability prediction is carried out through this life cycle as a guide to action. Accounts of reliability prediction include those given by von Alven (1964) and D.J. Smith (1985a).

7.22.1 Stages of reliability prediction

Reliability prediction passes through three broad stages, generally characterized as (1) pre-design, (2) interim and (3) final reliability prediction.

7.22.2 Pre-design reliability prediction

The pre-design reliability prediction has to be performed with limited information and involves in particular the feasibility evaluation and the reliability apportionment.

7.22.3 Reliability feasibility study

One of the first reliability prediction activities is the feasibility study. A pre-design estimate is made of the system reliability and is compared with the specification. This indicates whether or not the proposed design is at least within hailing distance of meeting the specification. If it is not, possible responses are modification to the design, or to the specification, or to both. Even if the reliability prediction indicates that the design will meet the specification, it is good practice to explore alternatives. The next step is to set reliability specifications for the subsystems.

7.22.4 Reliability apportionment

The fundamental reliability specification is that for the system as a whole. However, in order to achieve this it is necessary to decompose the system into subsystems and to determine the reliability specifications for the constituent parts. This is known as 'reliability apportionment', or 'reliability allocation'.

There are a number of models which may be used to apportion the reliability targets among the parts, as described by Anderson and Neri (1990). A model for the case where the parts, or subsystems, are similar is:

$$R_x = R^{1/n} \qquad [7.22.1]$$

where n is the number of subsystems, R_x the reliability of the system, and R_x the reliability of a single subsystem. For the case where the subsystems are different one model is:

$$R_x = R^{W_i} \qquad [7.22.2]$$

with

$$w_i = \frac{C_i}{\sum_{j=1}^{n} C_j} \qquad [7.22.3]$$

where C_i is a parameter representing the complexity of the ith subsystem and W_i is the weighting factor for that subsystem.

7.22.5 Interim reliability prediction

Once the design is under way, reliability prediction is used in support. As is usual in design, the process is iterative and involves various trade-offs.

7.22.6 Final reliability prediction

The final reliability prediction is made as part of the overall specification of the product. This prediction also serves as a measure of the success of the design process. There may be complications in producing a single final reliability prediction. The product may come in several versions and, over time, may be subject to modification.

7.23 Reliability Growth, Testing and Demonstration

In the achievement of reliability, design for reliability and reliability prediction need to be complemented by a programme of reliability testing and demonstration. In large part, reliability prediction and testing are directed to the growth in the reliability of the equipment Reliability growth is therefore conveniently considered along with testing.

7.23.1 Reliability testing

In reliability testing a distinction is made between (1) reliability development and demonstration testing, (2) qualification and acceptance testing and (3) operational testing.

Reliability development and demonstration testing is performed to determine (1) whether the design needs improvement, (2) to identify modifications which might lead to improvement and (3) to verify that the modifications made have led to improvement.

In high technology activities it is generally required that a design be accepted as qualified for the intended application. An example is the seismic qualification of equipment for nuclear plants. Similarly, there may be a requirement that the design be qualified with respect to reliability. This is the purpose of qualification testing.

Acceptance testing is concerned with the quality of manufacture of the equipment.

Operational testing provides information on the operation of the equipment, as verification of the design and feedback of information on performance for future use by the designers. This type of testing is less likely to be subject to the continuous process of modification that is characteristic of development testing.

Reliability testing is governed by a formal programme involving subcontractors as well as the lead manufacturer. The programme covers the stages of (1) design concept, (2) production prototype and (3) production testing. It is generally subject to frequent modification.

Further treatment of acceptance testing is deferred to later in the text in order to consider reliability growth.

7.23.2 Reliability growth

If the reliability development programme is effective, it should result in an increase in the reliability of the equipment. Experience with different products shows that the process of reliability growth has certain characteristic features. Accounts of reliability growth are given by Lloyd and Lipow (1962) and D.J. Smith (1985a). A relevant standard is BS 5760: Part 6: 1991 *Guide to Programs for Reliability Growth*.

The situation considered is the development phase of an equipment in which the manufacturer conducts field tests involving a continuous process of feedback of information on reliability performance and modification of the equipment to improve this reliability by reducing design-related failures.

Various models have been developed for reliability growth. Such models may be used to extrapolate in time to the point when the failure rate of an equipment under development should reach the specified value. They may also be used to make estimates of development times.

7.23.3 Duane method

A widely quoted method for the analysis of reliability growth during field testing has been given by Duane (1962). Further discussions of the method are given by Codier (1968), R.C.F. Hill (1977) and D.J. Smith (1985a). Duane found that a log-log plot of cumulative failure rate vs cumulative testing time tended to give a straight line. Codier (1968) modified this plot, replacing cumulative failure rate by cumulative MTBF, as shown in Figure 7.30. A straight line on this plot may be expressed as:

$$\text{MTBF} \propto T^{\alpha} \qquad [7.23.1]$$

The current MTBF is given by:

$$\text{MTBF}_{\text{cur}} = \frac{\text{MTBF}_{\text{cum}}}{1-\alpha} \qquad [7.23.2]$$

where the subscripts cum and cur indicate the cumulative and current values. Values of α tend to lie in the range 0.1–0.65.

The use of cumulative time in the Duane plot means that at long testing times changes in the reliability growth tend to be smoothed out and are difficult to discern.

7.23.4 Reliability acceptance testing

The decision of whether to accept or reject items on reliability grounds needs to be governed by a formal system of acceptance testing. Accounts of acceptance testing are given in texts on quality control (e.g., Burr, 1953; Moroney, 1956; E.L Grant, 1964). Treatments in the context of reliability engineering are given by von Alven (1964), Breipohl (1970) and D.J. Smith (1985a).

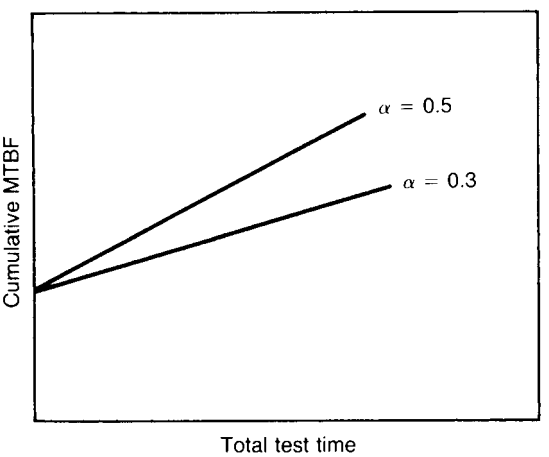


Figure 7.30 *Reliability growth plots: after Duane*

Acceptance testing is generally conducted by reference to an operating characteristic (OC) curve. For the case where such testing is performed by taking a sample of items from a production batch, the operating curve may be constructed from the binomial distribution:

$$P = \sum_{k=0}^{c} \binom{n}{k} q^k p^{n-k} \qquad [7.23.3]$$

where c is the allowable number of defective items in a sample of size n, p and q are the proportions in the batch of good and defective items, respectively ($p + q = 1$) and P is the probability of acceptance. The OC curve is a plot of P vs q for given values of n and c. A typical OC curve of this kind is shown in Figure 7.31(a).

In using a sample as the basis of acceptance, both producer and consumer accept a certain risk. The producer's risk is the probability that the batch is acceptable but fails the test, whilst the consumer's risk is the probability that the batch is unacceptable but passes the test.

The usual procedure is to set values for the acceptable quality level (AQL) and the lot tolerance per-cent defective (LTPD) which are entered on the OC curve as shown in Figure 7.31(a). The AQL is the batch, or lot, quality (q value) for which the probability of acceptance has some (high) specified value. The complement of this probability is the producer's risk (α). A typical value of the AQL is 95%, giving a producer's risk of 5% ($\alpha = 0.05$). Likewise, the LTPD is the lot quality (q value) for which the probability of acceptance has some (low) specified value. This probability is the consumer's risk (β). A typical value of LTPD is 10%, giving a consumer's risk of 10% ($\beta = 0.1$).

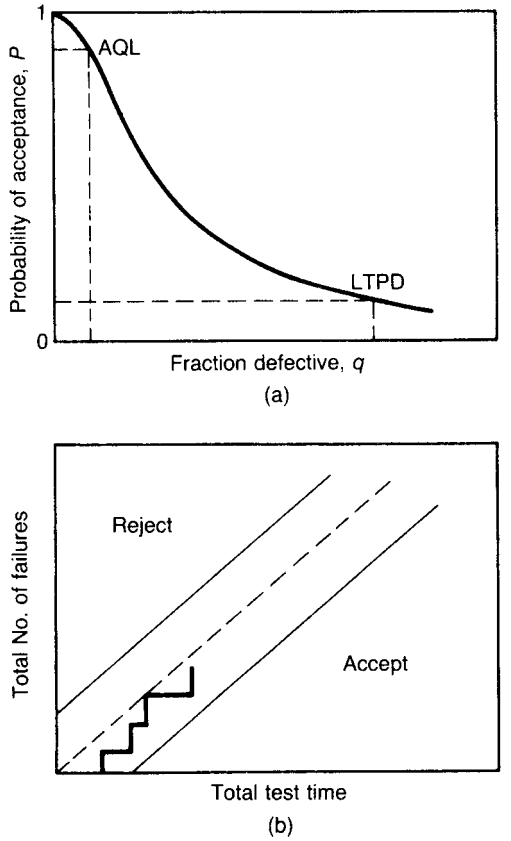


Figure 7.31 *Acceptance testing schemes: (a) operating characteristic curve for sinle sample plan; (b) operating limits for sequential sampling plan*

As just described, this scheme refers to the sampling of a single batch and provides lot quality protection (LQP). If the batch is then to be mixed with other batches, this degree of protection may not be necessary. An alternative scheme may be used which offers average quality protection (AQP).

An approach to acceptance testing for the case where the acceptance criterion is the failure rate of the equipment, which is based on the Poisson distribution, is described by Smith.

The binomial scheme just described involves single sampling. Another approach is the use of sequential sampling in which a series of tests is conducted, the decision after each test being (1) accept, (2) continue testing or (2) reject. This approach is illustrated in Figure 7.31(b).

An important issue in the design of an acceptance testing scheme is the degree of discrimination which it provides. This is discussed by Smith.

7.24 Maintainability

Accounts of reliability engineering generally include as a third theme, in addition to those of reliability and availability, that of maintainability. Maintainability is treated in the main reliability engineering texts cited here and in particular in *Maintainability* (Goldman and Slattery, 1964) and *Reliability, Maintainability and Availability Assessment* (Locks, 1973), and by von Alven (1964) and D.J. Smith (1985a).

The cost of maintaining equipment is a recurring theme in reliability work and was one of the original motivations for it. Although estimates vary, they are generally in agreement that the cost is high. Accounts of maintainability generally treat it as a property of the equipment. 'Maintainability' is therefore not synonymous with maintenance effectiveness, which includes other aspects such as organization and training.

7.24.1 Maintainability measures

The principal measures of maintainability of an equipment are its failure rate and repair time. Attention tends to centre mainly on the repair time, but the overall cost is also strongly influenced by the frequency at which repair is necessary.

The overall repair time is usually decomposed into several parts, a typical division being (1) active repair time, (2) logistics time and (3) administrative time. Essentially, logistics time is that spent waiting for spare parts, and administrative time is the balance of time spent on the repair which is not required for either active repair or logistics.

7.24.2 Maintainability principles

Some basic principles of maintainability are: (1) provision of good access; (2) minimization of the complexity of the task, tools and test equipment; (3) provision of good maintenance manuals; (4) clear criteria for recognition of faults

or marginal performance; and (5) optimization of the diagnosis and repair task.

The latter typically involves (1) preparation, (2) malfunction verification, (3) fault location, (4) fault isolation, (5) disassembly, (6) part procurement, (7) part interchange, (8) reassembly, (9) alignment and (10) checkout.

In many cases an approach based on simple checks to identify the malfunctioning module and replacement of that module is an appropriate strategy.

7.24.3 Maintainability prediction

Methods have been developed for the prediction of maintainability as measured by the repair time. The basic approach is to synthesize estimates of the repair time from a data bank of times for element of the repair task. Von Alven (1964) describes a number of data collections developed for this purpose. One is the ASB-4 system. Another system is that developed by the American Institute for Research (AIR).

7.24.4 Maintainability testing and demonstration

Major clients such as the armed services require the supplier to demonstrate maintainability as well as reliability. MIL-STD-471 *Maintainability Demonstration* states requirements for the US Armed Services, and is widely quoted.

Maintainability is generally demonstrated by conducting a series of tests. In the typical test a defined maintenance task is undertaken and measurements are made of the times taken to perform it. A plot is made of the probability of passing the test vs the MTTR (mean time to repair) which is then evaluated against a predefined criterion.

Comparability between tests depends crucially on holding constant the various factors which are known to exert a strong influence. These are listed by D.J. Smith (1985a) as (1) method of selecting the demonstration task, (2) tools and test equipment available, (3) PM given to test system, (4) maintenance documentation, (5) environment during test and (6) skill level and training of test subject.

7.25 Maintenance Activities and Policies

The maintenance analysis of a system has as its objective the identification of failure situations and the formulation of appropriate maintenance policies.

The theory of maintenance is a well-developed aspect of reliability engineering. Accounts are given in *Maintainability* (Goldman and Slattery, 1964), *Maintainability, Principles and Practice* (Blanchard and Lowery, 1969), *Maintenance, Replacement and Reliability* (Jardine, 1973) and *Maintainability Engineering* (D.J. Smith and Babb, 1973).

The management of maintenance is described in *Modern Maintenance* (J.E. Miller and Blood, 1963), *Effective Maintenance Organisation* (Newbrough, 1967), *Maintenance Engineering and Organisation* (Gradon, 1973), *Principles of Planned Maintenance* (Clifton, 1974), *Systematic Maintenance Organisation* (Priel, 1974), *Maintenance Management Techniques* (Corder, 1976), and *Maintenance Management and Terotechnology* (Husband, 1976).

The maintenance of plant to reduce failures and stoppages is discussed below. Some wider aspects of the maintenance function and of the information which it generates are described in Chapter 21.

7.25.1 Maintenance activities

Some maintenance activities which are carried out on process plants have traditionally been:

(1) production assistance – adjusting machine settings;
(2) servicing – replacement of consumables, including lubrication;
(3) running maintenance – running repairs with little interruption to production;
(4) shut-down maintenance – scheduled repair or overhaul with interruption to production;
(5) breakdown maintenance – unscheduled repair with interruption to production.

7.25.2 Failure regimes

Before considering maintenance policies, it is pertinent to consider briefly the issue of failure regimes. The measures which can be taken to reduce failure depend very largely on the failure regime of the equipment. As already discussed, the three regimes are: (1) early failure, (2) constant or random, failure and (3) wearout failure.

If the failure regime is established to be wearout failure, this points to a maintenance policy based on fixed interval replacement.

In many cases the equipment appears to be in the random failure regime. If the failures of the equipment are truly random, then there is little purpose in carrying out scheduled maintenance, because by definition the equipment is just as likely to fail afterwards as before. This is a fundamental point which it is difficult to overemphasize.

On the other hand, failure of an equipment is rarely truly random. If an equipment appears to be in the constant failure regime, it is usually worth probing further. Often the apparent constant failure characteristic is due to the non-constant failure characteristics of the large number of components of which it is constituted. This effect has been discussed in Section 7.18. Thus if the failures of components rather than those of the whole equipment are analysed, non-constant failure regimes may be revealed, although in many cases the number of failures of each component may be so small that analysis is difficult.

If the failure regime is established to be early failure, the choice of maintenance policy is again complex. In formulating a policy, account should be taken of the various factors which contribute to early failure, as described in Section 7.19. One of these may be failure induced by unnecessary scheduled maintenance.

7.25.3 Repair, reconditioning and replacement

Another preliminary matter is the issue of repair, reconditioning and replacement. If an equipment is found to have deteriorated to a point where its condition or performance is unsatisfactory, it is sometimes replaced, but is more often repaired or reconditioned with the aim of restoring it to the 'as new' condition.

Often this is not achieved. Failure to make full restoration can be serious. A policy where this tends to be the outcome can result in a higher overall level of faults on the plant. It is essential, therefore, that for equipments with fine tolerances the requirements for repair or reconditioning be properly specified. There should be a written specification for the task. The specification not only

should quote the original design information such as a drawing number but also should give the permissible wear tolerances.

It should be borne in mind that maintenance personnel deal with a wide range of equipment. On some of this equipment tolerances may not be particularly critical. It is important that they do not transfer the rough-and-ready methods which may be adequate there to equipment which requires more careful treatment.

Certain equipment designs allow for the rectification of a fault by simply removing a defective module from the equipment and replacing it with a new one. This is then generally the best action.

7.25.4 Maintenance policies

Some policies for maintenance are:

(1) scheduled maintenance:
  (a) inspection;
  (b) minor adjustment;
  (c) replacement;
(2) on-condition maintenance;
(3) opportunity maintenance;
(4) breakdown maintenance.

Maintenance policies can be classed as either PM or breakdown maintenance. All the policies except the last may be regarded as forms of PM.

7.25.5 Planned maintenance

In general, it is desirable that maintenance tasks be planned rather than undertaken *ad hoc*. The term 'planned maintenance' is widely used and refers to any maintenance which is planned. It includes some breakdown maintenance where the latter can be planned in advance.

7.25.6 Scheduled maintenance

A subset of PM policies is that comprising the variations on scheduled maintenance. There are several forms of scheduled maintenance, the distinction between them being the actions prescribed in advance. These may be (1) inspection, (2) adjustment or (3) replacement; the term 'adjustment' covering virtually any action beyond inspection but short of replacement.

If the policy is scheduled inspection and no problem is found, no further action is taken. However, if the inspection indicates that further action is required, it is taken, whether it be adjustment or replacement. Likewise, scheduled adjustment generally includes inspection and may involve replacement if the inspection so indicates.

7.25.7 Scheduled replacement

If it is established that an item exhibits wearout failure, it is possible in principle to determine the failure distribution and to adopt a policy of scheduled replacement based on this. If the parameters of the distribution are known, the probability of failure prior to replacement which is tolerable can be specified and the time interval for replacement read off from the failure distribution function, as shown in Figure 7.32.

Alternatively, the failure distribution may be assumed. In this case a common assumption is that the failure distribution is normal. This assumption together with knowledge of the value of the mean life and a further assumption about the variance allows an estimate to be made of the replacement interval. If the mean life to wearout is m and

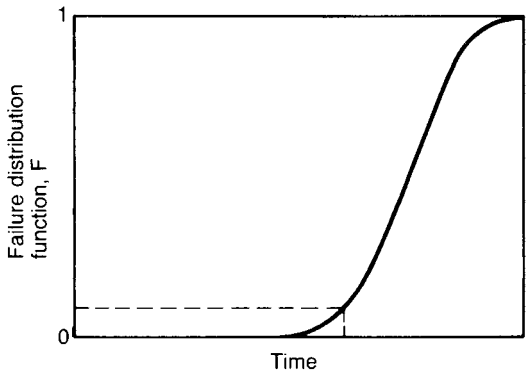


Figure 7.32 *Determination of the scheduled of replacement interval from the failure distribution*

the corresponding standard deviation is σ, then the maintenance policy is to replace at a time m_0 where

$$m_0 = m - k\sigma \qquad [7.25.1]$$

As a rule-of-thumb the value of σ is often taken as

$$\sigma = 0.1m \qquad [7.25.2]$$

A typical value of k is 6, so that Equation 7.25.1 becomes

$$m_0 = 0.4m \qquad [7.25.3]$$

Thus, for example, bearings are commonly replaced at a proportion of their mean life, the so-called 'B10 life'.

7.25.8 On-condition maintenance

An alternative to scheduled maintenance is on-condition or condition-based maintenance. On-condition maintenance (OCM) involves periodic inspection, and to this extent resembles scheduled inspection. Insofar as a difference can be drawn, the distinguishing features of OCM is that it tends to draw on the many powerful techniques now available for condition monitoring and, when deterioration is detected, to involve prediction of the expected time to failure. OCM has the advantage of averting failures by early action if inspection detects deterioration and of avoiding unnecessary maintenance if inspection reveals no deterioration.

An account of OCM is given by Moubray (1991). The essential conditions for its practice are there is a well-defined potential failure (PF) condition and that it is feasible to construct a dependable PF curve. In a PF diagram the fractional margin of acceptable performance (from 1 to 0) is plotted against time. This PF curve can then be used to predict the time of occurrence of total loss of margin, or failure. The time between first detection of PF and actual failure is the PF interval. For OCM to be practical, the PF curve must be reasonably reproducible. An inspection interval can then be chosen which is less than the PF interval. The time available for action to be taken is the difference between the PF and inspection intervals, or the net PF interval.

Moubray (1991) also gives an appendix containing brief summaries of the various condition monitoring techniques

and their applications. A further account of these techniques is given in Chapter 19.

OCM is a feasible policy only if an appropriate inspection or monitoring technique is available, but the development of new techniques is continually widening the scope of items which can be inspected for deterioration. However, since inspection incurs cost, there is an optimum degree of inspection. Optimal inspection policies are dealt with in standard texts on maintenance.

7.25.9 Opportunity maintenance

For equipments which are normally inaccessible, breakdowns or stoppages provide the occasion to practice 'opportunity maintenance'. This consists of doing PM work as and when the item becomes available.

Thus, for example, it is often normal practice that when a pump is opened up a check is made on alignment, bearings, seals and cooling water flow, but this check may be extended to other features such as the casing and the small bore connections.

7.25.10 Burn-in

As described above, one of the causes of early failure in a system with a large number of new components can be the presence of a proportion of weak components. An account of methods for dealing with this problem is given in *Burn-In* (Jensen and Petersen, 1982). These methods might be regarded as another type of maintenance policy. Jensen and Petersen describe a methodology for dealing with this kind of early failure problem by burn-in. Interest centres in large part on the prediction of the burn-in period required.

7.25.11 Selection of maintenance policies

There are considerable differences in the maintenance policies which may be followed on process plant. At one extreme the policy may be one of breakdown maintenance only, whilst at the other the policy may be one of extensive PM.

The terminology used for maintenance policies is defined in BS 3811: 1984 *Glossary of Maintenance Terms Used in Terotechnology.* An account of maintenance policies is given in *Maintenance Aspects of Terotechnology. 1, Planned Maintenance* (Department of Industry (DoI), 1975/4). A decision tree illustrating the relationships between the various forms of maintenance is given in Figure 7.33.

Over the years, maintenance policies have been subject to change, even fashions. Moubray (1991) distinguishes three stages. The first stage is that of breakdown maintenance, characterized by plant which was relatively simple, which was designed with large safety margins and which was usually not safety-critical. The second stage is that of PM, in response to pressures for longer equipment life, high availability and lower costs. The third stage is that of RCM, in response to intensification of the same pressure, as well as those of safety, health and environment.

At one time PM was very much in vogue. It was often taken to uneconomic lengths and, in consequence, the fashion faded. Most present policies in the process industries are a mix of preventive and breakdown maintenance.

If maintenance policies are considered from the safety and loss prevention viewpoint, it is apparent that it is desirable to forestall breakdown as far as possible and that it is prudent to identify critical equipments and to carry out appropriate inspection and PM on them.

Process plants tend to run for long periods between scheduled shut-downs, or turnarounds. There are many equipments, however, which are not accessible for maintenance except at shut-down. Thus the shut-down is extremely important from the maintenance viewpoint. In particular, the shut-down allows an opportunity for the maintenance of plant utilities.

7.25.12 Maintenance information

The formulation of maintenance policies and the monitoring of maintenance activities require that there be a suitable maintenance information system. The maintenance information system has as its main purpose the provision of data on which to base maintenance decision-making, but it also has the further important function of feeding back information on failure to the design department and information on failure and repair to the reliability engineering section.

Some information which is relevant to maintenance includes identification and quantification of (1) failures responsible for hazardous conditions, (2) failures responsible for plant downtime and (3) failures responsible for direct repair costs.

7.25.13 Maintenance effectiveness

Measurement and monitoring of the effectiveness of the maintenance system is necessary, but is often not straightforward. Maintenance costs break down into direct costs and indirect costs. The direct costs are (1) materials and (2) labour. Some indirect costs are those due to (1) plant unavailability, (2) loss of plant throughput, (3) loss of plant efficiency and (4) spares holdings. The overall effect of poor maintenance may result in a degree of disruption, the cost of which can exceeds the apparent sum of these factors.

These considerations are the basis of approaches to maintenance which concentrate on the three 'top tens', these being the top ten items which contribute most in each of the three categories: (1) direct cost, (2) indirect cost and (3) troublesomeness.

7.25.14 Maintenance indices

It is common practice to evaluate maintenance performance in terms of ratios, or indices. Such indices typically measure (1) relative maintenance cost, (2) proportion of PM, (3) plant availability, (4) breakdown rate, (5) breakdown repair time and (6) breakdown cost. Normalizing factors used include (1) plant capital cost, (2) plant operating cost, (3) maintenance man-hours and (4) number of breakdowns.

$$Index\ 1 = \frac{Total\ cost\ of\ maintenance}{Total\ capital\ cost\ of\ plant}$$

$$Index\ 2 = \frac{Total\ cost\ of\ maintenance}{Total\ cost\ of\ plant\ operation}$$

$$Index\ 3 = \frac{Total\ man\text{-}hours\ of\ preventive\ maintenance}{Total\ man\text{-}hours\ on\ all\ maintenance}$$

$$Index\ 4 = \frac{Plant\ up\text{-}time}{Plant\ up\text{-}time + Plant\ down\text{-}time}$$

$$Index\ 5 = \frac{Plant\ up\text{-}time}{Number\ of\ breakdowns} = MTBF$$

$$Index\ 6 = \frac{Plant\ down\text{-}time}{Number\ of\ breakdowns} = MTTR$$

$$Index\ 7 = \frac{Cost\ of\ breakdowns}{Number\ of\ breakdowns}$$

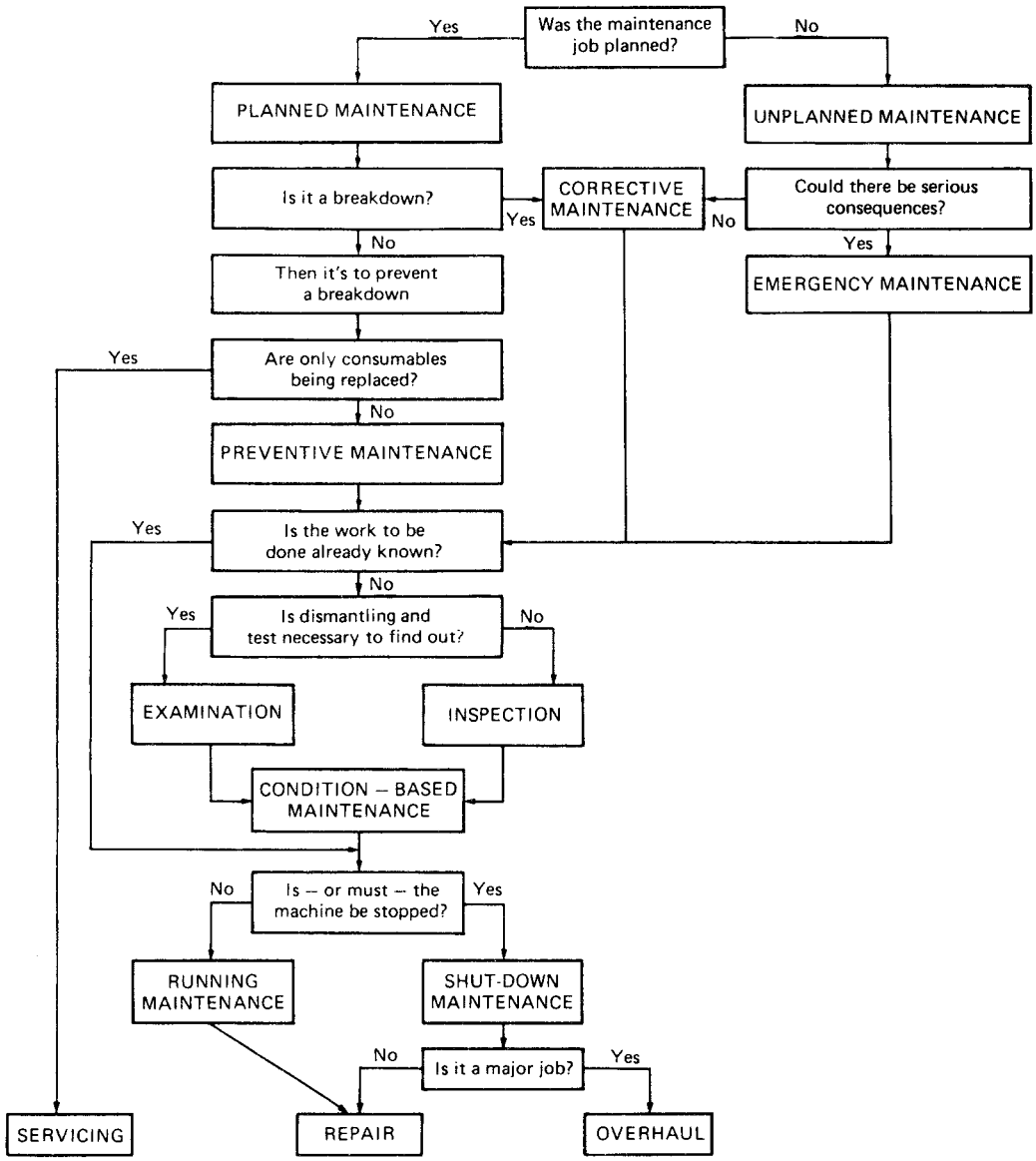


Figure 7.33 *Decision tree illustrating the relationship between the various forms of maintenance (Department of Industry, 1975/4). Terminology used is from BS 3811: 1974*

Such indices can be useful tools, but they may also imply unwarranted assumptions. Index 3, for example, appears to assume that PM is always a good thing, which is not necessarily the case.

A maintenance index may be evaluated by reference either to some absolute criterion value or to the historical trend. Both approaches have their uses.

7.26 Reliability-centred Maintenance

An approach to maintenance which is finding increasing acceptance is RCM. RCM is not a specific maintenance policy such as scheduled replacement or OCM, but an integrated method by which to select such policies. Accounts of this approach to maintenance are given in *Reliability-Centred Maintenance* (Anderson and Neri, 1990) and *Reliability-Centred Maintenance* (Moubray, 1991) and by Nowlan and Heap (1978), Sandtory and Rausand (1991) and Pradhan (1993).

RCM developed within the civil aircraft industry. In 1974, the Department of Defense commissioned a report on maintenance practice in that industry, published as *Reliability-centred Maintenance* (Nowlan and Heap, 1978).

The elements of RCM may be considered under the following headings: (1) functions, (2) function failures, (3) failures modes, (4) failure effects, (5) failure consequences, (6) preventive tasks and (7) default actions. This description suggests that RCM may be regarded as being based on a form of FMEA. This is broadly true, but it takes an approach to FMEA which places particular emphasis on function, function failure and prevention.

As described in the next chapter, FMEA is one of the prime tools of hazard identification used in safety and loss prevention work. Here it is sufficient to note that its growing use in maintenance is a major influence for the integration of safety and loss prevention (SLP) and maintenance.

7.26.1 Functions, functional failures and performance standards

Taking these elements in turn, RCM starts by establishing the functions of the equipment. The equipment will have some primary function which is its *raison d'etre,* but in addition it will generally have secondary functions. Thus, for example, a pump has the primary function of raising the pressure of the liquid, but it also has the secondary function of containing it. Satisfactory performance with respect to safety, health and environment may be treated as other secondary functions.

Increasingly, equipment comes with various kinds of protective device which serve to protect one or other of these functions. Protective devices are used to maintain the primary function by means such as bringing in standby equipment when the main equipment fails or to provide protection in relation to secondary functions such as safety or environment. For each function and each protective device there is a performance standard.

7.26.2 Failure modes and causes

It is necessary to identify the failure modes of the equipment. In general, failure modes may be described in terms of failure of performance or failure of condition. In RCM the former is the failure of function just described and it is the latter which is the failure mode. For example, if a pump becomes incapable of pumping the design flow of liquid, this might be expressed as a failure of pumping capability or a failure due to impeller wear. It is the failure of condition, the impeller wear, which is treated as the failure mode.

In the analysis of the failure modes it is important to uncover the root causes. Typical root causes include incorrect lubrication or maloperation. In the case of the pump impeller wear, the root cause might be cavitation due to partial blockages in the suction line.

7.26.3 Failure effects and consequences

The failure effects describe what happens when the failure occurs. They include the symptoms of failure and the effects on the process, on other equipment, safety and the environment. These failure effects are evaluated in order to assess the failure consequences. Here four types of consequence are distinguished: (1) hidden failure consequences, (2) safety and environmental consequences, (3) operational consequences and (4) non-operational consequences.

The term 'hidden failure' is that generally used in RCM to denote the unrevealed failure of protective devices. Most protective devices tend to fail without signalling the fact. In such cases the device then remains in the failed state until the failure is revealed either because the device is checked or because a demand occurs against which the device no longer provides protection. In other words, protective devices with this characteristic are not fail-safe. The treatment of unrevealed failure of protective devices is discussed in Chapter 13.

A hidden failure means that there is a risk of a demand occurring against which there is no protection, and hence of what in RCM is called 'multiple failure'.

The safety and environmental, operational and non-operational consequences are largely self-explanatory. The latter covers any damage to the equipment

7.26.4 Preventive tasks and default actions

The next step is to determine for each failure mode in turn whether a PM task exists which can eliminate or ameliorate the failure. For main equipment the approach followed is essentially that already described of establishing the failure characteristic (e.g., early failure, wearout failure) and identifying a corresponding appropriate preventive task. Consideration is also given to the appropriateness of OCM. For protective equipment, where the aim is to maintain an adequate availability, the main preventive action is to reduce the failure rate. The alternative measure is to alter the inspection interval, which counts as a default action.

In the RCM context, whether or not a preventive task is appropriate depends first on its technical feasibility and then on its worthwhileness. A task is undertaken only if it is feasible and worthwhile.

It is not appropriate to try to deal with every failure mode by a PM task. Where such a solution is not available, a default action is taken. Principal default actions are (1) redesign, (2) periodic inspection and (3) no action.

The typical account of RCM describes a rather formalized system with decision flow diagrams, FMEA worksheets, and so on. Commonly used abbreviations are: F, failure; FF, function failure; FM, failure mode; H, hidden failure; S, safety; E, environment; O, operation.

7.26.5 Illustrative example

The application of RCM to the process industries is illustrated by an example given by Pradhan (1993). The author deals with the use of RCM on a set of main reactor charge pumps handling vinyl chloride monomer (VCM) on a polyvinyl chloride (PVC) plant. Aims included the improvement of the pump system reliability and avoidance of the need for breakdown maintenance, and the prevention of VCM leaks and fires. He gives sample functions and failure analysis tables akin to those produced in FMEA, discusses in particular the hidden failure of protective devices, and describes the outcomes of the study in terms of the preventive tasks and default actions.

7.27 Life Cycle Costing

The concept of life cycle costing (LCC) is that ownership of an asset involves not only capital but also other costs, and that the aim should be to minimize these costs over the life cycle of the asset. An account of LCC in the context of process plants is given by Lees (1983d).

7.27.1 Management of life cycle costing

The practice of LCC is likely to be effective only if fully supported by management, whose attitude is crucial. Frequently

the issue which will reveal management's attitude will be the trade-off between higher initial cost and overall LCC. The role of management is to establish the policy of LCC and to set up formal systems to ensure that the policy is followed.

There are also other ways in which management can promote LCC. One is the rotation of personnel between the plant and the design function, so that plant experience is fed back into design. Failure to achieve such feedback, by this or other means, can be very costly.

There are a number of other activities to which LCC is related. They include (1) reliability and maintainability engineering, (2) value engineering and (3) process economics. It is unlikely that the practice of LCC will flourish unless the organization has a sufficient level of activity in such areas.

A practical policy for LCC needs to define clearly the items to which it is to be applied and needs to avoid excessive complication.

7.27.2 Applicability of life cycle costing

LCC is most readily applied to an asset which is 'free-standing', that is, one whose failure does not cause significant disruption. In this case the optimization of the life cycle cost is essentially a trade-off between the higher capital cost of an equipment with superior performance, including reliability, and the direct costs of inferior performance, including unreliability. Whatever the case with other equipment, and a truly free-standing equipment is perhaps not as common as might appear at first sight, that used in process plant does not fall into this category.

LCC is subject to the law of diminishing returns. A policy for LCC therefore needs to include some sort of stopping rule. The returns are likely to be greatest for two types of equipment: (1) major items and (2) minor items used in large numbers.

7.27.3 Decision process for life cycle costing

It is not uncommon in the acquisition of an asset that the decision is made by the wrong person at the wrong time on the basis of inadequate information, or even that it is made essentially by default. For LCC the decision process covers the stages of (1) specification, (2) design and (3) procurement.

Often the key decisions are those taken early in the project. Thereafter, many of the options which have the strongest influence on the LCC are foreclosed. That said, the importance of the procurement stage should not be underestimated.

7.27.4 Factors contributing to life cycle cost

Some of the factors which contribute to LCC are: for the equipment, (1) capital cost, (2) maintenance cost and (3) equipment life; and, for the plant, (1) plant availability, (2) plant instantaneous throughput, (3) plant efficiency and (4) plant flexibility. Safety, health, environment and other factors act as constraints which may have a strong influence on the LCC.

Often the main elements from this list are (1) capital cost, (2) maintenance cost and (3) plant availability.

7.27.5 Information for life cycle costing

The practice of LCC requires information on *inter alia* (1) failure rate, (2) repair time and (3) plant unavailability.

It is possible to construct a long list of information which in principle bears on LCC. However, not all this information is readily observable, at least without excessive cost. If the acquisition of information is considered in terms of the two attributes of importance and observability, the policy adopted might well be the following:

		Observability	
		High	*Low*
Importance	*High*	Y	?
	Low	?	N

where Y indicates that the information is sought, N that it is not sought and ? that the case is considered on its merits.

7.27.6 Essential and optional equipment functions

The functions of equipment divide into the essential and the desirable. Examples of essential functions include containment by materials of construction, material transfer by pumps and compressors, control by instruments and computers, protection by protective devices and thermal insulation by lagging. Other functions may be less essential, even optional. Examples are equipment for heat recovery or improved process yield.

The computation of LCC in these two cases is different. Where the function is essential, the decision is concerned with the alternative ways of providing the function, but where it is optional the decision is rather whether to provide it at all. The latter decision may well be more self-contained and easier to make.

7.27.7 Euipment functions involving availability

A further distinction to be made is that between those decisions which involve plant availability and those which do not. The effect of an equipment on plant availability is often quite difficult to assess. Intermediate storage is provided to improve plant availability, but its effectiveness is a function of the storage operating policy adopted. Stand by equipment is provided to cut in when the main equipment fails, but its reliability in responding to this demand depends largely on management factors.

A further complication arises when the plant is not operating at full capacity and its availability is at a discount. It is difficult to generalize about this situation, but one point is worth making. It can be of value to demonstrate that the plant can operate dependably at high availability, even if not currently required to do so, since this means that it is known that when demand picks up it can be met from the existing plant, thus allowing expenditure on a further plant to be deferred.

7.27.8 Equipment quality vs system configuration

It often occurs that a particular function can be provided by a single equipment or by several equipments in some suitable configuration. For a given level of reliability, the single equipment will need to be of higher quality. There is therefore a choice to be made between a single, high quality item and several items which could be of lower quality.

In making this decision, use may be made of simple models of system reliability and availability such as those given above, particularly in Sections 7.8 and 7.13. If the case is considered of a single equipment vs two parallel redundant equipments, the reliability of the single item needs to be very high to match that of a parallel system of two items of moderate reliability.

7.27.9 Assessment of equipment quality

The ability to assess the quality of equipment is clearly crucial to the practice of LCC. Some factors relevant to the assessment are (1) user experience, (2) vendor reputation, (3) design status (new, established), (4) capital cost, (5) material of construction and (6) engineering principles. Engineering principles include (1) the number of subsystems and components, (2) electronic vs mechanical subsystems, (3) moving parts and (4) stressing of parts. Also relevant are any quality assurance arrangements which exist between the vendor and the user.

7.28 Notation

Sections 7.1–7.13

a	constant; parameter in rectangular, gamma, Pareto and extreme value distributions
A	event A
$A(t)$	availability
$\mathbf{A}$	matrices defined by Equations 7.10.6 and 7.10.36
b	constant; parameter in rectangular, gamma and extreme value distributions
B	event B
C	event C; minimum cut set
$d(t)$	down-time
e	error
E	event E
$f(t)$	failure density function
$f_{\mathrm{d}}(d)$	down-time density function
$f_{\mathrm{r}}(t_{\mathrm{r}})$	repair time density function
$f_{\mathrm{w}}(w)$	throughput density function
$f_1(t), f_2(t)$	failure density function of subsystem
$F(t)$	failure distribution function
$F_{\mathrm{d}}(d)$	down-time distribution function
$F_{\mathrm{r}}(t_{\mathrm{r}})$	repair time distribution function
$\bar{g}(s)$	Laplace transform of $g(t)$
$H(t)$	cumulative hazard function
$\mathbf{I}$	identity matrix
k	counter; state counter; parameter in Weibull distribution (alternative form); parameters defined by Equations 7.13.28 and 7.18.5
m	mean life; parameter in Weibull distribution (alternative form); mean of normal distribution; number of repairmen
m^*	location parameter in log–normal distribution
m_{d}	mean down-time
m_i	ith moment (experimental)
m_{r}	mean repair time; mean of normal distribution of repair times
m_{r^*}	location parameter in log–normal distribution of repair times
m_{ru}	mean repair time of upstream unit
m_{u}	mean up-time
m_{z^*}	parameter in log-normal distribution of hazard rates
n	counter; number of items; number of states; number or trials; number of repairmen; number of applications of load
$n_f(t)$	number of items failed
n_i	number of times outcome i occurs
$n_{\mathrm{s}}(t)$	number of items surviving
p	probability; probability of success
P	probability; probability of success
$P(\|)$	conditional probability
P_k	probability of being in state k
$\boldsymbol{P}$	vector of probabilities
q	probability of failure
$Q(t)$	probability of failure, unreliability, failure distribution function
r	counter
$r_1 r_2$	equation roots defined by Equations 7.8.24 and 7.8.26
$R(t)$	probability of success or survival, reliability, reliability function
R_{sw}	probability of switchover
R_{x}	reliability of component
s	Laplace operator
t	time; failure time
t_{r}	repair time
T	time period; minimum tie set
T_{e}	time to empty tank
$u(t)$	up-time
$V(t)$	unavailability
V_{s}	unavailability of upstream unit
V_{st}	unavailability of upstream unit + tank
w	throughput
$z(t)$	hazard rate
$\mathcal{L}(\,)$	Laplace transform
α	parameter in Weibull distribution (alternative form); confidence level parameter
β	shape factor in Weibull distribution
γ	location parameter in Weibull distribution; number of standard deviations
Γ	gamma function
ζ	event rate
η	characteristic life in Weibull distribution
λ	failure rate; transition rate
λ'	failure rate
λ_{st}	failure rate of upstream unit + tank
λ_{u}	failure rate of upstream unit
μ	moment; mean number of events; repair rate
μ_{i}	ith moment (theoretical)
ξ	repair rate enhancement factor
ρ	parameter defined by Equation 7.13.24
σ	standard deviation of normal distribution; shape factor in log–normal distribution
σ_{L}	standard deviation of loading
σ_{r}	standard deviation of repair times; shape parameter in log–normal distribution of repair times
σ_{s}	standard deviation of strength
σ_z	parameter in log–normal distribution of hazard rates
τ	time; repair time; parameter defined by Equation 7.18.6
$\phi(\tau, t)$	joint density function

Superscripts

-	Laplace transform
Λ	estimated value

Section 7.14

E	event
$f_{T1}(t_1)$	density function of t_1
$f_{T1\|\Lambda}(t_1 \mid \lambda)$	density function of $t_1 \mid \lambda$
$f_X(x)$	density function of x
$f_{X\|Y}(x \mid y)$	density function of $x \mid y$
$f_Y(y)$	density function of y
$f_{Y\|X}(y \mid x)$	density function of $y \mid x$

$f_\Lambda(\lambda)$ density function of λ
$f_{\Lambda|T1}(\lambda \mid t_1)$ density function of $\lambda \mid t_1$
H hypothesis
n number of failures
t time
t_1 specific value of T_1 (time to failure)
T_1 random variable (time to failure)
x specific value of X
X random variable
y specific value of Y
Y random variable
λ specific value of Λ (failure rate)
Λ random variable (failure rate)
μ parameter in distribution of λ

Superscript
$\hat{}$ estimated value

Section 7.15

$E(\,)$ expected value
f_i density function of component i
$f_{\tau n}$ density function of τn
$F_{\tau n}$ distribution of function of τn
n counter for renewals
N number of renewals
P probability
s Laplace operator
t time
t_i time to failure of component i

Superscript
$-$ Laplace transform

Section 7.16

C average annualized cost of operation
C_c capital cost of equipment
$f(n)$ rate of expenditure on maintenance
$f(t)$ rate of expenditure on maintenance
n number of years equipment is to be in use
S scrap value of equipment
t time equipment is to be in use

Section 7.17

Subsection 7.17.5
$f(x)$ density function of load x
$f(y)$ density function of strength y
$g(z)$ density function of z
$G(z)$ distribution function of z
L load
m_x mean value of load x
m_y mean value of strength y
m_z mean value of z
n_x constant in Equation 7.17.4
n_y constant in Equation 7.17.5
S strength
u parameter defined by Equation 7.17.13
v parameter defined by Equation 7.17.14
x load
y strength
z difference between load and strength
σ_x standard deviation of load x
σ_y standard deviation of strength y
σ_z standard deviation of z
ϕ safety parameter

Subsection 7.17.6
$f(i)$ shaping factor
L load
n number of applications of load
ρ parameter defining shaping factor in Equation 7.17.21
$R(n)$ probability of survival after n applications of load
s stress (or strength)
s_0 initial strength
Δs_i decrement of strength
S strength
$z(t)$ hazard rate
σ scaling factor

Section 7.18

a, b constants
$H(t)$ cumulative hazard function
k parameter in Weibull distribution (alternative form)
m parameter in Weibull distribution (alternative form)
$R(t)$ probability of success or survival, reliability
$\bar{\lambda}$ parameter defined by Equation 7.18.4
τ parameter defined by Equation 7.18.6

Section 7.19

$f(t)$ density function
$f_1(t), f_2(t)$ constituent density functions
p weighting factor

Section 7.20

Subsection 7.20.6
f degrees of freedom
f_1, f_2 degrees of freedom
$L()$ lower limit
m mean life
n number of trials
N number of trials
S number of successes
T period of test
$U()$ upper limit
α confidence parameter
χ^2 chi square distribution

Superscript
$\hat{}$ estimated value

Subsection 7.20.8
as Sections 7.1–7.13 plus
F_{mean} mean rank
F_{med} median rank
m_j mean order number
m_0 replacement time
Δm mean order number increment
n number of items
$n_f(t)$ number of items failed
x number of items before jth failure

Subsection 7.20.11
as Sections 7.1–7.13 plus

a	parameter
a_i	parameters
b	parameter
L	likelihood function
t	time to failure
z_c	calculated hazard rate
μ_k	kth moment of distribution
$\mathcal{L}$	logarithm of likelihood function (= ln L)

Subsection 7.20.16
as Sections 7.1–7.13 plus

v	random number

Subsection 7.20.17

$z(t)$	hazard rate
z_i	ith influencing variable, or explanatory factor
$z_0(t)$	baseline hazard function
β_i	coefficient of z_i

Section 7.22
as Sections 7.1–7.13 plus

C_i	parameter representing complexity of ith subsystem
W_i	weighting factor for ith subsystem

Section 7.23

Subsection 7.23.3

T	period of test
α	index

Subscripts

cum	cumulative
cur	current

Subsection 7.23.4

c	allowable number of defects
n	number of items in sample
ρ	proportion of good items
P	probability of acceptance
q	proportion of defective items

Section 7.25

k	constant
m	mean life of component
m_0	replacement time of component
σ	standard deviation of life of component

8 Hazard Identification

Contents

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The identification of areas of vulnerability and of specific hazards is of fundamental importance in loss prevention. Once these have been identified, the battle is more than half won. Such identification is not a simple matter, however. In many ways, it has become more difficult as the depth of technology has increased. Loss prevention tends, increasingly, to depend on the management system and it is not always easy to discover the weaknesses in this. The physical hazards also no longer lie on the surface, accessible to simple visual inspection. On the other hand, there is now available a whole battery of hazard identification methods which may be used to solve these problems. Selected references on hazard identification are given in Table 8.1.

Different methods are required at different stages of a project. Table 8.2 lists some of these stages and the corresponding hazard identification techniques. The list is illustrative and, in particular, a technique quoted for one stage may also be applicable to another stage. There is no single ideal system of hazard identification procedures. The most appropriate system varies to some extent with the type of industry and process. Thus, for example, a firm involved in the batch manufacture of a large number of organic chemicals is likely to be much more interested in techniques of screening and testing chemicals and reactions than one operating ethylene plants.

The choice of hazard identification technique also depends on the purpose for which the study is done. For the identification of hazards and operating problems on a plant, a hazard and operability (HAZOP) study is suitable, while for the identification of sources of release for a hazard assessment, it is necessary to carry out a specific review of such sources. It is only sensible in hazard identification to make use of past experience. The use of standards and codes, of course, helps to avoid hazards of which people may not even be aware.

Many of the hazard identification techniques used, however, are concerned with situations, which have some element of novelty. Methods for screening and testing are used to detect hazardous runaways and decompositions in new chemicals and reactions. HAZOP studies are used to identify how often familiar hazards may be specifically realized in a new plant.

8.1 Safety Audits

One of the first systematic methods of hazard identification used in the chemical industry was the safety audit. Audits of various types are a normal management tool and are of considerable importance in safety.

An early account of safety audits in the United Kingdom was the BCISC report *Safe and Sound* (1969/9), which drew on the experience of the US chemical industry, where the safety audit was established as a prime means of ensuring safety. A full description of such an audit is given in the BCISC's *Safety Audits* (1973/12). A safety audit subjects every area of the organization's activity to a systematic critical examination. It aims, like other audits, to reveal the strengths and weaknesses and the areas of vulnerability. It is carried out by professionals and results in a formal report and action plan.

Safety Audits draws a distinction between a safety audit and a safety survey, which is a detailed examination of a narrow field such as specific procedures or a particular plant; safety inspection, which is a scheduled inspection of a unit carried out by the unit's own personnel; safety tour, which is an unscheduled tour of a unit carried out by

Table 8.1 *Selected references on hazard identification*

Albisser and Silver (1960, 1964); W.H. Richardson (1962, 1963); Carpenter (1964); Coulter (1965); Dow Chemical Co. (1966a,b, 1976, 1994); Fowler and Spegelman (1968); Leeah (1968–);British Chemical Industry Safety Council (BCISC) (1969/9,10, 1973/12,13); N.T. Freeman and Pickbourne (1971); Voigtsberger (1973); DOT, CG (1974a–d); D.W. Jones (1975); Harvey (1976, 1979); Heron (1976); Gelburd (1977); W.G. Johnson (1980); L. Kaplan (1981b); Gorbell (1982); Husman and van de Putte (1982); Kletz and Lawley (1982); Engineering Council (1983); W.B. Howard (1983, 1984); Kletz (1983d, 1984i, 1984 LPB 59, 1985e, 1986d, 1992b); Solomon (1983 LPB 52, 1984 LPB 54); Anon. (1984 LPB 60, p. 40); Embling (1986); CCPS (1985); Hoffmann (1985); Hoffmann and Maser (1985); van Horn (1985); Ducsherer and Molzala (1986); Flothmann and Mjaavatten (1986); Parry (1986 SRD R379); Pikaar *et al.* (1986); Pitblado (1986); Vervalin (1986b); Ozog and Bendixen (1987); Waite *et al.* (1988); Andreasen and Rasmussen (1990); Galagher and Tweeddale (1990, 1992); Tweeddale (1990a–c); Ahmed and Khan (1992); Argent *et al.* (1992); Kavianian *et al.* (1992); Pontiggia (1992); Sharkey *et al.* (1992); Toola (1992); Sankaran (1983); Knowlton (1993); Taylor (1993 LPB 112); Vincoli (1993)

CCPS Hazard Evaluation Guidelines
Witter (1992)

Physical and chemical properties (*see also* Tables 11.1, 11.18, 16.1, 16.3, 17.3, 17.62, 18.1)
National Institute for Occupational Safety and Health (NIOSH) (Crit. Doc. series, 1990/18); Nuckolls (1929); Mellan (1950, 1957, 1977); MCA (1952-SD series, 1972/21); NSC (1952–, Safety Data Sheets); DECHEMA (1953–); Sax (1957–, 1981, 1986); Kirk and Othmer (1963–, 1978–, 1991–); Marsden (1963); Shabica (1963); D.T. Smith (1965a); Anon. (1966–67); CGA (1966/1); G.D. Muir (1971–); Bahme (1972); FPA (1972– Meidl (1972); Bretherick (1974, 1975, 1976, 1987a,b, 1990); DOT, CG (1974a,b); Int. Tech. Inf. Inst. (Japan) (1975); DoE and Chemical Society (1976); Shieler and Pauze (1976); Redeker and Schebsdat (1977); Sittig (1979); Weiss (1981); Anon. (1985p); Sax and Lewis (1986); Reale and Young (1987); A. Allen (1988); Walsh (1988); National Fire Protection Association (NFPA) (1991/27); Carson and Mumford (1994)

Safety evaluation of chemicals
Cumberland and Hebden (1975); Brannegan (1985); A.S. West (1986, 1993a,b); Kohlbrand (1990)

Reactivity, instability, explosibility
ASTM (STP 394, 1975); Lothrop and Handrick (1949); Boynton *et al.* (1959); Steele and Duggan (1959); van Dolah (1961, 1965, 1969a); Mackenzie (1962, 1974); van Dolah *et al.* (1963); Shabica (1963); Wilcox and Bromley (1963); Cruise (1964); J.R. Marshall (1964); G.T. Austin (1965b); Garn (1965); Snyder (1965, 1982); Platt and Ford (1966); Sykes (1966); Prugh (1967); Silver (1967); Wankel (1967); Adams (1968); Lindeijer (1968); Roburn (1968); Settles (1968); Woodworth (1968); Brinkley (1969); Lindeijer and Pasman (1969); Spiegelman (1969); Flynn and Rossow (1970a); Stull (1970, 1973, 1976, 1977); Bersier *et al.* (1971); Gordon and McBride (1971, 1976); V.J. Clancey (1972a, 1974b); Coffee (1972, 1973, 1982a); Rollet and Bouzis (1972); Blazek (1973); Daniels (1973); E.J. Davis and Ake (1973);

Dehn (1973); Sheldon and Kochi (1973); Treweekef *et al.* (1973); Bowes (1974b); Carver *et al.* (1974); Groothuizen *et al.* (1974); A.J. Owen and von Zahn (1974); Porter (1974); Wendlandt (1974); Berthold *et al.* (1975); Burleson *et al.* (1975); Denn (1975); Keattch and Dollimore (1975); O'Driscoll (1975b); O'Neill (1975); Berthold and Loffler (1976); Brasie (1976a); Janin (1976); Lemke (1976); Riethmann *et al.* (1976); Grewer (1977); Pesata *et al.* (1977); Townsend (1977); Noronha and Juba (1980); G.F.P. Harris *et al.* (1981); Verhoeff (1981, 1983a,b); Hoffmann (1985); Hoffmann and Maser (1985); Bretherick (1987a, 1990); Hofelich and Thomas (1989); Kohlbrand (1990); Merrifield and Roberts (1991); NFPA (1991 NFPA 49, 325M, 491M); T.A. Roberts and Royle (1991); Frurip (1992); H.E. Fisher and Goetz (1993); Siwek and Cesana (1993); Fierz (1994); Wang, van Kiang and Merkl (1994)

Combustible solids, thermal explosion: (*see also* Table 16.28): Groothuizen *et al.* (1977); Beever (1981); Beever and Thorne (1981): Bishop (1981); Boddington *et al.* (1981); Bowes (1981); E.J. Davis *et al.* (1981); N. Gibson and Harper (1981b); Napier and Vlatis (1981); D.W. Smith (1982); Grewer (1987a,b); Cardillo (1988); de Faveri, Zonato *et al.* (1989); Fierz and Zwahlen (1989); Kotoyori (1989a); Tharmalingam (1989b); Liang and Tanaka (1990)

Test methods: V.J. Clancey (n.d.); A.K. Gupta (1949); Rapean *et al.* (1959); Koenen *et al.* (1961); Snyder (1965, 1982); Coffee (1969, 1972, 1973, 1976, 1982); MoD (1972); Connor (1974); Seaton *et al.* (1974); Berthold *et al.* (1975); Berthold and Loffler (1976); Eigenmann (1976); Janin (1976); Lemke (1976); Treweek *et al.* (1976); May (1978); Anon. (LPB 30 1979, p. 159); Dahn (1980); Myers (1980); Seyler (1980); D.W. Smith *et al.* (1980); Storey (1980, 1981); ABPI (1981, 1989); de Groot and Hupkens van der Elst (1981); Short *et al.* (1981); Townsend (1981); Mohan *et al.* (1982); Duch *et al.* (1982); Daugherty (1983); Pickard (1983); Fenlon (1984, 1987); C.A. Davies *et al.* (1985); Kohlbrand (1985, 1987a,b, 1989, 1990); Yoshida *et al.* (1985); Cutler (1986); UN (1986, 1988, 1990); Craven (1987); Cronin and Nolan (1987a,b); Grewer (1987a,b); Mellor *et al.* (1987); Snee (1987); Ducros and Sanner (1988); Health and Safety Executive (HSE) (1988 CRR 5); Mellor *et al.* (1988); Thomson and Zahn-Ullmann (1988); Boddington *et al.* (1989); Frurip *et al.* (1989); Hasegawa *et al.* (1989); Seaton and Harrison (1990); Uehara and Kitamura (1990); Ando *et al.* (1991); Cardillo and Cattaneo (1991); Cardillo and Nebuloni (1991); H.G. Fisher and Goetz (1991); Townsend and Valder (1993); Whitmore and Wilberforce (1993); Kossoy *et al.* (1994); Mores *et al.* (1994); Wan *et al.* (1994); Whitmore (1994)

Classification of materials: ACDS (1991); Merrifleld and Roberts (1991); T.A. Roberts and Royle (1991); UN (1991); Hofelich, Power and Frurip (1994)

Process chemical reactions

Schierwater (1971); Grewer (1974, 1975, 1976, 1991); Berthold and Loffler (1976); Eigenmann (1976, 1977); Janin (1976); Regenass (1976); Schleich (1976); Schofield (1976); Schildknecht (1977); Stull (1977); Husain and Hamilcar (1978); Dehaven (1979); Hub *et al.* (1979); Holzer *et al.* (1980); Noronha *et al.* (1980); D.W. Smith (1982, 1984); Hoffmann and Maser (1985); Zeller (1985); Grewer and Klais (1988); B. Rasmussen (1988); Verhoeff (1988); Gygax (1989, 1990); Palazzi and Ferraiolo (1989); Barton and Rogers (1993); Gustin (1993); Landau and Cutro (1993); S. Schwartz (1993); Stoessel (1993); Cardillo (1994)

Test methods: Snyder (1965, 1982); Hub (1975, 1976, 1977a–c, 1980, 1981); Berthold and Loffler (1976); Eigenmann (1976); Regenass (1976); Noronha *et al.* (1979); Grewer and Klais (1980, 1988); Hakl (1980, 1981); Noronha and Juba (1980); Townsend and Tou (1980); Verhoeff and Janswoude (1980); Brogli *et al.* (1981); Dollimore (1981); Grewer (1981, 1987a,b); Wilberforce (1982, 1984); Fierz *et al.* (1983, 1984); Giger *et al.* (1983); Grewer and Duch (1983); de Haven (1983); Klais and Grewer (1983); Coates (1984a,b); N. Gibson (1984); Verhoeff and Heemskerk (1984); Hub and Jones (1986); Ottaway (1986); Spence *et al.* (1986); Wendlandt (1986); T.K. Wright and Rogers (1986); Kirch *et al.* (1987); T.K. Wright and Butterworth (1987); Spence and Noronha (1988); Chaineaux and Dunnin (1989); Dixon-Jackson (1989); Fauske *et al.* (1989); Hofelich (1989); Hoppe and Grob (1989); Kohlbrand (1989); Kotoyori (1989b); Mix (1989); Rogers (1989a); Steele and Nolan (1989); Duswalt (1991); Vilchez and Casal (1991); Hoppe (1992); Lambert *et al.* (1992); Landau and Williams (1992); J. Singh and Boey (1992); Snee and Hare (1992, 1994); Suter *et al.* (1992); Cardillo *et al.* (1993); Gustin (1993); Snee *et al.* (1993); Steele *et al.* (1993) CCPS program: A.S. West (1993a)

Laboratories, pilot plants (***see also*** **Table A7.2**)

Fleming (1958); Gernand (1965); Gorman *et al.* (1965); Hudson (1967); Perciful and Edwards (1967); Katzen (1968); Anon. (1969a); Conn (1971); Katell (1973); Dollimore (1981); Hoffmann (1985); van Horn (1985); Kohlbrand (1985); Brummnel (1989)

Hazard indices

Pratt (1965); Stull (1970, 1973, 1977); DOT, CG (1974a,b); D.E. Miller (1976); C.J. Jones (1978); Pitt (1982); Embling (1986); Kletz (1988f); de Graaf (1989); Lapp (1990); NFPA (1991 NFPA 49); Kavianian *et al.* (1992)

Dow Index, Dow Guide: Dow Chemical Co. (1964, 1966a,b, 1976, 1980, 1987, 1994); van Gaalen (1974); Scheffler (1994)

Mond Index: D.J. Lewis (1979, 1980b, 1989b); Doran and Greig (1984 LPB 55); ICI (1985); Tyler (1985)

Instantaneous Fractional Annual Loss (IFAL) Index: J. Singh and Munday (1979); Munday *et al.* (1980); LTB (1981); Menashe and Berenblut (1981); Berenblut and Menashe (1982); Whitehouse (1985); Berenblut and Whitehouse (1988)

FIRST: Mudan (1989c)

Insurance assessments

Dow Chemical Co. (1964, 1966a,b, 1976, 1980, 1987, 1994); Fowler and Spiegelman (1968); Spiegelman (1969); Neil (1971); Drewitt (1975)

Ranking methods, rapid ranking

Mumford and Lihou (LPB 59 1984); Gillett (1985); Keey (1991); G. Stevens and Stickles (1992)

Process safety reviews, hazard studies

R.W. Henry (1979); Wells (1981); Anthony (1985); IMechE (1985/88); Oh and Husmann (1986); Vogler (1986); van Mynen (1990); Turney (1990a,b, 1991); Desjardin *et al.* (1991); Grossman and Fromm (1991); Wells *et al.* (1991); Burk (1992); Kolodji (1993); Heetveld (1993); R. James and Wells (1994); Wells *et al.* (1994)

HAZOP studies

Binsted (1960); Birchall (1960); Elliott and Owen (1968); Kletz (1972a, 1983d, 1984l, 1985e,i, 1986d, 1988b, 1992b); S.B. Gibson (1974, 1976a,b); ICI (1974); Lawley (1974a,b); Cowie (1976); Henderson and Kletz (1976); Knowlton (1976, 1979, 1981, 1989, 1992); Lock (1976); Chemical Industries Association (CIA) (1988 RC18); CISHC (1977/6); Rushford

(1977); Himmelblau (1978); Sachs (1978); Ministry of Social Affairs (1979a); A.F. Johnston, McQuaid and Games (1980); Lihou (1980a,b, 1990b, 1985 LPB 66); Wells (1980); Merriman (1982 LPB 48); Scott (LPB 48 1982); Anon. (LPB 49 1983, p. 1); IBC (1983/42, 1984/53); Illidge (1983 LPB 53); Lowe and Solomon (1983); Sinnott (1983); Solomon (1983 LPB 52, 1984 LPB 54); Bendixen and O'Neill (1984); Piccinnini and Levy (1984); Ozog (1985); Shafaghi and Gibson (1985); Flothmann and Mjaavatten (1986); Suokas (1986); Qureshi (1988); ILO (1989); Anon. (1991 LPB 98, p. 1); R.A. Freeman (1991); W.J. Kelly (1991); Black and Ponton (1992); Deshotel and Goyal (1992); Hendershot (1992); Isalski *et al.* (1992); Kavianian *et al.* (1992); G.C. Stevens and Humphreys (1992); D. Jones (1992); McCluer and Whittle (1992); Mitchell (1992 LPB 105); D. Scott and Crawley (1992); G.C. Stevens *et al.* (1992); Wells and Phang (1992); Willis (1992 LPB 108); Charsley and Brown (1993); Fully (1993); Sweeney (1993); Taylor (1993 LPB 112) CCPS Guidelines: Witter (1992)

Safety audits, including management audits, plant audits
MCA (SG-20); Stapleton (1963); J.U. Parker (1967, 1973); Whitehorn and Brown (1967, 1973); BCISC (1969/9, 10, 1973/12, 13); D. Williams (1971); Harvey (1976, 1979b); Kletz *et al.* (1977); R. King and Magid (1979); Kletz (1977h, 1981l); Anon. (LPB 60 1984); Conrad (1984); Scheid (1987); Anon. (1988 LPB 79, p. 25); Atallah and Guzman (1988); Luck and Howe (1988); Madhavan and Kirsten (1988a,b); Madhavan and Landry (1988); Monk (1988); Camp (1989); Stallworthy (1989); Kase and Wiese (1990); Scheimann (1990); Tweeddale (1990a, 1993d, 1994, 1994 LPB 117); I.G. Wallace (1990); NSW Government (1991); L.W. Ross (1991); Galagher and Tweeddale (1992); Ozog and Stickles (1992); D. Scott and Crawley (1992); Lockwood (1993); Ozog (1993); Sankaran (1993); Hurst and Ratcliffe (1994); Hurst *et al.* (1994)
Failure modes and effects analysis (FMEA, also failure modes, effects and criticality analysis, FMECA)
IEC (Std 812); US Armed Forces (MIL-STD-1629); Recht (1966b); Ostrander (1971); C.F. King and Rudd (1972); Jordan (1972); Taylor (1973, 1974c, 1975a); Himmelblau (1978); Lambert (1978a); Aldwinkle and Slater (1983); Flothmann and Mjaavatten (1986); Rooney *et al.* (1988); Arendt and Lorenzo (1991); Kavianian, Rao and Brown (1992); D. Scott and Crawley (1992); Andrews and Moss (1993); Goyal (1993); Vincoli (1993); BS 5760: Part 5: 1991

'What if?' method
Burk (1992); Zoller and Esping (1993)

Fault trees, event trees and cause–consequence diagrams (*see* Table 9.1)

Sneak path analysis
E.J. Hill and Bose (1975); Dore (1991); Hahn *et al.* (1991); Whetton (1993)

HAZCHECK
Wells and Phang (1992 LPB 105)

Hazard analysis
Kletz (1971, 1972a, 1973a, 1976d, 1983d, 1984b, 1986d, 1992b); S.B. Gibson (1976a, 1977a); Illidge (1983 LPB 53)
Computer HAZOP (CHAZOP) programs
Technica Ltd (1988); Andow (1991); Malagoli *et al.* (1992); Willis (1992 LPB 102); Burns and Pitblado (1993); Broomfield and Chung (1994); Chung and Broomfield (1994); Dyadem Ltd. (2001); Lihou Technical (2002)

Operator task analysis
Annett *et al.* (1971); Duncan (1974); Duncan and Gray (1975a); Duncan and Shepherd (1975a,b)

Emergency planning
Duff and Husband (1974)

Contractor hazard analysis
Whitaker (1993)

Pre-acquisition audits
Lloyds Register of Shipping (1992)

Quality assurance, completeness of identification
J.R. Taylor (1979, 1992); VTT (1985/1, 1988 Research Report 516); Rouhianen (1990)

Selection of method
CCPS (1989/7); Pontiggia (1992)

an outsider such as the works manager or a safety representative; and safety sampling, which is a specific application of a safety inspection/tour designed to measure accident potential.

A safety audit examines and assesses in detail the standards of all facets of a particular activity. It extends from complex technical operations and emergency procedures to clearance certificates, job descriptions, housekeeping and attitudes. It involves labour relations since people are asked about their training, their understanding of works policy and whether they think they are making their contribution in the right way.

An audit might cover a company-wide problem or a total works situation (say, its emergency procedures or effluent systems) or simply a single plant activity.

At any level an audit is carried out thoroughly by a team made up of people immediately concerned, assisted by experts in various fields and experienced people not connected with the area of audit, to ensure that a fresh and unbiased look is injected into the inspection process.

Safety audits thus cover the following main areas:

(1) site level
  (a) management system;
  (b) specific technical features;
(2) plant level
  (a) management system.

The audit has five main elements;

(1) identification of possible hazards;
(2) assessment of potential consequences of realization of these hazards:
(3) selection of measures to minimize frequency and/or consequences of realization;
(4) implementation of these measures within the organization;
(5) monitoring of the changes.

The audit is conducted in a fairly formal way, using a checklist, although experience-based approaches are used with appropriate protocols. Table 8.3, taken from *Safety*

Table 8.2 *Hazard identification techniques appropriate to different project stages*

Project stage	*Hazard identification technique*
All stages	Management and safety system audits
	Checklists
	Feedback from workforce
Research and development	Screening and testing for
	Chemicals (toxicity, reactivity, explosibility)
	Reactions (explosibility)
	Impurities
	Pilot plant
Pre-design	Hazard indices
	Insurance assessments
	Hazard studies (coarse scale)
Design	Process design checks
	Unit processes
	Unit operations
	Plant equipments
	Pressure systems
	Instrument systems
	Hazard and operability studies (fine scale)
	Safety Integrity Level Studies (SIL, SIS) and Level of Protection
	Chemical Interaction Matrix
	Failure modes and effects analysis
	Fault trees and event trees
	Hazard analysis
	Risk & Reliability assessments
	Operator task analysis and operating instructions
Commissioning	Checks against design, inspection, examination, testing
	Non-destructive testing, condition monitoring
	Pre-Startup Safety Review
	Plant safety audits
	Emergency planning
Operation	Inspection, testing
	Non-destructive testing, condition monitoring, corrosion
	Plant safety audits

Audits, gives a list of activities and activity standards. These standards can be used as the basis of a numerical rating scheme. If a safety audit is conducted, it is essential that the management act on it. This does not necessarily mean that every recommendation must be implemented, but there should be a reasoned response.

Safety audits are an important part of the activity of the safety function. In addition to identifying hazards, they play a major role in educating personnel at all levels. These aspects are discussed in more detail in Chapter 28. Safety audits of the organization and management system at site and at plant level are considered below.

Another form of audit is the insurance survey. Insurance surveys have been described in Chapter 5. Although the insurer is not able to go down to the lower levels of detail, his contribution is valuable in that it represents an independent assessment.

8.2 Management System Audits

The management system is crucial to loss prevention and it is essential that this system itself be monitored. The management system, and its auditing, have been described in Chapter 6. Management audit is so important, however, that a brief, summary account is in order at this point.

The management system may be audited in several ways. These include (1) self-checking procedures, (2) internal audit and (3) external audit. An illustration of a specific check built into the system is a formal requirement that a plant manager audit a proportion of the permits-to-work each week.

The safety audits described above include an internal audit of the overall system. In particular, there are checks on:

(1) overall management attitude, policies, systems and procedures, personnel selection;
(2) plant level management, attitude, systems, training and feedback;
(3) incident reporting, investigation and statistics.

External audit may be carried out by an outside body such as a firm of consultants.

There are now available a number of audit systems, including proprietary systems. Some of these yield quantitative factors applicable in quantitative risk assessment (QRA). Accounts of audit systems are given in Chapters 6, 9 and 28.

Table 8.3 *Activity standards for safety audits (British Chemical Industry Safety Council, 1973/12)*

Activity	*Poor*	*Fair*	*Good*	*Excellent*
A Organization and administration				
1 Statement of policy, responsibilities assigned	No statement of loss control policy. Responsibility and accountability not assigned	A general understanding of loss control, responsibilities and accountability, but not written	Loss control policy and responsibilities written and distributed to supervisors	In addition to 'good', loss control policy is reviewed annually and is posted. Responsibility and accountability is emphasized in supervisory performance evaluations
2 Safe operating procedures (SOPs)	No written SOPs	Written SOPs for some, but not all, hazardous operations	Written SOPs for all hazardous operations	All hazardous operations covered by a procedure, posted at the job location, with an annual documented review to determined adequacy
3 Employee selection and placement	Only pre-employment physical examination given	In addition, an aptitude test is administered to new employees	In addition to 'fair', new employees' past safety record is considered in their employment	In addition to 'good', when employees are considered for promotion, their safety attitude and record is considered
4 Emergency and disaster control plans	No plan or procedures	Verbal understanding on emergency procedures	Written plan outlining the minimum requirements	All types of emergency covered with written procedures. Responsibilities are defined with back-up personnel provisions
5 Direct management involvement	No measurable activity	Follow-up on accident problems	In addition to 'fair', management reviews all injury and property damage reports and holds supervision accountable for verifying firm corrective measures	In addition to 'good', reviews all investigation reports. Loss control problems are treated as other operational problems in staff meeting
6 Plant safety rules	No written rule	Plant safety rules have been developed and posted	Plant safety rules are incorporated in the plant work rules	In addition, plant work rules are firmly enforced and updated at least annually

B	Industrial hazard control				
1	Housekeeping storage of materials, etc.	Housekeeping is generally poor. Raw materials, items being processed and finished materials are poorly stored	Housekeeping is fair. Some attempts to adequately store materials are being made	Housekeeping and storage of materials are orderly. Heavy and bulky objects well stored out of aisles, etc.	Housekeeping and storage of materials are ideally controlled
2	Machine guarding	Little attempt is made to control hazardous points on machinery	Partial but inadequate or ineffective attempts at control are in evidence	There is evidence of control which meets applicable Federal and State requirements, but improvement may still be made	Machine hazards are effectively controlled to the extent that injury is unlikely. Safety of operator is given prime consideration at time of process design
3	General area guarding	Little attempt is made to control such hazards as: unprotected floor openings, slippery or defective floors, stairway surfaces, inadequate illumination, etc.	Partial but inadequate attempts to control these hazards are evidenced	There is evidence of control which meets applicable Federal and State requirements – but further improvement may still be made	These hazards are effectively controlled to the extent that injury is unlikely
4	Maintenance of equipment, guards, handtools, etc.	No systematic programme of maintaining guards, handtools, controls and other safety features of equipment, etc.	Partial but inadequate or ineffective maintenance	Maintenance programme for equipment and safety features is adequate. Electrical handtools are tested and inspected before issuance, and on a routine basis	In addition to 'good', a preventive maintenance system is programmed for hazardous equipment and devices. Safety reports filed and safety department consulted when abnormal conditions are found
5	Material handling – hand and mechanized	Little attempt is made to minimize possibility of injury from the handling of materials	Partial but inadequate or ineffective attempts at control are in evidence	Loads are limited as to size and shape for handling by hand, and mechanization is provided for heavy or bulky loads	In addition to controls for both hand and mechanized handling, adequate measures prevail to prevent conflict between other workers and material being moved
6	Personal protective equipment – adequacy and use	Proper equipment not provided or is not adequate for specific hazards	Partial but inadequate or ineffective provision, distribution and use of personal protective equipment	Proper equipment is provided. Equipment identified for special hazards, distribution of equipment is controlled by supervisor. Employee is required to use protective equipment	Equipment provided complies with standards. Close control maintained by supervision. Use of safety equipment recognized as an employment requirement. Injury record bears this out

Table 8.3 *(continued)*

Activity	*Poor*	*Fair*	*Good*	*Excellent*
C Fire control and industrial hygiene				
1 Chemical hazard control references	No knowledge or use of reference data	Data available and used by foremen when needed	In addition to 'fair', additional standards have been requested when necessary	Data posted and followed where needed. Additional standards have been promulgated, reviewed with employees involved and posted
2 Flammable and explosive materials control	Storage facilities do not meet fire regulations. Containers do not carry name of contents. Approved dispensing equipment not used. Excessive quantities permitted in manufacturing areas	Some storage facilities meet minimum fire regulations. Most containers carry name of contents. Some approved dispensing equipment in use	Storage facilities meet minimum fire regulations. Most containers carry name of contents. Approved equipment is generally used. Supply at work area is limited to one day requirement. Containers are kept in approved storage cabinets	In addition to 'good', storage facilities exceed the minimum fire regulations and containers are always labelled. A strong policy is in evidence relative to the control of the handling, storage and use of flammable materials
3 Ventilation – fumes, smoke and dust control	Ventilation rates are below industrial hygiene standards in areas where there is an industrial hygiene exposure	Ventilation rates in exposure areas meet minimum standards	In addition to 'fair', ventilation rates are periodically measured, recorded and maintained at approved levels	In addition to 'good', equipment is properly selected and maintained close to maximum efficiency
4 Skin contamination control	Little attempt at control or elimination of skin irritation exposures	Partial but incomplete programme for protecting workers. First-aid reports on skin problems are followed up on an individual basis for determination of cause	The majority of workmen instructed concerning skin-irritating materials. Workmen provided with approved personal protective equipment or devices. Use of this equipment is enforced	All workmen informed about skin-irritating materials. Workmen in all cases provided with approved personal protective equipment or devices. Use of proper equipment enforced and facilities available for maintenance. Workers are encouraged to wash skin frequently. Injury record indicates good control

5	Fire control measures	Do not meet minimum insurance or municipal requirements	Meet minimum requirements	In addition to 'fair', additional fire hoses and/or extinguishers are provided. Welding permits issued. Extinguishers on all welding carts	In addition to 'good', a fire crew is organized and trained in emergency procedures and in the use of fire fighting equipment
6	Waste – trash collection and disposal, air/water pollution	Control measures are inadequate	Some controls exist for disposal of harmful wastes or trash. Controls exist but are ineffective in methods or procedures of collection and disposal. Further study is necessary	Most waste disposal problems have been identified and control programmes instituted. There is room for further improvement	Waste disposal hazards are effectively controlled. Air/water pollution potential is minimal
D	**Supervisory participation, motivation and training**				
1	Line supervisor safety training	All supervisors have not received basic safety training	All shop supervisors have received some safety training	All supervisors participate in division safety training session a minimum of twice a year	In addition, specialized sessions conducted on specific problems
2	Indoctrination of new employees	No programme covering the health and safety job requirements	Verbal only	A written handout to assist in indoctrination	A formal indoctrination programme to orientate new employees is in effect
3	Job hazard analysis	No written programme	Job hazard analysis (JHA) programme being implemented on some jobs	JHA conducted on majority of operations	In addition, job hazard analyses performed on a regular basis and safety procedures written and posted for all operation
4	Training for specialized operations (fork trucks, grinding, press brakes, punch presses, solvent handling, etc.)	Inadequate training given for specialized operations	An occasional training programme given for specialized operations	Safety training is given for all specialized operations on a regular basis and retraining given periodically to review correct procedures	In addition to 'good', an evaluation is performed annually to determine training needs
5	Internal self-inspection	No written programme to identify and evaluate hazardous practices and/or conditions	Plant relies on outside sources, i.e. Insurance Safety Engineer, and assumes each supervisor inspects his area	A written programme outlining inspection guidelines, responsibilities, frequency and follow-up is in effect	Inspection programme is measured by results, i.e. reduction in accidents and costs. Inspection results are followed up by top management
6	Safety promotion and publicity	Bulletin boards and posters are considered the primary means for safety promotion	Additional safety displays, demonstrations films are used infrequently	Safety displays and demonstrations are used on a regular basis	Special display cabinets, windows, etc., are provided. Displays are used regularly and are keyed to special themes

Table 8.3 *(continued)*

Activity	*Poor*	*Fair*	*Good*	*Excellent*
7 Employee–supervisor safety contact and communication	Little or no attempt made by supervisor to discuss safety with employees	Infrequent safety discussions between supervisor and employees	Supervisors regularly cover safety when reviewing work practices with individual employees	In addition to items covered under 'good', supervisors make good use of the shop safety plan and regularly review job safety requirements with each worker. They contact at least one employee daily to discuss safe job performance
E Accident investigation, statistics and reporting procedures				
1 Accident investigation by line personnel	No accident investigation made by line supervision	Line supervision makes investigations of only medical injuries	Line supervision trained and makes complete and effective investigations of all accidents; the cause is determined; corrective measures initiated immediately with a completion date firmly established	In addition to items covered under 'good', investigation is made of every accident within 24 h of occurrence. Reports are reviewed by the department manager and plant manager
2 Accident cause and injury location analysis and statistics	No analysis of disabling and medical cases to identify prevalent causes of accidents and location where they occur	Effective analysis by both cause and location maintained on medical and first-aid cases	In addition to effective accident analysis, results are used to pinpoint accident causes so accident prevention objectives can be established	Accident causes and injuries are graphically illustrated to develop the trends and evaluate performance. Management is kept informed on status
3 Investigation of property damage	No programme	Verbal requirement or general practice to inquire about property damage accidents	Written requirement that all property damage accidents of US$50 and more will be investigated	In addition, management requires a vigorous investigation effort on all property damage accidents
4 Proper reporting of accidents and contact with carrier	Accident reporting procedures are inadequate	Accidents are correctly reported on a timely basis	In addition to 'fair', accident records are maintained for analysis purposes	In addition to 'good', there is a close liaison with the insurance carrier

The HSE is also concerned with auditing the management system. Indeed, it is fair to say that this is its most important function. When visiting a factory, an Inspector is very much concerned with the way the system works in practice. Audit by the HSE is another aspect discussed in Chapter 6.

8.3 Checklists

One of the most simplistic tools of hazard identification is the checklist. Like a standard or a code of practice, a checklist is a means of passing on lessons learned from experience. It is impossible to envisage high standards in hazard control unless this experience is effectively utilized. The checklist is one of the main tools available to assist in this.

Checklists are applicable to management systems in general and to a project throughout all its stages. Obviously the checklist must be appropriate to the stage of the project, starting with checklists of basic materials properties and process features, continuing on to checklists for detailed design and terminating with operations audit checklists.

There are a large number of checklists given in the literature – indeed a paper on practical engineering is quite likely to include a checklist. Selected references on checklists are given in Table 8.4, but these are only a tiny fraction of those available. A number of checklists are given in the present volume. These are collated in the index. A checklist should be used for just one purpose only – as a final check that nothing has been neglected. Also, it is more effective if the questions cannot be answered by a simple 'yes' or 'no' but require some thought in formulating an answer.

Checklists are effective only if they are used. There is often a tendency for them to be left to gather dust on the shelf. This is perhaps part of the reason for the development of other techniques such as HAZOP studies, as described below.

Table 8.4 *Selected references on checklists*

Dow Chemical Co. (1964, 1966a,b, 1976, 1980, 1987, 1994); Hettig (1966); Yelland (1966); J.U. Parker (1967, 1973); Fowler and Spiegelman (1968); Freddy (1969); MCA (1970/18); Klaassen (1971); R.L. Miller and Howard (1971); Whitehorn and Brown (1973); Balemans *et al.* (1974); Eberlein (1974); Kline *et al.* (1974); Henderson and Kletz (1976); Wells *et al.* (1976, 1977); Webb (1977); J.C. Rose *et al.* (1978); Wells (1980); Gorbell (1982); Flothmann and Mjaavatten (1986); Vervalin (1986b); Gordon and Moscone (1988); Wells *et al.* (1990); Kongso (1992); D. Scott and Crawley (1992); Oliver (1993); Anon. (1994 LPB 120, p. 13)
Insurance: Fowler and Spiegelman (1968); Spiegelman (1969); Ashe (1971); Neil (1971); Drewitt (1975)
Management systems: BCISC (1973/12, 13)
Physical and chemical properties: Dow Chemical Co. (1964, 1966a,b, 1976, 1980, 1987, 1994); Spiegelman (1969); Wells (1980)
Audits: Eley (1992)
HAZCHECK: Wells (1980); Wells *et al.* (1991)
Plant siting: Dow Chemical Co. (1964, 1966a,b, 1976, 1980, 1987, 1994); Spiegelman (1969); Balemans *et al.* (1974)
Plant layout: McGarry (1958); Dow Chemical Co. (1964, 1966a,b, 1976, 1980, 1987, 1994); Fowler and Spiegelman (1968); Spiegelman (1969); Balemans *et al.* (1974); Drewitt (1975); Wells (1980); Gorbell (1982); D. Scott and Crawley (1992)
Ventilation systems: BOHS (1987 TG7); HSE (1990 HS(G) 54)
Process design: Dow Chemical Co. (1964, 1966a,b, 1976, 1980, 1987, 1994); Spiegelman (1969); Wells *et al.* (1976); W.G. Johnson (1980); Well (1980); Gorbell (1982); D. Scott and Crawley (1992)
Operating parameters and deviations: Wells *et al.* (1976); Wells (1980); Gorbell (1982); Trask (1990)
Documentation: Wells *et al.* (1976); J.C. Rose *et al.* (1978); Wells (1980)
Statutory approvals: J.C. Rose *et al.* (1978)
Chemical reactors: Gorbell (1982)
Dust-handling plant: Anon. (1990 LPB 95, p. 7)
Utilities: Gorbell (1982)
Pressure systems design: Spiegelman (1969); Gorbell (1982); D. Scott and Crawley (1992)
Pressure relief: Gorbell (1982)
Instrumentation: Gorbell (1982)
Human factors, human error: SRD, Human Factors in Reliability Group (1985 SRD R347); HSE (1989 HS(G) 48); Brazendale (1990 SRD 510)
Training: FPA (1974/23)
Fire and fire protection: Dow Chemical Co. (1964, 1966a,b, 1976, 1980, 1987, 1994); FPA (1965/3, 1974/23); Wells (1980); Gorbell (1982); D. Scott and Crawley (1992)
Plant commissioning: Matley (1969); Buyers (1972); J.D. Baker (1974); Mackey (1974); Turnbull *et al.* (1974); Unwin *et al.* (1974); L. Pearso (1977a,b); J.C. Rose *et al.* (1978); Wells (1980); D. Scott and Crawley (1992)
Plant start-up and shut-down: Wells (1980); D. Scott and Crawley (1992)
Plant operation: D. Scott and Crawley (1992)
Plant maintenance: D. Scott and Crawley (1992)
Demolition: Stuart (1974)
Plant modifications: Henderson and Kletz (1976); Wells (1980); Anon. (1994 LPB 120, p. 13)
Storage: Dow Chemical Co. (1964, 1966a,b, 1976, 1980, 1987, 1994); Spiegelman (1969); Balemans *et al.* (1974); Drewitt (1975); Jager and Haferkam (1992)
Transport: Spiegelman (1969)
Personal safety: Gorbell (1982)
Pilot plants: Carson and Mumford (1989 LPB 89)
Incident investigation: M.E. Lynch (1967, 1973)

8.4 Materials Properties

8.4.1 Physical and chemical properties

It is obviously necessary to have comprehensive information on all the chemicals in the process: raw materials, intermediates and final products. A list of some important physical and chemical properties of any chemical is given in Table 8.5. The significance of most of the items in the list is self-evident.

Compilations of properties of hazardous substances are typically found in accompanying Material Safety Data Sheets (MSDSs). Other sources include those by the NFPA (NFPA 704) and the NIOSH.

Corrosivity, flammability, toxicity and radioactivity are considered in more detail in Chapters 12, 16, 18 and 25, respectively. Reactivity, instability and explosibility and

Table 8.5 *Some important physical and chemical properties of a chemical*

General properties	Molecular structure Freezing point Vapour pressure, boiling point Critical pressure, temperature, volume Vapour density, specific heat, viscosity, thermal conductivity Liquid density, specific heat, viscosity, thermal conductivity Latent heats of vaporization and fusion Dielectric constant, electrical conductivity
Flammability	Flammability limits Flash point Autoignition temperature Minimum ignition energy Maximum experimental safe gap Self-heating
Corrosion	Corrosiveness to materials of construction Incompatibility with particular materials
Polymerization, decomposition	Polymerization characteristics Decomposition, hydrolysis characteristics
Impurities	Impurities in: raw material plant material Mutual solubilities with water
Reaction, explosion	Heats of formation, combustion, decomposition Energy hazard potential Thermal stability Impact sensitivity
Toxicity	Threshold limit values, emergency exposure limits Lethal concentration LC_{50}, lethal dose LD_{50} Exposure effects (inhalation, ingestion, skin and eye contact) Long-term low exposure effects Warning levels (smell)
Radioactivity	Radiation survey α-particle, β- , γ- ray exposures

process chemical reactions are dealt with in the following sections.

8.4.2 Materials safety data sheets

Information on the physical and chemical properties of chemicals and on the associated hazards and the appropriate precautions cast in standard format is available in the form of MSDSs.

Safety data sheet compilations are prepared by various organizations and are available on the Internet.

An EC Directive (91/155/EEC) lays down the contents of a safety data sheet. In the United Kingdom, this is implemented by the Chemical Hazard Information and Packaging (CHIP) Regulations. HSE guidance: *Safety Data Sheets for Substances and Preparations Dangerous for Supply* (1993) has been amended on a regular basis since its inception and further guidance is available in *The EC Safety Data Sheet Directive* by CONCAWE (1992 92/55).

The Directive requires that the contents of a safety data sheet cover:

(1) identification of the substance/preparation and company;
(2) composition/information on ingredients;
(3) hazards identification;
(4) first-aid measures;
(5) firefighting measures;
(6) accidental release measures;
(7) handling and storage;
(8) exposure controls/personal protection;
(9) physical and chemical properties;
(10) stability and reactivity;
(11) toxicological information;
(12) ecological information;
(13) disposal considerations;
(14) transport information;
(15) regulatory information;
(16) other information.

Both the guides mentioned give detailed guidance on the material to be included under each of these heads. It is the responsibility of the supplier of a chemical to supply the safety data sheet.

8.4.3 Impurities

Impurities, foreseen or unforeseen, can have serious adverse effects on many aspects of process operation, including safety and loss prevention. These effects are discussed in more detail in Chapter 11. Here consideration

is confined to the identification of possible problems with impurities.

There is no established methodology of identifying impurities which may arise in the process, that is comparable with that for checking the reactivity of a chemical. Reliance usually has to be placed on the literature and on experience. As discussed below, however, indication of possible impurities and of their adverse effects is one of the particularly valuable features of a pilot plant.

8.5 Pilot Plants

Scale-up from laboratory to full-size plant has always been a difficult problem in the chemical industry. Indeed it is this problem which in large part is responsible for the profession of chemical engineering. An important tool for tackling the problem is the pilot plant. In the words of L.H. Baekeland, the philosophy of the pilot plant is: 'Make your mistakes on a small scale and your profits on a large scale'.

There are many reasons beside safety for using a pilot plant. They include the determination of the most economic design and operating parameters, the production of product for evaluation and trial marketing. Nevertheless, safety considerations constitute a substantial part of the case for the pilot plant.

A pilot plant is used principally to assist in the scale-up of the process design rather than the mechanical design, for example, reaction conditions rather than pump specifications.

Some types of information relevant to safety which a pilot plant may yield include:

(1) operating conditions (e.g. pressure, temperature);
(2) design parameters (e.g. reaction rates, heat transfer coefficients);
(3) reactor problems;
(4) unit operations problems;
(5) materials handling problems (e.g. foaming, solids handling, catalyst handling);
(6) decomposition;
(7) impurities;
(8) corrosion;
(9) fouling;
(10) analytical problems;
(11) operating problems;
(12) working environment problems (e.g. toxics);
(13) effluent and waste disposal problems.

Impurities can cause many problems, and a pilot plant is one of the most effective means of identifying these. There may be impurities in the feedstock which give unexpected effects. Impurities may arise through side reactions, decomposition or polymerization. Leaks into the system may bring in other impurities such as pump lubricant and seal fluids or heat transfer media, including water. Air and water from other sources are common impurities or sources of impurity. Impurities which in a one-pass process might not be significant can build up if there is recycle. The product may be contaminated with any of these impurities. Impurities may cause fouling, blockages, etc. Some impurities can explode or catalyse explosive reactions. Problems may arise in effluent disposal due to impurities. Operation of a pilot plant offers a high probability of detecting impurities problems. Similarly, a pilot plant often reveals corrosion problems. These are frequently associated not with the main materials and bulk chemicals, but with minor components such as gaskets and diaphragms or with impurities in the bulk chemicals.

If a pilot plant is used, it is essential, of course, that due attention be paid to safety in its design and operation. This rather different aspect is dealt with in Appendix 10.

8.6 Hazard Indices

There are a number of hazard indices which have been developed for various purposes. Mention has already been made at the level of the material processed of indices of energy hazard potential. There are other indices which are applicable to the process and plant as a whole. Some principal indices of process and plant hazard are the Dow Index, the Mond Index and the IFAL Index. Another technique of ranking hazards is that of rapid ranking.

8.6.1 Dow's Index

The Dow *Guide* was originally published in 1964 and has gone through seven editions (Dow Chemical Company, 1964, 1966a; AlChE, 1973, 40; Dow Chemical Company, 1976, 1980; AlChE, 1987, 1994). Descriptions of the first and third editions have been given by Pratt (1965) and van Gaalen (1974), respectively.

The original purpose of the Dow Fire and Explosion Index (F&EI) was to serve as a guide to the selection of fire protection methods. The index in the first edition was a modification of the Factory Mutual Chemical Occupancy Classification guide. In the first three editions, the methods of determining the index were developed and refined. Changes in the fourth edition were that the index was simplified and that two new features were introduced, the maximum probable property damage (MPPD) and a Toxicity Index. The fifth edition changes included a new framework for making the risk evaluation, improvements in the method of calculating the index and several new features, including Loss Control Credits and Maximum Probable Days Outage (MPDO), and omission of the Toxicity Index. In the sixth edition, a risk analysis package, including business interruption (BI) and a toxicity penalty to reflect emergency responses, was introduced. The seventh edition up-dates the sixth edition with respect to codes and to good practice, but includes no major conceptual changes.

The following account gives an overview of method. The figures are from the *Guide*, but the tables are summaries only. The account is intended to provide an understanding of the Dow *Guide*, but the guide itself should be consulted for determination of the index and, in particular, for fuller explanations, qualifications and illustrative examples.

The overall structure of the method is shown in Figure 8.1. The procedure is to calculate the F & EI and to use this to determine fire protection measures and, in combination with a Damage Factor, to derive the base MPPD. This is then used, in combination with the loss control credits, to determine the actual MPPD, the MPDO and the BI loss.

The procedure may be summarized as follows. The basic information required for the F & EI is the plot plan and flow sheet of the plant. For the economic losses, it is also necessary to know the value of the plant per unit area, or the 'capital density', and the monthly value of production.

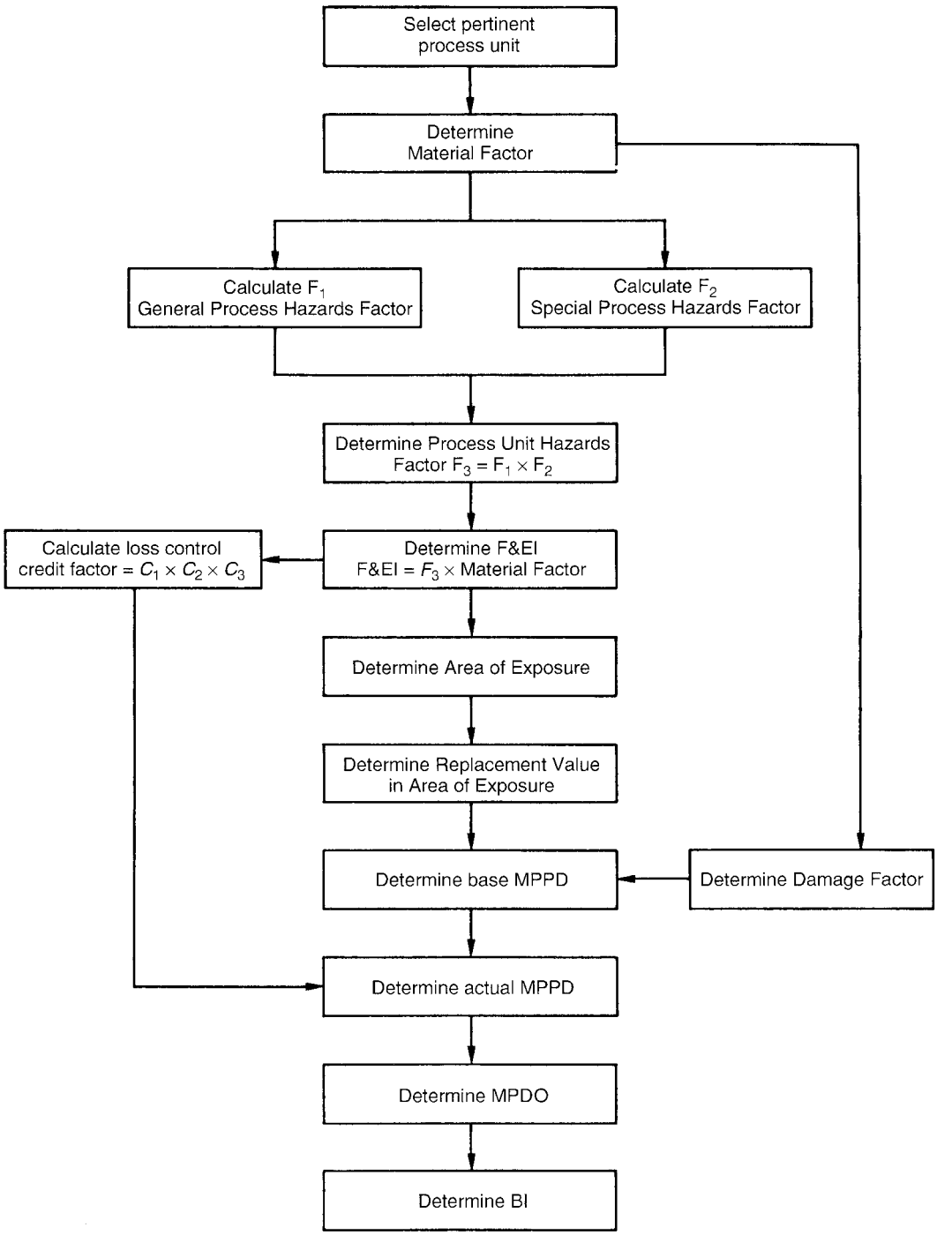

Figure 8.1 *Dow Fire and Explosion Index: procedure for calculating the Fire and Explosion Index and other quantities (Courtesy of the American Institute of Chemical Engineers)*

The plant is first broken down into process units. A process unit is an item of process equipment such as a reactor, distillation column, absorption column, compressor, pump, furnace, storage tank, etc. The process units are then identified which could have the most serious impact on the process area. The factors which identify a pertinent process unit include the inventory, chemical energy potential, operating conditions, capital density, loss history and potential for BI. Where equipment is arranged to give a single train, the decision on whether to treat the whole train or just a single vessel as a process unit is determined by the type of process. It is also necessary to make a judgement on the most appropriate stage of plant operation for the determination of the F&EI.

The F&EI is then determined for the process units. It should not normally be necessary to determine the F&EI for more than three or four process units in a single process area.

The F&EI assumes a minimum inventory of 5000 lb or 600 USgal of flammable, combustible or reactive material. If the inventory is less than this, the risk will generally be overstated.

The F&EI is calculated as follows. First a material factor (MF) is obtained. Then two penalty factors (F_1 and F_2), one for general process hazards (GPHs) and one for special process hazards (SPHs), respectively, are determined, and the process unit hazards factor (PUHF) (F_3), which is the product of these, is calculated. The product of the MF and PUHF is the F&EI. The assessment form used to calculate the index is shown in Figure 8.2.

The MF is a measure of the potential energy release from the material. It is obtained by considering the flammability and reactivity of the material and has a value in the range 1–40. Values of the MF for some 216 materials are given in Appendix A of the Dow *Guide* and values for selected chemicals are given in Table 8.6. For materials not listed, the procedure used to determine the MF is summarized in Table 8.7. Use is made of the NFPA fire rating N_F and reactivity rating N_R. Detailed guidance on the calculation of the MF using the procedure in the table is given in the Dow *Guide*.

The base MF is a measure of the hazard of the material at ambient temperature and pressure. If these are not the conditions applying, the base MF needs to be adjusted. The correction for temperature is shown in Table 8.8. Pressure is taken into account through the SPH. The Dow *Guide* also gives a method for the determination of the MF for a mixture.

The penalty factors applicable for GPHs and for SPHs are given in Tables 8.9 and 8.10 and Figure 8.3, respectively. The GPH factor (f_1) is the sum of all the GPH penalties, and the SPH factor (F_1) is the sum of all the SPH penalties. The PUHF factor (F_3) is the product of the GPH and SPH factors:

$$F_3 = F_1 \times F_2 \qquad [8.6.1]$$

The F&EI is the product of the MF and the PUHF:

$$\text{FEI} = F_3 \times \text{MF} \qquad [8.6.2]$$

The F&EI is of importance in its own right as a guide to the fire and explosion hazard.

The degree of hazard implied by the F&EI is shown by the relationships given in Table 8.11. The further use of the F&EI to undertake a process risk analysis, covering property damage and BI, is then as follows. The F&EI is used by itself to obtain the exposure radius (ER) and hence the area of exposure. The value of the area of exposure (VAE) is obtained from the area of exposure and the capital density, as described below. The F&EI and the PUHF are used in combination to obtain the damage factor (DF). The base MPPD is then obtained as the product of the VAE and the damage factor.

The exposure radius is a linear function of the F&EI, being 0 and 168 at values of the F&EI of 0 and 200, respectively. In other words:

$$\text{ER} = 0.84 \times \text{FEI} \qquad [8.6.3]$$

The value of the area of exposure is obtained as follows. The original value (OV) is obtained as the product of the area of exposure and the original capital density. The replacement value (RV) is then a function of the OV and the escalation factor (EF):

$$\text{RV} = 0.82 \times \text{OV} \times \text{EF} \qquad [8.6.4]$$

where 0.82 is an allowance for the cost of items which will not require replacement. The Dow *Guide* gives detailed guidance on the appropriate costs to use.

The damage factor is a function of the F&EI and the PUHF, as shown in Figure 8.4.

Then,

$$\text{Base MPPD} = \text{VAE} \times \text{DF} \qquad [8.6.5]$$

A credit factor (CF) is then obtained as the product of three individual loss control credit factors (C_1–C_3). The product of the base MPPD and the credit factor is the actual MPPD. The MPDO is a function of the actual MPPD. The BI is then obtained from the MPDO and the value of production per month (VPM). The credit factor is:

$$\text{CF} = C_1 \times C_2 \times C_3 \qquad [8.6.6]$$

The three loss control credit factors C_1–C_3 are each the product of a set of individual loss control credits. The ranges of these credit items are given in Table 8.12. Detailed guidance on the precise value of each credit within the range in Table 8.11 is given in the Dow *Guide*. Then

$$\text{Actual MPPD} = \text{CF} \times \text{Base MPPD} \qquad [8.6.7]$$

The MPDO is a function of the actual MPPD as shown in Figure 8.5. It is intended that judgement be exercised in selecting the line to be used in this figure. The upper and lower lines correspond to the cases where there are factors which would increase or reduce the period of interruption, respectively, and the central line corresponds to the case where neither of these applies. The BI is:

$$BI = 0.7 \times \frac{MPDO}{30} \times VPM \qquad [8.6.8]$$

where 0.7 is a factor which represents fixed costs plus profits, and 30 converts the number of days to months. The Dow *Guide* describes a risk analysis package which comprises: the simplified block flow sheet; the plot plan

FIRE & EXPLOSION INDEX

AREA / COUNTRY	DIVISION	LOCATION	DATE
SITE	MANUFACTURING UNIT	PROCESS UNIT	
PREPARED BY:	APPROVED BY: (Superintendent)	BUILDING	
REVIEWED BY: (Management)	REVIEWED BY: (Technology Center)	REVIEWED BY: (Safety & Loss Prevention)	
MATERIALS IN PROCESS UNIT			
STATE OF OPERATION ___ DESIGN ___ START UP ___ NORMAL OPERATION ___ SHUTDOWN	BASIC MATERIAL(S) FOR MATERIAL FACTOR		
MATERIAL FACTOR (See Table 1 or Appendices A or B) Note requirements when unit temperature over 140 °F (60 °C)			

1. General Process Hazards	Penalty Factor Range	Penalty Factor Used(1)
Base Factor	1.00	1.00
A. Exothermic Chemical Reactions	0.30 to 1.25	
B. Endothermic Processes	0.20 to 0.40	
C. Material Handling and Transfer	0.25 to 1.05	
D. Enclosed or Indoor Process Units	0.25 to 0.90	
E. Access	0.20 to 0.35	
F. Drainage and Spill Control _____ gal or cu.m.	0.25 to 0.50	
General Process Hazards Factor (F_1)		
2. Special Process Hazards		
Base Factor	1.00	1.00
A. Toxic Material(s)	0.20 to 0.80	
B. Sub-Atmospheric Pressure (< 500 mm Hg)	0.50	
C. Operation In or Near Flammable Range ___ Inerted ___ Not Inerted		
1. Tank Farms Storage Flammable Liquids	0.50	
2. Process Upset or Purge Failure	0.30	
3. Always in Flammable Range	0.80	
D. Dust Explosion (See Table 3)	0.25 to 2.00	
E. Pressure (See Figure 2) Operating Pressure _____ psig or kPa gauge Relief Setting _____ psig or kPa gauge		
F. Low Temperature	0.20 to 0.30	
G. Quantity of Flammable/Unstable Material: Quantity _____ lb or kg H_C = _____ BTU/lb or kcal/kg		
1. Liquids or Gases in Process (See Figure 3)		
2. Liquids or Gases in Storage (See Figure 4)		
3. Combustible Solids in Storage, Dust in Process (See Figure 5)		
H. Corrosion and Erosion	0.10 to 0.75	
I. Leakage – Joints and Packing	0.10 to 1.50	
J. Use of Fired Equipment (See Figure 6)		
K. Hot Oil Heat Exchange System (See Table 5)	0.15 to 1.15	
L. Rotating Equipment	0.50	
Special Process Hazards Factor (F_2)		
Process Unit Hazards Factor ($F_1 \times F_2$) = F_3		
Fire and Explosion Index ($F_3 \times MF$ = F&EI)		

(1) For no penalty use 0.00.

Figure 8.2 *Dow Fire and Explosion Index: assessment form for Fire and Explosion Index and other quantities (Courtesy of the American Institute of Chemical Engineers), (Figure and table references are to the Dow Guide)*

Table 8.6 *Dow Fire and Explosion Index: material factors for selected chemicals (Dow Chemical Company, 1994) (Courtesy of the Dow Chemical Company)*

	Heat of combustion[a] H_c (BTU/lb)	*NFPA classification*		*Reactivity,* N_R	*Material factor, MF*
		Health, N_H	*Fire,* N_F		
Acetone	12,300	1	3	0	16
Acetylene	20,700	0	4	3	29
Acrylonitrile	13,700	4	3	2	24
Ammonia	8,000	3	1	0	4
Ammonium nitrate	12,400[b]	0	0	3	29
Benzene	17,300	2	3	0	16
Benzylperoxide	12,000	1	3	4	40
1, 3-Butadiene	19,200	2	4	2	24
Butane	19,700	1	4	0	21
t-Butylhydroperoxide	11,900	1	4	4	40
Carbon disulfide	6,100	3	4	0	21
Carbon monoxide	4,300	3	4	0	21
Chlorine	0	4	0	0	1
Cyclohexane	18,700	1	3	0	16
Diesel fuel	18,700	0	2	0	10
Diethyl ether	14,500	2	4	1	21
Ethane	20,400	1	4	0	21
Ethylene	20,800	1	4	2	24
Ethylene dichloride	4,600	2	3	0	16
Ethylene oxide	11,700	3	4	3	29
Hydrogen	51,600	0	4	0	21
Kerosene	18,700	0	2	0	10
Methane	21,500	1	4	0	21
Methyl ethyl ketone	13,500	1	3	0	16
Naphtha (VM&P, regular)	18,000	1	3	0	16
Propane	19,900	1	4	0	21
Propylene	19,700	1	4	1	21
Styrene	17,400	2	3	2	24
Toluene	17,400	2	3	0	16
Vinyl acetate	9,700	2	3	2	24
Vinyl chloride	8,000	2	4	2	24

[a] This is the net heat of combustion, which is the value obtained when the water formed is considered to be in the vapour state.
[b] Heat of combustion H_c is equivalent to six times the heat of decomposition H_d.

showing areas of exposure, emergency isolation valves, and fire and gas detection equipment; the F&EI forms completed for the highest F&EI, the highest actual MPPD and the highest MPDO and BI; a risk analysis summary for the plant, based on the process units analyses as shown in Figure 8.2; and BI data. It recommends that each site maintain such a package for each of its plants.

The Dow *Guide* contains in Appendix C a set of basic preventive and protective features for fire protection. It states that many of the features should be provided regardless of the size of the F&EI, and that where they are not the hazard exposure will be greater than the F&EI indicates. These features are listed and discussed in Chapter 16.

There appears, in the successive editions, to be more emphasis on the use of the F&EI itself for risk management purposes and perhaps rather less on its use for the selection of fire protection measures. The Dow *Guide* also gives in Appendix D an extensive loss prevention checklist.

The current edition of the guide gives the correlations in terms of both graphical and equation form. The equations necessary for the determination of the F&EI are quoted here, but not those for MPPD, etc., for which the *Guide* should be consulted.

*The account given in this subsection is based on the seventh edition by permission of the Dow Chemical Company. The company accepts no liability for results of actions following the use of the *Guide*.

8.6.2 Mond Index

The Mond Fire, Explosion and Toxicity Index is an extension of the Dow Index. The index was developed at the Mond Division of ICI and the original version was described by D.J. Lewis (1979).

The principal modifications to the Dow method made in the Mond Index are:

(1) to enable a wider range of processes and storage installations to be studied;
(2) to cover the processing of chemicals which are recognized as having explosive properties;
(3) to offset difficulties raised by high heat of combustion per unit mass of hydrogen and to enable distinctions to be made between processes where a given fuel is reacted with different reactants;

Table 8.7 *Dow Fire and Explosion Index: Material Factor determination guide (Courtesy of the American Institute of Chemical Engineers)*

Liquids & gases flammability or combustibility[a]	*NFPA 325M or 49*	*Reactivity or instability*				
		$N_R = 0$	$N_R = 1$	$N_R = 2$	$N_R = 3$	$N_R = 4$
Non-combustible[b]	$N_F = 0$	1	14	24	29	40
FP > 200°F(> ≶.°C)	$N_F = 1$	4	14	24	29	40
FP > 100°F(> −. °°C) ≤ 200°F(≤93.3°C)	$N_F = 2$	10	14	24	29	40
FP ≥73°F(≥22.8°C) < Ø ≷ °Φ(<−.°°Ψ) or FP < 73°F(<.°°C) & BP ≥ 100°F(≥37.8°C)	$N_F = 3$	16	16	24	29	40
FP < 73°F(<.°°C) & BP < Ø ≷ ≷°Φ<−.°°Ψ)	$N_F = 4$	21	21	24	29	40
Combustible dust or mist[c]						
St-1 ($K_{St} \leq 200$ bar m/s)		16	16	24	29	40
St-2 ($K_{St} = 201–300$ bar m/s)		21	21	24	29	40
St-3 ($K_{St} > 300$ bar m/s)		24	24	24	29	40
Combustible solids						
Dense > 40 mm thick[d]	$N_F = 1$	4	14	24	29	40
Open < 40 mm thick[e]	$N_F = 2$	10	14	24	29	40
Foam, fibre, powder, etc.[f]	$N_F = 3$	16	16	24	29	40

FP = Flash point, closed cup; BP = boiling point at standard temperatures and pressure (STP).
[a] Includes volatile solids.
[b] Will not burn in air when exposed to a temperature of 1500°F (816°C) for a period of 5 min.
[c] K_{St} values are for a 16 l or larger closed test vessel with strong ignition source. See NFPA 68: *Guide for Venting of Deflagrations*.
[d] Includes wood – 2 in. nominal thickness, magnesium ingots, tight stacks of solids and tight rolls of paper or plastic film. Example: SARAN WRAP®.
[e] Includes coarse granular material such as plastic pellets, rack storage, wood pallets and non-dusting ground material such as polystyrene.
[f] Includes rubber goods such as tyres and boots. Styrofoam® brand plastic foam and fine material such as METHOCEL® cellulose ethers in dust/leak-free packages.
Note: N_F ratings can be found in NFPA 704.

Table 8.8 *Dow Fire and Explosion Index: material factor temperature adjustment*[a] *(Courtesy of the American Institute of Chemical Engineers)*

	N_F	St	N_R
(a) Enter N_F (St for dusts) and N_R			
(b) If temperature less than 140°F (60°C), go to (e)			
(c) If temperature above flash point or if temperature greater than 140°F (60°C), enter 1 under N_F			
(d) If temperature above exotherm start or autoignition, enter 1 under N_R			
(e) Add each column but enter 4 where total is 5			

(f) Using (e) and Table 8.7 determine Material Factor (MF) and enter on F&EI Form and Manufacturing Unit Risk Analysis Summary

[a] 140°F (60°C) can be reached in storage due to layering and solar heat.

(4) to include a number of additional special process type of hazard considerations that have been shown by a study of incidents to affect the level of hazard signifcantly;
(5) to allow aspects of toxicity to be included in the assessment;
(6) to include a range of offsetting factors for good design of plant and control/safety instrumentation systems to enable realistic hazard levels to be assessed for plant units under varying levels of safety features;

Table 8.9 *Dow Fire and Explosion Index: penalties for General Process Hazards (Courtesy of the American Institute of Chemical Engineers)*

A Exothermic chemical reactions

For reactions taking place in a reactor:

(1) Mild exotherms, e.g. hydrogenation, hydrolysis, isomerization, sulfonation and neutralization, penalty = 0.30
(2) Moderate exotherms, e.g. alkylation, esterification, oxidation,[a] polymerization, condensation, addition reactions,[b] penalty = 0.50
(3) Critical-to-control exotherms, e.g. halogenation, penalty = 1.00
(4) Particularly sensitive exotherms, e.g. nitration, penalty = 1.25

B Endothermic processes

(1) Endothermic process taking place in a reactor, penalty = 0.2
(2) Endothermic process taking place in a reactor where energy source is provided by combustion of solid, liquid or gaseous fuel, e.g. calcination, direct- fired pyrolysis, penalty = 0.4

C Material handling and transfer

For hazard of fire involving process unit during handling, transfer and warehousing of materials:

(1) Loading and unloading of Class I flammable liquids or liquefied petroleum gas (LPG)-type materials where transfer lines are connected and disconnected, penalty = 0.50
(2) Processes where introduction of air during manual addition may create a flammable mixture or reactivity hazard, e.g. centrifuges, batch reactions or batch mixing, penalty = 0.50
(3) Warehousing and yard storage:
  (a) Flammable liquids or gases $N_F = 3$ or 4,[c] penalty = 0.85
  (b) Combustible solids $N_F = 3$, penalty = 0.65
  (c) Combustible solids $N_F = 2$, penalty = 0.40
  (d) Combustible liquids (closed cup flash point > 100°F (37.8°C) and <140°F (60°C), penalty = 0.25

If any of (a)–(d) are stored on racks without in-rack sprinklers, add 0.20 to penalty

D Enclosed or indoor process units

For enclosed area, defined as any roofed area with three or more sides or an area enclosed by roofless structure with walls on all sides:

(1) Dust filters or collectors in an enclosed area, penalty = 0.50
(2) Process in which flammable liquids are handled above flash point in an enclosed area, penalty = 0.30; for quantities in excess of 10 M lb., penalty = 0.45
(3) Process in which LPG or flammable liquids are handled above boiling point in an enclosed area, penalty = 0.60; for quantities in excess of 10,000 lb (4536 kg), penalty = 0.90

If properly designed mechanical ventilation is installed, reduce penalties in (1) and (3) above by 50%

E Access

For inadequate access[d]

(1) Process area > 10,000 ft^2 (925 m^2) with inadequate access, penalty = 0.35
(2) Warehouse > 25,000 ft^2 (2312 m^2) with inadequate access, penalty = 0.35

F Drainage and spill control

For a flammable material in a process unit with a flash point <140°F or being processed above its flash point:

(1) Diking which exposes all equipment within dike to potential fire, penalty = 0.50
(2) Flat area around process unit which allows spills to spread, exposing large areas to potential fire, penalty = 0.50
(3) Diking around process unit which surrounds three sides of the area and directs spills to an impounding basin or non-exposing drainage trench, no penalty provided:
  (a) Slope to basin or trench is at least 2% for earthen surfaces or 1% for hard surfaces
  (b) Distance to equipment from nearest edge of trench or basin is at least 50 ft (15 m). This distance can be reduced if a firewall is installed
  (c) The impounding basin must have a capacity at least equal to the combined volume of flammable liquid and fire water[e]
(4) Basin or trench which exposes utility lines or does not meet distance requirements, penalty = 0.5

[a] In oxidation reactions involving combustion processes or vigorous oxidizing agents such as chlorates, nitric acid, hypochlorous acids and salts, etc., increase penalty to 1.00.
[b] When the acid is a strong reacting material, increase penalty to 0.75.
[c] This includes drums, cylinders and aerosol cans.
[d] For access to be adequate, there should be access from at least two sides. At least one of these should be a roadway. A monitor nozzle, which would remain easily accessible and operational during a fire could be considered a second access. Strong consideration should be given to this penalty for process units in an enclosed area.
[e] This volume is the sum of volume of the flammable liquid, which for process and storage facilities is 100% of the capacity of the unit's largest tank + 10% of the capacity of the next largest tank, and of the volume of a 30 min flow of firewater.

(7) to indicate how the results of using the method can be applied logically in the design of plants having a greater degree of 'inherent safety'.

The Mond Index was developed from the 1973 version of the Dow Index and the comparisons between the two given here relate to that version. Since then, there have been a number of developments in the Dow Index itself, in particular, the introduction of the loss control credit factors.

The Mond method involves making an initial assessment of hazard in a manner similar to that used in the Dow Index, but taking into account additional hazard considerations. The potential hazard is expressed in terms of the initial value of a set of indices for fire, explosion and toxicity. A hazard factor review is then carried out to see if there is scope to reduce the hazard by making

Table 8.10 *Dow Fire and Explosion Index: penalties for Special Process Hazards (Courtesy of the American Institute of Chemical Engineers)*

A Toxic materials

Penalty of $0.2 \times N_h$ is applied for a process involving toxic materials[a]

B Subatmospheric pressure[b]

Penalty of 0.5 is applied for processes in which air inleak could create a hazard and which operate at an absolute pressure < 500 mmHg[c]

C Operation in or near flammable range

For processes where air might enter the system and form a flammable mixture:

(1) Tank storage of $N_F = 3$ or 4 flammable liquids where air can be breathed into the tank during pump-out or sudden cooling of the tank, penalty = 0.50
For open vent or non-inert gas padded operating pressure-vacuum relief system, penalty = 0.50
Storage of combustible liquids above closed cup flash point, penalty = 0.50
No penalty is applied if an inerted, closed vapour recovery system is used and its air-tightness is assured
(2) Process equipment or process storage tanks which could be in or near the flammable range only in the event of instrument or equipment failure,[d] penalty = 0.30
(3) Processes or operations which are by nature always in or near the flammable range either because purging is not practical or because it was elected not to purge, penalty = 0.8

D Dust explosion[e]

For any process unit involving dust handling operations such as transferring, blending, grinding, bagging, etc.

Particle size[f] (mm)	*Tyler mesh size*	*Penalty*[g]
175+	60–80	0.25
150–175	80–100	0.50
100–150	100–150	0.75
75–100	150–200	1.25
<75	>200	2.00

E Relief pressure

For a process operating at a pressure above atmospheric, a penalty is applied which is a function of the operating pressure. Two pressure ranges are considered. For operating pressures in the range 0–1000 psig, the penalty is obtained using Figure 8.3(a)[1] in the manner described below. For pressures above 1000 psig, the penalty is

Pressure (psig)	*Penalty*
1000	0.86
1500	0.92
2000	0.96
2500	0.98
3000–10,000	1.0
>10,000	1.5

For the lower pressure range, the curve shown in Figure 8.3(a)[1] gives an initial penalty which is applicable for flammable and combustible liquids with flash point <140 °F (60 °C). For other materials, the initial penalty given by the curve is adjusted by a material adjustment factor as follows:

(1) Highly viscous materials,[h] multiply penalty by 0.7
(2) Compressed gases used alone or flammable liquids pressurized with any gas above 15 psig, multiply penalty by 1.2
(3) Liquefied flammable gases,[i] multiply penalty by 1.3
The actual penalty is obtained as follows. First determine from Figure 8.3(a)[1] the penalties associated with the operating pressure and with the set pressure of the relief device. Divide the operating pressure penalty by the set pressure penalty to obtain the final pressure penalty adjustment factor. Now multiply the operating pressure by the material adjustment factor given in (1)–(3) above and then by the final pressure penalty adjustment factor to obtain the final pressure penalty.

Example:
Vessel design pressure = 150 psig
Normal operating pressure = 100 psig; initial penalty = 0.31 (from Figure 8.3(a)[1])
Rupture disc set pressure = 125 psig; initial penalty = 0.34 (from Figure 8.3(a)[1])
Process with viscous material; penalty adjustment = 0.70
Adjusted initial penalty = $0.7 \times 0.31 = 0.22$
Actual penalty = $0.22 \times (0.31/0.34) = 0.20$

F Low temperature

For a process for which it has not been shown that there is no possibility of temperatures below the transition temperature due to normal or abnormal operating conditions:

(1) Process utilizing carbon steel and operated at or below the ductile/brittle transition temperature,[j] penalty = 0.30
(2) Process utilizing materials other than carbon steel where the operating temperature is at or below the transition temperature, penalty = 0.20

G Quantity of flammable and unstable material

A process involving flammable or unstable materials is classed as either:

(1) Liquids or gases in process;
(2) Liquids or gases in storage;
(3) Combustible solids in storage or dust encountered in process

and a single penalty is applied based on the material selected for the MF as follows:

The penalty is a function of the quantity of material which it is estimated might be released within 10 min.

For case (3) above, this quantity is used directly, whilst for cases (1) and (2) above, it is used in the form of the potential heat release.

Liquids or gases in process
This category applies to:

(a) Flammable liquids and those combustible liquids with flash point <140°F (60°C)
(b) Flammable gases

(c) Liquefied flammable gases
(d) Combustible liquids with closed cup flash points >140°F (60°C)
(e) Reactive materials, regardless of flammability

The penalty is a function of the potential heat release, which is the product of the quantity of material which it is estimated might be released within 10 min[k] and of the heat quantity H_c (BTU/lb),[l] as given in Figure 8.3(b)[1].

Liquids or gases in storage
This category applies to liquids or gases in storage and thus outside the process area. The penalty is a function of the potential heat release, which is the product of the quantity of material in storage[m] and of H_c[n] as given in Figure 8.3(c)[1].[o]

Combustible solids in storage or dust encountered in process
This category applies to combustible solids in storage and to dust in a process unit. The penalty is a function of the quantity of material[p] as given in Figure 8.3(d)[1].

H Corrosion and erosion[q]

For a corrosion rate, defined as the sum of the external and internal corrosion rates:

(1) Corrosion rate < 0.5 mil/year (0.127 mm/year) with risk of pitting or local corrosion, penalty = 0.10
(2) Corrosion rate > 0.5 mil/year (0.127 mm/year) and <1 mm/year, penalty = 0.20
(3) Corrosion rate > 1 mil/year (0.254 mm/year), penalty = 0.50
(4) Risk of stress corrosion cracking developing, penalty = 0.75
(5) Lining required to prevent corrosion,[r] penalty = 0.20

I Leakage – joints and packing

(1) Pump and gland seals are likely to give some leakages of a minor nature, penalty = 0.10
(2) Process known to give regular leakage problems at pumps, compressors and flange joints, penalty = 0.30
(3) Process in which thermal and pressure cycling occurs, penalty = 0.3
(4) Process material penetrating in nature or an abrasive slurry which causes intermittent problems of sealing, and process utilizing a rotating shaft seal or packing, penalty = 0.40
(5) Process with sight glasses, bellows assemblies or expansion joints, penalty =1.50

J Use of fired equipment

For a process unit which is in the vicinity of a fired heater or which is itself a fired heater, a penalty is applied which is a function of the distance from the air intake of the fired heater to a probable leak point as given in Figure 8.3(e)[1]. The two curves A-l and A-2 are applied as follows, where the material referred to is the material of the MF:

Curve A-l is used for:

(a) A process unit in which the material could be released above its flash point;
(b) A process unit in which the material is a combustible dust.

Curve A-2 is used for:

(a) a process unit in which the material could be released above its boiling point;

Note: If the material is below its flash point, the only situation which attracts a penalty is where the fired heater itself is the process unit being evaluated. In this case, the distance from the possible leak source is zero and even if the material is below its flash point, a penalty of 1.0 is applied.

K Hot oil exchange system

The penalty in this section is not applied:

(1) If the hot oil exchange system is the process unit being evaluated;
(2) If the hot oil is non-combustible or, if combustible, is always used below its flash point.

Otherwise, for a process unit utilizing a hot oil exchange system in which the heat exchange fluid is combustible:

Quantity[s] (US gal)	(m^3)	*Penalty oil > flash point*	*Oil ≥ flash point*
<5000	<18.9	0.15	0.25
5000–10,000	18.9–37.9	0.30	0.45
10,000–25,000	37.9–94.6	0.50	0.75
>25,000	>94.6	0.75	1.15

Note: (1) It is recommended that the F&EI also be determined for the hot oil system itself, including the process tank, pumps and distribution/return piping, but not the storage tank. (2) If a fired hot oil heat exchange system is actually located in the area of the process unit, the penalty in Section J applies.

L Rotating equipment[t]

Penalty of 0.5 is applied for a process unit, which utilizes, or is

(1) A compressor in excess of 600 hp;
(2) A pump in excess of 75 hp;
(3) Agitators and circulating pumps in which failure could produce a process exotherm;[u]
(4) Other large, high speed rotating equipment with a significant loss history, e.g. centrifuge

[a] For mixtures, the highest N_H value of the individual components should be used.
[b] If the penalty is applied, the penalty specified in Section C or E should not be duplicated or repeated.
[c] The main process units in this category are most stripping operations, some compressor operations and a few distillation operations.
[d] For a process unit which relies on inert purge to keep it out of the flammable range, penalty = 0.30. This penalty also applies to padded barges or tank cars. (*Note*: no penalty is applied here if the penalty in Section B has already been taken).
[e] Penalties should be applied unless it has been shown by testing that no dust explosion hazard exists.
[f] The particle size to be used is the 10% particle size, i.e. that at which 90% of the dust is coarser and 10% finer.
[g] If the dust is handled in an inert gas, the penalty should be halved.
[h] This includes materials such as tars, bitumen, heavy lubricating oils and asphalts.
[i] This includes all other flammable materials stored above their boiling point.
[j] If no data are available, a 50°F (10°C) transition temperature should be assumed.
[k] This figure should be based on the user's own judgement but, as a guide, experience shows that a reasonable estimate is the larger of

the quantity of material (1) in the process unit or (2) in the largest connected unit, disregarding any connected unit which can be isolated by an emergency isolation valve;
[l] For most materials, H_c is the heat of combustion, but for unstable materials ($N_r > 2$), it is six times the heat of decomposition or the heat of combustion, whichever is larger.
[m] In the case of portable drums, the relevant quantity is the total quantity in all the drums, and in the case where two or more vessels are in a common dike which would not drain adequately into an impounding basin, it is the quantity in all the vessels.
[n] See footnote l.
[o] If there is more than one class of material, the total heat release should be utilized in conjunction with the highest curve applicable to any of the individual materials.
[p] For unstable materials ($N_R > 2$), the quantity which should be used is the actual mass multiplied by six and the curve to be used is curve A.
[q] The *Guide* gives guidance on situations where corrosion or erosion is likely.
[r] This penalty does not apply if the lining is simply to prevent discolouration of the product.
[s] This quantity is defined as follows. It is the lesser of (1) a 15-min spill caused by a break in the lines servicing the process unit or (2) the oil inventory within the active circulating hot oil system, where the portion of the exchange system classed as storage is not included unless it is connected much of the time to the process unit.
[t] Formulae have not been developed for all types and sizes of rotating equipment, but there is evidence that equipments above a certain size are liable to contribute to an incident.
[u] Where the exotherm is due to lack of cooling from interrupted mixing or circulation of coolant or to interrupted and resumed mixing.

design changes, and intermediate values of the indices are determined. Offsetting factors for preventive and protective features are applied and the final values of the indices, or offset indices, are calculated.

In outline, the method of determining the Mond Index is as follows. The plant is divided into units, the demarcation between units being based on the feasibility of locating a separating barrier (open space, wall or floor) between the unit and its neighbours.

The material factor is determined as in the Dow method, but in addition, special material hazard factors are introduced. Again as in the Dow method, use is made of factors for GPHs and SPHs although the particular factors are different. A quantity factor, based on the inventory of material, and layout hazard factors are also introduced. There are also factors for toxicity hazard. The features taken into account in these factors are shown in Table 8.13.

The indices calculated are:

(1) overall index;
(2) fire load index;
(3) unit toxicity index;
(4) major toxicity incident index;
(5) explosion index;
(6) aerial explosion index;
(7) overall risk rating.

The degree of hazard associated with these indices is shown in Table 8.14.

The overall risk rating is then evaluated. If further action is judged appropriate, a hazard review is carried out to determine the scope for design modifications. Some examples of changes, which might be considered are given in Table 8.15. If design changes are made, the indices are recalculated.

The offsetting features shown in Table 8.16 are then brought into account. Some of these are preventive, reducing the frequency of incidents, and some are mitigating, reducing the consequences. Using the corresponding offsetting factors, final values of the indices are calculated.

The features to be taken into account in calculating the various factors are specified in detail in the *Technical Manual*, which contains a wealth of practical information, particularly in respect of the offsetting features.

As already mentioned, the plant is divided into individual units on the basis of the feasibility of creating separating barriers and one of the factors taken into account in the index is plant layout. The use of the method to assist in layout design is an important application. It is considered in more detail in Chapter 10.

8.6.3 IFAL Index

The IFAL index is a separate index developed by the Insurance Technical Bureau primarily for insurance assessment purposes. Accounts have been given by J. Singh and Munday (1979), Munday *et al.* (1980) and H.B. Whitehouse (1985). Calculation of the index is described in the *IFAL p Factor Workbook* (Insurance Technical Bureau, 1981).

The index was developed in order to provide a means of assessment that was more scientifically based and satisfactory than the historical loss record, which tends to be subject to chance fluctuations. An outline flow chart of the method is shown in Figure 8.6.

The method involves dividing the plant into blocks and examining each major item of process equipment in turn to assess its contribution to the index. The main hazards which contribute to the index are

(1) pool fires;
(2) vapour fires;
(3) unconfined vapour cloud explosions;
(4) confined vapour cloud explosions;
(5) internal explosions.

For hazards (2)–(5), emission frequency and hole size distributions are used, and for each case, emission, ignition, fire and explosion are modelled and the damage effects are estimated.

The IFAL Index is the product of the process factor p and of two modifying factors, the engineering factor e and the management factor m. For a process engineered and managed to 'standard good practice', the last two factors are unity and the IFAL Index equals the p factor.

In contrast to the Dow and Mond Index methods, the IFAL Index method is too complex for manual calculation and is carried out using a computer program.

Table 8.17 shows some results obtained using the IFAL method. Section A gives some relative p factors for 100,000 te/year petrochemical plants, and Section B gives the relative contribution of the five hazards to losses on an ethylbenzene plant.

8.6.4 Dow Chemical Exposure Index

As stated earlier, the main Dow Index contained at one time a Toxicity Index. Dow now uses a separate Chemical Exposure Index (CEI). An account of this index is given in *Dow's Chemical Exposure Index Guide* (AIChE 1994/39) (the Dow *CEI Guide*).

The CEI is a measure of the relative acute toxicity risk. It is used for initial process hazard analysis (PHA), in the calculation of its Distribution Ranking Index (DRI) and in emergency response planning.

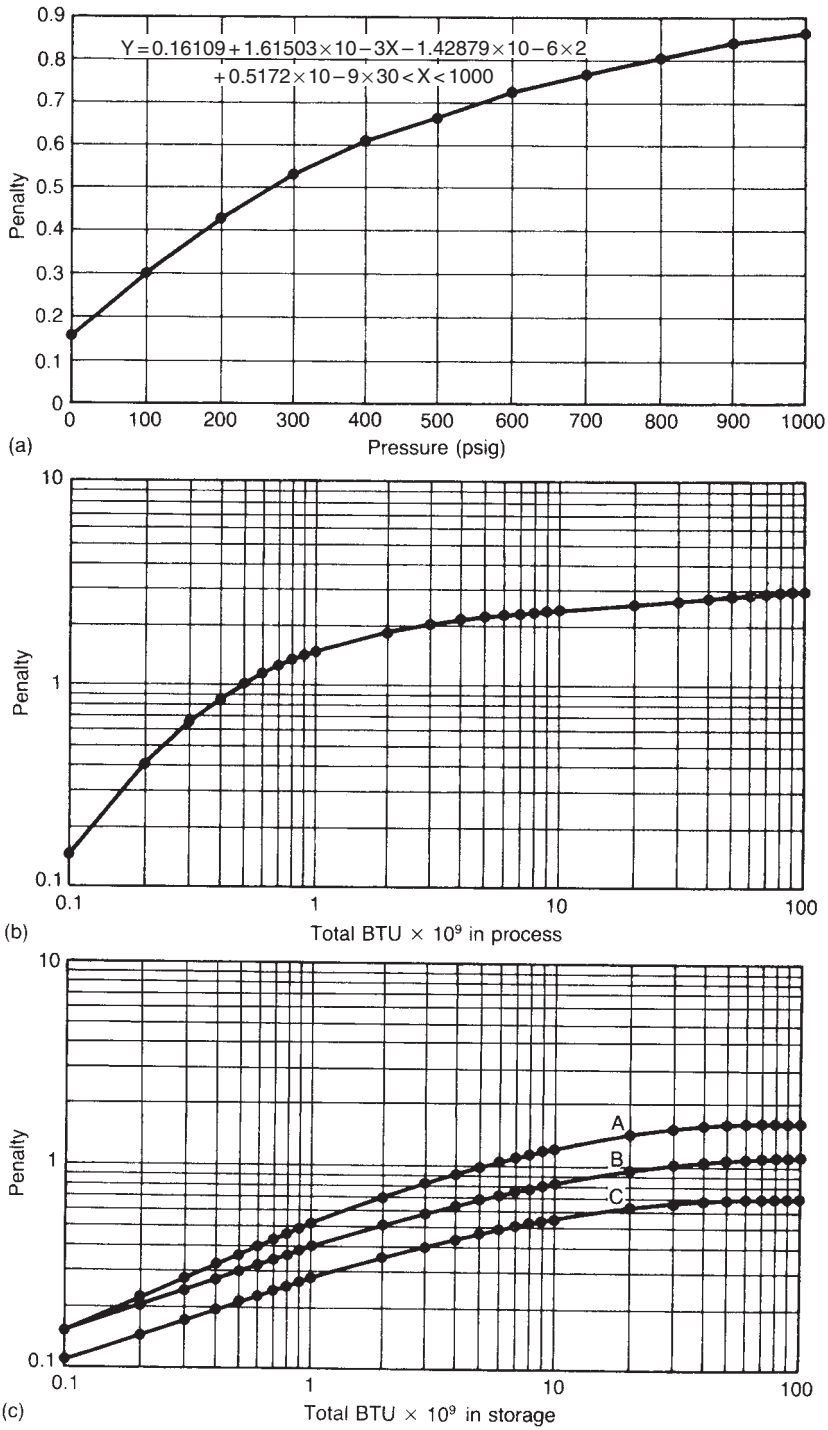

Figure 8.3 *Continued*

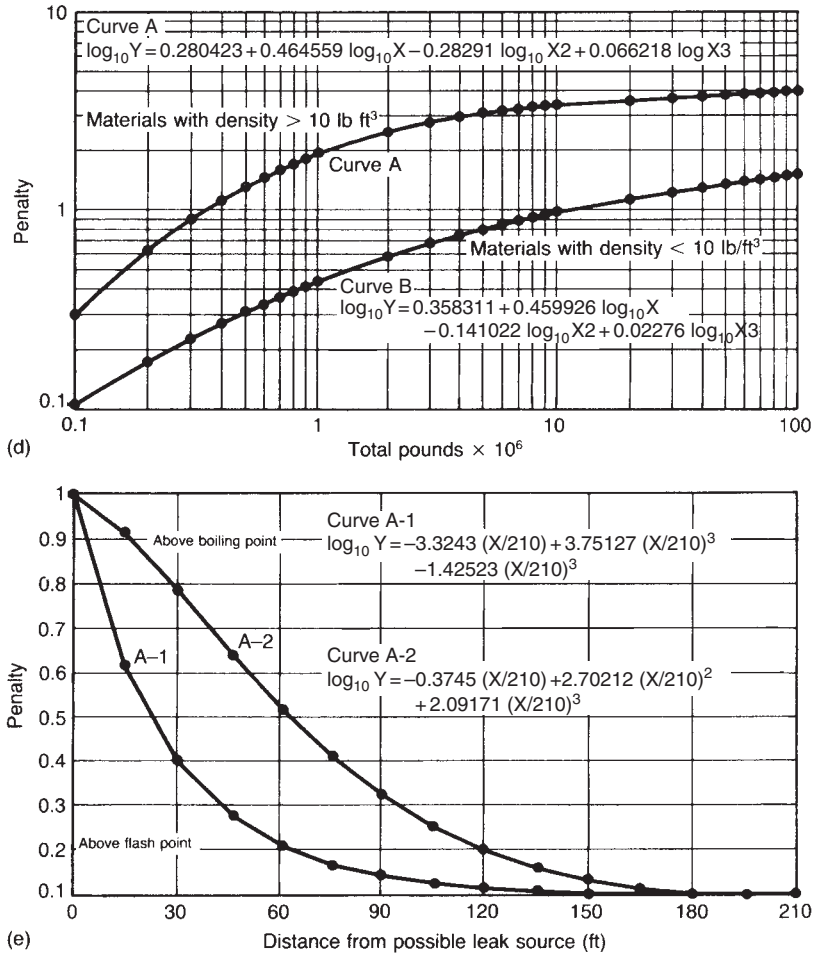

Figure 8.3 *Dow Fire and Explosion Index: penalties for special process hazards 1994: (a) penalty for pressure of flammable and combustible liquids; (b) penalty for potential heat release for liquids or gases in process; (c) penalty for potential heat release for liquids or gases in storage; (d) penalty for quantity of combustible solids in storage/dust in process; (e) penalty for location of fired equipment (Courtesy of the American Institute of Chemical Engineers)*

Table 8.11 *Dow Fire and Explosion Index: degree of hazard*

F&E index range	*Degree of hazard*	
	4th edition	*5–7th editions*[a]
1–50	1–60	Light
51–81	61–96	Moderate
82–107	97–127	Intermediate
108–133	128–158	Heavy
≥134	≥159	Severe

[a] Increase in range is due to new contribution factors and a correction for penalties in three contributing factor charts.

The information needed for the calculation of the CEI is: the physical and chemical properties of the material; a simplified process flow sheet, showing vessels and major pipework with inventories; and an accurate plot plan of the plant and the surrounding area.

It is also necessary to have toxicity limits in the form of the American Industrial Hygiene Association (AIHA) Emergency Response Planning Guidelines (ERPGs) for the material. There are three levels of ERPG (ERPG-1, ERPG-2 and ERPG-3), which are essentially the maximum airborne concentrations below which it is believed that nearly all individuals could be exposed without experiencing some defined effect, the effects being: for level 1, experience of something more than a mild transient health effect or odour; for level 2, serious or irreversible health effects; and for level 3,

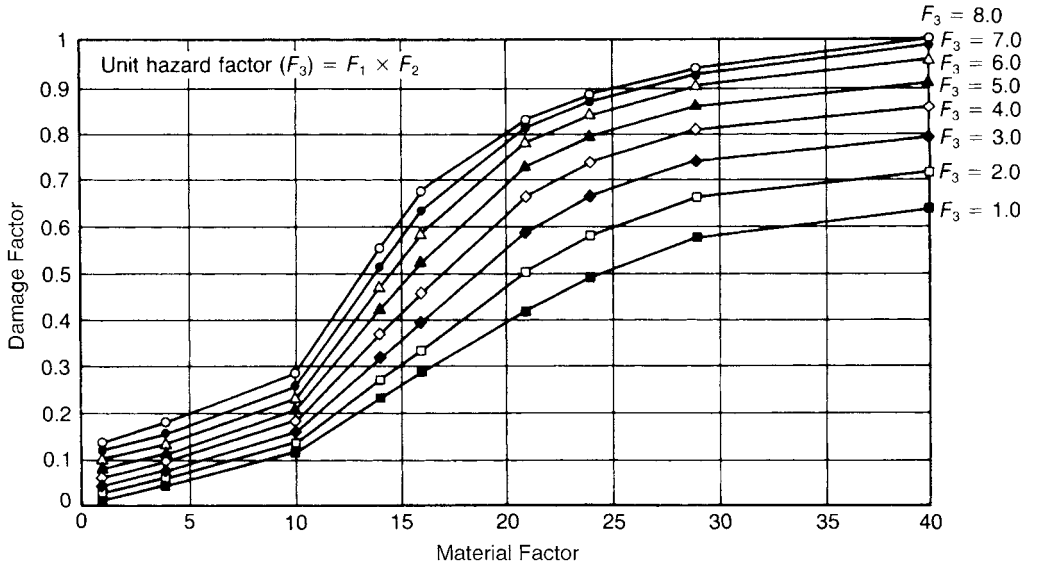

Figure 8.4 *Dow Fire and Explosion Index: damage factor (Courtesy of the American Institute of Chemical Engineers)*

Table 8.12 *Dow Fire and Explosion Index: loss control credit factor (Dow Chemical Company, 1994) (Courtesy of the Dow Chemical Company)*

A Process control (C_1)			
(a) Emergency power	0.98	(f) Inert gas	0.94–0.96
(b) Cooling	0.97–0.99	(g) Operating procedures	0.91–0.99
(c) Explosion control	0.84–0.98	(h) Reactive chemical review	0.91–0.98
(d) Emergency shut-down	0.96–0.99	(i) Other process hazard analysis	0.91–0.98
(e) Computer control	0.93–0.99		
B Material isolation (C_2)			
(a) Remote control valve	0.96–0.98	(c) Drainage	0.91–0.97
(b) Dump/blowdown	0.96–0.98	(d) Interlock	0.98
C Fire protection (C_3)			
(a) Leak detection	0.94–0.98	(f) Water curtains	0.97–0.98
(b) Structural steel	0.95–0.98	(g) Foam	0.92–0.97
(c) Water supply	0.94–0.97	(h) Hand extinguishers/monitors	0.93–0.98
(d) Special systems	0.91	(i) Cable protection	0.94–0.98
(e) Sprinkler systems	0.74–0.97		

life-threatening effects. ERPGs are considered further in Chapter 18.

The procedure for the calculation of the CEI is to determine (1) the release scenarios, (2) the ERPG-2, (3) the airborne quantities, (4) the CEI and (5) the hazard distance. The CEI is based on the scenario giving the largest airborne quantity (AQ).

The Dow *CEI Guide* gives a set of rules for defining release scenarios and of equations for estimating the AQ based on gas or liquid flow from vessels and pipes, liquid flash-off, and pool formation and evaporation. These, in effect, constitute a release model, description of which is deferred to Chapter 15.

The CEI is then calculated from the relationship:

$$\text{CEI} = 655.1\left(\frac{\text{AQ}}{\text{ERPG-2}}\right)^{1/2} \qquad [8.6.9]$$

where AQ is the airborne quantity (kg/s) and ERPG-2 is the relevant toxic limit (mg/m^3). If the calculated value of the CEI is greater than 1000, the CEI is set equal to 1000.

Table 8.13 *Mond Index: hazard factors (after D.J. Lewis, 1979)*[a]

A Special material hazards
Oxidizing materials
Reacts with water to produce a combustible gas
Mixing and dispersion characteristics
Subject to spontaneous heating
Subject to rapid spontaneous polymerization
Ignition sensitivity
Subject to explosive decomposition
Condensed phase properties
Other
B General process hazards
Handling and physical changes only
Single continuous reactions
Single batch reactions
Multiplicity of reactions or different process operations carried out in same equipment
Material transfer
Transportable containers
C Special process hazards
Low pressure (below 15 psia)
High pressure
Low temperature:
1: Carbon steel +10°C to −10°C
2: Carbon steel below −10°C
3: Other materials
High temperature:
1: Flammability
2: Construction materials
Corrosion and erosion
Joint and packing leakages
Vibration, load cycling, etc.
Processes or reactions difficult to control
Operation in or near flammable range
Greater than average explosion hazard
Dust or mist hazard
High strength oxidants
Process ignition sensitivity
Electrostatic hazards
D Layout hazards
Structure design
Domino effect
Below ground
Surface drainage
Other
E Toxicity hazards
TLV value
Material form
Short exposure risk
Skin absorption
Physical factors

[a] This table lists the hazard factors but not the associated numerical values. See *Technical Manual* (D.J. Lewis, 1979) for full details.

The hazard distance is then determined as:

$$HD = 6551\left(\frac{AQ}{ERPG}\right)^{1/2} \qquad [8.6.10]$$

where HD is the hazard distance (m) and ERPG is any one of three ERPG toxic limits (mg/m^3). If the calculated value of HD is greater than 10,000 m, HD is set equal to 10,000 m. There is thus a set of three HD values corresponding to the three levels of ERPG.

The Dow *CEI Guide* contains tabulations of relevant physical properties and ERPG values. It also gives CEI values for releases of different chemicals from a 2 in. hole together with worked examples. It provides a containment and mitigation checklist.

8.6.5 Mortality index

Another index which should be mentioned here is the Mortality Index proposed by V.C. Marshall (1977b). This is an index of the lethality of materials with major hazard potential, and is defined as the number of deaths per tonne of material involved. The index is discussed in Chapters 16–18.

8.7 Hazard Studies

There are now a number of methods that have been developed for the identification of hazards. A brief overview of these is given in this section, and a more detailed account of each method is then presented in the succeeding sections.

Overviews of hazard identification methods are available from numerous sources. Two primary information sources are the Chemical Industries Association (CIA) *HAZOP: Guide to Best Practice* (CIA, 1999) and *Guidelines for Hazard Evaluation Procedures* (AIChE/CCPS, 1992, 2nd edition).

Some of the methods described are complete methods. Methods in this category are What If? analysis, Preliminary Hazard Analysis (PHA), screening analysis techniques, HAZOP studies, and FMECA. Of these, PHA and screening analysis are designed for use at an early stage in the design.

Other methods, such as event tree, fault tree analysis, sneak analysis, computer control and human error analysis (known as CHAZOP), are specialist techniques used to complement or support more comprehensive methods. Scenario development and consequence analysis are part of hazard identification, but are also major features in hazard assessment.

The process safety system described in Subsection 8.7.12 combines a number of these techniques in an integrated system. Other aspects considered are the choice of method, the filtering and follow-up of the study results and formal safety review systems.

8.7.1 What if? analysis

An early method of hazard identification is to review the design by asking a series of questions beginning with What If? The method is a team exercise and typically makes use of pre-determined questions, but otherwise tends not to be highly structured. An account is given in Section 8.8.

8.7.2 Event tree and fault tree analysis

Event trees and fault trees are logic diagrams used to represent, respectively, the effects of an event and the

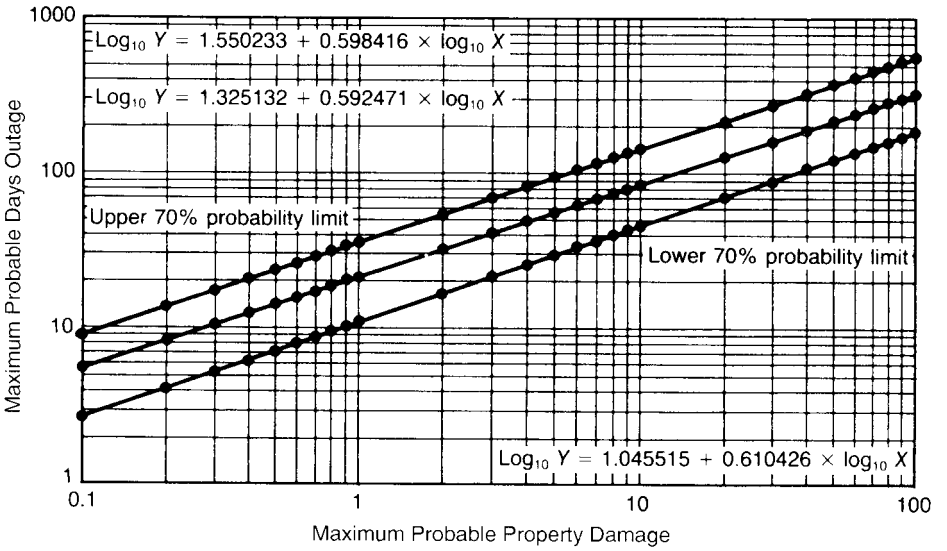

Figure 8.5 *Dow Fire and Explosion Index: maximum probable days outage. The MPPD is given as the actual MPPD in 10^{12} US$, 1986 basis. To update to 1993 basis, multiply by 359.9/318.4 = 1.130 (based on Chemical Engineering Plant Cost Index) (Courtesy of the American Institute of Chemical Engineers)*

contributory causes of an event. Accounts of event tree and fault tree analysis are given in Section 8.9 and Chapter 9.

8.7.3 Preliminary hazard analysis

'Preliminary hazard analysis' is a term normally used to describe a qualitative technique for identifying hazards relatively early in the design process. It is to be distinguished from the detailed hazard analysis, which employs a quantitative risk ranking technique. An account of PHA is given in Section 8.10.

8.7.4 Screening analysis techniques

A method of identifying hazards early in the design is through a screening analysis of anticipated hazards such as fire, explosion, reactivity, toxicity, etc. An account of screening techniques is given in Section 8.11.

8.7.5 Hazard and operability study

A method widely used by the process industries for the identification of hazards at, or close to, the engineering line diagram (ELD) stage is the HAZOP study. This technique is a development from critical examination. It is a team exercise, which involves examining the design intent in the light of guidewords. The technique has itself been subject to numerous variations.

For the process industries, the HAZOP study might fairly be described as the jewel in the crown of hazard identification methods. An account of the HAZOP study is given in Section 8.12.

8.7.6 Failure modes, effects and criticality analysis

Another method of hazard identification is the FMECA. It involves the analysis of the failure modes of an entity, their causes, effects, and associated criticality of the failure. An account of the FMECA technique is given in Section 8.13.

8.7.7 Sneak analysis techniques

There are a number of ways in which a hazard can 'sneak' into a complex electromechanical system. Sneak analysis is essentially a set of techniques for dealing with the various types of sneak. It is a complementary rather than a comprehensive method. An account of sneak analysis is given in Section 8.14.

8.7.8 Computer control and human error analysis

The conventional HAZOP study was developed for plants in which the control system was based on analogue controllers. It is not itself oriented to failures associated with computer control systems. CHAZOP has been developed to augment the process HAZOP in this respect. An account of CHAZOP is given in Section 8.15.

8.7.9 Human error analysis

It is well established that human actions play a large role in accidents. Human error analysis is used to take this aspect into account. As a hazard identification technique, human error analysis is qualitative, although a similar term is also sometimes used to describe a quantitative method. An account of human error analysis is given in Section 8.16.

8.7.10 Consequence analysis and modelling

Examination of different scenarios of plant disturbance and loss of containment is a central activity in hazard identification. The scenarios may relate to the events before release or to events involved in escalation after release. Hazard identification, therefore, includes methods of developing and structuring scenarios. Accounts of scenario development are given in Sections 8.17 and 8.19.

8.7.11 Process safety system

Hazard identification and hazard assessment are a part of the safety management system developed by the American

Table 8.14 *Mond Index: evaluation of index (after D.J. Lewis, 1979)*

A Overall index D

Range	*Overall degree of hazard*
0–20	Mild
20–40	light
40–60	Moderate
60–75	Moderately heavy
75–90	Heavy
90–115	Extreme
115–150	Very extreme
150–200	Potentially catastrophic
>200	Highly catastrophic

B Fire load index F

Fire load (10^3 BTU/ft^2)	*Expected fire duration* (h)	*Category*	*Comments*
0–50	0.25–05	light	
50–100	0.5–1	Low	Dwellings
100–200	1–2	Moderate	Factories
200–400	2–4	High	Factories
400–1000	4–10	Very high	Maximum for occupied buildings
1000–2000	10–20	Intensive	Rubber warehouses
2000–5000	20–50	Extreme	
5000–10000	50–100	Very extreme	

C Explosion indices

Internal unit explosion index, E range	*Aerial explosion index, A range*	*Category*
0–1	0–10	Light
1–2.5	10–30	Low
2.5–4	30–100	Moderate
4–6	100–500	High
>6	>500	Very high

D Toxicity indices

Unit toxicity index, U range	*Major toxicity incident index, C range*	*Category*
0–1	0–20	Light
1–3	20–50	Low
3–6	50–200	Moderate
6–10	200–500	High
>10	>500	Very high

E Overall risk factor R

Range	*Category*
0–20	Mild
20–100	Low
100–500	Moderate
500–1100	High (Group 1)
1100–2500	High (Group 2)
2500–12,500	Very high
12,500–65,000	Extreme
>65 000	Very extreme

Table 8.15 *Mond Index: some examples of potentially beneficial design changes (after D.J. Lewis, 1979)*

1. Changes to process whereby the key material is diluted by an inert at all times and so reducing the material factor
2. Use of effective stabilizer in all parts of the unit where polymerization hazards can exist
3. Alteration in process conditions (i.e. pressure, temperature or mixture composition) to avoid Special Material Hazards such as explosive decomposition, gaseous detonation (e.g. acetylene), condensed phase behaviour, etc.
4. Separation of unit into two or more units of reduced capacity or into units carrying out separate stages when such smaller units can be effectively separated from each other
5. Elimination of heated two phase storages
6. Elimination of multiple reactions within the same equipment
7. Replacement of removable connection systems by fixed fully closed pipework
8. Avoidance of use of open or semi-open equipment
9. Operation under less arduous pressure conditions (either vacuum or high pressure)
10. Selection of less arduous temperature conditions (avoidance of low temperature and high temperature operational hazards)
11. Use of materials of construction having reduced corrosion potential for vessels, pipework and fittings
12. Reduction in numbers of joint and packing leakage points and use of superior joint and packing designs and materials
13. Changes in design to reduce vibration or thermal cycling effects (e.g. elimination of bellows)
14. Adoption of more effective and safe control systems for the process
15. Change in operation to take conditions further away from flammable range
16. Use of some inert diluents where high strength oxidants are involved (i.e. oxygen enriched air in place of oxygen)
17. Selection of equipment requiring a smaller inventory of the key material in the unit
18. Changes to eliminate as much high level or below ground storage of flammable materials within the unit plan area as possible
19. Separation of as much storage capacity from process operations as possible
20. Placement of specific items behind blast or fire resistant walls
21. Addition of effective second containment walls to storage units
22. Changes to unit ventilation requirements

Petroleum Institute (API RP 750) and later evolved into the process safety management system enacted by USDOL OSHA (1992). An account of the hazard identification segments of the system is given in Section 8.19.

8.7.12 Choice of method

The number of techniques available for hazard identification is large and is still growing. Each has its own field of application. One relevant distinction is between methods

Table 8.16 *Mond Index: offsetting factors (after D.J. Lewis, 1979)*[a]

A Containment system
Pressure vessels
Non-pressure vertical storage tanks
Transfer pipelines
Additional containment vessels, sleeves and bund walls
Leakage detection systems and response
Disposal of relief, vented or dumped material
B Process control
Alarm systems
Emergency power supplies
Process cooling systems
Inert gas systems
Hazard study activities
Safety shut-down systems
Computer control
Explosion and incorrect reaction protection
Operating instructions
Plant supervision
C Safety attitude
Management involvement in safety
Safety training
Maintenance and safety procedures
D Fire protection
Structural fire protection
Fire walls, barriers and equivalent devices
Equipment fire protection
E Material isolation
Valve systems
Ventilation
F Fire fighting
Fire alarms
Hand fire extinguishers
Water supply
Installed sprinkler, water spray or monitor systems
Foam and inerting installations
Fire brigade attendance
Site cooperation in firefighting
Smoke ventilators

[a] This table lists the offsetting factors but not the associated numerical values. See *Technical Manual* (D.J. Lewis, 1979) for full details.

which are comprehensive and those which are not but which supplement the former. Another is between methods for use early and late in the design. A third is in the type of problem to which a method is best suited. Guidance on choice of method is given in Section 8.20.

8.7.13 Ranking and hazard resolution

Further aspects of hazard identification are the filtering or ranking of the hazard identified to determine those on which action is prioritized, and the recording and follow-up resolution of these actions. An account of filtering and follow-up is given in Section 8.21.

8.7.14 Safety review systems

The arrangements for hazard identification need to be embodied in a formal system, which ensures that the necessary studies are done and which covers the life cycle of the plant. An account of safety review systems is given in Section 8.22.

8.8 What If? Analysis

The What If? method involves asking a series of questions beginning with this phrase as a means of identifying hazards. Apart from checklists, What If? analysis is possibly the oldest method of hazard identification. The method is to ask questions such as,

What if the pump stops?
What if the temperature sensor fails?

The questions posed need not necessarily all start with What If?; other phrases may be used.

The method involves review of the whole design by a team using questions of this type, often using a list of pre-determined questions. A checklist for use in What If? analysis is given by Burk (1992) and is shown in Table 8.18

Table 8.19 gives an example of the results from a What If? study reported by Kavianian, Rao and Brown (1992).

8.9 Event Tree and Fault Tree Analysis

The event tree and fault tree methods may be used either qualitatively or quantitatively. The concept of the fault tree was introduced in Chapter 7 and a fuller treatment of both event trees and fault trees, including their application to quantitative assessment, is given in Chapter 9. Here it is sufficient to draw attention to the value of tree methods, particularly fault trees, in hazard identification.

An event tree involves the development of the consequences (outcomes) of an event. The overall approach is similar to that adopted in FMEA, which is described below.

A fault tree involves the development of the contributing causes of an undesirable event, often a hazard. The possibility of this event must be foreseen before the fault tree can be constructed. What the fault tree helps to reveal are the possible causes of the hazard, some of which may not have been foreseen.

Fault trees are used extensively in hazard assessment, but they are also of great value in hazard identification. In many cases, it is sufficient to be able to identify the fault paths and the base events, which can give rise to the top event, it being unnecessary to quantify the frequency of occurrence of these events.

In an FMEA or an event tree, the approach is 'bottom up', while in a fault tree, it is 'top down' (deductive). The HAZOP method involves both approaches, starting with the deviations and tracing down to the causes and up to the consequences.

8.10 Preliminary Hazard Analysis

PHA is a method for the identification of hazards at an early stage in the design process. Accounts of PHA are given in the CCPS *Hazard Evaluation Guidelines* and by Kavianian, Rao and Brown (1992). PHA is a requirement of the MILSTD-882D Standard Practice for System Safety.

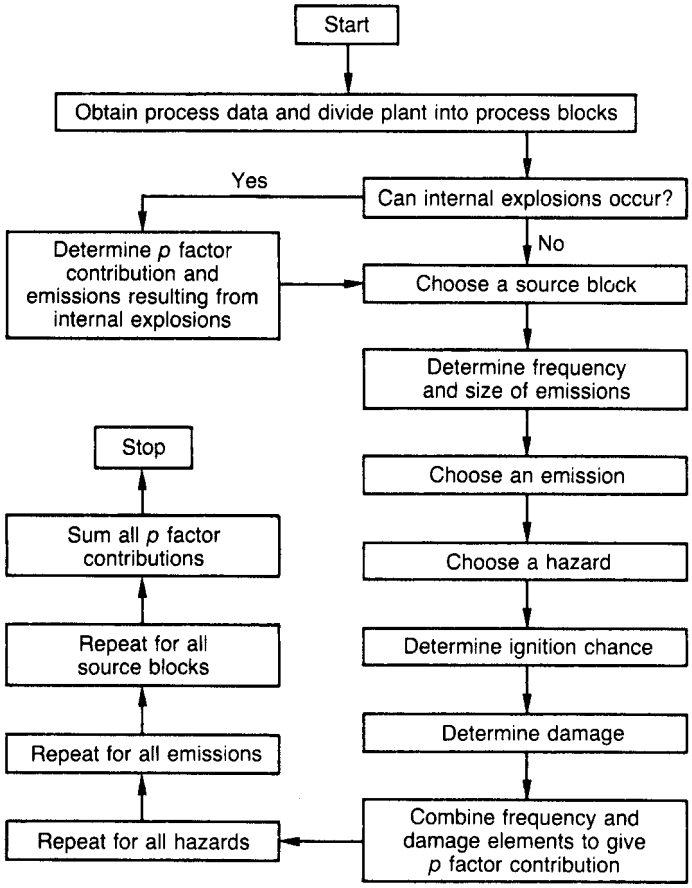

Figure 8.6 *IFAL Index: procedure for calculating p factor contributions (Munday et al., 1980)*

Since the early identification of hazards is of prime importance, many companies have some sort of technique for this purpose, a portion of which are called PHA; the use of the term tends to be fairly loose.

The CCPS *Guidelines* state that PHA is intended for use only in the preliminary stage of plant development, in cases where past experience provides little insight into the potential hazards, as with a new process. The information required for the study is the design criteria, the material and equipment specification, and so on. The *Guidelines* list the entities examined for hazards as: (1) raw materials, intermediates and final products; (2) plant equipment; (3) facilities; (4) safety equipment; (5) interfaces between system components; (6) operating environment and (7) operations (maintenance, testing, etc.).

The results from a PHA are illustrated in Table 8.20 (Kavianian, Rao and Brown, 1992).

8.11 Screening Analysis Techniques

One of the principal methods of identifying process hazards is the HAZOP study. Before describing this, however, it is appropriate to consider first the method developed for use in conjunction with, but earlier than the HAZOP.

The screen analysis is done at an early stage in the design where there is a block layout of plant items. The objective is to determine whether there are problems in areas such as data on the chemicals, information about the hazards, basic features of the process design, or layout and siting of the plant.

There are a number of advantages to be gained from conducting screening prior to the HAZOP study itself. It assists in the identification of those hazards and other problems which are quite basic and which are therefore capable, in principle, of being identified at this earlier stage. It reveals deficiencies in the design information. And it exposes hazards due to interactions between the plant and other plants or the environment, at which the HAZOP study is less effective. These features contribute to removing potential delays on the critical path of the project.

The conduct of a screening analysis involves compilation of two lists: (1) a database of hazards and nuisance properties of the material and (2) a list of potential hazards, nuisances and other matters of concern. The study

Table 8.17 *IFAL Index: value of index and relative contributions of hazards (after Munday et al., 1980)*

A Relative values of p factor for some 100,000 te/year plants

Plant	*p*
Acetic acid	1.7
Ethanol	2.4
Ethyl benzene	1.1
Ethylene oxide	2.1
Isopropanol	1.6
Styrene (1)	1.9
Styrene (2)	1.0
Vinyl chloride monomer	3.3

B Relative contribution of hazards on an ethylbenzene plant

Event	*Contribution* (%)
Pool fires	20
Vapour fires	30
Unconfined vapour cloud explosions	50
Confined vapour cloud explosions	0
Internal explosions	0

therefore covers, albeit in a different way from a HAZOP study, the two essential features of the design intent: (1) materials and (2) equipment and activities.

Use is made of a list of suitable guidewords. Guidewords may be generated by considering:

(1) energy sources;
(2) chemical interactions;
(3) environment.

Each of these headings may be broken down further. A suitable energy set is a list of the main forms of energy.

(1) People
(2) Materials
(3) Equipment.

The study results in a set of work assignments to follow-up the queries raised. As an illustration, the block layout might show a storage tank containing flammable liquids. The application of the guideword 'fire' to this tank might raise a number of queries. Amongst those that may be considered are (1) frequency of fire, (2) detection of fire, (3) access for firefighting, (4) method of firefighting, (5) source and disposal of fire water, (6) use of alternative firefighting agents, (7) nature of combustion products, (8) effects of radiant heat and (9) need for a disaster plan.

8.12 Hazard and Operability Studies

The HAZOP study is carried out when the ELD (piping and instrument diagram) of the plant becomes available. Accounts of HAZOP studies are given in the CIA *HAZOP: Guide to Best Practice* (CIA 1999), in HAZOP and Hazan (Kletz, 1983d, 1986d, 1992b), Guidelines for Hazard Evaluation Procedures (CCPS, 1985/1, 1992/9) (the CCPS *Hazard Evaluation Guidelines*) and *A Manual of Hazard and Operability Studies* (Knowlton, 1992), and by Kletz (1972a), S.B. Gibson (1974, 1976b,e), Lawley (1974a,b) and Kavianian, Rao and Brown (1992).

The following description is based on those given in the CIA *HAZOP: Guide to Best Practice* and by Lawley (1974b). The study is carried out by a multi-disciplinary team, which reviews the process to discover potential hazards and operability problems using a guideword approach. It is essentially an application of the technique of critical examination.

The basis of such a study may, in principle, be a process flow diagram (PFD), piping and instrument diagram (P&ID) or other information, which reveals the design intent. The basis of a HAZOP study is generally the ELD (P&ID) supplemented, as appropriate, by other information such as operating instructions, MSDSs, details of metallurgy, process control information, etc.

The HAZOP study technique is not a substitute for good design. There is something fundamentally wrong if the application of the method consistently reveals too many basic design faults.

8.12.1 Origins of HAZOP studies

The origins of HAZOP studies were in ICI in the 1960s. As with many techniques, there is more than one source which can lay claim to have been influential in its development. Accounts of the development of HAZOP have been given by Kletz (1986d) and in the Chemetics *Manual* (Knowlton, 1992).

The techniques, which eventually grew into HAZOP, developed at a time when the applications of method study, including critical examination, were being explored. Accounts of work in the Heavy Organic Chemicals Division of ICI (Binsted, 1960) and in the Mond Division (Elliott and Owen, 1968) describe the development of HAZOP in terms of critical examination.

8.12.2 Principle of HAZOP studies

The basic concept of the HAZOP study is to take a full description of the process and to question every part of it to discover what deviations from the intention of the design can occur and what the causes and consequences of these deviations may be. This is done systematically by applying suitable guidewords. Thus important features of the study are:

(1) design intent;
(2) deviations from intent;
(3) causes of deviations;
(4) consequences
  (a) hazards,
  (b) operating difficulties.

8.12.3 Design intent and entities examined

The design intent is examined in respect of the following entities:

(1) material;
(2) activity;
(3) equipment;
(4) source;
(5) destination.

In some applications, other relevant entities are:

(6) time;
(7) space.

Table 8.18 *What if method?: checklist for simplified process hazard analysis (Burk, 1992) (Courtesy of the American Institute of Chemical Engineers)*

Storage of raw materials, products, intermediates	
Storage tanks	Design separation, Inerting, Materials of construction
Dikes	Capacity, Drainage
Emergency valves	Remote control-hazardous materials
Inspections	Flash arresters, Relief devices
Procedures	Contamination prevention, Analysis
Specifications	Chemical, Physical, Quality, Stability
Limitations	Temperature, Time, Quantity
Materials handling	
Pumps	Relief, Reverse rotation, Identification of materials of construction
Ducts	Explosion relief, Fire protection, Support
Conveyors, Mills	Stop devices, Coasting, Guards
Procedures	Spills, Leaks, Decontamination
Piping	Rating, Codes, Cross-connections, Materials of construction
Process equipment, facilities and procedures	
Procedures	Start-up, Normal, Shut-down, Emergency
Conformance	Job audits, Shortcuts, Suggestions
Loss of utilities	Electricity, Heating, Coolant air, Inerts, Agitators
Vessels	Design, Materials, Codes, Access, Materials of construction
Identification	Vessels, Piping, Switches, Valves
Relief devices	Reactors, Exchangers, Glassware
Review of incidents	Plant, Company, Industry
Inspections, Tests	Vessels, Relief devices, Corrosion
Hazards	Hang-fires, Runaways
Electrical	Area classification, Conformance, Purging
Process	Description, Test authorizations
Operating ranges	Temperature, Pressure, Flows, Ratios, Concentrations, Densities, Levels, Time, Sequence
Ignition sources	Peroxides, Acetylides, Friction, Fouling, Compressors, Static electricity, Valves, Heaters
Compatibility	Heating media, Lubricants, Flushes, Packings
Safety margins	Cooling, Contamination
Personnel protection	
Protection	Barricades, Personal, Shower, Escape aids,
Ventilation	General, Local, Air intakes, Rate
Exposures	Other processes, Public environment
Utilities	Isolation: Air, Water, Inerts, Steam
Hazards manual	Toxicity, Flammability, Reactivity, Corrosion, Symptoms, First aid
Environment	Sampling, Vapours, Dusts, Noise, Radiation
Controls and emergency devices	
Controls	Ranges, Redundancy, Fail-safe
Calibration, Inspection	Frequency, Adequacy
Alarms	Adequacy, Limits, Fire, Fumes
Interlocks	Tests, Bypass procedures
Relief devices	Adequacy, Vent size, Discharge, Drain, Support
Emergencies	Dump, Drown, Inhibit, Dilute
Process isolation	Block valves, Fire-safe valves, Purging
Instruments	Air quality, Time lag, Reset windup, Materials of construction
Waste disposal	
Hatches	Flame traps, Reactions, Exposures, Solids
Vents	Discharge, Dispersion, Radiation, Mists
Characteristics	Sludges, Residues, Fouling materials
Sampling facilities	
Sampling points	Accessibility, Ventilation, Valving
Procedures	Pluggage, Purging
Samples	Containers, Storage, Disposal
Analysis	Procedures, Records, Feedback
Maintenance	
Decontamination	Solutions, Equipment, Procedures
Vessel openings	Size, Obstructions, Access
Procedures	Vessel entry, Welding, Lockout

Table 8.18 *(continued)*

Fire protection	
Fixed protection	Fire areas, Water demands, Distribution system, Sprinklers, Deluge, Monitors, Inspection, Testing, Procedures, Adequacy
Extinguishers	Type, Location, Training
Fire walls	Adequacy, Condition, Doors, Ducts
Drainage	Slope, Drain rate
Emergency response	Fire brigades, Staffing, Training equipment

Table 8.19 *What if? method: results for a high pressure/low density polyethylene plant (Kavianian, Rao and Brown, 1992)*

What if	*Consequence/hazard*	*Recommendations*
Coolant pump to reactor fails	Runaway condition in reactor explosion/fatality	• Provide accurate temperature monitoring in reactor • Employ backup pump/high temperature alarm • Relieve reactor pressure in reactor through automatic control to stop reactions • Provide automatic shut off of ethylene flow
Coolant temperature to jacket is high	Eventual runaway condition in reactor	• Provide adequate temperature control on coolant line • Use heat exchanger flow control to adjust inlet temperature
Runaway condition in reactor	Explosion; fire/fatality	• Provide adequate temperature control on coolant line • Use heat exchanger flow control to adjust inlet temperature • Install rupture disk/relief valve to relieve pressure to stop reactions • Emergency shut-down procedure
Recycle gas compressor 1 or 2 fails	None likely	• Provide spare compressor or shut-down procedure
Melt pump fails	High level in reactor causing more polymerization: runaway reaction eventually exceeds design pressure	• Provide level and flow control schemes to activate spare pump or shut the flow of monomer • Shut-down procedure if no spare pump
Leak at suction or discharge of compressors	Fire; explosion	• Use monitoring devices to ensure no flammable gas is released
Ethylene leaks out of process lines	Fire; explosion	• Provide adequate flammable gas monitoring devices
Monomer/initiator ratio out of control	Eventual runaway reaction causing fire and explosion	• Provide flow control on the initiator and monomer lines

8.12.4 Guidewords

To each of these above entities, there is applied a basic set of guidewords. These guidewords and their meanings are:

NO or NOT	Negation of intention
MORE	Quantitative increase
LESS	Quantitative decrease
AS WELL AS	Qualitative increase
PART OF	Qualitative decrease
REVERSE	Logical opposite of intention
OTHER THAN	Complete substitution

The application of these guidewords is illustrated by some of the examples discussed below. It is usually possible to apply all the guidewords intelligibly to activities and, with the possible exception of REVERSE, to substances.

In applying the guidewords to time, the following aspects may be relevant: duration, frequency, absolute time and sequence. The guidewords MORE and LESS are applicable for duration or frequency, while the guidewords SOONER and LATER may be more applicable than OTHER THAN for absolute time or sequence.

Similarly, in applying the guidewords to space, or place, the following aspects may be relevant: position, source and destination. The guidewords HIGHER or LOWER may be more applicable than MORE or LESS for elevation, while the guideword WHERE ELSE may be more applicable than OTHER THAN for position, source or destination.

Table 8.20 *Preliminary hazard analysis (Kavianian, Rao and Brown 1992)*

Hazard	*Cause*	*Major effects*	*Corrective/preventive measures*
Damage to feed reactor tubes	Feed compressor failure (no endothermic reactions in reactor)	Capital loss, down-time Damage to the furnace coils due to high temperature	• Provide spare compressor with automatic switch-off control • Develop emergency response system
Explosion, fire	Pressure build-up in the reactor due to plug in transfer lines	Fatalities, injuries	• Provide pressure relief valve on the reactor tubes • Provide warning system for pressure fluctuations (high-pressure alarm) • Provide auxiliary lines with automatic switch off
	Violent reaction of H_2 to acetylene converter with air in presence of ignition source	Potential for injuries and fatalities due to fire or explosion	• Provide warning system (hydrogen analyser) • Eliminate all sources of ignition near hydrogen gas storage area • Develop emergency fire response • Automatically shut off the H_2 feed • Provide firefighting equipment
Flammable gas release	Ethane storage tank ruptures	Potential for injuries and fatalities due to fire or explosion	• Provide warning control system (pressure control) • Minimize on-site storage • Develop procedure for tank inspection • Develop emergency response system • Provide gas monitoring system
Flammable gas release	CH_4 storage tank (line) leak/rupture (fuel for the furnace)	Potential for injuries and fatalities due to fire or explosion	• Provide warning system • Minimize on-site storage • Develop procedure for tank inspection • Develop emergency response system • Provide gas monitoring system
Flammable gas release	Radiant tube rupture in the furnace	Potential for injuries and fatalities due to fire	• Improve reactor materials of construction • Monitor design vs operating reactor temperature • Provide temperature control instrument
Employee exposure to benzene (carcinogen)	Leak in knock-out pots or during handling benzene	Chronic health hazard	• Install warning signs in the area • Provide appropriate PPE • Develop safety procedures for handling and cleanup • Monitor concentration of benzene in area to meet TLV requirements
Fire/explosion in acetylene converter	Runaway reaction (exothermic)	Fatality, injury, or loss of capital	• Install temperature control on converter • Install pressure relief on reactor responding to temperature control
Flammable atmosphere	Leak in transfer lines	Fire/explosion	• Install combustible gas meter in sensitive areas • Provide adequate firefighting equipment • Provide for emergency shut-down • Educate and train personnel on emergency procedures

Some additional guidewords include

STARTING
STOPPING
CONTROLLING
ISOLATION
INGRESS
ESCAPE
DECONTAMINATION

8.12.5 Illustrative example: reactor transfer system

The following example is given, which serves to illustrate both the basic examination principle and the detailed use of the guidewords. The flow sheet of a reactor system shows that raw material streams A and B are transferred by pump to the reactor, where they react to give product C. The flow of B should not exceed that of A, otherwise an explosion may occur. The flow sheet thus shows an intention to TRANSFER A to the reactor at the design flow. Applying the first guideword NO, NOT or DONT to this intention gives:

DON'T TRANSFER A

This is a deviation from intent. Some causes might be that the supply tank is empty, that the pipe is fractured or that an isolation valve is closed. A consequence might be an explosion due to an excess of B. Thus, the examination has discovered a hazard. The study is continued using further guidewords such as MORE, LESS, etc.

The application of the guidewords may be illustrated by the example already described: TRANSFER A. The guidewords may be applicable to either the word TRANSFER or to the word A. Thus, for this case, the meanings might include the following:

NO or NOT	No flow of A
MORE	Flow of A greater than design flow intent
LESS	Flow of A less than design flow intent
AS WELL AS	Transfer of some component other than A Occurrence some operation event additional to TRANSFER
PART OF	Failure to transfer all components of A Failure to achieve all that is implied by TRANSFER
REVERSE	Flow of A in direction opposite to design direction
OTHER THAN	Transfer of some material other than A Occurrence of some operation event other than TRANSFER

8.12.6 Organization and conduct of HAZOP studies

The stages in the conduct of a HAZOP study are:

(1) Definition of objectives and study scope;
(2) Selection of multi-disciplined team;
(3) Preparation;
(4) Conduct/facilitate;
(5) Record/document study;
(6) Preparation of HAZOP study report.

In general, the objectives of a HAZOP study as originally defined are to check the design intent and the operating procedures/conditions in order to identify hazards and operability problems, to which, increasingly, are added environmental issues.

Closely associated with these are checks on (1) information still lacking, (2) particular equipments, (3) supplier information, (4) plant phases (start-up, shut-down) and (5) maintenance procedures, and on entities to be protected such as (1) persons working on the unit, (2) others on the site, (3) the public, (4) the plant and (5) the environment.

A multi-disciplinary team is used to conduct the HAZOP study. The team should contain people from design and from operations who can cover the main relevant disciplines, who are senior enough to make on-the-spot decisions and who personally attend all the meetings, but the team size should be kept fairly small.

A good deal of preparation is needed prior to the HAZOP study. This includes (1) deciding on the type of study required, (2) acquisition of the information, (3) validation of the information, (4) conversion of the information to suitable form, (5) planning of the study sequence and (6) arrangement of the schedule of meetings. The detailed sequence of an examination is illustrated in Figure 8.7.

There are a number of factors, which are important for the success of the method. The study should have a clearly defined objective. The study leader (facilitator) should be experienced in the analysis technique but not necessarily in the particular process. The role of the study leader is crucial and the study leader must be adequately trained. The preparative work should be done carefully so that all the necessary documents are to hand and are accurate and up-to-date.

The study uses a formal, even mechanistic, approach and the questions raised may in some cases appear unrealistic or trivial. It is important to emphasize, however, that the approach is intended as an aid to the imagination of the team in visualizing deviations and their causes and consequences. The effectiveness of the technique depends very much on the spirit in which it is done.

More complete and detailed discussions of the organizational aspects of HAZOP studies are given in the CIA *Guide*.

8.12.7 Parametric method

As so far described, the focus of a HAZOP study is on the design intent. There is also a 'parametric method', distinguishable from the classic form, which concentrates on the deviations from design conditions.

This approach was originally developed in ICI Mond Division in response to the need to carry out a large number of HAZOP studies on existing plants. The method uses a hazard guide sheet. An early version of this guide sheet was reproduced in the first edition of this book, a later version from ICI is shown in Figure 8.8.

8.12.8 Illustrative example: continuous plant

As an illustration of a HAZOP study of a continuous process, consider the example given by Lawley (1974b). The proposed design is shown in Figure 8.9.

The process description is:

> An alkene/alkane fraction containing small amounts of suspended water is continuously pumped from bulk intermediate storage via a half-mile pipeline section into a buffer/settling tank. Residual water is settled out prior to passing via a feed/product heat exchanger and preheater to the reactor section. The water, which has an adverse effect on the dimerization reaction, is run off manually from the settling tank at intervals. Residence time in the reaction section must be held within closely

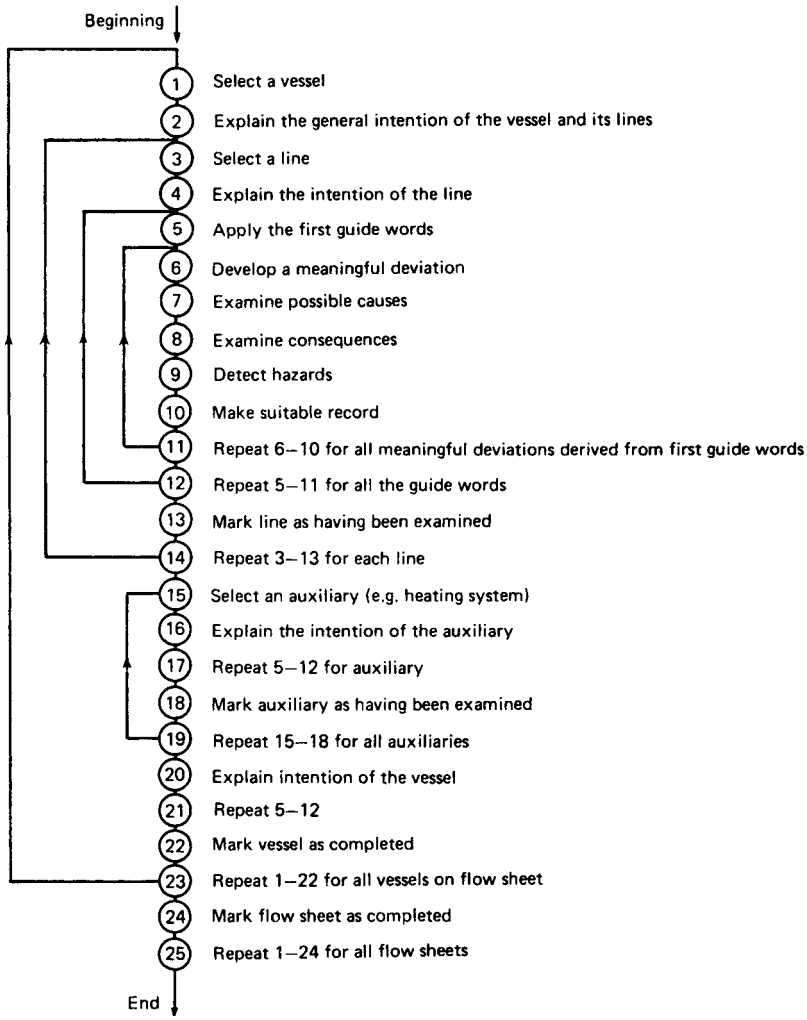

Figure 8.7 *Hazard and operability studies: detailed sequence of examination (Chemical Industry Safety and Health Council, 1977/3)*

defined limits to ensure adequate conversion of the alkene and to avoid excessive formation of polymer.

A summary of the results of a study for the first line section from the intermediate storage up to the buffer/settling tank is given in Table 8.21. A further table showing the results for the second line section is given in Lawley's paper.

For a continuous plant, the study should include the operability of the plant during commissioning and during regular start-up and shut-down. There are generally a number of operations, which are carried out only during these periods.

8.12.9 Time in HAZOP studies: sequences/batch processes

The HAZOP technique is applicable both to batch processes and to sequential operations on continuous plants such as start-up, shut-down and emergency shut-down. This introduces time as an additional factor to be taken into account. An adaptation of the set of guidewords applicable to time has been given in Section 8.12.4.

For batch and sequential operations, the following classification of activities are considered:

(1) make ready;
(2) key;
(3) put away.

'Key' is the activity which progresses the process, 'make ready' is the activity needed to prepare for the key activity, and 'put away' is the activity needed on completion of the key activity.

8.12.10 Illustrative example: batch plant

For a batch plant, the working documents comprise not only the flow diagram but also the operating procedures. Several documents may be needed to cover the latter, such

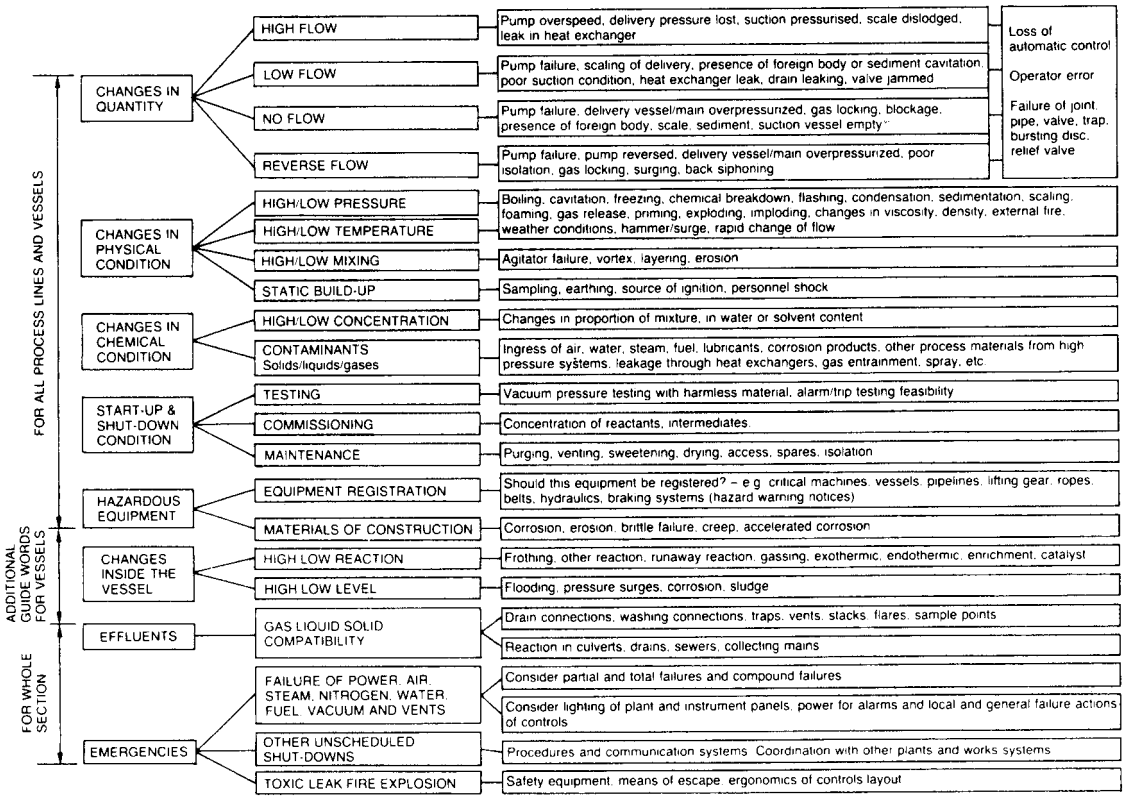

Figure 8.8 *Hazard and operability studies: hazard guide sheet (Imperial Chemical Industries Ltd, 1994)*

as tables giving the operating sequences, bar charts showing the states of equipment during the cycle and flow charts indicating the operator's movements.

As an illustration of a HAZOP study of a batch plant, consider the following example. The design is shown in a simplified diagram in Figure 8.10. The plant consists of two measure vessels, four reaction vessels, a condenser, an absorption tower with its circulation system and a Nutsche filter with its filtrate receiver.

The development of the study depends on the kind of sequence to be followed. In this case it is possible to follow a sequence derived from the flow diagram or one derived from the operating instructions. Assuming that the latter is used, an instruction part way through the sequence might be:

Instruction 23 Charge 100 l of material C from drum to the general purpose vessel using the air ejector.

Such an instruction is quite adequate for operational purposes, but it is too complex for the generation of deviations in the study, and needs to be broken down into the part dealing with the air ejector and that dealing with the liquid transfer. Thus the leader may ask a member of the team to describe the purpose of the air ejector, which might be stated as: 'Remove some air from measure vessel'. The guidewords may then be applied to the statement.

A summary of the results of a study of this batch plant for the operation 'Remove some air from measure vessel' is given in Table 8.22.

8.12.11 Illustrative example: proprietary equipment

As an illustration of a study of proprietary equipment, consider a sterilization autoclave design example given in Figure 8.11. The process description is:

> Sterilization of stillage-loaded materials is achieved by treatment with steam humidified sterilizing gas in a jacketed autoclave chamber under specified conditions. Two entries are provided to the chamber – from the sterile and from the non-sterile working areas of the facility.
> Steam is admitted to the chamber via a letdown system and sterilizing gas via a vaporizer. The chamber may be evacuated via a cooler either directly to drain or via a luted sealed catchpot to a vent stack. Filtered atmospheric air may be admitted via a non-return valve. A relief valve is fitted to the chamber, which exhausts to the vent stack and may be by-passed by opening a vent valve if it is required to dump the contents to stack. Water is circulated through the jacket and heated indirectly by means of steam.
> Once the autoclave is charged and the doors closed, automatic sequence control takes over and programmes the process as shown in Figure 8.12. The machine itself checks the progress of the process cycle, monitoring the status of the chamber and auxiliaries. Certain checks [see

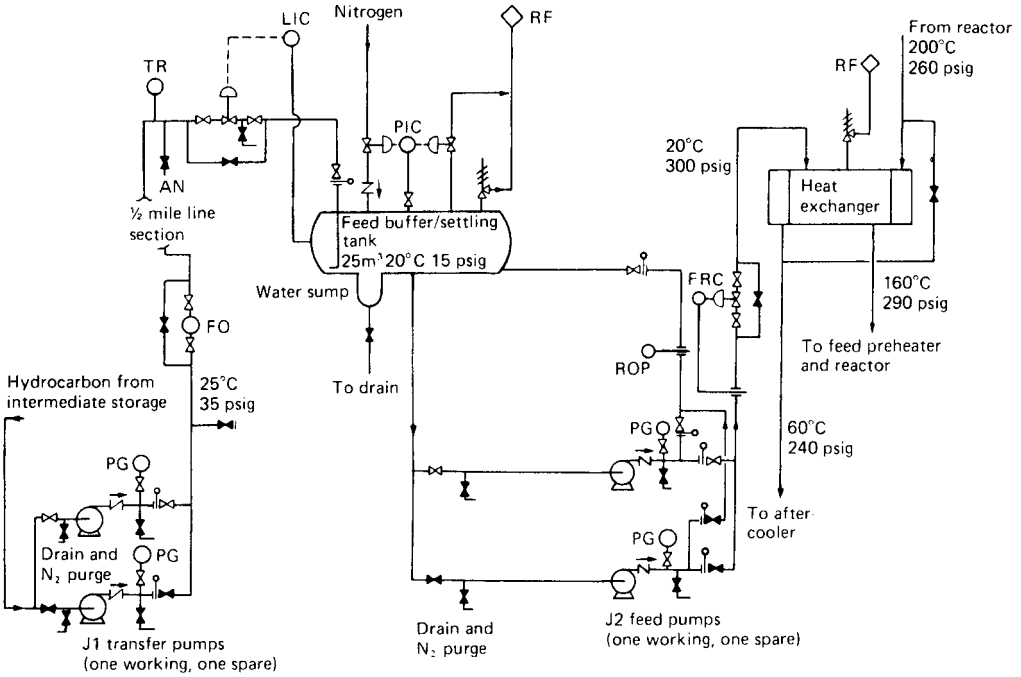

Figure 8.9 *Hazard and operability studies: feed section of proposed alkene dimerization plant (Lawley, 1974b) (Courtesy of the American Institute of Chemical Engineers)*

Figure 8.12: Autochecks] control progress in association with timers.

For an equipment of this kind, it is also possible to produce a flow process chart for the different operations of the cycle. A chart for the operation 'Charging autoclave' is shown in Figure 8.13.

The development of this study again depends on the choice of sequence to be followed. In this case there are a number of possible sequences that might be followed. Three of these are the flow diagram, the sequence diagram (dot chart) and the flow process chart shown in Figures 8.11–8.13, respectively.

A summary of the results of a study of this equipment for the operation 'Humidify autoclave chamber' derived from the flow diagram is given in Table 8.23.

8.12.12 Space and interactions in HAZOP studies: hybrid studies

In their classic form, HAZOP studies are essentially concerned with conditions inside the plant, including loss of containment from it. They do not address, however, any interaction in space between the plant and other plants nearby or the environment.

A technique for dealing with such problems is a hybrid approach, utilizing both creative checklists and guidewords. The method involves nominating a 'top event', which is then examined to identify its causes, using both a checklist of potential causes and guidewords.

8.12.13 Critical examination and HAZOP studies

As stated at the outset, HAZOP studies developed from the technique of critical examination. In some applications it may be useful to revert to the latter. A critical examination may be carried out by examining the design intent in respect of material, activities, equipment, source and destination.

The classic guidewords of critical examination may include:

WHAT	The design intent
HOW	Method and resources: materials, activities, equipments
WHEN	Time aspects: sequence, frequency, duration, absolute time
WHERE	Space aspects: relative location, sources and destinations, dimensions, absolute location
WHO	Persons or controls: person, skills, organization, control system

8.12.14 Control systems in HAZOP studies

The HAZOP study methodology was developed originally for plants operating under the control of analogue controllers. The methodology may be adapted to the examination of a plant operated through Distributive Control System (DCS).

8.12.15 Electrical systems in HAZOP studies

The treatment of electronic control and interlock systems and electrical distribution systems in a HAZOP is described by Mitchell (1992 LPB 105).

The headings used in his account for electronic control and interlock systems are: current, voltage, temperature, contamination, high current protection, instruments,

Table 8.21 *Hazard and operability studies: results for feed section of proposed alkene dimerization plant from intermediate storage to buffer/settling tank (Lawley, 1974b) (Courtesy of the American Institute of Chemical Engineers)*

Guide word	*Deviation*	*Possible causes*	*Consequences*	*Action required*
NONE	No flow	(1) No hydrocarbon available at intermediate storage	Loss of feed to reaction section and reduced output. Polymer formed in heat exchanger under no flow conditions	(a) Ensure good communications with intermediate storage operator. (b) Install low level alarm on settling tank LIC
		(2) J1 pump fails (motor fault, loss of drive, impeller corroded away, etc.)	As for (1)	Covered by (b)
		(3) Line blockage, isolation closed in error, or LCV fails shut	As for (1) J1 pump overheats	Covered by (b) (c) Install kick-back on J1 pumps (d) Check design of J1 pump strainers
		(4) Line fracture	As for (1) Hydrocarbon discharged into area adjacent to public highway	Covered by (b) (e) Institute regular patrolling and inspection of transfer line
MORE OF	More flow	(5) LCV fails open or LCV bypass open in error	Settling tank overfills	(f) Install high level alarm on LIC and check sizing relief opposite liquid overfilling (g) Institute locking off procedure for LCV bypass when not in use
			Incomplete separation of water phase in tank, leading to problems on reaction section	(h) Extend J2 pump suction line to 12 in. above tank base
	More pressure	(6) Isolation valve closed in error or LCV closes, with J1 pump running	Transfer line subjected to full pump delivery or surge pressure	(j) Covered by (c) except when kick-back blocked or isolated. Check line, FQ and flange ratings, and reduce stroking speed of LCV if necessary. Install a PG upstream of LCV and an independent PG on settling tank
		(7) Thermal expansion in an isolated valved section due to fire or strong sunlight	Line fracture or flange leak	(k) Install thermal expansion relief on valved section (relief discharge route to be decided later in study)
	More temperature	(8) High intermediate storage temperature	Higher pressure in transfer line and settling tank	(l) Check whether there is adequate warning of high temperature at intermediate storage. If not, install

Table 8.21 *(continued)*

Guideword	*Deviation*	*Possible causes*	*Consequences*	*Action required*
LESS OF	Less flow	(9) Leaking flange or valved stub not blanked and leaking	Material loss adjacent to public highway	Covered by (e) and the checks in (j)
	Less temperature	(10) Winter conditions	Water sump and drain line freeze up	(m) Lag water sump down to drain valve, and steam trace drain valve and drain line downstream
PART OF	High water concentration in stream	(11) High water level in intermediate storage tank	Water sump fills up more quickly. Increased chance of water phase passing to reaction section	(n) Arrange for frequent draining off of water from intermediate storage tank. Install high interface level alarm on sump
	High concentration of lower alkanes or alkenes in stream	(12) Disturbance on distillation columns upstream of intermediate storage	Higher system pressure	(o) Check that design of settling tank and associated pipework, including relief valve sizing, will cope with sudden ingress of more volatile hydrocarbons
MORE THAN	Organic acids present	(13) As for (12)	Increased rate of corrosion of tank base, sump and drain line	(p) Check suitability of materials of construction
OTHER	Maintenance	(14) Equipment failure, flange leak, etc.	Line cannot be completely drained or purged	(q) Install low point drain and N_2 purge point downstream of LCV. Also N_2 vent on settling tank

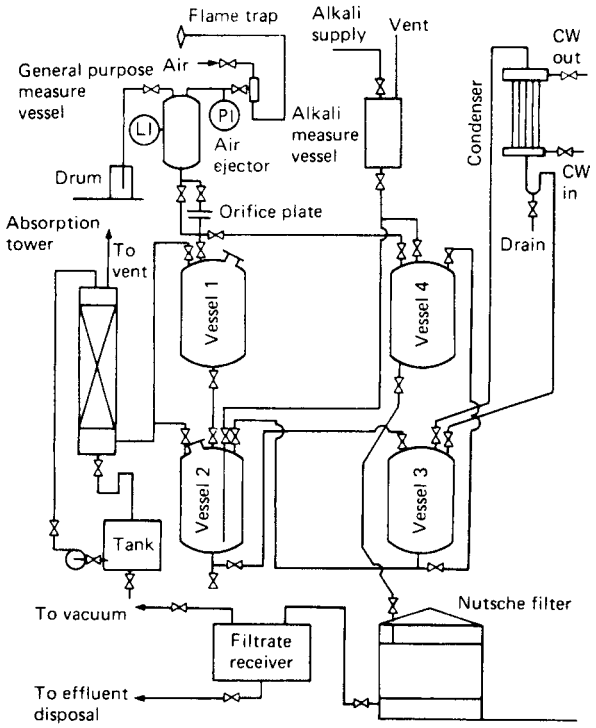

Figure 8.10 *Hazard and operability studies: batch plant (simplified diagram) (Chemical Industry Safety and Health Council, 1977/3)*

Table 8.22 *Hazard and operability studies: results for batch plant for operation 'Remove some air from measure vessel' (Chemical Industry Safety and Health Council, 1977/3)*

Deviations	*Causes*	*Consequences*
DON'T REMOVE AIR	No air supply Faulty ejector Value shut	Process inconvenience but no hazard
REMOVE MORE AIR	Completely evacuate measure vessel	Can vessel stand full vacuum?
REMOVE LESS AIR	Insufficient suck to transfer contents of drum	Process inconvenience but no hazard
AS WELL AS REMOVE AIR	Pull droplets of material C or other materials from drums or vessels 1 or 4 along exhaust line	Fire hazard? Static hazard? Corrosion hazard? Blocked flame trap? Will material be a hazard after leaving the flame trap? Where does it go?
REMOVE PART OF AIR	Remove oxygen or nitrogen only: not possible	
REVERSE REMOVAL OF AIR	If line form air ejector is blocked, compressed air will flow into measure vessel	Overpressure vessel? Blow air into drums and spray out contents? Put air into vessels 1 or 4?
OTHER THAN REMOVE AIR	Put air ejector on when measure vessel full	Spray contents along line and out through flame trap. Similar hazards to AS WELL AS

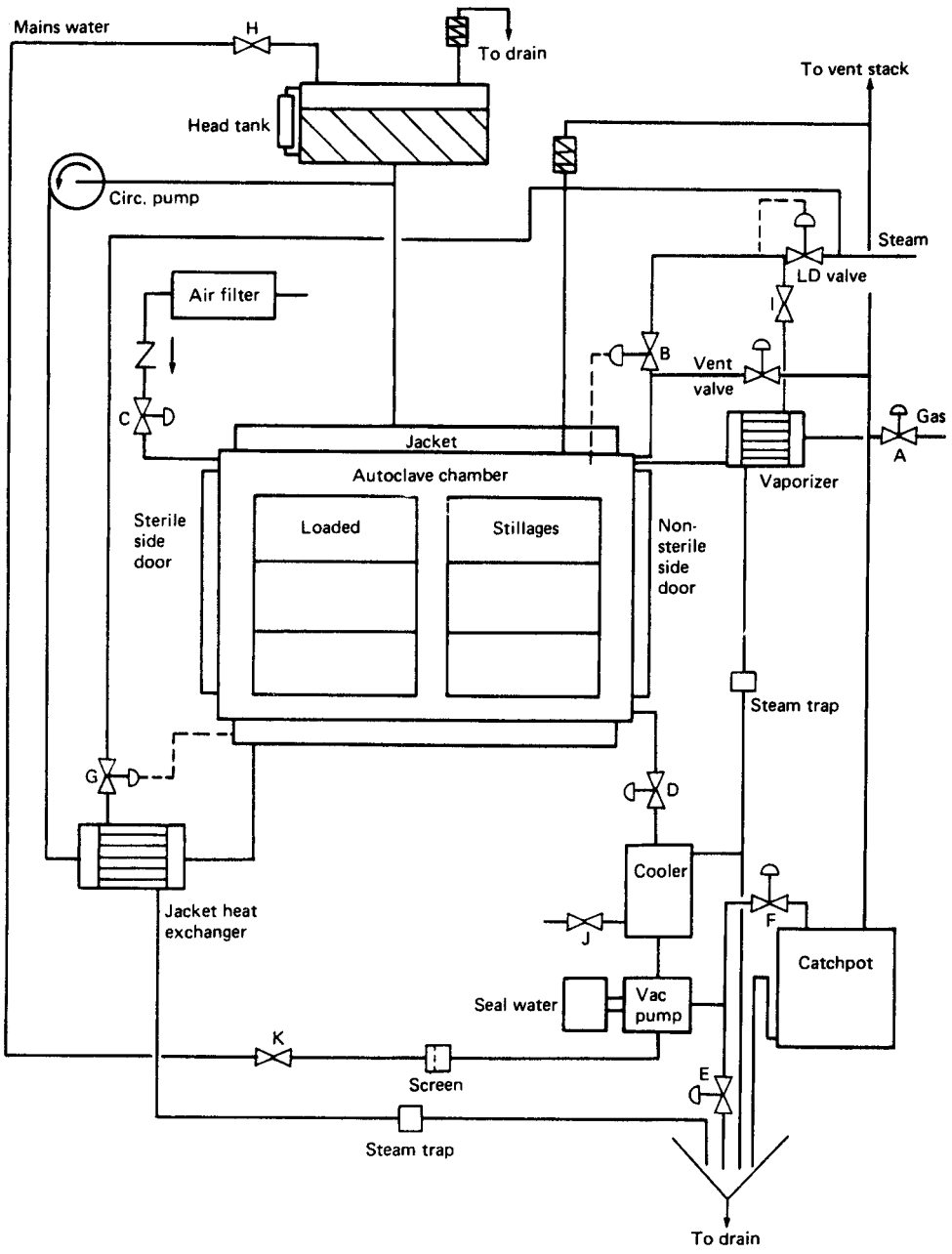

Figure 8.11 *Hazard and operability studies: autoclave arrangement (Chemical Industry Safety and Health Council, 1977/3)*

sampling, corrosion, services failure, maintenance, abnormal operations, spares, static electricity and safety. A short checklist is given under each heading. Where appropriate, as with current and voltage, guidewords such as NO, REDUCED, INCREASED, etc., are used. A basically similar list is used for electrical distribution systems.

8.12.16 Additional parameters and guidewords

Wider application of the HAZOP approach, to systems such as materials handling systems, has led to the creation of further lists of parameters and guidewords such as the one shown in Table 8.24, derived from the work by Tweeddale (1993e).

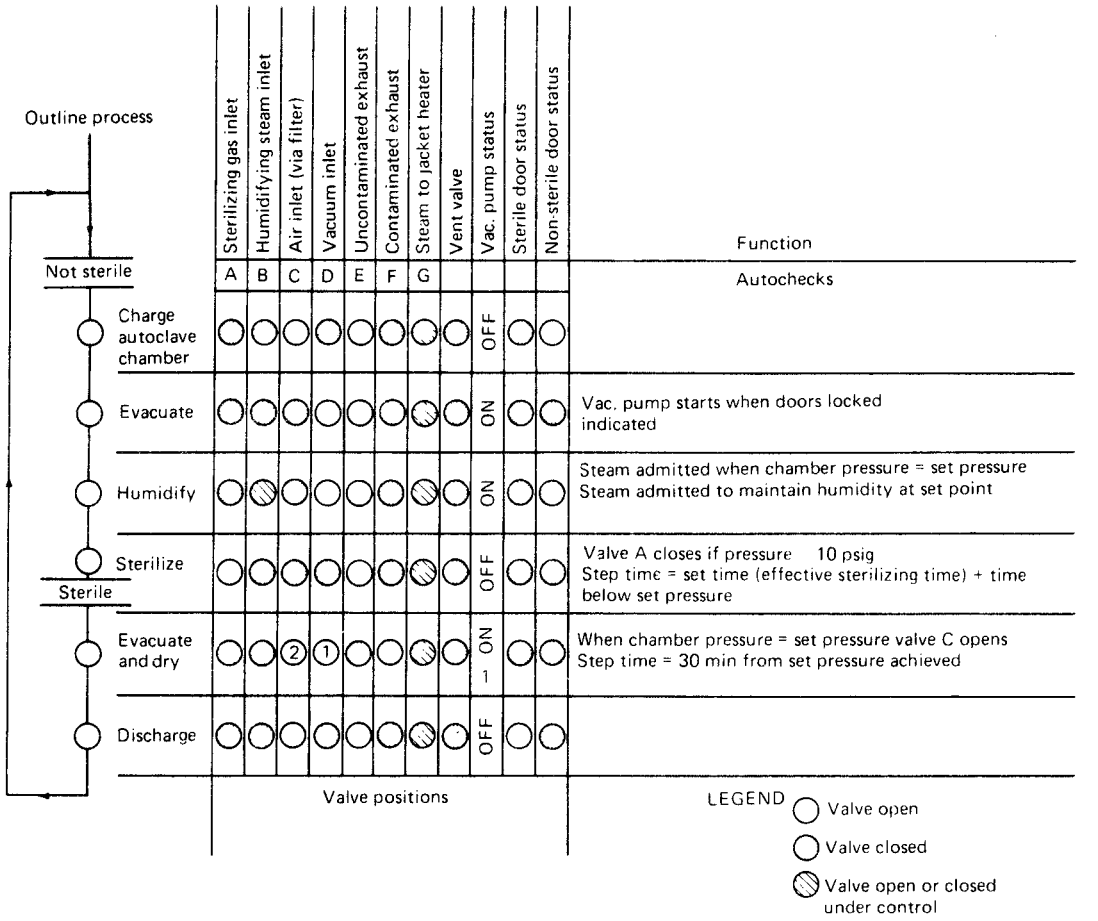

Figure 8.12 *Hazard and operability studies: sequence diagram (dot chart) for autoclave arrangement (Chemical Industry Safety and Health Council, 1977/3)*

8.12.17 Timing of HAZOP studies

The timing of a HAZOP study is an important issue. The disadvantages of an early study are that some of the information necessary to its effective conduct is not available and that there is a greater risk of design changes being made to the detriment of operability and/or safety. The advantages are that it is easier to incorporate in the design any changes arising out of the study and, in particular, to achieve an inherently safer design.

Conversely, the disadvantages of a late study are that the design response options will have been rendered more difficult and expensive to implement, or sometimes foreclosed altogether, and consequently there is a stronger tendency to solve safety problems by 'add-on' measures.

8.12.18 Documentation for hazard studies

As the design progresses, the documentation produced, including the process and plant diagrams becomes firmer and more detailed.

The most primitive document is a block diagram of the whole process, in which each block represents some operation, possibly a whole plant. Addition of flow quantities and utility usages to this diagram turns it into a quantities flowsheet.

Next come, for each of the blocks in the block diagram, the various versions of the PFD, these typically being concept, preliminary and final versions. The PFD shows the main items of equipment, utilities and effluents, and control loops.

As the design firms up, the ELD is produced, showing the in-line items, the materials of construction, the equipment sizings, the line specifications and sizings, the equipment and line code numbers, and more details of instrumentation and control loops, as well as of pipework features such as drains and lutes.

An ELD with full information on the instrumentation constitutes the P&ID.

The firm ELD or P&ID is the preferred diagram for a HAZOP study, but in some cases it may be necessary to initiate the study at some earlier stage. For a continuous process, the minimum documentation required is the ELD and the outline operating procedures. For a batch process, these need to be augmented by the operating sequence.

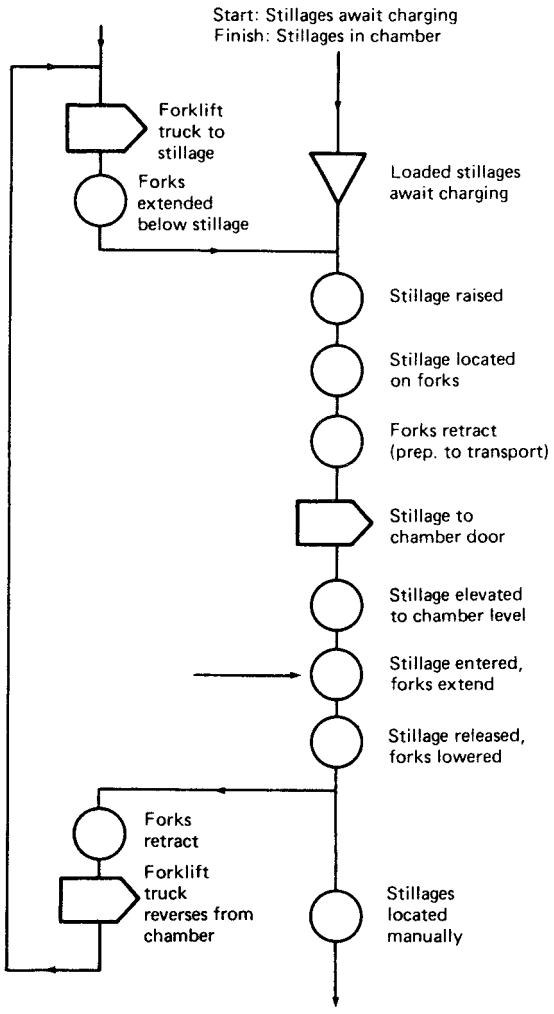

Figure 8.13 *Hazard and operability studies: flow process chart for autoclave arrangement for operation 'Charging autoclave' (Chemical Industry Safety and Health Council, 1977/3)*

8.12.19 Personnel involved in HAZOP studies

As stated earlier, a multi-disciplinary team performs the HAZOP. The team is normally composed of personnel responsible for design, commissioning and operation, but the detailed composition varies both between companies and with the type of project within a given company.

A typical team might comprise the study leader (facilitator), the project engineer, a process engineer, an instrument engineer and the commissioning manager. Other personnel who are often included, depending on the nature of the project, are a chemist, a civil engineer, an electrical engineer, a materials technologist, an operations supervisor, an equipment supplier's representative, and so on.

The technical team members provide the technical input in response to the guidewords. They are also able to amplify the information about the plant design given in the plant diagrams, operating instructions, etc. They may receive work assignments arising from the meetings and, as indicated below, one of their numbers may be appointed to act as the follow-up coordinator.

8.12.20 Leadership of HAZOP studies: the Facilitator

The role of the study leader is to act as a facilitator to bring to bear the expert knowledge of the technical team members in a structured interaction. It is not his role to identify hazards and operability problems, but rather to ensure that such identification takes place.

The study leader should be someone not directly involved in the design, but with skills as a HAZOP leader. The effectiveness of a HAZOP study is highly dependent on the skill of the study leader. Trained and experienced leaders are crucial.

The study leader is responsible for the definition of the project HAZOP; for the preparation of the meetings to be held; for arranging the schedules of meetings, and hence their timing and pacing; for assembling an appropriate team and ensuring that they understand their role, and receive training if necessary; for the provision to each study meeting of the necessary documents and other information; for the conduct and recording of the meetings; and for follow-up of matters raised during the meetings.

At the definition stage, the study leader should ensure that there is a satisfactory liaison with the client such that the latter will follow-up the results emerging from the study.

In the preparation stage, the study leader should review the extent to which the plant under consideration is similar to one already studied and how this should affect the study to be conducted. In many cases, the design is not a completely new one but constitutes a modification of an existing design. The study leader will then define the features, which are novel – raw materials, plant equipment, materials of construction, environmental conditions, etc. – and decide whether examination of certain parts can be omitted as unproductive. He should also ensure as part of the preparation that the necessary information is available and is correct.

The most elusive skill of the study leader lies in the conduct of the HAZOP meeting itself. One essential requirement is to ensure that the examination neither becomes too superficial nor gets bogged down in detail so that it identifies all the hazards but within a reasonable time-scale. Another is to manage the personal interactions between the team members, to obtain balanced contributions and to minimize the effect on individuals when the design is subject to criticism. These requirements are easily stated but constitute a significant skill.

8.12.21 Follow-up of hazard studies

The output of a HAZOP study is a set of queries concerning the design. There needs to be a formal arrangement to ensure that these are followed up. One method of doing this is to arrange that at each meeting every question raised is assigned to a specific individual to follow up and, in addition, to appoint a follow-up coordinator, preferably a member of the study team, to ensure that this is done. A common practice is to assign to this role a person with line responsibility such as the project manager.

Follow-up is one of the prime functions of computer packages developed to assist HAZOP.

Table 8.23 *Hazard and operability studies: results for autoclave arrangement for operation 'Humidify autoclave chamber' (Chemical Industry Safety and Health Council, 1977/3)*

Deviations	*Causes*	*Consequences*
DON'T HUMIDIFY	Valve B not open LD valve closed Steam line choked Vent valve open All steam to vaporizer Line fractured	Hazard to product – sterilizing gas not effective dry
MORE HUMIDIFY	Too much steam – LD valve failed open	Could chamber be overpressured? Is relief valve sized for full bore ingress of steam to chamber?
	Too high steam pressure/temperature	Is product temperature/pressure sensitive? Effect of high temperature and pressure on sealing components of autoclaves, e.g. door seals?
LESS HUMIDIFY	Too little steam, too low steam pressure/temperature	Is condensation on product deleterious?
AS WELL AS HUMIDIFY	Contaminants in steam, e.g. CO_2, condensation, air, rust, etc.	Effect on product?
	Sterilizing gas (valve A passing)	Waste gas by evacuation. Gas into plant atmosphere – is second isolation valve required?
	Air (valve C passing)	Reduces effectiveness of humidification
	Contaminants from vent stack (vent valve passing)	Might induce gases from other autoclaves
	Plant atmosphere (door seals leaking)	No hazard at this stage, but could be leak at sterilizing stage
	Vacuum pump fails	Contaminants from drain enter autoclave
PART OF HUMIDIFY	Steam in but loss of vacuum pump (or valve D closes)	Chamber will be partly pressurized. Load very wet, temperature too high. Chamber partly filled with water. Cycle will continue and sterilizing gas may not enter due to back pressure
	Vacuum, but no steam in	Cycle will continue; if lack of humidity is not detected and action taken, load will *not* be sterile
REVERSE HUMIDIFY	Vacuum drying	No steam in, as above
OTHER THAN HUMIDIFY	Sterilize by omission of humidifying step	Cycle will continue – load will not be sterile (as above)

8.12.22 Computer aids for HAZOP studies

There are a number of computer programs available to assist in the housekeeping aspects of HAZOP studies. These are covered in Chapter 29. These programs are distinct from codes, which perform hazard identification by emulating HAZOP studies. Developments in this area are described in Chapter 30.

8.12.23 Experience and further development of HAZOP studies

The HAZOP study has been found to be an effective technique for discovering potential hazards and operating difficulties at the design stage. Reductions of at least an order of magnitude in the number of hazards and problems encountered in operation due to such studies have been claimed.

The technique has become firmly established in the process industries, in small as well as large companies, as a prime, or the prime, method of hazard identification. In those companies where the method is used, HAZOP studies have tended to become an appreciable proportion of the design effort.

The account of the technique given above has followed the original emphasis on the deviations of process variables. Application of the technique has led to its extension particularly to the various activities of operation and maintenance, which are the source of many other deviations.

Not surprisingly, the widespread use of the technique has also led to the development of local variants and to adaptations to the needs of the particular companies using it. The HAZOP study technique has also been extended to cover other concerns such as the environment. In some cases, the same study is used to cover, on the one hand, safety and operability and, on the other, environment. Some HAZOP studies given in the literature are listed in Table 8.25.

Table 8.24 *Hazard and operability studies: some additional parameters and guidewords (after Tweedale, 1993e)*

Process variables	Flow	High; low; reverse; two-phase; leak
	Level	High; low
	Temperature	High; low
	Pressure	High; low; vacuun
	Load	High; low
	Viscosity	High; low
	Quality	Concentration/proportion; impurities; cross-contamination, side reactions; particle size; viscosity; water content; inspection and testing
Plant states	Commissioning and start-up	Statutory approvals; compliance checking; sequence of steps; supervision, training
	Shut-down	Isolation; purging; cleaning
	Breakdown	Fail-safe response; loss of utilities; emergency procedures
Production	Throughput	Sources of unreliability/unavaliability; bottlenecks
	Efficiency	
Materials of construction		Corrosion; erosion; wear; chilling; compatibility; sparking
Plant layout	Access	Operation; maintenance; escape; emergency response
	Space	(For housekeeping, work in progress, escape) Cramped; wasted
	Electrical safety	Hazardous area classification; electrostatic discharge and earthing: lightning protection
Utilities		Air; nitrogen; steam; electrical power; water: process, hot/cold, demineralized, drinking: drainage
Machinery	Machinery	Overload; malfunction; foreign body; rotation: fast, slow; jamming/seizing; frictional overheating; mechanical failure/fracture; impact; valve blockage: mechanical, low temperature; interlocks
	Assembly	Component missing, extra, or wrong; assembly sequence wrong; screwed wrong: (too tight, too loose): crossed/contaminated thread; shielding
	Incompatibility	Tools and equipment material: foreign objects
Materials handling	Speed	Fast; slow; unbalanced
	Packaging	Filling (over, under); damage (external, internal); poor sealing: legal requirements; labelling
	Physical damage	Impact; dropping; vibration
	Stoppages	Breakage; blockage; jamming; loss of feed; loss of packaging; advance warning; rectification
	Direction	Upwards; downwards: to one side; reverse
	Spillage	Spillage: into product, into other materials. Spillage: outside equipment, outside plant
	Location	Wrong: vertical, horizontal; orientation
Stockholding	Stockholding	Failed stock rotation: poor storage (water, vermin); storage of consumables (spares, tools, paints/solvents); storage of raw materials
Hazards	Fire and explosion	Prevention; detection; separation; protection; control
	Toxicity	Acute; long-term; ventilation; control
	Ignition	Friction: impact: static electricity; degraded electricals; failed earthing; mechanical sparling: misalignment; high temperature; dropped objects
	Environment	Housekeeping; dust, spillage, scrap/residues: humidity high, low; ventilation failure
	Environmental control	Effluents: gaseous, liquid, solid; noise; monitoring
Targets	Severity	Quantity exposed; protection and adequacy; venting; personnel escape: unplanned exposure: dust, maintenance, protection malfunction, propagation via duct
	Operator injury	Heavy lifting; repetitive motion; exposure: dust, fume, heat; falling, slipping, tripping
Reactions	Reaction rate	Fast; slow
Control and protection	Control	Sensor and display location; response speed; interlocks
	Protection	Response speed; element common with control loop: sensor, valve, operator; remote actuation; venting; testing
	Safety equipment	Personal equipment; showers
Sequences	Timing	Duration/dwell; rate of approach; sequence; start too early, late: stop too early, late
Testing	Testing	Raw materials; products; equipment; protective instrumentation: alarms, interlocks, trips; protective equipment

Table 8.25 *Selected hazard and operability studies*

Author(s)	*Subject of study*
Lawley (1974b)	Feed section of olefine dimerization plant
Lawley (1976)	Ethylene oxide feed system for batch reactors
CIHSC (1977/3)	Reactor transfer system; feed section of olefine dimerization plant; batch plant; autoclave
Rushford (1977)	Section of cracker unit
Austin and Jeffreys (1979)	Reactor section
Sinnott (1983)	Reactor section of nitric acid plant
Piccinini and Levy (1984)	Ethylene oxide reactor system
Kletz (1985e)	Liquid propane cross-country pipeline
Ozog (1985)	Flammable liquid storage tank
Flothmann and Mjaavatten (1986)	Refrigerated liquid ammonia storage
Kavianian, Rao and Brown (1992)	High pressure/low density polyethylene plant; metal organic chemical vapour deposition process
Knowlton (1992)	Reactor transfer system; batch plant; autoclave; interstage cooler; emergency shut-down and blowdown system; gas supply and oil storage system (hybrid study)

8.12.24 Activities in HAZOP studies

It is of interest to know the actual activities that are undertaken in a HAZOP study, particularly for the development of the HAZOP technique, including computer-aided activities (Table 8.26).

Figure 8.14 gives a flow chart for a typical study. A large proportion of the protocol consisted, in addition to selection of the item of plant and the parameter deviation for study, of the following activities:

(1) generation of possible causes and consequences of initial deviation;
(2) explanation of features of process material or plant item;
(3) estimation of quantitative aspects of plant dynamics, plant reliability and availability, hazard and risk;
(4) checks on features of design and operation and of potential HAZOP problems, including detectability of deviations/faults and final consequence hazards and methods for starting, controlling and stopping the operation;
(5) specification of any action to be taken.

The activity of generating causes and consequences triggered by the application of the guideword to the parameter was relatively unsystematic. The team explored fault paths as they occurred to individuals.

Explanation of features of process materials or plant items emerged as a significant activity. Generally, in a design there are (1) features that are ambiguous, (2) features that have to be modified and (3) features that have characteristics, which have not been considered. These features may require further explanation for several reasons: (1) the information may be documented but it is more convenient to retrieve it by verbal explanation, for example, philosophy of the design calculation; (2) the information is, or should be, part of the design, but it is not yet documented, for example, intended operating procedure; (3) the information is generated by the HAZOP team during the study. Some topics on which explanations were given are shown in Table 8.27, Section C.

Another significant activity was estimation of quantitative or semi-quantitative aspects of plant dynamics, plant reliability and availability, and hazard and risk. Some features on which estimates were made are given in Table 8.27, Section D.

The central activity was checks on features of design and operation and on hazards and operability problems. Some of these checks are listed in Table 8.27. The checks given are limited to those arising directly or indirectly from use of the guidewords, which were not instantly dismissed. An important class of check was those on the detectability of deviations/faults. A large proportion of operability problems are problems of deviation/fault detection. Some of the checks of this type are listed in Table 8.27, Section E.

Most of the hazards listed in Table 8.27 are intermediate events rather than final consequences. Table 8.27, Section F, gives some of the principal final consequences of ultimate interest in the study.

Some of the hazards considered would be identified only if two deviations/faults were to occur simultaneously. Some of the decisions made on such simultaneous deviations/faults are given in Table 8.27, Section G. In four out of the five cases shown in the table, the probability of simultaneous occurrence was assessed as negligible. In the fifth case, one of the faults is failure of a low flow alarm system. This type of failure could occur well before the low flow deviation but remain unrevealed so that the probability of 'simultaneous' deviations/faults could be much higher in this case unless the instrument was proof tested. The problem of unrevealed failure was evidently recognized by the team in assessing this risk as not negligible.

The analysis revealed several problems of design communication. Some of these are shown in Table 8.27, Section H.

8.12.25 Filtering in HAZOP studies

The account given so far of HAZOP studies has emphasized primarily the generation of deviations. But HAZOP is not in fact a pure identification technique. A significant part of the activity in a HAZOP is concerned with the filtering of the deviations identified. It is not the function of the HAZOP team to carry out 'instant design'. But it is a proper function to carry out a coarse filtering process on the deviations generated in order to prevent the design systems being swamped with insignificant items. The contribution of experienced people is probably at least as much in filtering as in generation.

8.12.26 Quality assurance

A survey of HAZOP studies conducted as part of the safety case for oil platforms in the North Sea has been

Table 8.26 *Hazard and operability studies: activities in a study*[a] *(Roach and Lees, 1981)*

A Features of design and operation
Plant and pipework configuration:
- Potential alternative pipework configuration
- Pipework configuration relative to intended flow

Equipment capacity, underdesign:
- Condenser
- Distillation column trays
- Pipe (6)
- Pressure relief valve
- Vent

Equipment overdesign:
- Pump
- Valve (2)

Plant turndown (2)
Materials of construction:
- Corrosion (2)
- High temperature
- Low temperature effect on lined pipe
- Low temperature embrittlement
- Product discolouration

Lagging:
- Frost protection (5)
- Heat conservation
- Personnel protection (4)

Equipment features and facilities:
- Access
- Analysis point (5)
- Break tank
- Bund
- Disengagement space
- Drain point (2)
- Droplet knockout facilities
- Drying facilities
- Gas balancing
- Isolation (4)
- Lute (4)
- NPSH
- Purging facilities (2)
- Self-draining:
  - Consenser fall
  - Pipe fall (3)
  - Restrictor orifice, effect of
- Siphon breaker (2)
- Slip plate facilities
- Spool piece (3)
- Venting facilities (3)
- Warming facilities

Instrumentation and control:
- Alarms on pumps
- Alarm dynamic response
- Alarm setting
- Flow measurement – full bore flow in pipe
- Interlocks (3)
- Potential correction
- Pressure deviation – effect on distillation column controllers
- Temperature measurement - full immersion of probe
- Trip dynamic response
- Trip setting

Pressure equipment:
- Pressure relief
- Pressure vessel design assumptions
- Pump delivery pipework rating for high pump suction pressure
- Rating of vessel as a pressure vessel

Pumps:
- Automatic vs manual changeover
- Configuration and layout
- Kickback
- Maintenance error – pump wrongly piped up
- Operating instructions
- Overdesign
- Pressure relief valve (positive displacement pump)
- Replacement error – pump of twice design capacity installed

Valves:
- Action on air failure
- Valve and bypass:
  - Interlock
  - Operating instructions
- Valve lock open
- Valve selection – isolation valve vs instrument valve
- Valve trim size

Power supply
Earthing, electrical continuity
Plant layout:
- Access (3)
- Floor levels, relative to operations
- Goggles area
- Manholes
- Overflows

Operating instructions:
- Additives
- Distillation column high level
- Effluent system operation
- Lute maintenance
- Pipe function and flow
- Pump maximum flow
- Pump operation
- Reverse flow hazard
- Valve and bypass

Sequential operations:
- Charging of acid and water

Additives:
- Operation instructions
- Pipework
- Pump interlocks

Pressure system register:
- Hazardous pipelines (3)
- Pipe acting as vent
- Vent

Maintenance, maintainability:
- Column repacking
- Equipment removal
- Pressurized equipment (2)

B Hazards and operability problems
Air ingress (3)
Blockage (6)
- Freezing (2)
- Icing
- Polymerization

Chemical reaction
Decomposition
Effluents
- Impurities
- Vented materials, fate of

Erosion
Explosion
Explosive impurities
External fire
Flammable atmosphere
Fluid flow phenomena:
- Boiling (2)
- Entrainment
- Erosion
- Flashing
- Flooding:
  - Condenser
  - Distillation column (2)
  - Gas absorption column

Frothing
Gas breakthrough
Gas evolution from liquid (2)
- Gas, Vapour lock (2)
- Hammerblow
- Inert gas blanketing of heat transfer surface
- Layering
- Liquid slugs, surges (2)
- Pressure surges (2)
- Reaction forces
- Siphon (3)
- Suction due to high downflow
- Suckback
- Vortexing

Heat effects:
- Heat of mixing (3)

Impurities:
- Effluents
- Process water
- Product

Leaks:
- to environment
- within heat exchanger (4)
- through Valve (3)

Lutes
Maloperation:
- Pumping of fluid from one pump back through another

Material deposits
Sample points:
Access (2)
- Air ingress
- Liquid circulation
- Pressurized system
- Wrong location

Sabotage
Static electricity (2)
Trip action effects
Utilities failure:
- Cooling water (3)
- Electrical power
- Instrument air
- Nitrogen

Vacuum:
- Absorption of soluble vapour
- Collapse of pipe lining

Valves:
- Heating up of fluid trapped between two closed valves
- Installed or replaced wrong way round
- Leaks

Water ingress (2)

[a] The categories listed are not all mutually exclusive, and a small proportion of checks are listed under more than one entry.

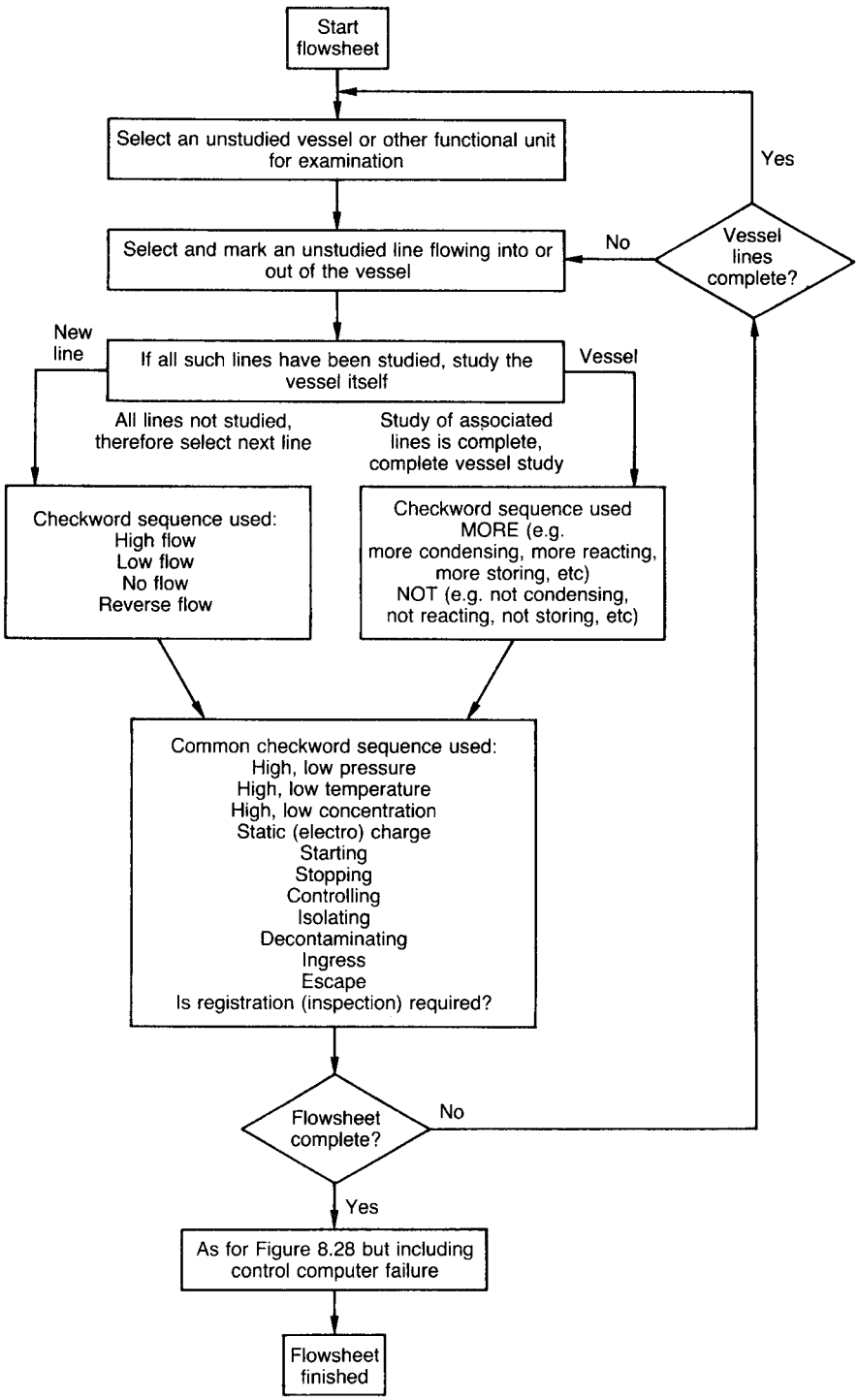

Figure 8.14 *Hazard and operability studies: sequence of activities in a study (Roach and Lees, 1981) (Courtesy of the Institution of Chemical Engineers)*

Table 8.27 *Hazard and operability studies: checks made in a study*[a] *(Roach and Lees,1981) (Courtesy of the Institution of Chemical Engineers)*

A Check words applicable to deviation of process variables

NO, NOT	Negation of intention
MORE	Quantitative increase
LESS	Quantitative decrease
AS WELL AS	Qualitative increase
PART OF	Qualitative decrease
REVERSE	Logical opposite of intention
OTHER THAN	Complete substitution

B Other check words

STARTING	ISOLATION
	ESCAPE
STOPPING	DECONTAMINATION
CONTROLLING	INGRESS

C Some topics on which explanations are given

Flowsheet discrepancies
Function of a unit:
  Drain/flushing point
  Valve
Modes of operation of unit
Design capacity/overdesign of unit
Materials of construction
Lagging
Physical characteristics of process materials:
  Miscibility
  Solubility
Chemical characteristics/reactions of process materials:
  Decomposition
Additives, functions of
Impurities, fate of
pressures and pressure drops:
  Gravity vs pumped flows (2)
  Units atmospheric pressure
System arrangements:
  Bypasses (2)
  Gas balancing
  Inserting/purging
  Isolation
  Lutes
  Purging (2)
  Sampling (2)
  Venting
Instrumentation, control and protection
  Conventional control system configuration, logic and behaviour (3)
  Computer control configuration logic and behaviour (3)
  Manual control loops
  Trip vs alarm setting
  Trip or pressure relief setting
Quality standards:
  Products
  Effluents (2)
Potential deviation:
  Pressure
Failure effects:
  Flow meter failure
  Pump corrosion
  Pump start failure
  Pump valve configuration errors
Failure data:
  Failure rate
  Repair time
Company practices:
  Lagging
  Overpressure protection
Statutory requirements
  Break tank

D Some features on which estimates are made

Fraction of time spent by unit in different operational modes
Magnitude of deviations (4)
Steady-state gain relating consequences
Time for deviation/fault to give rise to consequences (3) and cause deviations
Time for deviation/fault to be detected (2)
Performance of plant unit in face of deviation
Failure rate:
  Utilities (2)
Event rate
Repair time
Fractional dead time (3)
Degree of hazard/inoperability (4)
Frequency/probability of hazard/inoperability (8)

E Checks on detectability of deviations/faults and of correct operation

Deviations/faults checked for detectability
Process variable deviations:
  High flow (2)
  Low flow
  Reverse flow (2)
  High level (4)
  Low level (3)
  High pressure
  Low pressure (2)
  High temperature
  Low temperature
Contamination (3)
Additive deviations
Blockages:
  Blockages (3)
  Freezing (3)
Leaks
Flooding
Utility failures:
  Cooling water (2)
  Refrigeration set
  Steam
Instrument failure
Pump failure (2)
Valve fails open
Valve misdirected shut (2)
Valve installation errors on pump
Lute problems
Flow at pumps and valves checked for detectability
Pumps
Valves

F Principal final and intermediate consequences of deviations/faults

Overpressure (5)
Underpressure, vacuum collapse (2)
Overtemperature (3)
Undertemperature (2)
Corrosion (5)
Explosive mixture, confined
Explosion, confined
Equipment damage
Overflow (liquids) (11)
Boilover
Escape (gases)
Escape (liquids)
Product contamination (4)
Effluent (flow normally exists):
  Contamination (3)
  High flow
  High temperature
  pH deviation (2)
Effluent, (occasional venting flow occurs) (3):
  High flow (2)
Forced shut-down:
  Manual
  Automatic trip (2)
  Equipment failure
Personnel injury (6)

G Decisions on simultaneous deviations/faults

One of two pump motors down for maintenance AND electrical supply phased – no action
Process upset AND cooling water failure – no action
Steam flow high AND cooling water failure – no action
Pump failure AND low flow alarm failure – further investigation
Deviation in pH AND deviation in chemical decomposition with consequent possibility of SO_2 generation – no action

H Uncommunicated features, ambiguities and variations in the design

Uncommunicated design features
Uncommunicated design changes
Ambiguity about vessel design pressure
Equipment designed for throughputs other than flow sheet one
Potential variations in methods of plant operation not communicated

[a] Numbers in parentheses indicate the number of times an item occurs in the protocol. If no number is given, an item occurs once. Entries followed by a colon are headings, not specific items.

described by Rushton *et al.* (1994). The survey covered the context, policy, practical aspects and quality assurance of HAZOP.

A more detailed account of possible approaches to the quality assurance of HAZOP is given in a further report by Rushton (1995).

Quality assurance is discussed further in Sections 8.27–8.29.

8.12.27 Limitations of HAZOP studies

The HAZOP technique has been widely adopted and is the centrepiece of the hazard identification system in many companies. It does, however, have some limitations.

These limitations are of two kinds. The first type arises from the assumptions underlying the method and is an intended limitation of scope. In its original form, the method assumes that the design has been carried out in accordance with the appropriate codes. Thus, for example, it is assumed that the design caters for the pressures at normal operating conditions and intended relief conditions. It is then the function of HAZOP to identify pressure deviations which may not have been foreseen.

The other type of limitation is that which is not intended, or desirable, but is simply inherent in the method. HAZOP is not, for example, particularly well suited to deal with spatial features associated with plant layout and their resultant effects.

8.12.28 Variants of HAZOP studies

There are a large number of variants on the original HAZOP study. Many, perhaps most, companies have adapted the technique to their own needs. Many of these adaptations extend the method in respect of non-normal operation or of other activities such as maintenance, or to take account of other concerns such as environmental effects. Another type of variant is the application of the basic technique of HAZOP to systems other than process vessels and pipework. Some of these are described in Section 8.12.29. In this regard it should be remembered that HAZOP itself was an application of method study, and it may often be better to step back to this origin and then forward again from there rather than to try to apply HAZOP *per se*.

8.12.29 Other applications of HAZOP methodology

The methodology of HAZOP, or its parent critical examination, has been applied to a number of other situations, many of which are of interest in the process industries. These include (1) plant modification, (2) plant commissioning, (3) plant maintenance, (4) emergency shut-down and emergency systems, (5) mechanical handling, (6) tanker loading and unloading, (7) works traffic, (8) construction and demolition and (9) buildings and building services.

8.13 Failure Modes, Effects and Criticality Analysis

Another method of hazard identification is FMEA and its extension FMECA.

Accounts of FMEA and of FMECA are given in the CCPS *Hazard Evaluation Guidelines* (1985/1, 1992/9) and by Recht (1966b), J.R. Taylor (1973, 1974c, 1975a), Himmelblau (1978), Lambert (1978a), A.E. Green (1983), Flothmann and Mjaavatten (1986), Moubray (1991), Kavianian, Rao and Brown (1992), D. Scott and Crawley (1992) and Goyal (1993). A relevant code is BS 5760, which is described below.

FMEA involves reviewing systems to discover the mode of failure, which may occur, and the effects of each failure mode. The technique is oriented towards equipment rather than process parameters. Table 8.28 shows a set of typical results from an FMEA study on a process plant given by Recht (1966b).

8.13.1 BS 5760

Guidance on FMEA is given in BS 5760 *Reliability of Systems, Equipment and Components*, Part 5:1991 *Guide to Failure Modes, Effects and Criticality Analysis* (FMEA and FMECA). BS 5760: Part 5: 1991 deals with the purposes, principles, procedure and applications of FMEA, with its limitations and its relationship to other methods of hazard identification, and gives examples.

FMECA is an enhancement of FMEA in which a criticality analysis is performed. Criticality is a function of the severity of the effect and the frequency with which it is expected to occur. The criticality analysis involves assigning to each failure mode a frequency and to each failure effect a severity.

The purpose of an FMEA is to identify the failures which have undesired effects on system operation. Its objectives include: (1) identification of each failure mode, of the sequence of events associated with it and of its causes and effects; (2) a classification of each failure mode by relevant characteristics, including detectability, diagnosability, testability, item replaceability, compensating and operating provisions; and, for FMECA, (3) an assessment of the criticality of each failure mode.

The standard lists the information required for an FMEA, under the headings: (1) system structure; (2) system initiation, operation, control and maintenance; (3) system environment; (4) system modelling; (5) system software; (6) system boundary; (7) system functional structure; (8) system functional structure representation; (9) block diagrams and (10) failure significance and compensating provisions.

Core information on the items studied is the (1) name, (2) function, (3) identification, (4) failure modes, (5) failure causes, (6) failure effects on system, (7) failure detection methods, (8) compensating provisions, (9) severity of effects and (10) comments.

The main documentation used in an FMEA is the functional diagram. Use may also be made of reliability block diagrams.

The identification of the failure modes, causes and effects is assisted by the preparation of a list of the expected failure modes in the light of (1) the use of the system, (2) the element involved, (3) the mode of operation, (4) the operation specification, (5) the time constraints and (6) the environment.

The failure modes may be described at two levels: generic failure modes and specific failure modes. The standard gives as an example a set of generic failure modes: (1) failure during operation, (2) failure to operate at a prescribed time, (3) failure to cease operation at a prescribed time and (4) premature operation. As examples of specific failure modes, the standard gives: (1) cracked/fractured, (2) distorted, (3) undersized, and so on.

The failure causes associated with each mode should be identified. BS 5760 gives a checklist of potential failure causes under the headings: (1) specification, (2) design, (3) manufacture, (4) installation, (5) operation, (6) maintenance, (7) environment and (8) uncontrollable forces.

Table 8.28 *Failure modes and effects analysis: result for a process plant (after Recht, 1966b; Himmelblau, 1978)*

Component	*Failure or error mode*	*Effects on other system components*	*Effects on whole system*	*Hazard class*[a]				*Failure frequency*	*Detection methods*	*Compensating provisions and remarks*
				1	*2*	*3*	*4*			
Pressure relief valve	Jammed open	Increased operation of temperature sensing controller, and gas flow, due to hot water loss	Loss of hot water; greater cold water input, and greater gas consumption	1				Reasonably probable	Observe at pressure-relief valve	Shut off water supply, reseat or replace relief valve
	Jammed closed	None	None	1				Probable	Manual testing	Unless combined with other component failure, this failure has no consequence
Gas valve	Jammed open	Burner continues to operate. Pressure-relief valve opens	Water temperature and pressure increase. Water → steam			3		Reasonably probable	Water at faucet too hot. Pressure-relief valve open (observation)	Open hot water faucet to relieve pressure. Shut off gas supply. Pressure-relief valve compensates
	Jammed closed	Burner ceases to operate	System fails to produce hot water	1				Remote	Observe at output (water temperature too low)	
Temperature measuring and comparing device	Fails to react to temperature rise above preset level	Controller gas valve, burner continue to function 'on'. Pressure-relief valve opens	Water temperature too high. Water → steam			3		Remote	Observe at output (faucet)	Pressure-relief valve compensates. Open hot water faucet to relieve pressure. Shut off gas supply
Temperature measuring and comparing device	Fails to react to temperature drop below preset level	Controller, gas valve, burner continue to function off	Water temperature too low	1				Remote	Observe at output faucets	
Flue	Blocked	Incomplete combustion at burner	Inefficiency. Production of toxic gases				4	Remote	Possibly smell products of incomplete combustion	No compensation built in. Shut-down system
Pressure-relief valve and gas valve	Jammed closed	Burner continues to operate, pressure increases	Increased pressure cannot bleed at relief valve.				4	Probable	Manual testing of relief valve	Open hot water faucet. Shut off gas supply.
	Jammed open		Water → steam If pressure cannot back up cold water inlet, system may rupture violently					Reasonably probable	Observe water output	Pressure might be able to back into cold water supply, providing pressure in supply is not greater than failure pressure of system
								Reasonably probable	Temperature too high	

[a] 1, Negligible effects; 2, marginal effects; 3, critical effects; 4, catastrophic effects.

The failure effects involve changes in the operation, function or status of the system and these should be identified by the analysis. Failure effects can be classified as local or as end effects. Local effects refer to the consequences at the level of the element under consideration and end effects to those at the highest level of the system.

Where FMEA is to be applied within a hierarchical structure, it is preferable to restrict it to two levels only and to perform separate analyses at the different levels. The failure effects identified at one level may be used as the failure modes of the next level up, and so on.

BS 5760: Part 5: 1991 contains in Appendix B a number of tables illustrating the results of FMECAs conducted on various types of system. They include analysis of a subsystem of a motor generator set and of the fire protection system of an electric locomotive. Taking the latter as being most representative of process applications, the table is headed by a declaration that the system considered is the fire protection system and that its function is to detect and extinguish a fire within the locomotive. The columns of the table are headed as follows: (1) item, (2) item failure mode, (3) failure cause, (4) block function description, (5) functional failure mode, (6) effect on subsystem outputs, (7) effect on system reliability, (8) effect on system safety, (9) preventive action (design), (10) preventive action (quality assurance), (11) comment, (12) severity and (13) failure rate. Item failure mode is exemplified by 'failed to open circuit conditions', and functional failure mode by 'detection of false fire'.

FMEA is an efficient method of analysing elements which can cause failure of the whole, or of a large part, of a system. It works best where the failure logic is essentially a series one. It is much less suitable where complex logic is required to describe system failure.

FMEA is an inductive method. A complementary deductive method is provided by fault tree analysis, which is the more suitable where analysis of complex failure logic is required.

BS 5760: Part 5: 1991 states that FMEA can be a laborious and inefficient process unless judiciously applied. The uses to which the results are to be put should be defined. FMEA should not be included in specifications indiscriminately.

8.13.2 Application of FMEA

The range of applications of FMEA is very wide. At one end of the spectrum, A.E. Green (1983) has applied it to a pneumatic differential pressure transmitter, whilst at the other, Aldwinkle and Slater (1983) have described its application to a liquefied natural gas terminal. Table 8.29 lists some of the FMEA studies given in the literature.

Table 8.29 *Failure modes and effects analysis: selected studies*

Author(s)	*Subject of study*
Recht (1966b)	Hot water system
C.F. King and Rudd (1972)	Heavy water recovery plant
Eames (1973 UKAEA SRS/GR/12) Lambert (1978a)	Nuclear instrumentation
Aldwinkle and Slater (1983)	Liquified natural gas terminal
A.E. Green (1983)	Pneumatic differential pressure transmitter
Flothmann and Mjaavatten (1986)	Refrigerated liquid ammonia storage
BS 5760: Part 5:1991	Fire protection system of an electric locomotive; subsystem of a motor generator set
Kavianian, Rao and Brown (1992)	Metal organic chemical vapour deposition process

8.14 Sneak Analysis

In contrast to general methods such as HAZOP and FMECA, there are also niche methods. One of these is sneak analysis. Accounts of sneak analysis are given by E.J. Hill and Bose (1975), J.R. Taylor (1979, 1992), Rankin (1984), Dore (1991), Hahn *et al.* (1991), Hokstad, Aro and Taylor (1991) and Whetton (1993b).

Sneak analysis originated in sneak circuit analysis (SCA), a method of identifying design errors in electronic circuits (E.J. Hill and Bose, 1975). The technique was developed within a particular company and was slow to spread. An early use in the process industry was in the work of J.R. Taylor (1979) on sneak path analysis. A lead in encouraging the wider use of sneak analysis has been taken by the European Space Agency (ESA), as described by Dore (1991).

A review of sneak analysis is given by Whetton (1993b), who gives as a rough definition: 'A sneak is an undesired condition which occurs as a consequence of a design error, sometimes, but not necessarily, in conjunction with a failure'.

In sneak analysis generally, four recognized categories of sneak have emerged: (1) path, (2) indication, (3) label and (4) timing. Whetton refers to the following categories, which have developed from process work: (1) flow, (2) indication, (3) energy, (4) procedure, (5) reaction and (6) label.

8.14.1 Types of sneak

The different types of sneak which can occur are discussed by Whetton, with examples.

Sneak flow

Sneak flow is unintended flow from a source to a target. An example is the case where two vessels containing liquids, one at higher pressure than the other, are connected to a common drain header. If the bottom outlet valves on both vessels are open at the same time, liquid can flow from the higher to the lower pressure vessel.

Sneak indication

A sneak indication is one which is incorrect or ambiguous. An example is the power-operated relief valve (PORV) at Three Mile Island, where there was displayed an indication of 'Valve position' which was in fact the signal to, rather than the actual position of, the valve.

Sneak label

Likewise, a sneak label is one which is incorrect or ambiguous.

Sneak energy

Sneak energy is the unintended presence or absence of energy. An example is the energy release attendant on the

restart of agitation in a reactor where the agitator has been temporarily switched off.

Sneak reaction
Sneak reaction is an unintended reaction. Examples are a side reaction in a reactor and an undesired reaction between a fluid and a material of construction.

Sneak procedure or sequence
A sneak procedure or sequence is the occurrence of events in an unintended or conflicting order.

8.14.2 Sneak analysis methods

Whetton distinguishes three basic methods of sneak analysis: (1) topological, (2) path and (3) clue.

The original sneak analysis method was based on decomposing electrical circuits into standard subnetworks. According to Whetton, the method has proved difficult to adapt to process plants in that successful application depends on the ability of the analyst to cast process phenomena in the form of electrical analogues.

Sneak path analysis, developed by J.R. Taylor (1979, 1992), is the investigation of unintended flow between a source and a target. It is performed in a systematic manner by decomposing the P&ID into functionally independent sections and identifying sources and targets, source–target pairs and paths between sources and targets. One method of doing this is the use of coloured markers to trace the various paths, sometimes known as the 'rainbow' technique.

The clue method involves the use of a structured checklist. It is applicable to all types of sneak and examines each type by means of a question set.

8.14.3 Sneak-augmented HAZOP

Sneak analysis may be used as an enhancement of HAZOP. The techniques used are the path and clue methods. Whetton gives a detailed procedure for the conduct of a sneak-augmented HAZOP. All drawings used should be 'as built'. Information on labels should cover the as-built condition. Essentially, the sneak analysis aspect of the procedure involves an examination of the various types of sneak against the appropriate clue list. Among the other points made are the following:

Sneak flow
Examine all paths including utilities and drains, sewers and vents
Examine, in turn, all plant states such as normal operation, start-up, shut-down, etc.
Examine for each valve in turn the effect of unintended deviation in valve state.

Sneak indications
Examine each instrument
Examine control room, including humble lamps.

Sneak labels
Examine consistency of labels against as-built drawings
Examine consistency of labels on instruments.

Sneak procedures
Examine all procedures, including start-up, shut-down, etc., and maintenance.

Sneak energy
Examine, in turn, for all plant states, including start-up, shut-down, etc., and maintenance.

8.15 Computer HAZOP

The HAZOP study method just described was developed for plants in which predominantly the control system was based on analogue controllers. The advent of computer control has created the need for some method, which addresses the specific problems of this form of control.

In recent years, process engineers have increasingly chosen to use Programmable Logic Controllers (PLCs), DCSs and computers for process control. While these systems provide flexibility and close control of the process, they introduce an additional mode of failure to the plant. Modern HAZOP techniques including CHAZOP are used to consider such systems. This is quite distinct from computer-aiding of HAZOP.

An early expression of concern was that by Kletz (1982g), who highlights the human problem associated with computer control. The HSE has identified this as a topic requiring attention. One outcome has been its work on programmable electronic systems, leading to the HSE *PES Guide*, which deals with the reliability of the computer system itself, but the concern is wider than this, as described by P.G. Jones (1991).

8.15.1 Checklist and guideword methods

A method for CHAZOP that has the same general approach as conventional HAZOP has been described by Andow (1991). Like HAZOP, it is intended to be carried out by a multi-disciplinary team following a systematic methodology and using standard guidewords and questions.

Andow describes a two-part study format, comprising a preliminary study and then the main study. The purpose of the preliminary study is to identify critical features early in the design. The study covers (1) system architecture, (2) safety-related features, (3) system failure and (4) utilities failure. In the full study, attention is directed to (1) the computer-system environment, (2) input/output signals and (3) complex control schemes.

Study of the computer system environment involves examination of the machine itself and of cabinet, crates, etc.; control, input/output cards; communication links; operator consoles; power supplies; watchdog timers; and other utilities. It uses questions to establish design intent and then a question set to investigate failures:

(1) Does it matter?
(2) Will the operator know?
(3) What should he do?

The input/output signals are studied following rather more closely the HAZOP format, with examination of items such as the signal using guidewords such as LOW, HIGH, INVARIANT, DRIFTING and BAD followed up with the failure question set just quoted. Another item examined is the actuator.

Complex control schemes are examined using a list of potential weak points and corresponding problems:

Control tuning	Initialization and windup
Points of operator access	Set-points, cascades that may be made or broken
Interaction with other	schemes Start-up, normal operation, shut-down; synchronization and timing issues; expected or required operator actions

The approach described by Burns and Pitblado (1993) also follows that of HAZOP; it applies to features, such as signal or information, guidewords such as NO, MORE, LESS and WRONG.

8.15.2 Task analysis method

A quite different approach is that described by Broomfleld and Chung (Broomfleld and Chung, 1994; Chung and Broomfleld, 1994). The methodology developed by these authors is based on an analysis of some 300 incidents in two organizations – one a process industry and one an avionics company. As an example of a process industry incident, they quote the premature start of a control sequence due to inadequate specification of the preconditions for initiation.

The underlying premise of the method is that most incidents are the result of deficiencies in the software-hardware interface. The authors state that attempts to conduct separate analyses of the hardware and the software in order to simplify the task, actually complicates it.

This interface is represented by four concentric functional levels. Each level is associated with certain system components. Each component has a defined task. Starting at the periphery and working in to the centre, these are as follows:

Functional level	*Component*	*Task*
Intervention	Utility	Intervention
	Operator	Intervention
Input/output	Sensor	Input
	Human input device	Input
	Actuator	Output
	Display	Output
Communication	Communication link	Communication
Control and processing	Computer	Control and processing

There is for each task a guideword and question set. Those for the intervention task are shown in Table 8.30

8.16 Human Error Analysis

An important source of hazards and losses is maloperation of the plant, and other forms of operator error. There are a number of methods for addressing this problem. One of these is the HAZOP study which, as just described, utilizes aids such as the sequence diagram to discover potential for maloperation. Other methods which may be mentioned here are task analysis and action error analysis (AEA). The problem of human error is, however, very complex. It is considered in more detail in Chapter 14.

8.16.1 Task analysis

Task analysis is a technique, which was originally developed as a training tool. As applied to the process operator, it involves breaking down the task of running the plant into separate operations carried out according to a plan. The objective is to discover potential difficulties, and hence errors, in executing the individual operations or the overall plan. A detailed account is given in Chapter 14.

Clearly such task analysis also ranks as a hazard identification technique. Task analysis has been applied to process plants with good results, but is not in widespread use. It may also be noted in passing that the writing of operating instructions constitutes a less formalized type of task analysis, and may likewise serve to identify hazards.

8.16.2 Action error analysis

Another technique of identifying operating errors is AEA, developed by J.R. Taylor (1979). This is a method of analysing the operating procedures to discover possible errors in carrying them out.

The actions to be carried out on the process interface are listed in turn, each action being followed by its effects on the plant, so that a sequence is obtained of the form:

Action – Effect on plant – Action – Effect on plant …

The actions are interventions on the plant such as pushing buttons, moving valves, etc.

The errors handled in the method are shown in Table 8.31. The effects of possible errors are then examined using guidewords for action. The main guidewords are:

TOO EARLY
TOO LATE
TOO MUCH
TOO LITTLE
TOO LONG
TOO SHORT
WRONG DIRECTION
ON WRONG OBJECT
WRONG ACTION

In analysing the effects of an error, an important consideration is whether the effect can be observed and corrected.

It is necessary to limit the scope of the analysis. Consideration of actions on wrong objects may be confined to those, which are physically or psychologically close to the correct object. The number of wrong actions to be considered has to be kept small.

Multiple errors are considered only to a limited extent. Thus, in a large operating procedure, it would normally be practical to take into account only single initial errors, but in a few cases it may be possible to use heuristic rules to identify double errors, a factor which H is worthwhile to explore. For example, one error may result in material being left in a vessel, while a second error may result in an accident arising from this.

The technique of AEA appears to have been quite widely used in Nordic countries, but much less so elsewhere.

8.17 Scenario Development

8.17.1 Release scenarios

The methods just described are concerned with HAZOP problems, which occur on most plants. A rather different question is the identification of potential sources of major release of hazardous materials, which may pose a risk to the workforce and/or the plant, and in unfavourable circumstances may even affect the public.

Information on release sources is required for hazard assessment and for emergency planning. In order to identify such sources, it is necessary to carry out a review.

Table 8.30 *Computer hazop: task considerations and attributes for task 'intervention' (Chung and Broomfield, 1994)*

Task	*Task consideration*	*Task attributes*	*Questions*	*Incidents*
Intervention	Specification	Definition	...	...
		Objective	...	...
		Options	...	...
		Input/outputs	...	...
		Timing/control	...	...
		...	...	...
	Association	Tasks	...	...
		Devices	...	...
	Implementation	Selection	...	...
		Installation	...	...
		Testing	...	...
		Maintenance	...	...
		Environment	...	...
		Utilities	...	...
	Fail safe/protection	Failure detection	...	...
		Interlocks	...	...
		Trips	...	...
		Recovery procedure	...	...
		...	...	...
	Failure modes	Not initialized	...	...
		Incorrectly executed	...	...
		Not terminated	...	...
		...	...	...

Table 8.31 *Action error analysis: errors handled (J.R. Taylor, 1979)*

Cessation of a procedure
Excessive delay in carrying out an action or omission of an action
Premature execution of an action – timing error
Premature execution of an action – preconditions not fulfilled
Execution on wrong object of action
Single extraneous action
In making a decision explicitly included in a procedure, taking the wrong alternative
In making an adjustment or an instrument reading, making an error outside tolerance limits

Table 8.32 *Some sources of release on a plant*

Pipework:
Pipe rupture
Pipe flanges
Valves
Hoses
Compressors
Pumps
Agitators
Vessels and tanks:
Vessel/tank rupture
Vessel/tank overfilling
Reactors
Drain points
Sample points
Drains
Relief devices:
Pressure relief valves
Bursting discs
Vents
Flares
Operational release
Maintenance release

In principle, virtually all elements of the pressure system (vessels, pumps, pipework) are points at which a release may occur. Table 8.32 gives a list of some of these release sources. A more detailed checklist of release sources is given in the CCPS *QRA Guidelines* (1989/5). The identification of release sources in a hazard assessment is illustrated by the studies given in the *Rijnmond Report* described in Appendix 8.

The role of the HAZOP study in identifying such sources merits mention. A HAZOP study starts from the assumption that the plant is basically well designed mechanically and concentrates primarily on process parameter deviations. The type of release which a HAZOP study might identify would be overfilling of a tank as a result of maloperation, or brittle fracture of a pipe due to contact with cold liquefied gas, but the study is not normally concerned with mechanical failures which occur while the process parameters are within their design range. The points on the plant at which a release may occur can generally be identified by the release source review. What the HAZOP study does is to identify specific credible realizations of release from these points. For a potential release, it is necessary not only to identify a source but also to decide on the nature of the release, which could occur. The tendency is to assume that the fluid released is at its design conditions. A HAZOP study may reveal that this is not so. For example, materials may be released from a storage tank as a result of a chemical reaction in the tank, which causes the liquid to heat up considerably above its

storage temperature, and hence when released to give a much larger fraction of vapour.

8.17.2 Escalation scenarios

The identification process should not stop at the point where a release occurs, but in principle should be continued to embrace the consequences of the release and the failures and other events, which may allow these consequences to escalate. In practice, this aspect is usually treated as part of the hazard assessment. Whilst this is a reasonable approach, there is a danger that, unless the identification of the escalation modes is treated with a thoroughness matching that applied to the identification of the release modes, features which permit escalation and against which measures might be taken will be missed. The identification of the modes of escalation appears to be a rather neglected topic.

8.18 Consequence Modelling

For major hazard plants, it is common practice, following the development of the scenarios just described, to carry out some degree of quantitative modelling of the consequences. Such consequence modelling is described in more detail in the next chapter. Here it is sufficient to note its effect in giving a much better understanding of the likely development of the release and its potential for the identification both of hazards and of mitigatory measures.

8.19 Process Safety Review System

It is convenient at this point to consider under the heading of process safety reviews the family of techniques for hazard identification, hazard assessment, audit and accident investigation developed by Wells and co-workers.

8.19.1 General incident scenario

The next element is a method of defining incident scenarios, which is a necessary part of both hazard assessment and accident investigation. An account of this is given by Wells (1992) *et al.* The general incident scenario (GIS) described by these authors is a structure intended to be applicable to any incident.

The logic of an incident is also represented by the general incident structure shown in Figure 8.15. The GIS may be used for hazard identification, PHA or incident investigation.

8.19.2 Preliminary safety analysis

The GIS provides the basis for a set of techniques for PSA. Accounts of PSA are given by Wells, Wardman and Whetton (1993) and Wells, Phang and Wardman (1994). The PSA methods described are:

(1) concept safety review (CSR);
(2) concept hazard analysis (CHA);
(3) critical examination (CE);
(4) preliminary consequence analysis (PCA);
(5) preliminary hazard analysis (PHA).

These methods are now considered in turn, based on the account by Wells, Wardman and Whetton (1993).

8.19.3 Concept safety review (CSR)

The CSR is carried out as early as practical, possibly during the process development stage. Features of the CSR are review of the process and the alternatives, the safety, health and environment (SHE) information requirements, any previous incidents within the company and elsewhere, movement of raw materials and products, and organizational aspects.

8.19.4 Concept hazard analysis (CHA)

The CHA is an examination of the hazards of the process and is commenced as soon as the preliminary PFD becomes available. A checklist of keywords for a CHA is given in Table 8.33. Wells, Wardman and Whetton (1993) distinguish between a hazard and a hazardous condition. The former is purely qualitative, but the latter has a quantitative element. For example, a hazardous material constitutes a hazard.

The hazardous condition is determined by the quantity of the material. The CHA is akin to a coarse hazard study.

8.19.5 Critical examination (CE)

The CE of system safety is in large part a critical examination of the inherent safety of the system, and is therefore different from the critical examination involved in conventional HAZOP. The CE examines how the proposal is to be achieved and, in particular, (1) the materials, (2) the method and (3) the equipment. It also examines any dangerous condition and its cause. A checklist of keywords for the CE is shown in Table 8.34.

8.19.6 Preliminary consequence analysis (PCA)

The PCA, which may be started when the preliminary PED becomes available, is a hazard assessment kept at a fairly simple level. The main hazardous events considered are: (1) fire; (2) explosion, including missiles and (3) toxic release. The analysis covers the effects on the environment as well as on humans.

The analysis seeks to identify worst-case scenarios, to establish whether these could have impact outside the site and to define the types of emergency which might arise. The results from a PCA are illustrated in Table 8.35.

8.19.7 Preliminary hazard analysis (PHA)

The PHA is an analysis, which centres on the dangerous disturbance entry in the GIS. It involves estimating the frequency/probability of certain events and thus, in contrast to some other PHAs described in Section 8.10, it is a simplified form of conventional hazard analysis.

The results of a PHA are presented in tabular form, the core of which is the events:

(1) significant event to be prevented;
(2) failure to recover the situation;
(3) dangerous disturbance;
(4) inadequate emergency control or action;
(5) hazardous disturbances;

together with expansions at both ends, into causes of the set of hazardous disturbances and into escalation of the significant event. For each event, an estimate is given of the frequency/probability.

8.19.8 Short-cut risk assessment (SCRAM)

The SCRAM is essentially an extension of the PHA. It is described by Allum and Wells (1993). The SCRAM generates a set of significant events to be prevented, or top events, each of which is described in a risk evaluation

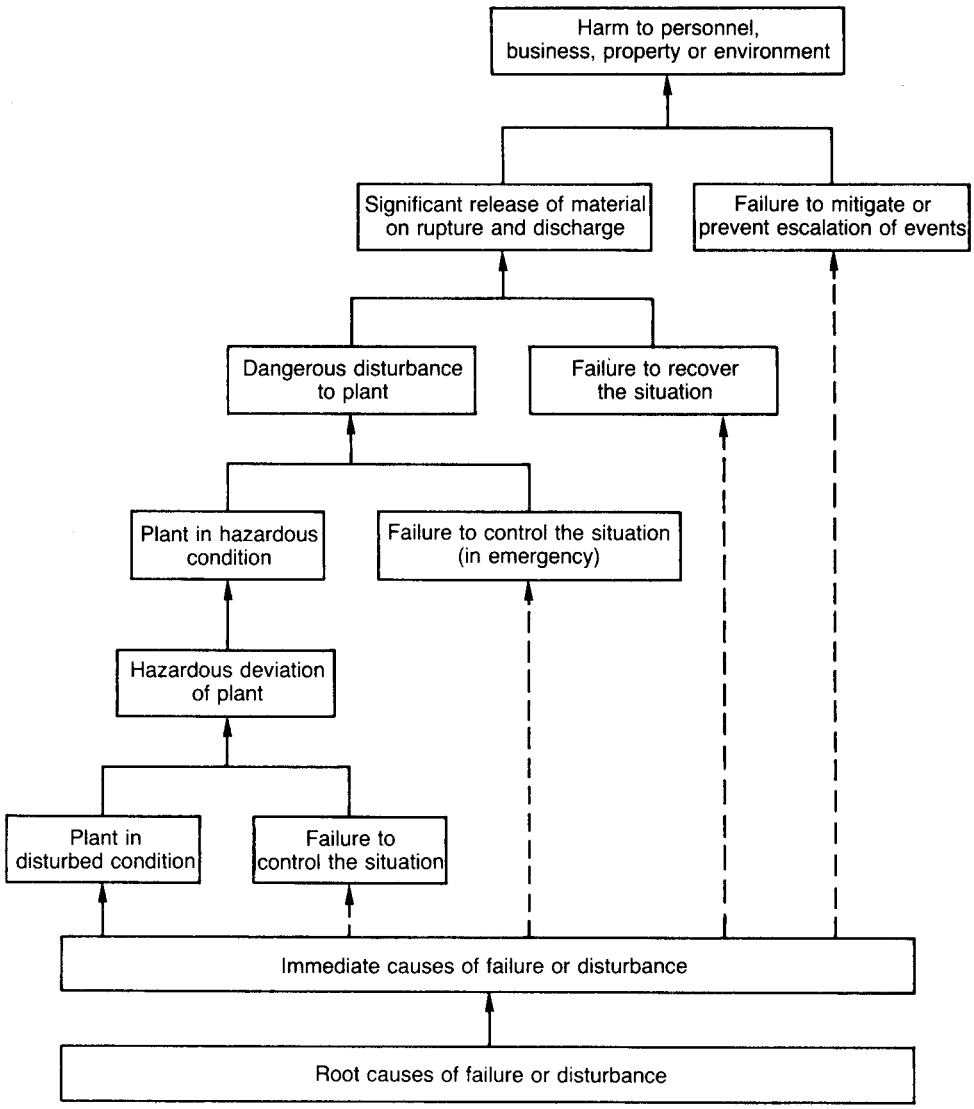

Figure 8.15 *Process safety review system: general incident structure (Wells et al., 1992) (Courtesy of the Institution of Chemical Engineers)*

sheet, which is essentially the tabulation of the PHA as just outlined. The risk assessment is developed using:

(1) target risk;
(2) severity categories;
(3) priority categories.

The target risk (TR) is defined as:

$$\mathrm{TR} = L + S \qquad [8.19.1]$$

where L is the exponent of likelihood as measured by frequency, and S is the severity category (described below).

The likelihood L is thus a negative number. If the frequency of the event is 10^{-2}, the likelihood has the value -2. The severity is the severity category number, which lies in the range 1–5. The authors give guidance on the estimation of event frequencies. This includes the adjustments to be made where the case under consideration is judged to depart from the average condition, as shown in Table 8.36. The target risk is taken as acceptable only if it is zero or less.

The severity categories are shown in Table 8.37. The severity category assigned to a given incident scenario is based on the highest level indicated by the entries in the category. The categories 'catastrophic' and 'severe' relate to very rare events, with a frequency of less than, say, 10^{-5}/year. The severity categories are not to be interpreted as implying that an event in a lower category is less serious

Table 8.33 *Process safety review system: concept hazard analysis – checklist of keywords (Wells, Wardman and Whetton, 1993)*

Keywords	*Undesired event*	*Consequences/problems*
Flammables	Release on rupture	Fire: flash, torch, pool
Ignition	Release by discharge	Chemical explosion
Fire	Entry of vessels	Physical explosion
Explosion	Handling	Vapour cloud explosion
	Ignition	Electrical explosion
Chemicals	Release on rupture	Absorption, inhalation, ingestion
Toxicity	Release by discharge	Contamination of environment
Corrosion	Entry of vessels	Disposal, incineration, storage, landfill
Pollutants	Handling	Asphyxia
Emissions	Fugitive emissions	Acidity, alkalinity, exposure effects
Effluents	Periodic emissions, washings	Separation or accumulation after discharge
Waste	Emergency emissions	
Health hazards	Human contact with chemicals	Effects of toxicity, biological activity
	Human contact with heat or cold	Effects of fire, contact with hot bodies, cold surfaces
	Noise	Effects of exceeding acceptable noise levels
	Illumination	Effect of glare, mist, fog, contrast, smoke
	Radiation	Effect of radioactive materials
External threats	Accidental impact, vibration	Harm, damage and removal of equipment
	Act of God, natural causes	Harm, damage and death of personnel
	Abnormal environmental extreme	Release of material
	External interference, loosening	Adverse discharge
	Drop, fail	Loss of supply
	Theft, hooliganism	Loss of services
	Force majeure, sabotage	Item breaks on impact
	External energetic events	
	External toxic events	
	External contamination	
	Corrosion, erosion	
Reactions	Unintended reactions	Release of material
	Difficulties with intended reactions	Dangerous disturbances
	Presence of dangerous (toxic) substances	Release of reaction energy
	Products of combustion	Defective materials
	Corrosion, etc.	
Thermodynamic hazards	Overpressure	Rupture of equipment
Overpressure	Underpressure	Impulse blows
Underpressure	Over-temperature	Weakening of materials of construction
Over-temperature	Under-temperature	Failure or damage of equipment
Under-temperature	Overheating	
	Overcooling	
	Fluid jet effects	
Abnormal opening to atmosphere	Inadequate mechanical integrity	Release of material
	Corrosion, erosion	Change in planned or emergency discharge
	Wrong status of equipment, valves, emergency relief, etc.	
Mechanical hazards	Overload/stress/tension	Rupture of equipment, change in material properties
Structural hazards	Mechanical energy/inertia	Failure of equipment or structure, transient effects, forces
Collapse, drop	Mechanical weakness	Impulse blows, fragility, vibration
	Loss of structural integrity	Failure of structure, collapse, object dropped
Electrical hazards	Charge, current, magnetism	Explosion, spark, shock, heat transfer, ionization
	High voltage	Shock to personnel

Table 8.33 *(continued)*

Keywords	*Undesired event*	*Consequences/problems*
Equipment problems	Dangerous disturbances or incident initiators	Release of material Off-specification material
Mode of operation Start-up Shut-down Maintenance Abnormal Emergency	Any notable disturbances or incident initiators Loss of supply Loss of services	Release of material Common cause failures Off-specification material

Table 8.34 *Process safety review system: critical examination – checklist of keywords (Wells, Wardman and Whetton, 1993) (Courtesy of Butterworth-Heinemann)*

Keyword	*Examples of use*
Eliminate	Eliminate by a completely different method or part of a method Eliminate certain chemicals, change the route, use a lean technology Eliminate additives, solvents, heat exchange mediums, additives Change the equipment or processing method Eliminate leakage points; use a weld not a bolted fitting, etc. Eliminate a prime mover or heat exchange or agitator Eliminate a separation stage or step Eliminate intermediate storage Eliminate an installed spare Eliminate manual handling Eliminate sneak paths, openings to atmosphere Eliminate waste Eliminate entry into vessels or disconnection Eliminate products that are harmful in use Eliminate an ignition source, particularly permanent flame
Avoid	Avoid extremes of operating conditions Avoid operating in a flammable atmosphere Avoid possible layering of materials, inadequate mixing Avoid flashing liquids, particularly in extensive heat exchanger networks Avoid production of large quantities of dangerous intermediates Avoid unwanted reactions within and outside reactors Avoid operating near extremes of materials of construction Avoid operating conditions leading to rapid deterioration of plant Avoid maintenance on demand and in short time periods Avoid items of plant readily toppled by explosions Avoid stage, step or activity by doing something as well as or instead of
Modify	Modify any topics above Modify batch operation to continuous operation, or vice versa
Prevent	Prevent emissions and exposure by totally enclosed processes and handling systems Prevent exposure by use of remote control
Increase	Increase heat transfer and separation efficiency or capacity Increase conversion in reactions
Reduce	Reduce inventory; less storage, hold-up, smaller size of equipment, less piping Reduce amount of energy in system Reduce pressure and temperature above ambient Reduce emissions and exposure by improved containment, piped vapour return, covers, condensation of return, use of reactive liquids, wetting dust Reduce frequency of opening, improve ventilation, change dilution or mixing Reduce size of possible openings to atmosphere
Segregate	Segregate by distance, barriers, duration and time of day Segregate plant items to avoid certain common-mode failures Segregate fragile items from roads, etc.
Isolate	Isolate plant by shut-down systems, emergency isolation valves
Improve	Improve plant integrity, reliability and availability Improve control or computer control; use user-friendly controls Improve response Improve quality of engineering, construction, manufacture and assembly

than one in a higher category. The categorization is for use solely as a practical design tool.

The priority categories are a function of the likelihood values and the severity categories. They are:

None	No action
A	Immediate attention needed
B	Further study probably required
C	Further study may be necessary

Table 8.35 *Process safety review system: results from a preliminary consequence analysis (Wells, Wardman and Whetton, 1993)*

What if undesired event?	*FR/PR*	*GA*	*Failure to mitigate*	*PR*	*L*	*S*	*P*	*Consequences*
Significant release of material: catastrophic failure of methanator circuit	10^{-3}	And	Countermeasures for a release fail: insufficient time for response	1	3	1		Release causes hazardous condition: cloud of flammable material
Ignition of flammable mixture: ignition and torch fire	0.5	And	Countermeasures fail to control fire: fire too great to be put out immediately	1	4	3	B	Escalation by torch fire
Escalation by fire: further spread of fire to pipe rack	0.2	And	Countermeasures fail to control fire: fire brigade fails to put out fire (no barrier)	0.5	5			Escalation by further release of material
Ignition of flammable mixture: ignition and pool fire	1.0	And	Countermeasures fail to control fire: fire brigade fails to put out fire	0.2	6	3	C	Escalation by pool fire, generating possible explosion with missiles
Escalation by explosion: missiles land on C plant	0.2	And	Countermeasures for a release fail	1	6	4	C	Escalation by further release of flammable material Aromatics washed into sewer

Note: GA, gate; FR, frequency; L, likelihood; P, priority; PR, probability; S, severity.

Table 8.36 *Process safety review system: short-cut risk assessment – adjustments to frequency estimates to allow for non-average conditions (Allum and Wells, 1993) (Courtesy of the Institution of Chemical Engineers)*

- Determine whether the plant conditions represent:
  - (a) Average duty or appropriate baseline failure rate data
  - (b) Excellent case conditions in which the internal duty is clean and maintenance performance is good on a well-established plant
  - (c) Worst-case conditions in which the duty is severe or maintenance performance poor or the plant is of novel technology or various combinations of similar effects
- Adjust the *likelihood* of failure in average duties as follows:
  - (a) In the worst case, multiply by 10
  - (b) In an average case, multiply by 1
  - (c) In an excellent case, multiply by 0.5
- Modify the *ineffectiveness* probabilities of control and mitigation:
  - (a) If a protective system is in the failed state, $P = 1$.
  - (b) In the worst case, *increase* values as follows: $0.01 \rightarrow 0.1$; $0.1 \rightarrow 0.5$; $0.5 \rightarrow 0.9$
  - (c) In an average case, do not adjust probabilities
  - (d) In an excellent case, *reduce* values as follows: 0.001 (no change); 0.01–0.005; 0.1–0.05; 0.5–0.1

The prioritization of risk is

Severity category	*Value of risk*			
	−2	−1	0	1
1	None	None	None	C
2	None	None	C	B
3	None	C/B	A/B	
4	C	B/C	B	A
5	B	B/C	A	A

The SCRA provides guidance on priorities to be addressed in the design. It also provides an indication as to whether more detailed QRA is appropriate.

8.19.9 Goal-oriented failure analysis (GOFA)

The GOFA technique is another based on the CIS checklists. An account is given by Reeves, Wells and Linken (1989). The method is described as a combination of fault tree analysis and checklists. The example given by the authors is loss of containment, the causes of which are traced through the checklist structure.

8.19.10 Socio-technical systems analysis

A socio-technical systems analysis is used to examine the preconditions for failure. An account is given by Wells, Phang and Wardman (1994). These authors describe the procedure and give the primary checklist. The main headings of this list are:

(1) system climate;
(2) communication and information systems;
(3) working environment;
(4) organization and management;
(5) management control;
(6) operator performance;
(7) external systems;
(8) procedures and practice;
(9) site and plant facilities;
(10) equipment integrity.

They also give the subsidiary checklist for external systems.

8.19.11 Illustrative example: methanator system

Some of the techniques which constitute the process safety review system just described have been illustrated by Wells and co-workers using the methanator system shown in Figure 8.16. Treatments which include examples involving the methanator system are given by Wells *et al.* (1992), Wells, Wardman and Whetton (1993) and Allum and Wells (1993).

Table 8.37 *Process safety review system: short-cut risk assessment – severity categories (Allum and Wells, 1993) (Courtesy of the Institution of Chemical Engineers)*

Catastrophic consequences: Severity 5
Catastrophic damage and severe clean-up costs
On-site: loss of normal occupancy > 3 months
Off-site: loss of normal occupancy > 1 month
Severe national pressure to shut-down
Three or more fatalities of plant personnel
Fatality of member of public or at least five injuries
Damage to Site of Special Scientific Interest or historic building
Severe permanent or long-term environmental damage in a significant area of land
Acceptable frequency 0.00001 per year
Severe consequences: Severity 4
Severe damage and major clean-up
Major effect on business with loss of occupancy up to 3 months
Possible damage to public property
Single fatality or injuries to more than five plant personnel
A 1-in-10 chance of a public fatality
Short-term environmental damage over a significant area of land
Severe media reaction
Acceptable frequency 0.0001 per year
Major consequences: Severity 3
Major damage and minor clean-up
Minor effect on business but no loss of building occupancy
Injuries to a maximum of five plant personnel with a 1-in-10 chance of fatality
Some hospitalization of public
Short-term environmental damage to water, land, flora or fauna
Considerable media reaction
Acceptable frequency 0.001 per year
Appreciable consequences: Severity 2
Appreciable damage to plant
No effect on business
Reportable near miss incident under CIMAH[a]
Injury to plant personnel
Minor annoyance to public
Acceptable frequency 0.01 per year
Minor consequences/near miss: Severity 1
Near-miss incident with significant quantity released
Minor damage to plant
No effect on business
Possible injury to plant personnel
No effect on public, possible smell
Acceptable frequency 0.1 per year

[a] Control of Industrial Major Accident Hazards Regulations 1984.

The methanator is a reactor, the feed to which contains H_2 97%, oxides of carbon 2% and methane 1%, and in which the oxides of carbon are converted to methane in a reaction which is exothermic. On occasion, the oxides of carbon in the feed can rise to 10–15%. In the examples quoted, the two dangerous disturbances explored for the reactor are overtemperature and overpressure.

The results of a concept hazard analysis for the system are shown in Table 8.38, those of a critical examination in Table 8.39 and those of a PHA in Table 8.40, as given by Wells, Wardman and Whetton (1993). The latter leads in to the risk evaluation sheet, given by Wells *et al.* (1992), shown in Table 8.41.

8.20 Choice of Method

A variety of methods of hazard identification applicable at the different stages of the project have been described. An overview of these methods is given in Table 8.2. In many cases, the aspect of hazard identification covered by a particular method is self-evident, but in others it is not. Some methods are alternatives or are complementary. Table 8.42 lists some of the principal methods as a guide to selection. The table gives the prime purpose(s) of each method. With regard to checklists, the applications shown in the table are limited, but some of the other methods such as HAZOP may also make use of a checklist specific to that method.

8.21 Filtering and Follow-up

Although it is convenient for purposes of exposition to treat hazard identification and assessment separately, the two are often interwoven. A process of filtering of the hazards takes place. Two forms of filtering, which occur with many of the identification methods described, may, be mentioned. The first involves discarding a hazard, which is considered to be unrealizable.

In the second form of filtering, a hazard is discarded if it is considered not to be sufficiently important. A measure of the need for action on an identified hazard which is widely used, albeit often not explicitly, is the product of the magnitude and frequency of the event. It is this criterion, which underlies the method of ranking described in Section 8.19.9. It is also used in task analysis as a stopping rule to decide how far to carry the process of subdivision of the task.

Filtering is an important feature of a HAZOP study. In such a study, a filtering process occurs whereby the hazards identified are assessed on the spot and only a proportion is passed on for further assessment.

Once a hazard has been identified and accepted, as worth further consideration, it is necessary to decide what to do about it. Figure 8.17 indicates four principal outcomes of the identification process. In many cases, once the problem has been identified, the solution is obvious or is known from experience. In many others it is taken care of by codes of practice. In a small proportion of cases, it may be appropriate to carry out a hazard analysis.

8.22 Safety Review Systems

Formal systems for the conduct of safety reviews appropriate to the stages of the project are now widespread in the process industries. These systems go by different names.

8.22.1 Hazard study systems

The system used in Mond Division of ICI has been described by several authors (N.C. Harris, 1975; S.B. Gibson, 1976a; Hawksley, 1984) and is shown in Figure 8.18 and Table 8.43. The system involves six hazard studies.

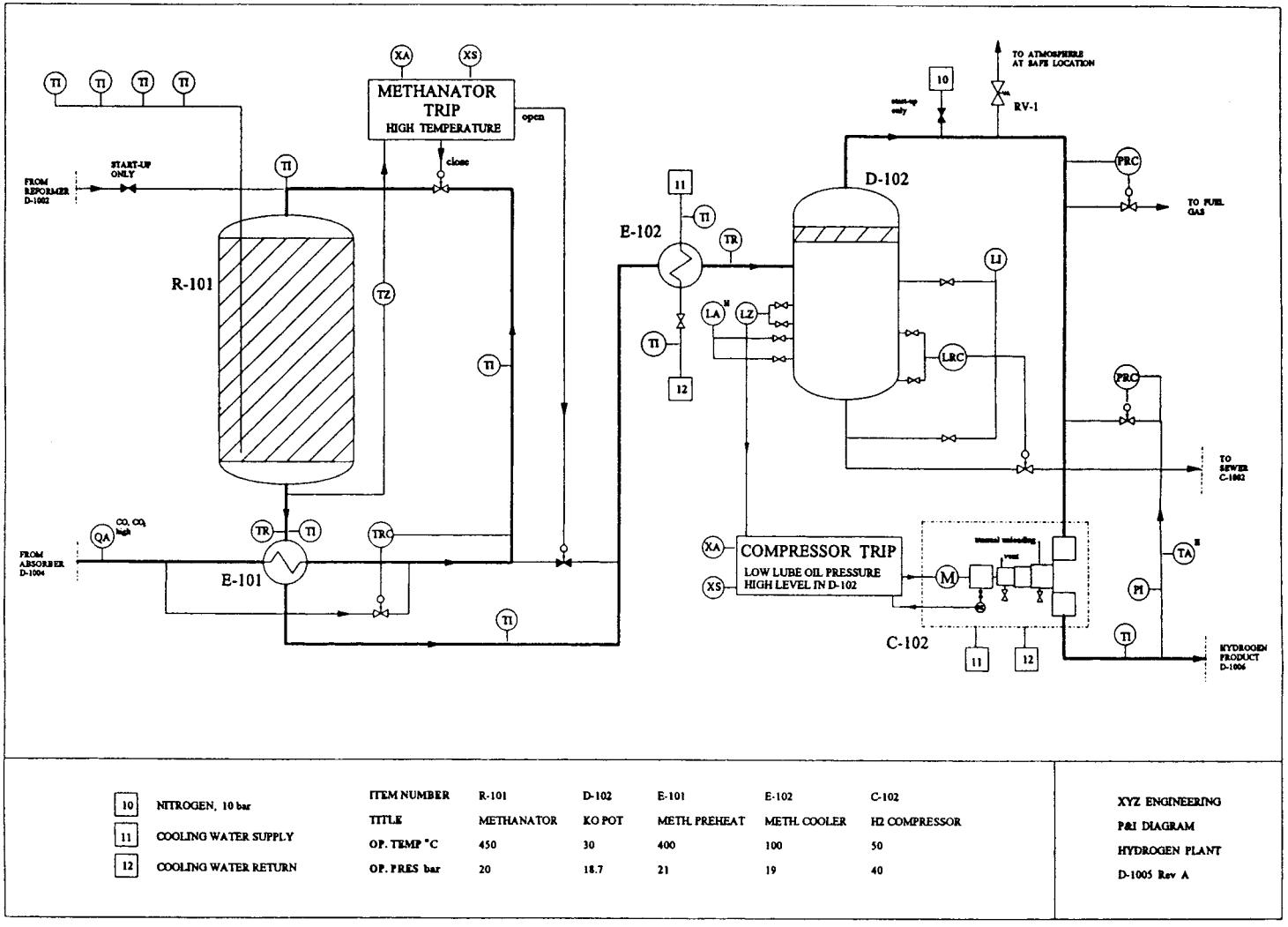

Figure 8.16 *Process safety review system: illustrative example – simplified piping and instrument diagram of a methanator system (Wells et al., 1992) (Courtesy of the Institution of Chemical Engineers)*

Table 8.38 *Process safety review system: methanator system – results of a concept hazard analysis (extract) (Wells, Wardman and Whetton, 1993)*

Ref. No	*Keyword*	*Dangerous disturbance*	*Consequences*	*Suggested safeguards*	*Comments/action*
1	Flammables	Release on rupture	Release may self-ignite torch fire. Escalation to pipe rack likely. Missile could affect C plant	Segregation by distance. Depressure or steam purge	Study best way of reducing damage
2	Flammables	Release on emergency discharge	Release at safe height: possible ignition and fire	Segregation by distance	Check possible radiation levels
3	Flammables	Normal discharge to sewer	Chemical explosion in sewer	Vent sewer with standpipes	Check other plants for incidents
4	Reaction	Exothermic runaway reaction in methanator	High level of oxides of carbon cause runaway with rupture and possible physical explosion	More robust design of absorber. Trip methanator on high temperature. Alarms on temperature and CO_2 high	Check action if trip fails
5	Reaction	Air in combustion vessels	Combustion in vessels. Causes chemical explosion	Purge plant before start-up. Ensure catalyst covered by N_2 as replaced	Get more information on catalyst
6	Reaction	Inadequate reaction Catalyst failure Low temperature feed Methanator bypassed	Off-specification H_2 to downstream plant. This can cause runaway reaction with chemical explosion	Alarm on high CO_2 outlet. Vent if off-specification and shut-down compressor. Ensure methanator warm enough to start-up. Connect methanator trip to compressor trip	Design heat exchanger circuit to preheat methanator
7	Pollutants	Effluent to sewer	Water with high sodium salts	Sewer to effluent treatment	Check effect on current treatment
8	Pollutants	Effluent caused by firewater	Fire-water will flood. River receives minor contamination		Check other sewers in area for contamination
9	Pollutants	Noise	Noise in compressor area	Building would cause explosion hazard	Operators to wear protection in danger area
10	Overpressure	Overpressure in hydrogen plant	High pressure caused by inadequate release of excess gas to fuel gas or blockage or incorrect valve status causes explosion	Two relief valves in circuit. High pressure alarm	Flare may be needed on fuel gas if demand low
11	Overtemperature	Overtemperature in methanator	Runaway reaction (see above)		
12	Overtemperature	Overtemperature in compressor	Excess recycle of hydrogen around compressor can result in physical explosion	High temperature alarm on loop	Evaluate as no safeguard provided
13	Mechanical hazard: overload	Overload of compressor	Stress in compressor caused by two phase feed due to liquid blowby from KO Pot can result in physical explosion	Trip on high level in KO Pot. Level alarm in KO Pot	Explosion unlikely but note compressor may be damaged
14	Abnormal opening	Vibration at compressor	Loosening of flange gives release. Possible torch fire	Vibration probe	
15	Abnormal opening	Spurious relief	Loss of material to safe point. Could ignite as minor torch fire		Consider need for lock open valve after RVs or bursting disc before RVs

Table 8.39 *Process safety review system: methanator system — results of a critical examination (Wells, Wardman and Whetton, 1993)*

DESIGN INTENT: A fixed-bed catalytic reactor, operating at 20 bar, 400°C inlet, 450°C outlet, converts the small amounts of oxides of carbon (maximum 2%) in a stream of hydrogen into a hydrogen product stream containing 10 ppm maximum of oxides of carbon

Query proposal	*Response*	*Generate alternatives*	*Comments*	*Recommendations*
Why remove oxides of carbon?	Oxides of carbon affect downstream catalyst on aromatics plant	Eliminate methanator here and install on aromatics plant only	No real saving on risk overall	Reject or change downstream catalyst
Why this process?	No addition of further materials	Alter by using pressure-swing adsorption system upstream	Lower yield of hydrogen but cheaper plant	Review for plant after next
Why at 400°C?	Optimized design for this catalyst	Alter the catalyst or use a larger size of bed	No safety advantage	Reject
Dangerous condition	*Cause*	*Modification/control*	*Comments*	*Recommendations*
Reactor runaway due to excess oxides of carbon in feed leading to reactor	Failure of absorption system	Increase capacity of absorption unit using an absorption train	Expensive but robust solution	Evaluate using quantitative risk analysis
		Isolate the methanator by shut-down system	Requires the diversion of upstream flow from methanator by shut-down system	Install bypass and vent off-specification material
Catastrophic failure of methanator circuit	Overtemperature due to reactor runaway	Improve metallurgy of reactor to withstand maximum temperature during upset condition	Long-term effort required	Review later
		Increasing cooling of reactor by external quench	Weakness in circuit may well not be the reactor	Consider under preliminary hazard analysis

Hazard Study I is the first formal study, carried out at the project exploration stage. Its purpose is to ensure that there is full understanding of the materials involved in the process and their potential interactions, and also the constraints on the project due to the particular site, not only in terms of safety but also in terms of environmental factors, including pollution and noise. This type of study was referred to above as a 'coarse hazard study'.

Hazard Study II is performed using the PFDs. Each section such as reaction, distillation, etc., is studied in turn and potential hazardous events such as fire, explosion, etc., are identified. At this stage it is often possible to eliminate such a hazard by means of design changes or to protect against it by the use of protective systems. In some instances, it may be necessary to study an event further. In this case, use may be made of fault tree analysis, with the hazardous event as the top event in the tree.

Hazard Study III is the HAZOP study, which has already been described.

Hazard Study IV involves a review of the actions generated in Hazard Studies I–III by the plant or commissioning manager, who also ensures that operating procedures, safe systems of work and emergency procedures are available.

Hazard Study V is the plant inspection carried out to ensure that the plant complies with the legal requirements on such matters as access and escape, guarding, emergency equipment, etc.

Hazard Study VI is undertaken during the commissioning and early operation of the plant and involves a review of changes made to the plant and its operating procedures, and of any differences between design intent and actual operation.

Once in operation, the plant is subject to further audits, but these fall outside the system as described.

8.22.2 Project safety review system

A broadly similar system is the project safety review system operated by BP. The reviews conducted in this system are:

(1) pre-project review;
(2) design proposal review;
(3) detailed design review;
(4) construction review;
(5) pre-commissioning review;
(6) post-commissioning review.

The two sets of safety review systems described above typify those in use.

Table 8.40 *Process safety review system: methanator system – preliminary hazard analysis (Wells, Wardman and Whetton, 1993)*

PROJECT: TOMHID PLANT: HYDROGEN UNIT: METHANATOR SECTION	REFERENCE: GLW LOCATION: SHEFFIELD EQUIPMENT: METHANATOR/PREHEAT		*Priority*			
			C			
FUNCTION: Fixed bed reactor converting oxides of carbon to hydrogen			*S*	*L*	*S*	*L*
Consequences of escalation	Fire escalates to pipe rack and C plant		4	E−6[a]	4	7
Failure to prevent further escalation	Failure to avoid domino due to lack of time and ineffective firefighting			0.01		0.01
Consequences of significant event	Torch fire on section of plant		3	E−4	3	E−5
Failure to mitigate or avoid escalation	Failure to avoid ignition: self-ignites as hot and release not attenuated in 15 min		3			1
Significant event to be prevented	Release through overtemperature	E−4	Release through overpressure			E−5
Failure to recover the situation	Operator fails to stop all plant flows	*	Operator action to depressure fails			0.1
		0.1				
Plant in danger: dangerous disturbance	Overtemperature in reactor	E-3	Overpressure in reactor			E−4
Inadequate emergency control or action	Failure of operator to stop flow to methanator	0.1	Pressure relief system fails			0.01
	Failure of shut-down system	0.2				
Hazardous disturbance	High temperature in reactor	0.1	High pressure in section			E−2
Inadequate control or action	Operator fails to reduce trend on TAH	1				0.01
Immediate causes	High inlet temperature (slow propagation)	E−1	Downstream blockage (clean duty)			E−4
Hazardous disturbance						
Inadequate control or action	Operator fails to reduce trend on CO_2 alarm or TAH	0.8	PRC closed			
			Fuel gas overpressure			0.01
Immediate causes	High CO_2 in stream from absorber	E−1	Lack of demand for product			E−0
Hazardous disturbance						
Inadequate control or action	Operator fails to reduce trend on CO_2 alarm or TAH or PAH	0.1	PRC closed			0.01
			Fuel gas overpressure			0.01
Immediate causes	Impurities in feed: sneak path down start-up line	E−2	Off-specification product			E−0

Recommendations/comments/actions:

1. Public not affected by domino escalation.
2. Business damage would be extensive if spread to complex.

*The operator can increase the probability of a release by wrong action and special supervision is required on any methanator problem.

1. Do not depressurize on high temperature unless sure of no flow through methanator.
2. Operator alert by several alarms. New TAH in and out.
3. Check if start-up line needed if heat exchange circuit modified.
4. Alter outlet location of start-up line. Add PAH and TR. Double block and bleed.
5. Check catalyst activation.
6. Improve absorber design to enhance reliability.

1. Operator also alerted by PAH.
2. Two relief valves in system and hydrogen is exceptionally free-flowing.
3. Add RV-1 and depressuring valve: locate before methanator.

[a] $E-n = 10^{-n}$.

Table 8.41 *Process safety review system: methanator system – risk evaluation sheet (Wells et al., 1992) (Courtesy of the Institution of Chemical Engineers)*

PSA: RISK EVALUATION SHEET	DATE: 11.7.92 PAGE: D1 of 2					
PROJECT: TOMHID PLANT: HYDROGEN UNIT: METHANATOR SECTION	REFERENCE: GLW LOCATION: SHEFFIELD EQUIPMENT: METHANATOR/PREHEAT		PRIORITY C			
FUNCTION: Fixed bed reactor converting oxides of carbon to hydrogen			*S*	*L*	*S*	*L*
CONSEQUENCES OF ESCALATION	Fire escalates to pipe rack and C plant		4	E−6[a]	4	7
FAILURE TO PREVENT FURTHER ESCALATION	Failure to avoid domino due to lack of time and ineffective firefighting			0.01		0.01
CONSEQUENCES OF SIGNIFICANT EVENT	Torch fire on section of plant		3	E−4	3	E−5
FAILURE TO MITIGATE OR AVOID ESCALATION	Failure to avoid ignition: self-ignites as hot AND release not attenuated in 15 min		3			1
SIGNIFICANT EVENT TO BE PREVENTED	Release through overtemperature	E−4	Release through overpressure			E−5
FAILURE TO RECOVER THE SITUATION	Operator fails to stop all plant flows	*	Operator action to depressure fails			0.1
		0.1				
PLANT IN DANGER: DANGEROUS DISTURBANCE	Overtemperature in reactor	E−3	Overpressure in reactor			E−4
INADEQUATE EMERGENCY CONTROL OR ACTION	Failure of operator to stop flow to Methanator Failure of shut-down system	0.1 0.2	Pressure relief system fails			0.01
HAZARDOUS DISTURBANCE	High temperature in reactor	0.1	High pressure in section			E−2
INADEQUATE CONTROL OR ACTION	Operator fails to reduce trend on TAH	1				
IMMEDIATE CAUSES	High inlet temperature (slow propagation)	E−1	Downstream blockage (clean duty)			E−4
HAZARDOUS DISTURBANCE						
INADEQUATE CONTROL OR ACTION	Operator fails to reduce trend on CO_2 alarm or TAH	0.8	PRC closed Fuel gas overpressure			0.01 0.01
IMMEDIATE CAUSES	High CO_2 in stream from absorber	E−1	Lack of demand for product			E−0
HAZARDOUS DISTURBANCE						
INADEQUATE CONTROL OR ACTION	Operator fails to reduce trend on CO_2 alarm or TAH or PAH	0.1	PRC closed Fuel gas overpressure			0.01 0.01
IMMEDIATE CAUSES	Impurities in feed: sneak path down start-up line	E−2	Offspec product			E−0
RECOMMENDATIONS/COMMENTS/ ACTIONS: 1. Public not affected by domino escalation. 2. Business damage would be extensive if spread to complex *The operator can increase the probability of a release by wrong action and special supervision is is required on any Methanator problem	1. Do not depressurize on high temperature unless sure of no flow through Methanator 2. Operator alert by several alarms. *New TAH in and out* 3. Check if start-up line needed if heat exchange circuit modified. 4. *Alter outlet location of start-up line. Add PAH and TR. Double block and bleed* 5. Check catalyst activation 6. Improve absorber design to enhance reliability		1. Operator also alerted by PAH. 2. Two relief valves in system and hydrogen is exceptionally free-flowing 3. *Add RV-1 and depressuring valve*: locate before *Methanator* E−2 = 10^{-2}			

[a] E−n = 10^{-n}.

Table 8.42 *Application of some techniques for hazard identification*[a]

Purpose	*Checklist*	*Safety review*	*Scenario development*[b]	*Hazard indices*	*Hazard ranking methods*	*Coarse hazard study*[c]	*Hazop*	*Failure modes, effects and criticality analysis*[d]	*Human error analysis*[e]	*Fault tree analysis*	*Event tree analysis*	*Consequence modelling*	*Hazard warning analysis*
Identification of:													
Deviations from good practice	Y	Y											
Hazards	Y	Y	Y	Y		Y	Y						
Hazards liable to threaten project viability			Y			Y							
Hazards with potential for large property damage loss				Y									
Hazards requiring priority					Y								
Worst-case accidents			Y	Y	Y								
Initiating events							Y	Y	Y	Y			
Pre-release accident path							Y	Y	Y	Y			
Measures to reduce probability of enabling condition, frequency of initiating event							Y	Y	Y	Y			
Post-release escalation paths and outcomes											Y		
Measures to reduce frequency of consequences											Y	Y	
Measures to mitigate effects of consequences												Y	
Precursor 'warning' events													Y

[a] The table is oriented towards hazard identification techniques for loss of containment events. It does not include hazard identification techniques the purpose of which is obvious, such as reaction screening or commissioning inspections.
[b] Also techniques such as 'What if?' method.
[c] Also techniques such as preliminary problems analysis (PPA).
[d] Also techniques such as action error analysis (AEA).
[e] Also techniques such as common mode failure analysis and cause–consequence analysis (CCA).

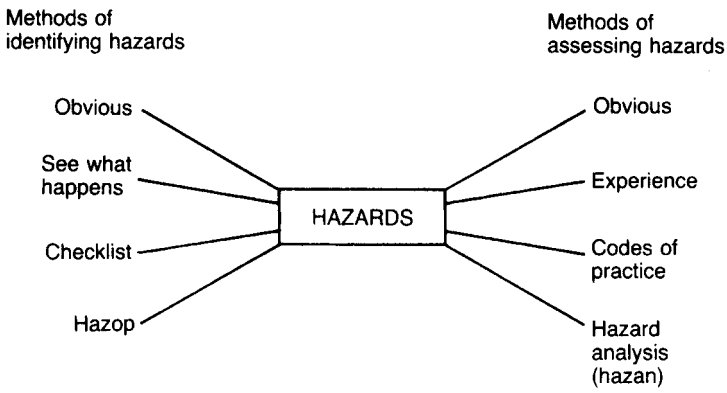

Figure 8.17 *Process of hazard identification and assessment (Klet, 1983d) (Courtesy of the Institution of Chemical Engineers)*

Project phase	Pre-sanction		Sanction obtained	Post-sanction			
Stage	Project exploration	Preliminary project assessment	Project definition	Design and procurement	Construction and safety check	Commissioning	Normal operation
Study No.	I		II	III	IV	V	VI

Figure 8.18 *System of hazard studies (after S.B. Gibson, 1976a; Illidge and Wolstenholme, 1979) (Reproduced by permission of the Institution of Chemical Engineers)*

8.23 Hazard Ranking Methods

There are available a number of hazard ranking methods for assigning priorities among hazards. Accounts include those of Gillett (1985), Ashmore and Sharma (1988), Rooney, Turner and Arendt (1988), Casada, Kirkman and Paula (1990), Eraser, Bussey and Johnston (1990) and Keey (1991).

8.23.1 Rapid ranking

Typical of these methods is that of rapid ranking described by Gillett (1985). The basis of the method is a trade-off between the consequence and the frequency of the event considered. The more serious the consequence, the lower the frequency, which is tolerable for the event. In principle, therefore, the criterion for action may be taken, as a first approximation, as some threshold level of the product of consequence and frequency.

The rapid ranking method actually utilizes a mixture of quantitative and qualitative measures. The cost of damage to the plant and the frequency of occurrence are expressed quantitatively and the other consequences qualitatively.

In the method, five hazard categories are defined. Table 8.44 defines the hazard categories in terms of the consequences. In determining the features of a particular hazard for comparison with the entries in the table, it is intended that the damage costs be estimated and that the other entries be obtained from expert judgement. The table also gives both relative guide frequencies and typical absolute frequencies for each hazard category.

For a particular hazard, a hazard category is obtained on the basis of the consequences. If different consequences yield different hazard categories, judgement must be exercised. The estimated frequencies derived from historical data are then compared with the absolute guide frequencies given in Table 8.44 and a hazard ranking obtained using Table 8.45.

Examples of the technique are given by Mumford and Lihou (1984 LPB 59). As an illustrative example, consider the hazard of fire in a pipe trench. In a particular application, it is estimated that a pipe trench fire will cause on average £10,000, damage and the following estimates are made of the frequency of the two hazards – (1) a fire without operator fatality and (2) a fire with a chance of an operator fatality:

Frequency of pipe trench fires without operator fatality $= 0.5$/year

Frequency of pipe trench fires with 1 in 10 chance of operator fatality $= 1.5 \times 10^{-2}$/year

Hazard 1, with an estimated damage cost of £10,000, is given by Table 8.44 as hazard category 2 and therefore has guide frequency of 10^{-1}/year. The expected frequency is 5×10^{-1}/year and thus exceeds the guide value by a factor of 5.

Table 8.43 *Rapid ranking of hazards: hazard categories (Gillet, 1985) (Courtesy of Process Engineering)*

Area at risk	*Description of risk*	*Hazard category*				
		1	*2*	*3*	*4*	*5*
Plant	Damage	Minor <£2000	Appreciable <£20,000	Major <£200,000	Severe <£2m	Total destruction >£2m
	Effect on personnel	Minor injuries only	Injuries	1 in 10 chance of a fatality	Fatality	Multiple fatalities
Works	Damage	None	None	Minor	Appreciable	Severe
Business	Business loss	None	None	Minor	Severe	Total loss of business
Public	Damage	None	Very minor	Minor	Appreciable	Severe
	Effects on people	None (smells)	Minor	Some hospitalization	1 in 10 change of public fatality	Fatality
	Reaction	None/ mild	Minor local outcry	Considerable local and national press reaction	Severe local and considerable national press reaction	Severe national (pressure to stop business)
Relative guide frequency of occurrence	—	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}
Typical[a] judgmental values for a plant/small works (years)	—	1	1/10	1/100	1/1000	$1/10^4$

[a] These typical comparative figures are given for illustration and should not be taken as applicable to all situations or taken to indicate absolute levels of acceptability.

From Table 8.45, the hazard ranking is A. Hazard 2, with the same damage cost but a 1 in 10 chance of fatality, is hazard category 3 and therefore has a guide frequency of 10^{-2}/year. The estimated frequency is 1.5×10^{-1}/year and thus exceeds the guide value by a factor of 1.5. The hazard ranking is again A, but only just. Action is indicated in both cases.

8.24 Hazard Warning Analysis

In some cases, analyses are carried out to identify the lesser events, which may serve as precursors to, or warnings of, more serious events. Such analyses clearly rank as hazard identification techniques. One such method is the technique of hazard warning analysis described by Lees (1982b). Like fault tree analysis, on which it is based, this technique may be used to obtain quantitative results. It is therefore described in the next chapter.

8.25 Plant Safety Audits

The conduct of some form of plant safety review is a normal part of plant commissioning. Traditionally this is a joint inspection by the plant manager and the plant safety officer and is concerned mainly with checking that the company complies with the legal and company safety requirements. Attention is directed to features such as: access and means of escape; walkways, stairs and floors; and firefighting and protective equipment.

There has developed from this, however, the more comprehensive plant safety audit. There is no uniform system for such audits. The BCISC publications *Safe and Sound* (1969/9) and *Safety Audits* (1973/12) give information on several systems. D. Williams (1971) gives a detailed des-cription of one system, including a comparison of one of the audits from *Safe and Sound* with a later audit by the same company, which illustrates the evolution of the method.

The general approach is on the following lines. The plant safety audit is conducted by a small, interdisciplinary team which is not connected with the plant. The members may come from the same works or from other works. The team may be led by a quite senior manager. The audit is carried out first during the plant commissioning, but is also repeated later at intervals. Typical intervals are a year after initial start-up and every 5 years thereafter.

The topics covered by the audit are illustrated by the checklists given in Tables 8.46 and 8.47. The former gives topics listed in *Safety Audits*. The latter is a checklist for both audits and surveys given by Williams. As already emphasized, it is essential that management act on any audit made.

8.26 Other Methods

8.26.1 Feedback from workforce

It is the responsibility of the management to create systems and attitudes which lead to the effective identification of

Table 8.44 *Rapid ranking of hazards: hazard ranking (Gillett, 1985) (Courtesy of Process Engineering)*

Hazard category (from Table 8.43)	*Expected frequency compared with guide frequency*			
	Smaller (−)	*Same (=)*	*Greater (+)*	*Uncertain (U)*
1	D	D	D/C at team's discretion	D/C at team's discretion
2	D	Normally C, but if upper end of frequency/ potential raised to B at team's discretion	Equally damaging hazard as those below, A, but if lower end of frequency/potential could be lowered to B at team's discretion	B Frequency estimate should not be difficult at this category; may be a lack of fundamental knowledge which requires research
3	C	B	A Major hazard	A/B at team's discretion. Such potential should be better understood
4 & 5	B/C at team's discretion	B, but can be raised to A at team's discretion	A Major hazard	A Such potential should be better understood

Table 8.45 *Checklist for a plant safety audit (after British Chemical Industry Safety Council, 1973/12)*

(1) Statutory requirements in the area under consideration
(2) Methods of process operation. Hazards of the materials involved and of the technology in use
(3) Material handling
(4) Tools, machinery, maintenance equipment
(5) Permit-to-work system, schedules for regular inspection of emergency equipment
(6) Personal protective equipment, its condition, care and suitability
(7) Plant tidiness, condition of floors, stairs, walkways, cleanliness of toilets and washing facilities, environmental factors, waste disposal
(8) Fire prevention and protection, alarm systems, emergency exits, flammable material storage
(9) Unsafe practices
(10) Arrangements for treating injuries, condition of safety showers, eye- and hand-wash cabinets, resuscitation equipment
(11) Involvement of employees in safety activities, their knowledge of the safety organization, attitudes, condition of displays and notices

Also
Electrostatic hazards
Alarms and trip systems and testing
Pressure vessels and relief valve inspections
Cable protection
Radiation hazards
Operation and maintenance of internal and external transport
Occupational health and hygiene standards
Electrical equipment maintenance
Major emergency arrangements
New projects and processes
Adherence to codes of practice (of internal or external origin)
Equipment faults
Labelling of products
Adherence to approved work and operational procedures
Training procedures/programmes and their effectiveness
Adequacy of safety procedures in office, administrative and ancillary buildings
Methods of communication and their success
Receipt, storage and transportation of chemicals and other materials
Extensions/alterations to existing production and storage facilities
Pollution/environmental control methods
Liaison with outside contractors
Safety standards in research, development and laboratory work
Consideration of safety and loss prevention at the design stage
Security arrangements covering the storage and issue of harmful substances
Safety advisory service to customers, covering products, their handling and use

Table 8.46 *Checklist for a plant safety audit or survey (D. Williams, 1971) (Courtesy of the Institution of Chemical Engineers)*

Buildings and surroundings:

(1) Are emergency exits adequate and accessible?
(2) Is lighting adequate for operations, walking, material handling?
(3) Is firefighting equipment adequate and accessible?
(4) Are aisles large enough? Marked? Clear?
(5) Is floor free of tripping or slipping hazards?
(6) Are floor loads within safe working loads? Are safe loading limits posted where necessary?
(7) Is general ventilation sufficient?
(8) Are stairs and platforms free of tripping hazards? Equipped with necessary guard rails?
(9) Are there any openings in fire walls? Are fire doors operable?
(10) Are hazardous areas provided with adequate explosion venting?
(11) Does building electrical service appear adequate? Does visual inspection reveal any maintenance problems?
(12) Is building trim (window sash, doors, rain gutters, fire escapes, etc.) in safe condition?
(13) Are lifts regularly inspected and adequately maintained between inspections? Are safe lifts loads posted? Adhered to?
(14) Are building approaches (outside steps, platforms, paths, etc.) in a safe condition?
(15) Are safety signs adequate and in good condition?

Equipment:

(1) Are danger points adequately guarded? Rotating parts? Pinch or nip points? Belts? Cutting edges? Hot surfaces? Open flames?
(2) Are operating controls positioned for safe use?
(3) Is there room for the operator to work safely?
(4) Are valves, switches, instruments, and other operating controls clearly identified? Are pilot lights working?
(5) Are safety alarms properly identified and tested regularly?
(6) Do automatic controls fail safe? (Can a hazardous condition be created by the failure of automatic controls?)
(7) Do wiring and piping appear to be in good condition and adequate for intended use?
(8) Is equipment rated and inspected for the service in which it is used? (Area engineers to provide list of pressure equipment rating.)
(9) If process presents corrosion problems, is equipment inspected regularly to anticipate and prevent failure in service?
(10) Are pressure relief devices adequately sized and accessible for inspection?
(11) Are overflow lines and breather vents adequate and clear? Equipped with flame arresters, liquid seals where needed? Do overflows and vents discharge at a safe location?
(12) Does equipment conform to grounding policy? Are grounds tested regularly? (Area supervisor to specify frequency of test.)
(13) Are drop lights and extension cords in good condition? Meet electrical standards?
(14) Are hand tools, portable tools and ladders inspected regularly? Are they proper for the intended use? In good condition?
(15) Can equipment be made safe for routine maintenance work? Electric lockouts? Lines blanked? Sufficient safe working area for mechanics? Adequate room and facilities for rescue?

Process:

(1) Is process safe under normal conditions?
  (a) Are toxic vapours normally present? Are safeguards adequate?
  (b) Are flammable vapours normally present? Are vapours confined? Are sources of ignition controlled?
  (c) Are operators or other employees normally exposed to toxic, corrosive or hot liquids? Is protective equipment properly stored, maintained and used? Are special physical examinations of employees conducted as recommended by the medical department?
  (d) Are sampling procedures safe?
  (e) Are safe storage conditions provided for hazardous raw materials and intermediates?
(2) Are abnormal conditions provided for?
  (a) Loss of utilities: Electricity – agitation, circulation, controls and instruments, light. Steam – heating, vacuum, pumps, steam snuffers. Air – instruments, pumps.Water – cooling, quenching. Gas – inert and illuminating.
  (b) Mechanical failures.
  (c) Operator errors – what can happen?
  (d) Are emergency venting facilities adequate? Inspected?
  (e) What sources of ignition may develop in this process? Are they guarded against?
  (f) Can a fire be controlled in this process?
  (g) Are operators or other employees unnecessarily exposed to serious injury in event of probable fire, explosion, large spills or mechanical failures?

Table 8.46 *(continued)*

(h) Are operators protected from probable leaks of steam, toxic or corrosive chemicals?
(i) Is quantity of exposed flammable or toxic liquids in populated areas kept to an absolute minimum consistent with production requirements?
(j) Is process subject to abnormal reactions?

ARE THERE ANY HAZARDS, WHICH WE HAVE NOT GUARDED AGAINST AND FROM WHICH OUR ONLY PROTECTION IS THE LAW OF CHANCE?

Operating instructions:
(1) Are operating instructions available in a written, legible, easily identified form?
(2) Are they up to date?
(3) Is there a procedure for keeping them up to date?
(4) Are they reviewed regularly with each employee?
(5) Are they accessible to operators for reference?
(6) Do the operating instructions spell out hazards of job and how to avoid them?
(7) Do operating instructions provide definite procedures for emergency situations where required?
(8) Is operator's performance checked regularly by supervision?
(9) Is there an effective system for notifying operators of non-standard conditions?
(10) Are operators permitted to take unauthorized short cuts in operations without reprimand?
(11) Are operators working in isolated locations checked regularly by supervision or the guard force?
(12) Do department supervisors know immediate first aid treatment required for exposure to toxic chemicals used in their departments?

Table 8.47 *System of hazard studies (after N.C. Harris, 1975; S.B. Gibson, 1976a; Hawksley, 1984)*

Study	*Project phase*	
I	Exploratory	Carried out at inception of project. Review of hazards of materials and process, of effluent and environmental problems and of site
II	Definition, preliminary design	Completed before sanction is sought. Examination of process flowsheets and assessment of ability of design to meet specifications
III	Detailed design	Takes place about time plant is sanctioned. Critical examination of hazards and operability of plant using Piping and instrument diagram, operating instructions, maintenance procedures, etc.
IV	Construction	Takes place during later stages of construction and early stages of commissioning. Review to ensure provisions of previous studies have been implemented
V	Commissioning	Carried out before initial start-up. Inspection to ensure safety systems are installed and operate as intended
VI	Operation	Carried out within a year of handover to operating team. Review of plant modifications, operating instructions, documentation

hazards, but it is the responsibility of everyone involved in the design and operation of the process to play his role in identifying and reporting any hazard of which he becomes aware.

This aspect has already been considered in the context of total loss control in Chapter 1 and of the safety system in Chapter 6, and is discussed again in Chapters 11 and 28.

8.26.2 Process design checks

There is an enormous amount of experience on the hazards associated with unit processes, unit operations, plant equipment, pressure systems, instrumentation, etc., and it is essential that this be utilized. It is not enough, therefore, to rely only on generalized methods of hazard identification. Full use needs to be made of what is already known. This may be done by methods such as the use of checklists for such processes, operations, etc. This aspect is discussed in more detail in Chapter 11.

8.26.3 Plant equipment checks

There are numerous types of check which are carried out on the plant equipment at various stages in the project. There are checks done before and during plant commissioning, including testing in manufacturers' works, checking the correct installation of the equipment, testing *in situ*, etc. There is a whole range of inspection and examination techniques, including non-destructive testing and condition monitoring, which are applied both during commissioning and in operation. Many items are checked or tested on a scheduled basis. While the results of some tests are unambiguous, others require careful interpretation and the application of sophisticated inspection standards.

8.26.4 Emergency planning

If a works contains hazardous plant, it is essential to plan for possible emergency situations. The first step in emergency planning is identification of those hazards, which are sufficiently serious to warrant such planning. Such a study is not necessarily an exercise separate from the other hazard identification procedures, but it does emphasize particular aspects, especially the development and scale of the emergency, the effects inside and outside the works boundary, the parties involved in dealing with the situation, etc. Emergency planning is treated in Chapter 24.

8.27 Quality Assurance

The quality of the hazard identification system should be assured by a suitable system of quality assurance. Normally this will be part of an accredited system covering the quality assurance of all aspects of company operation. Principles of quality assurance are discussed in Chapters 1 and 6 are therefore not repeated here, but it is appropriate to consider some aspects which apply to hazard identification.

There should be a formal system for hazard identification. For each stage of a project, a set of hazard identification techniques should be selected. The system should then ensure that these techniques are used.

Quality assurance may be based on inputs and process and/or outputs. It is generally prudent to utilize both. Inputs and process for hazard identification include: the qualifications, training, experience and plant knowledge of the team performing the task; the methods of hazard identification used and their suitability; the project documentation available, its comprehensiveness and accuracy; and the time available for the task.

Outputs include the whole range of information generated by the team. They are therefore not confined just to items such as release scenarios or deviations with associated causes and consequences, but extend also to the statements of scope, the report on the analysis and the follow-up measures.

Quality assurance of hazard identification requires documentation both of the hazard identification system and of the hazard identification activities conducted in a particular project. It should leave an audit trail which can be followed later if necessary.

8.28 Quality Assurance: Completeness

The quality of hazard identification virtually parallels the completeness of identification. It is of interest, therefore, to consider attempts made to assess the completeness of hazard identification. Some identified hazards are discarded as unrealizable. In discarding such hazards, discrimination is exercised. It is desirable to have some measure of this also.

A study of completeness and discrimination in hazard identification has been made by J.R. Taylor (1979; 1981 LPB 46). It is possible to specify a list of hazards which is complete. According to Taylor, process plant hazards are covered by the following list: fires, explosions, toxic releases, asphyxiations, drownings, and mechanical impact and cutting accidents. However, the price paid for completeness is a list so general that it is of little practical use. As soon as the list is developed into more specific categories, the degree of completeness is liable to decrease.

8.28.1 Criteria of completeness

The following criteria of completeness are defined:

Criterion	*Definition*
1	N_{id}/N_{tot}
2	$(N_{id})_m/N_{chl}$
3	$(\sum f_i c_i)_{id}/(Sf_i c_i)_{chl}$
4	N_{rl}/N_{id}

where c is a measure of consequence, f is the frequency of occurrence, and N is the number of hazards and where subscripts refer to the following:

id	identified
chl	identified in a case history list
m	identified by method m
rl	realizable
tot	total existing

Criterion 1 is the simple measure of completeness. Criterion 2 is a more practical criterion, which measures completeness obtained by a particular method in relation to hazards, which are ascertainable as having occurred historically. This requires the use of a large list of case histories.

Some hazards are expressly excluded from consideration in order to reduce the work involved. This is the case where a cut-off is applied to exclude combinations of hazards of order higher than 1 or 2. Criterion 3 is intended for use in such situations.

Some hazard identification methods possess internal completeness. They treat a specific class of hazard, which is logically complete. This is the case with a FMEA, where the set of failure modes is complete. Sources of incompleteness in such a method are errors in using the method or hazards, which lie outside the scope of the method.

Criterion 4 is a measure of discrimination. A hazard which has been identified may actually not be realizable, as may be demonstrated by further analysis.

There is a degree of conflict in the attempt to achieve both completeness and discrimination, particularly in industrial work where the time available for analysis is limited.

8.28.2 Studies of completeness

Taylor has extended this work to encompass a comparative study of the completeness of hazard identification on particular plants. The investigation covered four full-scale risk analysis projects plus a research study on a batch distillation plant.

In the batch plant study, various hazard identification techniques were applied successively. Starting with the HAZOP method, using a supporting checklist, the number of hazards identified was 30. A further two were identified by making some use of fault trees to explore causes and of consequence diagrams to explore consequences. Application of AEA then identified a further 82 hazards. Inspection of the actual plant using checklists identified a further 10 hazards. This gives a total of 124 hazards identified. A further three hazards were identified from disturbances during commissioning, making a total of 127.

The completeness of hazard identification was checked against a generic fault tree based on case histories. A further two hazards were identified using the tree. On this basis, therefore, the completeness of hazard identification obtained using the HAZOP, AEA and inspection was 97%.

Taylor also describes evaluation of completeness using manually and automatically constructed fault trees. For the former, he quotes a completeness of 80% as typical for analysis of a piping diagram, but states that the degree of completeness is much less for sequential operations and operating problems. For the latter, work was still in progress, but he quotes a completeness at the time of writing of some 94%.

The HAZOP method used in the study was based on vessels rather than lines and appears not to have been a version adapted for sequential operations, so that, as the author states, the results do not do justice to the HAZOP method.

8.29 Quality Assurance: QUASA

A formal method for quality assessment assurance of safety analyses (QUASA) has been developed by Rouhiainen (1990). The method covers both qualitative and quantitative aspects, but with emphasis on hazard identification, and it is therefore appropriate to consider it at this point.

8.29.1 Safety analysis

The content of safety analysis is considered in terms of four main elements: (1) hazard identification, (2) QRA (3) remedial measures and (4) resources.

The quality assessment examines fitness for purpose. The purposes of safety analysis considered include: assessment of risks in relation to plant siting; identification, elimination or reduction, and control of hazards in design of a new plant; and the same for an existing plant.

Safety analysis has potential deficiencies which it is the function of quality assessment to uncover. Some of these deficiencies are listed by Rouhiainen, as shown in Table 8.48.

Table 8.48 *Some potential deficiencies in a safety analysis (Rouhiainen, 1990)*

Phase of analysis	*Examples of possible deficiencies*
System definition	Correlation between the plant and its descriptions not checked Important parts of the production system not included in the analysis Important production situations not taken into account
Hazard identification	Important hazard types omitted Methods used do not cover all hazards
Accident modelling	Important accident chains not modelled Important contributing factors omitted
Estimation of accident frequencies	The data used inaccurate Incorrect subjective judgements used Accuracy of the results not evaluated
Estimation of accident consequences	Simplifications made incorrect Model used not suitable to the situation studied
Risk estimation	More reliable toxicity data might be available Emergency provisions overestimated or underestimated
Documentation	Description of the object inadequate Initial assumptions not presented
Measures after the analyses	Measures presented not implemented No plan for updating the analysis

8.29.2 QUASA

QUASA is based on quality theory. In accordance with this theory, methods for the assessment of the quality of a safety analysis may be based essentially on inputs and process and/or on outputs. The features assessed in QUASA are given in Table 8.49. As stated earlier, they include not just the immediate results of the hazard identification and risk assessment, but other features such as the statements of scope, the report on the analysis and the follow-up measures. The emphasis in the method is thus on outputs, broadly defined.

A core feature of the method is the assessment of the quality of the hazard identification and the QRA. Here consideration is confined to hazard identification, the treatment of the QRA in the method being deferred to the next chapter. The quality assessment in QUASA may be made by a single assessor or by a group of assessors.

8.29.3 Assessment models

Rouhiainen gives the following model of the accident process:

Hazard → Exposure → Consequences

with contributory factors influencing each stage. Two types of contributory factors are distinguished: determining factors and deviations. Essentially, determining factors are those governing the design of the system, and deviations are excursions in its operation.

For the assessment of a safety analysis, use is made of the further model shown in Figure 8.19, which gives an overview of limitations and deficiencies of the safety analysis process, cast in the form of a cause–consequence diagram.

8.29.4 Assessment checklist

The QUASA method is based on the checklist shown in Table 8.49. The checklist covers the various stages of the safety analysis, its preparation and initiation, conduct, reporting and follow-up. It draws on the method given in ISO 9002: 1987 for the assessment of the quality assurance system of a subcontractor.

8.29.5 Assessment measures

Assessment of quality involves a comparison of actual performance against some performance standard. Performance standards for some parts of the safety analysis are difficult to define. This is true particularly for hazard identification, since the complete list of hazards is not

Table 8.49 *Checklist for quality assessment of a safety analysis (Rouhiainen, 1990)*

(1) Preparation of the analysis
  (a) Selection of the object
  (b) Restriction and definition of the object
  (c) Definition of the goals
  (d) Organization of the safety analysis
(2) Initiating the safety analysis
(3) Selection of methods and performance of the analysis
  (a) Identification of hazards
    (i) General aspects
    (ii) Equipment
    (iii) Processes and materials
    (iv) Organization of the object
    (v) Human activities
  (b) Modelling of accidents
  (c) Estimation of accident frequencies
  (d) Estimation of consequences
    (i) Calculation of consequences
    (ii) Emergency preparedness
  (e) Estimation of risk
  (f) Planning of remedial measures
(4) Report of the safety analysis
  (a) Description of the object
  (b) Description of the analysis
  (c) Results of the analysis
  (d) Description of the proposed measures
(5) Measures after the analysis
  (a) Measures to be taken in the object under analysis
  (b) Information about analysis results
  (c) Plans for reviewing and updating the analysis
  (d) Follow-up

known. The approach taken in QUASA is to use a number of complementary methods of generating data alternative to that yielded by the original safety analysis with which the latter can then be compared. Some methods of generating such information for assessment of the hazard identification outputs include:

(1) parallel analysis
  (a) complete,
  (b) partial;
(2) comparison with operating experience;
(3) comparison with incident case histories.

Parallel analysis involves repeating the analysis using another analyst, either completely or in part. Full repeat analyses are time consuming and are rarely undertaken except in benchmark exercises, but sampling of the problem and partial analysis are more common.

A comparison may be made between the hazards identified in the safety analysis and incidents drawn from the operating experience of the plant. Since these cannot be expected to give the full range of potential incidents, particularly for rare events, a further comparison may be made by drawing on incident case histories for plants with similar features.

The safety analysis identifies deficiencies which in a proportion of cases will lead to incidents, but does not predict incidents as such. The same applies to the quality assessment of the safety analysis. The quality assessment, therefore, has to proceed by making a judgement as to which deficiencies have caused a particular incident. This then establishes the link between deficiencies and incidents.

8.29.6 Safety analysis performance

Thus, in general, there will be a number of deficiencies identified in the safety analysis, which may be compared with two other sets of identified deficiencies: those found by the quality assessor(s) and those inferred from incidents. There is no guarantee that these three sets comprise the total universe of deficiencies, but nevertheless the comparison gives a useful indicator of quality.

8.29.7 Assessor performance

Two indices of assessor performance are used which apply when there is more than one assessor. If a group of assessors is used, it is possible to compare the performance of the individual assessors. An interassessor reliability for a given assessor is defined as the ratio of the number of deficiencies identified by that assessor to the total number identified by all the assessors. The other index used is that of validity. This is defined as the ratio of the number of incidents illustrating deficiencies in the analysis identified by a given assessor to the total number identified by all the assessors. A high score by an assessor in interassessor reliability and a low score in validity means that a large proportion of the deficiencies identified are not significant causes of incidents.

8.29.8 Assessment studies

Four quality assessment studies were conducted and used to improve the checklist. The studies covered: (1) a pulp manufacturing process; (2) a chlorine liquefaction plant; (3) an liquefied petroleum gas storage and distribution system and (4) the First Canvey Report. All the studies involved quality assessment of the safety analysis as a whole, but in the first three the emphasis was on the quality of hazard identification, whilst in the fourth it was on the quality of the quantitative risk analysis.

In the original safety analysis of the pulp manufacturing process, the hazard identification methods used had been potential problem analysis (PPA), HAZOP and AEA. The PPA identified 30 hazards. The HAZOP identified over 150 hazards and gave 120 proposals for improvement. The AEA identified 25 opportunities for human error and gave 22 improvements.

In the quality assessment of this safety analysis, assessments were made by three assessors. The total number of deficiencies identified by the three assessors was as follows: system definition, 11; hazard identification, 24; accident modelling, 1; estimation of accident frequencies, 1; estimation of accident consequences, 3; risk estimation, 3; documentation, 9; and follow-up measures, 5. Assessor A found 36 deficiencies, assessor B found 17 of these same deficiencies and 13 new ones, assessor C found 20 of the deficiencies found by A and B and 8 new ones.

As far as concerns the checklist, out of the 138 questions, 70 were useful in revealing deficiencies in the safety analysis. Of these, 45 led to identification of deficiencies by one assessor, 28 to identification by two assessors and only 2 to identification by all three assessors.

The performance both of the safety analysis and of the quality assessors was checked against data obtained on operating experience on the plant. From these data, the assessors identified some 280 trivial incidents, which they classified under five headings, and 112 non-trivial

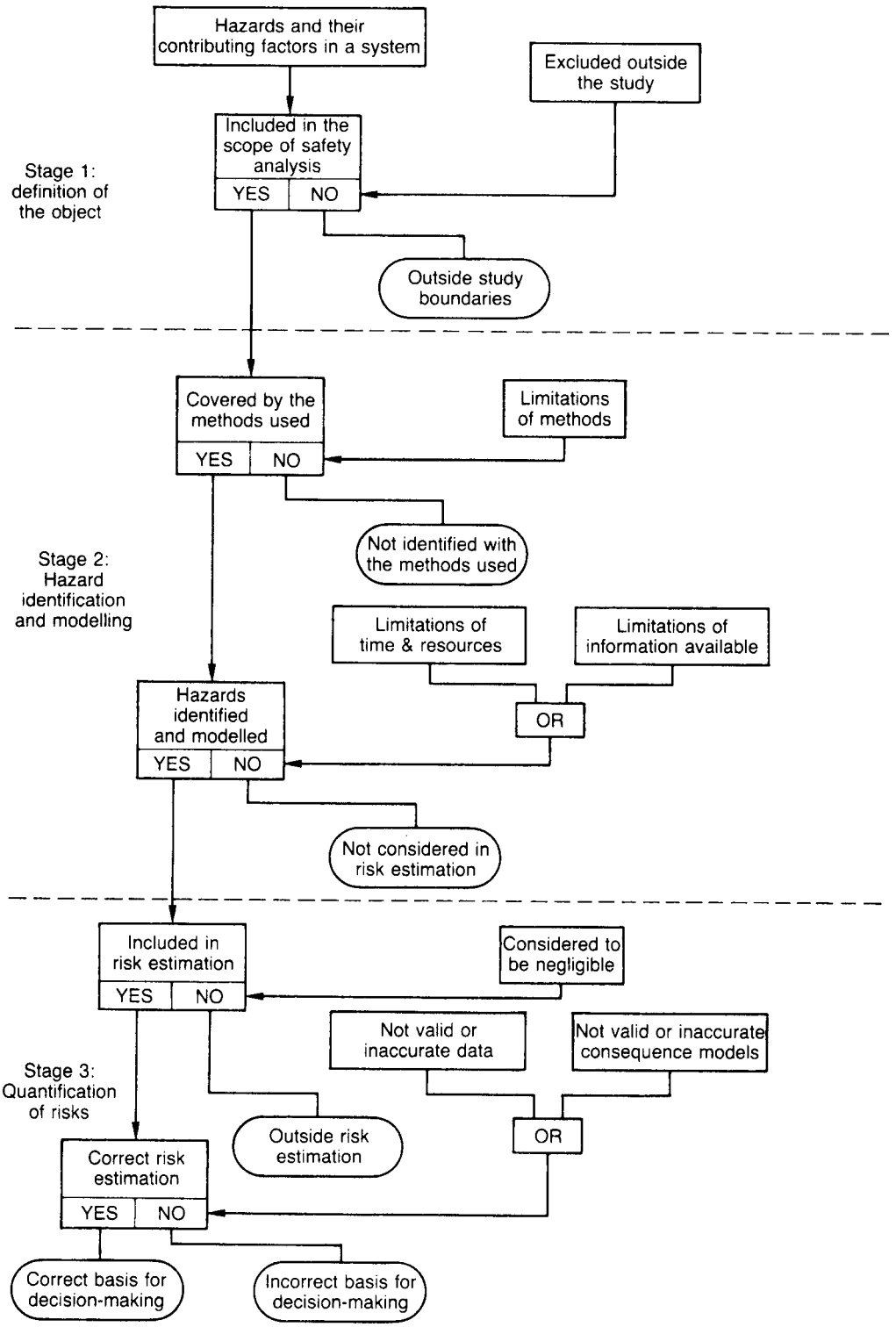

Figure 8.19 *Some potential limitations and deficiencies in a safety analysis (Rouhiainen, 1990)*

Table 8.50 *Identification of factors contributing to incidents by safety analysts and by quality assurance assessors: study of 117 incidents (after Rouhiainen, 1990)*

	Identified in safety analysis	*Not identified in safety analysis*		*Total*
		Identified by at least one assessor	*Not identified by any assessor*	
Physical subsystem	49	63	15	127
Environmental subsystem	7	4	2	13
Human subsystem	4	5	0	9
Managerial subsystem	2	10	1	13
Total	62	82	18	162
N	44	59	14	117

Table 8.51 *Some principal deficiencies in the First Canvey Report identified in two quality assessments (Rouhiainen, 1990)*

Author[a]	*(Analysis . . . 1980)*
Definition of the object	
– Definition of the area not clear	– Geographical limits should be applied only to fixed installations
– No definition of the residual regions	
– Employees and minor accidents excluded	– Minor events ignored – Office and factory workers excluded
Definition of the goals	
– No definition of the concept 'major interaction'	
– No definition of the types of hazards excluded	
– No criteria for choosing the accidents modelled	
– Cut-off criteria for risks which can be excluded not presented	– The analysis could have gone further
Organization of the risk analysis and methods used	
– Background of the team members not presented	
– Knowledge and experience of the team not presented	
– Incident statistics of the plants not used	– Comparison with accident statistics should have been made
Identification of hazards	
– Hazard identification not systematic	– Reference presents two hazards overlooked
– Not all factors affecting event-chains considered	– Smaller initiating events not considered
– Hazards caused outside the area not studied	– The same deficiency noted
– Not all materials taken into account	– Not all toxic chemicals included in the report
Estimation of accident frequencies	
– Not all assumptions and simplifications presented	– Assumptions and calculations criticized
– Reference for the data used not presented	– Noted that this prevents assessment of the data
– Statistical data used may in some cases be incorrect	– Reference presents examples of incorrect failure frequencies
– Effect of speed limit overestimated	– Noted as a source of inaccuracy – Basis of subjective judgements incorrect – Frequencies overestimated
Estimation of consequences	
– Not all principles and limitations of the models used presented	– Calculation methods not presented in enough detail – Reference presents many mistakes in the assumptions, simplifications and methods
– Estimation based only on average amounts of materials	
– The effect of the changes in the source term not estimated	
Estimation of risks	
– Not all assumptions, simplifications and calculations presented	– Many mistakes presented – Some serious arithmetic errors noted

Table 8.51 *(continued)*

– Cryogenic commission of LNG[b] tankers excluded – Risk estimated only for some regions – Not all aspects concerning emergency planning studied	– The same deficiency noted – Avoiding action of people not taken into account
Report of the risk analysis	
– Some characteristics of the analysis object not described – Accuracy of the results not presented	– The same deficiency noted – Results not presented in enough detail – No logical basis for selecting the remedies – No guidance for the future – The total impact of the hazards not estimated

[a] Author, single assessor; (Analysis, 1980), other critiques.
[b] Liquefied natural gas.

incidents, giving a total number of 117 different incidents in all. Of these 117 incidents, 73 had not been identified in the safety analysis.

Rouhiainen (1990) gives evaluations of the interassessor reliability and of the validity. The interassessor reliabilities were 58%, 53% and 49%. With regard to validity, of the 117 incidents, 59 illustrated deficiencies identified by at least one assessor and 30 deficiencies identified by all three assessors.

The number of factors considered to have contributed to these 117 incidents is given in Table 8.50.

The physical subsystem covered failures and malfunctions, structural defects, leaks within and from the system, pipe blockage and conveyor jamming, and process disturbances. The environmental subsystem covered environmental factors, weather and impurities.

Further aspects of the incidents identified were also analysed. Of the total 177 incidents, the effects on personnel safety were found to be as follows: leak of hazardous substance, 12; another immediate accident hazard, 5; hazard with a parallel failure, 19; increase in probability of hazard, 25; and no direct effect on safety, 56. The effects on plant operation were as follows: shut-down of whole plant, 8; shut-down of part of plant, 53; operating disturbance, 40; decrease in quality of pulp, 4; extra work only, 8; and no effect on production, 4. The account given by Rouhiainen (1990) of the other two plant studies follows this broad pattern.

After the second study, the checklist was revised. The aim of the revisions was to repair omissions, overlaps and obscurities and variability in level of detail.

The study of the Canvey Report was concerned with the quality of the QRA rather than with hazard identification. The checklist was applied by a single assessor and the deficiencies identified, which are shown in Table 8.51 were compared with those given in other critiques of the report, including the Second Canvey Report.

8.30 Notation

Section 8.6

AQ	airborne quantity (kg/s)
BI	Business interruption loss
C	Loss control credit factor
CEI	Chemical exposure index
CF	Credit factor
DF	Damage factor
EF	Escalation factor
EPRG	toxic limit (mg/m^3)
ER	Exposure radius
F_1	GPH factor
F_2	SPH factor
F_3	PUHF factor
F&EI	Fire and explosion index
GPH	General process hazard
HD	Hazard distance (m)
MF	Material factor
MPDO	Maximum probable days outage
MPPD	Maximum probable property damage
OV	Original value
PUHF	Process unit hazards factor
RV	Replacement value
SPH	Special process hazard
VAE	Value of the area exposed
VPM	Value of production per month

Section 8.19

L	Exponent of likelihood (where latter is expressed as a frequency)
S	severity category
TR	target risk

Section 8.28

c	measure of consequence
f	frequency of occurrence
N	number of hazards

Subscripts

chl	identified in a large case history list
id	identified
m	identified by method m
rl	realizable
tot	total existing

9 Hazard Assessment

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In the previous chapter, an account was given of the process of identifying hazards, of the methods available and of the follow-up. For the great majority of hazards the action to be taken is clear once the hazard is known. There are, however, some hazards that require further assessment. Originally, such hazard assessment was undertaken in order to assist in making engineering decisions in the 'grey' areas where further investigation is needed in order to decide on the most cost-effective measures. This is still the prime purpose of hazard assessment, but increasingly in recent years, this activity has been enlarged to deal with major hazards which are realized only very rarely but which present a threat to the public.

The aims and nature of these two activities are somewhat different. The terminology used to describe them also differs. In the United Kingdom, the practitioners of the first type of hazard assessment have tended to call it 'hazard analysis' (HAZAN). The second type is often called 'probabilistic risk analysis' (PRA), a term which came into use in the US nuclear industry, or simply 'risk analysis'.

Hazard assessment is introduced here, therefore, with an account of how it has developed historically. The use of hazard analysis as an aid to engineering decision-making is then described. As this account shows, the methods used in hazard analysis are often relatively simple.

Risk assessment is a more complex undertaking, as the account given indicates. The starting point is the identification of the hazards and definition of the hazard scenarios to be considered. For each hazard, the frequency and consequences are then estimated. The estimation of frequency may require the use of fault trees, event trees and/or cause–consequence diagrams. The estimation of the consequences involves the study of a sequence of events. Usually this is an emission of hazardous material which gives rise to certain physical effects. The estimation of these effects involves the use of a wide range of hazard models.

Some hazard assessments terminate at this point. If a full risk assessment giving risks to the public is required, however, it is necessary also to have models that define the characteristics of the population at risk, in order to allow for factors such as shelter and escape, which modify exposure to the physical effects, and then to estimate the proportion of people who suffer injury.

There are a number of forms in which the results of a risk assessment may be presented. It is desirable that information be presented on the degree of confidence in the results of the risk assessment. This is important both because there are inherent uncertainties in risk assessment and because the methodology is still developing. Although the numerical estimates produced by a quantitative hazard assessment may not be the most important outputs, it is necessary to have risk criteria by which to evaluate them.

Model hazard assessments for major hazards have been carried out by the Health and Safety Executive (HSE) to assist in land-use planning and by the Chemical Industries Association (CIA) to assist in emergency planning and in preparation of a safety case. The impact of a hazard on the surrounding area may be estimated using a hazard impact model.

A full risk assessment is a major undertaking. Various simplified techniques have been developed, involving a greater or lesser degree of approximation. These range from short-cut versions of the normal method to very simple and approximate methods. A major accident is usually preceded by a number of lesser events which may serve as warnings. The hazard warning structure may be analysed and used to enhance confidence that the hazard is under control.

A number of major risk assessments have been carried out, notably the two *Canvey Reports* and the *Rijnmond Report*. These are described in Appendices 7 and 8, respectively. Selected references on hazard assessment are given in Table 9.1.

Table 9.1 *Selected references on hazard assessment*

NRC (Appendix 28 *Probabilistic Risk Assessment*); Green and Bourne (1965 UKAEA AHSB(S) R91.1966 UKAEA AHSB(S) R117.1972); Recht (1965); F.R. Farmer (1967b, 1969a, 1971, 1975, 1981); Hensley (1967 UKAEA AHSB(S) R136, 1968); Buchanan and Hutton (1968); Fowler and Spiegelman (1968); A.E. Green (1968, 1969 UKAEA AHSB(S) R172, 1969–70, 1970, 1972, 1973, 1974a,b, 1976, 1982, 1983); R.L. Browning (1969a–c, 1970, 1973, 1980); O'Sell and Bird (1969); Benjamin and Cornell (1970); MCA (1970/18); Fine (1971, 1973); Houston (1971); Kletz (1971, 1972a, 1973a, 1974c, 1976d, 1977a,b,e,f, 1978a, 1979l,m, 1981d, 1983e,h,i, 1984b,h,j); Malloy (1971); R.M. Stewart (1971); J.R. Taylor (1973, 1974b,d, 1975a,b, 1976b, 1994); Apostolakis (1974, 1975, 1978, 1981, 1986, 1991); G.D. Bell and Beattie (1974); Bulloch (1974); DOT, CG (1974a–d); S.B. Gibson (1974, 1974b); Hoffman (1974); Krasner (1974); Lawley (1974a,b, 1976,1980); AEC (1975); Burgoyne (1975); Eisenberg, Lynch and Breeding (1975); Erdmann *et al.* (1975, 1977); D.O. Cooper and Davidson (1976); Critchley (1976); Kastenburg, McKone and Okrent (1976); M.J. Katz (1976); Sather (1976); Erdmann *et al.* (1977); Gangadharan and Brown (1977); Ravetz (1977b); Sacks and Liberty (1977); US Army Material and Development and Readiness Command (1977); US Congress, OTA (1977); Anon. (1978g); Cremer and Warner (1978); HSE (1978b, 1981a); Kumamoto and Henley (1978); Albaugh *et al.* (1979); Hanna (1979); R. King and Magid (1979); V.C. Marshall (1979a, 1980b, 1982a,b); Mumford and Lihou (1979a–c); Riso National Laboratory (1979/1); Anon. (1980m); Apostolakis, Garribba and Volta (1980); Bjordal (1980); Burke and Weiss (1980); Coiner, Cox and Sylvester-Evans (1980); Garribba and Ovi (1980); Jager (1980,1983); Lawley (1980); Lees (1980b,c, 1981b, 1982c); Opschoor and Hoftijzer (1980); Abramson (1981a,b); Apostolakis and Kaplan (1981); EPA (1981, 1987a); R.F. Griffiths (1981a,b, 1989, 1991a); Henley and Kumamoto (1981, 1985, 1992); Kaplan and Garrick (1981); Napier (1981); D.W. Pearce (1981); Slater, Ramsay and Cox (1981); J.M.T. Thompson (1981); W.A. Thompson (1981); F. Warner (1981b); Chatwin (1982a,b); CONCAWE (1982 10/82, 1984, 1988 88/56); Covello, Menkes and Nehnevajsa (1982); L.A. Cox (1982); R.A. Cox (1982a,b, 1986,1987, 1989a, 1990); R.A. Cox and Comer (1982); N.C. Harris (1982); Helmers and Schaller (1982); IBC (1982/38, 1989/77, 1991/85, 86, 1992/95, 1993/103); Kaiser (1982c, 1993); S. Kaplan (1982b); NRC (1982a); Rijnmond Public Authority (1982); Sancaktar (1982, 1983); R.F. White (1982); Barren, Daniels and Hagon (1983); Borse (1983a–c); Cardinale, Grille and Messina (1983); A.P. Cox and Pasman (1983); Coxon and Gilbert (1983); Daniels and Holden (1983); Eddershaw (1983 LPB 52); R.A. Freeman (1983, 1985, 1989);

IMechE (1983); Joschek (1983); Lans and Bjordal (1983); Lathrop and Linerooth (1983); S. Levine, Joksimovic and Stetson (1983); Mancini and Volta (1983); Opschoor and Schecker (1983); The Royal Society (1983, 1992); Considine (1984 SRD R310); Frankel (1984); Hawksley (1984, 1989); Lowe (1984); T. Redmond (1984); Waller and Covello (1984); Cullingford, Shah and Gittus (1985); Holden (1985, 1989); Nieuwhof (1985c); Olkkola *et al.* (1986); Rasbash (1986a); J.R. Taylor *et al.* (1986); Apostolakis and Moieni (1987); Boykin and Kazarians (1987); Guymer, Kaiser and Mckelvey (1987); Kanury (1987); Ozog and Bendixen (1987); Heising (1987); Paté-Cornell (1987); J.R. Thomson (1987); Andrews (1988); Burns (1988); CPD (1988, 1992a,b); Emerson, Pitblado and Sharif (1988); Nelms (1988); Suokas (1988); Waite, Shillito and Sylvester-Evans (1988); Wakeling (1988); Withers (1988); J.L Woodward and Silvestro (1988); Andow (1989); Bourdeau and Green (1989); FEMA (1989); Geary (1989); R.F. Griffiths (1989); Holden (1989 SRD R504); HSC (1989); ILO (1989); van Loo and Opschoor (1989); Prugh (1989); L.E.J. Roberts (1989); Rouhianen and Suokas (1989); Suokas and Kakko (1989); B. Rasmussen and Smith-Hansen (1989); Suokas and Rouhianen (1989); Anon. (1990h); Arendt (1990); Castleman (1990); Edmondson (1990); Fraser, Bussey and Johastone (1990); French, Olsen and Peloquin (1990a,b); Hirano (1990b); Pitblado, Williams and Slater (1990); Schaller (1990); Smith (1990 LPB 93); Turney (1990a,b); Bowonder, Arvind and Myake (1991); A. Fisher (1991); Greenberg and Cramer (1991); Hurst (1991); S. Brown (1991); Basta (1992); CIA (1992 SRD RCS4, RC55, RC56); S.J. Cox (1992); Fryer and Mackenzie (1992); Goodner (1992); Heinold (1992); IAEA (1992); Papazoglou *et al.* (1992); Peacock and White (1992); J.R. Taylor (1992); Tweeddale (1992, 1993a,c); Twisdale *et al.* (1992); Ziegler (1992); Claggett *et al.* (1993); Frank, Giffin and Hendershot (1993); Goldsmith and Schubach (1993); Melchers and Stewart (1993); Rimington (1993); M.W. Wright, Bellamy and Cox (1993); Christen, Bohnenblust and Seitz (1994); Eastwood (1994); Melville (1994); Pitblado (1994b); Rosenthal and Lewis (1994)
Terminology: Higson (1981); F.Warner (1981b); V.C. Marshall (1981a,b, 1982c); A.E. Green (1982a); R. Mitchell (1982); Rasbash (1982b); D. Jones (1992); Hotson (1994 LPB 120)
ISGRA: ISGRA (1982,1985); Holden, Lowe and Opschoor (1985); Clerinx (1986)
CONCAWE: Hope (1983)
CCPS: Goldthwaite *et al.* (1987); R.A. Freeman (1990)

Incident scenarios
Wells *et al.* (1992)

Hazard assessment priorities, preliminary hazard assessment
Harrington *et al.* (1986); Holloway (1989); Keey (1991); Bergmann (1993); Allum and Wells (1993); Ganger and Bearrow (1993); Wells, Wardman and Whetton (1993)

Event data (*see* Table A14.1)

Fault trees
IEC (Std 1205); NRC (Appendix 28 *Fault Tree Analysis*); Esary and Proschan (1963); Boeing Company (1965); Feutz and Waldeck (1965); Haasl (1965); Mearns (1965); Michels (1965); Recht (1966c); W.Q. Smith and Lien (1968); Crosetti and Bruce (1970); Mieze (1970); Vesely (1970a,b, 1977b, 1983); Crosetti (1971), Houston (1971); NTSB (1971); R.M. Stewart (1971,1974a,b); Bennetts (1972, 1975); Fussell and Vesely (1972); Andow (1973, 1976, 1980, 1981, 1989); Barlow and Chatterjee (1973); Fussell (1973a,b, 1975,1976,1978b); Henley and Williams (1973); Fussell, Henry and Marshall (1971); R.A. Evans (1974, 1975); Fussell, Powers and Bennetts (1974); Lawley (1974a,b, 1980); Malasky (1974); Phibbs and Kumamoto (1974); Powers and Tompkins (1974a,b, 1976); AEC (1975); Andow and Lees (1975); Barlow, Fussell and Singpurwalla (1975); Esary and Ziehms (1975); Lambert (1975, 1976, 1977, 1978b); R.L. Browning (1975, 1976, 1979, 1980); Nieuwhof (1975); Caceres and Henley (1976); Carnino (1976); Lambert and Yadigaroglu (1976); Y.T. Lee and Apostolakis (1976); Powers and Lapp (1976); Salem, Apostolakis and Okrent (1975a,b, 1977); Apostolakis and Lee (1977); Brock (1977 NCSR R14); Burdick *et al.* (1977); Doering and Gaddy (1977); Gangadharan, Rao and Sundarajan (1977); Garriba *et al.* (1977); Kolodner (1977b); Lambert and Gilman (1977a,b); Lapp and Powers (1977a, 1979); Martin-Soils, Andow and Lees (1977); Mingle, Chawla and Person (1977); NBA (1977); G.D.M. Pearson (1977); Vaillant (1977); Astolfi, Contini and van den Muyzenberg (1978); Astolfi *et al.* (1978); Chamow (1978); Himmelblau (1978); J.R. Taylor (1976c, 1978b, 1979, 1982); D.M. Brown and Ball (1980); Dasarathy and Yang (1980); Hauptmanns (1980, 1986); Piccinini *et al.* (1980); Pilz (1980a,b); D.J. Allen 1981); Prugh (1981, 1982, 1992a); Welsh and Lundberg (1980); Arendt and Fussel (1981); Henley and Kumamoto (1981, 1985, 1992); Kumamoto, Inoue and Henley (1981); Vesely *et al.* (1981); Kletz and Lawley (1982); Schreiber (1982); Alesso (1983, 1985); Hauptmanns and Yllera (1983); Johnston and Matthews (1983 SRD) R245); Bendixen and O'Neill (1984) Doelp *et al.* (1984); J.M. Morgan and Andrews (1984); Shafaghi, Andow and Lees (1984a,b); Slater (1984); Zipf (1984); Alesso, Prasinos and Smith (1985); Andrews and Morgan (1985, 1986); Bendixen, Dale and O'Neill (1985); BG (1985 Communication 1242); Camarinopoulos and Yllera (1985); Jiang Mingxiang (1985); Keey and Smith (1984); Laviron and Heising (1985); W.S. Lee *et al.* (1985); J.M. Morgan (1985); Yampolsky, Adam and Karahalios (1985); Flothmann and Mjaavatten (1986); Harron (1986); Page and Perry (1986); Ruan Keqiang (1986); Vervalin (1986b); R.P. Hughes (1987a); Jeong, Chang and Kim (1987); Limnios (1987b); Kohda and Henley (1988); Kohda, Henley and Inoue (1989); Kumar, Chidambaram and Gopalan (1989); Singer (1990); Aldersey, Lees and Rushton (1991); H. James, Harris and Hall (1992); Kavianian, Rho and Brown (1992); Minton and Johnson (1992); Andrews and Moss (1993); Bueker *et al.* (1993); D.A. Lee and Browne (1993); Vincoli (1993); ANSI Y32.14-1973; BS 5760: Part 7: 1991
Graph theory, graphical methods: Karnopp and Rosenberg (1968); Harary, Norman and Cartwright (1975); Biggs, Lloyd and Wilson (1976); Carre (1979); Chachra, Ghare and Moore (1979); Umeda *et al.* (1979, 1980); Boffey (1981); Temperley (1981); Khoda and Henley (1988)
Kinetic tree theory: Vesely (1969, 1970b); Vesely and Narum (1970); Vesely and Goldberg (1977a,b)
GO methodology: R.L. Williams (1977)

Fault free synthesis (*see also* Table 30.1)
Lapp-Powers method: Henley and Kumamoto (1977); Lapp and Powers (1977a, 1979); Locks (1979, 1980); Powers (1977); Shaeiwitz, Lapp and Powers (1977); Lambert (1979); Yellman (1979); Cummings, Lapp and Powers (1983); Ulerich and Powers (1988)

Event trees
NRC (Appendix 28 *Event Trees*); von Alven (1964); N.C. Rasmussen (1974); AEC (1975); Andow (1976); Vesely (1977b); HSE (1978b); Worledge (1979 SRD R128); Welsh and Lundberg (1980); Kaplan (1982a); Schreiber (1982); Slater (1984); Limnios and Jeannette (1987); Melo, Lima and Oliviera (1987); Aldersey, Lees and Rushton (1991); H. James, Harris and Hall (1992); Piccinini, Scarrone and Ciarambino (1994)

Cause–consequence diagrams
D.S. Nielsen (1971, 1974, 1975); R.A Evans (1974); J.R. Taylor (1974c,d, 1975a, 1976c, 1978a); D.S. Nielsen, Platz and Runge (1975); J.R. Taylor and Hollo (1977a,b); Himmelblau (1978)

Dependent failures
Epler (1969); Fleming (1974); AEC (1975); R.A. Evans (1975); Apostolakis (1975); Fleming and Hannaman (1976); J.R. Taylor (1976a); NEA (1977); Vesely (1977a); D.P. Wagner, Cate and Fussell (1977); D.P. Wagner and Fussell (1977); Fussell (1978a); Edwards and Watson (1979 SRD R146); Welsh and Lundberg (1980); Bourne *et al.* (1981 SRD R196); Johnston and Crackett (1985 SRD R383); Crackett (1986 SRD R411); B.D. Johnston (1987a,b); Humphreys (1987); R.P. Hughes (1987h); Humphreys and Johnson (1987 SRD R418); B.R. Martin and Wright (1987); G.T. Edwards (1988); Mosleh *et al.* (1988); Attwood (1991); Andrews and Moss (1993)

Escalation, domino effects
Labath and Amendola (1989); Bagster and Pitblado (1991); Four Elements Ltd (1991); Purdy, Pitblado and Bagster (1992); Latha, Gautam and Raghavan (1992); Scilly and Crowther (1992); Pettit, Schumacher and Seeley (1993)

Expert judgement (*see* Table 7.1)

Rare events
Pressure vessel failure (*see* Table 12.1)

External threats
NRC (Appendix 28 *External Hazards*)
Aircraft crashes: Chelapati, Kennedy and Wall (1972); Marriott (1987); Phillips (1987 SRD R435)
Weather: Eagleman, Muirhead and Williams (1975); Eagleman (1983); Page and Lebens (1986); Peters and Hansel (1992)
***Earthquakes* (*see* Table A15.1)**
Floods: McCullough (1968)
Hurricanes: L.R. Russell and Schueller (1974)
Landslides: Zaruba and Mencl (1982)
Tornadoes: Twisdale *et al.* (1978); Peters and Hansel (1992);Rutchef *et al.* (1992)

Management systems
Barrell and Thomas (1982); R.A. Cox and Comer (1982); Powell and Canter (1984); Pitblado, Williams and Slater (1990); Burge and Scott (1992); J.C. Williams and Hurst (1992); A.J. Smith (1992); Bellamy, Wright and Hurst (1993)

Human factors (*see also* Table 14.11)
Howland (1980); Ingles (1980); Welsh and Lundberg (1980); Spangler (1982); Rasmussen and Pedersen (1983); Melchers (1984); Ramsden (1985); Bellamy, Kirwan and Cox (1986); Bellamy and Geyer (1988); Delboy, Dubnansky and Lapp (1991); Banks and Wells (1992); Bridges, Kirkman and Lorenzo (1992); Yukimachi, Nagasaka and Sasou (1992); Zimolong (1992); Cameron (1993); Nawar and Samsudin (1993)

Hazard models (*see also* Tables in Chapters 15–18)
Longinow *et al.* (1973); Dunn (1974); AD Little Inc. (1974a); Benedict (1978); Cremer and Warner (1978); HSE (1978b, 1981a); R.A. Cox *et al.* (1980); Rijnmond Public Authority (1982); Bello and Romano (1983a); Crocker and Napier (1988a,b); Chhiba, Apostolakis and Okrent (1991); Pietersen (1990); Bagster (1993); Geeta, Tripathi and Narasimhan (1993); Mallet (1993); K.E. Petersen (1994)

Hazard model systems
Harding, Parnarouskis and Potts (1978); Jäger, Diedershagen and Kühnreich (1989); FEMA (1989); Pitblado and Nalpanis (1989); Raj (1991); Papazoglou *et al.* (1992)
CPD, TNO: Opschoor (1979); CPD (1992a,b)
DYLAM: Nivolianitou, Amendola and Reina (1986); Labath and Amendola (1989)
RISKAT: Pape and Nussey (1985,1989); Hurst, Nussey and Pape (1989); Nussey, Mercer and Clay (1990); Nussey, Pantony and Smallwood (1992, 1993)
SAFETI: Pitblado and Nalpanis (1989); Pitblado, Shaw and Stevens (1990)
Vulnerability model: DOT, CG (1974a–d); Raj and Kalelkar (1974); Eisenberg, Lynch and Breeding (1975); Enviro Control Inc. (1976, 1977); Rausch, Tsao and Rowley (1977); Rowley and Rausch (1977); Rausch, Tsao and Rowley (1977); Rausch, Eisenberg and Lynch (1977); Tsao and Perry (1979); USCG (1979); Parnarouskis, Perry and Articola (1980); Perry and Articola (1980); Dodge *et al.* (1983)
WHAZAN: Technica (1985); World Bank, Office of Environmental and Science Affairs (1985)
QRA Toolkit: Technica (1991)

Population characteristics, exposure
NRC (Appendix 28 *Population Distribution*); Robinson and Converse (1966); F.R. Farmer (1967b); Athey, Tell and Janes (1973); AEC (1975); Eisenberg, Lynch and Breeding (1975); Hewitt (1976); Chartered Institute of Building Services (1977b); Fitzpatrick and Goddard (1977); HSE (1978b); Hushon and Ghovanlou (1980); OPCS (1980,1981a–c); Rhind (1983); CSO (1985); Schewe and Carvitti (1986); Petts, Withers and Lees (1987); van Loo and Opschoor (1989); ACDS (1991)

Mitigation of exposure
NRC (Appendix 28 *Mitigation Systems*)
Evacuation: NRC (Appendix 28 *Evacuation*); Hans and Sell (1974); Westbrook (1974); Solomon, Rubin and Okrent (1976); HSE (1978b); Urbanik *et al.* (1980); A.F.C. Wallace (1980); Sorensen (1987); Duclos, Binder and Rieter (1989); G.O. Rogers and Sorensen (1989); P.J. Harrison and Bellamy (1989/90)
***Shelter* (*see* Table 15.10)**
Other measures: Tsuchiya *et al.* (1990)

Injury relations
Lees (1980b); Bourdeau and Green (1989); CPD (1992b); CCPS (1994/15)
Probit methods: R.A. Fisher and Yates (1957); Finney (1971); Eisenberg, Lynch and Breeding (1975); HSE (1978b, 1981a); Lees (1980b); Paradine and Rivett (1980); CPD (1988, 1992a,b); Emerson, Pitblado and Sharifi (1988); MacFarlane and Ewing (1990); V.C. Marshall (1989b); J. Singh and McBride (1990); R.F. Griffiths (1991b); de Weger, Pietersen and Reuzel (1991); Opschoor, van Lao and Pasman (1992)

Presentation of results
Rothschild (1993)

Frequency–number (FN) tables, curves: F.R. Farmer (1967b); Provinciate Waterstaat Groningen (1979); R.F. Griffiths (1981e); Okrent (1981); Rijnmond Public Authority (1982); Hagon (1983, 1984, 1986); Vervauin (1986b); Ormsby and Le (1988); J.L. Woodward and Silvestro (1988); Saccomano, Shortreed and Mehta (1990); ACDS (1991); Pietersen and van het Veld (1992); Prugh (1992c)

Uncertainty, confidence and sensitivity
AEC (1975); Jacobsen (1980); Parry and Winter (1980 SRD R190); Amendola (1983b); Nussey (1983); Olivi (1983); Unwin (1984 SRD R301); Siu and Apostolakis (1985); Crick, Morrey and Hill (1986); Garlick (1987 SRD R443); Baybutt (1989); I. Cook and Unwin (1989); Goosens, Cooke and van Steen (1989); S.R. Hanna, Chang and Strimaitis (1990); ACDS (1991); Chhiba, Apostolakis and Okrent (1991); S.R. Hanna, Strimaitis and Chang (1991b); Amendola, Contini and Ziomas (1992a,b); Kortner (1992); van Wees and Mercx (1992); Shevenell and Hoffman (1993); Quelch and Cameron (1994)
Error propagation: Barry (1978); Karlsson and Bjerle (1980); Park and Himmelblau (1980); Chang, Park and Kim (1985); Keey and Smith (1984); Asbjornsen (1986); Dohnal *et al.* (1992); Melchers (1993a); Quelch and Cameron (1993)

Evaluation of results (*see also* Table 9.36)
Harvey (1979b, 1984); Kastenberg and Solomon (1985); R.F. Griffiths (1989); HSE (1989c); Casada, Kirkman and Paula (1990); Lapp (1990)

Quality assurance of hazard assessment
J.R. Taylor (1979); Welsh and Debenham (1986); Rouhiainen (1990); Pitblado (1994a)

Validation of hazard assessments
A. Taylor (1979, 1981); Jenssen (1993); R.F. Evans (1994); Nussey (1994)

Follow-up, outcome of hazard assessments
HSE (1978b, 1981a); Rijnmond Public Anthority (1982); Baybutt (1983, 1986); J.R. Taylor (1984); Arendt (1986); Vestergaard and Rasmussen (1988); Desaedeleer *et al.* (1989); Cullen (1990); Schaller (1990); Kakko, Virtanen and Lautkaski (1992); Tweedale (1993b)

Hazard assessment in decision-making
HSE (1983e, 1989c); Kelly and Hemming (1983); Harbison and Kelly (1985); Blokker (1986)

Hazard assessment and emergency planning
Burns (1988); J. Singh and McBride (1990); Tavel, Maraven and Taylor (1989); Essery (1991)

Hazard impact model
Poblete, Lees and Simpson (1984); Lees, Poblete and Simpson (1986); Lees (1987)

Hazard warning
Warning events analysis: J.H. Bowen (1978); Page (1979); W.G. Johnson (1980); Slater and Cox (1984); van Kernel, Connelly and Haas (1990)
Hazard warning structure:
Lees (1982b, 1983b, 1985); Keey (1986a,b); Lake (1986); Pitblado and Lake (1986, 1987); E. Smith and Harris (1990)

Planning (*see also* Table 4.1)
Batstone and Tomi (1980); Brough (1981); Pantony and Smith (1982)

HSE
Harvey (1976, 1979b, 1984); HSE (1978b, 1981a, 1989c,e); Barrell (1980); Barrell and Thomas (1982); Pantony and Smith (1982); ACDS (1991)

Offshore
Borse (1979); Pyman and Gjerstad (1983); Vinnem (1983); Cullen (1990)

Civil and structural engineering
Blockley (1980); Ingles (1980); Melchers (1984)

Hazard assessment applications and case histories
McGillivray (1963a,b); Kletz (1971, 1972a); Ybarrando, Solbrig and Isbin (1972 AlChE/119); Siccama (1973); Lawley (1974a,b, 1976, 1980); N.C. Rasmussen (1974); AEC (1975); Dicken (1975); J.R. Campbell and Gaddy (1976); Moser, Moel and Heckard (1976); Sellers (1976, 1988); Shell UK Exploration and Production (1976); Lundquist and Laufke (1977); D.S. Nielsen (1977); D.S. Nielsen, Plate and Kongso (1977); Okrent (1977); Rasbash (1977b); HSE (1978b,d, 1981a); Blokker *et al.* (1980); Joschek *et al.* (1980); de Ruiter and van Lookeren Campagne (1980); van der Schaaf and Opschoor (1980); Sutcliffe (1980); van Vliet *et al.* (1980); Helmeste and Phillips (1981); Considine, Grint and Holden (1982); Huberich (1982); Piccinini *et al.* (1982); Solberg and Skramstad (1982); Belo and Romano (1983b); Bergmann and Riegel (1983); Considine (1983,1986); Jager (1983); D.A. Jones (1983); D.S. Nielsen and Platz (1983); White (1983 SRD R273); Arendt *et al.* (1984); O'Mara and Burns (1984); Prijatel (1984); L.B. Grant (1985); Arendt (1986); Arendt, Casada and Rooney (1986); Blything (1986); Gebhart and Caldwell (1986); D.A. Jones and Fearnehough (1986); Labath *et al.* (1986); Rochina (1986); Shea and Jelinek (1986); Al-Abdullally, Al-Shuwaib and Gupta (1987); Page (1987) R.A. Cox (1989b); Crossthwaite, Fitzpatrick and Hurst (1988); Ormsby and Le (1988); Rooney, Turner and Arendt (1988); Sellers and Picciolo (1988); J.L. Woodward and Silvestro (1988); Anon. (1989 LPB 96, p.19); Cassidy (1989, 1990); CIA, Chlorine Sector Group (1989); M.M. Grant (1989); Klug (1989); Kumar, Chidambaram and Gopalan (1989); Grint and Purdy (1990); Schaller (1990); Shei and Conradi (1990); M.P. Singh (1990); Tweeddale and Woods (1990); ACDS (1991); S. Brown (1991); Duong (1991); R.J. Clarke and Nicholson (1992); Myers, Mudan and Hachrnuth (1992); Sorenson, Carnes and Rogers (1992); Goyal (1993, 1993 LPB 1123); Mant (1993)
ISPRA Benchmark Studies: CEC (EUR 13386 EN, EUR 13597 EN); Amendola (1983a,b); Amendola, Contini and Ziomas (1992a,b)
Safety cases: Lees and Ang (1989b); Wiedeman (1992); R.F. Evans (1994)

Guide assessments, including safety case assessments
BCGA (1984); Crossthwaite (1984, 1986); Pape and Nussey (1985); CIA Chlorine Sector Gp (1986, 1989); Clay *et al.* (1988); LPGITA (1988); FMA (1989); Lees and Ang (1989b)

9.1 Background

An understanding of the way in which hazard assessment has developed historically is important in appreciating its present role. Hazard analysis was developed in the 1960s as part of the response to the problems that stimulated the

development of loss prevention in general, as described in Chapter 1.

One problem area was the availability of large, single stream chemical plants. Application of the techniques of reliability engineering was one of the measures taken to correct this. Closely related was the problem of high hazard plants. Several major protective systems were implemented. These were designed using fault trees and instrument failure data, and risk criteria were devised to evaluate them. Another matter of concern was the increasing quantity of chemicals being transported around the country by road, rail and pipeline. Assessments were made of these operations.

The industry was initially assisted in the use of reliability engineering by the UK Atomic Energy Authority (UKAEA), but soon began to develop its own approach. One innovation introduced was the use of the hazard and operability study as a means of identifying hazards. This technique was developed by the chemical industry. The industry also developed a rather distinctive approach to hazard assessment. It was clear that in order to improve plant reliability and safety it was necessary to modify the plant designs, by using more reliable equipment and/or configurations and by incorporating additional protective devices. There was a severe problem, however, in selecting from the large number of measures which might be taken, those which were most cost-effective.

In many cases, once a hazard had been identified, it was clear what action should be taken, but there were sometimes 'grey' areas where the decision was not clear-cut. This is the problem which hazard analysis addresses. Typically, the use of hazard analysis involves estimating the frequency of realization of the hazard without and with some protective measure, and then evaluating the results using an appropriate criterion. The frequency of the hazard is usually estimated directly from data for that event, but it sometimes has to be synthesized from a fault tree using data for events lower down the tree.

The spirit in which the early hazard analysis was developed was to use quantitative methods but to keep it simple. Fault trees were used, but they were usually nothing like as complex as those developed for nuclear plants. Often the calculations were almost of a 'back of the envelope' type. In this, the approach had much in common with that of early operational research. Some examples of such hazard analysis are given in the next section. They are estimates made in support of engineering decision-making.

9.2 Hazard Analysis

Hazard analysis is now a well-established method for aiding engineering decision-making. An account is given in *Hazop and Hazan: Notes on the Identification and Assessment of Hazards* (Kletz, 1983d, 1986d, 1992b). The activity of hazard analysis may best be described in terms of illustrative examples. A collection of such examples has been given by Kletz (1971). Before giving these examples, however, it is necessary to describe the risk criterion used in them.

9.2.1 Fatal Accident Rate criterion

A risk criterion is required for the evaluation of the estimates made in hazard analysis. The criterion which was developed in the original work and which is still in almost exclusive use is the Fatal Accident Rate (FAR). The FAR is defined as the number of fatalities per 10^8 exposed hours. The meaning of the FAR may perhaps be best understood by saying that if the actual FAR is, say, 4, and if 1000 men go into a chemical works at the age of 20 years, then at the age of 60 years 996 men will leave the works alive. At the time when it was developed as a criterion, the actual FAR for the UK chemical industry was about 3.5.

The way in which the FAR is applied is then as follows. The total FAR is divided into 10 parts. Five of these are allocated for everyday hazards such as falling downstairs or having a spanner dropped on the head. The other five parts are allocated to technological hazards specific to the plant on which the employee works. It is assumed that there are no more than five of these on a given plant. This then gives one part available for each technological hazard on that plant. Thus if, for example, the actual overall FAR of 3.5 is also taken as the overall target value which is not to be exceeded, the target FAR for a single, specific technological hazard will be 0.35.

The FAR was originally called the Fatal Accident Frequency Rate (FAFR), but since this is tautologous, the term Fatal Accident Rate (FAR) is preferred. The FAR criterion is discussed further in Section 9.21.

9.2.2 Pipeline fracture

A hazard identified on one particular plant was contact of refrigerated liquefied gas with a mild steel pipeline, leading to brittle fracture. One method of avoiding this hazard was to use stainless steel, which would be very expensive. A much cheaper method was to use a trip system to prevent the cold gas from contacting the line. The use of hazard analysis to tackle this problem is described by Kletz (1971) as follows:

> Using data on the reliability of the various components of the trip system and assuming the operator will ignore the initial alarm system on one occasion out of four, the 'fractional dead time' of the whole system (that is, the fraction of time it is not operating) was calculated. This depends on the frequency with which the trips are tested. The 'demand rate' on the system, the number of times per year it is called on to operate, was estimated from previous experience.

The failure rate of the whole system was then estimated as once in 10,000 years or once in 2500 years for the whole plant which contained four similar systems.

It was assumed that one tenth of the occasions on which the cold gas reached mild steel would result in a leak, an explosion and a fatality – almost certainly an overestimate. A fatality will then occur once in 25,000 years giving an FAFR of 0.45. It was therefore agreed that the control system was satisfactory and it was not necessary to replace the mild steel by stainless steel.

It might be argued that the latter course is preferable as it is 100% safe, the FAFR is zero. Had we done this, the cost of reducing the hazard rate to zero would have been equivalent to £150,000,000 per life saved.

This example illustrates many of the characteristic features of hazard analysis. The aim of the analysis is to select a measure to deal with a hazard. An estimate is made of the frequency of realization of the hazard, based on a simple calculation using field data. The estimate made is somewhat conservative. The result is evaluated using the FAFR criterion, this criterion not being applied slavishly but with regard to the uncertainty in the estimate. A further check

is done on the value of a life implied by the decision alternatives.

9.2.3 Crankcase explosions

Another example is the problem of possible crankcase explosions in a building housing 25 compressors. Data obtained from a survey showed that there was one explosion per 500 machine-years. In order to achieve an FAR of 0.35 the proportion of explosions causing fatalities would not have had to exceed 1 in 1650. As there were normally several men in the building, the risk was clearly too high. The risk had to be reduced; the method actually used being to fit a suitable relief valve.

9.2.4 Hazardous area classification

A third example relates to hazardous area classification. Flameproof or intrinsically safe electrical equipment is required in Division 1 areas in which flammable gas or vapour is likely to be present under normal operating conditions. Totally enclosed 'non-sparking' equipment may be used in Division 2 areas, in which flammable gas or vapour is likely to be present under abnormal conditions. It is more economic to use this latter type of equipment and it is therefore desirable to apply the Division 1 classification only to those areas where it is really necessary. Records indicate that Division 2 motors develop a fault that causes them to spark or overheat at a rate of once per 100 years. Observation indicates that the probability of a man being within 10 ft (3 m) of a given motor in a plant area is 1 in 20. If it is assumed that anyone within this distance is killed when an explosion occurs, that on half the occasions when a flammable atmosphere occurs there is no explosion because diffusion into the equipment is slow and short-lived concentrations of gas/vapour can be ignored and that there are 100 motors on the plant, then an area may be classed as Division 2 if it has a flammable mixture for less than 10 h/year. This is the figure that corresponds to an FAR of 0.35.

9.3 Risk Assessment

The hazards considered in hazard analysis as just described are typically accidents with the potential to cause one or two fatalities. By contrast, quantitative risk assessment (QRA), also known as probabilistic risk assessment (PRA) or probabilistic safety assessment (PSA), usually deals with major hazards that could cause a high death toll.

A full risk assessment involves the estimation of the frequency and consequences of a range of hazard scenarios and of individual and societal risk. This is a major undertaking. An outline of the classical procedure of risk assessment is given in Figure 9.1. The diagram shows the principal elements and the broad structure, but there are variations and there is a degree of iterations, which is not shown. A risk assessment should be undertaken only if the purpose of the study has been well defined. If this is not done, it is unlikely that full value will be derived from the results obtained.

Identification of the hazards is the essential first step. The quality of the assessment depends crucially on the comprehensiveness of the hazard identification. Techniques of hazard identification have been discussed in Chapter 8. The method most relevant to risk assessment is the review of release sources. It is also necessary to identify the vulnerable targets, both persons and property.

A scenario is then developed for each potential release. The scenario defines the nature of the release and thus determines the subsequent chain of consequences. Since there is an infinite number of potential releases, it is necessary to arrange them in a limited number of groups of broadly similar nature. Some factors affecting the scenarios include the hole size and the duration, which may depend on any emergency shut-off. This procedure gives the source terms.

For each release scenario, a set of consequence chains is developed showing the escalation of the event. The different chains arise from the influence of conditions that affect the development of the event, such as the wind direction and velocity and stability conditions and, for flammables, the ignition sources. A typical consequence chain is shown in Figure 9.2. The dotted line in the figure represents the widening of the confidence bounds as the successive events become more remote from the initial release.

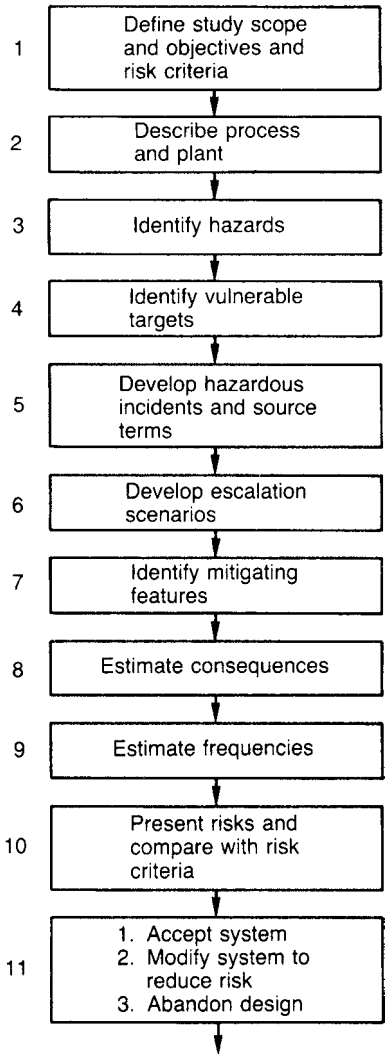


Figure 9.1 *The risk assessment process*

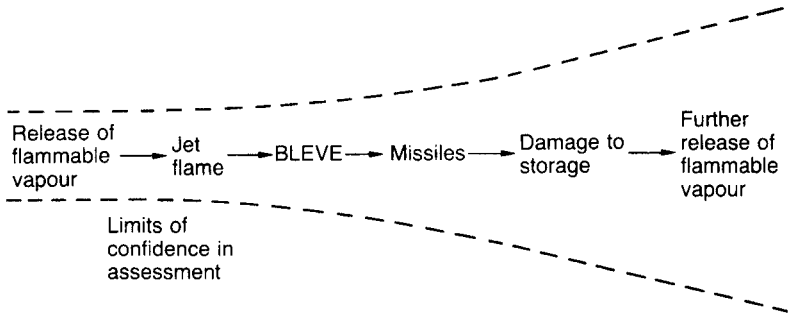


Figure 9.2 *A consequence chain*

Table 9.2 *Typical sequences of events in a risk assessment*

A	**Flammable release**
	Emission
	Vaporization (if liquid)
	Air entrainment
	Gas dispersion
	Ignition
	Flash fire or vapour cloud explosion
B	**Toxic release**
	Emission
	Vaporization
	Air entrainment
	Gas dispersion

The set of consequence chains is conveniently represented in the form of an event tree. Each of the branches of the event tree represents a single consequence chain. The outcomes are generally defined as events such as flash fire, vapour cloud explosion or toxic cloud. It is then necessary to identify any features that may mitigate the effects of these events on people or property. Factors that modify the exposure of the people include shelter, escape and evacuation.

In order to estimate injury or damage, it is necessary to model the sequence of events leading up to each outcome. Two typical chains of events are shown in Table 9.2, one for a flammable release and the other for a toxic release. Physical models are required which describe each stage in the sequence. Using these hazard models for the successive stages of the chain, the intensity of the physical effect is estimated.

The effect of a given outcome event on persons or property is estimated from the intensity of the harmful physical effect. These effects include:

(1) thermal radiation;
(2) explosion
    (a) overpressure,
    (b) impulse;
(3) toxic concentration
    (a) dosage,
    (b) concentration–time function.

The risk of injury is determined using injury relations that give the probability of a defined degree of injury as a function of the intensity of the physical effect. Similar procedures apply to property damage. Some hazard assessments are terminated at this point. The consequences are evaluated.

In other cases, an estimate is made of the frequencies of some or all of the outcomes. This involves first the estimation of the frequency of the release scenario. It may be possible to do this directly from failure data or it may be necessary to synthesize a value using fault tree methods. Then, using the event tree framework, an estimate is made of the probability of the various events constituting the branch points in the event tree and hence the frequencies of the outcomes. Other hazard assessments are terminated at this stage. The frequencies of the various consequences are evaluated.

Alternatively, the assessment is continued to provide a full risk assessment yielding individual and societal risks. Societal risk is expressed as a set of points representing increasingly serious events and relating the numbers of persons affected to the frequencies of the events. Estimation of societal risk involves determining the population at risk. The results of the assessment may be presented in a number of different forms such as risk contours on a map of the site or tables or graphs of individual and societal risks. Each stage of the assessment is attended by uncertainty. It is necessary, therefore, to provide measures of this uncertainty. Thus, the frequency of an outcome may be expressed as a frequency distribution or range of values rather than as a single figure. Finally, the results so obtained are evaluated using risk criteria.

The foregoing account is a simplified one. In particular, the information from a particular stage may lead to modification of the design and an iteration in which the results from that stage are recalculated. As indicated, the hazard assessment may be terminated short of a full risk assessment following assessment of the consequences. The consequences may be judged tolerably low for any foreseeable frequency.

In the scheme outlined, the estimation of the frequencies is deferred until a relatively late stage. An alternative approach is to perform this stage rather earlier. The hazard assessment may also be terminated following assessment of the frequencies. The frequencies may be judged tolerably low for any foreseeable consequences.

The individual aspects of QRA are discussed in more detail in the following sections.

There are differences of view on the value of such risk assessments. Some criticisms are directed to the basic philosophy underlying the methodology, others to the evaluation of the risk estimates generated. An account of the debate on risk assessment is given in Section 9.28.

Table 9.3 *Principal contents of NRC PRA Procedures Guide (Nuclear Regulatory Commission, 1982a)*

1.	Introduction
2.	PRA organization
3.	Accident-sequence definition and system modelling
4.	Human reliability analysis
5.	Database development
6.	Accident-sequence quantification
7.	Physical processes of core melt accidents
8.	Radionuclide release and transport
9.	Environmental transport and consequence analysis
10.	Analysis of external events
11.	Seismic, fire and flood risk analyses
12.	Uncertainty and sensitivity analysis
13.	Development and interpretation of results
Appendices, including:	
C	Sources indexes for availability and risk data
D	Issues in dispersion and deposition calculations
E	Evacuation and sheltering
F	Liquid pathway consequence analysis

9.3.1 NRC *PRA Procedures Guide*

Initially, guidance on the conduct of risk assessments had to be sought mainly in published studies such as the two *Canvey Reports*, the *Rijnmond Report* and the *Rasmussen Report*. More formal guidance appeared in the *PRA Procedures Guide* of the Nuclear Regulatory Commission (NRC, 1982). The coverage of the *PRA Procedures Guide* is indicated by the list of contents given in Table 9.3.

9.3.2 IAEA *PSA Procedures Guide*

A more recent nuclear industry guide is *Procedures for Conducting Probabilistic Safety Assessment of Nuclear Power Plant* by the International Atomic Energy Agency (IAEA, 1992). This guide is particularly strong on the development of accident scenarios.

9.3.3 CONCAWE *Guide*

Outline guidance for the process industries was published in *Methodologies for Hazard Analysis and Risk Assessment in the Petroleum Refining and Storage Industry* by CONCAWE (1982 10/82).

9.3.4 CCPS *QRA Guidelines*

A much more detailed QRA guide is given in *Guidelines for Chemical Process Quantitative Risk Analysis* by the Center for Chemical Process Safety (CCPS, 1989/5) (the CCPS *QRA Guidelines)*. The principal contents of the CCPS *Guidelines* are shown in Table 9.4 together with the location in this book where they are treated.

The *Guidelines* are oriented to the QRA practitioner. Discussion of the various consequence models and frequency estimation techniques typically has the following structure: (1) background (purpose, philosophy/ technology, application), (2) description (description of technique, theoretical foundation, input requirements and availability, outputs, simplified approaches), (3) sample problem and (4) discussion (strengths and weaknesses, identification and treatment of errors, utility, resources needed, available computer codes).

9.3.5 QRA in safety cases

In the United Kingdom, one of the principal applications of QRA in the process industries is in the safety case. An account of safety cases and, in particular, of the extent to which QRA is required is given in Chapter 4.

9.3.6 QRA and decision-making

A review by the HSE of the role of QRA in decision-making is given in *Quantified Risk Assessment: Its Input to Decision-making* (HSE, 1989c). The document is part of the HSE's response to the *Layfield Report* (Layfield, 1987) on Sizewell B, which called for studies both of the tolerability of risk from nuclear power stations and of the relationship of safety standards in the nuclear industry to those in other industries. It deals with the second of these topics, the first being treated in *The Tolerability of Risks from Nuclear Power Stations* (HSE, 1988c).

The study considers some 16 cases of the use of QRA. They include: in the process industries, the *Canvey Reports* (HSE, 1978b, 1981a), the St Fergus to Moss Morran pipeline (HSE, 1978a), the Moss Morran/Braefoot Bay development (HSE, 1983e), housing development near an ammonium nitrate plant in the Goole–Hook plan, major retail development near a chemical plant at Ellesmere Port, a harbour with a liquefied petroleum gas (LPG) shipping risk, an explosives wharf, a sulfonation reactor and a plastics injection moulding machine; in the nuclear industry, the Heysham/Torness AGR and Sizewell B; in civil engineering, Ronan Point and the River Thames Flood Defence scheme; in mining, Markham Colliery and, in the United States, Sunshine Mine; and in rail transport, automatic level crossings. In all cases, except apparently Sunshine Mine, the QRA was used as an input to decision-making. Details of these cases are given in Appendix 2 of the study.

There is, in general, considerable variation between one QRA and another. One cause of variation is the nature of the problem addressed. This may be, for example, a single machine, a whole plant or even a complex of plants. Another cause is the degree of conservatism in the estimates made. Furthermore, QRA is subject to quite large margins of error. The study makes the point that a QRA does not necessarily have to be a complex exercise. In some cases, a relatively simple QRA suffices.

In the cases considered, the main forms in which the risks were presented are individual fatal risk and societal fatal risk, the latter in the form of frequency–number (FN) curves. The study emphasizes the need to distinguish between the different bases on which FN curves are constructed. An FN curve may be based on (1) historical data, (2) design requirements or (3) predicted values. These three bases are quite different, and this needs to be borne in mind when using the curves derived.

The two latter types are illustrated by considering two FN curves produced for Sizewell B. One curve, by Harbison and Kelly (1985), is based on design requirements implied in the safety assessment principles of the Nuclear Installations Inspectorate (NII). The other curve, produced by the Central Electricity Generating Board (CEGB) (G.N. Kelly and Hemming, 1983) represents the predictions arising from the actual design. Another difference in the basis of FN curves is the fatalities on which the curve is based, which may be confined to immediate deaths or may also include delayed deaths.

The study gives a review of risk criteria, dealing in particular with the HSE criterion for a major civil nuclear

Table 9.4 *Principal contents of CCPS QRA Guidelines (Centre for Chemical Process Safety 1989/5)*

	Chapter/section[a]
1. Chemical process quantitative risk analysis	8, 9
2. Consequence analysis	15–18
3. Event probability and failure frequency analysis	9
4. Measurement, calculation and presentation of risk estimates	9
5. Creation of a CPQRA[b] database	Appendix 14
6. Special topics and other techniques	
Domino effects	9.14
Unavailability analysis of protective systems	13
Reliability analysis of programmable electronic systems	13
Other techniques	mainly 7–9
7. CPQRA application examples	–
8. Case studies	–
9. Future developments	passim
Appendices	
A Loss-of-containment causes in the chemical industry	15
B Training programs	14, 28
C Sample outline CPQRA results	9.19
D Minimal cut set analysis	7, 9.5
E Approximation methods for quantifying fault trees	9.5
F Probability distributions, parameters, and terminology	7
G Statistical distributions available for use as failure rate models	7
H Errors from assuming that time-related equipment failure rates are constant	7
I Data reduction techniques: distribution identification and testing methods	7
J Procedures for combining available generic data and plant-specific data	7

[a] Chapter or section of this book in which the topic is principally addressed.
[b] Chemical process quantitative risk analysis.

accident and the Advisory Committee on Major Hazards (ACMH) criterion for a major accident. The HSE nuclear criterion may be summarized as the requirement that an uncontrolled release from any of a family of reactors nationwide capable of giving doses of 100 mSv at 3 km, which pessimistically might cause eventual deaths of about 100 people, should be no more frequent than 10^{-4}/year and the ACMH major hazard criterion that a major accident such as Flixborough, involving say $\geq$10 deaths, should occur nationwide with a frequency no greater than 10^{-4}/year.

In Appendix 1, the study lists some 42 factors that seem important in judging the tolerability of risk, under the four headings of: (1) the hazard, the consequential risk and the consequential benefits, (2) the nature of the assessment, (3) the factors of importance to those generating the risk, to government or to regulators, and (4) public attitudes.

Although the results of a QRA are typically expressed in terms of deaths or of casualties, appropriately defined, there are generally other consequences that need to be considered. The study lists (1) the write-off of the plant, (2) the impact on the surrounding area, (3) the anxiety factor, (4) consequential detriments and (5) the 'What if?' factor. The write-off of a plant such as occurred at Three Mile Island or Chernobyl is costly in itself and harms the whole industry. The impact on the surrounding area can be severe, especially where land is rendered radioactive, and there may be consequent detrimental outcomes such as the increased number of miscarriages that took place after Seveso. The occurrence of a major accident may lead to concern arising from asking 'What if an even larger scale one were to occur?'

For the cases described, the study reviews the nature of the decision to be made, the risk estimates yielded by the QRAs and the decisions taken. Many of the decisions concerned the granting of planning permission. Others related to the safety of particular equipment or civil engineering designs. Two, Canvey and Sizewell, were much more complex than might appear. Canvey started from a planning application for a new plant but grew into an examination of the risks from an existing complex. Sizewell inevitably became a generic inquiry into the case for nuclear power in general and the pressurized water reactor (PWR) design in particular.

The study tabulates the QRA estimates of individual risk and gives for the societal risk estimates a FN curve in which the curves differ widely. For example, the frequency of $\geq$10 deaths varies from 10^{-1}/year for the historical data for flats of the Ronan Point type to somewhat over 10^{-7}/year for the implied design requirements of Sizewell B, with most cases clustering between about 10^{-3} and 10^{-4}/year.

The decision outcomes, as a decision proper or advice on a decision, include: granting of planning permission to a new development, without or with improvements (e.g. St Fergus to Moss Morran pipeline; Moss Morran Braefoot Bay development, harbour with LPG shipping, explosives wharf); requirement to make improvements to existing situation (e.g. Canvey); acceptance of a design (sulfonation reactor); and rejection of a design (e.g. Ronan Point).

Principal conclusions of the study are as follows. First, QRA is an element that cannot be ignored in decision-making about risk since it is the only discipline capable, however imperfectly, of enabling a number to be applied and comparisons of a sort to be made, other than of a purely qualitative kind. This said, the numerical element must be viewed with great caution and treated as only one parameter in an essentially judgmental exercise. Moreover,

since any judgement upon risk is distributional, risk being caused to some as an outcome of the activity of others, it is therefore essentially political in the widest sense of the word. Second, QRA illuminates some important components of a safety assessment but needs to be supplemented by other approaches particularly in the areas of management and human factors. Third, the fact that other factors need to be taken into account does not detract from the value of QRA as a decision input. Fourth, it is not legitimate to 'read across' QRA-derived risk figures from one hazardous situation to another. It follows that it is not possible to specify a universal upper limit for all societal risks. Fifth, it needs to be borne in mind that, although QRA sometimes gives predictions of very severe accidents, such accidents do occur, as instanced by events such as Mexico City, Bhopal and Piper Alpha.

9.4 Event Data

The methods that are used to estimate the frequency of an event depend somewhat on the nature of the event. The aim is usually to base the estimate on historical experience, but the precise way in which this is done varies.

In the simplest case, there may be available frequency data that apply directly to the event in question. This is likely to be the case if the event of interest is one that does sometimes occur, for example, the failure of a single item of equipment such as a pipeline fracture or pump leak. In other cases it may not be possible to obtain such direct data. This tends to be the case for complex systems and/or systems with multiple layers of protection. Thus the frequency of failure of a nuclear power reactor is a case in point. The presence of the protective systems has the effect both of rendering each system more or less unique and of reducing the frequency of system failure to a very low value. For both these reasons historical data on failure frequency are lacking. The frequency therefore has to be synthesized using a fault tree. Again historical data are used, but in this case the data are for the base events in the tree and so are used indirectly.

The choice of method for the estimation of frequency depends on the hazard under consideration. This is illustrated very clearly in the different methodologies used in the *Canvey Reports* and the *Rasmussen Report*. In the former, the typical events of interest were emissions from vessels, pipelines and pumps. For these events historical frequency data exist and were used. In the latter study, however, the events of interest were accidents on nuclear power plants. Historical data for the frequency of these events did not exist and estimates had to be synthesized. Thus, whereas the *Canvey Reports* contain very few fault trees, the *Rasmussen Report* has an appendix several centimetres thick and full of fault trees.

A particularly difficult problem is posed by the estimation of the frequency of a rare event where this is not amenable to synthetic methods. A typical example is the outright failure of a high quality pressure vessel. In many cases the estimates required are probabilities rather than frequencies. In the following, most of the comments made about frequency apply also to probability. Similarly, it is convenient to refer to failure frequency, but the account given applies in most instances to the frequency of other events.

There are a number of sources of historical data that can be used to obtain a frequency estimate. They include the literature, the works and data banks. The data which are often most easily obtained are the total number of events over a given time period. These do not in themselves give an event rate. To determine the event rate it is necessary to know the total number of items to which the data apply. It can be quite difficult to determine this inventory.

Given that these data are available, frequency is typically estimated by dividing the total number of events by the total number of equipment-years. The assumption underlying this procedure is that a constant event rate, or the exponential distribution, applies.

Where failure data are concerned, it is often necessary to have information not only on the overall frequency of failure but also on the composition of this frequency in terms of the individual failure modes. In hazards work the fail-to-danger mode is usually required.

The estimation of the frequency from historical data is in some cases straightforward, but in others not. Areas of difficulty include

(1) inapplicability of data;
(2) sparseness of data;
(3) status of data.

The first point that has to be ascertained is whether the data available are applicable to the case in hand. There are various reasons why they may not be. The data may apply to equipment and/or conditions that are out of date. There may be significant differences between the equipment and/or its situation.

The design and environment in which equipment is used have a major influence on its failure rate. High failure rates can occur if equipment is highly rated or used in the wrong application. Operating practices affect the failure rate. Above all, failure rates can vary widely, depending on the maintenance regime.

In some instances, it is possible to identify specific ways in which the situation to which the data apply differs from that under consideration. A not uncommon case is in which a particular failure mode is known to be much less frequent or even inapplicable. For example, pipeline failures due to corrosion have been much reduced by the use of cathodic protection. Similarly, changes to the design of rail tank cars for hazardous materials in the United States have reduced the probability of impact damage. It is, in principle, legitimate to adjust an estimate based on historical failure data to allow for changed conditions, although this should be done with care.

Another common problem is that the data available are sparse. As described in Chapter 7, methods exist which allow estimates to be made of the confidence bounds on such data, but the bounds may be wide, and in any case uncertainty in the basic data complicates the assessment.

Usually the frequency data used come from a number of different sources and have varying statuses. Data statuses include

(1) historical data
    (a) numerous,
    (b) sparse;
(2) synthesized values;
(3) expert judgements
    (a) amenable to improvement,
    (b) unamenable to improvement.x

If it is not practical to obtain direct data on the frequency of an event, it is often possible to obtain a value indirectly

by synthesis using tree methods. The most commonly used method is the fault tree, but the event tree can also be used.

A fault tree is typically used to estimate the frequency where the failure is such that the system or situation which gives rise to it is sufficiently complex as to render it relatively unique. In such a case historical failure data will not be available. One important feature that tends to render a system unique is the use of protective systems. Fault tree methods are described in Section 9.5.

Events that present a threat to the public are also relatively rare and unique, and again it may be necessary to resort to synthesis to obtain a value for the frequency. Such an event is the outcome of a chain of events following a release. The frequency may be obtained using an event tree. Event tree methods are described in Section 9.6.

In some cases historical data are not obtainable. In this case an approach that is increasingly used is that of expert judgement. Expert judgement methods are described in Section 9.9.

9.5 Fault Trees

A fault tree is used to develop the causes of an event. It starts with the event of interest, the top event, such as a hazardous event or equipment failure, and is developed from the top-down.

Accounts of fault trees are given in *Reliability and Fault Tree Analysis* (Barlow, Fussell and Singpurwalla, 1975), *Fault Tree Handbook* (Vesely *et al.*, 1981), *Engineering Reliability* (Dhillon and Singh, 1981), *Reliability Engineering and Risk Assessment* (Henley and Kumamoto, 1981), *Designing for Reliability and Safety Control* (Henley and Kumamoto, 1985) and *Probabilistic Risk Assessment, Reliability Engineering, Design and Analysis* (Henley and Kumamoto, 1992), and by Vesely (1969, 1970a,b), Vesely and Narum (1970), Fussell (1973a, 1975, 1976, 1978b), Lawley (1974b, 1980), Lapp and Powers (1977a, 1979), Vesely and Goldberg (1977b) and Kletz and Lawley (1982).

The fault tree is both a qualitative and a quantitative technique. Qualitatively it is used to identify the individual paths that led to the top event, while quantitatively it is used to estimate the frequency or probability of that event.

The identification of hazards is usually carried out using a method such as a hazard and operability (hazop) study. This may then throw up cases, generally small in number, where a more detailed study is required, and fault tree analysis is one of the methods that may then be used.

Fault tree analysis is also used for large systems where high reliability is required and where the design is to incorporate many layers of protection, such as in nuclear reactor systems.

With regard to the estimation of the frequency of events, the first choice is generally to base an estimate on historical data, and to turn to fault tree analysis only where data are lacking and an estimate has to be obtained synthetically.

9.5.1 Fault tree analysis

The original concept of fault tree analysis was developed at the Bell Telephone Laboratories in work on the safety evaluation of the Minuteman Launch Control System in the early 1960s, and wider interest in the technique is usually dated from a symposium in 1965 in which workers from that company (e.g. Mearns) and from the Boeing Company (e.g. Haasl, Feutz, Waldeck) described their work on fault trees (Boeing Company, 1965).

Developments in the methodology have been in the synthesis of the tree, the analysis of the tree to produce minimum cut sets for the top event, and in the evaluation of the frequency or probability of the top event. There have also been developments related to trees with special features, including repair, secondary failures, time features, etc.

A general account of fault tree methods has been given by Fussell (1976). He sees fault tree analysis as being of major value in

(1) directing the analyst to ferret out failures deductively;
(2) pointing out the aspects of the system important in respect of the failure of interest;
(3) providing a graphical aid giving visibility to those in system management who are removed from system design changes;
(4) providing options for qualitative or quantitative system reliability analysis;
(5) allowing the analyst to concentrate on one particular system failure at a time;
(6) providing the analyst with genuine insight into system behaviour.

He also draws attention to some of the difficulties in fault tree work. Fault tree analysis is a sophisticated form of reliability assessment and it requires considerable time and effort by skilled analysts. Although it is the best tool available for a comprehensive analysis, it is not foolproof and, in particular, it does not of itself assure detection of all failures, especially common cause failures (CCFs).

9.5.2 Basic fault tree concepts

A logic tree for system behaviour may be oriented to success or failure. A fault tree is of the latter type, being a tree in which an undesired or fault event is considered and its causes are developed. A distinction is made between a failure of and a fault in a component. A fault is an incorrect state that may be due to a failure of that component or may be induced by some outside influence. Thus fault is a wider concept than failure. All failures are faults, but not all faults are failures.

A component of a fault tree has one of two binary states: essentially it is either in the correct state or in a fault state. In other words, the continuous spectrum of states from total integrity to total failure is reduced to just two states. The component state that constitutes a fault is essentially that state which induces the fault that is being developed.

As a logic tree, a fault tree is a representation of the sets of states of the system that are consistent with the top event at a particular point in time. In practice, a fault tree is generally used to represent a system state that has developed over a finite period of time, however short. This point is relevant to the application of Boolean algebra. Strictly, the implication of the use of Boolean algebra is that the states of the system are contemporaneous.

Faults may be classed as primary faults, secondary faults or command faults. A primary fault is one that occurs when the component is experiencing conditions for which it is designed, or qualified. A secondary fault is one that occurs when the component is experiencing conditions for which it is unqualified. A command fault involves the proper operation of the component at the wrong time or in the wrong place.

A distinction is made between failure mechanism, failure mode and failure effect. The failure mechanism is the cause of the failure in a particular mode and the failure effect is the effect of such failure. For example, failure of a

light switch may occur as follows:

Failure mode – high contact resistance

Failure mechanism – corrosion

Failure effect – switch fails to make contact

Some components are passive and others active. Items such as vessels and pipes are passive, whilst those such as valves and pumps are active. A passive component is a transmitter or recipient in the fault propagation process, an active one can be an initiator. In broad terms, the failure rate of a passive component is commonly two or three orders of magnitude less than that of an active component.

There is a distinction to be made between the occurrence of a fault and the existence of a fault. Interest may centre on the frequency with which or probability that a fault occurs, that is, on the unreliability, or on the probability that at any given moment the system is in a fault state, that is, on the unavailability. The distinction between reliability and availability was discussed in detail in Chapter 7.

The simplest case is the determination of the reliability of a non-repairable system. This is sometimes known as the 'mission problem': the system is sent on a mission in which components that fail are not repaired. The obvious example is space missions, but there are cases in the process industries that may approximate to this, such as remote pumping stations or offshore subsea modules. The availability of a non-repairable system may also be determined, but the long-term availability, which is usually the quantity of interest, tends to zero.

Generally, however, process systems are repairable systems, and for these both reliability and availability may be of interest. If concern centres on the frequency of realization of a hazard, it is the reliability that is relevant. If, on the other hand, the concern is with the fractional downtime of some equipment, it is the availability that is required.

A fault tree may be analysed to obtain the minimum cut sets, or minimum sets of events that can cause the top event to occur. Discussion of minimum cut sets is deferred to Section 9.5.8, but it is necessary to mention them at this point since some reference to them in relation to fault tree construction is unavoidable.

9.5.3 Fault tree elements and symbols

The basic elements of a fault tree may be classified as (1) the top event, (2) primary events, (3) intermediate events and (4) logic gates.

The symbols most widely used in process industry fault trees are shown in Table 9.5. The British Standard symbols are given in BS logic 5760 *Reliability of Systems, Equipment and Components*, Part 7: 1991 *Guide to Fault Tree Analysis*. For the most part the symbols shown in Table 9.5 correspond to those in the Standard, but in several cases the symbols in the table are the Standard's alternative rather than preferred symbols.

The top event is normally some undesired event. Typical top events are flammable or toxic releases, fires, explosion and failures of various kinds.

Primary events are events that are not developed further. One type of primary event is a basic event, which is an event that requires no further development. Another is an undeveloped event, which is an event that could be developed, but has not been. One common reason for not developing an event is that its causes lie outside the system boundary. The symbol for such an undeveloped event is a diamond and this type is therefore often called a 'diamond event'. A third type of primary event is a conditioning event, which specifies conditions applicable to a logic gate.

Table 9.5 *Fault tree event and logic symbols*

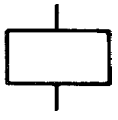
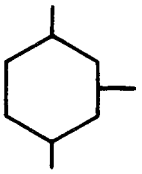
A Events	
Symbol	
	Primary, or base, event – basic fault event requiring no further development
	Undeveloped, or diamond, event – fault event which has not been further developed
	Intermediate event – fault event which occurs due to antecedent causes acting through a logic gate
	Conditioning event – specific condition which applies to a logic gate (used mainly with PRIORITY, AND and INHIBIT gates)
	External, or house, event – event which is normally expected to occur[a]

Table 9.5 *(continued)*

B Logic gates, etc.

Symbol	*Alternative symbol*	
		AND gate – output exists only if all inputs exist
		OR gate – output exists if one or more inputs exists
		INHIBIT gate – output exists if input occurs in presence of the specific enabling condition (specified by conditioning event to right of gate)
		PRIORITY AND gate – output exists if all inputs occur in a specific sequence (specified by conditioning event to right of gate)
		EXCLUSIVE OR gate – output exists if one, and only one, input exists
		VOTING gate – output exists if there exist *r*-out-of-n inputs[b]
		TRANSFER IN – symbol indicating that the tree is developed further at the corresponding TRANSFER OUT symbol
		TRANSFER OUT – symbol indicating that the portion of the tree below the symbol is to be attached to the main tree at the corresponding TRANSER IN symbol

[a] This is the definition given by Vesely *et al.* (1981). Other authors such as Henley and Kumamoto (1981) use this symbol for an event which is expected to occur or not to occur.
[b] See Chapter 13.

A fourth type of event is an external event, which is an event that is normally expected to occur.

Intermediate events are the events in the tree between the top event and the primary events at the bottom of the tree.

Logic gates define the logic relating the inputs to the outputs. The two principal gates are the AND gate and the OR gate. The output of an AND gate exists only if all the inputs exist. The output of an OR gate exists provided at least one of the inputs exists. The probability relations associated with these two gates are shown in Table 9.6, Section A. Other gates are the EXCLUSIVE OR gate, the PRIORITY AND gate and the INHIBIT gate. The output of an EXCLUSIVE OR gate exists if one, and only one, input exists. The output of a PRIORITY AND gate exists if the

Table 9.6 *Probability and frequency relations for fault tree logic gates (output A; inputs B and C)*

A Basic probability relations[a]

Logic symbol	*Reliability graph*	*Boolean algebra relation*	*Probability relations*
		A = BC	$P(A) = P(B)P(C)$
		A = B + C	$P(A) = P(B) + P(C) - P(B)P(C)$

B Relations involving frequencies and/or probabilities[a]

Gate	*Inputs*	*Outputs*
OR	P_B OR P_C	$P_A = P_B + P_C - P_B P_C \approx P_B + P_C$
	F_B OR F_C	$F_A = F_B + F_C$
	F_B OR P_C	Not permitted
AND	P_B AND P_C	$P_A = p_B p_C$
	F_B AND F_C	Not permitted; reformulate
	F_B AND P_C	$F_A = F_B P_C$

[a] F, frequency; P, probability.

inputs occur in the sequence specified by the associated conditioning event. The output of an INHIBIT gate exists if the (single) input exists in the presence of the associated conditioning event. There are also symbols for TRANSFER IN and TRANSFER OUT, which allow a large fault tree to be drawn as a set of smaller trees.

9.5.4 AND gates

One of the two principal logic gates in a fault tree is the AND gate. AND gates are used to represent a number of different situations and therefore require further explanation. The following typical situations can be distinguished:

(1) output exists given an input and fault on a protective action;
(2) output exists given an input and fault on a protective device;
(3) output exists given faults on two devices operating in parallel;
(4) output exists given faults on two devices, one operating and one on standby.

In constructing the fault tree the differences between these systems present no problem, but difficulties arise at the evaluation stage.

As already described, the probability p_0 that the output of a two-input AND gate exists, given that the probabilities of the inputs are p_1 and p_2, is

$$p_0 = p_1 p_2 \qquad [9.5.1]$$

The occurrence of events may be expressed quantitatively in terms of frequency or of probability. Failure of equipment is normally expressed as a frequency and failure of a protective action or device as a probability. A protective device is normally subject to unrevealed failure and needs therefore to be given a periodic proof test. Data for the failure of such a device may be available either as probability of failure on demand, or as frequency of failure. As described in Chapter 13, it can be shown that, subject to certain assumptions, the relationship between the two is

$$p = \lambda \tau_p / 2 \qquad [9.5.2]$$

where p is the probability of failure, λ is the failure rate and τ_p is the proof test interval.

Then for a Type 1 situation the frequency λ_0 of a fault is

$$\lambda_0 = \lambda_p \qquad [9.5.3]$$

where p is the probability of failure of the protective action, λ is the frequency of the input event and λ_0 is the frequency of the output event.

For a Type 2 situation, Equation 9.5.3 is again applicable, with the probability p of failure of protective action in this case being obtained from Equation 9.5.2.

The evaluation of a Type 3 situation is less straightforward. For this, use may be made of the appropriate parallel system model derived from either the Markov or joint density function methods, described in Chapter 7. These give the probability of the output event given the frequency of the input events. Where applicable, the rare event approximation may be used to convert from probability to frequency:

$$\lambda = p/t \qquad [9.5.4]$$

Similarly, for a Type 4 situation use may be made of the appropriate standby system model.

9.5.5 Fault tree construction

The construction of a fault tree appears a relatively simple exercise, but it is not always as straightforward as it seems and there are a number of pitfalls. Guidance on good practice in fault tree construction is given in the *Fault Tree Handbook*. Other accounts include that in the CCPS *QRA Guidelines*, and those by Lawley (1974b, 1980), Fussell (1976) and Doelp *et al.* (1984).

An essential preliminary to construction of the fault tree is definition and understanding of the system. Both the system itself and its bounds need to be clearly defined. Information on the system is generally available in the form of functional diagrams such as piping and instrument diagrams and more detailed instrumentation and electrical diagrams. There will also be other information required on the equipment and its operation, and on the environment. The quality of the final tree depends crucially on a good understanding of the system, and time spent on this stage is well repaid.

It is emphasized by Fussell (1976) that the system boundary conditions should not be confused with the physical bounds of the system. The system boundary conditions define the situation for which the fault tree is to be constructed. An important system boundary condition is the top event. The initial system configuration constitutes additional boundary conditions. This configuration should represent the system in the unfailed state. Where a component has more than one operational state, an initial condition needs to be specified for that component. Furthermore, there may be fault events declared to exist and other fault events not to be considered, these being termed by Fussell the 'existing system boundary conditions' and the 'not-allowed system boundary conditions', respectively.

Fault trees for process plants fall into two main groups, distinguished by the top event considered. The first group comprises those trees where the top event is a fault within the plant, including faults that can result in a release or an internal explosion. In the second group, the top event is a hazardous event outside the plant, essentially fires and explosions.

If the top event of the fault tree is an equipment failure, it is necessary to decide whether it is the reliability, availability, or both, which is of interest. Closely related to this is the extent to which the components in the system are to be treated as non-repairable or repairable.

As already described, the principal elements in fault trees are the top event, primary events and intermediate events, and the AND and OR gates. The *Handbook* gives five basic rules for fault tree construction:

Ground Rule 1	Write the statements that are entered in the event boxes as faults; state precisely what the fault is and when it occurs.
Ground Rule 2	If the answer to the question, 'Can this fault consist of a component failure?' is 'Yes', classify the event as a 'state-of-component fault'. If the answer is 'No', classify the event as a 'state-of-system fault'.
No Miracles Rule	If the normal functioning of a component propagates a fault sequence, then it is assumed that the component functions normally.
Complete-the-Gate Rule	All inputs to a particular gate should be completely defined before further analysis of any one of them is undertaken.
No Gate-to-Gate Rule	Gate inputs should be properly defined fault events, and gates should not be directly connected to other gates.

Each event in the tree, whether a top, intermediate or primary event, should be carefully defined. Failure to observe a proper discipline in the definition of events can lead to confusion and an incorrect tree.

The identifiers assigned to events are also important. If a single event is given two identifiers, the fault tree itself may be correct, if slightly confusing, but in the minimum cut sets the event will appear as two separate events, which is incorrect.

For a process system, the top event will normally be a failure mode of an equipment. The immediate causes will be the failure mechanisms for that particular failure. These in turn constitute the failure modes of the contributing subsystems, and so on.

The procedure followed in constructing the fault tree needs to ensure that the tree is consistent. Two types of consistency may be distinguished: series consistency within one branch and parallel consistency between two or more branches. Account needs also to be taken of events that are certain to occur and those that are impossible.

The development of a fault tree is a creative process. It involves identification of failure effects, modes and mechanisms. Although it is often regarded primarily as a means of quantifying hazardous events, which it is, the fault tree is of equal importance as a means of hazard identification. It follows also that fault trees created by different analysts will tend to differ. The differences may be due to style, judgement and/or omissions and errors.

It is generally desirable that a fault tree has a well-defined structure. In many cases such a structure arises naturally. It is common to create a 'demand tree', which shows the propagation of the faults in the absence of protective systems, and then to add branches, representing protection by instrumentation and by the process operator, which are connected by AND gates at points in the demand tree. An example of a fault tree constructed in this way has been given in Figure 2.2. Essentially the same fault tree may be drawn in several different ways, depending particularly on the location of certain events that appear under AND gates.

9.5.6 Dependence

A fundamental assumption in work on reliability generally, and on fault trees in particular, is that the events considered are independent, unless stated otherwise. Formally, the events are assumed to be statistically independent, or 's-independent'. In practice, there are many types of situation where events are not completely independent. In fault tree work this problem was originally known as 'common mode failure' (CMF), then as 'common cause failure', and now more usually as 'dependent failure'.

The problem is particularly acute in systems, such as nuclear reactor systems, where a very high degree of

reliability is sought. The method of achieving this is through the use of protective systems incorporating a high degree of redundancy. On paper, the assessed reliabilities of such systems are very high. But there has been a nagging worry that this protection may be defeated by the phenomenon of dependent failure, which may take many and subtle forms. Concern with dependent failure is therefore high in work on fault trees for nuclear reactors.

Dependent failure takes various forms. In most cases it requires that there be a common susceptibility in the component concerned. Some situations which can cause dependent failure include: (1) a common utility; (2) a common defect in manufacture; (3) a common defect in application; common exposure to (4) a degrading factor, (5) an external influence, or (6) a hazardous event; (7) inappropriate operation and (8) inappropriate maintenance.

Perhaps the most obvious dependency is supply from a common utility such as electric power or instrument air. Equipment may suffer common defects either due to manufacture or to specification and application. Common degrading factors are vibration, corrosion, dust, humidity and extremes of weather and temperature. External influences include such events as vehicle impacts or earthquakes. An event such as a fire or explosion may disable a number of equipments. Equipment may suffer abuse from operators or may be maintained incorrectly. It will be clear that in such cases redundancy may be an inadequate defence.

Generally, a common location is a factor in interpreting this fairly broadly. But it is by no means essential. In particular, incorrect actions by a maintenance fitter can disable similar equipments even though the separation between the items is appreciable.

A type of dependent failure that is important in the present context is that resulting from a process accident. A large proportion of equipments, including protective and fire fighting systems, may be susceptible to a major fire or explosion, just at the time when they are required.

There is some evidence that dependent failure is associated particularly with components where the fault is unrevealed. Thus a study of nuclear reactor accident reports by J.R. Taylor (1978b) showed that of the dependent failures considered only one was not associated with a standby or intermittently operated system.

Not all dependent failures involve redundant equipment. Another significant type of dependent failure is the overload that can occur when one equipment fails and throws a higher load on another operating equipment. Failures caused by domino effects, and escalation faults generally, may also be regarded as dependent failures.

Dependent failure, then, is a crucial problem in high reliability systems. A more detailed account is therefore given in Section 9.8. Here further discussion is confined to fault tree aspects.

Dependent failure can be taken into account in a fault tree only if the potential for it is first recognized. Given that this potential has been identified, there are two ways of representing it in the tree. One is to continue to enter each fault separately as it occurs in the tree, but ensuring that each such entry is assigned the same identifier, so that the minimum cut sets are determined correctly. The other approach is to enter the effect as a single fault under an AND gate higher up the tree. A further measure that may be taken to identify dependent failure is to examine the minimum cut sets for common susceptibilities or common locations.

9.5.7 Illustrative example: instrument air receiver system

As an illustration of fault tree analysis, consider the system shown in Figure 9.3(a). The vessel is an air receiver for an instrument air supply system. Air is let down from the receiver to the supply through a pressure reducing valve. The pressure in the receiver is controlled by a pneumatic control loop that starts up an air compressor when the receiver pressure falls below a certain value. The instrument air supply to the control loop is taken from the instrument air supply described, and if the pressure in the supply system falls below a certain value this too causes the control loop to start up the compressor. There is a pressure relief valve on the receiver. There is also a pressure relief valve (not shown) on the instrument air supply system. The design intent is that the pressure relief valve on the air receiver is sized to discharge the full throughput of the compressor and is set to open at a pressure below the danger level and that the pressure reducing valve is sized to pass the full throughput of the compressor if the instrument air pressure downstream falls to a very low value. One of the main causes of failure in the system is likely to be dirt.

The top event considered is the explosion of the air receiver due to overpressure. A fault tree for the top event of 'Receiver explosion' is shown in Figure 9.3(b).

One fault event occurs in two places – 'Pressure reducing valve partially or completely seized shut or blocked'. This is drawn as a subtree. One primary failure event appears at several points in the tree – 'Dirt'. As shown, this is treated in the tree as separate primary failures for the pressure reducing valve and the pressure relief valve.

Two of the events in the tree are mutually exclusive. These are 'Instrument air system pressure abnormally high' and 'Instrument air pressure abnormally low'. These events are denoted by B and B*, respectively.

The analysis of this fault tree to obtain the minimum cut sets and the probability of occurrence of the top event is described below.

9.5.8 Minimum cut sets

A fault tree may be analysed to obtain the minimum cut sets. A cut set is a set of primary events that is of basic or undeveloped faults, which can give rise to the top event. A minimum cut set is one that does not contain within itself another cut set. The complete set of minimum cut sets is the set of principal fault modes for the top event.

The minimum cut sets may be determined by the application of Boolean algebra. The procedure may be illustrated by reference to the fault tree shown in Figure 9.3(b). This may be represented in Boolean form as:

$$T = (A + B + C + D)(B^* + F)(G + H + I) \qquad [9.5.5]$$

Then substituting

$$B^* = C + D + E$$

and noting that: $BB^* = 0$

$$CC = C; DD = D$$

$$AC, CD, CE, CF \subset C$$

$$AD, DC, DE, DF \subset D$$

gives

$$T = (AE + AF + BF + C + D) \cdot (G + H + I) \quad [9.5.6a]$$
$$= [A \cdot (E + F) + BF + C + D] \cdot (G + H + I) \quad [9.5.6b]$$

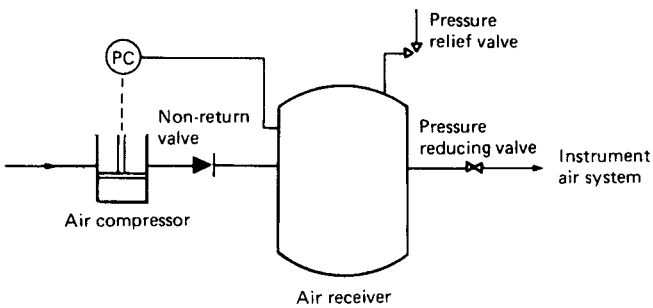
and thus the minimum cut sets are:

A E G	A E H	A E I
A F G	A F H	A F I
B E G	B F H	B F I
C G	C H	C I
D G	D H	D I

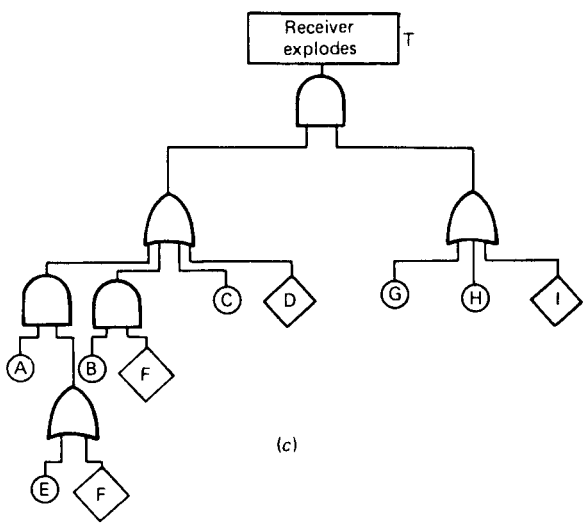
A simplified fault tree that corresponds to Equation 9.5.6b is shown in Figure 9.3(c).

Since fault trees for industrial systems are often large, it is necessary to have systematic methods of determining the minimum cut sets. Such a method is that described by Fussell (1976). As an illustration of this method, consider the motor system which is described by this author and which is shown in Figure 9.4(a). The top event considered is the overheating of the motor. The fault tree for this event is shown in Figure 9.4(b). The structure of the tree is:

Gate	*Gate type*	*No. of inputs*	*Input code*	*No.*
A	OR	2	1	B
B	AND	2	C	2
C	OR	2	4	3



(*a*)



(*c*)

Figure 9.3 *continued*

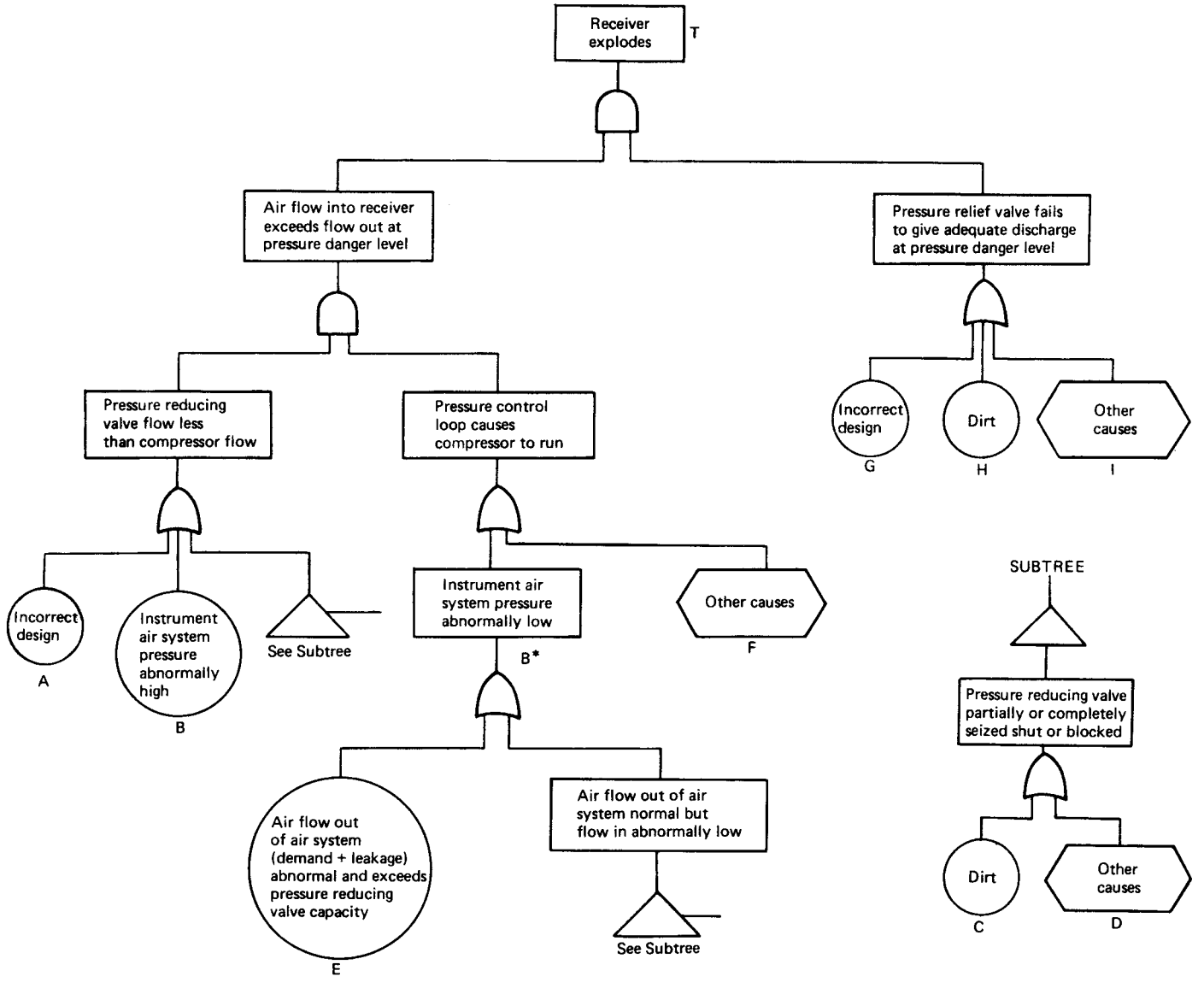


Figure 9.3 *Instrument air receiver system: flow diagram and fault trees for the explosion of an air receiver: (a) instrument air receiver system; (b) fault tree for top event 'Receiver explodes'; (c) equivalent but simplified fault tree for top event 'Receiver explodes'*

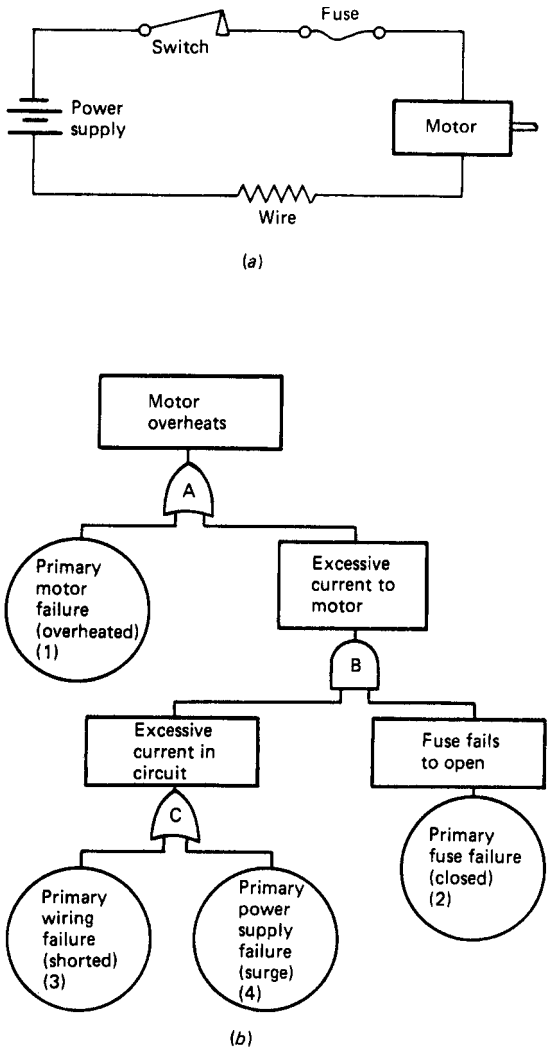


Figure 9.4 *Motor system: system diagram and fault tree for overheating of the motor (Fussell, 1976): (a) motor system; and (b) fault tree for top event 'Motor overheats' (Courtesy of the Sijthoff and Noordhoff International Publishing Company)*

The procedure is based on successive elimination of the gates. The analysis starts with a matrix containing the first gate, gate A, in the top left-hand corner:

A	

A is an OR gate and is replaced by its inputs listed vertically:

1	
B	

B is an AND gate and is replaced by its inputs listed horizontally:

1	
C	2

C is an OR gate and is replaced by its inputs listed vertically:

1	
4	2
3	2

It should be noted that when C is replaced by 4 and 3, the event 2, which is linked to C by an AND gate, is listed with both events 4 and 3. The minimum cut sets are then:

(1); (4,2); (3,2)

There are now a large number of methods available for the determination of the minimum cut sets of a fault tree. Methods include those described by Vesely (1969, 1970b), Gangadharan, Rao and Sundararajan (1977), Zipf (1984) and Camarinopoulos and Yllera (1985).

There are also a number of computer codes for minimum cut set determination. One of the most commonly used is the code set PREP and KITT. Another widely used minimum cut set code is FTAP.

9.5.9 Coherence of tree

The structure of a fault tree is either coherent or non-coherent. The property of coherence has been developed by Esary and Proschan (1963) as follows.

They define a structure function $\phi(\mathbf{x})$ such that it has three properties.

Property 1:

$$\phi(\mathbf{x}) \geq \phi(\mathbf{y}) \qquad \mathbf{x} \geq \mathbf{y} \qquad [9.5.7]$$

Property 2:

$$\phi(\mathbf{x}) = 1 \qquad \mathbf{x} = 1 \qquad [9.5.8]$$

Property 3:

$$\phi(\mathbf{x}) = 0 \qquad \mathbf{x} = 0 \qquad [9.5.9]$$

where $\mathbf{x}$ is the vector $[x_1, x_2, \ldots, x_n]$ and $\mathbf{y}$ the vector $[y_1, y_2, \ldots, y_n]$. For each component i, x_i has the value 1 if the component is functioning and 0 if it is failed; $\mathbf{x} \geq \mathbf{y}$ signifies $x_i \geq y_i$ for all i. A structure that has such a structure function is coherent or monotonic. In plain language, this means that:

(1) *Property 1* If sufficient components are functioning for the system to be functioning, the functioning of an additional component will not cause the system to fail; and if sufficient components are failed for the system to be failed, the failure of an additional com-ponent will not cause the system to function.
(2) *Property 2* If all the components are functioning, the system is functioning.
(3) *Property 3* If all the components are failed, the system is failed.

Coherence is of interest to reliability engineers because, given the property of coherence, it is possible to derive a number of useful relationships for bounds on the behaviour of large systems.

For fault trees the property of coherence depends partly on the logic gates and partly on the events. A fault tree structure which consists exclusively of AND and OR gates is generally coherent, but one which includes other types of gate may not be. Thus the presence of an EXCLUSIVE OR gate can render a structure non-coherent. For example for a two-input EXCLUSIVE OR gate, if one input fault to the gate exists, the output fault exists, but if a second input fault occurs, the output fault disappears.

However, coherence is also affected by the nature of the events. A structure that contains a secondary failure is generally non-coherent. As already described, a secondary failure is one that occurs because the component is over-stressed. This component is not necessarily restored by restoration of the other components.

An EXCLUSIVE OR gate was used in the classic nitric acid cooler problem considered by Lapp and Powers (1977a, 1979), which has been the subject of comment by Locks (1979) and others. A review of non-coherent structure and its bearing on fault tree work has been given by Johnston and Matthews (1983 SRD R245).

9.5.10 Fault trees and digraphs

A fault tree is one type of model of the propagation of faults in a process plant. The construction of the tree may be aided by the use of other models of fault propagation. A widely used method of constructing fault trees is to develop first a directed graph, or digraph, representing the fault propagation in the plant. A single digraph may be used to construct a number of fault trees, depending on the top events selected. Accounts of the use of digraphs for fault tree construction include those by Lambert (1975), Lapp and Powers (1977a, 1979), Chamow (1978), Andrews and Morgan (1986) and Kohda and Henley (1988).

9.5.11 Fault tree evaluation

A fault tree is a graphical representation of the fault paths and logic of a system and is of value as such. There are, however, a number of methods of fault tree evaluation that greatly enhance its utility. These methods are both qualitative and quantitative.

Qualitative evaluation is largely based on the determination of the minimum cut sets. The minimum cut sets and methods for their determination have been described in Section 9.5.8. One form of qualitative evaluation that is particularly useful is the determination of the importance of the primary events. This is described in Section 9.5.12.

Quantitative evaluation of a fault tree requires that numbers be put to the frequency or probability of the primary events. Given these quantitative data, there are several options for the evaluation of the frequency or probability of the top event.

Three methods of evaluation are considered here. These are the use of (1) the minimum cut sets, (2) the gate-by-gate method and (3) Monte Carlo simulation.

In the first of these methods, the probability of the top event may be evaluated from the probabilities of the minimum cut sets C_i

$$P(\mathrm{T}) = P\left(\bigcup_{i=1}^{n} \mathrm{C}_i\right) \qquad [9.5.10]$$

The events are not mutually exclusive and, therefore, strictly

$$\begin{aligned} P(\mathrm{T}) = {} & P(\mathrm{C}_1) + P(\mathrm{C}_2) + \cdots + P(\mathrm{C}_n) - P(\mathrm{C}_1)P(\mathrm{C}_2) \\ & - P(\mathrm{C}_1)P(\mathrm{C}_3) - \cdots - P(\mathrm{C}_{n-1})P(\mathrm{C}_n) \\ & + P(\mathrm{C}_1)P(\mathrm{C}_2)P(\mathrm{C}_3) + P(\mathrm{C}_1)P(\mathrm{C}_2)P(\mathrm{C}_4) \\ & + \cdots + P(\mathrm{C}_{n-2})P(\mathrm{C}_{n-1})P(\mathrm{C}_n) \\ & + \cdots + (-1)^{n-1} \prod_{i=1}^{n} P(\mathrm{C}_i) \end{aligned} \qquad [9.5.11]$$

But usually it is sufficient to use the low probability, or rare event, approximation

$$P(\mathrm{T}) = \sum_{i=1}^{n} P(\mathrm{C}_i) \qquad [9.5.12]$$

Equation 9.5.12 always gives a higher probability than Equation 9.5.11 and thus for failure oriented logic it is conservative.

As an illustration, consider the evaluation of the probability of the top event in the fault tree for the instrument air receiver system as given in Figure 9.3(c). The minimum cut sets have been listed above. Assume that

$$\begin{array}{lll} P_{\mathrm{A}} = 10^{-5} & P_{\mathrm{D}} = 2 \times 10^{-3} & P_{\mathrm{G}} = 10^{-3} \\ P_{\mathrm{B}} = 3 \times 10^{-5} & P_{\mathrm{E}} = 10^{-3} & P_{\mathrm{H}} = 8 \times 10^{-3} \\ P_{\mathrm{C}} = 2 \times 10^{-3} & P_{\mathrm{F}} = 5 \times 10^{-4} & P_{\mathrm{I}} = 2 \times 10^{-3} \end{array}$$

Then, for the first minimum cut set AEG,

$$\begin{aligned} P(\mathrm{C}_1) &= P_{\mathrm{A}} P_{\mathrm{E}} P_{\mathrm{G}} \\ &= 10^{-5} \times 10^{-3} \times 10^{-3} \\ &= 10^{-11} \end{aligned}$$

and so on for the other 14 cut sets. Alternatively, from Equation 9.5.12,

$$\begin{aligned} P(\mathrm{T}) = \sum_{i=1}^{n} P(\mathrm{C}_i) &= [P_\mathrm{A}(P_\mathrm{E} + P_\mathrm{F}) + P_\mathrm{B}P_\mathrm{F} + P_\mathrm{C} + P_\mathrm{D}] \\ &\quad \times (P_\mathrm{G} + P_\mathrm{H} + P_\mathrm{I}) \\ &= [10^{-5}(10^{-3} + 5 \times 10^{-4}) \\ &\quad + (3 \times 10^{-5} \times 5 \times 10^{-4}) \\ &\quad + (2 \times 10^{-3} + 2 \times 10^{-3})] \\ &\quad \times (10^{-3} + 8 \times 10^{-3} + 2 \times 10^{-3}) \\ &= 4.4 \times 10^{-5} \end{aligned}$$

This form of the minimum cut set method is applicable where the occurrence of the primary events can be characterized by simple probabilities. More commonly the occurrence of these events is characterized by a mix of frequencies and probabilities. Furthermore, it may be necessary to take into account repair of components. An account of an approximate method of handling systems in which event rates are expressed as frequencies and which involve repair is given in Section 9.5.15.

The second method is to work up the tree gate-by-gate from the bottom calculating the frequency or probability of the output event of each gate from those of the input events. The procedure is straightforward except where there occur at the gate, some input faults which are expressed in terms of frequency rather than probability.

The output–input relations which are permitted and those that are not are given for a two-input gate in Table 9.6, Section B. The main problem arises where the two inputs to an AND gate both have the dimensions of frequency. The output from the gate must also have the dimension of frequency. It is not permissible to multiply the two frequencies together.

The handling of an AND gate where the two inputs both have the dimension of frequency is discussed in Section 9.5.4. Two main situations occur: one is where both the components whose faults are the inputs to the gate are operating, and the other is where one component is operating and the other is on standby. As indicated in the Section 9.5.4, both situations can be handled by the use of suitable models derived from Markov modelling.

Use may also be made of the alternative model given in Equations 7.8.28–7.8.31, which in effect utilizes a repair time to convert one of the frequencies to a fractional downtime, or probability.

Accounts of the gate-by-gate method are given in the CCPS *QRA Guidelines* and by Doelp *et al.* (1984). The method is illustrated in the fault trees given by Lawley (1974b, 1980), one of which is described in Section 9.5.14.

There are advantages and disadvantages to both the gate-by-gate and minimum cut set methods. The former is the method traditionally used in manual evaluation of trees. It gives an evaluation of all the intermediate events as well as of the top event, which can be valuable. On the other hand, it tends to be error prone and becomes tedious for large trees.

The third method is the use of Monte Carlo simulation. The basic principle of this method has been described in Chapter 7. Its application to fault tree evaluation involves a series of trials. In a given trial each primary event either does or does not occur, the occurrence being determined by sampling, where the values returned by the sampling are, on average, in accordance with the frequency or probability data supplied. The outcome of each trial is the occurrence or non-occurrence of the top event. Provided a sufficient number of trials are used, the frequency or probability of the top event is then given by the proportion of trials in which it occurs. An account of the use of this method for fault tree evaluation has been given by Hauptmanns and Yllera (1983).

The use of Monte Carlo simulation is virtually unavoidable if the primary events are characterized by a range of values of probability, or frequency. The probability of a failure may be given not by a point probability value but by a probability density function. Obviously if the probabilities of the other events are expressed as density functions, then the probability of the top event must be expressed as a density function also.

A given Monte Carlo trial generates a set of probabilities for the primary failure events. The probability of the top event may then be evaluated by an analytical method, such as the minimum cut set method. The result of the series of trials is a probability density function for the top event. The principle of the method is illustrated in Figure 9.5. Monte Carlo simulation was used extensively for fault tree evaluation in the *Rasmussen Report*.

9.5.12 Importance of events

Since the number of primary events that, either serially or in combination, can cause the top event to occur can be large, it is very desirable to have means of assessing their relative significance. Primary events have the property of 'importance'. There are a number of measures of importance. Some of these rely solely on structural considerations, while others are based on probabilities. In other words, there are both qualitative and quantitative measures.

A simple approach to structural importance may be illustrated by the following minimum cut sets of events given in Section 9.5.8: (1); (4, 2); (3, 2).

The order of importance is then: events in one-event minimum cuts, events common to two-event minimum cut sets, events in two-event minimum cut sets, and so on. Thus, in the example given, the order of importance is:

1
2
3,4

There are a number of quantitative measures of importance that may be calculated if frequency or probability data are available. These include the Birnbaum criterion, which is the incremental reduction in the probability of the top event where the probability of the primary event is reduced incrementally, and the Vesely–Fussell criterion, which is the probability that a cut set containing the primary event has occurred given that the top event has occurred.

Formal methods of determining importance have been given by Lambert and Oilman (1977a,b), who have developed the computer code IMPORTANCE for such analysis.

9.5.13 Illustrative example: pressure tank system

As another illustration, consider the fault tree for the pressure tank system described by Vesely *et al.* (1981).

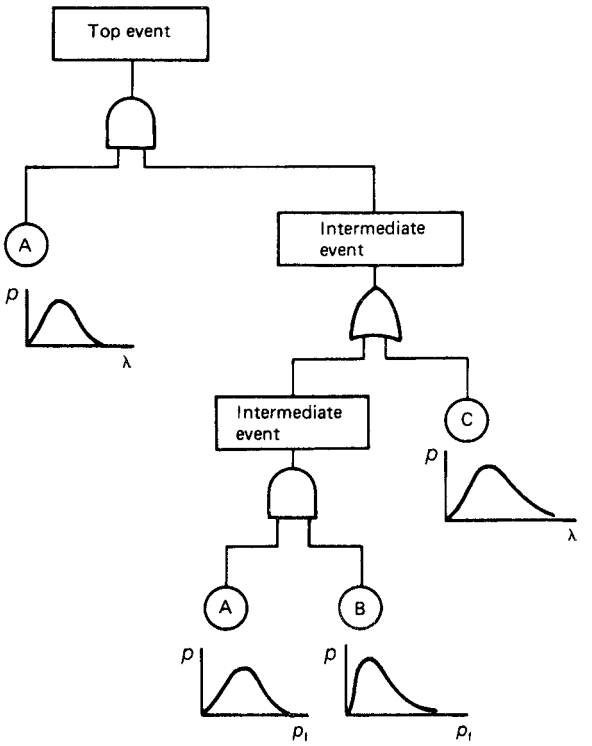


Figure 9.5 *Fault tree illustrating the principle of probabilities expressed in the form of density functions and of evaluation by Monte Carlo simulation, λ, Failure frequency; p_f, failure probability; p, probability of given value of λ or p_f*

This system is shown in Figure 9.6. The authors describe the system as follows:

The function of the control system is to regulate the operation of the pump. The latter pumps fluid from an infinitely large reservoir into the tank. We shall assume that it takes 60 seconds to pressurize the tank. The pressure switch has contacts that are closed when the tank is empty. When the threshold pressure has been reached, the pressure switch contacts open, removing power from the pump, causing the pump motor to cease operation. The tank is fitted with an outlet valve that drains the entire tank in a negligible time; the outlet valve, however, is not a pressure relief valve. When the tank is empty, the pressure switch contacts close and the cycle is repeated.

Initially the system is considered to be in its dormant mode: switch S1 contact open, relay K1 contacts open, and relay K2 contacts open: i.e., the control system is de-energized. In this de-energized state the contacts of the timer relay are closed. We will also assume that the tank is empty and the pressure switch contacts are therefore closed.

System operation is started by momentarily depressing switch S1. This applies power to the coil of relay K1, thus closing relay K1 contacts. Relay K1 is now electrically self-latched. The closure of relay K1 contacts allows power to be applied to the coil of relay K2, whose contacts close to start up the pump motor.

The timer relay has been provided to allow emergency shutdown in the event that the pressure switch fails closed. Initially the timer relay contacts are closed and the timer relay coil is de-energized. Power is applied to the timer coil as soon as relay K1 contacts are closed. This starts a clock in the timer. If the clock registers 60 seconds of *continuous* power application to the timer relay coil, the timer relay contacts open (and latch in that position), breaking the circuit to the K1 relay coil (previously latch closed) and thus producing system shutdown. In normal operation, when the pressure switch contacts open (and consequently relay K2 contacts open), the timer resets to 0 seconds.

The top event considered is 'Rupture of pressure tank after the start of pumping'. The fault tree developed by Vesely *et al.* for this event is shown in Figure 9.7. The detailed development of this fault tree is described by Vesely *et al.* and need not be given here, but the following points may be noted.

If the undeveloped events are disregarded, this fault tree reduces to that indicated by the events E1–E5, K1, K2, R, S, S1 and T shown in Figure 9.7. The top event E1 and the intermediate events E2–E5 in this tree are:

E1	pressure tank rupture
E2	excessive pressure to tank
E3	current to K2 relay coil for too long
E4	circuit B carries current for too long
E5	current to K1 relay coil for too long

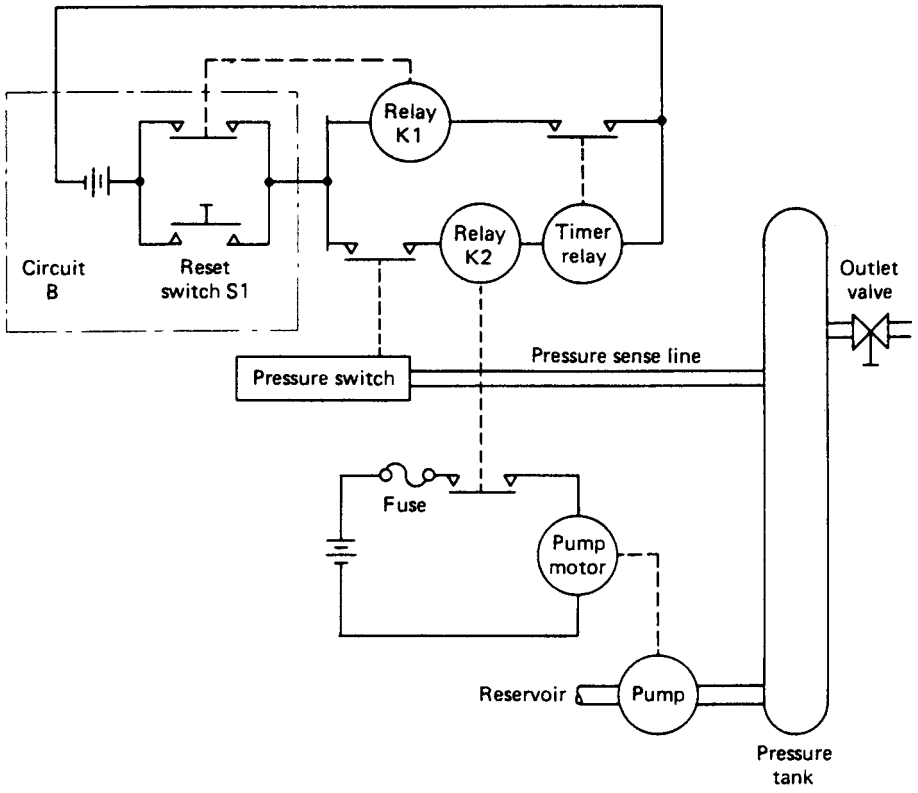


Figure 9.6 *Pressure tank system: system diagram (Vesely et al., 1981)*

E2 is equivalent to K2 relay contacts closed for too long, and E5 to timer relay contacts failing to open when pressure switch contacts have been closed for too long. The cut sets for the top event of this fault tree may be obtained by applying Boolean algebra. Starting with the top event E1:

$$
\begin{aligned}
\mathrm{E1} &= \mathrm{T} + \mathrm{E2} \\
&= \mathrm{T} + (\mathrm{K2} + \mathrm{E3}) \\
&= \mathrm{T} + \mathrm{K2} + (\mathrm{S} \cdot \mathrm{E4}) \\
&= \mathrm{T} + \mathrm{K2} + \mathrm{S} \cdot (\mathrm{S1} + \mathrm{E5}) \\
&= \mathrm{T} + \mathrm{K2} + (\mathrm{S} \cdot \mathrm{S1}) + (\mathrm{S} \cdot \mathrm{E5}) \\
&= \mathrm{T} + \mathrm{K2} + (\mathrm{S} \cdot \mathrm{S1}) + \mathrm{S} \cdot (\mathrm{K1} + \mathrm{R}) \\
&= \mathrm{T} + \mathrm{K2} + (\mathrm{S} \cdot \mathrm{S1}) + (\mathrm{S} \cdot \mathrm{K1}) + (\mathrm{S} \cdot \mathrm{R})
\end{aligned}
$$

There are therefore five minimal cut sets: T, K2, (S·S1), (S·K1) and (S·R).

Analysis of the tree at this stage gives qualitative information about the design of the system. The pressure tank system has in effect a single protective device, the timer relay, which protects against failure of the pressure switch. This is reflected in the fault tree which has a single AND gate.

With regard to the qualitative importance of the events, K2 and T both occur in single event cut sets, but K2 is an active failure and T a passive one, and hence K2 ranks higher than T. Events S, S1, K1 and R each occur in two-event cut sets, but of these S occurs in all three cut sets, whereas the other three faults each occur only in one cut set and hence S ranks higher than the other three, which all rank equally. The order of importance is thus: K2; T; S; and S1, K1 and R.

The failure probabilities given by Vesely *et al.* are:

Component	*Symbol*	*Failure probability*
Pressure	T	5×10^{-6}
Relay K2	K2	3×10^{-5}
Pressure	S	1×10^{-4}
Relay Kl	K1	3×10^{-5}
Timer relay	R	1×10^{-4}
Switch SI	S1	3×10^{-5}

Then the probabilities of the minimum cut sets are:

$$P(\mathrm{T}) = 5 \times 10^{-6}$$

$$P(\mathrm{K2}) = 3 \times 10^{-5}$$

$$P(\mathrm{S} \cdot \mathrm{K1}) = 1 \times 10^{-4} \times 3 \times 10^{-5} = 3 \times 10^{-9}$$

$$P(\mathrm{S} \cdot \mathrm{R}) = 1 \times 10^{-4} \times 1 \times 10^{-4} = 1 \times 10^{-8}$$

$$P(\mathrm{S} \cdot \mathrm{S1}) = 1 \times 10^{-4} \times 3 \times 10^{-5} = 3 \times 10^{-9}$$

and the probability of the top event is the sum of these

$$P(\mathrm{E1}) = 3.5 \times 10^{-5}$$

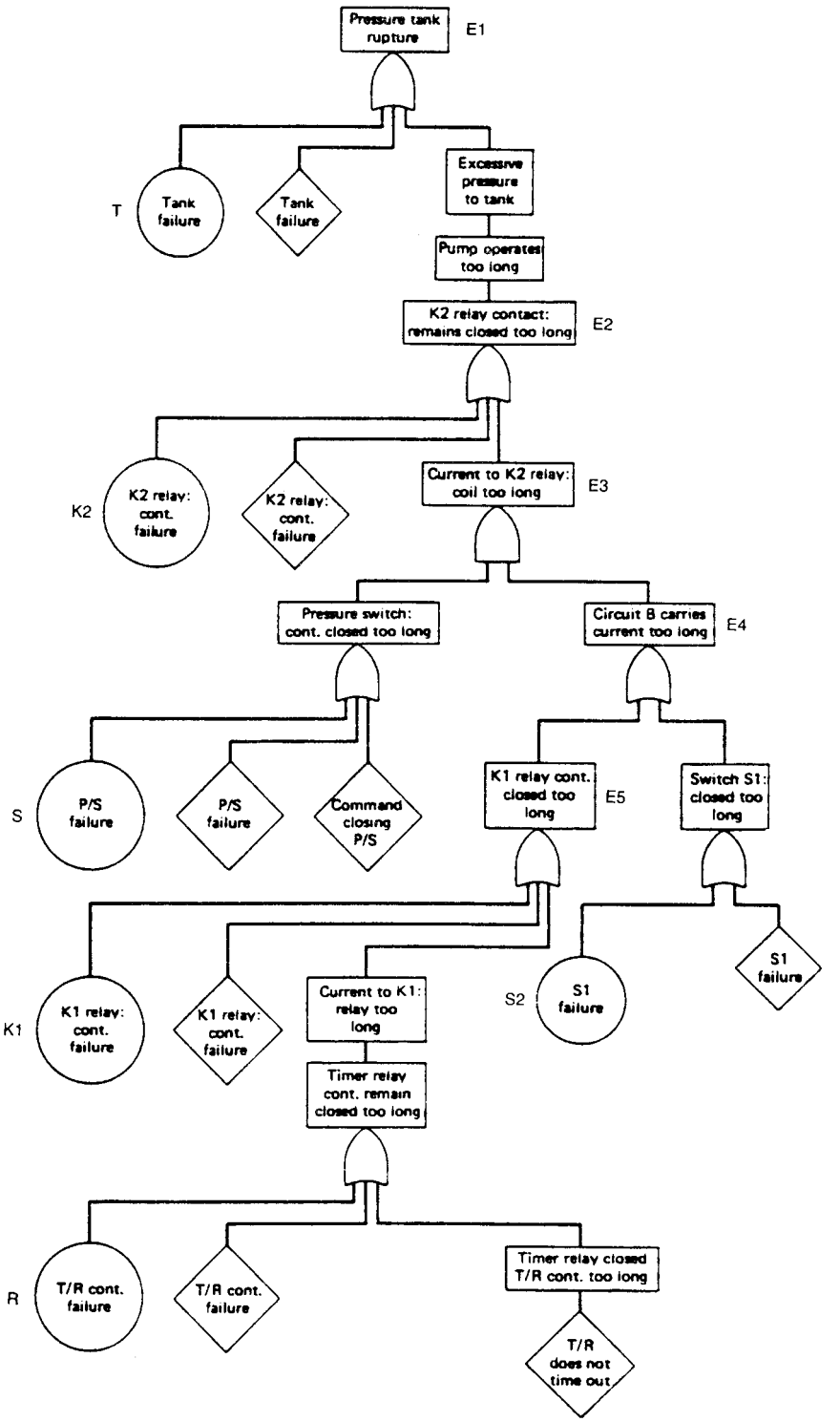


Figure 9.7 *Pressure tank system: fault tree for rupture of pressure tank (after Vesely et al., 1981; Henley and Kumamoto, 1981)*

The contribution of these minimum cut sets to the top event is a measure of their quantitative importance, and is:

Cut set	*Importance* (%)
T	14
K2	86
Other	<0.1

9.5.14 Illustrative example: crystallizer system

As a third illustrative example, consider the proposed crystallization plant system described by Lawley (1974b). This system is shown in Figure 9.8. The problem is to estimate the expected frequency of emission of the toxic and corrosive crystallizer slurry via the stack to the atmosphere. There are two ways in which this can occur – by discharge at about atmospheric pressure or by discharge at high pressure – but only the former is considered here. If the stack base and luted drain are properly designed for the flow from the three reactors, a discharge of slurry at only a few pounds per square inch pressure would normally pass via the pressure control valve (PCV) header or the relief header to the stack and hence to the drain. If a blockage occurs in the stack or the drain, the discharge from the crystallizer will result in a build-up of liquid in the stack and eventually to entrainment of the slurry to the atmosphere.

The top event considered is 'Low pressure discharge of slurry to the atmosphere'. The fault tree developed by the author for this event is shown in Figure 9.9. The tree is constructed by working from the top-down, but it is convenient here to explain it from the bottom-up. The level in No. 1 crystallizer can rise only if the outflow to No. 2 crystallizer is restricted. This can occur in three ways:

(1) Discharge line choked with slurry; frequency estimated from plant experience of similar materials, 5 occasions/year.
(2) Crystallizer level control valve (LCV) on discharge line shut or misdirected shut; frequency estimated from literature data, 0.5 occasions/year.
(3) Manual isolation valve on discharge line shut in error; frequency estimated from general plant experience, 0.1 occasions/year.

Thus the estimated frequency of restricted outflow is 5.6 occasions/year. The level will continue to rise only if:

(1) The operator fails to take action opposite a rising level signal; frequency estimated 4% of occasions.
(2) The level meter fails dangerous; failure rate estimated 2 failures/year, downtime 4 h/failure, dead time $2 \times 4 = 8$ h/year, fractional dead time $8/8760 \approx 0.1\%$ of time.

The slurry will only overflow into the PCV header and thence to the stack if

(1) The operator fails to take action opposite a high-level alarm signal; frequency estimated 3% of occasions.
(2) The high level alarm fails dangerous; fractional dead time estimated 1.25% of time.

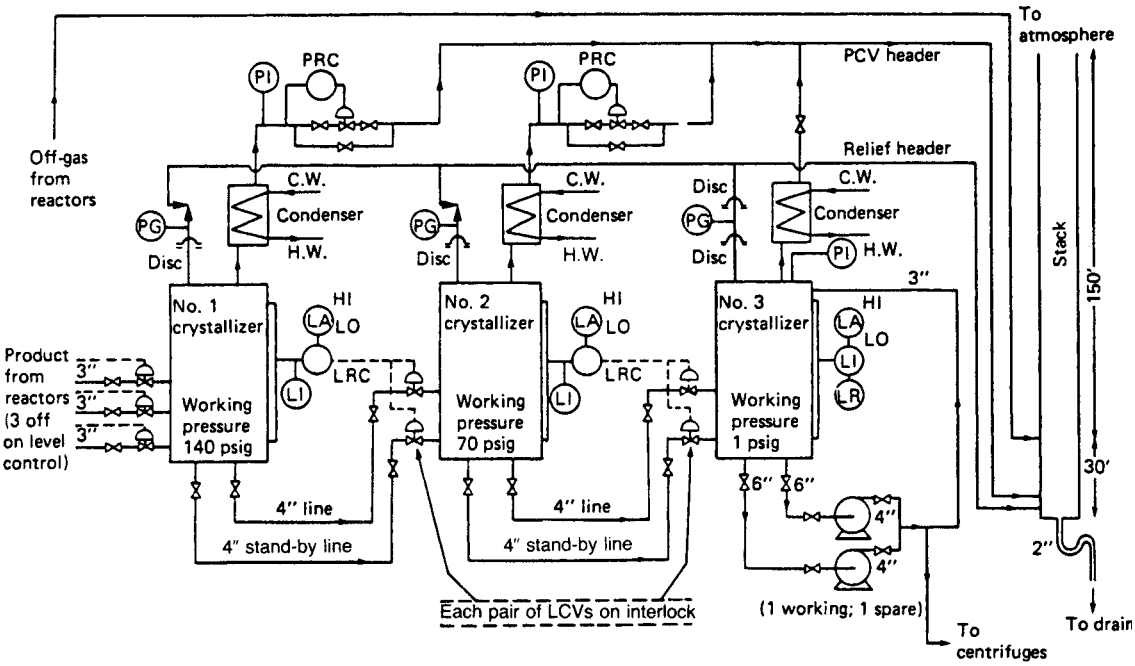


Figure 9.8 *Proposed crystallization plant: flow diagram (Lawley, 1974b) CW, cold water; HI, high; HW, hot water; LA, Level alarm; LO, low; LRC, level recorder controller; PCV, pressure control valve; PG, pressure gauge; PI, pressure indicator; PRC, pressure recorder controller (Courtesy of the American Institute of Chemical Engineers)*

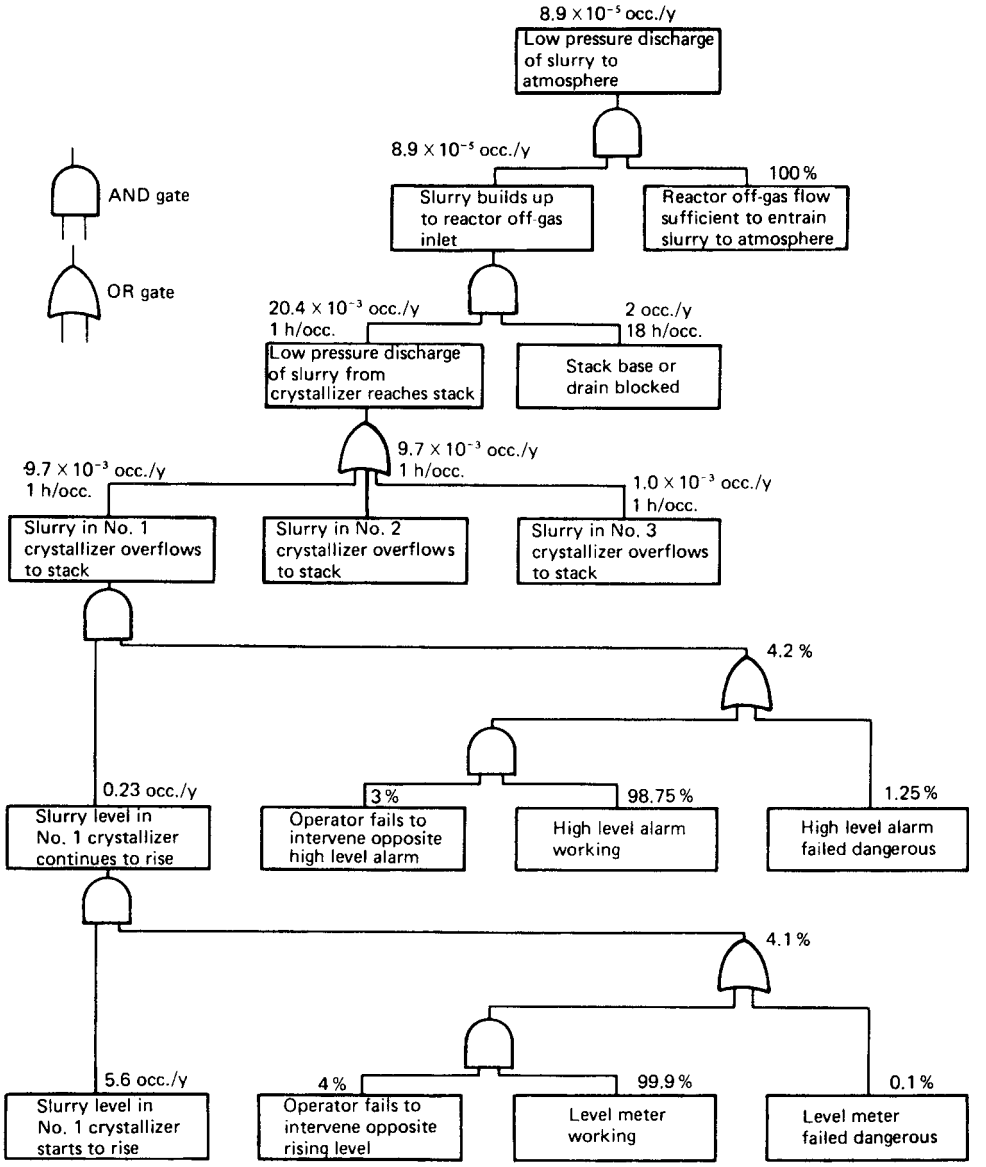


Figure 9.9 *Proposed crystallization plant: fault tree for low pressure discharge of crystallizer slurry to stack and entrapment to atmosphere (Lawley, 1974b) (Courtesy of the American Institute of Chemical Engineers)*

This fractional dead time calculation is as follows. The failure rate of the high level alarm (excluding the meter) is estimated as 0.2 failures/year and the proof test interval is 6 weeks. Thus the fractional dead time is:

$$\frac{1}{2} \times 0.2 \times \frac{6}{52} = 1.15 \times 10^{-2}$$
$$= 1.15\%$$

The fractional dead time of the meter has already been given as 0.1%. Thus the fractional dead time of the level meter and the high level alarm together is 1.25%.

If the slurry overflows, it is assumed that it continues to pass to the stack for up to 2 h maximum and thus for 1 h/occasion, on average.

Similarly, the level in No. 2 crystallizer can rise only if the outflow to No. 3 crystallizer is restricted. The treatment is identical to that for No. 1 crystallizer.

The level in No. 3 crystallizer can rise only if the outflow is restricted. This can occur in four ways:

(1) Discharge line or centrifuge feed line blocked; frequency estimated from plant experience of similar materials, 0.2 occasions/year.
(2) Failure of online circulation pump followed by failure to commission standby circulation pump in time; frequency estimated, 0.1 occasion/year.
(3) The operator fails to reduce the feed to the reaction section when there are problems on the centrifuges; frequency estimated 0.2 occasions/year.
(4) Manual isolation valve on discharge line shut in error; frequency estimated 0.1 occasion/year.

Thus the estimated frequency of restricted outflow is 0.6 occasions/year.

Since No. 1 crystallizer has restricted outflow on 5.6 occasions/year and overflow on 9.7×10^{-3} occasions/year, No. 3 crystallizer, which has restricted outflow on 0.6 occasions/year, will have overflow on:

$$\frac{0.6}{5.6} \times 9.7 \times 10^{-3} = 1 \times 10^{-3} \text{ occasions/year}$$

Thus the low pressure discharge of slurry from one of the crystallizers reaches the stack via the PCV header on

$$2 \times 9.7 \times 10^{-3} + 1 \times 10^{-3} = 20.4 \times 10^{-3} \text{ occasions/year}$$

Noxious discharge from the top of the stack occurs only if the stack base or drain is blocked. It is estimated that blockage will occur on 2 occasions/year. The stack drain is checked for blockage once per day so that, on average, a blockage would be unrevealed for 12 h. Allowing 6 h for clearing the blockage gives a mean downtime for the drain of 18 h/occasion. Then the low pressure discharge of slurry to atmosphere is

$$2 \times 20.4 \times 10^{-3}\left(\frac{1+18}{8760}\right) = 8.9 \times 10^{-5} \text{ occasions/year}$$

This is a fairly typical illustration of an industrial fault tree analysis. Some additional examples related to protective systems are given in Chapter 13.

9.5.15 Repairable systems

The treatment given so far has not taken into account the repair of failed components. For lack of exact solutions, approximate treatments have been developed which give the upper bounds on reliability and availability. A method of determining the reliability and availability for the top event that is based on this approach and that is suitable for manual calculation has been described by Fussell (1975).

The method is based on the crucial minimum cut sets, or collection of minimum cut sets that can be taken as adequately representing for quantitative evaluations the top event fault logic. It utilizes the rare event approximation, the principal condition being $0.1 < \lambda_i t$, where λ_i, is the failure rate of component i. The account given here is confined to the presentation of the results obtained by Fussell; full derivations are given by that author.

For the primary events:

$$\bar{r}_i \leq \lambda_i t \quad \text{non-repairable and repairable components} \qquad [9.5.13]$$

$$\bar{a}_i \leq \lambda_i t \quad \text{non-repairable components} \qquad [9.5.14a]$$

$$= r_i \qquad [9.5.14b]$$

$$\bar{a}_i \leq \lambda_i \tau_i \quad \text{repairable components} \qquad [9.5.15]$$

where, for component i, a_i and $\bar{a}_i$ are the availability and unavailability, r_i and $\bar{r}_i$ the reliability and unreliability, and λ_i, is the failure rate and τ is the restoration time. For the minimum cut sets:

$$\bar{A}_k = \sum_{i=1}^{n_k} \bar{a}_i \qquad [9.5.16]$$

$$f_k \leq \bar{A} \sum_{i=1}^{n_k} \frac{\lambda}{\bar{a}_i} \qquad [9.5.17]$$

$$\bar{R}_k = \int_0^t f_k(t')\mathrm{d}t' \qquad [9.5.18]$$

$$\Lambda_k = f_k/\bar{R} \qquad [9.5.19]$$

And for the top event

$$\bar{A}_t \leq \sum_{k=1}^{N} \bar{A}_k \qquad [9.5.20]$$

$$\bar{R}_t \leq \sum_{k=1}^{N} \bar{R}_k \qquad [9.5.21]$$

$$\Lambda_t \approx \sum_{k=1}^{N} \bar{\Lambda}_k \qquad [9.5.22]$$

where, $\bar{A}$ is the unavailability, f the failure density function, $\bar{R}$ the unreliability, Λ the failure rate, n_k the number of primary events in minimum cut set k, and N the number of crucial minimum cut sets; subscripts k and t refer to the minimum cut set and top event, respectively. For importance:

$$I_{ia} \approx \left(\sum_{k=1}^{m_i} \bar{A}_k\right) \Big/ \bar{A}_t \qquad [9.5.23]$$

$$I_{ir} \approx \left(\sum_{k=1}^{m_i} \bar{R}_k\right) \Big/ \bar{R}_t \qquad [9.5.24]$$

where, for event i, I_{ia} is the importance with respect to availability and I_{ir} is the importance with respect to reliability, and m_i is the number of minimum cut sets containing event i.

9.5.16 Illustrative example: pump set system

As a fourth illustrative example, consider the use of the relationships just given to determine the reliability of a pump set, consisting of two streams, each with a pump and a control valve (CV).

The basic components, their failure rates and restoration times, and hence their unavailabilities, obtained from

Equation 9.5.15, are:

Component	*Component no.*	*Failure rate,* λ_i (year^{-1})	*Restoration time,* τ_i		*Unavailability,* $\bar{a}_i$
			hours	(years)	
Power supply	1	0.08	1	1.1×10^{-4}	8.8×10^{-6}
Pump 1	2	2	6	6.8×10^{-4}	1.36×10^{-3}
Pump 2	3	2	6	6.8×10^{-4}	1.36×10^{-3}
Control valve 1	4	0.02	3	3.4×10^{-4}	6.8×10^{-6}
Control valve 2	5	0.02	3	3.4×10^{-4}	6.8×10^{-6}

The minimum cut sets are:

Minimum cut set no.	*Component failure no.*
1	1
2	2, 5
3	2, 3
4	3, 4
5	4, 5

Then from Equations 9.5.16 and 9.5.17:

$$f_1 = \bar{a}_1\lambda_1/\bar{a}_1 = \lambda_1 = 0.08$$
$$f_2 = \lambda_2\bar{a}_5 + \lambda_5\bar{a}_2 = 2.86 \times 10^{-5}$$
$$f_3 = \lambda_2\bar{a}_3 + \lambda_3\bar{a}_2 = 5.44 \times 10^{-3}$$
$$f_4 = \lambda_3\bar{a}_4 + \lambda_4\bar{a}_3 = 2.86 \times 10^{-5}$$
$$f_5 = \lambda_4\bar{a}_5 + \lambda_5\bar{a}_4 = 2.72 \times 10^{-7}$$

From Equation 9.5.18 for a time period of one year ($t = 1$), $R_k = f_k t$ is numerically equal to f_k. Then, from Equation 9.5.21,

$$\bar{R}_t \leq 0.085$$

9.5.17 Phased mission systems

In some cases the system passes through more than one phase of operation. Such a system is referred to as a 'phased mission system'. Typically, phased mission systems occur where the same equipment is used at different times in different configurations for different tasks.

Certain emergency core cooling systems (ECCSs) in US nuclear reactors are phased mission systems. After a loss-of-coolant accident (LOCA) the ECCS may have to go through the phases of (1) initial core cooling, (2) suppression pool cooling, and (3) residual heat removal (Burdick *et al.*, 1977). Similarly, on certain liquefied natural gas (LNG) installations the same equipment is used in different modes for normal operation and peak load operation.

In effect, therefore, the top event of the fault tree for a phased mission system is the output of an OR gate, the inputs to which are the top events of the several phases of the mission. This particular OR gate differs, however, from the conventional type in that its inputs are separated in time.

Although a phased mission system can be treated by constructing fault trees for the separate phases, there are certain problems which arise at the boundaries. Such a treatment is not conservative.

For non-repairable systems only, Esary and Ziehms (1975) have developed a transformation that converts the fault tree under the special type of OR gate just mentioned to a conventional fault tree. This transformation is not applicable, however, to repairable systems.

9.5.18 Protective systems

A large proportion of fault tree applications are for protective systems. The determination of the characteristics of systems of this type is therefore of particular interest. A treatment of this problem has been given by Kumamoto, Inoue and Henley (1981). The method given treats the system as a whole rather than the individual protective devices.

The states of the system are: 0, operational; 1, under a normal trip; 2, under a spurious trip; and 3, subject to destructive hazard. The system may then be described by the following equations:

$$\omega_{01}(t) = f_{01}(t,0) + \int_0^t f_{01}(t,u)[v_{10}(u) + v_{20}(u)]\,\mathrm{d}u \quad [9.5.25]$$

$$\omega_{02}(t) = f_{02}(t,0) + \int_0^t f_{02}(t,u)[v_{10}(u) + v_{20}(u)]\,\mathrm{d}u \quad [9.5.26]$$

$$\omega_{03}(t) = f_{03}(t,0) + \int_0^t f_{02}(t,u)[v_{10}(u) + v_{20}(u)]\,\mathrm{d}u \quad [9.5.27]$$

with

$$v_{10}(u) = \omega_{01}(u - \tau_\mathrm{n}) \quad [9.5.28]$$
$$v_{20}(u) = \omega_{02}(u - \tau_\mathrm{s}) \quad [9.5.29]$$

where: $F_{0j}(t, u)$ is the probability at time t that the system is in state j given that it entered state 0 at time u; $f_{0j}(t, u)$ is the time differential of $F_{0j}(t, u)$; $v_{j0}(t)$ is the transition rate, or intensity, at time t from state j to state 0; $w_{0j}(t)$ is the transition rate, or intensity, at time t from state 0 to state j; τ_n is the restoration time after a normal trip; and τ_s is the restoration time after a spurious trip. Then the expected numbers of the transition events are as follows:

$$N_\mathrm{n} = \int_0^t \omega_{01}(u)\,\mathrm{d}u \quad [9.5.30]$$

$$N_\mathrm{s} = \int_0^t \omega_{02}(u)\,\mathrm{d}u \quad [9.5.31]$$

$$N_\mathrm{h} = \int_0^t \omega_{03}(u)\,\mathrm{d}u \quad [9.5.32]$$

where N_h is the number of realized destructive hazards, N_n is the number of normal trips and N_s is the number of spurious trips.

Equations 9.5.25–9.5.27 are solved by numerical integration. The authors have written a code, PROTECT,

for this purpose. An application of this method, using PROTECT, has been described by Kumar, Chidambaram and Gopalan (1989).

9.5.19 Fault tree applications

Reviews of work on fault trees have been given by Arendt and Fussell (1981) and W.S. Lee *et al.* (1985). Accounts of industrial application of fault trees include those of Caceres and Henley (1976), Lihou (1980a,b), Pilz (1980a), Prugh (1981, 1982, 1992a) and Schreiber (1982). Some fault tree applications described in the literature are listed in Table 9.7.

9.6 Event Trees

An event tree is used to develop the consequences of an event. It starts with a particular initial event such as a power failure or pipe rupture and is developed from the bottom-up. The event tree is both a qualitative and a quantitative technique. Qualitatively it is used to identify the individual outcomes of the initial event, while quantitatively it is used to estimate the frequency or probability of each outcome.

An event tree is constructed by defining an initial event and the possible consequences that flow from this. The initial event is usually placed on the left and branches are drawn to the right, each branch representing a different sequence of events and terminating in an outcome. The main elements of the tree are event definitions and branch points, or logic vertices. The initial event is usually expressed as a frequency (events/year) and the subsequent splits as probabilities (events/demand), so that the final outcomes are expressed also as frequencies (events/year).

Each branch of the event tree represents a particular scenario. The tree is a means of estimating the frequency of the outcome for that scenario. It is used in conjunction with a set of hazard models for the determination of the physical consequences of that scenario. For example, for a flammable release, a typical series of models might be those for emission, gas dispersion, ignition, explosion and explosion injury.

Table 9.7 *Some fault trees for process industry systems*

System	*Reference*
Ethylene oxide plant trip system	R.M. Stewar (1971)
Pressure tank system	Fussell (1973a,b); Vesely *et al.* (1981)
Crystallization plant	Lawley (1974b)
Reactor system	Powers and Tompkins (1974a)
Nitric acid cooler	Lapp and Powers (1977a, 1979); Shaewitz, Lapp and Powers (1977)
Sulfur trioxide reactor	Lambert (1977)
Liquid propane pipeline system	Lawley (1980)
Motor system	Vesely *et al.* (1981)
Distillation column system	Kletz and Lawley (1982)
Power distribution network	Cummings, Lapp and Powers (1983)
Storage tank system	Ozog (1985)
Butane vaporizer system	Andrews and Morgan (1986)

In constructing an event tree, the normal convention is to use binary rather than multiple splits. For example, consider the representation of a release for which the immediate outcomes are that (a) the vapour cloud is ignited at the point of release, (b) it drifts towards housing and (c) it drifts away from housing, where the probabilities p_a, p_b and p_c of these three outcomes are 0.2, 0.2 and 0.6, respectively. Figure 9.10 shows two ways of representing this situation, but it is Figure 9.10(b) that is the preferred form. It should be noted that in this case the probability p_2 is obtained from

$$p_2 = p_b/(1 - p_a) \qquad [9.6.1]$$

In certain cases one event tree can be reduced to another, equivalent event tree. Examples of such reduction have been given by Schreiber (1982).

Figures 9.11–9.13 show event trees for the response of an operator to a nuclear reactor transient, a loss of grid power supply and a release of LPG, respectively. In the plant power supply system analysed in the event tree in Figure 9.12, power is supplied to a plant from the National Grid, but in the event of grid loss a standby generator is started up to supply power. The problem is to estimate the frequency of loss of power to the plant. In the event of diesel failure, a backup power supply is brought in. It is assumed in the example that the frequency of grid loss is 1×10^{-1} events/year, that the probability of diesel failure is 2.1×10^{-2} failures/ demand, made up of 2×10^{-2} failures/demand for start-up and 1×10^{-3} failures/demand for running for the required period, and that the backup power supply failure probability is 1×10^{-2} failures/demand. The event tree shows that the frequency of works power loss is 2.1×10^{-5} events/year.

Figure 9.13 shows an event tree analysis of a release of LPG near a detergent alkylate plant (DAP). The possibilities for the development of the release are then as follows. The release may ignite and, if it does, it will either explode or give a fireball. If it does not ignite, it may be borne by the wind towards the DAP and may then ignite and explode at the DAP. Alternatively, the cloud may drift in some other direction. The estimates are:

Frequency of large LPG release $1 = 68 \times 10^{-6}$/year

Probability of ignition $p_1 = 0.9$

Probability of explosion given ignition $p_2 = 0.1$

Probability of wind to DAP $p_3 = 0.4$

Probability of ignition and explosion at DAP $p_4 = 0.9$

Then the probabilities of the outcomes are:

Probability of hydrogen fluoride (HF) release (independent of wind direction) $p_5 = p_1 p_2 = 0.9 \times 0.1 = 0.09$

Probability of fireball $p_6 = p_1 \times (1 - p_2) = 0.9 \times 0.9 = 0.81$

Probability of HF release drifting north-east $p_7 = (1 - p_1) \times p_3 \times p_4 = 0.1 \times 0.4 \times 0.9 = 0.036$

Probability of drifting cloud $p_{10} = p_8 + p_9 = (1 - p_1) \times [p_3 \times (1 - p_4) + (1 - p_3)] = 0.1 \times (0.4 \times 0.1 + 0.6) = 0.064$

The outcome frequencies are then obtained by multiplying the initial event frequency by these outcome frequencies. Thus

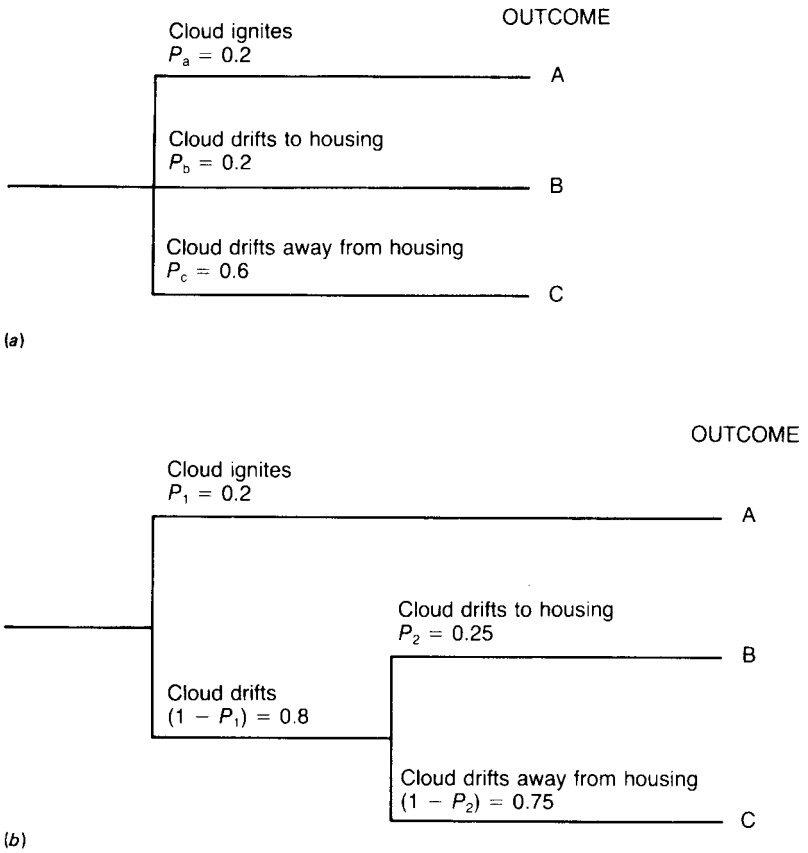


Figure 9.10 *Construction of an event tree: (a) multiple splits; (b) binary splits*

Frequency of HF release (independent of wind direction)

$$\lambda_5 = 0.09 \times 68 \times 10^{-6} = 6.1 \times 10^{-6}/\text{year}$$

and so on.

The outcome probabilities should sum to unity and the outcome frequencies to that of the initial event.

This last example also illustrates the need for care in the definition and interpretation of events. Outcome C is an HF release drifting north-east, but this is not the only outcome where this occurs. It occurs implicitly also in outcome A, so that the frequency of such a release is that of outcome C plus a contribution from that of outcome A.

Event trees are used particularly, but not exclusively, to analyse failures of utilities and outcomes of releases from plants. Other event trees are given in the literature (e.g. von Alven, 1964; N.C. Rasmussen, 1974; AFC, 1975; HSE, 1978b, 1981a; Cross, 1982; Rijnmond Public Authority, 1982).

9.7 Cause–Consequence Diagrams

A third technique that incorporates features both of the fault tree and of the event tree is the cause–consequence diagram. The cause–consequence diagram has been developed by D.S. Nielsen (1971, 1974, 1975) and by J.R. Taylor (1974d, 1978a).

A cause–consequence diagram is constructed by defining a critical event and then developing the causes and consequences of this event. The forward development has the features of an event or a decision tree and the backward development those of a fault tree. The main elements of the diagram are therefore event and conditions definitions and logic gates and vertices.

Some cause–consequence diagram symbols are given in Table 9.8. The logic symbols include both gates, which describe the relations between cause events, and vertices, which describe the relations between consequences. The event and condition symbols describe the type of event or condition. The symbols given are those that have been used by Nielsen and by Taylor.

The main logic gates are the AND gate and the OR gate. There are corresponding logic vertices in the form of the AND vertex and the OR vertex.

The EITHER/OR vertex, or decision box, is also very useful. It is utilized in particular to determine the effect of an event or condition on the paths that the system takes. If, as is often the case, the 'No' output from the decision box is the result of an abnormal condition, then the fault tree for this condition is developed. Thus fault trees occur on the diagram not only for the critical event but also for abnormal conditions throughout the diagram.

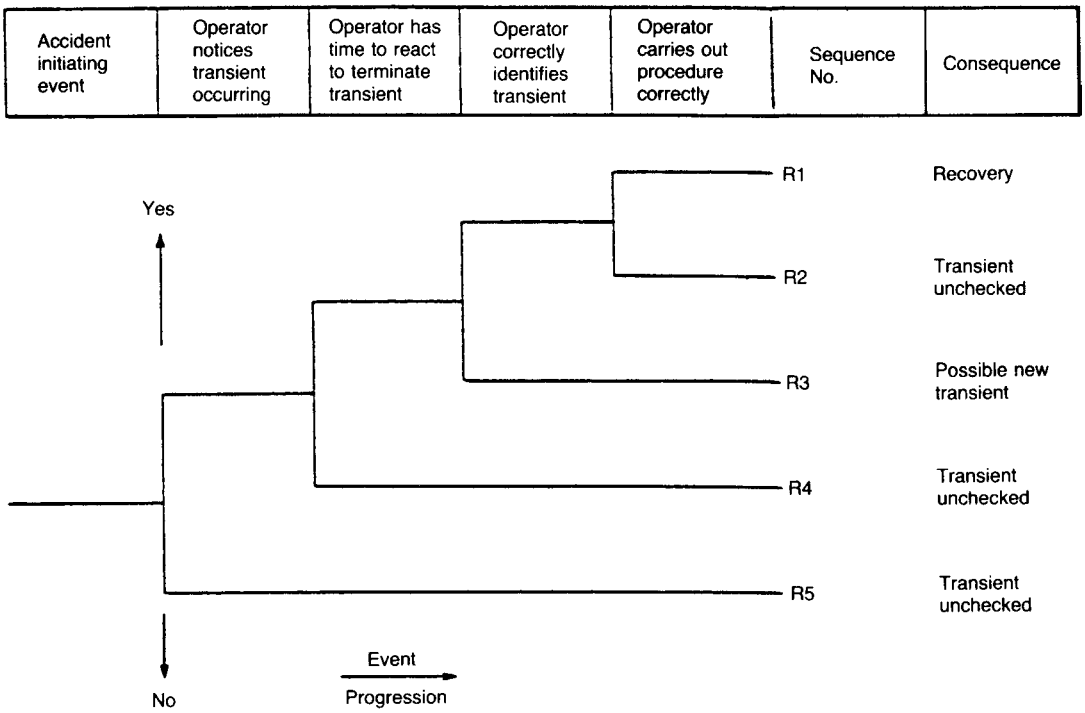


Figure 9.11 *Event tree for response of operator to nuclear reactor transient (Welsh and Lundberg, 1980) (Courtesy of Elsevier Science Publishers)*

Some important features of the cause–consequence diagram are its ability to handle alternative consequence paths and time delay and time order.

Examples of the use of cause–consequence diagrams in hazard assessment have been given by Nielsen and by Taylor. As an illustration consider the example of the surge tank system shown in Figure 9.14(a), which is adapted from a similar example by J.R. Taylor (1978a). The problem is to develop the diagram for the critical event of 'Flow controller fails'. The cause–consequence diagram is shown in Figure 9.14(b).

The cause–consequence diagram may also be used for quantitative assessment.

9.8 Dependent Failures

In the design of systems for reliability, use is made of redundancy and diversity of subsystems and components. In principle, the use of redundancy allows very high reliability to be obtained. The condition for this, however, is that the failures that occur are independent. If this is not so, then the design intent is defeated and the reliability may be less, sometimes dramatically less. In other words, the phenomenon of dependent failure tends to set a limit on the reliability that can be achieved. It is therefore a major concern for designers of high reliability systems.

Work on dependent failures has been described in *A Study of Common Mode Failures* (Edwards and Watson, 1979 SRD R146) and on defences against it in *Defences Against Common Mode Failures in Redundancy Systems* (Bourne *et al.* 1981 SRD R196) and *SRD Dependent Failure Procedures Guide* (Humphreys and Johnston, 1987 SRD R418).

The terminology used in the field has changed somewhat over the years. Initially, the term generally used was 'common mode failure' (CMF). The term 'common cause failure' (CCF) then gained currency. Some debate arose as to the difference between the two. The term 'dependent failure' (DF) is now preferred. A set of definitions is given by Humphreys and Johnston. They define dependent failure as 'the failure of a set of events, the probability of which cannot be expressed as the simple product of the unconditional failure probabilities of the individual events'. They treat CMF as a subset of CCF in which the failures are in the same mode and due to the same cause. They also refer to and include a fourth category, cascade failures or propagating failures.

9.8.1 Occurrence

Dependent failures are liable to occur in all sorts of ways. One of the most obvious is loss of a utility, such as failure of the power supply and hence simultaneous loss of power to all the instruments in a particular system. Another readily envisaged type of dependent failure is that due to some influence from the external environment. This may be freezing due to cold weather, or shock caused by an earthquake.

There are other causes of dependent failure which are less readily appreciated but which are just as important. One of these is human error, specifically systematic error. A systematic error in maintenance or testing may disable a complete system of redundant devices.

In general, a particular component will be potentially subject to a number of types of dependent failure. Typical

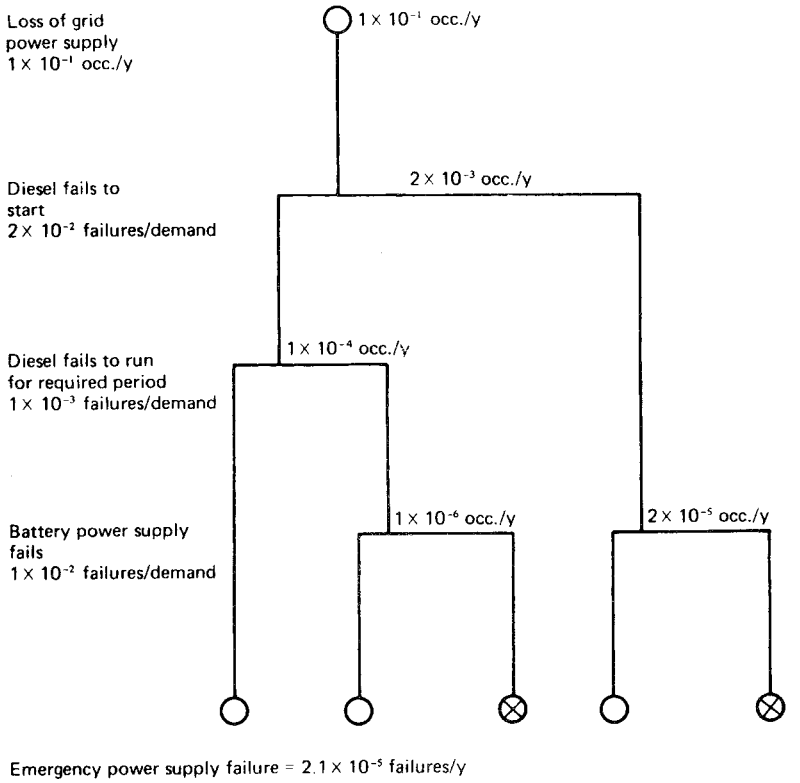


Figure 9.12 *Event tree loss of grid power supply (after Andow, 1976)*

dependencies are manufacture, maintenance and external events. Another form of dependent failure is damage caused by the accident event itself.

9.8.2 Significance

The significance of dependent failures is readily appreciated. There is a limit to the degree of reliability that can be achieved in a system by the use of single items of high reliability. For high system reliability it is necessary to exploit redundancy and diversity. In the absence of dependent failures, very high system reliabilities can be achieved by these means. The effect of dependent failures, however, is to set a limit to the increase in reliability that is obtainable in practice.

One type of system where this is important is protective, or trip, systems. High reliability protective systems tend to utilize more than one channel, typical configurations being $^1/_2$ systems and $^2/_3$ voting systems. Dependent failures can cause a significant increase in the probability of failure on demand for such systems.

Another type of system where the effect of dependent failures is significant is standby systems. There can be an appreciable increase in the probability of failure on demand due to dependent failures. One type of standby equipment where this effect has been repeatedly demonstrated is standby diesel generator sets for emergency power supply, where reliabilities have frequently fallen well below those estimated neglecting dependent failures.

9.8.3 Classification

A classification of causes of CMFs has been given by Edwards and Watson (1979 SRD R146) and is shown in Figure 9.15. Engineering failures are classed as those of design (ED), which is subdivided into functional deficiencies (EDF) and realization (EDR), and those of construction (EC), subdivided into manufacturing faults (ECM) and installation and commissioning faults (ECI). Operations failures are classed as procedural (OP), subdivided into maintenance and test (OPM) and operation (OPO), and environmental (OE), subdivided into normal extremes (OEN) and energetic events (OEE). Each of these classes is broken down into further detailed categories.

9.8.4 Failure data

Edwards and Watson review the data available on CMFs. Most of these data relate to aircraft systems and to nuclear reactor systems in the United States, France, Germany and the United Kingdom.

Data on abnormal occurrences in US nuclear power plants are available in the form of Licensee Event Reports (LERs). Two reactor systems for which high reliability is required are the automatic protective system (APS) and the emergency core cooling system (ECCS). The authors analyse the reports to identify CMFs.

CMF also figures prominently in the *Rasmussen Report* (AEC, 1975). This report contains (in Appendix III) CMFs identified in various data sources on reactor incidents and

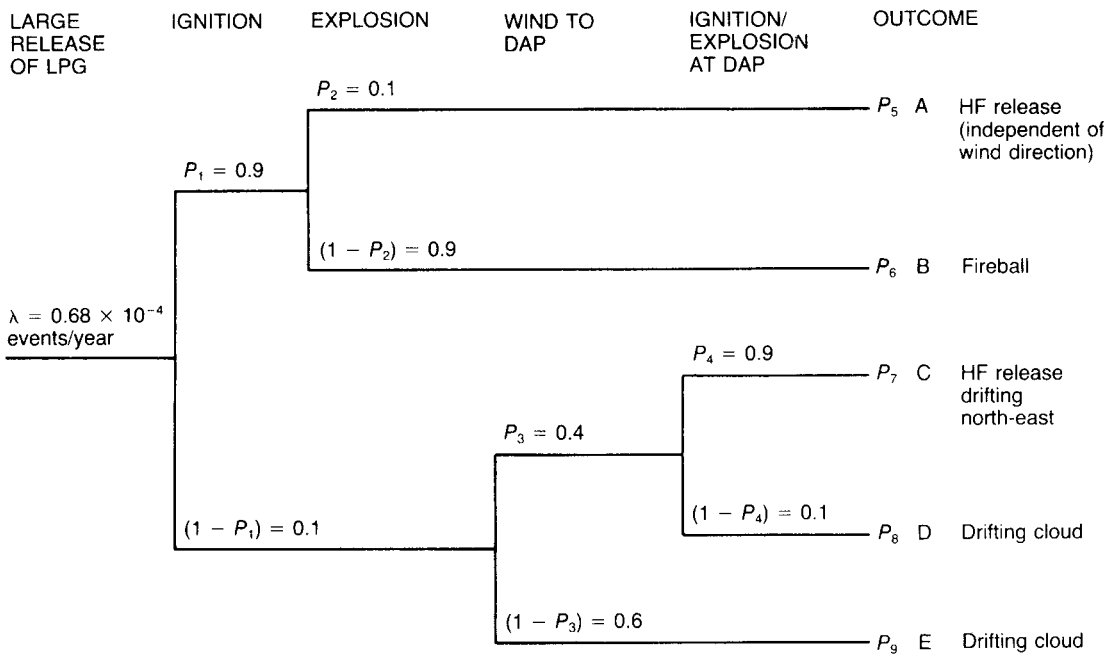


Figure 9.13 *Event tree for release of LPG (after HSE, 1981a)*

operation. Analysis of the data in the *Rasmussen Report* shows that of a total of 303 faults some 32 were CMFs. The causes of these CMFs include EDR (12 faults), OPM (6 faults) and OEN (5 faults).

Further discussions of data on dependent failures are given by Humphreys (1987) and G.T. Edwards (1988).

9.8.5 Beta factor

A quantitative measure of the prevalence of dependent failure is the ratio β of the dependent failures to the total failures, introduced by Fleming (1974). It is defined as:

$$\beta = \frac{\lambda_d}{\lambda_i + \lambda_d} + \frac{\lambda_d}{\lambda} \qquad [9.8.1]$$

with

$$\lambda = \lambda_i + \lambda_d \qquad [9.8.2]$$

where λ is the overall failure rate, λ_d is the rate of dependent failure, and λ_i is the rate of independent failure.

The beta factor may be used to quantify the contribution of dependent failures to overall system failure. Edwards and Watson have analysed the data and derived values of the beta factor for a number of subsystems and components. Particularly important are protective systems with redundancy. For such redundant systems typical values of the beta factor are 0.05 to 0.25.

Another important item is diesel generator sets for emergency power supply. In their study the authors identified 24 nuclear power plants that yielded usable data. For the diesel generators in these plants there were 67 failures recorded over a period of 238 operating years. There were six dependent failures over a period of 118 operating years. Each diesel generator was broken down into eight subsystems. The overall subsystem failure rate was therefore 0.035 failures/year ($67/(8 \times 238)$) and the dependent failure rate 0.0064 ($6/(8 \times 118)$). The resultant value of β is 0.18 (0.0064/0.035).

A further study of beta factors has been described by Humphreys (1987).

9.8.6 Protective systems

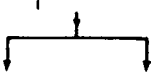
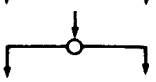
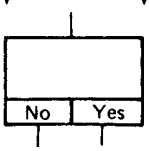
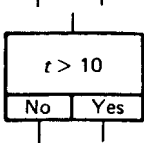
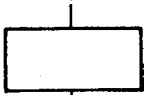
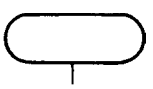
The type of system for which dependent failures are of particular concern is protective systems with a high degree of redundancy. The characteristics of such systems have been discussed by Bourne *et al.* (1981 SRD R196). The authors recognize five basic types of configuration for such systems: (1) a single channel, (2) a redundant system, (3) a partly diverse system, (4) a fully diverse system and (5) two diverse systems.

Thus, considering the measurement channels for a trip system, the authors give as an example of a redundant system a system with n identical redundant channels and m/n majority voting. As examples of partly diverse and fully diverse systems they give systems with two parallel channels, in which the channels are partly diverse and fully diverse, respectively. Two diverse systems are exemplified by a system with two complete subsystems in parallel, each of which is a half-identical redundant channel subsystem.

Bourne *et al.* gave the following approximate ranges for the probability of failure of these configurations, based on a typical proof test interval of 1–3 months:

Single channel	>0.5 to 5×10^{-3}
Redundant system	5×10^{-2} to 5×10^{-4}
Partly diverse system	10^{-2} to 5×10^{-5}

Table 9.8 *Cause–consequence diagram logic and event symbols (after D.S. Nielsen, 1974; J.R. Taylor (1974d)) (Courtesy of the Danish Atomic Energy Commission)*

Logic symbol	*Meaning of symbols*
	AND gate
	OR gate
	AND vertex
	Mutually exclusive, exhaustive OR vertex
	Mutually exclusive OR vertex (used after time delays)
	EITHER/OR vertex, decision box
	Condition vertex
Event and condition symbols	
	Basic condition
	Initiating event (may be critical event)
	Event
	Significant consequence
	Condition
	Fixed time delay
	Variable time delay

Fully diverse system	10^{-3} to 5×10^{-5}
Two diverse systems	5×10^{-5} to $< 10^{-6}$

The probabilities of failure of the systems therefore show considerable overlap.

9.8.7 Modelling for redundancy

A number of methods have been developed for the modelling of dependent failures in redundant systems. Accounts of such modelling are given by Edwards and Watson (1979 SRD R146), G.T. Edwards (1987a,b) and Humphreys and Johnston (1987 SRD R418). The methods include the beta factor method, the multiple Greek letter method, the binomial failure rate method and the Marshall–Olkin method. An account of these and other methods is given by Humphreys and Johnston.

One of the most widely used is the beta factor method. This has a single parameter β. Some of the other methods have several parameters. The use of a single parameter has the merit that only one parameter needs to be estimated from the data, but the corresponding limitation that it cannot, in principle, model the data as accurately as a multiple parameter method.

9.8.8 Beta factor method

As just stated, one of the most widely used models of dependent failure is the beta factor method of Fleming (1974). The beta factor was defined in Section 9.8.5. For a single component the overall failure rate may be written in terms of the beta factor as:

$$\lambda = \lambda_i + \lambda_d \qquad [9.8.3]$$

Then, writing

$$\lambda_i = (1 - \beta)\lambda \qquad [9.8.4]$$

$$\lambda_d = \beta\lambda \qquad [9.8.5]$$

Gives

$$\lambda = (1 - \beta)\lambda + \beta\lambda \qquad [9.8.6]$$

The simplest system to which CCF is applicable is the two-component parallel redundant system shown in Figure 9.16(a). The failure rate for a single component is λ. Then, applying the beta method and separating out the contributions of independent and CCFs, gives the system shown in Figure 9.16(b). The system now consists of a two-component parallel subsystem in series with a single component subsystem. The failure rate for the system λ_s is then given by the relation:

$$\lambda_s = \frac{1}{(1/(1-\beta)\lambda) + (1/(2-\beta)\lambda)} + \beta\lambda \qquad [9.8.7]$$

The fault trees for the two cases are given in Figures 9.16(c) and (d), respectively.

Models such as the beta model are applied particularly to protective systems. For such a system consisting of multiple redundant items in parallel, which is normally not operational but which is required to operate when a demand is placed on it, the probability of failure is equal to its unavailability, or fractional dead time. Since the probability of failure increases with time and since for such a

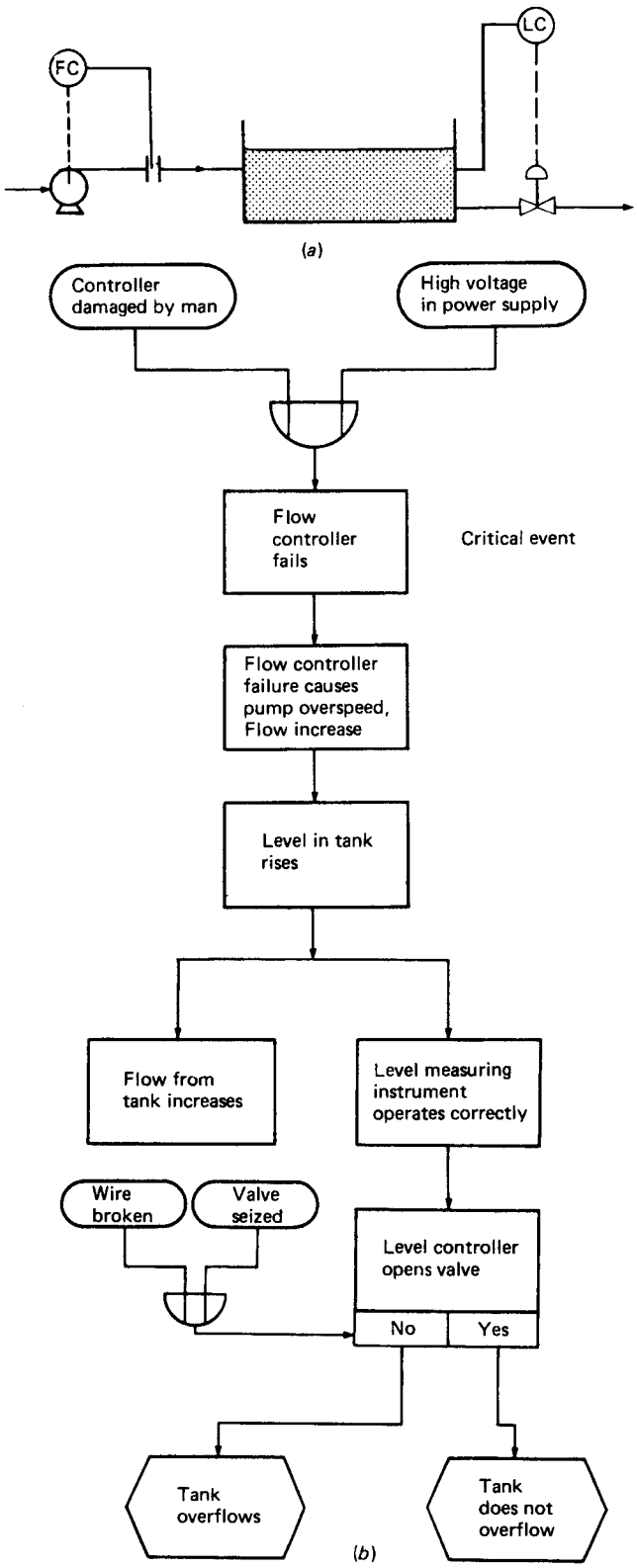


Figure 9.14 *Surge tank system and cause–consequence diagram for overfilling of a surge tank (after J.R. Taylor, 1978a): (a) surge tank system; (b) cause–consequence diagram of the surge tank system for the critical event 'Flow controller fails' (Courtesy of the Danish Atomic Energy Commission)*

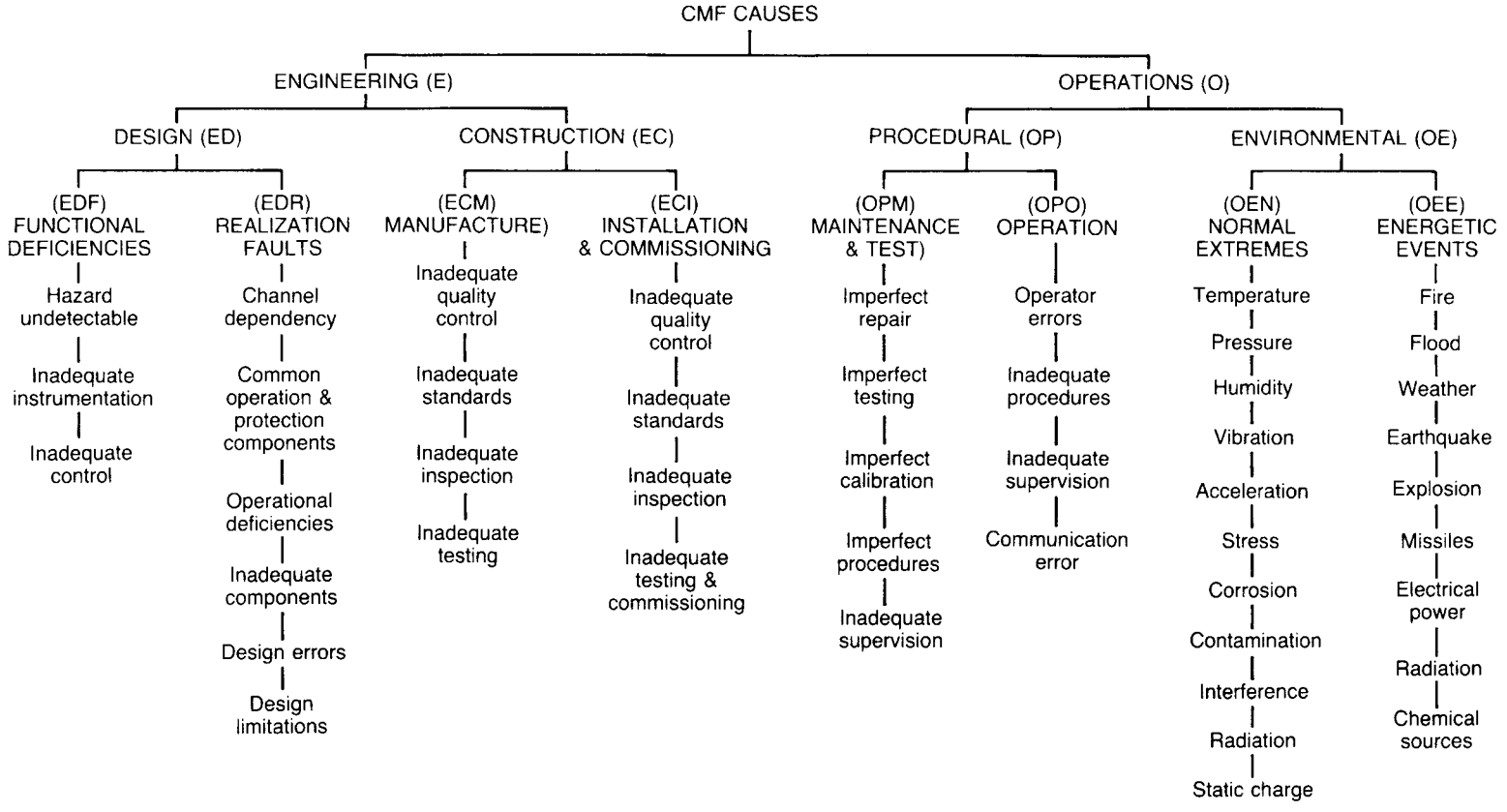


Figure 9.15 *Classification of common mode failures (Courtesy of the UKAEA Safety and Reliability Directorate)*

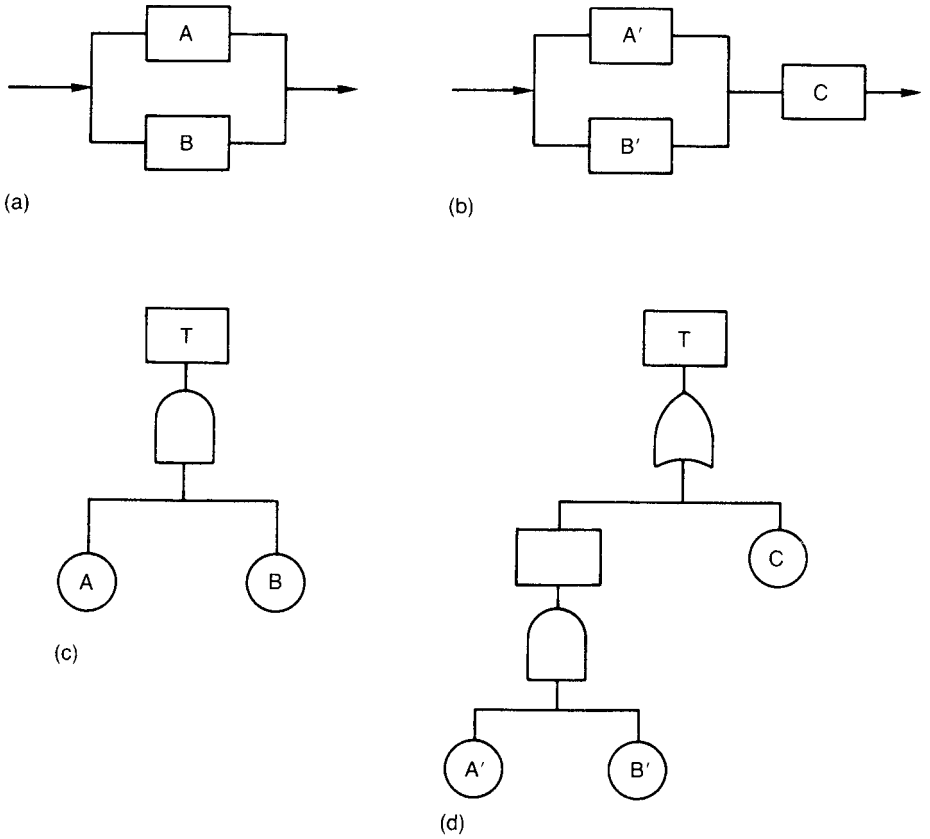


Figure 9.16 *Representation of dependent failure: (a) a two-component parallel system; (b) the two-component parallel system distinguishing between independent and common cause failures; (c) fault tree for system (a); (d) fault tree for system (b)*

system the failure will normally be unrevealed, it is necessary to perform a proof test at some fixed interval.

The application of the beta model may be illustrated as follows. It is shown in Chapter 13 that, subject to certain conditions, the fractional dead time for a single channel system is $\phi = \lambda\tau_p/2$ and that for a system of two parallel redundant channels it is $\phi = (\lambda\tau_p)^{2/3}/3$, where ϕ is the fractional dead time and τ_p the proof test interval. The corresponding expression for the latter case in terms of the beta factor is:

$$\phi = \frac{[(1-\beta)\lambda\tau_p]^2}{3} + \frac{\beta\lambda\tau_p}{2} \qquad [9.8.8]$$

The use of the beta factor method requires that a suitable value of β be known. As stated earlier, typical values for redundant systems are 0.05 to 0.25.

9.8.9 Geometric method

Another method of handling CCF is the geometric method. This utilizes the upper and lower bounds of failure of the system. The lower bound λ_l of the system failure rate is that assuming that there are no failures due to a CCF, and the upper bound λ_u is that assuming that all failures are due to the common cause. The system failure rate λ_s is

$$\lambda_s = (\lambda_l^n \times \lambda_u)^{1/(n+1)} \qquad [9.8.9]$$

where n is an index. The value of n is a function of the diversity of the components in the system and its value usually lies in the range 1–4.

9.8.10 Partial beta factor method

The partial beta factor method is not actually a separate method but rather a method of obtaining a more accurate value of the beta factor. The method is described by Humphreys and Johnston (1987 SRD R418). The authors suggest that a practical limit of the beta factor in a redundant subsystem is about 2×10^{-2} and that in a diverse subsystem is about 10^{-3}. They take the latter as the lower limit for a subsystem for which very high reliability is required and in which all defences are exploited.

The beta factor is decomposed into a set of partial beta factors, each of which corresponds to a particular defence. The beta factor is computed as the product of the partial beta factors. The procedure is as follows. For each partial beta factor, a minimum value β_{pm} is assigned. The product of the minimum values is 10^{-3}. Then for each partial beta factor the user assigns an actual value β_{pa}. The maximum in each case is unity, so that if this maximum is assigned in every instance, the product of these values is unity. Thus, in general, the beta value computed from the partial beta values will lie between 10^{-3} and 1.0.

The authors give a proforma for the determination of the beta factor from the partial beta factors, in which account is taken both of the causes of, and defences against, dependent failures. A further discussion of the partial beta factor method is given by B.D. Johnston (1987a,b).

9.8.11 Multiple Greek letter method

The beta factor method does not distinguish between different levels of redundancy in a subsystem. This deficiency is overcome in the multiple Greek letter method, in which a separate Greek letter is introduced for each component after the first. Thus for a four-component system one would use the letters β, γ and δ, where β is the conditional probability that a cause of component failure will be shared by one or more components, γ is the conditional probability that the cause of component failure which is shared by one or more components will be shared by two or more components, and δ is the conditional probability that the cause of component failure which is shared by two or more components will be shared by all components. It should be noted that the definition of β used here differs from that in the conventional beta factor method.

Humphreys and Johnston (1987 SRD R418) state that typical values of β, γ and δ are 0.1, 0.76 and 0.82, and that system failure probabilities computed by this method typically differ from those obtained by the conventional beta factor method by a factor of about 1.5.

9.8.12 Binomial failure rate method

In the binomial failure rate model developed by Vesely (1977a) and modified by Attwood (1991), multiple dependent failures in a redundant subsystem are treated as being either probabilistic (binomial) or deterministic (global) in nature. In this model, the external event is referred to as a 'shock'. Shocks are divided into non-lethal and lethal, the former being those which have a certain probability of causing subsystem failure and the latter being those which are certain to do so:

$$\lambda = \lambda_{si} + p\mu + \omega \qquad [9.8.10]$$

where p is the conditional probability that the external event will cause subsystem failure, λ is the overall failure rate of the subsystem, λ_{si} is the overall failure rate of the subsystem for independent failures, μ is the occurrence rate of non-lethal shocks, and ω is the occurrence rate of lethal shocks.

9.8.13 Revealed and unrevealed failure models

In the account given so far the emphasis has been on dependent failures in protective systems where failures are unrevealed when they occur and are detected only by proof testing. The probability of failure is a function of the failure rate and of the proof test interval.

In most plant systems, however, where an equipment is required to perform some active function on a continuous basis, failures are detected by the fact that this function is no longer being performed. In this case the failures are revealed. The probability of being in a failure state is a function of the failure rate and of the repair time, taking this as the total time for detection and repair. An example of a system in which failures are revealed is two pumps each of 50% capacity operating in parallel.

The models for the probability of failure in systems with revealed failures and in systems with unrevealed failures are different. Treatments are given in Chapters 7 and 13, respectively. Standby systems are an intermediate case. In the standby mode the failures are unrevealed, whilst in the operating mode they are revealed.

9.8.14 Diversity and its modelling

Diversity is recognized as one of the principal defences against dependent failures. A system with diversity is much less vulnerable to many of the events that can cause dependent failures in redundant systems. The modelling of diversity is, however, much less well developed than that of redundancy, and it is therefore less easy to obtain quantitative results for subsystems embodying diversity.

9.8.15 Fault tree analysis

One of the principal tools for the analysis of high reliability systems is fault tree analysis. The type of system to which fault tree analysis is typically applied is one in which undesirable events are protected against by the use of control loops and trip systems. In systems where very high reliability is required, use is generally made of redundancy in some of the trip systems. The benefit of redundancy may be negated if there is dependency between failures.

In fault tree analysis, dependent failures may be handled in two different ways. One is to construct the tree as normal, without explicit regard to dependency, but to flag each group of base events where a dependency exists and to deal with this dependency at the cut set stage. The alternative approach is to represent the dependent failure part of the subsystem failure as an explicit failure in its own right.

The two approaches are illustrated in Figure 9.17, which shows a fault tree for a system in which a measurement is made using a half-redundant system. The top event X is the failure of the measurement function. In Figure 9.17(a), the events A and B are defined as failure of measurement channel 1 and failure of channel 2, respectively. These failures include both independent and dependent failure contributions. If the dependency of A and B were to be dealt with at the cut set stage, the events would be flagged in some way.

In Figure 9.17(b), the failure that causes failure of the two channels, that is, the dependent failures, is isolated as event C. The events A and B are now redefined as, respectively, the failures of channels 1 and 2, excluding the dependent failure contribution. In this tree, the event C is shown accompanying both event A and event B. In the alternative, but equivalent, configuration shown in Figure 9.17(c), event C is separated out and shown only once.

Computer codes for the analysis of dependent failures have been described by Humphreys and Johnston (1987 SRD R418) and by B.D. Johnston (1987a,b). An account of these codes is given in Chapter 29.

9.8.16 Effect on reliability

The effect of dependent failures is seen most markedly in protective systems with a high degree of redundancy, where it can dominate. This may be illustrated by considering the half-redundant protective system described earlier. The expression for the fractional dead time ϕ of such a system is Equation 9.8.8. Typical values of the parameters are given by Humphreys and Johnston (1987 SRD R418) as follows: $\lambda = 10^{-6}$ failures/h; $\tau_p = 10^3$ h; and $\beta = 0.1$. The fractional dead time is then:

$$\phi = 0.27 \times 10^{-6} + 0.5 \times 10^{-4}$$

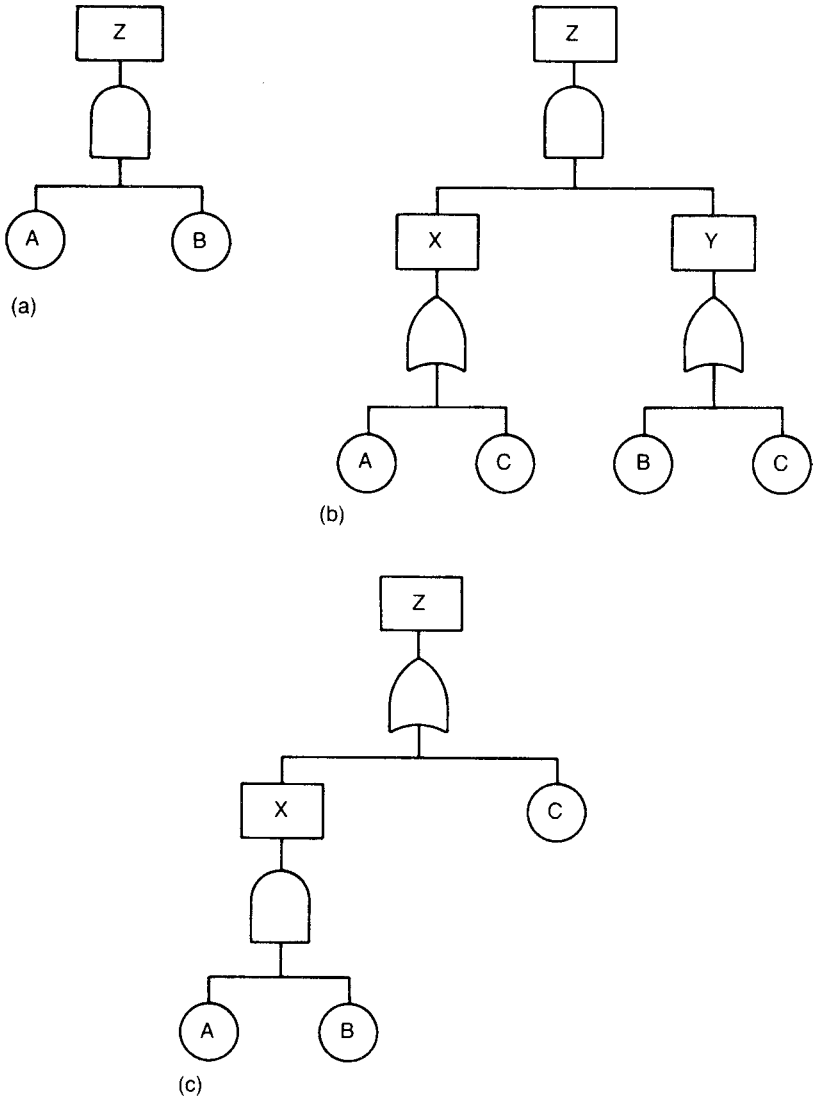


Figure 9.17 *Treatment of dependent failures in fault tree analysis: (a) tree with events A and B treated as independent events; (b) tree with events A and B treated as dependent on event C; (c) alternative form of tree in (b)*

where the first term is the contribution of the system for independent failures and the second that for dependent failures. The dominant contribution is that of the dependent failures.

The impact of dependent failures can be even greater. In the example just given the redundancy was minimal. Systems with higher degrees of redundancy are relatively even more vulnerable to dependent failures. One early study, by Epler (1969), stated that dependent failures might be dominant by a factor as high as 10^5.

9.8.17 Benchmark study

A benchmark study of CCF is described in *Common-cause Failure Reliability Benchmark Exercise* (*Gohnston* and Crackett, 1985 SRD R383). The study is one of a series of benchmark exercises conducted by the Commission of the European Communities (CEC) and organized by JRC-Ispra. A summary of this study is given by Humphreys and Johnston (1987 SRD R418). The situation investigated was dependent failures on the feedwater system of a PWR under emergency conditions. Of the ten teams whose studies are listed, five used the multiple Greek letter method and four the Marshall–Olkin method. The system is characterized by redundancy rather than diversity, and for this situation agreement was reasonably good. The three most structured presentations estimated the probability of failure as lying in the range 10^{-4} to 5×10^{-5}. The treatment of the rather limited amount of diversity in the system exhibited greater discrepancies.

9.8.18 Cascade failures

Cascade failures occur when a fault propagates through the plant and induces further failures. The conditions created by the fault may include abnormal process conditions, equipment overload, loss of potential correction on control loops, activation of trip systems and actions by the operator in response. The cascade failure problem appears to have received relatively little attention.

9.8.19 Defences

The defences available against dependent failures are described by Edwards and Watson (1981 SRD R146) and are further developed by Bourne *et al.* (1981 SRD R196) and Humphreys and Johnston (1987 SRD R418). The headings of the list given by Edwards and Watson are:

1.0 Design
- 1.1 Administration
- 1.2 Functional diversity
- 1.3 Equipment diversity
- 1.4 Fail-safe design
- 1.5 Redundancy and voting logic
- 1.6 Protection and segregation
- 1.7 Proven design and standardization
- 1.8 Equipment derating and simplicity
- 1.9 Operational interfaces
- 1.10 Quality control
- 1.11 Design review

2.0 Operation
- 2.1 Administration
- 2.2 Maintenance procedures
- 2.3 Proof testing
- 2.4 Operating procedures
- 2.5 Reliability performance monitoring

3.0 Reliability assessment

Detailed accounts of the elements of each of these defences are given by the three sets of authors quoted. Bourne *et al.* (1981 SRD R196) describe an overall defence strategy in terms of (1) general strategy, (2) management aspects and (3) technical aspects. The general strategy should be based on good administrative controls of both design and operations. There should be a specification for the reliability requirements of the system with particular reference to dependent failures (DFs). The design should be subject to reviews of dependent failures at appropriate stages. There should be an independent assessment of reliability in which dependent failures are considered. During the operational life of the plant, the continued effectiveness of the defences against dependent failures should be periodically reviewed.

Management should ensure that there is awareness of the problem of dependent failures among all personnel who have a contribution to make in minimizing it, and should give a lead. It should make defence against dependent failures an explicit objective in both design and operations stages. It should make it clear where the need for such defence imposes requirements additional to those of the regular standards and codes. It should assure the necessary reviews and independent assessment.

Technical aspects cover a wide range of measures. Probably the most effective is functional diversity, which is generally used only at system level. This defence may be enhanced by equipment diversity. Within subsystems fail-safe design may be exploited. Other measures are: redundancy and voting logic; protection and segregation; proven design and standardization; and equipment derating and simplicity. These design measures need to be complemented by adequate systems and procedures for defence during operations.

Bourne *et al.* suggest the following priorities. As the most significant contributors to dependent failures are errors in design and in maintenance and testing, the first priority should be the management of the design process and of design and operational tasks in relation to dependent failures. Of the technical measures, fail-safe characteristics offer the greatest potential for reliability enhancement. Next come measures to minimize human error at the interfaces of tasks such as maintenance and testing.

The defences most commonly applied are protection and segregation. Protection guards against influences from the external environment and segregation can be effective against most causes of dependent failure. Both have a contribution to make, but it is not a predominant one. The authors state that other design defences considered (redundancy and voting, proven design and standardization, derating and simplicity) are of less significance, but have a role to play.

9.9 Expert Judgement

It is sometimes difficult to obtain data on event frequency or probability. In such cases, a possible solution is the use of expert judgement to obtain the required estimates. This approach has been used particularly to obtain estimates for human error rates (HERs), where it is especially difficult to obtain field data, and for equipment failure rates, but it also has other applications.

An account of expert judgement is given in *Eliciting and Analysing Expert Judgement: A Practical Guide* (M.A. Meyer and Booker, 1990). A review of five areas of application of expert judgement methods is given by Mosleh, Bier and Apostolakis (1987). Further guidance on knowledge representation and elicitation is available in the literature on expert systems, though there the emphasis is generally more on expert rules rather than on quantification. Expert systems are discussed in Chapter 30.

9.9.1 Scope

Some purposes for which expert judgement has been used are given by M.A. Meyer and Booker (1990) as:

(1) to provide estimates on new, rare, complex or otherwise poorly understood phenomena;
(2) to forecast future events;
(3) to integrate or interpret existing data;
(4) to learn an expert's problem-solving processes or a group's decision-making processes;
(5) to determine what is currently known, what is not known, and what is worth learning in a field of knowledge.

A study in which expert judgement has been used for all these purposes in the context of the NUREG-1150 project is *Analysis of Core Damage Frequency from Internal Events: Expert Judgement Elicitation* by Wheeler *et al.* (1989).

9.9.2 Expert problem-solving

In solving a problem the tasks which an expert has to perform are essentially to (1) understand the question,

(2) retrieve the relevant information, (3) make a judgement and (4) formulate and report an answer.

It is to be expected that the results of an expert judgement exercise will be affected by bias. One form of bias is that arising from the elicitation process and from the expert's involvement with the project. Another form is a discrepancy between the expert's knowledge and some sort of norm. These two forms of bias are sometimes termed 'motivational bias' and 'cognitive bias', respectively.

Some forms of motivational bias are social pressure, misinterpretation or misrepresentation by the interviewer, and overoptimism by the expert. Forms of cognitive bias include inconsistency, anchoring, availability and underestimation of uncertainty. Anchoring is failure to make sufficient adjustment to an initial opinion in the light of further evidence. Availability is the difference in ease of retrieval of different types of information, infrequent catastrophic events being more readily retrieved than more frequent mundane ones.

The handling of bias is not well developed, but there are certain measures that can be taken. The elicitation process can be planned so as to minimize it. The expert can be made aware of the potential for bias. The elicitation process can be monitored for bias and, if necessary, adjustments made to counter it. The results can be analysed for the effect of bias.

9.9.3 Formulation of questions

The elicitation process involves asking the expert a number of questions. The quality of the results obtained depends in large part on the formulation of these questions. This involves defining the objectives of the project, selecting the general question areas and formulating the specific questions. Closely related to this is the selection of the experts who are to try to answer the questions. These may be in-house and/or external experts. Different options exist on the extent to which the experts are involved in the selection of the question areas and the formulation of the questions.

The questions are then refined by structuring them. Some aims of the refinement process are: to focus attention on what is required and to minimize misinterpretation; to present the question in a form that is assimilable by the expert; and to make the question acceptable to him. Some ways in which questions may be refined include decomposition, phrasing and use of representational aids such as diagrams.

There are certain circumstances in which the involvement of external experts in question refinement is critical. These are given by M.A. Meyer and Booker (1990) as those where the purpose is to capture the experts' problem-solving process, where there is evidence that the experts may not accept the questions, and where outside reviewers are likely to be concerned about bias in the questions.

9.9.4 Selection of experts

A basic distinction in the selection of the experts is between applications where the output is to be the experts' answers and those where the output is to be insight into the experts' problem-solving process. In most cases, it is the experts' answers that are of interest. In order to select an expert it is necessary to have some idea of what is to be regarded as constituting expertise. Two types of expertise are distinguished. One is the expert's experience in the domain, or substantive expertise. The other, or normative, expertise is his knowledge of the response mode, or form in which he is to be asked to give his answers, for example, as probabilities, odds or rankings. Both types of expertise are needed for satisfactory results. For certain projects, the credibility of the expert in the world at large may be a factor.

It is normally advisable to use multiple and diverse experts. Diversity of experts guards against the excessive influence of a single individual, and is particularly effective in face-to-face meetings. The number of experts is typically five to nine, the lower figure being about the minimum needed to obtain diversity and the upper one about the maximum that can be readily handled.

The diversity of expertise achieved depends on the selection of experts from the expert population; this is essentially a sampling problem. It is necessary to guard against overrepresentation of any particular tendency.

The success of the exercise depends on the motivation as well as the selection of the experts, and measures should be taken to motivate those participating.

9.9.5 Elicitation methods and planning

In designing the elicitation it is necessary to consider (1) the elicitation method, (2) the response mode and dispersion measures, (3) the aggregation of response, (4) the problem-solving process and (5) the documentation.

There are three principal methods of elicitation: the individual interview, the interactive group and the response of experts operating in isolation (the Delphi method). Each method has its advantages and disadvantages. The individual interview is the main method for obtaining detailed responses and insight into the expert's problem-solving process, but does not give interaction between experts and is time-consuming. The interactive group is claimed to give more accurate responses and to generate more ideas, but it can suffer from group bias. The Delphi method is freer from group bias. It can be framed so as to offer some insight into problem-solving or interaction.

Some response modes which may be used are: single probability values; odds ratios; sets of probability values, effectively a probability distribution; location on a continuous scale; location on a discrete scale, with ranking or rating; paired comparisons; and revisions of estimates. The expert may provide an indication of the uncertainty in the response in the form of a dispersion measures such as a range, or standard deviation.

Methods available for eliciting the expert's problem-solving process include verbal protocol, verbal probe and the ethnographic method. The first requires the expert to think aloud, the second is the questioning of the expert about his problem-solving process immediately after he has given his answer and the third involves transposing the expert's answers into questions, which draw from the expert elaboration of his answers. The use of verbal protocol avoids interviewer bias but is liable to disturb the expert's skilled problem-solving behaviour.

The answers given by a group of experts are likely to differ and need to be aggregated in order to obtain an overall response. This may be done by the experts themselves or by a mathematical technique.

The documentation required from the exercise should be specified. It may record the answers only, the answers and the problem-solving process or something intermediate such as the answers with a short explanation of the underlying reasoning.

The planning of the elicitation includes the logistics of involving the experts, the structuring of the elicitation process, the precautions against bias and the specification of the documentation to guide and record the elicitation. There will normally need to be some training and practice, probably with pilot testing, prior to the main elicitation exercise.

9.9.6 Analysis of responses

The data obtained from the elicitation normally consist of (1) answers to questions and (2) ancillary information. The latter is essentially information about (1) the experts and (2) the expertise.

The data obtained should be examined for two features in particular. One is the degree of detail, or granularity. Variations in the level of granularity can adversely affect the results. It is desirable in principle to operate in the analysis with a single level of granularity. There is, however, a loss of information in passing from the particular to the general and this may act as a constraint.

The other feature is conditionality. Answers are conditioned by the path by which they have been reached and it is desirable to make this explicit. Meyer and Booker comment that: 'Two experts could arrive at exactly the same final answer but for very different reasons, or two experts could arrive at different answers for exactly the same reasons'.

The analysis of the data is facilitated if they can be converted to quantitative form. There are a number of methods of doing this. One approach is to convert qualitative descriptors into values on some kind of scale. Another is to merge separate categories into a small number of broader ones. Another is the combination of quantitative data using weighting.

The data may be analysed to obtain relationships between different answers, between different ancillary variables and/or between answers and ancillary variables. One major aspect of such analysis is that concerned with lack of independence between experts' answers, or correlation, and with bias in these answers. There are various factors which experts may have in common, such as shared training, similar work experience and exposure to the same data sources. The biases that may be present include motivational and cognitive bias, as described earlier.

Another aspect of data analysis is the modelling of the experts' answers in terms of the ancillary data on the expert and his expertise.

A third aspect of the analysis is the application of aggregation methods to combine the answers of a number of experts into a single value or distribution of values. One particular application of aggregation occurs where there is a decision-maker and a single expert. The elements in this situation are the decision-maker's prior estimate, his choice of the expert, the aggregation of the prior estimate with the expert's information, and the inference. There are several quite different potential outcomes. Thus, the decision-maker may consider both items of information as valid and combine them, he may prefer one or the other or he may decide to adopt a range of values. Another situation occurs where there is a decision-maker and n experts. The potential outcomes are similar, but it is more likely that the decision-maker will not simply prefer his own prior.

A fourth aspect of the analysis is the handling of uncertainties in the data. Some sources of uncertainty are definitions, errors associated with small samples, non-sampling errors such as missing data, and deficiencies in scientific and modelling techniques. Methods are available which assist in the measurement, modelling and control of such uncertainties.

The purpose of the analysis is to reach conclusions by making inferences from the responses and analysis of these responses. What an expert judgement exercise does is to sample the world of experts and their expert knowledge. It does not sample the real world and the conclusions drawn may or may not represent the true state of nature. The validity of these conclusions depends very much on the quality of expert knowledge about the domain in question.

Critiques of expert judgement refer to the subjective nature of such judgement. The validity of subjective judgement is considered in more detail in Chapter 7.

9.9.7 Interviews

One of the main techniques of elicitation used in expert judgement work is the individual interview. There is a large literature on interview and questionnaire techniques. Guidance on interviewing is given by Kahn (1957), by Oppenheim (1966) and by Gorden (1987) and also in texts on expert systems.

9.9.8 Delphi method

Another of the principal techniques of expert judgement is the Delphi method. As already described, this method involves the use of multiple experts operating in isolation. This method is described in *The Delphi Method* (B. Brown, 1964), and by Linstone and Turoff (1975) and Dalkey (1969). The Delphi method was used for the estimation of failure rates in IEEE Standard 500: 1984, which gives an appendix on the procedure used.

9.9.9 Ranking and scaling

Work on ranking and scaling of expert judgement has been described by Thurstone (1927, 1931) and by Kendall (1948, 1955, 1970). An account of scaling methods has been given in *Theory and Method of Scaling* (Torgerson, 1967).

In general, the overall approach in expert judgement work is first to rank the items. From this ranking the items are then located on a numerical scale. If absolute values are known for some of the items on the scale, these may be used to calibrate the scale and thus obtain absolute values for the other items.

A distinction is made between psychological and probability scales. The responses from the judges lie on a psychological scale and have to be converted to a probability scale. The theory underlying the conversion of rankings to locations on the psychological scale is complex, but essentially, it is based on the concept that the responses for a particular item exhibit a Gaussian distribution about some point on the scale. Then if two items are located close together, there will be an overlap between the two distributions and hence a higher frequency of disagreement between judges, while if they are located far apart there will be little or no overlap between distributions and little or no disagreement between judges. The key result obtained by Thurstone is that

$$\mu_{k-j} \approx x_{kj} \qquad [9.9.1]$$

where μ_{k-j} is the mean separation on the scale between item j and item k, and x_{kj} is the unit normal deviation

corresponding to the probability that k will be ranked above j. This is the basis for the conversion of the rankings of the bench of judges into locations on the psychological scale.

9.9.10 Method of paired comparisons

A major difficulty in asking an expert to rank a number of items is that his preferences may not lie on a linear scale. If the interviewer insists on a simple ranking, the responses may be forced into too rigid a framework. This problem can be mitigated by asking the expert to express preferences between pairs of items only. This is the basis of the method of paired comparisons.

The method of paired comparisons was proposed by Thurstone (1927) and developed by Kendall (1948, 1955, 1970). Further accounts of the method are given by Guilford (1954), Keats (1971) and Hunns (1980, 1982).

In the method of paired comparisons, a bench of m judges is asked to rank a set of n items. The response of a single judge is considered first. For each item pair, say A and B, the judge is asked to express a preference. A preference for A over B is denoted by A → B or B ← A. An $n \times n$ matrix of responses is produced, as shown in the following illustrative example given by Kendall (1970):

	A	*B*	*C*	*D*	*E*	F
A	–	1	1	0	1	1
B	0	–	0	1	1	0
C	0	1	–	1	1	1
D	1	0	0	–	0	0
E	0	0	0	1	–	1
F	0	1	0	1	0	–

The diagonals are blocked out. An entry 1 in column Y, row X signifies X → Yand is therefore accompanied by the entry 0 in column X, row Y. In this example, A → B, A → C and A ← D. This $n \times n$ matrix provides the basic data from a single judge.

The responses of a judge often exhibit some degree of inconsistency. This is seen in its simplest form where a set of three pairs, or triad, is inconsistent, or circular. For example, the responses F → G → H → F are inconsistent.

In making paired comparisons, on n items a judge takes $n(n-1)/2$ decisions. The maximum number of circular triads is $(n^3-n)/24$ if n is odd and $(n^3-4n)/24$ if n is even. The minimum number is zero. A coefficient of consistency ζ for a single judge may then be defined

$$\zeta = 1 - 24d/(n^3 - n) \qquad n \text{ odd} \qquad [9.9.2a]$$

$$= 1 - 24d/(n^3 - 4n) \qquad n \text{ even} \qquad [9.9.2b]$$

where d is the observed number of circular triads. This may be obtained from the

$$d = \frac{n}{12}(n-1)(2n-1) - \frac{\sum a_i^2}{2} \qquad [9.9.3]$$

where a_i, is the sum of entries in row i.

The number of triads may also be analysed, as described by Kendall, using the chi-square distribution to determine the probability that the responses are random and could have arisen by chance.

The measure of agreement between the bench of judges is the coefficient of agreement u:

$$u = \frac{8\sum}{m(m-1)n(n-1)} - 1 \qquad [9.9.4]$$

where $\sum$ is the sum of agreements between pairs of judges. The maximum possible value *of* u is 1. The minimum possible value is not –1 but $-1/m$ for m odd and $-1/(m-1)$ for m even.

9.9.11 Saaty's method

One method for paired comparisons is that of Saaty (1977, 1980). His method is part of a methodology described in his book *The Analytic Hierarchy Process* (AHP) (Saaty, 1980). The problem is cast in hierarchical form and the paired comparison technique is then used at the successive levels of the hierarchy.

The following scheme is used in making the paired comparisons:

Number	*Description*
1	The two items are of equal importance or equally likely
3	A slight favouring of the first item over the second
5	A strong favouring of the first item over the second
7	A demonstrated dominance of the first over the second
9	An absolute affirmation of the first over the second

Values 2, 4, 6, 8 are used where the comparison is assessed as a case intermediate between the above descriptions. The comparsions are expressed as the number 1, for no preference, or the fractions 1/3, 1/5, 1/7, and 1/9 for positive preferences. Thus, for example, and entry 1/3 means that there is a slight preference for the second item over the first.

The expert proceeds by making all the possible comparisons and recording them in a $n \times n$ matrix with 1s down the diagonal and the comparisons in the upper triangular portion of the matrix. The reciprocals of the entries in the upper triangular portion are entered in the lower triangular portion. The relative weights of the n items are then obtained. These weights are the normalized eigenvectors of the principal eigenvalue of the matrix.

An index of consistency is obtained based on the deviation of the principal eigenvalue from the theoretical eigenvalue of a perfectly consistent matrix. If the consistency ratio is greater than 0.10, inconsistency is indicated.

As an illustration of Saaty's method, consider the example given by M.A. Meyer and Booker (1990). It is required to rank the following meteorological conditions in respect of the likelihood that they will cause a loss of off-site power to a plant:

(1) flash flooding at plant site with 0.5 to 2 in. of water;
(2) flash flooding with 2 to 4 in.;
(3) flash flooding with more than 4 in.;
(4) direct hit of lightning on power lines;
(5) direct hit by tornado;

(6) winds between 20 and 40 mph;
(7) winds higher than 40 mph.

The expert makes the following judgements:

1 vs 2.....1/3 2 vs 3.....1/2
1 vs 3.....1/4 2 vs 4.....1/3
1 vs 4.....1/5 2 vs 5.....1/3
1 vs 5.....1/5 2 vs 6.....1/2
1 vs 6.....1/3 2 vs 7.....1/3
1 vs 7.....1/4

3 vs 4.....1/2 4 vs 5.....1/3
3 vs 5.....1/2 4 vs 6.....1/5
3 vs 6.....1 4 vs 7.....1/4
3 vs 7.....1/2

5 vs 6.....5 6 vs 7.....1/2
5 vs 7.....4

and produces the following matrix:

	1	2	3	4	5	6	7
1	1	1/3	1/4	1/5	1/5	1/3	1/4
2	3	1	1/2	1/3	1/3	1/2	1/3
3	4	2	1	1/2	1/2	1	1/2
4	5	3	2	1	1/3	1/5	1/4
5	5	3	2	3	1	5	4
6	3	2	1	5	1/5	1	1/2
7	4	3	2	4	1/4	2	1

Eigenvalue analysis of this matrix gives the principal eigenvalue as 8.001. The weights for the seven items are obtained by normalizing the seven terms in the corresponding eigenvector. For this example the respective weights of the seven items are: 0.03, 0.06, 0.11, 0.11, 0.35, 0.15 and 0.19.

However, the consistency check gives a value of 0.13, indicating a degree of inconsistency. Examination of the initial judgements shows that the inconsistencies include the following: 1 vs 4 is the same as 1 vs 5; 2 vs 4 same as 2 vs 5; 3 vs 4 same as 3 vs 5; 6 vs 4 same as 6 vs 5 and 7 vs 4 same as 7 vs 5. These judgements imply that 4 and 5 are the same, but 4 vs 5 is given as 1/3. Furthermore they imply that $6 < 7$, but the judgements 4 vs 6 and 4 vs 7 imply that $6 > 7$. There may be other inconsistencies, but these three are major. The following corrections are made:

Comparison	*Correction*	*Objective*
4 vs 5	1	To make 4 and 5 the same
4 vs 6	5	To match 5 vs 6
4 vs 7	4	To match 5 vs 7

This now gives a consistency ratio of 0.06, which is much more acceptable, and yields the following revised weights: 0.03, 0.07, 0.11, 0.28, 0.28, 0.08 and 0.15.

These weights are to be interpreted solely as indicating the relative ranking. Thus the items judged most likely to cause loss of power are 4 and 5, whilst that judged least likely to do so is item 1. The weights must not be used to draw quantitative conclusions. It is not correct to infer that item 7 (weight 0.15) is five times as likely as item 1 (0.03).

Saaty's method has the advantages that it is easily used by an expert and that it monitors consistency. It is used primarily where the overall problem can be formulated to have a hierarchical structure. It has been widely used in decision analysis.

Many problems, however, are not readily cast in hierarchical form. Moreover, the forcing of a problem into such form is contrary to a philosophy of letting the data suggest the methods of analysis and the models to be used.

9.9.12 Hunns' method

A method for paired comparisons that allows items to be not only ranked but also scaled has been given by Hunns (1980, 1982). In order to calibrate the scale in terms of probability it is necessary to know the relationship between the scale units and the relative probability. Hunns suggests that there is evidence that this is a logarithmic one. Some support for the existence of a logarithmic scale has been given by Pontecorvo (1965) in a study involving comparison of expert judgements on repair times with field data. The relation may be expressed as:

$$\log_{10} P_x = k_1 + k_2 S_x \qquad [9.9.5]$$

where P is the relative probability of an item, S the scale value of the item, k_1 and k_2 are constants and the subscript x refers to item x.

Taking one scale unit to correspond to a ratio r of probabilities the following relations then apply:

$$\frac{P_u}{P_l} = r^{(S_u - S_l)} \qquad [9.9.6]$$

$$\frac{P_x}{P_l} = r^{(S_x - S_l)} \qquad [9.9.7]$$

$$= \left[\frac{P_u}{P_l}\right]^{(S_x - S_l)/(S_u - S_l)} \qquad [9.9.8]$$

Hence

$$r = \left[\frac{P_u}{P_l}\right]^{1/(S_u - S_l)} \qquad [9.9.9]$$

and

$$k_1 = \log_{10}(P_l r^{-S_l}) \qquad [9.9.10]$$

$$k_2 = \log_{10} r \qquad [9.9.11]$$

where subscripts l and u are to lower and upper.

If absolute probability values are known for two items on the scale, Equations 9.9.6–9.9.11 may be used to obtain absolute values for the others.

The application of Hunns' method is now described using the illustrative example given by him. A bench of 20 judges is asked to rank four items A, B, C and D. The results obtained are recorded in the raw frequency matrix **F**, which for this example is as follows:

	A	*B*	*C*	*D*
A	–	6	7	11
B	14	–	12	20
C	13	8	–	14
D	9	0	6	–

The entries give the number of judges out of 20 expressing the preference in question. An entry n in column Y, row X signifies that n judges prefer X to Y. Thus in this example all 20 judges prefer B to D. The entries on the diagonal are left blank. For an entry n in the upper triangular portion of the matrix there is an entry $20-n$ in the corresponding location in the lower triangular portion.

Next the probability matrix **P** is obtained by dividing the entries in the **F** matrix by 20 and thus normalizing them:

	A	*B*	*C*	*D*
A	–	0.30	0.35	0.55
B	0.70	–	0.60	1.0
C	0.65	0.40	–	0.70
D	0.45	0	0.30	–
Σ	1.80	0.70	1.25	2.25

The entries in each column are then summed as shown in the bottom additional row.

The transformation matrix **X** is then obtained as follows. The order of the columns is rearranged in the numerical order of the values of Σ in the **P** matrix, starting with the highest value. The entries in the **X** matrix are obtained by replacing the probability values from the **P** matrix by the values of the unit normal deviates. Thus for each entry value P the probability P' is obtained as follows:

$$\begin{aligned} P' &= P & P \le 0.5 \\ &= P - 0.5 & P > 0.5 \end{aligned}$$

From the value of P' the unit normal deviate is then determined. For this use is made of a table of the cumulative normal distribution function (e.g. A.E. Green and Bourne, 1972, p. 554). Thus for the entry in column A, row B in the **P** matrix, which has the value 0.70, the value of P' is 0.20 (=0.70 − 0.50) and that of the unit normal deviate is 0.53. The **X** matrix is:

	D	*A*	*C*	*B*
A	0.13	–	−0.38	−0.53
B	?	0.53	0.25	–
C	0.53	0.38	–	−0.25
D	–	−0.13	−0.53	?

The query signs occur where the judges were unanimous, namely in preferring B to D.

The column difference matrix **Z** is then obtained by taking the differences between entries in the adjacent columns of the **X** matrix:

	D–*A*	*A*–*C*	*C*–*B*
A	0.13	0.38	0.15
B	?	0.28	0.25
C	0.15	0.38	0.25
D	0.13	0.40	?
Σ/n	0.14	0.36	0.22

The entries in each column are then averaged as shown in the bottom additional row. These latter entries are the scale values that are used to locate the items on the ranking scale.

The range of the scale in this example, as given by the bottom additional row of the **Z** matrix, is 0.72 (=0.14 + 0.36 + 0.22). Item D has the lowest preference rating and is at the bottom of the scale and item B is at the top of the scale. The intervals between D and A, A and C, and C and C are, respectively, 0.14, 0.36 and 0.22.

This psychological scale may then be calibrated as a relative probability scale, as described above, and if the necessary absolute probability values are available for some of the items, absolute probabilities for the others may be calculated as described above. In performing this conversion, it is necessary to ensure that the upper limit of the scale is unity and to set some lower limit. For the latter Hunns uses a value of 10^{-6}. Hunns describes an application of his method but does not claim it to be well tested. It is, however, one of the methods referred to in the literature.

9.9.13 Applications

The use of expert judgement is now a well-established approach. A critical review of some principal applications has been given by Mosleh, Bier and Apostolakis (1987). Five types of application are reviewed.

The first is the assessment of component failure rates and other reliability parameters. Examples of the estimation of failure rates considered are those in the *Rasmussen Report* (AEC 1975), in IEEE Standard 500: 1984, and in the Seabrook Station PRA (Pickard, Lowe and Garrick, 1983).

The second type is the assessment of seismic hazard rates as exemplified in the studies by the Electrical Power Research Institute (EPRI, 1986) and Veneziano, Cornell and O'Hara (1984).

The third type is the assessment of nuclear reactor containment phenomenology as instanced by the work of the Steam Explosion Review Group of the NRC (1985 NUREG/CR 1116) and the Surry Station PRA by Benjamin *et al.* (1986).

The fourth type is modelling for the assessment of HERs. Examples considered here are: the approach described in the *Handbook of Human Reliability Analysis* (Swain and Guttman, 1983); the human cognitive reliability (HCR) model of Hannaman *et al.* (1986); the SLIM-MAUD method of estimating HERs of Embrey (1984); and, again, the Seabrook Station PRA.

The fifth type is studies of precursor events, which have been carried out by Minarick and co-workers (Minarick and Kukielka, 1982; Cottrell, Minarick *et al*, 1984; Minarick *et al.*, 1985).

These applications covered cases with a wide range of characteristics, including the following:

(1) cases involving single, as well as multiple, experts;
(2) cases involving structured group processes as well as unstructured ones;
(3) cases with a wide range of substantive problem areas;
(4) cases with and without availability of relevant empirical data;
(5) cases of varying degrees of complexity;
(6) cases involving varying degrees of mathematical sophistication in the aggregation of responses;

Some of the conclusions of the study are as follows. (1) An improvement in the quality of the results may often be obtained by decomposition of the problem into a set of more elementary problems. (2) Where experts are used to make estimates without the aid of formal methods, they tend to produce under- or overestimates and to underestimate the degree of uncertainty in these estimates. (3) Two effective techniques for reducing overconfidence are calibration training of the experts and exercises in which the experts are required to identify contrary evidence. (4) A structured group meeting tends to give better performance than an unstructured one. (5) Aggregation of multiple opinions tends to yield a more accurate result than the opinion of a single expert. (6) For aggregation of the opinions of multiple experts, mathematical methods of aggregation are to be preferred to behavioural methods of reaching a consensus.

Decomposition is identified as an effective strategy. The approach suggested by the authors is to enlist the experts in the decomposition process.

The use of multiple experts as opposed to a single expert is well established. But the methods of combining the responses of multiple experts need more development. Combination by an unstructured group does not give accurate results. On the other hand, the highly structured group used in the Delphi method seems cumbersome. The authors suggest the multiple team approach used by EPRI in the seismic hazard work.

9.9.14 Failure rates

As just described, one of the principal applications of expert judgement has been the estimation of failure and event rates. Experience in applications of this sort has been discussed by Apostolakis (1986). He distinguishes three general situations in which judgement is very prominent. These are where: (1) the probability distribution is developed solely from non-statistical knowledge, for example, human error distributions; (2) the advice of experts is incorporated, for example, generic failure rates in the *Rasmussen Report* and fragility curves in seismic work; and (3) the statistical evidence if available but subject to different interpretations. The author discusses some of the detailed features of the generic failure rate estimates in the *Rasmussen Report* and IEEE Standard 500: 1984.

Expert judgement may also be used in the utilization of such generic data. A common situation is in which plant data are available to supplement the generic data and it is then necessary to aggregate them. This may be done using Bayes' theorem. The generic data constitute the prior information that is adjusted using the plant data to obtain the posterior distribution.

Apostolakis draws attention to the fact that in some cases of failure rate estimation when this Bayesian approach is used, it is found that the posterior distribution lies in the tail region of the prior distribution on the high side, indicating bias in the prior distribution. He suggests that this points to the need to broaden the prior distribution, but acknowledges that this is a matter of debate (e.g. Apostolakis, 1982, 1985a; Martz, 1984).

9.10 Rare Events and External Threats

One of the most difficult problems in event frequency estimation is that of rare events. Such events come under the following headings:

(1) equipment failure;
(2) external events
    (a) natural,
    (b) man-made.

Usually it is necessary to take into account rare events only where the potential consequences may be very serious. The rare event problem is therefore essentially associated with major hazards.

9.10.1 Equipment failure

The failure rate of equipment is usually estimated from historical data. The difficulty in using this approach is that for rare events such data are sparse. This may render it necessary to resort to making an alternative estimate based on engineering principles.

It is not uncommon that the historical record appears to show there to be some cases of the event of interest, but that it is judged that many, or even all, of these do not apply to the particular situation of interest. Discarding of failures that are considered inapplicable reduces the data set further.

In the process, and nuclear, industries the rare event that has received most attention is almost certainly pressure vessel failure. The historical record shows only a handful of failures and some of these have been judged inapplicable for vessels designed to and operated at high standards.

Statistics exist which allow an estimate to be made of the failure rate of a device even if the data are limited to just a few, or even one, failure. The confidence limits, however, are a function of the number of failures, and if there are only one or two of these the bounds are wide. It is also possible to make an estimate of the failure rate, or rather its upper bound, even if there have been no failures, based on the number of failure-free years of the equipment. For a rare but high hazard event, however, it is generally necessary to accumulate a rather large number of years without failure before the failure rate estimate begins to approach an acceptable value, and often the number of equipment-years recorded is insufficient. Similarly, statistics exist which allow estimates to be made of failure probability on demand for a device, both with and without recorded failures. The appropriate statistics are given in Chapter 7.

If a statistical approach is considered inappropriate, it is necessary to resort to an attempt to make an estimate based on engineering principles. For example, for a pressure vessel use is made of estimates based on fracture mechanics and inspection considerations.

A prime example of equipment failure as a rare event is the failure of the nuclear reactor pressure vessel considered at the Sizewell inquiry, which is described in Appendix 26.

9.10.2 Natural hazards

There are various natural hazards that pose a threat to plant. Some of these are listed in Table 9.9. The relative importance of a particular natural hazard varies between different countries and between different locations within a country.

For some natural hazards, particularly those due to weather, there are historical records that for certain sites at least may allow a frequency estimate to be made. Others such as those involving surface instability tend to be one-off events that are not amenable to prediction. A third class are those involving subterranean stress where the probability of the event may increase over time until the stress is relieved and where the prediction techniques are still developing.

Information on recurring natural hazards is generally of two kinds. The hazard may be a discrete event that either occurs or does not occur and in this case, the data required are the frequency of occurrence. For such events the usual default assumption is that occurrence is random and that the data fit a Poisson distribution.

The other situation is where the hazard is an event that has associated with it a variable that has a range of values. In this case, the data required are the maximum values of the variable. For example, for wave hazard the required data are maximum wave heights. Data of this latter kind may relate either to maxima of events occurring at random or, where a number of such events always occur within a year, to annual maxima.

The statistical treatment of natural hazards is given in *Statistics of Extremes* (Gumbel, 1958). Descriptions are available of the application of such statistics to various natural hazards such as floods, hurricanes, waves and earthquakes. Further treatments are given by Perry (1981) and Schueller (1982).

In considering such natural phenomena the point of interest is to know the probability that a given value x of the variable, say wind speed or wave height, will be equalled or exceeded – this is the 'exceedance probability'. If the event occurs at random, then for an event rate λ and time period t the number of trials v in which exceedance may occur is

$$v = \lambda t \qquad [9.10.1]$$

If the event is the annual event for which the variable is the annual maximum, the number of trials θ equals the number of years in the time period t.

Table 9.9 *Some natural hazards which pose a threat to plant*

Subterranean stress:
Earthquakes
Volcanoes
Tsunamis
Surface instability:
Landslides and avalanches
Ground surface collapse
Weather:
Wind, storm
Tornadoes
Hurricanes
Floods
Fires

Considering first a general treatment, define $P(x)$ as the distribution of the probability that exceedance does not occur and p as the probability that in a single trial it does occur. Then,

$$p = 1 - P(x) \qquad [9.10.2]$$

Furthermore,

$$q = 1 - p \qquad [9.10.3]$$
$$= P(x) \qquad [9.10.4]$$

where q is the complement of p. The probability $W(v)$ of exceedance in v trials is

$$W(v) = 1 - q^v \qquad [9.10.5]$$

The mean number of trials $\bar{v}$ at which exceedance occurs is

$$\bar{v} = 1/p \qquad [9.10.6]$$

From Equations 9.10.3, 9.10.5 and 9.10.6:

$$W(v) = 1 - (1 - 1/\bar{v})^v \qquad [9.10.7]$$
$$= 1 - \exp(-v/\bar{v}) \qquad 1/\bar{v} = p << \phi \qquad [9.10.8]$$

A return period $T(x)$ may be defined as the mean time between exceedances, so that

$$T = \bar{v}$$

Then, from Equations [9.10.8] and [9.10.9]

$$W(v) = 1 - \exp(-v/T) \qquad 1/T << \text{ø} \qquad [9.10.10]$$
$$\approx v/T \qquad v/T << \text{ø} \qquad [9.10.11]$$

Equation 9.10.10 is independent of the form of the distribution $P(x)$.

Turning now to the assignment of a specific distribution to the event of interest, Gumbel gives a number of distributions, but that most commonly referred to as the 'Gumbel distribution' is as follows. For $P(x)$ he gives

$$P(x) = \exp\{-\exp[-\alpha(x - u)]\} \qquad [9.10.12]$$

where u is a location parameter and α is a scale parameter. This is the distribution of the probability that exceedance does not occur. The distribution of the probability that exceedance does occur is

$$F(x) = 1 - \exp\{-\exp[-\alpha(x - u)]\} \qquad [9.10.13]$$

It should be noted that Gumbel uses $F(x)$ for the distribution which is here denoted by $P(x)$. Since exceedance is akin to failure, $F(x)$ has been reserved here for the complement of $P(x)$ so that it is akin to the failure distribution functions given in Chapter 7.

Equation 9.10.13 is a form of the extreme value distribution that is described in Chapter 7. This distribution is the appropriate one to use for extreme values of a variable that follows the exponential distribution.

Observed values of the variable of interest may be plotted on special extreme value distribution graph paper, or 'Gumbel paper'. The vertical axis is a linear scale for the values of the variable. The horizontal axis is the probability scale. The observed values are first ordered in ascending order of magnitude. The ranks are then determined from

$$r = m/(n+1) \qquad [9.10.14]$$

where m is the order number, n the number of readings, and r the rank. The rank r is then equivalent to $P(x)$.

As an illustrative example, consider the determination of the distribution parameters for the wind gust data given in Table 9.10, where the data are already ordered and the rank calculated. The data are shown plotted in Figure 9.18. From this graph, at the 0.10 and 0.99 probability points (equivalent to $P(x)$) the values x of the wind speeds are 51 and 95 knots, respectively. Then the parameters u and α are 57.9 and 0.124, respectively.

The return period T of a particular wind speed is obtained as the reciprocal of $F(x)\,(=1-P(x))$. Consider the return period of a wind speed of 95 knots. Since for this wind speed $P(x)=0.99$, the probability of exceedance $F(x)$ is 0.01 and the wind speed has a return period of 100 years. This value is extrapolated from 23 data points in which the maximum observed wind speed is 81 knots and is about the limit of extrapolation.

If Gumbel paper is not available, the horizontal scale may be constructed using the reduced variate $y = -\ln(-\ln P(x))$, as shown in Figure 9.18.

Table 9.10 *Annual maximum wind gust velocities at Cardington 1932–54 (after Perry, 1981) (Courtesy of George Allen & Unwin)*

Order no. (m)	*Highest gust* (knots)	*Year*	*Rank (r)*
1	48	1953	0.042
2	51	1950	0.083
3	52	1941	0.125
4	53	1951	0.167
5	54	1952	0.208
6	55	1937	0.250
7	55	1939	0.292
8	56	1942	0.333
9	57	1933	0.375
10	58	1949	0.417
11	59	1948	0.458
12	60	1945	0.500
13	62	1940	0.542
14	63	1934	0.583
15	63	1944	0.625
16	66	1954	0.667
17	68	1943	0.708
18	68	1946	0.750
19	71	1932	0.792
20	72	1936	0.833
21	75	1938	0.875
22	77	1935	0.917
23	81	1947	0.958

9.10.3 Man-made hazards

Man-made hazards also pose a threat to plant. Some of these are listed in Table 9.11. The estimation of the frequency of events of this type is usually based on the use of historical data together with detailed consideration of the application of the data to the plant in question.

For example, an estimate of the frequency of aircraft crash on a plant would be made by using general data on aircraft crash frequency in combination with information for the particular location about such factors as aircraft flight paths at any nearby airport, deviations from such paths, etc.

9.11 Human Factors and Human Error

Human error and, more generally, human factors is a wide and complex topic and the treatment here is limited to the bare essentials necessary for a balanced treatment of hazard assessment. A more detailed account is given in Chapter 14. The account given there includes details of available techniques. The discussion in this section tries to set these techniques in the context of hazard assessment.

9.11.1 Human error in hazard assessment

Analyses of failures in technological systems generally conclude that in the vast majority of cases human error has played a predominant role. Insofar as any failure can be attributed to some form of human failing, human error in its broadest sense becomes, by definition, the basic cause of failures. An exception to this can occur in the case where a risk has been assessed and, after evaluation, accepted, but where the hazard nevertheless materializes, as statistically it must in a proportion of instances.

It is well appreciated by hazard analysts that it is necessary to take human error into account in hazard assessment work. The problem has been how to achieve this. As with other aspects of hazard assessment, there are two main motivations for investigating human error. One is to reduce it by identifying defects in the human factors environment and effecting improvements. The other is to obtain the data required to be able to quantify the human aspects of the assessment.

The implications of these two motivations for the hazard assessment as a whole are different. The purpose of hazard assessment is to assist decision-making. There is a danger that the second approach will furnish data for quantification, but that it may be relatively ineffective in indicating improvements in the human factors area.

It is fair to say that interest in human error in the process industries has been driven by the perceived need to address human error in hazard assessment, and in particular to obtain the human error data required for quantification.

9.11.2 Human error in operation

Historically, in hazard assessment most attention has been focused on human error in process operation. In the operation of a plant, human error may contribute to an incident either as an initiating or enabling cause or as a failure to achieve some form of prevention or mitigation.

Much of the early work on human error was concerned with estimating error rates in relatively well-defined activities such as detecting a signal, pressing a button or opening a valve. Work then moved on to human error in executing a whole task using a relatively well-defined plan. Both activities and plans may be relevant to either causation or prevention of an incident.

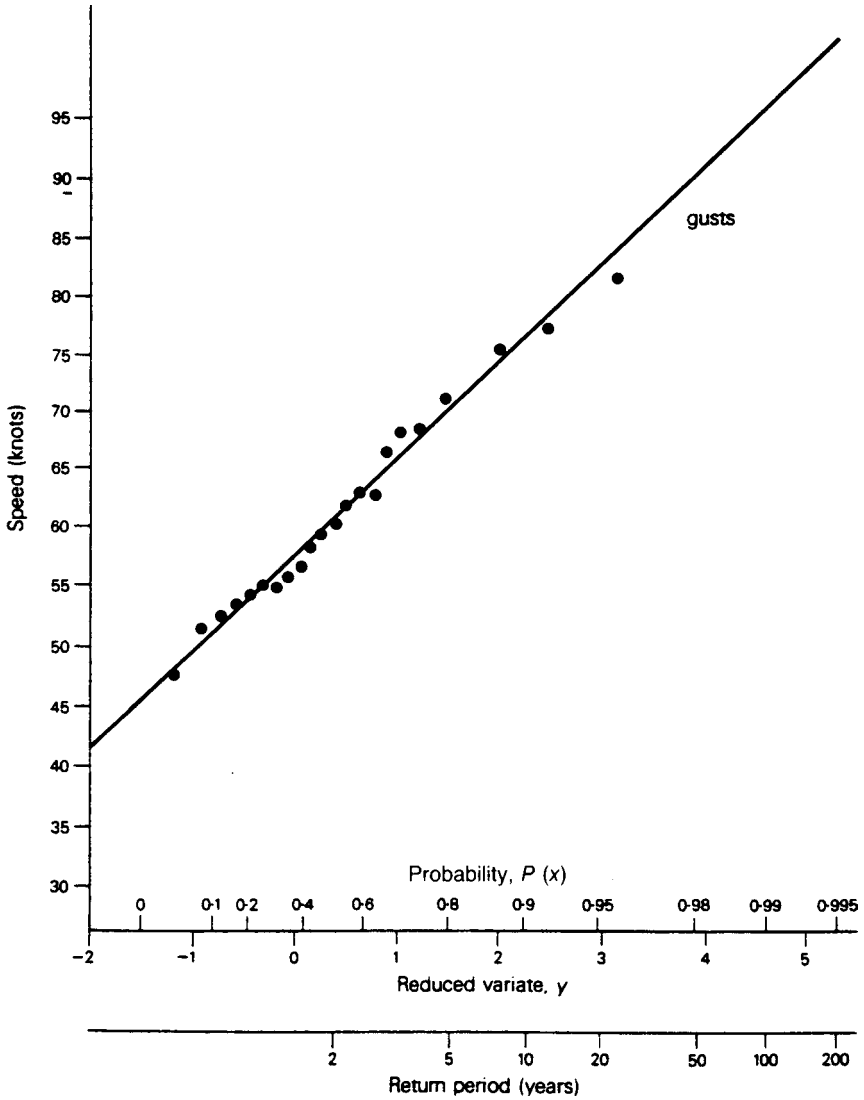


Figure 9.18 *Annual maximum gust velocities given in Table 9.10 plotted on extreme probability (Gumbel) paper (after Perry, 1981)*

Table 9.11 *Some man-made hazards that pose a threat to plant*

Dam bursts
Vehicle crashes
Aircraft crashes
Fires
Explosions

One method was to break a task down into its constituent elements, to collect data on the probability of error in the performance of these elements and to store these data in a human error data bank. This approach, however, tends to do less than justice to the operator's information processing and decision-making which are generally critical to the performance of the task. An alternative method, therefore, is to treat the task as a whole and to collect data on the probability of error in the performance of the task.

Both approaches make allowance for the influence of the work situation in which the task is performed by identifying performance shaping factors. The application of such factors requires the development for each factor of a measure of the strength of the factor and a relationship between the factor and the probability of error.

The most widely quoted method is the THERP technique developed by Swain and Guttman (1983). This technique makes widespread use of estimates of the probability of error in individual actions. A method that gives error estimates for whole tasks is the SLIM technique described by

Embrey (1983a,b). These and other methods are described in Chapter 14.

Human error often occurs in the development of a branch of a fault tree. The typical application of the methods just described is to obtain an estimate of the probability of failure, or error, for use at this point.

Another application of these methods is in the development of the branches of an event tree. Again the methods described have been used to estimate the probability of error at the branch points of an event tree. In particular, interest has centred on the prevention by the operator of escalation of the incident. The operator action event tree (OAET) is a particular form of event tree in which the branch points are defined in terms of failure of operator action.

As so far described, the assessment of operator error occurs within essentially predefined structures such as fault trees and event trees. In some cases, the situation is more complex. One such case is where the operator makes some fundamental error in assessing the situation and performs a series of actions, which may be quite complex, and which cause an incident. This is probably the most difficult case to handle and only limited progress has been made. One area where there has been some progress is in respect of communication errors, as described below.

Another case is where the operator is, in principle, able to prevent an incident but only by making a correct assessment of the situation and performing a series of actions, which may be quite complex and may involve initiative. This situation is sometimes dealt with by making a global estimate of the probability of no effective action. The probability is usually taken as a function that decreases quite strongly with time.

9.11.3 Human error in maintenance

Human error in maintenance has received rather less attention, although there is growing interest in it. Some maintenance errors result in an incident during plant operation. Insofar as the operations function has overall responsibility for safe operation, these may generally be regarded as operational failures. Other maintenance errors lead to an incident while the plant is shut-down. Maintenance errors are also an influencing factor on the failure rate of plant equipment.

9.11.4 Human error in communication

Analysis of incidents shows that an important contribution comes from errors of communication. It is fair to say that so far this work has contributed more to defining good practice in communications that to quantifying this aspect of human error.

9.12 Management Aspects

The prime determinant of the control over a hazard is the quality of management. The influence of management is all pervasive. In other words, it is a powerful cause of failure and has many of the features of a common cause. It is clearly desirable, therefore, to take the quality of management into account in any hazard assessment.

The first point to be made is that if the quality of management falls below a certain level, then there is generally little point in doing a hazard assessment at all. Hazard assessment should be able to start from the assumption that management meets at least some minimum standard of quality, particularly for major hazard installations. If this is not so, the effort would be better employed in remedying the defects than in estimating the probable results of those defects.

A second important point is that the use of management quality as an explicit input in a hazard assessment is a sensitive issue. This is so whether the assessment is being conducted by analysts within the organization concerned or by an outside body.

In general, the realization of a hazard involves the occurrence of an initial event followed by escalation of that event. Management influences both the frequency of the initial event and the effectiveness of measures taken to prevent its escalation.

9.12.1 Quantification of management influence

The attempt to make allowance for the effect of management quality involves both devising a measure of quality and a model for the impact of that quality on event frequency and escalation. Discussions of allowance for management quality in hazard assessment has been given by R.A. Cox and Comer (1982), Pitblado, Willliams and Slater (1990) and J.C. Williams and Hurst (1992).

Some limited progress has been made in this area. Aspects of the quality of management are considered in Chapter 6. Indices of quality may be devised for this specific purpose or, alternatively, use may be made of other indices such as the International Safety Rating System (ISRS).

The most straightforward application of such indices is to failure rates. Generic equipment failure rates may be regarded as being derived from organizations with 'average' quality management. These base failure rates may be adjusted according to the assessment made of management quality.

9.12.2 MANAGER model

The MANAGER model developed by DnV Technica and described by Pitblado, Williams and Slater (1990) exemplifies this approach.

A review was conducted of systems that might be adapted to provide modifiers for generic failure data to take into account management factors (MFs). Systems reviewed included the ISRS (Bird and Germain, 1985), the Management Oversight and Risk Tree (MORT) (W.G. Johnson, 1980) and the Technique for Human Error Rate Prediction (THERP) (Swain and Gutmann, 1983). The first two are described in Chapter 28 and the last in Chapter 14. It was concluded that ISRS would be relatively slow and costly to use and that it would not fit well with QRA, and that the strength of MORT is in accident investigation and that of THERP is in assessing the human error contribution in fault tree analysis. A requirement was defined for a modification of risk (MOR) method that would be simpler to use than human reliability assessment.

The properties that such a method should have were identified as the following. It should: (1) be based on a review of the role of safety management in actual accident causation, (2) address all areas shown to be important in accident causation, including human factors, (3) confirm that widely accepted management principles are suitably embedded in all key elements of the safety management system and (4) provide both a qualitative overview of safety management and an indication of quantitative modification to generic failure rates.

MANAGER is based on a questionnaire that utilizes the concept of performance shaping factors, which are

described in Chapter 14. The four most significant for this purpose were identified as (1) resources (manning, instrumentation), (2) system norms (incident reporting, safety policy, training), (3) communications (information flow, written documentation) and (4) pressures (stress, boredom). The questions are structured to conform with loss prevention principles as well as with these human factors influences. The questionnaire is structured into 12 broad topics, as shown in Table 9.12.

The responses to the questionnaire are scored as the proportion P which are rated as industry average (P_A), better than average (P_G) or worse than average (P_B) Use is made of a triangular diagram with these three proportions P_A, P_G and P_B at its corners. Values of a MF are located on the triangular diagram. A completely average plant ($P_A = 1$) has a value of MF = 1. This same value of the MF is also obtained by a plant with only good and bad responses ($P_A = 0$) at $P_G = 0.74$ and $P_B = 0.26$. A completely good plant has MF = 0.1 and for a completely bad plant MF = 100. In some 30 plant audits, values of MF ranged from 0.5 to 8.0.

The MF may then be used in QRA as a modifier for generic failure rates:

$$F_{est} = \text{MF} \times F_{gen} \qquad [9.12.1]$$

where F_{est} is the modified failure frequency and F_{gen} is the generic failure frequency.

A case study of the application of MANAGER has been described by J.C. Williams and Hurst (1992). A comparative investigation was made of two technically similar major hazard sites. The comparison was between the number of incidents reported under the RIDDOR regulations and the computed MF. The numbers of RIDDOR incidents per 1000 employees over the periods April 1986–March 1987, April 1987 –March 1988 and January –March 1991 were 8.7, 7.3 and 5.9 for company A and 12.5, 10.3 and 8.0 for company B. The computed MFs were 0.9 for company A and 1.7 for company B. Thus at site B the occupational incident rate was almost twice that at site A, and likewise the risk at site B as given by the MF was nearly twice that at site A. QRA showed that an individual risk of 10^{-5}/year occurred at site B at a distance of 400 m but at site A at 290 m. Further studies would be required to confirm the generality of the correlation.

As the study just described indicates, MANAGER may also be used for audit purposes.

Table 9.12 *Twelve topic areas of MANAGER questionnaire (after Pitblado, Williams and Slater, 1990)*

1.	Written procedures
2.	Incident and accident reporting
3.	Safety policy
4.	Formal safety studies
5.	Organization factors
6.	Maintenance
7.	Emergency resources and procedures
8.	Training
9.	Management of change
10.	Control room instrumentation and alarms
11.	Other human factors influences
12.	Fire protection systems

9.12.3 STATAS model

Another model that is relevant here is STATAS. This has been developed for the purposes of audit. However, just as MANAGER may also be applied to audit, so STATAS has a potential use in making allowance for MFs in QRA. It is described in Chapter 6.

9.13 Hazard Models

The estimation of the physical effects of a particular release scenario involves the use of a series of hazard, or consequence, models. Some of the models required are shown in Table 9.13. Most of the entries are straightforward,

Table 9.13 *Some principal hazard models*

Emission
Holes:
Gas flow
Liquid flow
Two-phase flow
Vessel rupture
Pipeline rupture
Vents
Relief valves
Vaporization
Flashing liquids
On land:
Spreading liquid
Volatile liquid
Cryogenic liquid
On sea:
Spreading of immiscible liquid
Mixing of miscible liquid
Volatile liquid
Cryogenic liquid
Air entrainment
(for each emission situation)
Source term
Gas cloud dispersion
Neutral density clouds
Heavy gas clouds
Buoyant gas clouds
Plumes
Neutral plumes
Heavy gas plumes
Buoyant plumes
Jets
Momentum jets
Fires
Pool fires
Fireballs
Flash fires
Jet flames
Engulfing fires
Explosions
Physical explosions of plant
Combustion explosions inside plant
Vapour cloud explosions
Explosions in buildings
Boiling liquid expanding vapour explosions

but the references to air entrainment and source term require some further explanation.

The models for emission allow an estimate to be made of the amount of material that is released or the rate at which it is released, but they do not in themselves necessarily give any information on the extent to which the emission entrains and mixes with the air. Dispersion models can be sensitive to the amount of air that mixes with the initial emission. It is necessary, therefore, to make some estimate of this.

The emission constitutes the source term for the dispersion models. A real emission does not usually correspond exactly to idealized source terms such as pure instantaneous or continuous sources, and a source term has to be selected which represents the situation as closely as possible but is suitable as input to the dispersion model.

Consequence models are described mainly in Chapters 15–17.

9.14 Domino Effects

Another aspect that needs to be taken into account in hazard assessment is the possibility of knock-on or 'domino' effects, leading to escalation. An event at one unit may be the cause of a further event at another unit, and so on.

The possibility of domino effects was one of the principal concerns that led to the hazard assessment of the complex of installations at Canvey, which was the subject of the two *Canvey Reports* described in Appendix 7.

The incident at Feyzin in 1968 (Case History A38) in which a fire on one storage sphere led to a series of fires and explosions involving other spheres illustrates the danger. Other subsequent incidents in which a domino effect has played an important role include Mexico City in 1985, Pasadena in 1988 and Piper Alpha in 1988. These incidents are described in Appendices 4, 6 and 19, respectively.

A method of handling potential domino effects in hazard assessment has been described by Bagster and Pitblado (1991). Table 9.14 shows a matrix of interactions between the process areas of two different operators obtained from the *Canvey Report* and quoted by these authors. A domino event may be treated either as an increase in the consequences of the event at the initiating unit, or as an increase in the frequency of events at the victim unit. The method described in this work adopts the latter approach.

Five events are included in the treatment: pool fire, explosion, boiling liquid expanding vapour explosion (BLEVE) giving rise to a fragment, jet fire and delayed explosion of a vapour cloud. The escalation is described in terms of a loss of containment at the victim unit. The following relation is used to describe loss of containment at unit j due to an event at the initiating unit i:

$$p_{\mathrm{loc};j;i} = \left[1 - \frac{r}{r_{\mathrm{lim};i}}\right]^2 \qquad [9.14.1]$$

where $p_{\mathrm{loc};j;i}$ is the probability of loss of containment at unit j due to an event at unit i, r is the distance of unit j from unit i, and $r_{\mathrm{lim};i}$ is the maximum distance at which the event at unit i can cause damage.

The basic relation for the frequency of loss of containment at the unit j due to an event at unit i is

$$F_{\mathrm{loc};j;i} = \mathrm{PI}_i \left(F_{\mathrm{cat};i} \sum_{m=1}^{3} p_{\mathrm{loc};j;m} P_{m;i} M_{m;i} + F_{\mathrm{leak};i} \sum_{m=4}^{5} p_{\mathrm{loc}rm;j;m} P_{m;i} M_{m;i} \right) \qquad [9.14.2]$$

with

$$M_{1;i} = M_{2;i} = 1 \qquad [9.14.3]$$

where $F_{\mathrm{cat};i}$ is the frequency of a catastrophic failure at unit i, $\mathrm{F}_{\mathrm{leak};i}$ is the frequency of a leak failure at unit i, $F_{\mathrm{loc};j;i}$ is the frequency of loss of containment at unit j due to an event at unit i, $M_{m;i}$ is the factor for mitigation of the event at unit $\imath$ due to its directionality, $p_{\mathrm{loc};j;i;\mathrm{m}}$ is the probability of loss of containment at unit j due to an event at unit i of type m, $P_{m;i}$ is the probability that the event at unit $\imath$ is an event of type m and PI_i is the probability of ignition following failure at unit i. The five events are pool fire (PF; $m = 1$), explosion (EX; $m = 2$), BLEVE fragment (BF; $m = 3$), jet fire (JF; $m = 4$) and delayed explosion (DEX; $m = 5$). The same probability of ignition is used for both types of failure and for all types of event.

In addition to this escalation of the primary event at unit i into a secondary event at unit j, the method also takes into account escalation of the latter into a tertiary event at unit k. In order to do this, it is necessary to make some assumption about the probability distribution of the failures induced at unit j. The assumption made is that the distribution between catastrophic failures and leak failures at unit j is the same as that at unit i. The relation for the probability of loss of containment at unit k due to an event at unit j, itself due to an event at unit i, is then

$$P_{\mathrm{loc};k;j;i} = \mathrm{PI}_{j\mathrm{loc};j;i} \left[\phi_j \sum_{m=1}^{3} p_{\mathrm{loc};k;j;m} P_{m;j} M_{m;j} + (1 - \phi_j) \sum_{m=4}^{5} p_{\mathrm{loc};k;j;m} P_{m;j} M_{m;j} \right] \qquad [9.14.4]$$

with

$$\phi_j = \frac{F_{\mathrm{cat}.j}}{F_{\mathrm{cat}.j} + F_{\mathrm{leak}.j}} \qquad [9.14.5]$$

$$M_{1;j} = M_{2;j} = 1 \qquad [9.14.6]$$

where $M_{m;j}$ is the factor for mitigation of the event at unit j due to its directionality, $P_{\mathrm{loc};k;j;i}$ is the probability of loss of

Table 9.14 *Matrix of potential interactions of process area explosions for two installations at Canvey: frequency of massive release of LPG per 10^6 years (Bagster and Pitblado, 1991) (Courtesy of the Institution of Chemical Engineers)*

Explosion at	*Fire spreading to LPG storage at*	
	Occidental	*URL*
Occidental process area	0.12	0.075
URL process area	0.09	0.065

LPG, liquefied petroleum gas; URL, United Refineries Ltd.

containment at unit k due to an event at unit j, itself due to an event at unit i, $p_{\mathrm{loc};k;j;m}$ is the probability of loss of containment at unit k due to an event at unit j of type m, P_m;j is the probability that the event at unit j is of type m, PI_j is the probability of ignition following failure at unit j, and ϕ_j, is the probability that the failure at unit j is catastrophic.

It is also necessary to take into account the fact that the damage zone of the event at unit j may be partially or totally within the damage zone of the event at unit i, or vice versa. This is taken into account by utilizing for each type of event a correction factor S_m. This correction factor is applied to the frequency of loss of containment at unit j for an event at unit i of type m. In effect, this is a correction to allow for overlap of the damage zones and thus to avoid double counting of the damage.

The three situations that are possible if overlap occurs are shown in Figure 9.19. An overlap factor q_m is defined which has the values

$q_m = 1$	damage zone of event i lies entirely within that of event j
$q_m = 1/2$	damage zones of event i and j partially overlap
$q_m = 0$	damage zone of event j lies entirely within that of event i

The overlap correction factor S_m is then

$$S_m = \frac{\sum_{m=1}^{5} P_m M_m q_m}{\sum_{m=1}^{5} P_m M_m} \qquad [9.14.7]$$

where M_m is the probability of mitigation of an event at unit j of type m, P_m is the probability that the event at unit j is an event of type m and q_m is the overlap factor for an event at unit j of type m.

The authors give the following illustrative example. They investigate the domino effects for two alternative layouts of a plant consisting of four items – an atmospheric storage tank, two storage spheres and a compressor. In one configuration the items are laid out in a square and in the other they are in a line. Details of the units are given in Table 9.15, Section A. The frequencies of loss of containment for three levels of escalation in the square layout case are shown in Table 9.15, Section B, and the corresponding first-order domino matrix in Section C. The results given in the domino matrix show, for example, that for unit 1 the base failure frequency of 6×10^{-6}/year is augmented by 0.893×10^{-6}/year due to domino effects.

9.15 Hazard Model Systems

There are a number of hazard model collections and complete hazard assessment systems. These include:

(1) the vulnerability model;
(2) the '*Yellow Book*';
(3) plant layout model;
(4) SAFETI system;
(5) WHAZAN system.

These are now described in turn.

9.15.1 Vulnerability model system

One major hazard assessment system is the vulnerability model (VM), later renamed the population vulnerability model (PVM), developed under contract for the US Coast Guard to investigate the possible effects of hazardous material spills. The basic VM is described by Eisenberg, Lynch and Breeding (1975) in a report entitled *Vulnerability Model: A Simulation System for Assessing Damage Resulting from Marine Spills*. Specific models developed in support of the VM are given by Raj and Kalelkar (1974). The second stage of the development of the VM is described by Rausch, Eisenberg and Lynch (1977) and the third stage by Rausch, Tsao and Rowley (1977). Modifications to the VM are described by Tsao and Perry (1979) and by Perry and Articola (1980) and a users' guide is given by Rowley and Rausch (1977). The VM and its applications have been reviewed by Parnarouskis, Perry and Articola (1980).

The VM is a consequence assessment system. It consists of a set of hazard models and injury/damage relations which are used in conjunction with meteorological and population data for a given site to assess the effects of specified releases of hazardous materials. The overall structure of the VM is shown in Figure 9.20. Within this structure, there are a number of decision trees for the selection of the scenarios and the corresponding hazard models. The decision tree for the behaviour of the cargo on release is shown in Figure 9.21. The information required by and obtained from the model is shown in Table 9.16. Figure 9.22 illustrates the simulation of a vapour cloud from a marine spill.

Some of the principal elements in the VM are shown in Table 9.17. As the table indicates, the VM is a prime source both of hazard models and of injury relations for both flammable and toxic releases. Many of these are considered in later chapters.

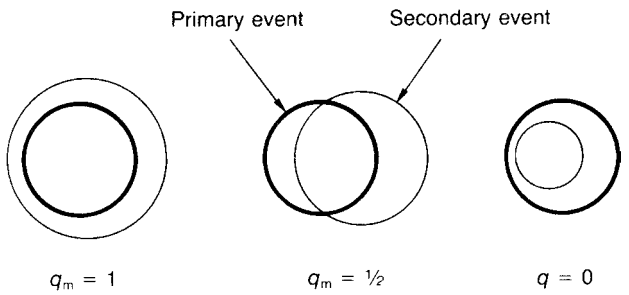


Figure 9.19 *Relationship between primary and secondary events in a domino incident (Bagster and Pitblado, 1991) (Courtesy of the Institution of Chemical Engineers)*

Table 9.15 *Illustrative example of potential interactions for four plant items on a single site (after Bagster and Pitblado, 1991) (Courtesy of the Institution of Chemical Engineers)*

A Data

Plant item number	1	2	3	4
Plant type	Atmospheric storage tank	Sphere	Sphere	Compressor
Toxic?	No	No	No	No
FC_{kt} (per million years)	1.0	1.0	1.0	50
F_{leak} (per million years)	5.0	1.0	1.0	100
Probability ignition, PI	0.1	0.2	0.2	0.1
Probability of pool fire, P_{pf}	0.3	0.25	0.25	0.1
Probability of explosion, P_{EX}	0.2	0.25	0.25	0.1
Probability of BLEVE, fragments, p_{bf}	0	0.1	0.1	0
Probability of jet fire, P_{JP}	0.05	0.2	0.2	0.1
Probability of delayed explosion, P_{DEX}	0.1	0.1	0.1	0.05
Mitigation factor for BLEVE fragments, M_{MBF}	0	0.005	0.005	0.05
Mitigation factor for jet, M_{JF}	0.01	0.01	0.01	0.05
Mitigation factor for drift of explosion, M_{DEX}	0.005	0.005	0.005	0.05
Pool fire range, r_{pl} (m)	25	20	15	25
Explosion range, r_{EX} (m)	30	40	25	30
Fragment range, r_{BF} (m)	0	1.0	1.0	0
Jet fire range, r_{JF} (m)	10	20	25	20
Delayed explosion range, r_{DEX} (m)	50	50	35	50

B Loss of containment frequencies: square configuration

Primary events	Primary loss of containment frequency
Item	
1	6
2	2
3	2
4	150
First-order knock-ons	Additional loss of containment frequency
Item	
1	0.89
2	0.48
3	0.36
4	0.11
Second-order knock-ons	Additional loss of containment frequency
Item	
1	2.8E-02[a]
2	7.8E-03
3	8.1E-03
4	2.2E-02
Third-order knock-ons	Additional loss of containment frequency
Item	
1	6.3E-04
2	2.6E-04
3	1.9E-04
4	4.7E-04

(Coordinates (m): 1(0, 0), 2(10, 0), 3(0, 10), 4(10, 10))
[a] E-n $= 10^{-n}$

C First-order domino matrix square configuration

Causing unit	*Victim unit*			
	1	2	3	4
1	6	0.021	0.015	0.026
2	0.061	2	0.019	0.038
3	0.070	0.024	2	0.051
4	0.762	0.432	0.326	150
First-order domino frequency (column sum minus major diagonal entry)	0.893[a]	0.477	0.360	0.115

Coordinates of units (m): 1(0, 0), 2(10, 0), 3(0, 10), 4(10, 10)
[a] 0.061 + 0.070 + 0.762.

The injury relations in the VM, given in the form of probit equations, have proved of particular interest, owing to the paucity of information on this aspect. The VM studies did pioneering work in defining the form of the causative factor and in deriving constants for the probit equations. Inevitably, some of these require modification in the light of more recent work. Table 9.18 lists some of the original probit equations in the model. In the later work, revisions and additions were made to the probits for toxic gases, as described in Chapter 18.

The principal application of the VM is consequence assessment for planning purposes. It is used to estimate for a particular site the effects of hazardous releases, to determine whether particular releases would cause casualties, and to give a hazard ranking. The VM is also used to compare the hazards of specified releases at different sites. For example, comparisons have been made of the relative hazards of LNG terminals at Point Conception and Oxnard in California.

9.15.2 '*Yellow Book*' models

A major collection of hazard models is given in *Methods for the Calculation of the Physical Effects Resulting from Release of Hazardous Material* by the Committee for the Prevention of Disasters (CPD, 1992a) in the Netherlands. The report is published by the Dutch Labour Inspectorate and the work was done by Toegepast-Natuurwetenschappelijk Onderzoek (TNO). It is usually referred to as the '*yellow Book*'. The principal contents of the *Yellow Book* are shown in Table 9.19.

9.15.3 Plant layout models

A set of hazard models for use in plant layout has been given in *Process Plant Layout* (Mecklenburgh, 1985). These models are listed in Table 9.20.

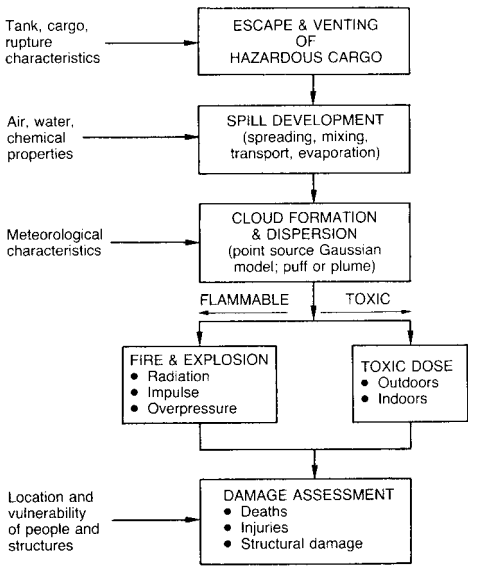


Figure 9.20 *Vulnerability model: structure of the model (Parnarouskis, Perry and Articola, 1980)*

9.15.4 SAFETI computer code

Another major collection of hazard models is that in the SAFETI computer code for risk assessment developed by Technica. The hazard models used, as described by Pitblado and Nalpanis (1989), are as follows. For gas dispersion, four regimes are recognized. These are (1) turbulent jet dispersion, (2) hydrid dispersion with both turbulent jet and dense gas behaviour, (3) dense gas cloud, and (4) passive dispersion. The dense gas dispersion model used is that of R.A. Cox and Carpenter (1980).

The other models cover: (1) vaporization from a pool using the model of O.G. Sutton (1953) or, for liquids with boiling points below ambient, that of Drake and Reid (1975); (2) vapour cloud explosion using the TNO correlation model by Opschoor (1979); (3) fireball, or BLEVE, based on the model of Moorhouse and Pritchard (1982); (4) pool fire, using an in-house model; and (5) jet flame, using the TNO free jet model to obtain the jet length combined with the American Petroleum Institute (API) model for thermal radiation. There is no flash fire model as such; it is assumed that the fire is co-terminus with the cloud and in determining injury a small additional increment is added to this contour to allow for the thermal radiation close to the cloud. Probit equations are used for injury and damage effects.

9.15.5 WHAZAN computer code

A set of hazard models is the core of another computer code WHAZAN developed by Technica for the World Bank. The package is described in *Manual of Industrial Hazard Assessment Techniques* (World Bank, 1985). This system allows the user to explore interactively the consequences of a set of release scenarios. The frequency of occurrence of the scenarios is not estimated and the hazard models are relatively simple. The package is not intended for probabilistic risk assessment.

The models used are given in Table 9.21 and a typical event tree which the user can explore using WHAZAN is illustrated in Figure 9.23. These relate to the initial version of the program. WHAZAN is therefore a much simpler package than SAFETI. It is described further in Chapter 29.

9.16 Population Characteristics

Information on the characteristics of the exposed population is frequently required in a hazard assessment. The people exposed consist of two groups, those working on the site and those living and/or working in the area around the site.

It is usually a straightforward matter to obtain the necessary information on the on-site workforce, but this is not so for the off-site population. Here the data required include

(1) population density;
(2) population composition;
(3) population changes by time of day;
(4) vulnerable population;
(5) population outdoors.

For estimation of societal risk information is required on all these items, but even for estimation of individual risk only it is still necessary to have data on the vulnerable population and the population outdoors.

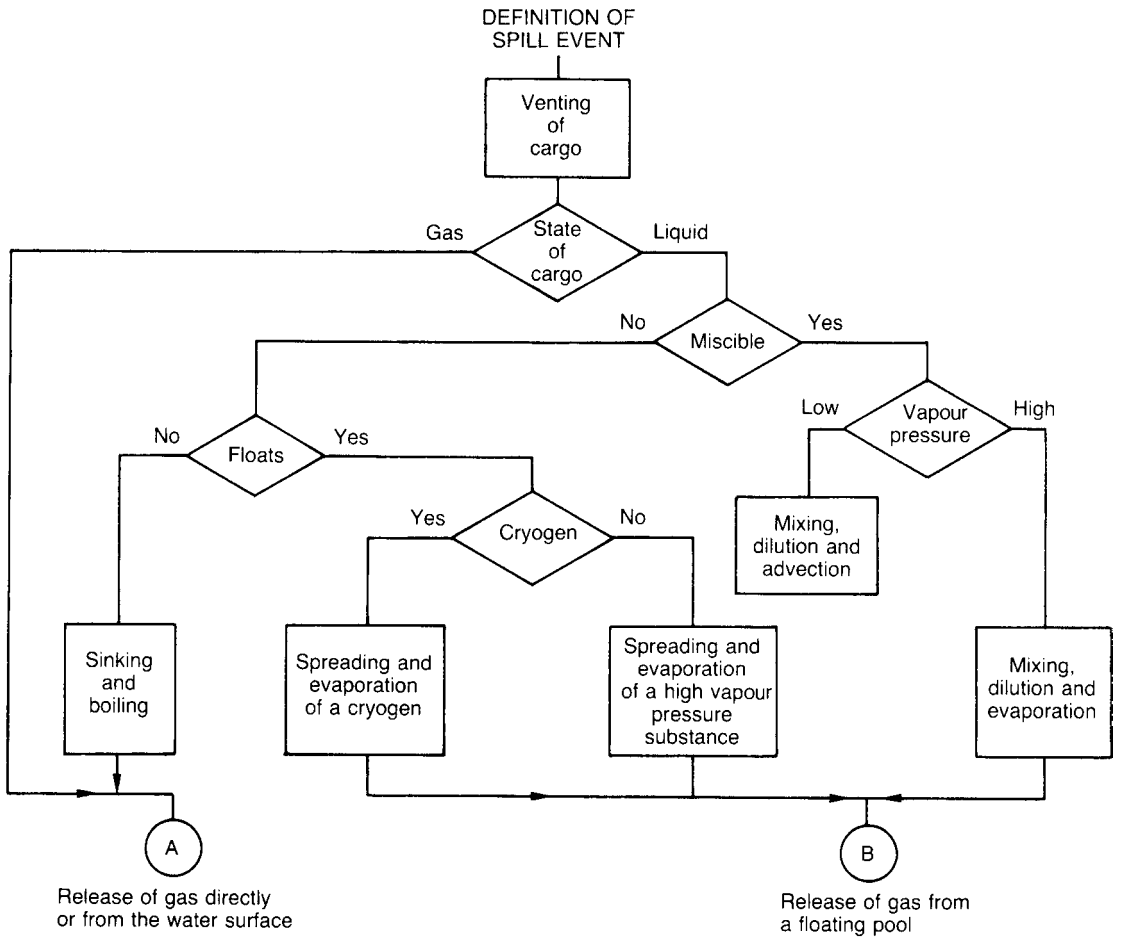


Figure 9.21 *Vulnerability model: decision tree for behaviour of cargo on release (Eisenberg, Lynch and Breeding, 1975)*

The accuracy of estimation of the density and other characteristics of the population should broadly match that of the other stages of the hazard assessment. A very refined estimate of the population characteristics will often not be justified. On the other hand, it should be borne in mind that some of the factors that characterize the population are not independent. Thus the number of people at home during the day is less than at night, but the proportion of vulnerable people is greater.

A method for the determination of the population characteristics for Britain has been given by Petts, Withers and Lees (1987). The method is intended primarily for use in estimating the societal risk of fatalities for sets of scenarios where typically in a large proportion of cases the fatal effects may not extend sufficiently far for more approximate methods of estimating population density to give sufficient accuracy.

9.16.1 Population density

Estimates of off-site population density have been made in the two *Canvey Reports* and in the *Rijnmond Report*. The *Canvey Reports* are mainly concerned with the off-site population, but the *Rijnmond Report* gives estimates of the on-site population density. For the on-site population, data on the number of workers at each site were obtained and the numbers present during the working day N_d and at other times N_n were determined. Then assuming three-shift, 7-day working, the number of manshifts worked per week is $5\,N_d + 16\,N_n$, and assuming that each employee has n_h weeks off for holidays and sickness, etc., and therefore works $(52 - n_h)$ weeks per year, the average number N_s of employees on site is

$$N_s = ((5N_d + 16N_n) \times 52)/(5 \times (52 - n_h)) \qquad [9.16.1]$$

The average number on site in the daytime for the six sites in this study was found to be 200 persons/km^2. The site area used in this computation appears from the map of the area to be filled with process plant and storage and does not contain much open space.

For the off-site population in the First *Canvey Report* the general approach is to define the built-up areas on the map and to use for these areas a uniform population density of

Table 9.16 *Vulnerability model: outline of information required by and obtained from the model (after Perry and Articola, 1980)*

A Information required
Characteristics of the cargo (e.g. chemical composition, size of tank, temperature of cargo)
Size and location of the rupture
Characteristics of the spill environment (e.g. marine characteristics and weather conditions)
Geographical location of the spill
Location and characteristics of the vulnerable resource (people and property) in the vicinity of the spill
B Information obtained
Size and characteristics of the spill
Disposition of the hazardous materials (e.g. mixing, sinking, dilution, vaporization, diffusion, dispersion)
Concentrations and hazardous effects of spilled material as a function of position and time (e.g. toxic concentration and dose, thermal intensity and dose, overpressure)
Number of people killed and injured and amount and value of property damage

4000 person/km^2. The population profile was obtained in some cases up to 32 km from the hazard source. In some of the studies in the report, however, there are variations. In Appendix 3, use is made of population densities of 5000 and 100 persons/km^2 for urban and rural areas, respectively. In Appendix 14, use is made of census data on the number of people in 100 m squares. In the Second *Canvey Report* it is this latter method that is used.

The *Rijnmond Report* also makes use of census data on the number of people in grid squares, in this case 500 m squares. This grid covered an area of some 75 km^2. Uniform population densities were assumed outside the grid.

The method for the estimation of the population density for British conditions given by Petts, Withers and Lees is as follows. Use is made of national census population data. In Britain, there is a full census every decade, the then most recent being in 1971 and 1981. The 1981 Census (OPCS, 1981a) is available as is the official user guide (OPCS, 1981b) and a further guide (Rhind, 1983). Other useful documents are the 1981 Labour Force Survey (OPCS, 1981c) and the Annual Abstract of Statistics (CSO, 1985). The basic small geographical unit for the census is the enumeration district (ED), which is an area of land defined in terms of the number of households representing a suitable census workload. The average population of an ED in England and Wales is about 500 in urban areas and 150 in rural areas. The local geography of the census in Scotland is slightly different in that EDs are built up from the Post Office postcode areas. The main small unit statistical output from the census is the small area statistics (SAS), which are supplied by the Census Office on magnetic tape, on microfilm or as paper copy. There are delays of several years in the publication of some census data. Naturally, the data become out of date, and this needs to be borne in mind.

The estimation of the population density off site requires the use of Ordnance Survey maps. Four principal map sizes relevant here are the 1 : 25,000, 1 : 10,000, 1 : 2500 and 1 : 1250 scale series. The 1 : 10,000 scale is that normally used by local authorities. It is also the size on which the census EDs are recorded and maps showing the boundaries of the EDs are available from the Census Office as paper copies of microfilmed 1 : 10,000 scale maps. The 1 : 2500 and 1 : 1250 scale maps can be useful in locating more accurately the boundaries between EDs; unfortunately the whole country is not covered by these series. These maps give the most detailed record of buildings. In the 1 : 10,000 and 1 : 25,000 series there is some loss of detail and accuracy with respect to buildings.

The method that gives the most accurate results for population density is the use of the census data. This should therefore be used where it is practical to do so. There may, however, be reasons for not using census data for the whole area of interest. One is that it can be time-consuming. Another is that the census may have become out of date.

In these circumstances, a rapid estimate of population may be made using a map to identify the built-up areas and assuming population densities of 4000 persons/km^2 for large built-up areas, 100 persons/km^2 for other inhabited areas, and zero population for uninhabited areas.

For more accurate work, a more detailed approach is necessary. It is recommended by Petts, Withers and Lees that three zones be defined around the hazard source, delimited by distances of 400 and 1000 m. For the outer zone ($>$1000 m) the rapid estimation method should be used. For the intermediate zone (400–1000 m) the map should be used to identify three types of residential area and the uninhabited area. These three types of residential development are: dense, usually in-town, terraced housing (and high-rise flats); semi-detached housing, usually suburban; and sparse, detached housing. Population densities of 15,000, 10,000 and 1000 persons/km^2, respectively, should be used.

For the inner zone ($<$400 m) the population should be estimated from census ED data. It is recommended, however, that for this inner zone this estimate should be checked against visual inspection and local inquiry. The radius of the inner zone was originally set at 250 m, but site inspection indicated that this may be too short a distance for acceptable accuracy. The distance of 400 m is therefore preferred as the boundary of the inner zone. This method for the estimation of the density of the population around a hazard source is summarized in Table 9.22.

It is necessary to define the point from which the circles defining these zones are drawn. There appears at present to be some difference of practice. In some cases this point is taken to be the plant itself, in others the site boundary. The former makes more sense for a plant at a specific point, but the latter allows for relocation of the plant within the site boundary.

The accuracy of the method described for the estimation of the population density in the middle zone was checked against the 1981 Census data for three hazardous sites. The average difference in the estimates of the numbers of people was 14%, one estimate being low and two high.

The use of the census data is not entirely straightforward. The approach used by the authors was first to identify the codes of the required EDs from 1 : 10,000 scale maps provided by the Census Office and then to obtain the ED data by interrogating the Census computer data bank.

There are in existence several computer programs that process population data. These use data on the numbers of people in each 100 m square. This information was provided in the 1971 Census, but is not available in the 1981 Census.

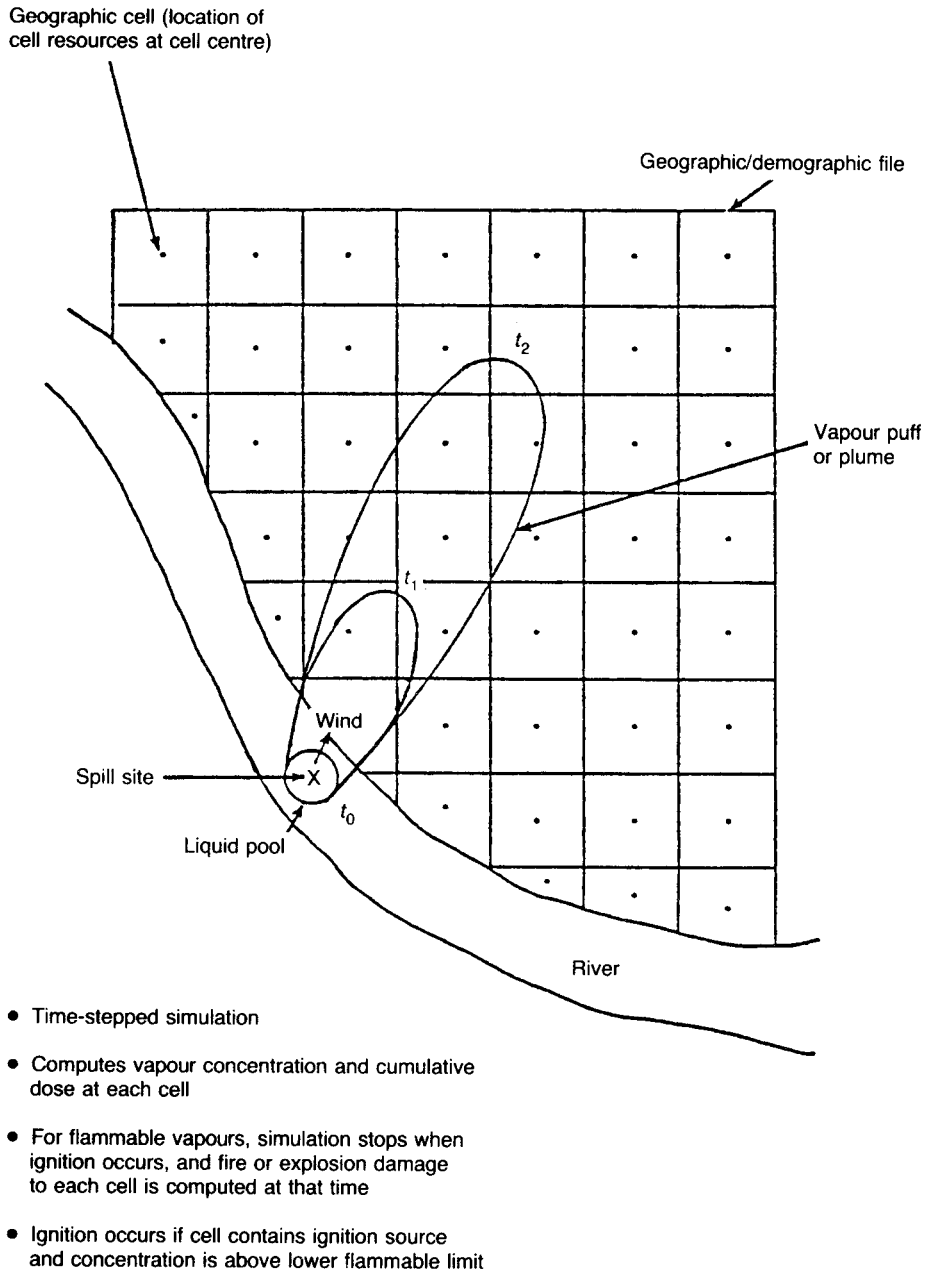


Figure 9.22 *Vulnerability model; simulation of vapour release from a marine spill (Parnarouskis, Perry and Articola, 1980)*

The basic case for the off-site population is the nighttime population. It is this that is given by the census data and by the method just described. An approximate estimate of the number of people over the whole 24 h is 80–85% of this value. However, the probability of some hazards may be a function of time of day and it then becomes necessary to estimate population by time of day also. The daytime population may be estimated more accurately, as described below.

Attention is drawn by Petts, Lees and Withers to the fact that errors in drawing the boundaries between areas of different population densities can easily lead to errors which are as great or greater than those which are due to errors in estimating those densities.

Table 9.17 *Vulnerability model (VM): some principal elements of the model*

A Reports on VM

Eisenberg, Lynch and Breeding (1975)	ELB
Raj and Kalelkar (1974)	RK
Rausch, Eisenberg and Lynch (1977)	REL
Rausch, Tsao and Rowley (1977)	RTR
Tsao and Perry (1979)	TP
Perry and Articola (1980)	PA
Rowley and Rausch (1977)	RR

B Elements of VM

	Reference/ page number
Overview	ELB
Computer programs	ELB; REL, 211; TP, 30
Emission and vaporization	
Overview	ELB, xi, xii
Spreading of liquid on land	
Spreading of liquid on water or other liquids	ELB, 20; RK, 19, 85, 113, 139, 228, 232, 234, 235
Mixing and dilution of soluble liquid in water	ELB, 21; RK, 29, 115, 228, 236
Boiling and sinking of heavy liquid in water	ELB, 22; RK, 171, 237
Gas/vapour dispersion	
Overview	ELB, xi, 23
Instantaneous release (puff)	ELB, 33; RTR, 16
Continuous release (plume)	ELB, 33; RTR, 15
Model selection	ELB, 195
Dispersion coefficients	ELB, 42
High concentration sources	ELB, 185
Area sources	RK, 55
Plume width	RK, 57
Meandering plume	ELB, 42
Fire	
Overview	ELB, xi, xiv, xviii, 92
Ignition, ignition sources	ELB, xiii, 49, 207; REL, 35
Flammable cloud size	ELB, 211
Flash fire	ELB, 59; REL, 31; RTR, 13; TP, 17
Pool fire	ELB, xiv, 66
Flame dimensions	ELB, xiv; RK, 63, 65, 230, 231; RTR, 12
Thermal radiation	ELB, xiv
View factor	ELB, xiv
Burning time	ELB, xiv
Fireball	RTR, 5
Jet flame	RK, 64, 231
Thermal radiation View factor	
Structure ignition	REL, 49
Secondary fires	REL, 5
Toxic combustion products	REL, 91, 114
Explosion	
Overview	ELB, xi
Explosion energy	ELB, 221
Explosion	ELB, xiii, xviii, 49, 90, 229; RTR, 18
Toxic release	
Overview	ELB, xi, xii, xviii, 49
Infiltration	REL, 137
Dosage: outdoor dosage	TP, 5
indoor dosage	TP, 6
Injury and damage relations	
Injury outdoors	
Fire	ELB, xi; TP, 12
Explosion	ELB, xi
Toxic gas	TP, 6
Injury indoors	REL, 137
Fire	REL, 202
Explosion	REL, 163
Toxic gas	REL, 137
Damage	ELB, 252
Structure ignition	ELB, 251
Fire	ELB, xi
Explosion	ELB, xi, 247; RTR, 23
Confined explosion	ELB, 226
Gas toxicity	
Overview	ELB, xvii, 83; REL, 73
Acrolein	REL, 76, 88; PA, C-2, C-3
Acrylonitrile	PA, C-2, C-3
Ammonia	ELB, 257; PA, C-2, C-4
Carbon monoxide	REL, 114
Carbon tetrachloride	REL, 81, 88; PA, C-2, C-5
Chlorine	ELB, xviii, 83, 257; PA, C-2, C-5
Hydrogen chloride	REL, 83, 88; PA, C-2, C-6
Hydrogen cyanide	PA, C-2, C-6
Hydrogen fluoride	RTR, 33; PA, C-2, C-7
Hydrogen sulfide	PA, C-2, C-7
Methane, propane	REL, 78
Methyl bromide	REL, 84, 89; PA, C-2, C-9
Phosgene	REL, 86, 89; PA, C-2, C-9
Propylene oxide	PA, C-2, C-9
Sulfur dioxide	PA, C-2, C-10
Toluene	PA, C-2, C-11
Hazard assessment	
Overview	
Double counting	ELB, 325
Case histories	ELB, 137, 269

Table 9.18 *Vulnerability model(VM) some probit equations in the original model (Eisenberg, Lynch and Breeding, 1975)*

Phenomenon and type of injury or damage	*Causative variable*	*Probit equation parameters*		*Per cent affected*	*Data from which the probit equation was derived*				
		k_1	k_2		*Value of variable*	*Per cent affected*	*Value of variable*	*Per cent affected*	*Value of variable*
Fire:									
Burn deaths from flash fire	$t_e I_e^{4/3}/10^4$	−14.9	2.56	1	1099	50	2417	99	7008
				1	1073	50	2264	99	6546
				1	1000	50	2210	99	6149
Burn deaths from pool burning	$tI^{4/3}/10^4$	−14.9	2.56	1	1099	50	2417	99	7008
				1	1073	50	2264	99	6546
				1	1000	50	2210	99	6149
Explosion:									
Deaths from lung haemorrhage	p°	−77.1	6.91	1	1.00×10^5	50	1.41×10^5	99	2.00×10^5
				10	1.20×10^5	90	1.76×10^5		
Eardrum ruptures	p°	−15.6	1.93	1	16.5×10^3	50	43.5×10^3		
				10	19.3×10^3	90	84.3×10^3		
Deaths from impact	J	−46.1	4.82	0	18.0×10^3	31	37.3×10^3	96	49.7×10^3
				8	28.6×10^3	63	45.2×10^3	100	60.7×10^3
Injuries from impact	J	−39.1	4.45	1	13×10^3	90	28×10^3		
				50	20×10^3				
Injuries from flying fragments	J	−27.1	4.26	1	1024	50	1877	99	3071
Structural damage	p°	−23.8	2.92	1	6.2×10^3	99	34.5×10^3		
				50	20.7×10^3				
Glass breakage	p°	−18.1	2.79	1	1700	90	6200		
Toxic release:									
Chlorine deaths	$\Sigma C^{2.75} T$	−17.1	1.69	3	14.1×10^4	50	34.05×10^4	97	105.8×10^4
				3	17.0×10^4	50	47.0×10^4	97	129.4×10^4
				3	21.5×10^4	50	64.7×10^4		
Chlorine injuries	C	−2.40	2.90	1	6	50	13		
				25	10	90	20		
Ammonia deaths	$\Sigma C^{2.75} T$	−30.57	1.385	3	37.3	50	74.6	99	411.8
				3	90.9	50	204.6	99	334.4
				3	44.6	50	148.6		

t_e = effective time duration (s)
I_e = effective radiation intensity (W/m^2)
t = time duration of pool burning (s)
I = radiation intensity from pool burning (W/m^2)
p° = peak overpressure (N/m^2)
J = impulse (Ns/m^2)
C = concentration (ppm)
T = time interval (min)

Table 9.19 *CPD models: principal contents of* Yellow Book *and* Green Book *(Committee for the Prevention of Disasters, 1992a,b)*

A Physical effects (*Yellow Book*)
Outflow
Turbulent free jet
Spray release
Evaporation
Heat radiation
Dispersion
Vapour cloud explosion
Consequences of rupture of vessels
B Damage effects (*Green Book*)
Damage caused by heat radiation
Consequences of explosion effects on structures
Consequences of explosion effects on humans
Survey study of the products which can be released during a fire
Damage caused by acute intoxication
Protection against toxic substances by remaining indoors
Population data

Table 9.20 *Plant layout models: principal models (after Mecklenburgh, 1985)*

1. Introduction
2. Instantaneous release of gas or vapour
   - 2.1 Size of cloud
   - 2.2 Dispersion of cloud to lower flammability limit
   - 2.3 Explosion overpressure
   - 2.4 Fireball size
   - 2.5 Dispersion of toxic cloud
3. Steady leak of gas or vapour
   - 3.1 Leakage rates
   - 3.2 Dispersion of jet to lower flammability limit
   - 3.3 Size of jet flame
   - 3.4 Dispersion of toxic plume
4. Loss of liquid
   - 4.1 Leakage rate, pool size and evaporation rate
   - 4.2 Pool and tank fires
5. Fire damage and protection
6. Implications for plant layout
   - 6.1 Risk criteria
   - 6.2 On-site and off-site effects
7. Blast effects
   - 7.1 Human and building tolerances
   - 7.2 Plant components
   - 7.3 Control rooms
8. Hazardous area classification
   - 8.1 Small continuous release of gas or vapour in the open
   - 8.2 Small release of liquid in the open
   - 8.3 Small continuous release of gas or vapour in a building
   - 8.4 Small release of liquid in a building

Table 9.21 *WHAZAN: principal models (Technica, 1985)*

Emission	
Liquid	
Gas	
Two-phase	Fauske–Cude model
Behaviour on release	
Spreading liquid	
Jet	
Flashing liquid	
Dispersion	
Heavy gas	Cox and Carpenter model
Neutral density gas	Pasquill–Gifford model
Buoyant plume	Briggs model
Fire	
Pool fire	
Jet fire	Modified API model
Fireball	API model
Flash fire	Gas dispersion model
Fire damage	
Explosion	
Explosion damage	DSM model
Toxic release	Gas dispersion model + probit equations

9.16.2 Population composition

In order to obtain a more detailed picture of the population it is necessary to define the population composition. This is relevant to the probability that an individual is at his home base, that he is a member of a more vulnerable population and/or that he is outdoors.

Information on population categories is available in the 1981 Labour Force Survey (OPCS, 1981c) as shown in Table 9.23. From these data Petts, Withers and Lees have derived the population composition model given in Table 9.24.

In order to use this population composition model it is necessary to define the times of day. The set of times of day used by the authors is shown in Table 9.25, Section A. These are to be used with the population categories at home by time of day given in Table 9.25, Section B.

9.16.3 Population change by time of day

Using the definitions of population composition and of times of day just given, estimates may be made of the population changes by time of day. The estimates based on the data given in Table 9.25, Sections A and B, are given in Section C of the table. It was found that for random sections of the Canvey and Rijnmond populations, the proportions of the nighttime population who were at home during the day were 42% and 46%, respectively.

9.16.4 Vulnerable population

Some members of the population are likely to be more vulnerable to the hazard than others and it may be necessary to take this into account. In general, it is children, old people and infirm people who tend to be most vulnerable, and the proportion of vulnerable people may be estimated as a first approximation by determining the proportion in these categories. However, vulnerability must be a function of the particular hazard. For example, children

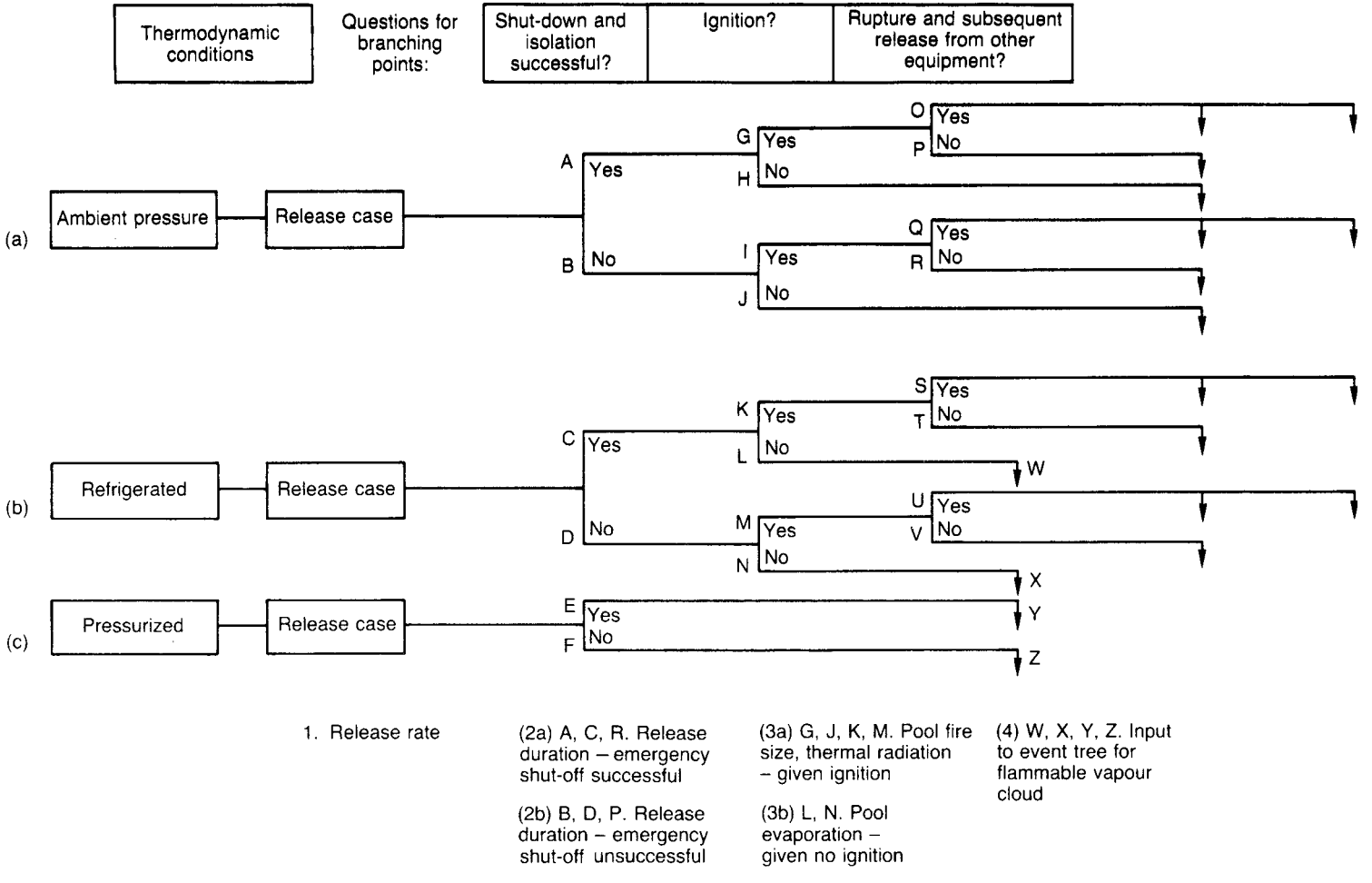


Figure 9.23 *WHAZAN: event trees for the models (after Technica, 1985): (a) tree for flammable gas release; (b) tree for flammable or toxic liquid release; (c) tree for toxic gas release*

Table 9.22 *Methodology for estimation of density of population around a hazard source (after Petts, Lees and Withers, 1987) (Courtesy of Elsevier Science Publishers)*

Distance from hazard source (m)	*Method*	*Population density* (persons/km^2)
<400	Use of Census data	From enumeration district data
400–1000	Use of Ordnance Survey maps	Dense terrace housing: 15,000 Semi-detached housing: 10,000 Sparse detached housing: 1000 Uninhabited areas: 0
>1000	Use of Ordnance Survey maps	Built-up areas: 4000 Other inhabited areas: 100 Uninhabited areas: 0

Table 9.23 *Population categories and composition based 1981 Labour Force Survey (after Petts, Lees and Withers, 1987) (Courtesy of Elsevier Science Publishers)*

	Number (thousands)	*No. per household*
Adults in full-time employment	16,595	0.85
Adults in part-time employment	4,042	0.21
Self-employed	2,164	0.11
Unemployed	2,447	0.13
Housewives	7,092	0.36
Children: 0–4 years	3,222	0.17
Children: school age	8,753	0.45
Students	1,415	0.07
Retired	6,266	0.32
Others (including permanently sick and disabled)	1,100	0.06
Total	53,096	2.73
Total no. of households	9,442	

may actually recover better from some burns than adults, and persons with respiratory disease are likely to be more susceptible to irritant toxic gas, but not necessarily to thermal radiation.

As a first approximation, therefore, the population may be divided into two broad groups: (1) adults of working age and older children and (2) young children and old people. The first group is some 75% and the second some 25% of the population. In general, the latter is the more vulnerable group, although for some hazards it may be necessary to have a more specific definition. In this case, the proportion of vulnerable people may be assessed in relation to the particular hazard considered using the population composition model given in Table 9.24.

Mention may be made here of estimates of the proportion of vulnerable people given by other workers. Table 9.26 shows some estimates made by Hewitt (1976) for the proportion of people vulnerable to a toxic irritant gas such as chlorine.

9.16.5 Population outdoors

Very little information was found by Petts, Withers and Lees on the proportion of the population which is outdoors at different times of the day. In the *Rijnmond Report*, the proportion of people indoors was taken in the context of toxic gas hazard as 99%, allowing for the fact that some people would seek shelter from this hazard indoors.

The population location model derived by the authors is shown in Table 9.27. It was assumed that the regular and vulnerable groups spend 1 and 1/2 h/day outdoors, respectively, that the proportion of the total population outdoors at night (18.30–08.00 h) is 1%, and that those outdoors are drawn exclusively from the regular population. Then the time outdoors and the proportions outdoors by day, by night and overall may be calculated for the regular, vulnerable and total populations. A partial cross-check on the model or, more specifically, a crosscheck on the lower bound of the proportion of the population outdoors, was obtained from wartime data on V-2 rocket bomb casualties.

9.17 Modification of Exposure

The characteristics of the population at risk may need to be modified to take account of changes in the exposure of the population that occur if there is warning of the hazard. There are a number of ways in which an individual who becomes aware of a hazard may modify his exposure. He may seek shelter indoors or he may try to distance himself from the hazard, either by individual escape or by participating in an organized evacuation.

While these are the principal actions, they are by no means the only ones. There are others that are more specific to the hazard concerned. For example, an individual may seek shelter from the thermal radiation of a fireball behind some

Table 9.24 *Population composition model (after Petts, Lees and Withers, 1987) (Courtesy of Elsevier Science Publishers)*

A Unemployment 5%

	No. per household	*Proportion* (%)
1. Adults in full time employment:		
(a) at work (including self-employed)	0.89	32.9
(b) sick, on holiday, working from home	0.10	3.7
2. Adults in part time employment:		
(a) at work	0.21	7.7
(b) sick, on holiday	0.02	0.7
3. Unemployed	0.07	2.6
4. Homekeepers	0.35	12.9
5. Children of school age:		
(a) at school	0.31	11.4
(b) sick, on holiday	0.14	5.2
6. Students:		
(a) at college	0.04	1.5
(b) sick at home, on vacation	0.03	1.1
7. Children under school age	0.17	6.3
8. Retired	0.32	11.8
9. Others (including permanently sick and disabled)	0.06	2.2
Total	2.71	100.0

B Unemployment 10%

	No. per household	*Proportion* (%)
1. Adults in full time employment:		
(a) at work (including self-employed)	0.84	31.0
(b) sick, on holiday, working from home	0.10	3.7
2. Adults in part time employment:		
(a) at work	0.19	7.0
(b) sick, on holiday	0.02	0.7
3. Unemployed	0.14	5.2
4. Homekeepers	0.35	12.9
5. Children of school age:		
(a) at school	0.31	11.4
(b) sick, on holiday	0.14	5.2
6. Students:		
(a) at college	0.04	1.5
(b) sick at home, on vacation	0.03	1.1
7. Children under school age	0.17	6.3
8. Retired	0.32	11.8
9. Others (including permanently sick and disabled)	0.06	2.2
Total	2.71	100.0

structure. Or he may try to reduce his vulnerability to the blast from an explosion by adopting a different body posture.

Some aspects of modification of exposure by escape and evacuation are considered here. Other aspects such as modification by shelter are treated in the chapters on particular hazards. Organized evacuation as part of emergency planning is discussed in Chapter 24.

9.17.1 Reaction

The most basic feature bearing on modification of exposure is the response time of humans.

Estimates of human response time in emergencies have been made by the British Compressed Gases Association (BCGA, 1984) in relation to response to ignition of clothing in an oxygen-enhanced atmosphere. Work on human factors (e.g. Denison and Tonkins, 1967) is quoted, to the effect that the time taken by humans to respond to an unexpected situation varies between 5 and 20s. The BCGA obtain from this the following response model:

(1) 5% of the population (i.e. babies and disabled persons) are incapable of any reaction
(2) 95% of the population are capable of reaction, of whom it is assumed: 80% can react within 15 s, 25% can react within 10 s, 10% can react within 7.5 s.

It is taken that none of the population can react within 5 s.

Table 9.25 *Population composition at home by time of day (after Petts, Lees and Withers, 1987) (Courtesy of Elsevier Science Publishers)*

A Time-of-day categories

	Time of day	*Duration*	
		(h)	(%)
School day	08.00–16.00	8	33
Work day	08.00–18.30	10.5	44
Night	18.30–08.00	13.5	56

B Population categories at home

	Categories
School day	1(b), 2(b), 3, 4(b), 5(b), 6(b), 7–9
Work day	All except 1(a)
Night	All

C Proportion of population at home

	Proportion at home (%)	
	Unemployment 5%	*Unemployment* 10%
School day	46.5	49.1
Work day	67.2	69.0
Night	100.0	100.0

9.17.2 Escape

A systematic treatment of individual escape is difficult. The principal case where this has been attempted is for escape from toxic gas by walking out of the cloud. The treatment of this problem given in the First *Canvey Report* is described in Appendix 7.

9.17.3 Evacuation

Organized evacuation is more readily analysed. A simple model for evacuation is:

$$\phi(t) = 1 \qquad t < t_d \quad [9.17.1a]$$

$$= \phi(\infty) + [1 - \phi(\infty)]\exp[-\lambda(t - t_d)] \qquad t \geq t_d \quad [9.17.1b]$$

where t_d is the time lag before any evacuation starts, λ is a constant, $\phi(t)$ is the fraction of population which has not evacuated at time t, and $\phi(\infty)$ is the fraction of population which does not evacuate at all. The constant λ is related to the evacuation half-life $t_{1/2}$ as:

$$\lambda = 0.693/t_{1/2} \qquad [9.17.2]$$

This model has been used by Solomon, Rubin and Okrent (1976) to allow for the effect of evacuation in hazard assessments of large toxic releases. Most other workers appear to have used a similar model.

A study of evacuation effectiveness in actual emergencies has been made by Hans and Sell (1974), who give details of evacuation from transportation, hurricane and flood emergencies. The transportation emergencies include the incidents shown in Table 9.28. The overall conclusion of these investigators is that behaviour in such emergencies is less irrational and more effective than is often supposed.

Table 9.26 *Vulnerable members of population (after Hewitt, 1976)*

	No. per 1000 people
Children:	
<6 months	8
<12 months	8
12 months–5 years	75
5–9 years	82
Old people (>70 years)	85
People with chronic heart trouble	5
People with respiratory diseases	9
People with restricted mobility	4
Blind people	2
Healthy youngsters and adults	722

The data presented in this work were analysed in the *Rasmussen Report* (AEC, 1975). The evacuation speed and time for each type of incident were found to be correlated by the equations:

$$v = kd^n \qquad [9.17.3]$$

$$t = d/v \qquad [9.17.4]$$

where d is the evacuation distance (mile), t is the evacuation time (h), v is the evacuation speed (mile/h), k is a constant and n is an index.

The type of incident that is most relevant in the present context appears to be the transportation emergency. For such incidents

$$v = 0.3\mathrm{d}^{1.02} \qquad [9.17.5]$$

The evacuation speeds were found to fit a log–normal distribution with the density function

$$f = \frac{1}{\sigma v(2\pi)^{1/2}} \exp\left[-\frac{(\ln v - m^*)^2}{2\sigma^2}\right] \qquad [9.17.6]$$

where m^* and σ are parameters in the log–normal distribution.

For transportation incidents $m^* = 0.20$ and $\sigma = 1.64$ and hence the modal and mean values of v are 0.08 and 4.7 mile/h, respectively.

There have been a number of more recent major evacuations. One of the largest was at Mississauga, Toronto, where a leaking chlorine rail tank car led to the evacuation of some 223,000 people (Case History A97). Another large evacuation took place at Bhopal, but in this case there was no chance of averting a major disaster. Bhopal is described in Appendix 5. At Chernobyl, after a delay in deciding to evacuate, some 40,000 people were evacuated in about 2 h. Chernobyl is described in Appendix 22.

The value of evacuation in modifying exposure was investigated in the First *Canvey Report*, as described in Appendix 7. Opportunity to evacuate depends on the hazard and on the way in which the incident develops. Although some hazards, such as a single, unexpected explosion may give little warning, in other cases there may be a substantial degree of warning. One example is an initial explosion in a works followed by a fire that may lead to further explosions and fires. Another is derailment of a rail tank car with the possibility of fireballs and toxic release. In both such cases evacuation may be beneficial.

Table 9.27 *Population outdoor exposure model (after Petts, Lees and Withers, 1987) (Courtesy of Elsevier Science Publishers)*

Population	*Time outdoors* (h/week)			*Proportion outdoors* (%)		
	Day	*Night*	*Overall*	*Day*	*Night*	*Overall*
Regular	0.81	0.19	1.0	7.70	1.33	4.17
Vulnerable	0.5	0	0.5	4.8	0	2.08
Total	0.74	0.14	0.88	7.05	1.0	3.67

Table 9.28 *Evacuation in some major transport emergencies (after Hans and Sell, 1974)*

Date	*Location*	*Incident*	*Number evacuated*	*Area evacuated* (mile^2)	*Evacuation distance* (mile)	*Evacuation period* (h)
1965	Baton Rouge, LA	Chlorine barge, no chlorine escape	150,000	8	30	2
1969	Glendora, MI[a]	Vinyl chloride escape from rail tankers	35,000	1200	20	4
1972	Louisville, KY	Chlorine barge, no chlorine escape	4,000	0.35	1	3
1973	Morgan City, LA	Chlorine barge, no chlorine escape	3,000	1.8	2	4

[a] The Glendora incident is described in Case History A43.

9.17.4 Incident control

Avoidance of casualties also has another aspect. Besides getting people who are exposed out of the danger zone, it is often necessary also to keep others from entering the danger zone. In particular, an incident may tend to attract spectators who thereby put themselves at risk. In 1947, ammonium nitrate explosions aboard the *Grandcamp* and the *High Flyer* in the harbour in Texas City killed 552 people (Case History A16). The explosion on the *Grandcamp* killed everyone in the dock, many of whom were spectators. Spectators also constituted a large proportion of the death toll of more than 150 at Caracas in 1982, when burning oil from a storage tank on fire at the top of a hill flowed down into a crowd below (Case History A102).

9.18 Injury Relations

The estimation of the injury or damage caused by a physical effect such as heat radiation intensity, overpressure or toxic concentration requires the use of injury or damage relations.

The normal method of formulating such relations is in three stages. The first is the determination of the causative (or injury or damage) factor which best correlates the data. The second is the determination of the probability distribution for this factor. The third is the conversion of this distribution into the more convenient form of a probit equation.

These steps are now described. In the account given reference is primarily to injury rather than damage relations, but the principles are the same for the latter. Injury and damage relations may be expressed in forms other than probit equations and these also are briefly mentioned.

9.18.1 Injury factors

The starting point for the derivation of an injury relation is a set of data giving the probability of a specified degree of injury as a function of some physical effect. Some typical physical effects are:

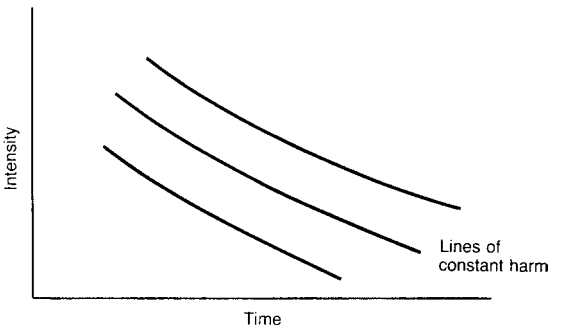


Figure 9.24 *Determination of the form of the injury factor*

Fire	Thermal radiation intensity	I
Explosion	Overpressure	p°
	Impulse	J
Toxic gas	Concentration	C
	Dosage	Ct

where t is time.

The probability of injury may or may not correlate directly with the physical effect. In some cases the correlation is with some power or time function of the effect. For example, probability of eardrum rupture does correlate with explosion overpressure p°, but probability of burn death correlates with the radiation intensity time function $I^{4/3}t$. The first step, therefore, is to determine the appropriate injury factor. It may be helpful to plot a graph of the form shown in Figure 9.24.

9.18.2 Injury distributions

Next it is necessary to determine the probability distribution of the injury factor. The distribution usually considered first is the log–normal distribution. The fit of the data to this distribution may be tested by plotting on log–probability paper. A plot of this type is shown in Figure 9.25.

The reason that data on probability of injury tend to give a log–normal distribution is that this distribution fits the case where the population contains a proportion of individuals who are unusually resistant. For example, the distribution is widely used to correlate the toxicity of an insecticide, where the dosage required to kill off the last few individuals is relatively high.

9.18.3 Probit equations

The injury distribution just described gives the information required on the probability of injury as a function of the injury factor. It is possible, however, to carry out a transformation that casts it in the more convenient form of a probit equation. An account of the probit method is given in *Probit Analysis* (Finney, 1971). One of the first major applications of the method to hazard assessment in the process industries was in the VM of Eisenberg, Lynch and Breeding (1975). The probit Y is an alternative way of expressing the probability P of injury. It is defined by the relation:

$$P = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{Y-5} \exp(-u^2/2)\,\mathrm{d}u \qquad [9.18.1]$$

The probit is a random variable with a mean 5 and variance 1. The probability range (0–1) is generally replaced in probit work by a percentage (range 0–100). The relationship between percentages and probits is shown in Table 9.29 and in Figure 9.26.

It is shown below that for an injury factor x which fits the log–normal distribution the probit equation has the form:

$$Y = k_1 + k_2 \ln x \qquad [9.18.2]$$

A typical probit transformation is illustrated in Figure 9.27. The sigmoidal curve of the log–normal distribution is transformed into the straight line of the probit. This makes it easier both to correlate the data in the first place and then to use the correlation.

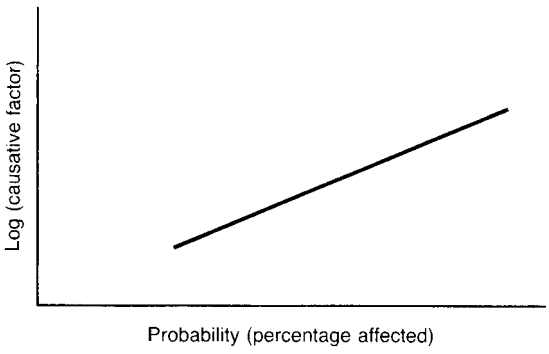


Figure 9.25 *Determination of the distribution of the injury factor*

The derivation of an equation of the general type given in Equation 9.18.2 is conveniently shown by considering first a normal distribution. The density function f is

$$f = \frac{1}{(2\pi)^{1/2}\sigma} \exp\left[-\frac{(x-m)^2}{2\sigma^2}\right] \qquad [9.18.3]$$

The distribution function F is

$$F = \int_{-\infty}^{x} f(x)\,\mathrm{d}x \qquad [9.18.4]$$

But the distribution function F is the same as the probability P of injury, so that entering Equation 9.18.3 in Equation 9.18.4 gives:

$$P = \frac{1}{(2\pi)^{1/2}\sigma} \int_{-\infty}^{x} \exp\left[\frac{-(x-m)^2}{2\sigma^2}\right]\mathrm{d}x \qquad [9.18.5]$$

Then equating Equation 9.18.5 with Equation 9.18.1 gives

$$u = (x - m)\sigma \qquad [9.18.6]$$

and

$$Y - 5 = u \qquad [9.18.7]$$

Hence

$$Y = (5 - m/\sigma) + (1/\sigma)x \qquad [9.18.8]$$

$$= k_1' + k_2' x \qquad [9.18.9]$$

Similarly, for the log–normal distribution:

$$Y = k_1 + k_2 \ln x \qquad [9.18.10]$$

with

$$k_1 = 5 - m^*/\sigma \qquad [9.18.11a]$$

$$k_2 = 1/\sigma \qquad [9.18.11b]$$

Equation 9.18.10 is the usual form of the probit equation.

The derivation of a probit equation from a set of data giving the probability of a specified injury as a function of the injury factor may be illustrated using the following data for eardrum rupture due to overpressure given by Eisenberg, Lynch and Breeding:

Percentage affected	*Probit*	*Peak overpressure* (N/m^2)
1	2.67	16.5×10^3
10	3.72	19.3×10^3
50	5.00	43.5×10^3
90	6.28	84.3×10^3

The corresponding probit equation given by these authors is

$$Y = -15.6 + 1.93 \ln p^{\circ} \qquad [9.18.12]$$

Table 9.29 *Transformation of percentages to probits (Finney 1971) (Courtesy of Cambridge University Press)*

%	0	1	2	3	4	5	6	7	8	9
0	–	2.67	2.95	3.12	3.25	3.36	3.45	3.52	3.59	3.66
10	3.72	3.77	3.82	3.87	3.92	3.96	4.01	4.05	4.08	4.12
20	4.16	4.19	4.23	4.26	4.29	4.33	4.36	4.39	4.42	4.45
30	4.48	4.50	4.53	4.56	4.59	4.61	4.64	4.67	4.69	4.72
40	4.75	4.77	4.80	4.82	4.85	4.87	4.90	4.92	4.95	4.97
50	5.00	5.03	5.05	5.08	5.10	5.13	5.15	5.18	5.20	5.23
60	5.25	5.28	5.31	5.33	5.36	5.39	5.41	5.44	5.47	5.50
70	5.52	5.55	5.58	5.61	5.64	5.67	5.71	5.74	5.77	5.81
80	5.84	5.88	5.92	5.95	5.99	6.04	6.08	6.13	6.18	6.23
90	6.28	6.34	6.41	6.48	6.55	6.64	6.75	6.88	7.05	7.33
–	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
99	7.33	7.37	7.41	7.46	7.51	7.58	7.65	7.75	7.88	8.09

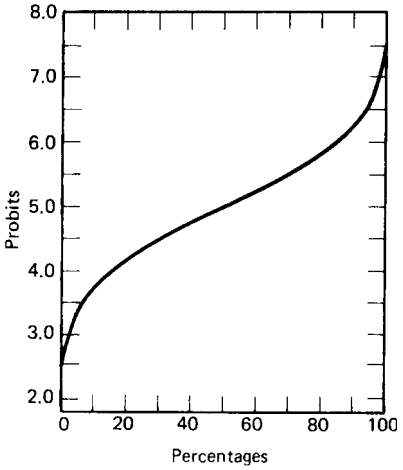


Figure 9.26 *Relationship between percentages and probits (Finney, 1971) (Courtesy of Cambridge University Press)*

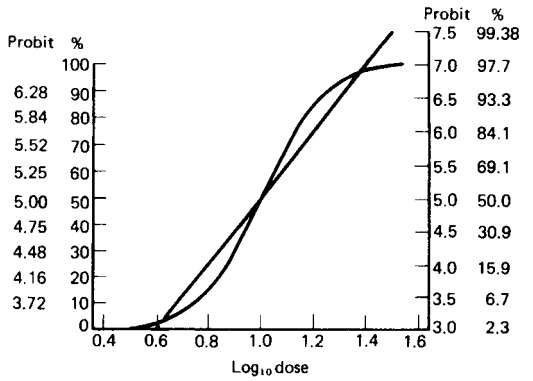


Figure 9.27 *Effect of the probit transformation (Finney, 1971). The figure illustrates a typical experiment on the toxicity of an insecticide. The logarithm of the lethal dose fits a normal distribution. The figure shows the distribution function and the corresponding probit function (Courtesy of Cambridge University Press)*

Probit equations for some major hazards given by Eisenberg, Lynch and Breeding are shown in Table 9.18. The derivation of these equations is discussed in more detail in Chapters 16–18.

It is emphasized that the probit equations given in Table 9.18 were early examples and were avowedly tentative and approximate, as will be clear from their derivations. They were developed essentially for use in the VM. Some have been superseded by improved equations. They are given here primarily as an illustration of the general form of injury factors and probit equations.

Probit equations were used in the *Canvey Reports* and the *Rijnmond Report* and have been widely used in many hazard assessments since then.

With respect to probit equations, there are several points that need to be borne in mind. First, any injury or damage correlation is only as good as the original data. Second, a check should be made that the data do actually fit the distribution implied, generally the log–normal distribution. Third, it is desirable to allow for the fact that data for probabilities in the middle of the probability range are likely to be more accurate than those for probabilities at the extremes of the range.

9.18.4 Probit equations: data weighting

Taking up this latter point, it is the case that given data for probabilities P near the centre of the range (say $P = 0.5$) and at an extreme of the range (say $P = 0.01$ or 0.99) obtained from samples of the same size, the level of confidence will be higher in the former. Or, to put the matter another way, for the same level of confidence it is necessary to have a larger sample size at an extreme of the range than near the centre.

This problem arises particularly in laboratory work on the toxicity of, say, pesticides. It has been addressed by Fisher and Yates (1957), who give a set of weighting coefficients for use in probit analysis. Table 9.30, Section A, gives a set of weighting coefficients interpolated from their values.

A technique described by Gilbert, Lees and Scilly (1994a) which is convenient in dealing with a set of data points and which gives an essentially similar weighting is to multiply each point by the weighting factor shown in Section B of Table 9.30. The point is discussed further in Chapter 18.

Table 9.30 *Weighting factors for construction of probit equations*

A Weighting coefficient (after R.A. Fisher and Yates, 1957)

Probability (%)[a]	*Probit*	*Weighting coefficient*
1	2.7	0.072
5	3.4	0.224
10	3.7	0.342
20	4.2	0.490
30	4.5	0.575
40	4.7	0.621
50	5.0	0.637

B Number of entries (after Gilbert, Lees and Scilly, 1994a)

Probability range (%)	*No. of times in which point is entered*
40–60	6
30–40; 60–70	5
20–30; 70–80	4
10–20; 80–90	3
5–10; 90–95	2
<5; >95	0

[a] The weighting coefficient for a percentage x greater than 50% may be obtained from that for $100 - x$.

9.18.5 Other relations

Not all correlations of injury and damage are in terms of probability distributions and probit equations. In particular, certain effects of explosions are often correlated in other ways. Among these effects are damage to plant and buildings, injury due to building collapse and damage and injury due to missiles. The treatment of explosion effects is described in Chapter 17.

9.18.6 Multiple injury and double counting

It is appropriate at this point to draw attention to some of the problems associated with multiple injury and double counting of injuries.

A treatment of double counting is given in the *Green Book*, (CPD, 1992b), which identifies three basic types of double counting. In double counting of the first type, a single injury mechanism due to a single event creates victims with several, successively more severe, degrees of injury. A problem arises where the number of victims with a lower degree of injury is also included in the number with the higher degree(s) of injury. The correct procedure is to subtract the number of victims with the higher degree(s) of injury from the number with the lower degree of injury.

In double counting of the second type, several injury mechanisms due to a single event create victims with the same degree of injury. The problem here is that a proportion of victims are injured by more than one of these mechanisms and that, mathematically, it is incorrect to obtain the probabilities of injury by simply summing the probabilities for each mechanism. The correct procedure mathematically is to utilize the expressions for the probability of a joint event, as given by Equations 7.5.5–7.5.8.

In double counting of the third type, several events, occurring in succession, each theoretically injure to a given degree the same person, whereas in reality the first event produces such injury that any subsequent event has no additional injurious effect. In this case, the correct procedure mathematically is to subtract the number of persons suffering this degree of injury after the first event from the population at risk for subsequent events.

This approach to the avoidance of double counting is essentially a mathematical one. It is valid for double counting of the first type and also for double counting of the second and third types where the degree of injury concerned is fatal injury. However, for degrees of injury that are less than fatal it fails for the second and third types to make sufficient allowance for physiological as opposed to mathematical factors.

As far as physiological factors are concerned, it is difficult to generalize. Each case needs to be considered on its merits. It might be thought that from a physiological rather than a mathematical viewpoint the overall probability of a given degree of injury from more than one event capable of causing that degree of injury might be greater, rather than less, than the sum of the individual probabilities, and also that there might be escalation to a more severe degree of injury, but this may not always be so.

Thus, on the one hand there is some evidence from battle casualties that the physiological effect of fragment wounds is not necessarily proportional to the number of fragments involved. On the other hand, the severity of burn wounds increases with the proportion of the body surface that is affected. A further discussion of combined injuries is given by R.K. Jones (1971).

9.18.7 Overview

It is peculiarly difficult to obtain injury relations for humans, since the normal method of establishing a correlation, that is direct experimentation, is ruled out. The approaches taken have often been opportunistic, seeking data wherever it may be found. For example, the correlation for burn injury that has long held the field is based on data on injuries caused by the atomic bombs at Hiroshima and Nagasaki. Not surprisingly, the derivation and use of injury relations has been subject to some criticism. Critiques include those of V.C. Marshall (1989b), Turner and Fairhurst (1989 HSE SIR 21) and R.F. Griffiths (1991b).

A general criticism is the relatively high uncertainty in injury relations. This is inherent in the problem and there is not very much that can be done about it. The degree of uncertainty may be quantified if it is possible to determine confidence bounds, but often it is not obvious how this is to be done. It may well be possible to give bounds for, say, the concentrations of a toxic gas which are lethal to a particular animal species, but these data have then to be extrapolated to humans, an operation which involves a good deal of judgement.

Another criticism concerns extrapolation from the region of 50% probability to those of 5% and or even 1%. Here there are two distinct problems. One is the confidence that can be placed in the slope of the probit relation on which such extrapolation is based. The other is the possibility that at low values of the physical effect the injury mechanisms that come into play may be qualitatively different. Since the level of physical effect which applies to the 5% or 1% probabilities is relatively low and thus applies to the far field, the area affected is large and differences in the value of the effect for these probability levels can have a significant impact on the estimate of the number injured.

Although in principle a similar problem of extrapolation exists for the region of 95% or 99% probability, in practice this is of less importance, because these probability values apply in the near field where the area affected is relatively small and because in consequence the difference in numbers of injured between estimated values of, say, 90% and 95% is not great.

9.19 Presentation of Results

There are a number of different outputs that may be obtained from a hazard assessment. These outputs may be, and often are, in the form of risk estimates, but other outputs may also be used. The results are sometimes presented in terms of the distance at which the hazard will cause a defined effect. Such a hazard range may be based on a worst-case scenario or on some less serious scenario. In the latter case there is an implied cut-off for the frequency of the event.

Alternatively, the results are presented in terms of risk. One form of risk is the frequency of a defined effect. In this case, no explicit computation is made of harm to people. If the risk to people is determined, the exercise becomes a full risk assessment. The risk may be expressed in terms of fatalities only, or of fatalities and injuries.

The risk of damage to property may also be determined, although such assessment appears to be less common as an end in itself than as a means of estimating the risk to people.

9.19.1 Types of risk to people

As just described, the results presented from a risk assessment may be confined to risk of death or may embrace risk of injury. Relying on the concept of a more or less fixed ratio of injuries to fatalities, the engineer may well consider that a risk profile of the plant formulated in terms of fatalities is usually sufficient as an aid to decision-making. As described below, however, risk of injury is also taken into account. In particular, the HSE are interested in the risk of receiving a 'dangerous dose'. This dose translates into different risks of death for vulnerable and non-vulnerable people.

9.19.2 Forms of presentation

There are a number of ways in which the results of a risk assessment may be presented. Some of the forms of presentation are shown in Table 9.31. For a fixed installation the risk will relate to some event that might occur on the site in question. The risk is generally measured from a particular point within the site. In some cases, the risk may be presented simply as the frequency of a defined event, usually a major accident, at the installation.

For individual risk to the workforce, the usual form is either an annual risk or the FAR. There is a straight conversion between the two. It is not usual to derive for the workforce any form of collective risk equivalent to the societal risk for the public described below.

The forms of presentation for risk to the public are more varied. For land-use planning, contours and transects (plan and elevation, respectively) may be given. These contours and transects may represent the frequency of a given intensity of a physical effect, or alternatively the frequency of individual fatality, or individual risk. Such contours and transects may relate to a single hazard or to the combined results of several hazards.

Table 9.31 *Forms of presentation of results of a risk assessment*

A Risk of workforce
Annual risk
Fatal accident rate (FAR)
B Risk to public
Physical effects
Contours on site map
Transects on site map
Individual risk
Contours on site map
Transects on site map
Annual risk at fixed location
Societal risk
FN table
FN curve
Equivalent annual fatalities

Note: Risk may be risk of fatality or injury, or other risk such as that of HSE dangerous dose.

Individual risk to members of the public may be presented as a function of distance from the site, but is more usually given as the average risk to groups at different locations around the site.

The main form in which societal risk is presented is as a relation between incidents that cause some number N or more fatalities and the frequency F of such incidents. These data may be given in tabular form, but are also often plotted as a FN curve. The basic FN data may be integrated to obtain a value for the equivalent annual fatalities. One use of this statistic is to compare the risks of different activities, for example coal mining vs nuclear energy. It is generally regarded as less appropriate for a hazard on a particular site, since it lumps together small incidents with relatively high frequency and large incidents with relatively low frequency. However, for such a hazard it is of some value in assessing the relative contribution of high frequency and low frequency events to the overall risk.

9.19.3 Risk contours and transects

The use of risk contours and transects is illustrated in Figures 9.28 and 9.29. Figure 9.28 gives overpressure risk contours for a natural gas liquids (NGL) plant and refrigeration facility. Figure 9.29 gives a risk transect for interaction between a vapour cloud from a pipeline and the public.

9.19.4 FN tables and curves

Table 9.32 shows some results of the risk assessment given in the First *Canvey Report*. Figure 9.30 shows the corresponding FN curve. This was one of the first FN curves published for the process industries. Also shown in Figure 9.30 are other curves given in the two *Canvey Reports*.

Figure 9.31 shows a set of FN curves given by the HSE for accidents, in the chemical and petrochemical industries, in the United Kingdom and worldwide.

If the FN relation is a straight line, it may be written as:

$$fN^{\alpha} = r = \text{Constant} \qquad [9.19.1]$$

where f is the frequency, N is the number of fatalities, r is a constant and α is an index.

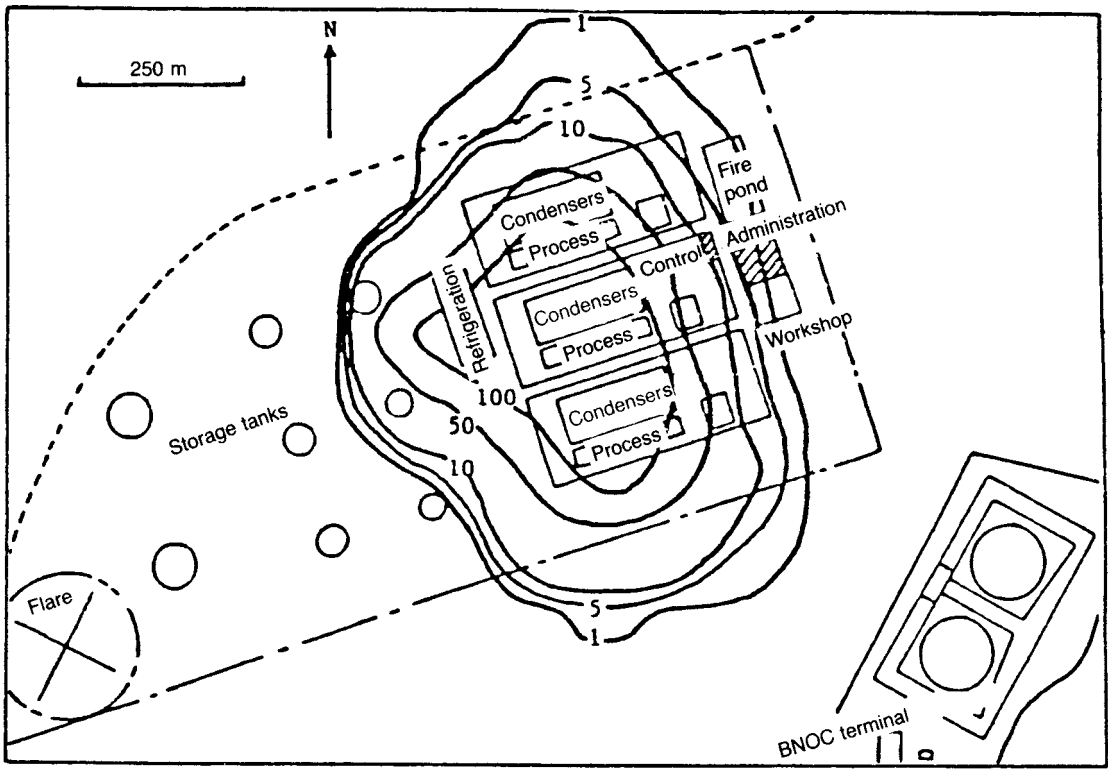


Figure 9.28 *Risk contours for a NGL plant and refrigeration facility (Ramsay, Sylvester-Evans and English, 1982) (Courtesy of the Institution of Chemical Engineers)*

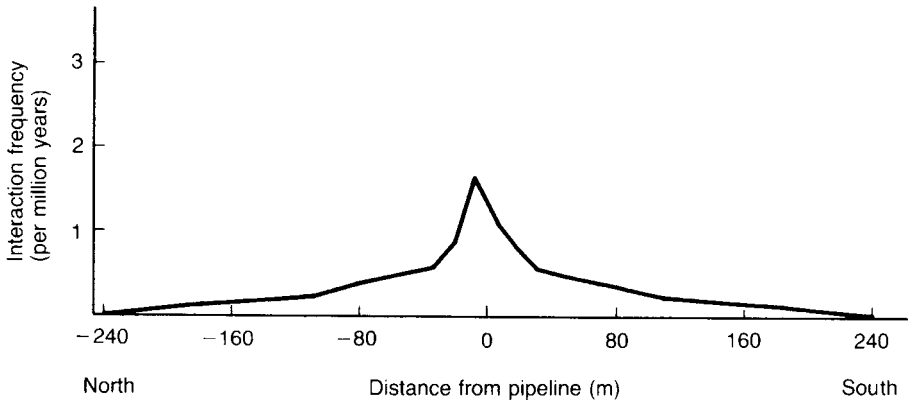


Figure 9.29 *Risk transect for interaction between a vapour cloud from a pipeline and the public (Ramsay, Sylvester-Evans and English, 1982) (Courtesy of the Institution of Chemical Engineers)*

9.19.5 Risk aversion in FN curves

Generally, society is more averse to a single very large accident than to a number of small ones. Such risk aversion has been discussed in Chapter 4. In simple terms, risk aversion exists if society regards a single accident with 100 fatalities as in some sense worse than 100 accidents with a single fatality each.

Risk aversion is seen most clearly in FN curves, where the slope of the curve indicates the degree of risk aversion. If the FN relation is in fact a straight line, its slope

Table 9.32 *Assessed risks for some principal hazards given in the First Canvey Report (before proposed modifications (after Lees, 1982b) Courtesy of the Institution of Chemical Engineers)*

Hazard	*Frequencies of initiating event* (10^{-6}/year)	*Frequenceis* (10^{-6}/year) *for number of offsite casualties exceeding*							
		0	10	1500	3000	4500	6000	12,000	18,000
Oil overtopping of bund by process explosion[a]	1000	975	25	18	8	4	–	–	–
LPG ship collision	6640	6490	196	124	64	31	–	–	–
LNG ship collision remote from jetty	50	45	5	3	1	0.5	0.3	0.2	0.1
LNG jetty incident	2000	1830	168	118	83	56	37	16	7
Ammonia storage sphere spontaneous failure	100	30	68	40	28	21	15	7	3
HF release[a]	200	30	168	144	132	120	114	80	70
Ammonium nitrate storage explosion	85	0	85	85	85	17	17	–	–

LNG, liquefied natural gas; LPG, liquefied petroleum gas.
[a] Occidental.

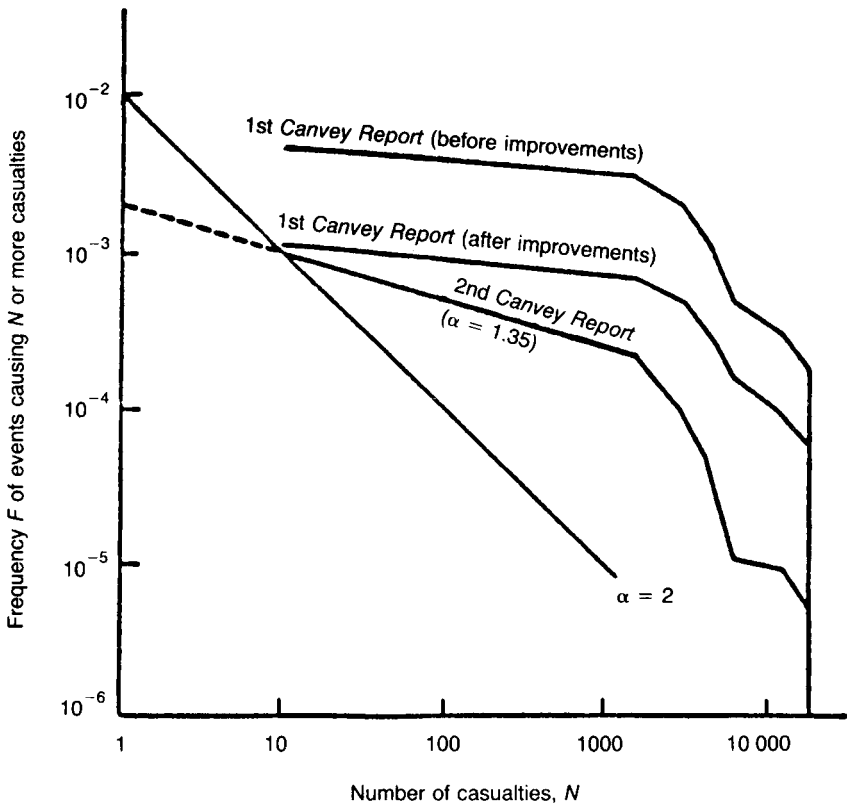


Figure 9.30 *FN curve for some principal hazards given in the First* Canvey Report*, (Hagon, 1984) (Reproduced by permission of the Institution of Chemical Engineers)*

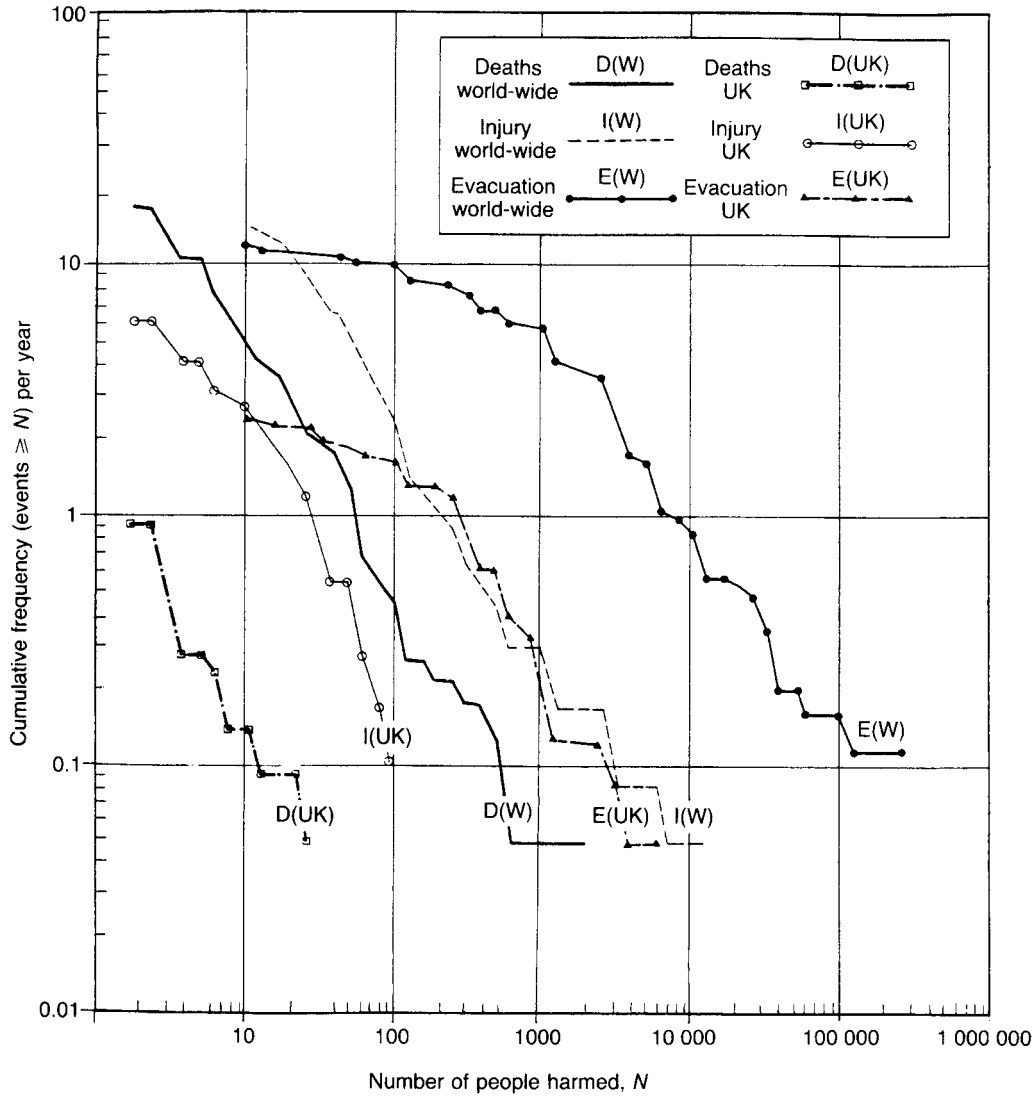


Figure 9.31 *Some FN curves for accidents in the chemical and petrochemical industries, in the United Kingdom and worldwide (HSE, 1989e) (Courtesy of the HM Stationery Office)*

is directly related to the parameter α, which is therefore known as the 'risk aversion index'.

9.19.6 Characteristics of FN curves

In order to make full use of the information given in FN curves and also to avoid certain misunderstandings that have arisen in their use, it is necessary to consider some of the characteristics of such curves. Accounts of FN curves include those given by R.F. Griffiths (1981e), the Royal Society Study Group (1983) and Hagon (1984).

As already stated, the normal FN curve is a plot of the frequency F of N or more events. Use has been made, however, particularly in early work, of alternative forms. The best known of these is the Farmer curve (F.R. Farmer, 1967b). This is a risk criterion curve and description of it is deferred until Section 9.21. However, it is appropriate to consider here the characteristics of the curve itself, that is whether the curve represents actual risk or a risk criterion. In a curve of this type, the consequence quantity plotted against frequency is not a cumulative quantity. There has been some confusion as to what this quantity should be. Accounts are given by R.F. Griffiths (1981e) and D.C. Cox and Baybutt (1982). The interpretation of Farmer himself is that it is a range of consequences, or a consequence interval, as shown in Figure 9.32. However, this type of curve is now rarely used.

Accounts of the relations underlying FN curves include those by R.F. Griffiths (1981e), D.C. Cox and Baybutt (1982) and Hagon (1984). The following treatment is based on the work of the latter.

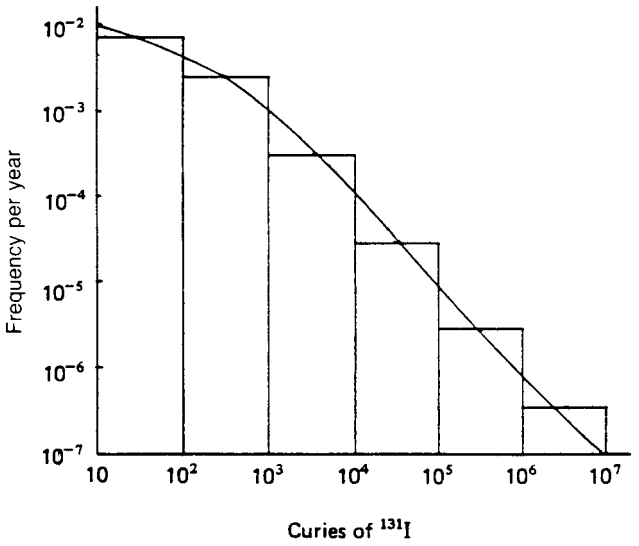


Figure 9.32 *Interpretation of the Farmer curve (R.F. Griffiths, 1981e) (Courtesy of Manchester University Press)*

From Equation 9.19.1, the following relations may be stated for cumulative frequency *F:*

$$F_1^K = \sum_{N=1}^{N=K} f \qquad [9.19.2a]$$

$$= r \sum_{N=1}^{N=K} (1/N^{\alpha}) \qquad [9.19.2b]$$

Defining

$$S(K,\ \alpha) = \sum_{N=1}^{N=K} (1/N^{\alpha}) \qquad [9.19.3]$$

gives

$$F_1^N = rS(N,\ \alpha) \qquad [9.19.4]$$

Also

$$F_{N_1}^{N_2} = r[S(N_2,\ \alpha) - S(N_1 - 1,\ \alpha)] \qquad [9.19.5]$$

Values of $S(N, \alpha)$ computed for ranges of values of N and α are shown in Figure 9.33.

The total annual fatalities D may be obtained in a similar manner:

$$D_1^K = \sum_{N=1}^{N=K} fN \qquad [9.19.6a]$$

$$= r \sum_{N=1}^{N=K} \left(1/N^{\alpha-1}\right) \qquad [9.19.6b]$$

$$D_1^N = rS(N,\ \alpha - 1) \qquad [9.19.7]$$

$$D_{N_1}^{N_2} = r[S(N_2,\ \alpha - 1) - S(N_1 - 1,\ \alpha - 1)] \qquad [9.19.8]$$

If f is treated as a continuous function of N, the following relations apply:

$$F_1^K = \int_1^K f\, \mathrm{d}N \qquad [9.19.9]$$

$$D_1^K = \int_1^K fN\, \mathrm{d}N \qquad [9.19.10]$$

The relations for these integrations are shown in Table 9.33. The relations change at $\alpha = 2$. The values based on the assumption that N is continuous are not accurate for N less than approximately 30.

The application of these equations to a set of FN curves given in an actual risk assessment has also been described by Hagon. Figure 9.34 shows the FN curves concerned which are for the ammonia storage sphere in the *Rijnmond Report.*

Also shown in Figure 9.34 is a dotted line that corresponds to

$$\alpha = 2$$

$$F_1^N = 10^{-3}$$

Then for r taking some large value of N, say 5000,

$$r = F_1^N / S(N,\ \alpha)$$

From Figure 9.30, for $N = 5000$

$$S(5000,\ 2) \approx 1.65$$

Hence

$$r = 10^{-3}/1.65 = 0.61 \times 10^{-3}$$

Then the cumulative frequency of accidents and expected annual fatalities may be estimated. Values of these quantities derived from (1) the exact relations and (2) the approximate relations given in Table 9.33 are shown in

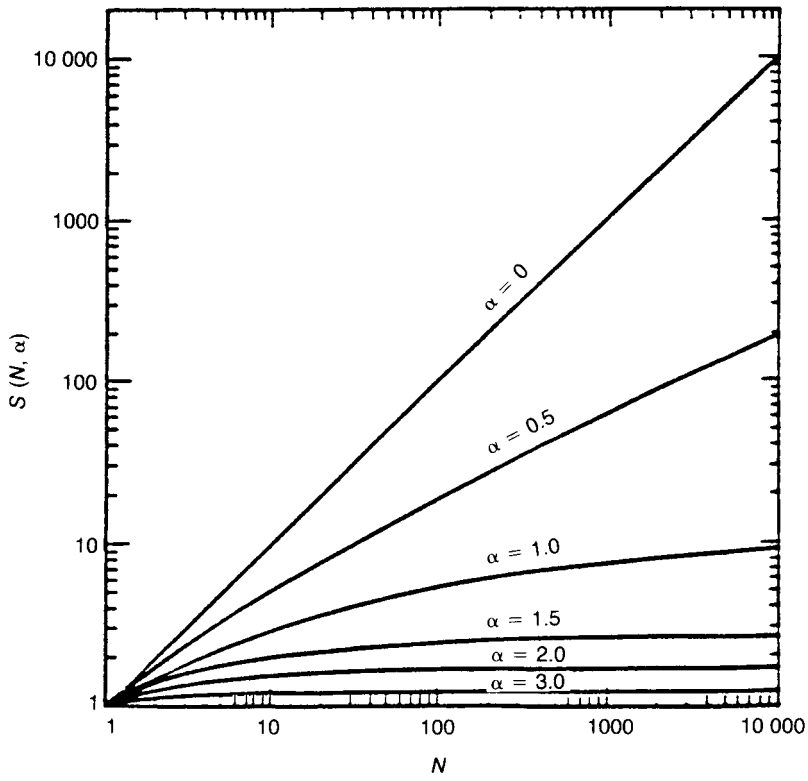


Figure 9.33 *Values of parameter S(N, α) (Hagon, 1984) (Courtesy of the Institution of Chemical Engineers)*

Table 9.33 *Approximate relations for cumulative frequencies and expected annual fatalities (Hagon, 1984). These relations approximate to the exact relations (Equations (9.19.3)–(9.19.6)) if N > 30 and limits are taken as $N_2 + 0.5$, $N - 1 - 0.5$ (Courtesy of the Institution of Chemical Engineers)*

Aversion index	*Cumulative frequency*		*Total deaths/year*
	$(F)_{N_1}^{N_2}$	$F_N = (F)_N^{\alpha}$	$(D)_{N_1}^{N_2}$
$\alpha = 1$	$r \ln \dfrac{N_2}{N_1}$	∞	$r(N_2 - N_1)$
$1 < \alpha < 2$	$\dfrac{r}{\alpha - q}\left(\dfrac{1}{N_1^{\alpha-1}} - \dfrac{1}{N_2^{\alpha-1}}\right)$	$\dfrac{r}{\alpha - 1}\left(\dfrac{1}{N^{\alpha-1}}\right)$	$\dfrac{r}{2-\alpha}\left(N_2^{2-\alpha} - N_1^{2-\alpha}\right)$
$\alpha = 2$	$r\left(\dfrac{1}{N_1} - \dfrac{1}{N_2}\right)$	$\dfrac{r}{N}$	$r \ln \dfrac{N_2}{N_1}$
$\alpha > 2$	$\dfrac{r}{\alpha - 1}\left(\dfrac{1}{N_1^{\alpha-1}} - \dfrac{1}{N_2^{\alpha-1}}\right)$	$\dfrac{r}{\alpha - 1}\left(\dfrac{1}{N^{\alpha-1}}\right)$	$\dfrac{r}{\alpha - 2}\left(\dfrac{q}{N_1^{\alpha-2}} - \dfrac{1}{N_2^{\alpha-2}}\right)$ $= \dfrac{r}{\alpha - 2}$ for $N_2 = \infty, N_2 = 1$

Note: The above relations approximate to the exact Equations 9.20.4, 9.20.5, 9.20.6 and 9.20.7 if $N > 30$ and limits are taken to be $N_2 + 0.5$, $N_1 - 0.5$.

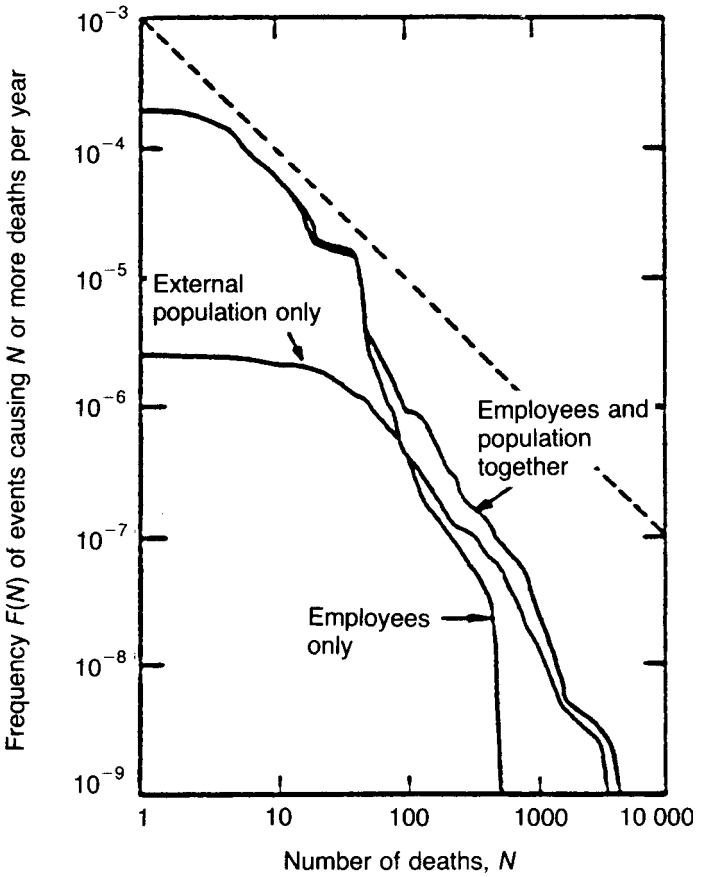


Figure 9.34 *FN curves for an ammonia storage sphere given in the Rijnmond Report (Hagon, 1984) (Courtesy of the Institution of Chemical Engineers)*

Table 9.34 *Cumulative frequencies and expected annual fatalities for an ammonia storage sphere (after Hagon, 1984) (Courtesy of the Institution of Chemical Engineers)*

	Approximate relation (per year)	*Exact relation* (per year)
F_3^{30}	1.8×10^{-4}	2.2×10^{-3}
F_3^{300}	1.8×10^{-5}	2.2×10^{-5}
D_1^{30}	3.5×10^{-3}	2.4×10^{-3}
D_1^{3000}	4.8×10^{-3}	5.2×10^{-3}

Table 9.34. These equations are considered further in Section 9.21 in relation to risk criteria.

9.20 Confidence in Results

The results of a hazard assessment are subject to uncertainty and it is necessary therefore to be able to estimate the extent of this uncertainty. Discussions of uncertainty in hazard assessment include those by Nussey (1983), Goosens, Cooke and van Steen (1989) and Chhibber, Apostolakis and Okrent (1991).

9.20.1 Sources of uncertainty

Sources of uncertainty in a hazard assessment may be classified under the following broad headings:

(1) scenarios for initial event;
(2) scenarios for escalation;
(3) event frequency, probability;
(4) models for physical events;
(5) models for injury;
(6) models for mitigation.

These sources of uncertainty are amplified in Table 9.35. An account of sources of uncertainty with special reference to toxic release has been given by Nussey (1983).

9.20.2 Characterization of uncertainty

Uncertainty may attach to a single event or to a chain of events. The approach taken to the characterization of uncertainty depends on the complexity of the problem. The conventional analytical approach to uncertainty in the frequency, or probability, of a single event is to utilize not a point value but a distribution of values. A distribution that is widely utilized is the log–normal distribution, described below.

Table 9.35 *Some sources of uncertainty in hazard assessment*

A Scenarios for initial event
Some uncertainties in the scenarios for the initial event, and thus the source term are:
Release sources and, for each source
Size
Orientation
Flash, rainout
Initial air entrainment
Duration
B Scenarios for escalation
Pool vaporization
Gas dispersion
Ignition
Jet flames
Pool fires
Fireballs
Flowing, burning liquid
BLEVEs
Missiles
Failure of emergency shut-down
Failure of fire protection system
Structural collapse
C Event frequency, probability
Failure frequency
Leak frequency
Ignition probability
Explosion probability
D Models for physical events
Flash fires
Pool fires
Fireballs
Jet flames
BLEVEs
Missiles
E Models for injury
Heat radiation
Explosion effects
Direct blast effects
Housing collapse
Missiles
Toxic effects
F Models for mitigation
Human behaviour
Escape
Shelter

Continuing with an analytical approach, the propagation of uncertainty is handled by utilizing relationships for the combination of distributions, principally relations for the sum and product of distributions. The result obtained is a distribution of the frequency, or probability, of the event of interest.

If the problem is too complex for analytical solution, use may be made of techniques such as Monte Carlo simulation to obtain frequencies and probabilities. Again a frequency, or probability, distribution is obtained. The Monte Carlo method was described in Chapter 7.

Moving on to uncertainty in the models, for physical effects, injury and mitigation, the analytical approach is to derive relations for the sensitivity of the results to changes in the models. One method is to determine the first derivative of the output of the model to its inputs, in other words the gains. Another is to express the parameters of the model as distributions rather than point values. A formal method of investigating the sensitivity of results to the parameters of physical models and injury relations is the hazard impact model, described in Section 9.23.

If again the problem is too complex to be handled analytically, the sensitivity of the results to the models may be investigated by Monte Carlo simulation or other methods. Again the parameters in the model may be given in the form of distributions.

The characterization of uncertainty in the scenarios is less well developed. One approach is to utilize expert judgement, as described below.

9.20.3 Log–normal distribution and error factor

A distribution which is widely used to characterize the spread of values of a variable is the log–normal distribution. The properties of the log–normal distribution were described in Chapter 7.

This distribution is used in particular for event frequency λ and probability p. For a failure rate λ, the log–normal distribution may be written as

$$f(\lambda) = \frac{1}{(2\pi)^{1/2}\sigma\lambda}\exp\left[-\frac{(\ln\lambda - m^*)^2}{2\sigma^2}\right] \qquad [9.20.1]$$

where m^* is the location parameter and σ the shape parameter.

The distribution is also frequently characterized in terms of the median λ_{med} and the shape parameter σ. The median λ_{med} of the distribution is

$$\lambda_{\text{med}} = \exp m^* \qquad [9.20.2a]$$

$$m = \ln\lambda_{\text{med}} \qquad [9.20.2b]$$

The mean λ_{mn} is

$$\lambda_{\text{mn}} = \exp\left(m^* + \sigma^2/2\right) \qquad [9.20.3]$$

where subscripts med and mn indicate the median and mean, respectively.

An important property of the log–normal distribution is its associated error factor. For lower and upper confidence bounds λ_{l} and λ_{u}, respectively, the median λ_{med} is related to the bounds by the error factor ϕ:

$$\lambda_{\text{med}} = \phi\lambda_{\text{l}} \qquad [9.20.4a]$$

$$= \lambda\text{u}/\phi \qquad [9.20.4b]$$

Hence

$$\lambda_{\text{med}} = (\lambda_{\text{l}}\lambda_{\text{u}})^{1/2} \qquad [9.20.5]$$

The relation between the spread parameter σ and the error factor ϕ is

$$\sigma = \ln \phi / k \qquad [9.20.6]$$

where k is a constant. The values of k for 90% and 95% of values that lie within the range are 1.64 and 1.96, respectively.

These equations have been written for further reference in terms of event frequency λ but they could equally well be written in terms of any variable x. In particular, they are also applicable to event probability p, and are so utilized below.

9.20.4 Propagation of uncertainty

A broad outline of approaches to the propagation of uncertainty was given above. An account is given here of the propagation of uncertainty in event rates.

Since a combination of events is considered, it is more appropriate to work in terms of probability p rather than frequency λ. For a variable p_3, which is the product of two independent variables p_1 and p_2 so that

$$p_3 = p_1 p_2 \qquad [9.20.7]$$

it can be shown that if variables p_1 and p_2 are log–normally distributed, the distribution of p_3 is also log–normal and the relations between the location parameters and the variances are

$$m_3^* = m_1^* + m_2^* \qquad [9.20.8]$$

$$\sigma_3^2 = \sigma_1^2 + \sigma_2^2 \qquad [9.20.9]$$

where subscripts 1–3 indicated events 1–3, respectively. Then it follows from Equations 9.20.2, 9.20.3, 9.20.8 and 9.20.9 that the median and mean of p_3 are given by:

$$p_{3,\text{med}} = p_{1,\text{med}} \times p_{2,\text{med}} \qquad [9.20.10]$$

$$p_{3,\text{mn}} = p_{1,\text{mn}} \times p_{2,\text{mn}} \qquad [9.20.11]$$

The propagation of uncertainty in a fault tree is considered in Section 9.20.7.

9.20.5 Scenarios

The basis of a hazard assessment is a set of scenarios. Both the completeness and the realism of these scenarios are subject to uncertainty.

Usually in hazard assessment the scenarios relate to loss of containment. There are then two sets of scenarios to be considered. The first set relates to the release itself. The second set relates to the escalation. Both release and escalation scenarios are subject to uncertainty.

In principle, completeness of the release scenarios may be achieved by considering release from each item of equipment. For this purpose, certain categories of equipment may be lumped together. On the other hand, it is necessary to consider not just a single size of release, but also a size distribution. There is, however, a further uncertainty concerning the geometry of the release. The material will not necessarily come out as, say, a free jet, but may issue at a downwards angle and hit the ground or may impinge on other equipment.

Completeness of the escalation scenarios is probably a more difficult problem. Much attention has been focused on the release and dispersion of flammable or toxic gas clouds. The generation of scenarios for such a hazard has not proved particularly difficult. However, the concentration on this rather stereotyped situation has perhaps masked the problem of defining the escalation in other, more varied, cases. Such a situation is exemplified by an offshore module.

Uncertainty concerning scenarios shades over into uncertainty concerning models, as described below.

9.20.6 Event rate

For an event rate, a frequency or probability, uncertainty may be taken into account by treating the event rate as a random variable with a distribution of values. This approach was used in the *Rasmussen Report* and since then has been widely adopted. In this study, data for both failure frequencies and probabilities were correlated using the log–normal distribution, as described in Section 9.20.3.

The procedure adopted was to consider for each equipment the available data on failure frequency or probability and to determine by expert judgement the lower and upper bounds for the range of values covering 90% of cases. The tables of failure data quote the lower and upper bounds, the median and the error factor.

9.20.7 Fault trees

It is also necessary to be able to obtain the probability distribution of the frequency of an event that has been synthesized using a fault tree. Where a measure of the uncertainty in the frequency estimate is made in a risk assessment, this is generally done numerically using Monte Carlo simulation. The frequencies of the base events in the tree are expressed in terms of probability distributions of frequency, such as the log–normal distribution as just described. Each simulation trial generates a set of frequencies for the base events. These are combined according to the tree structure to obtain a frequency of the top event. The result of a series of such trials is the probability density function for the top event. The principle of the method is illustrated in Figure 9.5.

Analytical treatments of the propagation of uncertainty through the logic gates of a fault tree are also available for certain defined cases. This approach is illustrated here by the work of Keey and Smith (1984). The problem considered is the combination at OR and AND gates of inputs which are normally distributed. Taking first an OR gate, consider two inputs whose frequencies take random values λ_1 and λ_2 with corresponding mean values $\bar{\lambda}_1$ and $\bar{\lambda}_2$ and standard deviations σ_1 and σ_2. The frequency λ of the output from the OR gate is

$$\lambda = \lambda_1 + \lambda_2 \qquad [9.20.12]$$

and the corresponding mean frequency $\bar{\lambda}$ is

$$\bar{\lambda} = \bar{\lambda}_1 + \bar{\lambda}_2 \qquad [9.20.13]$$

But mean values can be expressed as expected values. Then Equation 9.20.13 can be rewritten as

$$E[\lambda] = E[\lambda_1] + E[\lambda_2] \quad [9.20.14]$$

The variance of the output becomes

$$\sigma^2 = E\left[\lambda^2\right] - (E[\lambda])^2 \quad [9.20.15]$$

Then, from the properties of expected values.

$$E\left[\lambda^2\right] = E\left[\lambda_1^2 + 2\lambda_1\lambda_2 + \lambda_2^2\right] \quad [9.20.16]$$

$$= E\left[\lambda_1^2\right] + E[2\lambda_1\lambda_2] + E\left[\lambda_2^2\right] \quad [9.20.17]$$

Also

$$(E[\lambda])^2 = \bar{\lambda}^2 = \bar{\lambda}_1^2 + 2\bar{\lambda}_1\bar{\lambda}_2 + \bar{\lambda}_2^2 \quad [9.20.18]$$

From Equations 9.20.15 and 9.20.17

$$E\left[\lambda^2\right] = E\left[\bar{\lambda}_1^2 + \sigma_1^2\right] + E\left[\bar{\lambda}_2^2 + \sigma_2^2\right] + 2\bar{\lambda}_1\bar{\lambda}_2 \quad [9.20.19]$$

Substitution of Equations 9.20.18 and 9.20.19 into Equation 9.20.15 gives

$$\sigma^2 = \left(\bar{\lambda}_1 + \sigma_1^2\right) + \left(\bar{\lambda}_2 + \sigma_2^2\right) - \left(\bar{\lambda}_1 + \bar{\lambda}_2\right) \quad [9.20.20]$$

$$= \left(\sigma_1^2 + \sigma_2^2\right)^{1/2} \quad [9.20.21]$$

A measure of spread of the frequency is the coefficient of variation C:

$$C_i = \sigma_i/\lambda_i \quad [9.20.22]$$

The coefficient of variation of the output is

$$C = \sigma/\bar{\lambda} = (\sigma_1^2 + \sigma_2^2)^{1/2}/\left(\bar{\lambda}_1 + \bar{\lambda}_2\right) \quad [9.20.23]$$

One limiting case is where the two inputs have the same mean value ($\lambda_0 = \lambda_1 = \lambda_2$) and the same standard deviation ($\sigma_0 = \sigma_1 = \sigma_2$). Then

$$C = (2\sigma_0^2)^{1/2}/2\bar{\lambda}_0 = 2^{1/2}\sigma_0/2\bar{\lambda}_0 \quad [9.20.24]$$

or

$$C = C_0/2^{1/2} \quad [9.20.25]$$

Another limiting case is which one input becomes single valued ($\sigma_1 = 0$) and very small ($\lambda_1 \ll \lambda_2$):

$$C = (\sigma_2^2)^{1/2}/(\bar{\lambda}_1 + \bar{\lambda}_2) = \sigma_2/\bar{\lambda}_2 \quad [9.20.26]$$

or

$$C = C_2 \quad [9.20.27]$$

Hence the output coefficient of variation has the range:

$$(1/2^{1/2})\min(C_1, C_2) < \Psi < \mu\alpha\xi(\Psi_{\oslash}, \Psi) \quad [9.20.28]$$

Equation 9.20.18 shows that for an OR gate the coefficient of variation of the output is less than the larger of the coefficients of variation of the inputs, and that in this sense this gate reduces the uncertainty in the input data.

For an AND gate with an input of frequency λ_1 and another input of probability p_2, with corresponding standard deviations σ_1 and s_2, respectively, the frequency λ of the output is

$$\lambda = \lambda_1 p_2 \quad [9.20.29]$$

The corresponding mean frequency $\bar{\lambda}$ is related to the mean frequency $\bar{\lambda}_1$ and probability $\bar{p}_2$ of the inputs:

$$\bar{\lambda} = \bar{\lambda}_1\bar{p}_2 \quad [9.20.30]$$

Then

$$E\left[\lambda^2\right] = E\left[\lambda_1^2 p_2^2\right] \quad [9.20.31a]$$

$$= E\left[\lambda_1^2\right] \cdot E\left[p_2^2\right] \quad [9.20.31b]$$

$$= \left(\bar{\lambda}_1^2 + \sigma_1^2\right)\left(\bar{p}_2^2 + s_2^2\right) \quad [9.20.31c]$$

Also

$$(E[\lambda])^2 = \bar{\lambda}^2 = \bar{\lambda}_1^2\bar{p}_2^2 \quad [9.20.32]$$

Then, from Equation 9.20.15, the standard deviation of the output σ is

$$\sigma^2 = \left(\bar{\lambda}_1^2 + \sigma_2^2\right)\left(\bar{p}_2^2 + s_2^2\right) - \bar{\lambda}_1^2\bar{p}_2^2 \quad [9.20.33]$$

Hence

$$\sigma = \left(\sigma_1^2 s_2^2 + \bar{\lambda}_1^2 s_2^2 + \sigma_1^2\bar{p}_2^2\right)^{1/2} \quad [9.20.34]$$

The output coefficient of variation is then

$$C = \sigma/\bar{\lambda} = \left(\sigma_1^2 s_2^2 + \bar{\lambda}_1^2 s_2^2 + \sigma_1^2\bar{p}_2^2\right)^{1/2}/\bar{\lambda}_1^2\bar{p}_2 \quad [9.20.35]$$

Noting that

$$C_2 = s_2/\bar{p}_2 \quad [9.20.36]$$

Equation 9.20.35 can be recast in terms of the input coefficients of variation

$$C = (C_1^2 + C_2^2 + C_1^2 C_2^2)^{1/2} \quad [9.20.37]$$

One limiting case is where both input coefficients have the same value ($C_0 = C_1 = C_2$)

$$C = C_0(2 + C_0^2)^{1/2} \quad [9.20.38]$$

Another limiting case is in which one input coefficient becomes very small. Hence the output coefficient of variation has the range

$$C_m < \Psi < \Psi_{\gtrless}(+\Psi_{\gtrless})^{\oslash} \quad [9.20.39]$$

with

$$C_m = \max(C_1, C_2) \quad [9.20.40]$$

Relation 9.20.39 shows that for an AND gate the coefficient of variation of the output is more than the larger of the coefficients of variation of the inputs, and that in this sense this gate increases the uncertainty in the input data.

These results show that strictly in terms of error propagation for a sizeable fault tree a large number of initiating events may produce an outcome for which the uncertainty is relatively low, while a large number of mitigating or protective features may produce one for which the uncertainty is relatively high.

9.20.8 Event trees

An event tree consists of a series of binary splits. Each branch of the tree constitutes a separate escalation scenario. Uncertainty attaches both to the set of escalation scenarios and then, assuming that the set is correct, to the probability of each branch. The question of uncertainty in the escalation scenarios was discussed in Section 9.20.5. The probability distribution for the occurrence of a given branch may be obtained from probability distributions for each of the branch points.

9.20.9 Scenarios, models and parameters

The uncertainty in models has been discussed by Chhibber, Apostolakis and Okrent (1991), in the context of modelling of the fate of chemicals in the environment, particularly in geohydrochemical systems. They consider especially the following areas of uncertainty: (1) completeness of scenarios, (2) completeness of chains of consequences, (3) validity of individual models and (4) parameters in these models, with particular reference to expert judgement.

The formulation of scenarios by experts has been the subject of study. *The Reactor Risk Reference Document* of the Nuclear Regulatory Commission (NRC) (1989 NUREG-1150) gives an account of the expert treatment of scenarios in terms of 'issues' and levels' for a nuclear incident. The issues concern the scenarios that are credible. The levels represent different sets of assumptions about these scenarios.

Likewise, the models, whether for physical phenomena or for injury, may be based on a wide variety of assumptions and may thus be very disparate. Up to a certain point, variation may be handled by assigning different values to the parameters in the model, but beyond this point the model can be stretched no more, and a different model has to be used. There can be a thin dividing line between models and parameters.

Similarly, the value assigned to a parameter may depend on the model used. A well-known case is particle diameter, which may be characterized in different ways, depending on the situation being modelled. The relationships between models are a problem area. The models are not necessarily exclusive, exhaustive or independent.

9.20.10 Physical models

In general, the question of uncertainty in the models of physical phenomena is a relatively neglected one. Whereas treatments are available for uncertainty in event data and fault trees, there is no real equivalent for models. The problem is considered here first in terms of certain general principles. The role of expert judgement in selecting models is then described.

It is possible to identify certain features of models that bear on the degree of uncertainty. Models may be

(1) theoretical;
(2) empirical;
(3) semi-empirical.

They may also be

(1) deterministic;
(2) probabilistic.

The characteristics of these different types of model are well known. A theoretical model may have the weakness that it fails to take into account some relevant phenomenon. It may contain parameters to which it is difficult to assign accurate values or which it is impractical to quantify at all. The weakness of an empirical model may be that it has a limited, and poorly defined, range of applicability. A semi-empirical model, incorporating some combination of theory and experiment, may go some way to overcoming these weaknesses. Alternatively, a straight theoretical model may be validated by experiments.

A comprehensive model incorporates knowledge of the relevant regimes, the ranges of these regimes, and, in each regime, the mechanisms and the values of the parameters. Some factors that bear on the confidence that can be placed in a model include:

(1) theoretical basis;
(2) experimental validation;
(3) range of applicability;
(4) variety of tests;
(5) origin of model;
(6) life of, and interest in, model;
(7) number and convergence of competing models.

Confidence in a model must be greater if it has a theoretical basis. Equally, experimental validation increases confidence. It is, however, the quality of these two factors that matters. It is not uncommon that a theoretical model with some experimental support later proves inadequate.

The range of applicability is therefore important. Greater confidence can be placed in a model that covers a wide range and has been tested over this range. Testing using a variety of methods also increases confidence.

In assessing quality, the origin of the model is a crucial factor. Notwithstanding the challenge to conventional thinking that sometimes occurs from a previously unknown author, confidence is clearly greater if the worker(s) concerned are well established.

Where there is a single model, confidence should in principle increase with time. This will be true, however, only if there is some interest in the model so that the passage of time does actually result in activities which provide some degree of support for it.

A more encouraging situation is where there are a number of competing models that over a period of time yield results which converge. Whilst this by no means gives a guarantee of correctness, it does nevertheless build confidence.

These points are illustrated by the history of the development of models for heavy gas dispersion. In the early days, the models used for gas dispersion were neutral density models. These had both a strong theoretical basis and

extensive experimental support. They originated largely from the Meteorological Office and had a good scientific pedigree. It was shown by experiment, however, that the behaviour of a heavy gas cloud is quite different from that of a neutral density gas. It has some of the characteristics of the flow of a liquid, but differs in that air is entrained at the top and the edge of the cloud. This led to the development of a number of models for heavy gas dispersion.

Estimates of the travel distance of a flammable cloud were given in an early study, *Transportation of Liquefied Natural Gas* by the Office of Technology Assessment (OTA) of the US Congress (1977). The following estimates were quoted for the maximum downwind distance for a cloud from a 25,000 m^3 instantaneous spill of LNG onto water in a 5 mile/h wind for dilution to 5% concentration:

Travel distance (miles)	*Source*
0.75	Federal Power Commission
1.2[a]	Science Applications Inc.
5.2	American Petroleum Institute
16.3	US Coast Guard
25.2–50.3	US Bureau of Mines

[a] 37,500 m^3 release in a 6.7 mile/h wind.

The figures illustrate the wide spread given by the different early models. As the field has become more mature, this wide spread has disappeared. There are now available heavy gas dispersion models that have emerged from a large field of competitive models and for which there is experimental underpinning from both large-scale field trials and wind tunnel tests.

9.20.11 Injury relations

Many of the same general considerations that apply to physical models apply also to injury relations, but in addition the latter have some characteristics of their own. In general, an injury relation is obtained either from laboratory work on animals or from incident data affecting humans. In the former case, confidence limits are usually given for the results. Uncertainty arises, however, concerning the applicability of the results to man. If the data relate to an incident, there may be uncertainty concerning both the physical phenomenon and the exposure of humans to it. It is difficult to provide confidence limits. The uncertainty tends to be greatest at the two extremes of very low and very high probability of the injury effect and least at the 50% probability level. Often the injury relations are expressed as probit equations. The remarks just made apply equally to these.

9.20.12 Expert judgement

The choice of models to be used is normally made by a single expert. One of the main methods available to assess the uncertainty in the models is that of expert judgement, using a panel of experts.

Several studies of expert judgement in assessment of models have been made. One is the NRC study already mentioned (NUREG-1150).

Another is the work of Goossens, Cooke and van Steen (1989). This addresses uncertainty in the relative likelihood of different phenomena and in the values of parameters. The areas of application include failure rates, physical models and injury effects.

Models are developed by a domain expert. The uncertainty in the models may be assessed by a normative expert, whose expertise resides in such assessment.

One way of quantifying the uncertainty in a model is the error factor method. The error factor was described in Section 9.20.3. Consider a deterministic reference model (DRM) that yields some variable T. Then using an error factor E, T may be written as

$$T = ET_{\mathrm{DRM}} \qquad [9.20.41]$$

where T_{DRM} is the value of given by the DRM. The error factor is external to the model. It may be updated whilst the model remains unchanged. This error factor approach has been applied by Siu and Apostolakis (1985) in the context of fire growth in a building. It is described further by Chhibber, Apostolakis and Okrent (1991).

It can occur that experimental data become available that might be used to modify a model. In principle, such updating may be effected using Bayesian methods, but this may not be straightforward. In order to apply the Bayesian approach it is necessary to formulate a likelihood function and for a complex model it may not be easy to do this. In this case, one approach may be to use expert judgement methods to formulate a suitable likelihood function.

9.20.13 Results

The results of a hazard assessment should in principle include not only the best estimate of the risk but also a measure of the uncertainty that attaches to this estimate. There are, however, problems associated with providing such measures of uncertainty. These include: the difficulties of principle in assigning uncertainty, particularly to models; the effort required to compute the measures, which may be comparable with that of making the basic estimate; and an inability to make effective use of this additional information in decision-making.

9.21 Risk Criteria

In order to evaluate a risk assessment it is necessary to have appropriate risk criteria. Some of the more philosophical aspects of risk are considered in Chapter 4. The treatment here is confined to a consideration of some of the principles that should underlie the choice of risk criteria and of some of the types of criterion, systems and numerical criterion values used or proposed. Accounts of risk criteria include those given in *Dealing with Risk* (R.F. Griffiths, 1981c), *Risk Assessment. A Report of a Royal Society Study Group* (Royal Society Study Group, 1983) (the RSSG Report), the *Third Report of the Advisory Committee on Major Hazards* (Harvey, 1984), *The Tolerability of Risk from Nuclear Power Stations* (HSE, 1988c) and *Risk Criteria for Land-use Planning in the Vicinity of Major Industrial Hazards* (HSE, 1989c). Selected references on risk criteria are given in Table 9.36.

9.21.1 Royal Society Study Group

The *RSSG Report* sets out some possible quantitative guidelines for risk. It prefaces these by a number of qualifications. The risks considered are primarily risks of death, but in addition some suggestions are also made for criteria for non-fatal risks.

The RSSG define an upper bound of risk above which the risk is 'unacceptable in essentially all circumstances',

Table 9.36 *Selected references on toleration of risk and risk criteria*

Grosser *et al.* (1964); Sowby (1964, 1965); Crowe (1969); Starr (1969, 1970, 1972, 1985); Kletz (1971, 1976d, 1977c, 1980a,b, 1980–, 1981d,f,k,m, 1982e, 1983d,g); R.M. Stewart (1971); NAE (1972); Robens (1972); Sinclair (1972); Sinclair, Marstrand and Newick (1972a,b); Tudor-Hart (1972); Weinberg (1972a); Siccama (1973); Baldewicz (1974); Brook (1974); Hirschleifer, Bergstrom and Rappaport (1974); Koshland (1974); Lawless (1974); Sather (1974, 1976); AEC (1975); Chicken (1975); Linnerooth (1975); Otway (1975); R. Wilson (1975); Ash, Baverstock and Vennart (1976); J.H. Bowen (1976); Gibson (1976a,c,d,f, 1977a,b); C.H. Green and Brown (1976/77, 1978, 1980a,b); Hammond and Adelman (1976); Harvey (1976, 1979b, 1984); Kastenburg, McKone and Okrent (1976); Lowrance (1976); Slovic, Fischoff and Lichtenstein (1976, 1981, 1982); Solomon, Rubin and Okrent (1976); Starr, Rudman and Whipple (1976); Council for Science and Society (1977); F.R. Farmer (1977b); Glaser (1977); Mcginty and Atherley (1977); McLean (1977a, 1982); Mark and Stewart (1977); Rowe (1977); Adcock (1978); Boe (1978); Critchley (1978); HSC (1978c); HSE (1978b, 1981a); Rothschild (1978); Torodahl (1978); Dunster and Vinck (1979); C.H. Green (1979); Nelkin and Pollak (1979); Atallah (1980, 1981b–e); Brett-Crowther (1980a); Conrad (1980); Dierkes, Edwards and Coppock (1980); Dowie and Lefrere (1980): Giarini (1980); Goodin (1980); R.F. Griffiths (1980); Houston (1980); Risk Research Committee (1980); Schwing and Albers (1980); Starr and Ritterbush (1980); F. Warner (1980, 1981a,b); Weaver (1980); Zuckerman (1980); Berg and Maillie (1981); A.V. Cohen (1981); Cotgrove (1981); Fischhoff *et al.* (1981); Harvey (1981); Hildyard (1981); T.R. Lee (1981); McLoughlin (1981); Okrent (1981); Payne (1981); F. Warner and Slater (1981); von Winterfeldt, John and Borcherding (1981); Wu-Chien and Apostolakis (1981); Hohenemser and Kaspersen (1982); Lagadec (1982); Lind (1982); Kinchin (1982); Macgill (1982); W.W. May (1982); O'Riordan (1982); Otway and Thomas (1982); Covello *et al.* (1983); Giannini and Galluzzo (1983); The Royal Society (1983, 1992); Covello (1984); Jouhar (1984); Pierson (1984); Sass (1986); BMA (1987); Ashmore and Shama (1988); Corbett (1988 LPB 82); Cumo and Naviglio (1989); H.J.S. Petersen (1989); Smithson (1989); V.C. Marshall (1991a); Vlek and Keren (1991); Alder and Ashurst (1992); Engineering Council (1992); Philey (1992a); Council (1993); Irish (1993); Melchers (1993b); Melchers and Steward (1993); Song, Black and Dunne (1993)

Risk perception
Douglas (1966, 1982, 1985, 1987, 1990, 1992); Ashby (1997); ICRP (1977a,b); Fischhoff *et al.* (1978); C.H. Green and Brown (1978); Lichtenstein *et al.* (1978); Ravets (1979); Slovic, Fischhoff and Lichtenstein (1980); M. Thompson (1980); Wynne (1980, 1982, 1989, 1992); Fischhoff *et al.* (1981); Helms (1981); Watson (1981); Cotgrove (1982); Douglas and Wildavsky (1982a,b); Otway and Winterfeldt (1982); Fischhoff and Macgregor (1983); E.J. Johnson and Teversky (1984); Slovic, Lichtenstein and Fischhoff (1984); J.G.U. Adams (1985); Pidgeon, Blockley and Turner (1986); Slovic (1986); B.B. Johnson and Covello (1987); R. Wilson and Crouch (1987); Rip (1988); Wildavsky (1988); J. Brown (1989); Sharlin (1989); M. Thompson, Ellis and Wildavskay (1990); Beder (1991); C.H. Green, Tunstall and Fordham (1991); Slovic, Flynn and Layman (1991); Krimsky and Goldring (1992)

Risk communication
MCA (n.d./17); Wynne (1980, 1982, 1992); Dewhurst (1986); Plough and Krimsky (1987); Corbett (1988); Covello and Allen (1988); Covello, Sandman and Slovic (1988); Kasperson *et al.* (1988); Hadden (1989a,b); F.R. Johnson and Fisher (1989); NRC (1989); Otway and Wynne (1989); Siegel (1989); Bord and O'Connor (1990); Handmer and Penning-Rowsell (1990); Covello (1991); A. Fisher (1991); Kasperson and Stallen (1991); B.B. Johnson (1992); AIHA (1983/28)

Natural and man-made hazards
Macdonald (1972); Blume (1978); Burton, Kates and White (1978); M.G. Cooper (1985); C.H. Green, Tunstall and Fordham (1991)
Aircraft: North (1949); M. Hill (1971); Warren (1977)
Buildings: Flint (1981); Holdgate (1981)
Chemicals: McLean (1979, 1981)
Chronic hazards: Travis *et al.* (1987); J.B. Cox (1989)
Flooding (Dutch dikes): van Danzig (1960); Turkenburg (1974); Harvey (1976)
Foodstuffs: McLean (1977b)
Leisure: J. Wilkinson (1981)
Medical: Roach (1970); Leach (1972); H. Miller (1973); Pochin (1975, 1981a,b)
Nuclear radiation: Burhop (1977); Pochin (1983)
Roads: Reynolds (1956); Dawson (1967); Hayzelden (1968); A.D. Little (1968); Jones-Lee (1969); Thedie and Abraham (1969)

Major hazards
Harvey (1976, 1979b, 1984); S.B. Gibson (1978); Lowe (1980); Helsby and White (1985)

Nuclear industry
F.R. Farmer (1979b, 1971); AEC (1975); Weinberg (1976); Orr (1977); Pochin (1983); HSC (1978c); J. Hill (1981); W.L. Wilkinson (1981); Okrent and Baldewicz (1982); T.R. Lee, Brown and Henderson (1984); Franklin (1985); C. Tayler (1985f); Gunning (1987); HSE (1988c)

Conventional energy sources
Orr (1977); HSC (1978c); HSE (1978/4, 1980 RP 11); A.V. Cohen and Pritchard (1980); S. Russell and Ferguson (1980); Ferguson (1981, 1982); Inhaber (1981a,b); K. Thomas (1981); Dunster (1982); IAEA (1984); Fremlin (1985)

Fire, explosion
Melinek (1972 FRS Fire Research Note 950, 1973 FRS Fire Research Note 978, 1974 BRE CP 88/74); North (1973 FRS Fire Research Note 981); Coward (FRS 1973 Fire Research Note 982)

Chemical industry
F.R. Farmer (1971); Kletz (1971, 1972a, 1977a,f, 1980a,b, 1981a); Bulloch (1974); S.B. Gibson (1976a,c,d,f, 1977a,b); Harvey (1976); HSE (1978b, 1981a); de Heer, Kortlandt and Hansen (1980); Livingstone (1979); N.C. Harris (1982, 1986)

Gas terminals
Keeney (1980); Kunreuther, Linnerooth and Starnes (1981)

Offshore (*see* Table A18.1)

Environment
Sewell (1971); Programmes Analysis Unit (1972); Ashby (1976); Barker (1977); Fischoff *et al.* (1978); Kletz (1981b)

Fatality rates
Pochin (1973); Fryer and Griffiths (1978 SRD R110, 1979 SRD R149); Grist (1978 SRD R125) Anon. (1980n); C. Wright (1986)

Risk criteria
NRC (Appendix 28 *Risk* Criteria, *Safety Goals*); Kletz (n.d.b, 1971, 1977a,b, 1980a,b); Provinciate Waterstaat Groningen (1979); S.B. Gibson (1981); Lees (1980a); Lowe (1980); Rasbash (1980b, 1985); R.F. Griffiths (1981b–d); Petkar (1981); D.C. Cox and Baybutt (1982); Matthews (1982); Okrent and Baldewicz (1982); Hagon (1984); Holden (1984); Helsby and White (1985); Ministry of Housing (1985); R. Wilson and Crouch (1987); Directorate General for Environ. Prot. (1988–89); NSW Govt (1990); ACDS (1991); Cameron and Corran (1993)
***Fatal accident rate* (*FAR*):** Kletz (1971, 1978a); B.J. Wilson and Myers (1979); A.F.C. Wallace (1980); Harrod (1981); Lees (1981b)
Value of a life: Hayzelden (1968); Schelling (1968); FRS (1972 Fire Research Note 950, 1973 Fire Research Note 978, 982); Melinek (1974); Linnerooth (1975); Jones-Lee (1976, 1982, 1989); Mooney (1977); BRE (1978 CP52/78); Marin and Psacharoploulos (1982); Slovic *et al.* (1984); Jones-Lee, Hammerton and Philips (1985); Kletz (1985c); Moore and Viscusi (1988); A. Fisher, Chestnut and Violette (1989); Nawar and Salter (1993)
HSE criteria: D.A. Jones (1989); HSE (1988c, 1989c)
Delayed fatalities: R.F Griffiths (1994a)
Ring of igniters: Fallows (1982)

Cost benefit analysis
Jones-Lee (1969, 1976, 1982, 1989); Marin and Psacharopoulos (1982); May (1982); Jones-Lee, Hammerton and Philips (1985); Fleishman and Hogh (1989); Marin (1992)

except perhaps for activities entered into voluntarily or in wartime. It also defines a lower bound below which risks may 'legitimately be regarded as trivial by the decision-maker'. Between these two bounds there lies a region in which the risk needs to be assessed and all reasonably practicable steps taken to reduce it. This is referred to here as the 'three-region approach', as opposed to the point value, approach.

The RSSG suggest that most people regard as insignificant a risk of death below about 10^{-6}/year. This therefore constitutes a lower bound. For the upper bound the RSSG state that few would dissent from the proposition that imposing a continuing risk of 10^{-2}/year is unacceptable. The position is less clear with regard to a risk of 10^{-3}/year. For males only, those between 1 and 20 years of age have an annual risk of death markedly less than this. Therefore pre-existing levels of risk are more likely to cause death than a new imposed risk. The RSSG argue that an imposed risk of 10^{-3}/year can therefore hardly be called totally unacceptable provided that the individual is aware of the situation. The RSSG finally take this value of 10^{-3}/year as the upper bound. The central region contained within these bounds is therefore that where the risk lies between 10^{-6}/year and 10^{-3}/year. It is in this region that the concept of reducing risk 'as far as reasonably practicable' applies. As indicated, the upper bound of 10^{-3}/year is evidently associated with situations in which there is a degree of voluntary acceptance.

The risk criteria described are those that may be used by the decision-maker, particularly the central decision-maker in government. The categorization of a risk as insignificant does not necessarily imply that it will be perceived as such by those affected, but relates rather to the action that the decision-maker should require.

9.21.2 Advisory Committee on Major Hazards

In its First *Report* (Harvey, 1976), the ACMH made the statement

> If, for instance, such tentative conclusions indicated with reasonable confidence that in a particular plant a serious accident was unlikely to occur more often than once in 10,000 years (or – to put it another way – a 1 in 10,000 chance in one year), this might perhaps be regarded as just on the borderline of acceptability . . .

Insofar as the committee was set up following the Flixborough disaster, in which 28 people were killed, it may be assumed to have had in mind a similar accident, say one involving 30 fatalities. The above statement has been taken by a number of parties as a starting point for the development of criteria for societal risk. Otherwise, however, the ACMH proposed little by way of quantitative risk criteria. It did, however, in its Third *Report* (Harvey, 1984) state a number of principles, including the following:

1. The risk from a major hazard to an individual employee or member of the public should not be significant when compared with other risks to which a person is exposed in everyday life.
2. The risk from any major hazard should, whenever reasonably practicable, be reduced.
3. Where there is a risk from a major hazard, additional hazardous development should not add significantly to the existing risk.
4. If the possible harm from an incident is high, the risk that the incident might actually happen should be made very low indeed.

9.21.3 HSE nuclear installations risk criteria

The HSE have published two documents outlining their approach to the development of risk criteria. The first of these is *The Tolerability of Risk from Nuclear Power Stations* (HSE, 1988c). This document gives the following treatment of risk of death to workers and to members of the public. A distinction is made between risk from normal operation, due essentially to radiation dose, and risk from a nuclear accident.

At nuclear installations the actual risk to workers from the average levels of radiation dose lies between about 10^{-4}/year and 2.5×10^{-4}/year. A very small number of workers are exposed to a risk some ten times greater. The figure of 2.5×10^{-4}/year happens to correspond to the risk to workers in heavy manufacturing and mineral extraction and that of 10^{-4}/year to the average for manufacturing industry. The HSE conclude that, broadly, the limit of tolerable risk to a worker is 10^{-4}/year.

On the basis that the risk to a member of the public should be at least an order of magnitude lower than that to a worker, the limit of tolerable risk to a member of the public is taken as 10^{-4}/year. The risk to a member of the public that might be regarded as acceptable, as opposed to tolerable, is then taken 10^{-6}/year. This appears to be a level at

which in general a risk causes little concern. It happens to be approximately the risk of being electrocuted at home and one hundredth of the risk of dying in a traffic accident.

The actual risk to a member of the public from normal operation of a nuclear installation is well below 10^{-5}/year and that from a nuclear accident at an installation designed to Nuclear Installation Inspectorate (NII) principles is about 10^{-6}/year. The risk to a member of the public from both causes is assessed as 10^{-6}/year for most people in the vicinity of the installation, but for a small number it is about 10^{-5}/year and for a very few it may exceed this.

The document does not give a criterion for societal risk in terms of FN curves or the equivalent. Instead, it takes as a measure of societal risk three scenarios: (1) a limiting design basis accident, (2) an uncontrolled release and (3) an uncontrolled release large enough to produce doses of 100 mSv within 3 km. It suggests that the limit of tolerable risk of a considerable uncontrolled release anywhere in the United Kingdom might be about 10^{-4}/year. The assessed risk quoted for such a release is in fact 10^{-6}/year.

9.21.4 The ALARP principle

The HSE nuclear risk document also deals with the question of reducing the risk to a level that is as low as reasonably practicable (ALARP). The reduction of risk in accordance with the ALARP principle is a basic requirement of the Health and Safety at Work etc. Act 1974.

The ALARP principle is illustrated in Figure 9.35. There is some level, above which the risk is intolerable. Above this level, the risk cannot be justified on any grounds and must be reduced. There is another level below which the risk is negligible and no action is required, not even demonstration that the ALARP principle has been applied. Between these two levels lies the region in which there is a requirement to apply the ALARP principle.

9.21.5 HSE land-use planning risk criteria

The other HSE publication on risk criteria is *Risk Criteria for Land-use Planning in the Vicinity of Major Industrial Hazards* (HSE, 1989c). The risk criteria described in this document are strictly for land-use planning of new developments around major hazard installations. They are not intended to be used for (1) siting of a new major hazard installation, (2) new activities on an existing site or (3) an existing major hazard installation and existing development.

As described in Chapter 4, the basic approach to land-use planning adopted by the HSE is to divide the area around a hazardous installation into three zones. In the top zone risk is a major factor, in the bottom zone it is treated as insignificant and in the middle zone it is a consideration and further assessment is indicated.

The risk criteria given are largely determined by the use to which they are put in land-use planning and differ from the conventional criteria, which tend to be for risk of death. Instead the HSE have developed the concept of a 'dangerous dose'. This dangerous dose is effectively an injurious load imposed by some physical phenomenon such as thermal radiation, explosion overpressure or toxic concentration. The dangerous dose is that which will result in the death of a small proportion of the exposed population. It is

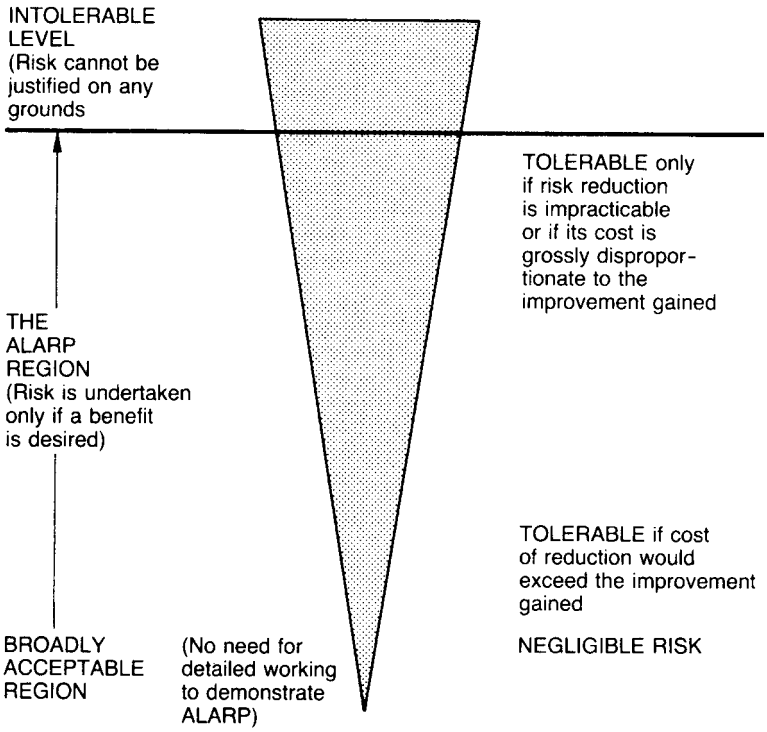


Figure 9.35 *The ALARP principle (HSE, 1988c) (Courtesy of HM Stationery Office. Copyright All rights reserved)*

assumed that the risk to a vulnerable person is an order of magnitude greater than that to the average person.

For the exposed population as a whole, the HSE take as the upper bound for the risk of a dangerous dose or worse 10^{-5}/year and as the lower bound 10^{-6}/year. This implies that these figures are also approximately the risk of death for vulnerable people. For the case where the exposed population contains a high proportion of vulnerable people the lower bound is taken instead as 0.33×10^{-6}/year. The upper bound risk is about one-tenth of the risk of death in a road traffic accident. The lower bound risk is about ten times the risk of death from lightning.

With regard to societal risk, the HSE rehearse the problems of risk aversion and of FN curves. Instead they elect to use a 'judgmental approach', in which qualitative factors are more prominent. The starting point is the individual risk. The element of societal risk is taken into account by applying a harsher judgement to larger developments in the middle zone. These risk criteria are intended to be used in conjunction with a risk assessment based on the 'cautious best estimate' approach.

The application of these criteria to various types of development, which is given in the document, is described in Chapter 4.

9.21.6 Factors restricting choice of individual risk criteria

A difficulty in the selection of risk criteria is that the choice of criteria is liable to appear arbitrary. The description just given of some systems of risk criteria hints at the fact that when account is taken of the various relevant factors, the scope for arbitrary choice is quite severely restricted. This aspect is now explored in more detail.

Considering risk of death, the average risk to a worker in manufacturing industry is about 3×10^{-5}/year. On the assumption that a new plant should be three times safer than the current average, the risk criterion for a worker on a new plant might be taken as 10^{-5}/year.

It is reasonable to assume that the risk to a worker on a potentially affected plant other than the plant under consideration should be less than that to a worker on the latter, and an order of magnitude reduction is often used. On this assumption, the risk criterion for a worker on another plant would be 10^{-6}/year.

Adopting the usual assumption that the risk to a member of the public should be less than that to a worker, the figure of 3×10^{-5}/year might also be taken as an upper bound for a member of the public. The risk of being killed by lightning, which is 10^{-7}/year, is often taken as one that causes little concern. On this basis, the lower bound for risk to a member of the public might be taken as 10^{-6}/year.

A further factor that needs to be taken into account is the risk from a complex of plants. It is assumed that where there is such a complex the risk is increased by a factor of 3.

Then, taking into account (1) new vs existing plants and (2) single plants vs a complex of plants, the risks obtained for a member of the public are as follows:

Single plant		*Complex*	
New plant	*Existing plant*	*New plant*	*Existing plant*
10^{-6}/year	3×10^{-6}/year	10^{-5}/year	3×10^{-5}/year

The highest and lowest risks here correspond exactly to the upper and lower bounds given above.

The foregoing account is given not primarily to suggest a further set of risk criteria, although the values given do not differ greatly from criteria often proposed, but rather to illustrate the fact that by the time account is taken of the relevant factors, the scope for arbitrary choice narrows appreciably.

9.21.7 FN curve criteria of societal risk

Given that a formal risk criterion is used at all for societal risk, the criterion most commonly used is the FN curve. The basic characteristics of FN curves were described in Section 9.19. The account given here is concerned with the parameters to be used in a risk criterion curve.

Like other forms of risk criterion, the FN curve may be cast in the form of a single criterion curve or of two criteria curves dividing the space into three regions – where risk is unacceptable, where it is negligible and where it requires further assessment. The latter approach corresponds to application to societal risk of the ALARP principle and is much to be preferred.

The characteristics of a FN relation are most easily appreciated by considering an FN line. The two defining parameters of such a line are the frequency of a single fatality accident, or intercept on the F axis, and the slope of the line. A characterization of FN curves, whether for actual risks or as risk criteria, has been given by Hagon (1984).

9.21.8 Farmer curve

Before considering the more usual type of FN curve, it is appropriate to refer to the risk criterion curve given by F.R. Farmer (1967b), which pioneered this form of criterion. Figure 9.36 shows the Farmer curve.

As explained in Section 9.19, the quantity plotted on the ordinate of this curve is accident intervals rather than accidents equal to or greater than the defined size.

The argument supporting this criterion (as developed in 1967) is roughly on the following lines. A release of a few thousand curies of ^{131}I constitutes an accident that could cause fatalities and would probably provoke public outcry. Programmes of reactor installation in several countries

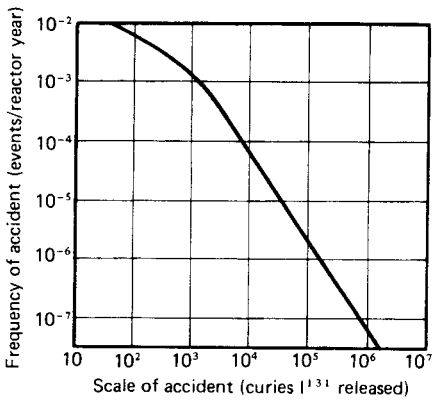


Figure 9.36 *Accident scale–frequency criterion for nuclear power reactors (the Farmer curve) (after F.R. Farmer, 1967b) (Courtesy of the British Nuclear Energy Society)*

will accumulate about 100 reactor-years operation before the turn of the century. The risk of one such event during this period is probably the limit of acceptability. This therefore gives one point on the graph, at the frequency of 10^{-3} accidents per reactor year. The slope of the main part of the graph, for large accidents, is -1.5 (on the log–log plot). This slope implies that if the severity of an event increases by two orders of magnitude, its frequency decreases by three orders of magnitude. This represents a weighting to reduce the probability of large-scale accidents that may be expected to give rise to severe public reaction. The curve on the graph in the smaller accident region represents a reduction in the frequency of small incidents, since numerous small incidents are also likely to cause public concern.

9.21.9 Criteria expressing risk aversion

Reference has already been made to risk aversion in respect of societal risk. The Farmer curve just described is an early illustration of such risk aversion. As mentioned above, a measure of risk aversion is the parameter α defined in Equation 9.19.1. This quantity is known as the 'risk aversion index'. Considering a FN line on a log–log plot, if the slope of the line is $-x$ the risk aversion index α is $1 + x$. A number of authors have discussed the appropriate value of this index, including Okrent (1981), D.C. Cox and Baybutt (1982) and Hagon (1984).

It is argued by Okrent that it is unlikely that society demands a value of $\alpha \geq 1.5$, that one of $\alpha = 2$ is certainly excessive and that even one of $\alpha = 1.2$ may not be of general applicability. On the other hand, as described below, Hagon has shown that at values of α of less than 2 the contribution of large accidents to the average risk tends to become relatively large, or even predominant.

9.21.10 Groningen FN curve risk criterion

An early societal risk criterion utilizing FN curves was that promulgated by the Provinciale Waterstaat Groningen (PWG, 1979), the 'Groningen criterion'. The Groningen criterion is illustrated in Figure 9.37. There are three zones and two bounding curves. In one zone the risk is unacceptable, in one it is acceptable and in one further assessment is required. For accidents with, on average, more than one fatality ($N > 1$) the slope of the two bounding curves corresponds to a degree of risk aversion in which the consequence is raised to the power 2 (N^2).

Some further characteristics of the Groningen criterion have been given by Hagon (1984), using his relations given in Section 9.19. For the upper curve over the range $N = 1$ to $N = 1000$

$$F_1 = 10^{-2}$$
$$F_{1000} = 10^{-8}$$

The risk aversion is therefore given by

$$FN^2 = \text{Constant}$$
$$\alpha = 3$$

Beyond $N = 1000$ the curve is vertical so that $\alpha = \infty$. For the lower curve over the range $N = 1$ to $N = 10$

$$F_1 = 10^{-6}$$
$$F_{10} = 10^{-8}$$

with the same degree of risk aversion. Beyond $N = 10$, the curve is again vertical.

9.21.11 Hagon FN curve risk criteria

Hagon has used his FN curve relations to describe the characteristics of several well known FN curves. His treatment of the Groningen criterion has just been described. For those given in the Second *Canvey Report*, shown in

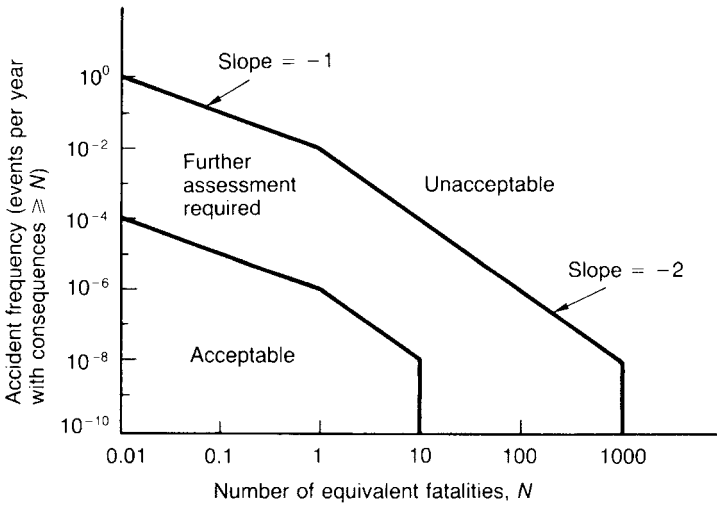


Figure 9.37 *Groningen FN curve risk criterion (Hagon, 1984; after PWG, 1979) (Courtesy of the Institution of Chemical Engineers)*

Figure 9.30 which gives a curve approximating to a straight line, for events up to $N > 1000$ he obtains:

$$F_{10} = 10^{-3}/\text{year}$$
$$F_{1000} = 2 \times 10^{-4}/\text{year}$$
$$\alpha = 1.35$$

This is a low degree of risk aversion.

For the ammonia storage sphere in the *Rijnmond Report*, the FN curves for which are shown in Figure 9.34, Hagon sets a bounding line characterized by $F_1 = 10^{-3}$/year and $\alpha = 2$. He then obtains:

$$F_3^{30} = 2.2 \times 10^{-3}$$
$$F_{30}^{300} = 2.2 \times 10^{-5}$$

and

$$D_1^{30} = 2.4 \times 10^{-3}$$
$$D_1^{3000} = 5.2 \times 10^{-3}$$

This indicates that large accidents are a significant contributor to the average risk of death.

Hagon takes as a prime determinant of the risk aversion index α the parameter F_N^M, which is the frequency of all accidents between one with N fatalities and one with the maximum number M of fatalities. Figure 9.23 shows that F_N^M increases only slowly with N, provided that $\alpha > 1.5$.

Hagon takes as another determinant of α the parameter D. From Figure 9.33 the increase of D with N is slow, provided that $\alpha > 2$.

With regard to the choice of F_N^M, Hagon takes as his starting point the Flixborough disaster, in which 28 men died. If there are assumed to be nationwide in the United Kingdom some 500 installations capable of giving an event such as Flixborough, and if such an event should occur no more often than once in 100 years, then for a single installation:

$$F_N^M = \frac{1}{500 \times 100} = 2 \times 10^5/\text{year}$$

The number of fatalities at Flixborough was 28. He takes the range of fatalities for a major hazard as 30–300, and thus sets $F_{30}^{300} = 2 \times 10^{-5}$/year. He sets $\alpha = 2$, and obtains for single fatality accidents and for total deaths due to the major hazard risk:

$$F_1 = 6.5 \times 10^{-4}/\text{year}$$
$$D_1^{300} = 4.1 \times 10^{-3}/\text{year}$$

9.21.12 Dutch risk criteria

Two more recent sets of risk criteria are the Dutch criteria and the Advisory Committee on Dangerous Substances (ACDS) FN curve. Provisional risk criteria according to Dutch law are quoted by Ale (1991). They are shown in Figure 9.38

9.21.13 ACDS FN curve

The ACDS *Transport Hazards Report* (1991) also gives a FN curve, shown in Figure 9.39. Arguments in support of the curve are given in detail in Appendix 6 of the report.

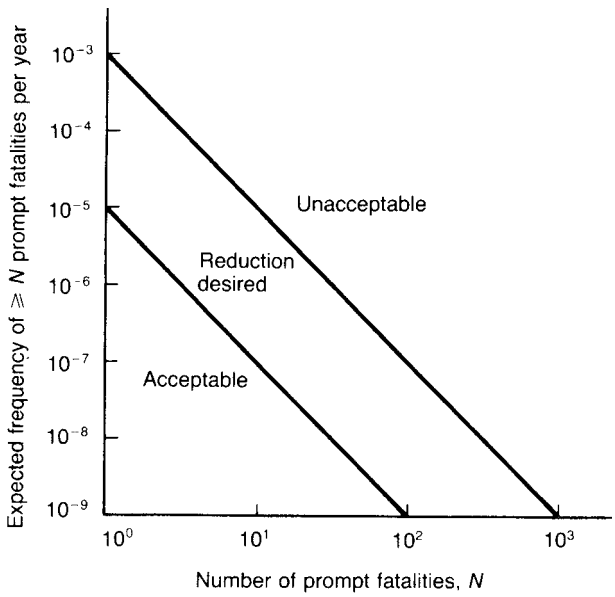


Figure 9.38 *Some risk criteria for the Netherlands (after Ale, 1991; Pasman, Duxbury and Bjordahl, 1992) (Courtesy of Elsevier Science Publishers)*

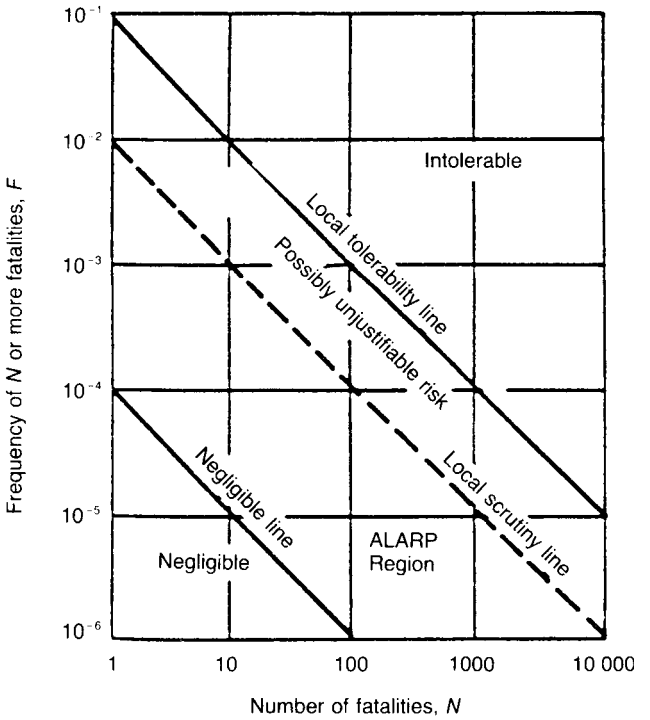


Figure 9.39 *ACDS FN curve risk criterion (after Advisory Committee on Dangerous Substances, 1991)*

9.21.14 Need for criteria in hazard assessment

In the method of hazard assessment described by Kletz (1971) he effectively recognizes four situations in respect of the probability of an event leading to a hazard:

(1) The probability of the event is low.
(2) The probability of the event can be made low by application of a standard or code of practice.
(3) The probability of the event can be made low by the application of measures that can be shown by a simple risk analysis to be of equivalent safety to the normal standard or code of practice.
(4) The probability of the event must be assessed quantitatively and must be reduced to conform to the risk criteria by measures indicated by the analysis. For a straightforward case use is make of a simple risk analysis while for a more complex one it is necessary to resort to a more detailed method such as fault tree analysis.

Risk criteria are needed mainly for the fourth case. The second and third cases are considered first.

9.21.15 Standards and codes

If the probability of the event that may lead to realization of the hazard is not intrinsically low, nevertheless it may often be reduced to a low level by the use of an appropriate standard or code of practice.

An example given by Kletz is that there is some probability of overpressure in a pressure vessel, but the use of pressure relief valves as specified in standards and codes for pressure vessels reduces this probability to a low level. Another example is that electrical equipment has some probability of acting as a source of ignition, but the application of codes for hazardous area classification and equipment safeguarding results in a low value of this probability.

The main *caveat* to be made here is that where major hazards are concerned it should not be assumed that the use of the standards and codes is sufficient.

9.21.16 Equivalent risk

It is sometimes not appropriate, or even possible, to use a standard or code. In this case it may be possible to devise an alternative method that can be shown to have a degree of safety at least equivalent to the standard or code. A simple risk analysis is carried out to demonstrate this. The analysis by Kletz (1974a) of the use of trips instead of pressure relief valves described in Chapter 13 is a case in point.

9.21.17 Individual and average risk

Before considering the evaluation of the more complex analyses mentioned using suitable risk criteria, there are some further preliminary points to be made.

In considering risk, it is necessary to distinguish between the average risk run by a group of people, whether employees or public, and the higher risk that may be run by some individuals within the group. Thus some employees may be exposed to a higher risk because the plant on which they work is more hazardous and some members of the public may be exposed to a higher risk because they live nearer the works. There is fairly general agreement that there should be a limit to the risk run by any individual.

Thus it is not sufficient to achieve a low average risk; it is necessary also to reduce to a minimal level the risk to the most exposed individual. In other words the risk to that person should not be 'lost' by combining it with the risk to a larger group most of whom are much less exposed.

9.21.18 Death and injury

Most treatments of risk deal primarily with the risk of death. This may appear somewhat arbitrary, but there is justification for this approach. Data on fatalities are recorded and are relatively straightforward. For other levels of injury, however, there can be problems. Often the data are not available, but even if they are, there tend to be difficulties in interpreting them. Moreover, for any given activity in industry there tends to be a relationship between fatalities and other injuries. The work of Heinrich (1959) on this ratio has been described in Chapter 1.

Measures that reduce deaths from a particular hazard tend to reduce injuries in proportion and it is this reduction that is important. The use of death rate as the main practical criterion does not therefore imply any disregard of the personal tragedy arising from serious injury.

Several indices of industrial injury risk are used in the literature. The lost time accident rate is expressed as the number of accidents per 10^5 exposed hours; this period corresponds approximately to a working lifetime. Fatal accidents are much less frequent and in order to avoid inconveniently small numbers the FAR is defined as the number of deaths per 10^8 exposed hours; this roughly corresponds to the number of deaths over a working lifetime of 1000 persons. Another index that is useful in relation to general fatality risks is the death rate per annum.

It should be recognized, however, that the use of fatality risk is not universally accepted as the most appropriate approach, and there is considerable literature on the subject. Some hazards are particularly likely to give rise to delayed, as opposed to prompt, deaths or to serious injury. A release of radioactivity from a nuclear reactor may have the potential to cause many deaths that are predominantly delayed.

9.21.19 Engineering feasibility

There is obviously a limit to the degree of plant reliability that can be achieved even by the best engineering practice and, equally important, to the degree of confidence that can be placed in estimates of that reliability.

A figure frequently quoted for the reliability to which plants can be engineered is a hazard rate for a major accident of 10^{-5} events/year. This is the figure given by J.H. Bowen (1976) from a nuclear industry perspective. The reason that it is difficult to achieve lower hazard rates is that at this level the risk begins to be affected by rather improbable failures and by dependent failures.

In this respect, a distinction may be made between a risk which is assessed as 10^{-5}/year as a single figure and a one which is also assessed as 10^{-5}/year but as the product of two separate risks of 10^{-2}/year and 10^{-3}/year; insofar as the two latter values represent figures that are known to be achievable in engineering terms, the second of the two risks of 10^{-5}/year may be considered to be a more robust estimate.

9.21.20 Value of a life

One criterion for evaluating measures available to reduce risk is the value of a life. A general discussion of this concept, and its difficulties, has been given in Chapter 4. The account here is confined to an overview of the principal approaches and of the values that emerge from them.

The cost of accidents and the cost-effectiveness of safety measures were major concerns of the Robens Committee (Robens, 1972). The *Robens Report* itself attempted to assess the cost of industrial accidents to the nation. The committee also supported work by Sinclair, Marstrand and Newick (1972a,b) on the cost-effectiveness of approaches to industrial safety. The problem is an important one and there is a large literature on the subject (e.g. National Academy of Engineering, 1972).

Some of the methods that can be used to estimate the value of a life have been reviewed by Melinek (1974 BRE CP88/74) and Kletz (1976d). The following account is based on their work and the figures quoted from it are taken unchanged and reflect the value of money at that time. The methods that they describe may be summarized as (1) future production, (2) administrative decisions, (3) consumer preference, (4) court awards and (5) life assurance.

Thus one method of assessing the value of a life is to calculate the future production or services which an individual may be expected to give to the community. A variant of this is to estimate future earnings, although these are not synonymous with the value of the work done. Most estimates of the value of future production lie in the range £10,000–£100,000. The Road Research Laboratory has given an estimate of £15,000 (R.F.F. Dawson, 1967).

There are many administrative decisions made by government that effectively set a particular value on life. Mellinek quotes:

Worker safety	£15,000–£20 million
Consumer safety	£0–£20 million
Medical care	up to £20,000

Similarly Kletz quotes:

Agriculture	£2000
Steel handling	£200,000
Pharmaceuticals	£5 million

The value set in medical work seems to be particularly low. Leach (1972) has shown that lives can be saved for very small expenditures:

Lung X-ray machines for older smokers	£400
Cervical cancer screening	£1400
Artificial kidney	£9500

Another approach is based on consideration of consumer preference. The following illustration is given by Melinek for the implicit valuation put on his own life by a pedestrian who crosses the road on the surface instead of using the safer subway:

Probability of being killed crossing a road	$\approx 10^{-8}$
Extra time taken by using subway	$\approx 15\text{ s} = 0.004\text{ h}$
Value which people put on own time	$\approx$ £0.25/h
Value of a life	$\approx \dfrac{0.25 \times 0.004}{10^{-8}} =$ £100,000

The value that people put on their own time is taken from transport studies. The value of a life as obtained from more extensive studies by the FRS is, as described by Melinek, about £50,000.

The damages which courts award for death or injury often include a sum for the reduction of life expectancy and are thus another means of estimating the value of a life. It has also been suggested that the value of a life may be determined from the sums covered by life assurance.

There are quite serious objections to some of these approaches. In the case of the valuation of life in terms of the value of the person's future production, the *reductio ad absurdam* is that this criterion puts a zero value on the life of a retired person. Society, however, is prepared to pay to preserve that life. Consumer preference seeks an objective basis in what people actually do, but hardly appears to reflect the way they actually think. Court awards set a notoriously low value on life expectancy and are thus a poor guide. Life assurance is taken out to protect dependants or as an investment and is not intended to compensate for death. The values implied in administrative decisions show a very wide spread and again are far from satisfactory as a guide.

A rather different, and more relevant, approach is described by Kletz (1976d). This is to consider the cost of achieving the risk target that he uses for process plants. He estimates this cost as equivalent to about £1 million per life and suggests that in general this is a reasonable figure to take as the value of a life. A valuation less than £100,000 would hardly be acceptable, while one more than £10 million would seem extravagant.

The value of a life criterion is applied as follows:

$$v = \frac{c}{h} \qquad [9.21.1]$$

where c is the annual cost of eliminating the hazard (£/year), h is the hazard rate (deaths/year) and v is the value of a life (£/death avoided). Thus, for example, if in a given case a particular hazard is assessed as presenting a hazard rate of 10^{-4} deaths/year, if the value of a life is taken as £1 million and if £1 million capital expenditure is equivalent to £200,000/year recurrent expenditure, then the application of the criterion indicates that it is appropriate to spend up to £20/year to eliminate the hazard.

9.21.21 Comparisons of process and other risks

Whereas the risk to which a member of the public is exposed from a hazardous installation is an involuntary one, it is generally considered that to some degree at least, an employee accepts voluntarily the risk associated with work on the plant.

Writers on hazard analysis such as Kletz (1971) and S.B. Gibson (1976a) have compared the risks to employees on process plant with other risks accepted voluntarily or borne involuntarily. Following Kletz (1976d) some data on voluntary and involuntary risk are

	Fatality rate (deaths/person-year)
Voluntary risk	
Taking a contraceptive pill[a]	2×10^{-5}
Playing football[b]	4×10^{-5}
Rock climbing[b]	4×10^{-5}
Car driving[c]	17×10^{-5}
Smoking (20 cigarettes/day)[b]	500×10^{-5}
Involuntary risk	
Meteorite[d]	6×10^{-11}
Transport of petrol and chemicals (UK)	0.2×10^{-7}
Aircraft crash (UK)[a]	0.2×10^{-7}
Explosion of pressure vessel (USA)[d]	0.5×10^{-7}
Lightning (UK)[e]	1×10^{-7}
Flooding of dikes (The Netherlands)[f]	1×10^{-7}
Release from nuclear power station (at 1 km) (UK)	1×10^{-7}
Fire[g]	150×10^{-7}
Run over by vehicle (UK)	600×10^{-7}
Leukaemia[a]	800×10^{-7}

[a] S.B. Gibson (1976c); [b] Pochin (1975); [c] Roach (1970); [d] Wall (1976); [e] Bulloch (1974); [f] Turkenburg (1974); [g] Melinek (1974 BRE CP 88/74).

The validity of such comparisons has been discussed in Chapter 4.

9.21.22 Computation of risk

The risk of an individual may be formulated in simple terms as:

$$r = \frac{1}{N}\sum_{i=1}^{n} x_i f_i \qquad [9.21.2]$$

where f_i is the frequency of accident type i, r is the individual risk of death, x_i, is the number of deaths for accident type i, n is the number of types of accidents and N the total number of persons at risk.

The calculation is concerned with the risk to the individual. All accidents that might have a significant effect on this individual risk should be taken into account. The estimate should not be distorted by inclusion of numbers of people who have a significantly lower exposure.

Often the relationship for individual risk is more complex than Equation 9.21.2. The ACDS *Transport Hazards Report* (1991) contains a number of examples of the more complex formulations necessary in certain cases.

9.21.23 Application of risk criteria

The foregoing treatment has outlined some approaches to the setting of individual and societal risk criteria. An account is now given of some of the practicalities of engineering design utilizing these and other criteria.

The treatment for risk to employees essentially follows the systems developed by Kletz (1971) and S.B. Gibson (1976a). Their approach is based on the use of hazard analysis and of the FAR criterion, as described in Section 9.2. For, say, an overall FAR of 3.5 the target value for a given plant hazard is 0.35, or one-tenth of the overall value. If some particular jobs on a process are more subject to this hazard than others, then the FAR is applied to the more hazardous ones; it is not averaged over all the jobs. Thus no one is exposed to a risk higher than the target value.

This *primary criterion* of maximum risk must normally be met and any expenditure required to meet it must be incurred.

It is not necessarily enough, however, to meet the FAR criterion. It still remains to determine whether all that is 'reasonably practicable' has been done to ensure safety. For this, use is made as a *secondary criterion* of the concept of the value of a life. The value of a life criterion is applied to evaluate additional expenditure aimed at eliminating hazards and reducing risk.

Various figures have been given for the value of a life for use in this context. As described in Section 9.21.20, the value suggested for the chemical industry by Kletz when he wrote in the mid-1970s was £1 million. Publications in the recent past, say 1990, have quoted for a wider range of activities a value of about £3 million.

This approach represents the practical application of the ALARP principle.

9.21.24 Safety improvement

It is often suggested that it would be unfortunate if the adoption of particular risk criteria was to lead to the situation where there ceased to be any improvement in safety standards. In fact the system described, based on the FAR, does tend towards a continuous improvement in safety standards provided the system is universally applied, that factors other than the plant design, particularly the standard of management, do not deteriorate and that the target FAR used is the moving average for the industry. For, while it is then not accepted that any plant have an FAR worse than the current average, some will have one which is better, so that the average will gradually improve. Moreover, the use of the value of a life as a secondary criterion injects a further degree of improvement. There is therefore a ratchet effect that tends to raise standards.

9.21.25 Allocation of resources

The problem of expenditure on safety measures is one of allocation of resources and of cost-effectiveness. As already indicated, the administrative decisions made by government and industry imply a wide range of valuations of human life.

Some of the examples quoted do at least prompt the question whether the chemical industry perhaps spends too much on safety. This may be so, but the hazards of the chemical industry tend to provoke a strong reaction and it is doubtful if much relaxation would be tolerated. This is doubly so following disasters such as that at Bhopal.

Moreover, it is probably of value to the community as a whole to have an industry that despite the high intrinsic hazards of its materials and processes is able to pioneer methods of improving control of hazards and to achieve high levels of safety.

Nevertheless, the allocation of resources to safety is a legitimate subject for public debate. The chemical industry can only try to respond responsibly to this.

9.22 Guide Assessments

The arrangements for the control of major hazards in the United Kingdom were described in Chapter 4. It was mentioned there that in order to give advice to local planning authorities the HSE has developed assessment methods for LPG and for chlorine installations.

An outline approach to assessment for emergency planning for a chlorine release has been given by the UK Chlorine Producers under the auspices of the CIA. The CIA has also issued a Control of Industrial Major Accident Hazards (CIMAH) guide for ammonia. Other CIMAH guides include those on LPG by the Liquefied Petroleum Gas Industry Technical Association (LPGITA), on liquid oxygen by the British Compressed Gases Association (BCGA) and on ammonium nitrate by the Fertilizer Manufacturers Association (FMA). These guide assessments are now described in turn. Some of the features mentioned draw on material described in Chapters 15–18.

9.22.1 HSE LPG methodology

The HSE methodology for the hazard assessment of LPG has been described by Crossthwaite (1984, 1986) and its further development has been described by Clay *et al.* (1988). It is embodied in the program RISKAT. The assessment has been carried out as part of the work done by HSE on their advice to local planning authorities on consultation distances. The overall approach taken is that described in the *Third Report* of the ACMH that states:

> It seems reasonable to aim for a separation which gives almost complete protection for lesser but more probable accidents and worthwhile protection for major but less probable accidents.

In applying this principle the HSE has judged that releases due to pipework failure fall in the first category and fireballs and vapour cloud explosions (VCEs) fall in the second.

The events considered by Crossthwaite (1984) are shown in Table 9.37. For thermal radiation from a fireball, the effects of different levels of received radiation are taken to be:

	kJ/m^2
50% fatalities	700
Blistering of exposed skin	200
Blistering of skin (threshold)	100

and of explosion overpressure:

	psi
5% fatalities	5
Injury due to flying glass	1
Injury but very unlikely to be serious	0.7

The distances at which and the areas over which these levels of effect are estimated to occur for the more serious accidents such as a release of 100 te of LPG are shown in Table 9.38.

The guidelines on consultation distances issued by the HSE on the basis of such assessments are described in Chapter 4.

9.22.2 HSE chlorine methodology

The HSE methodology for the hazard assessment of chlorine has been described by Pape and Nussey (1985). It is embodied in the program Risk Assessment Tool (RAT), now RISKAT. The type of installation considered is shown in Figure 9.40. The listing of hazard scenarios given is shown in Table 9.39. These releases were developed as shown in Figure 9.41 and the consequences analysed as

Table 9.37 *HSE guide assessment on LPG installations: hazardous events (after Crossthwaite, 1984)*

Event	*Consequences*	*Likelihood*
Small flange leak	Local effects only. No off-site hazard	Considerable number each year
Severe pipe leak (guillotine rupture)	If ignition occurs on site, then off-site consequences unlikely to be serious. If ignition occurs off site, a flash fire would injure persons in and near the cloud	Average of about 1/year in UK
BLEVE	High levels of thermal radiation at substantial distances from point of release	Two incidents known to have occurred in UK
Vessel rupture	Flash fire: persons within the (quasi-instantaneous) cloud likely to be killed. Explosion: this will have serious effects at substantial distances from release	No history in UK

Table 9.38 *HSE guide assessment on LPG installations: physical effects from a 100 te release of propane (after Crossthwaite, 1984)*

A Fireball from a BLEVE

Thermal radiation (kJ/m^2)	*Distance from installation* (m)	*Area of land* (hectacres)
(Fireball radius)	107	3.6
700	200	12.6
200	380	45
100	530	88

B Explosion of a vapour cloud

Overpressure (psi)	*Distance from installation* (m)	*Area of land* (hectacres)
5	176	9.7
1	513	83
0.7	675	143

shown in Figure 9.42. Some of the principal assumptions used in the analysis are given in Table 9.40.

The hazard scenarios to be considered were simplified by reducing the pipe failures to two cases: guillotine fracture with both ends open, and a split equivalent to a hole of half the pipe size. Each release was expressed as a vapour flow rate. It was assumed that small releases from pipes would vaporize completely. The justification for this was that for unbunded releases the SPILL computer code for vaporization predicts that the vaporization rate quickly reaches the release rate.

For convenience, large instantaneous releases were treated as pseudo-continuous. A rule of thumb was used that a release over 10 te is equivalent to a continuous release of 1.5 times the actual release with a duration of 10 min, and that smaller releases have an effective duration of 5 min. The heavy gas dispersion was modelled using the CRUNCH computer code for dispersion of a continuous release of heavy gas.

The results for the base case studied are shown in Table 9.41. They show that very close to the plant the principal risks are from gasket failures, pipe splits, coupling/hose failures and releases from the vaporizer unit. At 200 m, it is the last three that are the main risks, while at 300 m and beyond the risk of major vessel failures becomes dominant, with a contribution from uncontrolled gasket failures and pipe splits. A large proportion of the risk beyond 200 m occurs with Pasquill category F weather.

The assessment includes a sensitivity analysis on the following features:

(1) plant size;
(2) vessel failure rate;
(3) gasket size;
(4) proportion of time outdoors;
(5) ventilation rate;
(6) evacuation time;
(7) gas toxicity.

A plant larger than the base case was studied. The increase in risk was roughly proportional to the change in the numbers of components. A 10-fold increase in the vessel failure rate had a strong effect on the risks in the far field, doubling the range of the 10^{-7}/year risk. The effect of reducing gasket thickness was to cut release rates by a factor of 4 and to reduce risks at short ranges. The proportion of time spent outdoors was varied from 0 to 100%. Zero time outdoors gave results little different from the base case, while 100% time outdoors increased the risk by a factor of 2 at intermediate distances. Ventilation rate increases by factors of 4 in weather category D and 2 in category *F* resulted in risks at intermediate distances which were 2 or 3 times the base case, while decreases of the rate to 0.5 in D/2.4 weather and a halving of the rate in *F* weather gave reductions in the risk of up to 4 at intermediate distances. The effect of increasing to 60 min the time taken to evacuate the building after passage of the cloud was to increase the risk at intermediate distances by a factor of about 2.5. For gas toxicity several relations were investigated. The use of a toxicity estimate by ten Berge and van Heemst instead of the Dicken value had a dramatic effect on risks, reducing the range of the 10^{-7}/year risk from 750 to 300 m. In addition to the results given in Table 9.41 the results were also presented in the form of risk contours on a typical site plan and of a FN curve.

9.22.3 UKCP chlorine emergency planning guidelines

Guidelines for chlorine emergency planning are given in *General Guidance on Emergency Planning with the CIMAH Regulations for Chlorine Installations* by the UK Chlorine Producers (UKCP) (CIA, 1986) (the UKCP *Chlorine Guide*);

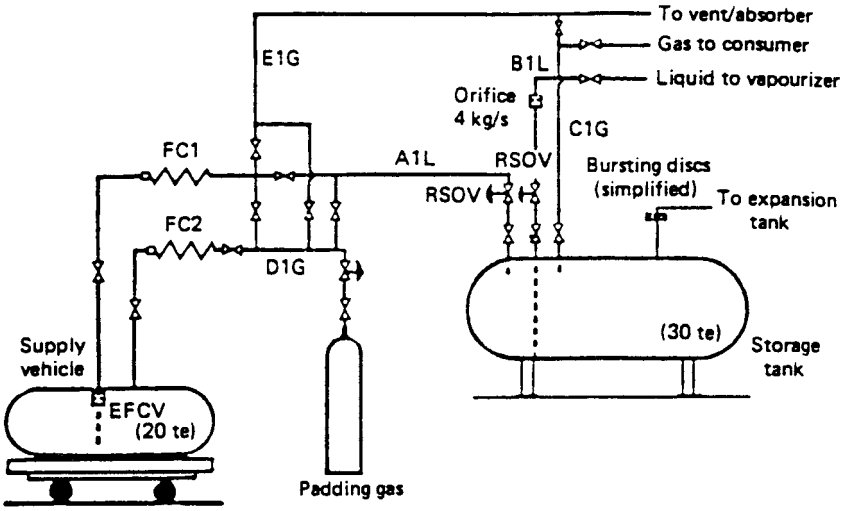


Figure 9.40 *HSE guide assessment on chlorine installations: typical installation (after Pape and Nussey, 1985) (Courtesy of the Institution of Chemical Engineers)*

an extract (CIA, 1989) is given in Lees and Ang (1989b). Although the guidelines are intended primarily for emergency planning, it is explicitly stated that the methods given may also be helpful in producing a safety case.

The type of installation considered is shown in Figure 9.43. Typical equipment and inventories at the installation and the process activities are shown in Table 9.42, Sections A and B, respectively. The steps in the hazard assessment are given in Section C of the table. A list of typical incidents to assist in hazard identification is given in Section D. The summary of possible incidents given in the guide and the interpretation of the terminology are given in Table 9.43, Sections A and B, respectively.

The guide gives, in addition, methods of estimating the emission rate and gas dispersion, using for the latter overlays that can be placed on a map of the site, and data on gas toxicity.

9.22.4 CIA ammonia CIMAH guidelines

The CIMAH Safety Case: Ammonia by the CIA (1988 PA9) (the CIA *Ammonia Guide*) gives guidance for that substance. The main body of the CIA *Ammonia Guide* is largely concerned with the safety report itself. It says relatively little about the frequency of events, but it gives in Chapter 5 a set of release scenarios for different storage conditions and some guide to toxic concentration estimates.

The guide contains a detailed table (15 pages) of causes of release. It gives five main release scenarios as follows: Scenario 1, release of liquid from a hole in pressurized storage; Scenario 2, release of liquid from a hole in refrigerated storage; Scenario 3, release of vapour from a relief valve; Scenario 4, failure of a refrigerated bunded storage tank; and Scenario 5, a spill of refrigerated liquid ammonia onto water. For the first two continuous releases, two flows (10 and 40 kg/s) are considered, and for the relief valve a flow of 6 kg/s is considered. In the fourth scenario, two subscenarios are considered: (1) a failure near the top of the tank and (2) a failure near the bottom; in the latter case a flash evaporation of 5 te is estimated. In the fifth scenario the evaporation rate is taken as 50 kg/s during the 2 min of the spill. Results are given without and with allowance for plume rise. The guide gives estimates of the ground level concentration of ammonia for the five scenarios, including the results given here in Table 9.44.

9.22.5 LPGITA LPG CIMAH guidelines

Guidance for LPG is given in *A guide to the writing of LPG safety reports* by the LPGITA (1988 GN1) (the LPGITA *LPG Guide*).

The LPGITA LPG *Guide* deals in the main body largely with the safety report. It has relatively little on the frequency of events, but it gives in Appendix 2, a set of graphs based on simplified hazard models for propane, butane and LPG.

These models appear broadly similar to those given in the Second *Canvey Report* and by Considine and Grint (1985) and the graphs are similar in form to those given by Grint (1989). The graphical correlations cover gas flow and two-phase flow from holes, distance to the LFL, mass of gas in cloud formed, distance to given levels of thermal radiation from a fireball, length of a jet flame and distance to given levels of thermal radiation from such a flame and distance to given overpressures from a vapour cloud explosion. There are also tables listing the injury effects at these levels of thermal radiation and overpressure.

9.22.6 BCGA liquid oxygen CIMAH guidelines

A method for estimating the Off-site Risks from Bulk Storage of Liquid Oxygen (*LOX*), by the British Compressed Gases Association (BCGA, 1984) (the BCGA *Guide*), gives guidance for that substance. The hazard of liquid oxygen is quite different from that for conventional flammables or toxics. Essentially it is the hazard due to enhancement of flammability in an oxygen-enriched atmosphere. This effect is discussed in Chapter 16.

The BGCA *Guide* deals with (1) the consequences of oxygen enrichment, (2) the chance of being injured, (3) the

Table 9.39 *HSE guide assessment on chlorine installations: hazard scenarios[a] (after Pape and Nussey, 1985) (Courtesy of the Institution of Chemical Engineers)*

Item	*Event*[b]	*Release* (kg/s)	*Duration*[d] (min)	*Frequency* (failures $\times 10^6$/year)	*Comments*
Storage vessels; only 1 live at once; typical stock 20 te	Burst	50[c]	10	1	Over bund, pseudo-plume
	Burst	25[c]	10	1	Into bund, pseudo-plume
	50 mm hole, L	25[c]	10	1.6	Pseudo-plume
	50 mm hole, G	6.4	20	2.4	2 × flash
	25 mm hole, L	19	8.8	3.2	
	25 mm hole, G	1.6	30	4.8	2 × flash
	13 mm hole, L	5	30	4	
	13 mm hole, G	0.25	30	6	
	6 mm hole, L	1.3	30	16	
	6 mm hole, G	0.06	30	24	
Tanker vessels	*Neglect*: only on site 2% of time, so probability of failure on site much less than for static tanks				
Other vessels					None on site
Pipelines, guillotine fractures	A1L (10 m)	1	5(C)	0.6	Tanker EFVC[h] works, live 2% of time
		9	20	0.006	Tanker EFVC fails, failure 10 × B1L/m[e]
	B1L (40 m)	4	5(C)	12	Normally live, limited to 4 kg/s by orifice plate
		4	20	0.12	
	C1G (20 m)	1	20	6	Normally live
	D1G (20 m)	1.25	20	0.3	Live as A1L[f]
	E1G	1.25	20	0.15	Live 0.1%; 10 × failure rate
Pipe splits	A1L	5	20	6	EFVC on tanker not actuated
	B1L	4	5(C)	120	
	C1G	0.25	20	60	
	D1G	0.25	20	3	
	E1G	0.25	20	1.5	
Gaskets, equivalent 9 mm diameter holes, 3 mm thick, $\frac{1}{4}$ of circumference	A1L	2.4	20	17	17 joints, live 2% of time, failure 10 × normal rate
	B1L	2	5(C)	220	47 joints (3 below RSOV so 'uncontrollable')
		2	20(U)	15	
	C1G	0.13	20	60	12 joints
	D1G	0.13	20	9	9 joints, live as A1L
	E1G	0.13	20	1.3	26 joints
Transfer coupling/ hose	FC1	1	5(C)	150	50 operations[g]
		9	20	1.5	EFVC fails
	FC2	1.25	20	150	50 operations[g]
Other vaporizer	Failure leads to liquid from	4	5(C)	100	
	B1L	4	20(U)	1	

[a] In deducing source terms, due account is taken of the possibilities for forward and back flow, and the differences between normally live and intermittent use items.
[b] L, liquid; G, gas.
[c] Equivalent continuous release.
[d] C, controlled by remotely operated shut-off valve (RSOV); U, RSOV fails or absent.
[e] Pipe used intermittently. Failure rate assumed to be 10× that of normal pipeline, then multiplied by fractional use.
[f] Pipe live when AIL is live.
[g] 50 operations per annum.
[h] EFVC, excess flow valve cut off.

dispersion of oxygen vapour and (4) the probability of the failure event and gives (5) examples of release and their range of hazard. It contains appendices on (1) the effect of oxygen enrichment on the burning characteristics of cloth materials, (2) the potential for low temperature and wind chill to cause injury, (3) the factors affecting the number of casualties, (4) the principles for validation of storage tank design and (5) release rate calculations and dispersion estimates.

The *Guide* treats three representative scenarios: (1) release of liquid from a hole in a 2 in. pipe, (2) release of liquid

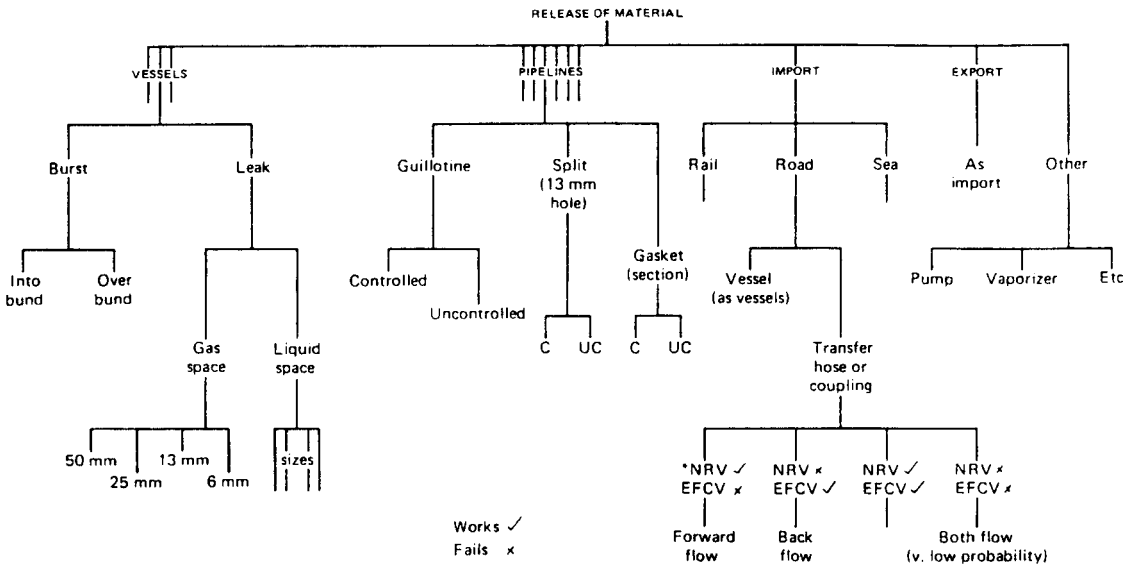


Figure 9.41 *HSE guide assessment on chlorine installations: releases (after Pape and Nussey, 1985) (Courtesy of the Institution of Chemical Engineers)*

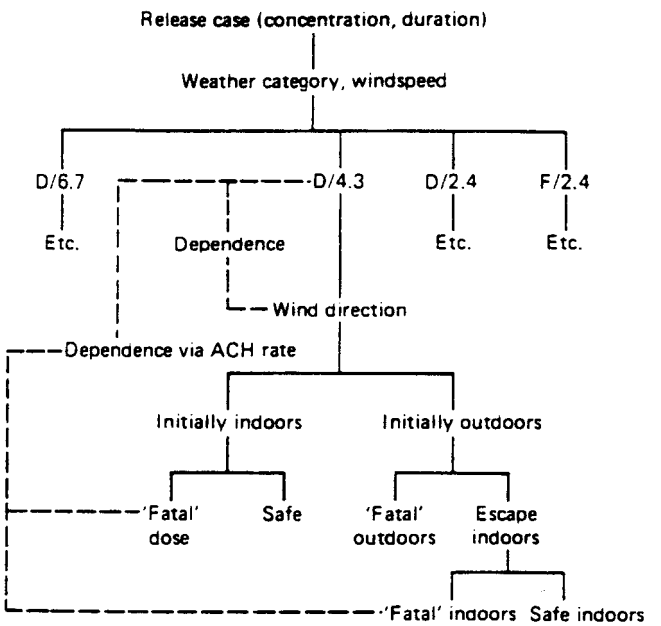


Figure 9.42 *HSE guide assessment on chlorine installations: consequences of release (after Pape and Nussey, 1985) (Courtesy of the Institution of Chemical Engineers)*

Table 9.40 *HSE guide assessment on chlorine installations: key assumptions (after Pape and Nussey, 1985) (Courtesy of the Institution of Chemical Engineers)*

A Failure frequency[a]

Vessels[b]
Frequency of near instantaneous release of whole contents $= 2 \times 10^{-6}$/year

Frequency lesser releases $= 6 \times 10^{-5}$/year partitioned as follows:

Equivalent hole diameter (mm)	*Frequency*
50	4×10^{-6}/year
25	8
13	10
6	40

and

Gas space 60%, liquid space 40%

Pipework
Frequency of guillotine fracture on 25 mm pipework = 0.3×10^{-6} years
Frequency of lesser releases (equivalent to 13 mm hole) = 0.3×10^{-5} years

Gaskets[c]
Frequency of failure for 0.6 mm thick gaskets $= 3 \times 10^{-6}$/year
Frequency of failure for 3 mm thick gaskets $= 5 \times 10^{-6}$/year

Tankers
Probability of failure of coupling/hose $= 3 \times 10^{-6}$/operation
Probability of failure of excess flow valve = 0.01/demand
Frequency of failure of tanker vessels same as vessels given above, but with allowance made for time on site

B Release duration

Vessels
For lesser releases duration is 30 min or time taken to release all the contents, whichever is less[d]

Pipework
For automatic shut-off duration[e] = 1 min
For remote manual shut-off duration[e] = 5 min
For local manual shut-off duration = 20 min

C Release rate

Vessels
For vessel bursts over bund, 100% of release vaporizes
For vessel bursts directed into bund, 50% vaporizes

Pipeline
For pipeline release, 100% vaporizes
For two-phase flashing flow from pipeline guillotine fracture in a 25 mm internal diameter pipe with flow driven by chlorine vapour pressure, flow rate = 4 kg/s
For single-phase liquid flow from tanker coupling failure in 25 mm pipe driven by padding pressure, flow rate = 9 kg/s
For single-phase liquid flow from pipework in 13 mm hole in pipe, flow rate = 4 kg/s

D Release dilution

For releases from pressurized containment initial release is diluted by a factor of 10

E Weather conditions

Pasquill category/ wind speed (m/s)	*Probability*
D/2.4	0.30
D/4.3	0.24
D/6.7	0.29
F/2.4	0.17

F Gas dispersion

Gas dispersion calculated using CRUNCH heavy gas dispersion model. Concentrations within the plume predicted by this model are assumed to be Gaussian, concentrations outside the plume are not considered. During the time of passage of the plume, the concentration at a particular location is assumed to be uniform for the duration of the release

G Modification of exposure

Probability of being initially outdoors = 0.1 Pasquill D
= 0.01 F

For person initially outdoors, probability of escape indoors after receiving significant dose:

Concentration outdoors (ppm)	*Probability of escape indoors*
>1000	0
570–1000	0.2
140–570	0.8
<140	1

Evacuation occurs 30 min after arrival of cloud, or later if cloud persists more than 30 min

H Effect of shelter

Concentrations indoors calculated using a single exponential stage model with following values for the product of the ventilation rate constant λ and the mixing efficiency factor k[f]:

Pasquill category/wind speed (m/s)	$k\lambda$(h^{-1})
D/2.4	0.7
D/4.3	1.0
D/6.7	1.5
F/2.4	0.5

I Gas toxicity

Significant exposure is $C^{1.67}t \geq 20{,}000$, equivalent to the Dicken 'fatal' dose

Threshold of significant dose is 140 ppm for 5 min

[a] Failure rates are based on aggregated data from various sources modified by judgement. Rates used are for sudden failures, that is leaks which can develop into major failures before preventive action can be taken.
[b] Vessel failure includes events up to and including the first flange on any nozzle or penetration.
[c] Gasket failure means loss of one section between two adjacent bolts. It should be checked whether the gasket internal diameter equals that of the pipeline. Actual frequency may depend on inspection and replacement practices.
[d] For leaks in gas space, the available contents for 50 and 25 mm holes are 2× the flash fraction and, for smaller holes, the flash fraction.
[e] Fractional dead time of automatic or remote shut-off is 0.01. Such a failure places a demand on the manual shut-off leading to a release duration of 20 min.
[f] These values are based on data modified by judgement and make some allowance for the possibility of a few windows being open.

Table 9.41 *HSE guide assessment on chlorine installations: risks (after Pape and Nussey, 1985) (Courtery of the Institution of Chemical Engineers)*

Rate (kg/s)	*Duration* (min)	*Frequency* ($\times 10^6$/year)	*Distance* (m)			*Risks* ($\times 10^6$/year)				
			50	100	200	300	500	750	1000	1500
50	10	1	0.29 (23)	0.23 (24)	0.17 (26)	0.13 (29)	0.08 (39)	0.04 (57)	0.01 (94)	0
22	10	5	1.29 (24)	0.99 (25)	0.68 (30)	0.46 (38)	0.18 (62)	0.06 (95)	0.02 (92)	0
6.4	20	2	0.5 (26)	0.35 (30)	0.18 (42)	0.08 (59)	0.02 (94)	0	0	0
5	30	4	0.82 (27)	0.56 (31)	0.28 (44)	0.11 (63)	0.03 (93)	0	0	0
1.25	20	156	23.8 (34)	9 (52)	1.46 (93)	0.04 (8)	0	0	0	0
4	5	232	44.6 (29)	22.4 (42)	4.33 (89)	0.13 (22)	0	0	0	0
5	20	7	1.44 (27)	0.98 (31)	0.43 (48)	0.17 (69)	0.04 (94)	0	0	0
0.2	20	141	3.04 (94)	0.04 (8)	0	0	0	0	0	0
2.4	20	17	3.09 (30)	1.73 (40)	0.42 (72)	0.14 (93)	0	0	0	0
2	5	220	33.05 (36)	7.36 (86)	0.15 (19)	0.04 (23)	0	0	0	0
1	5	150	13.64 (49)	1.36 (82)	0.03 (20)	0	0	0	0	0
9	20	1	0.33 (26)	0.24 (29)	0.14 (36)	0.07 (48)	0.01 (94)	0	0	0
1.4	30	20	3.38 (33)	1.55 (46)	0.26 (94)	0.08 (92)	0	0	0	0
2	20	15	2.63 (31)	1.37 (43)	0.23 (94)	0.09 (93)	0	0	0	0
Total			131.5 (35)	48.1 (51)	8.8 (76)	1.6 (53)	0.4 (66)	0.1 (80)	0	0

Note: The values in parentheses show the percentage contributions to risk levels due to accidents in stable weather conditions.

from a hole in a 6 in. pipe into a bund and (3) failure of a 135 te storage vessel. It gives for different air entrainment factors estimates of the distances to specified oxygen concentrations.

In determining the effect of enhanced oxygen concentration, the BCGA *Guide* assumes that clothing fires are the only type of fire that would increase casualties. It concentrates largely on the potential for persons who are smoking or using matches to ignite their clothing, the source of fuel closest to them.

9.22.7 FMA ammonium nitrate CIMAH guidelines

Guidance for ammonium nitrate is given in *Safety Case for Ammonium Nitrate Required by Regulation 7 of CIMAH* by the Fertilizer Manufacturers Association (the *FMA Ammonium Nitrate Guide*) (1989); an extract (FMA, 1989) is given in Lees and Ang (1989b). The FMA *Ammonium Nitrate Guide* is mainly concerned with the safety report and, in particular, with the properties of ammonium nitrate.

The *Guide* discusses the hazard of explosion of ammonium nitrate and considers the consequences of deflagration of a stack of 300 te of ammonium nitrate. It obtains for such an explosion a trinitrotoluene (TNT) equivalent of 41 te, based on an ammonium nitrate TNT equivalent of 55% and a maximum explosion efficiency of 25%, and hence at 600 m a scaled distance of 175 m. It reproduces the ACMH correlation for the overpressure from a TNT explosion (Harvey, 1979b) and utilizes this correlation to determine that for this explosion an overpressure of 1 psi occurs at 600 m.

9.23 Hazard Impact Model

The impact of a hazard on the surrounding area may be modelled analytically by making certain simplifying assumptions. The hazard impact model so derived may be

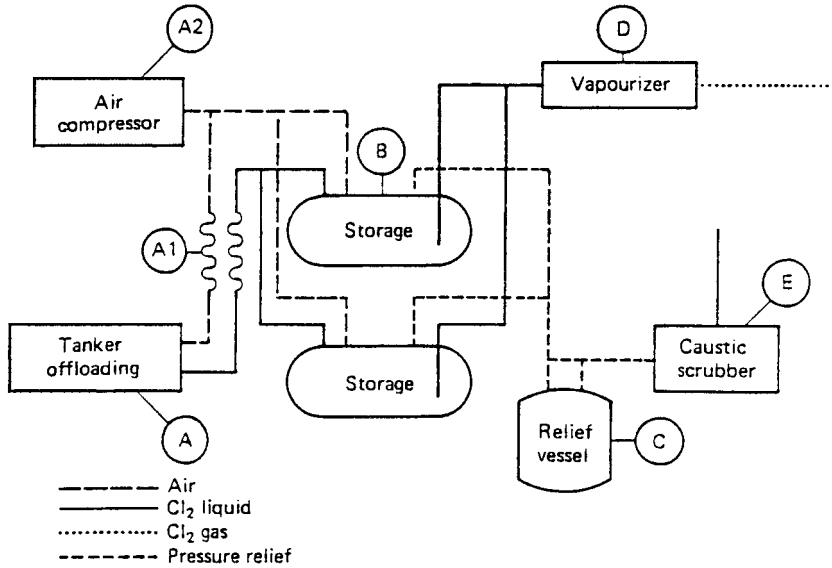


Figure 9.43 *UKCP guide on emergency planning for chlorine installations: typical installation (after Chemical Industries Association, Chlorine Sector Group, 1989)*

Table 9.42 *UKCP guidance on emergency planning for chlorine installations: typical installation (after Chemical Industries Association, Chlorine Sector Group, 1989)*

A Typical equipment and inventories

Equipment	*Pressure* (bar g)		*Size*	*Quantity*
	Normal	*Design*		
Stock tanks	7	13	20–200 te	2 × 35 te, typically
Expanse tanks	0	13	10% of stock tank	1 × 5 te, typically
Vaporizers	3	14	0.2–2 te/h	1, typically
Scrubbers	Pressurized			1
Air compressors	9	11	–	1
Piping:				
Gas	2–9			<20 m
Liquid	9 ASA 150 1 in. diam			<20 m
Vent	13			<20 m
Valves	Primary – globe		1 in. Table D	<20
	Isolation – ball		1 in. ASA 150	<20
'Flexibles' (liquid/vent)	2–9	25	1 in. ASA 150	<10 m

B Process activities

Air compression
Pressurization of tanker for offloading
Pressurization of storage tanks for chlorine transfer
Vaporization of chlorine
Controlled venting of tanker and storage tanks after transfer or for maintenance
Pressure relief
Possible interaction between the chlorine and its point of application

C Steps in hazard assessment

Examination of piping and instrument diagram
Systematic identification and listing of hazards
Assessment of credible size of leak
Definition of operating pressure

Table 9.42 *(continued)*

Assessment of extent of vaporization
Estimation of extent of gas concentrations at different locations
Estimation of potential duration of leak

D List of typical incidents[a]

1. Loss of containment of chlorine from pipework
   (a) Corrosion due to freeze/thaw conditions (particularly under lagging)
   (b) Pipe flange leaks (e.g. expansion of trapped liquid)
   (c) Flange gasket failure (due to incorrect gasket material)
   (d) Leak from pipework (e.g. spool fabricated/fitted to wrong specification, section of pipework not subject to routine inspection)
2. Loss of containment from the offloading installation
   (a) Leaks from flexibles (e.g. pinhole on weld)
   (b) Damage to filling/discharge connection due to transport container movement (e.g. collision)
   (c) Liquid chlorine ingress into vent/compressed air systems/absorption systems overloaded
3. Incidents involving bulk storage and relief systems
   (a) Contamination of stock tank contents (e.g. water ingress/incomplete drying out procedure)
   (b) Leaks from valves (incorrect valve specification)
   (c) Leaks from relief system/expanse vessel (valve maloperation, water ingress, etc.)
   (d) Total loss of containment from bulk storage needs to be considered in each case to estimate the likelihood of this event. In particular, the systems and procedures used in the operation and maintenance of the plant must be carefully reviewed
4. Loss of containment from the system supplying chlorine to the point of application
   (a) Internal chlorine iron fires (e.g. vaporizers)
   (b) Nitrogen trichloride explosion (e.g. drains from vaporizer)
   (c) Interaction in the chlorine delivery pipework, backflow of water/reagents

[a] These examples are of typical incidents but do not cover all possibilities, particularly those associated with site specific features.

used for various purposes, including estimating the number of injured and assessing the error in the estimates.

9.23.1 Approximate model

An approximate model that may be used to estimate the number of people who suffer injury is

$$N_i = \pi r_{50}^2 d_p \qquad [9.23.1]$$

where d_p is the population density (persons/m^2), N_i is the total number of injured and r_{50} is the radius (metres) at which the probability of injury is 50%.

In this model, the assumption is made that the number of people inside the circle of radius r_{50} who escape injury is equal to the number outside the circle who suffer injury. It is also assumed that the population density is uniform. The use of the radius r_{50} has some justification apart from computational convenience in that, although injury relations are usually subject to much uncertainty, the uncertainty tends to be least at the 50% injury level.

It can readily be appreciated that the degree of error in this approximate model depends on the relation between the distance and the probability of injury. Three possible cases are illustrated in Figure 9.44. In case (a), the transition from a probability of injury of unity to one of zero is very gradual, in case (b) more sharp, and in case (c) immediate. The error in the estimate reduces to zero for this latter case.

If the population density is not uniform, the approximate model given by Equation 9.23.1 cannot itself be used, but use may still be made of the radius r_{50} in conjunction with the site population density to obtain an approximate estimate of the number of injured, although in this case the number of injured inside the circle who escape injury and the numbers outside who suffer injury may not balance. As before the error in the estimate reduces to zero for case (c).

It has been shown, however, by Poblete, Lees and Simpson (1984) and Lees, Poblete and Simpson (1986) that it is possible to derive an alternative, more accurate model.

9.23.2 Intensity of physical effect

Some principal physical effects are:

Fire	
Thermal radiation	I
Thermal radiation dose	It
Thermal radiation-time function	$f(I, t)$
Explosion	
Overpressure	p^o
Impulse	I_p
Toxic release	
Concentration	C
Dose	Ct
Concentration–time function	$f(C, t)$

It is assumed in the model that the intensity of the physical effect decays with distance according to an inverse power law. Hence:

$$w = k_w / r^{n_\omega} \qquad [9.23.2]$$

where k_w is the intensity constant, n_w the intensity index and w the intensity.

The normalized intensity i is obtained by dividing the actual intensity w by the value w_0 of the intensity at the

Table 9.43 *UCKP guidance on emergency planning for chlorine installations: hazard scenarios[a] (after Chemical Industries Association, Chlorine Sector Group, 1989)*

Event	*Event likelihood*	*Pressure* (bar g)	*Hole size* (diameter) (mm)	*Leak rate* (kg/s)		*Consequence Downwind Distance affected* (m)			
				Liquid	*Gas*	*Neutral D*5 m/s		*Inversion F*2 m/s	
						140 ppm	15 ppm	140 ppm	15 ppm
Valves									
Leak from a packed gland	Quite likely	7	<2	0.1 NF[b]		–	200	130	400
Leak on a bolted tongue and groove flange									
Porosity in the value body or Bonnet									
Leak from flange (hole in 1.6 mm gasket)					0.01	–	–	–	100
Piping									
Small leak from liquid flange (1.6 mm gasket)	Likely	7	5		0.8 NF	200	600	400	1100
Small hole in liquid pipework wall (corrosion/erosion/defect)									
Small hole in gas pipework					0.05	–	150	100	300
Hole in pipework due to corrosion/erosion/defect. A full segment of 1.6 mm gasket expelled between adjacent bolts	Unlikely	7 sustained	12	3.5 NF	–	400	1300	800	>1500
Expansion of trapped liquid between closed valves (full segment of 1.6 mm gasket expelled between adjacent bolts)	Unlikely	7 reducing	12	1.2	–	200	700	500	1400
Hole in gas pipework (e.g. flange leak)	Likely	7 sustained	12	–	0.3	100	400	200	700
Storage									
T&G flange leak on liquid branch	Likely	7 reducing slowly	<2	0.1 NF		–	200	130	400
Flange leak on gas branch					0.01	–	–	–	100
Small leak from liquid branch	Unlikely	7 reducing slowly	5	0.8 NF		200	600	400	1100
Small leak from gas branch					0.05	–	150	100	300
Transfer equipment									
Flexible hose	Very likely		Pinhole	0.01	–	–	–	–	100
	Likely		2	0.1	–	–	200	130	400

B Interpretation of the qualitative frequency terms

Extremely unlikely	$<10^{-6}$/year
Very unlikely	$10^{-6} - 10^{-5}$/year
Unlikely	$10^{-5} - 10^{-4}$/year
Quite unlikely	$10^{-4} - 10^{-3}$/year
Somewhat unlikely	$10^{-3} - 10^{-2}$/year
Fairly probable	$10^{-2} - 10^{-1}$/year
Probable	$>10^{-1}$/year

[a] This table is appendix IV of the original document. The table is by way of example only.
[b] NF, non-flashing flow.

Table 9.44 *Ground level concentrations (ppm) for scenarios 1–5 in the CIA Ammonia Guide (CIA, 1988 PA49)*

Scenario	*D*5			*F*2		
	500 m	1000 m	2000 m	500 m	1000 m	2000 m
1: 10 kg/s	500–1000		50–100	1000–5000		200–600
40 kg/s	600–4000		150–300	3000–10^4		1000–3000
2	200–500		20–50	500–1000		100–200
3	150–250	80–150	30–70	50–100	200–300	250–350 (no plume rise)
	40–80	40–80	20–40	0	0	10–20 (plume rise)
4(b)	300–500	200–400	100–200	200–300	400–600	600–800 (no plume rise)
	50–100	60–120	30–60	0	0	10–20 (plume rise)
	Same order of magnitude as Scenario 1					

distance r_0, which is termed the 'radius of the physical effect', and which is discussed further below. Hence:

$$i = w/w_0 \qquad r = r \qquad [9.23.3a]$$

$$i = 1 \qquad r = r_0 \qquad [9.23.3b]$$

9.23.3 Injury factor

Some principal injury factors are

Fire	$I^{4/3}\,t$
Explosion	p°
	I_p
Toxic release	C
	Ct
	C^2t

It is assumed in the model that the injury factor is a power function of the intensity.

Hence:

$$v = k_{vw} w^{n_{vw}} \qquad [9.23.4]$$

where k_{vw} is the first injury factor constant, n_{vw} is the injury factor power index and v the injury factor.

Combining Equations 9.23.2 and 9.23.4 gives

$$v = k_v / r^n \qquad [9.23.5]$$

with

$$k_v = k_{vw} k_w^{n_{vw}} \qquad [9.23.6]$$

$$n = n_w n_{vw} \qquad [9.23.7]$$

where k_v is the second injury factor constant and n is the injury factor decay index.

The normalized injury factor x is obtained by dividing the actual injury factor v by the value v_o of the injury factor at the distance r_0:

$$x = v/v_0 \qquad r = r \qquad [9.23.8a]$$

$$x = 1 \qquad r = r_0 \qquad [9.23.8b]$$

9.23.4 Probability of injury

The relationship between the injury factor and the probability of injury is assumed to be the log–normal distribution:

$$P = \frac{1}{(2\pi)^{1/2}\sigma} \int_0^x \frac{1}{x} \exp\left[-\frac{\ln(x - m_n^*)^2}{2\sigma^2} \right] \mathrm{d}x \qquad [9.23.9]$$

where P is the probability of injury, m_n^* is the normalized location parameter of the distribution, and σ is the spread parameter of the distribution.

An alternative way of expressing this relation is in the form of a probit equation:

$$Y = k_{n1} + k_{n2} \ln x \qquad [9.23.10]$$

with

$$k_{n1} = 5 - m_n^*/\sigma \qquad [9.23.11a]$$

$$k_{n2} = 1/\sigma \qquad [9.23.11b]$$

The relation between the probability and the probit is given by Equation 9.18.1.

The probit equation given by Equation 9.23.10 is in normalized form. The unnormalized equation is

$$Y = k_1 + k_2 \ln v \qquad [9.23.12]$$

with

$$k_1 = 5 - m_\mathrm{u}^* \sigma \qquad [9.23.13a]$$

$$k_2 = 1/\sigma \qquad [9.23.13b]$$

The two forms are related through two location parameters

$$m_n^* = m_\mathrm{u}^* - n \ln v \qquad [9.23.14a]$$

$$v = \exp(m_\mathrm{u}^* - m_n^*) \qquad [9.23.14b]$$

9.23.5 Distances r_0 and r_{50}

The intensity of the physical effect and the injury factor are scaled in relation to the distance r_0. In principle, r_0 is intended to represent the radius of the physical effect, where this is a meaningful concept as with, say, a fireball, and hence the radius at which the probability of injury is unity. The choice of r_0 is, however, unrestricted. It is recommended that it be chosen so as to give a probability of injury close to unity.

Then the normalized injury factor decays with distance according to the relation

$$x = (r_0/r)^n \qquad r = r \qquad [9.23.15a]$$

$$x = x_0 = 1 \qquad r = r_0 \qquad [9.23.15b]$$

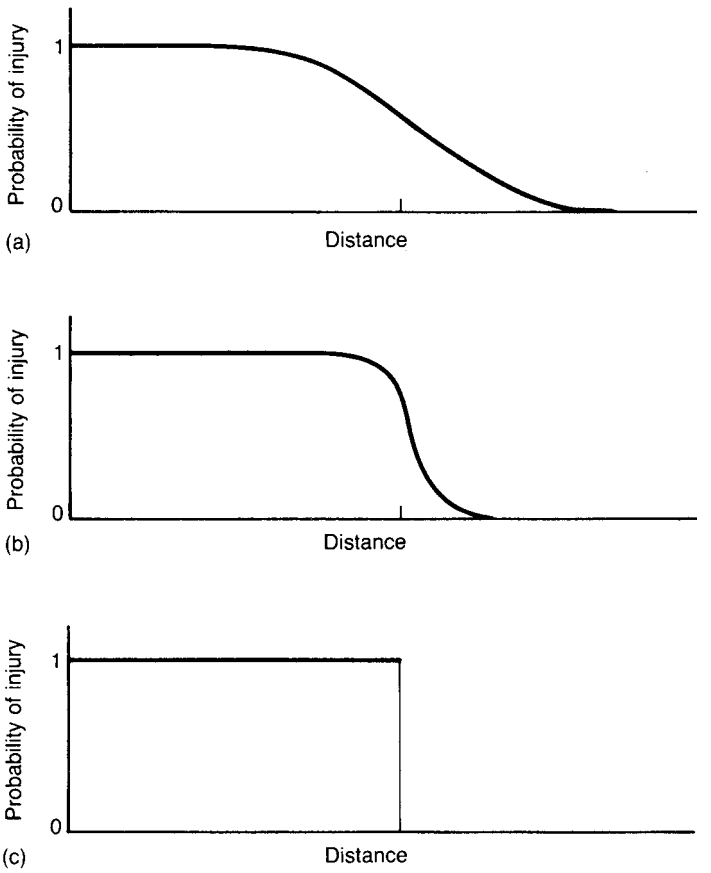


Figure 9.44 *Some hypothetical relations between distance and probability of injury*

The distance r_{50} has been defined as the radius at which the probability of injury is 50% ($P = 0.5$). The normalized injury factor x_{50} at this distance is then:

$$x_{50} = (r_0/r_{50})^n \qquad [9.23.16]$$

Also, putting $x = x_{50}$ and $Y = 5$ ($P = 0.5$) in Equation 9.23.10, gives

$$x_{50} = \exp(m_n^*) \qquad [9.23.17]$$

Hence from Equations 9.23.16 and 9.23.17

$$r_{50} = r_0/x_{50}^{1/2} \qquad [9.23.18a]$$

$$= r_0/\exp(m_n^*/n) \qquad [9.23.18b]$$

9.23.6 Number of injured

It is assumed that the density d_p of the population around the hazard source is uniform. This assumption can be relaxed in certain specific ways as described below. The number N_i of people injured is:

$$N_i = \int_0^\infty 2\pi d_p P(r) r \, dr \qquad [9.23.19]$$

It can be shown that the solution of Equation 9.23.19 is

$$N_i = \pi r_{50}^2 d_p \phi \qquad [9.23.20]$$

With

$$\phi = \exp(2\sigma^2/n^2) \qquad [9.23.21]$$

where ϕ is the correction factor for variance and decay. Equation 9.23.20 together with Equation 9.23.21 constitutes the hazard impact model derived by Lees, Poblete and Simpson.

9.23.7 Practical decay relations

An important feature of the model is the assumption that the intensity of the physical effect decays according to an inverse power law. It has been shown by Poblete, Lees and Simpson (1984) and Lees, Poblete and Simpson (1986) that a number of the simpler hazard models give such a decay relation. There are others, however, particularly some gas cloud models, which do not.

The question of the decay of the physical effect is considered in more detail in Section 9.25.

Table 9.45 *Hazard impact model sensitivity coefficients (after Lees, 1987) (Courtesy of Elsevier Science Publishers)*

$(\partial N_i/N_i)/(\partial d_p/d_p) = 1$
$(\partial N_i/N_i)/(\partial k_w/k_w) = 2/n_w$
$(\partial N_i/N_i)/(\partial n_w/n_w) = -(2/n)\ln k_v + (2/n)m_u^* - 4\sigma^2/n^2$
$(\partial N_i/N_i)/(\partial k_{vw}/k_{vw}) = 2/n$
$(\partial N_i/N_i)/(\partial n_{vw}/n_{vw}) = -(2/n)\ln k_{vw} + (2/n)m_u^* - 4\sigma^2/n^2$
$(\partial N_i/N_i)/(\partial m_u^*/m_u^*) = -2m_u^*/n$
$(\partial N_i/N_i)/(\partial \sigma/\sigma) = 4\sigma^2/n^2$

9.23.8 Sensitivity estimates

It has been shown by Lees (1987) that there can be derived from Equation 9.23.20 a set of sensitivity coefficients which can be used to determine the effect of errors in the various physical models and injury relations utilized on the estimate of the number of injured given by that model. The parameters of interest are: d_p, k_w, n_w, k_{vw}, n_{vw}, m_u^* and σ. The normalized partial derivatives, or sensitivity coefficients, of N_i with respect to these parameters are given in Table 9.45.

9.23.9 Applications of model

The hazard impact model presented in Equation 9.23.20 is more accurate than that given in Equation 9.23.1 and, if the assumptions hold exactly, the results given by the model are exact, but in most practical cases there is likely to be a degree of approximation in the assumptions and hence in the results.

One application of the model is to make a rapid estimate of the number of injured. The model may be used to make a quick, ranging estimate, usually prior to a more detailed assessment. The use of the model is straightforward, but there are two common situations where some modification is necessary. These are for population density and directional effects.

In many cases the population density is not uniform. Two specific deviations can readily be taken into account. One is the case where there is a different population density, perhaps zero, up to some distance r_w from the hazard source. If this is such that the probability of injury up to this point is virtually unity, it is straightforward to calculate the number of injured inside the circle radius r_w and to adjust the value of N_i accordingly. The other case is where there are different population densities in different sectors around the hazard source. Again it is straightforward to adjust the value of N_i. Combination of these two cases can also be handled and, taken together, these adjustments extend appreciably the scope of the model.

Some physical phenomena are directional and affect not a circular area around the hazard source but an area that is a sector with its apex at the source. The most important case here is a gas cloud.

Directional effects can be handled by the model by considering only the sector affected and, where necessary, dividing it into a sufficient number of subsectors such that the conditions along any arc in a subsector are essentially uniform.

Another, and perhaps more significant, application of the model is to determine the effect of errors in the physical models and injury relations on the estimate of the number of injured. This may be of value not only in the conduct of hazard assessments but also in the identification for research purposes of areas where improved models and correlations would, or would not, give significant improvements in the accuracy of the assessment.

9.24 Simplified assessment methods

A full hazard assessment is a major exercise. It is useful, therefore, to have short-cut methods. The short-cut methods described may be used to obtain an approximate estimate with economy of effort. The use of such a method may improve understanding of the hazards and may highlight unexpected features. But short-cut methods have their limitations. By definition they tend to be based on generalized relations and thus are much less effective in revealing critical features and assumptions in a specific design.

A study of simplified methods of hazard assessment has been described by R.A. Cox and Comer (1982). The study was commissioned following the *Rijnmond Report*. The aim of the work was to devise a method of hazard assessment that would yield risk contours, FN curves and individual and group risks. It was accepted that such a method would not be able to give individual risk for employees, since the degree of detail required to do this was not consistent with the simplicity sought. The method was required to yield intermediate as well as final results to permit checking and to improve confidence in the latter. Two methods were devised and compared:

(1) Simplified classical method.
(2) Parametric correlation method.

These are now described in turn.

9.24.1 Short-cut classical method

The short-cut classical method (SCM) is a simplified form of the full classical method in which individual failure scenarios are defined and estimates are made of their frequency and consequences.

The SCM approach involves three stages: failure case selection and frequency estimation; application of consequence submodels; and summarization of risks.

Crucial to the method is the selection of the failure cases. The original intent was to pick a set of representative cases. But it was concluded that it is necessary to start from the full set of failure cases. These cases are then reduced to a more limited set of equivalent discrete failures (EDFs). One method is to cluster together 'similar' failures, another is to compare each case with a standard EDF (SEDF). It was the latter approach that was adopted.

A standard EDF (SEDF) is defined by standard physical consequences such as the distance travelled by a vapour cloud in standard weather conditions. An SEDF list was created, giving for each EDF the distances for defined intensities of the relevant physical effects such as toxic concentration. For each EDF the consequences are determined by a once-and-for-all assessment. Then, in applying the method to a particular plant the actual EDF for a particular failure case is equated to one of the standard EDFs using consequence submodels. This is the only use of these submodels in the method.

Some of the principal elements in the method are shown in Table 9.46. Section A of the table lists the data schedules required to define the failure cases. They are schedules of the plant units, of the items on the plant and of the connections between items. Section B shows the six main categories of release considered, and section C gives the consequence submodels used. Figure 9.45 is a flow diagram

Table 9.46 *Some elements of the short-cut classical methods (SCM) of hazard assessment (after R.A. Cox and Comer, 1982) (Courtesy of the Institution of Chemical Engineers)*

A Schedule of item interconnections
Each item to item connection defined by:
Identification of items of either end of pipe
Pipe diameter
Location of connection at either end of pipe – in vapour Space or below liquid level
Presence of particular types of valving along pipe (excess flow, non-return and shut-off valves)
B Schedule of items
For each plant item:
Item identification
Materials and inventory contained
Temperature and pressure
The item location is specific by the item identification that identifies the plant unit on which the item is located
C Schedule of plant units
For each plant unit:
Set of parameters to define failure frequencies Location coordinates

of the algorithm for pipe failure and Figure 9.46 one for application of the method to an actual plant.

Up to this point the analysis is independent of the environment. Factors defining this environment, such as the weather, ignition sources, etc., are now brought in. The effect of introducing these factors is to alter not consequences, but the frequencies for each standard. From this information on the frequency and consequences of each standard EDF at the particular plant it is possible to obtain estimates of risk. The frequencies of the various physical outcomes, the areas affected and the number of casualties are determined, and risk estimates made in the usual way.

9.24.2 Parametric correlation method

The alternative method considered was the parametric correlation method (PCM). With this method there are two principal features that must be specified: the form of the correlation function and the method of determining its parameters.

One approach to selecting the form of the correlation function is to run a large number of full hazard assessments and derive a correlation function from these. Another is to use expert judgement to select suitable functional forms. The correlation function should be carefully chosen to give an appropriate number of parameters. There is a potential problem of escalation of the number of parameters required.

A possible form of correlation function might be:

$$R(d) = \frac{R(0)}{2}[1 + \cos(\pi d/d_{\max})] \qquad [9.24.1]$$

where d is the distance from the unit, R is the risk and the subscript max indicates the maximum at which any risk exists.

The correlation function given in Equation 9.24.1 has two parameters, $R(0)$ and $d_{\max}$. Its characteristics are shown in Figure 9.47. Since $R(0)$ is the risk at the unit itself, it is in effect a measure of frequency, while $d_{\max}$ is a measure of consequences. Thus the two parameters are independent. This correlation function therefore has the attraction of simplicity.

9.24.3 Comparison of methods

The two candidate methods were then compared both with the full classical method and with each other. The full method used in the Rijnmond study was considered to be accurate in most cases to within one order of magnitude in each direction, but in some cases only to within two orders of magnitude. The SCM approach was not expected to be appreciably less accurate. Insofar as a multiparameter PCM approach would be derived from full analyses, it too should have a similar accuracy, but it would have less transparency than the SCM. A two-parameter PCM would probably be appreciably less accurate.

With regard to cost, the capital cost of the SCM and two-parameter PCM were assessed as comparable and that of a multiparameter PCM as about double. On the other hand, the operating costs of the two-parameter PCM were estimated as half those of the SCM, with the multiparameter PCM costs lying in between.

9.24.4 Hazard impact model

The hazard impact model may be used as a short-cut method for hazard assessment. The method depends on the availability of decay and injury relations and on certain simplifying assumptions. The use of the model for this application is described in Section 9.23.

9.25 Decay Relations

Several of the methods described make use of decay relations. These may be generic relations intended to be applicable to any hazard with suitable choice of parameters or they may be specific to a particular hazard.

For the simpler hazard models decay may often be derived analytically, while for the more complex models embodied in computer codes it is necessary to obtain and then correlate numerical results. Similarly, correlations may be derived from experimental data.

9.25.1 Generic decay relations

Several decay relations have been given in the literature. They include: Equation 9.24.1, used by R.A. Cox and Comer (1982) for the parametric correlation model; Equation 9.23.20 used by Lees, Poblete and Simpson (1986) for the hazard impact model; and Equation 9.14.1, used by Bagster and Pitblado (1991) for the domino effect model.

9.25.2 Decay relations for specific hazards

Decay relations can be obtained from the simpler hazard models for fire, explosion and toxic release, as described by Poblete, Lees and Simpson (1984) and Lees, Poblete and Simpson (1986).

The intensity of heat radiation from a fireball is:

$$F = E/4\pi r^2 \qquad [9.25.1]$$

where E is the heat radiated (kW), F is the heat radiated on the target (kW/m^2), and r is the distance (m) from the centre of the fireball to the target. Similar equations apply to other types of fire, such as pool fires and flares.

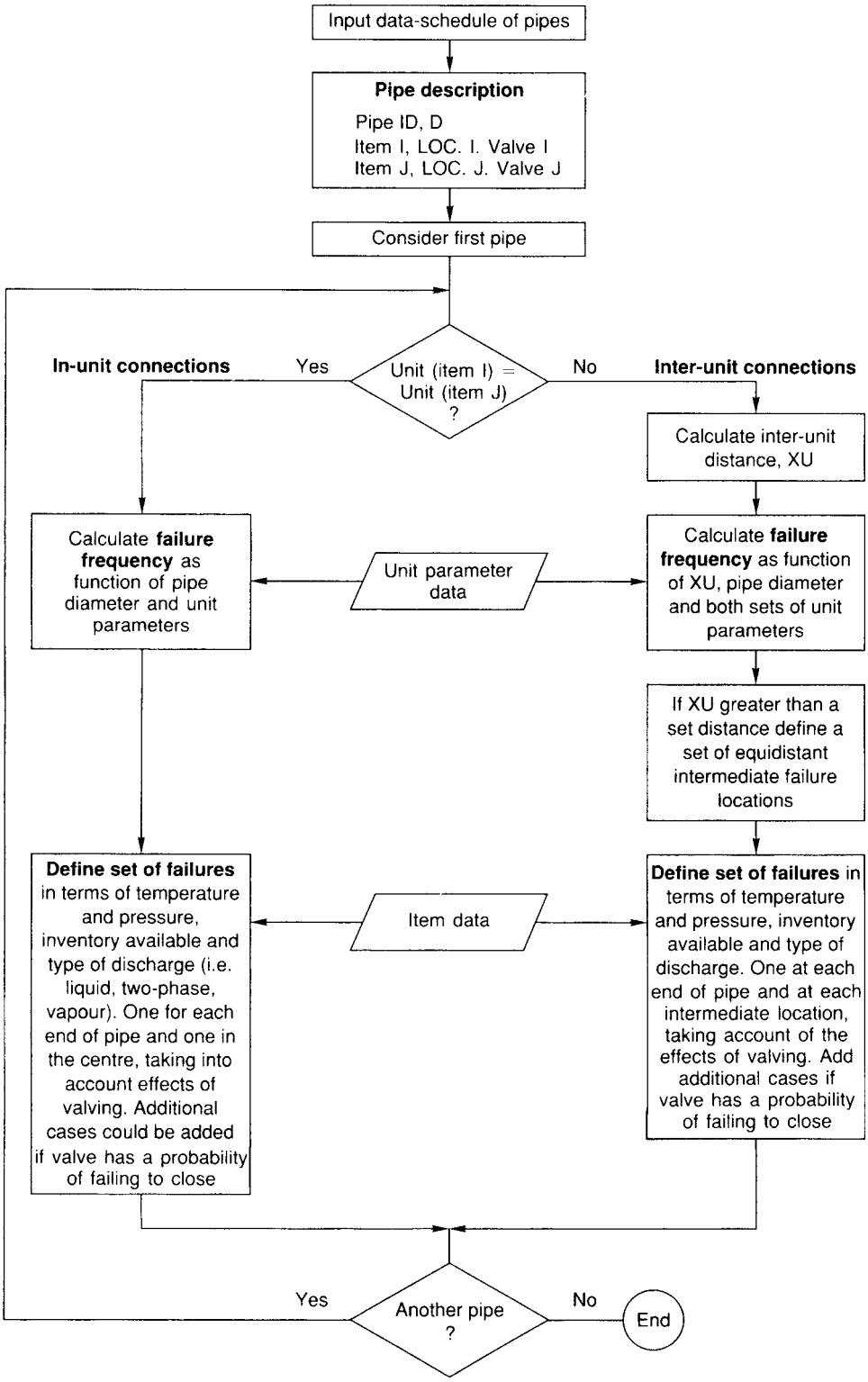


Figure 9.45 *Flow diagram of algorithm for pipe failure in short-cut classical method (SCM) (R.A. Cox and Comer, 1982) (Courtesy of the Institution of Chemical Engineers)*

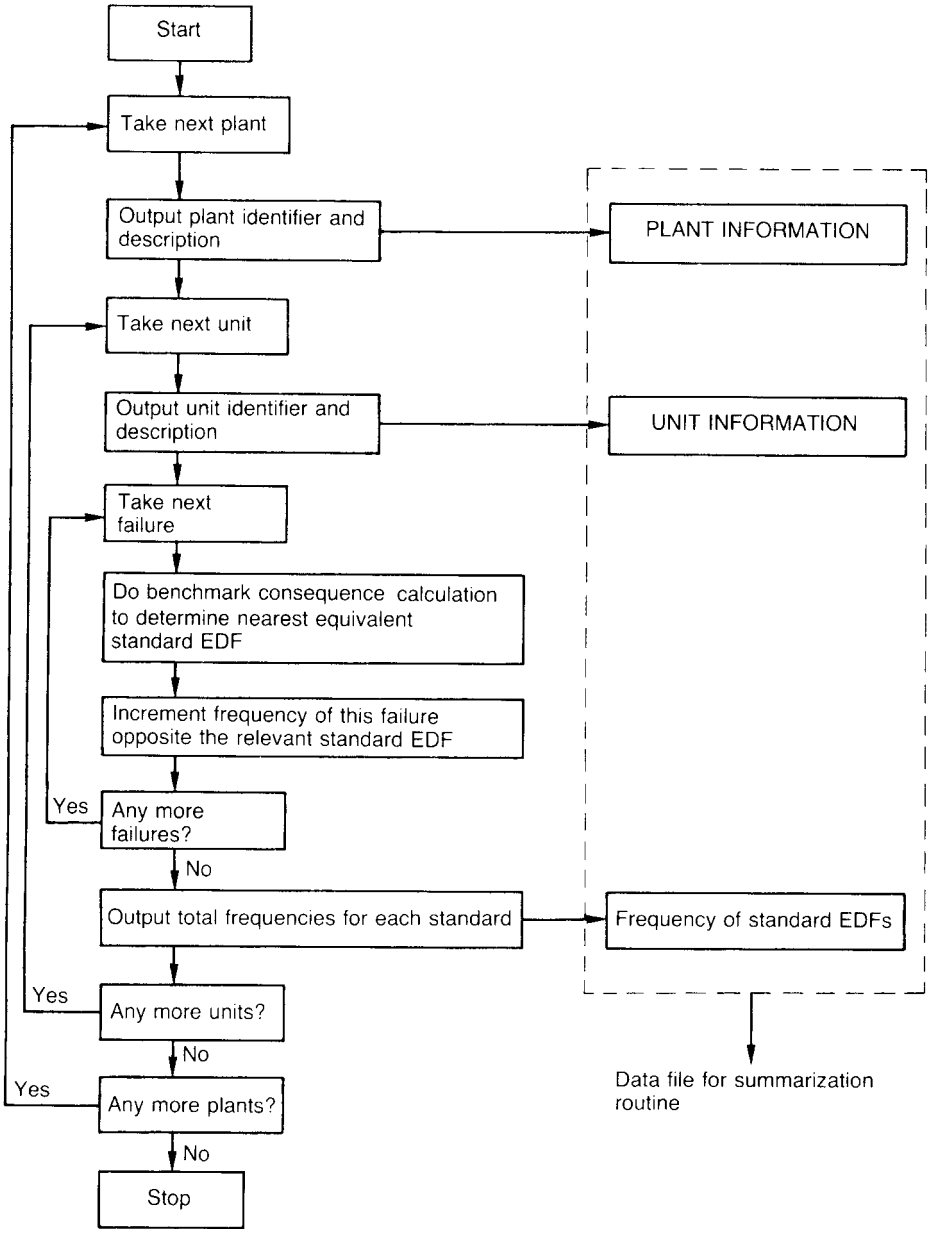


Figure 9.46 *Flow diagram of algorithm for analysis of an installation in short-cut classical method (SCM) (R.A. Cox and Comer, 1982) (Courtesy of the Institution of Chemical Engineers)*

The peak overpressure and impulse from the explosion of a high explosive are functions of scaled distance:

$$p^0 = f(z) \qquad [9.25.2]$$

$$I_p = f(z) \qquad [9.25.3]$$

with

$$z = r/W^{1/3} \qquad [9.25.4]$$

where I_p is the impulse (N s/m), p^o is the peak incident overpressure (N/m^2), W is the mass of explosive (kg) and z is the scaled distance ($m/kg^{1/3}$). The function in Equation 9.25.2 is usually provided in graphical form, such as the curves given by W.E. Baker *et al.* (1983). However, over a limited overpressure range it can be represented by the relation

$$p^0 = 1/r^{n_1} \qquad [9.25.5]$$

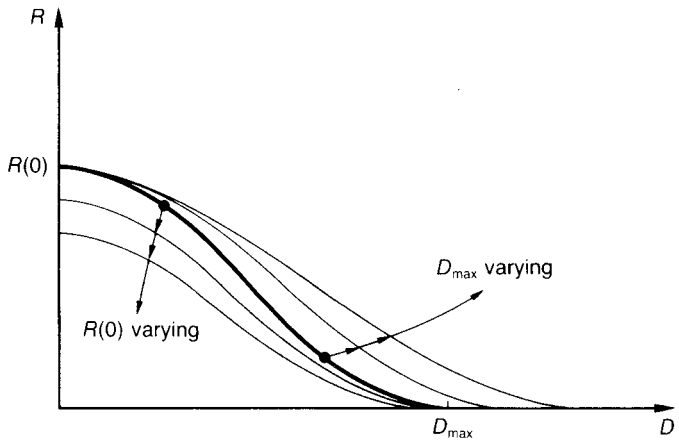


Figure 9.47 *Characteristics of the decay function R(d) used in the parametric correlation method (R.A. Cox and Comer, 1982) (Courtesy of the Institution of Chemical Engineers*

where n_1 is an index. The Baker curves correspond over the overpressure range 1.0–0.1 bar to decay indices of 1.7 and 0.9 for peak overpressure and impulse, respectively.

For VCEs there is no established model. Some theoretical models give a decay index of approximately unity. On the other hand, the decay curve established for the Flixborough explosion gives over the overpressure range 1.0–0.1 a decay index of 1.7.

Decay indices for dispersion of neutral density gas may be derived from the Sutton equations. For an instantaneous release the concentration at ground level on the centre line of the cloud and at cloud centre is

$$\chi = \frac{2Q^*}{\pi^{3/2}C^3(ut)^{3/2(2-n)}} \qquad [9.25.6a]$$

where C is the diffusion parameter ($m^{n/2}$), n is the diffusion index, Q^* is the mass released (kg), t is the time (s), u is the wind velocity (m/s) and χ is the concentration (kg/m^3). For neutral conditions, $n = 0.25$:

$$\chi \propto 1/x^{2.6} \qquad [9.25.6b]$$

where χ is the distance (m). The total integrated dosage D_{tid} ((kg/m^3) s) is

$$D_{tid} = \frac{2Q^*}{\pi C^2 u(ut)^{2-n}} \qquad [9.25.7a]$$

Setting $n = 0.25$:

$$D_{tid} \propto 1/x^{1.75} \qquad [9.25.7b]$$

For a continuous release the concentration at ground level on the centre line of the cloud is

$$\chi = \frac{2Q}{\pi C^2 u x^{2-n}} \qquad [9.25.8a]$$

where Q is the mass rate of release (kg/s) setting $n = 0.25$:

$$\chi \propto 1/x^{1.75} \qquad [9.25.8b]$$

The total integrated dosage is obtained by assuming that the continuous release lasts for some finite time. Then the total integrated dosage is:

$$D_{tid} \propto 1/x^{1.75} \qquad [9.25.9]$$

Models of heavy gas dispersion tend to be too complex to permit the analytical derivation of general decay indices, although an index may sometimes be derived for particular cases. Some decay indices for some principal hazards are given in Table 9.47.

The decay index for the physical effect can be combined with the power index for the injury factor to give an overall decay index for injury, as described the discussion of the hazard impact model in Section 9.23.

Another decay relation used is:

$$r = kM^{n_2} \qquad [9.25.10]$$

where M is mass released (kg), n_2 is a decay index, r is the distance for some physical effect (m) and k is a constant.

Equation 9.25.10 has been used to correlate results from numerical computations or empirical data. In particular, it has been used to give a correlation for the decay of the concentration of a flammable gas cloud to its lower flammability limit (LFL) or some fraction of this. For example, it was used in the Second *Canvey Report* to correlate distance to 0.5 LFL.

9.26 Hazard Warning

The use of hazard assessment of the kind so far described to provide assurance that a hazard is under control has certain weaknesses. One is the problem of credibility. The most difficult situation arises where there is a major hazard. Industry may attempt to argue qualitatively and then to demonstrate quantitatively that although in the most unfavourable circumstances the hazard has the

Table 9.47 *Decay indices for some principal hazards*

Hazard	*Model*	*Physical effect*	*Intensity*	*Decay index*
Fire	Fireball, pool fire	Thermal radiation	I	2
Explosion	TNT	Peak overpressure	p^o	1.7[a]
		Impulse	I_p	0.9[a]
	VCE (Flixborough)	Peak overpressure	p^o	1.7[b]
	VCE (models)	Peak overpressure	p^o	1.0[c]
				1.1[d]
Toxic release	Neutral density gas: instantaneous release	Concentration	C	2.6
		Dosage	Ct	1.75
	Neutral density gas: continuous release	Concentration	C	1.75
		Dosage	Ct	1.75
	Heavy gas: instantaneous release	Concentration	C	1.4[e]
	Heavy gas: continuous release	Concentration	C	1.7[f]

[a] Over the range 1.0–0.1 bar (W.E. Baker *et al.*, 1983).
[b] Over the range 1.0–0.1 bar (Sadee, Samuels and O'Brien, 1976–77).
[c] Model of Wiekema (1980).
[d] Model of Ebert and Becker (1982).
[e] Specific example of 200 te ammonia release using DENZ computer code (Fryer and Kaiser, 1979 SRD R152).
[f] Specific example of 23.9 kg/s chlorine release using CRUNCH computer code (Jagger, 1983 SRD R229).

potential to kill a large number of people, the probability that the hazard will be realized during the lifetime of the plant is very low. Frequently such arguments do not satisfy the objectors, who tend to concentrate exclusively on the hazard potential and to emphasize that the major accident could occur out of the blue at any time.

Another weakness is that when the plant comes to be operated, usually relatively little use is made of the information generated during the design, particularly the fault trees, for the control of hazards and the analysis of accidents and failures. These problems may be tackled using the concept of hazard warning structure described by Lees (1982b, 1983b, 1985). This is now outlined.

9.26.1 Hazard warning structure

If the structure of a major accident is analysed by constructing a fault tree, it is generally found that this event occurs as a result of a minor accident and of failure of a mitigating feature that is normally effective in preventing such escalation. In turn the minor accident may occur only if there is a lesser accident and failure of a second mitigating feature. Typically, there is a series of events that result in a major accident only if all the mitigating features fail. Generally, therefore, there are many more lesser accidents than major accidents. This high ratio of lesser to major accidents is the concept underlying the accident pyramid discussed in Chapter 1 and shown in Figure 1.4.

The major accident is likely therefore to be preceded by a number of lesser events, some of which may be regarded as 'near misses'. Thus the time order of the events is also important. The exploitation of the time order of major and lesser accidents underlies the concept of learning from near misses.

These ideas are well understood. What does not appear to have been sufficiently appreciated and exploited is the potential for using these concepts in conjunction with a formal analysis of accident structure such as the fault tree. A hazard possesses a characteristic warning structure. The hazard warning structure may be laid bare by casting the fault tree for the hazard in a particular way.

9.26.2 Hazard warning tree

A typical hazard warning tree is shown in Figure 9.48. An event at level 1, which has a frequency λ_1, escalates into a level 2 event only if there is failure of a level 1 mitigating feature, which has a probability p_1. Similarly, the level 2 event with frequency λ_2 escalates into a level 3 event with frequency λ_3 only if there is failure of the level 2 mitigating feature with probability p_2. The probabilities p_1 and p_2 are attentuation fractions associated with the mitigating features.

A simple illustration is a release from a large refrigerated atmospheric storage tank holding toxic liquefied gas towards a housing estate as shown in Figure 9.49. In this case, the first level event might be defined as a release of unspecified size that might have a number of possible causes. The first level feature might then be the size of release, since only a proportion of such releases would be large ones. Further mitigating features at higher levels in the tree would be the wind direction, the stability condition, the population exposure and the injury relations.

9.26.3 Events before and after release

For a major hazard the critical event is usually loss of containment, and consideration here is directed mainly to this.

Generally in hazard assessment the frequency of the critical event is estimated either directly from failure data or else the structure of the events leading up to the release is analysed and the frequency obtained indirectly using a fault tree, while the structure of the events following the release and the frequency of particular outcomes is determined using an event tree. For a particular outcome the event tree can then be recast in the form of a fault tree. In some cases, therefore, there are available, in principle, both pre-release and post-release fault trees, whilst in other cases only the latter are available.

Even where it is not normally considered necessary to construct a pre-release fault tree in order to estimate release

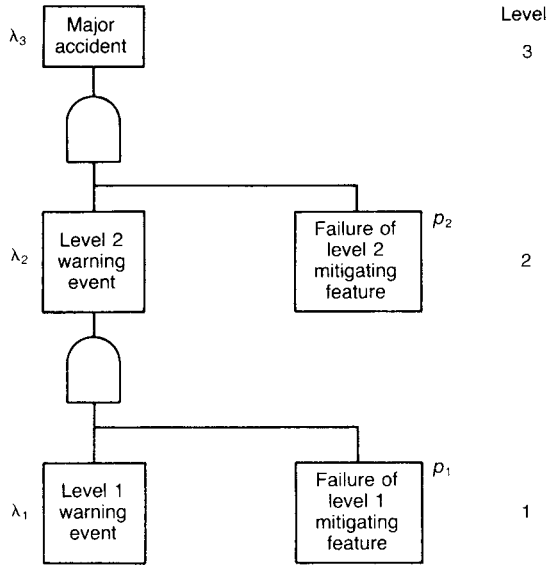


Figure 9.48 *A hazard warning tree (Lees, 1983b) (Courtesy of the Institution of Chemical Engineers)*

frequency, it may nevertheless by worth doing so for the purpose of analysing hazard warning structure. If both pre- and post-release fault trees are available, the two trees may be consolidated to form a single fault tree.

The concept of hazard warning was originally described primarily in terms of the critical event and the post-release tree, using the illustrative example of the release of refrigerated toxic liquefied gas as just described. The reason for this was simple. After the release the event/mitigating feature pairs are readily defined. They are features such as leak size, wind direction, stability condition, and so on. The hazard warning analysis is therefore relatively straightforward.

However, the application of hazard warning analysis to the situation prior to release is equally valid and may actually be of more value, since it deals with the features over which management has some control. Management can do little about the weather, but it can do something about plant design and operation. Pre-release analysis may therefore be more valuable, but it is usually more difficult.

9.26.4 Events, mitigating features and attenuation factors

The essential feature of a hazard warning analysis is that an event above the lowest level is defined as the outcome of a lower level event and of failure of a mitigating feature. The quality of the analysis depends largely on this first stage in which events, or in effect event/mitigating feature pairs, are defined.

In defining an event the object should be to give a definition that corresponds to an observable, and recordable, event. This is an essential condition both for the use of historical event data in conventional hazard assessment and for the use of event data from the operating plant. The definition of an event implies that of the associated mitigating feature. The term 'mitigating feature' is interpreted very broadly. For example, hole size for a noxious release is a mitigating feature on the basis that only a proportion of holes are large ones.

As in constructing a fault tree, with a hazard warning tree it is important that events be defined in such a way as to make the tree comprehensive and to guard against omissions. Such robustness of event definition may be achieved by working, at least in the first instance and at higher levels of the tree, in terms of generic failure modes rather than specific causes. For example, blockage may represent a generic mode of which solids deposition, freezing, crystallization and polymerization are specific causes. This approach is a safeguard against omissions insofar as it is much less probable that a generic mode will be overlooked than a specific, and perhaps low probability, cause.

Some events and mitigating features are under the influence of management, while others are not. Broadly speaking, management has relatively good control up to the point where loss of containment occurs, but much less thereafter. Management decides the hardware and software protection that is to be provided. The former includes both passive protection such as plant layout and active protection such as trip systems, while the latter covers a range of measures such as formal systems and procedures and training. Management is also able to influence the occurrence of initiating events. Once emission has occurred, the features that come into play are those such as weather conditions and exposure of people, factors over which management has little or no control.

Another important distinction is between predictable and unpredictable event rates and attenuation factors. It is much more difficult to make quantitative estimates for some event/mitigating feature pairs than for others.

Since there is a potential ambiguity it is necessary to define the sense in which 'attenuation' and associated terms are used here. The frequency of a lower level event is divided by the attenuation, or attenuation factor, associated with the mitigating feature in order to obtain the frequency of the higher level event. The attenuation is therefore greater than unity. The attenuation fraction, which is the probability of failure of the mitigating feature, is the reciprocal of the attenuation factor and is less than unity.

A hazard has a high or low warning structure depending on the total attenuation between the major accident and the lowest level of event that can serve as a warning. For a hazard to be classed as 'high warning', which is the desirable case, the total attenuation should ideally be several orders of magnitude. Generally, this means that the attenuation attributable to a single feature should be an order or magnitude or more. Attentuations of 2 or 3 are of limited value, although not completely worthless. Fortunately, for many hazards there are mitigating features that do tend to be associated with quite large attenuations. For example, the proportion of large leaks to total leaks, the probability of explosion rather than fire, the probability of particular meteorological conditions may each be quite low. If a mitigating feature represents a significant barrier to escalation and if it is one over which management has some control, it is important that it be identified

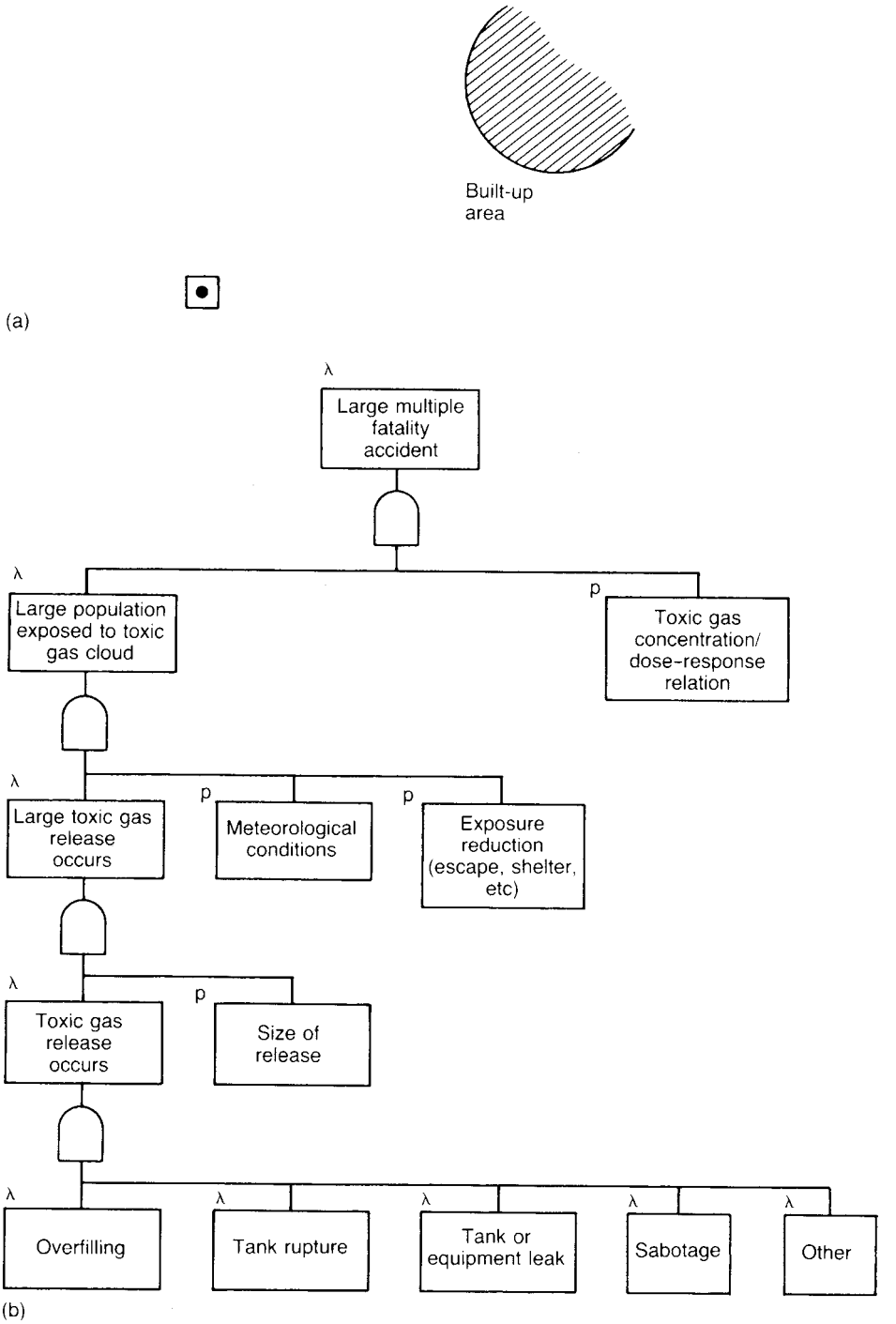


Figure 9.49 *Hazard warning tree for large multiple fatality accident due to large release of toxic liquefied gas: (a) storage tank with built-up area distant and in one sector only; (b) hazard warning tree (Lees, 1982b) (Courtesy of the Institution of Chemical Engineers)*

and that measures be taken to maintain or even improve its effectiveness.

Hazard warning is best viewed not so much as a property inherent in an installation but rather as one conferred on it by the observer. The property of hazard warning is conferred partly by recognition of features capable of giving warning and partly by the creation of such features. The principal means of creating a warning feature are, in the pre-release phase, the use of monitoring and inspection in some form and, in the post-release phase, the use of separation distances.

9.26.5 Post-release analysis

The starting point for the post-release analysis is the critical event, which is here taken as a loss of containment. In constructing the post-release tree, it is generally convenient to include as a mitigating feature the size of release, even though this could be regarded strictly as part of the pre-release tree, provided that double counting is avoided in the final assessment. The justification for this practice is that leak size is nearly always an important mitigating feature with a high attenuation factor, and that inclusion in the post-release tree ensures that it is taken into account even if no pre-release tree is developed.

Some principal mitigating features in a post-release tree are given in Table 9.48. The list is illustrative rather than exhaustive, and is self-explanatory. A post-release hazard warning analysis of the St Fergus to Moss Morran pipeline has been given by Lees (1985). A hazard assessment for this pipeline has been made by the HSE, as described in Chapter 23.

The hazard considered in the HSE report is a release of NGL from the pipeline, resulting in interactions with housing and hospitals. For this hazard there is a single base event that has 11 potential bad outcomes. The base event is a release of NGL from the pipeline. The pipeline is 220 km long. The frequency of the base event is:

$$\text{Frequency of release of NGL} = 2.32 \times 10^{-4}/\text{km-year} = 220 \times 2.32 \times 10^{-4} = 5.1 \times 10^{-2}/\text{years}$$

The bad outcomes are interactions with housing at eight locations and with hospitals at three locations. The frequencies of these bad outcomes are:

Location	*Frequency* (10^{-6} interactions/year)	*Location*	*Frequency* (10^{-6} interactions/year)
1	2.5	7	1.0
2	2.0	8	1.2
3	3.3	9	1.0
4	4.0	10	1.3
5	1.5	11	1.4
6	2.8		
Total			22.0

The frequency of all bad outcomes is 22×10^{-6}/year. The overall attenuation factor for all bad outcomes is:

$$\text{Overall attenuation factor} = (5.1 \times 10^{-2})/(22 \times 10^{-6}) = 2300$$

The individual attenuation factors that make up this overall attenuation factor may be derived from the report as follows. For each location there is an estimated length of pipeline that is capable of giving rise to an interaction. The total length for all locations is 32.5 km. Hence:

$$\text{Attenuation factor for location} = 220/32.5 = 6.8$$

There is no interaction for ruptures with hole sizes up to 20 mm, but there can be interactions for ruptures with hole sizes in the range 20–80 mm. The estimated frequencies for these two cases are:

$$\text{Frequency of rupture with hole size up to 20 mm} = 2.0 \times 10^{-4}/\text{km-year}$$
$$\text{Frequency of rupture with hole size 20–80 mm} = 2.2 \times 10^{-5}/\text{km-year}$$

and hence

$$\text{Attenuation factor for leak size} = (2.0 \times 10^{-4} + 2.2 \times 10^{-5})/(2.2 \times 10^{-5}) = 10.1$$

Interaction can occur only if the wind direction allows. The probability of such wind direction, weighted in accordance with the interaction frequencies, is 0.240. Hence:

$$\text{Attenuation factor for wind direction} = 1/0.240 = 4.2$$

Also, interaction can occur only if the stability condition allows. Interactions are possible at all locations for Pasquill

Table 9.48 *Some mitigating features for post-release hazard warning*

Size of leak
Employee exposure: workforce location
Distance to population
Direction of population
Density of population
Population exposure: siting
Distance to population
Direction of population
Density of population
Modification of exposure (employees and public):
Time of day
Escape, evacuation
Shelter
Protective clothing
Meteorology:
Wind direction
Wind speed
Stability category
Nature and intensity of failure
Nature and size of equipment failure:
Size of hole
Size of inventory
Flammable cloud behaviour
Ignition:
Probability
Time delay
Explosion:
Probability
Directionality

stability category *F* and at eight locations for category E, giving for the latter a weighting factor of 0.72 based on the length of line at each location over which interaction can occur. The probabilities of categories E and *F* are 0.06 and 0.08, respectively. Hence:

Attenuation factor for stability conditions $= 1/[(0.06 \times 0.72) + 0.08] = 8.1$

The overall attenuation factor from these four separate attenuation factors is 2300, which agrees with the figure derived earlier. In this case, therefore the overall attenuation factor is a very large one.

9.26.6 Pre-release analysis

It is generally much more difficult to carry out a pre-release analysis and the methods for doing this are not well developed. As before, the approach involves the definition of mitigating features. Some principal mitigating features are shown in Table 9.49. These features are rather less straightforward and require some explanation. The pre-release tree may be envisaged as consisting of the main potential hazard tree which has as its top event the hazard, namely a leak, which will be realized unless protection acts to prevent it, and as having grafted onto it two branches, one of hardware protection and one of software protection. These two latter modes of protection are effected by protective devices such as pressure relief valves, trips and interlocks and by the process operator, respectively. Within the potential hazard tree there are two main mitigating features. These are inspection and procedures. Inspection is the means of detecting and correcting mechanical failures. Procedures are the means of preventing human error. Both types of failure can constitute initiating events. The construction of a pre-release tree requires a degree of inventiveness. There is wide scope for creative definition of mitigating features. A pre-release hazard warning analysis of a hydrocarbon sweetening plant has been described by Lees (1985). The analysis is based on an account given by Kletz (1972a) of the use in the design of the plant of several trip systems to protect against the hazard of explosion.

The plant consists of a reactor that is fed with both hydrocarbon and air. The air is supplied from an air receiver, which is fed by an air compressor. There is a pressure relief valve on the air receiver and a non-return valve between the air receiver and the reactor. An explosion is assumed to occur if an explosive mixture develops, since an ignition source is assumed always to be present. An explosive mixture can occur if an air pocket develops and the feed is above its flashpoint or if backflow occurs from the reactor into the air receiver, which is at a temperature above the flashpoint. The combination of an air pocket and of a feed above its flashpoint can result from a high feed temperature, which is a common cause for both these conditions, or from other causes. The fault tree for the system is given by Kletz in his paper.

Table 9.49 *Some release modes and mitigating features for pre-release hazard warning*

A Release modes
Pressure envelope failure:
Equipment defect
External threat
Maintenance/modification activity
Process parameter deviation
B Mitigating features
Leak size
Protective devices
Operator action
Inspection procedures

The hazard warning tree derived by Lees from this fault tree is shown in Figure 9.50. The release mode in this case is a process parameter deviation. The initiating and enabling events are:

(1) relief valves fails open;
(2) compressor fault;
(3) mixer fault;
(4) supply fault;
(5) instrument fault;
(6) operator error.

The protective device failures are:

(1) non-return valve fails;
(2) high temperature trip fails;
(3) air pocket trip fails.

The procedure failures are

(1) purging procedure fails;
(2) flash point control procedure fails.

The mitigating features of protective devices and of procedures are underlined in Figure 9.50. Events that might be reduced in frequency by mitigating features such as inspection (equipment failures) and procedures (operator errors) are shown with broken underlining. This indicates points at which additional mitigating features might in some cases be created to give reduced frequency of occurrence and increased warning if these are judged desirable.

This hazard warning tree shows that there is one mitigating feature, the non-return valve and the high temperature trip, on the first and second branches, respectively, but two mitigating features, the air pocket trip and the flashpoint control procedure, on the third branch. In the event, it was decided to accept low flashpoint feeds as well, so that with this policy there was then one mitigating feature on the third branch also.

In general, the process operator appears both as a source of initiating events and as a form of protection. In the tree considered the protection afforded by the operator is limited to formal checking procedures. In principle, the operator might also intervene to effect protection at other points. For example, he may act as a further layer of protection against high feed temperature. However, for the operator to be able to give protection against a condition he must be able to observe or at least infer it. Observability is one of the principal aspects of operability, which in turn is one of the two main concerns of hazard and operability (hazop) studies.

Another illustrative example of pre-release analysis is shown in Figure 9.51 for the hazard of rupture of a batch reactor due to reaction runaway. Figure 9.51 (a) gives the master tree and Figures 9.51(b) and 9.51(c) show the subsidiary trees. The reactor is one for which only a proportion

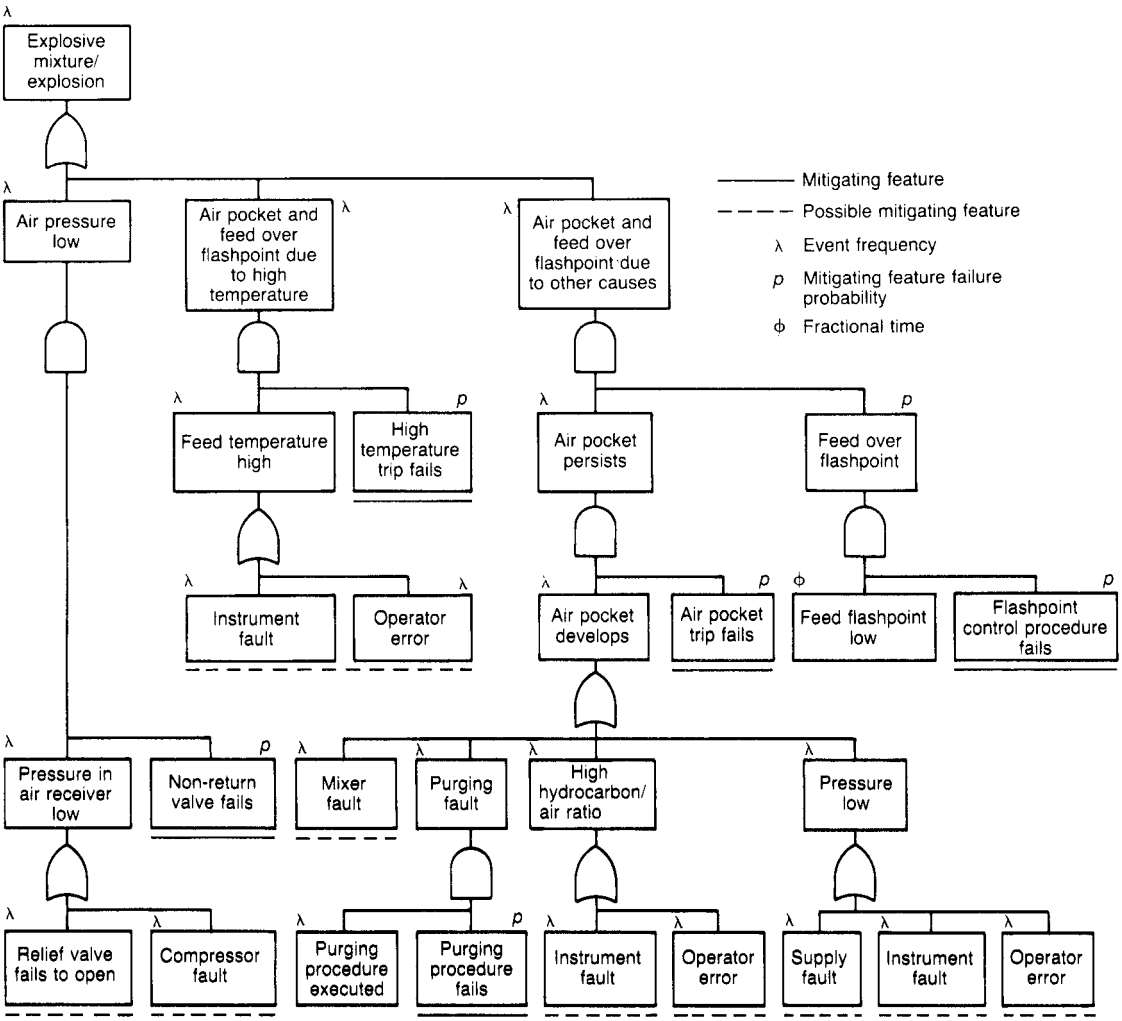


Figure 9.50 *Hazard warning tree for explosion in hydrocarbon sweetening plant (Lees, 1985) (Courtesy of the Institution of Chemical Engineers)*

of batches are prone to reaction runaway, which gives an additional mitigating feature.

Of particular interest in this tree is the fact that two of the initiating events may also cause failure of a mitigating feature. Thus loss of agitation is not only an initiating event but also prevents the use of shortstop, since without agitation distribution of the shortstop is poor. Similarly, if there is a single temperature measuring instrument both for the control loop and for display to the operator, failure of this instrument is not only an initiating event but may also cause a failure of operator intervention.

In the first example of pre-release analysis given above, the problem was of the type to which fault tree analysis is typically applied. There is a basic hazard and trip, and other protective systems are used to guard against it. The problem in the second example possesses a somewhat similar structure. It is also possible to apply hazard warning analysis to less explicitly structured problems, but the investigator must then impart much of the structure himself.

Of particular importance is loss of containment from the plant. Figure 9.52 gives an outline hazard warning tree for a major release of flammables from a plant, referred to as Plant EB. Figure 9.52(a) gives the master tree and Figures 9.52(b)–9.52(g) show the subsidiary trees. For example, for vessel corrosion (Figure 9.52(b)), the initiating event is vessel deterioration. Only if the mitigating feature of inspection fails does this escalate into a vessel leak. In turn, only in a proportion of cases will the leak be a major one, so that hole size is another mitigating feature.

For pipework rupture by maintenance or modification (Figure 9.52(c)), the initiating event is non-adherence to procedures anywhere in the works. Only in a proportion of cases will this lead to a leak, which gives a mitigating feature. Furthermore, only in a proportion of cases will

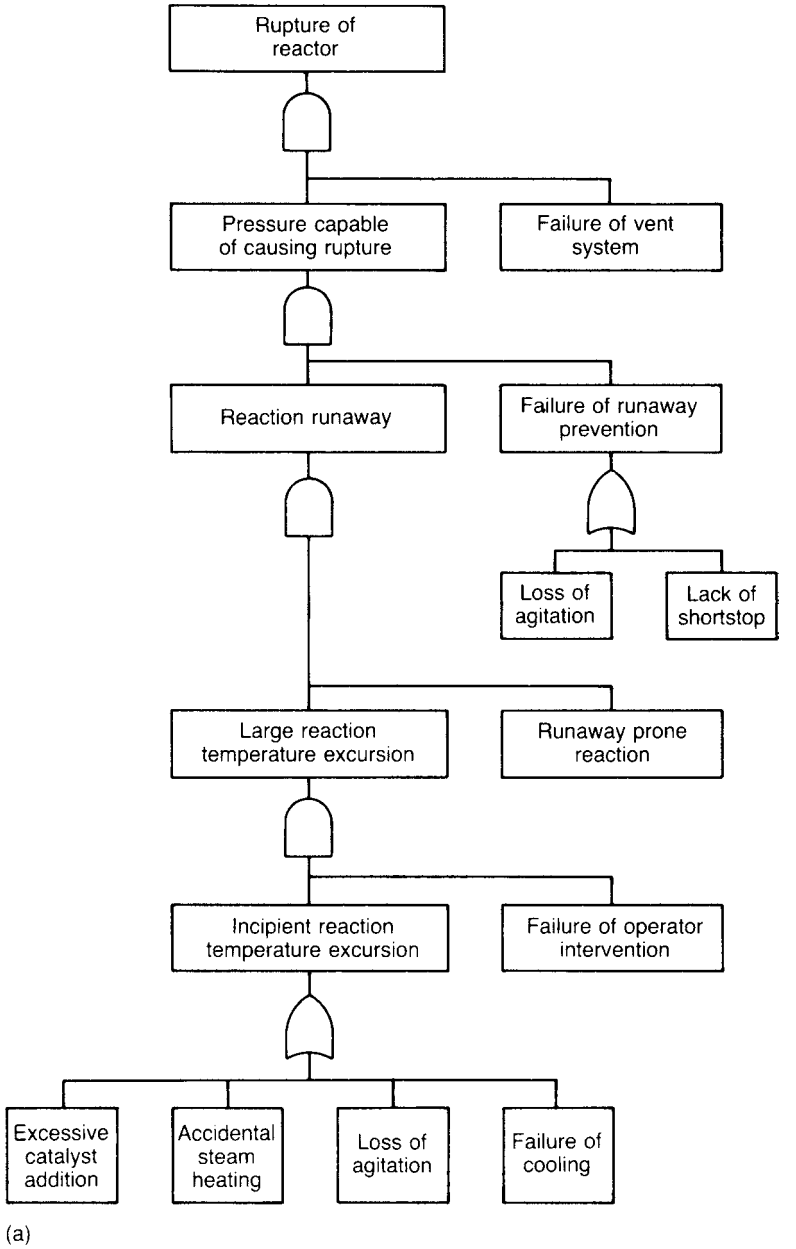


Figure 9.51 *Hazard warning tree for reaction runaway in a batch reactor, (a) Master tree, and subsidiary trees for (b) failure of operator intervention; (c) failure of cooling*

such a leak occur on Plant X, as opposed to elsewhere in the works, which gives a further mitigating feature. Finally, only in a proportion of cases will the leak be a major one, so that again hole size is another mitigating feature.

The other subsidiary trees for vehicle impact, missile impact and fire on the same plant and on another plant shown (Figures 9.52(d)–9.52(g)) follow the same principles. In some of the trees not all the branches are fully developed. In this example, therefore, the lowest level warnings even

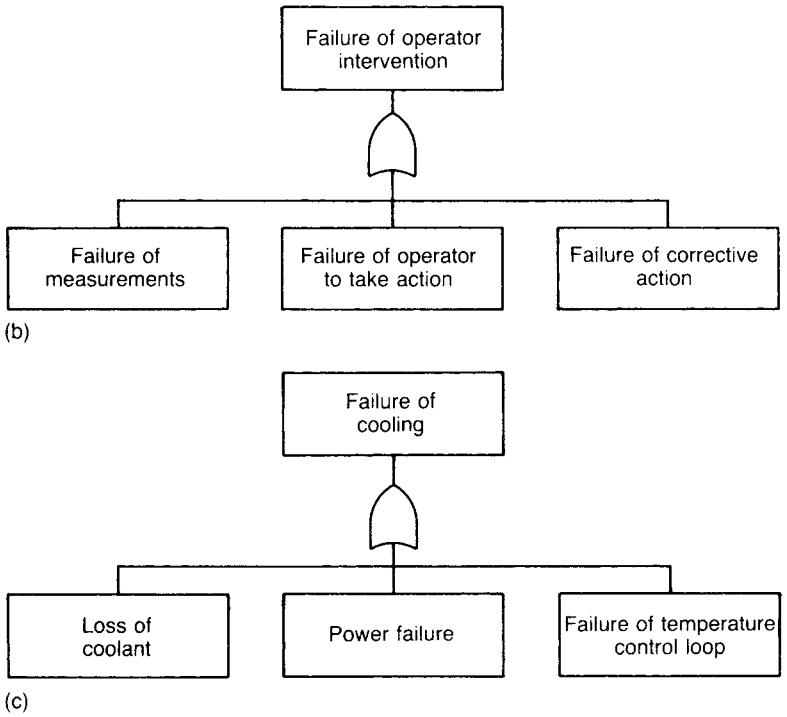


Figure 9.51 *continued*

include events that occur elsewhere on the works. It is quite legitimate to include these as warnings if they are indicators, for example, of non-adherence to procedures. The example illustrates the fact that it is up to the analyst to impose the hazard warning structure on the problem.

Another illustrative example of a similar type is that shown in Figure 9.53 for the hazard of failure of a materials testing system. Such failure may lead to a major leak from a pipework component. The initiating event is receipt of an unsuitable component. The materials testing system allows through only a proportion of defective components and acts as a mitigating feature. Only in a proportion of cases will the leak be a major one, which is a further mitigating feature. The failure of the mitigating feature of detection can occur as a result of failure of the detection procedure, but less obviously it can also be a result of failure to select the component for inspection in the first place.

9.26.7 Failure of warning

It is of interest to be able to estimate the probability that there may be a failure of hazard warning.

For a top event T of frequency λ_1 which is caused on a proportion p of occasions by a base event B of frequency λ_2:

$$\lambda_1 = p_1\lambda_2 \qquad [9.26.1]$$

Over a given time interval t the probability $P_T(t)$ that the top event will occur is:

$$P_T(t) = 1 - \exp(-\lambda_1 t) \qquad [9.26.2]$$

The probability $\bar{P}_T(t)$ that the top event will not occur is:

$$\bar{P}_T(t) = \exp(-\lambda_1 t) \qquad [9.26.3]$$

The probability $P_B(t,k)$ that the base event will occur exactly k times is:

$$P_B(t,k) = \exp(-\lambda_2 t)\frac{(\lambda_2 t)^k}{k!} \qquad [9.26.4]$$

The probability $P_B(t, k \leq n)$ that the base event will occur no more than n times is:

$$P_B(t,k \leq n) = \exp(-\lambda_2 t)\sum_{k=0}^{n}(\lambda_2 t)^k/k! \qquad [9.26.5]$$

The probability $P_B(t, k \leq n)$ that the top event will occur given that the base event occurs no more than n times is:

$$P_T(t,k \leq n) = \exp(-\lambda_2 t)\sum_{k=1}^{n}p(k)(\lambda_2 t)^k/k! \qquad [9.26.6]$$

where

$$p(k) = \sum_{j=1}^{k}(-1)^{j-1}\binom{k}{j}p^j \qquad [9.26.7]$$

Then the probability $W(t, k \geq n)$ that there will be a failure of hazard warning, in other words that the top event will occur and that the number of base events will be no more

than n when the top event occurs so that there will not be n clear warnings, is:

$$W(t, k \geq n) = P_T(k \leq n) \quad [9.26.8]$$

The ratio of the probability P_T of the top event to the hazard warning index W is the hazard warning ratio and it gives a measure of the degree of warning available.

As an illustrative example, Lees considers the case shown in Figure 9.54(a), for which:

$\lambda_1 = 0.001/\text{year}$

$\lambda_2 = 0.5/\text{year}$

$p = 0.002$

Then for a time period $t = 10$ years and $n = 2$

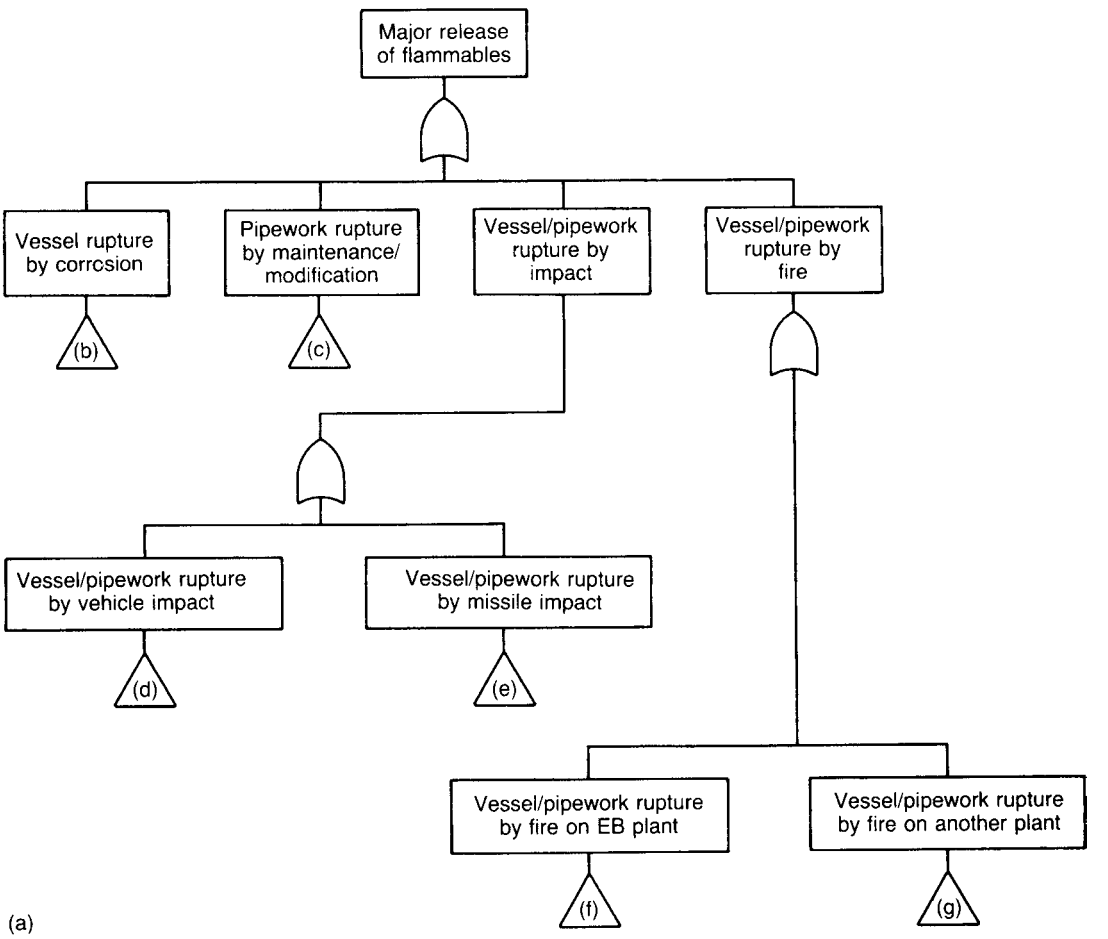
$P_T(t) = 0.01$

$W(t, k \geq n) = 0.0004$

Pitblado and Lake (1987) have derived an expression equivalent to Equation 9.26.8 and have explored the numerical implications using Lees' example. Their results are plotted in Figure 9.54 (b). They show that the value of the hazard warning ratio is lower in the early years and that it is reduced if the number of warnings specified is excessive, but that otherwise a worthwhile degree of warning is obtained.

9.26.8 High and low warning hazards

For many hazards the expected number of warnings is large, but for some it is not. The intention behind hazard warning analysis is to exploit the warnings, but analysis is not wasted if it reveals a low warning hazard. It is important to be aware of such a hazard, because it is unforgiving and needs special care.



(a)

Figure 9.52 *continued*

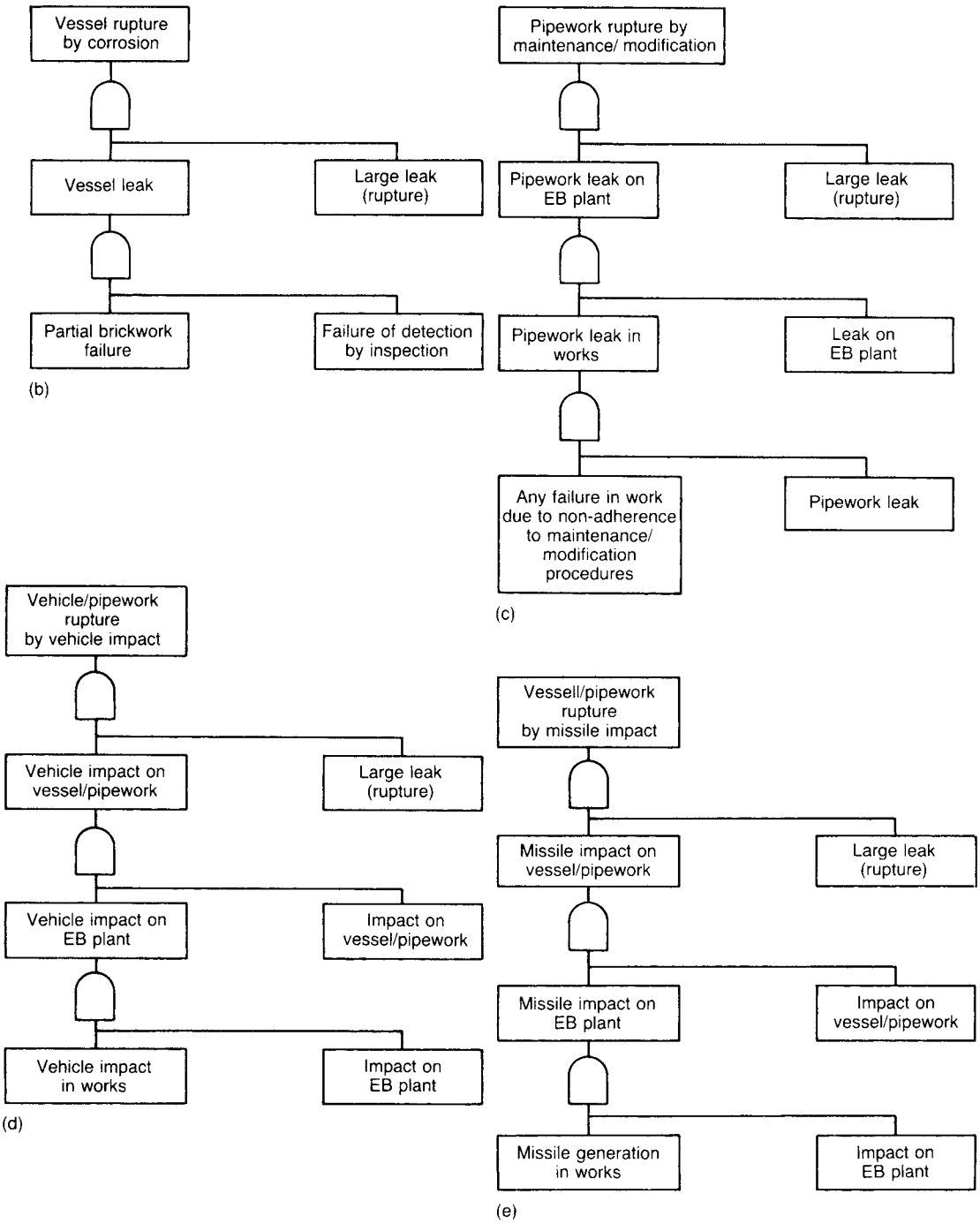
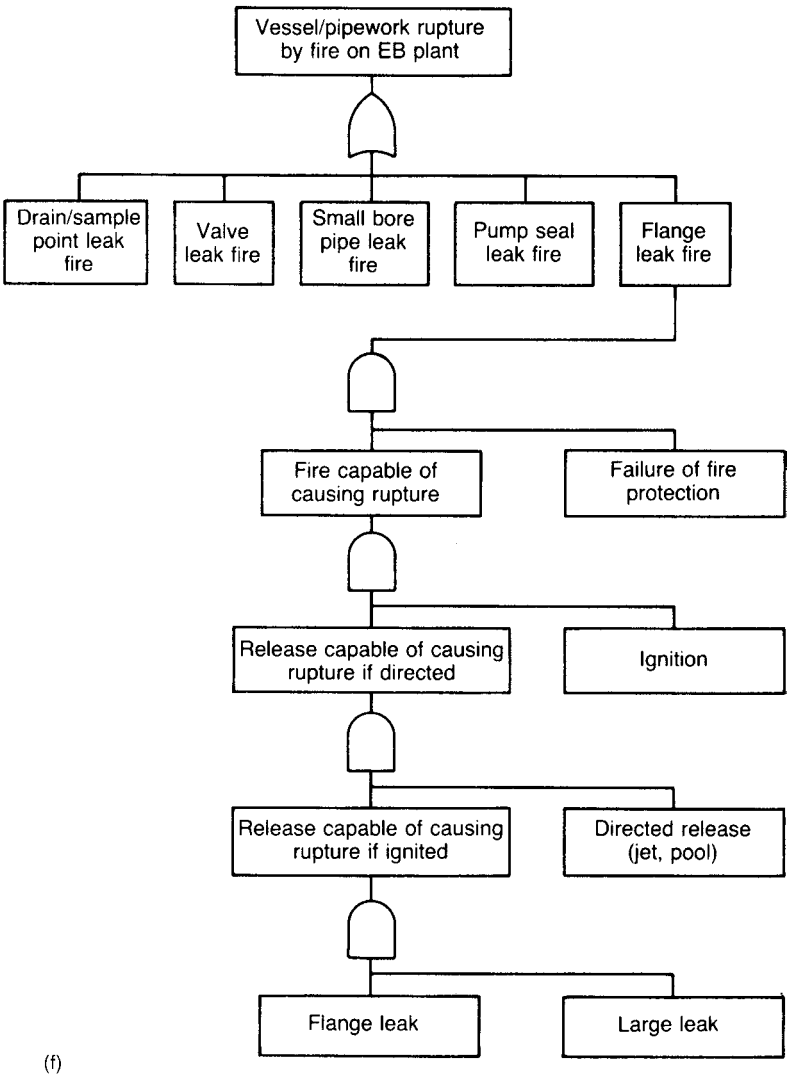


Figure 9.52 *continued*



(f)

Figure 9.52 *continued*

The degree of warning may be defined as follows (Lees, 1983b):

Degree of warning	*Attenuation factor*
Zero	1
Low	10
Medium	100
High	1000

An example of a low warning hazard was given in the First *Canvey Report*, where an ammonium nitrate explosion was identified as a hazard which, if it occurred at all, would cause casualties.

9.27 Computer Aids

Hazard assessment is an active field for the development of computer aids. Computer aiding has been applied to the following:

(1) fault tree analysis;
(2) fault tree synthesis;
(3) hazard models;
(4) hazard model systems;
(5) risk assessment.

These developments are described in Chapter 29. Also important in hazard assessment are computer data banks, which are described in Appendix 14.

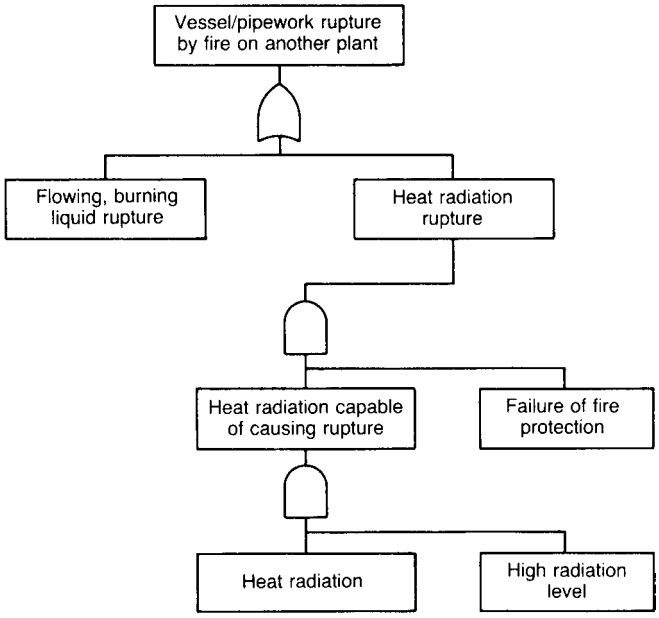


Figure 9.52 *Hazard warning tree for major release of flammables from a pressure system, (a) Master tree, and subsidiary trees for (b) vessel rupture by corrosion, (c) pipework rupture by maintenance/modification, (d) vessel/pipework rupture by vehicle impact, (e) vessel/pipework rupture by missile impact, (f) vessel/pipework rupture by a fire on same plant; and (g) vessel/pipework rupture by fire on another plant, EB, ethyl benzene*

9.28 Risk Assessment Debate

Almost from their inception, both the philosophy and methodologies of risk assessment have attracted criticism. The whole status of risk assessment as a scientific activity has been questioned by Weinberg (1972a,b). He argues that the assessed risks for very rare events are likely always to be derived by a process involving much subjective judgement and intractable for peer review and, therefore, to be subject to much uncertainty. In effect, it is possible to pose the problem in scientific terms, but the answer that can be given is not based on science but 'trans-science'. He quotes a major nuclear reactor accident as an example of this type of problem. He argues further that, insofar as in this area truth may be unattainable, the search should be rather for wisdom and that laymen have a correspondingly larger part to play in making the decision. Other critiques of risk assessment as applied to nuclear hazards include those by Hanauer and Morris (1971) and Critchley (1976).

Criticisms of specific techniques were also not slow to appear. Much of the initial work on the use of fault trees was done in the aerospace industry. The effectiveness of fault tree estimates in this work has been criticized by Bryan (1976), who was in charge of reliability assessment during testing of the Apollo Service Propulsion System (or SPS engine). He states:

> This optimism was soon dispelled by hundreds of cases of unexpected test and operational failures and thousands of system malfunctions. Many of the failures and malfunctions modes had either been previously analysed and seemed to be noncredible events or had come as a complete surprise which previous analyses had not identified at all. By the early 1960s, it had become apparent that the traditional method of identifying potential failure events and assigning historical probabilities of occurrence to these events . . . had consistently led to overly optimistic conclusions. Consequently, the failure rates were consistently underestimated.

Further discussion of experience in reliability assessment of the SPS engine is given by the Union of Concerned Scientists (1977).

The debate on the *Rasmussen Report*, described in Appendix 23, was in large part concerned with the validity of risk assessment. The use of risk assessment in the process industries has also had its critics, including Bjordal (1980), Pilz (1980a,b), Joschek (1983) and Lowe (1984). This criticism comes from experienced practitioners and is directed not at the use of quantitative methods but rather at what is considered to be their misuse.

It is argued by Lowe that hazard analysis and risk analysis are quite different activities. Whereas the former is action oriented, being undertaken to assist in making engineering decisions, the latter is information oriented, yielding little except very uncertain risk estimates. At first sight it appears that risk estimates, even if approximate, should be of value in assisting decisions in the public domain. Where most of the other factors, however, are unquantifiable, quantification of a single factor may actually be a hindrance by putting undue weight on and creat-

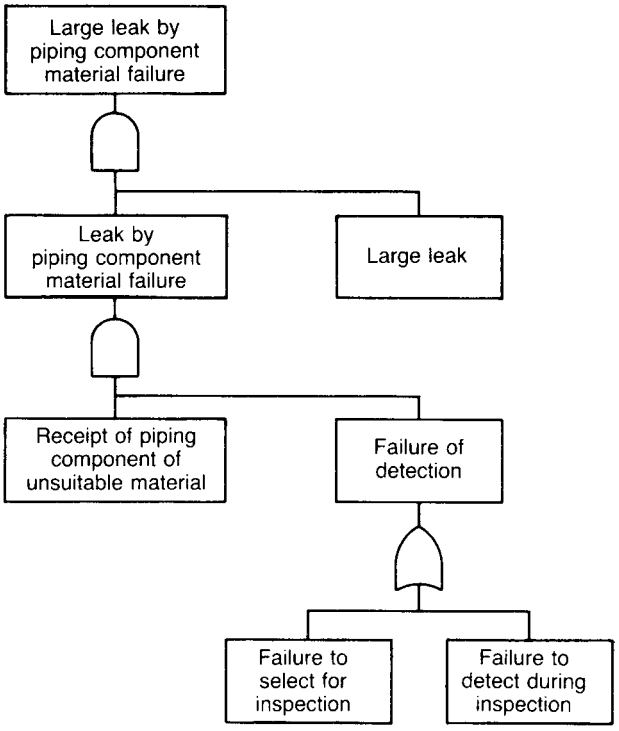


Figure 9.53 *Hazard warning tree for major leak by piping component due to failure of materials inspection*

ing excessive debate about that factor. He concludes:

> In my view risk analysis of the type considered here is to safety what the merry-go-round is to transport. We can spend a lot of time and money on it, only to go round in circles without really getting anywhere.

Bjordal's criticism is directed particularly to risk assessments that concentrate exclusively on fatalities. He draws attention to the wide variety of other factors that may concern the public, ranging from pollution to anxiety. He emphasizes the importance of defining beforehand the use to which the results are to be put, and cites one case where the point which the public were most anxious to have answered was not the risks as usually assessed, but the question: 'Is it more dangerous to live along the fjord than before?'

Pilz describes the many difficulties in the way of obtaining a meaningful risk assessment for a process plant. The value of the assessment is crucially dependent on the insight the analyst has regarding the system. Failure rates are usually assumed to be constant over time, but may well not be so. Failure data are often lacking and are strongly affected by the differences in aggressiveness of the chemicals handled and in operating and maintenance practices. Fault tree methods are based on classifying states that are essentially a continuum as discrete states of failure or success. Human error plays a critical role. It is necessary to consider not simply the steady-state operating condition but also other conditions such as start-up, shut-down, etc. He concludes that it is a virtually hopeless task to obtain a risk assessment that is meaningful in terms of the uses for which it is usually advocated and quotes the wide confidence bounds given by the authors of the *Nuclear Reactor Risk Study* in Germany.

In Pilz's view, fault tree analysis can nevertheless play a useful role. It is a valid technique for comparing different protective systems. It should be used to check different safety concepts and to discover weak points, but it should not be made to bear the burden of risk assessment. He points out that in Germany a risk assessment is not done for every nuclear reactor, and that indeed the *Reactor Risk Study* dismisses this as impossible. What is done is to study a number of typical plants and to determine the average risk from these.

The debate on risk assessment is reflected in the two guides *Methodologies for Hazard Analysis and Risk Assessment in the Petroleum Refining and Storage Industry* (CONCAWE, 1982 10/82) and *Risk Analysis in the Process Industries* by the International Study Group on Risk Assessment (ISGRA, 1985; Pitblado, 1994b). Both publications give guidance on the methodologies of hazard analysis and risk assessment. Neither recommend the universal use of risk assessment. The CONCAWE guide emphasizes the uncertainties inherent in risk assessment. The ISGRA guide explicitly states: 'Whilst a large number of companies have found benefit from the use of quantified risk analysis, it must be recognised that others in the process industries have not found it necessary'.

One aspect of quantification which has attracted less criticism is the modelling of consequences. Certainly there are many comments on the wide disparities in the results from different models of particular physical phenomena,

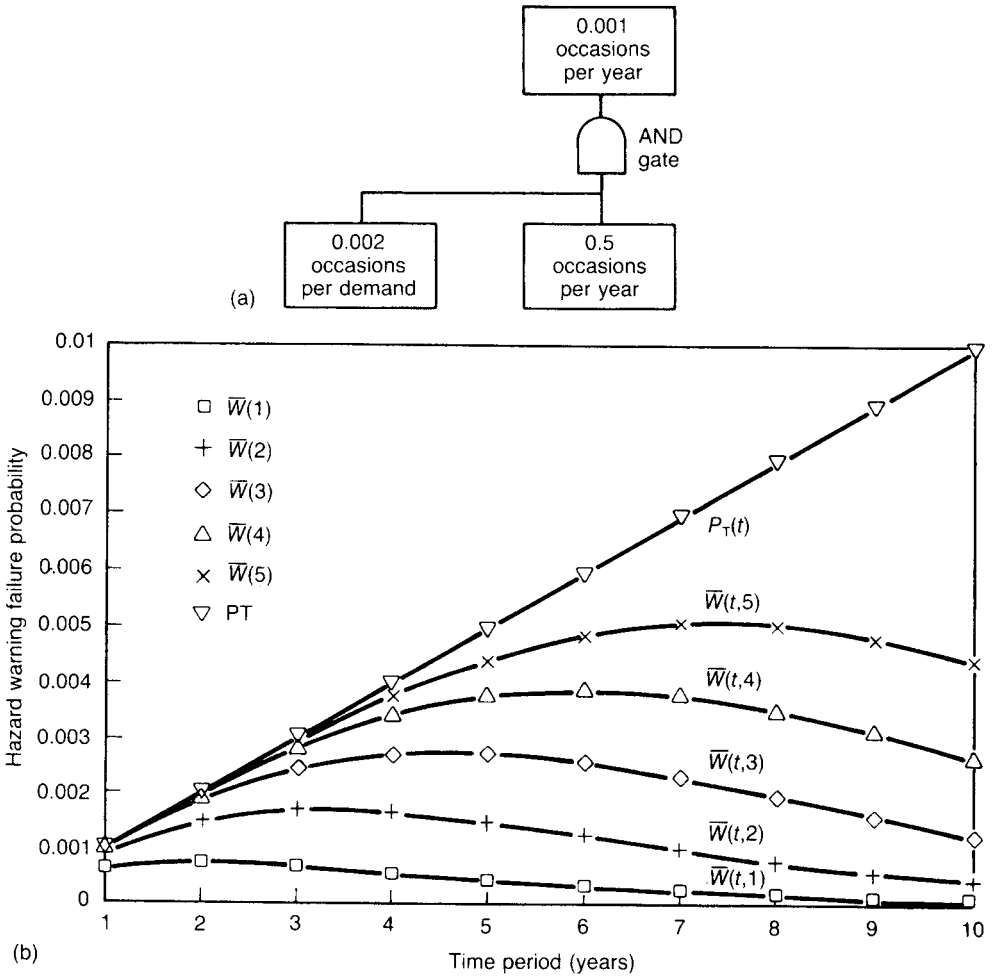


Figure 9.54 *Effectiveness of hazard warning (after Pitblado and Lake, 1987); (a) simple hazard warning tree; (b) probability of failure of warning (Courtesy of the Institution of Chemical Engineers), Note: In these authors' notation P_T is the probability of the top event, or hazard realization; W is the probability of failure of hazard warning and is thus equivalent to Lees' W*

but there is also perhaps a feeling that there is good prospect of resolving these differences in due course and that the models are already becoming sufficiently accurate to give useful results.

9.29 Overview

There are three principal reasons why hazard assessment may be undertaken:

(1) engineering decisions;
(2) public acceptance;
(3) regulatory requirements.

There are important differences between these three situations. The first two are voluntary, while the third is imposed. The first is in-company, while the last two are in the public domain.

Hazard assessment is undertaken by industry as an aid to decision-making. It assists in identifying the significant hazard, in choosing cost-effective countermeasures, and in bringing out the underlying assumptions and the conditions that must be met if the hazard is to be controlled. There is little dispute over its value for these purposes. Applied in this way hazard assessment has the aspect of hazard analysis (HAZAN).

Debate centres on the value of hazard assessment in the form of probabilistic risk assessment. Here the common features of risk assessments in respect of consequence modelling appear to have obscured the fact that there are major differences between assessments in the treatment of frequency estimation.

Assessments tend to vary in nature according to the system studied. As already pointed out, the *Canvey Reports* contain little in the way of fault trees, whereas the *Rasmussen Report* contains large numbers.

For a process plant it is possible to conduct a risk assessment that is based on a release source review and uses generic failure data. This overcomes many of the problems associated with completeness of hazard identification and with hazard assessment using fault tree methods. On the other hand, the information obtained from such a study is of limited use. Essentially what it reveals is the risks to be expected if the plant is designed and operated to some average standard. A study of this kind appears relevant primarily to decisions about the siting of and development around a major hazard.

A risk assessment for a process plant which starts from a release source review but also includes extensive hazard identification and assessment studies on the particular plant using methods such as hazop and fault trees and utilizing, as far as possible, plant specific data is another matter. Such a study involves much more work, but it also yields much more information and is of much greater assistance in engineering decision-making. It is convenient to refer to these two types of risk assessment as 'generic' and 'specific' assessments, respectively.

The use of risk assessments in the public domain arises from the demand that the operator of a major hazard plant should demonstrate that the hazards on its plant are under control. In making this demand, it seems probable that the public is seeking assurance in respect both of the magnitude of the hazard and of the risk of its realization. What the public gains from a generic assessment is a general picture of the hazard and the associated risks, the latter based on the assumption that the plant standards are average.

The value to the public of a specific risk assessment is rather different. In this case what the public gains is the assurance that the company has made a detailed study of the hazards of its plant and that, as a result, the standards should not be below average. The difference between generic and specific risk assessments, therefore, lies less in the assessment of the consequences than in that of the frequency.

A full risk assessment of a major hazard plant is a substantial undertaking. Much of the effort, however, lies in the assembly of data and models and is in some degree transferable to other assessments. Moreover, computer aids are now available which besides carrying out the actual calculations, also provide a framework and set of default data and models.

Some aspects of risk assessment, therefore, may become virtually routine, but care is needed in identifying those features for which in a given case a relatively routine treatment may be appropriate and those that require detailed study. The aim should be to free the engineer to concentrate on the latter. It is such detailed studies that are most likely to yield useful results.

A risk assessment should be realistic rather than conservative. In engineering design, it is not uncommon for a number of safety factors to be introduced at the various stages. This approach is not suitable in risk assessment. The use of excessively conservative assumptions leads to overly pessimistic and unrealistic risk estimates that are of little value for decision-making. The assessed risks should be 'best estimates'. The decision-makers can then treat these results with whatever degree of conservatism they think appropriate.

Risk assessment has undergone substantial development in recent years and the pace of change is still rapid. The methodology is still only barely adequate for the tasks often required of it. This should be borne in mind when evaluating the assessed risks.

The numerical risk results are only one of the outputs from a risk assessment. Equally important, and perhaps more so, are the other findings such as the identification and ranking of hazards, the identification and assessment of engineering measures to avoid, protect against and mitigate hazards, and an appreciation of the conditions necessary to keep hazards well controlled.

10 Plant Siting and Layout

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10.1 Plant Siting

Safety is a prime consideration in plant siting. Other important factors include: access to raw materials and to markets; availability of land, labour and cooling water; means of effluent disposal; interlinking with other plants; and government policies, including planning permission and investment incentives. It is only safety aspects which are considered here.

As far as safety of the public is concerned, the most important feature of siting is the distance between the site and built-up areas. Sites range from rural to urban, with population densities varying from virtually zero to high. Separation between a hazard and the public is beneficial in mitigating the effects of a major accident. An area of low population density around the site will help to reduce casualties. In the ideal case, the works is surrounded by fields or waste land forming a complete cordon sanitaire. In many situations, however, it is unattractive to 'sterilize' a large amount of land in this way, particularly in an urban area, where land is generally at a premium.

The physical effects of a major accident tend to decay quite rapidly with distance. Models for fire give an inverse square law decay, as do many of the simpler models for explosion and toxic release, though other explosion and toxic release models give different decay relations, some with less rapid decay. Decay laws were discussed in Chapter 9 and further treatments are given in Chapters 15–17.

Information on the potential effects of a major accident on the surrounding area is one of the main results obtained from a hazard assessment and such an assessment is of assistance in making decisions on plant siting.

Siting is not a substitute for high standards of design and operation of the plant. It should never be forgotten that the people most at risk are the people on site, and standards should be such as to safeguard this workforce. It is sometimes argued in fact that standards should be sufficiently high so that separation between site and public is not necessary. Such standards, however, are essentially a form of active protection, which depends crucially on the quality of management. In most countries, including the United Kingdom, the view is taken that it is prudent nevertheless to have a degree of separation. The provision of a separation distance is a form of passive protection which provides a further mitigating factor and which is relatively robust in the event of deterioration in the plant management.

In terms of hazard warning, separation tends to create a hazard, which will give more warnings and which is therefore less unforgiving.

Topography is another relevant feature. It is desirable to avoid terrain where hazardous fluids, whether liquids or dense gases, can flow down into populated areas. Another consideration to be taken into account is contamination of water courses by liquid spills.

In selecting a site, allowance should be made for site emergencies. One factor is the availability of emergency utilities such as electrical power and water. Another is the availability and experience of outside emergency services, particularly the fire service. A third is access for these services.

A discussion of siting for high toxic hazard materials (HTHMs) is given in the CCPS HTHM *Storage Guidelines* (1988/2). Siting policy for major hazard plants in the United Kingdom was discussed in Chapter 4. Selected references on plant siting are given in Table 10.1.

Table 10.1 *Selected references on plant siting*

NRC (Appendix 28: Siting); Cremer (1945); Mohlman (1950); Bierwert and Krone (1955); Greenhut (1956); von Allmen (1960); J.A. Gray (1960); Anon. (1964b); Risinger (1964i); Liston (1965); Fryer (1966); Farmer (1967a,b, 1969a,b); R. Reed (1967); Fowler and Spiegelman (1968); Kaltenecker (1968); G.D. Bell (1970); Otway and Erdmann (1970); Speir (1970); Tucker and Cline (1970); Yocom, Collins and Bowne (1971); Gronow and Gausden (1973); Balemans *et al.* (1974); Cross and Simons (1975); Roskffl (1976); Weismantel (1977); Cremer and Warner (1978); Slater (1979); Dalai (1980); Kletz (1980h); Granger (1981); Considine, Grint and Holden (1982); Lovett, Swiggett and Cobb (1982); Ramsay, Sylvester-Evans and English (1982); Landphair and Motloch (1985)

10.2 Plant Layout

Plant layout is a crucial factor in the economics and safety of process plant. Some of the ways in which plant layout contributes to safety and loss prevention (SLP) are:

(1) segregation of different risks;
(2) minimization of vulnerable pipework;
(3) containment of accidents;
(4) limitation of exposure;
(5) efficient and safe construction;
(6) efficient and safe operation;
(7) efficient and safe maintenance;
(8) safe control room design;
(9) emergency control facilities;
(10) fire fighting facilities;
(11) access for emergency services;
(12) security.

Plant layout can have a large impact on plant economics. Additional space tends to increase safety, but is expensive in terms of land and also in additional pipework and operating costs. Space needs to be provided where it is necessary for safety, but not wasted.

The topics considered under the heading of 'plant layout' are traditionally rather wide ranging. Many of these subjects are treated here in separate chapters and only a brief treatment is given in this one. This applies in particular to such topics as hazard assessment, emission and dispersion, fire and fire protection, explosion and explosion protection, storage and emergency planning.

A general guide to the subject is given in *Process Plant Layout* (Mecklenburgh, 1985). This is based on the work of an Institution of Chemical Engineers (IChemE) working party and expands an earlier guide *Plant Layout* (Mecklenburgh, 1973). The treatment of hazard assessment in particular is much expanded in this later volume. The loss prevention aspects of plant layout have also been considered specifically by Mecklenburgh (1976).

Other work on plant layout, and in particular SLP, includes that of: Armistead (1959), R. Kern (1977a–f, 1978a–f) and Brausbacher and Hunt (1993), on general aspects and spacing recommendations; Simpson (1971) and R.B. Robertson (1974a, 1976b), on fire protection; Fowler and Spiegelman (1968), the Manufacturing Chemists Association (MCA, 1970/18); Balemans *et al.* (1974) and Drewitt

(1975), on checklists; and Madden (1993), on synthesis techniques.

Plant layout is one of the principal aspects treated in various versions of the Dow *Guide* by the Dow Chemical Company (1994b). It is also dealt with in the *Engineering Design Guidelines* of the Center for Chemical Process Safety (CCPS, 1993/13). There are also a large number of codes relevant to plant layout, and particularly separation distances and area classification. These are described below.

The treatment given here for the most part follows that of Mecklenburgh, except where otherwise indicated. It is appropriate to repeat here, his caution that the practice described should be regarded only as typical and that it may need to be modified in the light of local conditions, legislation and established safe practices. In particular, the account given generally assumes a 'green-field' site, and some compromise is normally necessary for an existing site.

Selected references on plant layout are given in Table 10.2.

10.3 Layout Generation

10.3.1 Factory layout

For factories generally there are a number of different principles on which plant layout may be based (Muther, 1961).

Table 10.2 *Selected references on plant layout*

Cremer (1945); Mallick and Gaudreau (1951); Shubin and Madeheim (1951); Muther (1955,1961,1973); McGarry (1958); Armistead (1959); R. Reed (1961, 1967); EEUA (1962 Document 12, 1973 Hndbook 7); J.M. Moore (1962); ABCM (1964/3); Dow Chemical Co. (1964,1966a,b, 1976, 1980, 1987, 1994); Duggan (1964a); Jenett (1964c); Landy (1964a–c); Risinger (1964i); R. Wilson (1964b); Liston (1965, 1982); IP (1980 Eur. MCSP Pt 2,1981 MCSP Pt 3,1987 MCSP Pt 9, 1990 MCSP Pt 15); R. Kern (1966, 1977 series, 1978b): M.W. Kellogg Co. (1967); BCISC (1968/7); Fowler and Spiegelman (1968); Kaltenecker (1968); House (1969); Proctor (1969); British Cryogenics Council (1970); J.R. Hughes (1970); ICI/RoSPA (1970 IS/74); Kaess (1970); Sachs (1970); Tucker and Cline (1970); Bush and Wells (1971, 1972); Simpson (1971); Guill (1973); Mecklenburgh (1973, 1976, 1982, 1985); Pemberton (1974); R.B. Robertson (1974a,b, 1976a,b); Unwin, Robins and Page (1974); Falconer and Drury (1975); Beddows (1976); Harvey (1976, 1979b); Spitzgo (1976); Rigby (1977); Kaura (1980b); Kletz (1980h, 1987c); F.V. Anderson (1982); O'Shea (1982); Goodfellow and Berry (1986); Brandt *et al.* (1992); Meissner and Shelton (1992); Bausbacher and Hunt (1993); Madden (1993); Briggs (1994) ANSI A, A10, A37 and D series, BS 5930: 1981

Layout techniques
Mecklenburgh (1973, 1976, 1985); Sproesser (1981); Nolan and Bradley (1987); Madden, Pulford and Shadbolt (1990); Madden (1993).
Virtual reality: IEE (1992 College Digest 92/93)

Civil engineering, including foundations
ASCE (Appendix 27, 28); Urquhart (1959); Biggs (1964); ASTM (1967); MacNeish (1968); Benjamin and Cornell (1970); Tomlinson (1980); Carmichael (1982); M. Schwartz (1982a–c, 1983a–e, 1984); Pathak and Rattan (1985); Blenkinsop (1992); BS (Appendix 27 Civil Engineering, Construction), BS 6031: 1981, BS 8004: 1986, BS COP 2010: 1970–, BS COP 2012: 1974–

Equipment weights: El-Rifai (1979)

Hazardous area classification (*see* Table 16.2)

Materials handling
Woodley (1964); Smego (1966); R. Reed (1969); Department of Employment and Productivity (1970); Brook (1971); DTI (1974); Pemberton (1974); Sussams (1977); Chemical Engineering (1978b)

In-works transport, roads
HSE (1973 TON 44); Mecklenburgh (1973, 1985); HSE (1985 IND(G) 22 (L); 1992 GS 9)

Separation distances
C.W.J. Bradley (n.d., 1985); Armistead (1959); Dow Chemical Co. (1964, 1966a, 1976, 1980, 1987, 1994); Scharle (1965); Home Office (1968/1, 1971/2, 1973/4); Masso and Rudd (1968); Goller (1970); J.R. Hughes (1970); ICI/RoSPA (1970 IS/74); Laska (1970); Simpson (1971); OIA (1972 Publication 631); HSE (1973 HSW Booklet 30); Mecklenburgh (1973, 1976, 1985); Unwin, Robins and Page (1974); Butragueno and Costello (1978); IP (1980 Eur. MCSP R 2, 1981 MCSP R 3, 1987 MCSP R 9); API (1981 Refinery Inspection Guide Chapter 13, 1990 Std 620,1993 Std 650); Nolan and Bradley (1987); D.J. Lewis (1989b); Martinsen, Johnsen and Millsap (1989); NFPA (1989 NFPA 50A, 50B, 1992 NFPA 58, 59); IRI (1991, 1992); LPGLTA (1991–LPG Code)

Control rooms
Bradford and Culbertson (1967); Burns (1967); Prescott (1967); Schmidt (1971); E. Edwards and Lees (1973); Mecklenburgh (1973, 1976, 1985); V.C. Marshall (1974, 1976a,c,d); Kletz (1975e); Anon. (1976 LPB 11, p. 16); Gugan (1976); Harvey (1976, 1979b); Langeveld (1976); Anon. (1977 LPB 16, p. 24); Balemans and van de Putte (1977); CIA (1979); Cannalire *et al.* (1993)

Emergency shelters
Johnston (1968); Lynskey (1985)

Indoor plants
R. Kern (1978a); Munson (1980)

Storage
FPA (1964/1); IP (1980 Eur. MCSP R 2, 1981 MCSP R 3, 1987 MCSP R 9); Home Office (1968/1, 1971/2, 1973/4); J.R. Hughes (1970); ICI/RoSPA (1970 IS/74); HSE (1973 HSW Booklet 30); Wirth (1975); Hrycek (1978); D.W. Johnson and Welker (1978); Aarts and Morrison (1981); NFPA (1986 NFPA 43C, 1989 NFPA 50A, 50B, 1990 NFPA 43A, 50, 59A, 1992 NFPA 58, 59, 1993 NFPA 43B); LPGITA (1991 LPG Code 1 R 1)

Fire prevention and protection
FPA (CFSD FPDG 2); IRI (1964/5); BCISC (1968/7); IP (1980 Eur. MCSP R 2, 1981 MCSP R 3, 1987 MCSP R 9, 1993 MCSP R 19); Home Office (1974– Manual of Firemanship); J.R. Hughes (1970); ICI/RoSPA (1970 IS/ 74); Simpson (1971); Mecklenburgh (1973, 1976, 1985); R.B. Robertson (1974a,b, 1976a,b); Klootwijk (1976); Kaura (1980a)

Drains
J.D. Brown and Shannon (1963a,b); Seppa (1964); ICE (1969); Mecklenburgh (1973, 1976, 1985); Klootwijk (1976); Anon. (1978 LPB 19, p. 10); Elton (1980); Gallagher (1980); D. Stephenson (1981b); Easterbrook and Gagliardi (1984); Mason and Arnold (1984); Chieu and Foster (1993); Crawley (1993 LPB 111); BS 8005: 1987–

Barge mounted and ocean-borne plants
Birkeland *et al.* (1979); Charpentier (1979); Glaser, Kramer and Causey (1979); J.L. Howard and Andersen (1979); Jackson (1979); Jansson *et al.* (1979); Shimpo (1979); Ricci (1981); H.R. James (1982); de Vilder (1982)

Plant identification
NFPA (1990 NFPA 901); API (1993 RP 1109); BS (Appendix 27 Identification of Equipment), BS 1710: 1984, BS 5378: 1980–

Hazard assessment
Mecklenburgh (1982, 1985)

Thus, in light engineering, use is made of layouts in which the material fabricated remains in a fixed position and others in which a particular process or function is performed at a fixed point.

10.3.2 Flow principle

For process plants, however, the most appropriate method is generally to lay the plant out so that the material flow follows the process flow diagram. This is the process flow principle. This arrangement minimizes the transfer of materials, which is desirable both for economics and safety. It is difficult to overemphasize the importance of efficient materials handling. It has been estimated by the Department of Trade and Industry (DTI, 1974) that about a quarter of the production costs of manufacturing industry generally are for materials handling – an activity which in itself is totally unproductive.

Likewise, long runs of pipework with vulnerable features are an undesirable addition to the hazards of the plant. There are features which can lead to the layout sequence diverging from the process sequence. They relate particularly to: requirements for gravity flow; equipment needing specially strong foundations; access for construction, commissioning, operation and maintenance; future extension; operator protection; escape and fire fighting; containment of accidents; and environmental impact.

10.3.3 Correlation and compatibility

There are certain other layout approaches which are used for factory layouts generally and which merit mention. Correlation and compatibility techniques are used for the elimination of layout arrangements which are incompatible or impossible, and also for the preliminary formulation of compatible arrangements.

In the correlation chart method, for example, the procedure is as follows. The constraints and objectives are listed. The floor space is subdivided into a grid and for each item the grid divisions which violate the constraints are deleted. The permissible layouts are then determined. There is a corresponding algebraic method.

Proximity and sequencing techniques are available for the determination of the costs of material transfer with different layouts.

These general factory layout techniques are described in more detail by Mecklenburgh (1973), but he states that they appear to have found little application in process plant layout.

10.3.4 Process plant layout

As with design generally, the design of a process plant layout involves first synthesis and then analysis. Despite its importance, there is relatively little written on the generation of the layout. An indication of some of the principles which guide the designer has been given by Madden (1993). He describes a structured approach to the generation of the layout which has four stages: (1) three-dimensional (3D) model, (2) flow, (3) relationships and (4) groups.

10.3.5 Three-dimensional model

The first step is to produce a 3D model of the space occupied by each item of equipment. This 3D envelope should include space for (1) operations access, (2) maintenance access and (3) piping connections. The effect of allowing for these aspects is generally to increase several-fold the volume of the envelope.

10.3.6 Flow

The concept of 'flow' as used by Madden has two meanings: (1) progression of materials towards a higher degree of completion, and (2) mass flows of process or utility materials. Often the two coincide, but where there is a feature such as a recycle the relationship is less straightforward.

10.3.7 Relationships

A relationship exists between two items when they share some common factor. Relationships may be identified by considering the plant from the viewpoint of each discipline in turn. Broad classes of relationship are (1) process, (2) operations, (3) mechanical, (4) electrical, (5) structural and (6) safety.

Process relationships are exemplified by: direct flow diagram connectivity between items; gravity flow; hydraulics and net positive suction head (NPSH) requirements; and heat interchange and conservation. Operations relationships include multiple items with similar features, for example batch reactors and centrifuges. Examples of mechanical relationships are the space needed between items for piping and transmission or isolation of vibrations. Electrical relationships may be associated with electrical area classification and with high voltage or power features. Structural features include the grouping together of heavy items and the location of heavy items on good ground. Some safety features are separation between potential leak sources and ignition sources and the provision of a sterile area such as that around a flare.

10.3.8 Groups

From the relationships identified it is then necessary to select those which are to be given priority. It is then possible to arrange the items into groups. It is found by experience that a group size of about seven items is the largest which a layout designer can readily handle; above this number the arrangement of items within the group becomes excessively complex. A typical group is a distillation column group consisting of the column itself and its associated heat exchangers, etc.

10.3.9 Segregation

A relationship of particular importance in plant layout is that between a hazard and a potential target of that hazard. The minimization of the risk to the target is effected by segregating the hazard from the target. The requirement for segregation therefore places constraints on the layout.

10.4 Layout Techniques and Aids

There are a number of methods available for layout design. These are generally more applicable to the analysis rather than the synthesis of layouts, but some have elements of both. They include:

(1) classification, rating and ranking;
(2) critical examination;
(3) hazard assessment;
(4) economic optimization.

There are also various aids, including:

(5) visualization aids;
(6) computer aids.

10.4.1 Classification, rating and ranking

There are several methods of classification, rating and ranking which are used in layout design. The main techniques are those used for the classification of (1) hazardous areas, (2) storage, (3) fire fighting facilities and (4) access zones, together with methods based on hazard indices.

Hazardous area classification is aimed at the exclusion of ignition sources from the vicinity of potential leak sources and involves the definition of zones in which control of ignition sources is exercised to differing degrees. It is described in Section 10.12 and Chapter 16.

Storage classification is based on the classification of the liquids stored. Accounts are given in Section 10.10 and Chapter 22.

Closely related is classification based on fire fighting requirements, since this is applicable particularly to storage.

Restriction of access may be required near major hazard plants or commercially sensitive processes. Areas are therefore classified by the need to control access.

10.4.2 Critical examination

Critical examination, which is part of the technique of method study (Currie, 1960), may be applied to plant layout. This application has been described by Elliott and Owen (1968). In critical examination of plant layout, typical questions asked are: Where is the plant equipment placed? Why is it placed there? Where else could it go?

The technique therefore starts with and involves analysis of a proposed layout, but insofar as other possible solutions are suggested, it may be regarded also as a method for the generation of alternatives which can then be evaluated.

As already mentioned in Chapter 8, the working document in an early hazard study is a plant layout diagram, and to this extent such a hazard study may be regarded as a form of critical examination of layout.

10.4.3 Hazard assessment

Hazard assessment of plant layout is practised both in respect of major hazards which affect the whole site, and of lesser hazards, notably leaks and their escalation. The traditional method of dealing with the latter has been the use of minimum safe separation distances, but there has been an increasing trend to supplement the latter with hazard assessment. An account of hazard assessment is given in Chapter 9 and its role in plant layout is discussed in Sections 10.5 and 10.13.

10.4.4 Economic optimization

The process of layout development generates alternative candidate layouts and economic optimization is a principal method of selection from among these. The points at which such economic optimization is performed are described in Section 10.5. Some factors which are of importance for the cost of a plant layout include foundations, structures, piping and pipetracks, and pumps and power consumption.

10.4.5 Visualization aids

There are various methods of representing the plant to assist in layout design. These include drawings, cutouts, block models and piping models. Cutouts are a two-dimensional (2D) layout aid consisting of sheets of paper, cardboard or plastic which represent items in plan, whether whole plots or items of equipment, and are overlaid on the site or plot plan, as the case may be. The other main physical aids are 3D. Block models are very simple models made from wood blocks or the like which show the main items of equipment and are used to develop plot and floor plans and elevations. Piping models include the pipework, are more elaborate, and can constitute up to 0.5% of the total installed plant cost. They are useful as an aid to: doing layout drawings; determining piping layout and avoiding pipe fouls; positioning valves, instruments, etc.; checking access for operation and maintenance; planning construction and executing it; and operator training.

10.4.6 Computer aids

Plant layout is one of the areas in which computer aided design (CAD) methods are now widely used. One type of code gives visualization of the layout. This may take a number of forms. One is a 2D layout visualization equivalent to cutouts. Another is a 3D visualization equivalent to either a block model or a piping model, but much more powerful. The visualization packages available have become very sophisticated and it is possible in effect for the user to sit at the display and take a 'walk' through the plant. A recent development is enhancement by the use of the techniques of virtual reality. Typically, such CAD packages not only give 3D display but hold a large amount of information about the plant such as the coordinates of the main items and branches, the piping routes, the materials list, etc.

A particular application of 3D visualization codes is as input to other computer programs such as computational fluid dynamics codes for explosion simulation. The 3D layout required for the latter is provided by the 3D visualization code, which then forms the front end of the total package.

Another type of code tackles the synthesis of layouts. The general approach is to define a priority sequence for locating items of equipment inside a block and then for the location of the block. The pipework is then added and costed. Such a method has been described by Shocair (1978).

A third type of code deals with the analysis of layouts to obtain an economic optimum. Typical factors taken into account in such programs include the costs of piping, space and buildings. A program of this type has been described by Gunn (1970).

The extent to which computer aids are used in the design of plant layout is not great, but some visualization packages are very powerful and are likely to find increasing application. Computer techniques for plant layout are described in more detail in Chapter 29.

10.5 Layout Planning and Development

10.5.1 Layout activities and stages

Plant layout is usually divided into the following activities:

(1) site layout;
(2) plot layout;
(3) equipment layout.

The layout developed typically goes through three stages:

(1) Stage One layout;
(2) Stage Two layout;
(3) Final layout.

The sequence of layout development described by Mecklenburgh is:

(1) Stage One plot layout;
(2) Stage One site layout;
(3) Stage Two site layout;
(4) Stage Two plot layout.

Typical stages in the development of a plant layout are given in Table 10.3. The Stage Two and Final Stage design network is shown in simplified form in Figure 10.1. The process of layout development makes considerable use of guidelines for separation distances. These are described in Section 10.11

Table 10.3 *Typical stages in the development of a plant layout (after Mecklenburgh, 1985) (Courtesy of the Institution of Chemical Engineers)*

A	**Stage One plot layout**
1	Initial plot data
2	First plot layout
3	Elevation
4	Plot plan
5	Plot buildings
6	Second plot plan
7	Hazard assessment of plot layout
8	Layout of piping and other connections
9	Critical examination of plot layout
B	**Stage One site layout**
10	Initial site data
11	First site layout
12	Hazard assessment of site layout
13	Site layout optimization
14	Critical examination of site layout
15	Site selection
C	**Stage Two site layout**
16	Stage Two site data
17	Stage Two site layout
D	**Stage Two plot layout**
18	Stage Two plot layout data
19	Stage Two plot layout

Stage One is the preliminary layout, also known as the conceptual, definition, proposal or front end layout. In this stage consideration is given to the various factors which are important in the layout, which may threaten the viability of the project if they are not satisfactorily resolved and which are relevant to site selection.

10.5.2 Stage One plot layout

In the Stage One plot layout, the information available should include preliminary flow sheets showing the major items of equipment and major pipework, with an indication of equipment elevations, and process engineering designs for the equipment. The plot layouts are then developed following the process flow principle and using guidance on preliminary separation distances. The plot size generally recommended is 100 m × 200 m with plots separated from each other by roads 15 m wide.

For each plot layout the elevation and plan are further developed. The proposed elevation layouts are subjected to a review such as critical examination which generates alternatives, and these alternatives are costed. Similarly, alternative plan layouts are generated accommodating the main items of equipment, pipework, buildings and cable runs, and are reviewed to ensure that they meet the principal constraints. These include construction, operation, maintenance, safety, environment and effluents. The plan layouts are then costed. The justification for the use of buildings is examined. The civil engineering aspects are then considered, including foundations and support and access structures.

The outcome of this process for each plot is a set of candidate layouts. These are then presented for view as layout models in block model or computer graphics form. The different disciplines can then be invited to comment. These plot layouts are then costed again and a short list is selected, preferably of one.

The plot layouts are then subjected to hazard assessment. This assessment is concerned largely with the smaller, more frequent leaks which may occur and with sources of ignition for such leaks. The process of hazardous area classification is also performed. Hazard assessment and hazardous area classification are described in Sections 10.12 and 10.13.

Studies are carried out to firm up on piping and piping routes and on electrical mains routes. Finally, each plot layout is subjected to a critical examination, typically using a model and following a checklist.

10.5.3 Stage One site layout

The Stage One plot layouts provide the information necessary for the Stage One site layout. These include the size and shape of each plot, the desirable separation distances, the access requirements and traffic characteristics. The flow of materials and utilities on the site are represented in the form of site flowsheets.

The site layout is now developed to accommodate not only the process plots but also storage and terminals, utilities, process and control buildings, non-process buildings and car parks, and the road and rail systems. The flow principle is again followed in laying out the plots, but may need to be modified to meet constraints. Guidance is available on separation distances for this preliminary site layout.

Hazard assessment is then performed on the site layout with particular reference to escalation of incidents and to

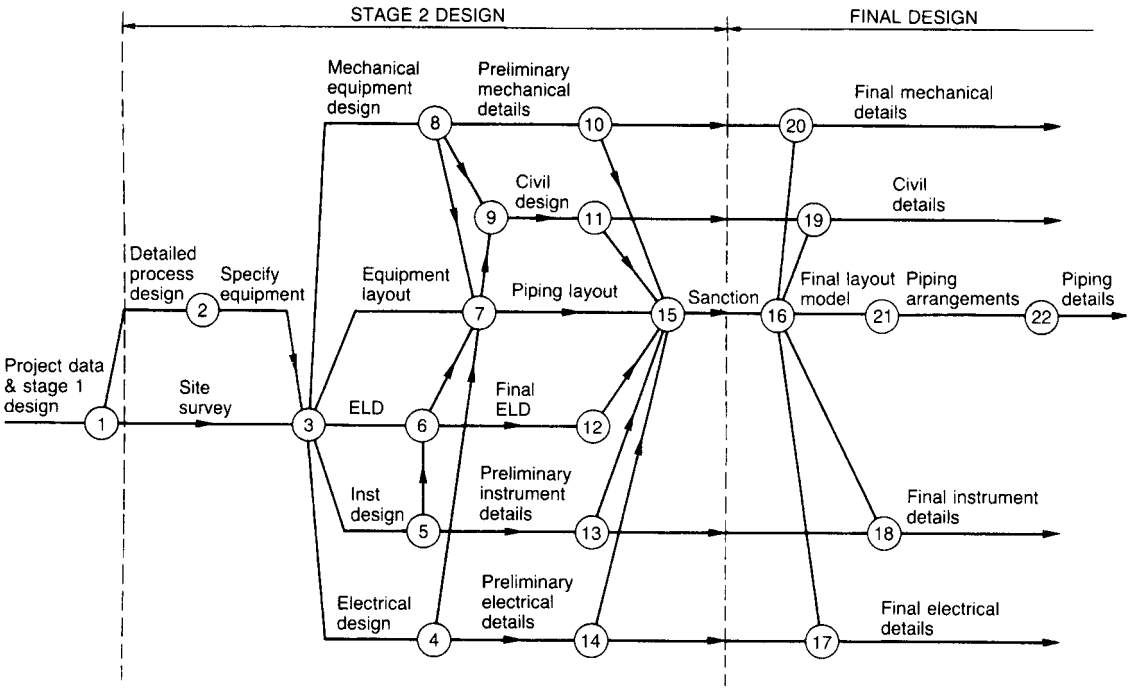


Figure 10.1 *Simplified Stage Two and Final Stage design network (Mecklenburgh, 1985). ELD (Courtesy of the Institution of Chemical Engineers) engineering line diagram*

vulnerable features such as service buildings and buildings just over the site boundary.

If alternative site layouts have been generated, they are then costed and the most economic identified. The site layout is then subjected to a critical examination. If there is a choice of site, the selection is made at this point.

10.5.4 Stage Two site layout

Stage Two layout is the secondary, intermediate or sanction layout. As the latter term implies, it is carried out to provide a layout which is sufficiently detailed for sanction purposes. It starts with the site layout and then proceeds to the layout.

At this stage information on the specific characteristics of the site is brought to bear, such as the legal requirements, the soil and drainage, the meteorological conditions, the environs, the environmental aspects and the services. Site standards are set for building lines and finishes, service corridors, pipetracks and roads.

Stage Two layout involves reworking the Stage One site layout in more detail and for the specific site, and repeating the hazard assessment, economic optimization and critical examination.

Features of the specific site which may well influence this stage are: planning matters; environmental aspects; neighbouring plants, which may constitute hazards and/or targets; other targets such as public buildings; and road, rail and service access points.

At this stage, there should be full consultation with the various regulatory authorities, insurers and emergency services, including the police and fire services.

A final site plan is drawn up in the form of drawings and models, both physical and computer-based ones, showing in particular the layout of the plots within the site, the main buildings and roads, railways, service corridors, pipetracks and drainage.

10.5.5 Stage Two plot layout

There then follows the Stage Two plot layout. The information available for this phase includes (1) standards, (2) site data, (3) Stage Two site layout, (4) process engineering design and (5) Stage One plot layout. The standards include international and national standards and codes of practice, company standards and contractor standards. The process engineering design data include the flowsheets, flow diagrams, equipment lists and drawings, process design data sheets and pipework line lists.

The Stage Two plot layout involves reworking in more detail and subject to the site constraints the plot plans and layouts and repeating the hazard assessment, piping layout and critical examination. The reworking of the plot layout, which occurs at node 7 in Figure 10.1, is a critical phase, requiring good coordination between the various disciplines.

10.6 Site Layout Features

10.6.1 Site constraints and standards

Once a site has been selected the next step is to establish the site constraints and standards. The constraints include:

(1) topography and geology;
(2) weather;
(3) environment;
(4) transport;
(5) services;
(6) legal constraints.

Topographical and geological features are those such as the lie of the land and its load-bearing capabilities. Weather includes temperatures, wind conditions, solar radiation, and thunderstorms. Environment covers people, activities and buiilidings in the vicinity. Services are power, water and effluents. Legal constraints include planning and building, effluent and pollution, traffic, fire and other safety laws, bylaws and regulations.

Site standards should also be established covering such matters as:

(1) separation distances;
(2) building lines;
(3) building construction, finish;
(4) road dimensions;
(5) service corridors;
(6) pipebridges.

Road dimensions include width, radius and gradient.

10.6.2 Site services

The site central services such as the boiler house, power station, switch station, pumping stations, etc., should be placed in suitable locations. This means that they should not be put out of action by such events as fire or flood and, if possible, not by other accidents such as explosion, and that they should not constitute sources of ignition for flammables.

Electrical substations, pumping stations, etc., should be located in areas where non-flameproof equipment can be used, except where they are an integral part of the plant.

Factors in siting the boiler house are that it should not constitute a source of ignition, that emissions from the stack should not give rise to nuisance and that there should be ready access for fuel supplies.

10.6.3 Use of buildings

Some or part of the plants may need to be located inside a building, but the use of a building is always expensive and it can create hazards and needs to be justified. Typically, a building is used where the process, the plant, the materials processed and/or the associated activities are sensitive to exposure. Thus the process may need a stable environment not subject to extremes of heat or cold or it may need to be sterile. The plant may contain vulnerable items such as high-speed or precision machinery. The process material may need to be protected against contamination or damage, including rain. The activities which the operators have to undertake may be delicate or skilled, or simply very frequent. Thus, a building may be used to encourage more frequent inspection of the plant. Similarly, there may be maintenance activities which are delicate or skilled or simply frequent. In some cases where there are high elevations, an indoor structure may be, or may feel, safer. The need to satisfy customers of the product and to keep unsightly plant out of view are other reasons. Examples of the use of buildings are the housing of batch reactors, centrifuges and analysis instruments.

Since ventilation in a building is generally less than that outdoors, a leak of flammable or toxic material tends to disperse more slowly and a hazardous concentration is more likely to build up. Moreover, if an explosion of a flammable gas or dust occurs the overpressure generated tends to be much higher. These are major disadvantages of the use of a building.

10.6.4 Location of buildings

Buildings which are the work base for a number of people should be located so as to limit their exposure to hazards.

Analytical laboratories should be in a safe area, but otherwise as close as possible to the plants served. So should workshops and general stores. The latter also require ready access for stores materials.

Administration buildings should be situated in a safe area on the public side of the security point. The main office block should always be near the main entrance and other administration buildings should be near this entrance if possible. Other buildings, such as medical centres, canteens, etc., should also be in a safe area and the latter should have ready access for food supplies.

All buildings should be upwind of plants which may give rise to objectionable features.

Water drift from cooling towers can restrict visibility and cause corrosion or ice formation on plants or transport routes, and towers should be sited to minimize this. Another problem is recycling of air from the discharge of one tower to the suction of another, which is countered by placing towers cross-wise to the prevailing wind. The entrainment of effluents from stacks and of corrosive vapours from plants into the cooling towers should be avoided, as should the siting of buildings near the tower intakes. The positioning of natural draught cooling towers should also take into account resonance caused by wind between the towers. The problem of air recirculation should also be borne in mind in siting air-cooled heat exchangers.

10.6.5 Limitation of exposure

An aspect of segregation which is of particular importance is the limitation of exposure of people to the hazards. The measures required to effect such limitation are location of the workbase outside, and control of entry to the high hazard zone. The contribution of plant layout to limitation of exposure, therefore, lies largely in work-base location. Limitation of exposure is considered more fully in Chapter 20.

10.6.6 Segregation

Although a layout which is economical in respect of land, piping and transport is in general desirable, in process plants it is usually necessary to provide some additional space and to practise a degree of segregation. The site layout should aim to contain an accident at source, to prevent escalation and avoid hazarding vulnerable targets. A block layout is appropriate with each plot containing similar and compatible types of hazard and with different types segregated in separate plots.

10.6.7 Fire containment

The site layout should contribute to the containment of any fire which may occur and to combating the fire.

Features of the site layout relevant to fire hazard are illustrated in Figures 10.2 and 10.3 (Simpson, 1971). Figure 10.2 shows a compact layout, which minimizes land usage and pipework, for a petrochemical plant consisting of a major process with several stages and a number of subsidiary processes. There are two main process areas and at right angles to these is an area with a row of fired heaters, and associated reactors, steam boilers and a stack.

This layout has several weaknesses. The lack of firebreaks in the main process blocks would allow a fire to propagate right along these, particularly if the wind is

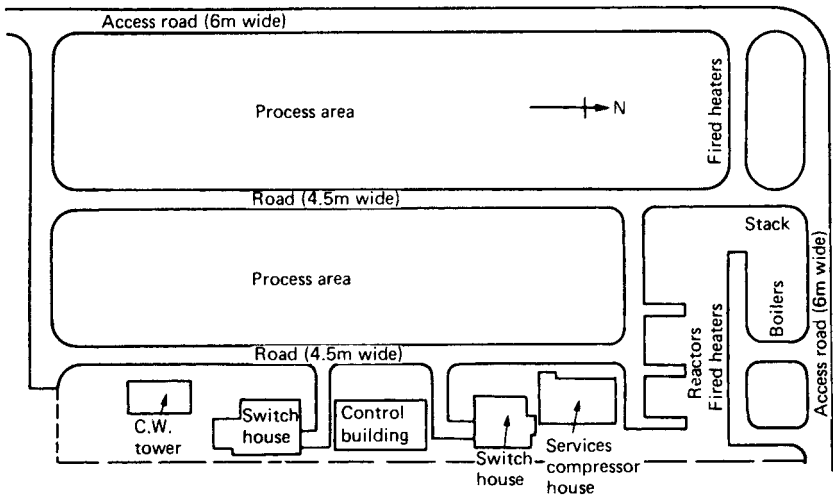


Figure 10.2 *Compact block layout system in the process area of a petrochemical plant with 4.5 m roads (Simpson, 1971) (Courtesy of the Institution of Chemical Engineers)*

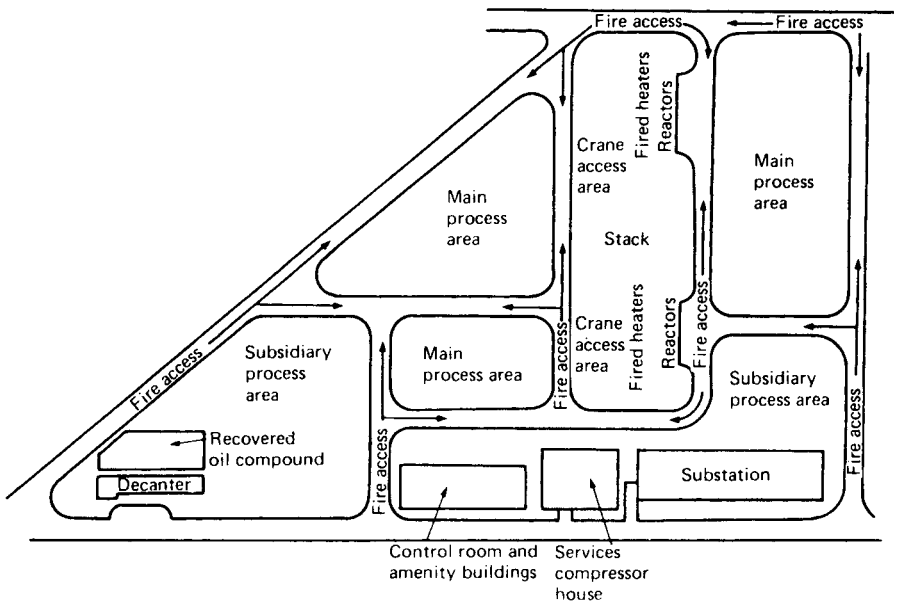


Figure 10.3 *Block layout system in the process area of a petrochemical plant with 6 m roads (Simpson, 1971) (Courtesy of the Institution of Chemical Engineers)*

blowing along them, which, on the site considered it does for 13% of the year. There is entry to the plant area from the 6 m roads from opposite corners, which allows for all wind directions. But the only access for vehicles to the process plots is the 4.5 m roads. In the case of a major fire, appliances might well get trapped by an escalation of the fire. The 4.5 m roads give a total clearance of about 10 m after allowance for equipment being set back from the road, but this is barely adequate as a firebreak. The layout is also likely to cause difficulties in maintenance work.

The alternative layout shown in Figure 10.3 avoids these problems. The process areas are divided by firebreaks. There are more entry points on the site and dead ends are eliminated. The roads are 6 m wide with an effective clearance of 15 m. The crane access areas provide additional clearances for the fired heaters.

Other aspects of fire protection are described in Section 10.15 and Chapter 16.

10.6.8 Effluents

The site layout must accommodate the systems for handling the effluents – gaseous, liquid and solid – and storm water and fire water. The effluent systems are considered in Section 10.16 and the drain system in Section 10.17.

10.6.9 Transport

It is a prime aim of plant layout to minimize the distances travelled by materials. This is generally achieved by following the flow principle, modified as necessary to minimize hazards.

Access is required to plots for transport of materials and equipment, maintenance operations and emergencies. Works roads should be laid out to provide this to plant plots, ideally on all four sides. Roads should be suitable for the largest vehicles which may have to use them in respect of width, radius, gradient, bridges and pipe-bridges. Recommended dimensions for works roads are given by Mecklenburgh (1973). Road widths of 10 m and 7.5 m are suggested for works' main and side roads, respectively. Standard road signs should be used. A road width of 7.5 m with the addition of free space and/or a pipe trench on the verges may be used to give a separation distance of 15 m between units.

There are various types of traffic in a works, including materials, fuel, wastes, stores, food and personnel. These traffic flows should be estimated and their routes planned. Incompatible types of traffic should be segregated as far as possible.

Road and rail traffic should not go through process areas except to its destination and even then should not violate hazardous area classifications. In this connection, it should be borne in mind that some countries still use open firebox engines. Railway lines should not cross the main entrance and should not box plants in. There should be as few railway crossings, crossroads, right angle bends, dead ends, etc., as possible.

There should be adequate road tanker parking and rail tanker sidings at the unloading and loading terminals, so that vehicles can wait their turn at the loading gantry or weighbridge without causing congestion at entrances, or on works or public roads.

Pedestrian pathways should be provided alongside roads where there are many people and much traffic. Bridges may need to be provided at busy intersections. Car and bus parks and access roads to these should be situated in a safe area and outside security points. The park for nightshift workers should be observable by the gatekeeper. There should be gates sited so that the effect of shift change on outside traffic is minimized.

10.6.10 Emergencies

There should be an emergency plan for the site. This is discussed in detail in Chapter 24. Here consideration is limited to aspects of layout relevant to emergencies.

The first step in emergency planning is to study the scenarios of the potential hazards and of their development. Plant layout diagrams are essential for such studies. Emergency arrangements should include an emergency control centre. This should be a specially designated and signed room in a safe area, accessible from the public roads and with space around it for emergency service vehicles.

Assembly points should also be designated and signed in safe areas at least 100 m from the plants. In some cases, it may be appropriate to build refuge rooms as assembly points. A control room should not be used either as the emergency control centre or as a refuge room.

The maintenance of road access to all points in the site is important in an emergency. The site should have a road round the periphery with access to the public roads at least at two points. The vulnerability of the works road system to blockage should be as low as possible. Data on typical fire services appliance dimensions and weights are given by Mecklenburgh (1985). For several of these the turning circle exceeds 15 m.

Arrangements should be made to safeguard supplies of services such as electricity, water and steam to plants in an emergency. Power cables are particularly vulnerable to fire and, if possible, important equipment should be provided with alternative supplies run through the plant by separate routes.

10.6.11 Security

The site should be provided with a boundary fence and all entrances should have a gatehouse. The number of entrances should be kept to a minimum. If construction work is going on in part of the works, this building site should have its own boundary fence and a separate entrance and gatehouse. If the works boundary fence is used as part of this enclosure, movement between the building site and the works should be through an entrance with its own gatehouse.

10.7 Plot Layout Considerations

Some considerations which bear upon plot layout are:

(1) process considerations;
(2) economic considerations;
(3) construction;
(4) operations;
(5) maintenance;
(6) hazards;
(7) fire fighting;
(8) escape.

10.7.1 Process considerations

Process considerations include some of the relationships already mentioned, such as gravity flow and availability of head for pump suctions, control valves and reflux returns. Under this heading come also limitations of pressure drop in pipes and heat exchangers and across control valves and of temperature drop in pipes, the provision of straight runs for orifice meters, the length of instrument transmission lines and arrangements for manual operations such as dosing with additives, sampling, etc.

10.7.2 Economic considerations

As already mentioned, some features which have a particularly strong influence on costs are foundations, structures, piping and electrical cabling. This creates the incentive to locate items on the ground, to group items so that they can share a foundation or a structure, and to keep pipe and cable runs to a minimum.

10.7.3 Construction

Additional requirements are imposed by the needs of construction and maintenance. The installation of large and

heavy plant items requires space and perhaps access for cranes. Such items tend to have long delivery times and may arrive late; the layout may need to take this into account.

Construction work may require an area in which the construction materials and items can be laid out. On large, single-stream plants major items can often be fabricated only on site. There needs to be access to move large items into place on the plant. If the plot is close to the site boundary, it should be checked that there will be space available for cranes and other lifting gear.

10.7.4 Operation

Access and operability are important to plant operation. Mention has already been made of the development of the 3D envelope of the main items of equipment to allow for operation. Hazop studies, described in Chapter 8, may be used to highlight operating difficulties in the layout.

The routine activities performed by the operator should be studied with a view to providing the shortest and most direct routes from the control room to items requiring most frequent attention. Clear routes should be allowed for the operator, avoiding kerbs and other awkward level changes.

General access ways should be 0.7 m and 1.2 m wide for one and two persons, respectively. Routes should be able to carry the maximum load, which often occurs during maintenance.

Stairways rather than ladders should be provided for main access, the latter being reserved for escape routes on outside structures and access to isolated points which are only visited infrequently. Recommended dimensions for stairways are an angle of 35–40° and overall width of 1 m with railings 0.85 m high and clearances 2.1 m. The height of single flights without a landing should not exceed 4.5 m. No workplace should be more than 45 m from an exit.

Ladders should be positioned so that the person using it faces the structure and does not look into space. A ladder should not be attached to supports for hot pipes, since forces can be transmitted which can distort the ladder. Recommended dimensions for ladders are given by appropriate codes.

If plant items require operation or maintenance at elevated levels, platforms should be provided. The levels are defined as 3.5 m above grade for vessels, 2 m above grade for instruments or 2 m above another platform. Platform floors are normally not less than 3 m apart. Headroom under vessels, pipes, cable racks, etc., should be 2.25 m minimum, reducing to 2.1 m vertically over stairways.

Good lighting on the plant is important, particularly on access routes, near hazards and for instrument reading.

Operations involving manipulation of an equipment while observing an indicator should be considered so that the layout permits this. Similarly, it is helpful when operating controls to start or stop equipment to be able to see or hear that the equipment has responded to the signal.

Hand valves need good access, particularly large valves which may require considerable physical effort to turn. Valves which have to be operated in an emergency should be situated so that access is not prevented by the accident through fire or other occurrences. For emergency isolation, however, it may be preferable to install remotely operated isolation valves, as described in Chapter 12.

Batch equipment such as batch reactors, centrifuges, filters and driers, tends to require more manual operation, so that particular attention should be paid to layout for such items.

Insulation is sometimes required on pipework to protect operating and maintenance personnel rather than for process reasons.

10.7.5 Maintenance

Plant items from which the internals need to be removed for maintenance should have the necessary space and lifting arrangements. Examples are tube bundles from heat exchangers, agitators from stirred vessels and spent catalyst from reactors.

10.7.6 Hazards

The hazards on the plant should be identified and allowed for in the plot layout. This is discussed in other sections, but some general comments may be made at this stage.

Plot layout can make a large contribution to safety. It should be designed and checked with an intent to reducing the magnitude and frequency of the hazards and assisting preventive measures. The principle of segregation of hazards applies also to plot layout.

Hazardous areas should be defined. They should not extend beyond the plot boundaries or to railway lines. It is economic to minimize the extent of hazardous areas and to group together in them items which give the same hazard classification.

Plants which may leak flammables should generally be built in the open or, if necessary, in a structure with a roof but no walls. If a closed building cannot be avoided, it should have explosion relief panels in the walls or roof with relief venting to a safe area. Open air construction ventilates plants and disperses flammables but, as already indicated, scenarios of leakage and dispersion should be investigated for the plant concerned.

Fire spread in buildings should be limited by design, as should fire spread on open structures. Sprinklers and other protective systems should be provided as appropriate. A more detailed consideration of fire hazards and precautions is given in Chapter 16.

Plants which may leak toxics should also generally be built in the open air. The hazardous concentrations for toxics are much lower than those for flammables, however, and it cannot be assumed that an open structure is always sufficiently ventilated. A wind of at least 8 km/h is needed to disperse most toxic vapours safely before they reach the next plant. Some toxic plants, however, require a building and in some cases there has to be isolation of the toxic area through the use of connecting rooms in which clothing is changed.

Ventilation is necessary for buildings housing plants processing flammables or toxics. Air inlets should be sited so that they do not draw in contaminated air. The relative position of air inlets and outlets should be such that short circuiting does not occur. Exhaust air may need to be treated before discharge by scrubbing or filtering.

Plants which are liable to leak liquids should stand on impervious ground with suitable slopes to drain spillages away. The equipment should be on raised areas which slope down to valleys and to an appropriate collecting point. Suitable slopes are about 1 in 40 to 1 in 60. Valleys should not coincide with walkways, and kerbs may be needed to keep liquid off these. The collecting points should be away from equipment so that this is less exposed to any fire in the liquid collected. The amount of liquid which may collect should be estimated and the collecting point should be designed to take away this amount. The heat generated if

the liquid catches fire should be determined and vulnerable items relocated if necessary.

The use of pervious ground, such as pebbles, to absorb leaks of flammable liquids should be avoided. Such liquid may remain on the water table and may be brought up again by water from fire fighting. Other hazards which are prevalent mainly outside the United Kingdom include earthquakes and severe thunderstorms. These require special measures.

Personal safety should not be overlooked in the plot layout. Measures should be taken to minimize injury due to trips and falls, bumping of the head, exposure to drips of noxious substances and contact with very hot or cold surfaces. Where such hazards exist, they generally present a threat not just on occasion but for the whole time.

10.7.7 Fire fighting

Access is essential for fire fighting. This is provided by the suggested plot size of 100 m×200 m with approaches preferably on all four sides and by spacing between plots and buildings of 15 m.

Fire water should be available from hydrants on a main between the road and the plant. Hydrant points should be positioned so that any fire on the plot can be reached by the hoses. Hydrant spacings of 48, 65 and 95 m are suitable for high, medium and low risk plots, respectively. Plants over 18 m high should be provided with dry riser mains and those over 60 m high or of high risk should be equipped with wet riser mains. The inlets on the ground floor to dry riser mains and the outlets on all floors to both types of main should be accessible.

Pipes for fire water supply should be protected against explosion damage. Isolation valves should be provided to prevent loss of fire water from damaged lines and, if these valves are above ground level, they should be protected by concrete blast barriers.

Fire extinguishers of the appropriate type and fire blankets should be placed at strategic points. There should be at least two extinguishers at each point. Some extinguishers should be located on escape or access routes, so that a person who decides to fight the fire using the extinguisher has a route behind him for escape. The location of other fire fighting equipment such as sprinklers and foam sprays is a matter for experts.

Fire equipment should be located so that it is not likely to be disabled by the accident itself. It should be accessible and should be conspicuously marked. The main switchgear and emergency controls should have good access, preferably on an escape route, so that the operator does not have to risk his life to effect shut-down.

There are numerous legal requirements concerning fire, fire construction and fire fighting. There should be full consultation on this at an early stage with the works safety officer and with other parties, such as the local authority services, the Factory Inspectorate and the insurers.

10.7.8 Escape

A minimum of two escape routes should be provided for any workspace, except where the fire risk is very small, and the two routes should be genuine alternatives. No workplace should be more than 12–45 m, depending on the degree of risk, from an exit, and a dead end should not exceed 8 m.

Escape routes across open mesh areas should have solid flooring. Escape stairways should be in straight flights. They should preferably be put on the outside of buildings. Fixed ladders may be used for escape from structures if the number of people does not exceed 10. Doors on escape routes should be limited to hinged or sliding types and hinged doors should open in the direction of escape. Handrails should be provided on escape routes across flat roofs. Escape routes should be signposted, if there is any danger of confusion, as in large buildings. They should be at least 0.7 m and preferably 1.2 m wide to allow the passage of 40 persons per minute on the flat and 20 persons per minute down stairways. Good lighting should be provided on escape routes and arrangements made to ensure a power supply in an emergency. The escape times of personnel should be estimated, paying particular attention to people on tall items such as distillation columns or cranes. Bridges between columns may be used.

10.8 Equipment Layout

10.8.1 General considerations

Furnaces and fired heaters are very important. Furnace location is governed by a number of factors, including the location of other furnaces, the use of common facilities such as stacks, the minimization of the length of transfer lines, the disposal of the gaseous and liquid effluents, the potential of the furnace as an ignition source and the fire fighting arrangements. Furnaces should be sited at least 15 m away from plant which could leak flammables.

No trenches or pits which might hold flammables should extend under a furnace, and connections with underground drains should be sealed over an area 12 m from the furnace wall. The working area of the furnace should be provided with ventilation, particularly where high temperatures and high sulfur fuels are involved.

On wall-fired furnaces there should be an escape route at least 1 m wide at each end and on top-fired furnaces there should also be an escape route at each end, one of which should be a stairway. The provision of peepholes and observation doors should be kept to a minimum. Access to these may be by fixed ladder for heights less than 4 m above ground, but platforms should be provided for greater heights.

Incinerators and burning areas for waste disposal should be treated as fired equipment. Waste in burning areas should be lit by remote ignition and, if it is an explosion hazard, blast walls should be provided.

Chemical reactors in which a violent reaction can occur, may need to be segregated by firebreaks or even enclosed behind blast walls.

Heat exchangers should have connecting pipework kept to a minimum, consistent with provision of pipe lengths and bends to allow for pipe stresses and with access for maintenance.

Equipments which have to be opened for cleaning, emptying, charging, etc., may need ventilation.

Driers in which volatile materials are driven off solids will generally need ventilation of the drying area and probably of the drier itself. If the materials are noxious, defraying booths may be necessary.

Dust-handling equipment such as driers, cyclones and ducts may constitute an explosion hazard, but tends to be rather weak. It should be separated from other plant by a wall and vented. Vents should be short and should go through the roof. Some equipment such as cyclones are often placed outside the building and this is preferable to ducting a vent to the outside. Vents should pass to a safe

area. Mills are relatively strong and are not usually provided with explosion relief. Dust should be transferred through chokes to prevent the transmission of fire or explosion. Surfaces which might collect dust should be kept to a minimum. Dust hazards are considered further in Chapter 17.

Pumps handling liquids which are hot ($> 60°C$) should be separated from those handling liquids which are flammable and volatile (boiling point $< 40°C$) or from compressors handling flammable gases. In the open, separation may be effected by a spacing of at least 7.5 m and in a pump room by a vapour-tight wall.

Hazards associated with particular plant equipment are also considered in Chapter 11.

10.8.2 Corrosive materials

If the process materials are corrosive, this aspect should be taken into account in the plant layout. The layout of plants for corrosive materials is discussed in Safety and Management by the Association of British Chemical Manufacturers (ABCM, 1964/3).

Corrosive materials are responsible for an appreciable proportion of accidents on chemical plants and of damage done to the plant. The presence of corrosive materials creates two particular hazards: (1) corrosion of materials of construction, and (2) contact of persons with corrosive materials. On a plant handling corrosive chemicals, the materials of construction should be chosen with particular care, should be protected by regular painting and should be checked by regular inspection.

Some features of plant layout which are particularly important in relation to corrosive chemicals are foundations, floors, walkways, staging, stairs, handrails, drains, ventilation.

Foundations of both buildings and machines, especially those constructed in concrete, may be attacked by leakage of corrosive materials, including leakage from drains. If the corrosion is expected to be mild, it may be allowed for by the use of additional thickness of concrete, but if it may be more severe, other measures are necessary. These include the use of corrosion resistant asphalt, bricks and plastics.

Floors should be sloped so that spillages are drained away from vulnerable equipment and from walkways and traffic lanes. The latter should generally be laid across the direction of fall and should, as far as possible, be at the high points of the slopes.

Severe corrosion of steel stanchions can occur between a concrete subfloor and a brick floor surface, and this possibility should be considered.

Pipe flanges which may drip corrosive substances should not be located over walkways. There should be guardrails around vessels or pits containing corrosive liquids. The floors and walkways should be of the 'non-skid' type.

Staging should not be located over an open vessel which may emit corrosive vapours.

Staircases and handrails should be designed to minimize corrosion. Stairheads should be located at the high points of sloping floors. Handrails tend to corrode internally and may collapse suddenly. They should be made of a suitable material. Aluminium is suitable, if it is not corroded by the atmosphere of the plant. Metal protectors of the vapour type are also available. These are put inside the pipe and the ends sealed. Alternatively, solid rails can be used. The rails should be protected against external corrosion by regular painting or other means. Regular inspection and maintenance is particularly important for staging, staircases and handrails on plants containing corrosive materials.

Drains should be designed to handle the corrosive materials, and mixtures of materials, which may be discharged into them.

Ventilation should be provided and maintained as appropriate. This requires as a minimum the circulation of fresh air. It may also involve local exhaust ventilation.

10.9 Pipework Layout

In general, it is desirable both for economic and safety reasons to keep the pipe runs to a minimum. Additional pipework costs more both in capital and operation, the latter through factors such as heat loss/gain and pumping costs. It is also an extra hazard not only from the pipe itself but more particularly from the joints and fittings.

The application of the flow principle is effective in minimizing pipe runs, but it is also necessary to practise segregation and this will sometimes lead to an unavoidable increase in the length of pipe runs. The design, therefore, involves a compromise between these two factors.

Piping for fluids servicing a number of points may be in the form of a ring main, which permits supply to most points, even if part of the main is disabled. Ring mains are used for steam, cooling water, process water, fire water, process air, instrument air, nitrogen and even chlorine.

Services such as steam and water mains and electricity and telephone cables should generally be run alongside the road and should not pass through plant or service areas.

Pipes may be buried, run at ground level, run on supports or laid in an open pipe trench. Open pipe trenches may be used where there is no risk of accumulation of flammable vapours, of the material freezing or of flooding.

Water mains should be buried below the frost line or to a minimum depth of 0.75 m to avoid freezing. If they run under roads or concreted areas, they should be laid in ducts or solidly encased in concrete.

Steam mains may be laid on the surface on sleepers. They should be run on the outside edge of the pipeway to allow the expansion loops to have the greatest width and to facilitate nesting of the loops. Steam mains may also be run in open pipe trenches.

Electrical power and telephone cables should be run in sand-filled trenches covered by concrete tiles or a coloured concrete mix. If possible, the cables should be run at the high point of paving leaving room for draw boxes. If use is made of underground piping and cabling, it should be put in position at the same time as the foundation work is being done. Alternatively, cables can be run overhead. Overhead cables are less affected by spillages and are easier to extend, but may require fire protection.

Electrical lines can give rise to fields of sufficient intensity to cause local overheating of adjacent metalwork or to induce static electricity in plant nearby, and this should be taken into account in positioning them. Pipes which are hot or carry solvents should be laid as far as possible from electrical cables.

Piping may be run as a double layer, but triple layers should be avoided. Double layer piping should be run with service lines on the upper and process lines on the lower deck.

Piping may require a continuous slope to permit complete drainage for process, corrosion or safety reasons;

other pipes should not be sloped. Sloped lines should be supported on extensions of the steel structure. The slope arrangement should not create a low point from which liquid cannot be drained.

Overhead clearances below the underside of the pipe, flange, lagging or support should have the following minimum values:

Above roads and areas with access for crane	7 m
Plant areas where truck access is required	4 m
Plant areas in general	3 m
Above access floors and walkways within buildings	2.25 m
Above railway lines (from top of rail)	4.6 m

Pipe flanges should be positioned so as to minimize the hazards from small leaks and drips. Flanges on pipework crossing roads on pipebridges should be avoided. Pipebridges over roads should be as few as possible. Every precaution should be taken to prevent damage from vehicles, particularly cranes and forklift trucks.

Attention should be paid to the compatibility of adjacent pipework, the cardinal principle being to avoid loss of containment of hazardous materials. Thus, it is undesirable, for example, to put a pipe carrying corrosive material above one carrying flammables or toxics at high pressure.

Emergency isolation valves should be used to allow flows of flammable materials to be shut off. Valves may be manually or power operated and controls for the latter may be sited locally or remotely. The use of such valves is described in more detail in Chapter 12.

If a manual valve is used for isolation, it should be mounted in an accessible position. Emergency operation of valves from ladders should be avoided. If the valve is horizontally mounted and its spindle is more than 2.1 m above the operating level, a chain wheel should be provided. A valve should not be mounted in the inverted position, since solids may deposit in the gland and cause seizure.

Discharges from pressure relief valves and bursting discs are normally piped away in a closed system. In particular, a closed system is necessary for hydrocarbon vapours with a molecular weight greater than 60, flammable liquids and toxic vapours and liquids. Pressure relief and flare systems are considered more fully in Chapter 12.

Liquid drains from drainage should also be taken to a safe point. Liquids which are not flammable or toxic may be discharged to grade.

Sample points should be 1 m above the floor and not at eye level.

Flexible piping should be kept to a minimum. Where such piping is used on vehicles, use may be made of devices which shut off flow if the vehicle moves away.

Instruments incorporating glass tubing, such as sight glasses and rotameters, are a source of weakness. In some cases the policy is adopted of avoiding the use of such devices altogether. If this type of instrument is used, however, it should be enclosed in a transparent protective case.

The layout for piping and cabling should allow for future plant expansion. An allowance for 30% additional pipework is typical. Full documentation should be kept on all piping and cabling.

10.10 Storage Layout

Treatments of plant layout frequently cover all aspects of storage, including bunding, venting, etc. In this book, storage is dealt with separately in Chapter 22, and only those features which are directly relevant to the layout of the plant as a whole are dealt with at this point.

The principal kinds of storage are bulk storage of fluids, bulk storage of solids and warehouse storage. The storage of main interest in the present context is storage of fluids, particularly flammable fluids. The types of storage include:

(1) liquid at atmospheric pressure and temperature;
(2) liquefied gas under pressure and at atmospheric temperature (pressure storage);
(3) liquefied gas at atmospheric pressure and at low temperature (refrigerated storage);
(4) gas under pressure.

There are also intermediate types such as semi-refrigerated storage.

For liquid storage it is common to segregate the liquids stored according to their class. The current classification, given in the *Refining Safety Code* of the Institute of Petroleum (IP, 1981 MCSP Part 3) and used in BS 5908: 1990, is

Class I	Liquids with flashpoint below 21°C
Class II (1)	Liquids with flashpoint from 21°C up to and including 55°C, handled below flashpoint
Class II (2)	Liquids with flashpoint from 21°C up to and including 55°C, handled at or above flashpoint
Class III (1)	Liquids with flashpoint above 55°C up to and including 100°C, handled below flashpoint
Class III (2)	Liquids with flashpoint above 55°C up to and including 100°C, handled at or above flashpoint

An earlier classification, given in the former BS CP 3013: 1974, was as follows:

Class A	Liquids with flashpoint below 22.8°C (73°F)
Class B	Liquids with flashpoint between 22.8 and 66°C (73 and 150°F)
Class C	Liquid with flashpoint above 66°C (150°F)

The classification given in the National Fire Protection Association's (NFPA 321: 1987) *Basic Classification of Flammable and Combustible Liquids* is:

Class I	Liquids with flashpoint below 37.8°C (100°F)
Class IA	Liquids with flashpoint below 22.8°C (73°F) and boiling point below 37.8°C (100°F)
Class IB	Liquids with flashpoint below 22.8°C (73°F) and boiling point at or above 37.8°C (100°F)
Class 1C	Liquids with flashpoint at or above 22.8°C (73°F) and below 37.8°C (100°F)
Class II	Liquids with flashpoint at or above 37.8°C (100°F) and below 60°C (140°F)
Class III	Liquids with flashpoint at or above 60°C (140°F)
Class IIIA	Liquids with flashpoint at or above 60°C (140°F) and below 93.4°C (200°F)
Class IIIB	Liquids with flashpoint at or above 93.4°C (200°F)

NFPA 321 distinguishes between flammable and combustible liquids. It defines a flammable liquid as one having a flashpoint below 37.8°C (100°F) and having a vapour

pressure not exceeding 40 psia at 37.8°C (100°F), and a combustible liquid as one having a flashpoint at/or above 37.8°C (100°F).

Quantities in storage are almost invariably much greater than those in process. Typical orders of magnitude for a large plant are several hundred tonnes in process and ten thousand tonnes in storage.

Storage is usually built in the open, since this is cheaper and allows dispersion of leaks. The site chosen should have good load-bearing characteristics, since tanks or vessels full of liquid represent a very heavy load. The design of foundations for storage tanks is a specialist matter.

The storage site should be such that the contour of the ground does not allow flammable liquid or heavy vapour to collect in a depression or to flow down to an area where it may find an ignition source. The prevailing wind should be considered in relation to the spread of flammables to ignition sources or of toxics to the site boundary.

Storage should be segregated from process. A fire or explosion in the latter may put at risk the very large inventory in storage, and a small fire in storage, which is otherwise easily dealt with, may jeopardize the process. The storage area should be placed on one or at most on two sides of the process and well away from it. This gives segregation and allows room for expansion of the process and/or the storage. The separation distance between process and storage has been discussed above. It should not be less than 15 m.

It is also necessary to keep terminals away from the process, since they are sources of accidents. A suitable layout is therefore to interpose the storage between the process and the terminals. The separation distance between storage and terminals should be not less than 15 m.

The storage tanks should be arranged in groups. The grouping should be such as to allow common bunding, if bunds are appropriate, and common fire fighting equipment for each group. There should be access on all four sides of each bund area and roads should be linked to minimize the effect if one road is cut off during a fire.

It is not essential that there be only one storage area, one unloading terminal or one loading terminal. There may well be several, depending on the materials and process, and the principle of segregation. The raw material unloading and the product loading terminals should be separate. Normally, both should be at the site boundary near the entrance. If the materials are hazardous or noxious, however, the terminal should not be near the entrance, although it may be near the site boundary, provided it does not affect a neighbour's installation.

10.11 Separation Distances

Plant layout is largely constrained by the need to observe minimum separation distances. For hazards, there are basically three approaches to determining a suitable separation distance. The first and most traditional one is to use standard distances developed by the industry. The second is to apply a ranking method to decide the separation required. The third is to estimate a suitable separation based on an engineering calculation for the particular case. Not all separation distances relate to hazards. Construction, access and maintenance are other relevant factors. The first two methods of determining separation distances are considered in this section, and the third is considered in Section 10.14.

10.11.1 Types of separation

The types of separation which need to be taken into consideration are illustrated by the set of tables of separation distances given by Mecklenburgh (1985) and include:

(1) site areas and sizes;
(2) preliminary spacing for equipment
  (a) spacing between equipment,
  (b) access requirements at equipment,
  (c) minimum clearances at equipment;
(3) preliminary spacings for storage layout
  (a) tank farms,
  (b) petroleum products,
  (c) liquefied flammable gas,
  (d) liquid oxygen;
(4) preliminary distances for electrical area classification;
(5) size of storage piles.

Further types of separation used by D.J. Lewis (1980b) are given in Section 10.11.4.

10.11.2 Standard distances

There are a large number of standards, codes of practice and other publications which give minimum safe separation distances. The guidance available relates mainly to separation distances for storage, either of petroleum products, of flammable liquids, of liquefied petroleum gas (LPG) or of liquefied flammable gas (LFG).

Recommendations for separation distances are given in: for petroleum products, *The Storage of Flammable Liquids in Fixed Tanks Exceeding 10,000 m^3 Total Capacity* (HSE, 1991 HS(G) 52), the *Refining Safety Code* (IP, 1981 MCSP Pt 3), the American Petroleum Institute (API) standards API Std 620: 1990 and API Std 650: 1988 and NFPA 30: 1990 *Flammable and Combustible Liquids Code*; for LPG, in *The Storage of LPG at Fixed Installations* by the HSE (1987 HS(G) 34), *Liquefied Petroleum Gas* by the IP (1987 MCSP Pt 9), the *Code of Practice, Part 1, Installation and Maintenance of Fixed Bulk LPG Storage at Consumers' Premises* by the Liquefied Petroleum Gas Industry Technical Association (LPGITA) (1991 LPG Code 1 Pt 1), API Std 2510: 1989 and 2510A: 1989 and NFPA 58: 1989 *Storage and Handling of Liquefied Petroleum Gases*; and for LFG, the ICI *Liquefied Flammable Gases, Storage and Handling Code* (the ICI LFG Code) (ICI/RoSPA 1970 IS/74). Another relevant code is BS 5908: 1990 *Fire Precautions in the Chemical and Allied Industries*. Separation distances are also given in many of the NFPA codes.

Further guidance on separation distances and clearances is given by Armistead (1959), House (1969), the Oil Insurance Association (OIA) (1972/6), Backhurst and Harker (1973), Mecklenburgh (1973, 1985), Kaura (1980b), F.V. Anderson (1982) and Industrial Risk Insurers (IRI) (1991, 1992).

Separation distances are specified in the *Fire and Explosion Index. Hazard Classification Guide* (*the Dow Guide*) (Dow Chemical Company, 1976) as a function of the Fire and Explosion Index (F&EI) and the maximum probable property damage (MPPD). These do not appear as such in the current edition of the *Guide* (Dow Chemical Company, 1994b), which is described in Chapter 8. Some tables of separation distances for storage of flammable liquids, for LPG and for LFG are reproduced in Chapter 22.

Separation distances for process units are usually given as the distances between two units or as the distance between a single unit and an ignition source. It is normal to quote distances between the edges of units and not centre to centre. There is generally little explanation given of the basis of the separation distances recommended.

The separation distances for liquids which have a lower vapour pressure, including the bulk of petroleum products and flammable liquids, tend to be less than those for liquids which have a high vapour pressure and so flash off readily, such as LPG and LFG. It is frequently stated that for LPG a smaller separation distance may be allowed if there is provision of adequate radiation walls and/or water drench systems.

There is naturally some tendency for separation distances to be reproduced from one publication to another. In general, however, there are differences between the various codes and guidelines, so that the overall situation is rather confused. This problem has been discussed by Simpson (1971).

Typical separation distances for preliminary site layouts are given by Mecklenburgh (1985). The table of spacings which he gives is shown in Table 10.4. Some interunit and interequipment separation distances given by IRI (1991, 1992) are shown in Table 10.5.

10.11.3 Rating and ranking methods

An alternative to the use of standard separation distances is the utilization of some form of rating or ranking method. The most widely applied method of this kind is that used in hazardous area classification. This method ranks items by their leak potential. An outline of the method is given in Section 10.12. Another such method is the Mond Index, which is now described.

10.11.4 Mond Index

The Mond Index is one of the hazard indices described in Chapter 8. A particular application of this index is the determination of separation distances as described by D.J. Lewis (1980b, 1989b). In the Mond Index method two values are calculated for the overall risk rating (ORR), those before and after allowance is made for offsetting factors. It is the latter rating R_2 which is used in applying the technique to plant layout. The ORR assigns categories ranging from mild to very extreme.

(1) Flare spacing should be based on heat intensity with a minimum space of 60 m from equipment containing hydrocarbons.
(2) The minimum spacings can be down to one-quarter these typical spacings when properly assessed.

The objectives of layout are: to minimize risk to personnel; to minimize escalation, both within the plant and to adjacent plants; to ensure adequate access for fire fighting and rescue; and to allow flexibility in combining together units of similar hazard potential.

Lewis enumerates the basic concepts underlying the initial layout. In addition to general layout principles, he includes several applications of the ORR. Control and other occupied buildings should be adjacent to low or medium risk units, the latter being acceptable only if a low risk unit is not available and if the R_2 value is just inside the medium risk band. Units with the highest value of the aerial explosion index A_2 should not be located near to the plant boundary but should be separated by areas occupied by low risk activities and with low population densities (up to 25 person/acre). Major pipebridges with medium to high R_2 should be located to reduce their vulnerability to incidents from tall process units and from transport accidents arising from normal vehicle traffic.

Units separately assessed can be combined into a single unit, providing that the hazards are compatible and the risks similar, the potential direct and consequential losses do not become excessive and the reassessed R_2 value is acceptable.

The initial layout is based on a nominal interunit spacing of 10 m. It includes pipebridges and vehicle routes. The nominal interunit distances are then replaced by those established by engineering considerations, including the use of guidance on minimum separation distances and of the ORR.

Lewis states that the minimum separation distances given in the relevant codes are absolute minimum distances and are not necessarily good practice for new installations. Some situations for which separation distances are required are given by Lewis as follows:

(1) distances between a unit of a particular degree of hazard and
    (a) another unit of the same degree,
    (b) another unit of lower or higher degree;
(2) distances between a process unit and
    (a) a storage unit,
    (b) the bund of a storage unit;
(3) distances between adjacent storage units containing materials of different flammability;
(4) distances between a unit and
    (a) occupied buildings,
    (b) potential ignition sources,
    (c) a plant boundary,
    (d) the works boundary.

For units, the relevant distance for the determination of separation is taken as that between the nearest wall, structural frame or free-standing equipment of the two units.

Separation distances for pipebridges receive particular attention. For a pipebridge between two units, the separation distance is between one side of the pipebridge and the adjacent unit. The distance should not include the plan area occupied by the pipebridge itself, but it is not normally necessary to provide two separation distances, one on each side of the pipebridge. A pipebridge which itself has significant potential for a hazardous release should not be located alongside a unit without a separation distance unless assessment shows that the hazard level of the combination of unit and pipebridge is acceptable. If it is not, there should be a separation between the pipebridge and all units, using the pipebridge separation distances given.

The spacings for storage units given in the initial treatment (D.J. Lewis, 1980b) were subsequently revised (D.J. Lewis, 1989b). The principal changes are considerable increases in separation distances for the extreme and very extreme values of R_2, exclusion of units which have potential for 'frothover' or for 'boilover' in a fire, and restriction to units which are on level ground.

The recommendations for separation distances for process units are shown in Table 10.6 and those for storage units in Tables 10.7 and 10.8. D.J. Lewis (1989b) gives further

Table 10.4 *Preliminary areas and spacings for site layout (Mecklenburgh, 1985) (Courtesy of the Institution of Chemical Engineers)*

Administration	10 m^2	per administration employee
Workshop	20 m^2	per workshop employee
Laboratory	20 m^2	per laboratory employee
Canteen	1 m^2	per dining space
	3.5 m^2	per place including kitchen and store
Medical centre	0.1–0.15 m^2	per employee depending on complexity of service
Minimum	10 m^2	
Fire-station (housing one fire, one crash, one foam, one generator and one security vehicle)	500 m^2	per site
Garage (including maintenance)	100 m^2	per vehicle
Main perimeter roads	10 m	wide
Primary access roads	6 m	wide
Secondary access roads	3.5 m	wide
Pump access roads	3.0 m	wide
Pathways	1.2 m	wide up to 10 people/min
	2.0 m	wide over 10 people/min (e.g. near offices, canteens, bus stops)
Stairways	1.0 m	wide including stringers
Landings (in direction of stairway)	1.0 m	wide including stringers
Platforms	1.0 m	wide including stringers
Road turning circles (90° turn and T-junctions)		radius equal to width of road
Minimum railway curve	56 m	inside curve radius
Cooling towers per tower	0.04 m^2/kW	mechanical draught
	to 0.08 m^2/kW	natural draught
Boiler (excluding house)	0.002 m^3/kW	(Height = 4 × Side)

Property boundary	*Control room (non-pressurized)*	*Control room (pressurized)*	*Administration building*	*Main substation*	*Shippings, buildings, warehouses*	*Loading facilities, road, rail, water*	*Fire pumphouse*	*Cooling towers*	*Process fired heaters*	*Gas compressors*	*Reactors*	*High pressure storage spheres, bullets*	*Atmospheric flammable liquid storage tanks*	*Aircoolers*	*Low pressure storage spheres or tanks < 1bar g*	*Plot limits*	*Process control station*	*Process unit substation*	*Process equipment (low-flashpoint)*	*Process equipment (high-flashpoint)*	*Cryogenic O_2^a plant*
NA																					
30	NA																				
8	NA	NA																			
8	8	8	NA																		
8	30	15	8	NA																	
8	15	NM	30	15	NA																
30	60	30	60	60	60	NA															
8	8	8	8	30	30	45	NA														
30	30	30	30	60	30	45	30	7.5													
30	30	30	75	60	75	60	60	30	7.5												
30	30	30	60	60	60	60	60	30	15	2											
60	30	30	60	60	60	60	60	30	15	10	2										
CP	60	30	75	75	75	CP	75	30	CP	75	60	CP									
CP	60	30	60	60	60	CP	60	30	CP	60	60	CP	CP								
60	30	30	60	60	60	60	60	30	15	7.5	5	60	60	NM							
CP	60	30	75	60	60	CP	60	30	CP	60	60	CP	CP	60	CP						
60	60	60	60	60	60	45	60	30	NA	NA	NA	CP	CP	NA	CP	15					
30	NA	NA	NA	30	NA	60	NA	15	15	15	15	60	60	15	60	NA	NA				
NM	NM	NA	NA	NM	NA	45	NM	15	15	15	15	NM	NM	15	NM	NM	NM	NA			
15	30	NM	60	60	60	60	60	30	30	7.5	5	CP	CP	5	CP	NA	15	15	2		
15	30	NM	60	60	60	60	60	30	15	7.5	5	CP	CP	5	CP	NA	15	15	2	2	
CP	30	NM	30	60	60	CP	45	30	CP	45	60	CP	CP	30	CP	CP	60	50	CP	CP	30

NA, not applicable since no measureable distance can be determined; NM, no minimum spacing established – use engineering judgement; CP, reference must be made to relevant Codes of Practice but see section C.6 of the original reference.

[a] *See also* section C.6 for minimum clearances.

Notes:

(1) Flare spacing should be based on heat intensity with a minimum space of 60 m from equipment containing hydrocarbons.

(2) The minimum spacings can be down to one-quarter these typical spacings when properly assessed.

Table 10.5 *Some separation distances for oil and chemical plants. The spacings given are applicable for items with potential for fire and vessel explosion. Spacings for items with potential for vapour cloud explosion should be obtained by other means*

A Interunit spacings (Industrial Risk Insures, 1991)

	Service buildings	*Motor control centres and electrical substations*	*Utilities areas*	*Cooling towers*	*Control rooms*	*Compressor buildings*	*Large pump houses*	*Process units moderate hazard*	*Process units intermediate hazard*	*Process units high hazard*	*Atmospheric storage tanks*	*Pressure storage tanks*	*Refrigerated storage tanks dome roof*	*Flares*	*Unloading and loading racks*	*Fire water pumps*	*Fire stations*
/	/	/															
50	50		/														
50	50		100	50													
/	/		100	100	/												
100	100		100	100	100	30											
100	100		100	100	100	30	30										
100	100		100	100	100	30	30	50									
200	100		100	100	200	50	50	100	100								
400	200		200	200	300	100	100	200	200	200							
250	250		250	250	250	250	250	250	300	350	*	*					
350	350		350	350	350	350	350	350	350	350	*	*	*				
350	350		350	350	350	350	350	350	350	350	*	*	*				
300	300		300	300	300	300	300	300	300	300	300	400	400	/			
200	200		200	200	200	200	200	200	200	300	250	350	350	300	50		
50	50		50	50	50	200	200	200	300	300	350	350	350	300	200	/	
50	50		50	50	50	200	200	200	300	300	350	350	350	300	200	/	/

B Interequipment spacings (Industrial Risk Insurers, 1992)

Compressors	*Intermediate hazard pumps*	*High hazard pumps*	*High hazard reactors*	*Intermediate hazard reactors*	*Moderate hazard reactors*	*Columns, accumulators drums*	*Rundown tanks*	*Fired heaters*	*Air cooled heat exchanger*	*Heat exchangers*	*Pipe racks*	*Emergency controls*	*Unit block valves*	*Analyser rooms*
30														
30	5													
50	5	5												
50	10	15	25											
50	10	15	25	15										
50	10	15	25	15	15									
50	10	15	50	25	25	15								
100	100	100	100	100	100	100	100							
50	50	50	50	50	50	50	100	25						
30	15	15	25	15	15	15	100	50	/					
30	10	15	25	15	10	10	100	50	15	5				
30	10	15	25	15	10	10	100	50	/	10	/			
50	50	50	100	50	50	50	100	50	50	50	50	/	/	/
50	50	50	100	50	50	50	100	50	50	50	50	/	/	
50	50	50	50	50	50	50	100	50	50	50	50	/		

1 ft = 0.305 m; /, No spacing requirements; ∗ Spacing given in Table 3 of the original reference.

recommendations for dealing with storage units with frothover or boilover potential and with units located on sloping ground.

10.11.5 Hazard models

Another approach to the determination of separation distances is to use hazard models to determine the separation distance at which the concentration from a vapour escape or the thermal radiation from a fire fall to an acceptable level. This is the other side of the coin to hazard assessment of a proposed layout. Early accounts of the use of hazard models to determine separation distances include those of Hearfield (1970) and Simpson (1971).

Two principal factors considered as determining separation are (1) heat from burning liquid and (2) ignition of a vapour escape.

Table 10.6 *Separation distances for process units: spacings between process units and other features obtained using the Mond Index (D.J. Lewis, 1980b) (Courtesy of the American Institute of Chemical Engineers)*

A Minimum spacings between one process unit A and another process unit B (m)

Overall risk rating R_2 of process unit A	*Overall risk rating R_2 of process unit B*						
	Mild	*Low*	*Medium*	*High*	*Very high*	*Extreme*	*Very extreme*
Mild	0	6	9	12	17	20	30
Low	6	8	10	15	20	25	40
Medium	9	10	15	18	25	30	50
High	12	15	18	20	30	40	60
Very high	17	20	25	30	40	50	80
Extreme	20	25	30	40	50	65	100
Very extreme	30	40	50	60	80	100	150

B Minimum spacings between a process unit and another feature (m)

Overall risk rating R_2 of storage unit	*Feature*							
	Works boundary	*Plant boundary works main road, works main railway*	*Control room*	*Offices, amenity, buildings, workshops, laboratories, etc.*	*Electrical switchgear, instrument houses*	*Electrical power lines and transformers*	*Process furnaces and similar ignition sources*	*Forced draught cooling towers*
Mild	20	15	9	12	5	0	7	10
Low	27	20	10	15	10	5	12	17
Medium	35	27	15	20	15	10	17	25
High	50	35	18	27	20	15	25	30
Very high	70	50	25	40	25	20	30	35
Extreme	120	75	30	60	30	25	40	40
Very extreme	200	100	50	75	40	30	60	50

Permissible heat fluxes are discussed by Simpson, who distinguishes three levels of heat flux: 12.5 kW/m^2 (4000 BHU/ft^{2}h), 4.7 kW/m^2 (1500 BTU/ft^{2}h) and 1.6 kW/m^2 (500 BTU/ft^{2}h). The first value is the limit given in the Building Regulations 1965 and is suggested as a suitable limit for buildings such as control rooms or workshops; the second is the threshold of pain after a short time and is suggested as the limit for workers out on the plant who must continue doing essential tasks; and the third is the level of minor discomfort and is suggested as the limit for people in adjoining areas. A more detailed discussion of thermal radiation criteria is given in Chapter 16.

Simpson also considers separation distances based on the dilution of a vapour leak to a concentration below the lower flammability limit. The estimates are based on calculations of leak emission flows, pool vaporization rate and vapour cloud dispersion, as described in Chapter 15. One problem which he discusses is the separation between storage and an ignition source for petroleum spirit and other flammable liquids of similar volatility. For this case, he concludes that in most instances a separation distance of 15 m is adequate.

Another problem is the separation distance between a petrochemical unit and an ignition source. The typical scenarios which he discusses give separation distances as high as 88 m, this being for a necked-off branch on a C_2 fractionator.

A further discussion of the basis for separation distances has been given by R.B. Robertson (1976b).

The principle of the use of hazard models to set separation distances is now recognized in codes. *Liquefied Petroleum Gas* (IP, 1987 MCSP Part 9) gives separation distances for liquid storage units based on hazard models, as described in Section 10.14.

10.11.6 Liquefied flammable gas

A separation distance of 15 m frequently occurs in codes for the storage of petroleum products, excluding LPG. For LPG and LFG, the separation distances are generally greater. Thus in the ICI *LFG Code* the separation distances recommended between a storage and an ignition source are, for ethylene, 60 m for pressure storage and 90 m for refrigerated storage, and for C_3 compounds, 45 m for both types of storage. The general approach there taken is that there is significant risk of failure for a refrigerated storage but negligible risk for a pressure storage vessel.

Separation distances are also implied in the ICI *Electrical Installations in Flammable Atmospheres Code* (the *ICI Electrical Installations Code*) (ICI/RoSPA 1972 IS/91) in that the code gives guidance on the radius of the electrical area classification zone from potential leak points. For a pump with a mechanical seal containing a flammable liquid with

Table 10.7 *Separation distances for process units: spacings between storage units and process units or other storage units obtained using the Mond Index (D.J. Lewis, 1989b) (Courtesy of the Norwegian Society of Chartered Engineers)*

A Minimum spacings between a storage unit and a process unit: spacing to tank wall (m)

Overall risk rating R_2 *of storage unit*	*Overall risk rating* R_2 *of process unit*						
	Mild	*Low*	*Medium*	*High*	*Very high*	*Extreme*	*Very extreme*
Mild	3	7	10	13	18	23	38
Low	6	9	12	17	23	30	50
Moderate	9	12	17	21	31	44	66
High	12	17	21	28	43	56	84
Very high	17	23	31	43	56	72	110
Extreme	23	30	44	56	72	97	145
Very extreme	38	50	66	84	110	145	197

B Minimum spacings between a storage unit and a process unit: spacing to bund wall (m)

Overall risk rating R_2 *of storage unit*	*Overall risk rating* R_2 *of process unit*						
	Mild	*Low*	*Medium*	*High*	*Very high*	*Extreme*	*Very extreme*
Mild	2	4	5	7	9	10	15
Low	3	5	6	8	10	13	20
Moderate	4	6	8	9	13	16	26
High	6	8	9	12	16	22	33
Very high	8	10	13	16	22	28	45
Extreme	10	13	16	22	28	36	58
Very extreme	15	20	26	33	45	58	90

C Spacings between two storage units: spacing between one tank wall and the other tank wall (m)

Overall risk rating R_2 *of storage unit A*	*Overall risk rating* R_2 *of storage unit B*						
	Mild	*Low*	*Medium*	*High*	*Very high*	*Extreme*	*Very extreme*
Mild	5	7	10	13	18	25	43
Low	7	10	13	19	26	36	55
Moderate	10	13	19	26	36	56	80
High	13	19	26	36	56	72	110
Very high	18	26	36	56	72	97	145
Extreme	25	36	56	72	97	130	185
Very extreme	43	60	80	110	145	185	225

a flashpoint below 32°C the radius of Zone 2 depends on the liquid temperature as follows:

Liquid temperature (°C)	*Radius of Zone 2* (m)
≤100	6
100–200	20
>200	30

10.12 Hazardous Area Classification

Plant layout has a major role to play in preventing the ignition of any flammable release which may occur. This aspect of layout is known as 'area classification'. One principal type of ignition source is electric motors, and area classification has its origins in the need to specify motors with different degrees of safeguard against ignition. As such, the practice was known as 'electrical area classification' and was usually performed by electrical engineers. The extension of this practice to cover the exclusion of all sources of ignitions is known as 'hazardous area classification' and is generally performed by chemical engineers.

Hazardous area classification is dealt with in BS 5345: 1977 *Code of Practice for the Selection, Installation and Maintenance of Electrical Apparatus for Use in Potentially Explosive Atmospheres (Other than Mining Applications or Explosive Processing and Manufacture)*, and in a number of industry codes, including the *Area Classification Code for Petroleum Installations* (IP, 1990 MCSP Pt 15).

The process of hazardous area classification involves assigning areas of the site to one of four categories. The international definition of these by the International Electrotechnical Commission (IEC), given in BS 5345: 1977, is:

Zone 0 A zone in which a flammable atmosphere is continuously present or present for long periods.

Table 10.8 *Separation distances for process units: spacings between storage units and other features obtained using the Mond Index (D.J. Lewis, 1989b) (Courtesy of the Norwegian Society of Chartered Engineers)*

A Spacings between a storage unit and another feature: spacing to tank wall (m)

Overall risk rating R_2 *of storage unit*	*Feature*[a]					
	Works boundary	*Plant boundary, works main road, works main railway*	*Control room*	*Offices, amenity, buildings, workshops, laboratories, etc.*	*Process furnaces, other ground level ignition sources, electrical switchgear, instrument houses*	*Flare stacks, of tip height H m above ground*[b]
Mild	20	15	7	12	10	$1.25H + 6$
Low	27	20	12	16	15	$1.25H + 10$
Moderate	35	25	20	24	22	$1.25H + 15$
High	55	41	28	36	33	$1.25H + 22$
Very High	81	70	41	58	52	$1.25H + 35$
Extreme	125	95	53	72	66	$1.25H + 45$
Very extreme	175	130	75	100	90	$1.25H + 60$

B Spacings between a storage unit and another feature: spacing to bund wall (m)

Overall risk rating R_2 *of storage unit*	*Feature*[a]					
	Works boundary	*Plant boundary, works main road, works main railway*	*Control room*	*Offices, amenity, buildings, workshops, laboratories, etc.*	*Process furnaces, other ground level ignition sources, electrical switchgear, instrument houses*	*Flare stacks, of tip height H m above ground*[b]
Mild	15	10	5	8	7	$H + 6$
Low	20	12	6	11	10	$H + 8$
Moderate	25	15	7	13	12	$H + 10$
High	38	22	9	20	18	$H + 16$
Very High	46	29	12	25	23	$H + 20$
Extreme	54	36	15	30	26	$H + 23$
Very extreme	65	45	20	40	32	$H + 28$

[a] In the case of a buried tank, the tank wall distance is measured to the position on the plan of the tank wall or other items not more than 10 m below ground level.
[b] In the case of a flare stack, the distances is a function of the flare stack tip height H, as shown in the last column.

Zone 1 A zone in which a flammable atmosphere is likely to occur for short period in normal operation.
Zone 2 A zone in which a flammable atmosphere is not likely to occur in normal operation and if it occurs only exist for a short time.

A non-hazardous area is an area not classified as Zone 0, 1 or 2. In the United Kingdom, this classification system replaces an earlier system based on three Divisions: 0, 1 and 2.

In the United States of America, hazardous area classification is covered in Article 500 of NPFA 70: 1993 *National Electrical Code* and in API RP 500: 1991 *Recommended Practice for Classification of Locations for Electrical Installations at Petroleum Facilities*.

The purpose of hazardous area classification is to minimize the probability of ignition of small leaks. It is not concerned with massive releases, which are very rare. This distinction is a necessary one, but the difference can sometimes be blurred. Mecklenburgh instances a pump seal which, if it leaks, will generally give a rather small release, but which may on occasion give a leak greater than that from the rupture of a small pipe. Because the leaks considered are small and because small flammable releases burn rather than explode, it is fire rather than explosion with which hazardous area classification is concerned.

Since it is difficult to specify leaks fully in terms of size, frequency and duration, the following grades of leak are defined:

(1) Continuous grade: release is continuous or nearly so.
(2) Primary grade: release is likely to happen regularly or at random times during normal operation.
(3) Secondary grade: release is unlikely to happen in normal operation and in any event will be of limited duration.

Broadly speaking, continuous, primary and secondary grade releases equate to Zones 0, 1 and 2, respectively.

Hazardous area classification proceeds by identifying the sources of hazard, or potential leak points, and the sources of ignition. Typical leak points include flanges, seals, sample points and temporary connections; typical ignition

sources include electric motors, burners and furnaces, engines and vehicles.

There are three main strategies available for the control of ignition sources: prevention, separation and protection. The approach to hazardous area classification based on these strategies is broadly as follows. First, the potential leak sources are identified. The characteristics of the leak are defined, for start-up, shut-down and emergency conditions as well as normal operation, and the grade of leak assigned. For each leak point, consideration is given to reducing or eliminating any leak. Guidance on separation distances is then used to determine the area around the leak source from which ignition sources should be excluded. Next the ignition sources near the leak point are identified. For each ignition source in turn, consideration is given to the possibility that it can be eliminated or moved. Where this is not applicable, the zone is specified and appropriate protection of the ignition source is determined. For electrical equipment this means specifying the type of safeguarding appropriate to the zone.

A check may be made on the separation distances used and on the degree of protection required by modelling the dispersion of the leak. Consideration should also be given to the effect of any pool fire arising from flammable liquid released at the leak point. In some instances this may require an increase in the separation distance or the use of protection measures such as insulation or water sprays.

The control of ignition sources reduces the risk of injury to personnel and the risk of property damage. The extent to which the plant design is modified for reasons of hazardous area classification is governed for personal injury by the usual risk criteria and considerations of what is reasonably practicable, and for property damage by economic considerations. In cases where property damage is the issue, it may be preferable to accept a certain risk rather than to undertake unduly expensive countermeasures.

The outcome of this exercise for all the ignition sources identified is the definition of the zones in three dimensions for the whole plant. Drawings are produced showing these zones in plan and elevation, both for individual items of equipment and for the plant as a whole. A typical plan drawing is illustrated in Figure 10.4.

Hazardous area classification provides the basis for the control of ignition sources both in design and in operation. A further discussion of hazardous area classification is given in Chapter 16.

10.13 Hazard Assessment

In the methodology for plant layout described by Mecklenburgh (1985), hazard assessment is used at several points in the development of the layout. In each case, the procedure is essentially an iterative one in which hazards are identified and assessed, modifications are made to the design and the hazards are reassessed. The nature of the hazard assessment will vary depending on whether it is done in support of site location, site layout, Stage One plot layout or Stage Two plot layout.

Hazard assessment in support of site location is essentially some form of quantitative risk assessment.

Hazard assessment for site layout concentrates on major events. It provides guidance on the separation distances required to minimize fire, explosion and toxic effects and on the location of features such as utilities and office buildings.

Hazard assessment for plot layout deals with lesser events and with avoidance of the escalation of such events. It is used as part of the hazardous area classification process and it provides guidance on separation distances to prevent fire spread and for control building location.

At the plot layout level, hazard assessment is concerned mainly with flammable releases. It is not usually possible at this level to do much about explosions and toxic releases.

10.14 Hazard Models

10.14.1 Early models

An account has already been given of the early work of Simpson (1971) on the use of models for plant layout purposes. The hazard models described by him include models for two-phase flow and for vapour dispersion and criteria for thermal radiation, as described in Section 10.11.

10.14.2 Mecklenburgh system

A set of hazard models specifically for use in plant layout has been given by Mecklenburgh (1985). A summary of the models in this hazard model system is given in Table 10.9. Some of the individual models are described in Chapters 15, 16 and 17. Although the modelling of some of the phenomena has undergone further development, this hazard model system remains one of the most comprehensive available for its purpose.

10.14.3 IP system

Another, more limited, set of hazard models for plant layout is that given in *Liquefied Petroleum Gas* (IP, 1987 MCSP Pt 9). The models cover:

(1) emission;
  (a) pressurized liquid,
  (b) refrigerated liquid,
(2) pool fire;
(3) jet flame.

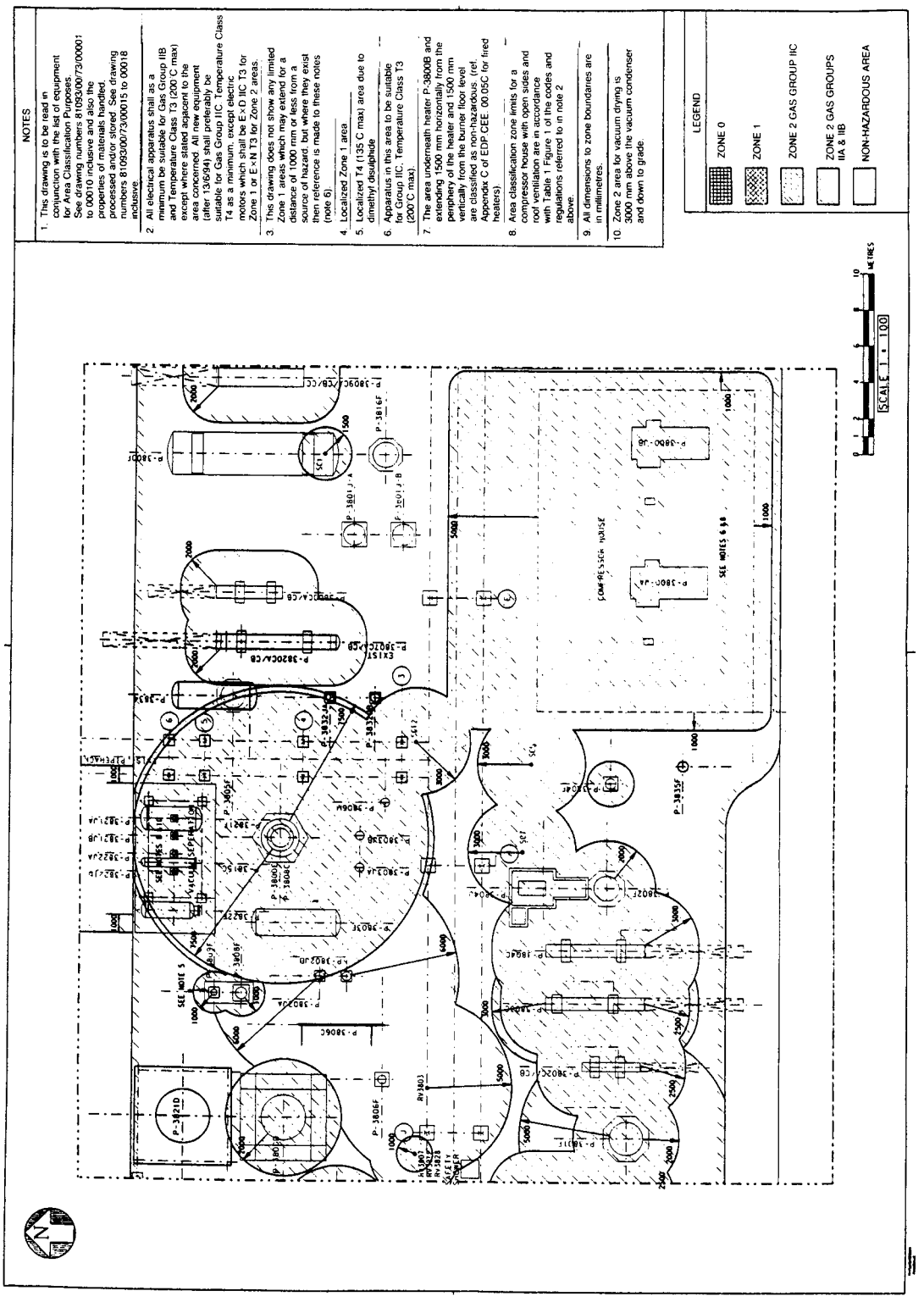
The models include view factors for thermal radiation from cylinders at a range of angles to the vertical and of positions of the target. The requirements for separation distances between storage units are based on thermal radiation flux criteria. These are given in Chapter 22. The code gives worked examples.

10.14.4 Injury and damage criteria

Criteria for injury and damage, principally the latter, are given by Mecklenburgh as part of his hazard model system.

For the heat flux from a flame or fire the tolerable intensities are given as follows:

	Heat flux (kW/m^2)
Drenched storage tanks	38
Special buildings	25
Normal buildings	14
Vegetation	12
Escape routes	6
Personnel in emergencies	3
Plastic cables	2
Stationary personnel	1.5


NOTES
1. This drawing is to be read in conjunction with the list of equipment for Area Classification Purposes. See drawing numbers 81093/00/73/00001 to 00010 inclusive and also the properties of materials handled, processed and/or stored. See drawing numbers 81093/00/73/00015 to 00018 inclusive.
2. All electrical apparatus shall as a minimum be suitable for Gas Group IIB and Temperature Class T3 (200°C max) except where stated apacent to the area concerned. All new equipment (after 13/6/94) shall preferably be suitable for Gas Group IIC. Temperature Class T4 as a minimum, except electric motors which shall be E x D IIC T3 for Zone 1 or E x N T3 for Zone 2 areas.
3. This drawing does not show any limited Zone 1 areas which may extend for a distance of 1000 mm or less from a source of hazard, but where they exist then reference is made to these notes (note 6).
4. Localized Zone 1 area
5. Localized T4 (135°C max) area due to dimethyl disulphide
6. Apparatus in this area to be suitable for Group IIC, Temperature Class T3 (200°C max).
7. The area underneath heater P-3900B and extending 1500 mm horizontally from the periphery of the heater and 1500 mm vertically from the burner floor level are classified as non-hazardous (ref. Appendix C of EDP CEE. 00.05C for fired heaters).
8. Area classification zone limits for a compressor house with open sides and roof ventilation are in accordance with Table 1 Figure 1 of the codes and regulations referred to in note 2 above.
9. All dimensions to zone boundaries are in millimetres.
10. Zone 2 area for vacuum drying is 3000 mm above the vacuum condenser and down to grade.
LEGEND
ZONE 0
ZONE 1
ZONE 2 GAS GROUP IIC
ZONE 2 GAS GROUPS IIA & IIB
NON-HAZARDOUS AREA
SCALE 1 : 100
METRES
SEE NOTES 5 & 8
SEE NOTE 5
SEE NOTES 5 & 8
COMPRESSOR HOUSE
SAFETY TOWER
P-3821D
P-3806F
P-3806C
P-3806E
P-3806W
P-3806K
P-3806J
P-3806H
P-3806L
P-3806M
P-3806N
P-3806P
P-3806R
P-3806S
P-3806T
P-3806U
P-3806V
P-3806Z
P-3807A
P-3807B
P-3807C
P-3807D
P-3807E
P-3807F
P-3807G
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P-3809W
P-3809X
P-3809Y

Table 10.9 *Hazard assessment in support of plant layout: Mecklenburgh hazard model system*

Table No.[a]	
B1	Source term: instantaneous release from storage of flashing liquid (catastrophic failure of vessel) Flash fraction Mass in, and volume of, vapour cloud
B2	Dispersion of flammable vapour from instantaneous release Distance to lower flammability limit (LFL)
B3	Explosion of flammable vapour cloud from instantaneous release Explosion overpressure Damage (as function of overpressure)
B4	Fireball of flammable vapour cloud from instantaneous release Fireball diameter, duration, thermal radiation
B5	Dispersion of toxic vapour from instantaneous release Peak concentration, time of passage Distance to safe concentration, outdoors and indoors
B6	Source term: continuous release of fluid (a) Gas (subsonic) (b) Gas (sonic) (c) Flashing liquid (not choked) (d) Flashing liquid (choked)
B7	Dispersion of flammable vapour jet Jet length, diameter (to LFL)
B8	Jet flame from flammable vapour jet Flame length, diameter Flame temperature, surface heat flux, distance to given heat flux
B9	Dispersion of toxic vapour plume Distance to given concentration Distance to safe concentration, outdoors and indoors
B10	Growth of, and evaporation from, a pool Pool diameter Evaporation rate
B11	Pool or tank fire Flame height Regression rate, surface heat flux View factor
B12	Effect of heat flux on targets Tolerable heat fluxes
B13	Risk criteria Individual risk to employees (as a range) Individual risk to public (as a range) Multiple fatality accident
B14	Explosion overpressure Damage (as function of overpressure) (*see also* B3)
B15	Dispersion of flammable vapour from small continuous release Jet dispersion: distance to given concentration, to LFL (*see* B7) Passive dispersion: distance to given concentration (*see* B9) Jet flame: distance to given heat flux (*see* B8)
B16	Evaporation and dispersion from small liquid pool Distance to given concentration
B17	Dispersion of flammable vapour from small continuous release in a building Jet dispersion: distance to given concentration Passive dispersion: distance to given concentration Jet flame: distance to given heat flux (*see* B8)
B18	Evaporation and dispersion from small liquid pool in a building Evaporation rate Mean space concentration Other parameters for (a) horizontal air flow and (b) vertical air flow

[a] In Mecklenburgh (1985).

For a fireball, the safe dose is given as $It_B^{2/3} < 47$, where I is the heat flux (kW/m^2) and t_B is the duration of the fireball (s).

For the peak incident overpressure from an explosion the limits which should not be exceeded are given as follows:

	Peak incident overpressure (bar)
Schools	0.02
Housing	0.04
Public roads	0.05
Offices	0.07
Shatter-resistant windows	0.10
Site roads, utilities	0.20
Hazardous plants	0.30–0.40
Protected control room	0.7

10.14.5 Illustrative example

Mecklenburgh illustrates the application of his hazard models by giving for each a scenario and worked example, and for some of the outdoor cases he combines these into an assessment of the effects on-site and off-site. For this latter assessment he considers a set of scenarios which may be summarized as follows:

(1) instantaneous release of flashing liquid from storage tank:
   (a) flammable liquid giving rise to unignited vapour cloud, or fireball or vapour cloud explosion,
   (b) toxic liquid giving rise to toxic gas cloud, in open and around building;
(2) residual liquid in tank:
   (a) flammable liquid giving rise to unignited vapour cloud, pool fire,
   (b) toxic liquid giving rise to toxic gas cloud;
(3) liquid pool from 10 cm leak in tank base following instantaneous release:
   (a) flammable liquid giving rise to unignited vapour cloud, or pool fire,
   (b) toxic liquid giving rise to toxic gas cloud;
(4) Continuous release of pressurized liquid from 2.5 cm hole:
   (a) flammable fluid giving rise to passively dispersing unignited vapour cloud, or jet fire,
   (b) toxic fluid giving rise to passively dispersing toxic gas cloud;
(5) continuous release of pressurized liquid from 10 cm hole:
   (a) flammable fluid giving rise to passively dispersing unignited vapour cloud, or jet fire,
   (b) toxic fluid giving rise to passively dispersing toxic gas cloud.

The overall results are summarized in Table 10.10. These results are discussed by Mecklenburgh in relation to both on-site and off-site effects and to the countermeasures which might be taken.

10.15 Fire Protection

Plant layout can make a major contribution to the fire protection of the plant. This has a number of aspects.

Plant layout for fire protection is covered in BS 5908: 1990 *Fire Precautions in the Chemical and Allied Industries*. Also relevant are BS 5306: 1976 *Fire Extinguishing Installations and Equipment on Premises*, particularly Part 1 on fire hydrants, and BS 5041: 1987 *Fire Hydrant Systems Equipment*. An important earlier code, BS CP 3013: 1974 *Fire Precautions in Chemical Plant*, is now withdrawn. The coverage of BS 5908: 1990 is indicated by the list of contents given in Table 10.11. Accounts of the fire protection aspects of plant layout include those by Simpson (1971), Hearfield (1970) and Kaura (1980a).

Some aspects of plant layout for fire protection may be classed as passive and others as active measures. The former include (1) separation of hazards and targets, (2) measures to prevent fire spread and (3) provision of access for fire fighting; the latter include provision of (4) fire water and (5) fire protection systems. The segregation of hazards and targets and the containment of fire are important aspects of site layout and are considered in Section 10.6. The provision and location of fire water hydrants and fire protection equipment are prominent features of plot layout and are discussed in Section 10.7. This section deals primarily with access, fire water and fire protection equipment. Fire protection is discussed further in Chapter 16.

Table 10.10 *Hazard assessment in support of plant layout: illustrative example (after Mecklenburgh, 1985) (Courtesy of the Institution of Chemical Engineers)*

A Off-site effects – summary of distances (m)

	All built-up area	*100m built-up, then country*	*All country*
1(a) Instantaneous release			
LFL	341	363	377
Fireball, safe dose	463	463	463
Blast, schools	500	500	500
housing	290	290	290
roads	240	240	240
Safe toxic, open	941	1034	1048
Safe toxic, building	35	–	54
1(b) Open tank after instantaneous release			
LFL	At tank	–	At tank
Fire, 1.5 kW/m^2	17	17	17
Safe toxic	Near tank	–	Near tank
1(c) Unconfined pool from 10 cm leak after instantaneous release			
Fire, 1.5 kW/m^2	83	–	83
Pool radius (fire)	9	–	9
LFL	37	–	41
Safe toxic	67	–	96
Pool radius (evap.)	33	–	33 (concrete)
2 2.5 cm steady release under pressure			
LFL (no jet)	16 (28)	–	16 (38)
Fire, 1.5 kW/m2	43	–	43
Safe toxic (no jet)	60 (72)	–	68 (92)
3 10 cm steady release under pressure			
LFL (no jet)	62 (159)	62 (172)	62 (200)
Fire, 1.5 kW/m^2	172	172	172
Safe toxic in open (no jet)	290 (403)	324 (461)	324 (489)
Safe toxic in building (no jet)	87 (126)	87 (131)	87 (159)

B On-site effects – summary of distances (m)

1(a) Instantaneous release	
LFL	341
Fireball, safe dose	463
Fireball radius	73
Blast-resistant control rooms	50
Hazardous plants	60–75
Shatter-resistant windows	150

Table 10.10 *(continued)*

Offices	180	
Safe toxic in buildings	35	
Safe toxic in open	941	
1(b,c) After instantaneous release		
	Open tank (m)	*Unconfined pool from 10 cm leak* (m)
LFL	Close	37
Pool radius (fire)	–	9
Fire, drenched tanks	8	30
Special buildings	9	33
Normal buildings	10	39
Vegetation	10	41
Escape routes	12	50
Personnel in emergencies	14	62
Plastic cables	15	73
Stationary personnel (1.5 kW/m2)	17	83
Safe toxic limit	3	67
Pool radius (evaporation)	–	33
2 and 3 Steady releases under pressure		
	2.5 cm	*10 cm*
LFL (no jet)	16 (28)	63 (159)
Fire, drenched tanks	29	116
Special buildings	30	120
Normal buildings	32	128
Vegetation	32	128
Escape routes	35	140
Personnel in emergencies	39	156
Plastic cables	41	164
Stationary personnel	43	172
Safe toxic limit in open (no jet)	60 (72)	290 (403)
Safe toxic limit in building (no jet)	60 (72)	87 (126)

LFL, lower flammability limit.
Note: Values in brackets are for the case where the release does not take the form of a jet.

Table 10.11 *Principal contents of BS 5908: 1990*

1. General
2. Legal background
3. Principles of initiation, spread and extinction of fire
4. Site selection and layout
5. Buildings and structures
6. Storage and movement of materials
7. Design of process plant
8. Operation of process plant
9. Maintenance of process plant
10. Fire prevention
11. Fire defence
12. Works fire brigades
13. Classification of fires and selection of extinguishing media
14. Fixed fire extinguishing systems
15. Portable and transportable appliances
16. Organization of emergency procedures

There are numerous legal requirements concerning fire, fire construction and fire fighting. There should be full consultation at an early stage with the works safety officer and with other parties such as the local authority services, the Health and Safety Executive (HSE) and the insurers.

10.15.1 Fire fighting access

Access is essential for fire fighting. Some basic principles are that it should be possible to get fire fighting equipment sufficiently close to the site of the fire and that there should be access from more than one side. Access should be provided within 18 to 45 m of a hazard and there should be water supplies and hard standing at these access points.

The site should have a peripheral road connected at not less than two points with the public road system. It may be necessary to provide a waiting area for fire fighting vehicles near each main gate. Site roads should be arranged to allow approach to a major fire from two directions. Major process or storage units should be accessible from at least two sides. Access is assisted by a plot size of 100 m×200 m with approaches preferably on all four sides and by spacing between plots and buildings of 15 m.

Access for fire fighting vehicles should be over firm ground, should have sufficient road and gate widths, should give adequate clearance heights and should allow for the necessary turning and manoeuvring. The vehicles requiring access may include heavy bulk foam or carbon dioxide carriers.

10.15.2 Fire water

In a fire, water is required for extinguishing the fire, for cooling tanks and vessels and for foam blanketing systems.

The quantities of water required can be large, both in terms of the instantaneous values involved and of the duration for which they may be needed. In some fires water sprinkler systems have been required to operate for several days.

The design of a fire water system requires the determination of the maximum fire water flow which the system should deliver. Some order of magnitude figures are given in the *Refining Safety Code* (IP, 1981 MCSP Pt 3). This states that for a major process fire the fire water flows required might be of the order of 750–1500 m^3/h. The code also quotes for a major fire on a 50 m diameter storage tank a fire water flow of 830 m^3/h for the application of foam to the burning tank and for the cooling of the adjacent tanks. R.B. Robertson (1974a) refers to investigation of the fire water actually used in major process plant fires and quotes water flows in the range of 900–2700 m^3/h.

It is also necessary to specify the length of time for which such fire water flows should be sustained. This specification also may be obtained using the design basis fire approach. Typically this length of time is recommended to be 2–3 hours. Robertson states that study of time taken to control fires points to a duration of 2 hours.

The fire water requirement may be based on the specification of a design basis fire. Kaura (1980a) suggests that this might be two simultaneous fires, one on a major process unit and the other at the storage tanks. The IP *Refining Safety Code* states, on the other hand, that it is usual to assume that there will be only one major fire at a time. The practical difference between these approaches depends on how generous an allowance is made for the single fire.

The fire water main may be fed from the public water supply, but for large works the public supply may well not be adequate to provide the quantities of water required. Additional water supplies may be drawn be the fire brigades from rivers, canals, reservoirs or static tanks, but such sources should be near enough to allow suction to be obtained directly, since reliance on relays is likely to involve undue delay. Cooling water should not be used, because loss of cooling on other plants is itself a hazard. Where the public supply is to be used, this should be done in accordance with BS 6700: 1987. The water and fire authorities should be consulted about fire water supplies.

Water supplies for water sprays and sprinklers may be provided in the form of elevated static water tanks. A typical capacity might be such as to supply water for 1 hour. Pumps should be provided to replenish the supplies.

Fire water should be available from hydrants adjacent to the fire hazards on a ring main running alongside the road and located between the road and the plant. The main should preferably be buried under ground. The installation should be generally in accordance with BS 5306: 1976–and fire water hydrants with BS 750: 1984 and BS 5306: Part 1: 1976. The main should take the form of a ring main encircling the plant, with cross-connections and with isolation valves to allow shut-off if a section of the main is damaged.

Hydrant intervals should be 45 m for high risk areas but may be up to 100 m for low risk ones. The distance between the hydrant, the plant structure or storage area should be not less than 18 m and may be up to 45 m. The hydrants should be provided with a hard standing and with signs in accordance with BS 5499: Part 1: 1990. The signs should indicate the quantity of water available.

Rising mains should be installed in a building or structure on any floor exceeding 18 m above ground level. Dry rising mains are suitable for heights up to 60 m, but above this height a wet main may be preferable. The inlets on the ground floor to dry riser mains and the outlets on all floors to both types of main should be accessible.

Fire water for sprinkler and water spray systems should be in accordance with BS 5908.

Pipes for fire water supply should be protected against explosion damage. Isolation valves should be provided to prevent loss of fire water from damaged lines and, if these valves are above ground level, they should be protected by concrete blast barriers. The fire water is normally pumped through the main by fixed fire pumps. There should be at least two full capacity pumps with separate power supplies. Cabling for electric pumps should not run through high risk areas or, if this is unavoidable, it should be protected. The location of the pumps is usually determined by that of the source of supply, but they should not be in a high risk area. The fire pumps should be housed to protect them from the weather. In a fire, mobile pumps may sometimes be used to boost the fire main pressure, though their principal use is to supply fire hoses from the main or other sources.

10.15.3 Fire protection equipment

The other aspects of fire protection of plant, including fire containment by layout, gas, smoke and fire detection, passive fire protection such as fire insulation, and active fire protection such as the use of fixed, mobile and portable fire fighting equipment, are considered in Chapter 16.

It is appropriate to mention here, however, the provision of certain minimal equipment which is generally treated as an aspect of plant layout. Fire extinguishers of the appropriate type and fire blankets should be placed at strategic points on the plant. There should be at least two extinguishers at each point. Some extinguishers should be located on escape or access routes, so that a person who decides to fight the fire using the extinguisher has a route behind him for escape.

Fire equipment should be located so that it is not likely to be disabled by the accident itself, should be accessible and should be conspicuously marked. The main switchgear and emergency controls should have good access, preferably on an escape route, so that the operator does not have to risk his life to effect shut-down.

10.16 Effluents

General arrangements for dealing with effluents are discussed by Mecklenburgh (1973, 1985). Pollution of any kind is a sensitive issue and attracts a growing degree of public control. There should be the fullest consultation with the local and water authorities and the Inspectorate of Pollution in all matters concerned with effluents.

Hazard identification methods should be used to identify situations which may give rise to acute pollution incidents and measures similar to those used to control other hazards should be used to ensure that this type of hazard also is under control.

10.16.1 Liquid effluents

Liquid effluents include soil, domestic and process effluents, and cooling, storm and fire water. Harmless aqueous effluents and clean stormwater may be run away in open sewers, but obnoxious effluents require a closed sewer. One arrangement is to have three separate systems: an open

sewer system for clean stormwater and two closed sewer systems, one for domestic sewage and one for aqueous effluent from the plant and for contaminated stormwater.

There are a number of hazards associated with liquid effluent disposal systems such as drains and sewers. One is the generation of a noxious gas by the mixing of incompatible chemicals. Another hazard is that a flammable gas may flow through the drains, become distributed around the plant and then find a source of ignition. This can give rise to a quite violent explosion, or even detonation. A flammable liquid which is immiscible with water flowing through the drains constitutes another hazard. Again it may become distributed around the plant and find an ignition source. If the liquid is already on fire, its entry into the drains may cause the fire to be distributed around the plant.

Other problems with sewers include overloading, blockage and back flow, each of which can be hazardous. Overloading or blockage can result in a liquid fire being floated across to other parts of the site. Some case histories of problems in sewers are given by Anon. (1978 LPB 19, p. 10).

There are also environmental factors to consider. It is necessary to avoid the discharge of untreated contaminated liquid.

As stated above, process effluents, essentially aqueous, and contaminated stormwater are collected in a common sewer. The liquids discharged to this sewer should be closely controlled. If different effluents are to be mixed together, it should be checked that this can be done safely. Chemical works effluents are quite prone, for example, to generate obnoxious gases.

Water-immiscible flammable liquids should not be allowed to enter the sewers, where they create the hazard of fire or explosion. In particular, open sewers with solvent floating on the water may transmit fires over long distances. There should be arrangements to prevent the entry of such liquids into the sewers. Runoff from the plant area should be routed to interceptors located at the edge of the fire risk area. In order to avoid overloading, use is made of primary interceptors to effect a preliminary separation. Measures may need to be taken to prevent sedimentation in, and freezing of, the interceptors.

It may be necessary to take measures to avoid flooding on process and storage plots. There is need for care to avoid the flooding by effluents of vulnerable points such as pump pits. Flooding of bunds can cause the tanks inside to float. Effluents should not be permitted to run off plant areas onto adjacent sites, or vice versa. If the site slopes or contains a natural water course, additional precautions are needed.

The traditional sewer is the gravity flow type. This should have a gradient and be self-cleaning. Sewer boxes should be used as interconnections with a liquid seal to prevent the transmission of gases and vapours and reduce the hazard of fire/explosion. Where noxious vapours might collect, the sewer box lids should be closed, sealed and vented to a safe place. A suitable point is above grade 3 m, horizontally 4.5 m from platforms and 12 m from furnaces walls. The routing of sewers should be parallel to the road system. They can go under the road, but for preference should be alongside it.

Sewers are considered in more detail in Section 10.17. The sewer system should be settled at an early stage. It is usually not practical to increase the capacity once the plant is built.

10.16.2 Gaseous effluents

Gaseous effluents should be burned or discharged from a tall stack so that the fumes are not obnoxious to the site or the public. The local Industrial Pollution Inspector is able to advise on suitable stack heights and should be consulted. It is also necessary to check whether a high stack constitutes an aerial hazard and needs to be fitted with warning lights.

Flare stacks are a particular problem, because they radiate intense heat and can be very noisy. Quite a large area of ground beneath a flare stack is unusable and is effectively 'sterilized'. A flare stack may have to be relegated to a distant site. A further discussion of flare stacks is given in Chapter 12.

The behaviour of airborne emissions of all types should be carefully considered. Although the prevailing wind is the main factor, other possible troublesome wind conditions should be taken into account. The effect of other weather conditions, such as inversions should also be considered.

10.16.3 Solid wastes

Solid waste should preferably be transferred directly from the process to transport. If intermediate storage is unavoidable, care should be taken that it does not constitute a hazard or a nuisance. If combustible solid and solvent wastes are burnt, the incinerator should be convenient to the process.

10.17 Drain Systems

The main plant sewers are of particular importance and merit further description. As already stated, it is common to have an open clean stormwater sewer and a closed contaminated stormwater sewer. These sewers also carry fire water runoff during fire fighting.

Accounts of sewer systems include those by J.D. Brown and Shannon (1963a,b), Seppa (1964), D'Alessandro and Cobb (1976a) and Anon. (1978 LPB 19, p. 10). These systems are also considered by Mecklenburgh (1973, 1985). Stormwater systems are discussed by Elton (1980), W.E. Gallagher (1980) and G.S. Mason and Arnold (1984).

10.17.1 Clean stormwater system

Clean stormwater is usually collected in an open sewer. The discharge may be to water courses or the sea, or to a holding pond. On large sites it is generally not practical to discharge it to the public system, due to overload of the latter.

10.17.2 Contaminated stormwater system

The contaminated stormwater system consists of the contaminated stormwater sewers together with an impounding basin to hold the contaminated water prior to treatment and discharge. The design of the impounding basin is discussed by Elton (1980) and W.E. Gallagher (1980) and that of the contaminated stormwater sewers themselves by G.S. Mason and Arnold (1984).

First it is necessary to determine the catchment area, or watershed, from which the stormwater will flow onto the plant site. The next step is to characterize the rainfall. A suitable starting point is a rainfall atlas such as the *Rainfall Frequency Atlas* in the United States of America. The available data may be used to make an estimate of the maximum 24 hour rainfall. For some locations information is available from which the recurrence interval of particular levels of 24 hour rainfall may be determined.

A gravity flow stormwater system allows nearly immiscible liquids such as chlorinated hydrocarbons to accumulate and to contaminate water passing through until they are gradually dissolved. It may also allow a light, nearly immiscible flammable liquid to float on the top of the water and pass through unless liquid seals are installed to prevent this.

The alternative type of system is the fully flooded system. The system is flooded by a dam at the entrance to the collection sump. As water enters, the sewer becomes fully flooded. The catchbasins and manholes used in this case are of the dry-box type. A fully flooded system prevents the passage of flammable vapours and of burning liquids. There is no accumulation of nearly immiscible liquids and thus no contamination of the stormwater by such liquids.

A flooded stormwater system may not be justified if the liquids handled on the plant are not flammable. Such a system may be impractical in a location sufficiently dusty to cause clogging.

The selection of the materials of construction for a fully flooded system is important and is considered by the authors. These need to withstand both corrosion and thermal shock. They also discuss the conversion of a gravity flow system to fully flooded system and give cost comparisons.

10.17.3 Firewater disposal

There should be arrangements for the disposal of fire water, but it is expensive to provide sewers for the very large quantities of water involved, and different views have been expressed on the necessity for this (e.g. Simpson, 1971; Mecklenburgh, 1976). A practical compromise is to design the sewers to take at any rate the initial 'first aid' fire fighting water (R.B. Robertson, 1974a).

There are also different estimates given of the quantities of fire water likely to be involved. Mecklenburgh (1985) states that the allowance for fire water is about five times the volume allowed for the stormwater. Presumably this refers to UK conditions. A different ratio may well apply in other parts of the world.

Consideration should be given to the fire water flow in all sections of the sewer system. The main trunk sewer usually receives water from a relatively large watershed, but branch sewers may well be prone to overloading from large fire water usage on particular parts of the site.

In view of the large quantities of fire water which can be generated, it may well not be practical to design the sewers for these flows, and other methods of disposal may be needed. These include measures to pump it away or to run it off onto other land.

10.18 Blast-Resistant Structures

It is sometimes necessary in the design of structures such as plant and buildings to allow for the effect of shocks from explosions and/or earthquakes. In both these cases, there is a strong probabilistic element in the design in that it is not possible to define the precise load to which the plant structure may be subjected. The starting point is therefore the definition of the design load in terms of the relation between the magnitude of the load and the frequency of occurrence.

The full design of shock-resistant structures is beyond the scope of this book, but some limited comments are made here. Further accounts of explosion-resistant structures are given in Chapter 17 and of earthquake-resistant structures in Appendix 15.

10.19 Control Buildings

Until the mid-1970s, there were few generally accepted principles, and many variations in practice, in the design of control buildings. Frequently the control buildings constructed were rather vulnerable, being in or close to the plant and built of brick with large picture windows.

10.19.1 Flixborough

The Flixborough disaster, in which 18 of the 28 deaths occurred in the control building, caused the Court of Inquiry to call for a fundamental reassessment of practice in this area.

The control building at Flixborough has been described by V.C. Marshall (1976a). It was constructed with a reinforced concrete frame, brick panels and considerable window area. It was 2½ storeys high in its middle section, the 1½ storeys over the control room consisting of a half-storey cable duct and a full-storey electrical switchgear room. The control room was part of a complex of buildings some 160 m long, which also housed managers' offices, a model room, the control laboratory, an amenities building and a production block.

This building complex was 100 m from the assumed epicentre of the explosion and was subjected to an estimated overpressure of 0.7 bar. The complex lay with its long axis at right angles to the direction of the blast. It was completely demolished by the blast and at the control room the roof fell in. The occupants of the control room were presumably killed mainly by the collapse of the roof, but some had been severely injured by window glass or wired glass from the internal doors. It took mine rescue teams 19 days to complete the recovery of the bodies.

The main office block, which was a 3-storey building, again constructed with a reinforced concrete frame, brick panels and windows, was only 40 m from the assumed epicentre and was also totally demolished.

The implications of the Flixborough disaster for control building location and design have been discussed by V.C. Marshall (1974, 1976a,c,d) and by Kletz (1975e).

10.19.2 Building function

The control building should protect its occupants against the hazards of fire, explosion and toxic release. Much the most common hazard is fire, and this should receive particular attention.

There are several reasons for seeking to make control buildings safer. One is to reduce to a minimum level the risk to which operators and other personnel are exposed. Another is to allow control to be maintained in the early stages of an incident and so reduce the probability of escalation into a disaster. A third is to protect plant records, including those of the period immediately before an accident.

It is sometimes suggested that another aim should be to equalize the risks to those inside and outside. Since those outside tend to be less at risk in an explosion, this means in effect reducing the risk to those inside. This objective is not self-evident, however. The philosophy of risk described earlier is that no one should be subjected to more than a specified risk, not that the risk should be equal for all. In any event, before designing a control room, it is necessary to be clear as to what the objectives are.

10.19.3 ACMH recommendations

Control building location and design is one of the topics raised by the Court of Inquiry on the Flixborough disaster

and considered in the First and Second *Reports* of the Advisory Committee on Major Hazards (ACMH) (Harvey 1976, 1979b). The recommendations of the committee are that control rooms which may be subject to explosion should not be built in brick with large picture windows, but in reinforced concrete with small, protected windows.

10.19.4 Control facilities

There is a tendency for control rooms to become part of a complex of facilities, as the buildings at Flixborough illustrate. As a result, more people are exposed to hazard than is necessary and/or the buildings must be of more elaborate and expensive construction. Some of the additional rooms often associated with the control room include computer room, locker room, mess room, toilets, supervisors' offices, analytical laboratories, test rooms, instrument workshops, electrical relay and switchgear rooms.

The proper policy is to build a secure control room in which the functions performed are limited to those essential for the control of the plant and to remove all other functions to a distance where a less elaborate construction is permissible. The essential functions which are required in the control room are those of process control. There are other types of control which are required for the operation of the plant, such as analytical control and management control, but they need not be exercised from the control room. Thus other facilities such as analytical laboratories, amenities rooms, etc., should be located separately from the control room.

The control room should not be used as a centre to control emergencies. There should be a separate emergency control centre, as described in Chapter 24. The control room should also not be used as an emergency assembly point or refuge room.

10.19.5 Location

The ability of a control building to give protection against a hazard such as an explosion depends not only on its design but also on its location. The siting of a control building can, therefore, be as important as its construction.

It is good practice to lay plant out in blocks with a standard separation distance. The control building should be situated on the edge of the plant to allow an escape route. Recommended minimum distances between the plant and the control building tend to lie in the range 20–30 m. If hazard studies indicate, however, that the standard separation distance may not be adequate, the distance between the control building and the plant should, of course, be increased.

The control building should not be so near the plant that its occupants are at once put at risk by a serious leak of flammable, toxic or corrosive materials. On the other hand, increasing the distance from the process may make the operators less willing to get out on the plant. Managers are generally opposed to control rooms which are too remote. This is important, because active patrolling by the operator is one of the main safeguards against plant failures.

A control building should not be sited in a hazardous area as defined in BS 5345: 1977–. Further guidance on location of the control building is given below.

10.19.6 Basic principles

Arising from the experience of Flixborough, V.C. Marshall (1976a) has suggested certain principles for control building design which may be summarized as follows:

(1) The control room should contain only the essential process control functions.
(2) There should be only one storey above ground.
(3) There should be only the roof above the operator's head. The roof should not carry machinery or cabling.
(4) The building should have cellars built to withstand earthshock and to exclude process leaks and should have ventilation from an uncontaminated intake.
(5) The building should be oriented to present minimum area to probable centres of explosion.
(6) There should be no structures which can fall on the building.
(7) Windows should be minimal or non-existent and glass in internal doors should be avoided.
(8) Construction should be strong enough to avoid spalling of the concrete, but it is acceptable that, if necessary, the building be written off after a major explosion.

10.20 Toxics Protection

Another hazard against which protection may be required is that posed by a release of toxic gas. In general, ordinary buildings off site and even on site can afford an appreciable degree of protection against a transient toxic gas release, but for certain functions enhanced protection is required. It is also necessary to ensure that the protection potentially available is not defeated. Buildings of particular interest here are (1) the control building, (2) the emergency control centre and (3) any temporary refuges.

10.20.1 Control room

The design of a control room for protection against toxic release is discussed in the CIA *Control Building Guide* (CIA, 1979). The design should start by identifying the release scenarios against which protection is required and by making some quantitative assessment of the dispersion of the gas. If persons outside exposed to the gas release would be incapacitated or unable to escape, protection is needed. The time for which protection is needed should also be defined. This will normally be governed by the time required to shut the plant down or the time needed to control the emergency.

The control building should be located at the edge of the plant, and its siting should take into account both fire/explosion and toxic gas hazards. There should be at least two escape routes, which should be chosen bearing in mind that they may need to be used by partially incapacitated people and by rescue teams wearing heavy breathing apparatus. They should be free from obstructions and well lit.

The construction of the building should be gas-tight. This means, among other things, that windows should be non-opening and that door and window frames should be designed and maintained to minimize entry of gas. There should be no more than two doors, each with an air lock and each gas-tight. The wedging open of these doors should not be tolerated.

The occupants of the control building should be provided with a supply of air sufficient for the time for which protection is required. Generally, it will be necessary to shut off the normal ventilation and the control building will

then lose any overpressure and may become contaminated. Self-contained breathing apparatus should be provided for each occupant.

In some cases, it may be possible to supply air from a source sufficiently far from the control building that the air from it is clean. The air supply should maintain within the building a positive pressure of 0.5–1.0 in. water gauge, which requires 2 to 15 air changes per hour, depending on building size, construction and gas-tightness.

There are various ways in which toxic gas may enter such a building. One is via service trenches and cellars. These should be avoided, but if used should incorporate sealed barriers and should be subject to a permit-to-work system. Another mode of entry is via instrument air lines and appropriate precautions should be taken. Instrument sample lines should not bring toxic process fluids into the control building.

Where available, gas detectors should be used to give warning of a toxic gas escape by activating an alarm in the control room, where there should be means of activating the toxic gas alarm. There should be in the control room an indication of wind direction.

It may be possible to provide protection to the control building using a water spray system. The gas detector signal may be used to activate such a water spray and to shut off the normal ventilation air.

The control building should have a priority communication link, other than the normal telephone system, to the emergency control centre.

Appropriate breathing apparatus or respirators should be provided in the control building to assist the escape of any persons who have to be evacuated in the emergency.

10.20.2 Emergency control centre

Protection of the emergency control centre from a toxic release will normally be in large part by location. It is necessary for the emergency controllers to gain access to the centre at the start of the emergency and it is undesirable that they should have to pass through a toxic gas cloud. Nevertheless, it may need to be designed to afford protection against toxic gas, in which case the points just made in relation to the control building are pertinent.

10.20.3 Refuges

A temporary refuge, or haven, has the quite different function of providing temporary shelter for personnel. The design of such havens is described in the *Vapor Release Mitigation Guidelines* (CCPS, 1988/3). The *Guidelines* distinguish between temporary and permanent havens, or more effective temporary havens. Virtually any weathertight building should suffice as a temporary haven. Personnel in such a haven should be notified to leave the building when the toxic gas cloud has passed. There should be arrangements for them to be rescued, if necessary, by well-equipped teams. It would also seem necessary that there be means whereby the emergency controllers know the location of personnel needing rescue.

For permanent havens, the CCPS *Guidelines* refer to the arrangements for control buildings as described in the CIA *Control Building Guide*. They also give a method of estimating the capacity of a haven. The conditions in the haven should not exceed the following limits: minimum oxygen concentration 18%; maximum carbon dioxide concentration 3%; maximum temperature 33°C; and maximum 100% relative humidity (RH).

10.21 Modular Plants

During the late 1950s and early 1960s, there was introduced a type of plant consisting of a number of modules and mounted on skids which could be transported by road from the fabrication to the operating site. The processes were straightforward and the plants were simple and cheap. From these early skid-mounted plants, there has developed a whole range of modular and barge-mounted plants, some of which are large and complex.

Accounts of modular plants have been given by Glaser, Kramer and Causey (1979), Zambon and Hull (1982), Glaser and Kramer (1983), Hulme and La Trobe-Bateman (1983), Kliewer (1983), Clement (1989), Hesler (1990) and Shelley (1990), and accounts of barge-mounted plants have been given by Birkeland *et al.* (1979), Charpentier (1979), J.L. Howard and Andersen (1979), R.G. Jackson (1979), Jansson *et al.* (1979), Shimpo (1979), Ricci (1981), Bolt and Arzymanow (1982), de Vilder (1982) and Glaser and Kramer (1983). Both types of plant are treated by Mecklenburgh (1985).

10.21.1 Skid-mounted plants

The early skid-mounted plants were typically natural gas processing plants and pipeline compressor stations mounted on skids. The plants had a quite small number of modules of limited dimensions. They were transported by truck from the fabrication works to the operating site. The plants were simple and were equipped to shut-down if an operating problem arose. The plant operator typically lived in a house close by. These plants were designed for a relatively short life and had low capital and running costs. A description of such skid-mounted plants is given by Kliewer (1983).

10.21.2 Modular plants

The late 1970s saw a significant extension of the scale and complexity of modular plants. Such plants were seen as offering benefits where site construction was unusually difficult, particularly on remote sites. Factors favouring modular plants include problems associated with (1) access difficulties, (2) severe weather and (3) the labour force.

Advantages of modular construction are those associated with (1) access for equipment suppliers, (2) work in sheltered conditions and (3) availability of a skilled workforce. Arising from these are (4) easier construction and testing, (5) improved quality assurance and (6) shorter project timescale. Construction of the plant at a dedicated fabrication site minimizes access difficulties for equipment suppliers, and allows the work to be done under cover and by a skilled workforce. Main items of equipment, pipework, supports, instrumentation and cabling can be installed and tested under essentially factory conditions. The project timetable can be shorter, both because work on foundations and on plant construction can proceed in parallel and because construction can be done in more favourable conditions.

Disadvantages of modular construction include those associated with (1) engineering design, (2) modifications, (3) steelwork and (4) transport. Modular construction necessitates high quality and more expensive engineering design. It is relatively unforgiving of modifications, which can therefore be disruptive and expensive. There are additional costs for steelwork but, because steel is relatively cheap, these may be modest. There are additional transport

costs which vary depending on the site and the plant, and which can be considerable.

Modular construction requires its own design approach. It is not effective to design a plant by conventional methods and then divide it into modules. It is necessary to design for a modular layout from the start. It is also necessary to accept that the main features affecting layout have to be frozen earlier than is often the case is normal design.

Plants have been constructed with some 200 modules and with modules stacked as high as 50 m. With regard to module dimensions and weight, in one project described by Kliewer (1983) the maximum module dimensions were set at 6.7 m wide × 4.0 m high × 30.5 m long. The weight limit was 125 ton, though most modules did not exceed 50 ton. Shelley (1990) describes rubber-track crawlers and trailers with up to 360 wheels capable of transporting 3000–4000 ton and cranes with lifting capacity of 5000 ton.

Advocates of modular design typically claim savings on project cost and time. Accounts of cost benefits include those of Kliewer (1983) and Shelley (1990). Broadly, capital costs are less, but design, steelwork and transportation cost more. Shelley quotes construction times shortened by up to 50% and capital cost savings of up to 20%.

Progress in modular construction has been reviewed by Shelley (1990). The image of modular plants has tended to be that of skid-mounted plants and plants shipped to remote locations. Modularization has generally been considered only for remote locations where the weather is hostile or skilled labour unavailable. The author discerns a trend towards increasing use of modular construction for regular projects, arising from its advantages of cutting capital costs and shortening construction times. Another stereotype which is somewhat outdated is that modular plants necessarily involve a cramped layout.

10.21.3 Barge-mounted plants

A particular type of modular plant is that mounted on a barge or other vessel. The development of such plants has received impetus from the need for shipyards to diversify. Features of the operating site which favour the use of a barge-mounted plant include: a seaboard inaccessible from the hinterland; a navigable, if shallow, river; or a delta unsuitable for land traffic.

A plant transported by sea may, in fact, be truly barge mounted or it may be self-floating. In the latter case it is effectively a sea-going object in its own right, must be fully seaworthy and must meet the requirements of the classification societies. The direct costs of transport of a barge-mounted plant may well be modest, but those of providing the stiff framing for, and the measures to counter stresses developed in, a sea voyage can be appreciable. A barge-mounted plant is a sea-going object so that it must be seaworthy and must meet the classification society specifications, which can be expensive.

One solution is to use a vessel designed specifically for the transport of modular plants. The Wijsmuller semi-submersible heavy lift vessel Super Servant, described by de Vilder (1982) is of this type. This is a development from the semi-submersible barges which have been in use for some decades, either unpowered or with auxiliary propulsion only.

The options for installation at the operating site have been discussed by Charpentier (1979), who lists four. One is a barge floating at sea or anchored. This means, in effect, a factory ship with its own propulsion and mooring systems. Another is a barge which floats but is moored along a quay, accessible from the sea on one side and from the land on the other. A third is a barge grounded on a dredged bed in a shelter site, possessing connections similar to those in the previous case but not subject to water movement. The fourth option is a barge grounded on a foundation sill and protected by some form of dike or dam.

The use of prestressed concrete hulls for barge-mounted plants has been described by Birkeland *et al.* (1979). They outline three options for installation at the operating site: a self-floating plant may be permanently floating or permanently grounded; a plant delivered by a barge is off-loaded and floated into position and then permanently grounded.

Reviews of projects on barge-mounted plants include those by Charpentier (1979) and Ricci (1981). Birkeland *et al.* (1979) describe several barge-mounted projects. They include a self-floating LPG refrigeration and storage barge, the *Ardjuna Sakti*, sited near Jakarta and permanently floating. Charpentier (1979) describes a number of projects involving barge-mounted plants. They include a refinery, a natural gas liquefaction plant, an ammonia plant and a methanol plant.

The design of a barge-mounted liquefied natural gas (LNG) liquefaction and storage plant, the marine LNG system (MLS), has been described by J.L. Howard and Andersen (1979); the project was intended for the Pars gas field off Kangan, Iran, but was interrupted by political factors. The authors give details of the process flow diagram, the LNG storage spheres and the fire protection and emergency shut-down systems. The design was done according to the requirements of the International Maritime Consultative Organization (IMCO) gas carrier codes. The installation was of the dredged basin type.

In the 1970s, the conversion of LNG to methanol prior to transport appeared to be a potentially attractive way of transporting energy on long hauls, and studies of barge-mounted plants for such conversion were carried out (R.G. Jackson, 1979). One application envisaged for such units was the exploitation for smaller, shorter life fields.

A somewhat similar motivation underlies the use of barge-mounted plants to process gas from fields for which a pipeline would be uneconomic and at which the gas would therefore be flared (Jansson *et al.*, 1979). These fields may include subsea completions where there is no production platform. The main design described is for an ammonia plant with the platform—a flat, broad barge moored at a single point mooring, but variations include barge-mounted urea, methanol, natural gas liquids (NGL) and LNG plants and beaching of the plant.

Ricci (1981) gives an account of a barge-mounted low density polyethylene (LDPE) plant for Bahia Blanca, Argentina. This plant was transported by the heavy lift semi-submersible described by de Vilder (1982) and referred to above. This author describes in detail the planning of the voyage in respect of the wind and acceleration forces and of the mechanical stresses to which the load would be subjected.

An account of a barge-mounted pulp plant installed in the upper reaches of the Amazon in Brazil using the industrial platform system has been given by Shimpo (1979). The site was one with no roads and accessible only by plane. There were two platforms, one for the pulp plant and one for the power plant. The platforms had to be designed for structural strength whilst being towed and during operation. Platform construction posed various difficulties. It proved impossible to set up a longitudinal

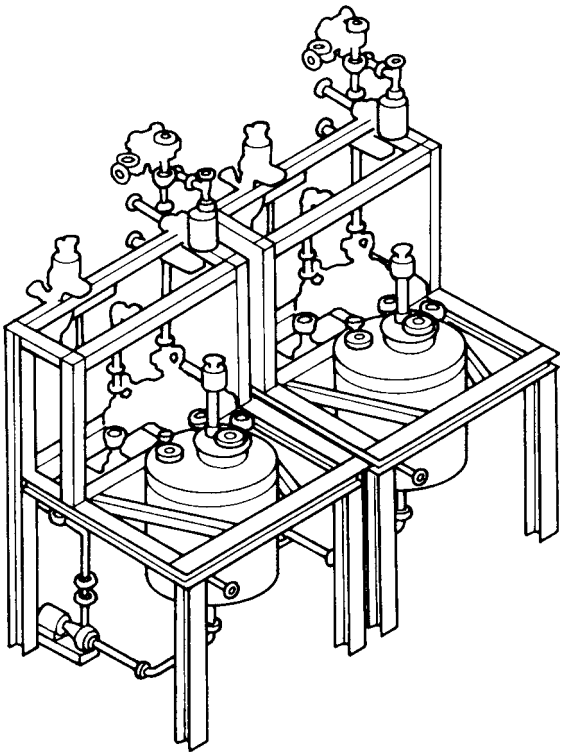

Figure 10.5 *Modular two-unit reactor train (Hester, 1990) (Courtesy of the American Institute of Chemical Engineers*

bulkhead and there were few straight transverse bulkheads. There were many large irregular openings in the main deck, especially close to the side. At the site the design was for the platform to be set on piles. There were problems arising from unbalanced soil strength and uneven live load on the platform. The project yielded much information on motions and stresses during the voyage and at the site.

10.21.4 Modular design

It is possible to adopt a modular approach to the design of plant, even if modular construction is not intended. An account of such modular design is given by Hesler (1990). A modular approach not only saves on design costs but also allows the design to be optimized and defects eliminated and, by offering equipment suppliers repeat runs, reduces equipment costs and procurement times. For some types of plant the normal design consists of replicated modules.

One type of plant for which modular design is often appropriate is a batch reactor system. Such plant generally consists of a number of similar reactor trains. Furthermore, these trains are frequently required to have the flexibility to permit changes in the raw materials used and products made and a modular design is able to accommodate such modifications. Typical units in such plant are reactors, columns, quench tanks, crystallizers, liquid-solid separators, and driers. Figure 10.5 illustrates the two-unit reactor train described by Hesler. Another example given by this author is the ICI FM-21 membrane chlorine cell.

10.21.5 Offshore modules

Another application of modular construction is on offshore oil and gas production platforms. The production deck of such a platform will typically consist of some four modules which are lifted whole onto the platform. The lifting capacity of the floating cranes used is now in fact such that a whole deck can be installed in one lift.

10.22 Notation

Section 10.14

I heat flux (kW/m^2)
t_B duration of fireball (s)

11 Process Design

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11.1 The Design Process

Process design designates the Chemical Engineering development aspects of a process plant. This is augmented by the classical related engineering disciplines: Mechanical, Electrical, Civil along with others, which provide constraints as to the availability and feasibility of industrial equipment, electrical hazards and siting issues covered in Chapter 10. Clearly, issues such as single or multiple trains; equipment topological aspects (layout); industrial availability of machinery; heat exchangers and process towers and reactors; influence and interact with the process design.

The design of a large process plant, or plant modification or extension is a complex activity involving engineers of many disciplines. The design process normally involves engineering organizations and expertise other than the operating company. This aspect is considered in Section 11.2, Conceptual Design, or in the current parlance of the industry front-end engineering.

The project evolves under the influence of: research and development, which define the technical possibilities and constraints; safety, health and environmental studies, which lead to further constraints; economic studies, which indicate the productions costs and sales returns together with their sensitivity to the various factors; and the financial approvals, which allow the project to proceed. The political, social and environmental issues at the location must be recognized. An overall risk of the plant to the community must be developed and agreed with the appropriate local, state and federal authorities before further process design can proceed. This will largely comply with regulations and avoid a Bhopal-type catastrophe. The infrastructure available will dictate whether the design is a self-supporting grassroots or an integrated facility. Of course, the additional constraint of the limited space and congestion affect the design of offshore facilities.

The decisions made in the early stages, particularly concerning the process route, the plant capacity and their locations, are crucial. Thereafter, many options are foreclosed such that further fundamental changes are difficult, if not simply impractical.

From the safety and loss prevention (SLP) viewpoint it is essential to get the process fundamentally right from the start, as illustrated above. The design should be to eliminate hazard rather than devise measures to control it. This aspect is discussed in Section 11.3, Detailed Design, and also in Section 11.6, Inherently Safer Design.

The safety of the plant is determined primarily by the quality of the basic design rather than by the addition of special safety features. It is necessary, however, to incorporate specific systematic safety checks throughout the design process at each level, generally termed hazard identification and assessment studies.

11.1.1 Process risk management strategies

Risk has been defined as a measure of economic loss or human injury in terms of both the incident likelihood and the magnitude of the loss or injury (CCPS, 1989). Thus, any effort to reduce the risk arising from the operation of a chemical processing facility can be directed toward reducing the likelihood of incidents (incident frequency), reducing the magnitude of the loss or injury should an incident occur (incident consequences), or some combination of both. In general, the strategy for reducing risk,

Table 11.1 *Examples of process risk management strategies*

Risk management strategy category	*Example*	*Comments*
1. Inherent	An atmospheric pressure reaction using non-volatile solvents which is incapable of generating any pressure in the event of a runaway reaction	There is no potential for overpressure of the reactor because of the chemistry and physical properties of the materials
2. Passive	A reaction capable of generating 150 psig pressure in case of a runaway, done in a 250 psig reaction	The reactor can contain the runaway reaction. However, 150 psig pressure is generated and the reactor could fail due to a defect, corrosion, physical damage or other cause
3. Active	A reaction capable of generating 150 psig reactor with a 5 psig high pressure interlock to stop reactant feeds and a properly sized 15 psig rupture disc discharging to an effluent treatment system	The interlock could fail to stop the reaction in time, and the rupture disk could be plugged or improperly installed, resulting in reactor failure in case of a runaway reaction. The effluent treatment system could fail to prevent a hazardous release
4. Procedural	The same reactor described in example 3 above, but without the 5 psig high pressure interlock. Instead, the operator is instructed to monitor the reactor pressure and stop the reactant feeds if the pressure exceeds 5 psig	There is a potential for human error, the operator failing to monitor the reactor pressure, or failing to stop the reactant feeds to stop the reactant feeds in time to prevent a runaway reaction

Note: These examples refer only to the categorization of the risk management strategy with respect to the hazard of high pressure due to a runaway reaction.The processes described may involve trade-offs with other risks arising from other hazards. For example, the non-volatile solvent in the first example may be extremely toxic, and the solvent in the remaining examples may be water. Decisions on process design must be based on a thorough evaluation of all the hazards involved.

whether directed toward reducing frequency or consequence of potential accidents, falls into one of the following categories (Table 11.1):

(1) Inherent, or Intrinsic – Eliminating the hazard by using materials and process conditions that are non-hazardous (e.g. substituting water for a flammable solvent).
(2) Passive – Eliminating or minimizing the hazard by process and equipment design features that do not eliminate the hazard, but do reduce either the frequency or consequence of realization of the hazard without the need for any device to function actively (e.g. the use of higher pressure-rated equipment).
(3) Active – Using controls, safety interlocks and emergency shut-down systems to detect potentially hazardous process deviations and take corrective action. These are commonly referred to as engineering controls.
(4) Procedural – Using operating procedures, administrative checks, emergency response and other management approaches to prevent incidents, or to minimize the effects of an incident. These are commonly referred to as administrative controls.

Risk control strategies in the first two categories, inherent and passive, are more reliable and robust because they depend on the physical and chemical properties of the system rather than the successful operation of instrument, devices and procedures. Inherent and passive strategies are not the same and are often confused. A truly inherently safer process will completely eliminate the hazard (Kletz, 1991a).

The design experience and know-how of the organization may be generalized in terms of its knowledge of the characteristics of particular chemicals,unit operations and unit processes and so on. Full use should be made of this information both for process design and for hazard identification.

Accounts of process design are given in *Applied Process Design for Chemical and Petrochemical Plants* (Ludwig, 1964–), *Equipment Design Handbook for Refineries and Chemical Plants* (Evans, 1971), *Applied Chemical Process Design* (Aerstin and Street, 1978), *Introduction to Chemical Process Technology* (van den Berg and Dejong, 1980), *Chemical Process Synthesis and Engineering Design* (Kumar, 1981), *Process Analysis and Design for Chemical Engineers* (Resnick, 1981) *Process Design for Reliable Operation* (Lieberman, 1983), *Introduction to Material and Energy Balances* (Reklaitis, 1983), *Scaleup of Chemical Processes* (Bisio and Kabel, 1985) *Chemical process Computations* (Raman, 1985), *The Art of Chemical Process Design* (Wells and Rose, 1986), *Process Modelling* (Dean, 1987), *Conceptual Design of Chemical Processes* (Douglas, 1988), *Foundations of Computer Aided Process Operations* (Reklaitis and Spriggs, 1988), *Chemical Process Equipment* (Walas, 1990) and *Dimensional Analysis and Scaleup in Chemical Engineering* (Zlokarnik, 1991).

Economic aspects of process design are treated in *A Guide to Chemical Engineering Process Design and Economics* (Ulrich, 1984), *Economic Evaluation of Projects* (D.H. Allen, 1988) and *A Guide to Capital Cost Estimating* (IChemE, 1982a,b).

Case studies of process design include *Process Design Case Studies* (R.Scott and McLeod, 1991) and the Institution of Chemical Engineers (IChemE) model design projects described by Jeffreys (1961), Austin and Jeffreys (1979) and Ray and Johnston (1990).

Treatment of the SLP aspects of process design is given in *Hazard Survey of the Chemical and Allied Industries* (Fowler and Spiegelman, 1968), *Flowsheeting for Safety* (Wells, Seagrave and Whiteway, 1976), *Industrial Hazard and Safety Handbook* (R. King and Magid, 1979), *Safety in Process Plant Design* (Wells, 1980), *Chemical Process Safety* (Crowl and Louvar, 1990), *Safety in the Process Industries* (R. King, 1990), *Safety at Work* (Ridley, 1994) and Austin (1965a, 1982a), Hudson (1965) and Fitt (1976a).

Selected references on chemical reactors, unit processes, unit operations and equipments, extreme operating conditions, utilities, particular chemicals, particular processes and plants, ammonia, urea and ammonium nitrate plants, and liquefied petroleum and natural gases (LPG and LNG) are given in further tables in this chapter.

11.1.2 Design stages

Some important stages of the design of a process plant are:

(1) research and development – pilot plant;
(2) process design;
  (a) selected process flowsheet,
  (b) detailed process design-simulation,
(3) front-end conceptual engineering;
  (a) Process development unit (new design),
(4) Engineering design and equipment specification – selection.

The current execution technique in virtually all organizations is not to have the discrete stages indicated which are designated silos, but to have engineering interaction at the earliest process stages to avoid subsequent pitfalls.

The design of a plant is an interactive and iterative process. Modifications are made as more information becomes available, as constraints or opportunities are recognized, and as the situation changes.

It is necessary to pay close attention to the scheduling and co-ordination of the project, which is a project management function to provide the guidelines required.

11.1.3 Design information

Process design can be properly done and executed only with adequate and correct design data. This should include as a minimum:

(1) the physical and chemical properties of the chemicals;
(2) the reaction characteristics, including mechanism, kinetics and thermal data for all likely reactions;
(3) fire, explosion and toxic hazards;
(4) the effect of trace impurities which may have a major impact on metallurgy.

Particularly relevant for safety and loss prevention are material safety data sheets (MSDSs). These data are legally required and must be available for operating plants.

The data used in the design must be consistent throughout the design team. It is necessary, therefore, to devote some effort to the provision and documentation of these data.

Beside special proprietary data, processes data are available on line from suppliers such as ASPEN.

11.1.4 Design standards and codes

The standards and codes which are to be used in the design should be specified from the start. Standards and codes give design requirements and guidance. They constitute both an aid to the designer and a means of communicating design requirements to other parties, with certain contractual implications. They embody the lessons which industry has learned from past incidents and are therefore a store of experience which the designer should draw on.

Consistency should be maintained both in the initial choice of standards and codes and in their subsequent use. A particular code or set of codes embodies a particular design philosophy. It is not good practice to use an indiscriminate mix of codes or to use a different code for a particular problem simply because its requirements are less onerous. This can cause difficulties not only at the design stage but also later in plant operation and maintenance when confusion may arise as to the design philosophy.

There is often some degree of overlap in the topics covered by different codes. Consideration should be given to areas where codes may conflict or where there may be gaps which are not covered.

An account of standards and codes is given in Appendix 27.

11.1.5 Design experience

It is useful to consider the forms in which process design experience and know-how are available. The information may relate to:

(1) chemical reactors;
(2) unit processes;
(3) unit operations and equipment;
(4) operating conditions;
(5) utilities;
(6) particular chemicals;
(7) particular processes and plants.

Thus, much information is available on: the characteristics of chemical reactors, including reactor protection; unit processes, such as oxidation; unit operations, such as distillation; operating conditions, such as high pressures and low temperature; utilities, such as electricity, steam and nitrogen; on particular chemicals such as ethylene or chlorine; and particular processes and plants, such as air and ammonia plants.

In particular, information is available in the form of national standards and codes of practice, in-house standards, procedures and reports and checklists. This documentation is the principal means whereby experience won at considerable expense of money, effort and sometimes life is made available for design of new plants. This information should be used in design, and in the reviews of the design.

11.1.6 Design communication and documentation

It is essential in the design process that there be effective communication. Much of this communication is done on an individual basis or in design committees. The most important channel of communication, however, is the documentation. Details of this have been given in Chapter 6 and are not repeated here. Of particular importance are the process flow sheet, the process flow diagram and the engineering line diagram. Examples of the two latter are shown in Figures 11.1 and 11.2.

One item of information which is often required for SLP work and which has frequently not been shown on flow diagrams is the inventory of the principal vessels. It is desirable that flow diagrams show the normal and maximum design inventories.

Of particular importance are the process flow diagram, process heat and mass balances, and the engineering flow sheets (piping and instrument diagram, P&ID). Typical examples are shown in Figure 11.1 process flow diagram and Figure 11.2 P&ID.

11.1.7 Design changes

At a critical point in the design, a freeze is instituted to complete the design effectively. Inevitably, changes occur subsequently, usually due to external factors which must be accommodated. A management of change (MOC) procedure is instituted to ensure all aspects of the change are properly reviewed, accredited and authorized, and communicated to all parties involved. This is also required for construction and commissioning activities. The control of plant changes or modifications is considered in Chapter 21.

11.1.8 Overdesign

Overdesign in engineering is often equivalent to the incorporation of an extra factor of safety, but this is by no means always so. In some cases such overdesign can reduce safety. There is an inherent tendency to overdesign in a project as the various individuals in the chain introduce factors of safety. In this context overdesign is taken to cover the purchasing as well as the design decisions. What matters is the item which is finally installed.

This is illustrated by two common items of process equipment, pumps and control valves. If a pump is required which has a certain characteristics relating to flow and pressure and if the pump installed is capable of a higher flow or pressure, this may introduce a hazard insofar as the rest of the plant is not designed for these conditions. Similarly, control valves are almost always oversized. If reliance has been placed on a valve of a certain size to limit flow to a maximum value and a larger valve is provided, a hazardous situation may result.

11.1.9 Design error propagation

It is sometimes appropriate to check the error associated with a design calculation, particularly if this has important safety aspects. If a calculated variable z is a function of two other variables x and y,

$$z = f(x, y) \qquad [11.1.1]$$

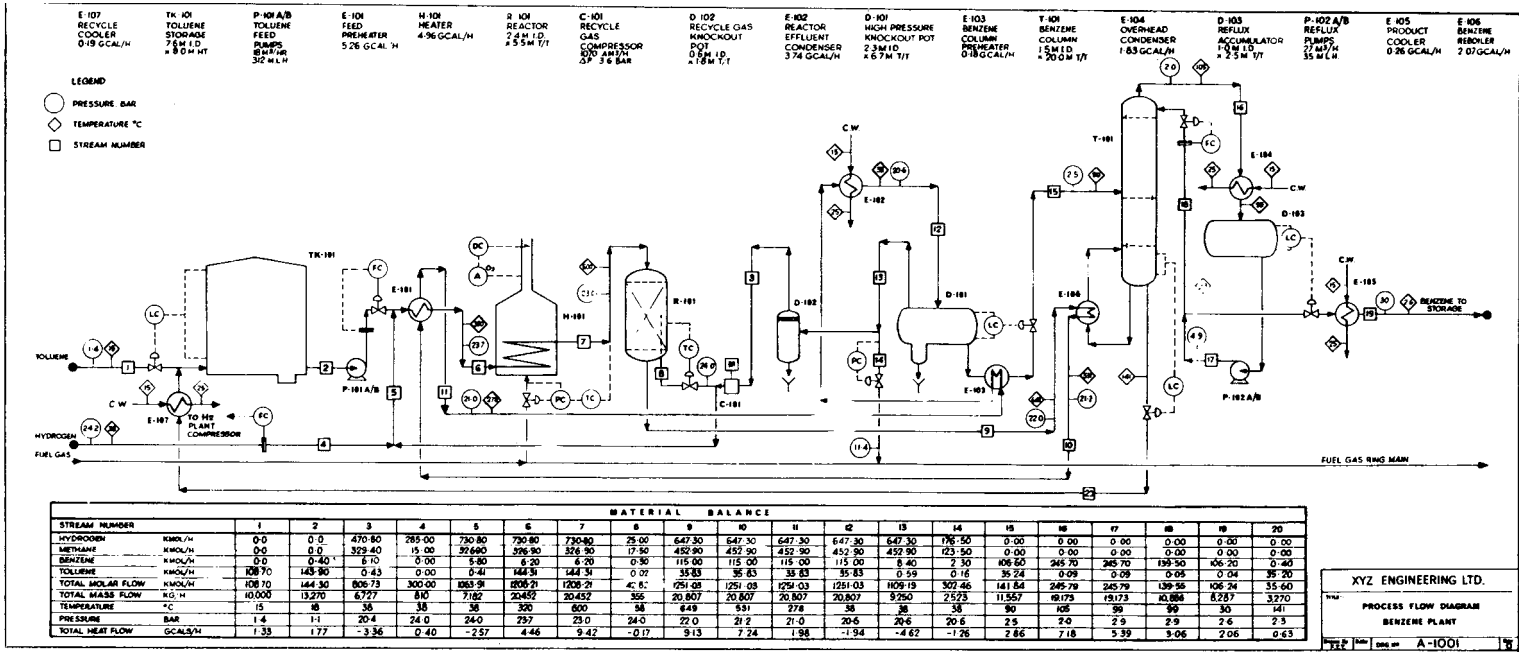
then the calculated value of z will have an error S_z which results from the errors δx and δy in x and y, respectively. There are two errors which are of interest. The maximum error is

$$\delta z = \left|\frac{\partial f}{\partial x}\right| \delta x + \left|\frac{\partial f}{\partial y}\right| \delta y \qquad [11.1.2]$$

A more realistic estimate is the probable error

$$\delta z = \left[\left(\frac{\partial f}{\partial x}\right)^2 \delta x^2 + \left(\frac{\partial f}{\partial y}\right)^2 \delta y^2\right]^{1/2} \qquad [11.1.3]$$

Further information is given in standard texts (e.g. Jenson and Jeffreys, 1963). A discussion of error propagation is given by Park and Himmelblau (1980).

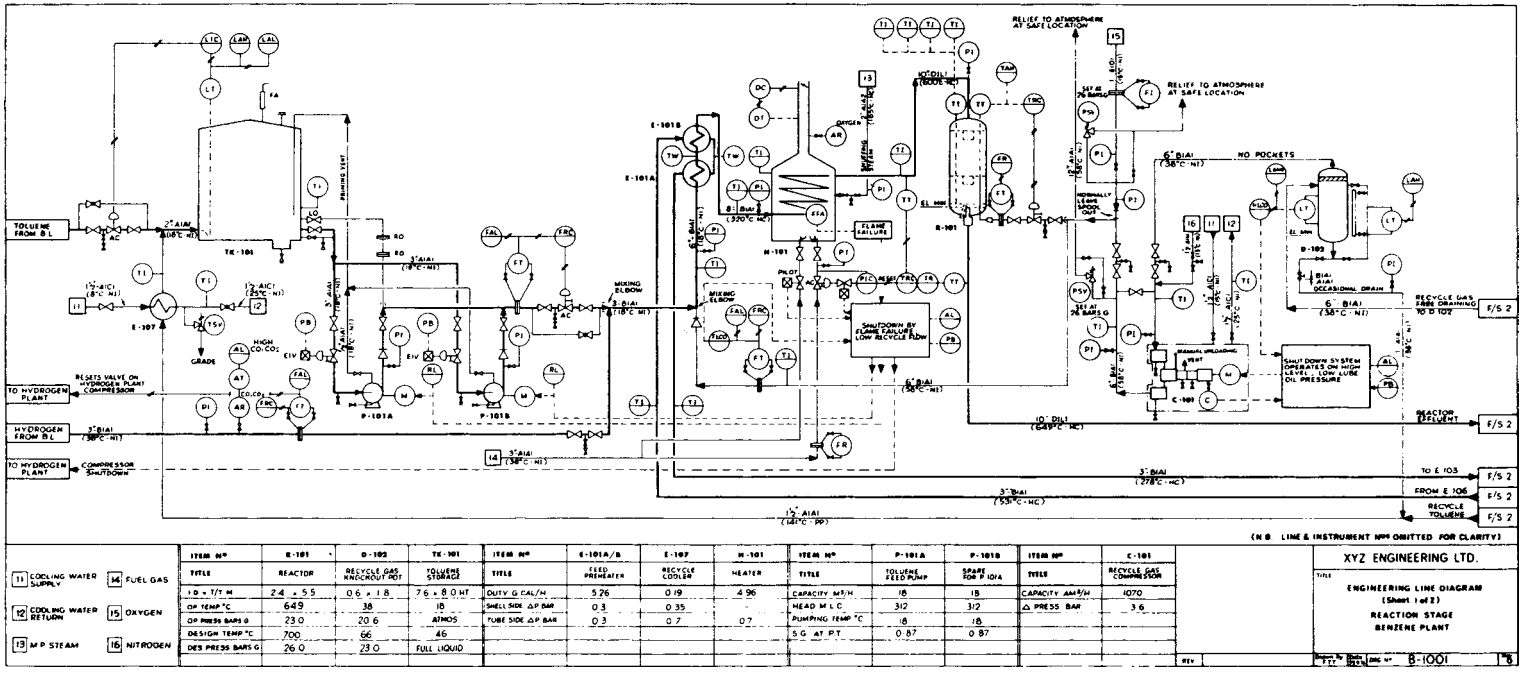


MATERIAL BALANCE

STREAM NUMBER		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
HYDROGEN	KMOL/H	0·0	0·0	470·80	285·00	730·80	730·80	730·80	25·00	647·30	647·30	647·30	647·30	647·30	176·50	0·00	0·00	0·00	0·00	0·00	0·00
METHANE	KMOL/H	0·0	0·0	329·40	15·00	32690	326·90	326·90	17·50	452·90	452·90	452·90	452·90	452·90	123·50	0·00	0·00	0·00	0·00	0·00	0·00
BENZENE	KMOL/H	0·0	0·40	8·10	0·00	5·80	6·20	6·20	0·30	115·00	115·00	115·00	115·00	8·40	2·30	106·60	245·70	245·70	139·50	106·20	0·40
TOLUENE	KMOL/H	108·70	143·90	0·43	0·00	0·41	144·31	144·31	0·02	35·83	35·83	35·83	35·83	0·59	0·16	35·24	0·09	0·09	0·05	0·04	35·20
TOTAL MOLAR FLOW	KMOL/H	108·70	144·30	806·73	300·00	1063·91	1208·21	1208·21	42·82	1251·03	1251·03	1251·03	1251·03	1109·19	302·46	141·84	245·79	245·79	139·55	106·24	35·60
TOTAL MASS FLOW	KG/H	10,000	13,270	6,727	810	7182	20452	20452	355	20,807	20,807	20,807	20,807	9250	2523	11,557	19173	19173	10,886	8287	3270
TEMPERATURE	°C	15	18	35	35	35	320	600	98	649	531	278	38	38	38	90	105	99	99	30	141
PRESSURE	BAR	1·4	1·1	20·4	24·0	24·0	257	23·0	24·0	22·0	21·2	21·0	20·6	20·6	20·6	2·5	2·0	2·9	2·9	2·6	2·3
TOTAL HEAT FLOW	GCAL/H	1·33	1·77	-3·36	0·40	-2·57	4·46	9·42	-0·17	9·13	7·24	1·98	-1·94	-4·62	-1·26	2·86	7·18	5·39	3·06	2·06	0·63

XYZ ENGINEERING LTD.
PROCESS FLOW DIAGRAM
BENZENE PLANT
DRG. NO. A-1001

Figure 11.1 *Process flow diagram of a benzene plant (Wells, Seagrave and Whiteway, 1976) (Courtesy of the Institution of Chemical Engineers)*



ITEM No	E-101	D-102	TK-101	ITEM No	E-101A/B	E-107	H-101	ITEM No	P-101A	P-101B	ITEM No	C-101
TITLE	REACTOR	RECYCLE GAS KNOCKOUT POT	TOLUENE STORAGE	TITLE	FEED PREHEATER	RECYCLE COOLER	HEATER	TITLE	TOLUENE FEED PUMP	SPARE FOR P 101A	TYPE	RECYCLE GAS COMPRESSOR
I.D. - T/T M	2.4 x 5.5	0.6 x 1.8	7.6 x 8.0 HT	DUTY G CAL/H	5.26	0.19	4.96	CAPACITY M³/H	18	18	CAPACITY AM³/H	1070
OP TEMP °C	649	38	18	SHELL SIDE ΔP BAR	0.3	0.35	-	HEAD M L C	312	312	Δ PRESS BAR	3.6
OP PRESS BARS G	23.0	20.6	ATMOS	TUBE SIDE ΔP BAR	0.3	0.7	0.7	PUMPING TEMP °C	18	18		
DESIGN TEMP °C	700	66	46					S.G. AT P.T.	0.87	0.87		
DES PRESS BARS G	26.0	23.0	FULL LIQUID									

11 COOLING WATER SUPPLY · 12 COOLING WATER RETURN · 13 M.P. STEAM · 14 FUEL GAS · 15 OXYGEN · 16 NITROGEN

Figure 11.2 *continued*

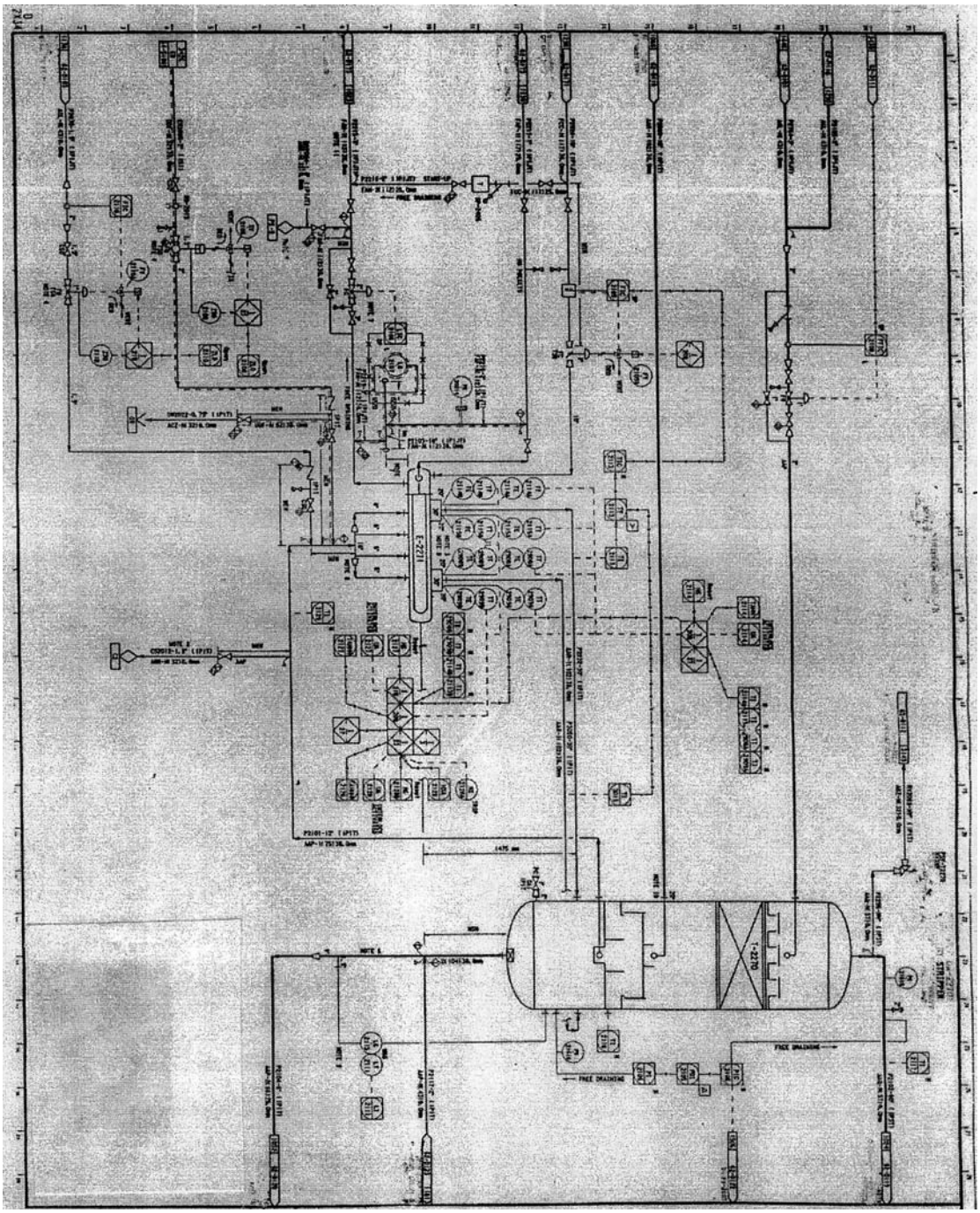


Figure 11.2 *Part of engineering line diagram of a benzene plant (Wells, Seagrave and Whiteway, 1976) (Courtesy of the Institution of Chemical Engineers)*

11.1.10 Computer-aided design

Modern process design involves considerable use of computer-aided design (CAD) techniques, particularly for flowsheeting, equipment design, plant layout, piping and instrument diagrams. Other applications continue to be developed. In particular, extensions of computer design are developing in the area of information flow in plants, leading to automatic hazard identification, fault tree analysis and reliability assessment.

In the design context, computer systems constitute a powerful tool not only for design but also for information storage and retrieval, and thus for communication. Here their effectiveness depends on the database. The design of databases which can be used by all members of the team and which can be quickly but securely updated is another area of development.

A fuller treatment of CAD is given in Chapter 29 and treatment of more advanced CAD developments is given in Chapter 30.

11.2 Conceptual – Front End Design

At the conceptual design stage the process concept is developed, its implications are explored and potential problems are identified. Design in general and conceptual design in particular is generally regarded as an art. Much work is going on, however, to put it on a more systematic basis. Early work is described in *Strategy of Process Design* (Rudd and Watson, 1968). A systematic approach is stated in *The Conceptual Design of Chemical Processes* (J.M. Douglas, 1988). A further discussion of fundamental developments is given in Chapter 30.

In most cases, the process is an established one, so that the conceptual design stage may be quite short. The nature of this stage is best appreciated, however, by considering the conceptual design of a new process. Elements of the process and plant considered in conceptual design are:

(1) process materials;
(2) chemical reaction;
(3) overall process;
(4) effluents;
(5) storage;
(6) transport;
(7) utilities;
(8) siting and layout.

The topics addressed in the conceptual design are principally:

(9) process design;
(10) mechanical design;
(11) pressure relief, blow down, venting, disposal and drains;
(12) control and instrumentation;
(13) plant construction and commissioning;
(14) plant operation;
(15) plant maintenance;
(16) health and safety;
(17) environment;
(18) costing.

The plant turn-down capability must be defined and the potential problems for each piece of equipment identified.

The philosophy underlying the conceptual design should be that of inherently safer design, which is applicable to virtually all aspects. Likewise, in regard to the environment, there should be a philosophy of inherently cleaner design.

The process materials include the raw materials, or feedstocks, the intermediates, and the products and also catalysts, additives and so on. Data are assembled on the physical and chemical properties, on the flammability and the health and toxicity, including material safety data sheets, and any special hazards of, or processing problems associated with, the materials. The composition of the raw materials is considered, including impurities which they may contain. The main chemical reaction of the process is reviewed with several aims in view. These are to ensure that the information available is adequate and that the reaction is sufficiently well understood; to identify the problems and hazards associated with the reaction; to define the reaction sequence and conditions; to examine the effect of the reaction stage on the later processing stages; to explore the possibility of alternatives and to determine the basis of safety of the reaction.

Processes which are likely to be particularly hazardous with respect to the reaction include those involving: highly reactive substances, such as those with a triple carbon bond; a high exotherm; unstable substances; thermally sensitive substances; substances sensitive to impurities, such as air, water, rust or oil and high pressure and/or high temperature.

The other stages of the process are reviewed in a similar way. Here the aims are: to ensure that there is sufficient design information available; to identify the problems and hazards associated with particular process conditions, unit operations and equipments; to define the operating conditions of the equipment; to explore alternatives and to determine the basis of safety of the equipment.

Some features of process conditions which may point to problems or hazards include: operation close to a phase change (boiling, condensation, freezing); operating conditions which give on release a flashing liquid and extreme requirements for exclusion of air or water, for leak tightness or for cleanliness. Corresponding features for equipment include: use of novel equipment; requirement for special materials of construction; pumping of difficult fluids; and unusual pressure relief requirements.

The gaseous and liquid effluents and solid wastes generated by the process are reviewed with a view to: reducing or eliminating them; rendering them less noxious and more easy to dispose of; to explore process alternatives which may be beneficial in this regard; and to decide on their handling and disposal.

A review is made of the requirements for storage of raw materials, intermediates and products. Storage is always a large contributor to costs and often to the hazards of the installation. Here the aims are: to define an operating philosophy for the plant in respect of storage and to match the storage provided to this; to determine the type of storage to be used for each material and the conditions under which it is to be stored and to decide in outline the siting and layout of the storage. The thrust should be to eliminate storage by the use of a 'just-in-time' approach.

The methods of transport of the raw materials and products are reviewed in order: to define material flows for delivery and shipping which match the process and storage requirements; to explore the implications of the different

modes of transport available; to select the mix of transport modes which best meets the governing factors; and to decide in outline the siting and layout of terminals and pipelines. Factors which need to be taken into account include the volume of materials transported, the hazards of these materials and of the modes of transport, the probable life and growth of the transport requirement, the effects of traffic on the environment outside the site, and the traffic flows and handling within the site. The review of storage and transport generally involves interactions particularly between these two but also with the process.

The utilities for the process are reviewed in order: to define the requirements not simply in terms of the nominal quantities but also of the quality and dependability of the supply; to identify any problems and hazards, including implications for existing plants; to explore alternatives; to determine the method of supply for each utility and to decide in outline on siting and layout. On the basis of the foregoing information, decisions may then be made concerning the siting and layout. An account has been given in Chapter 10 of the principles applicable at the conceptual design stage.

In the foregoing the conceptual design has been treated in terms of the process and the plant. In the following it is considered essentially in relation to the design disciplines. The first of these is process design. Some account of this has already been given above. In essence, process design at this stage involves consideration of the process and plant from a number of different viewpoints: the process flow sheet and process conditions; the unit processes and the unit operations and equipments. Two of the principal aims at this stage should be the minimization of hazards by inherently safer design and the minimization of effluents by inherently cleaner design. Regard should also be given to the location where the plant is to be built. Features such as the nature of the available workforce or the access for transport of plant equipment may be relevant. In some cases such factors may point to a more robust design.

The reliability and availability aspects of the plant need to be given some thought at this stage. Different philosophies may be adopted. Options are to accept loss of a function for a period or to minimize its downtime by use of a single high reliability unit or to use several units, with parallel redundancy or stand-by configurations. For some types of plant a single-stream philosophy is the norm. Even with such plants, however, there are certain types of units, such as furnaces, which are commonly multiple and others for which stand-by configurations are widely used.

The process designer is rarely a completely free agent. In most cases, the process in view is an established one, but even where this is not the case there tend to be numerous constraints. There is commonly within the company itself a preference for established technology and an aversion to innovation and the risk perceived to be associated with it. Generally, there are requirements imposed by outside parties. A licensor of a process usually imposes certain requirements which are a condition of the guarantees provided. Likewise, an equipment vendor generally makes his guarantees conditional on requirements such as use of certain ancillary equipment or of alarm and trip instrumentation. An insurer often has preferred arrangements for fire protection. Acceptance of various constraints may be a condition for raising the necessary finance.

Mechanical design at this stage is fairly limited, but consideration is given to materials of construction and to the principal vessels and other items of equipment.

The arrangements for pressure relief, blowdown and venting, for relief and vent disposal, and for drains are also addressed at this stage. These generally have a number of significant implications which it pays to explore at the conceptual stage, because changes later in the design tend to be either disruptive and costly or simply not possible. Thus, a decision to contain rather than to relieve a high pressure may entail a stronger vessel, but such vessels have to be ordered early. A decision to dispose of a relief flow by venting or flaring may require a sterile area which needs to be incorporated early in the layout.

Control and instrument system design is concerned at this stage with the philosophy in respect of allocation of function between the human operator and automatic systems and of the means of providing the latter. The process may be reviewed to assess unsteady-state features, including the dynamics of continuous processes, the sequential operation of batch processes, and start-up and shut-down, and to identify any particular control and instrument problems, including difficult measurements.

The conceptual design stage also covers consideration of the construction and commissioning, operation and maintenance of the plant. Construction creates requirements for space on site, for additional traffic and for lifting equipment, and may affect existing plants. Commissioning also may effect existing plants as the new plant is tied in and manned. The operation of the plant too has implications for other linked plants and for storage requirements.

The start-up and shut-down of the plant are considered at the conceptual design stage. Start-up involves taking the plant through a series of discrete stages. In general, some of these stages can be held indefinitely, whilst others are essentially transient, with no choice but to proceed to the next stage or revert to an earlier one. These stages need to be defined and holding states identified. Likewise, normal shut-down may be effected in a series of discrete stages and these need to be defined. It is also prudent to identify holding states, or fall-back positions, short of shut-down, to which the operator can move if abnormal conditions develop, thus taking pressure off him and making the plant more friendly. Definition of emergency shut-down is necessary since it is liable to involve abnormally high flows which have to be catered for.

The plant needs to be reviewed in respect of health, safety and environmental factors. Each of these aspects needs to be assessed using a formal method to identify the problems. Health factors may affect features such as the degree of leak-tightness required, the use of buildings and the need for particular operating practices.

The factors related to safety are discussed throughout this text and are not rehearsed here, but one particular aspect merits mention at this point. This is the major hazard potential of the plant, which needs to be addressed at the conceptual design stage. This evaluation is necessary because the information gained has a bearing on many fundamental aspects of the design. Methods of hazard identification and assessment appropriate to the conceptual design stage have been described in Chapters 8 and 9. Relevant techniques include the various preliminary hazard study and hazard ranking methods. The formal requirement for the use of such methods as part of the management system has been discussed in Chapter 6.

The approach to environmental aspects is essentially similar, with a formal requirement for the assessment of the major environmental impact potential using specified methods. There are now regulatory requirements for a safety case for major hazard installations and for an environmental impact statement for certain developments, as described in Chapters 3 and 4.

The conceptual design includes, as part of an overall economic assessment, an estimate of the costs of the various elements described.

11.3 Detailed Engineering

The detailed design stage involves the detailed process and mechanical design together with detailed design from a large number of supporting disciplines. The treatment given here is confined to a broad outline, with particular reference to features bearing on SLP.

Elements of the detailed design of the process and plant include:

(1) process design;
(2) mechanical design;
(3) storage;
(4) transport;
(5) utilities;
(6) layout;
(7) pressure relief, venting and disposal;
(8) control and instrumentation;
(9) fire protection;
(10) explosion protection;
(11) toxic emission protection;
(12) personnel protection;
(13) plant failures;
(14) plant operation;
(15) plant maintenance;
(16) plant reliability, availability and maintainability;
(17) equipment specification, selection and procurement;
(18) health and safety;
(19) environment.

Central to the process design is the chemical reactor. The design should minimize the probability of a hazardous excursion and provide means for dealing with one should it occur.

The process design should take full account of the experience available, both within the company and elsewhere, in respect of the unit processes, the unit operations and equipments, the operating conditions, the utilities, the particular chemicals and the particular processes and plants, as described in Sections 11.7–11.12, respectively.

The process design sets the operating conditions throughout the process for normal operation and defines the envelope of conditions within which the process can operate safely. This information governs the mechanical design. Consideration should be given in the process design to the various operational deviations which may occur and to the impurities which may be present, as described in Sections 11.13 and 11.14, respectively.

In the mechanical design, the materials of construction need to be compatible with the process materials not only at flow sheet conditions, but within the whole envelope of operating conditions, and compatible also with each other. Attention needs to be paid to impurities which may cause greatly increased corrosion. Consideration has to be given also to erosion. Major piping vessel codes have been rewritten and emphasis placed on low temperature design to avoid catastrophic low temperature material failure.

The design should ensure effective containment of the process fluids within the pressure system of vessels, pipework and rotating machinery. Piping design accounts for 50% of the reported loss of containment incidents. Detailed attention needs to be given to pipework, pipework joints and pipework supports, and to the numerous features which can cause damage, including vibration, thermal expansion and contraction, shut-in fluids, water hammer and external events. Likewise, weak points on rotating machinery such as pump seals require consideration.

In addition to avoidance of loss of containment, it is also necessary to design to minimize much smaller but continuous leaks, known as fugitive emissions. These are considered in Chapter 15.

There often arise situations where there is a trade-off to be made between flexibility and complexity. It may be possible to design manifolds which allow a more flexible use of certain items of equipment but at the price of a considerable increase in complexity of the pipework. Often complexity may be too high a price to pay for the additional flexibility. The mechanical design of the plant is dealt with in Chapter 12.

Features of the design of storage are the choice between pressure and refrigerated storage for liquefied gases, the specification of the design pressure and temperature, the venting and the operating and fire relief arrangements, the fire protection, the bunding or drain-off arrangements, and other aspects of storage layout.

For the loading and unloading terminals for the transport of raw materials and products, features are the fluid transfer arrangements, the fire protection, the emergency isolation, the control of ignition sources, including precautions against static electricity and hazardous area classification, and other aspects of terminal layout. Non-return or check valves must always be used at any connection between a utility and the process, often removable isolation spools are also provided.

Location of vent stacks, furnaces and boilers should take into account the prevailing wind. Seismic design is particularly relevant in storage tank areas.

Plant layout is considered in Chapter 10. Features which merit mention here are: the provision of separation to minimize both ignition of flammable leaks and the effects of fire and explosion, and hence domino effects; the control of ignition sources through hazardous area classification; the provision of a suitable drainage system; and the labelling of equipment to ensure positive identification in plant operation and maintenance; as well as the aspects of the layout of storage and terminals already mentioned.

The arrangements for venting, pressure relief and blowdown are a significant feature and have a pervasive influence on the overall design. It is normally necessary to cater: for venting from the process, either continuously or periodically; for pressure relief for operational conditions; and for pressure relief for fire conditions. Features are: the relief scenarios; the location, setting and capacity of relief devices; the selection of these devices; the relief collection system; the choice between relief to atmosphere or to a disposal system; and the selection of the disposal system.

It is also necessary to cater for the relief and blowdown which occurs during emergency shut-down. Venting and pressure relief are treated in Chapters 12 and 15.

Aspects of the control and instrumentation system which are particularly relevant here are the provision of: protective systems in the form of trips and interlocks; a fire and gas detection system; and an emergency shut-down system. Control and instrumentation are considered in Chapter 13.

The fire protection system will generally rely on a combination of passive features such as layout and fire insulation and active ones such as fire and gas detection, emergency blowdown, and fire fighting and equipment cooling systems using water spray, foam and other measures. Fire and fire protection are discussed in Chapter 16; layout aspects are treated in Chapter 10.

Protection may also be required against explosion of flammable vapours or dusts within the plant or inside buildings. Explosions and explosion protection are considered in Chapter 17; layout aspects are treated in Chapter 10.

If the substances handled are particularly toxic, it may well be necessary to design for an enhanced degree of protection against them. The first line of defence is a more leak-tight plant. Dilution and removal of any leaks which occur is assisted if the plant is located in the open, but if it is in a building ventilation may be necessary. Toxic releases and occupational health are dealt with in Chapters 18 and 25; fugitive emissions are considered in Chapter 15.

Personnel protection should not be neglected. Aspects include: access to equipment, particularly hand valves; layout to minimize contact with corrosive substances; guarding of moving machinery; insulation and other measures to prevent contact with hot surfaces; and safeguards to prevent injury due to the operation of fire extinguishing systems. Chapters 10, 16 and 25 in particular deal with such topics.

The design should cater for the requirements of plant operation, discussed in Chapter 20. The requirement to isolate items of equipment or sections of the plant should be studied and features such as high frequency of isolation or need for positive isolation identified and, where appropriate, measures taken or facilities provided. Thus flexibility may be built into the pipework to assist the insertion of slip plates, or isolation facilities, such as a spectacle plate or double block and bleed valves, may be provided.

The requirements for plant start-up, normal shut-down and emergency shut-down should be studied and facilities provided as necessary.

Facilities need to be available to dispose of any material which is off specification, contaminated, or otherwise unsatisfactory, which may be produced in the course of plant operation, whether in the plant itself or in storage. Inspection is practised on a range of plant equipment and using a variety of techniques, and for some of these it may be necessary to provide facilities, even if this amounts to no more than suitable access. Likewise, facilities may be required for various types of test on equipment. Plant inspection and testing are considered in Chapter 19.

For plant maintenance reference has already been made to isolation arrangements. Maintenance often involves emptying the plant of fluids and suitable vents and drains need to be provided for this purpose. It may also be necessary to clean the inside of the plant, and this too may require particular facilities. Plant maintenance is discussed in Chapter 21. Plant lock-out tag procedures must be in place to meet legislative requirements for the Occupational Safety and Health Laws.

The failures that may occur on the plant should be considered. The items of plant equipment should be identified which are particularly vulnerable to frequent failure and/or failure of which could have serious consequences. For plant systems failures, 'Hazop', 'what if', or check list techniques should be used. A technique particularly suitable for investigation of potential equipment failures is failure modes and effects analysis (FMEA).

Consideration should be given to hazardous passages of fluid through isolation, which include leaks through valves which are not leak-tight and opening of bypasses around equipment.

The effect on the plant of failure of utilities such as electrical power or cooling water should be reviewed. The need for emergency back-up supplies should be considered, as described earlier.

The effect of abnormal conditions and of start-up, normal shut-down and emergency shut-down on plant under design on other linked plants should receive attention. Links exist by virtue of the transfer of materials between the plants or common use of a utility. Likewise, the effect on the plant in question of such conditions on other plants should be considered.

For critical functions the reliability and availability required should be specified. Steps can then be taken to ensure that the specification is met by the elimination of causes of failure, the use of single, high reliability items, or the use of suitable configurations of multiple items, such as installed spares. This approach should also be applied to the utilities, including the emergency back-up supplies.

The specification, selection and procurement of equipment should receive its share of attention. The equipment specification should match the design of the plant into which it is to be incorporated. The initial specification may be defective in neglecting some important aspect. Alternatively, it may be unnecessarily restrictive. It may well pay to discuss the specification with other parties to the design and with the prospective manufacturer. In selecting the equipment, the experience of the manufacturer in supplying equipment for similar duties should be taken into account. It should be borne in mind, however, that whilst a manufacturer supplies a range of equipments which are suitable for a generic duty, he cannot be expected to know about special features or requirements which may exist on the plant in question.

The detailed design needs to be subjected to review in respect of health, safety and environment. The design assessments made of these and other aspects are now considered.

11.4 Design Assessments

As the design progresses, it is subject to various assessments, which draw on a number of specific techniques. Those considered here are: (1) critical examination, (2) value engineering assessment, (3) energy efficiency assessment, (4) reliability and availability assessment, (5) hazard identification and assessment, (6) occupational health assessment and (7) environmental assessment.

11.4.1 Critical examination

Critical examination, which is a structured method for asking basic questions about the plant, is an effective method for fundamental review, exposing assumptions and generating alternative options. There are in effect a family of techniques which have grown out of critical examination. One is hazop, which is directed to hazard identification, as described in Chapter 8. Another is value engineering, which is now considered; construction management; inspection and documentation.

Value engineering utilizes the techniques of reliability engineering and hazard identification such as Pareto analysis and FMEA. A large value engineering study may take approximately 300–400 h, a medium one 100–300 h and a small one 20–100 h. Others include value improving practices (VIPs), which are now considered.

11.4.2 Value improving practices

VIPs are formal structured practices applied to the front-end stages of any project to improve profitability above that attained through good engineering and project management practices. VIPs are also intended to challenge existing project and design premises to ensure the most robust and profitable facility results. Often, design deficiencies are revealed in these workshops and better alternates identified. Well-recognized VIPs include:

(1) classes of facility quality;
(2) technology selection;
(3) process simplification;
(4) constructability;
(5) customization of standards and specifications;
(6) predictive maintenance;
(7) process reliability simulation;
(8) value engineering;
(9) design to capacity;
(10) energy optimization;
(11) waste minimization;
(12) Three-dimensioanl-CAD.

All VIPs include key components that ensure that the design will result in a safe and predictably operable facility. Moreover, the practices all focus on identifying safe, technically viable and economically attractive improvements. To accomplish this, improvements are identified, analysed and recommended by multidiscipline expert teams composed project team members and experts from outside the project team. Experience has proven that including subject matter experts from the operating company involved, the engineering contractor and key technology licensors produce the best overall results. Experince has also shown that three of the VIPs are the most rigorous and consistently produce greater value improvements. They are the process simplification VIP, the constructability VIP, and the value engineering VIP.

11.4.3 The value methodology

The process simplification VIP and the value engineering VIP require the use of the value methodology. This methodology has been used extensively throughout industry since the 1940s and is supported by the Society of American Value Engineers (SAVE) International (see SAVE at http://www.value-eng.org). This methodology is now used worldwide and is an integral part of many major project plans in industry and government today.

The value methodology follows an established set of procedures that include: (1) pre-study planning and information gathering, (2) information analysis, (3) function identification and analysis, (4) identification of creative alternatives for key functions via brainstorming, (5) evaluation of selected alternatives, (6) development of selected alternatives to estimate costs, benefits, risks and other impacts to the project, (7) recommendation of the best alternatives, (8) implementation or approved recommendations by the project team and (9) post-study follow-up.

The value methodology differs from simple brainstorming session and simple cost-cutting exercises by emphasizing function analysis based on health, safety and environmental (HSE) requirements, required construction, operations and maintenance needs, project and market schedule constraints, all expected facility uses and operating conditions, and consideration of life-cycle costs and not just installed costs.

11.4.4 Function analysis

A function is the intent or purpose that the equipment, product or process is expected to perform best described using an active verb and a measurable noun. In the function analysis phase, each function is depicted in graphical intuitive-logic format known as a function analysis system technique (FAST) diagram. For example, one of a distillation column's functions could be to 'separate volatile compounds'. Another function might be 'separate final product.' Functions are obtained by confirming what the process system or equipment component must do or how it must perform under steady-state and non-steady-state conditions.

Once the functions of the design and project are identified in a collaborative team environment, alternatives for each function are sought in an open creative environment via various brainstorming techniques. These alternatives are then evaluated by the team. If they are found to offer higher overall value than the current design, they are recommended for further engineering analysis. If the analysis confirms that the life-cycle benefits outweigh the risks, then the change becomes a permanent part of the design or facility.

11.4.5 The process simplification VIP

The process simplification VIP consistently yields the greatest value improvements of the VIPs. It is a formal, rigorous process to search for opportunities to eliminate or combine process and utility system steps or equipment ultimately resulting in the reduction of investment and operating costs. The focus is the reduction of installed costs and critical path schedule while balancing these value improvements with expected facility operability, flexibility and overall life-cycle costs. The so-called value improvements that compromise safe operations or required environmental performance are not accepted or recommended from these formal studies. Critical analysis of each recommended improvement is required by the project team to verify that the risks associated with the recommended change are well understood and manageable.

Process simplification is executed in a formal workshop with an experienced facilitator. It insures that low- or zero-value functions or equipment included in the project scope are challenged to be the highest value possible for the project. Removal of these low- or zero-value functions from

the project scope, if possible, will most likely yield significant economic improvements to the overall project.

Process simplification results in reduced capital costs (CAPEX), improved critical-path schedule, reduced process inventory, increased yields, reduced operating and maintenance costs (OPEX), increased productivity, incremental capacity gains, reduced utility and support systems requirements and reduced waste generations. It also provides a means for integrating overall plant wide systems when applied at the block level in addition to the unit level.

11.4.6 The constructability VIP

The constructability VIP is the facilitated systematic implementation of the latest engineering, procurement and construction concepts and lessons learned consistent with the facility's operations and maintenance requirements to enhance construction safety, scope, cost, schedule and quality. This VIP involves planning, design, procurement, fabrication and installation to achieve the best overall project safety record, lowest installed costs and the shortest reasonable schedule. Constructability helps account for construction options and requirements during design, thus reducing re-work and delay in the construction and start-up schedules.

11.5 Licensors, Vendors and Contractors

The description of the design process which has just been given is based essentially on that which takes place in an operating company which is designing its own plant. The ultimate responsibility for the safe design and operation of plant lies with the operating company and the owner. It should take the appropriate steps to ensure that the processes designed and the equipment supplied by the other parties are safe.

Some design responsibility resides, however, with other parties. These may be (1) licensor, (2) vendor and (3) contractor. A treatment of licensing is given in *Licensing Technology and Patents* (V. Parker, 1991). Contractual arrangements are the subject of the series *Model Form of Conditions of Contract for Process Plants* in three volumes – (1) subcontracts, (2) lump sum contract and (3) reimbursable contracts – by the IChemE (1992a–c) (the 'Yellow Book', 'Red Book' and 'Green Book', respectively) with a guide by D. Wright (1993) (the 'Purple Book').

If the process has been bought under licence, then the licensor has some design responsibility. The extent of this depends on how much information the licensor releases as a result of the licence agreement. Normally the licensor is responsible for the basic process flowsheet, but he may also specify some detailed process design and safety features. It is important to ensure that the division of responsibilities is specified in the licence and that adequate information and documentation are made available.

There is a responsibility on the vendor to supply equipment which is safe. The equipment should conform to specified standards and codes and it should have adequate documentation such as fabrication records or operating instructions. The purchaser is responsible for specifying standards and codes to be used, for ensuring that the equipment delivered is that specified and for seeing that it is used as intended. If changes are required to a licensed process or to equipment, consideration should be given as to whether these constitute modifications on which consultation is required.

The responsibilities of the contractor depend on whether he is responsible for the whole process and engineering design on a turnkey basis or whether he is acting as an extension of the client's own organization and is thus undertaking detailed engineering only. In the first case the responsibility of the contractor is obvious, but even in the second he retains a residual responsibility. Again it is important for the contract to state clearly the division of responsibility. If the design responsibility lies primarily with the contractor, he should subject the design to safety checks using methods of hazard identification and assessment, as already described.

It may happen in some cases that the client proposes a feature which the contractor considers unsafe. If agreement cannot be reached, the contractor should not undertake this feature. Another point of difficulty can arise if the client wishes to make a modification. The contractor should make all reasonable checks that the modification does not introduce a hazard.

11.6 Inherently Safer Design

The best way of dealing with a hazard is to remove it completely. The provision of means to control a hazard is very much the second best solution. This has been succinctly stated by Trevor Kletz as 'What you don't have, can't leak'. This, of course, immediately eliminates fire and explosive hazards. A corollary to this is the importance of limiting inventory of hazardous materials, which is one of the lessons learned in the Flixborough disaster. This principle has been incorporated in the systematic application of inherent safety.

The terminology 'inherently safer design' is 'intrinsically safer design' which is associated with electrical power and control issues. The comparative term safer is used since no operating plant is absolutely or totally 'safe'.

11.6.1 Limitation of inventory

One of the principal ways in which a process may be made inherently safer is to limit the inventory of hazardous material. The scale of the Flixborough disaster was due to the fact that the holdup of flammable liquid at high pressure and temperature in the reactors was large. The inventory in the five reactors and one after-reactor operating at the time of the explosions was about 120 te. The *Flixborough Report* recommended that consideration be given to reducing the inventories on process plants.

It is a normal objective in design to minimize the volume of process vessels, as this saves on the cost both of the vessels themselves and of the supporting structures. But the reduction of holdup, though recognized as a generally desirable aim from the safety viewpoint, had not been particularly emphasized as an explicit aim in safe design.

This situation has been changing, largely as a result of Flixborough. The *Second Report of the ACMH* (Harvey, 1979b) states that limitation of inventory should be a specific design objective. The philosophy of limitation of inventory has been memorably captured by the motto of Kletz (1978c): 'What you don't have, can't leak'. It is better to have only a small inventory of hazardous material than a large one which can be rendered relatively safe only by highly engineered safety systems. In other words, it is better to keep a lamb than a caged lion.

Process inventories have been increasing proportionally to plant capacities based on fixed holdup time rules.

This has usually been based on pneumatic and direct controlled instrumentation with limited response times. Currently with electronic instrumentation, smart control valves and transmitters, DCS- and PC-integrated systems these rules no longer apply. This results in adequate controllability with much smaller inventories.

The advent of very large process plants has resulted in massive overhead distillation accumulators which require isolation safety systems as well. In many cases, the accumulators can be eliminated by providing judiciously reduced inventory in the wells of the overhead condensers. This principle has been utilized on a number of recent plant designs.

11.6.2 Some basic principles

Some basic principles of inherently safer design Kletz (1984a–m, 1991b) are:

(1) intensification;
(2) substitution;
(3) attenuation;
(4) simplicity;
(5) operability;
(6) fail-safe design;
(7) second chance design.

A plant which embodies these principles is described by Kletz (1989c, 1990f) as a 'friendly plant'. Some features of friendly plants are given in Table 11.2.

These basic principles have been distilled down to the following systemized approaches (CCPS, 1996 'Gold Book'):

(1) minimize;
(2) substitute;
(3) moderate;
(4) simplify.

Approaches to the design of inherently safer processes and plants have been grouped into four major strategies by IChemE and IPSG (1995) and Kletz (1984a–m, 1991b); and CCPS (1996 'Gold Book' 1993a).

11.6.3 Intensification

A principal route to limitation of inventory is intensification of the process. This means carrying out the reaction or unit operation in question in a smaller volume. Process intensification is applicable to a wide range of chemical engineering operations, including reactors, mass transfer operations such as distillation and gas absorption, and to heat exchange, as described below.

11.6.4 Substitution

Another principle of wide applicability is that of substitution, in which a hazardous feature is replaced by a less hazardous one. Applications described below include substitution in the main process reaction and in heat transfer media.

11.6.5 Attenuation

A third principle, that of attenuation, involves the use of less hazardous process conditions. Examples of its application are given below. What constitutes a less hazardous process condition, however, is not always obvious. The problem is a multidimensional one. This aspect is described below in the context of the hazards of compromise.

11.6.6 Selection of process

The starting point for inherently safer design is the selection of the process with a view to eliminating particularly hazardous chemicals and/or to operating under less hazardous conditions. Some examples of selection of inherently safer processes are given by Kletz. In dyestuffs production use is no longer made of benzidene and certain other intermediates because they are carcinogenic.

In the production of KA, a mixture of cyclohexanone and cyclohexanol, used in the manufacture of nylon, two routes are available. One is by air oxidation of cyclohexane, the process used at Flixborough. The other involves the hydrogenation of phenol, which occurs in the vapour phase and is less hazardous. That the choice of route cannot be considered in isolation, however, is illustrated by the fact that the usual process for the production of phenol involves oxidation of cumene, a process generally regarded as at least as hazardous as cyclohexane oxidation.

The compounds 4,4-diphenylmethane diisocyanate (MDI) and toluene diisocyanate (TDI) are made using phosgene as an intermediate, which is highly toxic. Efforts have been made to devise an alternative, but these have not been entirely successful. However, manufacturers using the original route have been able to reduce drastically the amount of phosgene stored, or even to eliminate phosgene storage completely by passing the gas direct from the production to the consumer unit.

Generation and immediate consumption, rather than storage, of the intermediate methylisocyanate (MIC) is one of the proposals made for inherently safer design of the process used at Bhopal. Other manufacturers are known to make use of much smaller storages of the intermediate.

11.6.7 Hazards of compromise

It is as well at this point to draw attention to the fact that, as far as operating conditions are concerned, a compromise solution may turn out to be the most hazardous. The hazard may be relatively low for a process with a large inventory but operating at low pressure and temperature such that if an escape occurs only a small amount of material will flash off. At the other extreme a process operating at high temperature and pressure may present only a low hazard, because the use of these operating conditions allows the inventory to be kept low. The compromise solution of moderate inventory at moderate pressure and temperature may actually be the most hazardous, if the conditions are such that on release a large fraction of the material will flash off and the inventory is such that the quantity escaping is likely to be large. In cyclohexane reactors, the reaction product still contained approximately 94% of unreacted cyclohexane. The holdup in the reactors and the circulation of unreacted material were both large.

Limitation of inventory in the reactor is illustrated by the evolution of the processes for the manufacture of nitroglycerine, which has been described by N.A.R. Bell (1971). The first stage of development was a batch process with a holdup of about 1000 kg. The second was a continuous process with a 200–300 kg inventory. The third, the NAB process, is again continuous, with reaction taking place in a nozzle and with a holdup of only about 5 kg.

Another example of inherently safer design of a reactor is the development of an alternative design of adipic acid reactor as described by Hearfield (1980a). The original

Table 11.2 *Some features of friendly plants (Kletz, 1990f) (Courtesy of Elsevier Publishing Company)*

Characteristic			*Friendliness*	*Hostility*
1.	Intensification	Distillation	Higee	Conventional
		Heat transfer	Miniaturize	Conventional
		Nitroglycerine manufacture	NAB process	Batch process
		Intermediate storage	Small or nil	Large
		Reaction	Vapour phase	Liquid phase
			Tubular reactor	Pot reactor
2.	Substitution	Heat transfer media	Non-flammable	Flammable
		Solvents	Non-flammable	Flammable
		Chlorine manufacture	Membrane cells	Mercury and asbestos cells
		Carbaryl production	Israeli process	Bhopal process
3.	Attenuation	Liquefied gases	Refrigerated	Under Pressure
		Explosive powders	Slurried	Dry
		Runaway reactants	Diluted	Neat
		Any material	Vapour	Liquid
4.	Simpler design with fewer leakage points or opportunities for error		Hazards avoided	Hazards controlled by added equipment
			Single stream	Multi-stream with many cross-overs
			Dedicated plant	Multi-purpose plant
			One big plant	Many small plants
		Spares	Uninstalled	Installed
5.	No knock-on effects		Open construction	Closed buildings
			Firebreaks	No firebreaks
		Tank roof	Weak seam	Strong seam
		Horizontal cylinder	Pointing away from other equipment	Pointing at other equipment
6.	Incorrect assembly impossible	Compressor valves	Non-interchangeable	Interchangeable
		Device for adding water to oil	Cannot point upstream	Can point upstream
7.	Status clear		Rising spindle valve or ball valve with fixed handle	Non-rising spindle valve
			Spectacle plate[a]	Slip plate
8.	Tolerant of maloperation or poor maintenance		Continuous plant	Batch plant
			Spiral wound gasket	CAF gasket
			Expansion loop	Bellows
			Fixed pipe	Hose
			Articulated arm	Hose
9.	Low leak rate		Spiral wound gasket	CAF gasket
			Tubular reactor	Pot reactor
			Vapour phase reactor	Liquid phase reactor
10.	Easier to control	Response to change	Flat	Steep
		Negative temperature coefficient	Processes in which rise in T produces reaction stopper	Most processes
			Most nuclear reactors	Chernobyl reactor
		Slow response	AGR	PWR
		Less dependent on added-on	AGR, FBR, HTGR	PWR
		Safety systems	PIUS	

Table 11.2 *continued*

Characteristic		*Friendliness*	*Hostility*
11. Software	Errors easy to detect and correct	Some PES	Some PES
	Training and instructions	Some	Most
	Gaskets, nuts, bolts, etc.	Few types stocked	Many types stocked
12. Other industries	Continuous movement[b]	Rotating engine	Reciprocating engine
	Helicopters with two rotors	Cannot touch	Can touch
	Chloroform dispenser	Reverse connection possible	Reverse connection impossible
13. Analogies		Lamb	Lion
		Bungalow	Staircase
		Tricycle	Bicycle
	Marble on saucer	Concave up	Convex up
	Boiled egg	Pointed end up, hard-boiled, medieval egg-cup	Blunt end up, soft-boiled, standard egg-cup

[a] A spectacle plate is easier to fit (in rigid piping) and easier to find.
[b] In practice reciprocating internal combustion engines are not less friendly than rotating engines, though one might expect that equipment which continually starts and stops would be less reliable.
AGR, advanced gas-cooled reactor; CAF, compressed asbestos fibre; HTGR, high temperature gas reactor; FBR, fast breeder reactor; PES, programmable electronic system; PIUS, process inherent ultimate safety reactor; PWR, pressurized water reactor.

design and the design finally adopted in 1980 are shown in Figure 11.3. In the latter the inventory is reduced and many of the sources of leaks – the agitator, pump, external cooler and connecting pipework – are eliminated.

11.6.8 Plate heat exchangers

Another application of process intensification is the use of plate heat exchangers, as described by C. Butcher (1992c). Plate heat exchanger technology is developing rapidly and exchangers are available for a much wider range of applications than previously. For example, the pressure range has been extended from about 80 to 100 bar.

The potential of plate heat exchangers goes beyond conventional heat transfer applications. One concept is the use of plate heat exchangers coated with catalyst as methane reformers. It is estimated that a plate heat exchanger reformer with capacity sufficient for a 1000 te/day methanol plant would be about 4 m^3; this contrasts with conventional reformers which are about 20 m high.

11.6.9 Combination of unit operations

Another form of intensification is the conduct of several unit operations in one equipment. Kletz (1992c) cites the example of a design in which the operations of drying, heat exchange and granulation are combined.

11.6.10 Applications of substitution

Some applications of substitution in the main reaction of the process have been described by S.E. Dale (1987). One is the process for acrylonitrile, which was originally manufactured from acetylene and hydrogen cyanide, both hazardous chemicals, but is now made from propylene, ammonia and air, all less hazardous. Another example is the production of ethylene glycol from ethylene rather than from ethylene oxide, another hazardous material. These are good examples of inherently safer design, even though they have been made for essentially economic reasons. Further

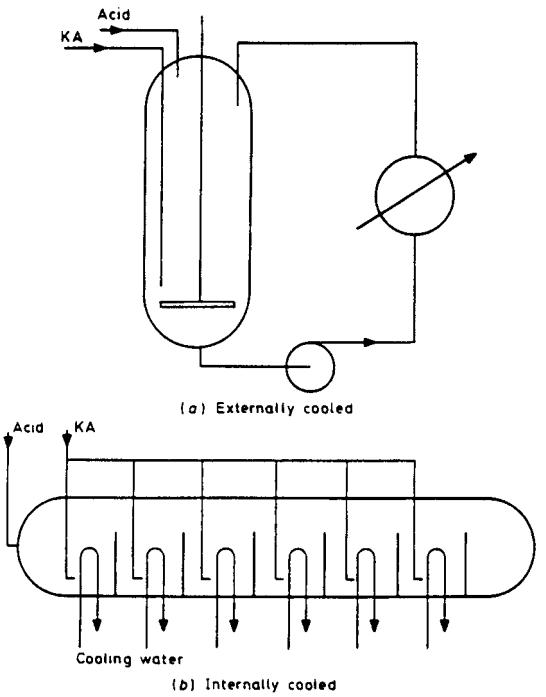


Figure 11.3 *Alternative designs of adipic acid reactors (Hearfield, 1980a): (a) original design with external cooling; (b) evolved design with internal cooling (Courtesy of the Institution of Chemical Engineers)*

illustrations of the substitution of less hazardous reactions have been given by R.L. Rogers and Hallam (1991). One case quoted is the manufacture of the synthetic nitrocarbamate shown in Figure 11.4(a). One of the routes considered involved the preparation and isolation of the nitrobenzoyl chloride intermediate shown in Figure 11.4(b). Experience indicated that this was likely to be thermally unstable. Further work identified a route in which the nitration is effected at a later stage. Another example involves the oxidation of a substituted acetophenone to a carboxylic acid. The reaction shown in Figure 11.4(c) involves hydrogen peroxide. This was replaced by that shown in Figure 11.4(d) with air and a catalyst.

11.6.11 Applications of attenuation

S.E. Dale (1987) has also described some applications of attenuation. He cites a number of processes which now operate at lower pressures, often due to improvements in the catalysts. Processes which he mentions include methanol synthesis, polyethylene and polypropylene processes, and the Oxo process.

Another process which he quotes is the production of butyl lithium, which is pyrophoric and thus liable to ignite when exposed to air. This hazard is minimized by producing the butyl lithium in dilute solution.

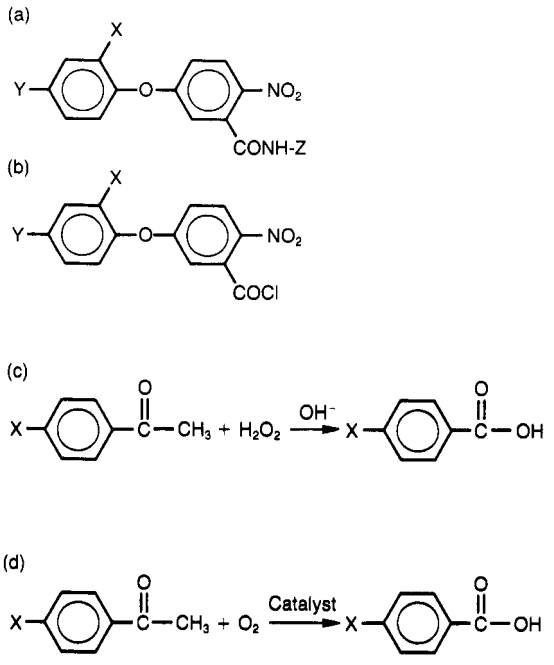


Figure 11.4 *Some reaction routes of varying degree of hazard (R.L. Rogers and Hallam, 1991): (a) substituted nitrocarbamide; (b) nitrobenzoyl chloride intermediate; (c) oxidation of a substituted acetophenone to a carboxylic acid using hydrogen peroxide; and (d) oxidation of the substituted acetophenone to the carboxylic acid using air and catalyst (Courtesy of the Institution of Chemical Engineers)*

11.6.12 Design of unit operations

Distillation units may contain appreciable inventories of hazardous materials. The quantities held up in a large modern unit are of the same order as those previously held in storage on smaller plants. Substantial reductions in the inventory in distillation units by better design have been demonstrated.

Column inventory may be reduced by the use of low holdup internals. The estimate given by Kletz (1975c) of the holdup per theoretical plate is:

Conventional trays (sieve, valve, etc.)	40–100 mm liquid
Packing	30–70 mm liquid
Film trays	10–20 mm liquid

Holdup in the column base may be reduced by the use of a narrow bottom section. Thermosiphon reboilers have a lower inventory than kettle reboilers. It may be possible to eliminate intermediate storages.

Original and revised designs of a distillation unit for separation of LPG described by Kletz are shown in Figure 11.5. The inventories in the two designs are:

	Original inventory (te)		*Revised inventory* (te)	
	Working	*Maximum*	*Working*	*Maximum*
Plant	85	150	50	80
Storage	425	850	–	–

In addition to reductions of inventory due to the use of low holdup packing and of a narrow column base, the revised design achieves even larger reductions by the eliminating intermediate storages. The reflux pump suction is taken from the condenser and the reflux drum is omitted. So also are the raw materials and product buffer storage.

Heat exchangers also offer scope for reduction of inventory. In the revised distillation unit design just described the fluids in the condenser were reversed so that the LPG and refrigerant are on the shell and tube sides, respectively. This has the effect of reducing the inventory of coolant and the total flammable inventory. A table of surface compactness of heat exchangers as a guide to inventories is given by Kletz.

11.6.13 Selection of heat transfer media

The refrigeration systems on olefins plants contain large inventories of flammables such as ethylene and propylene. Ammonia is a possible substitute, but in view of the toxic risk seems no safer. A viable alternative refrigerant, however, would make a real contribution to inventory reduction. Some alternative refrigerants have been discussed by Jacob (1991a).

Large inventories of flammables occur in heat transfer systems. For example, in an ethylene oxide plant using kerosene boiling under pressure as the heat transfer medium this may well constitute a greater hazard than the ethylene oxide mixture, which is very closely controlled. Use has been made of steam as an alternative, inherently safer heat transfer fluid.

Many alternative heat transfer fluid have been designed for specific temperature ranges and a high degree of safety in flammability or in some cases completely non-flammable (see Chapter 7 (CCPS, 1993b)).

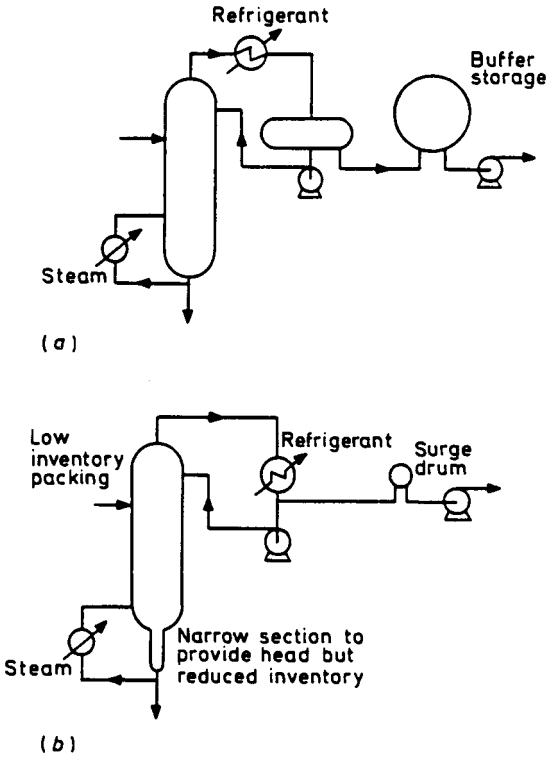


Figure 11.5 *Alternative designs of LPG distillation unit (Kletz, 1984d): (a) original design with high inventory; (b) revised design with low inventory (Courtesy of the Institution of Chemical Engineers)*

11.6.14 Design of storage

In general, storage capacity is of great assistance to plant management in the operation of the plant, but this has to be balanced against the cost and the hazard of storage. Application of inherently safer design to storage may involve:

(1) elimination of intermediate storage;
(2) reduction in storage inventory;
(3) storage under less hazardous conditions.

If the plant producing an intermediate can be located near the consumer plant, it may be possible to eliminate intermediate storage altogether. Mention has already been made of the elimination of intermediate storage of phosgene in the manufacture of MDI and TDI.

Even if it is not practical to eliminate storage it may be possible to reduce it. Kletz quotes the case of a company which used to hold several thousand tonnes of chlorine, but found it was in fact able to operate with only a few hundred tonnes.

A third approach is to store the material in a safer form. Examples given by Kletz include the storage and transport of acetylene in acetone, of organic peroxides as solutions and of hydrogen in the form of ammonia which is 'cracked' when the hydrogen is required.

The issue of inherently safer storage conditions arises most often, however, in relation to pressure and refrigerated storage. Considering the storage alone, for a liquefied gas refrigerated storage is safer than pressure storage. Large storages of such gases tend to be refrigerated. On the other hand, if the fluid is required as a gas and it is necessary to provide vaporizers and other equipment, it is the whole system which then needs to be considered and in this case refrigerated storage may be assessed as no safer. Pressure and refrigerated storage are considered further in Chapter 22.

The issue of centralized vs distributed smaller storage systems, such as chlorine, is highly controversial, dependent on a number of factors in the plant environment, engineering judgement, etc. and cannot be pontificated.

11.6.15 Major hazard storages

An account of the reductions in hazardous storage inventories at one's works in the context of the CIMAH Regulations has been given by Orrell and Cryan (1987). The principal hazardous chemicals involved were ethylene oxide, propylene oxide and sulfur trioxide. Disregarding the former, the use of which was discontinued on that site, the reductions achieved between 1980 and 1987 were as follows:

	Inventory (te)				
	1980		*1987*		*1987*
	Process	*Storage*	*Process*	*Storage*	*CIMAH level*
Propylene oxide	51	246	<0.2	<50	50
Sulfur trioxide	<0.5	75	<0.2	<50	75

11.6.16 Toxic storages

Following the Bhopal incident, many companies reviewed their inventories of toxic chemicals and achieved appreciable reductions. An account of one such exercise has been given by Wade (1987), who cites five examples of major reductions of inventory.

In one case, a large acrylonitrile plant, the purification section had a shorter time interval between scheduled shutdowns than the reaction section, and intermediate storage was used to allow the reaction section to continue running whilst the purification section was shut down. Practice was changed so that the reaction section ran at a lower, but safe, throughput whilst the purification section was down and until the latter had run the storage down again, thus effecting a large reduction in the average intermediate storage inventory.

In the second case, by-product hydrogen cyanide from a large acrylonitrile plant was sent to storage before being distributed to satellite plants. The intermediate storage was eliminated, the hydrogen cyanide being passed direct to the user plants. Elimination of the storage created some problems of composition control and of flow smoothing as user plants started up and shut-down, but these were met.

A third case involved the elimination of chlorine horizontal storage bullets and their replacement with smaller storage containers. In the fourth case, changes were made

to the practice of using as storage rail tank cars hooked up to the plant. One approach was to work more closely with the supplier to ensure that deliveries were made when needed. The other was to work with the railway company to locate areas where such tank cars could be held with minimal public exposure.

The fifth case, described earlier, involved the transfer of the first stage of a multi-step reaction process to the reactant supplier, thus giving more benign reactants for the remainder of the reaction sequence.

11.6.17 On-site production

Another way of eliminating a storage inventory is on-site production of the chemical. There are now available skid-mounted phosgene plants with a capacity of 2–15 te/day which can be installed at the user's work and obviate the need for phosgene storage. On-site production has the further advantage of eliminating the need to transport the chemical produced, although it does of course involve transport of the raw materials. On-site production of hydrogen is commonly employed.

11.6.18 Design against overpressure

Virtually all pumps installed in process plants are specified such that a future full-sized impeller can be installed in the future. In the majority of cases with centrifugal pumps this has no or a minor safety implication.

Control valve sizing is an industry-wide problem due to the cumulative effects of each discipline safety factor which result in a valve two to three times oversize. The valve exhibits poor controllability due to the low valve lift and the bath-tub stopper effect. The valve suppliers exacerbate the problem by providing the next size larger valve. Only careful surveillance of each process step will eliminate the problem. Oversize pressure relief valves are the safety implication.

11.6.19 Design for containment

Another aspect of inherently safer design is the prevention and reduction of loss of containment of the more hazardous materials. Three typical leak situations are illustrated in Figure 11.6. Figure 11.6(a) shows a leak of liquid petrol at high pressure but atmospheric temperature. For this case the fraction flashing off and the amount of vapour formed are small. Figure 11.6(b) shows a leak of propane gas at high pressure and temperature. The mass flow is much smaller but all the material is in gaseous form. The release may well be rapidly dispersed below its lower flammability limit by the momentum of the escaping jet. Figure 11.6(c) shows a leak of liquid petrol at high pressure and temperature. This is the most hazardous of the three cases. The fluid is a superheated liquid so that the mass flow is high and the flash fraction, and thus the vapour cloud formed, are large. It is therefore this third case which should receive particular attention. Utilizing excess flow valves can limit the risk.

Each leak situation must be analysed for its characterization for forming a flammable liquid pool or a potential vapour cloud explosion. The size of the leaks must be empirically assessed. It should be noted that leakage of an LPG, LNG or intermediate material can result in refrigeratioin of the metal to a low temperature resulting in a brittle fracture.

11.6.20 Simplicity in design

A fundamental principle of inherently safer design is simplicity. Many actual plant designs are extremely complex.

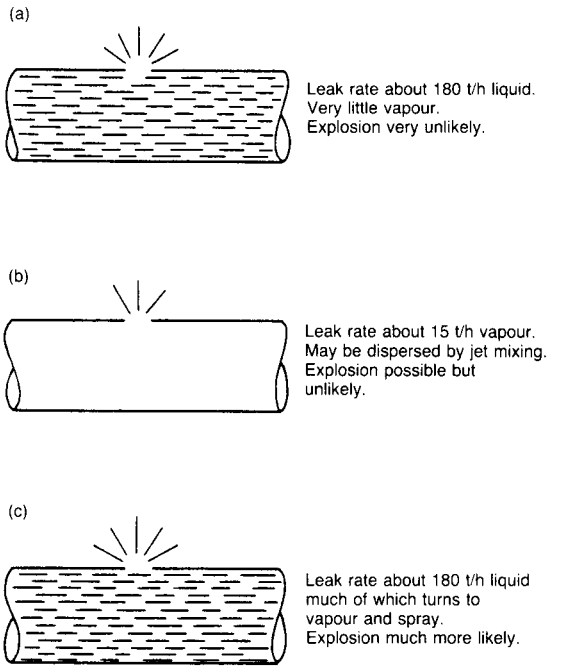


Figure 11.6 *Some typical leak situations (Kletz, 1984d): (a) petrol at 7 bar and 10°C; (b) propane gas at 7 bar and 100°C; (c) petrol at 7 bar and 100°C (Courtesy of the Institution of Chemical Engineers)*

That shown in Figure 11.7 is used by Kletz (1984d) to illustrate the problem of complexity. Aspects of simpler design instanced by Kletz include:

(1) design for full overpressure;
(2) design modification to avoid instrumentation;
(3) use of resistant materials of construction;
(4) use of simple alternatives to instrumentation.

Where a vessel may be subject to overpressure, the simplest solution may be to design it to withstand this overpressure. Most commonly, a pressure relief system is employed. The environmental and regulation issues must be addressed as well as the design.

Sometimes instrumentation is provided to overcome a problem for which the alternative solution is a design change. Kletz gives as an example a liquid phase oxidation plant. The oxidizing air was fed to the plant mixed with the hydrocarbon recycle and instrumentation was provided to keep the mixture outside the flammable range. An alternative design was to add the air directly to the liquid so that a flammable mixture could not form.

Another reason for installing instrumentation may be to prevent attack on materials of construction. Use of more resistant materials may avoid the need for the instruments. Whether this is the best solution depends on the particular case. A contrary example is given in Chapter 9, where hazard assessment showed that use of a trip was preferable to constructing a pipe in special steel.

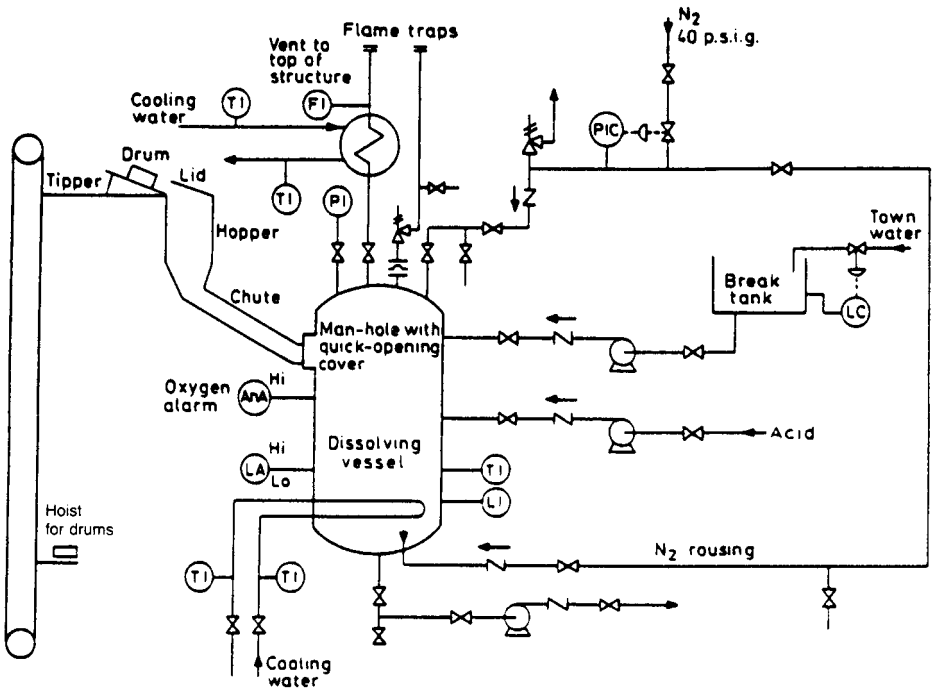


Figure 11.7 *A complex plant design involving instrumentation (Kletz, 1984d) (Courtesy of the Institution of Chemical Engineers)*

High integrity protective systems (HIPSs) are widely used to improve the safety (by orders of magnitude) and increasing the plant reliability (see Chapter 13).

11.6.21 Flexibility of plant

Flexibility is a valuable feature on a plant, but it can be taken too far. Not only can the interconnections needed to give such flexibility become very complex and costly but also they introduce further potential sources of leaks and human errors. General multiple single trains are employed rather than complex crossovers.

11.6.22 Modification chains

Another source of complexity is the modification chain: an initial modification is made which leads to others. This is a problem not only in design, but perhaps even more on existing plant, where a single *ad hoc* modification can lead to a whole series.

A simple modification chain is shown in Figure 11.8. The manhole cover in Figure 11.8(a) is not leak-tight and traces of flammable vapour escape into the plant. In order to reduce the probability that they will ignite or be inhaled, a vent 4 m high is fitted to the cover, as shown in Figure 11.8(b). In turn, as shown in Figures 11.8(c–e), a flame trap is fitted because the gas leaving the vent might be ignited by lightning, an access platform is provided to allow regular cleaning of the flame trap, and handrails and toe boards are fitted because it is realized that the platform is now a 'place of work'.

A more complex example is the system for transfer of slurry under pressure between the two vessels shown in

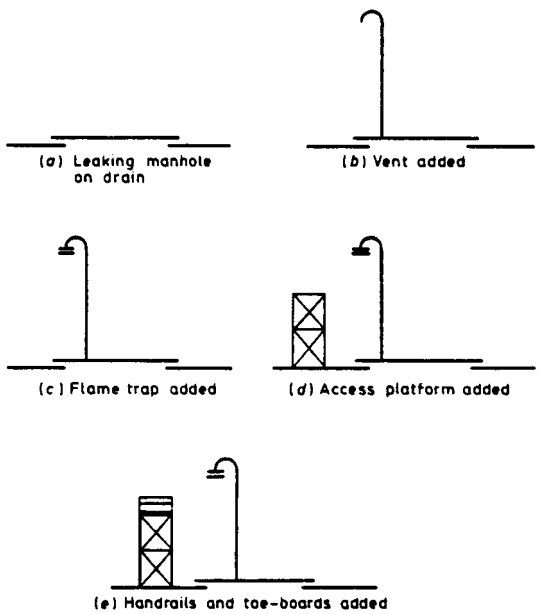


Figure 11.8 *A modification chain for a manhole cover (Kletz, 1984d): (a) manhole cover; (b) addition of vent; (c) addition of flame trap; (d) addition of platform; (e) addition of handrail and toe boards (Courtesy of the Institution of Chemical Engineers)*

Figure 11.9. Figure 11.9(a) shows the original design with a single transfer line and arrangements to blow the line with steam to clear the line of chokes and to clean it. The plant was the first version to be continuous, earlier plants being batch. In order to avoid downtime due to blockages in the transfer line, a second transfer line, Figure 11.9(b), was added. The relief and blow-down review revealed that the two transfer lines could be operated simultaneously and that in this situation the downstream vessels would require twice the relief capacity. In order to avoid this, the valves on the two lines were interlocked, Figure 11.9(c). This created two more dead legs in each line so it was necessary to add four more steam connections to allow steam flushing, Figure 11.9(d). It was then realized that in order to be sure that the stand-by line was ready for use it was necessary to keep steam flowing through it. The transfer line was protected against the pressure of the process but not against that of the steam. Whereas it was considered acceptable not to provide relief for occasional use of steam, it was necessary to do so for steam continuously in the line, and so a pressure relief valve was fitted to the steam line, Figure 11.9(e).

11.6.23 Process operability

Some processes are inherently more operable than others. This aspect should be borne in mind in the selection of the process. In particular, a process which has no 'fallback' positions and which in the extreme case presents the operator with a stark choice of continuing to run at a given set of conditions or of shutting down completely is not easy to operate. The operability of process and plant is one of the two main aspects which are examined in hazop studies.

11.6.24 Fail-safe design

The concept of fail-safe design is well established in the process industries. It refers to the design of equipment such as control and solenoid valves so that in the event of failure of a utility such as electricity or instrument air the plant moves to a safe state.

The decision of whether a valve should be open or closed on utility failure is made in the light of the consequences for the process. The fail-safe position, assuming there is one, is then determined. Thus pneumatic control valves, for example, are available as 'air-to-open' or 'air-to-close'; the former close and the latter open on air failure.

Current electronic components do not have identified fail-safe positions. See HSE 1987a–d *Programmable Electronic Systems* for random and systemic failures which are not fail-safe.

The principle of fail-safe design may be extended to include the action of whole control loops. This aspect is considered in Chapter 13.

11.6.25 Second chance design

Another relevant concept is that of 'second chance design'. This means the provision of a second line of defence to guard against an initial hazard or failure. Some features which are prominent in second chance design are:

(1) plant layout;
(2) pressure system design;
(3) materials of construction;
(4) isolation arrangements;
(5) alarms and trips;
(6) operating and maintenance procedures.

Second chance design is illustrated by: many of the normal features of plant layout such as bunding and drainaway arrangements; many normal features of pressure systems such as the installation on pressure vessels of pressure relief and blow-down systems and on pumps of double mechanical seals with monitoring of the pressure sealing system; the use of materials of construction which can withstand deviations from normal operating conditions such as a slug of low temperature liquid; the provision of arrangements for isolation if there is loss of containment; the use of alarms which warn of, and trips which take action against, hazardous conditions; and adherence to operating and maintenance procedures which reduce the probability of the hazard, such as purging again after a delay in lighting a furnace.

It will be apparent from these examples that second chance design is a rather general concept, embracing both preventive and mitigating features, but is a very valuable one.

11.6.26 Layers of protection

A newer concept, analogous to the previous paragraph on second change design, is layers of protection. This technique was introduced by Drake and Thurston in 1992 and is now widely adopted and included in safety codes such as ISA 84.01. The basic idea is illustrated plainly in the onion skin Figure 11.10 which is self-explanatory. This inner most layer is the process design, basic control systems (BPCS), critical alarms, automatic actions such as the safety interlock systems (SIS), emergency shut-down (ESD); physical protection, dikes, and emergency responses, both plant- and community-wide. This provides the multiple safety layers present to provide protection from a hazardous incident. Each safety layer must be independent, specific, dependable and auditable, providing an order of magnitude protection over the previous layer. Further detailed information is available in CCPS *Guidelines for Safe Automation of Chemical Processes*. This approach has been touted to be highly effective and has resulted in a significant reduction of incidents.

11.6.27 Single large vs multiple small systems

A question which occurs in the context of inherently safer design is whether it is preferable from this aspect to have a single large unit, plant or storage, or several smaller ones. Generally it is economically attractive to choose the single large unit. Many consider that this is usually the best choice for safety also. If several small units are built, the number of weak points such as pumps, flanges, etc., increases roughly in proportion to the number of units, and the management effort is more thinly spread. If a single large unit is built, the number of weak points is much reduced and the management can concentrate on this unit. For both these reasons the frequency of incidents with a single large unit should be less than with several smaller ones. The argument for the single large unit is thus, in part, that if one puts all one's eggs in one basket, one can afford a good basket. The drawback is that the scale of any incident which does occur is likely to be larger with the single unit. There is probably no general solution to this problem. Each case should be considered on its merits.

11.6.28 Limitation of exposure

A rather different aspect of inherently safer design is the limitation of exposure of personnel. This is another concept

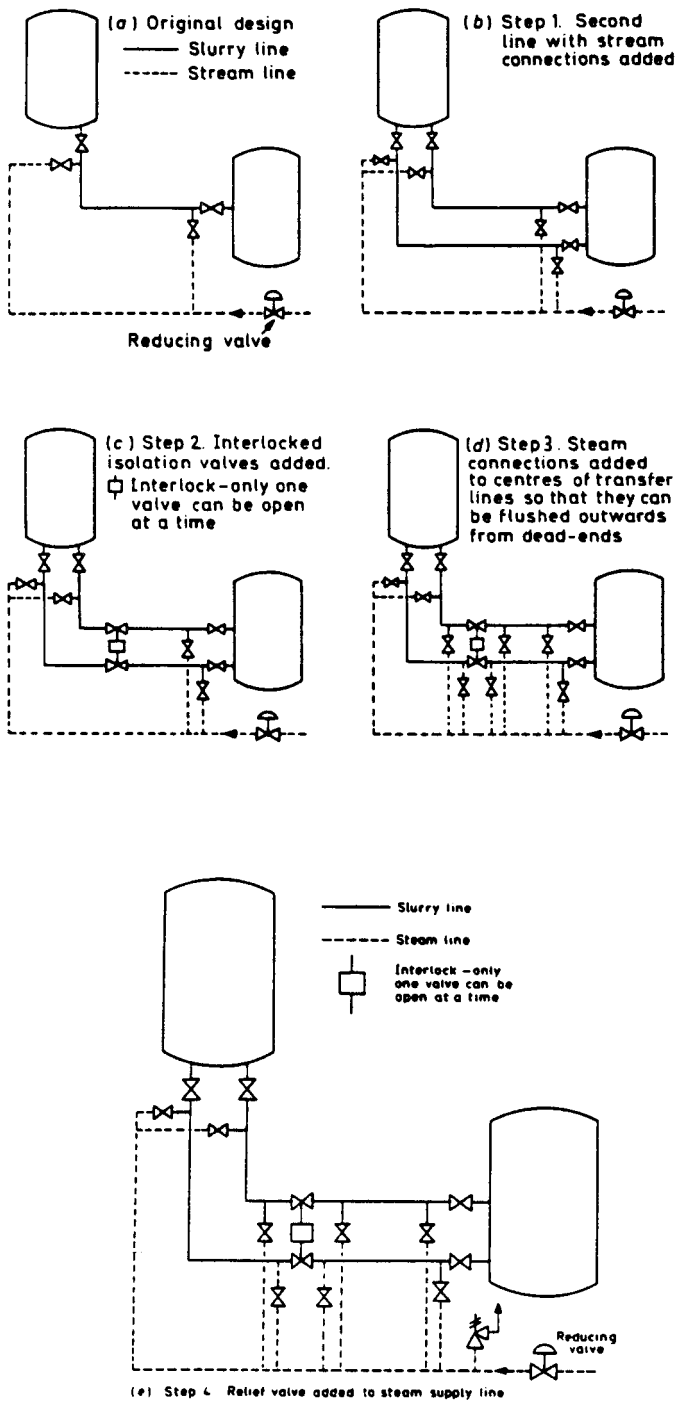


Figure 11.9 *A modification chain for a slurry transfer system (Kletz, 1984d): (a) slurry transfer system; (b) addition of second transfer line; (c) addition of interlock between values on two transfer lines; (d) addition of extra steam connections; (e) addition of pressure relief value on stream line (Courtesy of the Institution of Chemical Engineers)*

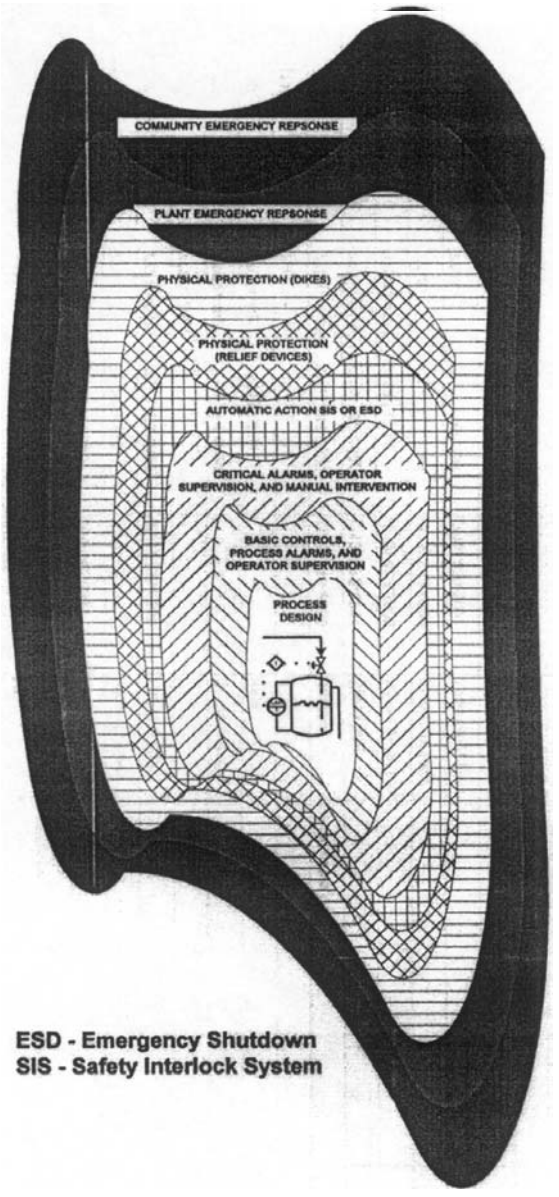


Figure 11.10 *Typical layers of protection in modern chemical plant (CCPS, 1993)*

which received impetus from the Flixborough incident, in which 18 of the 28 deaths occurred in the control room. The question was asked whether so many people really needed to be exposed to the hazard in this way. Limitation of exposure of personnel may be achieved by location of the workbase and by control of access to the high hazard zones. These aspects are considered in Chapters 10 and 20. This subject is covered in detail with a quantitative analysis in the CCPS *Guidelines for Evaluating Process Plant Buildings for External Explosion and Fires* (CCPS, 1996).

11.6.29 Inhibiting factors

Progress in the realization of inherently safer designs has not been as rapid as its advocates would wish. Some reasons for this have been examined by Kletz (1991h, 1992c) and Mansfield and Cassidy (1994).

The arguments advanced by Kletz have application particularly where an inherently safer alternative design involves a significant degree of innovation, which affects only a part of the whole plant and where the scale of production is large. Since, in general, technical and economic risk is increased by novel features, opponents will argue that a large project is being put at risk for relatively small gain.

Essentially, part of the problem is that a single project is being made to bear the 'cost' of an innovation which has the potential eventually to make a significant contribution to the reduction of costs and enhancement of safety over a range of processes operated by the company.

Another feature of the problem is that once plant design is under way, there is often not sufficient time to accommodate such innovation, and there is pressure to follow the previous design. This aspect has been addressed by Malpas (1983), who argues that whilst the design of the next plant is in progress thought should be given to the improvements which have been identified, which it is not practical to incorporate in the design but which, with forethought, could be implemented in 'the plant after next'.

The problem of furthering innovation is exacerbated, moreover, by the move towards business-centred rather than functional organization of companies. However, as Mansfield and Cassidy (1994) point out, inherently safer design is not necessarily radical but may involve incremental change. Among the reasons which they give for lack of progress are lack of awareness, lack of a recognized tool and failure to build the practice into company procedures. Moreover, even where what is in question is a radical change, the proposed process may be such as to constitute a minimal risk.

11.6.30 HSE initiatives

The Health and Safety Executive (HSE) now has an explicit policy of encouraging the application of inherently safer design concepts. Its philosophy and activity in this area have been described by Barrell (1988a) and P. Jones (1992). The work described by Mansfield and Cassidy (1994) is one aspect of this programme.

11.6.31 Inherently safer design methodology

The work of Mansfield and Cassidy is aimed at furthering the practice of inherently safer design by the development of suitable tools. The authors argue that there is need for a technique which will do for inherently safer design what hazop has done for hazard identification. Such a tool needs to address particularly the conceptual design stage. Concept design is generally done quite rapidly. The tendency is that thereafter the basic concept does not undergo any great change.

These authors suggest four broad categories of tool for inherently safer design: (1) brainstorming with a degree of structure, (2) a more highly structured hazop-style examination of flow sheets and process diagrams, (3) examination, using checklists, of the plant layout and (4) indices of inherent safety.

11.6.32 Inherently safer design index

The development of an index for inherently safer design has been described by D.W. Edwards and Lawrence (1993).

This index is intended for use early in the design, at the stage of process selection. The authors list a number of variables relevant to inherent safety, including: properties of the chemicals such as corrosiveness, flammability, explosibility and toxicity; operating conditions such as pressure and temperature; reaction conditions such as phase, rate, heat release, yield and side reactions; and effluents and wastes. At this early stage information on inventory, for example, is lacking and has to be represented by surrogates such as yield. The method involves assigning scores to the individual parameters. These are then used to compute a chemical score, a process score and an overall inherent safety index. A low value of this index means a high degree of inherent safety. The inherent safety index is obtained from the sum of the scores of the individual process stages. Hence the index penalizes processes with a large number of stages.

Edwards and Lawrence state that one of their aims is to test the hypothesis that inherently safer design means cheaper plants, and give as an illustrative example of a comparison of six routes to methylmethacrylate in respect of: (1) the estimated costs and (2) the inherent safety index. Perhaps the most salient point from this single example is the benefit of a smaller number of stages. They also refer to work on comparison of the index with expert rankings.

The *Dow Fire and Explosion Index – Hazard Classification Guide* which has been available for over 20 years, now in the eighth edition, provides also quantitative results based on the same issues previously described.

11.6.33 Miniaturized and distributed plants

In a speculative treatment, Benson and Ponton (1993) suggest that one future trend may well be towards distributed manufacture of chemicals using miniaturized plants at the users' sites. Such an approach chimes with demands for plants which are environmental friendly and deliver their products on a 'just-in-time' basis.

Development on these lines requires that the plants be fully automated and highly reliable. The authors envisage plants that operate at moderate pressure and temperature, are self-cleaning and are sealed for life. There is also an implication that there is no insuperable effluent problem.

Benson and Ponton list a number of types of equipment which have been the subject of much development in recent years but which have not realized their full potential because they come into their own in small scale rather than large scale production. Table 11.3 contrasts some of the characteristics of distributed plants and large scale plants.

11.7 Unit Processes

11.7.1 Chemical industry

The chemical and petrochemical industries are described in *The Petroleum Chemicals Industry* (Goldstein and Waddams, 1967), *The Petrochemical Industry* (Hahn and Williams, 1970), *Structure of the Chemical Processing Industries* (Wei, Fraser and Swartzlander, 1978), *The Chemical Industry* (Sharp and West, 1982), *Shreve's Chemical Process Industries* (G.T. Austin, 1984), *The Chemical*

Table 11.3 *Some characteristics of miniaturized and of large scale plants (Benson and Ponton, 1993) (Courtesy of the Institution of Chemical Engineers)*

Distributed plants	*Large site plants*
Feedstocks:	
Readily available at the customer's site (e.g. air, methane, water, electricity)	Available from other processes on the site (e.g. chlorine)
Safe to transport (e.g. CO_2, salt, lime, most solids)	Dangerous to transport (e.g. ethylene oxide)
Processes:	
That build new molecules from simple feedstocks (e.g. phosgene)	That involve cracking complex molecules to low molecular weight products (e.g. oil refining, olefins from naphtha)
Catalytic processes (e.g. ammonia from methane)	Low specificity, multi-product processes
Low pressure and temperature (e.g. bioprocesses)	High temperature or pressure (e.g. polyethylene)
Stand-alone processes (e.g. air liquefaction)	Highly integrated processes
Physical change processes (e.g. formulation, shredding)	
Customer products:	
Considered to be dangerous to transport (e.g. phosgene, bromine)	Involving a hazardous processing step (e.g. highly exothermic reaction)
Production state matches customer requirement, but would require change for transport (e.g. molten polymer, liquefied gases, many powders)	
Produced and required in dilute state, but normally concentrated for transport (e.g. aqueous HF)	
Waste products:	
Suitable, after treatment, for returning to the immediate environment (e.g. oxygen, water)	Requiring controlled thermal oxidation (e.g. tars, chlorinated wastes)
May be reacted with other customer waste to produce benign products (e.g. chlorine, caustic)	Treatment requires other plants on the site
Biodegradable waste (e.g. from biological processes)	

Industry (Heaton, 1985–), *Handbook of Chemicals Production Processes* (Meyers, 1986a) and *Petrochemicals* (Spitz, 1988). Further references are given in Section 11.11.

Accounts of the European chemical industry are given in the following: France, E. Johnson (1989c) and Redman *et al.* (1991); Germany, E. Johnson *et al.* (1990); Italy, Redman *et al.* (1990) and the Netherlands, Redman and Smith (1991).

11.7.2 Principal processes

Descriptions of unit processes and of their thermodynamics and kinetics are given in *Unit Processes in Organic Synthesis* (Groggins, 1952), *Industrial Chemicals* (Faith, Keyes and Clark, 1965), *Chemical Process Industries* (Shreve, 1967), *Organic Chemicals Manufacturing Hazards* (Goldfarb *et al.*, 1981), *Shreve's Chemical Process Industries* (G.T. Austin, 1984), *Survey of Industrial Chemistry* (Chenier, 1986) and *Introduction to Industrial Chemistry* (H.L. White, 1986). Further information is given in other standard texts, including encyclopaedias such as those by Kirk and Othmer (1963–, 1978–, 1991–) and Ullman (1969–, 1985–). Selected references on unit processes and their hazards are given in Table 11.4.

Unit processes are listed by Fowler and Spiegelman (1968) as follows: acylation, alkaline fusion, alkylation, animation, aromatization, calcination, carboxylation, causticization, combustion, condensation, coupling, cracking, diazotization, double decomposition, electrolysis, esterification, fermentation, halogenation, hydration, hydroforming, hydrogenation, hydrolysis, ion exchange, isomerization, neutralization, nitration, oxidation/reduction, polymerization, pyrolysis and sulfonation. The unit processes which are generally more hazardous are given by Fowler and Spiegelman as alkylation, animation, aromatization, combustion, condensation, diazotization, halogenation, hydrogenation, nitration, oxidation and polymerization. The unit processes considered here by way of illustration are (1) oxidation, (2) hydrogenation, (3) chlorination and (4) nitration.

A particular unit process tends to have certain characteristic features. These often relate to:

(1) reactant and product;
(2) reactor phase;
(3) main reaction
    (a) thermodynamic equilibrium,
    (b) heat of reaction,
    (c) velocity constant,
    (d) activation energy;
(4) side reactions;
(5) materials of construction.

Table 11.4 *Selected references on unit processes and their hazards*

Groggins (1952); Kirk and Othmer (1963–, 1978–, 1991–); Faith, Keyes and Clark (1965); Goldstein and Waddams (1967); Shreve (1967); Considine (1974); NFPA (1991 NFPA 491M)

Biotechnology, food processing
Tong (1978); Frommer and Kramer (1989); Palazzi *et al.* (1989); Jowitt (1980)

Alkylation
B. Scott (1992)

Carbonylation
Goldfarb *et al.* (1981)

Chlorine production
Eichelberger, Smura and Bergenn (1961); Pennell (1963); Chlorine Institute (1981 CPP, Pamphlet 67, 1986 Pamphlet 1); Sommers (1965); Schwab and Doyle (1967); Bunge and Honigh (1969); Elliott (1969); J.L. Wood (1969); Kuhn (1971); Stephens and Livingston (1973); C. Jackson and Kelham (1984); Means and Beck (1984); Coulter (1986); C. Jackson (1986); Wall (1986); I.F. White *et al.* (1986)

Chlorination
Groggins (1952); Daniel (1973); Goldfarb *et al.* (1981)

Electrochemical
Dotson (1978); AIChE (1981/76, 1983/80); Fleischmann and Overstall (1983); Fletcher (1984)

Hydrogenation
Groggins (1952); Augustine (1965); Gant (1978); Rylander (1985); Klais (1987)

Nitration
Groggins (1952); Albright (1966b,e,g); Dubar and Calzia (1968); Albright and Hanson (1969, 1976); Fritz (1969); Ventrone (1969); N.A.R. Bell (1971); Biasutti and Camera (1974); Biasutti (1976, 1979); F.W. Evans, Meyer and Oppliger (1977)

Oxidation
Burgoyne and Kapur (1952); Groggins (1952); Burgoyne and Cox (1953); Sittig (1961–, 1962); Salooja (1964a); Shtern (1964); Emanuel (1965); Papenfuss (1965); Zeelenberg and de Bruijn (1965); Berezin, Denisov and Emmanuel (1966); Albright (1967b,e); Farkas (1970); Prengle and Barona (1970); Haberle (1971); Pickles (1971); Talmage (1971); Alexander (1974,1990a,b); Dumas and Bulani (1974); Gugan (1974b); Hucknall (1974); Dragoset (1976); Nemes *et al.* (1976); Saunby and Kiff (1976); R. Davies (1979); Cans (1979); Weismantel and Ricci (1979); Hobbs (1980); Lyons (1980); Goldfarb *et al.* (1981); Crescitelli *et al.* (1982); Krzyrztoforski *et al.* (1986); Snee and Griffiths (1989); Franz and Sheldon (1991); Memedlyaev, Glikin and Tyulpinov (1992)

Oxychlorination
Quant *et al.* (1963); Illidge and Wolstenholme (1978); Goldfarb *et al.* (1981)

Oxyhydrochlorination
Illidge and Wolstenholme (1978); McNaughton (1983)

Oxo synthesis
Weber and Falbe (1970)

Plasma processing
Szekely and Apelian (1984)

Polymerization
Goldfarb *et al.* (1981)

11.7.3 Oxidation

The oxidation reactions considered here are those of an organic compound with molecular oxygen. Some principal industrial oxidation reactions include:

Vapour phase

Ethylene → ethylene oxide
Propylene → acrylic acid
Methanol → formaldehyde
Naphthalene → phthalic anhydride
Benzene, butenes → maleic anhydride

Liquid phase

Acetaldehyde → acetic acid
Butane → acetic acid and related products
i-Butane → *t*-butyl hydroperoxide
(and hence propylene oxide)
Cumene → cumene hydroperoxide
(and hence phenol, acetone)
Cyclohexane → cyclohexanone and cyclohexanol
(and hence adipic acid and caprolactam)
Ethylbenzene → ethylbenzene hydroperoxide
(and hence propylene oxide)
Naphtha → acetic acid
Toluene → benzoic acid (and hence phenol)
p-Xylene → terephthalic acid
p-Xylene → monomethylterephthalate
Higher hydrocarbons → primary hydroperoxides
(and hence primary alcohols, aldehydes and acids)
Higher hydrocarbons → secondary hydroperoxides
(and hence secondary alcohols and ketones)

The reactions are generally exothermic and sometimes highly so. There is frequently, therefore, a problem of heat removal and of temperature control.

Oxidation reactions tend not to be limited by thermodynamic equilibrium. There can be problems, however, of the reaction of complete combustion and of side reactions to unwanted by-products. Frequently, it is necessary to employ catalysts and to use only moderate temperatures in order to avoid these undesired reactions.

The heat generated in such oxidation processes may considerably exceed the theoretical heat of reaction. Thus the heat of oxidation of napthalene to phthalic anhydride is about 5460 BTU/lb of naphthalene, but for some reactor conditions it is reckoned that the occurrence of the complete combustion reaction can raise the effective heat of reaction to 10,000 BTU/lb of naphthalene-fed.

Vapour phase oxidations are carried out in various types of reactor, such as a reactor vessel with catalyst on a tray, a tubular packed bed reactor or a fluidized bed reactor. Tubular and fluidized bed reactors are suitable if the heat release is large. Thus, the oxidation of napthalene to phthalic anhydride is highly exothermic. Initially, this reaction was carried out in a tubular reactor, but is now usually done in a fluidized bed.

In vapour phase oxidation the reactor feed is generally kept outside the flammable range. This requires the use of well designed and highly reliable trip systems. The use of a high integrity protective system to maintain the ethylene and oxygen feeds in the ethylene oxide process on the ethylene-rich side has been described by R.M. Stewart (1971) and is considered in more detail in Chapter 13.

Another approach to the control of the feed composition has been outlined by Pickles (1971), who describes a method used in the production of formaldehyde by oxidation of methanol. The methanol–air feed is obtained by bubbling air through the methanol vaporizer. The feed is maintained on the methanol-rich side, mainly by ensuring that the temperature of the methanol in the vaporizer is sufficiently high.

The hazard of a flammable mixture is much less if the burning velocity is low, which it is near the flammability limits. In the methanol–air system the burning velocity is low not only at the upper flammability limit but also some way inside it. In the system described by Pickles this fact is exploited.

If the risk of ignition is judged sufficiently low, the reaction may be carried out within the flammable limits. R. Davies (1979) cites benzene and propylene oxidation as two processes which have been operated in this way.

Liquid phase oxidations are typically carried out in tank reactors at a pressure in the range 10–50 bar and a temperature in the range 100–200°C. Air is bubbled into the reactor by a sparge pipe.

One of the main liquid phase processes is the oxidation of cyclohexane to cyclohexanone and cylcohexanol. This was the process at Flixborough. It has been described in *The Oxidation of Cyclohexane* (Berezin, Denison and Emmanuel, 1966) and by Haberle (1971). In this process, which is carried out industrially at pressures in the range 10–25 bar and temperatures in the range 140–170°C, the conversion per pass has to be kept to a few per cent in order to minimize undesirable side reactions. Therefore, heat removal is fairly simple. The principal hazard is the large amount of cyclohexane liquid which is held in and circulated around the reactors.

The air inlet line can be a hazard in a liquid phase oxidation process. It is known that in the manufacture of KA, a mixture of cyclohexanone and cyclohexanol, by air oxidation of cyclohexane a blackened product is occasionally made. The conditions under which this 'black KA' is produced are always those of start-up. The cause is that liquid from the reactor flows back up the line, stays there until the plant is started up and then catches fire when the air flow resumes. The temperatures reached are sufficient to melt through the air pipe. There is a hazard, therefore, that the reactor contents may escape through this line. The phenomenon has been discussed by Alexander (1974).

The hazards of oxidation processes have been reviewed by R. Davies (1979). He describes the transition in liquid phase oxidations from batch reactors to large-scale continuous reactors. This growth was accompanied by an increasing number of incidents.

Davies identifies three principal hazards of oxidation processes, in the liquid or vapour phase: flammable release, internal ignition and unstable or reactive substances. The majority of liquid phase oxidation processes require a large inventory held at a temperature above the boiling point. This creates the potential for a large release of flashing flammable liquid. Moreover, the operating conditions are quite difficult, which increases the risk that such a release will occur.

A second hazard of liquid phase oxidations is internal ignition. This can occur if for any reason the concentration of oxygen builds up in the vapour space. Such build-up may happen if the dispersion of the air in the liquid is poor or if the oxygen is not immediately absorbed and reacted. In some processes a flammable mixture can occur where recycle offgas is mixed with the air prior to injection into the liquid.

Vapour phase oxidation processes have a low inventory of process fluids, but a flammable release hazard may still

exist where there is a large inventory of flammable heat transfer fluid. Single-pass, atmospheric processes may be protected against internal ignition by explosion venting, but this is more difficult to do where the process is at higher pressure or involves recycle.

The products of oxidation processes tend to contain unstable substances, which in some cases can constitute a severe hazard. These include cumene hydroperoxide and ethylene oxide. Another is acetaldehyde, though this is more readily controlled. Davies gives a detailed account of the characteristics of, and precautions against, these substances.

Davies identifies four oxidation processes which have been responsible for a relatively large number of incidents. They are the liquid phase oxidations of cyclohexane and cumene, the vapour phase oxidations of ethylene and naphthalene or *o*-xylene. He gives a list of incidents and identifies several factors which have contributed to such incidents. One is the use of a series of liquid phase reactors in cascade with insufficient attention paid to the interconnecting pipework. Another is modifications which are intended to increase yield or to improve thermal economy but which also increase inventory and complexity. A third is deficiencies of various kinds in the trip systems.

An account of the continuing problem of liquid phase oxidation processes has been given by Alexander (1990b,c). The loss potential in an oxidation process can be large and the margin between a minor and a major incident small. He deals in particular with internal ignition. Such incidents are relatively frequent, but tend not to be reported.

The author suggests that most internal ignitions are due to a common cause and puts forward the following hypothesis. Oxidizable material is exposed to air at a temperature high enough to initiate liquid phase oxidation. Poor dispersion of the air allows a high concentration of oxygen to build up close to the liquid–air interface and a flammable mixture forms. Free radicals from the oxidation reaction in the liquid phase evaporate into the flammable mixture near the interface and ignite it. He cites the work of Sokolik (1960) in support of the ability of free radicals to ignite a flammable mixture well below the autoignition temperature. Alexander argues that this proposed mechanism is consistent with the wide variety of conditions in which ignitions occur. He refers also to other proposed mechanisms of ignition, including deposits of peroxides, of pyrophoric materials, and of catalyst, and friction between metal surfaces. Alexander describes some of the situations in which internal ignitions occur, and gives explanations based on his hypothesis. These situations involve the formation of a flammable mixture, followed by ignition by free radicals from the liquid, present as bulk liquid or as liquid droplets. One is backflow of liquid into the air feed line. This can occur if the air flow is shut off but the isolation is not good enough to prevent the pressure of the air in the pipe in the reactor falling below that of the liquid. It can occur if the air flow is interrupted momentarily. If the air temperature is above the critical value, burning will occur. This may result only in a very hot pipe, but can cause pipe failure followed by release of the reactor contents. If under very unfavourable circumstances a flammable mixture occurs along a sufficient length of the air pipe, there is potential for detonation.

Another situation with potential for internal ignition occurs where there is a recycle of fuel-rich offgas back into the air pipe, designed so that under normal operation the gas mixture downstream of the mixing point is also fuel-rich. If there is an upset, the mixture may enter the flammable range. Another such situation is where a temporary liquid diversion is made to flush out blockages in the air line.

Alexander also describes precautions which can be taken. One is the design of the air line, which should be such that liquid is not likely to be held up if there is an interruption of the air flow. The line should not rise up through the bottom of the vessel. Nor should it enter through the top, since a leak from the pipe in the vapour space could give a flammable mixture there. The preferred configuration is for the air line to come down from a height, slope gently down to the vessel and then enter its side. Another precaution is positive isolation of the air line by a double block and bleed valve arrangement. Another is the use of cool air. Other precautions relate to recycle gas, liquid diversion, offgas analysis and explosion containment.

11.7.4 Hydrogenation

The hydrogenation reactions considered here are those of an organic compound with molecular hydrogen in the presence of a catalyst. Some principal hydrogenation reactions include:

Vapour phase
Carbon monoxide → methanol
Olefins → paraffins

Liquid phase
Coal → oil

The thermodynamic equilibrium in hydrogenation reactions is almost invariably such that the yield falls as temperature rises and therefore the reaction temperature is a compromise between high reaction yield and high reaction rate.

Hydrogenation reactions are generally exothermic. The reaction usually occurs only on the catalyst, so that the local surface temperature can be very high. This may result in undesirable side reactions and catalyst deterioration, and may have implications for reactor materials of construction and for control.

The activation energy of hydrogenation reactions is normally low. For most hydrogenation reactions an increase in temperature of 50°C or more is required to double the reaction rate. There are few for which an increase of 10°C is sufficient to do this.

Vapour phase hydrogenations are carried out typically in the pressure range from atmospheric to several hundred bar and in the temperature range 100–400°C. Most catalysts used in hydrogenations are also capable of promoting oxidation. Also catalysts can be rendered more pyrophoric by the adsorption of hydrogen. Hydrogenation involves the hazards of the use of hydrogen under pressure. These are considered elsewhere, but particularly in Section 11.9.

11.7.5 Chlorination

The chlorination reactions considered here are those of an organic compound with molecular chlorine. Some principal industrial chlorination reactions include:

Vapour phase
Methanol → chloromethanes

Liquid phase
Ethylene → ethylene dichloride

Chlorination reactions have many similarities with oxidation reactions. They tend not to be limited by

thermodynamic equilibrium, but there can be problems of the reaction of complete chlorination and of side reactions to unwanted by-products.

Again the reactions are generally exothermic and often highly so, with the result that there tends to be a problem of heat removal and temperature control. For the substitution reaction

$$RH + Cl_2 \rightarrow RCl + HCl$$

the heat of reaction is about 24,000 kcal/kmol of chlorine.

The vapour phase reaction of chlorine with paraffinic hydrocarbons is apt to become too violent and it may be necessary to take measures to prevent this. These include limiting the proportion of chlorine or admitting it in stages and using diluents such as nitrogen or recycle gases.

Vapour phase reactors are typically empty vessels or packed beds. Chlorine, like oxygen, forms flammable mixtures with organic compounds. Thus, for example, the following flammability limits have been quoted for methane:

	Oxygen	*Chlorine*
Lower flammability limit (%)	5.2	5.6
Upper flammability limit (%)	60.5	70.0

Further details are given by Daniel (1973).

The reactor feed in vapour phase chlorinations is kept outside the flammable range. Liquid phase reactions are frequently carried out by blowing the chlorine and organic reactants into liquid product in a tank reactor.

11.7.6 Nitration

The nitration reactions considered here are those of an organic compound with a nitrating agent such as nitric acid or mixed acid. Mixed acid is nitric acid admixed with a dehydrating acid such as sulfuric acid. Nitration accidents are among not only the most frequent but also the most destructive in the chemical industry. The processes for the manufacture of nitroglycerine (NG) and trinitrotoluene (TNT) are particularly sensitive.

The typical nitration is a batch process carried out in the liquid phase and it is this which is discussed first. Nitric acid is not only a nitrating agent but also an oxidizing agent. The nitration and the oxidation reactions both constitute a hazard. Nitric acid is itself a hazardous chemical, since it is not only a corrosive substance but also a strong oxidant. As indicated, it may react explosively with some organic liquids.

Both the nitration reaction itself and the oxidation reaction are strongly exothermic. Since nitration mixtures are often very sensitive and liable to explode, unless conditions are closely controlled, this strong heat generation is a problem. The heat evolved in a nitration reaction includes not only the heat of nitration but also the heat of dilution. Thus the heat of nitration of benzene is 761 BTU/lb, but under certain conditions the heat released by reaction and dilution is 895 BTU/lb.

Nitration reactions may constitute a hazard due to a reaction exotherm or a sensitive product. In some incidents the phenomena appear not to have been recorded previously, but in others the hazard was known in general terms, but its full implications have not been appreciated. There have been a number of explosions in nitration reactors which have subsequently been shown to have been due to the fact that the temperature of the reaction was too close to that at which a runaway reaction could start. The temperature differences between the main reaction and the runaway reactions have been typically of the order of 10–50°C. Similarly, explosions have occurred due to the sensitivity of the product of the nitration. Some nitro compounds have a quite low decomposition temperature, in the range 100–150°C, and are thus relatively hazardous. Information is available on this aspect (e.g. T.L. Davis, 1943; Kirk and Othmer, 1963–, 1978–, 1991–).

Rapid autocatalytic decompositions or 'fume-offs' of nitration products sometimes occur. Often they do not involve an explosion, but are nevertheless quite violent. Factors which have contributed to explosions due to runaway reactions or sensitive materials have included lack of knowledge and lack of appreciation of the need for particular precautions and for a wide margin of safety.

Nitrations are frequently carried out in stirred batch reactors. This type of reactor has certain characteristic hazards. These include the charging of reactants in incorrect quantities or sequence and the accumulation of unmixed reactants which react violently when the agitator is switched on.

Another hazard in nitration reactions is the ingress of water. The addition of water to the nitration mixture may result in a large release of heat which causes an explosion either directly or by initiating some other effect.

Whereas the other unit processes considered above are carried out in plants dedicated to that single process, nitrations are frequently performed in plants which make a number of products on a campaign basis. This method of manufacture introduces some additional opportunities for error.

Since nitration often presents problems both in respect of runaway exotherms and heat-sensitive products, it is especially important to have full information about the reaction and the products, particularly for a new reaction. Many of the problems of nitration are alleviated by the use of a continuous nitration process. The nitration is carried out in several vessels, each of which has a smaller holdup and time-invariant operating conditions. Many stages such as charging and discharging, precooling and preheating are eliminated, as are some items of equipment such as pumps. The process is more readily adaptable to automatic control. There is less human intervention and thus both less human error and less exposure of personnel. The evolution of nitroglycerine manufacture from a process using a batch reactor to a continuous process carried out in a nozzle has already been described.

Nitration is also carried out in the vapour phase. A further discussion of safety in nitration processes is given by Biasutti and Camera (1974). An accident in a nitration process is described in *Case History B22*.

11.8 Unit Operations and Equipments

Unit operations include: mixing, dispersion; distillation, gas absorption, liquid–liquid extraction; leaching, ion exchange; precipitation, crystallization; centrifugation, filtration, sedimentation; classification, screening, sieving; crushing, grinding; compacting, granulation, pelletizing; gas cleaning; heat transfer; and drying and dehydration. A further listing is given by Fowler and Spiegelman (1968).

Characteristic types of equipment are associated with these different operations. Accounts of unit operations are given in *Chemical Engineering* (Coulson and Richardson, 1955–, 1977–), *Unit Operations of Chemical Engineering* (McCabe and Smith, 1967), *Handbook of Separation Techniques for Chemical Engineers* (Schweitzer, 1979), *Principles of Unit Operations* (Foust *et al*., 1980), *Chemical Engineers Handbook* (Perry and Green, 1984) and *Handbook of Separation Processes* (Rousseau, 1987) and by McCabe, Smith and Harriott (1985).

The unit operations and equipments considered here by way of illustration are: (1) mixers, (2) centrifuges, (3) driers, (4) distillation columns and (5) activated carbon adsorbers. All five feature in the CCPS *Engineering Design Guidelines* (1993/13) and the first three are the subject of IChemE guides.

There is a large group of unit operations in which dusts are handled with the associated hazard of dust explosion. This includes driers, as described below. Further treatment of this and other operations involving dusts is given in Chapter 17.

Other equipments such as fired heaters, heat exchangers, pumps and compressors are treated in Chapter 12 as parts of the pressure system. Selected references on unit operations and equipments and their hazards are given in Table 11.5.

Table 11.5 *Selected references on unit operations and equipments and their hazards*

API (1979/1); McCabe, Smith and Harriott (1985); Elvers *et al.* (1988); CCPS (1993/13)

Adsorbers
Chapman and Field (1979); Anon. (1986 LPB 69, p. 257); CCPS (1993/13)

Agitation, mixing
Garrison (1981); Schofield (1982, 1983); Harnby, Edwards and Nienow (1985); Kneale (1985 LPB 62); Sandier and Luckiewicz (1987); Ulbrecht and Patterson (1985)

Autoclaves
HSE (1990 PM 73)

Centrifuges
Thrush and Honeychurch (1969); E.B. Price (1970); P. Peterson and Cutler (1973); Butterwick (1976); Funke (1976); Simon (1976); O'Shea (1983); Lindley (1985, 1987); IChemE (1987); Bange and Osman (1993); BS 767: 1983

Conveyors
Anon. (1977i); Ewart Chainbelt Co. Ltd (1977); Conveyor Equipment Manufacturers Association (1979); BS 490: 1975–, BS 2890: 1989

Crushing and grinding equipment
Anon. (1962b); Stern (1962); K.N. Palmer (1973a); Anon. (1979 LPB 26, p. 48); Moir (1984)

Distillation
Guerreri (1969); McLaren and Upchurch (1970); Frank (1977); R.G. Hill (1977); Shah (1978); G.F.P. Harris, Harrison and Macdermott (1981); Nisenfeld and Seeman (1981); Anon. (1983s, 1987g); L.M. Rose (1985); M.E. Harrison and France (1989); Strofer and Nickel (1989); Hower and Kister (1991); Love (1992)

Driers
Sloan (1967); Keey (1973, 1978); K.N. Palmer (1973a); Glatt (1977); Reay (1977); Grafton (1983); van't Land (1984); Walsh (1984); N. Gibson, Harper and Rogers (1985); Schacke and Falcke (1986); IChemE (1989/134); Abbott (1990); Papagiannes (1992)

Dust-handling plant
Merrill and Velentine (1942); Sargent (1969); K.N. Palmer (1973a); Schafer (1973b); Batel (1976); Horzella (1978); IChemE (1978/116, 1992/32); M.N. Kraus (1979a,b); Anon. (1981b); Bartknecht (1981a, 1989); M.A. Maxwell (1981); P. Swift (1984); D.M. Muir (1985); Mody and Jackhete (1988); Eggerstadt, Zievers and Zievers (1993); Opila (1993); VDI 2263: 1990–

Electrostatic coating
Luderer (1987)

Electrostatic precipitators
H.J. White (1963); H.E. Rose and Wood (1966); Hanson and Wilke (1969); K.N. Palmer (1973a); Schneider *et al.* (1975a,b); Bump (1977); Frenkel (1978); Lewandowski (1978); Oglesby and Nichous (1978); Bohm (1982); Coleman (1984); Jaasund (1987)

Evaporating ovens
HSE (1974 HSW Booklet 46, 1981 HS(G) 16)

Gas absorption
Astarita, Savage and Bisio (1983)

Heat treatment baths
HSE (1971 HSW Booklet 27, 1975 SHW 849); FPA (1974 S8)

Oil–water separators
Chambers (1978)

Polymer processing
Sullivan (1989)

Solids handling
Mechanical Handling Engineers Association (1962); Weisselberg (1967); Notman, Gerrard and de la Mare (1981); IChemE (1985/126); Grossel (1988)

Pneumatic conveying
EEUA (1963 Handbook 15); M.N. Kraus (1965, 1966a,b, 1986); Gluck (1968); D. Smith (1970); Stoess (1970); K.N. Palmer (1973a); Weston (1974a); Gerchow (1975); Caldwell (1976); Barker (1981); O.A. Williams (1983); Maunder (1985); D. Mills (1990); Dahn (1993)

Spray driers
Belcher, Smith and Cook (1963); Sloan (1967); Masters (1972, 1979); N. Gibson and Schofield (1977); Christiansen (1978); Long (1978); Bartknecht (1981a)

Vaporizers
G.T. Wright (1961); W.H. Doyle (1972a); E.R. Peterson and Maddox (1986); R.A. Smith (1987)

Vapour–liquid separators
Gerunda (1981); Purarelli (1982); Wu (1984); Tsai (1985)

Water treatment
Gilwood (1963); Boby and Solt (1965); Arden (1968); Seels (1973); Webb (1974); Betz Laboratories Inc. (1976); D.R. Smith (1976); Rue (1977)

Ancillary equipment
Anon. (1978 LPB 24, p. 167); API (1980/2); Klein (1993)

11.8.1 Mixers

Mixers present a variety of hazards. An account of hazards of, and precautions for, mixers is given in the *Guide to Safety in Mixing* (Schofield, 1982) (the IChemE *Mixer Guide*). The body of the *Mixer Guide* is in the form of a checklist of hazards and precautions under the headings: (1) equipment, (2) operations, (3) substances and (4) plant.

The equipment should be suitable for its purpose. Dead spaces where reactions may occur or material may solidify should be avoided. The mixer body may be subjected to pressure or vacuum and to fatigue due to any vibration. It may experience out-of-balance loads such as the dropping in or the shifting of the charge. It should be capable of withstanding these different effects.

The rotating parts may experience inertia loads on start-up and out-of-balance loads during operation. Loads may be imposed due to high liquid viscosity or high powder shear resistance. Other hazards include entry of foreign material such as tramp metal and contact between the impeller and the body of the vessel due to bending of the shaft. There is a critical speed for an impeller. It should normally not be run between 70 and 100% of this critical speed.

There are various features that may constitute weak points on a mixer. They include closures, sight glasses, instruments, sample points on the body, and bearings and seals on the agitator. The moving parts and the charge may present a hazard to personnel. The moving parts may include the mixer body or other features such as counterbalanced closures. Other hazards include unguarded impellers, splashing or even ejected material, or ejected objects.

Failure of utilities can cause problems for mixers. Some failures include loss of electrical power to the agitator, loss of cooling, loss of inerting and loss of exhaust ventilation. If there is loss of agitation, reactions may occur or material may solidify. Another hazard of failure of electrical power is unexpected restart of the mixer. It should be arranged that the mixer does not restart automatically following restitution of power after a power failure. Measures should also be taken to prevent other inadvertent start-up of the mixer.

Mixers sometimes handle flammable materials. Sources of ignition characteristic of mixers are hot surfaces, friction and impact, and static electricity. Hot surfaces include electric motor casings, drive components, bearings and lamps. Friction and impact can occur due to breakage of rotating parts, entry of foreign material or contact between the impeller and the vessel. Friction may also occur due to bearings or seals running dry. Static electricity may be generated during the loading or during mixing of liquids or powders. A principal precaution against ignition is inerting.

The plant layout should provide good access to the mixer for operation and maintenance and should cater for foreseeable leaks and spillages. Operational hazards include: overfilling, leading to overpressure or spillage; underfilling, leading to splashing or, if the mixer is nearly empty, mechanical damage; and overmixing, leading to thickening, overheating or overreaction of the mixture.

The *Mixer Guide* describes some of the principal types of mixer such as the rotating shape (double cone), orbiting screw, 'U' trough, high speed rotor, Muller, top entry agitator (stirred tank), agitated bead mill (attrition), change can, planetary, heavy paste (Z-blade), internal (Banbury), roll mills and mixer/extruder types, and gives a matrix of mixer types vs relevant hazards.

Two precautions which find widespread use on mixers are fixed guards and interlocks. Fixed guards include annular covers around agitators and bars to prevent entry of a limb into a running nip. These are complemented by non-manual methods of loading and discharging such as chutes and feed belts.

Interlocks are used to prevent a mixer from being started up or approached unless it is in a safe condition. One application is to ensure that the cover is closed, another to ensure that the agitator is properly centred in the body and another to prevent access either to the agitator shaft or to the mixer body while it is moving. The *Mixer Guide* gives a number of examples.

A further treatment of mixers is given in the CCPS *Engineering Design Guidelines*.

11.8.2 Centrifuges

Centrifuges likewise present a variety of hazards. The hazards of, and the precautions for, centrifuges are considered in the *User Guide for the Safe Operation of Centrifuges with Particular Reference to Hazardous Atmospheres* (Butterwick, 1976) and the later publication *User Guide for the Safe Operation of Centrifuges* (Lindley, 1987) (the IChemE *Centrifuge Guide*).

Centrifuges often handle volatile flammable liquids and, unless special precautions are taken, are almost certain to contain a flammable mixture at some stage in the operational cycle. The probability of ignition of the flammable mixture is quite high. Main sources of ignition are mechanical friction, hot surfaces and static electricity. A centrifuge rotates at high speed and a mechanical fault, leading to a spark, or a hot surface, can cause ignition.

The movement of the slurry in an operating centrifuge favours the generation of static electricity, particularly if the liquid has a high resistivity. Alternatively, if the centrifuge is stopped and open, a static electricity hazard may occur from an operator who has too high an insulation path to earth.

There is also a mechanical hazard from the high kinetic energy of the rotating centrifuge bowl. The main causes of mechanical failure are basket imbalance, incorrect assembly, corrosion and bearing failure.

Since centrifuge operations involve frequent opening of the centrifuge, there is with some substances a toxic hazard. This may be an immediate, acute hazard or a long-term cumulative one.

If there is an explosion hazard in a centrifuge, it should be blanketed with inert gas, usually nitrogen. The maintenance of an inert atmosphere should be monitored. The three monitoring systems commonly used are based on measurement of: (1) flow of inert gas into centrifuge, (2) pressure of gas in centrifuge and (3) oxygen concentration of gas in centrifuge. The most suitable system depends on the degree of hazard. But the system based on the measurement of oxygen concentration, which is the variable of direct interest, is the most positive and should be used for high risk situations.

If there is a toxic hazard, the centrifuge system should be enclosed as far as practicable. Local exhaust ventilation should be provided. Alternatively, it is possible to extract from the casing and operate under a negative pressure, provided that the liquid is not flammable. Other measures which may be required include provision of a forced air supply or of breathing equipment for the operator.

Centrifuges are treated further in the CCPS *Engineering Design Guidelines*.

11.8.3 Driers

The principal hazards presented by driers are those of fire and explosion. These hazards and the corresponding precautions are discussed in *Prevention of Fires and Explosions in Dryers* (Abbott, 1990) (the IChemE *Drier Guide*). This is the second edition of, and thus supersedes, the *User Guide to Fire and Explosion Hazards in the Drying of Particulate Materials* (Reay, 1977).

The *Drier Guide* states that each year in the United Kingdom driers are responsible for 30 fires and one explosion serious enough to be attended by the local fire brigade. A detailed account of the self-heating of combustible materials is given in Chapter 16 and of combustibility and explosibility of dusts and of dust fires and explosions and dust explosion venting in Chapter 17, and the treatment given here is correspondingly limited.

Differences between the first and second editions of the *Drier Guide* are in large part accounted for by the up-dating of the methods for explosibility testing and for explosion suppression and venting. The identification of hazards in powders which are to be dried is described in Chapter 8. The *Drier Guide* assumes that the materials processed are essentially materials which may be combustible but are not either explosive or liable to decomposition. The following discussion is concerned with such combustible materials.

With regard to the oxygen concentration to prevent ignition, the *Drier Guide* states that if the published values are unacceptably low for efficient plant operation, the minimum oxygen concentration to support combustion should be established by tests performed using the modified vertical tube apparatus described by Field (1982).

There are three forms in which a combustible material being processed in a drier may be ignited: (1) dust cloud, (2) dust layer and (3) bulk dust.

A dust cloud of explosible concentration will normally occur only in driers where the material is dispersed such as in a fluidized bed drier or a spray drier. In other types of driers such as tray and band driers there should be no dispersed dust, provided the air velocity is kept sufficiently low. If there is a dust cloud, it will almost certainly be within the explosible range. The dust cloud may be ignited by an ignition source. Alternatively, ignition may occur if the cloud is raised above its minimum ignition temperature.

Dust may also form in layers inside the drier. A dust layer may be ignited by an ignition source. Alternatively ignition by self-heating may occur if the dust layer is exposed to an ambient temperature above its minimum ambient temperature for self-ignition.

Ignition may also occur in the bulk dust, for which there is a separate minimum ignition temperature. Since the heat loss from the bulk material is less than from a layer, this minimum ignition temperature is lower than that for a dust layer.

A dust explosion may be prevented by the use of inerting. The concentration of inert gas should be such as to reduce the oxygen concentration below the minimum oxygen concentration required to support combustion.

Dust properties relevant to drier design, therefore, include in particular the minimum ignition temperature of the dust cloud, the minimum ambient temperature of ignition of a dust layer, the minimum ignition temperature for the bulk dust and the minimum oxygen concentration to support combustion. The minimum ignition energy of the dust cloud is also relevant. The design of dust explosion venting systems utilizes information on the dust K_{st} class. Particle size is a strong determinant of these properties. Account should also be taken of the fact that if the dust contains any significant amount of flammable liquid, there is a hybrid mixture, with enhanced explosibility.

Many of the regular ignition sources apply to driers. These include hot work, hot surfaces, electrical equipment, and friction and impact. A direct heating system may give rise to hot particles which can act as an ignition source and precautions are taken against this. Air for combustion should be drawn from a source free of dust. Avoidance of dust in this air should be a factor taken into account when considering recirculation of air from the drier. Burners should be cleaned regularly and operated so as to give complete combustion. Erratic operation and flame blow-off should be remedied without delay. Before entering the drier, the hot gases should be passed through a 3 mm mesh to screen out hot particles. The mesh should be able to withstand the high temperatures and should be cleaned regularly. A direct heating system should not be used to evaporate flammable vapours.

Precautions against explosion may be based on prevention or protection. The main preventive measure given in the *Drier Guide* is inerting. The guide gives three main protective measures: venting, suppression and containment.

On the basis of the hazard evaluation a basis of safety should be chosen. The *Drier Guide* states that one measure is sufficient. If inerting is used, there should be continuous on-line monitoring of the oxygen concentration. With some driers there is a facility to recirculate part of the exhaust air to improve thermal efficiency. The gas entering the drier will then have a higher concentration of water vapour and, if it is direct fired, a higher concentration of carbon dioxide also. This provides a degree of inerting and such driers are described as 'self-inertizing'.

The *Drier Guide* gives a detailed discussion of the application of explosion suppression and explosion venting methods to driers. It also discusses the applicability of explosion containment, including pressure shock containment, to which it adopts a cautious approach. It points out, however, that containment may well be a practical option for a vacuum drier, where the initial pressure is much lower.

Measures which protect against a dust explosion, whether explosion suppression, venting or containment, do not necessarily offer protection against a sudden decomposition of the material, with a massive evolution of gas. Measures should also be taken to prevent the spread of dust fire or explosion to other parts of the plant. The process should be specified so as to minimize the hazard. The inlet air temperature is a particularly important variable and the *Drier Guide* discusses in detail the relevant factors and safety margins for different types of drier.

There are various items of equipment which are common to drying plants. They include heating systems, feed systems, dust conveying and recovery systems, and product storage vessels. Dust recovery systems include cyclones, filters, electrostatic precipitators, and scrubbers and washers.

The heating system should be designed in accordance with the codes for gas or oil fired heaters, as the case may be. It should have the appropriate instrumentation, including alarms, trips and interlocks.

Protection should be provided against explosion of a fuel–air mixture in the firing space. Suitable relief should be provided against such an explosion, unless the drier is

designed for an explosible dust and is thus already provided with a dust explosion relief which can serve both purposes; where such a dust explosion relief exists, it will generally be adequate for the flammable gas explosion.

Self-heating of material passing hot from a drier to product storage is a hazard. The maximum safe temperature for discharge to storage may be determined for many situations from thermal ignition theory in combination with empirical tests. Measures to reduce the risk of self-heating include limitation of the size of storage vessel and monitoring of the temperature of the material in the vessel.

The operation and maintenance of driers also have certain common features. The *Drier Guide* discusses the operational aspects under the headings of pre-start-up checks, start-up, normal operation, normal shut-down and emergency shut-down. The guide gives what amount to checklists for pre-start-up checks and maintenance.

The *Drier Guide* describes some of the principal types of driers such as spray driers, pneumatic conveying driers, fluidized bed driers, rotary driers, band driers, batch atmospheric tray driers, batch vacuum driers and trough driers. For each type of drier it discusses the principle of operation, hazards, ignition sources, preventive and protective measures, process specification, equipment specification, and operation and maintenance. The CCPS *Engineering Design Guidelines* provide a further treatment of driers.

11.8.4 Distillation columns

Distillation columns present a hazard in that they contain large inventories of flammable boiling liquid, usually under pressure. There are a number of situations which may lead to loss of containment of this liquid.

The conditions of operation of the equipment associated with the distillation column, particularly the reboiler and bottoms pump, are severe, so that failure is more probable.

The reduction of hazard in distillation columns by the limitation of inventory has been discussed above. A distillation column has a large input of heat at the reboiler and a large output at the condenser. If cooling at the condenser is lost, the column may suffer overpressure. It is necessary to protect against this by higher pressure design, relief valves or HIPS. On the other hand, loss of steam at the reboiler can cause underpressure in the column. On columns operating at or near atmospheric pressure, full vacuum design, vacuum breakers or inert gas injection is needed for protection. Depostition of flammable materials on packing surfaces has led to many fires on opening of distillation column for maintenance.

Another hazard is overpressure due to heat radiation from fire. Again pressure relief devices are required to provide protection.

The protection of distillation columns is one of the topics treated in detail in codes for pressure relief such as API RP 521. Likewise, it is one of the principal applications of trip systems.

Another quite different hazard in a distillation column is the ingress of water. The rapid expansion of the water as it flashes to steam can create very damaging overpressures.

11.8.5 Activated carbon adsorbers

Experience with activated carbon adsorbers indicates that they are another potentially troublesome operation. An account of this type of adsorber is given in the CCPS *Engineering Design Guidelines*.

Activated carbon adsorbers are prone to fires in the adsorbent bed. This is so particularly where the substance being adsorbed is an oxidizable organic such as an aldehyde, ketone or organic acid. Fires are especially likely to occur during a shut-down.

Countermeasures evolved to minimize the risk of fire include: paying attention to adsorbent purity; maintaining the moisture content of the adsorbent; operating at less than 25% of the lower flammability limit; and avoiding dead spots. The adsorbers should be located outdoors and provided with pressure relief and fire protection.

Among the measures used to prevent fire during a shut-down are maintenance of a gas flow 75% of normal, use of water or steam spray to keep the bed moist, inerting of the bed and removal of the bed.

The *Guidelines* give a checklist of precautions for activated carbon adsorbers.

11.9 Operating Conditions

Operation at extremes of pressure and temperature has its own characteristic problems and hazards. Extreme conditions may occur at: (1) high pressure, (2) low pressure, (3) high temperature and (4) low temperature.

Some general characteristics of these operating conditions are described below, together with some of the associated literature. In relation to extreme operating conditions in general, mention may be made of *Chemical Engineering under Extreme Conditions* (IChemE, 1965/40) and of the series *Safety in Air and Ammonia Plants* (1960–69/17–26), *Operating Practices in Air and Ammonia Plants* (1961–62/27–28) and *Ammonia Plant Safety and Related Facilities* (1970–94/31–53) by the American Institute of Chemical Engineers (AIChE).

A newer development in extreme operating conditions is the use of plasma processing. Selected references on extreme operating conditions and their hazards are given in Table 11.6.

11.9.1 High pressure

The range of pressures handled in high pressure technology is wide. Three broad ranges of pressure may be distinguished: (1) pressures up to about 250 bar, (2) pressures of several thousand bar, and (3) pressures greater than 8000 bar. Most process plants operate at pressures below 250 bar, but certain processes such as high pressure polyethylene plants operate at pressures up to about 3000 bar. Ultra-high pressures begin at a pressure of about 8000 bar, which is the probable limit of the simple elastic cylinder and at which it becomes necessary to use other types of construction such as wire-wound vessels. It is therefore important to minimize leaks by eliminating potential sources such as flanges, vents, bonnet seals, etc.

In general, pressure vessels in process design are not designed for explosive over pressures such as deflagration or detonation with certain exceptions (acetylene). Deflagration can produce over pressure of a factor of 9–10 whereas detonations can lead to a factor 40 or higher. Detonations are not expected in pressure vessels and rarely in pipelines. Appropriate arrestors should be provided for this condition (CCPS, 2000).

Normal high pressure plant is dealt with in numerous standard texts. Mention may be made here of *Theory and Design of Modern Pressure Vessels* (Harvey, 1974) and *Pressure Component Construction* (Harvey, 1980).

Table 11.6 *Selected references on extreme operating conditions and their hazards*

IChemE (1965/40); Zabetakis (1965); Pilborough (1971, 1989)

High pressure
ASME (Appendix 28 *Pressure Vessels and Piping*, PVP 192, 1982/154, 1986 PVP 110, 1987 PVP 125, 1988 PVP 148, 1989 PVP 165); ASTM (STP 374, 1982 STP 755); Tongue (1934); Newitt (1940); Comings (1956); Stevenston (1959); AIChE (1960–69/3–12, 1961–62/13,14, 1967/71, 1970–94/17–38, 1973/62, 1974/63, 1978/64); SCI (1962); F.W. Wilson (1962); E.L. Clark (1963); Bett and Burns (1967); Buchter (1967); Weale (1967); Albright, van Munster and Forman (1968); Manning and Labrow (1971); Munday (1971a); Karl (1973); Witschakowski (1974); Sykes and Brown (1975); Gilbert and Eagle (1977); IMechE (1977/39); Spain and Paauwe (1977); Vodar and Marteau (1980); Homan, MacCrone and Whalley (1983); Boyer (1984); Livingstone (1984); Sherman and Stadtmuller (1987); Prugh, Howard and Windsor (1993)

High temperature
ASME (Appendix 28 *Materials, Pressure Vessels and Piping*, 1975/71, 1979/137, 1982/156, 1983/164, 1984/172, 1989 PVP 163); I.E. Campbell (1956); Goldberger (1966); Kamptner, Krause and Schilken (1966b); I.E. Campbell and Sherwood (1967); Clause (1969); Albrecht and Seifert (1970); ASME (1971/65); IChemE (1971/50, 1975/62); Zeis and Lancaster (1974); AIChE (1986/84)

Low pressure, vacuum
Avery (1961); Davy (1951); EEUA (1961 Handbook 11); Pirani and Yarwood (1961); Steinherz (1962); Spinks (1963); van Atta (1967); Roth (1967, 1990); Dennis and Heppel (1968); Carpenter (1970); Mangnall (1971); AIChE (1972/74); O'Hanlon (1980); Ryans and Croll (1981); Patton (1983); R.V. Parker (1984); Ryans (1984); Ryans and Roper (1986); EEMUA (1987 Publ. 152); IChemE (1987/130); Sandier and Luckiewicz (1987); N.S. Harris (1989); Wutz, Adam and Walcher (1989); Eckles and Benz (1992); R.E. Sanders (1993b)

Low temperature
ASME (Appendix 28 *Materials, Pressure Vessels and Piping*, 1980/49; 1984/195); British Cryogenics Council (n.d., 1970, 1975); M. Davies (1949); Ruhemann (1949); Anon. (1960e); J.D. Jackson (1961); Burgoyne (1965b); Krolikowski (1965); Barron (1966–); AIChE (1968/72, 1972/74, 1982/77, 1986/83); Codlin (1968); Harton (1968); Ligi (1969); IChemE (1970/49, 1972/53, 1975/ 59); V.C. Williams (1970); Haselden (1971); R.W. Miller and Caserta (1971); Edeskuty and Williamson (1983); Springmann (1985); CGA (1987 P-12)

Supercritical conditions
Korner (1985); Penninger *et al.* (1985); Randhava and Calderone (1985); McHugh and Krukonis (1986)

Plant for higher pressure is a more specialized technology. It is treated in *The Design and Construction of High Pressure Chemical Plant* (Tongue, 1934), *The Design of High Pressure Plant and Properties of Fluids at High Pressure* (Newitt, 1940), *High Pressure Technology* (Comings, 1956), *Apparate und Armaturen der Chemischen Hochdrucktechnik* (Buchter, 1967), *High Pressure Engineering* (Manning and Labrow, 1971), *High Pressure Technology* (Spain and Paauwe, 1977), *High Pressure in Science and Technology* (Vodar and Marteau, 1980) and *Experimental Techniques in High Pressure Research* (Sherman and Stadtmuller, 1987), and by Homan, Maccrone and Whalley (1983).

Further accounts of high pressure technology and its hazards are given by Stevenston (1959), Munday (1971a), Sykes and Brown (1975), B.G. Cox and Saville (1975), Boyer (1984), Livingstone (1984) and Prugh, Howard and Windsor (1993).

The relevant standard for high pressure plant is BS 5500: 1976 Unfired Fusion Welded Pressure Vessels. There is no UK standard for very high pressure plant.

High pressures are usually associated with high and/or low temperatures.

The use of high pressure greatly increases the amount of energy available in the plant. Whereas in an atmospheric plant stored energy is mainly chemical, in a high pressure plant there is, in addition, the energy of compressed permanent gases and of fluids kept in the liquid state only by the pressure.

Since the economies of scale apply very strongly to compression, the number of compressors used is generally small. Often there is a single compressor for a particular duty. The machines themselves are large and their technology is complex.

Although high pressures in themselves do not pose serious problems in materials of construction, the use of high temperatures, low temperatures or aggressive materials does. Thus, the problem is to obtain the material strength required by high pressure operation despite these factors.

With high pressure operation, the problem of leaks becomes much more serious. The amount of fluid which can leak out through a given hole is greater on account of the pressure difference. Moreover, the fluid may be a liquid which flashes off as the pressure is reduced.

11.9.2 Low pressure

The degrees of vacuum handled in low pressure or vacuum technology span many orders of magnitude. In the present context, it is relatively low vacuum from 760 torr (atmospheric pressure) to 1 torr and medium vacuum from 1–10^{-3} torr which are the ranges of prime interest.

Normal vacuum technology is treated in *Industrial High Vacuum* (Davy, 1951), *Principles of Vacuum Technology* (Pirani and Yarwood, 1961), *Vacuum Technology* (Spinks, 1963), *Vacuum Science and Engineering* (van Atta, 1967), *Vacuum Sealing Techniques* (Roth, 1967), *Vacuum System Design* (Dennis and Heppel, 1968), *A User's Guide to Vacuum Technology* (O'Hanlon, 1980), *Process Vacuum System Design and Operation* (Ryans and Roper, 1986), *Modern Vacuum Practice* (N.S. Harris, 1989), *Theory and Practice of Vacuum Technology* (Wutz, Adam and Walcher, 1989) and *Vacuum Technology* (Roth, 1990). Low pressures are not in general as hazardous as the other extreme operating conditions. But a hazard which does exist in low pressure plant handling flammables is the ingress of air, with consequent formation of a flammable mixture.

A major part of vacuum technology is concerned with detecting and preventing leaks. The techniques developed in this field may be relevant, therefore, to plants under positive pressure, particularly those handling very toxic materials.

11.9.3 High temperature

The literature on high temperature technology is relatively diffuse and deals mainly with particular types of plant (e.g. ammonia plants), or particular types of equipment (e.g. fired heaters). Mention may be made, however, of *High Temperature Materials and Technology* (I.E. Campbell and Sherwood, 1967).

As already mentioned, the use of high temperatures in combination with high pressures greatly increases the amount of energy stored in the plant. The heat required to obtain a high temperature is often provided by fired heaters. These have a number of hazards, including explosions in the firing space and rupture of the tubes carrying the process fluid.

There are severe problems with materials of construction in high temperature plants. The main problem is that of creep at high temperatures. But there are other problems also, such as hydrogen embrittlement. The use of high temperatures implies that the plant is put under thermal stresses, particularly during start-up and shutdown. It is essential to take these stresses fully into account in the design.

It is equally necessary to operate the plant with regard to the temperature effects. Its life can be much shortened by excursions inside the high creep range or by transients which cause high thermal stresses. Relatively low cyclical temperatures such as in driers, and absorbers when regenerating, can lead to greatly reduced service life.

11.9.4 Low temperature – cryogenics

The temperatures handled in low temperature technology are those below 0°C. There is a somewhat distinct technology dealing with ultra-low temperatures below 20 K, but this is not of prime interest in the present context.

Normal low temperature technology is dealt with in *The Physical Principles of Gas Liquefaction and Low Temperature Rectification* (M. Davies, 1949), *The Separation of Gases* (Ruhemann, 1949), *Cryogenic Systems* (Barron, 1966–), *Cryogenic Fundamentals* (Haselden, 1971) and *Liquid Cryogens* (Edeskuty and Williamson, 1983). Mention should also be made of the *Cryogenic Safety Manual* by the British Cryogenic Council (BCC, 1970).

Low temperature plants contain large amounts of fluids kept in the liquid state only by pressure and temperature. If for any reason it is not possible to keep the plant cold, then the liquids will begin to vaporize.

Impurities in the fluids in low temperature plant are liable to come out of solution as solids. This is particularly likely to happen if parts of the plant are allowed to boil dry. Deposited solids may be the cause not only of blockage but also, in some cases, of explosion. It is necessary, therefore, to ensure that the fluids entering a low temperature plant are thoroughly purified.

Careful attention must be paid to the establishment and compliance with the vessel operating parameters. In most cases low temperatures are the result of advertent or inadvertent depressurization of light hydrocarbon materials, which greatly reduces the hazard. Care must be taken on repressurization to allow the materials to reach a safe temperature.

A severe materials of construction problem in low temperature plants is low temperature embrittlement. The materials requirements, however, are well understood. The main difficulties arise from aspects such as installation of incorrect materials or flow of low temperature fluids into sections of the plant constructed in mild steel.

In low temperature as in high temperature operations the plant is subject to thermal stresses, especially during start-up and shut-down. These stresses need to be allowed for and, as far as possible, avoided.

The insulation on low temperature plant frequently takes the form of a cold box. It is not easy to gain access to equipment inside the cold box. It is important, therefore, for the equipment to be as reliable and the fluids processed as pure as possible.

In low temperature plant the temperature approaches used in the heat exchangers are very close, say 3°C. This is done to achieve maximum thermodynamic efficiency, since any inefficiency is paid for directly in the power required for compression. The use of such close temperature approaches is another reason for avoidance of fouling by keeping the fluids free of impurities.

The scale of operation in low temperature technology can be very large. In particular, the largest storages of hazardous liquids, both flammables and toxics, tend to be refrigerated storages.

11.10 Utilities

The process plant is dependent on its utilities. These include in particular:

(1) electricity
  (a) general,
  (b) uninterrupted power supplies,
  (c) electrical heating;
(2) fuels;
(3) steam;
(4) compressed air
  (a) plant air,
  (b) instrument air,
  (c) process air,
  (d) breathing air,
(5) inert gas;
(6) water
  (a) cooling water,
  (b) process water,
  (c) hot water,
  (d) fire water;
(7) heat transfer media
  (a) hot fluids,
  (b) refrigerants.

There may also be other special services on particular plants. Selected references on utilities are given in Table 11.7.

Important features of a utility are its: (1) security, (2) quality, (3) economy, (4) safety and (5) environmental effects.

One of the main causes of failure of supply of a utility is loss of part of the generating capacity followed by rapid overload of the rest, leading to total loss. In order to avoid this, measures may be taken to effect load shedding at the less essential points of consumption. Specific application of this principle is discussed below for electricity and steam.

It is often attractive to use a ring main layout to distribute a service. This allows the supply to a given point to be provided from either side and thus increases reliability. It is necessary, however, to give careful consideration to the flows which can occur in ring mains, particularly those handling steam.

Table 11.7 *Selected references on utilities and their hazards*

NRC (Appendix 28 *Utilities*); D.T. Smith (1965c, 1982); Butikofer (1974); Monroe (1970); W.B. Thomas (1981); API (1981/4); Kletz (1988m); Broughton (1993)

Electricity
American Oil Company (n.d./5); BG (Appendix 27 *Electrical*); EEUA (Doc. 37D, 1964 Doc. 17); HSE (HSW Booklet 31, 1970 HSW Booklet 24,1985 OP 10,1991 GS 47); ICI (n.d.b); IEEE (Appendix 27); IEE (1966 Conference Publ. 16, 1971 Conference Publ. 74, 93, 1974 Conference Publ. 108, 110, 1975 Conference Publ. 134, 1977 Conference Publ. 148, 1982 Conference Publ. 281, 1988 Conference Publ. 296, 1992 Conference Publ. 361); MCA (SG-8); NRC (Appendix 28 *Power Supply*); RoSPA (IS/73); Swann (1959); Abbey (1964); Jenett (1964a); Silverman (1964a–d); Tenneco Oil Company (1964a); R.Y. Levine (1965a); D.T. Smith (1965c, 1982); Edison Electric Institute (1966); Chopey (1967a); Kerkofs (1967); EPA (1968/6, 1974/25); House (1968a); Kullerd (1968); Haigh (1969); Hoorman (1969); R.H. Lee (1969); J.C. Moore (1969); Vaccaro (1969); Nailen (1970a, 1973a–c, 1974, 1975); Tucker and Cline (1970,1971); Yuen (1970); Yurkanin and Claussen (1970); A.H. Moore and Elonka (1971); API (1982 Refinery Inspection Guide Ch. 14, 1991 RP 540, 2003); Consumers Association (1972); Jolls and Reidinger (1972); Stover (1972); Anon. (1973i); Butler (1973); Huey (1973); Imhof (1973); IEEE (1973,1975a,b); Mattson (1974); Needle (1974); Lammartino (1975); Crom (1977); Fink and Beaty (1978); Margolis (1978); Morrison (1978); Roe (1978); Bos and Williams (1979); T. Brown and Cadick (1979–); Mueller (1980); Macpherson (1981); Wildi (1981); Cohn (1983); A. Jackson (1984); Nicholls (1984); Peate (1984); Goodchild (1985); Hobson and Day (1985); Fordham Cooper (1986); Sandier and Luckiewicz (1987); EEMUA (1988 Publ. 133); Kletz (1988m); UL (1988 UL 1012); Bro and Levy (1990); Anon. (1991 LPB 102, p. 21; 1991 LPB 102, p. 23; 1992 LPB 108, p. 28; 1994 LPB 118, p. 15); Kowalczyk (1992); J.A. McLean (1992); Broughton (1993); McLean (1993 LPB 110); NFPA (1993 NFPA 70, 496) ANSI (Appendix 27), ANSI C series, ANSI C2-1993 BS (Appendix 27 *Electrical*), BS CP 1003: 1964–, BS CP 1013: 1965, BS PD 2379: 1982

Emergency generators
NRC (Appendix 28 *Diesel Generators*); HSE (1985 PM 53); Kletz (1988m); NFPA (1989 NFPA 110A, 1993 NFPA 110, 111)

Uninterruptible power supply
Cullen (1990); UL (1991 UL 1778)

Electrical pipe tracing
Butz (1966); Ando and Othmer (1970); Ando and Kawahara (1976)

Electrical area classification
BASEEFA (n.d./1, SFA 3004, 3006, 3009, 3012); MCA (SG-19); IEE (1962 Conference Publ. 3, 1971 Conference Publ. 74, 1975 Conference Publ. 134, 1982 Conference Publ. 218, 1988 Conference Publ. 296, 1992 Conference Publ. 361); API (1973 RP 500B, 1982 RP 500A, 1984 RP 500 C, 1991 RP 500); IP (1990 MCSP Pt 15,1991 MCSP Pt 1); J.R. Hughes (1970); ICI/ RoSPA (1970 IS/74,1972 IS/91); EEUA (1973 Doc. 47D); LPGITA (1991 LPG Code 1 Pt 1); NFPA (1993 NFPA 70, 496); ANSI (Appendix 27), BS (Appendix 27), BS 4683: 1871–, BS 5345: 1977–, BS 5501: 1977–

Gas (*see* Table 11.10)

Steam, condensate, feedwater
American Oil Company (n.d./6); Lyle (1947); NRC (Appendix 28 *Steam Supply*); EEUA (1962 Handbook 8); Monroe (1970); Buffington (1973); IMechE (1974/12, 13, 1981/58, 1984/76, 1987/96, 98, 90/124); Anon. (1976 LPB 11, p. 5); Danekind (1976, 1979); Pitts and Gowan (1977); Reid and Renshaw (1977); Gambhir, Heil and Schuelke (1978); Bos and Williams (1979); J.K. Clark and Helmick (1980); J.J. Jackson (1980); Ward, Labine and Redfield (1980); Pybus (1981); Blackwell (1982b); Andrade, Gates and McCarthy (1983); ASME (1983/193); Freedman (1983); Monroe (1983a); J.F. Peterson and Mann (1985); T.J. Kelly (1986); Plummer (1986); A. Atkinson (1988); Heaton and Handley (1988); Gunn and Morton (1989); National Fuel Efficiency Service (1989); Istre (1992); Babcock and Wilcox (1993); Broughton (1993); C. Butcher (1993b); Ganapathy (1993); Spirax-Sarco (1993); Hahn (1994); BS 759: 1984–, BS 1113: 1992

Cooling water
American Oil Company (n.d./1); Partridge and Paulson (1963); M. Brooke (1970); Gazzi and Pasero (1970); Troscinski and Watson (1970); Silverstern and Curtis (1971); Klen and Grier (1978); Krisher (1978); Ward, Lee and Freymark (1978); Conger (1979); Veazey (1979); J.W. Lee (1980a,b); Burger (1982, 1983); Holiday (1982); W.J. Scott (1982); D.T. Smith (1982b); G.B. Hill (1983); Willa and Campbell (1983); IChemE (1987/131); Reidenbach (1988); Ellis (1990); G. Parkinson and Basta (1991); NFPA (1992 NFPA 214); Broughton (1993)

Process water
Holiday (1982)

Drinking water
BS 6700: 1987

Compressed air
American Oil Company (n.d./2); Weiner (1966); La Cerda (1968); A.G. Paterson (1969); McAllister (1970, 1973); ISA (1975 S7.3, 1984 RP 7.7); Allan (1986); Johnston (1990); Broughton (1993); O'Dell (1993)

Instrument air
Nielsen, Platz and Kongso (1977); Broughton (1993)

Inert gas
Hotchkiss and Weber (1953); P.A.F. White and Smith (1962); Funk (1963); Husa (1964); Sittig (1966); Penland (1967); Rosenberg (1968); H.A. Price and McAllister (1970); Loeb (1974); Anon. (1976 LPB 7, p. 11); Simon (1976); Kletz (1980f); Mehra (1982); Metzger *et al.* (1985); Hardenburger (1992); Broughton (1993)

Refrigeration
ASHRAE (Appendix 27, 28, n.d./2, 1972, 1992 ASHRAE 15, 34); Tanzer (1963); Ballou, Lyons and Tacquard (1967); Spencer (1967); Zaffi (1967); Kaiser, Salhi and Pocini (1978); Mehra (1978, 1979a–c, 1982); Marsh and Olivo (1979); O.K. Miller (1979); Baggio and Saintherant (1980); Sibley (1983); Jacob (1991a); R.W. James (1994)

Heat transfer media
Geiringer (1962); Seifert, Jackson and Sech (1972); Frikken, Rosenberg and Steinmeyer (1975); Anon. (1978i); Sheehan (1986); Dotiwala (1991); CCPS (1993/13)

Water treatment
Bellew (1978); Day (1978); Gasper (1978); Setaro (1980); W.B. Thomas (1980); Saffell (1992)

Since service pipes and trunking pass through the plant, they are vulnerable to damage from accidents. The routing of services should be planned so as to minimize such damage.

In particular, cabling for control instruments and other key services should be routed as safely as possible. For critical control functions requiring replication, the cables should go by different routes. A severe accident may well cause damage to certain key services. There may be serious consequences if there is loss of electrical power to machines or control instrumentation, of cooling water or of fire water.

11.10.1 IChemE *Utilities Guide*

A treatment of the principal utilities is given in *Process Utility Systems* (Broughton, 1993) (*The* IChemE *Utilities Guide*). The Utilities Guide deals with the following topics: (1) efficient use of utilities, (2) fuel, (3) compressed air, (4) inert gases, (5) thermal fluid systems, (6) water preparation, (7) the boiler house, (8) steam distribution, (9) electricity use and distribution, (10) air and water cooling, (11) refrigeration, (12) fire protection system, (13) building services, and (14) pipework and safety.

The *Guide* starts by outlining five broad principles of general applicability to process utilities. One is the need for critical examination of all aspects, both the requirements and the means of meeting them, with full exploration of alternatives. Another is integration of utilities not just with individual plants but across the site. The third is the appropriate sizing and location of the utilities units. The fourth is the use of modern, efficient systems. And the fifth, the need for performance targets and monitoring.

11.10.2 Electricity

Electricity is used for a number of different purposes on process plants. These include: (1) machinery, (2) heating and (3) instrumentation. The use of electricity in factories is governed by the Electricity at Work Regulations 1989, which supersede the former Electricity (Factories Act) Special Regulations 1908 and 1944.

UK standards on electrical equipment include: BS 2771: 1986– Electrical Equipment for Industrial Machines, replacing BS CP 1015: 1967; BS 4683: 1971– Specification of Electrical Apparatus for Use in Explosive Atmospheres; BS 5345: 1977– Code of Practice for the Selection, Installation and Maintenance of Electrical Apparatus for Use in Potentially Explosive Atmospheres (other than Mining Applications or Explosive Processing or Manufacture); BS 5501: 1977– Electrical Apparatus for Potentially Explosive Atmospheres, replacing BS CP 1003; and BS 7430: 1991 Code of Practice for Earthing, replacing BS CP 1013: 1965. Relevant UK codes of practice include the IP Electrical Safety Code (1991 MCSP Pt 1) and the IP Area Classification Code for Petroleum Installations (1990 MCSP Pt 15). The ICI Electrical Installations in Flammable Atmospheres Code (ICI/RoSPA, 1972 IS/91) has also been widely quoted in the safety and loss prevention literature.

Relevant US codes are: NFPA 70: 1993 National Electrical Code; API RP 540: 1991 Recommended Practice for Electrical Installations in Petroleum Processing Plants; and API RP 500: 1991 Recommended Practice for Classification of Locations for Electrical Installations at Petroleum Facilities, replacing API RP 500A, 500B and 500C.

Safety aspects of electricity and electrical equipment are dealt with in *Electrical Safety* (Swann, 1959), *Electrical Safety Engineering* (Fordham Cooper, 1986) and *Hazard of Electricity by the American Oil Company* (Amoco) (Amoco/5).

Electrical power in a chemical works may be provided from the National Grid or from a power station within the works. Since steam is also required, a large works usually has its own power station. There are frequently mutual back-up arrangements between the Grid and the works station.

On some processes loss of electrical power for machinery can be serious. This applies particularly where materials may solidify in the plant, liquefied gases may warm up and vaporize, and refractories may cool and collapse. It may be necessary in such situations to provide a stand-by power supply. This may be done by setting up mutual back-up arrangements, by providing stand-by generators, or by installing engine-driven equipment and/or batteries.

Fluctuations of power supply in the form of voltage dips and outages can also occur and cause motors to cut out, which may result in process upsets. Time delay relays are available which can be used to overcome brief fluctuations.

It is particularly important to ensure the removal of heat from the process, as heat exchange depends primarily on the continued operation of pumps, both those for the process fluid and those for the cooling water. The fans of air-cooled heat exchangers are also dependent on electrical power. The fans on fired heaters are important. Loss of power on these fans can lead to the formation of a flammable atmosphere.

In order to maintain power supply to essential equipment when partial loss of generating capacity occurs, it may be necessary to practice load shedding on other equipment. Load may be shed automatically, using load shedding relays which detect deterioration of the supply frequency and operate to shed the load according to a prearranged sequence.

Where electric motors are used to drive pumps, it is not uncommon for sudden overloads to occur on a pump and for the motor overload protection to cut the motor out. This situation tends to occur particularly during a transient condition such as the loss of one pump in a set. In consequence, the reliability of the redundant pumps is not always as good as theoretical reliability predictions suggest. It is necessary, therefore, to give careful consideration to possible causes of pump overload.

Electrical apparatus is a potential source of ignition. It is essential, therefore, to have a system of electrical area classification and to use appropriate equipment in each zone. This is a most important aspect and it is considered in Chapters 10, 16 and 22 in relation to plant layout, fire and storage, respectively.

Stray electrical currents may also be a problem. They can cause corrosion and can act as sources of ignition. The power supplies to instruments as well as to machinery should be such as not to constitute a source of ignition.

11.10.3 Electricity: uninterrupted power supplies

Instrumentation requires a power supply of high quality. Voltage fluctuations, for example, can cause upsets to process computers and programmable electronic systems and to some instrumentation. It is often necessary to provide for such equipment an uninterrupted power supply (UPS), also frequently called an 'uninterruptible power supply'. These terms are used to describe a supply which possesses both high reliability and high quality in the sense that it

does not have interruptions even for a few milliseconds. Designs of UPS system are described in the IChemE *Guide*.

The UPS may utilize rotating or static equipment. One method of providing a UPS is a motor–alternator set with diesel engine back-up, other components of the system being an electromagnetic clutch and a flywheel. In normal operation, the alternator is driven by the motor. On mains failure the diesel engine starts and the clutch engages, connecting the engine to the alternator, additional energy being supplied by the flywheel until the engine is up to full power.

An alternative method of providing a UPS is a static system using batteries. In one arrangement, the AC supply passes to the load via a rectifier and an inverter, with the batteries connected between these two. This design is intended to ensure that in normal operation the batteries are kept charged and that on mains failure the batteries maintain the supply. A further discussion of UPSs is given in the CCPS *Safe Automation Guidelines* (1993/14).

11.10.4 Electricity: electrical heating

Electricity may also be used for electrical heating, or electroheat. Although the efficiency of electrical heating is limited by thermodynamics, this factor may be more than offset by the ability of electroheat systems to deliver heat with greater flexibility and precision. Types of electrical heating include immersion heating, resistance heating of pipes, induction heating of vessel walls, and the various forms of surface heating using jackets, mantles, panels, tapes, etc. An account is given in the IChemE *Guide*. Electrical heating is also used instead of a fired heater in smaller heat transfer fluid systems.

11.10.5 Fuels

Process units use both gaseous fuels such as LPG and liquid fuels in the form of fuel oil. Fuel gas is often available as part of an integrated process, as in a refinery, but it is proper to treat it as a utility. A typical fuel gas supply system is illustrated in Figure 11.11, which shows supplies taken from a primary process source, a secondary source and an LPG vaporizer.

Fuel oil is used in burners on the process, in boilers and in fired heaters. The heavier fuel oils are cheaper but are viscous and require heated storage and preheaters so that for smaller systems it is often more economic to use light fuel oils.

11.10.6 Steam

Steam is used for: (1) machinery, (2) heating, (3) process, (4) purging and inerting and (5) snuffing. Steam may provide motive power in steam turbines and also in ejectors. It is extensively used for heating. It may be injected directly into the process as in operations such as steam stripping. It is a principal fluid used for purging and cleaning operations. It is used as a means of snuffing out the flame in fired heaters.

The main source of steam is usually the works power station, but there may be process sources such as waste heat boilers or chemical reactors. On smaller works steam may be supplied by boilers.

Steam systems are described in *The Efficient Use of Steam* (Lyle, 1947), *Industrial Boilers* (Gunn and Horton, 1989) and *Steam, Its Generation and Use* (Babcock and Wilcox, 1993). Hazards are reviewed in *Hazards of Steam by the American Oil Company* (Amoco/6).

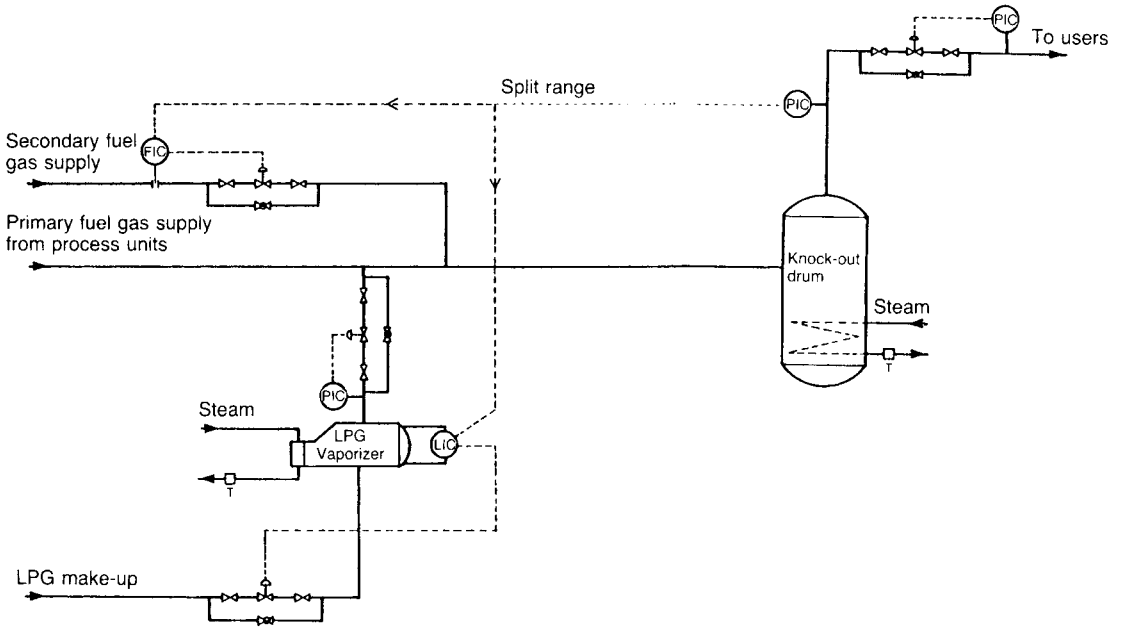


Figure 11.11 *Schematic diagram of a composite gaseous fuel supply system (Broughton, 1993). FIC, flow indicator controller; L/C, level indicator controller; PIC, pressure indicator controller (Courtesy of the Institution of Chemical Engineers)*

An overview of the boiler house on a process plant site is given in the IChemE *Guide*, which describes the common types of boilers and burners and the ancillary plant required, and gives a checklist for boiler selection.

Boilers are either shell boilers or water-tube boilers. In fire-tube boilers, the water is in the shell, the hot gases are burned in a combustion chamber inside the shell and then pass through the fire tubes, giving up more of their heat. In one arrangement, the boiler is set in brickwork, the Lancashire and Cornish boilers being early workhorses of this type with single and double internal flues, respectively. The economic boiler, by contrast, is self-contained. Package fire-tube boilers are widely used. Electrical boilers are of two types. One is heated by an immersion element akin to that used in domestic systems. The electrode boiler is heated by passage of current directly through the water between immersed electrodes. Both types come as package units. Finally, water-tube boilers are available in a variety of designs and in sizes from package units to the large-field assembled units used in power stations.

All boilers, including waste heat boilers, require feed water treated to prevent scaling. The feed water and boiler water qualities required for different steam pressures are listed in the IChemE *Guide*. Boiler feed water treatment is an important aspect of boiler operation. The reliability of the feedwater treatment plant, including the feedwater pumps, is therefore an issue.

The quantities of steam needed for purging can be large. It is necessary, therefore, to provide for this requirement, otherwise there may be a tendency to use insufficient steam in purging operations.

As with electrical power, it may be necessary to practice load shedding to protect the supply of steam to essential equipment on loss of part of the generating capacity.

Where there is a set of boilers and some are lost, the resultant demand on the remaining boilers is liable to cause fan overload and loss of these boilers also. A limit control system may be used to prevent such overload.

Loss of steam can normally be tolerated and it is not usual to have a stand-by steam supply. The steam system has some capacity, however, and can usually supply steam for a period. For more critical units, the period can be prolonged if steam to other units is cut off.

It is appropriate, however, to consider the effect on a unit if the heating steam is lost. The resultant cooling may lead to condensation of vapours and to underpressure of the unit, and it may be necessary to provide nitrogen injection to counteract this.

Steam from the main boilers, and any waste heat boilers, is distributed to user plants, by a distribution system which may provide steam at low, intermediate and high pressure, pressure being let down at let-down stations.

A serious hazard in steam systems is water hammer. A slug of condensate which has collected in the main may be flung by the steam against the pipework with a very destructive effect.

Steam distribution systems should be designed to effect efficient drainage of condensate. This means that: the lines should be sloped; drainage points should placed at suitable locations and provided with drain pockets so that the condensate collects and does not skim over the top of the drain point; and efficient steam traps should be installed for take-off of the condensate.

Guidance on steam traps is given in *Steam and Steam Trapping* by Spirax-Sarco Ltd (1993). Further treatments of the design and operation of steam distribution systems, with particular reference to the avoidance of condensate hammer, are given in Chapters 12 and 20, respectively.

Erosion is a common feature in steam systems. Steam can be a surprisingly erosive fluid, especially if it is wet.

Leaking steam can cause a build-up of static electricity and can thus constitute a source of ignition. This possibility should be considered where leaks of flammable vapours may also be present.

Air may be present in a steam system on start-up and manual vents located at high points should be provided to allow it to be removed. The IChemE *Guide* suggests this should be the limit of the problem.

In some cases, as discussed by Plummer (1986), the presence of air and other gases in steam does cause operating problems and needs to be addressed. There are various sources of air or other gas in plant. Air dissolved in the boiler feedwater may not be completely removed by deaeration. Chemical reactions in the boiler, such as the release of carbon dioxide from bicarbonates, can generate gas. Air may be drawn into spaces where steam is condensing at a pressure below atmospheric.

These permanent gases can then create problems. Temperature control is often based on pressure control and if, due to the presence of gas, the relation between pressure and temperature departs from the value corresponding to the steam tables, control is upset. Heat transfer across heat exchange surfaces may deteriorate due to blanketing of these surfaces by gas. Corrosion may be promoted by the presence of oxygen or carbon dioxide.

Unwanted gas may be removed by suitable venting. Vent valves are available which operate on temperature, opening when the temperature is below saturation and seating when saturation temperature is reached. Points where such valves may be located are at the boiler, at remote ends of lines, upstream of isolation valves and on heat exchangers.

11.10.7 Compressed air: plant air

Compressed air is required on process plants as plant air for general applications, instrument air, breathing air and process air. General applications include purging and driving pneumatic tools.

Typically plant air is filtered, compressed to 6–7 barg and then cooled in a heat exchanger with condensation of water, but is not dried. The air enters an air receiver which supplies the service stations on the compressed air main. Compressed air, therefore, should be free of solid matter but contains some oil and is saturated with water.

The demand for plant air is subject to large fluctuations and the supply should be able to cope with such peaks, but it is not generally necessary to install stand-by compressors.

11.10.8 Compressed air: instrument air

The requirements for instrument air are somewhat different. Instrument air needs to be dry and its supply reliable. It is important that the instrument air be of good quality and, in particular, that it be free from solids, oil and water. Dirty, oily or wet air is liable to cause instrument error and failure. It follows that it is not good practice to use ordinary plant air for instrumentation.

The IChemE *Guide* states that instrument air should be free of solids, oil, corrosive substances and noxious gases. The solids content should be less than 0.1 $g/N/m^3$ with particle sizes less than 3 μm. With regard to dryness, the Guide quotes the requirement for a dewpoint of −40°C

frequently suggested for UK sites, but adds that this can reduce the flexibility of vendor packages and proposes that for temperate climates such as those of central and southern Europe a dewpoint 10°C below the minimum ambient temperature suffices. The compressors used for instrument air should be of the oil-free type.

Instrument air is typically supplied at about 7 barg from an air receiver. The *Guide* states that a pressure of 4 barg is the minimum for satisfactory operation of the instrumentation and that it should not be allowed to fall below this. The supply needs to be adequate to cope with fluctuations. The *Guide* gives typical air consumption figures for instrumentation.

In most applications, the instrument air supply should have high reliability, which will normally mean the provision of stand-by equipment, separate power sources, and so on.

Avoidance of contamination, discussed in Section 11.10.18, is particularly important for instrument air. Connection of another system to the instrument air system creates the possibility of such contamination. It was contamination of the instrument air which initiated the train of events at Three Mile Island, as described in Appendix 21.

11.10.9 Compressed air: breathing air

If the extent of use of air-supplied breathing apparatus justifies it, a dedicated supply of air may be provided for breathing. This is considered in Chapter 25.

11.10.10 Compressed air: process air

Many processes use air as a raw material. Such air is usually obtained by compression of atmospheric air. Generally loss of process air is not critical and special measures are usually not required to ensure security of supply.

Air drawn by the process air compressors necessarily comes from some point in the works. There may be a degree of contamination due to leaks from plants, and in some cases the impurities may have an adverse effect on the process.

Hazards can arise from the build-up of oil from the compressors in the process air lines. Hazards are reviewed in *Hazards of Air by the American Oil Company* (Amoco/2).

11.10.11 Inert gas

The inert gases used in the process industries are mainly nitrogen and carbon dioxide. Alternatively, flue gas from an inert gas generator may be used. The inert gas principally considered here is nitrogen. This is described in *Nitrogen for Industry* (Sittig, 1966) and in the IChemE *Guide*.

Nitrogen is used for a large number of purposes. These include: (1) inerting, (2) process, (3) purging and (4) pressurizing. One main use of nitrogen is inerting. Inert atmospheres are often required in processes such as polymerization, catalyst preparation and drier regeneration, and in plant such as centrifuges and storage tanks. Storage tank atmospheres are frequently inerted with nitrogen.

Nitrogen has a number of process uses. In particular, it may be used to dilute the concentration of a reactant such as oxygen in an oxidation process. In high pressure processes the use of nitrogen permits the use of such pressures while limiting the partial pressure of oxygen.

Another use of nitrogen is as a purge gas. Purging of equipment is discussed in Chapters 16, 20 and 21 in relation to fire protection, plant operation and maintenance, respectively. Where purging is carried out to prevent entry of flammable gases into equipment which may spark, nitrogen is not always the most suitable gas to use. Often air is both cheaper and safer. The choice of purge gas for such applications is considered further in Chapter 16.

There are certain situations which can lead to the plant being underpressured so that it may collapse inwards. This may be countered by nitrogen injection. Another application of pressurizing is the use of nitrogen pressure to transfer liquids in order to avoid having to pump them.

The quality of the nitrogen required depends on the application. The IChemE *Guide* distinguishes between general purging (GP) nitrogen and high purity inert medium (HPIM) nitrogen. Supplies of nitrogen may be obtained from gas cylinders or ammonia dissociation; from an inert gas generator in which nitrogen is obtained from combustion of air and removal of other products of combustion; from air separation by pressure swing adsorption (PSA); from air separation by permeation through a membrane; from bulk gas or liquid storage or gas pipeline; or from a low temperature air separation plant on site. Cylinders are economic only for very small quantities and a low temperature air separation plant only for very large ones.

The choice of nitrogen supply method is discussed in the *Guide*. It is essentially a function of the purity and scale. A breakpoint occurs at a demand of about 300 Nm^3/h. Broadly, the *Guide* indicates that the demands below this can be met using a liquid nitrogen storage/vaporizer system and those above using a low temperature separation plant, with PSA and membrane methods an option for smaller demands of GP nitrogen. Thus, in contrast to the other services nitrogen is not always generated on site. Instead, it may be brought in and held in storage. In this case, it is essential to have a sufficient supply.

The Flixborough Inquiry revealed that the nitrogen required for inerting on the plant was sometimes in short supply and that as a result routine procedures were interrupted. The *Flixborough Report* drew attention to the importance of ensuring an adequate supply of nitrogen when plant safety is dependent on it.

11.10.12 Water: cooling water

Cooling water in the process industries is provided using one of three basic systems. One is the 'once-through' system, which is self-explanatory. The other two involve recirculation, either in an open system in which the water is cooled in cooling towers, or in a closed system in which it is cooled in heat exchangers using another fluid. The use of cooling towers is the normal method except where the site is such as to allow the once-through use of river or seawater.

Other cooling facilities may be provided by air-cooled heat exchangers, which depend on electric fans for air circulation.

Since it is essential to assure removal of heat from the process, the security of the cooling water supply is important. This may be achieved by making sure that the power supply is secure, by providing stand-by pumping arrangements and/or by the use of head tanks.

It is not good practice to use cooling water as fire water, as this may result in the loss of ability to ensure essential heat removal from process units. The cooling water system should be operated so that corrosion of process equipment by cooling water is kept to a minimum.

11.10.13 Water: process water

Water is an important raw material for many processes. It is usually taken from the public water supply or from company

sources such as reservoirs and springs. Generally, loss of process water is not serious and a stand-by supply is usually not necessary. High security may be needed, however, for the boiler feedwater supply. The water purity required depends upon the process. In some cases, special purification plant may be needed. Such purification is necessary in particular for boiler feedwater. It is not good practice to draw the process water from the cooling water system.

Hazards are reviewed in *Hazard of Water by the American Oil Company* (Amoco/1).

11.10.14 Water: hot water

A supply of hot water may be required for washing down plants. If this is generated by direct mixing of water and steam, a specially designed mixing nozzle system should be used which shuts off on loss of cold water. The water temperature should be controlled at a temperature which will not injure personnel using it. A water temperature exceeding 57°C can give first degree burns.

11.10.15 Water: fire water

The provision of fire water is treated in Chapters 10 and 16 in relation to plant layout and fire protection, respectively.

11.10.16 Heat transfer media: hot fluids

In addition to steam and cooling water, use may be made of other heat transfer fluids (HTFs) for heating or cooling. HTF, or thermal fluid, systems are used to supply heat to process fluids at temperatures up to about 300°C. Such HTF systems exhibit a number of problems which need to be addressed if they are to operate satisfactorily. Accounts are given in the IChemE *Guide* and the CCPS *Engineering Design Guidelines*; both devote a complete chapter to these systems.

The HTFs used are mainly mineral oils, synthetic aromatics, diphenyl–diphenyl oxide mixtures and silicones. Examples of mineral oils are BP's Transcal 65; of synthetic aromatics, Dew's Dowtherm Q and BP's Transcal SA; of diphenyl–diphenyl oxide mixtures, Dow's Dowtherm A and ICI's Thermex; and of silicone, Dow's Syltherm 800.

An HTF generally has a boiling point in the range 260–340°C, a maximum fluid temperature of 350°C and a vapour pressure at the operating temperature of 1–2 barg. Many are subject to autoignition on escape to atmosphere.

Since the fluid circulates continuously, it is subject to degradation, minimization of which is an important feature of the design and operation of HTF systems.

A typical HTF system consists of a heater, heat exchangers to transfer heat to the process fluid(s), a storage reservoir and an expanse tank. The storage vessel may double as a discharge vessel or there may be a separate discharge vessel. There may be an emergency cooler. Flow diagrams of HTF systems are given in the IChemE *Guide* and the CCPS *Guidelines*.

The heat input is provided by a heater, except for smaller units where electrical heating is used. It follows that an HTF system is subject to the various problems of fired heaters and that the precautions applicable to fired heaters in general, described in Chapter 12, are required for those in HTF systems. They include on the heater tubes trips on high temperature and low flow.

In contrast to most fired heaters, the fluid in an HTF system is recirculated. The conditions created by this combination of fired heating and recirculation are severe and fluid degradation is characteristic of HTF systems. One consequence can be coking and plugging of the heater tubes.

Heat transfer fluids tend to be 'searching' and HTF plants have a history of leaks, particularly at flanges. Ignition occurs where the leaking fluid is above its autognition temperature. Another problem due to leaks is saturation of the lagging, resulting in lagging fires.

Pressure relief valves on HTF systems have not always been well located, so that fluid has been discharged and has then found a source of ignition. Experience also shows that both out-leak of the HFT and in-leak of another fluid may occur. Precautions include the installation of a low level trip and a high level alarm on the expanse tank.

The need for security of supply of the hot fluid varies. A reliable system may be necessary, for example, in an application where heat is required to prevent a process fluid going solid in the plant.

11.10.17 Heat transfer media: refrigerants

Refrigerants are used to cool process fluids to temperatures lower than those achievable using cooling water. Accounts of refrigeration are given in the *ASHRAE Refrigeration Handbook* by the American Society of Heating, Refrigerating and Air-conditioning Engineers (ASHRAE, 1990/3). Other relevant ASHRAE publications are the *ASHRAE Thermodynamic Properties of Refrigerants* (ASHRAE/2) and the *ASHRAE Handbook of Fundamentals* (ASHRAE, 1993/7).

Basic methods of obtaining refrigeration are Joule–Thomson expansion, work expansion, evaporation refrigeration and absorption refrigeration. Joule–Thomson and work expansion may be used within the process to effect direct cooling of process fluids. Evaporation and absorption refrigeration sets are used to provide indirect cooling.

A variety of refrigerants are available, including: ammonia (R717); carbon dioxide; ethylene (R170), ethane (R1150), propylene (R1270) and propane (R290); and chlorofluorohydrocarbons (CFCs) such as dichlorodifluoromethane (R12) and chlordifluoromethane (R22). In selecting a refrigerant it is necessary to consider the general properties, the safety features and the environmental features.

Relevant general properties are the normal boiling point and refrigerant service temperature, the latent heat and the coefficient of performance (COP). Safety features include flammability and toxicity, in conjunction with the inventory required. The main environmental feature is the ozone depletion potential.

The replacement of materials with noxious properties such as ammonia (toxic) and ethylene (flammable) with non-toxic, non-flammable CFCs has been arrested by the environmental harm which the latter cause. The production and use of CFCs is restricted by the Montreal Protocols. New refrigerants to replace CFCs comprise an active area of development.

In some applications it may be necessary to consider other properties of the refrigerant, such as its interaction with the process fluid in the event of a pinhole leak.

A summary of general and environmental properties of refrigerants is given in the IChemE *Guide* and more detailed information in the ASHRAE handbooks. These publications also deal with refrigeration cycles and with package refrigeration sets.

Use is sometimes made in the process industries of systems in which a refrigerated heat transfer fluid is circulated between a refrigeration set and the process. A typical refrigerated fluid used in such applications is ethylene glycol.

11.10.18 Contamination hazards

Many of the services described are fluids. Hazards can arise from contamination of process materials by service fluids or contamination of service fluids by process materials. The contamination may occur through pipes and valves or by leakage in equipment.

Accidental entry of water, including steam, into the plant can have serious consequences. The water may vaporize, giving a large increase in pressure, or it may cause an oil–water 'slopover'. It may react violently with the process materials, it may ruin catalysts or adsorbents, it may give rise to very rapid corrosion and it may freeze and cause blockages. With accidental air ingress the main hazard is the formation of a flammable mixture.

In order to prevent unwanted entry of water and air into the plant through the pipework, it is necessary to provide positive isolation. This may require the use of double block and bleed valves rather than single valves. There need to be equally effective measures to prevent operational errors.

Contamination can also occur due to leakage of equipment. In particular, steam vaporizers and reboilers often develop pinhole leaks. If the consequences of such a leak might be serious, consideration should be given to the use of an alternative means of heating such as a heat transfer fluid.

The entry of process materials into lines carrying service fluids can have equally serious results. Toxic materials may enter the water supply, flammable vapours may pass into the air lines, or air may get into the nitrogen supply. In all these cases the hazard is obvious. It is essential, therefore, to check whether flow reversals into the service fluids could occur which might create a hazardous situation and to take any appropriate measures.

There is a particular obligation to ensure that the public water supply is not contaminated. If water is drawn from this for process use, positive means such as a break tank should be provided to prevent backflow and possible contamination.

11.11 Particular Chemicals

Accounts of the properties, manufacture and use of chemicals are given in the *Kirk–Othmer Encyclopaedia of Chemical Technology* (Kirk and Othmer, 1963–, 1978–, 1991–) and in *Ullmann's Encyclopaedia of Chemical Technology* (Ullmann, 1969–, 1985–). Selected references on particular chemicals and their hazards are given in Table 11.8.

The number of chemicals used in the process industries is very large. The few principal chemicals considered here are selected because they are important in their own right and because they illustrate the type of factors which have to be taken into account. The chemicals are:

(1) hydrocarbons;
(2) acetylene;
(3) acrylonitrile;
(4) ammonia;
(5) chlorine;
(6) ethylene dichloride;
(7) ethylene oxide;
(8) hydrogen;
(9) hydrogen fluoride;
(10) oxygen;
(11) phosgene;
(12) vinyl chloride.

Table 11.8 *Selected references on particular chemicals and their hazards*

Notes: (a) The former Manufacturing Chemists Association (MCA) SD series, given in the first edition of this book, is not included. (b)The FPA Compendium of Fire Safety Data, vol.4, H series is denoted by the H number. (c) Company materials safety data sheets are now a much improved source of detailed information.

General
Cloyd and Murphy (1965); DOT, CG (1974a,b); Goldfarb *et al.* (1981); Chissick *et al.* (1984); Keith and Walters (1985–); H.H. Fawcett (1988); Spitz (1988); Agam (1994)

Air sensitive compounds
Shriver (1969)

Acetaldehyde
Gemmill (1961a); Jira, Blau and Grimm (1976); Goldfarb *et al.* (1981); FPA (1986 H29)

Acetic acid
Claydon (1967); Ellwood (1969a); Schwerdtel (1970); Lowry and Aguilo (1974); Goldfarb *et al.* (1981); Aquilo *et al.* (1983); FPA (1988 H120)

Acetylene
Reppe (1952); Penny (1956); H. Watts (1956); Sargent (1957); Chemical Engineering Staff (1960); S.A. Miller and Penny (1960); S.A. Miller (1964); Hardie (1965); Mayes and Yallop (1965); Kamptner, Krause and Schilken (1966a); Stobaugh (1966a); Tedeschi *et al.* (1967); Zieger (1969); CGA (1970 G-1.3, 1990 G-1.1, SB-4); Schmidt (1971); Carver, Smith and Webster (1972); Sutherland and Wegert (1973); Holman, Rokstad and Solbakken (1976–); NIOSH (1976 Crit. Doc. 76-195); Stork, Hanisian and Bac (1976); Anon. (1978a); Manyik (1978); Tedeschi (1982); P.J.T. Morris (1983); Passler *et al.* (1985); FPA (1987 H6); Ashmore (1988 LPB 88); Hort and Taylor (1991); Conrad, Dietlen and Schendler (1992)

Acetylenic alcohol
Lorentz (1967, 1973)

Acids and alkalis
Anon. (1977 LPB 16, p. 3)

Acrylic acid
FPA (1986 H95); Levy (1987)

Acrylic monomers
Kirch *et al.* (1988)

Acrylonitrile
Guccione (1965a); S.G.M. Clark and Camirand (1971); Dalin, Kolchin and Serebryakov (1971); Caporali (1972); Pujado, Vora and Krueding (1977); CIA (1978 PAH); CIHSC (1978/4); NIOSH (1978 Crit. Doc. 78-116); Langveldt (1985); FPA (1986 H51); Brazdil (1991)

Air (*see* Table 11.10)

Alcohols
Courty *et al.* (1984); FPA (1986 H2)

Aluminium alkyls
Heck and Johnson (1962); Governale, Ruhlin and Silvus (1965); Albright (1967f); Schmit *et al.* (1978)

Ammonia (*see* also Tables 11.11, 18.1, 18.2, 22.1 and 23.1)
American Oil Company. (n.d./9); Slack and James (1973); NIOSH (1974 Crit. Doc. 74-136); CIA (1975/8, 11, PA1, 1988 PA9, 1990 RC3); Blanken (1978); HSE (1978b, 1981a); Strelzoff (1981); CGA (1984 G-2, 1989 G-2.1, TB-2); Bakemeier *et al.* (1985); FPA (1987 HIS); Kletz (1988a)

Ammonium nitrate (*see* also Table 11.11)
American Oil Company. (n.d./9); Burns *et al.* (1953 BM RI 5476); Sykes, Johnson and Hainer (1963); van Dolah *et al.* (1966 BM RI 6773); Watchorn (1966); HSE (1978b, 1981a); Keleti (1985); Zapp (1985); FPA (1987 H33); FMA (1989); NFPA (1990 NFC 490); ACDS (1991); Miyake and Ogawa (1992); Weston (1992)

Ammonium perchlorate
Bond (1990 LPB 93)

Aniline
HSE (TON 10, 1979 EH 4); Cans (1976b); FPA (1986 H80)

Arsine
HSE (1975 TON 6, 1990 EH11)

Asbestos (*see* Tables 18.1 and 25.1)

Benzene
Stobaugh (1965a); Remirez (1968b); Ockerbloom (1972); Hancock (1975); NIOSH (1976 Crit. Doc. 137); Kohn (1978c); Cheremisinoff and Morresi (1979); CIA (1980 PAS); Malow (1980); HSE (1982 TR4); FPA (1986 HIS)

Bischloromethyl ether
Ress (1982)

Bitumen
Swindells, Nolan and Pratt (1986); IP (1990 MCSP Pt 11)

Bromine
Jolles (1966); FPA (1986 H61); CIA (1989 RC4)

Butadiene
D.A. Scott (1940); Stobaugh (1967a); FPA (1987 H63); Glass (1987)

Calcium hypochlorite
V.J. Clancey (1975b,c, 1975/76, 1987); Uehara, Uematsu and Saito (1978); FPA (1987 H46)

Caprolactam
H.F. Steward (1974)

Carbon dioxide
CGA (1984 G-6, 1985 G-6.2)

Carbon disulfide
Thacker (1970); NIOSH (1977 Crit. Doc. 77-152); HSE (1981 SHW 932, TR3); FPA (1986 H43)

Carbon monoxide
HSE (HSW Booklet 29); NIOSH (1972 Crit. Doc. 73-110); Anon. (1975a); Ribovitch, Murphy and Watson (1977); FPA (1987 H57); CGA (1989 P-13)

Chlorine (*see* also Tables 18.1, 18.2, 22.1 and 23.1)
Chlorine Institute (Appendix 27, 28, 1971 BIBLL, 1986 Pamphlet 1); DoEm (Det. Booklet 10); HSE (HSW Booklet 37, 1978b); Brian, Vivian and Habib (1962); Johnsen and Yahnke (1962, 1973); Payne (1964); Brian, Vivian and Piazza (1966); de Nora and Gallone (1968); W.W. Lawrence and Cook (1970); Sconce (1972); Statesir (1973); BCISC (1975/1); NIOSH (1976 Crit. Doc. 76-110); H.E. Schwarz (1976); CIA (1980/10, 1986 PA 48); Meinhardt (1981); HSE (1986 HS(G) 28); Schmittinger (1986); FPA (1987 H39); J.L. Woodward and Silvestro (1988); CIA, Chlorine Sector Group (1989); Gustin (1989a); Klug (1989); Somerville (1990); Anon. (1991 LPB 98, p. 25); Curlin, Bommaraja and Hansson (1991)
Nitrogen trichloride: Chlorine Institute (1975 MIR-2)

Chlorine dioxide
Cowley (1993 LPB 113)

Chloromethanes
Akiyama, Hisamoto and Mochizuki (1981); FPA (1986 H68)

Cryogenic gases
Blakey (1981); Williamson and Edeskuty (1984)

Cyanuric chloride
Anon. (1979 LPB 25, p. 19)

Cyclohexane
Haines (1962); Dufau *et al.* (1964); Stobaugh (1965b); Berezin, Denisov and Emmanuel (1966); Alagy *et al.* (1968); Ishimoto, Sasano and Kawamura (1968); Craig (1970); Taverna and Chiti (1970); Alagy, Trambouze and van Landeghem (1974); Dragoset (1976); McCorkle (1980); Ciborowski and Krysztoforski (1981); FPA (1986 H25); Krysztoforski *et al.* (1986); Krysztoforski *et al.* (1992)

Diethyl ether
Redeker and Schebsdat (1977)

Dimethylsulfate
Anon. (1979 LPB 25, p. 24)

Dimethylsulfoxide (DMSO)
Gostelow (1983); Hall (1993 LPB 114)

Dimethylterephthalate (DMT)
Ueda (1980)

Ethyl acetate
Bond (1994 LPB 119)

Ethylene
Stobaugh (1966c); W.W. Lawrence and Cook (1967); S.A. Miller (1969); Strelzoff (1970); Fiumara and Cardillo (1976); MITI (1976); Ribovitch, Murphy and Watson (1977); Kniel, Winter and Chung-Hu Tsai (1980); Kniel, Winter and Stork (1980); Pike (1981); Tayler (1984a); C. Britton, Taylor and Wobser (1986); FPA (1987 H17); Glass (1987); Granton and Roger (1987)

Ethylene cyanide
Berthold and Loffler (1983)

Ethylene dichloride
CIA (1975 PA13); CISHC (1975/1); V.L. Stevens (1979); McNaughton (1983); FPA (1986 H77); Rossberg *et al.* (1986)

Ethylene oxide
Burgoyne and Burden (1948, 1949); Burden and Burgoyne (1949); Burgoyne and Cox (1953); Burgoyne, Bett and Muir (1960); Burgoyne, Bett and Lee (1967); Troyan and Levine (1968); Ray, Spinek and Stobaugh (1970); CISHC (1975/2); de Maglie (1976); Cans and Ozero (1976); S.C. Johnson (1976); Kiguchi, Kumazawa and Nakai (1976); NIOSH (1978 Crit. Doc. 77-200); CIA (1979 RC 14); Kuhn (1979, 1980b); Cause *et al.* (1980); Pesetsky and Best (1980); Pesetsky, Cawse and Vyn (1980); Chen and Faeth (1981b);

Ozero and Procelli (1984); FPA (1987 H79); Rebsdat and Mayer (1987); Kletz (1988m); de Groot and Heemskerk (1989); Siwek and Rosenberg (1989); Britton (1990b); Brockwell (1990); Grumbles (1990); June and Dye (1990); Conrad, Diellen and Schendler (1992); Ondrey (1992)

Fluorine
McGuffy, Paluzelle and Muldrew (1962)

Formaldehyde
NIOSH (1976 Crit. Doc. 77-126); HSE (1981 TR2); CIA (1983 PA21); Clary, Gibson and Waritz (1983); Dunn *et al.* (1983); FPA (1986 H54)

Formic acid
Aguido and Horlenko (1980); Czaikowski and Bayne (1980); Anon. (1984 LPB 56, p. 24); FPA (1986 H86)

Grignard reagents
Rakita, Aultman and Stapleton (1990)

Halogenated hydrocarbons
Santon and Wrightson (1989)

Hydrocarbons
WHO (EHC20); Wade (1963); Stobaugh (1966b); A. Brown (1964); Burgoyne (1965b); ICI/RoSPA (1970 IS/74); Binns (1978); Boesinger, Nielsen and Albright (1980); Maisel (1980); IP (1991 PUB 60, 61); API (1983/6)

Hydrogen
American Oil Company (n.d./9); Cronan (1960a); G.R. James (1960); Labine (1960); G.J. Lewis (1961); Vander Arend (1961); Zabetakis and Burgess (BM 1961 RI 5707); Zabetakis, Furno and Perlee (BM 1963 RI 6309); R.B. Scott, Denton and Nicholls (1964); Reiff (1965); Scharle (1965); Stoll (1965); Voogd and Tielrooy (1967); Chopey (1972); CGA (1974 G-5, 1985 P-6, 1990 G-5.3); Anon. (1977 LPB 15, p. 2); Anon. (1978 LPB 21, p. 85); K.E. Cox and Williamson (1977); Bassett and Natarajan (1980); W.N. Smith and Santangelo (1980); Donakowski (1981); Mandelik and Newsome (1981); Angus (1984); Mahmood *et al.* (1984); J.D. Martin (1984); Shields, Udengaard and Berzins (1984); FPA (1986 H20); Haussinger, Lohmuller and Watson (1989); NFPA (1989 NFPA 50A, SOB); Johansen, Raghuraman and Hackett (1992); Ondrey, Hoffinann and Moore (1992)

Hydrogen chloride, hydrochloric acid
BCISC (1975/2); CIA (1975 PA12); HSE (1981 BPM 5); FPA (1987 H41)

Hydrogen cyanide
Koberstein (1973); NIOSH (1976 Crit. Doc. 77-108); HSE (1983 SHW 385); FPA (1986 H94)

Hydrogen fluoride
Muehlberger (1928); Simons (1931); K.M. Hill and Knott (1960); NIOSH (1976 Crit. Doc. 76-143); HSE (1978b, 1980 BPM 4); Gall (1980); CIA (1987 PA14); Aigueperse *et al.* (1988); G. Parkinson (1990); van Zele and Diener (1990); Diener (1991)

Hydrogen peroxide
HSE (SIR 19); Schumb, Satterfleld and Wentworth (1955); Shell Chemical Corp. (1959); Rawsthorne and Williams (1961); Monger *et al.* (1964); G.A. Campbell and Rutledge (1972); Berthold and Loffler (1980); FPA (1987 H3); Mackenzie (1990, 1991)

Hydrogen sulfide
NIOSH (1977 Crit. Doc. 77-158); API (1981 RP 55); CGA (1981 G-12); Maclachlan (1985); FPA (1986 H78)

Insecticides, pesticides
Presidents Advisory Committee (1963); Brooks (1974)

Iron sulfide
Anon. (1976 LPB 12, p. 1)

Isocyanates
OSHA (OSHA 2248); Corbett (1963); HSE (1975 TON 41, 1983 MS 8, 1984 EH 16); British Rubber Manufacturers Association (1977); NIOSH (1978 Crit. Doc. 78-215); Chironna and Voelpel (1983); FPA (1986 H5); CIA (1989 RC29)

Isopropyl nitrate
Beeley, Griffiths and Gray (1980)

Lead (*see* also Table 18.1)
HSE (TON 16); DoE (1974 Poll. Paper 2); NIOSH (1978 Crit. Doc. 78-158); IP (1985)

Lead additives
Associated Octel Company (Appendix 28, n.d./1); HSE (1978b)

LNG (*see* Table 11.13)

LPG (*see* Table 11.12)

Maleic anhydride
Trivedi and Culbertson (1982)

Mercury
HSE (1975 TON 21, 1977 ED 17); DoE (1976 Poll. Paper 10); McAuliffe (1977); D. Taylor (1978); Okouchi and Sasaki (1984)

Methanol
Ferris (1974); Kugler and Steffgen (1980); Sherwin (1981); D.L. King, Ushiba and Whyte (1982); Chang (1983); EPA (1986 H42); Fielder *et al.* (1990)

Methylmethacrylate
EPA (1986 H67); Porcelli and Juran (1986)

Molten salts
HSE (1971 HSW Booklet 27); C.B. Allen and Janz (1980)

Monomethylamine nitrate
Miron (1980)

Naphthalene
Stobaugh (1966d); EPA (1987 H69)

NGL
Collins, Chen and Elliott (1985)

Nitric acid
Bingham (1966); van Dolah (1969a); Mandelik and Turner (1977); Bolme and Morton (1980); Calmon (1980); Marvin, Leray and Roudier (1980); Ohrui, Ohkubo and Imai (1980); Keleti (1985); EPA (1987 H23)

Nitrogen
CGA (1980 P-9, 1985 G-10.1); Anon. (1984 LPB 59, p. 30); Bond (1985 LPB 63); Hempseed (1991 LPB 97)

Nitrogen oxides
NIOSH (1976 Crit. Doc. 76-149); Ribovitch, Murphy and Watson (1977); Bretherick (1989 LPB 86); Currie (1989 LPB 88)

Nitrotoluenes
G.F.P. Harris, Harrison and Macdermott (1981)

Organic nitrates
Reboch (1976)

Organic peroxides
ASTM (STP 394); D.A. Scott (1940); National Board of Fire Underwriters (1956); Armitage and Strauss (1964); Castrantas, Banerjee and Noller (1965); Fine and Gray (1967); Bowes (1968); Hupkens van der Elst (1969); Swern (1970–); A.G. Davies (1972); Donaldson (1973); Home Office (1974/5); Interox Chemicals Ltd (1975); Wagle *et al.* (1978); de Groot, Groothuizen and Verhoeff (1980); de Groot and Hupkens van der Elst (1981); McCloskey (1989); Britton (1990b); T.A. Roberts, Merrifleld and Tharmalingham (1990); Tognotti and Petarca (1992)

Organic phosphorus compounds
MacDonald (1960)

Oxidizing substances
Uehara and Nakajima (1985)

Oxygen (*see* also Table 11.10)
CGA (1980 G-4.4, 1983 P-14, SB-2, 1985 G-4.1, 1987 G4, 1988 G-4.3); NASA (1972–); HSE (1977a); Newton (1979); A.H. Taylor (1981); D.A. Jones (1983); EPA (1987 H12); Kirschner (1991)

Perchlorates
Schumacher (1960)

Perchloric acid
Graf (1967); FPA (1987 H53)

Peroxidizable compounds
H.L. Jackson *et al.* (1970)

Pharmaceuticals
Dickson and Teather (1982); Handley (1985)

Phenol
Richmann (1964); Stobaugh (1966e); Fleming, Lambrix and Nixon (1976); Gelbein and Nislick (1978); HSE (1984 SHW 29)

Phosgene
CISHC (1975/3); NIOSH (1976 Crit. Doc. 76-137); Hardy (1982); Alspach and Bianchi (1984); Anon. (1986q); FPA (1988 H105); Somerville (1990); Schneider and Diller (1991)

Phosphorus
Lemay and Metcalfe (1964); FPA (1987 H19)

Phosphoric acid
Blumrich, Koening and Schwehr (1978)

Phosphorous compounds, chlorides
Anon. (1976 LPB 12, p. 11); Anon. (1977 LPB 13, p. 21); HSE (1994 TR30)

Phthalic anhydride
B. Shaw (1961); Ellwood (1969b); J.J. Graham (1970); Schwab and Doyle (1970); G.F.P. Harris and Macdermott (1980); FPA (1988 H130)

Polychlorinated biphenyls (PCBs)
Hutzinger (1974); Higuchi (1976); George *et al.* (1988); Derks (1991); Sundin (1991)

Polymers, including inhibitors
Mark *et al.* (1989); Redman (1991); Levy (1993); Vasile and Seymour (1993)
PVC: BCISC (1974/14); Nass (1976); Terwiesch (1976); Sittig (1978); HSE (1979 BPM 3); Nass and Heiberger (1986)

Propargyl bromide
Coffee and Wheeler (1967)

Propylene
Haines (1963); Stobaugh (1967b); Strelzoff (1970); Hancock (1973); FPA (1986 H75); Glass (1987); C. Butcher (1989b)

Propylene oxide
Jefferson Chemical Company (1963); Stobaugh *et al.* (1973); Simmrock (1978); Kuhn (1979, 1980b); FPA (1986 H88)

Silane, silane chlorides
Britton (1990a)

Sodium
Bulmer (1972); Zinsstag (1973); Parida, Rao and Mitragotri (1985); FPA (1987 H4)

Sodium borohydride
Duggan, Johnson and Rogers (1994)

Sodium chlorate
V.J. Clancey (1975b,c); Anon. (1980r); HSE (1985 CS 3); FPA (1987 H7)

Solvents
Ceilings and Luxon (1982); de Renzo (1986)

Styrene
Stobaugh (1965c); HSE (1981 TR1); Short and Bolton (1985); FPA (1986 H44); Anon. (1987 LPB 78, p. 23); Ayers (1988 LPB 84)

Sulfur
J.R. Donovan (1962); Palm (1972); Chao (1980); Parnell (1981); FPA (1986 H14)

Sulfur dioxide, sulfur trioxide
B.O. Davies and Royce (1961); NIOSH (1977 Crit. Doc. 74-11); CGA (1988 G-3)

Sulfuric acid
Biarnes (1982)

Terephthalic acid (TPA)
Derbyshire (1960); FPA (1991 H165)

***t*-Butylhydroperoxide (TBHP)**
Verhoeff (1981)

Toluene
Stobaugh (1966f); Hancock (1982); FPA (1986 Hll); HSE (1989 TR20)

Trichloroethylene
Institut National de Securite (1967); Tsuda (1970); HSE (1973 TON 17, 1985 EH 5); FPA (1990 H157)

Vinyl acetate
Reis (1966); Remirez (1968a); Stobaugh, Allen and van Sternbergh (1972); R.D. Brown and Bennett (1978); NIOSH (1978 Crit. Doc. 78-205); Goldfarb et al. (1981); Douglas, von Bramer and Jenkins (1982); Ehrler and Juran (1982); FPA (1986 H36)

Vinyl chloride (*see* also Table 18.1)
Gomi (1964); Buckley (1966); Albright (1967d,g); Arne (1967); Keane, Stobaugh and Townsend (1973); NIOSH (1974 Crit. Doc. 78-205); Z.G. Bell *et al.* (1975); CIA (1975/8, 1978 PA15, 1978/9); Reich (1976); Vervalin (1976a); Wimer (1976); Mukerji (1977); Sittig (1978); Mcpherson, Starks and Fryar (1979); Goldfarb *et al.* (1981); Cowfer and Magistro (1983); FPA (1990 H20)

Xylene
Stobaugh (1966g); Atkins (1970); Hancock (1982); FPA (1986 H76); HSE (1992 TR26)

Other chemicals
Bond (1987); L.E. Brown, Johnson and Martinsen (1987); Fitzer et al. (1988); Midgley (1989)

Deterioration of chemicals
Crowl and Louvar (1990); Kletz (1992a)

The emission and dispersion characteristics of materials are treated in Chapter 15 and flammability, explosibility and toxicity in Chapters 16–18, whilst storage, transport and emergency planning are treated in Chapters 22–24, respectively.

The accounts of particular chemicals given in the table are based mainly on the codes of practice and other guidance documents of the Chemical Industries Association (CIA) and the HSE. An overview of some principal topics covered in these publications is given in Table 11.9. Storage is dealt with in all the publications to some degree and in several it is the main content. It is convenient, if somewhat arbitrary, to cover it separately in Chapter 22. The treatment of the individual chemicals given here is intended to highlight their characteristic features; it is not a detailed summary of the codes and guidance. For LPG, there are codes issued by the Liquefied Petroleum Gas Association (LPGA) in the United Kingdom and the National Fire Protection Association (NFPA) in the United States.

Toxic limits are given in *Occupational Exposure Limits* (HSE, 1994 a,b EH 40/94). The normal limit is the long-term time-weighted average (TWA), but the limit given is in some cases the maximum exposure limit or the short-term exposure limit (STEL). Alternatively, the substance may be classed as an asphyxiant. The HSE has also given guidance on toxicity in relation to major hazards for several of the materials, namely acrylonitrile, ammonia, chlorine and hydrogen fluoride, as described in Chapter 18.

One topic treated in most of the publications mentioned is pressure relief and relief of thermal expansion of liquids. Overall, the treatments are broadly similar, but contain differences of detail, the reasons for which are not always clear. In the treatments given below some mention is made of such reliefs, but only to highlight certain points particular to the chemical in question. An account of pressure relief and thermal relief for chlorine systems, which contains many typical features, is given in Chapter 12.

Guidance on safety cases under the Control of Industrial Major Accident Hazards Regulations 1984 (CIMAH) and on quantitative risk assessment is available, from different sources, for several of the materials, as described in Chapter 9. These include LPG, ammonia, chlorine and oxygen.

11.11.1 Hydrocarbons, LPG and LNG

Some of the principal hydrocarbons processed in the petrochemical industry are as follows:

	Normal boiling point (°C)
Methane	−161.4
Ethane	−88.6
Propane	−42.2
n-Butane	−0.6
Ethylene	−103.9
Propylene	−47.7

Methane is the main component of natural gas, which in liquefied form is known as liquefied natural gas (LNG). Propane and butane are referred to as liquefied petroleum gas (LPG). LNG and LPG are treated more fully in Section 11.12.

The hydrocarbons listed above are all gases at normal temperature and pressure, but can all be liquefied with a greater or lesser degree of difficulty. All are handled industrially in the liquid phase by the use of low temperatures, high pressures or both.

In many cases these materials are held not only under pressure but also at the high temperatures necessary for processing. The handling of hydrocarbons in this way means that if containment is lost, dispersion may be quite rapid. In particular, a material held under pressure and above its normal boiling point will flash off when let down to atmospheric pressure.

The use of extremes of temperature, both high and low, creates difficulties in materials of construction. Some of these are discussed in Chapter 12. In particular, there are problems of brittle fracture at low temperature and of creep at high temperature. The use of low temperatures also means that there is continual heat in-leak into the plant, which can become a problem if there is an interruption to processing or if insulation is lost. The hydrocarbons are flammable and can therefore give rise to the hazards both of fire and of explosion.

In addition to their use in the process industries, several of these hydrocarbons are widely used as fuels. In particular, propane and butane enjoy widespread use as fuels in the form of LPG supplied from self-contained storage installations. Natural gas, which is mainly methane, is transmitted by high pressure pipeline to the public distribution system for industrial and domestic users. It is also transported and stored as LNG. Natural gas liquids (NGLs), which are mainly ethane, propane and butane, are also transported by pipeline. Again there are hazards of fire and explosion associated with these materials. Fire and explosion hazards of hydrocarbons are considered in detail in Chapters 16 and 17, respectively.

11.11.2 Acetylene

Accounts of acetylene are given in *Acetylene – Its Properties, Manufacture and Use* (S.A. Miller, 1964), *Acetylene Manufacture and Uses* (Hardie, 1965), *Acetylene by the*

Table 11.9 *Some topics covered in certain Codes of Practice, and guidance for particular chemicals*[a]

	Acrylonitrile	*Ammonia*	*Chlorine*	*Ethylene dichloride*	*Ethylene oxide*	*Hydrogen fluoride*	*Phosgene*	*Vinyl chloride*
Physical properties	2, 19	5	34	14, 15	7, 28	15, 16	5	App. I, II
Flammability	2	5			7		6	2
Toxicity, health effects	2	5, 6	36		8, 11	2	8	2
Special properties[b]		17			7, 8, 10		6, 18	7
Phase change: boiling, condensation				7		9		11
Plant design:	3				12	4		2
Siting and layout	4	6	1	3	12	4	3, 10	5
Ignition sources	4, 7	13		8	9			5, 13
Ventilation		13		8				3, 13, 14
Materials of construction	5	7, 12	35	3	13	3	12, 13	3
Material transfer, pumping	5	11	20, 22	8	14	10	9, 18	12
Pipework, pipelines	5	11	5	5	13	6	9, 13, 14	8
Valves	6		8	6		7	14	9
Heat exchange					15		13	
Instrumentation	8							
Backflow prevention					14			
Pressure relief and vents	6		7, 28	6	13	7	9, 12, 19	8, 10, 13
Explosion relief				6				11, 14
Disposal of vented material, absorbers and scrubbers			27	8		10	9, 20	
Disposal of contaminated liquids, drains	6, 15				25		11, 21	15
Vaporizers			23		17			
Plant operation:	10	15, 17	30	11	21	11	21	16
Protective clothing	3, 9, 11				22			
Isolation	12			7		9		11
Maintenance	11		30		23		22	
Emergency planning and procedures:	16	21	31	13	24	13	4, 23	20
Protective equipment	9		29	13		13	23	20
Emergency equipment	17		29	13		13		20
Leaks and spillages	15		29	12	25	12	27	18
Fire	16			12	24			19
First aid	13, 22		33		11	14, 19	28	

[a]The publications referred to are as follows: acrylonitrile (CIA, 1978 PA11); ammonia (HSE, 1986 HS(G) 30); chlorine (HSE, 1986 HS(G) 28); ethylene dichloride (CIA, 1975 PA13); ethylene oxide (CIA, 1992 RC14); hydrogen fluoride (CIA, 1978 PA14); phosgene (CIA, 1975 CPP5); vinyl chloride (CIA, 1978 PA15). The numbers in the body of the table refer to the page numbers of these publications. Storage is considered separately in Chapter 22.

[b]Special properties: ammonia (oxygen); chlorine (nitrogen trichloride); ethylene oxide (decomposition, polymerization); phosgene (decomposition in water, reaction with lubricating oils); vinyl chloride (polyperoxides).

Compressed Gas Association (CGA, 1990 G-1) and *Acetylene Transmission for Chemical Synthesis* (CGA, 1970 G-1.3) and by Sargent (1957), S.A. Miller and Penny (1960), Schmidt (1971), Manyik (1978), P.J.T. Morris (1983), Passler *et al.* (1985) and Hort and Taylor (1991).

Codes for the handling of acetylene in the United Kingdom are issued by the British Compressed Gases Association (BCGA, 1986 CP 5, 1986 CP 6), the successor to the British Acetylene Association.

Acetylene is produced from calcium carbide or by the cracking or oxidation of hydrocarbons. Acetylene is highly reactive due to its triple carbon–carbon bond and was for many years the basis of a whole branch of the chemical industry, including in particular products derived from the intermediate tetrachloroethane, and of vinyl chloride. Acetylene chemistry has always been particularly strong in Germany. Thus, in 1958 the production of calcium carbide in West Germany, East Germany, the United States and the United Kingdom was 979,000, 815,000, 805,000 and 145,000 ton, respectively. Since the 1960s acetylene has been largely replaced by ethylene as the raw material for these products. Production peaked in the United States in 1960 at 480,000 ton/year and in Germany in the 1970s at 350,000 ton/year. New processes have been developed for the manufacture of acetylene, but these have not arrested its decline. However, there is some evidence that this decline has slowed, partly because acetylene has always been the main route for some chemicals such as 1,4-butanediol and special vinyl esters, and partly because in Europe the relative cost of oil to natural gas feedstock rose.

In the United Kingdom, acetylene was brought under the provisions of the Explosives Act 1875 by an Order in Council in 1897. For pressures exceeding 24 psig the installation came under the control of the Explosives Inspectorate. The legal requirements associated with this regime are described in *The Law Relating to Petroleum Mixtures, Acetylene, Calcium Carbide, etc.* (H. Watts, 1956). Legislation on acetylene is discussed in Chapter 3.

Acetylene is a gas. It is a flammable and explosively unstable material. For occupational exposure it is classed as an asphyxiant. Acetylene undergoes explosive decomposition at any pressure and temperature and even without the presence of oxygen. Acetylene decomposition may be initiated by shock, temperature or reactive substances. The decomposition may range from a harmless puff of flame to a violent explosion.

In particular, acetylene reacts violently with substances such as chlorine. Thus in the production of vinyl chloride by the reaction of acetylene with hydrogen chloride, where the latter is produced by burning hydrogen and chlorine, it is essential to ensure that there is no free chlorine in the hydrogen chloride. On the other hand, acetylene and chlorine are bubbled into liquid tetrachloroethane in the process for the manufacture of the latter product.

The explosion hazard with pure acetylene is most severe in pipelines. Here a deflagration may travel down a pipe until it becomes a detonation, which is much more destructive. This is a well-known effect in pipeline explosions, but acetylene presents a particularly severe problem in this regard. Further information on acetylene decomposition in equipment and pipelines is given by Schmidt (1971) and by Carver, Smith and Webster (1972). Despite this hazard, long-distance acetylene pipelines have been developed in Germany. Precautions against explosions include the earthing of pipes against static electricity and the use of flame arresters. There are no long-distance acetylene pipelines in the United Kingdom.

The usual material of construction for plant handling acetylene is mild steel. It is necessary in such plant to eliminate copper and brass, which can give rise to the formation of the highly explosive compound copper acetylide.

In some processes, traces of acetylene may be present in the effluent gases. These gases are sometimes cooled to condense out other components. In such cases, consideration should be given to the possibility of forming solid acetylene. Although the literature suggests that pure solid acetylene is not hazardous, this may not be the case if the material is impure.

Bulk acetylene is stored in gasholders. Holders with a capacity of 1000 m^3 have been used in the United Kingdom. Acetylene is stored and distributed in cylinders containing acetone and is widely used in this form, particularly for oxyacetylene welding.

11.11.3 Acrylonitrile

A relevant code for acrylonitrile is the *Codes of Practice for Chemicals with Major Hazards: Acrylonitrile* (the Acrylotnitrile Code) by the CIA (1978). Accounts are also given in *Acrylonitrile* (Dalin, Kolchin and Serebryakov, 1971) and by Langvardt (1985) and Brazdil (1991).

Acrylonitrile is a liquid with a normal boiling point of 77°C. It has moderate solubility in water. It is flammable, the flammable range being 3–17% and the flashpoint −1°C. It is toxic and has a long-term maximum exposure limit of 2 ppm.

Acrylonitrile is liable to polymerize and thus in storage needs to be stabilized. Stabilizers used are methyl ether of hydroquinone (MEHQ), ammonia and water.

Materials of construction for acrylonitrile plants are carbon steel, and for polymerization plants stainless steel. Copper and its alloys should not be used, since they cause contamination which inhibits subsequent polymerization.

Pumps used for transfer may be of the centrifugal or positive displacement types. For centrifugal pumps located outdoors a single mechanical seal is usually adequate, but indoors consideration should be given to double mechanical seals. At normal pumping rates of about 3 m/s the generation of static electricity by acrylonitrile should be minimal, but plant handling this chemical should be earthed.

In relief systems for acrylonitrile, consideration should be given to possible condensation in the relief line.

11.11.4 Ammonia

There is no single code of practice applicable to ammonia, but there are several codes covering particular aspects. These include *Storage of Anhydrous Ammonia under Pressure in the United Kingdom* (HSE, 1986a–c HS(G) 30), *Anhydrous Ammonia – Guidance for the Large Scale Storage, Full Refrigerated, in the United Kingdom* (CIA, 1993 RC40) and *Code of Practice for the Safe Handling and Transport of Anhydrous Ammonia by Rail* (CIA, 1975 PA1). Accounts are also given in *Ammonia* (Slack and James, 1973) and by Bakemeier *et al.* (1985) and Czuppon, Knez and Rounes (1992).

Ammonia is produced by the reaction of hydrogen and nitrogen in converters at high pressure, as described in Section 11.12. Much of the largest use is for fertilizers, in the form of ammonium sulfate and ammonium nitrate and in anhydrous liquid form. It is used to make nitric acid and, in part via this, a range of plastics and fibres such as nylon, urea–formaldehyde resins, urethane, acrylonitrile and melamine. It is also used in the manufacture of explosives, hydrazine, amines, amides, nitriles and dyestuff intermediates and of urea, sodium cyanide and sodium carbonate.

Ammonia has a normal boiling point of −33.4°C and is therefore a gas. The vapour pressure at 20°C is 8.6 bar. It is frequently handled as a liquefied gas, either under pressure or refrigerated. Pressurized liquefied ammonia gives on release a flashing liquid.

Ammonia is flammable, but not readily so. The flammability range is 15–28%. The minimum ignition energy, however, is 100 mJ, which is high. The flammability and explosibility of ammonia is discussed by Kletz (1988a). The incident at Jonova (Case History A124) illustrates the flammability of ammonia.

Ammonia is a toxic irritant. Its long-term occupational exposure standard is 25 ppm. A concentration of about 1700 ppm can be fatal for a half-hour exposure. Its odour is detectable by most people at about 5 ppm.

After a large release of chlorine, a release of ammonia is potentially one of the worst toxic hazards from the common bulk chemicals in the chemical industry.

Ammonia is fully miscible with water. This creates the hazard that if there is water in a vessel containing ammonia vapour, the latter may dissolve, so that a vacuum is formed and the vessel collapses inwards.

Materials of construction for ammonia depend on the operating temperature. While mild steel may be used at ambient temperatures, special steels are necessary at low

temperatures to avoid embrittlement. Materials for ammonia processes are discussed in Section 11.12.

Ammonia is corrosive even in trace amounts to copper, zinc, silver and many of their alloys. It is necessary, therefore, in handling ammonia to avoid the use of valves and other fittings which contain these metals. Under certain conditions ammonia can react with mercury to form explosive compounds (Comings, 1956):

> 'Under pressure, mercury forms a compound with ammonia consisting of several molecules of ammonia per atom of mercury. This compound is apparently not explosive. However, as the pressure is lowered, the ratio of ammonia to mercury decreases and a compound similar to a fulminate is formed. This has been known to detonate and is a serious hazard. The hazard is greatest when a system containing mercury and ammonia is being depressured.'

Impurities in liquid anhydrous ammonia, such as air or carbon dioxide, can cause stress corrosion cracking of mild steel. This is largely inhibited, however, if the ammonia contains 0.2% water and this water content is therefore specified for some applications. This aspect is considered further in Chapters 22 and 23.

The production, storage and transport of ammonia are considered in Section 11.12, and Chapters 22 and 23, respectively, the toxic release hazard is discussed in Chapter 18 and emergency planning in Chapter 24.

11.11.5 Chlorine

Chlorine is treated in Chlorine (Sconce, 1972) and it is the subject of *Safety Advice for Bulk Chlorine Installations* (HSE, 1986a–c HS(G) 28). This code is based on an earlier CIA code and is the code now listed by the CIA; the earlier code *Codes of Practice for Chemicals with Major Hazards: Chlorine* (the *Chlorine Code*) by its predecessor, the British Chemical Industry Safety Council, (BCISC, 1975/1) is no longer listed. Further information is given in the *Chlorine Manual* (Chlorine Institute, 1986 Pamphlet 1). Accounts are also given by Schmittinger (1986) and Curlin, Bommaraju and Hansson (1991).

Chlorine is produced by the electrolysis of brine in mercury or diaphragm cells, with the co-products sodium hydroxide and hydrogen. It is used mainly for the manufacture of a wide range of organic and inorganic chlorine compounds and for the chlorination of water and for bleaching. Some principal organic compounds are chlorinated paraffins such as methyl chloride, methylene chloride, chloroform and carbon tetrachloride from methane and hexachlorobutadiene and hexachloropentadiene from butane and pentane, respectively. The main single organic chloride product is ethylene dichloride which is obtained by chlorination of ethylene and is used mainly to make vinyl chloride. Chlorination of ethylene also gives trichloroethylene and perchloroethylene. Products obtained via chlorination of propylene include propylene oxide, propylene glycol, carbon tetrachloride, glycerine and epoxy resins and synthetic rubber. Aromatic products of chlorination include monochlorobenzene, dichlorobenzene and hexachlorobenzene.

Chlorine has a normal boiling point of −34°C and is therefore a gas. The vapour pressure at 20°C is 6.7 bar. It has a very low solubility in water. Chlorine is frequently handled as a liquefied gas under pressure. In this condition liquefied chlorine gives on release a flashing liquid. Chlorine is not flammable in air, but is itself an oxidant. Chlorine is a toxic irritant. Its long-term occupational exposure standard is 0.5 ppm.

A large chlorine release is potentially one of the most severe hazards from a common bulk chemical presented by the chemical industry. As an oxidant chlorine is in many ways comparable with oxygen. Organic compounds may have flammability limits in chlorine rather similar to those which they have in oxygen. Reactions between organic compounds and chlorine are generally highly exothermic and tend to go to complete chlorination, often with some violence.

Chlorine also forms flammable mixtures with hydrogen. This is important in chlorine production, where both gases are evolved from the electrolysis cells. Hydrogen and chlorine may also be reacted together to produce hydrogen chloride.

Usually, liquid chlorine contains the impurity nitrogen trichloride, which decomposes explosively. Therefore, it is necessary when handling chlorine to prevent the accumulation of this substance. For example, a chlorine vaporizer should not be allowed to boil dry so that the nitrogen trichloride is concentrated and may explode.

Mild steel is a suitable material of construction for use with chlorine unless the water content or temperature renders it unsuitable. Wet chlorine corrodes mild steel rapidly. Mild steel should only be used if the chlorine is dry. For wet chlorine gas, ebonite-lined mild steel is commonly used.

There are both low and high temperature limitations on the use of mild steel with chlorine. Special steels are required at low temperatures to avoid embrittlement. At high temperatures, mild steel burns in chlorine and again special materials have to be used. Chlorine attacks mild steel significantly above 200°C and rapidly above 230°C. In order to prevent reaction, it is normal to limit the operating temperatures with mild steel. The *Chlorine Code* quotes a limit of 120°C.

The design of pressure systems for handling chlorine incorporates a number of special features. Many of these are generally applicable to the handling of a very toxic substance. They are discussed in Chapter 12. In view of the toxicity of chlorine, it is not appropriate to vent large quantities to atmosphere. Plants producing chlorine therefore require emergency gas absorption facilities. Chlorine from pressure relief devices should go to an expanse tank or to gas absorption plant.

Storage and transport of chlorine are treated in Chapters 22 and 23, respectively, the toxic release hazard in Chapter 18, and emergency planning in Chapter 24.

11.11.6 Ethylene dichloride

A relevant code for ethylene dichloride, or 1,2-dichloroethane, is the *Code of Practice for Chemicals with Major Hazards: Ethylene Dichloride* (CIA, 1975 PA13). Accounts are also given by V.L. Stevens (1979) and Rossberg *et al.* (1986).

Ethylene dichloride is made by the liquid phase chlorination of ethylene. It is used principally for the manufacture of vinyl chloride by cracking the ethylene dichloride to vinyl chloride and hydrogen chloride. Usually, the latter is then reacted in an oxychlorination process to produce more vinyl chloride.

Ethylene dichloride is a liquid with a normal boiling point of 84.4°C. It has a low solubility in water. Ethylene dichloride is flammable, the flammable range being 6–16%. The flash point is 13°C (closed cup) or 18°C (open cup).

Ethylene dichloride is toxic. It has a long-term maximum exposure limit of 5 ppm and carries the 'Skin' notation. Concentrations of about 3% can produce nausea, drowsiness and stupor. It is detectable by odour at a concentration of 50–100 ppm. The decomposition products of ethylene dichloride in a fire include hydrogen chloride, which is toxic.

Plant handling ethylene dichloride is usually constructed in mild steel. Mild steel is suitable for dry ethylene dichloride and also for wet saturated ethylene dichloride below 50°C, provided the aqueous phase is alkaline. But at temperatures above 80°C wet ethylene dichloride undergoes hydrolysis, forms acid and rapidly corrodes mild steel. Transfer of ethylene dichloride may be effected by pumping or inert gas padding.

11.11.7 Ethylene oxide

Ethylene oxide is the subject of the *Guidelines for Bulk Handling of Ethylene Oxide* (CIA, 1992 RC14) (the *CIA Ethylene Oxide Guidelines*), the earlier *Code of Practice for Chemicals with Major Hazards: Ethylene Oxide by the Chemical Industry Safety and Health Council* (CIHSC, 1975/1) (the *Ethylene Oxide Code*) is no longer listed. Accounts are also given by Cause *et al.* (1980), Ozero and Procelli (1984), Rebsdat and Mayer (1987), Ondrey (1992) and Siwek and Rosenberg (1993).

Ethylene oxide is produced by the vapour phase oxidation of ethylene. There are various processes; some use air and some use oxygen, but otherwise the processes are broadly similar. It is used primarily for the production of ethylene glycol, which in turn is used in roughly equal proportions as antifreeze and for production of polyesters. Other products obtained via ethylene oxide are ethanolamines, glycol ethers and surfactants.

Ethylene oxide is a toxic, flammable and explosively unstable material. Therefore it exhibits a rather unusual combination of hazards. The properties of ethylene oxide have been the subject of a series of investigations by Burgoyne and co-workers (e.g. Burgoyne and Burden 1948, 1949; Burden and Burgoyne, 1949; Burgoyne, Bett and Muir, 1960).

Ethylene oxide has a normal boiling point of 10.5°C. At atmospheric pressure it may therefore be a gas or a liquid, depending on the temperature, and in handling it may be treated as a liquefied gas. At higher ambient temperatures, a liquid leak undergoes a degree of flashing to vapour. This feature of a normal boiling point close to ambient temperature tends to increase the hazard.

Ethylene oxide is fully miscible with water. In contrast to other flammables such as hydrocarbons, therefore, liquid spills can readily be diluted with water to reduce the hazard of fire.

The lower flammability limit of ethylene oxide is 3%. There is no upper flammability limit as normally conceived, since at high concentrations up to pure ethylene oxide combustion is replaced by explosive decomposition. The flashpoint (open cup) is −17.8°C. The autoignition temperature in air is 429°C.

Ethylene oxide is toxic and has a long-term maximum exposure limit of 5 ppm. The odour of pure ethylene oxide is not detectable by many people below about 700 ppm, and whilst impurities present in the industrial material reduce the odour threshold considerably, odour is not a reliable guide to its presence, and artificial means are necessary. Ethylene oxide liquid or aqueous solution affect the skin.

Ethylene oxide vapour decomposes explosively even in the absence of air, if ignited or heated above about 560°C. The liquid is stable to decomposition.

Liquid ethylene oxide is very susceptible to polymerization. This may be initiated at ambient temperatures by acids, bases and anhydrous chlorides of iron and of some other metals. Also, iron rust is a moderate initiator, so that equipment should be substantially rust free. At around 100°C purely thermal initiation starts, and once this happens iron becomes a promoter. The polymerization is highly exothermic and can result in explosive decomposition. Slow polymerization can also occur, producing a solid polymer which does not decompose explosively.

Mild steel and stainless steel are used as materials of construction for plant handling ethylene oxide, but mild steel must be rust free. The internal surfaces of plant equipment for handling ethylene oxide should be carefully prepared before use and free from foreign matter which could cause slow polymerization such as welding slag, rust and debris. Cleaning may be by shot blasting or by chemical means. If shot blasting is used, it must be possible to remove the dust and debris created; otherwise chemical methods must be used. The stages of acid cleaning are: (1) degreasing, (2) acid pickling, using hydrochloric acid for mild steel and citric acid for stainless steel and (3) for mild steel, atmospheric passivation.

Flanged joints should have stainless steel, spiral wound, polytetrafluoroethene (PTFE) filled joint rings or trapped Fluon rings. Natural rubber joint rings should not be used. Compressed asbestos fibre (CAF) is suitable for use only below 25°C and is therefore not generally recommended. Joints should be kept to a minimum consistent with enabling lines to be opened for polymer clearance.

In order to avoid polymerization, pipework for handling liquid ethylene oxide should be laid out so that it can be completely drained during a shut-down. There should be facilities for blowing through with nitrogen. Lines of less than 25 mm (1 in) bore should not be used. Pipework should be designed to minimize the trapping of ethylene oxide between closed valves or in stagnant pockets. Relief is not normally required on in-plant pipework, but each case should be considered individually.

Ethylene oxide liquid has a high electrical conductivity, of the order of 10^6 pS/m ($1\ S = 1/\Omega^{-1}$). Since experience shows that buildup of electrostatic charge does not occur in a liquid with a conductivity greater than 300 pS/m, it is not necessary to take the usual precautions against the static electricity hazard, such as limitation of pipeline velocities and avoidance of splash filling. However, in order to maintain consistency with practice for flammable liquids generally, transport containers should be earthed during loading and discharge.

Transfer of liquid ethylene oxide may be by gravity, inert gas padding or pumping. For small quantities it may be preferable to use the first two methods. If a pump is used, it is essential for there to be no conditions which can cause an abnormal temperature rise. This requirement can be met by the use of a recycle system from the pump delivery to the suction when the pump is operating, with cooling of the recycle. The recycle system should be sized to handle all the heat which can be generated by the pump when operating against a closed delivery. If the recycle is to the suction tank, the latter acts as a thermal reservoir. If dead-heading can occur, the pump should be fitted with a high temperature trip,

which should shut the pump down if the temperature reaches 10°C above normal.

An in-line centrifugal pump with mechanical seals is the preferred type. It should be fitted with a single seal with a restrictor brush or a double seal flushed with water, which should be analysed regularly to detect leaks. A canned pump should not be used. If a reciprocating pump has to be used, it should be fitted with a double diaphragm seal with suitable sealant and rupture indication.

Refrigerant fluids used for direct heat exchange with ethylene oxide should not react with it and should not contain polymerization initiators.

Vaporizers for liquid ethylene oxide should be designed as once-through systems so as to prevent the accumulation of hazardous residues. The heating medium should be such as to keep the temperature well below that of decomposition. Direct flame or electrical heating should not be used.

Measures are required to prevent contamination of ethylene oxide in storage by backflow from consumer plants, by contamination of inert gas supplies or by flow from the loading terminal. Protection against backflow from the plant should be effected by means of two separate trip systems, the first based on the pressure difference between the ethylene oxide storage outlet and the supply line to the consumer plant and the second on that between the supply line and the inlet of the plant.

Prevention of contamination of the supply of inert gas, typically nitrogen, is ideally effected by the use of separate supplies for storage and process. The measures necessary where the supply is common are detailed in the *Ethylene Oxide Guidelines*.

Ethylene oxide should be stored separately from other flammable liquids. Terminals for loading and unloading ethylene oxide should also be segregated. Storage and transport of ethylene oxide are considered in Chapters 22 and 23, respectively, the toxic release hazard in Chapter 18 and emergency planning in Chapter 24.

11.11.8 Hydrogen

Hydrogen is the subject of the codes NPFA 50A: 1989 Gaseous Hydrogen Systems at Consumer Sites and NFPA SOB: 1989 Liquefied Hydrogen Systems at Consumer Sites and of Hydrogen by the CGA (1974 G-3). Accounts are also given in *Hydrogen* (K.E. Cox and Williamson, 1977–) and *Hydrogen* (W.N. Smith and Santangelo, 1980) and by Donakowski (1981), Mandelik and Newsome (1981), J.D. Martin (1984), Haussinger, Lohmuller and Watson (1989) and Johansen, Raghuraman and Hackett (1992).

Hydrogen is produced by steam reforming or partial oxidation of hydrocarbons or from a hydrogen-rich stream from a low temperature section of a petroleum plant or a coke oven plant or from a chlorine cellroom. It is used in many large-scale processes, notably in ammonia synthesis, refinery hydrogenation processes, and methanol synthesis, and in hydrogenation of coal and hydrogasification of coal to synthetic natural gas (SNG). It is also used in: hydroformylation of olefins, the Oxo synthesis; organic hydrogenations; and hydrogenation of fats and oils.

Hydrogen has a normal boiling point of −252.5°C and is therefore a gas. Hydrogen has a wide flammable range of 4–75%, a low minimum ignition energy of about 0.019 mJ and a high burning velocity. It is therefore easily ignited and burns rapidly. For occupational exposure hydrogen is classed as an asphyxiant.

In consequence of its flammability, hydrogen presents an explosion hazard and it is necessary to take suitable precautions. As far as the hazard of an open air explosion is concerned, hydrogen gas has a low density and tends to rise and dissipate rapidly unless it is very cold. Nevertheless, vapour cloud explosions of hydrogen have occurred. They are discussed in more detail in Chapter 17.

Hydrogen gas may burn in air, but hydrogen flames have low heat radiation, about one-tenth that of propane, and tend, therefore, to be less hazardous. The gap through which a hydrogen flame can travel is much smaller than with most other gases. It is therefore more difficult to make electric motors sufficiently flameproof for operation in atmospheres which may contain a flammable hydrogen–air mixture.

Hydrogen at elevated pressures and temperatures attacks mild steel severely, causing hydrogen decarburization and embrittlement, and it is necessary, therefore, to use special alloy steels in hydrogen service.

Leakage of hydrogen constitutes a problem. The pressures in plant handling hydrogen are commonly high and the gas diffuses readily through small holes. Hydrogen exhibits a reverse Joule–Thomson effect, so that leaking gas heats up and may ignite. Since the flame is non-luminous, it may not be visible. An operator may walk unawares into a hydrogen leak flame.

Hydrogen can also diffuse through solid metal. It can pass, for example, into a thermocouple pocket and thence through the connecting leads into the control room. Where this risk exists, therefore, it is good practice to arrange the connections so that there is no flow path for the hydrogen.

Liquid hydrogen is used in certain special applications, notably aerospace work. This is effectively a separate technology. It is described in *Handbook for Liquid Hydrogen Handling Equipment* (A.D. Little Inc., 1960), and by Cassut, Madocks and Sawyer (1964), Stoll (1965) and Scharle (1965).

11.11.9 Hydrogen fluoride

A relevant code for hydrogen fluoride is *Guide to Safe Practice in the Use and Handling of Hydrogen Fluoride* (CIA, 1978 PA14) (the CIA *Hydrogen Fluoride Guide*). Accounts are also given by Gall (1980) and Aigueperse *et al.* (1988).

Hydrogen fluoride is used industrially both as anhydrous hydrogen fluoride and as solution of hydrogen fluoride in water; the *Guide* recommends that the term 'hydrofluoric acid' be reserved for the latter. It is the former, anhydrous hydrogen fluoride, which is of interest here.

Hydrogen fluoride is produced by the reaction of sulfuric acid on fluorspar in a rotary furnace. There are a number of processes, broadly similar but with variations, involving mainly pre-heaters, pre-reactors and recycle. The main uses are for the manufacture of fluorocarbons and of aluminium fluoride and synthetic cryolite used in the aluminium industry. It is also used in refinery processes.

Anhydrous hydrogen fluoride has a normal boiling point of 19.5°C. At atmospheric pressure, it may therefore be a gas or a liquid, depending on the temperature and in handling it is conventionally treated as a liquefied gas. At higher ambient temperatures, a liquid leak undergoes a degree of flashing to vapour.

Hydrogen fluoride is fully miscible with water. This creates the hazard that if there is water in a vessel containing hydrogen fluoride vapour, the latter may dissolve, so that

a vacuum is formed and the vessel collapses inwards; the like hazard with ammonia has already been mentioned.

Hydrogen fluoride is toxic. It has a short–term occupational exposure standard of 3 ppm (as fluorine). It is detectable by odour at about 2–3 ppm, but reliance should not be placed on this. Aqueous solutions of hydrogen fluoride, anhydrous hydrogen fluoride liquid or, to a lesser extent vapour, affect the skin and eyes.

Hydrogen fluoride is highly corrosive, but its corrosivity depends on the water content. Mild steel is resistant to corrosion down to concentrations in water of about 70% hydrogen fluoride. Plant for the manufacture of hydrogen fluoride is largely made of mild steel, but is designed to allow for the foreseeable presence of water. Mild steel is also the material used for the storage and transport of anhydrous hydrogen fluoride. Mild steel becomes decreasingly suitable as the temperature increases. The *Guide* states that the upper limit is usually given as 50–65°C and recommends that this be observed. Silica and silica-containing materials, including metal slags, are attacked by hydrogen fluoride and welds should be such as to avoid slag inclusions.

Special process conditions, such as those that occur in the manufacture of hydrogen fluoride, may require the use of other materials of construction. The *Guide* gives a list of other materials which may be used for hydrogen fluoride. Pipework for hydrogen fluoride should have flanged or butt-welded joints. The range of materials which can be used for joint rings is narrow and measures are needed to ensure that only suitable materials are used.

Transfer of liquid hydrogen fluoride may be by gas padding or pumping. If pumping is used, measures are needed to prevent cavitation and leaks. A pump with double diaphragm or a canned pump may be used. Padding gas is usually dry air or nitrogen. Unless it is from a source which is inherently dry, the gas should be monitored for water content. The gas supply should have its own pressure control and pressure relief systems, and should not be subject to contamination by hydrogen fluoride.

A vent system is required to handle both normal process and emergency vent flows. The vent gases should pass to a gas absorption system. Water is generally used for absorption, with neutralization by lime slurry.

Methods of relief disposal mentioned in the *Guide* include: returning the relief flow back to a suitable point in the process, which in hydrogen fluoride production is often possible; the use of an expanse tank; and the use of a gas absorption system.

Since with hydrogen fluoride a pressure relief valve is liable to become corroded, the primary relief device used is a platinum bursting disc. A further relief device may be located after the disc to control the relief flow. The design of the relief system ducting should allow for the erosive effect of high velocity hydrogen fluoride gas on mild steel.

Storage and transport of hydrogen fluoride are considered in Chapters 22 and 23, respectively, the toxic release hazard in Chapter 18 and emergency planning in Chapter 24.

11.11.10 Oxygen

Relevant codes for oxygen are *Bulk Liquid Oxygen at Production Plants* (BCGA, 1990 Code 20) and *Bulk Liquid Oxygen at Users' Premises* (BCGA, 1992 Code 19). Oxygen is the subject of NFPA 50: 1990 Bulk Oxygen Systems at Consumer Sites. Accounts are also given by A.H. Taylor (1981) and Kirschner (1991).

Oxygen is produced by the liquefaction and separation of air. It is used in bulk quantities in iron and steel making and in chemical processes. It is also used in oxyacetylene welding.

Oxygen is the constituent in the air which supports combustion of fuels and other materials, and in the pure form it supports combustion even more effectively. Combustible materials of all kinds, ranging from hydrocarbons in chemical reactors to workmen's clothing, undergo combustion much more readily in oxygen-enriched air or in pure oxygen. The enhancement of flammability in oxygen-enriched atmospheres is described in Chapter 16.

Oxygen has a normal boiling point of −183°C (90.2 K) and is therefore a gas. It is frequently handled as a liquefied gas under pressure. In this condition liquefied oxygen gives on release a flashing liquid.

Oxygen is odourless and therefore gives no indication of its presence. Short exposure to air with some degree of oxygen enrichment does not appear to be harmful. Oxygen is used in breathing apparatus. The main hazard of an oxygen-enriched atmosphere is the enhancement of flammability.

The effect of a large release of oxygen would be to increase the combustibility of materials in the oxygen cloud. Such materials might include not only people's clothing but even steel equipment on the plant, since steel will burn in oxygen. A possible source of ignition in such circumstances might be a lagging fire. There appears, however, to be no recorded case of any such incident.

Air separation plants are discussed in Section 11.12.

11.11.11 Phosgene

A relevant code for phosgene is *Code of Practice for Chemicals with Major Hazards: Phosgene* (CIHSC, 1975/3) (the CIA *Phosgene Code*), but this code is no longer listed by the CIA. Accounts are also given by Hardy (1982) and Schneider and Diller (1991).

Phosgene is manufactured by passing carbon monoxide and chlorine over activated carbon. It is used mainly to make isocyanates, particularly toluene diisocyanate. It is also used for chloroformic esters, urea azo dyes, carbonate esters and Friedel Crafts acylations. There are available small tonnage phosgene plants which may be installed at a user's site and which avoid the need to transport and store large quantities of the material.

Phosgene has a normal boiling point of 8.2°C. It is not flammable. It is highly toxic and has a long-term occupational exposure standard of 0.02 ppm, which is a five-fold downwards revision from the previous value of 1 ppm and is very low indeed.

In contact with water phosgene undergoes slow decomposition to hydrochloric acid and carbon dioxide. It is essential, therefore, to keep plant handling phosgene dry in order to prevent such decomposition. Phosgene also reacts with most lubricating oils to form a black sludge.

For dry phosgene, carbon steel has proved a satisfactory material of construction, for both vessels and pipework. Where other substances are also present, it may be necessary to use other materials. The *Code* cautions against the use of non-metallic materials for pipework.

The *Code* gives detailed requirements for the design of storage vessels for liquid phosgene. Process vessels handling more than one tonne of liquid phosgene in normal operation should be designed to a standard similar to that for storage vessels.

For the pipework on a phosgene plant seamless tubes are preferred to seam-welded ones. The pipework should take into account both the maximum and minimum temperatures which may occur. Stress relieving heat treatment may be required. The pipework arrangement should have a good degree of natural flexibility, but bellows should not be used. Joints should preferably be welded, but otherwise flanged. Butt-welded joints should be radiographed. Compressed asbestos fibre gaskets have been used satisfactorily.

Liquid phosgene may be transferred by pumping or inert padding gas. For pumping, glandless pumps should be used. These are suitable for phosgene concentrations down to 5% and for lower concentrations also. Particular attention should be paid to avoidance of cavitation and provision of sufficient net positive suction head (NPSH).

Due to its high solubility in liquid phosgene, nitrogen may be unsuitable as a padding gas. Any gas used should be dry, with a dewpoint less than −30°C. Measures should be taken to prevent contamination of the padding gas supply, preferably by the use of a supply exclusive to the phosgene plant.

Reciprocating compressors are used to compress phosgene vapour, but it is necessary to take special measures to prevent contact between phosgene and lubricating oil. Use is also made in phosgene systems of fans and vacuum pumps.

Relief disposal should be to an expanse tank or to a gas absorption system, but not to atmosphere.

A phosgene plant should normally have two separate gas absorption systems, one to handle process vents and one for emergency reliefs. The former should be designed for flows with high concentrations of inerts but low concentrations of phosgene and the latter for flows with higher concentrations of phosgene. The use of a dedicated absorption system for relief flows guards against corrosion and blockage of the relief lines by materials vented from the process. The phosgene content of gas leaving the gas absorption system should be monitored.

With regard to relief devices, pressure relief valves and carbon bursting discs both have some disadvantages for phosgene duties, but either is suitable with good design. A bursting disc alone risks imposing a sudden high load on the gas absorption system. An acceptable arrangement is a bursting disc followed by a pressure relief valve with an alarm on the intermediate space to detect disc failure.

For pipelines an alternative relief device is an expansion bottle. These bottles are fitted to the top of the pipeline at regular intervals and each is isolated from it by a bursting disc. There should be an alarm on the bottle space to detect disc failure.

The use of water or steam in direct heat exchange with phosgene should be avoided due to the possibility that water will leak into the phosgene stream.

Liquid phosgene may be stored under pressure or refrigerated. The *Code* states that plant for handling and storage of phosgene should be kept simple, even if this means storing liquid phosgene under pressure, that storage vessels for liquid phosgene should be pressure vessels and that the contents of a pressure storage vessel should be kept below 8°C in order to reduce the risk of overloading the gas absorption system due to flash-off if pressure has to be reduced.

11.11.12 Vinyl chloride

Vinyl chloride (VC), or vinyl chloride monomer (VCM), is the subject of *Precautions against Fire and Explosion: Vinyl Chloride* (CIA, 1978 PA15) (the *CIA Vinyl Chloride Guide*). The toxicity of vinyl chloride is treated in *Vinyl Chloride: Toxic Hazards and Precautions* (HSE, 1992 a–d EH 63). Accounts are also given in *Vinyl Chloride and PVC Manufacture* (Sittig, 1978) and by Cowfer and Magistro (1983).

Vinyl chloride was originally produced by the gas phase reaction of acetylene and hydrogen chloride. It is now made almost entirely by the cracking of ethylene dichloride and oxychlorination of ethylene. These two processes are generally operated in combination, with the hydrogen chloride from the cracking of ethylene dichloride being reacted with air or oxygen in the oxychlorination process to produce more vinyl chloride. Vinyl chloride is polymerized to polyvinyl chloride (PVC) and also used to make copolymers.

Vinyl chloride has a normal boiling point of −13.9°C. It is frequently handled as a liquefied gas under pressure. In this condition, liquefied vinyl chloride gives on release a flashing liquid. Vinyl chloride is flammable, the flammable range being 3.6–33%.

Vinyl chloride is toxic and has a long-term maximum exposure limit of 7 ppm. The toxicity of vinyl chloride was not fully appreciated until the mid-1970s. The discovery of its toxicity, and in particular its carcinogenic properties, presented the industry with a problem which, although quite different in nature, was of the same order of magnitude as that caused by the vapour cloud explosion at Flixborough. The decomposition products of vinyl chloride in a fire include hydrogen chloride and phosgene, which are both toxic, particularly the latter. As its full title indicates, the *Vinyl Chloride Guide* deals with the fire and explosion but not the toxic hazards of vinyl chloride.

In the handling of vinyl chloride, it is necessary to ensure that air is excluded. Air can cause the formation of vinyl chloride polyperoxides, which appear as a yellow oil or rubbery solid and which detonate on mild impact. Oxygen also catalyses the polymerization of vinyl chloride. Vinyl chloride can be stored unstabilized if air is excluded, but addition of inhibitor should be considered if this cannot be assured. On the other hand, in the absence of other substances, water in vinyl chloride does not constitute any special hazard, although it may cause contamination of the product with rust.

Change of phase, either condensation or boiling, of vinyl chloride can be hazardous. One hazard is a sudden pressure rise, another concentration of impurities and a third polymerization. The *Code* details measures for safeguarding against these hazards.

Materials of construction for vinyl chloride plants are mild steel and for polymerization plants stainless steel. Other materials which may be used where other substances are present in addition are described in the *Code*. Joints on pipework should be welded or flanged.

Liquid vinyl chloride may be transferred by pumping or inert padding gas. Pumps with fine clearances should be avoided as these can give trouble due to polymerization. Particular attention should be paid to avoidance of cavitation and provision of sufficient NPSH and to the pump seals. For padding, the gas normally used is nitrogen.

Compressors used for the compression of vinyl chloride vapour should be such as to ensure exclusion of air.

Relief flows may be sent to a gas absorption system, a flare or an atmospheric vent, if permitted. Both combustion at a flare and combustion following accidental ignition of a vent generate hydrogen chloride, which is toxic.

A suitable relief device for vinyl chloride is a bursting disc followed by a pressure relief valve, or possibly a second bursting disc. The design should allow for the possibility of polymerization in the pipework leading to the relief device and at the device itself.

Plant handling vinyl chloride should preferably be located outdoors, but where it has to be indoors with the attendant hazard of an indoor release of flammable material, consideration should be given to requirements for ventilation and explosion relief of the building.

Storage of vinyl chloride may be in pressure or refrigerated storage.

11.11.13 Some other chemicals

Some other leading inorganic chemicals are covered in *Bromine and Its Compounds* (Qolles, 1966) and *Nitric Acid and Fertiliser Nitrates* (Keleti, 1985). Accounts of some principal organic chemicals include *Propylene Oxide* (Jefferson Chemical Company, 1963), *Propylene and its Industrial Derivatives* (Hancock, 1973), *Benzene and its Industrial Derivatives* (Hancock, 1975), *Benzene* (Cheremisinoff and Morresi, 1979), *Toluene, the Xylenes and their Industrial Derivatives* (Hancock, 1982), *Maleic Anhydride* (Trivedi and Culbertson, 1982), and *Formaldehyde* (Clary, Gibson and Waritz, 1983).

Polymers are treated in *Encyclopaedia of PVC* (Nass, 1976–), *Vinyl Chloride and PVC Manufacture* (Sittig, 1978), *Encyclopaedia of PVC* (Nass and Heiberger, 1986), *Encyclopaedia of Polymer Science and Engineering* (Mark *et al*., 1989) and *Handbook of Polyolefins* (Vasile and Seymour, 1993).

11.12 Particular Processes and Plants

The chemical and petrochemical industries operate a great variety of processes and plants, many of them highly interconnected. There are certain processes and plant which have particular hazards, which feature prominently in the safety and loss prevention literature and which are appropriate to consider here. These are:

(1) air and oxygen plants;
(2) ammonia plants;
(3) ammonium nitrate plants;
(4) methanol plants;
(5) olefins plants;
(6) LPG and LNG installations;
(7) petroleum refineries and gas processing plants.

Descriptions of the first three types of plants and the associated hazards and precautionary measures are given in *Operating Practices in Air and Ammonia Plants* (1961–62/27–28), in the series *Safety in Air and Ammonia Plants* (1960–69/17–26) and *Ammonia Plant Safety and Related Facilities* (1970–1994/31–52), in *Survey of Operating Practices in Thirty-one Ammonium Nitrate Plants* (AIChE, n.d./15), and in *Safe Operation of Ammonia and Ammonium Nitrate Plants* by the American Oil Company (Amoco/9).

Selected references on particular processes and plants and their hazards are given in Table 11.10 and selected references on ammonia, urea and ammonium nitrate plants and their hazards are given in Table 11.11.

11.12.1 Air separation plants

In addition to the references just given, there are accounts of air separation plants by Newton (1979), A.H. Taylor (1981) and Kirschner (1991).

Air separation plants can produce both oxygen and nitrogen. Each of these products may be in either gaseous or liquid form. Large amounts of oxygen are used in the chemical industry in oxidation processes and in the steel industry in both the blast furnace and steel-making processes. Nitrogen is used in large quantities as a synthesis gas and for gas washing, inerting and purging.

An air separation plant is an integral part of an ammonia plant where the hydrogen for the synthesis gas is obtained from a hydrogen-rich stream or by partial oxidation of hydrocarbons. Hydrogen from partial oxidation or from processes such as coke ovens, catalytic reformers or electrolysis plants is purified by washing in liquid nitrogen, which removes hydrocarbons and carbon monoxide. Nitrogen is then added to the hydrogen to form synthesis gas. The oxygen and nitrogen for these processes are obtained from an air separation plant.

Air separation is carried out by compression, liquefaction and distillation of air. If the products are gases near ambient temperature, the refrigeration required is small and is principally to cover heat inefficiencies and losses, but if they are liquids, there is a much larger refrigeration requirement. This refrigeration is produced by compressing the air and then expanding it through a valve, using the Joule–Thomson effect, or in an expansion engine. The plant is contained in an insulated cold box.

Low pressure plants operate in the approximate pressure range 5–10 bar and intermediate pressure range 10–45 bar. The temperatures are low with nitrogen being separated at about −190°C.

There are two main hazards in an air separation plant. These are that: (1) liquid oxygen reacts with any combustible material with explosive violence and (2) hydrocarbons may accumulate in the liquid oxygen and give an explosive reaction. Combustible materials with which liquid oxygen may react violently include wood, lubricating oils, greases and graphite.

Impurities which may enter the plant and accumulate in the liquid oxygen in the distillation column reboiler include methane, ethane, ethylene and acetylene. These hydrocarbons have a very low solubility in oxygen and therefore tend to precipitate out as solids. The solubility of acetylene in liquid oxygen, for example, is only 7 ppm. The solid hydrocarbons are then liable to react explosively with the oxygen. If nitrogen oxides, especially nitric oxides, are present, they catalyse this reaction.

Precautions which are necessary in liquid air plants, therefore, include the elimination of combustibles, both in the construction and operation of the plant, use of clean air and purification of this air, avoidance of build-up of contaminants in the liquid oxygen and safe disposal of the liquid oxygen.

In order to eliminate the combustible materials, equipment is degreased before installation. Grease and graphite materials are not used for pipe joints and gaskets containing graphite are not used for pipe flanges. Every effort is made to ensure that items such as wood, clothing or rags are not left inside the plant. Measures are taken to reduce the risk of hydrocarbon lubricating oils being carried into the low temperature section from the main compressors. Non-flammable lubricants are used for applications such as liquid oxygen pump seals.

Air is taken from an area which is not contaminated by hydrocarbons or nitrogen oxides. Methods of purifying the air in the air intake include catalytic combustion of

Table 11.10 *Selected references on particular processes and plants and their hazards*

Chemical processes
Groggins (1952); Santini (1961); Kirk and Othmer (1963–, 1978–, 1991–); Faith, Keyes and Clark (1965); Gait (1967); Goldstein and Waddams (1967); Long (1967); Shreve (1967); Hahn and Williams (1970); Kuhn (1971); Considine (1974); Hobson and Pohl (1975); Lowenheim and Moran (1975); British Petroleum Company (1977); Financial Times (1979); Wei, Eraser and Swartzlander (1978); E.R. Kane (1979); Benn Publications Ltd (1980); G.T. Austin (1984); Meyers (1986a)

Air and oxygen plants
American Oil Company (n.d./9); Anon. (1960d); AlChE (1960–69/3–12, 1961–62/13, 14); C.P. Anderson (1960); Rotzler *et al.* (1960); Gardner (1961); Matthews (1961); G.T. Wright (1961); Brink (1962); Lang (1962, 1965); T.R. McMurray (1962); Ball (1963, 1964, 1965, 1966a,b, 1968a); Guccione (1963); Matthews and Owen (1963); Rendos (1963, 1964, 1967); Calvert (1967); Eschenbrenner, Thielsch and Clark (1968); van der Ende (1969); Tanne (1970); NASA (1972–); Booth (1973); Goller (1974); L'Air liquide (1976); Honti (1976); Springman (1977); Newton (1979); Wolff, Eyre and Grenier (1979); C. Butcher (1989c); CGA (1989 P-8); NFPA (1990 NFPA 50); Dunrobbin, Werley and Hansel (1991); Kirschner (1991); Shelley (1991)
Impurities: Bollen (1960); Coleman (1961, 1962); Karwat (1961a,b, 1963); Kerry and Hugffl (1961); Ball (1962, 1965, 1966b); M.H. Jones and Sefton (1962); Schilly (1962); Hofmaier (1963); Parks and Hinkle (1963); McDonnell, Glass and Daues (1967)

Petrochemical plants, olefins plants
OIA (Loss Inf. Bull. 1, Publ. 301,1972 Loss Inf. Bull. 2, 1974 Publ. 101); Hydrocarbon Processing (1963–); Prescott (1966); Stobaugh (1966c, 1967a,b, 1988); R.F. Phillips (1967); Feldman and Grossel (1968); Lofthouse (1969); J.F. Tucker (1969); Loftus (1970); Sugai (1970); de Blieck, Cijfer and Jungerhans (1971); Silsby and Ockerbloom (1971); Gambro, Muenz and Abrahams (1972); Wilkson and Dengler (1972); Dewitt *et al.* (1974); Stork, Abrahams and Rhoe (1974); Zdonik, Bassler and Hallee (1974); Barlow (1975); Fuge and Sohns (1976); Barker, Kletz and Knight (1977); Hydrocarbon Processing (1977, 1981, 1985, 1987b, 1991b, 1993c); Barnwell (1979); Maples and Adler (1978); Boyett (1979); Geihsler (1979); Picciotti (1978, 1980); Wilkinson (1979); Burchell (1980); Bockmann, Ingebrigtsen and Hakstad (1981); Ahearne (1982); Albright, Crynes and Corcoran (1983); Ng, Eng and Zack (1983); Walter (1983); Zack and Skamser (1983); Zdonik and Meilun (1983); Eng and Barnes (1984); Gfflett (1984); Kister and Townsend (1984); Maddock (1984); R.V. Parker (1984); C. Tayler (1984a); API (1985 Std 2508); van Camp *et al.* (1985); Wett (1985); Anon. (1986o); List (1986); Redman (1986b); Short (1986); Kister and Hower (1987); Plehiers, Reyniers and Froment (1990); Wiedeman (1992); Olivo (1994a,b); Shelley (1994)

Gas, gas plants, including industrial utilization
AGA (Appendix 28); BG (Appendix 27, 28, 1978 Comm. 1110, 1989 Comm. 1404); IGasE (Appendix 28, n.d./6, 1978 IGE/TM/2,1985 IGE/TM/2A); Gas Council (1960); Kintz and Hill (1960 BM Bull. 588); Tiratsoo (1967); D.S. Wilson (1969); Anon. (19721); Bresler and Ireland (1972); Crossland (1972); Hart, Baker and Williams (1972); Thornton, Ward and Erickson (1972); BP Ltd (1973); J.A. Gray (1973); Jockel and Triebskorn (1973); Wall (1973); Walters (1973); Anon. (1974c); Medici (1974); API (1975 RP 50); Hydrocarbon Processing (1975,1984a, 1986b, 1988b, 1990b, 1992b); Franzen and Goeke (1976); IChemE (1976/65); Sharpe (1976); Detman (1977); Caldwell, Eifers and Fankhanel (1978); Pritchard, Guy and Connor (1978); UN (1978); J.A. Gray (1980); Meyers (1984); Reren (1987); Melvin (1988); NFPA (1992 NFPA 54, 1992/32)

Coal-based plants
Hoffman (1978); O'Hara *et al.* (1978); J.P. Leonard and Frank (1979); Pitt and Mfflward (1979); C.L. Reed and Kuhre (1979); IBC (1981/12); J.M. Evans and Verden (1982); Merrick (1983); Norton (1984)

Methanol plants
Royal and Nimmo (1969); AlChE (1970/73); Hedley, Powers and Stobaugh (1970); Killer and Marschner (1970); Mehta and Ross (1970); Prescott (1971); Pettman and Humphreys (1975); Supp (1981); Wade *et al.* (1981); Meinhold and Laading (1983); Kobayashi, Kobayashi and Coombs (1986)

Oil, oil refineries
API (Appendix 27, 28, 1983 Publ. 999); ASME (Appendix 28 *Hydrocarbon Processing*); HSE (Appendix 28 *Oil Industry*); IP (Appendix 27, 28, Oil Data Sheets, TP series, 1968–/1, 1980 Eur. MCSP, 1981 MCSP Pt 3, 1984/2); OIA (see Appendix 28); Shell International Petroleum Co. (1933–); W.L. Nelson (1958); Hydrocarbon Processing (1962–, 1984b, 1986c, 1988c, 1990c, 1992); J.R. Hughes (1967, 1970); Adelman (1972); Anon. (1975m); J.A. Price (1962); Vervalin (1964a, 1973a); Crowe and Marysiuk (1965); Albright (1966a,c); Forry and Schrage (1966); Bland and Davidson (1967); Good (1967); Dosher (1970); Hobson and Pohl (1975); Verde, Moreno and Riccardi (1977); Cantrell (1982); M. Sherwood (1982); Shell (1983); Gary and Handwerk (1984); IBC (1985/62, 1993/105); Loubet (1986); Meyers (1986b)

Polyethylene plants
Albright (1966d,f, 1967a,c); Foreman (1972); AlChE (1973/62, 1974/63, 1978/64); Fitzpatrick (1973, 1974); Guill (1973); Hatfield (1973); Marzais (1973); O'Hara and Poole (1973); O'Neal, Elwonger and Hughes (1973); Royalty and Woosley (1973); Ziefle (1973); Afzal and Livingstone (1974); Mauck and Tomita (1974); R.F. Murphy (1974); Prentice, Smith and Virtue (1974); Traversari and Beni (1974); Watson (1974); Beret, Muhle and Villamil (1978); Olivier and Scheuber (1978); H.S. Robinson (1978); Sandner (1978); Siegel (1978); Yasuhara, Kita and Hiki (1978); Chriswell (1983); Redman (1991)

hydrocarbons and adsorption of hydrocarbons and nitrogen oxides.

Build-up of contaminants in the liquid oxygen is minimized by the avoidance of pockets where liquid oxygen accumulates, by running oxygen reboiler tube plates always flooded and by continuous blowdown of liquid oxygen into an auxiliary vaporizer.

If the air supply becomes contaminated, it may be necessary to stop air supply to the plant. Under these conditions heat leaks into the plant and causes liquid oxygen to

Table 11.11 *Selected references on ammonia, urea and ammonium nitrate plants and their hazards*

Ammonia plants
American Oil Company (n.d./9); Anon. (1959b), 1960d); Harding (1959); AlChE (1960–69/3–12, 1961–62,13, 14, 1964/15, 1970–77/17–38); Bresler and James (1965); Guccione (1965b); Wrotnowski (1965); B. Powell (1967); Badger (1968); Eschenbrenner, Thielsch and Clark (1968); Finneran, Sweeney and Hutchinson (1968); Quartulli, Fleming and Finneran (1968); Vancini (1971); Finneran, Buividas and Walen (1972); Sawyer, Williams and Clegg (1972); K. Wright (1973); J.F. Anderson (1974); Sawyer and Williams (1974); Webb (1974); Atwood (1976); Butzert (1976); Hess (1976); Ostroot (1976a); Partridge (1976); Wheeler (1976); K.A. Carter *et al.* (1977); Gilbert and Eagle (1977); R.W. James (1977); Livingstone (1977, 1989); Akitsune, Takahashi and Jejuna (1978); Attwood, Lombard and Merriam (1978); Banks (1978); Gadsby and Livingstone (1978); Hager, Long and Hempenstall (1978); Kusha (1978); Nakano (1978); Wakabayashi (1978); G.P. Williams (1978); Bishop and Mudahar (1979); Czuppon and Buividas (1979); Farinola and Langana (1979); Ricci (1979b); Archambault, Baldini and Train (1980); Butwell, Kubek and Sigmund (1980); Colby, White and Notwick (1980); Handley (1980); Kokemor (1980); Setoyama, Wadar and Funakoshi (1980); Swanson (1980); Buividas (1981); Moon, Mundy and Rich (1981); Saviano, Lagana and Bisi (1981); C.P.P. Singh and Saraf (1981); Strelzoff (1981); Hodgson (1982); A. Nielsen *et al.* (1982); Reddy and Husan (1982); Anon. (1983q); Livingstone and Pinto (1983); G.P. Williams and Hoehing (1983); Atwood (1984); Facer and Rich (1984); Kolffand Mertens (1984); Prijatel (1984); Rohlflng (1984); Grotz, Gosnell and Grisolia (1985); Ruziska *et al.* (1985); Erskine (1986); Song (1986); Josefson (1987); Madhavan and Sathe (1987); W.K. Taylor and Pinto (1987); G.B. Williams, Hoehing and Byington (1987); Epps (1988); Madhavan and Kirsten (1988, 1989); Madhavan and Landry (1988); Mall (1988); Kershaw and Cullen (1989); Short (1989); Armitage *et al.* (1992); Czuppon, Knez and Rounes (1992)

Converters
W.D. Clark and Mantle (1967); Eschenbrenner and Wagner (1972); Appl, Feind and Liebe (1976); Casey (1976); Kusha and Lloyd (1976); W.D. Clark (1977); Dye (1977); J.A. Lawrence (1977); Patterson (1977); R.L. Thompson and Brooks (1977); Wahl and Neeb (1977); B.R. Phillips (1979); Rao, Wiltzen and Jacobs (1986); Karkhanis and van Moorsel (1987); Mack and Shultz (1987); Shimagaki *et al.* (1987); Veazey and Winget (1989)

Catalysts
A. Nielsen (1964); Comley (1968); D.W. Allen (1969); Cromeans and Knight (1969); J.W. Marshall (1969); Delong (1971); Fleming and Cromeans (1971); Scharle, Salot and Hardy (1971); Cromeans and Fleming (1972, 1976); K. Wright and Haney (1972); Salot (1973); R.L. Thompson (1973); P.W. Young and Clark (1973); Bridger (1976); Collard (1976); Lundberg (1979); Dybkjaer *et al.* (1980); Prince and Odinga (1986); Mukheriee *et al.* (1988)

Reformers
Francis (1964); Adams (1967); Pennington (1968); Kobrin (1969, 1978); Bongiorno, Connor and Walton (1970); Ballantyne (1972); Salot (1972, 1975); Lombard and Culberson (1973); Fuchs (1974); Demarest (1975); Fuchs and Rubinstein (1975); E.R. Johnson (1975, 1977); Leyel (1975); Sterling and Moon (1975); MacMfflan (1976); Tendolkar, Sitaraman and Ponnuswamy (1976); Blackburn (1977); Hundtofte (1978); Thuillier and Pons (1978); Hasaballa (1981); Connaughton and Clark (1984); Ennis and Le Blanc (1984); G.M. Lawrence (1984); Roney and Persson (1984); Schlichtharle (1984); Scherf and Novacek (1985); Schuchart and Schlichtharle (1985); Gupton, Stal and Stockwell (1986); McCoy, Dillenback and Traux (1986); Vick (1987); Orbons (1988); Cromarty (1992)

Materials of construction
Speed (1966); W.D. Clark and Mantle (1967); Dial (1968); G.R. James (1968); A. Nielsen (1971); Hutchings *et al.* (1972); van der Horst (1972); Atkins, Fyfe and Rankin (1974); Zeis (1975); Appl and Feind (1976); Tendolkar, Sitaraman and Ponnuswamy (1976); W.D. Clark and Cracknell (1977); Jordan and Rohlflng (1979); Moniz (1985); Barkley (1986); Krishr (1986); Shibasaki *et al.* (1987); van Grieken (1989); Vilkus and Severin (1989)

Pipework
Coats (1967); Chaffee (1970); Appl (1975); Luddeke (1975); Mitcalf (1975); Wicher (1975); Janssen (1976); Osman and Ruziska (1976); Hakansson (1977); Isbell (1977); Pebworth (1977); Batterham (1985); El Ganainy (1985); G.M. Lawrence (1986); Legendre and Solomon (1986); Prescott, Blommaeth and Grisolia (1986); Sotebier and Rail (1986); Schwarz and Spahn (1988); Veazey and Winget (1989); Nightingale (1990)

Compressors
Deminski and Hunter (1962); Penrod (1962); Deminski (1964a,b); Morain (1964); Ball (1965); Wrotnowski (1965); Hile (1967); Stafford (1971); Kusha (1977); Tipler (1979); Verduijn (1979); A.G. Smith *et al.* (1985); Fromm and Rail (1987a); G.R. Thomas (1987); Whiteside (1987); Kumar and Grewal (1988); J.B. Smith and Paulson (1989); Bergenthal, Fromm and Liebe (1990); Iliadis (1990); Leingang and Vick (1992)

Other equipments
Linton and Brink (1967); Roney and Acree (1973); W.D. Clark (1976a); Edmondson (1977); Rail and Fromm (1986); Karkhanis and van Moorsel (1987); Cagnolatti (1988); Mukherjee, Ghosh and Chatterjee (1992)

Control and instrumentation
Daigre and Nieman (1974); van Eijk (1975); Pebworth and Wickes (1975); Prijatel (1984)

Spillages
Kalelkar and Cece (1974); Feind (1975); O'Driscoll (1975a); Raj *et al.* (1975); W.D. Clark (1976b)

Urea plants
Reynolds and Trimarke (1962); Croysdale, Samuels and Wagner (1965); Walton (1965, 1966, 1967); J.F. Anderson (1967); Mavrovic (1974); Dooyeweerd (1975); W.D. Clark and Dunmore (1976); Otsuka, Inoue and Jojima (1976); Bress and Packbier (1977); Cabrini and Cusmai (1977); Jojima (1980); Khadra (1980); P.C. Campbell (1981); Luetzow (1989)

Ammonium nitrate plants
American Oil Company (n.d./9); Commentz *et al.* (1921); Cronan (1960c); AlChE (1966/16); van Dolah *et al.* (1966 BM RI 6773); Huijgen and Perbal (1969); Hansen and Berthold (1972); Perbal (1983); FMA (1989); NFPA (1993 NFPA 490)

evaporate and contaminants to concentrate. There is therefore a certain time period after which hazardous concentrations of contaminants may accumulate. Thus there need to be arrangements for the discharge of the plant liquids.

Contaminants which accumulate in the plant may be removed by regular cleaning. This involves heating up the plant with warm air, which vaporizes the contaminants. The accumulation of contaminants is reduced if the insulation is efficient. The cold box is kept at a positive pressure by air, so that water vapour does not enter and freeze in the insulation, thus making it less effective. The air used has to be free of hydrocarbons.

The small bore instrument and sampling pipework inside the cold box is vulnerable to fracture when insulation is being put in. A suitable precaution is to do this work with the lines under a low nitrogen pressure so that a fracture can be detected by a fall in pressure. A further hazard is the twisting of the tubing when work is being done on tubing which extends through the cold box wall. The likelihood of this may be reduced by the use of back-up wrenches.

Materials of construction used in air separation plants include aluminium, copper and stainless steel. Mild steel is not used in applications where it may undergo low temperature embrittlement or may oxidize as a result of a liquid oxygen leak. This applies to its use not only in vessels and pipework but in supports also.

Tarmacadam road surfaces are avoided in areas where liquid oxygen may spill. Oily or greasy clothing is also avoided.

11.12.2 Ammonia plants

Treatments of ammonia and ammonia plants have been referenced in Section 11.11. Additional accounts of ammonia manufacture are given in *Technology and Manufacture of Ammonia* (Strelzoff, 1981) and by Bakemeier *et al.* (1985) and Czuppon, Knez and Rounes (1992).

Large tonnages of ammonia are used directly in liquid form as a fertilizer and as a chemical raw material for the production of other fertilizers such as ammonium sulfate, ammonium nitrate and ammonium phosphate, of explosives such as ammonium nitrate, of inorganic chemicals such as nitric acid and hydrogen cyanide and of organic chemicals such as acrylonitrile. Other uses are described in Section 11.11. The basic ammonia synthesis reaction is:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

There are a number of processes for ammonia synthesis. The differences between these are partly in the source of hydrogen and partly in the operating conditions and synthesis converter design.

As already described, hydrogen is generally produced by steam reforming of natural gas or naphtha or partial oxidation of fuel oil or from a hydrogen-rich stream from the low temperature separation section of a petroleum or coke oven plant, or from a chlorine cell-room. Nitrogen is normally obtained either from an air separation plant or from air which has been burned to remove the oxygen. Some 75–80% of ammonia production worldwide uses steam reforming and of this some 65–70% is based on a natural gas feedstock.

In the steam reforming of natural gas, the principal process steps are feedstock purification, primary and secondary reforming, shift conversion, carbon dioxide removal, synthesis gas purification, synthesis gas compression, ammonia synthesis and recovery.

Following purification, the natural gas is reacted with steam in a primary reformer, which consists of a tubular reactor placed vertically in the furnace and packed with nickel catalyst. The reaction, which takes place in the temperature range approximately 700–800°C, is strongly endothermic, requires a substantial heat input and produces a mixture of hydrogen, carbon dioxide and carbon monoxide:

$$2CH_4 + 3H_2O \rightarrow 7H_2 + CO_2 + CO$$

Air is injected into this gas as it enters the secondary reformer, which is an internally insulated vessel filled with nickel catalyst operating at a temperature above 1100°C. Combustion of the air provides the heat for completion of the reaction and nitrogen to form the synthesis mixture. The air flow is adjusted to give this correct synthesis gas composition. The gas is then passed through a shift converter to assist the reaction of steam and carbon monoxide to hydrogen and carbon dioxide:

$$H_2O + CO \rightarrow H_2 + CO_2$$

Carbon dioxide and carbon monoxide are removed from the gas by various purification processes. The synthesis gas then passes to the compression section.

In the ICI LCA process a variation is introduced in which the primary reformer can be greatly reduced in size or even eliminated by waste heat reforming, in which part of the reforming is carried out in a reforming heat exchanger utilizing waste heat from the secondary reformer.

In partial oxidation, a similar hydrocarbon feed and oxygen from an air separation plant are preheated separately and reacted in non-catalytic gas generators at a temperature above 1100°C. The reaction is:

$$2CH_4 + O_2 \rightarrow 4H_2 + 2CO$$

The gas is cooled, followed by the shift reaction and purified of carbon dioxide and carbon monoxide by processes similar to those used in steam reforming. It is then cooled and washed with liquid nitrogen to remove traces of impurities. The gas is then adjusted in composition by addition of further nitrogen and passes to the compressors.

If the hydrogen is the off-gas from a refinery reformer, it is purified, dried and then washed with liquid nitrogen. After adjustment of the gas composition by further nitrogen addition, this synthesis gas enters the compressors.

The synthesis gas is then compressed. Whereas reciprocating compressors were a feature of earlier ammonia plants, on modern plants centrifugal compressors are used for compression of the synthesis gas. They are usually driven by steam turbines.

Following compression, the synthesis gas enters the ammonia converters, which on large plants are multiple-bed. There are a variety of designs which differ in respect of the flow pattern, the method of temperature control and the reaction heat recovery. The reaction takes place on an iron catalyst, is exothermic and gives a conversion of about 25%. The ammonia formed is condensed out by cooling the exit gases, which are recycled to the converter.

The ammonia synthesis is one of the classic high pressure processes, but the pressure at which ammonia converters operate has tended to fall. In plants designed before the mid-1960s synthesis converters operated at pressures up to about 340 bar (5000 psi), but the operating pressure in large plants is now of the order of 150 bar (2200 psi).

Up to about 1960, ammonia plants were of relatively low capacity operating at high pressures obtained using reciprocating machines. The early 1960s saw the introduction of the Kellogg single-stream ammonia plant using centrifugal compression and with an output of 544 t/day. This involved a step change in the scale and technology of ammonia plants and was one of the first examples of the large, single-stream plant. By the 1970s single-stream ammonia plants with a capacity of 1500 t/day were becoming common.

The hazards which are encountered in an ammonia plant depend somewhat on the process. But they include those of the chemicals (ammonia and hydrogen), of the operating conditions (high pressure, high temperature and low temperature), and of the pressure system components (furnaces and compressors).

The hazards of and the precautions necessary with ammonia and hydrogen were considered in Section 11.11. Those associated with extreme operating conditions were discussed in Section 11.9 and those associated with pressure systems are dealt with in Chapter 12.

11.12.3 Ammonium nitrate plants

Ammonium nitrate is the subject of NFPA 490: 1986 Storage of Ammonium Nitrate. Accounts of ammonium nitrate plants are given by Zapp (1985) and Weston (1992).

Ammonium nitrate is used in large quantities as an agricultural fertilizer. It is also used as an explosive. Some of the worst disasters in the chemical industry have been ammonium nitrate explosions. These include the explosion at Oppau in 1921, which killed 561 people, and that in Texas City in 1947, in which 522 died. Further details are given in Case Histories A5 and A16, respectively.

Despite these occurrences, ammonium nitrate is widely used. It is manufactured by neutralizing nitric acid with ammonia. The nitric acid is made by oxidation of anhydrous ammonia by air on a platinum–rhodium gauze catalyst. The reaction gases are cooled and absorbed in water to give about 56–60% nitric acid. The temperature of the ammonia entering this converter needs to be kept above 60°C in order to prevent liquid ammonia reaching the gauze and generating high temperatures, which may cause an explosion. The chloride content of the water entering the absorber has to be kept low to prevent formation of hydrochloric acid, and thus aqua regia, which is highly corrosive to stainless steel, and to avoid the catalysis by chloride of thermal decomposition of ammonium nitrate. Nitric acid is extremely corrosive and may react explosively with carbonaceous materials, so leaks require to be repaired promptly.

The nitric acid is neutralized with ammonia vapour. The reaction is exothermic and the heat liberated vaporizes water to produce 83–86% ammonium nitrate solution. Solutions of higher concentrations may be produced by further vaporization of water in evaporators. Concentrated ammonium nitrate solutions are blended with ammonia, additional water or urea as required to give ammonium nitrate–ammonia solutions. Alternatively, solid ammonium nitrate is produced by spray drying in a prilling tower or by concentrating to dryness and spraying the molten nitrate.

It is necessary to control closely the temperatures in ammonium nitrate neutralizers and evaporators. Although pure ammonium nitrate does not decompose rapidly below 200°C, impurities can cause a significant reduction in the decomposition temperature. The temperature in the neutralizers and evaporators is therefore generally kept below 135°C. In operating this plant, it is important not to produce dry ammonium nitrate, which can become hazardous if then heated further.

Limitation of impurities is equally essential, since they increase the tendency of the ammonium nitrate to decompose. Impurities which sensitize decomposition include copper and zinc as well as nitric acid and chlorides. Solid ammonium nitrate is very hygroscopic and tends to cake into a large mass which is difficult to handle. This is overcome by the use of a surface coating such as diatomaceous earth.

Addition of carbonaceous materials to ammonium nitrate can turn it into a blasting agent. It is necessary, therefore, to keep materials such as hydrocarbons away from ammonium nitrate. The sensitizing effect of hydrocarbon surface coatings used to prevent caking is partly responsible for some of the worst explosions which have occurred in the past. Other serious accidents have occurred from the former use of explosives to loosen caked ammonium nitrate, as at Oppau. This is no longer done.

The extent to which ammonium nitrate should be regarded as a high explosive was for some time a matter of debate. The matter was brought to a head when NFPA 490 was first adopted in 1963. A distinction was drawn between fertilizer grade and explosive grade ammonium nitrate, the latter containing some 1% of organic material. In effect, the former was treated in the code as not being a high explosive (W.H. Doyle, 1980). Furthermore, under certain circumstances ammonium nitrate exposed to fire can explode. For some time, the conditions necessary for an explosion were not well defined. Accounts of work on both these problems have been given by van Dolah (1966 BM RI 6903) and van Dolah *et al.* (1966 BM RI 6743, 1966 BM RI 6773).

If ammonium nitrate is heated to about 200°C, it begins to decompose and give off heat. This temperature may be lower if there are impurities present. Up to about 260°C the reaction is well behaved, but about this temperature decomposition becomes much more rapid. In a fire ammonium nitrate burns freely and does not explode. Thus over one three-year period records showed that 13 freight cars containing ammonium nitrate had burnt without explosion. Similarly, there have been several fires which have destroyed without explosion some five million pounds of ammonium nitrate stored in warehouses. But an explosion may occur if there is substantial confinement, so that high temperature and pressure can develop. The risk may be minimized by providing adequate spacing and ventilation in storages.

There are certain precautions which should be taken in the storage, transport and handling of ammonium nitrate. For aqueous solutions, the hazard is mainly that of evaporation of water to give a more concentrated solution. Precautions include limits on the strength of solutions stored and facilities for water addition. For bagged solids, the precautions required include spacing and ventilation, elimination of explosives and oxidizing materials, and avoidance of heat and ignition. In both cases, there should be prompt clearing up of spills.

Ammonium nitrate fires should be fought by the application of large volumes of water. Steam should not be used

on an ammonium nitrate fire. The nitrate itself can supply enough oxygen, so that steam does not smother the fire, but only increases the temperature and the degree of hazard. Water sprinklers, fog nozzles and fire extinguishants such as foam or dry powder tend to be ineffective. In contrast to the situation with other fires in confined spaces, it may be advisable with ammonium nitrate fires to provide ventilation, so as to the reduce the chance of pressure and temperature build-up.

11.12.4 Methanol plants

Accounts of methanol production processes are given by Wade *et al.* (1981) and Fielder *et al.* (1990). Methanol is used in the production of a large range of organic chemicals, notably formaldehyde, methyl-*t*-butyl ether (MTBF), acetic acid, methyl methacrylate (MM) and dimethyl terephthalate. It is also finding use as a fuel, for which it has considerable potential. The basic methanol synthesis reactions are:

$$CO + 2H_2 \rightarrow CH_3OH$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

There are a number of processes for methanol synthesis. All are based on the conversion of hydrogen, carbon monoxide and carbon dioxide to methanol in the presence of a catalyst. The main differences lie in the source of hydrogen and in the catalyst and operating pressure of the synthesis stage.

Sources of hydrogen were discussed above in the context of ammonia synthesis. For methanol, hydrogen is obtained mainly from natural gas, petroleum residues and naphtha. In 1980, some 70% of methanol production worldwide was based on steam reforming of natural gas.

The principal reactions occurring in steam reforming are for methane:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

and for heavy hydrocarbons

$$C_nH_{(2n+2)} + (n-1)H_2 \rightarrow nCH_4$$

and the water gas shift reaction

$$CO + H_2O \rightarrow H_2 + CO_2$$

The reaction is strongly endothermic, requires a substantial heat input and produces a mixture of hydrogen, carbon monoxide and carbon dioxide.

Steam reforming gives a hydrogen content higher than that required for the methanol reaction and processes differ in the way this feature is handled. In some, the hydrogen is burned whilst in others, an addition of carbon dioxide is made. The synthesis gas is then compressed by centrifugal compressors.

At the synthesis stage, the pressure required depends on the activity of the catalyst used and these are the main sources of difference between processes. Three pressure ranges are distinguished: low pressure (50–100 bar), medium pressure (100–250 bar) and high pressure (250–350 bar).

Up to the mid-1960s, methanol processes utilized relatively high pressures of the order of 350 bar obtained using reciprocating compressors. In 1966, ICI began operation of a low pressure methanol plant operating at 50 bar with an output of 400 t/day using all-rotating compression equipment. This plant set the pattern for subsequent developments. By 1980, a typical methanol plant was a single-stream plant, operating in the low–medium pressure range, using all-rotating compression equipment and with an output of 1000–2000 t/day.

11.12.5 Olefins plants

An account of olefins production processes is given in *Ethylene* (Kniel, Winter and Storck, 1980) and by Kniel, Winter and Chung-Hu Tsai (1980), Pike (1981) and Granton and Roger (1987). Olefins plants produce not only ethylene but other major co-products, including propylene and butadiene, and are the key units of a petrochemical works.

The main hazard on an olefins plant is that of the flammable hydrocarbons. This hazard is simply stated, but has many aspects. The hydrocarbons are processed under pressure at both low and high temperatures, which increase the risk both of loss of containment and of formation of a vapour cloud which may cause a fire or explosion.

Many aspects of olefins plants are discussed in Chapters 10, 12, 20 and 22, which deal with plant layout, pressure system design, plant operation and storage, respectively. A review of the evolution of safety aspects of olefins plants has been given by Barker, Kletz and Knight (1977), who consider in particular the following aspects: (1) plant layout, (2) plant equipment, (3) pressure relief and (4) leak control. The authors discuss these features in relation to differences of practice on ICI's successive olefins plants, particularly the then most recent plants, Nos 4 and 5. In the account given below, 'policy' refers to thinking described as 'current' in the paper by Barker, Kletz and Knight.

On plant layout the policy is to space units so that an expected leak does not find a source of ignition (rather than to use rules-of-thumb), to increase the number of fire breaks and to put more equipment at grade level, where it is more accessible to inspection and to fire fighting.

Electrical and instrument cables are vulnerable to flash fires and damage to cabling can cause extensive downtime. Whereas on No. 4 plant no special attention was paid to this aspect, on No. 5 plant in high risk areas cables are run in asbestos/galvanized steel troughs on the cable racks. Policy is to develop preformed reinforced concrete troughs.

Defects in the drainage systems of early olefins plants were that insufficient care was taken in siting low points and gullies and that drains did not have sufficient capacity to carry away fire water. These deficiencies were rectified on the No. 5 plant, in which the high and low points and the drains are located so as to avoid pools of liquid under equipment and the drains are sized to take the quantities of water used to cool major vessels in and near a fire area. The plant, however, has conventional luted drains and some drains from roads and pebbled areas do not pass through the oil–water separator. The policy is to use fully flooded drains with no vapour space in which explosion can occur and with no lutes which can choke, to make extensive use of paving, and to take all drainage from roads and pebbled areas to the oil–water separator.

With regard to process equipment, the early olefins plants had multiple reciprocating or spared centrifugal compressors. Current plants have single unspared machines. This requires the highest standard of design and operation. But it is very effective in reducing leaks.

Another area where leaks can occur is on cold pump glands. The use of O-rings and the elimination of routine

pump changeovers have greatly reduced such leaks. Leakage has been further reduced by the use of brazed aluminium plate fin heat exchangers instead of tubular heat exchangers on cold duties. It is necessary, however, to provide these finned tube exchangers with special protection against fire damage.

Developments in pressure relief include the reduction of the total amount of material to be released, reduction of the probability that hydrocarbons will be discharged to the atmosphere unburnt and improvements in the safety of unburnt discharges.

Measures which can be taken to reduce discharge to the flare system include the more extensive use of trip systems and of higher design pressures for vessels such as low pressure catchpots.

The No. 5 plant has two separate flare systems, and this practice would be repeated. One system is for wet streams and the other for cold, dry streams. Process gas can be dumped to either flare or via a process gas transfer system to the fuel gas system or to other flare systems.

Various measures have been developed to reduce and control leaks. Both plants No. 4 and 5 have a leak detection system using Sieger detectors. There is a total of 140 detectors on the two units. Both plants are also provided with a steam curtain to dilute any vapour cloud which may escape from the plant. Extensive use is made of emergency isolation valves. The valves on No. 5 plant have been individually listed and justified by Kletz (1975b).

The possibility of hydrocarbons entering steam or condensate systems is investigated and potential routes are classed as high or low risk. On high risk routes the risk is either eliminated completely or at least is reduced. Thus a tubular heat exchanger is high risk if it may be subjected to conditions such as low temperature, high pressure, vibration or intermittent use. If, for example, a steam-heated heat exchanger might reach subzero temperatures during plant upsets, the practice would be to fit the steam supply with a check valve and the condensate system with a trip valve closed as appropriate by low level and/or low temperature.

The authors list the following safety reviews which are made on olefins plants: (1) piping and instrument diagram, (2) electrical distribution, (3) relief and blow-down, (4) layout, (5) paving and drainage, (6) cable routing and protection, (7) means of escape from structures and buildings, (8) fire fighting and (9) fire protection.

The foregoing is a necessarily brief summary of the hazards of olefins plants and of some of the measures developed to deal with them. Many of the aspects mentioned are considered in more detail in other chapters.

A further account of loss prevention in an ethylene plant has been given by Olivo (1994a).

11.12.6 LPG and LNG installations

Propane and butane are stored in liquid form as LPG. They play an important part in the oil and chemical industries, which have large LPG storages.

LPG is treated in *An Introduction to Liquefied Petroleum Gas by the LPG Industry Technical Association* (LPGITA, n.d.) and are the subject of a set of codes of practice, notably Installation and Maintenance of Fixed Bulk LPG Storage at Consumer Premises (LPGITA, 1991 LPG Code pt 1); the LPGITA is now renamed the Liquefied Petroleum Gas Association (LPGA). LPG is also covered in Storage of LPG at Fixed Installations (HSE, 1987a–d HS(G) 34) and in the Liquefied Petroleum Gas Safety Code (IP, 1987 MCSP Pt 9). It is the subject of NFPA 58: 1989 Storage and Handling of Liquefied Petroleum Gases (also published as the *Liquefied Petroleum Gases Handbook*) and NFPA 59: 1989 Storage and Handling of Liquefied Petroleum Gases at Utility Plants. Further accounts of LPG are given by Selim (1981) and S.M. Thompson (1990).

LPG is widely used as a fuel in general manufacturing industry, which therefore has a large number of LPG storage installations of various sizes. In general, these industries are not as well versed in the hazards of flammable materials as the chemical industry.

Natural gas, which is mainly methane, has replaced coal gas as the gas supplied to industrial and domestic users by British Gas. Most of the gas is obtained from the North Sea, but some is imported as LNG. In contrast to LPG, the number of LNG installations is very small, but the quantities stored are large. There is sophisticated management of the hazard.

LNG is the subject of *NFPA 59A: 1990 Production, Storage and Handling of Liquefied Natural Gas and of LNG Materials and Fluids* by the National Bureau of Standards (NBS, 1978), *Liquefied Energy Gases Safety* by the General Accounting Office (GAO, 1978), *Liquefied Natural Gas: Safety, Siting and Policy Concerns* (US Senate, 1978) and *Liquefied Gas Handling Principles on Ships and in Terminals* (McGuire and White, 1986). Further accounts of LNG are given by Boesinger, Nielsen and Albright (1980) and Hammer *et al.* (1991). Selected references on LPG and on LNG and their hazards are given in Tables 11.12 and 11.13 respectively.

LPG and LNG installations present the hazards of fire and explosion. In view of the scale involved, the siting of a large LNG installation is a major planning matter, which is likely to involve a public inquiry.

LNG is shipped to the storage terminals by specially designed vessels. The shipping of LNG involves the hazard that LNG may be spilled on the sea, may evaporate rapidly and may give a vapour cloud fire or explosion. This hazard has been a matter of much concern and has been the subject of considerable investigation. It is considered further in Chapters 16 and 17.

Storages of LPG and LNG are among the installations which have been of particular concern in relation to interactions between hazardous plants. Thus, for example, LPG storages, if poorly sited, are a possible threat to nuclear reactors and LNG storages may be hazarded by other plants. The British Gas LNG terminal at Canvey was one of the installations investigated in the *Canvey Report*, which is described in Appendix 7.

Closely related are synthetic fuels, or synfuels, including SNG. An account is given in *Handbook of Synfuels Technology* (Meyers, 1984).

11.12.7 Petroleum refineries and gas processing plants

Petroleum refining and gas processing involve the handling of hydrocarbons in very large quantities. This industry has faced many of the classic problems in SLP and has contributed much to their solutions.

Accounts of petroleum refining include *The Petroleum Handbook* (Shell International Petroleum Company, 1933–), *Modern Petroleum Technology* (Hobson and Pohl, 1975), *Our Industry Petroleum* (British Petroleum Company, 1977), *Petroleum Refining Technology and Economics* (Gary and Handwerk, 1984) and *Handbook of Petroleum Refining Processes* (Meyers, 1986b).

Table 11.12 *Selected references on LPG and its hazards*

IGasE (n.d./5); LPGFTA (Appendix 27; n.d., 1974/1, 1991 Code Pt 1); Bray (1964); FPA (1964/1); van Fossan (1965); Eckhart (1969); Andrews (1970); Home Office (1971/2, 1973/4); T.H. Taylor (1971); HSE (1973 HSW Booklet 30); A.F. Williams and Lorn (1974); Heng-Joo Ng and Robinson (1976); Skillern (1976); Wesson (1976); Jensen (1978); Rasbash (1978/79); Steinkirchner (1978); Anon. (1979c); Craig and White (1980); Hogan, Ermak and Koopman (1981); C. Jones and Sands (1981); Luks and Kohn (1981a); Selim (1981); BG (1983 BGC/PS/ DAT24); Desteese and Rhoads (1983); Chowdhury (1984); Moodie, Billinge and Cutler (1985); Rammah (1985); Jenkins and Martin (1983); UL (1985 UL 144, 1986 UL 21); Avgerinos (1987); IP (1987 MCSP Pt 9); API (1989 Std 2510, Publ. 2510); Dunne and Higgins (1989); Pantony and Fullam (1989); B.M. Lee (1989); Vermeiren (1989); S.M. Thompson (1990); NFPA (1992 NFPA 58, 59)

Storage
ICI/RoSPA (1970 IS/74); Lafave and Wilson (1983); Fuvel and Claude (1986); Lagron, Boulanger and Luyten (1986); Blomquist (1988); Droste and Mallon (1989); ILO (1989)

Transport
Sea: Gosden, Smith and Elkington (1982); Lyon, Pyman and Slater (1982); Lakey and Thomas (1983); Buret, Hervo and Tessier (1985); Chauvin and Bonjour (1985); Pakleppa (1991)

Projects, installations, operations
Borseth, Huse and Olsen (1980); Shtayieh *et al.* (1982); Bonnafous and Divine (1986); Branchereau and Bonjour (1986); Bendani (1989); Pangestu (1991)

Fire protection (*see* also Tables 16.2 and 22.1)
J.M. Wright and Fryer (1982); Fullam (1987); S. Stephenson and Coward (1987); API (1989 Publ. 2510A); B.M. Lee (1989); NFPA (1992/31)

Hazard assessment and control
SAI (1974); van der Schaaf and Opschoor (1980); Romano, Dosi and Bello (1983); Wicks (1983); Crossthwaite (1986); Crocker and Napier (1988a); Droste and Mallon (1989)

Table 11.13 *Selected references on LNG and its hazards*

Abadie (1966); Gram (1968); IGU (1968–); P.C. Johnson (1968); Stark and Washie (1968); Bloebaum and Lewis (1969); Barren (1970); Cribb and Hildrew (1970); Haselden (1970, 1971); Potter and Bouch (1970); R. Shepherd (1970); IGasE (1971IGE/SR/11); AGA (1973); Thorogood, Davey and Hendry (1973); Wall (1973,1975); AGA (1974/18, 1979/5, 1981/6, 1984/10, 1986/11); Battison (1974); AD. Little (1974c); Lorn (1974); Sarkes and Mann (1974); ASCE (1976/6); Peebles (1977); Proes (1977); US Congress, OTA (1977); Whitlock (1977); P.J. Anderson and Daniels (1978); Ediger (1978); HSE (1978b); US Senate (1978); Arnoni (1979); Yamanouchi and Nagasawa (1979); Ait Laoussine (1980); Atallah (1982, 1983); Faridany (1982); Geist (1985); Gilbert *et al.* (1985); Rideout *et al.* (1985); Leray, Petit and Paradowski (1986a,b); McGuire and White (1986); Anon. (1987r); Melvin (1988); Hammer *et al.* (1991)

Physical and chemical properties
Gonzalez *et al.* (1968); Klosek and McKinley (1968); Huebler, Eakin and Lee (1970); Nakanishi and Reid (1971); Luks and Kohn (1981b); FPA (1987 CFSD H30)

Materials of construction
Burkinshaw (1968); Duffy and Dainora (1968); Lake, DeMorey and Eiber (1968); Cordea, Frisby and Kampschaefer (1972); ASTM (1975 STP 579); Khenat and Hasni (1977); NBS, Cryogenics Division (1978); Leeper (1980); Charleux and Huther (1983); Duffaut (1983); Krause (1986); Minoda *et al.* (1986); Ohsaki *et al.* (1986); Vercamer, Sauve and Lootvoet (1987)

Instrumentation
Blanchard (1975); Blanchard and Sherburne (1985); Broomhead (1986); Flesch and Dourche (1986); Saiga *et al.* (1991)

Heat exchangers
Merte and Clark (1964); Gaumer *et al.* (1972); O'Neill and Terbot (1972); Tarakad, Durr and Hunt (1987)

Process machinery
Bourguet (1968); Linhart (1970); Schlatter and Noel (1972); L.R. Smith (1972); Guguen and Cherifl (1974); Kato (1977)

Storage
IGasE (n.d./2–4); Tutton (1965); E.L. Smith (1966); Closner (1968, 1970); Ward and Egan (1969); Berge (1970); G.H. Gibson and Walters (1970); Hashemi and Wesson (1971); Geist and Chatterjee (1972); Gondouin and Murat (1972); Kiimper (1972); Lusk and Dorney (1972); Mansillon (1972); US Congress (1973); Schuller, Murphy and Glasser (1974); K.A. Smith and Germeles (1974); Stone, Hill and Needels (1974); Walters, Dean and Carne (1974); Ferguson (1975); Bellus *et al.* (1977); Fujita and Raj (1977); Haddenhorst and Lorenzen (1977); Ishimasa and Umemura (1977); US Congress, OTA (1977); Dinapoli (1978); HSE (1978b, 1981a); Bakke and Andersen (1982); Beevers (1982); Brumshagen (1982); van Hoof and Ofrenchk (1982); Yamakawa (1982); Zick and LaFave (1982); Boulanger and Luyten (1983a,b); Cheyrezy (1983); Closner and Wesson (1983); Collins *et al.* (1983); Lafave and Wilson (1983); de la Reguera *et al.* (1983); Steel, Faridany and Ffooks (1983); Steimer (1983); Capdevielle and Goy (1985); Fluggen, Niissbaumer and Reuter (1985); Huther, Zehri and Anslot (1985); Marchaj (1985); Speidel (1985); Vater (1985);

Gas processing is treated in *Gas Encyclopaedia* (L'Air liquide, 1976), *Handbook of Industrial Gas Utilization* (Pritchard, Guy and Connor, 1978) and *Natural Gas* (Melvin, 1988).

Reference to petroleum refining and gas processing is made throughout this book.

11.13 Operational Deviations

An important aspect of process design is consideration of possible deviations of operating parameters from their design values. Some of these deviations are listed in Table 11.14. A further list of deviations is given in the checklist for hazard and operability (hazop) studies shown in Figure 8.24.

The causes of deviation of a process variable are mostly specific to that variable, but there are some general causes of deviation. One is the deterioration or failure of equipment. Another is the maloperation of the control system, including in this the process operator.

Crawford, Durr and Handman (1986); Lagron, Boulanger and Luyten (1986); Leray, Petit and Paradowski (1986a,b); Acketts (1987); Bomhard (1987); Morrison (1987); Beese, Trollux and Jean (1989); Itoyama *et al.* (1989); A.L. Marshall (1989); NFPA (1990 NFPA 59A); Meratla (1990); Carre and Bre (1991); Neville and White (1991); Chen-Hwa Chiu and Murray (1992)
Rollover: J.S. Turner (1965); Hashemi and Wesson (1971); Chatterjee and Geist (1972); Maher and van Gelder (1972a,b); Sarsten (1972); Drake, Geist and Smith (1973); Germeles (1975a,b); K.A. Smith *et al.* (1975); Drake (1976); Takao and Narusawa (1980); Nakano *et al.* (1983); Takao and Suzuki (1983); Lechat and Caudron (1987); Benazzouz and Lasnami (1989); Marcel (1991)

Transport
Dyer (1969); A.E. Gibson and Pitkin (1972); Gondouin and Murat (1972); US Congress, OTA (1977); HSE (1978b, 1981b)
Road: Eifel (1968); Stahl (1968); Montet, Przydrozny and Inquimbert (1977)
Rail: Eifel (1968); Backhaus and Jannsen (1974)
Waterway: Kober and Martin (1972); Backhaus and Jannsen (1974); Backhaus (1982)
Pipelines: C.J. Gibson (1968); Gineste and Lecomte (1970); Hoover (1970); Ivantzov, Livshits and Rozhdestvensky (1970); Katz and Hashemi (1971); Dimentberg (1972); Ivantzov (1972); Walker, Coulter and Norrie (1972); Dumay (1982); Backhaus (1983); van Tuyen and Regnaud (1983); Kostering and Becker (1987)
Sea: Tutton (1965); Pilloy and Richard (1968); Ward and Hildrew (1968a); F.S. Atkinson (1970); Filstead and Rook (1970); Guilhem and Richard (1970); Rook and Filstead (1970); Gilles (1972); Kober and Martin (1972); Booz-Allen Applied Research Inc. (1973); H.D. Williams (1973); Soesan and Ffooks (1973); Hansen and Vedeler (1974); R.C. Hill (1974); Kniel (1974); AGA (1975/24); D.S. Allan, Brown and Athens (1975); Corkhill (1975); Eisenberg, Lynch and Breeding (1975); J.P. Johnson and Jamison (1975); Authen, Skramstad and Nylund (1976); Prew (1976); Department of Commerce, Maritime Administration (1977); DOT, CG (1977a); Eke and Gibson (1977); Ffooks (1977); Findlater and Prew (1977); Mathiesen *et al.* (1977); Schwendtner (1977); US Congress, OTA (1977); Vrancken and McHugh (1977); HSE (1978b, 1981a); Glasfeld (1980); F.S. Harris (1980); Bockenhauer (1980, 1981, 1985, 1987); Shumaker (1980); Bourguet (1981); Angas (1982, 1985); Armand (1982); Beevers (1982); Benoit (1982); Bojrkman (1982); Brumshagen (1982); Edinberg *et al.* (1982); Hillberg (1982); Holdsworth (1982, 1983, 1985); Lyon, Pyman and Slater (1982); Mabileau (1982); Mankabady (1982); Masaitis and Tornay (1982); van Mater *et al.* (1982); P.R. Mitchell (1982); Nagamoto *et al.* (1982); Nassopoules (1982); Peck and Jean (1982); Riou and Zermati (1982); Veliotis (1982); Aprea (1983); Berger (1983); Fujitani *et al.* (1983); Huther and Benoit (1983); Jean and Lootvoet (1983); Lakey and Thomas (1983); Murata *et al.* (1983); Nagamoto *et al.* (1983); van Tassel (1983); Vogth-Eriksen (1983); B. White and Cooke (1983); Aldwinckle and McLean (1985); Fujitani *et al.* (1985); Jean and Bourgeois (1985); Jenkin, Singleton and Woodward (1985); Latreille (1985); Tanaka and Umekawa (1985); Bakke (1986a); Betille and Lebreton (1986); J. Bradley (1986); J.A. Carter (1986); Itoyama *et al.* (1986); Lootvoet (1986); McLean and Cripps (1986); Ogawa *et al.* (1986); Ogiwara *et al.* (1986); Olschlager (1986); Rowek and Cook (1986); Schrader and Mowinckel (1986); Ackerman and Hutmacher (1987); Flesch and Lootvoet (1987); Huther, Anslot and Zehri (1987); Fujitani *et al.* (1987); Ferguson, McLean and Sakai (1989); Fujitani, Okumura and Ando (1989, 1991); Jean, Lootvoet and Bennett (1989); Meratla (1990); Claude and Etienne (1991); Itoyama *et al.* (1991); Mathiesen *et al.* (1991); Ogiwara *et al.* (1991); Pakleppa (1991); Tornay, Gilmore and Feskos (1991); Wayne, Bockenhauer and Gray (1991)
Shipping statistics: J.R. Evans (1987); Kolb and Boltzer (1987)
Ships engines: Engesser *et al.* (1987); Grøne and Pedersen (1987); Terashima *et al.* (1987)
Ship-shore transfer: Whitmore and Gray (1987)

Training
Blogg (1987); Karim *et al.* (1987)

Projects, installations, operations
Guccione (1964); Filstead (1965); IGasE (1965 Comm. 696); Culbertson and Horn (1968); Engler (1968); P.C. Johnson (1968); R.T. Miller (1968); Naeve (1968); Pierot (1968); Rerolle (1968); Stanfffl (1968); Ward and Hildrew (1968b); Bourguet, Garnaud and Grenier (1970); Gineste and Lecomte (1970); Laur (1970); Asselineau *et al.* (1972); Berge and Poll (1972); Bourguet (1972); C. Gibson (1973); Eke, Graham and Malyn (1974); Horn *et al.* (1974); Jenkins, Frieseman and Prew (1974); Purvin, Withington and Smith (1974); Anon. (1976c,e); Dolle and Gilbourne (1976); Daniels and Anderson (1977); Khenat and Hasni (1977); Ploum (1977); Seurath, Hostache and Gros (1978); Anspach, Baseler and Glasfeld (1979); Kime, Boylston and van Dyke (1980); Rust and Gratton (1980); KW. Edwards *et al.* (1982); Zermati (1982); Chauvin and Bonjour (1985); McKinney and Oerlemans (1985); Setters, Luck and Pantony (1985); de Sola (1985); Branchereau and Bonjour (1986); Colonna, Lecomte and Caudron (1986); Craker, Scott and Dutton (1986); Leray, Petit and Paradowski (1986); White-Stevens and Elliott (1986); Benazzouz and Albou (1987); Tarakad, Durr and Hunt (1987); Vik and Kjersem (1987); Bendani (1989); Dassonville and Lechat (1989)

Safety and environmental aspects
Copp (1971); Kober and Martin (1972); Mansfflon (1972); Napier (1972); J. Davis (1973); P.J. Anderson and Bodle (1974); FPC (1974); Stone, Hills and Needels (1974); Walters, Dean and Carne (1974); F.H. Warren *et al.* (1974); California State Legislature (1976, 1977); von Ludwig (1975); F.W. Murray, Jaquette and King (1976); FERC (1977); Comptroller General (1978); General Accounting Office (1978); US Senate (1978); L.N. Davis (1979); Ahern (1980); R.A. Cox *et al.* (1980); McGuire (1980); Rust and Gratton (1980); Atallah (1982,1983); Kotcharian and Simon (1982); Navaz (1987)

Leaks and spillages
R.O. Parker and Spata (1968); Humbert-Basset and Montet (1972); AGA (1974); Battelle Columbus Laboratories (1974); Fay and Lewis (1975); H.H. West, Brown and Welker (1975); Neff, Meroney and Cermak (1976); R.A. Cox and Roe (1977); HSE (1978b, 1981a)
Marine spillages: Burgess, Biordi and Murphy (1970 BM S4105); Burgess, Murphy and Zabetakis (1970 BM RI 7448); Enger and Hartman (1972a,b); Kneebone and Prew (1974); Raj and Kalelkar (1974); Eisenberg, Lynch and Breeding (1975); Germeles and Drake (1975); Havens (1977, 1978); US Congress, OTA (1977); HSE (1978b, 1981a)

Fires (*see* Tables 16.1 and 16.2)

Fire protection (see also Tables 16.2 and 22.1)
van Dyke and Kawaller (1980); Rudnicki and vander Wall (1980); H.H. West, Pfenning and Brown (1980); Sonley (1982); S. Stephenson and Coward (1987); B.M. Lee (1989); NFPA (1990 NFPA 59A)
Inerting: Johannessen (1987); Oellrich (1987); Tepper (1987)

Hazard assessment and control
F.H. Atkinson (1970); Nassikas (1970); Brubaker, Koerner and Mathura (1972); Burgess, Biordi and Murphy (1972); Crouch and Hillyer (1972); Mansillon (1972); Fay (1973); McKinley (1973); R.C. Hill (1974); Horner (1974); Horner and Ecosystems Inc. (1974); Raj and Kalelkar (1974); SAI (1974); Allan, Brown and Athens (1975); Eisenberg, Lynch and Breeding (1975); Fedor, Parsons and de Coutinho (1975); Gratt and McGrath (1975a,b, 1976); DOT, CG (1976, 1977b); van Horn and Wilson (1976); California Assembly (1977); California Energy Resources Conservation and Development Communication (1977); R.A. Cox and Roe (1977); DOT, OPSO (1977a); Fairley (1977); FPC, Bureau of Natural Gas (1977); Kopecek (1977); Mathiesen *et al.* (1977); John J. McMullen Associates Inc. (1977); Resource Planning Associates (1977); Snellink (1977); Socio-economic Systems (1977); US Congress, OTA (1977); Wesson and Associates Inc. (1977); BGC (1978); California Control Communication (1978); FERA (1978); HSE (1978b, 1981a); Nikodem (1978, 1980); Philipson (1978a,b, 1980); Rigard and Vadot (1979); R.A. Cox *et al.* (1980); Feely *et al.* (1980); Lautkaski and Fieandt (1980); Summer *et al.* (1980); Kunreuther and Lathrop (1981); Lyon, Pyman and Slater (1982); Roopchand (1983); Solberg and Skramstad (1982); Valckenauers (1983); Wicks (1983); Dale and Croce (1985); D.A. Jones (1985); Sellers, Luck and Pantony (1985); Valk and Sylvester-Evans (1985); Setters and Luck (1986); Schrader and Mowinckel (1986); Zehri *et al.* (1986); Navaz (1987)

The effects of deviations and the measures which may be taken to prevent them are also specific. But there are certain devices which are generally provided to give protection against extreme deviations, particularly of pressure and temperature. These are considered in the discussion of pressure systems and of control systems in Chapters 12 and 13, respectively. A further discussion of operating deviations is given by Wells, Seagrave and Whiteway (1976).

When a plant has been designed, it should be checked by some method such as a hazop study, as described in Chapter 8. Again this technique is based on consideration of operational deviations.

11.13.1 Pressure deviations

Pressure deviations can occur as a result of: changes in action of pumping equipment (e.g. failure of a pump or compressor), changes in flow (e.g. closure of a valve or pump outlet), changes of heat input (e.g. heat from sun or fire), changes in heat output (e.g. loss of condenser cooling), contacting of materials (e.g. hot oil and water), thermal expansion and contraction (e.g. liquid density changes in a pipeline), and chemical reaction and explosion (e.g. runaway reaction).

Effects of pressure deviations include overpressure and underpressure of equipment and changes of temperature, flow and level. Measures should be taken as appropriate to reduce the pressure deviations. In addition, it is essential to provide protective devices which prevent overpressure and underpressure.

11.13.2 Temperature deviations

Some causes of temperature deviations are: changes in heat input (e.g. loss of fuel), changes in heat output (e.g. loss of cooling), changes in heat transfer (e.g. fouling of heat exchangers), generation of heat (e.g. runaway reaction), changes of flow (e.g. flow to a reactor), changes of pressure (e.g. pressure reduction causing liquid flashing), thermal lags (e.g. lags in heat exchangers), hot spots (e.g. machinery in distress).

Table 11.14 *Some deviations of operating parameters from design conditions (after Wells, Seagrave and Whiteway, 1976) (Courtesy of the Institution of Chemical Engineers)*

Process variables	Pressure, temperature, flow, level, concentration
Pressure system	Mechanical stress, loading, expansion, contraction, cycling effects, vibration, cavitation, resonance, hammer; corrosion, erosion, fouling
Chemical reactions	Reactions in reactors: nature and rate of main reactions and side reactions Catalyst behaviour reaction, regeneration, poisoning, fouling, disintegration Unintended reactions elsewhere: explosion, heating, polymerization, corrosion
Material characteristics	Vapour density; liquid density, viscosity; melting point, boiling point; latent heat; phase change; critical point effects; solids physical state, particle size, water content
Impurities	Contaminants; corrosion products; air; water
Localized effects	Mixing effects, maldistribution; adhesion, separation, vapour lock, surging, siphoning, vortex generation, sedimentation, fouling, blockage, hot spots
Time aspects	Contact time, control lags, sequential order
Process disturbances	Operating point changes, changes in linked plants, start-up, shut-down, utilities failure, equipment failure, control disturbance, operator disturbance, blockage, leakage, climatic effect, fire
Constructional defects	Plant not complete, not aligned, not level, not supported, not clean, not leak-tight; materials of construction incorrect or defective
Loss of containment	Leakage, spillage

Temperature deviations in reactors can occur as a result of errors in the charging sequence, delays in initiating agitation, feed flow or temperature variations, maldistribution of reactants, development of catalyst hot spots, loss of cooling and fouling of heat transfer surfaces.

Effects of temperature deviations include overtemperature and undertemperature of equipment, changes of pressure and flow, and runaway reactions. The appropriate measures should be taken to reduce the deviations. In particular, attention should be paid to the heat input and output from the plant and to the control of reactors.

11.13.3 Flow deviations

Flow deviations may be too high, too low, zero, reverse or fluctuating. Changes in flow are generally the result of pressure changes and should be considered in conjunction with these.

Some causes of no flow are lack of feed material, lack of pressure difference, vapour effects and equipment failures. Vapour effects which can cause loss of flow include vapour locks and gassing up of pumps. Equipment failures include the stoppage of pumping equipment, the fracture of equipment resulting in leakage, and the blockage of equipment.

Blockage may occur in a number of ways. Items may be left in the plant after construction and maintenance work. Deposits may build up from liquid impurities, from solid particles, from corrosion or erosion products. The fluid may polymerize or solidify. Cessation of flow for other reasons can cause solidification or polymerization in a heat exchanger. Low ambient temperatures increase the risk of freezing, particularly of liquids which are solids under ambient conditions.

Equipment which is prone to blockage includes pipes, heat exchangers, packed beds and filters. Control valves may block or jam shut.

Reverse flow occurs if there is a reversal of the pressure differential. It should therefore be considered in conjunction with pressure changes. Failure of pumping equipment is a main cause of reverse flow.

Flow deviation can cause deviations of pressure, temperature and level. It can result in materials entering the wrong parts of the plant, can cause erosion, cavitation and hammer blow, and can result in pump overload and trip.

Complete stoppage of flow may cause disturbances to other parts of the plant. Restart after temporary interruption of flow can be hazardous also, as in the case of the extinction of a flame followed by a resumption of flow of unignited fuel.

The manipulation of fluid flows is the principal means by which control is exercised. There are many hazards which can arise if there is a loss of control. A particularly serious one occurs if it is no longer possible to effect necessary heat removal. Low flow may be as hazardous as zero flow, if the deviation is not sufficient to activate the protective devices.

Leakage flow may cause contamination between process streams or emission to the atmosphere. Contamination may result in blockages, corrosion, phase changes, chemical reaction and explosion. Water is the most common substance used in process plants and can give rise to all of these effects. It may enter other streams through pinholes or other tube failures, or through leaking shut-off valves.

The measures required to reduce flow deviations depend on the specific cause, but include attention to the reliability of pumping equipment, the provision of adequate storage and the elimination of blockages and of phenomena which have a similar effect.

Arrangements should be made for the easy removal of blockages at points where these are reasonably foreseeable. Provision should be made for cleaning pipes and heat exchangers by such methods as rodding out, chemical cleaning and burning of carbon deposits. Surfaces of packed beds may be protected from blinding by putting a filter layer such as ceramic packing on top. It may be necessary to install bypasses on equipments which are liable to blockage, but these may introduce their own hazards, which should be considered. Where fluids may freeze, it may be necessary to provide trace steam or electrical heating to prevent this.

11.13.4 Level deviations

Levels may be too high, too low, zero or fluctuating. Changes in level result from flow changes and should be considered in conjunction with these. Level deviations often occur as a result of changes in the flow in or out of a vessel. These may be controlled changes which result in overfilling or emptying of the vessel, or they may be caused by failure of equipment, such as the off-take pump, by vapour effects such as gassing up of that pump, or by blockages.

Changes in the pressure above the liquid, such as loss of vacuum, also affect the level. Some of the other causes of level deviations are surging, foaming and thermal expansion, siphoning and blown lutes. Excessive agitation or vibration of the vessel can also cause level deviations.

The measurement of liquid level is often difficult if there are solids, two liquid phases or foam, or if inerts, water or sediment accumulate. If the level is too high, liquid may overflow, the vessel may be overpressured or the weight of the system may become excessive. Where there is a gas flow through the vessel, a high level may cause liquid entrainment. If the level is zero, the outlet liquid flow is lost. Loss of liquid level can also result in breakthrough of high pressure gas to a part of the plant which is not designed for it. Measures to reduce level deviations depend on the specific case. In particular, attention should be given to the problems of level measurement.

It is not always the aim to eliminate level deviations completely. For some vessels, such as a chemical reactor, the level should normally be held constant, but other vessels are specifically used as surge vessels to smooth fluctuations of flow between units. Such vessels can fulfil their function only if the level in them does vary. They are usually provided with a low gain control loop which permits this.

In the case of level, control of the upper level limit may be achieved without resort to automatic controls by the simple and reliable device of an overflow pipe, and this should always be considered.

In addition to the levels in the main vessels, those in other equipments should be considered. These include levels in heat exchangers and on distillation trays.

11.13.5 Inhomogeneities and accumulations

There are many ways in which inhomogeneities of conditions and accumulations of material can arise. Poor mixing in reactors or other equipment can result in: side reactions and reaction runaway; hot spots, overheating and thermal degradation; and fouling. The accumulation of substances

which are relatively innocuous at high dilution but which when concentrated in some way, such as by vaporization with an insufficient bleed-off or by recycling of material, may present a hazard. Material which is held up in the system in a dead leg or elsewhere, for an abnormally long time may undergo degradation and become hazardous.

11.13.6 Control disturbances

The control system, including the process operator, may be a cause of operating deviations. One cause of this is errors, faults or lags in measurement. A level measurement based on liquid head may be in error due to frothing. The reading of a flow measuring instrument may be plausible, but the instrument may nevertheless have failed. There may be appreciable lags in the measurement of temperature.

Deviations may also be caused by the action of the automatic control system. The unsteady-state characteristics of the process such as the nature of the disturbances and of the time lags, the presence of dead time and loop interactions, and a requirement to operate at different throughputs, may make control inherently difficult. As a result, controller settings are sometimes inadequate. Other deviations may be introduced by the actions of the process operator, either through the control system or in other ways.

It is important for the process design to provide sufficient potential correction for control. If a variable is to be controlled, then there must be other variables which can be manipulated in order to achieve that control. This may seem obvious, but it is often not appreciated in practice. If, for example, a cement kiln is operated at maximum air flow, it is not possible to have close control of the outlet gas oxygen content by means of the air flow, since this requires that it be possible both to increase and decrease that flow.

11.14 Impurities

In the foregoing section frequent reference has been made to impurities. These merit some attention in their own right. The problem has been considered by Grollier-Baron (1992a,b), who gives a number of examples of incidents due to impurities, involving mainly explosion or corrosion. The use of nitrogen from ammonia cracking to inert a storage tank containing ethylene oxide led to decomposition of the latter due to traces of ammonia in the nitrogen. The presence of traces of acetylene in air passing over bronze fittings resulted in the formation of cuprous acetylide which then exploded. In a storage facility, replacement of demineralized water used in a heat exchanger for cooling acrolein with water from another source combined with a small leak in the exchanger allowed mineral ions to enter the acrolein, which polymerized exothermically so that the tank exploded. In catalytic crackers and methane reformers, unsaturated hydrocarbons and NCX are produced and when cooled to low temperature can form compounds, some of which are explosive. Mercury present in some natural gas condenses in the aluminium heat exchangers of the liquefaction units and forms an amalgam which corrodes the exchangers. Explosions can occur due to the accumulation of nitrogen trichloride in chlorine vaporizers.

Grollier-Baron outlines a formal approach to dealing with the problem of impurities based essentially on the following measures: (1) identification of the species present in trace quantities, (2) review of the fate of these species, (3) review of the hazards posed by the species, (4) formulation of corrective measures and (5) review to ensure that these countermeasures do not themselves create new hazards.

Identification involves consideration of the trace species in the raw materials, those created in the process and those which could be introduced accidentally. It also requires a review of the sensitivity of the raw materials, intermediates and products to these species. It cannot be assumed that the composition of the raw materials will necessarily remain constant with respect to trace species. There are many factors which may give rise to a change in composition of a raw material, ranging from minor changes in natural or quarried products or in inputs or process at the supplier plant to a complete change of supplier or of process.

There are a number of ways in which impurities may be formed in the process, including by side reactions and by corrosion. Impurities may also be introduced accidentally. One significant source is leaks. Another is deposits left behind in equipment or following maintenance.

It is desirable to have a material balance on, and to know the fate of, any impurities which may be significant. The hazard caused by impurities is increased by accumulation. This accumulation occurs because the impurity has some property different from that of the fluid in which it is present. Hydrogen from corrosion processes is light and may collect at the top of a tank or in a vent system. Nitrogen trichloride is less volatile than chlorine and can build up in a chlorine vaporizer. A difference in relative volatility can cause a compound to build up to quite a high concentration on the tray of a distillation column. Accumulation may also occur due to special circumstances. Cold weather can cause trace quantities to freeze out and cause blockages or worse.

Further treatment of contaminants is given by Tagoe and Ramharry (1993).

11.15 CCPS *Engineering Design Guidelines*

11.15.1 Guidelines for Engineering Design for Process Safety

Process design is one of the principal topics covered in the *Guidelines for Engineering Design for Process Safety* (CCPS, 1993/13) (the CCPS *Engineering Design Guidelines*). The scope of the *Engineering Design Guidelines* is, however, much broader. Table 11.15 gives the principal topics covered together with the location in this book where they are treated.

As far as process design is concerned, the *Guidelines* deal in particular with: (1) inherently safer design, (2) process equipment, (3) utilities, (4) heat transfer fluids, (5) effluent disposal and (6) documentation. The treatment of inherently safer design is organized around the themes of: (1) intensification, (2) substitution, (3) attenuation, (4) limitation of effects and (5) simplification and error tolerance, and includes an inherent safety checklist. The general approach is broadly similar to that taken in Section 11.6.

The items of process equipment treated in the *Guidelines* are: (1) chemical reactors, (2) columns, (3) heat exchangers, (4) furnaces and boilers, (5) filters, (6) centrifuges, (7) process vessels, (8) gas/liquid separators, (9) driers, (10) solids handling equipment, (11) pumps and compressors, (12) vacuum equipment and (13) activated carbon adsorbers.

Table 11.15 *Some principal topics treated in the CCPS Engineering Design Guidelines and their treatment in this text*

Topics	*Chapter*[a]
1. Overview	
2. Inherently safer plant	11
3. Plant design	10, 11
4. Equipment design	11, 12, 22
5. Material selection	12
6. Piping systems	12
7. Heat transfer fluid systems	11
8. Thermal insulation	12
9. Process monitoring and control	13, 14
10. Documentation	6, 11
11. Sources of ignition	10, 16
12. Electrical system hazards	10, 11, 16, 25
13. Deflagration and detonation flame arresters	17
14. Pressure relief systems	12, 15, 17
15. Effluent disposal systems	10, 11, 17
16. Fire protection	10, 16
17. Explosion protection	17

[a] Chapter in this book in which this topic is principally addressed.

The *Guidelines* give a table showing the common causes of loss of containment for different types of process equipment. They also include checklists for safe operation of fired equipment and activated carbon adsorbers. The treatment covers all the main utilities, with particular attention to reliability of electrical power supplies, and includes a checklist of possible utility failures and equipment liable to be affected.

The account of heat transfer fluid systems describes the fluids available and their applications, discusses the relative merits of steam, liquid and vapour–liquid systems, outlines the system design considerations and describes the system components, and considers the safety issues.

With regard to effluent disposal, the systems considered are: (1) flares, (2) blowdown systems, (3) incineration systems and (4) vapour control systems. The treatment does not extend to disposal of materials discharged in reactor venting.

The section on documentation covers: (1) design documentation, (2) operations documentation, (3) maintenance documentation and (4) record keeping.

12 Pressure System Design

Contents

12.1 Pressure Systems 12/5
12.2 Pressure System Components 12/8
12.3 Steels and Their Properties 12/8
12.4 Pressure Vessel Design 12/15
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12.6 Pressure Vessel Standards and Codes 12/18
12.7 Pipework and Valves 12/22
12.8 Heat Exchangers 12/32
12.9 Fired Heaters and Furnaces 12/34
12.10 Process Machinery 12/36
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12.12 Overpressure Protection 12/43
12.13 Overpressure Protection: Pressure Relief Devices 12/47
12.14 Overpressure Protection: Relief System Design 12/50
12.15 Overpressure Protection: Fire Relief 12/51
12.16 Overpressure Protection: Vacuum and Thermal Relief 12/53
12.17 Overpressure Protection: Special Situations 12/56
12.18 Overpressure Protection: Disposal 12/57
12.19 Overpressure Protection:Pressure Relief Valves 12/60
12.20 Overpressure Protection: Bursting Discs 12/64
12.21 Overpressure Protection: Installation of Relief Devices 12/65
12.22 Flare and Vent Systems 12/67
12.23 Blowdown and Depressuring Systems 12/72
12.24 Pressure Containment 12/72
12.25 Containment of Toxic Materials 12/73
12.26 Pressure Systems for Chlorine 12/75
12.27 Failure in Pressure Systems 12/79
12.28 Fracture Mechanics 12/87
12.29 Probabilistic Fracture Mechanics 12/92
12.30 Failure of Vessels, Equipment and Machinery 12/92

Process materials are normally contained within a pressure system. The main problem in loss prevention is the avoidance of loss of containment from this system. Thus, the First Report of the ACMH (Harvey, 1976) states: 'Containment is the very essence of the problem of control of dangerous materials, and therefore we regard the integrity of pressure systems as of the highest importance' (paragraph 64).

The report continues: 'Scrutiny of incidents suggests that the outright failure of properly designed, constructed, operated and maintained pressure vessels is rare, perhaps because of the lessons learned over many years from steam boiler practice. It is pipework, valves, pumps, etc., which are vulnerable and much more prone to failure' (paragraph 65).

Some of the principal features of pressure systems are briefly discussed in this chapter. It cannot be too strongly emphasized, however, that the discussion is limited to the background information necessary for the appreciation of the problems which occur in loss prevention and that many of the topics touched on, such as materials of construction, pressure vessels, piping, process machinery and overpressure protection, are complex matters which require specialist knowledge. The operation of pressure systems is at least as important as their design. This is considered in Chapter 6 on management systems and in Chapter 20 on plant operation. Selected references on pressure systems and components are given in Table 12.1 and on materials of construction for and corrosion in pressure systems in Table 12.2.

Table 12.1 *Selected references on pressure systems and components*

ASME (Appendix 27 *General and Safety Standards*, 1987–, Code for Pressure Piping B31, 1992, Boiler and Pressure Vessel Code; Appendix 28 *Pressure Vessels and Piping*); Associated Offices Technical Committee (n.d.); British Gas (Appendix 27 *Pressure Vessels*); IMechE (Appendix 28, 1970/3, 1975/16,18, 1976/27, 1977/33, 1979/50, 1981/57, 1991/130, 1993/148); Lloyds Register of Shipping (n.d.); NRC (Appendix 28 *Containment, Equipment Qualification, Pressure Systems, Pressure Vessels*); NSC (Safe Practice Pamphlet 68); Welding Inst. (Appendix 28, 1972/20); den Hartog (1952, 1956); Chuse (1954–); D.A.R. Clark (1956); Timoshenko and Young (1956); Manning (1957, 1960, 1978); Arnold (1959); Brownell and Young (1959); AIChE (1960–69/3–12, 1967/71, 1970–94/17–38, 1973/62, 1974/13, 1978/14); MacCary (1960a,b); Hughson (1961d, 1969); Begg (1963–64); Maynard (1963); Faupel (1964); Jenett (1964b); Voelker (1964); Blick (1965); IP (1980 Eur. MCSP Pt 2, 1981 MCSP Pt 3,1987 MCSP Pt 7,1993 MCSP Pt 13); Johns (1965); MacDermod (1965, 1982); Norden (1965); Thielsch (1965); Kemper *et al.* (1966–67); API (1967– Reflnery Inspection Guide, 1992 RP 510, Publ. 910); Bickell and Ruiz (1967); Canavan (1967); Canham (1967); Spence and Carlson (1967–68); Titze (1967); Eschenbrenner, Honigsberg and Impagliazzo (1968); Strelzoff and Pan (1968); Strelzoff, Pan and Miller (1968); T.E. Taylor (1968–69); Witkin (1968); Anon. (1969f); Fowler (1969); McCabe and Hickey (1969); McLeod (1969); Nichols (1969, 1976b, 1979a,b, 1980, 1983, 1987); Warwick (1969); J.S. Clarke (1970); Le Coff (1970); Franzel (1970); Gill (1970); Hearfield (1970); Kemp (1970); Losasso (1970); MacFarland (1970,1974); Pugh (1970); Dall'Ora (1971); F.L Evans (1971); Markovitz (1971, 1977); J.R. Palmer (1971); Pilborough (1971, 1989); Toogood (1972); Whenray (1972); Ford *et al.* (1973); Guill (1973); Jaeger (1973, 1975); Karl (1973); Timoshenko and Gere (1973); Dimoplon (1974); L. Evans (1974); Fitzpatrick (1974); Harvey (1974, 1980); M.R. Johnson *et al.* (1974); Stokes, Holly and Mayer (1974); Anon. (1975c,g,l); Berglund (1975, 1978); B.G. Cox and Saville (1975); ICI/RoSPA (1975 IS/107); Koike (1975a–c, 1978a–c); Mazzoncini (1975,1978); Roark and Young (1975); van Rossen (1975); Steffen (1975, 1978); Anon. (1976); Bhattacharyya (1976); Dickenson (1976); Logan (1976); Warburton (1976); Bacon and Stephen (1977); Gilbert and Eagle (1977); Heyman (1977); HSC (1977/1); Mahajan (1977b); Pludek (1977); Shigley (1977); Anon. (1978c); Baumeister (1978); Chambard (1978); Megyesy (1978,1983); Strawson (1978); Witkin and Mraz (1978); Blevins (1979); Heinze (1979); Koenig (1979); Mraz and Nisbett (1979); Puzak and Loss (1979); Unrug (1979); Vreedenburgh (1979); Widera and Logan (1979); D.J.D. White and Well (1979); Buhrow (1980); Facer (1980); Gerlach (1980); HSE (1980a,b EM 7); Kletz (1980i, 1984i,k); Wells and White (1980); Zeis and Eschenbrenner (1980); Azbel and Cheremisinoff (1981); Burr (1981); R. Cook and Guha (1981); Moy (1981); Collier, Davies and Game (1982); W. Marshall *et al.* (1982); Polak (1982); Smolen and Mase (1982); IAEA (1983); Rosaler and Rice (1983); Wicks (1983 LPB 53); Boyer (1984); Chuse and Eber (1984); Hurst (1984); Jawad and Farr (1984); Murray (1984); Arnold, Mueller and Ross (1986); Bednar (1986); Escoe (1986, 1992); J.P. Gupta (1986); Kutz (1986); Rogerson (1986); Yokell (1986); S.J. Brown (1987); Grosshandler (1987a,b); Kirkpatrick (1987); Kohan (1987); D.R. Moss (1987); Prugh (1987b); Sandler and Luckiewicz (1987); Coleman (1989 LPB 85); Trbojevic and Gjerstad (1989); K.P. Singh (1990); Factory Mutual Int. (1991b); LPGITA (1991 LPG Code 1 Pt 1); Snow (1991); EEMUA (1992 Publ. 162); HSE (1992 GS 4); Kassatly (1992); Batra et al. (1993); Chuse and Carson (1993); E.H. Smith (1993); Norton, Pilkington and Carr (1994); Pilkington, Platt and Norton (1994); Spence and Tooth (1994)

ANSI B series, BS (Appendix 27 *Pressure and Other Vessels*, PD series), BS 5500: 1991, VDI 2224: 1988

Prestressed concrete pressure vessels: IOCI (1968)

Composites, FRP

ASME (PVP 115, 1977/131, 1987 PVP 121, 1990 PVP 196, 1992 Boiler and Pressure Vessel Code Pt X, 1992 AMD 150); ASTM (1975 580, 1976 503, 1986 D4012, 1988 D4097,1991 D3517); Puckett (1976); IMechE (1977/35, 1984/77, 1990/116, 118); I.R. Miller (1979); Fasano and Eberhart (1980); IChemE (1980/119); Weatherhead (1980); Anon. (1986 LPB 70, p. 7); BG (1986 BGC/PS/ PL2); Institute of Materials (1986 B366); Maddison (1987 LPB 76); HSE (1991a,b PM 75); Britt (1993)

Foundations, structures

Brownell (1963); Deghetto and Long (1966); Pridgen and Garcia (1967); Tang (1968); A.A. Brown (1969, 1971, 1973, 1974); Czerniak (1969); G.B. Moody (1969, 1972); Youness (1970); Eichmann (1971); Molnar (1971); Arya, Drewyer and Pincus (1975, 1977); Mahajan (1975, 1977a); Raynesford (1975); K.P. Singh (1976); Simiu and Scanlon (1978); Faber and Alsop (1979); Faber and Johnson (1979); Moy (1981); Cowan (1982); Mosley and Bungey (1982); M. Schwartz (1982a–c, 1983a–e, 1984); Kong *et al.* (1983); HSE (1991a,b GS 49)

BS (Appendix 27 *Civil Engineering*), BS CP 2012: 1974–, BS 8004: 1986

Boilers
American Oil Co. (n.d./IO); Institute of Fuel (1963); Csathy (1967); FMEC (1967); van Loosen (1968); Attebery (1970); Impagliazzo and Murphy (1970); OIA (1971 Publ. 502); Horsler and Lucas (1972); API (1974 Refinery Inspection Guide Ch. 8); Vodsedalek and Bielak (1977); BRE (1978 CP59/78); Wilcox (1978); Needle (1979); A. Gibson (1980); W.S. Robertson (1981); Andrade, Gates and McCarthy (1983); Wilcox and Baker (1986); Harmsworth (1987); HSE (1987a–d PM 60, 1989a–f PM 5); Kauffman (1987); Hewett (1988); Kingshott (1988); Prescott, Podhorsky and Blommaert (1988); Gunn and Horton (1989); NFPA (1989 NFPA 85H); Kakac (1991); Anon (1992a); ASME (1984/174, 1988/201, 1992 Boiler and Pressure Vessel Inspection Code); Colannino (1993); Ganapathy (1994)
BS (Appendix 27 *Boilers*), BS 759: 1984–, BS 1113: 1992

Waste heat boilers, process heaters
Csathy (1967, 1981); Streich and Feeley (1972); Gupton and Kreisher (1973); Din (1975); T. Gibson (1975); Hinchley (1975, 1977, 1979a,b); W.P. Knight (1978); O'Sullivan, McChesney and Pollock (1978); Ozmore (1978); Salot (1978, 1982); Subramanyam, Pandian and Ganapathy (1979); Fuchs and Blanken (1986); Pariag, Welch and Kerns (1986); Sitaraman, Santoso and Sathe (1988)

Heat exchangers
ASME (Appendix 28 *Heat Transfer*, 1990 PVP 194); NRC (Appendix 28 *Steam Generators*); D.Q. Kern (1950, 1966); Drake and Carp (1960); Rubin (1960, 1961, 1980); Bohlken (1961); D.S. Morton (1962); E.M. Cook (1964); Fraas and Ozosik (1965); Gilmour (1965, 1967); P.R. Owen (1965); API (1967 Refinery Inspection Guide Ch. 7, 1982 Std 660, 1992 Std 661); R.B. Moore (1967); Y.N. Chen (1968); Gainsboro (1968); Hargis (1968); Small (1968); A.A. Thompson (1969); Lord, Minton and Slusser (1970a,b); Thongren (1970); EEMUA (1971 Publ. 135); Stuhlbarg (1971); D.Q. Kern and Kraus (1972); Knülle (1972); Simpson (1972); Taborek *et al.* (1972a,b); Barrington (1973, 1978); Doyle and Benkly (1973); Filers and Small (1973); J.A. Moore (1973); Song and Unruh (1974); P.M.M. Brown and France (1975); Char (1975b); Grossman (1975); Osman (1975); Piehl (1975); Anon. (1976 LPB 10, p. 1); Fanaritis and Bevevino (1976); G.W. Schwarz (1976); Blevins (1977); Cabrini and Cusmai (1977); R. Brown (1978); Ganapathy (1978, 1992, 1994); Glass (1978); Sueyama and Takami (1978); Rubin and Gainsboro (1979); Standiford (1979); Subramanyam *et al.* (1979); Needle (1979); Triggs (1979); W.J. Baker (1980); Butterworth (1980,1992); Devore, Vago and Picozzi (1980); Greene (1980); Gutterman (1980); Landrum and Watson (1980); Lufti, El-Migharbil and Hasaballah (1980); Malone (1980); Saunders (1980); Scaccia and Theoclitus (1980); Vukadinovic (1980); Kakac, Bergler and Mayinger (1981); Lopinto (1982); Schlunder (1982); TEMA (1982 B78.1); Wassom (1982); K. Bell (1983); Cizmar (1983); Crane and Gregg (1983); Mehra (1983); Shipes (1983); Yokell (1983); Knudsen (1984); Anon. (1985m); Rail and Spaehn (1985); J.P. Gupta (1986); Nieh and Zengyan (1986); R.G. Thomas (1986); Crittenden, Kolaczkowski and Hout (1987); Sandier and Luckiewicz (1987); Tammani (1987); Weaver (1987); Zakauskas, Ulinskas and Katinas (1988); Fraas (1989); Bott (1990); Mir and Siddiqui (1990); Crisi (1992); Love (1992); lian, Kawaji and Chan (1993)
BS (Appendix 27 *Heat Exchangers*), BS 3274: 1960

Pipework
ASME (Appendix 27, 1987– *Code for Pressure Piping B31*, 1992 Boiler and Pressure Vessel Code; Appendix 28 *Pressure Vessels and Piping*); British Cryogenics Council (n.d); IGasE (Appendix 28, n.d./7, 1967/8, 1976/10); NRC (Appendix 28 *Pipework, Pipe Whip*); M.W. Kellogg Co. (1956); G.N. Smith (1959); Bagnard (1960); R. Kern (1960, 1966, 1969, 1971, 1972a,b, 1974–, 1975b,c); Hilker (1962); Littleton (1962); Stubenrauch (1962); Whalen (1962); EEUA (1963 Handbook 18, 1965 Doc. 23., 1968 Handbook 23); Rase (1963); Francois (1964); Ingels and Powers (1964); Jenett (1964c); Masek (1964b, 1968); Surdi and Romaine (1964); Chapman and Holland (1965–); W.H. Doyle (1965); Thielsch (1965); Canham (1966, 1981); Judson (1966); Kiven (1966); Lancaster and Hoyt (1966); Koch (1966); Mallinson (1966a,b); W.C. Turner (1966); Cherrington and Ciuffreda (1967); R.C. King and Cracker (1967); Avery and Valentine (1968); Prescott (1968); Simpson (1968, 1969); Ward (1968); C.E. Wright (1968); L. Wright (1968); Yoder (1968); Anon. (1969c); Meador and Shah (1969); Aslam (1970); G.B. Moody (1970); Phelps (1970); Wills (1970); F.L. Evans (1971); Simmon (1972); Benson (1973); FPA (1973/21); Guffl (1973); O'Neal, Elwongerand Hughes (1973); Royalty and Woosley (1973); Holmes (1973); Styer and Weir (1973); Weaver (1973); API (1974 Refinery Inspection Guide Ch. 11); Mauck and Tomita (1974); W.W. Russell (1974); Ruziska and Worley (1974); Char (1975a, 1979); Lancaster (1976); Pothanikat (1976); Wachel and Bates (1976); D.W. Moody (1977); Surtees and Rooney (1977); Getz (1978); G.R. Kent (1978a); R. Kern (1978e); Constance (1979); J.D. Dawson (1979); Dilworth (1979); Lazzeri (1979); Marks (1979); Peng (1979); Stevens and littlewood (1979); API (1980 Std 605,1994 Bull. 6F2); Bedson (1980); Facer (1980); G. Montgomery (1980); Anon. (1981v); R.J. Cook (1981); D. Stephenson (1981a); Chlorine Institute (1982 Publ. 60); Hooper (1982); Kannappan (1982); Kentish (1982a,b); Rao (1982); Gardner (1983); Hills (1983); Anon. (1984n); Mikasinovic and Marcucci (1984); de Nevers (1984a); Broyles (1985); Hodge (1985); IGasE (1985 IGE/TD/12); IMechE (1985/86,89, 1989/112, 1993/158, 159); Hansen (1986); Hanson (1986); Helguero (1986); Prescott, Blommaert and Grisalia (1986); Sotebier and Rail (1986); G.Parkinson (1987); Sandier and Luckiewicz (1987); P.R. Smith and van Laan (1987); Towndrow (1987 LPB 73); Anon. (1988p); J. K Rogers (1988); Droste and Mallon (1989); Geyer *et al.* (1990); Hancock (1990a,b); Coker (1991a,b); Couch (1991); Hurst *et al.* (1991); Hartman (1993); Sixsmith (1993), Sadler and Matusz (1994)
ANSI B18 series; BS (Appendix 27 *Pipework*)
Reaction forces: F.J. Moody (1969, 1973); Stikvoort (1986); Hansen (1991)
Coaxial pipes, jacketed pipes: Anon. (1977 LPB 13, p. 17); Anon. (1977 LPB 18, p. 2); Stubblefleld (1993)
Plastic-lined pipes: J.R. Ward (1968); Chasis (1976); Spencer (1978); Anon. (1981s); Castro (1982); Carroll (1985); M.E. Jones (1990); Jeglic and lindley (1992, 1994)
Glass-lined pipes: Cowley, Dent and Morris (1978)

Plastic pipes: British Gas (1985 Comm. 1277); AGA (1989/12)
Gaskets: Rothman (1973); Stevens-Guille and Crago (1975); ASTM (1977 620); G.R. Kent (1978b); Payne (1980); Granek and Heckenkampf (1981); Payne and Bazergui (1981); API (1982 Std 601); G. Parkinson (1986); B. Singh (1991); ASME (1992 B16.2); Childs (1992); Crowley (1993)

Bellows, expansion joints: Anon. (1975 LPB 5, p. 19); Kobatake *et al.* (1975); British Gas (1977 TIN1); Engineering Appliances Ltd (1977); ASME (1981/147, 1984/175, 1989 PVP 168); Jetta, Brown and Pamidi (1981); McCulloch (1981); P.E. Smith (1983); C. Taylor (1985); Smith (1988 LPB 83); D.J. Peterson (1991), BS 6129: 1981
Hoses: C.W. Evans (1974)
Filters: Uberoi (1992); Artus (1976); Anon. (1977 LPB 13, p. 5); Anon. (1977 LPB 15, p. 35); Carriker (1979)
Sightglasses, rotameters: Anon. (1988 LPB 80, p. 19)
Thermowells: Masek (1964a, 1972, 1978)

Pipeline transients, water hammer
NRC (Appendix 28 *Water Hammer*); ASME (1933/21, 1961/22, 1984 ASME A112.26M, 1984/183); Thomson (1951); Lewitt (1952); Lupton (1953); Parmakian (1955); Marchal and Due (1959); Worster (1959); Hayashi and Ransford (1960); Karplus (1961); Harding (1964, 1965–66); Streeter (1964); Pearsall (1965–66); Fabic (1967); Streeter and Wylie (1967); Pickford (1969); Casto (1973); Ludwig and Ruijterman (1974); Anon. (1975 LPB 0, p. 6); Anon. (1975 LPB 1, p. 7); J.A. Fox (1977); Waiters (1979); Mukaddam (1982); Collier (1983); R. King (1983); Kremers (1983); K. Austin (1984); Crawford and Santos (1986); D. Clarke (1988a,b); Swierzawski and Griffith (1990); Kletz (1994 LPB 115)

Pipe tracing, steam tracing, steam traps
Bower and Petersen (1963); Eland (1966); House (1968b); Northcroft and Barber (1968); Bertram, Desai and Interess (1972); Mathur (1973); Anon. (1974a); Monroe (1975, 1976a–c, 1985); Cronenwett (1976); Mikasinovic and Dautovich (1977); Beatty and Kruger (1978); McWhorter (1978); Kohli (1979); Anon. (1981v); Blackwell (1982a,b); Lonsdale and Mundy (1982); Russo, Haydel and Epton (1984); HSE (1988 SIR 5); Haas (1990); David (1991); Kenny (1991, 1992); Lam and Sandberg (1992); Mackay (1992); O'Dell (1992); Radle (1992); C. Butcher (1993b); Morran (1993)

Insulation
British Gas (GBE/DAT30); Hughson (1961b); EEUA (1963 Handbk 12); Lawson (1964); Mathay and MacKnight (1966); W.C. Turner (1966, 1974); Hoffman (1967); House (1968b); Isaacs (1968); Ellis (1969); Malloy (1969); Marks and Holton (1974); ASTM (1975 581, 1980 718, 1983 789, 1984 826, 1985 880); Paros (1976); M.R. Harrison and Pelanne (1977); M.R. Harrison (1979); Webber (1979); Lang, Moorhouse and Paul (1980); McChesney and McChesney (1981, 1982); W.C. Turner and Malloy (1981); Nagl (1982); Schroder (1982); Kletz (1984m); Laxton (1985); Sandier and Luckiewicz (1987); Irwin (1991a,b); McMarlin and Gerrish (1992); Reddi (1992); Sloane (1992); Britton and Clem (1991); Gamboa (1993)
BS (Appendix 27 *Insulation*)

Valves (*see also* Table 13.2)
British Gas (Appendix 27 *Valves*); NRC (Appendix 28 *Valves*); Holmberg (1960); F.C. Price (1961); Antrim (1963); Calef (1964); Liptak (1964); Burger and Hoogendam (1965); Ciancia and Steymann (1965); Holmes and Ramaswami (1966); API (1974 Refinery Inspection Guide Ch. 11, 1984 Std 526, 1988 Std 599, 1989 Spec. 6A, Std 608, 1990 Std 598, 1991 Spec. 6D, Std 600); Boger (1969); Canon (1969); Driskell (1969, 1983); Glickman and Hehn (1969); Simon and Whelan (1970); Brodgesell (1971); Chemical Engineering (1971); Lawson and Denkowski (1971); Lovett (1971); Templeton (1971); British Valve Manufacturers Association (1972); G.W. Brown (1974); F.L. Evans (1974b); R. Kern (1975a); Wicher (1975); Wier (1975); Anon. (1976 LPB 10, p. 3); Bertrem (1976); Hays and Berggren (1976); Pikulik (1976); Babbidge, Partridge and d'Angelo (1977); Karcher and Ball (1977); Clayton and Johnson (1978); Constance (1979); Farley (1979); IMechE (1979/51, 1980/54, 1989/114, 1993/161, 1994/168); Anon. (1980 LPB 31, p. 17); Kaplan (1981a); Whitaker (1981); D.T. Cook (1982); Anon. (1984 LPB 59, p. 28); Ball and Howarth (1984); Stacey (1984); C. Tayler (1984c); Wallbridge and Gates (1984); Chowdhury (1985a); Greene *et al.* (1985b); Merrifleld (1985); Pittman (1985); ASME (1986 PVP 109, 1989 PVP 180); Bond (1986 LPB 69); Merrick (1986); Anon. (1987n); Latty (1987); Morley and Heasman (1987); Warring (1987); Anon. (1988p); Hunter (1988); T.M. Rogers (1988); Royce (1988b); Pinnington (1989); McGuinness (1990); Whitehouse (1990); Newby and Forth (1991); Hotchkiss (1991); Miles (1991); Ridey (1991); Zappe (1991); Anon. (1992 LPB 103, p. 25); Beasely (1992); Grumstrup (1992); Dana (1993); Fruci (1993); Graczyk and Hannon (1993); Kroupa (1993); T. Robinson (1993); J.B. Wright (1993); Hingoraney (1994); Peters (1994)
BS (Appendix 27 *Valves*)
Pressure regulators and reducers, restriction orifices: Fadel (1987); Liptak (1987); Baumann (1992); Khandelwal (1994)
Non-return valves and devices, blackflow protection: Malleck (1969); Fitt (1974); Nicholson (1974); Kletz (1976b); Cherry (1980); Emery (1983); K Austin (1984); Thorley (1984); Fluid Controls Institute (1985); Tomfohrde (1985); Anon. (1986 LPB 87, p. 1); Ellis and Mualla (1986); Anon. (1987b); Anon. (1988 LPB 83, p.9); Zappe (1991); Englund, Mallory and Grinwis (1992); Anon. (1993 LPB 111, p. 25)
Emergency isolation valves: Roney and Acree (1973); Kletz (1975b); Tomfohrde (1985); C. Butcher (1991b)
Excess flow valves: Anon. (1977 LPB 14, p. 15); Anon. (1977 LPB 18, p. 22); R.A. Freeman and Shaw (1988)
Fire safe valves: J.B. Wright (1981); Cory and Riccioli (1985); API (1993 Std 589, 607, 1994 Spec. 6FA)
Fluidic valves: J. Grant and Marshall (1976, 1977)

Lutes, seals
Anon. (1989 LPB 87, p. 1); Anon. (1992 LPB 104, p. 27)

Joining
Manning (1960); Hamm (1964); Matley (1965); Graves (1966); Canham and Hagerman (1970); Isaacs and Setterlund (1971); Vossbrinck (1973); Briscoe (1976); Cloudt (1978); Girin (1978); Pengelly (1978); Strawson (1978); ASME (1979– Code for Pressure Piping, 1988 B16.6, 1989 PVP 158); Stippick (1979); M.G. Murray (1980b); Anon. (1981 LPB 38, p. 23); Institute of Materials (1981 B349); Zelnick (1981); G. Thompson (1994)
ANSI B18 series, BS (Appendix 27 *Pipework*)

Welding (*see also* Table 25.1)
AGA (Appendix 28); AWS (Appendix 27, 28); ASTM (STP 11, 494); British Gas (Appendix 27); HSE (HSW Bklt 38); IMetall (Item/1); Welding Institute (Appendix 28); Voelcker (1964, 1965, 1973); ASME (1968/64, 1984/ 93, 1989 PVP 173, 1992 Boiler and Pressure Vessel Code Pt DQ); Maukonen and Vest (1973); Assini (1974); Houldcroft (1975); Schofield (1975); API (1978 Refinery Inspection Guide App., 1982 RP 942, 1988 Std 1104); Cary (1979); M.M. Schwartz (1979);

A.C. Davies (1984); Faltus (1985); J.E. Jones and Olsen (1986); D. Smith (1986); Hicks (1987); NFPA (1989 51B); W. Lucas (1991); Stippick (1992)
BS (Appendix 27 *Welding*)

Equipment identification
D.F. Allen (1976); API (1993 RP 1109) ANSI A13.1-1981, BS (Appendix 27 *Identification of Equipment*), BS 1710: 1984

Mechanical failure (*see also* Table 7.1)
SMRE (Engineering Metallurgy 4, 6); Thielsch (1965, 1968); Stokoe, Potts and Marron (1969); Weeks and Hodges (1969–70); Anon. (1970a); IMechE (1970/3, 1984/79, 1988/105, 1994/172); Loescher (1971); Pilborough (1971, 1989); Streich and Feeley (1972); Collins and Monak (1973); Colangelo and Heiser (1974); R.W. Wilson (1974); Lancaster (1975); Melville and Forster (1975); Hutchings (1976); Kletz (1980i, 1984k); Mischiatti and Ripamonti (1985); S.J. Brown (1987); Nishida (1991); Chapman and Lloyd (1992)

Pressure vessel failure, failure rates
Kellerman (1966); Kellerman and Seipel (1967); Phillips and Warwick (1968 UKAEA AHSB(S) R162); Slopianka and Mieze (1968); Butler (1974); Engel (1974); T.A. Smith and Warwick (1974, 1978, 1981 SRD R203); Boesebeck (1975); Bush (1975); Solomon, Okrent and Kastenberg (1975a,b); W. Marshall *et al.* (1976); Boesebeck and Homke (1977); Cottrell (1977); H.M. Thomas (1977); Arulanantham and Lees (1981); Harrop (1982 SRD R217); W. Marshall (1982); W. Marshall *et al.* (1982); Smith (1986 SRD R314, 1987 SRD R353); Kavianian, Rao and Brown (1990); Davenport (1991); Hurst (1991); Medhekar, Bley and Gekler (1993); Ardillon and Bouchacourt (1994); Crombie and Green (1994); Hurst, Davies *et al.* (1994)

Pipework failure
Janzen (n.d.); Gibbons and Hackney (1964); British Gas (1978 Comm. 1103); AGA (1981/34, 35, 1983/38); K.E. Petersen (1982, 1983); Cannon and Lewis (1987 NCSR/GR/71); Bellamy, Geyer and Astley (1989); Hancock (1990a,b); Geyer *et al.* (1990); Geyer and Bellamy (1991); Hurst *et al.* (1991); Medhekar, Bley and Gekler (1993); Hurst, Davies *et al.* (1994): Strutt, Allsop and Ouchet (1994); G. Thompson (1994)

12.1 Pressure Systems

Any system in which the pressure departs at all significantly from atmospheric, and which is therefore of rigid construction, needs to be considered as a pressure system. In the United Kingdom, pressure systems are covered by the Pressure Systems and Transportable Gas Containers Regulations 1989 (the Pressure Systems Regulations). For fixed plant the associated code is COP 37 *Safety of Pressure Systems* (HSE, 1990).

The definition of a 'pressure system' under the Pressure Systems Regulations is given in Regulation 2 and is: '(a) a system comprising one or more pressure vessels of rigid construction, any associated pipework and protective devices; (b) the pipework with protective devices to which a transportable gas container is, or is intended to be, connected; or (c) a pipeline and its protective devices; which contains or is liable to contain a relevant fluid, but does not include a transportable gas container'.

Regulation 2 defines 'relevant fluid' as: '(a) steam; (b) any fluid or mixture of fluids which is at a greater pressure than

Table 12.2 *Selected references on materials of construction for and corrosion in pressure systems*

Materials science
ASTM (Appendix 27, STP 289, 325, 1970 STP 466, 1981 STP 736, 1983 STP 806, 814); Institute of Materials (Appendix 28, B345); Godfrey (1959); Guy (1959, 1976); Jastrzebski (1959); Dieter (1961); W. Johnson and Meller (1962); Grossman and Bain (1964); Tweeddale (1964); Hull (1966); Prince (1966); Cottrell (1967); Honeycombe (1967); Spencer (1968); Gillam (1969); Gregory (1970); Timoshenko and Goodier (1970); van Vlack (1970); IMechE (1971/4); Chadwick (1972); Gabe (1972); Benham and Warnock (1973); J.D. Campbell (1973); C.T. Lynch (1974); Popov (1976); Summitt and Sliker (1980); Crane and Charles (1984); Wulpi (1985) ANSI Z178 series

Process plant materials
ASME (Appendix 27, 1992 Boiler and Pressure Vessel Code Pt II; Appendix 28 *Materials, Pressure Vessel and Piping*, 1986 PVP 111); ASTM (Appendix 28, STP 15C); EEMUA (Appendix 28); NRC (Appendix 28 *Materials of Construction*); DECHEMA (1953–); Greathouse and Wessel (1954); Aldrich (1960c); McConnell and Brady (1960); Norden (1960a,c); Rumford (1960); Chelius (1962); Chemical Engineering (1962–, 1970–, 1980, 1984); Heckler *et al.* (1962); Wyma (1962); Brauweiler (1963); Gleekman (1963, 1970); Kane and Horst (1963); J.F. Mason (1963); Samans (1963,1966); E.M. Sherwood (1963); Tracy (1963); Bulow (1964); Fenner (1964, 1967, 1968, 1970); Hughson and Labine (1964); Jaffee (1964); Juniere and Sigwalt (1964); Klouman (1964); Kuli (1964); Lancaster (1964, 1969, 1970, 1971); Renshaw (1964); Funk (1965); GA Nelson (1965); Anon. (1966a); Carmichael *et al.* (1966); Halbig (1966); IChemE (1966/42, 1978/71); C.M. Parker (1966); Petsinger and Marsh (1966); Speed (1966); Duhl (1967); Mara (1967); Sheets, O'Hara and Snyder (1967); Dukes and Schwarting (1968); R. Miller (1968); Leonard (1969); Schweitzer (1969); Skaudahl and Zebroski (1969); Anon. (1970c); Benzer (1970); Briton, Declerck and Vorhis (1970); Desenby (1970); Fontana (1970); Gregory (1970); Gulya and Marshall (1970); C.A. Robertson (1970, 1972); Skabo (1970); Tarlas (1970); Tator (1970); Tucker and Cline (1970, 1971); Zolin (1970); Anon. (1971b); IMechE (1971/4, 1982/63, 1989/107, 1992/139); F.E. Lawrence (1973); Smithells (1973); Tesmen (1973); L. Evans (1974); W. Lee (1974); McDowell (1974); Hughson (1976); Kerr (1976); McCandless and Ingram (1976); Mack (1976); Menzies (1976); Wyatt (1976); Bonner (1977); Grafen, Gerischer and Gramberg (1977); Anon (1978 LPB 23, p. 136); Brady and Clauser (1978); Cangi (1978); Chambard (1978); Hornbostel (1978); RE. Moore (1979); Schillmoller (1979); Weiner and Rogers (1979); Ashby and Jones (1980); Bro and Pfflsbury (1980); Gallagher (1980); Gramberg, Gunther and Grafon (1980); Greene (1980); Hagel and Miska (1980); Nichols (1980); Tvrdy *et al.* (1980); Beer and Johnstone (1981); W.W. Marshall (1981); Pollock (1981–); Weismantel (1981); Schiefer and Pape (1982); Crook and Asphahani (1983); Gackenbach (1983); Martino (1983); Murali (1983); Shuker (1983); Baker-Counsell (1984a); Fensom and Clark (1984); Horner (1984); Bayer and Khandros (1985); Kirby (1985b); Asphahani (1986); Declerck and Patarcity (1986); R. King (1986); Cornish (1987); Sandier and Luckiewicz (1987); M. Turner (1987); Dean (1989); Setter-kind (1991); Kane (1992); Pollock (1992); Puyear (1992) ANSI H series: BS (Appendix 27 *Concrete,*

Steels and Tubes, Test Methods), BS EN series Stainless steel: ASTM (STP 369, 1952 DS 5, 1965 DS 5-S1, 1969 DS 5-S2, 1982 STP 756); Hughson (1961b); Luce and Peacock (1962,1963); Bates (1963); Edstrom and Ljungberg (1964, 1965); Scharfstein (1964); Krisher (1965); McDowell (1965); Merrick and Mantell (1965); Keating (1968); Long (1968); Husen and Samans (1969); Kies, Franson and Coad (1970); Knoth, Lasko and Matejka (1970); Vandelinder (1970); Gaugh (1972, 1976); Pitcher *et al.* (1976); British Gas (1977 TIN2); Peckner and Bernstein (1977); Fowle (1978); Anon. (1979 LPB 28, p. 118); Davison and Miska (1979); Sedricks (1979); Truman and Haigh (1980); R. Brown (1981); R. Cook and Guha (1981); J.D. Redmond and Miska (1982, 1983); J.B. Wright (1982); Martenson and Supko (1983); J.R. Fletcher (1984); P. Marshall (1984); Schillmoller and Althoff (1984); J.D. Redmond (1986); Smith (1987 SRD R353); Institute of Materials (1988 B426); Henderson, King and Stone (1990); Avery (1991); Debold (1991); Warde (1991); Underwood (1992); Whitcraft (1992)

Titanium: R.S. Sheppard and Gegner (1965); Cotton (1970); Feige and Kane (1970); C.P. Williams (1970); W.D. Clark and Dunmore (1976); Covington, Shutz and Franson (1978); Seagle and Bannon (1982)

Clad materials: Beckwith (1987); Lednicky and Lindley (1991); Lerman and Carrabotta (1991); Henthorn and Lednicky (1992); B. Singh (1993)

Plastics including fibre reinforced plastics: Norden (1960c); P. Morgan (1961); Costello, Rhodes and Yovino (1965); Parkyn (1970); Parratt (1972); Catherall (1977); Cheremisinoff and Cheremisinoff (1978); Fasano and Eberhart (1980); N.J. Kraus (1980); McBride (1980); Piggott (1980); Puyear and Conlisk (1980); Rolston (1980); Margus (1982); Baines (1984); Dibbo (1984); Watt and Perov (1985); Rubin (1990); M. Schwartz (1991); M.A. Clark (1992); Goldsmith (1992b); Currieo (1993); W.A. Miller (1993)

Timber: Desch (1981); T. Smith (1987)

Glass: Lofberg (1965); Rawson (1980); Anon. (1981 LPB 41, p. 1; 1981 LPB 42, p. 11; 1982 LPB 44, p. 35); Bucsko (1983); Hoult (1983); Lerman and Carrabotta (1991)

Paints: Charlton (1963); British Gas (1983 BGC/PS/DAT12); Baker-Counsell (1985a); Foscante (1990)

High temperature materials

ASME (Appendix 28 *Materials, Pressure Vessels and Piping*, 1975/71, 1979/137, 1982/156, 1983/164, 1984/ 172, 1989 PVP 163); ASTM (Appendix 28, DS series); IMechE (Appendix 28, EGF and ESIS series); Institute of Materials (Appendix 28); Schley (1960); E.W. Ross and McHenry (1963); R. Miller (1968); Gaugh (1976); Mack (1976); Hasselman and Heller (1980); IMechE (1983/71, 1987/95, 1988/104); Gooch *et al.* (1983); Skelton (1983, 1987); Marriott *et al.* (1988)

Low temperature materials

ASTM (STP 47, 63, 78, 158, DS 22); E.W. Johnson (1960); R.J. Johnson (1960); Rote and Proctor (1960); Vanderbeck (1960); Zenner (1960); Hwoschinsky (1962); Hurlich (1963); C.M. Parker and Sullivan (1963); R.W. Campbell (1967); Wigley (1979); IMechE (1982/60); R.P. Reed and Clark (1983); British Gas (1990 TIN26)

Materials for particular applications

Acids: Falcke and Lorentz (1985); Ireland (1985)

Ammonia: W.L Ball (1968b); Inkofer (1969); Rohleder (1969); Kobrin and Kopecki (1978); van Grieken (1979); Ishimaru and Takegawa (1980); Prescott and Badger (1980); Prescott (1982); El Ganainy (1985)

Chlorine: Dukes and Schwarting (1968); BCISC (1975/ 1); Horowitz (1981); Chlorine Institute (1982 Pmphlt 60, 1985 Pmphlt 6, 1986 Pmphlt 1); Hamminck and Westen (1986); Royce (1988b)

Hydrogen: C.M.Cooper (1965, 1972a); API (1967 Publ. 940, 1971 Publ. 942, 1975 Publ. 945, 1978 Publ. 956, 1990 Publ. 941); G.A Nelson (1965, 1966); Molstad and Gunther (1967); Gorman (1962); Cracknell (1976); Bonner (1977); C.C. Clark (1978); Treseder (1981); ASME (1982/88); Webb and Gupta (1984)

Hydrogen sulfide: Sivalls (1985); Schwinn and Streisselberger (1993)

Oxygen: Lowrie (1987)

Materials control, identification

W.D. Clark and Sutton (1974); Duff (1976); Ostrofsky (1980-); Baker-Counsell (1985d)

Corrosion

ASTM (STP 179, 567,1972 STP 516, 1974 STP 534, 558); CONCAWE (23/70); Institute of Materials (Appendix 28); NRC (Appendix 28 Corrosion); Uhlig (1951); Greathouse and Wessel (1954); Chlorine Institute (1956 Publ. 18); Fontana (1957, 1986); Jelinek (1958–); J.E. Dawson (1960a); U.R. Evans (1960); Gladis (1960); Norden (1960b); Wachter (1960); Hughson (1963); J.D. Jackson (1961); Brooke (1962); Draley (1962); Swandby (1962); Tracy (1962a,b); Bergstrom and Ladd (1963); Charlton (1963); Fochtmann, Langion and Howard (1963); Hinst (1963); Krebs (1963); Wilder (1963); Wilten (1963, 1965); Ashbaugh (1965a); Menzies *et al.* (1965); Sorell (1965, 1968, 1970); E.H. Anderson (1966); Bates (1966); A.S. Cooper and McConomy (1966); T.A. Lees (1966); Sculley (1966); Canavan (1967); Dingman (1967); Falck-Muus (1967); Iverson (1968); Rabald (1968); D. Stewart and Kulloch (1968); Landrum (1969, 1970); Maylor (1969); Schweitzer (1969, 1976, 1989); J.M. Brooke (1970); Dunlop (1970); Fenner (1970); Husen and Samans (1970); Thornton (1970); Diamaui (1971); Henthorne (1971–); Hoar (1971); Lochmann (1971); Anon. (1972h); Bonar (1972); C.M. Cooper (1972b); P.O. Thomas (1972); Cantwell and Bryant (1973); IChemE (1973/54); Lux (1973); McDowell (1973); J.A. Richardson and Templeton (1973); F.L Evans (1974a); G.A. Nelson (1974); Rodgers (1974); Dol (1975); Appl and Feind (1976); Dragoset (1976); Lancaster (1976); Shreir (1976); Berger (1977, 1982); Brautigam (1977); Chadwick and Jamie (1977); Hawk (1977); Pludek (1977); Cangi (1978); Edeleanu (1978); Fontana and Greene (1978); Fryer (1978); Layton (1978); Leach (1978); Ueda *et al.* (1978); Chase (1979); Schumacher (1979); Sedriks (1979); Braunton (1980); J.M. West (1980); Danilov (1981); Rozenfeld (1981); A.E. Wallace and Webb (1981); Ailor (1982); Mclntyre (1982); Mallinson (1982); Parkins (1982); Bernie (1983); Stafford and Whittle (1983); Cihal (1984); Elliot (1984); NACE (1984); Baker-Counsell (1985b); Holmes (1985); Kyte (1985); Pelosi and Cappabianca (1985); R. Stevens (1985); Twigg (1985); Anon. (1986f); Dillon (1986); AGA (1987/ 48, 49,1988/51); Anon. (1987z); DECHEMA (1987–); R.W. Green (1987); Kofstad (1988); Munn (1988); Royce (1988a); Sathe and O'Connor (1988); M. Turner (1988, 1989a,b, 1990a–c); Avery (1991a); R.D. Kane (1991); Wilhelm (1991); Priest (1992); R.D. Kane *et al.* (1993)

Erosion: Thiruvengadam (1966); ASTM (1979 STP 664); Craig (1985)

External corrosion: Hughson (1961c); Figg (1979); SCI (1979); Anon. (1984 LPB 56, p. 1); Dorsey (1984); Batterham (1985); Liss (1987); Pollack and Steeley (1990)

Corrosion of steel in concrete: ASTM (1977 629, 1980 713, 1984 818)
Concrete: Figg (1979, 1983); Sheppard (1984); Closner (1987a)

Materials and corrosion problems
Field (1963); D.T. Williams (1963); Gleekman (1964); C.F. Lewis (1964); Heckler (1969); Capel and van der Horst (1970); Krystow (1971); Schwab (1971); J.L Cook (1972); R. Lee (1972); Rollins (1972); Spangler (1972); Butwell, Hawkes and Mago (1973); W.D. Clark and George (1973); Kussmaul and Kregeloh (1973); Lancaster (1973); Anon. (1975 LPB 6, p. 1); R.J. Parker (1975); Anon. (1976 LPB 9, p. 26); R.P. Lee (1976a,b, 1977a,b); Livsey and Junejo (1976); Anon. (1977 LPB 15, p. 23); B. Turner (1977); Anon. (1978 LPB 24, p. 172); Bognar, Peters and Schatzmayr (1978); Schmeal, MacNab and Rhodes (1978); K. Brown (1982); Hare (1982); Quraidis (1982); R.W. Clarke and Connaughton (1984); Sheilan and Smith (1984); W.L. Sheppard (1984); R. Stevens (1985); Anon. (1986f); Kolff (1986); A. Atkinson (1988); Schofield (1988); Schofield and King (1988); Cantwell (1989 LPB 89); Nightingale (1989a,b, 1990); Anon. (1990 LPB 92, p. 11); linstroth (1991)

Fracture, fracture mechanics
ASME (Appendix 28 *Applied Mechanics, Materials, Pressure Vessels and Piping*, 1975/72); ASTM (Appendix 27); IMechE (Appendix 28 EGF, ESIS series); Institute of Materials (Appendix 28); NRC (Appendix 28 *Crack Growth, Fatigue, Fracture Mechanics*); A.A. Griffith (1920–21); Neuber (1937); Westergaard (1939); Sneddon (1946, 1973); Irwin (1948, 1957, 1958, 1962, 1968); Dryden, Rhode and Kuhn (1952); E.R. Parker (1957); Dugdale (1960, 1968); A.A. Wells (1961, 1969); Bilby, Cottrell and Swinden (1963); Paris and Erdogan (1963); Hahn and Rosenfield (1965, 1967, 1968); R.E. Johnson (1965); Paris and Sih (1965); Burdekin and Stone (1966); Pratt (1966); Sih (1966, 1973a,b); Irwin *et al.* (1967); Tetelman and McEvily (1967); Liebowitz (1968); Rice (1968a,b, 1976); Sneddon and Lowengrub (1969); Pellini (1971); ASTM (1972 STP 513, 514,1974 STP 556, 559, 560); Battelle Columbus Labs (1972); Begley and Landes (1972); Bravenec (1972); Bucci *et al.* (1972); Eftis and Liebowitz (1972); Heald, Spink and Worthington (1972); Formby, Kirby and Ratcliffe (1973); Irvine (1973 SRD R21,1974 SRD R26,1977 SRD R48); Kiefner *et al.* (1973); Kihara and Ikeda (1973); Knott (1973); Nichols (1973); Tada, Paris and Irwin (1973); Broek (1974); Fearnehough (1974); Harvey (1974); Hood (1974); J.N. Robinson and Tetelman (1974); Shannon (1974a,b); Tanaka (1974); Cartwright and Rooke (1975); Crossley and Ripling (1975); Dumm and Fortmann (1975); Gibbons, Andrews and Clarke (1975); MacCary (1975); Pook (1975a,b, 1977, 1979); Underwood (1975); Dragoset (1976); Erdogan (1976); Rooke and Cartwright (1976); Eftis, Subramanian and Liebowitz (1977); Engineering Sciences Data Unit (1977); T.G.F. Gray (1977); Knowles, Tweedle and van der Post (1977); Rolfe and Barsom (1977, 1987); Sorenson and Besuner (1977); Stanley (1977); H.M. Thomas (1977, 1981); AGA (1978/28, 1988/50, 1991/72, 76, 1992/79, 84, 85); Chell (1978); Hudson and Seward (1978); Paris *et al.* (1978); Vosikovsky and Cooke (1978); Cesari and Hellen (1979); R.P. Harrison, Loosemore and Milne (1979); Nichols (1979a); AP. Parker (1979, 1981); Suzuki, Takahashi and Saito (1979); CEC (1980 EUR 6371 EN); HSE (1980 EM 4, EM 5); G.O. Johnson (1980); O'Neil (1980); Ponton (1980); Wiberg (1980); R.P. Harrison and Milne (1981); Kastmretal. (1981); Lorio and Crespi (1981); Shih, German and Kumar (1981); Ziebs *et al.* (1981); Johnston (1982); Ainsworth and Goodall (1983); Temple (1983, 1985); Haines (1983); Tomkins (1983); Arimochi *et al.* (1984); Ewalds and Gielisse (1984); Ichikawa (1984c, 1985, 1987); Imai et al. (1984); Latzko *et al.* (1984); Lidiard (1984); Saldanha Peres and Rogerson (1984); Funderburg (1985); Milne *et al.* (1986, 1988a,b); IMechE (1987/95); Jutla (1987); Thomson (1987); J.K.W. Davies (1989b); HSE (1989 Nuclear Installations 12); Tomkins, Lidbury and Harrop (1989); Schulz and Braun (1992); Medhekar, Bley and Gekler (1993)

Fatigue
ASME (Appendix 28 *Materials*, 1981/11, 84, 1984/92, 94); ASTM (STP 91, 237, 1972/ 513, 514, 1973 STP 520, 1974 STP 556, 559, 560); IMechE (Appendix 28 EGF, ESIS series, 1975/15, 1977/40); NRC (Appendix 28 *Crack Growth, Fatigue, Fracture Mechanics*); Dryden, Rhode and Kuhn (1952); Kooistra and Lemcoe (1962); Yao and Munse (1962); Manson (1966); Avery (1972b); Tomkins (1973); Harvey (1974); Frost, Marsh and Pook (1975); Pook (1975a,b, 1977); W.J. Harris (1976); Duggan and Byrne (1977); Linhart and Jelinek (1977); Bongers, Diols and Linssen (1978); Cowley and Wylde (1978); Michelini (1978); Klesnil and Lukas (1980); Skelton (1983, 1987); Larsson (1984); Younas and Sheikh (1987); Fromm, Liebe and Siegel (1988); J.KW. Davies (1989)

Ageing
NRC (Appendix 28 *Ageing*)

Embrittlement, brittle fracture
E.R. Parker (1957); Biggs (1960); Tipper (1962); Ladd (1966); W.D. Clark and Mantle (1967); W.J. Hall *et al.* (1967); Sorell and Zeis (1967); Harnby (1968); Madayag (1969); Boyd (1970); Karinen (1971); Moisio (1972); Anon. (1974Ï); ASTM (1974 STP 543, 1984 STP 844); Afzal and Livingston (1974); Harvey (1974); Lamberton and Vaughan (1974); Lonsdale (1975); Watanabe and Murakami (1981); Murza, Centner and McMahon (1981); B.J. Shaw (1981); AGA (1983/38); Merrick and Ciuffreda (1983); Maxey *et al.* (1985); Wilkie (1985a); Snyder (1988); API (1990 Publ. 920); Burke and Moore (1990)

Stress corrosion cracking
ASTM (STP 64, 264, 397, 1967 STP 425,1972 STP 518, 1976 STP 610, 1979 STP 665); Copson and Cheng (1957); Hughson (1961a); Loginow and Phelps (1962); Wilten (1962); Ashbaugh (1965b, 1970); Truman and Kirkby (1965); Logan (1966); Anon. (1972j); van der Horst (1972); Hutchings *et al.* (1972); Phelps (1972, 1974); Collins and Monack (1973); Creamer (1974); Harvey (1974); Zeis (1975); Zeis and Paul (1975); van Grieken (1976, 1979); Harvey (1976); HSE (1976 TON 53/2); Arup (1977); W.D. Clark and Cracknell (1977); Anon. (1979 LPB 28, p. 104); Karpenko and Vasilenko (1979); Cracknell (1980); Ishemaru and Takegawa (1980); Macintyre (1980); Takemura, Shibasaki and Kawai (1981); Gossett (1982); Anon. (1983r); AGA (1984/40, 1988/56, 1990/68, 70, 1991/71, 1992/87, 88); Blanken (1984); L. Lunde (1984); Orbons and Huurdeman (1985); Lemoine *et al.* (1986); Loginow (1986); Schillmoller (1986); L. Lunde and Nyborg (1987, 1989, 1990); Stephens and Vidalin (1988); Anon. (1989 LPB 89, p. 27); Bockenhauer (1989); Byrne, Moir and Williams (1989); Parkins (1989); Appl *et al.* (1990); Selva and Heuser (1990); Conley, Angelsen and Williams (1991); Crawley (1992 LPB 104)

Creep
ASME (Appendix 28 *Materials*, 1981/84, 1984/92, 94, 1988 PVP 35, 151) ASTM (STP 26, 37, 107, 325, 391); Institute of Materials (Appendix 28); Finnie and Heller (1959); Anon. (1969e); Lochmann (1972); Harvey (1974); IMechE (1974/7, 1975/15, 1977/36, 1978/47, 1994/162); HSE (1977 TON 53/3); Imoto, Terada and Maki (1982); Konoki, Shionohara and Shibata (1982); Ashby and Brown (1983); Tomkins (1983); H.E. Evans (1984); Kawai *et al.* (1984); Larsson (1984); Anon. (1986e)

Hydrogen corrosion
Anon. (1962d); Cooper (1965, 1972a); McDowell and Milligan (1965); McDowell (1967); Ciuffreda and Hopkinson (1968); Ciuffreda and Greene (1972); AGA (1974/19); Harvey (1974); K.L. Moore and Bird (1965); Bonner (1977); A.W. Thompson (1978); Truax (1978); Tvrdy *et al.* (1981); Timmins (1983, 1984); Webb and Gupta (1984); Genet and Perdrix (1987)

Liquid metal attack
British Gas (1982 TIN16)

Zinc embrittlement
Ball (1975a,b, 1976); Cottrell and Swann (1975a,b, 1976); Harvey (1976); HSE (1976 TON 53/1, 1977 PM 13); Anon. (1979 LPB 29, p. 149); Anon. (1979 LPB 30, p. 175); British Gas (1983 BGC/PS/DAT11); SETE Consultants and Services Ltd (1984 LPB 55)

Tribology, wear
ASTM (STP 30, 567, 1969 STP 446); Burwell (1957–58); Norden (1960a); MacGregor (1964); Furey (1969); Summers-Smith (1969); M.C. Shaw (1971); Avery (1972a); M.J. Neale (1973); Hailing (1975); IMechE (1975/17, 22, 1977/45, 1980/53, 1994/167); Engel (1976); P.R. Williams (1976); ASME (1977/74, 1979/80, 1980/10, 1981/87, 1983/91, 1985/96); Fenton (1977); Schumacher (1977); Sorenson and Besuner (1977); Sayles and Macpherson (1980); Suh and Saka (1980); Szeri (1980); Buckley (1981); Briscoe (1982)

0.5 bar above atmospheric pressure, and which fluid or mixture of fluids is – (i) a gas, or (ii) a liquid which would have a vapour pressure greater than 0.5 bar above atmospheric pressure when in equilibrium with its vapour at either the actual temperature of the liquid or 17.5°C; or (c) a gas dissolved under pressure in a solvent contained in a porous substance at ambient temperature and which could be released from the solvent without application of heat'.

Regulation 4 deals with the design, construction, repair and modification of pressure systems. Regulations 5–13 cover essentially operation, inspection and maintenance. Regulation 7 requires there to be safe operating limits. Regulation 5 requires marking of equipment, Regulation 8 a written scheme of examination, Regulation 9 examination in accordance with this scheme and Regulation 13 the keeping of records. Regulation 11 covers operation and Regulation 12 maintenance, whilst Regulation 10 deals with action in the case of imminent danger.

Requirements for the provision of protective devices are contained in Regulation 4 and also in Regulations 14 and 15. This aspect is discussed in more detail in Section 12.12.

12.2 Pressure System Components

The main components of pressure systems have been described by Dickenson (1976). They are:

(1) pressure vessels (reactors, distillation columns, storage drums and vessels);
(2) piping system components (pipes, bends, tees, reducers, flanges, valves, nozzles, nipples);
(3) means of adding, controlling or removing heat (fired heaters, reboilers, vaporizers, condensers, coolers, heat exchangers generally);
(4) means of increasing, controlling or reducing pressure (pumps, compressors, fans, letdown turbines, control valves);
(5) means of adding or removing fluids or solids to or from the process system (pumps, compressors, dump valves);
(6) measurement and control devices and systems (instrumentation);
(7) utilities and services (electricity, steam, water, air).

Item (7) was considered in Chapter 11 and item (6) is described in Chapter 13. The other items are dealt with in the following sections.

12.3 Steels and Their Properties

The main material of construction used in pressure systems is steel and it is necessary to consider some of the properties of steel which are particularly important in relation to pressure systems and which are the basis of pressure systems standards and codes of practice.

Steels and other materials are discussed in *Selecting Materials for Chemical and Process Plant* (L. Evans, 1974), *Handbook of Materials Science* (C.T. Lynch, 1974–), *Materials Handbook* (Brady and Clauser, 1978), *Construction Materials* (Hornbostel, 1978), *Materials for Low Temperature Use* (Wigley, 1979), *Mechanics of Materials* (Beer and Johnstone, 1981), *Physical Properties of Materials for Engineers* (Pollock, 1981–) and *Selection and Use of Engineering Materials* (Crane and Charles, 1984).

Accounts of the general properties of steels in relation to their use in pressure vessels are given in *Theory and Design of Modern Pressure Vessels* (Harvey, 1974), *Pressure Component Construction* (Harvey, 1980) and *Pressure Vessel Systems* (Kohan, 1987). The main steels used in process plant and their relation to the standards and codes are described by L. Evans (1974).

12.3.1 Stress, strain and elasticity

If a specimen test bar of a material is subjected to a tensile load in a tensile testing machine, stress is induced in the material and strain occurs.

The stress is:

$$\sigma = \frac{f}{a_0} \qquad [12.3.1]$$

where a_0 is the original cross-sectional area, f is the force and σ is the stress. The strain, or fractional elongation, is:

$$e = \frac{\delta}{l_0} \qquad [12.3.2]$$

where e is the strain, l_0 is the original length and δ is the elongation.

The typical load–extension, or stress–strain, diagram obtained for many metals, including mild steel, is shown in Figure 12.1. At low loads the material is elastic, returning to its original dimensions when the stress is removed, and the strain is proportional to the stress:

$$\frac{e}{\sigma} = \frac{1}{E} \qquad [12.3.3]$$

where E is the elastic modulus. Equation 12.3.3 is Hooke's law and the constant E is Young's modulus.

As the load increases, there is a change in material behaviour indicated by points A and B in Figure 12.1. The proportionality limit at A is the stress beyond which the strain is no longer proportional to the stress. The elastic limit at B is the stress beyond which the material no longer returns to its original dimensions, but undergoes some permanent deformation. For mild steel and many other materials the proportionality and elastic limits coincide, but for some, such as rolled aluminium, they are separate.

12.3.2 Yield and tensile strengths

The yield point C, which is close to points A and B, is the stress at which there occurs a marked increase in strain without an increase in stress. For many engineering applications it is not acceptable that the material should yield. The yield point represents the limit of strength in such applications.

As the load increases further, there is continued extension until point D is reached at which fracture occurs. The stress at fracture is the ultimate tensile stress, or strength:

$$\tau_u = \frac{f_u}{a_0} \qquad [12.3.4]$$

where f_u is the force at ultimate tensile stress and τ_u is the ultimate tensile strength.

The ultimate tensile strength given in Equation 12.3.4 is the engineering value based on the original cross-sectional area of the specimen. In fact, there is a reduction of this area prior to rupture so that the true tensile strength is:

$$\tau_{u,t} = \frac{f}{a} \qquad [12.3.5]$$

where a is the actual cross-sectional area and $\tau_{u,t}$ is the true ultimate tensile strength. The ultimate tensile stress represents the limit of strength in applications where yielding is acceptable, but rupture is not.

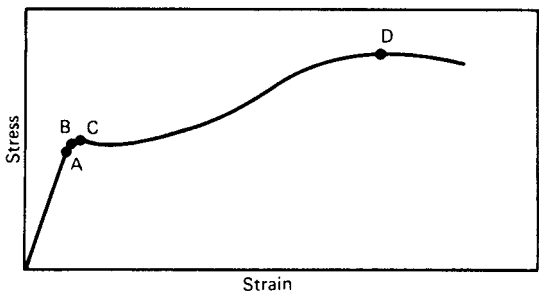


Figure 12.1 *Typical load–extension diagram for mild steel*

12.3.3 Ductility

Another important property of a material is its ductility, or its ability to undergo deformation. Ductility may be expressed as fractional elongation:

$$d_e = \frac{l_r - l_0}{l_0} \qquad [12.3.6]$$

or fractional reduction in area

$$d_a = \frac{a_0 - a_r}{a_0} \qquad [12.3.7]$$

where a_r is the cross-sectional area at rupture, d_a is the fractional reduction in area at rupture, d_e is the fractional elongation and l_r is the length at rupture.

Ductility is a very desirable property in a steel and is important for design and for fabrication. In pressure vessels, features such as joints, openings and nozzles create additional load stresses which may not be fully allowed for in the design. Ductility permits local yielding so that the stress is adjusted. Similarly, ductility allows material to undergo fabrication operations, such as rolling, forging, drawing and extruding, without fracturing.

12.3.4 Toughness and impact strength

A further property which is important in a material is its toughness, or ability to resist impact. Toughness is measured by the energy absorbed in stressing to fracture, which is the area under the stress–strain curve, and thus the modulus of toughness is given by the area:

$$T = \int_0^{e_r} \sigma \, de \qquad [12.3.8]$$

where e_r is the strain at rupture and T is the toughness. A material which has both high tensile strength and high ductility has high toughness. Toughness is another property which is very desirable in a steel, and loss of toughness, or embrittlement, is a serious defect.

12.3.5 Low temperature strength

At low temperatures, mild and other steels tend to suffer a loss of toughness as shown in Figure 12.2. For mild steel the ductile/brittle transition occurs at about 0°C; the precise transition temperature depends on the type and quality of the steel. An account of brittle fracture is given in *The Brittle Fracture of Steel* (Biggs, 1960). Since much process plant operates at low temperatures, such embrittlement is important. Low temperature embrittlement has been the cause of many failures, and is discussed further in Section 12.27.

12.3.6 High temperature strength

At high temperatures, the strength of many materials, including mild steel, tends to decrease, as illustrated in Figure 12.3. The yield point falls and becomes less pronounced, and the ultimate tensile strength also falls. Moreover, a further factor begins to limit strength at high temperature. This is creep.

12.3.7 Creep strength

Creep is an extension which occurs in metals, including mild steel, at high temperatures under constant load over

$$\sum_{i=1}^{n} \frac{t_i}{t_{ri}} = 1 \qquad [12.3.9]$$

where t_i, is the time at stress and temperature conditions i and t_{ri} is the creep life at stress and temperature conditions i. Similarly, for strain at different stresses and temperatures the condition is given by the 'strain fraction' rule:

$$\sum_{i=1}^{n} \frac{e_i}{e_{ri}} = 1 \qquad [12.3.10]$$

where e_i, is the strain at stress and temperature conditions i, and e_{ri} is the strain for rupture at stress and temperature conditions i.

Use is also made of the following equation which utilizes the geometric mean of these two approaches:

$$\sum_{i=1}^{n} \left(\frac{t_i}{t_{ri}} \frac{e_i}{e_{ri}} \right)^{1/2} = 1 \qquad [12.3.11]$$

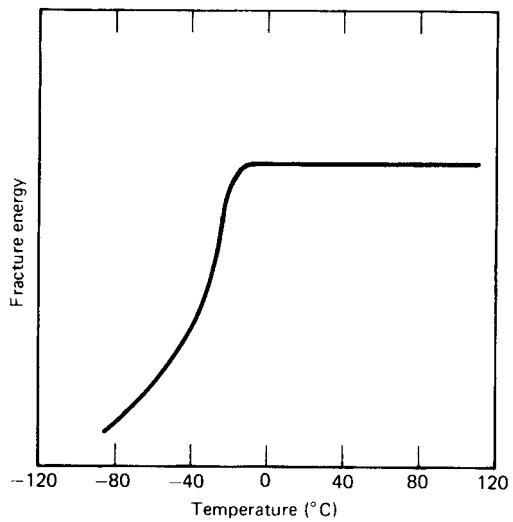


Figure 12.2 *Typical impact strength diagram for mild steel*

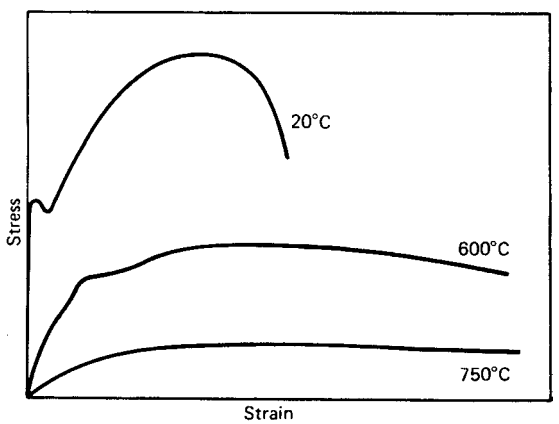


Figure 12.3 *Typical load–extension diagram at high temperatures for mild steel*

a period of time. Accounts of creep are given in *Perspectives in Creep Fracture* (Ashby and Brown, 1983) and *Mechanisms of Creep Fracture* (H.E. Evans, 1984).

The typical results of a creep test on mild steel carried out in a tensile testing machine at constant load and constant temperature are illustrated in Figure 12.4. There is a short primary phase (1) when the creep rate is fairly rapid, a long secondary phase (2) when it is approximately constant, and a short tertiary phase (3) when it accelerates to rupture.

The typical variation of creep rate with loading and temperature is illustrated by Figure 12.5. The creep strength of a material at a particular temperature is usually expressed either as the stress for 1% extension in 100,000 h or as the stress for rupture in 100,000 h. The former is normally taken as not less than two-thirds of the latter.

Frequently, a steel is subjected to a number of different temperatures and/or stresses. For such cases, it is common practice to calculate the fraction of creep life used up as follows. For time at different stresses and temperatures, the condition for exhaustion of the creep life is given by the 'life fraction' rule: it is emphasized that Equations 12.3.9–12.3.11 are approximate. The applicability of these equations is discussed in more detail by Harvey.

Since high temperatures are common in process plant, creep is very important. It is considered again in Section 12.27.

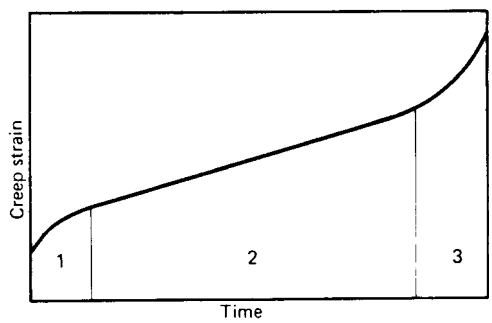


Figure 12.4 *Typical creep test at high temperatures for mild steel*

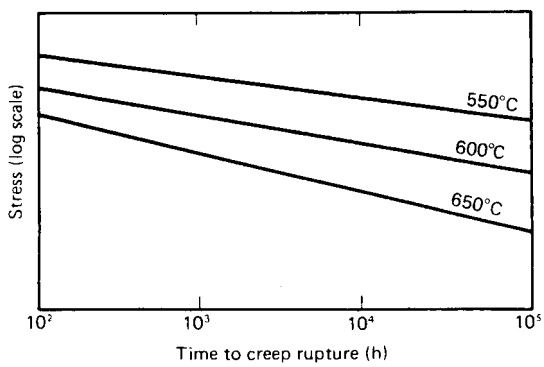


Figure 12.5 *Typical variation of creep rate with loading and temperature for mild steel*

12.3.8 Fatigue strength

Many ductile metals, including mild steel, can under certain conditions suffer fatigue failure at a stress well below the ultimate tensile strength if subjected to repeated cycles of stress. Accounts of fatigue are given in *Fatigue and Fracture of Metals* (Dryden, Rhode and Kuhn, 1952), *Fatigue of Metallic Materials* (Klesnil and Lukas, 1980), *The Mechanics of Fatigue and Fracture* (A.P. Parker, 1981), *Fatigue at High Temperatures* (Skelton, 1983) and *High Temperature Fatigue* (Skelton, 1987).

Whether fatigue failure occurs depends on the magnitude of the stress range which is applied and on the number of repetitions of the stress. The relationship between these two factors is shown in Figure 12.6, which illustrates the results of a typical fatigue test on mild steel. Fatigue testing is usually done using the reversed bending test, in which a load is applied at the end of a cantilever test specimen which is then rotated at constant speed, so that the full reverse bending stresses are created each revolution. The data from such tests may be plotted as maximum stress or as stress range. The stress range is the fundamental parameter, but the maximum stress is often plotted.

The curve given in Figure 12.6 has two distinct regimes. In the first region, to the left of the break point, failure occurs at decreasing stresses but increasing number of cycles, while in the second region to its right there is a stress level below which failure does not occur irrespective of the number of cycles. This stress level is the fatigue limit, or endurance limit, and is an important property. For most steels at room temperature a good estimate of the fatigue limit may be obtained from the ultimate tensile stress using the relation:

$$\sigma_E = d_a \sigma_u \qquad [12.3.12]$$

where σ_E is the fatigue limit and σ_u is the ultimate tensile stress. The fatigue limit for steels other than high strength steels is generally 40–55% of the ultimate tensile strength.

The number of cycles at which the fatigue limit occurs at room temperatures is of the order of 10^6–10^7. It is often convenient, therefore, to take the fracture stress at 10^8 cycles as the practical limit.

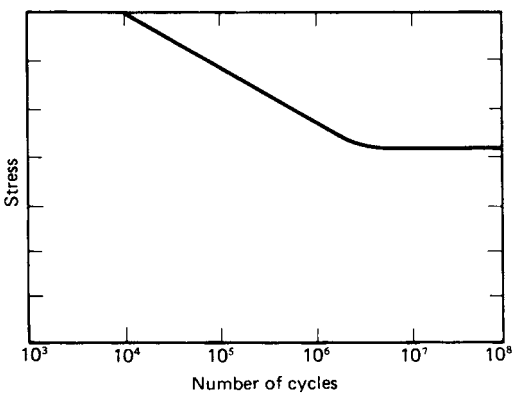


Figure 12.6 *Typical fatigue test for mild steel*

Although it is high cycle fatigue which has been most studied, low cycle fatigue is also important. This occurs at higher stresses and smaller number of cycles and corresponds to the first region in Figure 12.6. In this region, if the data are expressed as stress there is usually considerable scatter, but the scatter is reduced if the data are expressed as strain. A strain is often multiplied by one-half of the elastic modulus to give a pseudo-stress amplitude. Low cycle fatigue is generally considered to cover the region below 10^5 cycles.

It can be shown for many metals, including mild steel at room temperature, that the relation between the stress amplitude and the number of cycles N at fatigue failure can be described approximately by the equation:

$$\sigma = \frac{e}{4N^{1/2}} \ln\left(\frac{1}{1-d_a}\right) + \sigma_E \qquad [12.3.13]$$

This equation covers the range of both low cycle and high cycle fatigue. It may be used to calculate a fatigue life curve. A fatigue design curve may then be obtained using suitable factors of safety. Typical factors of safety are 2 on stress amplitude or 20 on the number of cycles, whichever is the more conservative.

A steel is generally subjected to a number of cycles at a number of different stresses. At each stress the fraction of life used up is given by the cycle ratio n/N. The condition for fatigue failure is given by the 'cycle ratio' rule:

$$\sum \frac{n}{N} = 1 \qquad [12.3.14]$$

where n is the actual number of cycles and N is the number of cycles at fatigue failure. It is emphasized that Equation 12.3.14 is approximate.

There are a number of other factors which also affect fatigue strength. They include (1) temperature, (2) corrosion and (3) surface condition. In the range from room temperature up to about 350°C many steels, including mild steel, show no loss of fatigue strength. In fact there is often a slight gain. But at higher temperatures fatigue strength begins to decrease. At higher temperatures still, creep becomes a significant factor. Reduction of fatigue strength by corrosion may be the result of surface roughening or of reduction of cross-sectional area. More serious is true corrosion fatigue, in which deterioration is due to the interaction of fatigue and corrosion.

The general effect of corrosion fatigue is to reduce the fatigue strength. With corrosion fatigue there is generally no definite fatigue limit. Corrosion fatigue tends to be worse if oxygen is present. Oxygen normally reduces the low cycle fatigue strength. Whether the fatigue limit is reduced depends on the surface condition. A reduction in fatigue strength due to oxygen tends to occur if very sharp cracks are present.

Fatigue strength is, in general, greatly reduced if there are cracks or similar surface defects. A high stress concentration occurs at the extremities of the crack and the crack grows a finite amount each cycle. The growth of fatigue cracks is the subject of fracture mechanics, which is considered in Section 12.28.

Another important factor in fatigue is the temperature changes which occur and which cause thermal stress fatigue. This is an effect quite separate from that of

temperature on fatigue strength. Thermal changes are a source of cycling and tend to be difficult to predict, but are often appreciable. If the thermal stress is large, it may cause the metal to deform. This deformation results in a more favourable stress distribution, and to this extent thermal stress is self-correcting, but there may also be some cracking. Cracks arising during thermal stress may grow as a result of mechanical stress.

An index of susceptibility to thermal stress is given by the thermal shock parameter

$$\phi = \frac{E\alpha}{k} \qquad [12.3.15]$$

where k is the thermal conductivity, α is the coefficient of thermal expansion, and ϕ is the thermal shock parameter.

The higher the thermal shock parameter, the more susceptible the metal is to thermal stress. The thermal shock parameter of mild steel is less than that of austenitic stainless steel by a factor of about 3 at room temperature. The difference decreases with temperature, but there is still a factor of about 2 at 350°C.

Mechanical and thermal stresses arising from the operation of process machinery, from pressure changes and from temperature changes are normal in process plant. Fatigue due to these stresses is one of the most common causes of failure and is very important. A further discussion is given in Section 12.27.

12.3.9 Types of steel

The main types of steel which are used in process plant are: (1) carbon steel, including mild steel, (2) low alloy steel and (3) stainless steel, including ferritic and austenitic types. Of prime importance is the temperature at which the steel begins to undergo creep. At room temperature, the strength of the steel is limited by the yield and/or tensile strengths. As the operating temperature increases, however, the creep strength becomes the limiting factor. Thus, the operating temperatures may be divided into (1) temperatures below the creep range and (2) temperatures above the creep range. The basis of design is different for these two cases.

The approximate threshold temperatures at which onset of creep occurs are:

Mild steel	400°C
Low alloy steel	500°C
Austenitic stainless steel	600°C

The change with temperature in the limiting strengths of these three types of steel is shown in Figure 12.7. The shape of the curve is broadly similar for all three types.

12.3.10 Carbon steel

Carbon steels are generally defined as those containing iron, carbon and manganese. Most steels have a carbon content of 0.1–0.9% carbon and 0.5–2.0% manganese.

The most common type of carbon steel is low carbon, or mild, steel with a carbon content up to 0.25%. Mild steel is described in the following subsection. High carbon steels are those with a carbon content above this figure, up to about 0.9%.

Steels containing more than 0.3% carbon are difficult to weld. High carbon steel is produced mainly as bar and forgings for uses such as shafts, bolts, etc. These steels require heat treatment by way of quenching and tempering to give their optimum properties.

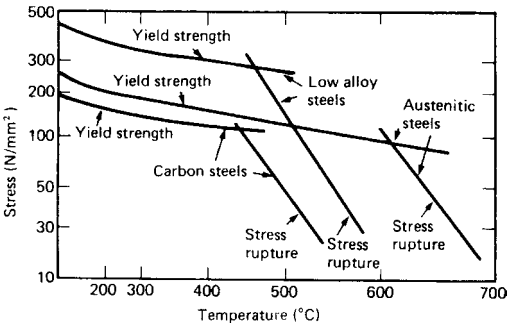


Figure 12.7 *Typical yield stress and creep rupture stress curves for mild, low alloy and austenitic steels. (L. Evans, 1974) (Courtesy of Business Books)*

12.3.11 Mild steel

Mild steel is low carbon steel with, as just stated, a carbon content less than 0.25%. It is the cheapest and commonest form of steel. The properties of mild steel may be illustrated by the room temperature properties given in BS 4360: 1990 for plate to grade 43EE:

Tensile strength	430/580 N/mm^2
Yield strength	265 N/mm^2
Elongation	20%

where the yield strength applies to thicknesses in the range 16–40 mm and the elongation applies over 200 mm. Mild steel is ductile and weldable, but it has certain limitations which are related to:

(1) corrosion resistance;
(2) strength at
  (a) room temperature,
  (b) high temperature,
  (c) low temperature.

There are many chemicals which corrode mild steel. Examples are dilute acids, such as sulfuric, nitric and hydrochloric acids, and chemicals containing water, such as wet chlorine.

For pressure vessels, it is often attractive to use a material which has a higher strength than mild steel and so to have a thinner walled vessel. Low alloy steel is generally used instead of mild steel in such applications.

At high temperatures, above about 400°C, mild steel suffers quite severe creep and it becomes necessary to use other steels. At low temperatures, below about 10°C, the ductility of mild steel falls off sharply, and brittle fracture can occur, as described above. Again, other steels have to be used.

Mild steel can be modified by the incorporation of small amounts of alloying elements. Addition of up to 0.1% niobium can increase yield strength and low temperature ductility. Addition of up to 1.5% manganese can give substantial increases in yield strength such as from 230 to 400 N/mm^2.

12.3.12 Low alloy steel

The low alloy steels which are important in process plant are mainly those which have a carbon content less than 0.2% and contain a total $< 12\%$ alloying elements (Ni, Cr, Mo, V, B, W or Cu).

Many low alloy steels are given a heat treatment of normalizing and tempering by the manufacturer, but there is an increasing tendency to a quenching and tempering treatment. Low alloy steels are all weldable, but for some steels pre- or post-weld heat treatment is necessary in order to avoid weld zone cracking.

Some principal low alloy steels are:

0.5 Mo	12 CrMoVW
1.25 CrMo	0.25 Cr 0.25 Mo 1.5 Ni
2.25 CrMo	

Some significant advantages of low alloy steels over mild steel are:

(1) yield strength;
(2) high temperature properties
  (a) creep strength,
  (b) oxidation resistance,
  (c) hydrogen resistance;
(3) low temperature ductility.

The improvement in yield strength and in creep strength is illustrated in Figure 12.7. Yield strength is the main design parameter used in advanced codes for pressure vessels and the gain in yield strength is valuable. Low alloy steels make it possible to have thinner walled pressure vessels. Low alloy steels such as 0.5 Mo, 1.25 CrMo, 2.25 CrMo and 12 CrMoVW are used for their creep properties in applications such as steam boilers and refinery crackers and reformers. The upper temperature limit for low alloy steels is about 600°C.

Oxidation resistance is another important property of low alloy steels. The principal alloying element which imparts oxidation resistance is chromium. Low alloy steels also offer greater resistance to hydrogen attack in such operations as cracking and reforming. Mild steel ceases to be suitable above 250°C, 0.5 Mo steel can used up to about 350°C, while 2.25 CrMo steel can go up to about 550–600°C. Apart from resistance to oxidation and hydrogen attack, low alloy steels do not offer much greater resistance to corrosion than does mild steel.

An increase in low temperature ductility down to −50°C can be obtained by addition of 1.5 Ni to 0.25 Cr 0.25 Mo steel. This is a most valuable modification, since low temperature embrittlement is a serious problem. Nickel is the main alloying element used to give low temperature ductility.

12.3.13 Stainless steel

The main alloying elements in high alloy steels are chromium and nickel. A stainless steel is one which contains 11% or more of chromium. The chromium forms an oxide film giving a passive surface, rendering it generally more resistant to corrosion than that on the lower alloy or carbon steels.

Accounts of stainless steels are given in *Handbook of Stainless Steels* (Peckner and Bernstein, 1977), *Corrosion of Stainless Steels* (Sedriks, 1979), *Austenitic Stainless Steels* (P. Marshall, 1984) and *High Temperature Alloys* (Marriott *et al.*, 1988) and by Redmond and Miska (1982), J.R. Fletcher (1984), Henderson, King and Stone (1990), and Warde (1991).

The review by Redmond and Miska (1982) covers: the role of the alloying elements; the classes of stainless steel; their corrosion resistance; their physical and mechanical properties; and their fabrication. It also gives numerous tables listing the American Iron and Steel Institute (AISI) types and Unified Numbering System (UNS) numbers for the different classes of stainless steel.

The principal alloying elements in stainless steel are chromium, nickel and molybdenum. Each has a number of effects, and mention is made here of only a few. As already stated, chromium gives a passive oxide layer which increases the corrosion resistance. It also promotes the formation of the ferrite phase. Nickel, by contrast, promotes the formation of the austenite phase and enhances toughness, ductility and weldability. It also increases resistance to strong acids. A principal function of molybdenum is to enhance the resistance of the stainless steel to pitting and crevice corrosion.

Broadly, stainless steels have four main advantages: (1) higher corrosion resistance, (2) higher resistance to heat, (3) higher creep and stress rupture resistance and (4) higher strength at ambient and intermediate temperatures.

For a long time the development of stainless steels was hampered by the presence of carbon and nitrogen, which can have deleterious effects, but the use of techniques such as argon–oxygen decarburization (AOD), vacuum–oxygen decarburization (VOD) and vacuum induction melting (VIM), which allow the production of steels with very low carbon and nitrogen contents, has largely obviated these difficulties.

Redmond and Miska distinguish five classes of stainless steel: (1) austenitic, (2) ferritic, (3) duplex, (4) martensitic, and (5) precipitation hardening. The last two classes are considered later in this subsection and the first three in the next three subsections. Heat treatment is essentially confined to the martensitic and precipitation hardening classes of stainless steel.

The AISI has defined standard types of stainless steel and these steels are commonly described in terms of the AISI types. Also widely used is the UNS of the American Society for Testing and Materials (ASTM). Relevant British Standards are BS 1449: Part 2: 1983 for stainless steel plate and BS 3605: 1973 for austenitic stainless steel pipe.

The stainless steels are dominated by austenitic stainless steels in the AISI 300 series and ferritic steels in the 400 series. The latter series is not confined, however, to steels of the ferritic class, but also includes some in other classes such as martensitic and superduplexes.

Martensitic stainless steels generally contain 11–18% chromium but little or no nickel, and have a structure which can be transformed by suitable cooling from austenite at high temperature to martensite at room temperature. They include a low carbon subclass and a high carbon one, the division occurring at a carbon content of about 0.15%. Martensitic steels, given suitable heat treatment, can have very high strength and hardness. They have a ductile–brittle transition temperature which is usually close to room temperature. A general purpose low carbon martensitic steel is type 410. Martensitic steels are used for such items as bolts, shafts and bearings.

Precipitation-hardening (PH) stainless steels contain both chromium and nickel, and other alloying elements such as copper or aluminium, which impart the precipitation hardening property, allowing the steel to be hardened to high strength for use in such applications as gears.

12.3.14 Austenitic stainless steel

The basic austenitic stainless steel may be regarded as containing 18% chromium and 8% nickel, but there is a whole family of such steels with variations about these values. These steels are described in *Chromium Nickel Austenitic Steels* by Keating (1968) and Redmond and Miska (1982).

The workhorse austenitic steels include AISI types 304, 304L, 316, 316L, 321 and 347. The suffix L denotes low carbon. As already mentioned, austenitic steels are covered in BS 1449: Part 2: 1983 and BS 3605: 1973.

Type 304 is a 19/10 (19 Cr 10 Ni) steel. It contains the minimum amount of alloying elements to give a stable austenitic structure under all fabrication conditions. Type 304L has a lower carbon content than type 304 and is used for applications involving the welding of plate thicker than about 6.5 mm in order to avoid intergranular corrosion, or weld decay.

Type 316 is a 17/12 steel with 2.5 Mo addition to improve resistance to reducing conditions such as brine and dilute sulfuric acid. Type 316L has a lower carbon content than type 316 and is used in applications where the heat input during fabrication will exceed the incubation period of the 316 grade, such as the welding of plate thicker than about 10 mm.

Type 321 is an 18/10 steel with titanium addition to prevent intergranular corrosion. Type 347 is an 18/11 steel with niobium addition to improve welding properties.

Standard austenitic stainless steels are subject to chloride-induced stress corrosion cracking, although certain types exist such as 904L and, particularly 825, which are resistant.

More highly alloyed austenitic stainless steels include the HyResist 317LM and 94L steels, with enhanced corrosion resistance, and the HyProof 3126L and 317L steels with higher proof strength.

The absence of ferrite means that austenitic stainless steels do not have a ductile–brittle transition temperature.

12.3.15 Ferritic stainless steel

Ferritic stainless steels contain chromium but little or no nickel. The class may be subdivided into two main subclasses: those with 11% Cr and those with 17% Cr. Ferritic stainless steels can be rendered brittle by even quite low contents of carbon and nitrogen (say 0.1% C + N), and for a long time this inhibited their use, but in manufacture this problem has been largely obviated by the techniques of AOD, VOD and VIM mentioned above.

The workhorse ferritic stainless steels include AISI types 409, 430, 434 and 444. Type 409 has 11% Cr and type 430 17% Cr.

The welding of ferritic steels poses a problem in that carbon or nitrogen pick-up can have serious effects. In the 11% Cr steels an improvement in weldability, and also an extension of the size of section which can be produced, has been achieved with the use of the SCR 12 type, which is so balanced that some austenite forms above about 800°C, which is beneficial both in welding and rolling.

Ferritic, and also martensitic, stainless steels are immune to chloride-induced stress corrosion cracking but are susceptible to sulfide-induced stress corrosion cracking. Ferritic stainless steels have a ductile–brittle transition temperature. There are also superferritic stainless steels with a high alloy content, which imparts enhanced resistance to pitting corrosion and crevice corrosion.

12.3.16 Duplex stainless steel

Duplex stainless steels contain both ferrite and austenite, in approximately equal amounts. Their properties reflect the fact that they contain both phases. The presence of ferrite means that duplex stainless steels have a ductile–brittle transition temperature.

The duplexes differ from standard austenitic stainless steels in that they have higher resistance to stress corrosion cracking and higher yield strength. They differ from the ferritic stainless steels in having higher low temperature toughness and in being more weldable. Some types of duplex stainless steels are 'lean duplex', 22/5 and 25 Cr.

For some time the use of duplex stainless steels was inhibited by fabrication difficulties. The addition of nitrogen substantially eased these constraints and reduced the need for post-weld heat treatment to restore corrosion resistance.

Recent years have seen the introduction of a new breed of duplex, the superduplex stainless steels. Standard duplexes have limited resistance to pitting and crevice corrosion. The superduplexes include Ferralium 255, Zeron 100 and Uranus 52N +. They are not yet widely used but are starting to find application offshore. They are described by Warde (1991).

12.3.17 Low temperature steel

For low temperature applications use is made of alloy steels or aluminium alloys. Two principal applications are in storage tanks and in liquefied gas carriers. Some of the materials used are illustrated by the following list taken from the IMO *International Gas Carrier Code* (1983 IMO 782):

Minimum design temperature (°C)	*Chemical composition and heat treatment*	*Impact test temperature* (°C)
−60	1.5% nickel steel, normalized	−65
−65	2.25% nickel steel, normalized or normalized and tempered	−70
−90	3.5% nickel steel, normalized or normalized and tempered	−95
−105	5% nickel steel, normalized or normalized and tempered	−110
−165	9% nickel steel, double normalized and tempered or quenched and tempered	−196
−165	Austenitic steels such as types 304, 304L, 316, 316L, 321 and 347 solution treated	−196
−165	Aluminium alloys such as type 5083 annealed	Not required
−165	Austenitic Fe-Ni alloys (36% nickel), heat treatment as agreed	Not required

The qualifications on the use of these materials are given in the code.

12.3.18 Heat treatment of steel

There are a number of processes to which steel may be subjected in order to obtain a better microstructure and enhanced mechanical and corrosion properties. An account oriented to pressure vessels is given by Kohan (1987).

Critical temperature and transformation range
A basic concept in heat treatment of steel is that of the critical temperature at which a transformation occurs in the steel. Actually changes occur over a range of temperature (the transformation range). There are separate transformation ranges for heating and for cooling.

Quenching
Quenching is rapid cooling of the steel by immersion in a medium such as oil or water.

Hardening
Hardening is the heating and quenching of the steel to produce an increase in hardness.

Normalizing
Normalizing involves heating the steel to about 100°F (38°C) above its critical temperature and cooling in still air to room temperature.

Annealing
Annealing involves heating and controlled cooling of the steel in order to refine its structure, modify its properties and/or remove stresses. There is a variety of annealing processes. Full annealing involves heating above the critical temperature and then slow cooling.

Tempering
Tempering is an operation performed after hardening of the steel, and involves heating to a temperature below the critical value and then cooling.

Stress relief heat treatment
Stress relief heat treatment involves uniform heating of all or part of a component to a temperature sufficient to relieve the major part of the residual stresses and then uniform cooling.

Post-weld heat treatment
Post-weld heat treatment (PWHT) refers to any heat treatment carried out following welding.

12.3.19 Steel coding systems

There are a number of systems for the coding of types of steel. These include British, European and American systems.

BS 5500: 1991 for pressure vessels refers to BS 1501–1504 and BS 3059 and BS 3601–3605. These standards designate steels by type and grade, for example, 224 grade 490. Another relevant standard is BS 4360: 1990 *Weldable Structural Steels*. This refers to grades, for example, 50EE. The 1990 edition gives cross-referencing to nomenclature used in earlier editions of this standard. The standards also use the following classification of steels:

Grade	
M0	Carbon steels
M1	Carbon and carbon manganese steels
M2–M10	Low alloy steels
–	High alloy steels

Details are given in Appendix H of BS 5500.

Currently, in the United Kingdom, transition is taking place to the European system. This is described in BS EN 10027 *Designation Systems for Steel*; this and BS 10028 *Flat Products Made of Steels for Pressure Purposes* give cross-referencing.

For the United States, the ASTM has established a unified numbering system (UNS) and issues standards for steel, for example, ASTM A-515/A515M-90. ASME utilizes these standards adding the prefix S, for example, SA-515. Principal steels for process plant are given in the ASME *Boiler and Pressure Vessel Code*, Section II: 1990 *Materials Specifications*. Reference has already been made to the AISI system, particularly in relation to stainless steels. A further discussion of steel coding is given by Pilborough (1989).

12.4 Pressure Vessel Design

Pressure vessels are subject to a variety of loads and other conditions which stress them and, in certain cases, may cause serious failure.

Accounts of pressure vessel design are given in *Pressure Vessels* (Chuse, 1954–), *Pressure Vessel Design and Analysis* (Bickell and Ruiz, 1967), *The Stress Analysis of Pressure Vessels and Pressure Vessel Components* (Gill, 1970), *Theory and Design of Modern Pressure Vessels* (Harvey, 1974), *Pressure Component Construction* (Harvey, 1980), *Chemical and Process Equipment Design*: *Vessel Design and Selection* (Azbel and Cheremisinoff, 1981), *Pressure Vessels* (Chuse and Eber, 1984), *Pressure Vessel Design Handbook* (Bednar, 1986), *Mechanical Design of Process Systems* (Escoe, 1986), *Fundamentals of Pressure Vessel and Heat Exchanger Technology* (J.P. Gupta, 1986), *Pressure Vessel Systems* (Kohan, 1987), *Pressure Vessel Design Manual* (D.R. Moss, 1987), *Pressure Vessels* (Chuse and Carson, 1993) and *Pressure Vessel Design* (Spence and Tooth, 1994).

In general, structures are subject to two types of loading: (1) static loading and (2) dynamic loading. For pressure vessels this loading is normally due to pressure. The load caused by the pressure creates stresses in the vessel. There may also be other stresses, which include (1) residual stress, (2) local stress and (3) thermal stress.

12.4.1 Design basis

The basis of the design of pressure vessels is the use of appropriate formulae for vessel dimensions in conjunction with suitable values of design strength. In determining the strength of materials, a basic distinction is drawn between (1) temperatures below the creep range and (2) temperatures inside the creep range.

For temperatures below the creep range two important properties are (1) tensile strength, R; and (2) yield strength, E. Different design methods may use these properties as measured at room temperature (generally 20°C) or at the operating temperature (f°C). Use has been made, therefore, of all the four properties:

(1) tensile strength at room temperature, R_{20},
(2) tensile strength at operating temperature, R_t,
(3) yield strength at room temperature, E_{20},
(4) yield strength at operating temperature, E_t.

For temperatures inside the creep range, two further important properties are (1) stress for 1% extension in 100,000 h at the operating temperature, S_c and (2) stress for rupture in 100,000 h at the operating temperature, S_r. These material strengths are divided by a factor of safety to obtain the design strengths for use in the design.

12.4.2 Static pressure loading

Pressure vessels may often be treated as thin-walled cylinders or spheres. For a thin-walled cylinder, a simple force balance gives the longitudinal stress:

$$p\pi r^2 = \sigma_1 t 2\pi r \quad [12.4.1]$$

$$\sigma_1 = \frac{pr}{2t} \quad [12.4.2]$$

where p is the pressure, r is the radius of the vessel, t is the wall thickness, and σ_1 is the longitudinal stress. The circumferential, or hoop, stress is:

$$\sigma_2 = \frac{pr}{t} \quad [12.4.3]$$

where σ_2 is the circumferential stress.

Similarly, for a sphere the longitudinal and circumferential stresses are:

$$\sigma_1 = \sigma_2 = \frac{pr}{2t} \quad [12.4.4]$$

Other methods are required for thick-walled vessels.

12.4.3 Dilation

If the pressure vessel is subject to stress, it exhibits dilation, or radial growth. For an element which is subject to tensile stress in two perpendicular directions, the strain in one direction depends not only on the stress in this direction but also on that in the perpendicular direction and is a function of Poisson's ratio μ:

$$e_1 = \frac{\sigma_1}{E} - \frac{\mu\sigma_2}{E} \quad [12.4.5]$$

$$e_2 = \frac{\sigma_2}{E} - \frac{\mu\sigma_1}{E} \quad [12.4.6]$$

where e_1 is the longitudinal strain, e_2 the circumferential strain and E is the elastic modulus.

The dilation, or radial growth, of a cylindrical pressure vessel may be determined by integrating the hoop strain in the wall from an axis through the centre of rotation and parallel to a radius. If the coordinates of a point in the wall are r, ϕ, the dilation δ is:

$$\delta = \int_0^{\pi/2} e_2 r \cos\phi \, \mathrm{d}\phi \quad [12.4.7a]$$

$$\delta = e_2 r \quad [12.4.7b]$$

Then from Equation 12.4.6

$$\delta = r\left(\frac{\sigma_2}{E} - \frac{\mu\sigma_1}{E}\right) \quad [12.4.8]$$

and from Equations 12.4.2 and 12.4.3

$$\delta = \frac{pr^2}{2tE}(2-\mu) \quad [12.4.9]$$

Similarly, for a spherical vessel the dilation is

$$\delta = \frac{pr^2}{2tE}(1-\mu) \quad [12.4.10]$$

12.4.4 Dynamic pressure loading

The behaviour of a material such as mild steel under dynamic loading differs considerably from its behaviour under static loading. The shape of the stress–strain diagram alters with the rate of loading. At very high strain rates (say $\mathrm{d}e/\mathrm{d}t = 300\ \mathrm{s}^{-1}$) the yield point more than doubles. There are also large increases in the ultimate tensile strength and elongation. In consequence of this characteristic, the loads which can be applied to the material without permanent deformation or rupture are considerably greater with dynamic loading than with static loading.

12.4.5 Residual stress

The basic design equations for pressure vessels assume that the stresses are caused only by external loads. They do not take into account residual stresses resulting from fabrication and construction processes such as heat treatment, weld shrinkage or casting cooling. These stresses are of great importance in brittle materials. They are usually rather less significant in ductile materials, which tend to yield and relieve the stress, but they can contribute to fatigue failure.

Moreover, in thick sections residual stresses can combine with load stresses to create a three-dimensional stress pattern which restricts the redistribution of the localized stresses by yielding. This is the reason why stress relieving is particularly important for thick vessels.

12.4.6 Local stress

Another assumption of the basic design equations is that there is continuity of stress. The localized stresses in a region where there is a discontinuity are therefore greater than those predicted. These localized stresses are more important in brittle than in ductile materials, but again they are significant for fatigue failure.

12.4.7 Thermal stress

Most materials undergo expansion if their temperature is raised and contraction if it is lowered. If an unrestrained body is subjected to non-uniform heating, the different parts experience different degrees of strain and these differential strains give rise to corresponding stresses. Such stresses do not develop if the body is heated up uniformly. If the body is restrained, however, stress is developed even though the heating is uniform. There are, therefore two basic causes of thermal stress, non-uniform temperature and restraint.

With a ductile material, thermal stresses do not on first application cause failure by rupture, because the material tends to yield and relieve the stress, but their repeated application can cause fatigue failure. In addition, the deflection or distortion due to normal stresses can render equipment unserviceable.

For a body which is restrained in one dimension only, the thermal stress σ is

$$\sigma = -E\alpha\Delta T \quad [12.4.11]$$

where ΔT is the temperature difference and α is the coefficient of thermal expansion. The product $E\alpha$ is the thermal stress modulus. The minus sign indicates that the body is in compression. For a body restrained in two dimensions

$$\sigma = -\frac{E\alpha\Delta T}{(1-\mu)} \quad [12.4.12]$$

and for one restrained in three dimensions

$$\sigma = -\frac{E\alpha\Delta T}{(1-2\mu)} \quad [12.4.13]$$

Pressure vessel conditions mainly correspond to two-dimensional constraint.

Non-uniform temperature distribution may be either steady or unsteady state. The thermal stresses caused by thermal gradients in a long thin-walled cylinder or pipe may be shown to be as follows. For a steady state, linear temperature gradient through the pipe wall the stress on the inside of the pipe is:

$$\sigma = -\frac{E\alpha\Delta T}{2(1-\mu)} \qquad [12.4.14]$$

For a transient in which a hot fluid is suddenly contacted with the pipe wall, which previously was at a uniform temperature, the initial stress is:

$$\sigma = -\frac{E\alpha\Delta T}{(1-\mu)} \qquad [12.4.15]$$

12.4.8 Design construction features

There are numerous design features which tend to create local stresses. These include:

(1) discontinuities:
  (a) vessel ends,
  (b) changes of cross-section,
  (c) changes of thickness;
(2) joints:
  (a) bolted joints,
  (b) welded joints;
(3) bimetallic joints;
(4) holes and openings;
(5) flanges;
(6) nozzles and connections;
(7) bolt seating and tightening;
(8) supports and lugs.

The minimization of the local stresses caused by these stress raisers is a major aspect of pressure vessel design. Some of the principal methods of minimizing local stresses are as follows. Discontinuities are made as gradual as possible and sudden discontinuities are avoided. Weld defects such as overfill are kept to a minimum. Holes are spaced relative to each other so as not to cause serious weakening. The same applies to the spacing of nozzles and other connections. Flanges and nozzles are reinforced so as to minimize stress. The reinforcement relies on good design rather than on massive addition of metal. Self-adjusting nut seats are provided for bolts which have to be tightened on sloping surfaces. Thermal stresses at supports are reduced by measures to allow heat to flow between the vessel and the support, and so avoid large temperature gradients.

12.4.9 Vessels in composite materials

Pressure vessels may also be constructed in composite materials, notably glass-reinforced plastic (GRP), or fibre-reinforced plastic (FRP). The main use of GRP in the process industries is for atmospheric, or near-atmospheric, storage tanks, but vessels can be built to withstand higher pressures.

Accounts of the use of composite materials are given in *Glass Reinforced Plastic* (Parkyn, 1970), *Fibre Reinforced Materials Technology* (Parratt, 1972), *Fibre Reinforcement* (Catherall, 1977), *FRP Technology* (Weatherhead, 1980), *Materials and the Designer* (Cornish, 1987), *Composite Materials Handbook* (M. Schwartz, 1991) and by Puckett (1976), I.R. Miller (1979) and Britt (1993).

The use of GRP for storage tanks is discussed in Chapter 22.

12.5 Joining, Fastening and Welding

There are two main methods by which materials may be joined: (1) mechanical fastening and (2) physical bonding. For pressure systems the main fastening methods are riveting and bolts and nuts, while the methods of bonding are soldering and brazing and fusion welding. Although riveting was used as a method of joining in older pressure vessels, some of which are still in use, the modern method of joining is by fusion welding. Fastening by bolts and nuts, however, is a widely used method of joining, particularly on flanged joints. Flanged joints are used mainly in pipework and are considered in Section 12.7.

Soldering and brazing are methods of bonding in which the joint is made by introducing molten metal between the two parts to be joined without deliberate fusion of the parent metal. With fusion welding, by contrast, the parts of the parent metal adjacent to the joint are brought to molten temperature and caused to fuse together, generally with the addition of molten filler material. Fusion welding is the principal method of making permanent joints in pressure vessels and pipework.

An account of methods of joining, fastening and welding is given by Pilborough (1971, 1989).

12.5.1 Fusion welding

In fusion welding, the parts to be welded are heated so that they are molten along the line of the joint, and then generally a filler rod, also raised to molten temperature, is brought over the joint. This forms a pool of molten metal which is made to run along the joint and fuse the two parts together so that when they cool and solidify a homogeneous joint is made.

Some of the main methods of fusion welding described are:

(1) oxyacetylene welding;
(2) metallic arc welding;
(3) inert gas shielded welding:
  (a) argon arc welding,
  (b) CO_2 gas shielded welding,
  (c) pulsed arc welding;
(4) electrical resistance welding:
  (a) spot welding,
  (b) seam welding,
  (c) projection welding,
  (d) butt welding,
  (e) flash welding.

Oxyacetylene welding is cheap and is widely used. It is suitable where high quality welds are not required and where corrosion is not a serious problem. In oxyacetylene welding heat is generated by combustion of acetylene in oxygen using a blowtorch and the weld is made using a filler rod. The flame should be kept as nearly neutral as possible. Excess acetylene tends to cause carburization of the weld, leading to lower corrosion resistance and possibly embrittlement, while excess oxygen generally gives an oxidized and porous weld.

Metallic arc welding is perhaps the most commonly used method. It is suitable for welding a wide range of plate thicknesses, from thin plate up to plate many centimetres thick, and a wide range of materials including stainless steel. In metallic arc welding, an electrode of the same

metal as the work is used and an arc is struck between the two. The heat of the arc melts both the tip of the electrode and the parent metal beneath it, and metal drops across the arc from this electrode to the parent metal. Both a.c. and d.c. are used, the former being cheaper, but the latter being more suitable for some high quality work and for stainless steel.

Inert gas shielded welding is widely used to obtain a high quality weld. In the United Kingdom, the inert gas used is generally argon and the method is also known as 'argon arc welding'. Helium is normally used in the United States. The two main methods used are tungsten inert gas (TIG) and metal inert gas (MIG) welding. In the TIG technique, an arc is struck between the tungsten electrode and the work in an inert atmosphere. Filler is added as necessary in the form of a bare wire. In the MIG process, the arc is struck and a bare wire filler and inert gas are fed in through a feeder gun or head.

An alternative gas used in inert gas shielded welding is CO_2, which is much cheaper than argon. CO_2 gas shielded welding tends to be used for high quality work on ferrous metals and argon shielded welding for high quality work on stainless steel and on other materials.

The quality of the weld in MIG welding is affected by the mode of transfer of the molten metal to the work. The most desirable mode is spray transfer, in which the metal passes from the wire to the weld pool as small drops, but there occur also dip transfer, in which metal is deposited when the wire is dipped in the pool and which causes irregularity, and globular transfer, in which large drops are released. Spray transfer is favoured by high current, but the latter tends to burn through on thin material and a compromise is necessary.

Pulsed arc welding overcomes this problem and gives spray transfer without burn-through by using a high pulsed current to effect transfer, while maintaining a relatively low mean welding current.

There are a number of electrical resistance welding processes in which an electric current is passed through the work to be joined; the material is heated and rendered molten by the electrical resistance at the joint and is thus welded together.

In spot welding, the points to be joined are clamped together between two shaped electrodes. A heavy surge of current is passed between these electrodes and welds the work together by a small spot.

In seam welding, a series of spot welds is produced by a pulsed current from a rotating disc electrode. This method does not give a completely continuous weld. There is some tendency, therefore, for seam welds to leak and to entrap materials and corrode.

In projection welding, projections are raised on the parts to be joined, the parts are pressed together between the electrodes and the projections are fused by the weld current.

In butt welding, special projections are not used. The parts are pressed together between the electrodes and the adjoining surfaces are fused by the welding current. The adjoining faces in butt welding should be flat and parallel. In flash, or flash-butt, welding the parts are again pressed together between electrodes, a current is passed which causes the slight roughnesses of finish to melt and flash-off, the parts are pressed closer and more flashing occurs and, at the right moment, further pressure is applied, the parts fuse together and the current is switched off. Butt welding is used to join smaller components and flash welding large ones.

The terminology used in arc welding in the United States is described in the account by J.E. Jones and Olson (1986). They classify arc welding processes by type of shielding and by whether or not the electrode is consumed; they distinguish the following principal types:

Method	*Shielding*	*Electrode type*	*Usual thickness* (in.)
1. Shielded-metal arc welding (SMAW)	Flux plus coating; some generated gas	Solid wire, coated with flux	0.25–4
2. Submerged arc welding (SAW)	Granulated flux	Solid wire, maybe copper flashed	0.1–2
3. Gas-metal arc welding (GMAW)	Inert gas or gas mixture	Solid wire, maybe copper flashed	0.05–2
4. Fluxed-core arc welding (FCAW)	Flux and/or gas; may be self-shielding	Hollow electrode with core of metal powder	0.05–1.5
5. Gas-tungsten arc welding (GTAW)	Inert gas or gas mixture	Solid tungsten wire, water or air cooled	0.05–0.4
6. Plasma arc welding (PAW)	Inert gas or gas mixture	Solid tungsten wire, water cooled	0.04–0.24

In the first four of these methods the electrode is consumed, whilst in the last two it is not. The authors give details of the materials for which the different methods are suitable and of typical applications.

The American Welding Society (AWS) issues standards for most of these methods, with individual standards covering the arc welding of different materials such as carbon steel, stainless steel, etc. Thus, for example, AWS B2.1.001–90, B2.1.002–90 and B2.1.008–90, and B2.1004–90 cover welding of carbon steel by the SMAW, GTAW and GMAW methods, whilst B2.1.0013-91 and B2.1.005-90 cover welding of austenitic stainless steel by the SMAW and GMAW methods, respectively.

The qualifications of welders, the inspection of welds and defects in welds are considered in Chapter 19.

12.6 Pressure Vessel Standards and Codes

The design, fabrication and construction of pressure vessels is a subject which is particularly well covered by standards and codes of practice. Pressure vessel codes fall into two main types. The first type is the conventional codes, the second the so-called 'advanced codes'. The differences between the two types of code are considered below.

In the United Kingdom, the main pressure vessel codes until 1976 were BS 1500: 1958 *Fusion Welded Pressure Vessels for General Purposes* and BS 1515: 1965 *Fusion Welded Pressure Vessels for Use in the Chemical, Petroleum and Allied Industries*. BS 1500 was a conventional code and BS 1515 was an advanced code. In 1976, both these codes were superseded by a new pressure vessel code BS 5500.

The current version of this code is BS 5500: 1991 *Specification for Unfired Fusion Welded Pressure Vessels*.

The corresponding US code is the ASME *Boiler and Pressure Vessel Code*: 1992; this is described in Subsection 12.6.5.

Another code is ISO R831: 1968 *Recommendations for Stationary Boilers*, which is applicable to pressure vessels also.

There is an EC Directive 77/767/EEC on pressure vessels.

12.6.1 Conventional and advanced codes

The maximum design stresses allowed in a code either are tabulated in the code or are calculated from materials properties using factors of safety given in the code. The difference between the conventional and the advanced codes lies mainly in the design stress considered. These differences may be illustrated by considering on the one hand BS 1500: 1958 and ASME Section VIII, Division 1, and on the other BS 1515: 1965 and ASME Division 2.

At temperatures below the creep range the conventional codes BS 1500: 1958 and ASME Division 1 use as the design stress the tensile strength divided by a factor of safety, which is 4 in both codes, whilst the advanced codes BS 1515: 1965 and ASME Division 2 use the yield stress at design temperature divided by a factor of safety, which in BS 1515: 1965 is 1.5. This different design criterion favours the use of steel with high yield strength such as low alloy steels. The use of low alloy steels makes possible the design of thinner walled pressure vessels.

At temperatures within the creep range the design stress used is the creep strength, again in conjunction with a suitable factor of safety. The difference between the two types of code may be seen in the comparisons of design strengths given in the earlier BS codes by L. Evans (1974) and in the ASME code by Pilborough (1989). For a particular material at a particular temperature, the maximum permissible design strength is the lowest strength obtained by dividing the specified properties by the specified factor of safety. For BS 1500 and BS 1515 Evans gives the design strengths in terms of the material tensile strengths R_{20}, and R_t, the yield strengths E_{20} and E_t and the creep strengths S_r and S_c (as defined in Section 12.4), and an appropriate factor of safety.

BS 1500: 1958	$\frac{R_{20}}{4}$	$\frac{R_t}{4}$			$\frac{S_c}{1}$
BS 1515: 1965	$\frac{R_{20}}{2.35}$		$\frac{E_t}{1.5}$	$\frac{S_r}{1.5}$	$\frac{S_c}{1}$

The comparison given by Pilborough (1989) for the two divisions of the ASME code and also for ISO R831 may be summarized as follows. For each code the design strength is the lowest of:

ASME Section VIII Division 1	$\frac{R_{20}}{4}$	$\frac{R_t}{4}$	$\frac{E_{20}}{1.6}$	$\frac{E_t}{1.6}$	$\frac{S_r}{1.25}$	$\frac{S_c}{1}$
ASME Section VIII Division 2		$\frac{R_t}{3}$	$\frac{E_t}{1.5}$			$\frac{S_c}{1.5}$
ISO R831		$\frac{R_t}{2.7}$		$\frac{E_t}{1.5}$	$\frac{S_r}{1.5}$	$\frac{S_c}{1}$

The design strengths laid down in BS 5500: 1991 and the ASME code are given below.

12.6.2 Pressure vessel classification

BS 5500: 1991 gives a classification of pressure vessels. An earlier classification was given in BS 1500: 1958. The latter classified pressure vessels as Class I, II or III. For a Class I vessel the requirements include full radiography of the main seam welds, while Classes II and III have less stringent requirements. A Class I vessel also requires PWHT for stress relief.

BS 5500: 1991 places pressure vessels in three construction categories. For a Category 1 vessel full non-destructive testing of the main seam welds is required, while for Categories 2 and 3 the requirements are limited to spot non-destructive testing and visual examination, respectively. The PWHT requirements are related to steel type and thickness rather than to vessel category.

12.6.3 BS 5500

The coverage of BS 5500: 1991 *Specification for Unfired Fusion Welded Pressure Vessels* is indicated by the list of contents given in Table 12.3. The standard applies to the design, construction, inspection, testing and certification of pressure vessels. It does not cover certain defined types

Table 12.3 *Principal contents of BS 5500: 1991*

1. General
   - 1.1 Scope
   - 1.2 Interpretation
   - 1.3 Definitions
   - 1.4 Responsibilities
   - 1.5 Information and requirements to be agreed and documented
2. Materials
   - 2.1 Selection of materials
   - 2.2 Materials for low temperature applications
   - 2.3 Carbon, carbon manganese and alloy steels
3. Design
   - 3.1 General
   - 3.2 Application
   - 3.3 Corrosion, erosion and protection
   - 3.4 Construction categories and design stresses
   - 3.5 Vessels under internal pressure
   - 3.6 Vessels under external pressure
   - 3.7 Supports, attachment and internal structures
   - 3.8 Bolted flanged connections
   - 3.9 Flat heat exchanger tubesheets
   - 3.10 Design of welds
   - 3.11 Jacket construction
   - 3.12 Manholes and inspection openings
   - 3.13 Protective devices for excessive pressure or vacuum
4. Manufacture and workmanship
   - 4.1 General aspects of construction
   - 4.2 Cutting, forming and tolerances
   - 4.3 Welded joints
   - 4.4 Heat treatment
   - 4.5 Surface finish
5. Inspection and testing
   - 5.1 General
   - 5.2 Approval testing of fusion welding procedures
   - 5.3 Welder and operator approval
   - 5.4 Production control test plates
   - 5.5 Destructive testing
   - 5.6 Non-destructive testing
   - 5.7 Acceptance criteria for weld defects revealed by visual examination and non-destructive testing
   - 5.8 Pressure tests

Also various appendices including:

B Recommendations for cylindrical, spherical and conical shells under combined loadings, including wind and earthquakes.
C Recommendations for the assessment of vessels subject to fatigue.
D Requirements for ferritic steels in bands M0–M*E* inclusive for vessels required to operate below 0°C
E Recommendations for welded connections of pressure Vessels.
G Recommendations for methods of calculation of stresses from local lads, thermal gradients, etc.
H Recommendations for post-weld heat treatment of dissimilar ferritic steel joints.
J Recommendations for pressure relief protective Devices.
K Requirements for the derivation of material nominal design strengths for construction Category 1 and 2 vessels.
U Guidance on use of fracture mechanics analysis.

of vessel, which may be summarized as atmospheric storage tanks, vessels for very high pressure (e.g. strip wound compound vessels), vessels in which the stresses are less than 10% of the permitted design stress, vessels for specific applications covered by other British Standards and pressure vessels used in transport.

Specific recognition is given in the standard to the Inspecting Authority, which acts on behalf of the purchaser, and the Regulating Authority, which enforces the laws and regulations in the country concerned.

With respect to materials of construction the standard allows the use either of materials specified in British Standards or of other materials, provided these meet specifications agreed between the manufacturer and the user for certain specified properties as tested by specified methods listed in the standard. The latter should cover as a minimum the manufacturing process, compositional limits for all constituents, deoxidation practice, heat treatment and appropriate mechanical properties.

BS 5500: 1991 lists in its table 2.3 and appendix K the other standards which it uses for the design strength of steels. These include BS 1501–1504, BS 3059 and BS 3601–3605. It gives in tables 2.3(a)–(j) extensive tabulations of design strengths from these standards.

The basis for the determination of design strengths in the standards just listed is described in appendix K of BS 5500. A distinction is made between (1) the time-independent design strength and (2) the time-dependent design strength, in the creep region. For the former, distinctions are made between materials with and without specified elevated temperature properties and between carbon, carbon manganese and low alloy steels and austenitic stainless steels. Thus, for the time-independent strength, relations are given for the following four cases:

(1) carbon, carbon manganese and low alloy steels
  (a) materials with specified elevated temperature properties,
  (b) materials without specified elevated temperature properties;
(2) austenitic stainless steels
  (a) materials with specified elevated temperature properties,
  (b) materials without specified elevated temperature properties.

The nominal design strength f is taken as the lesser of the nominal design strength f_e corresponding to the short-time tensile strength characteristics and the nominal design strength f_F corresponding to the creep characteristics. The material strengths used are as follows. R_m is the minimum tensile strength at room temperature. R_e is the minimum yield strength at room temperature. Where a standard specifies minimum strength values of R_{eL} or $R_{p,0.2}$, these values are taken as corresponding to R_e. $R_{e(T)}$ corresponds to R_{eL}, or $R_{p,0.2}$ a temperature T. S_{Rt} is the mean stress required to produce rupture at time t at temperature T. The relations given in appendix K of the standard for the determination of the nominal design strength f are shown in Table 12.4. The design strength for a typical steel, BS 1501 26B, in plate form up to a thickness of 32 mm, which has a minimum tensile strength of 402 N/mm^2, is given in Table 12.5.

The equations given in the standard for minimum shell thickness for pressure loading only are as follows:

Cylinder:

$$e = \frac{pD_i}{2f - p} \qquad [12.6.1a]$$

or

$$e = \frac{pD_o}{2f + p} \qquad [12.6.1b]$$

Sphere:

$$e = \frac{pD_i}{4f - 1.2p} \qquad [12.6.2]$$

or

$$e = \frac{pD_o}{4f + 0.8p} \qquad [12.6.3]$$

where D_i is the internal diameter of the shell, D_o is the external diameter of the shell, e is the minimum thickness of the shell, f is the nominal design stress, and p is the design pressure. The dimensions do not include corrosion allowances.

The standard gives guidance on the design pressures and temperatures to be used. For the maximum design pressure it states that the design pressure, or the pressure to be used in the equations for the purposes of calculation, should not be less than:

(a) the pressure which will exist in the vessel when the pressure relieving device starts to relieve, or the set pressure of the pressure relieving device, whichever is the higher (see Appendix J of standard);
(b) the maximum pressure which can be attained in service where this pressure is not limited by a relieving device.

The static head should be taken into account.

For the minimum design pressure, the standard recommends that vessels subject to vacuum should be designed to a full negative pressure of 1 bar.

The maximum design temperature should not be less the actual metal temperature expected in service, allowing adequate margin for uncertainties in predicting this temperature. An appropriate design lifetime should be agreed between purchaser and manufacturer. No vessel designed

Table 12.4 *Design strengths given in BS 5500: 1991*

Material	*Regime*	*Temperature range* (°C)	*Design strength lowest of*
Carbon, carbon manganese and low alloy steels	Time-independent[a]	≤50	$f_E = \frac{R_e}{1.5}$ or $\frac{R_m}{2.35}$
		>150[b]	$f_E = \frac{R_{e(T)}{}^{c}}{1.5}$ or $\frac{R_m}{2.35}$
Austenitic stainless steel	Time-independent	≤50	$f_E = \frac{R_e}{1.5}$ or $\frac{R_m}{2.35}$
		>150[b]	$f_E = \frac{R_{e(T)}{}^{d}}{1.5}$ or $\frac{R_m}{2.35}$
Both types of steel	Time-dependent		$f_F = \frac{S_{R_t}}{1.3}$

[a] Values given for time-independent nominal design strengths are for material with specified elevated temperature values.
[b] For temperatures between 50 and 150°C values are interpolated.
[c] For materials without specified elevated temperature values, value is $R_{e(T)}/1.6$.
[d] For materials without specified elevated temperature values, values is $R_{e(T)}/1.45$.
[e] See detailed notes in Appendix K of the standard.

Table 12.5 *Design strengths (f, N/mm²) for steel 224, 490 M1 (A and B) for plates up to 40 mm thick, as given in BS 5500: 1991 (Courtesy of the British Standards Institution)*

R_m (N/mm²)	R_e (N/mm²)	*Thickness* (mm)	*Design temperatures* (°C) *not exceeding*						*Design lifetime* (h)
			50	*100*	*150*	*200*	...	*480*	
490	325	3–16	208	192	177	160	...	42	100,000
	315	40	208	190	173	158	...	38	150,000
	305	63	204	187	171	156	...	34	200,000
	281	100	187	176	164	153	...	34	250,000
	250	150	167	162	157	150			

on this basis should remain in service beyond the agreed lifetime without a review as specified in the standard.

The minimum design temperature, which is used to assess the suitability of the material to resist brittle fracture, should be the lowest metal temperature expected in service. In the case of components with external thermal insulation, this temperature is that of the contents of the vessel under the appropriate loading conditions, whilst in the uninsulated case the minimum temperature is a matter for agreement.

Some of the topics on which the standard gives guidance are (1) local stresses, (2) low temperature properties, (3) corrosion and (4) fatigue. The calculation of local stresses is covered rather comprehensively in the standard, which gives a large number of charts for particular cases.

The standard deals in appendix D with the suitability of steels in bands M0–M4 for low temperature service, below 0°C. A design reference temperature #R is defined such that

$$\theta_R \leq \theta_D + \theta_S + \theta_C + \theta_H \qquad [12.6.4]$$

where θ_D is the minimum design temperature (°C), and θ_R is the design reference temperature (°C), and θ_S, θ_C and θ_H are temperature adjustments. θ_C is an adjustment which depends on the construction category and has the values 0, −10 and −20°C for Category 1, 2 and 3 vessels, respectively. θ_H is an adjustment in applications where all plates incorporating subassemblies undergo PWHT before they are butt welded together, but the main seams do not subsequently undergo PWHT. In these applications θ_H is +15°C. θ_S is an adjustment depending on the calculated membrane stress which has the value 0°C when this stress is equal to or exceeds $2f/3$, +10°C when the stress is equal to or exceeds 50 N/mm² but does not exceed $2f/3$; and +50°C when the stress does not exceed 50 N/mm². In the latter case, the membrane stress should take into account internal and external pressure, static head and self-weight.

Where the calculated membrane stress can vary with the minimum design temperature, for example in autorefrigeration during depressurization, the standard requires that the coincident values of θ_D and θ_S be evaluated, where appropriate, allowing for the possibility of repressurization whilst still cold, and gives detailed guidance.

The standard gives graphs showing the permissible design reference temperature/reference thickness/material impact test temperature relationships for (1) as-welded and (2) PWMTcomponents.

Guidance on corrosion given in the standard is fairly general. It is recommended that the possible forms of corrosion such as chemical attack, rusting, erosion and high temperature oxidation be reviewed, that particular attention be paid to impurities and to fluid velocities, and that where doubt exists corrosion tests be done. If corrosion is expected to be negligible, no corrosion allowance is required, but where this is not the case, the recommended minimum allowance is 1 mm.

The standard deals in Appendix C with fatigue, for which it lists the following causes: (1) periodic temperature transients, (2) restrictions of expansion or contraction during normal temperature variations, (3) applications or fluctuations of pressure, (4) forced vibrations and (5) variations in external loads. Attention is drawn to the influence on fatigue of corrosion and of creep.

The standard requires that the design stress be kept reasonably below the fatigue limit if the expected number of cycles during the service life of the vessel might otherwise lead to fatigue failure. A detailed fatigue analysis is not required, however, where the design is based on previous and satisfactory experience of strictly comparable service or where certain alternative conditions are satisfied. A generalized chart for a design fatigue curve is given in the standard. It also gives a recommended method of constructing a design fatigue curve from test data.

The standard gives requirements for protective devices and for inspection. These are described here in Section 12.12 and Chapter 19, respectively.

12.6.4 Standards committees

Support for BS 5500: 1991 is provided by the Pressure Vessels Technical Committee (PVTC) (PVE/1) of the British Standards Institute (BSI). There is also a Pressure Vessel Quality Assurance Board (PVQAB) set up under the sponsorship of the Institution of Mechanical Engineers (IMechE).

12.6.5 ASME Boiler and Pressure Vessel Code

Another principal code is the American Society of Mechanical Engineers (ASME) *Boiler and Pressure Vessel Code*: 1992. The 11 sections of the code are shown in Table 12.6. Of particular relevance here are Sections II and VIII which deal, respectively, with materials specifications and with pressure vessels themselves. Section VIII has two parts: *Pressure Vessels, Division 1* and *Pressure Vessels, Division 2 – Alternative Rules*. Division 1 is a conventional code and Division 2 an advanced code.

Table 12.6 *Principal contents of the ASME Boiler and Pressure Vessel Code*

Section No.	
I	Power boilers
II	Material specification
III	Nuclear power plant components
IV	Heating boilers
V	Non-destructive examination
VI	Recommended rules for care and operation of boilers
VII	Recommended rules for care of power boilers
VIII	Pressure vessels: Division 1 Division 2 – Alternative rules
IX	Welding and brazing qualifications
X	Fibre-glass reinforced plastic pressure vessels
XI	Rules for in-service inspection of nuclear power plant components

12.6.6 Fibre-reinforced plastic vessels

There are also a number of standards and codes for the design of vessels and tanks in FRP. Relevant standards and codes are BS 4994: 1987 *Specification for Design and Construction of Vessels and Tanks in Reinforced Plastic;* the ASME *Boiler and Pressure Vessel Code*, Part X, *Fiber-Glass Reinforced Plastic Pressure Vessels* (1992); ASTM D 4021-86 *Standard Specification for Contact Moulded Glass-fiber-reinforced Thermosetting Resin Underground Petroleum Storage Tanks* and ASTM D 4097-88 *Standard Specification for Contact Moulded Glass-fiber-reinforced Thermosetting Resin Chemical Resistant Tanks*. HSE guidance is given in PM 75 *Glass Reinforced Plastic Vessels and Tanks: Advice to Users* (1991).

12.6.7 Limitations of standards

It is important to appreciate that standards and codes of practice have certain inevitable limitations. They are by their nature generalized and cannot readily cover all situations that may arise. They are prepared by committees and may represent the minimum standard on which agreement can be obtained. Their revision is a time-consuming task and they can become out of date. A fuller discussion of standards and codes is given in Appendix 27. These points have particular relevance to plants which have major hazards and/or novel technology. In these cases it should be appreciated that the standards represent a minimum requirement. Nevertheless, standards and codes of practice have an essential role to play in the design and operation of process plant.

12.7 Pipework and Valves

Loss of containment from a pressure system generally occurs not from pressure vessels but from pipework and associated fittings. At least as much attention should be paid to the pipework and fittings as to the vessels.

The cause of the Flixborough disaster was a modification to a 28 in. pipe connection between two reactors. The modification involved the installation of a temporary 20 in. pipe with bellows at each end. The design of the pipe system was defective in that it did not take into account the bending moments on the pipe due to the pressure in it. The bellows were not installed in accordance with the manufacturer's instructions. The pipework assembly was not adequately supported. The relevant British Standards, notably BS 3351 and 3974, were not followed. Further details are given in Appendix 2.

12.7.1 Pipework

The plant pipework and fittings include the piping itself, flanges and joints, and fittings, such as the many types of valves, bellows, etc., together with the pipe supports.

Accounts of pipework on process plants include those given in the *Handbook of Industrial Pipework Engineering* (Holmes, 1973), *Process Piping Design* (Weaver, 1973), *Handbook of Pipeline Engineering Computations* (Marks, 1979), *Piping Stress Handbook* (Helguero, 1986), *Piping and Pipe Support Systems* (P.R. Smith and van Laan, 1987) and

the *Engineering Design Guidelines of the Center for Chemical Process Safety* (CCPS, 1993/13).

Pipework in process plant in the United Kingdom has been covered by BS 3351: 1971 *Piping Systems for Petroleum Refineries and Petrochemical Plants* and by BS 3974: 1966 *Pipe Supports*, together with numerous other British Standards for pipework and fittings, some of which are listed in Appendix 27.

BS 3351: 1971 is now withdrawn. The code now commonly used is the ASME B31 *Code for Pressure Piping*. Also relevant until its withdrawal was the American Petroleum Institute *Guide for Inspection of Refinery Equipment*, Chapter 11, *Pipes, Valves and Fittings* (API, 1974). ASME B31.3 is described below, but first there are some preliminary points to be made.

A large proportion of failures of containment in process plants occur on the pipework and fittings. Some suggestions for reducing pipework failures have been given by Kletz (1984k) as part of a survey of such failures, which is described in Section 12.30. The design of pipework should be done by a fully integrated design organization working in a structured manner. There should be a relatively small number of designers of high quality making full use of computer aids. Similar principles should apply to the fabrication and construction stages.

Kletz recommends detailed design of even small bore pipework, though he recognizes that some organizations consider this impractical. He states that efforts should be made to reduce the number of grades of steel required so as to reduce the chance of installation of the incorrect grade, and instances restriction of steam temperatures so as to avoid the need for creep resistant steel. His survey highlights the high proportion of failures which are attributable to the construction phase and he makes suggestions for improved inspection during and after construction. Kletz states that the incidents which he lists suggest that of all the measures proposed this would be the most effective.

The pipework should be designed for ease of maintenance. If a joint may have to be broken, there should be adequate access and sufficient 'spring' in the pipework. If the insertion of a slip plate into a joint is likely to be a frequent operation, consideration should be given to installing a slip ring or spectacle plate.

Work on safe piping systems has been the subject of a study by the Institution of Chemical Engineers (IChemE), as described by Hancock (1990a). The principal features considered were (1) layout, (2) quality control, (3) construction, (4) pipe supports, (5) dead ends and (6) vibration and the principal causes of failure (1) vibration, (2) external corrosion, (3) temporary supports, (4) blocked in liquids, (5) water hammer, (6) steam hammer, (7) cavitation and (8) pressure surge.

12.7.2 ASME B31.3

The ASME B31 *Code for Pressure Piping* includes, in particular, Sections B31.1: 1992 *Power Piping*, B31.3: 1990 *Chemical Plant and Petroleum Refinery Piping*, B31.4 *Liquid Transportation Systems for Hydrocarbons, Liquid Petroleum Gas, Anhydrous Ammonia, and Alcohol*, B31.5: 1987 *Refrigeration Piping*, B31.8 *Gas Transmission and Distribution Systems*, and B31.9: 1988 *Building Services Piping*. In this chapter it is B31.3, the ASME *Chemical Plant and Refinery Piping Code*, which is the most relevant. The principal contents of ASME B31.3 are shown in Table 12.7.

Table 12.7 *Principal contents of ASME B31.3*

Chapter	
I	Scope and definition
II	Design
	Part 1 Conditions and criteria
	Part 2 Pressure design of piping components
	Part 3 Fluid service requirements for piping components
	Part 4 Fluid service requirements for piping joints
	Part 5 Flexibility and support
	Part 6 Systems
III	Materials
IV	Standards for piping components
V	Fabrication, assembly and erection
VI	Inspection, examination and testing
VII	Non-metallic piping and piping lined with non-metals[a]
VIII	Piping for Category M fluid service[a]
IX	High pressure piping[a]
Also various appendices, including:	
A	Allowable stresses and quality factors for metallic piping and bolting materials
B	Stress tables and allowable pressure tables for non-metals
C	Physical properties of piping materials
E	Reference standards
F	Precautionary considerations
G	Safeguarding
K	Allowable stresses for high pressure piping
M	Owner's guide to classifying fluid services
X	Metallic bellows expansion joints

[a] Chapters VII–IX have a structure broadly similar to, but in some cases more detailed than, that of Chapter II.

B31.3 defines the following categories of fluid service: (1) Category D, fluid service; (2) Category M, fluid service; (3) high pressure fluid service and (4) normal fluid service. Category D applies where: (1) the fluid handled is non-flammable, non-toxic and not damaging to human tissues; (2) the design pressure does not exceed 150 psig (10.3 barg) and (3) the design temperature is in the range −20 to 366°F (−29 to 186°C). The term 'damaging to human tissues' describes a fluid such that 'exposure to the fluid, caused by leakage under expected operating conditions, can harm skin, eyes, or exposed mucous membranes so that irreversible damage may result unless prompt restorative measures are taken'.

Category M, which is particularly relevant here, is 'a fluid service in which the potential for personnel exposure is judged to be significant and in which a single exposure to a very small quantity of a toxic fluid, caused by leakage, can produce irreversible harm to persons on breathing or bodily contact, even when prompt restorative measures are taken'.

High pressure fluid service is one for which the owner specifies the use of chapter DC of the code. Normal fluid service is fluid service not covered by the other three categories and not subject to severe cyclic conditions, and is the most commonly occurring service.

Appendix M of the code gives a guide to classification of fluid services (Figure M-l). The code utilizes a system of

listed materials and components, which are those conforming to a specification given in appendices A, B or K or to certain listed standards (tables 326.1, A326.1 and K326.1).

It also utilizes certain prefixes. These include A for entries in chapter VII on non-metallic piping, M for those in chapter VIII on Category M fluid service piping, and K for those in chapter DC on high pressure piping.

Dealing first with the provisions for metallic pipework, the code gives guidance in chapter II on design pressures and temperatures. Essentially, the design pressure of a component should not be less than the pressure at the most severe condition to which the equipment may be subject, the most severe condition being that combination of pressure and temperature which requires the greatest component thickness and highest component rating.

For a straight pipe under internal pressure the code gives for the pipe thickness:

$$t_m = t + c \qquad [12.7.1]$$

where c is the sum of mechanical, corrosion and erosion allowances, t is the pressure design thickness and t_m is the minimum required thickness. The pressure design thickness t is given by:

$$t = \frac{PD}{2(SE + PY)} \qquad [12.7.2]$$

It also allows three alternative equations, one of which is

$$t = \frac{PD}{2SE} \qquad [12.7.3]$$

where D is the outside diameter of the pipe, E is the quality factor, P is the internal design gauge pressure, S is the stress value for the material and Y is a coefficient. Values for the quality factor E are given in appendix A of the code and those for the coefficient Y are given in a table. These equations apply for $t < D/6$. For $t > D/6$ or $P/SE > 0.385$ the design is more complex and requires account to be taken of factors such as thermal stress and fatigue, and application of failure theory.

The design temperature of a component should be that at which, in combination with the relevant pressure, the greatest component thickness and highest component rating are required. In determining the design temperatures, factors to be considered include fluid temperatures, ambient temperatures, solar radiation, and heating and cooling medium temperatures.

The code gives guidance on the component temperatures to be assumed for uninsulated, externally insulated and internally insulated components. For the former, for fluid temperatures below 150°F (65°C) the component temperature is taken as that of the fluid, unless there are factors such as solar radiation which indicate that a higher value should be taken. For fluid temperatures above 150°F the component temperature is taken as a given fraction of the fluid temperature, as follows: (1) 95% of the fluid temperature for pipes, valves, lapped ends, welding fittings, and other components of wall thickness comparable to that of the pipe; (2) 90% for flanges, except lap joint flanges; (3) 85% for lap joint flanges and (4) 80% for bolting. For externally insulated pipework the component temperature should be taken as the fluid temperature unless some other temperature can be justified by calculation, test or experience.

The code deal with materials in chapter III, in appendices A–C and also in other parts. For severe cyclic conditions only certain types of pipe may be used, as listed in chapter II (paragraph 305.2.3). The code gives guidance on materials suitable for use at high temperatures and those suitable for low temperatures. It contains a table of requirements for low temperature toughness tests for metals (table 323.2.2). This table gives design minimum temperatures.

Flanges, valves and other fittings are dealt with in chapter II of the code and also in chapter IV and appendix F. Chapter IV gives for flanges, valves and other fittings, listed components, each with its appropriate standard (table 326.1), together with guidance on the use of unlisted components.

Appendix F of the code on precautionary considerations provides guidance on certain potential hazards and weak points in pipework. It highlights certain hazards such as expansion of trapped liquids and fluid transients including geysering and bowing during cooldown, but is mainly concerned with: (1) valves; (2) flanged joints, including flanges, gaskets and bolting and (3) materials.

The integrity of a flanged joint depends on the flanges, the gasket and the bolting. For the flanges themselves, the code gives guidance on flange rating, type, facing and facing finish. It also gives guidance on selection of gaskets.

Bolting covers bolts, bolt studs, studs, cap screws, nuts and washers. The codes gives listed bolting. It also gives guidance for conditions subject to high pressure, to high and low temperatures and temperature cycling and to vibration. For high, low and cycling temperatures and for vibration conditions consideration should be given to the use of controlled bolting procedures to reduce (1) joint leakage due to differential thermal expansion and (2) stress relaxation and loss of bolt tension.

With respect to valves, the use of extended bonnet valves is recommended where appropriate to establish a differential between the temperature of the valve stem packing and that of the fluid. This can be an effective way of avoiding problems of packing shrinkage, leakage and icing. Attention is also drawn to the potential for entrapment of liquids in valves such as double-seated valves, with its attendant liquid expansion problem.

Metallic bellows expansion joints are treated in the code in Appendix X, which delineates the relative responsibilities of the pipework designer and the expansion joint manufacturer, and gives guidance on: expansion joint design conditions; joint design, including fatigue analysis; joint support and restraint; and fabrication, examination and pressure and leak testing. Reference is made to the standards of the Expansion Joint Manufacturers Association (EJMA). The use of expanded joints is not allowed in Category M (fluid service) or high pressure piping.

Appendix G of the code on safeguarding deals with measures to protect pipework against accidental damage and to minimize the consequences of pipework failure. Normal safeguards listed include: (1) plant layout; (2) equipment, such as instrumentation, ventilation and fire protection; (3) systems of access and of work; (4) means for fluid containment, recovery or disposal and (5) operating procedures. Whilst in most cases additional engineered safeguards are not necessary, in some they may be. Engineered safeguards listed include: (1) temperature protection by instruments, thermal insulation or thermal shields; (2) mechanical protection by shields, barricades, etc.;

(3) vibration protection; and (4) measures to mitigate pipework failure.

The code addresses the question of the use of isolation valves, or stop valves, in pressure relief piping. Stop valves between the piping being protected and the protective device (s) and between the latter and the point of discharge are not allowed, except subject to conditions. Essentially these are: (1) the stop valves are so constructed and subject to such positive control that any closure made does not reduce the pressure relief capacity; (2) the stop valves are either full-area valves or are such that they will not affect either the operation or the capacity of the pressure relief device(s); and (3) the stop valves are so arranged that they can be locked or sealed in both the open and closed positions. The procedures to be followed if stop valves installed according to these principles are to be closed whilst the plant is operating are given in appendix F of the code. This requires the presence of an authorized person who has the means to observe the pressure in the equipment and to relieve it in the event of overpressure. Before leaving the scene, this person should lock or seal open the stop valves.

The requirements for examination of the pipework are given in chapter VI of the code. For piping for normal fluid service the minimum requirements are certain specified visual examinations, covering materials, fabrication, longitudinal welds, assemblies and erection and examination by radiographic or ultrasonic methods of a random sample of 5% of circumferential butt welds and mitre groove welds.

Chapter VI also contains the provisions for testing. For normal fluid service piping the essential requirement is for a hydrostatic test. The test is performed using water and the test pressure is 1.5 times the design pressure, but with an adjustment for the difference between the test and design temperatures and with a limitation to ensure that the yield strength is not exceeded. There are various alternative provisions such as those for the use of a pneumatic test and of hydraulic test fluids other than water.

High pressure pipework is dealt with in chapter IX of the code. The basic approach is similar, but the requirements are more stringent in respect of a number of features. There is a different formula for the thickness of straight pipe under internal pressure.

Piping for Category M fluid service is treated in chapter VIII. Again, the requirements for certain features are more stringent.

12.7.3 Pipe supports

Pipe supports are dealt with in BS 3974: 1974. This standard lists the following loads for which supports are required: (1) mass of the pipe, including operating or testing medium, insulation and associated equipment; (2) expansion and contraction; (3) reaction due to pumping effects and discharge to atmosphere and (4) wind, snow or ice loads.

Equations are given for the calculation of maximum bending stresses and deflections based on a single span simply supported or a continuous beam. Pipes are usually assumed to be simply supported or unrestrained rather than supported as beams with fixed ends. Concentrated loads, direction changes and pipe joints require special attention. Increase in pipe diameter is sometimes used to obtain a greater distance between supports.

Some devices used to support horizontal pipes include pipe hangers, slider supports and roller supports. Spring and turnbuckle hangers are used for suspending hot insulated pipes. For vertical pipes methods of support include trunnions supported on guide lugs, and sling rods supported by pipe hangers.

Pipe clips or hangers should be in direct contact with the pipe or insulation, but should not be too tight around them. Distance pieces are generally used to prevent this. The insulating material should be capable of bearing the compression load imposed. Pipe guides are used to restrain sideways movement of pipes. Anchors are used where it is necessary to provide fixed points for pipe bends and loops.

Pipework supports are also dealt with in ASME B31.3. This code gives separate treatments for pipe supports for piping for normal fluid service, Category M fluid service and high pressure service, and for non-metallic piping.

12.7.4 Gaskets

Flanged joints in process plant are sealed mainly by gaskets or ring seals. Gaskets are considered in this subsection and ring seals in the next.

Two commonly used types of gasket are compressed asbestos fibre (CAF) gaskets and metallic spiral wound gaskets. These are covered in BS 1832: 1972 *Specification for Oil Resistant Compressed Asbestos Fibre Jointing* and BS 3381: 1989 *Specification for Spiral Wound Gaskets for Steel Flanges* to BS 1560. There is a trend towards the use of metallic spiral wound gaskets instead of CAF gaskets for many of the more severe and hazardous duties. A metallic spiral wound gasket takes the form of a ring made out of metal windings, with a V-shaped cross-section, wrapped in a continuous spiral with soft filler between the metal plies, all encased in an outer wrap.

The features of metallic spiral wound gaskets are discussed by Granek and Heckenkamp (1981). Such spiral wound gaskets have many merits. They provide a relatively simple and low cost joint. They offer the elasticity and material flow required for good sealing. They are well suited to high pressures. They are resistant to high temperature and corrosive conditions. They are resilient to thermal shock and vibration. The method of construction and the permutations of metal and filler support a family of gaskets with shapes compliant to different flange configurations and with properties such as the stiffness matched to the application. On the other hand, they have certain disadvantages. They are not readily tightened up to stop leaks and they are not resusable. They are also relatively sensitive to the quality control on the gasket itself, the application in which it is used and the manner in which it is bolted up. These authors also discuss the extent of confinement of the gasket, favouring the practice of confining it so that it has no freedom to move and immobilizing it to prevent leak paths when pressurized. Metallic spiral wound gaskets are resistant to blowout, and this is often an important factor in their selection.

12.7.5 Ring seals

The other main kind of seal for flanged joints is the ring seal, also known as a lens or ring type joint (RTJ). This type of seal is used particularly for high pressure plant. A ring seal is a ring with an approximately ovoidal cross-section which fits into two grooves, one on each of the two flanges. The seal is made at the edges rather than at the bottom of the groove. The ring is capable of a degree of deformation to make a good seal. It is good practice to use a new ring seal

when remaking a joint. Ring seals are another form of blowout-resistant sealing.

12.7.6 Bellows

Pipework needs to incorporate means of accommodating expansion and contraction. One method of doing this is by utilizing bellows. A bellows assembly may be used, for example, between two pipe sections, between two vessels or between a pipe and a vessel.

After the Flixborough disaster in 1974, referred to above, the use of bellows came under a cloud. It is now subject to much stricter control. Typically, proposals to use bellows in pipework with potential for hazardous release are reviewed individually during design, and in some cases there may be restrictions on their use. An account of one company's policy on bellows is given by Boyett (1979).

Following Flixborough, a British Standard on bellows was issued. This is BS 6129: 1981 *Code of Practice for the Selection and Application of Bellows Expansion Joints for Use in Pressure Systems*, which has a single part, Part 1: 1981 *Metallic Bellows Expansion Joints*. In the United States, standards for bellows are issued by the EJMA.

An account of the design and application of bellows as expansion joints is given by C. Taylor (1985). The bellows itself consists of a convolution. The convolution may be 'thick-walled' or 'thin-walled', the latter term covering multi-wall construction which may be thicker than a 'thick-walled' unit. Its stiffness is expressed as a spring rate.

The design of a bellows assembly has to take into account: the forces on, and stresses induced in, the bellows, and its movement; the forces and moments on equipment connected to it; the external forces such as wind loads on it; its stability; and its fatigue performance. The design requires also to cover the anchors and guides.

The EJMA method gives relations for determining the spring rate of the convolution. It treats the bellows as an elastic shell with stresses induced by pressure and deflection. It deals with the stability of the bellows and gives a fatigue curve.

Taylor describes three types of system used to compensate for expansion: (1) compression systems, (2) tension systems and (3) pressure balanced systems. The compression system is the simplest: the bellows is placed between the two pipe sections and, when expansion occurs, the bellows is compressed. The fixed pipe section is held by an anchor which resists the compressive forces and the moving section may be provided with a guide.

In a tension system, the pressure end load is taken up not by anchors but in some other way. The arrangement exploits angulation, or slight off-axis movement of the bellows. Three tensile systems are hinged assemblies, gimbal assemblies and tied double assemblies. Hinged units give movements in one plane by angulating the bellows; the pressure end load is contained by the hinge parts. Gimbal assemblies allow angular movements. Tied double assemblies permit large movements in a plane and, using two tie bars, angulation.

In a pressure balanced system, the force induced by the pressure in the bellows is balanced so that only the spring rate needs to be accommodated by external means. Two commonly used systems are the in-line assembly and the elbow-type assembly. Systems of this kind tend to be relatively bulky and expensive, but find application where movements are small and space is restricted, and also on high pipework where anchors are impractical. They are widely used on compressors and turbines.

Hydrostatic testing requirements can present a difficulty in bellows design. Whereas with most pipework fittings there is no fundamental problem in increasing the strength, a bellows is unique in that there is a tradeoff to be made between strength and deflection. An increase in thickness of the bellows gives an increase in strength, but a decrease in allowable deflection, the limiting factor being squirm. The point is discussed by D.J. Peterson (1991), who instances design of bellows for piping on a fluid catalytic cracker unit with gas at 45 psig and 1300°F. He argues that in practice the metal temperature of such bellows would be 1000°F. Design for a test pressure of 76 psig and the actual operating temperature of 1000°F yields a bellows thickness of 0.048 in. However, if the test pressure is taken as that for the nominal operating temperature of 1300°F and, furthermore, as that applicable to the material of construction of the pipework rather that of the bellows, this results in a test pressure of 343 psig and a corresponding bellows thickness of 0.150 in. The spring rate is increased by a factor of 28 and the cycle life is reduced by a factor of 317.

12.7.7 High integrity pipework

Where the consequences of pipework failure could be especially serious, the pipework should be of high integrity. Measures to improve pipework integrity are discussed by numerous authors. A convenient summary of many of these is given for highly toxic materials in the CCPS *HTHM Guidelines* (1988/3).

Measures should be taken to reduce the stresses to which the pipework is liable to be subjected and to give it robustness in the face of such stresses. Sources of vibration and of severe cycling should be minimized and, if necessary, countermeasures taken. A flexibility analysis of the pipework should be carried out.

Joints on pipework should be welded or flanged, and threaded joints should be avoided. Features which may prove to be weak points should be minimized; these include expansion bellows, hoses and sight glasses.

Gaskets should be suitable for the fluid handled and the temperatures, and should be resistant to blowout. Blowout resistant-gaskets include metal reinforced, spiral wound and ring joint types.

Fittings, particularly valves, are potential weak points and should receive attention both in respect of fugitive emissions and outright failure. Leakage can be reduced by the use of double packing boxes or bellows seals.

The design should seek to limit the size of any release which may occur. One measure is the avoidance on vessels of nozzles larger than is strictly necessary. Another is the use of flow restrictor orifices in pipes. The approach taken here is to make the pipe of larger diameter, and thicker walled, with a lower normal flow velocity.

The pipework should be protected against overtemperature, particularly from fire. Methods of protection include fire insulation and water sprays used as alternatives or in combination. The fire insulation should not only possess a suitable nominal fire resistance but also should remain in place under fire conditions, which include the use of water jets for fire fighting. With respect to fire insulation there is a balance to be struck between fire protection which it affords and the threat of external corrosion beneath it.

Where the pipework may be subjected to low temperature, whether this be the normal operating temperature or one resulting from a deviation such as sudden depressurization, the constructional materials should have sufficient impact resistance to prevent low temperature brittle fracture.

If the material in the pipe may freeze at the lowest temperatures expected, countermeasures such as trace heating are necessary. Freezing poses two distinct threats. One is expansion on freezing. The other is uneven thawing and expansion of the unfrozen liquid.

The pipework should be protected against overpressure, using a suitable combination of protective measures. These may include trips, expansion chambers and pressure relief devices.

With respect to physical abuse the CCPS *Guidelines* state that a properly supported NFS 1.5 in. steel pipe is generally accepted as being resistant to loads such as being stepped on or struck by a heavy pipe wrench. It is desirable that piping of other materials be similarly resistant, whether by materials selection, pipe thickness or protection.

Impurities may constitute a threat to pipework integrity, particularly where the materials handled are highly reactive, which includes those which are strong oxidizers. The system may therefore need to be cleaned after construction. This can be assisted by a design which avoids dead spaces and provides adequate vents and drains.

In supporting pipework carrying a corrosive fluid, the hangers which support the pipe from above by rods are liable to suffer corrosion of these rods, and the arrangement is generally to be avoided. An arrangement which supports the pipe from below is less liable to fail. In more critical duties, it may be necessary to consider protection of the pipe support themselves against very low or high temperatures, including those occurring in fire conditions.

The routing of pipes should take account of the threat from tanks and vessels, pumps and pipework holding flammables and, generally, of the threat from fire. Routes should pass through protected areas and away from roads. It may be appropriate to furnish protection against vehicle impact and against physical abuse. In some cases, piping is armoured and extra protection is provided for nozzles and small bore pipework.

The pipework should be designed with a view to maintenance of the valves, important aspects being access and ease of slip plating. Attention should also be paid to the avoidance of unbolting errors in the maintenance of valves, so the bolts necessary to containment of the pressure are not removed in the mistaken belief that they are associated only with, say, the actuator or with a spool piece.

Tanks and vessels should be provided where necessary with remotely operated emergency isolation valves, as described below. Open-ended external valves should be fitted with a blind flange or plug.

Another potential weak point is the pumps. These should be designed to withstand the highest pressures and most extreme temperatures to which they may be subject.

Construction of the pipework should also be to high standards. This aspect is dealt with in Chapter 19. Aspects mentioned in the CCPS *Guidelines* include: colour coding for identification; cleaning after construction, and design to facilitate this; procedures for controlled bolting; and access for inspection.

12.7.8 Fibre reinforced plastic pipework

There are also a number of standards and codes for the design of pipework in FRP. Relevant standards and codes are BS 6464: 1984 *Specification for Reinforced Plastics Pipe, Fittings and Joints for Process Plants*, BS 7159: 1989 *Code of Practice for Design and Construction of Glass-reinforced Plastic (GRP) Piping Systems for Individual Plants or Sites*, and ASTM D 3517-91 *Standard Specification for 'Fiberglass' (Glass-fiber-reinforced Thermosetting Resin) Plastic Pipe*. ASME B31.3, the *Chemical Plant and Refinery Piping Code*, deals with non-metallic piping.

12.7.9 Valves

Valves constitute another important class of component in pipework systems. There is a wide variety of valves in use, and only a few types, that is, those with an essentially protective function, are considered here. They are (1) non-return valves, (2) excess flow valves and (3) emergency isolation valves. Regular control valves are dealt with in Chapter 13. Another aspect of protection is the interlocking of valves to prevent their being operated in an incorrect sequence. This is discussed in Subsection 12.7.13.

12.7.10 Non-return valves

Non-return valves (NRVs), or check valves, are used to prevent undesired reverse flows. Reverse flow can have serious consequences and some form of protection is often necessary. Some situations in which reverse flow occurs have been described by Kletz (1976b). They include: (1) flow into plant from storage vessels or blowdown lines, (2) flow from plant into service lines, (3) reverse flow through a pump and (4) reverse flow from reactors. An NRV is a prime means of preventing reverse flow in many of these situations, although it is not always an adequate, or even the most appropriate, method in all cases.

Process materials can flow back into service lines with disastrous results if a pressure reversal occurs. AN NRV should be installed on service lines, but other measures are also necessary. If the service line is in continuous use, it may be necessary to have low service pressure and high process pressure alarms/trips. If the service line is used intermittently, it should be isolated when not in use by positive means such as hose disconnection or double block and bleed valves.

NRVs are widely used on the discharge of pumps to prevent reverse flow through the pump. If reverse flow occurs, it can disintegrate the impeller and damage the motor. Consideration should also be given to reverse rotation locks on pumps.

Reverse flow of one reactant from a reactor into the feed pipe of another reactant is likely in many cases to result in an explosion. NRVs may be appropriate on the feed pipes. Another precaution is the use of a small inventory feed tank. This limits the scale of any possible explosion, although it also lessens the degree of dilution of a contaminant and may thus increase the probability of a reaction.

NRVs are not a fully reliable means of eliminating reverse flow. Numerous instances have occurred in which materials have travelled back not just through one but several NRVs in series. According to Ellis and Mualla (1986), a survey of stoppages in Central Electricity Generating Board (CEGB) power stations showed that some 16% were connected with NRVs.

NRVs on critical duties are important pressure system components and should be included in the pressure system register and regularly tested and maintained.

Leakage from storage vessels or blowdown lines into the plant tends to occur when the latter is shut-down, and can have serious consequences. It is usually due to leaks through closed but defective valves. The remedy is more positive isolation by means such as blanking off.

Increasingly, environmental considerations lead to requirements for vents from storage tanks and other equipment to be routed to a disposal system. It is necessary to ensure that reverse flow does not occur in such a system. However, reverse flow protection for storage tank vents is not readily effected by the use of NRVs, because the storage tank pressures are low and the flows are often very low and intermittent. The problem is discussed by Englund, Mallory and Grinwis (1992), who describe instrument systems for this duty. These authors also describe reverse flow protection arrangements, including NRVs, for a number of other situations, such as pump and reactor systems.

In some cases, it is necessary to take quite elaborate precautions to prevent reverse flow. The importance of avoiding reverse flow in ethylene oxide plants was emphasized in Chapter 11. Figure 12.8 shows a reverse flow protection system for the ethylene oxide feed to a reactor. There is a kick-back line around the pump to prevent overheating and an NRV on the pump delivery. There are two trip initiators and two shut-down valves with both initiators and valves arranged as 1-out-of-2 systems, as described in Chapter 13. One of the valves is also used as a control valve. There are two further NRVs. Diversity of the types of NRV is used to reduce the probability of common cause failure.

Reverse flow of ammonia into an ethylene oxide feed tank on a reactor was responsible for the disaster in 1962 at Doe Run, Kentucky (Case History A31). Appendix 1 also describes various other incidents involving reverse flow and NRVs. Further case histories are given by Kletz (1976b).

12.7.11 Excess flow valves

Another type of valve with a protective function is the excess flow valve (EFV). Such a valve is used to shut off flow in a situation where the flow has suddenly risen far in excess of its normal value. The rise in flow which triggers the operation of an EFV is generally 50% or more above the normal value.

EFVs are used at loading facilities to give flow shut-off in the event of rupture of a filling line hose. The EFV on a filling line may be installed internally in the storage vessel.

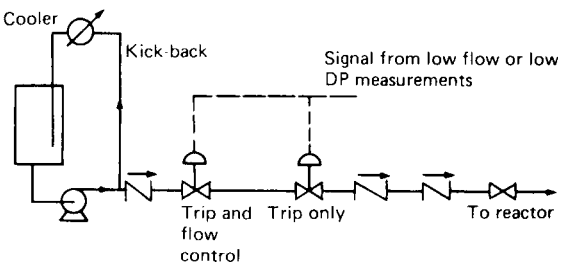


Figure 12.8 *Ethylene oxide feed system to a reactor (Kletz, 1976b) (Courtesy of Hydrocarbon Processing)*

Where the fluid is held as a superheated liquid under pressure and will flash when released to atmosphere, the flow will become two-phase. The sizing of the EFV thus involves a two-phase flow calculation. A calculation method for two-phase flow in this application has been described by R.A. Freeman and Shaw (1988). The method is presented as an alternative to testing of excess flow valves, which is a code recommendation for liquefied petroleum gas (LPG), but which the authors consider to be potentially hazardous.

12.7.12 Emergency isolation valves

Emergency isolation valves (EIVs) are used in process plant to prevent the loss from containment of large quantities of flammable or toxic substances. An account of EIVs has been given by Kletz (1975b). Kletz gives rules for deciding whether to install an EIV, and illustrations of the application of these rules in particular plants. Points where large escapes of material are liable to occur include (1) pumps, (2) drain points and (3) hose connections.

Large leakages can occur from pump glands and seals. Some cases of pump leakage are quoted by Kletz. In one instance there was a 3 ton escape of ethylene over a period of 20 min.

Drain points are also liable to large escapes. Again a number of examples are given by Kletz. The drainage of water from hydrocarbons can take some minutes, so that an operator tends to go and do something else. Then, if there is less water than he expected, or if he forgets to return, there may be a leak of hydrocarbons.

Another problem is the blockage of drain lines and drain valves by ice or hydrate formation. In some cases, a drain valve freezes open and the operator is unable to close it. In others, a blockage occurs and the operator clears it, but is then unable to approach to close the valve on account of the material escaping. The Feyzin disaster in 1966 (Case History A38) began with a blockage in the drain line from a propane storage sphere, due almost certainly to ice or hydrate.

EIVs may be installed between the inventory and the point of expected leakage, but it is unnecessary to install an emergency isolation valve between every inventory and every leakage point. In fact, it is undesirable to do so, since every such device itself introduces further chances of leakage. The decision as to whether an emergency isolation valve is required in a given case depends, therefore, on the expected scale and effects of a leakage and on its probability. Inventory is an important factor, but it is not the only one.

In many cases, a rough estimate of the probability of a leak may be sufficient to show that an EIV is or is not needed. In cases where the decision is not clear-cut, it may be helpful to do a hazard assessment as described in Chapter 9. Relevant to such assessment is the probability of pump fires. Some estimates given by Kletz (1971) are quoted in Table 16.55.

The condition of the material should also be taken into account in determining the need for an emergency isolation valve. A cold liquid that is well below its atmospheric boiling point is less hazardous than one which is superheated and will flash off when let down to atmospheric pressure. Other factors which may be taken into account include the possibility of isolating the inventory by other means, such as on the feed to the unit, or of pumping the inventory away.

Kletz (1975b) gives some examples of the need for emergency isolation valves, which illustrate the fact that inventory is not the only criterion. An emergency isolation valve is recommended for a 10 ton inventory on an ethylene sidestream pump which in the past has leaked and ignited, whereas one is not recommended for a 70 ton inventory on a naphtha feed pump which contains cold material and has not leaked.

An emergency isolation valve may be installed as a new valve or by motorization of an existing valve. Figure 12.9 illustrates the two methods for two pumps piped up in parallel. In this case the use of existing valves requires the motorization of two valves. But there are some advantages in this method in that the amount which can leak out after the valves are closed is much reduced and that the valves are more easily tested.

The valve may be arranged so that air, hydraulic or electrical power is required to keep it open or, alternatively, to close it. The normal arrangement is closure on power failure, unless this is undesirable for some reason. Valves which are very large and existing valves which have to be motorized, however, require power to move them either to open or close.

If the emergency isolation valve closes on loss of power, it is not generally necessary to provide fire protection on the air or electrical power lines to it. But if power is needed to close the valve, the power lines should be provided with 15-min protection and a latching device installed to keep the valve closed if the power lines are destroyed. The 15-min protection allows the operator time to decide whether to close the valve.

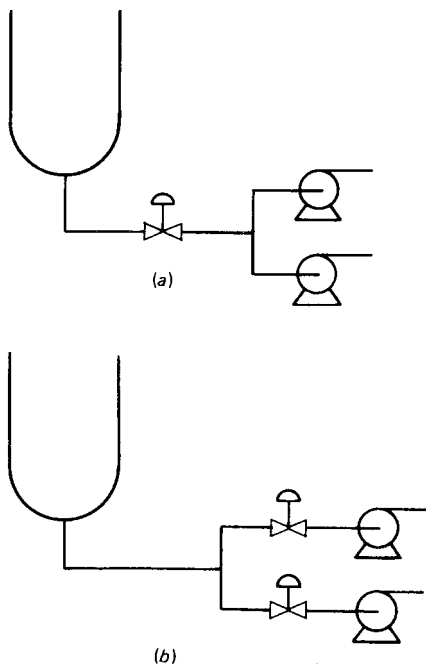


Figure 12.9 *Emergency isolation valves between a vessel and pumps: (a) new isolation valve; (b) existing isolation valves motorized, (after Kletz, 1975b) (Courtesy of the American Institute of Chemical Engineers*

There appears to be little evidence to suggest that either pneumatic or electrical operation is more reliable, but it is desirable to ensure that the valve actuator is sufficiently powerful, particularly on dirty fluids, slurries, and so on. An oversized actuator may well be worthwhile.

Operation of the emergency isolation valve should be sufficiently remote that the operator can close it readily in an emergency. He or she should not have to approach a gas cloud or a fire or to go up on higher level platforms or to stand on a ladder. The most suitable arrangement is often remote operation from the control room. Emergency isolation valves which are controlled remotely are also known as remotely operated valves (ROVs) and remotely operated block valves (RBVs).

For EIVs it is recommended by Kletz that two switches should be provided at a safe distance from potential leak points and separated by at least 30 ft. Where there is more than one device to be operated remotely, such as an emergency isolation valve and a pump shut-off, it will generally be desirable to group the switches for the different devices together.

In some older plants, the handles of emergency isolation valves are taken through a wall, which thus provides protection for the operator. This method is not recommended, however, since walls interfere with ventilation and hinder the dispersal of leaks. Remote operation is better.

Where an emergency isolation valve is fitted on the suction of a pump, operation of the valve should cause the pump motor to trip so that the pump does not overheat and ignite the leak.

The closure of an EIV is not instantaneous. An electrically operated valve typically takes about 1 min to close, a pneumatically operated ball valve somewhat less and a pneumatically operated gate valve somewhat more.

In some cases, an automatic control valve is used for emergency isolation. Such a valve is not an ideal isolation valve, because a characterized valve often does not give a tight shut-off, especially after a period of operation. But where a control valve is installed, it may be difficult to justify a separate emergency isolation valve. If a control valve is used for this purpose, there should be a separate manual control for isolation; the manual mode of the controller should not be used.

EIVs have not been widely used on compressors, but their installation on a new compressor plant has been described by Kletz. He makes the point that, since the valves are very large and are motorized, they are useful for plant operation as well as for emergencies, and this makes their installation easier to justify.

The Flixborough disaster involved the escape of large quantities of superheated flammable liquid from a train of high inventory reactors in series. It has been suggested that it would have been desirable to have an emergency isolation valve between each reactor. Conversely, it has also been argued that the probability of an escape from a pipe between two reactors in the original, as opposed to the modified, plant was remote and that the introduction of emergency isolation valves might have increased rather than decreased the hazard; the latter is probably the more widely held view.

EIVs may be used to prevent low temperature fluids getting into mild steel plant and causing low temperature embrittlement, but in general where this hazard exists it is

better to use materials which can withstand the lower temperatures.

The most positive method of ensuring isolation of the bottom offtake from a storage vessel is to have a single offtake pipe with an EIV on it and with all other devices such as sample points or drain points downstream of this.

Self-closing valves using the dead-man's handle principle may be used for drains, but they are liable to be wired open by operators. Drain points which are required only for maintenance should be blanked off.

With regard to the type of valve used as an emergency isolation valve, relevant features are the torque required to operate it, the propensity to trap liquid and the leak tightness. Valves should be provided with power operated actuators, but should be capable of being operated manually. Valves which do not trap liquid include globe, ball and high pressure butterfly types. Leak-tightness cannot be assumed in an emergency isolation valve and the pipework arrangements should be such that positive isolation can be effected by methods such as double block and bleed systems or slip plates.

EIVs with potential exposure to flammables, and hence fire, should be fire resistant or should have fire protection in the form of fire shields and insulation or water deluge.

EIVs are also installed on pipelines as described in Chapter 23.

EIVs are important components of the pressure system. They should be included in the pressure system register and should be regularly tested and maintained.

12.7.13 Valve interlocks

In some cases, it is critical that operations in a pressure system take place in a specified sequence. This applies particularly to the opening and closing of valves. The control of such operations may be effected using interlocks. This topic is treated in Chapter 13, but it is convenient here to consider the more specialized matter of mechanical interlocks, particularly for valves.

Some principal forms of mechanical interlock are those used for (1) supply, (2) access and (3) exchange. In supply there is a choice between two mutually exclusive conditions. An example might be where two different fluids may be admitted to a system, but where only one is to be admitted at a time. One interlock system that can ensure this is to fit each of the two valves with a single lock and to provide a single key. The two states of the lock are (1) switch on with the key turned and trapped in the lock and (2) switch off with the key removable. When the key is turned and trapped the valve is closed and when it is removed the valve is open. Another example might be two power supplies that are configured in parallel but only one of which should be connected at a given time.

With regard to access, there is to be no access unless there is a safe condition. The safe condition generally depends on the isolation of a power supply or other source of energy or pressure. One interlock system that can ensure this is to fit both the access point and the power supply point each with a lock and to provide a single key. The basic principle is similar to that in the case of the two-valve system just described.

An alternative method, which is applicable to the systems just described but comes into its own particularly in more complex systems, is exchange. Some interlock systems based on key exchange may be illustrated by reference

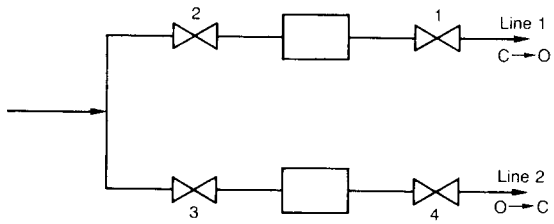


Figure 12.10 *Valve system controlled by key interlocks. C, closed; O, open*

to the system shown in Figure 12.10 in which there are two lines, only one of which is operational at a given time.

The particular interlock system to be used for such a system will depend on whether it is critical that one line always be open or that one line always be closed. It is the first case which is considered here for illustrative purposes. One interlock system is: to fit each of the four valves with a single lock, valves 1 and 2 being fitted by key type A, and valves 3 and 4 by key type B such that when a key is turned and trapped the valve is locked and when the key is removed the valve is open; to provide two keys of each type, A and B; and to provide also a key exchange box with four locks which contains at any one time the pair of keys of one type such that the pair of keys in residence (say type B) are removable only when the pair of keys of the other type (A) are inserted, turned and trapped. For the case where the initial state is line 1 closed and line 2 open and the system is to be moved under interlock to the final state of line 1 open and line 2 closed, the procedure is to open valves 1 and 2, remove the two A keys, insert, turn and trap them in their locks in the key exchange, thus allowing the B keys to be removed from the exchange and inserted, turned and trapped in valves 3 and 4, thus closing it. The sequence is then as follows:

	Initial state		*Final state*	
	Key	*Valve*	*Key*	*Valve*
Key exchange	B, B	–	A, A	–
Valve 1	A	Closed	–	Open
Valve 2	A	Closed	–	Open
Valve 3	–	Open	B	Closed
Valve 4	–	Open	B	Closed

Another interlock system applicable to the same valve system is as follows. Each of the four valves is fitted with a double lock with two different keys such that when the first key is turned and trapped the valve is open and the second key is removable, and when the second key is turned and trapped the valve is closed and the first key is removable. Thus, for valve 1 the first key might be A and the second B. Five keys are used for the four valves. The keys overlap around the system so that for valve 2 the two keys are B and C, for valve 3 keys C and D, and for valve 4 keys D and E; key A would then be held in the key box. For the case where the initial state is line 1 closed and line 2 open with keys B and C turned and trapped to hold closed valves 1 and 2, respectively, with keys D and E turned and trapped to hold open valves 3 and 4, respectively, and with key A in the key box, and the system is to be moved under interlock to the final

state of line 1 open and line 2 closed, the procedure is to insert, turn and trap key A in valve 1, thus opening it; this allows key B to be removed and inserted, turned and trapped in valve 2, thus opening it; this allows key C to be removed and inserted, turned and trapped in valve 3, thus closing it; this allows key D to be removed and inserted, turned and trapped in valve 4, thus closing it; and this allows key E to be removed and returned to the key box. The sequence is then as follows:

	Initial state		*Final state*	
	Key	*Valve*	*Key*	*Valve*
Key exchange	A	–	E	–
Valve 1	B	Closed	A	Open
Valve 2	C	Closed	B	Open
Valve 3	D	Open	C	Closed
Valve 4	E	Open	D	Closed

12.7.14 Fluid transients

There are a number of flow phenomena which can constitute a threat to the piping system. They include various forms of hammer, two-phase flow, and geysering. Some of these fluid transients are referred to in codes such as ASME B31.3: 1990 and API RP 521: 1990.

The best known of the hammer phenomena is water hammer, which occurs when the closure of a valve at the end of a pipe is too rapid. Steam hammer is another rather similar effect in high pressure steam mains. Steam flow may also accelerate condensate causing another hammer phenomenon which is referred to here as 'condensate hammer'.

The terminology used to describe these effects reflects the fact that, in many cases, the fluids concerned are water and/or steam, but similar effects can occur with other substances. Thus, for example, water hammer may more generally be termed 'hammerblow'. Another form of hammer which occurs when an NRV is slow to close, so that a return velocity builds up and the fluid movement is then arrested. It is referred to here as 'reverse flow hammer'.

12.7.15 Water hammer

If a valve on a liquid pipeline is closed quickly, a large change in momentum of the liquid column occurs in a short period of time and a large force is exerted on the valve. This is known as 'water hammer' and it can have a very destructive effect, resulting in the shattering of the valve and/or the line.

Accounts of water hammer are given in *Hydraulics* (Lewitt, 1952), *Hydraulic Transients* (Streeter and Wylie, 1967), *Analysis of Surge* (Pickford, 1969), *Hydraulic Analysis of Unsteady State Flow in Pipe Networks* (Q.A. Fox, 1977) and by Hayashi and Ransford (1960), Streeter (1964), Pearsall (1965–66), Ludwig and Ruiterman (1974), Ardron, Baum and Lee (1977), Kremers (1983) and D. Clarke (1988a,b).

Following Lewitt (1952), a simple treatment of hammer blow in a pipelines is as follows. Consider the pipeline system shown in Figure 12.11. If the valve at A is closed suddenly, there will be a rapid rise in pressure at this point due to the change in momentum of the column of liquid in the pipe. This sudden pressure rise at A causes a pressure wave

Figure 12.11 *Simple pipeline system*

to pass back down the pipe to B at the velocity of sound in the liquid. When this pressure wave reaches B, the liquid in the pipe surges back in the direction of B and causes the pressure at A to fall. The time for this to happen is

$$t = \frac{l}{u_s} \qquad [12.7.4]$$

where l is the length of column of liquid, t is the time for the pressure wave to travel the length of the column of liquid, and u_s is the velocity of sound in the liquid. For any closure time less than this the pressure at A has its maximum value. Thereafter, the pressure at A oscillates as the pressure waves pass back and forth between A and B, the oscillation being damped by friction in the pipe.

For an inelastic pipe, the pressure on the valve may be obtained by equating the loss of kinetic energy of the liquid to the gain in the strain energy of the liquid. The latter is

$$W = \frac{1}{2}PV \qquad [12.7.5]$$

where P is the pressure of the liquid, V is the volume of the liquid, and W is the strain energy of the liquid.

The bulk modulus K of the liquid is defined as:

$$K = \frac{P}{(\mathrm{d}V/V)} \qquad [12.7.6]$$

Hence:

$$W = \frac{1}{2}\frac{P^2V}{K} \qquad [12.7.7]$$

Then, equating the kinetic energy loss to the strain energy gain for a differential element:

$$\frac{\rho a\,\mathrm{d}l}{2}u^2 = \frac{1}{2}\frac{P^2}{K}a\,\mathrm{d}l \qquad [12.7.8]$$

$$P = u(K\rho)^{1/2} \qquad [12.7.9]$$

$$\frac{\rho a\,\mathrm{d}l}{2}u^2 = \frac{1}{2}\frac{P^2}{K}a\,\mathrm{d}l + \left(\frac{1}{2}\frac{\sigma_1^2}{E} + \frac{1}{2}\frac{\sigma_2^2}{E} - \frac{\mu\sigma_1\sigma_2}{E}\right)a\,\mathrm{d}l \qquad [12.7.10]$$

with

$$\sigma_1 = \frac{Pr}{2h} \qquad [12.7.11]$$

$$\sigma_2 = \frac{Pr}{h} \qquad [12.7.12]$$

where E is the elastic modulus of the pipe, h is the thickness of the pipe wall, r is the radius of the pipe, μ is Poisson's ratio of the pipe, σ_1 is the longitudinal stress in the

pipe, and σ_2 is the circumferential stress in the pipe. Hence, assuming $\mu = 1/4$:

$$\frac{\rho u^2}{2} = \frac{1}{2}\frac{P^2}{K} + \frac{P^2 r}{Eh} \qquad [12.7.13]$$

$$P = u\left[\frac{\rho}{(1/K + 2r/Eh)}\right]^{1/2} \qquad [12.7.14]$$

Equation 12.7.14 reduces to Equation 12.7.9 as the elastic modulus E goes to infinity. A treatment of the case where the fluid flow is two-phase bubbly flow has been given by Karplus (1961).

A principal means of avoiding water hammer is the limitation of the rate of closure of the valve in question. There are available computer codes for the analysis of liquid flows in networks which can be used to analyse the system and determine the safe rate of closure of the valve.

12.7.16 Steam hammer

A treatment of transients in lines containing a steam–water mixture is given by Karplus (1961). An account of the occurrence in high pressure steam lines of a steam hammer effect on rapid closure of the stop valves to a steam turbine has been given by Crawford and Santos (1986). The closure time of the valves was very short, some 50–100 ms.

12.7.17 Condensate hammer

Another hammer effect can occur when steam is admitted, typically after a shut-down, into a line which contains condensate. The condensate can be propelled along the line with tremendous and destructive force.

This effect is treated in *Avoiding Water Hammer in Steam Systems* by Mortimer and Edwards (1988 HSE SIR 5). They distinguish three cases: (1) condensate driven by steam, (2) condensate drawn by vacuum and (3) flash steam effects. In the first case, condensate collects in a pipe or at fittings. When steam is admitted and flows past, at velocities which can be up to 40 m/s, waves are set up on the condensate surface and, in due course, slugs of condensate are formed. When a liquid slug encounters an obstruction, such as a sharp bend or valve, it strikes it with a 'hammer blow'. The second case is where the steam is admitted to a space where it is cooled in some way and condenses, drawing condensate at high speed towards the space. The third case occurs in a pipe containing superheated water which is let down in pressure so that some vaporizes as flash steam and drives the water away. The flash steam then condenses, creating a vacuum with the effects described in the second case. Frequently, the damage done is slight, but in some instances it is severe. It does not necessarily manifest itself at the point of hammer, but sometimes a metre or more away.

The principal measure taken to avoid condensate hammer is design to prevent the build-up of condensate. Provision of adequate fall in the pipe is one aspect, avoidance of fittings which collect condensate another and provision of means to remove condensate a third. Fittings such as globe valves and strainers are liable to collect condensate. With a globe valve, for example, the depth of water collecting behind the weir even when the valve is open can exceed half the pipe diameter. In this particular case, the problem can be avoided by mounting the valve with its spindle horizontal. Manual drain points may be appropriate at some locations, but automatic steam traps are the principal means of draining condensate.

There are also operational measures which can be taken. One is to drain condensate before starting up. Another is to exercise care in the admission of steam. It should be appreciated that condensate may form from leaks through closed steam valves, even several closed valves in series, while the pipe is shut-down.

12.7.18 Reverse flow hammer

Another form of hammer is that which occurs when an NRV does not close rapidly enough. This is referred to here as 'reverse flow hammer'. The effect is described by Ellis and Mualla (1986). If the closure of an NRV is not sufficiently rapid there is an appreciable 'reverse velocity', the arrest of which, when the valve does close, gives rise to a high pressure transient on one side of the valve and a low pressure one on the other. Incorrect selection of NRVs has for a long time been a source of troublesome pressure transients. In order to make the correct choice, it may be necessary to conduct tests and to model valve behaviour. The trend is to present the valve characteristics as a plot of reverse velocity on closure vs the rate of velocity reversal. The lack of a standard definition of the latter has caused some variability in treatments.

12.7.19 Two-phase flow effects

Two-phase flow can often give rise to pressure oscilllations and surges. Another phenomenon associated with such flow is 'bowing', which occurs when a refrigerated liquid is introduced at such a rate that two-phase stratified flow occurs, with attendant large temperature differences.

12.7.20 Geysering

Geysering is a phenomenon which occurs when a liquid near its boiling point is handled in a vertical, or sometimes in an inclined, pipe. It involves a rapid evolution of vapour, expelling liquid from the pipe and causing a destructive pressure surge.

12.8 Heat Exchangers

Heat exchangers are components of importance in pressure systems. They include (1) vaporizers, (2) reboilers, (3) condensers, and (4) waste heat boilers, as well as heat exchangers on general heat interchange duties. The design of heat exchangers is dealt with in *Process Heat Transfer* (D.Q. Kern, 1950) and in *Process Heat Transfer* (Hewitt *et al.* 1993).

Relevant standards are BS 3274: 1960 *Tubular Heat Exchangers for General Purposes*, API Std 660: 1973 *Heat Exchangers for General Refinery Services* and the Tubular Exchangers Manufacturers Association (TEMA) *Standards of the Tubular Heat Exchangers Manufacturers Association* (n.d.). Until its withdrawal, heat exchangers were dealt with in the API *Guide for Inspection of Refinery Equipment*, Chapter 7, *Heat Exchangers, Condensers and Cooler Boxes*.

Some problems that occur in heat exchangers and which may affect safe operation are (1) fouling, (2) polymerization and solidification, (3) leakage, (4) tube vibration and (5) tube rupture.

12.8.1 Fouling

If fouling occurs in a heat exchanger, it may affect (1) heat transfer and (2) pressure drop. Reduction of heat transfer

capacity may be particularly serious if the heat exchanger is a cooler on a critical duty such as removal of heat from a reactor in which an exothermic reaction is carried out. Effects of increasing pressure drop which may be serious are reduction in the maximum flows which can be passed through the exchanger and reduction in the pressure drop across the control valve and hence deterioration in the tightness of control. In the extreme, fouling can result in complete blockage of the exchanger.

Fouling may be reduced by correct selection of tube and shell side fluids and by the use of appropriate fluid velocities. Thus, for example, D.Q. Kern (1950) gives separate tabulations of fouling factors for water velocities below and above 3 ft/s. An allowance may be made for fouling by the use of a fouling factor which is equivalent to a heat transfer coefficient. This may be a general value taken from the literature or a specific value determined on the plant.

Generally, the so-called 'fouling factor' measures all the deficiencies of the heat exchanger, not just fouling. Often these deficiencies are much more significant than fouling itself. Thus, for example, a symmetrical positioning of the inlet and outlet on a two-pass heat exchanger can cause bypassing of the tubes below and above the level of these connections and a consequent reduction in heat transfer. Or again, a vertical condenser tends to have an inferior performance if it is updraft rather than down-draft.

It is claimed, however, that it is possible by good design virtually to eliminate the features which tend to cause serious reductions in heat transfer. Detailed design aspects have been described by Gilmour (1965). He states that where heat transfer deficiencies do still occur, they are usually on the shell side.

The use of a large fouling factor is not necessarily conservative. It may give a degree of overdesign which results in higher than expected temperatures and greater corrosion or coke deposition in the equipment. An example is discussed by Small (1968).

The use of very compact equipment can give rise to fouling due to lack of turbulence. Gilmour quotes a case in which reboiler tubes were very tightly packed and tended to foul by polymerization with bridging of polymer between tubes. The original tubes were replaced by half the number of finned tubes so that turbulence was increased and satisfactory heat transfer restored. This point is clearly relevant to design for limitation of inventory.

Fouling can also occur due to operational factors such as stoppage of a pump, omission of a filter, transfer of debris from other equipment, and so on. If this can have a serious effect, it may be necessary to take appropriate precautions, but the incorporation of a fouling factor in the design is of little use in this situation.

12.8.2 Tube vibration

The use of high capacity, compact heat exchangers with long tubes and high fluid velocities has intensified the problem of tube vibration. Tube vibration can cause damage to the tubes themselves and possibly to the exchanger shell and its supports or to the pipework connected to it, can transmit destructive pressure fluctuations from the exchanger and can generate considerable noise. Vibration can be sufficiently severe to lead to shut-down with multiple tube failure within 1 or 2 days. Two such cases are quoted by Gainsboro (1968) and by Eilers and Small (1973).

A heat exchanger tube may be regarded as a beam clamped at both ends and with distributed load. For such a system the natural frequency f_n is:

$$f_n = k\frac{\pi}{l^2}\left(\frac{EI}{w}\right)^{1/2} \qquad [12.8.1]$$

with $k = 1.136$ and where E is the elastic modulus, I is the moment of inertia, l is the length of the beam, and w is the mass per unit length. In a more detailed treatment A.A. Thompson (1969) gives a value of the constant k for heat exchanger tubes in the range 0.781–1.125.

The tube may be excited to resonance by vortex shedding. The vortex shedding frequency f_v has been studied by Y.N. Chen (1968), who obtained for gases a correlation in terms of the Strouhal number S:

$$f_v = \frac{Su}{d} \qquad [12.8.2]$$

where d is the diameter of the tube and u is the fluid velocity (based on the minimum flow area between tubes of a row).

The Strouhal number was correlated by a relation of the following form:

$$S = f(x_l, x_t) \qquad [12.8.3]$$

where x_l is the longitudinal spacing ratio, and x_t is the transverse spacing ratio.

The problem of tube vibration in heat exchangers has been investigated by P.R. Owen (1965), Y.N. Chen (1968), Gainsboro (1968), A.A. Thompson (1969) and Eilers and Small (1973).

Also relevant is the acoustic frequency. The acoustic resonant frequency f_a in a cavity is

$$f_a = \frac{nc}{2z} \qquad [12.8.4]$$

where c is the velocity of sound, n is the wave mode (integer), and z is the characteristic dimension.

If the vortex shedding frequency approaches the acoustic resonant frequency, loud noise may be generated. Acoustic resonance in heat exchangers has been described by Barrington (1973). Resonance may be avoided by alteration of the parameters in Equations 12.8.1–12.8.4.

In one case quoted by Barrington, a heat exchanger with an operating weight of 125,000 lb suffered displacements of 1 mil (0.001 in.) at the anchor bolts with accelerations up to 175 ft/s. A force of 340 ton was applied to the foundations at a frequency of about 350 Hz. He found that few foundations can withstand such forces without damage. The monitoring of heat exchanger vibration is discussed in Chapter 19.

12.8.3 Tube rupture

In a heat exchanger with high pressure gas or vapour in the tubes and low pressure liquid in the shell, tube rupture can lead to overpressure of the shell. The need for protection of the heat exchanger shell is recognized in pressure vessel codes such as BS 5500 and the ASME *Boiler and Pressure Vessel Code*. The latter states: 'Heat exchangers and similar vessels shall be protected with a relieving device of sufficient capacity to avoid overpressure in the case of an internal failure'.

More specific guidelines are given in API RP 520: 1990. This recommends that it be assumed that the area available for flow of gas or vapour from the high pressure tube into the shell be taken as twice the cross-sectional area of the tube, which is the worst case for failure of a single tube.

The pressure rise in the shell caused by a tube rupture is not a simple matter, however. The problem has been investigated by Simpson (1972), who distinguished two effects: (1) local pressure rise at point of rupture and (2) overall peak pressure rise in shell. The time-scale of these two phenomena differs by an order of magnitude; the first occurs in about 1 ms, and the second in about 10 ms. But these times are very dependent on the precise conditions in the shell, particularly the amount of gas or vapour present initially. As little as 1% of inert gas in the shell can increase by a factor of 3 the time required to reach peak shell pressure.

Simpson presents a calculation of the bubble pressure created by the rupture in 1 ms of a tube at 10,000 psia. The peak bubble surface pressures reached at 1 tube diameter and 5 tube diameters from the rupture were about 900 and 550 psia, respectively. In other words, the peak bubble pressure was less than 10% of the tube pressure. The pressure experienced by the shell wall is the reflected pressure P_r:

$$P_r \approx 2P_i - P_0 \qquad [12.8.5]$$

where P_i is the incident pressure and P_0 is the initial liquid pressure. Here the effective incident pressure is that of the bubble surface. If the rupture time was halved, the peak bubble pressure was increased by about 50%.

Although the localized overpressure is less than the overall peak pressure rise in the shell which occurs later, the latter is normally catered for by a pressure relief device, while the former is not. The effect of local overpressure on the shell and its implications for the positioning of tubes relative to the shell should be considered as a separate matter. The pressure relief of heat exchangers is discussed in Section 12.12.

12.8.4 Waste heat boilers

Process heat recovery boilers, or waste heat boilers, are widely used, particularly on ethylene and ammonia plants and on sulfuric acid and nitric acid plants. This type of boiler has developed as a cross between a conventional shell-and-tube heat exchanger and a firetube boiler. Its original function was to cool high temperature process gas and, as a by-product, to generate low pressure steam. The steam generation aspect, however, has grown in importance and the operating conditions have become increasingly severe. Moreover, as with heat recovery schemes in general, the use of waste heat boilers increases the degree of interlinking of plant and its vulnerability to failure.

Waste heat boilers and their problems have been discussed by Streich and Feeley (1972). A comparison given by these authors of the typical process waste heat boiler with the traditional Scotch marine boiler is instructive:

Typical conditions	*Process waste heat boiler*	*Scotch boiler*
Heat load (BTU/ft^2 h)	11,000	15,000
Steam pressure (psig)	$\leq$2300	200–225

Waste heat boilers do not have a raw flame licking at the tube seats, but otherwise experience conditions at least as severe.

Firetube boilers tend to leak at the tube inlets and this problem occurs in waste heat boilers also. Tube size is a compromise between the conflicting requirements for low velocity at the high temperature inlet and high velocity at the low temperature outlet.

12.9 Fired Heaters and Furnaces

Fired heaters are another important component in pressure systems. They include pipe stills on crude oil units, furnaces on olefins plants, and heaters for reactors and for heat transfer media.

General treatments of fired heaters are given in *Safe Furnace Firing* by the American Oil Company (Amoco/3), *Handbook of Industrial Loss Prevention* by the Factory Mutual Engineering Corporation (FMEC, 1967), *Heaters for Chemical Reactors* by Lihou (IChemE 1975/61) and the *CCPS Engineering Design Guidelines* (1993/13).

Relevant codes include BS: 799: 1981– *Oil Burning Equipment* and 5410: 1976– *Code of Practice for Oil Firing*, and the British Gas (BG) *Code of Practice for Large Gas and Dual Fuel Burners* (the BG Burner Code) (1976/1). National Fire Protection Association (NFPA) codes include the NFPA 31, 85 and 86 series.

Selected references on furnaces, fired heaters and flare systems are given in Table 12.8.

Fired heaters are a prime source of hazards. These hazards are principally (1) explosion in firing space and (2) rupture of tubes. Explosion in the firing space occurs mainly either during lighting up or as the result of flame failure. Rupture of tubes is usually caused by loss of feed or by overheating. In addition, heaters are a source of ignition for escapes of flammable materials from other parts of the plant.

The elimination of hazards in fired heaters is a good illustration of the need for measures both in design and operation. The design aspects are considered here and the operating aspects in Chapter 20.

Many explosions in the firing space take place during start-up when an attempt is made to light a burner. The usual situation is that fuel leaks and forms a flammable atmosphere in the firing space while the plant is shut-down and an explosion occurs when an attempt is made to light a burner. There are a number of measures which should be taken to prevent this hazard. The most important is to eliminate the admission of unburnt fuel into the firing space. This is principally a matter of achieving a positive isolation on the main fuel feed pipe to the burner. The importance of this is strongly emphasized.

For isolation it is not sufficient to rely on a single valve. Use should be made either of double block and bleed valves or of slip plates. There are different views on which of these methods is preferable and in any case the choice is affected by the fuel. For gas, double block and bleed valves should be used and for oil either double block and bleed valves or slip plates.

Where oil is used, the configuration of the pipe between the shut-off valve and the burner should be such that oil does not flow from this section of pipe into the firing space after the valve has been shut. In addition, the entry of fuel from the main feed pipe during the few seconds while the burner is shutting down after flame failure or from the subsidiary feed pipe to the pilot burner should be avoided.

Table 12.8 *Selected references on furnaces, fired heaters and flare systems*

American Oil Co. (n.d./3, 9); ASME (Appendix 28 Heat Transfer, 1984/55,1985/56, 57, 1992 CSD-1); Griswold (1946); Thring (1952); Krebs (1962); Finnie (1963); Wimpress (1963); lichtenstein (1964); Charlton (1965); Runes and Kaminsky (1965, 1973); F.A. Williams (1965); Backensto, Prior and Porter (1966); Ellwood and Danatos (1966); FMEC (1967); Loftus, Schutt and Sarofim (1967); Maddock (1967); Lenoir (1969); C. Davies (1970); von Wiesenthal and Cooper (1970); Demarest (1971); Mack (1971, 1976); OIA (1971 Publ. 501); Siegel and Howell (1972); J. Chen and Maddock (1973); Fitzsimmons and Hancock (1973); R.D. Reed (1973); Ulrich (1973); Chambers and Potter (1974); Mol and Westenbrink (1974); Taube (1974); Fertilio and Princip (1975); IChemE (1975/61); Mitcalf (1975); Ashbaugh (1976); Coulter and Tuttle (1976); Krikke, Hoving and Smit (1976); Anon. (1977l); Hoffman (1977); Lihou (1977); Tuttle and Coulter (1977); Berman (1978); Hougland (1978); Jensen (1978); R. Kern (1978f); Ministry of Social Affairs (1979b); Goyal (1980); API (1981 Refinery Inspection Guide Ch. 9, 1986 Std 560, 1988 RP 530); Lovejoy and Clark (1983); Schillmoller and van den Bruck (1984); Gomes (1985); Institute of Materials (1985 B367); Kauffman (1987); TO. Gibson (1988); NFPA (1985 NFPA 85E, 1987 NFPA 85A, 85G, 1988 85F, 1989 NFPA 85B, 85D, 1990 NFPA 86,1991 NFPA 86C, 1992 NFPA 31, 54); Ghosh (1992); L. Thomas (1992)

Reformers
Francis (1964); Axelrod and Finneran (1966); Avery and Valentine (1968); Kratsios and Long (1968); Pennington (1968); Jacobowitz and Zeis (1969); Kobrin (1969); Bongiorno, Connor and Walton (1970); F.W.S. Jones (1970); Zeis and Heinz (1970); Holloway (1971); Nisbet (1971); Attebery and Thompson (1972); Salot (1972, 1975); Strashok and Unruh (1972); A.J.P. Tucker (1972); Fuchs (1974); Ruziska and Bagnoli (1974); Demarest (1975); Fuchs and Rubinstein (1975); van der Horst and Sloan (1975); E.R. Johnson (1975); Leyel (1975); Sterling and Moon (1975); Sparrow (1986)

Burners
British Gas (Appendix 27, 28); Anon. (1957–58); P.G. Atkinson, Grimsey and Hancock (1967); FMEC (1967); Gas Council (1969 GC166); Brook (1978); Elias (1978); J.A. Wagner (1979); Murphy (1988); NFPA (1992 NFPA 31, 52)
ANSI Z83; BS (Appendix 27 *Burners*)

Refractories
Chesters (1961, Institute of Materials 1974 B135); Burst and Spieckerman (1967); Crowley (1968); McGreavy and Newmann (1974)

Flare systems
Zink and Reed (n.d.); P.O. Miller, Hibshman and Connell (1958); Hajek and Ludwig (1960); Bluhm (1961, 1964b); Husa (1964); G.R. Kent (1964, 1968, 1972); Kevil (1967); P. Peterson (1967); Tan (1967a,b); Kilby (1968); R.D. Reed (1968,1972); Grumer *et al.* (1970 BM RI 7457); F.R. Steward (1970); Escudier (1972); Lauderback (1972); Seebold (1972a,b, 1984); Swithenbank (1972); Brzustowski (1973, 1976, 1977); Brzustowski and Sommer (1973); Peters (1973); H.M. Chief Alkali Inspector (1974 annual report); Kletz (1974b); Vanderlinde (1974); Brzustowski *et al.* (1975); Klooster *et al.* (1975); Ito and Sawada (1976); Bonham (1977); Jenkins, Kelly and Cobb (1977); Schmidt (1977a,b); R. Schwartz and Keller (1977); Straitz (1977); Straitz and O'Leary (1977); Straitz *et al.* (1977); Agar (1978); Bonilla (1978); McGffl and McGffl (1978); Anon. (1979 LPB 28, p. 97); Boeye (1979); Paruit and Kimmel (1979); Anon. (1980 LPB 31, p. 27); Oenbring and Sifferman (1980a,b); Kandell (1981); E.B. Harrison (1982); McMurray (1982); P.J. Turner and Chesters (1982); Anon. (1983n); G.D. Allen, Wey and Chan (1983); Beardall (1983); Blanken and Groefsma (1983); Chung-You Wu (1983); B.C. Davis (1983, 1985); Fumarola *et al.* (1983); Lutzow and Hemmer (1983); Max and Jones (1983); Romano (1983); Alcazar and Amillo (1984); Coulthard (1984); Vaughan (1984); Banerjee, Cheremisinoff and Cheremisinoff (1985); Boix (1985); Chunghu Tsai (1985); Cindric (1985a); Corbett (1985); de Faveri *et al.* (1985); Herbert and Rawlings (1985); Narasimhan (1986); Pohl *et al.* (1986); Swander and Potts (1986, 1989); British Gas (1987 Comm. 1349); D.K. Cook, Fairweather, Hammonds and Hughes (1987); D.K Cook, Fairweather, Hankinson and O'Brien (1987); Straitz (1987); Leite (1988, 1990); de Suva (1988); Tite, Greening and Sutton (1989); API (1990 RP 521); Crawley (1993 LPB 111); Niemeyer and Livingston (1993); Bryce and Fryer-Taylor (1994)

Explosions (*see* Table 17.1)

Before a burner is started up, the firing space should be purged with air. The atmosphere in the space should then be sampled to confirm that it is not flammable. The purging of the firing space is essential. It is emphasized, however, that it is in no way a substitute for elimination of leakage of fuel into this space.

Means for lighting a burner include a poker, a spark igniter, a permanent pilot burner and an interrupted pilot burner. An interrupted pilot burner is extinguished a few seconds after main flame ignition. The use of a poker is not a good method of ignition. An interrupted pilot burner may be more satisfactory than a permanent pilot burner, since the latter tends to go out.

The ignition period is a critical one. The approach adopted is illustrated by the procedures given in the BG *Burner Code*. The burner is started up on a start-gas flow which is less than the normal flow. The establishment of the start flame consists of two periods: an initial period of not more than 5 s in which ignition is checked and a second period of at least 5 s during which flame stability is checked.

It is essential that if the flame fails, the burner should be shut-down immediately. A flame failure detector is used to monitor the flame and to initiate the trip. Loss of combustion air also necessitates immediate shut-down. Methods of detecting this condition are measurement of static pressure or of air flow.

The sequence of operations for the start-up of a burner should be carefully specified. In particular, the following operations should be carried out in sequence and the start-up should not proceed unless this has been done: establishment of air flow; purging of firing space; testing of atmosphere in space; and establishment of flame. Some detailed start-up sequences are given in the BG *Burner Code* and by the FMEC (1967). It is necessary to ensure that any start-up sequence specified is rigidly adhered to. Generally, the reliability of execution of these sequences can be improved by the use of automatic operation or of interlocks.

Many cases of tube rupture in fired heaters occur because the flow of process fluid through the tubes either falls too low or ceases altogether. If this happens, it is essential for the flame to be extinguished immediately. It should be appreciated that in a furnace where at normal throughput the ratio of the heat required to vaporize liquid to that required to superheat vapour is high, a given reduction in feed flow can result in a disproportionate increase in outlet tube temperature. Overheating of the tubes is another cause of rupture. It is necessary, therefore, to have measurements of tube temperature.

Instrumentation should be provided to measure and control the main operating parameters and, if necessary, to trip the furnace. Measurements should normally include: fuel pressure and flow; combustion air flow and fuel/air ratio; combustion gas oxygen content; process fluid pressure, flow and outlet temperature; flame state; and tube temperatures. There should be appropriate alarms based on these measurements.

The fail-safe principle should be applied in the design of the control system. Thus there is frequently a control loop which manipulates the feed flow in order to control the temperature of the process fluid leaving the furnace. If the instrument measuring this outlet temperature fails, the control loop may increase the fuel flow, which is a hazardous condition. It is essential, therefore, that the measurement on which any alarm or trip is based be separate from that used for control.

There should be trip systems which shut off the fuel flow to the furnace and inject snuffing steam (1) if the electrical power fails, (2) if the fuel pressure and/or flow is low, (3) if the flame goes out, (4) if the combustion air pressure and/or flow is low, or (5) if the process fluid pressure and/or flow is low or its outlet temperature high.

The provision of automatic sequence controls or interlocks for burner start-up has already been mentioned. The safe operation of burners depends critically on the reliability of the instrumentation and it is essential for this to be high.

Difficulties are sometimes experienced with the flame failure device. One problem is instrument failure. Flame failure devices are available with some degree of self-checking. Another is sighting of a pilot burner flame instead of the main flame. If this situation might arise, the flame failure detector should be fitted in such a way that it cannot 'see' the pilot flame.

The foregoing indicates some of the general safety aspects of the design of fired heater systems, but it should be emphasized that this is a specialist matter.

12.10 Process Machinery

Process machines such as compressors and pumps are particularly important items in pressure systems. Not only are they themselves potential sources of loss of containment, but they also affect the rest of the plant by imposing pressure and/or flow fluctuations and by causing vibrations.

The size, complexity and severe operating conditions of many process machines create numerous problems. Much attention is devoted to critical machinery, however, as much for economic as for safety reasons. In consequence, the level of reliability attained is generally rather high. Nevertheless, a failure of a process machine can be serious.

An account of some of the problems associated with process machinery is given in *Safe Operation of Air, Ammonia and Ammonium Nitrate Plants* by the American Oil Company (Amoco/9). Selected references on process machinery are given in Table 12.9.

Table 12.9 *Selected references on process machinery*

ASME (Appendix 28 *Applied Mechanics, Design Engineering, Fluids Engineering*, 1981/85); ASTM (STP 231); IMechE (Appendix 28, 1987); Routh (1882, 1905); Riegel (1953); EEUA (1960 Doc. 15); Meyer (1961); Everett (1964); Axelrod, Daze and Wickham (1968); Sternlicht, Lewis and Rieger (1968); Blubaugh and Watts (1969); Scheel (1970); Tucker and Cline (1970, 1971); Carrier (1971); Perkins and Stuhlbarg (1971); Bultzo (1972); Weaver (1972); Abraham (1973); Dziewulski (1973); J.E. Ross (1973); Barnes (1974); Ryder (1975); API (1976 Refinery Inspection Code Ch. 10); HSE (1978b); Sohre (1977, 1979, 1981); C. Jackson (1976a,b, 1981); Bloch and Geitner (1983, 1990); Bloch (1988, 1989); IEE (1991/5); Oberg *et al.* (1992); Rutan (1993) BS (Appendix 27 *Machinery*), BS 5304: 1988; VDI 2224: 1988

Turbines, turbomachinery
Keith (1965); Shield (1967, 1973); Naughton (1968); Purcell (1968); Swearingen (1970, 1972); Farrow (1971); ASME (1972/28, 1977/189, 1982/43); H. Cohen, Rogers and Saravanamuttoo (1972); Wachel (1973); B. Turner (1974); Bloch (1976); IMechE (1976/29); Leonard (1976); Millar (1978); Simmons (1978); Athearn (1979); Bergmann and Mafi (1979); C. Jackson and Leader (1979); Molich (1980); Neerken (1980b); Fielding and Mondy (1981); Harman (1981); Nippes (1981); Sohre (1981); Nicholas (1983); L.L. Fisher and Feeney (1984); Turton (1984); Campagne (1985); Rail and Fromm (1986); API (1987 Std 612, 1988 Std 611, 1992 Std 616); Lake (1988); AGA (1989/13) BS 132: 1983, BS 3863: 1992

Compressors
American Oil Co. (n.d./9); Horlock (1958); Coopey (1961); Troyan (1961c); Younger and Ruiter (1961); Esplund and Schildwachter (1962); Borgmann (1963); Anon. (1964a); Chlumsy (1966); Bultzo (1968); Telesmanic (1968); Kauffmann (1969); Bresler (1970); R.N. Brown (1972, 1974); Hallock, Farber and Davis (1972); Mehta (1972); Dwyer (1973); D.F. Neale (1973, 1976); H.M. Davis (1974a,b); P. Lewis (1974); Bauermeister (1975); C. Jackson (1975,1978); Neerken (1975); Sayyed (1976, 1978); Bryson and Dickert (1977); Cordes (1977); IMechE (1977/34, 1989/108); Kusha (1977); W. E. Nelson (1977); Dimoplan (1978); Winters (1978); Matley and Chemical Engineering Staff (1979–); van Ormer (1979); Stokes (1979); Broekmate (1980); Haselden (1980); Burke (1982); AGA (1983/39, 1988/52, 58, 1989/12); G. Bowen (1984); Greene *et al.* (1985a); Zafar (1986); Ablitt (1987): EEMUA (1987 Publ. 152); Sandier and Luckiewicz (1987); ASME (1990 19.1, 1991 19.3); Nissler (1991); B.C. Price (1991); Bloch and Noack (1992); Hallam (1992); Livingstone (1993); O'Neill (1993)
Centrifugal compressors: Schildwachter (1961); Church (1962); Sedffle (1965–66); Hile (1967); Badger (1968); Chodnowsky (1968); Morrow (1968); Moschini and Schroeder (1968); Scheel (1968,1971); Zech (1968); Sohre

(1970, 1977); ASME (1971/25, 1976/36, 1984/46, 1990 19.1, 1991 B19.3); Burns (1971); H.M. Davis (1971); Dwyer (1971a,b, 1974); C.Jackson (1971b, 1975); D.LE. Jacobs (1971); D.F. Neale (1971); Rassman (1971); Schirm (1971); Stafford (1971); Wachel (1973); Cameron and Danowski (1974); B. Turner (1974); Lapina (1975, 1982); Strub and Matile (1975); Leonard (1976); Sayyed (1976,1985); Boyce (1978); Gupta and Jeffrey (1979); Rehrig (1981); H. Davis (1983); API (1988 Std 617)

Reciprocating compressors: Deminski and Hunter (1962); Deminski (1964a,b); Morain (1964); Chlumsy (1966); Scheel (1967a,b); Gallier (1968); F.G. Jones (1971); Bultzo (1972); Dziewulski (1973); Prentice, Smith and Virtue (1974); Traversari and Beni (1974); ASME (1975/33); Whittaker (1975); Barnes (1976); Messer (1979); Schiffhauer (1984); API (1986 Std 618); Dube, Eckhardt and Smalley (1991); WooUatt (1993) BS 7322: 1990

Rotary compressors: Scheel (1969b); van Ormer (1980); API (1990 Std 619); IMechE (1994/163) Compressor control: Claude (1959); Hagler (1960); R.N. Brown (1964); Daze (1965); Marton (1965); Hatton (1967); Magliozzi (1967); Gallier (1968); Labrow (1968); Spence (1972); Staroselsky and Carter (1990)

Fans

NRC (Appendix 28 *Fans and Blowers*); Woods Ltd (1960); Scheel (1969a); Pollak (1973); Eck (1974); IMechE (1974/8, 1975/24, 1977/34, 1984/78, 1990/119, 1993/ 151); Martz and Pfahler (1975); J.P. Lee and Chockshi (1978); Matley and Chemical Engineering Staff (1979); Summerell (1981); J.E. Thompson and Trickier (1983); Fringe and Kasthuri (1986); ASHRAE (1992 ASHRAE 87.1)

Pumps

ASME (Appendix 28 *Fluids Engineering*, 1991 B73.1, B73.2M); ASTM (STP 307, 408); IMechE (Appendix 28, 1974 Item 11,1975 Items 14, 24,1976 Item 25, 1977 Item 34); NRC (Appendix 28 *Pumps*); Church (1944); Hicks (1957, 1958); Stepanoff (1957); Minami *et al*. (1960); Doolin (1961, 1963, 1978, 1984, 1990); Korzuch (1961); Younger and Ruiter (1961); Troyan (1961c); Anon. (1962g); Niemkiewicz (1962); T.E. Johnson (1963); Pollak (1963); C. Jackson (1965, 1972a, 1973); J.K Jacobs (1965); Thurlow (1965, 1971); Addison (1966); Chapman and Holland (1966); Holland and Chapman (1966a,b); Hummer (1966); R. Montgomery (1967); I. Taylor (1967); EEUA (1968 Hndbk 26); Hernandez (1968); Rost and Visich (1969); Hattiangadi (1970b); Chemical Engineering (1971); Glikman (1971); R. Kern (1971); Knoll and Tinney (1971); J.A. Reynolds (1971); Stindt (1971); Anon. (1972h); H.E. Doyle (1972); D'Innocenzio (1972); Karassik (1972, 1977, 1982, 1993); Platt (1972); Ramsden (1972); C.A. Robertson (1972); M.G.Murray (1973); Simo (1973); Black *et al*. (1974); van Blarcom (1974, 1980); British Pump Manufacturers Association (1974); Hancock (1974); Neerken (1974, 1980a, 1987); Waring (1974); Yedidiah (1974); Buse (1975, 1985, 1992); Karassik and Krotsch (1975); Anon. (1976d); R. James (1976); Makay (1976); de Santis (1976); Bloch (1977a, 1978, 1980, 1982, 1983a, 1989); R.J. Meyer (1977); Rinard and Stone (1977); Sparks and Wachel (1977); W.H. James (1978); McLean (1982); Morlock (1978); Panesar (1978); Penney (1978); Tinney (1978); Tsai (1982); Anon. (1979 LPB 29, p. 139); Grohmann (1979); Henshaw (1979,1981); Lightle and Hohman (1979); Panesar (1979a); Poynton (1979); A.P. Smith (1979a,b); Webster (1979); Mattley and Chemical Engineering Staff (1979–); API (1980 Std 674, 676,1989 Std 610); IChemE (1980/121,1985/127); Krienberg (1980); Vetter and Hering (1980); Anon. (1981f); Bristol (1981); Ekstrum (1981); Eraser (1981); J.D. Johnson (1981); Lapp (1981); Mikasinovic and Tung (1981); W.V. Adams (1982); Hallam (1983); F.J. Hill (1983); R. King (1983); Krutzsch (1983); R.R. Ross (1983); Talwar (1983); Baker-Counsell (1984b); Dobrowolski (1984); Hornsby (1984); Vlaming (1984); Bloch and Johnson (1985); Cody, Vandell and Spratt (1985); Etheridge (1985); S. Hughes (1985, 1987); Lobanoff and Ross (1985); Nevffl (1985); Rattan and Pathak (1985); Lonel (1986); Karassik *et al*. (1986); Nasr (1986,1992); R. Edwards (1987); EEMUA (1987 Publ. 157); Reeves (1987); Sandier and Luckiewicz (1987); I. Taylor (1987); T. Martin (1988a,b, 1989a); Rendell (1988b); API (1990 Std 610); Dufour (1989); Garbers and Wasfi (1990); Gravenstine (1989); Giilich and Rosch (1989); Lahr (1989); Luetzow (1989); McCaul (1989); G. Parkinson and Johnson (1989); J.A. Reynolds (1989); H. Davis (1990); Doolin and Teasdale (1990); Flyght Pumps Ltd (1990); Mabe and Mulholland (1990); Anon. (1991i); C. Butcher (1991d); Doolin *et al*. (1991); Jaskiewicz (1991); Margus (1991); Newby and Forth (1991); Wild (1991); Hawks (1992); G. Parkinson and Ondrey (1992); Schiavello (1992); UL (1992 UL 51); Bitterman (1993); Blair (1993); Buck (1993); Chyuan-Cheng Chen (1993); Cleary (1993); J.R. Peterson and Davidse (1993); Vandell and Foerg (1993); Vetter *et al*. (1993); BS 4082: 1969–, BS 5257: 1975

Agitators

N.H. Parker (1960); Troyan (1961c); EEUA (1962 Hndbk 9); Penney (1970); Gates, Hicks and Dickey (1976); Hicks and Dickey (1976); R.S. Hill and Kime (1976); Ramsey and Zoller (1976); Ketron (1980)

Centrifuges

IChemE (1976/67, 1987/81); Crosby (1979); BS 767: 1983

Conveyors

EEUA (1965 Doc. 30); ASME (1990 B20.1-1990); BS 490: 1975–, BS 2890: 1989

Drives

NRC (Appendix 28 *Electric Motors*); Gillett (1960); H.H. Meyer (1961); Cunningham (1962); Lane and Holzbock (1962); Olson (1963, 1979); ASME (1966/122); Caplow (1967); Olson and McKelvy (1967); EEUA (1968 Hndbk 29); Roe (1969); Nailen (1970a,b, 1973a–c, 1974, 1975, 1978); E.F. Cooke (1971, 1973); P. Bell (1971b); Cates (1972); Hallock, Faber and Davis (1972); IEE (1972 Conf. Publ. 93); Platt (1972); Pritchett (1972); J.C. Moore (1975); Plappert (1975); Bloch (1977a); M.G. Murray (1977); Constance (1978); Albright (1979); Deutsch (1979); Fishel and Howe (1979); Kohn (1979b); Panesar (1979b); Basta (1980); Finn (1980); M.N. Kraus (1980); Pollard (1980); Anon. (1981e); IMechE (1981/55, 1983/ 69, 1985/85); Antony and Gajjar (1982); Doll (1982); Hartmann (1984); Long (1984); Beevers (1985b); API (1987 Std 541); Feldman (1987); Sandier and Luckiewicz (1987); EEMUA (1988 Publ. 132); I. Evans (1988); Ranade, Robert and Zapate-Suarez (1988); UL (1988 UL 1004, 1991 UL 1247); Anon. (1989a); Burton (1989); Mabe and Mulholland (1990); Basso (1992); Patzler (1992);Thibault (1993) BS (Appendix 27 *Electrical*)

Power transmission

North and Parr (1968); Anon. (1973h); Beard (1973); E.F. Cooke (1973); Dubner (1975); Finney (1973); Shipley (1973);

Thoma (1973); Bloch (1974); Kraemer (1974); Arndt and Kiddoo (1975); Calistrat (1975, 1978–); Roney (1975); Wattner (1976); Vanlaningham (1977); Coupland (1980); Renold Ltd (1980); J.D. Smith (1983); ASME (1985 B106.1M); C.M. Johnson (1985); Polk (1987); API (1988 Std 613, 1989 Std 677); Mancuso (1988); Timmerman (1989); Horrell, Neal and Needham (1991); IMechE (1993/153); Thibault (1993) ANSI B93 series, BS (Appendix 27 *Machinery*)

Bearings, seals, lubrication
ASME (Appendix 28 *Applied Mechanics, Fluids Engineering*); ASTM (STP 77, 84, 88, 437); IMechE (Appendix 28); Whalen (1963); Anon (1964d); Coopey (1965, 1967, 1969); EEUA (1965 Handbook 10, 1971 Handbook 27); LH. Price (1965); Koch (1966); Stock (1966); Lindsey (1967); C. Jackson (1968, 1970, 1972a, 1975); N.H. Miller (1968); Samans (1968); Samoiloff (1968); Furey (1969); Yaki and Carpenter (1970); Battilana (1971, 1989); C.P. Shaw (1971, 1977); E. Meyer (1972); Ruckstuhl (1972); EEMUA (1973 Publ. 115); Bushar (1973); Kellum (1973); M.J. Neale (1973); Rothman (1973); J.O.S. MacDonald (1973); Tinney, Knoll and Diehl (1973); B. Turner (1973); R.M. Austin and Nau (1974); Miannay (1974); Nisbet (1974); Anon. (1975k); Pattinson (1975); J. Wright (1975); Anon. (1976 LPB 9, p. 12); Cameron (1976); Fern and Nau (1976); Houghton (1976); M.G. Murray (1976); Ramsey and Zoller (1976); Summers-Smith and Livingstone (1976); Czichos (1978); Hills and Neely (1978); Hoyle (1978); Ramsden (1978); Barwell (1979); McNally (1979); J. Phillips (1979); Tipler (1979); Ummarino (1979); Hawk (1980); P.T. Jones (1980); Mendenhall (1980); Panesar (1980); P. Rogers (1980); Sangerhausen (1981); Warring (1981); Kerklo (1982); Lansdown (1982); Summers-Smith (1982, 1988); Anon. (1983g); W.V. Adams (1983, 1987); Bloch (1983b, 1989); Booser (1983); Cameron and McEttles (1983); Cleaver (1983); Higham (1983); M.H. Jones and Scott (1983); BOHS (1984 TG3); Fuller (1984); W.S. Robertson (1983); Dunhill (1984b); Wallis (1984); Wong and Ansley-Watson (1985); Baker-Counsell (1985h); Buse (1985); Wallace and David (1985); Flitney (1986,1987); Trade and Technical Press (1986); Anon. (1987e); Chynoweth (1987); Mattel, Botte and Regazzacci (1987); Abrams and Olson (1988); Ferland (1988); Fort and Jehl (1988); Newby (1988); API (1992 Std 614); Gregory (1993); Wells (1993) BS 1399: 1970

Vibration (*see also* Table 19.9)
ASME (Appendix 28 *Applied Mechanics, Design Engineering, Dynamic Systems and Control, Flow Induced Vibration and Noise, Fluids Engineering, Heat Transfer, Pressure Vessels and Piping*, 1988/197); Church (1963); Summers-Smith (1969); Ker Wilson (1970–71); R.H. Wallace (1970); Anon. (1973h); IMechE (1975/24, 1977/ 43, 1979/49, 1984/84, 1988/100, 106, 1991/131, 1992/145); J.M. Baker (1976); R.J. Meyer (1977); Sallenbach (1980); M.H. Jones and Scott (1983); J.D. Smith (1983)

Alignment and balancing
Blake (1967); C. Jackson (1971a,b, 1976a,b); Essinger (1973, 1974); M.G. Murray (1974, 1979); Ryman and Steenbergen (1976); Kirlan (1977); AGA (1985/44); Horrell (1991); IMechE (1991/128)

12.10.1 Process compressors

The process industries use both positive displacement and centrifugal compressors, some of which are very large machines with high throughputs and energy. An account of compressors is given in *Industrial Compressors* (O'Neffl, 1993).

The three principal types of compressor are centrifugal compressors, reciprocating compressors and screw compressors. Both the last two are positive displacement machines, but with reciprocating and rotary motions, respectively.

Reciprocating compressors have long been used for high pressure duties. There has been a trend, however, towards centrifugal compressors and, although these machines were originally used mainly for relatively low compressions, the pressures for which they are used have tended to increase. Some centrifugal compressors are now very big. A large ethylene plant may depend on single large compressors not only for main gas compression but also for refrigeration compression. Another trend is the increase in the application of screw compressors. The range of throughput and compression of these machines has extended so that they now constitute a significant third option.

Compressors are complex machines and their reliability is crucial. It is essential, therefore, to put much effort into the specification of the machine and to liaise with the manufacturer. It is equally necessary to maintain high standards in the operation of compressors. Some general features of compressors which are important are (1) lubrication, (2) protection, (3) isolation, (4) purging, (5) liquid slugs, (6) housekeeping and (7) observation.

The lubrication systems are an integral part of the compressor. It is essential for them to be well engineered and reliable if they are not to be a weak link.

Compressors are provided with protective devices such as pressure relief valves and pressure, temperature and vibration measuring instruments which activate alarms and trips. These are particularly important instruments and they should be reliable.

There need to be arrangements for the isolation of the compressor. Isolation may be by a single block valve and blind or by double block and bleed valves. It may also be appropriate to have an emergency isolation valve on the compressor suction.

Facilities should be provided to allow the compressor to be purged. A permanent purge connection is often considered undesirable because of the hazard of reverse flow from the compressor into the purge gas main. If a permanent connection is installed, it should be shut off when not in use by a blind.

A slug of liquid entering a compressor can be as destructive as a lump of metal. It is important, therefore, for the system to be designed so that this does not happen. It is also necessary before start-up to check that there is no liquid in the inlet or interstage piping, intercoolers, knock-out drums or pulsation bottles.

A high standard of housekeeping around compressors is very desirable. Leaks of oil or water should be eliminated and cleaned up promptly.

The process operators should, and usually do, learn to detect changes in external appearance, noise and vibration as well as in the pressure and temperature measurements. This monitoring by the operators often gives early detection of malfunction and allows corrective action to be taken in time. For large compressors, however, it is now usual to monitor condition and performance using instrumentation.

It is essential to have the highest standard of maintenance on compressors. The maintenance methods need to be thought out thoroughly and the maintenance personnel well trained in them. The conditions under which the maintenance is done should be suitable both with respect to weather and to cleanliness.

Prime movers for compressors include electric motors, turbines and gas engines.

12.10.2 Reciprocating compressors

Reciprocating compressors are utilized for high compressions. They have long been the machines used for compression to the high pressures required in ammonia plants and on offshore platforms. Accounts of reciprocating compressors are given by Whittaker (1975), Barnes (1976), Messer (1979) and Woollat (1993). Relevant standards are BS 7322: 1990 *Specification for the Design and Construction of Reciprocating Type Compressors for the Process Industry* and API Std 618: 1986 *Reciprocating Compressors for General Refinery Services*.

Reciprocating compressors can be provided with capacity control, or turndown, by the use of volume pockets and by drive speed control. Some principal malfunctions on reciprocating compressors are (1) valve leakage, (2) cylinder/piston scoring, (3) piston ring leakage, (4) gasket failure, (5) tail rod failure, and (6) vibration, as well as the general compressor failures such as those caused by liquid slugs or loss of lubricating oil or cooling water.

Leakage of the suction or discharge valves is one of the commonest failures. There are a number of symptoms of valve malfunction. The valve may become unusually hot, the cylinder capacity may fall, the discharge temperature may rise and the interstage pressures may be abnormal. The suction pressure may rise and the discharge pressure fall unless automatically controlled.

On some machines, there is nothing to prevent a suction valve being fitted on the discharge, or vice versa, by mistake. If this happens, it is possible to create very high pressures in the cylinder, particularly the high pressure cylinder, and so cause failure of the cylinder, the piston or the drive system. Preferably, this feature should be designed out. Where this is not the case, there should be procedures to minimize the probability of error.

The piston rod in high pressure cylinders is sometimes balanced by a tail rod on the other side of the piston. There have been some serious accidents in which the tail rod has broken off and flown out like a projectile. There should be a 'catcher' of sufficient strength to prevent escape of the tail rod if it does break. Tail rods are frequently surface hardened and it is important for them to be free of surface cracks. They should be regularly inspected. A tail rod failure allows the escape of high pressure gas.

The reciprocating movement of the piston inevitably causes some degree of vibration. This vibration may be transmitted to, and cause failures in, the process pipework. Small auxiliary piping on the machine tends to be particularly vulnerable to fracture from this vibration. It should be anchored to reduce vibration and inspected regularly.

Changes in the discharge temperature are often a sign of malfunction on a reciprocating compressor. High discharge temperature may be associated with valve failure, piston ring leakage, increased compression ratio, gas composition change or loss of cooling water.

On air compressors lubricated with oil, a high discharge temperature can result in an explosion. Such air compressor explosions, and the discharge temperature limits necessary to avoid them, are discussed in Chapter 17. Some compressors are required to produce compressed air which is free of oil. It is very desirable, for example, that instrument air be oil-free. Carbon ring compressors are often used for this purpose.

The reciprocating compressors were one of the potential sources of the gas leak investigated in the Piper Alpha Inquiry (Cullen, 1990). The questions of the tolerance of such machines to ingestion of liquid slugs and of the bolt tightening practices used were considered in evidence by Bett (1989).

12.10.3 Centrifugal compressors

Centrifugal compressors are the main workhorse machines in the process industries. They can be built for very high throughputs. Although the compression obtained has been lower than that given by reciprocating machines, the range of pressures attainable has gradually been extended. As mentioned, centrifugal compressors are used for the main duties on ethylene plants, both for process gas and for refrigeration.

Accounts of centrifugal compressors are given by Rehrig (1981), H. Davis (1983) and Sayyed (1985). A relevant standard is API Std 617: 1988 *Centrifugal Compressors for General Refinery Services*.

Centrifugal compressors have relatively limited turndown. On centrifugal compressors some of the main malfunctions are (1) rotor or shaft failure, (2) bearing failure, (3) vibration and (4) surge, as well as the general compressor failures mentioned earlier.

In some duties the rotor suffers relatively little attack, but rotors sometimes have flaws or suffer embrittlement or debris deposition. Rotors can become unbalanced or displaced axially. Shafts may contain flaws.

The various kinds of bearing failure are one of the commonest faults in centrifugal compressors. Shaft or casing misalignment and rotor imbalance are frequent causes of bearing failure.

Vibration can cause damage to parts of the compressor itself, such as the bearings. It may also be transmitted to and induce failure in the pipework.

Surging can cause serious damage on a centrifugal compressor. Surge is a condition which occurs when the machine is operating on too low a load, generally in the range 50–85% of normal capacity, which gives rise to violent rapid flow changes and vibration. It is usually prevented by automatic controls which detect the near-surge condition and bypass gas from the discharge to the suction of the compressor. A further discussion of surge control is given in Chapter 13.

12.10.4 Screw compressors

Screw compressors are positive displacement machines with rotary motion, and are also known as 'helical screw' or 'spiral lobe' compressors. They are relatively simple and low in capital cost. They have gradually extended their range of application to emerge as a third force in process industry compression. They are now in widespread use for lower compression and refrigeration duties.

Accounts of screw compressors are given by B.C. Price (1991) and Bloch and Noack (1992). A relevant standard is API Std 619: 1985 *Rotary Type Positive Displacement Compressors for General Refinery Services*.

The original screw compressors were oil-free, or dry, machines. They ran at high speed to minimize internal gas

bypassing and were very noisy. In the 1950s, oil-injected machines came in and found application in natural gas compression and refrigeration.

Capacity control on screw compressors is effected by the use of a slide valve which moves axially along the housing. They have good turndown, being able to operate at loads as low as 10% of the normal throughput. Another feature of screw compressors is that they can tolerate relatively large changes in suction pressure, a characteristic useful in refrigeration duties.

Screw compressors have the advantage over reciprocating compressors that they require no suction or discharge valves. By comparison with centrifugal compressors, the spares problem with screw compressors tends to be less severe. Since screw compressors are designed for oil-injection, they have some tolerance to a liquid slug, although continuous liquid slugging can cause problems.

A large proportion of the heat of compression in a screw compressor is absorbed by the oil. This characteristic may be advantageous if it is desirable to avoid high gas compression temperatures, as in cases where the gas may polymerize or explode if overheated.

12.10.5 Gas engines

Gas engines are used to drive compressors. Some principal failures which occur are explosions of (1) starting air line, (2) fuel line and (3) crankcase. A number of explosions have occurred in the starting line to gas engines. Generally, these have been the result of leakage from the power cylinder through a defective NRV. Preventive measures include regular inspection and maintenance of the NRV on the starting line, elimination of oil from this line and venting of the header when the engine is in normal operation.

When the engine is shut-down, it is desirable that the fuel be shut off also. If this is not done, fuel may collect in the engine and the exhaust system, and may explode when the engine is restarted. There have been a number of explosions of combustible mixtures of oil or gas and air in crankcases during operation. Crankcase explosions may be minimized by ventilating the crankcase or purging it with inert gas and fitting an explosion relief device. A further discussion of crankcase explosions is given in Chapter 17.

12.10.6 Process pumps

Most process pumps are centrifugal machines, although reciprocating machines are used in some cases. Where the application is severe and/or critical, a degree of redundancy may be provided, using one or more standby pumps or using several pumps operating at less than full capacity. Thus, for example, the equipment to perform the duty of a single pump may be one pump operating at 100% throughput and a similar pump on stand-by or two pumps each rated for 100% capacity, but both operating at 50% throughput. Diversity of the power supply may also be provided using as drives steam turbines as well as electric motors, thus reducing dependence on electrical power.

If a stand-by pump is provided, it is necessary to ensure that it can be started up rapidly and dependably. The reliability of the pump set can be seriously degraded by pump changeover failure. The arrangements for pump shut-down also need to be reliable. This is particularly the case where there is a potential weak point in the discharge piping such as a flexible hose at a loading facility.

As described earlier, it will often be appropriate to install an emergency isolation valve between a pump and its feed vessel. It is good practice to group together controls for both items.

12.10.7 Centrifugal pumps

The principal malfunctions on centrifugal process pumps are:

(1) bearing failure;
(2) gland/seal failure;
(3) maloperation damage
    (a) cavitation,
    (b) deadheading,
    (c) dry running.

The most common pump faults are failures of bearings or of glands or seals. A common cause of failure is shaft misalignment. Also, a bearing failure can induce a gland or seal failure. If seal failure is particularly undesirable, a type of pump may be used which has a more reliable sealing arrangement. Such pumps include:

(1) pumps with mechanical seals
    (a) single mechanical seals,
    (b) double mechanical seals;
(2) seal-less pumps.

The pump sealing arrangements should both minimize fugitive emissions and have a low probability of catastrophic failure. Gland seals and single mechanical seals leak to some degree. Leaks may be minimized by the use of double mechanical seals or of seal-less pumps. As a precaution against catastrophic failure, use may be made of a double mechanical seal with monitoring of the atmosphere between the two seals. Another arrangement with the same purpose is a single mechanical seal with a packing gland backup.

Seal-less pumps are also referred to as 'glandless pumps' or 'canned pumps'. In a canned pump, the impeller of the pump and the rotor of the motor are mounted on an integral shaft, the rotor and stator being encased, or canned, so that the process fluid can circulate in the space which is normally the air gap of the motor. The bearings are lubricated by the process fluid. Pumps with mechanical seals and seal-less pumps are less liable to leakage, but are also more expensive.

Pumps are particularly liable to be damaged by maloperation. Cavitation, deadheading and dry running can have destructive effects and failure can be catastrophic. Not infrequently, pumps are allowed to run whilst cavitating. Cavitation occurs if the liquid is close to its boiling point and involves incipient vaporization in the pump, the bubbles formed collapsing on the pump impeller due to the pressure induced condensation. This causes pitting and, eventually, more serious damage to the impeller, and can be very destructive. It is avoided by provision of adequate net positive suction head. In order to ensure this it is helpful to keep the suction lines to the pump short. Another measure which may be taken is the provision of a bypass.

Deadheading involves pumping against a closed outlet, or possibly a closed outlet with a closed inlet also. The pump may then generate enough heat and/or pressure to rupture. Cases have occurred of a runaway reaction in the pump or a reaction between the pump material and the fluid. Although avoidance of deadheading is principally an operations matter, there are countermeasures which can be taken in the design. One is a trip system, based on rise in

temperature or pressure in the pump. Another is a bypass line free of valves from the pump delivery to the feed tank, or 'kickback' line.

The provision of bypasses on centrifugal pumps is discussed by I. Taylor (1987). Apart from boiler feed-water pumps, centrifugal pumps have traditionally not been equipped with a bypass. Over the last 20 years, however, this has changed. It remains true that most centrifugal pumps do not need a bypass. In order to decide whether one is needed, it is necessary to establish the expected frequency and extent of low flow operation, including shut-off of a downstream control valve, and the extent of any hazard if failure occurs. Centrifugal pumps can generally tolerate '1-min' periods of low flow immediately after start-up. The cases where bypasses are required tend to be those involving pumps which are of large size, high horsepower and high head, and are in continuous low flow operation. The author gives some 10 reasons for installing a bypass, the two principal ones being to prevent excessive temperature rise and to avoid unstable flow conditions. For pump thermal control a bypass flow of 10% is generally sufficient.

Taylor discusses the net positive suction head (NPSH) required to prevent Cavitation. In the 1960s and the early 1970s a spate of problems occurred on high head and high horsepower pumps, involving excessive vibration and pulsation at low flows. Work by Minami *et al.* (1960) and others showed that, whereas traditionally a 3% reduction of first stage head had been taken as an indication of impairment of pump performance by cavitation due to lack of NPSH, at low flows incipient cavitation can occur even at a much higher suction head. In fact, the NSPH required to suppress 'low flow' cavitation in such cases could be two to five times as much as the conventional figure. Subsequently, Fraser (1981) presented a method of estimating the minimum continuous flow based on the suction specific speed index number N_{ss}.

Incorrect design of a bypass, however, can itself be a cause of failure at pumps. Taylor recommends that, with certain exceptions, an automatic bypass should branch off on each pump upstream of the first valve, whether this be an isolation valve, NRV or control valve. Whilst it is true that in many cases involving two motor driven pumps, a common bypass has often been satisfactory, there are two dangers. One is that if one pump stops or trips out and the other, on stand-by, cannot be started up, the bypass opens and connects the high pressure of the delivery side to the suction side. The other danger is that if both pumps are running but with one at a higher speed, perhaps because one is driven by a motor and the other by a steam turbine, the difference in speed may be sufficient to hold closed the NRV valve of the lower speed pump, so that it overheats.

Pumps are sometimes allowed to run completely dry, often due to loss of head in a feed tank. Under these conditions the pump can be wrecked very quickly. Pumps which are not operating can suffer damage due to vibration of the plant, which causes 'brinelling' at one particular point. Such pumps may be turned over periodically to prevent this.

12.10.8 Positive displacement pumps

Positive displacement pumps are less common in process plant than are centrifugal pumps, and, apart from metering applications, are used mainly for high pressure work. In particular, reciprocating pumps are used to obtain high pressures. The discharge side of a positive displacement pump requires protection against overpressure. The usual arrangement is the provision of a pressure relief valve with its discharge returned to the suction side.

12.11 Insulation

Another element of the pressure system on process plants is the insulation. Insulation is employed to control heat transfer both in normal operation and in fire conditions. It has more implications for safety than might at first appear. Accounts of insulation are given in *Thermal Insulation* (Malloy, 1969), in the *CCPS Engineering Design Guidelines* (1993/13) and by Britton (1991), Britton and Clem (1991), Irwin (1991a,b), McMarlin and Gerrish (1992), Reddi (1992) and Gamboa (1993).

There are two basic types of insulation: thermal insulation and fire insulation. There is potential for confusion in that many types of thermal insulation have fire-resistant properties. Thermal insulation is used to (1) reduce heat loss from plant operating at temperatures above ambient, (2) reduce heat gain from plant at temperatures below ambient, (3) protect personnel from hot or cold surfaces on the plant and (4) attenuate sound from the plant. Two particular reasons for reducing heat loss are to prevent (1) freezing of liquid and (2) condensation of vapour.

12.11.1 Safety aspects of insulation

Some of the principal safety aspects of insulation are (1) corrosion beneath insulation, (2) self-heating in insulation, (3) insulation against fire and (4) effect on the process of inadequacies, defects or failures of insulation. Corrosion beneath insulation is considered in Section 21.11.4, self-heating in insulation in Section 12.11.6, fire insulation in Section 12.11.7 and fire properties of thermal insulation in Section 12.11.8. The effects on process or storage of defects in insulation depend on the particular case, but may include hazards from freezing, condensation, rollover, etc.

12.11.2 Materials for thermal insulation

The thermal conductivity is by no means the sole criterion in selecting an insulation. Materials with similar thermal conductivities may differ widely in their other relevant properties. Categories of non-combustible insulation material are (1) calcium silicate, (2) expanded perlite, (3) expanded vermiculite, (4) mineral fibre, and (5) cellular glass.

Some properties of thermal insulation which are important in the present context, in addition to its thermal conductivity, are its characteristics in respect of fire resistance, liquid absorption, fabrication, durability and damage resistance. The liquid absorptivity and fire resistance of insulation are considered in Sections 12.11.3 and 12.11.8, respectively.

The insulation should provide complete cover of the areas of the equipment which it is intended to insulate. Properties which bear on this are dimensional stability and shrinkage. Furthermore, it should be sufficiently easy to fabricate that gaps do not occur as a result of fabrication difficulties. Insulation is often subject to conditions which lead to its being crushed or torn, damage from feet being quite common. Vibration may lead to degradation of short-fibre insulation.

12.11.3 Absorption of liquids in insulation

An important property of an insulation is the extent to which it retains liquid that it already contains or that leaks

into it. This property is relevant to the insulation in respect of its (1) thermal performance, (2) mechanical performance and (3) weight, and to (4) corrosion beneath the insulation and (5) self-heating in the insulation.

Water absorption is greatest for calcium silicate and least for cellular glass, whilst for the other types it is variable, depending in part on any added water repellent. Water may enter the insulation as rain or washing water or in other ways such as a steam leak from a trace heating system. Water present in insulation can cause a marked increase in the effective thermal conductivity of the latter, as spaces which should be filled with air become filled with water, with a thermal conductivity more than 20 times that of air. Water also has the potential to cause disruption of the insulation, a typical situation being that which occurs when water freezes to ice and then melts. Since some insulation materials can absorb twice their mass in liquid, water absorption can cause a significant increase in the weight of the insulated system.

Another effect of water is to cause external corrosion of the equipment beneath the insulation, as discussed in Section 12.11.4.

With some insulations the moisture can be driven out and thermal performance restored, but with others this is not so. Calcium silicate, which has a high propensity to absorb water, falls in this latter group.

Process liquids may enter from pipework as may heat transfer fluids. Possible sources of in-leak are flanges and drain and sample points. Some liquids react with the binder in the insulation and promote its disintegration. Flammable liquid entering insulation can give rise to self-heating, as described in Section 12.11.6.

12.11.4 External corrosion beneath insulation

Factors which determine the extent of external corrosion beneath insulation include (1) the insulation material, (2) the equipment material, (3) the equipment configuration, (4) the equipment coating, (5) the equipment stress, (6) the service temperature, (7) any temperature transients and (8) the climate and location.

One important factor governing external corrosion is the insulation material. An insulation which absorbs a large amount of water is likely to cause increased corrosion. One which contains chloride is liable to cause corrosion of stainless steel. The extent to which water is excluded by efficient cladding is another significant factor in external corrosion.

The material of construction of the equipment insulated is another factor. In particular, stainless steel is prone to corrosion by chloride in the insulation. A further factor is the equipment configuration. There are a number of equipment features where corrosion is especially likely to occur. On a vessel these might include nozzles, manholes, supports, brackets, lifting lugs and small bore and instrumentation piping. There are also features such as flanges and drain and sample points which may allow entry of liquids into the insulation. The extent of external corrosion under insulation also depends on the degree of protection afforded by any coating such as paint. External corrosion may be increased by residual stress in the equipment. This is a factor particularly in the stress corrosion cracking of stainless steel.

External corrosion under insulation occurs mainly on equipment operating in the range −5 to 105°C, and especially in the range 60–80°C. At lower temperatures the reaction rate is slower, whilst at higher temperatures water tends to be driven off. Much equipment is subject to temperature transients, which can increase external corrosion. These may be major changes occurring during the start-up and shut-down of high or low temperature plants, or they may take the form of temperature cycling. High plant temperatures can cause concentration of salts which then cause severe corrosion when rewetted.

Corrosion occurs on low temperature plant at thawing zones which tend to remain wet and corrosive.

External corrosion can be aggravated by the presence of salt, as at a coastal location, especially in combination with water precipitating, say, from cooling towers, or condensing, say, from low temperature plant. Pollack and Steely (1990) have described a case in which a large steel column had to be replaced due to corrosion underneath the insulation.

One of the proposals put to the Piper Alpha Inquiry (Cullen, 1990) was that gas risers on production platforms should be provided with passive fire protection in the form of lagging. However, the Inquiry heard evidence that there were also potential problems with this approach – a riser could be put at risk by corrosion beneath the lagging. It made no recommendation on the fire insulation of risers.

It is also convenient to mention at this point the tendency of some insulation to cause abrasive wear of equipment.

12.11.5 External corrosion beneath insulation: protective measures

Measures to prevent external corrosion under insulation relate broadly to (1) the insulation material, (2) the cladding, (3) the equipment coating and (4) the equipment design features. The insulation material should match the equipment to be insulated. For example, an insulation for stainless steel should contain minimal amounts of chloride. The insulation should be one with low water content and absorption capacity.

The insulation should be designed to exclude water. It should be provided with weatherproof cladding. This should permit water entering to be drained and water in the insulation to vaporize and exit when the insulation is heated. The equipment should be protected by coating with paint or other suitable covering.

The design should assist inspection for external corrosion. Inspection ports are available which are specifically designed for this purpose. With regard to abrasive wear of the equipment, there are available anti-abrasive coatings which can be used to reduce this.

12.11.6 Self-heating in insulation

Another insulation issue related to fire is self-heating in insulation soaked with a flammable liquid. Above a critical temperature, which depends on the liquid–substrate system and on the geometry, self-heating initiates and smouldering occurs, limited both by heat transfer from the combustion zone and mass transfer of oxygen into the zone. The explosive destruction of an ethylene oxide column at Antwerp in 1989 was found to be due to self-heating of a leak of the fluid into the insulation (Case History A122).

Accounts of self-heating in insulation are given by Gugan (1974a), Britton (1991) and Britton and Clem (1991). The latter authors discuss the spontaneous ignition temperature (SIT) of liquid in insulation. Values of the SIT range from above 180°C down to near ambient temperature.

Precautions against self-heating include (1) use of a non-porous insulation, (2) exclusion of flammable liquids, and (3) use of a geometry less favourable to its occurrence. One non-porous insulation is cellular glass. However, its fire resistance properties leave something to be desired. Measures for the exclusion of flammable liquids have been discussed in Section 12.11.3. Both self-heating in general and lagging fires in particular are discussed in more detail in Chapter 16.

12.11.7 Fire insulation

Fire insulation proper is provided on equipment which requires fire protection but not thermal insulation. For fire insulation use is made of material which is generally cementitious, such as vermiculite cement. A further discussion of fire insulation, including criteria and tests, is given in Chapter 16.

12.11.8 Fire performance of thermal insulation

On equipment which does require thermal insulation, fire protection may be provided by a fire resistant thermal insulation system. This phrasing is used advisedly, since the effectiveness of the protection is a function of the whole system rather than of the insulation alone.

From the fire protection viewpoint, the ideal thermal insulation is one which does not burn or melt and is non-absorbent. To the extent that it does undergo combustion, it should not give off toxic fumes. Some insulating materials such as polyisocyanurate foam are not suitable. The main categories of non-combustible insulation are listed in Section 12.11.2.

Standard tests of fire properties such as those for flame spread and smoke development are applicable to the insulation materials. There are also standard fire tests such as ASTM E-119 and other tests which seek to simulate more closely hydrocarbon fires. Tests for the insulation material itself and for the insulation system are discussed in the CCPS *Guidelines* and by Britton and Clem (1991). A review of insulation materials for fire protection has been given by Wright and Fryer (1982).

The insulation needs to be protected against the weather. Methods of weatherproofing include the use of caulking, of mastic or of metal jacketing. Metal jacketing is to be preferred. Stainless steel provides a quality jacket, with galvanized steel being a less expensive alternative. There is some experimental evidence of good fire performance of galvanized steel jackets, but it is uncertain how far this can be generalized. Aluminium jackets melt on exposure to fire, in some cases within minutes.

The jacket should have points through which any water entering can drain away and should allow for the egress of any water vaporized when the insulation is heated. In a fire the insulation system may be subject to quite severe conditions, including impingement by flame and/or water jets. These need to be borne in mind in the design.

Britton and Clem (1991) describe the measures used in Union Carbide for certain situations where fire insulation is regarded as particularly critical. One such case is fire insulation of equipment handling reactive chemicals. An example of such a chemical is acetylene. For such reactive chemicals a double layer of insulation is used with staggered joints. Stainless steel is specified for the metal jacketing.

12.11.9 Personnel protection by insulation

One function of thermal insulation is to prevent injury to personnel. Hazard exists not only on high temperature plants but also on those operating at low temperatures which can cause 'cold burns'. The usual method of protection is to make the insulation sufficiently thick to prevent injury. For high temperatures, a criterion commonly used is that the external surface of the insulation should not exceed 60°C. Britton and Clem (1991) discuss the effect on the outer surface temperature of the insulation of its emissivity and absorptivity. An alternative means of protecting personnel from hot or cold equipment is the use of guards to prevent access to the hazardous surface.

12.11.10 Design of insulation systems

As already emphasized, design must address the total insulation system rather than just the insulation itself. It needs to have regard to the several goals of thermal insulation, fire protection and personnel protection and to the avoidance of corrosion beneath the insulation, self-heating and hazardous effects on the process. It is likely to involve a number of trade-offs. Attention should be paid to any special situations. These include, as discussed above, the insulation of stainless steel equipment and of equipment handling reactive chemicals.

Some of the errors commonly made in insulation, not all in design, are rehearsed by Irwin (1991a,b). They include (1) using the wrong insulation material, (2) installing the wrong thickness, (3) struggling with difficult calculations, (4) specifying the wrong thickness for jacketing, (5) laying insulation over jacketing, (6) poor workmanship, (7) hiding damage and (8) no insulation at all.

12.12 Overpressure Protection

Pressure systems need to be provided with protection against failure, particularly from overpressure. Standards and codes which deal with overpressure include: BS 5500: 2003; the ASME *Boiler and Pressure Vessel Code* 2001; the ASME B31 *Code for Pressure Piping*, particularly B31.3: 2002 *Process Piping*; API RP 520: 2000 *Sizing, Selection, and Installation of Pressure-Relieving Devices in Refineries*; API RP 521: 1997 *Guide for Pressure-Relieving and Depressuring Systems*; and API Std 2000: 1998 *Venting Atmospheric and Low-Pressure Storage Tanks*.

Accounts of pressure relief include those given in *Relief Systems Handbook* (Parry, 1992) (the IChemE Relief Systems Guide), *Guidelines for Pressure Relief and Effluent Handling Systems*, (CCPS, 1998/nn) (the CCPS Guidelines for PRS), and by Isaacs (1971), Fitt (1974), Duxbury (1976), Crawley and Scott (1984), A. Moore (1984), Cunningham (1985), Tomfohrde (1985), Crooks (1989), Duckworth and McGregor (1989), and Parry (1989).

The overpressure protection considered here applies to situations in which the pressure rise is relatively gradual. Protection against explosion overpressure is treated in Chapter 17. A number of equations given in the standards and codes are quoted in the following sections. Particular symbols may have different meanings in different equations, but in all cases the symbols are fully defined with the equation and in the notation at the end of the chapter. Selected references on overpressure protection, pressure relief and blowdown are given in Table 12.10.

Table 12.10 *Selected references on overpressure protection, pressure relief and blowdown*

Overpressure protection
Sylvander and Katz (1948); C.G. Weber (1955); Conison (1960,1963); Block (1962); Jenett (1963a–c); Loudon (1963); Driskell (1964, 1976); Ruleo (1964); Rearick (1969); Warwick (1969); Hattiangadi (1970a); Heitner (1970); ICI/RoSPA (1970 IS/74); Wittig (1970); Isaacs (1971); Pilborough (1971, 1989); Fitt (1974, 1976b, 1983); Kletz (1974a,d,e, 1989); BCISC (1975/1); Whelan and Thomson (1975); Anon. (1976m); Duxbury (1976); Henderson and Kletz (1976); Huff (1977a, 1988); Jenkins, Kelly and Cobb (1977); Frankland (1978); Wia-Bu Cheng and Mah (1976); Richter (1978a,b); Sengupta and Staats (1978a,b); IMechE (1979, 1984); J.S. Parkinson (1979); Sallet (1979a); Anon. (1980 LPB 36, p. 1); Chambard (1980); IP (1980 Eur. MCSP Pt 2,1981 MCSP Pt 3,1987 MCSP Pt 9); D. Scott (1980,1980 LPB 34, 36); Gerardu (1981); P.L Jones (1981); Kauders (1980–1984); Chen-Hwa Chiu (1982); Doelp and Brian (1982); McKinley (1982); Uchiyama (1982); Badami (1983); IMechE (1984/ 81); Knox (1984); Middleton and Lloyd (1984); A. Moore (1984); Cunningham (1985); Francis and Shackleton (1985); Poole (1985); Tomfohrde (1985); Valdes and Svoboda (1985); Politz (1988); Crooks (1989); Duckworth and McGregor (1989); IChemE (1989/136); Parry (1989, 1992); LPGITA (1991 LPG Code Pt 1); Ridey (1991); Aarebrot and Svenes (1992); Prugh (1992b); Cassata, Dasgupta and Gandhi (1993); Nichols (1994); Schiappa and Winegardner (1994); Tanner (1994); CCPS (1998/nn); BS 5500: 2003

Fire relief
Fitt (1974); A.F. Roberts, Cutler and Billinge (1983); Grolmes and Epstein (1985); Moodie *et al.* (1988); Morris (1988b); Wilday (1988); Epstein, Fauske and Hauser (1989): Venart (1990b)

Containment
Bartknecht (1981a); Wilday (1991)

Particular equipment
Gas filled vessels: Heitner, Trautmanis and Morrissey (1983a,b)
Heat exchangers: Case (1970); P.M.M. Brown and France (1975); Sumaria *et al.* (1976); W.Y. Wong (1992a,b)
Storage vessels: Kutateladze (1972)
Offshore: Crawley and Scott (1984)

Pressure relief valves, liquid relief valves, relief pipework
NRC (Appendix 28 *Safety Relief Valves*); Burgoyne and Wilson (1957); Conison (1960); Missen (1962); Porter (1962); Boyle (1967); Rearick (1969); Hattiangadi (1970a); Wissmffler (1970); Klaassen (1971); K. Wood (1971); Anon. (1972k); G.F. Bright (1972); Beck and Raidl (1973); Bodurtha, Palmer and Walsh (1973); API (1974 *Refinery Inspection Guide* Ch. 16, 1984 Std 526, 1988- RP 520, 1990 RP 521,1991 Std 527); Forrester (1974); Kletz (1974a,d,e, 1985l, 1986a,g, 1987J, 1989a); Pasman, Groothuizen and de Gooijer (1974); Anon. (1975 LPB 6, p. 12); ASME (1975/ 130,1983/168); Chlorine Institute (1975 Pamphlet 41,1982 Pamphlet 39); Schampel and Steen (1975, 1976); Anon. (1976); Anon. (1976 LPB 10, p. 15); F.E. Anderson (1976); Anon. (1977 LPB 17, p. 5); R. Kern (1977f); D. Martin (1977); Welsh (1977); Frankland (1978); Sallet (1978, 1979a,b, 1990a–c); Sengupta and Staats (1978a,b); Bourdelon and Lai (1979); Coffman and Bernstein (1979); Ezekoye (1979); Haupt and Meyer (1979); Moody, Wheeler and Ward (1979); Sallet, Weske and Giihler (1979); Semprucci and Holbrook (1979); Strong and Baschiere (1979); Wheeler and Moody (1979); CGA (1980 S-l.l, S-1.3,1989 S-1.2); Copigneux (1980, 1982); Crozier (1980,1985); Dockendorff (1980); Mukerji (1980); Weighell (1980); O.J. Cox and Weirick (1981); Scully (1981); Aird (1982, 1983); van Boskirk (1982); AGA (1983/ 39, 1988/58); Heller (1983); Huff (1983); Papa (1983a,b, 1991); Bradford and Durrett (1984); Brahmbhatt (1984); J.A. Fuller (1984); S.F. Harrison (1984); Chester and Phillips (1985); Emerson (1985,1988); I.D. Pearce (1985); Sallett and Somers (1985); Anon. (1986t); Bayliss (1987); DIERS (1987); DnV (1987 RP C202); Maher *et al.* (1988); Chambers and Fisher (1989); Desaedeleer *et al.* (1989); Morley (1989a,b); W.W. Wong (1989); Anon. (1990 LPB 92, p. 1); Kast (1990 LPB 95); Gavrila and Sethi (1991); Glinos and Miers (1991); Ridey (1991); Zappe (1991); Coker (1992); Lai (1992); Leung (1992a); W.Y. Wong (1992a–c); Bravo and Beatty (1993); W.E. Nelson (1993); British Gas (1994 BGES/DAT44); Crombie and Green (1994); Hanks (1994); D.W. Thompson (1994); BS 1123: 1987–, BS 5500: 1991.
Relief pipework: Duxbury (1976); Friedel and Schmidt (1993); S.M. Hall (1993); Perbal (1993)

Bursting discs
CGA (S-3); Fire Metal Products Corp. (n.d.); Bonyun (1935, 1945); Creech (1941); Murphy (1944a,b); Bigham (1958); J.F.W. Brown (1958); Lowenstein (1958); Luker and Leibson (1959); Diss, Karam and Jones (1961); Franks (1961); Block (1962); Solter, Fike and Hansen (1963a,b); Ruleo (1964); liptak (1965); Myers and Wood (1965); Sestak (1965); L.E. Wood (1965); Boyle (1967); Alba (1970); C.R.N. Clark (1970); Harmon and Martin (1970); Kayser (1972); Brodie (1973); Huff (1973, 1977a); Anon. (1975 LPB 6, p. 12); Anon. (1976l); Zook (1976); Ganapathy (1976); Cockram (1977); Anon. (1978 LPB 23, p. 125); Fitzsimmons and Cockram (1979); Beese, Organ and Wade (1980); Hoffman, Hansen and Doelling (1980); L. Wood (1981); Anon. (1982 LPB 45, p. 1, 7); Falconer *et al.* (1982 LPB 45); L.R. Harris (1983a,b); Mathews (1983); Phadke (1983); British Gas (1984 TIN20); Prickett (1984); Watton and Brodie (1984); Zanetti (1984b); Beveridge (1985); Walker (1985); Anon. (1989 LPB 90, p. 30); Zappe (1991); Brazier (1993); Anon. (1994a) BS 2915: 1990

Fusible plugs
Warwick (1969)

Venting and blowdown
Rudinger (1959); API (1988- RP 520, 1990 RP 521); Grote (1967); Klaassen (1971); Craven (1972); Simon and Thomson (1972); Fitt (1974, 1976b); BCISC (1975/1); Wia-Bu Cheng and Mah (1976); Pilz (1977); von Boskirk (1987); Haque *et al.* (1990); Haque, Richardson and Savffle (1992); Haque et al. (1992); Perbal (1992); Mahgerefteh, Giri and Wong (1993); N.E. Stewart and McVey (1994)
Vents: Cindric (1985a,b); P. Watts (1985); Burgoyne (1986a); P.F. Thorne (1986)
Depressuring: Chiu (1982); Sonti (1984)

Relief disposal
Kneale (1984, 1989, 1984 LPB 59); Grossel (1986); DnV (1987 RP C202)

Trip systems
Kletz (1974a,d,e); Lawley and Kletz (1975)

12.12.1 Requirements for protection

The statutory requirements for protection of pressure vessels and the legislative background to these were outlined in Chapter 3. As described in Section 12.1, the principal legislation in the United Kingdom covering pressure systems is the Pressure Systems and Transportable Gas Containers Regulations 1989 (the Pressure Systems Regulations), with, for fixed plant, the associated code COP 37 Safety of Pressure Systems (HSE, 1990).

The requirement for protection is given in Regulation 4(5) which states 'The pressure system and transportable gas container shall be provided with such protective devices as may be necessary for preventing danger; and any such device designed to release contents shall do so safely, so far as is practicable.' It is also required by Regulations 14 and 15 that a permanent outlet to the atmosphere, or to a space at atmospheric pressure, be kept open and free of obstruction at all times.

It has been a requirement of the Factories Act 1961 in Sections 32, 35 and 36 that steam boilers and receivers and air receivers have a safety valve to prevent overpressure. These sections of the act were revoked by the Pressure Systems Regulations 1989.

Relevant to disposal is the legislation dealing with pollution. The Control of Pollution Act 1974 requires the use of best practicable means for preventing emission of noxious or offensive substances and for rendering harmless and inoffensive any which may be emitted. There is also the general duty to provide safe equipment, which is reinforced by the Health and Safety at Work, etc. Act 1974.

The statutory controls are not the only external influence to which industry is subject. Provision of protection similar to the statutory requirements is normally a condition of obtaining insurance for other vessels.

It is necessary to define both the conditions against which protection is required and the nature of the system to be protected. PD 5500: 2003 requires that every pressure vessel be protected from excessive pressure or vacuum. If the source of pressure or temperature, however, is external to the vessel and is controlled so that overpressure of the vessel cannot occur, then the standard does not require the use of a protective device. Thus, overpressure protection is not required, for example, if the source of pressure is a pump which has a maximum delivery pressure less than the design pressure of the vessel.

For a vessel that is subdivided, each compartment should be treated as a separate vessel and suitably connected to a protective device. On the other hand, PD 5500 states: 'Vessels connected together in a system by piping of adequate capacity, free from potential blockages and which does not contain any valve that can isolate any vessel may be considered as a system of vessels for the application of pressure relief.' The protective device should have adequate capacity to prevent overpressure in the face of failure of any heating coil or other similar element in the vessel.

The protective devices envisaged in the standard are primarily safety valves and bursting discs complying with BS 6759: 1984 and BS 2915: 1990, respectively, but it also allows other devices provided they are suitable and reliable. It requires the maintenance of a register of all protective devices fitted to the vessel. The standard states 'Where the total capacity of the devices necessary to protect an installation from overpressure requires appropriate account to be taken of operating and fault conditions, the register should also include a record of the relevant calculations.'

12.12.2 API RP521

Guidance on protection of plant against overpressure is given in API RP 521: 1997. The contents are (1) general, (2) causes of overpressure, (3) determination of individual relieving rates, (4) selection of disposal systems, (5) disposal systems, and (6) bibliography. The appendices are: A, determination of fire relief requirements; B, special system design considerations; C, sample calculations for sizing a flare stack; and D, typical details and sketches. This is supplemented by the information on the relief devices themselves given in API RP 520, Part I: 2000, and Part II: 1994.

12.12.3 IChemE Relief Systems Guide

Further guidance is available in the *Relief Systems Handbook* by Parry (1992) (IChemE *Relief Systems Guide*). The contents are (1) introduction, (2) relief devices, (3) determining the set pressure and bursting pressure, (4) total relief systems, (5) vacuum relief, (6) thermal relief, (7) fire relief, (8) reliability of relief systems, (9) performance of relief systems, (10) installation of relief devices, (11) operation and maintenance, (12) current and future developments and (13) concluding remarks. The Guide contains some 19 appendices covering the legislation and (1) causes of relief situations, (2) relief rates, (3) minimum discharge velocity for dispersion, (4) Mach number, (5) atmospheric dispersion from a relief, (6) heat radiation at ground level from an elevated flare, (7) steam supply for smokeless flare operation, (8) flare purge gas velocity, (9) knockout drum droplet drag coefficient, (10) ground flares, (11) elevated flares, (12) thermal relief rate, (13) classification of liquids for thermal relief, (14) reliability data and (15) discharge reaction force. The Guide gives a brief summary of eighteen pressure relief case histories, classifying them as (1) safety valve failures, (2) bursting disc failures or (3) failures of containment systems.

12.12.4 Sources of overpressure

API RP 521 gives detailed guidance on causes of overpressure. The principal events may be summarized as follows: (1) connection to a high pressure source, (2) disconnection from a low pressure sink, (3) increased heat input, (4) decreased heat output, (5) vapour evolution, (6) absorbent failure, (7) heat exchanger tube failure, (8) expansion of blocked-in liquid, (9) reverse flow, (10) fluid transients and (11) plant fire.

Connection to a high-pressure source can occur if a valve is opened in error. Likewise, loss of connection to a low-pressure sink can occur if a valve is erroneously closed.

Increased heat input can occur due to malfunction of heating equipment or to chemical reaction. A heat exchanger such as a reboiler when just cleaned may temporarily have a high heat transfer capacity.

Decreased heat output, or loss of cooling, can occur in numerous ways. Malfunction of cooling equipment such as a heat exchanger is an obvious case. Distillation columns particularly can lose cooling in a number of ways. In a single column, loss of cooling can occur not only due to malfunction of the condenser but also due to loss of reflux or of subcooled feed. Where there is a set of columns in series, loss of heat input to one column can cause overpressure of the next column, due to carry forward of light ends in the bottoms from the first column which then overload the second column.

Overpressure can be caused by admission of water or light hydrocarbons to hot oil resulting in rapid evolution of vapour. Failure to remove sufficient gas due to loss of flow of absorbent can also cause overpressure. Failure of a tube in a heat exchanger so that the low-pressure shell is exposed to the high-pressure tube fluid can cause overpressure. This has been discussed in Section 12.8. Overpressure can be caused by expansion of liquid in a section of line between two closed block valves.

A particular case of increased heat input is a fire on the plant. In this case the potential heat input is so great that it is accorded special treatment, as described in Section 12.14. Failure of a pressure raiser and reverse flow from the high-pressure discharge to the low-pressure suction can cause overpressure of the latter. Fluid transients, such as those described in Section 12.7, can be another source of overpressure.

Some of these events may themselves be caused by failure of a utility such as electrical power to equipment or cooling water, or other coolant, or by failure of air or electrical power to instruments. The actions of control loops and those of the process operator are further causes. API RP 521 gives a table (table 1) of possible utility failures and the equipment affected.

12.12.5 Identification of relief requirements

An account of the identification of the nature and magnitude of the sources of overpressure has been given by Fitt (1974), with emphasis on practical interpretation. The first step in dealing with hazards is to ensure that they have been fully identified. The overview of sources of overpressure presented in API RP 521: 1997 and summarized above provides an excellent starting point and 'check list' for the task of identifying potential overpressure scenarios. Hazard identification, which has been described in Chapter 8, is an essential part of the design of protection for pressure systems. The technique of hazard and operability (hazop) studies can be helpful in ensuring that all potential overpressure scenarios have been considered.

Once the hazards have been identified, it is appropriate to consider whether measures other than overpressure protection are more suitable. Some alternatives are to make the plant inherently safer by means such as increasing vessel strength or limiting the delivery pressure of pumps. It must be emphasized that typical process and safety controls (such a pressure or level alarms or trips), while reducing the probability of an overpressure scenario, are not sufficiently reliable to remove the need for overpressure protection by a pressure relief valve, a bursting disc or a device with equivalent reliability.

Full consideration should be given to the action of the process operator. He or she is an integral part of the hazard situation. It is usually reasonable to place some reliance on operator action in averting a hazard, but the extent of such reliance depends on such factors as ease of recognition of the existence of the hazard, instructions and training for dealing with it, and difficulty of and time available for this task. The possibility that the operator would do something positively harmful has to be allowed for, although this is less probable than that he will fail to take some beneficial action. Problems associated with action by the process operator are discussed in Chapter 14.

Some hazards may have such a low probability that they can be disregarded. The cut-off level is commonly determined by the consequences of a failure, which in turn depend on factors such as the number of people exposed to the hazard. Overpressure protection should be considered at an early stage in the design so that unnecessarily severe demands can be identified and averted, but the main work has to be done at a relatively late stage.

Pressure relief becomes necessary when plant conditions are abnormal. Thus, flow sheet quantities provide only a partial guide to the required relief capacities and conditions. Some cases discussed by Fitt to illustrate the practical application of pressure relief are (1) shut-down pumps and compressors, (2) pressure let-down, (3) continuous distillation columns, (4) isolable equipment, (5) low pressure storage tanks, (6) control loop failures, (7) power turbines and let-down engines, (8) heat exchanger tube bursts, and (9) batch operations.

For a pump discharging into a receiver, the pressure relief valve should pass the volume of fluid that the pump could deliver if the feed valve is open and the receiver discharge is blocked. While it is common to assume normal operating (i.e. flow sheet) suction conditions, some designers assume more conservative conditions, such as a suction pressure at alarm or trip value.

Failure of pressure let-down devices can cause a large and sudden rise in downstream pressure, particularly where a liquid line is blown down by gas. Therefore, consideration should always be given to making the downstream section capable of withstanding the upstream pressure. An alternative policy is to size the downstream pressure relief device to handle the combination of let-down valve and bypass valve both fully open. Neither of these valves should be oversized and bypasses should be avoided or limited in capacity (e.g. by a reduced trim or installation in series with a restriction orifice) wherever practicable.

On a continuous distillation column, overpressure may be created by an increase in heat input. Some causes of increased heat input include increase in temperature difference in the reboiler, loss of cooling, loss of reflux and loss of subcooled feed. Loss of cooling is often, but not always, the worst case. In some columns, a subcooled feed provides as much cooling as the condenser.

The case of a column with a subcooled feed also provides an illustration of the need to consider the action of the process operator. If there is a loss of reflux on the column, he may well shut off the feed while he tries to re-establish normal conditions. This then represents a worse case for pressure relief than loss of either reflux or feed alone.

Pressure relief should be provided between isolations if the equipment is subject to pressure from a source of high pressure or of process heat and, generally, if the equipment can be isolated when the plant is operating and it is in a fire zone. Relief need not be provided, however, between isolations if there is no such high pressure or process heat source and if either there is no significant fire risk or the equipment cannot be isolated while the plant is on line, there is adequate provision of vents and drains between the isolations, and operating and maintenance procedures ensure that the segment is drained and vented upon isolation. This philosophy applies to all fluids, including steam and water. It is particularly applicable to valved spare heat exchanger sets.

Low-pressure storage tanks are capable of withstanding only a very low pressure. It is important, therefore, to avoid exposing them to high pressure. The problem is discussed in Chapter 20 on plant operation and in Chapter 22 on storage.

Failure in a control loop may occur in the measuring element, in the controller, in the control valve or its actuator, in the transmission lines or by operator action. The possible failures and combinations of failure should be reviewed and the worst case considered. In evaluating the relief load upon control failure, a credible set of simultaneous occurrences must be selected. Is the upstream pressure at the normal operating, high-pressure alarm, or high-pressure trip value? Should the bypass be assumed fully or partially opened when the control failure occurs? In the design of new facilities, it is usually assumed that both the control valve and the bypass may be fully open, if this constitutes a worst case. It need not be assumed that all control valves on equipment will fail to danger simultaneously, but neither should it be assumed that all control loop actions will be favourable. In considering control loops, it should be assumed that flow may not be fully controlled by the control valve, either because the bypass is open or because the controller is on manual setting.

The system downstream of a power turbine or let-down engine is liable to be subjected to the upstream pressure. Such machines often have a low resistance to flow when stopped. Flow may also occur through an open bypass. The pressure relief valve on the downstream system should be sized to handle the maximum flow from the combination of let-down engine and open bypass. Sentinel 'relief valves' function merely as mechanical high-pressure alarms; they are not intended as, nor are they capable of serving as, a means of pressure relief.

For the bursting of a high-pressure tube in a heat exchanger, the pressure relief valve on the low-pressure side should be sized to handle the flow from twice the cross-sectional area of the tube. If the high-pressure fluid is gas or vapour and the low-pressure side contains liquid, particular attention must be given to the potential for a water-hammer effect as the compressible fluid contacts the incompressible fluid as it flows through the rupture. Pressure increase rates in the liquid-filled low-pressure side can be very high; for many such scenarios designers prefer the high response rate of a bursting disc over the relatively slow-opening pressure relief valve (IP, 2000). The internal failure of a heat exchanger may also bring a hot fluid into direct contact with a highly volatile one. Consideration should be given to the potential for a greatly increased rate of vaporization upon such direct contact.

Batch operations require special consideration, because the conditions change throughout the cycle.

12.13 Overpressure Protection: Pressure Relief Devices

12.13.1 Pressure relief valves

Valves for the relief of pressure are referred to by a number of names and there is no universally agreed terminology. Two names commonly used as generic terms are 'pressure relief valve' and 'safety valve'.

A set of definitions is given in the successive editions of API 520. These are very similar to those given in ASME documents, primarily PTC 25-2001. These documents use 'pressure relief valve' as the generic term. API RP 520: 2000 defines it as a pressure relief device designed to open and relieve excess pressure and to reclose and prevent further flow of fluid after normal conditions have been restored. RP 520 proceeds to make the following distinctions. A 'relief valve' is a spring-loaded pressure relief valve actuated by the static pressure upstream of the valve. It opens normally in proportion to the increase in pressure over the opening pressure. It is used mainly for incompressible fluids. A 'safety valve' is a spring-loaded pressure relief valve actuated by the static pressure upstream of the valve and characterized by rapid opening or pop action. Normally it is used for compressible fluids. A 'safety relief valve' is a spring-loaded pressure relief valve that can be used as either a safety or a relief valve, depending on the application.

According to the IChemE *Relief Systems Guide*, the BSI has decided that the use of these definitions is impossible without ambiguity. The relevant standard, BS 6759: 1984, describes any mechanical valve designed for the automatic relief of pressure as a 'safety valve'. Similarly, BS 5500: 1990 refers to 'safety valve'. This term is also that adopted in the *Guide*. The generic term used here is 'pressure relief valve'.

BS 5500 requires that safety valves comply with BS 6759 *Safety Valves*. BS 6759 has three parts, the most relevant here being BS 6759: Part 3: 1984 *Specification for Safety Valves for Process Fluids*. Part 1: 1984 deals with steam and hot water and Part 2: 1984 with compressed air or inert gases. The installation is required to comply where appropriate with these standards and with BS 1123: 1961 *Safety Valves, Gauges and Other Safety Fittings for Air Receivers, and Compressed Air Installations*, which has one part, Part 1: 1987 *Code of Practice for Installation*.

There are a number of different types of pressure relief valve. Three broad categories of valve are (1) the conventional, direct-loaded valve, (2) the balanced valve, and (3) the pilot-operated, indirect-loaded valve.

A conventional pressure relief valve, the simplest type, is a spring-loaded valve. The pressure at which the valve relieves is affected by the back pressure.

The direct-loaded pressure relief valve has a number of variants. One is the assisted-opening valve, which has power-assisted opening. One use of this type of valve is to give depressurization down to a predetermined level. In a supplementary-loaded pressure relief valve, an external power source is used to impose an additional sealing force, which is released automatically when the set pressure is reached. This arrangement gives an improved degree of leak-tightness.

A third variant is the pilot-assisted valve, which is a different type from the pilot-operated valve. A pilot-assisted valve is a direct-loaded valve in which some three-quarters of the load is due to the spring and the rest to the pressure of the fluid from the pilot valve. When the set pressure is reached, the pilot opens and that part of the load contributed by it is removed.

A balanced pressure relief valve is one that incorporates means of minimizing the effect of back pressure on performance. With this type of valve the back pressure has little effect on the pressure at which the valve relieves. A balanced relief valve is used to accommodate the back pressure in a relief header.

The principal type of balanced pressure relief valve is the balanced bellows valve. The valve incorporates a bellows with an effective area equal to that of the valve seat so that it counteracts the effect of back pressure on the set pressure. The balanced pressure relief valve also comes in a number of variants. They include the balanced piston valve, in which the counteracting balance is effected by a piston, and the balanced bellows valve with auxiliary piston.

A pilot-operated, indirect-loaded pressure relief valve is one in which the main valve is combined with and controlled by an auxiliary direct-loaded pressure relief valve. The whole load on the main valve is provided by the fluid pressure from the pilot valve. When the set pressure is reached, the pilot valve opens and releases the loading pressure.

A pilot-operated pressure relief valve may be used where the margin between the operating and set pressures is narrow or where the set pressure is low. It is also used when discharging direct to atmosphere to ensure high discharge velocity and hence good jet mixing. The principal drawback of a pilot-operated pressure relief valve is that the small passages of the pilot valve are liable to become blocked if the process fluid is dirty, so that is suitable only for relatively clean duties.

Some pressure relief valves are illustrated in Figure 12.12. Figure 12.12(a) shows a conventional pressure relief valve and Figure 12.12(b) a pilot-operated pressure relief valve. Further accounts of pressure relief valves are given in API RP 520 and the IChemE *Guide*. Each of these documents includes diagrams of the various types.

12.13.2 Bursting discs

As for reclosing pressure relief devices, there is no universally agreed terminology for non-reclosing diaphragm-type devices. In API and ASME parlance, such devices are 'rupture disks'. According to the BSI, they are 'bursting discs', which is the term used here.

The conventional bursting disc is the simple disc illustrated in Figure 12.13(a). The disc has its dome with the direction of the bursting pressure. Conventional bursting discs tend to be very thin. Many are less than 0.05 mm in thickness.

A conventional bursting disc should be carefully installed. Manufacturers provide disc mountings that have a number of fool proofing features of which the following are typical. The ring holding the disc on the vent side is made thicker than the dome in order to protect the latter. The disc has an identification tag with full details stamped on. The tag neck serves to centre the disc in place and is notched on one side so that, if correctly installed, the disc does not seat properly and, if not readjusted, will vent at a low pressure. Discs with different pressures have pegs located at different points so that a disc for one pressure will not fit into a holder for a different pressure. Conventional bursting discs are normally made of metal, but graphite discs are also used.

Some other types of disc which are used in general applications include:

(1) composite slotted disc;
(2) reverse buckling disc.

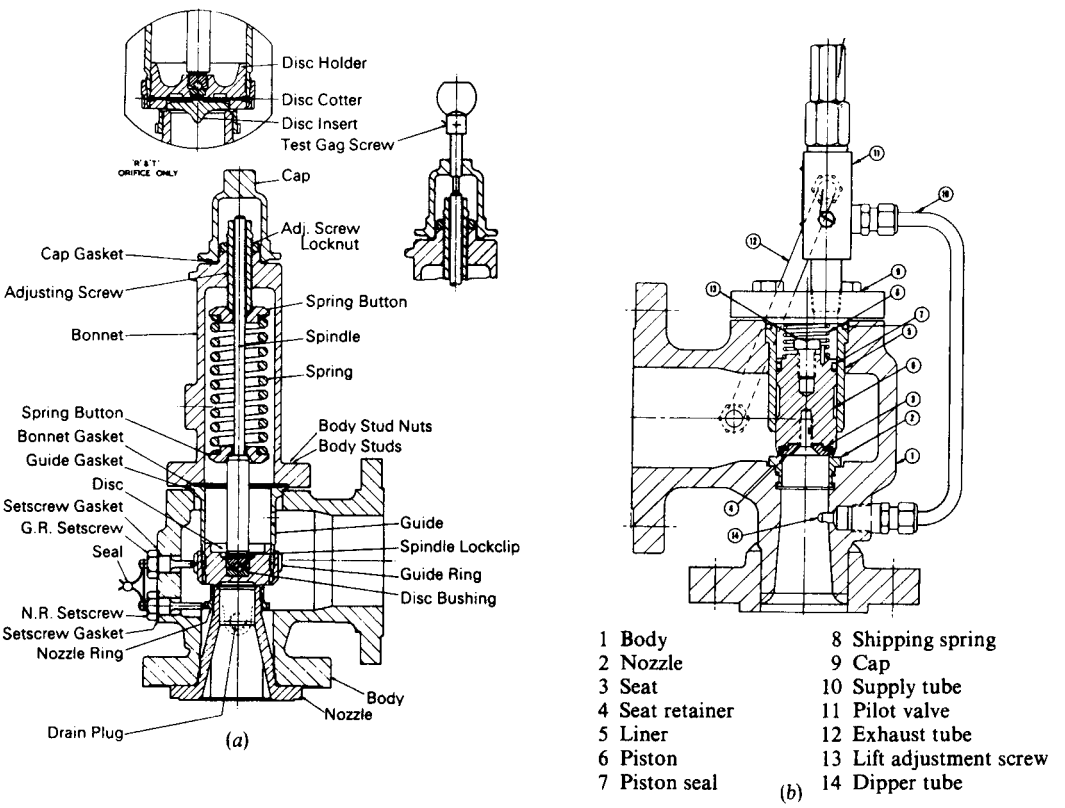


Figure 12.12 *Some typical pressure relief valves: (a) conventional pressure relief valve (Crosby Valve and Engineering Company Ltd); (b) pilot-operated relief valve (Anderson Greenwood Company)*

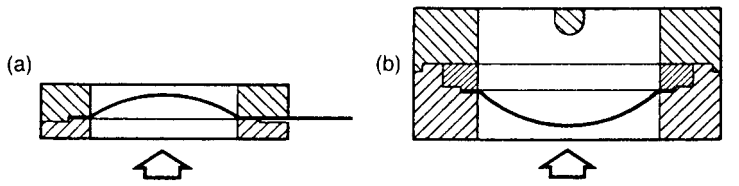


Figure 12.13 *Some typical bursting discs: (a) conventional bursting disc; and (b) reverse buckling bursting disc*

A composite slotted disc is a variation on the conventional disc. It consists of the main disc, which is slotted to burst at the rated pressure, and a protective membrane, in plastic or metal. The use of slotting allows the disc to be made of thicker material so that it is less liable to fatigue, while the use of the membrane gives protection against corrosion by the process fluid. There are also grooved discs, which are less deeply scored.

A reverse buckling disc has its dome against the direction of the bursting pressure, as shown in Figure 12.13(b). An account of reverse buckling discs is given by Watton and Brodie (1984), who list the following types:

(1) disc that, on reversal, bursts by being sheared either radially or circumferentially by serrated cutters mounted on the vent side;
(2) disc with preformed diametral grooves which, on reversal, opens at the grooves;
(3) disc that, on reversal, slips out of the holder;
(4) disc that, on reversal, shears around the dome.

The latter type is available in metal or graphite.

A reverse buckling disc is thicker than a conventional disc for the same duty. Watton and Brodie quote for 50 mm diameter discs rated for a burst pressure of 20 bar at 20°C thicknesses for stainless steel of 0.04 and 0.3 mm for conventional and reverse buckling discs, respectively. The latter is thus 7.5 times thicker than the former. The greater thickness of a reversed buckling disc makes it less liable to failure by fatigue, creep or corrosion.

The reversal time of a reverse buckling disc bursting as designed is very short. For 450 mm diameter discs, Watton and Brodie quote reversal times of 40 ms at 0.035 bar and 5 ms at 10 bar. In order for the disc to be cut by the knife there needs to be sufficient energy. The disc may fail to burst properly if the pressure rise is too slow. If the disc is damaged, even by a quite small dent, in the dome, it may 'roll through' and lie on the knife without being cut. The disc may then fail to burst at the design burst pressure. Furthermore, the knife blades generally must receive routine sharpening to maintain their cutting edge. For these reasons, designers have begun to prefer reverse-buckling discs equipped with preformed grooves.

A reverse-buckling disc should be carefully installed and securely mounted. The following fool proofing features are typically provided by the manufacturer. The disc is preassembled in the holder and pretorqued. The holder is provided with a pin to ensure that it is mounted the right way up. The screws in the holder are of a special type that can require the use of a special tool. Another device to prevent the holder being installed the wrong way up is the use of a J-bolt. Only when the bolt is in can the holder be centred and the flange bolts tightened. This arrangement is particularly useful where frequent cleaning of discs to remove blockages is necessary.

In addition to its use as the primary relief device a bursting disc may also be used mounted in series below a pressure relief valve to protect the latter from corrosion. This arrangement is suitable only if the bursting of the disc will not cause obstruction of the relief valve, and is effective only as long as there are no pinhole leaks in the disc. A pressure gauge is usually mounted on the space between the valve and the disc to detect any rise of pressure due to leakage. This 'tell-tale' gauge is one of several alternative installation details required by ASME Section VIII to ensure proper operation of a pressure relief valve/bursting disc series combination.

In a similar arrangement, a bursting disc is sometimes installed on the discharge side of a pressure relief valve to provide isolation between the valve and a collection system. In this arrangement, the burst pressure of the disc is typically a minimal value, as there is little to no static pressure at the discharge of the pressure relief valve.

There are also available disc assemblies based on the reverse buckling principle that give protection against both overpressure and underpressure, or vacuum. An arrangement described by Watton and Brodie consists of a reverse buckling metal disc perforated with a number of holes and sealed with a graphite membrane. If overpressure occurs, the metal disc and graphite membrane burst in the normal reverse buckling mode; in effect, the system has the characteristics of the metal disc. If underpressure occurs, the graphite membrane bursts, acting like a simple domed disc.

Bursting discs can be made in quite large diameters. Manufacturers are able to supply discs up to some 1.2 m. There are a number of other applications for which special bursting disc systems are available. They include (1) high temperature gas relief, (2) general liquid relief, (3) liquid relief, (4) pulsating liquid relief and (5) two-way relief.

12.13.3 Other relief devices

In addition to pressure relief valves and bursting discs, there are a number of other devices that may be used to relieve pressure. One such device is the buckling pin device (Taylor and Austin, 1992), which is classified by ASME Section VIII – along with the bursting disc – as a 'non-reclosing' pressure relief device. In such a device, sanctioned by the ASME under Code Cases 2091 and 2169, a pressure-containing member (e.g. a piston) is held closed against the system pressure by a thin, typically metal, pin. When installed, the pin is held in compression; it has been engineered (and tested) to fail when the force exerted upon it by the system pressure reaches a specified value. Following an overpressure event, such a device can be restored to its closed position by simply sliding the piston back against the process and inserting a new pin with the correct failure pressure. This convenience is touted relative to the

bursting disc, which requires separation of flanges to restore the process to operability following an overpressure event.

A variety of devices is used to provide overpressure protection of low-pressure and atmospheric storage tanks. The simplest of these devices is the atmospheric vent, typically a short pipe. An atmospheric vent is used on atmospheric storage tanks where there is minimal hazard from the ingress of air or egress of vapour.

On an atmospheric storage tank where the liquid held is more volatile, use is generally made of pressure-vacuum valves, which allow the tank to 'breathe'. Another device that can be used to provide pressure relief on low-pressure tanks is the liquid seal. Fire relief for an atmospheric storage tank may be provided in the form of a weak roof-to-shell seam, or rupture seam. For a pressure vessel a device that can provide fire relief is the fusible plug, a non-reclosing device actuated by high temperature.

12.14 Overpressure Protection: Relief System Design

12.14.1 Location of relief devices

In some cases, the provision of a pressure relief device on a particular kind of equipment is a legal or code requirement. An example is the requirement in the Factories Act 1961 for a pressure relief device on a steam boiler, steam receiver or air receiver. ASME Section VIII states: 'All pressure vessels . . . shall be provided with pressure relief devices in accordance with the requirements' of the subsequent approximately fifteen pages of the code. It must be noted directly that those pages include the statement that vessels connected together by adequate piping not containing isolation valves may be considered as one unit in evaluating the pressure relief requirements. But furthermore, in appendix M, it is noted that an isolation valve would be permissible in such a collection of vessels if, when isolating one component vessel from its protective relief device, the valve also isolated the vessel from all source of overpressure.

The only logical method for determining the required location of pressure relief devices is by starting with the identification of potential sources of overpressure. This is best done for each equipment item in the process unit. When this task has been completed, relief devices are then 'located' on equipment or associated piping in such a way that they will be accessible to provide relief for each potential overpressure scenario identified. The relief devices should be installed not simply to protect the particular points at which they are located, but to provide protection for all vulnerable points. Generally, a process vessel is provided with a pressure relief device, but, as described below, there are exceptions, as noted above for section VIII, and discussed further below for API RP 521.

Conditions for the protection of several components in a pressure system by a single pressure relief device are given in API RP 521: 1997 in appendix B. Four criteria are given. The first is that there should not exist any means for blocking in any of the components so protected. The other three criteria, given in detail in the code, have to do with the set pressure, the accumulation pressure and the operating pressure. RP 521 gives an example of a hydrotreater–reactor–recycle gas loop system that has a compressor and six process vessels/units but is protected by a single pressure relief device on the last vessel in the train, and lists the conditions for the acceptability of such protection in this case.

12.14.2 Selection of relief devices and systems

Guidance on the selection of the pressure relief devices to be used for a particular duty is given in the IChemE *Relief Systems Guide*. The first decision is whether to make use of a bursting disc, either alone or in combination with a pressure relief valve. It advises the use of a bursting disc if there is a completely free choice and if this is the more economic option or if either (1) the pressure rise is too rapid for a pressure relief valve or (2) the process fluid properties make a pressure relief valve unsuitable (toxicity, corrosiveness, blockage-forming components, aggressiveness).

If a system based on pressure relief valves alone is indicated, this may be a single valve or a set of multiple valves in parallel, depending on whether a single valve can provide the necessary capacity. The principal types of pressure relief valve are (1) conventional valves, (2) balanced valves, and (3) pilot-operated valves. The characteristics and applications of these different valves are described in Section 12.13.

One fundamental factor that affects the choice of relief valve type is the sink to which the valve will discharge. If this is a relief header and therefore exerts a back pressure, a balanced valve may be indicated. On the other hand, if discharge is to atmosphere, a pilot-operated valve may be selected for its high discharge velocity. Other factors that affect the choice are (1) the margin between operating and the set pressure, (2) the required speed of opening and (3) the required valve tightness. The first and third cases favour a pilot-operated valve.

If the discharge is into a header where the built-up back pressure is expected to exceed 10% of the gauge set pressure, a balanced pressure relief valve is needed, the workhorse valve being of the balanced bellows type. In this case, consideration should be given to the effects of bellows failure in altering the set pressure or leaking process fluid into the valve bonnet.

If the system is to incorporate a bursting disc, it is necessary to consider whether, following operation of the relief, (1) the loss of the plant contents is acceptable and (2) the plant can be shut-down to replace the disc. If neither is acceptable, a system incorporating a bursting disc in series with a pressure relief valve is indicated. If only the first is acceptable, use may be made of two bursting disc systems in parallel. If both are acceptable, a bursting disc system alone suffices. For a bursting disc system, use may be made of a single bursting disc or, if the process conditions are aggressive, two bursting discs in series. The latter case would require installation details as shown in Figure 12.14 and as described above in Section 12.13.2 for the series combination of a bursting disc and a pressure relief valve.

For a bursting disc/pressure relief valve system, the valve may have a bursting disc (1) upstream, (2) downstream, or (3) on both sides, depending on whether it is the process-side fluid, the discharge-side fluid or both fluids that are aggressive.

The principal types of bursting disc are (1) conventional domed disc, (2) reverse domed disc and (3) composite slotted disc; these are discussed in further detail in Section 12.13.2. Use of the conventional type is suitable provided that there is a wide margin, say 30%, between the operating and design pressures and that the pressure does not pulsate. If these conditions are not met, if a long life is required or if the disc is to be used in series with a safety valve, consideration should be given to the other two types.

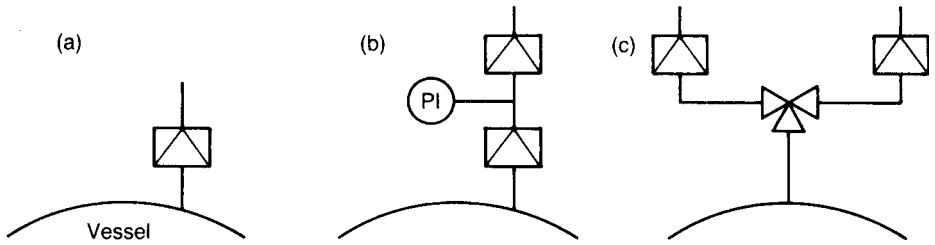


Figure 12.14 *Some typical bursting disc arrangements: (a) single bursting disc; (b) two bursting discs in series with pressure indicator (PI) on intermediate space; (c) two bursting discs in parallel with three-way valve to allow replacement without plant shut-down*

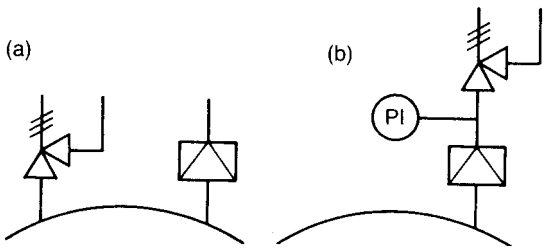


Figure 12.15 *Some typical pressure relief valve + burst-bursting disc arrangements: (a) pressure relief valve and bursting disc in parallel; and (b) pressure relief valve in series with bursting disc upstream and with pressure indicator on intermediate space*

12.14.3 Relief device configurations

Figure 12.14 illustrates some relief configurations based on bursting discs only. Figure 12.14(a) shows a single bursting disc. Figure 12.14(b) shows two bursting discs in series with a pressure indicator on the space between to detect pinholes leaks. Figure 12.14(c) shows two bursting disc in parallel with a three-way valve.

Figure 12.15 illustrates some pressure relief valve + bursting disc configurations. Figure 12.15(a) shows a pressure relief valve and bursting disc in parallel and Figure 12.15(b) a pressure relief valve with an upstream bursting disc to protect against aggressive process conditions. Other arrangements (not shown) are a pressure relief valve with a downstream bursting disc to protect against aggressive discharge conditions, and one with both upstream and downstream bursting discs to protect against aggressive conditions on both sides.

12.14.4 Setting of relief devices

Once the location of the relief system and the type of system to be used have been decided, it is possible to determine the setting and capacity of the device. Guidance on the set pressure for pressure relief valves and for bursting discs is given in the codes. Discussion of this aspect is deferred to Sections 12.19 and 12.20, respectively.

12.14.5 Sizing of relief devices

Guidance on the sizing of individual pressure relief valves in given in API RP 521, which considers in detail the assumptions to be made in relation to each of the sources of overpressure listed in Section 12.12. The situations treated are similar to those discussed in Section 12.12. The approach taken is to describe the scenario and to define a basis for the determination of the relief capacity, indicating whether credits can be taken for particular mitigating factors and discussing features to be taken into account. The account given in Section 12.15 of the treatment of external fire illustrates the general approach. An essentially similar philosophy is applicable to the sizing of bursting discs.

12.15 Overpressure Protection: Fire Relief

The pressure relief requirements just discussed are those for relief of conditions that may arise during operation. In addition to such operational relief, there is a requirement for fire relief. 'Fire relief' refers to an overpressure scenario in which flames external to an equipment item heat the contained fluid, producing a pressure increase either via vaporization of liquid or thermal expansion of gas or vapour. Except in storage areas, operational upsets are more likely to give rise to a requirement for pressure relief than are fires. But fires tend to require a larger pressure relief capacity. In cases where fire can affect a number of vessels, the requirement for fire relief is very much greater than that for operational relief.

Equipment for which fire relief may be required includes atmospheric storage tanks, pressure storage vessels and process systems. For pressure vessels there are two distinct cases: vessels containing gas, vapor, or supercritical fluids only and vessels containing liquids. Guidance on fire relief for pressure storage vessels has been given in the successive editions of API RP 520 and RP 521. In the most recent editions of these documents (RP 521: 1997 and RP 520: 2000), the fire relief guidance appears only in RP 521. There are also a number of other codes which give recommendations on fire relief. A critique of these codes and summary of the current situation is given in the IChemE *Relief Systems Guide*, as described below.

The account of fire relief given here is supplemented by the further discussion in Chapter 22 of fire relief for storage.

12.15.1 Scenarios for fire relief

The first step in design for fire relief is to define the scenarios for which such relief is to be provided. A discussion of this aspect is given by Fitt (1974). The amount of fire relief required depends on the surfaces which may be exposed to fire. The requirement is greatest for groups of process vessels and of storage vessels. If the scenario indicates that the fire would develop slowly and would cause

overpressure only after a long period, say several hours, it is sometimes assumed that the fire would be brought under control by fire fighting before overpressure occurs.

12.15.2 Fire protection measures

Some methods of protection against fire in addition to pressure relief are (1) inventory reduction, (2) fire insulation, and (3) water sprays. These alternative protection methods have been the subject of recent experimentation and recommendations (IP 2002, Salater, Overaa and Kjensjord 2002, Bjorn Hekkelstrand and Skulstad 2002; Roberts, Medonos and Shirvill 2000). Inventory reduction is discussed in the following section. Fire insulation and water sprays are discussed in Chapter 16 and fire insulation and water sprays for storage vessels in Chapter 22.

12.15.3 Inventory reduction in fire

Consideration also needs to be given to measures for limitation of developed pressure and for reduction of inventory in fire conditions. One method of limiting the overpressure which can develop is vapour depressurization, or blowdown. Vapour is blown down to a suitable disposal system through a depressurization valve which is separate from any pressure relief device and which is normally operated before the pressure reaches the set pressure of the relief device. This reduces the stress on the vessel walls, reducing the likelihood of their failure as the fire increases their temperature. It also reduces the potential consequences if failure should occur. The depressurization valve needs to be capable of remote operation. Depressurization systems are discussed further in Section 12.23.

Provision may also be made for the removal of the liquid inventory. One reason for doing this is to limit the amount of vapour which has to be handled. Another is to limit the release of material which could then feed the fire if the vessel should fail. The preferred means of removal is the normal liquid withdrawal system, but a separate liquid pulldown system may be used. However, removal of the liquid inventory is not necessarily the best policy. Liquid remaining in the vessel provides effective cooling for the portion of the walls which it wets. Each case needs to be considered on its merits.

12.15.4 Fire relief of pressure vessels containing liquid: API RP 521

A method for determining of the requirement for fire relief of a pressure vessel is given in section 3.15 and appendix A of API RP 521: 1997.

API RP 521 gives one treatment for a vessel containing liquid and another for a vessel containing only gas, vapor, or supercritical fluid when exposed to fire. For the former, it is the wetted surface which is effective in generating vapour. The code states that the portion of the vessel to be considered is that which is wetted by the liquid and which is at a height equal to or less than 25 ft (7.6 m) above the source of the flame, usually, but not necessarily, the ground surface. For the heat absorbed, two cases are considered. For the case where there is drainage of flammable liquid away from the vessel and fire fighting is prompt, the relation given is:

$$Q = 21000\, FA^{0.82} \qquad [12.15.1]$$

where A is the total wetted surface (ft^2), F is the environment factor and Q is the total heat absorption to the wetted surface (BTU/h). For the case where these conditions are not met:

$$Q = 34500\, FA^{0.82} \qquad [12.15.2]$$

The heat absorbed per unit area q is therefore proportional to $A^{-0.18}$, which is termed the 'area exposure factor'; it accounts for the fact that a large vessel is less likely than a small one to be completely exposed.

From Equation 12.15.1 or 12.15.2, the flow of vapour generated may be obtained and hence the capacity required of the pressure relief valve determined. The two important parameters of this model, therefore, are the wetted area A and the environment factor F.

For the wetted area, the standard gives guidance (table 4) on the degree of fill to be assumed for various vessels, including storage vessels, process vessels, distillation columns, etc.

The environment factor F is, in principle, a function of a number of variables related to fire protection: (1) insulation, (2) water application, and (3) depressurizing and emptying facilities. The factor F has a value of unity for bare metal and 0.3, 0.15, 0.075 and 0.03 for insulations with conductances of 4, 2, 1 and 0.4 BTU/(ft^2 h °F), respectively. A full set of values is given in the code (table 5). No credit is given by way of reduction of this factor (i.e. F is unity) for depressurizing and emptying facilities or for water sprays on a bare vessel. The reason given is that neither of these mitigation steps is sufficiently reliable to reduce the relief requirement.

As described below, differences between API RP 521 and other codes in respect of fire relief are in large part associated with differences in the credit given for fire protection by way of the environment factor F.

12.15.5 Fire relief of pressure vessels containing no liquid: API RP 521

For a vessel containing only gas, vapour, or fluid above the critical pressure and exposed to fire, API RP 521 gives the following simplified method, which in this case gives directly the required discharge area of the pressure relief valve:

$$A = F'A'/P_1^{1/2} \qquad [12.15.3]$$

with

$$F' = \frac{0.1406}{CK_d}\left[\frac{(T_w - T_1)^{1.25}}{T_1^{0.6506}}\right] \qquad [12.15.4]$$

$$T_1 = T_\eta(P_1/P_\eta) \qquad [12.15.5]$$

where A is the effective discharge area of the valve ($in.^2$), A' is the entire exposed surface area of the vessel (ft^2), C is a coefficient, F' is a parameter, K_d is the coefficient of discharge, P_1 is the upstream relieving pressure (psia), P_η is the normal operating pressure (psia), T_1 is the upstream relieving temperature (°R), T_w is the vessel wall temperature (°R) and T_η is the heated fluid's normal operating temperature (°R). RP 521 states that the recommended minimum value of F' is 0.01 and when the minimum value is unknown, a value of 0.045 should be used. Then, from

Equations 12.15.3 and 12.15.4 together with Equation 12.19.15 given below the relief load is:

$$W = 0.1406\left(\frac{MP_1}{Z}\right)^{1/2}\left[A'\frac{(T_w - T_1)^{1.25}}{T_1^{1.1506}}\right] \qquad [12.15.6]$$

where M and Z are, respectively, the molecular weight and compressibility of the fluid at relief conditions and W is the required mass flow (lb/h).

This simple method is based on the assumption that the gas behaves as an ideal gas, that the vessel is uninsulated and has negligible mass, that the gas temperature does not change and that the vessel wall temperature does not reach its rupture value. The document states that these assumptions should be reviewed and, if necessary, use made of a more rigorous method, on which it gives some further guidance.

It must be emphasized that the heat flux modelling used in the fire relief methods described in API RP 521: 1997 are based on empirical observations of heat flux to pressure vessels from fires of pools of flammable liquids. Therefore, the heat flux correlations above are not appropriate for fire scenarios involving jet fires. In jet fire cases, particularly those in which the fire may impinge upon a vessel, the intense, localized heating of the vessel wall may cause vessel failure before the relief pressure is reached. In such cases, depressurization and fireproofing may present the only feasible means of protection.

12.15.6 Fire relief of pressure vessels: other codes

There are several other codes which give guidance on fire relief. A critical review is given in the IChemE *Guide*. The other major code discussed in the Guide is NFPA 30: 1981, together with the Occupational Safety and Health Administration code (OSHA) 1910.106: 1981, which is essentially similar. It states that for storage equipment with wetted areas below 2000 ft^2, NFPA 30 appears to give heat fluxes twice those of API RP 521, but that this difference gradually reduces for wetted areas between 2000 and 2800 ft^2 so that for wetted areas above the latter value the two coincide.

It is also necessary, however, to consider the environmental factor. For good drainage, NFPA 30 gives credit in the form of a value of 0.5 for this factor. As stated above, API RP 521 gives no explicit credit for good drainage, the existence of good drainage being a condition of the use of Equation 12.15.1. Thus for wetted areas of less than 2000 ft^2 the heat fluxes given by the method of API RP 521 and that of NFPA 30 are the same. The *Guide* concludes that the method of API RP 521 is to be preferred. A further discussion of heat fluxes to pressure vessels is given in Chapter 16.

The *Guide* also considers the Compressed Gas Association code CGA S-1.3: 1980 for gas cylinders, together with the Chlorine Institute code CI 5.3.3: 1977, which is essentially similar. CGA S-1.3 utilizes for gas cylinders the more conservative Equation 12.15.2. The *Guide* argues that cylinders may well be exposed to higher heat fluxes so that a case can be made for this approach.

12.15.7 Fire relief of atmospheric storage tanks: API Standard 2000

Guidance on fire relief for atmospheric and low pressure storage tanks is given in API Std 2000: 1998. This standard distinguishes between tanks with a weak roof-to-shell attachment, or rupture seam, and those without. For tanks with a rupture seam, the standard does not require any further emergency venting for fire relief. For tanks without a rupture seam, the standard provides a table of relieving requirements given as a function of the wetted area of the tank. It should be noted that recent reports indicate that the rupture of seams on tanks with diameters less than 50 ft cannot be sufficiently relied upon to remove the need for separate relief devices. (Ferry, 2002).

For a vertical tank, the wetted area is taken as the total cylindrical surface area of the shell up to height of 30 ft above grade. For a horizontal tank, it is the greater of 75% of the total surface area or the surface area to a height of 30 ft (9.14 m) above grade. For a sphere or spheroid it is the greater of 55% of the total surface area or the surface area to a height of 30 ft above grade.

The value of the wetted area used in API Std 2000 reflects the fact that such an atmospheric storage tank normally stands in a bund in which there could be a liquid fire. This contrasts with the values of the wetted area in API RP 521, which reflect the fact that the ground under a pressure storage vessel is normally sloped to drain any liquid away. Fire relief for atmospheric storage is discussed further in Chapter 22.

12.15.8 Effect of fire on relief devices

It is also necessary to consider the effect of fire on pressure relief devices. On a pressure relief valve there are two main effects of fire. One is to cause thermal expansion of the spring, which reduces the force on the valve and is a deviation in the safe direction. The other is to cause thermal expansion of the valve spindle which can lead to jamming. However, if the valve is immersed in the fire so that the temperatures in it are equalized, this effect may be minimal. On a bursting disc the effect of fire is to reduce the bursting pressure or to cause rupture, both of which are effects in the safe direction.

12.15.9 Heating of unwetted surfaces

Provision of fire relief does not give full protection against fire. Unwetted surfaces which are exposed to fire may experience overtemperature and may rupture, even though overpressure of the vessel has not occurred. API RP 521 gives a graph for the time taken by steel plate of different thicknesses to reach particular temperatures when exposed to an open gasoline fire on one side, and another graph for the time to rupture at different rupture stresses and temperatures. These two graphs are shown in Figure 12.16(a) and (b), respectively. RP 521 quotes the example of an unwetted steel vessel of plate thickness 1 in. and with a stress of 15,000 psi in an open fire. The time for the vessel wall to heat up to 1300°F is 17 min and the time for rupture to occur at that temperature is 2.5 min.

The failure of LPG pressure storage vessels in 1966 at Feyzin (Case History A38) was due to the effect of fire on the unwetted walls, even though the pressure relief valves operated.

12.16 Overpressure Protection: Vacuum and Thermal Relief

12.16.1 Vacuum relief

Vacuum collapse of equipment is destructive and hazardous, despite the fact that in some instances the pressure differential may appear relatively small. There is a wide variety of situations that can lead to at least a partial

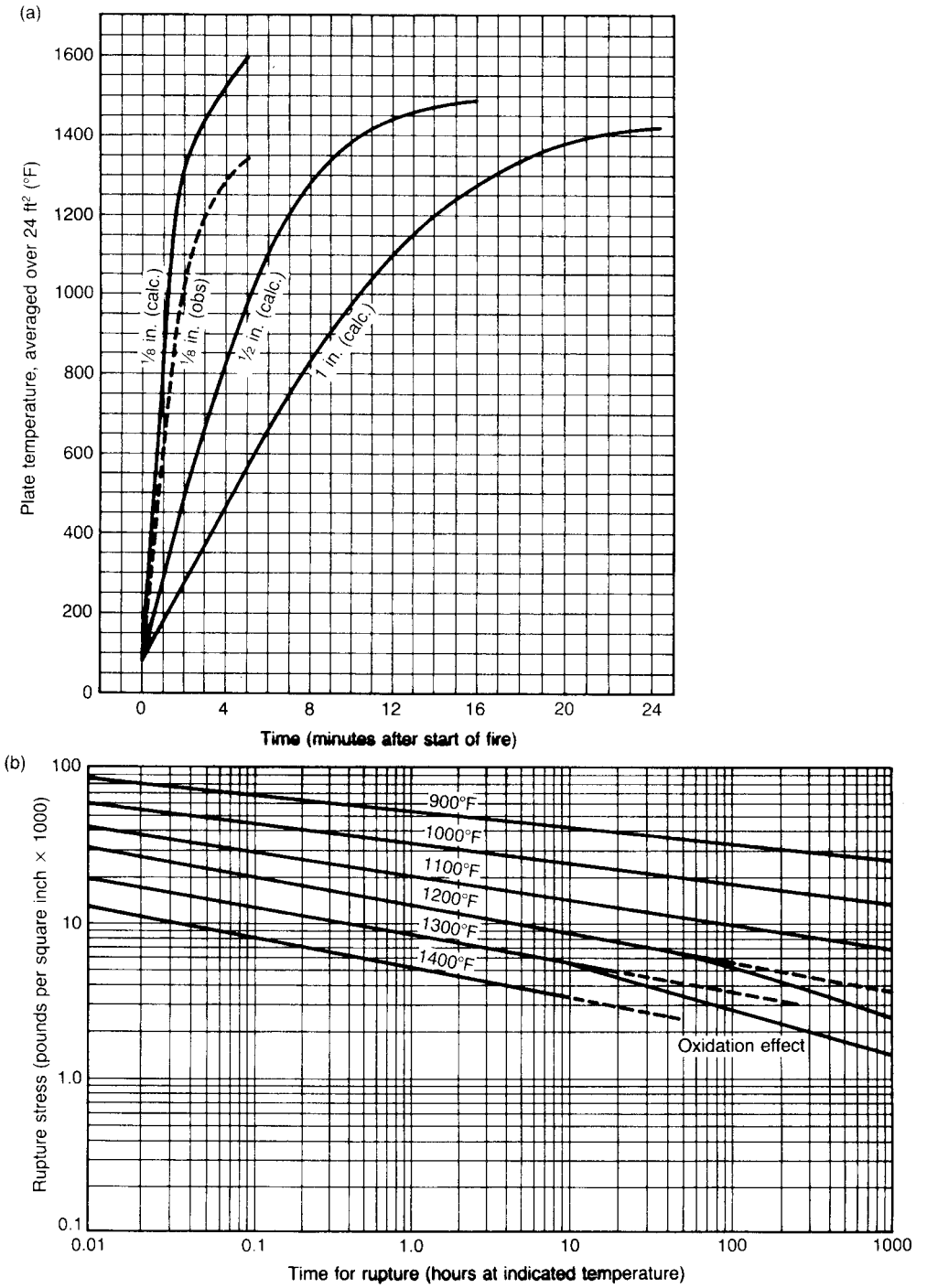


Figure 12.16 *Effect of fire engulfment on steel plate (American Petroleum Institute, 1997 API RP 521): (a) average rate of heating of steel plates of different thickness exposed to an open gasoline fire on one side; and (b) time to rupture of steel plate (ASTM A515 grade) as a function of temperature and stress (Courtesy of the American Petroleum Institute)*

vacuum. They include (1) pumping out with inadequate vent opening, (2) condensation of a vapour, (3) absorption of a vapour, (4) cooling of a volatile liquid, (5) connection to a source of vacuum or suction, (6) depletion of oxygen in air by rusting, and (7) sudden arrest of a moving column of liquid. Some scenarios of storage tank collapse due to such situations are illustrated in Chapter 22.

Some equipment is capable, as designed, of withstanding full vacuum. This is often the case with steel pressure vessels. Other equipment such as plastic storage tanks or large diameter pipework may not have full vacuum strength.

The IChemE *Guide* states that a cylindrical pressure vessel with a length/diameter ratio not exceeding about three and a design pressure of 3.5 barg can generally withstand full vacuum, but that it is prudent to make the check. An increase in the vacuum strength of a vessel can often be obtained by a quite small increment in wall thickness or addition of a stiffening ring.

Vacuum relief devices include vacuum valves and bursting discs. A vacuum valve is a direct-loaded valve which opens to admit air. An alternative is a vacuum bursting disc, which may be preferred where the fluid is corrosive or liable to create blockage, or where it is sufficiently toxic that even a small leak is unacceptable. Bursting disc arrangements are also available which provide both overpressure and vacuum protection, as described in Section 12.13.

On atmospheric storage tanks widespread use is made of pressure/vacuum valves which allow flow in either direction. These are discussed in more detail in Chapter 22. In some cases, vacuum protection may be provided by way of a liquid seal. Where it is not acceptable for air to be admitted to the equipment, inert gas may be used. A typical inert gas arrangement on a storage tank is illustrated in Figure 12.17.

In such an installation, the tank pressure is maintained within acceptable limits primarily by inflow or venting of the inert 'blanket' gas. Installation of pressure and vacuum vents is still required, however, as these provide the ultimate means of protection in the event of failure of the blanketing system. Inflow of air or venting of tank vapours is generally to be preferred over tank rupture or implosion.

12.16.2 Thermal relief

Another form of pressure relief which may be required is thermal hydraulic relief. This is the relief of pressure due to expansion of a liquid that is blocked in and then heated. The pressure generated by a blocked-in and heated liquid is independent of the volume, but the latter does affect the consequences of any escape.

A treatment of thermal relief is given in the IChemE *Relief Systems Guide*. The factors governing the decision as to whether to provide thermal relief are (1) the nature of the liquid, (2) the heat source, (3) the volume of the plant section or system, (4) the tightness of the closure, (5) the probability of blocking in, (6) the location of the system, and (7) the availability of other means of relief.

The *Guide* divides liquids into the following categories: (1) cryogenic, (2) low boiling point, (3) volatile, (4) flammable, (5) toxic, (6) other liquids, and (7) water.

Sources of heat are classified as (1) process heat, (2) heat tracing, (3) solar radiation, and (4) ambient temperature. Subject to the volume exemption described below, the first of these cases should be provided with relief, as should the second, unless the controls are such as to make it unnecessary, whilst the third and fourth cases require the exercise of judgement. For liquids in categories 1–5 relief should generally be provided except for insignificant volumes, that is, volumes $<0.1\,m^3$ (perhaps less for toxic compounds). The location of the system may strengthen the case for relief, which is indicated if the system is located in an unmanned offsite area (where corrective action is unlikely) or on public property.

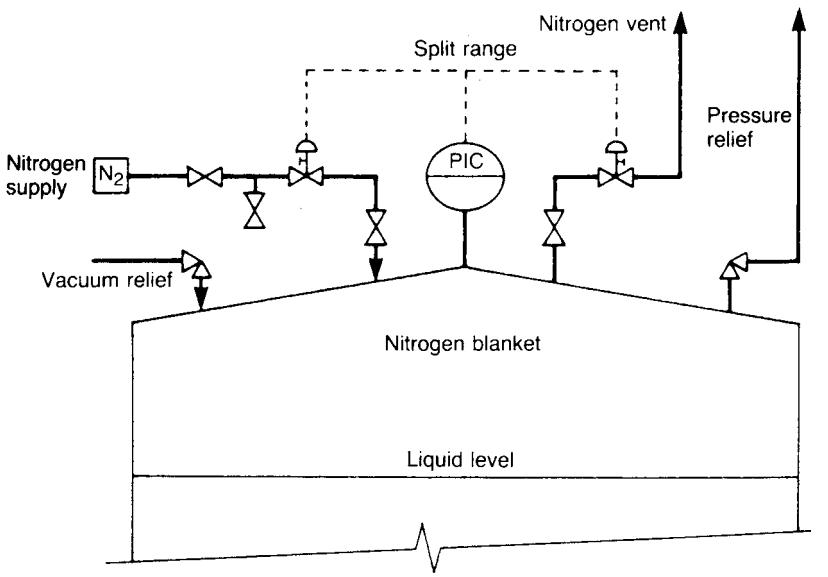


Figure 12.17 *Storage tank system showing inert gas blanketing and arrangements for pressure and vacuum relief (Parry, 1992). PIC, pressure indicator controller (Courtesy of the Institution of Chemical Engineers)*

Turning to category 6 liquids, these require judgement. Account may be taken of the frequency with which the system may be blocked in and the degree of control. If the frequency is judged sufficiently low, it may be possible to dispense with relief.

The *Guide* advises that in borderline cases account may be taken of the volume of the system. The volume which may be regarded as insignificant is related to the tightness of closure. The following tightness categories are given:

Construction	*Valves*		
	Bubble	*Soft*	*Metal*
All welded	A	A	B
Class 300 flanges or higher	A	B	C
Class 150 flanges	B	C	D

It also gives the following relationships between tightness category and limiting volume requiring thermal relief:

Tightness category	*Limiting volume* (m^3)
A	0.1
B	1.0
C	5.0
D	10.0

Separate thermal relief may not be needed if other means of relief exist. These may include a small hole in the valve or a small bore bypass around it, bellows, or relief provided for other purposes.

The following equation is given in the IChemE *Relief Systems Guide* for the thermal relief requirement:

$$W = Q\beta/S \qquad [12.16.1]$$

where Q is the heat input rate (W), S is the specific heat of the fluid (J/kg°C), W is the required relief rate (kg/s) and β is the coefficient of volumetric expansion ($°C^{-1}$).

12.17 Overpressure Protection: Special Situations

There are a number of special situations in pressure relief which require separate consideration. They include (1) extreme operating conditions, (2) aggressive fluids, (3) multiphase fluids, and (4) uncontrolled chemical reaction.

12.17.1 Extreme operating conditions

Extreme operating conditions that can affect pressure relief include (1) high pressure, (2) high temperature, and (3) low temperature.

With high pressure relief valves factors to be considered are valve tightness and precision of lift. Increased tightness may be obtained by the use of a supplementary-loaded valve. In high pressure processes, it is usual to operate close to the design pressure and precision of lift becomes important. A pilot-operated valve may meet the case for clean fluids. Advice on selection of valves for dirty fluids is given in the IChemE *Guide*. There are also available bursting discs for high pressure duties. A feature of relief flows at high pressure is that the gas behaviour may not be ideal.

For a high temperature pressure relief valve relevant factors are materials of construction, spring relaxation, the hot set pressure and the difference between the operating temperature and the relieving temperature. A valve spring subject to high temperature may suffer relaxation. The problem, and work on it, have been described by Aird (1982, 1983). A method of minimizing the effect by the hot set procedure has been described by Weighell (1980). The hot set procedure is specified by the valve manufacturer and should be followed.

If the process fluid has to travel any significant distance before reaching the valve, there may be a difference between the operating temperature and the relieving temperature. It is the latter which is to be used in performing the sizing calculations.

For a pressure relief valve on low temperature duty, factors to consider are materials of construction, the low temperature set pressure, the difference between the operating temperature and the relieving temperature and icing. The low temperature set pressure may be obtained by using a correction on the ambient set pressure but it is also practice to adjust a valve in place at the operating temperature. Icing is countered in various ways. Use may be made of insulation or trace heating. If the plant is in a cold box, the valve may be mounted outside it so that it is at a temperature close to ambient.

For a bursting disc on high or low temperature duty the important feature is the material of construction.

12.17.2 Aggressive fluids

Where a fluid is corrosive, it may be possible to use a pressure relief valve on its own if suitable materials of construction are available. Otherwise, options are the use of a bursting disc upstream of the valve, a bursting disc on its own, or, if the fluid is especially corrosive, two bursting discs in series.

Where the fluid is liable to cause blockage, a pressure relief valve alone may not be suitable. One option is to install a bursting disc upstream of the valve. Another is to use a bursting disc on its own.

If the fouling could be severe, further steps may need to be taken to keep the disc clear. Methods include the use of a coating or anti-fouling compound on the disc, or even water sprays to wash the disc clean.

12.17.3 Multiphase fluids

In some applications, the fluid flowing through the pressure relief valve will be a two-phase vapour–liquid mixture, either because the fluid is two-phase at the valve inlet or because it becomes so in passing through the valve. Two-phase flow through a pressure relief valve is a specialist topic of active current research. It is discussed further in Chapter 15.

Another type of two-phase system is a liquid containing solid particles. There are two potential effects of such solid matter. One is blockage, which has just been discussed. The other is any effect on the flow properties of the fluid.

12.17.4 Runaway reactions

Chemical reaction has long been recognized as a potential source of overpressure in equipment and piping elements. It is unavoidably a specialized domain within the field of overpressure protection, because the rate at which pressure builds – and must be relieved – is inextricably connected to the kinetics of each particular reactive system. Furthermore, reactions that may lead to overpressure include not only reactions intentionally carried out but control of which

is lost, but also unintended reactions that occur due to feeding incorrect compounds, impurities, or failing to maintain process parameters within specified limits. An ongoing thrust of the DIERS User's Group – with worldwide participation – is to share, compare and validate experimental and theoretical studies of reactive systems of wide industrial relevance. A series of international symposia has featured reports of data for 'runaway reactions' (Runaway Reactions 1–3).

12.18 Overpressure Protection: Disposal

12.18.1 Disposal and disposal systems

Pressure relief necessarily involves the provision of arrangements for the disposal of the material vented. The selection of the method of relief disposal and the design of any relief disposal system are integral to the overall design.

With all credible overpressure scenarios as a starting point, the nature, temperature, phase and flow rate of the each relief stream are defined. Fluids may be flammable, toxic and/or corrosive. Some may be at high or low temperature. Some flows may be two-phase or liable to condense on release.

For each relief location there will be a flow profile with time. There may also be contributions to the total flow from other devices such as depressuring valves. If the overall profile shows too high a peak, measures may be taken to shave the peaks by means such as the staggering of pressure relief valve settings.

Discharge of gas or vapour to atmosphere is relatively simple and dependable, but its use may be constrained by regulatory and other requirements. API RP 521 recognizes this method for use where it is acceptable. The code also deals with some of the problems which can arise with atmospheric discharge, including formation of flammable plumes, ignition of such plumes, toxic or corrosive plumes, noise and pollution. Its guidance on avoidance of flammable plumes is discussed in the next subsection.

Another option for gas or vapour, which is applicable in some cases, is disposal to a lower pressure system. Minimum requirements in this case are that the unit have the capacity to receive the relief safely and that it be available to do so, bearing in mind that the lower-pressure system may be affected by the same conditions that created the need for relief in the first place.

If these methods of disposal are not appropriate, other methods available include: scrubbing, followed by discharge of the scrubbed gas; discharge from a vent stack; or burning from a flare stack. In these cases, the necessary pipework has to be provided in the form of a relief header, or headers. Here a basic distinction is between single- and multiple-valve disposal systems. In the design of the latter there are a number of features which need to be taken into account.

It is common practice to use a common header both for normal vents and for emergency relief. In this case the normal vent flows should be added to the emergency relief flows in designing the header. Alternatively, separate headers may be provided for normal vents, for gas/vapour relief and for liquid blowdown. Separate headers for gas/vapour and for liquid permit separate disposal arrangements such as a flare stack and blowdown drums, respectively. It may be necessary to consider segregation of streams which are in some way incompatible. Such incompatibility may have to do with fluids that react together, with a low-temperature fluid that requires a more expensive material of construction, or with a fluid that is susceptible to freezing by another, colder fluid.

As far as liquids are concerned, some may be suitable for disposal to the drains. Others may need to be routed to a liquid blowdown receiver or disposed of in an earth burning pit.

12.18.2 Load on disposal system

If the relief flows are discharged to a closed system rather than to atmosphere, it becomes necessary to define the load the system is required to handle. The determination of the flow for which the relief header should be designed is not a simple matter. Its capacity must lie somewhere between the largest single relief flow and the sum of all relief flows. Except for very small plants the latter solution is too conservative and uneconomic.

Before the total design load of the disposal system can be determined, credible 'global scenarios' must be defined. These are scenarios in which multiple relief devices can credibly be expected to discharge simultaneously into the disposal system as a result of a single initiating event. All sources tied to the disposal system – which typically include relief devices, blowdown valves, and process control valves (e.g. pressure bleeds to flare) – must be considered in this evaluation.

Guidance on the identification of global scenarios and determination of the associated loads on the disposal system is given in API RP 521. The essential principle is to design for the set of individual contingencies, rather than for coincident occurrence of multiple independent contingencies. However, each contingency should be carefully examined, because the consequences of certain events can be very widespread.

The code gives guidance particularly on loss of utilities. For failure of electrical power to equipment, the design is commonly based on failure of one bus, or possibly of the distribution centre or the incoming line. Sudden total or partial loss of instrument air or instrument electrical power is also typically considered. The presence of large reservoirs of instrument air may provide for the failure of an air compressor, but cannot protect against the rupture of an air manifold.

Definition of the load resulting from fire requires a specific study taking into account the plant layout, including location of potential sources of release, natural barriers and drainage, etc. The fire on a plant handling only gas can generally be assumed to be more localized than on one handling liquids. RP 521 states that in the absence of special factors the ground area of fire is often taken as being limited to 2500–5000 ft^2 (230–460 m^2).

Fitt (1974) describes an approach to this problem based on certain 'standard hazards'. These are (1) fire, (2) electrical power failure, (3) instrument air failure and (4) cooling water failure.

Fire may affect a group of vessels. It should be assumed, therefore, that there would be simultaneous relief on these vessels. It is usually not necessary to assume a process upset at the same time.

Failures of electrical power, instrument air or cooling water are all obvious causes of simultaneous relief. Total power failure can cause failures on a large number of equipments and all electronic instrumentation. Partial power failure can be even more hazardous. Thus, for example, reboiler fuel pumps might continue to operate after reflux pumps have stopped.

Total instrument air failure disables all pneumatic instrumentation. It is normal practice, however, to design instrument systems so that the control valves 'fail safe' on air failure. Thus again, it may be more hazardous if the air failure is partial. In this case the movement of valves may be in the directions opposite to those on total air failure. In addition, a control valve with an open bypass will not shut off flow completely even if it does close.

Failure of cooling water is usually a consequence of power failure and should be assumed unless the supply can be maintained by pumps with prime movers which have an independent power supply. Note that RP 521 recommends against taking credit for independent-driver pumps not normally operating, stating that their start-up upon power failure has proven not sufficiently reliable.

According to Fitt (1974), once the credible standard hazards have been identified, the flows expected to occur over three different time periods (1) less than 10 min, (2) 10–30 min, and (3) up to 1 h (4 h for fire), are determined.

12.18.3 Disposal to atmosphere

Disposal of gas or vapour by direct discharge to atmosphere possesses the virtue of being relatively simple and dependable, and may be used where it is acceptable. A method for the design of atmospheric discharge arrangements is given in API RP 521. The case considered is that of a safety relief valve discharging a flammable vapour upwards through a vertical tail pipe. The vapour is discharged at a velocity sufficiently high that it is rapidly diluted below the lower flammability limit (LFL).

The criterion for the vapour to be diluted below the LFL whilst the mixing is still dominated by the momentum of the jet is that the Reynolds' number, Re, exceed following value:

$$Re > 1.54 \times 10^4 \rho_j / \rho_\infty \qquad [12.18.1]$$

where ρ_j is the density of the vapour at the vent outlet and ρ_∞ is the density of the air.

The code quotes the work of Taylor, Grimmett and Comings (1951) and gives for the dilution of the discharged vapour the relation:

$$\frac{W}{W_0} = 0.264 \frac{y}{D} \qquad [12.18.2]$$

where D is the diameter of the nozzle (ft), W is the mass flow of vapour–air mixture at distance y from the tail pipe (lb/h), W_0 is the mass flow of vapour from the safety relief valve (lb/h), and y is the distance from the end of the tail pipe (ft).

On this basis it is calculated that, provided that the velocity of the discharged material leaving the tail pipe is more than 500 ft/s (150 m/s) so that sufficient energy is supplied for mixing to occur, a hydrocarbon discharging from a safety relief valve into the atmosphere will entrain enough air to become diluted below its LFL at a distance of approximately 120 diameters from the end of the tail pipe.

The code recognizes that, whilst this is fine as long as the valve discharges at this high rate, it cannot be assumed that the flow through a safety relief valve is the full capacity flow. Once a spring-loaded valve has opened, the force exerted on it by the flowing fluid is sufficient to prevent reclosure until the flow has fallen to about 25% of capacity. However, the code quotes a study by Hoehne, Luce and Miga (1970) which has shown that even at flows of 25% of capacity the vapour is safely dispersed.

API RP 521 also refers to studies on venting of oil tankers (ICS, 1978) which indicate that dilution is effective at release velocities exceeding 100 ft/s (30 m/s). It gives a set of graphs for the estimation, for petroleum gases, of the maximum vertical and downwind horizontal distances from the jet exit to the LFL and of the axial distances to the upper flammability limit (UFL) and LFL. For the vertical distance the correlation is:

$$\frac{y}{d_j(\rho_j/\rho_\infty)^{1/2}} \quad \text{vs} \quad U_\infty / U_j \qquad [12.18.3]$$

where d_j is the inside diameter of the tip, or jet exit diameter, U_j is the jet exit velocity, U_∞ is the wind speed and y is the vertical distance to the LFL. The correlations for horizontal distance x and axial distance S are of similar form, with y replaced by x and S, respectively.

The code comments that the studies demonstrate the adequacy of the industry practice of locating the discharge of a safety relief valve at a horizontal distance of at least 50 ft (15 m) from any equipment or structure above the discharge level.

API RP 521 also gives consideration to the case in which the vapour discharged condenses to form a mist. In principle, condensation can occur if the ambient temperature is below the dewpoint of the vapour. However, there are two factors that may mitigate this situation. One is that condensation does not necessarily occur and the other is that, even if it does, the droplets may coalesce and fall out.

Vapour let down in pressure through a safety relief valve becomes superheated and this may prevent condensation. Furthermore, the vapour may be diluted so rapidly that condensation is avoided. A method of determining whether condensation occurs has been given by Loudon (1963). It shows that condensation does not occur with most hydrocarbons, though it may with some of high molecular weight, a finding which is in accord with industrial experience.

RP 521 states that, whilst conclusive data are lacking, condensation at a hydrocarbon partial pressure of 5 psi (0.34 bar) or less should be assumed to result in a fine mist, the dispersion and flammability of which are similar to those of a vapour. A further discussion of discharge to atmosphere and from vents is given in Chapter 15.

12.18.4 Design of a relief header

The use of a closed system involves the design of the relief discharge pipework. In certain cases, use may be made of individual discharge lines, but commonly there is a relief header taking discharges from a number of points.

A discussion of relief headers is given by Fitt (1974) in the study mentioned. As stated above, he considers for a given standard hazard the flows occurring over the three time periods (1) less than 10 min, (2) 10–30 min, and (3) up to 1 h (4 h for fire). The relief header is designed to handle the sum of the flows of the largest of these groups. The header may be required to handle both gas/vapour and liquid flows.

If conventional relief valves are used, relief headers should be so sized that the back pressure developed is limited to 10% of the set pressure. This requirement can be relaxed, however, if balanced relief valves are used. The latter thus permit a more economical design of the relief header.

The pressure drop in the header is sometimes high and the changes in gas density and velocity are correspondingly large. Not infrequently, sonic flow conditions occur. The design of relief headers is therefore relatively complex.

The gas flow in the header may be treated either as isothermal or as adiabatic. For an ideal gas the flow is greater under adiabatic than under isothermal conditions, but for a ratio of specific heats $\gamma < 1.8$ this difference does not exceed 23%. Frequently, calculations are done on the basis of isothermal flow.

API RP 521 gives in Section 5.4.1 guidance on the design basis for a relief header. Essentially, the flows are determined for each credible global scenario and the design is based on the most severe flow condition. This is the condition which gives the highest pressure drop, which is not necessarily that with the highest mass flow; the volumetric flow is relevant, and hence so are molecular weight and temperature.

Once the design loadings are determined, then for each global scenario the maximum allowable back pressure on each pressure relief valve should be calculated. The code gives detailed guidance on these back pressures.

In addition to the flows from the pressure relief valves, there may be flows from depressuring valves. Normally, a depressuring valve is treated as fully open or fully closed and the maximum flow from it taken as the flow capacity of the valve at the maximum pressure of the equipment that it protects, which may be the maximum accumulated pressure. However, the code advises that where the same equipment is protected by both a pressure relief valve and a depressuring valve, only the larger of the two flows is to be considered.

API RP 521 gives a method for the design of the relief header, which is based on the method of Lapple (1943) for isothermal flow of gas through pipes at high pressure drop. The design of relief headers is a specialist matter. It is also an economically important one, since relief headers can be expensive items, particularly if it is necessary to use special materials of construction. Some of the specialist topics in the sizing of relief headers, including non-ideal gas flow and pipe section changes, are discussed by Duxbury (1976).

12.18.5 Disposal to a flare stack

Guidance on the design of a flare for the disposal of gas or vapour is given in API RP 521. The code gives methods for the determination of the diameter and height of the flare stack, the fuel gas supply to the flare, and the steam requirement for a smokeless flare.

The selection of flare stack diameter and height is treated in appendix C of the code. As described there, the diameter is chosen to give a particular Mach number at the flare tip and the height is chosen to limit thermal radiation at ground level. Appendix D of the code gives typical sketches and details of a complete flare system, and of seal drums and knockout drums.

The code also deals with thermal radiation and pollution from the flare. Appendix C gives two models for the flame on the flare, a simple model and the model of Brzustowski and Sommer. These API flare models are described in Chapter 16.

API RP 521 gives information on the exposure times necessary to reach the threshold of pain (table 7) and recommended design radiation levels (table 8). RP 521: 1997 differs from previous editions in that table 8 specifies recommended design values of total radiation; in previous editions the corresponding table explicitly excluded solar radiation from the design values. These and other thermal radiation limits are discussed in Chapter 16.

With regard to the estimation of ground level concentrations of combustion products from the flare, the code refers to the method of Gifford (1960a).

Methods for dispersion from elevated stacks are considered in Chapter 15.

12.18.6 Disposal to a vent stack

API RP 521 also contains guidance on the design of a vent stack for the disposal of gas or vapour. It gives methods for the determination of the diameter and height of the stack.

The diameter is chosen to give a high exit velocity. As discussed above, the code states that excellent dispersion is obtained with a velocity of 500 ft/s (150 m/s). However, sonic velocity should be avoided, or else allowance made for the effect on the pressure drop of the pressure discontinuity at the discharge. The choice of the height of the stack is governed by the need to ensure acceptable concentrations at the points of interest. The code gives guidance on the level of noise from such a stack.

An equation for the maximum ground concentration of a gas downwind of a vent stack is:

$$C_{\max} = \frac{W}{VH^2M} \qquad [12.18.4]$$

where $C_{\max}$ is the maximum ground concentration (% v/v), H is the height of the stack (ft), M is the molecular weight, V is the wind velocity (mile/h) and W is the mass flow rate of gas (lb/h).

There are a number of restrictions on the use of Equation 12.18.4. It assumes that the air velocity increases with height above the ground and that the gas–air mixture is not much heavier than air itself. It is not applicable if the wind velocity is zero or very low, or if the discharge velocity is much below 500 ft/s.

12.18.7 Selection of disposal system

Guidance on the selection of a disposal system is given in the IChemE *Relief Systems Guide*. The disposal systems considered in the guide are to (1) atmosphere, (2) quench vessel, (3) process, (4) storage, (5) dump tank, (6) sewer, (7) elevated flare, (8) ground flare, (9) incinerator, or (10) scrubber.

The selection scheme passes through four broad stages. If the fluid to be disposed of is mainly vapour and if it is lighter than air or can be discharged at high velocity, disposal to atmosphere is a technical option. If the fluid contains both vapour and liquid and needs to be cooled, disposal to a quench vessel is indicated. Otherwise, if a sink for the fluid is available in process or in storage, it may be disposed of to that sink. If the fluid is mainly liquid and it is suitable for discharge to a plant sewer, it may be so disposed of. Otherwise it should be discharged to a dump tank.

If the fluid is both vapour and liquid and cannot be disposed of as described above, other options must be considered. Flammable vapours with some liquid may be sent to a flare. If the fluid contains toxic and/or particulate matter which can be scrubbed out, treatment in a scrubber is suitable. Otherwise the fluid should be sent to an incinerator.

Guidance on selection and design of systems for dipsosal of relief streams is also provided in the CCPS *Relief*

Guidelines (CCPS/NN). This work considers a wide variety of collection, treatment, and containment equipment. It also makes brief mention of several treatment and disposal alternatives that may be applied in special circumstances, noting that the highly variable flow rates associated with relief systems limit the general applicability of these alternatives.

12.19 Overpressure Protection: Pressure Relief Valves

The basics of pressure relief valves have been outlined in Section 12.13. In this section, consideration is given to valve set pressure, sizing and failure.

12.19.1 Valve set pressure

A pressure vessel has a design pressure. The definition of design pressure given in PD 5500: 2003 was quoted in Section 12.6. The set pressure of a safety valve is defined in codes by reference to a specific terminology. The pressure relationships used in PD 5500: 2003 for a safety valve on a vessel are indicated in Figure 12.18(a), which shows the case of a safety valve on gas or vapour service with a 10% overpressure. The pressures on the left-hand side refer to the vessel, whilst those on the right-hand side refer to the safety valve. For the vessel, the normal operating pressure lies between 90 and 95% of its design pressure. The maximum permitted regulated pressure is 110% of the design pressure, the difference between the two being the accumulation. For the safety valve, the set pressure is equal to the design pressure. The relieving pressure is 110% of the set pressure, the difference between the two being the overpressure. Where the set pressure of the valve is the design pressure of the vessel, the overpressure equals the accumulation.

PD 5500: 2003 states that a safety valve should normally be set to operate at a nominal pressure not exceeding the design pressure of the vessel at the operating temperature. However, if the capacity is provided by more than one safety valve, it is permissible for only one of the valves to be set to operate in this way and for the additional valve (s) to be set to operate at a pressure not more than 5% high. The pressure relationships given in BS 5500: 1991 for a safety valve for liquid service with a 25% overpressure are shown in Figure 12.18(b).

Figure 12.18(c) gives the pressure relations for pressure relief valves on a vessel used in API RP 520: 2000. Again, pressures pertaining to the vessel are shown on the left of the figure, whilst those on the right refer to the relief device. For the vessel, the maximum expected operating pressure is 90% of the maximum allowable working pressure (MAWP), which is not less than the design pressure at a coincident design temperature. The figure shows several values of the maximum allowable accumulation, for the following three cases: (1) non-fire exposure with a single valve, (2) non-fire exposure with multiple valves, and (3) fire exposure. The accumulation values are 110, 116 and 121%, respectively. For the pressure relief valve, a similar set of distinctions apply. The maximum set pressure and maximum relieving pressure are equal, respectively, to 100 and 110% of the design pressure for case 1; 105 and 116% for case 2; and 110 and 121% for case 3. Note that in all cases, at least one pressure relief valve must be set no higher than the vessel MAWP. Where the set pressure of the valve is the design pressure of the vessel, the overpressure equals the accumulation. RP 520 states that Figure 12.18(c) conforms to the ASME *Boiler and Pressure Vessel Code*, Section VIII.

Note that all applicable codes would require that where a single relief device or set of devices is designed to protect multiple equipment items, the set pressure of at least one relief device be no higher than the equipment with the lowest design pressure.

For further details of, and qualifications and variations on, the above pressure relief requirements, such as the use of multiple pressure relief valves, reference should be made to the appropriate codes, including the codes just mentioned, and other codes such as API RP 521 and Std 2000.

12.19.2 Valve sizing: BS 5500

Equations for pressure relief valve sizing were given in BS 5500: 1976. PD 5500: 2003 simply refers to the standards for pressure relief valves BS 6759. The equations given in PD 5500: 2003 are widely quoted and are given here for reference.

For a gas or vapour under critical flow conditions:

$$W = \frac{KAp}{C}\left(\frac{M}{T}\right)^{1/2} \qquad [12.19.1]$$

where A is the actual discharge area (m^2), K is the coefficient of discharge for gas flow, M is the molecular weight, p is the absolute accumulation pressure (N/m^2), T is the inlet temperature (K), W is the rated capacity (kg/s) and C is a constant.

For saturated steam:

$$W_s = \frac{KAp}{686} \qquad [12.19.2]$$

and for air at 20°C

$$W_a = \frac{KAp}{423} \qquad [12.19.3]$$

where W_a is the rated capacity for air at 20°C (kg/s) and W_s is the rated capacity for saturated steam (kg/s).

The coefficient of discharge, K, may vary. The standard quotes a value of 0.25 for a parallel inlet guided wing type valve of high lift and 0.97 for a nozzle inlet type valve with flat disc. The value of the coefficient should be provided by the manufacturer. The value of C is 133 for a ratio of specific heats of 1.4.

For liquid flow:

$$W = KA(2\Delta pG)^{1/2} \qquad [12.19.4]$$

where G is the density (kg/m^3) at the inlet temperature, K is the coefficient of discharge for liquid flow and Δp is the pressure drop (N/m^2).

12.19.3 Valve sizing: BS 6759: 1984

The relations given for pressure relief valve sizing in BS 6759: Part 3: 1984 are as follows. For air or any gas at critical flow conditions:

$$q_{mg} = pC\left(\frac{M}{ZT}\right)^{1/2} \qquad [12.19.5]$$

$$= 0.2883\ C\left(\frac{p}{v}\right)^{1/2} \qquad [12.19.6]$$

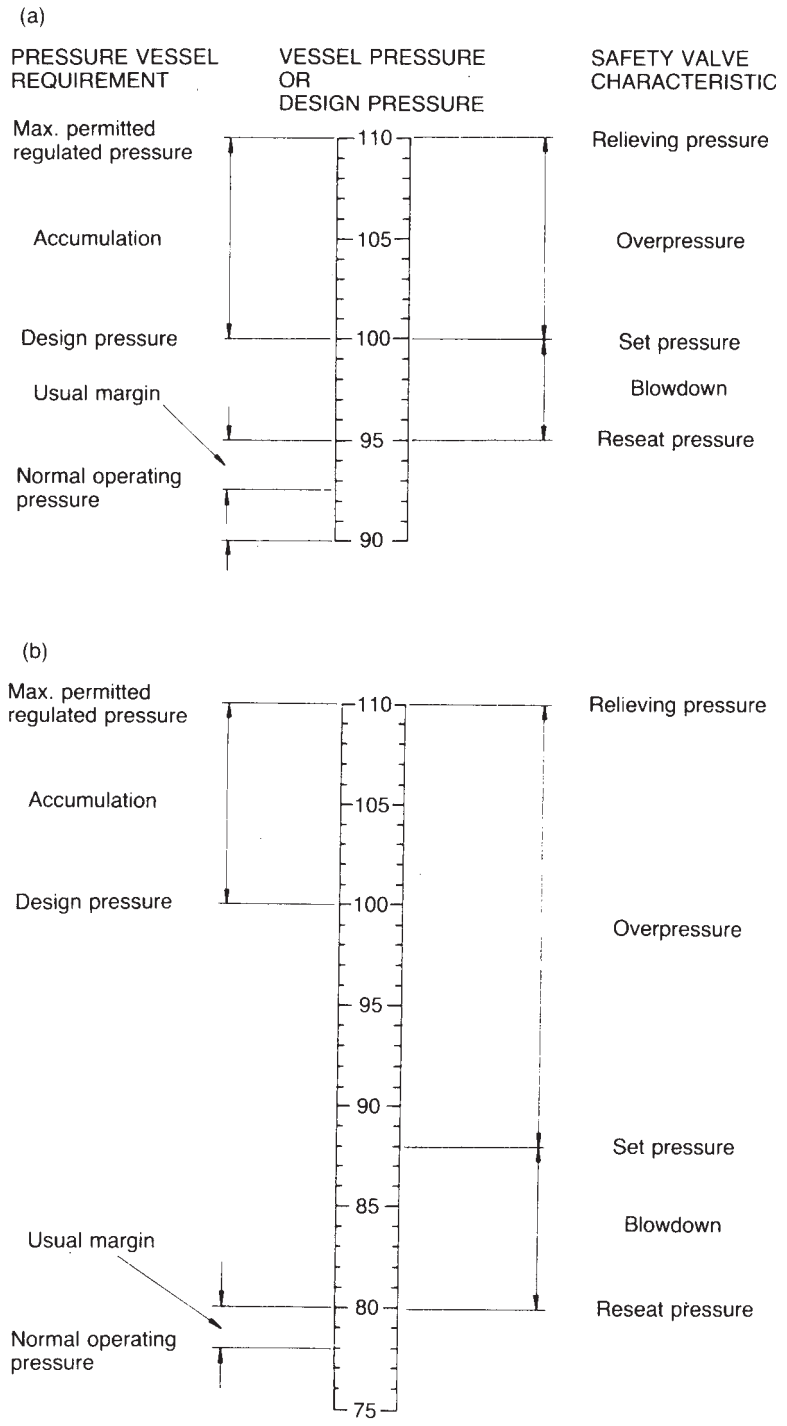
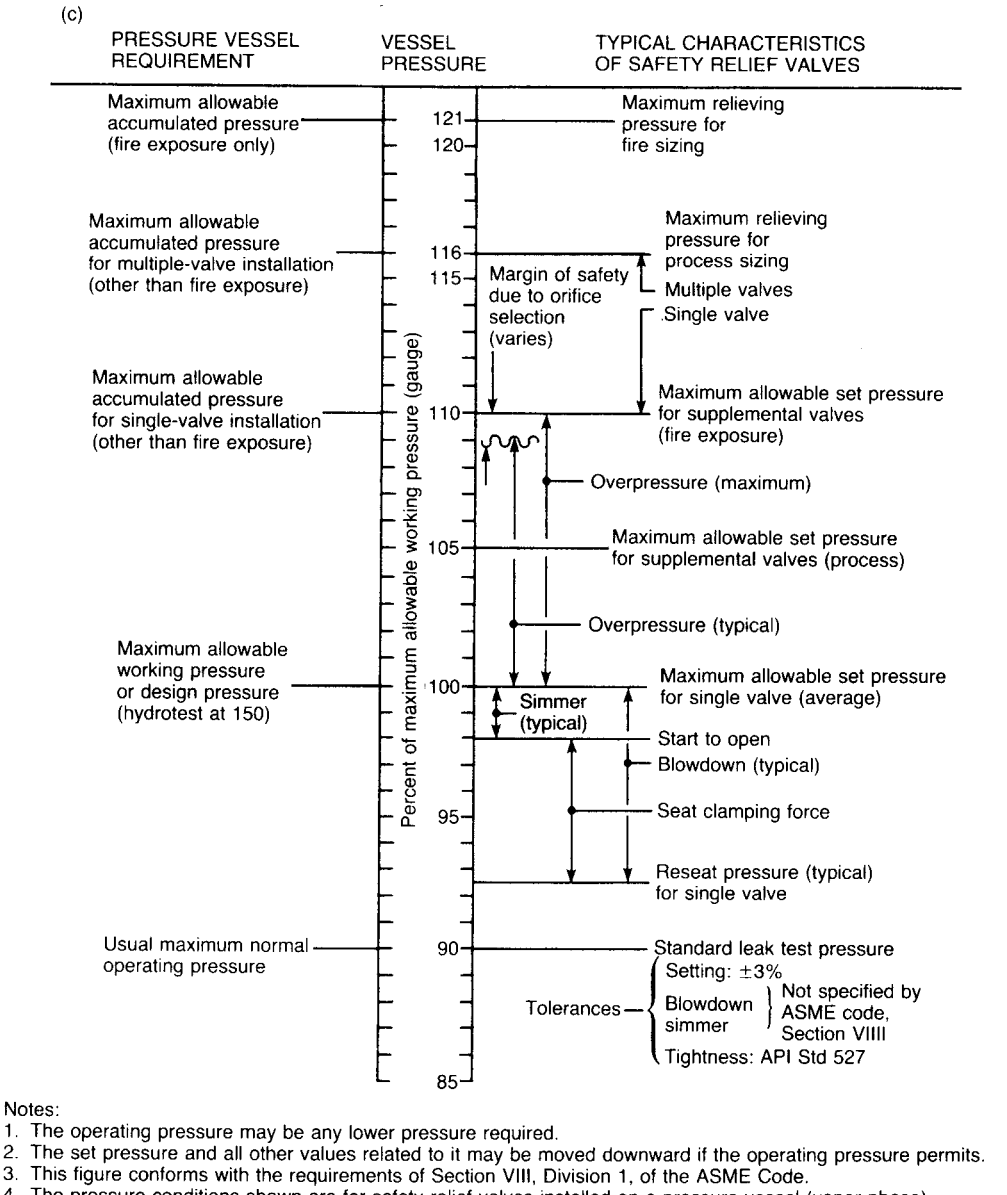


Figure 12.18 *continued*



Notes:
1. The operating pressure may be any lower pressure required.
2. The set pressure and all other values related to it may be moved downward if the operating pressure permits.
3. This figure conforms with the requirements of Section VIII, Division 1, of the ASME Code.
4. The pressure conditions shown are for safety relief valves installed on a pressure vessel (vapor phase).

Figure 12.18 *Settings for pressure relief valves: (a) safety valve with 10% overpressure for gas or vapour service (BS 5500: 1991) (Courtesy of the British Standards Institution); (b) safety valve with chosen 25% overpressure for liquid service (BS 5500: 1991) (Courtesy of the British Standards Institution); and (c) pressure relief valve for vapour or liquid service (API RP 520: 2000) (Courtesy of the American Petroleum Institute)*

with

$$C = 3.984\left[k\left(\frac{2}{k+1}\right)^{(k+1)/(k-1)}\right]^{1/2} \qquad [12.19.7]$$

where q_{mg} is the theoretical flowing capacity (kg/h/mm^2 of flow area), M is the molecular mass of gas (kg/kmol), p is the actual relieving pressure (bara), T is the actual relieving temperature (K), v is the specific volume at the actual relieving pressure and temperature (m^3/kg), Z is the compressibility factor, k is the isentropic expansion coefficient at the relieving inlet conditions and C is a parameter which is a function of that coefficient.

For air or any gas at subcritical conditions:

$$q_{mg} = pCK_b\left(\frac{M}{ZT}\right)^{1/2} \quad [12.19.8]$$

$$= 0.2883\ CK_b\left(\frac{p}{v}\right)^{1/2} \quad [12.19.9]$$

with

$$K_b = \left\{\frac{(2k)/(k-1)[(p_b p)^{2/k} - (p_b/p)^{(k+1)/k}]}{(k(2/(k+1)))^{(k+1)/(k-1)}}\right\}^{1/2} \quad [12.19.10]$$

where K_b, is the capacity correction factor for back pressure and p_b is the back pressure (bara).

For liquids:

$$q_{ml} = 1.61(\rho\Delta p)^{1/2} \quad [12.19.11]$$

with

$$\Delta p = p - p_b \quad [12.19.12]$$

where Δp is the pressure difference (bar), q_{ml} is the theoretical flowing capacity (kg/h/mm^2 of flow area) and ρ is the mass density (kg/m^3).

For dry saturated steam with a minimum dryness fraction of 0.98 or a maximum superheat of 10°C:

$$q_{ms} = 0.525p \quad p \le 110 \quad [12.19.13]$$

where q_{ms} is the theoretical flowing capacity of dry saturated steam (kg/h/mm^2 of flow area).

The coefficient of discharge K_d is the ratio of the actual to the theoretical flow capacity. A derated coefficient of discharge K_{dr} is also defined as $0.9K_d$.

12.19.4 Valve sizing: API RP 520

The relations given in API RP 520: 2000 for sizing of pressure relief valves are as follows. The critical flow pressure ratio is estimated as:

$$\frac{P_{CF}}{P_1} = \left(\frac{2}{k+1}\right)^{k/(k-1)} \quad [12.19.14]$$

where k is the ideal gas ratio of specific heats, p_{CF} is the absolute critical flow throat pressure (lb$_f$/in.^{2}) and P_1 is the absolute upstream relieving pressure (lb$_f$/in.^{2}). The code gives values of the ratio of specific heats k for a number of gases.

For critical flow conditions:

$$W = CK_dAK_bP_1\left(\frac{M}{ZT}\right)^{1/2} \quad [12.19.15]$$

or, in the form actually given

$$A = \frac{W}{CK_dP_1K_b}\left(\frac{ZT}{M}\right)^{1/2} \quad [12.19.16]$$

with

$$C = 520\left[k\left(\frac{2}{k+1}\right)^{(k+1)/(k-1)}\right]^{1/2} \quad [12.19.17]$$

where A is the effective discharge area (in.^{2}), K_b is the capacity correction factor due to back pressure, K_d is the effective coefficient of discharge, M is the molecular weight of the gas, T is the relieving temperature (°R), W is the required flow rate through the valve (lb/h), Z is the compressibility factor and C is a coefficient. The effective coefficient of discharge K_d has the value 0.975. Two further equations are also given for volumetric flows, one for air and one for gas.

The capacity correction factor due to back pressure is obtained from manufacturer's literature or from a graph given in the code; the graph is for balanced bellows pressure relief valves. The correction factor is not a means of extending Equation 12.19.15 to subcritical flow, for which separate equations are given.

For subcritical flow:

$$W = 735F_2K_dA\left[\frac{MP_1(P_1 - P_2)}{ZT}\right]^{1/2} \quad [12.19.18]$$

or, in the form given

$$A = \frac{W}{735F_2K_d}\left[\frac{ZT}{MP_1(P_1 - P_2)}\right]^{1/2} \quad [12.19.19]$$

with

$$F_2 = \left[\left(\frac{k}{k-1}\right)r^{2/k}\left(\frac{1 - r^{(k-1)/k}}{1-r}\right)\right]^{1/2} \quad [12.19.20]$$

$$r = P_2/P_1 \quad [12.19.21]$$

where F_2 is the coefficient of subcritical flow, P_2 is the absolute back pressure (lb$_f$/in.^{2}) and r is the ratio of back pressure to upstream pressure.

For liquid flow:

$$A = \frac{Q}{38K_dK_wK_v}\left(\frac{G}{P_1 - P_2}\right)^{1/2} \quad [12.19.22]$$

where G is the specific gravity of the liquid at the flowing temperature relative to water at 70°F, K_d is the effective coefficient of discharge, K_v is the viscosity correction factor, K_w is the back pressure correction factor and Q is the required flow (USgal/min). For the effective coefficient of discharge, the value should be obtained from the manufacturer; for preliminary estimates a figure of 0.65 can be used. For the viscosity correction factor, K_v, the code gives a graph. For the correction factor due to back pressure, K_w, the approach is as follows. If the back pressure is atmospheric $K_w = 1$. If a balanced bellows valve is used, the correction factor may be obtained from a graph given in the code. If a conventional valve is used, no correction is necessary.

12.19.5 Valve sizing: two-phase flow

With the publication of its seventh edition, API RP 520: 2000 includes for the first time two-phase flow sizing methods designed to include the effects of vapour generation as the fluid flows through the relief valve. The equations presented in appendix D of the code are based on the omega method of Leung (1995), which explicitly assumes both thermal and mechanical equilibrium are maintained as the fluid passes through the safety valve. RP 520 notes that these assumptions are equivalent to those made in the development of the homogeneous equilibrium model (HEM). The code makes note of the fact that the methods presented have not been validated experimentally, principally because there is no recognized procedure for certifying the flow capacity of relief devices in two-phase service.

RP 520 distinguishes among four potential types of two-phase flow scenarios, depending on the character of the fluid entering the relief valve. These are: (1) vapour and liquid at equilibrium, containing no non-condensable gas, (2) highly subcooled liquid with either non-condensable gas or condensable vapour or both, (3) subcooled liquid with no gases or vapours, and (4) subcooled or saturated liquid, with either non-condensable gas or condensable vapour or both. Mixtures (1), (3) and (4) are expected to flash as they flow through the relief valve, but mixture (2) will not flash, due to its high degree of subcooling. Having classified his fluid into one of these categories, the designer is directed to one of three procedures for evaluating the mass flux through the relief valve. Appendix D includes examples of the application of each of these three calculation procedures.

Additional discussion of two-phase flow, and of methods for calculating relevant flow rates, including the cases of relief flow and of reactor venting, appears in Chapter 15.

12.19.6 Valve sizing: safety factors

A discussion of safety factors applicable to pressure relief valves and relief systems is given in Appendix 13.

12.19.7 Valve failure

Pressure relief valves are relatively reliable equipment and the incidence of overpressure due to failure of a relief valve appears low. Accounts of pressure relief valve failure are given by Aird (1982), Maher *et al.* (1988), Crombie and Green (1994), D.W. Thompson (1994), A.B. Smith (1995) and Parr (1998). Modes of failure of pressure relief valves include:

(1) failure to open on demand
  (a) total failure to open,
  (b) opening at a pressure higher than set pressure (lifting 'heavy');
(2) opening in the absence of demand
  (a) opening at a pressure lower than set pressure (lifting 'light'),
  (b) chattering,
  (c) failure to reseat after a correct opening on demand,
  (d) leakage;
(3) disabling of valve inlet or outlet.

Failure to open is a functional failure and opening in the absence of demand an operational, or spurious, failure.

Information on the failure rates of pressure relief valves is given in Appendix 14.

API RP 576: 2000, *Inspection of Pressure Relieving Devices*, provides a detailed discussion of failure modes of both pressure relief valves and bursting discs, and provides guidance on frequency and methods of inspection and maintenance of these devices.

12.20 Overpressure Protection: Bursting Discs

An alternative pressure relief device is a bursting disc. The circumstances under which a bursting disc may be applicable are given in PD 5500: 2003 as those where the pressure rise may be so rapid that the inertia of a relief valve may be a disadvantage, where even minute leakage cannot be tolerated, or where blockage may render a valve inoperative.

The relevant standard is BS 2915: 1990 *Specification for Bursting Discs and Bursting Disc Devices*. The basics of bursting discs have been outlined in Section 12.13. In this section, consideration is given to disc set pressure, sizing and failure.

12.20.1 Bursting disc sizing: BS 2915

For a bursting disc it is usual to specify a range of pressures within which the disc will burst. Therefore, a disc has minimum, mean and maximum bursting pressures.

Equations for the sizing of bursting discs are given in BS 2915: 1990. Earlier editions of this standard contained the following treatment, given here for reference. For gas or vapour:

$$W = CKAP\left(\frac{M}{T}\right)^{1/2} \qquad [12.20.1]$$

where A is the actual orifice area (mm^2), K is the coefficient of discharge, M is the molecular weight of the gas, P is the absolute vessel pressure (bara), T is the inlet temperature (K), W is the rated capacity (kg/h) and C is a constant. For saturated steam

$$W_s = 0.535KAP \qquad [12.20.2]$$

and for air at 20°C

$$W_a = 0.85KAP \qquad [12.20.3]$$

where W_a is the rated capacity for air at 20°C (kg/h) and W_s is the rated capacity for saturated steam (kg/h). The coefficient of discharge is usually taken as 0.6 and the value of C is 2.7 for a ratio of specific heats of 1.4.

These equations have similarities with Equations 12.19.1–12.19.3.

BS 2915: 1990 gives the following relations for bursting disc sizing.

For compressible fluids:

$$Q_{mg} = A_0 pF\alpha(M/ZT)^{1/2} \qquad [12.20.4]$$

where A_0 is the required minimum cross-sectional area (mm^2), M is the molecular mass (kg/kmol), p is the relieving pressure (bara), Q_{mg} is the required flow of gas (kg/h), T is the relieving temperature (K), Z is the compressibility factor, α is the coefficient of discharge of the branch/nozzle type and bursting disc combined and F is a correction factor (described below).

For steam

$$Q_{mw} = 0.2883A_0(F/x)\alpha(p/v)^{1/2} \quad 0.9 \leq x < 1.0 \qquad [12.20.5]$$

and for saturated or superheated steam ($x = 1$)

$$Q_{ms} = 0.2883A_0F\alpha(p/v)^{1/2} \qquad [12.20.6]$$

where Q_{mw} is the required flow of wet steam (kg/h), Q_{ms} is the required flow of saturated or superheated steam (kg/h), x is the dryness fraction and v is the specific volume at the relieving pressure and temperature (m^3/kg).

The standard gives a graph for the coefficient of discharge α. The correction factor F is:

$$F = 3.984\left\{\frac{2k}{k-1}\left[(p_b/p)^{2/k} - (p_b/p)^{(k+1)/k}\right]\right\}^{1/2} \qquad [12.20.7]$$

where k is the isentropic expansion exponent and p_b is the back pressure (bara). For steam, the standard gives a graph for the isentropic exponent k.

For incompressible fluids:

$$Q_{ml} = 1.610A_0f_\mu\alpha(\Delta p \cdot \rho)^{1/2} \qquad [12.20.8]$$

where f_μ is the correction factor for liquid viscosity, Q_{ml} is the required flow of liquid (kg/h), Δp is the pressure difference (bar) and ρ is the mass density (kg/m^3). The pressure difference term should take account of any static head. The standard gives a graph for the correction factor for liquid viscosity f_μ. The coefficient of discharge has the value of 0.5 or 0.62, depending on the type of branch/nozzle; details are given in the standard.

12.20.2 Bursting disc sizing: API RP 520

API RP 520: 2000 presents two methods for sizing bursting discs used as independent relief devices. The first method is essentially identical to that used for pressure relief valves (as embodied in Equations 12.19.16, 12.19.19 and 12.19.22). The sole distinction is that for bursting disc sizing, a value of 0.62 is to be used for the coefficient of discharge K_d. Consistent with the requirements of ASME Section VIII: 2001, this method is applicable only for bursting disc installations in which:

(a) piping from the protected vessel to the bursting disc and from the disc to the atmospheric discharge location has a nominal diameter at least as large as the disc, and
(b) the bursting disc is installed within 8 pipe diameters of the protected vessel, and
(c) the length of the discharge pipe is less than 5 pipe diameters.

The second sizing method described by RP 520: 2000, is applicable to all installations in which a bursting disc is used as the sole pressure relief device. In this method, the flow capacity of the entire piping system, of which the bursting disc is one component, is calculated using accepted engineering practices. The calculation is to take into consideration the flow resistance of the bursting disc device, piping and piping components (tees, elbows, reducers, valves, etc.), and entrance and exit losses. Per ASME Section VIII, the calculated flow capacity is to be multiplied by 0.9 to determine the relief capacity of the bursting disc system. Finally, the flow resistance coefficient, K_R, of the bursting disc device is typically to be supplied by the manufacturer (who will have measured it per the certification requirements of ASME VIII). If manufacturer's data are not available, a value of 2.4 is to be used for K_R.

12.20.3 Bursting disc sizing: two-phase flow

The standards and codes described refer to, but do not give calculation methods for, two-phase flow in bursting discs. Methods for two-phase flow, including the case of reactor venting, are considered in Chapter 15.

12.20.4 Bursting disc sizing: safety factors

A discussion of safety factors applicable to bursting discs and relief systems is given in Appendix 13.

12.20.5 Bursting disc failure

Like a relief valve, a bursting disc may suffer functional or operational failures. In other words, it may fail to burst at the set burst pressure and thus fail to danger, or it may burst below that pressure and thus fail prematurely but, generally, be safe.

Some of the principal modes of failure of a conventional bursting disc are fatigue, creep and corrosion. Pulsation of the fluid pressure induces fatigue, while high temperature causes creep and contributes to fatigue.

Another type of failure is caused by blockage. Blockage may occur on the process side and may be caused by corrosion, crystallization or polymerization. It can also occur on the vent side.

Malinstallation constitutes a third type of failure. The disc may be installed upside down. Another example of malinstallation is putting more than one disc in the holder. Discs are sometimes supplied in stacks and in this case duplication may be a simple error. In other cases, the use of more than one disc is done deliberately to avoid frequent bursting, particularly during commissioning.

Reverse buckling discs are thicker and less prone to fatigue, creep and corrosion, but they have their own characteristic failures. One of these is 'roll through'. The dome of the disc becomes dented and it rolls through onto the knife but with insufficient energy to cause bursting.

In a reverse buckling disc equipped with knife blades, the condition of the knife is critical. It may suffer corrosion, cracking or blunting so that it is no longer capable of cutting. Failure of a reverse buckling disc may also occur if there is insufficient energy to cause cutting of the disc. This is particularly liable to occur on liquid systems.

Malinstallation is another type of failure with a reverse buckling disc. Again the disc may be put in upside down. This may occur where the fitter is accustomed to installing conventional discs and is insufficiently alert to the difference between the two.

Information on the failure rate bursting discs is given in Appendix 14.

12.21 Overpressure Protection: Installation of Relief Devices

In addition to the factors already considered, it is necessary in the design of a relief system to pay close attention to the installation of the relief devices. The installation of relief

devices is treated in API RP 520 Pt II, the CCPS *Engineering Design Guidelines* (CCPS/13), the IChemE *Relief Systems Guide*, and the CCPS *Relief Systems Guidelines* (CCPS/NN).

12.21.1 API RP520: Part II

A prime source of guidance on the installation of relief devices is API RP 520 Pt II: 1994 *Sizing, Selection and Installation of Pressure-relieving Devices in Refineries*, Part II, *Installation*. This deals with the following topics: (1) general, (2) inlet piping, (3) discharge piping, (4) isolation valves, (5) bonnet or pilot vent piping, (6) drain piping, (7) valve location and position, (8) bolting and gasketing, (9) multiple pressure-relieving devices with staggered settings, and (10) pre-installation handling and inspection.

12.21.2 Inlet piping to pressure relief valves

A pressure relief valve should be mounted directly on the vessel which it protects at a dedicated nozzle unless there is good reason to do otherwise. Similar considerations apply to bursting discs.

Cases where a pressure relief valve may be positioned at some short separation from the vessel include those where this improves access, allows the valve to be put outside the insulation, reduces the valve temperature, minimizes the vibration to which the valve is subject, or permits improved drainage of the discharge pipework.

Where a pressure relief valve is connected to the vessel by piping, the desirable features of this piping are that it should be short, full bore, vertical and self-draining with low pressure drop and exerting minimum stress on the equipment.

12.21.3 Reaction force from pressure relief valve discharge

The reaction forces due to discharge from a pressure relief valve can be appreciable and need to be allowed for in the design. Accounts of reaction forces are given in API RP 521 Pt II: 1994 and the IChemE *Relief Systems Guide* and by Moody (1969, 1973), Stikvoort (1986), Huff (1990, 1991), Hansen (1991), and Leung (1992, 1998).

API RP 520 Pt II gives a relationship for the reaction force for the case where the pressure relief valve is mounted vertically with its discharge entering a pipe which runs a short distance horizontally, then through a 90° elbow, and vertically upwards. The equation is:

$$F = \frac{W}{366}\left(\frac{kT}{(k+1)M}\right)^{1/2} + A_0 P_2 \qquad [12.21.1]$$

where A_0 is the area of the outlet at the point of discharge (in.^{2}), F is the reaction force (lb$_f$), k is the ratio of specific heats of the gas, M is the molecular weight of the gas, P_2 is the static pressure at the point of discharge (lb$_f$/in.^{2}), T is the absolute temperature (°R) and W is the mass flow of gas (lb/h). The reaction force is exerted downwards on the horizontal section. The code shows a support between this section and the vessel.

12.21.4 Isolation of relief devices

There are certain circumstances in which it would be convenient to be able to isolate a relief device on an operating vessel. This is particularly the case where the device needs to be removed for maintenance. Any such isolation is restricted by regulatory requirements and by good practice.

In British legislation, as described in Section 12.12, steam boilers and air receivers have long been subject to specific requirements. It has not been permitted even to install an isolation valve between a steam boiler and its safety valve. For air receivers, BS 1123: Part 1: 1987 permits the installation of an isolation valve between the vessel and its safety valve, provided (1) that the source of supply is also isolated by the same valve and (2) the receiver is fitted with a fusible plug. For process vessels, the installation of an isolation valve between the vessel and its relief valve without further precaution is regarded as bad practice.

BS 5500: 1991 does, however, provide in appendix J for installation of isolation valves subject to the following conditions: 'Intervening stop valves or cocks may be installed provided that they are so constructed and controlled by mechanical interlocks that a limited number only can be closed at any one time and that those stop valves or cocks which remain open are adequately sized to permit the unaffected pressure relieving devices to discharge at the required capacity for the vessel'. Thus, there must be at least duplicate pressure relief valve systems and there must be a mechanical interlock between the two systems.

ASME Section VIII specifies that there shall be no intervening stop valves between a vessel and its relief device except when (1) the stop valves are constructed or positively controlled such that closing the maximum number of stop valves at one time will not reduce the available relief capacity below the required value, or (2) the stop valve is installed for inspection or repair purposes only, is installed such that it can be locked or sealed open, and shall be closed only by an authorized person who shall remain stationed at the stop valve during the period of the vessels operation while the valve remains closed and who shall relock or reseal the valve open before leaving that station.

The fitting of an isolation valve on a single relief device is permitted in some companies, provided that there are strict administrative controls. A case in point might be the fitting of an isolation between a liquid relief device and the space protected. It may be a condition of such exemption that it be shown by hazard assessment that the probability of a demand during the period of valve isolation is acceptably low.

The requirements of the Pressure Systems Regulations 1989 given in Regulation 4(5) have been quoted in Section 12.12. Guidance is given in COP 37: 1990. This states: 'every plant item in which the pressure can exceed the safe operating limit for pressure should be protected, whenever operational, by at least one pressure relieving or pressure limiting device.'

12.21.5 Overpressure protection: design basis documentation

The design basis of a process unit's pressure relief system is widely recognized as a key element of the unit's process safety information (see Chapter 6, and CCPS nn/YYYY, OSHA 29 CFR 1910.119, EPA 40 CFR 68). The US EPA, in guidance materials for its Risk Management Program (EPA, 'General Guidance for Risk Management Programs' (40 CFR Part 68)), has defined the relief systems design basis in the following manner:

> Design basis means documenting how the loads and sizes of the relief system, as well as inlet and outlet sizes, were determined. This includes a description of overpressure scenarios considered, the scenario that creates

the largest load to be relieved, the assumptions used, and if the device meets a certain code. . . . Industry codes (e.g. API RP 520) also provide guidance on scenarios that should be considered and on equations for sizing of devices.

In documenting pressure relief systems, Berwanger and Kreder, (Kreder and Berwanger, 1995; Berwanger and Kreder, 1998) have argued that an equipment-based rather than a relief-device-based approach is necessary, giving two central reasons. First, the purpose of the relief system is to ensure that the entire process unit – that is, every pressure-containing component – is protected against potential overpressure. Accordingly, the rationale for each equipment item's need for – or lack of need for – overpressure protection must be documented. Second, having the relief device, with its specification and purchase, be central to the documentation of the relief system design has traditionally placed exclusive emphasis on documentation of the 'worst-case' overpressure scenario. Subsidiary cases that may have been considered in the original system design are documented insufficiently, or not at all (particularly when the relief device specification sheet is the only piece of documentation that is maintained). When process changes are considered years after original commissioning, these subsidiary cases may become governing. Because of their poor or missing documentation, these cases are then overlooked by plant engineers – rarely experts in relief system design – contemplating the consequences of the process change under consideration.

As evidence of the need for an equipment-based approach, Berwanger and Kreder cite statistical analysis of their findings in detailed revalidations of the pressure relief systems in over 400 process units in the chemicals, refining, and oil production sectors of the process industries during the period 1994 through 2002 (Berwanger *et al.,* 2000; Berwanger, 2002). These studies reviewed the overpressure protection of some 42,000 equipment items, provided by approximately 25,000 relief devices. Evaluating these relief systems against design standards specified by the owner/operators of the process units, these studies found that 12% of the equipment items analysed were left unprotected against one or more credible overpressure scenario. These results are in substantial agreement with those of Parr (1998), who reports one study in which 25% of the relief systems evaluated were found to be inadequately documented (i.e. the basic purpose of the design was unclear), and another study in which UK HSE personnel over a 10-year period found that nearly 40% of reportable pressure systems incidents were associated with equipment not fitted with a relief valve. Berwanger *et al.* (2000) note that nearly all of the process units in their studies found to have unprotected equipment had recently undergone Process Hazard Analysis (PHA) studies, and conclude that this finding is attributable to the 'traditional' approach of documenting the adequacy of each relief device. The authors reiterate the need for a paradigm shift to documenting the adequacy of the protection of each plant equipment item.

The core purpose of the relief system design basis documentation is two-fold: (1) to ensure that the entirety of the process unit is adequately protected against all credible sources of overpressure, and (2) to ensure that this design basis information is available to all interested parties throughout the operating life of the unit. These goals may be satisfied if the documentation captures the analysis process of the original designers of the unit's pressure relief system. The key steps in this design process given by Kreder and Berwanger (1995) are:

(a) for each equipment item, identify all potential scenarios that can credibly lead to overpressure; for these, and for commonly occurring scenarios that may have been deemed not credible, document the rationale for the identification of the scenario as potentially causing overpressure (or not)
(b) for each overpressure scenario identified as credible in (a), calculate the required relief flow rate
(c) for each flow rate calculated in (b), specify a relief device with the set pressure, flow capacity, and installation location required to protect the associated equipment item(s) against overpressure.
(d) for each credible overpressure scenario and combination of scenarios, ensure that the relief devices are equipped with effluent handling systems to dispose safely of the relief streams while not compromising the performance of the relief devices.

The Process Safety Management committee of the DIERS Users Group has recommended a list of information to be included in all pressure relief system documentation (Lee, 1996). In addition to data concerning the individual relief device, the equipment it protects, and the inlet and outlet piping associated with the device, the list includes 'summary of all relief cases considered, including the worst credible design case', and a description of 'containment, handling, and treatment of relief device effluents'.

12.22 Flare and Vent Systems

A principal method of disposal of gases and vapours discharged from the process is flaring. The function of a flare system is generally to handle materials vented during (1) normal operations, particularly start-up and (2) emergency conditions.

Guidance on flare system design is given in API RP 521: 1990, on which much of the other literature draws heavily. Accounts of flare systems are given in *Flare Gas Systems Pocket Handbook* (Bannerjee, Cheremisinoff and Cheremisinoff, 1985), the CCPS *Engineering Design Guidelines* and the IChemE *Relief Systems Handbook* and by Bluhm (1961, 1964b), Husa (1964), G.R. Kent (1964, 1968, 1972), P. Peterson (1967), Tan (1967a,b), Kilby (1968), Seebold (1984), Straitz (1987), Swander and Potts (1989) and Tite, Greening and Sutton (1989).

12.22.1 Types of flare system

There are three main types of flare system: (1) elevated flare, (2) ground flare, and (3) low pressure flare. The last two are described first.

12.22.2 Ground flares

A ground flare generally consists of a battery of tubular burners contained in a short refractory-lined stack, which serves as combustion chamber and windshield. The bottom of the stack is above grade so that the combustion air can enter. Typically, this air inlet is provided with a louvred shield to maintain flame stability and masks the glare from the flame; the stack is circular or square in cross-section

and it is set inside an octagonal windshield. The elements of a ground flare system are knockout drum, seal drum, burner system, ignition system, stack and windshield.

In one design of ground flare systems, the height H of the stack is about $0.3D$, where D is the diameter of the combustion chamber, and the bottom of the stack wall is also about $0.3D$ from grade. Other designs of ground flare are described by Swander and Potts (1989), who give illustrations of designs ranging from a completely open flare to one with a quite high stack. There are also variations in the number of burners, some low volume ground flares having just a single burner. Details of ground flare systems are given in the IChemE *Guide*.

A ground flare may be favoured where there is a limitation on the height of the flare which can be installed. Insofar as the products of combustion are discharged relatively close to ground level, a ground flare is not suitable if these gases are noxious or pollutant. Flare glow and noise may also be limiting factors.

12.22.3 Low pressure flares

There are in process plants various low pressure units which may produce an off-gas stream. These include storage tanks, and oil–water separator and wastewater treatment units. These off-gases may be routed to a low pressure flare. The tightening of controls on the emission of volatile organic compounds increases the number of situations where a low pressure flare may be needed. There are available a number of designs of low pressure flare such as small 'stick' flares.

The principal problems and hazards of a low pressure flare arise from the fact that the pressure in the discharging unit may be barely sufficient to maintain the flow. The pressure drop in the low pressure header should be calculated with care and the header adequately sized. Not all computer programs used for header design are suitable for this case, and it may be necessary to resort to hand calculation.

Where the discharge source pressure is insufficient, use may be made of a blower installed in the off-gas line. The use of an off-gas blower, however, is not an ideal arrangement in that it introduces rotating equipment which may fail and which may have the potential to act as a source of ignition. Designs based on off-gas blowers are discussed in the CCPS *Guidelines*.

12.22.4 Elevated flares

Elevated flares are used to handle both normal and emergency loads and are generally the system of choice except where environmental considerations prevent their use. An elevated flare is a normal feature of a refinery or a petrochemical plant.

A flare system consists of a flare stack and of gathering pipes which collect the gases to be vented. Other features include the flare tip, which typically has steam nozzles to assist entrainment of air into the flare, seals installed on the stack to prevent flashback of the flame and a knockout drum at the base of the stack to remove the liquid from the gases passing to the flare.

A typical elevated flare system is illustrated in the widely quoted diagram from API RP 521 shown in Figure 12.19. The elements of this system are gas collection pipework, knockout drum, seal drum, flare stack, flare tip, molecular seal, ignition system, steam injection system and purge system.

12.22.5 Flaring policy

The type of flare system required and the associated hazards depend very much on the venting and flaring policies adopted. Thus, for example, the decision to vent certain cold columns of an ethylene plant direct to the atmosphere can greatly reduce the size of the system and avoid the need to use the special steels required to handle cold gases.

The emergency load on the flare is highly dependent on factors such as the extent to which trip systems are used to reduce the frequency of discharges from pressure relief valves and on the staggering of such discharges.

Descriptions of practice in flaring include those given in the CCPS *Guidelines*, and the IChemE *Guide*, and by Barker, Kletz and Knight (1977), Bonham (1977), R. Schwartz and Keller (1977) and Straitz *et al.* (1977).

12.22.6 Flare system hazards

There are a number of hazards associated with a flare system. These include (1) failure of the collection system pipework due to low temperature embrittlement or corrosion, (2) obstruction in the flare system, (3) explosion in the flare system, (4) heat radiation from the flare, (5) liquid carryover from the flare, and (6) emission of toxic materials from the flare.

Even if these features are not such as to present a hazard, the latter three may be environmentally objectionable. Other features which cause environmental problems are (1) smoke in the flare, (2) glare from the flare, and (3) noise from the flare.

12.22.7 Flare collection system

The collection system which gathers the gas and vapour to be flared may comprise a single system or a set of systems in which different types of stream are segregated. Brittle fracture of the pipework in the gathering system is a hazard if the temperature of the steel is taken below its transition value. It may be necessary to use stainless steel in parts of the pipework where this condition may occur. Stainless steel may also be required for highly corrosive gases. The use of such steel is expensive, however, and the amount used is kept to a minimum. The extent to which stainless steel is required depends on the discharge and segregation policies adopted.

The CCPS *Guidelines* distinguish the following cases: (1) cold gas, (2) intermediate gas, (3) hot gas and (4) sour gas. Typical cold gas is ethane and lighter hydrocarbons flashing at or below $-45°C$. The material of construction used for the header is commonly austenitic stainless steel. Most gaseous effluents are hot wet gases above $0°C$ which are generally collected in a header made of carbon steel. Liquid droplets are separated in the knockout drum. A third class of gaseous effluent is cold dirty gases at a temperature intermediate between 0 and $-45°C$. For these use is frequently made of a header constructed in killed carbon steel.

Certain processes give rise to sour gas streams containing appreciable concentrations of hydrogen supplied which are toxic and corrosive. A sour gas stream is often provided with its own header, made of stainless steel. This segregation avoids the use of an expensive steel for the whole gas collection system. Frequently a separate flare is also used, which gives better control of the flaring.

Separate collection systems may also be provided for low and high pressure gas streams. The size of the system is generally governed by the low pressure streams, but if the system is to take all the discharges, it must be designed for

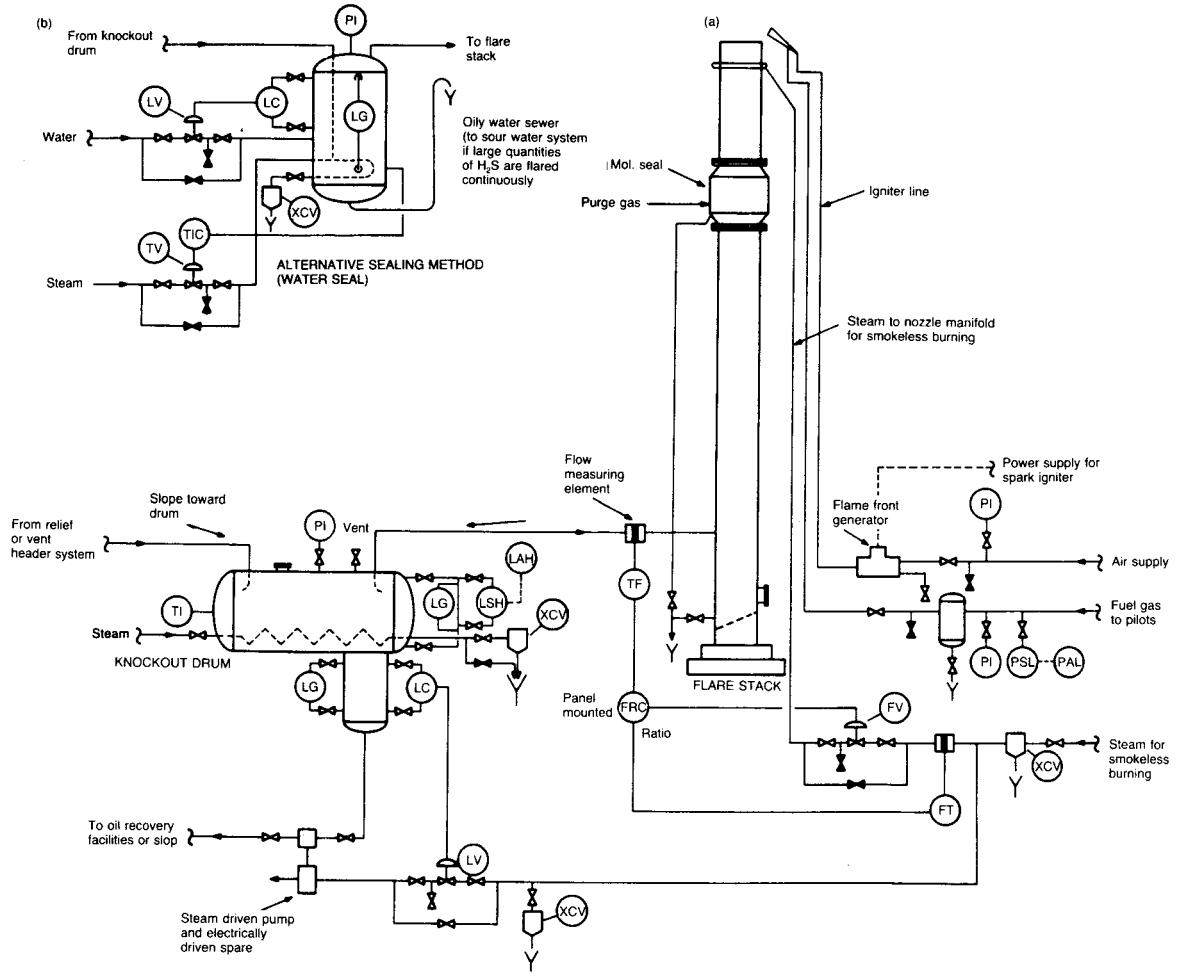


Figure 12.19 *Typical flare system (American Petroleum Institute, 1990 API RP 521): (a) flare system; and (b) alternative sealing system. Note: this figure represents an operable system arrangement and its components. The arrangement of the system will vary with the performance required. Correspondingly, the selection of types and quantities of components, as well as their applications, should match the needs of the particular plant and its specifications. FRC, flow recorder controller; FT, flow transmitter; FV, flow valve; LAH, level alarm (high); LC, level controller; LG, level gauge; LSH, level switch (high); LV, level valve; PAL, pressure alarm (low); PI, pressure indicator; PSL, pressure switch (low); TIC, temperature indicator controller; TV, temperature valve; XCV, steam trap*

the highest pressure which it could experience. It can be more economic to use a separate high pressure collection system with smaller piping.

Elements of the collection system are the various relief headers, the piping from the individual valves discharging into these headers and the flare header connecting these relief headers to the flare itself.

12.22.8 Flare system

The flare system consists of the collection system, the liquid knockout and seal drum system, the flare assembly and the ancillary equipment. The collection system is described in the next section. The flare assembly comprises the flare stack itself and the associated components, notably (1) the flare tip, (2) the pilot burners, (3) the pilot igniters, and (4) the steam injection system. Between the collection system and the flare stack comes the knockout and seal drum system. This typically includes a knockout drum and a seal drum, and may also have a quench drum.

12.22.9 Flare stack

The flare stack itself is tyically self-supporting or supported by guy wires. Associated components are (1) the flare tip, (2) the pilot burners, (3) the pilot igniters, (4) the steam injection system, and (5) the flame monitoring instrumentation.

The process design of the flare stack is essentially the determination of the stack height and diameter. API RP 521 gives one design method. The stack height is basically governed by the heat radiation from the flare, which is described below.

The stack diameter is set by the gas velocity. API RP 521 suggests that the design aim for a flare tip Mach number of 0.2 at normal gas flows and 0.5 for short, infrequent peak flows. It also states that a smokeless flare should be sized for the conditions under which it will operate smokelessly.

Flare stack conditions are discussed further in Chapter 16. Discussion of the other elements in the flare system is deferred until the flare stack obstruction and explosion hazards have been considered.

12.22.10 Flare system obstruction

Obstruction of the flare system is a hazard which can occur in a number of ways. One is the blockage of devices such as flame arresters and molecular seals. Another is the freezing of water seals in cold weather.

In some flare systems steam is injected at the base of the stack. The combination of contact with a cold gas such as ethylene and of cold weather may cause the water injected to freeze. There may also be other fluids in the flare system which are liable to freeze in cold weather. Freezing points of two common hydrocarbons are: benzene 5°C and cyclohexane 6.5°C.

The solidification of heavy oils can create blockage. Blockage can also be caused by refractory debris at the base of the flare stack, unless this is catered for in the design.

12.22.11 Flare system explosion

In a flare system there is a hazard that air will enter and form a flammable mixture. The hazard is particularly serious, because a source of ignition is always present in the form of the flame on the flare tip. Air may enter the flare system due to factors such as open valves or corrosion, or by diffusion down from the flare tip when the flame is not operating.

There are three specific conditions which are conducive to entry of air into the flare stack. One is when flaring has just ceased and cooling and shrinkage of the gas column in the stack draws air in. Another is when the gas being flared is light, especially if it is hydrogen, so that the pressure at the bottom of the stack is lower than atmospheric and air may enter through any apertures. The third is when the flare stack creates a natural draught and air leaks in at the bottom.

The precautions taken against the hazard of an explosion in a flare system divide into those aimed at avoiding a flammable mixture, such as (1) use of purge gas, (2) elimination of leaks, (3) monitoring the oxygen concentration, and those directed to mitigating the results of any ignition which may occur, such as (4) the use of flame arresters. Associated measures include the use of (5) molecular seals and (6) seal drums.

The discharge of waste gas to the flare system is inevitably somewhat erratic. If the gas flow falls too low and if there are air leaks into the system, a flammable mixture may form. Also if the gas flow is too low, the flame may go out, flash back down the stack or start pulsating. It is common practice, therefore, to maintain the gas flow in the flare system. This purge is usually a fuel gas. A method of calculating the purge gas rate is given by Husa (1964).

The best approach to the prevention of explosions in flare systems, however, is to prevent air from getting into the system in the first place and to monitor the oxygen content to check that this has been achieved. The elimination of air inleak into the pipework should be a specific objective. The prevention of air inleak through open valves is particularly important.

Air may also enter the system by diffusion down the stack when the flare is not operating. A molecular seal is often installed to prevent this. The use of molecular seals (described below) effects a large reduction in the purge gas flow required to prevent air diffusion down the stack.

The oxygen concentration in the flare system should be monitored. This is necessary in order to ensure that a large air inleak does not develop undetected.

The elimination of air inleak by the measures just described is preferable to the use of large purge gas flows to dilute such inleak. Devices which are used to guard against flashback of the flame down the stack are flame arresters and water seals.

12.22.12 Seal drums

A device widely used to prevent ingress of air from the flare stack into the gas collection system is a seal drum in which the gas passes through a water seal. API RP 521 gives one design for a seal drum together with the method of sizing. The IChemE *Guide* gives further design details.

A seal drum is generally designed for an internal pressure of at least 50 psig in order to withstand an internal explosion. Two problems with water seals are the creation of an uninterrupted gas passage through the water at high gas flows, which can render the seal ineffective, and the tendency to surge, which can affect operation of the flare. Proprietary water seals are available which are designed to overcome both these difficulties.

Another difficulty with water seals is the loss of the water from the seals. A further disadvantage of water seals is that they tend to freeze in cold weather. This problem is sufficiently serious that some operators prefer not to use them at all.

12.22.13 Molecular seals

A molecular seal is a device designed to limit the rate at which air can flow back into the flare stack. The principle of operation is to make the air flow through a set of concentric tubes in which it suffers reversals of direction so that its flow is reduced. A molecular seal is best located close to the top of the stack.

The benefit of a molecular seal is economy of purge gas. Molecular seals have the disadvantage that they tend to block up. One cause of blockage is corrosion products from the stack. Another is blockage by water or ice. In cold climates, prevention of ice formation requires the use of heating.

12.22.14 Flashback arresters

One common device for preventing passage of a flame along a pipe or stack is the flame, or flashback, arrester. A disadvantage of flame arresters is the tendency for the small passages to become obstructed. This problem is sufficiently serious that some companies do not use them.

12.22.15 Flare combustion and smoke control

Brzustowski and co-workers (Brzustowski, 1973, 1977; Brzustowski and Sommer, 1973; Brzustowski *et al.*, 1975) have studied the fundamentals of combustion in flare systems. Efficient combustion in the flame depends on achieving good mixing between the fuel gas and the air, and avoidance of a pure diffusion flame. Failure to achieve efficient combustion results in a smoky flame.

There are various methods which are used to promote efficient combustion. One of the principal methods is steam injection. The main function of the steam is to increase the entrainment and mixing of the air. The steam also takes part in the water gas shift reaction

$$C + H_2O = CO + H_2$$

and the steam reforming reaction

$$C_xH_y + H_2O = xCO + zH_2$$

Alternatively, low pressure air may be used to assist the entrainment and mixing of the atmospheric air.

There are available a number of proprietary flare tips for steam injection. One which is widely used is the Zink S type, which has a ring of small jets around the tip of the flare.

The equation given in API RP 521 for the amount of steam injection required to give a smokeless flare is that of Tan (1967):

$$W_{st} = W_{HC}\left(0.68 - \frac{10.8}{M}\right) \quad M > 16 \qquad [12.22.1]$$

where M is the molecular weight of the gas, W_{HC} is the mass flow of hydrocarbons (kg/s) and W_{st} is the mass flow of steam (kg/s). This is based on maintaining a steam/CO_2 mass ratio of about 0.7.

The control of the state of the flame by the manipulation of the steam supply has traditionally been done by the process operator relying on visual observation. Automatic control is difficult, because it is not easy to obtain a good measure of the state of the flame. One automatic system now in use is based on the measurement of the heat radiation at the root of the flame, where the difference in the heat radiated by a smoky and by a non-smoky flame is particularly pronounced.

There are a number of problems involved in achieving positive ignition and in retaining a flame on the flare tip as well as in preventing flashback. These problems are particularly difficult where the turndown ratio is high, which is often the case.

12.22.16 Flare heat radiation

The flare stack radiates intense heat which constitutes a potential hazard. The flame on a flare stack is often several hundred feet long and has a heat release of the order of 10^7 BTU/h. There is intense heat radiation from a flare. It is generally necessary, therefore, to have an area around the flare in which people do not normally work. A large flare can thus sterilize a sizeable area of land. It may be acceptable in some cases, however, to locate certain types of equipment within the flare compound, provided that the time which personnel have to spend in the compound is strictly limited.

Methods of caculating the heat radiated from a flare are given in API RP 521: 1990. This code gives the following equation based on the work of Hajek and Ludwig (1960):

$$D = \left(\frac{\tau F Q}{4\pi K}\right)^{1/2} \qquad [12.22.2]$$

where D is the distance from the centre of the flame, F is the fraction of heat released which is radiated, K is the allowable intensity of heat radiation, Q is the net heat release rate and τ is the atmospheric transmissivity.

Combustion in the flare is a complex process. In Equation 12.22.2 this complexity is subsumed in the factor F. This factor has traditionally been taken as a property of the fuel only. Some typical values of F are:

Gas	*F*	*Reference*
Methane	0.16	Brzustowski and Sommer (1973)
Propane	0.33	G.R. Kent (1964)
Butane	0.30	Brzustowski and Sommer (1973)
Ethylene	0.38	Brzustowski and Sommer (1973)

It has been shown, however, that the F factor depends also on other features of the flame such as the Reynolds number. The F factor is discussed by Brzustowski (1977) and Straitz *et al.* (1977).

Models of the flame on a flare are considered in Chapter 16.

Guidance on the permissible level of heat radiation from a flare in different situations is given in API RP 521 and BS 5908: 1990. Further discussions of acceptable levels of heat radiation are given by G.R. Kent (1964), R. Schwartz and Keller (1977) and Straitz *et al.* (1977). This aspect is considered in Chapter 16.

12.22.17 Liquid carryover in flares

Liquid carryover from the flare stack may result in a more smoky flame, in dispersion of burning drops of flammable material or dispersion of drops of toxic material. Liquid drops as small as 15 μm can negate the devices used for smokeless operation and give a smoky flame. The principal means used to prevent liquid drops reaching the flame is

the use of a knockout drum at the base of the stack. It is sometimes difficult, however, to eliminate completely spray and condensation.

12.22.18 Toxics in flares

In some flares, gases containing materials such as chlorine and sulfur are burned, giving compounds such as HCl and SO_2. In such cases the flare stack should be sufficiently high to prevent unacceptable ground level concentrations of these toxic gases.

12.22.19 Flare environmental problems

Smoke, glare and noise from a flare are environmentally objectionable. The elimination of smoke has already been discussed. There is relatively little which can be done to eliminate light from the flame. If this is a serious problem, it may be necessary to use a low level enclosed burning system instead of a flare. Flare noise is discussed in Appendix 12.

12.22.20 Combined flare systems

In some installations, the flaring arrangements consist of an elevated flare combined with a ground flare. Normal operating and start-up loads are handled by the ground flare, while both flares are used to handle the relatively infrequent high volume emergency loads. In this way the environmental impact of the flaring is kept to a minimum.

12.23 Blowdown and Depressuring Systems

The response to a plant emergency may require the disposal of hazardous inventories. This is effected by the emergency blowdown and depressuring systems.

12.23.1 Blowdown systems

Disposal of liquid streams in an emergency is through the blowdown system. An emergency blowdown system has two basic features: treatment and disposal. An account of blowdown systems is given in the CCPS Engineering Design Guidelines.

Fluids which may require disposal are, in general, streams containing volatile organics or mixtures of volatile organics and water. More specific cases are reaction fluids vented from a reactor and cooling water contaminated with organics following a tube burst in a heat exchanger where the process fluid is at the higher pressure. The streams to be disposed of may contain flammable, toxic, corrosive or pollutant substances.

Blowdown streams may be unsuitable for immediate disposal, and may therefore require treatment. Principal types of treatment are disengagement of gases and vapours from liquid, and quenching to cool and partially condense hot vapours.

Disengagement is effected in a disengagement drum. The CCPS *Guidelines* refer to the API RP 521 knockout drum design. In a typical disengagement operation, involving a mixture of organics and water, the vapour is sent to a flare and the organic and water phases are separated by gravity in the drum.

Quenching is carried out in a quench nozzle, a quench drum or a blowdown drum. In a quench nozzle, water is injected to effect at least partial condensation of the blowdown fluid. In a quench drum, condensation of the blowdown fluid is effected by spraying water or other liquid onto it. The CCPS *Guidelines* refer to the API RP 521 quench drum design (figure D-2).

A blowdown tank is charged with an inventory of solvent through which the blowdown fluid is sparged, effecting condensation. The design of blowdown tanks for high rate releases of short duration has been discussed by Fauske and Grolmes (1992).

The sinks to which the liquid effluent part of a blowdown stream may be sent include a clean water sewer, an oily water sewer, a closed drain header and a tank for further treatment. The CCPS *Guidelines* give a detailed discussion.

12.23.2 Depressuring systems

Disposal of vapours from equipment at pressures below those of the pressure relief devices is by means of the emergency depressuring system. Depressuring is used to reduce hazard by removing vapour or gas from an equipment. This may be necessary where the equipment may fail at a pressure below the set pressure of the pressure relief valve, as in fire engulfment of a vessel which is filled with gas or one which contains some liquid but in which part of the walls is unwetted. Another situation where depressuring may be appropriate is where there may be benefit in anticipating the operation of the relief, as in the depressuring of a reaction runaway. A third case is where the equipment pressure is very high (say, 1000 psig) where depressuring reduces both the inventory and the stress in the equipment.

12.24 Pressure Containment

An alternative to pressure relief is pressure containment. This may be effected by ensuring that the system is sufficiently strong that any pressure generated is contained. This approach is currently applied only to a relatively limited extent. A discussion of the potential for wider application is given by Wilday (1991).

12.24.1 Problems of pressure relief

Protection against overpressure by the provision of pressure relief has a number of disadvantages. In general, pressure relief involves the use of an active system which is subject to failure and has to be inspected and maintained, and which may operate spuriously.

Pressure relief creates the problem of relief disposal. Environmental pressures make this an increasingly onerous matter. The basis for the design of the disposal train is often not well defined. The demands on the disposal train will be rare and its reliability in responding to them uncertain.

In some cases pressure relief is not a practical option. This is the case, for example, where the vent area on a reactor is simply too large to fit on the vessel.

12.24.2 Inherently safer design

The containment approach to overpressure protection requires that all the potential sources of overpressure be identified. Generic sources include (1) flow in, (2) momentum effects, (3) heat input, and (4) chemical reaction.

Likewise, in principle, it is necessary to identify all the potential sources of underpressure. Generic causes of underpressure include (1) flow out, (2) heat removal, and (3) chemical reaction. However, vacuum-causing events, such as vapour condensation, are often difficult to quantify. Thus in the case of underpressure the practical approach is

often to design for full underpressure. The pressure deviation scenarios, including combinations, should then be considered and a credible worst case determined as the basis of design.

Design for full overpressure is assisted if sources of overpressure can be designed out. Wilday (1991) gives as examples (1) heat exchanger tube failure, (2) process heating, and (3) runaway reactions. A heat exchanger with high pressure gas in the tubes and liquid in the shell can present a difficult case for pressure relief. If the design is to be based on the common assumption of full bore rupture of a single tube, a large two-phase flow may be generated and the pressure relief requirement is severe. One solution may be to eliminate the pressure differential by raising the liquid pressure.

Other aspects of heat exchanger tube failure considered by Wilday include the use of a non-reactive cooling medium to eliminate reaction between the material cooled and cooling water and the merits of using air-cooled heat exchangers.

In the heating of a liquid, the total pressure due to the vapour pressure of the liquid and the partial pressure of non-condensable gases can be high. Methods of dealing with this problem include the use of a lower vapour pressure liquid, the provision of adequate gas space, the limitation of the heat input, the prevention of isolation of the equipment, and the use of a sufficiently high design pressure.

The measures suggested for avoidance of high pressure in reactors include laboratory screening to identify reaction exotherms and decompositions, use of a low vapour pressure solvent, avoidance of accumulation of reactants, use of a semi-batch configuration with one component fed continuously, and provision of a trip to cut off the feed.

12.24.3 Safety instrumented systems

One approach to the elimination of sources of overpressure is the use of safety instrumented systems. The use of such systems as an alternative to pressure relief is relatively limited and generally subject to strict conditions. Several international standards for the criteria and methods for the design and application of these systems have recently been promulgated by the ASME (Code Case 2211, 1996), the ISA (S84.01, 1996), and the IEC (IEC 61511, 2003). Guidance is provided by CCPS (2001/MM), Karcher *et al.* (1996).

The use of an instrumented protective system requires that all the sources of high pressure be identified and protected against. Another problem is that such a system is an active one, with the disadvantages already mentioned. Nevertheless, where the pressure relief option also poses severe difficulties, as in some reactor relief situations, there has been considerable interest in the use of instrumented protective systems. Work on the options for overpressure protection of reactors is described in Chapter 11.

Examples of the use of instrumented protection given by Wilday are (1) the protection of plant downstream of a pressure letdown valve by a trip which shuts a trip valve and (2) the protection of a reactor by a trip which shuts off the feed.

IEC 61511, *Functional Safety – Safety Instrumented Systems for the Process Industry Sector* is published in three parts. Part 1 provides the overview and core of the standard; it is entitled *Framework, Definitions, System, Hardware and Software Requirements*. It is divided into 19 sections, which deal with issues such as safety life cycle requirements, process hazard and risk analysis, allocation of safety functions to protective layers, SIS safety requirements specification, SIS design and engineering, factory acceptance testing, and SIS installation and commissioning, safety validation, operation and maintenance, modification, and decommissioning. This overview document describes the framework of the standard and the relationship between IEC 61511 and IEC 61508.

Part 2, referred to as 61511-2, is titled *Guidelines for the Application of 61511-1*. It has an organizational structure that is clause-by-clause identical to that of 61511-1, so as to provide clear, concise guidance on the application of that Part 1.

Part 3, 61511-3, is called *Guidance for the Determination of the Required Safety Integrity Levels*, and is divided into only three sections – scope, terms and definitions, and risk and safety integrity – general guidance. It also contains six informative annexes.

12.24.4 Problems of, and scope for, containment

Containment also has its problems. One general problem is protection against external fire. If a vessel is engulfed in a fire it is liable to fail due to overtemperature of the metal, even though the normal failure pressure has not been attained. There may also be additional hazards such as a liability of the material held to decompose.

There are certain measures which may be taken in some cases to limit the degree of potential fire exposure such as elimination or reduction of flammable materials near the vessel, provision of fire insulation and, possibly, location of the vessel above the level at which flame impingement could occur, but the overall conclusion is that it is very difficult to protect against external fire by containment.

There are certain types of equipment, such as atmospheric storage tanks, to which overpressure protection by containment is not applicable. The same applies to certain reactors. Wilday suggests that a plant protected solely by containment would be likely to be designed for a relatively high pressure and for full vacuum and would require to be engineered so as effectively to eliminate the external fire hazard or the need for fire relief. However, even if a policy of full containment is not adopted, the principles described may be used to limit the extent of pressure relief needed.

12.25 Containment of Toxic Materials

Some plants handle substances which rank as high toxic hazard materials (HTHMs) and the pressure system must ensure their containment. Guidance is given in the CCPS *Guidelines for Safe Storage and Handling of High Toxic Hazard Materials* (1988/3) (the CCPS *HTHM Guidelines*), which covers a wide range of topics. These guidelines are considered in Chapter 22. Many aspects are dealt with in other parts of the present text. Table 22.10 gives an indication of the chapter or section where relevant material is to be found.

Containments for HTHMs should be designed and constructed to standards which are higher than average. This applies to, among other things, the vessel wall thickness and connections, the materials of construction, the welds and the quality control.

12.25.1 Storage tanks and vessels

US standards and codes applicable to the storage of HTHMs include API Std 620: 1990, API Std 650: 1988 and the ASME *Boiler and Pressure Vessel Code* 1992. Also

relevant is the ASME B31.3: 1990 *Chemical Plant and Petroleum Refinery Piping Code*.

API Std 650 is the standard for large oil storage tanks and has limited relevance to HTHMs. The safety factors and welding standards are less stringent and the tank relief is to atmosphere. The more relevant standard is API Std 620. For storage of larger quantities of HTHMs the preferred method will often be the use of refrigerated storage. This is dealt with in the standard in appendices R and Q which treat, respectively, tanks for refrigerated liquids stored in the temperature range 40 to −60°F and those stored at temperatures in the range down to −270°F.

Tank designs for refrigerated storage given in API Std 620 include both single and double wall metal tanks, but in the latter the outer wall is not intended to withstand major failure of the inner tank, either in respect of the hydrostatic head or of the temperature of the liquid stored. A more suitable design is one incorporating a high bund close to the metal tank. The CCPS *Guidelines* refer to that given the CIA *Refrigerated Ammonia Storage Code*, which is considered in Chapter 22. Materials of construction for refrigerated storage of HTHMs need to possess both the necessary impact toughness and corrosion resistance.

In design of storage tanks for HTHMs, particular attention should be given to features such as the foundations, the weld radiography and the pressure testing. API Std 620 contains stress relief requirements which are given in appendices H and I.

With a storage tank designed to API Std 620 the pressure relief is generally designed for normal 'breathing'; and for operational variations. These arrangements are less suitable for HTHMs, for which there are more severe restrictions on release to atmosphere. It may be necessary to use a closed relief and vent system. If direct relief to atmosphere is permissible, a rupture disc should not be used alone, as it does not reclose after opening.

API Std 620 contains provisions by which fire relief may be provided by a rupture seam. The CCPS Guidelines state that a rupture seam is not normally acceptable for HTHMs. The implication of this is that there need to be specific alternative arrangements for fire relief. Whatever arrangements are adopted, it is essential to ensure that the tank does not rupture at the wall–floor seam, which would allow discharge of its entire contents.

For storage vessels, the ASME Boiler and Pressure Vessel Code recognizes lethal service. It states that 'by lethal substances are meant poisonous gases or liquids of such a nature that a very small amount of gas or of the vapour of the liquid, mixed or unmixed with air, is dangerous to life when inhaled ... this class includes substances of this nature which are stored under pressure or which may generate a pressure if stored in a closed vessel.'

The minimum wall thicknesses given in pressure vessel codes may yield for small vessels at low pressure relatively thin walls, and it may be prudent for certain HTHMs to use a thicker walled container. A suggestion made in the CCPS Guidelines is the use of compatible DOT cylinders.

The nozzles are frequently the weak points on a vessel and for containment of HTHMs they need to be of high integrity. Measures to ensure this include high nozzle specifications, use of sufficient thickness and of suitable welds and avoidance of small nozzles and of excessive projection. The CCPS Guidelines recommend that: nozzles should preferably be to Class 300 flanged welding necks; all nozzle-to-shell welds be full penetration welds; nozzles of less than 1–1.5 in. nominal bore (NB) be avoided, or at least protected; and nozzles less than 2 in. NB do not project more than 6 in., or be provided with additional strength or protection.

Since for HTHMs avoidance of catastrophic failure is of particular importance, use should be made of fracture mechanics so that, where practical, the vessel operates in the lower risk 'leak-before-break' regime. This is discussed in Section 12.28.

12.25.2 Pipework

As for tanks and vessels, so for piping – design and construction for HTHM service should be to high standards. Some features of high integrity pipework have been discussed in Section 12.7. Only those aspects are considered here where the toxicity of the material is of particular relevance.

ASME B31.3 recognizes a Category M Fluid Service in which the potential for personnel exposure is judged to be significant, and in which a single exposure to a very small quantity of a toxic fluid, caused by leakage, can produce serious irreversible harm to persons upon breathing or bodily contact, even when prompt restorative measures are taken. Chapter VIII of the code deals with Category M Fluid Service.

It is preferable that filling and discharge lines enter a storage tank through the top, thus avoiding piping penetration below the liquid level. However, for discharge this requires the use of submerged pumps, which may constitute a maintenance problem.

The pipework should have an adequate degree of fire protection. Whereas, in general, the emphasis in fire protection is avoidance of further releases which could feed the fire, in the case of HTHMs it shifts rather to the avoidance of serious toxic release. It follows that for HTHMs it may be necessary to provide pipework with protection which would otherwise be considered unnecessary. The CCPS Guidelines recommend a fire resistance of at least 30 min at 1100°F.

12.25.3 Limitation of release

There are a number of devices which may be used to shut off or reduce releases of HTHMs. These include EIVs, NRVs, excess flow valves, restrictor orifices and pump trips.

Storage tanks and vessels for HTHMs should be provided with emergency isolation valves or control valves with separate shut-off facilities. Other situations which may merit an emergency isolation valve are a large vapour line on a pressurized storage vessel and a long pipeline.

NRVs, or check valves, can be used with the purpose of preventing back flow out of a tank in the event of rupture of a liquid line on it, but are notoriously unreliable and are not suitable as the sole device in a critical duty. The flow from a line may be reduced by the use of an excess flow valve or a restrictor orifice. Another measure is remote shut-off of pumps providing the pressure behind the release.

12.25.4 Secondary containment

There are a number of arrangements which can be used to contain a release and prevent its escape to atmosphere. Such secondary containments include double-walled equipment, enclosures and bunds. Pressure relief and vent systems are also sometimes so classified. Common to all

these arrangements is the need to provide in addition some form of disposal system.

Double-walled equipment is used particularly for storage tanks. In particular, the principle is exploited in the design of large refrigerated ammonia storage tanks. This is described in Chapter 22.

The double-wall principle is also used to a limited extent for pipework. One system involves the enclosure of the pipe carrying the HTHM in a second, concentric pipe. The annular space between the two pipes is filled with inert gas either at a pressure higher than that in the inner pipe or at a lower pressure with monitoring to detect leakage of the toxic fluid. An alternative system involves the use of double seals on flanges and of bellows seals on valves, both purged with monitored inert gas.

The use of an enclosure building provides another form of secondary containment but allows accumulation of small leaks. It therefore requires the provision of toxic detectors and alarms and of ventilation and disposal systems. Where toxic liquids are handled, it is also necessary to provide for their retention, collection and disposal. The sump should be of small cross-sectional area but deep, in order to minimize vaporization. If there is a possibility of an internal overpressure sufficient to cause structural damage, consideration should be given to this.

Material from the pressure relief and depressuring, or blowdown, devices should be collected in a closed relief or vent header system. This is usually a common header, though in some instances this approach may need to be modified in order to avoid a problem arising from the interconnection of systems. The header typically passes to a knockout drum or catchpot and then to the disposal system, usually a flare or scrubber. Disposal systems are considered in Chapters 11 and 22.

12.26 Pressure Systems for Chlorine

As just described, the design of pressure systems for hazardous materials requires special consideration. This is illustrated by the requirements for chlorine, which is highly toxic and, if wet, very corrosive, and which is produced in large tonnages.

The handling of chlorine is treated in the publications of the Chlorine Institute, including the *Chlorine Manual* (1986 Pamphlet 1). The generally used code has been the Chemical Industries Association (CIA) *Code of Practice for Chemicals with Major Hazards: Chlorine* (BCISC, 1975/1) (the CIA Chlorine Code). Another CIA publication has been *Guidelines for Bulk Handling of Chlorine at Customer Installations* (1980/9). These are both now superseded by HS(G) 28 *Safety Advice for Bulk Chlorine Installations* published by the Health and Safety Executive (HSE, 1986) in cooperation with the CIA; it is this document which now appears in the CIA publication list.

An account of chlorine as a chemical is given in Chapter 11. The storage of chlorine is considered in Chapter 22 and its transport, including pipeline transport, is discussed in Chapter 23. The principles of chlorine handling are, in large part, applicable to the handling of many other chemicals which are toxic, irritant and non-flammable, and are made on a large scale.

12.26.1 Chlorine and chlorine plants

Typically, chlorine is produced in integrated systems in which part of the production is liquefied and transported away and part is consumed as gas in user plants within the works. Such a system is illustrated in Figure 18.11.

The quantity of chlorine handled in a producer plant, or cell room, is generally much greater than in a user plant. In a producer plant the important thing is to be able in an emergency to stop the production of the gas quickly and so avoid a large release to atmosphere. This requires that means be provided to detect this need, to communicate it and to shut-down rapidly and safely. There should be facilities for emergency venting of the chlorine to gas absorption plant.

In a user plant, the size of potential chlorine release is usually less, but the operating conditions tend to be more arduous. In such a works chlorine is handled both as gas and as liquid (see Chapter 11). Particularly important in chlorine handling are the facts that wet chlorine attacks mild steel and that chlorine forms the unstable explosive compound nitrogen trichloride.

12.26.2 Materials of construction

The usual material of construction for dry chlorine is mild steel. If the chlorine is wet, however, it attacks mild steel severely. It is essential, therefore, for water to be excluded if mild steel is to be used for handling chlorine. Corrosion is particularly severe with liquid chlorine if there is a separate water phase. The corrosiveness of wet chlorine also depends on the temperature.

The *Chlorine Code* states that the normal dissolved water content of chlorine is 20–60 ppm and that this is satisfactory for the common materials of construction. In conformity with BS 3947, commercial chlorine should have a maximum water content of 100 ppm.

Mild steel equipment for use with dry chlorine itself needs to be dried out before commissioning. HS(G) 28 recommends purging with air or inert gas down to a dewpoint of −40°C.

Corrosion of mild steel by chlorine is also affected by temperature. The *Chlorine Code* states that attack is significant at about 200°C and rapid at about 230°C and that it is normal practice to impose a limit of 120°C. This is the normal limit advised by HS(G) 28, for example, for steel tubes in chlorine vaporizers.

Materials widely used for handling wet or dry chlorine gas include ebonite-lined mild steel or reinforced polyester resin. Glass and stoneware may also be used in appropriate applications. With certain exceptions, plastic materials are unsatisfactory for liquid chlorine. Another material which can be used for chlorine gas or liquid up to about 100°C is titanium, but only provided that the fluid is wet; titanium is attacked by dry chlorine. If this material is used for wet chlorine, therefore, there must be assurance that it will not be contacted with dry chlorine, even under fault conditions, otherwise some alternative material should be selected. There are available carbon steels which are suitable for the low temperatures found in the normal handling of chlorine.

12.26.3 Vessels, pipework and equipment

Pressure systems for handling chlorine should be of a particularly high standard, with appropriate attention paid to control of impurities, isolation arrangements, protective devices, pressure relief arrangements and protection against external damage.

Chlorine vessels are designed to normal pressure vessel codes but with the additional requirements stated in

HS(G) 28. Storage tanks and vessels for chlorine are discussed in Chapter 22. For chlorine process vessels, particular consideration should be given to possible impurities in the chlorine, which are a more severe problem in process than in storage.

Chlorine pipework may carry chlorine gas in which the presence of liquid is excluded, chlorine gas which may contain some liquid, or liquid chlorine. Pipelines are designed for dry gas, wet gas and dry liquid. HS(G) 28 gives guidance on pipework for liquid chlorine. The pipework should be designed, fabricated, inspected and tested to a recognized code. The design pressure should be in accordance with the code, but in any case not less than 12 barg which corresponds to a design temperature of 45°C.

Seamless steel tubing is preferred, but resistance seam welded tubing that has been welded and stress relieved automatically during manufacture is acceptable. The number of flanged joints should be kept to a minimum. All butt welds should be fully radiographed or ultrasonically examined.

Gaskets used for liquid chlorine are of compressed asbestos fibre and should be to BS 2815 Grade A. The use of an incorrect gasket for chlorine can be hazardous and gaskets should be tabbed if there is any possibility of misidentification.

Pipelines should be sited so as to be as safe as possible from impact, fire or other threats. They should be protected from external corrosion, but accessible for inspection and maintenance.

HS(G) 28 gives less guidance on lines for chlorine gas. The following guidance is given in the *Chlorine Code*, but it should be borne in mind that it is somewhat dated. Gas pipelines in which it is known with confidence that there will be no liquid chlorine are usually designed so that they are sufficiently strong to withstand the highest pressure which can be applied or so that relief is inherent in the design, and do not normally require relief devices. Pipelines for gas which may contain liquid are operated at rather higher pressures than the previous ones, but are not necessarily designed for the full pressure which could arise from the vaporization of trapped liquid chlorine. Usually some relief capacity is necessary to cater for any liquid present and this should be considered in relation to the gas absorption facilities. Often such pipelines contain vaporized chlorine. It may be appropriate to provide trace heating. This is necessary if the lowest winter temperature to which the pipeline is exposed could cause formation of the liquid. The gaskets used for dry gas are compressed asbestos fibre, whilst those for wet gas are a special rubber. Although the latter is suitable for low pressure dry gas, it is quite unsuitable for liquid or high pressure gas. It is essential, therefore, that means such as tabbing be provided to ensure that the correct gasket is used.

Liquid pipelines may be subject to overpressure caused by hammer blow resulting from rapid closure of valves and by thermal expansion of the liquid. Slow-acting valves and surge vessels may be used to protect against hammer blow from liquid chlorine. Good communication between operators is also helpful in reducing this problem.

Liquid chlorine has a high coefficient of thermal expansion and the possible effects of liquid thermal expansion should always be considered in liquid chlorine pipework systems. The trapping of liquid between two valves should be minimized by a combination of design and operations measures. Liquid trapping is particularly likely to occur if there is a proliferation of valves which can close automatically. This may be avoided by the judicious use of a proportion of valves which are manually operated.

Traditionally, for small lines the industry has placed some reliance on liquid thermal relief by the springing of flanged joints. Thus, the *Chlorine Code* states that on smaller systems the release may be relatively small and harmless, and indicates that in order to provide such relief flanged joints should not be eliminated completely.

HS(G) 28 states that if the capacity of the system is such that a release could have serious consequences, automatic means of relief should be provided and that reliance on the springing of flanged joints for thermal relief is not acceptable. It refers to two means of relief: (1) a bursting disc discharging to a suitable disposal system and (2) an expansion tank designed to accommodate the gas phase.

The *Chlorine Code* states that an expansion bottle or other relief device is normally used if:

(1) the system is fully welded and includes no flanged joints;
(2) there is a substantial length of pipework involved such that the volume of chlorine released in easing a potential pressure would be significant;
(3) the two valves, the closure of which traps the liquid chlorine, are under the control of different operators and there is a reasonable chance of this occurring without either being aware of it;
(4) overpressure due to external causes can be foreseen.

However, it also states that an expansion bottle is effective only provided it contains non-condensable inert gas and does not fill up with liquid. HS(G) 28 states that, in view of the difficulty in determining whether the gas space contains chlorine or inert gas, the use of such a device is not recommended for new installations.

Arrangements for pressure relief of chlorine pipelines using these two systems are given in HS(G) 28. In both cases the relief volume needs to be at least 20% of the line volume. Figure 12.20 shows the two systems. Figure 12.20(a) gives the bursting disc system. The disc relieves into a pressure vessel fitted with a pressure alarm and vents from there to the disposal system. Figure 12.20(b) gives the expansion vessel system. There is a heating system to maintain the temperature at around 60°C. There are a number of further design requirements, which are given in the guide. In each case the vessel used should be a pressure vessel and entered as such in the pressure vessel register.

The possibility of low temperature embrittlement should be considered carefully for pipelines carrying liquid chlorine. The line may be subjected to temperatures down to the normal boiling point of chlorine (−34°C) or even lower. Pipelines carrying liquid chlorine are liable to ice up on the outside and to corrode under the ice, and require to be protected by suitable wrapping or painting.

Valves for chlorine pipelines should be carefully chosen, particularly in respect of corrosion resistance, strength against possible overpressures, leak-tightness of the gland and ease of removal and maintenance. Some requirements for valves in liquid chlorine systems are given in HS(G) 28. Such valves should preferably be in forged steel, and in any event not in cast iron. If the valve is of a type in which liquid chlorine may become trapped, measures need to be taken to prevent the development of excessive pressure due to temperature rise. The types of valve referred to in HS(G) 28 as

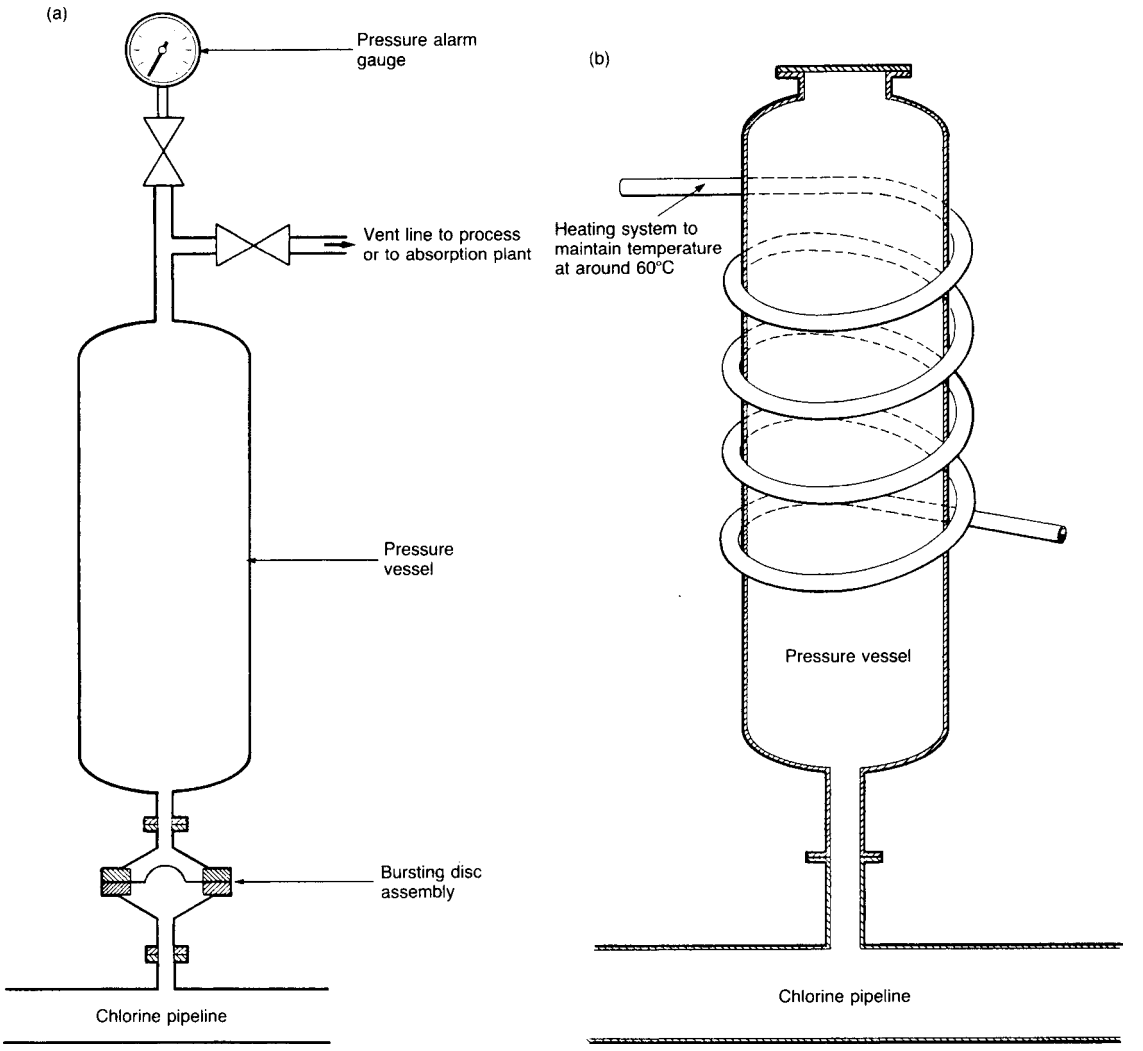


Figure 12.20 *Overpressure protection arrangements for chlorine pipelines (Health and Safety Executive, 1986 HS(G) 28): (a) bursting disc system; and (b) expansion vessel system (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

suitable for liquid chlorine or dry chlorine gas are (1) vertical globe valves, (2) conical plug valves and (3) ball valves. Detailed guidance is given on each type.

Isolation arrangements are particularly important in chlorine systems. A single valve should not be relied on to give complete isolation. More positive isolation is required using means such as the provision of spool pieces which can be removed and replaced by blanks and the use of slip plates. Where the latter are to be utilized, the layout and piping should provide for this. Large low-pressure chlorine gas mains are particularly difficult to isolate effectively due to the size of the line and the dirtiness of the gas. Ease of removal of valves and of insertion of slip plates is especially important in such systems.

Every item of equipment which contains, and could release, a significant quantity of chlorine should have a means of isolation and a means of venting to a gas absorption unit. Stop valves at inlet and outlet are the normal means provided for effecting immediate isolation, but the arrangements should facilitate the insertion of slip plates.

Chlorine liquefiers are subject to the general requirements for chlorine vessels, but involve some special considerations. The operating temperatures are low and require suitable materials of construction. The chlorine gas, even after drying, is not completely clean and tends to cause blockage and corrosion, so that ease of cleaning is important. The refrigerant used should not react with the chlorine if there is a leak.

Likewise, there are some particular considerations in chlorine vaporizers. There is a potential for creating overpressure. The higher temperatures are conducive to

increased corrosion. The impurities, particularly nitrogen trichloride, may concentrate and explode. There is a possibility of failure of the heating surfaces. Materials of construction for chlorine vaporizers should withstand both the temperatures and impurities. There should be effective control on pressure, temperature and level. Pressure relief should be provided and should take account of the possibility of heating surface failure. There should be specific arrangements to prevent concentration of nitrogen trichloride. The effects of heating surface failure should be thoroughly reviewed and means provided for its prompt detection. Chlorine vaporizers are utilized by users of chlorine which are not necessarily large chemical works. A robust design is therefore important. A further discussion of chlorine vaporizers is given in Chapter 22.

12.26.4 Compressors, pumps and padding

Compressors are used to re-compress chlorine vapour and need to be suitable for intermittent operation. Dry carbon ring and diaphragm types are used, the latter having double stainless steel diaphragms with inert fluid in between. The shaft of a carbon ring compressor needs to be sealed so as to prevent escape of chlorine and ingress of moist air. The shaft glands should be pressurized during operation with dry inert gas. After use the compressor should be purged with dry air to prevent leakage of residual chlorine.

The temperature rise in the compressor may need to be controlled. The cooling arrangements should take account of the possibility of water leaks. Direct water cooling should be avoided. It is preferable to use air cooling. The compressor should have a bypass allowing the chlorine to be recycled so that its temperature is high enough to avoid liquefaction in the delivery lines. There should, however, be an alarm which will activate if the temperature exceeds 90°C.

In general, transfer of liquid chlorine may be effected by the use of (1) chlorine vapour at the vapour pressure of the liquid, (2) dry compressed chlorine vapour, (3) dry compressed padding gas, and (4) pumping. The choice of method for different applications such as transfer from storage to consuming units and unloading from tankers to storage is discussed in HS(G) 28. For the former, all four methods are listed, but with the first two preferred, whilst for the latter the third method is the preferred one, with the second as a possible alternative.

In many cases, transfer of liquid chlorine from storage may be effected under the vapour pressure of the liquid. If this method is used, factors to be taken into account are the effect on the vapour pressure of low external temperatures and the need to maintain in the vessel a positive pressure, which should be specified. Alternatively, liquid chlorine may be transferred by pressure of gas, such as dry air or nitrogen, or of chlorine vapour from a vaporizer or compressor. HS(G) 28 gives the following guidance.

Gas used for transfer of liquid should be a dedicated supply. Nitrogen at pressure may be obtained from a liquid nitrogen vaporizer. Compressed air can be provided by an air compressor. It is highly desirable that this be an oil-free machine; if oil lubrication is used, the machine should have an oil filter which is regularly maintained. Measures should be taken to ensure that the air is dried to a dewpoint of −40°C. The padding gas, nitrogen or air, should have its own pressure control and pressure relief arrangements. It should be held in a gas receiver with a relief valve set to operate at the safe working pressure of the chlorine plant or 150 psig, whichever is the lesser. Further detailed requirements are given in the guide.

Chlorine vapour for padding may be obtained by recompression of vapour from a storage vessel or by vaporization of liquid chlorine. The storage vessel from which transfer is made should have a design pressure and pressure relief arrangements which protect against pressures which the padding gas or vapour can develop. It should also have a relief to the gas absorption facilities.

It may be necessary to pump liquid chlorine if it has to be delivered at a higher pressure (say, 100 psig) or if the use of dry padding gas is for some reason inappropriate. Some of the problems in pumping chlorine are discussed in the *Chlorine Code*. Pump cavitation can be a problem in pumping chlorine, which tends to vaporize. It is essential to provide sufficient liquid head on the suction side to avoid liquid flashing. Severe cavitation can damage the pump or even cause the casing to fail. Another problem in pumping chlorine is seal leakage. This virtually rules out the use of rotating shaft seals. Liquid chlorine pumps are generally canned, diaphragm or submersible types. The code recommends that centrifugal pumps should be provided with a bypass to a pumping tank to prevent liquid boiling and that a positive displacement pump should have a pressure relief valve on the outlet bypassing to the suction.

HS(G) 28 describes the use of an arrangement in which liquid chlorine is transferred from a storage vessel using a canned pump. There should be sufficient NPSH and a remotely operated emergency isolation valve installed either inside the vessel or between it and the pump. The guide also discusses the use of submersible pumps.

12.26.5 Pressure relief and gas absorption

The philosophy of pressure relief for chlorine has traditionally been somewhat different from that for most other materials. It is stated in the Chlorine Code thus:

(1) Any relief system shall be regarded as a safeguard of last resort; its existence shall not be regarded as an alternative to providing protective systems and operating instructions such that process conditions cannot, in the absence of human or equipment failure, lead to the relief conditions arising.
(2) Relief to atmosphere shall be sanctioned only as a last resort when the consequences of not doing so would be worse.
(3) A relief device shall not be isolated unless approved alternative arrangements to protect the vessel have been made.

Likewise, the philosophy in HS(G) 28 for chlorine systems lays emphasis on prevention of overpressure with pressure relief as a last resort. These measures include (1) prevention of overfilling of storage tanks by use of weighing systems or of ullage pipes giving warning of entry of liquid into vent lines, combined in both cases with alarms and (2) prevention of overpressure by pressure control and relief on the padding gas system and storage vessel high-pressure alarms.

As a last line of defence, a chlorine storage vessel should be provided with pressure relief. This pressure relief should be provided by a bursting disc rather than a relief valve, because chlorine tends to corrode the latter. The relief should normally pass to an expansion vessel. For a simple system consisting of a single storage tank and expansion

tank, a single bursting disc system may suffice, installed directly on the storage vessel without isolation valves. A system commonly found on much existing plant is two bursting discs in series with a pressure alarm on the intervening space and with isolation valves upstream and downstream of this assembly, with both valves locked open. The preferred arrangement is two such assemblies of bursting discs and isolation valves in parallel. In this case one arrangement is that the valves are interlocked and another that the upstream valves and at least one downstream valve are locked open.

Where there are several storage vessels, they may each be provided with an expansion vessel or there may be a common expansion vessel. An expansion vessel should have a capacity at least 10% of the largest storage vessel. It should be capable of being vented manually to an absorption system. It should be fitted with a high pressure alarm to indicate build-up of chlorine. Any necessary measures should be taken to ensure that the expansion vessel is not itself overpressurized.

Arrangements should be made to ensure that facilities exist for absorption of chlorine gas vented by the pressure relief system. In some installations, there are chlorine-consuming plants to which the relief gas can be routed, and a separate gas absorption facility may be deemed unnecessary. In this case, it is essential to ensure that the absorption capability is available whenever it may be required. Usually it is necessary to provide a separate gas absorption facility. This should be a high reliability plant with adequate redundancy and comprehensive instrumentation. HS(G) 28 gives detailed recommendations.

The pressure relief arrangements should cater for fire relief as well as operational relief. In some cases it may be necessary to provide protection against the risk of explosion of chlorine with other gases, particularly hydrogen. The design of such explosion relief is a specialist matter. The Chlorine Code refers to the possible need for explosion relief to atmosphere in unavoidable cases, and states that this a matter for expert advice. HS(G) 28 does not consider this eventuality.

12.27 Failure in Pressure Systems

Maintenance of the integrity of the pressure system and avoidance of loss of containment is the essence of the loss prevention problem. It is necessary, therefore, to consider the failures which occur in pressure systems. Of particular importance are catastrophic failures in service.

Catastrophic failure of a properly designed, constructed and operated pressure vessel is comparatively rare. The most common cause of such failure is inadequate operational procedures. Most failures in pressure systems occur, however, not in pressure vessels but in the rest of the system, which includes pipework, valves and fittings and equipment such as heat exchangers and pumps.

The problem of failure in pressure systems is treated here by first describing some principal causes of failure, particularly sudden failures, and then giving some historical data on failure. In the present context it is service failures which are of prime importance. Service failures of pressure systems are generally caused by exposure to operating conditions more severe than those for which the system was designed.

It is usual to classify service failures as (1) mechanical failure, through stress and fatigue and (2) corrosion failure, although many failures have an element of both of these. Accounts of causes of failure in pressure systems are given in *Defects and Failures in Pressure Vessels and Piping* (Thielsch, 1965) and *Inspection of Chemical Plant* (Pilborough, 1971, 1989).

12.27.1 Materials identification errors

Mistakes in identifying materials of construction which result in the construction of plant using the wrong materials are a significant problem. Such errors are particularly likely to occur where the materials have a somewhat similar appearance, for example low alloy steel and mild steel, or stainless steel and aluminium-painted mild steel. It is necessary, therefore, to exercise careful control of materials. Methods of reducing errors involve marking, segregation and instrument spot checks. For critical applications, is may be necessary to carry out a full 100% *in situ* check on materials using an instrument such as a Metascope.

Misidentification of materials and some accidents caused by it have been described by W.D. Clark and Sutton (1974). In 1984, a leak due to erosion failure on a hydrocarbon liquid line at Fort McMurray, Alberta, resulted in a major fire (Case History A109). The investigation found that inadvertently an 18 in. long section of carbon steel had been inserted into an alloy steel line.

12.27.2 Mechanical failure

Some common causes of mechanical failure in process plant are:

(1) excessive stress;
(2) external loading;
(3) overpressure;
(4) overheating;
(5) mechanical fatigue and shock;
(6) thermal fatigue and shock;
(7) brittle fracture;
(8) creep;
(9) hydrogen attack.

Excessive stress in equipment may be caused by factors such as stress raisers or by malpractices such as uneven tightening of flanges.

Equipment may be externally loaded by loads carried on additions such as lugs, supports, brackets and hangers. Common sources of external loads are platforms, stairs and ladders. Movement of foundations may cause external loads, as may restraint on thermal expansion of pipework passing through concrete walls. Wind and occasionally ice may contribute a significant external load.

Overpressure may occur due to failure of a pressure relief valve to fulfil its function. Such failures may be due to poor design or incorrect operation, or to relief valve failure. Freezing of liquid, particularly in pipework, is another cause of overpressure.

Gross overheating may cause rapid failure due to operation well outside the temperature range of the material. In particular, direct flame impingement can give rise to sudden failure. Less severe overheating can cause creep as discussed below.

The other causes of mechanical failure are now considered.

12.27.3 Mechanical fatigue and shock

Conditions which give rise to mechanical fatigue include (1) pressure variations, (2) flow variations, (3) expansion effects, and (4) imposed vibrations. Stress cycling can be caused by normal changes of pressure in the process. Normal flow fluctuations or effects such as hammer blow or cavitation also give rise to stress cycles. So do differential expansions and contractions of the process plant. Other stress cycling is imposed by vibrations from such equipment as compressors, pumps or valves.

Although there is often some degree of vibration in pressure vessels and pipework, it is usually at a sufficiently low level as not to cause fatigue failure. In some cases, however, fatigue can progress very rapidly. Thielsch quotes the case of the fatigue failure of a carbon monoxide generator which was subjected in a period of only 17 days to several hundred million stress cycles.

Mechanical shock differs from mechanical fatigue in that the load is greater and causes failure within only one or a few cycles. Shock is often caused by hammer blow or liquid slugs. In 1975 at Antwerp, Belgium, a leak of ethylene at high pressure due to fatigue failure of a vent connection on the suction of a compressor led to an explosion and fire at a low-density polyethylene plant (Case History A74). Six persons were killed and extensive damage was done.

12.27.4 Thermal fatigue and shock

Similarly, the distinction between thermal fatigue and thermal shock is that in the latter the applied temperature difference and the rate of change of temperature are greater and cause failure in one, or a few, cycles. A given temperature cycle may give rise to thermal fatigue or shock, depending on the material. It may constitute thermal fatigue for a ductile material, but shock for a brittle one. Thermal cycling is caused by (1) intermittent operation and (2) particular equipment conditions.

There are many types of intermittent operation ranging from batch processes to throughput changes and including forced shut-downs. These all create thermal stress cycles. This source of thermal fatigue is much reduced if the plant is operated continuously, even though the operating temperatures may be relatively high.

Thermal fatigue is also caused by the conditions in particular types of equipment. Steam desuperheaters using direct water spray cooling may suffer thermal fatigue failures. Thermal fatigue occurs in reducing valves due to repeated flow changes. Slugs of condensate can cause thermal fatigue in steam lines.

12.27.5 Brittle fracture

The materials used in plant handling low temperature fluids should have a ductile–brittle transition temperature below not only the normal operating temperature but also the minimum temperature which may be expected to occur under abnormal conditions. If this requirement is not observed and cold fluid contacts metal below the transition temperature, brittle fracture may occur. Brittle fracture is catastrophic, since the fracture can propagate at a velocity close to that of sound.

In 1973 at Potchefstroom, South Africa, an ammonia tank suffered brittle fracture, which resulted in the release of some 30 ton of ammonia (Case History A65). The fracture occurred in a dished end which was fabricated in carbon steel and which had not been stress relieved after manufacture. The minimum transition temperatures obtained by subsequent testing were 20°C for the fragment and 115°C for the remaining part of the dished end. Thus, the metal was below its transition temperature under normal operating conditions.

The possibility of accidental entry of cold fluids into parts of the plant where they are not normally present and the resultant hazard of brittle fracture present a difficult problem. In general, the best practice is to use suitable materials in any part of the plant where it is realistic to expect that low temperature fluids could enter under abnormal conditions. But alternative means of protection such as trip systems may be used in some cases. An example of the application of hazard analysis to this problem was discussed in Chapter 9.

Where a liquefied gas is held under pressure, sudden depressurization to atmospheric pressure will cause the temperature of the gas to fall to its normal boiling point. This could be below the transition temperature of the metal unless this has been taken into account in the design.

It is not only the vessels and pipework which may suffer low temperature embrittlement, but also features such as vessel supports and flange bolts. It is essential, therefore, for these latter also to be made of the appropriate material.

12.27.6 Creep

The problem of creep at high temperatures has already been discussed in Section 12.3. Since design for high temperatures is based on creep strength, failure due to creep is usually unlikely under normal operating conditions and is generally caused by abnormal conditions such as maloperation or fire. It is appropriate to emphasize here the very rapid increase in creep rate with temperature. For mild steel in the creep range, a temperature increase of about 10–15°C is sufficient to double the creep rate. A stress which gives an 11-year life at 500°C can result in rupture in 1 h at 700°C.

Creep involves plastic deformation and, eventually, rupture. However, some metals have a very low ductility in the normal creep range, although they are more ductile at low and at very high temperatures. Low ductility fractures with an elongation of less than 1% are frequently associated with the formation of cavities at the grain boundaries. The development of cavities can occur at low stress over long time periods. The application of higher temperatures and higher strain rates, as in a fire, can accelerate cavitation and cause low ductility failure.

Creep cavitation of stainless steel occurred on the plant at Flixborough, as described in Appendix 2. The 8 in. pipe, which was made of 316L stainless steel, had a 50 in. rupture which was initiated by creep cavitation. It was estimated that for failure in 20 min, a temperature of 900–950°C would have been needed.

If there has been overheating, there may be creep effects such as deformation and distortion which can be detected by visual examination and by measurement. Often there are also oxidation and scaling. But, since creep can occur with very little deformation, it may not be readily detectable. Expert advice should be sought if this is a possibility.

Fire on a process plant may result in local overheating and hence creep. Equipment should be protected against overheating by fixed protection such as fire insulation and by fire fighting. If equipment has been exposed to fire so that creep may have occurred, expert advice should be sought before it is put back into service.

The process should be operated at the temperatures specified. If an alteration is proposed, its effect on creep

should be checked. This includes such alterations as change in lagging thickness, since this affects equipment temperature.

Further information on creep is given in TDN 53/3 *Creep of Metals at Elevated Temperatures* (HSE, 1977).

12.27.7 Hydrogen attack

Mild steel is subject to the following types of hydrogen attack: (1) hydrogen blistering and (2) hydrogen embrittlement and damage.

Hydrogen blistering can occur when atomic hydrogen diffuses into steel. Normally the atomic hydrogen diffuses right through, but if it encounters voids it forms molecular hydrogen, which can generate pressures of several hundred bar. Internal splitting of the steel occurs and gives surface blisters. Steels which are dirty and contain numerous voids, laminations and inclusions are especially prone to hydrogen blistering. Hydrogen blistering has been a quite common problem in catalytic reformers and has occurred at temperatures as low as low as 315°C. It has also been reported in butane storage tanks with butane run down from a gas separation treatment plant at 21°C. The butane was sometimes contaminated with small amounts of water with traces of hydrogen sulphide. When corrosion occurs, the latter favours the evolution of atomic rather than molecular hydrogen.

At high temperatures and high hydrogen partial pressures, steels can suffer hydrogen embrittlement and damage. The steel suffers decarburization by the hydrogen, which causes a loss of ductility, and development of microfissures at the grain boundaries, which leads to loss of strength. The decarburization reaction is reversible, but the formation of cracks is not. These two effects are sometimes distinguished as hydrogen embrittlement and hydrogen damage, but often one of these terms is used to describe both phenomena. Both effects are referred to here as 'hydrogen attack'.

Hydrogen attack has been a relatively common problem in equipment handling hydrogen at high temperatures such as refinery boilers and catalytic reformers. Failures usually occur in the temperature range 300–550°C. The resistance of steel to hydrogen attack can be greatly increased by the addition of suitable alloying elements, and CrMo steels are widely used for hydrogen service. Operating limits for steels in hydrogen service have been given by a number of workers, notably G.A. Nelson (1966). The Nelson curves are published with periodic amendments in *Steels for Hydrogen Service at Elevated Temperatures and Pressure in Petroleum Refineries and Petrochemical Plants* (API, 1991 Publ. 941). Typical Nelson limit curves are illustrated in Figure 12.21. These are used to select a suitable material. The basis of design for equipment in which hydrogen attack may occur is therefore selection of a suitable material and use of a design stress less than the lower critical stress.

In 1984 at Romeoville, Illinois, an absorption column came apart at the weld and rocketed up, initiating a vapour cloud explosion and a series of fires and boiling liquid expanding vapour explosions (BLEVEs), in which 17 people were killed (Case History A111). The vessel had a history of hydrogen attack problems.

12.27.8 Corrosion failure

A large proportion of failures in process plant are due to corrosion Accounts of corrosion include *Deterioration of Materials* (Greathouse and Wellel, 1954), *Seawater Corrosion Handbook* (Schumacher, 1979), *Basic Corrosion and Oxidation* (Q.M. West, 1980), *Corrosion Inhibitors* (Rozenfeld, 1981), *Corrosion Processes* (R.N. Parkins, 1982), *Intergranular Corrosion of Steels and Alloys* (Cihal, 1984), *Corrosion Control in the Chemical Process Industries* (Dillon, 1986), *Corrosion Engineering* (Fontana, 1986), *DECHEMA Corrosion Handbook* (DECHEMA, 1987–), *The Chemical Engineering Guide to Corrosion Control in the Process Industries* (R.W. Green, 1987), *High Temperature Corrosion* (Kofstad, 1988) and *Corrosion and Corrosion Protection Handbook* (Schweitzer, 1989).

Corrosion occurs as (1) general corrosion, (2) local corrosion and (3) erosion. In general corrosion, there is a fairly uniform deterioration of the overall surface. In contrast, localized corrosion involves little generalized corrosion but severe local attack, often at points of surface defects or stress. Erosion is also localized at points of high velocity or impact.

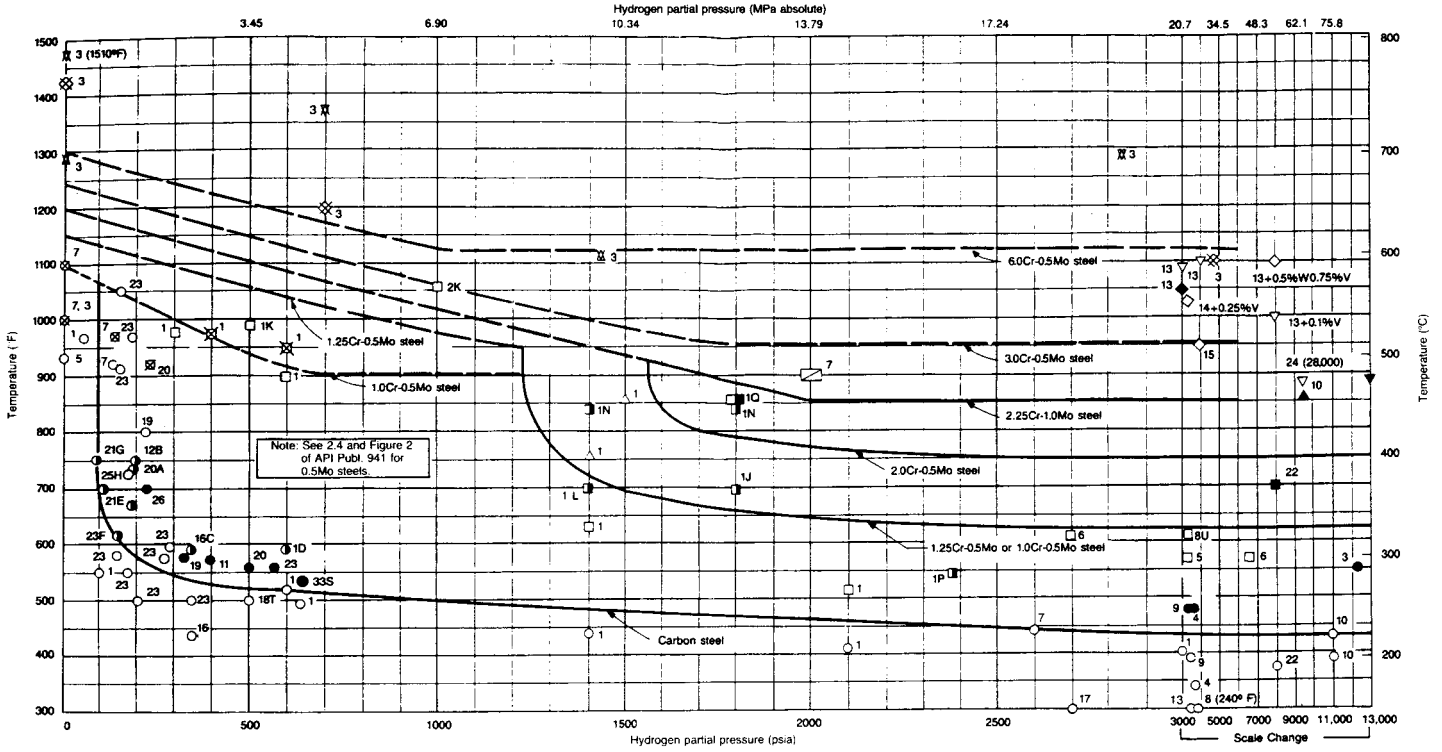
Some common types of corrosion in process plant, following Thielsch (1965), are

(1) general corrosion;
(2) scaling;
(3) exfoliation;
(4) galvanic corrosion;
(5) crevice corrosion;
(6) corrosion pitting;
(7) stress-related corrosion
  (a) stress corrosion cracking,
  (b) corrosion fatigue,
  (c) stress-enhanced corrosion;
(8) intergranular corrosion;
(9) knife-line corrosion;
(10) erosion;
(11) external corrosion.

It should be emphasized, however, that many corrosion failures are not easily classified and may involve more than one type of corrosion. Corrosion frequently occurs at welds rather than in the parent metal and corrosion at welds ranks as a topic in its own right. Accounts of the practical treatment of corrosion problems in process plants have been given by M. Turner (1987, 1988, 1989a,b, 1990a,b).

General corrosion often results from attack by a corrosive chemical or impurity over the whole exposed surface. Scaling corrosion is the result of oxidation in a gaseous atmosphere caused by exposure to high temperatures. It occurs particularly in steam boilers. Exfoliation is another type of scaling corrosion caused again by oxidation, but in a steam atmosphere. Steam-heated boiler feedwater heaters exhibit exfoliation.

There are several kinds of corrosion which are associated with concentration cells. In the salt concentration cell, which involves a dissolved salt containing ions of the metal, there is a difference of salt concentration at two parts of the exposed surface. The metal in contact with the lower salt concentration becomes the anode and corrodes preferentially. In the differential aeration cell, two parts of the exposed surface are subject to a difference of oxygen concentration. The metal in contact with the lower oxygen concentration becomes anodic and corrodes. Such corrosion takes two forms: pitting corrosion of an exposed surface, and crevice corrosion in a crevice. The detailed mechanisms are described further in relation to crevice



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Notes:
1. The limits described by these curves are based on service experience originally collected by G. A. Nelson and on additional information gathered by or made available to API.
2. Austenitic stainless steels are generally not decarburized in hydrogen at any temperature or hydrogen pressure.
3. The limits described by these curves are based on experience with cast steel as well as annealed and normalized steels at stress levels defined by Section VIII, Division 1, of the ASME Code. See 2.7 and 2.8 in text for additional information.

Legend:
Surface decarburization
Internal decarburization (Hydrogen attack)

	Carbon steel	1.0 Cr 0.5 Mo	2.0 Cr 0.5 Mo	2.25 Cr 1.00 Mo	3.0 Cr 0.5 Mo	6.0 Cr 0.5 Mo
Satisfactory	○	□	△	▭	◇	▽
Hydrogen attack	●	■	▲	▬	◆	▼
Surface decarburization	⊠	⊠	⊠	▨	⊠	⊠
See comments	◑	◨	◭	◨	◆	▼

Figure 12.21 *Recommended operating limits of steel for hydrogen service to avoid decarburization and hydrogen attack: Nelson curves (American Petroleum Institute, 1991 Publ. 941) (Courtesy of the American Petroleum Institute)*

corrosion. Both types of concentration cell corrosion occur in water containing chloride ions. Galvanic corrosion is considered in Section 12.27.9; crevice corrosion in Section 12.27.10; corrosion pitting in Section 12.27.11; stress-related corrosion, including stress corrosion cracking, corrosion fatigue and stress-enhanced corrosion, in Section 12.27.12; particular forms of stress corrosion in Sections 12.27.13 and 12.27.14; and inter-granular corrosion, or weld decay, in Section 12.27.18.

Knife-line corrosion takes place between the parent and weld metals. It occurs mainly in austenitic stainless steels. Erosion and external corrosion are discussed in Sections 12.27.16 and 12.27.17.

In 1970 in Brooklyn, New York, a road tanker carrying liquid oxygen ruptured violently causing a number of fires, with two deaths (Case History A48). The investigation found, amongst other things, that there had been a appreciable loss of metal from the aluminium tank shell, even though the tank had been in service for only a month.

In 1988 at Norco, Louisiana, an explosion occurred on a catalytic cracker (Case History A121). The cause was a release due to internal corrosion of an elbow in the depropanizer overhead piping. Some 9 te of hydrocarbons was released and there was a vapour cloud explosion. Seven people were killed and damage was extensive.

Some of the types of corrosion mentioned are now considered in more detail.

12.27.9 Galvanic corrosion

Galvanic corrosion is caused by current flowing between two dissimilar metals which form a galvanic cell, or bimetallic couple. A discussion of galvanic corrosion in process plants is given by M. Turner (1990c).

A typical pair of dissimilar metals which exhibits galvanic corrosion is copper and iron, typically in steel. In this case it is the steel which corrodes. The electromotive series gives the ranking of metals in descending order of their electrode potential relative to that of the hydrogen electrode, the metals higher in the series being the more noble. If a galvanic cell is set up, it is the less noble metal which suffers the corrosion. The noble metal forms the cathode and the less noble one the anode.

The electromotive series is an imperfect indicator of what happens in practice. For this a more relevant guide is the galvanic series which ranks metals according to their nobility in seawater. Some materials in this series, in descending order of nobility, are 316 stainless steel > ferritic stainless steel > copper > low alloy steel > carbon steel > aluminium > zinc. However, while the galvanic series is applicable to an aqueous medium of wide interest, the ranking in other solutions is not necessarily the same.

In galvanic corrosion, the corrosion rate is a function of the potential difference between the two surfaces and the slope of the cathodic and anodic polarization curves, which may be analysed using the Evans diagram. In neutral solutions, particularly with dissolved oxygen, the cathodic polarization is crucial. The relative sizes of the cathode and anode are also important in this situation. Features which reduce cathodic polarizations, and can therefore greatly increase the corrosion rate, include agitation and air sparging. A large surface area of the cathode favours an increased corrosion rate.

Galvanic corrosion may occur in equipment incorporating two dissimilar metals. It can also occur when two such metals are joined together at a weld. It may also result from the utilization of a second metal as a plated surface. But such corrosion can also occur with minor dissimilarities in composition such as different metallurgical phases.

Measures which can be taken against galvanic corrosion include the selection of compatible materials and the insertion in the circuit of an ohmic resistance, either in the metal path or in the ionic path. Examples of the insertion of a resistance for these two paths are the use of an insulated gasket in pipework and the coating of one of the metal surfaces, respectively.

The purpose of such coating is to protect the less noble metal, but it does not follow that it is this metal which should be coated. The coating is liable to contain holes, or 'holidays'. A couple of coats of paint may still leave gaps of perhaps 1% of the area. If the coating is put on the less noble metal and gaps exist amounting to 1% of the area, the corrosion at these gaps will simply be enhanced by a factor of about 100.

12.27.10 Crevice corrosion

Crevice corrosion of steel occurs in crevices sufficiently narrow for an oxygen deficiency to occur which leads in due course to a build-up of acidity. Its occurrence in process plant is described by M. Turner (1989a).

It is exemplified by the corrosion of carbon steel in salt water. In general corrosion of an exposed surface, part of the surface acts an anode and part as a cathode. The corrosion can be represented as:

$Fe \rightarrow Fe^{2+} + 2e^-$	Anodic reaction
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	Cathodic reaction

The location of the anodes and cathodes shifts with time.

Where the metal surface is within a crevice the situation is quite different. The cathodic reaction consumes oxygen and the concentration falls, since the rate of diffusion into the crevice is slow. A differential aeration cell is set up. The metal surface in the crevice becomes anodic relative to the exposed surface. The anodic reaction creates ferrous ions, which combine with chloride ions to give ferrous chloride; this oxidizes to ferric chloride, which combines with hydroxyl ions from the cathodic reaction to form ferric hydroxide. This insoluble hydroxide in turn forms ferric oxide, or rust, and hydrochloric acid. The chloride ions are attracted to the anode. The water in the crevice can become so acidic that corrosion then occurs simply by acid attack.

From this point on, the rate of corrosion is determined by the acidity, which depends on the particular solution. In the example just given the solution contained chloride. There is a rank order of aggressiveness, headed by chlorides, then sulfates, phosphates, etc. With crevice corrosion, the corrosion rate can be orders of magnitude greater than with general corrosion.

Crevice corrosion can occur where the two surfaces forming the crevice are of the same metal, where they are of different metals or where one is non-metallic. In the second case there may be bimetallic corrosion as well.

Many of the situations where crevice corrosion occurs involve single-sided fillet welds. It occurs, for example, on lap joints with such a weld. On process plants, use is often made of a support ring welded around the inside of a vessel. The use of a full penetration weld instead of a single-sided fillet weld can minimize such corrosion. Another support

detail in plants is a pad seal welded to the inside of a thin walled vessel to support a heavy internal member. In this case, crevice corrosion may be reduced by making the seal weld a continuous one. In some cases, a 'sentinel hole' is drilled from the outside through the vessel wall to leak test the weld; it also serves to provide warning of any leak during service. Crevice corrosion occurs at the tube–tube plate joints of heat exchangers. It is fairly common in threaded joints.

12.27.11 Corrosion pitting

Corrosion pitting also involves concentration cell corrosion by a differential aeration cell, but in this case without crevice effects. The anode and cathode move over the surface of the exposed metal, with the oxygen-lean area acting as the anode and suffering preferential corrosion. Pitting is favoured by no-flow conditions and by surface defects. It occurs in boiler feedwater heaters during shut-down if the oxygen content of the feedwater is high. This type of corrosion may be prevented by chemical treatment.

The resistance of steels to pitting and crevice corrosion can be characterized by the pitting index (Henderson, King and Stone, 1990)

$$PRE_N = \%Cr + 3.3(\%Mo) + 16(\%N) \qquad [12.27.1]$$

Broadly, alloy steels with an index value below 32 are susceptible to pitting and crevice corrosion in salt water, whilst those with a value of 36 are resistant. A minimum value of 40 is quoted for resistance to hot seawater.

12.27.12 Stress-related corrosion

Often failure results from a combination of corrosion and stress. Stress corrosion cracking (SCC) is non-ductile failure caused by the combination of corrosion and static tensile stresses. Corrosion fatigue is caused by corrosion and stress cycling. An account of stress corrosion is given in *The Stress Corrosion of Metals* (Logan, 1966).

Many types of steel are liable to SCC, including mild steel and austenitic stainless steel. The stresses necessary to cause SCC may be internal or due to externally applied loads. Generally, normal operating pressures are not alone sufficient to cause such cracking and appreciable internal stress must be present. SCC can occur in the parent metal of vessels and pipes, in welds and on nozzle connections and support attachments. In welds the cracks may be transverse or longitudinal.

Chlorides are a common cause of SCC. They are a very widespread impurity and are rather difficult to eliminate. SCC due to chlorides is discussed in Section 12.27.13. There is also a form of SCC due to nitrates, which is considered in Section 12.27.14.

SCC caused by an alkaline solution is known as 'caustic embrittlement', which has been a frequent cause of failure in boilers. It is normal to treat boiler feedwater to reduce the risk of caustic embrittlement. SCC, particularly by chlorides, can occur externally as well as internally. A common cause is the leaching of chlorides from lagging. Some failures caused by SCC have been described by Ashbaugh (1970) and M. Turner (1989b).

Corrosion fatigue involves a mutual interaction between corrosion and fatigue. Corrosion occurs in the fatigue cracks. Alternation of stress prevents the build-up of films which protect against corrosion. Thus, corrosion reduces the fatigue limit and fatigue speeds up the corrosion. In consequence, corrosion tends to occur with a wider range of chemicals and concentrations than is the case in the absence of fatigue.

Stress-enhanced corrosion describes corrosion at features where there are high residual stresses, such as welds, nozzles and attachments. Measures to counter stress-related corrosion depend on the particular case, but include selection of suitable materials, operation in a suitable temperature range, elimination of corrodants, reduction of residual stresses, reduction of vibrations, and close control of operations.

12.27.13 Chloride stress corrosion cracking

Chloride SCC occurs in austenitic stainless steels. A discussion of this form of SCC is given by M. Turner (1989b). When a dislocation propagates and a slip plane forms, there is a rupture of the protective oxide layer. Although the passive film usually reforms on the surface thus exposed, in an aqueous solution of chloride ions the repair is imperfect and the film contains chloride ions, so that the renewed surface has a different composition. The repaired surface constitutes an anode and, since it is small relative to the rest of the surface which becomes the cathode, rapid corrosion occurs. This in turn creates a crack, which propagates along the slip plane. The corrosion is further promoted by the build-up of acidity at the anodic crack and now becomes well established.

There are four main factors which influence SCC: (1) the temperature, (2) the chloride ion concentration, (3) the stress, and (4) the grade of steel. SCC rarely occurs at temperatures below 60°C, but above 200°C it can progress rapidly, the relevant temperature being that of the metal rather than of the liquid. The rate at which SCC occurs is a function of the chloride ion concentration, the relevant concentration being that in the liquid film at the metal surface. The stress causing SCC may sometimes be the tensile stress in the metal surface at the operating pressure, but a more common cause is residual stresses. Stainless steels such as the commonly used 304, 321 and 347 types are susceptible, and the 316 and 317 types are only marginally less so.

Where SCC is detected, specialist advice is required. If the cracks are sufficiently deep, immediate shut-down is necessary. If they are more shallow, the advice may be that it is possible to continue in operation with appropriate monitoring and perhaps that the cracks may be dealt with in due course by grinding out.

Prevention of SCC by elimination of stress is generally difficult. Stress relief may be practised, although the temperatures required are high and can cause distortions. On the other hand, operation with a metal temperature below 60°C eliminates the problem. Control of chloride ion concentration is more problematic, particularly if chlorides can concentrate by evaporation. Selection of an appropriate stainless steel is an effective measure. The steels which show resistance to SCC are those with higher nickel contents: the 904L grade is resistant and the 825 grade highly so.

Other measures of protection include exclusion of oxygen, use of inhibitors and cathodic protection. A critique is given by M. Turner (1989b), who rehearses some drawbacks of these methods. The quantity of oxygen required to initiate SCC is very small. Inhibitors have not proved universally effective. Cathodic protection requires very

precise control. Failures due to SCC are mostly not catastrophic, though hey can be. They tend to exhibit leak-before-break behaviour.

12.27.14 Nitrate stress corrosion cracking

A particular type of SCC is the nitrate SCC of mild steel. It was nitrate stress corrosion which caused the crack in No. 5 Reactor at Flixborough and led to the removal of the reactor and the installation of the 20 in. pipe. The cracking occurred because cooling water treated with nitrite had been played on the reactor to dilute small leakages of cyclohexane.

The conditions for nitrate cracking of mild steel to occur are a high concentration of nitrate, a low pH, a temperature above 80°C and high stress. This combination of features is not often present and nitrate cracking is not common outside plants handling nitric acid and nitrates. Most water contains some nitrates. In particular, water treatment of industrial cooling water results in an appreciable nitrate concentration. But such cooling water does not normally cause nitrate cracking. It is concentration of nitrates which presents the main hazard of nitrate cracking. Concentration may occur on a nitric acid plant or a plant producing nitrates, inside a crack which has been created by some other mechanism such as fatigue, or due to evaporation.

Contamination with nitrates should be avoided as far as practicable. In particular, it is not good practice to let water penetrate thermal insulation. This creates a risk of various kinds of corrosion apart from nitrate cracking. If heavy contamination may occur, equipment should be stress relieved. This is not a full answer for all fittings, since some items such as bolts have a high working stress. These need to be checked by regular inspection.

Where it is not possible to rely on either avoidance of contamination or stress relief, some protection may be obtained by the use of certain paint coatings. On plants handling nitric acid and nitrates, nitrate cracking is a well-known problem and special procedures have been evolved.

Further information on nitrate cracking is given in TON 53/2 *Nitrate Stress Corrosion of Mild Steel* (HSE, 1976).

12.27.15 Zinc embrittlement

At high stresses and temperatures, traces of other metals such as copper or zinc can cause rapid and severe embrittlement of some types of steel. The effects of zinc embrittlement of austenitic stainless steel were illustrated at Flixborough. Many of the stainless pipes found on the site had suffered zinc embrittlement.

For zinc embrittlement of stainless steel to occur it is necessary for the material to be under high stress and at a high temperature, but given these conditions the quantity of molten zinc required to cause embrittlement is very small and failure can occur in seconds. The features which determine zinc embrittlement of stainless steel are (1) temperature, (2) applied stress, (3) wetting, (4) type of steel, and (5) time.

Austenitic stainless steel is not used in process plant above 750°C except in certain specialized applications. Zinc embrittlement is not likely to occur below this temperature. Zinc has a melting point of 419°C and molten zinc penetrates stainless steel above 450°C, but embrittlement is improbable below 750°C. Investigations by Cottrell and Swann (1976), after Flixborough, showed that the most favourable metal temperature for rapid attack is 800–900°C. Thus zinc embrittlement is unlikely to occur under normal operating conditions, but requires temperatures such as usually occur only in a fire.

High stress is also a condition for zinc embrittlement to occur. In Cottrell and Swann's work zinc embrittlement did not occur at low stress, even though the temperature was 1050°C and the specimen was coated on all sides by a pool of zinc.

Wetting of the steel by the molten zinc is the condition most favourable to zinc embrittlement. Surface layers such as metal oxides can prevent penetration, but if the layer is broken in some way, such as by abrasion or a reducing atmosphere, wetting can occur. There is some evidence that embrittlement can be caused by contamination from zinc vapour, but this is unlikely to occur, unless the molten zinc is at a distance of no more than an inch or so.

The type of stainless steel affects its susceptibility to zinc embrittlement. The latter is believed to be the result of interaction between zinc and nickel in the steel. It is the austenitic chromium nickel steels which are particularly affected.

Given conditions favourable to zinc embrittlement failure can be rapid. Cottrell and Swann obtained failures in a matter of seconds.

There are a number of possible sources of zinc on process plants. Zinc is used in galvanized, sprayed and painted coatings. Typical zinc-coated items are galvanized fittings, walkways, wire and finned tubes. Paints which contain zinc compounds but not metallic zinc are not a serious risk in this respect.

The principal hazard posed by zinc embrittlement is rapid and catastrophic failure as a result of a fierce local fire on the plant. Zinc embrittlement also creates the problem that, after a general plant fire, stainless steel equipment which has a nearby source of zinc is suspect. The problem of zinc embrittlement, however, should be kept in perspective. It is significant mainly as a secondary effect which can increase the severity of a local fire.

On stainless steel plant where zinc embrittlement could have serious consequences in the event of fire, zinc should be eliminated as far as possible. In particular, zinc-coated items should not be placed in direct contact with stainless steel or in positions where they could drip molten zinc onto it. Thus, for example, galvanized wire netting used in insulation should not be in direct contact with stainless steel pipe. Similar considerations apply to stainless steel plant which has a normal operating temperature above 400°C. Care should also be taken to prevent zinc contamination of stainless steel in welding and other fabrication or maintenance activities.

If plant made of stainless steel is subjected to fire, it should be examined by experts to check that it has not suffered zinc embrittlement. Deterioration is difficult to determine by normal inspection methods and requires metallurgical examination. Further information on zinc embrittlement is given in TDN 53/1 *Zinc Embrittlement of Austenitic Stainless Steel* (HSE, 1976).

12.27.16 Erosion

Erosion is a common form of corrosion and takes many forms. It occurs particularly at sites where there is a flow restriction or change of direction. These included nozzle-sand valves, elbows, tees and baffles, and points opposite to inlet nozzles. It is enhanced by the presence of solid particles in gas or liquid, by drops in vapours or by bubbles in liquids and by two-phase flow. Conditions which can

cause severe erosion include pneumatic conveying, wet steam flow, flashing flow and pump cavitation.

12.27.17 External corrosion

External corrosion can be caused by components in insulation and in fireproofing. The leaching of chloride salts from insulation by dripping water corrodes pipework. An account of corrosion beneath lagging has been given in Section 12.11. External corrosion is also considered in relation to maintenance in Chapter 21.

Underground pipework can be corroded by the soil. This form of corrosion is often electrochemical, and cathodic protection is used to combat it.

12.27.18 Corrosion at welds

In much process equipment, the welds constitute both a potential fault line and a line of common cause failure, in that if there is corrosion at one point in the weld it is quite likely to be occurring along much of it. It is this combination, with its potential for catastrophic failure, which makes corrosion at welds so serious. An account of corrosion at welds is given by M. Turner (1990a), who distinguishes three basic causes of such corrosion: (1) hydrodynamics, (2) differences in composition and (3) differences in metallurgical structure.

Corrosion due to hydrodynamic effects is seen in butt welds on pipes. One cause is lack of root fusion, such that there is a small hollow at the root of the weld on the inner surface of the pipe, which then becomes the site of turbulence and impingement corrosion. Another cause is protrusion of a weld bead, which gives rise to impingement pitting in the pipe surface beyond the protrusion. In both cases, attack can be rapid and can accelerate. If the defect extends sufficiently far round the pipe, it may result in pipe rupture. In addition to control of welding to eliminate such defects, countermeasures may include the use of a backing ring; for a small bore connection, the use of an undersized connection which is then drilled out to size; and the limitation of fluid velocity.

A weld has the structure of cast metal and, if made of the same material as the parent metal, will generally be weaker. In order to compensate for this, use is commonly made of a weld metal of different composition. However, this difference in composition can be another cause of weld attack, by galvanic cell, or bimetallic couple, corrosion. The corrosion effects are governed by the ionic conductivity of the liquid which determines the extent of the pipe which participates as an electrode. If the weld metal is more noble, it is cathodic towards the parent metal, and it is principally the latter which will corrode, but even if the corrosion zone is relatively narrow, the rate of corrosion will tend to be limited by the small area of the cathode. If the weld metal is less noble and is therefore anodic, corrosion will occur mainly at the weld, with the rate of corrosion being dependent on the area of the pipe acting as the cathode. If the ratio of this area to that of the weld is high, corrosion can be rapid.

During welding a zone of the parent metal is affected by the heat. This heat affected zone (HAZ) can be some 20 mm wide and usually it is more susceptible to corrosion. Early stainless steels suffered serious problems of grain boundary corrosion, or weld decay, which led to brittle failure. The cause was depletion of chromium at the grain boundaries, due to the fact that under these conditions the carbon in solid solution migrates to the boundaries and forms chromium carbide, which precipitates, whilst chromium migrates more slowly and thus the chromium deficiency is not made good. The solution was the production of stainless steels with low carbon contents.

In steels, generally, the high temperatures involved in welding cause a number of metallurgical changes in the HAZ, many of which make it more susceptible to corrosion. One mechanism of corrosion is a bimetallic couple. Control of the welding, including the heat input and interpass temperatures, can minimize, but generally not totally eliminate, the corrosion susceptibility. This susceptibility is, however, little affected by post-weld heat treatment, which is a form of tempering aimed at partial stress relief of the weld to reduce its brittleness, and is conducted at temperatures below those required to reverse changes in the metallurgical structure of the heat affected zone.

In 1984, an oil line fracture at Las Piedras, Venezuela, sprayed hot oil across a roadway onto hydrogen units, causing a major fire (Case History A110). The pipe failure was a circumferential fracture in the parent metal in the heat affected zone about 1.5 in. from the weld.

12.27.19 Corrosion testing

Corrosion is generally a function of a number of variables and can be very sensitive to the particular process conditions. It is not always easy to predict, and in some cases corrosion testing is necessary. As described by M. Turner (1988), there are essentially two distinctly different types of corrosion test. The first type is standard tests, which are characterized by the fact that they apply essentially to a set of relatively straightforward conditions and are precise, reproducible, rapid and cheap, and require neither skilled supervision and interpretation nor input from the client. Plant simulation tests, on the other hand, which simulate actual plant conditions, are not very precise or reproducible, can be prolonged and expensive, and require close supervision, skilled interpretation and client input.

Since in a candidate design corrosion is likely to proceed relatively slowly, testing can take a long time. It is therefore not uncommon to use some form of accelerated test. As with any form of accelerated testing, this can be misleading. An alternative is the use of corrosion rate monitoring for which instrumentation now exists. This allows information to be obtained in tests which simulate the plant conditions. However, since the corrosion rate can vary with time, if this method is used it is necessary to ensure that the steady-state rate has been reached. It is desirable that the design of corrosion tests be a joint exercise between the chemical engineer and the corrosion specialist.

12.27.20 Corrosion policy

In establishing a policy on corrosion, there is a need to strike a balance between neglect and excessive caution. Process plants live with corrosion. The important thing is to identify, and act on, those cases where corrosion can be especially hazardous or costly. Some of the factors to be considered are discussed, with illustrations, by M. Turner (1987, 1990b). Most experienced corrosion engineers will themselves admit to cases where they have been surprised by the rapid corrosion which has occurred and others where they anticipated corrosion which never materialized.

The *Report of the Committee on Corrosion and Protection* (Hoar, 1971) (the *Hoar Report*) reviewed national policy on corrosion. It made the point that there were substantial gains to be made simply by applying existing knowledge; in other words, there is a need for 'corrosion awareness' on the

part of engineers. However, there has to be an economic balance. Corrosion technologists for their part need a keen appreciation of the practicalities of the economics of process plants. For example, in many applications the choice of carbon steel will be the right one, even though it will corrode faster than an alternative, more expensive material.

As an instance of living with corrosion, M. Turner (1987) cites the case of the steam reforming process for hydrogen. Theoretically, this should have been severely inhibited by the problem of creep rupture of the catalyst tubes, which, since creep is a probabilistic process, was liable to cause disruption due to premature failures. The solution was the use of 'pigtails' which could be nipped closed, allowing the furnace to continue in operation.

Corrosion is another area in which it is important that engineers know enough to recognize those situations in which specialist advice is necessary.

12.28 Fracture Mechanics

A very powerful tool for the avoidance of catastrophic failure in pressure equipment is fracture mechanics. In this section an account is given of deterministic fracture mechanics, which deals essentially with the propagation of cracks, whilst the following section treats probabilistic fracture mechanics, which deals with the probabilistic aspects of equipment failure due to cracks such as the probabilities of prior existence of defects, of failure to detect them, and so on.

Accounts of fracture mechanics are given in *Fracture of Structural Materials* (Tetelman and McElivy, 1967), *Elements of Elasticity* (Dugdale, 1968), *Fracture – An Advanced Treatise* (Liebowitz, 1968), *Fundamentals of Fracture Mechanics* (Knott, 1973), *Elementary Engineering Fracture Mechanics* (Broek, 1974), *Fracture and Fatigue Control in Structures* (Rolfe and Barsom, 1977, 1987), *The Mechanics of Fracture and Fatigue* (A.P. Parker, 1981) and *Engineering SafetyAssessment* (Thomson, 1987). Background treatments of elasticity and plasticity include those by Godfrey (1959), W. Johnson and Meller (1962), Spencer (1968), Timoshenko and Goodier (1970) and Benham and Warnock (1973).

Fracture mechanics deals with the initiation and growth of cracks to a critical size and with failure due to cracks. It identifies different regimes of crack growth, and the effect of material properties, plate thickness, and so on. It provides the basis for strategies for the avoidance, control and mitigation of crack propagation.

As such it provides a tool not only for the avoidance of catastrophic failure, but also for discrimination between those defects which require prompt action and those which do not. The failure mechanism mainly treated in fracture mechanics is fatigue, but it is applicable to other mechanisms also.

12.28.1 Loading regimes

The account of fracture mechanics given here is concerned essentially with steel plate such as is used in pressure vessels. An applied load gives rise in a body to stress σ and strain ϵ. The general problem of determining the stresses and strains within a loaded body is a complex one. A considerable simplification can be obtained if for a body of coordinates *x, y, z* it can be assumed that there is no change in the distribution of stress in the *z* direction. Then for deformation in the *x, y* plane two cases may be distinguished: plane stress and plane strain.

Plane stress is applicable to the case of a plate sufficiently thin that it can be assumed incapable of supporting stress σ_z through the thickness (the *z* direction) so that $\sigma_z = 0$. Plane strain applies in the case of a plate sufficiently thick that it prevents strain t_z through the thickness so that $\epsilon_z = 0$.

In most engineering applications, the combination of the dimensions of the structure and the steels used is such that at normal service temperatures the thickness of the steel is not sufficient to ensure plane strain under slow loading conditions. The material exhibits a behaviour which is not purely elastic but is to some degree elastic–plastic. Another distinction is in the mode of crack surface displacement. Three such modes are commonly treated. The modes involve opening (Mode I), shearing (Mode II) and tearing (Mode III). It is the first mode which is of interest here.

12.28.2 Modelling of crack behaviour

In describing the modelling of the stresses and strains caused by an applied load, and of the effect on cracks, it is usual to start by considering purely elastic behaviour. Models of loading are based on equations of equilibrium and compatibility. There are a number of stress functions which can be shown to satisfy the equilibrium conditions. One of these is the Airy stress Function *F*. There are also a number of complex stress functions which satisfy both the equilibrium and compatibility conditions. It can be shown that both sets of conditions are satisfied by the solution

$$F + \mathrm{i}B = \bar{z}\phi(z) + \int \psi(z)\,\mathrm{d}z \qquad [12.28.1]$$

where F is the Airy function, B is some other function, ϕ and ψ are analytic functions, and $z = x + \mathrm{i}y$ and $\bar{z} = x - \mathrm{i}y$.

12.28.3 Stored energy

When a body is loaded the movement caused by the applied load does work which is stored as strain energy. For uniaxial tension this work is:

$$U = \sigma^2/2E \qquad [12.28.2]$$

where E is the modulus of elasticity, or Young's modulus and U is the energy stored per unit volume of material.

12.28.4 Griffith crack model

Early work on fracture faced the apparent paradox that a sharp notch is capable of producing very high stress concentration, yet an infinitely sharp one does not necessarily lead to failure. This problem was addressed by Griffith (1920–21), who for the case of a single crack of length $2a$ in a brittle material considered the energy changes associated with an incremental extension of that crack and showed that

$$U = \frac{\sigma^2}{2E}\pi a^2 \qquad \text{plane stress} \qquad [12.28.3]$$

$$U = \frac{\sigma^2}{2E}\pi a^2(1 - v^2) \qquad \text{plane strain} \qquad [12.28.4]$$

since for plain strain

$$\epsilon = (1 - v^2)\sigma/E \qquad [12.28.5]$$

where a is the crack half-length and v is Poisson's ratio. The energy release rate for crack extension G is defined as

$$G = \partial U/\partial a \qquad [12.28.6]$$

Hence from Equations 12.28.3, 12.28.4 and 12.28.6

$$G = \frac{\pi\sigma^2 a}{E} \quad \text{plane stress} \qquad [12.28.7]$$

$$G = \frac{\pi\sigma^2 a}{E}(1 - v^2) \quad \text{plane strain} \qquad [12.28.8]$$

The energy absorption rate for crack extension

$$R = \partial W/\partial a \qquad [12.28.9]$$

where W is the energy absorbed in producing crack extension.

At the threshold condition for unstable crack growth $\mathrm{d}U/\mathrm{d}a = \mathrm{d}W/\mathrm{d}a$ and hence $G = R$. But since R is a constant, there is a critical value G_{cr} at which such growth will occur and this value is a constant. Then from Equations 12.28.7 and 12.28.8

$$G_{cr} = G_c = \frac{\pi\sigma_c^2 a}{E} \quad \text{plane stress} \qquad [12.28.10]$$

$$G_{cr} = G_{IC} = \frac{\pi\sigma_c^2 a}{E}(1 - v^2) \quad \text{plane strain} \qquad [12.28.11]$$

where G_c and G_{IC} are the critical values of G for plane stress and plane strain, respectively, and U_c is the critical value of the stress. Equations 12.28.10 and 12.28.11 give

$$\sigma_c^2 = \frac{EG_c}{\pi a} \quad \text{plane stress} \qquad [12.28.12]$$

and

$$\sigma_c^2 = \frac{EG_{IC}}{\pi a(1 - v^2)} \quad \text{plane strain} \qquad [12.28.13]$$

Equation 12.28.12 is sometimes written as

$$\sigma_c = \left(\frac{2\gamma E}{\pi a}\right)^{1/2} \qquad [12.28.14]$$

with

$$G_c = 2\gamma \qquad [12.28.15]$$

where γ is the surface energy per unit area.

12.28.5 Stress intensity factor

For a body containing a crack the magnitude of the stress field at the crack tip may be characterized by the stress intensity factor K. For the first mode of crack surface displacement, Mode I, which is that of interest here, the stress intensity factor is K_I.

This stress intensity factor K_I has a critical value K_c at which unstable crack propagation occurs. As the plate thickness is increased, the value of K_c decreases asymptotically to a minimum value K_{IC}. In other words, under plain strain conditions K_c has a minimum value K_{IC} the plane strain fracture toughness or, simply the fracture toughness.

For biaxial loading an expression for the stress intensity factor is

$$K_I = \sigma(\pi a)^{1/2} \qquad [12.28.16]$$

Then from Equations 12.28.7, 12.28.8 and 12.28.16

$$K_I = (GE)^{1/2} \quad \text{plane stress} \qquad [12.28.17]$$

$$K_I = \left(\frac{GE}{1 - v^2}\right)^{1/2} \quad \text{plane strain} \qquad [12.28.18]$$

Compilations of stress intensity factors are given by Sih (1973a), Rooke and Cartwright (1976) and Hudson and Seward (1978).

The fracture toughness is a property of the material, and plays a crucial role in fracture mechanics. It is discussed further below.

12.28.6 Westergaard stress function

Mention has already been made of the Airy function. Another stress function, or rather family of functions, which has proved fruitful is the Westergaard stress function Z_I, where the subscript I refers to the x axis of symmetry. The stress intensity factor k_I may be expressed in terms of a Westergaard function:

$$K_I = (2\pi)^{1/2} \lim_{z \to a}(z - a)^{1/2} Z_I(z) \qquad [12.28.19]$$

It can be shown that using the appropriate Westergaard function the stress intensity factor for a biaxially loaded crack in a plate is given by

$$K_I = \sigma(\pi a)^{1/2} \qquad [12.28.20]$$

as already given.

Another situation of interest is that of an array of cracks aligned in the same direction. Then, using the Westergaard function appropriate to this case, it can be shown that

$$K_I = \sigma(\pi a)^{1/2}\left[\frac{2b}{\pi a}\tan\left(\frac{\pi a}{2b}\right)\right]^{1/2} \qquad [12.28.21]$$

where the distance between the centres of the cracks is $2b$. Equation 12.28.21 reduces to Equation 12.28.20 as $b/a \to \infty$.

12.28.7 Geometric factor

Equation 12.28.20 may be generalized to cover other cases such as that given in Equation 12.28.21 by the introduction of a configuration correction factor, or geometric factor Q, so that

$$K_I = Q\sigma(\pi a)^{1/2} \qquad [12.28.22]$$

Then, for example, for the case of an array of cracks given by Equation 12.28.21

$$Q = \left[\frac{2b}{\pi a}\tan\left(\frac{\pi a}{2b}\right)\right]^{1/2} \qquad [12.28.23]$$

The geometric factor Q has the value unity for a central through crack in a thick plate. Values for other configurations are given by Harvey (1974).

12.28.8 Fracture toughness

The fracture toughness K_{IC} is a property of the material and there are standard tests for it. They include BS 5447: 1977 and ASTM Test Method E-399: 1990. There are also relations between fracture toughness and other parameters such as the Charpy V-notch (CVN) toughness and the crack opening displacement (COD). Both tests and relationships are described by Rolfe and Barsom (1987).

As described earlier, below the transition temperature there is a marked fall in the toughness of a ferritic steel. Typically the fracture toughness is reduced by a factor of about four. Hydrogen embrittlement and impurities can also cause a pronounced reduction in fracture toughness.

12.28.9 Modelling of crack behaviour: plastic deformation

In the account given so far the assumption has been made that the behaviour of the material is elastic. In practice, most materials exhibit at some critical combination of stresses a degree of plastic deformation, or yielding.

There are two principal criteria for the onset of yielding. These are the Tresca criterion

$$|\sigma_1 - \sigma_3| = \sigma_{ys} \qquad [12.28.24]$$

and the von Mises criterion

$$(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 = 2\sigma_{ys}^2 \qquad [12.28.25]$$

where σ_{ys} is the yield stress and $\sigma_1 > \sigma_2 > \sigma_3$.

Some principal models of crack tip plastic behaviour are those given by Irwin (1958) and Dugdale (1960).

12.28.10 Irwin model

A model of crack tip plastic behaviour has been given by Irwin (1958). If the plastic zone is treated as a circle of radius λ, the model gives

$$\lambda = \frac{1}{2\pi}\left(\frac{K_I}{\sigma_{ys}}\right)^2 \qquad [12.28.26]$$

The crack may be envisaged as having a notional length $(a + \lambda)$. Then, following Equation 12.28.22, an alternative stress intensity factor K^* may be defined as

$$K^* = Q\sigma[\pi(\alpha + \lambda)]^{1/2} \qquad [12.28.27]$$

12.28.11 Dugdale model

Another model for crack tip plasticity is that of Dugdale (1960). In this model the notional length of the crack is taken as $(a + \rho)$, where ρ is the length of the plastic zone. The model yields the relation:

$$\rho = \frac{\pi}{8}\left(\frac{K_I}{\sigma_{ys}}\right)^2 \qquad [12.28.28]$$

which may be compared with Equation 12.28.26 in the Irwin model.

12.28.12 Modelling of critical crack length

There are a number of models for the critical length of crack for fracture. They include the following: the linear elastic fracture mechanics (LEFM) model, the stress concentration theory (SCT) model, the Bilby, Cottrell and Swinden (BCS) model, and the J integral model.

An early model for failure at the crack tip was that of Neuber (1937). In this model failure is considered to occur when, over some characteristic distance b from the crack tip, the average stress, or stress integrated over the distance from a to $(a + b)$, reaches a critical value.

The characteristic distance b has a critical value b_{cr}, such that at shorter distances the stress concentration at the crack becomes critical. Following the treatment of Thomson (1987), itself based on that of Irvine (1977 SRD R48), when the average stress over the characteristic distance reaches a critical value

$$\frac{\sigma_u}{\sigma_c} = \left(\frac{2a}{b_{cr}} + 1\right)^{1/2} \qquad [12.28.29]$$

where b is a 'spreading length', b_{cr} its critical value and σ_u is the ultimate tensile stress.

Use is also made of another parameter S, effectively an alternative critical spreading length, where

$$b_{cr} = \frac{2}{3}S \qquad [12.28.30]$$

An account is now given of the first three models mentioned earlier. The fourth is the J integral model of Rice (1968a,b).

12.28.13 LEFM model

The linear elastic fracture mechanics (LEFM) model follows directly from Equation 12.28.29. If the spreading length is much less than the crack size ($b_{cr} \ll a$), then from that equation:

$$\frac{\sigma_u}{\sigma_c} = \left(\frac{2a}{b_{cr}}\right)^{1/2} \qquad [12.28.31]$$

and from Equations 12.28.30 and 12.28.31

$$\frac{a}{S} = \frac{1}{3}\left(\frac{\sigma_u}{\sigma}\right)^2 \qquad [12.28.32]$$

12.28.14 SCT model

The stress concentration theory (SCT) model is a modification of the LEFM model. It may be expressed in the form of Equation 12.28.29 or, using equation 12.28.30, as:

$$\frac{a}{S} = \frac{1}{3}\left[\left(\frac{\sigma_u}{\sigma}\right)^2 - 1\right] \qquad [12.28.33]$$

12.28.15 BCS model

The third model, that of Bilby, Cottrell and Swinden (1963), or the BCS model, may be stated as:

$$\frac{a}{S} = \frac{\pi}{8}\left[\ln \sec\left(\frac{\pi\sigma}{2\sigma_u}\right)\right]^{-1} \qquad [12.28.34]$$

12.28.16 Crack opening displacement

In the extension of the modelling of fracture into the region of elasto-plastic behaviour, an important concept is the crack opening displacement (COD), or crack tip opening displacement (CTOD), proposed by Wells (1961). In this region, if a crack is envisaged as a triangular wedge extending some distance λ into a circular plastic zone, such that the effective half-length is $(a + \lambda)$, then at the distance a from its centre, where it enters the plastic zone, it must have a certain width. This width is the COD.

The COD is a property of the material, is the subject of standard tests and may be related to other properties such as the fracture toughness. Standard tests include BS 5762: 1979 and ASTM Test Method E1290: 1990 and relations exist between the COD and other parameters; the tests and relationships are discussed by Rolfe and Barsom (1987).

Expressions for the COD δ may be obtained from the models of crack tip plastic behaviour. For the model of Dugdale (1960):

$$\delta = \frac{8}{\pi}\frac{\sigma_{ys}}{E} a \ln\left(\frac{a+\rho}{a}\right) \qquad [12.28.35]$$

and also

$$\delta = \frac{8}{\pi}\frac{\sigma_{ys}}{E} a \ln\left[\sec\left(\frac{\pi a}{2\sigma_{ys}}\right)\right] \qquad [12.28.36]$$

This last equation may be

$$\delta \approx \frac{\pi\sigma^2 a}{E\sigma_{ys}} \quad \sigma < 0.7\sigma_{ys} \qquad [12.28.37]$$

Then from Equations 12.28.16 and 12.28.37

$$\delta = K_I^2/E\sigma_{vs} \qquad [12.28.38]$$

The crack opening displacement δ has a critical value δ_C corresponding to the critical stress σ_c.

In line with the foregoing, a general relation for the critical crack opening displacement has been given by J.N. Robinson and Tetelman (1974)

$$\delta_c = \frac{K_{IC}^2}{\lambda' E\sigma_{ys}} \qquad \text{plane stress} \qquad [12.28.39]$$

$$\delta_c = \frac{K_{IC}^2(1-v^2)}{\lambda' E\sigma_{ys}} \qquad \text{plane strain} \qquad [12.28.40]$$

where λ' is a constraint factor.

12.28.17 Fatigue crack growth

A principal mechanism of crack propagation is fatigue. If a crack is subjected to a cyclic stress of amplitude $\Delta\sigma$ this induces a corresponding range of the stress intensity factor ΔK. Then from Equation 12.28.22

$$\Delta K = Q\Delta\sigma(\pi a)^{1/2} \qquad [12.28.41]$$

If the rate of increase da/dN of the crack length is plotted against the stress intensity factor range ΔK on a log–log plot, then as shown in Figure 12.22, the curve has three regions. In the first region (1) there is rapid crack growth; in the second region (2) the crack growth is slower and more predictable; and in the third region (3) the crack growth accelerates again to failure. Over the second region the curve is given by the Paris equation:

$$\frac{da}{dN} = C(\Delta K)^m \qquad [12.28.42]$$

where N is the number of loading cycles, C is a constant, and m is an index. For most ferrous and non-ferrous metals $m \approx 4$.

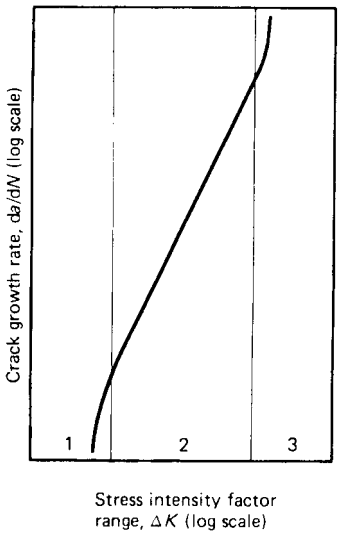

Figure 12.22 *Typical crack growth rate for mild steel*

Equation 12.28.42 may be integrated as follows:

$$N = \int_{a_i}^{a_f} \frac{1}{C(\Delta K)^m}\, da \qquad [12.28.43]$$

where subscripts f and i indicate final and initial, respectively. Fatigue is not, however, the only mechanism of crack propagation. At high temperatures, crack growth can occur by creep. In this case the rate of growth is expressed not in terms of the number N of cycles but of time t, hence as da/dt. Treatments have been given by Tomkins (1983) and by Ainsworth and Goodall (1983).

12.28.18 Failure assessment diagram

A method for the assessment of the regime in which a particular equipment is operating has been developed at the CEGB, and is described by R.P. Harrison and Milne (1981).

Linear elastic failure and fully plastic failure represent two limiting cases. Two parameters are defined as follows. For linear elastic failure

$$K_r = K_I(a)/K_{IC} \qquad [12.28.44]$$

and for fully plastic failure

$$S_r = \sigma/\sigma_1(a) \qquad [12.28.45]$$

where K_r is a measure of the proximity to linear elastic failure, S_r is a measure of the proximity to fully plastic failure and $\sigma_1(a)$ is the plastic collapse stress. As indicated, both K, and σ_1 are functions of the crack half-length.

Figure 12.23 illustrates the failure assessment diagram (FAD) given by the authors and based on these two parameters. The failure assessment line in the diagram is constructed using an elastic-plastic model from the work of Dugdale (1960), Bilby, Cottrell and Swinden (1963) and Heald, Spink and Worthington (1972) to interpolate

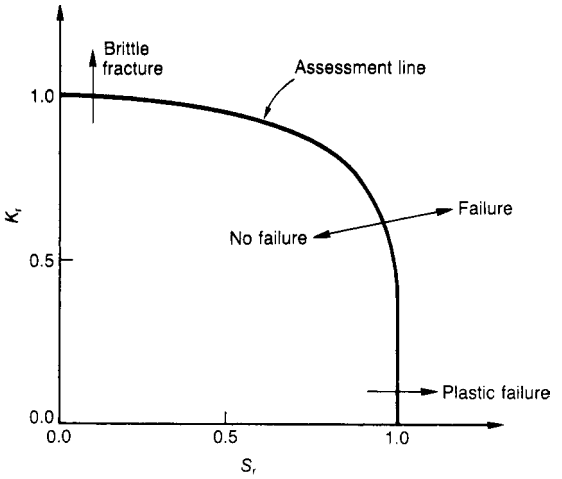

Figure 12.23 *Failure assessment diagram (after R.P. Harrison and Milne, 1981) (Courtesy of The Royal Society)*

between the two limiting behaviours. It has been shown by Chell (1978) that this approach is a reasonable approximation to the failure curve for any structural geometry. It is supported by tests on laboratory specimens and on structures as described by R.P. Harrison, Loosemore and Milne (1979). Failure is conceded if the assessment point lies outside (to the right) or on the curve. If lower bound data areused, the curve may be regarded as a failure avoidance line.

The method has been developed to support a comprehensive system of fracture mechanics used in the CEGB and elsewhere. This system is referred to as the 'R6 Procedure'. Its third revision is given in a CEGB report by Milne *et al.* (1986) and in the open literature by Milne *et al.* (1988b).

12.28.19 Fracture analysis diagram

Another widely used diagram is the fracture analysis diagram (also FAD). This was developed by Pellini (1971) as a means of providing guidance on steels which exhibit a transition temperature. The diagram is a plot of stress vs temperature and has four reference points: the null ductility transition (NDT), fracture transition elastic (FTE) and fracture transition plastic (FTP) points and midrange point between NDT and FTE. As described by the author, restricting the service temperature to just above the NDT provides fracture initiation protection for most common failures; restricting it to the mid-range between NDT and FTE provides fracture arrest protection for $\sigma \leq 0.5\sigma_{ys}$; restricting it to above the FTE provides fracture arrest protection for $\sigma \leq \sigma_{ys}$; and restricting it above the FTP ensures that the fracture is fully ductile.

12.28.20 Through-thickness yielding

It is of interest to be able to establish in a given case whether through-thickness yielding will occur before fracture. Such yielding is a function of plate thickness. As already described, the two limiting conditions are those of plane stress in thin plates and plane strain in thick plates. Practical situations to lie between these two extremes.

Through-thickness yielding is generally treated in terms of the dimensionless parameter β

$$\beta = \frac{1}{B}\left(\frac{K_{IC}}{\sigma_{ys}}\right)^2 \qquad [12.28.46]$$

where B is the plate thickness.

A discussion of the values given by various workers for the parameter β and their interpretation is given by Rolfe and Barsom (1987). They quote ASTM Committee 24 on Fracture Testing as advising that to ensure plain strain behaviour it is necessary to have $\beta \geq 0.4$. Hahn and Rosenfield (1968) found a significant increase in the rate at which through-thickness deformation occurs for $\beta \geq 1$. Irwin (1962) used a value of $\beta = 1.4$ in his leak-before-break model, described below.

12.28.21 Leak-before-break behaviour

If a crack grows to the point where it will cause failure, it is obviously desirable that it give warning of impending failure by leaking. It is possible using fracture mechanics to assess whether or not in a given situation the crack will exhibit such leak-before-break (LBB) behaviour. This behaviour is also sometimes called leak-before-fracture (LBF) and its obverse as fracture-before-leak (FBL).

The LBB criterion was proposed by Irwin *et al.* (1967) with the aim of predicting the toughness required in a pressure vessel so that before fracture occurs a surface crack will grow through the wall and give a leak. Another way of putting this is that the critical crack size is greater than the wall thickness.

An account of the LBB criterion is given by Rolfe and Barsom (1977). It is assumed that a surface crack might grow through a wall of thickness B into a through-thickness crack of length $2B$. Hence the LBB criterion is $2a \approx 2B$. The authors use for the stress intensity factor K_I, the relation

$$K_I^2 = \frac{\sigma^2 \pi a}{1 - 0.5(\sigma/\sigma_{ys})^2} \qquad [12.28.47]$$

or, for low stress

$$K_I = \sigma(\pi a)^{1/2} \qquad [12.28.48]$$

as given earlier. Then for the critical stress $K_I = K_c$. The critical stress intensity factor K_c is obtained using the following relation:

$$K_c^2 = K_{IC}^2(1 + 1.4\beta_{IC}^2) \qquad [12.28.49]$$

with

$$\beta_{IC} = \frac{1}{B}\left(\frac{K_{IC}}{\sigma_{ys}}\right)^2 \qquad [12.28.50]$$

where B is the wall thickness and β_{IC} a dimensionless parameter.

Another treatment of LBB is given by Harvey (1974), who deals with practical aspects such as allowance for residual stress.

One use of the LBB method is in the design of a vessel to ensure that it operates in the LBB region. Another is to calculate the allowable stress in a vessel where a crack has been observed. Another is to check that the size of crack

which requires a reduction in operating stress is detectable by the inspection methods used.

12.28.22 Some design features

The fracture characteristics just described have a number of implications for the design of pressure systems. They include: the effects of plate thickness and through-thickness yielding; the effect of the use of advanced design codes; and the LBB principle.

If a plate is sufficiently thin, fracture is ductile; if it is sufficiently thick, fracture is brittle. Much equipment in pressure systems will lie somewhere in between. The relations for through-thickness yielding provide a means of quantifying this behaviour.

Advanced design codes such as BS 5500 and ASME *Boiler and Pressure Vessel Code*, Section VIII, Division 2, permit the use of a stress which constitutes a higher proportion of the ultimate tensile stress; in other words the ratio σ_u/σ is lower, so that instead of being 4 it lies in the range 2–3. Whilst this gives economies in equipment design, it means that the length of the critical crack is appreciably reduced, thus making it more difficult to ensure detection of such a crack.

For critical equipment, such as a vessel containing a large inventory of a hazardous material, it is possible to identify the region in which a fracture will exhibit LBB behaviour, with a view to designing to ensure that the equipment operates always in that region.

There are also implications for inspection. Fracture mechanics can indicate the size of crack which needs to be detected by the inspection procedures and the inspection interval necessary to ensure that no crack grows to its critical value before the next inspection.

12.29 Probabilistic Fracture Mechanics

A comprehensive approach to equipment failure from crack propagation requires that the deterministic treatment just described be complemented by probabilistic methods. Probabilistic fracture mechanics addresses such questions as the probability that a crack will be present, that it is not detected on a given inspection and that it grows to a critical size before the next inspection, causing failure. Accounts of probabilistic fracture mechanics include those by O'Neil (1980), Temple (1983, 1985), Haines (1983), Lidiard (1984) and Thomson (1987).

The probability that a pressure vessel, or similar equipment, will fail due to crack propagation may be expressed as follows:

$$P_f = P_{x0}(x) P_{nf} P_{gc} \qquad [12.29.1]$$

where P_f is the probability that the vessel fails, P_{gc} is the probability that the defect grows to critical size before the next inspection, P_{nf} is the probability that the defect is not detected by non-destructive examination (NDE) at a given inspection, $P_{x0}(x)$ is the probability that the vessel has an initial defect of depth $> x$, and x is the crack depth (mm).

Work in this area has focused particularly on pressure vessels for nuclear pressurized water reactors (PWRs). In a study of this problem, Lidiard (1984) obtained the relation

$$P_{x0}(x) = \frac{A}{\Theta} \exp(-\Theta x) \qquad [12.29.2]$$

where A and Θ are constants (both mm^{-1}). He obtained for such vessels values of A and Θ of 0.59 and 0.16, respectively. These values imply, for example, that the probability of such a vessel having a crack of depth exceeding 25 mm is 0.067 and the probability of one exceeding 50 mm is 1.24×10^{-3}.

The reliability of detection by NDE was the subject of a study by the European Community Plate Inspection Steering Committee (PISC). Information obtained on defect detection probability (DDP) is described by O'Neil (1980) and an analysis is given by Haines (1983).

The data on the probability of detection, or DDP, may be fitted to an appropriate distribution. That used by W. Marshall (1982) is the exponential distribution. Thomson (1987) proposes, for a simplified analysis, that the probability of detection by NDE, P_n may be fitted to a log–normal distribution, as given by Equation 7.7.20. He gives for the parameters of the distribution m^* and σ the values 3.135 and 0.667 mm, respectively. The probability P_{nf} of failure to detect is the complement of P_n.

The probability that a crack will grow to critical size may be obtained deterministically by the method described in the previous section. Alternatively, it too may be treated probabilistically. This approach has been described by Temple (1985). The probability P_{gc} that the crack grows to critical size given that it has an initial depth x_0 and stress intensity factor range ΔK and is subject to N loading cycles may be written as $P_{gc}(x/x_0, \Delta K, N)$. Then, taking for this probability a log-normal distribution, Temple obtains for PWR vessels:

$$m^* = x_0 + 6.56 \times 10^{-5} \Delta K \cdot N \text{ mm}$$

$$\sigma = 2.93 \times 10^{-5} \Delta K \text{ mm}$$

where ΔK is the stress intensity factor range ($MPa/m^{1/2}$). The application of the relations just described to obtain the probability of vessel failure is discussed, with illustrative examples, by Thomson. He casts Equation 12.29.1 in the form

$$P_f = \int_0^{x_c} P_{x0}(x) P_n(x) p_{gc}(x)\, dx \qquad [12.29.3]$$

where p_{gc} is the probability density function corresponding to the probability distribution P_{gc} and x_c is the critical crack length.

H.M. Thomas (1981) describes an approach to the determination of the probability ρ_c of catastrophic failure and ρ_L of leak which starts with generic estimates but involves a learning process using data from the actual plant to obtain more refined estimates.

12.30 Failure of Vessels, Equipment and Machinery

There is a certain amount of statistical information available on the failure of pressure system components.

12.30.1 Failure of pressure vessels

Work on the failure rates and modes of pressure vessels has been driven initially by the needs of the nuclear industry.

Information on pressure vessel failure is given in *A Survey of Defects in Pressure Vessels Built to High Standards of Construction and its Relevance to Nuclear Primary Circuit Envelopes* by Phillips and Warwick (1968 UKAEA AHSB(S) R162). The survey deals with pressure vessels built to Class 1

requirements of BS 1500, BS 1515 and comparable standards. It classifies failures as catastrophic or potentially dangerous. The former are disruptions of the vessel which require major repair or scrapping; the latter are defects which might deteriorate under the working conditions and which require remedial action. The following information is given on failures prior to service and in service:

	Sample size	*Failure rate* (failures/year)	
		Potentially dangerous failures	*Catastrophic failures*
Failure in construction	12,700 vessels	5.5×10^{-4}	2.3×10^{-4}
Failure in service	100,300 vessel-years	1.25×10^{-3}	0.7×10^{-4}

For all the service failures the causes were classified. The results are shown in Table 12.11. The vast majority of failures, some 89.3%, were due to cracks. The causes of cracks were therefore analysed separately as shown in the table. The table also gives the methods by which the failures were detected.

In addition, Phillips and Warwick analysed the effects of other variables such as materials of construction, design conditions, fluid handled, component state and age. The results are given in Table 12.12. As indicated in Table 12.12, there were seven catastrophic failures. The causes of these failures were: maloperation (four cases), fatigue (two cases), and pre-existing from manufacture (one case). The authors comment: 'Most of these catastrophic failures are due to inadequate operational procedures and highlight the need for more consideration of control techniques.'

The authors then analyse the data to assess the failure frequency of the pressure vessels used in nuclear reactor primary circuit envelopes. They conclude that many of the failures given in the survey would not apply in such vessels, for example, cracks in boiler furnaces, and reduce the total number of applicable service failures from 132 to 62 and the number of applicable catastrophic failures from 7 to 2. Then the failure frequencies become:

	Failure rate (failures/year)	
	Potentially dangerous failures	*Catastrophic failures*
Failure in service	6×10^{-4}	2×10^{-5}

These results agree reasonably well with the catastrophic failure frequencies estimated for nuclear vessels by Kellerman and Seipel (1967). This study provides a good illustration of the determination of failure data and of the derivation from crude data of failure data applicable to the

Table 12.11 *Causes and methods of detection of service failure in pressure vessels (after Phillips and Warwick, 1968 UKAEA AHSB(S) R162) (Courtesy of the UK Atomic Energy Authority)*

	No. of cases	*Percentage of total cases*
Causes of failures:		
Cracks	118	89.3
Maloperation	8	6.1
Pre-existing from manufacture	3	2.3
Corrosion	2	1.5
Creep	1	0.8
	132	100.0
Causes of cracks:		
Fatigue	47	35.6
Corrosion	24	18.2
Pre-existing from manufacture	10	7.6
Miscellaneous	2	1.5
Not ascertained	35	26.5
	118	89.4
Method of detection:		
Visual examination	75	56.9
Leakage	38	28.8
Non-destructive testing	10	7.5
Hydraulic tests	2	1.5
Catastrophic failure	7	5.3
	132	100.0

Table 12.12 *Other variables relevant to service failure in pressure vessels (after Phillips and Warwick, 1968 UKAEA AHSB(S) R162) (Courtesy of the UK Atomic Energy Authority)*

Variables	*Failures*			
	Potentially dangerous failures[a]		*Catastrophic failures*[a]	
	No.	(%)	*No.*	(%)
Materials of construction:				
Mild steel	105	79.5	5	3.9
Alloy steel	20	15.1	2	1.5
Design pressure:				
<500 lb/in.^{2}	41	31.1	4	3.1
≥ 500 lb/in.^{2}	84	63.5	3	2.3
Design temperature:				
$<600°$F	15	11.4	1	0.7
$\geq 600°$F	69	52.5	1	0.7
Not stated	41	31.1	5	3.9
Age:				
<10 years	59	45.0	6	5.0
≥ 10 years	64	48.5	1	0.7
Not stated	2	1.5		
Component state:				
Fired	29	22.0	4	3.1
Unfired	96	72.6	3	2.3
Fluid handled:				
Gas (including steam)	69	52.2	4	3.1
Liquid	14	10.6		
Mixture	42	31.8	3	2.3

[a] These columns give alternative breakdowns of the 125 potentially dangerous and seven catastrophic failures.

case which is of interest. The survey just described has been updated by a further survey by Smith and Warwick (1974 SRD R30). Again this survey dealt only with pressure vessels built to Class 1 requirements. The period covered by the survey was from the latter half of 1967 to the end of 1972. The information shown in the table below was obtained on failures prior to service and in service:

Sample size		*Failure rate* (failures/year)	
		Potentially dangerous failures	*Catastrophic failures*
Failure in construction	8,823 vessels	2.1×10^{-3}	–
Failure in service	105,402 vessel-years	1.1×10^{-3}	1.5×10^{-4}

In this latter survey, therefore, there were no catastrophic failures in construction, but the failure rates of potentially dangerous failures in construction and catastrophic failures in service are appreciably greater than in the earlier survey. The failure rate of potentially dangerous failures in service is similar. The survey includes further tables giving the classifications of service failures and the variables relevant to service failures similar to Tables 12.11 and 12.12.

A further analysis of pressure vessel failure statistics made by the Atomic Energy Commission (AEC) Advisory Committee on Reactor Safety (ACRS) has been described by Engel (1974). This work refers to further large collections of pressure vessel failure data by the Edison Electric Institute-Tennessee Valley Authority (EEI-TVA), by the American Boiler Manufacturers Association (ABMA) and by the Institut fur Reactorsicherheit der Technischen Uberwachungs-Verein (TUV). The EEI-TVA data are effectively a subset of the ABMA data. Studies based on the TUV2 data have been published by Kellerman (1966), Kellerman and Seipel (1967) and Slopianka and Mieze (1968).

The most severe category of failure used by Engel is a disruptive failure, which is breaching of the vessel accompanied by the release of a large volume of contained fluid. He treats this as a more restrictive category other than of catastrophic failure used by Phillips and Warwick. Engel considers failures of non-nuclear vessels applicable to nuclear reactor vessels. The largest data collections are as tabulated below:

Data source	*Sample size* (vessel-years)	*Disruptive failures* (failures/year)	
		No. of failures	*Upper bound of failure rate at 99% confidence*
Phillips and Warwick (1968)	100,300	0	4.6×10^{-5}
ABMA (Marx, 1973)	723,000	0	0.64×10^{-5}
Kellerman and Seipel (1967)	1,700,000	0–49	0.27×10^{-5}–4.0×10^{-5}

The work by Kellerman and Seipel does not indicate how many of the 49 failures reported might be classified as disruptive and therefore the number of failures and the upper bound on this failure rate are shown in the table as ranges. The upper bound of the failure rate in the table is determined by the statistical methods described in Chapter 7 and for zero disruptive failures is equal at the 99% confidence level to 4.6 (9.2/2) divided by the number of vessel-years.

Engel concludes that the ABMA data are the most useful and significant. These data are for pressure vessels designed to the ASME *Boiler and Pressure Vessel Code*, Section I or Section VIII, version 1956 or later, for pressures and temperatures equal to or exceeding those in light water reactors (LWRs) and with wall thicknesses exceeding 1.5 in. He states that the data support the conclusion that for failure of pressure vessels applicable to nuclear reactors the disruptive failure rate is less than 1×10^{-5} failures/year.

In a further survey, Smith and Warwick (1981 SRD R203) obtained for the period 1962–78 the following failure rates for pressure vessel failures in service. For some 20,000 vessels they obtained the results given below. Of the 229 failures, 206 were cracks.

Sample size (vessel-years)	*No. of failures*		*Failure rate* (failures/year)	
	Potentially dangerous failures	*Catastrophic failures*	*Potentially dangerous failures*	*Catastrophic failures*
310,000	216	13	6.9×10^{-4}	4.2×10^{-5}

A survey of pressure vessel failures in process plants has been reported by Arulanantham and Lees (1981). The work covered process pressure vessels, pressure storage vessels, non-pressure storage vessels, heat exchangers and fired heaters. The plants studied were four olefins plants and one plant handling a toxic and corrosive material, in a single works. Two of the olefins plants were commissioned in the 1950s and closed down in the 1960s, one was commissioned in the 1960s and closed in the 1970s and one was commissioned in the 1960s and was still operating. The toxics plant was also commissioned in the 1960s and was still operating. The olefins plants operated at about 3.5 and 35 barg at the hot and cold ends, respectively, except that at the hot end there was steam generation at about 85 barg. The temperatures ranged from −100° to 800°C. The toxics plant operated at relatively low pressures and mild temperatures. Excluded from the survey were failures in steam boilers and steam and air receivers and in pipework and also heat exchanger tube failures. The authors define failure as a condition in which a crack, leak or other defect has developed in the equipment so that repair or replacement is required, a definition which they treat as including some of the potentially dangerous as well as all the catastrophic failures in that of Phillips and Warwick. They report failure rates classified by type of vessel, operating conditions and causes of failure.

For pressure vessels other than fired heaters, that is, process pressure vessels, pressure storage vessels and heat exchangers they obtain:

Sample size		*No. of failures*	*Failure rate* (failures/year)
Vessels	Vessel-years		
1216	16,417	70	4.3×10^{-3}

Other failure data given are as follows. For the olefins plants:

Vessel	*Sample size*		*No. of failures*	*Failure rate* (failures/year)
	Vessels	Vessel-years		
Process pressure vessel	415	5535	15	2.7×10^{-3}
Pressure storage vessel	129	2220	4	1.8×10^{-3}
Heat exchanger	446	5950	10	1.7×10^{-3}
Fired heaters	36	447	181	405×10^{-3}
High temperature vessel, except fired heater	58	809	6	7.4×10^{-3}
Low temperature vessel	147	1941	3	1.5×10^{-3}

Here the pressure storage vessel data are for the whole works and the fired heater data are for the toxics plant also. For the toxics plant:

Vessel	*Sample size*		*No. of failures*	*Failure rate* (failures/year)
	Vessels	Vessel-years		
Process pressure vessel	131	1572	15	26×10^{-3}
High temperature vessel, except fired heater	16	192	7	36×10^{-3}
Vessel in corrosive duty	45	540	21	39×10^{-3}
Vessel subject to stress corrosion	49	588	12	20×10^{3}

Davenport (1991) has reported a survey involving some 360,000 vessels and 1.8×10^6 vessel-years over the period 1983–88, which is a much larger sample than that obtained by Smith and Warwick. The survey was not confined to Class 1 vessels, but took in a much larger range, and in fact is dominated by relatively thin-walled air receivers, so that the two surveys are not comparable. In the survey by Davenport there were 92 failures, of which 60 were cracks.

The distribution of pressure vessel disruptive failure rates from a number of sources has been analysed by Hurst, Davies *et al.* (1994). In this work the authors give various sets of failure rate data as plots of $\log_{10}\lambda$ vs normal quantiles, where λ is the failure rate of the exponential distribution, in order to check whether the failure rates are log-normally distributed. Their plot for pressure vessels is shown in Figure 12.24(a), the straight line confirming that the distribution of the failure rates is log–normal. The mean pressure vessel disruptive failure rate obtained from this plot is $\lambda \approx 10^{-5}$/year. The failure rates vary, however, by some five orders of magnitude at the 95% confidence level.

With regard to pressure vessel failure rates used in hazard assessments, the First *Convey Report* gives for spontaneous failure of a pressure vessel a failure rate of some 10^{-5}–10^{-4} failures/year. A failure rate of 10^{-5} failures/year is used in the study, but the sensitivity of the results to the higher failure rate is also given. The treatment of pressure vessel failure rates in the report is described in Appendix 7.

The *Rijnmond Report* gives for catastrophic failure and for serious leakage of a pressure vessel failure rates of 10^{-6} and 10^{-5} failures/year, respectively.

The estimated failure rate of a pressure vessel is given by Batstone and Tomi (1980) as 10^{-6} failures/year.

12.30.2 Failure of pipework

There is a considerable amount of data available on pipework failures, but the range of values quoted is wide and tends to be confusing. There are several important distinctions to be made. One concerns the type of failure. Complete pipe breaks, or guillotine fractures, constitute only a small proportion of failures. Another relates to the pipe size. The failure rate tends to be higher for small than for large diameter pipes. A further difference in the figures arises from the basis on which figures are quoted, which may be per unit length of pipe run, per pipework section or per plant.

Even so, the quoted failure rates of pipework show considerable variation. Table 12.13 shows some estimates of the failure rate of pipework on nuclear plants quoted in the Rosmussen Report. Similarly, Figure 12.25 has been given by Hawksley (1984) to illustrate the variability of pipework failure rates.

As with pressure vessels, so with piping, early work on failure rates and modes was directed to nuclear industry needs. Data on pipework failure have been given by a number of authors, particularly those concerned with nuclear systems, such as Smith and Warwick (1974 SRD R30) and Bush (1977).

Smith and Warwick (1974 SRD R30), applying definitions of catastrophic and potentially dangerous failures, similar to those which they used for pressure vessels as described in the previous section, obtained for reactor systems the data contained in the table below.

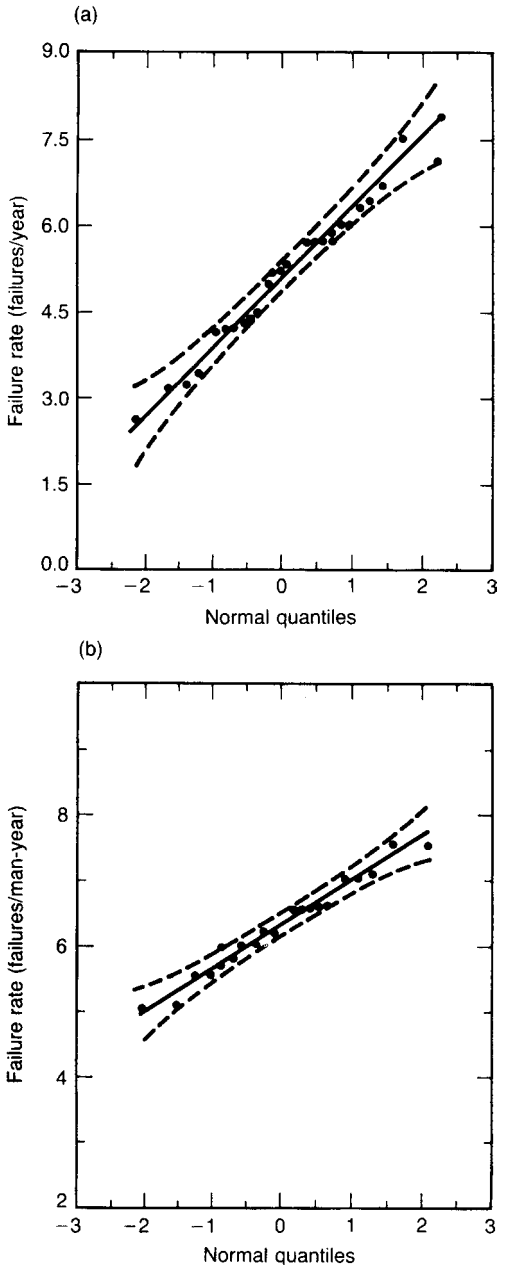

Figure 12.24 *Distribution of disruptive failure rates of pressure vessels and pipework (Hurst Davies et al., 1994): (a) pressure vessel disruptive failure rates (failures/year); and (b) pipework guillotine fracture failure rates (failures/m-year). In these graphs the variable of interest is the logarithm of the exponential failure rate, which is shown plotted against the quantiles of the normal distribution. A straight line through the points indicates that this variable is log-normally distributed. The value corresponding to the zero value of the normal quantile is the mean of the failure rate values.*

Sample size (reactor system-years)	*No. of failures*		*Failure rate* (failures/year)	
	Potentially dangerous failures	*Catastrophic failures*	*Potentially dangerous failures*	*Catastrophic failures*
2397	35	6	1.5×10^{-2}	2.5×10^{-3}

The reactor system included reactors and other equipment such as heat exchangers as well as pipework, but the failures were predominantly in the latter.

The failure rate of pipework in nuclear plants is given by Bush (1977) as 4.3×10^{-5} failures/man-year derived from eight failures, which are individually described and of which four were due to water hammer.

A survey of pipework failure in nuclear plants to provide information more up-to-date than that given in *Rosmussen Report* has been described by R.E. Wright, Steverson and Zuroff (1987). They distinguish between pipework for which a failure would result in a loss-of-coolant accident (LOCA), which they term 'LOCA-sensitive', and other pipework. Their summary of the pipework failure rates used in the *Rosmussen Report* is shown in Table 12.14.

The authors obtained data for US nuclear reactors with a total operating time of nearly 800 reactor-years, covering both PWRs and boiling water reactors (BWRs). They consider three pipe ranges: 0.5–2 in. > 2–6 in. and > 6 in. For LOCA-sensitive systems they defined a failure as a leak flow ≥ 50 US gal/min for PWRs and ≥ 500 US gal/min for BWRs. For non-LOCA-sensitive systems all pipe break failures were collected which had a leak flow ≥ 1 US gal/min for pipes ≥ 2 in. diameter or which had a leak flow of ≥ 50 US gal/min for all pipe sizes.

For PWRs with a total period of operation of 485 years and BWRs with a period 313 years, there were no failures of LOCA-sensitive pipework. There were, therefore, 798 years of operation of the two types of (LWR) free of failure. The point estimates of the failure rate based on this information were 0.0005, 0.0007 and 0.0003 failures/reactor-year for PWRs, BWRs and LWRs, respectively. The value for LWRs is evidently not the average of the values for the two types of LWR, but a value determined in its own right and based on the total of 798 years accumulated by both reactor types.

For the non-LOCA-sensitive pipework there were nine failures in PWRs and 10 in BWRs, making a total of 19 failures for LWRs. Pipe length and weld population data were available for 18 plants. The authors used these data to give the pipe length and weld populations of a nuclear plant. The mean pipe lengths and weld numbers obtained are given in Table 12.15, Sections A and B. Breakdowns of the failures by plant type and pipe size, by leak flow and by operational mode are given in Sections C, D and E of Table 12.15, respectively. The causes of failure were mainly vibration (10 cases) and water hammer (3 cases). The other cases were attributed one each to pump seizure, corrosion, fatigue, impact, operator error and unknown cause.

In the survey of failure rates of pressure equipment in process plants described in the previous section, Arulanantham and Lees (1981) also report data on major failures of pipework in one of the olefins plants. Over a 9.5-year period there were seven failures, giving a failure rate of 0.74 failures/plant. The failures are described

Table 12.13 *Estimates of failure rates of pipework in nuclear plants given in the Rasmussen Report (after Atomic Energy Commission, 1975)*

	Failure rate
'Probability of large scale rupture of primary coolant system' (A.E. Green and Bourne) (1968)	$3 \times 10^{-6} - 2 \times 10^{-3}$/plant-year
'Catastrophic rupture of primary system pipes' (Salvatory) (1970)	1×10^{-4}/plant-year
'Pipe rupture' (Erdmann) (1973):	1.5×10^{-6}/section-year
which corresponds roughly to	1×10^{-4}–1×10^{-2}/plant-year
'Pessimistic probability for catastrophic failure of primary system of PWR' (Otway)	1.7×10^{-7}/plant-year
Total probability of severence anywhere in primary system piping' (General Electric Report) (1970):	
Without ultrasonic testing	1×10^{-3}/plant-year
With ultrasonic testing	1×10^{-4}/plant-year
'Failure rate for rupture of primary coolant system piping' (Wells-Knecht) (1965)	1×10^{-7}/plant-year

Note: The references given in this table refer to those in the *Rasmussen Report*, not this book.

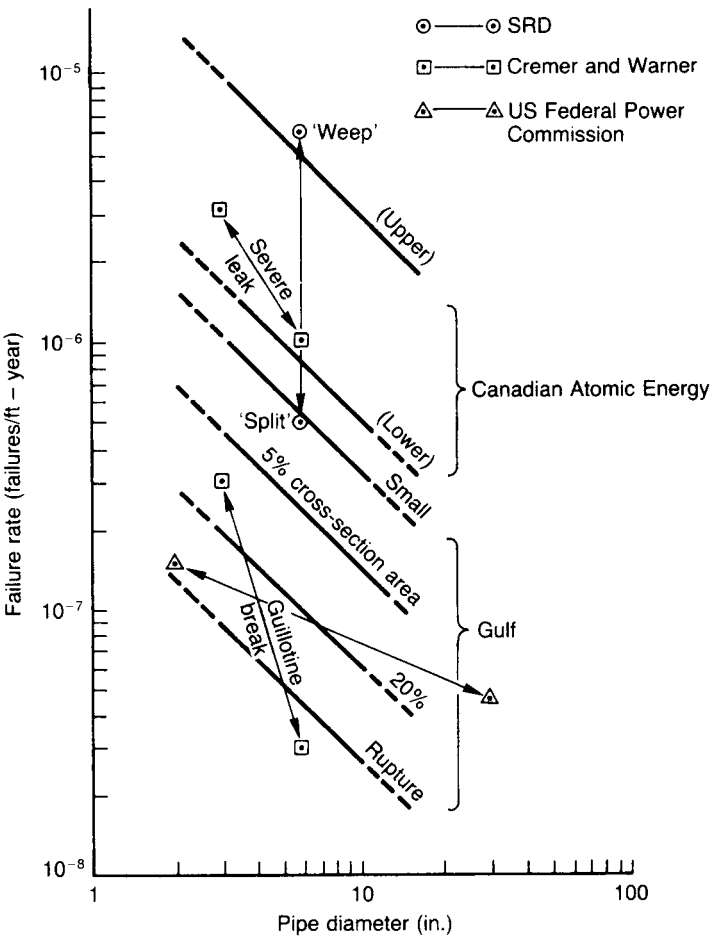

Figure 12.25 *Some data on pipework failure rates (Hawksley, 1984)*

Table 12.14 *Failure rates for LOCA-initiating ruptures used in the Rasmussen Report (after R.E. Wright, Steverson and Zuroff, 1987)*

Pipe repture size (in.)	*LOCA-initiating rupture rates* (failures/plant-year)	
	Median	*Range*
$\frac{1}{2}-2$	1×10^{-3}	1×10^{-4}–1×10^{-2}
2–6	3×10^{-4}	3×10^{-5}–3×10^{-3}
>6	1×10^{-4}	1×10^{-5}–1×10^{-3}

individually: two were due to water hammer, two to vibration-induced fatigue, one to brittle fracture resulting from admission of freezing hydrocarbon and one to overpressure of a pump suction line.

A survey of pipework failure in plants in the nuclear, chemical and other industries had been described by Blything and Parry (1988 SRD R411). The data sources were as follows. For chemical plants use was made of data from a medium-sized plant and of incident data from four separate sources; for refineries data were obtained from the plants of an oil company and from incidents; for nuclear plants data sources were a study by Riso National Laboratory and a presentation by the Nuclear Installations Inspectorate (NII); for steam plants the data were taken from T.A. Smith and Warwick (1974) and Gibbons and Hackney (1964).

The data were analysed by 'failure cause' and 'root cause'. Essentially, failure causes are the mechanical causes, such as corrosion, fatigue and water hammer, and root causes are activities such as error in design, operation and maintenance. Their results are summarized in Table 12.16, which gives the failure causes vs root causes for chemical plants and refineries (Section A) and for nuclear plants and steam plants (Section B).

The severity of failure expressed as leak flow is shown in Table 12.17 for the medium-sized chemical plant in Section A and for the GEC steam plant survey in Section B. The mechanical failures for the five chemical plant sources were as follows:

	No.	*Proportion* (%)
Weld failure	45	33.1
Stress rupture	30	22.1
Bending stress	2	1.5
Fatigue	3	2.2
External load	4	2.9
Bellows failure	3	2.2
Valve failure	27	19.9
Seal failure	15	11.0
Miscellaneous	7	5.1
Total	136	100.0

Kletz (1984k) has given information on some 50 major pipe failures in process plants as shown in Table 12.18. Section A of the table gives general failures, Section B gives failures in dead ends, and Section C gives bellows failures. The suggestions which Kletz makes for prevention of each failure are given in Table 12.19. He also makes proposals for reduction of pipework failures by improved design and describes some points to look for in inspection of pipework. These aspects are described in Section 12.7 and Chapter 19, respectively.

A study of pipework failures in process plants has been described by Bellamy and co-workers (Bellamy, Geyer and Astley 1989; Geyer *et al.*, 1990; Geyer and Bellamy, 1991; Hurst *et al.*, 1991). This work was concerned particularly with human factors as a cause of failure. This study reviewed 921 incidents from incident data bases such as the HSE MARCODE, the Safety and Reliability Directorate (SRD) MHIDAS and (the Toegepast-Natuurwetenschappelijk Onderzoek (TNO) FACTS data bases. Some analysis was undertaken on all 921 incidents, and some 500 of these incidents were selected as suitable for further analysis. Pipelines and flexible hoses were excluded.

The data were biased towards failures in larger pipes, as the following breakdown of pipework failures shows:

Pipe size (mm)	*Frequency of failure*
>150	70
51–149.9	31
26–50.9	19
13.1–25.9	22
≤13	3
Total	145

This reflects the fact that the study was based on incidents held in data bases.

Incidents were classified under the three headings: (1) direct cause, (2) origin of failure or underlying cause, and (3) recovery from failure or preventive mechanism. Detailed accounts of these definitions are given by Bellamy and Geyer (1989) and by Hurst *et al.* (1991).

Table 12.20 gives the direct causes of failure and Table 12.21 the underlying causes vs the recovery failure.

Table 12.22 gives a breakdown of the failures of pipes, valves and other equipment, for those incidents where the information was available. Table 12.23 shows the state of the equipment, again for those cases where there was information. The survey also yielded information on various aspects of the releases, some of which is described in other chapters.

In the work already described, Hurst Davies *et al.* (1994) also plotted the distribution of pipework guillotine failure rates from a number of sources, in order to check whether the failure rates are log-normally distributed. Their plot for pipework guillotine failure rates is shown in Figure 12.24(b), the straight line confirming that the distribution of the failure rates is log–normal. The mean pipework guillotine failure rate obtained from this plot is $\lambda \approx 4.6\times10^{-7}$/m-year. The failure rates vary, however, by some 2.5 orders of magnitude at the 95 % confidence level.

Further values for pipework failure are quoted in work on hazard assessment. Estimated failure rates of pipework quoted by Batstone and Tomi (1980) are given in Table 12.24.

Pape and Nussey (1985) in a hazard assessment of a chlorine installation have used for 25 mm diameter pipe the following values:

Frequency of guillotine fracture
$= 3\times10^{-7}$ failures/m-year

Table 12.15 *Failure rates for rupture in non-LOCA-sensitive pipework in US nuclear plants (after R.E. Wright, Steverson and Zuroff, 1987)*

A Pipe length populations (ft)[a]

	Pipe size (in.)[2]				
	2	*>2–6*	*>6*	*No. of plants*	*Total length* (in.)
PWRs:					
LOCA-sensitive	212	338	209	6	1,834
Non-LOCA-sensitive[b]	6,312	11,883	15,021	2–8 (av. 4.7)	33,239
BWRs:					
LOCA-sensitive	2,603	3,024	4,427	1–2 (av. 1.7)	5,803
Non-LOCA-sensitive[b]	–	5,906	6,577	0–2 (av. 1.0)	3,045

B Pipe weld populations (no. of welds)[a]

	Pipe size (in.)[2]				
	2	*> 2–6*	*> 6*	*No. of plants*	*Total*
PWRs:					
LOCA-sensitive	123	161	100	8	579
Non-LOCA-sensitive[b]	2,914	3,862	3,800	3–10 (av. 5.2)	12,289
BWRs:					
LOCA-sensitive	870	448	622	2	1,078
Non-LOCA-sensitive[b]	–	1,915	2,114	1–2 (av. 1.7)	861

C Failures by plant type and pipe size

Pipe size (in.)	*No. of failures*	*No. of reactor-years*	*Failure rate* (failures/reactor-year)
PWRs:			
½–2	2	484	0.0041
≥2–6	4	484	0.0083
≥6	3	484	0.0062
Total			0.0186
BRWs:			
½–2	3	313	0.0096
≥2–6	2	313	0.0064
≥6	5	313	0.0160
Total			0.0320
LWRs:			
Total	19	798	0.0238

D Failures by leak flow

Leak flow (US gal/min)	*No. of failures*	*No. of reactor-years*	*Leak frequency* (leaks/reactor-year)
PWRs:			
>1–<15	5	484	0.0103
>15	4	484	0.0083
BWRs:			
>1–<15	1	313	0.0032
>15	9	313	0.0287

E Failures by operational mode

Plant type	*No. of failures*			*Total*
	Starting up	*Normal operation*	*Whilst shut-down*	
PWR	2	5	2	9
BWR	0	8	2	10

[a] The figures in Sections A and B of the table are for background information only. They give an indication of the population of pipe lengths and welds on which data were available. They were not used as such in determining failure rates, which are given as failures/ reactor-year. The total in the final columns is not necessarily the sum of those in the earlier columns. A full explanation of these data is given by the authors.
[b] For PWRs this is primary circuit pipework, for BWRs it is recirculation, main steam and main feed (interpreted as feedwater) pipework.

Table 12.16 *Failure of pipework in chemical, refinery, nuclear and steam plants: failure cause vs root cause (after Blything and Parry, 1986 3 RD R 441) (Courtesy of the UKAEA Safety and Reliability Directorate)*

A Failures in chemical plants and refineries – 'failure cause' vs 'root cause'

	Design	*Installation*	*Design/ installation*	*Operation*	*Maintenance*	*Manufacture*	*Unknown*	*Unspecified*	*Total*
Corrosion:									
External	18	8	–	2	4	–	–	1	33
Internal	56	1	2	1	1	1	–	3	65
Stress	15	–	1	–	–	–	–	–	16
Erosion	2	1	–	–	1	–	–	–	4
Restraint	1	2	4	–	–	–	–	–	7
Vibration	9	1	3	1	–	–	–	1	15
Mechanical	28	10	5	11	12	18	2	21	107
Material	5	7	10	–	4	2	–	21	49
Freezing	13	1	–	2	–	–	–	1	17
Thermal fatigue	2	1	–	2	–	1	–	1	7
Water hammer	2	1	1	4	–	–	–	–	8
Work systems	6	4	36	47	49	–	–	2	144
Unknown	–	–	–	–	–	–	29	1	30
Unspecified	1	1	13	3	3	–	–	33	54
Total	158	38	75	73	74	22	31	85	556

B Failures in steam plan is – 'failure cause' vs 'root cause'

Corrosion:									
External	–	–	–	–	–	–	–	–	–
Internal	16	–	–	14	–	1	–	–	31
Stress	5	–	–	–	–	1	–	–	6
Erosion	13	–	–	53	–	1	–	–	67
Restraint	2	–	2	–	–	–	–	–	4
Vibration	7	1	–	–	–	–	–	–	8
Mechanical	11	6	–	4	1	22	1	–	45
Material	3	–	–	–	–	14	–	–	17
Freezing	1	–	–	–	–	–	–	–	1
Thermal fatigue	7	–	–	–	–	3	–	–	10
Water hammer	–	–	–	2	–	–	–	–	2
Work systems	–	2	1	–	–	–	–	–	3
Unknown	–	–	–	–	–	–	4	–	4
Unspecified	–	–	–	–	–	4	–	–	4
Total	65	9	3	73	1	46	5	–	202

Frequency of lesser failure
$= 3 \times 10^{-6}$ failures/m-year

Frequency of gasket failure
Gaskets 0.6 mm thick $= 3 \times 10^{-6}$ failures/year
Gaskets 3 mm thick $= 5 \times 10^{-6}$ failures/year

The authors state that these data include valve leaks.

The failure rates given by Hawksley (1984) in Figure 12.25 yield the values given in Table 12.25. Comparison of the frequency of a guillotine rupture for pipe diameters > Sin. quoted by some of these sources gives:

	Failure frequency (failures/year)
Gulf	3×10^{-7}
Pape and Nussey	3×10^{-7}
Cremer and Warner	$\approx 1 \times 10^{-6}$
Batstone and Tomi	3×10^{-6}

In converting the data of Batstone and Tomi, it has been assumed that a connection is a pipe section 10 m long.

From these data it might be estimated that for regular pipework the frequency of guillotine rupture for a pipe > 3 in. diameter is 1×10^{-6} failures/m-year and that for more critical pipework it is some three times less.

12.30.3 Failure of process equipment

A survey of the causes of service failure in process equipment generally has been given by Collins and Monack and this has been further analysed by Lancaster (1975). Some 685 failures were recorded. The results of the survey are shown in Table 12.26. Causes of general service failure which are emphasized by this work are general corrosion, stress corrosion cracking and mechanical failure. The number of failures caused by brittle fracture is small.

12.30.4 Failure of process machinery

The results of a survey of causes of service failure in process machinery are shown in Table 12.27. The importance of misalignment as a cause of failure is brought out strongly.

Table 12.17 *Failure of pipework in chemical, refinery, nuclear and steam plants: leak flows (after Blything and Parry, 1986 SRD 441) (Courtesy of the UKAEA Safety and Reliability Directorate)*

A Failures in a chemical plant

Pipe	*No. of leaks*	*No. of ruptures*
$d < 6$	29	2
$10 < d < 15$	12	–
Total	41	2

B Failures of steam plant (GEC study)

Pipe size (in.)	*No. of leaks*	*No. of ruptures*
$d \leq 6$	115	9
$10 < d \leq 15$	26	7
$d > 15$	6	1
Unspecified	18	2
Total	165	19

Table 12.18 *Some pipework failures in process plants: individual cases (after Kletz, 1984k) (Courtesy of the American Institute of Chemical Engineers)*

A General failures

1. A pipe was secured too rigidly by welding to supports; vibration caused a section to be torn out
2. Thermal expansion of a pipe caused a $\frac{3}{4}$-in. branch to press against a girder on which the pipe rested; the branch was torn off
3. A batch of pipe-hangers were too hard and many cracked
4. A crane was used to move a live line slightly so that a joint could be remade
5. An old pipe was reused after being on corrosive/erosive service; it failed
6. A pipe was laid on the ground and corroded badly. Construction team may have used a pipe which was already corroded
7. Water injection caused excessive corrosion/erosion because the mixing arrangements were poor
8. Water injection caused excessive corrosion/erosion because the mixing arrangements were poor
9. A temporary support was left in position
10. The exit pipe from a converter was made of carbon steel instead of $\frac{1}{2}$% Mo; the pipe fragmented and the reaction force caused the converter to fall over
11. A crane hit an overhead pipeline
12. Vibration caused fatigue failure of a 2-in. long pipe
13. The wrong valve was opened and liquid nitrogen entered a mild-steel line causing it to disintegrate
14. Vibration caused fatigue failure of a 1-in. long pipe
15. An underground pipeline corroded and leaked
16. Vibration caused a fatigue failure at a badly designed joint
17. A construction worker cut a hole in a pipeline in the wrong place and, discovering his error, patched the pipe. The repair was substandard, corroded, and leaked badly
18. A heat transfer oil line failed by fatigue as the result of repeated expansion and contraction. There should have been more expansion bends in the line
19. Water froze in an LPG drain line. A screwed joint fractured. Screwed joints should not be used for LPG
20. A section of steam tracing was isolated, causing a blockage. Expansion of the liquid in the rest of the pipe caused it to burst
21. A level controller fractured at a weld, the result of poor workmanship. According to the report, the failure 'emphasizes the need for clear instructions on all drawings and adequate inspection during manufacture'
22. A 1-in. screwed nipple blew out of a hot oil line. It was installed 20 years before, during construction, for pressure testing and was not shown on any drawing
23. Water injection caused corrosion/erosion because a properly designed mix nozzle was installed pointing in the wrong direction (see (7))
24. A Be/Cu circlip was used in an articulated arm carrying ammonia instead of a stainless steel one. The joint blew wide open
25. Decomposition of the contents caused a pipeline to fail
26. An LPG line corroded because it passed through a pit full of water contaminated with acid
27. The tail pipe from a relief valve came down to the ground and dipped into a pool of water which froze
28. Underground propane and oxygen lines leaked causing an underground explosion, the report states, 'During execution of the pipework, doubts were expressed by the works management as to the quality of the workmanship and the qualifications of those employed'
29. A little-used line was left full of water. Frost split it
30. A portable hand-held compressed air grinder being used on a new pipeline was left resting between two live lines. When the air compressor was started the grinder, which had been left switched on, started to turn and ground away part of a live line
31. A new line had the wrong slope so the contractors cut and welded some hangers. They failed. Other hangers failed due to incorrect assembly and absence of lubrication
32. The space between a reinforcement pad and the pipe was not vented. Water in the space vaporized causing collapse of a pipe
33. An old pipe was reused after use on duty which used up most of its creep life (see (5))
34. Two pipe-ends which were to be welded together did not fit exactly and were welded with a step between them
35. An ice/hydrate plug blocked a blowdown line. It was cleared by external steaming. When the choke cleared the pressure above it caused it to move with such force that the line fractured at a T
36. A carbon steel line was installed instead of $1\frac{1}{4}$ Cr $\frac{1}{2}$ Mo and ruptured after 16 years by H_2 attack (see (10))

B Failures in dead ends

1. Water collected in a dead end branch 10 ft long and caused corrosion. Five men were killed when the branch failed and the escaping gas ignited
2. Water collected in a dead end branch and froze, breaking the branch

3. Water collected in the dead end branch leading to a flowmeter which had been removed. It froze and damaged a valve
4. Corrosion products collected in the branch leading to a spare pump which was never used; the branch failed
5. A stainless steel line operating at 360°C was fitted with a branch leading to a relief valve. The branch was made of stainless steel for 1 m and then mild steel. The temperature of the mild steel exceeded the 100°C estimate and the line failed by hydrogen attack
6. Corrosive by-products collected in a blanked branch; the branch failed
7. Water collected in a branch on the feed line to a furnace; the branch was permanently connected to a steam supply. The water froze and fractured the line
8. Water collected in an open-ended branch which was welded onto a pipeline as an instrument support. After 4 years the process line had corroded right through

C Bellows failures

1. A bellows was damaged before delivery
2. A Fluon bellows failed because the pipe was free to move sideways
3. Two pins in a hinged bellows failed by fatigue and the bellows became distorted
4. A bellows was designed for normal operating conditions but distorted under abnormal, but foreseeable, conditions
5. A bellows blew apart a few hours after installation. The split rings around the convolutions which support them and equalize expansion were slack
6. Flixborough – two 28-in. bellows failed completely

Table 12.19 *Some pipework failures in process plants: preventive measures (after Kletz, 1984k) (Courtesy of the American Institute of Chemical Engineers)*

A Points to look for during construction

1. Equipment is made of the grade of steel specified and has received the right heat treatment
2. Old pipe is not being reused without checking that it is suitable
3. Pipes are not laid underground
4. Workmanship is of the quality specified and tests are carried out as specified
5. Purchased equipment is undamaged

B Points to look for after construction

1. Pipes are not secured too rigidly (by welding or clamping) so that they are not free to expand
2. Pipes will not foul supports or other fixtures when they expand
3. Pipes are not in contact with the ground
4. Temporary supports have been removed
5. Pipes are free to expand
6. Screwed joints have not been used
7. Steam tracing cannot be isolated on different sections of the same process line
8. Temporary branches, nipples, and plugs have been removed and replaced by properly designed welded plugs
9. Equipment has not been assembled wrongly (First identify equipment which can be assembled wrongly)
10. Pipes do not pass through pits or depressions which will fill with water
11. Relief-valve tail pipes are not so close to the ground that they may be blocked by ice or dirt
12. Lines which may contain water can be drained
13. The slope of lines is correct (for example blowdown line should slope towards the blowdown drum)
14. There is no 'bodging'
15. Reinforcement pads are vented
16. There are no dead ends in which water or corrosive materials can collect (Note: dead ends include little used branches as well as blanked lines)
17. There are no water traps formed by brackets, etc., fixed to equipment
18. Bellows are not bent because the two pipe ends are not in line
19. The support rings on bellows are not loose

C Points to look for after start-up

1. Pipes are not vibrating

Table 12.20 *Failures of pipework in incidents: direct causes (after Bellamy, Geyer and Astley, 1989) (Courtesy of the Health and Safety Executive)*

	No. of incidents	*Contribution*	
		Normalized No.[a]	*Proportion (%)*
Corrosion	92	85.5	9.3
Erosion	11	7.3	0.8
External load	35	27.5	3.0
Impact	49	43.8	4.8
Overpressure	129	111.8	12.1
Vibration	16	14.0	1.5
Temperature (high or low)	44	34.8	3.8
Wrong or incorrectly located in-line equipment	44	36.8	4.0
Operator error	190	167.8	18.2
Defective pipe or equipment	303	293.5	31.9
Other	17	14.0	1.5
Unknown	84	84.0	9.1
Total	1014	921.0	100.0

[a] Some incidents were assigned to more than one direct cause so that the total number of entries in the first column is 1014. The second column gives the number of incidents normalized to a total of 921.

Table 12.21 *Failures of pipework in incidents: underlying cause vs recovery failure (after Geyer et al., 1990)*

Underlying cause	*Recovery failure* (%)						
	Not recoverable	*Hazard study*	*Human factors review*	*Task checking*	*Routine checking*	*Unknown recovery*	*Total*
Natural causes	1.8	–	–	0.2	–	–	2.0
Design	–	24.5	2.0	–	0.2	–	26.7
Manufacture	–	–	–	2.4	–	–	2.4
Construction	0.1	0.2	1.9	7.5	0.2	0.4	10.3
Operation	–	0.1	11.0	1.6	0.2	0.8	13.7
Maintenance	–	0.4	14.5	12.7	10.3	0.8	38.7
Sabotage	1.2	–	–	–	–	–	1.2
Domino	4.5	0.2	–	–	0.3	–	5.0
Total	7.6	25.4	29.5	24.4	11.1	2.0	100.0

Table 12.22 *Failures of pipework in incidents: failures of pipes, valves and other equipment (after Bellamy, Geyer and Astley, 1989) (Courtesy of the Health and Safety Executive)*

A Pipe failures

	Frequency
Full bore release:	
Spontaneous rupture	165
Release during line opening or other human activity	25
Leak:	
Spontaneous leak	85
Leak during line opening or other human activity	5
Failure	99
Total	379

B Valve failures

Valve operation mode:	
Manual	7
Automatic	4
Remotely operated	2
Valve function:	
Flow control	20
Isolation	7
Drain	5
Emergency shut-down	2
Safety/relief	6
Other	3
Valve position:	
Valve failed open	2
Valve failed closed	25

C Failure of other equipment[a]

Bellows	5
Coupling	6
Drum	3
Elbow	2
Gasket	10
Joints	20
Compressor	2
Filter	4
Flange	48
Fitting	2
Gasket	10
Packing	14
Gland (gland packing)	2
Pump	10
Rupture/bursting disc	5
Seal	9
Shell	5
Sightglass	2
T pieces	3
Weld	17
Total	179

[a] Only equipment with more than one reported failure is listed.

Table 12.23 *Failures of pipework in incidents: equipment in incorrect status (after Bellamy, Geyer and Astley, 1989) (Courtesy of the Health and Safety Executive)*

A Type of equipment

	Frequency
Pipe	76
Valve	53
Flange	5
Pump	4
Other	9
Total	147

B Nature of incorrect status

Disconnected/connected	4
Removed	10
Not bled/ drained/cleaned	35
Not effectively isolated	25
Open/on	50
Closed/ off	8
Other/unknown	8
Total	140

Table 12.24 *Some failure rates of pipework used in hazard assessment (after Batstone and Tomi, 1980)*

Pipe diameter (mm)	*Failure rate per connection* (failures/10^6 years)
≤ 25	30
40	10
50	7.5
80	5
100	4
≥ 150	3

Table 12.25 *Some failure rates (failures/ft-year) of pipework given in the literature (after Hawksley, 1984)*

Source	*Type of failure*	*Pipe diameter* (in.)		
		3	6	10
Canadian Atomic Energy	Upper line	10^{-5}		3×10^{-6}
	Lower line	1.7×10^{-6}		4×10^{-7}
Gulf	Small	10^{-6}		3×10^{-7}
	5%	5×10^{-7}		1.3×10^{-7}
	20%	2×10^{-7}		6×10^{-8}
	Rupture	9×10^{-8}		2.5×10^{-8}
Cremer and Warner	Severe leak	3×10^{-6}	10^{-6}	
	Guillotine break	3×10^{-7}		3×10^{-8}
SRD	Weap		6×10^{-6}	
	Split			5×10^{-7}
FPC	Undefined	1.3×10^{-7}		10^{-7}

FPC, Federal Power Commission; SRD, Safety and Reliability Directorate.

Table 12.26 *Causes of service failure in metal equipment and piping in chemical plants (Collins and Monack, 1973) (Courtesy of Materials Protection and Performance)*

Corrosion	*(%)*
Cavitation	0.3
Cold wall	0.4
Cracking, corrosion fatigue	1.5
Cracking, stress corrosion	13.1
Crevice	0.9
Demetallification	0.6
End grain	0.4
Erosion-corrosion	3.8
Fretting	0.3
Galvanic	0.4
General	15.2
Graphitization	0.1
High temperature	1.3
Hot wall	0.1
Hydrogen blistering	0.1
Hydrogen embrittlement	0.4
Hydrogen grooving	0.3
Intergranular	5.6
Pitting	7.9
Weld corrosion	2.5
Subtotal	55.2
Mechanical failure	
Abrasion, erosion or wear	5.4
Blisters, plating	0.1
Brinelling	0.1
Brittle fracture	1.2
Cracking, heat treatment	1.9
Cracking, liquid metal pen	0.1
Cracking, plating	0.6
Cracking, thermal	3.1
Cracking, weld	0.6
Creep or stress rupture	1.9
Defective material	1.6
Embrittlement, sigma	0.3
Embrittlement, strain age	0.4
Fatigue	14.8
Galling	0.1
Impact	0.1
Leaking through defects	0.4
Overheating	1.9
Overload	5.4
Poor welds	4.4
Warpage	0.4
Subtotal	44.8
No. of failures: 685	
Period: 1968–71	

Table 12.27 *Causes of service failure of rotating machinery in the process industries (after Anon., 1970a)*

Cause	(%)
Misalignment between machines	> 50
Ingestion of solid materials	10
Portions of rotating element thrown	10
Vibration causing seal loss, causing thrust bearing failure	10
Various other sources: lubrication failures, internal misalignment, piping vibration, overspeed, slugging with liquid, chemical attack, surge	10
Design and manufacturing errors	< 10

13 Control System Design

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The operation of the plant according to specified conditions is an important aspect of loss prevention. This is very largely a matter of keeping the system under control and preventing deviations. The control system, which includes both the process instrumentation and the process operator, therefore has a crucial role to play. Selected references on process control are given in Table 13.1.

Table 13.1 *Selected references on process control*

NRC (Appendix 28 Control Systems); A.J. Young (1955); Ceaglske (1956); D.F. Campbell (1958); Grabbe, Ramo and Wooldrige (1958); Macmillan (1962); Buckley (1964); R.J. Carter (1964, 1982); Harriott (1964); Hengstenberg, Sturm and Winkler (1964); Coughanowr and Koppel (1965); Perlmutter (1965); Franks (1967); IChemE (1967/45); C.D. Johnson (1967); E.F. Johnson (1977) H.S. Robinson (1967b); Shinskey (1967, 1977, 1978, 1983); Himmelblau and Bischoff (1968); Chemical Engineering (1969c); Gould (1969); McCoy (1969); Soule (1969–); Himmelblau (1970); Considine (1971); Hartmann (1971); Pollard (1971); Luyben (1973); C.A.J. Young (1973); C.L. Smith and Brodman (1976); Lees (1977a); R.E. Young (1977, 1982); C.L. Smith (1979); Dorf (1980); L.A. Kane (1980); Basta (1981d); Frankland (1981); Auffret, Boulvert and Thibault (1983); Stephanopoulos (1984); Hydrocarbon Processing (1986a–); Tsai, Lane and Lin (1986); Benson (1987); Prett and Morari (1987); W.R. Fisher, Doherty and Douglas (1988); Prett and Garcia (1988); Asbjornsen (1989); T. Martin (1989b); K. Pritchard (1989); R. Hill (1991); Ayral and Melville (1992); Y.Z. Friedman (1992); T. Palmer (1992); C. Butcher (1993c); Holden and Hodgson (1993); Ponton and Laing (1993); Roberson, O'Hearne and Harkins (1993)

Sequence control, batch control, including computer control
Kochhar (1979); Thome, Cline and Grille (1979); Ghosh (1980); Rosenof (1982b); Armstrong and Coe (1983); Severns and Hedrick (1983); Anon. (1984ii); M. Henry, Bailey and Abou-Loukh (1984); Bristol (1985); Cherry, Preston and Frank (1985); E.M. Cohen and Fehervari (1985); Krigman (1985); Namur Committee (1985); Preston and Frank (1985); Egli and Rippin (1986); Love (1987a,b, 1988); Rosenof and Ghosh (1987); ISA (1988); Kondili, Pantiledes and Sargent (1988); Cott and Macchietto (1989); IChemE (1989/135); T.G. Fisher (1990); Crooks, Kuriyna and Macchietto (1992); Wilkins (1992); Sawyer (1992a,b, 1993a,b); Hedrik (1993)

Reactor control (*see also* Table 11.4)
Aris and Amundson (1957, 1958); Harriott (1961, 1964); Levenspiel (1962); Dassau and Wolfgang (1964); Coughanowr and Koppel (1965); Denbigh (1965); Perlmutter (1965); Shinskey (1967); Buckley (1970); Schottle and Hader (1977); Rosenhof (1982a,b); R. King and Gilles (1986); Rosenof and Ghosh (1987); Craig (1989)

Compressor control, turbine control
Claude (1959); Hagler (1960); Tezekjian (1963); R.N. Brown (1964); Daze (1965); Marton (1965); Hatton (1967); Magliozzi (1967); Hougen (1968); Labrow (1968); M.H. White (1972); Nisenfeld *et al.* (1975); Sweet (1976); IEE (1977 Coll. Dig. 77/38); Nisenfeld and Cho (1978); Staroselsky and Ladin (1979); D.F. Baker (1982); Bass (1982); Gaston (1982); Maceyka (1983); B. Fisher (1984); Rana (1985); AGA (1988/52)

Process instrument and control systems
Isaac (1960); Anon. (1962a); Fusco and Sharshon (1962); Richmond (1965); Fowler and Spiegelman (1968); Byrne (1969); Frey and Finneran (1969); Klaassen (1971); Hix (1972); Nisenfeld (1972); Jervis (1973); K. Wright (1973); Calabrese and Krejci (1974); Wilmot and Leong (1976); Gremillion (1979); Mosig (1977); Redding (1977); Shinskey (1978); Kumamoto and Hensley (1979); Rinard (1982); Cocheo (1983); Rindfleisch and Schecker (1983); Swanson (1983); Galuzzo and Andow (1984); Love (1984); E.M. Cohen (1985); B. Davis (1985); S.J. Brown (1987); Cluley (1993); I.H.A. Johnston (1993)

Traditionally, control systems have tended to grow by a process of accretion as further functions are added. One of the thrusts of current work is to move towards a more systematic design approach in which there is a more formal statement of the control objectives, hierarchy, systems and subsystems.

Once the objectives have been defined, the functions of the systems and subsystems can be specified. Typical subsystems are those concerned with measurement, alarm detection, loop control, trip action, etc. The next step is the allocation of function between man and machine – in this case the instrumentation and the operator. This allocation of function and the human factors aspects of process control are discussed in Chapter 14.

It is convenient to distinguish several broad categories of function that the control system has to perform: these are (1) information collection, (2) normal control and (3) fault administration. A control system is usually also an information collection system. In addition to that required for immediate control of the process, other information is collected and transmitted. Much of this is used in the longer term control of the process. Another category which is somewhat distinct from normal control is the administration of fault conditions which represent disturbances more severe than the control loops can handle.

13.1 Process Characteristics

The control system required depends very much on the process characteristics (E. Edwards and Lees, 1973). Important characteristics include those relating to the disturbances and the feedback and sequential features. A review of the process characteristics under these headings assists in understanding the nature of the control problem on a particular process and of the control system required to handle it.

Processes are subject to disturbances due to unavoidable fluctuations and to management decisions. The disturbances include:

(1) raw materials quality and availability;
(2) services quality and availability;
(3) product quality and throughput;
(4) plant equipment availability;
(5) environmental conditions;

and due to

(6) links with other plants;
(7) drifting and decaying factors;

(8) process materials behaviour;
(9) plant equipment malfunction;
(10) control system malfunction.

Quality may relate to any relevant parameter such as the composition or particle size of the material, the voltage level of a power supply or the specification of a product. Plant equipment may be taken off or brought back into service. Links with other plant may require changes in the operation of the process. Typical drifting and decaying factors are fouling of a heat exchanger and decay of catalyst. Process materials introduce disturbances through such behaviour as the clogging of solids on weighbelts or the blocking of pipes. Plant equipment failures constitute disturbances, as do those of the control system such as instrument faults, measurement noise, control loop instability or operator error.

Certain trends in modern plants tend to intensify the process disturbances. They include use of continuous, high throughput processes, existence of recycles, elimination of storage and interlinking of plants.

Some process characteristics which tend to make feedback control more difficult include:

(1) measurement problems;
(2) dead time;
(3) very short time constants;
(4) very long time constants;
(5) recycle;
(6) non-linearity;
(7) inherent instability;
(8) limit cycles;
(9) strong interactions;
(10) high sensitivity;
(11) high penalties;
(12) parameter changes;
(13) constraint changes.

Measurement has always been one of the principal problems in process control. A measurement may be difficult to make; it may be inaccurate, noisy, or unreliable; or it may be available in sampled form only. Even if the measurement itself is satisfactory, it may not be the quantity of prime interest. An 'indirect' or 'inferred' measurement may have to be computed or otherwise obtained from the actual plant measurement(s). Feedback control is totally dependent on measurement.

Dead time or time delay arises in various ways in processes. It may be introduced by the distance–velocity lag in pipework, the nature of distributed parameter systems or the time to obtain a sample or laboratory analysis. Dead time makes feedback control more difficult, owing to the delay before any error is measured and corrective action is initiated.

Processes with very short time constants are obviously difficult to control, because the speed of response required for control decisions and actions is rapid. But so also are processes with very long time constants, where the problems have to do with the increased chance of disturbances and other control interactions upsetting the control action taken and with the difficulty of remembering all the relevant factors.

Recycle takes a number of forms, including recycle of a process stream to an earlier point in the process and internal recycle within a vessel.

If a process is very non-linear, its behaviour tends to vary with throughput, its responses to disturbances and corrective actions differ, and it becomes difficult to find satisfactory controller settings.

Some processes, notably certain chemical reactors, are inherently unstable over a certain range of operation. If the process enters the unstable region, variables such as temperature and pressure may increase exponentially, leading to an explosion. In other cases, the process enters a limit cycle and oscillates between definite limits.

The relationships between the input and output variables of a process are often complex and there may be strong interactions. One input may change several outputs and one output may be changed by several inputs. Where the output variables are controlled by single loops, severe interactions may occur between these loops.

Some processes are very sensitive and this clearly intensifies the difficulty of control. So also does the existence of very high penalties for excursions outside the control limits.

Process parameter changes tend to reduce the effectiveness of controller settings and may make the process inherently more difficult to control. Constraint changes alter the envelope within which the process is to be controlled.

The sequential control characteristics of a process include:

(1) plant start-up;
(2) plant shut-down;
(3) batch operation;
(4) equipment changeover;
(5) product quality changes;
(6) product throughput changes;
(7) equipment availability changes;
(8) mechanical handling operations.

The sequential element in the start-up and shut-down of continuous processes and in batch processes is obvious, but there are other operations with sequential features. Continuous processes often contain semi-continuous equipment, particularly where regeneration is necessary. Deliberate changes in product quality or throughput or in equipment status involves sequential operation. In general, a sequence consists of a series of stages, of which some are initiated by events occurring in the process and others are initiated after the lapse of a specified time.

Some other process characteristics which may be significant include requirements for:

(1) monitoring;
(2) feedforward control;
(3) optimization;
(4) scheduling;
(5) process investigation;
(6) plant commissioning.

Monitoring is usually a very important function in the control system. The monitoring requirements posed by a process vary, but in cases such as multiple identical units or batch operations, they can be very large.

Feedforward control may be appropriate if there are difficulties in feedback control due to measurement problems or process lags. It is applicable where the disturbances can be measured but not eliminated, and where a model exists

which makes possible the prediction of the effect on the controlled variable of both the disturbing and correcting variables.

If the plant has a time-varying operating point, continuous optimization may be appropriate. Although optimization is carried out normally for economic reasons, it is characterized by adherence to a set of constraints. Operation within the envelope of constraints contributes to process safety.

Some processes pose a scheduling requirement, particularly where batch operations are concerned. There is normally some element of novelty in the process or plant equipment, and this may give rise to a requirement for process investigation and collection of information which is not otherwise needed for control.

The investigative element is particularly important during plant commissioning. So also is the need for facilities which assist in bypassing problems on plant equipment or control instrumentation, while solutions are sought or equipment ordered.

13.2 Control System Characteristics

The characteristics of process control systems have passed through three broad phases: (1) manual control, (2) analogue control and (3) computer control (covering all forms of programmable electronic system). However, such a classification can be misleading because it does not bring out the importance of measuring instrumentation and displays, because neither analogue nor computer control is a homogeneous stage and because it says very little about the quality of control engineering and reliability engineering and the human factors involved.

The sophistication of the measuring instrumentation greatly affects the nature of the control system even at the manual control stage. This covers instruments for measuring the whole range of chemical and physical properties. The displays provided can also vary widely. These are discussed in more detail in the next chapter.

The stage of analogue control implies the use of simple analogue controllers, but may also involve the use of other special purpose equipment. Most of this equipment serves to facilitate one of the following functions: (1) measurement, (2) information reduction and (3) sequential control.

The first two functions, therefore, improve the information available to the operator and assist him to digest it, but leave the control to him. The equipment typically includes data loggers and alarm scanners. The third function does relieve the operator of a control function. Batch sequential controllers exemplify this sort of equipment.

Another crucial distinction is in the provision of protective or trip systems. In some cases, the safety shut-down function is assigned primarily to automatic systems; in others it is left to the operator. Similarly, computer control is not a homogeneous stage of development. In some early systems, the function of the computer was limited to the execution of direct digital control (DDC). The real control of the plant was then carried out by the operator with the computer as a rather powerful tool at his disposal. In other systems the computer had a complex supervisory program which took most of the control decisions and altered the control loop set points, leaving the operator a largely monitoring function. The two types of system are very different.

The quality of the theoretical control engineering is another factor which distinguishes a system and largely determines its effectiveness in coping with problems such as throughput changes, dead time and loop interactions.

Equally important is the reliability engineering. Unless good reliability is achieved nominally automated functions will be degraded so that they have to be done manually or not at all. Control loops on manual setting are the typical result.

The extent to which human factors has been applied is another distinguishing feature. This aspect is considered further in Chapter 14. The general trend in control systems is an increase in the degree of automation and a change in the operator's role from control to monitoring.

Computer control itself has progressed from control by a single computer, or possibly several such computers, to distributed control by programmable electronic systems (PESs). These are described further in Section 13.4.

13.3 Instrument System Design

The design of process instrument systems, like most kinds of design, is largely based on previous practice. The control panel instrumentation and the control systems on particular operations tend to become fairly standardized. Selected references on process instrumentation are given in Table 13.2.

13.3.1 Some design principles

There are some basic principles which are important for control and instrument systems on hazardous processes. The following account has been given by Lees (1976b):

(1) There should be a clear design philosophy and proper performance and reliability specifications for the control and instrumentation. The design philosophy should deal among other things with the characteristics of the process and of the disturbances to which it is subject, the constraints within which the plant must operate, the definition of the functions which the control system has to perform, the allocation of the function of these between the automatic equipment and the process operator, the requirements of the operator and the administration of fault conditions. The philosophy and specification should cover: measurements, displays, alarms and control loops; protective systems; interlocks; special valves (e.g. pressure relief, non-return, emergency isolation); the special purpose equipment; and the process computer(s).

(2) The process should be subjected to a critical examination such as a hazop study to discover potential hazards and operating difficulties.

(3) If a process contains serious hazards and requires an elaborate instrument system, it should be re-examined to determine whether the hazards can be reduced at source.

(4) If the process continues to contain serious hazards, these should be assessed and protective systems provided as appropriate. If necessary, these should be high integrity protective systems (HIPS).

(5) For pressure systems it is necessary to provide protection not just against overpressure, but also against other conditions such as underpressure, overtemperature, undertemperature, overfilling, etc.

Table 13.2 *Selected references on process instrumentation*

British Gas (Appendix 27 Instrumentation); Institution of Electrical Engineers (IEEE) (Appendix 27); ISA (Appendix 27); Gillings (1958); Howe, Drinker and Green (1961); Jenett (1964a); J.T. Miller (1964); O.J. Palmer (1965); Richmond (1965, 1982); Holstein (1966); Liptak (1967, 1970, 1993); Regenczuk (1967); Considine (1968, 1971, 1985); Fowler and Spiegelman (1968); EEUA (1969 Doc. 32, 1970 Doc. 37D, 1973 Hndbk 34); Health and Safety Executive (HSE) (1970 HSW Bkit 24); Tully (1972); Whitaker (1972); Zientara (1972); Engineering Equipment and Materials Users Association (EEMUA) (1973 Publ. 120); Perry and Chilton (1973); Weston (1974a,b); Anon. (1975i); Andrew (1975); Doebelin (1975); Anon. (1976 LPB 7, p. 1); J. Knight (1976); Benedict (1977); Hayward (1977, 1979); C.D. Johnson (1977); Yothers (1977); Anon. (1978 LPB 21, p. 68); Cavaseno (1978b); C. Tayler (1987a); Verstoep and Schlunk (1978); Cheremisinoff (1979, 1981); B.E. Cook (1979); Hayward (1979); Hougen (1979); Marcovitch (1979); Ottmers *et al.* (1979); Andrew and Williams (1980); Chemical Engineering Staff (1980); Coppack (1980); IChemE (1980/73); Medlock (1980); Messniaeff (1980); Hewson (1981); Cramp (1982); Liptak and Venczel (1982); R.J. Smith (1982); R.H. Kennedy (1983); Anon. (1984gg); IBC (1984/51); Klaassen (1984); Perry and Green (1984); Atkinson (1985); Borer (1985); Cahners Exhibitions Ltd (1985); Demorest (1985); M.J. Hauser, McKeever and Stull (1985); Higham (1985a,b); Langdon (1983); Leigh (1985); Challoner (1986); A. Moore (1986); A. Morris (1986); Tily (1986); Leigh (1987); Sinnott (1988); C. Butcher (1990b, 1991c); Bosworth (1991); Burchart (1991); Bond (1992 LPB 106); Krohn (1992); Nimmo (1992); K. Petersen (1992); API (1993 RP 551); Goodner (1993); Chilton Book Co. (1994); McClure (1994)

BS (Appendix 27 Instrumentation), VDI (see Appendix 27)

Symbols
ISA (1976, 1982)

Measurement
Flow: IBC (1982/26, 1984/54); IMechE (1989/100)
Level: IBC (1982/28)
Pressure, vacuum: Waters (1978); Pressure Gauge Manufacturers Association (1980); Masek (1981, 1982, 1983); Demorest (1985); Liptak (1987); Roper and Ryans (1989)
Temperature: ASTM (1974 STP 470A)
Process analysers: Huyten (1979); Verdin (1973, 1980); Huskins (1977); Carr-Brion (1986); Clevett (1986); EEMUA (1988 Publ. 138); Dailey (1993)

Non-invasive instruments
Asher (1982)

Intelligent and self-checking instruments
Hasler and Martin (1971, 1973, 1974); J.O. Green (1978); R.E. Martin (1979, 1980); Barney (1985); Dent (1988); Anon. (1994b)

Control valves
ISA (Appendix 27); Charlton (1960); Liptak (1964, 1983); EEUA (1969 Hndbk 32); Driskell (1969, 1983, 1987); Baumann (1971,1981); Baumann and Villier (1974); Hays and Berggren (1976); Hutchison (1976); Forman (1978); R.T. Wilson (1978); Kawamura (1980); Perry (1980); Royle and Boucher (1980); Whitaker (1981); Langford (1983); M. Adams (1984); Kerry (1985); Kohan (1985); Vivian (1988); Barnes and Doak (1990); Bhasin (1990); Fitzgerald (1990); Luyben (1990); B.A. White (1993); Anon. (1994b) BS 5793: 1979–

Fluidics
J. Grant and Marshall (1976, 1977); Grant and Rimmer (1980); Anon. (1981 LPB 40, p. 7)

Sampling
Cornish, Jepson and Smurthwaite (1981); Strauss (1985)

Signal transmission, cabling
Berry (1978); Garrett (1979); Kaufman and Perz (1978); Boxhorn (1979); Anon. (1984cc); K. Hale (1985); Higham (1985a,b); Mann (1985); C. Tayler (1986e); P. Reeves (1987); Fuller (1989)

Sneak circuits
McAlister (1984); Rankin (1984)

Intrinsic safety (*see* Table 16.2)

Fail-safe philosophy
Fusco and Sharshon (1962); Axelrod and Finneran (1965); Hix (1972); Nisenfeld (1972); Bryant (1976); Ida (1983)

Instrument commissioning
Cans and Benge (1974); Spearing (1974); Shanmugam (1981); Meier (1982)

Instrument maintenance
Upfold (1971); Skala (1974); Denoux (1975); van Eijk (1975); R. Kern (1978d)

Instrument failure (*see also* Appendix 14) Scientific Instrument Research Association(SIRA)(1970); Anyakora, Engel and Lees (1971); A.E. Green and Bourne (1972); Lees (1976b); Cornish (1978a–c); English and Bosworth (1978); H.S. Wilson (1978); Mahood and Martin (1979); Kletz (1981i); Perkins (1980); Weir (1980); R.I. Wright (1980); Vannah and Calder (1981); Rooney (1983); Prijatel (1984); May (1985)

Logic systems
Hodge and Mantey (1967); F.J. Hill and Peterson (1968); Maley (1970); Steve (1971); D. King (1973); E.P. Lynch (1973, 1974, 1980); Zissos (1976); Kampel (1986); S.B. Friedman (1990)

Protective systems, trip systems
Bowen and Masters (1959); Obermesser (1960); Barnes (1965 UKAEA AHSB(S) R99, 1966 UKAEA AHSB(S) R119, 1967 UKAEA AHSB(S) R122, R131); A.E. Green and Bourne (1965 UKAEA AHSB(S) R91, 1966 UKAEA AHSB(S) R117, 1972); L.A.J. Lawrence (1965–66); Bourne (1966 UKAEA AHSB(S) R110, 1967); A.E. Green (1966 UKAEA AHSB(S) R113, 1968, 1969 UKAEA AHSB(S) R172, 1970); Hensley (1967 UKAEA AHSB(S) R136, 1968, 1971); Hettig (1967); Vaccaro (1969); Schillings (1970); M.R. Gibson and Knowles (1971, 1982 LPB 44); Kletz (1971, 1972a, 1985n, 1987J, 1991n); R.M. Stewart (1971, 1974a,b); Stewart and Hensley (1971); Tucker and Cline (1971); Wood (1971); Bennet (1972); R.L. Browning (1972); Herrmann (1972); Nisenfeld (1972); Ruziska (1972); J.T. Fisher (1973); de Heer (1973, 1974, 1975); J.R. Taylor (1973, 1976c); AEC (1975); van Eijk (1975); Lawley and Kletz (1975); E.J. Rasmussen (1975); Hullah (1976); B.R.W. Wilson (1976); Giugioiu (1977); Quenne and Signoret (1977);

B.W. Robinson (1977); Suss (1977); Troxler (1977); M.R. Gibson (1978); Kumamoto and Henley (1978); Verde and Levy (1979); Chamany, Murty and Ray (1981); Wheatley and Hunns (1981); Aitken (1982); Lees (1982a); Rhodes (1982); Ciambarino, Merla and Messina (1983); Jonstad (1983); Yip, Weller and Allan (1984); Enzina (1985); Lihou and Kabir (1985); Hill and Kohan (1986); Onderdank (1986); C. Tayler (1986c); Zohrul Abir (1987); Barclay (1988); R. Hill (1988, 1991); Kumar, Chidambaram and Gopalan (1989); Oser (1990); Papazoglu and Koopman (1990); Rushton (1991a,b, 1992); Argent, Cook and Goldstone (1992); Beckman (1992a,b, 1993); Englund and Grinwis (1992); S.B. Gibson (1992); Gruhn (1992a,b); Kobyakov (1993); R.A. Freeman (1994); VDI 2180 (1967)

Interlocks
D. Hughes (n.d.); Richmond (1965, 1982); E.G. Williams (1965); Platt (1966); Holmes (1971); Rivas and Rudd (1974); Rivas, Rudd and Kelly (1974); Becker (1979); Becker and Hill (1979); E.P. Lynch (1980); Kohan (1984); Rhoads (1985)

Control system classification
W.S. Black (1989); EEMUA (1989 Publ. 160)

Emergency shut-down (ESD)systems
DoEn (1984); AGA (1988/52); Cullen (1990); HSE (1990b); J. Pearson (1992)

Leak detection
ISA (1982 S67.03)

Gas, smoke and fire detectors (*see* **Table 16.2)**

Toxics detectors (*see* **Table 18.1)**

Reaction runaway detectors
Hub (1977c); Wu (1985)

Fracture detectors
Ponton (1980); Wilkie (1985a)

Instrument air (*see* **Table 11.17)**

(6) The measurements should be as far as possible on the variable of direct interest. If this variable has to be inferred from some other measurement, this fact should be made clear. It is also important that the measurement should be at the right location.

(7) If the variable is critical for process safety, the same measurement should not be used for control and for an alarm or trip.

(8) If the variable is critical for operator comprehension, it may be desirable to provide additional integrity.

(9) The alarm system should have a properly thought out philosophy, which relates the variables alarmed, the number, types and degrees of alarm, and the alarm displays and priorities to factors such as instrument failure and operator confidence, the information load on the operator, the distinction between alarms and statuses, and the action which the operator has to take.

(10) The control loops should have fail-safe action as far as possible, particularly on loss of instrument air or electrical power to the control valves. The action for other equipment should also be fail-safe where applicable.

(11) Those control loops which can add material or energy to the process are particularly critical and it may be desirable to provide additional integrity.

(12) The control system as a whole and the individual instruments should have the 'rangeability' necessary to maintain good measurement and control at low throughputs.

(13) The control system should be designed for off-normal as well as normal conditions, for example, start-up and shut-down.

(14) Restart situations, such as restarting after a trip or restarting an agitator, tend to be particularly hazardous.

(15) Manual stations should be provided which allow the operator to manipulate control valves in situations such as the failure of the automatic controls.

(16) The fact of instrument failure should be fully taken into account. The reliability of critical instrumentation should be assessed quantitatively where possible.

(17) The ways in which dependent failures can occur and the ways in which the instrument designer's intentions may be frustrated should be carefully considered.

(18) Instrumentation which is intended to deal with a fault should not be disabled by the fault itself. And if the process operator has to manipulate the instrumentation during the fault, he should not be prevented from doing so by the condition arising from the fault.

(19) The services (instrument air, electrical power, inert gas) on which instruments depend should have an appropriate degree of integrity.

(20) The instrument system should be checked regularly and faults repaired promptly. It should not be allowed to deteriorate, even though the process operator compensates for this. The process operator should be trained not to accept instrumentation unrepaired over long periods.

(21) Ease of detection of instrument faults should be an objective in the design of the instrument system. The process operator should be trained to regard detection of malfunction in instruments as an integral part of his job.

(22) Instruments which are required to operate only under fault conditions, and which may therefore have an unrevealed fault, require special consideration.

(23) Important instruments should be checked regularly. The proof test interval should, where possible, be determined from a reliability assessment. The checks should not be limited to protective systems and pressure relief valves, but should include non-return valves, emergency isolation valves, etc., and often also measurements, alarms, control loops, etc.

(24) Tests should correspond as nearly as possible to the expected plant conditions. It should be borne in mind that an instrument may pass a workshop test, but still not perform satisfactorily on the plant.

(25) Valves, whether control or isolation valves, are liable to pass fluid even when closed. Characterized control valves in particular tend not to give a tight shut-off. More positive isolation may require measures such as the use of double block and bleed valves or of slip plates.

(26) Valves, particularly control valves, also tend to stick. This can give rise to conditions which do not always emerge from a simple application of fail-safe philosophy. Jamming in the open position is often particularly dangerous.
(27) Practices which process operators tend to develop in their use of the instrumentation should be borne in mind, so that these practices do not invalidate the assumptions made in the reliability assessments.
(28) The fact of human error should be fully taken into account. To the extent that is practical, human factors principles should be applied to reduce human error, and the reliability of the process operator should be assessed quantitatively.

It is also necessary to pay careful attention to the details of the individual instruments used. Some features which are important are as follows:

(1) Instruments are a potential source of failure, either through a functional fault on the instrument or through loss of containment at the instrument.
(2) Use of inappropriate materials of construction can lead to both kinds of failure. Materials should be checked carefully in relation to the application, bearing in mind the possible impurities as well as the bulk chemicals. It should be remembered that the instrument supplier usually has only a very general idea of the application.
(3) Instruments containing glass, such as sight glasses or rotameters, can break and give rise to serious leaks and should be avoided if such leaks could be hazardous.
(4) Instruments may need protection against the process fluid due to its corrosiveness. Examples of protection are the use of inert liquids in the impulse lines on pressure transmitters or of chemical diaphragm seals on pressure gauges.
(5) Sampling and impulse lines should be given careful attention. Purge systems are often used to overcome blockages in impulse lines. Freezing is another common problem, which can be overcome by the use of steam or electrical trace heating.
(6) Temperature measuring elements should not normally be installed bare, but should be protected by a thermowell. A thermowell is frequently exposed to quite severe conditions such as erosion/corrosion or vibration and should be carefully designed.
(7) Pulsating flow is a problem in flowmeters such as orifice plate devices and can give rise to serious inaccuracies. This is a good example of a situation where replication of identical instruments is no help.
(8) Pressure transmitters and regulators are easily damaged by overpressure and this needs to be borne in mind.
(9) Complex instruments such as analysers, speed controllers, vibration monitors and solids weighers are generally less reliable than other instruments. This requires not only that such instruments should receive special attention but also that the consequences of failure should be analysed with particular care.
(10) Different types of pressure regulators are often confused, with perhaps a pressure reducing valve being used instead of a non-return valve, or vice versa. It is specially necessary with these devices to check that the right one has been used. Also, bypasses should not be installed across pressure regulators.
(11) Selection of control valves is very important. A control valve should have not only the right nominal capacity but also appropriate rangeability and control characteristics. It should have any fail-safe features required, which may include not only action on loss of power but also a suitable limit to flow when fully open. It should have any necessary temperature protection, for example cooling fins. Bellows seals may need to be provided to prevent leaks. The valve should have a proper mechanical balance for the application, so that it is capable of shutting off against the process pressure. It should be borne in mind that any valve, but particularly a characterized valve, may not give completely tight shut-off, and also that a badly adjusted valve positioner can prevent shut-off.
(12) Instruments should not be potential sources of ignition and should conform with the hazardous area classification requirements.

Further discussions of the safety and loss prevention(SLP) aspects of instrument systems are given by Mix (1972) and the Center for Chemical Process Safety (CCPS, 1993/14).

13.3.2 Instrument distribution

A feel for the distribution of types of instrument on a process plant may be obtained from the following figures given by Tayler (1987a):

	Overall (%)	*Monitoring* (%)	*Control* (%)
Pressure	40	26	21
Temperature	32	56	15
Flow	20	8	47
Level	8	4	8
Analysis		3	4
Miscellaneous		3	5

The first column evidently refers only to the four main types. It can be seen that, whereas temperature is dominant for monitoring, it is flow which predominates in control.

13.3.3 Instrument accuracy

Most process plant instrumentation are quite accurate provided they are working properly. Information on the expected error limits of commercially available instrumentation has been given by Andrew and Williams (1980), who list limits for over 100 generic types of instrument. Some ranges of total error quoted by these authors are:

Pressure:

Bellows transmitter ±0.5%

Temperature:

Thermocouple ±0.25–5%
Resistance thermometer ±0.2–0.5

Flow:

Orifice meter ±0.5–1%

Level:

Differential pressure ±0.5–2%

Analysis:

Gas chromatograph ±0.5–1%

13.3.4 Instrument signal transmission

Pneumatic instrument signals are transmitted by tubing, but several means are available for the transmission of electrical signals: wire, fibre optics and radio waves. The signals from measuring instruments can become corrupted in transmission. Pneumatic signals may be affected by poor quality instrument air, while electrical signals are liable to be subject to electromagnetic interference.

Both pneumatic and electrical instrument signals utilize live zero, standard ranges being 3–15 psig for pneumatic instruments and 4–20 mA for electronic ones. This avoids the situation where a zero signal is ambiguous, meaning either that the measured variable actually has a zero value or that the instrument signal has simply gone dead.

13.3.5 Instrument utilities

Instrument systems require high quality and high reliability utilities. A general account of instrument utilities has been given in Chapter 11. As far as quality is concerned, pneumatic systems require instrument air which is free of dirt and oil. Many electronic instrument systems can operate from an electrical feed which does not constitute an uninterruptible power supply (UPS). But computers and PESs are intolerant of even millisecond interruptions, unless they have their own in-built means of eliminating them. A further treatment of instrument utilities is given by the CCPS (1993/14).

13.3.6 Valve leak-tightness

In many situations on process plants, the leak-tightness of a valve is of some importance. The leak-tightness of valves is discussed by Hutchison (1976) in the *ISA Handbook of Control Valves*.

Terms used to describe leak-tightness of a valve trim are (1) drop tight, (2) bubble tight or (3) zero leakage. Drop tightness should be specified in terms of the maximum number of drops of liquid of defined size per unit time and bubble tightness in terms of the maximum number of bubbles of gas of defined size per minute.

Zero leakage is defined as a helium leak rate not exceeding about 0.3 cm^3/year. A specification of zero leakage is confined to special applications. It is practical only for smaller sizes of valves and may last for only a few cycles of opening and closing. Liquid leak-tightness is strongly affected by surface tension.

Specifications for leak-tightness of a stop, or isolation, valve are given in SP-61 by the US Valve Manufacturers Standardization Society, and are quoted in the *ISA Handbook*. In respect of control valves, the *Handbook* states:

> Properly designed control valves can achieve stop valve tightness and maintain it throughout a long service life before trim replacement; particularly with cage guided, balanced trim having elastomer plug-to-cage seals. The control valve, however, is expected to throttle and often shuts off much more frequently than stop valves. For example, some dump valves may have from 4000 to 7000 opening and closing cycles per day, handling high pressure and erosive fluids at 1000 to 4000 psi pressure drop. Few stop valves could match this performance and remain tight.

It is normal to assume a slight degree of leakage for control valves. It is possible to specify a tight shut-off control valve, but this tends to be an expensive option. A specification for leak-tightness should cover the test fluid, temperature, pressure, pressure drop, seating force and test duration. For a single-seated globe valve with extra tight shut-off, the *Handbook* states that the maximum leakage rate may be specified as 0.0005 cm^3 of water per minute per inch of valve seat orifice diameter (not the pipe size of the valve end) per pound per square inch pressure drop. Thus, a valve with a 4 in. seat orifice tested at 2000 psi differential pressure would have a maximum water leakage rate of 4 cm^3/min.

13.3.7 Hazardous area compatibility

The instrument system, including the links to the control computers, should be compatible with the hazardous area classification. Hazardous area classification involves first zoning the plant and then installing in each zone instrumentation with a degree of safeguarding appropriate to that zone. Since much instrumentation is of low power, an approach based on inherent safety is often practical. These various aspects of hazardous area classification are dealt with in Chapter 16.

13.3.8 Multi-functional vs dedicated systems

An aspect of basic design philosophy which occurs repeatedly in different guises is the choice which has to be made between a multi-functional and a dedicated system. Some basic functions which are typically required are (1) monitoring, (2) control, (3) trips and interlocks, (4) fire and gas detection, (5) ESD and (6) communication. The trip system may well be separate from the monitoring and control system and the ESD system trips separate from the other trips.

The situation which develops is illustrated in Figure 13.1(a) which shows a traditional design for an offshore production platform system (A. Morris, 1986). The alternative design which he proposes for consideration is shown in Figure 13.1(b). To the objection that this latter design puts all its eggs in one basket, the author puts two arguments. First, the overall reliability has been improved to such an extent that the frequency of a complete system failure will be very low. Second, in the majority of cases, the process should be able to survive such failure because it can be brought to a safe state by simple measures, notably by shutting off the heat input and depressurizing.

A particular but common example of the multi-functional vs dedicated system problem is the choice between a computer-based and a hardwired trip system. This aspect is discussed further in Sections 13.9, 13.12 and 13.15.

13.4 Process Computer Control

The use of computers in control systems began in the late 1950s and is now a mature technology. Process control computer systems and applications are described in *Computer Control of Industrial Processes* (Savas, 1965), *Computer Control of Industrial Processes* (Lowe and Hidden, 1971), *Handbook of Industrial Control Computers* (Harrison, 1972), *Understanding Distributed Process Control* (Moore and Herb, 1983), *Computer Systems for Process Control* (Giith, 1986) and *Industrial Digital Control Systems* (Warwick and Rees, 1986), while a description of computer control and its relation to operator control has been given in *Man and Computer in Process Control* (E. Edwards and Lees, 1973). Selected references on process computer control are given in Table 13.3.

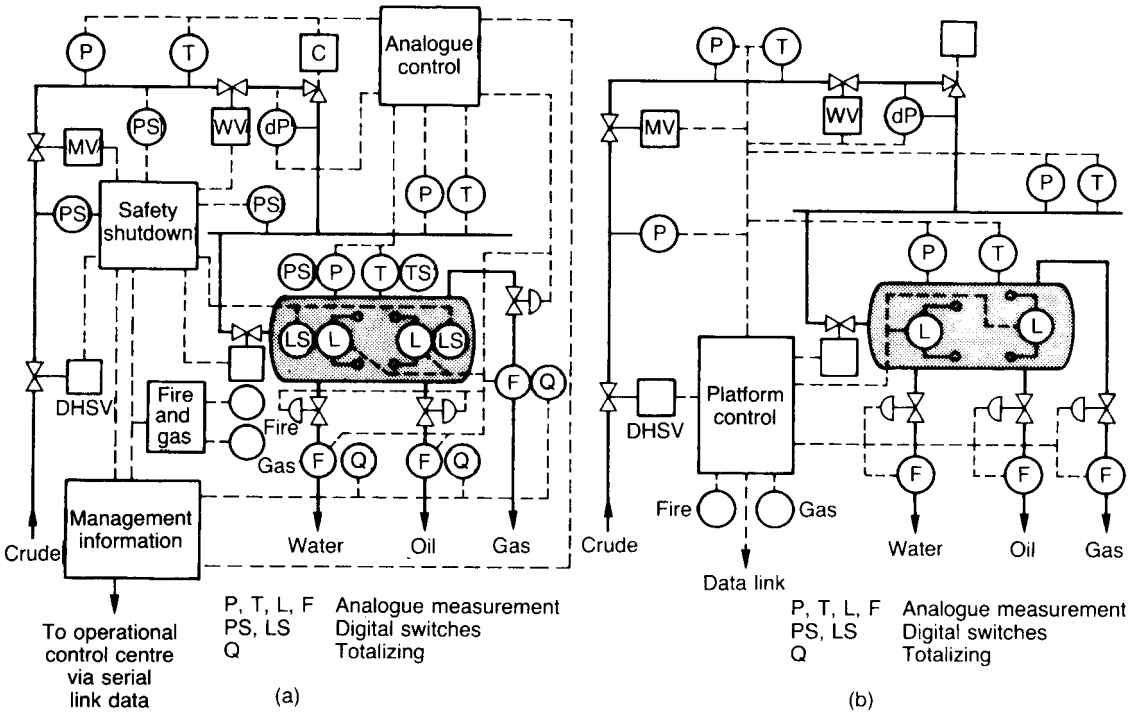


Figure 13.1 *Instrumentation for a system on an offshore production platform (A. Morris, 1986): (a) conventional system and (b) alternative system (Courtesy of Process Engineering)*

The inclusion of a process control computer greatly extends the capabilities, but also affects the reliability, of the control system. These two aspects are now considered.

13.4.1 Computer configurations and reliability

There are several ways in which a computer may be incorporated in a process control system. The approaches originally used are illustrated in Figure 13.2. If there is no computer, then the loops are controlled by analogue controllers as shown in Figure 13.2(a).

The configuration given in Figure 13.2(b) is set-point control. The computer takes in signals from measuring instruments and sends signals to the set points of analogue controllers. If there is a computer failure, control is still maintained by the analogue controllers. Figure 13.2(c) shows DDC. The computer again takes in signals from measuring instruments, but now sends signals direct to the control valves; there are no analogue controllers. If there is a computer failure, control is lost on all loops, unless standby arrangements have been made. Although set-point control developed first, it was followed quickly by DDC, and both methods came into use.

The first large DDC installation on a chemical plant was on the ammonia soda plant of Imperial Chemical Industries (ICI) at Fleetwood (Burkitt, 1965; A. Thompson, 1965). The computer carried out DDC on 98 loops and achieved an availability of about 99.8%. Further accounts of DDC systems have been given by Barton *et al.* (1970) and by Higson *et al.* (1971).

Although the initial intention was for DDC to save the cost of analogue controllers, it soon became apparent that many other factors were involved in the choice between set-point control and DDC. Since, with DDC, computer failure leads to loss of control, it may be necessary to achieve a much higher reliability than with set-point control. The effort required to implement a DDC installation tends, therefore, to be much greater. It is necessary to pay very careful attention to details of the computer, the power supply and the environment, the input–output equipment and the programming. Usually DDC does not reduce the cost of adding computer control to the control system much below that for set-point control. Savings in costs per loop tend to be slight, because the equipment needed to get measurements into the computer and to position the control valves from it is quite expensive. It is necessary to provide standby analogue controllers for critical control loops and change-over equipment to transfer between computer and analogue control. The extra general effort required to assure integrity in DDC is also significant.

On the other hand, DDC does offer some advantages, not only over conventional control but also over set-point control. The advantages derive from the fact that the computer takes in signals from the measuring instruments and can process them in all sorts of ways before sending out the results as signals to the control valves. It makes it possible to: carry out operations on the measurements, such as

Table 13.3 *Selected references on process computer control*

Process computer control, including distributed control
Savas (1965); Anke, Kaltenecker and Oetker (1970); Lowe and Hidden (1971); T.J. Harrison (1972); Lees (1972); E. Edwards and Lees (1973); IEE (1977 Conf. Publ. 153, 1982 Control Ser. 21, 1988 Control Ser. 37, 1989 Conf. Publ. 314, 1990 Control Ser. 44, 1993 Control Ser. 48); R.E. Young (1977); Bader (1979); Sandefur (1980); Cocheo (1981); IMechE (1982/61); Petherbridge (1982); Helms (1983); D.R. Miller, Begeman and Lintner (1983); J.A. Moore and Herb (1983); Rembold, Armbruster and Ulzmann (1983); Anon. (1984rr); Nordic Liaison Committee (1985 NKA/LIT (85)5); C. Tayler (1985b, 1986d); Giijth (1986); Hide (1986); Morrish (1986); Warwick and Rees (1986); J. Pearson and Brazendale (1988); D.L. May (1988); Strock (1988); Eddershaw (1989 LPB 88); J.A. Shaw (1991); Livingston (1992); Ray, Cary and Belger (1992); Wadi (1993) BS (Appendix 27 Computers)

Computer integrated processing
Zwaga and Veldkamp (1984); C. Tayler (1985d); O'Grady (1986); T.J. Williams (1989); W. Thompson (1991); Canfield and Nair (1992); Conley and Clerrico (1992); Mehta (1992); Nair and Canfield (1992); Sheffield (1992); Stout (1992); Bernstein *et al.* (1993); Koppel (1993); Mullick (1993); Yoshimura (1993)

Programmable electronic systems
Zielinski (1978); Bristol (1980); Sargent (1980); EEMUA (1981 Publ. 123); HSE (1981 OP 2, 1987/21, 22); Dartt (1982); IBC (1982/39); Devries (1983); Martinovic (1983); Martel (1984); Lihou (1985b, 1987); Skinner (1985 LPB 62); Weiner (1985); Wilkinson and Balls (1985); R. Bell (1986); Daniels (1986); Fulton and Barrett (1986); Holsche and Rader (1986); Margetts (1986a,b, 1987); Pinkney (1986); Wilkinson (1986); Anon. (1987u); Pinkney and Hignett (1987); Wilby (1987); Bellamy and Geyer (1988); Clatworthy (1988); D.K. Wilson (1988); Deja (1989); IGasE (1989 IGE/SR/15); Max-lino (1989); Oser (1990); British Gas (1991 Comm. 1456); Borer (1991); J. Pearson (1991); Sawyer (1991a); Gruhn (1992b); Prugh (1992d)

Control rooms, computer displays
Bernard and Wujkowski (1965); Wolff (1970); IEE (1971 Conf. Pub. 80, 1977 Conf. Pub. 150); Dallimonti (1972, 1973); E. Edwards and Lees (1973); Strader (1973); Lees (1976d); Bonney and Williams (1977); Jervis and Pope (1977); Hammett (1980); Burton (1981); Lieber (1982); C.M. Mitchell and Miller (1983); Banks and Cerven (1984); Jansen (1984); Mecklenburgh (1985); C. Tayler (1986a); Gilmore, Gertman and Blackman (1989)

Computer system reliability, including safety critical systems (SCS), fault tolerant systems, computer system security (*see also* Table 7.1)
Hendrie and Sonnenfeldt (1963); R.J. Carter (1964); Sonnenfeldt (1964); Burkitt (1965); A. Thompson (1965); Lombardo (1967); Regenczuk (1967); Amrehn (1969); Stott (1969); Anon. (1970d); Barton *et al.* (1970); Hubbe (1970); Luke and Golz (1970); H.F. Moore and Ballinger (1970); Parsons, Oglesby and Smith (1970); J. Grant (1971); J.A. Lawrence and Buster (1972); E. Edwards and Lees (1973); Daniels (1979 NCRS 17, 1983, 1986); N.R. Brown (1981); Wong (1982); Anon. (1984cc); Hura (1984); Bucher and Frets (1986)

Computer-based trips
Wilkinson and Balls (1985); Wilkinson (1986); Cobb and Monier-Williams (1988)

Computer-based 'black box' recorder
Anon. (1977a)

Safety of computer-controlled plants
Kletz (1982g, 1991g, 1993a); Pitblado, Bellamy and Geyer (1989); P.A. Bennett (1991a); Frank and Zodeh (1991); P.G. Jones (1991); Pearson (1991) BS (Appendix 27 Computers)

Computer control applications
W.E. Miller (1965); UKAC (1965); Control Engineering (1966); IEE (1966 Conf. Pub. 24, 1967 Conf. Pub. 29, 1968 Conf. Pub. 43, 1969 Coll. Dig. 69/2, 1971 Conf. Pub. 81, 1972 Conf. Pub. 83, 1973 Conf. Pub. 103, 1975 Conf. Pub. 127, 1977 Coll. Dig. 77/30); Washimi and Asakura (1966); IChemE (1967/45); M.J. Shah (1967); Whitman (1967); Barton *et al.* (1970); Higson *et al.* (1971); Sommer *et al.* (1971); E. Edwards and Lees (1973); Daigre and Nieman (1974); St Pierre (1975); Tijssen (1977); P.G. Friedman (1978); Weems, Ball and Griffin (1979); British Gas (1983 Comm. 1224); IBC (1983/40); Seitz (1983); C. Tayler (1984b); Tatham, Jennings and Klahn (1986)

calculation of indirect measurements and filtering of measurement signals; ensure that the control algorithm is truly proportional, integral and derivative without the inaccuracies and interactions which tend to occur in analogue controllers; use different control algorithms such as non-linear or asymmetrical algorithms or algorithms with some logic in them; eliminate features such as integral saturation and derivative kick; position valves more accurately; alter the control configuration; and so on.

There are several ways in which the reliability of DDC systems can be improved. One of these, as mentioned earlier, is the use of standby controllers on critical loops. But this is by no means a complete answer to the problem. The system may still be upset by intermittent faults, there may be difficulties in keeping the standby instrumentation maintained and avoiding degradation, and the operator is faced with a different interface to use on loss of computer control. Another approach is the use of duplication. In this case it is necessary not only to use dual computers, but also to duplicate other parts of the system such as power supplies and input–output equipment. Various configurations are possible and in normal operation the work may be divided either on a parallel or a hierarchical basis, but in all cases the essential principle is that the surviving computer takes over the critical control functions. The reliability of dual computer systems is undoubtedly higher, but it can still be affected by factors such as intermittent failures, data link troubles, hardware faults in common, such as earthing, and software faults in common, such as programming errors. With regard to reliability, for the type of system just described, the most reliable systems achieved a mean time between failures (MTBF) and an availability of not less than 2000 h and 99.9%, respectively.

Advances in process control systems, and particularly the trend towards distributed PESs, have largely resolved

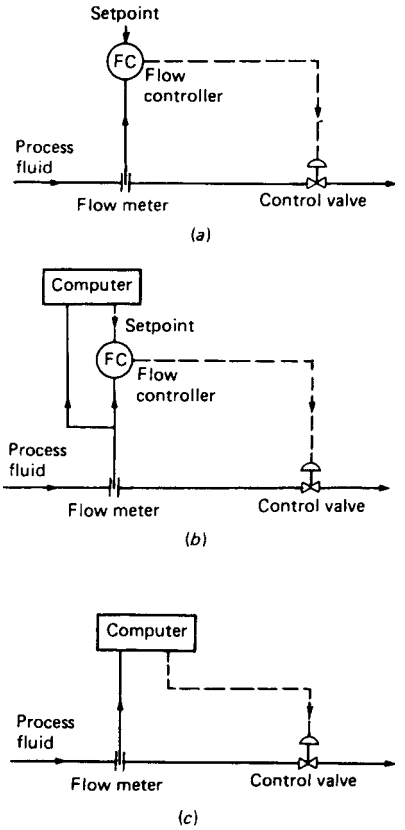


Figure 13.2 *Process computer control systems: set-point and direct digital control: (a) analogue control; (b) set-point control by computer; (c) direct digital control by computer*

the dilemmas described and have gone far towards solving the reliability problems. Figure 13.3 shows schematically a system configuration typical of these developments. The backbone of the system is a data highway to which various devices are connected. The individual PES controllers are capable of operating as DDC controllers in the stand-alone or set-point control modes. The VDU display can also operate independently of the computer. Thus, the system allows the full facilities of DDC if the computer is working, but on computer failure, the controllers maintain control and the VDU display continues to provide the operator with the usual interface.

Various configurations may be used to obtain back-up control of critical loops. Where a loop is backed up, it is desirable to ensure 'bumpless' transfer when the standby equipment assumes control. This involves a process of initialization before control is transferred.

Accounts of computer-based and PES-based process control systems based on these principles include those by E. Johnson (1983), Tatham, Jennings and Klahn (1986), Cobb and Monier-Williams (1988) and the CCPS (1993/14). PESs for process control are considered further in Section 13.12. Data on the reliability of computer systems are given in Appendix 14.

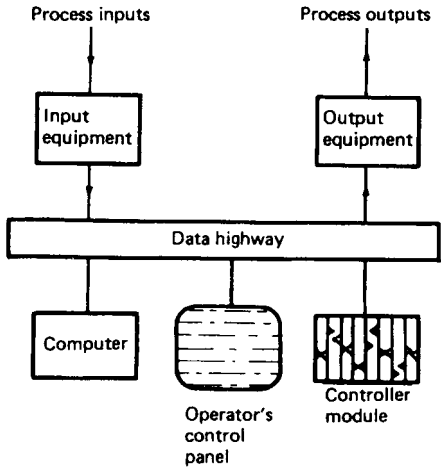


Figure 13.3 *Process computer control systems: distributed control system*

13.4.2 Computer functions

If the computer carries out DDC, then this is its most important function. The facilities and flexibility which DDC offers have already been described. However, as just described, modern process control systems are generally based on distributed PESs.

The other main functions which a process control computer or PES performs are:

(1) measurement;
(2) data processing and handling;
(3) monitoring;
(4) other control;
(5) sequential and logical control;
(6) optimization;
(7) scheduling;
(8) communication.

Several of these functions are important in relation to SLP.

The measurements on which control depends are critical. The computer is often used to carry out certain checks on the measurements as described in Chapter 30. It can also upgrade them in various ways such as by extraction of non-linearities, zero or range correction, or filtering.

The computer's ability to calculate 'indirect' or 'inferred' measurements is widely used. These are calculated from one or more process measurements and possibly other data inserted into the computer, for example, laboratory analyses. Thus, the mass flow of a particular component may be calculated from a total mass flow and a concentration measurement. It is often such indirect measurements which are of principal interest and their use represents a real advance in control. An indirect measurement can be subjected to all the operations which are carried out on direct measurements: it can be displayed, logged, monitored, controlled and used in modelling and optimization.

The computer usually logs data and provides summaries for the process operator and management. These logs often contain important information on equipment faults, operator interventions, etc. Arrangements are also sometimes made for a post-mortem log in the event of a serious

incident on the process. This usually involves holding a continuously updated set of data on process instrument readings so that it can be replayed if necessary.

The computer almost invariably carries out monitoring of the process measurements and statuses to detect abnormal conditions. This constant scanning of the operating conditions is invaluable in maintaining control of the process. Computer alarm scanning is considered, together with other aspects of the alarm system with which the operator interacts, in more detail in Chapter 14.

Frequently, there are one or two process variables, equipments or operations which are particularly difficult to control, and for these, more advanced control methods may be appropriate. These methods are usually difficult to implement without a computer. The following appear to be especially useful: (1) indirect variable control, (2) automatic loop tuning, (3) control of dead time processes and (4) non-interacting control.

The execution by the computer of sequential operations in a reliable manner is another common function which is invaluable in maintaining trouble-free operation of the process. Such sequential control involves much more than simply sending out control signals. It is essential for checks to be made to ensure that the process is ready to proceed to the next stage, that the equipment has obeyed the control signals, and so on. There is, therefore, a liberal sprinkling of checks throughout the sequence. Thus, sequential control involves continuous checking of the state of the process and the operation of equipment.

Using a computer, it is possible to carry out more complex sequences with greater reproducibility. This is particularly useful in operations where it is necessary to follow a rather precise schedule in order to avoid damage to the equipment.

On some processes where there is a time-varying optimum, the computer carries out continuous optimization. Optimization is usually performed with a set of constraints. Computer optimization therefore provides as by-product, a more formal definition of, and adherence to, process constraints.

There are several other computer functions which are particularly relevant to SLP. These include computer alarm analysis, valve sequencing and malfunction detection. These are dealt with in Chapter 30.

For many years there was very little use of computers to carry out the protective function of tripping plant when a hazardous condition occurs. The protective system has almost invariably been a system separate from the control system, whether or not the latter contains a computer, and engineered for a greater degree of integrity. There is now movement towards the use of PESs for the trip functions also, but only where it can be demonstrated that the system has a reliability at least equal to that of a conventional hardwired system.

13.4.3 Computer displays and alarms

Process computers, as just indicated, are powerful tools for the support of information display and alarm systems. The design of such systems is intimately bound up with the needs of the process operator, and discussion is therefore deferred to Chapter 14.

13.4.4 Fault-tolerant computer systems

To the extent practical, process computer systems should be fault tolerant. A fault-tolerant system is one which continues to perform its function in the face of one or more faults. Accounts of fault-tolerant design of computer systems, including process computer systems, are given by Shrivastava (1991), the CCPS (1993/14) and Johnston (1993).

The creation of a fault-tolerant system involves a combination of approaches. A necessary preliminary effort is to obtain high reliability and thus to eliminate faults. The methods of reliability engineering may be used to model the system and to identify weak points. The use of redundancy and diversity is a common strategy. Dependent failures and methods of combating them should receive particular attention.

Prompt detection and repair of faults is an important part of a strategy for a fault-tolerant system. A fault-tolerant system should degrade gracefully, and safely. One important aspect is the fail-safe action of the system.

13.4.5 Computer power supplies

Process computers and PESs require a high reliability and high quality power supply. A general account of power supplies is given in Chapter 11. The operation of such equipments can be upset by millisecond interruptions, unless they have in-built means of dealing with them. They therefore generally require a UPS. Devices used to provide a UPS include motor generators, DC/AC inverters and batteries.

The power supply also needs to be uninterruptible in the sense that it has high reliability. One option is the use of batteries, another is some form of redundancy or diversity of supply.

A treatment of power supplies for PESs is given by the CCPS (1993/14). A relevant code for UPSs is IEEE 446.

13.4.6 Computer system protection

Process computers and PESs require suitable protection against fire and other hazards.

For fire protection, the relevant codes are BS 6266: 1992 Code of Practice for Fire Protection of Electronic Data Processing Installations, NFPA 75: 1992 Protection of Electronic Computer/Data Processing Equipment and NFPA 232: 1991 Protection of Records.

Lightning protection is covered in NFPA 78: 1989 Lightning Protection Code.

Codes for earthing are BS 1013: 1965 Earthing and IEEE 142: 1982 Grounding of Industrial and Commercial Power Systems (the IEEE Green Book).

These hazards and protection against them are treated by the CCPS (1993/14).

13.5 Control of Batch Processes

The control of batch processes involves a considerable technology over and above that required for the control of continuous processes. Accounts of batch process control are given in *Batch Process Automation* (Rosenof and Ghosh, 1987), *Batch Control Systems* (T.G. Fisher, 1990) and *Computer-Controlled Batch Processing* (Sawyer, 1993a) and by Love (1987a–c, 1988).

Batch processes constitute a large proportion of those in the process industries. Sawyer (1993a) gives the following figures:

Many batch plants are multi-purpose and can make multiple products. Their outstanding characteristic is their flexibility. They differ from continuous plants in that: the operations are sequential rather than continuous; the

environment in which they operate is often subject to major variability; and the intervention of the operator is to a much greater extent part of their normal operation rather than a response to abnormal conditions. A typical batch plant is shown in Figure 13.4.

13.5.1 Models of batch processing

There are a number of models which have been developed to represent batch processing. Three described by T.G. Fisher (1990) are (1) the recipe model, (2) the procedure model and (3) the unit model.

The recipe model centres on the recipe required to make a particular product. Its elements are the procedures, the formula, the equipment requirements and the 'header'. The procedure is the generic method of processing required to make a class of product. The formula is the raw materials and operating conditions for the particular product. The equipment requirements cover the equipment required to execute the formula, including materials of construction. The header is the identification of the batch in terms of product, version, recipe and so on.

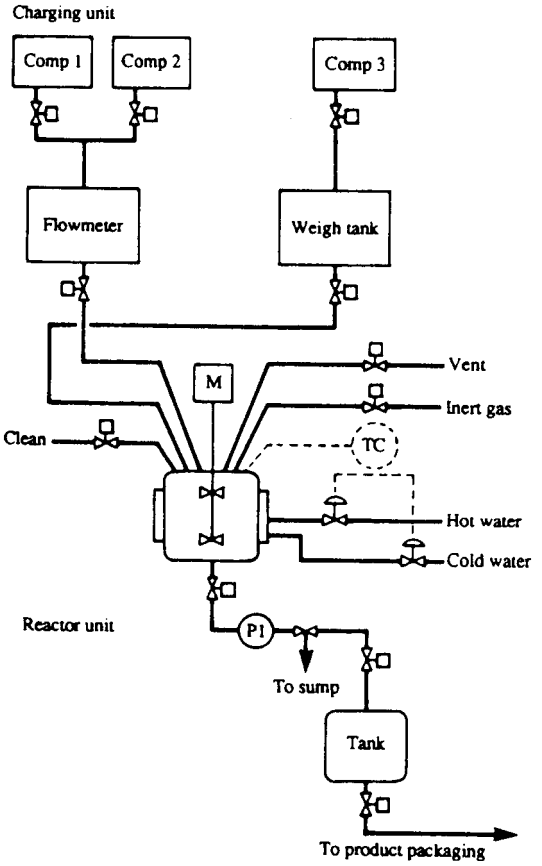


Figure 13.4 *A typical batch plant (Sawyer, 1993) (Courtesy of the Institution of Chemical Engineers)*

The procedure model has the form:

Procedure → Operation → Phase → Control step

The overall procedure consists of a number of operations, akin to the unit operations of continuous processes, except that they may be carried out by the same equipment. The phase is a grouping of actions within an operation. The control step is the lowest level of action, typically involving the movement of a small number of final control elements.

The concept of phase is a crucial one in batch processing. A phase is a set of actions which is logical to group together and which ends at a point where it is logical and safe for further intervention to take place. It is closely connected, therefore, with the concept of 'hold' states at which it is safe for the process to be held. The possibility that other facilities on which the progress of the batch depends may not be immediately available makes such hold states essential.

The unit model is equipment-oriented and has the form:

Unit → Equipment module → Device/loop → Element

The unit is broken down into functional equipment modules such as vessels and columns. These in turn are decomposed into devices and loops which are groupings of elements such as sensors and control valves.

13.5.2 Representation of sequential operations

The control of a batch process is a form of sequential control. A typical sequential control procedure, expressed in terms of the procedure model, is shown in Table 13.4. Various methods are available for the specification of sequences. They include (1) flowcharts, (2) sequential function charts and (3) structured plain language.

The flowchart is a common method of representing sequences, but its successful use requires that: a consistent style be adopted; that the method cater to the procedure hierarchy by the use of a hierarchy of charts for operations, phases and control steps; it also allows for parallel activities and for actions prompted by alarms and failures; and is supplemented by information on recipes, units, etc., and by other representations such as structured language. Computer-based drafting aids are invaluable in creating flowcharts.

The sequential flowchart has been developed expressly to describe sequential control and has three basic features: (1) steps, (2) transitions and (3) directed links. A step is an action and ends with a conditional transition. If the condition is satisfied, control passes to the next step. This latter step then becomes active and the previous step inactive. A directed link creates a sequence from steps and transitions. Figure 13.5 shows a sequential flowchart together with the standard symbols used in the creation of such charts.

With regard to the use of structured language, Rosenof and Ghosh advise that: (1) simple statements should be used; (2) the required function should be clearly defined in a statement; (3) the plant hardware addressed should, where possible, be identified; (4) text should be indented where necessary; (5) negative logic should be avoided and (6) excessive nested logic should be avoided.

13.5.3 Structure of batch processing

The overall structure of batch processing is commonly represented as a hierarchy. The following structure and

Table 13.4 *Typical sequential control procedure (Sawyer, 1993a) (Courtesy of the Institution of Chemical Engineers)*

Operations	*Phases*	*Controls steps*
Initialize	Initialize	Start jacket circulation pump. Put reactor temperature controller in SECONDARY AUTO mode with set-point of 120°C
Weigh	Weigh Component 3	Initialize (tare-off weigh tank). Open outlet valve from head tank. When weight of component 3 equals preset, close outlet valve from head tank
Charge	Add Component 3	Open outlet valve from weigh tank. When enough of component 3 has been added, start the agitator. When weigh tank is empty, close outlet valve
	Add Component 1	Initialize (reset flow totalizer to zero). Open outlet valves from head tank to flowmeter and from flowmeter to reactor. When volume of Component 1 charged equals preset, close outlet valves
React	Heat	Initialize (put reactor temperature controller in CASCADE mode with set-point of 120°C)
	Hold Sample	Initialize (reset timer). Start timer
Discharge	Cool	Initialize (set reactor temperature set-point to 35°C)
	Transfer	Initialize (set reactor outlet valves to correct destination, i.e. storage tank). Start discharge pump. Set reactor temperature controller to MANUAL mode with output at zero (full cooling). Before agitator blades are uncovered, stop agitator. When reactor is empty, close reactor outlet valves, stop discharge pump, stop jacket circulation pump

terminology by Rosenof and Ghosh (1987) is widely used:

Production planning → Production scheduling
→ Recipe management → Batch management
→ Sequential control → Discrete/regulatory control
→ Process interlocks → Safety interlocks

A treatment of batch processing as a form of computer integrated manufacturing (CIM) is given in Section 13.7.

13.5.4 Batch control systems

Batch processing may be controlled by the process operator, by a system of single controllers or by a programmable logic control (PLC) system, a distributed control logic system (DCL) or a centralized control system (CCS). The selection of the system architecture and hardware is discussed by Sawyer (1993).

Recommendations for batch control have been made in Europe by the NAMUR committee (1985), which addresses particularly the need for standard terminology and for a hierarchical structure of the control system which reflects that of batch processing itself.

In the United States, guidance is available in the form of ISA SP88: 1988 Batch Control Systems.

13.6 Control of Particular Units

The safe operation of process units is critically dependent on their control systems. Two particularly important features of control in process plant are (1) compressor control and (2) chemical reactor control. These are now considered in turn.

13.6.1 Compressor control

Centrifugal and axial compressors are subject to the phenomenon of surging. Surging occurs when flow through the compressor falls to a critical value so that a momentary reversal of flow occurs. This reversal of flow tends to lower the discharge pressure and normal flow resumes. The surge cycle is then repeated. Severe surging causes violent mechanical shock and noise, and can result in complete destruction of parts of the compressor such as the rotor blades.

A typical centrifugal compressor characteristic showing the surge limit is illustrated in Figure 13.6(a). A centrifugal compressor is usually fitted with antisurge controls which detect any approach to the surge conditions and open the bypass from the delivery to the suction of the machine, thus increasing the flow through the machine and moving it away from the surge conditions.

The compressor delivery and suction pressures P_d and P_s are related to the gas flow Q as follows:

$$P_d - P_s \propto Q^2 \qquad [13.6.1]$$

The shape of the surge curve is therefore parabolic as shown in Figure 13.6(a). An expression of this form is generally inconvenient in instrumentation, for which linear relations are preferred. A linear relation can be obtained by making use of the relation for pressure drop ΔP across the orifice flowmeter on the compressor suction:

$$Q^2 \propto \Delta P \qquad [13.6.2]$$

Hence from relations 13.6.1 and 13.6.2,

$$P_d - P_s \propto \Delta P \qquad [13.6.3]$$

Figure 13.6(b) shows the compressor characteristics redrawn in terms of this pressure drop. The surge condition is now given by a straight line. The antisurge control system is set to operate on a line somewhat in advance of the

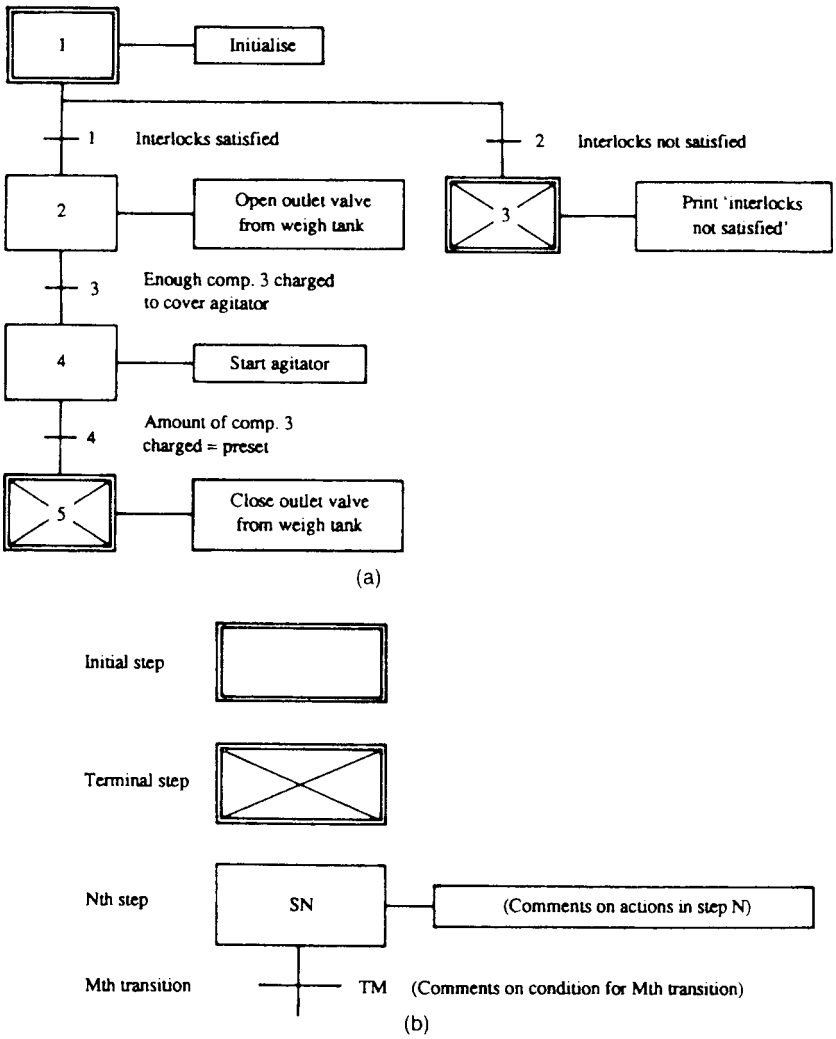


Figure 13.5 *Sequential function chart (Sawyer, 1993): (a) chart for control steps ADD COMPONENT; and (b) basic symbols (Courtesy of the Institution of Chemical Engineers)*

surge limit, as shown in Figure 13.6(b). The antisurge controller is usually a P+I controller and, since it operates only intermittently, it needs to have arrangements to counteract integral saturation.

Accounts of centrifugal and axial compressor control are given by Claude (1959), R.N. Brown (1964), Daze (1965), Hatton (1967) and Magliozzi (1967), and accounts of reciprocating compressor control are given by Hagler (1960) and Labrow (1968). Multi-stage compressor control is discussed by D.F. Baker (1982), Maceyka (1983) and Rana (1985), and control of compressors in parallel by Nisenfeld and Cho (1978) and B. Fisher (1984).

13.6.2 Chemical reactor control

The basic characteristics of chemical reactors have already been described in Chapter 11, in which, in particular, an account was given of the stability and control of a continuous stirred tank reactor. It is appropriate here to consider some additional aspects of reactor control.

A continuous stirred tank reactor is generally stable under open-loop conditions, but in some cases, a reactor may be unstable under open-loop but stable under closed-loop conditions. Some polymerization reactors and some fluidized bed reactors may be open-loop unstable under certain conditions.

The reactor should be designed so that it is open-loop stable unless there is good reason to the contrary. One method of achieving this is to use jacket cooling with a large heat transfer area. Another is to cool by vaporization of the liquid in the reactor. This latter method gives a virtually isothermal reactor.

If the reactor is or may be open-loop unstable, the control system should be very carefully designed. The responses of the controls should be fast. One method of achieving this

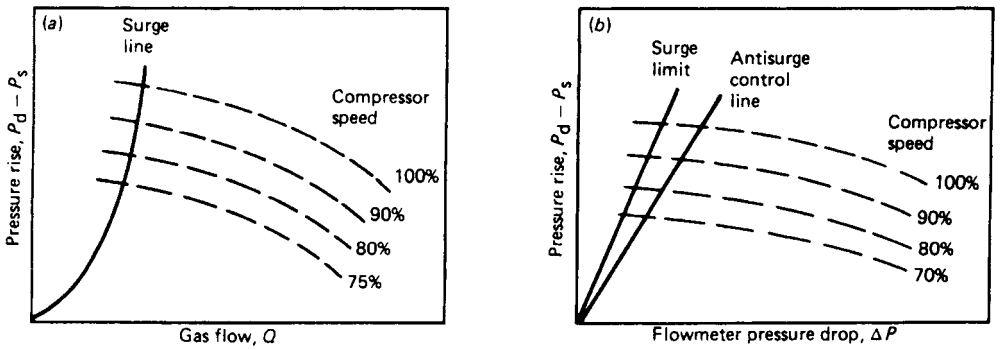


Figure 13.6 *Centrifugal compressor characteristics illustrating surge and antisurge control: (a) conventional characteristic; (b) characteristic for antisurge control*

is the use of cascade control for the reactor temperature to the coolant temperature. The dead time should be minimized. A high coolant flow assists in reducing dead time.

Continuous stirred tank reactors and batch reactors have their own characteristic control problems. Some of the control problems of continuous stirred tank reactors are as follows. A reaction in a continuous reactor is often carried out in a single phase in one pass. This requires accurate control of the feed flows to the reactor. Failure to achieve such control may have effects such as unconverted reactant leaving the reactor, undesirable side reactions or rapid corrosion.

It is often possible for impurities to build up in a continuous reactor. Where this is the case, arrangements should be made to purge the impurities. If the reactants to a continuous reactor need to be preheated, this should be done before they are mixed, unless the reaction requires a catalyst. A continuous reactor is sometimes provided with regenerative preheating. It should be borne in mind that such preheating constitutes a form of positive feedback.

As described in Chapter 11, batch reactors are of two broad types. In the first, the 'all-up' batch reactor, the main reactants are all charged at the start. In the semi-batch reactor, one reactant is not charged initially but is fed continuously.

The reaction mass in a batch reactor cannot necessarily be assumed to be completely mixed. It is not uncommon for there to be inhomogeneities, hot spots and so on. This has obvious implications for reactor control.

Some of the control problems of batch reactors are as follows. In a typical all-up batch cycle, the reactants and catalyst are charged, the charge is heated to reaction temperature, and the reaction mass is then cooled and discharged. In some cases the reaction stage is followed by a curing stage which may be at a temperature below or above the reaction temperature.

In the initial heating up period, the temperature of the charge should be brought up to the operating point rapidly, but it should not overshoot. If the reactor temperature is controlled by an ordinary three-term controller, integral saturation in the controller will cause overshoot. It is necessary, therefore, to employ a controller which is modified to avoid this. Alternatively, the heating up may be controlled in some other way which avoids overshoot. Once the reaction is under way in a batch reactor, the initial heat release is large. The cooling system should be adequate for this peak heat release.

Semi-batch reactors have different problems. The addition of the continuously fed reactant before the batch is up to temperature should be avoided, otherwise it is liable to accumulate and then react rapidly when the operating temperature is reached.

If agitation is interrupted and then resumed, there may be a sudden and violent reaction of reactants which have accumulated. There should be suitable alarms, trips and interlocks to signal loss of agitation, to cut off feed of reactant, and to ensure an appropriate restart sequence.

In both types of reactors, there should be arrangements to prevent material from the reactor passing back into reactant storage tanks where this could constitute a hazard. The control of flows in the reactant feed pipes is important. It is necessary to ensure tight shut-off of the reactants and to prevent flow from the reactor into the reactant feed system.

The reactor should be provided with suitable display and alarm instrumentation, so that the process operator has full information on the state of the reactor. Important variables are typically the flows of the reactants and of the coolant, the pressure in the reactor and the temperature of the reactor and of the coolant. Important statuses are the state of the agitator, of the pumps and of the valves.

The reactor should have a control system which is fully effective in preventing a reaction runaway. The main reactor control is usually based either on reactor temperature or on reactor pressure. The dynamic response of the loop is especially important. There should be adequate potential correction on the control loops. In other words, the steady-state gain between the manipulated variable and the controlled variable should be high enough to ensure that control of the latter is physically possible.

The instrumentation should possess both capability and reliability for the duty. Important aspects of capability are accuracy and dynamic response. The effects of instrument failure should be fully considered. In particular, failure in the measurement and control of the main variable, which is usually temperature, should be assessed. The ease of detection of instrument malfunction by the process operator should be considered. Factors which assist in malfunction detection include the use of measuring instruments with a continuous range rather than a binary output and

the provision of recorders and of indications of valve position.

Trip systems should be provided to deal with potentially hazardous conditions. These typically include loss of feed, loss of coolant, loss of agitation and rise in reactor temperature. ESD arrangements for reactors are discussed in Chapter 11.

Use should be made of interlocks to ensure that critical sequences which have to be carried out on the reactor are executed safely and to prevent actions which are not permissible. Many of these control functions are facilitated by the use of a process control computer. A fuller discussion of instrumentation is given in Section 13.8.

13.7 Computer Integrated Manufacturing

There is now a strong trend in the process industries to integrate the business and plant control functions in a total system of CIM. Accounts of CIM are given by T.J. Williams (1989), Canfield and Nair (1992), Conley and Clerico (1992), Mehta (1992), Nair and Canfleld (1992), Bernstein *et al.* (1993) and Koppel (1993).

The aim of CIM is essentially to obtain a flexible and optimal response to changes in market demand, on the one hand, and to plant capabilities on the other. It has been common practice for many years for production plans to be formulated and production schedules to be produced by computer and for these schedules to be passed down to the plant. In refineries, use of large scheduling programmes is widespread. In addition to flexibility, other benefits claimed are improved product quality, higher throughputs, lower costs and greater safety.

A characteristic feature of CIM is that information also flows the other way, that is, up from the plant to the planning function. This provides the latter with a continuous flow of up-to-date information on the capability of the plant so that the schedule can be modified to produce the optimal solution. A CIM system may therefore carry out not only the process control and quality control but also scheduling, inventory control, customer order processing and accounting functions.

The architecture of a CIM system is generally hierarchical and distributed. Treatments of such architecture are given in Controlling Automated Manufacturing Systems (O'Grady, 1986) and by Dempster *et al.* (1981).

For such a system to be effective, it is necessary that the data passing up from the plant be of high quality. The system needs to have a full model of the plant, including the mass and energy balances and the states and capabilities of the equipment. This involves various forms of model-based control, which is of such prominence in CIM that the two are sometimes treated as if they are equivalent.

Plant data are corrupted by noise and errors of various kinds, and in order to obtain a consistent data set, it is necessary to perform data reconciliation. Methods based on estimation theory and other techniques are used to achieve this. Complete and rigorous model-based reconciliation (CRMR) is therefore a feature of CIM. Data reconciliation is discussed further in Chapter 30. One implication of CIM is that the plant is run under much tighter control, which should be beneficial to safety.

13.7.1 Batch plants

Batch processing involves not only sequential operations but also a high degree of variability of equipment states and is particularly suited to CIM. Accounts of integrated batch processing include those by Rosenof (1982b), Armstrong and Coe (1983), Rippin (1983), Severns and Hedrick (1983), Bristol (1985), Krigman (1985), Egli and Rippin (1986), Kondili, Panteides and Sargent (1988), Cott and Macchietto (1989) and Crooks, Kuriyna and Macchietto (1992).

In the system described by Cott and Macchietto (1989), use is made of three levels of control, which are, in descending order: plant level control, batch level control and resource level control, operating respectively on typical time-scales of days, minutes and seconds. A comprehensive approach to batch processing requires the integration of tools for plant design, automation and operating procedures.

13.8 Instrument Failure

Process plants are dependent on complex control systems and instrument failures may have serious effects. It is helpful to consider first the ways in which instruments are used. These may be summarized as follows:

Instrument	*System application*
Measuring instrument	Input to:
	Display system-measurement/status/alarm
	Control loop
	Trip system
	Computer model
Control element	Output from:
	Control loop
	Trip system

Measuring instruments are taken to include digital as well as analogue outputs. Control elements are normally control valves, but can include power cylinders, motors, etc.

The important point is that some of these applications constitute a more severe test of the instrumentation than others. The accuracy of a flowmeter may be sufficient for flow control, but it may not be good enough for an input to a mass balance model in a computer. The dynamic response of a thermocouple may be adequate for a panel display, but it may be quite unacceptable in a trip system.

This leads directly, of course, to the question of the definition of failure. In the following sections, various kinds of failure are considered. It is sufficient here to emphasize that the reliability of an instrument depends on the definition of failure, and may vary depending on the application.

13.8.1 Overall failure rates

There are more data on the failure rates of instrumentation than on most other types of plant equipment. It is now usually possible to obtain sufficient data for assessment purposes, though there are inevitably some gaps. There are two types of failure data on instruments. The first relates to performance in standard instrument tests and the second to performance on process plant. It is the latter which is of primary interest here.

Many of the data on the failure rates of instruments on process plants derive from the work of the UK Atomic Energy Authority (UKAEA). Table 13.5 gives data quoted in early investigations by UKAEA workers. Table 13.6 shows data in another early survey by Anyakora, Engel and Lees

Table 13.5 *Some data on instrument failure rates published by the UKAEA*

Instrument	*Failure rate* (faults/year)		*Reference*[a]
	Observed	*Assumed/predicted*	
Control valve[b]	0.25		1–4
		0.26	5, 6
Solenoid valve		0.26	5, 6
Pressure relief valve		0.022	5, 6
Hand valve		0.13	5, 6
Differential pressure transmitter[b]	0.76		1–4, 7, 8
Variable area flowmeter transmitter[b]	0.68		1–4, 8
Thermocouple		0.088	5, 6
Temperature trip amplifier:			
Type A	2.6		7
Type B	1.7		7
Pressure switch		0.14	1–4, 8
Pressure gauge		0.088	5, 6
O_2 analyser	2.5		1, 2, 4, 8
Controller[b]	0.38		7
Indicator (moving coil meter)		0.026	5, 6, 8
Recorder (strip chart)		0.22	5, 6, 8
Lamp (indicator)		0.044	5, 6, 8
Photoelectric cell		0.13	5, 6
Tachometer		0.044	5, 6
Stepper motor		0.044	5, 6
Relay[b]	0.17		7
Relay (Post Office)		0.018	5, 6

[a] (1) Hensley (1967 UKAEA AHSB (S) R136); (2) Hensley (1968); (3) Hensley (1969 UKAEA AHSB (S) R178); (4) Hensley (1973 SRS/GR/1); (5) Green and Bourne (1966 UKAEA AHSB (S) R117); (6) A.E. Green and Bourne (1972); (7) Eames (1966); (8) Green (1966 UKAEA AHSB (S) R113).
[b] Pneumatic.

(1971) in three works in the chemical industry. The first (works A) was a large works producing a wide range of heavy organic chemicals. The second (works B) made heavy inorganic chemicals. The third (works C) was two sites in a glass works. The failures were defined as and derived from job requests from the process operators. The failure rates were calculated on the assumption of a constant failure rate. The environment factor quoted in Table 13.6 is explained below.

The failure rates given in Table 13.6 are in broad agreement with other work published about the same time, such as that of Skala (1974). It should be emphasized that, of the failures given in the tables, only a very small proportion resulted in a serious plant condition. In most cases the failures were detected by the process operator, who then called in the instrument maintenance personnel.

The failure rates quoted are those for normal commercial instruments in the process industries. In certain other applications where higher instrument costs are acceptable, the failure rates are lower. Thus, instruments used in some defence applications are of an order of magnitude more expensive, but have a much higher reliability. Further data on instrument failure rates are given in Appendix 14.

13.8.2 Factors affecting failure

Some of the factors which affect instrument failure are listed below.

(1) System context:
  (a) application (display, control, etc.);
  (b) specification (accuracy, response, etc.);
  (c) definition of failure.
(2) Installation practices.
(3) Environmental factors – process materials:
  (a) degree of contact (control room, plant);
  (b) material phase (gas, liquid, solid);
  (c) cleanliness;
  (d) temperature;
  (e) pressure;
  (f) corrosion;
  (g) erosion.
(4) Environmental factors – ambient and plant conditions:
  (a) temperature;
  (b) humidity;
  (c) dust;
  (d) frost exposure;
  (e) vibration;
  (f) impact exposure.
(5) Operating factors:
  (a) movement, cycling.
(6) Maintenance practices.

There is little information available on which to assess the effect of these factors. In the survey by Anyakora, Engel and Lees, an attempt was made to assess the effect of environment, defining this rather loosely in terms of both ambient conditions and process materials. Two approaches were tried. One was to compare the effect of being or not being in contact with process fluids. Table 13.7 shows this effect for two groups of instruments, one consisting of those which are in contact and one consisting of those which are not. The instruments which are not in contact with process fluids show a much lower failure rate,

Table 13.6 *Some instrument failure rate data from three chemical works (Anyakora, Engel and Lees, 1971) (Courtesy of the Institution of Chemical Engineers)*

Instrument	*No. at risk*	*Instrument years*	*Environment factor*	*No. of faults*	*Failure* (faults/year)
Control valve	1531	747	2	447	0.60
Power cylinder	98	39.9	2	31	0.78
Valve positioner	334	158	1	69	0.44
Solenoid valve	252	113	1	48	0.42
Current/pressure transducer	200	87.3	1	43	0.49
Pressure measurement	233	87.9	3	124	1.41
Flow measurement (fluids):	1942	943	3	1069	1.14
Differential pressure transducer	636	324	3	559	1.73
Transmitting variable area flowmeter	100	47.7	3	48	1.01
Indicating variable area flowmeter	857	409	3	137	0.34
Magnetic flowmeter	15	5.98	4	13	2.18
Flow measurement (solids):					
Load cell	45	17.9	–	67	3.75
Belt speed measurement and control	19	7.58	–	116	15.3
Level measurement (liquids):	421	193	4	327	1.70
Differential pressure transducer	130	62	4	106	1.71
Float-type level transducer	158	75.3	4	124	1.64
Capacitance-type level transducer	28	13.4	4	3	0.22
Electrical conductivity probes	100	39.8	4	94	2.36
Level measurement (solids)	11	4.38	–	30	6.86
Temperature measurement (excluding pyrometers):	2579	1225	3	425	0.35
Thermocouple	772	369	3	191	0.52
Resistance thermometer	479	227	3	92	0.41
Mercury-in-steel thermometer	1001	477	2	13	0.027
Vapour pressure bulb	27	10.7	4	4	0.37
Temperature transducer	300	142	3	124	0.88
Radiation pyrometer	43	30.9	4	67	2.17
Optical pyrometer	4	3.4	4	33	9.70
Controller	1192	575	1	164	0.29
Pressure switch	549	259	2	87	0.34
Flow switch	9	3.59	–	4	1.12
Speed switch	6	2.39	–	0	–
Monitor switch	16	6.38	–	0	–
Flame failure detector	45	21.3	3	36	1.69
Millivolt-current transducer	12	4.78	–	8	1.67
Analyser:	86	39.0	–	331	8.49
PH meter	34	15.8	–	93	5.88
Gas–liquid chromatograph	8	3.43	–	105	30.6
O_2 analyser	12	5.67	–	32	5.65
CO_2 analyser	4	1.90	–	20	10.5
H_2 analyser	11	5.04	–	5	0.99
H_2O analyser (in gases)	3	1.38	–	11	8.00
Infrared liquid analyser	3	1.43	–	2	1.40
Electrical conductivity meter (for liquids)	5	1.99	–	33	16.70
Electrical conductivity meter (for water in solids)	3	1.20	–	17	14.2
Water hardness meter	3	1.20	–	13	10.9
Impulse lines	1099	539	3	416	0.77
Controller settings	1231	609	–	84	0.14

although control valves and temperature measurements are exceptions.

The other approach, which was applied to instruments which are in contact with process fluids, was to distinguish between 'clean' and 'dirty' fluids. A fluid was regarded as dirty if it contained 'gunk', polymerized, corroded, etc. Table 13.8 gives data for instruments in these two cases.

From this work it was concluded, as a first approximation and for the instruments considered, that the severity of the environment of an instrument depends on the aggressiveness of any process materials with which it is in contact and that other factors are generally of secondary importance.

If the failure rate is taken to be a product of a base failure rate and of an environment factor, then Tables 13.7 and 13.8 suggest that a maximum value of about 4 is appropriate. Environment factors are given in Table 13.6; the failure rates given in the table are the original data and should be

Table 13.7 *Effect of environment on instrument reliability: instruments in contact with and not in contact with process fluids (Anyakora, Engel and Lees, 1971) (Courtesy of the Institution of Chemical Engineers)*

Instrument	*No. at risk*	*No. of faults*	*Failure rate* (faults/year)
Instruments in contact with process fluids:	2285	1252	1.15
Pressure measurement	193	89	0.97
Level measurement	316	233	1.55
Flow measurement	1733	902	1.09
Flame failure device	43	28	1.37
Instruments not in contact with process fluids:	2179	317	0.31
Valve positioner	320	62	0.41
Solenoid valve	168	24	0.30
Current-pressure transducer	89	23	0.54
Controller	1083	133	0.26
Pressure switch	519	75	0.30
Control valve	1330	359	0.57
Temperature measurement	2391	326	0.29

Table 13.8 *Effect of environment on instrument reliability: instruments in contact with clean and dirty fluids (Anyakora, Engel and Lees, 1971) (Courtesy of the Institution of Chemical Engineers)*

Instrument	*No. at risk*	*No. of faults*	*Failure rate* (faults/year)
Control valve:			
Clean fluids	214	17	0.17
Dirty fluids	167	71	0.89
Differential pressure transmitter:			
Clean fluids	27	5	0.39
Dirty fluids	90	82	1.91

divided by the environment factor to give the base failure rate. It should also be noted that the sampling/impulse line failure rates given in Table 13.6 should be added to the failure rates of the instruments themselves to obtain the failure rates of installations.

13.8.3 Failure modes

The overall failure rate of an instrument gives only limited information. It is often necessary to know its failure modes. Failure modes can be classified in several ways. Some important categories are (1) condition, (2) performance, (3) safety and (4) detection.

In a failure classification based on conditions, a failure mode is exemplified by a faulty bellows on a flowmeter or a broken diaphragm in a control valve. In a classification by performance, illustrations of failure are a zero error in a flowmeter or the passing of fluid when shut by a control valve. A performance classification emphasizes effects and a condition classification emphasizes causes, but the distinction is not rigid: a blockage in a control valve could reasonably be classed either way. The safety classification divides faults into fail-safe and fail-dangerous. The detection classification distinguishes between revealed and unrevealed faults: a revealed fault signals its presence and is at once detectable, an unrevealed fault is not immediately detectable, but is usually detected by a proof check.

Condition and performance may be regarded as the primary types of failure. Safety and detection modes may be obtained from these and from the system context of the instrument.

Table 13.9 *Failure modes of some instruments (Lees, 1973b) (Courtesy of the Institution of Chemical Engineers)*

Instrument failure mode	*No. of faults*
Control valve:	
Leakage	54
Failure to move freely:	
Sticking (but moving)	28
Seized up	7
Not opening	5
Not seating	3
Blockage	27
Failure to shut off flow	14
Glands repacked/tightened	12
Diaphragm fault	6
Valve greased	5
General faults	27
Thermocouple:	
Thermocouple element faults	24
Pocket faults	11
General faults	20

Table 13.9 shows some data obtained by Lees (1973b) in the survey already described on failure modes in thermocouples and control valves. These failure modes are essentially classified by condition, although the condition is often revealed by a performance failure. Similar data for other instruments are given in the original paper. Some

data used in reliability studies described in the literature on failure modes of instruments and control loops are shown in Table 13.10.

If information is available on overall but not on mode failure rates, it is sometimes assumed that about one third of the faults are in the fail-dangerous mode. The safety and detection failure modes of the temperature trip amplifier shown in Figure 13.7 have been analysed by Eames (UKAEA 1973 SRS/GR/12) as shown in Table 13.11. The fault is described by a four-letter code. The first indicates that it is fail-safe (S), fail-dangerous (D) or a calibration shift in the dangerous direction (C). The second is the number of the equipment adversely affected by the fault. The number 1–5 refers to, respectively, the main trip, the excess margin alarm the low margin alarm and the indicating meter shown in the figure and the indicating lamp (not shown). The third letter indicates that the fault is revealed (r) or unrevealed (u). The fourth is the number of the equipment which reveals the fault; the numbering code is as before. The various failure rates of the equipment are as follows:

Faults	*Failure rate*	
	(faults/10^6 h)	(faults/year)
Fail-dangerous (D1)	9.85	0.086
Fail-dangerous, unrevealed (D1u)	4.6	0.040
Total	145.5	1.27

Thus, the total fail-dangerous and fail-dangerous unrevealed faults are, respectively, 6.8% and 3.2% of the total faults, which is one measure of the success of the fail-safe design of the equipment.

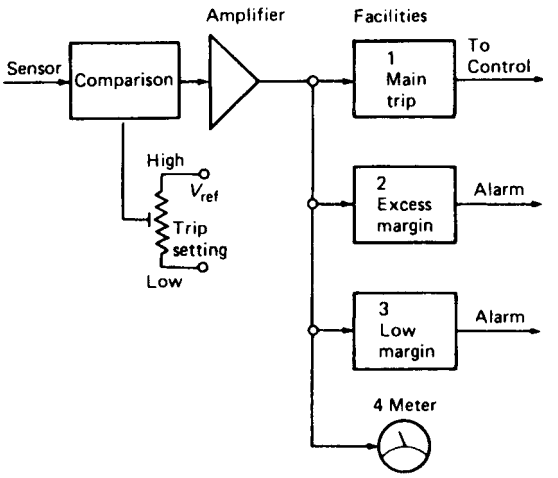


Figure 13.7 *Temperature trip amplifier (Fames, 1973 UKAEA SRS/GR/12) (Courtesy of the UK Atomic Energy Authority, Systems Reliability Directorate)*

Table 13.10 *Failure modes of some instruments defined by performance*

		Reference
Level measurement and alarm:	*Failure rate* (faults/year)	Lawley (1974b)
Level indicator fails to danger	2	
High level alarm fails	0.2	
	Probability	
Operator fails to observe level indicator or take action	0.04	
Operator fails to observe level alarm or take action	0.03	
Flow measurement and control:	*Failure rate* (faults/year)	S.B. Gibson (1977b)
For an FRC where high flow is undesirable:		
Flow element fails giving low reading	0.1	
Flow transmitter fails giving low reading	0.5	
FRC fails calling for more flow	0.4	
Flow control valve fails towards open position	0.1	
	Fractional dead time	
High flow trip fails to operate	0.01	
For an FRC where low flow is undesirable:	*Failure rate* (faults/year)	
Flow element fails giving high reading	0.2	
Flow transmitter fails giving high reading	0.4	
FRC fails calling for less flow	0.4	
Flow control valve fails towards closed position	0.2	
	Fractional dead time	
Low flow trip fails to operate	0.01	
Low flow trip left aborted after start-up	0.01	
Manual and control valves:	*Failure rate* (faults/year)	Lawley (1974b)
Manual isolation valve wrongly closed	0.05 and 0.1	
Control valve fails open or misdirected open	0.5	
Control valve fails shut or misdirected shut	0.5	

FRC, flow recorder controller.

13.8.4 Prediction of failure rates

It is sometimes necessary to know the failure rate of an instrument for which field data are not available. To meet this situation, methods have been developed for estimating the failure rate of an instrument from those of its constituent parts. Table 13.12 shows part of a prediction by Hensley (UKAEA 1969 AHSB(s) R178) of the failure rate of a pressure switch.

A comparison of some observed and predicted failure rates is given in Table 13.13. It can be seen that the agreement is quite good. A more quantitative measure of the effectiveness of the technique is Figure 13.8, which is given by A.E. Green and Bourne (1972) and shows the ratio of observed and predicted failure rates for a number of equipments. The median value of this ratio is 0.76 and the probabilities of the ratio being within factors of 2 and 4 of this value are 70% and 96%, respectively.

13.8.5 Loop failure rates

Data on failure rates of complete control loops have been the given by Skala (1974) and are shown in Table 13.14. Loop failure rates can be calculated from the failure rates of the constituent instruments. The failure rates of a loop with a pneumatic flow indicator controller, as calculated from the

Table 13.11 *Failure modes and rates of a temperature trip amplifier (Eames, 1973 UKAEA SRS/GR/12) (Courtesy of the UK Atomic Energy Authority, Systems Reliability Directorate)*

				Failure rate (faults/10^6h)			
Sr1	53.89	D1r2	4.85	D2r3	9.95	C1u	3.15
Sr2	2.1	D1r3	0.4	D2r4	0.15	C2u	6.79
Sr3	7.4	D1u	4.6	D2u	6.0	C3u	5.77
Sr5	5.0			D3r2	0.35		
Su	15.84			D3u	3.3		
				D4r4	5.8		
				D5u	10.2		
Total S	84.23	Total D1	9.85	Total other D	35.75	Total C	15.71

Table 13.12 *Predicted failure rates of a pressure switch (Hensley, 1969 UKAEA AHSB(S) R178) (Courtesy of the UK Atomic Energy Authority, Systems Reliability Directorate)*

Component	*Fault*	*Category*	*Failure rate* (faults/10^6 h)		
			Dangerous	*Safe*	*Total*
Spring	Fracture	Dangerous	0.2		
Bellows	Rupture	Safe		5.0	
Screws – pivot (2 items)	Loosen	Dangerous	1.0		
Microswitch	Random	Dangerous 25%	0.5		
		Safe 75%		1.5	
Total of above 5	—	—	1.7	6.5	
Total for 30 components in instrument			2.9	11.7 (faults/year)	14.6
Total for 30 components in instrument			0.025	0.10	0.13

Table 13.13 *Observed and predicted instrument failure rates*

Instrument	*Failure rate* (faults/year)		*Reference*[a]
	Observed	*Predicted*	
Control valve[b]	0.25	0.19	1–3
Differential pressure transmitter[b]	0.76	0.45	1–4
Variable area flowmeter transmitter[b]	0.68	0.7	1–3
Temperature trip amplifier:			
Type A	2.6	2.8	1, 2, 4
Type B	1.7	2.1	4
Controller	0.38	0.87	4
Pressure switch	0.14	0.13	1–3
Gas analyser	2.5	3.3	1,2
Relay[b]	0.17	0.35	4

[a] (1) Hensley (1967 UKAEA AHSB (S) R136); (2) Hensley (1968); (3) Hensley (1969 UKAEA AHSB (S) R178); (4) Eames (1966).
[b] Pneumatic.

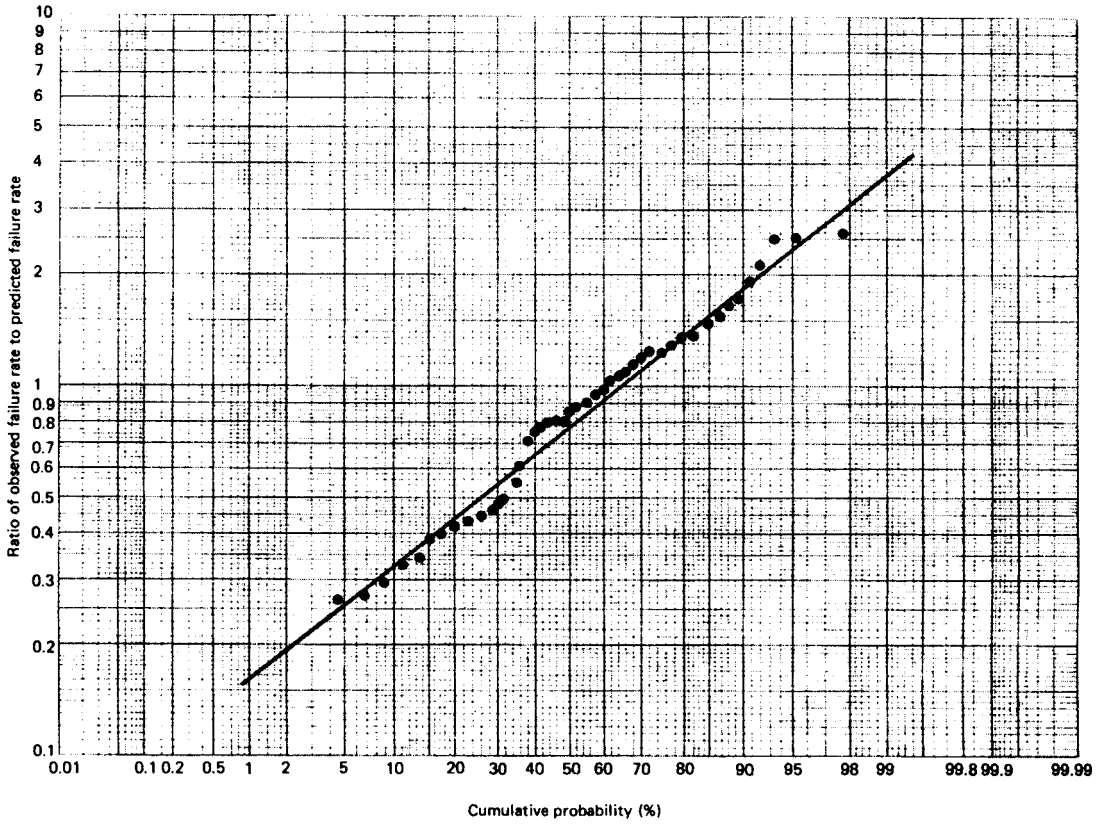


Figure 13.8 *Ratio of observed to predicted equipment failure rates (A.E. Green and Boume, 1972) (Reproduced with permission from Reliability Technology by A.E. Green and J.R. Boume, Copyright ©, 1972, John Wiley & Sons Inc.)*

data in Table 13.5 (UKAEA), as calculated from the data in Table 13.6 (Anyakora, Engel and Lees), and as given by Skala, are shown in Table 13.15.

Again it should be emphasized that, of the failure rates for loops given in these tables, only a very small proportion results in a serious plant upset or trip. In one study of the control loop failures on a large chemical plant quoted by M.R. Gibson (1978), it is found that there had been three control loop failures which resulted in plant trips and that the frequency of such failures was one failure every 20 years per loop.

13.8.6 Detection of failure

If instrument failure occurs, it is important for it to be detected. The ease of detection of an instrument failure depends very much on whether the fault is revealed or unrevealed. Unrevealed faults are generally detectable only by proof testing.

An instrument fault which is revealed is usually detected by the process operator either from the behaviour of the instrument itself or from the effect of the failure on the control system. There are, however, developments in the use of the process computer to detect instrument faults. Fault detection by the operator and by the computer is discussed in Chapters 14 and 30, respectively.

The detection of failure in instruments which have a binary output such as pressure or level switches is particularly difficult, because the fault if generally unrevealed, but is particularly important, because such instruments are frequently part of an alarm or trip system. One approach to the problem is to use an instrument with a continuous range output rather than a binary output. Thus, a level measuring instrument may be used instead of a level switch. In this way, many of the faults on the instrument which would otherwise be unrevealed become revealed.

13.8.7 Self-checking instruments

Developments are also made in instruments which have a self-checking capability. Principles on which such instruments are designed include (1) multiple binary outputs and (2) electrical sensor check.

A self-checking level measuring instrument which uses multiple binary outputs has been described by Hasler and Martin (1971). The instrument has a series of binary output points, which measure the liquid level at different heights. These points provide a mutual check. Thus, for example, if there are 10 points and the liquid level is up to point 5, so that this point gives a positive output, the absence of a positive output from point 4 indicates a failure on that point

A self-checking level switch in which electronic signals are used to check the state of the sensor has been described by J.O. Green (1978).

Increasingly, instruments are also being provided with the enhanced capabilities available from the incorporation of microprocessors. Self-checking is one such capability.

A general account of such instruments is given in Intelligent Instrumentation (Barney, 1985). A further discussion of intelligent, or smart, instruments is given by the CCPS (1993/14).

13.8.8 Fault-tolerant instrumentation

Instrument systems should have a degree of fault tolerance. The need for fault-tolerant systems has already been mentioned in relation to computer systems, where certain basic principles were outlined. These principles are equally applicable to the design of fault-tolerant instrument systems. Two main features of such instrumentation are redundancy and/or diversity and fail-safe operation. Fault-tolerant design of instrument systems is discussed by Bryant (1976), Ida (1983), Frederickson and Beckman (1990) and the CCPS (1993/14).

Table 13.14 *Control loop failure rates (after Skala, 1974) (Reproduced from Instrument Technology with permission of the publisher, Copyright ©, Instrument Society of America, 1974)*

Loop failures (by type of loop):	(faults/year)
PIC	1.15
PRC	1.29
FIC	1.51
FRC	2.14
LIC	2.37
LRC	2.25
TIC	0.94
TRC	1.99
Loop failures (by frequency per loop): [a] (% loops)	(faults/year)
25	0
34	1
14	2
9	3
5	4
4	5
3	6
2	7
1	8
1	9
0	10
0	11
2	12
Loop failures (by element in loop): (loop element)	(% faults)
Sensing/sampling	21
Transmitter	20
Transmission	10
Receiver[b]	18
Controller	7
Control valve	7
Other	17

[a] These data have been read from figure 2b of the original paper.
[b] Presumably indicators, recorders.

13.8.9 Instrument testing

Information is also available on the performance of instruments when subjected to a battery of standard tests. The evaluation of instruments is carried out both by special testing organizations and by major users. In the United Kingdom, the main organization concerned with instrument evaluation is the SIRA. Some of the tests carried out by SIRA have been described by Cornish (1978a). The instruments tested are normal production models.

Results of instrument evaluations by SIRA for the period 1971–76 have been given by Cornish (1978b) and are shown in Table 13.16. The reference conditions are the manufacturer's specification or, where no specification is quoted, an assumed specification based on current practice. The influence conditions refer to variations in electrical power or instrument air supply, high and low temperature, and humidity. These failure rates under test are high, but similar results are apparently obtained in other industrial countries.

Table 13.15 *Failure rates for a pneumatic flow indicator control loop*

UKAEA data:	(faults/year)
Differential pressure transmitter	0.76
Controller	0.38
Control valve	0.25
	1.39
Anyakora, Engel and Lees' data:	
Impulse lines	0.26
Differential pressure transmitter[a]	0.58
Controller[a]	0.29
Control valve[a]	0.30
Valve positioner[a]	$0.09(0.2 \times 0.44)$[b]
	1.52
Skala's data:	
FIC Loop[c]	1.51

[a] Pneumatic.
[b] It is assumed that 20percent of the valves have positioners.
[c] FIC, Flow indicator controller.

Table 13.16 *Instrument test failures (after Cornish, 1978b)*

Fault	*Instruments Subject to fault* (%)
Instruments faulty as received	21
Outside specification under reference conditions	27
Outside specification under influence conditions	30
Component failure during evaluation	27
Inadequate handbook/manual	26
Modification to design or manufacturing method after evaluation	33

13.9 Trip Systems

It is increasingly the practice in situations where a hazardous condition may arise on the plant to provide some form of automatic protective system. One of the principal types of protective system is the trip system, which shuts down the plant, or part of it, if a hazardous condition is detected. Another important type of protective system is the interlock system, which prevents the operator or the automatic control system from following a hazardous sequence of control actions. Interlock systems are discussed in Section 13.10.

Accounts of trip systems are given in *Reliability Technology* (A.E. Green and Bourne, 1972) and by Hensley (1968), R.M. Stewart (1971), Kletz (1972a), de Heer (1974), Lawley and Kletz (1975), Wells (1980), Barclay (1988), Rushton (1991a,b) and Englund and Grinwis (1992).

The existence of a hazard which may require a protective system is usually revealed either during the design process, which includes, as routine, consideration of protective features, or by hazard identification techniques such as hazop studies.

The decision as to whether a trip system is necessary in a given case depends on the design philosophy. There are quite wide variations in practice on the use of trip systems. There is no doubt, however, about the general trend, which is towards the provision of a more comprehensive coverage by trip systems. The problems are considered further in Chapter 14. The decision as to whether to install a trip system can be put on a less subjective basis by making a quantitative assessment of the hazard and of the reliability of the operator in preventing it.

13.9.1 Single-channel trip system

A typical, single-channel trip system is shown in Figure 13.9. It consists of a sensor, a trip switch and a trip valve. The configuration of a trip loop is therefore not dissimilar to that of a control loop. The difference is that, whereas the action of a control loop is continuous, that of a trip loop is discrete.

The trip switch may be of a general type, being capable of taking an electronic or pneumatic signal from any type of sensor. Thus, in a pneumatic system, a pressure switch would serve as the trip switch. Alternatively, the trip switch and the sensor may be combined to give a switch dedicated to a particular variable. Thus, common types of trip switch include flow, pressure, temperature, level and limit switches.

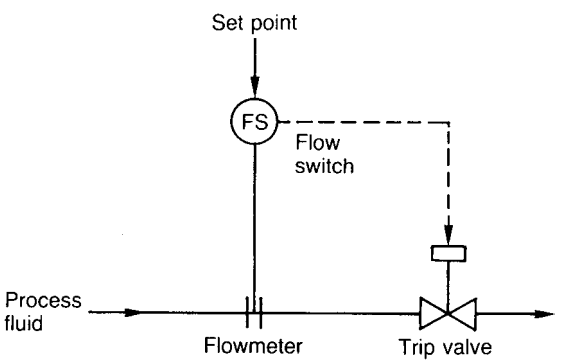


Figure 13.9 *A trip system*

13.9.2 Dependability of trip systems

Since a trip system is used to protect against a hazardous condition, it is essential for the system itself to be dependable. The dependability of a trip system depends on (1) capability and (2) reliability. Thus, it is necessary both for the system to have the capability of carrying out its function in terms of features such as accuracy, dynamic response, etc., and for it to be reliable in doing so. The reliability of the trip system may be improved by the use of (1) redundancy and (2) diversity. Thus, one approach is to use multiple redundant instruments, which generally give a reliability greater than that of a single instrument. But redundancy is not always the full answer, because there are some dependent failures which may disable the whole set of redundant instruments. This difficulty can be overcome by the use of diversity, which is exemplified by the use of different measurements to detect the same hazard and by the use of different instruments to measure the same variable.

Most trip systems consist of a single channel comprising a sensor, a switch and a shut-off valve, but where the integrity required is higher than that which can be obtained from a single channel, redundancy is generally used.

A trip system should be reliable against functional failure, that is, failure which prevents the system shutting the plant down when a hazardous condition occurs. Such a condition is not normally present and its rate of occurrence, which is the demand rate on the trip system, is usually very low. Thus, functional failures of the system are generally unrevealed failures. The trip system should also be reliable against operational failure, that is, failure which causes the system to shut the plant down when no hazardous condition exists. Thus operational failures of the system are always revealed failures.

It is the object of trip system design and operation to avoid both loss of protection against the hazardous condition due to functional failure and plant shut-down due to operational failure, or spurious trip. Since functional failure of the system is generally unrevealed, it is necessary to carry out periodic proof testing to detect such failure.

The simpler theoretical treatments of trip systems usually assume that the functional failures are unrevealed and the operational failures revealed and that the failure rates are constant; this approach is followed here. The treatment draws particularly on the work of A.E. Green and Bourne (1966 UKAEA AHSB(S) R117), some of which was later published by the same authors in *Reliability Technology* (1972).

13.9.3 Fractional dead time

The fractional dead time (FDT) of an equipment or system gives the probability that it is in a failed state. If the failure of an equipment is revealed with a revealed failure rate λ, the FDT ϕ depends on the failure rate and the repair time τ_r:

$$\phi = \lambda\tau_r \qquad \tau_r \ll 1 \qquad [13.9.1]$$

For a series system with revealed failure, the FDT ϕ of the system is related to the FDT ϕ_i of the constituent equipments as follows:

$$\phi = \sum_{i=1}^{n} \phi_i \qquad \lambda_i\tau_{ri} \ll 1 \qquad [13.9.2]$$

For a parallel system with revealed failure, the FDT ϕ of the system is related to the FDT ϕ_i of the equipments as follows:

$$\phi = \prod_{i=1}^{n} \phi_i \qquad \lambda_i \tau_{ri} \ll 1 \qquad [13.9.3]$$

For a parallel redundant, or 1/n (1-out-of-n), system with revealed failure, the FDT $\phi_{1/n}$ of the system is related to the FDT $\phi_{1/1}$ of a single equipment as follows:

$$\phi_{1/n} = \phi_{1/1}^{n} \qquad [13.9.4]$$

If, however, the failure of an equipment is unrevealed with an unrevealed failure rate λ, the FDT depends on this failure rate and on the proof test interval τ_p. The probability q of failure within time period t is:

$$q = 1 - \exp(-\lambda t) \qquad [13.9.5]$$

or, for small values of λt

$$q = \lambda t \qquad \lambda t \ll 1 \qquad [13.9.6]$$

Then the FDT is:

$$\phi = \frac{1}{\tau_p} \int_0^{\tau_p} q \mathrm{d}t \qquad [13.9.7]$$

For a $1/n$ system with unrevealed failure, the FDT $\phi_{1/n}$ of the system is obtained from the probability $q_{1/n}$ of failure of the system within the time period t:

$$\phi_{1/n} = \frac{1}{\tau_p} \int_0^{\tau_p} q_{1/n} \mathrm{d}t \qquad [13.9.8]$$

A detailed account of FDTs is given by A.E. Green and Bourne (UKAEA 1966 AHSB(S) R117).

13.9.4 Functional reliability of trip systems

Functional failure of a trip system here is assumed to be unrevealed. The failure rate λ used in the equations in this section is that applicable to these unrevealed fail-dangerous faults.

For a simple trip system consisting of a single channel 1/1 (1-out-of-1) system with a failure rate λ, the probability q of failure within proof test interval τ_p is:

$$q = 1 - \exp(-\lambda \tau_p) \qquad [13.9.9]$$

For small values of $\lambda \tau_p$:

$$q = \lambda \tau_p \qquad \lambda \tau_p < 1 \qquad [13.9.10]$$

The trip system is required to operate only if a hazardous plant condition occurs. The probability p_δ that such a plant demand, which has a demand rate S, will occur during the dead time τ_0 after the failure is:

$$P_\delta = 1 - \exp(-\delta \tau_0) \qquad [13.9.11]$$

But, on average, the dead time I_o is half the proof test interval τ_p:

$$\tau_0 = \frac{\tau_p}{2} \qquad [13.9.12]$$

Hence:

$$P_\delta = 1 - \exp(-\delta \tau_p / 2) \qquad [13.9.13]$$

For small values of $\delta \tau_0$:

$$p_\delta = \frac{\delta \tau_p}{2} \qquad \delta \tau_\rho \ll 1 \qquad [13.9.14]$$

The probability p, that a plant hazard will be realized can be written in terms of the plant hazard rate η:

$$P_\eta = 1 - \exp(-\eta \tau_p) \qquad [13.9.15]$$

For small values of $\eta \tau_p$:

$$P_\eta = \eta \tau_p \qquad \eta \tau_p \ll 1 \qquad [13.9.16]$$

Frequently, some or all of the approximations of Equations 13.9.10, 13.9.14 and 13.9.16 apply. If all do, then taking

$$P_\eta = q p_\delta \qquad [13.9.17]$$

gives

$$\eta = \frac{\delta \lambda \tau_p}{2} \qquad \lambda \tau_p \ll 1; \quad \delta \tau_p \ll 1; \quad \eta \tau_p \ll 1 \qquad [13.9.18]$$

If the assumptions underlying Equation 13.9.18 are not valid, an expression which has been commonly used is:

$$\eta = \lambda p_\delta \qquad [13.9.19]$$

Alternatively, the plant hazard rate can be expressed in terms of the FDT ϕ of the system:

$$\eta = \delta \phi \qquad [13.9.20]$$

As given earlier, the probability q of failure of the simple trip system within the time period t is:

$$q = 1 - \exp(-\lambda t) \qquad [13.9.21]$$

For small values of λt:

$$q = \lambda t \qquad \lambda \mathrm{t} \ll 1 \qquad [13.9.22]$$

Then the FDT ϕ of the simple trip system is:

$$\phi = \frac{1}{\tau_p} \int_0^{\tau_p} q \mathrm{d}t \qquad [13.9.23]$$

Hence:

$$\phi = \frac{\lambda \tau_p}{2} \qquad [13.9.24]$$

and

$$\eta = \frac{\delta\lambda\tau_p}{2} \qquad [13.9.25]$$

as before.

For a parallel redundant, or $1/n$ (1-out-of-n), system, or for an m/n (m-out-of-n) system, which may be a majority voting system, the following treatment applies. If there are n equipments of which m must survive for the system to survive and r must fail for the system to fail*:

$$r = n - m + 1 \qquad [13.9.26]$$

The probability $q_{m/n}$ of failure of this system within the proof test interval is:

$$q_{m/n} = \sum_{k=r}^{n} \binom{n}{k} q^k (1-q)^{n-k} \qquad [13.9.27]$$

For small values of q:

$$q_{m/n} = \binom{n}{r} q^r \qquad q \ll 1 \qquad [13.9.28]$$

The FDT $\phi_{m/n}$ of the system is:

$$\phi_{m/n} = \frac{1}{\tau_p} \int_0^{\tau_p} q_{m/n} \mathrm{d}t \qquad [13.9.29]$$

Then, from Equations 13.9.22, 13.9.28 and 13.9.29, the FDT $\phi_{m/n}$ of the system is:

$$\phi_{m/n} = \binom{n}{r} \frac{(\lambda\tau_p)^r}{r+1} \qquad [13.9.30]$$

Thus, for a 2/3 majority voting system:

$$\phi_{2/3} = (\lambda\tau_p)^2 \qquad [13.9.31]$$

For the special case of a parallel redundant, or $1/n$ (1-out-of-n), system, Equation 13.9.30 reduces to give the FDT $\phi_{1/n}$:

$$\phi_{1/n} = \frac{(\lambda\tau_p)^n}{n+1} \qquad [13.9.32]$$

Thus, for a 1/2 parallel system:

$$\phi_{1/2} = \frac{(\lambda\tau_p)^2}{3} \qquad [13.9.33]$$

and for a 1/3 system

$$\phi_{1/3} = \frac{(\lambda\tau_p)^3}{4} \qquad [13.9.34]$$

* In this trip chapter, the number of equipments which must fail for the system to fail is r. This notation differs from that used in Chapter 7 for r-out-of-n parallel systems, in which r was used for the number of equipments which must survive for the system to survive. These two notations are used in order to preserve correspondence with established usage in texts on general reliability (e.g. Shooman, 1968) and on trip systems (e.g. A.E. Green and Bourne, 1972).

FDTs calculated from Equation 13.9.30 are shown in Table 13.17, both as functions of $\lambda\tau_p$ and of the FDT $\phi_{1/1}$ for a single channel. Table 13.17 assumes that the instruments are tested simultaneously at the end of the proof test interval. Some improvement can be obtained by staggered testing, as shown by the data in Table 13.18, which are taken from A.E. Green and Bourne (1972).

13.9.5 Operational reliability of trip systems

It is also necessary to consider operational failure of trip systems. Operational failure here is assumed to be revealed. The failure rate λ used in the equations in this section is that applicable to these revealed fail-safe, or fail-spurious, faults.

For a simple trip system consisting of a single channel 1/1 system with a failure rate λ the operational failure, or spurious trip, rate γ is:

$$\gamma = \lambda \qquad [13.9.35]$$

For a parallel redundant, or $1/n$, system the operational failure rate $\gamma_{1/n}$ is:

$$\gamma_{1/n} = n\lambda \qquad [13.9.36]$$

For an m/n system, which may be a majority voting system, the following treatment applies. The rate at which the first operational failure of a single channel occurs is $n\lambda$.

Table 13.17 *Fractional dead times for trip systems with simultaneous proof testing*

System	n	m	r	ϕ	
1/1	1	1	1	$\frac{\lambda\tau_p}{2}$	$\phi_{1/1}$
1/2	2	1	2	$\frac{(\lambda\tau_p)^2}{3}$	$\frac{4}{3}\phi_{1/1}^2$
1/3	3	1	3	$\frac{(\lambda\tau_p)^3}{4}$	$2\phi_{1/1}^3$
2/2	2	2	1	$\lambda\tau_p$	$2\phi_{1/1}$
2/3	3	2	2	$(\lambda\tau_p)^2$	$4\phi_{1/1}^2$

Table 13.18 *Fractional dead times for trip systems with staggered proof testing (A.E. Green and Bourne, 1972) (Reproduced with permission from Reliability Technology by A.E. Green and J.R. Bourne, Copyright © , 1972, John Wiley and Sons Inc.)*

System	ϕ^*	ϕ/ϕ^*
1/1	$\frac{\lambda\tau_p}{2}$	1
1/2	$\frac{5}{24}(\lambda\tau_p)^2$	1.6
1/3	$\frac{1}{12}(\lambda\tau_p)^3$	3.0
2/2	$\lambda\tau_p$	1
2/3	$\frac{2}{3}(\lambda\tau_p)^2$	1.5

ϕ, Fractional dead time for simultaneous testing; ϕ^*, fractional dead time for staggered testing.

This first failure only results in a system trip if further operational failure of single channels sufficient to trip the system occurs within the repair time τ_r. The probability q_γ that this will occur is:

$$q_\gamma = \binom{n-1}{m-1}(\lambda\tau_r)^{m-1} \qquad \lambda\tau_r \ll 1 \qquad [13.9.37]$$

Then the operational failure rate $\gamma_{m/n}$ of the system is:

$$\gamma m/n = n\lambda q_\gamma \qquad [13.9.38]$$

$$\gamma_{m/n} = n\lambda\binom{n-1}{m-1}(\lambda\tau_r)^{m-1} \qquad [13.9.39]$$

Thus, for a 2/3 majority voting system:

$$\gamma_{2/3} = (3\lambda)\cdot(2\lambda\tau_r) \qquad [13.9.40]$$

$$\gamma_{2/3} = 6\lambda^2\tau_r \qquad [13.9.41]$$

Operational failure, or spurious trip, rates calculated from Equations 13.9.36 and 13.9.39 are shown in Table 13.19. It is emphasized again that the foregoing treatment is a simplified one. The expressions derived here appear, however, to be those in general use (e.g. Hensley, 1968; Kletz, 1972a; de Heer, 1974; Lawley and Kletz, 1975). Full theoretical treatments of trip systems have been given by A.E. Green and Bourne (1966 UKAEA AHSB(S) R117) and Wheatley and Hunns (1981). The latter gives expressions for a wide variety of trip systems.

13.9.6 Proof testing of trip systems

The treatment of the functional reliability of trip systems which has just been given demonstrates clearly the importance of the proof test interval. The expressions derived show that the condition for high functional reliability is

$$\lambda\tau_p < 1 \qquad [13.9.42]$$

As an illustration of the effect of the proof test interval, consider a simple trip system which has a failure rate of 0.67 faults/year on a duty where the demand rate is 1 demand/year:

$\delta = 1$ demand/year

$\lambda = 0.67$ faults/year

If the proof test interval is 1 week:

$\tau_p = 0.0192$ year

Table 13.19 *Spurious trip rates for trip systems*

System	γ
1/1	λ
1/2	2λ
1/3	3λ
2/2	$2^2\tau_r$
2/3	$6\lambda^2\tau_r$

Then the FDT is:

$$\phi = \frac{\lambda\tau_p}{2} = 0.0064$$

and the plant hazard rate is

$\eta = \delta\phi = 0.0064$ hazards/year

The plant hazard rate for a range of proof test intervals is:

τ_p	η (hazards/year)
1 week	0.0064
1 month	0.027
1 year	0.26

For the longer proof test intervals, the approximate Equation 13.9.18 is not valid and Equation 13.9.19 was used.

Some additional factors which affect the choice of proof test interval are the facts that, while it is being tested, a trip is disarmed and that each test is an opportunity for an error which disables the trip, such as leaving it isolated after testing.

Thus, for a simple trip system with a trip disarmed period τ_d and an isolation dead time ϕ_{is}, the FDT becomes:

$$\phi = \frac{\lambda\tau_p}{2} + \frac{\lambda_d}{\tau_p} + \phi_{is} \qquad [13.9.43]$$

This expression has a minimum at:

$$(\tau_p)_{min} = \left(\frac{2\tau_d}{\lambda}\right)^{1/2} \qquad [13.9.44]$$

The effect of these factors can be illustrated by considering the trip system described in the previous example. If the trip disarmed period is 1 h and the isolation dead time is 0.001:

$\tau_d = 1.14 \times 10^{-4}$ year

$\phi_{is} = 0.001$

$(\tau_p)_{min} = 0.0184$ year = 0.96 weeks

Assume that a proof test interval of 1 week is chosen:

$\tau_p = 0.0192$ year

Then the FDT is

$\phi = 0.013$

and the plant hazard rate is

$\eta = 0.013$ hazards/year

In some instances it is not possible to test all parts of the trip system every time a proof test is carried out. For example, it is often not permissible to close the shut-off

valve completely. In such cases a partial test is done, checking out the system to demonstrate valve movement but not valve shut-off.

If for a simple trip system the functional failure rate and proof test interval of the first part of the system are λ_A and τ_{pA} respectively, and those of the second part are λ_B and τ_{pB}, respectively, then:

$$q_A = 1 - \exp(-\lambda_A t) \qquad [13.9.45]$$

$$q_A = \lambda_A t \qquad \lambda_A t \ll 1 \qquad [13.9.46]$$

Similarly

$$q_B = \lambda_B t \qquad \lambda_B t \ll 1 \qquad [13.9.47]$$

Then the FDT is:

$$\phi = \frac{1}{\tau_{pA}} \int_0^{\tau pA} q_A dt + \frac{1}{\tau_{pB}} \int_0^{\tau pB} q_B dt \qquad [13.9.48]$$

$$\phi = \frac{1}{2}(\lambda_A \tau_{pA} + \lambda_B \tau_{pB}) \qquad [13.9.49]$$

There appears to be some variability in industrial practice with respect to the proof test interval. Generally a particular firm tends to have one longer interval, which is the standard one, and a shorter interval which is used for more critical cases. One such pair of intervals is 3 months and 1 month. Another is 1 month and 1 week. Thus, 1 month and 1 week proof test intervals are mentioned in many of the trip system applications described by Lawley and Kletz. In some cases the policy is adopted that if analysis shows that the proof test interval for a single trip is short, a redundant trip system is used.

13.9.7 Some other trip system characteristics

There are certain general characteristics which are desirable in any instrument system, but which are particularly important in a trip system. A trip system should possess not only reliability but also capability. In other words, when functional, it should be capable of carrying out its function. If it is not, then no amount of redundancy will help. The measuring instrument of the trip system should be accurate. This is particularly important where the safety margin is relatively fine.

The trip system should have a good dynamic response. What matters here is the ability of the trip to give rapid detection of the sensed variable and to effect rapid correction of that variable or rapid plant shut-down. This response therefore depends on the trip system itself, but also on the dynamic response of the plant. This aspect is considered further in Section 13.9.16.

The trip system should have sufficient rangeability to maintain accuracy at different plant throughputs. Another important property of a trip system is the ease and completeness with which it can be checked. It is obviously desirable to be able to check all the elements in a trip system, but this is not always easy to arrange.

13.9.8 Trip system applications

Some illustrations of the specification and design of protective systems have been given by Kletz (1972a, 1974a) and by Lawley and Kletz (1975). As already mentioned in Chapter 12, the use of trip systems instead of pressure relief valves is sometimes an attractive proposition, particularly where the relief valve solution involves large flare or toxic scrubbing systems. This is considered by Kletz (1974a) and by Lawley and Kletz (1975), who suggest that if a trip system is used instead of a relief valve, it should be designed for a reliability 10 times that of the latter. The reason for this is the uncertainty in the figures and the difference in the modes of failure; a relief valve which fails to operate at the set pressure may nevertheless operate at a higher pressure, whereas a trip is more likely to fail completely.

The fail-dangerous failure rates of a pressure relief valve and of a simple 1/1 trip system are quoted by these workers as 0.01 and 0.67 faults/year, respectively (Kletz, 1974a). Then, using these failure rates and assuming a demand rate of 1 demand/year, the plant hazard rates shown in Table 13.20 are obtained. For the longer proof test interval, $\delta\tau_p \ll 1$ and $\lambda\tau_p \ll 1$ do not apply, and for this case, the data in the table are obtained not from the approximate Equation 13.9.18, but from Equation 13.9.19. Thus, to meet the design criterion suggested for functional reliability, a 1/2 trip system with weekly testing is required. The spurious trip rate for this system, however, might be unacceptable, leading to a requirement for a 2/3 system.

Another example of the use of trip systems is the hydrocarbon sweetening plant shown in Figure 13.10 (Kletz, 1972a). The hydrocarbon is sweetened with small quantities of air which normally remain completely dissolved, but conditions can arise in which an explosive mixture may be formed. Initially it was assumed that the principal problem lay in a change in the air/hydrocarbon ratio but a hazop study revealed that a hazard could arise in a number of ways. One is for an air pocket to be formed, which can occur as follows:

(1) the temperature can be so high that the amount of air normally used will not dissolve;
(2) an air pocket can be left behind when a filter is recommissioned;
(3) the pressure can fall, allowing air to come out of solution;
(4) a fault in the mixer can prevent the air being mixed with hydrocarbon, so that the pockets of air can be carried forward;
(5) a fault in the air/hydrocarbon ratio controller can result in the admission of excess air.

Table 13.20 *Plant hazard rates for pressure relief valves and for trip systems (after Kletz 1974a) (Courtesy of Chemical Processing)*

System	*Plants hazard rate,* η (hazards/year)	(years/hazard)
No relief valve or trip	1	say, 1
Relief valve:		
Annual testing	0.004	250
Single 1/1 trip:		
Annual testing	0.264	4
Monthly testing	0.027	36
Weekly testing	0.0064	180
Duplicate 1/2 trip:		
Weekly testing	5.5×10^{-5}	18,000

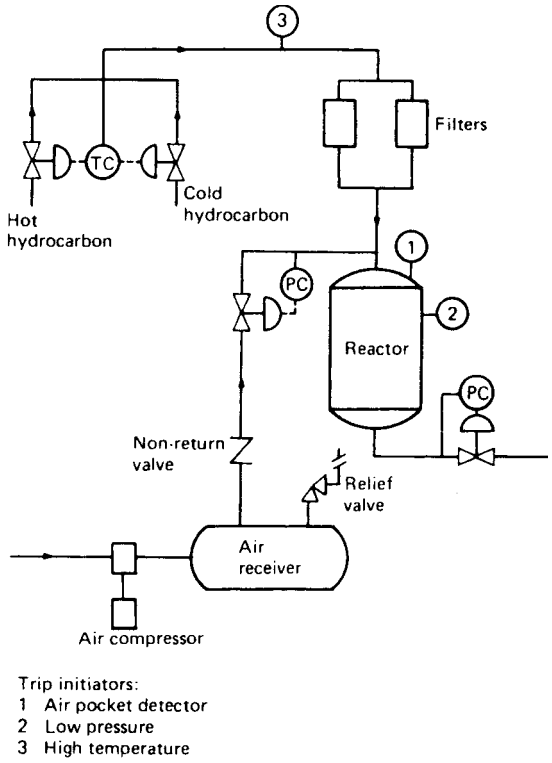


Figure 13.10 *Hydrocarbon sweetening plant (Kletz, 1972a) (Courtesy of the American Institute of Chemical Engineers)*

In this case it is also necessary for the feed to be above its flashpoint, which can occur in a number of ways: (1) the temperature can be above the normal flashpoint and (2) the feed can contain low flashpoint material. Alternatively, if there is both a loss of pressure in the receiver and a failure of the non-return valve, hydrocarbon may find its way into the air receiver.

The fault tree for the hazard is shown in Figure 13.11. The probabilities of the various fault paths were evaluated from this and the trip requirements were identified. The trip initiators considered, shown by the circles in Figures 13.10 and 13.11, were

(1) a device for detecting a pocket of air in the reactor;
(2) a pressure switch for detecting a low pressure in the receiver;
(3) a temperature measurement device for detecting a high temperature in the feed;
(4) laboratory analysis for detecting a low flashpoint feed;
(5) a device for detecting a high air/hydrocarbon ratio.

As the latter condition is detected by the trip initiator 1 anyway, trip initiator 5 was not used. The shut-down arrangement was that any of the trip initiators 1–3 shuts a valve in the air line and shuts down the compressor. The use of the laboratory analysis of feed flashpoint was restricted to ensuring that low flashpoint feeds were only present a for sufficiently small fraction of the time to meet the system specification.

A third example is the distillation column heating system shown in Figure 13.12 (Lawley and Kletz, 1975). Heat was supplied to the distillation column from an existing steam-heated reboiler and a hot-water-heated feed vaporizer. The plant was to be uprated by the addition of another reboiler and vaporizer.

The existing pressure relief valve was a 2/2 system and was adequate to handle overpressure from the existing reboiler and vaporizer. The problem was to cope with the overpressure which the new reboiler and vaporizer might give rise to. Both re-sizing of the existing relief valves and the addition of a third were unattractive in the particular situation. There was therefore a requirement for a trip system which would shut-down both the steam to the new reboiler and the hot water pump on the new vaporizer.

Both 1/1 and 1/2 trip systems were considered. The 1/1 system consisted of a pressure switch for detecting a high pressure on the overhead vapour line, a relay and a contact on the power supply to the hot water pumps and a relay and contact on that to the solenoid-operated shut-off valve on the reboiler steam supply. The 1/2 system consisted of a duplication of the 1/1 system. The summary of the failure rates of a simple trip system for this case is shown in Table 13.21.

The functional reliability of the existing 2/2 relief valve system was calculated as follows:

$$\lambda = 0.005 \text{ faults/year}$$
$$\tau_p = 2 \text{ years}$$
$$\phi = \lambda\tau_p = 0.01$$

The target FDT for the new trip system was taken as a factor of 10 less than this, namely 0.001, for the reasons already explained. The functional reliability of a 1/1 trip system was calculated as follows:

$$\lambda = 0.42 \text{ faults/year (from Table 13.21)}$$
$$\phi = \frac{\lambda\tau_p}{2}$$
$$= 0.21\tau_p$$

Then, taking into account also the disarmed time and the isolation dead time:

$$\tau_d = 1 \text{ h/test}$$
$$\approx 0.0001 \text{ years/test}$$
$$\phi_{is} = 0.001$$
$$\phi = 0.21\tau_p + \frac{0.0001}{\tau_p + 0.001}$$

The minimum FDT is at a proof test interval of

$$(\tau_p)_{min} = (2\tau_p/\lambda)^{1/2}$$
$$= 0.022 \text{ years}$$
$$= 8 \text{ days}$$

Assuming a proof test interval of 1 week, the FDT is

$$\phi = 0.01$$

This does not meet the target.

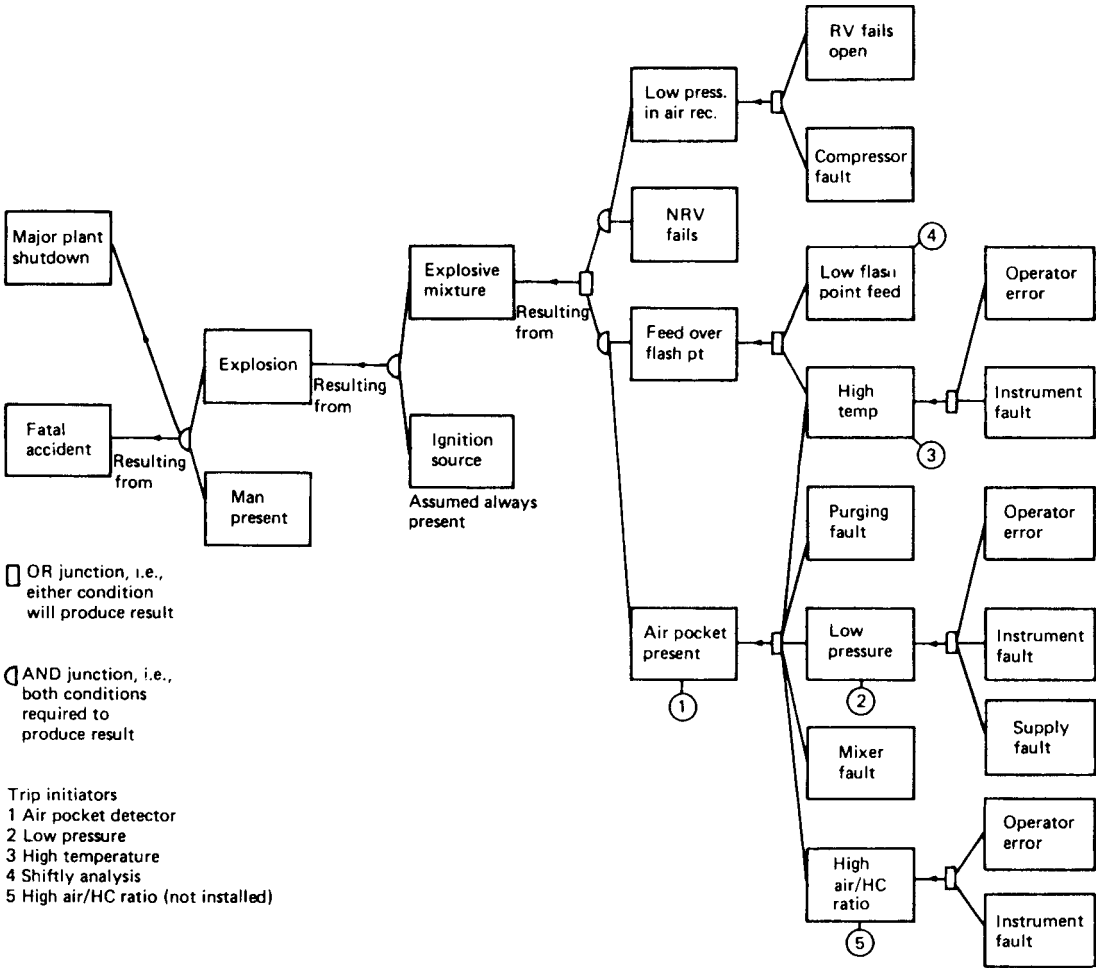


Figure 13.11 *Fault tree for explosion on a hydrocarbon sweetening plant (after Kletz, 1972a) (Courtesy of the American Institute of Chemical Engineers)*

The authors therefore consider a 1/2 trip system. The analysis for this system is more complex and takes into account the fact that the complete shut-off of the valves can be checked only on a proportion of the tests. It is concluded that a 1/2 system does just meet the target set.

13.9.9 High integrity trip systems

The trip system applications described so far have been 1/1 or 1/2 systems. The more complex system with 2/3 majority voting is now considered.

A major system of this kind, which appears to be the then most sophisticated on a chemical plant and which has been influential in the general development of protective systems in the industry, is that on the ethylene oxide process of ICI described by Stewart and co-workers (R.M. Stewart, 1971, 1974a; R.M. Stewart and Hensley, 1971). The ethylene oxide process is potentially extraordinarily hazardous: it operates with a reaction mixture very close to the explosive limit, there is a fire/explosion hazard and a toxic release hazard.

The design of the protective system followed the methods already outlined. The risk criterion was set at a probability of one fatality of 3×10^{-5} per year. The hazards were assessed by means of a fault tree, part of which is shown in Figure 13.13.

The system devised is a HIPS, consisting of the high integrity trip initiators (HITIs), the high integrity voting equipment (HIVE) and the high integrity shut-down system (HISS). A schematic system diagram, which omits replicated signal connections, is shown in Figure 13.14.

Redundancy is fully exploited throughout the system. Against each logic path to fire/explosion in the fault tree at least one parameter was selected initially to be a trip initiator. The integrity specified in fact required the use of at least two parameters. The choice of the trip initiating parameters is important but difficult. Some are obvious such as high oxygen concentration, high reactor temperature, low recycle gas flow. Others are far less obvious, but are needed to guard against combinations of faults or to substitute for other parameters. The latter occurs, for

example, where the measurement response is too slow, for example oxygen concentration, or where the trip could result in a hazardous condition, for example recycle compressor trip.

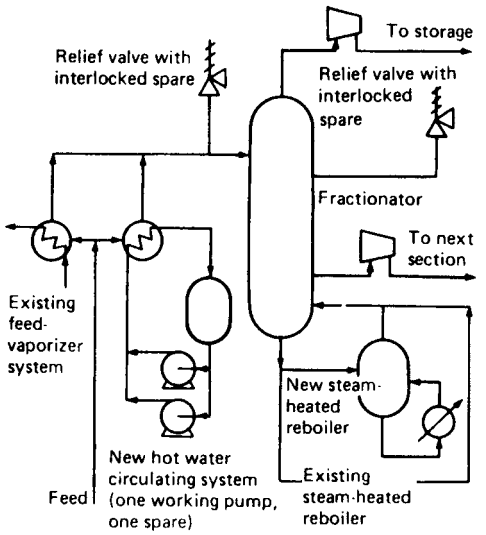


Figure 13.12 *Distillation column heating system (Lawley and Kletz, 1975) (Courtesy of Chemical Engineering)*

The measuring instruments used are carefully selected and, if necessary, modified to ensure high reliability. Each parameter is measured by triplicate instruments. The cables from each trip initiator on a parameter go by different routes so that there is less chance of all three being disabled by an incident such as a flash fire; the equipments have separate power supplies; and so on. The arrangement of the shut-down valves in the oxygen line illustrates further the use of redundancy. There are two lines each with three valves. A single line represents a 1/3 shut-down system. Duplication is provided to permit complete testing without disarming.

The advantages of the system are that the failure of one trip initiator in the fail-safe mode does not cause the plant to be tripped spuriously, the failure of one trip initiator in the fail-dangerous mode does not prevent the plant from being tripped, and the proof testing can be done without disarming the system.

The design of the system was subjected to an independent assessment by assessors within the company who were advised by the UKAEA. The assessors checked all feasible faults which could lead to hazardous conditions: the capability of the HIPS to carry out the protective action against the hazardous conditions arising from such faults and the occurrence rate of other hazardous conditions which the HIPS would not prevent, in relation to the design target Table 13.22 shows an extract from the table produced during this assessment.

The assessment showed that at this stage the plant hazard rate was 4.79×10^{-5}/year, which was higher than the target of 3×10^{-5}/year. An extra HITI was used to reduce the contribution of fault 3 from 2.72×10^{-5} to

Table 13.21 *Failure rates of trip systems for a distillation column heating systems (Lawley and Kletz, 1975) (Courtesy of Chemical Engineering)*

Components	*Failure rate* (faults/year)		
	Fail-to-danger	*Fail-safe*	*Total*
Trip initiator:			
Impulse lines – blocked	0.03	–	0.03
– leaking	0.06	–	0.06
Pressure switch (contacts open to give trip signal on rising pressure)	0.10	0.03	0.13
Cable fractured or severed	–	0.03	0.03
Loss of electrical supply	–	0.05	0.05
Total	0.19	0.11	0.30
Steam shut-off system:			
Relay coil (de-energize to trip)	–	0.05	0.05
Relay contact	0.01	0.01	0.02
Relay terminals and wire	–	0.01	0.01
Solenoid valve (de-energize to trip)	0.10	0.20	0.30
Loss of electrical supply (to solenoid valve)	–	0.05	0.05
Trip valve (clothes on air failure)	0.10	0.15	0.25
Air supply line – blocked or crushed	0.01	–	0.01
– fractured or holed	–	0.01	0.01
Loss of air supply	–	0.05	0.05
Total	0.22	0.53	0.75
Pump shut-off system:			
Relay coil, contact, terminals and wire (as above)	0.01	0.07	0.08
	0.01	0.07	0.08

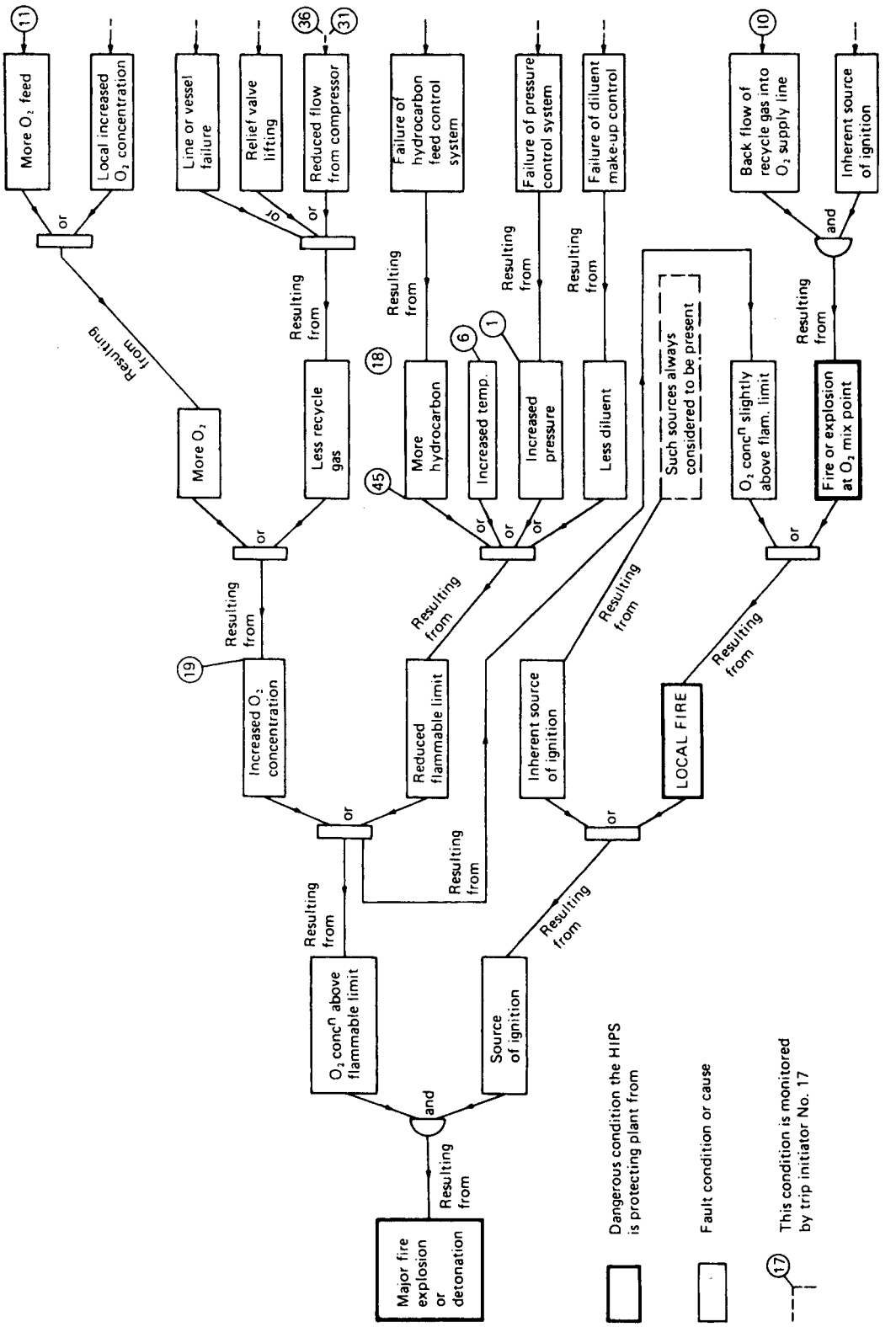


Figure 13.13 *Fault tree for fire/explosion on an ethylene oxide plant (after R.M. Stewart, 1971) (Courtesy of the Institution of Chemical Engineers)*

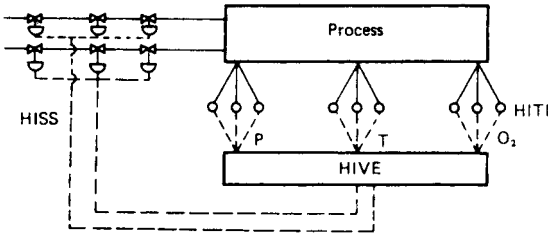


Figure 13.14 *High integrity protective system (after Stewart, 1971) (Courtesy of the Institution of Chemical Engineers)*

0.8×10^{-5}/year, which brought the system within specification.

The assessors also examined the HIPS as installed to ensure that there were no significant deviations from design and reviewed the maintenance, calibration and testing procedures. The quality of the maintenance and testing is crucial to the integrity of a protective system and much attention was paid to this aspect.

It was estimated that an alternative system with $70^1/_1$ single trip initiators would result in some 30 spurious trips a year and that the system used reduced this by a factor of over 12. Since the cost of a trip was estimated as £2000, the saving due to avoidance of spurious trips was about £55,000 per annum. The cost of £140,000 for the installation was therefore considered justified on these grounds alone.

A coda to this account has been given by A. Taylor (1981), who describes the operation of the trip system over the period 1971–80. The information on the performance of the trip system is of two kinds: operations of and tests on the system. Events were classified as spurious, genuine and deliberate, the last being initiations by the operators.

Analysis of these events revealed that in a few cases the demand frequency was greater than that originally estimated by orders of magnitude. The author gives a table listing seven fault conditions, with the event numbering rising to 53, which exemplify the worst discrepancies. The two fault conditions which show the greatest discrepancies are the opening of a certain relief valve and loss of reaction:

Fault description		*Fault condition*		
		Predicted frequency (events/year)	*Actual frequency* (events/year)	*Ratio of actual/predicted frequency*
15	A certain relief valve opens	0.001	1.68	1680
48b	Loss of reaction	0.01	1.16	116

The relief valve fault was due to 'feathering', which had not been anticipated. The loss of reaction fault is not explicitly explained, but references by the author to the effect of modifications in reaction conditions may bear on this. It is noteworthy that of the seven fault conditions, it is those for which the original frequency estimates were lowest which are most in error.

With regard to instrument failure rates, in the case of magnetic float switches, three different failure mechanisms, and three different failure rates, were observed. Switches operating submerged in clean lubricating oil recorded no failures; those operating in recycled gas with occasional slugs of dirty water choked up; and a new type of switch was found to suffer from corrosion.

The author quotes three examples of dependent failure. One of these relates to the choked level switches just mentioned, which were all on one vessel. On four occasions, testing of the switches revealed that all were choked. The test procedure was altered to require that if one switch was found to be choked, the others should be tested.

There were also mistakes made in the installation of the instruments. In one case, pneumatic pressure switches, of a flameproof type which is not waterproof, were located downwind of a low pressure steam vent pipe, and suffered water ingress and corrosion.

13.9.10 PES-based trip systems

A trip system needs to be highly reliable. For this reason, it has been the practice to design trip systems as separate, hardwired systems. The acceptability of using a PES to implement the trip functions has long been a matter of debate. There has been a marked reluctance to abandon dedicated, hardwired systems.

The most constructive approach to the problem is to try to define the conditions which must be met by a PES-based trip system. As described in Section 13.12, the Health and Safety Executive (HSE, 1987b) has issued guidance based on this approach. Further guidance is given in the CCPS *Safe Automation Guidelines* described in Section 13.15, which are largely concerned with this topic.

An account of a computer-based trip system on an ammonia plant has been given by Cobb and Monier-Williams (1988). The reason given for moving to such a system is the avoidance of spurious trips. Design options were considered based on PLC and computer systems. The latter was selected largely because it offered a better interface with the operator. The system uses two computers operating in parallel. Some features of the system are: the ability to use inferred measurements; improved reliability of the trips; decreased defeating, or disarming, of the trips; and better control of any disarming which does occur.

13.9.11 Disarming of trip systems

It may sometimes be necessary to disarm a trip. This need arises particularly where a transition is being made between one state and another such as during start-up. The disarming of a trip should be assessed to ensure that it does not negate the design intent, whether this check is made at the time of the original design or subsequently. Such disarming should be the subject of a formal authorization procedure. This may be supplemented by hardware measures such as a key interlock.

If a trip proves troublesome, it is liable to be disarmed without such authorization. This is particularly likely to occur if there are frequent spurious trips, due to sensor failure or other causes. In order to disarm a trip, it may not be necessary to interfere with the hardware. It is often sufficient simply to alter to set-point.

13.9.12 Restart after a trip

Once a trip has operated, it is necessary to reset the system so that a safer restart can be made. Therefore, the trip action which has driven the plant to a safe state should not simply be cancelled, but instead a planned sequence of

Table 13.22 *Assessment of reliability of a high integrity trip system (after R.M. Stewart, 1971) (Courtesy of the Institution of Chemical Engineers)*

Description	*Fault condition*				*Relevant trip initiator No.*	*Fractional deed time*				*Hazard rate* ($\times 10^5$) (hazards/year)
	Occasions per year	*Probability that it leads to rupture*	*Probability that operator's intervention fails*	*Demand rate* (demands/year)		*HITI*	*HIVE*	*HISS*	*Overall*	
	a	*b*	*c*	*(d = a × b × c)*		*e*	*f*	*g*	*(h = e + f + g)*	*(i = d × h)*
1 Feed filters blocked	0.001	0.2	0.1	0.00002	10 & 12	10^{-4}	10^{-5}	10^{-5}	1.2×10^{-4}	0.00024
2 Oxygen supply failure	2.0	0.2	0.1	0.04	10 & 38	10^{-4}	10^{-5}	10^{-5}	1.2×10^{-4}	0.48
3 PCV fails open	0.25	0.1	1.0	0.025	11	10^{-3}	8.3×10^{-5}	10^{-5}	1.09×10^{-3}	2.72
4 Compressor antisurge bypass fails open	0.2	1.0	0.1	0.02	18 & 36	10^{-4}	10^{-5}	10^{-5}	1.2×10^{-4}	0.24
5 Gross carryover from absorber	0.1	1.0	0.1	0.01	18, 24	10^{-4}	10^{-5}	10^{-5}	1.2×10^{-4}	0.12
6 etc.										etc.

PCV, pressure control valve.

actions taken to effect the restart. One situation which has frequently led to incidents is the restart of agitation in a batch reactor following an interruption of agitation.

A case history caused by restart after a trip has been described by Kletz (1979a). A cumene oxidation reactor was fitted with a high temperature trip for which the trip action was to shut off the air and dump the contents of the reactor into a water tank. A spurious trip occurred, the air valve closed and the dump valve opened. The trip condition cleared itself, the dump valve remained open, but the air valve reopened. Air passed into the reactor, creating a flammable mixture.

13.9.13 Restart after a depressurization

A particular case of restart after a trip is the repressurization of a vessel following emergency depressurization (EDP). The effect of rapid reduction of pressure in a vessel containing a material such as liquefied gas may be to chill the vessel below the transition temperature, thus creating the hazard of brittle fracture. Too prompt a repressurization, before the vessel has warmed up sufficiently, can result in realization of this hazard.

Cases where this has occurred are mentioned by Valk and Sylvester-Evans (1985). Treatment of the problem using a model of blowdown has been described by S.M. Richardson and Saville (1992).

13.9.14 Hazard rate of a single-channel trip system

In the relations for the functional reliability of a single-channel trip given in Section 13.9.3:

$$\eta = \frac{\delta\lambda\tau_p}{2} \qquad [13.9.50]$$

The assumptions made are that $\lambda\tau_p \ll 1$; $\delta\tau_p \ll \eta\tau_p \ll 1$, as stated.

If Equation 13.9.50 is used outside its range of validity, the results obtained can be not only incorrect but also nonsensical. Consider the case where the failure rate is $\lambda = 0.01$ failures/year, the demand rate is $\delta = 3$ demands/year and the proof test interval is $\tau_\rho = 1$ year. Then, Equation 13.9.50 gives for the hazard rate η a value of 0.015 hazards/year, which is actually greater than the failure rate λ.

A treatment is now given for the more general case, based on the work of Lees (1982a) as extended by de Oliveira and Do Amaral Netto (1987). For a single-channel trip, one formulation of the possible states is: (1) trip operational; (2) trip failed but failure undetected and (3) trip failed, failure detected and trip under repair. The corresponding Markov model is:

$$\dot{P}_1(t) = -\lambda P_1(t) + \mu P_3(t) \qquad [13.9.51a]$$

$$\dot{P}_2(t) = \lambda P_1(t) - \delta P_2(t) \qquad [13.9.51b]$$

$$\dot{P}_3(t) = \delta P_2(i) - \mu P_3(t) \qquad [13.9.51c]$$

where P_n is the probability that the trip is in state n.

With the initial condition that the trip is operational, the solution of Equation 13.9.51 is as follows:

$$P_1(t) = \frac{\mu\delta}{r_1 r_2} + \frac{(r_1+\mu+\delta)+\mu\delta}{r_1(r_1-r_2)}\exp(r_1 t) - \frac{r_2(r_2+\mu+\delta)+\mu\delta}{r_2(r_1-r_2)}\exp(r_2 t) \qquad [13.9.52a]$$

$$P_2(t) = \frac{\lambda\mu}{r_1 r_2} + \frac{\lambda(r_1+\mu)}{r_1(r_1-r_2)}\exp(r_1 t) - \frac{\lambda(r_2+\mu)}{r_2(r_1-r_2)}\exp(r_2 t) \qquad [13.9.52b]$$

$$P_3(t) = \frac{\lambda\delta}{r_1 r_2} + \frac{\lambda\delta}{r_1(r_1-r_2)}\exp(r_1 t) - \frac{\lambda\delta}{r_2(r_1-r_2)}\exp(r_2 t) \qquad [13.9.52c]$$

with

$$\gamma_1 = \frac{-(\mu+\lambda+\delta) - [(\lambda+\delta-\mu)^2 - 4\lambda\delta]^{1/2}}{2} \qquad [13.9.53a]$$

$$r_2 = \frac{-(\mu+\lambda+\delta) - [(\lambda+\delta-\mu)^2 - 4\lambda\delta]^{1/2}}{2} \qquad [13.9.53b]$$

Then the FDT and hazard rate obtained from Equations 13.9.52b and 13.9.52c are instantaneous values, and are:

$$\varphi(t) = P_2(t) + P_3(t) \qquad [13.9.54]$$

$$\eta(t) = \delta[P_2(t) + P_3(t)] \qquad [13.9.55]$$

The FDT and the hazard rate given in Equations 13.9.54 and 13.9.55 are functions of time. The average value of the hazard rate over the proof test interval is:

$$\eta = \frac{1}{\tau_p}\int_0^{\tau_p} \eta(t)\mathrm{d}t \qquad [13.9.56]$$

Then, substituting Equation 13.9.55 in Equation 13.9.56 and integrating gives the average hazard rate:

$$\eta = \frac{\lambda\delta(\mu+\delta)}{r_1 r_2} + \frac{\lambda\delta(r_1+\mu+\delta)}{r_1^2\tau_p(r_1-r_2)}[\exp(r_1\tau_p) - 1] - \frac{\lambda\delta(r_2+\mu+\delta)}{r_2^2\tau_p(r_1-r_2)}[\exp(r_2\tau_p) - 1] \qquad [13.9.57]$$

The foregoing treatment is based on the assumptions that the trip is always operational after a proof test is performed and that the test duration is negligible compared with the proof test interval.

Although this model has a high degree of generality, it is based on the assumption that, following detection of a trip failure, the plant continues to operate while the trip is repaired. If in fact the policy is that the plant operation does not continue while the trip is being repaired, different expressions apply. If the state $P_3(t)$ is dropped from the instantaneous hazard rate $\eta(t)$ in Equation 13.9.55 and if the repair rate $\mu = 0$, Equation 13.9.57 for the average hazard rate, then becomes:

$$\eta = \frac{1}{\tau_p}\left\{1 - \frac{1}{\lambda - \delta}[\lambda \exp(-\delta\tau_p) - \delta \exp(-\lambda\tau_p)]\right\} \qquad \lambda \neq \delta \qquad [13.9.58a]$$

$$\eta = \frac{1}{\tau_p}[1 - (1 + \lambda\tau_p)\exp(-\lambda\tau_p)] \qquad \lambda = \delta \qquad [13.9.58b]$$

This case is essentially that considered by Lees (1982a), who used the joint density function method. Two of the relations which he gives, for the failure density function f_η, and the probability ρ_η of realization of the hazard, are also of interest and are

$$f_\eta = \frac{\lambda\delta}{\lambda - \delta}[\exp(-\delta\tau_p) - \exp(-\lambda\tau_p) \qquad \lambda \neq \delta \qquad [13.9.59a]$$

$$f_\eta = \lambda^2\tau_p \exp(-\lambda\tau) \qquad \lambda = \delta \qquad [13.9.59b]$$

and

$$\rho_\eta = 1 - \frac{1}{\lambda - \delta}[\lambda \exp(-\delta\lambda_p) - \delta \exp(-\lambda\tau_p)] \quad \lambda \neq \delta \qquad [13.9.60a]$$

$$\rho_\eta = 1 - (1 + \lambda\tau_p)\exp(1 + \lambda\tau_p) \qquad \lambda = \delta \qquad [13.9.60b]$$

A number of other relations have been given in the literature for situations where Equation 13.9.50 is not valid. An expression given by Kletz and Lawley (Kletz, 1972a; Lawley and Kletz, 1975; Lawley, 1976) is

$$\eta = \lambda[1 - \exp(-\delta\tau_p/2)] \qquad [13.9.61]$$

This is in effect Equation 13.9.19. It may be derived from Equation 13.9.17 together with Equations 13.9.10, 13.9.13 and 13.9.16. It is applicable for small $\lambda\tau_p$ and $\eta\tau_p$, but higher $\delta\tau_p$.

Lawley (1981) has subsequently given the more accurate Equation 13.9.58. The assumptions underlying this equation have just been described.

Wells (1980) has given an expression

$$\eta = \frac{\delta\lambda}{\delta + \lambda} \qquad [13.9.62]$$

as an upper bound on the hazard rate for higher values of $\delta\tau_p$ (>2). This expression is equivalent to taking the FDT as $\varphi = \lambda/(\lambda + \delta)$. De Oliveira and Do Amaral Netto give the relation:

$$\eta = \delta\left\{1 - \frac{1}{\lambda\tau_p}[1 - \exp(-\lambda\tau_p)]\right\} \qquad [13.9.63]$$

for low values of δ but higher values of $\lambda\tau_p$.

Numerical results for some of these expressions have been given by Lees and by de Oliveira and Do Amaral Netto. Table 13.23 shows some comparative results obtained, mainly by the latter workers.

13.9.15 Frequency of events in a trip system

A method of determining for a trip system the frequency of the events of principal interest has been described by Kumamoto, Inoue and Henley (1981). These events are the demand, the functional failure and the operational failure of the trip. The method is implemented in the program PROTECT.

The procedure is to designate each of these events in turn as the top event of a fault tree, to create the fault tree and to determine its cut sets. These cut sets together with the proof test interval for the trip are the inputs used by the model to provide estimates of the frequency of the events mentioned.

The application of this program to determine the expected frequency of these events for an ammonia–air mixing plant as a function of the proof test interval has been described by Kumar, Chidambaram and Gopalan (1989).

13.9.16 Time response of a trip system

The point has already been made that the dependability of a trip system is a function not only of its reliability but also of its capability. An important aspect of capability is the dynamic response. The effect of the dynamic response of the instrument is illustrated in Figure 13.15. It is assumed in the figure that, when a fault occurs, the variable increases linearly from its normal level to the danger level. The nominal trip point is set part way up the ramp, but the trip will not usually occur at the point in time corresponding to this level of the variable. There will normally be delays due to sampling and the dynamic response of the measuring instrument and there may be an instrument error. After the measuring instrument has responded, there will be delays in the safety circuitry and the shut-down valve. There will be a further delay in the process itself, before the effect of the shut-off is felt on the variable measured. All these factors, delays and errors, erode the nominal safety margin and should be considered carefully. The original assumptions concerning the maximum rate of rise of the variable are clearly critical also.

Further reduction of the nominal trip point may be appropriate, but the setting should not be put so low that noise on the variable at its normal level activates the trip. A spurious trip can arise from too low a level of the trip setting as well as from instrument unreliability.

The dynamic response of the complete situation against which the trip system is designed to protect may be modelled using standard methods. An account of unsteady-state modelling of plant is given in *Mathematical Modeling in Chemical Engineering* (Franks, 1967) and the modelling of instrumentation is treated in texts on process control such as those by Harriott (1964) and Coughanowr and Koppel (1965).

Table 13.23 *Some numerical values given by expressions for the average hazard rate of a single-channel trip system (after de Oliveira and Do Amaral Netto, 1987) (Courtesy of Elsevier Science Publishers)*

Parameter			*Equation*[a]				
τ_p (year)	λ (year^{-1})	δ (year^{-1})	13.9.57	13.9.58	13.9.61	13.9.63	13.9.18
0.0192	0.1	0.1	0.958×10^{-4}	0.958×10^{-4}	0.958×10^{-4}	0.958×10^{-4}	0.958×10^{-4}
		1.0	0.954×10^{-3}	0.952×10^{-3}	0.954×10^{-3}	0.958×10^{-3}	0.959×10^{-3}
		10	0.919×10^{-2}	0.900×10^{-2}	0.914×10^{-3}	0.958×10^{-2}	0.959×10^{-2}
	1.0	0.1	0.952×10^{-3}	0.952×10^{-3}	0.958×10^{-3}	0.953×10^{-3}	0.959×10^{-3}
		1.0	0.949×10^{-2}	0.947×10^{-2}	0.954×10^{-2}	0.953×10^{-2}	0.959×10^{-2}
		10	0.913×10^{-1}	0.895×10^{-1}	0.914×10^{-1}	0.953×10^{-1}	0.959×10^{-1}
	10	0.1	0.900×10^{-2}	0.900×10^{-2}	0.958×10^{-2}	0.900×10^{-2}	0.959×10^{-2}
		1.0	0.897×10^{-1}	0.895×10^{-1}	0.954×10^{-1}	0.900×10^{-1}	0.959×10^{-1}
		10	0.864	0.845	0.914	0.900	0.959
1.0	0.1	0.1	0.468×10^{-2}	0.468×10^{-2}	0.488×10^{-2}	0.484×10^{-2}	0.5×10^{-2}
		1.0	0.359×10^{-1}	0.355×10^{-1}	0.393×10^{-1}	0.484×10^{-1}	0.5×10^{-1}
		10	0.916×10^{-1}	0.860×10^{-1}	0.993×10^{-1}	0.484	0.5
	1.0	0.1	0.358×10^{-1}	0.355×10^{-1}	0.488×10^{-1}	0.368×10^{-1}	0.5×10^{-1}
		1.0	0.284	0.264	0.393	0.368	0.50
		10	0.847	0.591	0.993	3.68	5.0
	10	0.1	0.892×10^{-1}	0.860×10^{-1}	0.488	0.900×10^{-1}	0.5
		1.0	0.827	0.591	3.93	0.900	5.0
		10	4.82	1.00	9.93	9.00	50

[a] In equations where μ is used, $\mu = 365$/year.

The following treatment is confined to the dynamic response of the measuring instrument, or sensor. The inputs to a sensor are generally characterized by a set of idealized forcing functions, of which the main types relevant here are (1) the step function, (2) the ramp function and (3) the impulse function. The unit step function changes suddenly at time zero from a value of zero to one of unity. The unit ramp function increases linearly with time and has a slope t. The unit impulse is a function which is infinitely large at time zero and zero elsewhere, but which also has an area which is unity. These three forcing functions are shown in Figure 13.16(a)–(c).

The instrument itself is typically modelled as either a first- or second-order system. Thus, a temperature sensor might be modelled as a first-order system:

$$Mc_p \frac{dT}{dt} = UA(T_i - T) \qquad [13.9.64]$$

where A is the area for heat transfer to the sensor, c_p is the specific heat of the sensor, M is the mass of the sensor, t is time, T is the temperature of the sensor, U is the overall heat transfer coefficient, and the subscript i indicates input, or forcing. Thus, T_i is the temperature of the surrounding fluid.

Equation 13.9.64 may be written in the more general form for a first-order system as:

$$\tau \frac{dT}{dt} = T_i - T \qquad [13.9.65]$$

where

$$\tau = Mc_p/UA \qquad [13.9.66]$$

and τ is a time constant. A lag of the form given by Equation 13.9.65 is known as a 'transfer lag'.

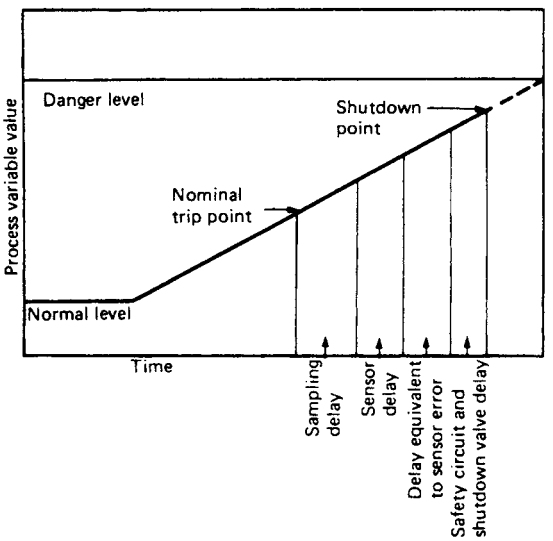


Figure 13.15 *Effect of instrument error and dynamic response on the safety margin in a trip system (after Hensley, 1988) (Courtesy of the Institute of Measurement and Control)*

In this case, the model obtained is a linear one. If the model obtained is non-linear, it needs first to be linearized. A non-linear model is obtained, for example, if the mode of heat transfer to the sensor is radiation rather than conduction.

The normal approach is then to express each term in the linear model as the sum of the steady-state value and of

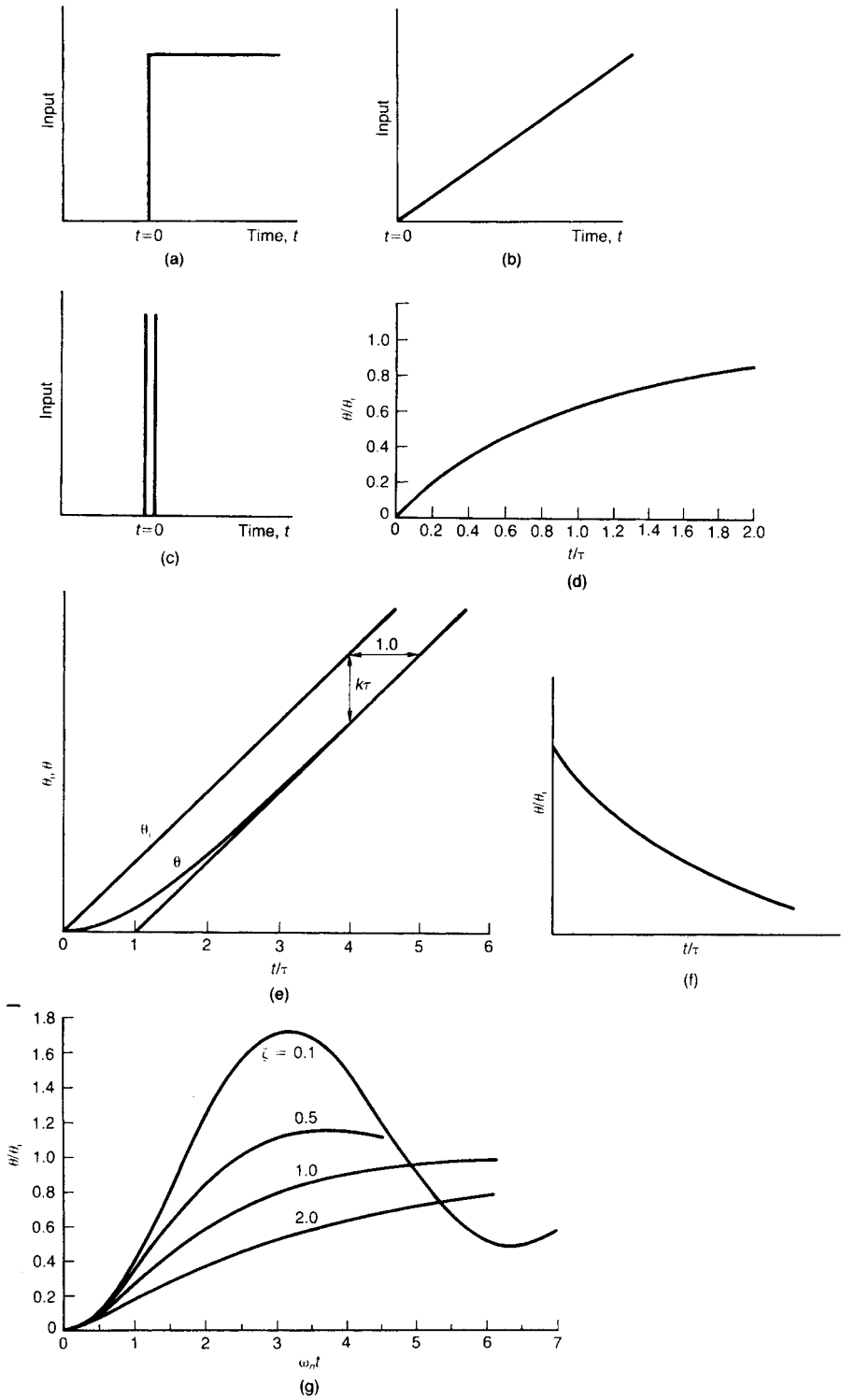


Figure 13.16 *Dynamic response of sensor systems: (a) step forcing function; (b) ramp forcing function; (c) impulse forcing function; (d) response of first-order system to step forcing function; (e) response to first-order system to ramp forcing function; (f) response to first-order system to impulse forcing function; (g) response of second-order system to step forcing function. For second order system: ω_n natural frequency: ζ, damping factor*

a transient component. Equation 13.9.65 then becomes:

$$\tau\frac{\mathrm{d}(T_{ss}+\theta)}{\mathrm{d}t}=(T_{i,ss}+\theta_i)+(T_{ss}+\theta) \quad [13.9.67]$$

The corresponding steady-state equation is:

$$0=\mathrm{T}_{i,ss}-\mathrm{T}_{ss} \quad [13.9.68]$$

Subtracting Equation 13.9.68 from Equation 13.9.67 gives:

$$\tau\frac{\mathrm{d}\theta}{\mathrm{d}t}=\theta_i-\theta \quad [13.9.69]$$

where θ is the transient component of temperature and the subscript ss indicates steady state.

Equation 13.9.69 is then transformed into the Laplace, or s, domain by taking the Laplace transform:

$$s\bar{\theta}-\theta(0)=\bar{\theta}_i-\bar{\theta} \quad [13.9.70]$$

Taking the initial condition as the steady state with zero deviation gives $\theta(0)=0$, and hence the ratio of the output to the input, or the transfer function, is:

$$\frac{\bar{\theta}}{\theta_i}=\frac{1}{1+\tau s} \quad [13.9.71]$$

The response of the first-order system to the three forcing functions is then as follows. For the step response:

$$\theta_i=k \quad [13.9.72]$$

where k is a constant. Taking the Laplace transform of Equation 13.9.72 gives

$$\bar{\theta}_i=\frac{k}{s} \quad [13.9.73]$$

Substituting Equation 13.9.73 in Equation 13.9.71 gives:

$$\bar{\theta}=\frac{k}{(1+\tau s)s} \quad [13.9.74]$$

Inverting the Laplace transformed expression 13.9.74 back into the time domain:

$$\theta=k[1-\exp(-t/\tau)] \quad [13.9.75]$$

Equation 13.9.75 is sometimes written as:

$$\frac{\theta}{\theta_i}=1-\exp(-t/\tau) \quad [13.9.76]$$

Where this is done, it should be noted that θ_i is a constant, defined by Equation 13.9.72, whereas in Equation 13.9.69, it was a variable. For the ramp response, proceeding in the same way:

$$\theta_i=kt, \text{ say} \quad [13.9.77]$$

$$\bar{\theta}_i=\frac{k}{s^2} \quad [13.9.78]$$

$$\bar{\theta}=\frac{k}{(1+\tau s)s^2} \quad [13.9.79]$$

$$\frac{\theta}{\theta_i}=\tau\left\{\frac{t}{\tau}-[1-\exp(-t/\tau)]\right\} \quad [13.9.80]$$

The ramp response has the important property that

$$\frac{\theta}{\theta_i}=t-\tau \qquad t\to\infty \quad [13.9.81]$$

In other words, after an initial transient, the measured value lags the actual value by a time equal to the time constant τ. For the impulse response:

$$\theta_i=k\delta(t), \text{ say} \quad [13.9.82]$$

$$\bar{\theta}_i=k \quad [13.9.83]$$

$$\bar{\theta}=\frac{k}{1+\tau s} \quad [13.9.84]$$

$$\frac{\theta}{\theta_i}=\frac{1}{\tau}\exp(-t/\tau) \quad [13.9.85]$$

where $S(t)$ is the impulse function. The step, ramp and impulse responses of a first-order system are shown in Figure 13.16(d)–(f).

An overdamped second-order system is equivalent to two transfer lags in series. The basic model is therefore

$$\tau_1\frac{\mathrm{d}T_1}{\mathrm{d}t}=T_i-T_1 \quad [13.9.86]$$

$$\tau_2\frac{\mathrm{d}T_2}{\mathrm{d}t}=T_1-T_2 \quad [13.9.87]$$

where subscripts 1 and 2 indicate the first and second stages, respectively. The transfer function of the second-order system is:

$$\frac{\bar{\theta}_2}{\theta_i}=\frac{1}{(1+\tau_1 s)(q+\tau_2 s)} \quad [13.9.88]$$

The step response is:

$$\frac{\theta_2}{\theta_i}=1-\frac{1}{\tau_1-\tau_2}[\tau_1\exp(-t/\tau_1)-\tau_2\exp(-t/\tau_2)] \quad [13.9.89]$$

The impulse response is:

$$\frac{\theta_2}{\theta_i}=\frac{1}{\tau_1-\tau_2}[\exp(-t/\tau_1)-\exp(-t/\tau_2)] \quad [13.9.90]$$

The step response of a second-order system is shown in Figure 13.16(g).

It is sometimes required to provide an unsteady-state model of the sensor for incorporation into an unsteady-state model of the total system. In this case, an equation such as Equation 13.9.65 may be used for a first-order system and a pair of equations such as Equations 13.9.86 and 13.9.87 for a second-order system.

The three forcing functions may be illustrated by the example of a flammable gas cloud at a gas detector. The gas cloud may present to the sensor as any one of these forcing functions. The gas concentration may rise suddenly from zero to a value which then remains constant (step function), it may rise linearly (ramp function) or it may rise momentarily from zero to a high value and then subside as rapidly (approximated by an impulse function).

An account of the time lags which occur in practical trip systems has been given by R. Hill and Kohan (1986), who characterize the dynamic response of a trip by a ramp function similar to that shown in Figure 13.15 and consider in turn the individual time lags. If the total interval from the time when the process starts to deviate to the time when it reaches the danger point exceeds 2 min, there is normally no problem in designing a trip system, but if the interval is less than this, there is a potential problem, and, if it is of the order of seconds, a trip solution may well not be practical.

The signal transmission lags to and from the logic system, and the logic system delay itself is normally negligible, even for pneumatic systems. Exceptions may occur where there are very long pneumatic transmission lines or where the logic is executed on a time-shared device. The more significant lags are likely to be in the sampling and the sensor, in the final control element, and in the process itself. Sampling lags may amount to a dead time of 10–30 s. Transfer lags in sensors vary, with temperature measurement lags often being large due to the thermal inertia of the measuring pocket. The lag at the control valve can vary from a fraction of a second up to several minutes, depending on the valve size. The lag in the process is also highly variable.

13.9.17 Configuration of trip systems

Inspection of Tables 13.17 and 13.19 indicates that the use of parallel redundant, or $1/n$, systems gives an increase in functional reliability, but a decrease in operational reliability compared with a 1/1 system. Better overall reliability characteristics can be obtained by the use of a majority voting system, of which the 2/3 system is the simplest. A comparison of a 2/3 system with a 1/1 system shows that the 2/3 system has a high functional and operational reliability, while a comparison with a 1/2 system shows that the 2/3 system has a slightly lower functional reliability, but a much higher operational one. The 2/2 system is little used for trip systems but has some interesting characteristics. It is effectively a series system which has a rather lower functional reliability than a 1/1 system, but its operational reliability exceeds not only that of the 1/1 but also that of the 2/3 system.

The configuration of trip systems has been discussed by Rushton (1991a,b), who describes a formal approach. According to Rushton, for typical systems, the ranking of trip systems with respect to their functional and operational reliability is invariant and is as shown in Table 13.24. The trip systems most commonly used are the 1/1, 1/2 and 2/3 systems. The requirement for functional reliability is rarely such as to justify a $\frac{1}{3}$ system and that for operational reliability rarely such as to justify a 2/2 or 3/3 system.

Table 13.24 *Ranking of trip system configurations with respect to functional and operational failure (Rushton, 1991b) (Courtesy of the Institution of Chemical Engineers)*

Functional ranking		*Operational ranking*	
$\phi_{m/n}$	*System*	$\gamma_{m/n}$	*System*
Low	1/3	Low	3/3
↓	1/2	↓	2/2
	2/3		2/3
	1/1		1/1
↓	2/2	↓	1/2
High	3/3	High	1/3

The criterion given by Rushton for selection of the trip system configuration is an economic one and is:

$$V = nC + \delta\phi_s H + \gamma_s S + \delta(1 - \phi_s)G \qquad [13.9.91]$$

where C is the annualized cost of a single channel trip, G is the cost of a genuine trip, H is the cost of realization of a hazard, S is the cost of a spurious trip, V is the overall annual cost, and the subscript s indicates the trip system (as opposed to a single channel). The most economic solution is that which minimizes V.

For a genuine trip, there is an element of loss related to the process failure which causes the demand. If, for purposes of comparison, this element (which will occur in all cases) is neglected, the cost of a genuine trip is approximately the same as that of a spurious one ($G = S$), so that Equation 13.9.91 becomes:

$$V = nC + \delta\phi_s H + [\gamma_s + \delta(1 - \phi_s)]S \qquad [13.9.92]$$

If the basic parameters of a particular application are known, namely the demand rate δ, the fail-to-danger and spurious failure rates λ_s and γ_S, the proof test interval τ_p, the repair time τ_r and the costs of hazard realization H and spurious trip S, then a plot of H/C vs S/C gives a map showing the regions where a particular configuration is optimal. The boundaries of the regions are curves of constant V/C.

As an illustration, consider the case given by Rushton where the application is characterized by $\delta = 0.01$ demands/year, $\lambda = 0.2$ failures/year, $\gamma = 0.5$ failures/year, $\tau_p = 1/12$ and $\tau_r = 1/52$. The map giving the optimal configurations for this case is shown in Figure 13.17(a). If δ is increased to 1.0 demands/year, the map becomes that shown in Figure 13.17(b).

Rushton also treats the case where there is an element of common cause failure (CCF) and uses for this the beta method described in Chapter 9. He considers the simplest trip configuration to which such failure applies, the 1/2 system. For such a system:

$$\phi_{1/2} = \frac{[\lambda(1 - \beta_1)\tau_p]^2}{3} + \frac{\beta_1 \lambda \tau_p}{2} \qquad [13.9.93]$$

$$\gamma_{1/2} = 2 \times (1 - \beta_2)\gamma + \beta_2\gamma \qquad [13.9.94a]$$

$$= (2 - \beta_2)\gamma \qquad [13.9.94b]$$

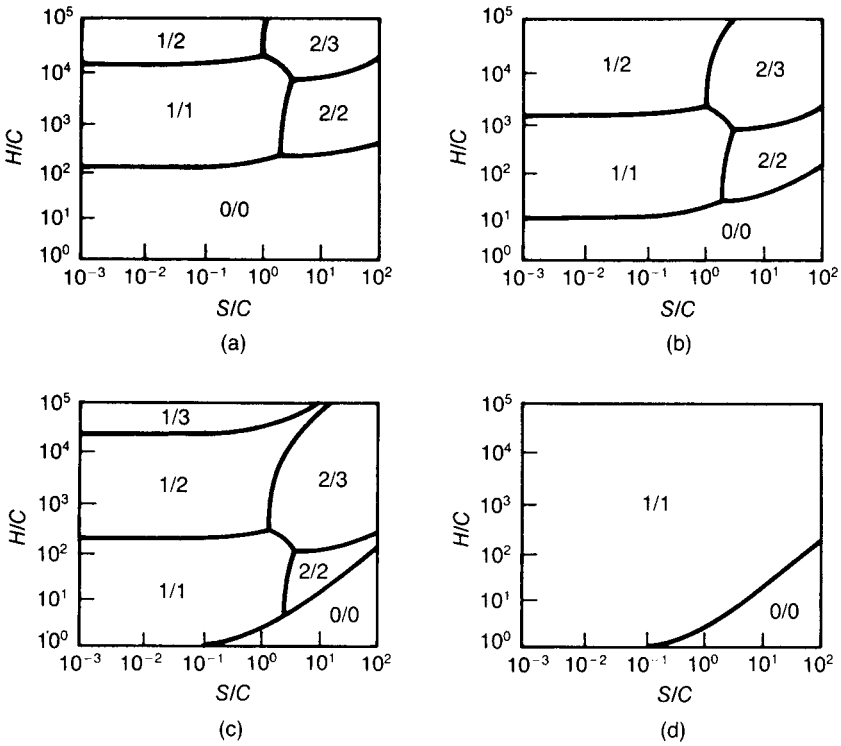


Figure 13.17 *Configuration selection map for trip systems: illustrative examples (Rushton, 1991b): (a) case with $\delta = 0.01$, $\beta = 0$; (b) case with $\delta = 0.1$, $\beta = 0$; (c) case with $\delta = 1$, $\beta = 0.3$ and (d) case with $\delta = 1$, $\beta = 1$. See text for further details (Courtesy of the Institution of Chemical Engineers)*

where β_1 is the fraction of the functional failure rate which is common cause, or the beta value for that failure rate, and β_2 is the operational beta value.

The effect of CCF may be illustrated by considering the extension given by Rushton of his example to the case of a 1/2 trip system where $\delta = 1$ demand/year, $\lambda = 0.2$ failures/year, $\gamma = 0.5$ failures/year, $\tau_p = 1/12$, $\tau_r = 1/52$ and where $\beta_1 = \beta_2 = \beta_3$. Maps of the configuration space for this case are shown in Figure 13.17(c) and (d) for different values of β. Table 13.25 gives expressions for the FDT and spurious trip rate for different trip configurations.

This cost-based approach allows the different trip system configurations to be put on a common basis for purposes of comparison. Where the hazard includes one to human life, there will be a certain level of functional reliability which must be achieved and this should be a factor in the choice of configuration. The approach described may still be applicable with adaptation in judging which configurations are reasonably practicable.

13.9.18 Integration of trip systems

As already described, a trip system is normally dormant and comes to life only when a demand occurs. An element of the trip system such as a sensor or a valve may experience failure and such a failure will lie unrevealed unless detected by proof testing or some other means. By contrast, equivalent elements in a control system are exercised continuously, and failure in such an element is liable to cause an operational excursion of some kind. The failure in this case is a revealed one. Yet the actual physical fault in the two cases may well be identical. A sensor may fail giving a low/zero or high reading, or a valve may jam open or shut. The concept of trip integration, which has been described by Rushton (1992), is based on this contrast between a fault which lies unrevealed in a trip system but is revealed in a measurement and control system. The principle applies to any system which has a protective function. The system is regarded as integrated provided it is regularly exercised, which generally means that it is in use during the normal operation of the plant. As an illustration, Rushton describes a refrigerated storage tank for a toxic liquid, equipped with a cooling system and a pressure relief valve. Both are protective systems, but the cooling system is in more or less continuous use and is thus integrated, whereas the relief valve is not.

In this case the integration is benign, but it can also be malignant. As an example of the latter, the author cites the case of a sensor which is common to both a level control loop and a high level alarm. Failure of the sensor results in failure not only of the control loop but also of the alarm.

It should be an aim of trip system design to convert unrevealed failures into revealed failures, and hence to enhance reliability, by the judicious exploitation of benign integration.

Table 13.25 *Fractional dead times and spurious trip rates for trip systems with simultaneous proof testing and common cause failures accounted for by the beta method (Rushton, 1991b) (Courtesy of the Institution of Chemical Engineers)*

System	$\phi_{m/n}$	$\gamma_{m/n}$
1/1	$\frac{\lambda\tau_p}{2}$	γ
1/2	$\frac{[\lambda\tau_p(1-\beta_1)]^2}{3}+\frac{\beta_1\lambda\tau_p}{2}$	$(2-\beta_2)\gamma$
2/2	$\lambda\tau_p(1-\beta_1/2)$	$2\gamma^2(1-\beta_2)^2\tau_r+\beta_2\gamma$
1/3	$\frac{(\lambda\tau_p)^3}{4}(1-\beta_1)^3+\frac{\beta_1\lambda\tau_p}{2}$	$(3-2\beta_2)\gamma$
2/3	$(\lambda\tau_p)^2(1-\beta_1)^2+\frac{\beta_1\lambda\tau_p}{2}$	$6\gamma^2(1-\beta_2)^2\tau_r+\beta_2\gamma$
3/3	$\frac{\lambda\tau_p}{2}(3-2\beta_1)$	$3\gamma^3(1-\beta_2)^3\tau_r^2+\beta_2\gamma$
m/n	$\binom{n}{r}\frac{[\lambda\tau_p(1-\beta_1)]^r}{r+1}+\frac{\beta_1\lambda\tau_p}{2}$	$n\gamma(1-\beta_2)\binom{n-1}{m-1}[\gamma(1-\beta_2)\tau_r]^{m-1}+\beta_2\gamma$

13.9.19 Maintenance of trip systems

The foregoing account of trip systems has brought out the importance of proof testing. This testing and, more generally, the maintenance of trips needs to be of a high standard if the design reliabilities are to be achieved. Accounts of the testing and maintenance of trip systems have been given by R.M. Stewart (1971), A. Taylor (1981) and Barclay (1988).

The system described by Barclay is broadly as follows. The trips on a plant are covered by a testing schedule which specifies a test interval for each trip system. A common test interval is 12 months, but the interval is established for each trip individually. A change to the test interval, or complete removal of the trip, are governed by formal procedures which involve consultation with the interested parties.

There is a written procedure for the test which details the actions to be taken. This is necessary because the procedure can be quite complex, because the individual performing the test may not be familiar with the particular trip and because in many cases the test is one of the last tasks done prior to a start-up when there may be considerable pressure. This procedure can be changed only after formal consultations.

The test should cover the whole trip from initial to final element. From the point of view of testing, the preferred method is an actual test in which the procedure is to take the process to the trip point and verify the trip action. The alternative is a simulated test which is performed by simulating process conditions using test equipment.

In many cases it is impractical to carry out an actual test. In the case of a hazardous process, the reasons are obvious. But even for a less hazardous process, the number of trips may be such that repeated shut-down and start-up is not practical. On a plant with 30 or 40 trips the equipment may be worn out just by testing.

It can be misleading to rely on a single-point trip as a sufficient test. And particularly where there is complex logic, it is necessary to exercise all the steps in the chain; omission of intermediate steps can be misleading.

Instruments which are part of a trip system are provided with identification, both on circuit diagrams and in the field by a tag. This helps avoid shut-downs caused by work on such instruments.

The trip system is maintained in good condition by preventive maintenance. Equipment is inspected for deterioration. Critical equipment is classified as such and subject to periodic overhaul. It is required that following maintenance work a function check be carried out on the equipment. A trip which is out of service or fails to operate is not tolerated. It is classed as a hazard and action is taken.

At the site described by Barclay, there are some 35,000–40,000 instruments with more than 5000 trips and interlocks. Trip maintenance is handled by a computerized system. The responsibility for testing in this works lies with the operations rather than the mechanical function. Essentially similar considerations apply to the maintenance of interlocks.

13.10 Interlock Systems

Interlocks are another important type of protective device. They are used to control operations which must take place in a specified sequence and equipments which must have specified relations between their states. This definition of an interlock differs from that often used in the American literature, where the term 'interlock' tends to be applied to both trip and interlock systems (as defined here).

Accounts of interlock systems are given in *Applied Symbolic Logic* (E.P. Lynch, 1980) and *Logical Design of Automation Systems* (V.B. Friedman, 1990) and by D. Richmond (1965), E.G. Williams (1965), Becker (1979), Becker and Hill (1979), Kohan (1984) and the CCPS (1993/14).

There are various kinds of interlock The original type is a mechanical device such as a padlock and chain on a hand valve. Another common type is the key interlock. Increasing use is made of software interlocks based on process computers.

Some typical applications of interlocks are in such areas as:

(1) electrical switchgear;
(2) test cubicles;
(3) machinery guards;
(4) vehicle loading;
(5) conveyor systems;
(6) machine start-up and shut-down;
(7) valve systems;
(8) instrument systems;
(9) fire protection systems;
(10) plant maintenance.

An interlock is often used to prevent access as long as an equipment is operating. Thus, electrical switchgear may be installed in a room where an interlock prevents the door opening until there is electrical isolation. Similarly, an interlock prevents access to a test cubicle for operations involving high pressure or explosive materials until safe conditions pertain. An interlock may be used to stop access to a machine or entry into a vessel unless the associated machinery cannot move. In vehicle loading, interlocks are used to prevent a tanker moving away while it is still connected to the discharge point.

Where synchronized operation of equipment is necessary, as in a conveyor system, interlocks are used to ensure this. Interlocks are used for the start-up of machinery to ensure that all the prestart conditions are met, that the correct sequence is followed and that conditions for transition from stage to stage are met. For large rotating machinery, key factors are process conditions and oil pressures.

Pressure relief valves have interlocks to prevent all the valves being shut off simultaneously. There may be interlocks on other critical valve systems. Interlocks are also a part of instrument systems. An interlock may be used to prevent the disarming of a trip system unless certain conditions are met. Fire protection systems are provided with interlocks as a safeguard against leaving the system disabled, particularly after testing or maintenance. Plant maintenance operations make much use of interlocks to prevent valves being opened or machinery started up while work is in progress.

Some features of a good hardware interlock are that it (1) controls operations positively, (2) is incapable of defeat, (3) is simple, robust and inexpensive, (4) is readily and securely attachable to engineering devices and (5) is regularly tested and maintained.

Some interlocks are quite simple, but some interlock systems are quite complex. Such systems are often not confined to interlocks, but incorporate other logic functions. Interlock systems therefore shade over into general logic control systems. In particular, there are some very large interlock systems on boilers and gas turbines.

An especially important type of logic control is the control of sequential operations. Sequential control systems usually have numerous checks which must be satisfied before the next stage is initiated and checks that equipment has obeyed the control signals. These checks constitute a form of interlock.

Since an interlock can bring the process to a halt, it is important to provide adequate status and alarm signals to indicate which feature is responsible for the stoppage. It will be apparent that some interlocks are effectively trips. The distinction between the two is often blurred.

The interlocks described so far are simple rather than high integrity systems, but the latter can, of course, be used, if the situation warrants it. The general approach is similar to that described for trip systems.

13.10.1 Interlock diagrams

As with protective systems so with interlock systems, the design may involve a number of parties and a common language is needed. Unfortunately, this is an area of some difficulty, for three reasons. The description of interlock systems involves the use of several different types of diagram; there appears to be considerable variability in the types of diagram employed and in the nomenclature used to describe them. The symbols for use in these diagrams are given in standards; however, not only are these standards subject to continuous revision, but also the symbols given are often not those in common use. Interlock systems are not well served with textbooks. In particular, there is in electrical engineering a large literature on switching systems, but very little of this addresses process interlock systems as such.

Three types of diagrams commonly used in the design of interlock systems in the process industries are (1) the process flowchart, (2) the logic diagram and (3) the ladder diagram. The last two are sometimes referred to as the 'attached logic diagram' and the 'detached logic diagram', respectively.

The starting point for design of an interlock system is a description of a sequence of operations. A diagram showing this is a process chart. Process chart symbols have been given in *Work Study* (Curie, 1960) and are shown in Table 13.26, Section A.

The logic required to implement this sequence may be shown in a logic diagram. This utilizes standard symbols for functions such as OR, AND and NOT, similar to those used in fault tree work, as described in Chapter 9. Standard symbols for fault trees are given in BS 5760 *Reliability of Systems, Equipment and Components*, Part 7: 1991 *Guide to Fault Tree Analysis*. For some functions, two sets of symbols are given, the preferred and the alternative. It is the latter which is commonly used in the process industries and which is used here. The logic symbols used here are the alternative symbols given in BS 5760 and are shown in Table 13.26, Section B.

The logic diagram may then be converted to a ladder diagram. Standard symbols for protective logic systems are given in BS 3939: 1985 *Graphical Symbols for Electrical Power, Telecommunications and Electronic Diagrams*. The relevant IEC standard is IEC 617 Graphical Symbols for Diagrams. BS 3939: Part 7: 1985 *Switchgear, Controlgear and Protective Devices*, which is identical to IEC 617-7, gives relevant symbols. Other sets of symbols include those given by E.G. Williams (1965) and those of E.P. Lynch (1980). An account of the evolution of logic symbols is given in *An Introduction to the New Logic Symbols* (Kampel, 1986). Table 13.26, Section C, shows a selection of symbols, including those used here, from those given by Lynch.

13.10.2 Some basic systems

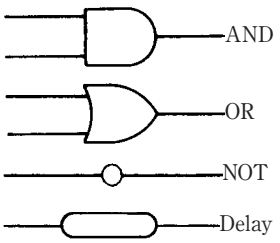
Some of the basic building blocks of interlock systems are illustrated in Figure 13.18. Figure 13.18(a) shows a simple starting circuit. Activation of the circuit occurs if there is a signal due to depression of the start pushbutton AND a signal due to non-depression of the stop pushbutton. Since the signal from the start pushbutton will disappear when it

Table 13.26 *Interlock logic symbols*

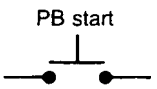
A Work study symbols[a]

Symbol	*Activity*	*Predominant result*
	Operation	Produces accomplishes changes further the process
	Inspection	Verifies quantity or quality
	Transport	Moves or carries
	Delay	Interferes or delays
	Storage	Holds, retains or stores

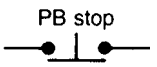
B Logic symbols[b]



C Ladder diagram, symbols[c]

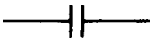


Pushbutton start



Pushbutton stop

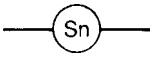
Position, or limit, switch


Relay or solenoid contracts, normally open, closed when relay or solenoid is energized

Relay or solenoid contacts normally closed, opened when relay or solenoid is energized

Motor *n*

Relay *n*



Solenoid *n*

[a] These symbols are given by Currie (1960), who attributes them without reference to the American Society of Mechanical Engineers.
[b] These symbols are given in BS 5670: Part 7: 1991. The alternative symbols for NOT is a common alternative and is that used by E.P. Lynch (1980).
[c] These symbols are those used by E.P. Lynch (1980).

is no longer being depressed by the operator, it is necessary to provide the feedback signal shown, which ensures that there continues to be an output signal. If the stop pushbutton is depressed, the output signal is extinguished.

Figure 13.18(b) shows a time delayed holding circuit. If following activation by the start pushbutton, the signal X does not appear within the time interval specified, the output signal disappears. A typical application of this circuit is start-up of a motor-driven pump which is supplied with lubricating oil by a lube oil pump driven from the same motor. If the lubricating oil pressure signal is still absent after the time interval specified, the pump is shut-down.

Figure 13.18(c) shows a self-extinguishing circuit. Activation of the pushbutton gives an output signal which continues until the time interval specified has elapsed, when the output signal is extinguished. This circuit might typically be used to have a motor-driven equipment run for a period and then shut-down.

13.10.3 Illustrative example: conveyor system

As an illustration of an interlock system, consider the conveyor system described by Lynch. A screw conveyor A feeds material from a car vibrator to an elevator, which discharges to screw conveyor B above two storage bins A and B. There is a slide gate on the pipe between conveyor B and each bin, with a limit switch on each gate. Material is fed from a bin by a star feeder into screw conveyor C. The loading equipment can fill the bins at several times the rate at which it can be withdrawn.

Figure 13.19(a) shows a logic diagram for the interlocks for manual operation of this system. Conveyor B can be started only if either A or B slide gate is open. The elevator can be started only if conveyor B is running. Conveyor A can be started only if the elevator is running. The diagram also shows the simple non-interlocked starting circuit for the car vibrator.

The corresponding ladder diagram is shown in Figure 13.19(b). The diagram shows six circuits A–F. Certain relays occur in more than one circuit, for example, relay Rl in circuits A and D, and it is this which imparts the interlocking feature. Circuit A is the starting circuit for conveyor B. This circuit can be activated only if either relay R2 or R3, the relays for the slide gates limit switches (LS), is closed. If this condition is met, depression of the start pushbutton (PB) energizes relays R1 and M1 and causes R1 to close and Ml to operate a relay in the power circuit. When the stop pushbutton is pressed, the circuit is de-energized and Rl opens.

In circuit B, closure of the slide valve limit switch LSI energizes relay R2 and causes it to close, and opening of the switch causes R2 to open. Circuit C implements a similar relationship between limit switch LS2 and relay R3. Circuit D is the starting circuit for the elevator. The circuit can be activated only if relay R1 is closed. If this condition is met, depression of the start button energizes relays R4 and M2 and causes R4 to close and M2 to operate. Circuit E is the starting circuit for conveyor A, and is similar to circuit D. The circuit can be activated only if relay R4 is closed. Circuit F is a simple starting circuit and is not interlocked.

13.10.4 Illustrative example: reactor system

Another example of a simple interlock system is illustrated in Figures 13.20 and 13.21. Figure 13.20 shows a plant consisting of a water-cooled reactor in which a batch reaction is carried out. The reactor is charged with chemical A and

chemical B is then fed in gradually from a weigh tank as the reaction proceeds. The interlock system is required to cut off the supply of B from the weigh tank if any of the following conditions apply: (1) the shut-off valve V3 on reactor 2 is open; (2) the agitator is not operating; (3) the agitator paddle has fallen off or (4) the reactor temperature has risen above a fixed limit. The loss of the agitator paddle is detected by a current-sensitive relay on the motor.

An interlock system for carrying out these functions is shown in Figure 13.21. The start input opens valve 1, unless valve 3 is open or the agitator is stopped, which conditions inhibit start-up. If these conditions occur later or if the reactor temperature rises or the agitator paddle falls off, valve 1 is closed. The interlock causing the closure is signalled by a status or alarm display. There is a 10 s delay on the reactor high temperature interlock to

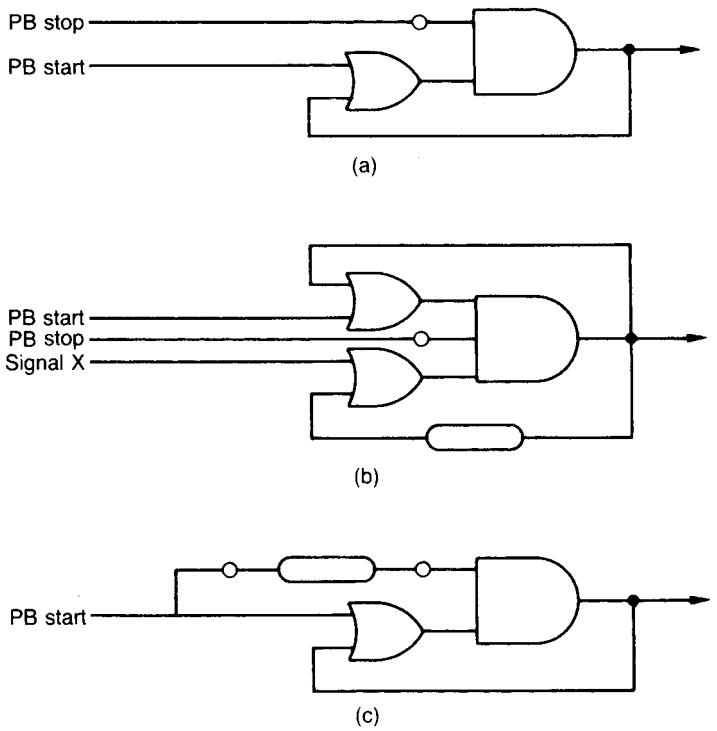


Figure 13.18 *Some basic interlock system logic diagrams: (a) simple starting circuit; (b) time delayed holding circuit and (c) self-extinguishing circuit. PB, pushbutton*

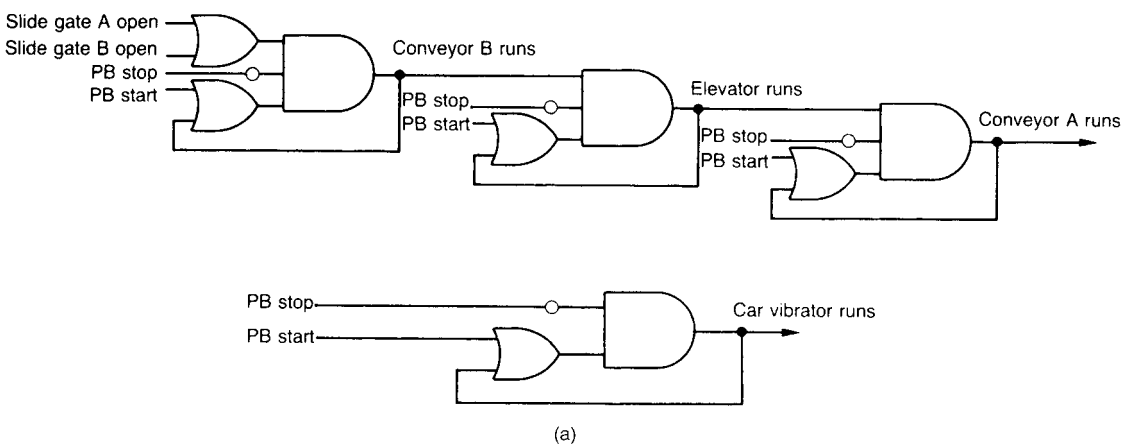


Figure 13.19 *continued*

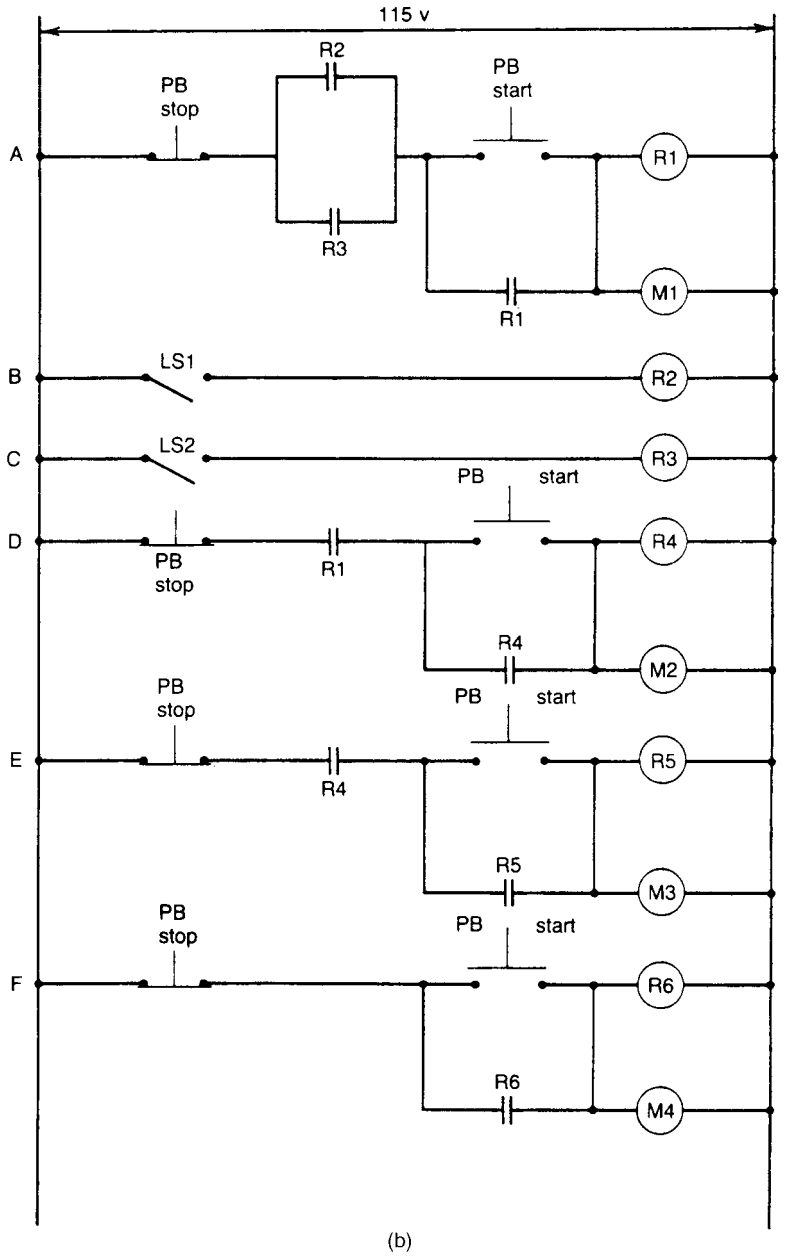


Figure 13.19 *Conveyor interlock system diagrams: (a) logic diagram; and (b) ladder diagram (E.P. Lynch, 1980) (Reproduced with permission from Applied Symbolic Logic by E.P. Lynch, Copyright © , 1980, John Wiley & Sons Inc.)*

allow for noise on that signal. If operation is inhibited by the reactor high temperature or agitator stoppage interlocks, these inhibitions are removed 5 and 10 min, respectively, after the inhibiting condition has disappeared. An account of the reliability of interlock systems is given by R.A. Freeman (1994).

13.11 Programmable Logic Systems

As already indicated, increasing use is made in process control systems of PLCs. An account of the application of PLCs to functions such as pump change over, fire and gas detection and ESD has been given by Margetts (1986a,b). He describes the planning of an operation such as pump

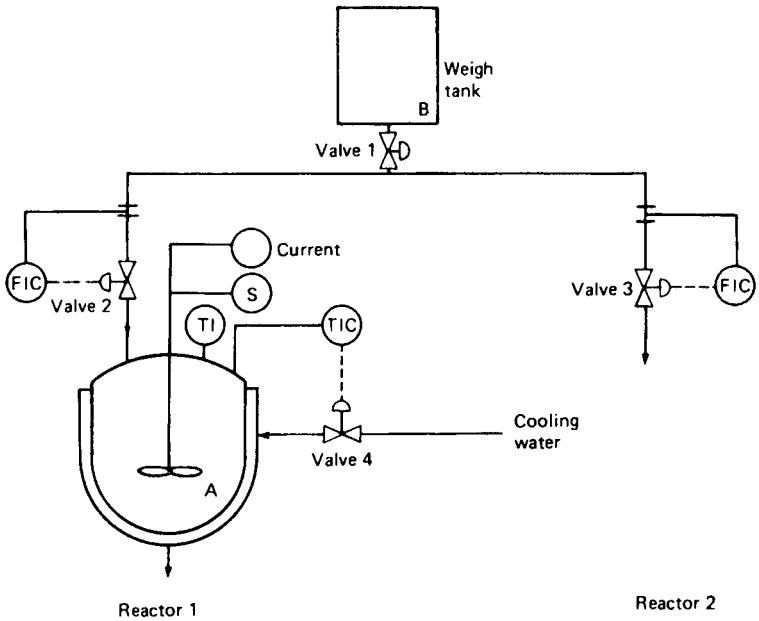


Figure 13.20 *Batch reactor system. FIC, flow indicator controller; S, speed measurement; TI, temperature indicator; TIC, temperature indicator controller*

change over using hierarchical task analysis, in which the change over task is successively redescribed until it has been broken down into executable elements, and the application of the hazard and operability (hazop) method to assess the adequacy of the resultant design.

He also deals with the reliability of the PLC system. For the system which he considers, the MTBFs of the input device, the control logic and the output device are 100,000, 10,000 and 50,000 h, respectively, giving an overall system MTBF of 7690 h. Use of as many as four control logic units in parallel would raise the system MTBF to 14,480 h, but this is not the complete answer. The method described by the author for the further enhancement of reliability is the exploitation of the ability of the PLC to test the input and output devices and also itself.

13.12 Programmable Electronic Systems

Increasingly, the concept of computer control has become subsumed in the broader one of the PES. The account given here is confined to the safety aspects of PESs and is based on the *HSE PES Guide*. The treatment in the *CCPS Safe Automation Guidelines* is discussed in Section 13.15.

13.12.1 HSE PES Guide

An account of PESs and their safety implications is given in *Programmable Electronic Systems in Safety Related Applications* (HSE, 1987b) (the *HSE PES Guide*), of which Part 1 is an *Introductory Guide* (PES 1) and Part 2 the *General Technical Guidelines* (PES 2). The general configuration of a PES is shown in Figure 13.22.

Whereas in a safety-related system the use of conventional hardwired equipment is routine, the use of a PES in such an application has been relatively unknown territory. The approach taken, therefore, has been to assess the level of integrity required in the PES by reference to that obtained with a conventional system based on good practice. This level of integrity is referred to as 'conventional safety integrity'.

PES 2 gives three system elements which should be taken into account in the design and analysis of safety-related systems:

(1) configuration;
(2) reliability;
(3) overall quality.

Safety integrity criteria for the system should be specified which cover all three of these system elements.

13.12.2 Configuration

The configuration of the system should be such as to protect against failures, both random and systematic. The former are associated particularly with hardware and the latter with software. PES 2 lays down three principles which should govern the configuration:

(1) the combined number of PES and non-PES safety-related systems which are capable, independently, of maintaining the plant in a safe condition, or bringing it to a safe state, should not be less than the number of conventional systems which have provided conventional safety integrity;
(2) no failure of a single channel of programmable electronic (PE) hardware should cause a dangerous mode of failure of the total configuration of safety-related systems;
(3) faults within the software associated with a single channel of PE should not cause a dangerous mode of failure of the total configuration of safety-related systems.

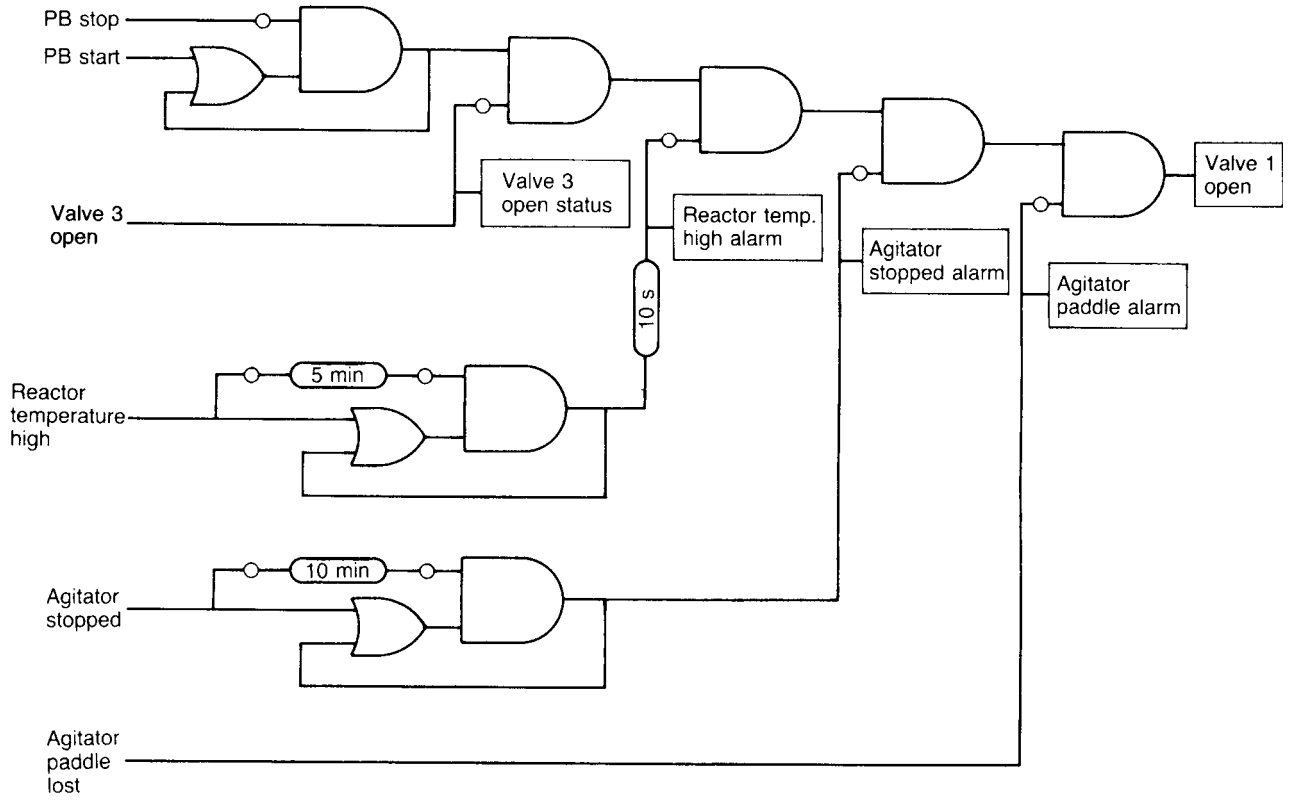


Figure 13.21 *Batch reader interlock system logic diagram*

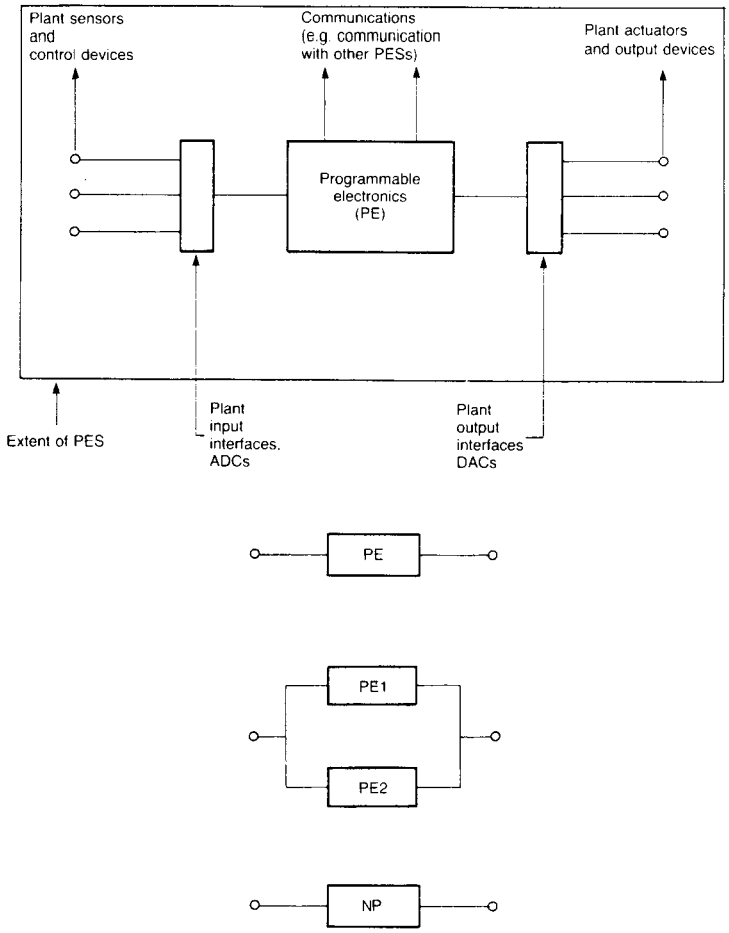


Figure 13.22 *A programmable electronic system (HSE, 1987b). ADC, analogue-to-digital converter; DAC, digital-to-analogue converter; NP, non-programmable hardware; PE, programmable electronics (Courtesy of HM Stationery Office)*

Observance of the second principle may require that, in addition to the single channel of PE hardware, there should be at least one additional means of achieving the required level of safety integrity. Three such means might be:

(1) additional non-programmable hardware;
(2) additional programmable hardware of diverse design;
(3) additional PE hardware of same design.

The latter is applicable only where the design is well established and there is a record of reliable operation in an environment similar to that under consideration.

Observance of the third principle may require that where a single design of software is used, there should be an additional means of achieving safety integrity. Such means may be:

(1) additional software of diverse design;
(2) additional non-programmable hardware.

Diversity of software is required only where:

(1) PES safety-related systems are the sole means of achieving the required level of safety integrity;
(2) faults in the software of a single channel of PE might cause a dangerous mode of failure of the total configuration of safety-related systems.

This strategy is intended to protect against systematic failures and, in particular (a) software errors in the embedded or applications software; (b) differences in the detailed operation of microprocessor and other large-scale integrated circuits from that specified; (c) incompatibility between original and replacement hardware modules and (d) incompatibility of updated or replacement embedded software with original software or hardware.

The extent to which it is necessary to have diversity of software depends on the application. As a minimum, the safety-related function should use diverse applications software. For higher reliability it may be necessary to consider also diverse embedded software. The safety

requirements specification is necessarily a common feature of the diverse software implementations. It is therefore important that it be correct.

PES 2 recognizes that there may exist other ways of providing against failure. In some applications it may be possible to achieve the required level of safety integrity by adopting a formal approach to the software design and testing. Furthermore, for situations where a relatively low level of reliability is acceptable, the use of a single PE channel may be acceptable provided there is extensive self-monitoring of the hardware and automatic safety action on detection of failure.

13.12.3 Reliability

The governing principle for reliability of the hardware is that the overall failure rate in a dangerous mode of failure, or, for a protection system, the probability of failure to operate on demand, should meet the standard of conventional safety integrity. PES 2 specifies three means of meeting this criterion:

(1) a qualitative appraisal of the safety-related systems, using engineering judgement;
(2) a quantified assessment of the safety-related systems;
(3) a quantified assessment of the safety of the plant.

Essentially, the level of reliability should be governed by the conventional safety integrity principle. Where the acceptable level of reliability is relatively low, the first method may suffice, but where a higher reliability is required, the second and third methods will be appropriate.

13.12.4 Overall quality

Whilst the foregoing measures concerning configuration and reliability are a necessary framework, they are not in themselves sufficient. In particular, systematic errors creep in due to deficiencies in features such as the safety requirements specification and software faults. They need, therefore, to be supplemented by the third system element, overall quality. Overall quality is concerned essentially with high quality procedures and engineering. These should cover the quality of the specification, design, construction, testing, commissioning, operation, maintenance and modification of the hardware and software.

In determining the level of overall quality to be aimed for, regard should be paid to the level which would be appropriate for conventional safety integrity and to the level determined for the system elements of configuration and reliability. As a minimum, attention should be paid to (1) the quality of manufacture and (2) the quality of implementation. For overall quality to match a higher level of reliability (3) each procedural and engineering aspect should be reviewed.

Qualitative assessment checklists in support of such a review are included in PES 2 in Appendix 7. Three sets of checklists are given for (1) a control computer, (2) PLC and (3) CCF. The headings of these checklists are (1) safety requirements specification, (2) hardware specification, (3) hardware design, (4) hardware manufacture, (5) hardware test, (6) installation, (7) system test, (8) operations, (9) hardware maintenance and modification, (10) software specification, (11) software design, (12) software coding, (13) software test, (14) embedded software, (15) application programming and (16) software maintenance and modification. The applicable headings are: for a control computer, all except (14)–(15); for a PLC, all except (10)–(13); and for CCF, all.

13.12.5 Design considerations

PES 2 describes a number of design considerations which are particularly relevant to the safety integrity of PESs. The replacement of a control chain in which the sensor sends a signal directly to the actuator by one which involves analogue-to-digital (A/D) converters and PEs may reduce the safety integrity. Unless there is a positive contribution to safety by doing otherwise, the direct route between sensor and actuator should normally be retained. An additional signal may be taken from the sensor with suitable isolation to the PEs.

For the execution of safety functions, it may be necessary to have a shorter sampling interval than is required for normal measurement and control functions.

There should be hardware or software to ensure that on switch-on or on restart after a power failure, the resetting of the system is complete and the point in the program at which entry occurs is a safe one. Interruptions of the power supply should be catered for and should not lead to unidentified or unsafe conditions.

As far as practicable, safety critical functions should be automatically monitored or should be self-checking. The emergency ESD systems should be proof checked at appropriate intervals to discover unrevealed failures.

PES 2 also gives detailed guidance on the environmental aspects of PESs, particularly in respect of electrical interference and of electrostatic sensitive devices.

13.12.6 Software considerations

The software for use in safety-related applications needs to be of high quality and PES 2 gives an account of some of the measures which may be taken to achieve this. These include:

(1) safety requirement specification;
(2) software specification;
(3) software design, coding and test;
(4) system test.

They also include:

(5) software modification procedures.

For all these aspects, there should be

(6) Formal documentation.

PES 2 puts considerable emphasis on the safety requirements specification, as already described. It also devotes a good deal of space to the control of software changes.

A further account of software reliability is given in Section 13.13.

13.12.7 Illustrative example

PES 2 gives as an illustrative example part of the safety integrity assessment of a plant for the manufacture of the explosive pentaerythritol tetranitrate (PETN). Figure 13.23 shows a schematic diagram of one of the nitrators.

A particularly critical parameter is high temperature in the nitrator, the limit being 35°C. For this, protection is provided in the form of a dump valve, which opens to dump the reactor contents to a drowning tank. The conventional control and protection system for such a plant is a control system incorporating some protection features and a single dedicated protection system.

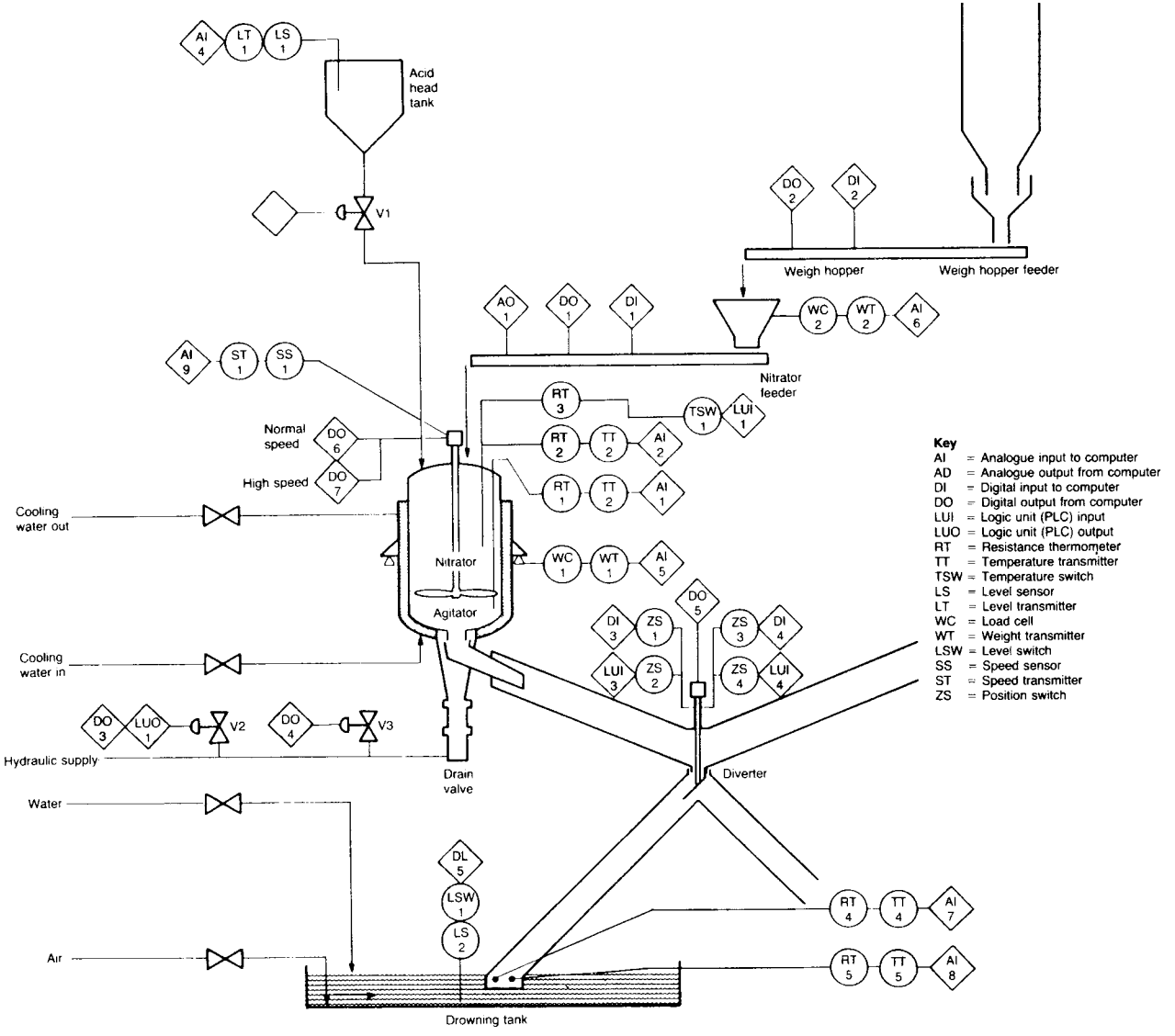


Figure 13.23 *A nitrator unit under control of a PSE (HSE, 1987b) (Courtesy of HM Stationery Office)*

In the design considered, the plant is controlled by a control computer which performs the basic control of the operating sequence. At each stage of the sequence the computer performs checks to ensure that the previous stage is complete and that the plant is in the correct state and ready to proceed to the next stage.

On each of the critical parameters there are duplicate sensors. The signal from one sensor goes to the computer and that from the other to a PLC. The computer and the PLC operate their own relays in the appropriate interlock system. An attempt by the computer to take an action is inhibited if: (1) the PLC relay contact is not closed in agreement with the computer; or (2) the combination of permissives being sent to the computer is correct but indicates that the action is to be inhibited; or (3) the combination of permissives being sent to the computer is incompatible with the inputs to the PLC. The latter occurrence is assessed by the computer. Thus, the control of critical parameters and sequences is by the computer monitored by the PLC, which is in turn monitored by the computer.

For the critical parameter of high temperature in the nitrator, the computer and PLC act in effect as a 1/2 protective system. If either detects a high temperature, it acts to open the dump valve on the reactor.

A hazard analysis of the nitrator system was performed and a fault tree developed for the top event 'Decomposition', as shown in Figure 13.24(a). This event occurs if there is a demand in the form of high temperature and a failure of the top level of protection ('protection fails'). The guide includes the further fault trees for the events C1–C4 and B4–B8.

Figure 13.24(b) shows one of these constituent fault trees, subtree B5 for the event 'no dump signal'. This has several interesting features. The top event in the subtree will occur if both the computer and the PLC fail to send a trip signal. Among the causes for the computer failing to send this trip signal are various combinations of instrument failure, including CCF of all the instruments in one group, for example, resistance thermometers RT1 and RT2. In the tree the failures of RT1 and RT2 are regular random failures, whilst the failure 'CCF of RTs' is the CCF for this group. The separation of the CCF in this way both highlights it as a specific event and assists in assigning to it a numerical value.

Other CCFs occur higher up the subtree just beneath the top event. These are the CCFs of: (1) all three resistance thermometers, RT1 and RT2 on the computer and RTS on the PLC; (2) the hydraulic valves and (3) both the computer and the PLC.

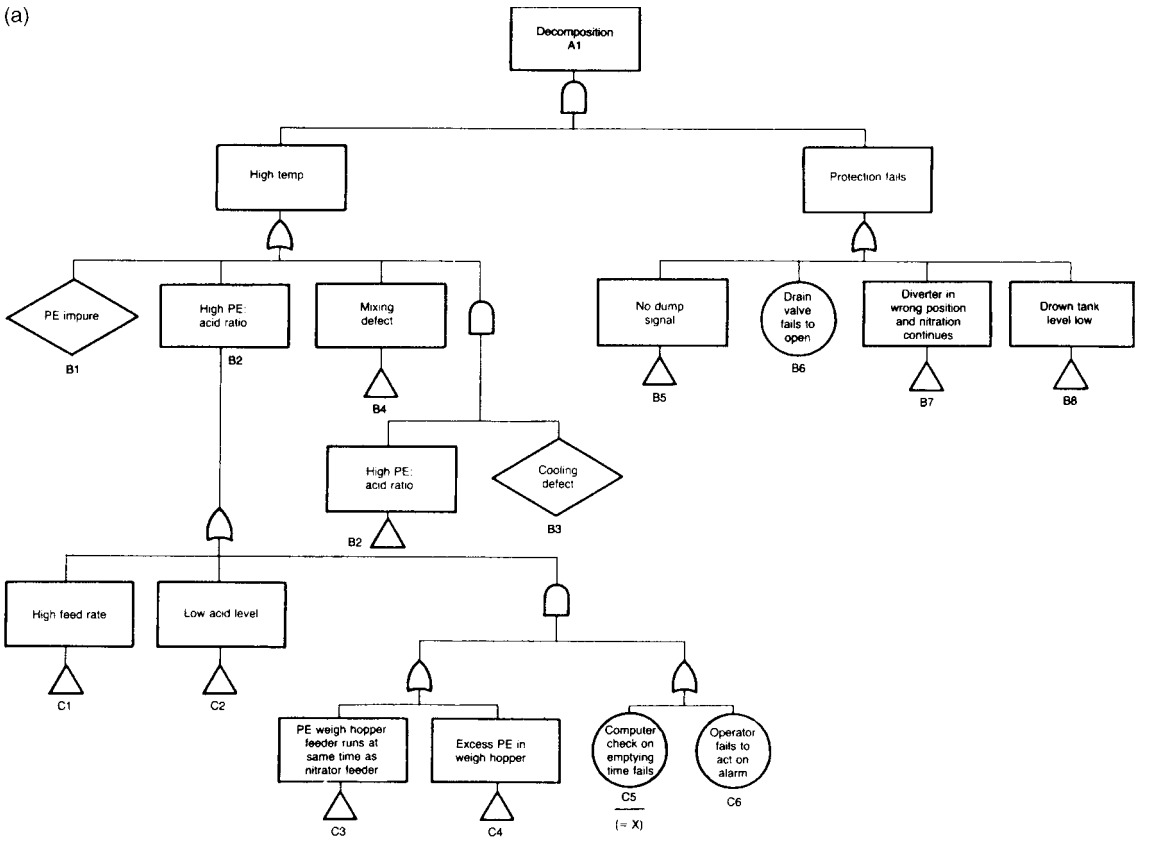


Figure 13.24 *continued*

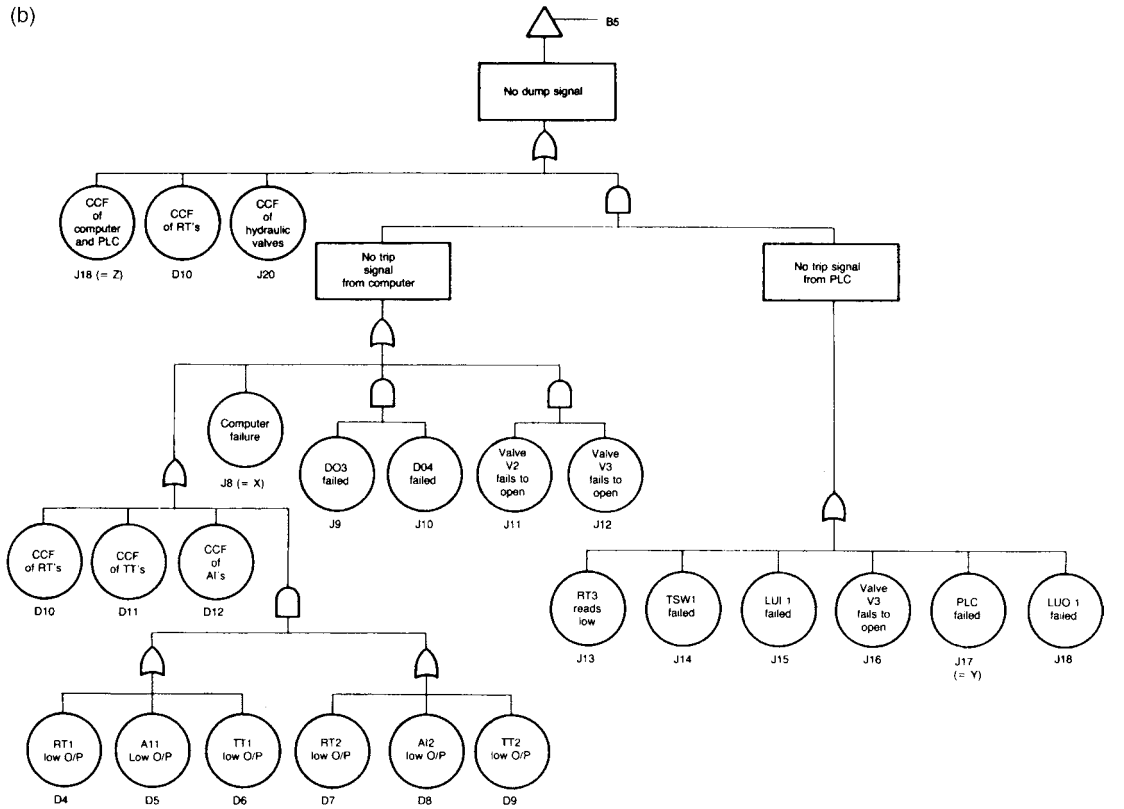


Figure 13.24 *Sections of fault tree for the top event 'Decomposition' for the nitrator unit shown in Figure 13.23 (HSE, 1987b): (a) top section of fault tree; and (b) subtree for event B5 (Courtesy of HM Stationary Office)*

A safety integrity analysis of the system is given in which each of the three system elements (configuration, reliability and overall quality) are examined. For configuration, a check is made against each of the three principles given in Section 13.12.2. In respect of criterion 1, the combined number of PES and non-PES systems is two, as in the conventional system, so this criterion is met. For criterion 2, failure of no single channel, computer or PLC, will cause loss of protection, so criterion 2 is met. For criterion 3, failure of no single set of software, on the computer or on the PLC, will cause loss of protection, so criterion 3 is met.

For reliability, the fault tree is analysed to produce the cutsets and it is shown that the Boolean relation for the top event A1 is:

$$\begin{aligned} A1 = {} & D10 + Z + X(B6 + J13 + J14 + J15 + J16 + J18 + J20 \\ & + L1 + L2 + Y) + Y(D11 + D12) + (B1 + D1 + D2 \\ & + D11 + D12 + HI + H2)(J20 + B6) \end{aligned} \qquad [13.21.1]$$

The frequency of the top event A1 was then estimated by applying data on the frequency of failures and, for protective features, by utilizing Equation 13.9.18 with data on proof test intervals. Table 13.27 shows the numerical values obtained for the events given in Equation 13.12.1. The frequency of the top event was found to be 8.8×10^{-4}/year. This was based on a number of pessimistic assumptions and on this basis was deemed an acceptable frequency.

For overall quality, it was considered necessary to examine not only the quality of manufacture and implementation, but also the procedures and engineering. For this the checklists given in appendix 7 of PES 2 were used and the results obtained for each item in this example are shown in that appendix. This check led to consideration of the following modifications: (1) addition of software limits on programmable alarm and trip levels; and (2) provision of test signal injection and monitoring points, particularly on the resistance thermometers measuring high temperature in the nitrator.

13.13 Software Engineering

The use of various types of computer aid in process plant design and operation is now routine. The dependability of these aids is determined by the quality of the computer programs. The dependability of this software is therefore important and may be critical. This is especially the case in real-time, on-line computer-based systems.

The dependability of software, particularly in SCS, is a major topic in software engineering and is beyond the scope of this book. However, it cannot be neglected, and

Table 13.27 *Some results obtained in the estimation of the hazard rate of the nitrator shown in Figure 13.23 (HSE, 1987b) (Courtesy of HM Stationery Office)*

Event reference	*Event description*	*Failure rate* (failures/10^6 h)	*Test interval*	*Probability of failure on demand*
D10	Common cause failure of resistance thermometers RT1, RT2 and RT3 giving low output	0.06		
Z	Common cause failure of computer and PLC	Not quantified		
X	Failure in a dangerous mode of control computer	7.5		
B6	Drain valve fails to open			3.8×10^{-4}
J13	Failure of resistance thermometer RT3 giving tow output	2.0	1 month	7.3×10^{-4}
J14	Temperature switch TSW1 fails to operate on high temperature	3.4	1 month	1.2×10^{-4}
J15	Logic unit (PLC) input LUI 1 failed; does not respond to TSW1	1.0	1 month	3.7×10^{-4}
J16	Valve V3 fails to open			7.5×10^{-4}
J18	Logic unit (PLC) output LUO 1 failed; does not de-energize	1.0	1 month	3.7×10^{-4}
L1	Drowning tank leaking			Negligible
L2	Drowning tank drain valve opened			1×10^{-3}
Y	PLC failed in dangerous mode	2.5	1 month	9.1×10^{-4}
Σ_1				5.7×10^{-3}
$X \cdot \Sigma_1$		0.042		
Y	PLC failed in dangerous mode	2.5	1 month	9.1×10^{-4}
D11	Common cause failure of temperature transmitters TT1, TT2 giving low output	0.06		
D12	Common cause failure of control computer analogue inputs All and A12 giving low reading	0.03		
Σ_2		0.09		
$Y \cdot \Sigma_2$		8.2×10^{-5}		
B1	PE impure	Not quantified		
D1	Feeder fails at high speed	2.6		
D2	Control computer analogue output A01 fails to high O/P	1.0		
D11	Common cause failure of temperature transmitters TT1, TT2	0.06		
D12	Common cause failure of control computer analogue inputs A11, A12	0.03		
H1	Hydraulic failure of agitator causing high speed	Negligible		
H2	Stirrer breaks from shaft	Negligible		
Σ_3		3.7		
J20	Common cause failure of hydraulic valves V2 and V3	2.3×10^{-6}		
B6	Drain valve fails to open	3.8×10^{-4}		
Σ_4		3.8×10^{-4}		
$\Sigma_3 \cdot \Sigma_4$		1.4×10^{-3}		
Total	$(D10 + Z + X\Sigma_1 + Y\Sigma_2 + \Sigma_3\Sigma_4)$	0.1		

therefore a brief description is given of some of the principal issues of which engineers in the process industries should be aware.

Accounts of software engineering and software reliability are given in *Software Engineering* (Bauer, 1975a), *Software Reliability, Principles and Practice* (Meyers, 1976), *Quality Assurance for Computer Software* (Dunn and Ullman, 1982), *Program Verification Using ADA* (McGettrick, 1982), *Software Engineering* (Shooman, 1983), *Software Defect Removal* (Dunn, 1984), *Program Construction and Verification* (Backhouse, 1986), *Systematic Software Development Using VDM* (C.B. Jones, 1986), *The Spine of Software: Designing Probably Correct Software – Theory and Practice* (Baber, 1987), *Achieving Safety and Reliability with Computer Systems* (Daniels, 1987), *The Craft of Software Engineering* (Macro and Buxton, 1987), *Software Reliability* (Littlewood, 1987b), *Software Reliability* (Musa *et al*., 1987), *Handbook of Software Quality Assurance* (Schulmeyer and MacManus, 1987), *Software Diversity in Computerised Control Systems* (Voges, 1987), *Managing the Software Process* (Humphrey, 1989), *High Integrity Software* (Sennett, 1989), *Software Engineering* (Somerville, 1989), *Case Studies in Systematic Software Development* (C.B. Jones and Shaw, 1990), *Deriving Programs from Specifications* (C. Morgan, 1990), *Software Quality and Reliability* (Ince, 1991a), *Software Engineers Reference Book* (McDermid, 1991), *Developing Safety Systems: A Guide Using ADA* (Pyle, 1991), *Reliability in Instrumentation and Control* (Cluley, 1993) and *Safety Aspects of Computer Control* (P. Bennett, 1993).

13.13.1 Software dependability

The software provided should be dependable in serving the purposes of the system. The dependability of the software has two aspects: (1) specification and (2) reliability. The requirements of the system need to be defined and then converted into a specification. Both the formulation of the requirements and the conversion into a specification are critical features. It is then necessary to ensure that the software conforms with the specification to a high degree of reliability. One of the recurring themes in discussions of software dependability is that reliability alone is not enough. If the specification is defective, the software will be so too, however high its reliability.

13.13.2 Some software problems

There are some persistent problems associated with software. A review of these problems by Bauer (1975b) gives the following tendencies: (1) software is produced in a relatively amateurish and undisciplined way, (2) it is developed in the research environment by tinkering or in industry by a human wave approach, (3) it is unreliable and needs permanent maintenance, (4) it is messy, opaque and difficult to modify or extend and (5) it arrives later, costs more and performs less well than expected.

13.13.3 Software error rates

There are a number of rules-of-thumb used in the software industry for the error rates which occur in programming. An account is given by Cluley (1993). For software, an important distinction is that made between a fault and failure. A fault is an error in the program. A failure occurs when the program is run and produces an incorrect result for software reasons. It is a common occurrence that a program which contains a fault may be run many times before a failure occurs.

A rule-of-thumb widely used in the industry is that a program typically contains 1 fault per 1000 instructions. This is supported by data given by Musa *et al.* (1987) to the effect shown that for programs of some 100,000 lines of source code, when, first operational, the incidence of faults varies between 1.4 and 3.9 faults per 1000 lines. For programs when first written, the number of faults is much higher.

Faults may be corrected, but correction is not always straightforward and the potential exists to introduce other faults. The data of Musa *et al.* indicate that between 1 and 6 new faults are introduced for every 100 faults corrected.

Musa *et al.* also quote data for the number of failures per fault for a single run of a program. The average value of this ratio is 4.2×10^{-7} failures/fault. In other words, this implies that in order to detect a fault by triggering a failure, it is necessary on average to run a program 2.4×10^{-6} times.

In real-time applications of SCS, another metric of concern is the failure intensity, or frequency of failure per unit time, or per mission. For passenger aircraft, an error rate used has been 10^{-9} per mission, where the mission is a flight of 1–10 h.

The progress of a debugging task may be monitored by 'seeding' the program with deliberate errors which are not known to the team engaged in the work. Thus, if 35 faults have been introduced deliberately and 25 genuine and 7 deliberate faults are found, the estimated number of original faults is 125 ($= 25 \times 35/7$).

There exist reliability growth models for software which may be used by management to estimate the time necessary to debug a program. One such model is described by Cluley.

13.13.4 Software management

Management commitment is crucial in achieving dependability in software, as in other fields. Management needs to create a culture which gives priority to, and so ensures, dependability of the software. The management of a software project includes the following aspects:

(1) project management;
(2) software quality assurance (QA);
(3) software standards;
(4) system requirements and software specifications;
(5) software development;
(6) software documentation;
(7) software verification;
(8) software modification control;
(9) software validation and testing;
(10) software maintenance.

Accounts of project management are given by Tsichritzis (1975a) and P.A.V. Hall (1991). The other aspects are considered below.

13.13.5 Software quality assurance

There should by a system of QA for the software. The extent of this system will depend on the scale of the operation, and in some cases will be governed by standards and/or user requirements, but as a minimum, there should be a formal system and an independent QA function. Some of the methods of assuring quality are described below.

13.13.6 Software standards

Use has long been made in software development of the traditional quality standards such as BS 5750 and ISO 9000, but there are an increasing number of standards specific to software. Accounts of developments in these standards are given by P. Bennett (1991a), the CCPS (1993/14) and Rata (1993). In the United Kingdom, standards and guidance include: BS 5887: 1980 *Code of Practice for Testing of Computer-Based Systems*, BS 6238: 1982 *Code of Practice for Performance Monitoring of Computer-based Systems*, BS 5515: 1984 *Code of Practice for Documentation of Computer-based Systems and* BS 6719: 1986 *Guide to Specifying User Requirements for a Computer-based Systems; Programmable Electronic Systems in Safety Related Applications* (HSE, 1987b) (the HSE *PES Guide*); the Ministry of Defence (MoD) Interim Defence Standards 0055: 1989 *Requirements for the Procurement of Safety Critical Software in Defence Equipment* (MoD, 1989c) and 0056: 1989 *Requirements for the Analysis of Safety Critical Hazards* (MoD, 1989b).

Relevant US standards are IEEE 1058-1987 *Software Project Management Plans*, IEEE 1012-1987 *Software Verification and Validation Plans*, IEEE 1028-1988 *Software Reviews and Audits*, IEEE 730-1989 *Software Quality Assurance Plans* and IEEE 1063-1989 *Software User Documentation*, as well as the guides IEEE 830-1984 *Guide to Software Requirement Specifications* and IEEE 1042-1987 *Guide to Software Configuration Management*. An international standard is IEC SC65A WG9: 1991 *Software for Computers in the Application of Industrial Safety-related Systems*.

The *PES Guide* has been described in Section 13.12.

MOD 0055 is in three main sections. The first deals with the project management, the parties involved and the documentation; the second with the software engineering; and

the third relates the requirements of these two sections to the life cycle of the project.

MOD 0056 gives requirements for the hazard analysis of SCS.

There are also two IEC working groups, WG9 and WG1O, which deal with software for safety-related applications and with generic safety aspects, respectively. WG9 is responsible for IEC SG65A.

13.13.7 Software development

The process of software development is generally described broadly in the following terms:

(1) requirements specification;
(2) system specification;
(3) program specification;
(4) program design;
(5) program production;
(6) program verification;
(7) program validation and testing;
(8) system integration and testing.

In software development, two terms that are widely used are 'Verification' and 'Validation' (V&V). Verification is the process of determining whether the product of a given phase of development meets the requirements established in the previous phase. Validation is the process of evaluating software at the end of the software development process to ensure compliance with software requirements.

It is good practice to verify the software produced in each phase of the project before proceeding to the next phase. Another aspect of good practice is the production of good documentation.

One method of software development which is found useful in many cases is prototyping. There is more than one kind of prototype. An account of prototyping is given by Ince (1991b).

13.13.8 Software specification

The conversion of the user's requirements into an unambiguous specification for the system and then for the software is one of the most important, but difficult, tasks in software development. There is a high degree of formality in the approach taken to the specification of the software and a number of formal methods have been developed. An account is given by Webb (1991). Use is made of mathematically based languages such as VDM, Z and OBT and of mathematically based methodologies such as JSD, EPOS and Yourdan Structural Development. For many SCS, such formal methods are a requirement

13.13.9 Software design, production and verification

There are a number of basic principles governing software design. They include (1) modularity and (2) hierarchy.

The computer program required for even a moderately sized project may be large. A large program needs to be subdivided into manageable parts, or modules. Whilst subdivision into modules is necessary, problems arise if the interfaces between modules are poorly defined. The specification of the interfaces between modules requires careful attention. In some applications, it may be possible to exploit the use of verified modules and of a module library.

The program will generally have a hierarchical structure, with the higher level modules controlling the lower level ones. Structured programming involves the use of a hierarchy of conceptual layers and provides a formal approach to the creation of hierarchical software.

As already mentioned, verification of the programs produced at each phase should not be relegated until the end but should be performed before proceeding to the next phase.

13.13.10 Software modification control

A major software project will generally be subject to modifications. Demands to make modifications may occur at any level, starting with the system requirements. There should be a system for the control of such modifications. The ease with which such a system can be created and operated depends very much on the quality of the software design and documentation.

13.13.11 Software reliability

The point has already been made that 'software reliability' is not the same as 'software dependability'. It is nevertheless an essential feature. Accounts of software reliability are given in the quoted texts and by Tsichritzis (1975b). Some aspects of software reliability are:

(1) programming language;
(2) programming practice;
(3) software design;
(4) measurement of reliability;
(5) assessment of reliability.

The programming language used can influence the reliability of the software produced. A number of examples of differences between languages in this respect are given by Tsichritzis.

Likewise, the programming style can affect reliability. One aspect is the naming of items. It is usually recommended that semantic naming be practised in which the name is a meaningful one. Another aspect is the length of sections of the program. Here the recommendation is to keep the verification length short. A practice which tends to increase the verification length is the use of GO TO statements.

One aspect of good design practice which contributes to software reliability is a strong structure. Another is transparency of the programs. A third is well-defined interfaces between modules.

In principle, improvement of reliability depends on the ability to measure it. Traditionally, metrics have been concerned primarily with aspects of performance such as execution time rather than with reliability. Measures for reliability are discussed by Tsichritzis. Software protection contributes to reliability by providing barriers to the transmission of errors between different features of the system.

13.13.12 Software testing and debugging

The traditional way of dealing with errors in a program is testing and debugging. An account of this aspect is given by Poole (1975). Debugging and testing are greatly facilitated if they are planned for in the design phase. Another feature which can make a major contribution is documentation written with this requirement in mind.

Debugging tends to be a difficult task and various aids are available. One is the system dump, activated by a call in, or by catastrophic failure of, the program. Another is the snapshot, similar to a dump, but occurring during execution. The trace mode of program execution causes an output to be made for each statement in the section traced. The traceback facility shows how control reached the point in the program where the error has occurred.

It is helpful to debugging if key quantities in the program are made parameters which the user can alter. This permits a fuller exploration of the program characteristics. Debugging is also assisted by the incorporation of debugging code in the program. The use of such code is discussed by Poole.

Testing is assisted by subdivision of the program into modules. It is not, however, a straightforward matter to devise test beds and test strategies for modules.

13.13.13 Software protection

Software protection may be regarded as an aspect of software reliability. The aim of software protection is to guard against error and malice. There are a variety of items, such as files and programs, which need to be protected and a corresponding variety of means of achieving protection.

Protection establishes barriers to the transmission of an error between one part of the system and another. It therefore contributes to reliability by limiting the effect of an error. Protection contributes to reliability in another way. The occurrence of an error usually results in an attempt to violate a protection barrier. This can be used as a means of error detection.

Closely related to software protection is software security. The aim of software security is to guard against unauthorized use.

13.13.14 Software assessment

There are a number of methods available for the assessment of the software reliability. Accounts of these techniques are given in the texts mentioned and by Tsichritzis (1975b), Fergus *et al.* (1991), Webb (1991) and M.R. Woodward (1991). Three main approaches are:

(1) auditing;
(2) static analysis;
(3) dynamic analysis.

Auditing particularly addresses aspects such as the QA and standards, the comprehensibility and readability of the program, and the documentation.

Static analysis involves analysing the program without running it. Some methods which may be used include:

(1) semantic checking;
(2) control flow analysis;
(3) data use analysis;
(4) information flow analysis;
(5) semantic analysis;
(6) compliance analysis.

The program compiler is generally utilized to perform checks on statements in the program, or semantic checks. The power of this facility depends on the programming language used.

The control flow of the program may be analysed to reveal its structure and to detect undesirable features such as multiple starts, multiple ends, unreachable code, etc. One method of doing this is to represent the program as a graph of nodes joined by arcs, where initially each node represents a statement. A process of reduction is then applied whereby nodes are successively eliminated to reveal the underlying structure.

The data use of the program may be analysed to identify incorrect uses of data such as attempts to read data which are not available or failure to utilize data which have been generated.

The information flow in the program may be analysed to identify the dependence of output variables on input variables.

Semantic analysis determines the mathematical relationship between the input and output variables for each semantically feasible path. It can be used to determine the outputs for the whole input space, including unexpected inputs.

Compliance analysis compares the program with the specification and reveals discrepancies. The specification is expressed as a statement in the predicate calculus of the pre-conditions and post-conditions to be satisfied by the program. For a complex program, assertions may be provided about the functionality of the program for intermediate stages.

Use may also be made of diagrams showing the logic of the program, such as fault trees, event trees, Petri nets, and state transition diagrams, as described by P. Bennett (1991a). The application of fault tree analysis to programs has been developed by Leveson and co-workers (Leveson and Harvey, 1983; Leveson and Stolzy, 1983). Figure 13.25 shows the analysis of an IF . . . THEN . . . ELSE statement by fault tree, Petri net and event tree methods.

Fault trees and event trees are described in Chapter 9, but the Petri net representation requires brief explanation. A Peiri net consists of the quintuple C:

$$C = (P, T, I, O, u) \qquad [13.13.1]$$

where P is a place, T a transition, I an input, O an output and u an initial condition. Initialization of a Petri net is called 'marking' it. A transition is said to 'fire'. Assigning a value is referred to as 'passing' a 'token' to a place.

Software tools have been developed to assist in the static analysis of software. Some of the tools available are described by Fergus *et al.* (1991). They include MALPAS, SPADE and the LDRA testbed. An account of MALPAS, which includes control flow, data use, information flow, semantic and compliance analysers, is given by Webb (1991).

Dynamic analysis, or testing, involves running the program and analysing the results. The basic technique is to force situations where errors are revealed. There are two main approaches. One is 'black box' testing and the other 'white box' testing. The distinction is that the latter relies on knowledge of the structure of the program, whilst the former has no such knowledge but tests the performance against the requirements and relies essentially on knowledge of the application domain. Dynamic testing may be control flow or data flow driven. A discussion is given by M.R. Woodward (1991).

One aim of testing is to remove whole classes of error. A technique for doing this is mutation testing. An account is given by Woodward. The basic concept is to make a small change to the program in the expectation that this will make an observable difference in its performance.

It should be appreciated that good results from a validation test do not necessarily indicate high reliability.

This is so only if the exercise of the control path in the validation test corresponds to that which will occur in practice.

The level of assessment should be matched to the application. This aspect is discussed by P. Bennett (1991a). He lists five classes of assessment:

0 System overview.
1 System structure analysis.
2 System hazard analysis.
3 Rigorous analysis.
4 Formal mathematical methods.

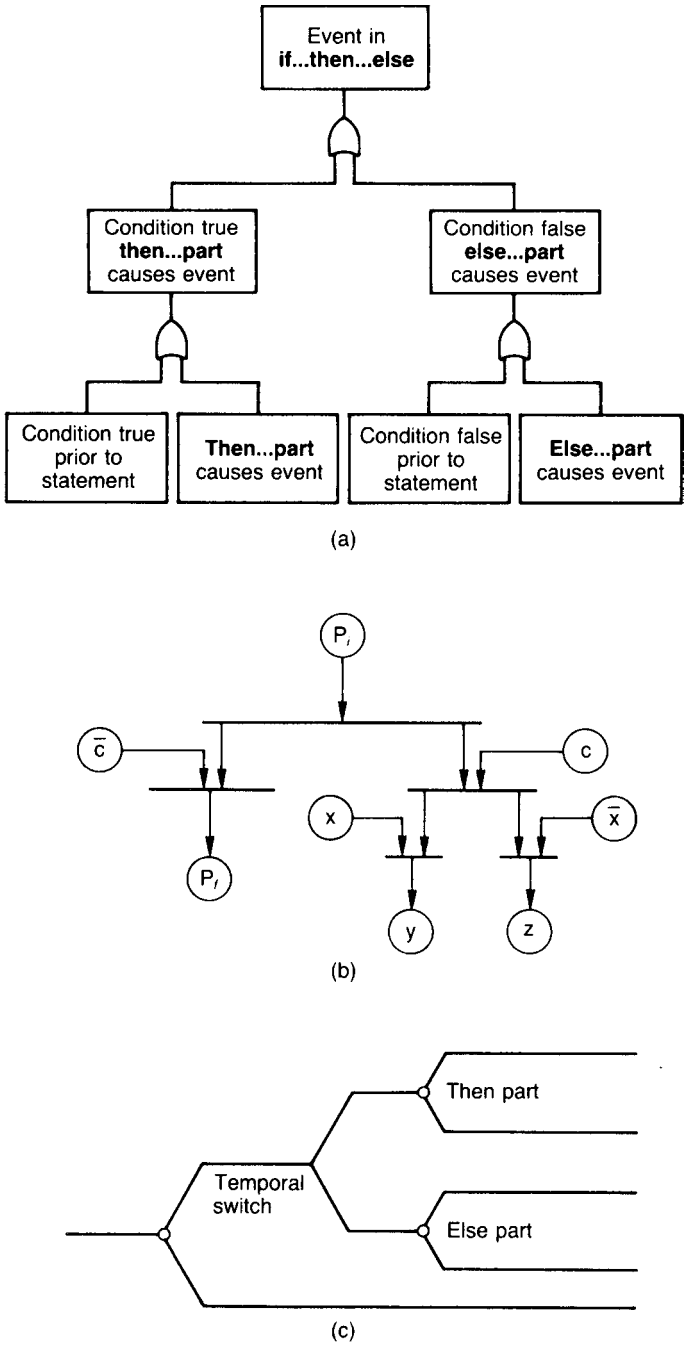


Figure 13.25 *Some representations used in error analysis of an IF... THEN... ELSE statement in a computer program (after P. Bennett, 1991a): (a) fault tree; (b) Petri net and (c) event tree (Courtesy of Butterworth-Heinemann)*

13.13.15 Software correctness

The use of formal methods to prove the correctness of the program has already been mentioned. This is a major area of research. There are differing views as to the feasibility of such proof.

The methods used to prove correctness may be informal or formal. The informal method derives from the work of Naur (1966), Floyd (1967) and London (1968), following von Neumann. Points are selected on all the control paths at which assertions can be made about the variables. Then if

A is an assertion at one point in a control path and B an assertion at the following point, the approach taken is to prove that the code is such that if A is true, B is true. If this verification is performed for all adjacent pairs of assertions and for all control paths, the partial correctness of the program is proved. Proof of complete correctness requires a separate proof of halting. It tends to be a substantial task, however, to develop the assertions and to perform the proofs.

The formal method of proving correctness is based on the demonstration by Floyd (1967) that proof of partial correctness is equivalent to proving corresponding theorems in the first order-predicate calculus. Manna and Pnueli (1969) extended such proof to include halting. The approach taken is to formulate the problem so that it is possible to apply automatic theorem-proving techniques.

13.13.16 Software maintenance

Software generally requires a good deal of maintenance. This is particularly true of safety-related software, especially real-time software. The project management should make suitable provisions for software maintenance. The quality of the software, and the associated documentation, largely determines the ease of maintenance.

13.13.17 Software for real-time systems

Real-time, on-line systems controlling process plants place even more stringent demands on software. An account of the software aspects is given by Fergus *et al.* (1991).

The characteristics of real-time systems have been described by Quirk (1985). In such systems the demands are driven in timing and sequencing by the real world, they may occur in parallel and they may be unexpected and even conflicting. The software must satisfy time constraints and it must continue to operate. Moreover, the software is part of a total system and is difficult to validate in isolation.

Work on the methods of describing the behaviour of real-time systems typically deals with issues such as concurrency and synchronization, resource scheduling, and liveness and deadlock.

The dynamic testing of a real-time program may be carried out using an off-line host machine. Such testing is described by Fergus *et al.*

13.13.18 Safety critical systems

If the consequences of failure of a real-time computer system are sufficiently serious, the system is a SCS. SCSs are of particular concern in the military, aerospace and nuclear fields, but are of growing importance in the process industries.

SCSs are treated in *Safety Aspects of Computer Control* (P. Bennett, 1993). Other accounts are given in the texts cited at the start of this section and by P. Bennett (1991a,b), Bologna (1993), Ehrenberger (1993), Malcolm (1993), McDermid (1993) and Pyle (1993). Standards are particularly important for SCSs. Some relevant standards and guidance are detailed in Section 13.13.6. Practical guidance is available in the *HSE PES Guidelines* and the *CCPS Safe Automation Guidelines*, described in Sections 13.12 and 13.15, respectively.

There are a number of real-time languages and environments which have special safety-related features. One such is ADA. Accounts are given in *Program Verification Using ADA* (McGettrick 1982), *ADA for Specification and Design* (Goldsack, 1985), *ADA in Industry* (Heilbrunner, 1988) *and Developing Safety Systems: A Guide Using ADA* (Pyle, 1991). Pyle (1993) discusses the guidance given in the *HES PSE Guide* in the context of ADA.

Where the process is dependent on a computer or PES, methods are required to identify the associated hazards. The application of hazop to process computers (chazop) is described in Chapter 8.

13.14 Safety-related Instrument Systems

It will be apparent from the foregoing that it is necessary to adopt a systematic approach to the whole system of instrumentation, control and protection.

13.14.1 EEMUA Safety-related Instrument System Guide

A scheme for this is described in *Safety-related Instrument Systems for the Process Industries* by the EEMUA (1989 Publ. 160) (the *EEMUA Safety-related Instrument System Guide*). This document complements the *HSE PES Guide* by proving additional guidance specific to the process industries. The background to, and an account of, the scheme is given by W.S. Black (1989).

The starting point is the practice in conventional systems of separating the protective functions from the control functions. Whereas in such systems control functions may be performed by a PES, it has been almost universal practice to use hardwired systems for protective functions.

13.14.2 Categories of system

Four categories of system are defined:

0 Self-acting devices.
1 Non-self-acting devices.
2 System which protects against damage to environment.
3 System which ensures reliable production and keeps plant operation with operational limits.

These categories are amplified in Table 13.28

13.14.3 Categorization process

Assignment of systems to these categories should be made on the basis of a review, involving consideration of the plant line by line. A schedule should be prepared of all the failures which result in excursions outside normal process operating limits. The process conditions after failure should be determined. Cases where the process conditions are unacceptable with respect to safety should be identified. The option of making a modification to eliminate the unacceptable condition should be considered. If it is decided to rely on the instrument system to prevent the unacceptable condition, the system should be listed together with the potential hazard.

The review may be part of a hazop study or it may be separate. A separate review has the advantage that any rethinking can be done outside the hazop. If a separate review is undertaken, the results should be considered in the hazop.

13.14.4 Selection of systems

In selecting a system for a Category 1, 2 or 3 duty, consideration should be given as to whether the system should be programmable or non-programmable. The IEE classification of programmable systems recognizes three types:

(1) fixed program system;
(2) limited variability system;
(3) full variability system.

Table 13.28 *Categories of control and protective system given in the EEMUA Guide (after EEMUA, 1989) (Courtesy of the Engineering Equipment Manufacturers and Users Association)*

Category	*Type of system*	*Purpose*	*Consequence of failure*	*Requirements*
0[a]	Self-acting device such as PRV, BD, or containment	Safety	Hazard to persons	Relevant BSs
1[b]	Instrument safety system	Safety	Hazards to persons	PES Guide: *EEMUA Guide*
2[c]	Protective system	Economic or environmental	Loss of production or harm to environment	Reliability comparable to conventional analogue systems so that demands on protective devices are limited
3[c]	Control system	Operational	Loss of production and possible demand on category 0, 1, of 2 system	

[a] Where Category 0 devices are installed and their capability and integrity alone are adequate to ensure safety, Category 1 systems will be unnecessary.
[b] Where mechanical devices cannot be used or are not adequate alone to ensure safety, category 1 systems will be necessary.
[c] If programmable systems are used for Category 2 or 3 systems, a full assessment of the system according to the *PES Guide* or the *EEMUA Guide* will be unnecessary.

Table 13.29 *Selection scheme for control and protective systems given in EEMUA Guide (EEMUA, 1989) (Courtesy of the Engineering Equipment Manufacturers and Users Association)*

System	*Self-acting*	*Non-programmable*	*Fixed program*	*Limited variability*	*Full variability*
Ultimate safety, Category 0	Preferred	–	–	–	–
Ultimate safety, Category 1	–	Preferred	Acceptable	Acceptable	Avoid
Protection, Category 2	–	Preferred	Preferred	Acceptable	Avoid
Regulatory, Category 3	–	Acceptable	Acceptable	Preferred	Avoid
Supervisory control	–	–	Avoid	Preferred	Acceptable
Information	–	–	–	Acceptable	Preferred

Examples of these three types are a three-term controller which emulates its analogue equivalent, a PLC and a minicomputer. Table 13.29 gives the selection scheme presented in the *EEMUA Guide*.

13.14.5 Review of systems

Once the systems have been selected, the arrangements should be subjected to a review by a team including process engineers, control engineers and operations managers. It should be established that the requirements given in the *PES Guide* for configuration, reliability and quality are met The *EEMUA Guide* refers to the checklists in the *PES Guide* and gives its own checklists.

13.14.6 Implementation of systems

A Category 0 or 1 system should have the capability and reliability to deal with the foreseeable failure modes and failure frequency of the plant itself and of the Category 2 and 3 systems.

Where a Category 1 system is used, the system should be engineered in accordance with the *PES Guide* and the *EEMUA Guide*. The requirements in these documents relating to hardware, quality and reliability are applicable both to programmable and non-programmable systems. For the latter, however, the requirements relating to software are not applicable.

Failure of a Category 2 or 3 system may put a demand on a Category 0 or 1 system. Where a Category 0 or 1 system is used which is based on a PES, the failure rate should not exceed that of the equivalent conventional system.

13.14.7 Failures in systems

The *EEMUA Guide* gives an account of, and guidance on, the failures which occur in conventional and programmable systems. In conventional systems, a single output failure is usually to the zero or low states. This is the mode of failure on loss of air or power. Systems are designed so that the plant goes to a safe state on this failure mode. In such systems the usual assumption is that multiple failures are in the zero or low mode. This is commonly the basis on which relief capacity is sized.

In programmable systems, a single output failure will be due to failure in an input or output channel. The failure rate to the high state is unlikely to exceed that in a conventional system. There is potential, however, in a programmable system for multiple failures to the high state due to random hardware failure or systematic software failure. An assessment should be made of the system to ensure that the

probability of multiple failure to the high state due to random hardware failure is low.

Failures of software may be failures of system software or of applications software. It is rare for system software to be fault free, although a mature system can be expected to contain fewer faults than a new one. The system software for any control system to be used in a safety-related application should be evaluated. The alternative means given are formal evaluation and user experience.

Failure in the applications software should be minimized by good software engineering. The *EEMUA Guide* gives guidance on software development and testing.

13.14.8 Loop allocation strategies

There are two basic strategies for loop allocation: (1) outputs distributed and (2) outputs grouped. The principles are that, in the first case, the outputs from a single PES unit are distributed around a number of process units, whereas in the second they are concentrated at a single process unit or at least at a minimum number of units.

If the outputs are distributed, loops which may fail simultaneously are not concentrated on the same process unit. The resultant problem at any given unit will therefore be less severe. In particular, this policy allows the pressure relief system to be designed for a single failure on each unit. On the other hand, there may then be a quite large number of process units with some degree of problem. Alternatively, the outputs may be grouped. The problem of multiple failures of loops is then concentrated on one process unit.

The choice between these strategies depends on the characteristics of the process and the probability of multiple failure. A distributed strategy may be suitable for a simple, slow-responding process, but a grouped strategy for a fast-acting process. With a well-designed instrument system, particularly with redundancy, the probability of multiple failure may be small compared with failures of the process unit for other causes.

13.15 CCPS Safe Automation Guidelines

13.15.1 Guidelines for Safe Automation of Chemical Processes

The safety aspects of process control systems are the subject of *Guidelines for Safe Automation of Chemical Processes* (CCPS, 1993/14) (*the CCPS Safe Automation Guidelines*). The *Safe Automation Guidelines* cover the safety aspects of the whole process control system, including the basic process control system (BPCS), the safety interlock system (SIS) and the human operator. Two types of interlock are distinguished: (1) failure interlocks and (2) permissive interlocks. The distinction corresponds to that used here between trips and interlocks proper.

The headings of the *Guidelines* are: (1) overview; (2) the place of automation in chemical plant safety – a design philosophy; (3) techniques for evaluating integrity of process control systems; (4) safety considerations in the selection and design of BPCSs; (5) safety considerations in the selection and design of SISs; (6) administrative controls to ensure control system integrity; (7) an example involving a batch polymerization reactor and (8) the path forward. Appendices deal with SIS technologies, separation of the BPCS and SIS, watchdog timer circuits, communications, sensor fail-safe considerations, SIS equipment selection, PES failure modes and factory acceptance test guidelines.

The *Guidelines* are concerned particularly with PES-based SISs. As described earlier, at least until recently, the normal approach has been to use for the safety interlock (SI) a hardwired system separate from the rest of the control system, whether or not this be computer based. The *Guidelines* describe a design philosophy in which the system of choice for an SIS is a PES-based system. In large part the guidance is concerned with ensuring that a PES-based system has the availability and reliability required for this duty.

This section gives an outline of the *Guidelines*. The latter contain a wealth of practical guidance on the various topics which are touched on here.

13.15.2 Basic design method

The design requirements for the SIS arise out of the process hazard analysis (PHA). The *Guidelines* require that the SIS should be designed by a formal method, but are flexible with respect to the method used. They give a basic design method, which includes what they term a 'qualitative approach to specification' of the SIs required but which allows for the use of alternative quantitative approaches.

The basic design method given in the *Guidelines* is based on the following features:

(1) independent protection layers;
(2) process risk ranking;
(3) SI integrity level specification;
(4) SI integrity level implementation.

This philosophy is outlined in Table 13.30 Section A of the table lists the features which are treated as layers of protection and Section B gives the criteria for a layer or combination of layers to constitute an independent layer of protection (IPL). An IPL protects against a particular type of hazardous event. The event severity and event likelihood are obtained from the process hazard analysis as shown in Section C. The scheme given in Section D indicates the integrity level (IL) required for any SI. There are three integrity levels: Levels 1, 2 and 3 (IL1, IL2 and IL3). As stated in the footnotes, the number of IPLs to be used in the table is the total number of IPLs, including the SI being classified. The implementation of a SIS of specified integrity level is indicated in Section E and an example of the determination of the integrity level of a SI is given in Section F.

13.15.3 Evaluation of control system integrity

The *Guidelines* review the various safety and integrity evaluation techniques applicable to process control systems, including under the qualitative techniques operating experience, standards and codes, design guidelines, checklists, What-If analysis, failure modes and effects analysis (FMEA) and hazop and under the quantitative techniques trip capability analysis, fault tree analysis, event tree analysis, reliability block diagrams, Markov models, Monte Carlo simulation, non-destructive fault insertion testing and QRA.

The BPCS and SIS should both be certified, either by self-certification or third party certification. For PES devices, three maturity levels are recognized: user-approved

Table 13.30 *Basic design philosophy of the safety interlock system in the CCPS safe Automation Guidelines (CCPS, 1993/14) (courtesy of the American Institute of Chemical Engineers)*

A Layers of protection

1. Process design
2. Basic controls, process alarms, operator supervision
3. Critical alarms, opearator supervision and manual intervention
4. Automatic SIS
5. Physical protection (relief devices)
6. Physical protection (containment dikes)
7. Plant emergency response
8. Community emergency response

B Criteria for independent layers of protection

The criteria for a protection layer or a combination of protection layers to qualify as an independent protection layer (IPL) are:

1. The protection provided reduces the indentified risk by large amount that is, at least by a 100-fold reduction
2. The protective function is provided with a high degree of availability – 0.99 or greater
3. The protection has the following characteristics:
   – *Specificity*. An IPL is designed solely to prevent or to mitigate the consequences of one potentially hazardous event (e.g. a runaway reaction, release of toxic material, a loss of containment, or a fire). Multiple causes may lead to the same hazardous event and therefore multiple event scenarios may initiate action of one IPL
   – *Independence*. An IPL is indepentent of the other protection layers associated with the identified danger
   – *Dependability*. It can be counted on to do what it was designed to do. Both random and systematic failure modes are addressed in the design
   – *Auditability*. It is designed to facilitate regular validation of the protective functions. Functional testing and maitenance of the safety system is necessary

C Process risk ranking

An event is assigned a severity and a likelihood:

Event severity	
Minor incident	Impact initially limited to local area of the event with potential for broader consequences if corrective action is not taken.
Serious incident	One that could cause: – any serious injury or fatality on-site or off-site – property damage of $1 million off-site or $5 million on-site
Extensive incident	One that is five more times worse than a serious incident
Event likelihood	
Low	A failure or series of failures with a very low probability of occurrence within the expected lifetime of the plant ($<10^{-4}$failures/year). Exambles: (1) three or more simultaneous instrument, valve or human failures; (2) spontaneous failure of single tanks or process vessels
Moderate	A failure or series of failures with a very low probability of occurrence within the expected lifetime of the plant (10^{-4} to 10^{-2} failures/year). Examples: (1) dual instrument failures; (2) combination of instrument failures and operator errors; (3) single failures of small process lines or fittings
High	A failure can reasonably be expected to occur within the expected lifetime of the plant ($>10^{-2}$ failures/year). Examples: (1) process leaks; (2) single instrument or valve failures; (3) human errors that could result in material releases

The event is designated low risk for any of the following combinations: (1) severity low, likelihood low; (2) severity serious, likelihood low; (3) severity low, likelihood moderate. It is designated high risk for any of the following combinations (1) severity extensive, likelihood high; (2) severity serious, likelihood high; (3) severity extensive.Likelihood moderate. It is designated moderate risk for the other three combinations.

D Safety interlock integrity level specification[a]

	Event severity								
	Minor			*Serious*			*Extensive*		
Event likelihood	Low	Moderate	High	Low	Moderate	High	Low	Moderate	High
No. of IPLs[b]3	(5)	(5)	(5)	(5)	(5)	(5)	(5)	1	1
2	(5)	(5)	1	(5)	1	2	1	2	3 (2)
1	1	1	3	1	2	3 (2)	3 (2)	3 (2)	3 (1)

[a] The values in the table without brackets refer to the integrity level (IL) required; the values in brackets refer to the number of the note given below.
[b] Total number of IPLs, including the safety interlock being classified.

Table 13.30 *(continued)*

Notes:
1. One Level 3 safety interlock does not provide sufficient risk reduction at this risk level. Additional PHA modifications are required.
2. One Level 3 safety interlock may not provide sufficient risk reduction at this risk level. Additional PHA review is required.
3. Event likelihood – likelihood that the hazardous event occurs without any of the IPLs in service (i.e. the frequency of demand).
4. Event likelihood and total number of IPLs are defined as part of the PHA team work.
5. SIS IPL is probably not needed.

Integrity level availability

	Availability (%)
Level 1	about 99
Level 2	99–99.9
Level 3	up to 99.9–99.99

E Safety interlock integrity level implementation

Integrity level (IL)	*Minimum interlock design structure*
1	Non-redundant: best single path design
2	Partially redundant: redundant independent paths for elements with lower availability
3	Totally redundant: redundant, independent paths for total interlock system. Diversity should be considered and used where appropriate. A single fault of an SIS component is highly unlikely to result in a loss of process protection

F Illustrative example

Event severity	Extensive
Event likelihood without benefit of either IPL	Moderate
Total number of IPLs (non-SIS IPL + SIS interlock)	2
Required SIS interlock integrity level	2

(for BPCS), user-approved safety (UAS) (for SIS) and user-obsolete. The *Guidelines* give criteria for user approvals.

13.15.4 Basic process control system

The BPCS is not usually an IPL. It is, nevertheless, the next line of defence after the process design and has an important part to play. The *Guidelines* therefore deal with the safety considerations in the selection and design of the BPCS. The account given covers (1) the technology selection, (2) the signals, (3) the field measurements, (4) the final control elements, (5) the process controllers, (6) the operator/control interfaces, (7) communication considerations, (8) electrical power distribution systems, (9) control system grounding, (10) batch control, (11) software design and data structures and (12) advanced computer control strategies, and contain much practical material on these features.

The *Guidelines* advise that use of a supervisory computer should be subject to a discipline which restricts it to manipulation of loop set points. It should not normally be able to change the operational mode of the loops except for transfer to the back-up mode on computer failure or to computer mode on initialization. It should not compromise the integrity of the back-up controls.

The design philosophy of the *Guidelines* requires that the BPCS and the SIS should be separate systems. The BPCS should not be relied on to protect against unsafe process conditions. The integrity of the SIS should not be compromised by the BPCS. Appendix B of the *Guidelines* gives detailed guidance on separation.

13.15.5 Safety interlock system

As far as safety considerations in the selection and design of the SIS are concerned, the *Guidelines* cover (1) the design issues, (2) the requirements analysis, (3) the technology selection, (4) the architecture selection, (5) the equipment selection and (6) the system design. The necessary preliminaries are to determine the need for SIs and to establish their integrity levels.

Design issues

Design issues are of two main kinds: function and integrity. Issues concerning function include the parameters to be monitored, the trip actions to be taken, the testing facilities and policy. Among those bearing on integrity are the number of integrity levels required, which affects the choice of technology.

Some specific design issues addressed in the *Guidelines* are (1) the fail-safe characteristics, (2) logic structures, (3) fault prevention and mitigation, (4) separation of the BPCS and SIS, (5) diversity, (6) software considerations, (7) diagnostics, (8) the human/machine interface and (9) communications.

The fail-safe issue involves the choices de-energize-to-trip vs energize-to-trip. There is also the question of the failures modes of PES-based devices. Even at the chip level, probable states are equally likely to be on or off. The problem is even more severe at the level of a PES-based device. Effectively, the *Guidelines* suggest alternative approaches based on the use of equipment of proven reliability, capable of self-diagnosis and of proof-testing, with judicious use of redundancy.

There should be a separation between the SIS and BPCS such as to ensure the integrity of the former. Conventional SISs have long utilized separate sensors and power supplies. The *Guidelines* also bring into consideration the input/output system, the software and the human/machine interface.

Diagnostics may be used to detect fail-to-danger failures in the SI equipment including the sensor, the logic solvers, the final control elements and the energy sources. The *Guidelines* distinguish between passive and active diagnostics. In passive diagnostics, the failure is revealed only when a demand is imposed, either by the system or by a user test. In active diagnostics, the device is subjected continuously to testing by input of out-of-range conditions and its response monitored, but over a time interval short enough not to upset the SI loop. The example quoted is the perturbation of a solenoid valve on a control valve with sufficient rapidity that the control valve is not affected.

Requirements analysis
The requirements analysis determines the targets for availability and reliability (or functional and operational reliability).

Technology selection
The SIS technologies given in the *Guidelines* include: (1) fluid logic (pneumatic, hydraulic); (2) electrical logic, including direct-wired systems, electromechanical devices (relays, timers), solid state relays, solid state logic and motor-drive timers; (3) PES technology, involving PLCs and distributed control systems (DCSs) and (4) hybrid systems. The technologies are detailed in appendix A of the *Guidelines*.

The hardware of a typical SIS as envisaged in the *Guidelines* might consist of a logic solver with input modules receiving sensor signals, output modules sending out signals to final control elements, a BPCS interface, a human/machine interface and an engineer's interface.

Architecture selection
Under architecture selection, the *Guidelines* discuss the various ways of achieving an integrity appropriate for the integrity level determined. Thus, for IL1, redundancy is usually not necessary, though it may be appropriate for a lower reliability element. For IL3, on the other hand, there should be full redundancy. Other features mentioned for IL3 are use of analogue sensors so that active diagnostics can be practised, monitoring of the logic solver outputs by the BPCS and consideration of the use of diversity in the sensors. For both high availability and high reliability, use may be made of a triple modular redundant (TMR) system, or $\frac{2}{3}$ voting system.

Equipment selection
The equipment selected for a PES-based SIS should be of user-approved safety.

System design
The basic design method for the SIS has already been described, but the design involves more than this. The design should allow for the special features of PES-based systems. One of these, the difficulty of determining fail-safe states, has already been mentioned. Another feature is false 'turn-ons' of inputs or outputs.

Another problem in PES-based systems is that the life of a given version of the software is relatively short so that the version initially used is liable to become out of date and, after a time, no longer supported by the vendor. The problem then arises that insertion of an updated version constitutes a software modification, with all that that entails. There are various approaches to the problem, none entirely satisfactory.

The design should take into account the potential impacts of the SIS on the other components of the process control system, including the alarm system, the communications system and the human/machine interfaces.

Most process control systems involve some sequential control even if it is largely limited to start-up and shut-down. The sequential logic should operate in such a way as not to cause any safety problems. Its operation should be tested against the SI logic to ensure that normal operation of the sequential control does not trigger interlock action.

The documentation for the SIS specified in the *Guidelines* includes (1) the operational description, (2) the schematic diagrams, (3) the binary logic diagrams and (4) the single line diagrams. Examples are given of these different types of diagrams.

13.15.6 Administrative actions

In order to ensure the control system integrity, the design process just described needs to be supported by administrative actions The *Guidelines* outline minimum procedural requirements, the scope of which includes (1) operating procedures, (2) maintenance facilities, (3) testing of the BPCS, (4) testing of the SIS and alarms, (5) test frequency requirements, (6) testing facilities, (7) operations training, (8) documentation and (9) auditing of maintenance and documentation.

The test frequency indicated in the *Guidelines* for SIS functional testing is, for minimal risk systems, testing once every 2 years or at major turnarounds, whichever is more frequent, and for high risk systems, testing at least once a year or on major maintenance, whichever is more frequent.

13.16 Emergency Shut-down Systems

In quite a large proportion of cases, the plant is provided not just with individual trips but with a complete automatic emergency shut-down (BSD) system. There is relatively little written about BSD systems. One of the principal accounts is that given in *Offshore Installations: Guidance on Design and Construction, Guidance Notes to the Offshore Installations (Construction and Use) Regulations 1974* issued by the Department of Energy (1984) followed now by *Offshore Installations: Guidance on Design, Construction and Certification* (HSE, 1990b) (the HSE *Design, Construction and Certification Guidance Notes*).

13.16.1 Conceptual design of ESD

The function of an ESD system is to detect a condition or event sufficiently hazardous or undesirable as to require shut-down and then to effect transition to a safe state. The potential hazards are determined by a method of hazard identification such as hazop. Estimates are then made of the frequency and consequences of these hazards. The hazards against which the ESD system is to protect are then defined.

This protection is effected by identifying the operating parameters which must be kept within limits if realization of the hazards is to be avoided and selecting shut-down actions which will achieve this. A shut-down sequence is determined and the shut-down logic formulated. It is not always necessary to shut-down the whole plant and there are different levels of ESD which fall short of this, such as shut-down of an individual unit or of a section of plant.

13.16.2 Initiation of ESD

The arrangements for initiation of the ESD are critical. If these are defective, so that the system is not activated when it should be, all the rest of the design goes for nothing. There is a balance to be struck between the functional and operational reliability of the ESD system. It should act when a hazard arises, but should not cause unnecessary shut-downs or other hazards.

One factor which affects this balance is the fact that usually the plant is safest in the normal operating mode and that transitions such as shut-down and start-up tend to be rather more prone to hazards and are to be avoided unless really necessary. Another, related factor is that shut-down of one plant may impose shut-down on other, linked plants.

Initiation may be manual, automatic or, more usually, both. The usual arrangement is a manual initiation point, or shut-down button, in the control centre, other manual initiation points located strategically throughout the plant and initiation by instrumentation. Such automatic initiation may be effected by the fire and gas system and/or by process instruments. Measures should be taken to avoid inadvertent activation, including activation during maintenance and testing.

13.16.3 Action on ESD

There are a variety of actions which an ESD system may take. Three principal types are:

(1) flow shut-off;
(2) energy reduction;
(3) material transfer.

Flow shut-off includes shut-off of feed and other flows. It often involves shut-down of machinery and may include isolation of units. Energy reduction covers shut-off of heat input and initiation of additional cooling. Material transfer refers to pressure reduction, venting and blow-down.

A fundamental principle in ESD is failure to a safe state. The overall aim is failure to a safe state for the system as a whole. This is normally effected by applying the principle to individual units, but there may be exceptions, and cases should be considered individually. Each required action of the ESD system should be effected by positive means. Reliance should not be placed on the cascading effect of other trip actions.

13.16.4 Detail design of ESD system

It is a fundamental principle that protective systems be independent of the rest of the instrument and control system, and this applies equally to an ESD system. The design of the ESD system should follow the principles which apply to trip systems generally, as described in Section 13.9. There should be a balance between functional and operational reliability. Dependent failures should be considered. The reliability may be assessed using fault tree and other methods. The techniques of diversity and redundancy should be used as appropriate. Use may be made of majority voting systems.

The emergency shut-down valves (ESVs) should have a high degree of integrity. Such valves are frequently provided with pneumatic or hydraulic power supplies in addition to electrical power supply. An ESV should be located so that it is unlikely to be disabled by the type of incident against which it is intended to protect.

The ESD system should be provided with power supplies which have a high degree of integrity. The normal approach is to provide a UPS. This supply should be designed and located so that it is unlikely to be disabled by the incident itself. The cables from the power supply to the final shut-down elements should be routed and protected to avoid damage by the incident.

13.16.5 Operation of ESD system

The status of the ESD system should be clear at all times. There should be a separate display showing this status in the control centre. This display should give the status of any part of the EDS system which is under test or maintenance and of any part which is disarmed. Initiation of ESD should activate audible and visual alarms in the control centre. There should be an indication of the source of the initiation, whether manual or instrument. BSD should also be signalled by an alarm which is part of the general alarm system.

It may be necessary in certain situations such as start-up, changeover or maintenance to disarm at least part of the BSD system, but such disarming should be governed by formal arrangements. The principles are essentially similar to those which apply to trip systems generally, as described in Section 13.9.

13.16.6 Testing and maintenance of ESD system

The ESD system should be subject to periodic proof testing and such testing should be governed by a formal system. The principles of proof testing were discussed in Section 13.9. As far as is practical, the test should cover the complete system from initiation to shut-down condition.

The need for proof testing and, more generally, for the detection of unrevealed failure should be taken into account in the design. The equipment should be designed for ease of testing. It should be segregated and clearly identified. Techniques for detection of instrument malfunction should be exploited. In voting systems, the failure of a single channel should be signalled.

13.16.7 Documentation of an ESD system

The ESD system should be fully documented. *The HSE Design, Construction and Certification Guidance Notes* give details of recommended documentation.

13.16.8 ESD of a gas terminal

The design of systems for ESD and EDP of a gas terminal has been described by Valk and Sylvester-Evans (1985). The design philosophy described is that the ESD system should operate only in an extreme emergency, that the ESD and EDP systems are separate from the control, trip and relief systems, and that the systems should be simple and reliable.

The preliminary design of the ESD and EDP systems was reviewed by means of a hazop study. Potential operational failures were studied using general reliability engineering methods and functional failures were studied using, in particular, fault tree analysis. A further hazop was conducted on the final design for the ESD and EDP system.

Design studies showed that a totally fail-safe concept would result in a relief and flare system of exceptional size. Alternatives considered were to allow an increase in the depressurization time for certain critical equipment beyond that recommended in the codes and to control the peak

depressurization flow in the relief and flare system. In the design adopted, the plant was divided into sections such that the depressurization of each section could be done independently and the operation of the sections was interlocked. The depressurization time of certain items was extended to 30 min as opposed to the 15 min recommended in API 521, but the design compensated for this extension by provision of additional fireproofing and water cooling arrangements.

The authors highlight the differences of philosophy between companies on whether the ESD and EDP systems should be used for normal shut-down and depressurization or reserved as systems dedicated for emergency use. This project reaffirmed the need to consider the ESD and EDP systems at an early stage and to avoid treating them as an 'add-on' feature to be dealt with late in the design.

13.16.9 ESD on Piper Alpha

The ESD system on Piper Alpha illustrates a number of the points just made. Overall, the system was largely effective in achieving shut-down and venting and blow-down, but there were a number of features which are of interest.

The main button for the initiation of the ESD caused closure of the ESV on the main oil pipeline but not on the three gas pipelines. One reason for this was that closure of these latter ESVs would impose a forced shut-down on the linked platforms. There were three separate shut-down buttons, one for each of these valves, and shut-down depended on manual action by the control room operator – he was thrown across the control room by the explosion.

The ESVs on the risers of the gas pipelines were so located that they were vulnerable to the fires that developed. This defect was widespread throughout the North Sea and regulations were introduced without delay to require such valves to be relocated. There was also evidence that some of the ESVs did not achieve tight shut-off. The explosion damaged power supplies, and in some cases closure of ESVs occurred, not due to survival of the intended power supply, but fortuitously. Further details are given in Appendix 19.

13.17 Level of Automation

The allocation of function between man and machine is a principal theme in human factors and is discussed in the next chapter. Of particular interest here is the allocation of control and protective functions to the process operator or the instrument system. This was touched on above and is now considered in more detail by means of a industrial example.

13.17.1 Illustrative example: steam boiler protective system

A case study of the optimum level of automation has been described by Hunns (1981). The system investigated was the protective system of a large steam plant. The plant consisted of a 100 MW boiler operating at 1500–2000 psi and producing 500 ton/h of steam, the boiler being dual fired with oil and gas. The principal relevant features of the three candidate control and protective systems are shown in Table 13.31.

Each system was assessed for its reliability in the start-up and operational phases of the plant. A variety of start-up sequences were considered, each related to the event which had caused the previous shut-down. Some 200 logic diagrams were produced.

The criterion used to determine the optimum system was a function of the expected shut-downs. These were classified as low penalty and high penalty. Low penalty shut-downs were unwanted shut-downs due to spurious trips and correct shut-downs in response to a demand, whilst high penalty, or catastrophic, shut-downs were those caused by a demand to which the protective system did not respond.

One such case is an excessive release of unignited fuel into the combustion chamber. Figure 13.26 shows a section of the logic, which the authors term 'matrix logic'. Events envisaged by the analyst are shown in the left-hand column. A particular event sequence is shown by a vertical column of the matrix containing one or more dots. The circle enclosing the '&' symbol at the head of the column indicates that the events are ANDed together. The set of event sequences is collected under the OR symbol, which indicates that these event sequences are related to the top event, the unignited release, by OR logic.

The equipment failure data were taken from the Safety and Reliability Directorate SYREL data bank, whilst the human error estimates were obtained by expert judgement. There were some 180 elements in the latter list. Estimates of the values in the list were made by two experienced analysts. Use was made of performance shaping factors such as 'time to react','prior expectancy','conspicuity of task'and 'perception of consequence'. Good agreement was obtained between the two. Those estimates which were particularly critical or where a divergence had emerged were mediated by a third, independent, analyst.

The results of the study were expressed in terms of the number of low and high penalty shut-downs per year and the corresponding mean outage time. The mean outage of

Table 13.31 *Elements of three candidate protective systems for a large steam boiler plant (after Hunns, 1981) (Courtesy of Elsevier Science Publishers)*

Control and protective features	*Protective system design*[a]		
	Manual	*Medium automated*	*Higly automated*
Trip parameters[b]	A	A	A
Boiler purge sequence	M	A	A
Burner flame failure detection	M	A	A
Gas valves leak test	M	M	A
Ignition burner control	M	M	A
Burner fuel valves operation	M	A	A

[a] A, automated; M, manual.
[b] Low boiler drum level; low combustion air flow; low instrument air pressure; low level fuel oil pressure; low atomizing steam pressure; low fuel gas pressurel; high fuel gas pressure; high knockout drum level; and loss of 110 DC supplies.

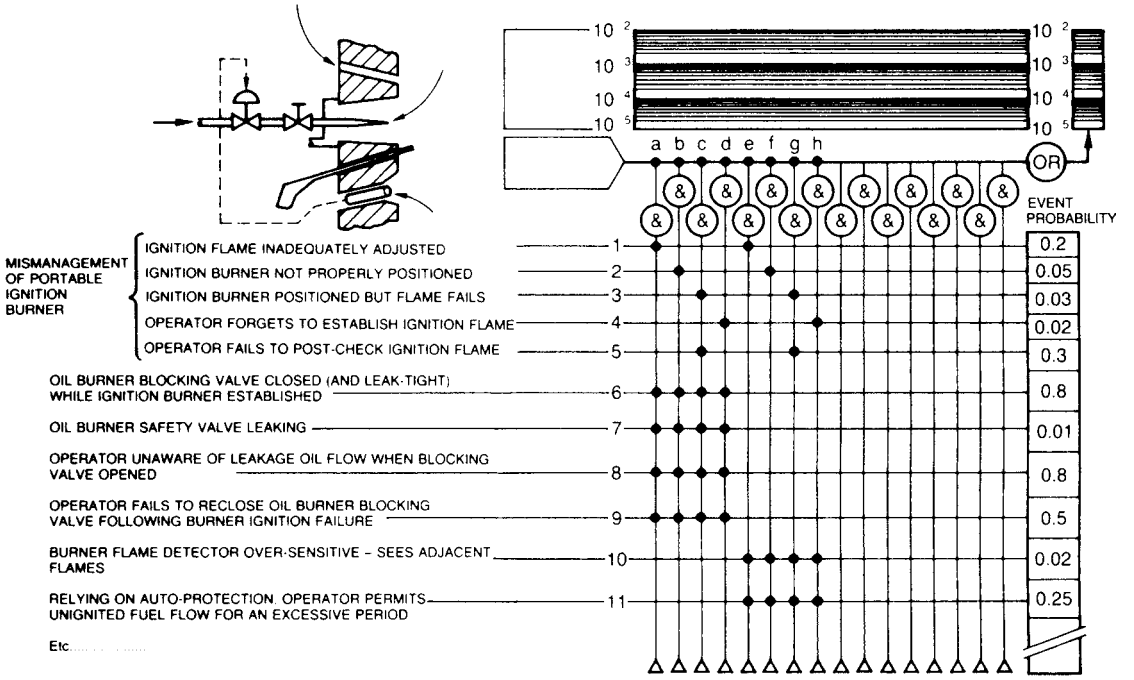


Figure 13.26 *Matrix logic diagram for a steam boiler protective system: event 'excessive unignited fuel release' (Hunns, 1981) (Courtesy of Elsevier Science Publishers)*

low penalty events was taken as 1/3 days/event and that of high penalty events as 60 days/event. The manual system gave appreciably more high penalty shut-downs but fewer low penalty ones and overall a higher outage than the other two systems. The medium automated system gave slightly more high penalty shut-downs and fewer low penalty ones than the highly automated one, but the same outage time. On a life cycle cost basis, for which the highly automated system had higher capital and maintenance costs, the medium automated system was superior. The total life cycle costs of the three systems – manual, medium automated and highly automated – were £0.122, 0.095 and 0.099 million/year, respectively.

13.18 Toxic Storage Instrumentation

On plants handling high toxic hazard materials (HTHMs), the instrumentation and control system assumes particular importance. Some relevant considerations are outlined in *Guidelines for Safe Storage and Handling of High Toxic Hazard Materials* by the CCPS (1988/2) (the CCPS HTHM Guide).

Depending on the degree of hazard, the instrumentation and control system should be a high integrity one. This requires adherence to the various principles already described for high integrity design, including the application of principles such as fail-safe and second chance design and the use, as appropriate, of high reliability instrumentation, instrument diversity and redundancy, and high quality maintenance. It also involves the application of the techniques of hazard identification and assessment to the design.

In respect of measurement, principal considerations are that the potential for release from the instrument, or its fittings, should be minimized, that the instrument be reliable and that the measurement be accurate. For flow measurement this favours the use of non-invasive sensors such as magnetic flowmeters and avoidance of glass in instruments such as rotameters. Orifice flowmeters also have the disadvantage of an extra flange and associated piping. For pressure measurement, diaphragm pressure sensors are preferred to direct-connected gauges of the Bourdon tube type. Precautions to be taken where the latter have to be used include protection by inert liquid filling in corrosive service and installation of shut-off valves and, possibly, flow limiters in the form of restriction orifices. For level measurement, weighing methods have advantages, but use of sightglasses should be avoided. For temperature measurement, particular care should be taken in the design of the thermowell, which can be a weak point.

The arrangements for control and protection should address the hazards of particular importance for the storage of tonics. These include (1) overpressure, (2) overfilling, (3) overtemperature and (4) high release flow. For overpressure, the main requirements are the provision of overpressure protection and of means of disposal for the relief flows. For overfilling, a significant role is likely to be played by trip systems. For temperature deviations, which may indicate reaction runaway or thermal stratification with its attendant risk of rollover, the need is for warning. Some methods of dealing with overtemperature are described below. High releases flow following a failure of containment may be mitigated by the use of suitable control valve trims and of restrictor orifices or excess flow valves.

Storage of a reactive chemical requires close control in respect both of temperature and of contamination. Methods of temperature control include the use of cooling coils, a reflux condenser, a quench system and short stop arrangement. All these methods of temperature control require for their effective functioning good mixing in the tank.

A toxic gas detection system should be provided, on the lines described in Chapter 18. Toxic gas detectors should also be installed on vents on which breakthrough of a toxic gas may occur. The sensors should have a range adequate for this duty. Instrumentation may also be required to ensure that the pilot burner remains lit on any flare which has the function of destroying by combustion any toxic gas routed to it.

13.19 Notation

Section 13.6

P_d delivery pressure
P_s suction pressure
ΔP pressure drop
Q gas flow

Section 13.9

f_η density function for a plant hazard occurring
m number of equipments which must survive for trip system to survive
n number of identical equipments
P_η probability of a plant hazard occurring
r number of equipments which must fail for trip system to fail
t time
γ spurious trip rate
δ plant demand rate
η plant hazard rate
λ equipment failure rate
τ_p proof test interval
τ_r repair time
ϕ fractional dead time (with simultaneous testing)

Subsections 13.9.1–13.9.13

p_δ probability of a plant demand occurring
q probability of a single channel failing
q_γ probability defined by Equation 13.9.37
τ_d disarmed time
τ_0 dead time
ϕ^* fractional dead time (with staggered testing)
ϕ_{is} isolation dead time

Subscripts

m/n for an m/n (m-out-of-n) system
min minimum

Subsection 13.9.14

P_n probability that system is in state n
r_1, r_z terms defined by Equation 13.9.53

Subsection 13.9.16

A heat transfer area of sensor
c_p specific heat of sensor
k constant
M mass of sensor
s Laplace operator
t time
T temperature
T_i input temperature
U overall heat transfer coefficient of sensor
$\delta(t)$ delta function
ζ damping factor
ϕ temperature division
ϕ_i input temperature deviation
I time constant of sensor
ω_n natural frequency

Subscripts

i input
ss steady-state
1,2 first, second stage

Superscripts

– Laplace transform

Subsection 13.9.17

C annualized cost of a single channel trip
G cost of genuine trip
H cost of realization of hazard
S cost of spurious trip
V overall annual cost
β_1 functional beta value
β_2 operational beta value

Subscripts

s trip system
1/2 1/2 system

14 Human Factors and Human Error

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14.23 Assessment of Human Error 14/53
14.24 Assessment of Human Error: Task Analytic Approach 14/53
14.25 Assessment of Human Error: Process Operation 14/54
14.26 Assessment of Human Error: Qualitative Methods 14/57
14.27 Assessment of Human Error: *Human Reliability Analysis Handbook* 14/59
14.28 Assessment of Human Error: Success Likelihood Index Method (SLIM) 14/73
14.29 Assessment of Human Error: Human Error Assessment and Reduction Technique (HEART) 14/74
14.30 Assessment of Human Error: Method of Dougherty and Fragola 14/74
14.31 Assessment of Human Error: CCPS Method 14/80
14.32 Assessment of Human Error: Other Methods 14/80
14.33 Assessment of Human Error: Performance Shaping Factors 14/82
14.34 Assessment of Human Error: Human Error Data 14/84
14.35 Assessment of Human Error: SRD Human Error Guides 14/87
14.36 Assessment of Human Error: Benchmark Exercise 14/87
14.37 Assessment of Human Error: ACSNI *Study Group Report* 14/88
14.38 CCPS *Human Error Prevention Guidelines* 14/90
14.39 Human Factors at Sizewell B 14/91
14.40 Notation 14/92

It is appropriate at this point to deal with the topic of human factors, and one important aspect of that, human error. Human factors considerations are relevant to all aspects of the design and operation of process plants. The topic is, however, a vast one and the account given here is necessarily limited. The approach taken is to consider in particular the process operator and then to touch on certain other aspects such as communications, maintenance and construction.

Overviews of human factors are given in *Biotechnology* (Fogel, 1963), *Human Factors Engineering* (McCormick, 1957b), *Human Engineering Guide to Equipment Design* (C.T. Morgan *et al.*, 1963), *Human Engineering Guide for Equipment Designers* (Woodson and Conover, 1964), *Human Factors Evaluation in System Development* (Meister and Rabideau, 1965), *Ergonomics* (Murrell, 1965a), *Human Performance in Industry* (Murrell, 1965b), *Human Factors* (Meister, 1971), *Handbook of Human Factors* (Salvendy, 1987), *Applied Ergonomics Handbook* (Burke, 1992 ACGIH/76) and *Human Factors in Design and Engineering* (Sanders, 1993). Accounts of human factors with specific reference to safety are given in *Ergonomics Guides* (AIHA, 1970–/1), *Human Aspects of Safety* (Singleton, 1976b) and *Human Factors in Process Operations* (Mill, 1992). HSE guidance is given in HS(G) 48 *Human Factors in Industrial Safety* (HSE, 1989).

Selected references on human factors are given in Table 14.1 and references on the process operator are given in Table 14.2.

Table 14.1 *Selected references on human factors*

IOHSI (Inf. Sht 15); NRC (Appendix 28 *Human Factors*); Chapanis, Garner and Morgan (1949); Grossman (1956); McCormick (1957, 1976); Institute of Personnel Management (1961); Bennett, Degan and Spiegel (1963); Fogel (1963); C.T. Morgan *et al.* (1963); E. Edwards (1964, 1973); Woodson and Conover (1964); Chapanis (1965); Meister and Rabideau (1965); Murrell (1965a,b); Edholm (1967); Sackman (1967, 1970); Singleton, Easterby and Whitfield (1967); Kelley (1968); Hands (1969); Hurst (1969); Ragsdale (1969); Siegel and Wolf (1969); Bongard (1970); De Greene (1970, 1974); Meister (1971, 1987); Poulton (1971); Sayers (1971 SRS/GR/9); Singleton, Fox and Whitfield (1971); E. Edwards (1973); E. Edwards and Lees (1973, 1974); R.G. Mills and Hatfield (1974); Christensen (1976); Singleton (1976a,b); Towill (1976); Welford (1976); S. Brown and Martin (1977); Jennings and Chiles (1977); Rouse and Gopher (1977); Craig (1978); Jagacinski and Miller (1978); Stammers (1978); V.R. Hunt (1979); Kiguchi and Sheridan (1979); Anon. (1980i); Shackel (1980); McCormick and Sanders (1982); M.S. Sanders (1982–, 1993); J.C. Williams (1982); S. Cox and Cox (1984); Helmreich (1984); Nordic Liaison Committee (1986 NKA/LTT(85)1); L.E. Davis and Wacker (1987); Goldstein (1987); Lehner and Zirk (1987); Parasuraman (1987); Salvendy (1987); Sanders and McCormick (1987); Swain (1987c); de Vries-Griever and Meijman (1987); Wiener (1987); Woodson (1987); Holloway (1988); Grollier-Barron (1989); HSE (1989b); Bond (1990 LPB 92); Broadbent, Reason and Baddeley (1990); J.R. Wilson and Corlett (1983); A.F. Sanders (1991); Mill (1992); Moraal (1992); Needham (1992)

Allocation of function
Fitts (1962); Ephrath and Young (1981); Bainbridge (1983); H.E. Price (1985); Kantowitz and Sorkin (1987); Kletz (1987b); Swain (1987b); J. Lee and Moray (1992)

Human information processing, including decision-making, control tasks
Wald (1947); Heider (1958); Newell, Shaw and Simon (1960); Sinaiko (1961); Senders (1964); W. Edwards (1965); Zadeh (1965); Dreyfus (1972); Newell and Simon (1972); Kelley (1973); Ince and Williges (1974); Levine and Samet (1974); Pew (1974); Sheridan and Ferrell (1974); Tversky and Kahneman (1974); McLeod and McCallum (1975); J. Anderson (1976); W. Edwards and Tversky (1976); Gaines (1976); Keeney and Raiffa (1976); Senders and Posner (1976); Gaines and Kohout (1977); Janis and Mann (1977); Rouse (1977); Schank and Abelson (1977); Jagacinski and Miller (1978); Feigenbaum (1979); Kochhard and All (1979); Ringle (1979); Hammond, McClelland and Mumpower (1980); Cuny and Boy (1981); Barnett (1982); Baron *et al.* (1982); Rasmussen and Lind (1982); Rasmussen (1983); Eberts (1985); Friedman, Howell and Jensen (1985); Sayers (1988); Moray *et al.* (1991); Thimbleby (1991); Bainbridge (1993b); Bainbridge *et al.* (1993); van der Schaaf (1993); Sünderstrom (1993)

Vigilance
Levine and Samet (1974); Wiener (1974, 1987); Kvalseth (1979); Mackie (1977); Loeb (1978); Craig (1979, 1980, 1981, 1987); Curry (1981); Fisk and Schneider (1981); Kessel and Wickens (1982); Anon. (1984s); Wiener (1987); Wogalter *et al.* (1987)

Inspection tasks
Mackenzie (1958); Drury and Addison (1973); Drury and Fox (1975); Yao-Chung Tsao, Drury and Morawski (1979); Gallwey (1982); Geyer and Perry (1982); Drury and Sinclair (1983)

Displays, controls, display-control relations
Sleight (1948); Murrell (1952a,b, 1965a); Sinaiko (1961); Loveless (1962); Fogel (1963); Ziebolz (1964); Carbonell (1966); H.H. Bowen (1967); Meister (1967); Kelley (1968); Luxenberg and Kuehn (1968); Singleton (1969); Bainbridge (1971); Bernotat and Gartner (1972); Ince and Williges (1974); Jacob, Egeth and Bevan (1976); Seeberger and Wierwille (1976); Sheridan and Johanssen (1976); Curry, Kleinman and Hoofman (1977); Potash (1977); Demaio, Parkinson and Crosby (1978); B. Gibson and Laios (1978); Cakir, Hart and Stewart (1980); Penniall (1980); Petropoulos and Brehner (1981); Goodstein (1984); Kautto *et al.* (1984); Bullinger, Kern and Muntzinger (1987); Downing and Sanders (1987); Helander (1987); Triggs (1988); Whalley (1989); Buttigieg and Sanderson (1991); Dillon (1992)

Diagnostic tasks
Dale (1958, 1964, 1968); Shriver, Fink and Trexler (1964); Tilley (1967); Rasmussen and Jensen (1973, 1974); Gai and Curry (1976); Brooke and Duncan (1980a,b, 1981, 1983a,b); Bond (1981); Brehmer (1981); Brooke (1981); Freedy and Lucaccini (1981); Gaddes and Brady (1981); R.M. Hunt and Rouse (1981); Leplat (1981); Moray (1981); Patrick and Stammers (1981); Sheridan (1981); Syrbe (1981); W.B. Johnson and Rouse (1982); Rouse and Hunt (1982); Brooke, Cook and Duncan (1983); N.M. Morris and Rouse (1985); Patrick *et al.* (1986); Toms and Patrick (1987, 1989);

Carlson, Sullivan and Schneider (1989); Brinkman (1993); Patrick (1993); Reinartz (1993); Schaafstal (1993)

Emergency actions
Haas and Bott (1982); Lester and Bombaci (1984)

Shiftwork
HSE (1978 Research Review 1, 1992 CRR 31); Folkard and Monk (1979); Akerstedt and Torsvall (1981); Tilley *et al.* (1982); Folkard and Condon (1987); Costa *et al.* (1989); Folkard (1992); Wedderburn (1992); Wilkinson (1992a,b); Rosa and Bonnet (1993)

Workload, mental load, stress, fatigue, boredom
Bartlett (1943); Berkun *et al.* (1962); Berkun (1964); Bainbridge (1978); Goldstein and Dorfman (1978); Leplat (1978); Welford (1978); Moray (1979); R.P. Smith (1981); Sharit and Salvendy (1982); Anon. (1984ss); Braby, Harris and Muir (1993); Dorner and Pfeifer (1993); Gaillard (1993); HSE (1993 CRR 61)

Drink, drugs
NTSB (annual reports); HSE (1981 OP 1)

Task sharing
Goldstein and Dorfinan (1978); Cellier and Eyrolle (1992)

Teamwork
D.P. Baker and Salas (1992); Driskell and Sals (1992); Reinartz (1993); Rogalski and Samurcay (1993)

Personnel selection
Mallamad, Levine and Fleishman (1980); Gallwey (1982); Osburn (1987); HSE (1993 CRR 58)

Training
Holding (1965, 1987); Boydell (1970, 1976); Patrick (1975, 1992); API (1977 Publ. 756, 1979 Publ. 757); S.L. Johnson (1981); Nawrocki (1981); Svanes and Delaney (1981); Towne (1981); Wickens and Kessel (1981); W.B. Johnson and Rouse (1982); Kessel and Wickens (1982); Buch and Diehl (1984); Gagne (1985); Cannon-Bowers *et al.* (1991); Bainbridge (1993a); Kozak *et al.* (1993)

Task analysis
Annett *et al.* (1971); Leplat (1981); Piso (1981); Drury (1983); Kirwan and Ainsworth (1992)

Operating instructions
S. Jones (1968); Booher (1975); Kammann (1975); Anon. (1976 LPB 8, p. 19); Duffy, Curran and Sass (1983); Krohn (1983); Berkovitch (1985); Hartley (1985); R.C. Parker (1988); DTI (1989); Chung-Chiang Peng and Sheue-Iing Hwang (1994)

Computer aids
Mitter (1991); Marmaras, lioukas and Laios (1992); Adelman *et al.* (1993); Kirlik (1993)

Air traffic control systems
Whitfield, Ball and Ord (1980); Wiener and Curry (1980)

Formal safety assessment (FSA)
Bellamy, Kirwan and Cox (1986); Bellamy and Geyer (1991)

Evacuation
Bellamy and Harrison (1988)

Offshore (*see* Table A18.1)

Table 14.2 *Selected references on the process operator, including fault administration and computer aids (see also Table A14.1)*

NRC (Appendix 28 *Operating Personnel, Simulators, Training*); Riso National Laboratory (Appendix 28); Crossman (1960); W.R. King (1965); Rasmussen (1968a–c, 1969, 1971, 1973, 1974, 1976a,b, 1977, 1981a,b, 1983, 1986, 1988); Beishon (1969); Lees (1970, 1974c); E. Edwards and Lees (1971a,b, 1973, 1974); E. Edwards (1973); IEE (1975 Coll. Dig. 75/12); Purdue Europe (1977); A. Shepherd (1979, 1993); SN (1979 123); Lenior, Rijnsdorp and Verhagen (1980); Bainbridge (1981); Ergonomics Society (1983); Boel and Daniellou (1984); Brouwers (1984); Daniellou and Boel (1984); EPRI (1984); IChemE (1984/77); Kragt and Daniels (1984); S.B. Gibson (1987); Hoyos (1987); Bellamy and Geyer (1988); Sanderson, Verhage and Fuld (1989); J.R. Wilson and Rutherford (1989); ACSNI (1990, 1991, 1993); Mill (1992); Hoc (1993)

Manual vs automatic systems
Hunns (1981); Bessant and Dickson (1982); Bainbridge (1983); Rijnsdorp (1986); Visick (1986); Bodsberg and Ingstad (1989)

Operator activities
Troyan (1963); Lees (1970); E. Edwards and Lees (1973, 1974); Skans (1980)

Control tasks
E. Edwards and Lees (1973, 1974); Patternotte (1978); Umbers (1979, 1981)

Information display
Rasmussen (1968a–c, 1969, 1971, 1973, 1976b); Rasmussen and Goodstein (1972); E. Edwards and Lees (1973, 1974); Pedersen (1974); A. Shepherd (1979); Pew, Miller and Feehler (1981); Buttigieg and Sanderson (1991)

Fault administration
Annett *et al.* (1971); CAPITB (1971 Inf. Pap. 8); E. Edwards and Lees (1973, 1974); Rasmussen and Jensen (1973, 1974); Duncan (1974); Goodstein *et al.* (1974); Lees (1974c); Duncan and Gray (1975a,b); Duncan and Shepherd (1975a,b); A. Shepherd (1976); Rouse (1977, 1979a,b, 1981); A. Shepherd *et al.* (1977); Himmelblau (1978); Landeweerd (1979); Lihou (1979, 1981); A. Shepherd and Duncan (1980); Christeansen and Howard (1981); Duncan (1981); Johannsen (1981); B.C. Marshall, Duncan and Baker (1981); B.C. Marshall and Shepherd (1981); B.C. Marshall *et al.* (1981); Patrick and Stammers (1981); Process Control Training (1981); Rasmussen and Rouse (1981); D.A. Thompson (1981); Rouse and Hunt (1982); Embrey (1986); P.J. Smith *et al.* (1986); Toms and Patrick (1987, 1989); Vermeulen (1987); Malaterre *et al.* (1988); Morrison and Duncan (1988); Patrick and Haines (1988); Moray and Rotenberg (1989); Patrick *et al.* (1989); Yukimachi, Nagasaka and Sasou (1992); Decortis (1993); Hukki and Norros (1993); Patrick (1993); Chung-Chiang Peng and Sheue-Ling Hwang (1994)

Alarm systems
Andow and Lees (1974); Hanes (1978); E. Edwards (1979); Hanes (1980); Kortlandt and Kragt (1980a,b); Benel *et al.* (1981); Dellner (1981); Andow (1982, 1985a,b); Kragt (1982, 1983, 1984a,b); Kragt and Bonten (1983); Renton (1984); Schellekens (1984); J.A. Shaw (1985); British Gas (1986

Comm 1296); Arnold and Darius (1988); Sorkin, Kantowitz and Kantowitz (1988); Fort (1989); Edworthy, Loxley and Dennis (1991); Fordestrommen and Haugset (1991)

Batch processes
Lihou and Jackson (1985); Rayment (1986)

Operator-computer interaction
Rasmussen (1968b, 1981a); Rasmussen and Goodstein (1972); Goodstein (1981, 1982, 1984); Kletz (1982g, 1991g); Rasmussen and Lind (1982); Goodstein *et al.* (1983); Hollnagel (1984); J.C. Shaw (1985); Rayment (1986); Gilmore, Gertman and Blackman (1989); Hockey *et al.* (1989)

Control room design
NRC (Appendix 28 *Control Rooms*); Ergonomics Society (1983); Stumpe (1984); Nordic Liaison Committee (1985 NKA/LLT(85)4); Singleton (1986); Wanner (1986); Pikaar *et al.* (1990); HSE (1993 CRR 60); Ainsworth and Pendlebury (1995); Umbers and Rierson (1995); Whitfield (1995)

Operator training, including simulators
MCA (SG-15); NRC (Appendix 28 *Operating Personnel, Simulators, Training*); Pontius, van Tassel and Field (1959); Crossman (1960); S.D.M. King (1960, 1964); Crossman and Cooke (1962); Stapleton (1962); Crossman, Cooke and Beishon (1964); Weltge and Clement (1964); BCISC (1965/5); Whitesell and Bowles (1965); Carmody and Staffin (1970); Annett *et al.* (1971); Atherton (1971); CAPITB (1971 Inf. Paps 6–10, 1972 Inf. Pap. 13); PLTB (1971/1, 2, 1972/3, 1975/6); Biggers and Smith (1972); City and Guilds Institute (1972); E. Edwards and Lees (1973, 1974); Duncan (1974, 1981); Goodstein *et al.* (1974); Lees (1974c); Duncan and Gray (1975a,b); Duncan and Shepherd (1975a,b); Patrick (1975, 1992); Barber and Tibbets (1976); A. Shepherd (1976, 1982b, 1986, 1992); J. Davies (1977); Doig (1977); A. Shepherd *et al.* (1977); Shindo and Umeda (1977); Stephens (1977); Crawford and Crawford (1978); Goldstein (1978, 1987); Duncan, Gruneberg and Willis (1980); Landeweerd, Seegers and Praagma (1981); Process Control Training (1981); Vervalin (1981c, 1984); Sorotzkin and Lock (1983); Demena *et al.* (1984); Madhavan (1984); Clymer (1985); Pathe (1985); Tomlinson (1985); Embrey (1986); Marcille (1986); Nordic Liaison Cttee (1986 NKA/LLT(85)6); Wetherill and Wallsgrove (1986); Drury *et al.* (1987); Elshout and Wetherill (1987); Flexman and Stark (1987); Avisse (1989); IAEA (1989); Patrick *et al.* (1989); ACSNI (1990); Mani, Shoor and Petersen (1990); Ferney (1991); Grossman and Dejaeger (1992); IEE (1992 Coll. Dig. 92/123); Sanquist (1992)

Operating procedures, instructions
Oriolo (1958); Troyan (1961a); Minich (1979); Lopinto (1983); S.T. Wood (1984); Kujawski (1985); Bardsley and Jenkins (1991 SRDA Rl); Connelly (1992); McIntyre (1992); I.S. Sutton (1992); Swander and Vail (1992)

Three Mile Island (*see also* Table A21.1)
Livingston (1980); Malone *et al.* (1980); Kletz (1982l)

14.1 Human Factors in Process Control

In the previous chapter the importance of plant operation was emphasized and the automatic control system was described. Consideration is now given to the other element in the overall control system – the process operator.

Although modern control systems achieve a high degree of automation, the process operator still has the overall immediate responsibility for safe and economic operation of the process. There are different philosophies on the extent to which the function of safety shut-down should be removed from the operator and assigned to automatic trip system. In general, the greater the hazards, the stronger the argument for protective instrumentation. This question is considered in more detail later. But, whatever approach is adopted, the operator still has the vital function of running the plant so that shut-down conditions are avoided.

The job of the process operator is therefore a crucial one, but it is also rather elusive in that it presents the engineer with a type of problem with which he is not normally required to deal. The study of industrial jobs and work situations is the province of ergonomics or, its American near-equivalent, human factors. It is appropriate, therefore, to consider the contribution which this discipline can make to the problems associated with the work of the process operator.

It should be said, however, that the chemical industry in general appears to make little use of human factors in this area. There is considerable willingness to do so among engineers, but perhaps also some lack of appreciation of the scope of human factors as a discipline.

14.2 Human Factors in System Design

The pace of technological change and the scale of systems have now become so great that it is often not possible to rely on evolutionary trial and error to achieve the proper adaptation of human tasks. Instead, it is necessary to try to foresee the problems and to design to overcome them. The discipline that is concerned with this on the human side of systems is human factors.

The development of human factors has been strongly influenced by the problems of large, complex man–machine systems that occur in the fields of defence, aerospace and computers. Much of the fundamental research and design experience are in these areas.

An important area of study in the early work on human factors was the compatibility of man and machine, with its emphasis on 'knobs and dials'. More recent work has laid a greater stress on system design. In consequence, the ergonomist has concerned himself increasingly with all stages of the design process, particularly the early stages where the crucial decisions are made.

Human factors is now established, therefore, as an aspect of systems engineering. An outline of the human factors activities in system design is shown in Figure 14.1. Two main points may be noted: (1) human factors play a role at all stages of the design; and (2) the decisions taken early on, such as those on allocation of function, are especially important and the design process is a highly interactive and iterative one. Only one iteration loop is shown, but in fact iteration occurs at all stages of the design process. Important emphases in human factors, therefore, are the system criteria and the system design process.

The engineer unfortunately frequently misunderstands human factors. The view of the subject as being concerned with knobs and dials is entrenched. The application of human factors is too often ineffective because it is called upon too late in the day to fulfill a rescue or cosmetic function. Its greatest contribution should in fact come earlier, particularly at the allocation of function stage.

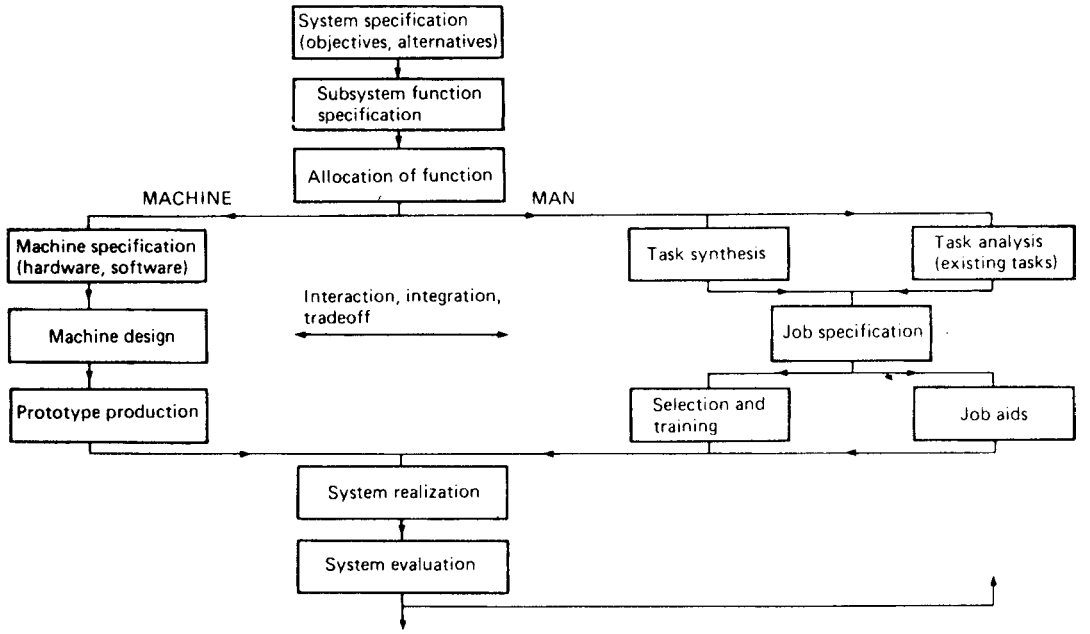


Figure 14.1 *Human factors activities in system design (Lees, 1974c) (Courtesy of Taylor & Francis Ltd)*

Like the engineer, the ergonomist is concerned with solving problems, particularly those arising in design. He draws on the work of psychologists and others, much as the engineer draws on that of physicists.

14.3 Themes in Human Factors

It is appropriate at this point to give a very brief account of some of the themes in human factors work which have obvious relevance to process control. Some of these are shown in Table 14.3. This is an abstract from a fuller table, which gives detailed references, in an account of the development of human factors in this context by Lees (1974c).

Much of the early work on human factors was concerned with physical tasks, but in more recent years, the emphasis has been increasingly on mental tasks. This is certainly more relevant as far as the process operator is concerned, since his job is essentially decision-making.

The question of the sampling and processing of information by the human operator is therefore of great importance. Work in this area largely evolved from study of the skills involved in physical tasks to investigation of those required for perceptual and decision-making tasks (Crossman, 1956). The model of man as an information processor has proved fruitful, although the application of information theory to the problem has not been entirely successful. Work in the area has emphasized: the ability of man to accept information coming through many sensory channels and coded in many different ways, and his ability to compensate for errors in the information; the differences in the amounts of information which can be handled by the various channels; the sampling of information and the updating of his mental model of the environment; the effect of information overload, resulting in selective omission of parts of the task; and the characteristics of memory, particularly short-term memory such as is exercised in remembering a telephone number to make a phone call.

Table 14.3 *Selected topics in human factors*

Information sampling and processing
Learning
Skill
Stress, fatigue
Decision-making
Diagnostic tasks
Motivation
Performance assessment
Task analysis
Man–machine systems
Manual control, tracking
Man–machine system reliability, human error
Emergency situations
Air traffic control
Aircraft pilot's task
Dynamic modelling of operator
Man–computer systems
Displays
Vigilance, signal detection
Inspection tasks
Controls
Control–display relations
Control panels, computer consoles
Personnel selection
Training
Organizational factors, job enrichment
Repetitive work, boredom, rest pauses, shift work

The ergonomist's approach to a particular job tends to be to enquire into the skill involved, including the nature of

the skill, its acquisition through the learning process and its disintegration under stress. Skills differ greatly in their amenability to study; some skills, such as that of the process operator, are particularly inaccessible. Nevertheless, skilled performance does exhibit certain common characteristics. Skill seems to lie largely in the timing and co-ordination of activities to give a smooth and effortless performance. It is highly learned and barely accessible to consciousness, as indicated by the fact that the attempt to describe it, as in instructing a novice, often leads to actual degradation in performance.

The effects on skill of various forms of stress such as fatigue, workload and anxiety, have been investigated both on account of the importance of these effects in themselves and of the light which they throw on the nature of skill as it degrades under stress. An important finding is that skilled performance tends to improve with moderate stress, but that beyond a certain threshold, which varies greatly with the individual, it deteriorates rapidly.

The characteristics of human as opposed to mathematically optimal decision-making have been studied (W. Edwards, 1965). Interesting results are man's tendency to make decisions that are based on rather small samples, that is to jump to conclusions, and to make decisions that are biased towards optimism, that is to gamble on beating the odds.

A type of decision-making that is rather important is diagnosis (Dale, 1958, 1964; Tilley, 1967). Studies of this indicate that man does not so much follow through the decision tree irrespective of the probabilities of the various paths, but rather moves about the tree, testing first the high probability paths, and only goes to the low probability ones when the former have been exhausted.

Human performance in manual control tasks has been much studied. Early work evolved a transfer function model of the operator:

$$H(s) = K\frac{\exp(-\tau_d s)(1+\tau_L s)}{(1+\tau_N s)(1+\tau_I s)} \qquad [14.3.1]$$

where $H(s)$ is the transfer function; K the gain; s the Laplace operator; τ_d the reaction time (usually 0.1–0.3 s); τ_L the lead time constant (0.2–2.5 s); τ_N the neuromuscular lag time constant (0.1–0.2 s); and τ_I the compensatory lag time constant (5–20 s). Of these parameters, the gain is particularly significant, alteration of gain being a favoured response of the human operator to a changing situation. This approach has been developed by later workers to take account of non-linearities, sampled data features, etc.

Work in this area shows clearly the increased difficulty which the human operator has in controlling processes with an increasing number of transfer lags or integrations or with dead time. Certain systems are virtually uncontrollable by the operator, unless he is provided with specially processed information. In particular, systems with more than three integrations in series tend to be beyond the limits of manual control. For systems such as submarines, which have this feature, the technique of quickening has been developed, in which the signal displayed to the operator is a weighted sum of signals from various points in the series of integrations. Another feature of man as a controller is his ability to carry out predictive and feedforward control functions. This is a rather characteristic feature of operator control.

Much work has been done on displays, in terms both of detailed design of dials, etc., and of the display layout, and it is perhaps this aspect which the engineer most readily identifies as human factors. Particularly relevant here is the classification of the uses of displays (Murrell, 1965a). These are:

(1) Indicating, that is the operator perceives one of two binary states.
(2) Quantitative reading, that is the operator requires a precise numerical value.
(3) Check reading, that is the operator requires confirmation that value lies within an acceptable range.
(4) Setting, that is the operator manipulates his machine controls in order to achieve a predetermined display state.
(5) Tracking, that is the operator carries out an on-going control task in order to achieve certain display conditions which may vary as a function of time.

These are very different uses and a display which is optimal for one is not necessarily so for another. There is some work which suggests that some 75% of industrial applications is accounted for either by check reading alone or by check reading and setting combined (Murrell, 1952b).

The acquisition of information from large display layouts is another important problem. Work in this area tends to emphasize the value to the operator of being familiar with the position of dials which give particular readings. Such spatial coding is lost, for example if the same instrument is used to display different variables at different times. The operator then has to devote more effort to finding out which variable is on a particular display and he is less able to recognize patterns.

Control–display relations can be important. In a given culture, there tend to be expectations of particular relations between control movements and display readings. A typical stereotype of a control–display relation is shown in Figure 14.2. Although an operator can be trained to use equipment that embodies faulty control–display relations in its design, he may tend under stress to revert to the expected relation. Violation of the stereotype can result in severe penalties.

Monitoring, signal detection and vigilance is another related and important area on which a large amount of work has been done. Some of this has been concerned with the fall-off in attention over the watch-keeping period, that is the vigilance effect. The application of this to process control is doubtful, but perhaps more relevant is the well-established relation between the frequency of a signal and

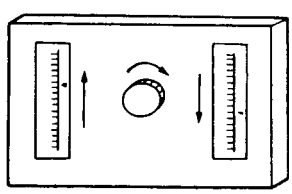


Figure 14.2 *Expected relationships between control and display movements (E. Edwards and Lees, 1973) (Courtesy of the Institution of Chemical Engineers)*

the probability of its detection. The probability of detection of a rare signal is rather low. This has been studied both in dial monitoring and in inspection tasks.

The problems of man–computer systems have been studied quite extensively. These include allocation of function between man and machine, man–computer interaction and man–computer problem-solving. For many functions the emphasis has moved away from early attempts at complete automation towards computer-assisted operator decision-making.

This rather brief survey is intended to show that the problems with which human factors deals are very relevant to process control by the human operator. These and other topics such as learning and training, organizational and social factors, and human error are now considered more specifically in relation to process control.

14.3.1 Human factors in process control

The task of process control is of interest to workers in human factors as an example of a task involving cognitive rather than manipulative skills and was the subject of a series of early classic studies by Crossman. Since then there have been numerous investigations of the process control task. This work is described below.

A review of the control of processes by operators and computers is given in *Man and Computer in Process Control* and some of the classic papers on the process operator are collected in *The Human Operator in Process Control,* both by E. Edwards and Lees (1973, 1974).

14.4 Process Operator Functions

The job of the process operator has developed over the years from one based largely on manual work to one consisting primarily of decision-making. The physical work content is now frequently vestigial.

The process operator is part of the control system. The primary functions of the control system and, therefore, of the operator, depend on the nature of the process. In a chlorine cellroom, it may be the monitoring of alarm conditions, and in a batch reactor plant the conduct of sequential operations.

The nature of the control system provided also influences strongly the operator's functions. The stages of development of control systems have already been described in Chapter 13. The job of the operator is generally different in systems based on analogue and on computer control. The job of the process operator, at least in the control room, is essentially decision-making in a rather artificial situation, involving the manipulation of symbolic displays.

If the process control task as a whole is considered, a number of distinct operator functions may be identified (E. Edwards and Lees, 1973; Lees, 1974c):

(1) goal formulation;
(2) measurement;
(3) data processing and handling;
(4) monitoring;
(5) single variable control;
(6) sequential control;
(7) other control;
(8) optimization;
(9) communication;
(10) scheduling;
(11) manual operations.

These functions have been discussed in detail by E. Edwards and Lees (1973). Although most process control tasks have elements of all these functions, the relative importance varies widely.

The state of the process also affects the operator's task. If process conditions are abnormal, he has the crucial function of fault administration. In simple terms, this may be regarded as having three stages: (1) fault detection, (2) fault diagnosis and (3) fault correction. But this can be an oversimplification, in that following fault detection the priority is often to move to a safe condition rather than to diagnose the fault. As control systems achieve increasing automation, the function of fault administration tends to grow in importance. It is a crucial one in relation to loss prevention.

14.5 Process Operator Studies

In a review in 1974 of studies of the process operator, Lees (1974c) listed some 140 items. This list was limited to work directly concerned with the process operator and did not include work on more general but related problems such as vigilance or manual control. There exists, therefore, a quite substantial body of work on the process operator and his problems, although it is not well known among engineers. Selected studies of the process operator are given in Table 14.4. Some of the salient points from these studies are now considered.

It may be mentioned at this point that the compilation of this list appears to have coincided with the end of that phase in the development of human factors in which studies were conducted of the process operator *per se*. Subsequent research has been directed rather to specific tasks, particularly fault diagnosis, to methodologies such as task analysis and to training.

Much of the pioneering work on the process operator was initiated by Crossman and his co-workers. His interest in process control was that it is a good example of an industrial skill that is predominantly cognitive rather than physical. Crossman (1960) did an investigation of a number of process control tasks and concluded that it is particularly difficult to control the following processes:

(1) where several display and control variables depend on one another;
(2) where the process has a long time constant;
(3) where important variables have to be estimated by the operator rather than measured by an instrument;
(4) where the readings of instruments at widely separated points have to be collated, and the operator has to remember one while going to another ('short-term memory');
(5) where the operator gets imperfect knowledge of the results of his performance, or where the knowledge arrives late;
(6) where the basic process is either difficult to visualize, for example chemical reactions, or contradicts 'common-sense' assumptions, or is too complicated to be held in mind at one time.

One aspect of process control skill, which was investigated by Crossman and his colleagues is information sampling (Crossman, Cooke and Beishon, 1964). The information sampling behaviour of the operator was studied in the laboratory task of controlling the temperature of a water bath

Table 14.4 *Selected studies of the process operator*

Author	*Subject of study*	*Type of study*
Hiscock (1938)	Selection tests for process operators	Industrial study
Crossman (1960)	Process control task and skill in plants of different types	Industrial study
Kitchen and Graham (1961)	Decision-making and mental load of process operators in 50 chemical plants	Industrial study
Crossman and Cooke (1962)	Manual control by process operator	Experimental laboratory study
Sell, Crossman and Box (1962)	Evaluation of human factors aspects of control system of hot strip mill	Industrial study
Spencer (1962)	Manual control by process operator on liquid washing plant	Experimental in-plant study
Crossman, Cooke and Beishon (1964)	Information sampling by process operator	Experimental laboratory and in-plant studies
Vander Schraaf and Strauss (1964)	Acceptability of process computer to process operator	Industry study
Bernard and Wujkowski (1965)	Acceptability of process computer to process operator	Industry study
CEGB (1966)	Evaluation of human factors aspects of control room of nuclear reactors	Industry study
Sinclair *et al.* (1966)	Evaluation of human factors aspects of control room of Linz-Donau (LD) converter waste heat boilers	Industrial study
Beishon (1967)	Manual control by process operator on paper machine	Experimental in-plant study
Davies (1967)	Selection tests for process operators	Industrial study
Bainbridge *et al.* (1968); Bainbridge (1971, 1972, 1974)	Decision-making by process operator in scheduling electric arc furnaces	Experimental simulation study
Crawley (1968)	Allocation of function between process operator and process computer and computer graphic displays for process operator on LD converter	Industrial study
Munro, Martin and Roberts (1968)	Workload of process operator	Experimental simulation study
Rasmussen (1968a–c, 1971, 1973, 1974, 1976a,b, 1977, 1978); Rasmussen and Goodstein (1972); Rasmussen and Jensen (1973); Goodstein *et al.* (1974); Rasmussen and Taylor (1976)	Control and surveillance by process operator, displays for process operator, fault diagnosis by process operator, reliability of process operator	Experimental, industrial and general studies
Beishon (1969)	Manual control and decision-making by process operator on baking ovens	Experimental in-plant studies
Whitfield (1969)	Evaluation of human factors aspects of control room of nuclear reactor	Industrial study
Attwood (1970)	Manual control by process operator on paper machine	Experimental laboratory and in-plant studies
Engelstad (1970)	Social and organizational features in process control in paper mill	Experimental in-plant study
Ketteringham, O'Brien and Cole (1970); Ketteringham and O'Brien (1974)	Computer-aided scheduling by process operator in steel mill soaking pits	Experimental simulation study
Annett *et al.* (1970); Duncan (1974); Duncan and Gray (1975); Duncan and Shepherd (1975a,b)	Task analysis and training for process control tasks	Experimental in-plant studies
Daniel, Puffier and Strizenec (1971)	Mental load of process operator in four chemical plants	Experimental in-plant studies
de Jong and Köster (1971)	Process operator in computer-controlled refinery	Review
Anyakora and Lees (1972a)	Detection of instrument malfunction by process operator in chemical plants	Experimental in-plant study

Table 14.4 *(continued)*

Dallimonti (1972, 1973)	Design of man–computer interface and acceptability of process computer to process operator	Industrial study
E. Edwards and Lees (1973, 1974)	The human operator in process control, including process computer systems	Review
Lees (1973a, 1976a)	Design for human reliability and human reliability assessment in process control	Review
Duncan (1974); Duncan and Gray (1975); Duncan and Shepherd (1975a,b); Shepherd (1976); Shepherd *et al.* (1977)	Training of process operator in fault diagnosis	Experimental in-plant studies
Kragt and Landeweerd (1974)	Manual control and surveillance by process operator	Experimental laboratory and in-plant studies
West and Clark (1974)	Information display for and manual control and fault administration by process operator in computer-controlled pilot plant	Experimental in-plant study
Brigham and Laios (1975)	Manual control by process operator	Experimental laboratory study
Lees and Sayers (1976)	Emergency behaviour of process operator	Experimental simulation study

and the industrial one of controlling the basis weight on a paper machine. It was found that the Shannon–Wiener sampling theorem did give a basic minimum sampling rate, provided a system bandwidth modified for error tolerance was used. But many other factors were identified which tend to increase the sampling rate. Sampling behaviour depends on the operator's uncertainty and its growth over time and on the cost of sampling, and it cannot be separated from the control problem, which raises questions of the control accuracy required, the penalty for error, the operator's understanding of the system, the nature and predictability of the disturbances and the lags in the process. Five factors were identified as governing the sampling rate: (1) bandwidth, (2) noise, (3) tolerance, (4) predictability and (5) control calibration.

Bandwidth is a function of the maximum possible rate of change of the signal. Noise on the signal causes excursions of the signal near the tolerance limit. Tolerance limits depend on the importance of the variable, its possible rate of change and the signal noise. Predictability of the signal allows extrapolation and reduces the need for sampling. Control calibration, which gives the relation between the change of the manipulated variable and that of the controlled variable, assists predictability.

In the light of this work the authors criticized the use of displays which show only a deviation between the set point and a measured value. Such displays greatly reduce the operator's ability to learn the signal characteristics such as noise, predictability and control calibration. This problem has also been considered by de Jong and Köster (1971) in terms of the sampling of information from chart recorders.

Crossman and his colleagues also studied manual control of the laboratory water bath and the paper machine (Crossman and Cooke, 1962; Beishon, 1967). The control action required in both cases was to bring the system to a new operating point. The work showed that a good subject often begins with a closed-loop strategy that tends to produce the oscillatory response shown in Figure 14.3, but soon learns to use an open-loop approach, limiting the use of feedback to fine tuning as in Figure 14.3(b).

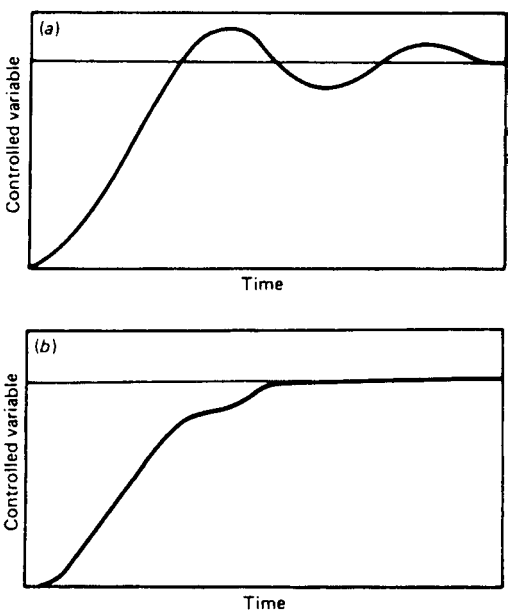


Figure 14.3 *Change of operating point in a manually controlled system: (a) closed-loop behaviour; (b) open-loop behaviour*

Similar work has been done by Attwood (1970), also on a laboratory water bath and a paper machine, by Kragt and Landeweerd (1974) on a laboratory heater and by B. West and Clark (1974) on a distillation column in a computer-controlled pilot plant. This work further confirms the importance of the open-loop strategy.

Crossman also raised the question of the operator's mental model of the process and investigated the difference in performance between subjects who were given an

account of the physics of the plant and those who were simply told to control calibration settings. The performance of the former was much less effective. He concluded that the results cast some doubt on the practice of instructing operators in the physics and chemistry of the process. Similar results were obtained by Attwood and by Kragt and Landeweerd.

Brigham and Laios (1975) have studied manual control of level in a laboratory rig consisting of three tanks in series, with interaction between the levels. The tanks were glass, so that the operator also had feedback of information from intermediate points in the process. Cross-correlation of his control manipulations with level error showed little correlation between the two, indicating that the control was based on predictive rather than feedback strategy.

The effect of the number and types of lag in the process has also been studied. Crossman and Cooke added further lags to their laboratory apparatus by putting additional sheaths round the thermometer and found that control became more difficult and response was more oscillatory. Attwood introduced dead time into his water bath and found a similar effect. Control behaviour on paper machines observed by Crossman, Cooke and Beishon and by Attwood shows similar oscillatory responses.

Manual control of a liquid washing plant has been studied by Spencer (1962). This work highlighted the difficulties of control in the absence of feedback of information on the results of control actions and the wide differences between operators in terms of the control gain which they employ.

The mental load on the operator has been studied by Kitchin and Graham (1961) in an investigation covering some 50 plants. The decision-taking load was analysed under the following five headings: (1) number of factors in the situation; (2) complexity of comprehension of each factor; (3) memory; (4) interdependence of factors and (5) delay characteristics of situation. This is somewhat similar to Crossman's description of the factors which make process control difficult, as described earlier.

Another study which involved sampling of the operator's activities and assessment of the mental workload imposed by the work is that done by Daniel, Puffier and Strizenec (1971) on four chemical plants. The Monte Carlo simulation of the workload on the operator has been described by Munro, Martin and Roberts (1968).

There have been a number of studies by ergonomists of industrial control rooms. Examples are those of a hot strip mill by Sell, Crossman and Box (1962), of an Linz-Donau (LD) converter waste heat boiler control room by Sinclair *et al.* (1966) and of nuclear power station control rooms by the Central Electricity Generating Board (1966) and by Whitfield (1969).

Decision-making by the operator has been investigated by Bainbridge *et al.* (1968) in a simulation study of electric arc furnace scheduling. A running commentary, or verbal protocol, was given by the subjects as they performed the task and has since been analysed in detail by Bainbridge (1971, 1972, 1974). This analysis identifies subroutines which the operator uses and attempts to describe the executive programme which organizes these.

An important aspect of this work is the light which it throws on the way in which the operator keeps track of the state of the process and so updates his mental model of it. In general, he tends to predict the future of the process state and then subsequently samples only enough readings to confirm that his prediction was correct. This is in line with other work such as that of Crossman, Cooke and Beishon (1964) referred to earlier. This work has significant implications for displays. Good display facilities allow the operator to survey the state of the process as a whole with minimum effort.

The advent of the process computer has brought profound changes in the work of the operator. A number of investigations have been done (e.g. Vander Schraaf and Strauss, 1964; Bernard and Wujkowski, 1965) on the reaction of process operators to computers. Another such study is that by Dallimonti (1972, 1973), which was particularly concerned with the design of computer facilities.

The problem of system objectives and allocation of function in computer control of a basic oxygen furnace has been discussed by Crawley (1968). He gives as an example of a function that is more appropriately allocated to man the interpretation of the noise signal given by a bomb thermocouple. The point is also made, however, that the optimal allocation of function changes continuously as technology progresses.

The difficulty of automating certain functions is further illustrated by the work of Ketteringham, O'Brien and Cole (Ketteringham, O'Brien and Cole, 1970; Ketteringham and O'Brien, 1974) on the scheduling of soaking pits using a man–computer interactive system. Problems of providing all the necessary information to the computer and of complexity in the decision-making make it difficult to automate this function, but it is possible to provide computer facilities, which by storage of large amounts of information, the use of predictive models and the provision of appropriate displays, greatly assist the operator to make decisions. The work involved simulation using a realistic interface and actual steel works schedulers. The problem is very similar to that of air traffic control, which has been extensively investigated in human factors.

The importance of organizational and social factors is shown by the work of Engelstad (1970), who investigated these in a paper mill. The work revealed that individuals tended to operate too much in isolation and to have goals that were not necessarily optimal as far as the system was concerned. It sought to encourage communication by treating the control room as an information and control centre, which all concerned should use, and by designing jobs to give greater variety, responsibility, learning opportunity and wholeness. Other workers too have commented on the losses that can occur in continuous flow processes, if there are poor relationships between the men controlling the process at different points.

Other studies have been concerned with task analysis, fault administration, displays, selection and training and human error. These topics are considered below.

14.6 Allocation of Function

As already emphasized, human factors has at least as important a role to play in matters of system design, such as allocation of function as in those of detailed design. The classic approach to allocation of function is to list the functions which machines perform well and those which men perform well and to use this as a guide. One of the original lists was compiled by Fitts (1962) and such a list is often referred to as a 'Fitts' list'. However, this approach needs some qualification. As Fitts pointed out later, the

functions which should be allocated to man are not so much those which he is good at as those which it is best from the system point of view that he perform, which is slightly different. The question of motivation is also important. De Jong and Köster (1971) have given a similar type of list showing the functions which man is motivated to perform. Further accounts of allocation of function is given by H.E. Price (1985) and Kantowitz and Sorkin (1987). Particularly important in relation to loss prevention are functions concerned with fault administration, fault diagnosis, plant shut-down and malfunction detection.

14.7 Information Display

Once the task has been defined, it is possible to consider the design of displays. Information display is an important problem, which is intensified by the increasing density of information in modern control rooms. The traditional display is the conventional control panel. Computer graphics now present the engineer with a more versatile display facility, offering scope for all kinds of display for the operator, but it is probably fair to say that he is somewhat uncertain what to do with it.

The first thing that should be emphasized is that a display is only a means to an end, the end being improved performance by the operator in executing some control function. The proper design of this function in its human factors aspects is more important than the details of the display itself. Some types of display that may be provided are listed in Table 14.5.

The provision of displays that the operator deliberately samples with a specific object in view is only part of the problem. It is important also for the display system to cater both for his characteristic of acquiring information 'at a glance' and for his requirement for information redundancy. There is a need, therefore, for the development of displays that allow the operator to make a quick and effortless survey of the state of the system. As already described, the operator updates his knowledge of system state by predicting forward, using a mental model of the process and sampling key readings to check that he is on the right lines. He needs a survey display to enable him to do this.

This need still exists even where other facilities are provided. Facilities, such as alarm systems are based on a 'management by exception' approach, which is essential if the large amounts of information are to be handled. But when the exceptional condition has been detected, the operator must deal with it and for this he needs knowledge of the state of the process, which a survey display provides. A display of system state also allows the operator to use his ability to recognize patterns. This aspect is considered below.

Table 14.5 *Some displays for the process operator*

Displays of flow and mimic diagrams
Displays of current measurements, other variables, statuses (other variables include indirect measurements, valve positions, etc.)
Displays of trends of measurements, other variables, statuses
Displays of control loop parameters
Displays of alarms
Displays of reduced data (e.g. histograms, quality control charts, statistical parameters)
Displays of system state (e.g. mimic diagrams, 'status *array*', 'surface' and polar plots)
Displays for manual control (e.g. predictive displays)
Displays for alarm analysis
Displays for sequential control
Displays for scheduling and game-playing
Displays for valve sequencing
Displays for protective system checking
Displays of maloperation
Displays for malfunction detection
Command displays

14.7.1 Regular instrumentation

It will be apparent from the foregoing that the conventional control panel has certain virtues. The panel shown in Figure 14.4 is typical of a modern control panel. The conventional panel does constitute a survey display, in which the instruments have spatial coding, from which the operator can obtain information at a glance and on which he can recognize patterns. These are solid advantages not to be discarded lightly. This is only true, however, if the density of information in the panel is not allowed to become too great. The advantages are very largely lost if it becomes necessary to use dense blocks of instruments which are difficult to distinguish individually.

An important individual display is the chart recorder. A trend record has many advantages over an instantaneous display. As the work of Crossman, Cooke and Beishon (1964) shows, it assists the operator to learn the signal characteristics and facilitates his information sampling. Both Attwood (1970) and B. West and Clark (1974) found that recorders are useful to the operator in making coarse adjustments of operating point, while the latter authors also noted the operator's use of recorders in handling fault conditions. Anyakora and Lees (1972a) have pointed out the value of recorders in enabling the operator to learn the signal characteristics and so recognize instrument malfunctions.

14.7.2 Computer consoles

The computer console presents a marked contrast to conventional instrumentation. This is illustrated with particular starkness in Figure 14.5(a), which shows the console of the original ICI direct digital control (DDC) computer. Some of the features of ergonomic importance in this panel are: (1) specific action is required to obtain a display; (2) there is no spatial coding and the coding of the information required has to be remembered or looked up; (3) only one variable is displayed at a time; (4) only the instantaneous value of the variable is displayed and (5) the presentation is digital rather than analogue.

This is a revolutionary change in the operator's interface. While there is, among engineers, a general awareness that the change is significant, its detailed human factors implications are not so well appreciated. The subsequent refinement of process computer consoles and the introduction of computer graphics have somewhat mitigated these features. A more modern computer console is shown in Figure 14.5(b). Moreover, the facilities that the computer offers in functions such as alarm monitoring or sequential control are powerful new aids to the operator.

It remains true, however, that the transition from the conventional panel to the computer console involves some

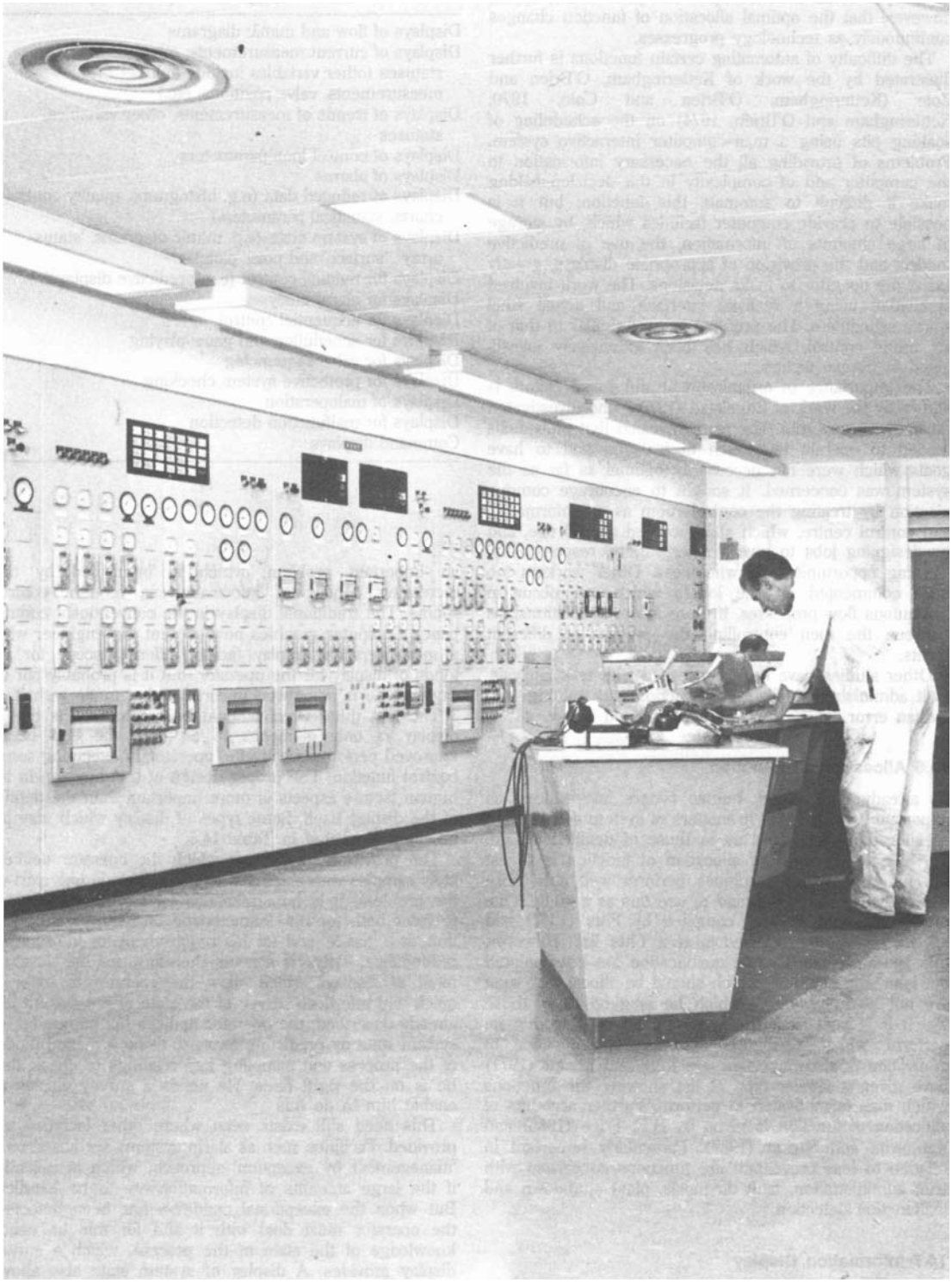


Figure 14.4 *Control panel in a chemical plant (Courtesy of Kent Instruments Ltd)*

serious human factors losses, particularly in information display. This does not necessarily mean that the change should not be made. Conventional panels are expensive and lose much of their advantage if the information density becomes too high. Computers offer some very worthwhile additional facilities. But the change should at least be made in the full awareness of its implications and with every effort to restore in the new system the characteristic advantages of the old.

14.8 Alarm Systems

As stated in the previous chapter, the progress made in the automation of processes under normal conditions has focused attention on the monitoring and handling of abnormal or fault conditions. It is the function of the control system to prevent, if possible, the development of conditions which will lead to plant shut-down, but to carry out the shut-down if necessary. The responsibility for averting shut-down conditions falls largely to the operator. The principal automatic aid provided to assist him is the alarm system. Alarm systems are an extremely important but curiously neglected and often unsatisfactory aspect of process control.

An alarm system is a normal feature of conventional control systems. If a process variable exceeds specified limits or if an equipment is not in a specified state, an alarm is signalled. Both audible and visual signals are used.

Accounts of alarm systems include those by E. Edwards and Lees (1973), Andow and Lees (1974), Hanes (1978), Swain and Guttman (1983), Schellekens (1984), Shaw (1985) and the Center for Chemical Process Safety (CCPS, 1993/14). There have also been investigations of the operation of alarm systems, as described below.

14.8.1 Basic alarm systems

The traditional equipment used for process alarms is a lightbox annunciator. This consists of a fascia, or array, of separate small rectangular coloured glass panels, behind each of which there is a lamp that lights up if the alarm is active. Each panel is inscribed with an alarm message. The panels are colour coded, usually with red being assigned the highest priority. This visual display is complemented by a hooter. When a new alarm occurs, the hooter sounds and the fascia light flashes until the operator acknowledges receipt by pressing a button. The panel then remains lit until the alarm condition is cleared by operator action or otherwise, as described below.

There are a number of variations on this basic system. An account of some of these is given by Kortland and Kragt (1980a). One is a two-level hierarchical arrangement in which there is a central fascia and a number of local

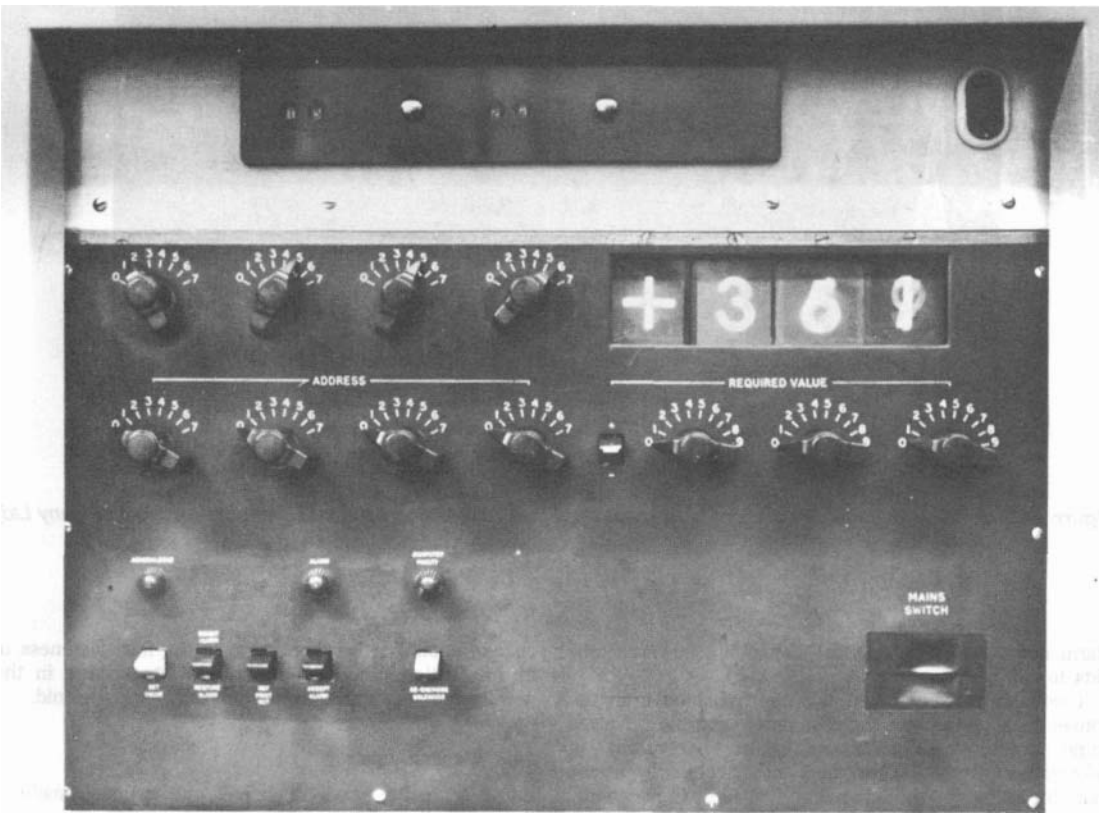


Figure 14.5(a) *Control panel of the direct digital control (DDC) computer on ICIs ammonia soda plant at Fleetwood, 1961 (Courtesy of Ferranti Ltd and Imperial Chemical Industries Ltd)*

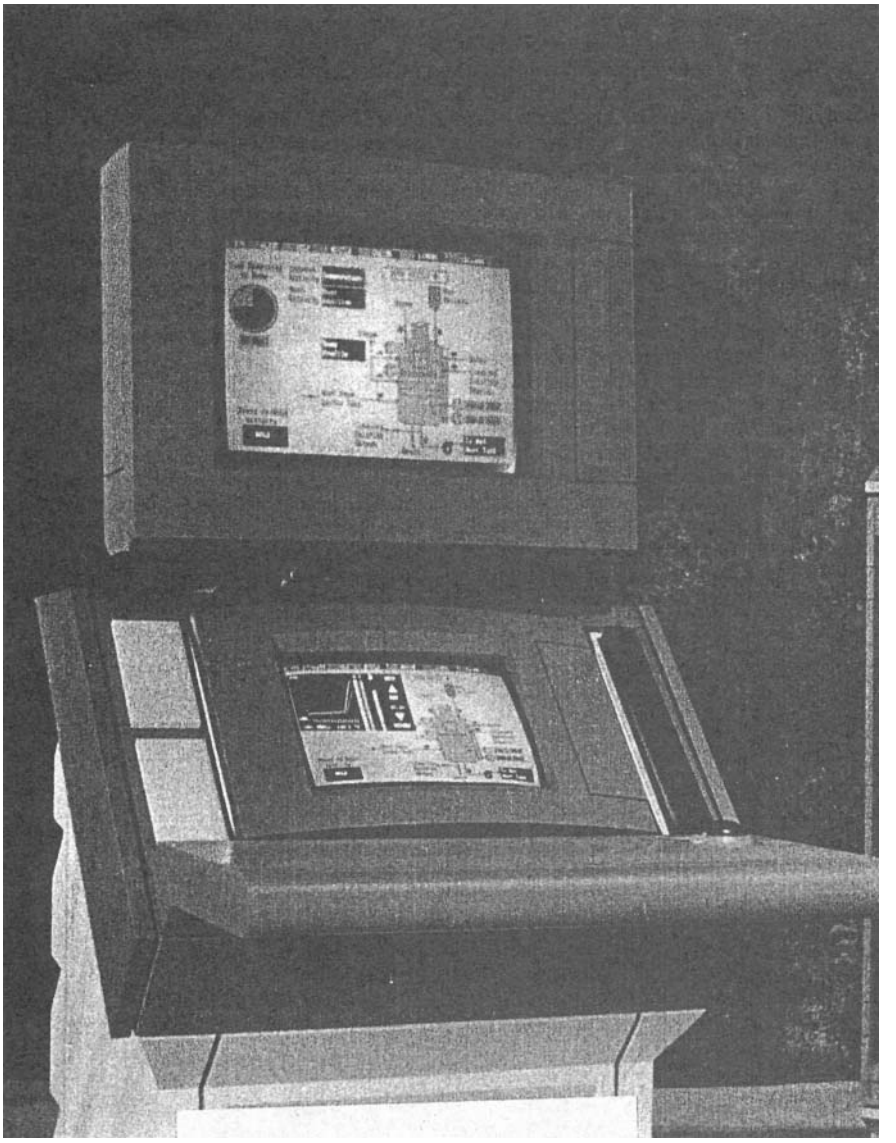


Figure 14.5(b) *Control panel and display of Foxboro Intelligent Automation computer system (Foxboro Company Ltd)*

fascias, the light on the former indicating the number of the local fascia on which the alarm has occurred. These authors also describe hierarchical systems with additional levels. Another arrangement is a mimic panel with alarms located at the relevant points on the flow diagram.

In computer-controlled systems alarms are generally printed out on hard copy in the time sequence in which they occur and are also displayed on the VDU. On the latter there are numerous display options, some of which are detailed by Kortlandt and Kragt. One is the use of a dedicated VDU in which the alarms come up in time sequence, as on the printer. Another is a group display in which all the alarms on an item of equipment are shown with the active alarms(s) highlighted. Another is a mimic display akin to the hardwired mimic panel.

The occurrence of an alarm is normally accompanied by an audible warning in the form of the sounding of the hooter and a visual warning in the form of a flashing light. On a computer system, the sound of the printer serves as another form of audible signal. The operator 'accepts' the alarm by depressing the appropriate pushbutton.

Annunciator sequences are given in ISA Std S18.1: 1975 *Annunciator Sequences and Specifications,* which recognizes three types: (1) automatic reset (A), (2) manual reset (M) and (3) ringback (R). Automatic reset returns to the normal state automatically once the alarm has been acknowledged

and the process variable has returned to its normal state. Manual reset is similar except that return to the normal state requires operation of the manual reset pushbutton. Ringback gives a warning, audible and/or visual, that the process condition has returned to normal.

There are alarms on the trips in the Safety Interlock System (SIS). Operation of a trip is signalled by an alarm. The SIS alarm system, like the rest of the SIS, should be separate from the basic process control system (BPCS).

In a conventional instrument system, the hardware used to generate an alarm consists of a sensor, a logic module and the visual display. The sensor and the logic elements may be separate or may be combined in an alarm switch. Such combined switches are referred to as flow switches, level switches and so on.

In a computer-based system there are two approaches that may be used. In one, the computer receives from the sensor an analogue signal to which the program applies logic to generate the alarm. In the other, the signal enters in digital form. The latter can provide a cheaper system, but reduces the scope for detection of instrument malfunction.

Some basic requirements for an alarm are that it attracts the attention of the operator, that it be readily identifiable and that it indicate unambiguously the variable which has gone out of limit.

14.8.2 Alarm system features

As just described, an alarm system is a normal feature of process computer control. The scanning of large numbers of process variables for alarm conditions is a function very suitable for a computer. Usually the alarm system represents a fairly straightforward translation of a conventional system on to the computer. Specified limits of process variables and states of equipment are scanned and resulting alarms are displayed on a typewriter, necessarily in time order, and also on a VDU, where time order is one of a number of alarm display options.

The process computer has enormous potential for the development of improved alarm systems, but also brings with it the danger of excess. There is first the choice of variables which are to be monitored. It is no longer necessary for these to be confined to the process variables measured by the plant sensors. In addition, 'indirect' or 'inferred' measurements calculated from one or more process measurements may be utilized. This considerably increases the power of the alarm system.

Then there are a number of different types of alarm which may be used. These include absolute alarms, relative, deviation or set-point alarms, instrument alarms and rate-of-change alarms, in which the alarm limits are, respectively, absolute values of the process variable, absolute or proportional deviations of the process variable from the loop set-point, zero or full-scale readings of the instrument and rate of change of the process variable.

The level at which the alarm limits are set is another important feature. Several sets of alarm limits may be put on a single variable to give different degrees of alarms such as early warning, action or danger alarms. The alarms so generated may be ordered and displayed in various ways, particularly in respect of the importance of the variable and the degree of alarm.

The conventional alarm system, therefore, is severely limited by hardware considerations and is relatively inflexible. The type of alarm is usually restricted to an absolute alarm. The computer-based alarm system is potentially much more versatile.

The alarm system, however, is frequently one of the least satisfactory features of the control system. The most common defect is that there are too many alarms and that they stay active for too long. As a result, the system tends to become discredited with the operator, who comes to disregard many of the alarm signals and may even disable the devices which signal the alarms.

Computer-based alarm systems also have some faults peculiarly their own. It is fatally easy with a computer to have a proliferation of types and degrees of alarm. Moreover, the most easily implemented displays, such as time-ordered alarms on a typewriter or a VDU, are inferior to conventional fascias in respect of aspects such as pattern recognition.

The main problem in alarm systems is the lack of a clear design philosophy. Ideally, the alarm system should be designed on the basis of the information flow in the plant and the alarm instrumentation selected and located to maximize the information available for control, bearing in mind instrumentation reliability considerations. In fact, an alarm system is often a collection of subsystems specified by designers of particular equipment with the addition of some further alarms.

An alarm system is an aid for the operator. An important but often neglected question is therefore what action he is required to take when an alarm is signalled.

There are also specific problems which cause alarms to be numerous and persistent. One is the confusion of alarms and statuses. A status merely indicates that an equipment is in a particular state, for example that an agitator is not running. An alarm, by contrast, indicates that an equipment is in a particular state and should be in a different one, for example, that an agitator is not running but should be. On most plants there are a number of statuses that need to be displayed, but there is frequently no separate status display and so the alarm display has to be used. As a result, if a whole section of plant is not in use, a complete block of alarms may be permanently up on a display, even though these are not strictly alarm conditions. The problem can be overcome by the use of separate types of display, for example yellow for alarms, white for statuses, in conventional systems and by similar separate displays in computer systems, but often this is not done.

A somewhat similar problem is the relation of the alarms to the state of the process. A process often has a number of different states and a signal which is an alarm in one state, for example normal operation, is not a genuine alarm in another, as with, say, start-up or maintenance. It may be desirable to suppress certain alarms during particular states. This can be done relatively easily with a computer but not with a conventional system. It should be added, however, that suppression of alarms needs to be done with care, each case being considered on its merits.

On most plants there is an element of sequential control, for example start-up. As long as no fault occurs, control of the sequence is usually straightforward, but the need to allow for faults at each stage of the sequence can make sequential control quite complex. With sequential operations, therefore, the sequential control and alarm systems are scarcely separable. A computer is particularly suitable for performing sequential control.

The state of the art in alarm system design is not satisfactory, therefore. In conventional systems this may be ascribed largely to the inflexibility of the hardware, but the

continuance of the problem in computer systems suggests that there are also deficiencies in design philosophy.

The process computer provides the basis for better alarm systems. It makes it possible to monitor indirect measurements and to generate different types and degrees of alarm, to distinguish between alarms and statuses and to adapt the alarms to the process state. It is also possible to provide more sophisticated facilities such as analysis of alarms, as described below. However, there is scope for great improvement in alarm systems even without the use of such advanced facilities.

14.8.3 Alarm management

It will be apparent from the foregoing that in many systems some form of alarm management is desirable. Alarm management is discussed by the CCPS (1993/14). Approaches to the problem include (1) alarm prioritization and segregation, (2) alarm suppression and (3) alarm handling in sequential operations.

Alarms may be ranked in priority. The CCPS suggests a four level system of prioritization in which critical alarms are assigned to Level 1 and important but non-critical alarms to Level 2, and so on. The alarms are then segregated by level.

With regard to alarm suppression, the CCPS describes two methods. One is conditional suppression, which may be used where an alarm does not indicate a dangerous situation and where it is a symptom which can readily be deduced from the active alarms. The other is flash suppression, which involves omitting the first stage in the alarm annunciation sequence, namely the sounding of the hooter and flashing of the fascia lamp. Instead, the alarm is shown illuminated, as if already acknowledged.

As already discussed, sequential operations such as plant start-up tend to activate some alarms. With a computer-based system arrangements may be made for appropriate suppression of alarms during such sequences.

Alarm management techniques need to be approached with caution, taking account of the overall information needs of the operator, of the findings of research on the operation of alarm systems and of other factors such as the fact that an alarm which is less important in one situation may be more so in another.

14.8.4 Alarm system operation

Studies of the operation of process alarm systems have been conducted by Seminara, Gonzalez and Parsons (1976) and Kragt and co-workers (Kortlandt and Kragt, 1980a,b; Kragt, 1983, 1984a,b; Kragt and Bonten, 1983; Kragt and Daniels, 1984).

The work of Seminara, Gonzalez and Parsons (1976) was a wide-ranging study of various aspects of control room design. On alarms, two features found by these authors are of particular interest. One is that, in some cases, the number of alarms was some 50–100 per shift, and in one case 100 in an hour. The other is the proportion of false alarms, for which operator estimates ranged from 'occasional', through 15% and 30%, up to 50%.

Kortland and Kragt (1980a,b) studied five different control room situations, by methods including questionnaire and observation, two of the principal investigations being in the control rooms of a fertilizer plant and a high pressure polyethylene plant. On both plants, the authors identified two confusing features of the alarms. One was the occurrence of oscillations in which the measured values moved back and forth across the alarm limit. The other was the occurrence of clusters of alarms. The number of alarms registered on the two plants was as follows:

	Fertilizer plant	*Polyethylene plant*
Observation period (h)	63	70
Single alarms, not occurring during clusters or oscillations	816	1714
Single alarms during clusters or oscillations	280[a]	325[a]
Signals during oscillations	410[a]	NA
Signals from clusters	1288[a]	1300[a]
Total	2794	3339

[a] Estimated from analysis of the data.

The authors suggest that oscillations can be overcome by building in hysterisis, which is indeed the normal approach, and that clusters may be treated by grouping and suppression of alarms. The intervals between successive signals, disregarding oscillations and clusters, were analysed and found to fit a log–normal distribution. The response of the operators to the alarms was as follows:

	Fertilizer plant	*Polyethylene plant*
Signal followed by action (%)	47	43
Action followed by signal (%)	46	50
No action (%)	7	7

Thus about half the alarms were actually feedback cues on the effects of action taken by the operators, who in many cases would have been disturbed not to receive such a signal. Further evidence for this is given by the fact that on the fertilizer plant 55% of the alarm signals were anticipated. On this plant, the operators judged the importance of the signals as follows: important 13%, less important 36%, not important 43% and unknown 8%.

Kragt (1984a) has described an investigation of the operator's use of alarms in a computer-controlled plant. The main finding was that sequential information presentation is markedly inferior to simultaneous presentation.

14.9 Fault Administration

As already stated, it is the function of the control system to avert the development of conditions which may lead to shut-down, but if necessary to execute shut-down. Generally, there are automatic trip systems to shut the plant down, but the responsibility of avoiding this situation if at all possible falls to the operator.

Fault administration can be divided into three stages: fault detection, fault diagnosis and fault correction or shut-down. For the first of these functions, the operator has a job aid in the form of the alarm system, while fault correction in the form of shut-down is also frequently automatic, but for the other two functions, fault diagnosis and fault correction less drastic than shut-down, he is largely on his own.

14.9.1 Fault detection

The alarm system represents a partial automation of fault detection. The operator still has much to do, however, in detecting faults. This is partly a matter of the additional

sensory inputs such as vision, sound and vibration that the operator possesses. But it is also partly due to his ability to interpret information, to recognize patterns and to detect instrument errors.

14.9.2 Fault diagnosis

Once the existence of some kind of fault has been detected, the action taken depends on the state of the plant. If it is in a safe condition, the next step is diagnosis of the cause. This is usually left to the operator. The extent of the diagnosis problem may vary considerably with the type of unit. It has been suggested, for example that whereas on a crude distillation unit the problem is quite complex, on a hydrotreater it is relatively simple (Duncan and Gray, 1975a).

There are various ways in which the operator may approach fault diagnosis. Several workers have observed that an operator frequently seems to respond only to the first alarm which comes up. He associates this with a particular fault and responds using a rule-of-thumb. This is an incomplete strategy, although it may be successful in quite a high proportion of cases, especially where a particular fault occurs repeatedly.

An alternative approach is pattern recognition from the displays on the control panel. The pattern may be static or dynamic. The static pattern is obtained by instantaneous observation of the displays, like a still photograph. The operator then tries to match this pattern with model patterns or templates for different faults. Duncan and Shepherd (1975b) have developed a technique for training in fault diagnosis in which some operators use this method. The alternative, and more complex, dynamic pattern recognition involves matching the development of the fault over a period of time.

Another approach is the use of some kind of mental decision tree in which the operator works down the paths of the tree, taking particular branches, depending on the instrument readings. Duncan and Gray (1975a) have used this as the basis of an alternative training technique. Yet another method is the active manipulation of the controls and observation of the displays to determine the reaction of the plant to certain signals. Closely related to this is the situation where no fault has been detected, but the operator is already controlling the process when he observes some unusual feature and continues his manipulation to explore this condition.

Whatever approach is adopted by the operator, fault diagnosis in the control room is very dependent on the instrument readings. It is therefore necessary for the operator to check whether the instruments are correct. The problem of checking to detect malfunctions is considered later, but attention is drawn here to its importance in relation to fault diagnosis.

These different methods of fault diagnosis have important implications for aspects such as displays and training. The conventional panel assists the recognition of static patterns, whereas computer consoles generally do not. Chart recorders aid the recognition of dynamic patterns and instrument faults. The question of training for fault diagnosis is considered later.

Fault diagnosis is not an easy task for the operator. There is scope, therefore, for computer aids, if these can be devised. Some developments on these lines are described below.

14.9.3 Fault correction and shut-down

When, or possibly before, a fault has been diagnosed, it is usually possible to take some corrective action which does not involve shutting the plant down. In some cases, the fault correction is trivial, but in others, such as operating a complex sequence of valves, it is not. Operating instructions are written for many of these activities, but otherwise this is a relatively unexplored area.

Fault correction is one of the activities for which interlocks may be provided. Conventional interlocks were described in the previous chapter and developments in computer software interlocks are outlined below.

Some fault conditions, however, require plant shut-down. Although fault administration has been described in terms of successive stages of detection, diagnosis and correction, in emergency shut-down usually little diagnosis is involved. The shut-down action is triggered directly when it is detected that a critical process limit has been passed.

There are differing philosophies on the problem of allocation of responsibility for shutting down the plant under fault conditions. In some plants, the operator deals with fault conditions with few automatic aids and is thus required to assure both safety and economic operation. In others, automatic protective systems are provided to shut the plant down if it is moving close to an unsafe condition and the operator thus has the economic role of preventing the development of conditions which will cause shut-down.

In a plant without protective systems the operator is effectively given the duty of keeping the plant running if he can, but shutting it down if he must. This tends to create in his mind a conflict of priorities. Usually, he will try to keep the plant running if he possibly can and, if shut-down becomes necessary, he may tend to take action too late. Mention has already been made of the human tendency to gamble on beating the odds. There are numerous case histories which show the dangers inherent in this situation (Lees, 1976b).

The alternative approach is the use of automatic protective systems to guard against serious hazards in the plant. The choice is made on the basis of quantitative assessment of the hazards. This philosophy assigns to the operator the essentially economic role of keeping the plant running.

Although the use of protective systems is rapidly increasing, the process operator usually retains some responsibility for safe plant shut-down. There are a number of reasons for this. In the first place, although high integrity protective systems with 2/3 voting are used on particularly hazardous processes (R.M. Stewart, 1971), the majority of trip systems do not have this degree of integrity. The failure rate of this simple 1/1 trip system has been quoted as 0.67 faults/year (Kletz, 1974d).

Protective systems have other limitations that apply even to high integrity systems. One is that it is very difficult to foresee and design for all possible faults, particularly those arising from combinations of events. It is true, of course, that even if a process condition arises from an unexpected source a protective system will usually handle it safely. But there remains a residual of events, usually of low probability, against which there is no protection, either because they were unforeseen or because their probability was estimated as below the designer's cut-off level.

Another problem is that a protective system is only partially effective against certain types of fault, particularly failure of containment. In such an event, the instrumentation can initiate blowdown, shut-off and shut-down sequences,

but while this may reduce the hazardous escape of materials, it does not eliminate it.

Yet another difficulty is that many hazards occur not during steady running but during normal start-up and shut-down or during the period after a trip and start-up from that condition. A well designed protective system caters, of course, for these transitional regimes as well as continuous operations. Nevertheless, this remains something of a problem area. Even with automatic protective systems, therefore, the process operator tends to retain a residual safety function. His effectiveness in performing this is discussed later.

14.10 Malfunction Detection

Another aspect of the administration of fault conditions by the control system is the detection of malfunctions, particularly incipient malfunctions in plant equipment and instruments. These malfunctions are distinguished from alarms in that although, they constitute a fault condition of some kind, they have not as yet given rise to a formal alarm.

Malfunction detection activities are not confined to the control system, of course. Monitoring of plant equipment by engineers, as described in Chapter 19, is a major area of work, usually independent of the control system. Insofar as the control system does monitor malfunctions, however, this function is primarily performed by the operator. The contribution of the computer to malfunction detection is considered later.

Detection of instrument malfunction by the operator has been investigated by Anyakora and Lees (1972a). In general, malfunction may be detected either from the condition of an instrument or its performance. Detection from condition is illustrated by observation on the plant of a leak on the impulse line to a differential pressure transducer or of stickiness on a control valve. Detection from performance is exemplified by observation in the control room of an excessively noise-free signal from the transducer or of an inconsistency between the position of a valve stem and the measured flow for the valve. Most checks on instrument condition require the operator to visit the equipment and use one of his senses to detect the fault. Most performance checks can be made from the control room by using instrument displays and are based on information redundancy.

Some of the ways in which the operator detects malfunction in instruments are illustrated by considering the way in which he uses for this purpose one of his principal detection aids – the chart recorder. Some typical chart records are shown in Figure 14.6. The operator detects error in such signals by utilizing some form of redundant information and making a comparison. Some types of redundant information are (1) *a priori* expectations, (2) past signals of instrument, (3) duplicate instruments, (4) other instruments and (5) control valve position.

Thus it may be expected *a priori* that an instrument reading will not go 'hardover' to zero or full scale, that it will give a 'live' rather than a 'dead' zero, that it will exhibit a certain noise level, that its rate of change will not exceed a certain value and that it is free to move within the full scale of the instrument. On the basis of such expectations, the operator might diagnose malfunction in the signals shown in Figures 14.6(b–f). However, the firmness of such expectations may vary with the plant operating conditions. For example, during start-up, zero readings on some instruments may be correct.

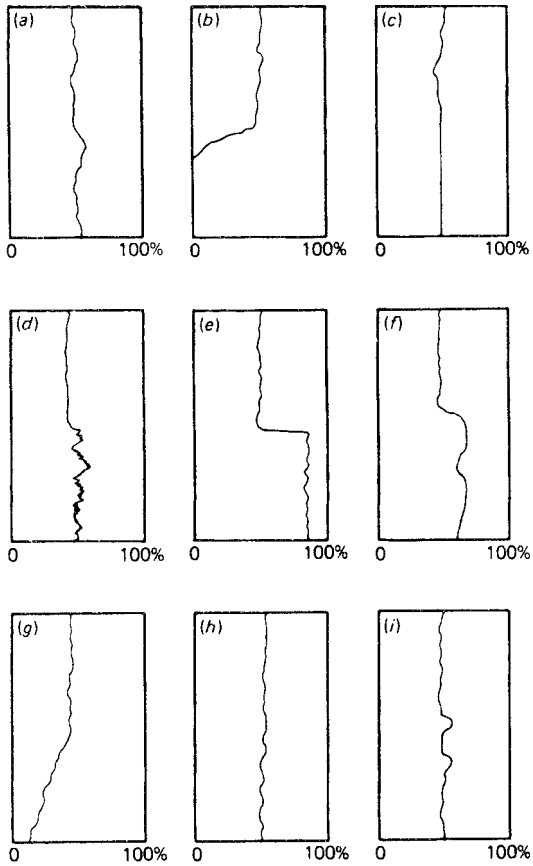


Figure 14.6 *Typical chart recorder displays of measurement signals (Anyakora and Lees, 1972a): (a) normal reading; (b) reading zero; (c) reading constant; (d) reading erratic; (e) reading suddenly displayed; (f) reading limited below full scale; (g) reading drifting; (h) reading cycling; (i) reading with unusual features (Courtesy of the Institution of Chemical Engineers)*

It may not be possible to decide *a priori* what constitutes a reasonable expectation. The level of noise, for example tends to vary with the individual measurement. In this case, the operator must use his knowledge of the range of variation of the noise on a particular instrument in the past. Thus, Figures 14.6(c) and 14.6(d) might or might not indicate malfunction.

If there is a duplicate instrument, then detection of the fact that one of the instruments is wrong is straightforward, although it may not be possible to say which. However, duplication is not usual in the normal instrument systems that are of primary concern here. On the other hand, near duplication is quite common. For example, the flow of a reactant leaving a vaporizer and entering two parallel reactors may be measured at the exit of both the vaporizers and the reactors, and the flow measurement systems provide a check on each other.

What constitutes a reasonable signal may depend on the signals given by other instruments. Thus, although a signal

that exhibits drift, such as that in Figure 14.6(g), may appear incorrect, a check on other instruments may show that it is not.

Some types of variation in a signal, such as a change in the noise level, appear easy to detect automatically. Others, such as that shown in Figure 14.6(i), are probably more difficult, especially if their form is not known in advance. Here the human operator with his well developed ability to recognize visual patterns has the advantage.

There are a number of ways in which the readings of other instruments can serve as a check. Some of these are (1) near-duplication, (2) mass and heat balances, (3) flow–pressure drop relations and (4) consistent states. This last check is based on the fact that certain variables are related to each other and at a given state of operation must lie within certain ranges of values.

The position of control valves also provides a means of checking measurements. This is most obvious for flow measurement but it is by no means limited to this.

These remarks apply essentially to measuring instruments, but checks can also be developed for controllers and control valves. A general classification of instrument malfunction diagnoses by the operator is shown in Table 14.6.

Many of the checks described do not show unambiguously that a particular instrument is not working properly; often they indicate merely that there is an inconsistency that needs to be explored further. However, this information is very important.

Another kind of information that the operator also uses in checking instruments is his knowledge of the probabilities of failure of different instruments. He usually knows which have proved troublesome in the past.

The detection of instrument malfunction by the process operator is important for a number of reasons. Instrument malfunctions tend to degrade the alarm system and introduce difficulties into loop control and fault diagnosis. Their detection is usually left to the operator and it is essential for him to have the facilities to do this. This includes appropriate displays and may extend to computer aids.

14.11 Computer-based Aids

There are some functions that the computer can perform automatically, whereas there are others which at present are performed by the operator, but for which computer aids have been, or may be, developed to assist him. Some computer-based aids to assist the operator which have been described include:

(1) system state display;
(2) alarm diagnosis;
(3) valve sequencing;
(4) malfunction detection.

The provision of such an aid is not solely a matter of engineering. There is an essential human factors angle also. A facility that is intended to assist the operator to perform a particular function, as opposed to replacing him by executing that function automatically, must conform to the requirements of the operator.

The main account of computer-based aids is given in Chapter 30. The treatment at this point is confined to consideration of one particular aid, computer-based alarm diagnosis. This, is in its own right, one of the most

Table 14.6 *General classification of methods of instrument malfunction detection (Anyakora and Lees, 1972a) (Courtesy of the Institution of Chemical Engineers)*

Measuring instruments

M1 Measurement reading zero or full scale
- M1.1 Reading zero
- M1.2 Reading full scale

M2 Measurement reading noise or dynamic response faulty
- M2.1 Reading constant
- M2.2 Reading erratic
- M2.3 Reading sluggish

M3 Measurements reading displaced suddenly
- M3.1 Reading fell suddenly
- M3.2 Reading rose suddenly

M4 Measurement reading limited within full scale
- M4.1 Reading limited above zero
- M4.2 Reading limited below full scale

M5 Measurement reading drifting
- M5.1 Reading falling
- M5.2 Reading rising

M6 Measurement reading inconsistent with duplicate measurement

M7 Measurement reading inconsistent with one other measurement
- M7.1 Reading inconsistent with near-duplicate measurement
- M7.2 Reading inconsistent with level-flow integration
- M7.3 Reading otherwise inconsistent

M8 Measurement reading inconsistent with simple model
- M8.1 Reading inconsistent with mass balance
- M8.2 Reading inconsistent with heat balance
- M8.3 Reading inconsistent with flow–pressure drop relations
- M8.4 Reading otherwise inconsistent

M9 Measurement reading inconsistent with plant operating state
- M9.1 Reading zero but variable not zero
- M9.2 Reading not zero but variable zero
- M9.3 Reading low
- M9.4 Reading high
- M9.5 Reading otherwise inconsistent

M10 Measurement reading inconsistent with control valve position
- M10.1 Reading (flow) zero with valve open
- M10.2 Reading (flow) not zero with valve closed
- M10.3 Reading otherwise inconsistent

M11 Measurement reading periodic or cycling

M12 Measurement reading showing intermittent fault

M13 Measurement reading faulty

M14 Measurement instrument tested by active tests

M15 Measuring instrument condition faulty

Control action and controllers

C1 Control action faulty
- C1.1 Control erratic
- C1.2 Control sluggish
- C1.3 Control cycling
- C1.4 Control unstable

C1.5 Control error excessive
C1.6 Control otherwise faulty
C2 Controller performance faulty
C3 Controller tested by active tests
C4 Controller condition faulty

Control valves and valve positioners
V1 Valve position inconsistent with signal to valve (this requires independent measurement of position)
V2 Valve position inconsistent with flow (but not necessarily flow measurement)
V2.1 Valve passing fluid when closed
V2.2 Valve not passing fluid when open
V2.3 Valve position otherwise inconsistent with flow measurement
V2.4 Valve position inconsistent with one other measurement
V2.5 Valve position inconsistent with simple model
V3 Valve not moving
V3.1 Valve stays closed
V3.2 Valve stays open
V3.3 Valve stays part open
V4 Valve movement less than full travel
V4.1 Valve not closing fully
V4.2 Valve not opening fully
V4.3 Valve travel otherwise limited
V5 Valve movement faulty
V5.1 Valve movement erratic
V5.2 Valve movement sluggish
V5.3 Valve movement otherwise faulty
V6 Valve movement cycling
V7 Valve or positioner performance faulty
V8 Valve or positioner tested by active tests
V9 Valve or positioner condition faulty

significant aids, but in addition it also illustrates the human factors problems which can arise.

14.11.1 Alarm analysis

In some process systems, the number of alarms that can be generated is large and it seems desirable to help the operator to assimilate these by an analysis of the alarms using a process computer. The problem is most acute in nuclear power stations and alarm analysis has been pioneered by the nuclear industry. Computer-based alarm systems, which include alarm analysis, were installed on the nuclear reactors at Oldbury (Kay, 1966; Kay and Heywood, 1966; Patterson, 1968) and at Wylfa (Jervis and Maddock, 1965; Welbourne, 1965, 1968).

The number of alarms in the systems described is very large. At Wylfa, for example, there are two reactors with some 6000 fuel channels, 2700 mixed analogue inputs and 1900 contacts on each reactor. These systems, therefore, represent an extreme form of the problem of potential information overload that is always encountered when a wide span of control is concentrated in one centralized control station. Some kind of information reduction is required if overload is to be avoided. Thus, alarm analysis was undertaken not as a desirable optional facility but rather as a matter of necessity. There are two possible objectives of alarm analysis that are related but distinct. The weaker one is to interpret fresh alarms as they appear in the real-time situation, whilst the stronger one is to identify the original, usually mechanical, cause.

On the Oldbury system, as described by Patterson (1968), the method of analysis is 'alarm tree analysis' in which the propagation of a fault is followed up through successively higher levels of the tree. A prime cause alarm is an active alarm at the lowest level. All important alarms are displayed together, with the cause alarm at the head of the group and the effect alarms beneath it. Other associated effect alarms that are not considered important for the operator's understanding of the fault are not displayed but are 'suppressed' or 'inhibited' by 'darkening'.

Initially, the alarms displayed were the prime cause alarms and the uninhibited alarms; the highest level alarm reached was not shown, unless it was an uninhibited alarm. It was found, however, that this system led to an excessive demand for more uninhibited alarms. It was, therefore, modified so that the highest alarm reached is always displayed. The operator thus knows how far the fault has propagated.

The analysis method at Wylfa, as described by Welbourne (1965, 1968) is rather similar. When a fresh alarm occurs, it is classed as a prime cause alarm, unless it could have been caused by an existing prime cause alarm, in which case it is classed merely as a new alarm. There are separate VDU displays for prime cause and new alarms. There is, however, no suppression of intermediate alarms.

At Oldbury, in addition to real process alarms based on plant sensors, messages may be generated based on such alarms. If the message relates to a fault, it is in effect a 'deduced alarm'. Similarly, at Wylfa there are 'synthetic' alarms. The number of alarms to be displayed at Oldbury proved to be rather larger than expected. It was necessary to increase the number of 32-line pages of alarms from 3 to 9. The number of alarms is also large at Wylfa, where there is no suppression of alarms.

It is apparent that there are a number of problems in the provision and use of an alarm analysis facility. They fall into two broad categories: those that are concerned with the engineering work involved in conducting a comprehensive analysis, and those that concern the use of the analysis by the operator.

The method of conducting the analysis in the systems described is that a team of experienced engineers studies systematically and in detail the various situations which can occur on the plant and the alarms to which these give rise. The engineering effort in the system described by Patterson was a team of five for 2 years.

As far as concerns process plants, an early exploration was undertaken by Barth and Marleveld (1967), but was not apparently followed through.

One of the main obstacles to the use of an aid such as alarm analysis is the large effort required to create the alarm data structure. It is clear that progress in its application to process plants would be greatly assisted by the development of a systematic and economical method of creating the alarm data structure. By the mid-1970s, there were indications of work in this area (Andow, 1973; Powers and Tompkins, 1974b; Andow and Lees, 1975).

Since that time, as described in Chapter 30, the development of real-time aids to assist the operator in handling fault conditions, including expert system aids, has been an active area of investigation, but progress is perhaps best described as sporadic.

Turning to the human factors aspects, alarm analysis is a facility to assist the operator. It is essential, therefore, to give the fullest consideration to the human factors problems that arise. Otherwise, the engineering effort is largely wasted.

The objective of alarm analysis is principally to assist the operator in handling rarely occurring but seriously hazardous situations. These occur typically as a result not of a single fault but of a combination of faults. If an analysis is to be useful, it must be sufficiently comprehensive to include these low probability but hazardous conditions, and it must do this in such a way as to convince the operator, who may be disinclined initially to believe in the existence of a low probability event or combination of events until he has exhausted the more familiar high probability causes. The point is well put by Rasmussen (1968b):

> It may be extremely difficult, if not impossible, for the designer of a large plant to carry through an analysis that takes into account not only all failures in the plant itself and the instrumentation, but also the combination of failures.
>
> One has to realize that direct automatic identification of the primary fault based on a not completely comprehensive analysis, which assumes that the operator critically evaluates the results of the analysis, involves a great risk of further decreasing that probability that the operator takes into consideration very improbable but hazardous failures not dealt with in the simplified analysis of the designer and thus of the instrumentation.
>
> If one utilizes a simplified analysis of failure conditions in this way, one may therefore be in the paradoxical situation that it is as risky for the operator to trust the analysis too much when it indicates a probable cause of failure as to incline towards distrusting it when it indicates an *a priori* improbable cause.

In addition to this problem of the confidence that the operator can place in the analysis, there is the question of the way in which the results are to be displayed. Moreover, the display of the analysis itself is not the whole of the display problem. A knowledge of the current state of the process is also necessary to the operator when a fault is detected. Both his own diagnosis and his corrective action depend very much on this background information. It is not satisfactory that he should have to begin his evaluation of the process state *ab initio* on detection of a fault before he can take action.

An additional aspect is the phenomenon of operator indecision. It has been found by several workers that an operator may have difficulty in bringing himself to actually take a control action. Thus Bainbridge (1974) describes this situation, which in her work occurred even in a simulation study:

> Another type of poor performance, independent of ability to think about the task, is shown by the subjects who can choose the action to take, considering more and more refined dimensions of this choice, but have difficulty in committing themselves to making it.

It seems reasonable to assume that this inability to come to the point of decision is largely a matter of the confidence that the operator has in his assessment of the situation and in his intended remedial action. This in turn depends to a considerable extent on his knowledge of the state of the process, on information redundancy in the displays, and so on.

14.12 Human Information Processing

At this point, it is necessary to devote some consideration to the topic of human information processing, some appreciation of which is essential to the understanding of modern developments in areas such as training and human error. The task of the process operator is largely one of processing information. An understanding of the characteristics of human information processing in such a task is therefore crucial to the design of his work situation. In particular, it can contribute to the design of the interface and to assessment of human error. The process operator as an information processor is described in *Information Processing and Human–Machine Interaction* (Rasmussen, 1986). The following is a simplified account of this work.

14.12.1 Cognitive task analysis

An account has already been given of the use of task analysis as an aid to understanding the task of the process operator and its role in design of the system and provision of assistance to the operator. Figure 14.7 shows a generalized framework for task analysis in process operation in the form of information processing activities required to pass from one state of knowledge to the next. The left-hand, upwards ladder gives the activities leading to evaluation of some plant state which requires action. The activities are (1) detection, (2) observation, (3) identification, (4) interpretation and (5) evaluation. The right-hand, downwards ladder gives the activities leading to action in response to that state. They are (1) evaluation, (2) interpretation, (3) definition of task, (4) formulation of procedure and (5) execution of procedure. Also shown in the diagram are some of the links that allow bypassing of intermediate stages.

Several different types of information processing are involved. There is analysis of the current state of the system, evaluation both of the current state and of the ultimate goal and planning of the task to be undertaken in response to that state.

14.12.2 Level of abstraction

The operator may think about the system at several different levels of abstraction: (1) physical form, (2) physical function, (3) generic function, (4) abstract function and (5) functional purpose. Consider the example of a pump. The level of physical form corresponds to the appearance of the pump. A typical representation at this level might be the symbol for a pump on the flow diagram. The level of physical function corresponds to the pumping function of the pump. The level of generic function corresponds to the maintenance of flow and that of abstract function to the maintenance of the mass and/or heat balance. These functions in turn contribute to the ultimate functional purpose of the plant. The levels of abstraction constitute a means–ends hierarchy, with the functional end at the top and the physical means of fulfilling this at the bottom.

In making decisions about the system, the operator may need to move between the different levels of abstraction. In an emergency situation, for example, he may have to step back and consider the ultimate functional purpose. If he decides that this is best served by maintaining the heat balance, he may consider whether to reconfigure the system. This is a decision at a lower level of abstraction. He may then decide to effect this by altering a flow and may alter this flow by making a physical change to a pump system. This takes the decision-making to still lower levels.

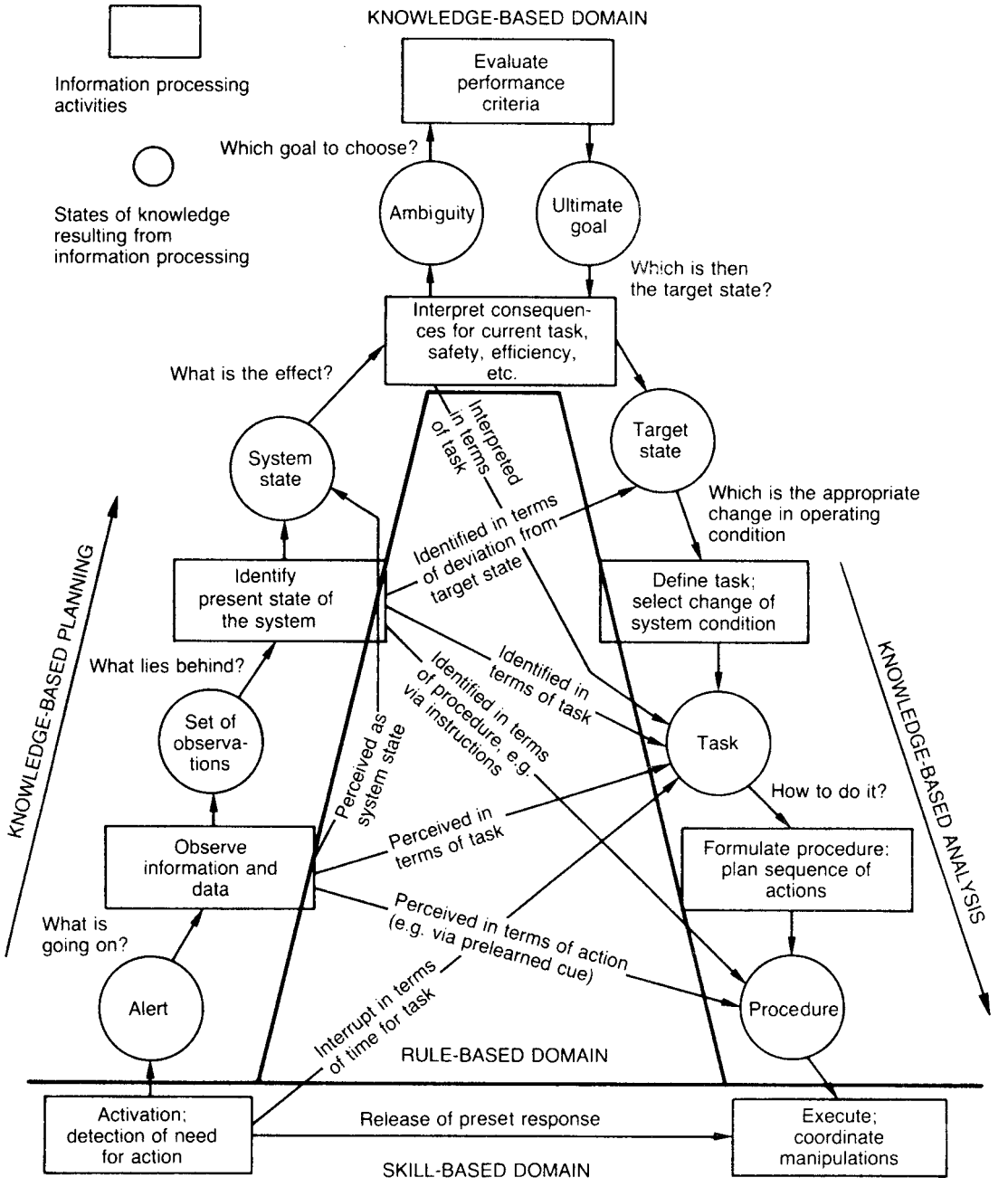


Figure 14.7 *The information processing activities of the operator in making a control decision represented as a ladder diagram (Rasmussen, 1986), The diagram also shows (a) bypassing of certain stages and (b) the domains of skill-based, rule-based and knowledge-based behaviour (Reproduced with permission of John Wiley & Sons Ltd from Information Processing and Human–Machine Interaction by J. Rasmussen, 1986, Copyright ©)*

14.12.3 Human behaviour in diagnostic tasks

One of the principal functions of the process operator is diagnosis. On a process plant, however, diagnosis is not entirely straightforward. If an equipment is known to have a fault, the response required from the maintenance technician is relatively simple. It is to identify the fault and repair it. With a fault on a process plant, fault matters are not quite so simple. The identification of the fault is typically not the

first priority. The priority is generally to evaluate the situation, decide whether the ultimate goal is to be modified, decide the new target state of the plant and define the tasks, and formulate and execute the procedures required to bring the plant to that state. Only if diagnosis of the fault is necessary to this sequence need it be undertaken at this stage.

A study of trouble-shooting in electronic equipment was undertaken by Rasmussen and Jensen (1973, 1974) as an example of human behaviour in a diagnostic task. They identified two broad search strategies:

(1) functional search;
(2) topographic search.

Functional search involves detailed observation of the specific characteristics of the fault, followed by interpretation in the light of a model of the system. It requires relatively few items of data but a possibly quite complex model. It is characteristic of the expert designer.

Topographic search is quite different. It involves a search through the system making a rapid sequence of good/bad checks until the fault is located. It requires a large number of items of data, on average, but only simple good/bad decisions. It is characteristic of the expert maintenance technician.

The maintenance technician is able to operate successfully a topographic search strategy using a rather general search procedure that is not dependent on the specific equipment or fault. The task is viewed not as one of solving a problem but of locating a faulty item. Aspects of the search strategy include search along the main flow path and hierarchical ordering of the search. The technician is also able to make do with a very generalized model of the system. In electronic trouble-shooting, the circuit diagram is used for simple purposes such as identification of the main signal paths rather than to obtain a full functional understanding.

In performing topographic search, the maintenance technician follows a strategy that he finds to be broadly optimal in terms of time and trouble. It may not appear optimal in terms of the conventional measures. He will tend to follow the line of least resistance and to take apparently impulsive decisions.

Behaviour in topographic search may sometimes appear to display a fixation. The search may come to an impasse. Even in these circumstances there is relatively little tendency to resort to the use of functional reasoning. The technician is likely to take a break and then to resume using a topographic search strategy again.

Functional search is often used to identify the subsystem that is faulty, prior to the use of topographic search on the subsystem. A common example is trouble-shooting on a TV set where the behaviour of the 'picture' may provide an indication of the type of fault and the associated faulty subsystem.

This work provides background to the diagnostic tasks performed by the process operator. The operator may utilize one of two broad strategies:

(1) topographic search;
(2) symptomatic search:
    (a) pattern recognition,
    (b) sequential decision-making.

The topographic search is based on a map of the system that shows the location of items the state of which can be observed and subjected to a good/bad check.

The symptomatic search may take two forms. It may involve assessment of the state of the system by some form of pattern recognition. Or it may involve a sequential process of decision-making equivalent to logical forms such as truth tables, fault trees and event trees. An alternative sequential approach is search by hypothesis and test.

These considerations have implications for various aspects affecting the operator such as information display, computer aiding and training.

14.12.4 Design of overall control system

Design of the overall control system for a process plant is seen by Rasmussen as involving three principal stages:

(1) definition of control requirements;
(2) analysis of the decision tasks;
(3) cognitive task analysis and design.

The designer defines the control requirements by moving down through the levels of abstraction, defining at each level the context of the control task, including the task specification from the level above and the resources available at the level below. The decision tasks implied in this scheme of control are then analysed. The decision ladder diagram given in Figure 14.7 provides a framework for such analysis.

In the cognitive task analysis, the designer formulates the possible information-processing strategies that the operator may use. System design does not require knowledge of the detailed mental models used by the operator. Rather it can be based instead on knowledge of the higher level, more generic, models which operators can and do use. The fact that different operators may use different detailed models also argues for a higher level approach.

Rasmussen gives several ladder diagrams illustrating the decision task analysis for different tasks and in different systems. These all have the same broad structure but differ in detail. For example, different diagrams apply for fully and partially automated systems.

14.12.5 Human behaviour in cognitive tasks

Rasmussen distinguishes three types, or levels, of human behaviour in tasks such as process control. Such behaviour may be:

(1) skill-based;
(2) rule-based;
(3) knowledge-based.

The relation between the three types is shown in Figure 14.8.

This description of operator behaviour by Rasmussen is frequently referred to as the skill-rule-knowledge, or SRK model. Skill-based, or skilled, behaviour occurs without conscious attention and is data-driven. Rule-based behaviour is consciously controlled and goal-oriented. Knowledge-based behaviour is also conscious and involves reasoning. These three types of behaviour apply to both parts of the decision ladder diagram, as shown in Figure 14.7.

Another, closely related distinction is that between (1) a signal, (2) a sign and (3) a symbol, illustrated in Figure 14.9. The distinction lies in the way in which the input is perceived. A signal is an input perceived simply as a continuous quantitative indicator of system state. A sign is perceived as an indication of some discrete state and often of the need for action. A symbol relates to some functional

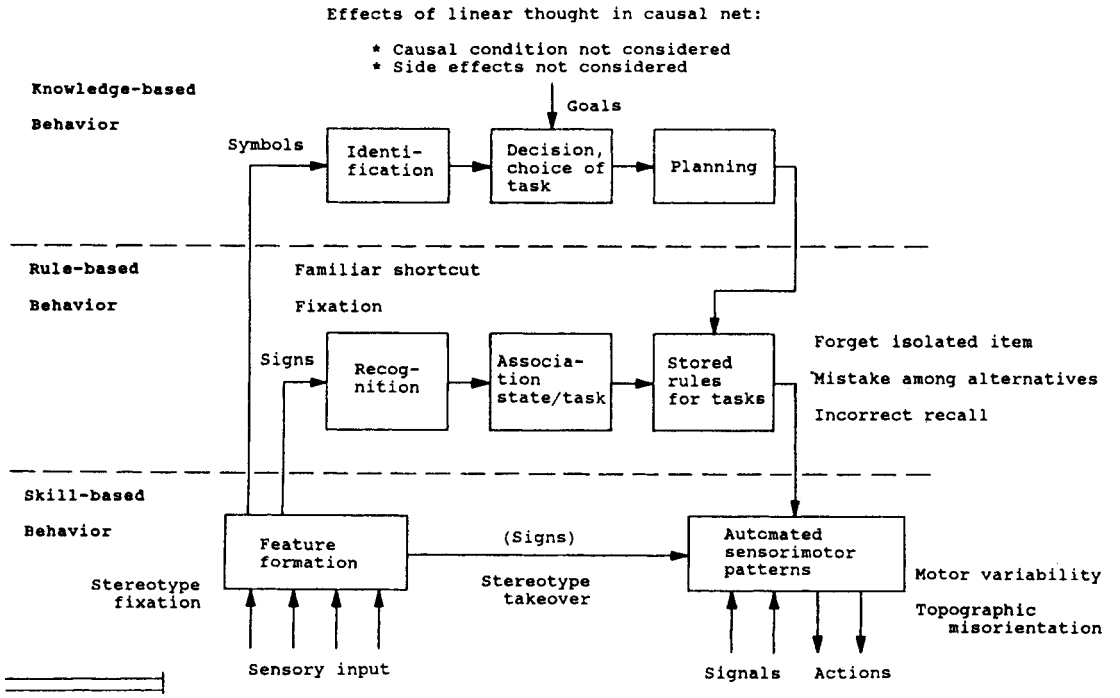


Figure 14.8 *The three levels of control of human actions: skill-based, rule-based and knowledge-based behaviour (Rasmussen, 1986) (Reproduced with permission of John Wiley & Sons Ltd from Information Processing and Human–Machine Interaction by J. Rasmussen, 1986, Copyright ©)*

property of the system. A sign cannot be used for functional reasoning about the system, which is the province of the symbol. Signs belong essentially to the domain of rule-based behaviour, and symbols to that of knowledge-based behaviour, as shown in Figure 14.8.

14.12.6 Human as control system component

Much work has been done on human behaviour in control tasks generally and in process control tasks in particular, and various characterizations have been developed of man as a component in a control system.

Rasmussen discusses the behaviour of the human as a component in a control loop, and his needs for aiding, in relation to the successively more difficult tasks of (1) direct manipulation, (2) indirect manipulation, (3) remote manipulation and, finally, (4) remote process control. In the first three cases, the operator receives information in analogue form and exercises a basic sensorimotor skill in a relatively simple space-time loop. This may not be so in the fourth case, where the signals on both the input, or sensory, channel and the output, or manipulative, channel, are likely to be symbolic and therefore to require translation. Such translation is a relatively high-level activity and therefore breaks the simple space-time loop.

In this light, the aim of the designer should be to restore to the operator the ability to apply to the task the basic sensorimotor skill. This requires that the designer do at least two things. On the sensory channel, the information presented should be based on symbols directly related to the function to be controlled. On the manipulative channel, the information presented should provide symbols and structure which allow the symbolic representation of the space-time feature to be directly manipulated.

14.12.7 Mental models used in cognitive tasks

At the level of knowledge-based behaviour, the operator requires to effect transformation between different types of model. Rasmussen identifies three strategies which he uses to do this: (1) aggregation, (2) abstraction and (3) analogy.

If a system is viewed with a high degree of resolution, it may appear complex. This complexity, however, is not an inherent property. If the elements of the system are aggregated into a larger whole by reducing the degree of resolution, a simplification may be achieved.

The apparent complexity of a typical control system is largely due to the one-sensor-one indicator technology. Given this technology, the operator has to transform the information by aggregation in order to reduce the complexity. Alternative forms of display can be devised which effect this aggregation for him. Another basic transformation strategy is shifting the level of abstraction. The operator moves between different levels of abstraction, as already discussed. The third strategy is analogy. This may be regarded as a special case of shifting the level of abstraction. Since systems that are physically different may have the same higher level model, a shift to this higher level may provide a useful analogy.

These considerations have implications for the decision support systems provided for the operator. Traditionally, displays consist mainly of measured values and some

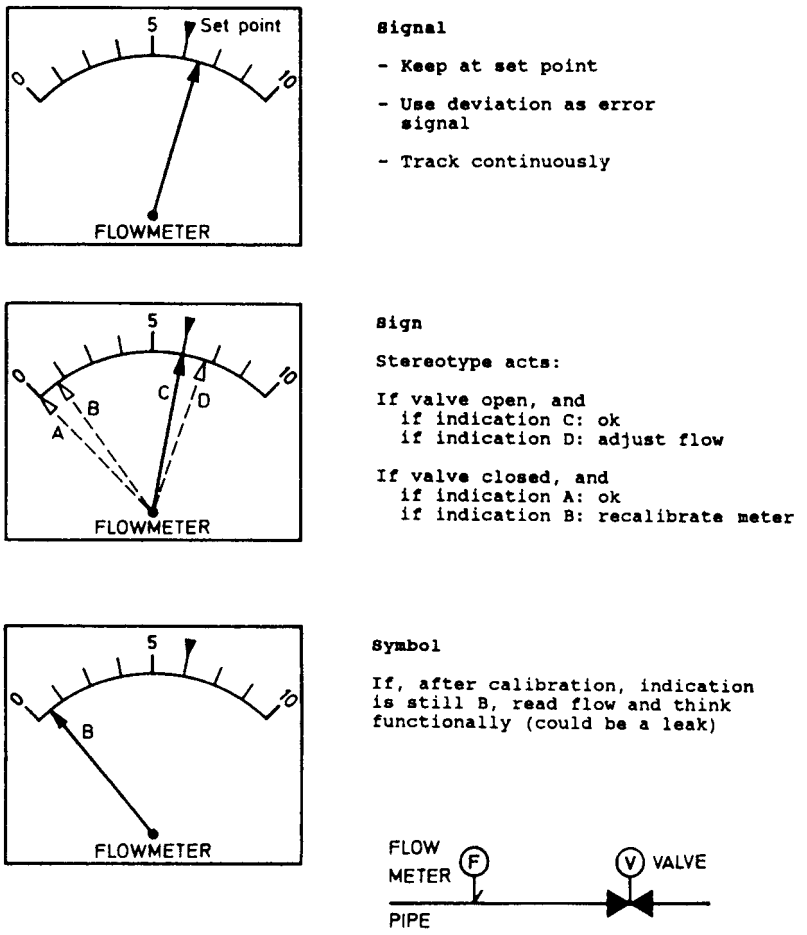


Figure 14.9 *Three perceptions of the same indication (Rasmussen, 1983): as a signal; as a sign; and as a symbol (Courtesy of the Institute of Electrical and Electronic Engineers)*

structural information such as mimic diagrams. There is relatively little that relates directly to the various levels of the means–ends hierarchy. There is need for displays to support decision-making at the different levels.

Lind (1981) has developed a description of process systems in terms of the mass and energy balances which has several levels and maps well onto the means–ends hierarchy. Goodstein (1984) has done work on multilevel displays. The provision at a higher level of abstraction of displays which give a one-to-one mapping between the appearance of the display and the properties of the process to be controlled allows rule- and skill-based behaviour to be extended to this higher level.

A functional representation can serve as a set of prescriptive signs. Cuny and Boy (1981) have shown that an electrical circuit diagram can be analysed as a set of signs controlling activities in design, installation and repair. A closely associated topic is co-operative decision-making where the computer supports human decision-making by undertaking parts of the information processing.

With regard to the form of mental models, the model used by man tends to be based on common-sense reasoning, or causal reasoning. As a model at the purely physical level, this does not have the precision of a formal mathematical model such as a set of differential equations, but it is serviceable and can be extended to higher levels of reasoning.

14.12.8 Human error in cognitive tasks

The causes of unsatisfactory system performance are technical faults and human error. The tracing of the causes of poor performance by an investigator is arbitrary to a degree. Rasmussen points out that there is a strong tendency for the trace to terminate if it reaches a human; it does not often pass through.

He discusses human error mainly in terms of human variability and of human–machine mismatch. This variability is a desirable characteristic. It is an important ingredient in human adaptability. In particular, it plays an important part in the learning processes. Small excursions outside limits are needed in order to learn where limits lie.

Similar experimentation underlies the development of rules-of-thumb.

If the environment is unforgiving, however, so that if such excursions prove to have bad effects it is not possible to recover, error becomes a problem. Overall, it is generally more fruitful both for error prevention and error prediction to concentrate on recovery from error than on the initial error.

At the level of knowledge-based behaviour, error may occur due to selection of an inappropriate goal or selection of an appropriate goal followed by incorrect implementation.

At the level of rule-based behaviour a prime cause of error is a change in the environment. Practice of a task leads to a tendency for knowledge-based behaviour to be replaced by rule-based behaviour and use of signs. If the environment changes so that the signs do not alter but the rules are no longer appropriate, error is liable to occur. This may be compounded by the tendency to utilize convenient, informal signs instead of formal signs and to modify rules to give more convenient sequences.

Human error may occur in a normal situation in the execution of familiar tasks. Some of the mechanisms include (1) motor variability, (2) topographic misorientation, (3) stereotype take-over, (4) forgetting an isolated item and (5) selecting an incorrect alternative.

Motor variability is exemplified by an operator applying different degrees of force to a set of valves so that one of them is not leak-tight. Selecting the wrong pump in a set of pumps is an example of topographic misorientation. Stereotype take-over is illustrated by switching during an emergency shut-down sequence to the regular shut-down sequence.

Forgetting an isolated item can take many forms. A typical form is omission of an isolated act. An analysis of nuclear plant test and calibration reports by Rasmussen (1980b) found that this category accounted for 50% of errors. Precisely because the act is an isolated one, the probability of initial error tends to be high and that of recovery low. Another form of forgetting an isolated item is incorrect recall of a number. Insertion by an operator of a wrong set-point is an example. An example of incorrect selection between alternatives is adding to a figure a correction factor which should in fact be subtracted.

Other types of human error occur in off-normal situations. Skill-based behaviour is appropriate to the normal situation, but if the situation changes it may no longer be appropriate. Generally, however, adaptation tends not to take place until a mismatch has occurred.

Rule-based behaviour is liable to two types of mismatch: (1) stereotype fixation and (2) stereotype take-over. An example of stereotype fixation is execution of a sequence of operations appropriate to normal dusts when in fact the dust being handled is radioactive and calls for additional precautions. Stereotype take-over, by contrast, is exemplified by an operator initially conscious of the need to vary a sequence of operations to suit the particular circumstances, such as the dust-handling task just described, but then relapsing into the normal sequence. Such interference is more likely to occur in situations where the mind is occupied by forward planning of other activities before the action concerned has been executed.

Another form of failure in rule-based behaviour is failure to switch to knowledge-based behaviour even though this is what the situation warrants. If the system has changed but the signs remain unchanged, rule-based behaviour based on the signs may no longer be appropriate.

An operator is typically faced with the display of a set of measurements. It is apparently the expectation of the designer that he will interpret them using knowledge-based behaviour. In fact, an operator relies not so much on sets of relationships between variables as on linear sequences of events. He does not derive states and events from sets of relations but utilizes state and event indicators. Thus, if the system changes, the operator is required not only to shift to knowledge-based behaviour but also to cease interpreting information as signs and to interpret it instead as symbols. His difficulty is compounded if the information sources are attended to sequentially.

Once the domain of knowledge-based behaviour is entered, it becomes much more difficult to characterize the mechanisms leading to mismatch. Some types of human error which may occur in this situation include the following: (1) slips, mistakes and interference; (2) premature selection of a hypothesis; and (3) inappropriate testing of a hypothesis and (4) failure to map/match resource to goal. Rasmussen concludes that given current types of display, the situation is generally too unstructured to permit the development of a model of the problem-solving process and hence the identification of typical error modes.

The taxonomy for description and analysis of events involving human malfunction given by Rasmussen is shown in Figure 14.10. Human malfunctions are classified as external or internal malfunctions. An external malfunction relates to omission or commission of acts that affect the state of plant equipment. An internal malfunction relates to decisions made at some level on the decision ladder. The scheme is not hierarchical. It allows quite a high degree of resolution. It is based on internal rather then external malfunctions, which retains the internal structure of the error, allows a reasonably economical description of it and avoids the combinatorial explosion that is liable to occur in a scheme based on external malfunctions.

One of the factors which affect the probability of error is stress. However, although much work has been done on the effects of stress, relatively little is applicable to cognitive tasks. An abnormal situation tends to result in a modification of behaviour even if there is little stress. But frequently in an abnormal situation, there is an increase in stress. Apart from the effect of anxiety, there are some specific effects related to the cognitive task itself. The need to apply functional reasoning to a disturbed function increases the workload and reduces the time available for general monitoring of the state of the system. At the same time, the existence of abnormal conditions means that familiar indicators may be less reliable as guides to the state of the system. There is a tendency for the operator to focus on the disturbed function and thus to exhibit the cognitive tunnel effect. The need for shifts of strategy is another factor increasing stress.

Work on pilot performance by Bartlett (1943) indicates that under stress the tendency is for skilled subroutines to be retained but for the higher level co-ordination of these routines to deteriorate.

14.12.9 Models of human information processing

There exist a variety of models of human information processing activities which may have a contribution to make in the present context. These are reviewed by Rasmussen in respect of the characteristics of each model and of its relationships with the other models. The models are summarized in Table 14.7.

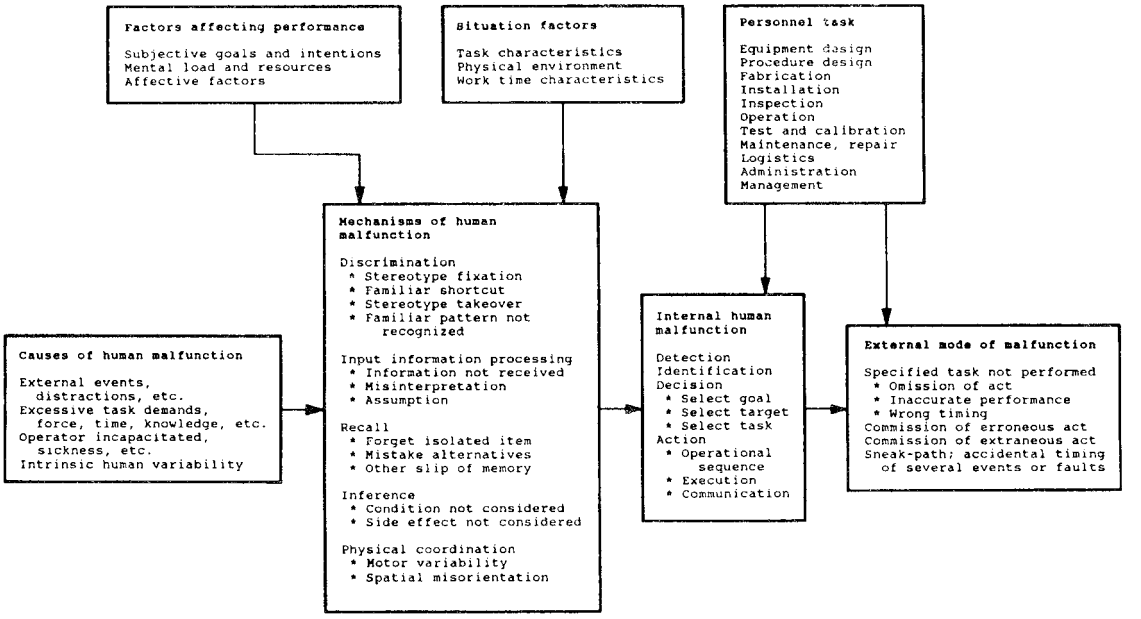


Figure 14.10 *A taxonomy for description and analysis of events involving human malfunction (Rasmussen, 1982b) (Reproduced with permission of John Wiley & Sons Ltd from High Risk Safety Technology By A.E. Green, 1982, Copyright©)*

Table 14.7 *Some models of human information processing*

Model	*Further description*	*References*
Attention allocation	Queueing theory	Carbonell (1966); Senders and Posner (1976); Rouse (1977)
	Sampling theory	Senders (1964)
Detection	Signal detection	Wald (1947); Sheridan and Ferrell (1974)
	Estimation theory	Gai and Curry (1976)
Manual control		Crossman and Cooke (1962); Pew (1974); Sheridan and Ferrell (1974); Baron *et al.* (1982)
Human judgement		Hammond, McClelland and Mumpower (1980)
Decision theory		Keeney and Raiffa (1976)
Behavioural decision theory	Subjective probability and its revision by Bayesian approach	W. Edwards and Tversky (1976)
Psychological decision theory	Subjective probability	Tversky and Kahneman (1974)
Social judgement	Expert judgement	Hammond, McClelland and Mumpower (1980); Brehmer (1981)
Information integration theory	Cognitive algebra of stimulus–response	N. Anderson (1974)
Attribution theory		Heider (1958); Kelley (1973)
Fuzzy set theory		Zadeh (1965); Gaines (1976); Gaines and Kohout (1977)
Artificial intelligence models	Expert systems	Ringle (1979); Schank and Abelson (1977); Feigenbaum (1979)
	Problem-solving	Newell, Shaw and Simon (1960); Newell and Simon (1972); Dreyfus (1972)

14.13 Task Analysis

The analysis of the task to be done logically precedes other stages of the design process, such as interface or training design, as shown in Figure 14.1. Insofar as any analysis of the operator's task is made in the process industries, this has traditionally tended to be done implicitly in the course of writing the plant operating instructions. Increasingly, however, use is being made of more fundamental approaches, mainly based on the various forms of task analysis.

14.13.1 Hierarchical task analysis

Early work was given in *Task Analysis* (Annett *et al.,* 1971). The method described by these authors is hierarchical task analysis (HTA), in which the task is broken down into a hierarchy of task elements. The hierarchical task analysis method of Annett *et al.* has been developed by Duncan and co-workers (Duncan, 1974; Duncan and Gray, 1975a,b; Duncan and Shepherd, 1975a,b).

The method adopted is to break the task down into a hierarchy. The elements of the hierarchy are a goal, plans and operations. The task involves a goal and this is then redescribed in terms of the plans and operations necessary to achieve it. Operations are units of behaviour, typically with an action–information feedback structure. The main operations in the task of controlling an acid purification plant are shown in Figure 14.11, the full hierarchy of operations in Figure 14.12 and representative subordinate operations in a start-up procedure in Figure 14.13.

One of the difficulties in any task analysis is to know when to stop. Unless there is a suitable stopping rule, the redescription gets out of hand. The rule used is that redescription stops when the product of the probability p and the cost c of failure is acceptably low. The application of the rule is shown by the underlining in Figure 14.11. Double underlining indicates that this product has an acceptably low value. This is usually because the action required is trivial and does not call for training. Single underlining denotes a possible difficulty and perhaps need for training.

Thus, as mentioned in Chapter 8, this method is a type of hazard identification procedure and should take its place along with other such techniques. It conforms to the loss prevention approach of taking into account both the magnitude and probability of the hazard. Although the technique is intended primarily to assist in the design of training, it is not assumed that training is in all cases the right solution. On the contrary, in some instances other measures such as design alteration may be more appropriate.

The type of material that the method produces is shown in Table 14.8. The numbers in the left-hand column identify the operation in the corresponding box diagram of Figure 14.12. Thus 3/1.2 (Run plant) is operation 3, which is the second subdivision of operation 1. The column on the extreme right refers to further breakdown. Thus operation 4 is broken down into operations 11–13, which are detailed further down the table. The notes in the main body describe the operation, mentioning particularly any constraints or tolerance limits and also tentative suggestions for a training method. The columns headed I or F, and A, are checked with a cross if any difficulty has been found in the input or feedback to the operator (that is a sensory or perceptual difficulty) or if an action difficulty (inability to perform the motor act) has been found. The letter R indicates that the operation is redescribed elsewhere in the table.

The task analysis breaks the task down into operations which are carried out according to a plan. The simplest plan is a fixed sequence, but variable sequences may be handled, and training may be particularly important for these. One problem that task analysis studies reveal is the identification of equipment, such as bypass and isolation valves around control valves. Figure 14.14 shows a typical plant control valve and Figure 14.15 some representative bypass and isolation configurations, the variety of which can lead to confusion. Another problem is fault diagnosis, which is considered below.

14.13.2 Development of task analysis

Task analysis has now developed into a family of techniques, undertaken for a variety of purposes and employing different methodologies. Thus, for example, task analysis may be used as an aid to identifying information requirements, writing operating procedures, defining training

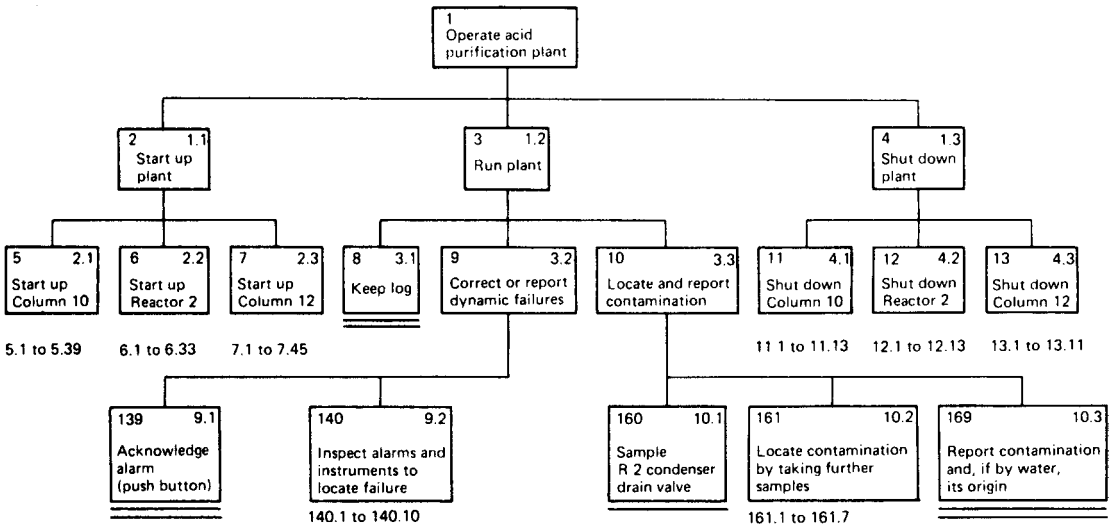


Figure 14.11 *Main operations in an acid purification task (Duncan, 1974) (Courtesy of Taylor & Francis Ltd)*

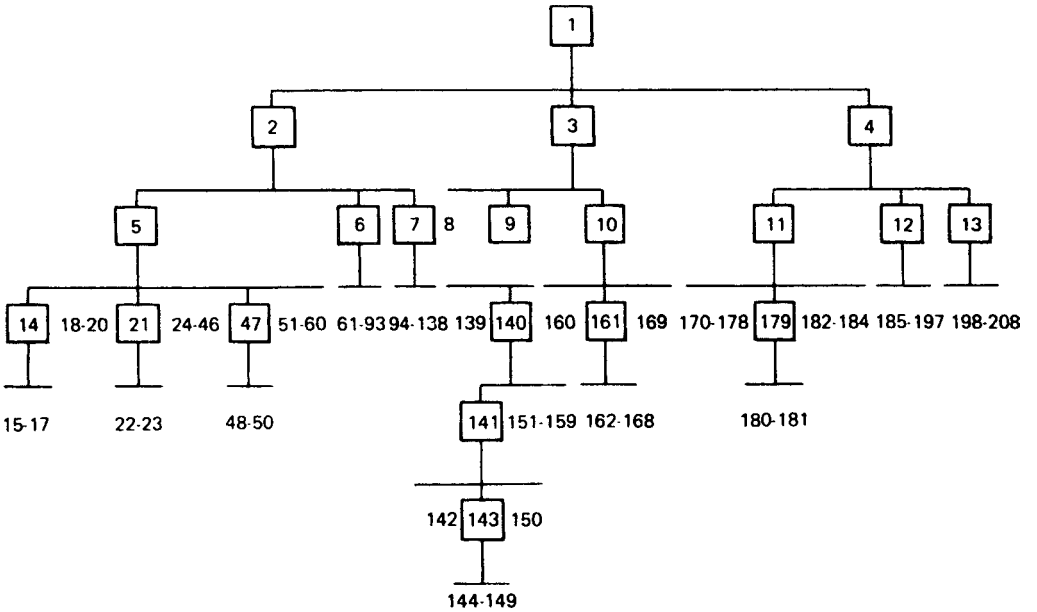


Figure 14.12 *Hierarchy of operations in an acid purification task (Duncan, 1974) (Courtesy of Taylor & Francis Ltd)*

needs, specifying manning levels, estimating human reliability in probabilistic safety assessment and investigating problems.

As far as concerns the methods, there are some 25 or more major techniques available. In effect, therefore, in many areas of human factors in the process industries, task analysis has become an indispensable tool.

14.13.3 Hierarchical task analysis: standard task elements

An approach to rendering hierarchical task analysis more systematic has been described by A. Shepherd (1993), with special reference to the information requirements of the process operator, as described below. In HTA, the task is decomposed into a set of subgoals for each of which there is a set of information requirements, which the author calls 'subgoal templates' (SGTs). He identifies five broad classes of task element:

(1) sequence elements (S);
(2) action elements (A);
(3) communications elements (C);
(4) monitoring elements (M);
(5) decision-making elements (D).

He further divides each class of element into subclasses to give the scheme shown in Table 14.9.

Shepherd illustrates the translation of a conventional HTA into his standard form by reference to the simple example shown in Figure 14.16. The original plan is:

> *Upon instructions from supervisor, do 1, then do 2, then when temperature = 100 degrees, do 3. Then if pH is within specification, do 4, otherwise do 5.*

This plan is translated into standard task elements as follows, where the left-hand side shows the plan and the right-hand side the standard elements:

Upon instruction from supervisor	—receive instruction (C4)
do	—then do (S1)
1 (Establish feeds)	—redescribed
then do	—then do (S1)
2 (Open steam valve to 7 psi)	—redescribed
then	—then do (S1)
when temperature = 100 degrees	—monitor to anticipate change (M2)
do	—then do (S1)
3 (Switch steam to 'automatic')	—activate (A1)
then	—then do (S1)
If pH is within specification	—monitor to anticipate change (M2)
do	—then do . . . either (S2)
4 (Switch feeds to 'automatic')	—activate (A1)
otherwise do	—then do . . . or (S2)
5 (Adjust feeds)	—redescribed

In this method sequence elements need to be introduced between each of the other elements. This serves to clarify for each subgoal in the task the information required and the time when it is needed. Another feature is that monitoring elements and decision-making elements need to be introduced within sequences to handle contingencies that may arise. Frequently in task analyses these elements are not made explicit.

14.13.4 Applications of task analysis: operator information requirements

A methodology for the definition of the information requirements of the process operator where he is part of a

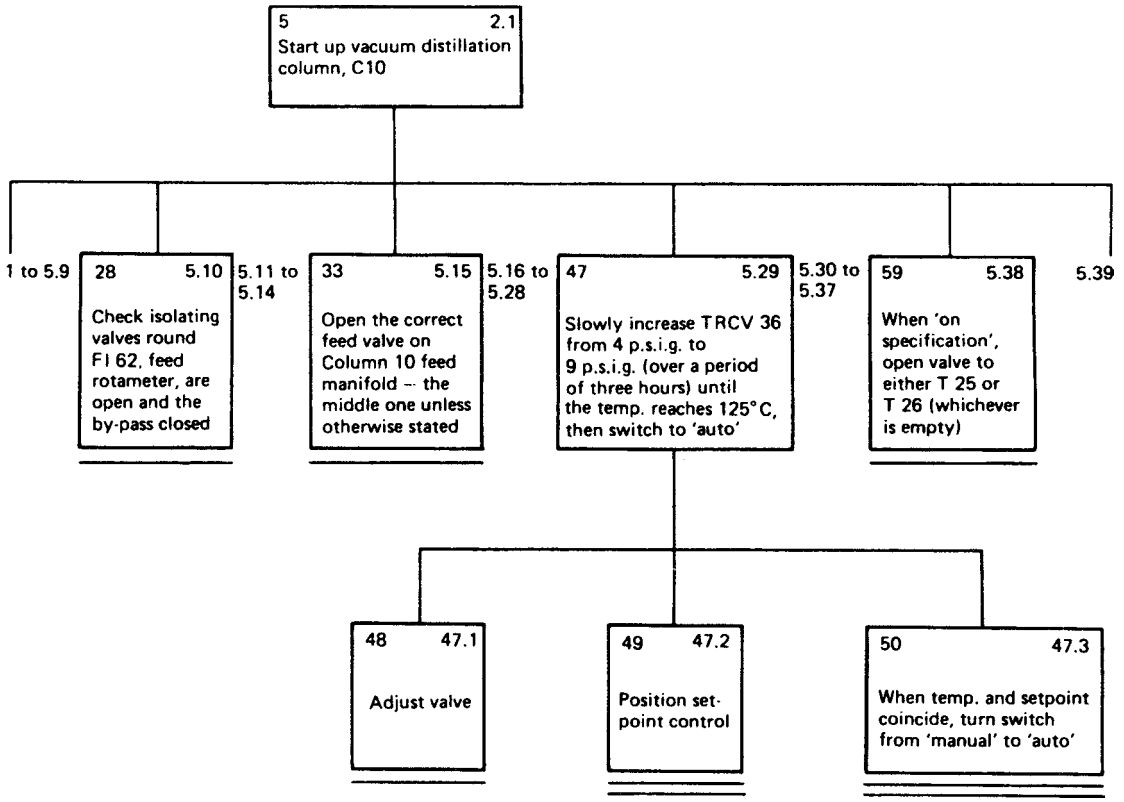


Figure 14.13 *Representative subordinate operations in a start-up procedure (Duncan, 1974) (Courtesy of Taylor & Francis Ltd)*

control loop has been described by A. Shepherd (1993) in the work just referred to. He describes a number of operator information acquisition problems found in industrial studies. One is 'breaking the loop'. In one case, the display of information on the effect of control actions was distant from the controls to be manipulated, being two floors up from the controls. In another, the problem was that the control actions on a rather sensitive distillation process on a batch plant had to be performed by interrupting work on preparation of batches and going to another part of the plant, with the result that the operators tended to adopt a rather conservative and uneconomic control strategy. In a third example, the target information and the controls – required to effect changes were shown on different VDUs because the VDUs were arranged to display information by geographical area on the plant and the equipments were in different areas, with the result that in order to make a change, two operators, each viewing one screen, had to shout across the control room to each other.

Another problem identified was 'information fragmentation'. This can arise where the operator has to examine several items of information before making a decision. In one case the operator was required to deal with disturbances in a particular part of the plant but in order to do so required information from points throughout the plant. This was not too difficult to do using the original conventional control panel but with a new VDU system it became very difficult, because the menu hierarchy was organized geographically and considerable search activity was involved in order to locate the necessary data.

14.13.5 Applications of task analysis: emergency stand-by system

Umbers and Reiersen (1994) have described the application of task analysis to assessment of an emergency stand-by system. This arose as part of the long-term safety review (LTSR) of the UK Magnox nuclear reactors, which includes the installation of a new, tertiary feed water system as stand-by for the two existing systems. Several task analysis techniques were used, including hierarchical task analysis and timeline analysis.

Information for the work was drawn from a wide variety of sources. The documentation consulted included the outline design specification, summary of safety arguments, fault study results, station operating procedures, site drawings and plant system drawings. Discussions were held with operations staff, the feed system designers and fire service teams. A timed walk-through was done.

Also of interest are the topics on which assumptions had to be made, including: plant status following a fault; system

Table 14.8 *Extracts from the analysis of an acid purification task (Annett et al., 1971) (Courtesy of HM Stationery Office)*

No.	*Description of operation and training notes*	*I or F*	*A redescribed*
1	Operate acid purification plant. R Instructions when to start-up or shut-down the whole process given by supervisor	–	X 2 to 4
2/1,1	Start-up plant. R Must memorize order of units, i.e. C10, R2, C12	–	X 5 to 7
3/1,2	Run plant. R Log keeping and sampling tests for contamination at intervals fixed by supervisor. Alarms signal dynamic failure	–	X 8 to 10
4/1,3	Shut-down plant. R Must memorize order of units for *routine* shut-down, i.e. C10, R2, C12. In an *emergency* units may be shut-down in any order depending on instructions, and an abbreviated procedure is followed	–	X 11 to 13
5/2,1	Start-up vacuum distillation column, C10. R Invariant order 5,1 to 5,39. Very long fixed procedure. Use job aid? Group steps under headings and learn order of headings? Few opportunities to practise in a continuous process plant. Delays due to plant response could be avoided and practice speeded on a simulator	–	X 14 18 to 21 24 to 47 51 to 60
6/2,2	Start-up hydrogenerator reactor, R2. R Invariant order 6,1 to 6,35. *See* 5	–	X 61 to 93
7/2,3	Start-up final water distillation column, C12. R Invariant order 7,1 to 7,45. *See* 5	–	X 94 to 138
8/3,1	Keep log		–
9/3,2	Locate and correct or report dynamic failures. R Acknowledge – first accept responsibility – then locate	–	X 139 and 140
10/3,3	Locate and report product contamination. R *Only report* contaminants other than water; *report and locate* water contamination	–	X 160, 161 and 169
11/4,1	Shut-down C10. R Invariant order 11,1 to 11,13. *See* 5. In emergency, procedure is abbreviated to suboperations 172, 170, 171, 174 *in that order.* This procedure and locations of console instruments must be overlearned	–	X 170 to 179 182 to 184
12/4,2	Shut-down R2. R Invariant order 12,1 to 12,13. *See* 5. In emergency, procedure is abbreviated to suboperations 188 to 193 *in that order. See* 11	–	X 185 to 197
13/4,3	Shut-down C12. R Invariant order 13,1 to 13,11. *See* 5. In emergency, procedure is abbreviated to suboperations 198 to 203 *in that order. See* 11	–	X 198 to 208
23/21,2	Turn switch from 'manual' to 'auto'		
25/5,7	Open inlet valve to reflux pump in use and check outlet, drain and valves about stand-by pump are closed (P66/67). I Must find way through plant to pump plinth 66/67 – 'landmarks' for learning plant geography? Pumps are labelled but inlet valve is one of six unlabelled hand valves on pump lines. Rote learn which is which, OR learn generalization and discrimination of classes of valves, i.e. *inlet, outlet or discharge*, and *drain!* Sketch to indicate relevant valves and lines against cluttered plant background?	X	– –
48/47,1	Adjust valve. A Compensatory tracking of pen movements to produce an acceptable slope on recorder. Plant control law might be simulated, but expense justifiable? Practice on the job under supervision feasible, but would be infrequent. F Examples of 'acceptable' and 'unacceptable' slopes could easily be provided	X	X –
78/6,18	Set up a pressure of 1 psig on the gauge after the block valve. Then check that there is a purge through the system by putting a hand over the outlet vent. F Must find way through plant to outlet valve. Once pointed out, vent is easily identified	X	– –
161/10,2	Locate origin of water contamination by taking further samples from other points on the plant. R The number and order of samples taken, i.e. suboperations, varies. Given (a) a relative cost index for each of 7 sampling points and (b) for each of 8 plant components, estimated probability of failure (i.e. contaminating product), the operator must apply a search strategy which minimizes sampling costs. Need flow	–	X 162 to 168

Table 14.8 *(continued)*

No.	*Description of operation and training notes*	*I or F*	*A redescribed*
	diagram showing only relevant information, i.e. (a) and (b). Simulation inevitable – in this case instructor might provide 'lab reports' for a series of 'faults' (occurring with a frequency proportional to their probabilities). Should trainee (1), be told efficient strategy, e.g. decision tree-prescribing branching sequence of samples? or (2), attempt unaided to minimize his sampling costs?		

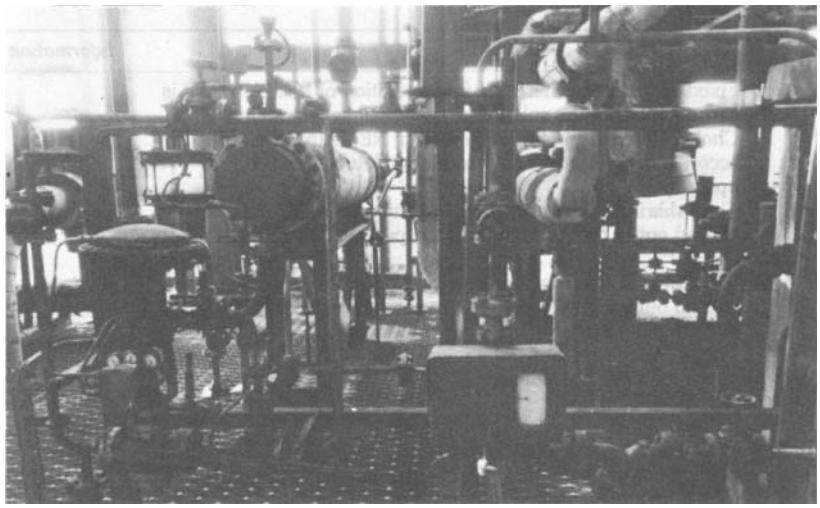
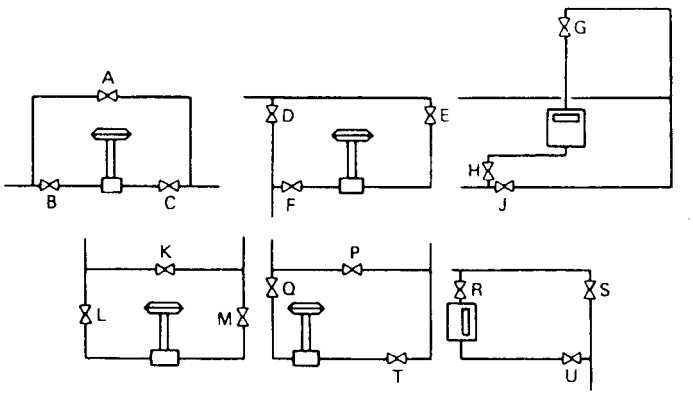


Figure 14.14 *A slave valve and sensing device with bypass and isolating configurations (Duncan, 1974) (Courtesy of Taylor & Francis Ltd)*



By-pass valves	Corresponding isolating valves
A	B,C
D	E,F
J	G,H
K	L,M
P	Q,T
S	R,U

Figure 14.15 *Some bypass and isolating configurations (Duncan, 1974) (Courtesy of Taylor & Francis Ltd)*

design aspects; maintenance and testing aspects; and the number, training and responsibilities of personnel.

The study had a number of outcomes. It gave estimates of the time to commission the tertiary feed water system in an emergency. It highlighted the importance of avoiding delay in establishing loss of the primary and secondary feeds and identified the indications of such loss, some of which varied as between one plant and another. It showed up potential errors and simple design enhancements to avoid them.

The work included a comparison of the commissioning times predicted by the task analysis with those found in

Table 14.9 *Standard task elements for hierarchical task analysis (A. Shepherd, 1993) (Courtesy of Taylor & Francis Ltd)*

Code	*Label*	*Description*	*Information suggestion*
S1	then do	Fixed sequence – where the first operation of REMAINDER is carried out upon completion of the previous operation	
S2	then do either . . . or . . .	Choice – where the first operation of REMAINDER varies in accordance with a specified condition detected in the first operation	
S3	Then do together . . . and . . .	Time sharing – where the first operation of REMAINDER is carried out at the same time as the previous operation	
S4	do in any order . . .	Sometimes it does not matter which order suboperations are carried out in. This is the case in setting-up operations, e.g. prior to plant start-up	
A1	Prepare equipment	The operator sets items of equipment, e.g. valves, in readiness for subsequent operations	Indication of alternative operating states. Feedback that equipment is set to required state
A2	Activate	The operator carries out an act locally on plant or on a central or local control panel to bring an item of equipment on-line or take it off-line, e.g. open valve, switch on centrifuge	Auditory or mechanical feedback that the action has been effective
A3	Adjust	The operator carries out an act locally or on a central or local control panel to adjust an item of equipment to modify operating rates, e.g. increase amps, adjust valve controller, decrease feed-pump rate	Feedback confirming controller position
A4	De-activate	The converse of A1	Auditory or mechanical feedback that the action has been effective
C1	Read	The operator reads a value of a parameter or listens to a sound, e.g. read pressure indicator	Indication of item
C2	Record	The operator records items of information for managerial purposes or to provide data for later stages in processing (e.g. remember, record)	Location of record for storage and retrieval
C3	Wait for instruction	The operator waits for an instruction before commencing the next action	Project wait time. Contact point
C4	Receive	The operator receives instructions pertinent to operation, e.g. to proceed or not proceed, adjustment to targets, priorities, running conditions, potential hazards	Channel for confirmation
C5	Give instruction/ information	The operator gives instructions or provides information (e.g. to management, other operators in plant, operators on other plants outside, suppliers, customers, services)	Feedback of receipt
C6	Remember	The operator commits information to memory (e.g. times to act, operating values, operating constraints)	
C7	Retrieve	The operator may be required to retrieve previously stored information to provide current operating information	Location of information for retrieval
M1	Monitor to detect deviance	Target values of particular parameters are to be maintained through specified	Key parameters to monitor

Table 14.9 *(continued)*

Code	*Label*	*Description*	*Information suggestion*
		phases of processing, usually as a precautionary action. This form of monitoring is usually intermittent, with low expectancy of deviation, unless certain preconditions have occurred. Often this form of monitoring is dealt with by attention grabbing alarms	
M2	Monitor to anticipate change	The operator anticipates change to detect a cue for a subsequent action. In contrast to M1, the operator expects change, usually after the passing of some time or the occurrence of an intermediate event	Key parameters
M3	Monitor rate of change	Where the current plant status is changing over time (e.g. during a plant start-up or other change of operating conditions), the operator may have to ensure that rates of change are within tolerance	Key parameters to monitor Change rates
M4	Inspect plant and equipment	The satisfactory state of equipment may only be determined by human inspection via the human senses	Access to symptoms
D1	Diagnose process problems	Operators must diagnose situations judged out of tolerance to determine a course of compensatory or corrective action	Information requirements must be identified in conjunction with training strategies
D2	Plan adjustment	The operator must observe conditions and work out a sequence of steps to move to a desired (safe) state in an acceptable fashion. Planning must anticipate the consequence of choices of intermediate actions and select only those which lead to acceptable conditions	Planning information deriving from analysis of typical cases
D3	Locate contaminant	In plants where there may be problems associated with contaminants entering pipework, through impure feeds or leaks in heat exchangers, there may be a need for examination of samples at various points in order to detect the site of the problem	Sample points in the system enabling the problem, eventually to be bracketed between a clean input and a contaminated output
D4	Judge adjustment	Often operators are required to make an adjustment to an item of equipment to affect processing conditions. The degree of adjustment must be judged prior to the action	The target indicator Adjustment values

demonstration exercises. The differences were attributable mainly to pessimistic assumptions made by the analysis.

14.13.6 Task Analysis Guide

A full treatment of the topic is given in *A Guide to Task Analysis* (Kirwan and Ainsworth, 1992) (the *Task Analysis Guide*). Other accounts include those by Drury *et al.* (1987) and A. Shepherd (1992).

The *Task Analysis Guide* divides task analysis methods into five broad categories: (1) task data collection, (2) task description, (3) task simulation, (4) task behaviour assessment and (5) task requirement evaluation. The *Guide* gives short accounts of a number of techniques under each of these headings. For task data collection the techniques are (1) activity sampling, (2) critical incident technique, (3) observation, (4) questionnaire, (5) structured interview and (6) verbal protocol. The task description techniques are (1) charting and networking methods, (2) decomposition methods, (3) hierarchical task analysis, (4) link analysis, (5) operational sequence diagram and (6) timeline analysis.

Task simulation is represented by (1) computer modelling and simulation, (2) simulator and mock-up, (3) table top analysis and (4) walk-through and talk-through. Techniques considered under task behaviour assessment are (1) barrier and works safety analysis, (2) event tree, (3) failure modes and effects analysis, (4) fault tree, (5) hazard

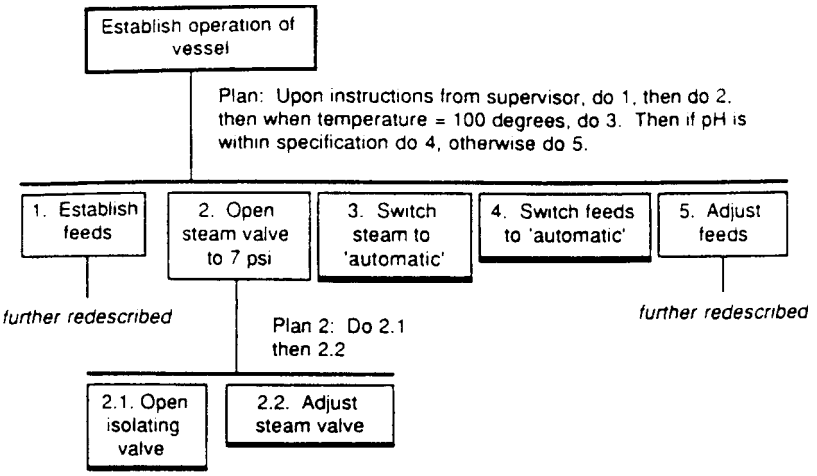


Figure 14.16 *Hierarchical task analysis of part of a process control operation (A. Shepherd, 1993) (Courtesy of Taylor & Francis Ltd)*

and operability (hazop) study, (6) influence diagram and (7) management oversight and risk tree (MORT). The task requirement techniques treated are (1) ergonomics checklists and (2) interface surveys.

The *Guide* also gives some 10 case histories of the application of task analysis to (1) allocation of function between humans and automatic systems, (2) preliminary communications system assessment, (3) plant local panel review, (4) staffing assessment for a local control room, operator workload assessment in a command system, (5) analysis of operator safety actions, (7) maintenance training, (8) quantification of effectiveness of ultrasonic inspection, (9) operations safety review and (10) a task analysis programme for a large plant.

14.13.7 CCPS *Guidelines*

Other task analysis methods are described in the *Human Error Prevention Guidelines* (CCPS, 1994/17), described in Section 14.38. Under the heading of 'action oriented techniques' they give an account of hierarchical task analysis, operator action event trees, decision/action flow diagrams, operational sequence diagrams and signal flow graph analysis. The two cognitive task analysis techniques given are the critical action and decision evaluation technique (CADET) and the influence modelling and assessment system (IMAS).

14.14 Job Design

Job design involves the arrangement of the individual tasks which the man has to do into a job which he is capable of doing and from which he obtains satisfaction. An account of job design is given by L.E. Davis and Wacker (1987).

As the control system becomes more automatic, the active control work of the operator is reduced and his function is increasingly one of monitoring. Such passive monitoring, however, is not a function to which man is well suited.

There is, therefore, a potential problem of job design. An entry to this problem is to consider why man is part of the control system at all. To a large extent, he is there as the component used by the designer to give the system a self-repairing capability. An approach to job design that starts from this fact is to develop explicitly those functions of the operator that are concerned with handling faults and keeping the plant running, notably fault administration and malfunction detection. These are tasks for which, in general, man has the ability and the motivation and they are entirely in line with the aims of loss prevention.

Such an approach requires more attention to be given to these functions of the operator and that he be given the necessary training and job aids. Training should emphasize the importance of running a tight ship and not tolerating degraded equipment. Job aids, including computer-based aids, should assist him in fault administration and malfunction detection.

Other aspects of job design such as workload and organization and social factors have been considered above.

14.15 Personnel Selection

There does not appear to be very much guidance available on selection methods for process operators. This is no doubt largely due to the difficulty of defining criteria for operator performance.

One of the first studies of the process operator was in fact that by Hiscock (1938), who described the development of a set of selection tests, but subsequent work by D.G. Davies (1967) showed little correlation between performance assessed by a selection test battery and by the judgement of supervisors.

It is probably true that enough is now known about process control skill to offer a better prospect of success in developing selection tests. The abilities that an operator needs are better understood. They include signal detection, signal filtering, probability estimation, system state evaluation, manual control and fault diagnosis. Tests may be devised to measure these abilities, using perhaps a computer-based simulator.

It is also important, however, to take into account in selection personal qualities. Crossman (1960) suggested that it is desirable that a process operator should be:

(1) Responsible – able to make satisfactory judgements on matters of discretion, so that his work does not need frequent checking by superiors.

(2) Conscientious – ready to take extra trouble and care, without direct instructions, when the situation demands it.
(3) Reliable – never making mistakes, forgetting instructions, overlooking important indications, etc., or otherwise failing in his prescribed duties.
(4) Trustworthy – honest and truthful in reporting to superiors; not concealing the facts when his own actions may have had adverse effects.

Other important factors are temperament, motivation and social skills. Temperament includes response to monotony and to stress. Motivation is partly an individual matter, but is also influenced by job design. Social skills cover the wide range of communication activities that the work entails.

The operator's job requires a reasonably high level of intelligence, particularly on large plants, but it is not necessary to look for a high intelligence score or university degree. The graduate sometimes makes a rather poor operator. The question of education is considered below together with that of training. A further account of personnel selection is given by Osburn (1987).

Selection for process control tasks is touched on in a study by the Advisory Committee on the Safety of Nuclear Installations (ACSNI, 1990) in relation to testing for trainability. The authors emphasize the need for the formulation of criteria for operator performance applicable to both training and selection, and thus imply that full development of selection tests must wait on the availability of such criteria. They do, however, consider it practical to select out individuals who have chronic stress problems or are unable to cope with high levels of stress. This aspect is also addressed by Weisaeth (1992), who describes the variability of individual response to the stress of emergency conditions.

The elimination of completely unsuitable individuals is probably the most useful feature of selection tests in other fields, such as those for aircraft pilots, which might appear to be a suitable model for some process situations.

A review of the state of knowledge and current practice on operator selection has been published by the HSE (1993 CRR 58).

14.16 Training

The training of process operators is an area in which more can be achieved and, in general, industry devotes considerable effort to this. An overview of training applicable to the process industries is given in *Training* (Patrick, 1992).

14.16.1 Training and education

There is a distinction to be made between training and education: the former is specific to a particular task or job, the latter is more general. The difference may be seen clearly in the evolution of training for electronic maintenance technicians in the US armed services (Shriver, Fink and Trexler, 1964). Initially, this involved a general education in electronics, but this did not prove very effective in training people to repair equipment. Latterly, the emphasis has been on specific training for the diagnostic tasks involved.

The question of the operator's mental model of the process and of his need for a scientific understanding of it was raised in the work of Crossman and Cooke (1962) on manual control and has been extensively discussed by subsequent workers (Attwood, 1970; Kragt and Landeweerd, 1974). Investigations in fairly simple manual control tasks do tend to suggest that it is better to train the operator in control strategies, controller settings, etc., but it is not clear how far this can be generalized to other tasks such as fault diagnosis.

In the United Kingdom, the City and Guilds Institute runs a Chemical Technicians Certificate (1972) that constitutes a substantial education in chemical processes. Such an educational background probably is beneficial, but it is not a substitute for specific training in process tasks.

General guidance on the training of process operators is given in the publications of the former Industry Training Boards (ITBs), in particular the Chemical and Allied Products ITB (CAPITB) and the Petroleum ITB (PITB). For example, CAPITB *Training Recommendation 12* (1971/9) contains *Information Papers* which represent outline approaches to job analysis, training needs, training programmes and fault analysis which the user should apply to his own plant, while other *Information Papers* such as that on distillation (1972/6) represent outline subject syllabuses. Another *Information Paper* (1971/5) deals with safety training. The work of Duncan and his colleagues has been supported by the CAPITB and has been published partly as reports of that body (Duncan and Shepherd, 1975a).

14.16.2 Training principles

> The job of the trainer is to observer and analyse, and to arrange to supply the right amount of the right kind of information to the learner at the right time. He must know a great deal about the task being trained, but the kind of knowledge needed is what comes from careful, objective analysis of the job and of the necessary skill rather than from the experience of becoming personally proficient. His task is to find out what factors affect the learning of the skill with which he is concerned, to watch the effects of varying them and to try to arrange the best combination.

This account by Holding (1965) highlights some of the important features in training. It brings out clearly the importance of the prior task analysis to determine where the operator may have difficulty and where training may be necessary. The content of training should be appropriate, which in effect means it should be related to these difficulties. The training should be at a suitable pace. It should provide feedback of results, since this is essential for learning.

Motivation of the trainee is another important factor and this can be strengthened by recognizing successful performance and treating failures objectively by explaining the cause in a non-condemnatory manner.

There are a number of classic problems in training. The training period may be spaced out or massed together. The task may be learned whole or in parts. The task may have to be done under some form of stress and this may need to be taken into account.

A particularly important question is the transfer of skill from one task to another. It is possible, for example, to achieve good performance in a particular task using methods such as decision trees that leave relatively little to the operator, but the penalty tends to be that he cannot transfer the skill to other tasks.

Many of these problems are discussed in the specific context of process control in the work of Duncan and

his colleagues (Duncan, 1974; Duncan and Shepherd, 1975a,b). A further account of concepts of training is given by Holding (1987). The relationship between training goals and training systems is described by Goldstein (1987) and the use of training simulators by Flexman and Stark (1987).

14.16.3 Process operator training

The process operator needs to have the safety training received by other employees also, but in addition has certain specific needs of his own. In this section, consideration is given to the content of training for process operators. A further account of operator training is given in Section 14.17. Safety training is considered in Chapter 28. Some topics for training are listed in Table 14.10.

In general, it is usually a mistake to provide numerous lectures on areas such as details of the process design or of the process computer program. It is better to stick fairly closely to the operator's own problems. Nevertheless, he does need to understand the process flow diagram, the unit operations which compose it and the control system. In addition, a basic understanding of the goals and constraints with which the plant manager operates and the possible changes of priorities that may occur is necessary.

The operator also requires some knowledge of the plant equipment and the instrumentation. In particular, he needs to be able to identify items and to carry out the manipulations for which he is responsible.

There are numerous operating procedures with which he has to become familiar. These include start-up, shut-down, batch operation and all other sequential routines.

The operator needs to learn to administer faults and, in particular, to interpret the alarm system, to diagnose faults and to detect incipient malfunction. He must also be thoroughly conversant with the emergency procedures.

The system of permits-to-work on a plant is extremely important and the operator requires to have a full grasp of the system used.

Training in fire fighting is a particularly important aspect of emergency work. The best training is provided by realistic fire fighting exercises in a training area dedicated to this purpose.

Operational malpractices develop on most plants. A typical example is the operation of furnaces at temperatures that drastically reduce creep life. If this can be foreseen, training may be given to counter this.

The operator has quite an important role to play in communicating information about plant operation to other people and it may be appropriate to include this in training.

Table 14.10 *Some aspects of the training of process operators*

Process goals, economics, constraints and priorities
Process flow diagram
Unit operations
Process reactions, thermal effects
Control systems
Process materials quality, yields
Process effluents and wastes
Plant equipment
Instrumentation
Equipment identification
Equipment manipulation
Operating procedures
Equipment maintenance and cleaning
Use of tools
Permit systems
Equipment failure, services failure
Fault administration
Alarm monitoring
Fault diagnosis
Malfunction detection
Emergency procedures
Fire fighting
Malpractices
Communications, record-keeping, reporting
See also Table 28.5

14.16.4 Fault diagnosis

Fault diagnosis is a particularly important activity of the process operator. It has been studied in detail by Duncan and his co-workers (Duncan, 1974; Duncan and Gray, 1975a,b; Duncan and Shepherd, 1975a,b) and is considered here as an example of training in a specific task.

Fault diagnosis is usually carried out by the operator at the control panel. Frequently, therefore, use is made of a panel simulator for training. The simulator used at the beginning of Duncan's work is shown in Figure 14.17. It represents a typical panel and the trainer sets up manually combinations of instrument readings corresponding to particular process conditions. The training is interrupted, however, by the rather slow process of resetting the simulator to represent the next set of conditions. Duncan and Shepherd (1975b) have overcome this problem by using a mock-up of the panel, shown in Figure 14.18, and back-projecting this on to a full-size screen in front of which the trainee operator can stand. Different sets of instrument readings can be brought up by projection without delay.

Using this device, Duncan and Shepherd have studied the training of operators to recognize different fault patterns on the panel. A cumulative part-training method was used in which the number of sets of faults was progressively increased. The subjects achieved encouragingly high rates of success in diagnosing faults. Debriefing of the subjects suggested that different diagnosis strategies were used. One was a pattern recognizer, looking first at the alarms and then considering possible failures consistent with these. Another examined first the instruments and then used hueristics based on plant functions.

An alternative approach is the use of decision trees as described by Duncan and Gray (1975a). Figures 14.19 and 14.20 show for a crude distillation column the decision tree and fault-symptom matrix, respectively. The operators were taught to use the decision tree to diagnose faults. Again a high success rate was achieved.

There are various ways in which the information in the decision tree in Figure 14.19 may be presented and learned. The tree as shown gives the faults in the 'natural' grouping. An alternative tree can be constructed in which the maximum number of decisions is reduced from 8 to 3, but the rationale of such a tree is no longer apparent, and the tree would be more difficult to remember. The method actually adopted was to retain the tree in its natural form and to use the 'linked lists' shown in Figure 14.21 to assist in learning it.

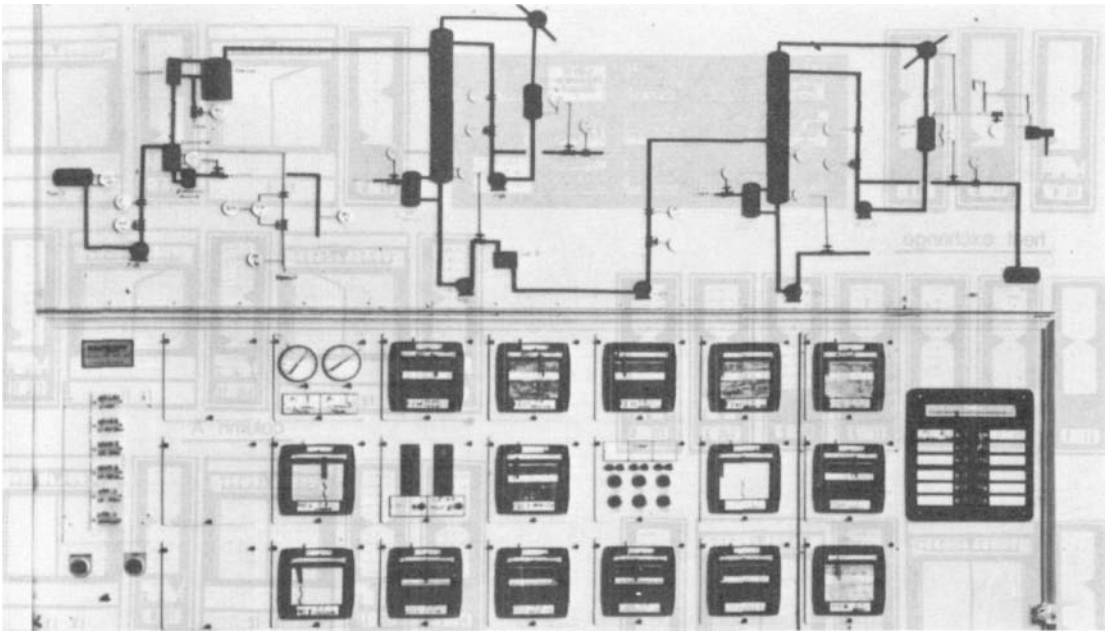


Figure 14.17 *The Carmody 'Universal Process Trainer' (Courtesy of Taylor & Francis Ltd; photograph courtesy of BP Chemicals (International) Ltd)*

Some of the decisions in the tree depend on the instrument readings, which may be in error. Training in the checking of instruments was therefore developed also. The emphasis here was on determining the true value of a parameter rather than on deciding the instrument failure. The following general principles were evolved for checking:

(1) Direct observation – represents truth.
(2) An outside report, such as a sight glass reading, is a direct observation only if the correct procedure for reading is followed.
(3) Two control instruments that agree represent truth.
(4) The costs (time, effort, danger) must be taken into account, and the cheapest route to truth taken.
(5) Only independent indicators of the same parameter can be used for checking.
(6) Where only two indicators of a parameter are available, the more reliable of the two is to be believed.
(7) An individual instrument may show itself to be faulty by deviant behaviour; for example, a straight line on a pen record.

This work brings out the importance of verifying the instrument readings before embarking on the main diagnosis. The need for this in the automated equivalent of computer alarm analysis was mentioned earlier.

This work also included the development of programmed learning texts to assist the operator to learn both the linked lists of the main decision tree and the instrument verification procedures. These developments in training do not of course solve the problem of diagnosing very rare but very hazardous fault conditions. It is doubtful if training is the proper approach to this problem. Such faults are better dealt with by the protective system; since they are very rare, the shut-downs involved are probably acceptable.

14.17 Training: ACSNI *Study Group Report*

A review of training is given in the *First Report: Training and Related Matters* of the ACSNI (1990). Although this is a report to the nuclear industry, it is applicable in large part to the process industries also. The report starts from the point that human error is the major source of accidents and refers to the cases of Three Mile Island and Chernobyl.

The authors treat the topic under the following headings: (1) definition of training, (2) the safety culture, (3) initiation of training, (4) internal monitoring, (5) training needs analysis, (6) criteria for operator performance, (7) standards for training, (8) methods of training, (9) central vs site-based simulators, (10) individual vs team training, (11) training for stress, (12) training of management, instructors, etc., (13) certification and (14) privatization. They state:

> It is misleading to think of training solely in terms of the transfer of items of verbal knowledge or technical skill from instructor to pupil. Although both knowledge and skill are necessary, they are not on their own sufficient to assure safety. They must be augmented by different qualities: habits of forethought and precaution that place minimization of risk first, and other goals such as short term performance or convenience, second.

The main purpose of training is to create a safety culture. The report rehearses some of the elements of this, which have already been described in Chapter 6. It is necessary that senior management give a lead and take certain specific measures. Line management should have operational

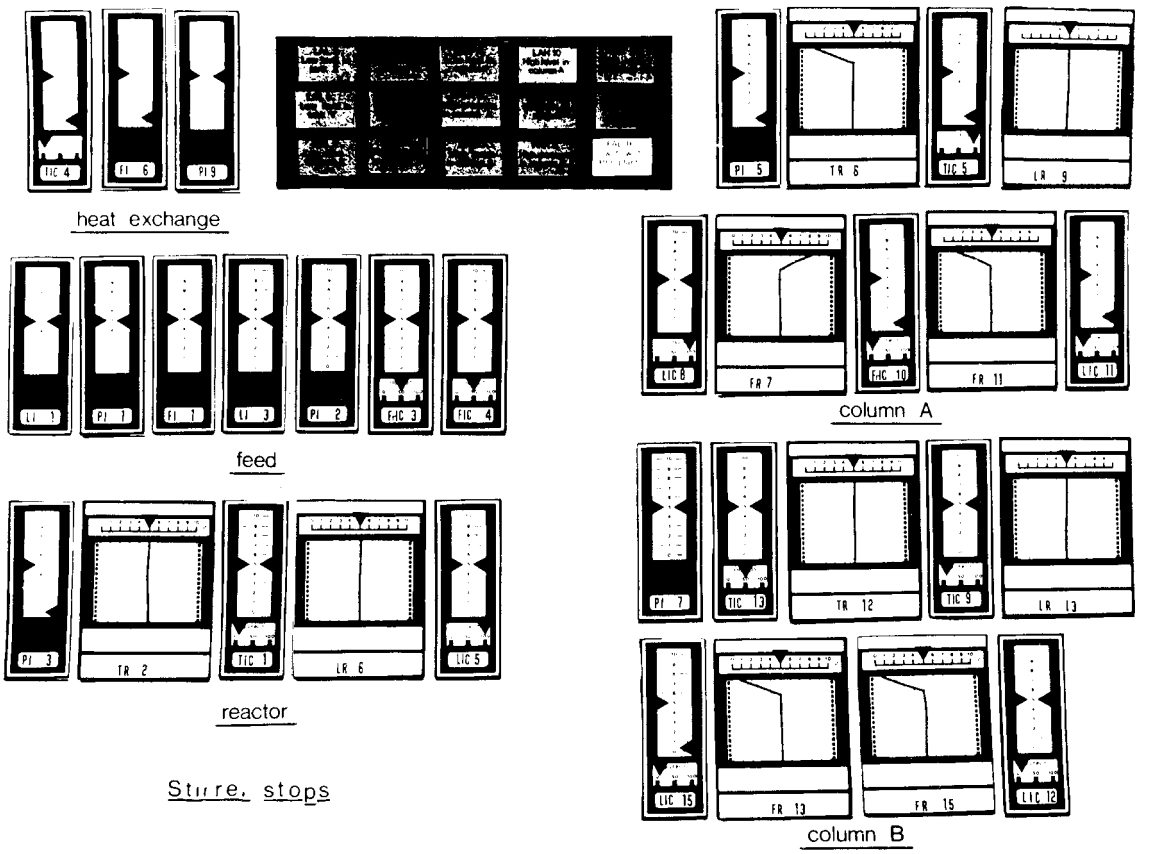


Figure 14.18 *Control panel display used for operator training (Duncan and Shepherd, 1975b) (Courtesy of Taylor & Francis Ltd)*

responsibility *inter alia* for safety and training. There should be monitoring of the safety culture using objective measures and independent assessment and a policy of continuous improvement with specific targets and with feedback to the workforce. Training should aim to rehearse the individual's experience deliberately so as to reinforce compliance and self-monitoring and awareness and reporting of hazards. Senior management should ensure not only that the organization has a suitable formal training system, but that it is operating effectively in practice.

Training should be monitored. One method of monitoring is the use of objective measures such as the frequency of accidents, incidents, operational deviations, trips, etc. Another method is to sample regularly what people say about the safety culture and about their own attitudes. The monitoring should be done by an assessor who is independent both of the local line management and of the training specialists.

Task analysis should be used to establish training needs. The analysis should specify in concrete terms the information to be supplied, the alternative actions that can be taken, and the quality of calculation or judgement the task requires. It may reveal different needs such as knowledge about equipment or practice in control skills, and thus point to different types of training such as lectures or use of a simulator.

Evidence from a number of industries shows that, even after quite thorough training, an individual may have little idea of the hazards of the job. The training should aim to raise the awareness of these hazards.

The report states that performance on the job should be not only monitored but also measured. This implies that there should be criteria of operator performance. Closely related to this is standards for training. The report accepts that it may be unrealistic to seek totally objective measures. Where these are not practical, it suggests that the assessment take the form of two independent assessments by supervisory staff using carefully defined rating scales and that these staff themselves receive training to ensure that the criteria used are consistent.

With regard to methods of training, the report refers to the distinction between skill-based, rule-based and knowledge-based behaviour and between responses to signal and to signs. Control skills such as making adjustments to maintain constant a single variable have become relatively less important on automated plant, but there are a range of control room skills which still need to be learned. Skills used in normal operation may perhaps be adequately learned on the job, but this is not so for skills required in

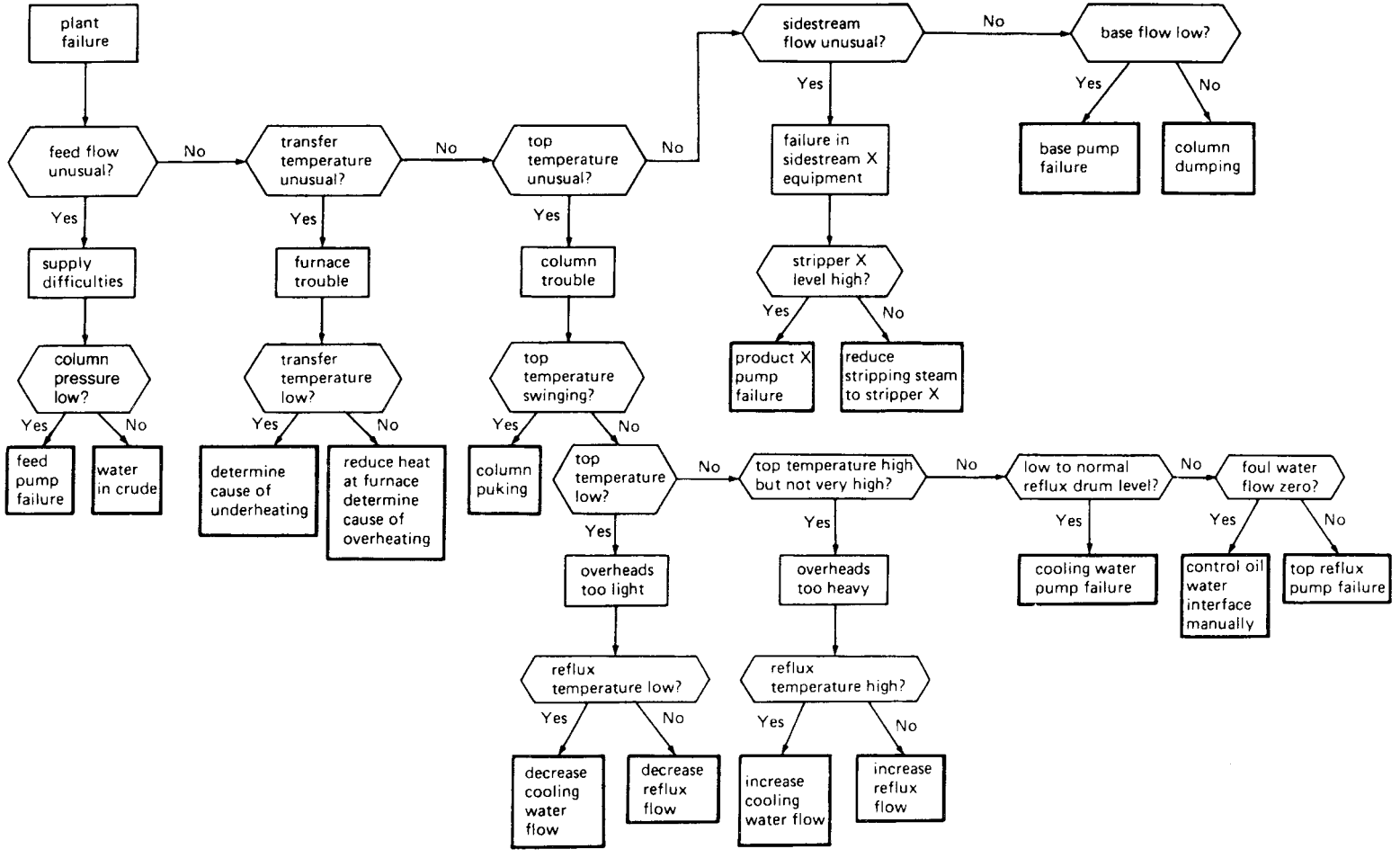


Figure 14.19 *Decision tree for fault diagnosis on a crude oil distillation unit (Duncan and Gray, 1975a) (Courtesy of the Journal of Occupational Psychology)*

an emergency situation, for which simulator training is appropriate.

The report argues that for the control of nuclear plants, an average level of performance is not good enough. It follows that training may have to seek to change certain patterns of highly learned skilled-based behaviour.

The report places particular emphasis on the rule-based level of control. Here the operator responds to signs rather than signals and has to categorize the situation. Whilst rules may be learned to some degree in the classroom, practice in the use of rules to categorize the situation is most effectively given on a simulator.

The report gives high priority to the provision of simulators for each type of control room, since there are aspects of task that cannot readily be taught without them. It discusses the merits of local vs off-site simulators, but regards this question as less important that clear specification of the skills to be learned and the level of competence to be achieved.

With regard to individual vs team training, the authors suggest that the initial emphasis should be on individual training, with team training introduced later. Simulator training is treated as a form of team training.

Operator performance is affected by the level of stress experienced. It is not desirable that any operator of a nuclear plant should have to carry out the job under an abnormal degree of stress. This has implications for selection and for monitoring of individuals. The individual should be free from chronic stress symptoms and be able to tolerate acute stress. Given this, the training should give practice in performing the task in realistic conditions and with a raised level of stress so that the trainee learns to handle it. Factors that affect stress include the level of demand and the degree of control over the task that the person feels he has. The individual's confidence that he is in control may be built up by experience of successful handling of similar problems. This experience can be given using a simulator. The level of demands should be built up until it reaches that experienced in real operation.

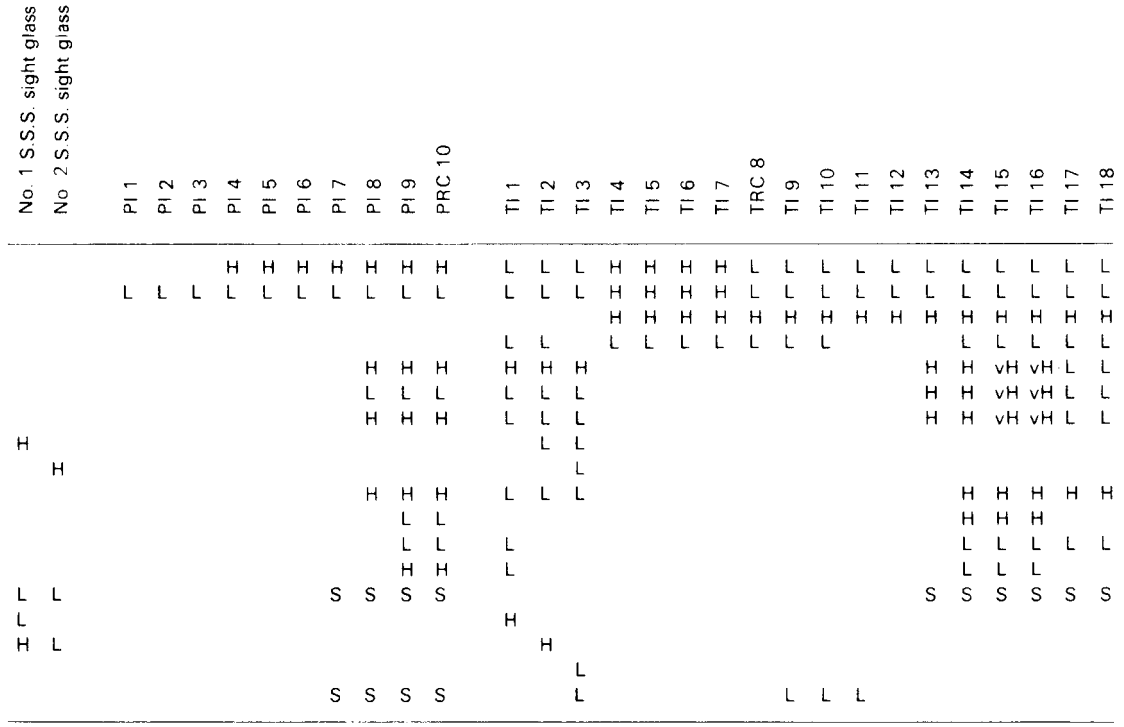
Another aspect of stress is the danger inherent in a major incident. The reports acknowledge that this aspect is difficult to simulate in an exercise, but refers to the expectation of possible criticism. In a healthy safety culture criticism of the performance of an individual or team can be made and accepted constructively. The report urges that management

FAULT	FI 1	FI 2	FI 3	FI 4	FI 5	FI 6	FIC 7	FIC 8	FI 9	FI 10	FRC 11	FRC 12	FRC 13	FRC 14	FR 15	Foul water to drain	Gas flow	Overheads	No. 1 S.S	No. 2 S.S.	Bottoms	LI 1	LIC 2	LIC 3	LIC 4	LIC 5	Feed tank sight glass	Column base sight glass	R/X drum sight glass
1	ø	L	L	L	L	L	L	L	L	L	L	L	L	L	ø	L	L	L	L	L	L		H	L				H	L
2	ø	L	L	L	L	L	L	L	L	L	L	L	L	L	ø	L	L	L	L	L	L			L					L
3																													
4				L	L	L		L	L								L	L	L					L					L
5					H	H	ø	H								ø	H	H						H					H
6					ø	H		ø									H	ø						H					H
7					L	H	L	L	H	H						L	H	L											
8				ø															ø							H			
9			ø																	ø					H				
10						H	L	L								L	H												
11								L																					
12				H	L			L	H									L	H					L					L
13				H	L			H	H									L	H										
14					S	H	S	S								S	H	S						H	L	L			H
15				L	H			H	L									H	L							L			
16			L							L										L					L	H			
17		ø																			ø		H				H		
18		S																			S		B				B		

FAULT:

1 Water in crude
2 Feed pump failure
3 Furnace overheating—reduce furnace heat
4 Furnace underheating—determine cause
5 Accumulator boot valve shut—control oil water interface manually
6 Top reflux pump failure
7 Cooling water pump failure
8 No. 1 sidestream pump failure

Figure 14.20 *continued*



9 No. 2 sidestream pump failure
10 Too little cooling water—increase flow
11 Too little reflux—increase flow
12 Too much cooling water—decrease flow
13 Too much reflux—decrease flow
14 Column puking
15 Too much stripping steam (S.S.S.1)—reduce
16 Too much stripping steam (S.S.S.2)—reduce
17 Base pump failure
18 Column dumping

Figure 14.20 *Fault-symptom matrix for faults on a crude oil distillation unit (Duncan and Gray, 1975a): ø, zero; L, low; H, high; vH, very high; S, swinging; B, swinging and high (Courtesy of the Journal of Occupational Psychology)*

at all levels should be periodically assessed for training need and that no-one should be 'above it.'

The report devotes considerable attention to the question of certification, which is supported by some and opposed by others. In order to disentangle the argument, it is necessary to assign a clear meaning to the word 'certification'. The report gives some eight possible definitions, together with comments. These may be summarized as follows: (1) specification of the content of training and clear responsibility for authorization of an individual to undertake certain actions; (2) separation between individuals who undertake (1) and line management; (3) a requirement that line management accept without further question separate assessment of the individual competence; (4) a requirement that line management authorize only persons from amongst those who have satisfied a separate assessment; (5) a rule that (3) or (4) apply only at the stage common to all reactors with different procedures thereafter; (6) a requirement that separate assessment should not mean simply testing by the training function but by another part of the organization; (7) a requirement that separate assessment should not be carried out by the licensee's organization at all but by a separate body and (8) a requirement that assessment should include observation of performance on the job and not merely verbal knowledge.

The report suggests that the first two interpretations would attract widespread consent. Opponents of certification may understand it in the third sense, but the authors doubt whether this view has proponents. A more serious argument turns on the fourth definition. Here opponents of certification argue that the trend is towards more involvement by line management in any matter which affects production and that there are dangers if it is not involved in training, whilst proponents emphasize that line management is liable to develop blind spots. The authors suggest that this points to the need for a 'two key' system, in which an operator needs to satisfy both an independent assessment and local line management. They argue that given the wide variety of reactor types in Britain the fifth definition would effectively rule out independent assessment. With regard to the sixth and seventh definitions, the report supports an assessment of the trainee performed by assessors who are independent both of the local line management and of the training function, but is unconvinced that the independent assessors need to come from outside the licensee. The authors support the type of assessment

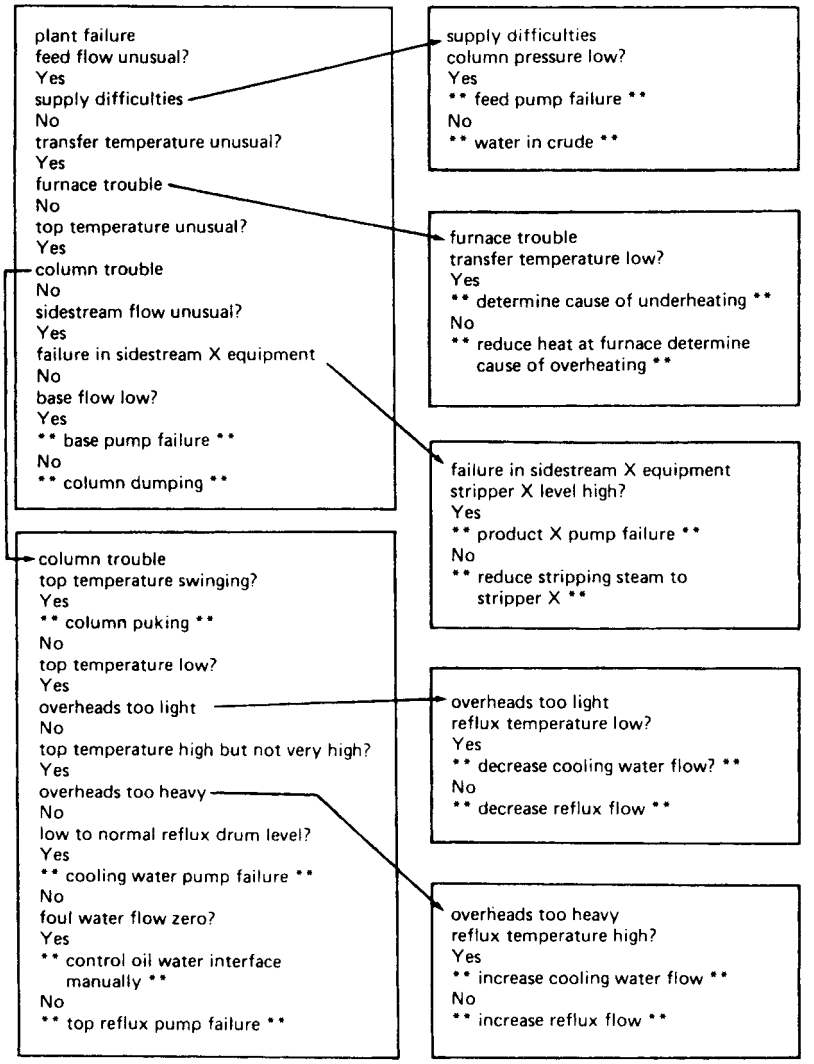


Figure 14.21 *Linked lists for learning fault diagnosis on a crude oil distillation unit (Duncan and Gray, 1975a) (Courtesy of the Journal of Occupational Psychology)*

given in the eighth definition. With regard to privatization, the report makes the point that, in order to support the type of training envisaged, a certain minimum size of training establishment is required.

The framework for training developed in the report is therefore broadly on the following lines. The starting point is task analysis. On the basis of this a specification for training is formulated by line management and the training is carried out by the training function. It is monitored by assessors independent of both local line management and the training establishment. Assessment of the trainee contains a component of actual or simulated performance. The trainee first has to satisfy the independent assessors and is then authorized by line management. Assessment is a continuing process.

The report deals particularly with the training of process operators. However, it emphasizes that training should not be confined to process operators but should also cover instrument artificers, maintenance personnel, etc.

Under the guise of trainability testing, the report touches on the question of personnel selection. It states:

> The Study Group believes it is important to find a valid way of deciding the relative success of different individuals, and that thereby it will become possible to devise satisfactory selection procedures. In other occupations it has frequently been found that systematic assessment of individuals can significantly improve trainability and subsequent performance. The potential of such methods should be explored further.

14.18 Human Factors and Industrial Safety

An account of the role of human factors in safety is given in *Human Factors in Industrial Safety* (HSE, 1989 HS(G) 48). This study sets out the factors that emerge most frequently from accident investigations and gives numerous case histories to illustrate the points made. Some of these case histories are given in Appendix 1.

It refers to the disaster at Chernobyl as an illustration. The background to the incident was serious defects in the management culture and in the regulatory system. The personnel conducting the test on the reactor were under pressure to complete the test in a short time. They failed to distinguish between small and large risks. They removed layer upon layer of protection and violated operational rules. The incident has many lessons, but the authors warn against treating it as a universal model.

The study starts from the viewpoint that the human operator is basically a positive rather than a negative factor in process plants. The operator gives the system a much enhanced ability to deal with abnormal situations. But it is necessary to design systems which protect against, and are tolerant of, human error and to train operators to improve their decision-making in these situations. Above all, the operator needs the support of a good safety culture.

The authors describe case histories that illustrate three aspects of human factors in particular: inadequate information, inadequate design and minimization of the consequences of human error. Human error is classified, with examples, under the headings of slips and lapses, mistakes, misperceptions, mistaken priorities and violations.

Measures for the prevention of human error, and an overall strategy for this, are considered under the headings of the organization, the job and personal factors. In this strategy, the organization is considered in terms of the safety climate, standard setting, monitoring, supervision and incident reports; the job is considered in terms of task analysis, decision-making, man–machine interfaces, procedures and operating instructions, the working environment, tools and equipment, work patterns and communication; and personal factors are considered in terms of personnel selection, training, health assessment and monitoring. Checklists are given under each of these headings.

Many of the examples given in this study are drawn from the process industries. The application of human factors to the process industries specifically is treated in *Human Factors in Process Operations* (Mill, 1992). This is a report of the Human Factors Study Group of the Loss Prevention Panel of the European Federation of Chemical Engineering (CEFIC).

The study covers a number of topics dealt with elsewhere in the present text, notably: management; accident models; control room design; operator control, mental models and workload; operating and emergency procedures; and human error.

A five-step strategy is described for modification of human behaviour in relation to accidents and hazards. These steps are: (1) identification and analysis of accidents and hazards; (2) revision of safety rules concerning working behaviour; (3) development of a plan of measures; (4) implementation of the plan and (5) follow-up – assessing the effectiveness of the measures taken.

14.19 Human Error

The topic of human error as such is a vast one and beyond the scope of the present work. The treatment here is limited to consideration of the effect of human error on the performance of process systems and on methods of dealing with it.

Accounts of human error include *Handbook of Human Reliability Analysis with Emphasis on Nuclear Power Plant Applications* (Swain and Guttmann, 1983), *Information Processing and Human-Machine Interaction* (Rasmussen, 1986), *Human Reliability* (Park, 1987), *Human Reliability Analysis* (Dougherty and Fragola, 1988), *Human Error* (Reason, 1990) and *An Engineers View of Human Error* (Kletz, 1991e). Selected references on human error and operator error are given in Table 14.11.

Table 14.11 *Selected references on human error, operator error*

NRC (Appendix 28 *Human Error*); Riso National Laboratory (Appendix 28); Flanagan (1954); Lincoln (1960); Rook (1962, 1964); Irwin, Levitz and Ford (1964); Irwin, Levitz and Freed (1964); Leuba (1964); Swain (1964a,b, 1968, 1969, 1972, 1973a,b, 1982); Chase (1965); Pontecorvo (1965); Blanchard *et al.* (1966); Rigby (1967, 1971a,b); Rasmussen (1968a–c, 1969, 1976b, 1978, 1980a,b, 1982a,b, 1985, 1987, 1990); Rigby and Edelman (1968a); Askren and Regulinski (1969); Faverge (1970); Sayers (1971 UKAEA SRS/GR/9, 1976); E. Edwards and Lees (1973); Kletz and Whitaker (1973); Lees (1973a, 1976b, 1983a); Regulinski (1973); Finley, Webster and Swain (1974); AEC (1975); Anon. (1976 LPB 7, p. 15); Apostolakis and Bansal (1976); R.L. Browning (1976); Embrey (1976a,b, NCSR RIO, 1979a,b, 1981, 1983a,b, 1984, 1985, 1992a–c); Rasmussen and Taylor (1976); Hopkin (1977); Reason (1977, 1979, 1986, 1987a,b, 1990); Skans (1978); Bello and Colombari (1980); J. Bowen (1980); Griffon (1980); R.A. Howard and Matheson (1980); W.G. Johnson (1980); Kletz (1980c,e, 1982g, 1985d,f, 1987f,h, 1989d, 1990c, 1991e,g, 1993a); Senders (1980); Swain and Guttman (1980, 1983); B.J. Bell and Swain (1981, 1983); J.A. Adams (1982); Carnino and Griffon (1982); Rasmussen and Pedersen (1982, 1983); Singleton (1982, 1984); Beare *et al.* (1983); Brune, Weinstein and Fitzwater (1983); Embrey and Kirwan (1983); HSE (1983a); Mancini and Amendola (1983); Nieuwhof (1983a); Seaver and Sitwell (1983); J.C. Williams (1983, 1985a,b, 1986, 1988a,b, 1992); Embrey *et al.* (1984); Siegel *et al.* (1984); Willey (1984); Ball (1985 LPB 62); Dhillon and Misra (1985); Leplat (1985); Carnino (1986); Dhillon (1986); Dhillon and Rayapati (1986); Hannaman *et al.* (1986); P. Miller and Swain (1987); Park (1987); Rasmussen, Duncan and Leplat (1987); J.B. Smith (1987); Whalley (1987); D.D. Woods, O'Brien and Hanes (1987); Bercani, Devooght and Smidts (1988); Bersini, Devooght and Smidth (1988); Dougherty and Fragola (1988); Drager, Soma and Falmyr (1988); Humphreys (1988a,b); Kirwan (1988); D. Lucas and Embrey (1988); Purdy (1988); Whittingham (1988); Worledge *et al.* (1988); Whalley and Kirwan (1989); ACSNI (1990, 1991, 1993); CMA (1990); Gall (1990); Kirwan *et al.* (1990); Lorenzo (1990); Ball (1991 SRDA R3); Bellamy (1991); Masson (1991); Hollnagel, Cacciabue and Rouhet (1992); Ishack (1992); Paradies, Unger and Ramey-Smith (1992); Samdal, Kortner and Grammeltvedt (1992); Sten and Ulleberg (1992); Vestrucci (1992); Welch (1992); Yukimachi, Nagasaka and Sasou (1992); Nawar and

Samsudin (1993); Wreathall (1993); Wreathall and Reason (1993); CCPS (1994/17)

Organizational factors as cause of human error
Bellamy (1983, 1984, 1986)

Data banks
Payne and Altaian (1962); Altaian (1964); Meister (1964); Rigby (1967); Swain (1970); Topmiller, Eckel and Kozinsky (1982)

Vigilance tasks
Ablitt (1969 UKAEA AHSB(S) R160); A.E. Green (1969 UKAEA AHSB(S) R172, 1970); Kantowitz and Hanson (1981)

Inspection tasks
Mackenzie (1958); McCornack (1961); Rigby and Edelman (1968a); Drury and Addison (1973); Rigby and Swain (1975); Drury and Fox (1978); Pedersen (1984); Murgatroyd *et al.* (1986)

Emergency situations
Fitts and Jones (1947); Ronan (1953); Rigby and Edelman (1968b); Lees (1973a); AEC (1975); Lees and Sayers (1976); Danaher (1980); Apostolakis and Chu (1984); Giffin and Rockwell (1984); Woods (1984); Briggs (1988); Waters (1988b)

Deliberate violations
W.B. Howard (1983, 1984); Zeitlin (1994)

Human reliability assessment
NRC (Appendix 28 *Human Reliability Assessment*); R.A. Howard and Matheson (1980); Swain and Guttman (1980, 1983); R.G. Brown, von Herrman and Quilliam (1982); R.E. Hall, Fragola and Wreathall (1982); Rasmussen and Pedersen (1982); Hannaman *et al.* (1983); L.D. Phillips *et al.* (1983); Weston (1983); Anon. (1984aa); Watson (1984 LPB 58); White (1984 SRD R254); Hannaman *et al.* (1985); Hayashi (1985); Heslinger (1985); Pedersen (1985); Soon Heung Chang, Myung Ki Kim and Joo Young Park (1985); L.A. Watson (1985); R.F. White (1986); Hannaman and Worledge (1987); Murgatroyd and Tate (1987); Dougherty and Fragola (1988); Humphreys (1988a); Purdy (1988); Kirwan (1990); Oliver and Smith (1990); L.D. Phillips *et al.* (1990); Delboy, Dubnansky and Lapp (1991); Paradies, Unger and Ramey-Smith (1991); Banks and Wells (1992); Bridges, Kirkman and Lorenzo (1992); Zimolong (1992); J.C. Williams (1993); CCPS (1994/17)

Benchmark exercise
Waters (1988a, 1989); Poucet (1989)

Pipework failures
Bellamy, Geyer and Astley (1991); Geyer and Bellamy (1991); Hurst *et al.* (1991)

Computer control (*see also* Table 8.1)
Bellamy and Geyer (1988); Kletz (1993a)

Effect of human error on system performance
J. Cooper (1961); Cornell (1968); Ovenu (1969); R.L. Scott (1971); S. Brown and Martin (1977); Burkardt (1986); Gerbert and Kemmler (1986); Hancock (1986); B.J. Bell (1987); Latino (1987); Whitworth (1987); Holloway (1988); Suokas (1989); Rasmussen (1990); Vervalin (1990b); Pyy (1992); Rothweiler (1994 LPB 118)

14.19.1 Engineering interest in human error

Engineering interest in human error derives from two principal sources. One is accident investigation, where the apparent salience of human error gives rise to concern. The other is hazard assessment, where the requirement to quantify the effect of human error on system performance creates a demand for a methodology capable of doing this.

In certain areas, such as an aircraft flightdeck, the prime emphasis has been on the application of human factors in system design to improve performance and reduce human error. In the nuclear field, however, there has been a much greater emphasis on the development of methodology for the assessment of the effect of human error on system performance. This has been the case in the process industries also.

There are, therefore, two distinct sources of interest in human error in engineering. Design seeks to improve the work situation and should not too readily accept the inevitability of human error. Assessment must to a considerable extent accept the situation as it is and seek to evaluate human error.

Work both on features that cause human error and on the methods of assessing it is a well established aspect of human factors.

14.19.2 Human error as a cause of accidents

Human error often figures as a major factor in analyses of incidents. Such an attribution appears in large part to derive from the nature of the investigative process. Reference has already been made to the comment by Rasmussen that in the investigation of accidents the tracing of the causes is generally terminated when it reaches a human, as if this was a stopping rule of the tracing process.

When a failure occurs, there is frequently an administrative requirement to determine the cause, and allocation to human error is notorious. In fact, the incident has occurred in a specific set of circumstances involving men, machines, systems and procedures, physical and social factors, and their interactions. Often the error is more truly that of another party who is responsible for some aspect of the work situation. This point is important because, whereas assignment to human error suggests little can be done, recognition of the effect of the work situation does tend to indicate the possibilities for improvement.

It is relevant to remember that experimental psychologists frequently conduct experiments in which various aspects of the work situation are altered and the subject's error rate is evaluated. This demonstrates clearly the importance of these factors in determining human error.

The reporting of errors in man–machine systems is often deficient, because reporting systems are frequently designed essentially to give information on equipment failure. The reporting of malfunctions in missile systems was studied by J. Cooper (1961), who found that, whilst the reporting system did reveal failures involving equipment only, it was deficient in discovering those involving man as well. He found that man appeared to be involved in 20–53% of all malfunctions for the systems studied, and this result is probably typical.

Thus, other investigations of the contribution of man to system failure have been made – in aerospace by Cornell (1968), on nuclear reactors by R.L. Scott (1971) and on industrial boilers by Ovenu (1969). These studies too attribute a large proportion of failures in the system to human error.

The contribution of human error to major accidents appears to be greater than it is to less serious failures. It has

been estimated by Rasmussen (1978) that whereas human error probably contributes about 10% to general failures, it contributes about 50–80% to major accidents.

14.19.3 Approaches to human error

In recent years, the way in which human error is regarded, in the process industries as elsewhere, has undergone a profound change. The traditional approach has been in terms of human behaviour, and its modification by means such as exhortation or discipline. This approach is now being superseded by one based on the concept of the work situation. This work situation contains error-likely situations. The probability of an error occurring is a function of various kinds of influencing factors, or performance shaping factors.

The work situation is under the control of management. It is therefore more constructive to address the features of the work situation that may be causing poor performance. The attitude that an incident is due to 'human error', and that therefore nothing can be done about it, is an indicator of deficient management. It has been characterized by Kletz (1990c) as the 'phlogiston theory of human error'.

There exist situations in which human error is particularly likely to occur. It is a function of management to try to identify such error-likely situations and to rectify them. Human performance is affected by a number of performance shaping factors. Many of these have been identified and studied so that there is available to management some knowledge of the general direction and strength of their effects.

The approach to the work situation has itself undergone development. Three phases may be distinguished. In the first phase, the concern was with error-likely situations and performance shaping factors in general and on the application of ergonomic and human factors principles. The second phase saw greater emphasis on cognitive and decision-making aspects of the task. The third phase seeks the root causes in the organizational and, more generally, socio-technical background.

The approaches taken to human error may therefore be summarized as:

(1) behavioural approach;
(2) work situation approach:
    (a) general work situation,
    (b) cognitive features,
    (c) organizational features.

Any approach that takes as its starting point the work situation, but especially that which emphasizes organizational factors, necessarily treats management as part of the problem as well as of the solution. Kipling's words are apt: 'On your own heads, in your own hands, the sin and the saving lies!'

14.20 Models and Classifications of Human Error

A systematic approach to human error must involve the classification of errors and must, therefore, be based on appropriate models, either explicitly or implicitly. The classification is not necessarily along a single dimension. Most workers in the field have found it necessary to classify in terms of at least two dimensions: (1) human behaviour and (2) task characteristics.

An early detailed classification of operator error, which was developed for use in analysing licensee event reports (LERs) for nuclear plants by Rasmussen, quoted by J.R. Taylor (1979), is shown in Table 14.12. Also shown in the table is an analysis of 200 such reports. A more comprehensive version of this analysis is given by Rasmussen (1980). This classification includes categories both of behaviour and of task.

14.20.1 Task analysis framework and model

The general framework in which most models and classifications of human error are applied is that of task analysis. That is to say, the task is decomposed into elements such as plans and actions and the errors associated with these are modelled and classified. The extent of the decomposition varies, some approaches being highly decompositional and others more holistic, as discussed below.

In addition to being a general framework within which particular models are applied, task analysis, particularly hierarchical task analysis, may be regarded as a model in its own right. One common classification of human error is in terms of actions. This type of classification refers to acts of omission, acts of commission, and also delays in taking action and so on. It does not attempt to explain them in terms of any other model, such as one involving skills or absentmindedness, although it make take into account various types of influencing factor. This approach has much in common with hazop in the way in which action errors are classified. The similarity between the task analysis scheme and the human error classification shown in Tables 14.9 and 14.18 respectively, makes the point.

14.20.2 Work situation framework and models

Another general framework in the modelling of human error is the work situation, which covers the task itself and the various influencing factors including the ergonomic, the cognitive and the organizational. Where an approach is adapted to human error which accords a central role to the work situation, or some aspect of it such as communication, the work situation virtually becomes the model. In such a model, the emphasis tends to be on identifying, classifying and quantifying the strength of the factors influencing human error rather than on seeking a more fundamental explanation.

14.20.3 Demand-capacity mismatch model

Turning now to other models of human error, or human reliability, one early model views it as a mismatch between the demands of the task and the capacity of the human to perform the task. The mismatch may arise in various ways. It may be due, for example, to physical incapacity. Or it may arise from lack of training.

A particular case, which is properly regarded as involving human reliability rather than human error, is where sudden death or incapacity, such as a heart attack, occurs. This may need to be taken into account in relation to crucial functions.

14.20.4 Tolerance-variability model

Another early model starts from the viewpoint that fundamental to human error is variability, both of people and of tasks. Variability in performance is associated with the desirable human feature of adaptability. Variability is also present in the task. Even a standardized assembly operation involves some variability. More complex industrial tasks are much more variable.

Table 14.12 *Classification of operator error in 200 licensee event reports (J.R. Taylor, 1979; after Rasmussen)*

	No.
Task condition	
Routine task on schedule	89
Routine task on demand	11
Special task on schedule	51
Ad hoc, improvization	21
Various, not mentioned	27
Task control	
Paced by system dynamics	9
Paced by program, orders	4
Self-paced	166
Various, not mentioned	21
Error situation	
Spontaneous error in undisturbed task	93
Change in condition of familiar task	27
Operator distracted in task, preoccupied	10
Unfamiliar task	22
Various, not mentioned	48
Task	
Monitoring and inspection	3
Supervisory control	13
Manual operation, manual control	17
Inventory control	30
Test and calibration	47
Repair and modification	60
Administrative, recording	4
Management, staff planning	13
Various, not mentioned	13
Effect from	
Specified act not performed	103
Positive effect of wrong act	65
Extraneous effect	15
Sneak path	12
Various, not mentioned	6
Potential for recovery	
Effect not immediately reversible	29
Effect not immediately observable	137
Various, not mentioned	34
Error categories	
Absent-mindedness	3
Familiar association	6
Capability exceeded	1
Alertness low	10
Manual variability, lack of precision	10
Topographic, spatial orientation inadequate	10
Familiar routine interference	0
Omission of functionally isolated act	56
Omission of administrate act	12
Omission, other	9
Mistake, interchange among alternative possibilities	11
Expect, assume rather than observe	10
System knowledge, insufficient	2
Side-effects of process not adequately considered	15
Latent causal condition or relations not adequately considered	20
Reference data recalled wrongly	1
Sabotage	1
Various, not mentioned	17

Some variations in the performance of the task can be tolerated. It is only when some limit is overstepped that error is said to occur. The definition of error is therefore critical. The limits may be defined in various ways such as physical barriers, warning signs, operating procedures, production tolerances and standards, process conditions, and social and legal codes.

Swain (1972) distinguishes between random, systematic or sporadic errors. Random and systematic errors can usually be corrected by reducing, respectively, the variance and the bias in the performance of the task, but it may be more difficult to understand and correct sporadic errors, which typically involve sudden and often large excursions out of limits.

14.20.5 Time availability model

Another type of model is based on the premise that human reliability in certain tasks, particularly emergency response, increases with the time available to perform the task. This model might be regarded as a particular case of the demand–capacity mismatch model.

14.20.6 Skills-rules-knowledge model

The skills-rules-knowledge (SRK) model, developed by Rasmussen (1986), treats the human as operating on the three levels of skills, rules and knowledge. Each level has its characteristic types of error. An account of this model has been given in Section 14.12.

14.20.7 Absentmindedness model

The absentmindedness model, developed by Reason (1990), distinguishes between slips, lapses and mistakes. A slip is either (1) an error in implementing a plan, decision or intention, where the plan is correct but the execution is not or (2) an unintended action. A lapse is an error in which the intended action is not executed due to a failure of memory. A mistake is an error in establishing a course of action such as an error in diagnosis, decision-making or planning. This model is described more fully in Chapter 26.

14.20.8 Organizational model

The organizational, or socio-technical system, model stresses the contribution of organizational and wider socio-technical factors to human error. It may be regarded as a version of the work situation model that puts particular emphasis on these factors.

14.20.9 Violations

It is recognized that some actions are not strictly human errors but outright violations. There appears to be no developed model for violations. Whilst it is now accepted that human error is something that is under the influence of management, this is less so for violations. In this respect, the treatment of violations seems to be at the point where that of human error was some two or three decades ago. There is a need for a better understanding of why violations occur and how they may be designed out.

14.20.10 Decompositional and holistic approaches

Along a different dimension, approaches to human error may be characterized either as decompositional or as holistic. In the decompositional approach, also referred to as 'reductionist', 'mechanistic' or 'atomistic', the task is decomposed into its constituent elements, and for each element the probability of failure is estimated. The probability of failure for

the task overall is taken as the product of the individual probabilities. Allowance may be made for certain features such as dependent failure, but for the most part other aspects of task failure such as errors in decision-making are not well handled. The holistic approach by contrast takes high level elements of the work and thus covers features such as decision-making.

14.20.11 Classifications of human error

Classifications of human error flow from the above described models. A common distinction, based essentially on the task analysis model, is between errors of omission, transformation or commission. A human may fail to execute a required action, or he may execute it but incorrectly or out of sequence or too slowly, or he may execute an unwanted action. Errors of omission may involve failures of attention or memory, and errors of commission failures in identification, interpretation or operation. Error classifications along these lines have been given by Lincoln (1960) and Swain (1970).

Classifications related to the work situation model are typically in terms of the influencing factors. The SRK model of Rasmussen gives rise to a classification based on distinction between errors arising at the levels of skill, rules and knowledge. The classification deriving from Reasons's absentmindedness model is into slips, lapses and mistakes.

Another classification of human error is based on the relationship in time of the error to the initiating event in an incident sequence. If the error precedes the initiating event, it is a latent, or enabling, error. If it is the direct cause of the event, it is an initiating error. And if it follows the event, it is a response or recovery error.

14.21 Human Error in Process Plants

14.21.1 Human error in general and in plant operation

An overview of human error in process plants is given in *An Engineer's View of Human Error* (Kletz, 1991e). This work provides a useful account of the practicalities of human error in the various activities occurring on such plants. Kletz describes the following types of human error:

(1) simple slips;
(2) errors due to poor training or instructions;
(3) errors due to lack of physical or mental ability;
(4) wrong decisions;
(5) management errors.

He treats human error in:

(6) design;
(7) construction;
(8) operation;
(9) maintenance.

Kletz also gives numerous examples.

The basic approach that he adopts is that already described. The engineer should accept people as they are and should seek to counter human error by changing the work situation. In his words: 'To say that accidents are due to human failing is not so much untrue as unhelpful. It does not lead to any constructive action'.

In designing the work situation the aim should be to prevent the occurrence of error, to provide opportunities to observe and recover from error, and to reduce the consequences of error.

Some human errors are simple slips. Kletz makes the point that slips tend to occur not due to lack of skill but rather because of it. Skilled performance of a task may not involve much conscious activity. Slips are one form of human error to which even, or perhaps especially, the well trained and skilled operator is prone. Generally, therefore, additional training is not an appropriate response. The measures that can be taken against slips are to (1) prevent the slip, (2) enhance its observability and (3) mitigate its consequences.

As an illustration of a slip, Kletz quotes a incident where an operator opened a filter before depressurizing it. He was crushed by the door and killed instantly. Measures proposed after the accident included: (1) moving the pressure gauge and vent valve, which were located on the floor above, down to the filter itself; (2) providing an interlock to prevent opening until the pressure had been relieved; (3) instituting a two-stage opening procedure in which the door would be 'cracked open' so that any pressure in the filter would be observed and (4) modifying the door handle so that it could be opened without the operator having to stand in front of it. These proposals are a good illustration of the principles for dealing with such errors. The first two are measures to prevent opening while the filter is under pressure; the third ensures that the danger is observable; and the fourth mitigates the effect.

One area of process operation where slips are liable to occur is in the emptying and filling of equipment. It is often necessary to drain a vessel or other equipment such as a pump. Not infrequently, fluid is admitted to the equipment while the drain valve is still open. In some applications, an interlock may be the appropriate solution, as described in Chapter 13.

Misidentification of the equipment to be worked on is another fertile source of error. Kletz gives as an example a plant that had an alarm and trip on the same process variable and where the technician who intended to work on the alarm in fact disabled the trip. He also gives a number of examples of the operation of the wrong press button or the wrong valve caused by inconsistent labelling. The identification of equipment for maintenance is considered in more detail in Chapter 21.

Another type of slip is failure to notice. This is particularly liable to occur if some item is similar but not identical. A case in point is where an operator draws from a drum which contains the wrong chemical but where the drums containing the right and the wrong chemicals have similar markings.

The need to calculate some process quantity introduces a further opportunity for error. In some cases, the result may be sufficiently unusual as to highlight the error, but in others it may not.

Many human errors in process plants are due to poor training and instructions. In terms of the categories of skill-, rule- and knowledge-based behaviour, instructions provide the basis of the second, whilst training is an aid to the first and the third, and should also provide a motivation for the second. Instructions should be written to assist the user rather than to hold the writer blameless. They should be easy to read and follow, they should be explained to those who have to use them, and they should be kept up to date.

Problems arise if the instructions are contradictory or hard to implement. A case in point is that of a chemical

reactor where the instructions were to add a reactant over a period of 60–90 min, and to heat it to 45°C as it was added. The operators believed this could not be done as the heater was not powerful enough and took to adding the reactant at a lower temperature. One day there was a runaway reaction. Kletz comments that if operators think they cannot follow instructions, they may well not raise the matter but take what they believe is the nearest equivalent action. In this case, their variation was not picked up as it should have been by any management check. If it is necessary in certain circumstances to relax a safety-related feature, this should be explicitly stated in the instructions and the governing procedure spelled out.

Certain features of the operation and maintenance of process plants should be covered in elementary training. Incidents occur because operators do not fully appreciate the basic properties and hazards of flammable and toxic chemicals and the precautions necessary in handling them, the operation and hazards of pressure systems, the reasons for the principal procedures and the importance of adherence to all procedures. This elementary training is discussed in more detail in Chapter 28.

There are a number of hazards which recur constantly and which should be covered in the training. Examples are the hazard of restarting the agitator of a reactor and that of clearing a choked line with air pressure.

Training should instil some awareness of what the trainee does not know. The modification of pipework that led to the Flixborough disaster is often quoted as an example of failure to recognize that the task exceeded the competence of those undertaking it.

Kletz illustrates the problem of training by reference to the Three Mile Island incident. The reactor operators had a poor understanding of the system, did not recognize the signs of a small loss of water and they were unable to diagnose the pressure relief valve as the cause of the leak.

Installation errors by contractors are a significant contributor to failure of pipework. Details are given in Chapter 12. Kletz argues that the effect of improved training of contractors' personnel should at least be more seriously tried, even though such a solution attracts some scepticism.

Human error may occur due to physical or mental inability to perform the task. Even if there is not total inability, the task may be very difficult and therefore liable to error. Physical difficulties can arise in the manipulation of controls and valves. The task may require the operator to observe a display whilst manipulating a control, but the display may be too far from the control to do this. Manual valves on the plant may be inaccessible or stiff to turn. The need to use protective equipment such as breathing apparatus may introduce physical difficulties.

There are a number of situations that may create mental difficulties. Mental overload is one such situation that may come in various forms. The operator may suffer overload due to an excessive number of alarms. A supervisor may be overloaded by the number of permits-to-work. Another type of mental difficulty occurs where the operator is required to undertake tasks that are not his *forte*. One case is detection of rare events. Another is taking over in an emergency from a totally automated system.

Another category of human error is the deliberate decision to do something contrary to good practice. Usually it involves failure to follow procedures or taking some other form of short-cut. Kletz terms this a 'wrong decision'. W.B. Howard (1983, 1984) has argued that such decisions are a major contributor to incidents, arguing that often an incident occurs not because the right course of action is not known but because it is not followed: 'We ain't farmin' as good as we know how'. He gives a number of examples of such wrong decisions by management.

Other wrong decisions are taken by operators or maintenance personnel. The use of procedures such as the permit-to-work system or the wearing of protective clothing are typical areas where adherence is liable to seem tedious and where short-cuts may be taken.

A powerful cause of wrong decisions is alienation.

Wrong decisions of the sort described by operating and maintenance personnel may be minimized by making sure that rules and instructions are practical and easy to use, convincing personnel to adhere to them and auditing to check that they are doing so.

Responsibility for creating a culture that minimizes and mitigates human error lies squarely with management. The most serious management failing is lack of commitment. To be effective, however, this management commitment must be demonstrated and made to inform the whole culture of the organization.

There are some particular aspects of management behaviour that can encourage human error. One is insularity, which may apply in relation to other works within the same company, to other companies within the same industry or to other industries and activities. Another failing to which management may succumb is amateurism. People who are experts in one field may be drawn into activities in another related field in which they have little expertise.

Kletz refers in this context to the management failings revealed in the inquiries into the Kings Cross, *Herald of Free Enterprise* and Clapham Junction disasters. Senior management appeared unaware of the nature of the safety culture required, despite the fact that this exists in other industries.

14.21.2 Human error and automation

The automation of functions previously performed by the human operator can give rise to certain characteristic problems. These ironies of automation have been discussed by Bainbridge (1983), who identifies four areas of concern. One is the potential for deterioration of the skills of the process operator. Another is the need for the operator to monitor the functioning of the automatic equipment, a role to which he is not particularly well suited. The third is the difficulty for the operator of maintaining an up-to-date mental model of the status of the process in case he has to intervene. The fourth is the tendency of automated systems to reduce small variations at the price of occasionally introducing very large ones.

These characteristics of automated systems were discussed in general terms in the early part of this chapter. Here attention is drawn to their potential to induce human error.

14.21.3 Human error in plant maintenance

Much of the literature on human error in process plants is devoted to the process operators. However, a large proportion of serious incidents is attributable to errors in maintenance work. Maintenance errors may endanger those doing the work, the plant, or both.

Several treatments of human error in maintenance work have been published by the Health and Safety Executive (HSE). Accounts illustrated with case histories are given in *Deadly Maintenance* (HSE, 1985b) and *Dangerous*

Maintenance (HSE, 1987a). *Human Factors in Industrial Safety* (HSE, 1989 HS(G) 48) gives general guidance on human factors relevant *inter alia* to maintenance work.

Here again it is appropriate to start with the designer. If it is practical to design out the need for maintenance, the problem disappears.

One cause of error in maintenance is lack of understanding either of the process and chemicals or of the equipment. This is exemplified by a number of incidents where the wrong bolts have been loosened on a valve, resulting in a release.

Maintenance is an area where poor practices can easily creep in. An example is breaking a flange the wrong way. Maintenance personnel on process plants spend a large proportion of their time dealing with heavy, dirty equipment. It is not easy to make the transition required when they have to work on relatively delicate items. A case in point is leaving flameproof equipment with loose screws and an excessive gap so that it is no longer flameproof.

In some cases defects of workmanship in maintenance are gross. Kletz cites a case where a fitter had to remake a flanged joint using a new spiral wound gasket. Since it was too large, he ground depressions in the outer metal ring of the gasket so that it would fit between the bolts. He made matters worse by making only three depressions so that the gasket did not fit centrally between the bolts.

Maintenance is an activity which can often be frustrating and short-cuts may be taken. Use of protective clothing, isolation procedures and the permit-to-work system are areas where such short-cuts tend to be taken.

Reference has already been made to errors in identification of equipment. Measures need to be taken to ensure effective identification.

An overview of the management of maintenance to ensure safe working is given in Chapter 21.

14.21.4 Human error in pipework failure

In construction, errors in the installation of pipework loom large. The problem was highlighted in a survey by Kletz (1984k), who has given a checklist aimed at eliminating such defects. Two of the measures proposed by Kletz to reduce pipework construction errors are improved training of the construction workforce, as already described, and the use of the barrier principle. A more detailed treatment of Kletz' work on pipework errors is given in Chapter 12.

This theme has been taken up again in the study of pipework failure, and human error as cause of such failure, described by Bellamy and co-workers (Bellamy, Geyer and Astley, 1989; Geyer *et al.*, 1990; Geyer and Bellamy, 1991; Hurst *et al.*, 1991). This study has already been referred to in Chapter 12 in dealing with failure of pipework, where a number of tables are given based on this study.

A total of 921 incidents from incident data bases were reviewed, some analysis was done on all 921 incidents and further analysis on some 502 incidents. Incidents were classified in three ways: (1) 'direct cause', (2) 'origin of failure' or underlying cause and (3) 'recovery failure' or preventive mechanism.

The crude data showed that operator error contributed 18.2% to the direct causes of pipework failure, whilst defective pipe or equipment contributed 31.9% and unknown causes 9.1%. If the last two categories are removed from consideration, operator error then contributes 30.9%. Table 14.13, Section A, shows the contribution to the direct causes of operator error and of two other human errors. Sections B and C of the table give the distribution of human error among the underlying causes and the recovery failures, respectively. For the former, the predominant errors are in maintenance and for the latter, in human factors review and task checking.

Table 14.13 *Human error as a cause of pipework failure (after Bellamy, Geyer and Astley, 1989) (Courtesy of the Health and Safety Executive)*

A Direct causes

Cause	*Contribution of human error* (%)
Operator error	30.9
Wrong or incorrectly located in-line equipment	4.5
Human-initiated impact	5.6
Total	41.0

B Underlying cause

Cause	*Distribution of human error between underlying causes* (%)
Design	8
Manufacture	2
Construction	8
Operation	22
Maintenance	59
Sabotage	1
Total	100

C Recovery failures

Failure	*Distribution of human error between recovery failures* (%)
Not recoverable	1
Hazard study	6
Human factors review	60
Task checking	31
Routine checking	2
Total	100

14.21.5 Human error and plant design

Turning to the design of the plant, design offers wide scope for reduction both of the incidence and consequences of human error. It goes without saying that the plant should be designed in accordance with good process and mechanical engineering practice. In addition, however, the designer should seek to envisage errors that may occur and to guard against them.

The designer will do this more effectively if he is aware from the study of past incidents of the sort of things that can go wrong. He is then in a better position to understand, interpret and apply the standards and codes, which are one of the main means of ensuring that new designs take into account, and prevent the repetition of, such incidents.

A significant contribution can be made by the designer to the elimination of errors leading to pipework failures.

One is to remove situations vulnerable to an operator error such as opening the wrong valve so that the plant suffers overpressure or undertemperature. Another is to counter errors in construction and maintenance by applying the barrier principle so that it is literally impossible to assemble an item in a manner other than the correct one.

Another area where the designer has a large contribution to make is in facilitating maintenance activities on the plant. This includes: provision of access to equipment, pipework and valves; pipework arrangements which assist isolation of sections of plant; and measures to prevent of misidentification of equipment.

An aspect of operation that provides a new field for human error is computer control of process plants. This is considered in Chapter 13.

14.21.6 Human error and organizational factors

At a fundamental level human error is largely determined by organizational factors. Like human error itself, the subject of organizations is a wide one with a vast literature, and the treatment here is strictly limited.

It is commonplace that incidents tend to arise as the result of an often long and complex chain of events. The implication of this fact is important. It means in effect that such incidents are largely determined by organizational factors. An analysis of 10 incidents by Bellamy (1985) revealed that in these incidents certain factors occurred with the following frequency:

Interpersonal communication errors	9
Resources problems	8
Excessively rigid thinking	8
Occurrence of new or unusual situation	7
Work or social pressure	7
Hierarchical structures	7
'Role playing'	6
Personality clashes	4

The role of organizational factors is a principal theme in the work of Kletz, who has described a number of incidents that appear to arise from failures which at the superficial level might be assigned to hardware or humans, but which on deeper investigation can be attributed to organizational aspects. He describes the process of seeking out these more fundamental causes as 'peeling the onion'.

Organizational factors are to a degree taken into account in current methods of human reliability analysis (HRA) in several ways. In particular, allowance is made for these factors in relation to oral and written procedures and to factors that influence task performance.

14.21.7 Human error in communications

One aspect of organizational factors is interpersonal communication. Communications is one of the relatively few topics in human error in process plants that has been the subject of study. Work on communication errors has been described by Bellamy (1983, 1984, 1985). She found that interpersonal communication errors played a part in nine out of the ten incidents which she studied (Bellamy, 1985). The errors might be associated with either enabling or initiating events.

Incidents studied by Bellamy (1983) include the explosion at Flixborough, the explosion at Houghton Main colliery and the radioactive release at Sellafield. Figure 14.22 shows her analysis of the chain of events at Houghton Main in which communication errors were prominent.

It is normal to place considerable reliance on communication as a line of defence. Where this is the case it is necessary to take steps to ensure that the communication is effective. In order to ensure the integrity of communication, there is need for a considerable degree of formality in the communication procedures. In certain fields, such as air traffic control, this is normal practice. In the process industries, the degree of formality in communication tends to be variable. Two important features include the handover procedures and permit-to-work system. Other aspects of communication may be less formal.

Table 14.14 is a list given by Bellamy (1983) of some of the errors that may occur in interpersonal communications. One feature prominent in the incidents that she describes is ambiguous or incomplete messages occurring within a formal system. The existence of a formal system such as handover with associated logbooks may not, therefore, be sufficient if in practice the quality of communication within it is poor.

Two central features of the system of communication on a plant are the permit-to-work system and the handover system. It is not surprising, therefore, that many communications errors are associated in some way with one or other of these systems. Kletz (1991e) gives as an illustration the instance of the failure of a permit-to-work system, described in Chapter 20.

14.22 Prevention and Mitigation of Human Error

There exist a number of strategies for prevention and mitigation of human error. Essentially these aim to:

(1) reduce frequency;
(2) improve observability;
(3) improve recoverability;
(4) reduce impact.

Some of the means used to achieve these ends include:

(1) design-out;
(2) barriers;
(3) hazard studies;
(4) human factors review;
(5) instructions;
(6) training;
(7) formal systems of work;
(8) formal systems of communication;
(9) checking of work;
(10) auditing of systems.

The *Guide to Reducing Human Error in Process Operation* compiled by the Human Factors in Reliability Group (HFRG), (1985 SRD R347) gives guidance in check-list form. The checklists cover (1) operator-process interface, (2) procedures, (3) workplace and working environment, (4) training and (5) task design and job organization.

14.22.1 Role of engineering measures

There is some danger that emphasis on the apparently dominant role of human error in major incidents may induce in the engineer a feeling of helplessness. This is misplaced. As this chapter indicates, there is a variety of methods, from the managerial to the technical, which can

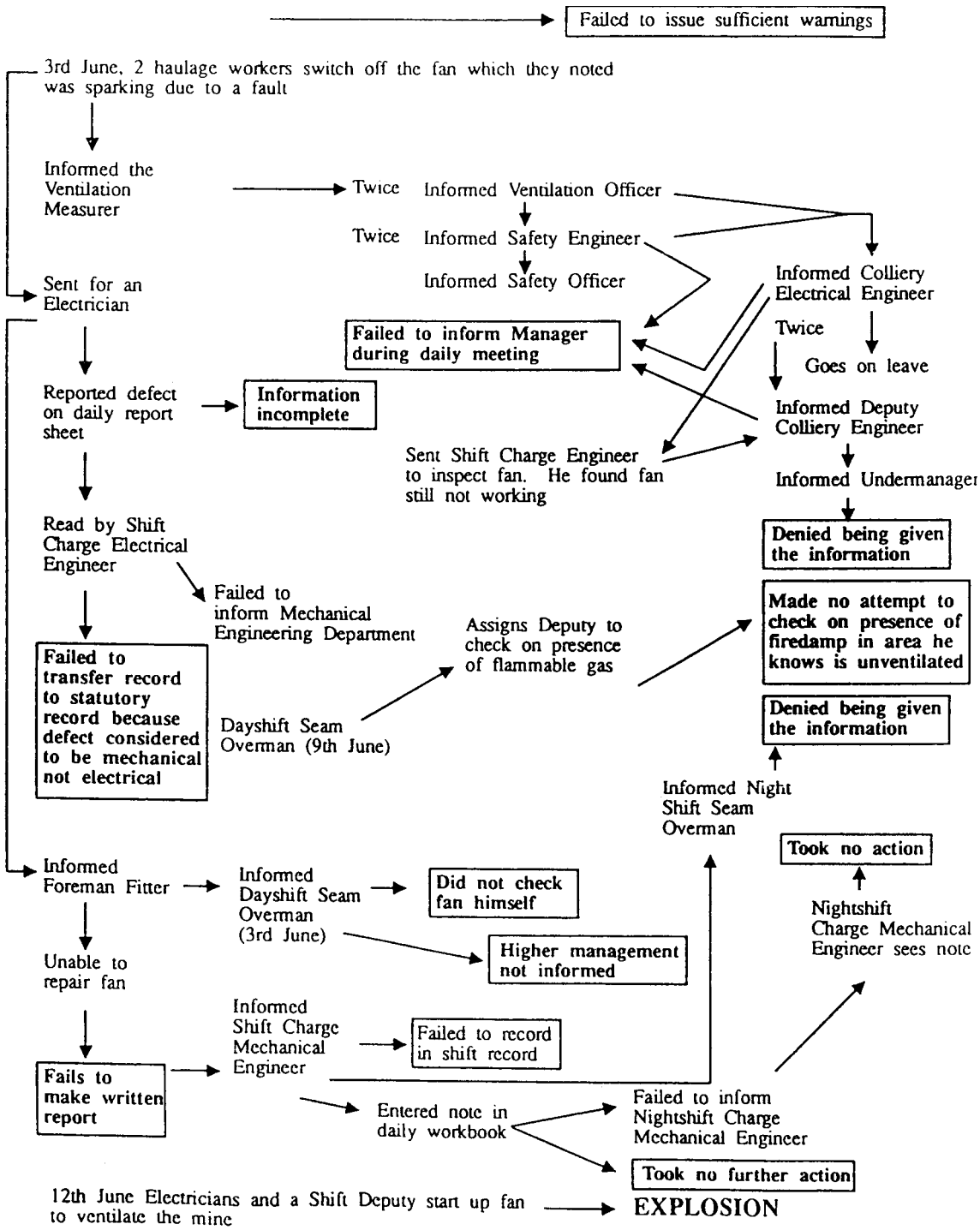


Figure 14.22 *Chain of events in the Houghton Main colliery accident illustrating communication errors (Bellamy, 1983. Reproduced by permission.)*

Table 14.14 *Some human errors in interpersonal communication (Bellamy, 1983. Reproduced with permission.)*

1. *Sender errors*
   (a) *In encoding information*
   Information not encoded (e.g. message contains no information)
   Information ambiguous (e.g. semantic ambiguity)
   Information incomplete (e.g. details omitted)
   Information or code incorrect (e.g. wrong values given, wrong terms used)
   Code inappropriate (e.g. code foreign to intended receiver)
   (b) *In transmitting information*
   Information not transmitted (e.g. not sent, not recorded)
   Information not transmitted in time (e.g. too late for action to be taken)
   Information transmitted via incorrect channel (e.g. standard channel not used)
   Unacknowledged transmission not repeated (e.g. repeat not possible)
   Acknowledged transmission not corrected (e.g. error in the acknowledgement not noticed)
2. *Receiver errors*
   Failure to acquire message (e.g. does not read record book, ignores message)
   Incomplete decoding of message (e.g. forgets details)
   Incorrect decoding of message (e.g. misinterprets meaning)
   Receipt of message not acknowledged (does not give feedback to sender)
   Receipt of message acknowledged but no feedback of decoded message (e.g. does not repeat back interpreted content of message)
   Feedback of decoded message is ambiguous (e.g. semantic ambiguity)
3. *Errors in additional recording of sent or received messages*
   Sent information not recorded (e.g. not written down)
   Received information not recorded (e.g. not written down)
   Information recorded but poorly encoded (*see* l(a)) (e.g. in written report)

be used to reduce the frequency with which human error gives rise to an initiating event. But it may well be in his contribution to the mitigation of the consequences that the engineer comes into his own.

14.23 Assessment of Human Error

Turning now to the assessment of human error, the growing use of quantitative risk assessment has created a demand for the development of techniques for the assessment of human error to complement those available for the assessment of hardware failures.

In the following sections an account is given of developments in the assessment of human error. First, the task analytic approach is described in which a task is decomposed into its elements and error rates are assigned to each of these elements (Section 14.24). Next, an overview is given of early attempts to decompose the process control task into elements for which there might be available information on human error probabilities (Section 14.25). The account then reverts to qualitative methods developed to ensure that the analyst has a sound understanding of the problem before embarking on quantification (Section 14.26). There follow descriptions of some of the principal methods of estimating human reliability (Sections 14.27–14.32), of performance shaping factors (Section 14.33) and of human error data (Sections 14.34). Treatments are then given of certain guides and overviews, including a benchmark exercise, and of applications at Sizewell B (Sections 14.35–14.39). The topic of human reliability assessment is replete with acronyms and the account here necessarily reflects this.

14.24 Assessment of Human Error: Task Analytic Approach

Turning then to the methods available for making a quantitative assessment of human error in process plant operation, the starting point is analysis of the task.

14.24.1 Task analysis

Early work on discrete tasks generally took as its starting point some form of task analysis in which the task was broken down into its component parts. The probabilities of error in the performance of these component subtasks were then estimated and the probability of error in the complete task then assessed.

A methodology based on the task analytical approach, the technique for human error rate prediction (THERP), developed by Swain and co-workers is described below. An overview of this type of approach is given here based on an early account by Swain (1972).

Estimates of the probability of success in a planned discrete task may be made at different levels of sophistication. At one extreme, an average task error rate of, say, 0.01 is sometimes quoted. This is apparently based on the assumption that the average element error rate is 0.001 and that there are, on average, 10 elements per task. At the other extreme is the collection and application of experimental data on error rates as a function of the performance shaping factors.

An important aspect of task reliability is the possibility of recovery by detection and correction of the error. If an error is retrievable in this way, the error rate for the task may be reduced by orders of magnitude. The probability of recovery depends very much on the cues available concerning the error, whether from displays and controls or from the system generally.

The effect of an error is also relevant, since only a proportion of errors have significant effects. Swain suggests that if the probability that an error will occur is between 10^{-4} and 10^{-3}, that it will be corrected is between 0.02 and 0.2 and that it will have a significant effect is between 0.2 and 0.3, then the probability that an error will occur, will remain undetected and will have a significant effect is of the order 0.4×10^{-6} to 60×10^{-6}.

The application of task reliability calculation to process control is exemplified by the work of Ablitt (1969 UKAEA AHSB(S) R160) on the estimation of the reliability of execution of a schedule of trip and warning tests involving some 55 items.

14.25 Assessment of Human Error: Process Operation

It was recognized early on that the above approach, based as it is on routine tasks such as equipment assembly, was of dubious applicability to the overall task of process control, and attempts were made to classify tasks in process control so as to make the links between these tasks and relevant areas of research in human factors.

One such classification is that given by Lees (1973a, 1980b), who breaks the overall process control tasks down into three categories on which information is available: (1) simple tasks, (2) vigilance tasks and (3) emergency behaviour – and two further more difficult categories – (4) complex tasks and (5) control tasks. In this classification, simple tasks are essentially the planned, usually routine, discrete tasks of the type just described, whereas complex tasks are those which are not routine but require some element of decision-making. The control task is essentially the residual of the operator's overall task in supervising the process, after exclusion of the specific simple and complex tasks, the vigilance, or monitoring, task and emergency response. The classification was an early attempt to decompose the process control task into categories that are recognized in work on human factors and on which there is therefore some prospect of obtaining data, or at least guidance.

A more recent but somewhat similar classification is that given by Dougherty and Fragola (1988). They give the following analogy between hardware failures and human error:

Hardware failure	*Human activity*
Demand failure	Plan-directed behaviour
Stand-by failure	Vigilance behaviour
Running failure	Event-driven behaviour

To the above list might be added, for hardware, emergency response failure and, for human activity, emergency response behaviour.

Other techniques which take a more holistic approach to complex tasks are the goal-directed activity (GDA) technique and success likelihood index method (SLIM) of Embrey and the human error assessment and reduction technique (HEART) of Williams, described below.

14.25.1 Routine tasks

As described above, the usual approach to the estimation of human error rates in simple, or routine, tasks is to break the task down into its constituent elements and to derive an estimate of the reliability of the task from that of its constituent elements. The deficiencies of this rather mechanistic approach have long been recognized for any task that involves decision-making, but it may serve to the degree that a routine task may be defined as one that does not require decision-making so that errors are confined to slips rather than mistakes. Given this restriction, the methods developed in THERP may be used. Alternatively, use may be made of the methods developed for complex, or non-routine tasks, as described below.

14.25.2 Vigilance tasks

A vigilance task involves the detection of signals. There is a large body of work on the performance of vigilance tasks. Some of the factors that affect performance in such tasks are:

(1) sensory modality;
(2) nature of signal;
(3) strength of signal;
(4) frequency of signal;
(5) expectedness of signal;
(6) length of watch;
(7) motivation;
(8) action required.

Sight and hearing are the main channels for receiving the signal. The signal itself may be a simple GO–NO GO one or a complex pattern. In this latter case, the out-of-limit condition may not be well defined in advance, but may have to be judged by the subject at the time. The signal may be strong and noise-free or weak and noisy, it may be frequent or infrequent and it may be an expected or unexpected type. The performance of the subject is affected by such factors as length of watch, degree of motivation and the action required on receipt of the signal.

Some general conclusions may be drawn from the work on vigilance. In general, the auditory channel is superior to the visual for simple GO–NO GO signals such as alarms. The probability of detection of a signal varies greatly with signal frequency; detection is much more probable for frequent than for infrequent signals. A vigilance effect exists so that performance tends to fall off with time.

There is an appreciable amount of data on vigilance tasks such as scanning displays, responding to alarms, and so on. A typical piece of work on vigilance in process control is that described by A.E. Green (1969 UKAEA AHSB(S) R172, 1970). The equipment used was the Human Response Analyser and Timer for Infrequent Occurrences (HORATIO), which automatically produces signals that are reasonably representative in form and time distribution of certain types of fault indication, and measures the time interval between the onset of the signal and the operator's response to it. Experiments were conducted in nuclear reactor control rooms in which operators were asked to respond to a simultaneous visual indication and an audible alarm signal by pressing a button. The signal rates were between 0.35 and 1.5 events/h. The probability of failure to respond to signals within the allowed response time was about 10^{-3}.

Another related type of task is inspection, which has also been much studied. In general, there is a greater probability of error in an inspection task where it is rather passive, the discrimination required is simple, the defect rate is low and the inspection is continuous. If there are more active features, such as taking measurements to detect the defect, the defect rate is high and inspection is alternated with another task, the error rate is reduced. A survey by McCornack (1961) suggests that with a defect probability of 0.01 the average inspection error is about 0.15, but inspection error probabilities vary widely and Swain (1972) quotes the range 0.01–0.6.

14.25.3 Emergency behaviour

Another definable task is response to an emergency. This is treated here as a situation which requires decision-making under stress. Here a certain amount of information is available from military and aerospace sources. One source of information is the critical incident technique that

involves debriefing personnel who have been involved in critical incidents.

Two studies in particular on behaviour in military emergencies have been widely quoted. One is an investigation described by Ronan (1953) in which critical incidents were obtained from US Strategic Air Command aircrews after they had survived emergencies, for example loss of engine on take-off, cabin fire or tyre blowout on landing. The probability of a response which either made the situation no better or made it worse was found to be, on average, 0.16.

The other study, described by Berkun (1964), was on army recruits who were subjected to emergencies, which were simulated but which they believed to be real, such as increasing proximity of mortar shells falling near their command posts. As many as one-third of the recruits fled rather than perform the assigned task, which would have resulted in a cessation of the mortar attack.

Information is also available from work on simulators. In process control, a typical study is the bounding study on operator response to emergencies done with reactor operators on a process simulator in the UKAEA and described by Lees and Sayers (1976). The simulation involved typical faults, for example control rod runout, blower failure and gas temperature rise. The fault rate was high at 10 faults/h. The response was to push a single button. These conditions were favourable and the result may therefore be regarded as an upper limit to the operator reliability that can be expected. For response times in the range 0–30 s the error probability was 0.24, and for those in the range 60–90 s it was zero.

14.25.4 Non-routine tasks

For complex, or non-routine, tasks the mechanistic approach of subdividing the task into its constituent elements is inappropriate. The appropriate approach is to treat the task in a more holistic way. Using this approach, it is necessary to obtain estimates for the reliability of the whole task.

One method of doing this is to obtain estimates of task reliability from the judgement of experts. Early work on this was done by Rook (1964), who developed a method in which tasks were ranked by experts in order of their error-likeliness, and ranking techniques were used to obtain error rates.

Embrey (1979b) has developed this line of approach in his work on GDA. Whole tasks which are undertaken in process control are identified and estimates made of task reliability by a combination of data collection and expert judgement.

The other main method of determining the reliability of the whole task is the use of simulation. The information from simulation is generally a correlation between the probability of failure and the time available to perform the task.

14.25.5 Overall control task

There remains an overall control task that is essentially the residual remaining after the above activities have been treated. The effect of progress in the treatment of human error in process control has been to reduce this undefined residue.

14.25.6 Isolated acts of commission

There is a finite possibility that in performing his overall control task the operator will intervene unnecessarily, with unfortunate results. Such an event is not brought out by analyses that consider only activities which the operator is required to perform.

There are also other possibilities, including deliberate damaging action by the operator. One such action is suicide by destruction of the plant which is discussed by Ablitt (1969 UKAEA AHSB(S) R190):

> The probability per annum that a responsible officer will deliberately attempt to drop a fuel element into the reactor is taken as 10^{-3} since in about 1000 reactor operator years there have been two known cases of suicide by reactor operators and at least one case in which suicide by reactor explosion was a suspected possibility. The typical suicide rate for the public in general is about 10^{-4} per year although it does vary somewhat between countries.

The report on the underground tube train crash at Moorgate Station in London (DoE, 1976/7) drew attention to the possibility of suicide by the driver. Sabotage is another type of action by the operator that is not unknown in process plants.

14.25.7 Time–reliability correlations

Error in executing a task is in general, a function of the time available to perform it. There has been a growing tendency to use time as a principal correlator of operator error.

Thus error in vigilance situations depends very much on the response time that is allowed. Ablitt (1969 UKAEA AHSB(S) R190) tentatively proposed the following estimates of the error probability q for operator action in response to an alarm signal as a function of response time t:

t	1 s	10 s	60 s	5 min	10 min	>10 min
q	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}–10^{-6}

A similar type of correlation underlies the estimates of the general probability of ineffective behaviour in emergencies used in studies such as the *Rasmussen Report*. In that study the error probability q used for operator action in response to an emergency as a function of response time t is:

t	60 s	5 min	30 min	Several hours
q	1	0.9	10^{-1}	10^{-2}

14.25.8 Human error probabilities: *Rasmussen Report*

One of the earliest sets of estimates for the probability of human error was that given in the *Rasmussen Report* as shown in Table 14.15. These estimates are mostly of the type used in THERP, but they include the time reliability correlation just referred to.

14.25.9 Human error probabilities: hazard analysis

Estimates of human error probability (HEP) are given in a number of fault trees. Operator error occurs in the tree as errors that either initiate or enable to the fault sequence and as errors that constitute failures of protection. Table 14.16 is a summary by Lees (1983a) of the estimates used in two fault trees published by Lawley (1974b, 1980). Errors that result in failure of protection (expressed as probabilities) predominate over errors that initiate or enable the fault sequence (expressed as frequencies). Initiating and enabling errors tend to be associated with an item of

Table 14.15 *General estimates of error probability used in the Rasmussen Report (Atomic Energy Commission, 1975)*

Estimated error probability	*Activity*
10^{-4}	Selection of a key-operated switch rather than a non-key switch (this value does not include the error of decision where the operator misinterprets situation and believes key switch is correct choice)
10^{-3}	Selection of a switch (or pair of switches) dissimilar in shape or location to the desired switch (or pair of switches), assuming no decision error. For example, operator actuates large-handled switch rather than small switch
3×10^{-3}	General human error of commission, e.g. misreading label and therefore selecting wrong switch
10^{-2}	General human error of omission where there is no display in the control room of the status of the item omitted, e.g. failure to return manually operated test valve to proper configuration after maintenance
3×10^{-3}	Errors of omission, where the items being omitted are embedded in a procedure rather than at the end as above
3×10^{-2}	Simple arithmetic errors with self-checking but without repeating the calculation by re-doing it on another piece of paper
$1/x$	Given that an operator is reaching for an incorrect switch (or pair of switches), he selects a particular similar-appearing switch (or pair of switches), where $x =$ the number of incorrect switches (or pairs of switches) adjacent to the desired switch (or pair of switches). The $1/x$ applies up to 5 or 6 items. After that point, the error rate would be lower because the operator would take more time to search. With up to 5 or 6 items he does not expect to be wrong and therefore is more likely to do less deliberate searching
10^{-1}	Given that an operator is reaching for a wrong motor operated valve (MOV) switch (or pair of switches), he fails to note from the indicator lamps that the MOV(s) is (are) already in the desired state and merely changes the status of the MOV(s) without recognizing he had selected the wrong switch(es)
~1.0	Same as above, except that the state(s) of the incorrect switch(es) is (are) *not* the desired state
~1.0	If an operator fails to operate correctly one of two closely coupled valves or switches in a procedural step, he also fails to correctly operate the other valve
10^{-1}	Monitor or inspector fails to recognize initial error by operator. *Note:* With continuing feedback of the error on the annunciator panel, this high error rate would not apply
10^{-1}	Personnel on different work shift fail to check condition of hardware unless required by checklist or written directive
5×10^{-11}	Monitor fails to detect undesired position of valves, etc., during general walk-around inspections, assuming no checklist is used
0.2–0.3	General error rate given very high stress levels where dangerous activities are occurring rapidly
$2^{(n-1)}x$	Given severe time stress, as in trying to compensate for an error made in an emergency situation, the initial error rate, x, for an activity doubles for each attempt, n, after a previous incorrect attempt, until the limiting condition of an error rate of 1.0 is reached or until time runs out. This limiting condition corresponds to an individual's becoming completely disorganized or ineffective
~1.0	Operator fails to act correctly in first 60 s after the onset of an extremely high stress condition, e.g. a large LOCA
9×10^{-1}	Operator fails to act correctly after the first 5 min after the onset of an extremely high stress condition
10^{-1}	Operator fails to act correctly after the first 30 min in an extreme stress condition
10^{-2}	Operator fails to act correctly after the first several hours in a high stress condition
x	After 7 days after a large LOCA, there is a complete recovery to the normal error rate, x, for any task

Notes:
(1) Modifications of these underlying (basic) probabilities were made on the basis of individual factors pertaining to the tasks evaluated.
(2) Unless otherwise indicated, estimates or error rates assume no undue time pressures or stresses related to accidents.

equipment, and protection errors with a process variable. Such a variable may have (1) no measurement, (2) measurement only or (3) measurement and alarm, and this is an important feature influencing the error rate.

The great majority of figures given are assumed values, with a few values being obtained from the literature and a few from the works. Engineering judgement is used in arriving at these values and the values selected take into account relevant influencing factors such as variable measurement and alarm and time available for action. The way in which allowance is made for these influencing factors is illustrated by the following extracts from the supporting notes:

> There is therefore a very high probability that the operator would be made aware of a spurious Slowdown condition by the alarms and this would be augmented by observation of excessive flaring and header noise that would highlight the cause of the problem. Because alarms will be set quite close to normal operating pressure and

Table 14.16 *Some estimates[a] of operator error used in fault tree analysis (Lees, 1983a; after Lawley, 1974, 1980) (Courtesy of the Institution of Chemical Engineers)*

Crystallizer plant

	Probability
Operator fails to observe level indicator or take action	0.04
Operator fails to observe level alarm or take action	0.03 *Frequency* (events/year)
Manual isolation valve wrongly closed (p)	0.05 and 0.1
Control valve fails to open or misdirected open	0.5
Control valve fails shut or misdirected shut (l)	0.5

Propane pipeline

	Time available	*Probability*
Operator fails to take action:		
To isolate pipeline at planned shut-down		0.001
To isolate pipeline at emergency shut-down		0.005
Opposite spurious tank blowdown given alarms and flare header signals	30 min	0.002
Opposite tank low level alarm		0.01
Opposite tank level high given alarm with	5–10 min	
(a) controller misdirected or bypassed when on manual		0.025
(b) level measurement failure		0.05
(c) level controller failure		0.05
(d) control valve or valve positioner		0.1
Opposite slowly developing blockage on heat exchanger revealed as heat transfer limitation		0.04
Opposite pipeline fluid low temperature given alarm	5 min	0.05
Opposite level loss in tank supplying heat transfer medium pump given no measurement (p)	5 min	0.2
Opposite tank blowdown without prior pipeline isolation given alarms which operator would not regard as significant and pipework icing	30 min	
(a) emergency blowdown		0.2
(b) planned blowdown		0.6
Opposite pipeline fluid temperature low given alarm		0.4
Opposite pipeline fluid temperature low given alarm	Limited	0.8
Opposite backflow in pipeline given alarm	Extremely short	0.8
Opposite temperature low at outlet of heat exchanger given failure of measuring instrument common to control loop and alarm		1
Misvalving in changeover of two-pump set (stand-by pump left valved open, working pump left valved in)		0.0025/changeover
Pump in single or double operation stopped manually without isolating pipeline		0.01/shut-down
Low pressure steam supply failure by fracture, blockage or isolation error (p)		0.1/year
Misdirection of controller when on manual (assumed small proportion of time)		1/year

[a] l, Literature value; p, plant value; other values are assumptions.

level, there would be almost 30 min available for action before the pipeline is chilled to −15°C.

and

The probabilities quoted are based on experience assuming that 5 min would be available for action, and including allowance for failure of the alarm. They take into account factors such as whether or not the operator would be in close attendance at the time of the fault, ease of diagnosis of the problem, whether or not the fault could be corrected from the control room or only by outside action, reluctance to shut-down the export pumps until correction of the fault has been attempted because back-up trip protection is provided, etc.

14.26 Assessment of Human Error: Qualitative Methods

The foregoing account has described some early approaches to human reliability assessment in support of probabilistic risk assessment (PRA). It is now necessary to backtrack a little and revert to a consideration of qualitative methods for analysis of human error.

Methods are available which may be utilized to identify and so reduce error-likely situations and also to support incident investigation. The elements of such methods are the underlying model of human reliability, the taxonomy of human error and the analysis technique.

These methods may be used in their own right to reduce error or as a stage in a human reliability assessment method. Their significance in the latter application is that they provide a structured approach to gaining understanding of the problem. In the absence of a high quality technique for this essential preliminary stage, quantification is premature.

Task analysis may be regarded as the prime technique, or rather family of techniques, but there are also a number of others. Early work in this area was that of J.R. Taylor (1979), who described a variety of approaches.

A method based on hierarchical task analysis is predictive human error analysis, described below. Another method is the work analysis technique described by Pedersen (1985).

A fuller discussion of human error analysis methods is given by Kirwan (1990) and the CCPS (1994/17).

14.26.1 Some error analysis strategies

Against the background of a long-term programme of work on human error, J.R. Taylor (1979) has developed a set of four error analysis strategies:

(1) action error method;
(2) pattern search method;
(3) THERP;
(4) sneak path analysis.

The third of these has already been outlined and is considered further below. The others are now described.

14.26.2 Action error method

The action error method is applicable to a sequence of operator actions that constitute intervention on the plant. The structure of the sequence takes the form: action/effect on plant/action/effect on plant. An outline of the structure of the procedure in the form of a cause-consequence diagram is shown in Figure 14.23. The range of errors handled is shown in Table 14.17.

Usually it is found that for any reasonably large operating procedure, it is practical to take into account only single initial errors, although in a few cases it may be possible to use heuristic rules to identify double errors that it is worthwhile to explore. For example, one error may result in material being left in a vessel, while a second error may result in an accident arising from this.

Taylor states that the method is not suitable for quantitative assessment, because the spread of error rates on the individual elements is considered to be too wide. Factors mentioned as influencing these error rates are cues, feedback and type of procedure (freely planned, trained).

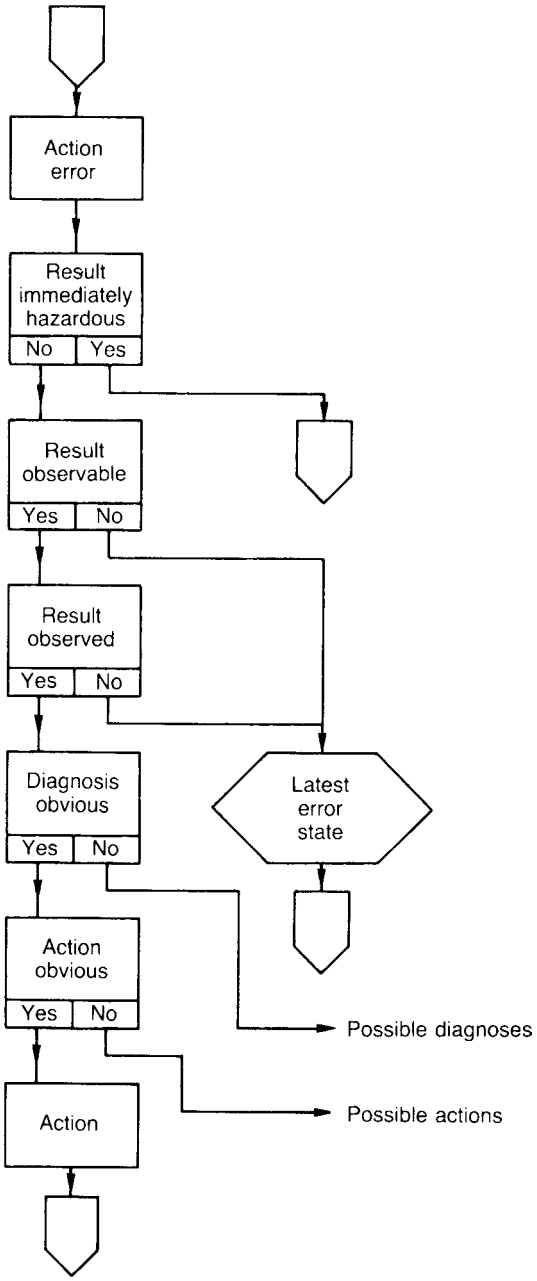


Figure 14.23 *Outline structure of action error method (J.R. Taylor, 1979. Reproduced by permission.)*

14.26.3 Pattern search method

The pattern search method is addressed to the problem that an accident is typically the result of a combination of operator errors. For such cases, detailed analysis at the task element level is impractical for two reasons. One is the combinatorial explosion of the number of sequences. The other is that the error rates, and above all the error rate dependencies, are not determinable.

An important feature of such accidents is that they may have a relatively long sequence of errors, say 3–5, which have a common cause, such as error in decision-making, in work procedure or in plant state assessment. Often the sequence is associated with an unrevealed plant failure.

Table 14.17 *Operator errors addressed in action error method (J.R. Taylor, 1979. Reproduced by permission.)*

Cessation of a procedure
Excessive delay in carrying out an action or omission of an action
Premature execution of an action – too early
Premature execution of an action – preconditions not fulfilled
Execution on wrong object of action
Single extraneous action
In making a decision explicitly included in a procedure, taking the wrong alternative
In making an adjustment or an instrument reading, an error outside tolerance limits

The pattern search method is based on identifying a common cause error, developing its consequence, perhaps using an event tree, and using the results to 'steer' the construction of the fault tree.

14.26.4 Sneak path analysis

Sneak path analysis is concerned with the identification of potential accident situations. It is so called by analogy with sneak circuits. It seeks to identify sources of hazard such as energy or toxins and targets such as people, critical equipment or reactive substances. The standpoint of the analysis is similar to the accident process model of Houston (1971) described in Chapter 2.

For an accident to occur, it is necessary for there to be some operator action, operator error, equipment failure or technical sequence. A search is made to determine whether any of these necessary events can occur. In examining operator error, attention is directed particularly to actions that are 'near' to the necessary error. Nearness may be temporal, spatial or psychological. Often such an action is very near to the normal operator action.

14.26.5 Predictive human error analysis (PHEA)

Predictive human error analysis (PHEA) is described by Embrey and co-workers (e.g. Murgatroyd and Tait, 1987; Embrey, 1990) and by the CCPS (1994/17). PHEA uses hierarchical task analysis to discover the plan involved in the task, combined with the error classification shown in Table 14.18. The task is then analysed step by step in terms of the task type, error type, task description, consequences, recovery and error reduction strategy.

In a validation study of PHEA, Murgatroyd and Tait (1987) found that the proportion of errors with potentially significant consequences that actually occurred in an equipment calibration task over a 5-year-period was 98%.

14.26.6 System for predictive error analysis and reduction (SPEAR)

The system for predictive error analysis and reduction (SPEAR) is a set of qualitative techniques, of which PHEA is one. It is described by the CCPS (1994/17). SPEAR comprises the following techniques: (1) task analysis, (2) performance influencing factor (PIF) analysis, (3) PHEA, (4) consequence analysis and (5) error reduction analysis.

Consequence analysis involves consideration not just of the consequences of failure to perform the task but also of the consequences of any side-effects that may occur whether or not the task is executed. Error reduction analysis is concerned with measures to reduce those errors that do not have a high probability of recovery. Task analysis and PHEA have already be described and PIF analysis is treated in Section 14.33.

Table 14.18 *Error classification for predictive human error analysis (Center for Chemical Process Safety, 1994/17) (Courtesy of the American Institute of Chemical Engineers)*

Action	
A1	Action too long/short
A2	Action mistimed
A3	Action in wrong direction
A4	Action too little/too much
A5	Misalign
A6	Right action on wrong object
A7	Wrong action on right object
A8	Action omitted
A9	Action incomplete
A10	Wrong action on wrong object
Checking	
C1	Checking omitted
C2	Check incomplete
C3	Right check on wrong object
C4	Wrong check on right object
C5	Check mistimed
C6	Wrong check on wrong object
Retrieval	
R1	Information not obtained
R2	Wrong information obtained
R3	Information retrieval incomplete
Transmission	
T1	Information not transmitted
T2	Wrong information transmitted
T3	Information transmission incomplete
Selection	
S1	Selection omitted
S2	Wrong selection made
Plan	
P1	Plan preconditions ignored
P2	Incorrect plan executed
P3	Correct but inappropriate plan executed
P4	Correct plan executed too soon/too late
P5	Correct plan executed in wrong order

14.27 Assessment of Human Error: *Human Reliability Analysis Handbook*

The first systematic approach to the treatment of human error within a PRA was the Technique for Human Error Rate Prediction (THERP). An early account of THERP was given by Swain (1972). Its origins were work done at Sandia Laboratories on the assessment of human error in assembly tasks. This work was then extended to human error in process control tasks, with particular reference to nuclear reactors. This extension to nuclear reactor control was used in the *Rasmussen Report,* or WASH-1400 (AEC, 1975), which contains generic PRAs for US commercial nuclear reactors.

The accident at Three Mile Island gave impetus to work in this area and led to the publication of the *Handbook of Human Reliability Analysis with Emphasis on Nuclear Power Plant Applications. Final Report* (the *HRA Handbook*) by Swain and Guttmann (1983). This report was widely circulated in draft form in 1980 and many literature references are to the draft. Further work is described in *Accident Sequence Evaluation Program. Human Reliability Analysis Procedure* (Swain, 1987a).

The *HRA Handbook* gives a complete methodology for addressing the human error aspects of a PRA, but THERP is central to the approach, and the methodology as a whole is generally referred to by that acronym. However, the *Handbook* represents a considerable extension of the original THERP methodology, particularly in respect of its adoption of the time reliability correlation method.

A further review of HRA and THERP is given by P. Miller and Swain (1987). Table 14.19 gives the contents of the *HRA Handbook* and Figure 14.24 shows the structure of the principal data tables. An account is now given of THERP. The *HRA Handbook* should be consulted for a more detailed treatment.

Table 14.19 *HRA Handbook: contents (Swain and Guttmann, 1983)*

1. Introduction
2. Explanation of Some Basic Terms
3. Some Performance Shaping Factors Affecting Human Reliability
4. Man–Machine Systems Analysis
5. A Technique for Human Reliability Analysis
6. Sources of Human Performance Estimates
7. Distribution of Human Performance and Uncertainty Bounds
8. Use of Expert Opinion in Probabilistic Risk Assessment
9. Unavailability
10. Dependence
11. Displays
12. Diagnosis of Abnormal Events
13. Manual Controls
14. Locally Operated Valves
15. Oral Instructions and Written Procedures
16. Management and Administrative Control
17. Stress
18. Staffing and Experience Levels
19. Recovery Factors
20. Tables of Estimated Human Error Probabilities
21. Examples and Case Studies
22. Concluding Comments

Appendices

A Methods for Propagating Uncertainty Bounds in a Human Reliability Analysis and for Determining Uncertainty Bounds for Dependent Human Activities
B An Alternative Method for Estimating the Effects of Dependence
C Calculations of Mean and Median Trials to Detection
D Calculations of Basic Walk-around Inspections as a Function of Period between Successive Walk-arounds
E Reviews of the Draft Handbook
F A Comparison of the October 1980 and Present Versions of the Handbook

14.27.1 Overall approach

The overall approach used in the *Handbook* is shown in Figure 14.25. The tasks to be performed are identified as part of the main PRA. The HRA involves the assessment of the reliability of performance of these tasks.

14.27.2 Technique for human error rate prediction (THERP)

The starting point is a task analysis for each of the tasks to be performed. The method is based on the original THERP technique and uses a task analytic approach in which the task is broken down into its constituent elements along the general lines described above. The basic assumption is that the task being performed is a planned one.

The task is described in terms of an event tree as shown in Figure 14.26. This figure gives the event tree for two tasks A and B which are performed sequentially and which constitute elements of a larger overall task. In reliability terms, the relationship between the two constituent tasks to the overall task may be a series or a parallel one.

The probability that task A will be performed successfully is a and the probability that it will not be performed successfully is A. Since task A is the first in the sequence it is assumed to be independent of any other task and the probabilities a and A are therefore unconditional probabilities. The probability that task B will be performed successfully is b and the probability that it will not be performed successfully is B. Since task B is performed after task A it is assumed to be dependent in some degree on task A and the probabilities b and B are therefore conditional probabilities. Thus for b it is necessary to distinguish between $b \mid a$ and $b \mid A$ and for B between $B \mid a$ and $B \mid$A. The probabilities to be used are therefore as shown in Figure 14.26.

The structure of the tree is the same whether the configuration is a series or parallel one but the status of the outcomes is different. As shown in Figure 14.26 for a series system in which it is necessary for both tasks to be successful, there is only one which rates as a success, whilst for a parallel system in which it is sufficient for only one of the tasks to be successful, there are three outcomes which rate as success.

A distinction is made between step-by-step tasks and dynamic tasks. The latter involve a higher degree of decision-making. The approach just described is most readily justified for step-by-step tasks.

14.27.3 Human error probability

The event tree so produced, and the corresponding equations, are then used to determine the probability of failure for the overall task. For this estimates are required of the HEP for each of the constituent tasks.

Several different human error probabilities are distinguished: nominal, basic, conditional and joint. A nominal HEP is a generic value before application of any performance shaping factors. A basic HEP (BHEP) is the basic unconditional HEP after application of performance shaping factors. A conditional HEP (CHEP) is a BHEP adjusted to take account of dependency. A joint HEP (JHEP) is the HEP for the overall task.

The simple application of HEP values that make no allowance for dependence tends to give very low probabilities of failure which do not accord with experience and carry little conviction. Allowance for dependence is therefore important. There is in any event some value of the HEP below which the estimate is no longer credible. A cut-off

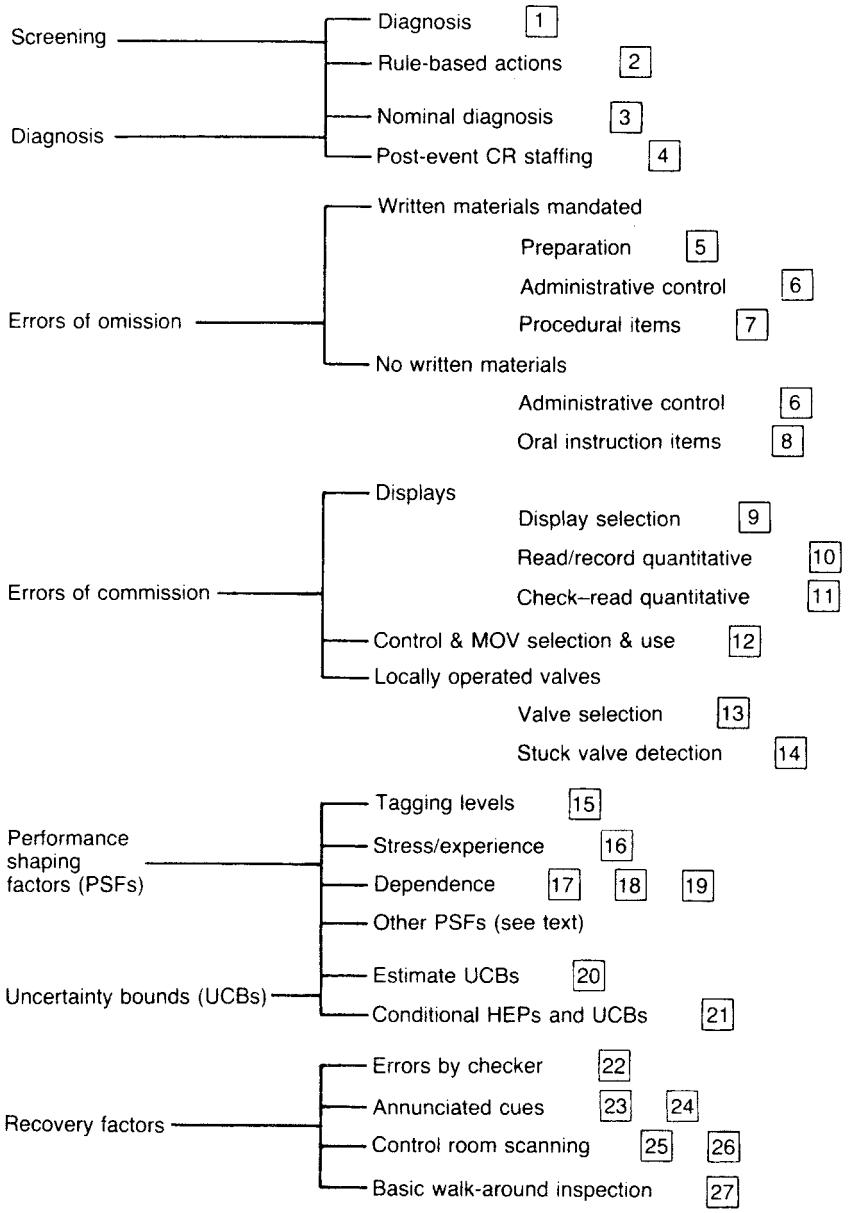


Figure 14.24 *HRA Handbook: structure of principal data tables (Swain and Guttmann, 1983). CR, control room; HEP, human error probability; MOV, motor operated valve*

value is therefore applied. Reference is made to a cut-off of about 5×10^{-5}.

Many of the HEPs in the *Handbook* are expressed as log–normal distributions, quoted in terms of the two parameters – median and error factor (EF).

14.27.4 Dependence model

The dependence model is an important feature of the methodology. A significant proportion of the *Handbook* is concerned with dependency. There are two basic forms of dependence: dependence between tasks and dependence between people.

Where two tasks are performed in sequence the second task may be influenced by the first. Dependence is likely, for example, where an operator has to change two valves one after the other.

The other situation is where two people are involved in the same task. The form of the involvement may vary.

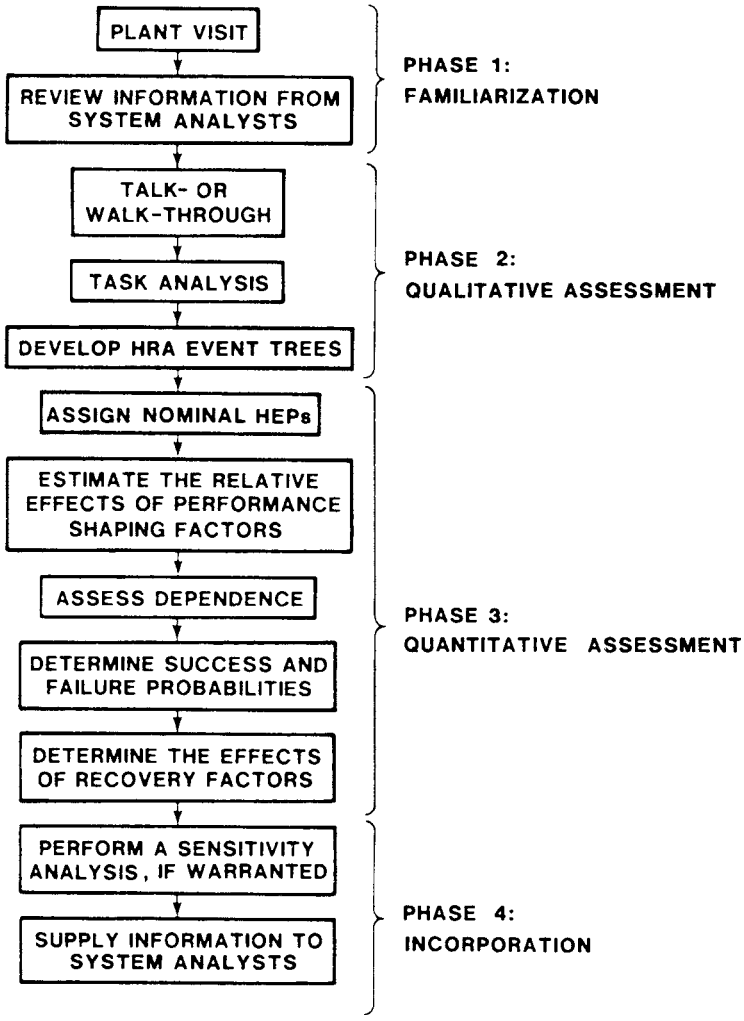


Figure 14.25 *HRA Handbook: methodology for human reliability analysis (Swain and Guttmann, 1983)*

The two persons may be involved in a joint task such as calibrating an instrument. They may perform separate but closely linked functions such as those of two operators sharing a control room but controlling different sections of the plant. The work of one person may be subject to the general supervision of another person. Or it may be formally checked by another.

There are various approaches that may be used to quantify dependence, including data and expert judgement. There are few relevant data. Expert judgement can be used to a limited extent. An example is given of the use of expert estimates of dependence in a calibration task.

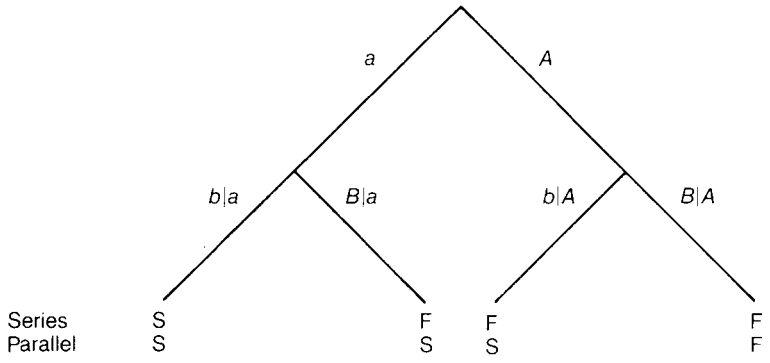
The approach used in the *Handbook*, therefore, is the development of a generalized dependence model. The degrees of dependence used are zero, low, medium, high and complete. The determination of the appropriate degree of dependence depends on the situation under consideration. The *Handbook* gives quite extensive guidance. Here it is possible only to give a few examples.

In some cases, there may be judged to be zero dependence. An example given of a situation where zero dependence between two tasks would be assumed is check-reading of one display followed by check-reading of another display as part of periodic scanning of the displays. Zero dependence is not normally assumed for persons working as a team or for one person checking another's performance.

The assumption of even a low level of dependence tends to result in an appreciably higher HEP than that of zero dependence. If there is any doubt, it is conservative to use low dependence rather than zero dependence.

A level of dependence between people that would be assessed as low is illustrated by the checking of the work of a new operator by a shift supervisor. In this situation, the shift supervisor has an expectation that the new operator may make errors and is more than usually alert.

A moderate level of dependence is usually assessed between the shift supervisor and the operators for tasks where the supervisor is expected to interact with them.



Task A = The first task
Task B = The second task
a = Probability of successful performance of task A
A = Probability of unsuccessful performance of task A
$b|a$ = Probability of successful performance of task B given a
$B|a$ = Probability of unsuccessful performance of task B given a
$b|A$ = Probability of successful performance of task B given A
$B|A$ = Probability of unsuccessful performance of task B given A

FOR THE SERIES SYSTEM:
$\Pr[S] = a(b|a)$
$\Pr[F] = 1 - a(b|a) = a(B|a) + A(b|A) + A(B|A)$

FOR THE PARALLEL SYSTEM:
$\Pr[S] = 1 - A(B|A) = a(b|a) + a(B|a) + A(b\,A)$
$\Pr[F] = A(B|A)$

Figure 14.26 *HRA Handbook: event tree for two tasks in sequence illustrating conditional probabilities (Swain and Guttmann, 1983); F, failure; S, success*

A high level of dependence, or even complete dependence, would be assigned for the case where the shift supervisor takes over a task from a less experienced operator, since the latter may well defer to the supervisor both because of his greater experience and his seniority.

The other aspect of the dependence model is the quantification of the adjustment to be made given that the degree of dependency has been determined. The adjustment is made to the BHEP. The relation used is:

$$P_c = (1 - kP_b)/(k + 1) \qquad [14.27.1]$$

where P_b, is the BHEP and P_c is the CHEP, k is a constant which has the following values: low dependency $k = 19$; medium dependency $k = 6$; high dependency $k = 1$.

Equation 14.27.1 and the values of the constant k are selected to give CHEPs of approximately 0.05, 0.15 and 0.50 of the BHEP for low, medium and high dependency, respectively, where BHEP ≤ 0.01. Where BHEP > 0.01, the effective multiplying factor is slightly different. Thus, for example, for a BHEP of 0.1 the values of the CHEP are 0.15, 0.23 and 0.55, respectively, for these three levels of dependency.

14.27.5 Displays, annunciators and controls

Common tasks in process control are obtaining information from displays, responding to annunciators and manipulating controls. This is very much the home ground of human factors and there is a good deal of information available on response times and probabilities of error in such tasks. The *Handbook* gives a number of tables for HEPs for these tasks.

For unannunciated displays, the *Handbook* gives the following HEP values for selection of a display (Table 20.9). The HEP depends on the existence of similar adjacent displays. It is assumed to be negligible if the display is dissimilar to adjacent displays and the operator knows the characteristics of the display he requires. The HEP is taken as 0.005 (EF 10) if it is from a group of similar displays on a panel with clearly drawn mimic lines which include the displays; as 0.001 (EF 3) if it is from a group of similar displays which are part of a well-delineated functional group on the panel; and as 0.003 (EF 3) if it is from an array of similar displays identified by label only. These HEP values do not include recovery from any error. The probability that this will occur is high if the reading obtained is grossly different from that expected.

For check reading from displays the HEPs given are as follows (Table 20.11). The HEP is taken as 0.001 for digital displays and for analogue meters with easily seen limit marks; as 0.002 for analogue meters with limits marks which are difficult to see and for analogue chart recorders with limits marks; as 0.003 for analogue meters without limit marks; and as 0.006 for analogue chart recorders without limit marks. In all cases, the EF is taken as 3. The HEP for confirming a status change on a status lamp and that for misinterpreting the indications an indicator lamp are assumed to be negligible. These HEPs apply to the individual checking of a display for some specific purpose.

14.27.6 Oral instructions and written procedures

Communication in process control includes both oral instructions and written procedures. For oral instructions, a distinction is made between general and detailed instructions. Table 14.20 gives some HEP estimates for these two cases.

For written instructions, the types of HEP treated include error in the preparation of the instructions, failure to refer to them and error in their use. Table 14.21 gives some HEP estimates for these three cases, respectively.

14.27.7 Locally operated valves

Another common task in process control is the manipulation of locally operated valves (LOVs). This task, therefore, receives special treatment in the *Handbook*. The valves concerned are manually operated. They include valves with or without a rising stem and with or without position indicators.

Three principal errors are distinguished. One is selection of the wrong valve. Here the base case is a single isolated valve. Where there are other valves present, the possibility exists that the wrong valve will be selected. Another type of error is reversal, or moving the valve in the wrong direction. The operator opens it instead of closing it, or vice versa. One form of this error is to reverse the state of a valve, which is in fact already in the desired state. The third type of error is failure to detect that the valve is stuck. A common form of this error is to fail to effect complete closure of a valve. Table 14.22 gives some HEP estimates for selection of a valve, for detection of a stuck valve and for checking a valve. The manipulation of valves is a particular case where there may exist a strong dependence, or coupling, between two tasks. This case is one that was taken into account in the *Rasmussen Report*. An operator may be required to cut off flow by closing two valves, closure of either of which is sufficient to stop the flow. If the probability of error in closing one valve is 10^{-2} and there is zero dependence, the probability of error in the overall task is 10^{-4} ($10^{-2} \times 10^{-2}$). On the other hand, if there is complete coupling, the probability of error is 10^{-2} ($10^{-2} \times 1$). These two cases represent the two extremes and constitute lower and upper bounds on the probability of failure. For the more realistic case of loose coupling, the approach used in WASH-1400 was to take for the probability of error the log−normal median or square root of the product of the two bounds: $(10^{-2} \times 10^{-4})^{1/2} = 10^{-3}$. The dependence model

Table 14.20 *HRA Handbook: human error probability (HEP) estimates and error factors (EFs) for oral instructions*[a] *(after Swain and Guttmann, 1983)*

Item[b]	*Number of oral instruction items or perceptual units*	*(a) Pr(F) to recall item 'N', order of recall not important*		*(b) Pr(F) to recall all items, order of recall not important*		*(c) Pr(F) to recall all items, order of recall is important*	
		HEP	*EF*	*HEP*	*EF*	*HEP*	*EF*
Oral instructions are detailed:							
(1)	1[c]	0.001	3	0.001	3	0.001	3
(2)	2	0.003	3	0.004	3	0.006	3
(3)	3	0.01	3	0.02	5	0.03	5
(4)	4	0.03	5	0.04	5	0.1	5
(5)	5	0.1	5	0.2	5	0.4	5
Oral instructions are general:							
(6)	1[c]	0.001	3	0.001	3	0.001	3
(7)	2	0.006	3	0.007	3	0.01	3
(8)	3	0.02	5	0.03	5	0.06	5
(9)	4	0.06	5	0.09	5	0.2	5
(10)	5	0.2	5	0.3	5	0.7	5

[a] It is assumed that if more than five oral instruction items or perceptual units are to be remembered, the recipient will write them down. If oral instructions are written down, use Table 20.5 in the *Handbook* for errors in preparation of written procedures and Table 20.7 for errors in their use.

The first column of HEPs (a) is for individual oral instruction items, e.g. the second entry, 0.003 (item 2a), is the Pr(F) to recall the second of two items, given that one item was recalled, and order is not important. The HEPs in the other columns for two or more oral instruction items are joint HEPs, e.g. the second 0.004 in the second column of HEPs is the Pr(F) to recall both of two items to be remembered, when order is not important. The 0.006 in the third column of HEPs is the Pr(F) to recall both of two items to be remembered in the order of performance specified. For all columns, the EFs are taken from Table 20.20.

[b] The term 'item' for this column is the usual designator for tabled entries and does *not* refer to an oral instruction item.

[c] The Pr(F) values in rows 1 and 6 are the same as the Pr(F) to initiate the task.

Table 14.21 *HRA Handbook; human error probability (HEP) estimates and error factors (EFs) for written procedures (after Swain and Guttmann, 1983)*

A Preparation of written procedures[a]

Item	*Potential errors*	*HEP*	*EF*
(1)	Omitting a step or important instruction from a formal or *ad hoc* procedure[b] or a tag from a set of tags	0.003	5
(2)	Omitting a step or important instruction from written notes taken in response to oral instructions[c]	Negligible	
(3)	Writing an item incorrectly in a formal or *ad hoc* procedure or a tag	0.003	5
(4)	Writing an item incorrectly in written notes made in response to oral instructions[c]	Negligible	

[a] Except for simple reading and writing errors, errors of providing incomplete or misleading technical information are not addressed in the *Handbook*. The estimates are exclusive of recovery factors, which may greatly reduce the nominal HEPs.
[b] Formal written procedures are those intended for long-time use; *ad hoc* written procedures are one-of-a-kind, informally prepared procedures for some special purpose.
[c] A maximum of five items is assumed. If more than five items are to be written, use 0.001 (EF = 5) for each item in the list.

B Neglect of written procedures

Item	*Task*	*HEP*	*EF*
(1)	Carry out a plant policy or scheduled tasks such as periodic tests or maintenance performed weekly, monthly or at longer intervals	0.01	5
(2)	Initiate a scheduled shiftly checking or inspection function[a]	0.001	3
	Use written operations procedures under:		
(3)	Normal operating conditions	0.01	3
(4)	Abnormal operating conditions	0.005	10
(5)	Use a valve change or restoration list	0.01	3
(6)	Use written test or calibration procedures	0.05	5
(7)	Use written maintenance procedures	0.3	5
(8)	Use a checklist properly[b]	0.5	5

[a] Assumptions for the periodicity and type of control room scans are discussed in Chapter 11 of the *Handbook* in the section, 'General Display Scanning Model'. Assumptions for the periodicity of the basic walk-around inspection are discussed in Chapter 19 of the *Handbook* in the section, 'Basic Walk-around Inspection'.
[b] Read a single item, perform the task, check off the item on the list. For any item in which a display reading or other entry must be written, assume correct use of the checklist for that item.

C Use of written procedures[a]

Item[b]	*Omission of item*	*HEP*	*EF*
When procedures with check-off provisions are correctly used:[c]			
(1)	Short list, ≤10 items	0.001	3
(2)	Long list, >10 items	0.003	3
When procedures without check-off provisions are used, or when check-off provisions are incorrectly used:[d]			
(3)	Short list ≤ 10 items	0.003	3
(4)	Long list, >10 items	0.01	3
(5)	When written procedures are available and should be used but are not used[d]	0.05[e]	5

[a] The estimates for each item (or perceptual unit) presume zero dependence among the items (or units) and must be modified by using the dependence model when a nonzero level of dependence is assumed.
[b] The term 'item' for this column is the usual designator for tabled entries and does *not* refer to an item of instruction in a procedure.
[c] Correct use of check-off provisions is assumed for items in which written entries such as numerical values are required for the user.
[d] Table 20.6 in the *Handbook* lists the estimated probabilities of incorrect use of check-off provisions and of non-use of available written procedures.
[e] If the task is judged to be 'second nature', use the lower uncertainty bound for 0.05, i.e. use 0.01 (EF = 5).

given in the *Handbook* allows the use of more levels of dependence.

14.27.8 Time ± reliability correlation

As already mentioned, there has been an increasing tendency, associated mainly with experimental work with operators on simulators, to correlate the probability of operator failure with time. In particular, use is made of the time–reliability correlation (TRC) to obtain human error probabilities for complex, or non-routine, tasks, including handling an emergency. The assumption underlying such a TRC is that, although there are in principle other factors

Table 14.22 *HRA Handbook; human error probability (HEP) estimates and error factors (EFs) for manipulation and checking of locally operated valves (after Swain and Guttmann, 1983)*

A Selection of valve

Item	*Potential errors*	*HEP*	*EF*
Making an error of selection in changing or restoring a locally operated valve when the valve to be manipulated is:			
(1)	Clearly and unambiguously labelled, set apart from valves that are similar in *all* of the following: size and shape, state and presence of tags[a]	0.001	3
(2)	Clearly and unambiguously labelled, part of a group of two or more valves that are similar in *one* of the following: size and shape, state or presence of tags[a]	0.003	3
(3)	Unclearly or ambiguously labelled, set apart from valves that are similar in *all* of the following: size and shape, state and presence of tags[a]	0.005	3
(4)	Unclearly or ambiguously labelled, part of a group of two or more valves that are similar in *one* of the following: size and shape, state or presence of tags[a]	0.008	3
(5)	Unclearly or ambiguously labelled, part of a group of two or more valves that are similar in *all* of the following: size and shape, state and presence of tags[a]	0.001	3

[a] Unless otherwise specified, level 2 tagging is presumed. If other levels of tagging are assessed, adjust the tabled HEPs according to Table 20.15 in the *Handbook*.

B Detection of stuck valves

Item	*Potential errors*	*HEP*	*EF*
Given that a locally operated valve sticks as it is being changed or restored,[a] the operator fails to notice the sticking valve, when it has:			
(1)	A position indicator[b] only	0.001	3
(2)	A position indicator[b] and a rising stem	0.002	3
(3)	A rising stem but no position indicator[b]	0.005	3
(4)	Neither rising stem nor position indicator[b]	0.01	3

[a] Equipment reliability specialists have estimated that the probability of a valve's sticking in this manner is approximately 0.001 per manipulation, with an error factor of 10.
[b] A position indicator incorporates a scale that indicates the position of the valve relative to a fully opened or fully closed position. A rising stem qualifies as a position indicator if there is a scale associated with it.

C Checking, including valves[a]

Item	*Potential errors*	*HEP*	*EF*
(1)	Checking routine tasks, checker using written materials (includes over-the-shoulder inspections, verifying position of locally operated valves, switches, circuit breakers, connectors, etc., and checking written lists, tags or procedures for accuracy)	0.1	5
(2)	Same as above, but without written materials	0.2	5
(3)	Special short-term, one-of-a-kind checking with alerting factors	0.05	5
(4)	Checking that involves active participation, such as special measurements	0.01	5
Given that the position of a locally operated valve is checked (item (1) above), noticing that it is not completely opened or closed:		0.5	5
(5)	Position indicator[b] only	0.1	5
(6)	Position indicator[b] and a rising stem	0.5	5
(7)	Neither a position indicator[b] nor a rising stem	0.9	5
(8)	Checking by reader/checker of the task performer in a two-man team, *or* checking by a second checker, routine task (no credit for more than 2 checkers)	0.5	5
(9)	Checking the status of equipment if that status affects one's safety when performing his tasks	0.001	5
(10)	An operator checks change or restoration tasks performed by a maintainer	Above HEPs/2	5

[a] This table applies to cases during normal operating conditions in which a person is directed to check the work performed by others either as the work is being performed or after its completion.
[b] A position indicator incorporates a scale that indicates the position of the valve relative to a fully opened or fully closed position. A rising stem qualifies as a position indicator if there is a scale associated with it.

that affect operator performance in such tasks, time is the dominant one.

An aspect of operator performance of particular concern to the nuclear industry is behaviour following the initial event. One of the main methods used to study such behaviour is the use of simulators. Work on simulators has shown that the probability of success in post-event behaviour correlates strongly with time. Early work on this was done by R.E. Hall, Fragola and Wreathall (1982). A number of TRC models have since been produced based on simulator results.

Figure 14.27 shows some TRCs given by Hall, Fragola and Wreathall for operator vigilance and for particular events to which a nuclear reactor operator may have to respond.

14.27.9 Nominal diagnosis model

The task analysis approach on which THERP is based is not well adapted to handling the behaviour of the operators in an abnormal situation. For this, use is made of the TRC approach. Several TRCs are given in the *Handbook*. Two are used for screening: one for diagnosis and one for post-diagnosis performance. The main TRC is the nominal diagnosis model that is applicable to diagnosis only and not to post-diagnosis performance. This TRC is shown in Figure 14.28. In contrast to the other HEP relations, which refer to individuals, the TRCs refer to the behaviour of a team. The nominal diagnosis model, therefore, implies a particular manning model. This is described in the next section.

Figure 14.28 includes curves for the upper and lower bounds. The *Handbook* gives guidance on the choice of curve. Essentially the lower bound is applicable if the event is a well-recognized one and the operators have practised on a simulator and demonstrate by interview that they know how to handle it. The upper bound is applicable if the event is not covered by training or is covered only in initial training or if the operators demonstrate by interview that they do not know how to handle it. The main, or nominal, curve is applicable if the operators have practised the event only on simulator requalification exercises or if none of the rules for the lower or upper bound apply.

The nominal diagnosis TRC does not itself fit a log–distribution, but it may be approximated by such a distribution. The parameters of the log–normal distribution approximating to this TRC have been estimated by Dougherty and Fragola (1988), who obtain values for the median and the EF of $m = 4$ and $f = 3.2$, respectively. The relation between the nominal diagnosis TRC and the approximating log–normal distribution is:

Time (min)	*Human error probability*	
	Nominal diagnosis TRC	*Approximating log–normal distribution*
5	0.9	0.4
10	0.1	0.1
20	0.01	0.01
30	0.001	0.002
60	0.0001	0.00006

14.27.10 Manning model

The nominal diagnosis TRC just described applies to a whole team and is in fact postulated on a particular team composition. In other words there is an implied manning model.

The manning model used is shown in Table 14.23. The team consists of operators 1 and 2, the shift supervisor and the shift technical advisor. At 10 min into the incident for operator 1 the BHEP is 0.1. Operator 2 has complete dependency. The shift supervisor has high dependency. At this stage, no credit is taken for the shift technical advisor. For operator 1, the BHEP remains constant at 0.1. At 20 min for operator 2, the dependency reduces to the high level and

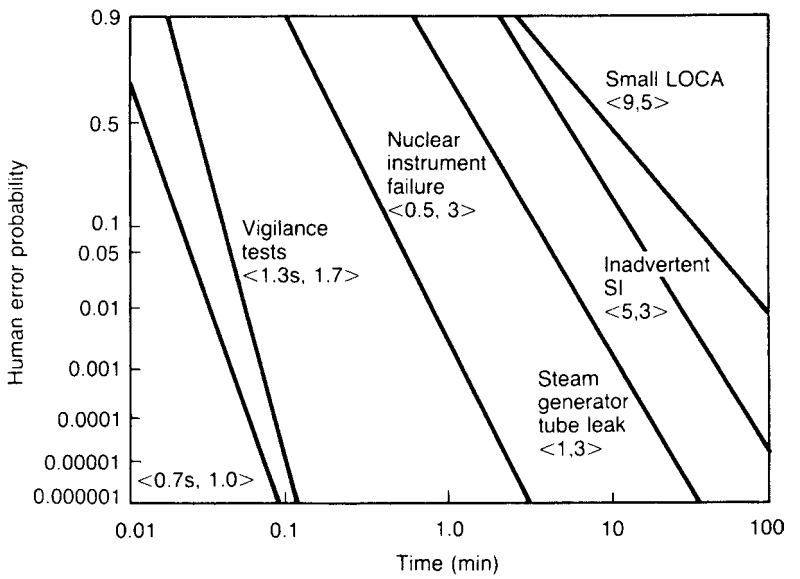


Figure 14.27 *Some time–reliability correlations relevant to nuclear power plants (R.E. Hall, Fragola and Wreathall, 1982). LOCA, loss of coolant accident; SI, safety interlock. Notation <x, y> denotes median m, error factor f of log–normal distribution*

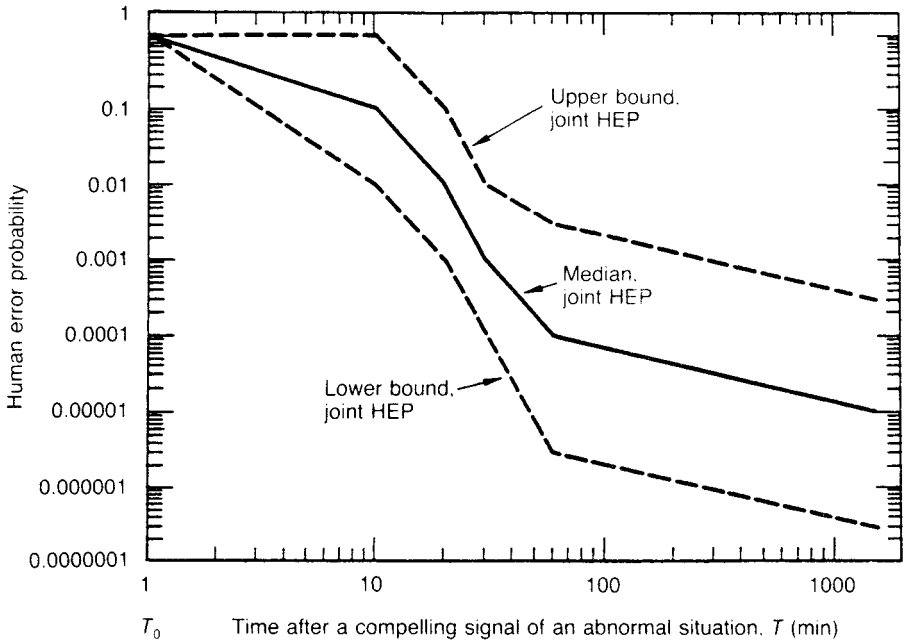


Figure 14.28 *HRA Handbook: nominal diagnosis model (Swain and Guttmann, 1983): human error probability (HEP) of diagnosis of one abnormal event by control room personnel*

Table 14.23 *HRA Handbook: manning model for nominal diagnosis model – illustrative example (after Dougherty and Fragola, 1988, from Swain and Guttmann, 1983)*

Time (min)	*Conditional probability of error*		*Joint probability of error*	*TRC value*
10	Operator 1	0.1 (basic probability)	0.055	0.1
	Operator 2	1.0 (complete dependence)		
	Shift supervisor	0.55 (high dependency)		
	Shift technical adviser	1.0 (no credit)		
20	Operator 1	0.1 (basic probability)	0.007	0.01
	Operator 2	0.55 (high dependency)		
	Shift supervisor	0.23 (moderate dependency)		
	Shift technical adviser	1.0 (high dependency)		
30	Operator 1	0.1 (basic probability)	0.0012	0.001
	Operator 2	0.55 (high dependency)		
	Shift supervisor	0.15 (low dependency)		
	Shift technical adviser	0.15 (low dependency)		

for the shift supervisor it reduces to medium level. The shift technical advisor is now taken into account with a high dependency. At 30 min for operator 2, the dependency remains at the high level but for the shift supervisor it reduces again to the low level. For the shift technical advisor, the dependency reduces to the low level. The CHEPs shown are those given by Equation 14.27.1. The JHEPs shown are the products of the BHEP for operator 1 and the CHEPs for the other members of the team. These JHEPs are then rounded to give the actual values used in the nominal diagnosis TRC.

14.27.11 Recovery model

Some errors are not recoverable, but many are and the recovery model is therefore another important feature of the methodology. The probability of recovery depends on the opportunities for detection, the use made of these opportunities and the effectiveness of the recovery action. Recovery mechanisms include:

(1) human actions – checking;
(2) plant states – panel indications;
(3) equipment states – inspections.

Recovery is treated under the headings:

(1) human redundancy;
(2) annunciated indications;

(3) active inspections;
(4) passive inspections.

Human redundancy is essentially the checking of one person's work by another person. For checking, the *Handbook* gives the following HEP values (Table 20.22). The HEP for checking is taken as being determined by two distinct errors, failure to execute the check at all and error in performing it. The HEP is taken as 0.1 if a written procedure is used; as 0.2 if a written procedure is not used; as 0.05 if the check is a one-off with alerting factors; and as 0.01 if the check involves active participation. The HEP is taken as 0.5 for checking by a second member of a two-man team or by a second checker. It is taken as 0.001 for checking of equipment which affects the safety of the checker. In all cases, the EF is taken as 5. These HEPs apply where a person is directed to check the work of others, either as the work is being performed or after its completion. Credit for checking is limited to the use of two checkers. The HEP of the second checker in a routine task is taken as 0.5.

Recognition is given to a number of problems associated with checking. Checking is particularly affected by psychological considerations. There is an expectation that an experienced person will not make errors. Conversely, there is an expectation that an inexperienced person may well do so.

It is often suggested that if a person knows that his work is to be checked he may perform it with less care and that the end result may be a lower task reliability than if checking were not employed. This view is rejected. It is argued that for any credible values of the BHEP and the CHEP for checking the JHEP will be lower with checking.

The possibility exists that on a particular plant checking may have fallen into disuse. This is one feature in particular which it is prudent for the analyst to observe and check. There is a tendency in some situations for the task and its checking to become elided and for the whole to become a joint operation. Where this occurs, there is no longer an independent check.

Annunciated indicators, or alarms, are treated at two levels. The HEP for taking the prescribed corrective action in response to a single alarm is 0.0001, but this may be drastically modified for other alarm situations.

An annunciator response model is used which applies to multiple alarms and is expressed by two equations. The probability P_i of failure to initiate action in response to the ith alarm in a group of n alarms is:

$$P_i = 10^{-4} \qquad i = 1 \qquad [14.27.2a]$$

$$P_i = 2^{i-2} \times 10^{-3} \qquad 1 < i \leq 10 \qquad [14.27.2b]$$

$$P_i = 0.25 \qquad i > 10 \qquad [14.27.2c]$$

The probability P_r of failure to initiate action in response to a randomly selected alarm in a group of alarms and is:

$$P_r = \sum_{i=1}^{n} P_i / n \qquad [14.27.3]$$

Active inspection is defined as inspection for a specific purpose. The main forms are prescribed periodic logging of readings and prescribed audit of indications with written instructions, both in the control room, and a walk-around inspection on the plant with instructions. The inspection may be based on oral instructions or written instructions. The HEP for an active inspection is that applicable to oral instructions and written procedures, already described.

Passive inspection is defined as a casual type of inspection. There are no written instructions and no instructions to look for any particular feature. The main forms are scanning of the control room displays and a walk-around on the plant.

As described above, HEPs are given for detection of deviant unannunciated displays in a periodic scan.

For passive inspection by walk-around, the *Handbook* gives the following HEP values (Table 20.27). The event concerned is failure to detect a particular deviant state within 30 days. It is assumed that there is one inspection per shift. The HEPs are taken as 0.52, 0.25, 0.05, 0.003, 0.002, 0.001 and 0.001 for periods between walk-around of 1, 2, 3, 4, 5, 6 and 7 days, respectively.

For a planned task recovery may be introduced into the task event tree. This is illustrated in the event tree shown in Figure 14.29, which shows recoveries from error represented by tasks C and G. C is a recovery from failure at task B. G is a recovery from failure at task E and also at task H.

14.27.12 Performance shaping factors

The performance shaping factors (PSFs) are divided into the following classes:

(1) external factors:
  (a) situational characteristics,
  (b) task and equipment characteristics,
  (c) job and task instructions,
(2) internal factors;
(3) stressors.

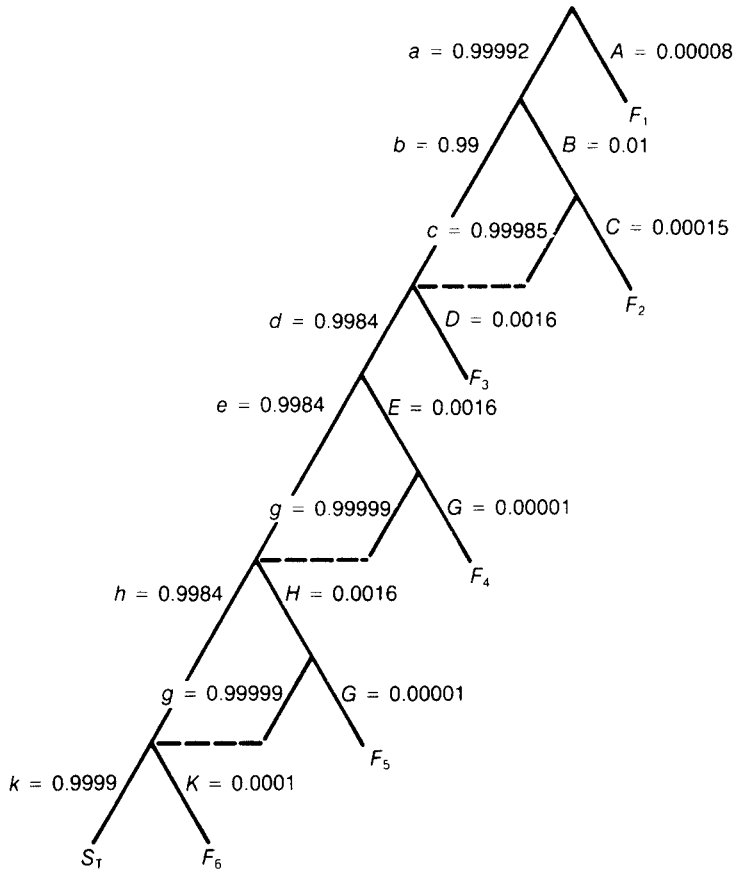
Stressors are treated separately and are considered in the next section.

The PSFs used listed in the *Handbook* are shown in Table 14.24. Each PSF is discussed in some detail. The *Handbook* does not, however, appear to give any simple method of adjusting the nominal HEPs by way of a multiplying factor or otherwise. It is evidently up to the analyst to judge the quality of a particular PSF for the situation concerned and to make a suitable adjustment.

However, some estimates, described as speculative and conservative, are given of the potential benefit of the adoption of good ergonomic practices. The authors state that in nuclear power plants violations of conventional human factors practices are the rule rather than the exception. The *Handbook* indicates that a reduction in HEP by a factor in the range 2–10 might be attained by adoption of good human factors practices in the design or displays and controls, and a similar reduction can be achieved by the use of checklists and well-written procedures instead of narrative procedures (Table 3.8). The EFs given alongside the nominal HEPs also provide further guidance for the analyst.

14.27.13 Stress

As already described, stress is an important determinant of performance and must be taken into account. It is one of the PSFs, but is accorded special treatment. Stress may be caused by both external and internal factors. Some of these



JHEP	EVENTS	JOINT HEPs FOR 3 OPERATORS
A	Fail to initiate action to annunciators	0.00008
B	Misdiagnosis	0.01
C	Fail to initiate action to annunciator	0.00015
D	Omit step 2.4	0.0016
E	Omit step 2.5	0.0016
G	Fail to initiate action to annunciator	0.00001
H	Omit step 2.6	0.0016
K	Fail to initiate high-pressure injection	0.0001

Figure 14.29 *HRA Handbook: event tree for task of handling loss of steam generator feed in a nuclear power plant, illustrating recovery from error (Swain and Guttmann,1983)*

stressors are listed in Table 14.24 for stress that could potentially be rather complex.

The approach adopted in the *Handbook* is to simplify and to treat stress as a function of workload. The assumption underlying this approach is that, although there are in principle other factors that affect stress, workload is the dominant one.

At a very low workload, performance is less than optimal. There is some higher workload at which it is optimal. At a higher workload yet, performance again deteriorates. Finally, the situation may induce threat stress, which is qualitatively different and is accorded separate treatment.

The four levels of stress are therefore defined as:

(1) very low task load;
(2) optimum task load;
(3) heavy task load;
(4) threat stress.

A heavy task load is one approaching the limit of human capacity.

For the first three levels of stress, the *Handbook* gives multiplying factors which are applied to the nominal HEP (Table 20.16). The multiplying factors for an experienced

Table 14.24 *HRA Handbook: some performance shaping factors (PSFs)*[a] (after Swain and Guttmann, 1983)

External PSFs		*Stressor PSFs – psychological stressors: PSFs which directly affect mental stress*	*Internal PSFs – organismic factors: characteristics of people resulting from internal and external influences*
Situational characteristics: those PSFs general to one or more jobs in a work situation	*Task and equipment characteristics: those PSFs specific to tasks in a job*		
Architectural features	Perceptual requirements	Suddenness of onset	Previous training/experience
Quality of environment	Motor requirements (speed, strength precision)	Duration of stress	State of current practice or skill
Temperature, humidity, air quality, and radiation	Control–display relationships	Task speed	Personality and intelligence variables
Lighting	Anticipatory requirements	Task load	Motivation and attitudes
Noise and vibration	Interpretation	High jeopardy risk	Emotional state
Degree of general cleanliness	Decision-making	Threats (of failure, loss of job)	Stress (mental or bodily tension)
Work hours/work breaks	Complexity (information load)	Monotonous, degrading or meaningless work	Knowledge of required performance standards
Shift rotation	Narrowness of task	Long, uneventful vigilance periods	Sex differences
Availability/adequacy of special equipment, tools and supplies	Frequency and repetitiveness	Conflicts of motives about job performance	Physical condition
Manning parameters	Task criticality	Reinforcement absent or negative	Attitudes based on influence of family and other outside persons or agencies
Organizational structure (e.g. authority, responsibility, communication channels)	Long- and short-term memory	Sensory deprivation	Group identifications
Actions by supervisors, co-workers, unions representatives and regulatory personnel	Calculational requirements	Distractions (noise, glare, movement, flicker, colour)	
Rewards, recognition, benefits	Feedback (knowledge or results)	Inconsistent cueing	
	Dynamic vs step-by-step activities		
Job and task instructions: single most important tool for most tasks	Team structure and communication	*Physiological stressors: PSFs which directly affect physical stress*	
Procedures required (written or not written)	Man-made interface factors: design of prime equipment, test equipment, manufacturing equipment, job aids, tools, fixtures	Duration of stress	
Written or oral communications		Fatigue	
Cautions and warnings		Plain or discomfort	
Work methods		Hunger or thirst	
Plant policies (shop practices)		Temperature extremes	
		Radiation	
		G-force extremes	
		Atmospheric pressure extremes	
		Oxygen insufficiency	
		Vibration	
		Movement constriction	
		Lack of physical exercise	
		Disruption of circadian rhythm	

[a] Some of the tabled PSFs are not encountered in present-day nuclear power plants (e.g. *g*-force extremes), but are listed for application to other man–machine systems.

operator are: 2 for a very low task load and for a heavy task load of a step-by-step task; and 5 for a heavy task load of a dynamic task and for a threat stress condition of a step-by-step task. The multiplier for optimum workload is unity. Different factors are given for an inexperienced operator.

A situation that can arise is where an error is made and recognized and an attempt is then made to perform the task correctly. Under conditions of heavy task load the probability of failure tends to rise with each attempt as confidence deteriorates. For this situation the doubling rule is applied. The HEP is doubled for the second attempt and doubled again for each attempt thereafter, until a value of unity is reached. There is some support for this in the work of Siegel and Wolf (1969) described above.

For a dynamic task or for diagnosis under threat stress the approach is different. A multiplier is not used, but instead a HEP value is given. The HEP for these cases is taken as 0.25 for an experienced operator and as 0.5 for an inexperienced one (both EF 5). The *Handbook* gives guidance on the assignment of the levels of workload, and hence stress.

The basis of the HEP value of 0.25 is the work on behaviour in emergencies by Ronan and Berkun already described. The probability of ineffective behaviour from the work on in-flight emergencies is about 0.15. The training of a pilot is particularly intensive. Operators are not expected to perform as well. Hence, the HEP value of 0.25 is used for operators.

This HEP for threat stress conditions applies to dynamic tasks and to diagnosis, not to step-by-step tasks, for which, as already stated, a multiplier of 5 is used.

A different treatment again is applied to a loss-of-coolant accident (LOCA).

14.27.14 Sources of human performance estimates

Ideally, the data on human performance used in this study would have been obtained from the nuclear industry alone. In fact, the data from this source were very limited and a much wider range of sources was used, as follows: nuclear power plants (NPPs); NPP simulators; process plants; other industrial and military sources; experiments and field studies on real tasks; and experiments on artificial tasks. This list is in order of decreasing relevance but, unfortunately, of increasing data availability. Some 29 'experts' on human error were approached for assistance in providing HEP estimates, but virtually none were forthcoming.

For the nuclear industry the main potential source of human error data is licensee events reports (LERs). These contain an entry 'Personnel error'. HEPs were determined from these LERs for tasks involving operation, maintenance and testing of manual isolation valves, motor operated valves (MOVs) and pumps. The HEP values obtained were low. Work by Speaker, Thompson and Luckas (1982) on valves has shown, however, that for every LER classification of 'Personnel error', there were some 5–7 additional reportable events that in their judgement involved human error. Multiplication of the original HEP estimates by a correction factor of 6 brought them much closer to those from other sources.

Most studies on NPP and other simulators have not yielded usable human error data. The first systematic study found which does was that of Beare *et al.* (1983). This work came too late for incorporation in the *Handbook* but was used as a cross-check. Extensive use was made of HEP data from the process industries given by Kletz and Whitaker (1973), E. Edwards and Lees (1974) and the *ICI Safety Newsletter* (1979). Other industrial HEP data mentioned are those of Rook (1962), Rigby and Edelman (1968a,b) and Rigby and Swain (1968, 1975) on the production and testing of military systems.

A number of field studies and experiments in industrial settings were conducted and yielded usable data. These were subject, however, to the usual caution that the very fact that an experiment is being conducted tends to distort the results.

There is a large amount of experimental data on artificial tasks such as those conducted in laboratories. This work suffers from the fact that not only is it artificial, but also the limits of acceptable performance are often very narrow. It tends to be a poor indicator of absolute performance in real situations, but is a much more reliable guide to comparative performance. The correction that needs to be applied to such data to allow for the broader tolerances in industrial situations was the subject of a study by Payne and Altaian (1962), who obtained an average correction factor of 0.008. The *Handbook* states that using this factor the HEP values obtained are similar to those found in field operations.

Expert judgement was utilized extensively to obtain HEP estimates where hard data were not available. Use was made of scaling techniques to calibrate HEPs for tasks estimated by the experts against known task HEPs. For the HEP in an emergency or highly stressed situation use was made of the work of Ronan (1953) and Berkun and co-workers (Berkun *et al.*, 1962; Berkun, 1964).

The *Handbook* discusses the estimation of HEPs where these are a function of time. For such tasks the three relevant features are: the time to begin the task, essentially the response time and the time required for diagnosis, if any; the time required to do the task correctly; and the time available to do the task correctly. Data on the time to perform the task were obtained from operating records and from experts. The time available was often determined by the characteristics of the plant.

The *Handbook* also gives an account of the determination of HEPs for: displays and controls; LOVs; oral instructions and written procedures; administrative controls; and abnormal events.

14.27.15 Human performance estimates from expert judgement

The estimates of human performance given in the *Handbook*, whether for human error probabilities or performance shaping factors, are based on expert judgement. A discussion of expert judgement techniques applicable to human factors work is given in the *Handbook* by Weston (1983). He discusses the following methods: (1) paired comparisons, (2) ranking and rating procedures, (3) direct numerical estimation and (4) indirect numerical estimation. In dealing with estimates of human error, it is particularly important to give a full definition of the task for which the estimate is to be made. If the definition is poor, the estimates obtained are liable to exhibit wide differences.

A study is quoted by Seaver and Sitwell (1983) in which these methods were compared in respect of six criteria. For the three criteria selected by Weston (quality of judgements, difficulty of data collection and empirical support) the rankings obtained by these workers were as follows: (1, best; 4, worst):

Criterion	*Type of procedure*			
	Paired comparisons estimation	*Ranking/ rating estimation*	*Direct numerical*	*Indirect numerical*
Quality of judgement	1	2	4	3
Difficulty of data collection	4	1	2	3
Empirical support	3	4	1	1

14.27.16 Uncertainty bounds and sensitivity analysis

It is normal to include in a hazard assessment a sensitivity analysis and this creates a requirement to express an estimate of HEP not just as a point value but as a distribution. The distribution that is generally used is the log–normal distribution. As described in Chapter 7, the log–normal distribution is characterized by the two parameters m^* and σ Alternatively, it may be defined instead in terms of the log–normal median m and the EF f. Often only a point value is available, and generalized values of σ or f are used to give the spread.

The log–normal distribution is that used in the *Handbook*. It is admitted that the basis for preferring this distribution is not strong. The experimental support that exists relates to distributions of response times. On the other hand, it is argued that the choice of distribution does not appear critical. It is also the case that the log–normal distribution is a convenient one to use. Uncertainty arises from (1) lack of data, (2) deficiencies in the models used, (3) the effects of the PSFs and (4) the variable quality of analysts.

Using the log–normal distribution, characterized by the log–normal median m and the EF f the uncertainty bounds (UCBs) are expressed in terms of the error factor. As an illustration, consider the following case:

Nominal HEP $= 0.01$
Lower UCB $= 0.003$
Upper UCB $= 0.03$
Error factor $f = (0.03/0.003)^{1/2} \approx 3$

For the most part symmetrical UCBs are used, but there are exceptions. If the median value is low, the use of symmetrical UCBs may give a lower bound which is below the HEP cut-off, whilst at the other extreme for an HEP ≥ 0.25 it may give an upper bound which exceeds unity. In these cases asymmetrical bounds are used.

The general guidelines given in the *Handbook* for estimating the EF (Table 20.20) are given in Table 14.25.

14.27.17 Validation

A methodology of the type just described is clearly difficult to validate. There is a good deal of information provided in the *Handbook* in support of individual HEP estimates and some of this is described above. An account is also given of validation exercises carried out in support of the original THERP methodology, but these relate to tasks such as calibration and testing rather than process control.

14.28 Assessment of Human Error: Success Likelihood Index Method (SLIM)

A method of obtaining HEP estimates based on PSFs is the success likelihood index (SLI) which is incorporated in the SLI method (SLIM). Accounts are given in *SLIM-MAUD: An Approach to Assessing Human Error Probabilities using Structured Judgement* by Embrey *et al.* (1984 NUREG/CR-3518) and by Embrey (1983a,b) and Kirwan (1990).

SLIM treats not only the quality of the individual PSFs but also the weighting of these in the task. It is thus a complete method for assessing of human error, and not merely a technique for determining values of the PSFs. The basic premise of SLIM is that the HEP depends on the combined effects of the PSFs. A systematic approach is used to obtain the quality weightings and relevancy factors for the PSFs, utilizing structured expert judgement. From these PSFs the SLI for the task is obtained.

As defined by Embrey (1983a) the SLI for n PSFs is:

$$\mathrm{SLI} = \sum_{i=1}^{n} r_i w_i \qquad [14.28.1]$$

where r is a relevancy factor and w a quality weighting. Thus, the SLI approach makes explicit the distinction between quality and relevance.

The quality weighting is obtained from the judgement of a panel of experts and is assigned a value on the scale 1–9.

Table 14.25 *HRA Handbook: general guidelines on estimation of the error factor (EF)[a] (after Swain and Guttmann, 1983)*

Item	*Task and HEP guideline*[b]	*EF*[c]
	Task consists of performance of step-by-step procedure[d] conducted under routine circumstances (e.g. a test, maintenance or calibration task); stress level is optimal:	
(1)	Estimated HEP < 0.001	10
(2)	Estimated HEP 0.001–0.01	3
(3)	Estimated HEP > 0.01	5
	Task consists of performance of step-by-step procedure[d] but carried out in non-routine circumstances such as those involving a potential turbine/reactor trip; stress level is moderately high:	
(4)	Estimated HEP < 0.001	10
(5)	Estimated HEP ≥ 0.001	5
	Task consists of relatively dynamic[d] interplay between operator and system indications, under routine conditions, e.g. increasing or reducing power; stress level is optimal:	
(6)	Estimated HEP < 0.001	10
(7)	Estimated HEP ≥ 0.001	5
(8)	Task consists of relatively dynamic[d] interplay between operator and system indications but carried out in non-routine circumstances; stress level is moderately high	10
(9)	Any task performed under extremely high stress conditions, e.g. large LOCA, conditions in which the status of ESFs is not perfectly clear, or conditions in which the initial operator responses have proved to be inadequate and now severe time pressure is felt (see text of *Handbook* for rationale for EF = 5)	5

[a] The estimates in this table apply to experienced personnel. The performance of novices is discussed in Chapter 18 of the *Handbook*.
[b] For UCBs for HEPs based on the dependence model, see Table 7.3 of the *Handbook*.
[c] The highest upper UCB is 1.0.
See Appendix A to calculate the UCBs for $P_T(F_T)$, the total-failure term of an HRA event tree.
[d] See Table 18.1 of the *Handbook* for definitions of step-by-step and dynamic procedures.

The relevancy factor, which again is obtained from the judgement of the expert panel, is a measure of the contribution of that PSF, the sum of the relevancy factors being unity. The SLI so obtained is a relative value.

In order to convert an SLI into a HEP, it is necessary to calibrate it against tasks for which the HEP is known. The relation used is:

$$\log_{10}(\mathrm{HEP}) = a\mathrm{SLI} + b \qquad [14.28.2]$$

where a and b are constants. These constants are obtained from two tasks of known HEP. Due to the logarithmic relationship, SLI values that do not differ

greatly (e.g. 5.5 and 5.75) may correspond to very different HEPs.

The SLI methodology has two modules. The first is the multi-attribute utility decomposition (MAUD), usually referred to as SLIM-MAUD. The second is the systematic approach to the reliability assessment of humans (SARAH). The former is used to obtain the SLI and the latter to perform the calibrations. Both are embodied in computer programs. Accounts of work done to validate this approach have been given by Embrey (1983a) and Embrey and Kirwan (1983). Illustrative examples of SLIM are given by Dougherty and Fragola (1988), as described below, and Kirwan (1990).

14.29 Assessment of Human Error: Human Error Assessment and Reduction Technique (HEART)

In the HEART, described by J.C. Williams (1986, 1988a,b, 1992), the HEP of the task is treated as a function of the type of task and of associated error producing conditions (EPCs), effectively PSFs. The method is based on a classification of tasks into the generic types shown in Section A of Table 14.26, which also gives the proposed nominal human unreliabilities for execution of the tasks. There is an associated set of EPCs, for each of which is given an estimate of the maximum predicted normal amount by which the unreliability might change going from 'good' to 'bad'. Section B of the table shows the first 17 EPCs listed, those with the strongest influence; entries 18–38 list further EPCs with a weaker influence.

In applying an EPC use is made of a weighting for the proportion of the EPC that is effective. Thus, for a task of type D with a nominal unreliability of 0.09, a single EPC of 4 and a weighting of 0.5, the resultant unreliability is:

$$0.09[(4-1) \times 0.5 + 1] = 0.23 \qquad [14.29.1]$$

The method also includes a set of associated remedial measures to be applied to improve the reliability.

HEART has been designed as a practical method, and is easy to understand and use. It was on of the principal techniques used in the quantitative risk assessment for Sizewell B, as described in Section 14.39.

14.30 Assessment of Human Error: Method of Dougherty and Fragola

The deficiencies of THERP in respect of non-routine behaviour have led to the development of alternative methods. One of these methods is that described in *Human Reliability Analysis* by Dougherty and Fragola (1988). Like THERP, this method has been developed essentially as an adjunct to fault tree analysis, but the approach taken is rather different.

The earlier approach associated human errors essentially with equipment or procedure failures. One effect was the generation of a large number of human events linked to the equipment failures. Another was the neglect of more significant but complex human errors. The approach taken in the HRA of Dougherty and Fragola is to concentrate on a smaller number of more significant failures and human errors. There is also strong emphasis on integrating the HRA into the PRA.

14.30.1 Overall approach

The HRA process is shown in Figure 14.30. The generation of the human events to be considered is part of the PRA. As with physical hazards, identification has a good claim to be the most difficult stage of the process. Error classification schemes have been developed as an aid, but give no guarantee of completeness.

The human events are identified, characterized and quantified according to the scheme shown in Figure 14.31.

Certain principles have been identified to guide the development of the PRA so that there is compatibility with the HRA. In broad outline these guidelines include the following:

(1) The description of the human event should refer to failure of a function rather than to some lower level of abstraction.
(2) The human events should be confined to the three categories of pre-initiator (or latent) events, human-induced initiator events and post-initiator events.
(3) Human events in the latent category should be incorporated in the fault tree at the highest appropriate level.
(4) A human-induced initiator event should be subsumed in the initiator type which includes the human event. The data required should be expressed as a probability and not as a frequency.
(5) A human event in the post-initiator category which relates to failure of a system should be modelled as a single event under the gate below the top event of the fault tree for that system, the gate being (a) an OR gate if the system is manually activated or (b) an AND gate if the system is automatically activated.

14.30.2 Task analysis

The starting point is again a task analysis. A typical task analysis is outlined in Table 14.27.

14.30.3 Response and recovery events

Human events that occur in the post-initiator period are treated as either response or recovery events. The nuclear industry has gone to some pains to provide a rather comprehensive set of emergency response guidelines. Following such guidelines, a planned activity is classed as a response, whilst an unplanned activity is classed as a recovery. Recovery activity is applicable only to those events from which recovery is possible; there are some events for which there is no recovery.

The incorporation of recovery is not undertaken during the development of the main fault tree but is deferred until the tree, and its cut sets, are available. There are two reasons for this. One is that introduction of recovery during the main synthesis tends to result in an undue increase in the size of the tree. The other is that recovery analysis is an iteration through much of the PRA/HRA process, embraces system and human aspects, and tends to be highly specific to the set of events from which the recovery is to be made. It is therefore better to consider the set of events and the associated recovery as a separate exercise at the end.

14.30.4 Operator action event trees

Some of the activity of the operator consists of planned tasks, but he may also have to respond to an abnormal condition on the plant. Thus, although some events can be incorporated into the main fault tree of the PRA, post-initiator events involving action by the operator require the introduction of a specific event tree – the operator action event tree (OAET).

Table 14.26 *Classification of generic tasks and associated unreliability estimates (J.C. Williams, 1986)*

A Generic classifications

Generic task		*Proposed nominal human unreliability (5th–95th percentile boundaries)*
A	Totally unfamiliar, performed at speed with no real idea of likely consequences	0.55 (0.35–0.97)
B	Shift or restore system to a new or original state on a single attempt without supervision or procedures	0.26 (0.14–0.42)
C	Complex task requiring high level of comprehension and skill	0.16 (0.12–0.28)
D	Fairly simple task performed rapidly or given scant attention	0.09 (0.06–0.13)
E	Routine, highly practised, rapid task involving relatively low level of skill	0.02 (0.007–0.045)
F	Restore or shift a system to original or new state following procedures, with some checking	0.003 (0.0008–0.007)
G	Completely familiar, well-designed, highly practised, routine task occurring several times per hour, performed to highest possible standards by highly motivated, highly trained and experienced person, totally aware of implications of failure, with time to correct potential error, but without the benefit of significant job aids	0.0004 (0.00008–0.009)
H	Respond correctly to system command even when there is an augmented or automated supervisory system providing accurate interpretation of system stage	0.00002 (0.000006–0.00009)
M	Miscellaneous task for which no description can be found. (Nominal 5th to 95th percentile data spreads were chosen on the basis of experience suggesting log-normality)	0.03 (0.008–0.11)

B Error-producing conditions[b]

Error-producing condition		*Maximum predicted nominal amount by which unreliability might change going from 'good' conditions to 'bad'*
1.	Unfamiliarity with a situation which is potentially important but which only occurs infrequently or which is novel	× 17
2.	A shortage of time available for error detection and correction	× 11
3.	A low signal-to-noise ratio	× 10
4.	A means of suppressing or overriding information or features which is too easily accessible	× 9
5.	No means of conveying spatial and functional information to operators in a form which they can readily assimilate	× 8
6.	A mismatch between an operator's model of the world and that imagined by the designer	× 8
7.	No obvious means of reversing an unintended action	× 8
8.	A channel capacity overload, particularly one caused by simultaneous presentation of non-redundant information	× 6
9.	A need to unlearn a technique and apply one which requires the application of an opposing philosophy	× 6
10.	The need to transfer specific knowledge from task to task without loss	× 5.5
11.	Ambiguity in the required performance standards	× 5
12.	A mismatch between perceived and real risk	× 4
13.	Poor, ambiguous or ill-matched system feedback	× 4
14.	No clear direct and timely confirmation of an intended action from the portion of the system over which control is to be exerted	× 3
15.	Operator inexperienced (e.g. a newly qualified tradesman, but not an 'expert')	× 3
16.	An impoverished quality of information conveyed by procedures and person–person interaction	× 3
17.	Little or no independent checking or testing of output	× 3

Table 14.26 *(continued)*

18.	A conflict between immediate and long-term objectives.	× 2.5
19.	No diversity of information input for veracity checks	× 2.5
20.	A mismatch between the educational achievement level of an individual and the requirements of the task	× 2
21.	An incentive to use other more dangerous procedures	× 2
22.	Little opportunity to exercise mind and body outside the immediate confines of the job	× 1.8
23.	Unreliable instrumentation (enough that it is noticed)	× 1.6
24.	A need for absolute judgements which are beyond the capabilities or experience of an operator	× 1.6
25.	Unclear allocation of function and responsibility	× 1.6
26.	No obvious way to keep track of progress during an activity	× 1.4
27.	A danger that finite physical capabilities will be exceeded	× 1.4
28.	Little or no intrinsic meaning in a task	× 1.4
29.	High-level emotional stress	× 1.3
30.	Evidence of ill-health amongst operatives, especially fever	× 1.2
31.	Low workforce morale	× 1.2
32.	Inconsistency of meaning of displays and procedures	× 1.2
33.	A poor or hostile environment (below 75% of health or life-threatening severity)	× 1.15
34.	Prolonged inactivity or highly repetitious cycling of low mental workload tasks	× 1.1 for first half-hour × 1.05 for each hour thereafter
35.	Disruption of normal work-sleep cycles	× 1.1
36.	Task pacing caused by the intervention of others	× 1.06
37.	Additional team members over and above those necessary to perform task normally and satisfactorily	× 1.03 per additional man
38.	Age of personnel performing perceptual tasks	× 1.02

[a] If none of the task descriptions A–H fits the task under consideration, the values given under M may be taken as reference points.
[b] Conditions 18–38 are presented simply because they are frequently mentioned in the human factors literature as being of some importance in human reliability assessment. To a human factors engineer, who is sometimes concerned about performance differences of as little as 3%, all these factors are important, but to engineers who are usually concerned with differences of more than 300%, they are not very significant. The factors are identified so that engineers can decide whether or not to take account of them after the initial screening.

The response of the operator to an abnormal condition may be described in terms of an event tree. The use of event trees for this purpose has been formalized as the OAETor, simply, the operator action tree (OAT) technique.

The OAET method has been described by R.E. Hall, Fragola and Wreathall (1982). Three basic features are recognized: (1) perception, (2) diagnosis and (3) response. Figure 14.32 shows a typical OAET for a nuclear reactor coolant pump seal LOCA. The OAET tends to be used in conjunction with a time–reliability correlation.

14.30.5 Modelling of human events

The classification of human events and the associated event models used in the HRA are shown in Figure 14.31. The human activity is divided into three classes which are specifiable and one that is not. The three definable activities are planned tasks, response and recovery. Each of these definable activities is further divided into slips and mistakes, and these in turn are divided into errors of omission or commission.

In each case a slip is modelled using a modified version of THERP. Mistakes of response and recovery are modelled using TRCs. Other mistakes are not modelled, except that response mistakes of commission may be modelled. Recovery mistakes of commission may be estimated as described below.

14.30.6 Filtering of human events

The human events identified are subjected to both a qualitative and a quantitative filter. This process is assisted if the analysis of the hardware and human aspects proceeds simultaneously. This is the most effective way to apply a qualitative filter to the large proportion of the human events identified.

A quantitative filter is then applied. This means that an approximate estimate is made of the probability of each human event and, if at this level of probability the event has negligible effect on the fault tree, it is not pursued.

The approach used draws on THERP. A probability of 0.001 is used as a basic screening value for the probability of a human event for latent or human-induced initiator failures. If there is redundancy so that a second error must occur for the failure to occur, a conditional probability of value of 0.1 is used, corresponding to moderate dependency. For post-initiator events, use is made of the appropriate TRC, taking the probability at 5 min as the screening value.

14.30.7 Modelling of slips

Slips are errors in an activity that has to some degree been planned. This applies even to recovery, where the operator first formulates and then executes a plan. The method used to model slips is a modified version of THERP. One modification is to consider only one slip per task. The probability of the slip is taken as a basic value of 0.001 or, if there is

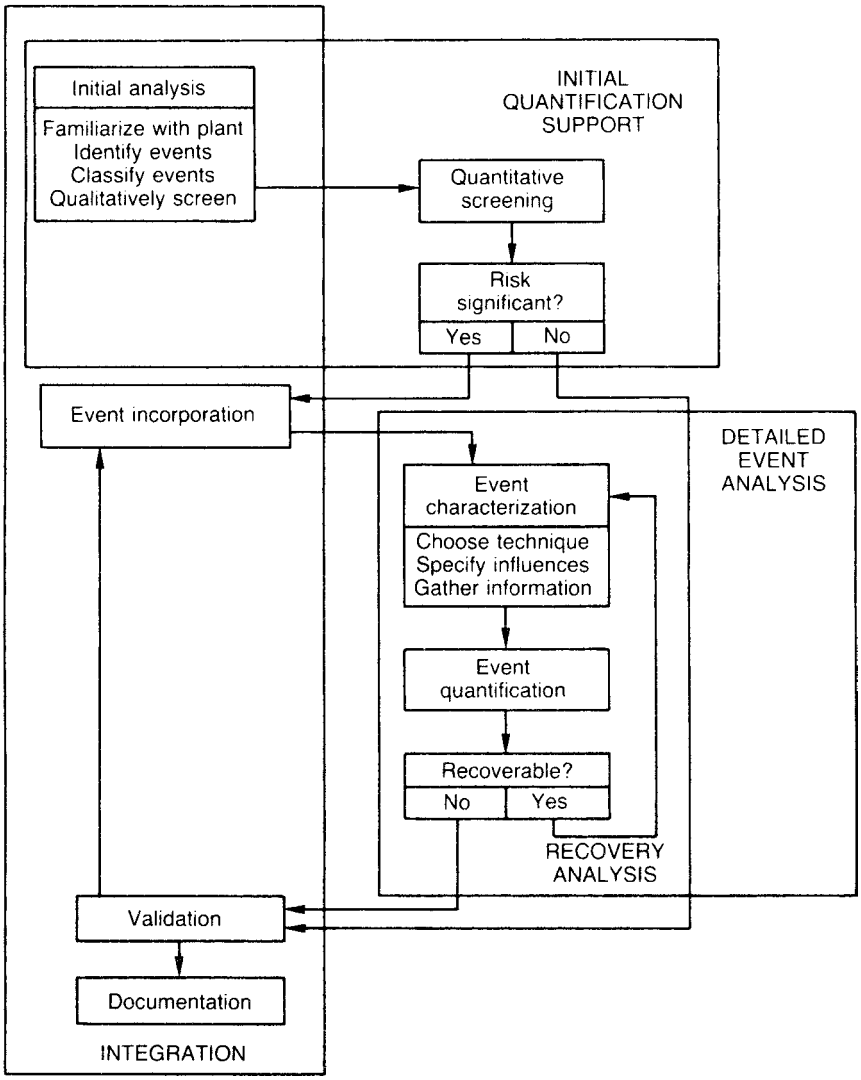


Figure 14.30 *Method of Dougherty and Fragola: methodology for human reliability analysis (Dougherty and Fragola, 1988) (Reproduced with permission of John Wiley & Sons Ltd from Human Reliability Analysis by E.M. Dougherty and J.R. Fragola, 1988, copyright ©)*

redundancy, 0.0001. These values are the same as those used for screening. They are then adjusted using appropriate performance shaping factors. The authors also describe alternative, more complex methods of estimating the probability of slips.

14.30.8 Modelling of mistakes

Response and recovery mistakes are modelled using time–reliability correlations. The underlying assumption in this approach is that, although the probability of success depends, in principle, on many factors, the time available is the dominant one. Four separate TRCs are used. These are for the cases

(1) response without hesitancy;
(2) response with hesitancy;
(3) recovery without hesitancy;
(4) recovery with hesitancy.

Hesitancy is associated with the burden of the task that in turn depends on a number of factors as described below. Account is also taken of the effect of PSFs. The incorporation of these two features into the TRCs is described below.

14.30.9 Time–reliability correlations

It is found empirically that response times tend to fit a log–normal distribution. The TRC models used are based

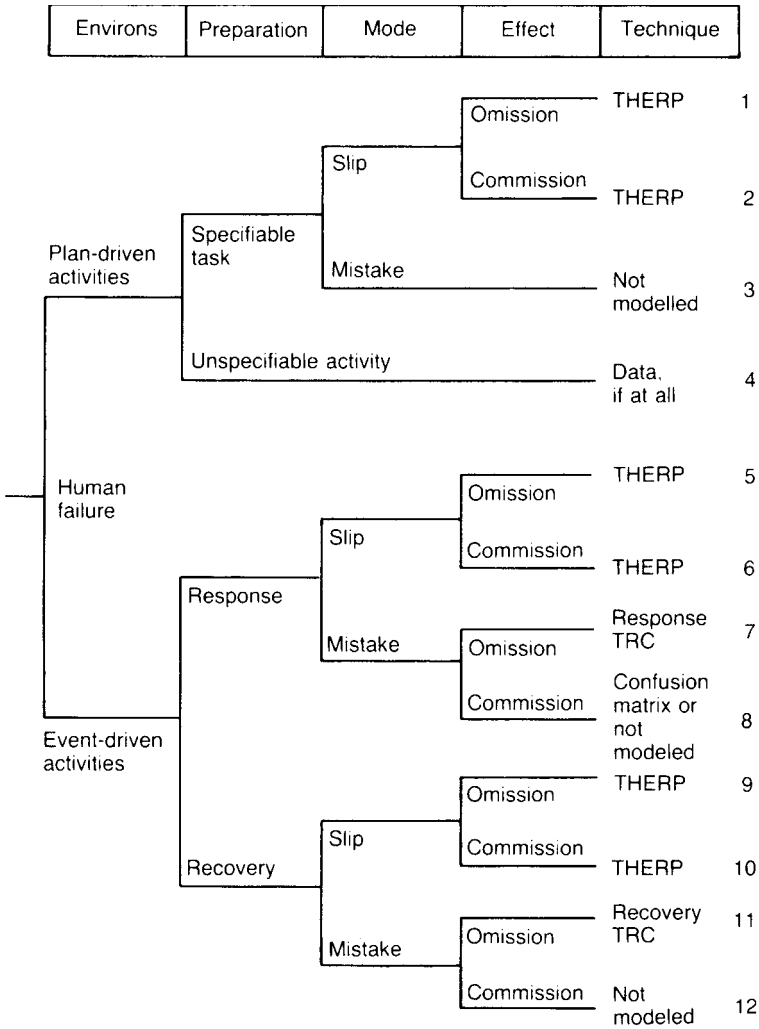


Figure 14.31 *Method of Dougherty and Fragola: classification of human events (Dougherty and Fragola, 1988) (Reproduced with permission of John Wiley & Sons Ltd from Human Reliability Analysis by E.M. Dogherty and J.R. Fragola, 1988, Copyright ©)*

on the assumption that the log-normal distribution is applicable. They are characterized by a log–normal median m and an EF f and give a straight line when plotted on log–probability paper. The basic response time τ is given by:

$$\tau_r = k_1 k_2 \tau \qquad [14.30.1]$$

where τ is the median response time, τ_r is the adjusted median response time and k_1 and k_2 are adjustment factors. The value of m used is the adjusted median response time.

The first factor k_1 takes account of the availability or otherwise of a rule, in other words of the difference between response and recovery. It has the values:

$k_1 = 1$ Rule available [14.30.2a]

$k_1 = 0$ no rule available [14.30.2b]

The second factor k_2 takes account of the performance shaping factor as measured by the SLI. It is assumed that at best (SLI = 1), the median response time is halved and at worst (SLI = 0), it is doubled. The factor is defined as:

$$k_2 = 2^{(1-2x)} \qquad [14.30.3]$$

where x is the SLI.

The base TRC is the nominal diagnosis curve given in THERP. This curve has a median m of 4 and an EF f of 3.2. It, therefore, has a relatively high median and low EF. The high median corresponds to a recovery rather than a response and the low error factor to absence of hesitancy. On this basis this curve is taken as that for recovery without hesitancy.

The other TRC curves are then obtained from this basic curve. The curve for response without hesitancy has the

Table 14.27 *Task analysis in support of a human reliability analysis for a task in nuclear power plant operation (Dougherty and Fragola, 1988) (Reproduced with permission of John Wiley & Sons Ltd from Human Reliability Analysis by E.M. Dougherty and J.R. Fragola, 1988, Copyright ©)*

Goal
Obtain reactor core system water make-up and cooling following a small loss of coolant accident (LOCA)

Step	*Means*
Diagnose event	
Detect plant upset condition	Several alarms
Observe RCS level indicator	Pressurizer or reactor level
Observe decreasing RCS pressure	Pressure indicator
Observe sump level increasing	Level indicator
Observe containment pressure increasing	Pressure indicators
Observe no secondary side radiation	Radiation monitors
Isolate the LOCA	
Close PORV block valve 1	One valve control
Close PORV block valve 2	Another valve control
Close letdown line	One valve control
Close RCP seal isolation valve 1	One valve control
Close RCP seal isolation valve 2	Another valve control
Verify safety system actuation	
Observe HPI pump meters	Two flow indicators
Start HPI pumps	Two pump start controls
Observe AFW pump meters	Two flow indicators
Start AFW pumps	Two pump start controls
Obtain long-term cooling	
Await low level tank alarm	One level indicator
Open sump valve 1	One valve control
Open sump valve 2	One valve control
Open tank valve 1	One valve control
Open tank valve 2	One valve control

AFW, auxiliary feed water; HPI, high pressure injection; PORV, power operated relief valve; RCP, reactor coolant pump; RCS, reactor cooling system.

parameters $m = 2$ and $f = 3.2$; that for response with hesitance $m = 2$ and $f = 6.4$; and that for recovery with hesitance $m = 4$ and $f = 6.4$.

The TRC curves so derived are shown in Figure 14.33. These curves already incorporate the factor k_1 but not the factor k_2. The response time obtained from the curves should be multiplied by k_2.

14.30.10 Performance shaping factors

PSFs are treated using SLIM. In the format given by the authors the SLI is defined as:

$$\text{SLI} = \sum_{i=1}^{n} r_{ni} q_i \qquad [14.30.4]$$

with

$$r_{ni} = r_i / \sum_{i=1}^{n} r_i \qquad [14.30.5]$$

where q is the quality, r the rank and r_n the normalized rank.

In general, q has a value in the range 0–1. This is so if the PSF can have either a bad or a good influence. If it can have only a bad influence, the range of q is restricted to 0–0.5 and if it can have only a good influence the range is restricted to 0.5–1.

The determination of the SLI is illustrated in Table 14.28, which gives the SLI for a human error in a recovery mistake. The SLI is can be used to adjust probabilities of slips or mistakes. In the latter case it is applied to the median response time of the TRC, as described below.

14.30.11 Recovery mistakes of commission

In an incident situation, the possibility exists that the operator will take some action which actually makes the situation worse. As so far described, the methodology does not include a model for such an action which is called a 'recovery mistake of commission'.

A method is given, however, for estimating the probability that such an error will occur. This probability is the product of three probabilities. The first is the probability of a significant and extended commission error, the second the probability that the emergency response guidelines (ERGs) do not cover the resulting situation, and the third the probability that the senior reactor operator (SRO) or other personnel fail to recover the situation.

The values of these three probabilities are estimated as follows. At the time of writing there had been 10,000 reactor scrams. Two involved misdiagnoses that led to core melt, including Chernobyl. The probability of a significant and extended commission error is thus estimated as 0.0002 (2/10,000). It is assumed that ERGs would effect a reduction in probability of between one and three orders of magnitude and a reduction of two orders of magnitude is selected so that the second probability is estimated as 0.01. The action of the SRO, whose function is to stand back and monitor plant status, is assumed to have only low dependency with that of the crew and the probability that he will fail to effect recovery is estimated as 0.05. From these figures the authors derive a figure for the frequency of unrecovered mistakes of commission.

14.30.12 Computer aids

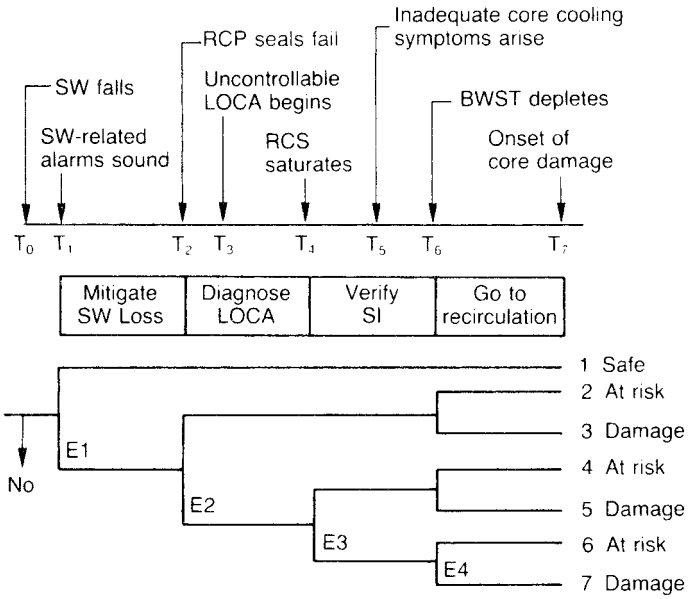
The documentation required of the HRA by the PRA is quite extensive and a computer program ORCA (Operator Reliability and Assessment) has been developed to assist in producing it. Table 14.29 shows a typical document for a recovery mistake.

14.30.13 Application to nuclear power plants

Detailed illustrations of the application of the HRA technique to particular nuclear power plants are given by the authors.

14.30.14 Validation

The HRA method just outlined is described by its authors as speculative. In other words, it lacks validation. In this it is on a par with most of the techniques used for quantifying human error in nuclear and process plants. Nevertheless,



Event	Most likely error modes
E1	Fail to recover SW in time
E2	Cannot stop LOCA in time
E3	Fail to follow ICC rule
E4	Fail to respond to low level alarm

Figure 14.32 *Operator action event tree for a nuclear reactor pump seal loss-of-coolant accident (LOCA) (Dogherty and Fragola, 1988). BWST, borated water storage tank; RCP, reactor coolant pump; RCS, reactor cooling system; SI, safety interlock; SW, seal water (Reproduced with permission of John Wiley & Sons Ltd from Human Reliability Analysis by E.M. Dougherty and J.P. Fragola, 1988, Copyright ©)*

this general type of approach represents the most systematic method currently available for the treatment of the human error aspects of a PRA.

14.31 Assessment of Human Error: CCPS Method

Another methodology for human reliability assessment is that described in the CCPS *Human Error Prevention Guidelines* (1994/17). The structure of the method is shown in Figure 14.34. The core is the four stages of (1) critical human interaction identification and screening, (2) qualitative prediction of human error, (3) representation of event development and (4) quantification of significant human errors.

The qualitative error prediction stage utilizes the SPEAR method involving task analysis, PIF analysis, PHEA, consequence analysis and error reduction analysis. The representation of event development typically takes the form of fault trees and event trees. The techniques described for the quantitative error prediction stage are THERP, SLIM and influence diagram analysis (IDA). The latter is described in the next section.

The CCPS HRA methodology has the important characteristic that it requires the analyst to start by acquiring a thorough understanding of the system first by critical human interaction identification and then by detailed qualitative analysis. Only then does the work progress to the use of the quantitative methods.

14.32 Assessment of Human Error: Other Methods

The following methods also merit mention. A brief account of each is given in the *Second Report* of the Study Group on Human Factors of the ACSNI (1991). Accounts are also given by J.C. Williams (1985), Waters (1989) and Brazendale (1990 SRD R510).

14.32.1 TESEO method

A simple model for the estimation of the probability of operator error is that used in TESEO (Tecnica Empirica

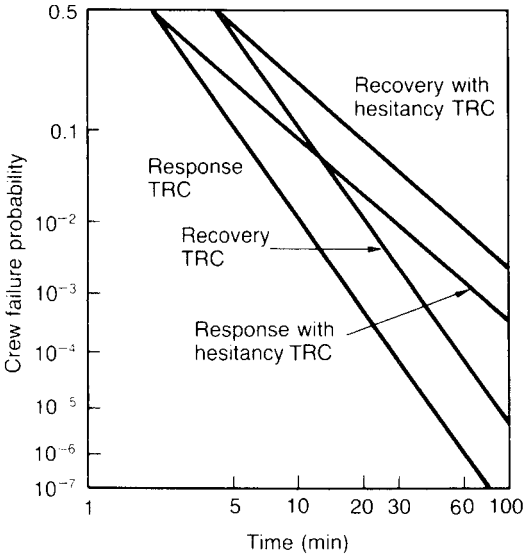


Figure 14.33 *Method of Dougherty and Fragola: time–reliability correlations (Dougherty and Fragola, 1988) (Reproduced with permission of John Wiley & Sons Ltd from Human Reliability Analysis by E.M. Dougherty and J.R. Fragola, 1988, Copyright ©)*

Stima Errori Operatori) developed by Bello and Colombari (1980). The probability, q, of error is assumed to be the product of five parameters K_1-K_5 as follows:

$$q = K_1K_2K_3K_4K_5 \qquad [14.32.1]$$

Definitions and values of the parameters are given in Table 14.30.

An illustration of the use of TESEO has been given by Kletz (1991e). He considers a daily task of filling a tank by watching the level and closing a valve when the tank is full. He suggests that a reasonable estimate of failure is 1 in 1000, or once in 3 years. In practice, men operate such systems without incident for periods of 5 years. Using the TESEO approach he sets K_1 as 0.001, K_2 as 0.5 and the other parameters as unity, obtaining a probability of failure of 1 in 2000, or once every 6 years.

14.32.2 Absolute probability judgement (APJ) method

In the absolute probability judgement (APJ) method, described by Seaver and Sitwell (1983), experts are asked to make direct estimates of human error probabilities for the task.

14.32.3 Method of paired comparisons (PCs)

The use of the method of paired comparisons (PCs) in expert judgement was outlined in Chapter 9. It may be applied to the estimation of HEPs, as described by Blanchard *et al.* (1966) and Hunns (1980, 1982).

14.32.4 Influence diagram approach (IDA)

Influence diagram analysis is a tool developed in the context of decision analysis (R.A. Howard and Matheson, 1980). It has been adapted for work on human factors by L.D. Phillips, Humphreys and Embrey (1983). Essentially, it is a form of logic tree showing the relations between particular performance shaping factors. As such it may be used to obtain quantitative estimates based on expert judgement of the effects of these factors.

14.32.5 Human Cognitive Reliability (HCR) correlation

The human cognitive reliability (HCR) correlation of Hannaman and co-workers (Hannaman *et al.*, 1985; Hannaman and Worledge, 1987) is a method in which the actions of the operating crew are represented in the form of an extended operator action tree and the probability of failure to respond is assessed using a set of three time–reliability correlations.

14.32.6 Systematic human error reduction and prediction approach (SHERPA)

The systematic human error reduction and prediction approach (SHERPA), and its application to human performance in ultrasonic inspection, has been described by Murgatroyd *et al.* (1986). SHERPA involves the three stages of identification of the set of tasks, hierarchical task analysis and human error analysis. HTA is used to identify the two main types of task element handled: those involving manual skills, and those involving the application of condition–action rules. The human error analysis utilizes a flowchart technique to identify the external error modes of the actions comprising the task and the psychological error mechanisms which give rise to these modes. Other types of task element are dealt with by some other appropriate method.

SHERPA is one of the two methods cited in the SRDA *Operating Procedures Guide* (Bardsley and Jenkins, 1991 SRDA-R1) for the treatment of human error in the development of operating procedures.

14.32.7 Critical action and decision approach (CADA)

The other method quoted by these authors is the critical action and decision approach (CADA) of Gall (1990). This is a technique for systematic examination of decision-making tasks and is thus complementary to SHERPA. CADA utilizes checklists to classify and examine decision errors and to assess their likelihood.

14.32.8 Maintenance personnel performance simulator (MAPPS)

The maintenance personnel performance simulator (MAPPS) method is concerned principally with the effect of manning levels on maintenance tasks. The basic premise is that the probability of failure is a function of the loading on the personnel.

14.32.9 Comparative evaluations

Comparative evaluations of sets of human reliability techniques have been given by several authors, including Brune, Weinstein and Fitzwater (1983), J.C. Williams (1983, 1985a), Bersini, Devooght and Smidts (1988), Humphreys (1988a,b) and Kirwan (1988). J.C. Williams (1985b) has compared six methods of human reliability assessment, including the AIR data bank, APJ, PC and SLIM.

The methods treated in the comparative evaluation by Humphreys (1988a,b), described more fully in Section 14.35, are APJ, PC, TESEO, THERP, HEART, IDA, SLIM

Table 14.28 *Success likelihood index calculation for a recirculation event in nuclear power plant operation (Dougherty and Fragola, 1988) (Reproduced with permission of John Wiley & Sons Ltd from Human Reliability Analysis by E.M. Dougherty and J.R. Fragola, 1988, Copyright ©)*

Influence	*Type*	*Rank*	*Relative rank*	*Quality*	*Product*	*%*
Competing resources	Bad	10	0.05	0.4	0.02	3
Tank level indication	Good	50	0.23	0.9	0.21	31
Size of LOCA	Both	10	0.05	0.2	0.01	1
Expectation of failure	Both	50	0.23	0.3	0.07	10
Training on contingencies	Both	100	0.45	0.8	0.36	54
		220		SLI = 0.67		

Table 14.29 *Proforma for a mistake in a recovery event in nuclear power plant operation (Dougherty and Fragola, 1988) (Reproduced with permission of John Wiley & Sons Ltd from Human Reliability Analysis by E.M. Dougherty and J.R. Fragola, 1988, Copyright ©)*

Event designators	NDXOVERH	**Event type:**	Recovery
Event description			
The crew fails to realign equipment following recirculation hardware failures			
Option information:		**Screening value:**	4E−1
Rule based?		No	
Hesitancy?		No	
SLI calculated?		Yes	
Standard TRC?		Yes	

Influences

	Rank	*Normed-rank*	*Quality*	*Product*
1. Display adequacy	10	0.06	70	4.2
2. Procedure adequacy	40	0.24	30	7.2
3. Team effectiveness	20	0.12	80	9.6
4. Communication effectiveness	10	0.06	80	4.8
5. Workload	40	0.24	30	7.2
6. Training adequacy	50	0.29	70	20.3
7.				
8.				
9.				
10.				
				53.3

SLI	50.3
Available time (min)	20
Mean probability and statistics	1E−2
Lower bound	4E−4
Upper bound	4E−2
Median time (min)	4.0
Error factor	3.2

E$-n = 10^{-n}$

and HCR. Another account of this work is given by Kirwan (1988).

A comparative evaluation was also made in the Benchmark Exercise described in Section 14.36.

14.33 Assessment of Human Error: Performance Shaping Factors (PSFs)

14.33.1 THERP method

The use of PSFs in the THERP methodology as given in the *HRA Handbook* has been outlined above. The factors are listed and described but a formal quantitative method of determining for each PSF an adjustment factor to be applied to the human HEP does not appear to be used.

14.33.2 SLIM

PSFs are the basis of SLIM, as described above. In this method the value, or quality, of a PSF is determined by structured expert judgement. The influence diagram technique is used to show the structure of the relationship between PSFs.

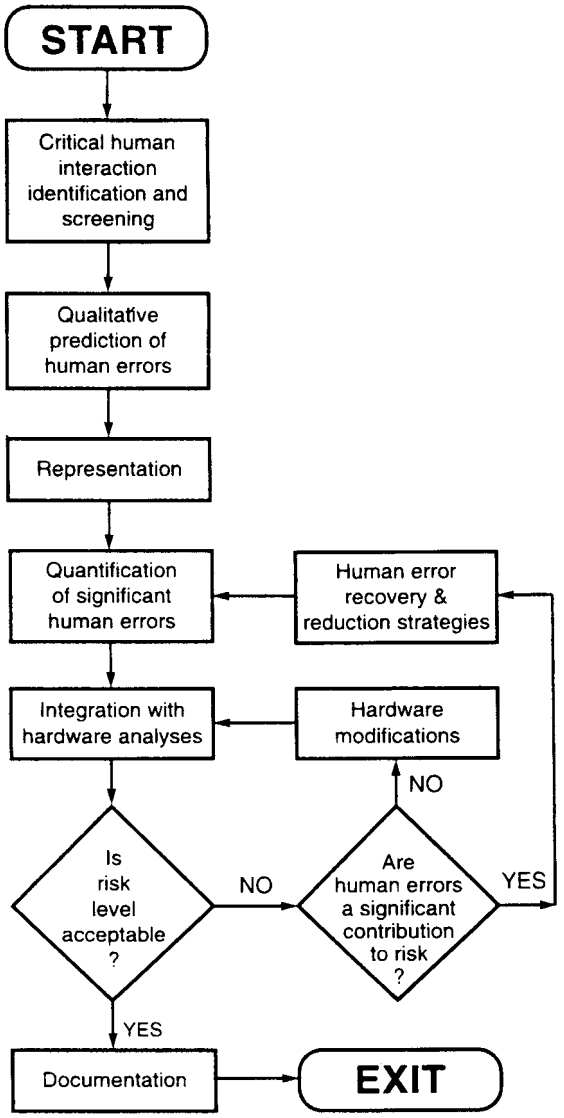


Figure 14.34 *A methodology for human reliability assessment (CCPS, 1994/17) (Courtesy of the American Institute of Chemical Engineers)*

Table 14.30 *Operator error probability parameters used in TESEO (Bello and Colombari, 1980) (Courtesy of Elsevier Applied Science Publishers Ltd)*

Type of activity	
	K_1
Simple, routine	0.001
Requiring attention, routine	0.01
Not routine	0.1
Temporary stress factor for routine activities	
Time available (s)	K_2
2	10
10	1
20	0.5
Temporary stress factor for non-routine activities	
Time available (s)	K_2
3	10
30	1
45	0.3
60	0.1
Operator qualities	
	K_3
Carefully selected, expert, well trained	0.5
Average knowledge and training	1
Little knowledge, poorly trained	3
Activity anxiety factor	
	K_4
Situation of grave emergency	3
Situation of potential emergency	2
Normal situation	1
Activity ergonomic factor	
	K_5
Excellent microclimate, excellent interface with plant	0.7
Good microclimate, good interface with plant	1
Discrete microclimate, discrete interface with plant	3
Discrete microclimate, poor interface with plant	7
Worst microclimate, poor interface with plant	10

14.33.3 HEART

HEART is another method in which PSFs play a central role. The classification of the generic tasks is itself based on PSF-like distinctions and the EPCs that are applied to the basic generic task reliability estimates are in effect PSFs.

14.33.4 White method

R.F. White (1984 SRD R254) has described a form of PSF, the observable operational attribute (OOA) in which, as the name implies, the emphasis is on the observability of the attribute. He provides a checklist of attributes, broken down into (1) plant attributes and (2) main- tenance attributes. Examples of attributes listed as observable are:

(1) What is the time-scale of a filling operation of one tank (or two at a time)? (e.g. Within one shift? Longer than one shift?)
(2) Is formal training given at instrument fitter level?

14.33.5 Whalley model

A methodology for identifying error causes and making the link between them and the PSFs has been developed by

Whalley (1987). The classification structure of the PSFs used is shown in Figure 14.35. A total of 146 PSFs is defined. The PSFs influence the error causes. Each error cause may be affected by several PSFs and each PSF may affect several error causes.

The method utilizes classifications of (1) task types, (2) response types, (3) error types, (4) error mechanisms and (5) error causes. There are seven task types (TTs), which are shown in Table 14.31, Section A. There are also seven response types (RTs) as shown in Section B of the table. The ten error types (ETs) are shown in Section C. The error mechanisms and error causes are shown in Figure 14.36. There are 10 error mechanisms (EMs) and 37 error causes (ECs) (including causes 23a and 30a).

The task types may be summarized as follows. TT 1 is response to a familiar input and requires essentially no decision-making. TT 2 is response to several familiar inputs, matches the mental model and requires no decision-making. TT 3 is interpretation of, and response to, a developing situation using the mental model. TT 4 is a predetermined response to a recognized situation. TT 5 is a self-determined activity that may involve planning. TT 6 is selection of one of several alternative plans. TT 7 is correction of error, and thus differs from the other types. For the response types the primary classification is into discrete or sequence responses, the former involving a single unit of performance, the latter a sequence. The secondary classification is into action and communication activities. The error types are cast as guidewords that are broadly similar to those used in Hazop studies.

The overall structure of the method is shown in Figure 14.37. The primary linkages are from TT, RT and ET to possible ECs. Each TT can be mapped to a set of ECs, either through an information processing chain (IPC) (TT → IPC → EC) or through a set of error mechanisms (TT → EM → EC). Each response type can be mapped to a set of error causes either through a set of error types (RT → ET → EC) or directly (RT → EC).

The analyst uses these various routes to identify the ECs for the task under consideration and then determines for each cause the relevant PSFs and their impact. A computer aid has been developed to assist in identifying the ECs, linking these to the PSFs and quantifying the effect of the latter.

14.33.6 CCPS method

Another set of PSFs are those given in the *Human Error Prevention Guidelines* by the CCPS (1994/17), which refers to them as performance influencing factors (PIFs). The PIF classification structure is shown in Table 14.32. The *Guidelines* give a detailed commentary on each of these factors.

14.34 Assessment of Human Error: Human Error Data

The various methods described for quantitative assessment of human reliability give rise to a demand for data on human error. Some aspects of this are now considered. Human error data and its acquisition has been discussed by a number of workers. The account given in *Human Error Prevention Guidelines* by the CCPS (1994/17) deals with the essentials.

14.34.1 Human error data

Data on human error may be acquired by a number of methods. One approach involves study of the task from

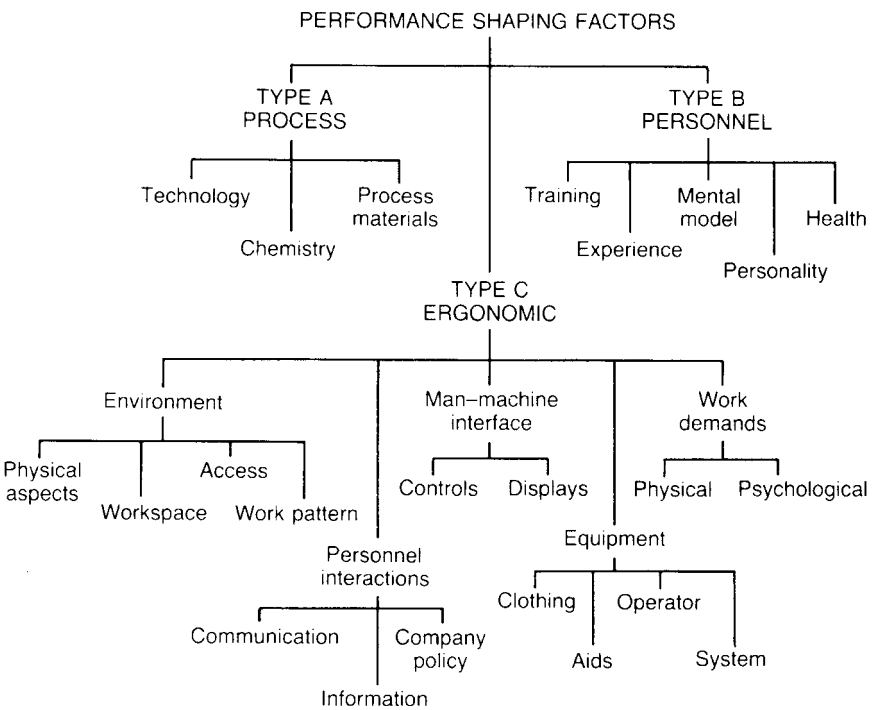


Figure 14.35 *Classification structure of performance shaing factors (Whalley, 1987. Reproduced by permission.)*

Table 14.31 *Some classifications of task, response and error for the human operator (Whalley, 1987. Reproduced with permission.)*

A Task types		
1. Stimulus		
2. Integration		
3. Interpretation		
4. Requirement		
5. Self-generation		
6. Choice		
7. Correction required		
B Response types[a]		
	Discrete	*Sequence*
Action	Y	Y
No action	Y	N
Give information	Y	Y
Get information	Y	Y
C Error types		
1. Not done		
2. Less than		
3. More than		
4. As well as		
5. Other than		
6. Repeated		
Timing errors		
7. Sooner than		
8. Later than		
9. Misordered		
10. Part of		

[a] Y, valid combination; N, invalid combination.

documentation, which may be aided by task analysis. Another group of methods are those based on some form of direct observation. This may be informal or may utilize formal techniques such as activity sampling, verbal protocol, or withholding of information.

A third group of methods are based on debriefing. One technique here is the critical incident technique, originally used by Flanagan (1954), in which a person who has experienced a near miss is debriefed. Debriefing may also be used to gain information about more normal tasks and situations. A fourth approach is the elicitation of information from experts.

The situation studied may be that on real plant or on a simulator. Simulation is widely used to present situations representative of real life in a compressed time-scale. A review of these and other methods of acquisition of data on human error is given by the CCPS.

14.34.2 Human error data collection

The acquisition of high quality data on human error is clearly of central importance. Human error data collection and data collection systems are also treated by the CCPS. The account deals with (1) types of data collection system, (2) design principles for data collection systems, (3) organizational and cultural aspects of data collection, types of data collected, (5) methods of data collection and storage and (6) data interpretation.

The CCPS distinguishes between consequence-driven and causally oriented systems. The traditional reporting system in the process industries is one triggered by incidents. It is often largely a matter of chance, however, whether or not an error has significant consequences. For this reason the *Guidelines* concentrate on causally oriented systems. Some types of data collection system that are described are (1) the incident reporting and investigation system (IRIS), (2) the root cause analysis system (RCAS), (3) the near miss reporting system (NMRS) and (4) the quantitative human reliability data collection system (QHRDCS).

It is primarily the latter type of system that has the potential to generate data for HRA. There is little evidence of the development of such systems. The CCPS sees them as most likely to emerge in the first instance at in-house level.

The type of data collected will depend on the perspective dominant in the organization, on the human error model implied and on the associated error classification. The CCPS list the following types of causal data. Data may refer to (1) event sequence and structure, (2) human error tendencies, (3) performance-influencing factors and (4) organizational issues.

14.34.3 Human reliability data banks

Human error data banks were a relatively early development. The data entered into these data banks were of the type necessary to support techniques such as THERP. One such data bank is the American Institute for Research (AIR) data bank developed by Altaian and co-workers (Payne and Altaian, 1962; Altaian, 1964) and also described by Meister (1964) and others (Swain, 1968; De Greene, 1970). The store provides data for the execution time and probability of success of task 'elements' or 'steps'. Each step has an input, a mediating and an output component. Typical input components are indicators such as scales and lights; typical output components are controls such as knobs and push buttons, and the two mediating components are identification/recognition and manipulation. Each component has several parameters. Those for a light include size, number and brightness. Each parameter has several discrete levels or 'dimensions'. Data on time and reliability for each parameter are recorded as functions of its dimensions. The time and reliability of the component are estimated by summing and multiplying, respectively, the time and reliability of the parameters. The time and reliability of the element are obtained from those of the components in a similar way.

Two other data banks from this era are the Aerojet-General data bank, described by Irwin and co-workers (Irwin, Levitz and Ford, 1964; Irwin, Levitz and Freed, 1964), and the Bunker-Ramo data bank, described by Meister (1967). These three data banks have been reproduced in Topmiller, Eckel and Kozinsky (1982). Another somewhat similar data bank is the Sandia Human Error Rate Bank (SHERB) described by Rigby (1967) and Swain (1970).

It will be clear that the development of these data banks was largely driven by the needs of the defence and aerospace industries.

Work on the cognitive and socio-technical aspects of human error is almost certainly too recent for the emergence of data banks utilizing classifications based on these approaches. Nor is it clear whether the needs of the process industries are perceived as sufficiently urgent to support

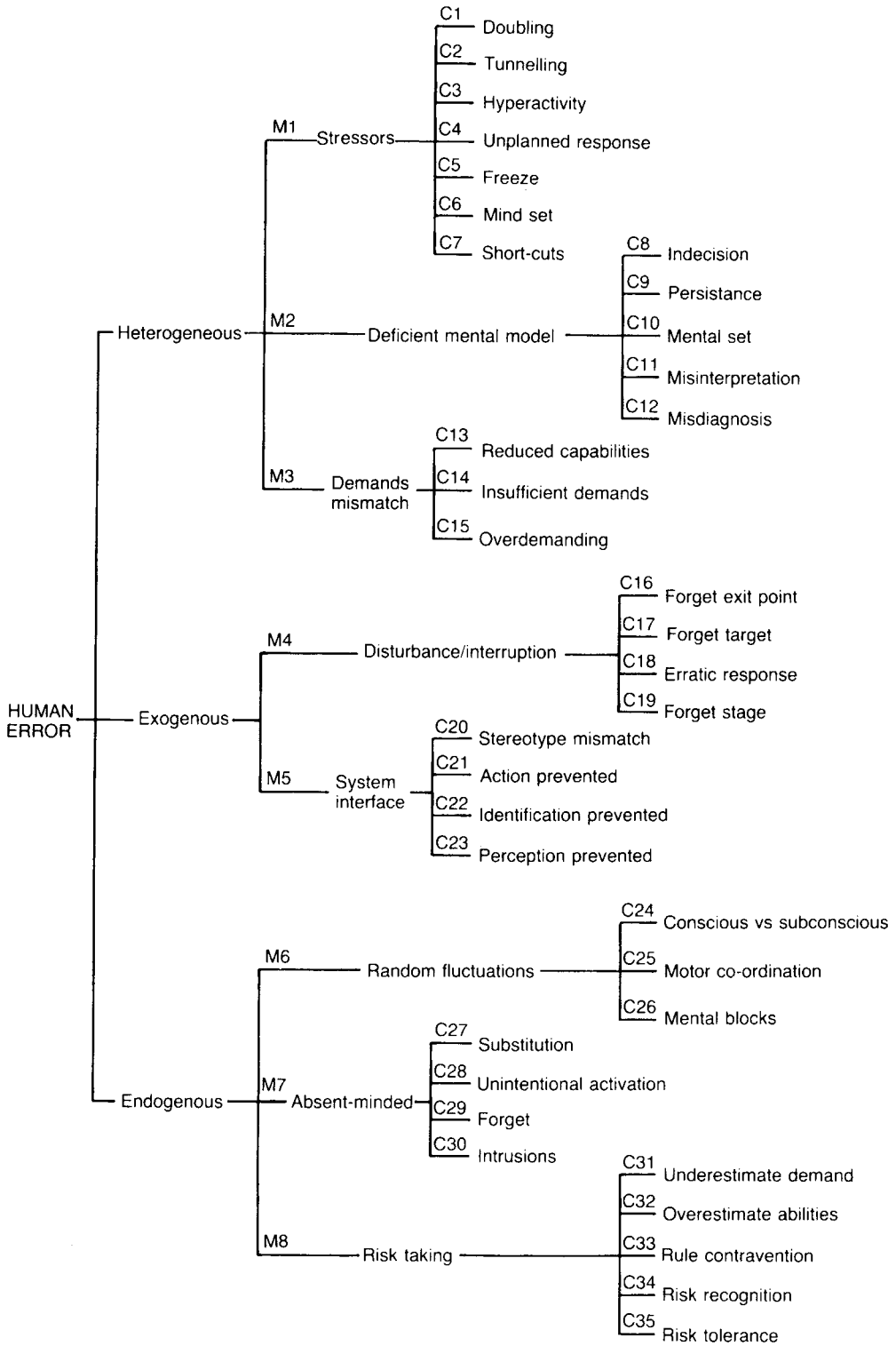


Figure 14.36 *Structure of error mechanisms and error causes (Whalley, 1987. Reproduced by permission.)*

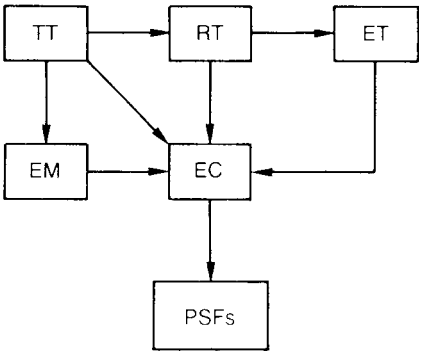


Figure 14.37 *Relations between task and response types, error causes and other quantities (Whalley, 1987. Reproduced by permission.)*

the creation of data banks which are both based on this more recent work and applicable to those industries.

14.34.4 Human error database (HED)

The Human Error Database (HED), described by Kirwan (1988), is based on the HEP data given in the *Rosmussen Report*, tempered by expert judgement. In that it derives from that report, it has similarities to THERP, but it is less decompositional and is not dependent on any specific model.

14.34.5 Accident and human error classification system (TAXAC)

A design for an accident and human error classification system, TAXAC, as the basis of a human error data bank, has been given by Brazendale (1990 SRD R510). The accident classification is obtained as a function of the accident signature (a skeletal account) S, and the accident causes and conducive factors. The features which contribute to the latter are grouped under the headings: activity A, man M, organization O, and plant P. Accidents are also categorized by industry I. Checklists are given for features I, S, A, M, O and P. The author also reviews the requirements and prospects for a human error data bank. Such a venture should not be an isolated entity but should be part of a wide activity on human performance.

14.35 Assessment of Human Error: SRD Human Error Guides

Guidance on several aspects of human error in design and assessment has been issued by the Safety and Reliability Directorate (SRD).

Design is dealt with in *Guide to Reducing Human Error in Process Operation (short version)* by the Human Factors in Reliability Group (HFRG) (1985 SRD R347) (the *HFRG Guide*) and *The Guide to Reducing Human Error in Process Operation* by P. Ball (1991 SRDA-R3), the short and full versions.

The treatment of human error in hazard assessment is covered in *A Suggested Method for the Treatment of Human Error in the Assessment of Major Hazards* by R.F. White (1984 SRD R254), *Human Reliability Assessors Guide* by Humphreys (1988a) and *Human Error in Risk Assessment* by Brazendale (1990 SRD/HSE/510).

A related publication is *Developing Best Operating Procedures* by Bardsley and Jenkins (1991 SRDA-R1). This is considered in Chapter 20.

The *HFRG Guide* (1985 SRD R347), as its title indicates, is concerned with qualitative measures for reducing human error rather than with predicting it. It is essentially a collection of checklists under the following headings: (1) operator–process interface, (2) procedures, (3) workplace and working environment, (4) training and (5) task design and job organization.

The *Guide* distinguishes three meanings of procedure: (1) general guidance, (2) an aid and (3) prescribed behaviour. With regard to the latter, it states the following principles: (1) there should be no ambiguity about when a procedure is to be used, (2) if a procedure is mandatory there should be no incentive to use another method, (3) where possible a procedure should support the operator's skill and discretion rather than replace them and (4) a procedure should be easy to understand and to follow.

R.F. White (1984 SRD R254) describes the use of event tree and fault tree methods to identify the points at which a human action occurs which has an effect on the outcomes. As described earlier, he uses a form of PSF, the OOA, which is distinguished by the fact that it is observable and for which he provides a checklist. He gives as an illustrative example the analysis of the filling of an liquefied natural gas tank.

The *Human Reliability Assessors Guide* (Humphreys, 1988a), given in overview by Humphrey (1988b), is in two parts, the first of which gives a summary of eight techniques for human reliability assessment and the second evaluation criteria for selection and a comparative evaluation based on these criteria. The eight techniques are APJ, PC, TESEO, THERP, HEART, IDA, SLIM and HCRM. For each technique the *Guide* gives a description and a statement of advantages and disadvantages. The evaluation criteria used relate to (1) accuracy, (2) validity, (3) usefulness, (4) effective use of resources, (5) acceptability and (6) maturity. Accuracy has to do with correspondence with reality and with consistency; validity with incorporation of human factors knowledge and of the effect of appropriate PSFs.

The report by Brazendale (1990 SRD/HSE/510) presents a taxonomy for an accident classification scheme, TAXAC, intended for use in connection with a human error data bank. The classification is preceded by a discussion of models of human error. An account of this work is given in Section 14.34.

14.36 Assessment of Human Error: Benchmark Exercise

A benchmark exercise of human reliability is described in *HF-RBE: Human Factors Reliability Benchmark Exercise: Summary Contributions of Participants* (Poucet, 1989). The study is one of a series of benchmark exercises conducted by the Commission of the European Communities (CEC) and organized by the Joint Research Centre (JRC) at Ispra, Italy. The exercise was carried out over 1986–88 with 13 participants. The system studied was the emergency feedwater system (EFS) on a nuclear reactor at the Kraftwerk Union (KWU) site at Grohnde. Two studies were performed: a routine test and an operational transient.

The study carried out by SRD is described in Poucet's volume by Waters. The work showed the importance of the

Table 14.32 *Classification structure of performance influencing factors (CCPS, 1994/17) (Courtesy of the American Institute of Chemical Engineers)*

Operating environment	*Task characteristics*
Chemical process environment: Frequency of personnel involvement Complexity of process events Perceived danger Time dependency Suddenness of onset of events Physical work environment: Noise Lighting Thermal conditions Atmospheric conditions Work pattern: Work hours/rest hours Shift rotation	Equipment design: Location/access Labelling Personal protective equipment Control panel design: Content and relevance of information Identification of displays and controls Compatibility with user expectations Grouping of information Overview of critical information and alarms Job aids and procedures: Clarity of instructions Level of description Specification of entry/exit conditions Quality of checks and warnings Degree of fault diagnostic support Compatibility with operational experience Frequency of updating Training: Clarity of safety and production requirements Training in using new equipment Practice with unfamiliar situations Training in using emergency procedures Training in using automatic systems
Operator characteristics	*Organizational and social factors*
Experience: Degree of skill Experience with stressful process events Personality: Motivation Risk taking Risk homeostasis Locus of control Emotional control Type A vs type B Physical condition and age	Teamwork and communications: Distribution of workload Clarity of responsibilities Communications Authority and leadership Group planning and orientation Management policies: General safety policy Systems of work Learning from operational experience Policies for procedures and training Design policies

qualitative modelling stage prior to any quantification and the value of event trees as a tool for such modelling. Methods investigated included APJ, TESEO, THERP, HEART and SLIM. No single method appeared superior in all applications.

14.37 Assessment of Human Error: ACSNI *Study Group Report*

The accounts given of attempts to assess human error illustrate the difficulties and raise the question of whether such assessment is even feasible. The use of quantitative risk assessment has created a demand for the development of techniques for the assessment of human error and this demand has been satisfied by the development of methods, which have just been described, but the validation of these methods leaves much to be desired.

This problem is addressed in *Second Report* of the ACSNI (1991) entitled *Human Reliability Assessment – A Critical Review*. The study deals with the control of the process, but emphasizes that the question is wider than this, embracing also maintenance and other activities. Although it is a report to the nuclear industry, its findings are in large part applicable to the process industries also.

As systems become more automated and reliable, but still vulnerable to human error, the relative importance of human error increases.

The report quotes the view expressed to the Sizewell B Inquiry by the Nuclear Installations Inspectorate (HSE, 1983e) that it was 'considered that comprehensive quantification of the reliability of human actions was not, with

current knowledge, meaningful or required', and considers how far the situation has changed since that time.

The report describes the basic procedure of HRA. This is the breakdown of the task into a series of events, each of which has two alternative outcomes and the assignment to these events of basis error probabilities (HEPs). These HEPs are then modified in respect of dependencies and of PSFs. The HEP for the task is then determined. The robustness of the result is assessed by means of a sensitivity analysis.

The variations on this basic procedure lie in the areas of the data sources, the rules for combination and the handling of time. The different techniques vary in the use which they make of field data, data banks, and expert judgement. They also differ in the way in which they combine the influencing factors. In one method some factors may be taken into account by making distinctions in the basic tasks, whilst in another they may be handled as PSFs. The effect of time may be taken into account by treating it simply as another PSF, or, alternatively, it may be accorded a special status. In this latter case the favoured method is the time response correlation, in which time is the principal independent variable determining the HEP, the HEP decreasing as the time available increases.

The report examines some of the areas of HRA in which problems arise or over which care must be taken. The include (1) classification of errors, (2) modelling and auditing, (3) operator error probabilities, (4) maintenance error probabilities, (5) interaction between PSFs, (6) sensitivity analysis and (7) changes in management and organization.

It adopts the distinction between skill-based, rule-based and knowledge-based behaviour and that between slips and mistakes. Essentially it argues that slips, associated with skilled behaviour, are amenable to prediction, but mistakes, associated with rule-based behaviour, are harder to predict, whilst for errors in knowledge-based behaviour there is currently no method available. It also draws attention to wilful actions, or violations, which again are not well covered in current methods.

The first step in an assessment of HEPs is the modelling of the task. There is evidence that for skill-based errors at least, the variability between techniques is less than that between analysts. This points to the need for training of analysts and for an independent check. For auditing it is necessary that the analyst record sufficient detail on his procedures and reasoning.

The report cites estimates of HEPs given in the literature such as the *Rasmussen Report*, described below. It draws attention to the importance of dependency between human actions. It is characteristic of human error that the probability of a further error following an initial one is often not independent but conditional on, and increased by, the occurrence of the first error. On the other hand, humans have the capability to recover from error. It is also necessary to consider the HEP for tasks where more than one operator is involved.

With regard to maintenance error, the report makes the point that hardware failure rate data already include the effects of maintenance errors. Nevertheless, it is prudent to make some assessment of the maintenance error. In particular, there is the possibility that such errors may be a source of dependent failures, as described in Chapter 9.

Most methods make the assumption that the PSFs are independent of each other. Yet, the effects of lack of supervision and of training, for example, are likely to be greater when they occur in combination. An exception is SLIM, which does allow for this effect. The HEP estimates should be explored using sensitivity analysis.

The HRA is likely to more affected than the PRA as a whole by changes in the management and organization of the company, but the assessment of such changes on HEPs is not straightforward. It seems likely that certain types of error will be more affected than others and, therefore, that their relative importance will change. Skill-level errors may be less influenced by management changes than by knowledge-level ones. Violations might well be sensitive to such changes.

The report reviews the strengths and limitations of HRA. It is accepted that PRA has an essential role to play in improving reliability; HRA is a logical and vital extension. Its use has been given impetus by the retrospective assessments conducted after the Three Mile Island incident. A HRA contributes to system design in three ways: it provides a benchmark for designs and safety cases; it gives a quantitative assessment of alternative design or organizational solutions; and it provides a means and a justification for searching out the weak points in a system.

The limitations of HRA principally considered are those of HEP data and of validation. There is a wealth of data from various kinds of human factors experiments, but the situations in which they are obtained are usually to a degree artificial and their applicability is questionable. They provide guidance on the relative importance of different PSFs but generally need to be supplemented by information from other sources. The quantity and quality of field data are relatively low. Those data that do exist are predominantly for slips rather than mistakes or violations. Again they are a guide to the relative importance of different PSFs, but need to be supplemented. A third source of data is expert judgement. The methods for maximizing the quality of assessments and avoiding pitfalls are discussed. The importance is emphasized of the experts having full information on the operational context, such as normal operation or abnormal conditions.

The report addresses the question of the lack of validation of HRA methods. It quotes the following critique of J.C. Williams (1985b): 'It must seem quite extraordinary to most scientists engaged in research in other areas of the physical and technological world that there has been little or no attempt made by human reliability experts to validate the human reliability assessment techniques which they so freely propagate, modify and disseminate'.

Four kinds of validity are considered by the authors: (1) predictive validity, (2) convergent validity, (3) content validity and (4) construct validity. Essentially, for the prediction of a given analyst, predictive validity is concerned with agreement with the real situation, convergent validity is concerned with agreement with the predictions of other analysts, content validity is concerned with agreement between the elements of the model and the features which are critical in real life, and construct validity is concerned with agreement between the structure of the model and that of the real-life situation.

A study of predictive validity has been made by Kirwan (1988). He compared six HRA methods in respect of their ability to predict accident data from experimental, simulator and plant sources, and found that on some criteria some methods seemed reasonably successful. The work was limited, however, to the assessment of the HEP for specified errors and did not deal with modelling of tasks. Two studies of convergent validity, by Brune, Weinstein

and Fitzwater (1983) and Bersini, Devooght and Smidts (1988), have found that different assessors give widely differing estimates, even when using the same method. Content validity is probably best assessed by peer review. A study by Humphreys (1988a) based on a comparison of eight methods against a checklist concluded that the relative performance of the methods depends on the problem and that few are completely comprehensive. The report states that construct validity does not appear to have been applied in HRA and that it may not be applicable at this stage of development.

Considering the areas where work is required, the report suggests that one important topic is the development of an improved model of operator behaviour. Here it is the high level decision-making processes which are of prime importance, since it is failures at this level which have the most serious consequences. There is a hierarchy of patterns of learned behaviour, highly learned at the lower levels and but less so towards the upper ones. It is the conservatism of these processes which is responsible for behaviour such as 'mind set' and switch to 'automatic pilot' and for slips when the mind 'jumps the points' and then continues with a whole series of inappropriate actions. Another area where work is needed is the creation of a data set which may be used for validation studies.

The report supports the development and use of methods of HRA. It is an essential element of PRA and is beneficial in its own right. But the techniques available for predicting slips are better than those for mistakes, and particular caution should be exercised with the latter. It should be recognized that HRA is still in its infancy.

It rejects the view that HRA in the nuclear industry should be optional and supports a requirement for its use. HRA provides a structured and systematic consideration of human error. It is already a valuable tool and has the potential to become an invaluable one. A requirement for its use is necessary to provide the necessary impetus for this. The report emphasizes, however, that effort should not be concentrated exclusively on assessment; there is equal need for a systematic approach to the reduction of human error.

The report contains appendices (Appendices 1–4) on HRA methods and their evaluation, dependability of human error data, attempts to establish validity of HRA methods, and approaches to reducing human error. Some of the procedures reviewed in Appendix 1 are APJ, IDA, TESEO, THERP, HEART, SLIM, TRCs, MAPPS and HED.

Appendix 4 of the report gives guidance on approaches to the reduction of human error. It discusses accident chains and latent and active (enabling and initiating) failures and gives the accident model shown in Figure 2.5 which shows the 'shells of influence' for the PSFs. The approach is based on the identification by the HRA, including the sensitivity analysis, of the features where human error is critical, the application of human factors methods and the implementation of the improvements indicated by these methods. The role of human factors both in system design and in the design of the man–machine interface and the workplace is described.

14.38 CCPS *Human Error Prevention Guidelines*

14.38.1 CCPS *Guidelines for Preventing Human Error in Process Safety*

The prevention of human error on process plants is addressed in the *Guidelines for Preventing Human Error in Process Safety* edited by Embrey for the CCPS (1994/17) (the CCPS *Human Error Prevention Guidelines*).

The *Human Error Prevention Guidelines* are arranged under the following headings: (1) the role of human error in chemical process safety, (2) understanding human performance and error, (3) factors affecting human performance in the chemical industry, (4) analytical methods for predicting and reducing human error, (5) qualitative and quantitative prediction of human error in risk assessment, (6) data collection and incident analysis methods, (7) case studies and (8) setting up an error reduction program in the plant.

14.38.2 Approaches to human error

The *Guidelines* distinguish four basic perspectives on human error, which they term: (1) the traditional safety engineering approach, which treats the problem as one of human behaviour and seeks improvement by attempting to modify that behaviour; (2) the human factors engineering and ergonomics (HF/E) approach, which regards human error as arising from the work situation which it therefore seeks to improve; (3) the cognitive engineering approach, which again accords primacy to the work situation, but places its main emphasis on the cognitive aspects; and (4) the socio-technical systems approach, which treats human error as conditioned by social and management factors. Until quite recently, it has been the HF/E approach which has made the running. In the last decade, however, the last two approaches, cognitive engineering and socio-technical systems, have emerged strongly.

The stance of the *Guidelines* is one of system-induced error. This is akin to the work situation approach but enhanced to encompass the cognitive and socio-technical approaches.

14.38.3 Performance influencing factors

The factors shaping human performance are referred to in the *Guidelines* as PIFs. They give a PIF classification structure and a detailed commentary on each factor.

14.38.4 Methods of predicting and reducing human error

The *Guidelines* deal with methods for predicting and reducing human error in terms of (1) data acquisition techniques, (2) task analysis, (3) human error analysis and (4) ergonomics checklists.

They describe a number of methods of task analysis, grouped into action-oriented techniques and cognitive techniques. The former include HTA and operation action event trees (OAETs). The two representatives of the latter are the critical action and decision evaluation technique (CADET) and the influence modelling and assessment system (IMAS). A critical review is given of each method.

Human error analysis is represented by PHEA and work analysis. The PHEA method is that utilized in the *Guidelines'* methodology for HRA.

14.38.5 Methods of predicting HEP for risk assessment

The *Guidelines* describe a methodology for HRA, as part of quantitative risk assessment, utilizing both qualitative and quantitative methods for predicting human error. They begin with an illustrative example of fault tree analysis in which the prime contributors are human error events.

The HRA methodology presented in the *Guidelines* is that already described in Section 14.31 and outlined in Figure 14.34. A detailed commentary is given on each of the

stages involved. The core of the method is the four stages of (1) critical human interaction identification and screening, (2) qualitative prediction of human error, (3) representation of event development and (4) quantification of significant human errors.

It is a feature of this HRA methodology that it directs the analyst to acquire understanding of the system and its problems by critical human interaction identification and to undertake a detailed qualitative analysis to further enhance this understanding before embarking on the use of the quantitative methods. It is this rather than the introduction of any new quantitative technique which is its most distinctive characteristic of the method.

14.38.6 Methods for data collection and incident analysis

The *Guidelines* review the collection of data on human error. The treatment given is outlined in Section 14.34.

The *Guidelines* give a number of methods of incident analysis. They are (1) the causal tree/variation diagram, (2) the management oversight and risk tree (MORT), (3) the sequentially timed events plotting procedure (STEP), (4) root cause coding, (5) the human performance investigation process (HPIP) and (6) change analysis. They also refer to the CCPS *Incident Investigation Guidelines*, where most of these techniques are described. A relatively detailed account is given of HPIP by Paradies, Unger and Ramey-Smith (1991); HPIP is a hybrid technique combining several of those just mentioned. The CCPS treatment of incident investigation both in these *Guidelines* and in the *Incident Investigation Guidelines* is described Chapter 27.

14.38.7 Case studies

A feature of the *Human Error Prevention Guidelines* is the number of case histories given. The section on case studies gives five such studies: (1) incident analysis of a hydrocarbon leak from a pipe (Piper Alpha); (2) incident investigation of mischarging of solvent in a batch plant; (3) design of standard operating procedures for the task in Case Study 2; (4) design of VDUs for a computer controlled plant; and (5) audit of offshore emergency blowdown operations. Other case studies occur throughout the text. One illustrates system induced error. Other scene-setting case studies cover (1) errors occurring during plant changes and stressful situations, (2) inadequate human–machine interface design, (3) failures due to false assumptions, (4) poor operating procedures, (4) routine violations, (5) ineffective organization of work, (6) failure explicitly to allocate responsibility and (7) organizational failures. There are case studies illustrating the application of models of human error such as the step ladder and sequential models.

The importance of human error in QRA is illustrated by the case study, already mentioned, dealing with the prevalence of human error in fault trees. Other case studies illustrate HTA, SPEAR, THERP and SLIM.

14.38.8 Error reduction programmes

The *Guidelines* provide guidance on the implementation of an error reduction programme in a process plant. A necessary precondition for such a programme is a management culture that provides the background and support for such initiatives. The general approach is essentially that given in the CCPS *Process Safety Management Guidelines* described in Chapter 6.

Since both safety-related and quality-related errors tend to have the same cause, an error reduction programme may well run in parallel with the quality programme. An error reduction programme should address both existing systems and system design. The tools for such a programme given in the *Human Error Prevention Guidelines* include (1) critical task identification, (2) task analysis, (3) PIE analysis and (4) error analysis, as described in Sections 14.38.3 and 14.38.4. System design should also address allocation of function. Error reduction strategies for these two cases are presented in the *Guidelines*.

14.39 Human Factors at Sizewell B

14.39.1 Sizewell B Inquiry

The potential contribution of human factors to the design and operation of nuclear power stations was urged in evidence to the Sizewell B Inquiry by the Ergonomics Society, as described by Whitfield (1994).

The Society saw this contribution as being in the areas of: (1) setting operational goals; (2) allocation of function between humans, hardware and software; (3) definition of operator tasks; (4) job design; (5) overall performance assessment and monitoring of operational experience; (6) operator-plant interface and workplace conditions; (7) pperator support documentation; (8) selection and training of operating staff; (9) human reliability assessment; and (10) construction and quality assurance. The Nuclear Installations Inspectorate also laid emphasis on human factors aspects (HSE, 1983e).

The report of the Inquiry Inspector (Layfield, 1987) states: 'I regard human factors as of outstanding significance in assessing the safety of Sizewell B since they impinge on all stages from design to manufacture, construction, operation and maintenance.' (paragraph 25.90). It recommended the involvement of the discipline.

The plan put forward by the Central Electricity Generating Board in support iof its licence application included commitments to an extensive schedule of training and to the use of probabilistic safety assessment, including quantification of human error.

14.39.2 Human factors studies

A review of the applicability of ergonomics at Sizewell B was undertaken by Singleton (1986), who identified applications in control room design, use of VDU displays, documentation, fault diagnosis, maintenance and task analysis. He stated: 'We know that human operators can achieve superb performance if they are given the right conditions. Appropriate conditions in this context can be listed within the four categories: the information presentations, the training, the support systems and the working conditions and environment'.

An overview of the application of human factors at Sizewell B has been given by Whitfield (1994).

Human factors specialists are involved in extensive work on training, supported by task analysis, as described below. In the main control room one feature is the use of a plant overview panel, separate from the other displays, for the monitoring of safety critical parameters. Another area of involvement is in operating instructions. Use is made of 'event-based' instructions to diagnose a fault and to initiate recovery. But in addition, for safety critical functions, there are 'function-based' procedures, which assist in restoring the plant to a safe condition if for some reason the event-based instructions are inappropriate. Further details are given by McIntyre (1992).

HRA within the PSA utilizes OAETs and the HEART method, with some use of THERP. An account is given by Whitworth (1987). The application of task analysis at Sizewell B is described by Ainsworth (1994). The programme for this comprised five stages:

(1) preliminary task analysis of critical tasks;
(2) task analysis of selected safety critical tasks;
(3) preliminary talk-through/walk-through evaluations of procedures in a control room mock-up;
(4) validation of procedures on a control room simulator;
(5) task analysis of tasks outside the main control room.

One crucial task on which task analysis was performed was the cooling down and depressurization of the reactor. This was a major study involving some 60 task elements and taking some 44 person-weeks. Time line analysis was used to address issues such as manning.

A review of procedures revealed a number of defects. Besides obvious typographical errors, they included: (1) incorrect instrument numbering (in procedures); (2) incorrect instrument labelling (on panels and in procedures); (3) omission of important clarifiers such as 'all', 'or', 'either' and 'if available'; (4) omission of important cautions and warnings; (5) requirements for additional information; and (6) lack of consistency between procedures, panels and VDU displays. Overall, the task analyses identified a number of mismatches between task requirements and man–machine interfaces.

Ainsworth makes the point that the ergonomists were often better at identifying problems than in devising solutions, those which they proposed often being impractical, but that it is possible to achieve a mode of working in which these problems are communicated to the designers who take them on board and come up with effective solutions.

14.40 Notation

Section 14.3

$H(s)$	operator transfer function
K	gain
τ_d	reaction time (s)
τ_I	compensatory lag time constant (s)
τ_L	lead time constant (s)
τ_N	neuromuscular lag time constant (s)

Section 14.27

Subsection 14.27.4

k	constant
P_b	basic human error probability
P_c	conditional human error probability

Subsection 14.27.11

n	number of alarms in group
P_i	probability of failure to initiate action in response to ith alarm
P_r	probability of failure to initiate action in response to a randomly selected

Section 14.28

a, b	constants
HEP	human error probability
n	number of performance shaping factors
r	relevancy factor
SLI	Success Likelihood Index
w	quality weighting

Section 14.30

f	error factor
k_1, k_2	constants
m	median
q	quality
r	rank
r_n	normalized rank
x	Success Likelihood Index
τ	mean response time
τ_r	adjusted median response time

Section 14.32

K_1–K_5	parameters
q	probability of error

15 Emission and Dispersion

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The three major hazards – fire, explosion and toxic release – usually involve the emission of material from containment followed by vaporization and dispersion of the material. The treatment given here is relevant to all three hazards; in particular, the development of the emission and dispersion phases is relevant to such situations as:

(1) Escape of flammable material, mixing of the material with air, formation of a flammable cloud, drifting of the cloud and finding of a source of ignition, leading to (a) a fire and/or (b) a vapour cloud explosion, affecting the site and possibly populated areas.
(2) Escape of toxic material, formation of a toxic gas cloud and drifting of the cloud, affecting the site and possibly populated areas.

15.1 Emission

There is a wide range of circumstances which can give rise to emission. The situation which appears to be most frequently discussed is a failure of plant integrity, but it is important to consider other occurrences, including escape from valves which have been deliberately opened and forced venting in emergencies. Thus on a low pressure refrigerated liquefied petroleum gas (LPG) installation, for example, a large quantity of flammable vapour may be released by failure of a pressure vessel or of pipework. But loss of refrigeration with resultant forced venting could also give a large release of vapour. Finally, emissions caused by terrorist acts are of growing concern.

In view of the many different situations which can give rise to emission, it is peculiarly difficult to obtain meaningful estimates of the quantity and duration of emissions. The emission stage is therefore subject to great uncertainty. It is nevertheless very important, because the way in which emission occurs can greatly influence the nature and effect of the release, and particularly of any vapour cloud which is formed.

Emission flows may be determined by the basic relations of fluid mechanics. Fundamentals of fluid flow are treated in such texts as *Hydraulics* (Lewitt, 1952), *Thermodynamics Applied to Heat Engines* (Lewitt, 1953), *The Dynamics and Thermodynamics of Compressible Flow* (Shapiro, 1953–), *Chemical Engineering* (Coulson and Richardson, 1955–, 1977–), *Machanics of Fluids* (Massey, 1968–) and *Chemical Engineers Handbook* (Perry and Green, 1984). Selected references on emission are given in Table 15.1.

Table 15.1 *Selected references on emission*

Cremer and Warner (1978); HSE (1978b, 1981a); Rosak and Skarka (1980); McQuaid and Roberts (1982); O'Shea (1982); Pikaar (1985); Ramskffl (1986 SRD R352)

Liquid, gas and vapour flow
Stanton and Pannell (1914); Lacey (1922/23); Lea (1930); Lapple (1943); Streeter (1951–); Lewitt (1952,1953); Shapiro (1953-); Coulson and Richardson (1955–, 1977–); Bulkley (1967); Grote (1967); Massey (1968–); Tate (1970); Simpson (1971); V.J. Clancey (1974a); Loeb (1975); Levenspiel (1977); HSE (1978a, 1981a); Pham (1979); Nowak and Joye (1981); Gyori (1985); Lipowicz (1985); Belore and Buist (1986); Pirumov and Roslyakov (1986); Leung and Epstein (1988); J.L. Woodward and Mudan (1991)

Coefficient of discharge
Perry (1949); Arnberg (1962); S.D. Morris (1990a)

Friction factor
Colebrook and White (1937); LF. Moody (1944); Colebrook (1939); Churchill (1973, 1977, 1980); Jain (1976); N.H. Chen (1979–); Serghides (1984)

Slow leaks
D.H. Jackson (1948); Mencher (1967); Pilborough (1971, 1989)

Vessel drainage times
Loiacono (1978); T.C. Foster (1981); Schwartzhoff and Sommerfeld (1988); Sommmerfeld (1990); J.L. Woodward and Mudan (1991); Papas and Sommerfeld (1991); Crowl (1992b); Hart and Sommerfeld (1993); Sommerfeld and Stallybrass (1993); K.S. Lee and Sommerfeld (1994)

Bund overflow
Michels, Richardson and Sharifl (1988); Phelps and Jureidni (1992)

Pipelines
Cronje, Bishnoi and Svrcek (1980); T.B. Morrow (1982a,c); Fayed and Olten (1983); Oranje (1983); Lagiere, Miniscloux and Roux (1984); Battarra *et al.* (1985); Cawkwell and Charles (1985); Maddox and Safti (1985); Schweikert (1986); Picard and Bishnoi (1988, 1989); Clerehugh (1991); Olorunmaiye and Imide (1993)

Two-phase flow (*see* Table 15.2)

Vessel venting, blowdown
Zuber and Findlay (1965); DNV (1983 83–1317); Fauske, Grolmes and Henry (1983); Swift (1984); Grolmes and Epstein (1985); Fauske (1988a); Evanger *et al.* (1989); Haque *et al.* (1990); Haque, Richardson and Saville (1992); Haque *et al.* (1992); S.M. Richardson and Saville (1992)

Pressure relief valves
F.J. Moody (1966); Richter (1978b); Sallett (1978, 1979a,b, 1990a–c); Lyons (1979); Sale (1979a,b); Sallet, Weske and Giihler (1979); L. Thompson and Buxton (1979a,b); Z. Chen, Govind and Weisman (1983); Heller (1983); Rommel and Traiforos (1983); Cloutier (1985); Forrest (1985); Sallett and Somers (1985); Moodie and Jagger (1987); Wilday (1987); Morley (1989a,b)

Bursting discs
Huff and Shaw (1992)

Vessel rupture
Artingstall (1972); Hardee and Lee (1974, 1975); Hess, Hoffman and Stoeckel (1974); J.D. Reed (1974); Lonsdale (1975); Maurer *et al.* (1977); HSE (1978b); Bongers, ten Brink and Rulkens (1980); R.A. Cox and Comer (1980); Leiber (1980); A.F. Roberts (1982); Drivas, Sabnis and Teuscher (1983); Friedel (1986, 1987a); CEC (1990 EUR 12602 EN); Nolan *et al.* (1990); Schmidli, Bannerjee and Yadigaroglu (1990); J.L. Woodward (1990); Nolan, Hardy and Pettitt (1991); Bettis and Jagger (1992); Pettit *et al.* (1992)

Pipeline rupture
Inkofer (1969); Westbrook (1974); R.P. Bell (1978); HSE (1978d); D.J. Wilson (1979b, 1981b); Morrow (1982a,c); Morrow, Bass and Lock (1982); Grolmes, Leung and Fauske (1983); Tarn (1989); Tarn and Higgins (1990); J.R. Chen, Richardson and Saville (1992)

Fugitive emissions (*see* Table 15.70)

15.1.1 Emission situations

Emission situations may be classified as follows:

(1) Fluid
  (a) gas/vapour,
  (b) liquid,
  (c) vapour–liquid mixture;
(2) Plant
  (a) vessel,
  (b) other equipment,
  (c) pipework;
(3) Aperture
  (a) complete rupture,
  (b) limited aperture;
(4) Enclosure
  (a) in building,
  (b) in open air;
(5) Height
  (a) below ground level,
  (b) at ground level,
  (c) above ground level;
(6) Fluid momentum
  (a) low momentum,
  (b) high momentum.

Some typical emission situations are shown in Figure 15.1.

The fluid released may be gas, vapour, liquid or a two-phase vapour–liquid mixture, as shown in Figure 15.1(a). If the escape is from a container holding liquid under pressure, it will normally be liquid if the aperture is below the liquid level and vapour or vapour–liquid mixture if it is above the liquid level. For a given pressure difference the mass of release is usually much greater for a liquid or vapour–liquid mixture than for a gas or vapour.

The plant on which the release occurs may be a vessel, other equipment such as a heat exchanger or a pump, or pipework, as shown in Figure 15.1(b). The maximum amount which can escape depends on the inventory of the container and on the isolation arrangements.

The aperture through which the release occurs may range from a large fraction of the envelope of the container in the case of complete rupture of a vessel to a limited aperture such as a hole, as shown in Figure 15.1(c). An aperture on a vessel may be (1) a sharp-edged orifice, (2) conventional pipe branch, (3) a rounded nozzle branch, or (4) a crack. The flow through a rounded nozzle is greater than through a conventional pipe branch, but it is the latter which is generally used. Other apertures on vessels, equipment and pipework include: (5) drain and sample points; (6) pressure relief devices – (a) pressure relief valves, (b) bursting discs, and (c) liquid relief valves; (7) seals; (8) flanges and (9) pipe ends.

The relief may take place from plant in a building or in the open air, as shown in Figure 15.1(d). This greatly affects the dispersion of the material. A large proportion of escapes to the open air are dispersed without incident.

The height at which the release occurs also has a strong influence on the dispersion, as shown in Figure 15.1(e). A liquid escape from plant below ground level may be completely contained. An escape of gas or vapour from above ground level may be dispersed over a considerable distance.

Dispersion is further affected by the momentum of the escaping fluid, as shown in Figure 15.1(f). Low and high momentum releases of gas or vapour form a plume and a turbulent momentum jet, respectively. Low and high momentum releases of liquid form a liquid stream and a high 'throw' liquid jet, respectively, both of which then form a liquid pool.

A generalized chart for the calculation of the discharge of liquids and gases under pressure has been given by Pilz and van Herck (1976) and is reproduced in Figure 15.2.

15.1.2 Elementary relations

For flow of a single fluid

$$W = Q\rho \qquad [15.1.1]$$

$$Q = uA \qquad [15.1.2]$$

$$G = W/A \qquad [15.1.3]$$

$$G = u\rho \qquad [15.1.4a]$$

$$G = u/v \qquad [15.1.4b]$$

where A is the cross-sectional area of the pipe, G is the mass flow per unit area, Q is the total volumetric flow, u is the velocity, v is the specific volume of fluid, W the total mass flow, and ρ is the density of the fluid.

The general differential form of the energy balance for the flow of unit mass of fluid is

$$-\mathrm{d}q + \mathrm{d}W_\mathrm{s} + \mathrm{d}H + \mathrm{d}\left(\frac{u^2}{2}\right) + g\,\mathrm{d}z = 0 \qquad [15.1.5]$$

where g is the acceleration due to gravity, H is the enthalpy, q is the heat absorbed from the surroundings, W_s is the work done on the surroundings (shaft work), and z is the height.

It is often convenient to eliminate H from Equation 15.1.5 using the relation:

$$\mathrm{d}H(= T\,\mathrm{d}S + v\,\mathrm{d}P) = \mathrm{d}q + \mathrm{d}F + v\,\mathrm{d}P \qquad [15.1.6]$$

where F is the mechanical energy irreversibly converted to heat (frictional loss) and P is the absolute pressure.

Then, combining Equations 15.1.5 and 15.1.6 gives

$$\mathrm{d}W_\mathrm{s} + v\,\mathrm{d}P + \mathrm{d}F + \mathrm{d}\left(\frac{u^2}{2}\right) + g\,\mathrm{d}z = 0 \qquad [15.1.7]$$

For the discharge processes considered here, the work done on the surroundings W_s is zero. Then Equation 15.1.7 becomes:

$$v\,\mathrm{d}P + \mathrm{d}F + \mathrm{d}\left(\frac{u^2}{2}\right) + g\,\mathrm{d}z = 0 \qquad [15.1.8a]$$

or, alternatively,

$$v\,\mathrm{d}P + \mathrm{d}F + u\,\mathrm{d}u + g\,\mathrm{d}z = 0 \qquad [15.1.8b]$$

In some applications the friction loss and potential energy terms may be neglected, in which case Equation 15.1.8b reduces to:

$$v\,\mathrm{d}P + u\,\mathrm{d}u = 0 \qquad [15.1.9]$$

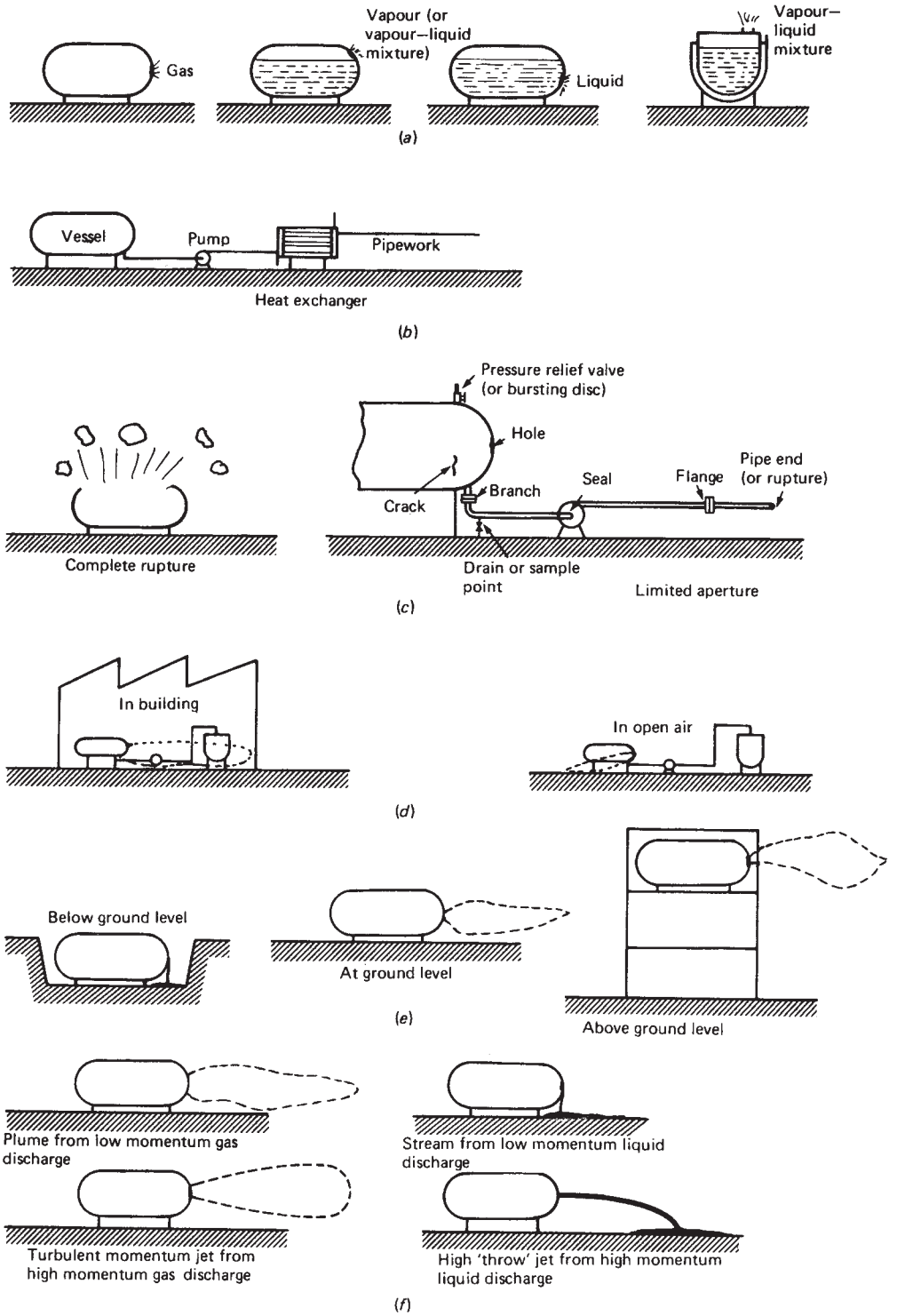


Figure 15.1 *Some emission situations*

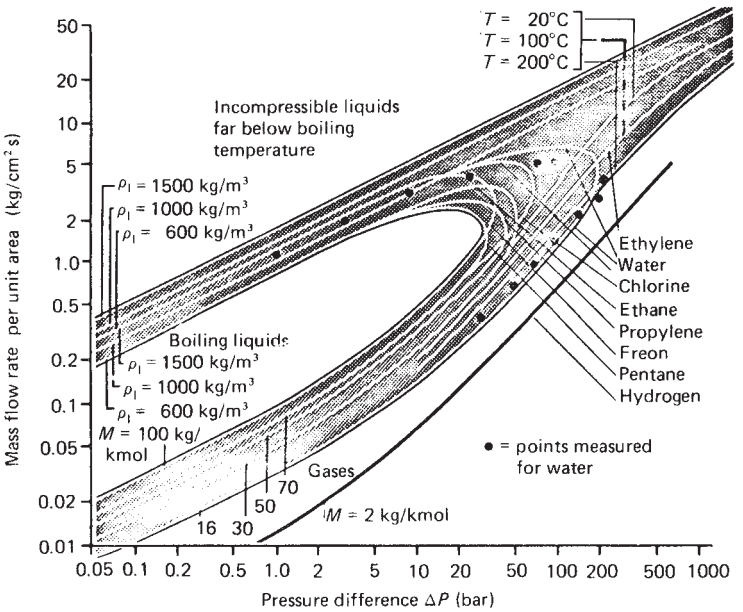


Figure 15.2 *Mass flow vs pressure difference for flow of gases, vapours and liquids through an orifice (Pitz and van Herck, 1976; reproduced by permission)*

Equation 15.1.8b may also be expressed in the form of a pressure drop relation:

$$\frac{\mathrm{d}P}{\mathrm{d}l}+\frac{1}{v}\frac{\mathrm{d}F}{\mathrm{d}l}+G\frac{\mathrm{d}u}{\mathrm{d}l}+\frac{g}{v}\frac{\mathrm{d}z}{\mathrm{d}l}=0 \qquad [15.1.10a]$$

or

$$\frac{\mathrm{d}P}{\mathrm{d}l}+\rho\frac{\mathrm{d}F}{\mathrm{d}l}+G\frac{\mathrm{d}u}{\mathrm{d}l}+\rho g\frac{\mathrm{d}z}{\mathrm{d}l}=0 \qquad [15.1.10b]$$

or

$$\frac{\mathrm{d}P}{\mathrm{d}l}+\frac{1}{v}\frac{\mathrm{d}F}{\mathrm{d}l}+\frac{u}{v}\frac{\mathrm{d}u}{\mathrm{d}l}+\frac{g}{v}\frac{\mathrm{d}z}{\mathrm{d}l}=0 \qquad [15.1.10c]$$

where l is the distance along the pipe.

A relation for pressure drop may also be obtained from the momentum balance:

$$\frac{\mathrm{d}P}{\mathrm{d}l}+\frac{S}{A}R_\mathrm{o}+G\frac{\mathrm{d}u}{\mathrm{d}l}+\rho g\frac{\mathrm{d}z}{\mathrm{d}l}=0 \qquad [15.1.11]$$

where R_o is the shear stress at the pipe wall and S is the perimeter of pipe. The term $\mathrm{d}z/\mathrm{d}l$ in Equations 15.1.10 and 15.1.11 is often replaced by the term $\sin\theta$, where θ is the angle between pipe and horizontal.

Comparing Equations 15.1.10b and 15.1.11, which each give the pressure drop, it follows that:

$$\frac{S}{A}R_\mathrm{o}=\rho\frac{\mathrm{d}F}{\mathrm{d}l} \qquad [15.1.12]$$

The pressure drop $\mathrm{d}P/\mathrm{d}l$ may also be expressed in terms of its constituent elements:

$$-\frac{\mathrm{d}P}{\mathrm{d}l}=-\frac{\mathrm{d}P_\mathrm{f}}{\mathrm{d}l}-\frac{\mathrm{d}P_\mathrm{a}}{\mathrm{d}l}-\frac{\mathrm{d}P_\mathrm{g}}{\mathrm{d}l} \qquad [15.1.13]$$

where $\mathrm{d}P_\mathrm{f}/\mathrm{d}l$ is the frictional pressure change, $\mathrm{d}P_\mathrm{a}/\mathrm{d}l$ is the accelerational pressure change and $\mathrm{d}P_\mathrm{g}/\mathrm{d}l$ is the gravitational pressure change.

For flow in pipes, the friction term $\mathrm{d}F$ is:

$$\mathrm{d}F=4\phi\frac{\mathrm{d}l}{d}u^2 \qquad [15.1.14a]$$

$$=8\phi\frac{\mathrm{d}l}{d}\frac{u^2}{2} \qquad [15.1.14b]$$

with

$$\phi=\frac{R}{\rho u^2} \qquad [15.1.15]$$

where d is the diameter of the pipe, R is the shear stress at the pipe wall and ϕ is the friction factor.

The most commonly used friction factor f is twice the friction factor ϕ:

$$f=2\phi \qquad [15.1.16]$$

Hence from Equations 15.1.14b and 15.1.16

$$\mathrm{d}F=4f\frac{\mathrm{d}l}{d}\frac{u^2}{2} \qquad [15.1.17]$$

Another form of the pressure drop equation which is derived from Equation 15.1.10b together with Equations 15.1.14 and 15.1.17 is:

$$\frac{dP}{dl} + G^2\left(\frac{dv}{dl} + \frac{4fv}{2d}\right) + \frac{g}{v}\frac{dz}{dl} = 0 \qquad [15.1.18]$$

The equations just given are in differential form. In order to obtain relations useful in engineering, they need to be integrated. Integrating the energy balance Equation 15.1.8a

$$\int_1^2 v\,dP + F + g\Delta z + \Delta\left(\frac{u^2}{2}\right) = 0 \qquad [15.1.19]$$

where limit 1 is the initial state and limit 2 is the final state.

Integration of the first term in Equation 15.1.19 requires a relation between pressure P and specific volume v. Three principal relations are those for incompressible, isothermal and isentropic flow:

$$v = \text{Constant} \quad \text{Incompressible flow} \qquad [15.1.20a]$$

$$Pv = \text{Constant} \quad \text{Isothermal flow} \qquad [15.1.20b]$$

$$P\gamma = \text{Constant} \quad \text{Isentropic flow} \qquad [15.1.20c]$$

where γ is the ratio of the gas specific heats. Also, for an adiabatic expansion:

$$Pv^k = \text{Constant} \quad \text{Adiabatic flow} \qquad [15.1.20d]$$

where k is the expansion index.

Then it can be shown that for these flow regimes:

$$\int_1^2 v\,dP = v(P_2 - P_1) \quad \text{Incompressible flow} \qquad [15.1.21a]$$

$$= P_1 v_1 \ln\left(\frac{P_2}{P_1}\right) \quad \text{Isothermal flow} \qquad [15.1.21b]$$

$$= \frac{\gamma}{\gamma - 1} P_1 v_1 \left[\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} - 1\right] \quad \text{Isentropic flow} \qquad [15.1.21c]$$

$$= \frac{k}{k - 1} P_1 v_1 \left[\left(\frac{P_2}{P_1}\right)^{(k-1)/k} - 1\right] \quad \text{Adiabatic flow} \qquad [15.1.21d]$$

It is frequently convenient to work in terms of the head h rather than the pressure P of the fluid. The relation between the two is:

$$P = h\rho g \qquad [15.1.22]$$

It is generally necessary to define the flow regime. The principal criterion of similarity is the Reynolds number Re which is

$$\text{Re} = \frac{Gd}{\mu} \qquad [15.1.23]$$

where d is the diameter of the orifice or pipe, and μ is the viscosity of the fluid.

The discharge of liquids and of gases and vapours is now considered.

15.1.3 Liquid or incompressible fluid discharge

For the flow of a liquid, or incompressible fluid, the term $\int_1^2 (1/\rho)\,dP$ is given by Equation 15.1.21a. Substituting this term in Equation 15.1.19 gives

$$\frac{1}{\rho}(P_1 - P_2) + g(z_1 - z_2) = \Delta\left(\frac{u^2}{2}\right) + F \qquad [15.1.24]$$

When flow is on a horizontal axis, the left-hand side simplifies to $(P_1 - P_2)/\rho$. When flow is not on a horizontal axis, variation in elevation can be incorporated in subsequent equations by replacing P with $P + \rho gz$ where z is based on a common reference height. The first term on the right hand side of Equation 15.1.24, $\rho\,(u^2/2)$, represents the increase in kinetic energy of (final) state 2 from (initial) state 1. Many authors include a coefficient on the kinetic energy term correcting for non-uniform velocity distributions

$$\left\{\frac{\text{kinetic energy}}{\text{mass of fluid}}\right\} = \frac{\int u^3\,da}{2\int u\,da} = \alpha\left(\frac{u^2}{2}\right) \qquad [15.1.25]$$

where integration is over the cross-sectional area of the flow and u is defined by Equation 15.1.2. For laminar flow in pipes, $\rho = 2$, and McCabe, Smith and Harriott (1956–) state that ρ is about 1.05 for fully developed turbulent flow in pipes.

For the flow of liquid through a pipe, the frictional loss F is given by

$$F = F_c + F_f + F_{ft} \qquad [15.1.26]$$

where F is the total frictional loss, F_c is the frictional loss due to sudden contraction, F_f is the frictional loss due to the pipe (or skin friction), and F_{ft} is the frictional loss due to fittings. In this expression, expansion losses have been ignored, but expressions for the expansion loss can be found in standard texts. Expansion losses cannot exceed the kinetic energy of the fluid and do not apply at the point of discharge to the atmosphere.

McCabe, Smith and Harriott (1956–) give the friction loss from contraction as

$$F_c = 0.4\left(1 - \frac{A_2}{A_1}\right)\left(\frac{u^2}{2}\right) \qquad [15.1.27]$$

where u is the velocity in the (smaller) pipe with cross-sectional area A_2. The frictional loss due to the pipe is:

$$F_f = \frac{4fl}{d}\left(\frac{u^2}{2}\right) \qquad [15.1.27]$$

The friction coefficient f is described in Section 15.1.5. The friction loss from pipe fittings is usually expressed as a number of velocity heads:

$$F_{ft} = K_{ft}\left(\frac{u^2}{2}\right) \qquad [15.1.28]$$

where K_{ft} is the friction coefficient for pipe fittings (expressed as the number of velocity heads) and is discussed in Section 15.1.5.

All of the frictional losses can be expressed in terms of the number if velocity heads. For flow from a vessel through a pipe of a single diameter, the total number K of velocity heads lost, excluding any exit, is

$$K = K_c K_f + K_{ft} \quad [15.1.30]$$

where K_c is the number of velocity heads lost at the contraction (pipe entrance), K_f is the number of velocity heads lost due to skin friction and K_{ft} is the number of velocity heads lost due to fittings. Comparing with Equation 15.1.27, K_c is

$$K_c = 0.4\left(1 - \frac{A_2}{A_1}\right) \quad [15.1.31]$$

and K_f is

$$K_f = \frac{4fl}{d} \quad [15.1.32]$$

15.1.4 Liquid discharge rates

Equation 15.1.24 can be used to predict the discharge rate from a vessel at (stagnation) pressure $P_1(+\rho gz)$ to ambient pressure $P_2(+\rho gz)$. As discussed above, the frictional loss due to a sudden pipe expansion does not apply at pipe openings to the atmosphere. This section discusses liquid discharge rates through an orifice, an external mouthpiece, and a constant diameter pipe system.

For discharge through an orifice or nozzle, changes in elevation are negligible, and frictional losses are much less than the flow kinetic energy. Based on vessel (stagnation) pressure P_1, Equation 15.1.24 shows that the velocity of a liquid through an orifice with a cross-sectional area A, which is small relative to that of the vessel, is

$$u = C_D\left[\frac{2}{\rho}(P_1 - P_2)\right]^{1/2} \quad [15.1.33]$$

or, in terms of the mass rate W,

$$W = C_D A[2\rho(P_1 - P_2)]^{1/2} \quad [15.1.34]$$

where C_D is the coefficient of discharge.

For orifice flow, the coefficient of discharge C_D is the ratio of the actual to the theoretical discharge. This actual discharge is the product of the actual cross-sectional area of the jet and the actual velocity of the jet. Then defining a coefficient of contraction C_c as the ratio of the actual to the theoretical area, and a coefficient of velocity C_v ($= 1/\rho$ in Equation 15.1.25) as the correction factor for non-uniform velocity profile at the actual cross-sectional area of the jet gives

$$C_D = C_c C_v \quad [15.1.35]$$

The coefficient of contraction C_c is defined as

$$C_c = A_c/A_o \quad [15.1.36]$$

where A_o is the cross-sectional area of the orifice and A_c is the cross-sectional area of the vena contracta. For a sharp-edged orifice in the side of a vessel there are available theoretical expressions for the coefficient of contraction. Thus for a two-dimensional sharp-edged orifice for liquid

$$C_c = \frac{\pi}{\pi + 2} = 0.61 \quad [15.1.37]$$

and for gas

$$C_c = \frac{\pi}{\pi + 2(\rho_2/\rho_1)} \quad [15.1.38]$$

where the subscripts 1 and 2 refer to stagnation and outlet conditions, respectively.

An average experimental value of C_c for sharp-edged orifices for liquids is 0.64. The difference between the actual and theoretical velocities for a sharp-edged orifice for liquid is very small. An average experimental value of C_v for sharp-edged orifices for liquids is 0.97. Thus for a sharp-edged orifice for liquids an average experimental value of the coefficient of discharge C_D is 0.62 ($= 0.97 \times 0.64$).

Studies on the coefficient of discharge from sharp-edged orifices for water have been described by Lea (1930). The coefficient of discharge for sharp-edged orifices for gases has been studied by Perry (1949). He found that the coefficient of discharge is a function of the ratio of the outlet to the stagnation pressure, or pressure ratio, as shown in Figure 15.4. The limiting values of the coefficient are 0.6 and 0.84 at high and low pressure ratios, respectively. Similar results have been obtained for short pipe outlets by Arnberg (1962). Values of the coefficient of discharge used in hazard assessment work range between 0.6 and 1.0. A value of 0.6 is frequently used for orifices. Coefficients of discharge are treated in more detail in standard texts (e.g. Lewitt, 1952; Coulson and Richardson, 1977–).

Another common discharge situation is that of an external mouthpiece on the side of a vessel, such as a short nozzle or pipe stub, as shown in Figure 15.3.

For short pipe stubs with l/d at least about 10, the frictional loss can be approximated as that of a flow contraction per Equation 15.1.27 or 15.1.31. Based on vessel (stagnation) pressure P_1, Equation 15.1.24 shows that the liquid velocity through an opening with cross-sectional area A which is small relative to that of the vessel is

$$u = \frac{[(2/\rho)(P_1 - P_2)]^{1/2}}{(1 + K_c)^{1/2}} \quad [15.1.39]$$

In a similar fashion to Equations 15.1.33 and 15.1.34, the discharge rate can be calculated using an effective

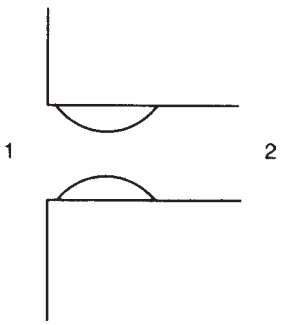


Figure 15.3 *External mouthpiece*

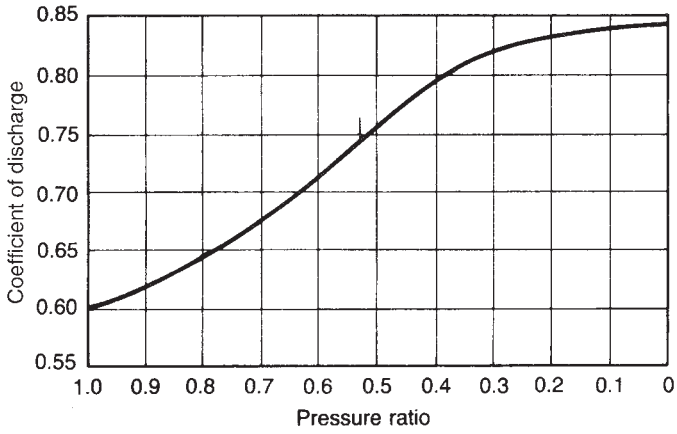


Figure 15.4 *Coefficient of discharge for gas flow through an orifice (after J.A. Perry, 1949) (Courtesy of the American Society of Mechanical Engineers)*

discharge coefficient, and using the number of velocity heads lost, the effective discharge coefficient is

$$C_D = \frac{1}{(1+K_c)^{1/2}} \qquad [15.1.40]$$

Using Equation 15.1.31 and considering discharge from a small opening in a large vessel,

$$C_D = \frac{1}{(1+0.4)^{1/2}} = 0.85 \qquad [15.1.41]$$

An average experimental value of the coefficient of discharge is 0.81 that applies to mouthpieces for which the length/diameter ratio of the pipe is not less than 3. A value of 0.8 is frequently used for short nozzles and pipe stubs.

Similarly for constant diameter pipe systems, an effective coefficient of discharge C can be defined as

$$C = \frac{1}{(1+K)^{1/2}} \qquad [15.1.42]$$

where K is given by Equation 15.1.30.

15.1.5 Friction, friction factor and fittings loss

The friction loss in a pipe is given by Equation 15.1.27, where the friction factor f is obtained from Equations 15.1.15 and 15.1.16. The relationship between the friction factors θ and f is given by Equation 15.1.16.

Relationships between the principal friction factors used are given by Churchill (1977). The friction factor f as defined above is identical to the Fanning friction factor f_F so that

$$f_F = 2\phi \qquad [15.1.43]$$

Another friction factor is the Darcy friction factor f_D. This is related to the other friction factors as follows:

$$f_D = 8\phi \qquad [15.1.44a]$$

$$= 4f \qquad [15.1.44b]$$

$$= 4f_F \qquad [15.1.44c]$$

Graphs of the friction factor are available based primarily on the work of Stanton and Pannell (1914) and of L.F. Moody (1944) and are given in standard texts (e.g. Coulson and Richardson, 1977–, Perry and Green, 1984).

It is also desirable to have equations for the friction factor, and a number of these are available. Some of the equations are implicit, others explicit. Some are more convenient for use if the flow is known, others if the pressure drop is known.

The friction factor depends on the flow regime, the three regimes being those of laminar, transitional and turbulent flow. In the laminar regime the friction factor may be obtained from the Poiseuille equation and may be written as:

$$\phi = \frac{8}{\mathrm{Re}} \qquad [15.1.45]$$

In the other regimes the friction factor is, in general, a function of the Reynolds number Re and of the roughness ratio e/d, where e is the pipe roughness.

A correlation of the friction factor for these regimes has been given by Colebrook (1939) as follows:

$$\frac{1}{f_D^{1/2}} = -2\log_{10}\left(\frac{e}{3.7d} + \frac{2.51}{\mathrm{Re}\, f_D^{1/2}}\right) \qquad [15.1.46]$$

He states that Equation 15.1.46 reduces for smooth pipes to

$$\frac{1}{f_D^{1/2}} = 2\log_{10}\left(\frac{\mathrm{Re}\, f_D^{1/2}}{2.51}\right) \qquad [15.1.47]$$

and for rough pipes to

$$\frac{1}{f_D^{1/2}} = 2\log_{10}\left(\frac{3.7d}{e}\right) \qquad [15.1.48]$$

Colebrook also gives as an alternative to Equation 15.1.47 which avoids the implicit formulation by means of the following approximate equation:

$$\frac{1}{f_D^{1/2}} = 1.8\log_{10}(\mathrm{Re}/7) \qquad [15.1.49]$$

Coulson and Richardson (1977–) state that the transition regime occurs at $2000 < \mathrm{Re} < 3000$ and give the following equations for the turbulent regime.

Smooth pipes:

$$\phi = 0.0396/\mathrm{Re}^{0.25} \quad 2.5 \times 10^3 < \mathrm{Re} < 10^5 \qquad [15.1.50]$$

$$\phi^{-0.5} = 2.5 \ln (\mathrm{Re}\,\phi^{0.5}) + 0.3 \quad 10^5 < \mathrm{Re} < 10^7 \qquad [15.1.51]$$

Rough pipes:

$$\phi^{-0.5} = -2.5 \ln [0.27e/d + 0.885/(\mathrm{Re}\,\phi^{-0.5})] \qquad [15.1.52]$$

$$\phi^{-0.5} = 3.2 - 2.5 \ln (e/d) \quad (e/d)\mathrm{Re}\,\phi^{0.5} \gg 3.3 \qquad [15.1.53]$$

Equation 15.1.50 is the Blasius equation.

Churchill (1977) has given an explicit equation for the friction factor ϕ for all three regimes as follows:

$$\phi = \left[\left(\frac{8}{\mathrm{Re}}\right)^{12} + \frac{1}{(A+B)^{3/2}}\right]^{1/12} \qquad [15.1.54]$$

with

$$A = \left[2.457 \ln\left(\frac{1}{(7/\mathrm{Re})^{0.9} + 0.27e/d}\right)\right]^{16} \qquad [15.1.55]$$

$$B = (37530/\mathrm{Re})^{16} \qquad [15.1.56]$$

where A and B are constants. Elsewhere, Churchill (1980) states that the transition regime occurs at $1800 < \mathrm{Re} < 4000$.

Another explicit equation for the friction factor for all three regimes, expressed this time in terms of the Darcy friction factor, is that of N.H. Chen (1979):

$$\frac{1}{f_\mathrm{D}^{1/2}} = -2.0 \log\left\{\frac{e}{3.7065d} - \frac{5.0452}{\mathrm{Re}} \times \log\left[\frac{1}{2.8257}\left(\frac{e}{d}\right)^{1.1098} + \frac{5.8506}{\mathrm{Re}^{0.8991}}\right]\right\} \qquad [15.1.57]$$

The relative merits of the equations for the friction factor are considered in the discussion on the work of N.H. Chen (1980).

Tabulations are available for the pressure drop across the various types of pipe fitting such as elbows, tees, valves, etc. A prime source is *Flow of Fluids through Valves, Fittings and Pipe* (Crane Company, 1986), which gives the loss in terms of the number of velocity heads. Tables are given in standard texts (e.g. Perry and Green, 1984) and appear mostly to be based on the data given in the various editions of the Crane Company publication.

An alternative formulation of fittings loss is in terms of number of pipe diameters. A table giving for selected fittings both the number of velocity heads and the number of pipe diameters is given by Coulson and Richardson (1977–). For many of the entries in this table the number of pipe diameters equivalent to one velocity head is about 50.

15.1.6 Critical flow

For compressible fluids, including gases and two-phase mixtures, it is necessary to consider critical flow. If, for such a fluid, the upstream pressure is high relative to the downstream pressure, the flow is choked. The flow is then no longer a function of the pressure difference but is a function of the upstream pressure alone and has a maximum or critical value. This is the condition of critical or choked flow. For a gas this flow is then sonic and the condition is also referred to as sonic flow.

The measure of approach to sonic conditions is the Mach number Ma which is

$$\mathrm{Ma} = \frac{u}{c} \qquad [15.1.58]$$

where c is the velocity of sound. For sonic flow the Mach number is unity and the velocity u of the fluid equals the velocity of sound c. The velocity of sound in a gas of absolute pressure P and specific volume v is given by the relation

$$c = (kPv)^{1/2} \qquad [15.1.59]$$

where k is the expansion index. Hence under critical conditions

$$u = (kP_1v_1)^{1/2} \qquad [15.1.60]$$

where subscript 1 indicates upstream (stagnation) conditions. A pressure ratio η may be defined

$$\eta = \frac{P_2}{P_1} \qquad [15.1.61]$$

Then it can be shown that the critical pressure ratio η_c is

$$\eta_\mathrm{c} = \left(\frac{2}{k+1}\right)^{k/(k-1)} \qquad [15.1.62]$$

Equation 15.1.62 is often used to determine the downstream, or choke, pressure under critical conditions.

For a given upstream pressure, the flow is zero both when $\eta = 0$ and when $\eta = 1$. At some intermediate value of η, and P, the flow passes through a maximum, which occurs when

$$\frac{\mathrm{d}G}{\mathrm{d}P} = 0 \qquad [15.1.63a]$$

or

$$\frac{\mathrm{d}G}{\mathrm{d}\eta} = 0 \qquad [15.1.63b]$$

Differentiating Equation 15.1.4b with respect to P and applying Equation 15.1.63a gives for the critical flow G_c

$$\frac{\mathrm{d}u}{\mathrm{d}P} = G_\mathrm{c}\frac{\mathrm{d}v}{\mathrm{d}v} \qquad [15.1.64]$$

Then from Equations 15.1.64 and 15.1.9

$$G_\mathrm{c}^2 = -\frac{\mathrm{d}P}{\mathrm{d}v} \qquad [15.1.65]$$

Critical flow is discussed further in the following sections.

15.1.7 Gas and vapour discharge

For the flow of a gas, or compressible fluid, through an orifice it is necessary to define the type of fluid and the type of expansion. For an ideal gas

$$P_v = \frac{RT}{M} \qquad [15.1.66]$$

and for a non-ideal gas

$$P_v = \frac{ZRT}{M} \qquad [15.1.67]$$

where M is the molecular weight, R is the universal gas constant, T is the absolute temperature, and Z is the compressibility factor.

The flow of an ideal gas may be calculated using Equation 15.1.21 with a suitable expression for $\int_1^2 v\,\mathrm{d}P$. The flow of a non-ideal gas may be obtained from Equation 15.1.5 using enthalpy values from thermodynamic tables.

The expansions which take place in discharge situations are normally throttling expansion or free expansion. Throttling expansion occurs when gas issues through a very narrow aperture or crack. There is high frictional resistance and low kinetic energy. When applied to vapour, the process is sometimes called 'wire-drawing'.

The frictional resistance of a fluid passing through a pipe varies inversely with the fifth power of the pipe diameter. Similarly, as an aperture becomes larger a situation is quickly reached where there is free expansion. The frictional resistance is low and the kinetic energy is high. In the present context it is free expansion which is of prime interest and which is considered in the treatment given below.

The free expansion of an ideal gas is usually treated as an approximately adiabatic expansion with some degree of irreversibility. The entropy change $\mathrm{d}S$ for the expansion is

$$\mathrm{d}S = \frac{\mathrm{d}q}{T} + \frac{\mathrm{d}F}{T} \qquad [15.1.68]$$

If the expansion is adiabatic $\mathrm{d}q = 0$, and if it is reversible $\mathrm{d}F = 0$. If the expansion is reversible adiabatic $\mathrm{d}S = 0$. The free expansion of an ideal gas is usually treated by the use of the Equation 15.1.21d.

If the expansion process is reversible and adiabatic or intermediate between adiabatic and isothermal, Equation 15.1.21d is applicable. If the expansion is not reversible, it may not be possible to give a continuous function for the relation between pressure and volume, but Equation 15.1.21d is often applied over a limited range of conditions. If the expansion is isentropic, then the index k is equal to the ratio of specific heats γ. If the expansion is not isentropic, then k is less than γ.

If the absolute upstream pressure P_1 is only slightly greater than the absolute downstream pressure P_2, in other words for low values of the pressure ratio P_1/P_2, it may be adequate to assume an isothermal expansion according to Equation 15.1.20b. For isothermal flow of an ideal gas ($Pv = P_1v_1$)

$$\int_1^2 v\,\mathrm{d}P = P_1v_1\int_1^2 \frac{1}{P}\mathrm{d}P \qquad [15.1.69a]$$

$$= P_1v_1 \ln\frac{P_2}{P_1} \qquad [15.1.69b]$$

Then, assuming flow on a horizontal axis ($\Delta z = 0$) and using a coefficient of discharge C_D to take account of the friction term F in Equation 15.1.19, it can be shown from Equations 15.1.4a, 15.1.19 and 15.1.76b that for the flow of an ideal gas through an orifice with a cross-sectional area A which is small relative to that of the vessel

$$u = C_D\left[2P_1v_1\ \ln\left(\frac{P_1}{P_2}\right)\right]^{1/2} \qquad [15.1.70]$$

$$G = C_D\left[\frac{2P_2^2}{P_1v_1}\ \ln\left(\frac{P_1}{P_2}\right)\right]^{1/2} \qquad [15.1.71]$$

For adiabatic flow of an ideal gas ($Pv^k = P_1{v_1}^k$),

$$\int_1^2 v\,\mathrm{d}P = \int_1^2 \left(\frac{P_1v_1^k}{P}\right)^{1/k}\mathrm{d}P \qquad [15.1.72a]$$

$$= \frac{k}{k-1}P_1v_1\left[\left(\frac{P_2}{P_1}\right)^{(k-1)/k} - 1\right] \qquad [15.1.72b]$$

$$= \frac{k}{k-1}(P_2v_2 - P_1v_1) \qquad [15.1.72c]$$

Following the same approach, it can be shown from Equations 15.1.4, 15.1.19 and 15.1.72b that for the adiabatic flow case

$$G = \frac{C_d}{v_2}\left\{\frac{2P_1}{v_1}\cdot\frac{k}{k-1}\left[1 - \left(\frac{P_2}{P_1}\right)^{(k-1)/k}\right]\right\}^{1/2} \qquad [15.1.73]$$

Introducing the pressure ratio η from Equation 15.1.61 in Equation 15.1.73 gives

$$G = C_d\left\{\frac{2P_1}{v_1}\cdot\frac{k}{k-1}[\eta^{2/k} - \eta^{(k+1)/k}]\right\}^{1/2} \qquad [15.1.74]$$

If the ratio of the upstream pressure P_1 to that downstream P_2 is sufficiently high, the flow is choked, or sonic. Under these conditions Equation 15.1.62 applies. Then, taking friction into account the maximum discharge G_c under these conditions is

$$G_c = C_d\left[\frac{P_1}{v_1}k\left(\frac{2}{k+1}\right)^{(k+1)/(k-1)}\right]^{1/2} \qquad [15.1.75]$$

Equation 15.1.75 shows that, under sonic conditions, the flow depends on the upstream pressure P_1, but is independent of the downstream pressure P_2.

Equations 15.1.73 and 15.1.75, for subsonic and sonic flow of gas, respectively, are those normally required here for the calculation of high pressure gas discharges both from vents and pressure relief valves and from ruptures.

Equation 15.1.20d and the expressions based on it should be used only within the range of their validity. The equation is based on a modification of the equations for isentropic expansion of an ideal gas, in which the index k is equal to the ratio of specific heats γ. The index k is used instead of γ to take account of a degree of non-ideal behaviour. The value of

k is obtained from thermodynamic charts by fitting Equation 15.1.20d to the appropriate constant entropy line. In addition, the index k is also used to take into account a degree of friction energy loss in expansion. In this case the value of k is determined empirically for the system concerned. The use of Equation 15.1.20d is not suitable for gases at very high pressures. These require separate treatment, as discussed in standard texts (e.g. Shapiro, 1953–; Massey, 1968–).

The use of Equation 15.1.20d is less appropriate for vapour which becomes wet when expanded. This case may be treated by the direct use of Equation 15.1.5. The work done on the surroundings is zero, and neglecting potential energy changes ($dz = 0$) along with heat transfer to the fluid, for finite changes, Equation 15.1.5 becomes

$$\Delta H + \Delta\left(\frac{u^2}{2}\right) = 0 \qquad [15.1.76]$$

Hence for negligible upstream velocity,

$$G = \rho_2[2(H_1 - H_2)]^{1/2} \qquad [15.1.77]$$

In order to solve Equation 15.1.77 it is necessary to determine the mass fraction constituted by the vapour phase, or quality, x. This can be obtained from the assumption of isentropic expansion which from the entropy balance gives

$$S_1 = S_2 \qquad [15.1.78a]$$

$$S_1 = S_{v2}x + S_{l2}(1 - x) \qquad [15.1.78b]$$

where subscripts l and v refer to the liquid and the vapour, respectively. The enthalpy after expansion H_2 is then given by:

$$H_2 = H_{v2}x + H_{l2}(1 - x) \qquad [15.1.79]$$

The effect of friction may be taken into account by applying to the enthalpy change $(H_1 - H_2)$ an efficiency factor. Efficiencies of orifices and nozzles are discussed in standard texts (e.g. Lewitt, 1953).

If the vapour flow is sonic, as determined by Equations 15.1.61 and 15.1.62, then, as for a gas, the flow is independent of the downstream pressure. In this case, the pressure P_2 for the calculation of the terminal conditions of the fluid is that obtained from Equation 15.1.61 with $\eta = \eta_c$. An illustrative example is given by Lewitt (1953, p. 275).

A vapour undergoing sudden expansion tends, however, to be supersaturated with less than the equilibrium quantity of condensed liquid droplets. It is frequently assumed that such a vapour does in fact follow a path given by Equation 15.1.20d.

A calculation which is sometimes required is the flow of vapour from a liquid vaporizing adiabatically in a vessel. The pressure in the vessel decreases as the temperature of the liquid falls due to the removal of the latent heat of vaporization.

Further discussions of methods of calculating the expansion of gases and vapours are given in the *High Pressure Safety Code* (E.G. Cox and Saville, 1975) and by Lapple (1943).

15.1.8 Temperature effects

For an adiabatic expansion the absolute temperature after expansion T_2 is

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k} \qquad [15.1.80]$$

For sonic flow the pressure ratio P_2/P_1 is given by Equation 15.1.62. Hence for this case

$$\frac{T_2}{T_1} = \frac{2}{k+1} \qquad [15.1.81]$$

15.1.9 Vessel discharge: gas flow through pipe

It is sometimes necessary to calculate the flow of high pressure gas from a vessel. The pressure in the vessel decreases as the mass of gas decreases. Equation 15.1.82, for sonic flow, can be used until the upstream pressure falls to the value at which flow becomes subsonic, at which point Equation 15.1.80 is used. An illustrative example is given by Coulson and Richardson (1977–, vol. 1, p. 110).

Another problem that may occur is the flow of gas from a vessel through a pipe, as shown in Figure 15.5. In this case, the calculation involves simultaneous solution of the equations for flow through the aperture at the entrance to the pipe and through the pipe itself.

Charts to facilitate the calculation have been constructed by Lapple (1943) and are widely used. It has been pointed out by Levenspiel (1977), however, that this work is in error due to the assumption that sonic flow can be isothermal. Corrected charts given by Levenspiel are reproduced in Figure 15.6. The parameters used in the charts are the pressures shown in Figure 15.5 and

d = diameter of pipe (m)
f_F = Fanning friction factor
G = mass velocity of gas (kg/m^2 s)
G^* = critical mass velocity of gas through an adiabatic nozzle (kg/m^{2}s)
k = expansion index (= ratio of gas specific heats)
L = length of pipe (m)
N = pipe resistance factor (= $(4f_FL)/d$)
P = absolute pressure (N/m^2)

Figure 15.6(a) is useful for finding the length of pipe for a given flow rate and Figure 15.6(b) for finding the flow rate for a given length of pipe. Note that the pipe resistance factor does not include entrance loss effects. Also, this method relies on the pipe having a uniform diameter. Changes in pipe diameter may result in multiple shocks in the discharge pipe.

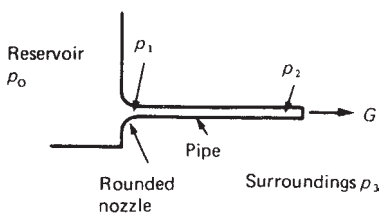


Figure 15.5 *Vessel with connected discharge pipe (Levenspiel, 1977) (Courtesy of the American Institute of Chemical Engineers)*

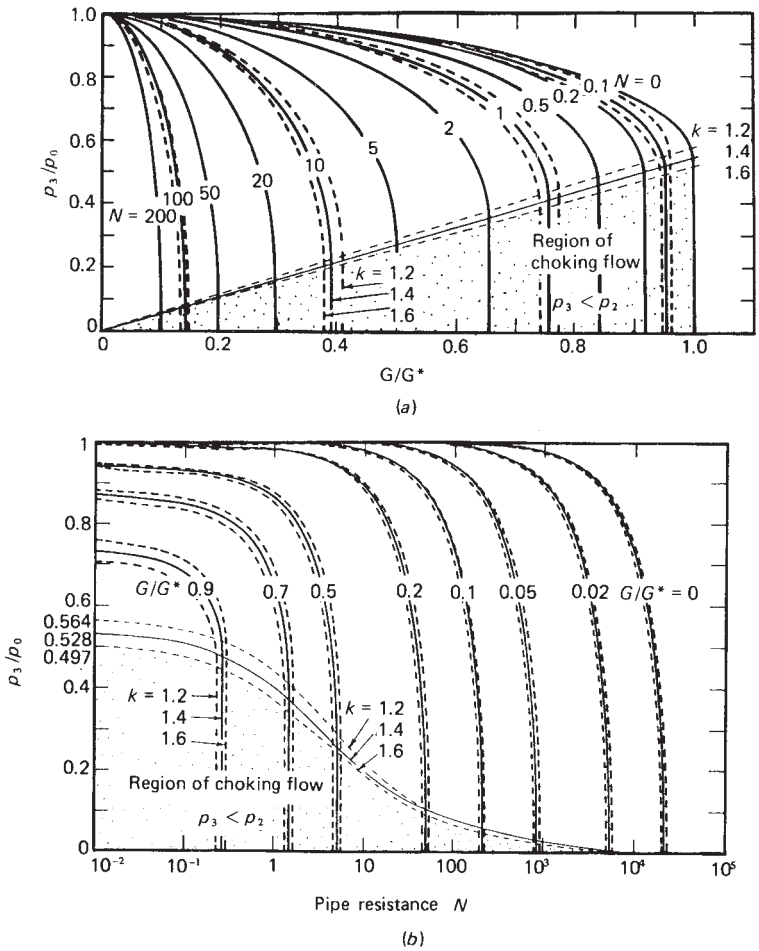


Figure 15.6 *Charts for calculation of adiabatic flow of gas from a vessel to atmosphere (Levenspiel, 1977): (a) chart useful for finding the allowable length of pipe for a given flow rate; (b) chart useful for finding the flow rate for a given length of pipe (Courtesy of the American Institute of Chemical Engineers)*

Expressions exist for the calculation of the fraction of fluid left in a vessel after a given discharge time. Such relations are given in the Rijnmond Report and by Mecklenburgh (1985).

15.1.10 Vessel discharge: liquid discharge time

It is convenient to have expressions for the time taken for a vessel containing liquid to discharge its contents. Treatments of liquid discharge times for vessels have been given in the Rijnmond Report and by Lewitt (1952), T.C. Foster (1981), Mecklenburgh (1985), Loiacono (1987), Sommerfeld and co-workers (Schwartzhoff and Sommerfeld, 1988; Sommerfeld, 1990; Papas and Sommerfeld, 1991; Hart and Sommerfeld, 1993; Sommerfeld and Stallybrass, 1993; K.S. Lee and Sommerfeld, 1994), Crowl and Louvar (2002), J.L. Woodward and Mudan (1991) and Crowl (1992b).

In the most elementary case, the vessel is of simple geometry and the outflow is through a hole at the bottom and is due solely to the head of liquid. Complexity is introduced by the following features: (1) pressure above the liquid in the vessel, (2) hole at an arbitrary height in the liquid space and (3) outflow through a pipe rather than an orifice.

The basic relations for liquid outflow, taking account of the pressure on the liquid surface and for a hole of arbitrary height, are

$$-A\frac{\mathrm{d}h}{\mathrm{d}t} = Q \qquad [15.1.82]$$

$$Q = C_D A_o\{2[g(h-h_0) + \Delta P/\rho]$$

where A is the cross-sectional area of the vessel at height h (m^2), A_o is the cross-sectional area of the orifice (m^2), C_D is the coefficient of discharge, g is the acceleration due to gravity (m/s^2), h is the height of the liquid above the bottom of the vessel (m), h_o is the height of the orifice above the bottom of the vessel (m), Q is the outflow through the orifice (m^3/s), ΔP is the pressure difference between the liquid surface and atmosphere, or gauge pressure (Pa), t is the time (s) and ρ is the density of the liquid (kg/m^3).

Rearranging and integrating Equations 15.1.82 and 15.1.83 gives the general relation for the time for discharge, or efflux time t_e (s), as:

$$t_e = \frac{1}{C_D A_o (2)^{1/2}} \int_{h_o}^{h_i} \frac{A(h)}{[g(h-h_o) + \Delta P/\rho]^{1/2}} dh \qquad [15.1.84]$$

for liquid with initial height above the bottom of the vessel h_i (m). The solution of this equation requires the specification of the terms $A(h)$ and $\Delta P/\rho$. The function $A = f(h)$ depends on the geometry of the vessel; specific cases are given below.

As for the term $\Delta P/\rho$, this is zero for the case where there is no imposed pressure on the liquid surface. The other simple case is where the pressure is maintained constant, as with an inert gas padding system, so that the term may be expressed as $\Delta P/\rho = g h_p$, where h_p is an equivalent liquid head (m).

Some expressions for the vessel cross-sectional area $A(h)$ are:

$$A = \frac{\pi}{4} D^2 \quad \text{vertical cylindrical vessel} \qquad [15.1.85]$$

$$A = 2L(hD - h^2)^{1/2} \quad \text{horizontal cylindrical vessel (flat ends)} \qquad [15.1.86]$$

$$A = \frac{\pi}{4} C^2 \quad \text{spherical vessel} \qquad [15.1.87]$$

with

$$C = 2(hD - h^2)^{1/2} \qquad [15.1.88]$$

$$A = \pi h^2 \tan^2 \theta \quad \text{vertical conical vessel, tip down} \qquad [15.1.89]$$

where L is the length of the vessel (m) and θ is the half-angle of the vessel tip(°).

It may sometimes be helpful to derive the cross-sectional area from the volume using the relation

$$A = \frac{dV}{dh} \qquad [15.1.90]$$

where V is the volume of the vessel (m^3). A number of specific cases are now considered.

Vertical cylindrical vessel, finite imposed pressure

Crowl and Louvar (2002) have treated the case of a vertical cylindrical vessel with a finite imposed pressure on the liquid surface. For this case, Equation 15.1.84 yields

$$t_e = \frac{1}{C_D g} \left(\frac{A}{A_o}\right) \left(\frac{2\Delta P}{\rho}\right)^{1/2} \left[\left(1 + \frac{\rho g (h_i - h_o)}{\Delta P}\right)^{1/2} - 1\right] \qquad [15.1.91]$$

where A is given by Equation 15.1.85. For the case where there is no imposed pressure $\Delta P = 0$:

$$t_e = \frac{1}{C_D g} \left(\frac{A}{A_o}\right) [2g(h_i - h_o)]^{1/2} \qquad [15.1.92]$$

And for the case where the hole is at the bottom of the vessel ($h_o = 0$)

$$t_e = \frac{1}{C_D} \left(\frac{A}{A_0}\right) \left(\frac{2h_i}{g}\right)^{1/2} \qquad [15.1.93]$$

Horizontal cylindrical vessel, no imposed pressure

The alternative case of a horizontal cylindrical vessel has been treated by Sommerfeld and Stallybrass (1993), who consider the case of a vessel with flat ends and no imposed pressure. Then from Equations 15.1.84 and 15.1.86

$$t_e = \frac{2L}{C_D A_o (2g)^{1/2}} \int_{h_o}^{h_i} \frac{[(D-h)h]^{1/2}}{(h-h_o)^{1/2}} dh \qquad [15.1.94]$$

The authors obtain an analytical solution, albeit a somewhat complex one.

Spherical vessel, no imposed pressure

The case of a spherical vessel with no imposed pressure has been described by Hart and Sommerfeld (1993). For this case, from Equations 15.1.94 and 15.1.87

$$t_e = \frac{2\pi}{15 C_D A_o (2g)^{1/2}} (5Dh_i + 10Dh_o - 3h_i^2 - 4h_i h_o - 8h_o^2)(h_i - h_o)^{1/2} \qquad [15.1.95]$$

For the case where the hole is at the bottom of the vessel ($h_o = 0$):

$$t_e = \frac{2\pi}{3 C_D A_o (2g)^{1/2}} \left[\left(D - \frac{3h}{5}\right) h_i^{3/2}\right] \qquad [15.1.96]$$

Vessels with other geometries

K.S. Lee and Sommerfeld (1993) have obtained analytical solutions for vessels with a number of other geometries with no imposed pressure. These are conical, paraboloid and ellipsoid vessels, both with the tapering end at the bottom and with it at the top.

Vessel drainage times and flows

Expressions have just been given for vessel drainage time. The average drainage flow is then obtained as the initial volume of liquid in the vessel divided by the drainage time. Expression of the drainage relations in dimensionless form allows some more general conclusions to be drawn. K.S. Lee and Sommerfeld (1993) define a dimensionless drainage time τ as the ratio of the time to drain the vessel with the liquid at the actual height h and the hole at the actual height h_o to the time to drain a full vessel with the hole at the bottom ($h_a = 0$). They also define a dimensionless hole height x as the ratio of the hole height h_o to the vessel diameter D or height H.

They show that for certain vessel geometries the variation of the dimensionless drainage time τ with the dimensionless hole height x is such that it passes through a maximum. The geometries where this occurs are those where the cross-sectional area of the vessel $A(h)$ decreases as the height h_a decreases. They give a tabulation of values

of the maximum dimensionless drainage time τ_{max}, which includes the following:

Vessel geometry	*Dimensionless drainage time maximum*, τ_{max}	*Corresponding dimensionless height of hole*, x
Vertical cylindrical	None	–
Horizontal cylinidrical	1.161	0.17
Spherical	1.299	0.25
Cone, tip down	1.776	0.683
Paraboloid, tip down	1.414	0.50
Vertical ellipsod	1.299	0.25
Horizontal ellipsoid	1.299	0.25

The sphere may be considered a special case of the ellipsoid.

The authors state that in no case does the maximum dimensionless drainage time attain a value of 2.

Vessels with pipe attached

Treatments for the case where the outflow is through a pipe attached to the vessel are given by Loiacono (1987), Sommerfeld (1990), Papas and Sommerfeld (1991) and Sommerfeld and Stallybrass (1992).

15.1.11 Model systems

There are available a number of model systems for determining the emission of fluid from vessels. These include those of the two *Canvey Reports* and the *Rijnmond Report* and of the Committee for the Prevention of Disasters (CPD), (1992a), Solberg and Skramstad (1982), Considine and Grint (1985), Mecklenburgh (1985) and Napier and Roopchand (1986). There are also the model systems associated with computer codes for hazard assessment such as WHAZAN and SAFETI.

15.2 Two-phase Flow

In some cases the fluid is neither a pure gas (or vapour) nor a pure liquid, but is a vapour–liquid mixture, and it is then necessary to use a correlation for two-phase flow.

The behaviour of fluids in two-phase flow is complex and by no means understood. Of the large literature on the topic mention may be made of the accounts in *One Dimensional Two-Phase Flow* (Wallis, 1969), *Two-Phase Flow and Heat Transfer* (Butterworth and Hewitt, 1977), in *Two-Phase Flow in Pipelines and Heat Exchangers* (Chisholm, 1983) and *Emergency Relief Systems for Runaway Reactions and Storage Vessels: A Summary of Multiphase Flow Methods* (AIChE, 1992/149) and of the work of Benjaminsen and Miller (1941), Burnell (1947), Lockhart and Martinelli (1949), Pasqua (1953), Schweppe and Foust (1953), O. Baker (1954, 1958), Isbin, Moy and da Cruz (1957), Zaloudek (1961), Fauske (1962, 1963, 1964), Isbin *et al.* (1962), Fauske and Min (1963), Dukler, Wicks and Cleveland (1964), Levy (1965), F.J. Moody (1965), Baroczy (1966), Chisholm and Watson (1966), Chisholm and Sutherland (1969–70), R.E. Henry and Fauske (1971), M.R.O, Jones and Underwood (1983, 1984), van den Akker, Snoey and Spoelstra (1983), Nyren and Winter (1983), B. Fletcher (1984a,b), B. Fletcher and Johnson (1984), Leung (1986a, 1990a,b, 1992a) and S.D. Morris (1988a,b, 1990a,b).

Work on two-phase flow, particularly in pipelines, has been carried out by the American Institute of Chemical Engineers (AIChE) Design Institute for Multiphase Processing (DIMP). An important distinction in two-phase flow is that between one-component systems, such as steam and water, and two-component systems, such as air and water. It is the former which is of prime concern here and, unless otherwise stated, it is to these systems that the account given here refers. Two situations which are of particular interest in the present context are the escape of a superheated, flashing liquid and the venting of a chemical reactor. Selected references on two-phase flow are given in Table 15.2.

Table 15.2 *Selected references on two-phase flow*

ASME (Appendix 28 *Applied Mechanics*, 1984/53, 183); NRC (Appendix 28 *Two-Phase Flow*); Schiller (1933); Benjaminsen and Miller (1941); Burnell (1947); Lockhart and Martinelli (1949); W.F. Allen (1952–); Pasqua (1953); Schweppe and Foust (1953); O. Baker (1954,1958); Lottes and Flynn (1956); Brigham, Holstein and Huntington (1957); Isbin, Moy and da Cruz (1957); Chisholm and Laird (1958); Hesson and Peck (1958); Fauske (1961, 1962, 1963, 1964, 1983, 1985a,b, 1986a–c, 1987a,b, 1988a); Zaloudek (1961); R. Brown and York (1962); Friedrich and Vetter (1962); Isbin *et al.* (1962); Fauske and Min (1963); D.S. Scott (1963); Dukler, Wicks and Cleveland (1964); Starkman *et al.* (1964); R.J. Anderson and Russell (1965–); Lacey (1965); Levy (1965); F.J. Moody (1965); Baroczy (1966); Chisholm and Watson (1966); Gouse (1966); Min, Fauske and Petrick (1966); Romig, Rothfus and Kermode (1966); Uchida and Nariai (1966); Cruver and Moulton (1967); Paige (1967); Collier and Wallis (1968); R.E. Henry (1968, 1970); Hubbard and Dukler (1968); Ogasawara (1969); Simpson (1968,1991); Chisholm and Sutherland (1969–70); Schicht (1969); Wallis (1969, 1980); Degance and Atherton (1970); R.E. Henry, Fauske and McComas (1970); Flinta, Gernborg and Adesson (1971); Greskovich and Shrier (1971); R.E. Henry and Fauske (1971); Klingebiel and Moulton (1971); Collier (1972); Beggs and Brill (1973); Choe and Weisman (1974); T.W. Russell *et al.* (1974); Cude (1975); Dukler and Hubbard (1975); Ishii (1975); Sozzi and Sutherland (1975); Isii, Chawla and Zuber (1976); Kopalinsky and Bryant (1976); Taitel and Dukler (1976); Ardron, Baum and Lee (1977); Butterworth and Hewitt (1977); Kevorkov, Lutovinov and Tikhonenko (1977); Ardron (1978); Wallis and Richter (1978); Fauske, Grolmes *et al.* (1980); Rassokhin, Kuzevanov and Tsiklauri (1980); Azbel (1981); Bergles, Collier and Delhaye (1981); Bergles and Ishigai (1981); Blackwell (1981); Chisholm (1981,1983); B. Fletcher (1982, 1984a,b); Hewitt (1982); IBC (1982/31, 1984/55); Landis (1982); S. Levy Inc. (1982); Sabnis, Simmons and Teuscher (1982); Fernandes, Semiat and Dukler (1983); Azzopardi and Gibbons (1983); van den Akker, Snoey and Spoelstra (1983); El-Emam and Mansour (1983); Friedel and Purps (1983,1984a,b); Grolmes and Leung (1983,1984); Hutcherson, Henry and Wollersheim (1983); M.R.O. Jones and Underwood (1983,1984); R. King (1983); Nyren and Winter (1983,1987); Veziroglu (1983); AGA (1984/43,1989/66); van den Akker (1984); Botterill, Williams and Woodhead (1984); Duiser (1984); Dukler and Taitel (1984); B. Fletcher and Johnson (1984); S.D. Morris and White (1984); Nicholson, Aziz and Gregory (1978); Soliman (1984); Berryman and Daniels (1985); Grolmes and Epstein (1985);

Huff (1985, 1990); D.A. Lewis and Davidson (1985); Olujic (1985); D.A. Carter (1986 LPB 70,1988); Friedel (1986,1987a, 1988); S.C. Lee and Bankoff (1986); Leung (1986a, 1990a,b, 1992a); Orell and Rembrand (1986); Yamashiro, Espiell and Farina (1986); Bettis, Nolan and Moodie (1987); Cindric, Gandhi and Williams (1987); Leung and Grolmes (1987–, 1988); Ewan, Moodie and Harper (1988); Hardekopf and Mewes (1988); S.D. Morris (1988a,b, 1990a,b); First and Huff (1989b); Leung and Fisher (1989); Nyren (1989); Eggers and Green (1990); Hague and Pepe (1990); Haque *et al.* (1990, 1992); Leung and Epstein (1990a,b, 1991); D.S. Nielsen (1991); Nolan, Pettit and Hardy (1991); Sumipathala, Venart and Steward (1990a,b); J.L. Woodward (1990,1993); Haque, Richardson and Saville (1992); Lantzy (1992); Giot (1994); Khajehnajafi and Shinde (1994); Seynhaefve *et al.* (1994); Holland and Bragg (1995)
Control valves: Ziegler (1957); Hanssen (1961); Sheldon and Schuder (1965); Romig, Rothfus and Kermode (1966)

Pressure relief valves
Tangren, Dodge and Seifert (1949); Richter (1978); Sallet (1978, 1979a,b, 1984, 1990a–c); Sallet, Weske and Guhler (1979); Simpson, Rooney and Grattan (1979); Fauske *et al.* (1980); O.J. Cox and Wierick (1981); Zahorsky (1983); J.W. Campbell and Medes (1985); Fauske (1985b, 1990); Forrest (1985); Sallet and Somers (1985); DnV (1982 RP C202); Friedel and Kissner (1987, 1988); Banerjee (1988); Friedel (1988); Morris (1988a,b, 1990a,b); M. Epstein, Fauske and Hauser (1989); Friedel and Molter (1989); Morley (1989a,b); Alimonti, Fritte and Giot (1990); API (1990 API RP 520); Bilicki and Kestin (1990); Curtelin (1991); M.R. Davis (1991); Lemonnier *et al.* (1991); Selmer-Olsen (1991, 1992); Simpson (1991); Leung (1992a); Wehmeier, Westphal and Friedel (1994) ISO 4126: 1991
Computer codes: Nylund (1983 DnV Rep 83–1317, 1984); Middleton and Lloyd (1984); Bayliss (1987); Klein (1987); Evanger *et al.* (1990); Haque, Richardson and Saville (1992); Haque *et al.* (1992)
Benchmark study: Skouloudis (1992)

Reactor venting (*see also* Table 17.13)
DIERS: Klein (1987); Wilday (1987); Fauske (1988a, 1989a); Leung and Fisher (1989)
Liquid swell: Grolmes (1983); Grolmes and Fauske (1983); Friedel and Purps (1984a,b)

Storage vessel venting
Fauske, Epstein *et al.* (1986)

Leaks through cracks
Pana (1976); Amos *et al.* (1983); Abdollahian *et al.* (1984); Collier (1984); John *et al.* (1986); Kefer *et al.* (1986); Friedel (1987b); Friedel and Westphal (1987, 1988, 1989)

15.2.1 Experimental studies

Much work on two-phase flow has been done on two-component systems, for example, air and water, but for the two cases mentioned the more relevant work is that on one-component systems, for example, steam and water. The bulk of the experimental work has been done on small pipes, often 25 mm diameter or less, but more recent work has been done on pipes of larger diameter. Details of some of the experimental work are given in Table 15.3.

15.2.2 Two-phase flow phenomena

Some characteristic features of, and problems in, two-phase flow are:

(1) flow pattern;
(2) phase equilibrium;
(3) phase velocity;
(4) critical flow;
(5) friction factor.

There are a variety of flow patterns in two-phase flow, the pattern depending on the mass flow and on the mass fraction of vapour, or quality, and also on whether the pipe is horizontal or vertical. The flow patterns are considered in the next section.

For very short flow outlets, there may be insufficient time for relaxation to occur and equilibrium between the liquid and vapour phase to be established. In this case it is necessary to make some assumption about the degree of equilibrium attained. One limiting assumption is that of frozen flow in which there is no interchange between the phases. The alternative limiting assumption is that equilibrium is attained.

Another principal feature is the relative velocity between the two phases. One limiting assumption is that of zero slip in which the relative velocity of the two phases is the same.

Critical flow occurs in two-phase flow but it is a much more complex phenomenon than in gas flow, and it tends not to be well defined. The essential feature, however, is that, as in gas flow, the flow is independent of the downstream pressure.

For flow in long pipes, it becomes necessary to take friction into account. Pressure drop due to friction is characterized in two-phase as in single-phase flow by a friction factor, but again this is somewhat more complex than in single-phase flow.

The types of two-phase flow calculation which are of interest here are primarily releases from plant and venting of reactors and vessels. An assumption which is conservative for one of these cases is not necessarily conservative for the other.

15.2.3 Two-phase flow patterns

There are a number of different flow patterns in two-phase flow. Among the numerous descriptions are those by O. Baker (1954, 1958), D.S. Scott (1963), Schicht (1969), Choe and Weisman (1974), Butterworth and Hewitt (1977), Chisholm (1983), and Cindric, Gandhi and Williams (1987).

The flow patterns for horizontal two-phase flow in pipelines were identified and correlated by O. Baker (1954, 1958). Figure 15.7, after Coulson and Richardson (1977–), shows a set of flow patterns denoted in accordance with Baker's terminology.

Figure 15.8 shows the correlation of flow patterns given by Baker in terms of the gas and liquid mass velocities G and L and the parameters λ and ψ, where the latter are defined as

$$\lambda = \left[\frac{\rho_g \rho_l}{\rho_a \rho_w}\right]^{0.5} \qquad [15.2.1]$$

$$\psi = \frac{\sigma_w}{\sigma_l}\left[\frac{\mu_l}{\mu_w}\left[\frac{\rho_w}{\rho_l}\right]^2\right]^{0.33} \qquad [15.2.2]$$

where μ is the viscosity, ρ is the density, σ is the surface tension, and the subscripts a, g, l, and w denote air, gas, liquid and water, respectively.

Table 15.3 *Some experimental studies on two-phaseflow*[a]

Investigator(s)	*System fluid*[b]	*Geometry*
W. Schiller (1933)		
Benjaminsen and Miller (1941)	Single component	Orifices
Burnell (1947)	Single component	Orifices, nozzles, pipes
Lockhart and Martinelli (1949)	Two components	Horizontal pipes
Pasqua (1953)	Single conponent	
Schweppe and Foust (1953)	Single components	Vertical tubes
Brigham, Holstein and Huntington (1957)	Two components	Inclined pipes
Isbin, Moy and da Cruz (1957); Isbin *et al.* (1962)	Single component	
Chisholm and Laird (1958)	Two components	Horizontal pipes
Zaloudek (1961)	Single component	Pipes
Fauske (1962, 1963, 1964)	Single component	Horizonal pipes
Friedrich and Vetter (1962)	Single component	Nozzles, short tubes
Baroczy (1966)	Single and two component systems	
Chisholm and Watson (1966)	Single component	Orifices
Uchida and Nariai (1966)	Single component	Orifices, nozzles, pipes
Finta, Gernborg and Andesson (1971)	Single component	Horizontal pipes
Beggs and Brill (1973)	Two components	Inclined pipes
Sozzi and Sutherland (1975)	Single conponent	Horizontal pipes
Kevorkov, Lutovinov and Tikhonenko (1977)	Single component	Horizontal pipes
Sallet (1979b); Sallet, Weske and G¨hler (1979); Sallet and Sommers (1985)	Single component	Safety valve
van den Akker, Snoey and Spoelstra (1983)	Single component	Vertical then horizontal section
Fermandes, Semiat and Dukler (1983)	Two components	Vertical tubes
Hutcherson, Henry and Wollersheim (1983)	Single component	Horizonal pipes
Nyren and Winter (1983)	Single component	Horizonal pipes
B. Fletcher (1984a,b); B. Fletcher and Johnson (1984)	Single component	Horizonal pipes
M.R.O. Jones and Underwood (1984)	Single component	Nozzles, short tubes
D.A. Lewis and Davidson (1985)	Single component	Orifices, nozzles
Friedel (1988)	Two components	Bursting disc, safety valve

[a] See also work of Fauske and coworkers (Section 15.3) and work on relaxation length (Table 15.4), on pressure relief valves (Section 15.6), on vessel blowdown (Section 15.7) and in the DIERS project (Chapter 17).
[b] Single-component systems are those with a single saturated or superheated liquid, typically water. Two-component systems are those with a gas and a liquid, typically air and water.

The Baker curves have been widely used to correlate the flow patterns in two-phase flow. A set of equations for the Baker curves has been given by Yamashiro, Espiell and Farina (1986).

The flow patterns for horizontal two-phase flow given by Butterworth and Hewitt are similar except that they omit dispersed flow. Figure 15.9 shows the flow patterns for vertical two-phase flow and Figure 15.10 a flow pattern map given by Butterworth and Hewitt.

There is a considerable variation in the terminology used for the flow patterns in two-phase flow. A summary of the terminology and a classification has been given by Chisholm (1983).

A simplified classification scheme for horizontal two-phase flow has been proposed by Choe and Weisman (1974), following earlier work by Hubbard and Dukler (1968). They identify four flow patterns, which correlate as follows with mass velocity G and with mass fraction of vapour, or quality, x.

Flow pattern	*Mass velocity,* G $(\mathrm{kg/m^2\,s})$	*Quality,* x
Homogeneous	$G > 2700$	0–1.0
Intermittent	$94 < G < 2700$	0–0.8
Annular	$94 < G < 2700$	$>0.8\ (\pm 0.1)$
Separated	$G < 94$	0–1.0

In terms of the relations given by Chisholm between the usual terms and those of Choe and Weisman, homogeneous flow corresponds to bubble flow, intermittent flow to plug and slug flow and separated flow to stratified flow; annular flow is the same in both cases.

Olujic (1985) has given a classification of flow patterns in horizontal two-phase flow based on a distinction between high and low quality. He defines parameters α and β:

$$\alpha = \left(1 + \beta \frac{u_g}{u_l}\right)^{-1} \qquad [15.2.3]$$

$$\beta = \frac{1-x}{x}\,\frac{\rho_g}{\rho_l} \qquad [15.2.4]$$

where u is the velocity. In the β regime, the velocity of the two phases is approximately equal, while in the α regime that of the gas is much higher. The β regime corresponds to bubble and slug flows, and the α regime to wavy, slug and annular flows. The author gives a map of the two regimes, plotting $1/\beta$ vs the Froude number Fr.

Cindric, Gandhi and Williams (1987) discuss the work of DIMP and present flow pattern maps, one for horizontal and one for vertical two-phase flow. The former is a plot of certain flow parameters vs the Martinelli parameter

(described below), and the latter a plot of superficial liquid velocity vs superficial gas velocity.

15.2.4 Modelling of two-phase flow

Two-phase flow is a complex phenomenon and has given rise to a large number of models. Of particular interest here are models for critical two-phase flow. A review of such models has been given by Wallis (1980). Wallis distinguishes essentially three types of model for critical two-phase flow:

(1) homogeneous equilibrium model;
(2) models incorporating limiting assumptions
  (a) frozen flow models,
  (b) slip flow models,
  (c) isentropic stream tube models;
(3) equilibrium models,
  (a) empirical models,
  (b) physically based models for thermal equilibrium,
  (c) two fluid models.

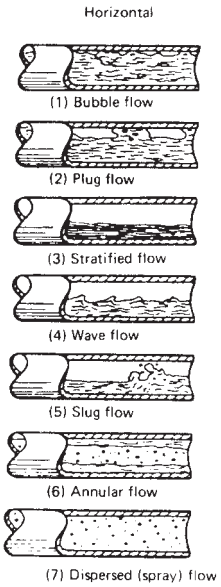


Figure 15.7 *Flow patterns in two-phase flow: horizontal flow (Coulson and Richardson, 1977–) (Courtesy of Pergamon Press)*

The homogeneous equilibrium model (HEM) is based on the two limiting assumptions: that the flow is homogeneous, that is, there is no slip between the two phases; and that the flow is in equilibrium, that is, there is effectively perfect transfer between the two phases.

This is a well-established and widely used model; it is used in a number of computer codes. Wallis states that the model gives reasonably good predictions for the mass velocity under conditions where the pipe is long enough for equilibrium to be established and the flow pattern is such as to suppress relative motion. For short pipes where there is insufficient relaxation time the flow can be in error by a factor of about 5. For longer pipes with a flow pattern which allows large relative velocity, such as annular flow, the error factor tends to be somewhat less than 2.

The homogeneous equilibrium model is based on limiting assumptions. The second group of models are based on alternative limiting assumptions. The limiting assumption made in the frozen flow model is that there is no transfer between phases so that flow is effectively frozen and quality remains constant. This assumption is most nearly met if the outlet is short. While no interphase transfer is the key assumption in this model it may be combined with other assumptions such as those of no slip or isentropic expansion.

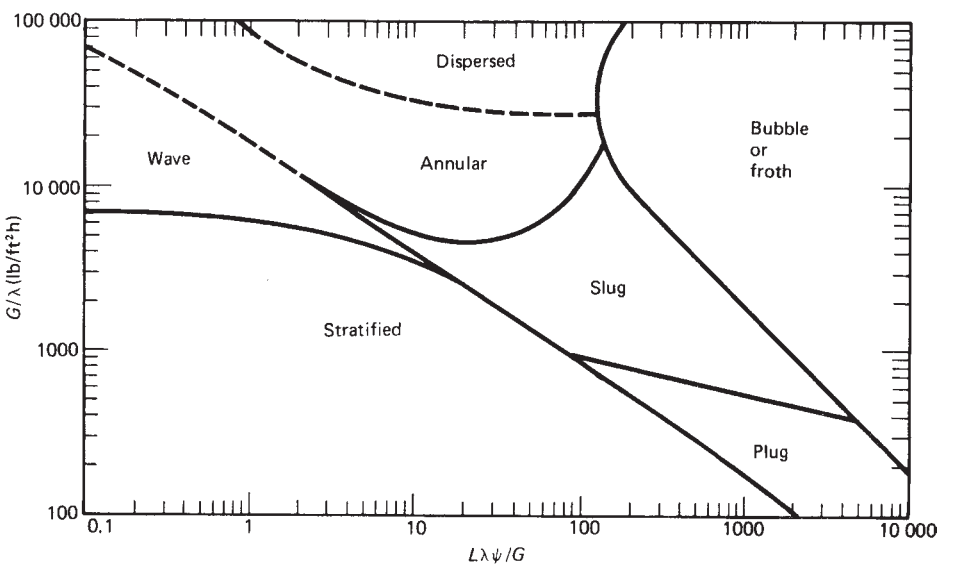


Figure 15.8 *Regimes in two-phase flow; the Baker diagram (O. Baker, 1954) (Courtesy of the Oil and Gas Journal)*

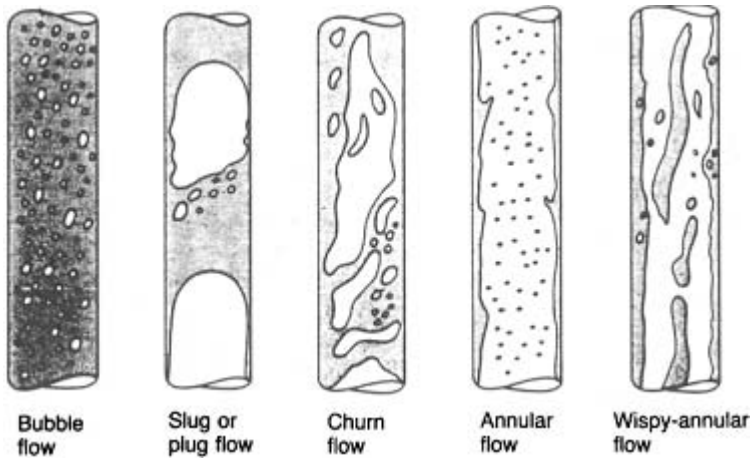


Figure 15.9 *Flow patterns in two-phase flow: vertical flow (Butterworth and Hewitt, 1977) (Courtesy of Oxford University Press)*

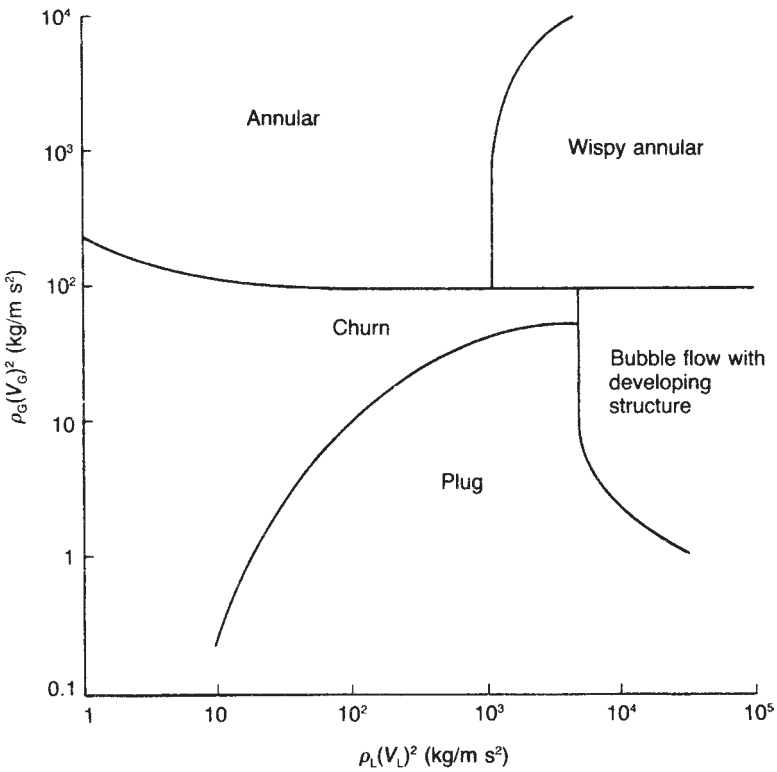


Figure 15.10 *Regimes in two-phase flow: flow patterns map for vertical flow (Butterworth and Hewitt, 1977) V_G velocity of gas (m/s); V_L, velocity of liquid (m/s); ρ_G density of gas (kg/m^3); ρ_L density of liquid (kg/m^3). (Courtesy of Oxford University Press)*

The limiting assumption made in the slip equilibrium model is that there is equilibrium between the phases, which is the opposite of the previous case. Two principal slip equilibrium models are those by Fauske (1962, 1963) and F.J. Moody (1965). These two models differ in terms of the way in which the exit condition is determined. In the Moody model, the exit conditions are determined by an energy balance and the maximum flow occurs at a slip ratio

$k = (\rho_l/\rho_g)^{1/3}$, while in the Fauske model the exit conditions are determined by a momentum balance and the maximum flow occurs at $k = (\rho_l/\rho_g)^{1/2}$.

The slip equilibrium models just described treat the velocity ratio k as a parameter to be adjusted to obtain the maximum flow, without indicating how this condition is actually achieved. Wallis and Richter (1978) have described an isentropic stream tube model, based on isentropic expansion of individual stream tubes originating from the vapour–liquid interface, which attempts to address this point.

The third group of models incorporate non-equilibrium effects. One approach used to handle such effects is the use of empirical correction factors. This is the basis of the model by RE. Henry and Fauske (1971).

Other non-equilibrium models are based on physical descriptions of the processes of bubble nucleation and vapour generation. Wallis concludes that the development of such models is not such as to offer much improvement on the purely empirical models.

Another type of non-equilibrium model is the two fluid, or separated flow, model, in which effects such as interphase drag are taken into account, but again Wallis concludes that the stage of development is not such as to make these models more useful than the empirical ones.

15.2.5 Elementary relations

For a two-phase system the following equations apply for continuity and other relations:

$$W_g = Wx \quad [15.2.5]$$

$$W_l = W(1-x) \quad [15.2.6]$$

$$G_g = u_g \rho_g \quad [15.2.7]$$

$$G_g = \frac{Gx}{\alpha} \quad [15.2.8]$$

$$G_l = \frac{G(1-x)}{1-\alpha} \quad [15.2.9]$$

$$Q_g = \frac{W_x}{\rho_g} \quad [15.2.10]$$

$$Q_l = \frac{W(1-x)}{\rho_l} \quad [15.2.11]$$

$$u_g = \frac{Gx}{\alpha \rho_g} \quad [15.2.12]$$

$$u_l = \frac{G(1-x)}{(1-\alpha)\rho_l} \quad [15.2.13]$$

$$k = \frac{u_g}{u_l} \quad [15.2.14]$$

$$k = \frac{x}{1-x}\ \frac{1-\alpha}{\alpha}\ \frac{\rho_l}{\rho_g} \quad [15.2.15]$$

$$\alpha = \left(1 + \frac{1-x}{x} k\ \frac{\rho_g}{\rho_l}\right)^{-1} \quad [15.2.16a]$$

$$\alpha = \left(1 + \frac{1-x}{x} k\ \frac{v_l}{v_g}\right)^{-1} \quad [15.2.16b]$$

$$\beta = \frac{Q_g}{Q_l + Q_g} \quad [15.2.17]$$

$$\beta = \left(1 + \frac{1-x}{x}\ \frac{\rho_g}{\rho_l}\right)^{-1} \quad [15.2.18]$$

where Q is the volumetric flow, v is the specific volume, W is the mass flow, ρ is the fraction of volume occupied by vapour, or void fraction, and β is the vapour phase volumetric flow fraction.

The pressure drop derived from the energy balance for two-phase flow, analogous to Equation 15.1.10b for single phase flow, is

$$\frac{dP}{dl} + \rho_h \frac{dF}{dl} + G\frac{du}{dl} + \rho_h g \frac{dz}{dl} = 0 \quad [15.2.19]$$

with

$$\rho_h = \left[\frac{x}{\rho_g} + \frac{1-x}{\rho_l}\right]^{-1} \quad [15.2.20]$$

where F is the friction loss, g is the acceleration due to gravity, l is the distance along the pipe, P is the absolute pressure, z is the vertical distance, and subscript h denotes homogeneous flow.

The pressure drop derived from the momentum balance for two-phase flow, analogous to Equation 15.1.11 for single phase flow, may be written as

$$\frac{dP}{dl} + \frac{S}{A}R_0 + \frac{d[G_g \alpha u_g + G_l(1-\alpha)u_l]}{dl} + g[\alpha\rho_g + (1-\alpha)\rho_l]\frac{dz}{dl} = 0 \quad [15.2.21]$$

where A is the cross-sectional area of the pipe, R_0 is the shear stress at the pipe wall and S is the perimeter of the pipe.

Comparing Equations 15.2.19 and 15.2.21, which each give the pressure drop, it follows that, in a manner analogous to the derivation of Equation 15.1.12,

$$\frac{S}{A}R_0 = \rho_h \frac{dF}{dl} \quad [15.2.22]$$

As with Equation 15.1.19 for single-phase flow, the pressure drop given in Equation 15.2.19 may also be expressed in terms of its constituent elements, as given in Equation 15.1.13.

15.2.6 Homogeneous flow

If the gas and liquid velocities are equal and the slip ratio k therefore unity, the flow is said to be homogeneous. The specific volume for homogeneous flow v_h is defined as

$$v_h = \frac{Q_g + Q_l}{W} \quad [15.2.23]$$

and hence

$$v_h = \frac{x}{\rho_g} + \frac{1-x}{\rho_l} \quad [15.2.24]$$

or

$$v = v_g x + v_l(1-x) \quad [15.2.25]$$

where v is the specific volume.

The density for homogeneous flow ρ_h is defined as the reciprocal of the specific volume

$$\rho_h = 1/v_h \quad [15.2.26a]$$

$$= \left[\frac{x}{\rho_g} + \frac{1-x}{\rho_l}\right]^{-1} \quad [15.2.26b]$$

It may be noted that Equation 15.2.26b is the same as Equation 15.2.20. This is the reason for the use of the symbol ρ_h to define the density in Equation 15.2.20. In that case, however, there was no implication that Equation 15.2.20 is restricted to homogeneous flow. Also for homogeneous flow:

$$\alpha = \left(1 + \frac{1-x}{x}\,\frac{\rho_g}{\rho_l}\right)^{-1} \quad [15.2.27a]$$

$$\alpha = \left(1 + \frac{1-x}{x}\,\frac{v_l}{v_g}\right)^{-1} \quad [15.2.27b]$$

$$\beta = \left(1 + \frac{1-x}{x}\,\frac{\rho_g}{\rho_l}\right)^{-1} \quad [15.2.28]$$

$$\beta = \alpha \quad [15.2.29]$$

For homogeneous flow, since $\rho_h = 1/v_h$, Equation 15.2.19 may be written as

$$\frac{dP}{dl} + \frac{1}{v_h}\frac{dF}{dl} + G\frac{du}{dl} + \frac{g}{v_h}\frac{dz}{dl} = 0 \quad [15.2.30]$$

15.2.7 Non-homogeneous flow

If the gas and liquid velocities are different, the flow is non-homogeneous. For non-homogeneous flow the specific volume of the two-phase mixture v_m is not equal to the reciprocal of the density of the two-phase mixture ρ_m:

$$v_m \neq 1/\rho_m \quad [15.2.31]$$

The specific volume for non-homogeneous flow is often defined as

$$v_m = [\rho_g \alpha + \rho_l(1-\alpha)]^{-1} \quad [15.2.32]$$

The use of this relationship for specific volume has been criticized by Fauske (1962). His alternative treatment is described in the following section.

15.2.8 Critical flow

As an introduction to critical two-phase flow, the condition is derived for critical flow in homogeneous flow. The acceleration pressure drop term in Equation 15.1.13 may be written as

$$-\frac{dP_a}{dl} = G^2\frac{dv_h}{dl} \quad [15.2.33]$$

But

$$v_h = f(P, x) \quad [15.2.34]$$

Hence

$$\frac{dv_h}{dl} = \frac{dv_h}{dP}\frac{dP}{dl} + \frac{dv_h}{dx}\frac{dx}{dl} \quad [15.2.35]$$

But, from Equation 15.2.25.

$$\frac{dv_h}{dx} = v_g - v_l \quad [15.2.36]$$

Then, from Equations 15.2.30, 15.2.33 and 15.2.36

$$-\frac{dP}{dl} = -\frac{dP_f}{dl} + G^2\left[\frac{dv_h}{dP}\frac{dP}{dl} + (v_g - v_l)\frac{dx}{dl}\right] + \frac{g}{v_h}\frac{dz}{dl} \quad [15.2.37a]$$

$$= -\frac{dP_f/dl + G^2(v_g - v_l)(dx/dl) + (g/v_h)(dz/dl)}{1 + G^2\left(\frac{dv_h}{dP}\right)}$$

where dP_f/dl is the pressure drop due to friction.

The critical condition occurs where the pressure gradient becomes infinite

$$1 + G^2\frac{dv_h}{dP} \quad [15.2.38a]$$

$$-\frac{dv_h}{dP} = \frac{1}{G^2} \quad [15.2.38b]$$

15.2.9 Empirical friction correlations

The solution of the equations for pressure drop in two-phase flow requires a relation for the friction loss term. Much effort has been devoted to obtaining a correlation for this. Typically, the two-phase pressure drop has been correlated in terms of some single phase pressure drop. One pair of relations used for correlation is

$$\frac{dP_f}{dl} = \phi_g^2\left(\frac{dP_f}{dl}\right)_g \quad [15.2.39a]$$

$$\frac{dP_f}{dl} = \phi_l^2\left(\frac{dP_f}{dl}\right)_l \quad [15.2.39b]$$

where dP_f/dl is the actual two-phase pressure drop, $(dP_f/dl)_g$ is the pressure drop which would occur if the gas phase were flowing alone in the pipe, $(dP_f/dl)_l$ is the pressure drop which would occur if the liquid phase were flowing alone and ϕ_g^2 and ϕ_l^2 are friction parameters.

Another pair of relations are

$$\frac{dP_f}{dl} = \phi_{go}^2\left(\frac{dP_f}{dl}\right)_{go} \quad [15.2.40a]$$

$$\frac{dP_f}{dl} = \phi_{lo}^2\left(\frac{dP_l}{dl}\right)_{lo} \quad [15.2.40b]$$

where $(dP_f/dl)_{go}$ is the pressure drop which would occur if the whole fluid were flowing as gas in the pipe, $(dP_f/dl)_{lo}$ is the pressure drop which would occur if the whole fluid were flowing as liquid ϕ_{go}^2 and ϕ_{lo}^2 are further friction parameters.

Lockhart and Martinelli (1949) introduced the parameter

$$X^2 = \frac{(dP_f/dl)_l}{(dP_f/dl)_g} \quad [15.2.41]$$

Chisholm and Sutherland (1969–70) utilized the parameter

$$\Gamma^2 = \frac{(dP_f/dl)_{go}}{(dP_f/dl)_{lo}} \qquad [15.2.42]$$

This parameter was also used by Baroczy (1966) in the form

$$\frac{1}{\Gamma^2} = \frac{\rho_g}{\rho_l}\left(\frac{\mu_l}{\mu_g}\right)^{0.2} \qquad [15.2.43]$$

The friction factor may be expressed in a generalized form of the Blasius equation

$$f \propto \mathrm{Re}^{-n} \qquad [15.2.44]$$

where n is an index. Then the parameters X and Γ are related to the quality x as follows:

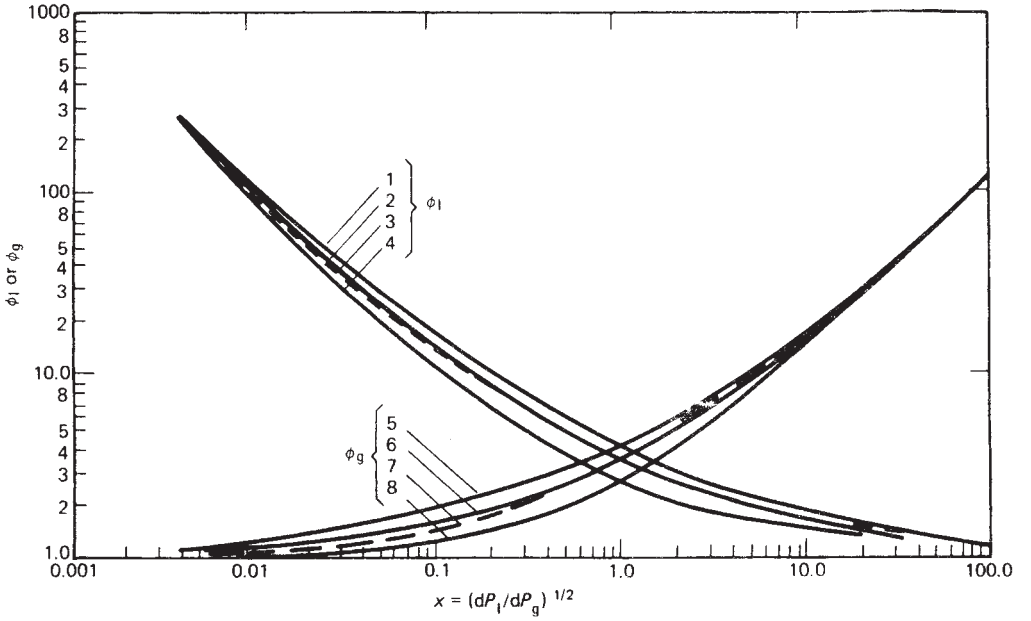
$$X^2 = \frac{1}{\Gamma^2}\left[\frac{1-x}{x}\right]^{2-n} \qquad [15.2.45]$$

15.2.10 Lockhart–Martinelli model

A method for determining the pressure drop in two-phase, two-component flow has been given by Lockhart and Martinelli (1949), who correlated ϕ_g^2 and ϕ_l^2 with X^2. The equations of the model are Equations 15.2.39 and 15.2.41. The relations given by Lockhart and Martinelli between the parameters ϕ_g, ϕ_l and X are shown in Figure 15.11.

The method is to calculate the single-phase gas and liquid Reynolds numbers Re_g and Re_l and pressure drops $(dP_f/dl)_g$ and $(dP_f/dl)_l$, to calculate X from Equation 15.2.41, to obtain from Figure 15.11 either ϕ_g or ϕ_l, depending on the value of X, and then to calculate (dP_f/dl) from Equation 15.2.39a or 15.2.39b. The curves given in Figure 15.11 for ϕ_g and ϕ_l depend, as shown, on whether the gas and liquid flow regimes are viscous or turbulent.

Equations for the Lockhart–Martinelli parameters, which may be used instead of Figure 15.11, have been given by Degance and Atherton (1970). Although it is one of the earlier two-phase flow correlations, the method of Lockhart and Martinelli remains one of the most widely used.



Reynolds No.	*Regime*			
	Turbulent–turbulent	*Viscous–turbulent*	*Turbulent–viscous*	*Viscous–viscous*
Re_l	> 2000	< 1000	> 2000	< 1000
Re_g	> 2000	> 2000	< 1000	< 1000
Curve for ϕ_l	1	2	3	4
Curve for ϕ_g	5	6	7	8

If $X \geqslant 1.0$ use ϕ_l
If $X < 1.0$ use ϕ_g

Figure 15.11 *Pressure gradient in two-phase flow: the Lockhart–Martinelli correlation (after Lockhart and Martinelli, 1949) (Courtesy of the American Institute of Chemical Engineers)*

15.2.11 Other friction correlation methods

Baroczy (1966) obtained a correlation in terms of ϕ_{lo}, x, and the group which is defined as $1/\Gamma^2$ in Equation 15.2.43. A further more economical correlation was derived by Chisholm and Sutherland (1969–70). The correlation depends on the value of n in relation 15.2.44. For the case of $n = 0$ their correlation is

$$\phi_g^2 = 1 + CX + X^2 \qquad [15.2.46a]$$

$$\phi_l^2 = 1 + \frac{C}{X} + \frac{1}{X^2} \qquad [15.2.46b]$$

with

$$C = \frac{1}{k}\left(\frac{\rho_l}{\rho_g}\right)^{1/2} + k\left(\frac{\rho_g}{\rho_l}\right)^{1/2} \qquad [15.2.47]$$

The parameter C is a function of the mass velocity G and the parameter Γ.

15.2.12 Friction factor

The friction factor to be used in two-phase flow equations depends on the particular correlation. Use is often made of a single-phase flow friction factor, obtained from one of the relations given in Section 15.1. In some cases, the approach taken is even simpler. The friction factor recommended by Perry and Green (1984) for use with Equation 15.2.48 below is the single value of 0.003.

15.2.13 DIMP project

A study of non-flashing two-phase flow has been conducted by the Design Institute for Multi-phase Processing (DIMP) of the AIChE. An account of the DIMP work has been given by Cindric, Gandhi and Williams (1987).

15.2.14 Homogeneous flow models

Much of the recent development in two-phase flow which is of interest here relates to homogeneous equilibrium flow models.

15.2.15 Homogeneous equilibrium flow model

The homogeneous equilibrium model has been described by a number of workers. The minimal assumptions in this model are that the phase velocities are equal and that thermal equilibrium exists.

From Equation 15.1.18 but substituting v_h for v it is possible to derive for a horizontal pipe

$$G = \left[\frac{-1}{\mathrm{d}v_h/\mathrm{d}P + (4fv_h)/2d(\mathrm{d}P/\mathrm{d}l)}\right]^{1/2} \qquad [15.2.48]$$

This appears to be the form most commonly quoted (e.g. Perry and Green, 1984).

For critical flow the following relation is given by Fauske (1962). From Equation 15.2.38b utilizing the definition of v_h in Equation 15.2.25 and assuming isentropic expansion, the critical mass velocity G_c is

$$G_c = \left[\frac{-1}{x(\mathrm{d}v_g/\mathrm{d}P)_s + (v_g - v_s)(\mathrm{d}x/\mathrm{d}P)_s + (1-x)(\mathrm{d}v_l/\mathrm{d}P)_g}\right]^{1/2} \qquad [15.2.49]$$

where subscript s indicates constant entropy.

A third form of the model is that given by Starkman *et al.* (1964), as quoted by R.E. Henry and Fauske (1971). Again, the additional assumption of isentropic expansion is made:

$$G_c = \frac{\{2[h_o - (1-x_E)h_{lE} - x_E h_{gE}]\}^{1/2}}{(1-x_E)v_{lE} + x_E v_{gE}} \qquad [15.2.50]$$

where h is the specific enthalpy and subscripts c, E and o indicate critical, equilibrium, and stagnation conditions, respectively.

15.2.16 Homogeneous frozen flow model

The homogeneous frozen flow model has also been described by a number of workers. In the form given by R.E. Henry and Fauske (1971), the model is based on the two necessary assumptions for this type of model, that the phase velocities are equal and that there is no transfer between phases so that thermal equilibrium does not exist, but also on the assumption that the vapour expansion is isentropic and that the critical flow is determined by gas dynamic principles. The expression for the critical mass velocity is

$$G_c = \frac{1}{v}\left[2x_o v_{go} P_o \frac{\gamma}{\gamma - 1}\left(1 - \eta_c^{(\gamma-1)/\gamma}\right)\right]^{1/2} \qquad [15.2.51]$$

where γ is the ratio of gas specific heats, η_c is the critical pressure ratio and subscript o indicates the stagnation condition. The critical pressure ratio is the ratio of the throat pressure to the downstream pressure, and the expression given for it is relatively complex.

15.2.17 Two-phase flashing flow

The two-phase flow which is of particular interest here is single-component, two-phase flashing flow. This is the type of flow which occurs when liquefied gas is released to the atmosphere, whether in a controlled manner through a relief device or due to an accident. A number of models have been developed for two-phase flashing flow, particularly through the work of Fauske and co-workers in the DIERS project, as described below.

The type of model characteristic of this work is a homogeneous equilibrium model for a very short pipe. The presence of the pipe makes it possible to assume equilibrium conditions, but the pipe is sufficiently short that frictional effects can still be neglected. Allowance is then made for frictional pressure drop by the use of empirical correlations.

The assumption of negligible pipe length leads to much simpler expressions for the critical flow. Initially, the length of pipe at which equilibrium is established was assumed to be defined by a length/diameter, or l/d, ratio. As described below, it has been shown that equilibrium is reached as a fixed length of some 0.1 m.

Two models, or rather families of models, of the type described are those of Fauske and of Leung. These are described in Sections 15.3 and 15.4, respectively.

15.2.18 Maximum critical flow

The maximum possible flow of a two-phase fluid in a pipe is obtained if it is assumed that friction can be neglected and that the energy released by the drop in pressure is converted to kinetic energy. At the critical flow conditions $\mathrm{d}G/\mathrm{d}P = 0$ or, alternatively, $\mathrm{d}G/\mathrm{d}\eta = 0$.

For a horizontal pipe Equation 15.1.77 yields $v\,dP = u\,du$ ($dW_s = dF = dz = 0$). Noting that the velocity $u = Gv$, it can readily be shown that at the critical flow conditions ($dG/dP = 0$) the maximum, or critical, mass velocity G_c is given by the relation $G_c^2 = -(dP/dv)$, where the pressure P and the specific volume v refer to the inlet conditions.

Critical flow conditions can occur at quite a high value of the ratio of the downstream pressure to the upstream pressure, or critical pressure ratio. A value as high as 0.7 in some cases is quoted by Coulson and Richardson (1977–, p. 95). The Leung model, described below, includes correlations for the critical pressure ratio.

15.2.19 Relaxation length

As already mentioned, it was initially believed that in two-phase flow the length of pipe over which equilibrium becomes established, or relaxation length, is a function of the length/diameter ratio. However, it has been shown in a number of studies that it is the absolute length which matters.

Work designed specifically to elucidate this point has been described by B. Fletcher (1984a,b) and B. Fletcher and Johnson (1984). Experiments were carried out on discharges of Refrigerant 11 through sharp edged orifices and tubes in the diameter range 3.2–10.8 mm and length/diameter ratio (l/d) range 0.88–200. In this work it was found that the onset of flashing was favoured by higher excess pressure, and hence superheat, and by increased tube length. It was also found that as the tube length was increased the flow at first decreased rapidly but then much more gradually. The transition point marking the end of the rapid decrease in flow with length occurred at a length of about 75 mm. Figure 15.12 shows the jet in some of Fletcher and Johnson's experiments.

At the time when this work was done one of the most widely used models for two-phase flow was the empirical model of Fauske (1964)

$$G = C_d[2\rho_l(P_0 - P_c)]^{1/2} \quad l/d < 3 \qquad [15.2.52]$$

where C_d is the coefficient of discharge, P_c is the absolute critical outlet pressure and P_0 is the absolute upstream pressure.

As described below, Fletcher and Johnson are somewhat critical of Equation 15.2.52. The correlation preferred is based on the assumption that for a given length

$$G \propto C_d P_0^{1/2} \qquad [15.2.53]$$

Figure 15.13 shows the results of discharge experiments correlated in this way. Figure 15.13(a) shows Fletcher's own results for Refrigerant 11 and Figure 15.13(b) shows the results of other workers. Thus, in this work, relation 15.2.53 is used for excess pressures in the range 1–102 bar.

Fletcher points out that the transition distance of 75 mm found in his work corresponds in Fauske's work to a length/diameter ratio of 12, a ratio which Fauske treats as a transition point.

Fletcher discusses the point at which all liquid flow ceases and flashing begins. He refers to the assumption in the Rijnmond Report that all liquid flow can be assumed to exist for $l/d < 2$ and states that he has observed flashing at $l/d < 1$ if the excess pressure is sufficiently high.

In presenting their own correlation, Fletcher and Johnson state certain criticisms of Equation 15.2.52. Two of these have already been discussed: the use of l/d instead of l as a correlator and the assumption of all liquid flow for $l/d < 2$. Another is the assumption that $P_c = 0.55P_d$ for all fluids. They refer to the use in the *Second Canvey Report* of Equation 15.2.52, but point out that this applies strictly only to the all gas, or vapour, condition.

Confirmation that the relaxation length is a function of the absolute length of pipe for large pipe diameters is provided by the work at Marviken by S. Levy Inc. (1982). The available data on relaxation length has been reviewed by Fauske (1984c), who quotes the data shown in Table 15.4. The later models of Fauske incorporate the absolute length method of correlation. This method is now generally adopted. The value of the relaxation length is taken as 0.1 m.

15.2.20 Critical pressure ratio

As the foregoing account indicates, a crucial parameter in two-phase flow is the critical pressure ratio (CPR), defined as the ratio of the critical pressure to the upstream, or stagnation pressure. A review of the CPR is given by Hardekopf and Mewes (1988).

For the fluid, they distinguish between a saturated liquid, a two-phase mixture and a superheated vapour and for the outlet between an orifice, a pipe, and a nozzle. They state that for orifices and long pipes there is no single CPR, but that for nozzles, including outlets with short pipes, a CPR can be calculated. They refer particularly to the work of Schiller (1933) and Friedrich and Vetter (1962), as well as that of Fauske and coworkers.

For an orifice with saturated liquid or two-phase flow there is no readily calculable CRP, whilst for superheated vapour they give the CPR as zero. For a pipe with any of the three fluid conditions the CPR is a function of pipe length; they suggest that for two-phase flow use be made of the model by R.E. Henry and Fauske (1971), described in the next section, or of the homogeneous equilibrium model (HEM). For a nozzle with saturated liquid or two-phase flow, they again refer to these two models and quote typical values for a saturated liquid of CPR $\sim$ 0.85 and for two-phase flow of $0.85 <$ CPR < 0.55, whilst for superheated vapour they give the adiabatic expansion equation with a typical CPR of 0.55.

15.2.21 Two-phase flow transients

The two-phase flow models described apply to steady-state conditions. The steady state is preceded and followed by transients. A treatment of such transients in pipelines is given by Seynhaefve *et al.* (1994).

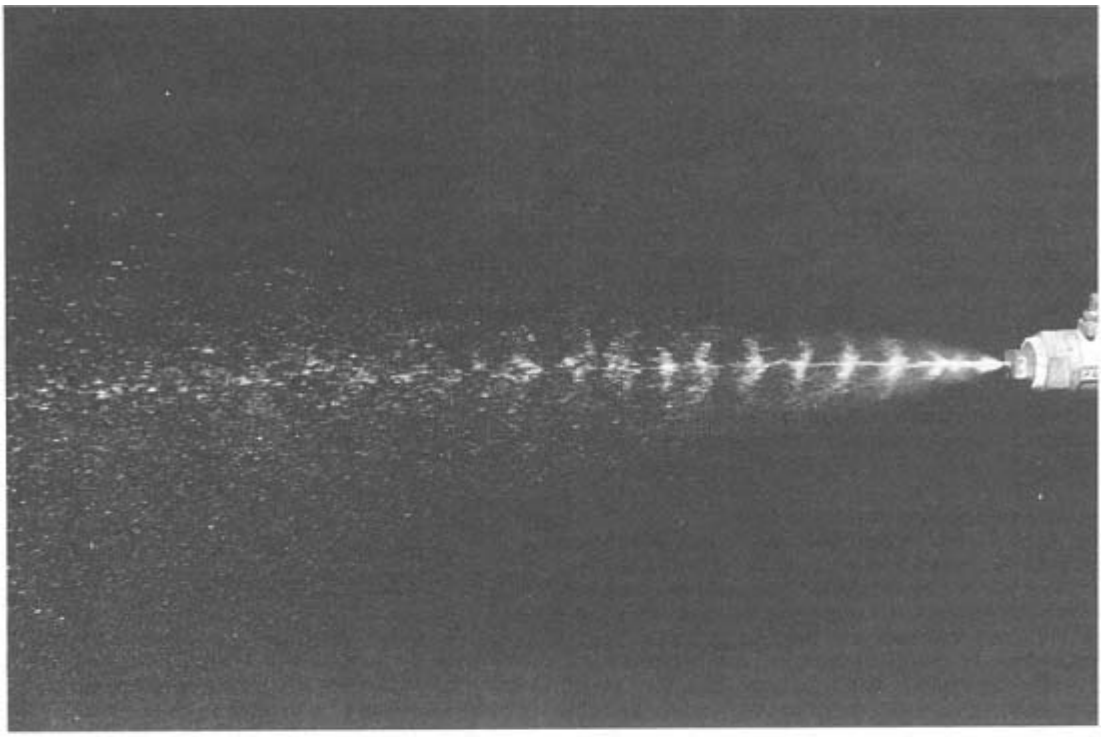
15.2.22 DIERS project

Two-phase flow was a major aspect of the project by the Design Institute for Emergency Relief Systems (DIERS) of the AIChE. Although it was not intended that the project should produce new relations for two-phase flow, much work was done to investigate the suitability of the various correlations, and new methods have resulted. This work is described in the DIERS Technical Summary and in a series of papers by Fauske, Epstein, Grolmes, Leung and co-workers.

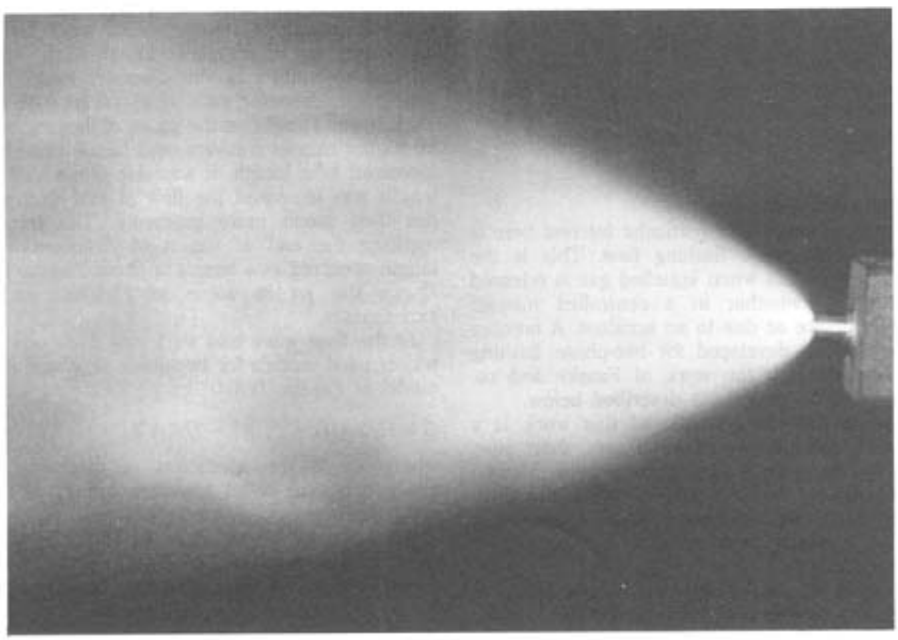
15.2.23 Choice of model

With regard to choice of model, it is relevant to distinguish between one-component, two-phase flashing flow, mainly in controlled or accidental releases from plant, and two-component, two-phase non-flashing flow, mainly of fluids in pipelines. It is the former which is of prime interest here.

Guidance on the choice of model for non-flashing two-phase flow based on the work of DIMP has been given by



(a)



(b)

Figure 15.12 *Discharge of Refrigerant 11 through 3.2 mm pipe (B. Fletcher and Johnson, 1984): (a) excess pressure of 0.7 bar; (b) excess pressure of 2.5 bar (Courtesy of HM Stationery Office)*

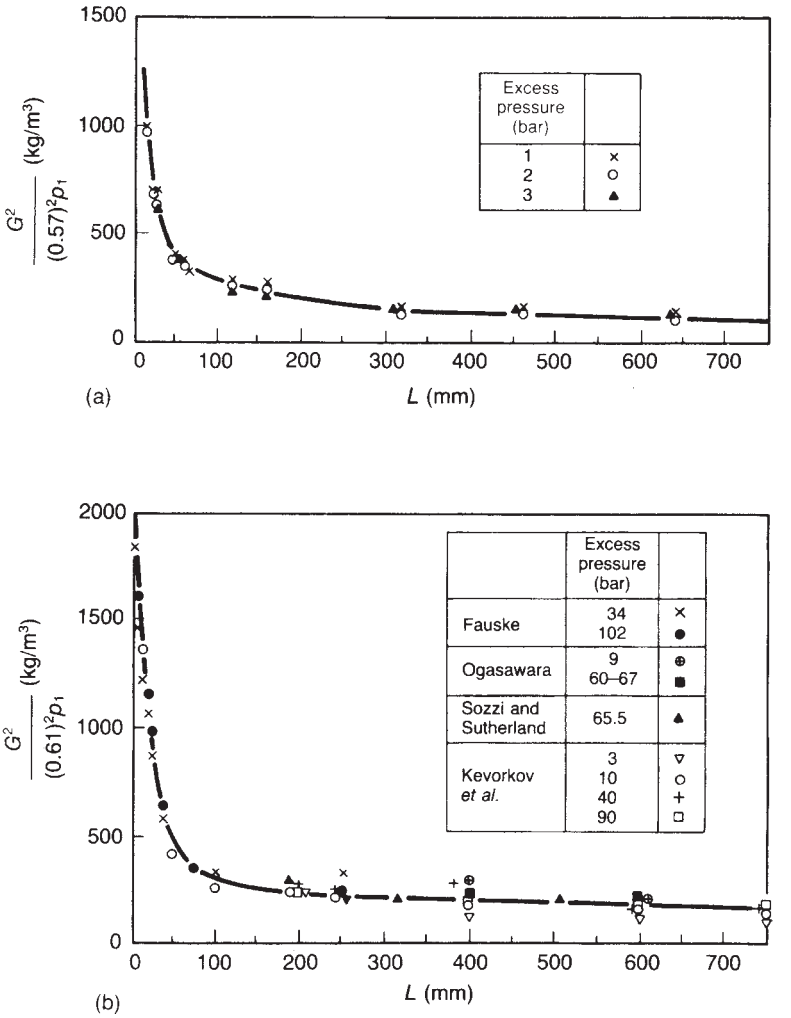


Figure 15.13 *Correlations for discharge of Refrigerant 11 and of saturated water (B. Fletcher and Johnson, 1984): (a) Refrigerant 11; (b) saturated water. G, mass velocity (kg/m² s); p_1 upstream pressure (N/m²) (Courtesy of HM Stationery Office)*

Table 15.4 *Relaxation length observed in some critical two-phase flow experiments*

Source	*Fluid*	*Diameter* (mm)	*Length* (mm)	*Length/diameter*
Fauske (1964)	Water	6.35	≈100	≈16
Sozzi and Sutherland (1975)	Water	12.7	≈127	≈10
Flinta, Gernborg and Adesson (1971)	Water	35	≈100	≈3
Uchida and Nariari (1966)	Water	4	≈100	≈25
B. Fletcher (1984)	Freon 11	3.2	≈105	≈33
van den Akker, Snoey and Spoelstra (1983)	Freon 12	4	90	≈22
S. Leavy Inc. (1982)[a]	Water	500	<166	<0.33

[a] Marviken data.

Cindric, Gandhi and Williams (1987). For horizontal flow the following models are recommended:

Flow	*Model*	
Stratified	Stratified	Taitel and Dukler (1976)
Stratified wavy	Stratified	Taitel and Dukler (1976)
Intermittent slug	Horizontal slug	Dukler and Hubbard (1975) Nicholson, Aziz and Gregory (1978)
Intermittent elongated bubble	Similarity	Dukler, Wicks and Cleveland (1964)
Annular	Similarity	Dukler, Wicks and Cleveland (1964)
Dispersed bubble	Similarity	Dukler, Wicks and Cleveland (1964)

The choice of model for two-phase flashing flow is discussed below, in particular in Sections 15.3 and 15.4 which deal with families of models of Fauke and Leung, Section 15.6 which treats the model given by Leung for pressure relief valves and Chapter 17 which covers venting of reactors.

For reactor venting, Fauske (1985b) suggests: for orifices, the non-equilibrium model; for short outlets, the equilibrium rate model (ERM); and for longer outlets, where friction is significant, the homogeneous equilibrium model (HEM).

15.2.24 Design conservatism

In considering what constitutes a conservative assumption, it is necessary to make a number of distinctions. In determining the flow through a relief such as a pressure relief valve or a reactor vent, for the purpose of sizing the relief, it is conservative to use a method which tends to underestimate the flow. However, this approach is not conservative with respect to aspects such as the reaction forces on the vessel, the pressure drop in the relief header or the flow through the relief disposal train, for all of which it is conservative to use a method which tends to overestimate the flow.

For an accidental release to atmosphere, it is generally conservative to use a method which tends to overestimate the flow. However, this may not always be true. For example, if the release gives a jet flame, a smaller flame of longer duration could be a worse case.

15.2.25 Two-phase flow in valves

Two-phase flashing flow occurs in valves, both control valves and pressure relief valves. Accounts of methods used to calculate such flow through control valves have been given by W.F. Allen (1952–), Ziegler (1957), Hanssen (1961), Sheldon and Schuder (1965) and Romig, Rothfus and Kermode (1966). Flow through pressure relief valves is considered in Section 15.6.

15.2.26 Two-phase flow through cracks

It is convenient to deal at this point with flow, particularly two-phase flow of a flashing liquid, through cracks in pressure vessels such as may be relevant to the leak-before-break condition. A number of workers have studied the leak rate through such cracks and have modelled it using various two-phase flow models (e.g. Amos *et al.*, 1983; Abdo Uahian *et al.*, 1984; R.P. Collier, 1984; John *et al.*, 1986; Kefer *et al.*, 1986). The two-phase flow models used by the workers cited are principally those of R.E. Henry (1970), Pana (1976) and Levy (1982).

The work has been reviewed by Friedel (1987b) and Friedel and Westphal (1987, 1988, 1989). They observe that there are a number of features, such as viscosity changes, surface tension and wetting effects, and non-equilibrium conditions, which current models tend not to account for and that no model can be regarded as universally valid, even for water.

15.3 Two-phase Flow: Fauske Models

15.3.1 Fauske empirical model

An early empirical model for two-phase flow was that described by Fauske (1964). The model is relatively simple and readily adaptable, and has been widely used. The general form of the model is

$$G = C_d[2\rho_l(P_o - P_*)]^{1/2} \qquad [15.3.1]$$

where C_d is the coefficient of discharge, G is the mass velocity, P_o is the absolute stagnation pressure, P_* is the effective downstream pressure and ρ_l is the density of the liquid.

A correlation for the transition from single-phase to two-phase flow in fluid flowing from a vessel through an aperture or short pipe to atmosphere has been given by Min, Fauske and Petrick (1966). The transition is correlated in terms of a modified cavitation number C'_a:

$$C'_a = \frac{2\Delta P}{\rho_l U^2}\frac{l}{d} \qquad [15.3.2]$$

where d is the diameter of the pipe, l is the length of the pipe, ΔP is the pressure difference, U is the average velocity of fluid and ρ_l is the density of the saturated or subcooled fluid in the vessel. Flow is single-phase for values of C'_a less than 9 and two-phase for values greater than 15. At values between 9 and 15, unstable transitional flow occurs.

The empirical model given by Fauske (1964) is based on experimental work on the flow of a saturated liquid from a vessel through an aperture or an aperture connected to a short pipe to atmosphere. For a system in which the aperture was a sharp edged orifice, the following equations were obtained:

$$G = C_d[2\rho_l(P_o - P_b)]^{1/2} \qquad [15.3.3a]$$

$$G = C_d[2\rho_l(P_o - P_c)]^{1/2}, \quad l/d < 3 \qquad [15.3.3b]$$

where subscripts b and c denote the downstream and critical values, respectively. The value of the coefficient of discharge was 0.61.

Equation 15.3.3a applies to an orifice without a pipe and Equation 15.3.3b to an orifice with a pipe attached. For this latter case the critical exit pressure P_c was found to be a function of the length/diameter ratio l/d of the pipe. Fauske considered separately the regions $3 < l/d < 12$ and $12 < l/d < 40$. He found that in the latter region there was very little decrease in flow with l/d, indicating a relatively small friction effect. His data over the two regions may be represented by the approximate equation

$$\frac{P_c}{P_o} = 0.55[1 - \exp(-1/3d)] \qquad [15.3.4]$$

Equation 15.3.3 was derived from experiments on saturated water flowing through a sharp-edged orifice of 0.25 in.

diameter with an upstream pressure of up to 2000 psi. This model has been used extensively in industry to determine the two-phase flow from pipe ruptures. An account of such application has been given by Simpson (1971).

Equation 15.3.3 is that used in the *Second Canvey Report* for estimation of two-phase flow from pipe ruptures. The report uses for the critical pressure ratio Equation 15.1.69.

15.3.2 Relaxation length

As described earlier, Fauske (1964) correlated his results in terms of the length/diameter ratio. Subsequent work indicates, however, that it is the absolute length l rather than the length/diameter ratio l/d which is the appropriate correlator and this position has been adopted by Fauske.

15.3.3 Jones and Underwood model

The Fauske empirical model has been widely used and has been subject to various adaptations. M.R.O. Jones and Underwood (1983) refer to Fauske's empirical model and point out that the use of an average density ρ_m implies the assumption of homogeneous equilibrium flow. They present as an alternative relations derived from the theory for critical annular flow given by Fauske (1961):

$$G = C_{DM}\left[\frac{\rho_l\rho_n}{\rho_l-\rho_n}(P_0-P_c)\right]^{1/2} \qquad [15.3.5]$$

with

$$\rho_n = \left[\frac{x_c^2}{\rho_g R_g} + \frac{(1-x_c)^2}{\rho_l(1-R_g)}\right]^{-1} \qquad [15.3.6]$$

$$R_g = \left[\frac{(1-x_c)}{x_c}\left(\frac{\rho_g}{\rho_l}\right)^{1/2} + 1\right]^{-1} \qquad [15.3.7]$$

where C_{DM} is the modified coefficient of discharge, R_g is the fraction of the cross-sectional area occupied by vapour, x is the mass fraction of the vapour, and subscripts c, g, l, and n denote the pipe exit, vapour, liquid and two-phase annular value, respectively.

The authors describe experimental work on Freons 12, 22, and 114 discharging through pipes of diameter 0.5 and 4 mm and length/diameter ratios between 10 and 617. The authors found that the coefficient of discharge C_{DM} in Equation 15.3.5 was a function of the length/diameter ratio and obtained the relation

$$C_{DM} = 5.46\left(\frac{l}{d}\right)^{-0.77} + 0.29 \qquad [15.3.8]$$

Equation 15.3.8 actually gives a coefficient of discharge greater than unity for $l/d < 15$ and the coefficient so obtained should be treated as a purely empirical one.

In a further study, M.R.O. Jones and Underwood (1984) investigated releases from apertures rather than full bore ruptures. Experiments were carried out using Freons and propane with pipes 4.3–4.5 mm in diameter and ending in a ball valve followed by one of the following apertures:

(1) circular aperture, $d = 0.5$–4.4 mm, $l/d < 3$;
(2) circular aperture, $d = 0.5$ mm, $l/d = 10$;
(3) rectangular aperture, height/width ratio 5.5, 10.2 and 25.6.

It might be expected that for pipes of cross-sectional area A_p and apertures of area A_a the flow would be proportional to the area ratio A_a/A_p, but the correlation obtained was in fact in terms of $(A_a/A_p)^{1/2}$. Three regions were observed:

$0 < (A_a/A_p)^{1/2} < 0.25$ Flow effectively metastable.
$0.25 < (A_a/A_p)^{1/2} < 0.9$ Ratio of actual flow to maximum flow proportional to $(A_a/A_p)^{1/2}$. Constant of proportionality 1.15.
$0.9 < (A_a/A_p)^{1/2} < 1.0$ Flow equal, or close, to maximum flow.

The authors warn, however, that their experiments were small scale and that caution should be exercised in extrapolating the results to the large scale.

15.3.4 Henry–Fauske non-equilibrium model

A non-equilibrium model for outlets with short pipes has been given by R.E. Henry and Fauske (1971). The model receives frequent mention. The assumption is made that flow is homogeneous but not that it is in equilibrium. The expansion of the vapour is assumed to be polytropic. The model gives the flow in terms of the stagnation conditions.

For critical two-phase flow the authors derive the relation

$$G_c^2 = \left(\frac{-\mathrm{d}}{\mathrm{d}P}\left\{\frac{[xk+(1-x)]}{k}[(1-x)kv_l + xv_g]\right\}\right)_t^{-1} \qquad [15.3.9]$$

where k is the slip ratio, v is the specific volume and subscript t indicates the throat. The equations of the model are:

$$G_c^2 = \frac{(1-x_o)v_{lo}(P_o-P_t) + [x_o\gamma/(\gamma-1)](P_o v_{go} - P_t v_{gt})}{[(1-x_o)v_{lo} + x_o v_{gt}]^2/2} \qquad [15.3.10]$$

$$\frac{\eta = [((1-\alpha_o)/\alpha_o)(1-\eta) + \gamma/(\gamma-1)]^{\gamma/(\gamma-1)}}{1/(2\beta\alpha_t^2) + \gamma/(\gamma-1)} \qquad [15.3.11]$$

$$\beta = \left\{\frac{1}{n} + \left(1-\frac{v_{lo}}{v_{gt}}\right)\left[\frac{(1-x_o)NP_t}{x_o(s_{gE}-s_{lE})_t}\frac{\mathrm{d}s_{lE}}{\mathrm{d}P}\right]_t - c_{pg}\frac{1/n-1/\gamma}{s_{go}-s_{lo}}\right\} \qquad [15.3.12]$$

$$\alpha_o = \frac{x_o v_{go}}{(1-x_o)v_{lo} + x_o v_{go}} \qquad [15.3.13]$$

$$\alpha_t = \frac{x_o v_{gt}}{(1-x_o)v_{lo} + x_o v_{gt}} \qquad [15.3.14]$$

$$v_{gt} = v_{go}\eta^{-1/\gamma} \qquad [15.3.15]$$

$$\eta = \frac{(1-x)c_l/c_{pg} + 1}{(1-x)c_l/c_{pg} + 1/\gamma} \qquad [15.3.16]$$

$$N = \frac{x_{Et}}{0.14} \quad x_{Et} \le 0.14 \qquad [15.3.17a]$$

$$N = 1 \quad x_{Et} > 0.14 \qquad [15.3.17b]$$

$$x_E = \frac{s_o - s_{lE}}{s_{gE} - s_{lE}} \qquad [15.3.18]$$

where c is the specific heat, n is the polytropic index, N is a non-equilibrium parameter, s is the specific entropy, α is the void fraction, γ is the isentropic index and the subscript E denotes equilibrium (corresponding to local static pressure).

For $N = 1$ the model reduces approximately to the homogeneous equilibrium model, while for $N = 0$ it reduces approximately to the homogeneous frozen model. For inlet quality greater than $x_o = 0.1$, corresponding to throat quality x_{Et} in the range 0.125–0.155, with an assumed average of 0.14, the homogeneous equilibrium model is assumed, so that $N = 1$, as given in Equation 15.3.17b. For inlet qualities less than $x_o = 0.1$, Equation 15.3.17a is used.

15.3.5 Fauske slip equilibrium model

In the models described so far, the usual assumptions are thermal equilibrium and homogeneous flow. Fauske (1962, 1963) has developed a slip equilibrium model in which the latter assumption is relaxed. The model is applicable essentially to annular flow, in which the vapour and liquid flows are largely separate so that the vapour velocity is likely to exceed that of the liquid. The starting point of the model is the momentum balance:

$$\mathrm{d}P + \mathrm{d}F' + \mathrm{d}(G_g u_g + G_l u_l) = 0 \qquad [15.3.19]$$

where $\mathrm{d}F'$ is the friction term. Differentiating Equation 15.3.19 with respect to the quality x gives

$$\frac{\mathrm{d}P}{\mathrm{d}x} + \frac{\mathrm{d}F'}{\mathrm{d}x} + \frac{\mathrm{d}(G_g u_g + G_l u_l)}{\mathrm{d}x} = 0 \qquad [15.3.20]$$

It is assumed that the friction term can be expressed as

$$\mathrm{d}F' = \frac{f^* G^2 v\, \mathrm{d}l}{2d} \qquad [15.3.21]$$

where f^* is a friction factor for two-phase flow.

Substituting for u_g, u_l and $\mathrm{d}F'$ in Equation 15.3.20 from Equations 15.2.12, 15.2.13 and 15.3.21 gives, eventually,

$$\frac{\mathrm{d}P}{\mathrm{d}l} + G^2\left\{\frac{\mathrm{d}}{\mathrm{d}l}\left[\frac{x^2 v_g}{\alpha_g} + \frac{(1-x)^2}{(1-\alpha_g)}\frac{v_l}{\rho_l}\right] + \frac{fv}{2d}\right\} = 0 \qquad [15.3.22]$$

But the corresponding equation for single-phase flow is

$$\frac{\mathrm{d}P}{\mathrm{d}l} + G^2\left[\frac{\mathrm{d}v}{\mathrm{d}l} + \frac{fv}{2d}\right] = 0 \qquad [15.3.23]$$

where f is the friction factor.

Equations 15.3.22 and 15.3.23 become identical because the specific volume v is defined as

$$v = \frac{v_g x^2}{\alpha_g} + \frac{v_l (1-x)^2}{1-\alpha_g} \qquad [15.3.24]$$

This definition of the specific volume is a crucial feature of the model.

In the model, the slip ratio k is treated as a variable to be adjusted to obtain the maximum flow. The specific volume v can be expressed as a function of k by combining Equations 15.2.16b and 15.3.24 to give

$$v = \frac{[(1-x)v_l k + x v_g][1 + x(k-1)]}{k} \qquad [15.3.25]$$

Differentiating Equation 15.3.22 with respect to k gives

$$G^2\left[\frac{\delta}{\delta l}\left(\frac{\delta v}{\delta k}\right) + \frac{f}{2d}\frac{\delta v}{\delta k} + \frac{v}{2d}\frac{\delta f}{\delta k}\right] = 0 \qquad [15.3.26]$$

In order to obtain from Equation 15.3.26 an expression for the maximum flow it is necessary to make some limiting assumptions. One limit is that of isentropic flow ($f = 0$, $\delta v/\delta k = 0$), but this is rejected because of the irreversibilities inherent in different phase velocities. Instead, the assumption made is isenthalpic flow ($\delta f/\delta k = 0$, $\delta v/\delta k = 0$).

Differentiating Equation 15.3.25 with respect to k gives

$$\frac{\delta v}{\delta k} = (x - x^2)\left(v_l - \frac{v_g}{k^2}\right) \qquad [15.3.27]$$

Then the values of k for which Equation (15.3.27) is equal to zero are

$$k = 1 \quad x = 0, 1 \qquad [15.3.28a]$$

$$k = \left(\frac{v_g}{v_l}\right)^{1/2} \quad 0 < x < 1 \qquad [15.3.28b]$$

Integrating Equation 15.3.22 over the length l of the pipe gives

$$\int_{P_o}^{P} \frac{\mathrm{d}P}{v} + G^2\left(\frac{\ln v}{v_o} + \frac{f_m l}{2d}\right) = 0 \qquad [15.3.29]$$

with

$$f_m = \int_{P_o}^{P} f \frac{\mathrm{d}}{\mathrm{d}P}(1/l)\, \mathrm{d}P \qquad [15.3.30]$$

where f_m is the average friction factor.

Differentiating Equation 15.3.30 with respect to P and setting $\mathrm{d}G/\mathrm{d}P = 0$ and then combining the result with Equation 15.3.29 gives

$$G_c = \left[\frac{-1}{v[\mathrm{d}\ln v/\mathrm{d}P + (1/2d)\,\mathrm{d}f_m/\mathrm{d}P]}\right]^{1/2} \qquad [15.3.31]$$

But

$$\left(\frac{\delta f_m}{\delta P}\right)_c = \frac{\delta f_m}{\delta k}\frac{\delta k}{\delta P} \qquad [15.3.32]$$

and, since, $\delta f_m/\delta k = 0$, it follows that $\delta f_m/\delta P = 0$.

Then from Equations 15.3.31 and 15.3.25

$$G_c = \left(\frac{-k}{\mathrm{d}/\mathrm{d}P\{[(1-x)v_l k + x v_g][1 + x(k-1)]\}}\right)^{1/2} \qquad [15.3.33]$$

Completing the differentiation of the denominator of Equation (15.3.33) with respect to P gives

$$G_c = (-k/\zeta)^{1/2} \quad [15.3.34]$$

with

$$\zeta = [(1 - x + kx)x]\frac{dv_g}{dP} + [v_g(1 + 2kx - 2x) + v_l(2xk - 2k - 2xk^2 + k^2)]\frac{dx}{dP} + [k(1 + x(k - 2) - x^2(k - 1)]\frac{dv_l}{dP} \quad [15.3.35]$$

Equation 15.3.34 is the required relation for the critical two-phase flow.

The derivative terms in Equation 15.3.35 are calculated under isenthalpic conditions as follows:

$$\frac{dv_g}{dP} \approx \left(\frac{\Delta v_g}{\Delta P}\right)_h \quad [15.3.36]$$

$$\frac{dv_l}{dP} \approx \left(\frac{\Delta v_l}{\Delta P}\right)_h \quad [15.3.37]$$

$$\frac{dx}{dP} \approx -\frac{1}{h_{fg}}\left(\frac{dh_f}{dP} + x\frac{dh_{fg}}{dP}\right) \quad [15.3.38a]$$

$$\frac{dx}{dP} \approx -\frac{1}{h_{fg}}\left(\frac{\Delta h_f}{\Delta P} + \frac{\Delta h_{fg}}{\Delta P}\right) \quad [15.3.38b]$$

where the subscripts f, fg and h denote the liquid, the liquid–vapour transition and constant enthalpy, respectively.

The method of calculation is as follows. For a given pressure P and given value of the quality x, the quantities v_g, v_l, h_{fg}, $\Delta v_g/\Delta P$, $\Delta v_l/\Delta P$, $\Delta h_f/\Delta P$ and $\Delta h_{fg}/\Delta P$ are obtained from thermodynamic tables. As an illustration, consider the calculation (in British units) given by Fauske for the maximum mass velocity of a steam–water mixture at a pressure of 600 psi. From steam tables

$$v_g = 0.7698$$
$$v_l = 0.0201$$
$$h_{fg} = 731.6$$

and for $\Delta P = 40$

$$\Delta v_g = 0.7440 - 0.7973$$
$$\Delta v_l = 0.0202 - 0.0201$$
$$\Delta h_f = 727.2 - 736.1$$
$$\Delta h_{fg} = 475.2 - 467.4$$

Hence

$$\frac{dx}{dP} = \frac{10^{-6}}{4.214}(-8.3 + 8.9x)$$
$$\frac{dv_g}{dP} = -9.2535 \times 10^{-6}$$
$$k = 6.19$$

Then the maximum mass velocity G_c for different values of quality x is

x	G_c
0.01	8960
0.05	7605
0.10	6510
0.20	5100
0.40	3570
0.60	2740
0.80	2235

The term (dv_l/dP) can often be neglected. In the calculation given for a value of the pressure P of 600 psi, the error in neglecting the term is 3%. At 400 psi the error reduces to 1%.

A further illustrative calculation has been given by Ramskill (1986 SRD R352) for an ammonia flow problem.

In the Fauske slip-equilibrium model, the friction factor defined is relatively complex and is unique to that model, although this does not present a problem since it is eliminated in the manipulations and does not appear in the final equation for the critical mass velocity.

15.3.6 Fauske non-equilibrium model

A model for critical two-phase flow in short outlets which has both non-equilibrium and equilibrium versions has been given by Fauske (1985b). The model is suitable for venting of vessels such as reactors and storage vessels where the outlet is sufficiently short for friction to be neglected. The general, or non-equilibrium, form of the model is:

$$G \approx \frac{h_{fg}}{v_{fg}}\left(\frac{1}{NTC}\right)^{1/2} \quad [15.3.39]$$

with

$$N \approx \frac{h_{fg}^2}{2\Delta P \rho_l K^2 v_{fg}^2 TC} + l/l_e \quad 0 < l/l_e < 1 \quad [15.3.40]$$

where C is the specific heat of the liquid, K is the coefficient of discharge, l_e is the equilibrium or relaxation length, N is a non-equilibrium parameter and ΔP is the total available pressure drop. The discharge coefficient K is the usual coefficient of discharge; it is given by Fauske variously as 0.6 and 0.61. The relaxation length l_e is 0.1 m.

Equation 15.3.39 is applicable over the range $0 < l/l_e < 1$. For $l/l_e = 0$, it reduces to

$$G = K(2\Delta P \rho_l)^{1/2} \quad [15.3.41]$$

with

$$\Delta P = P_o - P_a \quad [15.3.42]$$

where P_a is the absolute atmospheric pressure.

15.3.7 Fauske equilibrium rate model

If, on the other hand, the pipe length is sufficient for equilibrium to be reached, which occurs at $l/l_e > 1$, then in Equation 15.3.39 $N = 1$, and hence

$$G \approx \frac{h_{fg}}{v_{fg}}\left(\frac{1}{TC}\right)^{1/2} \quad [15.3.43]$$

Fauske (1985b) terms Equation 15.3.43 the equilibrium rate model (ERM).

An alternative form of Equation 15.3.43 which is often more convenient is

$$G \approx \frac{dP}{dT}\left(\frac{T}{C}\right)^{1/2} \quad [15.3.44]$$

Equation 15.3.44 gives a good estimate of two-phase flashing flow, provided the mass fraction x of vapour does not exceed a limiting value. The condition for its validity is given by Fauske and Epstein (1989) as

$$x < \frac{Pv_{fg}}{h_{fg}^2} TC \quad [15.3.45]$$

This condition implies a corresponding value of the void fraction α, since

$$\alpha = \frac{xv_g}{(1-x)v_f + xv_{fg}} \quad [15.3.46]$$

For a liquid with a small degree of subcooling, and thus in the transition zone between a saturated and strongly subcooled liquid:

$$G = \{2[P_o - P_v(T_o)]\rho_l + G_{ERM}^2\}^{1/2} \quad l/l_e \geq 1 \quad [15.3.50]$$

with

$$G_{ERM} = \frac{P_v}{P}\frac{dP}{dT}\left(\frac{T}{C}\right)^{1/2} \quad [15.3.51]$$

where P_v is the absolute vapour pressure.

Equation 15.3.50 reduces to Equation 15.3.44 for zero subcooling and to Equation 15.3.49 for strong subcooling.

15.3.10 Source term models

From this family of models, Fauske (1985b) and Fauske and Epstein (1988) have summarized those which may be used for the source term of an accidental release. They are:

Liquid condition		*Equation*
Saturated stagnation	Orifice (non-equilibrium, frictionless, $l/l_e = 0$)	15.3.41
	Nozzle (non-equilibrium, frictionless, $0 < l/l_e < 1$)	15.3.39
	Nozzle/short pipe (equilibrium, frictionless, $l/l_e > 1$)	15.3.44
	Longer pipe (equilibrium, frictional effecs, $l/l_e > 1$)	15.3.47
Week subcooling	Nozzle (non-equilibrium, $l/l_e < 1$)	15.3.50 (with G_{ERM} replaced by G from 15.3.39)
	Longer pipe (equilibrium, $l/l_e > 1$)	15.3.50 (with G_{ERM} from 15.3.51)
Strong subcooling	Nozzle/longer pipe	15.3.49

15.3.8 Flow through a pipe

The equilibrium rate model applies essentially to flow through a nozzle just long enough for equilibrium conditions to be established but sufficiently short that frictional effects can be neglected. The flow is only weakly dependent on the length of the outlet, but if it is necessary to take friction into account, Fauske suggests two approaches.

One is the use of the homogeneous equilibrium model. discussed in Section 15.2.15.

The other approach given by Fauske (1989a) is the use of a flow correction factor F to the ERM so that Equation 15.3.44 becomes

$$G = F\frac{dP}{dT}\left(\frac{T}{C}\right)^{1/2} \quad [15.3.47]$$

with

$$F = f(l/d) \quad [15.3.48]$$

In the context of venting of reactors with vapour pressure, or tempered systems, Fauske (1989a) has reported the values of F given here in Table 15.5.

15.3.9 Subcooled liquids

For flow of a liquefied gas which is initially subcooled, Fauske (1985b) gives the following relations. For a liquid with a large degree of subcooling:

$$G = K[2(P_o - P_a)\rho_l]^{1/2} \quad [15.3.49]$$

15.4 Two-phase Flow: Leung Models

Another family of models for two-phase flow is that given by Leung, another contributor to the DIERS project. The model of particular interest here is the homogeneous equilibrium model (HEM) for one-component two-phase flashing flow (Leung, 1986a). In addition to the basic model, the author has treated two-phase flashing flow in a horizontal duct (Leung, 1990a; Leung and Grolmes, 1987–), in an inclined duct (Leung, 1990a; Leung and Epstein, 1990a), with a subcooled liquid (Leung and Grolmes, 1988) and with non-condensable gas (Leung and Epstein, 1991), has presented a unified approach for nozzles and pipes (Leung, 1990b) and an overall comparison of flashing flow methods (Leung and Nazario, 1990). He has also given a model for two-phase non-flashing flow (Leung and Epstein, 1990b) and has shown the similarity between the flashing and non-flashing flow models (Leung, 1990a).

Table 15.5 *Flow correction factor for Fauske equilibrium rate model (after Fauske, 1989a)*

l/d	F
0	1.0
50	0.85
100	0.75
200	0.65
400	0.55

Applications of the model given by Leung include its use for: two-phase flow in storage vessels (Leung, 1986b); pressure relief valves (Leung, 1992a); and venting of reactors (Leung and Fauske, 1987; Leung and Fisher, 1989). These applications are described in Sections 15.5, 15.6 and Chapter 17, respectively.

15.4.1 Flow through a nozzle

The homogeneous equilibrium flow model of Leung (1986a) follows on from an earlier model by Grolmes and Leung (1984) which was restricted to an inlet condition of all liquid flow. This has been generalized by Leung to allow the handling of two-phase flow at the inlet.

The basic momentum and energy balance relations are:

$$v\,\mathrm{d}P + G^2\left(v\,\mathrm{d}v + 4fv^2\frac{\mathrm{d}L}{2D}\right) = 0 \qquad [15.4.1]$$

$$h_\mathrm{o} = h + \frac{G^2v^2}{2} \qquad [15.4.2]$$

where D is the diameter of the pipe, f is the friction factor, h is the specific enthalpy, L the length of the pipe and subscript o denotes stagnation. The situation considered is frictionless flow through a nozzle. This is treated as an isentropic process.

For a nozzle ($L = 0$), Equation 15.4.1 becomes

$$G = (-\mathrm{d}v/\mathrm{d}P)^{-1/2} \qquad [15.4.3]$$

The relations for specific enthalpy h, specific entropy s and specific volume v are:

$$h = h_\mathrm{f} + xh_\mathrm{fg} \qquad [15.4.4]$$

$$s = s_\mathrm{f} + xs_\mathrm{fg} \qquad [15.4.5]$$

$$v = v_\mathrm{f} + xv_\mathrm{fg} \qquad [15.4.6]$$

where subscripts f and fg indicate the liquid and the liquid–vapour transition, respectively.

Equation 15.4.2 for the energy balance can be written as

$$G = \frac{[2(h_\mathrm{o} - h)]^{1/2}}{v} \qquad [15.4.7]$$

But

$$h_\mathrm{o} - h = -\int_{P_\mathrm{o}}^{P} v\,\mathrm{d}P \qquad [15.4.8]$$

Then from Equations 15.4.7 and 15.4.8

$$G = \frac{(-2\int_{P_\mathrm{o}}^{P} v\,\mathrm{d}P)^{1/2}}{v} \qquad [15.4.9]$$

In order to solve Equation 15.4.9, use is made of an equation of state proposed by M. Epstein *et al.* (1983) for isentropic expansion from (all) liquid stagnation conditions:

$$\frac{v}{v_\mathrm{fo}} = \omega\left(\frac{P_\mathrm{o}}{P} - 1\right) + 1 \qquad [15.4.10]$$

where ω is a parameter. Grolmes and Leung (1984) utilized Equation 15.4.10 to obtain the flow through a nozzle for an all liquid inlet condition.

For isentropic expansion, the correlating parameter ω in Equation 15.4.10 is

$$\omega = \frac{C_\mathrm{fo}T_\mathrm{o}P_\mathrm{o}}{v_\mathrm{fo}}\left(\frac{v_\mathrm{fgo}}{h_\mathrm{fgo}}\right)^2 \qquad [15.4.11]$$

where C_f is the specific heat of the liquid and T is the absolute temperature.

The critical mass velocity G_c is

$$G_\mathrm{c} = \eta_\mathrm{c}\left(\frac{P_\mathrm{o}}{\omega v_\mathrm{fo}}\right)^{1/2} \qquad [15.4.12]$$

where η_c is the critical pressure ratio. The pressure ratio η is defined as

$$\eta = \frac{P}{P_\mathrm{o}} \qquad [15.4.13]$$

The critical pressure ratio η_c was found to be the value of η satisfying the relation

$$\eta^2 + (\omega^2 - 2\omega)(1-\eta)^2 + 2\omega^2\ln\eta + 2\omega^2(1-\eta) = 0 \qquad [15.4.14]$$

Further, for the all liquid inlet condition

$$\omega = \frac{P_\mathrm{o}}{v_\mathrm{fo}G_\mathrm{lm}^2} \qquad [15.4.15]$$

and hence from Equations 15.4.11 and 15.4.15

$$G_\mathrm{lm} = \left(\frac{1}{C_\mathrm{fo}T_\mathrm{o}}\right)^{1/2}\frac{h_\mathrm{fgo}}{v_\mathrm{fgo}} \qquad [15.4.16]$$

where G_lm is the mass velocity at this limiting condition. Starting from these relations, Leung extends the treatment to the case of a two-phase inlet condition. Equation 15.4.10 becomes

$$\frac{v}{v_\mathrm{o}} = \omega\left(\frac{P_\mathrm{o}}{P} - 1\right) + 1 \qquad [15.4.17]$$

which is also given as

$$\omega = \frac{(v/v_\mathrm{o} - 1)}{(P_\mathrm{o}/P - 1)} \qquad [15.4.18]$$

and Equation 15.4.12 becomes

$$G_\mathrm{c} = \eta_\mathrm{c}\left(\frac{P_\mathrm{o}}{\omega v_\mathrm{o}}\right)^{1/2} \qquad [15.4.19]$$

Introducing a dimensionless mass velocity G^*

$$G^* = \frac{G}{(P_\mathrm{o}/v_\mathrm{o})^{1/2}} \qquad [15.4.20]$$

the critical value G_c^* becomes

$$G_\mathrm{c}^* = \frac{G_\mathrm{c}}{(P_\mathrm{o}/v_\mathrm{o})^{1/2}} \qquad [15.4.21]$$

At this point, the assumption is made that the process is isenthalpic. This approximation allows ω to be expressed more readily in terms of the stagnation properties. The relations for the specific enthalpy, specific entropy and specific volumes are:

$$h_o = h_{fo} + x_o h_{fgo} \quad [15.4.22]$$

$$s_o = s_{fo} + x_o s_{fgo} \quad [15.4.23]$$

$$v_o = v_{fo} + x_o v_{fgo} \quad [15.4.24]$$

where x is the mass fraction of the vapour.

It is shown that with the isenthalpic assumption and certain other approximations:

$$\omega = \frac{x_o v_{fgo}}{v_o} + \frac{C_{fo} T_o P_o}{v_o}\left(\frac{v_{fgo}}{h_{fgo}}\right)^2 \quad [15.4.25]$$

Starting from Equation 15.4.19 and utilizing data for two-phase flow of water and nine other fluids, Leung obtains the following empirical correlation:

$$\frac{G_c}{(P_o/v_o)^{1/2}} = \frac{\eta_c}{\omega^{0.5}} \quad \omega > 4.0 \quad [15.4.26a]$$

$$= \frac{0.66}{\omega^{0.39}} \quad \omega < 4.0 \quad [15.4.26b]$$

The critical pressure ratio η_c was found to be the value of η satisfying the following relations. For a stagnation pressure of $P_o = 5$ bara (absolute bar)

$$\eta = 0.6055 + 0.1356 \ln\omega - 0.131(\ln\omega)^2 \quad [15.4.27]$$

and for $P_o = 15$ bara (absolute bar)

$$\eta = 0.55 + 0.217 \ln\omega - 0.046(\ln\omega)^2 + 0.004(\ln\omega)^3 \quad [15.4.28]$$

This correlation was found to apply up to a reduced temperature $T_r = 0.9$ and reduced pressure $P_r = 0.5$.

The most general formulation of the parameter ω is:

$$\omega = \alpha_o + (1-\alpha_o)\rho_{fo} C_{fo} T_o P_o \left(\frac{v_{fgo}}{h_{fgo}}\right)^2 \quad [15.4.29]$$

where α is the void fraction. For the all liquid condition $\alpha_o = 0$, and for the all vapour condition $\alpha_o = 1$. The parameter ω takes the following values:

$x_o = 1$	$\alpha_o = 1$	all vapour $\omega = 1$
$0 < x_o < 1$	$\alpha_o < 1$	but flashing $\omega > 1$
$0 < x_o < 1$	$\alpha_o < 1$	but non-flashing $\omega = \alpha_o < 1$

The larger the value of ω, the greater the increase in specific volume upon depressurization and the more readily the flow attains the choking condition.

15.4.2 Flow through a pipe

The case of flow through a horizontal pipe as opposed to a nozzle has been treated by Leung and Grolmes (1987–), whilst Leung and Epstein (1990a) have considered flow through a pipe inclined upwards. The results of this work have been summarized by Leung (1990a).

For the inclined pipe, use is made of the flow inclination number Fi defined as:

$$\mathrm{Fi} = \frac{gD\cos\theta}{4fP_o v_o} \quad [15.4.30]$$

where g is the acceleration due to gravity and θ is the angle between the pipe axis and the vertical.

Figure 15.14 shows the ratio G/G_o of the mass velocity through a pipe G to that through a nozzle G_o, or flow reduction factor. Figure 15.14(a) is for a horizontal pipe (Fi = 0) and Figure 15.14(b) for an inclined pipe with Fi = 0.1.

For the case of all liquid inlet flow ($\omega = 0$):

$$\frac{G}{G_o} = \left(\frac{1 - N\mathrm{Fi}}{1+N}\right)^{1/2} \quad [15.4.31a]$$

$$= \frac{1}{(1+N)^{1/2}} \quad \mathrm{Fi} = 0 \text{ (horizontal pipe)} \quad [15.4.31b]$$

$$\to 0 \quad N\mathrm{Fi} = 1 \quad [15.4.31c]$$

with

$$N = 4f\frac{L}{D} \quad [15.4.32]$$

where N is the pipe resistance factor.

15.4.3 Subcooled liquids

The case of flashing critical flow of an initially subcooled liquid is considered by Leung and Grolmes (1988). A more general relation which applies to such flow as well as flow of an initially two-phase mixture is

$$G^* = \frac{G}{(P_o/v_o)^{1/2}} = \frac{\{2(1-\eta_s) + 2[\omega\eta_s \ln(\eta_s/\eta) - (\omega-1)(\eta_s - \eta)]\}^{1/2}}{\omega((\eta_s/\eta) - 1) + 1} \quad [15.4.33]$$

with

$$\eta_s = \frac{P_s}{P_o} \quad [15.4.34]$$

where the subscript s denotes saturation.

Setting $dG^*/d\eta = 0$ gives for the critical mass velocity

$$G_c^* = \frac{\eta_c}{(\omega\eta_s)^{1/2}} \quad [15.4.35]$$

The flow behaviour depends on the degree of subcooling. The critical value η_{sc} separating the two regimes is

$$\eta_{sc} = \frac{2\omega - 1}{2\omega} \quad [15.4.36]$$

For low subcooling ($\eta_s \geq \eta_{sc}$), the fluid attains flashing before reaching the choked location. For high subcooling

$$\eta_c = \eta_s \quad [15.4.37]$$

$$G_c^* = [2(1-\eta_s)]^{1/2} \quad [15.4.38]$$

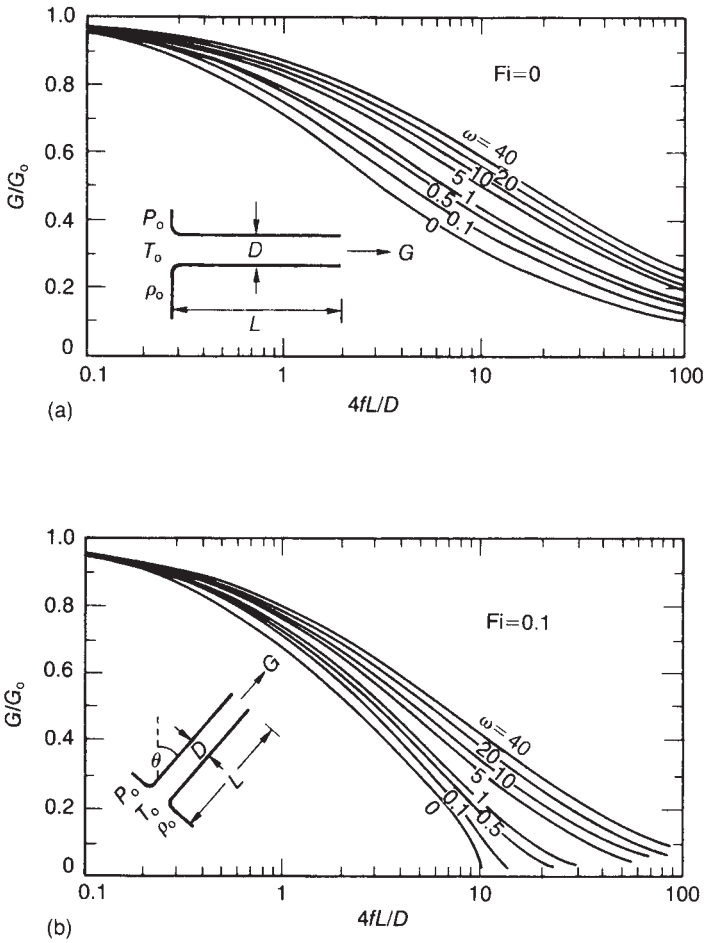


Figure 15.14 *Leung homogeneous equilbrium flow model: critical flow for discharge through a pipe (Leung, 1990a): (a) horizontal pipe; and (b) inclined pipe Fi = 0.1 (Courtesy of the American Institute of Chemical Engineers)*

or, from a relation similar to Equation 15.4.21 but with v_{fo} instead of v_{o},

$$G_{\mathrm{c}} = [2\rho_{\mathrm{fo}}(P_{\mathrm{o}} - P_{\mathrm{s}})]^{1/2} \qquad [15.4.39]$$

which is the usual equation for liquid flow through an orifice.

15.4.4 Subcritical flow

The case of flashing subcritical flow is treated by Leung (1992a). A more general relation which applies to such flow as well as critical flow is

$$G^* = \frac{G}{(P_{\mathrm{o}}/v_{\mathrm{o}})^{1/2}} = \frac{\{-2[\omega \ln \eta + (\omega - 1)(1 - \eta)]\}^{1/2}}{\omega(1/\eta - 1) + 1} \qquad [15.4.40]$$

Setting $\mathrm{d}G^*/\mathrm{d}\eta = 0$ gives for the critical mass velocity

$$G_{\mathrm{c}}^* = \frac{\eta_{\mathrm{c}}}{\omega^{1/2}} \qquad [15.4.41]$$

15.4.5 Non-flashing flow

The case of non-flashing critical flow has been dealt with by Leung and Epstein (1990b). Non-flashing two-phase flow is exemplified by two-phase flow of a two-component mixture such as air and water. A comparison of flashing and non-flashing flows is given by Leung (1990a).

Figure 15.15 shows the correlation given by Leung (1990a) for the dimensionless mass velocity G_{c}^* and the critical pressure ratio η_{c} in two-phase critical flow in both the flashing and non-flashing regimes.

15.5 Vessel Depressurization

Some of the most complex fluid flow problems arise in the depressurization or venting of vessels, particularly reactors and storage vessels. In order to specify the venting arrangements for a vessel, it is necessary to determine the flow, the phase condition of fluid and the vent area required for this flow. The venting of vessels is complicated by the fact that in many situations the flow is likely to be two-phase. It is necessary therefore, to be able both to estimate

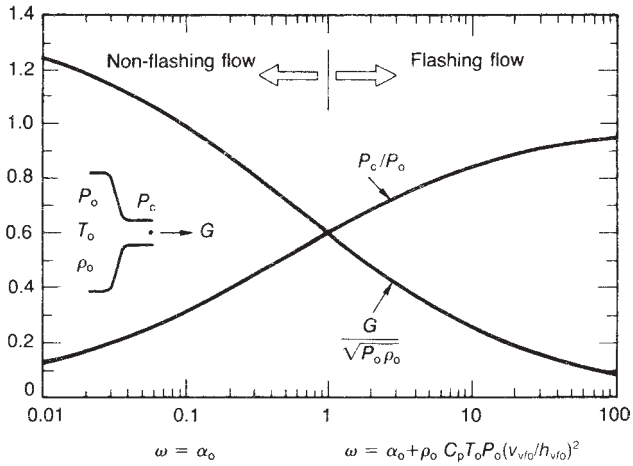


Figure 15.15 *Leung homogeneous equilibrium flow model: critical flow for discharge through a frictionless nozzle (Leung, 1990a) (Courtesy of the American Institute of Chemical Engineers)*

the vapour mass fraction, or quality, of the fluid entering the vent and the flow through the vent.

The need to determine the quality of the fluid vented has been highlighted during the work of the DIERS project. The quality of the fluid entering the vent is determined by liquid swell and vapour disengagement. There are two principal regimes that are recognized as occurring when a vessel is depressurized. If the liquid is non-foaming the regime tends to be churn turbulent, whereas if it is foaming the regime is bubbly.

For a non-foaming liquid, methods have been developed to predict the onset of two-phase flow. In the depressurization of a vessel containing such a liquid there will, in general, be a region in which the flow is all vapour and another region in which it is two-phase. A large initial vapour space, or freeboard, will favour all vapour flow. For a foaming liquid it is necessary to assume two-phase flow. Broadly, a pure liquid held in a storage vessel may well be non-foaming. It is to this situation that the methods developed principally apply.

An otherwise non-foaming liquid may be rendered foaming by the presence of impurities. Quite small quantities of a surface active agent may suffice to effect this. Since impurities are likely to be present in the liquid in a reactor, it is usual to treat a reaction mass as foaming.

In this section an account is given of models of liquid swell and vapour disengagement. Models have been given in the DIERS Technical Summary and by Fauske, Grolmes and Henry (1983), Swift (1984) and Grolmes and Epstein (1985). The application of these models to venting, particularly of storage vessels, is described in Chapter 17.

15.5.1 Liquid swell

Depressurization of a vessel containing superheated liquid or addition of heat to liquid in a vessel gives rise to the formation of vapour bubbles, which results in liquid swell. If this is severe, the level of the swollen liquid may reach the vent. But even if this is not so, there may be carryover of droplets into the vent. Liquid swell and vapour disengagement therefore affect the vapour mass fraction entering the vent. Some of the flow regimes that can occur on operation of the relief are shown in Figure 15.16.

For a liquid subject to swell, the average void fraction is

$$\bar{\alpha} = 1 - \frac{H_o}{H} \qquad [15.5.1]$$

with

$$H_o = \frac{V_l}{A_x} \qquad [15.5.2]$$

where A_x is the cross-sectional area of the vessel (m^2), H is the height of the liquid (m), H_o is the height of the liquid without swell (m), V_l is the volume of the liquid (m^3) and $\bar{\alpha}$ the average void fraction. A distinction is made between the average void fraction $\bar{\alpha}$ and the local void fraction α.

The initial void fraction in the vessel, or freeboard, α_o is

$$\alpha_o = 1 - \frac{H_o}{H_x} \qquad [15.5.3]$$

where H_x is the height of the vessel (m).

15.5.2 Gas or vapour generation

Gas or vapour may be present in the liquid because gas is injected into the liquid or because gas or vapour is generated in the liquid, due either to exothermic reaction or to an external heat source. The first case is that of uniform flux (UF) and the second that of a uniform volumetric source (VS). It is the latter that is of principal interest here.

The vapour superficial velocity above the height of the swelled liquid is

$$j_{g\infty} = \frac{S}{A_x} \qquad [15.5.4]$$

where j_g αis the vapour superficial velocity (m/s) and S is the volumetric source strength (m^3/s).

A dimensionless source strength ψ is defined as

$$\psi = \frac{j_{g\infty}}{U_\infty} \qquad [15.5.5]$$

where U_∞ is the bubble rise velocity (m/s). The parameter ψ is also referred to as the 'dimensionless velocity'.

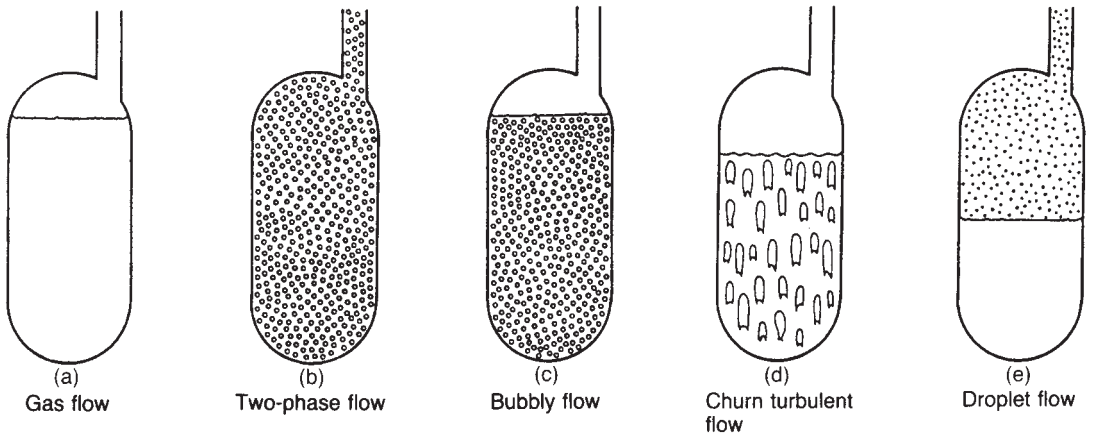


Figure 15.16 *Some flow regimes in venting of vessels (Swift, 1984) (Courtesy of the Institution of Chemical Engineers)*

The volumetric source strength is a function of the heat input. For an external heat source

$$q = \frac{FQ_{ex}}{\rho_l D} \qquad [15.5.6]$$

where D is the vessel diameter (m), q is the heat input per unit mass (kW/kg), Q_{ex} is the external heat input flux (kW/m^2), ρ_l is the density of the liquid (kg/m^3) and F is a geometric factor. For the geometric factor F the *Technical Summary* gives for a sphere $F = 6$, for a vertical cylinder $F = 4$ and for a horizontal cylinder with hemispherical ends $F = (L/D + 1)/(3L/D + 2)$, where L/D is the length/diameter ratio.

15.5.3 Drift flux

A drift flux model for the behaviour of the liquid in a vessel subject to vapour generation has been described in the *Technical Summary*. The concept of drift flux has been described in work by Zuber and Findlay (1965) and Wallis (1969). The local gas and liquid superficial velocities are:

$$j_g = \alpha U_g \qquad [15.5.7]$$

$$j_l = (1 - \alpha)U_l \qquad [15.5.8]$$

$$j = j_g + j_l \qquad [15.5.9]$$

where j is the total volume flux, or superficial velocity (m/s), j_g is the superficial gas velocity (m/s), j_l is the superficial liquid velocity (m/s), U_g is the area average gas velocity (m/s), and U_l is the area average liquid velocity (m/s).

From these relations is derived the expression for the drift flux:

$$j_{gl} = j_g(1 - \alpha) - \alpha j_l \qquad [15.5.10]$$

where j_{gl} is the superficial drift velocity, or drift flux (m/s).

It has been shown by Wallis that the drift flux j_{gl} can be expressed as a function of the bubble rise velocity U_∞. The particular relation adopted in the *Technical Summary* differs slightly from that of Wallis and is

$$j_{gl} = \frac{\alpha(1 - \alpha)^n U_\infty}{1 - \alpha^m} \qquad [15.5.11]$$

where U_∞ is the bubble velocity (m/s) and m and n are indices. The velocity U_∞ is also variously termed the 'particle velocity' and the 'characteristic velocity'. The bubble velocity is given by

$$U_\infty = \frac{k[\sigma g(\rho_l - \rho_g)]^{1/4}}{\rho_c^{1/2}} \qquad [15.5.12]$$

where $U\rho$ is the density (kg/m^3), σ is the surface tension of the liquid (N/m), k is a constant, and subscript c denotes the continuous phase.

The values of the indices m and n and of the constant k depend on the regime as follows:

	n	m	k
Bubbly regime	2	3	1.18
Churn turbulent regime	0	$\rightarrow \infty$	1.53

Substituting these values in Equation 15.5.11 gives

$$j_{gl} = \frac{\alpha(1 - \alpha)^2}{1 - \alpha^3} U_\infty \quad \text{bubbly regime} \qquad [15.5.13]$$

$$j_{gl} = \alpha U_\infty \quad \text{churn turbulent regime} \qquad [15.5.14]$$

A further drift flux is defined j_{lg}, complementary to j_{gl}, such that

$$j_{gl} + j_{lg} = 0 \qquad [15.5.15]$$

The two drift fluxes are given by

$$j_{gl} = \alpha(1 - \alpha)(U_g - U_l) \qquad [15.5.16a]$$

$$j_{lg} = -\alpha(1 - \alpha)(U_g - U_l) \qquad [15.5.16b]$$

where j_{lg} is the superficial drift velocity of the liquid phase relative to the gas phase (m/s).

The foregoing treatment does not take account of the radial distribution of the void fraction. In order to obtain better correlations Zuber and Findlay (1965) introduced the distribution parameter C_o. Equation 15.5.10 for the drift flux then becomes

$$j_{gl} = (1 - C_o\alpha)j_g - C_o\alpha j_l \qquad [15.5.17]$$

For the case of no radial void distribution C_o is unity. In general, the value of C_o used tends to lie in the range 1.0–1.5. For C_o a best estimate is 1.2 and 1.5 for the bubbly and churn turbulent regimes, respectively, and a conservative estimate is 1.0 for both regimes.

This drift flux model is now applied to three situations: (1) an open system with a uniform gas injection flow, (2) an open system with uniform volumetric gas generation and (3) a closed system with a uniform volumetric gas generation.

15.5.4 Superficial velocity: open system with uniform injection flow

For an open system with uniform gas injection at the bottom of the vessel, the steady state condition is $j_l = 0$ and Equation 15.5.17 with Equation 15.5.11 then gives

$$j_g = \frac{\alpha(1-\alpha)^n U_\infty}{(1-\alpha^m)(1-C_o\alpha)} \qquad [15.5.18]$$

But, since the gas flow is constant throughout the height, $j_g = j_{g\infty}$, and hence from Equation 15.5.5:

$$\psi = \frac{\alpha(1-\alpha)^n}{(1-\alpha^m)(1-C_o\alpha)} \qquad [15.5.19]$$

Then for the two regimes

$$\psi = \frac{\alpha(1-\alpha)^2}{(1-\alpha^3)(1-C_o\alpha)} \quad \text{bubbly regime} \qquad [15.5.20]$$

$$\psi = \frac{\alpha}{1-C_o\alpha} \quad \text{churn turbulent regime} \qquad [15.5.21a]$$

$$\psi \to \alpha \quad \text{churn turbulent regime; } \alpha \ll 1 \qquad [15.5.21b]$$

15.5.5 Superficial velocity: open system with uniform volume source

For an open system with uniform volumetric gas generation throughout the liquid, the vapour flux varies with height. The energy balance is:

$$\rho_g h_{fg} \mathrm{d}j_g = q\rho_l(1-\alpha)\,\mathrm{d}H \qquad [15.5.22]$$

where h_{fg} is the latent heat of vaporization (kJ/kg). Limiting the treatment to the churn turbulent regime, differentiation of Equation 15.5.18 with respect to α and combination with Equation 15.5.22 yields

$$\psi \frac{\mathrm{d}H^*}{\mathrm{d}\alpha} = (1-\alpha)^{-3} \qquad [15.5.23]$$

with

$$H^* = H/H_o \qquad [15.5.24]$$

$$\psi = \frac{q(\rho_l/\rho_g - 1)H_o}{h_{fg}U_\infty} \qquad [15.5.25]$$

where H^* is the dimensionless liquid height. Equation 15.5.23 may then be integrated:

$$\psi H^* = \int_0^\alpha (1-\alpha)^{-3}\,\mathrm{d}\alpha \qquad [15.5.26]$$

Two successive integrations are then performed. The first gives α as a function of H^*:

$$\alpha = 1 - (1 + 2\psi H^*)^{-1/2} \qquad [15.5.27]$$

The second gives α as a function of H^*, subject to the condition

$$H^*_{max} = 1/(1-\bar{\alpha}) \qquad [15.5.28]$$

This second integration yields

$$\bar{\alpha} = \frac{\psi}{2+\psi} \qquad [15.5.29a]$$

or

$$\psi = \frac{2\bar{\alpha}}{1-\bar{\alpha}} \qquad [15.5.29b]$$

Introducing the distribution parameter C_o, Equation 15.5.29 becomes

$$\bar{\alpha} = \frac{\psi}{2+C_o\psi} \qquad [15.5.30a]$$

$$\psi = \frac{2\bar{\alpha}}{1-C_o\bar{\alpha}} \qquad [15.5.30b]$$

The corresponding equation for bubbly flow is

$$\psi = \frac{\bar{\alpha}(1-\bar{\alpha})^2}{(1-\bar{\alpha}^3)(1-C_o\bar{\alpha})} \qquad [15.5.31]$$

15.5.6. Superficial velocity: closed system with uniform volume source

The case of a closed system is also relevant, since it represents the condition just before the relief device operates. It is used for the analysis of transient conditions. For this case j_l is not equal to zero.

For a closed system with uniform volumetric gas generation throughout the liquid, the treatment is as follows. Continuity of flow gives:

$$j_l = aj_g \qquad [15.5.32]$$

with

$$a = \frac{1-x_e}{(\rho_l/\rho_g)^{x_e}} \qquad [15.5.33]$$

where a is a parameter and x_e is the mass fraction of vapour at the vent. Then from Equations 15.5.11, 15.5.17 and 15.5.32:

$$j_g = \frac{\epsilon\lambda U_\infty}{1-C_o\lambda a} \qquad [15.5.34]$$

with

$$\epsilon = \frac{(1-\alpha)^n}{1-\alpha^m} \quad [15.5.35]$$

$$\lambda = \frac{\alpha}{1 - C_o\alpha} \quad [15.5.36]$$

where ϵ and λ are parameters.

For the two regimes, the values of the parameters, α, ϵ and λ are as follows. For the bubbly regime:

$$\alpha = \bar{\alpha} \quad [15.5.37]$$

$$\epsilon = \frac{(1-\alpha)^2}{1-\alpha^3} \quad [15.5.38]$$

$$\lambda = \frac{\bar{\alpha}}{1 + C_o\bar{\alpha}} \quad [15.5.39]$$

For the churn turbulent regime:

$$\alpha = \frac{2\bar{\alpha}}{1 + C_o\bar{\alpha}} \quad [15.5.40]$$

$$\epsilon = 1 \quad [15.5.41]$$

$$\lambda = \frac{2\bar{\alpha}}{1 - C_o\bar{\alpha}} \quad [15.5.42]$$

A mass balance on the vapour at the vent gives:

$$j_g = \frac{Gx_e\Omega}{\rho_g} \quad [15.5.43]$$

with

$$\Omega = A/A_x \quad [15.5.44]$$

where A is the area of the vent (m^2) and Ω is the ratio of the vessel area to the vent area. Then from Equations 15.5.34–15.5.43:

$$\frac{Gx_e\Omega}{U_\infty\rho_g} = \frac{\epsilon\lambda}{1 - C_o\lambda a} \quad [15.5.45]$$

Equation 15.5.45 provides an expression coupling between the vessel and the vent line description. As described by Grolmes and Leung (1985), it is used for this purpose in numerical models of vessel venting.

The value of ψ at the all vapour flow condition with $x_e = 1$ may be obtained as follows. Noting that Equation 15.5.43 is for the vent point and hence $j_g = j_{g\infty}$, then Equations 15.5.43 and 15.5.5 give

$$\psi = \frac{G\Omega}{U_\infty\rho_g} \quad [15.5.46]$$

15.5.7 Vapour generation by external heat

From Equations 15.5.3, 15.5.6 and 15.5.25 it may be shown that for an externally heated vessel

$$\psi = \frac{FQ_{ex}(1-\alpha_o)H_x}{U_\infty h_{fg}\rho_g D} \quad [15.5.47]$$

15.5.8 Criterion for two-phase flow

These relations may be used to indicate the boundary between all vapour venting and two-phase venting. The criterion for two-phase flow into the vent is that the average void fraction is greater than the vessel freeboard

$$\bar{\alpha} > \alpha_o \quad [15.5.48]$$

The value of the average void fraction $\bar{\alpha}$ for use in relation 15.5.48 is obtained as follows. The actual value of the dimensionless velocity ψ is determined from the appropriate equation. The corresponding value of $\bar{\alpha}$ is then determined from the appropriate relation between ψ and $\bar{\alpha}$. For example, for an externally heated vessel with a churn turbulent regime, Equation 15.5.47 gives ψ and Equation 15.5.30a the corresponding value of $\bar{\alpha}$.

Alternatively, the criterion for two-phase flow to occur may be formulated in terms of the dimensionless velocity ψ. The criterion is then

$$\psi(\bar{\alpha}) > \psi(\alpha_o) \quad [15.5.49]$$

For example, for the externally heated vessel with churn turbulent regime ($\bar{\alpha}$) is obtained as before from Equation 15.5.47 $\psi(\alpha_o)$ and from Equation 15.5.30b with α_o instead of $\bar{\alpha}$.

15.5.9 Criterion for two-phase flow: illustrative example

An illustrative example of the determination of the quality of the vapour entering the vent is given in Table 15.6. The case considered is a vertical cylindrical vessel with external heating. The calculation shows that the flow entering the vent is two-phase.

15.5.10 Vapour carryunder

A model based on vapour carryunder has been developed and applied to an externally heated vessel by Grolmes and Epstein (1985). A dimensionless heat flux J_o is defined as

$$J_o = \frac{Q_{ex}}{U_\infty h_{fg}\rho_g} \quad [15.5.50]$$

The external heating at the vessel walls creates a boiling two-phase boundary layer in the liquid which generates vapour bubbles that rise. This rise is balanced by liquid downflow in the centre of the vessel, which creates the potential for vapour carryunder. Vapour carryunder is assumed to occur if the downward recirculating velocity U_c exceeds the bubble rise velocity U_∞. The conditions which can occur are shown in Figure 15.17, where Figure 15.17(a) shows no vapour carryunder ($U_c < U_\infty$ throughout) and Figure 15.17(b) shows vapour carryunder to a level H_{BL} (where $U_c = U_\infty$).

The downward liquid recirculating velocity U_c is related to the upward liquid superficial velocity U_s, evidently the same as the bubble rise velocity U_∞, by a geometric factor ϵ:

$$U_c = \epsilon U_s \quad [15.5.51]$$

The geometric factor ϵ is the ratio of the area for downward recirculation flow to the boundary layer area for upward flow. It is a function of the boundary layer thickness $\delta(H)$ measured at the height H of the liquid, which itself is a function of the heat flux:

$$\epsilon = f[\delta(H)] \quad [15.5.52]$$

$$\delta(H) = f(J_o) \quad [15.5.53]$$

The interface height H_{BL} below which there is no vapour carryunder is determined as the height at which $U_c = U_s$ or $\epsilon = 1$.

Table 15.6 *Illustrative calculation for occurrence of two-phase flow of fluid entering the vent of an externally heated storage vessel*

A Scenario

Liquid density, $\rho_l = 750\ \text{kg/m}^3$
Vapour density, $\rho_g = 4.5\ \text{kg/m}^3$
Latent heat of vaporization, $h_{fg} = 900\ \text{kJ/Kg}$
Surface tension, $\sigma = 0.02\ \text{N/m}$
Vessel type: vertical cylindrical
Vessel diameter, $D = 1.0\ \text{m}$
Vessel height, $H_x = 2.0\ \text{m}$
Vessel freeboard, $\alpha_o = 0.16$
Vessel geometric factor, $F = 4$
External heat input, $Q_{ex} = 60\ \text{kJ W/m}^2$
Vessel regime: churn turbulent
$k = 1.53$
$C_o = 1$

B Fluid phase

From Equation 15.5.12:
$U_\infty = 1.53[0.02 \times 9.81(750 - 4.5)]^{1/4}/750^{1/2} = 0.19\ \text{m/s}$
From Equation 15.5.47

$$\psi = \frac{4 \times 60(1 - 0.16) \times 2.0}{0.19 \times 900 \times 4.5 \times 1.0} = 0.51$$

From Equation 15.5.5

$$j_{g\infty} = 0.51 \times 0.19 = 1.097\ \text{m/s}$$

From Equation 15.5.29a

$$\bar{\alpha} = \frac{0.51}{2 + 0.51} = 0.20$$

But

$$\alpha_o = 0.16$$

Hence $\bar{\alpha} > \alpha_o$, indicating that flow entering vent is two phase. Alternatively, from Equation 15.5.29b with α_o instead of $\bar{\alpha}$:

$$\psi(\alpha_o) = \frac{2 \times 0.16}{1 - 0.16} = 0.38$$

Hence $\psi(\bar{\alpha}) > \psi(\alpha_o)$, again indicating that flow entering vent is two phase.

The authors give a graphical relation of the form

$$U_s = f(J_o, z) \qquad [15.5.54]$$

where z is the height (m). Using this relation, the height H_{BL} can be determined.

Using this model, the authors derive the following results for the fraction H_{BL}/H of vessel height where there is no vapour carryunder:

Heat flux, J_o	*Vessel diameter* (m)			
	0.61	1.52	3.05	6.1
0.310	0.41	0.32	0.26	0.22
0.062	0.62	0.48	0.39	0.33
0.006	1	0.86	0.69	0.58

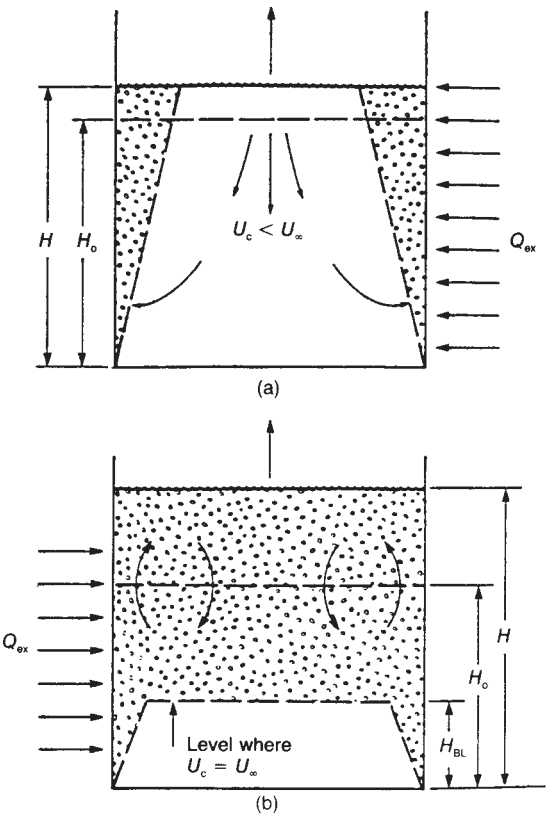


Figure 15.17 *Vapour carryunder in venting of a vessel (Grolmes and Epstein, 1985): (a) case where the recirculating liquid velocity U_c is less than the bubble rise velocity U_∞ throughout the vessel; and (b) case where the recirculating liquid velocity U_c is not less than the bubble rise velocity U_∞ throughout the vessel (Courtesy of the American Institute of Chemical Engineers)*

The results show that the proportion of the liquid subject to vapour carryunder increases with heat flux and with vessel size. Thus large vessels are more prone than small ones to vapour carryunder.

The potential significance of these models for large atmospheric storage tanks is discussed by Fauske *et al.* (1986). Assuming that vapour carryunder could cause sufficient liquid swell to give a two-phase mixture at the vent inlet, then since in such tanks the permissible overpressure is very low, the ratio of the vent area required for two-phase flow to that for all vapour flow is, to first order, proportional to $(\rho_g/\rho_i)^{1/2}$, which implies augmentation by a factor of 10–30.

The authors suggest, however, that while vapour carryunder is possible hydrodynamically, the vapour bubbles will in fact tend to collapse as they are carried down into liquid, the subcooling of which increases with depth, and state that, to first order, liquid swell is determined by the boiling two-phase boundary layer without vapour carryunder.

They describe experimental work on the measurement of liquid swell in vessels heated externally. The measured

liquid swells agree well with those predicted neglecting vapour carryunder. They suggest, therefore, that in the sizing of vents for atmospheric storage tanks for liquids that are not highly viscous or foaming, the assumption of all vapour flow will normally be valid.

For reactors, the situation is quite different, as discussed by Fauske (1985a). He states that it is a hopeless task to seek to generalize the results just described to reacting systems, or indeed to any system with traces of impurities. For such systems, the appropriate assumption is that there will be two-phase homogeneous flow at the vent inlet.

15.6 Pressure Relief Valves

As components of a pressure system, pressure relief valves have been treated in Chapter 12. In this section some further consideration is given in respect of the flow through such devices. Dispersion of the discharge is considered in Section 15.20 and, for dense gases in Section 15.43.

15.6.1 Single-phase flow

Relations for single-phase flow of gases and liquids have been presented in Section 15.1. Formulae derived from these are given in the codes for pressure relief. The API and BS formulae are stated in Chapter 12.

15.6.2 Two-phase flow

Two-phase vapour–liquid flow has been discussed in Sections 15.2–15.4, from which it will be apparent that this is a much more complex topic. The various models for two-phase flow do not lend themselves to formulae for calculating the area of the pressure relief valve orifice that are comparable in simplicity with those for single-phase flow. Moreover, with two-phase flow the determination of the flow through the valve orifice by no means exhausts the problem. The flows in the inlet and outlet lines are also complex.

The treatment here deals primarily with flow through the valve orifice and is confined to an account of the widely used American Petroleum Institute (API) method and of a method given by Leung which has gained some acceptance, together with a overview of the wider aspects of the design.

15.6.3 Two-phase flow: API method

API RP 520 Part 1: 1990 gives the following method for sizing a two-phase gas–liquid relief. It describes the method as reasonably conservative. The method is to calculate separately the cross-sectional areas required for the vapour and the liquid flows. The quantity of vapour formed is determined by assuming an adiabatic, isenthalpic expansion from the relieving condition down to the critical downstream pressure or the back pressure, whichever is the greater. The area for the vapour flow is then obtained using the equations given for all vapour flow, supercritical or subcritical, as the case may be. Likewise, the area for liquid flow is obtained from the equation for liquid flow, taking as the downstream pressure the back pressure. The areas for vapour and for liquid flow are then summed to give the required area of the valve orifice. The valve selected will have an area greater than or equal to this required area. The quantity of vapour formed downstream of the orifice of the actual valve should then be rechecked.

Whilst this method is probably the most widely used, it is commonly criticized by workers in the field as lacking theoretical basis and experimental validation. Critiques of the API method have been given by Leung and Nazario (1989) and Leung (1992a).

15.6.4 Two-phase flow: Leung method

As described in Section 15.4, a comprehensive set of models for two-phase flow has been developed by Leung. These have been applied by the author to the problem of two-phase flow through a safety relief valve (Leung, 1992a).

The treatment described by Leung is essentially the application of his homogeneous equilibrium model (HEM) to the safety relief valve (SRV) design requirements of API RP 520: 1990 and RP 521: 1990. The equations used are a subset of those given in Section 15.4, based mainly on Leung (1986a). For clarity, this subset is given again here together with an explanation of their use in SRV system design and with the illustrative examples given by Leung.

In his method, Leung distinguishes four initial states of the liquid in the vessel:

(1) saturated liquid;
(2) two-phase gas–liquid mixture;
(3) subcooled liquid
    (a) low subcooling,
    (b) high subcooling.

Each of these cases is treated differently.

The model utilizes the parameter ω which determines the equation of state

$$\frac{v}{v_o} = \omega\left(\frac{P_o}{P} - 1\right) + 1 \qquad [15.6.1]$$

and is given by

$$\omega = \frac{x_o v_{go}}{v_o} + \frac{C_{fo} T_o P_o}{v_o}\left(\frac{v_{fgo}}{h_{fgo}}\right)^2 \qquad [15.6.2]$$

where C is the specific heat (J/kg K), h is the specific enthalpy (J/kg), P is the absolute pressure (Pa), T is the absolute temperature (K), v is the specific volume (m^3/kg), x is the mass fraction of vapour, and subscripts f, fg, g and o indicate the liquid, the liquid–vapour transition, the vapour and stagnation, respectively. The inlet void fraction α_o is

$$\alpha_o = \frac{x_o v_{go}}{v_o} \qquad [15.6.3]$$

The specific volume of the fluid is

$$v_o = x_o v_{go} + (1 - x_o) v_{fo} \qquad [15.6.4]$$

The following pressures are defined: P the pressure, P_b the back pressure at the orifice, P_c the critical pressure, P_o the stagnation pressure in the vessel and P_s the saturation pressure of the liquid (all pressures absolute in Pa). Subscripts 1 and 2 denote upstream and downstream ends of the outlet line, respectively. The corresponding pressure ratios are:

$$\eta = \frac{P}{P_o} \qquad [15.6.5]$$

$$\eta_c = \frac{P_c}{P_o} \qquad [15.6.6]$$

$$\eta_s = \frac{P_s}{P_o} \qquad [15.6.7]$$

where the subscripts c and s denote critical and saturation, respectively.

For the outlet line the following expression is used for the critical pressure at the downstream end:

$$P_{2c} = \frac{W_{act}}{A_2}\left(\frac{P_o\omega}{\rho_o}\right)^{1/2} \quad [15.6.8]$$

where A_2 is the cross-sectional area of the outlet line (m^2), W is the mass flow (kg/s), ρ is the density (kg/m^3) and the subscript act indicates actual.

Saturated liquid

For the case where the inlet fluid condition is a saturated liquid, the vapour fraction $x_o = 0$.

A value of the parameter ω is calculated from Equation 15.6.2. This value is then used in the following equation to determine the critical pressure ratio η_c:

$$\eta_c^2 + (\omega^2 - 2\omega)(1-\eta_c)^2 + 2\omega^2 \ln\eta_c + 2\omega^2(1-\eta_c) = 0 \quad [15.6.9]$$

From the value of η_c so obtained, the critical pressure P_c is calculated using Equation 15.6.6.

If $P_c < P_b$ the flow is not choked, and P is set equal to P_b. The mass flux is then calculated from the following equation:

$$\frac{G}{(P_o/v_o)^{1/2}} = \frac{(-2\{\omega\ln(P/P_o) + (\omega-1)[1-(P/P_o)]\})^{1/2}}{\omega(P_o/P-1)+1} \quad [15.6.10]$$

where G is the mass velocity (kg/m^2 s). If $P_c > P_b$ the flow is choked and the mass flux may be obtained either from Equation 15.6.10 or from

$$\frac{G_c}{(P_o/v_o)^{1/2}} = \frac{\eta_c}{\omega^{1/2}} \quad [15.6.11]$$

Two-phase mixture

For the case where the inlet fluid condition is a two-phase gas–liquid mixture, the vapour fraction x_o has a finite value. Otherwise the calculation procedure is essentially the same as for the case of a saturated liquid.

Subcooled liquid

For the case where the inlet fluid condition is a subcooled liquid, a distinction is made between a low degree of subcooling and high subcooling.

A form of the parameter ω appropriate to the saturated condition is defined as

$$\omega_s = \frac{C_{fo}T_oP_s}{v_{fo}}\left(\frac{v_{fgo}}{h_{fgo}}\right)^2 \quad [15.6.12]$$

The condition for low subcooling is

$$\eta_s \geq \frac{2\omega_s}{1+2\omega_s} \quad [15.6.13]$$

If the case is one of low subcooling, the fluid flashes in the throat.

The value of the parameter ω_s is then used to determine the critical pressure ratio η_c:

$$\frac{\omega_s + (1/\omega_s) - 2}{2\eta_s}\eta_c^2 - 2(\omega_s - 1)\eta_c + \omega_s\eta_s\ln\left(\frac{\eta_c}{\eta_s}\right) + \frac{3}{2}\omega_s\eta_s - 1 = 0 \quad [15.6.14]$$

From the value of η_c so obtained, the critical pressure P_c is calculated using Equation 15.6.6.

The mass flux is calculated from the following equation:

$$\frac{G}{(P_o/v_{fo})^{1/2}} = \frac{\{2(1-\eta_s)+2[\omega_s\eta_s\ln(\eta_s/\eta)-(\omega_s-1)(\eta_s-\eta)]\}^{1/2}}{\omega_s(\eta_s/\eta-1)+1} \quad [15.6.15]$$

As the condition of a saturated liquid is approached $P_o \to P_s$ and $\eta_s \to 1$, so that Equations 15.6.14 and 15.6.15 reduce to Equations 15.6.9 and 15.6.10.

If the case is one of high subcooling, no flashing occurs at the throat. The critical pressure ratio is

$$\eta_c = \frac{P_s}{P_o} \quad [15.6.16]$$

and the critical pressure is the saturation pressure P_s.

The mass flux is given by Equation 15.6.15, which for this case reduces to

$$\frac{G_c}{(P_o/v_{fo})^{1/2}} = [2(1-\eta_s)]^{1/2} \quad [15.6.17]$$

or

$$G_c = [2\rho_{fo}(P_o - P_s)]^{1/2} \quad [15.6.18]$$

This completes the set of expressions for the mass flow through the valve orifice. It remains to consider the valve sizing and selection and the effect of the inlet and outlet lines.

Valve sizing

The pressure relief requirement is specified as a required mass flow. The actual mass flux is obtained by the methods just described. The required area of the valve orifice is then

$$A_{req} = \frac{W_{req}}{KG_{act}} \quad [15.6.19]$$

where A is the cross-sectional area of the valve (m^2), K is the valve discharge coefficient and the subscript req denotes required.

A valve size is then selected. Since, in general, this will have an orifice cross-sectional area slightly larger than that required, the actual mass flow will also be larger:

$$W_{act} = KA_{act}G_{act} \quad [15.6.20]$$

It is this actual mass flow, which is used in the piping calculations which follow.

Inlet line

The treatment of the inlet and outlet piping conforms to the API requirements. For the inlet piping, these are that the piping be as short as possible with the recommendation that the line losses be limited to 3% of the gauge set pressure.

The pressure drop in the inlet line is determined from the equation

$$\Delta P_{in} = \frac{1}{2}\bar{v}_{in}\left(\frac{W_{act}}{A_{in}}\right)^2\left[4f\left(\frac{L_{in}}{D_{in}}\right)\right] + \frac{gH}{\bar{v}_{in}} \qquad [15.6.21]$$

where A_{in} is the cross-sectional area of the inlet pipe (m^2), D_{in} is the diameter of the inlet pipe (m), f is the Fanning friction factor, g is the acceleration due to gravity (m/s^2), H is the change in elevation (m), L_{in} is the length of the inlet pipe (m), ΔP_{in} is the total pressure difference across the inlet pipe (Pa) and $\bar{v}_{in}$ is the average specific volume in the inlet pipe (m^3/kg). The value of K is taken as 0.95.

The average specific volume in the inlet is evaluated at 0.98 of the stagnation pressure, so that

$$\bar{v}_{in} = v_{fo}\left[\omega\left(\frac{1}{0.98} - 1\right) + 1\right] \qquad [15.6.22]$$

However, if the liquid is subcooled and $P_s/P_o < 0.98$, then $v_{in} = v_{fo}$.

Outlet piping

For the outlet piping, a calculation is made to determine the maximum allowable length of the pipe. This is governed by the maximum allowable back pressure on the valve. This back pressure is specified by the SRV manufacturer and is typically 10% of the differential set pressure for unbalanced valves and up to 50% for balanced valves.

The maximum allowable length of the outlet line is determined from the equation

$$4f\left(\frac{L_2}{D_2}\right) = 2\frac{P_o\rho_o}{(W_{act}/A_2)^2}\left\{\frac{\eta_1-\eta_2}{1-\omega} - \frac{\omega}{(1-\omega)^2} \times \ln\left[\frac{(1-\omega)\eta_1+\omega}{(1-\omega)\eta_2+\omega}\right]\right\} + 2\ln\left[\frac{(1-\omega)-\eta_1+\omega}{(1-\omega)\eta_2+\omega}\left(\frac{\eta_2}{\eta_1}\right)\right] \qquad [15.6.23]$$

with

$$\eta_1 = \frac{P_1}{P_o} \qquad [15.6.24]$$

$$\eta_2 = \frac{P_2}{P_o} \qquad [15.6.25]$$

where D_2 is the diameter of the outlet pipe (m) and L_2 is the length of the outlet pipe (m).

Illustrative example

As an illustration of this method, consider the example given by Leung, which is the design of an SRV for the venting of liquefied ammonia. The example is given in two parts, Part A being the determination of the mass flux for the specified liquid condition and Part A the sizing of the valve itself and of the inlet and outlet lines.

Part A: mass flux

The initial, or stagnation, state of the liquid is

$P_o = 1 \times 10^6$ Pa
$T_o = 298$ K
$v_{fo} = 0.001658\ m^3/kg$
$v_{go} = 0.1285\ m^3/kg$
$v_{fgo} = 0.1268\ m^3/kg$
$C_{fo} = 4806$ J/kg K
$h_{fgo} = 1165430$ J/kg

The mass flux is calculated for two liquid conditions: (1) saturated liquid, $x_o = 0$; and (2) two-phase gas–liquid mixture, $x_o = 0.1$. The latter is included to illustrate how this liquid condition is tackled, but is not strictly relevant to the main problem.

Case 1: saturated liquid

$x_o = 0$
$v_o = 0.001658\ m^3/kg$
$\rho_o = 603\ kg/m^3$
$\alpha_o = 0$
$\omega = 10.2$ (from Equation 15.6.2)
$\eta_c = 0.85$ (from Equation 15.6.9)
$G_c = 6510\ kg/m^2\,s$ (from Equation 15.6.11)

Case 2: two-phase mixture

$x_o = 0.1$
$v_o = 0.014\ 34\ m^3/kg$ (from Equation 15.6.4)
$\rho_o = 69.7\ kg/m^3$
$\alpha_o = 0.9$ (from Equation 15.6.3)
$\omega = 2.1$ (from Equation 15.6.2)
$\eta_c = 0.7$ (from Equation 15.6.9)
$G_c = 6010\ kg/m^2\,s$ (from Equation 15.6.11)

Part B: sizing of valve and piping

The pressures around the SRV are:

Atmospheric pressure = 0.101 MPa (a)
Backpressure = 0.0101 MPa (a)
Set pressure = 0.915 MPa (a) = 1.016 (g)
Differential set pressure = 0.915 − 0.101 = 0.814 MPa
Relieving pressure = 1.0 MPa (a)

The gauge relieving pressure is 110% of the differential set pressure ($1.1 \times 0.814 = 0.90$) and thus the absolute relieving pressure is 1.0 MPa. The details of the SRV piping are:

Elevation of valve, $H = 1$ m
Length of inlet pipe, $L_{in} = 1$ m
Equivalent length of outlet pipe, $L_2 = 20$ m
Outlet pipe Fanning friction factor, $f = 0.005$

The SRV is sized for the saturated liquid condition. The valve is required to vent a mass flow W_{req} of 1.0 kg/s, the actual mass flux G_{act} is 6510 kg/s and the value of the valve coefficient K is 0.95. Then from Equation 15.6.19 the required area A_{req} of the valve orifice is $1.62 \times 10^{-4}\ m^2$. Consulting the table of standard valve orifice sizes, the next size up is an F size valve with an actual area A_{act} of $1.98 \times 10^{-4}\ m^2$. This is the valve size selected.

Then from Equation 15.6.20 the actual mass flow is $W_{act} = 1.22$ kg/s.

For the size-F valve the diameter D_{in} and cross-sectional area A_{in} of the inlet are 0.0409 m and 1.313×10^{-3} m^2, respectively. An inlet line of the same diameter is used and a check is made that the inlet line losses do not exceed 3% of the gauge set pressure. Then Equation 15.6.22 with $\omega = 10.2$ and $v_o = 0.001658$ m^3/kg yields $\bar{v}_{in} = 0.002$ m^3/kg.

The pressure drop ΔP_{in} in the inlet line is calculated from Equation 15.6.21. For the vertical line the length L_{in} and the elevation H are identical at 1 m. The value obtained for ΔP_{in} is 5328 Pa. The inlet line losses are thus much less than 3% of the gauge set pressure of 1.016×10^6 Pa.

For the outlet line, the calculation required is to establish that the equivalent length of 20 m is within the maximum allowable length of the line. The first step is to determine the values to be used for the pressures P_1 and P_2 at the inlet and outlet of the line, respectively. For P_1 the value is 10% of the gauge set pressure and is thus 0.183 MPa. For P_2, from Equation 15.6.8 $P_{2c} = 5.64 \times 10^4$ Pa. The back pressure P_b is 10.1×10^4 Pa. Hence $P_{2c} < P_b$ and thus P_2 is set equal to P_b. Then from Equations 15.6.24 and 15.6.25 $\eta_1 = 0.183$ and $\eta_2 = 0.101$.

The line diameter D_2 is taken as that of the valve outlet, which is 0.0629 m, giving a corresponding cross-sectional area A_2 of 3.089×10^{-3} m^2. Then with a value of the Fanning friction factor f of 0.005, Equation 15.6.23 yields a maximum allowable line length of 28 m. The actual equivalent line length is 20 m, which is within the allowable range.

15.6.5 Two-phase flow: overall system

As indicated earlier, there is more to the design of a pressure relief for a two-phase vapour–liquid mixture than the sizing of the valve orifice. Accounts of overall design for pressure relief include those by Crawley and Scott (1984) and S.D. Morris (1988b). An overview, with particular reference to offshore systems, has been given by Selmer-Olsen (1992).

Selmer-Olsen identifies a number of difficulties: (1) there is no accepted method of deciding when two-phase flow needs to be considered; (2) there is no accepted design method for two-phase flow; (3) the widely used API method may be inadequate; (4) the methods available are generally not sufficiently validated by experimental work, particularly on the large scale and (5) there is a strong coupling between the thermohydraulic behaviour of the fluid system and the flow through the pressure relief device for which the commonly used modular approach may be inappropriate.

The occurrence of two-phase flow can completely alter the characteristics of the relief system, in particular the behaviour of the fluid in the pipework downstream of the pressure relief valve. This can result in increased back pressure or in choking in the relief header, possibly with oscillating location of the choking throat between the valve and the pipe – the multiple choke effect. Potential consequences of such flow effects are prolonged depressurization times, intermittent flows, high header pressures and blowback to lower pressure sources, and high thermal and mechanical loads.

The author identifies the following work relevant to the design of a pressure relief system for two-phase flow. Work on the sizing of the valve itself includes that of Simpson, Rooney and Grattan (1979), Sallet and co-workers (Sallet, 1984, 1990b,c; Sallet and Somers, 1985), Campbell and Medes (1985), Friedel and Kissner (1985, 1987, 1988), S.D. Morris (1988b, 1990a,b), Morley (1989a,b), Alimonti, Fritte and Giot (1990), Curtelin (1991), M.R. Davis (1991), Simpson (1991) and Leung (1992a).

Treatments of the inlet line to the valve are given by O.J. Cox and Weirick (1980), Zahorsky (1985), S.D. Morris (1988b) and Leung (1992a) and treatments of the outline line are given by Richter (1978b), Friedel and Lohr (1982), S.D. Morris (1988b, 1990b) and Leung (1992a).

The author states that the method of Leung (1992a), based on the homogeneous equilibrium model (HEM) of two-phase flow appears to be the increasingly preferred choice for flow through the valve, for which it is said to be reasonably conservative. He comments, however, that it may well not be conservative for the associated inlet and outlet lines and downstream tanks.

The effects of non-equilibrium assumptions are discussed by Bilicki and Kestin (1990) and Lemonnier *et al.* (1991).

Experimental work on the flows through a configuration relevant to pressure relief has been done by Selmer-Olsen (1991, 1992), using a converging–diverging nozzle with inlet and outlet lines. For short nozzles and low pressures the flows exceeded those predicted by the HEM by a factor of up to 2. As the throat length and pressure were increased the predictions of the HEM were approached, but never reached. The concomitant of this is that the flows in the inlet and outlet lines may be higher than predicted by the HEM.

15.6.6 Two-phase flow: computer codes

A number of computer codes have been developed for pressure relief flows. An account is given by Selmer-Olsen (1992).

One of these codes is BLOW-DOWN by Nylund (1983 DnV Rep. 83-1317, 1984). Another is the BLOWDOWN code of Haque, Richardson and Saville (1992), described in the next section. Other codes include those by Middleton and Lloyd (1984), Bayliss (1987), Klein (1987), Evanger *et al.* (1990) and the NEL code PIPES.

A benchmark exercise on vessel depressurization methods is described by Skouloudis (1990 CEC EUR 12602 EN).

15.7 Vessel Blowdown

Emergency shut-down of a hydrocarbon processing plant may involve the depressurization of major process vessels by blowdown to the flare. On offshore production platforms blowdown is a normal part of emergency shut-down.

In many cases, blowdown will be two-phase. One aspect of the treatment of blowdown is therefore the estimation of the flow. The account of flow in relief systems given in the previous section is applicable to blowdown. The other aspect is the hazards associated with blowdown, particularly the fall in the temperature of the gas.

15.7.1 BLOWDOWN

A treatment which covers both aspects has been given by Richardson, Saville and co-workers (S.M. Richardson, 1989; Haque *et al.*, 1990; Haque, Richardson and Saville, 1992; S.M. Richardson and Saville, 1992).

The hazards arise essentially due to the large temperature drop associated with the sudden depressurization of a vessel containing gas or vapour. Thus, for example, if nitrogen at 150 bar and atmospheric temperature is expanded adiabatically down to atmospheric pressure the isentropic expansion gives a final gas temperature of 78 K.

The type of vessel of interest is one that retains, under pressure, a vapour space, a layer of liquid hydrocarbon and beneath that a layer of water. The potential effects of the

temperature drop associated with sudden depressurization are chilling of the vessel walls, condensation of vapour to form droplets with carryover of these droplets into the flare header and formation of hydrates in the hydrocarbon liquid. It is therefore of practical interest to be able to predict the temperature profiles of the fluid phases and of the vessel walls.

An account of a model for vessel blowdown has been given by Haque, Richardson and Saville (1992). The model is embodied in the code BLOWDOWN. For a non-condensable gas, an acceptable estimate of the time profiles of pressure in and of flow from the vessel can generally be obtained assuming choked adiabatic flow. For this case the authors give:

$$P = P_o\left[1 + \frac{\gamma - 1}{2}\frac{A}{V}t\left(\frac{\gamma R T_o}{M}\right)^{1/2}\left(\frac{2}{\gamma+1}\right)^{(\gamma+1)/(2\gamma-2)}\right]^{-2\gamma/(\gamma-1)} \quad [15.7.1]$$

$$W = A\rho_o\left(\frac{\gamma R T_o}{M}\right)^{1/2}\left(\frac{2}{\gamma+1}\right)^{(\gamma+1)(2\gamma-2)}\left(\frac{P}{P_o}\right)^{(\gamma+1)/2\gamma} \quad [15.7.2]$$

where A is the cross-sectional area of the choke (m^2), M is the molecular weight of the gas, R is the absolute pressure in the vessel (Pa), R is the universal gas constant (J/kg mole K), T is the absolute temperature of the gas (K), V is the volume of the vessel (m^3), W is the mass flow from the vessel (kg/s), γ is the ratio of the gas specific heats, ρ is the density of the gas (kg/m^3), and the subscript o indicates initial conditions in the vessel.

Since in this model the conditions are adiabatic, it excludes heat transfer between the gas and the wall of the vessel. By definition, therefore, it cannot be used to determine the temperature of the vessel wall. On these grounds alone a fuller model is needed. Moreover, it turns out that this model is also inadequate for the representation of the more complex vessel blowdown scenarios of the kind described earlier. The BLOWDOWN model has been developed to meet this requirement. It consists of a thermophysical model in combination with relationships for heat, mass and momentum and for flow through the choke. The thermophysical properties are calculated using the computer package PREPROP.

The vessel is modelled as a set of three fluid zones (gas, liquid hydrocarbon and water), three corresponding vessel wall zones, and the outflow system consisting of the pipework between the vessel and the choke, the choke itself and the pipework downstream of the choke.

The outflow from the vessel is modelled as follows. It is assumed that the pressure drop at the orifice is such that the flow is critical. For a gas the flow is choked and is determined by its velocity through the choke which is equal to the velocity of sound in the gas:

$$a = \left[\left(\frac{\partial P}{\partial \rho}\right)_s\right]^{1/2} \quad [15.7.3]$$

where a is the velocity of sound in the gas at the choke (m/s), P is the absolute pressure at the choke (Pa), ρ is the density of the gas at the choke (kg/m^3) and subscript s denotes isentropic conditions. The expansion is isentropic so that

$$S_i = S_c \quad [15.7.4]$$

where S is the entropy of the gas (kJ/kmol K) and the subscripts c and i denote choke and vessel, respectively. The energy balance is

$$H_i = H_c + a^2/2 \quad [15.7.5]$$

where H is the enthalpy of the gas (J/kg). These three equations are solved simultaneously using the thermophysical package. The mass flow is then obtained as

$$W = C_D A a \rho_c \quad [15.7.6]$$

where C_D is the coefficient of discharge. The value of C_D at the choke is generally taken as 0.8.

For a gas–liquid, thus two-phase, fluid the flow is again assumed to be critical, but in this case the velocity does not equal the speed of sound. Consider changes in the overall pressure difference caused by, say, decreasing the downstream pressure. At small overall pressure differences the liquid is in the metastable condition and does not flash as it passes through the orifice. As the overall pressure difference increases, the limit of meta-stability is reached. There is then no further change either in the flow through the orifice or the pressure at the orifice. The fluid downstream of the orifice undergoes flashing. The behaviour of the fluid is therefore analogous to that of a gas in that a critical condition is reached, but differs from it in that the speed of sound plays no role.

For the pressure at which metastability can no longer be supported, the authors give the following relation, generalized from the work of Abuaf, Jones and Wu (1983):

$$P_s - P_{ms} = 1.1 \times 10^{11}\frac{\sigma^{1.5}(T/T_c)^8(1 + 2.2 \times 10^{-8}\Pi^{0.8})^{0.5}}{T_c^{0.5}[1 - (\rho_g/\rho_l)]} \qquad T < 0.85T_c \quad [15.7.7]$$

where P_{ms} is the absolute pressure at which metastability is no longer supported (Pa), P_s is the absolute saturated vapour pressure of the liquid at temperature T (Pa), T is the absolute temperature of the liquid upstream of the orifice (K), T_c is the absolute critical temperature of the liquid (K), Π is the depressurization rate (N/m^2 s), ρ_g is the density of the gas (kg/m^3), ρ_l is the density of the liquid (kg/m^3), is the surface tension of the liquid (N/m), and subscripts g and l denote the gas and liquid, respectively. The depressurization rate Π is approximated as the pressure difference across the orifice divided by the time required to traverse twice the diameter of the orifice.

The flow conditions are then as follows. For the range

$P_u > P_s,\ P_d < P_s$:

$P_d > P_{ms}$ flow unchoked

$P_d \le P_{ms}$ flow choked

where subscripts d and u denote downstream and upstream, respectively. The mass flow through the orifice is given by

$$W = C_D A[2\rho_l(P_u - P_x)]^{1/2} \quad [15.7.8]$$

where C_D is the coefficient of discharge and P_x is an appropriate absolute orifice pressure (Pa). The pressure P_x is the greater of P_{ms} and P_d. The coefficient of discharge is taken as approximately 0.65 for an orifice and unity for a properly formed nozzle.

The situations treated in this work are complex and it is not practical to construct a model that represents in equal detail all the relationships involved. Rather, the authors proceeded by seeking to identify the more significant phenomena and to model these accurately.

Experiments done to validate the model are described by Haque *et al.* (1990, 1992) and S.M. Richardson and Saville (1992). Two vessels were utilized, one 1.52 m long and the other 3.24 m long. In some tests the fluid used was nitrogen, in others it was a mixture of light hydrocarbons. The papers cited present for selected experiments a number of time profiles of the pressure in the vessel and of the temperatures of the gas and the vessel walls.

Some of these time profiles for tests of blowdown through a top outlet are shown in Figure 15.18. Figures 15.18(a) and

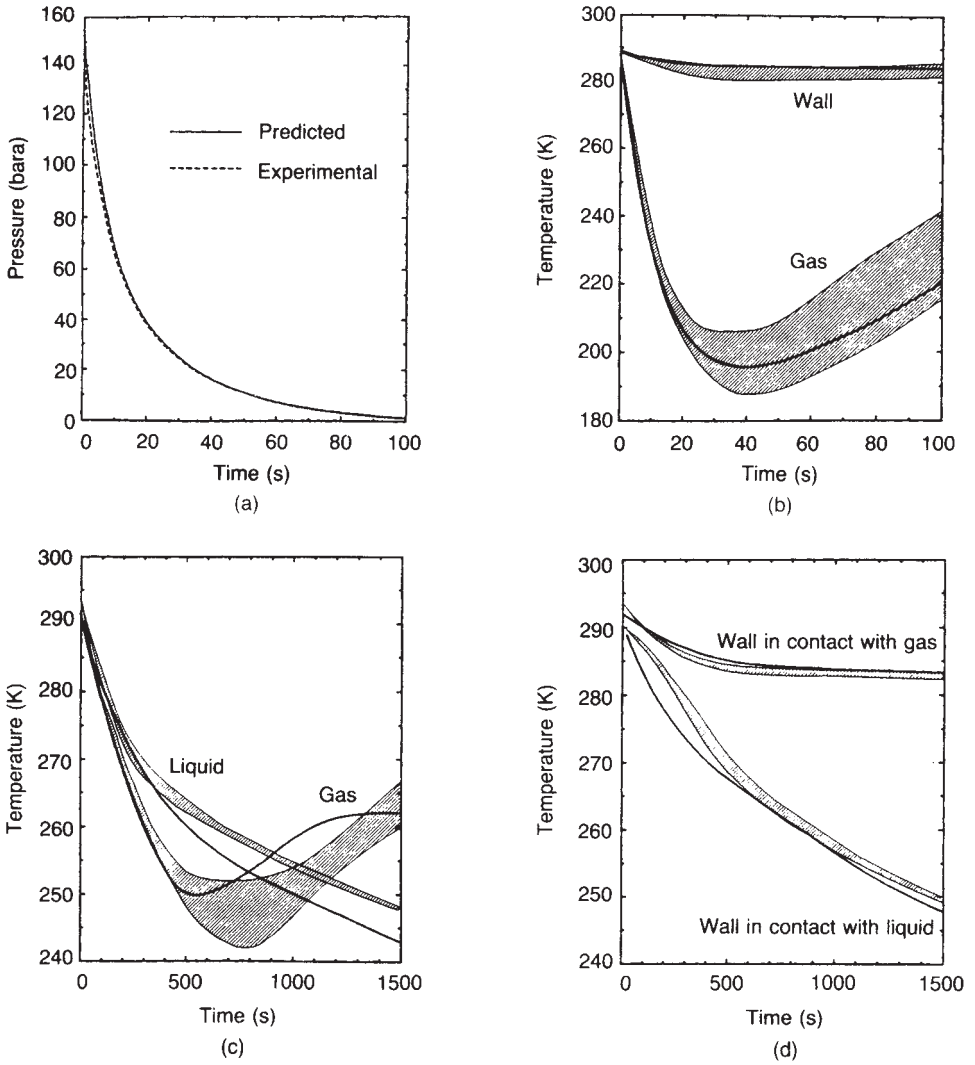


Figure 15.18 *Profiles of pressure and temperature in blowdown of a vessel (Haque et al., 1992): (a) pressure in vessel for nitrogen; (b) temperatures of bulk gas and of vessel wall for nitrogen; (c) temperatures of bulk gas and of bulk liquid for hydrocarbon mixture (C_1, 66.6%; C_2, 3.5%; and C_3, 30.0%); (d) temperature of sections of vessel inside wall in contact with (1) gas and (2) liquid for hydrocarbon mixture (C_1, 66.6%; C_2, 3.5%; and C_3, 30.0%). Vertical vessels, top outlets. Hatched regions span experimental measurements; solid lines are predictions (Courtesy of the Institution of Chemical Engineers)*

(b) are for a vessel containing nitrogen; the first shows the profiles of the vessel pressure, the second those of the temperatures of the gas and of the vessel wall Figures 15.18(c) and (d) are for a vessel containing hydrocarbons with the composition C_1 66.5%, C_2 3.5% and C_3 30.0%; the first shows the profiles of the gas and the liquid and the second those of the vessel wall in contact with these two phases.

Case studies of the application of the model are also described. One is for the blowdown of the suction scrubber of a gas compressor and another for the blowdown of a gas–condensate separator. The model is also applicable to the prediction of an accidental release from a vessel.

15.8 Vessel Rupture

In certain circumstances a vessel may rupture completely. If vessel rupture occurs, a large vapour cloud can be formed very rapidly. Accounts of vessel rupture include those by Hardee and Lee (1974, 1975), Hess, Hoffmann and Stoeckel (1974), J.D. Reed (1974), Maurer *et al.* (1977), AF. Roberts (1981/82) and B. Fletcher (1982).

15.8.1 Vaporization

If a vessel containing a superheated liquid under pressure ruptures, a proportion of the liquid vaporizes. This initial flash fraction is determined by the heat balance, the latent heat of vaporization being supplied by the fall in the sensible heat of the liquid. The rapid formation of vapour bubbles also generates a spray of liquid drops so that typically most or all of the remaining liquid becomes airborne, leaving little or no residue in the vessel.

This effect has been demonstrated by J.D. Reed (1974), who carried out experiments on sudden vessel depressurization. In one series of experiments, 3.5 kg of liquid ammonia contained at an absolute pressure of 3 bar and a temperature of $-9°C$ in a vessel 15 cm diameter and 45 cm high was released using a quick release lid. One of the experiments is shown in Figure 15.19, in which the time interval between the first and last frame is one-sixth of a second. In all the experiments at least 90% of the liquid ammonia was vaporized.

Similarly, Maurer *et al.* (1977) have carried out experiments (described below) on the rapid release of propylene held at pressures of 22–39 bar and temperatures of 50–80°C. The flash fraction of vapour was 50–65% and the remaining liquid formed spray.

An investigation of the extent of vapour and spray formation and of retained liquid has been made by B. Fletcher (1982), who carried out experiments, principally in a vertical vessel of 127×47 mm cross-section, in which a charge of superheated Refrigerant 11 was depressurized and the liquid residue was determined. The results are correlated in terms of the ratio (h_b/h_o) of the height reached by the liquid on depressurization h_b to the initial height of the liquid h_o, as shown in Figure 15.20. The parameter in the figure is the ratio K of the vent area to the vessel cross-sectional area. The mass of retained liquid is given by the relation

$$\frac{m_r}{m_o} = \frac{1}{K}\left[\frac{m_v \rho_l}{m_o \rho_v} + \left(1 - \frac{m_v}{m_o}\right)\right]^{-1} \qquad [15.8.1]$$

where m is the mass of fluid, ρ is the density, and subscripts l, o, r and v denote the liquid, initial, retained and vapour, respectively. For a full bore release the value of the constant K is unity.

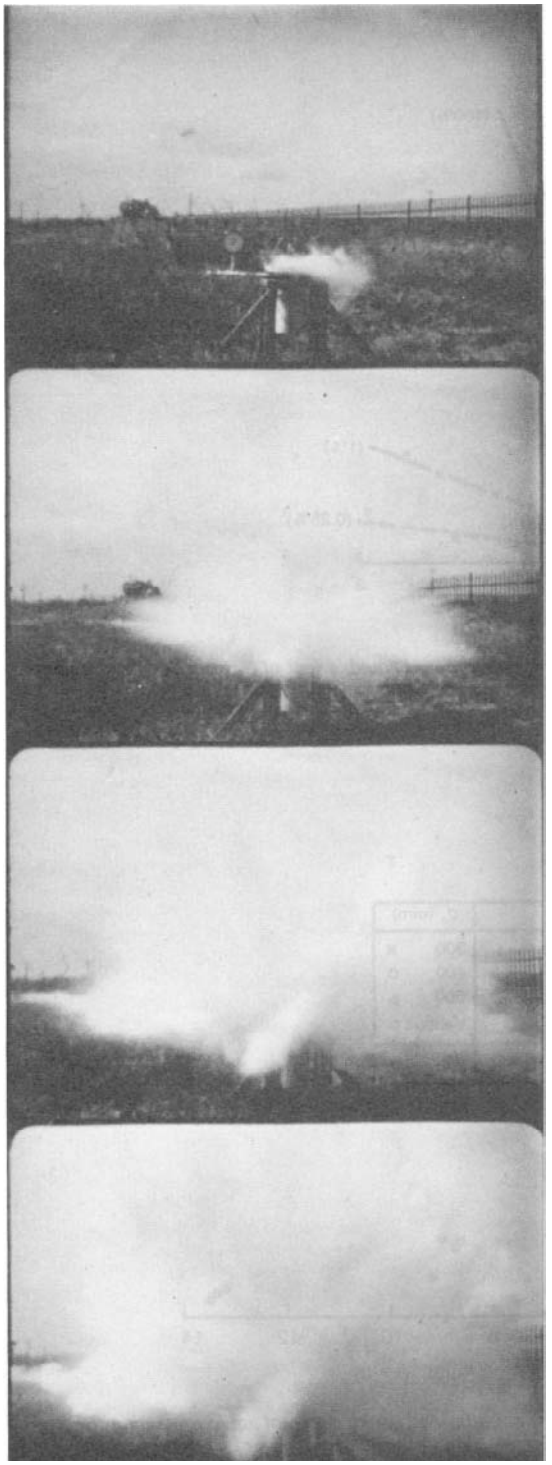


Figure 15.19 *Sudden depressurization of a vessel containing liquid ammonia under pressure (J.D. Reed, 1974) (Courtesy of Elsevier Publishing Company)*

Further correlation of the results is given in terms of the superheat ΔT_{onb} required for vapour nucleation, and hence nucleate boiling. The expression for superheat is

$$\Delta T \approx \frac{4RT_{sat}\sigma}{\Delta H_v M \delta P_l} \quad \rho_l \gg \rho_v;\ 4\sigma/P_l\delta \ll 1 \qquad [15.8.2]$$

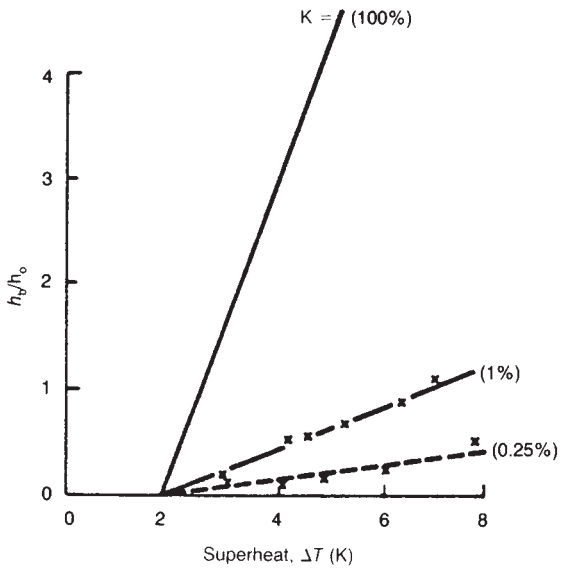


Figure 15.20 *Sudden depressurization of a vessel containing superheated liquid: effect of a restriction on the height to which the liquid rises (B. Fletcher, 1982) (Courtesy of the Institution of Chemical Engineers)*

where ΔH_v is the latent heat of vaporization, M is the molecular weight, P is the absolute pressure, R is the universal gas constant, T is the absolute temperature, ΔT is the superheat, δ is the diameter of the vapour nucleus, σ is the surface tension and subscripts onb and sat denote onset of nucleate boiling and saturation, respectively.

The proportion of retained liquid was expressed in terms of the ratio (h/h_v) of the height h of the liquid residue to the height h_v of the vessel. The limiting value of the superheat, or value at the onset of nucleate boiling (ΔT_{onb}), corresponds to the situation where all the liquid is retained and thus $h/h_v = 1$.

For Refrigerant 11 the value of ΔT_{onb} is about 1.9 K. Using this value in Equation 15.8.2 with the appropriate physical value for Refrigerant 11 a value of δ can be obtained. Then, utilizing this value, the superheat ΔT_{onb} for other substances can be obtained.

The correlation given by Fletcher for the superheat effect is shown in Figure 15.21. The proportion of retained liquid h/h_v falls off rapidly with increase in the ratio $\Delta T/\Delta T_{onb}$ and for values in excess of about 12 falls to less than 5%.

A comparison of the proportion of liquid retained in the tank cars in several transport incidents with that estimated from Equation 15.8.1 is given as:

Incident	*Liquid*	*Mass fraction retained* (%)	
		Reported	*Estimated*
Pensacola	Ammonia	50	40
Mississauga	Chlorine	10	13
Youngstown	Chlorine	44	37

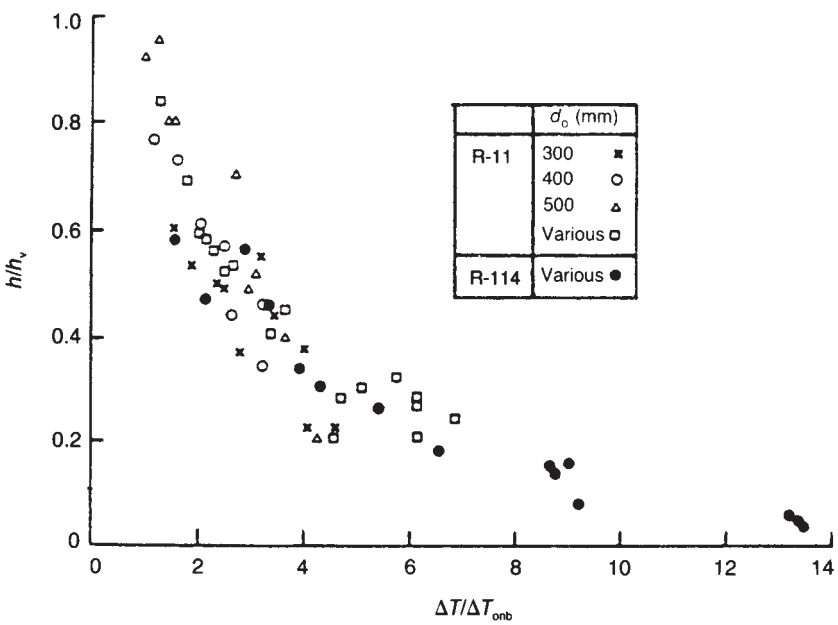


Figure 15.21 *Sudden depressurization of a vessel containing superheated liquid: depth of liquid remaining (B. Fletcher, 1992) (Courtesy of the Institution of Chemical Engineers)*

Further work on vaporization following vessel rupture has been described by Schmidli, Bannerjee and Yadigaroglu (1990).

15.8.2 Hardee and Lee model

An investigation of the rapid depressurization of a vessel containing a superheated liquid has been described by Hardee and Lee (1975). The growth of the cloud is considered to occur in three stages, as shown in Figure 15.22. The first stage is the expansion of the fluid from the original vessel pressure to atmospheric pressure, the second the entrainment of air, and the third the dispersion of the cloud.

For the first stage, the expansion is assumed to be isentropic and the flash fraction at the end of the expansion is given by the entropy balance

$$x_1 s_{v1} + (1 - x_1)s_{f1} = x_2 s_{v2} + (1 - x_2)s_{f2} \qquad [15.8.3]$$

where s is the specific entropy, x is the mass fraction of vapour and subscripts f and v denote liquid and vapour and 1 and 2 initial and final states, respectively.

The velocity of the expanding fluid may then be obtained from the energy balance. Taking the initial velocity u_1 of the liquid as zero,

$$x_1 h_{v1} + (1 - x_1)h_{f1} = x_2 h_{v2} + (1 - x_2)h_{f2} + u_2^2/2 \qquad [15.8.4]$$

where h is the specific enthalpy and u is the velocity.

The first stage is evidently to be regarded as virtually instantaneous. At the end of this stage the fluid consists of vapour and spray. In the second stage air is entrained, the spray is vaporized and the cloud grows. At the end of this stage the cloud has attained a height that thereafter does not increase. In the third stage the cloud grows, but only in the radial direction.

In the second stage, the momentum of the cloud increases linearly with time until the end of the stage is reached at the depressurization, or dump, time t_d. In the third stage, the momentum remains constant. For the second stage the volume of the expanding fluid is

$$V_2 = u_2 A_2 t \qquad [15.8.5]$$

where A_2 is the area of cloud perpendicular to direction of expansion at end of the second stage, t is the time and V is the volume of fluid; subscript 2 denotes the value at the end of expansion down to atmospheric pressure. At the end of the second stage, and hence at time t_d

$$V_2 = u_2 A_2 t_d \qquad [15.8.6]$$

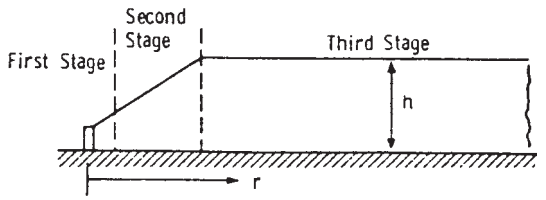


Figure 15.22 *Rupture of a vessel containing superheated liquid: cloud expansion process (Hardee and Lee, 1975) (Courtesy of Pergamon Press)*

The initial mass of fluid W may be expressed in terms of the volume given in Equation 15.8.6 as follows:

$$W = \rho_2 V_2 \qquad [15.8.7a]$$

$$= \rho_2 u_2 A_2 t_d \qquad [15.8.7b]$$

where ρ is the density. Then, during the second stage, the momentum ψ is

$$\psi = \rho_2 u_2^2 A_2 t \quad t < t_d \qquad [15.8.8a]$$

$$= \rho_2 u_2^2 A_2 t_d \quad t > t_d \qquad [15.8.8b]$$

$$= W u_2 \qquad [15.8.8c]$$

The momentum may be obtained via the momentum balance from the initial pressure P_1 and final pressure P_2 as follows:

$$(P_1 - P_2)A_1 = \rho_2 u_2^2 A_2 \qquad [15.8.9]$$

where A_1 is the area of the vessel aperture. Also, from Equations 15.8.8 and 15.8.9

$$\frac{A_1 t_d}{W} = \frac{u_2}{P_1 - P_2} \qquad [15.8.10]$$

For the momentum of a general moving vortex

$$\psi = c\rho u V \qquad [15.8.11]$$

where c is a constant. The value of the constant c is shown by the authors to be approximately 3/2. Then, from Equation 15.8.11:

$$\frac{dr}{dt} = u \qquad [15.8.12]$$

$$= \frac{2\psi}{3\rho V} \qquad [15.8.13]$$

where r is the radius of the cloud.

For a hemispherical cloud

$$V = \frac{2}{3}\pi r^3 \qquad [15.8.14]$$

Hence substituting from Equations 15.8.8a and 15.8.14 in Equation 15.8.13 and integrating

$$r = \left(\frac{2\rho_2 u_2^2 A_2}{\rho\pi}\right)^{1/4} t^{1/2} \qquad [15.8.15]$$

or, from Equation 15.8.8b

$$r = \left(\frac{2\psi}{\rho\pi t_d}\right)^{1/2} t^{1/2} \qquad [15.8.16]$$

At the end of this stage

$$r = \left(\frac{2\psi}{\rho\pi t_d}\right)^{1/4} t_d^{1/2} \qquad [15.8.17]$$

For the third stage, the height h of the cloud is constant at the value of the radius r reached at the end of the second stage. Then for a cylindrical cloud

$$V = \pi r^2 h \qquad [15.8.18]$$

Since the cloud is now relatively dilute it is possible to set, $\rho \approx \rho_a$, where ρ_a is the density of air. Then from Equations 15.8.13 and 15.8.18:

$$\frac{dr}{dt} = \frac{2\psi}{3\rho_a \pi r^2 h} \qquad [15.8.19]$$

and integrating

$$r = \left(\frac{2\psi}{\rho_a \pi h}\right)^{1/3} t^{1/3} \qquad [15.8.20]$$

The use of the model is assisted by the graphs given in Figures 15.23 and 15.24, which give the momentum and the dump time, respectively.

For a hazardous release there will be some concentration, corresponding to a cloud volume V, below which the cloud no longer presents a hazard. The model may be used to

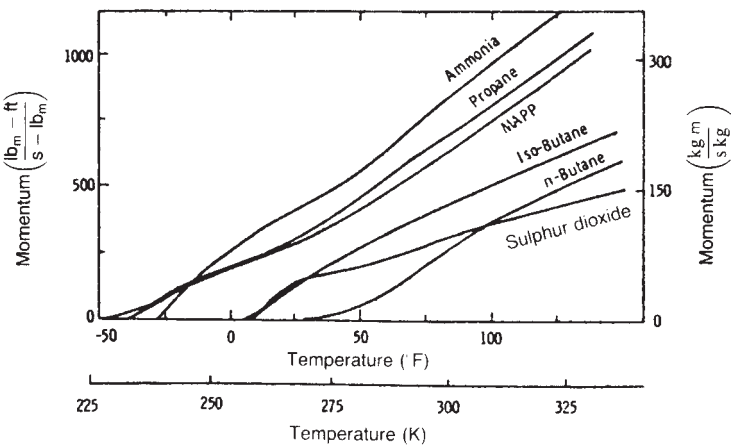


Figure 15.23 *Rupture of a vessel containing superheated liquid: momentum release per pound of fuel (Hardee and Lee, 1975) (Courtesy of Pergamon Press)*

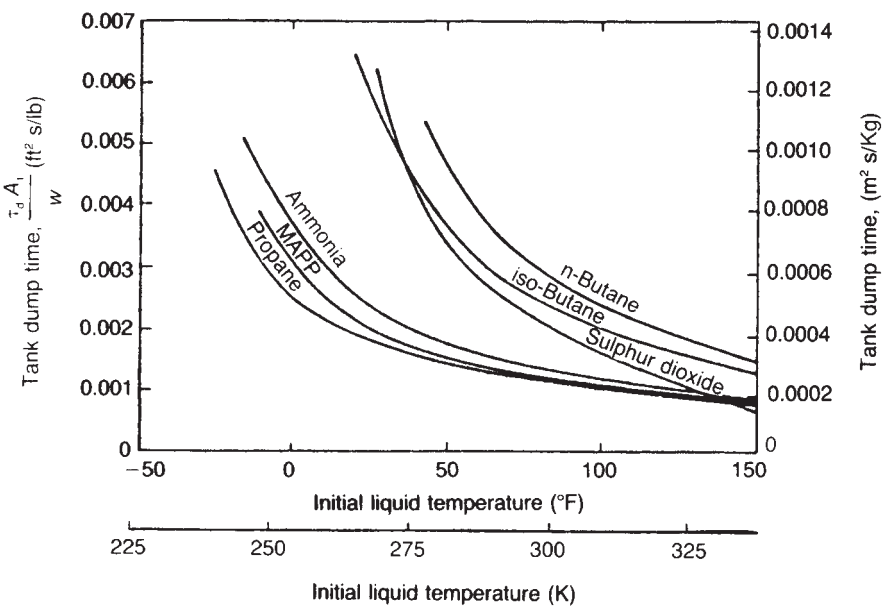


Figure 15.24 *Rupture of a vessel containing superheated liquid: vessel dump time (Hardee and Lee, 1975) (Courtesy of Pergamon Press)*

determine the range r and time t at which the concentration falls below this critical value.

The authors carried out experiments in which vessels containing up to 422 kg of propane and 436 kg of a methyl acetylene–propylene–propadiene (MAPP) mixture were suddenly depressurized and obtained good agreement for the increase of the cloud radius with time and for the cloud height.

Thus for a release of 29 kg of MAPP at a temperature of 284 K through an aperture of 0.728 m^2 the relation for the growth of the cloud radius, derived from Equation (15.8.20), is

$$r = 8.84t^{1/3} \qquad [15.8.21]$$

where r is the radius (m) and t the time (s). The cloud height is 2.74 m.

Hardee and Lee also describe the use of the model to determine cloud growth for the incidents of propane release at Lynchburg, Virginia, and of ammonia at Crete, Nebraska.

15.8.3 Model of Hess, Hoffman and Stoeckel

Another model for vessel rupture has been given by Hess, Hoffmann and Stoeckel (1974). The situation modelled is again the depressurization of a superheated liquid.

After the vessel burst the growth of the cloud is considered to occur in three stages. The first stage is expansion down to atmospheric pressure with flash-off of vapour and formation and partial evaporation of spray and some admixture of air. The second stage is the evaporation of the remaining spray and entrainment of air into the cloud. The third stage is the further entrainment of air and, if the fluid is flammable, the formation of a flammable mixture.

The model deals primarily with this third stage. For this stage, using spherical symmetry, the basic equation describing the variation of concentration c with radial distance r and time t is:

$$\frac{dc}{dt} = \epsilon\left[\frac{d^2c}{dr^2} + \frac{2}{r}\frac{dc}{dr}\right] \qquad [15.8.22]$$

where ϵ is eddy diffusion coefficient. Time zero is taken as the start of the third stage. The boundary conditions used are as follows: $0 < r < a$, $t = 0$, $c = c_0$; $r > a$, $t = 0$, $c = 0$. Then from a standard solution given by Carslaw and Jaeger (1959, p. 257), Equation 15.8.22 can be integrated to give

$$\frac{c}{c_o} = \frac{a^3}{6(\epsilon t)^{3/2}\pi^{1/2}}\exp\left(\frac{-r^2}{4\epsilon t}\right) \qquad [15.8.23]$$

where a is the radius of the initial cloud formed on completion of the bursting process and c_o is the concentration of vapour in the initial cloud.

The authors carried out experiments in which 40 and 60 mm diameter cylindrical vessels with a length/diameter ratio of 3.5 : 1, filled with liquid propane, were heated until they burst. The bursting of the vessels was recorded by high speed photography. They describe in detail the bursting of a 40 mm cylinder. The time for the vessel itself to burst was less than 1 ms. Following bursting the vapour cloud formed in two phases. In the first phase the propane expanded to ambient pressure and about half the liquid flashed off as vapour with the temperature dropping to about 230 K. It was estimated that without admixture of air the vapour would form a hemisphere with a radius of about 20 cm, but the actual radius was somewhat larger, implying that some air had already been mixed in. This phase was complete within about 3 ms. In the second phase the remaining liquid propane vaporized on mixing with air, from which it obtained the necessary heat of vaporization. It was estimated that from the energy balance the vapour–air mixture would form a hemisphere with a radius of about 46 cm. The average concentration of propane was then 20%. This phase was complete in about 8 ms.

The concentrations of vapour obtained following this bursting process were compared with those predicted by using Equation 15.8.23. The radius of and concentration in the initial cloud were obtained from the experiment. The eddy diffusion coefficient ϵ was obtained from the Prandtl mixing length formula:

$$\epsilon = lu' \qquad [15.8.24]$$

where l is the mixing length and u' the fluctuating velocity. The mixing length l was taken as the average eddy diameter and the fluctuating velocity u' was taken as the speed at which the eddies moved, both quantities being obtained from photographs. The parameters required for solution of Equation 15.8.23 were then

$c_o = 20\%$
$a = 46\,\text{cm}$
$\epsilon = 0.52\,m^2/s$

Using these values in the model, good agreement was obtained with the results of this experiment.

15.8.4 Model of Maurer *et al.*

A development of the model of Hess, Hoffman and Stoeckel has been described by Maurer *et al.* (1977). In the second model it is again assumed that there is a central highly mixed core at uniform concentration and that the concentration outside this core decays in a Gaussian manner, but the second model differs in that it allows for the variability of the eddy diffusion coefficient, which in the first model is assumed to be constant.

For the air entrainment stage, using spherical symmetry, the basic equations given are:

$$\frac{c}{c_c} = \exp\left\{X_c^2\left[1 - \left(\frac{r}{r_g}\right)^2\right]\right\} \quad r > r_g \qquad [15.8.25]$$

$$c_c = f(X_c)\frac{V_g}{(4\epsilon t)^{1.5}} \qquad [15.8.26]$$

$$r_g = X_c(4\epsilon t)^{1/2} \qquad [15.8.27]$$

where V_g is the effective volume of vapour, X_c is a parameter characterizing the mass fraction of gas in the core, and subscripts c and g denote the core concentration and the core radius, respectively. The volume V_g is taken as twice the mass divided by the density at standard pressure and temperature; this allows for the use of spherical symmetry to model a hemispherical cloud.

The parameter $f(X_c)$ is obtained experimentally. The value used is 1.36, which corresponds to a fraction of vapour in the core of 50%.

In addition, as observed by A.F. Roberts (1981/82), the following additional relation for the eddy diffusion coefficient may be obtained from a graph of experimental results given by the authors:

$$\epsilon = 0.75 V_g^{1/3} \left(\frac{t}{V_g^{1/3}} \right)^{-1/4} \qquad [15.8.28]$$

Experiments were carried out in which cylindrical vessels containing propylene were heated up and then made to burst by mechanical means or by a small explosive charge. The quantities of propylene used ranged from 0.124 to 452 kg, the vessel in this latter case being 0.7 m diameter × 2.8 m long. The propylene was heated to temperatures of 50–80°C corresponding to pressures of 22–39 bar. After rupture and flash evaporation the vapour was ignited and overpressure generated was recorded. Some 50–65% of the liquid vaporized and the rest formed spray. The propagation velocity of the cloud boundary was followed by the condensation contours, which correspond to vapour concentrations of 1–3%.

The expansion velocities obtained, and the turbulence generated, were high. Only a very small proportion of the mechanical energy available was required to generate this turbulence.

The authors correlate their results in terms of a reduced time, $t/V_g^{1/3}$, a dimensionless time $\tau = \epsilon t/V_g^{2/3}$ and a scaled distance $r/V_g^{1/3}$. Some of these results are shown in Figures 15.25 and 15.26. Figure 15.25 shows the propagation velocity w of the cloud boundary. The plateau at short times corresponds to the expansion velocities predicted thermodynamically, which ranged from 240 to 370 m/s for vessel preheats of 35 and 80°C, respectively. Figure 15.26 gives the overpressures measured due to flash evaporation.

Figure 15.27 shows the concentration profiles and contours predicted by the model. Figure 15.28 shows the ratio $V_{g,ign}/V_g$ of the flammable volume $V_{g,ign}$ to the total volume V_g as a function of t. The maximum flammable fraction is 70% and the period during which a flammable mixture exists at all is $0.15 < t < 0.4$ s.

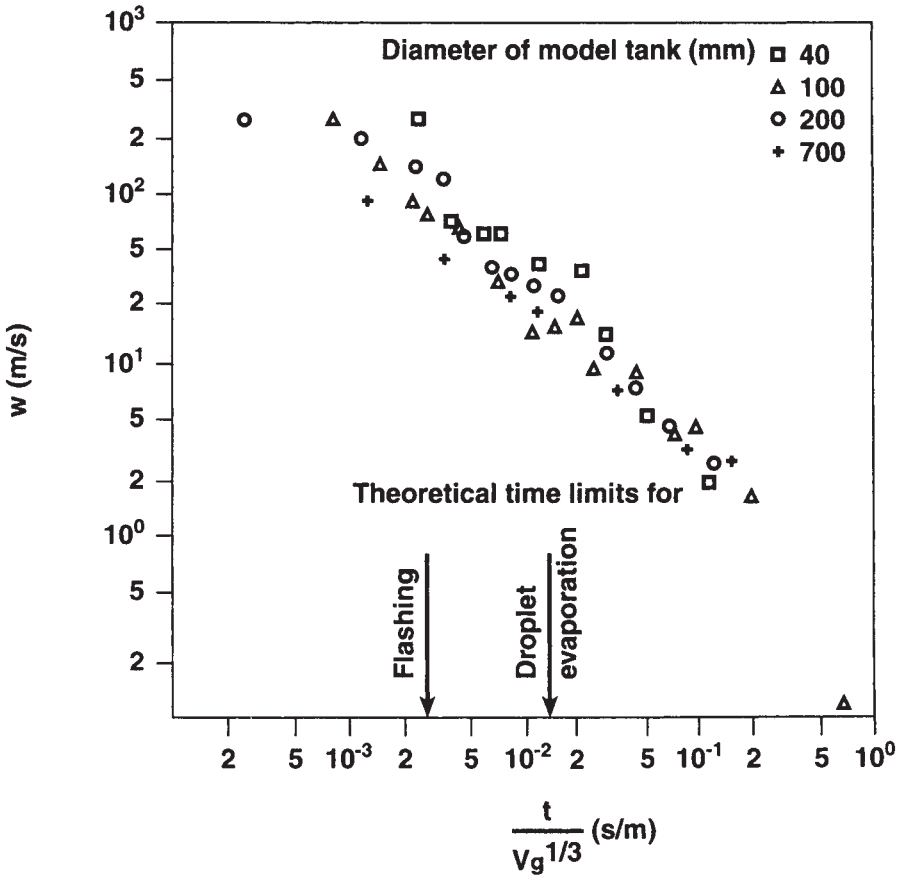


Figure 15.25 *Rupture of a vessel containing superheated liquid (Maurer et al., 1977): propagation velocity of vapour cloud boundary due to condensation from humid air (Courtesy of DECHEMA)*

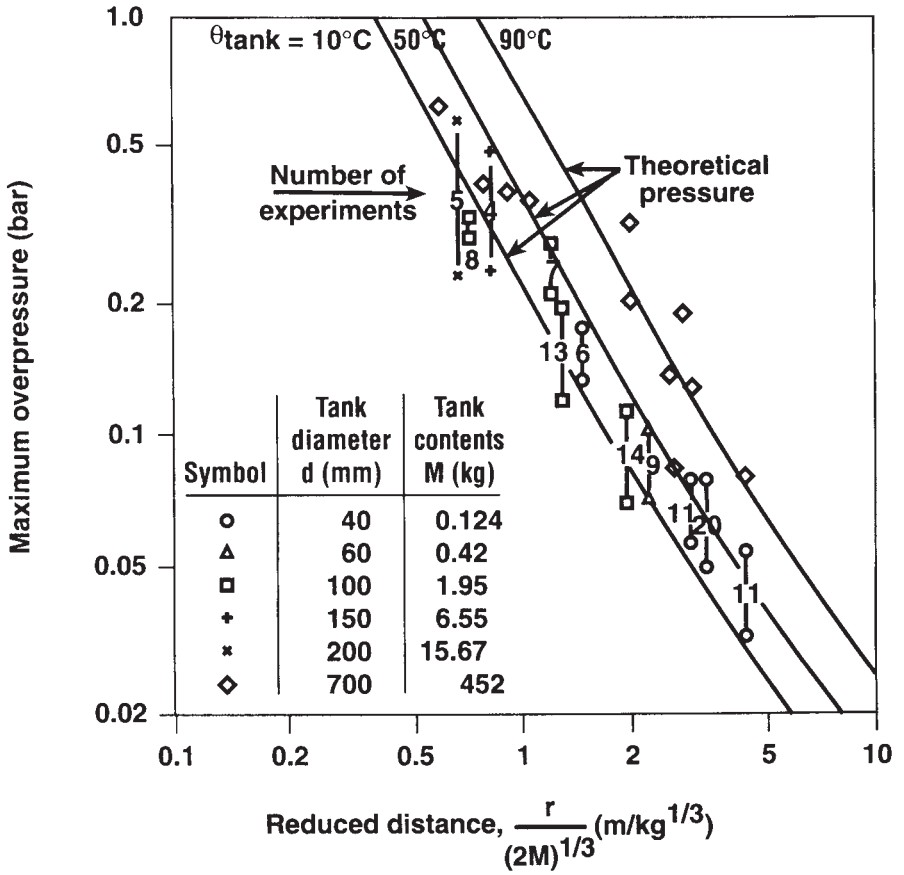


Figure 15.26 *Rupture of a vessel containing superheated liquid: blast wave overpressure due to flash expansion (Maurer et al., 1977) (Courtesy of DECHEMA)*

The flammable mixture showed considerable unmixedness, as evidenced by the afterburning of the cloud subsequent to the pressure-generating combustion. Investigation revealed that only some 30–50% of the macromixed gas participated in the pressure-generating combustion. Then taking the maximum flammable fraction as 70% and the fraction of the latter participating in pressure-generating combustion as 40%, the maximum fraction of the original contents participating in pressure-generating combustion is 0.28 (= 0.4 × 0.7). The authors therefore quote a round figure for this fraction of 30%.

15.8.5 Roberts model

A discussion of vessel rupture in the context of the fireballs has been given by A.F. Roberts (1981/82). Roberts compares the models of Hardee and Lee and of Maurer *et al.* in respect of the predictions of the transition from control by diffusion to control by gravity slumping, using the transition criterion – proposed by Jagger and Kaiser (1981):

$$N = \frac{gr\Delta}{(\mathrm{d}r/\mathrm{d}t)^2} \qquad [15.8.29]$$

with

$$\Delta = \frac{\rho_v - \rho_a}{\rho_a} \qquad [15.8.30]$$

where g is the acceleration due to gravity, r is the radial distance, Δ is a relative density, ρ is the density, and subscripts a and v denote air and vapour, respectively. The value of N at the transition point is taken to be unity. For the Hardee and Lee model, Roberts obtains

$$N = \frac{6g\Delta \cdot t}{\alpha} \qquad [15.8.31]$$

and for the model of Maurer *et al.*

$$N = 0.6\frac{\rho_v^{5/6}}{\rho_a}\left(1 - \frac{\rho_a}{\rho_v}\right)M^{1/6}t^{1/2} \qquad [15.8.32]$$

where M is the initial mass of liquid and α is the momentum per unit mass.

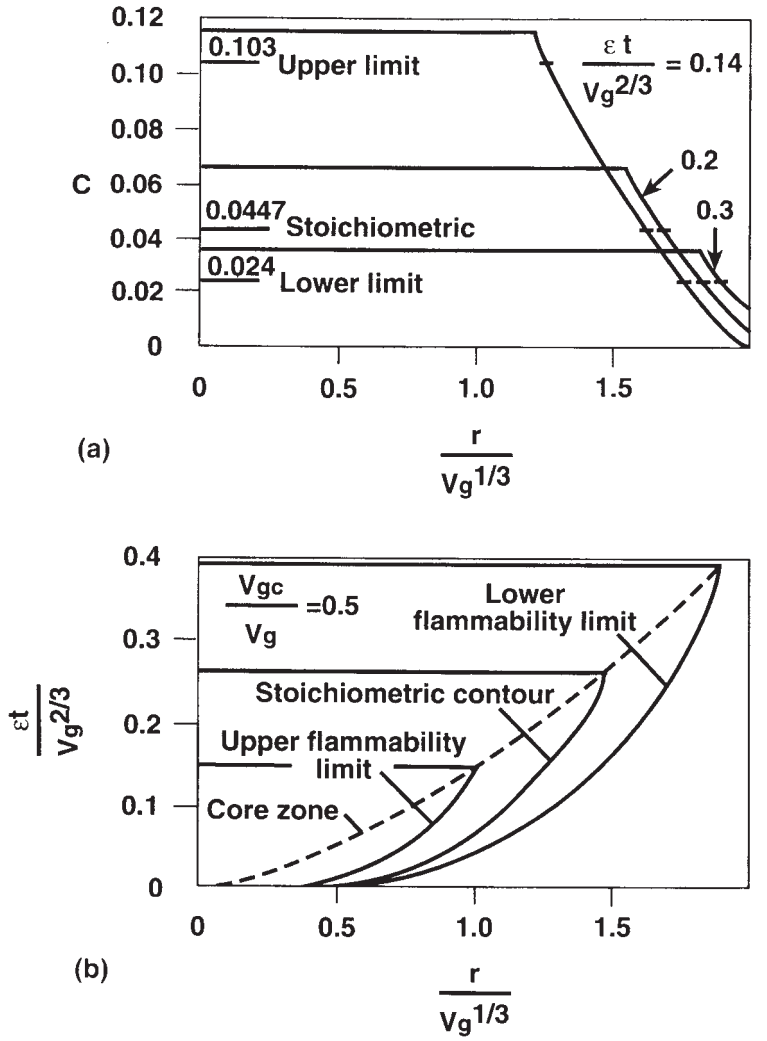


Figure 15.27 *Rupture of a vessel containing superheated liquid – model predictions (Maurer et al., 1977): (a) concentration profiles; (b) concentration contours (Courtesy of DECHEMA)*

Then, for a transition with $N = 1$, Roberts obtains for propane for the time t_g to transition for the Hardee and Lee model

$$t_g = 0.05\alpha \qquad [15.8.33]$$

and for that of Maurer *et al.*

$$t_g = 10M^{-1/3} \qquad [15.8.34]$$

Also in the Hardee and Lee model the concentration c at transition is

$$c = 22M^{1/4}\alpha^{-3/2} \qquad [15.8.35]$$

Thus, in both models gravity slumping becomes more important as the release size increases. With increase in release size the concentration at transition to gravity slumping also increases.

Roberts also gives the following expression for the radial velocity w in the Hardee and Lee model:

$$w = \left(\frac{\alpha\rho_v}{128\pi\rho_a}\right)^{1/4}\left(\frac{t}{V_g^{1/3}}\right)^{-3/4} \qquad [15.8.36]$$

with

$$V_g = 2M/\rho_v \qquad [15.8.37]$$

where V_g is the volume of vapour released and the factor of 2 is included to allow for the hemispherical symmetry. Substituting values for propane of $\rho_v/\rho_a = 2$ and $\alpha = 220$ m/s gives

$$w = 1.0 - \left(\frac{t}{V_g}\right)^{-3/4} \qquad [15.8.38]$$

He comments that this also agrees well with the data of Maurer *et al.*

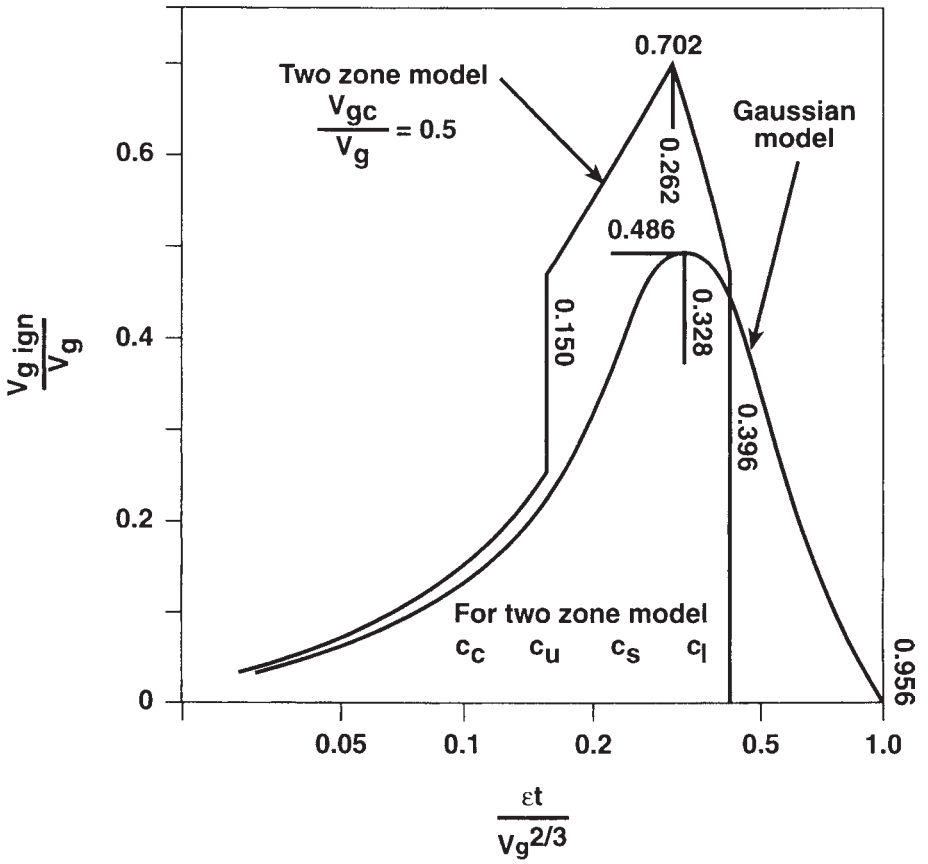


Figure 15.28 *Rupture of a vessel containing superheated liquid – model predictions (Maurer et al., 1977): fractions of flammable and reacting gas (Courstey of DECHEMA)*

15.8.6 Other treatments

A further discussion of vessel rupture has been given by Appleton (1984 SRD R303).

15.8.7 Entrainment of air

The cloud formed from a vessel rupture entrains air. The determination of the amount of air entrained is important, because the cloud constitutes the source term for dispersion models and these models are rather sensitive to the degree of air entrainment. The air entrained may be estimated using the models just described. Alternatively, use may be made of empirical relations.

Air entrainment has been discussed by Griffiths and Kaiser (1979 SRD R154) in relation to rupture of vessels containing liquefied ammonia. They propose for ammonia the rule-of-thumb that in such a release the ammonia mixes with ten times as much air by mass. They also state: 'to the accuracy that is possible here, this is also equivalent to mixing in about ten times as much air by volume'.

This estimate is based partly on the incident at Potchefstroom in which a horizontal pressure vessel burst, releasing 38 te of ammonia through a hole some 7 m^2. From eyewitness accounts the immediate resulting gas cloud was 'about 150 m in diameter and about 20 m in depth'. They also refer to the work of van Ulden (1974) in which 1 te of Freon 12 was poured onto water, giving immediate vigorous boiling and rapid formation of a gas cloud in which the volume of air was about 10 times that of the Freon.

The rule-of-thumb that for a vessel rupture the volume of air entrained is some 10 times that of the gas released has been widely used in the modelling of heavy gas dispersion.

Griffiths and Kaiser give an example of a release of 20 te of liquefied ammonia, giving 4 te of vapour and 16 te of spray. If sufficient dry air is entrained at 20°C just to evaporate the drops, this requires 400 te of air, or a factor of 20 on the mass of ammonia released. This gives a cloud at a temperature of −33°C and a relative density of 1.18. The density of the cloud is greatly in excess of that of air and the cloud will exhibit heavy gas behaviour.

15.8.8 Storage tank rupture

A quite different problem arises when rupture of an atmospheric storage tank occurs. If the rupture is sufficiently sudden and complete, a wave of liquid surges outwards and may overflow the bund. This hazard is considered further in Chapter 22.

15.9 Pipeline Rupture

Another situation that can lead to a large release of gas or vapour is rupture of a pipeline. Pipelines that may give rise to such a release are principally those carrying either high pressure gas or liquefied gas. In each case, while the determination of the initial emission rate is relatively straightforward, the situation then becomes rather more complex.

15.9.1 Gas pipelines

Accounts of emission from pipelines containing high pressure gas have been given by R.P. Bell (1978), D.J. Wilson (1979b), Picard and Bishnoi (1988, 1989) and J.R. Chen, Richardson and Saville (1992).

An empirical model for flow from a pipeline rupture has been given by R.P. Bell (1978). This model may be written as

$$m = \frac{m_o}{m_o + m_r}[m_o \exp(-t/\tau_2) + m_r \exp(-t/\tau_1)] \qquad [15.9.1]$$

with

$$m_r = A\left(\frac{2P\rho d}{flN}\right)^{1/2} \qquad [15.9.2]$$

$$\tau_1 = \frac{W_o}{m_r} \qquad [15.9.3]$$

$$\tau_2 = \frac{W_o m_r}{m_o^2} \qquad [15.9.4]$$

where A is the cross-sectional area of the pipeline, d is the diameter of the pipeline, f is the friction factor, l is the length of the pipeline, m_o is the initial mass flow from the pipeline, m_r is a steady-state, or reference, flow from the pipeline defined by Equation 15.9.2, N is a correction factor, P is the absolute pressure, W_o is the initial mass holdup in the pipeline, ρ is the density and τ_1 and τ_2 are time constants. The friction factor f is evidently the Darcy friction factor f_D ($=8\phi$).

For the correction factor N, Bell gives the empirical formula

$$N = 8[1 - \exp(-26400d/l)] \qquad [15.9.5]$$

He also states that he used a value of 0.02 for the friction factor f.

Bell also discusses the dispersion from the pipeline.

D.J. Wilson (1979b) has derived a rather more complex model, but also states that Bell's model compares quite well.

A formulation of the Bell model has been given by the CCPS (1987/2) and this may be put in the following form:

$$m = \frac{m_o}{1+\psi}[\exp(-t/\tau_2) + \psi \exp(-t/\tau_1)] \qquad [15.9.6]$$

with

$$\psi = m_r/m_o \qquad [15.9.7a]$$

$$\psi = W_o/m_o\tau_1 \qquad [15.9.7a]$$

$$\tau_1 = W_o/m_r \qquad [15.9.8]$$

$$\tau_2 = \psi^2\tau_1 \qquad [15.9.9]$$

where ψ is a parameter. Furthermore,

$$\tau_1 = 0.67\left(\frac{\gamma fl}{d}\right)^{1/2}\frac{1}{u_s} \qquad [15.9.10]$$

with

$$u_s = \left(\frac{\gamma RT}{M}\right)^{1/2} \qquad [15.9.11]$$

where M is the molecular weight, R is the universal gas constant, T is the absolute temperature, u_s is the velocity of sound and γ is the ratio of the gas specific heats.

More complex treatments are given by Picard and Bishnoi (1988, 1989) and J.R. Chen, Richardson and Saville (1992). The work of the latter authors is treated in Section 15.9.3.

15.9.2 Liquefied gas pipelines

Accounts of emission from pipelines containing liquefied gas are given by Inkofer (1969), Westbrook (1974) and T.B. Morrow, Bass and Lock (1982).

Inkofer (1969) discusses the factors determining the rate of emission in a liquid ammonia pipeline rupture. He envisages an initial spurt of liquid followed by a period of prolonged and spasmodic ejection of liquid and vapour due to the effect of vapour locks at humps along the pipeline.

Estimates of the rate of emission from a rupture in a chlorine pipeline have been given by Westbrook (1974). These estimates are an initial escape rate of 60.3 ton/h from each of two 4 in. orifices and a total escape of 28.4 ton in 24 min.

T.B. Morrow, Bass and Lock (1982) have given a method of estimating the flow from a pipeline containing liquefied gas. They consider two cases: complete rupture and partial rupture. For the two-phase critical flow at the rupture point the method utilizes Fauske's slip equilibrium model. Upstream of the rupture point it is assumed that there is a transition, or interface, point at which the flow changes from liquid flow to two-phase flow and that this point is that at which the pressure corresponds to the bubble point of the liquid. The basic equation for the two-phase pressure drop is

$$\frac{dP}{dz} = \frac{\phi_g^2 4f u_{fs}}{2dv_f} \qquad [15.9.12]$$

where f is the friction factor, u is the velocity, v is the specific volume, z is the distance along the pipe from the rupture point, ϕ_g is a parameter, and subscripts f and fs denote liquid and superficial value for liquid, respectively. The friction factor f is the Fanning friction factor ($=2\phi$).

The actual liquid velocity u_f is

$$u_f = \frac{u_{fs}}{1-Y} \qquad [15.9.13]$$

where Y is the void fraction. The parameter ϕ_g is

$$\phi_g^2 = \frac{1}{(1-Y)^2} \qquad [15.9.14]$$

Then from Equations 15.9.12–15.9.14

$$\frac{dP}{dz} = \frac{2fu_f^2}{dv_f} \qquad [15.9.15]$$

Using the same assumption for slip as made by Fauske in the derivation of the slip equilibrium model, namely

$$\frac{u_g}{u_f} = \left(\frac{v_g}{v_f}\right)^{1/2} \quad [15.9.16]$$

where subscript g denotes vapour. Expressing the quality in terms of the fluid enthalpies, and hence of pressure, the authors obtain

$$\left(\frac{mv_f}{Au_f}\right)^2 = f(P) \quad [15.9.17]$$

Hence

$$\frac{dP}{dz} = \frac{2fm^2v_f}{A^2df(P)} \quad [15.9.18]$$

In order to integrate Equation 15.9.18 the mass flow m is expressed as a function of the distance z from the rupture point:

$$m = m_e\left(\frac{m_e - m_i}{z_i}\right)z \quad [15.9.19]$$

where subscript e denotes the rupture point, or exit, and i denotes the transition, or interface, point. Expressions are also given for the volume of the vapour space, and hence of the liquid removed, between the transition and rupture points. The model allows the mass flow from the rupture point and the position of the transition point to be determined as a function of time.

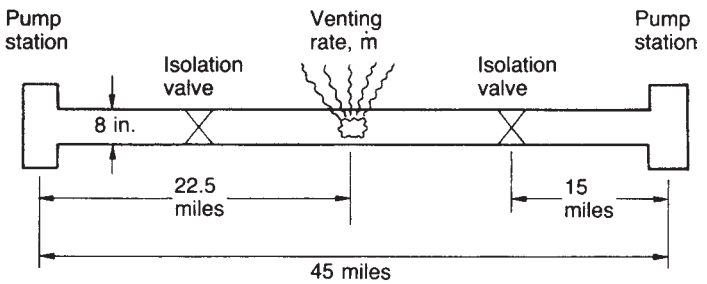
The authors have used the model to study ruptures in the propane pipeline system shown in Figure 15.29. They investigated different pumping station distances, valve spacings and shut-down times of the upstream pump, with valves shut down 5 min after the pump. Typical results for the flow profiles given by ruptures are shown in Figure 15.30. Curve A shows the flow for a complete rupture. This flow is for some time unaffected by pump shut-down and valve closure, since the two-phase interface moves relatively slowly. For example, for a spacing between pumps of 15 miles the interface is estimated to reach the isolation valves at 7½ miles only after some 25 min. Curve B in Figure 15.30 shows the flow for a partial rupture. In this case the pressure is maintained at the value before rupture until the pump shuts off, then falls, and finally reaches a new steady value corresponding to the bubble point. The fall may approximate to a ramp or may change to a steeper slope as the isolation valve shuts.

A description of the actual pipeline break at Port Hudson has been given by the NTSB (1972 PAR-72-01) and Burgess and Zabetakis (1973 BM RI 7752). The event is described in Case History A52.

15.9.3 BLOWDOWN

An account has been given in Section 15.8 of the model BLOWDOWN developed for the prediction of conditions during blowdown of, or release from, a vessel. This model has also been adapted for use in the determination of conditions arising during outflow of fluid from a pipeline, whether as intentional blowdown or accidental release.

One of the topics in which the Piper Alpha Inquiry was interested was the explanation of the change in pressure that occurred during the accident in the gas pipelines connected to the platform. Evidence on this topic, based on the use of the BLOWDOWN code, was presented to the inquiry by Richardson (1989b).



- Pipeline flow rate — 40 000 bbl/day
- Isolation valve spacing — 45, 15 and 5 miles
- Pump stations — 45 miles apart
- Pump shut-off time — 5 min and 20 min after rupture
- Valve closure time — 5 min after pump shut-off time
- Break sizes — Complete break (venting from both ends), and partial break (initial venting rate 10 000 bbl/day)

Figure 15.29 *Emission from an LPG pipeline: configuration of pipeline studied (T.B. Morrow, Bass and Lock, 1982) (Courtesy of the American Society of Mechanical Engineers)*

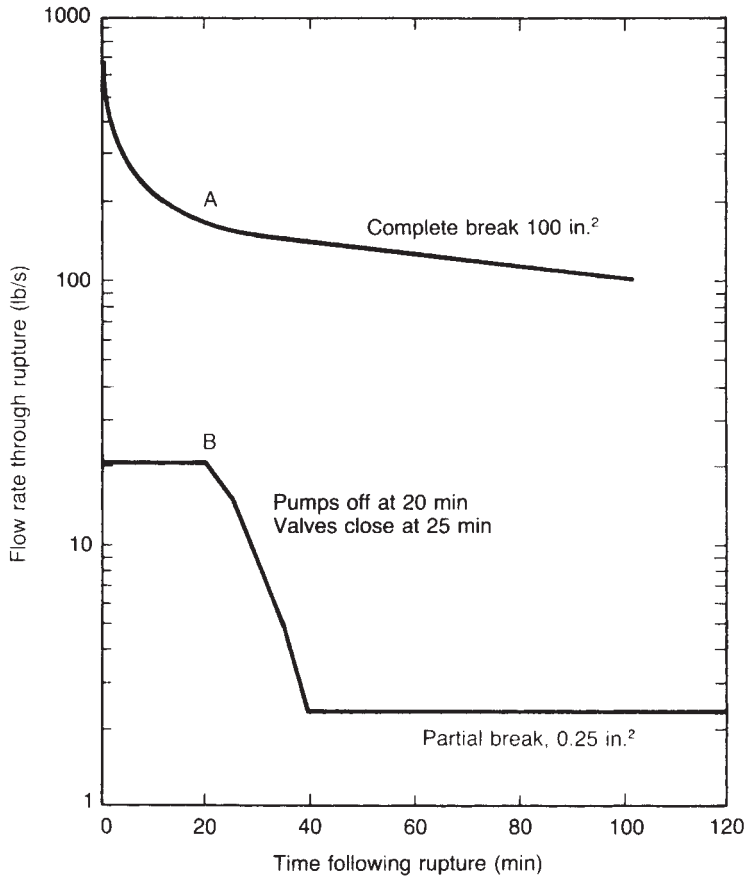


Figure 15.30 *Emission from an LPG pipeline: flow of propane for partial and complete ruptures. Isolation value spacing = 45 miles (T.B. Morrow, Bass and Lock, 1982) (Courtesy of the American Society of Mechanical Engineers)*

An account of the extensions made to the BLOWDOWN model to allow it to be applied to a gas pipeline has been given by J.R. Chen, Richardson and Saville (1992). The basic model comprises the unsteady one-dimensional Euler equations supplemented by friction and heat transfer relations. Chen *et al.* describe the investigation of a number of methods for the solution of these equations, including finite difference methods (FDMs), the method of characteristics (MOC), a hybrid method and a wave tracing method. The technique found to be most efficient and accurate was the multiple wave tracing method.

The investigation made use of the test problem of Picard and Bishnoi (1989) and of data on the depressurization of the pipeline between Piper Alpha and MCP-01 on the night of the accident. Results are presented which include values of the intact end pressure, the open end pressure and the release rate.

15.9.4 Pipeline isolation

The quantity of material released from a pipeline rupture depends on whether the section of line is isolated or not. The arrangements for line break detection and isolation are therefore of the greatest importance in minimizing escapes.

15.10 Vaporization

If the fluid that escapes from containment is a liquid, then vaporization must occur before a vapour cloud is formed. The process of vaporization determines the rate at which material enters the cloud. It also determines the amount of air entrained into the cloud. Both aspects are important for the subsequent dispersion. Selected references on vaporization are given in Table 15.7

15.10.1 Vaporization situations

In considering the generation of a vapour cloud from the liquid spillage, the following situations can be distinguished:

(1) A volatile liquid at atmospheric temperature and pressure, for example, acetone.
(2) A superheated liquid
  (a) at ambient temperature and under pressure, for example, butane;
  (b) at high temperature and under pressure, for example, hot cyclohexane.
(3) A refrigerated liquefied gas at low temperature but at atmospheric pressure, for example, cold methane.

Table 15.7 *Selected references on vaporization*

Liquid spreading
Stoker (1957); Abbott (1961); Fay (1969); Hoult (1969, 1972b); Fannelop and Waldman (1972); Webber and Brighton (1986 SRD R317)

Spillage and evaporation
Hinchley and Himus (1924); O.G. Sutton (1934); R.W. Powell and Griffiths (1935); Lurie and Michailoff (1936); R.W. Powell (1940); T.K. Sherwood (1940); Wade (1942); Pasquill (1943); Linton and Sherwood (1950); Langhaar (1953); Burgoyne (1965b); Humbert-Basset and Montet (1972); Pancharatnam (1972a,b); Mackay and Matsugu (1973); AGA (1974); V.J. Clancey (1974a, 1977c); Kalelkar and Cece (1974); Drake and Reid (1975); Feind (1975); Opschoor (1975b, 1978); Japan Gas Association (1976); Meadows (1976); Bellus, Vincent *et al.* (1977); Deacon (1977); HSE (1978b); Reid and Wang (1978); Shaw and Briscoe (1978 SRD R100); Flothmann, Heudorfer and Langbein (1980); N.C. Harris (1980, 1982); Reijnhart *et al.* (1980); Reijnhart and Rose (1980); Raj (1981, 1991); Brutsaert (1982); Drivas (1982); Hilder (1982); O'Shea (1982); Jensen (1983); Kunkel (1983); Webber and Brighton (1986, 1987 SRD R390); Anon. (1985i); Brighton (1985b, 1986 SRD R371, 1987 SRD R375, 1990); Pikaar (1985); Prince (1985 SRD R324); Lebuser and Schecker (1986, 1987); Moorhouse and Carpenter (1986); Kawamura and Mackay (1987); Webber (1987 SRD R421, 1988 SRD R404, 1989); Webber and Jones (1987); Studer, Cooper and Doelp (1988); Deaves (1989); Lantzy *et al.* (1990); Raj and Morris (1990); J. Singh and McBride (1990); J.L Woodward (1990); Alp and Matthias (1991); Mikesell *et al.* (1991); Angle, Brennan and Sandhu (1992); Frie *et al.* (1992); Stramigioli and Spadoni (1992); J. Cook and Woodward (1993a,b); Leonelli, Stramigioli and Spadoni (1994); Takeno *et al.* (1994)

Solar radiation, solar constant
Fritz (1954); C.O. Bennett and Myers (1962); N. Robinson (1966); Coulson (1975); L.B. Nielsen *et al.* (1981); Multer (1982); Lide (1994)

Burning spills
Opschoor (1975a,b, 1980)

Spillage and vaporization on water
Blokker (1964); Burgess, Murphy and Zabetakis (1970 RI 7448); Enger and Hartman (1972a,b); Hoult (1972a); Kneebone and Boyle (1973); Mackay and Matsugu (1973); Raj and Kalelkar (1973, 1974); Raj, Hagopian and Kalelkar (1974); Drake, Jeje and Reid (1975); Eisenberg, Lynch and Breeding (1975); Opschoor (1975a, 1977, 1980); Raj *et al.* (1975); Dincer, Drake and Reid (1977); Griffiths (1977 SRD R67); Havens (1977, 1980); HSE (1978b); Shaw and Briscoe (1978 SRD R100); Raj and Reid (1978a,b); Reid and Smith (1978); Raj (1979, 1981, 1991); Shell Research Ltd (1980); Anon. (1982f); Chang and Reid (1982); Dodge *et al.* (1983); Hirst and Eyre (1983); Waite *et al.* (1983); Prince (1985 SRD R324); Zumsteg and Fannelop (1991); J. Cook and Woodward (1993a)

Flash-off, flash fraction, aerosol
NRC (Appendix 28 *Aerosols*); Pinto and Davis (1971); A.R. Edwards (1978); Mesler (1985); API (1986 Publ. 4456); Ramsdale (1986 SRD R382, 1987 SRD R401); Emerson (1987b); Bache, Lawson and Uk (1988); Britter and McQuaid (1988); I. Cook and Unwin (1989); Lantzy *et al.* (1990); Schmidli, Bannerjee and Yadigaroglu (1990); D.W. Johnson (1991); D.W. Johnson and Diener (1991); Raj (1991); Kukkonen and Vesala (1991, 1992); J.L. Woodward and Papadourakis (1991)

Vaporization in jets (*see* Table 15.40)

Spill control
BDH (1970); Anon. (1972b); May, McQueen and Whipp (1973); AIChE (1974/99, 1988/100, 1989/70); May and Perumal (1974); University Engineers Inc. (1974); Weismantel (1974); Welker, Wesson and Brown (1974); Lindsey (1975); Otterman (1975); Wirth (1975); L.E. Brown *et al.* (1976); W.D. Clark (1976b); Martinsen and Muhlenkamp (1977); D.P. Brown (1978); Harsh (1978a,b); Norman and Dowell (1978, 1980); Whiting and Shaffer (1978); Kletz (1982i); Jeulink (1983)

Vaporization suppression
R.H. Hiltz (1982, 1987); Dilwali and Mudan (1986, 1987); Norman (1987); ASTM (1988 F1129); Dimaio and Norman (1988, 1990); Norman and Dimaio (1989); Leone (1990); Norman and Swihart (1990); Martinsen (1992); Howell (1993); Scheffler, Greene and Frurip (1993)

The vaporization of the liquid is different for these three cases. In the first case the liquid after spillage is approximately at equilibrium and evaporates relatively slowly. In the second case the liquid is superheated and flashes off when spilt, and then undergoes slower evaporation. The first category of a superheated liquid, at ambient temperature but under pressure, is that of a liquefied gas, while the second, at high temperature and under pressure, is that of a liquid heated above its normal boiling point. The third case is that of a refrigerated liquefied gas that on spillage evaporates rapidly at first and then more slowly.

15.10.2 Vaporization of a superheated liquid

If the liquid released from containment is superheated, a proportion flashes off as vapour. The remaining liquid is cooled by the removal of the latent heat of vaporization and falls to its atmospheric boiling point.

The theoretical adiabatic flash fraction (TAFF) of vapour so formed is usually determined by the simple heat balance

$$\phi = \frac{c_{\mathrm{pl}}}{\Delta H_{\mathrm{v}}}(T_{\mathrm{i}} - T_{\mathrm{b}}) \quad T_{\mathrm{i}} > T_{\mathrm{b}} \qquad [15.10.1]$$

where c_{p} is the specific heat, T is the absolute temperature, ΔH_{v} is the latent heat of vaporization, ϕ is the fraction of liquid vaporized and subscripts b, i and l denote boiling point, initial and liquid, respectively.

An alternative expression that takes account of the differential nature of the vaporization is

$$(1 - \phi)c_{\mathrm{pl}}(-\mathrm{d}T) = \Delta H_{\mathrm{v}}\,\mathrm{d}\phi \qquad [15.10.2]$$

and hence

$$\phi = 1 - \exp\left[-\frac{c_{\mathrm{pl}}}{\Delta H_{\mathrm{v}}}(T_{\mathrm{i}} - T_{\mathrm{b}})\right] \quad T_{\mathrm{i}} > T_{\mathrm{b}} \qquad [15.10.3]$$

Equations 15.10.1 and 15.10.3 give the theoretical fraction of vapour formed. The sudden growth and release of vapour

bubbles also results in the formation of liquid droplets, or spray. The mass of liquid in spray form is generally of the same order as that in the initial vapour flash and may exceed it.

This spray then either vaporizes, increasing the vapour cloud, or rains out as liquid, forming a pool on the ground. The total amount of vapour formed, both that from the initial flash and that from the evaporation of spray, constitutes the ultimate flash.

For the fraction of liquid which forms spray a rule-of-thumb frequently used is that it is equal to the initial vapour flash (Kletz, 1977J). Another rule-of-thumb is that if the fraction flashing off is small it may be appropriate to assume that the spray fraction is two or three times the initial vapour flash-off (W.G. High, 1976).

A discussion of spray and rainout following the discharge of a flashing liquid, with particular reference to liquid ammonia, has been given by Wheatley (1986). Two discharge situations may be distinguished: meta-stable flow of a superheated liquid and choked two-phase flow. These two cases have been modelled by Wheatley. As shown in Table 15.8, the flow characteristics obtained are significantly different.

In the non-choked liquid flow case there is a large increase in diameter of the flow at the outlet. Such large increases have been observed in the Desert Tortoise tests (Koopman *et al.*, 1986). In the choked two-phase flow case the flow velocity is much higher. The flash fraction is similar in the two cases.

The drops formed are subject to shear stress and there is a maximum size of drop given by the drop Weber number:

$$\mathrm{We_d} = \frac{u_\mathrm{d}^2 d \rho_\mathrm{d}}{\sigma_\mathrm{d}} \qquad [15.10.4]$$

where d is the diameter of the drop, u is the velocity, ρ is the density, σ is the surface tension and subscript d denotes drop. Table 15.8 shows the drop sizes obtained for the two cases.

The extent to which rainout of the drops occurs depends on a balance between the inertial and gravity forces. The drops will have higher inertia than the vapour but will be more affected by gravity. Wheatley treats rainout in terms of the inclination of the bounding drop trajectory, which is obtained from the ratio of the settling velocity to the horizontal velocity of the drops. The settling velocity and inclination of the drops for the cases considered are shown in Table 15.8. Both for the superheated liquid flow and the choked two-phase flow the inclinations are too small to give significant rainout, but for the refrigerated liquid flow the inclination is much larger and rainout could be significant.

Following flash-off, the residual liquid is at its normal boiling point. Vaporization then continues as a rate-limited process. This secondary stage of rate-limited vaporization is usually regarded as relatively less important compared with the initial flash-off, particularly with respect to the formation of flammable gas clouds.

The spray fraction from a ruptured vessel was considered in Section 15.7. Frequently, very little liquid is left in the vessel. The spray fraction in fireballs is discussed in Chapter 16.

15.10.3 Mass and heat transfer for a pool

In general, vaporization from a pool is a mass and heat transfer limited process, but in a specific case there may be one dominant transfer mode. Thus for vaporization of a cryogenic liquid it is the heat transfer from the ground to the pool which governs the rate of vaporization.

For a pool there is only one mode of mass transfer, that between the liquid surface and the atmosphere. By contrast, for heat transfer there are several modes, namely heat transfer by convection between the liquid surface and the atmosphere, by conduction between the liquid and the ground, and by radiation, both solar and between the liquid surface and the atmosphere.

The heat balance on the pool is thus

$$wc_\mathrm{pl}\frac{\mathrm{d}T}{\mathrm{d}t} = -A_\mathrm{p}(q_\mathrm{v} - q_\mathrm{cn} - q_\mathrm{cd} - q_\mathrm{r}) \qquad [15.10.5]$$

with

$$q_\mathrm{r} = q_\mathrm{rs} + q_\mathrm{ra} - q_\mathrm{rl} \qquad [15.10.6]$$

$$q_\mathrm{v} = m_\mathrm{v}\Delta H_\mathrm{v} \qquad [15.10.7]$$

where A_p is the area of the pool, c_pl is the specific heat of the liquid, m_v is the mass vaporization rate per unit area, q_cd is the heat flow per unit area by conduction from the ground to the pool, q_cn is the heat flow per unit area by convection from the atmosphere to the pool, q_r is the net heat flow per unit area by radiation to the pool, q_ra is the heat flow per unit area by radiation from the atmosphere to the pool, q_rl is the heat flow per unit area by radiation from the pool to the atmosphere, q_rs is the heat flow per unit area by solar radiation to the pool, q_v is the heat required per unit area for vaporization, t is the time and w is the mass of liquid.

The mass balance on the pool is

$$-\frac{\mathrm{d}w}{\mathrm{d}t} = A_\mathrm{p} m_\mathrm{v} \qquad [15.10.8]$$

Table 15.8 *Flow characteristics of discharge of liquid ammonia (after Wheatley, 1986) (Courtesy of the Institution of Chemical Engineers)*

Storage temperature (°C)	*Flow type*	*Axial velocity* (m/s)	*Flow diameter* (cm)	*Flash fraction* (%)	*Spray characteristics*		*Inclination* (°)
					Drop size (μm)	*Settling velocity* (m/s)	
20	Liquid	154	13	17.6	25	0.013	0.0048
20	Two-phase	37.7	61	18.7	420	1.4	2.1
−34	Liquid				1900	5.2	16

with

$$m_v = \frac{k_m M (p^o - p_\infty)}{RT} \quad [15.10.9]$$

where k_m is the mass transfer coefficient, p° is the vapour pressure of the liquid and p_∞ is the partial pressure of the liquid outside the influence of the pool. The partial pressure p_∞ can usually be set equal to zero. For a multi-component liquid Drivas (1982) has modified Equation 15.10.9 as follows:

$$m_v = \frac{k_m M_T^o}{RTn_T} \frac{\sum x_i^o M_i p_{is}}{\sum x_i^o M_i} \exp(-kp_{is}t) \quad [15.10.10]$$

with

$$k = \frac{k_m A_p}{RTn_T} \quad [15.10.11]$$

where M_i is the molecular weight of component i, M_T^o is the initial mass of the liquid, n_T is the number of moles of the liquid, p_{is} is the vapour pressure of component i, x_i^o is the initial mole fraction of component i in the liquid and k is a constant.

In general, heat transfer may be correlated by the factor j_h of Chilton and Colburn (1934) and mass transfer by the corresponding factor j_m. For a geometry where the characteristic dimension is the diameter d these j factors are defined as

$$j_h = \mathrm{St}\,\mathrm{Pr}^{0.67} \quad [15.10.12]$$

$$j_m = \frac{k_m}{u} \frac{C_{Bm}}{C_T} \mathrm{Sc}^{0.67} \quad [15.10.13]$$

where C_{Bm} is the log mean concentration difference, C_T is the total concentration and k_m is the mass transfer coefficient. The term C_{Bm}/C_T is the drift factor.

The definitions of, and relations between, the Reynolds number Re, the Prandtl number Pr, the Nusselt number Nu, the Schmidt number Sc and the Stanton number St are

$$\mathrm{Re} = \frac{ud\rho}{\mu} \quad [15.10.14]$$

$$\mathrm{Pr} = \frac{c_p \mu}{k} \quad [15.10.15]$$

$$\mathrm{Nu} = \frac{hd}{k} \quad [15.10.16]$$

$$\mathrm{Sc} = \frac{\mu}{\rho D} \quad [15.10.17]$$

$$\mathrm{St} = \frac{h}{c_p \rho} \quad [15.10.18]$$

$$\mathrm{St} = \frac{\mathrm{Nu}}{\mathrm{RePr}} \quad [15.10.19]$$

where d is the pool diameter, D is the diffusion coefficient, k is the thermal conductivity and μ is the viscosity.

Given a correlation for j_h, the heat transfer coefficient h may be obtained from the definition of j_h in Equation 15.10.12. Then, using the approximate equality,

$$j_m \approx j_h \quad [15.10.20]$$

and using the definitions of j_h, and j_m in Equations 15.10.12 and 15.10.13

$$k_m = \frac{hC_T}{c_p \rho C_{Bm}} \left(\frac{\mathrm{Pr}}{\mathrm{Sc}}\right)^{0.67} \quad [15.10.21]$$

Alternatively, if the correlation available is for j_m this may be used to obtain j_h. For other geometries the diameter d is replaced by the characteristic length.

A number of workers have measured mass transfer from a plane liquid surface to a gas stream above, particularly in the evaporation of water. An account is given by Coulson and Richardson (1977–). Their results have been correlated by T.K. Sherwood (1940) in terms of a point Reynolds number Re_x where the characteristic dimension is the distance across the liquid surface to the point considered. His results may be expressed as

$$j_m = 0.0415 \mathrm{Re}_x^{-0.21} \quad [15.10.22]$$

over the approximate range $10^4 < \mathrm{Re}_x < 10^5$. Equation 15.10.22 may be used, in conjunction with Equation 15.10.20, to obtain both the mass and heat transfer coefficients.

The mass transfer coefficient may also be correlated directly in terms of the Sherwood number Sh:

$$\mathrm{Sh} = \frac{k_m d}{D} \quad [15.10.23]$$

Fleischer (1980) has given the following correlation for the Sherwood number over a plane liquid surface:

$$\mathrm{Sh} = 0.037 \mathrm{Sc}^{1/3} (\mathrm{Re}^{0.8} - 15,200) \quad [15.10.24]$$

The transition from the laminar to the turbulent regime is taken here to occur at $\mathrm{Re} = 320{,}000$.

In the case of the plane liquid surface there is also available for the mass transfer a specific correlation for the evaporation rate derived by Sutton and Pasquill. This is described in Section 15.10.4.

Heat transfer from the ground is complex, because it involves an unsteady-state process. An account of unsteady-state heat transfer, including many standard cases, is given by Carslaw and Jaeger (1959). The basic equation is

$$\frac{\mathrm{d}^2\theta}{\mathrm{d}z^2} = \frac{1}{\alpha_s} \frac{\mathrm{d}\theta}{\mathrm{d}t} \quad [15.10.25]$$

with

$$\theta = T - T_s \quad [15.10.26]$$

$$\alpha_s = \frac{k_s}{\rho_s c_{ps}} \quad [15.10.27]$$

where α is the thermal diffusivity, θ the temperature above the datum, or soil, temperature and subscript s denotes soil.

For the case of constant liquid temperature, Equation 15.10.25 may be solved with the boundary conditions $z = 0$, $\theta = \theta_1$; $z = \infty$, $\theta = \theta_s$. For temperature this gives

$$\frac{\theta}{\theta_1} = \text{erf}\, c\left[\frac{z}{2(\alpha_s t)^{1/2}}\right] \quad [15.10.28]$$

where z is the vertical distance down into the ground and subscript l denotes liquid.

For the heat flow per unit area q

$$q = -k\frac{\mathrm{d}\theta}{\mathrm{d}z} \quad [15.10.29]$$

Then from Equations 15.10.28 and 15.10.29 and

$$q = \left(\frac{k_s \rho_s c_{ps}}{\pi}\right)^{1/2} \frac{\theta_1}{t^{1/2}} \quad [15.10.30]$$

For the total heat transferred per unit area Q

$$Q = \int_0^t q\,\mathrm{d}t \quad [15.10.31]$$

and from Equations 15.10.30 and 15.10.31

$$Q = 2\left(\frac{k_s \rho_s c_{ps}}{\pi}\right)\theta_1 t^{1/2} \quad [15.10.32]$$

For the more complex case of varying liquid temperature, Equation 15.10.25 may be solved with the boundary conditions $t = 0$, $\theta = 0$; $z = 0$, $\theta = \theta_l(t)$; $z = \infty$, $\theta = 0$. For temperature this gives

$$\theta = \frac{z}{2(\pi\alpha_s)^{1/2}} \int_0^t \frac{\theta_1}{(t-\tau)^{3/2}} \exp\left[-\frac{z^2}{4\alpha_s(t-\tau)}\right]\mathrm{d}\tau \quad [15.10.33]$$

The decrease in temperature of a vaporizing pool will be approximately exponential. An analytical solution of Equation 15.10.33 for the case $\theta_l = \exp(-\lambda t)$, where λ is a constant, is given by Carslaw and Jaeger.

For heat transfer by radiation the net heat radiated to the pool is given by Equation.15.10.6. The individual terms in the equation are given by

$$q_{rs} = \psi(1 - a) \quad [15.10.34]$$

$$q_{ra} = \epsilon_a \sigma T_a^4 \quad [15.10.35]$$

$$q_{rl} = \epsilon_l \sigma T_l^4 \quad [15.10.36]$$

where a is the albedo of the liquid surface, ϵ is the emissivity, σ is the Stefan–Boltzmann constant, ψ is the solar constant and subscript a denotes atmosphere. The value of the solar constant is 1373 W/m^2 (Lide, 1994).

The albedo and emissivities have been discussed by Mackay and Matsugu (1973), who propose for the albedo a value of 0.14 and for the emissivities of the atmosphere and of the liquid values of 0.75 and 0.95, respectively.

The albedo of a plane water surface has also been discussed by Shaw and Briscoe (1978 SRD R100). The albedo is actually a function of the sun's elevation. They give the following values:

Elevation (°)	90	50	40	20	10	0
Albedo	0.02	0.025	0.034	0.134	0.348	1.0

Data on the albedo for different surfaces are given by Oke (1978). A further discussion of albedo is given by Byrne *et al.* (1992 SRD R553).

15.10.4 Sutton–Pasquill model

A model for mass transfer in evaporation from a liquid surface at constant temperature has been derived by O.G. Sutton (1934). Sutton's model was subsequently modified by Pasquill (1943) and the modification was accepted by O.G. Sutton (1953). In the form given by Pasquill, the relations for evaporation from a rectangular and a circular pool are:

$$E = K u_1^{(2-n)/(2+n)} x_o^{2/(2+n)} y_o \quad \text{rectangular pool} \quad [15.10.37]$$

$$E = K' u_1^{(2-n)/(2+n)} r^{(4+n)/(2+n)} \quad \text{circular pool} \quad [15.10.38]$$

with

$$K = \chi_o \left(\frac{2+n}{2-n}\right)^{(2-n)/(2+n)} \left(\frac{2+n}{2\pi}\right) \sin\left(\frac{2\pi}{2+n}\right) \Gamma\left(\frac{2}{2+n}\right) \times a^{2/(2+n)} z_1^{-n^2/(4-n^2)} \quad [15.10.39]$$

$$K' = \frac{2^{2+n}\pi^{1/2}\Gamma(3 + n/2 + n)K}{\Gamma(8 + 3n/2(2+n))} \quad [15.10.40]$$

$$a = \left|\frac{[(\pi/2)]^{1-n}(2-n)^{1-n}n^{1-n}}{(1-n)(2n-2)^{2(1-n)}}\right| k^{2(1-n)} \lambda^n z_1^{(n^2-n)/(2-n)} \quad [15.10.41]$$

$$\chi_o = \frac{Mp^o}{RT} \quad [15.10.42]$$

where E is the evaporation rate (g/s), k is the von Karman' constant, M is the molecular weight, n is the diffusion index, p^o is the vapour pressure of the liquid (dyn/cm^2), r is the radius of the pool (cm), R is the universal gas constant (erg/gmol K), T is the absolute temperature (K), u_1 is the wind speed at height z_1 (cm/s), x_o is the downwind length of the pool (cm), y_o is the crosswind width of the pool (cm), z_1 is the height at which the wind speed u_1 is measured (cm), λ is a parameter (cm^2/s), χ_o is the concentration (g/cm^3) and a, K and K' are constants. The constant K may be written as:

$$K = \chi_o f_1(n) a^{2/(2+n)} z_1^{-n^2/(4-n^2)} \quad [15.10.43]$$

$$= \chi_o f_1(n)^{2/(2+n)} f_2(n)^{2/(2+n)} k^{4(1-n)/(2+n)} \times \lambda^{2n/(2+n)} z_1^{-n/(2+n)} \quad [15.10.44]$$

with

$$f_1(n) = \left[\frac{2+n}{2-n}\right]^{(2-n)/(2+n)} \left[\frac{2+n}{2\pi}\right] \sin\left[\frac{2\pi}{2+n}\right] \Gamma\left[\frac{2}{2+n}\right] \quad [15.10.45]$$

$$f_2(n) = \frac{(\pi/2)^{1-n}(2-n)^{1-n}n^{1-n}}{(1-n)(2-2n)^{2-2n}} \quad [15.10.46]$$

Sutton's treatment is based on the wind velocity profile:

$$\frac{u}{u_1} = \left[\frac{z}{z_1}\right]^{n/(2-n)} \quad [15.10.47]$$

where u is the wind speed (cm/s) and z is the height (cm).

Sutton identified the parameter λ with the kinematic viscosity of the air v. Pasquill gives a table of values for the constants K and K' for the following case:

$k = 0.4$

$\lambda = v = 0.147\ \text{cm}^2/\text{s}$

$\chi_o = 1\ \text{g/cm}^3$

$z_1 = 1\ \text{cm}$

$u_1 = 500\ \text{cm/s}$

Hence

n	K	K'
0.20	0.0094	0.0283
0.25	0.0180	0.0537
0.30	0.0313	0.0926

He also gives the results of an experiment for which

$M = 157$

$T = 290\ \text{K}$

$x_o = 10\ \text{cm}$

$y_o = 20\ \text{cm}$

$n = 0.219$

Hence

$K = 0.0122\chi_0$

and

$$\frac{E}{p^o} = 1.89 \times 10^{-6}\ (\text{g/s})/(\text{dyn/cm}^2)$$

However, Pasquill argued that the parameter should properly be the diffusion coefficient D of the vapour in air and this argument was accepted by O.G. Sutton (1953). Hence in Equations 15.10.39–15.10.44, λ should be set equal to D.

Equations for the Sutton–Pasquill model have been given by V.J. Clancey (1974a) in the following form. For a rectangular pool set square to the wind direction:

$$E = 1.2 \times 10^{-10} \frac{Mp^o}{T} u^{0.78} x_o^{0.89} y_o \quad \text{rectangular pool} \quad [15.10.48]$$

$$E = 3.6 \times 10^{-10} \frac{Mp^o}{T} u^{0.78} r^{1.89} \quad \text{circular pool} \quad [15.10.49]$$

Clancey states that in deriving Equations 15.10.48 and 15.10.49 he has used values $\lambda = 0.147\ \text{cm}^2/\text{s}$ and $D \approx 0.075\ \text{cm}^2/\text{s}$, the latter being typical for hydrocarbons. In determining K from Equation 15.10.39 he appears to have included both the terms $\lambda^{2n/(2+n)}$ and $D^{2n/(2+n)}$, which for $n = 0.25$ have the values 0.653 and 0.56, respectively. Equations 15.10.48 and 15.10.49 may be corrected for this by dividing by 0.653.

Relations for the Sutton–Pasqill model in SI units are given in the *Rijnmond Report*. The report gives Equations 15.10.37 and 15.10.38 together with the equations

$$K = a\chi_o D^{2n/(2+n)} z_1^{-n/(2+n)} \quad [15.10.50]$$

$$K' = a'\chi_o D^{2n/(2+n)} z_1^{-n/(2+n)} \quad [15.10.51]$$

where D is the diffusion coefficient of vapour in air (m^2/s), E is the evaporation rate (kg/s), r is the radius of the pool (m), x_o is the downwind length of the pool (m), y_o is the crosswind width of the pool (m), χ_o is the concentration of the vapour in the air (kg/m^3), u is the wind speed at height z_1(m/s), z_1 is the height at which the wind speed is measured (m) and a and a' are constants. The constant a is different from that given in Equation 15.10.41. The following values are given for the groups K/χ_o and K'/χ_o:

n	K/χ_o	K'/χ_o
0.20	1.278×10^{-3}	3.846×10^{-3}
0.25	1.579×10^{-3}	4.685×10^{-3}
0.30	1.786×10^{-3}	5.285×10^{-3}

15.10.5 Vaporization of a volatile liquid

Vaporization of a volatile liquid is governed by the mass and heat transfer rate processes described in Section 15.10.3. If the vaporization rate is low so that the heat transfer to the pool is sufficient to prevent a fall in the temperature of the liquid, the vaporization is a mass transfer limited process that depends on the vapour pressure of the liquid and the wind flow across the pool. At higher vaporization rates, where the heat transfer to the pool is insufficient to prevent chilling, the liquid temperature will fall, approaching asymptotically to a steady-state value. The approach will generally be approximately exponential.

It has been shown theoretically by Flothmann, Heudorfer and Langbein (1980) that for pools of liquids such as hydrogen cyanide and acrolein, neglect of heat transfer from the ground can lead to appreciable error in the estimation of the vaporization rate, particularly under conditions of low solar radiation and/or low wind speeds. Vaporization from a pool of a volatile liquid constitutes a steady, continuous source of vapour.

Higher vaporization rates still occur where the liquid is at or close to its boiling point. There is relatively little information available on vaporization under these conditions. This situation has been discussed by Shaw and Briscoe (1978 SRD R100), who consider the vaporization of a liquid such as butane (b.p. −0.5°C) on a cold surface at 0°C. The liquid boils and the vaporization is limited by heat transfer, the heat transfer being by convection from the air and by radiation, that from the ground being minimal.

They propose the use of the relations of Mackay and Matsugu (1973), given in Section 15.10.6, both for convective heat transfer from the air to the pool and for the net radiative heat transfer. For the former the heat transfer coefficient may be obtained from the expression for the mass transfer coefficient. They also discuss the question of the concentration and temperature at which the necessary physical properties should be determined.

A correlation for the vaporization rate for a liquid at a temperature above ambient has been given by the Centre for Chemical Process Safety (CCPS, 1987/2):

$$m_v = C_D u(\rho_{gs} - \rho_g) \qquad [15.10.52]$$

where C_D is the drag coefficient, u is the wind speed, ρ_g is the density of gas 10 m above the pool and ρ_{gs} is the saturation density of the gas at ambient conditions. The value of C_D is about 10^{-3} if u is measured 10 m above the pool.

15.10.6 Mackay and Matsugu model

A model for the vaporization of a volatile liquid from a circular pool has been given by Mackay and Matsugu (1973). The authors carried out experiments on the evaporation of water, gasoline and cumene from 4×4 ft and 4×8 ft pans.

In their model the heat balance on the pool is given by Equation 15.10.5, except that the term for heat conduction from the ground is omitted. For mass and heat transfer between the pool and the atmosphere:

$$N = \frac{k_m(p - p_\infty)}{RT_l} \qquad [15.10.53]$$

$$q_{cn} = h(T_a - T_l) \qquad [15.10.54]$$

with

$$k_m = Cu^{0.78}x^{-0.11} \qquad [15.10.55]$$

$$h = k_m \rho_v c_v (\mathrm{Sc}/\mathrm{Pr})^{0.67} \qquad [15.10.56]$$

$$C = k\mathrm{Sc}^{-0.67} \qquad [15.10.57]$$

where c is the specific heat, h is the heat transfer coefficient, k_m is the mass transfer coefficient, N is the mass transferred per unit area, p is the partial pressure of the vapour, q_{cn} is the heat flow per unit area by convection from the atmosphere to the pool, u is the wind speed, x is the diameter of the pool, C and k are constants and subscripts a, l, v and ∞ are air, liquid, vapour and atmosphere beyond influence of pool, respectively. In SI units, the value of k is $0.00482\ \mathrm{m}^{0.33}/\mathrm{s}^{0.22}$.

Equation 15.10.55 is based on the Sutton–Pasquill model with the diffusion index $n = 0.25$. The authors state that in terms of the factor j_m their correlation for the mass transfer coefficient is equivalent to

$$j_m = 0.0565\mathrm{Re}^{-0.22} \qquad [15.10.58]$$

where Re is in the range $7 \times 10^4 - 4.6 \times 10^5$.

For the net radiation the authors use Equations 15.10.34–15.10.36 with the values of the parameters quoted in Section 15.10.3.

As stated earlier, the model given by these authors does not include a term for heat transfer from the surface beneath the pool. This term was presumably not significant in their particular experiments, which involved evaporation pans.

15.10.7 Spreading of a liquid

Accounts of the spreading of liquids are given in *Water Waves* (Stoker, 1957) and *Oil on Sea* (Hoult, 1969) and by Abbott (1961) and Webber and Brighton (1986). Much of the work is concerned with the spreading of oil slicks, which is treated by Fay (1969, 1973) and by Hoult (1969, 1972b).

If the liquid is not confined within a hollow or a bund, but is free to spread, it is usually necessary to take account of such spreading and to use a treatment based on simultaneous spreading and vaporization. Spreading of a liquid on land and on sea differ somewhat and may require separate treatment.

The volume V of the liquid pool is a function of its radius r and height h

$$V = \pi r^2 h \qquad [15.10.59]$$

The growth of the pool may be expressed in terms either of the velocity u of the pool edge

$$\frac{dr}{dt} = u \qquad [15.10.60]$$

or of its acceleration.

As the pool spreads, it passes through different spreading regimes. Initially the frictional resistance may be negligible so that the gravity force is balanced by the inertia force. At a later stage, the inertia may be negligible so that the gravity force is balanced by the resistance force.

The pool growth has most commonly been modelled by the energy balance relation

$$\frac{dr}{dt} = (2g'h)^{1/2} \qquad [15.10.61a]$$

or, more generally,

$$\frac{dr}{dt} = c(g'h)^{1/2} \qquad [15.10.61b]$$

with

$$g' = g \quad \text{on land} \qquad [15.10.62a]$$

$$g' = g\Delta \quad \text{on water} \qquad [15.10.62b]$$

$$\Delta = \frac{\rho_w - \rho_l}{\rho_w} \qquad [15.10.63]$$

where g is the acceleration due to gravity, g' is the reduced gravity, Δ is the reduced density, c is a constant and subscripts l and w denote liquid and water, respectively.

The value of the constant c in Equation 15.10.61b has been extensively treated in the literature. A value of c of 1.4 is often used. This value is close to the value of $2^{1/2}$ implied in Equation 15.10.61a.

It may be noted that Equations 15.10.59 and 15.10.61 give

$$\frac{dr}{dt} \propto r^{-1} \qquad [15.10.64]$$

A treatment which takes account of both the gravity–inertia and gravity–viscous regimes has been given by Raj and Kalelkar (1974). In the former the gravity force F_g is opposed by the inertial force F_i

$$F_g = \pi \rho g' h^2 r \qquad [15.10.65]$$

$$F_i = -C\pi\rho h r^2 \frac{d^2 r}{dt^2} \qquad [15.10.66]$$

where C is a constant. The constant C represents the ratio of the inertia of the liquid system to the inertia that would exist if all the liquid were moving at the acceleration of the spill edge. The value given for C is 0.754.

Then, equating the two forces F_g and F_i gives

$$r\frac{d^2 r}{dt^2} = -\frac{g' h}{C} \qquad [15.10.67]$$

The authors also give a treatment of the gravity–viscous regime.

A relation that takes account of the frictional resistance has been given by Webber and Brighton (1986). They suggest that the natural model to use for the spreading of a thin layer of liquid is the shallow water, or shallow layer, equations (Stoker, 1957). From these equations they derive the relation

$$\frac{d^2 r}{dt^2} = \frac{4g' h(1-s)}{r} - F \qquad [15.10.68]$$

where F is a friction term and s is a shape factor. The friction factor is

$$F = C_L \frac{u^2}{h} + \left(\frac{3}{2}\right)^5 \frac{vu}{h^2} \quad \text{on land} \qquad [15.10.69a]$$

$$F = C_W \frac{u^2}{h} + 1.877\frac{vu}{h^2}(1-f) \quad \text{on water} \qquad [15.10.69b]$$

where v is the kinematic viscosity and C_L and C_W are constants for land and sea, respectively. The factor f allows for the effect on the shear stress on the pool of the radial motion in the water beneath it. In Equation 15.10.69 the right-hand side contains both a turbulent and a laminar term.

In a further treatment, Webber and Brighton (1986 SRD R371) have expressed their results in the form

$$\frac{d^2 r}{dt^2} = -\frac{gV}{\pi}\frac{\beta}{r^3} \qquad [15.10.70]$$

where β is a shape factor. The shape factor β determines the edge height of the pool and its value depends on the pool boundary conditions. Relevant factors include the surface tension of the liquid and the resistance of the ambient medium. For a convex pool $\beta < 0$, for a concave pool $\beta > 0$, for a cylindrical pool $\beta = 0$. A value of $\beta = -4$ corresponds to a pool with zero edge height (zero surface tension) and one of $\beta = 4$ corresponds to a pool with its centre tending to zero thickness. Hence from Equation 15.10.70

$$\frac{d^2 r}{dt^2} \propto r^{-3} \qquad [15.10.71]$$

15.10.8 Vaporization of a cryogenic liquid

In the general case of vaporization of a cryogenic liquid, or refrigerated liquefied gas, it is necessary to consider simultaneous spreading and vaporization. Considering initially just the vaporization, this is governed by heat transfer from the ground to the liquid. There is a short period of very rapid vaporization followed by a relatively steady lower rate of vaporization.

The rate of vaporization is obtained from the heat flux as given by Equation 15.10.30:

$$q = \left(\frac{k_s \rho_s c_{ps}}{\pi}\right)^{1/2} \frac{\theta_l}{t^{1/2}} \qquad [15.10.72]$$

Equation 15.10.72 may be written as

$$q = A_v t^{1/2} \qquad [15.10.73]$$

with

$$A_v = \left(\frac{k_s \rho_s c_{ps}}{\pi}\right)^{1/2} \theta_l \qquad [15.10.74]$$

where A_v is the vaporization parameter. Equation 15.10.73 has been confirmed experimentally.

It should be noted that for zero time Equation 15.10.72 gives an infinite heat transfer rate and is not applicable, but the period over which the heat transfer rate is overestimated is very short.

Most studies of the vaporization of cryogenic liquids have been concerned with liquefied natural gas (LNG) or liquefied ammonia. These are considered in the following sections.

Large-scale tests on the vaporization of refrigerated liquid ethylene have been conducted in Japan by a working group headed by Professor Hikita Tsuyoshi under the auspices of the Ministry of International Trade and Industry (MITI) (1976) and other bodies. This work was part of a programme of tests on various aspects of hazards of liquid ethylene.

In one test, 392 kg of liquid ethylene at a temperature of −104°C was poured into a 2.5 m diameter bund with a pebble floor. There was violent boiling of the liquid that caused an estimated 66% of it to vaporize or form spray within the first minute. The spillage gave rise to a cloud of ethylene with regions of mist and vapour.

The contours of the mist and of the vapour concentrations corresponding to lower explosive limit were similar, but not identical. The maximum distances reached by vapour concentrations of 2.7% (the lower explosive limit),

2.0% and 1.0% were 60, 80 and 86 m, respectively, all attained after 70 s. The mean wind speed was approximately 2.5 m/s.

The initial vaporization rate of the liquid ethylene over the first minute was fitted by the equation

$$v = 0.625\exp(-0.0507t) \qquad [15.10.75]$$

where t is the time (s) and v is the regression rate (cm/s). After the first minute the rate of vaporization was much reduced.

A collection of experimental data for the validation of models of spills of cryogenic liquids on land and water has been made by Prince (1985 SRD R324).

Vaporization from a pool of a cryogenic liquid constitutes initially a near-instantaneous source of vapour followed by steady, continuous source.

15.10.9 Spreading and vaporization of LNG

Accounts of the spreading and vaporization of LNG have been given by a number of workers including Burgess, Murphy and Zabetakis (1970 BM RI 7448), Humbert-Basset and Montet (1972), Kneebone and Boyle (1973), Feldbauer *et al.* (1972), Raj and Kalelkar (1973), the American Gas Association (AGA) (1974), Drake and Reid (1975), Opschoor (1977, 1980), Shaw and Briscoe (1978 SRD R100) and Raj (1979, 1981).

A general account of the spreading of a liquid such as LNG has been given in Section 15.10.7. In this section a description is given of work on the vaporization rate of a pool of LNG of fixed area on land or on water and of some simple treatments of simultaneous spreading and vaporization of LNG. Some principal models for the latter are given in the following sections.

Evaporation of liquid methane on common surfaces such as soil has been investigated by Burgess and Zabetakis (1962 BM RI 6099). They found that initially the vaporization rate v was limited by the rate of heat transfer from the substrate and was given by the relation

$$v = \frac{k_s}{\rho_l \Delta H_v}\frac{T_s - T_l}{(\pi\alpha_s t)^{1/2}} \qquad [15.10.76]$$

Equation 15.10.76 applied only to the initial rapid vaporization period, which did not exceed 1 min.

Values of the thermal conductivity and thermal diffusivity for different substrates are given by Carslaw and Jaeger (1959), as described below. There is relatively little difference between the values for average soil and normal concrete.

During the initial period the vaporization rate for liquid methane is high. Thereafter it decays and becomes dependent on the wind speed and is thus convection controlled. It approaches a constant value of approximately 0.02 in./min at low wind speeds after periods of 0.25–2 h. A log – log plot of vaporization rate vs time gives a straight line.

The evaporation of LNG on various surfaces has been investigated by Drake and Reid (1975). These authors describe experimental work at MIT and refer also to other experimental work by the American Gas Association (AGA) (1974) and work done by Gaz de France (Humbert-Basset and Montet, 1972). They found that the initial transfer and vaporization rates are in accordance with Equation 15.10.73, but that they vary considerably, depending on the nature of the substrate.

Drake and Reid quote both calculated and experimental values of the vaporization parameter A_v in Equation 15.10.73. Values of the parameters ρ_s, c_{ps} and k_s for various substrates are given by Carslaw and Jaeger (1959). From these parameters the corresponding values of A may be calculated. It is assumed that the substrate is at 16°C (60°F) and the LNG is at −162°C (−260°F) so that $(T_s - T_l)$ is 178°C. These calculated values of A_v are compared by Drake and Reed with experimental values for LNG spills obtained in the AGA and Gaz de France tests, as shown in Table 15.9. By contrast the value of A given for insulating concrete is 0.61.

Drake and Reid state that the rate of vaporization of LNG is greater than that of pure methane. It is greater on surfaces such as crushed rock or pebbles than on compacted soil. On soils, the vaporization rate is enhanced by percolation if the soil is dry. The extent of percolation in most soils is limited by the formation of a frozen barrier. Foaming is another factor that may increase the vaporization rate of LNG. A marked reduction in the vaporization rate of LNG may be obtained by the use of insulating concrete.

V.J. Clancey (1974a) has developed equations for the vaporization of a cryogenic liquid such as LNG. For the initial rapid vaporization

$$E_i = \frac{k_l(T_s - T_l)^2}{\Delta H_v} \qquad [15.10.77]$$

Table 15.9 *Vaporization parameters for LNG on different substrates (after Drake and Reid, 1975) (Courtesy of the American Institute of Chemical Engineers)*

	ρ_s (g/cm)	c_{ps} (cal/g°C)	k_s (cal/s cm°C)	A_v (cal/s$^{1/2}$cm^2)
Carslaw and Jaeger (1959, p. 497)				
Soil (average)	2.5	0.2	0.0023	3.41
Soil (sandy, dry)	1.65	0.19	0.00063	1.40
Soil (sandy, 8% moist)	1.75	0.24	0.0014	2.45
Concrete (1 : 2 : 4)	2.3	0.23	0.0022	3.39
AGA tests				
Soil (compacted)				8.5
Gaz de France				
Soil (dry, 15°C)				18.2
Soil (wet, 50°C)				12.7
Soil (wet, 15°C)				5.68

and for the steady continuous vaporization

$$E_s = \frac{k_2(T_s - T_l)}{\Delta H_v} \qquad [15.10.78]$$

where E_i is the mass vaporized per unit area within 1 min (g/cm^2), E_s is the steady-state mass vaporization rate per unit area (g/cm^2 min), ΔH_V is the latent heat of vaporization (cal/g) and k_1 and k_2 are constants. The values of the constants k_1 and k_2 are as follows:

Substrate	k_1	k_2
Average soil	7.1×10^{-4}	1.5×10^{-2}
Concrete	7.5×10^{-4}	1.5×10^{-2}
Sandstone	1.3×10^{-3}	2.6×10^{-2}

Equation 15.10.77 is applicable where the temperature difference $(T_s - T_l)$ is large, as for a spillage of liquid methane. It is assumed in Equation 15.10.77 that the depth of ground which gives up heat to the pool is proportional to $(T_s - T_l)$; this accounts for the occurrence in Equation 15.10.77 of the term $(T_s - T_l)^2$.

For a large spillage the time that elapses before the vaporization rate reaches a quasi-steady state may be an hour or more. Clancey suggests that the values of the vaporization rate in this intermediate period may be obtained by logarithmic interpolation between the initial and steady vaporization rates.

Vaporization rates of LNG on water are relatively high. Work has been carried out by a number of investigators, including Burgess, Murphy and Zabetakis (1970 BM RI 7448), Kneebone and Boyle (1973), Feldbauer *et al.* (1972), Germeles and Drake (1975) and Opschoor (1977, 1981).

Burgess, Murphy and Zabetakis obtained a mass vaporization rate of 0.18 kg/m^2 s and Feldbauer *et al.* (1972) one of 0.20 kg/m^2 s. The First *Canvey Report* states that the vaporization rate obtained in such work is of the order of 0.19 kg/m^2 s.

For the vaporization rate, Opschoor (1980) quotes the following relation of J.S. Turner (1965):

$$q_w = 0.085 k_w \left(\frac{g\beta\Delta T^4}{\alpha_w \nu_w}\right)^{1/3} \qquad [15.10.79]$$

where q_w is the heat flow per unit area by conduction from the water to the spill, ΔT is the temperature difference between the water and the liquid, β is the coefficient of cubical expansion and ν is the kinematic viscosity. For LNG, taking $\Delta T = 47.4$ K, Equation 15.10.79 gives

$$q_w = 2.3 \times 10^4 \text{ W/m}^2$$

which corresponds to a mass vaporization rate of

$$m_v = 0.045 \text{ kg/m}^2 \text{ s}$$

This value agrees well with the experimental results of Kneebone and Boyle (1973). Opschoor gives a preferred value of 0.05 kg/m^2 s.

Shaw and Briscoe (1978 SRD R100) use a regression rate based on the Esso work of 4.7×10^{-4} m/s. The regression rate used by Raj (1979) is 6.5×10^{-4} m/s.

Opschoor also gives relations for the estimation of the mass vaporization rate with ice formation beneath the LNG. It is found that an ice layer forms in about 20 s. Before the ice forms, film boiling pertains; once the film has formed heat transfer is by conduction through the ice. He gives for these two regimes the following mass vaporization rates:

$$m_v = 0.008t \quad 0 \le t \le 25 \qquad [15.10.80a]$$

$$m_v = \frac{0.517}{(t-20)^{1/2}} \quad t > 25 \qquad [15.10.80b]$$

where m_v is the mass vaporization rate per unit area (kg/m^2 s) and t is the time (s).

For simultaneous spreading and vaporization of LNG, Burgess, Murphy and Zabetakis (1970) have given the relations

$$r = k_3 t \qquad [15.10.81]$$

$$\frac{dm}{dt} = \pi \rho v r^2 \qquad [15.10.82]$$

$$m = \pi \rho v \int_0^t r^2(t)\, dt \qquad [15.10.83]$$

$$m = \frac{\pi}{3} \rho v k_3^2 t^3 \qquad [15.10.84]$$

where m is the total mass vaporized, r is the radial distance and k_3 is a constant. The value of the constant k_3 is 0.381. Then, taking the density of LNG as 416 kg/m^3, Equation 15.10.84 becomes

$$m = 63.2 v t^3 \qquad [15.10.85]$$

Lind (1974) has given a similar treatment but uses a value of k_3 of 0.635 based on the Esso experiments described by Feldbauer *et al.* (1972). From Equation 15.10.84 this gives

$$m = 175.7 v t^3 \qquad [15.10.86]$$

Fay (1973) has used Equations 15.10.59 and 15.10.61a, integrating the latter with the boundary conditions $t = 0$ and $r = 0$ to obtain

$$r = \left(\frac{8 g' V}{\pi}\right)^{1/4} t^{1/2} \qquad [15.10.87]$$

Equation 15.10.87 may be used with Equation 15.10.83 to determine the mass vaporized. Fay assumes in his treatment that ice forms beneath the spill, and that this determines the vaporization rate. Raj and Kalelkar (1973) obtained the relation

$$m = 1.712 \pi \rho v A^{1/2} t^2 \qquad [15.10.88]$$

where A is the volume of liquid for an instantaneous spill.

These and other models have been reviewed by Shaw and Briscoe (1978 SDR R100).

15.10.10 Shaw and Briscoe model

A series of models for simultaneous spreading and vaporization of continuous and instantaneous spills of LNG on land and on water has been given by Shaw and Briscoe (1978 SRD R100).

For the vaporization of LNG on land in a fixed area such as a bund they give

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{A_\mathrm{p} X k_\mathrm{s}(T_\mathrm{s} - T_\mathrm{b})}{\Delta H_\mathrm{v}(\pi\alpha_\mathrm{s})^{1/2} t^{1/2}} \qquad [15.10.89]$$

where A_p is the area of the pool, ΔH_v is the latent heat of vaporization, k is the thermal conductivity, m is the total mass vaporized, α is the thermal diffusivity, and subscripts b and s denote the boiling point and soil, respectively. The factor X takes account of surface roughness. In the tests by the Japan Gas Association, after 1 s the regression rate was some three times the theoretical value ($X = 1$), and on this basis the authors suggest a value for X of 3.

In general, for an LNG spill the volume V of the pool is

$$V = A + Bt - m/\rho \qquad [15.10.90]$$

where A is the volume of liquid for instantaneous spill and B is the volumetric flow for a continuous spill.

From Equations 15.10.59 and 15.10.61

$$\frac{\mathrm{d}r}{\mathrm{d}t} = \left(\frac{2g'V}{\pi r^2}\right)^{1/2} \qquad [15.10.91]$$

where r is the radius of the pool.

Analytical solutions of Equation 15.10.91 are obtained by neglecting the term m/ρ in Equation 15.10.90.

For an LNG spill on water the heat transfer rate, and hence the vaporization rate, is taken as constant and is characterized by the regression rate v. The authors use Equations 15.10.90 and 15.10.91 together with the relation

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \pi r^2 \rho v \qquad [15.10.92]$$

For an instantaneous spill on water, Equation 15.10.91 is solved with the condition $B = 0$ (and hence $V = A$), $t = 0$ and $r = r_\mathrm{o}$, where r_o is the initial radius of the pool. Then, integrating Equation 15.10.91

$$r = \left[\left(\frac{8g'A}{\pi}\right)^{1/2} t + r_\mathrm{o}^2\right]^{1/2} \qquad [15.10.93]$$

and using Equations 15.10.92 and 15.10.93 and integrating the former

$$m = \pi\rho v\left[\left(\frac{2g'A}{\pi}\right)^{1/2} t^2 + r_\mathrm{o}^2 t\right] \qquad [15.10.94]$$

For a continuous spill on water, Equation 15.10.91 is solved with the condition $A = 0$ (hence $V = Bt$), $t = 0$ and $r = 0$. Then, as before, integrating Equation 15.10.91 followed by Equation 15.10.92 gives

$$r = \left(\frac{2}{3}\right)^{1/2}\left(\frac{8g'B}{\pi}\right)^{\frac{1}{8}} t^{3/2} \qquad [15.10.95]$$

$$m = \frac{4}{15}\pi\rho v\left(\frac{8g'B}{\pi}\right)^{1/2} t^{5/2} \qquad [15.10.96]$$

For an LNG spill on land the vaporization rate is determined by the heat transfer, and hence the vaporization rate decreases with time. The relation used for the vaporization rate is

$$\frac{\mathrm{d}m}{\mathrm{d}t} = 2\pi\theta\int_0^{r_2} \frac{r_1}{(t_2 - t_1)^{1/2}}\,\mathrm{d}r_1 \qquad [15.10.97]$$

with

$$\theta = \frac{X k_\mathrm{s}(T_\mathrm{s} - T_\mathrm{b})}{\Delta H_\mathrm{v}(\pi\alpha_\mathrm{s})^{1/2}} \qquad [15.10.98]$$

where r_1 is the radius at time t_1, r_2 is the radius at time t_2 ($t_2 > t_1$) and θ is a parameter. Equations 15.10.90 and 15.10.91 are again used.

For an instantaneous spill on land, Equation 15.10.91 is solved with the conditions $B = 0$ (hence $V = A$), $t = 0$ and $r = r_\mathrm{o}$ Also on land, $g = g'$. Then, integrating Equation 15.10.91 gives

$$r = \left[\left(\frac{8gA}{\pi}\right)^{1/2} t + r_\mathrm{o}^2\right]^{1/2} \qquad [15.10.99]$$

For small r_o, Equation 15.10.99 becomes

$$r^2 \approx \left(\frac{8gA}{\pi}\right)^{1/2} t \qquad [15.10.100]$$

Hence

$$t = \beta_1 r^2 \qquad [15.10.101]$$

with

$$\beta_1 = \left(\frac{\pi}{8gA}\right)^{1/2} \qquad [15.10.102]$$

where β_1 is a constant.

Utilizing Equation 15.10.101 and integrating Equation 15.10.97 gives

$$m = \frac{8}{3}\theta(2\pi gA)^{1/2} t^{3/2} \qquad [15.10.103]$$

For a continuous spill on land, Equation 15.10.91 is solved with the conditions $A = 0$ (hence $V = Bt$), $t = 0$ and $r = 0$. Then, as before, integrating Equation 15.10.91 gives

$$r = \frac{2}{3}\left(\frac{8gB}{\pi}\right)^{1/4} t^{3/4} \qquad [15.10.104]$$

Hence

$$t = \beta^2 r^{4/3} \qquad [15.10.105]$$

with

$$\beta^2 = \left(\frac{9}{32}\frac{\pi}{gB}\right)^{1/3} \qquad [15.10.106]$$

where β^2 is a constant.

Utilizing Equation 15.10.105 and integrating Equation 15.10.97 gives

$$m = \pi^{3/2}\theta\left(\frac{gB}{2}\right)t^2 \qquad [15.10.107]$$

As stated above, the authors use for the regression rate for LNG on water the value from the Esso work of 4.7×10^{-4} m/s.

The authors also performed numerical integration of the full equations and obtained for the radius r_e and time t_e at the end of evaporation:

$$\ln r_e = 1.5 \ln t_e - 2.45 \qquad [15.10.108]$$

$$\ln t_e = 0.25(\ln M_s + 6) \qquad [15.10.109]$$

where M_s is the mass of the spill.

They also confirmed that it is justifiable to neglect the term m/ρ.

15.10.11 Raj model

Another series of models for simultaneous spreading and vaporization of continuous and instantaneous spills of LNG on land and on water has been given by Raj (1981), developing the earlier work of Raj and Kalelkar (1974). For a continuous spill on land the basic equation is

$$\frac{dq}{dt} = \frac{k_s \Delta T}{(\pi\alpha_s)^{1/2}(t - t_1)^{1/2}} 2\pi r_1 d_r \qquad [15.10.110]$$

with

$$\Delta T = T_s - T_l \qquad [15.10.111]$$

where k is the thermal conductivity, q is the heat flux per unit area, r is the radial distance, ΔT is the temperature difference between the liquid and the soil at distance r_1, and subscript 1 denotes at distance r_1.

Then, equating the steady-state vaporization rate per unit area and the volumetric flow of liquid into the spill V_c:

$$V_c = \frac{2\pi k_s \Delta T}{\Delta H_v \rho_l (\pi\alpha_s t)^{1/2}} \int_0^{r(t)} \frac{r_1}{(1 - t_1/t)^{1/2}} dr_1 \qquad [15.10.112]$$

where subscript l denotes the liquid.

Integration of Equation 15.10.112 gives

$$r(t) = \left(\frac{2\Delta H_v \rho_l V_c}{\pi^2 S \Delta T}\right)^{1/2} t^{1/4} \qquad [15.10.113]$$

with

$$S = \left(\frac{k_s \rho_s c_s}{\pi}\right)^{1/2} \qquad [15.10.114]$$

where c is the specific heat and ρ is the density.

Raj also shows that

$$V_c = \frac{\pi r^2 S \Delta T}{(2/\pi)\Delta H_v \rho_l} t^{1/2} \qquad [15.10.115]$$

The regression rate v is

$$v = \frac{V_c}{\pi r^2} \qquad [15.10.116]$$

For a continuous spill of finite size on land, using the result just given in Equation 15.10.115

$$V(t) + \frac{\pi^2 S \Delta T}{2\Delta H_v \rho_l} \int_0^t \frac{r^2}{t^{1/2}} dt = V_c t \quad t \le t_{sp} \qquad [15.10.117a]$$

$$= V_c t_{sp} \quad t > t_{sp} \qquad [15.10.117b]$$

where V is the volume of the pool and the subscript sp denotes the spill duration. The first term on the left-hand side of Equation 15.10.117 is the volume of liquid remaining and the second the volume vaporized.

Raj utilizes the liquid spreading relations 15.10.59 and 15.10.61b to obtain a numerical solution of Equation 15.10.117. For an instantaneous spill of LNG on land the basic equation is

$$V(t) + \int_0^t v(t)\pi r^2(t)\, dt = V_i \qquad [15.10.118]$$

with

$$v(t) = \frac{S\Delta T}{(2/\pi)\Delta H_v \rho_l t^{1/2}} \qquad [15.10.119]$$

where V_i is the volume of liquid in the instantaneous spill.

The relations utilized for the liquid spreading are Equations 15.10.59 and 15.10.67, together with Equation 15.10.118. From these relations are obtained for the final evaporation radius r_e and time t_e:

$$r_e = 1.248\left(\frac{\Delta H_v \rho_l}{S\Delta T}\right)^{1/3} V_i^{4/9} \qquad [15.10.120]$$

$$t_e = 0.639\left(\frac{\Delta H_v \rho_l}{S\Delta T}\right)^{2/3}\left(\frac{1}{g}\right)^{1/2} V_i^{7/18} \qquad [15.10.121]$$

For a continuous spill on water the basic equation is

$$\dot{V}(t) + \pi r^2 v = V_c \qquad [15.10.122]$$

The relations utilized for liquid spreading are Equations 15.10.59 and 15.10.61. The following relation is obtained for the final evaporation radius r_e:

$$r_e = \left(\frac{V_c}{\pi v}\right)^{1/2} \qquad [15.10.123]$$

For an instantaneous spill on water the basic equation is

$$V(t) + \pi \int_0^t v(t) r^2(t)\, dt = V_i \qquad [15.10.124]$$

The relation utilized for spreading is Equation 15.10.67.

The following relations are obtained for the final evaporation radius and time:

$$r_e = \left(\frac{V_i^3 g'}{v^2}\right)^{1/8} \quad [15.10.125]$$

$$t_e = 0.6743\left(\frac{V_i}{g' v^2}\right)^{1/4} \quad [15.10.126]$$

Raj (1979) has also given a criterion for classifying a spill of LNG on water as instantaneous or continuous. He defines the following dimensionless quantities:

$$L = V_i^{1/3} \quad [15.10.127]$$

$$t_{ch} = L/v \quad [15.10.128]$$

$$\xi = r/L \quad [15.10.129]$$

$$\tau = t/t_{ch} \quad [15.10.130]$$

where L is a characteristic length, t_{ch} is a characteristic evaporation time, ξ is a dimensionless maximum spread and τ is a dimensionless time.

Utilizing Equations 15.10.123 and 15.10.125 for the final spill radii for the two types of spill together with the fact that $V_c = V_i/t$, he obtains

$$\xi = \left(\frac{Lg'}{v^2}\right)^{1/8} \quad \text{instantaneous spill} \quad [15.10.131]$$

$$\xi = \frac{1}{(\pi\tau)^{1/2}} \quad \text{continuous spill} \quad [15.10.132]$$

Then from Equations 15.10.131 and 15.10.132 a value of τ may be obtained for the point at which the value of ξ is the same for the two equations.

Using a typical value of the regression rate v of LNG on water of 6.5×10^{-4} m/s gives a value of τ of 2×10^{-3} s. Then for the crossover time t_{cr} Raj gives the following values:

Volume spilled (m^3)	1000	10,000	25,000	50,000
Crossover time (s)	31	68	92	116

15.10.12 Opschoor model

A model for the simultaneous spreading and vaporization of an instantaneous spill of LNG on water has been given by Opschoor (1977, 1980).

For an instantaneous spill of LNG on water

$$V(t)\rho_l + \pi \int_0^t m_v r^2(t)\mathrm{d}t = V_i \rho_l \quad [15.10.133]$$

where m_v is the mass rate of vaporization per unit area.

Integration of Equation 15.10.133 gives

$$r = \left[0.44\frac{m_v g'}{\rho_l} t^3 + 1.3(g' V_i)^{1/2} t\right]^{1/2} \quad [15.10.134]$$

For the final evaporation radius and time

$$r_e = 1.02\left(\frac{g' \rho_l^2 V_i^3}{m_v^2}\right)^{1/8} \quad [15.10.135]$$

$$t_e = 0.67\left(\frac{\rho_l^2 V_i}{g' m_v^2}\right)^{1/4} \quad [15.10.136]$$

Opschoor also considers an LNG spill on a water surface of limited area A_o. Using Equation 15.10.134, but neglecting the first term on the right-hand side, the following relation is obtained for the time t_o for a water surface of area A_o to be fully covered:

$$t_o = 0.24\left(\frac{A_o^2}{g' V_i}\right)^{1/2} \quad [15.10.137]$$

The work of Opschoor on the mass vaporization rate of LNG on water has already been described in Section 15.10.9.

15.10.13 Spreading and vaporization of ammonia

Work on the spreading and vaporization of liquefied ammonia (LNH_3) on water has been described by Raj, Hagopian and Kalelkar (1974). Experiments were carried out in which quantities of ammonia up to 50 US gal were spilled on water.

When ammonia is spilled on water, part of it vaporizes and part goes into solution in the water. Defining a partition coefficient p as the proportion that dissolves, the authors obtained a value of $p \approx 0.6 \pm 0.1$. The remainder $(1-p)$ vaporizes.

The authors modelled the release assuming that the ammonia was at a temperature of −33°C, there was no initial entrainment of air and no spray formation. Under these conditions the cloud is buoyant. They treated the dispersion in terms of a buoyant plume model. For the final evaporation radius and time they give:

$$r_e = 2.5V^{0.375} \quad [15.10.138]$$

and

$$t_e = 0.674\left(\frac{V}{g' v^2}\right)^{1/4} \quad [15.10.139]$$

where r_e is the final evaporation radius (ft), t_e is the final evaporation time (s), v is the regression rate (ft/s), and V is the volume spilled (US gal). The authors obtained a regression rate of 2.8 in./min.

Using a thermodynamic analysis, Raj and Reid (1978a) have shown that it is possible to determine the point at which further addition of water simply dilutes the solution without causing any further evolution of ammonia and to obtain the value of the partition coefficient. For the illustrative example considered the experimental partition coefficient was 0.73 and the theoretical value 0.715.

Griffiths (1977 SRD R67) has criticized the interpretation given by Raj, Hagopian and Kalelkar and gives an alternative interpretation of the results assuming that spray formation occurs and that the plume is not buoyant.

15.10.14 Computer codes

A number of computer codes have been written for vaporization. A review of these has been given by the CCPS (1987/2). The Safety and Reliability Directorate (SRD) code SPILL is based on the model of Shaw and Briscoe (1978 SRD R100). It has been described by Prince (1981 SRD R210). Another program is the Shell SPILLS code which is described by Fleischer (1980).

15.11 Dispersion

Emission and vaporization are followed by dispersion of the vapour to form a vapour cloud.

Accounts of gas dispersion of particular relevance here include those given in *Micrometeorology* (O.G. Sutton, 1953), *Atmospheric Diffusion* (Pasquill, 1962a, 1974) *Meteorology and Atomic Energy* (Slade, 1968), *An Evaluation of Dispersion Formulas* (Anderson, Hippler and Robinson, 1969), *Recommended Guide for the Prediction of the Dispersion of Airborne Effluents* (ASME, 1969/1, 1973/2, 1979/4), *Workbook of Atmospheric Dispersion Estimates* (D.B. Turner, 1970), *Turbulent Diffusion in the Environment* (Csanady, 1973) and *Handbook on Atmospheric Diffusion* (Hanna, Briggs and Hosker, 1982), and those given by Pasquill and Smith (1983).

Dispersion models used in the nuclear industry are described in the Nuclear Regulatory Commission (NRC) *Regulatory Guide 1.111 Methods for Estimating Atmospheric Transport and Dispersion of Gaseous Effluents in Routine Releases from Light-water-cooled Reactors* (1974) and the NRC *Regulatory Guide 1.145 Atmospheric Dispersion Models for Potential Accident Consequence Assessments at Nuclear Power Plants* (1979a). The NRC has also published an account of the basis for *Regulatory Guide 1.145* (1981 NUREG/CR-2260). Another nuclear industry dispersion model is *A Model for Short and Medium Range Dispersion of Radionuclides into the Atmosphere* by Clarke (1979 NRPB R91).

Work on dispersion is primarily concerned with the dispersion of pollutants from industrial chimney stacks. Most of the fundamental work on dispersion relates to this problem. There is, however, an increasing amount of work on dispersion of hazardous releases from process plant.

Selected references on dispersion are given in Table 15.10.

Table 15.10 *Selected references on dispersion*

Meteorology

NRC (Appendix 28 *Meteorology,* 1972); Lamb (1932); Nikuradse (1933); Prandtl (1933); Schlichtling (1936, 1960); Brunt (1934); Milne-Thomson (1938); O.G. Sutton (1949, 1953, 1962); Geiger (1950); Hewson (1951); Malone (1951); Batchelor (1953, 1956, 1964, 1967); Brooks and Carruthers (1953); Singer and Smith (1953, 1966); Clauser (1954, 1956); G.F. Taylor (1954); AEC (1955); Townsend (1956); Haltiner and Martin (1957); Scorer (1958, 1978); Byers (1959); Priestley (1959); Chandrasekhar (1961); Monin (1962); Ogura and Phillips (1962); Pasquill (1962, 1974); Lumley and Panofsky (1964); Roll (1965); Munn (1966); Wu (1965); Bowne, Ball and Anderson (1968); Meteorological Office (1968, 1972, 1975, 1991, 1994); Slade (1968); Swinbank (1968); Trewartha (1968); ASME (1969/1, 1975/2, 1979/3, 4); Mclntosh and Thorn (1969); Monin (1970); D.B. Turner (1970); R.J. Taylor, Warner and Bacon (1970); Bradshaw (1971, 1978); Businger and Yaglom (1971); B.J. Mason (1971); Monin and Yaglom (1971); Tsang (1971); Launder and Spalding (1972); Mclntosh (1972); Tennekes and Lumley (1972); Zilitinkevich (1972a); Busch (1973); Blackadar (1976); Oke (1978); Caughey, Wyngaard and Kaimal (1979); Sethuraman and Raynor (1979); Cermak (1980); Kreith (1980); Venkatram (1980b, 1981a); A.E. Mitchell (1982); Plate (1982); Tennekes (1982); Volland (1982); Pasquffl and Smith (1983); Panofsky and Dutton (1984); Houghton (1985); J.C.R. Hunt (1985); Page and Lebens (1986); Anfossi (1989); Bartzis (1989); A.D. Young (1989); Lindzen (1990); Swaid (1991)

Lagrangian length scale: J.S. Hay and Pasquill (1959); J.D. Reid (1979); Hanna (1979a, 1981b); Hanna, Briggs and Hosker (1982)

Atmospheric boundary layer: Panofsky (1968, 1973, 1978); Deardorff (1970, 1973, 1974); Pasquill (1972); Zilitinkevich (1972b); Businger (1973, 1982); Csanady (1973); Tennekes (1973a); Wyngaard (1973, 1982); Wyngaard, Arya and Cote (1974); Wyngaard and Cote (1974); Wyngaard, Cote and Rao (1974); Counihan (1975); Kaimal *et al.* (1976); H.N. Lee (1979); Nichols and Readings (1979); Caughey (1982); Nieuwstadt (1984a,b); Holtslag and Nieuwstadt (1986)

Wind characteristics: Irwin (1979b); Wieringa (1980); Oehlert (1983); Nitz, Endlich and Ludwig (1986); R. Weber (1992)

Roughness length, friction velocity: Paeschke (1937); O.G. Sutton (1953); Plate (1971); Mulhearn (1977); Oke (1978); Wieringa (1981); Brutsaert (1982); Venkatram and Paine (1985); San Jose *et al.* (1986)

Wind velocity profile: Frost (1947); Deacon (1949, 1957); Lettau (1959); Panofsky, Blackadar and McVehil (1960); McVehil (1964); Swinbank (1964); Bowne and Ball (1970); Dyer and Hicks (1970); Paulson (1970); Webb (1970); Businger *et al.* (1971); P.M. Jones, Larrinaga and Wilson (1971); Colder (1972); Tennekes (1973a); Dyer (1974); Sethuraman and Brown (1976); Touma (1977); Yaglom (1977); Carson and Richards (1978); H.N. Lee (1979); Sethuraman and Raynor (1979); Skibin and Businger (1985); Hanafusa, Lee and Lo (1986); Leahey (1987)

Mixed layer height: Holzworth (1967, 1972); Zilitmkevich (1972a,b); Businger and Arya (1974); Tennekes and van Ulden (1974); Gryning *et al.* (1987)

Mixed layer scaling, convective velocity scale: Wyngaard, Cote and Rao (1974); Deardorff and Willis (1975); Wyngaard (1975); Willis and Deardorff (1976, 1978); Panofsky *et al.* (1977); Venkatram (1978); Nieuwstadt (1980b)

Exchange coefficients: O.G. Sutton (1953); Pasquill (1974); Mizuno and Yokoyama (1986)

Stability criteria: L.F. Richardson (1920, 1925, 1926); Monin and Obukhov (1954); Kazanski and Monin (1960); Monin (1970); Obukhov (1971); Willis and Deardorff (1976, 1978)

Stability classification: O.G. Sutton (1953); M.E. Smith (1956); Singer and Smith (1953, 1966); Cramer (1957, 1959a,b, 1976); Pasquill (1961); D.B. Turner (1961, 1964); Klug (1969); Carpenter *et al.* (1971); Colder (1972); Luna and Church (1972); F.B. Smith (1973, 1979); Liu *et al.* (1976); Hanna *et al.* (1977); AMS (1978); Clarke (1979 NRPB R91); Sedeflan and Bennett (1980); Schacher, Fairall and Zannetti (1982); Taglizucca and Nanni (1983); Kretschmar and Mertens (1984); Skupniewicz and Schacher (1984, 1986); Hasse and Weber (1985); Larsen and Gryning (1986); Ning and Yap (1986); Draxler (1987)

Vertical heat flux: Caughey and Kaimal (1977); Clarke (1979 NRPB R91); Maul (1980); Holtslag and van Ulden (1983)

Atmospheric visibility: Horvath (1981)

Dispersion
NRC (Appendix 28 *Gas Dispersion,* 1974,1979a); G.I. Taylor (1915,1921,1927); O.F.T. Roberts (1923); LF. Richardson and Proctor (1925); Schmidt (1925); LF. Richardson (1926); O.G. Sutton (1932,1947,1953); Dryden (1939); Bakhmeteff (1941); Katan (1951); Batchelor (1952,1953,1956,1964); Frenkiel (1952); Chamberlain (1953); AFC (1955); Bodurtha (1955); Gosline, Falk and Helmers (1955); Crank (1956); Cramer (1957, 1959a,b); Gifford (1957, 1960a, 1961,1962a,b, 1968,1976a,b,1977,1986,1987); H.L. Green and Lane (1957–); Cramer, Record and Vaughan (1958); Hilst and Simpson (1958); Hinze (1959); Ellison and Turner (1960); Bowne (1961); Friedlander and Topper (1961); Pasquill (1961, 1962, 1965, 1975, 1976a,b); P.M. Roberts (1961); Monin (1962); Beattie (1963 UKAEA AHSB(S) R64); Bryant (1964 UKAEA AHBS(RP) R42); Cramer *et al.* (1964); Panofsky and Prasad (1965); Yih (1965); Kreyzig (1967); Hansen and Shreve (1968); D.O. Martin and Tikvart (1968); R.O. Parker and Spata (1968); Ross (1968); Slade (1968); Anderson, Hippler and Robinson (1969); API (1969 Publ. 4030,1982 Publ. 4360,1987 Publ. 4457); ASME (1969/1,1975/2,1979/3, 4); Briggs (1969); Csanady (1969,1973); Fay and Hoult (1969); Larsen (1969); Burgess, Murphy and Zabetakis (1970); A.J. Clarke, Lucas and Ross (1970); Hearfield (1970); MCA (1970/16); D.B. Turner (1970); Pasquill and Smith (1971); Ramsdell and Hinds (1971); Simpson (1971); Beryland (1972,1975); J.T. Davies (1972); Monji and Businger (1972); Tennekes and Lumley (1972); Yang and Meroney (1972); Calder (1973); Haugen (1973, 1976); Leslie (1973); Mathis and Grose (1973); Ragland (1973); F.B. Smith (1973); J.S. Turner (1973); Winter (1973); V.J. Clancey (1974a, 1976a, 1977a,c); Deardorff and Willis (1974); J.D. Reed (1974); Eisenberg, Lynch and Breeding (1975); R.W. McMullen (1975); Runca and Sardei (1975); Drysdale (1976a); Nappo (1976,1981); Willis and Deardorff (1976,1978); Bass, Hoffnagle and Egan (1977); Comer (1977); S.K Friedlander (1977); Griffiths (1977 SRD R85); Kletz (1977–78); US Congress, OTA (1977); AMS (1978); R.P. Bell (1978); Carson and Richards (1978); HSE (1978b); Nieuwstadt and van Ulden (1978); Slater (1978a); Venkatram (1978,1980a); Beychok (1979); Bowne and Yocom (1979); Dobbins (1979); S.R. Hanna (1979b); C.J. Harris (1979); Harvey (1979b); Nieuwstadt and van Duuren (1979); Raj (1979); TNO (1979); T.B. Morrow *et al.* (1980); Nieuwstadt (1980a,b); Reijnhart, Piepers and Toneman (1980); Reijnhart and Rose (1980); Rodi (1980); Spencer and Farmer (1980); Arya and Shipman (1981); Arya, Shipman and Courtney (1981); Bower and Sullivan (1981); Dunker (1981); Holtslag, de Bruin and van Ulden (1981); Nappo (1981); Steenkist and Nieuwstadt (1981); Venkatram (1981b, 1988a,b); D.J. Wilson (1981a); de Wispelaere (1981,1983,1984,1985); S.R. Hanna (1982); S.R. Hanna, Briggs and Hosker (1982); N.C. Harris (1982); J.C.R. Hunt (1982); Lamb (1982,1984); Mecklenburgh (1982,1985); Nieuwstadt and van Dop (1982); O'Shea (1982); Comer *et al.* (1983); C.D. Jones (1983); Ludwig, Listen and Salas (1983); Ludwig and Livingston (1983); Diedronks and Tennekes (1984); Panofsky and Dutton (1984); Pendergrass and Arya (1984); Zeman (1984); Cogan (1985); Hukkoo, Bapat and Shirvaikar (1985); Lupini and Tirabassi (1985); K.R. Peterson (1985); Carson (1986); Davidson (1986); Enger (1986); Hamza and Golay (1986); Jakeman, Taylor and Simpson (1986); Mizuno and Yokoyama (1986); de Wispelaere, Schiermeier and Gillani (1986); Zanetti (1986, 1990); Andren (1987); Irwin *et al.* (1987); Li Zong-Kai and Briggs (1988); Lawson, Snyder and Thompson (1989); Nema and Tare (1989); Underwood (1989 SRD R483); Finch and Serth (1990); S.R. Hanna, Chang and Strimatis (1990); Linden and Simpson (1990); Guinnup (1992); Runca (1992); van Ulden (1992); Verver and de Leeuw (1992); Eckman (1994); Straja (1994)

Lagrangian models: van Dop (1992); Runca (1992)

Large eddy simulation: Henn and Sykes (1992); Nieuwstadt (1992); Sykes and Henn (1992)

Models, codes
Kaiser (1976 SRD R63); NRC (1972); Church (1976); Tennekes (1976); Benson (1979); D.B. Turner and Novak (1978); NRPB (1979 R91); AGA (1980/31, 32); Pierce and Turner (1980); Schulman and Scire (1980); Zanetti (1981, 1990); Hanna *et al.* (1984); Doron and Asculai (1983); Mikkelsen, Larsen and Thykierg-Nielsen (1984); Ames *et al.* (1985); Irwin, Chico and Catalano (1985); Berkowitz, Olesen and Torp (1986); EPA (1986); Layland, McNaughton and Bodner (1986); H.N. Lee (1986); W.B. Petersen (1986); Benarie (1987); API (1988 Publ. 4461, 1989 Publ. 4487); Doury (1988); Freiman and Hill (1992); Seigneur (1992); Bianconi and Tamponi (1993)

Experimental trials
M.E. Smith (1951); Pasquill (1956, 1962); Lettau and Davidson (1957); Barad (1958); Haugen (1959); Islitzer (1961, 1965); MacCready, Smith and Wolf (1961); F.B. Smith and Hays (1961); Barad and Fuquay (1962); Haugen and Fuquay (1963); Haugen and Taylor (1963); Islitzer and Dumbauld (1963); Cramer *et al.* (1964); Fuquay, Simpson and Hinds (1964); Gartrell *et al.* (1964); Islitzer and Markee (1964); Islitzer and Slade (1964, 1968); T.B. Smith *et al.* (1964); J.H. Taylor (1965); Lapin and Foster (1967); McElroy and Pooler (1968); Seargeant and Robinett (1968); Carpenter *et al.* (1971); Halitsky and Woodward (1974); van der Hoven (1976); Nickola (1977); Nieuwstadt and van Duuren (1979); AGA (1980/31); Defense Technical Information Center (1980); Doury (1981); Dabberdt *et al.* (1982); Dabberdt *et al.* (1983); Yersel, Goble and Merrill (1983); Vanderborght and Kretschmar (1984); Ramsdell, Glantz and Kerns (1985); Briggs *et al.* (1986); Schiermeier, Lavery and Dicristofaro (1986)

Meandering plumes
Falk *et al* (1953); M.E. Smith (1956); Gifford (1959, 1960b); Csanady (1973); Vogt, Straka and Geiss (1979); Zanetti (1981); S.R. Hanna (1984, 1986); Ride (1988)

Inversion conditions, non-Gaussian models
Gifford (1960b); Sagendorf (1975); van der Hoven (1976); Tennekes (1976); Robson (1983); Hukkoo, Bapat and Shirvaikar (1985); Venkatram and Paine (1985)

Calm conditions
Sagendorf (1975); Gifford (1976a,b); van der Hoven (1976)

Time-varying conditions
Ludwig (1981, 1984, 1986); Skibin (1983)

Puff vs plume criterion
Eisenberg, Lynch and Breeding (1975); Hesse (1991b)

Similarity models
Townsend (1956); Panofsky and Prasad (1965); Gifford (1968); Csanady (1973); PasquiU (1974, 1976b); Scorer (1978); Horst (1979); S.R. Hanna, Briggs and Hosker (1982)

Gradient transfer models, *K* models
O.F.T. Roberts (1923); Nieuwstadt and van Ulden (1978); Dvore and Vaglio-Laurin (1982); S.R. Hanna, Briggs and Hosker (1982); Runca (1982); Gryning, van Ulden and Larsen (1983); Gryning and Larsen (1984); Larsen and Gryning (1986); Gryning *et al.* (1987)

Urban areas
D.B. Turner (1964); PasquiU (1970); S.R. Hanna (1971, 1976); W.B. Johnson *et al.* (1971); Gifford (1972, 1976a,b); Ragland (1973); Bowne (1974); Chang and Weinstock (1974); Dabberdt and Davis (1974); D.S. Johnson and Bornstein (1974); Yersel, Goble and Morrill (1983); Depaul and Sheih (1985,1986); Oerlemans (1986); Jakeman, Jun and Taylor (1988); Surridge and Goldreich (1988); Bachlin, Plate and Theurer (1989); Gatz (1991); Grimmond, Cleugh and Oke (1991)

Coastal areas, sea
Roll (1965); Sethuraman, Brown and Tichler (1974); Kondo (1975); Gifford (1976a,b); Lyons (1976); Sethuraman, Meyers and Brown (1976); Nichols and Readings (1979); Cooper and Nixon (1984 SRD R307); S.R. Hanna, Paine and Schulman (1984); Manins (1984); Hasse and Weber (1985); Larsen and Gryning (1986); Stunder and Sethuraman (1986); Gryning *et al.* (1987); S.R. Hanna (1987a); Spangler and Johnson (1989); Khoo and Chew (1993)

Model comparisons
Nappo (1974); Gifford (1976a,b); Long and Pepper (1976); Venkatram (1981b); EPA (1984a,b); W.M. Cox and Tikvart (1986); Hayes and Moore (1986); Hinrichsen (1986); Layland, McNaughton and Bodmer (1986); M.E. Smith (1986); Stunder and Sethuraman (1986); Irwin *et al.* (1987); Zannetti (1990); Cirillo and Poll (1992); Dekker and Sliggers (1992); Poli and Cirillo (1993)

Diffusion parameters
O.G. Sutton (1953); Haugen, Barad and Athanaitas (1961); PasquiU (1962, 1974, 1976a); Hogstrom (1964); Beals (1971); Eimutis and Konicek (1972); Montgomery *et al.* (1973); Hosker (1974b); Pendergast and Crawford (1974); R.W. McMullen (1975); Draxler (1976, 1979); Gifford (1976a,b, 1980, 1987); AH. Weber (1976); Doran, Horst and Nickola (1978); Horst, Doran and Nickola (1979); Sedefian and Bennett (1980); D.J. Wilson (1981a); S.R. Hanna (1981a); S.R. Hanna, Briggs and Hosker (1982); Schayes (1982); Comer *et al* (1983); Pasquill and Smith (1983); Irwin (1984); Venkatram, Strimaitis and Dicristoforo (1984); Atwater and Londergan (1985); Bowling (1985); Henderson-Sellers (1986); San Jose *et al.* (1986); Gryning *et al.* (1987); Wratt (1987); Georgopoulos and Seinfeld (1988); R.F. Griffiths (1994b)

Estimation schemes: AMS (1977); Hanna *et al.* (1977); Irwin (1979a, 1983); Randerson (1979)

Urban areas: D.B. Turner (1964); McElroy (1969); Bowne (1974); Gifford (1976a,b); Santomauro, Maestro and Barberis (1979); Yersel, Goble and Morrffl (1983)

Complex terrain: Kamst and Lyons (1982)

Dispersion over water: Hosker (1974a); Kondo (1975); Ching-Ming Sheih (1981); Hanna, Paine and Schulman (1984); Hasse and Weber (1985); Skupniewicz and Schacher (1984); Larsen and Gryning (1986)

Dispersion over short ranges
O.G. Sutton (1950); Long (1963); G.A. Briggs (1974); Hanzevack (1982); Palazzi *et al.* (1982); Yersel, Golle and Morrill (1983); R. Powell (1984); CaUander (1986); Kaufman *et al.* (1990)

Dispersion from pipelines
D.J. Wilson (1979b, 1981b)

Concentration fluctuations, peak-mean concentrations
Gosline (1952); Fuquay (1958); Gifford (1960b, 1970); Becker, Hottel and Williams (1965); Hinds (1969); Barry (1971, 1972); Ramsdell and Hinds (1971); Csanady (1973); C.D. Jones (1979, 1983); Fackrell and Robins (1982); D.J. Wilson (1982, 1986, 1991a); D.J. Wilson, Robins and Fackrell (1982, 1985); D.J. Wilson, Fackrell and Robins (1982); Deardorff and WilUs (1984); R.F. Griffiths and Megson (1984); S.R. Hanna (1984, 1986); Ride (1984a,b, 1988); R.F. Griffiths and Harper (1985); D.J. Wilson and Sims (1985); Apsimon and Davison (1986); Georgopoulos and Seinfeld (1986); Lewellen and Sykes (1986); S.T. Brown (1987); Derksen and Sullivan (1987); Bara, Wilson and Zelt (1992)

Emergency gas dispersion modelling (*see also* Table 29.1)
M.E. Smith *et al.* (1983); Mudan (1984b); Lynskey (1985); Nitz, Endlich and Ludwig (1986); McNaughton, Worley and Bodmer (1987); Mulholland and Jury (1987)

Jets and plumes (see Table 15.40)

Obstacles, buildings
Gifford (1960a, 1976a,b); Halitsky (1963, 1968, 1977); Barry (1964); Hinds (1967, 1969); van der Hoven (1968); Slade (1968); Dickson, Start and Markee (1969); J.C.R. Hunt (1971,1985); Meroney and Yang (1971); AEC (1975); Cagnetti (1975); Huber and Snyder (1976, 1982); D.J. Wilson (1976, 1979a); Vincent (1977, 1978); Brighton (1978,1986); J.C.R. Hunt, Snyder and Lawson (1978); D.J. Wilson and Nettervffle (1978); Hosker (1979, 1980); Huber (1979, 1984, 1988, 1989); Ferrara and Cagnetti (1980); J.C.R. Hunt and Snyder (1980); C.D. Barker (1982); Castro and Snyder (1982); Fackrell and Robins (1982); Ogawa and Oikawa (1982); Ogawa *et al.* (1982); D.J. Wilson and Britter (1982); Li and Meroney (1983); Ogawa, Oikawa and Uehara (1983); Fackrell (1984a,b); Snyder and Hunt (1984); C.D. Jones and Griffiths (1984); Ryan, Lamb and Robinson (1984); M.E. Davies and Singh (1985a); Rottman *et al.* (1985); Arya and Gadiyaram (1986); Bachlin and Plate (1986, 1987); Boreham (1986); McQuaid (1986); Maryon, Whitlock and Jenkins (1986); R.S. Thompson and Shipman (1986); M. Epstein (1987); G.A. Briggs *et al.* (1992); R.S. Thompson (1993)

Complex terrain
Egan (1976); Egan, d'Errico and Vaudo (1979); Reible, Shair and Kauper (1981); Lett (1984, 1986); Callander (1986); P.A. Davis *et al.* (1986); Dawson, Lamb and Stock (1986); Dicristofaro and Egan (1986); Horst and Doran (1986); Lavery *et al.* (1986); Massmeyer *et al.* (1986); Rowe and Tas (1986); Schiermeier, Lavery and Dicristofaro (1986); Strimaitis and Snyder (1986); R.S. Thompson and

Shipman (1986); Arya, Capuana and Fagen (1987); Snyder and Britter (1987); Castro, Snyder and Lawson (1988); Lawson, Snyder and Thompson (1989); Ohba, Okabayashi and Okamoto (1989); Spangler and Johnson (1989); Ohba *et al.* (1990); Ramsdell (1990); Snyder (1990); Yoshikawa *et al.* (1990)

Physical modelling, wind and water tunnel experiments
Strom and Halitsky (1955); Strom, Hackman and Kaplin (1957); Meroney and Yang (1971); Hoot, Meroney and Peterka (1973); Meroney, Cermak and Neff (1976); Britter (1980); Castro and Snyder (1982); Huber and Snyder (1982); Meroney (1982); Ogawa *et al.* (1982); Bradley and Carpenter (1983); Cheah, Cleaver and Milward (1983a,b); Chea *et al.* (1984); Wighus (1983); Ogawa, Oikawa and Uehara (1983); Meroney and Lohmeyer (1984); T.B. Morrow, Buckingham and Dodge (1984); D.J. Hall and Waters (1985); van Heugten and Duijm (1985); Milhe (1986); RiethmuUer (1986); Schatzmann, Lohmeyer and Ortner (1987); Snyder and Britter (1987); Bara, Wilson and Zelt (1992)

Flammable cloud formation
Hess and Stickler (1970); Hess, Leuckel and Stoeckel (1973); Burgess *et al.* (1975); V.J. Clancey (1974a, 1977a,c); Eisenberg, Lynch and Breeding (1975); Sadee, Samuels and O'Brien (1976–77); R.A. Cox (1977); J.G. Marshall (1977, 1980); Harvey (1979b); van Buijtenen (1980); T.B. Morrow (1982b); Hesse (1991a)

Infiltration into buildings
Dick (1949, 1950a,b), Dick and Thomas (1951); BRE (1959); Megaw (1962); Slade (1968); Handley and Barton (1973); AEC (1975); Ministry of Social Affairs (1975); CIBS (1976); Brundrett (1977); HSE (1978b); Gufflaume *et al.* (1978); KronvaU (1978); Jackman (1980); Warren and Webb (1980a,b); Terkonda (1983); Haastrup (1984); Pape and Nussey (1985); Sinclair, Psota-Kelty and Weschler (1985); P.C. Davies and Purdy (1986); Pietersen (1986c); British Gas (1987 Comm. 1355); ASHRAE (1988 ASHRAE 119); El-Shobosky and Hussein (1988); Deaves (1989); Jann (1989); van Loo and Opschoor (1989); D.J. Wilson (1990, 1991b); D.J. Wilson and Zelt (1990); Zelt and Wilson (1990); McQuaid (1991); Engelmann (1992); McCaughey and Fletcher (1993); Rosebrook and Worm (1993)

Infiltration into cars: M. Cooke (1988)

Dispersion in buildings
B.R. Morton, Taylor and Turner (1956); Baines and Turner (1969); L.A. Wallace *et al.* (1985); Loughan and Yokomoto (1989); Cleaver, Marshall and Linden (1994)

Safe discharge and dispersion
Bosanquet (1935, 1957); Bosanquet and Pearson (1936); Chester and Jesser (1952); Bodurtha (1961, 1980, 1988); Long (1963); Loudon (1963); ASME (1969/1); Cairney and Cude (1971); Bodurtha, Palmer and Walsh (1973); Cude (1974a,b); Nonhebel (1975); de Faveri, Hanzevack and Delaney (1982); Hanzevack (1982); Palazzi *et al.* (1982); Jagger and Edmundson (1984); Palazzi *et al.* (1984); Burgoyne (1987); Moodie and Jagger (1987)

Deposition and removal
Gregory (1945); Bosanquet, Carey and Halton (1950); Chamberlain (1953, 1959, 1961, 1966a,b, 1975); Chamberlain and Chadwick (1953,1966); N.G. Stewart *et al.* (1954); Csanady (1955, 1973); F.G. May (1958); P.A. Sheppard (1958); E.G. Richardson (1960); Leighton (1961); Gifford and Pack (1962); F.B. Smith (1962); Hage (1964); Calvert and Pitts (1966); Engelmann (1968); van der Hoven (1968); Slade (1968); Marble (1970); Beadle and Semonin (1974); Demerjian, Kerr and Clavert (1974); Hosker (1974b); Krey (1974); AEC (1975); McEwen and Phillips (1975); Dana and Hales (1976); Hales (1976); Heicklen (1976); Overcamp (1976); V.J. Clancey (1977b); Horst (1977, 1980); Sehmel and Hodgson (1978,1980); Slater (1978a); McMahon and Denison (1979); Jensen (1980); NRPB (1980 R101); Sehmel (1980); Corbett (1981); Lodge *et al.* (1981); Meszaros (1981); P.M. Foster (1982); Garland and Cox (1982); S.R. Hanna, Briggs and Hosker (1982); Hosker and Lindberg (1982); Sievering (1982, 1989); R.M. Williams (1982a,b); Bartzis (1983); Ibrahim, Barrie and Fanaki (1983); Murphy and Nelson (1983); Pruppacher, Semonin and Slinn (1983); Cadle, Dasch and Mulawa (1985); Cher (1985); Doran and Horst (1985); El-Shobosky (1985); Schack, Pratsinis and Friedlander (1985); Sinclair, Psota-Kelty and Weschler (1985); Kumar (1986); Bettis, Makhviladze and Nolan (1987); Underwood (1987, 1987 SRD R423, 1988 SRD R442); Bache, Lawson and Uk (1988); M. Bennett (1988); El-Shobosky and Hussain (1988); Joffre (1988); Nicholson (1988, 1993); Venkatram (1988b); Dugstad and Venkatram (1989); Adhikari *et al.* (1990); M.P. Singh, Kumari and Ghosh (1990); A.G. Allen, Harrison and Nicholson (1991); Schorling and Kardel (1993)

Vapour solubility and chemical reactions
Clough and Garland (1970); Murata *et al.* (1974); HSE (1978b); Burton *et al.* (1983); Das Gupta and Shen Dong (1986); Raj (1986); Shi and Seinfeld (1991)

Topics common to passive and dense gas dispersion, including source terms, mitigation systems and hazard assessment (*see* Table 15.42)

15.11.1 Dispersion situations

Dispersion situations may be classified as follows. The fluid and the source may be classified as:

(1) Fluid buoyancy
  (a) neutral buoyancy,
  (b) positive buoyancy,
  (c) negative buoyancy.
(2) Momentum
  (a) low momentum,
  (b) high momentum.
(3) Source geometry
  (a) point source,
  (b) line source,
  (c) area source.
(4) Source duration
  (a) instantaneous,
  (b) continuous,
  (c) intermediate.
(5) Source elevation
  (a) ground level source,
  (b) elevated source.

The dispersion takes place under particular meteorological and topographical conditions. Some principal features of these are as follows:

(1) Meteorology
  (a) wind,
  (b) stability.
(2) Topography
  (a) surface roughness,
  (b) near buildings and obstructions,
  (c) over urban areas,
  (d) over coastal zones and sea,
  (e) over complex terrain.

These aspects of the dispersion situation are now considered.

15.11.2 Buoyancy effects

The fluid may have neutral, positive or negative buoyancy. Neutral density is generally the default assumption and applies where the density of the gas–air mixture is close to that of air. This is the case where the density of the gas released is close to that of air or where the concentration of the gas is low. In determining the density of the gas it is necessary to consider not only molecular weight but also the temperature and liquid droplets. Gases with positive buoyancy include those with low molecular weight and hot gases. Many hazardous materials, however, form negatively buoyant gases, or heavy gases.

Much of the fundamental work on dispersion, and the models derived from this work, relate to the dispersion of gas of neutral density, or neutral buoyancy. This work is relevant to dispersion from stacks once buoyancy effects have decayed. There are separate models that treat gases of positive buoyancy, which apply to releases close to stacks, and gases of negative buoyancy. Dispersion of gases that do not exhibit positive or negative buoyancy is generally referred to as 'passive dispersion'.

15.11.3 Momentum effects

A continuous release of material with low kinetic energy forms a plume that tends to billow. If the kinetic energy is high, however, a momentum jet is formed which has a well-defined shape.

The momentum of the release has a marked effect on the extent of air entrainment. If the kinetic energy is high, large quantities of air are entrained. The degree of air entrainment affects the density of the cloud and is important in its further dispersion.

15.11.4 Source terms

The principal types of source used in idealized treatments of dispersion are the point source, the line source and the area source. An escape from a pipe is normally treated as a point source, while vaporization from a pool may be treated as an area source. There may also be some situations that may be modelled as an infinite or semi-infinite line source.

A very short and a prolonged escape may approximate to an instantaneous release and to a continuous release, respectively. An escape of intermediate duration, however, may need to be treated as a quasi-instantaneous or, alternatively, quasi-continuous release.

The most common scenarios considered are an instantaneous release from a point source, or 'puff', and a continuous release from a point source, or 'plume'.

It will be apparent that the source terms described are idealizations of the actual situation.

15.11.5 Source elevation

Another distinction is the elevation of the source. Sources are classed as ground level or elevated. Most hazardous escapes are treated as ground level sources. Stacks are the principal elevated sources.

15.11.6 Meteorology and topography

The two main meteorological conditions that affect the dispersion are the wind direction and speed and the stability conditions.

The stability of the atmosphere determines the degree of mixing. The simplest classification of stability is:

(1) unstable;
(2) neutral;
(3) stable.

Dispersion is greatest in unstable conditions and least in stable conditions.

With respect to topography the default condition may be regarded as dispersion over flat grassland of moderate roughness, but there are many other situations, including dispersion over surfaces with very low or very high roughness, at buildings or other obstacles, over urban areas, over coastal zones and sea, and over other complex terrain.

Meteorology and topography are discussed further in Sections 15.12 and 15.13, respectively.

15.11.7 Dispersion of passive gas plume

As already mentioned, the dispersion situation that has been studied most extensively is the dispersion of a plume of neutral density gas from a continuous point source. It is convenient at this point to consider some basic features of gas dispersion in relation to this source term.

It has frequently been shown by experiment that for such a plume both the crosswind and vertical concentration distributions are approximately Gaussian, as illustrated in Figure 15.31(a).

By convention, the boundaries of a cloud are defined in dispersion work as the locus of the points at which the concentration has fallen to 1/10 of that at the centre. For a plume at ground level the horizontal and vertical cloud boundaries are given by the envelope at which the concentrations are 1/10 of those down the centre line. This defines the cloud width w, the lateral spread θ and the cloud height h, as shown in Figure 15.31(b).

Since the concentration distribution is Gaussian, the cloud spread may also be defined in terms of the standard deviations of concentration in the crosswind y and vertical z directions σ_y and σ_z. The relation between the cloud height h and vertical standard deviation σ_z is

$$h = 2.15\sigma_z \qquad [15.11.1]$$

The factor of 2.15 derives from the Gaussian distribution and corresponds to the 1/10 maximum value.

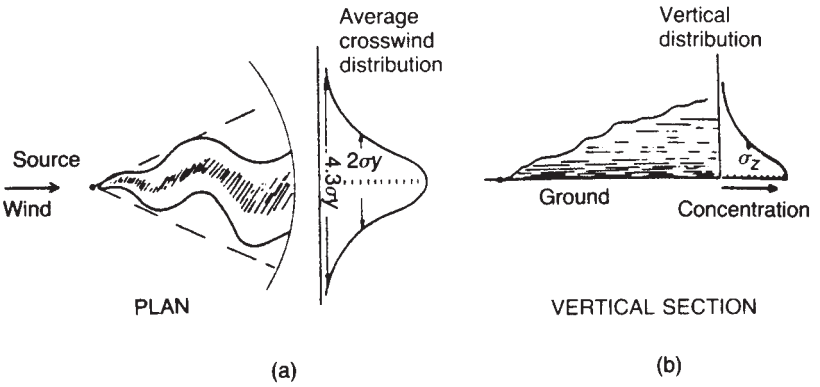


Figure 15.31 *Plume from a continuous release: definition of plume (Pasquill and Smith, 1983; reproduced by permission)*

15.11.8 Co-ordinate systems for gas dispersion

Three widely used co-ordinate systems are (1) the rectangular, (2) the spherical and (3) the cylindrical systems. A treatment of their use in chemical engineering is given by Bird, Stewart and Lightfoot (1960).

Most gas dispersion modelling utilizes rectangular coordinates (x, y, z). For dispersion of instantaneous releases it is sometimes convenient to use spherical co-ordinates (r, θ) . Models for instantaneous releases may use a coordinate system moving with the cloud. Some use is made of special coordinate systems. An example is that used in the DRIFT model described in Section 17.35.

15.11.9 Concentration fluctuations and sampling

It is found experimentally that if the concentration in a gas cloud from a continuous point source under near neutral conditions is measured at points along an arc across wind, the distribution of concentration obtained is Gaussian, but the shape of the distribution depends on the sampling interval. If the sample is virtually instantaneous, the distribution has a relatively narrow spread and a high maximum, while if the sample is averaged over a time period the distribution has a wider spread and a lower maximum. This behaviour is illustrated in Figure 15.32.

Typically, at 100 m the total width of the cloud as measured by instantaneous samples is about 20 m, but the width as measured by time mean samples is about 35 m. The width of the cloud increases rapidly as the interval over which the sample is averaged increases from zero to 2 min. For intervals greater than 3 min the concentration distribution remains fairly constant, provided the wind direction does not alter.

Over longer periods, however, the wind does alter direction and there is a further but more gradual increase in the spread of the concentration distribution. The variation of concentration with sampling period may be taken into account using a relation of the form

$$\frac{\chi}{\chi_r} = \left(\frac{t_r}{t}\right)^p \qquad [15.11.2]$$

where t is the sampling period which yields concentration χ, p is an index and subscript r denotes the reference value.

There can be considerable differences between peak and time-mean concentrations. Values of the peak/mean ratio of 50 or more have been reported in some investigations. The concentrations given by the common dispersion models for passive dispersion gas are time-mean values. In some applications it is necessary also to consider the peak values.

15.11.10 Models for passive gas dispersion

The modelling of dispersion, particularly that of neutral density gas, and passive gas dispersion models are discussed further in Sections 15.15 and 15.16, respectively. Passive gas dispersion over particular surfaces and in particular conditions is considered in Sections 15.17 and 15.18, while dispersion parameters for passive gas dispersion models are described in Section 15.19.

15.11.11 Models for dense gas dispersion

For high concentration releases of many of the *hazardous* materials of interest in process plants the assumption of neutral density gas behaviour is not valid. In particular, the gas cloud is often heavier than air. In this situation the common neutral density gas models are not applicable. However, the behaviour of dense gases has been the subject of much work in recent years and dense gas dispersion models have been developed. Dispersion of dense gas is discussed further in Section 15.22 and succeeding sections.

15.11.12 Other topics

Other topics in gas dispersion considered below include dispersion of buoyant plumes and momentum jets, concentration fluctuations, dispersion over short distances, transformation and removal mechanisms, flammable and toxic clouds, infiltration into buildings, fugitive emissions, dispersion by fluid curtains and leaks and spillages.

15.12 Meteorology

Gas dispersion depends on meteorology and, in particular, on turbulence. Both the form of the models used to describe dispersion and the values of the parameters in them derive from meteorological considerations.

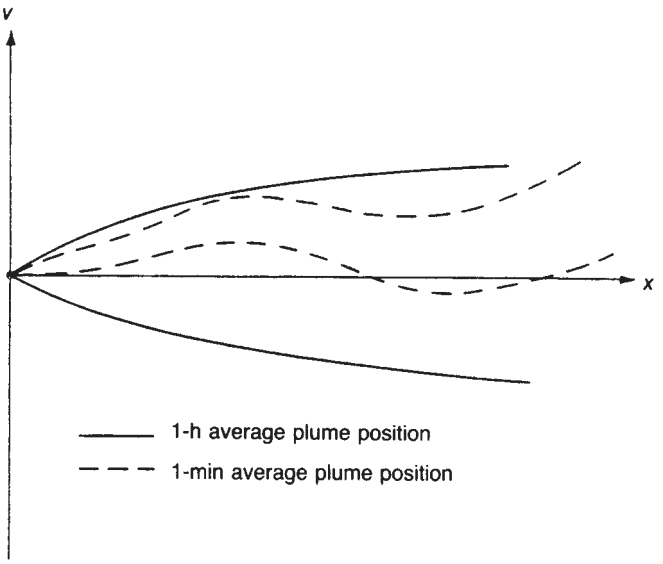


Figure 15.32 *Plume from a continuous release: effect of meandering of plume (S.R. Hanna, Briggs and Hosker, 1992)*

Accounts of meteorology include those given in *Physical and Dynamical Meteorology* (Brunt, 1934), *The Climate Near the Ground* (Geiger, 1950–), *Micrometeorology* (O.G. Sutton, 1953), *The Challenge of the Atmosphere* (O.G. Sutton, 1962), *Elementary Meteorology* (G.F. Taylor, 1954), *Exploring the Atmosphere's First Mile* (Lettau and Davidson, 1962), *Natural Aerodynamics* (Scorer, 1958), *Environmental Aerodynamics* (Scorer, 1978), *General Meteorology* (Byers, 1959), *Atmospheric Diffusion* (Pasquill, 1962a, 1974; Pasquill and Smith, 1983), *An Introduction to Climate* (Trewartha, 1968), *Essentials of Meteorology* (McIntosh and Thorn, 1969), *Evaporation into the Atmosphere* (Brutsaert, 1982), *CRC Handbook of Atmospherics* (Volland, 1982), *Engineering Meteorology* (Plate, 1982) and *Meteorological Glossary* (McIntosh, 1972), *Dynamics in Atmospheric Physics* (Lindzen, 1990), and in the *Meteorological Glossary* (McIntosh, 1972). An account specific to the United Kingdom is available in *Climate in the United Kingdom* (Page and Lebens, 1986).

Works on turbulence and related phenomena include *Massenaustausch in freier Luft and verwandte Erscheinungen* (Schmidt, 1925), *Turbulence* (Hinze, 1959), *Turbulent Transfer in the Lower Atmosphere* (Priestley, 1959), *Boundary Layer Theory* (Schlichtling, 1960), *Turbulence: Classic Papers on Statistical Theory* (Friedlander and Topper, 1961), *The Structure of Atmospheric Turbulence* (Lumley and Panofsky, 1964), *Introduction to Turbulence and Its Measurement* (Bradshaw, 1971), *Statistical Fluid Mechanics: Mechanics of Turbulence* (Monin and Yaglom, 1971), *Turbulence Phenomena* (J.T. Davies, 1972), *A First Course in Turbulence* (Tennekes and Lumley, 1972), *Turbulent Diffusion in the Environment* (Csanady, 1973), *Buoyancy Effects in Fluids* (U.S. Turner, 1973), *Mathematical Modelling of Turbulent Diffusion in the Environment* (C.J. Harris, 1979) and *Turbulence and Diffusion in Stable Environments* (Q.C.R. Hunt, 1985).

Treatments of gas dispersion, with particular emphasis on air pollution, include those given in *Atmospheric Pollution: Compendium of Meteorology* (Hewson, 1951), *Air Pollution* (Scorer, 1968), *Contemporary Problems of Atmospheric Diffusion and Pollution in the Atmosphere* (Beryland, 1975), *Atmospheric Motion and Air Pollution* (Dobbins, 1979), *Air Pollution Modelling and its Application* (de Wispelaere, 1981, 1983, 1984, 1985; de Wispelaere, Schiermeier and Gillani, 1986), *Atmospheric Diffusion* (Pasquill and Smith, 1983), and *Atmospheric Turbulence and Air Pollution Modelling* (Nieuwstadt and van Dop, 1982).

15.12.1 Atmospheric boundary layer

The meteorological conditions that are of prime relevance here are those within the atmospheric boundary layer (ABL), or planetary boundary layer (PEL). In unstable, or convective, conditions this layer is also known as the convective boundary layer (CBL).

The ABL has an outer and an inner region, as shown in Figure 15.33. The outer region, or defect layer, has a height of some 10^2–10^3 m and the inner region, or surface layer, one of some 10 m. There is within the surface sublayer a dynamic sublayer with a height of 1–10 m. Between the dynamic sublayer and the surface is the interfacial layer, the height of which depends on the surface roughness.

Within the PEL, the surface layer is of particular importance. Within this layer stress is virtually constant and it is also termed the constant stress layer, or surface stress layer. Considering the PEL over land, conditions in the layer depend on the stability conditions. The simplest case is that of neutral conditions where buoyancy forces are negligible. It is to this case that the classical treatments primarily apply.

In the neutral PEL turbulent energy derives from two main sources. One is due to the mechanical drag of the wind over the surface, and the other to the turning of the wind direction with height. In the unstable boundary layer

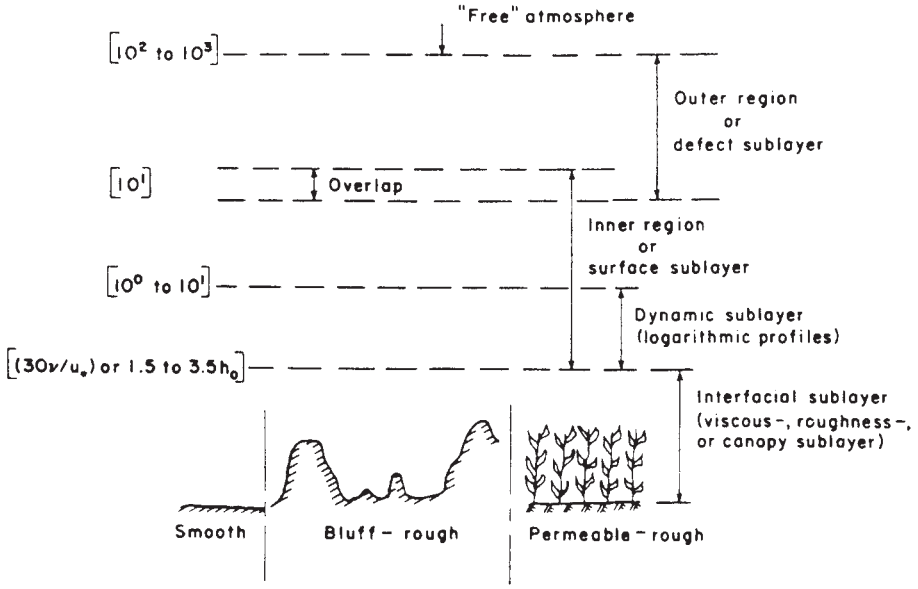


Figure 15.33 *Atmospheric boundary layer: orders of magnitude of the heights of the sublayers (Brutsaert, 1982). The vertical scale (m) is distorted; h_o is the height of the roughness obstances (Courtesy of Reidel Publishing Company)*

a further source of turbulent energy is that due to buoyancy. Over land, such buoyancy is mainly caused by vertical flux of sensible heat into the air at the surface. Over sea, vertical flux of latent heat associated with water vapour plays a significant role.

Stable conditions occur mainly at night. In the stable boundary layer the surface is cool relative to the air and the vertical heat flux is in the reverse direction so that the mechanical and buoyancy forces are opposed. At some height above the surface turbulence becomes very weak and is virtually suppressed.

15.12.2 Wind characteristics

Wind is a main factor in determining dispersion. Some principal wind characteristics are:

(1) direction;
(2) speed
  (a) at surface,
  (b) above ground;
(3) persistence;
(4) turbulence.

Wind direction is defined as the direction from which the wind is blowing. Information on wind direction and speed at a given location is conveniently summarized in the form of a 'wind rose'. This is a polar diagram in which the length of the sections of the spokes is proportional to the observed frequencies of wind direction and speed. The period for which the wind rose is drawn is typically a month or a year. Some monthly wind roses show a marked degree of seasonal variation, others do not. The degree of symmetry in wind roses also varies considerably. A table of percentage frequency of wind direction and speed and corresponding wind rose for Watnall is shown in Figure 15.34.

The predominant wind direction is usually called the 'prevailing wind'. This wind direction only applies, however, for a relatively limited proportion of the time, and it is usually necessary in dispersion calculations to consider other directions also.

Persistence of the wind direction is important in assessing dispersion. This is often expressed in the form of a persistence table such as that shown for Watnall in Table 15.11, which gives the number of occasions during the given period in which the wind remained within the sectors indicated for the number of hours in sequence indicated.

Alternatively, the persistence of wind direction may be expressed in terms of the constancy, which is based on the ratio of the vector and scalar winds and has a value of 1 for an invariant wind direction and 0 for a completely uniform distribution of wind directions. This measure has the advantage that, unlike persistence, it is relatively little affected by brief excursions outside the 45° sector.

Localized variations of wind direction and speed can occur and may affect dispersion. Features that can give rise to these variations include irregularities in terrain and differences in surface temperature. Where there is a marked slope, a drainage wind can occur. This is a downhill flow of air cooled by radiation at night and it may be in a direction quite different from the gradient wind. In well-defined valleys there are usually complex flow patterns. Typically, at night there is a drainage wind from the sides and down the bottom of the valley and during the day a tendency for wind to flow up the valley bottom. On the coast the land is warmer in daytime and the sea at night. Hence during the day there tends to be a sea breeze blowing onto the land and during the night a land breeze blowing towards the sea.

Turbulence is another feature of wind variation. In the present context turbulence includes wind fluctuations with

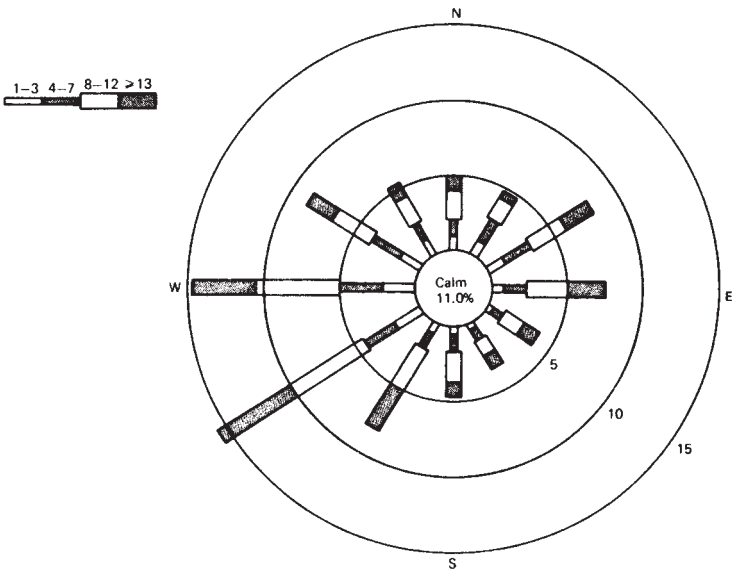


Figure 15.34 *Table of percentage frequency of wind direction and speed and corresponding wind rose for Watnall, 1959–68 (Meteorological Office, 1977; reproduced by permission)*

Table 15.11 *Table of wind persistence for Watnall, 1974–76 (Meteorological Office, 1977; reproduced by permission)*

No. of hours in sequence	*Direction*							
	N	*NE*	*E*	*SE*	*S*	*SW*	*W*	*NW*
1	756	565	510	411	587	1043	1087	721
7	91	110	64	29	82	176	202	46
13	27	49	29	4	49	97	72	12
25	14	8	8	2	6	15	9	2
37	2	7	1	0	0	6	5	0
>49	0	5	0	0	0	2	3	0
Total no. of hours	3374	4007	2404	1190	3106	6503	6153	2202

Watnall: latitude 53° 01′ N, longitude 01° 15′ W

a frequency of more than 2 cycle/h, the most important fluctuations lying in the range 0.1–1 cycle/s. The main factors that determine the turbulence are the gradient wind speed and the roughness of the terrain, and the temperature differences between the surface and the air. Turbulence tends to increase as the gradient wind speed increases, or as the temperature of the air close to the surface increases, relative to that of the air aloft. A measure of turbulence is given by the standard deviation, or, σ, value of the wind fluctuations over a 1 h period. These wind speed σ values can be related to the dispersion σ values in the models of gas dispersion.

Before leaving wind characteristics, it is convenient to give at this point the method of characterizing high wind speeds. This is the Beaufort scale, developed originally for use at sea. It is shown in Table 15.12. The scale is not used in work on gas dispersion, but is relevant to wind hazard.

15.12.3 Geostrophic wind and Ekman spiral

In the free atmosphere above the PEL it is usual to assume that the wind is horizontal and free from friction. In this situation the wind velocity becomes a function of the pressure gradient and of the forces arising from the rotation of the Earth. The wind that satisfies these conditions is known as the gradient level wind.

Where the lines of constant pressure, or isobars, are straight so that any centripetal acceleration is negligible, the gradient level wind is known as the geostrophic wind. The direction of the geostrophic wind is not the same as the surface wind. An idealized representation of the wind velocity vectors at different heights is given by the Ekman spiral, developed originally in relation to ocean currents, as shown in Figure 15.35. The Ekman spiral is the locus of the end points of the wind velocity vectors. These vectors approach the geostrophic wind velocity at the mixed layer

Table 15.12 *The Beaufort Scale*

Force	*Wind speed*[a] (mile/h)		*Description*	*Specification (land)*	*Weather forecast*
	Average	*Limits*			
0	<1		Calm	Calm; smoke rises vertically	Calm
1	2	1–3	Light air	Wind shown by smoke drift, not wind vanes	Light
2	5	4–7	Light breeze	Wind felt on face; leaves rustle	Light
3	10	8–12	Gentle breeze	Leaves and small twigs in constant motion	Light
4	15	13–18	Moderate breeze	Raises dusts and loose paper	Moderate
5	21	19–24	Fresh breeze	Small trees in leaf begin to sway	Fresh
6	28	25–31	Strong breeze	Large branches in motion; whistling heard in telegraph	Strong
7	35	32–38	Near gale	Whole trees in motion; inconvenience when walking against the wind	Strong
8	42	39–46	Gale	Breaks twigs off trees; generally impedes progress	Gale
9	50	47–54	Strong gale	Slight structural damage	Severe gale
10	59	55–63	Storm	Trees uprooted; considerable structural damage	Storm
11	68	64–72	Violent storm	Very rarely experienced; accompanied by widespread damage	Violent storm
12	>73		Hurricane	As Force 11	Hurricane

[a] Wind speeds are average speeds measured at a height of 10 m.

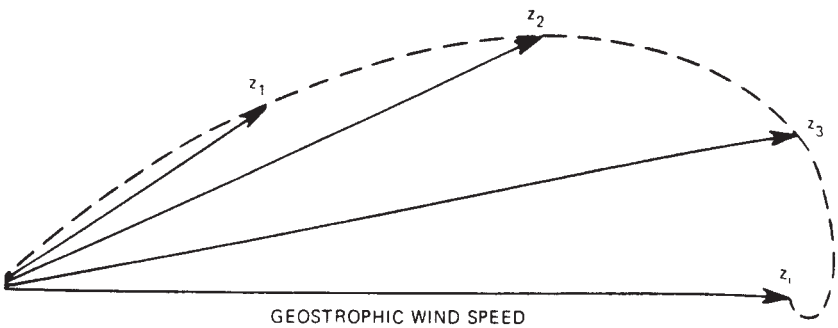


Figure 15.35 *Geostrophic wind and Ekman spiral (S.R. Hanna, Briggs and Hosker, 1982). The wind velocity vectors (z_1, z_2, z_3) approach the geostrophic wind velocity vector at the top of the mixed layer z_i*

height. The angle of a vector is the angle by which it is backed from the direction of the geostrophic wind. The angle of the surface wind vector is backed 45° from this direction. Actual observed angles between the geostrophic and surface winds are typically 5–10°, 15–20° and 30–50° for unstable, neutral and stable conditions, respectively.

Wind direction shear affects dispersion, particularly over large distances, where the top and bottom of a plume can move with a difference of direction of some 40–50°, which gives a much larger plume spread than would be obtained by diffusion alone.

15.12.4 Force balance equation

The balance of forces acting horizontally on the air in free stream conditions is given by the relations

$$\frac{\partial u}{\partial t} + fv = \frac{1}{\rho}\frac{\partial p}{\partial x} + X \qquad [15.12.1a]$$

$$\frac{\partial v}{\partial t} + fu = \frac{1}{\rho}\frac{\partial p}{\partial y} + Y \qquad [15.12.1b]$$

where f is the Coriolis force, p is the pressure, t is the time, u and v are the wind velocity components in the downwind and crosswind directions, respectively, X and Y are accelerations representative of forces not due to pressure and gravity, and ρ is the air density. The Coriolis force, or parameter, f is

$$f = 2\omega \sin \phi \qquad [15.12.2]$$

where ϕ is the latitude and ω is the angular velocity of the Earth. The Coriolis force has a value of approximately $10^{-4}\,s^{-1}$ at intermediate latitudes and tends to zero at the equator.

15.12.5 Turbulent exchange, momentum flux, eddy viscosity and mixing length

The theory of turbulence derives from the work of Schiller (1932), Nikuradse (1933), Prandtl (1933) and Schlichtling (1936) on the boundary layer for flow in pipes. The extension of this theory for flow over open ground is described by O.G. Sutton (1953) and Pasquill (1962a). The theories of turbulence which describe the mixing that occurs when

wind passes over a surface are complex. The treatment given here is limited to the description of a few simple concepts and relations. The momentum flux is given by the equation

$$\frac{\tau}{\rho} = (\nu + K_M)\frac{du}{dz} \qquad [15.12.3a]$$

The eddy viscosity K_M is generally much greater than the kinematic viscosity ν, and hence

$$\frac{\tau}{\rho} = K_M\frac{du}{dz} \quad \nu \ll K_M \qquad [15.12.3b]$$

where K_M is the eddy viscosity, u is the mean wind speed, z is the height, ν is the kinematic viscosity of air, ρ is the density of air and τ the mean momentum flux per unit area.

The constant K_M is variously described as the coefficient of exchange for momentum, the eddy diffusivity for momentum, or the eddy viscosity. In terms of the mixing length theory of Prandtl,

$$K_M = l^2\frac{du}{dz} \qquad [15.12.4]$$

where l is the mixing length. The momentum flux is then

$$\frac{\tau}{\rho} = l^2\left(\frac{du}{dz}\right)^2 \qquad [15.12.5]$$

On the assumption that the mixing length is proportional to the distance from the surface,

$$l = kz \qquad [15.12.6]$$

where the constant k is von Karman's constant. The value usually quoted for von Karman's constant is 0.4. A value of 0.35 has been given by Businger *et al.* (1971).

From Equation 15.12.3b and the relation $u_*^2 = \tau/\rho$, described below,

$$K_M = \frac{u_*^2}{du/dz} \qquad [15.12.7]$$

Then from Equations 15.12.7 and the 'law of the wall' Equation 15.12.15, given below,

$$K_M = ku_*z \qquad [15.12.8]$$

In terms of mixing length theory, using Equation 15.12.6, Equation 15.12.15 may be rewritten as

$$\frac{l}{u_*}\frac{du}{dz} = \frac{1}{l} \qquad [15.12.9]$$

and Equation 15.12.8 as

$$K_M = u_*l \qquad [15.12.10]$$

15.12.6 Friction velocity

Closely related to the momentum flux is the friction velocity u, defined by the relations

$$\frac{\tau}{\rho} = u_*^2 \qquad [15.12.11a]$$

or

$$u_* = (\tau/\rho)^{1/2} \qquad [15.12.11b]$$

The friction velocity may be obtained from the geostrophic wind velocity using the relation

$$u_* = c_g u_g \qquad [15.12.12]$$

where c_g is the drag coefficient and u_g is the geostrophic wind speed.

An empirical relation for the drag coefficient c_g in neutral conditions has been given by Lettau (1959) as follows:

$$c_g = \frac{0.16}{\log_{10}\mathrm{Ro} - 1.8} \qquad [15.12.13]$$

with

$$\mathrm{Ro} = \frac{u_g}{fz_o} \qquad [15.12.14]$$

where Ro is the Rossby number and z_o is the roughness length.

For other stability conditions Lettau uses the following approximate ratios of the drag coefficient to that in neutral conditions:

Unstable	1.2
Slightly stable	0.8
Stable	0.6

The value of the friction velocity u_* varies between about 3 and 12% of the mean wind speed, the lower values being associated with smooth surfaces. It is often taken as one-tenth of the wind speed. The friction velocity is generally tabulated together with the surface roughness as a function of the type of surface, as described below.

15.12.7 Law of the wall

On the assumption that the flow at the surface depends only on the shear stress and the distance from the wall

$$\frac{du}{dz} = \frac{u_*}{kz} \qquad [15.12.15]$$

This is the so-called 'law of the wall'. The term $(kz\mathrm{d}u/u_*\mathrm{d}z)$ is a non-dimensional wind shear. Equation 15.12.15 is applicable to adiabatic, or neutral, conditions.

15.12.8 Empirical vertical wind velocity profile

The gradient wind is, by definition, uninfluenced by friction effects, but at lower heights the wind velocity is reduced by such effects. Figure 15.36 illustrates some vertical profiles of wind speed.

A widely used empirical relation for the vertical wind velocity profile is

$$u = u_r\left(\frac{z}{z_r}\right)^p \quad z < z_r \qquad [15.12.16]$$

where u is the wind speed, u_r is the wind speed at the reference height, z is the height, z_r the reference height and p is an index.

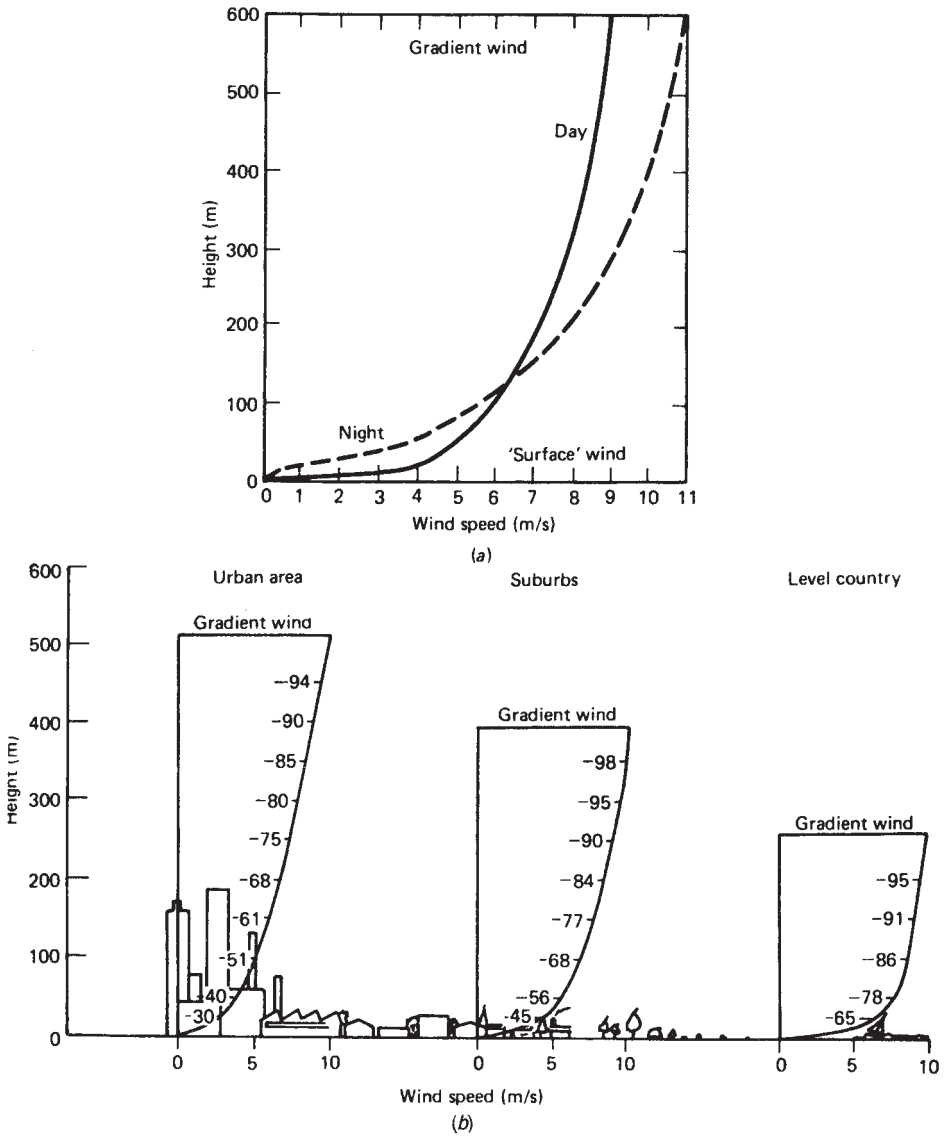


Figure 15.36 *Wind speed vs height above ground (American Society of Mechanical Engineers, 1973/2): (a) effect of stability conditions on wind speed; (b) effect of terrain on wind speed*

The gradient level reference height z_r lies approximately in the range 300–750 m, being typically 300 m over level ground and 500 m over an urban area.

The value of the index p generally lies in the range $0.11 < p < 0.65$, and invariably in the range $0 < p < 1$. Range values obtained include: $0.145 < p < 0.77$ by Frost (1947); $0.10 < p < 0.63$ by Touma (1977); and $0.11 < p < 0.65$ by Hanafusa, Lee and Lo (1986).

As pointed out by O.G. Sutton (1953), the generally accepted value of the index p for the turbulent boundary layer of a flat plate in a wind tunnel is 1/7 (0.142).

Touma states that in the absence of measured values the wind speed is generally estimated using the 1/7 wind profile and assuming neutral stability conditions. He presents experimental data, however, which indicate that the index p has a value of about 0.10 at Pasquill stability category A, may pass at some sites through a weak minimum and then increases markedly through categories D–F to a value of up to 0.62.

In further experimental work in Japan by Hanafusa, Lee and Lo (1986), the value of the index p varied with the Pasquill stability categories approximately

as follows:

Pasquill stability category	*Index, p*
A	0.33
B	0.26
C	0.20
D, E	0.38
F	0.42
G	0.57

The strong increase in the index p with stability categories D–F broadly confirmed that found by Touma, but the values of p for categories A and B were higher than those obtained by the latter. The authors suggest that the difference may be due to the different methods used to define the stability category. The index p may also be written as

$$p = n/(2-n) \qquad [15.12.17]$$

where n is an index. This index is one of the parameters in the Sutton model for neutral density gas dispersion, as described below.

15.12.9 Empirical vertical wind velocity profile: Deacon relation

An empirical relation for the vertical wind velocity gradient was formulated by Deacon (1949) as follows:

$$\frac{\mathrm{d}u}{\mathrm{d}z} = az^{-\beta} \qquad [15.12.18]$$

where a is a constant and β an index. He gave the following values of the index β:

$\beta > 1$ superadiabatic conditions
$\beta = 1$ adiabatic conditions, or small temperature gradients
$\beta < 1$ inversion conditions

Then for $\beta = 1$

$$\frac{\mathrm{d}u}{\mathrm{d}z} = \frac{a}{z} \qquad [15.12.19]$$

Equation 15.12.19 is an alternative form of the law of the wall given above as Equation 15.12.15.

15.12.10 Logarithmic vertical wind velocity profile

Another vertical wind velocity profile is the logarithmic profile. This is applicable to adiabatic, or neutral, conditions. The logarithmic vertical wind velocity profile is obtained by integration of Equation 15.12.15 to give

$$u = \frac{u_*}{k}\ \ln\left(\frac{z}{z_o}\right) \qquad [15.12.20]$$

where z_o is a constant of integration. This constant is termed the 'roughness length'.

15.12.11 Modified logarithmic vertical wind velocity profiles

For non-adiabatic, or diabatic, conditions a different treatment is required. The analysis is complicated by buoyancy effects. For diabatic conditions Equation 15.12.15 may be modified by the inclusion of the similarity factor introduced by Monin and Obukhov (1954). It then becomes

$$\frac{\mathrm{d}u}{\mathrm{d}z} = \frac{u_*}{kz}\phi_M \qquad [15.12.21]$$

where ϕ_M is the similarity factor. These authors take

$$\phi_M = f(z/L) \qquad [15.12.22]$$

They also use the relation

$$\phi_M = 1 + \alpha\frac{z}{L} \qquad [15.12.23]$$

which yields for Equation 15.12.21

$$\frac{\mathrm{d}u}{\mathrm{d}z} = \frac{u_*}{kz}\left(1 + \alpha\frac{z}{L}\right) \qquad [15.12.24]$$

where L is a characteristic length (the Monin–Obukhov length), and α is the Monin–Obukhov coefficient. Integrating Equation 15.12.24

$$u = \frac{u_*}{k}\left[\mathrm{In}(z/z_o) + \alpha\,\frac{z - z_o}{L}\right] \qquad [15.12.25]$$

and taking $z \gg z_o$ yields

$$u = \frac{u_*}{k}\left[\ln(z/z_o) + \alpha\,\frac{z}{L}\right] \qquad [15.12.26]$$

This is the log–linear vertical wind velocity profile. The log–linear velocity profile is applicable over a limited range of unstable conditions and a wide range of stable conditions. In a further treatment Ragland (1973) has given

$$\phi_M = 1 \quad \text{neutral conditions} \quad z < (ku_*/f) \qquad [15.12.27a]$$

$$= 1 + \alpha\frac{z}{L} \quad \text{stable conditions} \quad 0 < \frac{z}{L} < 1 \qquad [15.12.27b]$$

$$= 1 + \alpha \quad \text{neutral conditions} \quad 1 < \frac{z}{L} < 6 \qquad [15.12.27c]$$

$$= \left(1 - 15\frac{z}{L}\right)^{-0.25} \quad \text{stable conditions} \quad -2 < \frac{z}{L} < 0 \qquad [15.12.27d]$$

He quotes for α the value of 5.2 given by Webb (1970).

15.12.12 Surface roughness and roughness length

A surface is aerodynamically rough when the flow is turbulent down to the surface itself. Over such a surface the velocity profile and surface drag are independent of viscosity and depend on the roughness length. In meteorology, nearly all surfaces are aerodynamically rough for any significant wind speed. The roughness length depends on the height and spacing of the roughness elements.

From work on pipe roughness, the roughness length z_o and the mean height ϵ of the roughness elements are related approximately as follows:

$$z_o = \epsilon/30 \qquad [15.12.28]$$

Roughness of flow may be defined in terms of the roughness Reynolds number $u_* z/\nu$. For fully rough flow the criterion obtained from Nikuradse's work is

$$\frac{u_* \epsilon}{\nu} > 75 \qquad [15.12.29a]$$

or, using Equation 15.12.28,

$$\frac{u_* z_o}{\nu} > 2.5 \qquad [15.12.29b]$$

Paeschke (1937) correlated roughness length z_o with the mean height ϵ of roughness elements on a larger scale and obtained for various grass and field surfaces

$$z_o = \epsilon/7.35 \qquad [15.12.30]$$

Other workers have obtained similar results, while yet others have found it to be a more complex function. Some typical values of the roughness length given in the literature are shown in Table 15.13.

For very rough surfaces the logarithmic wind profile of Equation 15.12.20 may be extended using the empirical modification

$$u = \frac{u_*}{k} \ln\left(\frac{z-d}{z_o}\right) \quad z > (d + z_o) \qquad [15.12.31]$$

where d is the zero plane displacement, or displacement height.

The displacement height d is the datum level above which normal turbulent exchange occurs. Using the displacement height concept the base of the roughness elements is at $z = 0$.

Table 15.13 *Some values of roughness length*

A Values given by O.G. Sutton (1953)

Type of surface	z_o (cm)	u_* (cm/s)
Very smooth (mud flats, ice)	0.001	16
This grass upto 10 cm high	0.7	36
Thick grass upto 50 cm high	9	63

B Values given by Pasquill and Smith (1983)

Type of surface	z_o (m)
Grass: closely mown	10^{-3}
short (*c.* 10 cm)	10^{-2}
long	3×10^{-2}
Agricultural–rural complex	0.2
Towns, forests	1

15.12.13 Vertical temperature profile

The stability of the atmosphere is essentially the extent to which it allows vertical motion by suppressing or assisting turbulence. One source of turbulence is the mechanical turbulence due to wind movement. Another is the turbulence associated with the vertical temperature gradient. Traditionally stability has been expressed primarily in terms of the latter.

If a small volume of air is taken vertically upward in the atmosphere, it meets lower pressure and therefore expands and cools. The rate of decrease of temperature with height is known as the lapse rate. If the air were dry and the process adiabatic, then the rate of decrease would have a particular value which is known as the dry adiabatic lapse rate of temperature. Although such a process does not occur in the atmosphere, the dry adiabatic lapse rate provides a standard of comparison for real atmospheric conditions.

The rate of change of temperature with height $\mathrm{d}T/\mathrm{d}z$ under adiabatic, or neutral, conditions is approximately $-0.01°\mathrm{C/m}$. The definition of lapse rate as a rate of decrease of temperature, and thus as a positive quantity under adiabatic conditions, is a potential source of confusion. It is appropriate, therefore, to quote the following statement by O.G. Sutton (1953, p. 9): '$\mathrm{d}T/\mathrm{d}z = -1°\mathrm{C}$ per 100 m. This particular rate of decrease of temperature with height, known as the dry adiabatic lapse rate and denoted by the symbol Γ (gamma), is one of the fundamental constants of meteorology'.

The potential temperature θ of dry air is the temperature attained if a small volume of the air is taken adiabatically from its existing pressure to a standard pressure, usually that at the surface. Then

$$\theta = T\left(\frac{p_o}{p}\right)^{(\gamma-1)/\gamma} \qquad [15.12.32]$$

where p is the absolute original pressure, p_o is the absolute pressure at the surface, T is the absolute temperature of the volume of air and θ is the potential temperature of this air.

Taking logarithms of Equation 15.12.32 and differentiating with respect to z:

$$\frac{1}{\theta}\frac{\mathrm{d}\theta}{\mathrm{d}z} = \frac{1}{T}\frac{\mathrm{d}T}{\mathrm{d}z} - \frac{\gamma-1}{\gamma}\,\frac{1}{p}\,\frac{\mathrm{d}p}{\mathrm{d}z} \qquad [15.12.33]$$

and noting that

$$\mathrm{d}p = g\rho(-\mathrm{d}z) \qquad [15.12.34]$$

and

$$\rho = \frac{p}{RT} \qquad [15.12.35]$$

where g is the acceleration due to gravity, R is the universal gas constant and γ is the ratio of the specific heats of air, the following relation is obtained:

$$\frac{1}{\theta}\frac{\mathrm{d}\theta}{\mathrm{d}z} = \frac{1}{T}\left(\frac{\mathrm{d}T}{\mathrm{d}z} + \Gamma\right) \qquad [15.12.36]$$

with

$$\Gamma = \frac{\gamma - 1}{\gamma}\frac{g}{R} \qquad [15.12.37]$$

The term $(dT/dz + \Gamma)$ is the difference between the actual temperature gradient and the dry adiabatic lapse rate. Under adiabatic conditions it is zero, so that $dT/dz = -\Gamma$.

At the surface the potential temperature θ and the absolute temperature T are equal by definition, so that Equation 15.12.36 becomes

$$\frac{d\theta}{dz} = \frac{dT}{dz} + \Gamma \qquad [15.12.38]$$

The relation between the vertical temperature gradient and the stability condition is described below.

15.12.14 Vertical heat flux and the Bowen ratio

Another feature that affects turbulence is buoyancy effects associated with the vertical heat flux. As already mentioned, in neutral conditions this heat flux is negligible, but in unstable and stable conditions it is significant. The vertical heat flux consists of a sensible heat flux and a latent heat flux. The ratio of the vertical sensible heat flux to the vertical latent heat flux is given by the Bowen ratio Bo:

$$\text{Bo} = \frac{H}{L_e E} \qquad [15.12.39]$$

where H is the sensible heat flux into the air, E is the evaporation rate and L_e is the latent heat of evaporation. Over land, the latent heat flux is usually small compared to the sensible heat flux.

There are several empirical methods of estimating the vertical heat flux H (e.g. Holtslag and van Ulden, 1983). For the United Kingdom, the following equation is given by Clarke (1979, NRPB R91):

$$H = 0.4(S - 100) \qquad [15.12.40]$$

where H is the vertical heat flux (W/m^2) and S the incoming solar radiation (W/m^2).

The incoming solar radiation (ISR) may be estimated from Figure 15.37. Figure 15.37(a) gives the value of the ISR for a cloudless day as a function of time of day and month. For cloudy conditions this value is multiplied by the correction factor given in Figure 15.37(b).

15.12.15 Stability conditions

As stated earlier, stability has traditionally been described primarily in terms of the vertical temperature gradient. The theoretical adiabatic condition and some of the other conditions that occur in practice are illustrated in Figure 15.38. Curve 1 shows the dry adiabatic condition. Curve 2 shows a superadiabatic condition which can result from strong sunlight, or insolation, or from passage of cold air over a warm surface and which promotes convection and favours instability. Curve 3 shows a neutral condition which is associated with overcast skies and moderate to strong wind speeds and which is neutral with respect to stability. Curve 4 shows a subadiabatic condition that favours stability. Curve 5 shows an isothermal condition that favours stability strongly. Curve 6 shows an inversion condition that suppresses convection and is most favourable to stability.

There are several different types of inversion condition. One is surface inversion, as shown by Curve 6 in Figure 15.38. This tends to occur at night with clear skies and light winds when the ground and the air near to it lose heat by radiation. The condition is therefore also referred to as radiation inversion.

Another type of inversion is elevated inversion, as illustrated in Figure 15.39.

There are a number of causes for such inversions. One is subsidence of air from greater heights, which results in compression and hence warming. Another is a sea breeze, which may introduce a layer of cold air beneath a warm air mass. A third is a meteorological front, which also constitutes a boundary between cold air below and warm air above.

An inversion layer inhibits vertical motion. Surface inversion suppresses upward dispersion of a gas release at ground level and also downward dispersion of a release at elevated level. Elevated inversion acts as a 'lid', inhibiting further upwards dispersion. There is a virtually permanent inversion lid on the atmosphere at a height of about 10,000 m.

If in any layer the rate of change of temperature with height is negative, that layer is effectively a 'mixing layer' There is diurnal variation of stability within the lowest few hundred metres above the ground. The rate of change of temperature with height tends to be negative by day and positive by night giving, respectively, a lapse and an inversion condition. The latter is a surface inversion. Figure 15.40(a) illustrates a typical diurnal variation. An elevated inversion, however, can last for days or even weeks on end.

There are several special features that can affect stability. These include (1) semi-permanent pressure areas, (2) sea–land locations and (3) urban areas. Some areas are subject to a relatively fixed high or low pressure system. The United Kingdom, for example, is often under the influence of the Icelandic semi-permanent low pressure area, with cloudy weather and near neutral stability. Stability in coastal locations is strongly influenced by sea–land interactions. One effect may be the complete suppression of surface inversion during winter due to relatively warm sea breezes, as illustrated in Figure 15.40(b). Urban areas affect stability in various ways. One major aspect is the 'heat island' effect, which prevents the development of surface inversion at night.

15.12.16 Stack plume regimes

The effect of stability conditions on dispersion has been studied extensively and is most readily illustrated in relation to the behaviour of the plume from an elevated source such as a factory chimney. Some of the principal types of plume behaviour are shown in Figure 15.41.

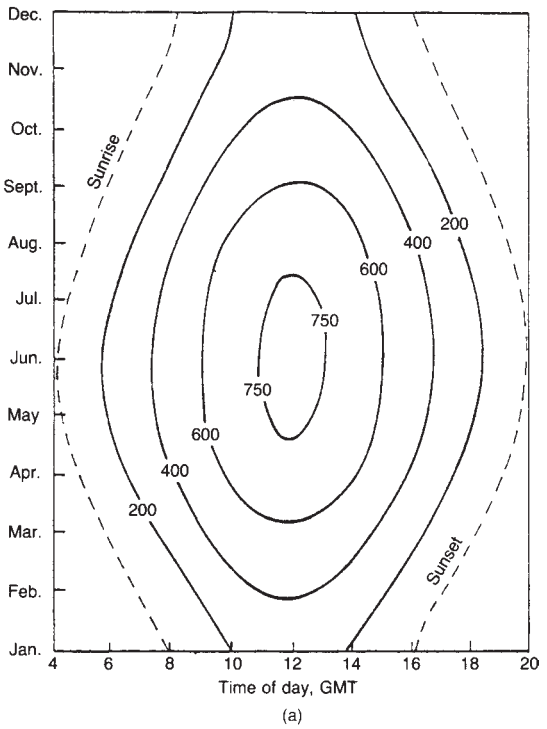
15.12.17 Stability criteria

A simple stability parameter, the environmental stability s, may be defined:

$$s = \frac{g}{T}\left(\frac{dT}{dz} + \Gamma\right) \qquad [15.12.41a]$$

$$= \frac{g}{\theta}\left(\frac{d\theta}{dz}\right) \qquad [15.12.41b]$$

This parameter is proportional to the rate at which the generation of turbulence is suppressed.



Cloud amount (eighths)	*Multiply ISR by*
0	1.07
1	0.89
2	0.81
3	0.76
4	0.72
5	0.67
6	0.59
7	0.45
8	0.23

(b)

Figure 15.37 *Incoming solar radiation (ISR) at Cambridge (after Clarke, 1979 NRPB R91; reproduced by permission): (a) ISR on a cloudless day (W/m^2); (b) correction factor by which ISR for cloudless day is multiplied to allow for cloudy conditions*

15.12.18 Richardson number

The rate at which mechanical turbulence is generated by wind shear is proportional to $(\mathrm{d}u/\mathrm{d}z)^2$. A criterion for the stability of the atmosphere that is effectively the ratio of the rates of suppression and generation of turbulence, as just described, was proposed by L.F. Richardson (1920, 1925) and is known as the Richardson number.

There are several forms of the Richardson number. The gradient Richardson number Ri is defined as

$$\mathrm{Ri} = \frac{g}{T}\left[\frac{\mathrm{d}T/\mathrm{d}z + \Gamma}{(\mathrm{d}u/\mathrm{d}z)^2}\right] \qquad [15.12.42a]$$

$$= \frac{g}{\theta}\left[\frac{\mathrm{d}\theta/\mathrm{d}z}{(\mathrm{d}u/\mathrm{d}z)^2}\right] \qquad [15.12.42b]$$

The bulk Richardson number $\mathrm{Ri_B}$ is defined as

$$\mathrm{Ri_B} = \frac{g}{T}\frac{\Delta\theta/\Delta z}{u^2}z^2 \qquad [15.12.43]$$

This form of the Richardson number is convenient for use where the value is determined experimentally from measurements made at two heights. The value of z is usually taken as the geometric mean of these heights and the value of u as that at the upper level. The flux Richardson number $\mathrm{Ri_F}$ is defined as

$$\mathrm{Ri_F} = -\frac{gH}{Tc_\mathrm{p}\tau(\mathrm{d}u/\mathrm{d}z)} \qquad [15.12.44]$$

where c_p is the specific heat of air, H is the vertical heat flux and τ is the Reynolds stress.

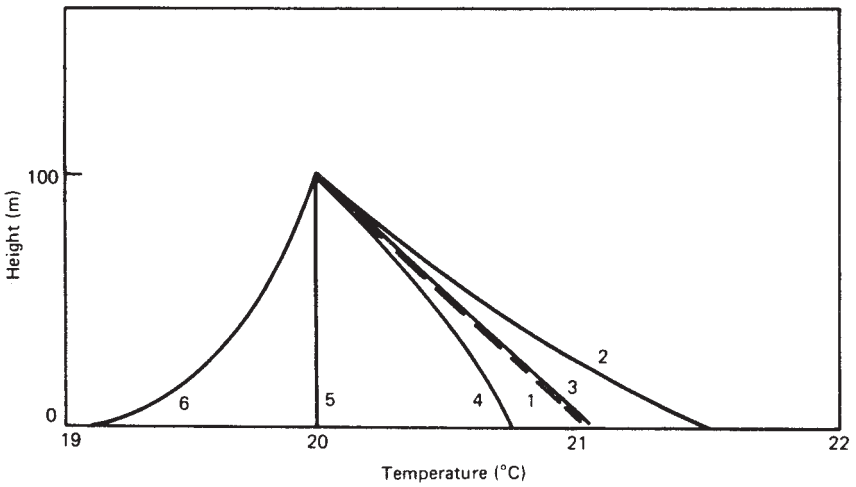


Figure 15.38 *Vertical temperature profiles and lapse rates (American Society of Mechanical Engineers, 1973/2; reproduced by permission): (1) dry adiabatic condition; (2) super-adiabatic condition; (3) neutral condition; (4) subadiabatic condition; (5) isothermal condition; (6) inversion condition*

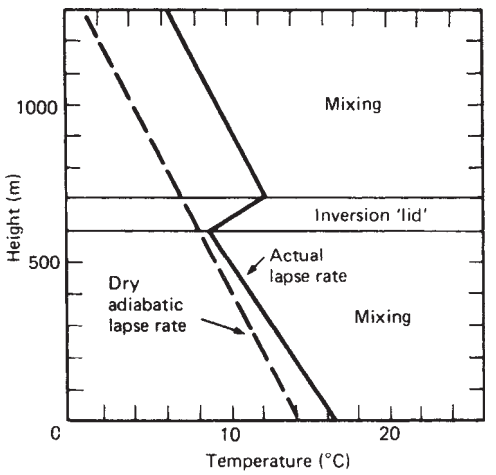


Figure 15.39 *Elevated inversion (American Society of Mechanical Engineers, 1973/2; reproduced by permission)*

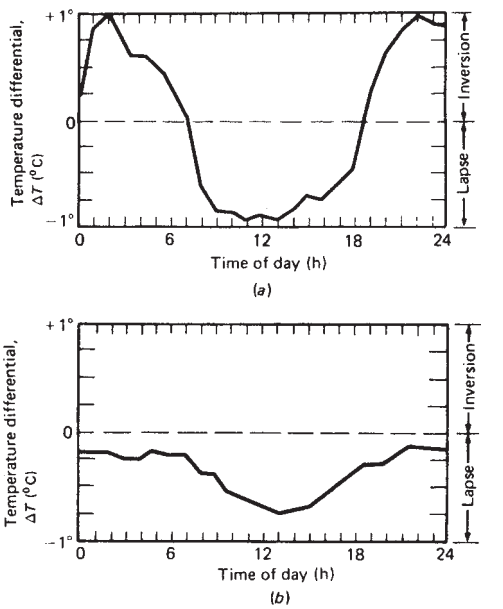


Figure 15.40 *Diurnal variation of vertical temperature profile (American Society of Mechanical Engineers, 19731/2; reproduced by permission): (a) open country site all year; (b) coastal site in winter*

A modified Richardson number $\mathrm{Ri}_{\mathrm{mod}}$ which is also used is

$$\mathrm{Ri}_{\mathrm{mod}} = g\frac{\Delta\rho}{\rho_{\mathrm{a}}}\frac{l}{u^2} \qquad [15.12.45]$$

where l is the mixing length and $\Delta\rho$ is the density difference between the cloud and the air.

The Richardson number Ri is the ratio of the buoyancy to the turbulent stress and is a criterion of similarity for turbulent motion. In his original treatment, Richardson suggested that there is a critical value $\mathrm{Ri}_{\mathrm{cr}}$ at which motion becomes turbulent and postulated that this value is unity. Then for $\mathrm{Ri} < 1$ motion is laminar and for $\mathrm{Ri} > 1$ it is turbulent.

Subsequent work indicates other values for the critical Richardson number. Obukhov (1971) quotes various values derived from theory including 1/2 (Prandtl), 1/4 (Taylor) and 1/24 (Tollmien) as well as an experimental value of 1/11 (Sverdrup).

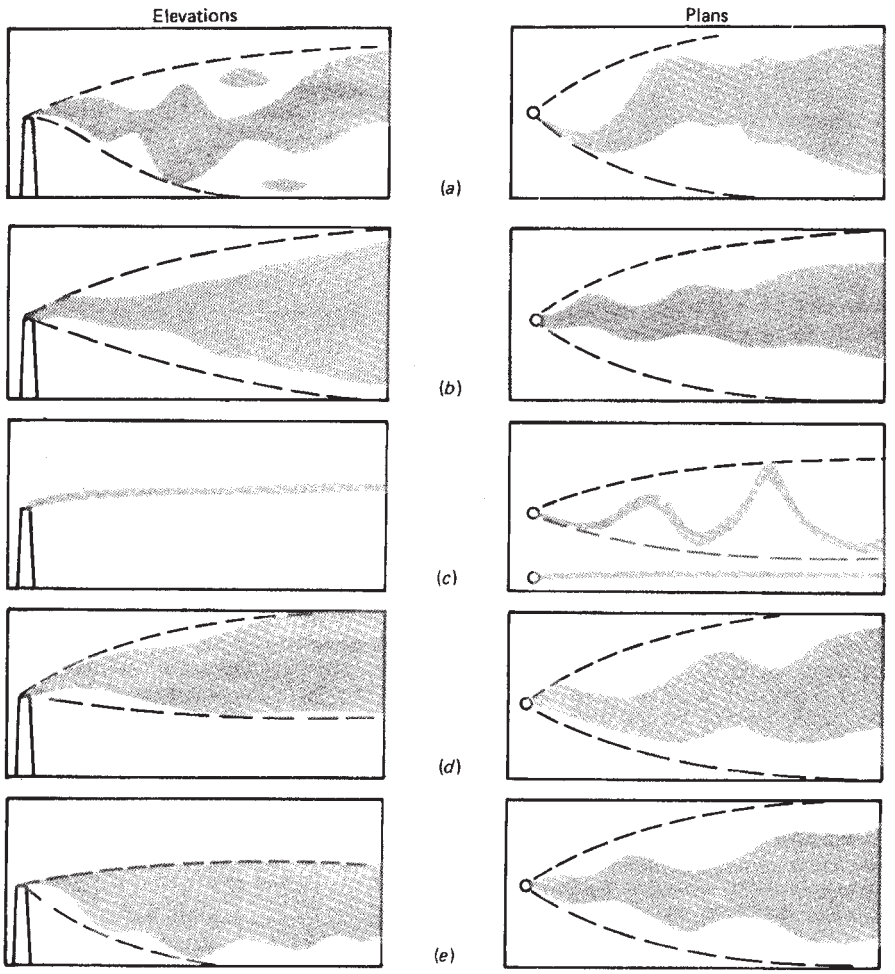


Figure 15.41 *Plume behaviour as a function of atmospheric stability conditions: (a) unstable ('looping'); (b) neutral ('coning'); (c) stable above and below source; surface inversion ('fanning'); (d) stable below source only: surface inversion ('lofting'); (e) stable above source only – elevated inversion ('fumigation')*

Since mechanical turbulence decreases quite rapidly with increase in height, the Richardson number is a function of height.

15.12.19 Monin–Obukhov length

The stability criteria just described take no account of two parameters that are now known to be important determinants of similarity in the surface layer. These are the vertical heat flux H and the friction velocity u_*.

These parameters are taken into account in another criterion of stability that is now increasingly used. This is the Monin–Obukhov length scale L (Monin and Obukhov, 1954; Obukhov, 1971), which is defined as

$$L = -\frac{u_*^3 c_p \rho T}{kgH} \qquad [15.12.46]$$

This parameter has the dimensions of length. It may be regarded as a measure of the depth of the mechanically mixed layer near the surface.

The Monin–Obukhov length L is negative for unstable and positive for stable conditions and infinite for adiabatic conditions. A dimensionless parameter, the Monin–Obukhov parameter ζ is obtained by taking the ratio of the height ζ to the Monin–Obukhov length L:

$$\zeta = z/L \qquad [15.12.47]$$

The Monin–Obukhov parameter is thus directly proportional to the height. Thus both the Richardson number and the Monin–Obukhov parameter are functions of the height.

The Richardson numbers and the Monin–Obukhov length and parameter are related, but the relations depend on stability conditions. Colder (1972) gives the following relations. For unstable conditions the Pandolfo–Businger hypothesis gives a good approximation:

$$\frac{z}{L} = \mathrm{Ri} \qquad [15.12.48a]$$

For stable conditions use may be made of the empirical relation given by McVehil (1964):

$$\frac{z}{L} = \frac{\mathrm{Ri}}{1 - \beta \mathrm{Ri}} \qquad [15.12.48b]$$

Values of the constant β are reviewed by Colder who uses $\beta = 7$.

The relation between the Richardson number and the Monin–Obukhov parameter may also be written in alternative form as given by Tagliazucca and Nanni (1983). For unstable conditions

$$\mathrm{Ri} = \frac{z}{L} \qquad [15.12.49a]$$

$$= \frac{z/L}{1 + \gamma z/L} \qquad [15.12.49b]$$

where γ is a constant.

The following empirical relation for the Monin–Obukhov length has been obtained by Venkatram (1980b):

$$L = 1100 u_*^2 \qquad [15.12.50]$$

15.12.20 Other stability criteria

Another stability parameter is the Kazanski–Monin parameter μ (Kazanski and Monin, 1960). This is defined as

$$\mu = \frac{k u_*}{f L} \qquad [15.12.51a]$$

$$= \frac{h'}{L} \qquad [15.12.51b]$$

where f is the Coriolis parameter and h' is the scale height of the neutral ABL. This parameter is also sometimes denoted by the symbol S.

A further stability criterion that is sometimes used is the non-dimensional windshear S:

$$S = \frac{kz}{u_*} \frac{\mathrm{d}u}{\mathrm{d}z} \qquad [15.12.52]$$

The condition $S = 1$ corresponds to the law of the wall as given in Equation 15.12.15.

15.12.21 Stability classification

The stability conditions have a strong influence on dispersion. The principal dispersion relations contain parameters that are functions of these conditions. Stability is a complex phenomenon, however, and its characterization is a difficult problem. There is a large literature dealing with approaches to turbulence typing or stability classification. Accounts are given by Pasquill (1962a), Gifford (1976b) and Sedefian and Bennett (1980).

A simple set of stability categories is:

(1) unstable conditions – lapse conditions;
(2) neutral conditions;
(3) stable conditions – including inversion conditions.

These categories are used to define the diffusion parameters in the Sutton equations, as described below.

A stability classification based on insolation and wind speed has been given by Pasquill (1961, 1962a) and is shown in Table 15.14. Night refers to the period from 1 h before sunset to 1 h after sunrise. Strong insolation corresponds to sunny, midday conditions in midsummer England and slight insolation to similar conditions in midwinter. If during day or night, there are overcast conditions then, regardless of wind speed, category D should be assumed.

Stability conditions in terms of the Pasquill stability categories are approximately:

A Unstable conditions
D Neutral conditions
F Stable conditions

The frequency of the different Pasquill stability categories in Great Britain is shown in Table 15.15. The contours on the map given in Figure 15.42 show the percentage of time during which the neutral category D prevails.

The Pasquill stability categories are used to define the dispersion coefficients in the Pasquill–Gifford equations and the parameters in the Pasquill equations, as described below.

An additional stability category G is used by some workers (e.g. Bryant, 1964 UKAEA AHSB(RP) R42).

Relations between the Pasquill stability categories and the two main stability criteria, the Richardson number Ri and the Obukhov length L have been given by Pasquill and Smith (1971) and are shown in Table 15.16.

There are a number of other stability classifications schemes. A review of these has been given by Gifford (1976b). Some of schemes are shown in Table 15.17.

The scheme of Brookhaven National Laboratory (BNL) (Singer and Smith, 1966) is based on the fluctuations of the horizontal wind direction trace recorded over a 1 hour period. The categories are

A Fluctuations $>90°$ peak to peak,
B2 Fluctuations $40–90°$,
B1 Fluctuations $15–45°$,
C Fluctuations $>15°$ distinguished by unbroken solid core of trace,
D Trace approximates a line, short-term fluctuations $<15°$.

Typical wind direction traces illustrating these wind gustiness categories given by Singer and Smith are shown in Figure 15.43.

The BNL scheme makes it possible to classify turbulence using relatively simple wind direction measurements and to relate the stability categories to experimental dispersion data obtained at a site. Strictly the categories are site specific and those published for BNL apply to the BNL site. The relations between the BNL categories and the wind speed and temperature gradient is shown in Table 15.18.

The scheme proposed by D.B. Turner (1961, 1964) is a version of Pasquill's scheme in which the insolation is according to the amount and height of cloud cover and the solar elevation angle.

The scheme developed by Klug (1969) is similar to that of Pasquill, but differs in that the categories are defined using more detailed rules for cloud cover, wind speed, time of day and season.

The scheme of Cramer (1957, 1959b) is based on correlation of stability with the azimuth σ_A and the elevation angle σ_E. Cramer's turbulence categories are shown in Table 15.19.

Table 15.14 *Pasquill's stability categories (Pasquill, 1961) (Courtesy of HM Stationery Office)*

Surface wind speed at 10 m *height* (m/s)	*Insolation*			*Night*	
	Strong	*Moderate*	*Slight*	*Thinly overcast or ≥4/8 cloud*	*<3/8 cloud*
<2	A	A–B	B	–	–
2–3	A–B	B	C	F	F
3–5	B	B–C	C	D	E
5–6	C	C–D	D	D	D
>6	C	D	D	D	D

Table 15.15 *Pasquill stability categories for Great Britain (see also Figure 15.42) (Meteorological Office, 1977; reproduced by permission)*

Surface wind speed at 10 m *height* (mile/h)	*Frequency of stability category* (%)						
	A	*B*	*C*	*D*	*E*	*F*	*G*
16	0	4	11	80	3	2	0
14.5	0	4	13	75	4	3	1
13	0	4	14	70	5	5	2
11.5	1	5	15	65	6	6	2
10	1	6	17	60	7	7	2
9	2	7	19	55	7	7	3
8	2	9	21	50	6	8	4

The Tennessee Valley Authority (TVA) scheme, described by Carpenter *et al.* (1971) is concerned with stability classification for buoyant plumes from tall chimneys. It is based on lapse rate $\Delta\theta/\Delta z$. The TVA stability categories are given in Table 15.20.

Relationships between some of these stability classification, or turbulence typing, schemes have been given by Gifford and are shown in Table 15.21.

The Pasquill scheme has been modified by F.B. Smith (1973) so that the stability is described in terms of a continuous index P rather than by discrete categories. The P value is a function of the wind speed, the upward heat flux and the incoming solar radiation, and also of the roughness length. P values of 0.5–6.5 correspond to the Pasquill categories A–G as follows:

	P
A	0.5
B	1.5
C	2.5
D	3.6
E	4.5
F	5.5
G	6.5

The graph given by Smith for the determination of the P value is shown in Figure 15.44.

There are a number of other stability classification schemes based on relations between the Pasquill stability categories and particular parameters. A review of several such schemes has been given by Sedefian and Bennett (1980), as shown in Table 15.22. The authors also analysed dispersion data and derived relations for the P value in some of the schemes.

In the σ_θ, or sigma theta, method the stability category is taken as a function of the wind direction standard deviation σ_θ. This method is one of two that has been recommended by the Nuclear Regulatory Commission and is widely used.

Sedefian and Bennett give the following relation involving σ_θ:

$$\sigma_\theta(z_2) = \sigma_\theta(z_1)(z_2/z_1)^{P_\theta} \qquad [15.12.53]$$

where P_θ is an index and where the heights z_1 and z_2 are 10 and 50 m, respectively. The values of P_θ corresponding to Pasquill categories A–F are −0.06, −0.15, −0.17, −0.23, −0.38 and −0.53, respectively.

The temperature difference ΔT method is the other method recommended by the NRC.

The wind speed ratio U_R is a parameter devised by Sedefian and Bennett and is the ratio of the wind speeds at 50 and 10 m height. The authors give the following relation involving U_R

$$U_R = (z_2/z_1)^{P_u} \qquad [15.12.54]$$

where P_u is an index and U_R is the wind speed ratio and where the heights z_1 and z_2 are 10 and 50 m, respectively. The values of P_u are related to the Pasquill stability categories.

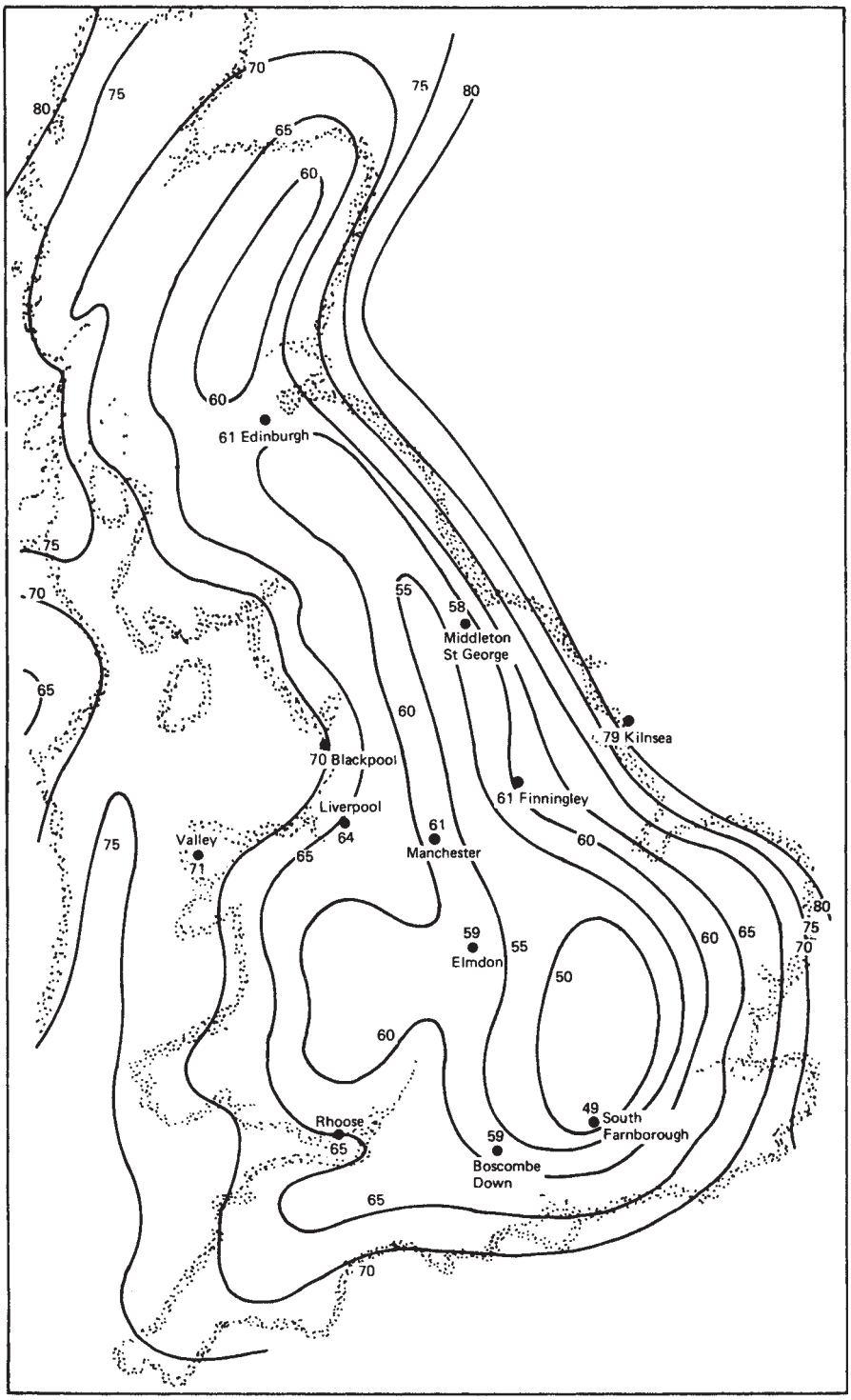


Figure 15.42 *Frequency of occurrence of Pasquill stability categories over Great Britain (Meteorological Office, 1977; reproduced by permission). Contours showing percentage of time during which Pasquill stability category D prevails (see Table 15.15)*

Table 15.16 *Relations between Pasquill stability categories and stability criteria (after Pasquill and Smith, 1971) (Courtesy of Academic Press)*

Pasquill stability category	*Richardson No.* Ri	*Obhukov Length L*
A	−1.0 to −0.7	−2 to −3
B	−0.5 to −0.4	−4 to −5
C	−0.17 to −0.13	−12 to −15
D	0	∞
E	0.03 to 0.05	35 to 75
F	0.05 to 0.11	8 to 35

Table 15.17 *Some stability classification schemes*

Stability classification scheme	*Categories*	*Reference(s)*
Pasquill	A–F	Pasquill (1961, 1962)
Brookhaven National Laboratory (BNL)	A–D	M.E. Smith (1951), Singer and Smith (1953, 1966)
Turner	1–7	D.B. Turner (1961, 1964)
Klug		Klug (1969)
Cramer	σ_A, σ_E	Cramer (1957, 1959b)
Tennessee Valley Authority (TVA)	A–F	Carpenter *et al.* (1971)

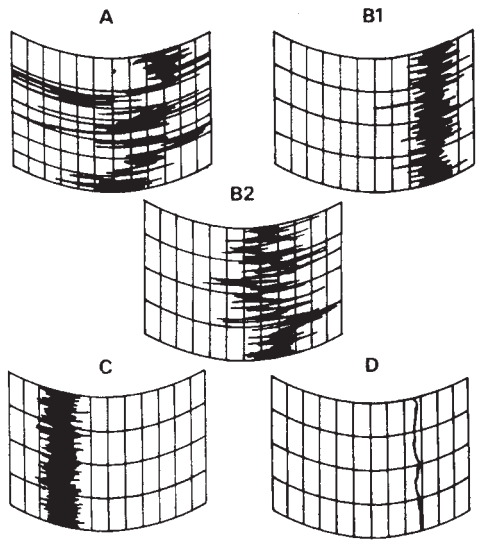


Figure 15.43 *Typical wind direction traces illustrating wind gustiness categories (Singer and Smith, 1966) (Courtesy of Brookhaven National Laboratory)*

The stability array (STAR) method is based on cloud cover, solar altitude and wind speed.

The relation between the Pasquill stability categories and the parameters of these various methods as determined by Sedefian and Bennett is shown in Table 15.23.

Table 15.18 *BNL turbulence categories (after Gifford, 1976b) (Courtesy of Nuclear Society)*

Turbulence category	*Wind speed* (m/s)		*Temperature gradient* ($\Delta T/\Delta z$) (°C/123 m)
	9 m	*108* m	
A	–	1.8 ± 1.1[a]	-1.25 ± 7[a]
B2	2.5	3.8 ± 1.8	-1.6 ± 0.5
B1	3.4	7.0 ± 3.1	-1.2 ± 0.65
C	4.7	10.4 ± 3.1	-0.64 ± 0.52
D	1.9	6.4 ± 2.6	-2.0 ± 2.6

[a] Standard deviation.

Table 15.19 *Cramer's turbulence categories*

Stability	*Azimuth,* σ_A (°)	*Elevation angle,* σ_E (°)
Extremely unstable	30	10
Near neutral (rough surface; trees, buildings)	15	5
Near neutral (very smooth grass)	6	2
Extremely stable	3	1

Table 15.20 *TVA stability categories (after Carpenter et al., 1971) (Courtesy of the Air Pollution Control Association)*

Stability category	*Lapse rate,* $\Delta\theta/\Delta z$ (K/100 m)
A Neutral	0
B Slightly stable	0.27
C Stable	0.64
D Isothermal	1.00
E Moderate inversion	1.36
F Strong inversion	1.36

Table 15.21 *Relations between turbulence typing schemes (Gifford, 1976b) (Courtesy of Nuclear Safety)*

Stability	*Scheme*			
	Pasquill	*Turner*	*BNL*	σ_A
Very unstable	A	1[a]	B2	25
Moderately unstable	B	2	B1	20
Slightly unstable	C	3	B1	15
Neutral	D	4	C	10
Moderately stable	E	6	–	5
Very stable	F	7	D	2.5

[a] After Golder (1972).

Pasquill related his stability categories to the lateral spread of the wind θ. The relations are given in Table 15.24.

There have been a number of studies in which stability classification schemes have been compared with

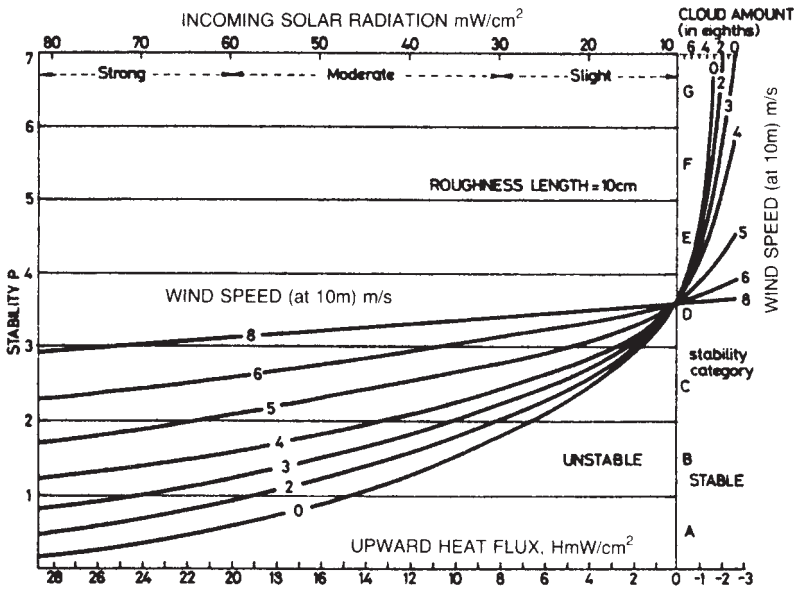


Figure 15.44 *Stability parameter, or P value (after F.B. Smith, 1973; Clarke, 1979 NRPB R91; reproduced by permission)*

Table 15.22 *Some schemes for assigning Pasquill stability categories (after Sedefian and Bennett, 1980)*

Scheme	*Comment*
Wind direction standard deviation σ_θ	One of two methods given in NRC *Guide* 1.23
Temperature difference, ΔT	Other method given in NRC *Guide* 1.23
Richardson number, Ri	Authors' own method,utilizing relations given by Golder (1972) between Pasquill categories and Monin–Obukhovlength L and roughness length z_o
Bulk Richardson number, Ri_B	Authors' own method
Wind speed ratio U_R	Authors' own method, based on ratio of wind speed sat heights of 10 and 50 m
Stability array (STAR)	Author's own method, based on wind speed at 10 m, solar altitude and cloud cover

experimental measurements, including those done by Sedefian and Bennett (1980) and A.E. Mitchell (1982).

An alternative approach to stability is to treat it as primarily a function of the Obukhov length L and the roughness length z_o. Colder (1972) has developed relationships between the Pasquill stability categories and these two parameters. Figure 15.45 shows these relations. Colder also concluded that the most appropriate conversion between the Pasquill and Turner categories is A to 1, B to 2, C to 3, D to 4, E to 6 and F to 7.

Relations between the Turner stability categories and the Monin–Obukhov length, inferred from the work of Colder (1972) have been given by Ning and Yap (1986). These are given in Table 15.25.

Another stability classification scheme is that of Holtslag and van Ulden (1983). This is based on the sensible heat flux.

The stability classifications just described were developed for use over land. They do not necessarily hold over water.

A stability classification scheme for use over water has been developed at the Naval Postgraduate School (NFS), Monterey, by Schacher, Fairall and Zannetti (1982).

Following Colder, stability is treated as primarily a function of the Monin–Obukhov length and the roughness length. The Monin–Obukhov length is determined from air-sea temperature difference, wind speed and relative humidity. Figure 15.46, given by Skupniewicz and Schacher (1986), illustrates the classification for 50% relative humidity. A somewhat similar scheme has been given by Hasse and Weber (1985). In that stability is characterized by the Monin–Obukhov length, the derivation and use of this parameter may be regarded as a stability classification 'scheme'.

The selection of a stability classification method scheme for gas dispersion modelling is exemplified by the set of schemes used in the DRIFT dense gas dispersion model described in Section 15.35. The model can accommodate three schemes. One is the use of the Monin–Obukhov length, valid for all locations and all times. The others are the Pasquill scheme, used for day on land, and the Holtslag and van Ulden scheme, used for neutral or unstable conditions for day on land.

Table 15.23 *Relations between Pasquill stability categories and parameters of some typing schemes (after Sedfian and Bennett, 1980)(Courtesy of Pergamon Press)*

Pasquill stability	σ_θ (10 and 50 m) (°)	σ_θ (50 m)[a] (°)	$\Delta T/\Delta z$ (°C/100 m)	Ri[b]	Ri_B[b]	U_R[b]
A	$22.5 < \sigma_\theta$	$20.0 < \sigma_\theta$	$\Delta T/\Delta z < -1.9$	$Ri < -2.51$	$Ri_B < -0.0016$	$U_R < 1.18$
B	$17.5 < \sigma_\theta \leq 22.5$	$13.75 < \sigma_\theta \leq 20.0$	$-1.9 \leq \Delta T/\Delta z < -1.7$	$-2.51 \leq Ri < -1.07$	$-0.0016 \leq Ri_B < -0.009$	$1.18 \leq U_R < 1.21$
C	$12.5 < \sigma_\theta \leq 17.5$	$9.5 < \sigma_\theta \leq 13.75$	$-1.7 \leq \Delta T/\Delta z < -1.5$	$-1.07 \leq Ri < -0.275$	$-0.009 \leq Ri_B < -0.003$	$1.21 \leq U_R < 1.26$
D	$7.5 < \sigma_\theta \leq 12.5$	$5.0 < \sigma_\theta \leq 9.5$	$-1.5 \leq \Delta T/\Delta z < -0.5$	$-0.275 \leq Ri < 0.089$	$-0.003 \leq Ri_B < 0.0075$	$1.26 \leq U_R < 1.56$
E	$3.75 < \sigma_\theta \leq 7.5$	$2.0 < \sigma_\theta \leq 5.0$	$-0.5 \leq \Delta T/\Delta z < 1.5$	$0.089 \leq Ri < 0.128$	$0.0075 \leq Ri_B < -0.05$	$1.56 \leq U_R < 2.28$
F	$2.0 < \sigma_\theta \leq 3.75$	$0.75 < \sigma_\theta \leq 2.0$	$1.5 \leq \Delta T/\Delta z < 4.0$	$0.128 \leq Ri < 0.134$	$0.05 \leq Ri_B < -0.075$	$2.28 \leq U_R < 3.28$
G	$\sigma_\theta \leq 2.0$	$\sigma_\theta \leq 0.75$	$\Delta T/\Delta z \geq 4.0$	$Ri \geq 0.134$	$Ri_B \geq 0.075$	$U_R \geq 3.28$

[a] Corrected for height variation of σ_θ.
[b] Ri, Ri_B and U_R limits based on Businger formulation for 22 m.

Table 15.24 *Relations between Pasquill stability categories and lateral spread of wind*

Pasquill stability category	*Lateral spread* θ (deg)	
	$d = 0.1$ km	$d = 100$ km
A	60	(20)
B	45	(20)
C	30	10
D	20	10
E	(15)	(5)
F	(10)	(5)

The stability category is the other main piece of information which is required, in addition to the wind characteristics, for the estimation of dispersion at a given location.

15.12.22 Flux–gradient relations

In the surface layer it is assumed that stress does not vary with height. Similar arguments based on the work of Monin and Obukhov lead to the conclusion that for any transferable property S the relation between vertical flux and vertical gradient is determined by the following parameters: z, ρ, g/T, τ/ρ, and $H/c_p\rho$.

The flux–gradient relations may be expressed in the form:

$$\frac{dS}{dz} = \frac{S_*}{kz}\phi_s\left(\frac{z}{L}\right) \qquad [15.12.55]$$

where S is the mean quantity of the property per unit mass of air, S_* is a scale parameter with the same dimensions as S, ϕ is a similarity factor, and the subscript s denotes the property specified.

The scale parameter S_* is defined by the relation to the vertical flux F_s:

$$S_* = \frac{F_s}{\rho u_*} \qquad [15.12.56]$$

The vertical flux is given by the relation:

$$F_s = -\rho K_s \frac{dS}{dz} \qquad [15.12.57]$$

where K is a turbulent exchange coefficient.

For momentum, heat and water vapour the flux relations are:

$$\tau = \rho K_M \frac{du}{dz} \qquad [15.12.58]$$

$$H = -\rho c_p K_H \frac{d\theta}{dz} \qquad [15.12.59]$$

$$E = -\rho L_W K_W \frac{dq}{dz} \qquad [15.12.60]$$

where c_p is the specific heat of air, E is the vertical flux of water vapour, H is the vertical heat flux, L_W is the latent heat of water vapour, q is the specific humidity, or

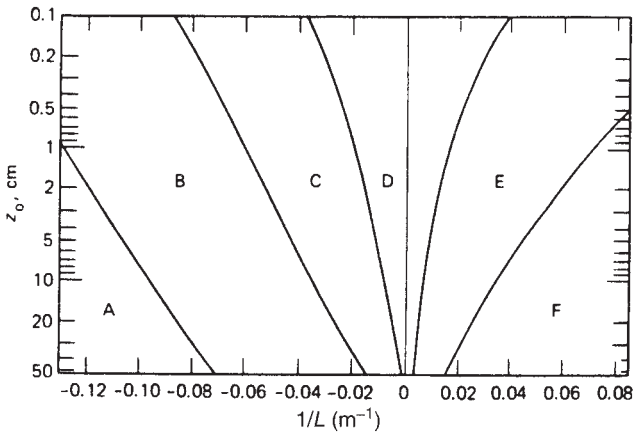


Figure 15.45 *Relations between Pasquill stability categories and Monin–Obukhov length and surface roughness (Golder, 1972) (Courtesy of Kluwer Academic Publishers)*

Table 15.25 *Relations between Turner stability categories and Monin–Obukhov length (after Ning and Yap, 1986) (Courtesy of Pergamon Press)*

Turner stability category[a]	$1/L$ (m^{-1})
A	$1/L \leq -0.087$
B	$-0.087 \leq 1/L < -0.028$
C	$-0.028 \leq 1/L < -0.005$
D	$-0.005 \leq 1/L$

[a] D.B. Turner (1964) denoted his stability categories 1–7.
Ning and Yap state that the Turner stability categories A–D are derived from the work of Golder (1972) for a roughness length z_o of 20 cm on land, and the Holtslag and van Ulden scheme, used for neutral or unstable conditions for day on land.

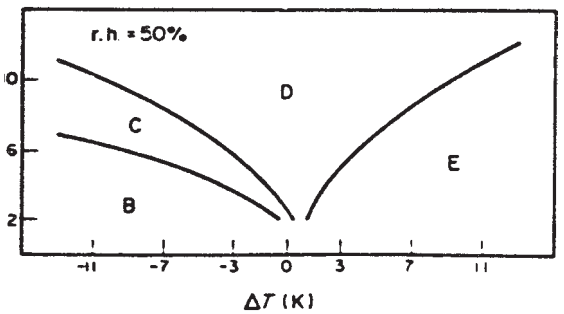


Figure 15.46 *Illustration of the NPS stability classification scheme over water (Skupniewicz and Schacher, 1986) (Courtesy of Pergamon Press)*

concentration of water vapour, u is the wind velocity, θ is the potential temperature, ρ is the density of air, and the subscripts H, M and W denote heat, mass and water vapour, respectively.

The corresponding equations for the turbulent exchange coefficients are then

$$K_M = \frac{\tau}{\rho \mathrm{d}u/\mathrm{d}z} \quad [15.12.61]$$

$$K_H = -\frac{H}{\rho c_p \mathrm{d}\theta/\mathrm{d}z} \quad [15.12.62]$$

$$K_W = -\frac{E}{\rho L_W \mathrm{d}q/\mathrm{d}z} \quad [15.12.63]$$

Then, applying Equations 15.12.56 and 15.12.57 to momentum and noting that for this case

$$S = u \quad [15.12.64]$$

and

$$F_s = -\rho u_*^2 \quad [15.12.65]$$

gives

$$\frac{\mathrm{d}u}{\mathrm{d}z} = \frac{u_*}{kz}\phi_M \quad [15.12.66]$$

Similarly, the gradient relations for heat and water vapour are:

$$\frac{\mathrm{d}\theta}{\mathrm{d}z} = -\frac{H}{\rho c_p k u_* z}\phi_H \quad [15.12.67]$$

$$\frac{\mathrm{d}q}{\mathrm{d}z} = -\frac{E}{\rho L_W k u_* z}\phi_W \quad [15.12.68]$$

The relations for the turbulent exchange coefficients become:

$$K_M = ku_*z/\phi_M \quad [15.12.69]$$

$$K_H = ku_*z/\phi_H \quad [15.12.70]$$

$$K_W = ku_*z/\phi_W \quad [15.12.71]$$

Also from the definitions of the Richardson number Ri and the Monin–Obukhov parameter z/L, as given by Equations 15.12.42b and 15.12.46, and from Equations 15.12.66 and 15.12.67

$$\mathrm{Ri} = \frac{z}{L}\frac{\phi_\mathrm{H}}{\phi_\mathrm{M}^2} \qquad [15.12.72]$$

15.12.23 Universal functions

Monin and Obukhov expanded the function $\phi_\mathrm{M}(z/L)$ as the power series

$$\phi_\mathrm{M} = 1 + \alpha_1\left(\frac{z}{L}\right) + \alpha_2\left(\frac{z}{L}\right)^2 + \cdots \qquad [15.12.73]$$

where α_1 and α_2 are coefficients. They truncated the series after the first term in (z/L) to give

$$\phi_\mathrm{M} = 1 + \alpha\left(\frac{z}{L}\right) \qquad [15.12.74]$$

where α $(=\alpha_1)$ is the Monin–Obukhov coefficient. This coefficient is to be determined empirically.

An alternative relation for ϕ_M is the exponential relation proposed by Swinbank (1964):

$$\phi_\mathrm{M} = \left[1 - \exp(z/L)\right]^{-1} \qquad [15.12.75]$$

Relations for the universal functions have been derived by a number of authors and have been reviewed by Dyer (1974). Some of these relations are given in Table 15.26. Obukhov (1971) has defined an alternative universal function by the relation

$$K_\mathrm{M} = K_\mathrm{Mo}\phi(\mathrm{Ri}) \qquad [15.12.76]$$

where K_Mo is the adiabatic value of K_M. He gives the following relations for ϕ (Ri):

$$\phi(\mathrm{Ri}) = 1 \qquad \mathrm{Ri} = 0 \qquad [15.12.77a]$$

$$= \left(1 - \frac{\mathrm{Ri}}{\mathrm{Ri_{cr}}}\right)^{1/2} \qquad \mathrm{Ri} < \mathrm{Ri_{cr}} \qquad [15.12.77b]$$

$$= 0 \qquad \mathrm{Ri} > \mathrm{Ri_{cr}} \qquad [15.12.77c]$$

where the subscript cr denotes critical.

Equation 15.12.77a follows from the definition of ϕ (Ri) and from the fact that for adiabatic conditions $\mathrm{Ri} = 0$, and Equation 15.12.77c follows from the fact that turbulence is suppressed for $\mathrm{Ri} > \mathrm{Ri_{cr}}$.

As already described, the Monin–Obukhov form of the universal function ϕ_M gives for the wind velocity gradient Equation 15.12.24, which on integration yields Equation 15.12.25 or, for $z \gg z_\mathrm{o}$, Equation 15.12.26.

15.12.24 Turbulent exchange coefficients

The turbulent exchange coefficients are:

K_M Turbulent exchange coefficient for momentum; eddy viscosity.
K_H Turbulent exchange coefficient for heat; eddy thermal diffusivity.
K_W Turbulent exchange coefficient for water vapour; eddy diffusivity.

These coefficients are defined by Equations 15.12.58–15.12.60, respectively. It was assumed in early work by Schmidt (1925) that

$$K_\mathrm{M} = K_\mathrm{H} = K_\mathrm{W} \qquad [15.12.78]$$

The identity of the three exchange coefficients is still a common assumption for neutral conditions. According to Dyer (1974), however, there is evidence that for such conditions the ratio $K_\mathrm{H}/K_\mathrm{M}$ is equal to 1.35.

From Equations 15.12.69–15.12.71, the ratio of the exchange coefficients may be expressed in terms of the ratios of the universal functions ϕ_M, ϕ_H and ϕ_W. For neutral conditions the latter approach unity. For other conditions the ratios $K_\mathrm{H}/K_\mathrm{M}$ and $K_\mathrm{W}/K_\mathrm{M}$ will be unity only if the asymptotic approach to unity of the ϕ_H and ϕ_W is identical with that of ϕ_M. For unstable conditions there is evidence that this is not so.

The identity of the exchange coefficients for mass and heat transfer implies, from Equations 15.12.58 and 15.12.59,

$$\frac{H}{C_\mathrm{p}\tau} = -\frac{\mathrm{d}\theta/\mathrm{d}z}{\mathrm{d}u/\mathrm{d}z} \qquad [15.12.79]$$

Equation 15.12.79 is a form of the Reynolds analogy.

Table 15.26 *Some forms of the universal functions (after Dyer, 1974) (Courtesy of Kluwer Academic Publishers)*

ϕ_M	ϕ_H	ϕ_W	*Regime*	*Reference*
A Unstable conditions				
$(z/L)[1-\exp(z/L)]^{-1}$	–	–	–	Swinbank (1964)
$0.613(-z/L)^{0.20}$	$0.227(-z/L)^{-0.44}$	–	$-0.1 > (z/L) > -2$	Swinbank (1968)
$1+4.5(z/L)$	$1+4.5(z/L)$	$1+4.5(z/L)$	$(z/L) > -0.03$	E.K. Webb (1970)
$[1-16(z/L)]^{-1/4}$	$[1-16(z/L)]^{-1/2}$	$[1-16(z/L)]^{-1/2}$	$0 > (z/L) > -1$	Dyer and Hicks (1970)
$[1-15(z/L)]^{-1/4}$	$0.74[1-9(z/L)]^{-1/2}$		$(z/L) > -2$	Businger *et al.* (1971)
B Stable conditions				
$1+5.2(z/L)$	$1+5.2(z/L)$	$1+5.2(z/L)$	$(z/L) > -0.03$	E.K. Webb (1970)
$1+4.7(z/L)$	$0.74+4.7(z/L)$		$(z/L) > -2$	Businger *et al.* (1971)

15.12.25 Wind direction fluctuations

Wind direction fluctuations may be defined in terms of the standard deviation of the horizontal direction and inclination of the wind:

σ_θ Standard deviation of the horizontal direction of the wind.
σ_ϕ Standard deviation of the inclination to the horizontal of the wind.

Alternative notation for these quantities is for σ_θ the standard deviation of the azimuth σ_A and for σ_ϕ the standard deviation of the elevation σ_E. Distributions of the standard deviations σ_θ and σ_ϕ by Pasquill stability category have been given by Luna and Church (1972) and are shown in Figure 15.47.

As described above, the concentration measured in a plume varies with the sampling time. Similarly, the value measured for σ_θ varies with sampling time. Slade (1968) suggests that a correction for sampling time may be made using the following approximate relation:

$$\frac{\sigma_\theta}{\sigma_{\theta r}} = \left(\frac{t}{t_r}\right)^p \qquad [15.12.80]$$

where t is the sampling period which yields σ_θ, p is an index and subscript r denotes the reference value. The value of p is of the order of 0.2.

The standard deviations σ_θ and σ_ϕ are used in the Pasquill model for passive gas dispersion.

15.12.26 Wind velocity fluctuations

The wind velocities u, v and w in the downwind, crosswind and vertical directions respectively, may be written as the sum of a mean velocity and a velocity fluctuation:

$$u = \bar{u} + u' \qquad [15.12.81a]$$

$$v = \bar{v} + v' \qquad [15.12.81b]$$

$$w = \bar{w} + w' \qquad [15.12.81c]$$

where $\bar{u}$, $\bar{v}$ and $\bar{w}$ are the mean values and u' v' and w' the fluctuations of u, v and w, respectively.

Wind velocity fluctuations may be defined in terms of the standard deviations σ_u, σ_v and σ_w of the velocities as follows:

$$\sigma_u = \left(\overline{u'^2}\right)^{1/2} \qquad [15.12.82a]$$

$$\sigma_v = \left(\overline{v'^2}\right)^{1/2} \qquad [15.12.82b]$$

$$\sigma_w = \left(\overline{w'^2}\right)^{1/2} \qquad [15.12.82c]$$

where $\overline{u^2}$, $\overline{v^2}$ and $\overline{w^2}$ are the variances of u, v and w, respectively.

Relationships for σ_u, σ_v and σ_w derived from the work of Wyngaard, Cote and Rao (1974) and Wyngard (1975) have been given by S.R. Hanna, Briggs and Hosker (1982). For σ_u:

$$\frac{\sigma_u}{u_*} = \left(12 - 0.5\frac{z_i}{L}\right)^{1/3} \quad \text{unstable} \qquad [15.12.83]$$

$$= 2.0\exp\left(-3\frac{fz}{u_*}\right) \quad \text{neutral} \qquad [15.12.84]$$

$$= 2.0\left(1 - \frac{z}{z_i}\right) \quad \text{stable} \qquad [15.12.85]$$

where f is the Coriolis parameter, L is the Monin–Obukhov length and z_i is the mixed layer height. The authors also give relationships for σ_v and σ_w.

15.12.27 Turbulence intensity

Intensities of turbulence are defined as:

$$i_y = \left(\overline{v'^2}\right)^{1/2}/\bar{u} \qquad [15.12.86a]$$

$$i_z = \left(\overline{w'^2}\right)^{1/2}/\bar{u} \qquad [15.12.86b]$$

where i_y and i_z are the intensities of the lateral and vertical components of turbulence, respectively.

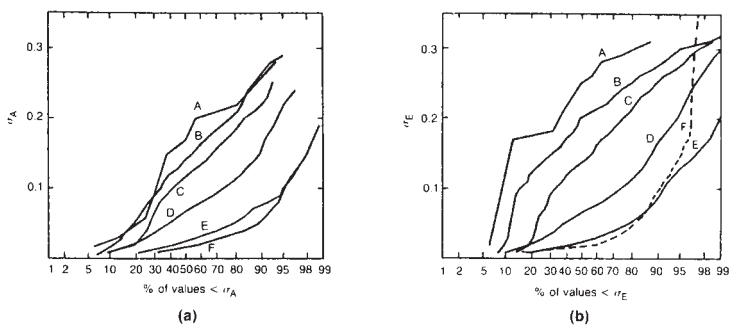


Figure 15.47 *Standard deviations of wind direction fluctuations (Luna and Church, 1972): (a) distribution of σ_A by stability class; (b) distribution of σ_A by stability class. A–F, Pasquill stability categories. Reproduced by permission*

The root-mean-square turbulent velocities are related to the friction velocity:

$$\left(\overline{v'^2}\right)^{1/2} = 2.2u_* \qquad [15.12.87a]$$

$$\left(\overline{w'^2}\right)^{1/2} = 1.25u_* \qquad [15.12.87b]$$

For neutral conditions, combining Equations 15.12.86, 15.12.87 and 15.12.20:

$$i_y = \frac{0.88}{\ln(z/z_o)} \qquad [15.12.88a]$$

$$i_z = \frac{0.5}{\ln(z/z_o)} \qquad [15.12.88b]$$

Also, combining Equations 15.12.82 and 15.12.86:

$$i_y = \sigma_v/\bar{u} \qquad [15.12.89a]$$

$$i_z = \sigma_w/\bar{u} \qquad [15.12.89b]$$

15.12.28 Eddy dissipation rate

The eddy dissipation rate t is the rate at which on the small scale turbulence is dissipated into heat. In the surface layer:

$$\epsilon = \frac{u_*^3}{kz}(\phi_M - z/L) \qquad [15.12.90]$$

For neutral conditions:

$$\epsilon = \frac{u_*^3}{kz} \qquad [15.12.91]$$

15.12.29 Lagrangian turbulence

Turbulence may be measured at a fixed point or by reference to a particle moving through the turbulent field. The types of turbulence measured in these two different ways are known as Eulerian and Lagrangian turbulence, respectively. The dispersion of a gas in air is a Lagrangian process, but it is generally observed by Eulerian measurements.

The difference between the two types of turbulence may be illustrated by the following simplified argument. Consider a wind speed u carrying a circular eddy radius r and tangential velocity ω. The Eulerian time scale t_E is the time for the eddy to pass a fixed point:

$$t_E = 2r/u \qquad [15.12.92]$$

The Lagrangian time scale t_L, is the time for a particle on the circumference of the eddy to travel once round the eddy:

$$t_L = 2\pi r/\omega \qquad [15.12.93]$$

The ratio β of the Lagrangian to the Eulerian time scale is then

$$\beta = \frac{t_L}{t_E} \qquad [15.12.94a]$$

$$= \frac{\pi}{\omega/u} \qquad [15.12.94b]$$

$$= \frac{\pi}{i} \qquad [15.12.94c]$$

with

$$i = \omega/u \qquad [15.12.95]$$

where i is the intensity of turbulence.

The ratio β decreases as the intensity of turbulence increases. Reid (1979) gives the relation

$$\beta = 0.5/i \qquad [15.12.96]$$

This suggests that, although the form of Equation 15.12.93 derived from the crude model is correct, the equation overestimates β. An average value given by Pasquill (1974) for β is 4.

A study of the time scales over water is described by Sethuraman, Meyers and Brown (1976).

15.12.30 Autocorrelation function

If in a field of homogenous turbulence measurements are made at two points of the instantaneous components of velocity u_1' and u_2' and, if the position of the second point is moved while that of the first is kept fixed, a correlation coefficient $R(x)$ may be defined as

$$R(x) = \overline{u_1'u_2'}/\overline{u'^2} \qquad [15.12.97]$$

For eddy sizes which are large compared with the distance x this correlation coefficient is high, and vice versa.

The correlation coefficient may also be expressed in terms of time. This time correlation coefficient $R(\tau)$, which is also known as the autocorrelation coefficient, is defined as

$$R(\tau) = \overline{u(t)u(t+\tau)}/\overline{u^2} \qquad [15.12.98]$$

The two correlation coefficients are identical:

$$R(\tau) = R(x) \qquad [15.12.99]$$

with $x = u\tau$.

Properties of the autocorrelation coefficient are:

$$R(\tau) = 1 \quad \tau = 0 \qquad [15.12.100a]$$

$$= 0 \quad \tau \to \infty \qquad [15.12.100b]$$

The form of the autocorrelation coefficient is not fully understood. One model commonly used is the Markov model for which

$$R(\tau) = \exp(-\tau/t_L) \qquad [15.12.101]$$

15.12.31 Taylor's theorem

A relation between the autocorrelation function and the dispersion parameters has been derived by G.I. Taylor (1921). The displacement x of a particle is related to its velocity u as follows:

$$x(t) = \int_0^t u(t')\,dt' \qquad [15.12.102]$$

Then

$$\frac{d\left[x^2(t)\right]}{dt} = 2x\frac{dx}{dt} \qquad [15.12.103a]$$

$$= 2\int_0^t u(t)u(t')\,dt' \qquad [15.12.103b]$$

Substituting the autocorrelation coefficient from Equation 15.12.98 in Equation 15.12.103 yields

$$\frac{\mathrm{d}\overline{x^2}}{\mathrm{d}t} = 2\overline{u^2}\int_0^t R(\tau)\,\mathrm{d}\tau \qquad [15.12.104]$$

But it can be shown that

$$\sigma_x^2 = \overline{x^2} \qquad [15.12.105]$$

Hence

$$\frac{\mathrm{d}\sigma_x^2}{\mathrm{d}t} = 2\overline{u^2}\int_0^t R(\tau)\,\mathrm{d}\tau \qquad [15.12.106]$$

and

$$\sigma_x^2 = 2\overline{u^2}\int_0^t\int_0^{t'} R(\tau)\,\mathrm{d}\tau\,\mathrm{d}t' \qquad [15.12.107]$$

Equation 15.12.107 is Taylor's theorem.

If a form of the autocorrelation coefficient is assumed, such as that given in Equation 15.12.101, it is possible to derive from Equation 15.12.107 an expression for the dispersion coefficient. The application of Taylor's theorem for this purpose is described below.

15.12.32 Mixed layer scaling

Much of the foregoing treatment has been concerned with the properties of, and similarity within, the surface stress layer. In mixed layer scaling, similarity is extended to the whole boundary layer.

The initial treatment by Deardorff (1970) was for the convective boundary layer, in other words, for the planetary boundary layer in convective, or unstable, conditions, and is also termed convective layer, or convective velocity, scaling.

Scaling has also been extended by other workers such as Caughey, Wyngaard and Kaimal (1979) to stable conditions and for this the term 'mixed layer scaling' is perhaps more appropriate. A parameter widely used in mixed layer scaling is

$$X = \frac{w_* x}{u z_i} \qquad [15.12.108]$$

where w_* is the convective velocity and z_i the mixed layer height.

15.12.33 Mixed layer height

Over land the mixed layer has a height of some 1000–2000 m by day but about an order of magnitude less by night. Over sea the diurnal variation is much less. By day the mixed layer height is usually set by an inversion layer capping the well mixed layer above the ground surface. By night, when there is some degree of inversion at all levels, the height of the mixed height may be taken as that at which surface induced mechanical turbulence dies out. Extensive data on the mixed layer height in the United States have been published by Holzworth (1972).

The mixed layer height z_i has been investigated by Zilitinkevich (1972a), who gives the following relations:

$$z_i = \frac{k u_*}{f} \qquad \text{neutral conditions} \qquad [15.12.109a]$$

$$= c\left(\frac{u_* L}{f}\right)^{1/2} \qquad \text{stable conditions} \qquad [15.12.109b]$$

where c is a constant. Values of the constant c are quoted by Venkatram and Paine (1985) as varying between 0.4 and 0.7.

Another correlation, applicable to stable conditions at night in high wind, is that of Venkatram and Paine (1985):

$$z_i = 2300 u_*^{3/2} \qquad [15.12.110]$$

They state that the constant, given here as 2300, tends to be site specific and quote a value of 1300 at another site.

15.12.34 Convective velocity scale

The convective velocity, or velocity scale, w_* is defined as

$$w_* = \frac{g Q_\mathrm{o} z_i}{T_\mathrm{o}} \qquad [15.12.111]$$

where Q_o is the surface heat flux and T_o is the absolute average temperature of the mixed layer.

The convective velocity w_* may be estimated from correlations for the quantity σ_w/w_*, together with correlations for σ_w or, more directly, from correlations for w_* itself. A correlation of the first type has been given by Irwin (1979a) and is shown in Figure 15.48. Correlations for σ_w have been discussed above.

Direct relations for w_* have been given by Venkatram (1978) in terms of the maximum surface heat flux Q_m and the maximum mixed layer height $z_{i\mathrm{m}}$ as follows:

$$w_* = A Q_\mathrm{m}^{1/2} \qquad [15.12.112]$$

with

$$Q_\mathrm{m} = Q_\mathrm{o}\sin(\pi t/2\tau) \qquad [15.12.113]$$

And

$$w_* = B z_{i\mathrm{m}} \qquad [15.12.114]$$

where τ is the time after sunrise when Q_o is a maximum, and A and B are constants. The values of the constants are $A = 4.74$ and $B = 1.12 \times 10^{-3}$.

15.12.35 Density effects

In some conditions the density of the air may be assumed to be a function of temperature and humidity, but not of pressure. This is the Boussinesq approximation. Then the buoyancy of the air, which is a function of the ratio of the density difference to the mean density, may be assumed to be a function of the ratio of the temperature difference to the mean absolute temperature. The Boussinesq approximation is generally valid when the ratio of the density difference to the mean density is 0.1 or less.

15.12.36 Meteorological variables

The meteorological variables of particular interest here in respect of gas dispersion are (1) wind speed and (2) stability category. Other variables that are of interest in hazard assessment generally include: (1) minimum temperature, (2) maximum temperature, (3) maximum wind speed and (4) maximum rainfall. The behaviour of the variable may be expressed in terms of the values averaged over a fixed period such as an hour, day, month or year.

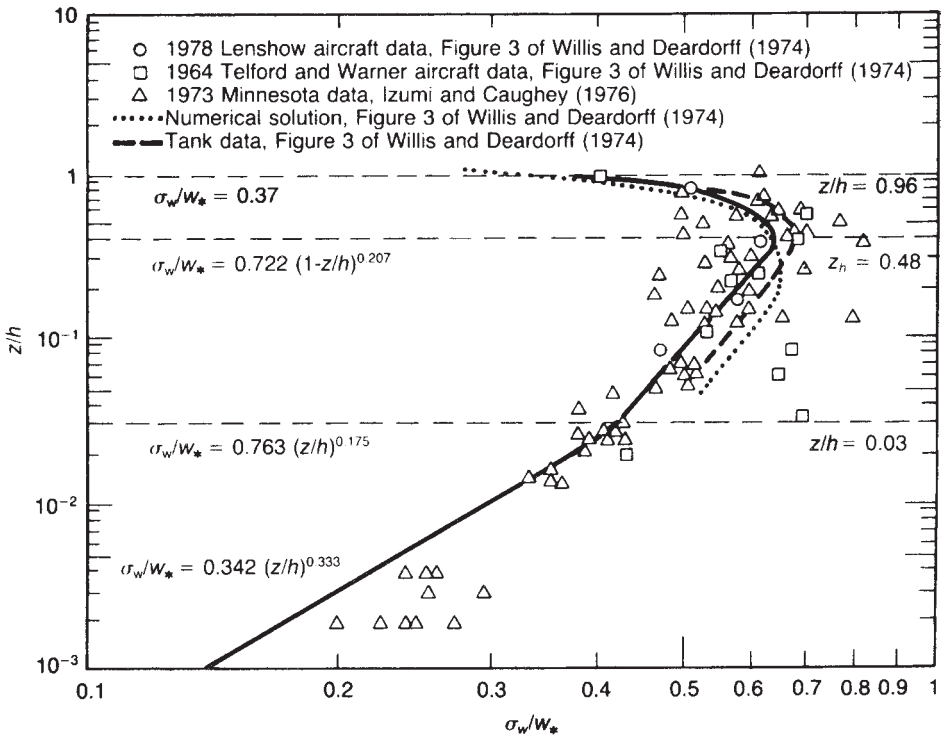


Figure 15.48 *Relation between the standard deviations of the vertical velocity fluctuations σ_w and the convective velocity w_* for fully convective conditions (Irwin, 1979a; reproduced by permission)*

15.12.37 Meteorology of the United Kingdom

Information on the meteorological characteristics of the United Kingdom is available from the Meteorological Office. A simple introduction is given in *Climate of the British Isles* (Meteorological Office, 1994), which contains a number of maps of wind speed, minimum temperature, maximum temperature, rainfall and snowfall. An account of British meteorology with particular reference to the hazards that it poses is given in *Environmental Hazards in the British Isles* (Perry, 1981).

15.13 Topography

In dispersion work the ground surface that may be regarded as the base case is flat grassland such as that on Salisbury Plain, where much of the early work on dispersion was done. Terrain may differ from this base case in a number of ways, particularly in respect of:

(1) surface roughness;
(2) urban areas;
(3) coastal zones and sea;
(4) complex terrain;
(5) buildings and obstructions.

General aspects of such terrain are considered briefly in this section. Models for dispersion over such terrain are treated in Section 15.14 and the corresponding dispersion parameters in Section 15.16.

15.13.1 Surface roughness

There is a wide range of surface roughness that is of interest in dispersion work. At one extreme ice has a very low value of the roughness length, while trees or urban areas have a very high value. There are also considerable differences in the roughness length of fields. For example, that for short grass is much lower than for wheat. The surface roughness of sea is affected by the wave motion and requires special treatment.

15.13.2 Urban areas

Accounts of dispersion over urban areas have been given by Gifford (1976a,b) and by S.R. Hanna (1976). An urban area acts as a heat island. It also constitutes terrain with a high surface roughness. Over an urban area the principal meteorological features such as wind speed, air and surface temperatures, mixing height and stability, are different from those over rural terrain.

Stable air from the surrounding rural area is modified as it approaches an urban area. Stability near a city tends to be nearly neutral, however stable the rural area may be. Hence the more stable conditions associated with Pasquill categories F and G tend not to occur. An urban area also tends to give increased turbulence. Measurements by Bowne, Ball and Anderson (1968) at Fort Wayne showed that the

intensity of turbulence was some 40% above that of the surrounding area.

15.13.3 Coastal areas and water

Dispersion over coastal areas and water has been described by Gifford (1976a,b) and Lyons (1976). Water in this context includes both sea and lakes, but unless otherwise stated reference here is to sea. Much of the experimental work described by Lyons, however, relates to the Great Lakes, which constitute a feature well suited to the study of coastal area dispersion.

Conditions at the coastline may exhibit extreme variations of wind pattern, temperature and humidity. In fact radical changes of stability and turbulence are the rule. Dispersion under such conditions is much more complex than over flat rural terrain and Lyons places some emphasis on what is not known as well as what is.

In general, turbulence, and hence dispersion, is often less over sea than over land. In particular, this is so when warm air is advected over colder water. On the other hand, when colder, or drier air, is advected over warmer water, strong turbulence can occur. Lyons distinguishes three situations:

(1) dispersion over water;
(2) dispersion over the coastline
    (a) with gradient wind,
    (b) with sea breeze.

The surface of the sea tends to be more uniform than that of land, but sharp differences of water temperature and the sudden discontinuity at the coastline introduce complications not met on a land mass.

For dispersion over water, in unstable and neutral conditions, with a flow of cold air over warmer water, intensity of turbulence is high. Water spouts and steam devils, may occur. In stable conditions, with a flow of warm air over colder water, intense inversion can occur. Conditions in which conduction of heat from the air to the water below is a dominant influence on the over-water air temperature are termed by Lyons 'conduction inversions'.

For dispersion in a gradient onshore flow, without a sea breeze, the low level flow crossing the coastline reacts to the changes in surface roughness, temperature and evaporation. This creates internal boundary layers for momentum, heat and water vapour that do not necessarily coincide.

Two conditions are of particular interest: plume trapping and fumigation. As described above, plume trapping occurs when a plume is trapped beneath an elevated inversion, while fumigation is of several types, that of interest here being coastline fumigation in which cold sea air is heated rapidly by the ground.

Sometimes a sea breeze blows onshore at low level while the gradient wind above blows in the opposite direction. This condition tends to occur in very light gradient winds, strong insolation and daytime air temperatures greater than the sea surface temperature. The condition, known as a 'sea breeze', is therefore something different from a simple onshore wind. The sea breeze inflow layer has a depth of some 100–1000 m, typically 500 m, and the peak wind speed is about 7 m/s.

Dispersion in a sea breeze is often regarded as the least favourable condition for dispersion of pollutants from a source near the coastline, in that the breeze will tend to blow these back on shore. In practice, along shore air movements, wind shear and other effects can cause appreciable dispersion. The effects of sea breeze tend to be varied.

Over the sea, most of the meteorological parameters, and their diurnal variation, tend to differ from those over land. The stability categories required to classify stability are different, as are the roughness length and friction velocity, and the mixed layer height.

15.13.4 Complex terrain

An account of dispersion over complex terrain has been given by Egan (1976) and Gifford (1976a,b). Urban and industrial development often occurs at sites that have some special geographical feature, such as along rivers, in valleys, or at the base of mountains beside a lake or the sea or at the end of a plain. Thus complex terrain is likely to be encountered quite frequently. The type of terrain principally discussed by Egan is mountainous areas.

In complex terrain there are a number of effects that tend to increase dispersion. One is wind shear due to the variation of wind speed and wind direction with height. Another is distortion of the plume.

There are significant distortions of flow in complex terrain. Flow separation, which occurs when the streamlines no longer follow the shape of an obstacle, may take place. Separation tends to be less severe for flow around an isolated three-dimensional object such as a hill than for flow normal to an object that is effectively two-dimensional such as a ridge. Separation is more pronounced for unstable or neutral conditions than for stable conditions, which tend to suppress it.

The difference between complex and level terrain in respect of stability is most marked for stable conditions. Stable stratification is liable to produce shearing motions and thus to promote turbulence. The effect of the terrain is less pronounced for unstable and neutral conditions.

Air flow in stable stratified conditions has been the subject of considerable work, since the phenomenon constitutes a hazard to aircraft, but this work tends to concentrate on the two-dimensional aspects, and there is less work available on three-dimensional stratified flow.

In valleys there tend to be local variations of wind direction and velocity. Typically there are upslope winds during the day and downslope winds at night. Two issues in air pollution in complex terrain are the impingement of a plume from an elevated source on the ground and episodes of high pollution in stagnant regions.

15.13.5 Buildings and obstructions

Dispersion at buildings and other obstructions has been described by Halitsky (1968), Gifford (1976a,b) and S.R. Hanna, Briggs and Hosker (1982). The presence of buildings or other obstructions in the path of the gas cloud has a marked influence on its flow and dispersion. Buildings act as obstacles to the flow of gas. They also give rise to flow distortions with local pressure and velocity fluctuations.

In considering the effect of a building in the near field, therefore, there is a distinction to be made between its influence on a release from a source some distance upwind and its influence on one from a source at a point near the building such as on its roof or in its lee. In the far field the influence of a number of buildings may often be treated in terms of their effect on the surface roughness.

Diagrams and photographs showing the flow patterns around buildings have been given by a number of authors, including Halitsky (1968), Hosker (1979) and D.J. Wilson (1979a). The flow pattern for conditions where the wind is perpendicular to the upwind face of a rectangular building are shown in Figure 15.49. This shows several important features. There is a roof cavity at the front edge of the building. Above this cavity, starting at about its maximum height, is a high turbulence layer boundary and a roof wake boundary. In the lee of the building there is a wake cavity.

15.14 Dispersion Modelling

There are a number of different approaches to the modelling of dispersion. These include:

(1) gradient transfer models;
(2) statistical models;
(3) similarity models;
(4) top hat, box and slab models.

These are now described in turn.

15.14.1 Diffusion equation

The fundamental equation for diffusion of a gas, in rectangular coordinates, is

$$\frac{d\chi}{dt} + u\frac{d\chi}{dx} + v\frac{d\chi}{dy} + w\frac{d\chi}{dz} = K_x\frac{d^2\chi}{dx^2} + K_y\frac{d^2\chi}{dy^2} + K_z\frac{d^2\chi}{dz^2} \qquad [15.14.1]$$

where x, y, z are the rectangular coordinates (m), K_x, K_y, K_z are the diffusion coefficients in the x, y, z directions (m^2/s), t is the time (s), u, v, w are the mean wind speeds in the x, y, z directions (m/s) and χ is the concentration (kg/m^3). The coordinate system is shown in Figure 15.50(a).

If the wind speed in the y and z directions is zero ($v = w = 0$) and the diffusion coefficients are the same in each direction ($K_x = K_y = K_z = K$), Equation 15.14.1 becomes

$$\frac{d\chi}{dt} + u\frac{d\chi}{dx} = K\left(\frac{d^2\chi}{dx^2} + \frac{d^2\chi}{dy^2} + \frac{d^2\chi}{dz^2}\right) \qquad [15.14.2]$$

where x, y, z are the distances in the downwind, crosswind and vertical directions (m) and K is the diffusion coefficient (m^2/s).

If the wind speed in the x direction is also zero ($u = 0$), Equation 15.14.2 reduces to

$$\frac{d\chi}{dt} = K\left(\frac{d^2\chi}{dx^2} + \frac{d^2\chi}{dy^2} + \frac{d^2\chi}{dz^2}\right) \qquad [15.14.3]$$

The corresponding equation for a symmetrical spherical system is

$$\frac{d\chi}{dt} = \frac{K}{r^2}\frac{d}{dr}\left(r^2\frac{d\chi}{dr}\right) \qquad [15.14.4]$$

with

$$r^2 = x^2 + y^2 + z^2 \qquad [15.14.5]$$

where r is the radial coordinate (m).

Analytical solutions of the above equations with a constant value of the diffusion coefficient K have been given by O.F.T. Roberts (1923) as described below.

15.14.2 Gradient transfer models

Gradient transfer models, or K models, are solutions of the diffusion equation. Although the assumption of a constant diffusion, or turbulent exchange, coefficient was made in the early work, it is known that this is an oversimplification that

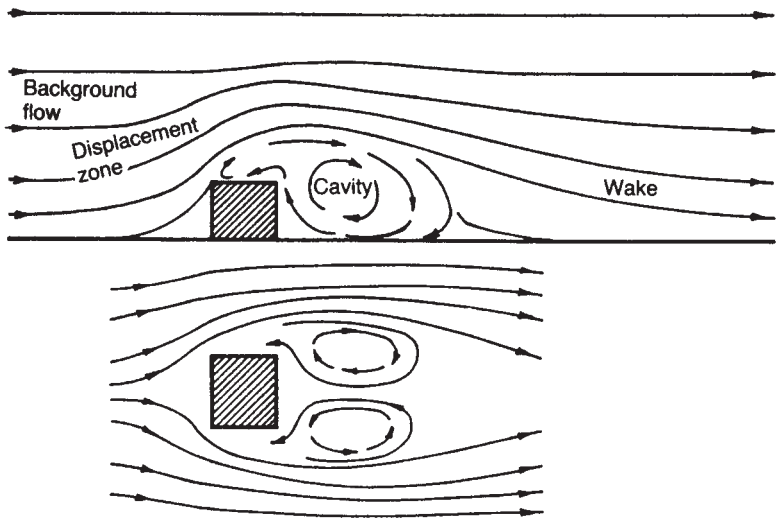


Figure 15.49 *Simplified flow pattern around a sharp-edged building (Pasquill and Smith, 1983; after Halitsky, 1968; reproduced by permission)*

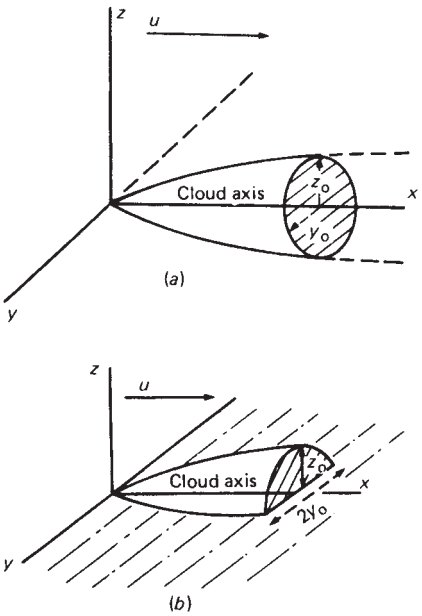


Figure 15.50 *Coordinates for dispersion equations: (a) elevated source; (b) ground level source*

yields unsatisfactory results. The approach now adopted is to solve the diffusion equation using relationships for the variation of the individual exchange coefficients K_x, K_y and K_z and for the wind speed u. If the form of these relations is amenable, an analytical solution may be obtained, but usually it is necessary to resort to numerical solution.

15.14.3 Statistical models

Analytical solution of the diffusion equation with a constant exchange coefficient K shows that the concentration profiles obtained for releases such as plumes and puffs are Gaussian in form and may therefore be characterized by standard deviations for dispersion, or dispersion coefficients, σ_x, σ_y and σ_z.

The statistical properties of turbulence may be described in terms of quantities such as the Lagrangian time scale and the autocorrelation function. Moreover, using Taylor's theorem the autocorrelation function may be related to the standard deviations of the wind velocity fluctuations, which in turn may be related to the standard deviations for dispersion.

In the model developed by O.G. Sutton (1953) the diffusion parameter C is related to the dispersion coefficients, while in the Pasquill–Gifford model these dispersion coefficients are used directly. These models therefore possess a statistical basis.

15.14.4 Similarity models

Another approach is the use of dimensional analysis to derive similarity, or self-similar, models. Typically, the basis of a similarity model is an equation, derived from dimensional analysis, for the rate of growth of some characteristic dimension of the cloud, such as the height of a plume. This part of the model, however, gives no information about the concentration distribution within the cloud; for this, additional relations are required, which tend to have an empirical basis.

Similarity models are used particularly for buoyant plumes and momentum jets, but such models also exist for plumes and puffs. The similarity approach is also used to obtain relationships for the dispersion coefficients used in the Gaussian models.

15.14.5 Similarity criteria

There are a number of dimensionless groups which constitute criteria of similarity and which are particularly relevant in dispersion work.

The Reynolds number Re is defined as

$$\mathrm{Re} = \frac{ul\rho}{\mu} \qquad [15.14.6a]$$

$$= \frac{ul}{\nu} \qquad [15.14.6b]$$

where l is a characteristic dimension, u is the velocity of the fluid, μ its viscosity, ν its kinematic viscosity and ρ its density. The Reynolds number is the ratio of the inertial forces to the viscous forces and is a criterion for similarity of flow regime. The Peclet number Pe is

$$\mathrm{Pe} = \frac{ul}{D} \qquad [15.14.7]$$

where D is the diffusion coefficient, or diffusivity.

The Peclet number characterizes the ratio of the inertial forces to the diffusivity and is a criterion for the relative importance in mass transfer of bulk transport and diffusive transport.

The Schmidt number Sc is

$$\mathrm{Sc} = \frac{\mu/\rho}{D} = \frac{\mu}{\rho D} \qquad [15.14.8a]$$

$$= \frac{\nu}{D} \qquad [15.14.8b]$$

It is thus the ratio of the Peclet and Reynolds numbers

$$\mathrm{Sc} = \mathrm{Pe}/\mathrm{Re} \qquad [15.14.9]$$

The Schmidt number is the ratio of the kinematic viscosity to the diffusivity and is a criterion for similarity of mass transfer. The Prandtl number Pr is

$$\mathrm{Pr} = \frac{\mu/\rho}{k/c_\rho\rho} = \frac{c_\mathrm{p}\mu}{k} \qquad [15.14.10]$$

where c_p is the specific heat of the fluid and k its thermal conductivity. The Prandtl number is the ratio of the kinematic viscosity to the thermal diffusivity and is a criterion of similarity for heat transfer, corresponding to the Schmidt number for mass transfer.

The Froude number Fr is

$$\mathrm{Fr} = \frac{u}{(gl)^{1/2}} \qquad [15.14.11]$$

It is the ratio of the inertial force to the gravitational force and is a criterion of similarity where buoyancy is significant.

15.14.6 Top hat, box and slab models

Another family of models is that comprising the models referred to as top hat, box and slab models.

A top hat model has an essentially flat top, although vertical mixing takes place at the top surface. The cloud can therefore be considered to have a defined height.

In a box model the cloud is treated as a vertical cylinder that at a given instant has a uniform concentration throughout. A source cloud is defined, which may or may not contain some initial entrained air, and the subsequent development of the cloud is described in terms of its advection and of the entrainment of air into it. In a slab model the concentration in the cloud is a function of distance. However, the terms 'box' and 'slab' are not invariably used in this way. A model in which the concentration in the cloud varies with distance is sometimes called a box model.

The principal application of box and slab models in hazard assessment is to the dispersion of dense gases. Such box models are usually solved numerically, although some analytical solutions have been obtained.

The term 'box model' is also applied to models of passive gas dispersion in a defined zone such as an urban area. The zone is modelled as a perfectly mixed box in which the concentration is uniform. This use of the term appears to antedate its application to dense gas dispersion.

The box model has also served as a starting point for the development of models in which the concentration profile is based on similarity.

15.14.7 Physical modelling

Complex situations that are not readily handled by the various types of model described may be investigated by physical modelling using wind tunnels or water flumes. In such a study it is necessary to establish similarity of conditions. This means that the relevant dimensionless similarity criteria should ideally have identical values in the scenario investigated and in the tunnel experiments. Since in some cases several such groups may be involved, it may not be possible to achieve complete identity of all the groups.

15.15 Passive Dispersion

The dispersion of gases with neutral buoyancy, or passive dispersion, has been the subject of a very large volume of work. Some of the early work was oriented to gas warfare, but latterly air pollution has been the principal concern.

Neutral buoyancy is commonly due to the low concentration of the contaminant gas released, although it may also occur if the density of the gas is close to that of air. The neutral buoyancy condition may be negated if the gas release causes a large change in the temperature of the resultant cloud.

Hazard assessment utilizes, but has not greatly contributed to, work on neutral density gas dispersion. Most of the work has therefore been concerned with dispersion of continuous releases from an elevated point source, as represented by an industrial chimney stack. The two other main types of release studied that are of industrial relevance are continuous and instantaneous point source releases at ground level. There is some work on continuous line sources at ground level, relevant to gas warfare, but also to industrial area releases.

Early work on the subject includes that of G.I. Taylor (1915) and O.F.T. Roberts (1923). The models that are most widely used, however, are those of O.G. Sutton (1953) and of Pasquill (1961, 1962a) and the Pasquill–Gifford model (Pasquill, 1961; Gifford, 1961).

In this section an account is given of experimental studies and empirical features of passive dispersion. Section 15.16 describes passive dispersion models and Sections 15.17–15.19 describe dispersion over particular surfaces, dispersion in particular conditions and dispersion parameters, respectively.

15.15.1 Experimental studies

Passive gas dispersion has been the subject of a large volume of experimental work. Accounts of this work include those by Islitzer and Slade (1968), Slade (1968), Colder (1972), Gifford (1976a,b) and A.E. Mitchell (1982). Some experimental studies of such dispersion are listed in Table 15.27. More detailed listings are given by Islitzer and Slade (1968).

Work on passive gas dispersion on Salisbury Plain at Porton Down established what may be regarded as a base case for terrain. The terrain at Porton is open country with some clumps of trees. The work at Porton provides the experimental background for the work of O.G. Sutton (1953) and Pasquill (1962a).

An important set of experiments carried out on this terrain are those used by Pasquill to derive parameters in his dispersion models. In this work there was a continuous release from a point source at ground level, the distance to which concentration measurements were made was 800 m and the sampling period was 10 min.

15.15.2 Empirical features

Experiments on passive gas dispersion indicate several important empirical features. The fundamental features have been described by O.G. Sutton (1953).

One of the most important features is that, for both continuous and instantaneous releases from a point source at ground level, the concentration profiles are Gaussian. Another basic feature is that for both types of release the spread of the measured concentration increases as the sampling period increases. It is observed that the plume from a continuous point source release tends to meander and that the dispersion due to turbulence is augmented by that due to this meandering.

The concentration downwind of a continuous or instantaneous point source at ground level is found to vary according to the strength of the source, provided that the latter does not itself cause appreciable convection. For a continuous point source the concentration is also inversely proportional to the mean wind speed.

The concentration on the centre line of a continuous point source is

$$\chi \propto x^{-1.76} \qquad [15.15.1]$$

and that on the centre plane of a continuous infinite line crosswind source is

$$\chi \propto x^{-1.09} \qquad [15.15.2]$$

This information on the variation of concentration with distance has played an important role in guiding the development of dispersion models.

Table 15.27 *Some experimental studies of passive gas dispersion*

Location	*Experiment*	*Reference*
A Continuous elevated sources[a]		
Porton Down	Porton	J.S. Hay and Pasquill (1957)
Idaho Falls, ID	National Reactor Testing Station (NRTS)	Islitzer (1961)
Richland, WA	Hanford	Hilst and Simpson (1958); Nickola (1977)
Harwell	Harwell (BEPO)	Stewart *et al.* (1954)
Long Island, NY	Brookhaven National Laboratory (BNL)	Gartrell *et al.* (1964); Carpenter *et al.* (1971)
Tennessee Valley, TN	Tennessee Valley Authority (TVA)	
B Continuous ground level releases[a]		
Porton Down	Porton	J.S. Hay and Pasquill (1959)
Cardington	Cardington	Pasquill (1962)
O'Neill, NE	Prairie Grass	Cramer (1957); Lettau and Davidson (1957); Barad (1958); Islitzer and Slade (1964)
Round Hill	Round Hill	Islitzer and Slade (1964)
Richland, WA	Green Glow	Barad and Fuquay (1962); Fuquay, Simpson and Hinds (1964)
Cape Kennedy, FL	Ocean Breeze	Haugen and Fuquay (1963); Haugen and Taylor (1963)
Vandenberg AFB, CA	Dry Gulch	Haugen and Fuquay (1963); Haugen and Taylor (1963)
Idaho Falls, ID	NRTS	Islitzer and Dumbault (1963)
C Instantaneous ground level releases[b]		
Porton Downs	Porton	F.B. Smith and Hay (1961)
Edwards AFB, CA	Sand Storm	J.H. Taylor (1965)
Agesta and Studsvik, Sweden		Högström (1964)
Dugway Proving Grounds, Utah	Dugway	Cramer *et al.* (1964)
Point Arguello, CA	Naval Missile Facility (NMF)	T.B. Smith *et al.* (1964)
Idaho Falls, ID	NRTS	Islitzer and Markee (1964)
Dallas, TX	Cedar Hill	McCready, Smith and Wolf (1961)
D Releases in urban areas		
Worcester, MA		Yersel, Goble and Morrill (1983)
St Louis, MO		McElroy and Pooler (1968)
E Releases over water		
Cameron, LA		Dabberdt *et al.* (1982)
Pismo Beach, CA		Dabberdt *et al.* (1982)

[a] Many of these experiments are also described by Slade (1968).
[b] These releases are more accurately described as 'quasi-instantaneous'.

15.16 Passive Dispersion: Models

Some principal models for passive dispersion are:

(1) Roberts model;
(2) Sutton model;
(3) Pasquill model;
(4) Pasquill–Gifford model.

An account is now given of each of these models in turn.

15.16.1 Roberts model

The fundamental diffusion equation has been given in Section 15.14. Solutions of this equation have been given by O.F.T. Roberts (1923), who analysed the behaviour of smoke from various types of release. The following treatment is based on Roberts' work and on modifications of it derived by O.G. Sutton (1953).

For dispersion from an instantaneous point source under windless conditions Equation 15.14.4 is applicable. The

relevant boundary conditions are:

$$\chi \to 0 \quad \text{as} \quad t \to 0, \quad r > 0 \qquad [15.16.1a]$$

$$\chi \to 0 \qquad t \to \infty \qquad [15.16.1b]$$

The continuity condition is

$$\int_{-\infty}^{\infty} \iint \chi \, dx \, dy \, dz = Q^* \qquad [15.16.2]$$

where Q^* is the mass released instantaneously (kg). The solution of Equation 15.14.4 is then

$$\chi(r,t) = \frac{Q^*}{8(\pi K t)^{3/2}} \exp\left(-\frac{r^2}{4Kt}\right) \qquad [15.16.3a]$$

$$\chi(x,y,z,t) = \frac{Q^*}{8(\pi K t)^{3/2}} \exp\left[-\frac{(x^2+y^2+z^2)}{4Kt}\right] \qquad [15.16.3b]$$

Equation 15.16.3b may also be applied to an instantaneous point source with a wind speed in the x direction by measuring the coordinates from an origin moving with the cloud at the mean wind speed.

For dispersion from a continuous point source under windless conditions, Equations 15.16.3, with Equation 15.14.5, may be integrated with respect to time to give

$$\chi(r,t) = \frac{Q}{(4\pi K r)} \operatorname{erfc}\left[\frac{r}{2(Kt)^{1/2}}\right] \qquad [15.16.4a]$$

$$\chi(x,y,z,t) = \frac{Q}{4\pi K (x^2+y^2+z^2)^{1/2}} \operatorname{erfc}\left[\frac{(x^2+y^2+z^2)^{1/2}}{2(Kt)^{1/2}}\right] \qquad [15.16.4b]$$

where Q is the continuous mass rate of release (kg/s). At steady state, Equation 15.16.4 becomes

$$\chi(r) = \frac{Q}{4\pi K r} \qquad [15.16.5a]$$

$$\chi(x,y,z) = \frac{Q}{4\pi K (x^2+y^2+z^2)^{1/2}} \qquad [15.16.5b]$$

Equation 15.16.5b may be applied to a continuous point source with a wind speed u in the x direction by a transformation of coordinates. This gives

$$\chi(x,y,z) = \frac{Q}{4\pi K (x^2+y^2+z^2)^{1/2}} \times \exp\left\{-\frac{u}{2K}\left[(x^2+y^2+z^2)^{1/2} - x\right]\right\} \qquad [15.16.6]$$

If the concentrations considered are those not too far from the x axis so that

$$\frac{y^2+x^2}{x^2} \ll 1 \qquad [15.16.7]$$

then for all but the lightest winds Equation 15.16.6 becomes

$$\chi(x,y,z) = \frac{Q}{4\pi K x} \exp\left[-\frac{u}{4Kx}(y^2+z^2)\right] \qquad [15.16.8]$$

For dispersion from a continuous infinite line source at right angles to the wind direction, Equation 15.16.6 can be modified and integrated in the y direction to give

$$\chi(x,z) = \frac{Q'}{2\pi K} \exp\left(\frac{ux}{2K}\right) K_o\left[\frac{u(x^2+z^2)^{1/2}}{2K}\right] \qquad [15.16.9]$$

where Q' is the continuous mass rate of release per unit length (kg/ms). K_o is the modified Bessel function of the second kind. Provided the term $u(x^2+z^2)^{1/2}/2K$ is sufficiently large, Equation 15.16.9 may be approximated by

$$\chi(x,z) = \frac{Q'}{(2\pi K x)^{1/2}} \exp\left(-\frac{uz^2}{4Kx}\right) \qquad [15.16.10]$$

For the case where dispersion is anisotropic the equations are as follows. For an instantaneous point source:

$$\chi(x,y,z,t) = \frac{Q'}{8(\pi t)^{3/2}(K_x K_y K_z)^{1/2}} \times \exp\left[-\frac{1}{4t}\left(\frac{x^2}{K_x}+\frac{y^2}{K_y}+\frac{z^2}{K_z}\right)\right] \qquad [15.16.11]$$

For a continuous point source

$$\chi(x,y,z) = \frac{Q}{4\pi x (K_x K_y)^{1/2}} \exp\left[-\frac{u}{4x}\left(\frac{y^2}{K_y}+\frac{z^2}{K_z}\right)\right] \qquad [15.16.12]$$

For a continuous infinite line crosswind source:

$$\chi(x,z) = \frac{Q'}{(2\pi x K_z x)^{1/2}} \exp\left(-\frac{uz^2}{4K_z x}\right) \qquad [15.16.13]$$

The equations derived so far apply to an elevated source dispersion which is unaffected by the ground. If the source is on the surface, the ground forms an impervious boundary. The coordinate system is shown in Figure 15.50(b). The effect of the ground is to double the concentration. Thus Equations 15.16.11–15.16.13 become: for an instantaneous point source

$$\chi(x,y,z,t) = \frac{Q^*}{4(\pi t)^{3/2}(K_x K_y K_z)^{1/2}} \times \exp\left[-\frac{1}{4t}\left(\frac{x^2}{K_x}+\frac{y^2}{K_y}+\frac{z^2}{K_z}\right)\right] \qquad [15.16.14]$$

for a continuous point source

$$\chi(x,y,z) = \frac{Q}{2\pi x (K_y K_z)^{1/2}} \exp\left[-\frac{u}{4x}\left(\frac{y^2}{K_y}+\frac{z^2}{K_z}\right)\right] \qquad [15.16.15]$$

and for a continuous infinite line crosswind source

$$\chi(x,z) = \frac{2Q'}{(2\pi x K_z x)^{1/2}} \exp\left(-\frac{uz^2}{4K_z x}\right) \qquad [15.16.16]$$

An intermediate situation occurs where the ground forms an impervious barrier to the material from an elevated

source such as a chimney or high vent. For this case it can be shown that for a continuous elevated point source

$$\chi(x,y,z) = \frac{Q}{4\pi Kx}\exp\left(-\frac{uy^2}{4Kx}\right) \times \left\{\exp\left[-\frac{u}{4Kx}(z-h)^2 + \exp\left[-\frac{u}{4Kx}(z+h)^2\right]\right\} \quad [15.16.17]$$

where h is the height of the source (m). Equation 15.16.17 reduces to Equation 15.16.15 if h is set equal to zero.

The equations for continuous sources are steady-state equations and therefore apply only to fully established plumes. The concentrations given by the equations are applicable only if the duration of the release t is equal to or greater than the ratio of the distance x at the location of interest to the wind speed u ($t \geq x/u$).

Equations 15.16.14–15.16.17 give the concentrations at all distances from the source. For practical purposes it is convenient to define some boundaries for the cloud. The convention adopted is to take the cloud boundaries y_o and z_o as a fixed proportion, usually one-tenth, of the maximum concentration at distance x. If y_o and z_o are the semi-lateral and semi-vertical dimensions of the cloud, as shown in Figure 15.50, then from Equation 15.16.15, for a continuous point source

$$y_o = \left(\frac{4}{u}K_y x \ln 10\right)^{1/2} \quad [15.16.18]$$

$$z_o = \left(\frac{4}{u}K_z x \ln 10\right)^{1/2} \quad [15.16.19]$$

Hence

$$y_o \propto z_o \propto x^{1/2} \quad [15.16.20]$$

The ground level concentration on the centre line ($y = z = 0$) of a continuous point source is given by Equation 15.16.15 as

$$\chi(x) = \frac{Q}{2\pi x(K_x K_y)^{1/2}} \quad [15.16.21]$$

and that on the centre plane ($z = 0$) of a continuous infinite line crosswind source is given by Equation 15.16.16 as

$$\chi(x) = \frac{2Q'}{(2\pi K_z x)^{1/2}} \quad [15.16.22]$$

The visible outline of the cloud is not determined as simply, but depends on the theory of opacity.

An important implication of Equations 15.16.15 and 15.16.16 is that for Equation 15.16.15 at a fixed distance x from the source the concentration distribution in both the crosswind and the vertical directions is a Gaussian, or normal, distribution. Similarly, Equation 15.16.16 gives a concentration distribution that is Gaussian in the vertical direction. This feature is important in the further development of dispersion equations, as described below.

It can also be seen from Equations 15.16.15 and 15.16.16 that the ground level concentration downwind along the centre line, or axis, of a continuous point source ($y = z = 0$), is

$$\chi \propto x^{-1} \quad [15.16.23]$$

and that the ground level concentration downwind over the centre plane of a continuous infinite line crosswind source is

$$\chi \propto x^{-1/2} \quad [15.16.24]$$

Comparison of relations 15.16.23 and 15.16.24 with the relations 15.15.1 and 15.15.2 obtained by experiment shows that this model is unsatisfactory.

Thus, it is not appropriate to model dispersion in the atmosphere using the constant Fickian diffusion coefficient K. Nevertheless, the equations given form the basis for most subsequent developments in work on passive dispersion.

15.16.2 Sutton model

The failure of the simple Fickian diffusion model has prompted the search for more realistic models of dispersion. The first model considered here is that of O.G. Sutton (1953).

The basic equation derived by Sutton for an instantaneous point source at ground level is

$$\chi(x,y,z,t) = \frac{2Q^*}{\pi^{3/2}C_x C_y C_z (ut)^{3/2(2-n)}} \times \exp\left[-(ut)^{n-2}\left(\frac{x^2}{C_x^2} + \frac{y^2}{C_y^2} + \frac{z^2}{C_z^2}\right)\right] \quad [15.16.25]$$

where C_x, C_y, C_z are diffusion parameters in the downwind, crosswind and vertical (x, y, z) directions ($m^{1/2n}$), n is the diffusion index, and the coordinates x, y, z are measured from an origin moving with the cloud at the mean wind speed u.

Equation 15.16.25 is related to Equation 15.16.14 in the Roberts model and becomes identical with it by putting

$$n = 1 \quad [15.16.26a]$$

$$C^2 = \frac{4K}{u} \quad [15.16.26b]$$

The equation for a continuous point source at ground level is

$$\chi(x,y,z) = \frac{2Q}{\pi C_y C_z u x^{2-n}}\exp\left[-x^{n-2}\left(\frac{y^2}{C_y^2} + \frac{z^2}{C_z^2}\right)\right] \quad [15.16.27]$$

and that for a continuous infinite line crosswind source at ground level is

$$\chi(x,y,z) = \frac{2Q'}{\pi C_z u x^{1/2(2-n)}} \times \exp\left[-x^{n-2}\left(\frac{y^2}{C_z^2}\right)\right] \quad [15.16.28]$$

The equation for a continuous elevated point source is

$$\chi(x,y,z) = \frac{Q}{\pi C_y C_z u x^{(2-n)}}\exp\left(-x^{n-2}\frac{y^2}{C_y^2}\right) \times \left\{\exp\left[-x^{n-2}\frac{(z-H)^2}{C_z^2} + \exp\left[-x^{n-2}\frac{(z+H)^{1/2}}{C_z^2}\right]\right\} \quad [15.16.29]$$

where H is the height of the source (m).

As mentioned above, the concentrations given by the equations for continuous sources are applicable only if the duration t of the release is equal to or greater than the ratio of the distance x to the wind speed u ($t \geq x/u$).

Equations 15.16.27–15.16.29 correspond to Equations 15.16.15–15.16.17 in the Roberts model. Equations 15.16.25 and 15.16.27–15.16.29 are frequently written with the assumption of isotropic conditions, for which the diffusion parameters are

$$C_x = C_y = C_z = C \qquad [15.16.30]$$

The index n and the generalized diffusion parameter C are meteorological constants. Values of these constants have been discussed in detail by O.G. Sutton (1947, 1953). The index n is a function of the stability conditions. The limiting values of n are zero and unity under conditions of very high and very low turbulence, respectively. In average conditions n has a value of approximately 1/4. The value of the generalized diffusion parameter C is a function of the height above ground and of the stability conditions. Values of these parameters given by Sutton are shown in Table 15.28. Further values are given in Section 15.28.

15.16.3 Pasquill model

Another general system of dispersion equations has been derived by Pasquill (1961, 1962a, 1965) and is generally referred to as the Pasquill model. The basis of the system is a modification of Equation 15.16.29 for a continuous point source at ground level:

$$C_o = \frac{2.8 \times 10^{-3} Q}{udh\theta} \qquad [15.16.31]$$

where C_o is the ground level concentration on the axis of the plume (units/m^3), d is the distance in the downwind direction (km), h is the vertical spread (m), Q is the mass rate of release (units/min), u is the mean wind speed (m/s) and θ is the lateral spread (degrees).

Equation 15.16.31 is based on Equation 15.16.29, generalized to allow for relatively slow changes of wind direction. The lateral spread θ and the vertical spread h define an envelope at the edge of which concentrations are one-tenth of the axial or ground level values, respectively, that is, the envelope of the cloud defined by the usual convention.

Equation 15.16.31 is for a continuous source and hence, as mentioned above, the concentrations given are applicable only if the duration of the release is equal to or greater than the ratio of the distance to the wind speed u ($t > d \times 10^3/u$).

Table 15.28 *Meteorological parameters for Sutton model*[a] *(after O.G. Sutton, 1947)*

Source height (m)	n	C_y (m$^{1/8}$)		C_y (m$^{1/8}$)
0	0.25	0.21		0.12
10	0.25	0.21		0.12
25	0.25		0.12	
30	0.25		0.10	
75	0.25		0.09	
100	0.25		0.07	

[a] Values are for small lapse rate and wind speed of 5 m/s.

For the lateral spread θ used in Equation 15.16.31, Pasquill recommends that if suitable data are available the following relations should be used:

$$\theta = 4.3\sigma_\theta \qquad [15.16.32]$$

with

$$\sigma_\theta \approx \sigma_y/x \qquad [15.16.33]$$

where x is the downwind distance (m), σ_y is the standard deviation of concentration in the crosswind direction (m) and σ_θ is the standard deviation of wind direction (degrees).

If such data are not available, he suggests that approximate estimates of θ for a long release, lasting 1 h or more, may be made from wind direction traces using the following rules:

$d =$ 0.1 km
$\theta =$ difference between maximum and minimum trace over period of release
$d =$ 100 km
$\theta =$ difference between maximum and minimum '15-min averages' of wind direction

For a short release, lasting a few minutes, Pasquill gives the estimates of θ shown in Table 15.29.

The vertical spread used in Equation 15.16.31 increases with distance d at a rate that depends on the extent of vertical mixing. If, however, vertical convection is suppressed by an isothermal or inversion layer, the height of this layer sets a limit to h. Ultimately, the concentration between the ground and the layer becomes uniform.

For the vertical spread h, Pasquill recommends that if suitable data are available the following relation be used:

$$h = 2150 d\sigma_\phi \qquad [15.16.34]$$

where σ_ϕ is the standard deviation of the wind inclination (rad) and ϕ is the wind inclination (rad).

If such data are not available, he suggests that tentative estimates of h be made using the graph shown in Figure 15.51. These estimates are applicable only to open country. The curves given in the graph are fitted by the approximate equations given in Table 15.29. The limits of the equations are as shown in the table.

In the stable conditions of a clear night with very light winds (<2 m/s), and thus under conditions conducive to sharp ground frost or heavy dew, the vertical spread h may be even less than that given for stability category F.

In unstable conditions, the vertical spread h may be estimated by the methods just described only until it reaches a value h' equal to the estimated vertical extent of convection which will occur at some distance d'. Under these conditions at the distance d' there is a concentration profile with a limiting vertical spread h'. For approximate work it may be assumed that over a further interval d', and therefore at a distance $2d'$, a uniform concentration develops. Thus for distances greater than $2d'$ the vertical spread h used in Equation 15.16.31 may be taken as $2h'$.

The wind speed u and the wind direction used in Equation 15.16.31 at distances 0.1 and 1 km are the usual

Table 15.29 *Meteorological parameters for Pasquill model (after Pasquill, 1961)*

A Lateral spread for a short release, θ

Pasquill stability category	*Lateral spread θ* (deg)	
	$d = 0.1$ km	$d = 100$ km
A	60	(20)
B	45	(20)
C	30	10
D	20	10
E	(15)	(5)
F	(10)	(5)

B Vertical spread, h

Pasquill's values, shown in Figure 15.51, are fitted by the following approximate equations:

A	$\log_{10} h = 2.95 + 2.19 \log_{10} d + 0.723(\log_{10} d)^2$	$0.1 < d < 2$
B	$\log_{10} h = 2.36 + 1.05 \log_{10} d + 0.067(\log_{10} d)^2$	$0.1 < \mathrm{d} < 10$
C	$\log_{10} h = 2.14 + 0.919 \log_{10} d - 0.017(\log_{10} d)^2$	$0.1 < d < 30$
D1	$\log_{10} h = 1.85 + 0.835 \log_{10} d - 0.0097(\log_{10} d)^2$	$0.1 < d < 100$
D2	$\log_{10} h = 1.83 + 0.754 \log_{10} d - 0.087(\log_{10} d)^2$	$0.1 < d < 100$
E	$\log_{10} h = 1.66 + 0.670 \log_{10} d - 0.100(\log_{10} d)^2$	$0.1 < d < 100$
F	$\log_{10} h = 1.48 + 0.656 \log_{10} d - 0.122(\log_{10} d)^2$	$0.1 < d < 100$

surface values. At distances of 10 and 100 km, the wind speed and direction used are the averages of the surface and geostrophic values, but in addition the latter is backed (i.e. moved anticlockwise) by 10°.

For an elevated source, Equation 15.16.31 is modified by the stack correction factor F_1 to give

$$C_c = \frac{2.8 \times 10^{-3} \times QF_1}{udh\theta} \qquad [15.16.35]$$

with

$$F_1 = \exp\left[-2.303\left(\frac{H}{h}\right)^2\right] \qquad [15.16.36]$$

where C_c is the ground level concentration on the axis of the plume for the elevated source (units/m^3), and H is the height of the stack (m).

Equations 15.16.31 and 15.16.35 give the concentration on the axis of the plume. Other concentrations may be calculated by multiplying the values given by these equations by the off-axis correction factor F_2:

$$F_2 = \exp\left[-2.303\left(\frac{2\alpha}{\theta}\right)^2\right] \qquad [15.16.37]$$

where α is the deviation from the axis (degrees). Thus Equation 15.16.31 becomes

$$C = \frac{2.8 \times 10^{-3} QF_1F_2}{udh\theta} \qquad [15.16.38]$$

where C is the ground level concentration (units/m^3).

The parameters θ and h are functions of distance and should be determined for the distance d at which the concentration C_o or C_c is to be calculated. It is convenient to tabulate and plot base values of C_o or C_c at distances d of 0.1, 1, 10 and 100 km and to obtain other values by interpolation. lines of equal concentration, or isopleths, may be calculated from Equation 15.16.38 by fixing the concentration C and determining the corresponding distance d and deviation α.

As an illustration of the application of the method the example described by Pasquill (1961, 1962a) is given. The problem is the determination of the ground level concentration for a prolonged release from continuous point sources (1) at ground level and (2) above ground level. A statement of the problem is given in Section A of Table 15.30. The results of the calculations for the solution of the problem are shown in Section B of the table and in Figures 15.52 and 15.53.

It may be noted that, although Equation 15.16.31 is for a continuous point source, so that the concentration given is applicable only if the duration t is equal to or greater than the ratio of the distance to the wind speed ($t \geq d \times 10^3/u$), it nevertheless gives the correct value of the total dosage for the total mass released, and may therefore be used to calculate dosage for a nearly instantaneous point source.

Graphical solutions of the Pasquill model have been presented by Bryant (1964 UKAEA AHSB(RP) R42).

15.16.4 Pasquill–Gifford model

An alternative form of the Sutton equations has been presented by Pasquill (1961, 1962a) and values of the dispersion coefficients used in this model have been obtained by Gifford (1961). This alternative form is often referred to as the Pasquill–Gifford model, as described below.

In this formulation, use is made of the relations given by O.G. Sutton (1953, p. 286):

$$\sigma_x^2 = \frac{C^2}{2}(ut)^{2-n} \qquad [15.16.39]$$

Similar expressions apply for σ_y and σ_z where σ_x, σ_y and σ_z are the standard deviations, or dispersion coefficients, in

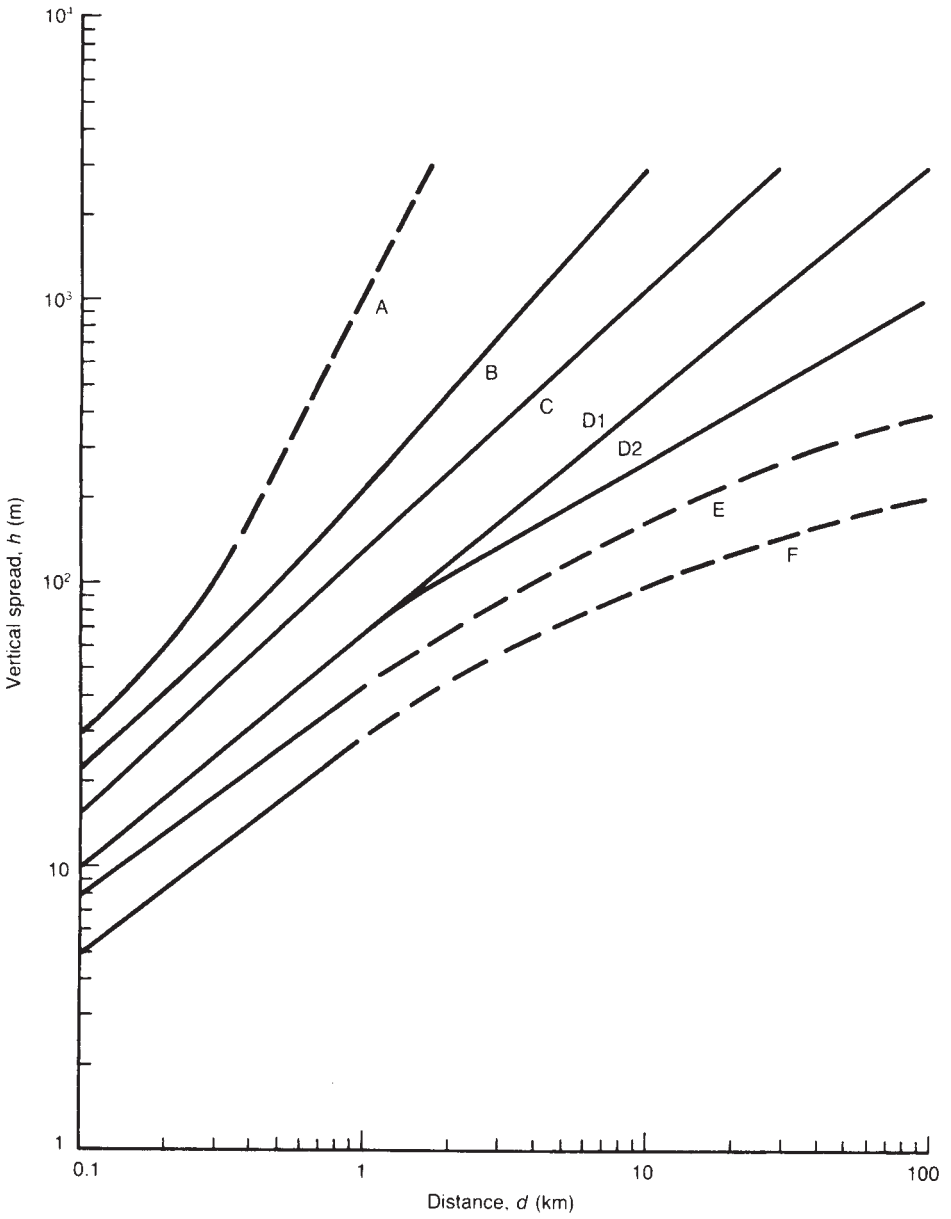


Figure 15.51 *Vertical spread h for Pasquill equation (Pasquill, 1961) (Courtesy of HM Stationery Office)*

the downwind, crosswind and vertical (x, y, z) directions (m).

The equation for an instantaneous point source at ground level then becomes

$$\chi(x,y,z,t) = \frac{2Q^*}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z} \times \exp\left[-\frac{1}{2}\left(\frac{x^2}{\sigma_x^2}+\frac{y^2}{\sigma_y^2}+\frac{z^2}{\sigma_z^2}\right)\right] \quad [15.16.40a]$$

where the coordinates x, y, z are measured from an origin moving with the cloud at the mean wind speed u. Alternatively, if the coordinates are measured from the point of release

$$\chi(x,y,z,t) = \frac{2Q^*}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z} \times \exp\left\{-\frac{1}{2}\left[\frac{(x-ut)^2}{\sigma_x^2}+\frac{y^2}{\sigma_y^2}+\frac{z^2}{\sigma_z^2}\right]\right\} \quad [15.16.40b]$$

Table 15.30 *Illustrative example of the application of the Pasquill equation for a prolonged release from continuous point sources at and above ground level (after Pasquill, 1961)*

A Problem

Effective height of elevated source H	100 m
Stability category	B–C
Surface wind speed	4 m/s
Surface wind direction	275°
Geostrophic wind direction	8 m/s
Geostrophic wind speed	325°
Vertical extent of convection	1000 m
Source strength	1 unit/min

B Solution

Distance at which vertical spread h equals vertical extent of convection h': 5.5 km

1 Ground level source

Distance d, km	0.1	1	10	100
Effective wind speed u, m/s	4	4	6	6
Effective wind direction, deg	275	275	290	290
Lateral spread θ[a], deg	120	93	67	40
Effective vertical spread h, m	20	170	2000	2000
Concentration along axis C_0, units/m^3	2.9×10^{-6}	4.4×10^{-8}	3.5×10^{-10}	5.8×10^{-11}

2 Elevated source

Arbitrary values of h/H	1/2	2/3	4/5	1	$1\frac{1}{2}$	2	4
Corresponding values of:							
Effective vertical spread h, m	50	67	80	100	150	200	400
Distance d, km	0.28	0.37	0.46	0.59	0.86	1.15	2.20
Concentration along axis C_0, $\times 10^{-10}$ units/m^3	4600	2700	1800	1200	580	330	82
Stack correction factor F_1	10^{-4}	5.6×10^{-3}	0.027	0.10	0.36	0.56	0.87
Corrected concentration C_c, $\times 10^{-10}$ units/m^3	0.46	15	49	120	210	185	71

[a] These values are obtained from wind direction traces.

The equation for a continuous point source at ground level becomes

$$\chi(x,y,z) = \frac{Q}{\pi\sigma_y\sigma_z u} \times \exp\left[-\frac{1}{2}\left(\frac{y^2}{\sigma_y^2}+\frac{z^2}{\sigma_z^2}\right)\right] \qquad [15.16.41]$$

The equation for a continuous infinite line crosswind source at ground level becomes

$$\chi(x,z) = \frac{2Q'}{(2\pi)^{1/2}\sigma_z u} \times \exp\left(-\frac{1}{2}\frac{z^2}{\sigma_z^2}\right) \qquad [15.16.42]$$

The equation for a continuous elevated point source becomes

$$\chi(x,y,z) = \frac{Q}{2\pi\sigma_y\sigma_z u}\exp\left(-\frac{y^2}{2\sigma_y^2}\right) \times \left\{\exp\left[-\frac{(z-h)^2}{2\sigma_z^2}+\exp\left[-\frac{(z+h)^2}{2\sigma_z^2}\right]\right]\right\} \qquad [15.16.43]$$

As mentioned above, the concentrations given by the equations for continuous sources are applicable only if the duration t of the release is equal to or greater than the ratio of the distance x to the wind speed u ($t \geq x/u$). Equations 15.16.40–15.16.43 correspond to Equations 15.16.25 and 15.16.27–15.16.29, respectively. As stated above, Equations 15.16.40–15.16.43 are often referred to as the Pasquill–Gifford model. Pasquill (1962a, p. 190) himself states that an equation of the particular form of Equation 15.16.40a appears to have been first given by Frenkiel (1952), but that Equations 15.16.41 and 15.16.42 are implicit in the equations given by O.G. Sutton (1947). D.B. Turner (1970, p. 3) states that values of the dispersion coefficient σ have been obtained by Cramer and co-workers (Cramer, Record and Vaughan, 1958; Cramer, 1959a,b) and by Gifford (1961), the tetter's values for continuous releases being converted from Pasquill's values of angular spread and height for similar releases, which were described above. It is the latter that are recommended for use by D.B. Turner (1970, p. 3).

Again the dispersion coefficients σ_x, σ_y and σ_z are meteorological constants. Different values are used for

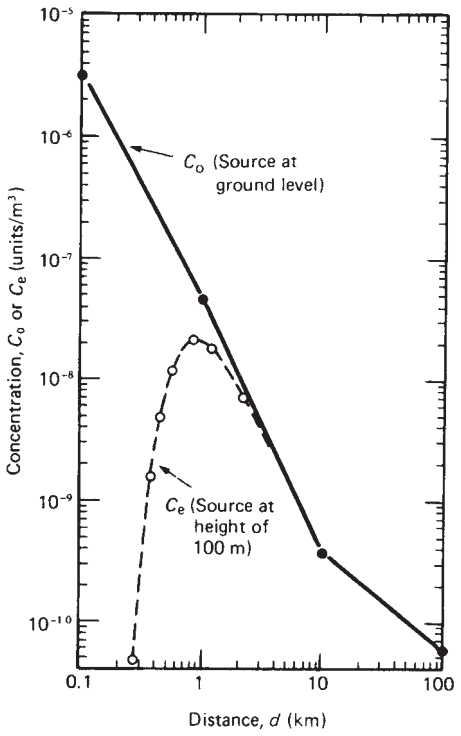


Figure 15.52 *Illustrative example of Pasquill equation: ground level concentrations along axis for a prolonged release from continuous point sources at and above ground level (Pasquill, 1961) (Courtesy of HM Stationery Office)*

Equations 15.16.40 for an instantaneous point source and for Equations 15.16.41–15.16.43 for a continuous source. The values of the dispersion coefficients σ_y and σ_z for a continuous point source have been discussed in detail by D.B. Turner (1970, p. 7). The values given by the latter, which are based on the work of Gifford (1961), are shown in Figures 15.54(a) and (b). These estimates are applicable only to open country. The curves in the graph are fitted by the approximate equations given in Table 15.31, Section A. The limits of the equations are as shown in the table.

The values given for the dispersion coefficients are best estimates (D.B. Turner, 1970, p. 7). In unstable and in stable conditions several-fold errors may occur in the estimate of σ_z. There are some circumstances, however, when the estimate of σ_z may be expected to be within a factor of 2. These are (1) for all stability conditions up to a few hundred metres, (2) for neutral or moderately stable conditions at distances up to a few kilometres and (3) for unstable conditions in the lower 1000 m of the atmosphere with a marked inversion above at distances up to 10 km or more. The uncertainty in the estimation of σ_y is, in general, less than that in the estimation of σ_z. Equations 15.16.41 and 15.16.43 are applicable only for time periods up to about 10 min. For time periods exceeding 10 min the concentration downwind of the source is somewhat less, due to alteration of the wind direction. This effect can be taken into account for time periods of between 10 min and 2 h using the following approximate relation suggested by D.B. Turner (1970, p. 38):

$$\chi \propto t^{-0.17} \qquad [15.16.44]$$

The concentration from a continuous point source at ground level or at an elevation obtained from Equations

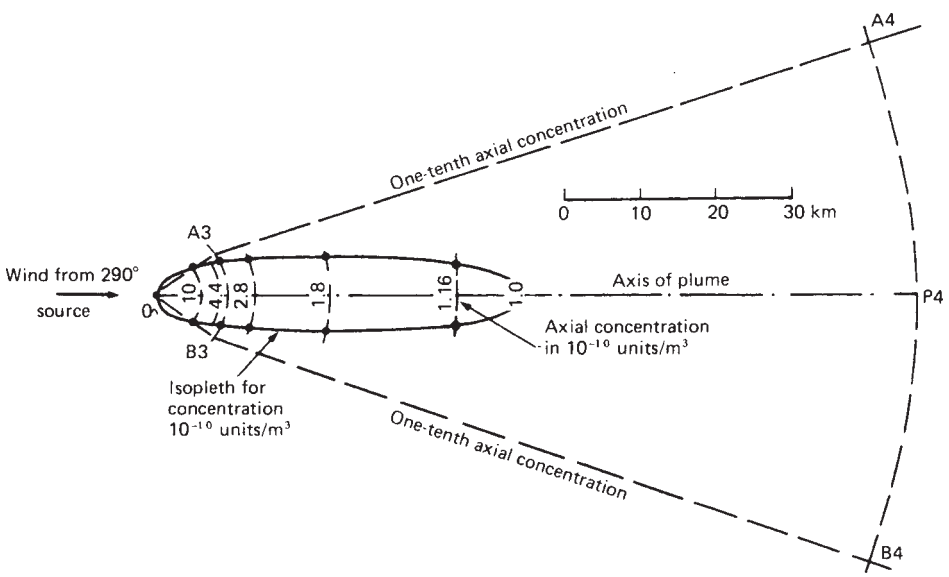


Figure 15.53 *Illustrative example of Pasquill equation: ground level concentration profile for a prolonged release from a continuous point source at ground level (Pasquill, 1961; reproduced by permission of HM Stationery Office)*

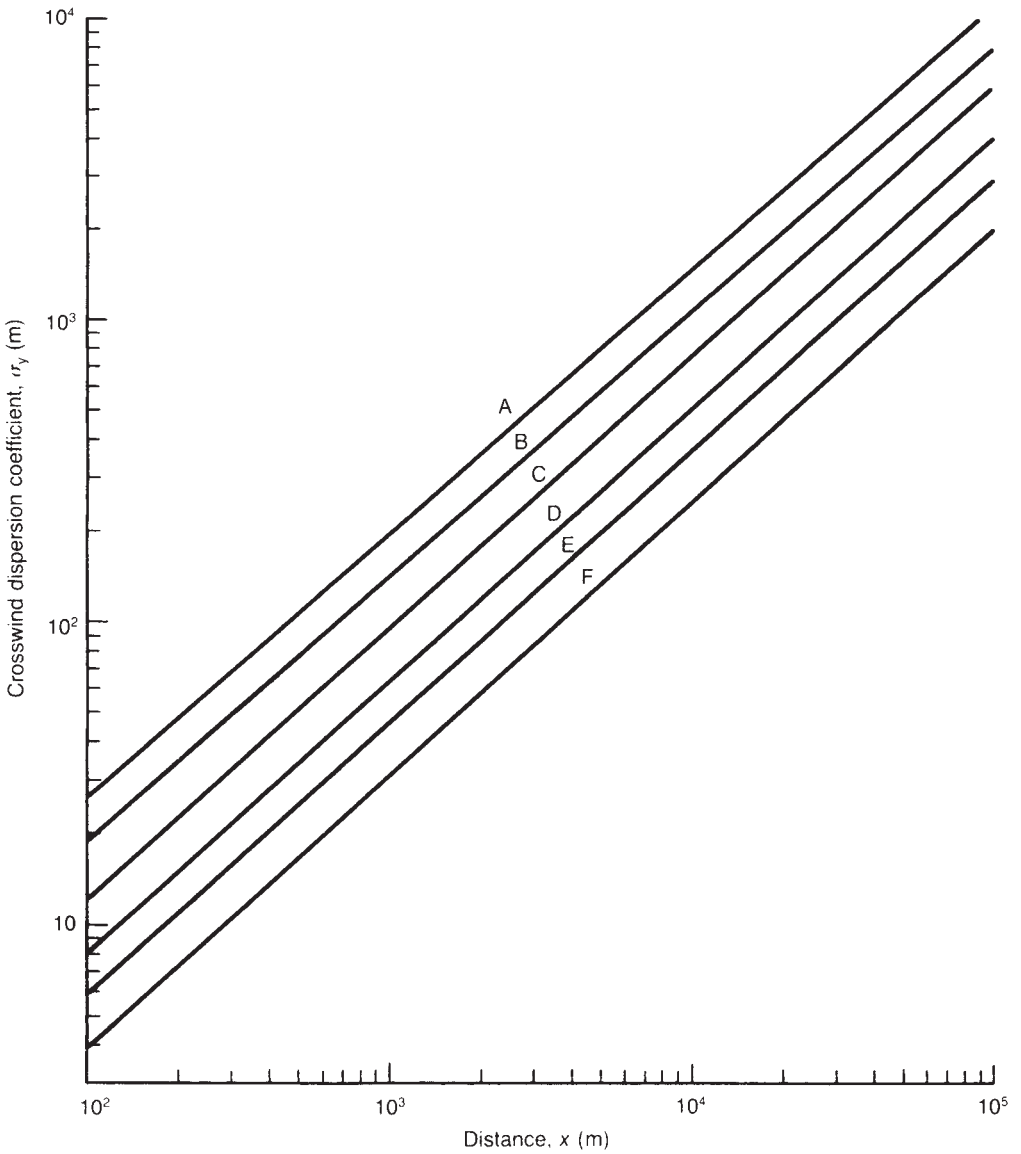


Figure 15.54(a) *Meteorological parameters for Pasquill–Gifford equations for continuous source: crosswind dispersion coefficient σ_y (D.B. Turner, 1970). A–F refer to Pasquill stability categories.*

15.16.41 and 15.16.43, respectively, is often plotted as xu/Q vs distance x.

The values of the dispersion coefficients σ_x, σ_y and σ_z for an instantaneous point source, which differ from those for continuous sources, are discussed by Slade (1968). The values of σ_y and σ_z given by the latter are shown in Table 15.31, Section B. It is normally assumed that σ_x is equal to σ_y.

15.16.5 Effect of sampling period

As described above, if the concentration in a plume is sampled virtually instantaneously, the concentration distribution has a relatively narrow spread, while if the sample is taken over a longer time period, the distribution has a wider spread. D.B. Turner (1970) quotes the following estimates by Meade of the effect of sampling period t on the concentration χ at ground level expressed as the ratio χ/χ_3, where χ_3 is the concentration for a sampling period of 3 min.

t	χ/χ_3
3 min	1.00
15 min	0.82
1 h	0.61
3 h	0.51
24 h	0.36

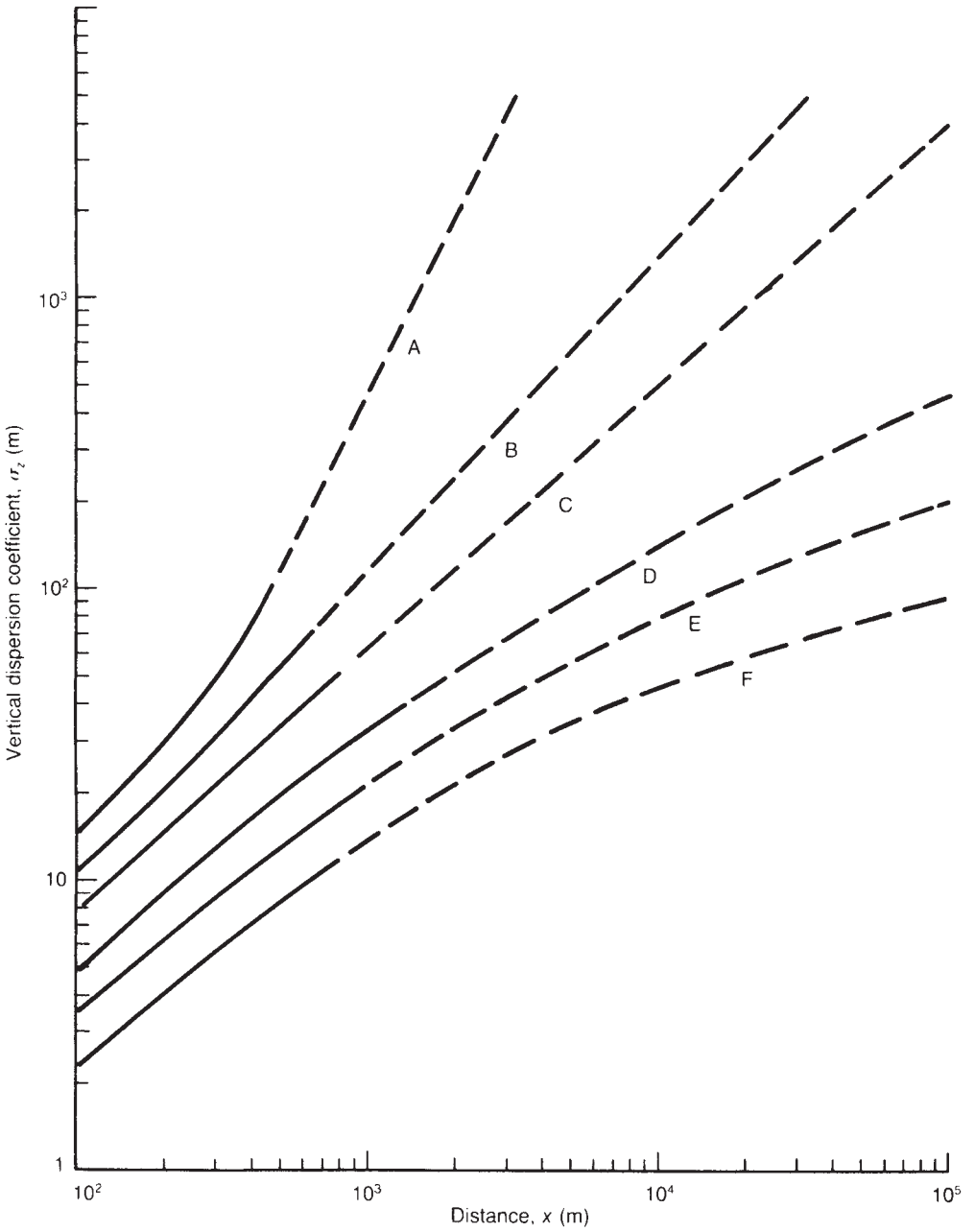


Figure 15.54(b) *Meteorological parameters for Pasquill–Gifford equations for continuous source: vertical dispersion coefficient σ_ζ (D.B. Turner, 1970). A–F refer to Pasquill stability categories*

He suggests that the variation of concentration with sampling period may be taken into account using the following approximate relation:

$$\frac{\chi}{\chi_r} = \left(\frac{t_r}{t}\right)^p \qquad [15.16.45]$$

where t is the sampling period which yields concentration χ, p is an index and subscript r denotes the reference value. Equation 15.16.45 is intended for use for sampling periods up to 2 h using a typical reference sampling period of 10 min. The value of index p is between 0.17 and 0.2.

Table 15.31 *Meteorological parameters for the Pasquill–Gifford model*

A values of σ_v and σ_z for continuous sources given by Turner (1970) are shown in Figure 15.54. Turner's values are fitted by following approximate equations:

Pasquill stability category	*Dispersion Coefficient*		
	σ_y	σ_z (m)	
A	$\sigma_y = 0.493x^{0.88}$	$\sigma_z = 0.087x^{1.10}$	$100 < x < 300$
		$\log_{10}\sigma_z = -1.67 + 0.902\log_{10}x + 0.181(\log_{10}x)^2$	$300 < x < 3000$
B	$\sigma_y = 0.337x^{0.88}$	$\sigma_z = 0.0135x^{0.95}$	$100 < x < 500$
		$\log_{10}\sigma_z = -1.25 + 1.09\log_{10}x + 0.0018(\log_{10}x)^2$	$500 < x < 2 \times 10^4$
C	$\sigma_y = 0.195x^{0.90}$	$\sigma_z = 0.112x^{0.91}$	$100 < x < 10^5$
D	$\sigma_y = 0.128x^{0.90}$	$\sigma_z = 0.093x^{0.85}$	$100 < x < 500$
		$\log_{10}\sigma_z = -1.22 + 1.08\log_{10}x - 0.061(\log_{10}x)^2$	$500 < x < 10^5$
E	$\sigma_y = 0.091x^{0.91}$	$\sigma_z = 0.082x^{0.82}$	$100 < x < 500$
		$\log_{10}\sigma_z = -1.19 + 1.04\log_{10}x - 0.070(\log_{10}x)^2$	$500 < x < 10^5$
F	$\sigma_y = 0.067x^{0.90}$	$\sigma_z = 0.057x^{0.80}$	$100 < x < 500$
		$\log_{10}\sigma_z = 1.91 - 1.37\log_{10}x - 0.119(\log_{10}x)^2$	$500 < x < 10^5$

B Values of σ_y and σ_z for instantaneous sources given by Slade (1968)

Stability condition	$x = 100$ m		$x = 400$ m		*Approximate equation*	
	σ_y (m)	σ_z (m)	σ_y (m)	σ_z (m)		
Unstable	10	15	300	220	$\sigma_y = 0.14x^{0.92}$	$\sigma_z = 0.53x^{0.73}$
Neutral	4	3.8	120	50	$\sigma_y = 0.06x^{0.92}$	$\sigma_z = 0.15x^{0.70}$
Very stable	1.3	0.75	35	7	$\sigma_x = 0.024x^{0.89}$	$\sigma_z = 0.05x^{0.61}$

15.16.6 Plume model characteristics

The Sutton equations for instantaneous and continuous point sources are models of the behaviour of a 'puff' and a 'plume' of gas, respectively. The equations are convenient in form for the calculation of various derived quantities and have been used extensively. Some important characteristics in the plume model of dispersion from a ground level source are (1) the concentration on the axis of the plume and (2) the dimensions of the plume. Again, these quantities are mainly of interest at ground level.

Applying the Sutton model, for a continuous point source at ground level use is made of Equation 15.16.27 with Equation 15.16.30. If the concentration considered is that at ground level $z = 0$, then

$$\chi(x,y,0) = \frac{2Q}{\pi C^2 u x^{2-n}} \exp\left(-x^{n-2}\frac{y^2}{C^2}\right) \qquad [15.16.46]$$

For the ground level concentration χ_{cl} on the axis $y = 0$

$$\chi_{cl} = \chi(x,0,0) = \frac{2Q}{\pi C^2 u x^{2-n}} \qquad [15.16.47]$$

For $n = 0.25$ and $C = 0.14$

$$\chi_{cl} = \frac{32Q}{ux^{1.75}} \qquad [15.16.48]$$

The cloud boundary concentration χ_{cb} may be defined as either one-tenth of the axial concentration χ_{cl} or as the extinction concentration χ_{ex}. For the dimensions of the cloud at ground level the coordinates (x, y) of a point of concentration χ_{cb} are obtained from Equation 15.16.46.

The plume model for dispersion from an elevated source is also relevant. In this case two important characteristics are (1) the maximum concentration on the axis at ground level and (2) the distance at which the maximum ground level concentration occurs.

For a continuous elevated point source, use is made of Equation 15.16.29 with Equation 15.16.30. If the concentration considered is that at ground level on the axis $y = 0$ and $z = 0$, then

$$\chi_{cl} = \chi(x,0,0) = \frac{2Q}{\pi C^2 u x^{2-n}} \exp\left(-x^{n-2}\frac{H^2}{C^2}\right) \qquad [15.16.49]$$

For the maximum ground level concentration χ_{mgl} on the axis the appropriate equation may be shown to be

$$x_{mgl} = \frac{2Q}{e\pi u H^2}\frac{C_z}{C_y} \qquad [15.16.50]$$

where e is the base of natural logarithms.

The distance χ_{mgl} at which the maximum ground level concentration χ_{mgl} occurs may be shown to be given by the equation

$$\chi_{mgl} = \left(\frac{H}{C_z}\right)^{2/(2-n)} \qquad [15.16.51]$$

The corresponding equations based on the Pasquill–Gifford model are as follows. For a continuous point source at ground level use is made of Equation 15.16.41. If the concentration considered is that at ground level $z = 0$, then

$$\chi(x,y,0) = \frac{Q}{\pi\sigma_y\sigma_z u}\exp\left(-\frac{1}{2}\frac{y^2}{\sigma_y^2}\right) \quad [15.16.52]$$

For the ground level concentration on the axis

$$\chi_{cl} = \frac{Q}{\pi\sigma_y\sigma_z u} \quad [15.16.53]$$

For the dimensions of the cloud at ground level, the coordinates (x, y) of a point of concentration χ_{cb} are obtained from Equation 15.16.52.

For a continuous elevated source use is made of Equation 15.16.43. If the concentration considered is that at ground level on the axis $y = z = 0$, then

$$x_{cl} = \frac{Q}{\pi\sigma_y\sigma_z u}\exp\left(-\frac{1}{2}\frac{h^2}{\sigma_z^2}\right) \quad [15.16.54]$$

For the maximum ground level concentration χ_{mgl} on the axis the appropriate equation may be shown to be

$$\chi_{mgl} = \frac{2Q}{e\pi u h^2}\frac{\sigma_z}{\sigma_y} \quad [15.16.55]$$

The distance at which the maximum ground level concentration occurs may be shown to be the point at which

$$\sigma_z = \frac{h}{2^{1/2}} \quad [15.16.56]$$

15.16.7 Puff model characteristics

Some important quantities in the puff model of dispersion from a ground level source are (1) the concentration at the centre of the cloud, (2) the dimensions of the cloud, (3) the maximum distance travelled and (4) the total integrated dosage given by the cloud. These quantities are mainly of interest at ground level.

Applying the Sutton model, for an instantaneous point source at ground level use is made of Equation 15.16.25 with Equation 15.16.30. If the concentration considered is that at ground level $z = 0$, then

$$\chi(x,y,0,t) = \frac{2Q^*}{\pi^{3/2}C^3(ut)^{3/2(2-x)}} \times \exp\left[-(ut)^{x-2}\left(\frac{x^2}{C^2}+\frac{y^2}{C^2}\right)\right] \quad [15.16.57]$$

For the ground level concentration χ_{cc} at the centre of the cloud $x = y = 0$

$$\chi_{cc} = \chi(0,0,0,t) = \frac{2Q^*}{\pi^{3/2}C^3(ut)^{3/2(2-n)}} \quad [15.16.58]$$

For $n = 0.25$ and $C = 0.14$

$$\chi_{cc} = \frac{131Q^*}{(ut)^{2.62}} \quad [15.16.59]$$

For the other quantities mentioned it is necessary to define the cloud. If the definition used is the convention that the concentration χ_{cb} at the cloud boundary is one-tenth of that at the centre, then

$$\frac{\chi_{cb}}{x_{cc}} = 0.1 \quad [15.16.60]$$

Alternatively, the cloud boundary concentration may be defined as some extinction value χ_{ex} at which the concentration is no longer of interest:

$$\chi_{cb} = \chi_{ex} \quad [15.16.61]$$

A typical extinction concentration is the lower flammability limit for a flammable gas.

For the dimensions of the cloud at ground level the cloud radius x is determined by calculating χ_{cc} from Equation 15.16.58, χ_{cb} from Equation 15.16.60 or 15.16.61 and χ from Equation 15.16.57, setting $\chi = \chi_{cb}$.

For the maximum distance travelled by the cloud the group ut is calculated from Equation 15.16.58 with χ_{cc} set equal to χ_{ex}.

The corresponding equations based on the Pasquill–Gifford model are as follows. For an instantaneous point source at ground level use is made of Equation 15.16.40. If the concentration considered is that at ground level $z = 0$, then

$$\chi(x,y,0,t) = \frac{2Q^*}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z} \times \exp\left[-\frac{1}{2}\left(\frac{x^2}{\sigma_x^2}+\frac{y^2}{\sigma_y^2}\right)\right] \quad [15.16.62]$$

For the ground level concentration χ_{cc} at the centre of the cloud $x = y = 0$

$$\chi_{cc} = \frac{2Q^*}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z} \quad [15.16.63]$$

For the dimensions of the cloud at ground level the cloud radius x is determined by calculating χ_{cc} from Equation 15.16.63, χ_{cb} from Equation 15.16.60 or 15.16.61 and χ from Equation 15.16.62, setting $\chi = \chi_{cb}$.

For the maximum distance travelled by the cloud use is made of Equation 15.16.63 with χ_{cc} set equal to χ_{ex}.

15.16.8 Dosage and dosement

The total integrated dosage D_{tid}, or more simply the dosage D, is

$$D = \int_0^\infty \chi\,dt \quad [15.16.64]$$

In the Sutton model for a puff release, the dosage at ground level on the axis may be obtained by integrating Equation 15.16.57 to obtain

$$D(x,0,0) = \frac{2Q^*}{\pi C^2 u(ut)^{2-n}} \quad [15.16.65]$$

In the Pasquill–Gifford model for a puff release, the dosage D at ground level and at ground level on the axis, the appropriate equations may be shown to be, respectively,

$$D(x,y,0) = \frac{Q^*}{\pi\sigma_y\sigma_z u}\exp\left(-\frac{1}{2}\frac{y^2}{\sigma_y^2}\right) \quad [15.16.66a]$$

and

$$D(x,0,0) = \frac{Q^*}{\pi\sigma_y\sigma_z u} \qquad [15.16.66b]$$

For some materials it is necessary to work in terms not of the dosage D as defined by Equation 15.16.64 but of a load, or dosement, defined as

$$L = \int_0^\infty \chi^n \mathrm{d}t \qquad [15.16.67]$$

where n is an index.

For the Pasquill–Gifford model it has been shown by Tsao and Perry (1979) that for a puff release the dosement at ground level is

$$L = \left[\frac{2Q^*}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z}\frac{\pi^{1/2}}{(2\pi)^{1/2}}\right]^n \frac{\sigma_x}{u}\left[1+\mathrm{erf}\left(\frac{n^{1/2}x}{2^{1/2}\sigma_x}\right)\right] \times \exp\left(-n\frac{y^2}{2\sigma_y^2}\right) \qquad [15.16.68]$$

For a plume release the load, or dosement, is obtained from the steady-state concentration and the period of exposure to that concentration.

15.16.9 Virtual sources

In the models just described, it is assumed that the sources are point sources, instantaneous or continuous. If the source is of finite size, it may be necessary to allow for this using the virtual source method. An account of the method has been given by Mecklenburgh (1985).

The need to allow for finite source size may occur, for example, as the result of the instantaneous flashing off of vapour at the source to form a relatively large cloud. A change of surface roughness, and hence of the dispersion parameter, may also require the use of the virtual source method.

Mecklenburgh treats the determination of the ground level concentration at the centre of the cloud formed from an instantaneous release. For this he utilizes Equation 15.16.63 rewritten in the form

$$\sigma_x\sigma_y\sigma_z = \frac{2V}{(2\pi)^{3/2}C} \qquad [15.16.69]$$

where C is the volumetric concentration (v/v) and V is the volume of gas released (m^3), together with the following relationships for the dispersion parameters:

On site:

$\sigma_x = 0.13x$; $\sigma_y = 0.064x^{0.905}$; $\sigma_z = 0.395x^{0.701}$;

$(\sigma_y\sigma_z)^{1/2} = 0.159x^{0.803}$; $(\sigma_x\sigma_y\sigma_z)^{1/3} = 0.149x^{0.869}$

Off site:

$\sigma_x = 0.13x$; $\sigma_y = 0.064x^{0.905}$; $\sigma_z = 0.200x^{0.760}$;

$(\sigma_y\sigma_z)^{1/2} = 0.113x^{0.833}$; $(\sigma_x\sigma_y\sigma_z)^{1/3} = 0.118x^{0.888}$

The equations are for Pasquill stability category D and a surface roughness of 0.1 on site and 1.0 (urban) off site. The method involves the repeated use of Equation 15.16.69, sometimes to determine the group $\sigma_x\sigma_y\sigma_z$ from C and sometimes vice versa.

Consider as an illustration the example given by Mecklenburgh, which is the determination of (1) the concentration of gas at the works boundary and (2) the distance to the lower flammability limit for a release of 8240 m^3 of gas from a point where the distance in the downwind direction between that point and the works boundary is 100 m.

The release gives a cloud of finite size. Equation 15.16.69 is strictly applicable to an instantaneous point source. In order to allow for the finite size of the cloud, the release is assumed to originate from a point source VS1 located at a virtual distance v_1 upwind of the actual release point. Then

$$x_{v1} = v_1 + x_s \qquad [15.16.70]$$

where v_1 is the distance between the virtual and actual sources (m), x_s is the distance between the actual source and the point of interest (m) and x_{v1} is the distance between the virtual source and the point of interest (m). These distances are shown in Figure 15.55(a). The concentration of the cloud at the actual source is taken as pure gas so that $C = 1$ v/v.

Then Equation 15.16.69 with $V = 8240$ m^3 and $C = 1$ v/v yields $(\sigma_x\sigma_y\sigma_z) = 1046$ m^3. The on-site equations for the σ values (with x in these relations equal to v_1) give $v_1 = 129$ m. The virtual source VS1 is thus 129 m upwind of the actual source.

For the concentration at the works boundary, the distance x_{v1} between the virtual source and the boundary is given by Equation 15.16.70 with $x_s = x_b$, so that

$$x_{v1} = v_1 + x_b \qquad [15.16.71]$$

where x_b is the distance between the actual source and the boundary (m). Using the on-site σ equations (with $x = x_{v1}$) yields $(\sigma_x\sigma_y\sigma_z) = 4696 m^3$. Then from Equation 15.16.69 at the boundary $C = 0.223$ v/v.

Across the boundary the surface roughness changes and it is necessary to utilize a second virtual source VS2, determining its distance upwind from conditions at the works boundary. Utilizing again $C = 0.223$ v/v, and hence $(\sigma_x\sigma_y\sigma_z) = 4696 m^3$, but this time using the off-site σ equations (with $x = x_{v2}$), gives $x_{v2} = 365$ m. At the boundary

$$x_{v2} = v_2 + x_b \qquad [15.16.72]$$

where v_2 is the distance between the virtual and actual sources (m). Then, from Equation 15.16.72, $v_2 = 365 - 100 = 265$ m.

For the distance to the lower flammability limit, the distances are shown in Figure 15.55(b). Setting $C = 0.0355$ v/v in Equation 15.16.69 yields $(\sigma_x\sigma_y\sigma_z) = 29{,}475$ m^3. Using the off-site σ equations (with $x = x_{v2}$) gives $x_{v2} = 528$ m. But

$$x_{v2} = v_2 + (x_s - x_b) \qquad [15.16.73]$$

Hence $x_s = 528 - (265 - 100) = 363$ m.

15.16.10 *K*-theory models

An alternative approach to that given in the Sutton, Pasquill and Pasquill–Gifford models is the direct solution of the fundamental diffusion equation in which the dispersion is characterized by the parameter K. As mentioned

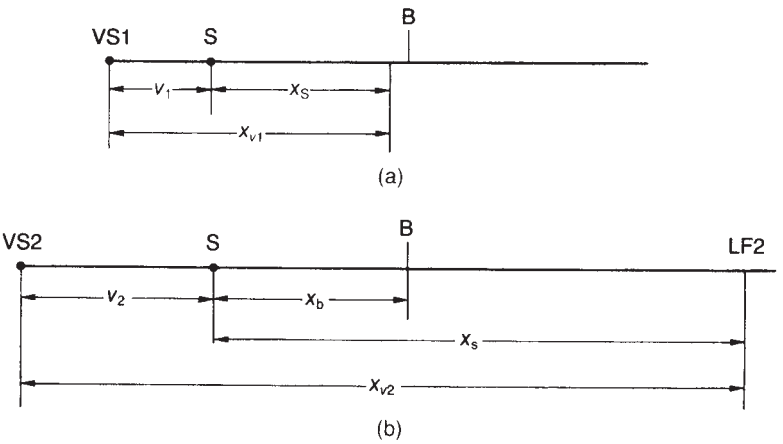


Figure 15.55 *Virtual source method: (a) use of virtual source to allow for finite size of initial cloud; and (b) use of virtual source to allow for change in surface roughness*

above, early work on this, in which K was assumed to be a constant, such as that of Roberts, gave unsatisfactory results, but more modern models, which take into account the variation of K, have been more successful and find use alongside the models already described.

Accounts of such gradient transfer, or K-theory, models are given by S.R. Hanna, Briggs and Hosker (1982), by Runca (1982) and Gryning, van Ulden and Larsen (1983). These if-theory models may be solved analytically, if correlations of a suitable form are available for K. Alternatively, they may be solved numerically.

For analytical solutions the profiles of the wind velocity u and of the parameter K may be expressed as power functions of the height z.

$$u = u_r \left(\frac{z}{z_r}\right)^m \qquad [15.16.74]$$

$$K = K_r \left(\frac{z}{z_r}\right)^n \qquad [15.16.75]$$

where m and n are indices and r denotes the reference value.

A further discussion of values of the parameter K is given in Section 15.24. Various analytical solutions for K-theory models are given by S.R. Hanna, Briggs and Hosker (1982).

Numerical solution of K-theory models tends to involve severe problems both of numerical inaccuracy and numerical instability. The effect of the former is to give a spurious diffusion which arises solely from the numerical method of solution. The effect of the latter is to require very small step lengths and hence very long computation times.

15.16.11 Criterion for type of release

The dispersion situations that occur in practice often correspond not to the puff or the plume model but to the intermediate case. The usual method of dealing with this problem is to calculate dispersion using both models and to take the worst case.

The alternative approach is to select the model on the basis of a suitable criterion. A criterion for deciding whether to use the puff or the plume model, as given by the respective Pasquill–Gifford equations, has been suggested by Eisenberg, Lynch and Breeding (1975). The puff model is preferable if the diffusion in the downwind, or x, direction is large relative to the length of the plume. A measure of diffusion in the downwind direction is the dispersion coefficient σ_x, where this is evaluated using the puff data, and a measure of the length of the plume is ut_e, where u is the wind speed and t_e is the time taken for total discharge or evaporation of the gas. The coefficient σ_x is evaluated using the puff data at $ut_e/2$. The authors suggest the following criteria:

$ut_e < 2\sigma_x$	Use puff model
$ut_e > 5\sigma_x$	Use plume model
$2\sigma_x < ut_e < 5\sigma_x$	Neither model entirely appropriate

In addition, the plume model is undefined for zero wind speeds, is inaccurate for low wind speeds and is therefore not recommended for use at wind speeds of less than 2 m/s. Further criteria for model selection are given in relation to some of the model systems described below.

15.17 Passive Dispersion: Dispersion over Particular Surfaces

15.17.1 Dispersion over urban areas

Accounts of dispersion over and in urban areas have been given by Gifford (1972, 1976a,b), S.R. Hanna (1976) and S.R. Hanna, Briggs and Hosker (1982). There are two rather different types of model that are used to describe the concentration of pollutant in an urban area. The first type is concerned with the overall concentration of the pollutant in the urban atmosphere as required for pollution studies. The second describes the dispersion and gives concentration profiles.

Models used for dispersion over and within an urban area include the Pasquill–Gifford model and K models. D.B. Turner (1964) carried out a study to validate the use of the Pasquill–Gifford model over and within a city, and various other workers have carried out studies to determine the parameters of this model in the urban situation.

Models used for pollution studies include rollback models, statistical correlations and box models. In a rollback model it is assumed that the concentration is proportional

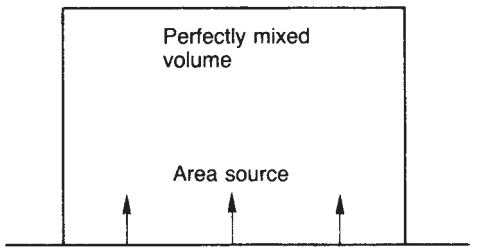


Figure 15.56 *Box model for dispersion over an urban area*

to the strength of the emission source(s). A rollback model therefore focuses attention on the level of emissions. Statistical correlations are used to relate concentrations to meteorological variables such as solar radiation, wind speed and temperature.

In a box model the urban area is treated as a box as shown in Figure 15.56. The basic equation is

$$\Delta x z_i \frac{\mathrm{d}\chi}{\mathrm{d}t} = \Delta x Q_\mathrm{a} + u z_i(\chi_\mathrm{b} - \chi) + \Delta x \frac{\mathrm{d}z_i}{\mathrm{d}t}(\chi_\mathrm{a} - \chi) \qquad [15.17.1]$$

where Q_a is the mass rate of release per unit area, Δx is an incremental length, z_i is the mixed layer height, χ is the concentration, χ_a is the concentration above the mixed layer height and χ_b is the concentration upwind of the city, or background concentration.

With zero background concentration and at steady state, Equation 15.17.1 becomes

$$\chi = \frac{\Delta x Q_\mathrm{a}}{z_i u} \qquad [15.17.2]$$

In some versions of the box model it is assumed that the pollutant is mixed not to the mixed layer height z_i, but to some other height. A correlation for this height is given by S.R. Hanna (1976).

Dispersion coefficients for use in the Pasquill–Gifford model in urban areas are discussed in Section 15.19.

15.17.2 Dispersion over coastal areas and water

An account of the meteorology relevant to coast and sea is given in *Physics of the Marine Atmosphere* (Roll, 1965). The modelling of dispersion over coastal areas and water has been described by Gifford (1976a,b) and by Lyons (1976).

Dispersion over coastal areas and water is most often modelled using the Pasquill–Gifford method. It is pointed out by Lyons that this involves use of the model outside the range of conditions for which it was developed, which were flat rural terrain. Moreover, a further weakness is that the assumption of a steady state is less valid in the more variable wind conditions characteristic of coastal areas. Nevertheless, this is the model that is most widely used. Dispersion coefficients for this model are described in Section 15.19.

Several other models are described by Lyons. These include a model for conduction inversion and one for shoreline fumigation based on a modification of the nocturnal inversion breakup model of Turner.

15.17.3 Dispersion over complex terrain

A description of the modelling of dispersion over complex terrain has been given by Egan (1976).

A model which has been used for complex terrain is the model of Environmental Research and Technology Inc. (ERT) which is based on the Pasquill–Gifford equation for a release from an elevated continuous point source as given in Equation 15.16.43. The effective stack height h_o is taken as usual as the sum of the actual stack height h and the plume rise Δh. Then an effective plume height, essentially the height of the centre line of the plume, is defined as follows. For a receptor on a hill, the height h_1 of which is lower than the effective stack height h_0, the effective plume height h_p is taken as

$$h_\mathrm{p} = h_0 - h_1/2 \quad h_1 < h_0 \qquad [15.17.3a]$$

whilst for a receptor on a hill height h_2, which is higher than h_0, the expression used for h_p is

$$h_\mathrm{p} = h_0/2 \quad h_2 < h_0 \qquad [15.17.3b]$$

The model has been used for unstable, neutral and stable conditions. For a hill higher than the effective stack height this model is the so-called 'half-height' model.

Flow in complex terrain may be modelled using potential flow theory. Standard cases in potential flow are treated by Lamb (1932) and Milne-Thomson (1938). Two cases relevant to complex terrain are the half circular cylindrical ridge and the hemispherical hill. Potential flow theory may be extended to include diffusion.

Thus the Pasquill–Gifford equation giving the ground level centre line concentration from an elevated point source may be modified to give

$$\chi = \frac{Q}{(\pi\sigma_y\sigma_x z_u)_\mathrm{f}(D_y D_z)} \exp\left[-\frac{(\eta h_0)^2}{2\sigma_{z\mathrm{f}}^2 \zeta^2 D_z^2}\right] \qquad [15.17.4]$$

with

$$D_y = \sigma_y/\sigma_{y\mathrm{f}} \qquad [15.17.5a]$$

$$D_z = \sigma_y/\sigma_{z\mathrm{f}} \qquad [15.17.5b]$$

$$\eta = (h_\mathrm{p} - z)/h_0 \qquad [15.17.6]$$

$$\zeta = (\mathrm{d}\psi/\mathrm{d}h_\mathrm{p})_\mathrm{o}/(\mathrm{d}\psi/\mathrm{d}h_\mathrm{p}) \qquad [15.17.7]$$

where h_p is the local height of the plume, z is the local height of the terrain, ψ is the stream function and subscripts f and o denote flat terrain and effective source height, respectively, ζ is the ratio of the average vertical gradient of the stream function at the effective source height to the gradient at the plume centre line over the surface.

For flat terrain, D_y, D_z, η and ζ are all unity. For two-dimensional flow, as over a ridge, it can be shown that near the surface η and ζ are approximately equal and, assuming that D_y and D_z are also equal to unity, Equation 15.17.4 reduces to Equation 15.16.43. For three-dimensional flow, as over a hill, the parameters η and ζ have the values

$$\eta = h_0/3a \qquad [15.17.8]$$

$$\zeta = 2h_0/3a \qquad [15.17.9]$$

where a is the radius of the hill. Then, again assuming that D_y and D_z are unity, Equation 15.17.4 becomes

$$\chi = \frac{Q}{(\pi\sigma_y\sigma_z u)_\mathrm{f}} \exp\left[-\frac{(h_0/2)^2}{2\sigma_{z\mathrm{f}}^2}\right] \qquad [15.17.10]$$

Comparing Equation 15.17.10 with Equation 15.16.43 it can be seen that the effect of the hill is to give an equivalent source height h_e half the effective source height h_o. Thus Equation 15.17.10 is another form of the 'half-height' equation for complex terrain.

Another approach is physical modelling using wind and water tunnels. As described above, Egan discusses the requirements of similarity in such work. He gives several examples of tunnel studies for complex terrain.

15.17.4 Dispersion at buildings and obstacles

Accounts of models available for dispersion at buildings and obstacles are given by Halitsky (1968), Gifford (1976a,b), Vincent (1977), S.R. Hanna, Briggs and Hosker (1982) and Fackrell (1984a). A review of the aerodynamics of flow around buildings has been given by J.C.R. Hunt (1971).

Treatments of the effect of a building on release from an upwind source are mainly concerned with the case of an elevated source. A rule-of-thumb applicable to this situation is that the plume will rise over the building if the distance from the source to the building is greater than $2h$, where h is the height of the building, and if the height h_s of the source exceeds two-thirds that of the building ($h_s > 2h/3$).

The overall effect of the building is to enhance the dispersion of the plume. D.J. Wilson and Netterville (1978) found that the main effect is to increase the mixing between the roof and ground levels. Around the building itself aerodynamic effects may give high local concentrations.

For groups of buildings or buildings of less regular shape, the flow patterns tend to be complex. It has been shown by Cagnetti (1975) for a reactor site that dispersion may vary markedly for relatively small changes in wind direction. Dispersion from sources close to a building has been modelled more extensively, since this is relevant to the siting of vents and stacks.

Rules for the siting of roof stacks for the case of wind impinging perpendicularly on the face of a rectangular building, as shown in Figure 15.57, have been derived by D.J. Wilson (1979a). For a building with height h, crosswind width w and alongwind length l, he defines a scaling factor R such that

$$R = D_s^{0.67} D_l^{0.33} \qquad [15.17.11]$$

where D_s is the smaller dimension of the height h and the width w, and D_l is the larger of these two. He gives the following correlations for the roof cavity length l_c and height h_c:

$$l_c = 0.9R \qquad [15.17.12]$$

$$h_c = 0.22R \qquad [15.17.13]$$

The upper boundary Z_{II} of the high turbulence layer, which starts near the maximum roof cavity height, is given as

$$\frac{Z_{II}}{R} = 0.27 - 0.1\frac{x}{R} \qquad [15.17.14]$$

and that of the roof wake Z_{III} as

$$\frac{Z_{III}}{R} = 0.28\left(\frac{x}{R}\right)^{1/3} \qquad [15.17.15]$$

where x is the downwind distance.

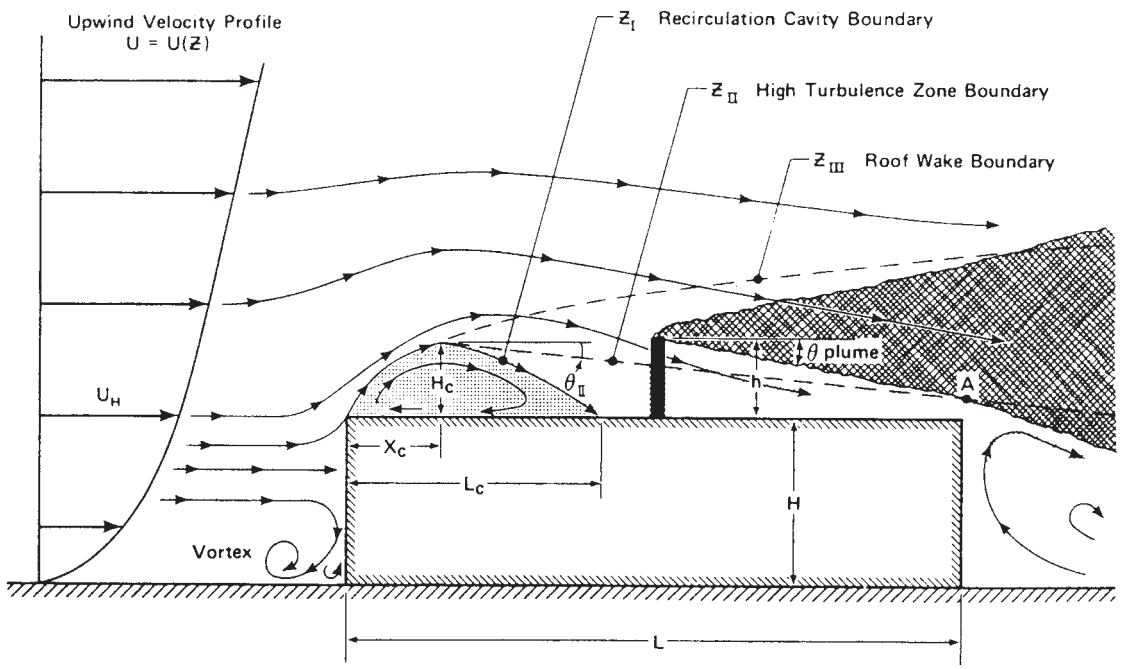


Figure 15.57 *Flow pattern and flow zones around the roof of a square edged building for wind perpendicular to the upwind face (D.J. Wilson, 1979a) H, H_c, L, L_c in the figure are denoted in the text by h, h_c, l, l_c (Courtesy of the American Society of Heating, Refrigerating and Air Conditioning Engineers)*

Wilson suggests that for a roof-mounted stack there is little risk of high pollutant concentrations on the roof if plume clears the boundary of the high turbulence zone and virtually no risk if it clears the roof wake boundary.

Concentrations arising from vents on roofs have been studied in wind tunnel investigations as described by Halitsky (1963, 1968) and D.J. Wilson (1976). Results of such studies are plotted in terms of the dimensionless concentration K defined as

$$K = \frac{\chi A u}{Q} \qquad [15.17.16]$$

where A is a characteristic area, Q is the mass rate of release and u is the wind speed. A typical characteristic area is wh.

Wilson gives the following correlation for the maximum value of the concentration $\chi(x)$ from a roof vent:

$$\frac{\chi(x)}{\chi(0)} = 9.1\frac{w_o A_v}{u x^2} \qquad [15.17.17]$$

where A_v is the vent area, u is the wind speed, w_o is the effluent velocity, x is the downwind distance, and $\chi(0)$ is the effluent concentration.

For a roof stack, a widely used rule-of-thumb is the '2 ½' rule that to avoid downwash problems the stack height should be 2 ½ times the building height. This height will cause the plume to clear the wake cavity.

Another model is that of G.A. Briggs (1974), which applies to a stack located upwind of the building. For such a stack of height h the effective stack height h' is taken as

$$h' = h - h_d \qquad [15.17.18a]$$

with

$$h_d = 2\left(\frac{w_o}{u} - 1.5\right)D_s \qquad [15.17.18b]$$

where D_s is the diameter of the stack outlet, h_d is the downwash, or initial fall in the plume, and w_o is the efflux velocity from the stack. The equation reflects the fact that downwash does not occur if the efflux velocity is maintained above a critical level, generally taken as $w_o/u = 1.5$. The plume is out of the building wake if $h' > (h + 1.5D_s)$. If this condition does not apply, the plume is to some degree affected by the building and if $h_o < 0.5D_s$, it is assumed to be trapped by the wake cavity. Then

$$h_0 = h' \qquad h' > (h + 1.5D_s) \qquad [15.17.19a]$$

$$= 2h' - (h + 1.5D_s) \qquad h' < (h + 1.5D_s) \qquad [15.17.19b]$$

$$= h' - 1.5D_s \qquad h' < h \qquad [15.17.19c]$$

If the plume is trapped it may be treated as a ground level source with initial area D_s^2.

If a plume is entrained into the wake cavity ($h_0 < 0.5D_s$), the dimensionless concentration tends to lie in the range 0.2–2. Given that the plume is entrained into the wake cavity, the precise height of the stack makes little difference to the ground concentrations. There is, however, one particular case where stack height can have a marked effect. If the stack height is about the same height as the wake cavity, the effluent may be carried directly to the ground along the boundary of the cavity.

There have been a number of treatments of the wake cavity in the lee of the building. These include studies of the characteristics of the wake cavity itself and of the concentrations resulting from a release within the cavity. The wake cavity approximates a perfectly mixed zone with the concentration being nearly the same throughout.

A review of models for building-influenced dispersion has been given by Fackrell (1984a). These include: the model of Gifford (1960a), described below; the models of D.B. Turner (1970) and Barker (1982), which involve the use of a virtual source; and those of Ferrara and Cagnetti (1980) and Huber and Snyder (1976), which involve modification of the dispersion coefficients. Both the models that use a virtual source and those that use modified dispersion coefficients correlate the parameters in terms of the building width w and height h.

For the wake cavity itself, Hosker (1979, 1980) has developed the following correlations for the length x_r:

$$\frac{x_r}{h} = \frac{A(w/h)}{1 + B(w/h)} \qquad [15.17.20]$$

with

$$A = -2.0 + 3.7(l/h)^{-1/3} \qquad l/h < 1 \qquad [15.17.21a]$$

$$= 1.75 \qquad l/h > 1 \qquad [15.17.21b]$$

$$B = -0.15 + 0.305(l/h)^{-1/3} \qquad l/h < 1 \qquad [15.17.22a]$$

$$= 0.25 \qquad l/h > 1 \qquad [15.17.22b]$$

As far as concerns the width y_r and height z_r of the cavity, these rarely exceed the building width w and height h, respectively.

For a plume from a source in the wake cavity, the following treatment by Gifford (1960a, 1976a,b) is widely quoted. Following an approach by Fuquay, an atmospheric dilution factor D_A is defined as

$$D_A = Q/\chi \qquad [15.17.23a]$$

$$= \pi\sigma_y\sigma_z u \qquad [15.17.23b]$$

where Q is the mass rate of release, u is the wind speed, and σ_y and σ_z are the downwind and crosswind dispersion coefficients, respectively. But a building dilution factor D_B can be defined as

$$D_B = cAu \qquad [15.17.24]$$

where A is the cross-sectional area of the building normal to the wind ($= wh$) and c is a constant. The total dilution factor D_{tot} is

$$D_{tot} = D_A + D_B \qquad [15.17.25a]$$

$$= (\pi\sigma_y\sigma_z + cA)u \qquad [15.17.25b]$$

$$= Q/\chi \qquad [15.17.25c]$$

Hence

$$\chi = \frac{Q}{(\pi\sigma_y\sigma_z + cA)u} \qquad [15.17.26]$$

Gifford (1960a) has estimated that the value of c lies in the range 0.5–2. He states (Gifford, 1976b) that this estimate, though widely quoted, was purely intuitive and that there are other studies that support a value of about 0.5.

There is evidence that the dispersion coefficients σ_y and σ_z applicable in Equation 15.17.26 differ somewhat from the regular values. The latter tend to give downwind concentrations that vary with distance to a power lying between −1.3 and −1.6, depending on the stability condition. Laboratory studies by Meroney and Yang (1971) and Huber and Snyder (1976) have found this power to be close to −0.8 to a distance of 50 h, although field studies such as those by Dickson, Start and Markee (1969) have given the power as about −1.3.

Gifford (1976b) draws attention to other conditions in which dispersion deviates from that predicted by Equation 15.17.26.

Barry (1964) has reviewed published expressions for the concentration given by pollutants in the lee of a rectangular block of square cross-section (alongwind length = height = S) and found them to be of the general form

$$\bar{C} = k\left(\frac{Q}{S^2 u}\right) \qquad [15.17.27]$$

where $\bar{C}$ is the mean concentration, Q is the source strength, u is the main stream air velocity and k is a constant. The value of the constant k is in the range 0.5–20.

Vincent (1977) has described wind tunnel work on the dispersion of pollutant near buildings, and particularly in building wakes. He uses dimensional analysis to derive the principal parameters governing flow around a rectangular block. These are X/S and

$$H = \frac{u t_d}{S} \qquad [15.17.28]$$

$$\Lambda = \frac{l_f k_f^{1/2}}{Su} \qquad [15.17.29]$$

where k_f is the characteristic energy of free stream turbulence, l_f is the characteristic length scale of free stream turbulence, t_d is the mean residence time of the scalar entities in the wake bubble, X is the length of the wake 'bubble' and Λ is a free stream turbulence parameter. Vincent gives results of wind tunnel work correlating H and X/S against Λ.

For a pollutant source wholly contained within the bubble he derives the relation

$$\bar{C} \approx \frac{QSH}{Vu} \qquad [15.17.30]$$

But

$$V \approx \left(\frac{X}{S}\right) S^3 \qquad [15.17.31]$$

where V is the volume of the wake bubble. Then from Equations 15.17.30 and 15.17.31

$$\bar{C} \approx \left(\frac{Q}{S^2 u}\right)\left(\frac{H}{X/S}\right) \qquad [15.17.32]$$

Vincent points out that Equation 15.17.32 gives for k in Equation 15.17.27 the explicit expression $H/(X/S)$.

Fackrell (1984b) has derived a model for a building wake and for the concentration in this wake and has used wind tunnel experiments to obtain values of the parameters involved. For flow out of the wake

$$F = \alpha S u_h C_w \qquad [15.17.33]$$

where C_w is the average concentration in the near-wake region, F is the flow out of the wake, S is the surface area of the near-wake region, u_h is the wind speed at the building height in undisturbed flow, and α is a flux constant. If there is a source of strength Q in the wake

$$F = Q \qquad [15.17.34]$$

so that from Equations 15.17.33 and 15.17.34

$$Q = \alpha S u_h C_w \qquad [15.17.35]$$

The residence time in the wake is

$$t_r = \frac{V}{\alpha S u_h} \qquad [15.17.36]$$

where t_r is the residence time in the near-wake region and V is the volume of the near-wake region.

Fackrell defines the following dimensionless quantities for the recirculation, or near-wake, region:

$$\beta = \frac{AL_r}{V} \qquad [15.17.37]$$

$$\lambda_r = L_r/h \qquad [15.17.38]$$

$$\tau_r = \frac{u_h t_r}{h} \qquad [15.17.39]$$

$$\chi_w = \frac{C_w u_h A}{Q} \qquad [15.17.40]$$

where A is the frontal area of the building, h is the height of the building, L_r is the length of the recirculation region, β is the wake shape parameter, λ_r is the dimensionless length of the recirculation region, τ_r is the dimensionless residence time in the recirculation region and χ_w is the dimensionless average concentration in the near-wake region.

Then from Equations 15.17.35–15.17.40

$$\chi_w = \frac{A}{\alpha S} \qquad [15.17.41]$$

$$= \beta \frac{\tau_r}{\lambda_r} \qquad [15.17.42]$$

Fackrell reviews the correlations available for λ_r and τ_r. He modifies Equation 15.17.20 of Hosker to give

$$\lambda_r = \frac{1.8(b/h)}{\left[(l/h)^{0.3}\right][1 + 0.24(b/h)]} \quad 0.3 \le \frac{l}{h} \le 3 \qquad [15.17.43]$$

where b is the crosswind breadth of the building. He also obtains

$$\tau_r = \frac{11(b/h)^{1.5}}{\left[1 + 0.6(b/h)^{1.5}\right]} \qquad [15.17.44]$$

15.18 Passive Dispersion: Dispersion in Particular Conditions

The other type of special situation is determined not by the terrain but by the meteorological conditions. Two such situations are considered here:

(1) dispersion in calm conditions;
(2) dispersion in a uniformly mixed layer.

15.18.1 Dispersion in calm conditions

For a small proportion of the time, calm, near windless, conditions prevail. These occur typically on clear nights with frost or heavy dew.

Conditions that are usually classified as Pasquill category F apply in the United Kingdom for some 20% of the time. Included in these are the periods of calm. Beattie (1963 UKAEA AHSB(S) R64) found that the proportion of time for which such conditions apply is about 5–8%. Pasquill actually excluded such conditions from his original categories because dispersion then tends to be irregular.

Beattie has classified such conditions as category G, but does not give the associated dispersion coefficients. It is natural to assume that dispersion is less in G than in F conditions. This assumption is made, for example, in NRC *Regulatory Guide* 1.21. However, there is evidence to show that under G conditions dispersion is ill-defined. Work on such conditions by Sagendorf (1975) has shown that a plume is subject to considerable meander, while work by van der Hoven (1976) has indicated values of dispersion coefficients which correspond to those found across the whole range from A to F conditions.

15.18.2 Dispersion in a uniformly mixed layer

Another meteorological condition that requires special treatment is that of limited mixing fumigation, where there is an elevated inversion which acts as a 'lid'. There is then a well mixed layer of height H in which, beyond a certain distance, the concentration is uniform. For this condition Gifford (1976a) gives the relation

$$\chi = \frac{Q}{(2\pi)^{1/2}\sigma_y u H} \qquad [15.18.1]$$

where, in this case, H is the height of the 'lid', Q is the mass rate of release, u is the wind speed, σ_y is the crosswind dispersion coefficient and χ is the concentration.

15.19 Passive Dispersion: Dispersion Parameters

The dispersion models described contain parameters that are functions of the meteorological variables and of the distance from the source. The Sutton model contains the diffusion parameter C, the Pasquill model the parameters θ and h, and the Pasquill–Gifford models the dispersion coefficient σ. The values of, and correlations for, these parameters proposed by the authors of the models were given in the overall account of these models in Section 15.16. There is, in addition, a considerable literature on these parameters, especially the Pasquill–Gifford dispersion coefficients, ranging from fundamental relations to empirical correlations, which is now described.

In the estimation of dispersion parameters a crucial aspect is the definition of the stability condition. It is argued by Atwater and Londergan (1985) that the representation of stability is of more importance than the correlation of dispersion coefficients with stability. In some cases, there are differences of two or more stability classes between the class based on the meteorology and that inferred from the observed dispersion coefficients and between that inferred from the horizontal dispersion coefficient and that inferred from the vertical dispersion coefficient. The discussion of dispersion parameters is confined initially to those for a plume. Those for a puff are considered in Section 15.19.12.

15.19.1 Fundamental relations

The relations between the turbulent exchange coefficient K, the Sutton diffusion parameter C, the Pasquill parameters θ and h, and the Pasquill–Gifford dispersion coefficient σ may be summarized as follows.

As described above, the condition for the reduction of the Sutton model to the K-model is

$$n = 1 \qquad [15.19.1]$$

$$C_x^2 = \frac{4K_x}{u} \qquad [15.19.2]$$

Similar equations apply relating σ_y to c_y, and σ_z to c_z.

The relation between the Pasquill–Gifford dispersion coefficients and the Sutton diffusion parameters is

$$\sigma_x = \frac{1}{2}C_x^2(ut)^{2-n} \qquad [15.19.3]$$

Similar equations apply relating σ_y to C_y and σ_z to C_z.

The relation between the Pasquill–Gifford dispersion coefficients and the turbulent exchange coefficients is

$$\sigma_x^2 = 2K_x t \qquad [15.19.4]$$

Similar equations apply relating σ_y to K_y and σ_z to K_z.

The Pasquill parameters are related to the Pasquill–Gifford dispersion coefficients as follows:

$$\sigma_y = \sigma_\theta x \qquad [15.19.5]$$

with

$$\sigma_\theta = \frac{\theta}{4.3} \qquad [15.19.6]$$

and

$$\sigma_z = \frac{h}{2.15} \qquad [15.19.7]$$

The constants 4.3 and 2.15 in Equations 15.19.6 and 15.19.7 are the values derived from the Gaussian distribution corresponding to the cloud boundary as defined by convention.

The physical meaning of the dispersion coefficient may be interpreted as follows. For diffusion through a vertical plane in the x direction, the dispersion variance σ_x^2 is the second moment of the concentration with respect to distance x, normalized with respect to concentration:

$$\sigma_x^2 = \frac{\int_{-\infty}^{\infty}\chi^{x^2}\mathrm{d}x}{\int_{-\infty}^{\infty}\chi\,\mathrm{d}x} \qquad [15.19.8]$$

Similar expressions apply to σ_y and σ_z.

Following Csanady (1973), consider the one-dimensional diffusion of a mass Q^*_{ps} of material (kg/m^2) initially concentrated in a thin sheet at $x = 0$, in an instantaneous plane source. Then the diffusion is given by the relationship

$$\frac{\partial \chi}{\partial t} = K_x \frac{\partial^2 \chi}{\partial x^2} \qquad [15.19.9a]$$

The mass released is

$$Q^*_{ps} = \int_{-\infty}^{\infty} \chi \mathrm{d}x \qquad [15.19.9b]$$

and the solution is

$$\chi = \frac{Q^*_{ps}}{2(\pi K_x t)^{1/2}} \exp\left(\frac{-x^2}{4K_x t}\right) \qquad [15.19.9c]$$

Furthermore, it may be shown that

$$Q^*_{ps} = \frac{1}{2K_x t} \int_{-\infty}^{\infty} \chi x^2 \mathrm{d}x \qquad [15.19.10]$$

Hence from Equations 15.19.8, 15.19.9b and 15.19.10

$$\sigma_x = (2K_x t)^{1/2} \qquad [15.19.11]$$

Moving on, if the exponential form of the autocorrelation coefficient $R(\tau)$ given in Equation 15.12.101 is used in Taylor's theorem as given in Equation 15.12.107, the solution obtained is

$$\sigma_x^2 = 2\sigma_u^2 t_L^2 \left[\frac{t}{t_L} - 1 + \exp\left(-\frac{t}{t_L}\right)\right] \qquad [15.19.12]$$

where t_L is the Lagrangian time scale.

Then for a short time t ($t \to 0$)

$$\sigma_x \propto t \qquad [15.19.13a]$$

while for a long time ($t \to \infty$)

$$\sigma_x \propto t^{1/2} \qquad [15.19.13b]$$

Since the distance x is proportional to the time t ($x = ut$), at short times

$$\sigma_x \propto x \qquad [15.19.14]$$

Similar relations apply for σ_y and σ_z.

The dispersion coefficients may be related to the standard deviations of the wind velocity (σ_v, α_w) as follows:

$$\sigma_y = \sigma_v t f_1(t/T_y) \qquad [15.19.15a]$$

$$\sigma_z = \sigma_w t f_2(t/T_z) \qquad [15.19.15b]$$

where f_1 and f_2 are universal functions and T_y and T_z are the time scales (s) for lateral and vertical dispersion, respectively. But

$$\sigma_v t \approx \sigma_\theta x \qquad [15.19.16a]$$

$$\sigma_w t \approx \sigma_\phi x \qquad [15.19.16b]$$

Hence from Equations 15.19.15 and 15.19.16

$$\sigma_y = \sigma_\theta x f_1(t/T_y) \qquad [15.19.17a]$$

$$\sigma_z = \sigma_\phi x f_2(t/T_z) \qquad [15.19.17b]$$

The universal functions f_1 and f_2 may be derived from theoretical considerations or expressed as empirical correlations. Pasquill (1976a) has tabulated values of f_1, which is taken as independent of stability and source height and as a function of distance only. Irwin (1979a) has correlated these values as follows:

$$f_1 = \left(1 + 0.031x^{0.46}\right)^{-1} \quad x \le 10^4 \qquad [15.19.18a]$$

$$= 33x^{-1/2} \quad x > 10^4 \qquad [15.19.18b]$$

Correlations for both f_1 and f_2 have been given by Draxler (1976). He obtains for f_1 the relation

$$f_1 = \frac{1}{[1 + 0.9(t/T_i)]^{1/2}} \qquad [15.19.19]$$

where T_i is the dispersion time. He states that the function f_2 may be assumed equal to f_1 except for a ground level source in unstable conditions and an elevated source in stable conditions. For the former case it was difficult to obtain a correlation, but for a limited set of data

$$f_2 = \frac{0.3(t/T_i - 0.4)^2}{0.16} + 0.7 \qquad [15.19.20a]$$

For the latter case he obtained

$$f_2 = \frac{1}{1 + 0.945(t/T_i)^{0.806}} \qquad [15.19.20b]$$

The dispersion time T_i is the time for f_1, or f_2, to become equal to 0.5. Draxler gives the following values for T_i (in seconds)

Source height	*Horizontal dispersion*		*Vertical dispersion*	
	Stable	*Unstable*	*Stable*	*Unstable*
Ground level	300	300	50	100
Elevated	1000	1000	100	500

A further discussion of these universal functions is given by Gryning *et al.* (1987).

15.19.2 Sutton diffusion parameters

Sutton's original values for the diffusion parameters C_y and C_z have been given in Section 15.16. Values have also been given by other workers as shown in Table 15.32.

15.19.3 Pasquill cloud parameters

Pasquill's original values for the cloud parameters θ and h have been given in Section 15.16.

For a long release where wind direction traces are not available, Beattie (1963 UKAEA AHSB(S) R64) has suggested the use of the following values for θ:

$d = 0.1$ km, $\theta = 30°$

$d = 100$ km, $\theta = 15°$

Table 15.32 *Sutton diffusion parameters*

A Values given by N.G. Stewart, Gale and Crooks (1958)
Source height: 68 cm

Downwind distance (m)	*Stability condition*	C_y	C_z
150–1000	Unstable		0.27
	Neutral		0.22
	Stable		0.12
590–620	Unstable, neutral	0.46	
880–1050	Unstable, neutral	0.28	
1200	Unstable, neutral	0.33	
2400–2800	Unstable, neutral	0.26	
6000–9700	Unstable, neutral	0.18	

B Values of Brookhaven National Laboratory (after Slade, 1968)[a]
Source height: Elevated and ground level sources

Wind gustiness Category	n	C_y	C_z
B2	0.15	0.48	0.50
B1	0.26	0.44	0.38
C	0.48	0.54	0.32
D	0.57	0.41	< 0.08

C Values of Barad and Fuquay (1962)

Stability condition	*Wind speed* (m/s)	n	C_y	C_z
Source height: elevated				
Unstable	1	0.20	0.30	0.30
	5		0.26	0.26
	10		0.24	0.24
Neutral	1	0.25	0.15	0.15
	5		0.12	0.12
	10		0.11	0.11
Source height: ground level				
Unstable	1	0.20	0.35	0.35
	5		0.30	0.30
	10		0.28	0.28
Neutral	1	0.25	0.21	0.17
	5		0.15	0.14
	10		0.14	0.13

D Values of V.J. Clancey (1974a)

Stability condition	n	C
Lapse	0.17	0.2
Neutral	0.25	0.14
Inversion	0.35	0.09

E Values of Long (1963)

Stability condition	n	C_y $(m^{n/2})$	C_z $(m^{n/2})$
Large lapse	1/5	0.37	0.21
Neutral	1/4	0.21	0.12
Moderate inversion	1/3	0.13	0.08
Large inversion	1/2	0.11	0.06

[a] A slightly different set of values are given by Gifford (1976b).

These values of θ are based on neutral weather conditions with Pasquill stability category *D* and relatively invariant wind direction, but are also applicable to stable weather conditions with Pasquill stability category F if the wind direction is variable. The values quoted are three times greater than those given by Pasquill for a short release in stability category F conditions, as shown in Table 15.29. The difference may be regarded as allowing for the variability of wind direction which tends to apply to this type of weather. If, however, the wind direction is invariant, then the lower values given in Table 15.29 for stability category F should be used.

15.19.4 Pasquill–Gifford dispersion coefficients

The dispersion coefficients most often used with the Pasquill–Gifford model are probably those of D.B. Turner (1970), as given in Section 15.16. There are, however, several other sets.

Correlations of the dispersion coefficients in terms of the Brookhaven National Laboratory (BNL) stability categories have been given by Singer and Smith (1966) as shown in Table 15.33 and in Figure 15.58.

Correlations have also been given by Carpenter *et al.* (1971) of the Tennessee Valley Authority (TVA) in terms of temperature gradient categories as shown in Figure 15.59.

Table 15.33 *Pasquill–Gifford dispersion coefficients: BNL formulae (Singer and Smith, 1966) (Courtesy of International Journal of Air and Water Pollution)*

BNL gustiness class	*Dispersion coefficient* (m)	
	σ_y	σ_z
B2	$0.40x^{0.91}$	$0.41x^{0.91}$
B1	$0.36x^{0.86}$	$0.33x^{0.86}$
C	$0.32x^{0.78}$	$0.22x^{0.78}$
D	$0.31x^{0.71}$	$0.06x^{0.71}$

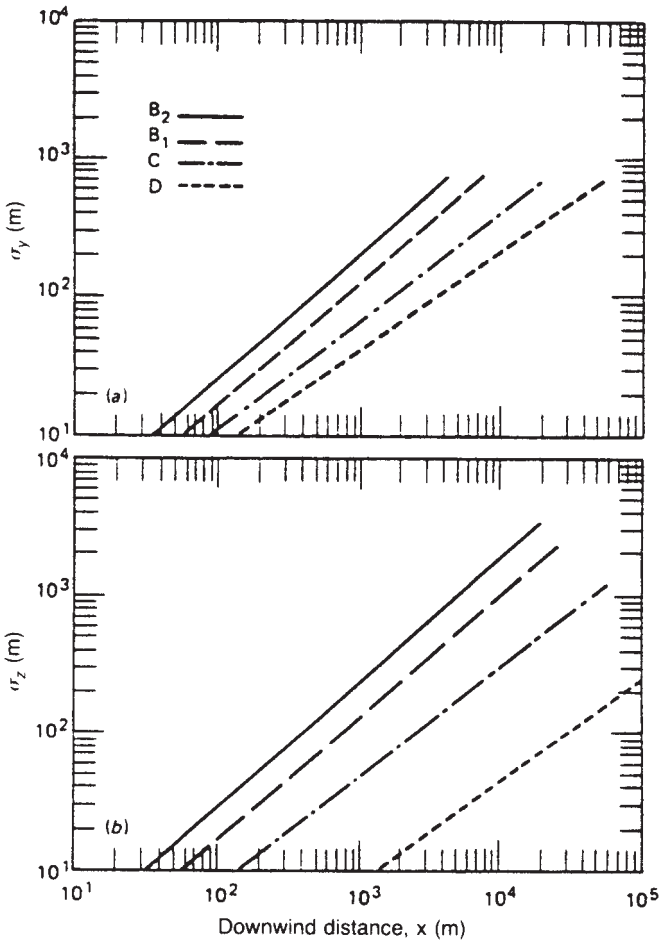


Figure 15.58 *Meteorological parameters for Pasquill–Gifford equations for continuous source: dispersion coefficients based on BNL scheme (Gifford, 1976b; after Singer and Smith, 1966) (Courtesy of Nuclear Safety)*

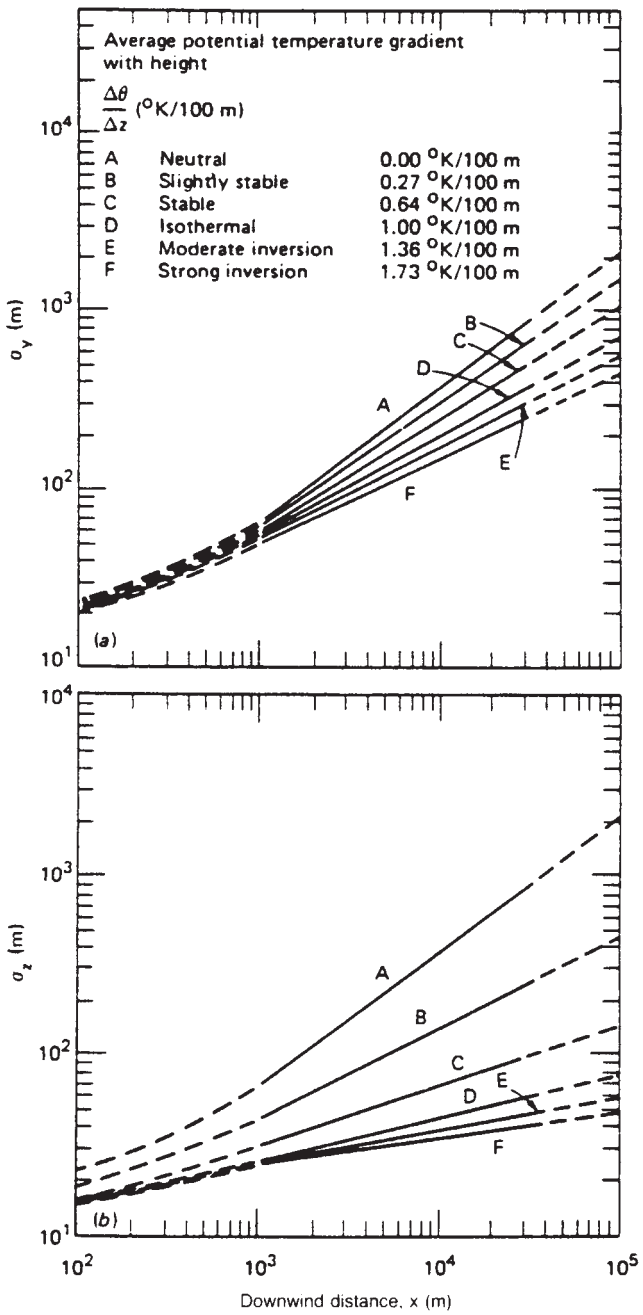


Figure 15.59 *Meteorological parameters for Pasquill–Gifford equations for continuous source: dispersion coefficients based on TVA scheme (Gifford, 1976b; after Carpenter et al., 1971 (Courtesy of Nuclear Safety)*

It can be seen from comparison of Figure 15.54 and Figures 15.58 and 15.59 that the correlations for the dispersion coefficients differ. An attempt to resolve these differences has been made by G.A. Briggs (1974). His work has been summarized by Gifford (1976b).

The Pasquill–Gifford curves are based on experiments on dispersion of non-buoyant gas over flat ground up to a downwind distance of 800 m. The BNL curves are for dispersion of a non-buoyant plume from an elevated stack (108 m) out to a distance of several kilometres with few

measurements taken within 800 m. The TVA curves are for dispersion of a buoyant plume with stack heights of 75–250 m, and with effective stack heights at least twice these values, and to a distance of up to some tens of kilometres. The dispersion of this latter type of plume is a function more of buoyancy and entrainment effects than of atmospheric turbulence.

Briggs therefore proposed a set of interpolation formulae with properties conformable to these three sets of results. They would agree with the Pasquill–Gifford curves for downwind distances over the range 100–10,000 m except that for A and B stability classes and for σ_z 100, the σ_z curves would be based on the values given by the American Society of Mechanical Engineers (ASME) (1968/1), which reflect mainly BNL data. The BNL and TVA curves agree reasonably well with each other, except at short distances where the latter are influenced by buoyancy; they also agree reasonably well with the Pasquill–Gifford curves at about 10 km, except for the A and B conditions, as just described.

Briggs' formulae are shown in Table 15.34 and curves given by Hosker (1974b) based on these are shown in Figure 15.60. The formulae are applicable up to 10 km.

15.19.6 Pasquill–Gifford dispersion coefficients: NRPB scheme

A scheme for the estimation of the Pasquill–Gifford dispersion coefficients based on F.B. Smith's P stability classification and his correlation of the vertical coefficient σ_z and on allowance for plume meandering for the horizontal dispersion σ_y has been developed at the National Radiological Protection Board (NRPB), as described by Clarke (1979 NRPB R91).

Following F.B. Smith (1973), the vertical dispersion coefficient σ_z is a function of the distance, the P class and the roughness length z_o. The value of σ_z is obtained from Figures 15.61–15.63. Figure 15.61 gives σ_z as a function of distance for $P = 3.6$ and $z_o = 0.1$ m. Figure 15.62 gives the correction for other P values at the same value of z_o. Figure 15.63 gives the correction for other values of z_o for all P values.

Table 15.34 *Pasquill–Gifford dispersion coefficients: Briggs interpolation formulae for open country (G.A. Briggs, 1974)*

Pasquill stability class	*Dispersion coefficient* (m)	
	σ_y	σ_z
A	$0.22x(1+0.0001x)^{-1/2}$	$0.20x$
B	$0.16x(1+0.0001x)^{-1/2}$	$0.12x$
C	$0.11x(1+0.0001x)^{-1/2}$	$0.08x(1+0.0002x)^{-1/2}$
D	$0.08x(1+0.0001x)^{-1/2}$	$0.06x(1+0.0015x)^{-1/2}$
E	$0.06x(1+0.0001x)^{-1/2}$	$0.03x(1+0.003x)^{-1}$
F	$0.04x(1+0.0001x)^{-1/2}$	$0.016x(1+0.0003x)^{-1}$

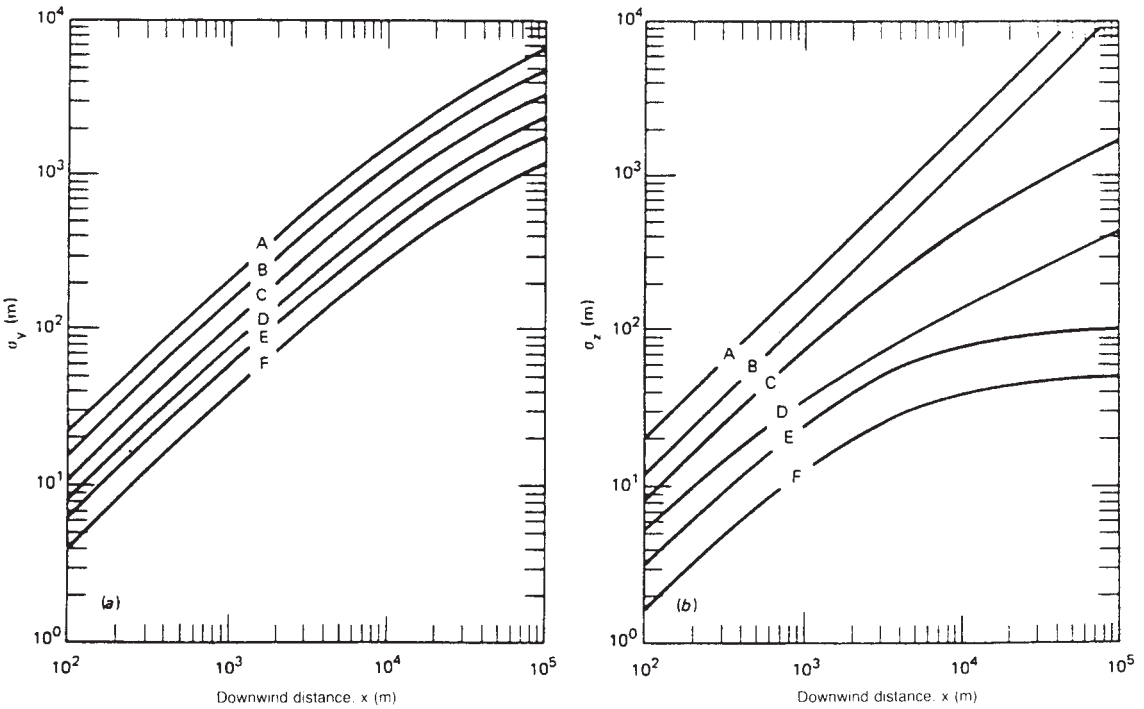


Figure 15.60 *Meteorological parameters for Pasquill–Gifford equations for continuous source: dispersion coefficients based on Briggs' interpolation formulae for open country (Gifford, 1976b; after Hosker, 1974b) (Courtesy of Nuclear Safety)*

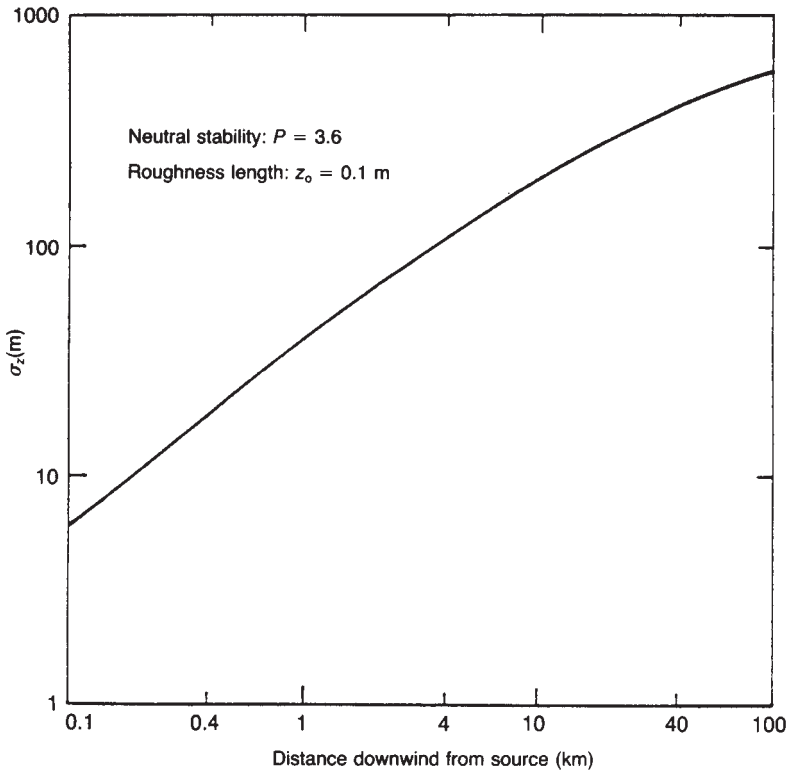


Figure 15.61 *Meteorological parameters for Pasquill–Gifford equations for continuous source: dispersion coefficients based on NRPB scheme (Clarke, 1979 NRPB R-91): vertical dispersion coefficient σ_z for stability parameter $P = 3.6$ and surface roughness $z_0 = 0{,}1$ m*

Formulae for σ_z for the discrete Pasquill classes, or P values, and for discrete values of z_o have been given by Hosker (1974b). These are

$$\sigma_z = \frac{ax^b}{1+cx^d} F(z_o, x) \qquad [15.19.21]$$

with

$$F(z_o, x) = \ln\left\{ fx^g \left[1 + \left(hx^j \right)^{-1} \right] \right\} \qquad z_o \geq 0.1 \qquad [15.19.22a]$$

$$= \ln\left[fx^g \left(1 + hx^j \right)^{-1} \right] \qquad z_o < 0.1 \qquad [15.19.22b]$$

where $F(z_o, x)$ is the roughness length correction factor and a–j are constants or indices. Values of the constants and indices for use in Equations 15.19.21 and 15.19.22 are given in Table 15.35.

Figure 15.64 shows the values of σ_z given by Smith's scheme for roughness length $z_o = 0.1$ m.

For the horizontal dispersion coefficient σ_y the regular Pasquill–Gifford values, which apply for very short releases, typically of 3 min duration, are used for releases of up to 30 min duration. For longer releases, account is taken of meandering using the relation

$$\sigma_y^2 = \sigma_{yt}^2 + \sigma_{yw}^2 \qquad [15.19.23]$$

where σ_{yt} is the turbulent diffusion (or 3 min) term and σ_{yw} is the term due to fluctuations in wind direction.

The values used for σ_{yt} are the regular Pasquill–Gifford values. For σ_{yw} two relations are given. If the standard deviation of the horizontal wind direction σ_θ is known, use is made of the equation

$$\sigma_{yw} = \sigma_\theta x \qquad [15.19.24a]$$

and if it is not, the equation used is

$$\sigma_{yw} = 0.065 \left(\frac{7T}{u_{10}} \right)^{1/2} x \qquad [15.19.24b]$$

where T is the duration of the release (h), x is the downwind distance (m), u_{10} is the wind speed at 10 m height (m/s) and σ_θ is the horizontal standard deviation of the wind direction averaged over 3 min periods and sampled over the duration of the release (rad).

15.19.7 Pasquill–Gifford dispersion coefficients: other correlations

Various authors have given for the Pasquill–Gifford coefficients power law formulae of the form

$$\sigma_y = ax^b \qquad [15.19.25a]$$

$$\sigma_z = cx^d \qquad [15.19.25b]$$

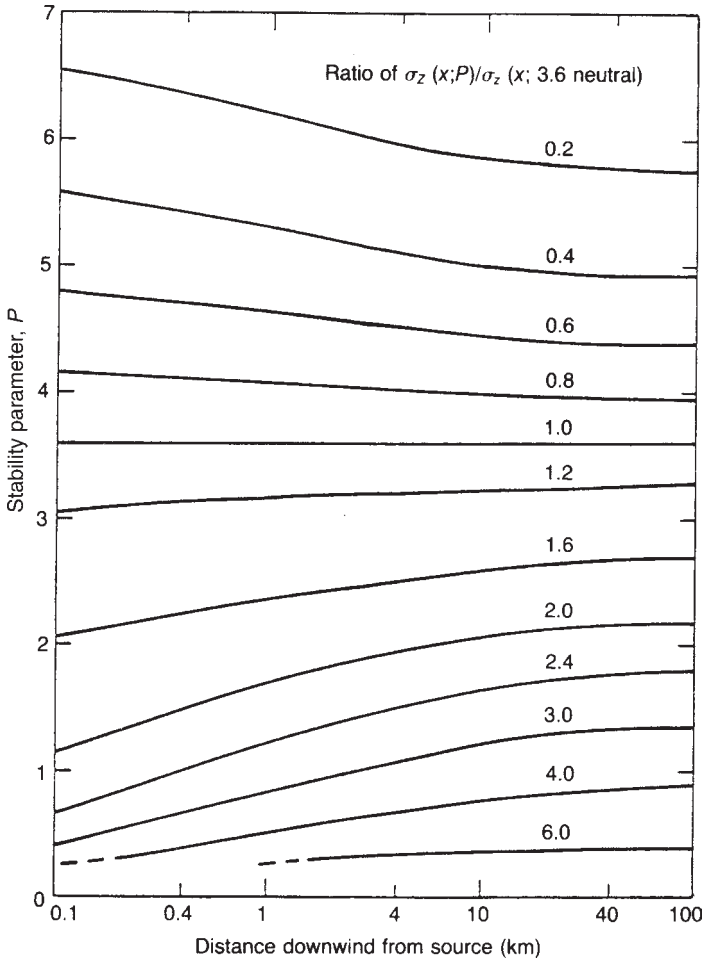


Figure 15.62 *Meteorological parameters for Pasquill–Gifford equations for continuous source: dispersion coefficients based on NRPB scheme (Clarke, 1979 NRPB R91): correction factor to vertical dispersion coefficient σ_z for stability parameter P*

Many of the Pasquill–Gifford curves given in Figures 15.54 and 15.58–15.60 clearly cannot be fitted over their whole range by such formulae, but provided they are used over the range of their validity such equations have their use in making it possible to obtain analytical solutions to dispersion problems.

R.W. McMullen (1975) has given the following formulae for both dispersion coefficients:

$$\sigma = \exp\left[a + b\ \ln x + c(\ln x)^2\right] \qquad [15.19.26]$$

where σ may be either σ_y or σ_z. The values of the constants a–c are given in Table 15.36.

15.19.8 Dispersion coefficients for urban areas

Work on dispersion coefficients for use in the Pasquill–Gifford model over and in urban areas has been described by a number of workers, including D.B. Turner (1964), Bowne, Ball and Anderson (1968), Bowne and Ball (1970) and Bowne (1974), McElroy and Pooler (1968), McElroy (1969) and Yersel, Goble and Morrill (1983). In general, dispersion over or within an urban area is greater than over a flat rural area. Mechanical turbulence is enhanced by the increase surface roughness and thermal turbulence by the heat island effect.

Summaries of experimental work on dispersion over urban areas have been given by Gifford (1972, 1976a,b). The experimental work of McElroy and Pooler (1968) over St Louis has provided dispersion data. These data have been used by Pasquill (1970) to compare dispersion over urban and rural terrains. Further data have been analysed by W.B. Johnson *et al.* (1971). On the basis of this work, G.A. Briggs (1974) has proposed relations for the dispersion coefficients. Table 15.37 gives information on the vertical dispersion coefficient σ_z and Table 15.38 gives

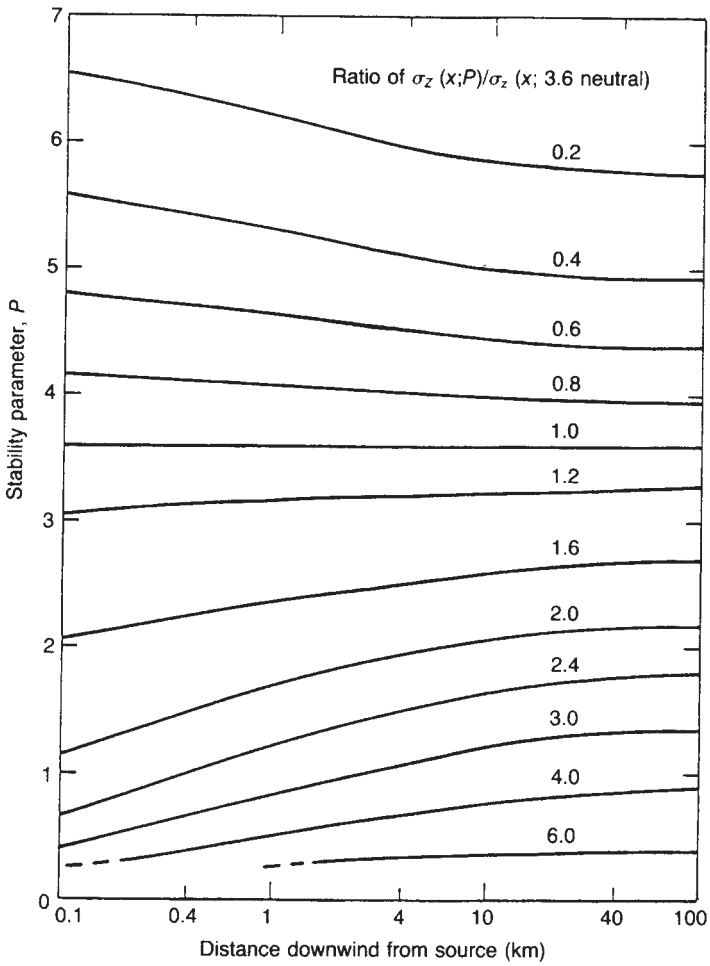


Figure 15.63 *Meteorological parameters for Pasquill–Gifford equations for continuous source: dispersion coefficients based on NRPB scheme (Clarke, 1979 NRPB R91): correction factor to vertical dispersion coefficient σ_z for surface roughness z_0*

the Briggs' formulae for both the horizontal and the vertical dispersion coefficients σ_y and σ_z. Figure 15.65 shows graphs obtained by Hosker from Briggs' equations.

Experimental work on dispersion over short distances within an urban area at Worcester, Massachusetts, has been conducted by Yersel, Goble and Morrill (1983). They carried out releases in a parking lot, with the nearest building 40 m away, and measured the concentration at distances up to 600 m. Their results for σ_y and σ_z are shown in Figure 15.66. For σ_y the values for stability class B are well described by the regular Pasquill–Gifford curves for class A, a shift of one class, while for classes C and D the values are best described by a shift of two classes. For σ_z, however, the data differ significantly in magnitude and slope and around 200 m are substantially higher than even the class A curve.

15.19.9 Dispersion coefficients for coastal areas and water

A number of authors have described work on dispersion coefficients for the Pasquill–Gifford model for coastal areas and water, including Kondo (1975), Gifford (1976a,b), Lyons (1976), S.R. Hanna, Paine and Schulman (1984), Hasse and Weber (1985), Larsen and Gryning (1986) and Skupniewicz and Schacher (1986). In general, dispersion over water tends to be less than over land but, as described above, this generalization needs heavy qualification.

The surface roughness of the sea may be characterized by a roughness length, but waves do not behave as simple roughness elements. This problem is discussed by Gifford (1976a,b).

In order to use the Pasquill–Gifford model it is necessary to define the stability classes. The Pasquill classes over land are not necessarily applicable without

Table 15.35 *Pasquill–Gifford dispersion coefficients: Hester's formulae (Hosker, 1974b) (Courtesy of International Atomic Energy Agency)*

A Vertical dispersion coefficient

Stability class	*a*	*b*	*c*	*d*
A	0.112	1.06	5.38×10^{-4}	0.815
B	0.130	0.950	6.52×10^{-4}	0.750
C	0.112	0.920	9.05×10^{-4}	0.718
D	0.098	0.889	1.35×10^{-3}	0.688
E	0.0609	0.895	1.96×10^{-3}	0.684
F	0.0638	0.783	1.36×10^{-3}	0.672

B Roughness length correction factor

Roughness length (m)	*f*	*g*	*h*	*i*
0.01	1.56	0.0480	6.25×10^{-4}	0.45
0.04	2.02	0.0269	7.76×10^{-4}	0.37
0.1	2.72	0	0	0
0.4	5.16	−0.098	18.6	−0.225
1.0	7.37	−0.0957	4.29×10^{3}	−0.60
4.0	11.7	−0.128	4.59×10^{4}	−0.78

modification over sea. The definition of suitable classes for use over sea was discussed in Section 15.12.

Empirical correlations for the Pasquill–Gifford dispersion coefficients for use over water have been given by Skupniewicz and Schacher (1986) in terms of the NFS stability classification. The relations are

$$\sigma_y = \sigma_y(R)\left(\frac{x}{R}\right)^{\alpha} \qquad [15.19.27a]$$

$$\sigma_z = \sigma_z(R)\left(\frac{x}{R}\right)^{\beta} \qquad [15.19.27b]$$

where $\sigma_y(R)$ and $\sigma_z(R)$ are the values of σ_y and σ_z at the reference distance R (= 100 m), and α and β are indices. Values of σ_y and σ_z at 100 m and of the indices α and β are given in Table 15.39.

These equations are empirical correlations. The data for σ_y exhibit considerable scatter. The authors state that stability classification can reasonably be used to characterize σ_z but not σ_y.

An alternative treatment for the estimation of dispersion coefficients for use over water based on the AMS Workshop scheme has been given by S.R. Hanna, Paine and Schulman (1984).

15.19.10 Dispersion coefficients for complex terrain

Dispersion coefficients for complex terrain are discussed by Egan (1976). In general, dispersion over complex terrain tends to give complex dispersion patterns. The overall effect is generally to increase dispersion, but, as described below, there are two features that may lead to local high concentrations.

There tends to be enhancement of both the dispersion coefficients, but the crosswind dispersion coefficient σ_y is enhanced more than is the vertical dispersion coefficient σ_z. This is often attributed mainly to plume meandering and splitting. For a ground level source the implication is that the ground level centre line concentration will be less than for flat terrain.

For an elevated source the situation is not quite so straightforward. The Pasquill–Gifford Equation 15.16.55 for the maximum ground level concentration for a release from an elevated continuous point source shows that, if there is an increase in the ratio σ_z/σ_y, this maximum concentration increases. Therefore, in principle, if σ_z increases and there is no compensating increase in σ_y, there will be an increase in the maximum ground level concentration and a decrease in the distance at which this occurs. The other feature that can give rise to a high local concentration is a stagnant pocket.

15.19.11 Effect of sampling period

As described above, if the concentration in a plume is sampled virtually instantaneously, the concentration distribution has a relatively narrow spread, while if the sample is taken over a longer time period the distribution has a wider spread. It follows that the dispersion coefficients are a function of the sampling period. The following relation has been proposed by Gifford (1976a) to take account of this variation:

$$\frac{\sigma_y}{\sigma_{yr}} = \left(\frac{t}{t_r}\right)^{p} \qquad [15.19.28]$$

where t is the sampling period which yields dispersion coefficient σ_y, p is an index, and subscript r denotes the reference value. The value of p is approximately 0.2 for sampling periods between 3 min and 1 h and in the range 0.25–0.3 for periods between 1 and 100 h.

Gifford states that similar considerations apply to σ_z, except that the effect of variations in σ_z should not extend beyond downwind distances of a few kilometres.

The regular Pasquill–Gifford curves correspond to a sampling period of about 10 min.

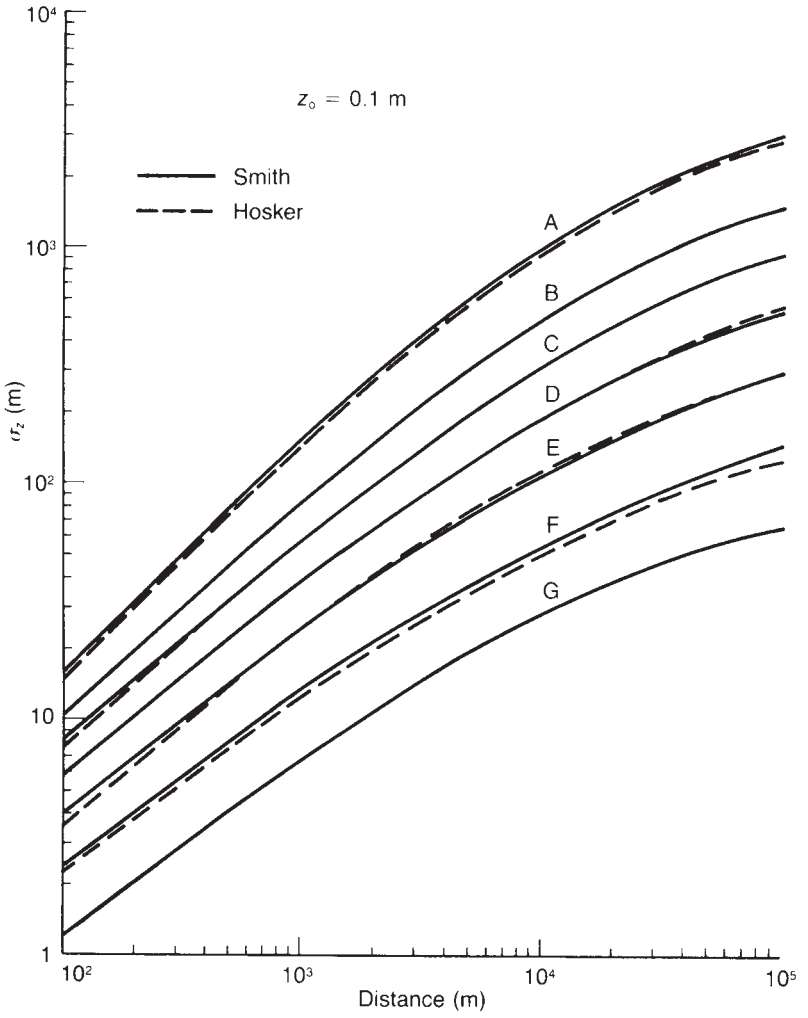


Figure 15.64 *Meteorological parameters for Pasquill–Gifford equations for continuous source: dispersion coefficients based on NRPB scheme (Clarke, 1979 NRPB R91): vertical dispersion coefficient σ_z as a function of stability*

Table 15.36 *Pasquill–Gifford dispersion coefficients: McMullen's formulae (R.W. McMullen, 1975) (Courtesy of Air Pollution Control Association)*

Pasquill stability class	*Formulae parameters*					
	σ_y			σ_z		
	a	*b*	*c*	*a*	*b*	*c*
A	5.357	0.8828	−0.0076	6.035	2.1097	0.2270
B	5.058	0.9024	−0.0096	4.694	1.0629	0.0136
C	4.651	0.9181	−0.0076	4.110	0.9201	−0.0020
D	4.230	0.9222	−0.0087	3.414	0.7370	−0.0316
E	3.922	0.9222	−0.0064	3.057	0.6794	−0.0450
F	3.533	0.9181	−0.0070	2.621	0.6564	−0.0540

Table 15.37 *Pasquill–Gifford dispersion coefficients for urban areas: comparison of vertical dispersion coefficient for rural and urban terrain (after Gifford, 1976b)[a] (Courtesy of Nuclear Safety)*

Downwind distance (km)	*Terrain*	*Ratio of σ_z for following stability classes to value in neutral conditions*			
		B	*C*	*D*	*E–F*
1	City[b]	4.5	2.7	1.7	0.7
	City[c]	4.0	2.4	1.5	0.6
	Open country	3.2	1.9	1.0	0.5
10	City[b]	9	3.4	1.0	0.3
	City[c]	11	4.1	1.2	0.4
	Open country	6	2.4	1.0	0.3

[a] Based on work of McElroy and Pooler (1968) at St. Louis and analysis by Pasquill (1970).
[b] Based on McElroy and Pooler's figure 2 using curve for bulk Richardson number $B = \pm 0.01$.
[c] Using data for $B = \pm 0.01$ in evening conditions only.

Table 15.38 *Pasquill–Gifford dispersion coefficients for urban areas: Briggs interpolation formulae (after G.A. Briggs, 1974)*

Pasquill stability class	*Dispersion coefficient* (m)	
	σ_y	σ_z
A–B	$0.32x(1+0.0004x)^{-1/2}$	$0.24x(1+0.001x)^{-1/2}$
C	$0.22x(1+0.0004x)^{-1/2}$	$0.20x$
D	$0.16x(1+0.0004x)^{-1/2}$	$0.14x(1+0.0003x)^{-1/2}$
E–F	$0.11x(1+0.0004x)^{-1/2}$	$0.08x(1+0.0015x)^{-1/2}$

15.19.12 Puff dispersion coefficients

For a puff, the size of eddy that mainly influences dispersion lies within a limited range, approximately 1/3 to 3 times the size of the puff. A smaller eddy effects little dispersion, while a larger one moves the whole cloud.

Relations for a puff dispersion coefficient σ have been derived by Batchelor (1952) from similarity considerations. It can be shown that

$$\sigma^2 = \sigma_0^2 + c_1(\epsilon\sigma_0)^{2/3}t^2 \quad \text{short times} \quad [15.19.29a]$$

$$= c_2\epsilon t^3 \quad \text{intermediate times} \quad [15.19.29b]$$

$$= c_3 t \quad \text{long times} \quad [15.19.29c]$$

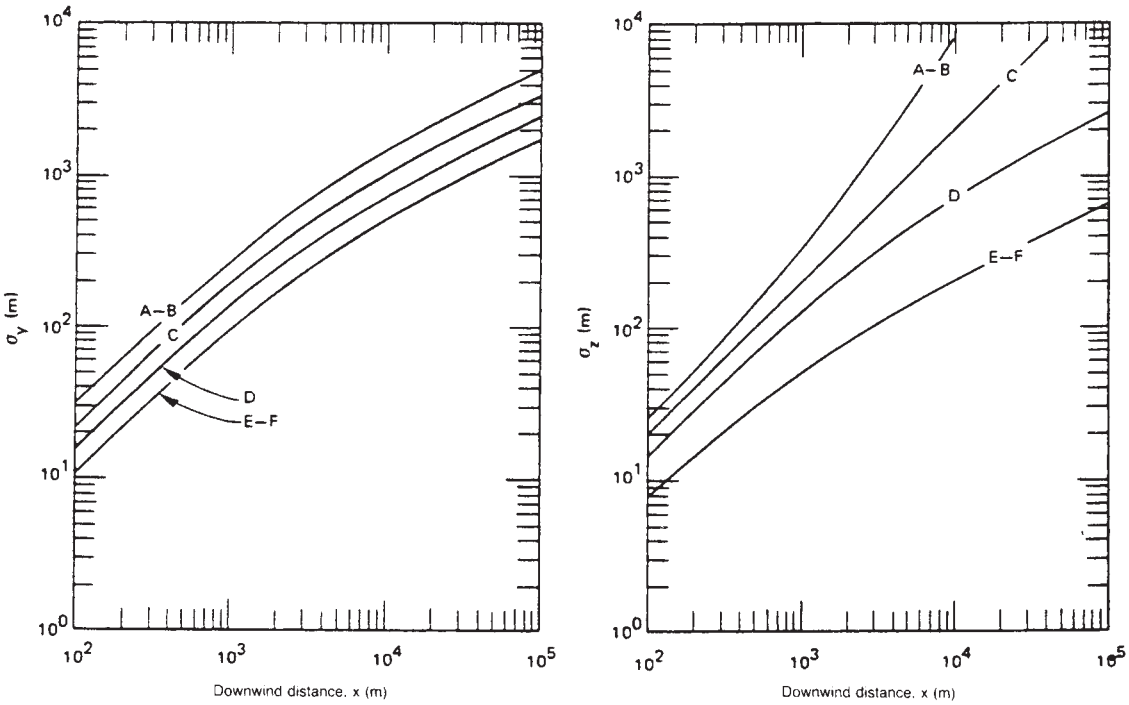


Figure 15.65 *Meteorological parameters for Pasquill–Gifford equations for continuous source: dispersion coefficients based on Briggs' interpolation formulae for urban areas (Gifford, 1976b; after Hosker, 1974b) (Courtesy of Nuclear Safety)*

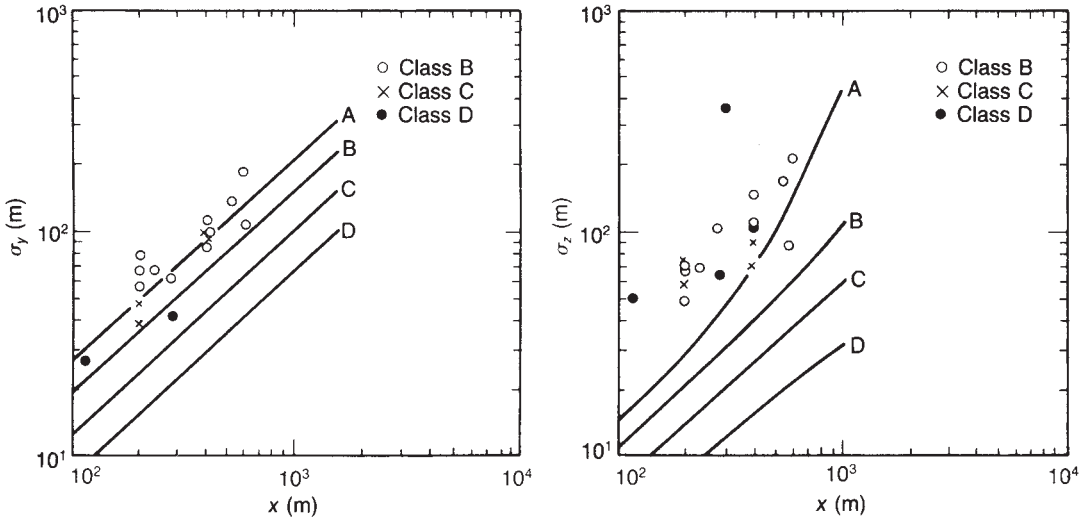


Figure 15.66 *Meteorological parameters for Pasquill–Gifford equations for continuous source: dispersion coefficients for urban areas (Yersel, Goble and Morill, 1983) (Courtesy of Pergamon Press)*

Table 15.39 *Pasquill–Gifford dispersion coefficients over water: empirical formulae (after Skupniewicz and Schacher, 1986) (Courtesy of Pergamon Press)*

NPS class	*Dispersion coefficient*[a] (100 m)				*Indices*			
	σ_y		σ_z		α		β	
	Water	*Land*	*Water*	*Land*	*Water*	*Land*	*Water*	*Land*
B	25.0	19.0	10.0	11.0	0.75[b]	1.00	0.75[b]	1.00
C	20.0	12.5	8.0	7.5	0.70[b]	1.00	0.70[b]	0.90
D	15.1	8.0	3.2	4.5	0.69	0.90	0.65	0.85
E	16.1	6.0	1.8	3.5	0.65	0.80	0.62	0.80

[a] Over land values are those given by DTIC (1980).
[b] Insufficient data for verification.

where ε is the eddy dissipation rate, σ_0 is the initial size of the cloud, and c_1, c_2 and c_3 are constants.

The constant c_2 is generally found to lie in the range 0.5–2 and is often taken as unity.

Then, from Equation 15.19.29,

$$\sigma \propto t \quad \text{short times} \qquad [15.19.30]$$

$$\propto t^{3/2} \quad \text{intermediate times} \qquad [15.19.30b]$$

$$\propto t^{1/2} \quad \text{long times} \qquad [15.19.30c]$$

Also at long times

$$\sigma^2_{\text{puff}} \rightarrow \sigma^2_{\text{plume}} \quad t \rightarrow 0 \qquad [15.19.31]$$

Here short times may be interpreted as a few seconds and long times as greater than 10^4 s. Generally it is the intermediate times that are of most interest. The number of data sets available on which to base estimates of the puff dispersion is very much less than for plume dispersion. Work on puff dispersion coefficients has been described by Islitzer and Slade (1968), who give the (σ_y and σ_z values shown in Table 15.31.

A somewhat different variation of the puff dispersion coefficients with distance, or time, is suggested by the work of Gifford (1977). One of his plots showing experimental data on the relation between σ_y and t is given in Figure 15.67. For times up to about 10^4 s the data give a reasonably good fit to relation 15.19.30b for intermediate times.

A method of estimating the dispersion coefficients based on Equation 15.19.29 has been given by S.R. Hanna, Briggs and Hosker (1982). For σ_y, Equation 15.19.29b is used up to a travel time of 10^4 s, the eddy dissipation rate ϵ being initially determined locally and then, as σ_y approaches $0.3z_i$ where z_i is the mixed layer height, at a height midway in the boundary layer. At a travel time equal to 10^4 s, the constant c_3 in Equation 15.19.29c is evaluated by equating the values of σ_y obtained from Equations 15.19.29b and 15.19.29c, and thereafter Equation 15.19.29c is used with this value of c_3. For σ_z, a similar procedure is used, except that once σ_z attains a value of $0.3z_i$ that value is used for all times thereafter.

15.19.13 Turbulent exchange coefficients

The foregoing account of dispersion parameters has concentrated mainly on those for the Pasquill–Gifford model.

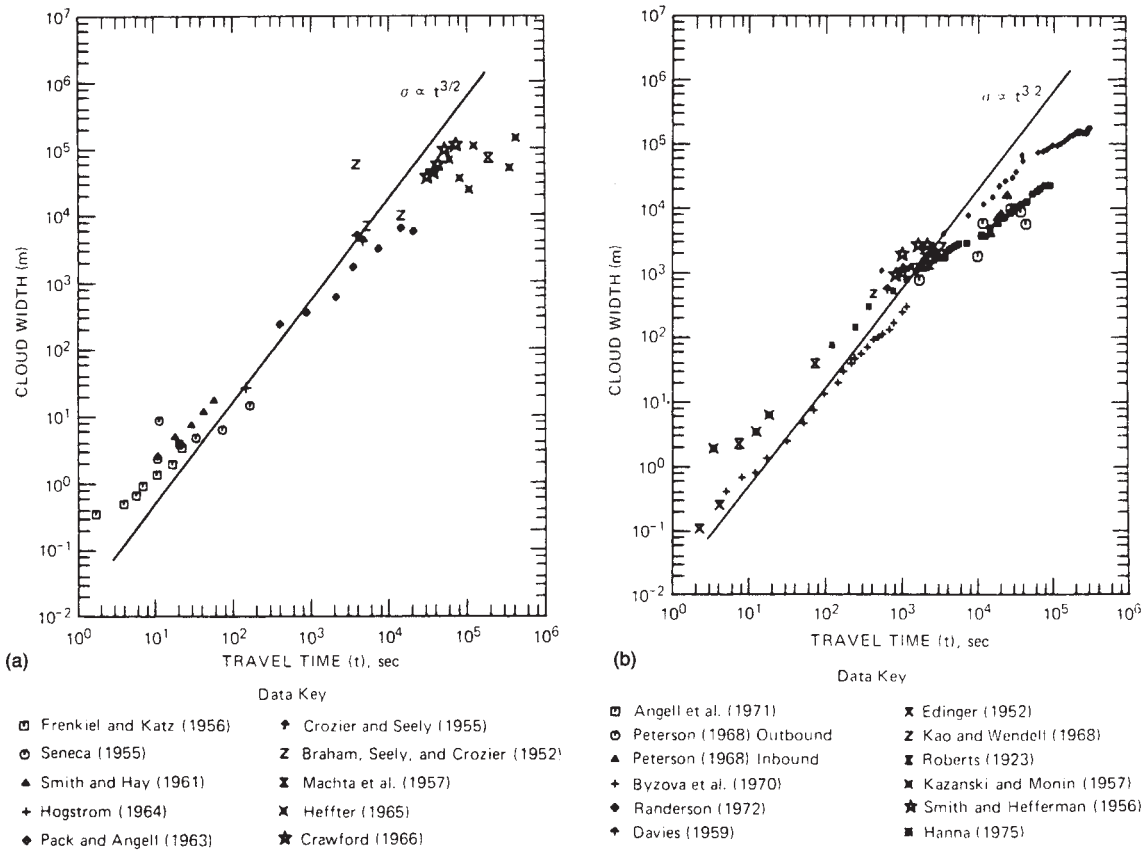


Figure 15.67 *Meteorological parameters for Pasquill–Gifford equations for instantaneous source: dispersion coefficient σ (Gifford, 1977): (a) selection of original data of Crawford (1966); (b) collection of subsequent data by Gifford. The references quoted are those given by Gifford and do not all appear in this text*

The turbulent exchange coefficients K used in K-theory models have been discussed in Section 15.12. Accounts of K-theory models commonly include a discussion of the estimation of the K values used in the models.

15.20 Dispersion of Jets and Plumes

The dispersion of material issuing as a leak from a plant is determined by its momentum and buoyancy. If momentum forces predominate, the fluid forms a jet, while if buoyancy forces predominate, it forms a plume. Such dispersion contrasts with the dispersion by atmospheric turbulence considered so far. However, once the momentum or buoyancy decay dispersion by atmospheric turbulence becomes the predominant factor for leaks also.

Emission situations were classified in Section 15.1. In respect of jets and plumes the following distinctions may be made:

(1) Fluid
  (a) gas,
  (b) liquid,
  (c) two-phase vapour–liquid mixture;
(2) Fluid momentum
  (a) low momentum,
  (b) high momentum;
(3) Fluid buoyancy
  (a) positive buoyancy,
  (b) neutral buoyancy,
  (c) negative buoyancy;
(4) Atmospheric conditions
  (a) low turbulence,
  (b) high turbulence.

If the momentum of the material issuing from an orifice on a plant is high, the dispersion in the initial phase at least is due to the momentum, and the emission is described as a momentum jet. If the momentum is low, either because the initial momentum is low or because it has decayed, the dispersion is due to buoyancy and atmospheric turbulence, and, if buoyancy is involved, the emission is described as a buoyant plume: the buoyancy may be positive or negative.

An account is now given of dispersion by momentum jets and buoyant plumes. Both types of emission are sometimes described as plumes, the jet being a forced plume. The forces in a buoyant plume are often of the same order as

those in a momentum jet. Selected references on jets and plumes are given in Table 15.40. Some jet and plume dispersion situations are illustrated in Figure 15.68. The figure shows schematically instances of releases issuing as jets and becoming plumes as the influence of buoyancy takes over from that of momentum.

Table 15.40 *Selected references on jets and plumes (See also Table 15.42 for dense gas)*

Turbulent momentum jets, buoyant plumes, plumes dispersed by wind

Abraham (n.d., 1970); Albertson *et al.* (1948, 1950); O.G. Sutton (1950); J.F. Taylor, Grimmett and Comings (1951); Yih (1951); Gosline (1952); Nottage, Slaby and Gojsza (1952); Rouse, Yih and Humphreys (1952); Tuve (1953); Priestley and Ball (1955); B.R. Morton, Taylor and Turner (1956); W.R. Warren (1957); B.R. Morton (1959, 1961, 1965); Ricou and Spalding (1961); Abramovich (1963, 1969); Keffer and Baines (1963); Long (1963); Kleinstein (1964); R.A.M. Wilson and Danckwerts (1964); Becker, Hottel and Williams (1965, 1967); Heskestad (1965, 1966); Schmidt (1965); J.S. Turner (1966, 1973); Baines and Turner (1969); Spalding (1971); Ballal and Lefebvre (1973); Gugan (1976); Rajaratnam (1976); Sadee, Samuels and O'Brien (1976–77); J.G. Marshall (1977); Birch *et al.* (1978); Meroney (1979a); TNO (1979); Birch, Brown and Dodson (1980); C.J. Chen and Rodi (1980); Delichatsios (1980, 1988); Gartner, Giesbrecht and Leuckel (1980); R.M. Harrison and McCartney (1980); Lehrer (1981); Anfossi (1982); Davidson and Slawson (1982); de Faveri, Hanzevack and Delaney (1982); Fumarola *et al.* (1982); Golay (1982); Hanzevack (1982); List (1982); O'Shea (1982); Rittman (1982); Rodi (1982); Whaley and Lee (1982); Barr *et al.* (1983); Epstein *et al.* (1983); Giesbrecht, Seifert and Leuckel (1983); Kerman (1983); Willis and Deardorff (1983, 1987); Khalil (1983); Badr (1984); Baines and Hopflnger (1984); Brennan, Brown and Dodson (1984); Leahy and Davies (1984); D.B. Turner (1985); Hsu-Cherng Chiang and Sill (1986); Hwang and Chaing (1986); Overcamp and Ku (1986); Pierce (1986); Birch, Hughes and Swaffleld (1987); Krishnamurty and Hall (1987); Pfenning, Millsap and Johnson (1987); Technica (1987); P.A. Clark and Cocks (1988); Fairweather, Jones and Marquis (1988); Haroutunian and Launder (1988); Shaver and Fornery (1988); Subramanian *et al.* (1988); Birch and Brown (1989); Birch and Hargrave (1989); Emerson (1989); G.K Lee (1989); Loing and Yip (1989); Vergison, van Diest and Easier (1989); J.L. Woodward (1989a); Arya and Lape (1990); Cleaver and Edwards (1990); M. Epstein, Fauske and Hauser (1990); Moodie and Ewan (1990); Nettervffle (1990); Anfosssi *et al.* (1993); Bagster (1993); Lane-Serff, Linden and Hillel (1993); Webber and Wren (1993 SRD R552); Landis, Linney and Hanley (1994).

Sonic jets: Hess, Leuckel and Stoeckl (1973); Ramskill (1985 SRD R302); Ewan and Moodie (1986)

Elevated plumes, stacks, chimneys

Bosanquet (1935, 1957); Bosanquet and Pearson (1936); Church (1949); Barad (1951); Gosline (1952); N.G. Stewart *et al.* (1954); Strom and Halitsky (1955); F.B. Smith (1956); O.G. Sutton (1956); Best (1957); Hay and Pasquill (1957); Hilst (1957); Strom, Hackman and Kaplin (1957); N.G. Stewart, Gale and Crooks (1958); Strauss and Woodhouse (1958); Nonhebel (1960); Bodurtha (1961, 1988); Bowne (1961); Scorer and Barrett (1962); Briggs (1965, 1968, 1969, 1974, 1976); D.J. Moore (1969, 1975); Slawson and Csanady (1971); Ooms (1972); Cude (1974a,b, 1975); Hoot and Meroney (1974); Ooms, Mahieu and Zelis (1974); Readings, Haugen and Kaimal (1974); Bowne, Cha and Murray (1978); Lamb (1979); Venkatram and Kurtz (1979); Venkatram (1980a,c); P.M. Foster (1981); Nonhebel (1981); Kerman (1981, 1982); Reible, Shair and Kauper (1981); Venkatram and Vet (1981); Fumarola *et al.* (1982); Londergan and Borenstein (1983); Robson (1983); R.F. Griffiths (1984a); Carras and Williams (1984); Deardorff and Willis (1984); Leahey and Davies (1984); Manins (1984); Ooms and Duijm (1984); Venkatram, Strimaitis and Dicristoforo (1984); Venkatram and Paine (1985); Li Xiao-Yun, Leijdens and Ooms (1986); Paine, Insley and Eberhard (1986); R.L. Petersen (1986); Pierce (1986); Rowe and Tas (1986); Weil, Corio and Brower (1986); Willis (1986); S.R. Hanna and Paine (1987); Havens, Spicer and Layland (1987); J.L. Woodward (1989a)

Liquid jets

Holly and Grace (1921); Rayleigh (1932); Lewitt (1952); Brodkey (1967); Bushnell and Gooderum (1968); Benatt and Eisenklam (1969); van de Sande and Smith (1976); Suzuki *et al.* (1978); Engh and Larsen (1979); Blanken (1990); Tilton and Farley (1990)

Flash-off (*see* Table 15.7)

Two-phase jets

R. Brown and York (1962); Bushnell and Gooderum (1968); Hetsroni and Sokolov (1971); Gyarmathy (1976); Suzuki *et al.* (1978); Melville and Bray (1979a,b); Koestel, Gido and Lamkin (1980); Tomasko, Weigand and Thompson (1981a,b); M. Epstein *et al.* (1983); Appleton (1984 SRD R303); Kitamura, Morimatsu and Takahashi (1986); Wheatley (1986, 1987 SRD R410); Fauske and Epstein (1988); Tarn and Cowley (1989); M. Epstein, Fauske and Hauser (1990); Hague and Pepe (1990); Webber (1990); Webber and Kukkonen (1990); J.L. Woodward (1990, 1993); D.W. Johnson and Diener (1991); Papadourakis, Caram and Earner (1991); Webber *et al.* (1992 SRD R584, R585); J. Cook and Woodward (1993b); DunbarefeZ. (1994)

15.20.1 Jets

Accounts of jets are given in *The Theory of Turbulent Jets (Abramovich, 1963), Turbulent Jets of Air, Plasma and Real Gas (Abramovich, 1969), Turbulent Jets* (Rajaratnam, 1976), *Vertical Turbulent Buoyant Jets* (C.J. Chen and Rodi, 1980) and *Turbulent Buoyant Jets and Plumes* (Rodi, 1982). Work on jets includes that by Albertson *et al.* (1948), O.G. Sutton (1950), J.F. Taylor, Grimmett and Comings (1951), Nottage, Slaby and Gojsza (1952), Tuve (1953), B.R. Morton, Taylor and Turner (1956), B.R. Morton (1959, 1961), Ricou and Spalding (1961), Long (1963), Kleinstein (1964), Heskestad (1965, 1966), J.S. Turner (1966), Spalding (1971), Hess, Leuckel and Stoeckl (1973), Birch *et al.* (1984); Ramskill (1985 SRD R302), Ewan and Moodie (1986), Birch, Hughes and Swaffold (1987), Birch and Brown (1989) and Birch *et al.* (1989).

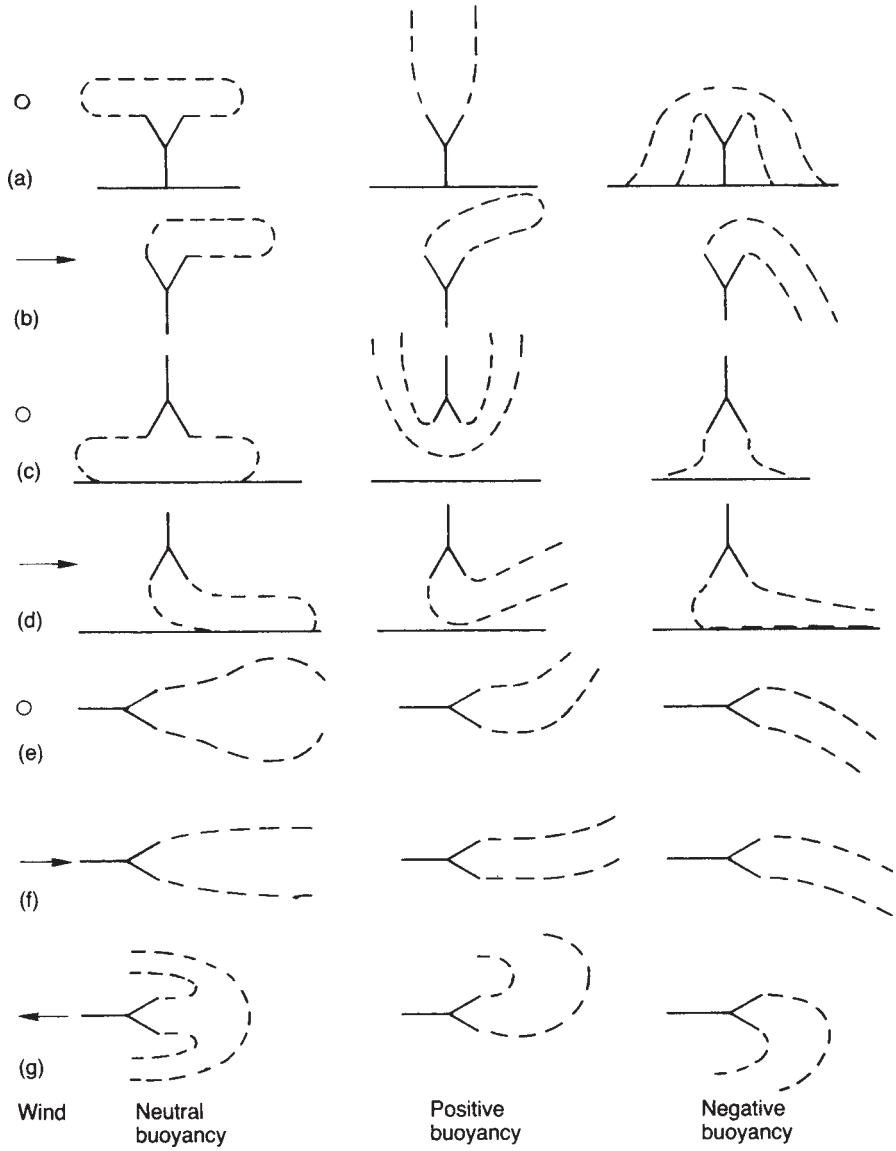


Figure 15.68 *Some jet and plume dispersion situations (after TNO, 1979): (a) upwards vertical release, zero wind speed; (b) upwards vertical release, finite wind speed; (c) downwards vertical release, zero wind speed; (d) upwards vertical release, finite wind speed; (e) horizontal release, zero wind speed; (f) horizontal release, wind speed in direction of release; and (g) horizontal release, wind speed in direction opposed to release*

15.20.2 Gas jets

The behaviour of a circular, or conical, turbulent momentum gas jet has been studied by Ricou and Spalding (1961), Long (1963) and Cude (1974b).

Long summarizes the empirical features of such a jet. The characteristics that he enumerates include the following. The jet is conical and apparently diverges from a virtual point source upstream of the orifice; dilution occurs by turbulent mixing; the time–mean velocity and time–concentration profiles are similar after 10 diameters and are approximately Gaussian; the concentration profile is wider than the velocity profile; the jet entrains air, but conserves its momentum, so that the momentum flux at any plane normal to the axis is constant.

Models of a momentum jet have been given by Ricou and Spalding, Long and Cude. The following treatment is based on these models, particularly that of Long. A momentum

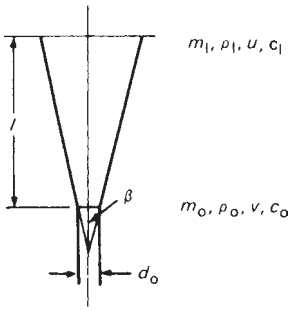


Figure 15.69 *Momentum jet*

jet is shown schematically in Figure 15.69. For such a jet the mass discharge flow is

$$m_o = \frac{\pi}{4} d_o^2 p_o u_o \qquad [15.20.1]$$

the mass balance is

$$m_x = \frac{\pi}{4} (2x \tan \beta) 2\rho_x u \qquad [15.20.2]$$

and the momentum balance is

$$\frac{m_x}{m_o} = \frac{u_o}{u} \qquad [15.20.3]$$

where d_o is the diameter of the outlet, m is the mass flow, u is the velocity of the gas, x is the axial distance from the outlet, β is the half-angle of the jet, ρ is the density of the gas and subscripts o and x denote the orifice and the mean value axial distance x, respectively. Then from Equations 15.20.1–15.20.3 the mass flow ratio is

$$\frac{m_x}{m_o} = k_1 \frac{x}{d_o} \left(\frac{\rho_x}{\rho_o} \right)^{1/2} \qquad [15.20.4]$$

with

$$k_1 = 2 \tan \beta \qquad [15.20.5]$$

In modelling a gas jet, it is necessary to distinguish for velocity u at distance x between the mean value (u_x), the value on the axis (u_{xo}) and the value at radial distance r (u_{xr}). A similar notation is used for concentration c and density η From Equation 15.20.4 the velocity ratio is

$$\frac{u_x}{u_o} = \frac{1}{k_1} \left(\frac{x}{d_o} \right)^{-1} \left(\frac{\rho_x}{\rho_o} \right)^{-1/2} \qquad [15.20.6]$$

The mean volumetric concentration is inversely proportional to the volumetric flow of the gas–air mixture and hence

$$\frac{c_x}{c_o} = \frac{1}{k_1} \left(\frac{x}{d_o} \right)^{-1} \left(\frac{\rho_x}{\rho_o} \right)^{1/2} \qquad [15.20.7]$$

where c is the volumetric concentration. Long proposes for the constant k_1 the value of 0.32 obtained by Ricou and Spalding.

If a Gaussian radial concentration profile is assumed, Equation 15.20.7 may be rewritten as

$$\frac{c_{xr}}{c_o} = k_2 \left(\frac{x}{d_o} \right)^{-1} \left(\frac{\rho_{xo}}{\rho_o} \right)^{1/2} \exp \left[- \left(\frac{k_3 r}{x} \right)^2 \right] \qquad [15.20.8]$$

where k_2 and k_3 are constants.

From the work of a number of experimenters Long proposes for constants k_2 and k_3 values of 6 and 5, respectively. The density η_{xo} is not readily calculated, but it is frequently set equal to the density of air (e.g. Cude, 1974b). The point is discussed by Gugan (1976).

The length of the jet may be obtained by combining Equations 15.20.3 and 15.20.4 to give

$$\frac{x}{d_o} = \frac{u_o}{k_1 u_x} \left(\frac{\rho_x}{\rho_o} \right)^{-1/2} \qquad [15.20.9]$$

The end of the jet is usually defined (e.g. Cude, 1974b) as the point at which the jet velocity u_x equals the wind speed w. Then

$$\frac{x_{tr}}{d_o} = \frac{u_o}{k_1 w} \left(\frac{\rho_x}{\rho_o} \right)^{-1/2} \qquad [15.20.10]$$

where x_{tr} is the length of the jet at the transition point and w is the wind speed. For the purpose of determining this transition in relatively still air, the wind speed is generally taken as 2 m/s.

As already mentioned, the axial gas concentration c_{xo} is found to be twice the mean gas concentration c_x:

$$c_{xo} = 2c_x \qquad [15.20.11]$$

The minimum discharge velocity of the jet to obtain a safe value c_s of the concentration c_{xo} may be obtained by combining Equations 15.20.7, 15.20.9 and 15.20.11 and so that

$$\frac{u_o}{u} = \frac{2c_o \rho_{xo}}{c_{xo} \rho_o} \qquad [15.20.12]$$

The behaviour of the momentum jet was studied experimentally by Ricou and Spalding (1961). In addition to air, they also used hydrogen, propane and carbon dioxide. As already mentioned, they obtained for the constant k_1 the value of 0.32. They verified Equation 15.20.4 up to 418 diameters. These authors also discuss the ratio of the widths of the concentration and velocity profiles and make the assumption that this has a value of 1.17.

In their theoretical analysis they point out that another feature of the momentum jet is that at high Reynolds number and uniform fluid density and at a distance along the axis that is large compared with the outlet diameter the mass flow m of entrained air is proportional to the axial distance x. They give the relations

$$\frac{dm}{dx} = k(M\rho_a)^{1/2} \qquad [15.20.13a]$$

$$\frac{m}{x} = k(M\rho_a)^{1/2} \qquad [15.20.13b]$$

with

$$M = M_o = \frac{\pi}{4} d_o^2 \rho_o u_o^2 \qquad [15.20.14]$$

where M is momentum flux and k is a constant. They give for k a value of 0.282.

For work on jets, Mecklenburgh (1985) introduces the air/fuel mass ratio θ. For this ratio

$$\theta = \left(\frac{1}{c_x} - 1\right)\frac{\rho_a}{\rho_x} \qquad [15.20.15]$$

$$u = \frac{u_o}{1+\theta} \qquad [15.20.16]$$

A set of equations for velocity ratio u_{xo}/u_o and the concentration ratio c_{xo}/c_o for circular and planar jets has been given by C.J. Chen and Rodi (1980). These are, for a circular jet

$$\frac{u_{xo}}{u_o} = 6.2\left(\frac{x}{d_o}\right)^{-1}\left(\frac{\rho_o}{\rho_a}\right)^{1/2} \qquad [15.20.17]$$

$$\frac{c_{xo}}{c_o} = 5\left(\frac{x}{d_o}\right)^{-1}\left(\frac{\rho_o}{\rho_a}\right)^{1/2} \qquad [15.20.18]$$

and for a planar jet

$$\frac{u_{cl}}{u_o} = 2.4\left(\frac{x}{d}\right)^{-1/2}\left(\frac{\rho_o}{\rho_a}\right)^{1/2} \qquad [15.20.19]$$

$$\frac{c_{cl}}{c_o} = 2\left(\frac{x}{d}\right)^{-1/2}\left(\frac{\rho_o}{\rho_a}\right)^{-1/2} \qquad [15.20.20]$$

where d is the width of the slot and the subscript cl denotes the centre line.

A set of equations for the velocity ratio u_m/u_o only for circular, planar and radial jets for air has been given by Rajaratnam (1976). These are, for a circular jet

$$\frac{u_m}{u_o} = 6.3\left(\frac{x}{d_o}\right)^{-1} \qquad [15.20.21]$$

for a planar jet

$$\frac{u_m}{u_o} = 3.5\left(\frac{x}{b_o}\right)^{-1} \qquad [15.20.22]$$

and for a radial jet

$$\frac{u_m}{u_o} = 3.5\frac{r_p}{b_o}\left(\frac{r}{b_o}\right)^{-1} \qquad [15.20.23]$$

where b_o is the half-width of the slot (for a planar or radial jet), r is the radial distance, r_p is the radius of the pipe or flange in which the outlet exists and the subscript m denotes the centre line, and hence the maximum.

Hess, Leuckel and Stoeckl (1973) have given relations for both subsonic and sonic gas jets. For the subsonic flow the condition is

$$\frac{P_v}{P_a} < \left(\frac{\gamma+1}{2}\right)^{\gamma/(\gamma+1)} \qquad [15.20.24]$$

At the exit plane after isentropic expansion

$$P_E = P_a \qquad [15.20.25]$$

$$T_E = T_v\left(\frac{P_a}{P_v}\right)^{(\gamma-1)/\gamma} \qquad [15.20.26]$$

$$\rho_E = \rho_v\left(\frac{P_a}{P_v}\right)^{1/\gamma} \qquad [15.20.27]$$

$$u_E = \left\{\frac{2\gamma}{\gamma-1} R T_v\left[1 - \left(\frac{P_a}{P_v}\right)^{(\gamma-1)/\gamma}\right]\right\} \qquad [15.20.28]$$

where P is the absolute pressure, R is the universal gas constant, T is the absolute temperature, γ is the ratio of the gas specific heats, and subscripts a, E and v denote atmospheric conditions, exit conditions and vessel conditions, respectively.

Some illustrative calculations on momentum jets have been given by Cude (1974b), Gugan (1976) and Mecklenburgh (1985).

15.20.3 Gas jets: sonic jets

The models just given apply to a gas jet with subsonic flow. A different treatment is necessary for sonic flow conditions. Models for underexpanded sonic jets have been reviewed by Ramskill (1985 SRD R302). The structure of an underexpanded sonic jet is shown in Figure 15.70.

As already mentioned, Hess, Leuckel and Stoeckl (1973) have also given a treatment for circular jets with sonic flow. For sonic flow the condition is

$$\frac{P_v}{P_a} \geq \left(\frac{\gamma+1}{2}\right)^{\gamma/(\gamma-1)} \qquad [15.20.29]$$

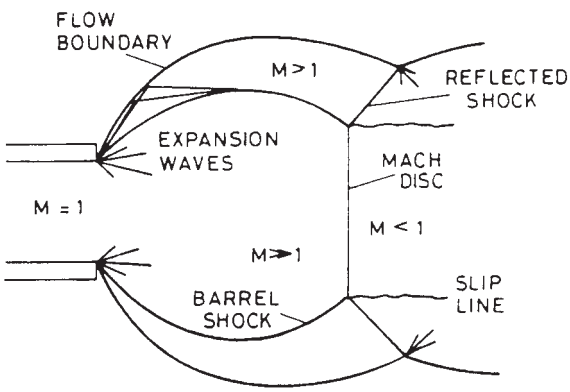


Figure 15.70 *Underexpanded momentum jet (Ewan and Moodie, 1986). M, Mach number (Reproduced by permission of Gordon and Breach Science Publishers, ©)*

At the exit plane, after isentropic expansion $P_E > P_a$, and the conditions are:

$$P_E = P_v\left(\frac{2}{\gamma+1}\right)^{\gamma/(\gamma-1)} \quad [15.20.30]$$

$$T_E = T_v\left(\frac{2}{\gamma+1}\right) \quad [15.20.31]$$

$$\rho_E = \rho_v\left(\frac{2}{\gamma+1}\right)^{\gamma/(\gamma-1)} \quad [15.20.32]$$

$$u_E = \left(\frac{2\gamma}{\gamma+1}RT_v\right)^{1/2} \quad [15.20.33]$$

At the shock plane downstream of the exit, Hess, Leuckel and Stoeckl define an equivalent diameter:

$$D_s = \frac{2M_s}{(\pi\rho_s M_s u_s)^{1/2}} \quad [15.20.34]$$

where D is the diameter, M is the mass flow and subscript s denotes the shock plane.

It has been shown by Ramskill that the equivalent diameter may also be expressed as

$$D_s = D_N\left[\left(\frac{P_v}{P_a}\right)^{(\gamma-1)/\gamma}\right]^{1/2} \quad [15.20.35]$$

where subscript N denotes the nozzle.

The term 'equivalent diameter' is generally used in work on underexpanded jets and is used here also. It should not be confused with the equivalent diameter used to relate non-circular to circular orifices and ducts.

For the velocity at this plane it is assumed that all the excess pressure goes to increase the momentum of the jet:

$$u_s = u_E + \frac{P_E - P_a}{\rho_E u_E} \quad [15.20.36]$$

Also

$$\rho_s = \frac{\rho_E u_E D_N^2}{u_s D_s^2} \quad [15.20.37]$$

Another model based on the apparent diameter is that given in the TNO *Yellow Book* (1979). The equations of this model are as follows. In the model use is made of gas densities normalized with respect to the density of air, these densities being denoted by a prime. The radial velocity and concentration are expressed as

$$\frac{u_{xy}}{u_m} = \exp(-b_1 b_3^2) \quad [15.20.38]$$

$$\frac{j_{xy}}{j_m} = \exp(-b_2 b_3^2) \quad [15.20.39]$$

with

$$b_3 = y/x'' \quad [15.20.40]$$

$$x'' = x + x' \quad [15.20.41]$$

where j is the volumetric concentration of the gas, u is the velocity of the gas, x is the axial distance from the outlet, x' is the distance between the virtual source and the outlet, y is the radial distance, b_1 and b_2 are constants, b_3 is defined by Equation 15.20.40 and subscript m denotes the centre line, and hence maximum, and subscript xy denotes point (x, y).

The following relations are given for the constants b_1 and b_2

$$b_1 = 50.5 + 48.2\rho'_{ga} - 9.95(\rho'_{ga})^2 \quad [15.20.42]$$

$$b_2 = 23 + 41\rho'_{ga} \quad [15.20.43]$$

where ρ'_{ga} is the normalized density of the gas at atmospheric conditions.

The equivalent diameter d_{eq} is defined as

$$d_{eq} = d_o\left(\frac{\rho'_{go}}{\rho'_{oeq}}\right)^{1/2} \quad [15.20.44]$$

where ρ'_{go} is the normalized density of the gas at the outlet and ρ'_{oeq} is the normalized density of the gas at the equivalent diameter. The velocity ratio is

$$\frac{u_m}{u_o} = \frac{b_1}{4}\left(\frac{d_{eq}}{x''}\right)^2\left[0.32\frac{x}{d_{eq}}\frac{\rho'_{ga}}{\left(\rho'_{oeq}\right)^{1/2}} + 1 - \rho'_{ga}\right]\frac{\rho'_{oeq}}{\rho'_{ga}} \quad [15.20.45]$$

and the concentration ratio is

$$\frac{j_m}{j_o} = \frac{(b_1+b_2)/b_1}{0.32\ (x/d_{eq})(\rho'_{ga}/\rho'_{oeq}) + 1 - \rho'_{ga}} \quad [15.20.46]$$

Ewan and Moodie (1986) have given a treatment of underexpanded sonic jets based on the work of Kleinstein (1964). For fully expanded supersonic jets Kleinstein obtained the relation

$$\frac{u_m}{u_n} = 1 - \exp\left[\frac{1}{k(\rho_a/\rho_e)^{1/2}(z/r_n) - x_c}\right] \quad [15.20.47]$$

where k is a compressible eddy coefficient, r_n is the equivalent radius, u is the velocity of the gas, x_c is a dimensionless core length, z is the distance along the axis from the outlet and subscripts e, m and n denote the exit, the maximum and the nozzle, respectively.

They also quote the following equation given by Warren (1957) and based on a different analysis for the radial variation of velocity in fully developed flow

$$\frac{u}{u_m} = \exp\left\{-\ln\left[2\left(\frac{r}{r_{0.5}}\right)^2\right]\right\} \quad [15.20.48]$$

where $r_{0.5}$ is the radius at which the velocity is half the centre line value.

Ewan and Moodie have adapted the Kleinstein model to an underexpanded jet by introducing the equivalent diameter. For the expansion

$$N = \frac{P_v}{P_a} \quad [15.20.49]$$

$$P_e = P_v\left(\frac{2}{\gamma+1}\right)^{\gamma/(\gamma-1)} \quad [15.20.50]$$

$$\rho_e = \rho_v\left(\frac{2}{\gamma+1}\right)^{1/(\gamma-1)} \quad [15.20.51]$$

$$\rho_{eq} = \rho_e\left(\frac{P_a}{P_e}\right) \quad [15.20.52]$$

where N is the ratio of the vessel pressure to atmospheric pressure and subscripts eq and v denote equivalent and vessel, respectively. Equivalent conditions are based on the sonic jet at ambient pressure, nozzle exit temperature and nozzle mass flow. They obtain for the velocity ratio

$$\frac{u_m}{u_n} = 1 - \exp\left[\frac{1}{k(\rho_a/\rho_{eq})^{1/2}(z^*/r_{eq}) - x_c}\right] \quad [15.20.53]$$

with

$$k = 0.08(1 - 0.16\,\mathrm{Ma}) \quad [15.20.54]$$

$$z^* = z - 2z_b \quad [15.20.55]$$

$$z_b = 0.77\,d_n + 0.068\,d_n^{1.35}N \quad [15.20.56]$$

where d is the diameter, Ma is the Mach number, z_b, is the barrel length and z^* is the modified axial distance. The unit of length in Equations 15.20.55 and 15.20.56 is millimetres.

The equivalent diameter d_{eq} is derived as follows. For continuity

$$\rho_e u_n A_e = \rho_{eq} u_{eq} A_{eq} \quad [15.20.57]$$

where A is the cross-sectional area of flow. But

$$\rho u = \frac{Pu}{RT} \quad [15.20.58a]$$

$$= \frac{Pu}{(\gamma RT)^{1/2}}\left(\frac{\gamma}{RT}\right)^{1/2} \quad [15.20.58b]$$

$$= P\,\mathrm{Ma}\left(\frac{\gamma}{R}\right)^{1/2}\frac{1}{T^{1/2}} \quad [15.20.58c]$$

Then from Equation 15.20.57

$$\frac{\rho_e u_n}{\rho_{eq} u_{eq}} = \frac{A_{eq}}{A_e} = \frac{P_e}{P_a} \quad [15.20.59]$$

Hence

$$d_{eq} = d_n\left(\frac{P_e}{P_a}\right)^{1/2} \quad [15.20.60]$$

In calculating the equivalent diameter the authors apply to the flow a discharge coefficient C_D so that Equation 15.20.60 becomes

$$d_{eq} = d_n\left(\frac{C_D P_e}{P_a}\right)^{1/2} \quad [15.20.61]$$

They quote the value of C_D of 0.85 assumed by Birch *et al.* (1984). For the concentration ratio they obtain

$$\frac{m_{cl}}{m_e} = 1 - \exp\left[\frac{1}{k'(\rho_a/\rho_{eq})^{1/2}(z^*/r_{eq}) - x_c}\right] \quad [15.20.62]$$

where k' is another eddy viscosity coefficient and m is the mass fraction. The constant k' has the value 0.104.

15.20.4 Liquid jets

It is also necessary to consider liquid jets. The 'throw' of a liquid jet can be quite large. Such a jet may reach beyond the limit of the area classification zone or may jump over a bund.

The simplest treatment of a liquid jet is based on the assumption that the jet suffers no drag and does not disintegrate. For a jet at ground level, as shown in Figure 15.71(a) the motion in the horizontal direction is given by

$$\frac{dx}{dt} = u\cos\alpha \quad [15.20.63]$$

where t is time, u is the horizontal velocity of the liquid, x is the horizontal distance and α is the angle between the jet and the horizontal. At $t = 0$, $x = 0$ and hence

$$x = ut\cos\alpha \quad [15.20.64]$$

For motion in the vertical direction

$$\frac{d^2z}{dt^2} = -g \quad [15.20.65]$$

Integrating Equation 15.20.65 gives

$$\frac{dz}{dt} = -gt + c \quad [15.20.66]$$

where g is the acceleration due to gravity, z is the vertical distance and c is a constant of integration. At $t = 0$, $dz/dt = u\sin\alpha$ and hence

$$\frac{dz}{dt} = u\sin\alpha - gt \quad [15.20.67]$$

At $t = 0$, $z = 0$ and hence

$$z = ut\sin\alpha - \frac{1}{2}gt^2 \quad [15.20.68]$$

The jet returns to the ground at $t = t$, $z = 0$ and hence

$$t = \frac{2u\sin\alpha}{g} \quad [15.20.69]$$

Then from Equations 15.20.64 and 15.20.69 the horizontal distance travelled is

$$x = \frac{u^2\sin^2\alpha}{g} \quad [15.20.70]$$

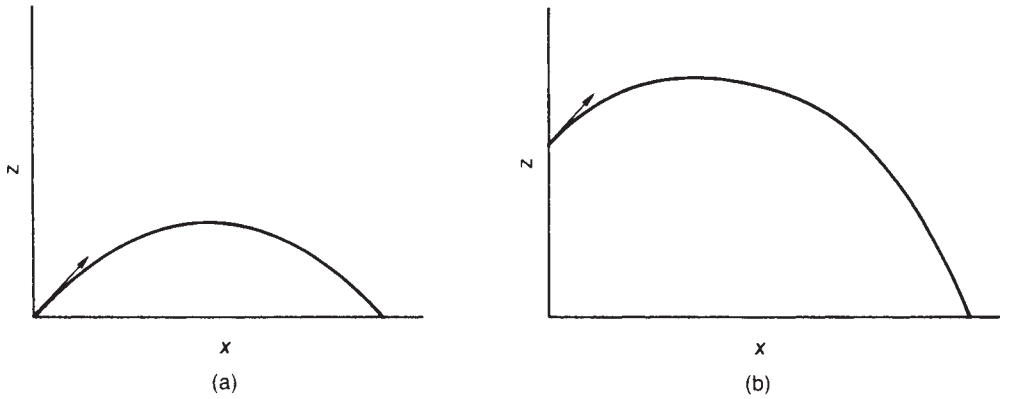


Figure 15.71 *Travel range of a liquid jet, neglecting air resistance and break up: (a) jet from ground level source; (b) jet from elevated source*

The maximum distance of travel x_{max} occurs at $\alpha = 45°$ and is

$$x_{max} = \frac{u^2}{g} \qquad [15.20.71]$$

where the subscript max denotes maximum.

For an elevated jet, as shown in Figure 15.71(b), the jet returns to the ground at $t = t$, $z = -l$ and, following the same approach, it may be shown that

$$x = \frac{u^2}{g}\left\{\frac{\sin 2\alpha}{2} + \left[\left(\frac{\sin 2\alpha}{2}\right)^2 + \frac{2\,lg\cos 2\alpha}{u^2}\right]^{1/2}\right\} \qquad [15.20.72]$$

where l is the height above the ground of the outlet and z is the vertical distance above the outlet. Equation 15.20.72 reduces to Equation 15.20.70 for $l = 0$.

For a horizontal elevated jet the following simple treatment is applicable.

$$x = ut \qquad [15.20.73]$$

$$l = \frac{1}{2}gt^2 \qquad [15.20.74]$$

From Equations 15.20.73 and [15.20.74]

$$x = u\left(\frac{2l}{g}\right)^{1/2} \qquad [15.20.75]$$

Equation 15.20.72 reduces to Equation 15.20.75 for $\alpha = 0$.

In practice, the travel distance of the liquid jet will be less than that predicted by the expressions just given, because the jet is subject to air resistance and to disintegration. It is often assumed that the actual travel distance is halved by these factors.

A treatment that takes air resistance into account is as follows. It is assumed that the resistance is proportional to the velocity. Then for motion in the horizontal direction

$$\frac{d^2x}{dt^2} = -k\frac{dx}{dt} \qquad [15.20.76]$$

Following the same approach as previously, it can be shown

$$x = \frac{u\cos\alpha}{k}[1 - \exp(-kt)] \qquad [15.20.77]$$

with

$$t = \frac{(ku\sin\alpha + g)[1 - \exp(-kt)]}{kg} \qquad [15.20.78]$$

where k is a constant representing air resistance.

The disintegration of a liquid jet under air resistance has been studied by a number of workers including Rayleigh (1932), van de Sande and Smith (1976) and Engh and Larsen (1979). The following treatment is based on the work of the latter.

The disintegration of a jet is determined by the Weber number We, which gives the ratio of the momentum to the surface tension forces. The Weber number is

$$\mathrm{We} = \frac{\rho u^2 d}{2\sigma} \qquad [15.20.79]$$

where d is the diameter of the jet, u is the velocity of the jet and σ is the surface tension.

The propagation of a disturbance in a liquid jet leading to its break up was studied by Lord Raleigh. In his model the amplitude δ of a surface disturbance of initial amplitude δ_o increases exponentially with time t:

$$\delta = \delta_o \exp(\alpha t) \qquad [15.20.80]$$

where α is a constant. When the amplitude δ of the disturbance is equal to the jet radius a, disintegration into drops begins. Drops are therefore formed at time

$$t = \ln(a/\delta_o)/\alpha \qquad [15.20.81]$$

Then the break-up length Z is

$$Z = ut \qquad [15.20.82]$$

$$= u\ln(a/\delta_o)/\alpha \qquad [15.20.83]$$

From this starting point Engh and Larsen derive the following expression for break-up length:

$$\frac{Z}{d} = 1.03 \ln(a/\delta_o)(2\mathrm{We})^{1/2} \qquad [15.20.84]$$

For an inviscid jet it has been found that

$$\ln(a/\delta_o) \approx 12 \qquad [15.20.85a]$$

Other values of the term $\ln(a/\delta_o)$ have been given by various workers.

Engh and Larsen conducted experiments on water and molten steel. They state that the term $\ln(a/\delta_o)$ decreases with increasing length/diameter (l/d) ratio of the nozzle, tending for $l/d \geq 13$ to a value

$$\ln(a/\delta_o) \approx 4 \qquad [15.20.85b]$$

They also state that for water their results give

$$\frac{z}{d} \approx 100 \qquad [15.20.86]$$

The relations for jet travel and for jet disintegration depend on different parameters, but for many cases of practical interest the jet will start to disintegrate within a short distance of the orifice.

15.20.5 Two-phase jets

Work on two-phase jets includes that by R. Brown and York (1962), Bushnell and Gooderum (1968), Hetsroni and Sokolov (1971), Gyarmathy (1976), Suzuki *et al.* (1978), Melville and Bray (1979a,b), Koestel, Gido and Lamkin (1980), and Tomasko, Weigand and Thompson (1981a,b). A review has been given by Appleton (1984 SRD R303). Two-phase jets may be classified as non-flashing or flashing.

A liquid jet in air tends to disintegrate. Break up may occur due either to air resistance or to vapour bubble formation. The break up of a non-flashing jet due to air resistance was considered in the previous section.

A two-phase non-flashing jet consists of a gas flow with entrained droplets. Characteristics of interest are: for the gas phase, the centre line and the radial velocities; and for the liquid phase, the radial mass flux of the droplets. Relations for these may be found in the work of Hetsroni and Sokolov (1971) and Melville and Bray (1979a,b).

It is two-phase flashing jets, however, which are of prime interest here. An account of such jets is given in Section 15.21.

15.20.6 Plumes

The principal types of jet and plume that occur are illustrated in Figure 15.72. Figure 15.72(a) shows a non-buoyant jet, or pure jet, or simply a jet. Figure 15.72(b) shows a pure plume with no momentum. This figure, therefore, shows as the source not a discharge orifice, but a heated surface. Figure 15.72(c) shows a buoyant plume, with some initial momentum, or forced plume. Figure 15.72(d) shows a negatively buoyant plume.

Accounts of plumes are given in *Plume Rise* (G.A. Briggs, 1969), *Vertical Turbulent Buoyant Jets* (C.J. Chen and Rodi, 1980) and *Handbook on Atmospheric Diffusion* (S.R. Hanna, Briggs and Hosker, 1982). Work on plumes includes that by O.G. Sutton (1950), Yih (1951), Rouse, Yih and Humphreys (1952), B.R. Morton (1959, 1961), Long (1963), Schmidt (1965), J.S. Turner (1966), G.A. Briggs (1965, 1968, 1976), Ooms (1972), Cude (1974a,b), Ooms, Mahieu and Zelis (1974), Davidson and Slawson (1982) and Frick (1984).

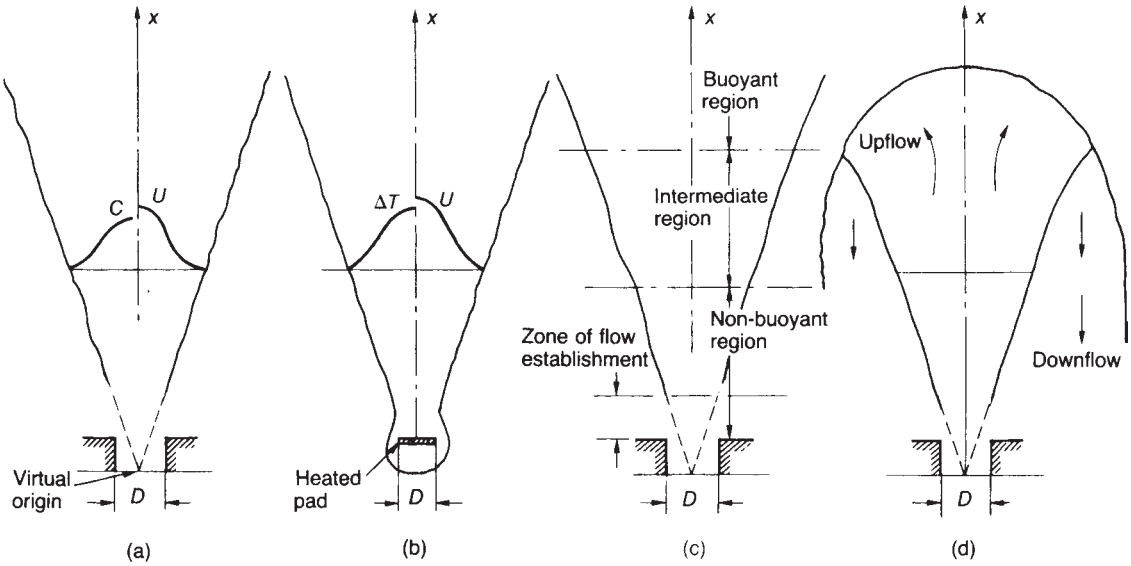


Figure 15.72 *Principal types of jet and plume (after C.J. Chen and Rodi, 1980): (a) pure, non-buoyant jet; (b) pure plume; (c) buoyant jet (forced plume); (d) negatively buoyant jet*

Most models of plumes deal with the case of an initial jet in which the momentum decays so that the emission undergoes transition to a buoyant plume. Much of the work on plumes relates to elevated emissions from stacks and is concerned primarily with pollution rather than with hazards. Fundamental quantities in models of dispersion of forced and buoyant plumes are the momentum and buoyancy fluxes.

The momentum flux at the outlet orifice is

$$M_o = \pi r_o^2 \rho_o u_o^2 \qquad [15.20.87]$$

where M is the momentum flux, r_o the radius of the outlet, u is the velocity of the gas, ρ is the density and subscript o denotes the outlet. The buoyancy flux at the outlet is

$$F_o = \pi r_o^2 g(\rho_a - \rho_o)u_o \qquad [15.20.88]$$

where F is the buoyancy flux and subscript a denotes air.

Use is frequently made of momentum and buoyancy fluxes which are normalized with respect to density, for example,

$$M_o = \pi r_o^2 \frac{\rho_o}{\rho_a} u_o^2 \qquad [15.20.89]$$

$$F_o = \pi r_o^2 g \frac{\rho_a - \rho_o}{\rho_a} u_o \qquad [15.20.90]$$

This then gives for momentum and buoyancy the SI units m^4/s^2 and m^4/s^3, respectively. In addition, π is sometimes omitted from the definitions of momentum and buoyancy.

In expressions for buoyancy flux, use is sometimes made of the relation

$$\frac{\rho_a - \rho}{\rho_r} = \beta(T - T_a) \qquad [15.20.91]$$

where β is the coefficient of cubical expansion ($\approx 1/T_r$) and subscript r denotes the reference.

The measure of the ratio of the momentum forces to the buoyancy forces is given by the Froude number Fr. The Froude number is defined as

$$\mathrm{Fr} = \frac{u}{(gl)^{1/2}} \qquad [15.20.92]$$

where l is a characteristic length.

In the context of plumes, the Froude number is more usually defined as

$$\mathrm{Fr} = \frac{u}{(g d_o(\rho_a - \rho_o/\rho_a))^{1/2}} \qquad [15.20.93]$$

where d_o is the diameter of the outlet.

Use is also sometimes made of the following Froude group (e.g. C.J. Chen and Rodi, 1980):

$$\mathrm{Fr} = \frac{u^3}{g d_o((\rho_a - \rho_o)/\rho_a)} \qquad [15.20.94]$$

In some definitions of the Froude number the divisor of the term $\rho_a - \rho_o$ is ρ_o rather than ρ_a. The Froude number is a criterion for the transition from momentum control to buoyancy control.

Some principal characteristics of a plume have been described by Long (1963). He summarizes the empirical features of a buoyant plume as follows. Under turbulent conditions the plume is conical and apparently diverges from an equivalent point source, the position of the point source depending on the point of transition from laminary to turbulent flow; the time–mean velocity and time–concentration profiles are similar and are approximately Gaussian.

Under adiabatic conditions buoyancy is conserved within the plume and the buoyancy flux remains constant with distance. The momentum flux therefore increases with distance. For the distance within which turbulence sets in for a pure plume Long gives the following relation based on the work of Yih (1951) on plumes from cigarettes:

$$x_{lt} = \left(\frac{\mu^3}{\rho_a^2 Q \Delta\rho_o g}\right)^{1/2} \times 10^5 \qquad [15.20.95]$$

where Q is the volumetric flow, x_{lt} is the distance for transition from laminar to turbulent flow, μ is the viscosity and Δ is the density difference. For most plumes of practical interest this transition distance is very short.

For the concentration ratio and radial distribution of a plume, Long gives:

$$\frac{c_{xr}}{c_o} = k_4 \left(\frac{Q^2 \rho_a}{\Delta\rho_o g x^5}\right)^{1/3} \exp\left[\left(\frac{k_5 r}{x}\right)^2\right] \qquad [15.20.96]$$

where c is the volumetric concentration, r is the radial distance, k_4 and k_5 are constants, and subscript xr denotes at the axial distance x and radial distance r.

Long suggests that, from the work of Yih, the time mean values of the constants k_4 and k_5 may be taken as 11 and 8.4, respectively.

For a forced plume with both momentum and buoyancy, Long proposes as the criterion of transition from momentum to buoyancy control the following modified Froude number:

$$\mathrm{Fr} = \frac{\rho_o^{3/2} u_o^2}{\rho_a^{1/2} \Delta\rho_o g d_o} \qquad [15.20.97]$$

He obtains an approximate value for the transition point by equating Equations 15.20.8 and 15.20.9. Then the transition point occurs at $2.4\mathrm{Fr}^{1/2}$ diameters from the source. This criterion is confirmed by the work of Ricou and Spalding (1961) in that the point of equal entrainment in the jet and plume regimes occurs at $2.3\,\mathrm{Fr}^{1/2}$ diameters. The jet persists at least to $0.5\,\mathrm{Fr}^{1/2}$ diameters and the plume is fully developed beyond $3\,\mathrm{Fr}^{1/2}$ diameters.

With the exception of last point, the treatment just given applies to a pure plume in a still atmosphere. In many practical applications the case to be considered is more complex. The emission may have both momentum and buoyancy, starting off as a jet and undergoing transition to a plume. The plume may be affected by the various weather conditions. In addition, the plume may have heavy gas characteristics requiring special treatment.

15.20.7 Plumes in atmospheric turbulence

A different situation occurs where a higher wind speed results in atmospheric turbulence. If conditions are such

that the discharge momentum and buoyancy effects are negligible relative to atmospheric turbulent diffusion, the dispersion may be estimated using the methods described in Section 15.10 such as the Sutton and Pasquill–Gifford models.

Using the Sutton model, Long (1963) gives the following equations for an elevated vent, derived from Equation 15.16.2(c) The full equation is

$$\chi(x,y,z) = \frac{Q}{\pi C_y C_z u x^{2-n}} \exp\left(-\frac{y^2}{C_y^2 x^{2-n}}\right) \times \left[\exp\left(-\frac{z^2}{C_z^2 x^{2-n}}\right) + \exp\left(-\frac{(z+2h)}{C_z^2 x^{2-n}}\right)^2\right] \quad [15.20.98a]$$

and that for the axial concentration at ground level ($y = z = 0$)

$$\chi(x,0,0) = \frac{Q}{\pi C_y C_z u x^{2-n}} \left[1 + \exp\left(\frac{4h^2}{C_z^2 x^{2-n}}\right)\right] \quad [15.20.98b]$$

where x, y and z are the downwind, crosswind and vertical distances, C is the diffusion parameter, h is the height of the outlet, Q is the volumetric flow from the outlet, u is the wind speed, χ is the concentration, n is the diffusion index and subscripts x and y denote downwind and crosswind, respectively. The origin of the coordinates in Equation 15.20.98, but in this equation only, is the outlet of the vent. The maximum ground level concentration χ_{mgl} is

$$\chi_{mgl} = 0.234 \frac{Q}{uh^2} \frac{C_z}{C_y} \quad [15.20.99]$$

The distance χ_{mgl} from the source at which the maximum ground level concentration occurs is

$$\chi_{mgl} = \left(\frac{h^2}{C_z^2}\right)^{1/(2-n)} \quad [15.20.100]$$

Values of the index n and of the generalized diffusion parameters C_y and C_z for the first 10 m above ground are given by Long as follows:

Stability condition	n	C_y ($m^{n/2}$)	C_z ($m^{n/2}$)
Large lapse rate	1/5	0.37	0.21
Neutral condition	1/4	0.21	0.12
Moderate inversion	1/3	0.13	0.08
Large inversion	1/2	0.11	0.06

The Sutton equation (15.20.98) was not originally intended for use over the very short distances involved in vent calculations, and its use demands some justification. This point has been discussed by Long, who concludes that the use of the equation is justified. A further discussion of this aspect is given in Section 15.48.

15.20.8 Plumes with negative buoyancy

In many practical situations the emission of interest is that of a dense gas. Plumes with negative buoyancy are therefore of particular interest. A study of a plume with negative buoyancy has been made by J.S. Turner (1966). He carried out experiments in which a dense liquid was injected into a less dense one. The flow pattern obtained is illustrated in Figure 15.72(d).

For this case Turner obtained the following expression for maximum plume rise z_{max}:

$$z_{max} = C \frac{M^{3/4}}{F^{1/2}} \quad [15.20.101]$$

with

$$F = \pi r_o^2 g \left(\frac{\rho_o - \rho_1}{\rho_1}\right) u_o \quad [15.20.102]$$

$$M = \pi r_o^2 u_o^2 \quad [15.20.103]$$

where F is the buoyancy flux, M is the momentum flux, u_o is the outlet velocity of the gas, ρ_o is the density of the outlet gas, ρ_1 is the density of ambient fluid and C is a constant. Turner gives the value of the constant C as 1.85.

15.20.9 Cude model

A model for jets and plumes has been given by Cude (1974b). The Cude model distinguishes between a jet, a buoyant plume, a negatively buoyant plume and a buoyant plume at low wind speed.

Plume in still air

A treatment of the rise or fall of a buoyant plume in low wind speed conditions has been given by Bosanquet (Bosanquet 1935, 1957; Bosanquet and Pearson, 1936). In the simplified form given by Cude, the rise or fall of the plume is

$$i = -wAF_1(x_1) \quad [15.20.104]$$

with

$$A = 9.42 \frac{gN}{w^4} \frac{\rho_g - \rho_a}{\rho_a} \quad [15.20.105]$$

$$x_1 = t_1/A \quad [15.20.106]$$

where A is a time parameter, $F_1(x_1)$ is a function that expresses the change in density of the plume as a result of dilution by air, i is the rise or fall of the plume at a distance wt_1 from the source, N is the volumetric flow from the outlet, t_1 is an arbitrarily chosen time interval, w is the wind speed and ρ_g is the density of the gas at the outlet. The time t_1 is taken by Cude as 100 s.

If the gas density is greater than that of air, the plume falls and i has a negative numerical value, while if the gas density is less than that of air the plume rises and i has a positive value.

The function $F_1(x_1)$ is a complicated one. Some values are

x_1	F_1	x_1	F_1
$<10^{-3}$	$1.0543 x_1^{0.75}$	10	2.33
10^{-3}	0.0059	10^2	4.50
10^{-2}	0.0323	10^3	6.79
10^{-1}	0.170	10^4	9.09
1	0.767	$>10^4$	$= \ln x_1 - 0.12$

Plume in atmospheric turbulence

For conditions of atmospheric turbulence with higher wind speeds Cude gives the following equations. For the axial concentration p_a from an elevated source

$$p_a = \frac{5.82J}{wx^{1.75}} \quad [15.20.107]$$

for the maximum ground level concentration p_{mgl}

$$p_{mgl} = \frac{0.234J}{w(H+l)^2} \quad [15.20.108]$$

and for the distance x_{mgl} at which the maximum ground level concentration occurs

$$x_{mgl} = 5.3(H+l)^{1.14} \quad [15.20.109]$$

where H is the height of the outlet (m), J is the volumetric flow from the outlet referred to the ambient temperature (m^3/s), l is the height of the jet (and of the horizontal axis of the plume above the outlet) (m), p_a is the concentration of gas along the axis at a distance x (mole fraction), p_{mgl} is the maximum ground level concentration of the gas (mole fraction), w is the wind speed (m/s), x is the downwind distance (m) and x_{mgl} is the distance at which the maximum ground level concentration occurs (m).

Momentum jet

For a momentum jet the model given by Cude is that already described in Equations 15.20.1–15.20. The height of the jet at which transition occurs is calculated as follows. It is assumed that at the transition point the mass flow of the gas–air mixture m_1 can be approximated by the mass flow of air m_a

$$m_1 \approx m_a \quad [15.20.110]$$

and that the velocity of the jet u is equal to that of the wind w

$$u \approx w \quad [15.20.111]$$

Then for still air, substituting in Equation 15.20.4 for d_o from Equation 15.20.1 and for m_1 from Equation 15.20.110

$$\frac{m_a}{l} = k_1 k_6 (m_o v)^{1/2} \quad [15.20.112a]$$

$$= k_1 k_6 \psi^{1/2} \quad [15.20.112b]$$

with

$$k_6 = \left(\frac{\pi p_1}{4}\right)^{1/2} \quad [15.20.113]$$

$$\psi = m_o v \quad [15.20.114]$$

where m_o is the mass flow at the outlet, v is the velocity of the gas at the outlet, ψ is the momentum flux in the still air, ρ_1 is the density of the jet at distance l, and k_6 is a constant.

Forced plume in wind

For a momentum jet that undergoes transition to a plume in a wind, Cude gives the following treatment. The situation is illustrated in Figure 15.73. The transition from momentum to buoyancy control is obtained as follows. For windy

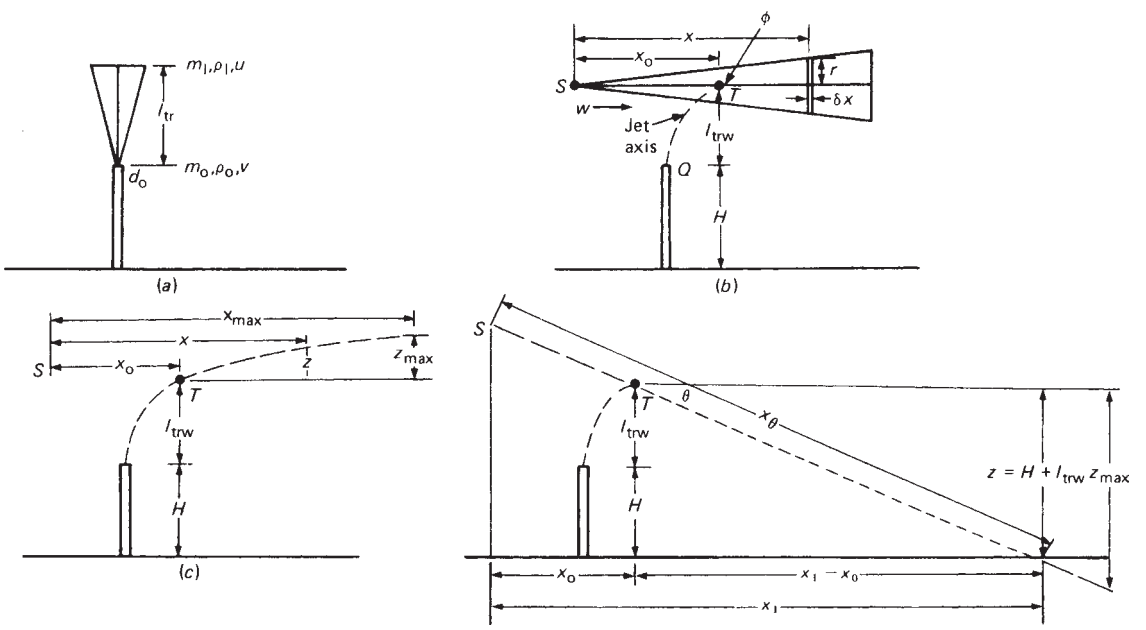


Figure 15.73 *Cude model of dispersion as jet and plumes from a stack (after Cude, 1977): (a) turbulent momentum jet; (b) and (c) buoyant plumes; (d) negatively buoyant plume with steep descent*

conditions the momentum flux is a vector quantity. In this treatment it is assumed that

$$\psi_w = \left[(m_o v)^2 + (m_a w)^2\right]^{1/2} \quad [15.20.115]$$

where ψ_w is momentum flux in windy conditions. But from Equations 15.20.3, 15.20.110 and 15.20.111

$$\frac{m_o v}{m_a w} = 1 \quad [15.20.116]$$

Hence from Equations 15.20.114–15.20.116

$$\psi_w = 2^{1/2}\psi \quad [15.20.117]$$

Then, since from Equation 15.20.112b the length of the jet is inversely proportional to the root of the momentum flux, the transition heights of the jet in still air conditions l_{tr} and in windy conditions l_{trw} are related as follows:

$$l_{trw} = \frac{l_{tr}}{2^{1/4}} = \frac{l_{tr}}{1.2} \quad [15.20.118]$$

The following relation is given by Cude for the horizontal displacement of the transition point x_{trw}:

$$x_{trw} \approx 0.5\, l_{trw} \quad [15.20.119]$$

The height reached by the plume from the transition point is calculated as follows. It is assumed that, as shown in Figure 15.73(b), there is a virtual source for the plume at point S that is a distance x_o upwind from the transition point T. This assumption allows for the mixing effect of the jet. The distance x_o is that which would be necessary to achieve the same concentration at the transition point if the mixing were done by the wind. Then, consider the element δx in Figure 15.73(b):

Volume of element $= \pi r^2 \delta x$

Volume of pure gas in element $= Q\delta x/w$

Volume of air in element $= \pi r^2 \delta x - Q\delta x/w$

Mass of pure gas in element $= Q\rho_o \delta x/w$

Mass of air in element $= \pi r^2 \rho_a \delta x - Q\rho_a \delta x/w$

Mass of air displaced by element $= \pi r^2 \rho_a \delta x$

$$\text{Buoyancy force on element} = g[\pi r^2 \rho_a \delta x - (\pi r^2 \rho_a \delta x - Q\rho_a \delta x/w) - Q\rho_o \delta x/w] = \frac{gQ\delta x}{w}(\rho_a - \rho_o)$$

where Q is the volumetric flow of the gas at the outlet, r is the radius of the plume and x is the downwind distance from the virtual source.

The rising plume experiences a resistance due to the shear stress in the air adjacent to it. Equating the buoyancy force and the shear stress

$$\frac{gQ\delta x}{w}(\rho_a - \rho_o) = 2\pi r \delta x u_b^2 \rho_a D_c \quad [15.20.120]$$

where D_c is the drag coefficient and u_b is the buoyancy, or upward, velocity of the plume.

But

$$r = x \tan\phi \quad [15.20.121]$$

where ϕ is the angle between the axis and the edge of the plume, or half-angle of plume. Hence Equation 15.20.120 can be rearranged to give

$$u_b = k_7 x^{-1/2} \quad [15.20.122]$$

with

$$k_7 = \left(\frac{gQ}{2\pi D_c w \tan\phi}\frac{\rho_a - \rho_o}{\rho_a}\right)^{1/2} \quad [15.20.123]$$

The half-angle of a plume from a stack is generally 5° or 6° so that $\tan\phi \approx 1$. The drag coefficient D_c is estimated by Cude from the work of Bodurtha, Palmer and Walsh (1973) as 0.4.

The treatments given by Cude for rising and for falling plumes are slightly different. The condition for a rising plume is $\rho_o < \rho_a$. The treatment for a rising plume shown in Figure 15.73(c) is as follows. The rise of the plume is given by

$$dz = \frac{u_b dx}{w} \quad [15.20.124a]$$

$$= \frac{k_7 x^{-1} dx}{w} \quad [15.20.124b]$$

where z is the vertical distance above the transition point. Integrating Equation 15.20.124 with the boundary conditions

$$z = 0, \quad x = x_o$$

gives

$$z = \frac{2k_7}{w}\left(x^{1/2} - x_o^{1/2}\right) \quad [15.20.125]$$

The maximum rise z_{max} of a plume occurs at a distance x_{max} where

$$x_{max} = k_8 w + x_o \quad [15.20.126]$$

where k_8 is a constant. The value of the constant k_8 may be obtained from the observation that a plume generally reaches its maximum rise after 200 s so that $k_8 = 200$. Then from Equation 15.20.125

$$z_{max} = \frac{2k_7}{w}\left(x_{max}^{1/2} - x_o^{1/2}\right) \quad [15.20.127]$$

The distance x_o is obtained from Equation 15.20.107:

$$x_o = \left(\frac{5.82J}{w p_a}\right)^{1.75} \quad [15.20.128]$$

The concentration p_a is, in this case, the concentration on the axis at the transition point and, assuming that the axial concentration is twice the mean concentration in the jet,

$$p_a = \frac{2M_a m_o}{M m_a} \quad [15.20.129]$$

$$= \frac{2M_a \omega}{Mv} \quad [15.20.130]$$

where M is the molecular weight of the gas and M_a is the molecular weight of the air.

The total effective height h_{pl} reached by the plume is thus

$$h_{pl} = H + l_{trw} + z_{max} \quad [15.20.131]$$

The maximum ground level concentration p_{mgl} is calculated from an equation similar to Equation 15.20.108, using the total effective height of the plume:

$$p_{mgl} = \frac{0.234J}{wh_{pl}^2} \quad [15.20.132]$$

and the distance x_{mgl} at which the maximum ground level concentration occurs is calculated from an equation similar to Equation 15.20.109:

$$x_{mgl} = 5.3h_{pl}^{1.14} \quad [15.20.133]$$

The treatment for a falling plume, which is an approximate one, is as follows. The condition for a falling plume is $\rho_o > \rho_a$. As before, calculations are made of the distances z and z_{max}, but in this case the quantities denote vertical distances below the transition point. In calculating k_7, the term $[(\rho_a - \rho_o)/\rho_a]$ is replaced by the term $[(\rho_o - \rho_a)/\rho_a]$.

For a falling plume there are two situations that can arise. If conditions are favourable

$$z_{max} < (H + l_{trw}) \quad [15.20.134]$$

The plume tends to become horizontal as it approaches the ground. In this case the method is to determine the total effective height h_{pl} from Equation 15.20.131 but with the modification that the term z_{max} is subtracted not added. The maximum ground level concentration z_{max} is then calculated as before from Equation 15.20.132.

It should be noted that Equation 15.20.132, which is approximate, gives very large values for p_{mgl} for very small values of h_{pl} and is not valid for such values. A check may be made by substituting x_{max} instead of x_o into Equation 15.20.128 and calculating p_a. If $p_a < p_{mgl}$, the value of p_{mgl} is rejected and the value of p_a is accepted in its place.

If conditions are unfavourable

$$z_{max} > (H + l_{trw}) \quad [15.20.135]$$

The plume approaches the ground at an angle. The maximum ground level concentration is the axial concentration in the plume when it reaches ground level. The situation is shown in Figure 15.73(d). In this case the method is to make the substitution

$$z = (H + l_{trw}) \quad [15.20.136]$$

The distance x_1 from the virtual source at which the plume axis reaches the ground is then calculated from Equation 15.20.125, using Equation 15.20.13. Then from the geometry of Figure 15.73(d)

$$\tan\theta = \frac{H + l_{trw}}{x_1 - x_o} \quad [15.20.137]$$

where θ is angle between axis of plume and horizontal. The horizontal component of the plume velocity is w and the vertical component is $w\tan\theta$. The resultant velocity u_θ is

$$u_\theta = w\left(1 + \tan^2\theta\right)^{1/2} \quad [15.20.138]$$

The distance x_θ from the virtual source S to the point where the plume reaches the ground measured along the axis of the plume is

$$x_\theta = \frac{x_1}{\cos\theta} = x_1\left(1 + \tan^2\theta\right)^{1/2} \quad [15.20.139]$$

The maximum ground level concentration p_{mgl} may be estimated by substituting u_θ and x_θ for w and x_o in Equation 15.20.128. The distance x_{mgl} at which the maximum ground level concentration is reached is

$$x_{mgl} = x_1 - x_o \quad [15.20.140]$$

Cude has compared his method with that of Bosanquet and with experimental data on plume paths given by N.G. Stewart *et al.* (1954) and quoted by Pasquill (1962a, p. 221). It predicts a plume rise approximately twice that of Bosanquets method and apparently more in accordance with the experimental data of Stewart *et al.* It gives a maximum ground level concentration which is approximately half that obtained by Bosanquets method, although Cude emphasizes that this difference is well within the range of variations which arise as a result of different atmospheric conditions. The method is applicable where the density difference between the plume and the air is zero, a condition where Bosanquets method is unreliable.

15.20.10 Briggs models

A model for jet and plumes and, in particular, for plume rise has been given by G.A. Briggs (1965, 1968, 1969, 1976), and S.R. Hanna, Briggs and Hosker (1982). The Briggs model distinguishes between a plume dominated by momentum and a plume dominated by buoyancy; between a vertical plume and a bent-over plume; and between a plume near the source and a plume in the three main stability conditions (stable, near neutral and convective, or unstable). The plume scenarios described in Briggs' models are illustrated in Figure 15.74.

In these models, the prime concern is with stack gases that have a temperature much greater than that of air but a molecular weight that does not differ greatly from that of air. For such gases Briggs defines the momentum flux as

$$M = wV \quad [15.20.141]$$

and the buoyancy flux as

$$F = g\frac{(T_p - T_{en})}{T_p}V \quad [15.20.142]$$

where F is the buoyancy flux, M is the momentum flux, V is the volumetric flow, w is the velocity in the vertical direction and the subscripts en and p denote environment and plume, respectively. The volumetric flow V is defined as

$$V = wr^2 \quad \text{Vertical plume} \quad [15.20.143a]$$

$$V = ur^2 \quad \text{Bent-over plume} \quad [15.20.143b]$$

where r is the radius and u is the wind speed.

Thus, in definition 15.20.143 Briggs omits the term π and in definitions 15.20.141 and 15.20.142 the term πr^2.

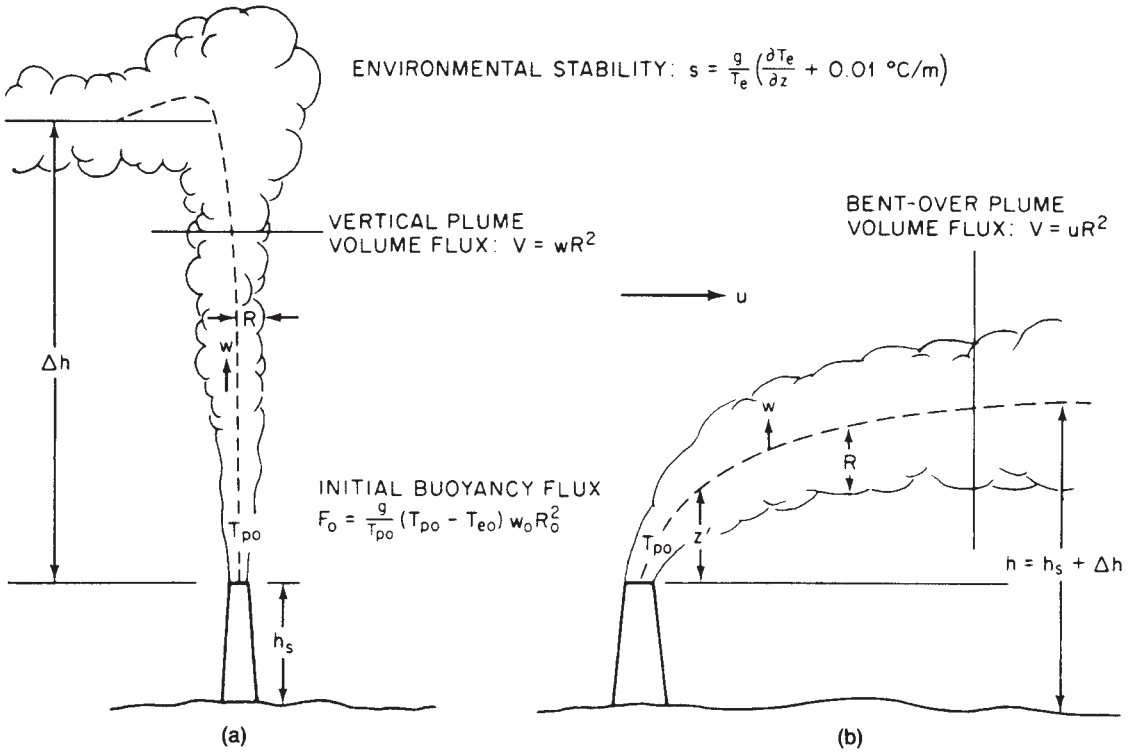


Figure 15.74 *Briggs model of dispersion of plumes from a stack (S.R. Hanna, Briggs and Hosker, 1982): (a) vertical plume; and (b) bent-over plume h and R in the figure are denoted in the text by h_e and r, respectively*

He adopts a similar approach to the definition of other quantities.

The initial momentum flux is

$$M_o = w_o V_o \qquad [15.20.144]$$

and the initial buoyancy flux is

$$F_o = g\left(\frac{T_{po} - T_{eo}}{T_{po}}\right) V_o \qquad [15.20.145a]$$

$$F_o = g\left(1 - \frac{T_{eo}}{T_{po}}\right) V_o \qquad [15.20.145b]$$

where subscripts eo, o and po denote the initial environment, the outlet and the initial plume, respectively.

If the molecular weight of the gas emitted differs significantly from that of air, the initial momentum and buoyancy may be modified as follows:

$$M_o = \frac{\rho_o}{\rho_a} w_o V_o \qquad [15.20.146]$$

$$F_o = g\left(1 - \frac{T_{eo}\, m_p}{T_{po} m_o}\right) V_o \qquad [15.20.147]$$

where m is the molecular weight.

The basis of the Briggs model is the equations for conservation of momentum and of buoyancy, together with additional relations required for the solution, or closure, of the equations. The closure relation is the Taylor entrainment assumption.

The basic equations are as follows. For conservation of momentum

$$\frac{dM}{dz} = \frac{F}{w} \quad \text{Vertical plume, bent-over plume} \qquad [15.20.148]$$

For conservation of buoyancy

$$\frac{dF}{dz} = -sV \quad \text{Vertical} \qquad [15.20.149a]$$

$$\frac{dF}{dz} = -\frac{sV}{S} \quad \text{Bent-over plume} \qquad [15.20.149b]$$

with

$$s = \frac{g}{T_e}\left(\frac{dT_e}{dz} + \Gamma\right) \qquad [15.20.150]$$

where s is the environmental stability, S is the ratio of the effective area influenced by the plume momentum to the cross-sectional area of the so-called thermal plume, T_e is the absolute temperature of the environment, z is the

vertical distance above the outlet and Γ is the dry adiabatic lapse rate. The value of S is found to be 2.3. For closure

$$\frac{dV}{dz} = 2r\alpha w \quad \text{Vertical plume} \qquad [15.20.151a]$$

$$\frac{dV}{dz} = 2r\beta w \quad \text{Bent-over plume} \qquad [15.20.151b]$$

where α and β are constants.

The velocities are

$$w = \frac{dz}{dt} \qquad [15.20.152]$$

$$u = \frac{dx}{dt} \qquad [15.20.153]$$

An alternative form of the equation for conservation of momentum, utilizing Equations 15.20.141 and 15.20.152, is

$$\frac{d(wV)}{dt} = F \qquad [15.20.154]$$

The derivation of the model equations is largely based on solutions of Equation 15.20.154 for the various conditions.

Plume near source: vertical plume

At the source there is a momentum-dominated plume, or jet. Then, taking the buoyancy as zero, or setting $F = 0$, gives

$$wV = \text{constant} \qquad [15.20.155a]$$

Hence

$$(wV)^{1/2} = \text{constant} \qquad [15.20.155b]$$

Then from Equation 15.20.143a

$$(wV)^{1/2} = wr \qquad [15.20.156a]$$

$$= w_o r_o \qquad [15.20.156b]$$

But for a jet

$$r = \beta z \qquad [15.20.157]$$

The constant β has the value 0.16 for the jet phase. Then

$$wz \propto w_o r_o \qquad [15.20.158]$$

From the work of Pai, the centre line velocity w_{cl} of a jet is

$$w_{cl} = 13\frac{w_o r_o}{z} \qquad [15.20.159]$$

But the mean velocity is about half the centre line velocity and hence

$$w = 6.25\frac{w_o r_o}{z} \qquad [15.20.160a]$$

$$= 6.25\frac{M^{1/2}}{z} \qquad [15.20.160b]$$

Transition from momentum to buoyancy control occurs at time

$$t = \frac{M}{F_o} \qquad [15.20.161]$$

Typically, the time to transition is less than 10 s.

After transition there is a buoyancy dominated plume, or buoyant plume. For this

$$w = 2.3\frac{F_o^{1/2}}{z} \qquad [15.20.162]$$

The radius r is again given by Equation 15.20.157, but the constant β has a value of 0.15 for the plume phase.

Plume near source: bent-over plume

Near the source, setting $F =$ constant in Equation 15.20.154 gives on integrating

$$wV = M_o + F_o t \qquad [15.20.163]$$

But for a bent-over plume

$$r = \beta z \qquad [15.20.164]$$

Then from Equations 15.20.143b, 15.20.152, 15.20.163 and 15.20.164

$$u(\beta z)^2 \frac{dz}{dt} = M_o + F_o t \qquad [15.20.165]$$

$$\int_0^z z^2\, dz = \int_0^t \left(\frac{M_o}{\beta^2 u} + \frac{F_o t}{\beta^2 u}\right) dt \qquad [15.20.166]$$

$$z = \left(\frac{3M_o t}{\beta^2 u} + \frac{3F_o t^2}{2\beta^2 u}\right)^{1/3} \qquad [15.20.167]$$

Alternatively, since

$$u = x/t \qquad [15.20.168]$$

Equation 15.20.167 can be written as

$$z = \left(\frac{3M_o x}{\beta^2 u^2} + \frac{3F_o x^2}{2\beta^2 u^3}\right)^{1/3} \qquad [15.20.169]$$

For the momentum-dominated plume, setting $F_o = 0$, gives

$$z = \left(\frac{3M_o t}{\beta^2 u}\right)^{1/3} \qquad [15.20.170]$$

or from Equation 15.20.168

$$z = \left(\frac{3M_o x}{\beta^2 u^2}\right)^{1/3} \qquad [15.20.171]$$

Equation 15.20.171 is the 1/3 law for a bent-over momentum plume.

For the buoyancy-dominated plume, setting $M_o = 0$, gives

$$z = \left(\frac{3F_o t^2}{2\beta^2 u}\right)^{1/3} \qquad [15.20.172]$$

and

$$z = \left(\frac{3}{2}\frac{F_o x^2}{\beta^2 w^3}\right)^{1/3} \quad [15.20.173]$$

But for a buoyant plume the constant β has the value 0.6. Substituting in Equation 15.20.173 gives

$$z = C_1 \frac{F_o^{1/3}}{u} x^{2/3} \quad [15.20.174]$$

with

$$C_1 = 1.6 \quad [15.20.175]$$

where C_1 is a constant. Equation 15.20.174 is the 2/3 law for a bent-over buoyant plume. A table of values of the constant C_1 is given by G.A. Briggs (1976). His preferred value is 1.6.

Plume rise in stable conditions

In stable conditions the environmental stability s is constant. Then from Equations 15.20.148, 15.20.149 and 15.20.152

$$\frac{d^2M}{dt^2} = -sM \quad [15.20.176]$$

This is the equation of a harmonic oscillator.

Briggs introduces a correction to the environmental stability s to allow for the effective vertical momentum flux M_{eff} and defines a modified stability s' such that

$$s' = s \quad \text{Vertical plume} \quad [15.20.177a]$$
$$= \frac{M}{M_{eff}} s \quad \text{Bent-over plume}$$

The ratio M/M_{eff} has the value 2.3. Then from Equations 15.20.141 and 15.20.176, and using s' rather than s,

$$\frac{d^2(wV)}{dt^2} = s' w V \quad [15.20.178]$$

Integrating Equation 15.20.178 with the initial conditions

$t = 0; \quad d(wV)/dt = F_o; \quad wV = M_o$

gives

$$wV = M_o \cos(w't) + \frac{F_o}{w'} \sin(w't) \quad [15.20.179]$$

with

$$w' = s'^{1/2} \quad [15.20.180]$$

In Briggs' model use is made of several plume heights. One is the maximum rise z_{max}. Another is the 'equilibrium' height z_{eq}, defined as the point at which $F = 0$. A third is the 'falling back' height z_{fb} defined as the height where the plume at maximum rise would be in equilibrium if no further mixing were to take place. Both z_{eq} and z_{fb} are fractions of z_{max}, as described below.

Plume rise in stable conditions: vertical plume

For the momentum plume, G.A. Briggs (1976) gives

$$z_{max} \approx 4\left(\frac{M_o}{s}\right)^{1/2} \quad [15.20.181]$$

and also

$$z_{eq} = 0.77 z_{max} \quad [15.20.182a]$$

$$z_{fb} = 0.8 z_{max} \quad [15.20.182b]$$

S.R. Hanna, Briggs and Hosker (1982) also give

$$z_{eq} = 2.44\left(\frac{M_o}{s}\right)^{1/4} \quad [15.20.183]$$

For the buoyant plume G.A. Briggs (1976) gives

$$z_{max} = 5\frac{F_o^{1/4}}{s^{3/8}} \quad [15.20.184]$$

S.R. Hanna, Briggs and Hosker (1982) also give

$$z_{eq} = 5.3\frac{F_o^{1/4}}{s_o^{3/8}} - 6r_o \quad [15.20.185]$$

The last term in Equation 15.20.185 is a correction to allow for the virtual source.

Plume rise in stable conditions: bent-over plume

For the buoyant plume, Equation 15.20.178 may be reformulated using Equations 15.20.143, 15.20.152 and 15.20.157. Then integrating the equation and taking the maximum value of z gives

$$z_{max} = \left(\frac{3F_o}{\beta^2 u s'}\right)^{1/3} \left\{1 + \left[1 + \left(\frac{w' M_o}{F_o}\right)^2\right]^{1/2}\right\}^{1/3} \quad [15.20.186]$$

But for $F_o \gg (M_o/w')$ Equation 15.20.186 reduces to

$$z_{max} = \left(\frac{6F_o}{\beta^2 u s'}\right)^{1/3} \quad [15.20.187]$$

Taking the constant β as 0.6 in Equation 15.20.187 gives

$$z_{max} = 2.6\left(\frac{F_o}{u s'}\right)^{1/3} \quad [15.20.188]$$

Also

$$z_{eq} = 0.79 z_{max} \quad [15.20.189a]$$
$$z_{fb} = 0.83 z_{max} \quad [15.20.189b]$$

G.A. Briggs (1976) also gives the following equation for plume rise Δh:

$$\Delta h = C_2\left(\frac{F_o}{u s}\right)^{1/3} \quad [15.20.190]$$

where C_2 is a constant. Values of the constant C_2 are tabulated by Briggs (1976). His preferred value is 2.6.

Plume rise limited by atmospheric turbulence

For conditions other than stable conditions, Briggs' treatment utilizes a 'break-up' model in which it is assumed that the plume rise terminates when the internal plume eddy dissipation rate equals the ambient eddy dissipation rate ϵ Then

$$\frac{\eta w^3}{z} = \epsilon \qquad [15.20.191]$$

where η is a constant. The constant η has the value 1.5. The term on the left-hand side of Equation 15.20.191 is the internal plume eddy dissipation rate. For a stack, the effective stack height (ESH) is

$$h_e = h_s + \Delta h \qquad [15.20.192]$$

where Δh is the plume rise above the stack outlet, h_e is the ESH and h_s is the actual stack height.

The plumes considered are momentum and buoyant plumes, both bent over.

Near neutral conditions

In near neutral conditions the ambient eddy dissipation rate is

$$\epsilon = \frac{u_*^3}{k h_e} \qquad [15.20.193]$$

where u_* is the friction velocity and k is von Karman's constant. The constant k has a value of 0.4.

Near neutral conditions: momentum plume

For a momentum plume for which the first phase of rise is given by Equation 15.20.171

$$\Delta h = \left(\frac{M_o}{\beta^2 u}\right)^{3/7} \left(\frac{\eta}{\epsilon}\right)^{1/7} \qquad [15.20.194]$$

From Equations 15.20.192 and [15.20.193]

$$\Delta h = \left(\frac{M_o}{\beta^2 u u_*}\right)^{3/7} (\eta k)^{1/7} \left(1 + \frac{h_s}{\Delta h}\right)^{1/7} \Delta h^{1/7} \qquad [15.20.195]$$

and hence

$$\Delta h = \frac{(\eta k)^{1/6}}{\beta} \left(\frac{u}{u_*}\right)^{1/2} \left(\frac{M_o}{u^2}\right)^{1/2} \left(1 + \frac{h_s}{\Delta h}\right)^{1/6} \qquad [15.20.196]$$

Assuming $\Delta h \gg h_s$ so that the last term of Equation 15.20.196 can be neglected and substituting for η and k values of 1.5 and 0.4, respectively, gives

$$\Delta h = \frac{0.9}{\beta} \left(\frac{u}{u*}\right)^{1/2} \frac{M_o^{1/2}}{u} \qquad [15.20.197]$$

From Equations 15.20.141, 15.20.143a and 15.20.197, taking the constant β as 0.6 and the ratio u/u_* as 15,

$$\Delta h = 2.9 \frac{w_o d_o}{u} \qquad [15.20.198]$$

where d_o is the diameter of the source.

G.A. Briggs (1982) also gives

$$\Delta h = 3 d_o \left(\frac{w_o}{u} - 1\right) \qquad [15.20.199]$$

The additional term is evidently a virtual source correction.

Near neutral conditions: buoyant plume

For a buoyant plume for which the first phase of rise is given by Equation 15.20.173]

$$\Delta h = \left(\frac{2F_o}{3\beta^2 u}\right)^{3/5} \left(\frac{\eta}{\epsilon}\right)^{2/5} \qquad [15.20.200]$$

Proceeding as before, it can be shown that

$$\Delta h = \frac{2}{3\beta^2} (\eta k)^{2/3} \left(\frac{F_o}{u u_*^2}\right) \left(1 + \frac{h_s}{\Delta h}\right)^{2/3} \qquad [15.20.201]$$

Neglecting the last term of Equation 15.20.201 and taking for the constants β, η and k values of 0.6, 1.5 and 0.4, respectively, gives

$$\Delta h = 1.3 \left(\frac{F_o}{u u_*^2}\right) \qquad [15.20.202]$$

Briggs also gives as an approximation for Equation 15.20.201 the following equation:

$$\Delta h = 1.54 \left(\frac{F_o}{u u_*^2}\right)^{2/3} h_s^{1/3} \qquad [15.20.203]$$

Convective conditions

For convective, or unstable, conditions Equation 15.20.193 does not apply. Instead, the relation used is

$$\epsilon = 0.25 H \qquad [15.20.204]$$

where H is surface buoyancy flux. The resultant equation for plume rise is

$$\Delta h = 3 \left(\frac{F_o}{u}\right)^{3/5} H^{-2/5} \qquad [15.20.205]$$

but this equation is to be regarded as tentative.

Ground level concentration

Once the plume rise Δh and hence the ESH h_e have been obtained, the maximum ground level concentration χ_{mgl} may be found in the usual way, using Equation 15.16.55, which may be written in the form

$$\chi_{mgl} = \frac{2Q}{e\pi u h_e^2} \frac{\sigma_z}{\sigma_y} \qquad [15.20.206a]$$

or

$$\chi_{mgl} = 0.234 \frac{Q}{u h_e^2} \frac{\sigma_z}{\sigma_y} \qquad [15.20.206b]$$

where e is the base of natural logarithms, Q is the mass rate of release and σ_y and σ_z are the longitudinal and vertical dispersion coefficients, respectively.

The maximum ground level concentration χ_{mgl} is low both at low and at high wind speeds, because in the first case the plume rise is high and in the second dilution is high. It therefore passes through a maximum value χ_{max} at some critical wind speed u_c.

A minimum value of the term uh_e^2 is obtained from Equation 15.20.201 when $\Delta h = h_s/3$. The following relations can then be derived:

$$u_c = 2.15\left(\frac{u}{u_*}\right)^{2/3}\left(\frac{F_o}{h_s}\right)^{1/3} \qquad [15.20.207]$$

$$u_c h_e^2 = 3.8\left(\frac{u}{u_*}\right)^{2/3} F_o^{1/3} h_s^{5/3} \qquad [15.20.208]$$

15.20.11 Jet transients

The jet and plume models described apply to steady-state conditions. The steady state is preceded and followed by transients that are much less well defined. In particular, the decay can result in a plume with a relatively low momentum. A study of gas jet transients has been described by Landis, Linney and Hanley (1994).

15.21 Dispersion of Two-phase Flashing Jets

The type of jet considered here is the jet resulting from a release of superheated liquid at high pressure, with choked liquid or two-phase flow. Such a jet may be divided into a number of zones, as shown in Figure 15.75. One common division is into two zones, a depressurization zone and an entrainment zone. In the depressurization zone, which is some two orifice diameters in length, the pressure falls essentially to atmospheric pressure, but there is little air entrainment. This occurs in the entrainment zone.

A modification of this scheme is to introduce between the depressurization and entrainment zone an intermediate zone in which deposition of liquid droplets, or rainout, is completed but negligible entrainment of air occurs. This is referred to here as the deposition zone.

The jet is commonly considered to end at the point where the jet velocity has fallen to a minimum value or to the wind speed, whichever is higher.

15.21.1 Disintegration of jets

Two-phase jets in general were considered in Section 15.2. The two-phase jets of main interest here are those of superheated liquids, which give flashing jets. A review of such jets has been given by Appleton (1984 SRD R303).

The break-up of a flashing jet will, in general, be due both to air resistance and vapour bubble formation. Appleton states that for most situations of interest in the process industries the latter will usually be the more important effect.

Work by Bushnell and Gooderum (1968) has shown that there is a critical degree of superheat above that the jet will disintegrate due to vapour bubble formation. They define a shattering temperature as follows:

$$\frac{T_{sh} - T_{sat}}{T_{sh}} = \epsilon \qquad [15.21.1a]$$

Hence

$$T_{sh} = \frac{T_{sat}}{1 - \epsilon} \qquad [15.21.1b]$$

where ϵ is a constant and subscripts sat and sh denote saturation and shattering, respectively. They give for the value of the constant ϵ the range 0.07–0.1.

Below the shattering temperature the jet remains well formed, while above it the jet shatters. In their work break-up did not appear to be affected by outlet diameter or liquid velocity. In the work of R. Brown and York (1962), however, for experiments where the Weber number was high, shattering occurred at lower values of the superheat. Mention should also be made of work by Suzuki *et al.* (1978), which has shown that, even when the jet conditions are held constant, large variations can occur in break-up length and pattern.

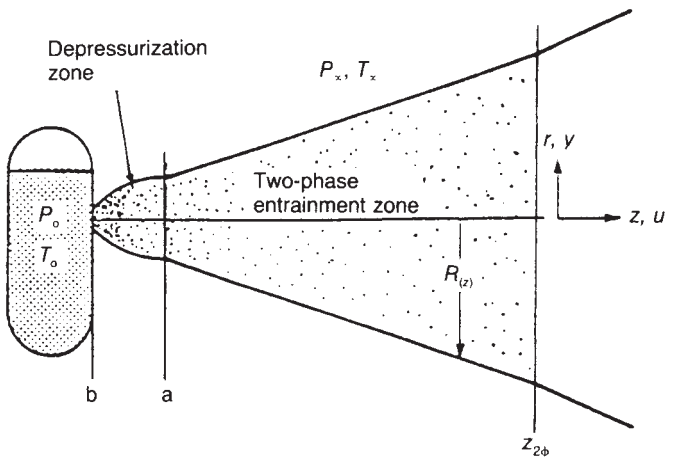


Figure 15.75 *Two-phase momentum jet (Fauske and Epstein, 1988). Subscript 2ϕ in the figure is denoted in the text by subscript tp.*

For a two-phase flashing jet the characteristics of interest are similar, but in this case the mass flow of droplets increases along the axis, so that in addition information is required on the production rate of droplets and on droplet size.

For droplet size relations for minimum and for maximum droplet size have been given by Koestel, Gido and Lamkin (1980) and by Gyarmathy (1976), respectively. Appleton has compared theoretical estimates from the methods of these authors with values obtained by Brown and York as follows:

Brown and York:	
Smooth orifice	34.7 μm
Rough orifice	54.5 μm
Koestel *et al.* (for minimum size)	19 μm
Gyarmathy (for maximum size)	31 μm

Quantitative treatment of the production rate of droplets is sparse. In Brown and York's experiments there was initial flashing and jet expansion some 0.15 m downstream from the outlet and there was then rapid evaporation of the droplets, so that by 1.2–1.5 m downstream practically all the liquid phase had disappeared.

15.21.2 Wheatley model

A model for a two-phase jet of liquefied ammonia has been given by Wheatley (1986, 1987 SRD R410). The model deals with: jet disintegration; gravitational settling of liquid droplets, or rainout; entrainment of air; and thermodynamics of mixing ammonia and moist air. It is not concerned with the effect on the jet of gravity or wind speed.

Wheatley's treatment of jet disintegration and rainout was considered in Section 15.1. The account given here is confined to his model for air entrainment. The situation that he considers is that in which the aerosol particles are sufficiently small for motion in the jet to be taken as homogeneous.

The basic relations of the model are

$$G_d = AuC \qquad [15.21.2]$$

$$G_d u_d = Au^2\rho \qquad [15.21.3]$$

and

$$G = G_d + G_a \qquad [15.21.4]$$

$$G = Au\rho \qquad [15.21.5]$$

Furthermore, from Equations 15.21.3 and 15.21.5

$$G_d u_d = Gu \qquad [15.21.6]$$

where A is the cross-sectional area of the jet, C is the concentration (mass per unit volume), G is the mass flow in the jet, u is the velocity of the jet, ρ is the density of the jet and subscripts a and d denote air and the end of deposition zone, respectively.

The relation for the growth of the jet due to air entrainment is

$$\frac{dG_a}{dz} = 2\pi Ru\rho_a f(\rho/\rho_a) \qquad [15.21.7]$$

where R is the radius of the jet and z is the distance downstream of the source. Here $f(\rho/\rho_a)$ is a function yet to be defined.

Wheatley considers two models of air entrainment. The first is that of Ricou and Spalding (1961). These workers give for an isothermal gas jet over a limited range of initial densities

$$\frac{dG_a}{dz} = \pi^{1/2}\tan\beta_\infty \rho_a^{1/2} u^{1/2} G^{1/2} \qquad [15.21.8]$$

where β_∞ is the asymptotic half-angle of the jet.

It is found empirically that $\beta_\infty = 9.1°$ and hence $\tan\beta_\infty = 0.15$. An entrainment coefficient $\propto$ is sometimes defined as

$$\alpha = 1/2\tan\beta_\infty \qquad [15.21.9]$$

Comparison of Equations 15.21.7 and 15.21.8 implies

$$f(\rho/\rho_a) = 1/2(\rho/\rho_a)^{1/2}\tan\beta_\infty \qquad [15.21.10]$$

This equation indicates that entrainment is affected by the density of the jet.

A density effect is indicated in the following equation obtained for isothermal gas jets:

$$\tan\beta = 1/2\left(\frac{\rho_a}{\rho} + 1\right)\left(\frac{\rho}{\rho_a}\right)^{1/2}\tan\beta_\infty \qquad [15.21.11]$$

Wheatley quotes experimental work to the effect that, where the density ratio ρ/ρ_a is appreciably greater than unity, β can be smaller than β_∞ by a factor of about 2, which is not consistent with Equation 15.21.1. He notes that in the work of Ricou and Spalding the density ratio ρ/ρ_a was at most about 1.05 and concludes that Equation 15.21.8 is not valid where ρ differs significantly from ρ_a.

Work by B.R. Morton, Taylor and Turner (1956) has shown that f is independent of ρ/ρ_a. Thus, Equation 15.21.10 becomes

$$f(\rho/\rho_a) = 1/2\tan\beta_\infty \qquad [15.21.12]$$

and Equation 15.21.11 becomes

$$\tan\beta = 1/2(\rho_a/\rho + 1)\tan\beta_\infty \qquad [15.21.13]$$

This equation gives the decrease of β with increasing ρ found experimentally.

Wheatley concludes that the treatment of Morton, Taylor and Turner should be used in preference to that of Ricou and Spalding. This model forms the basis of the computer code TRAUMA developed by Wheatley (1987 SRD R393, SRD R394). The code was developed initially for ammonia but was subsequently generalized to handle other liquefied gases.

15.21.3 Webber and Kukkonen model

A generalized model of a two-phase jet has been given by Webber and Kukkonen (1990). The model is intended as an exploration of basic principles. Most attempts to model two-phase jets have been partial ones, concentrating on particular aspects and neglecting others. The aim of the work was to determine which are the important phenomena and hence how comprehensive a realistic model needs to be.

In this model the depressurization zone is ignored. For the entrainment zone the basic relations are:

$$\frac{\mathrm{d}(CuA)}{\mathrm{d}x}) = 0 \qquad [15.21.14]$$

$$\frac{\mathrm{d}(\phi uA)}{\mathrm{d}x} = 2\pi R u_{\mathrm{E}} \qquad [15.21.15]$$

$$\frac{\mathrm{d}(\phi u^2 A)}{\mathrm{d}x} = 0 \qquad [15.21.16]$$

with

$$A = \pi R^2 \qquad [15.21.17]$$

where A is the cross-sectional area of the jet, C is the concentration of the contaminant, R is the radius of the jet, u is the velocity of the jet, u_{E} is the entrainment velocity, x is the downstream distance and ϕ is the ratio of the densities of the jet and air.

For the density of the jet, two cases (A and B) are considered. For Case A the density of the jet is the same as that of the ambient air

$$\phi = 1 \qquad [15.21.18]$$

For Case B the jet is an isothermal mixture of contaminant and air:

$$\phi = 1 + C \qquad [15.21.19]$$

Two entrainment models are considered. These are the models of B.R. Morton, Taylor and Turner (1956) and Ricou and Spalding (1961), as treated by Wheatley. The authors state these models in the form

$$u_{\mathrm{E}} = \alpha u \qquad [15.21.20]$$

and

$$u_{\mathrm{E}} = \alpha \phi^{1/2} u \qquad [15.21.21]$$

where α is an entrainment coefficient. These two entrainment models are identical for Case A, but not for Case B.

For Case A of a jet of ambient density, the solution of Equations 15.21.14–15.21.16 with incorporation of either entrainment model is

$$R = 2\alpha x \qquad [15.21.22]$$

$$u = UL(2\alpha x) \qquad [15.21.23]$$

$$C = L/(2\alpha x) \qquad [15.21.24]$$

where L and U are length and velocity scales determined by conditions at the source, and x is the downstream distance.

The solution for Case B of a dense jet before incorporation of the entrainment model is

$$(\phi - 1)uA = B \qquad [15.21.25]$$

$$\phi u^2 A = f \qquad [15.21.26]$$

where B and f are the buoyancy and momentum flux, respectively. The quantities L and U are defined as

$$L = \left(\frac{B^2}{\pi f}\right)^{1/2} \qquad [15.21.27]$$

$$U = f/B \qquad [15.21.28]$$

With incorporation of the first entrainment model, Equation 15.21.20, Equations 15.21.25 and 15.21.26 yield for Case

$$R = L(q/p) \qquad [15.21.29]$$

$$1 - \phi = 1/q^2 \qquad [15.21.30]$$

$$\phi = 1/(pq)^2 \qquad [15.21.31]$$

with

$$p^2 = u/U \qquad [15.21.32]$$

$$q^2 = Au/\left(\pi L^2 U\right) \qquad [15.21.33]$$

$$p^2 = \left(1 + q^2\right)^{-1} \qquad [15.21.34]$$

$$q\left(1 + q^2\right)^{1/2} + \ln\left[q + \left(1 + q^2\right)^{1/2}\right] = 2\alpha x/L \qquad [15.21.35]$$

where p and q are dimensionless variables.

For the Case B Equations 15.21.25 and 15.21.26 with the second entrainment model, Equation 15.21.21, the result is

$$R = 2\alpha x[1 + L/(2\alpha x)]^{1/2} \qquad [15.21.36]$$

$$u = U[L/(2\alpha x)][1 + L/(2\alpha x)]^{-1} \qquad [15.21.37]$$

$$\phi = 1 + L/(2\alpha x) \qquad [15.21.38]$$

For a two-phase jet that is not dense initially, L is rather smaller than R, and U is larger than u at the end of the depressurization zone. For an initially dense jet, L can be somewhat larger than R, whilst U approximates to u at the end of the zone.

The authors then develop the model to treat the effects of gravity, wind speed and liquid deposition. They give illustrative estimates from this model, utilizing the TRAUMA code to determine the conditions at the end of the deposition zone.

15.21.4 Fauske and Epstein model

Fauske and Epstein (1988) have described a more specific two-phase jet model, shown in Figure 15.75. They point out that, although in laboratory work the shattering temperature exceeds the saturation temperature, in practice due to factors such as vaporization upstream, roughness of the hole and air resistance, the extent of superheat without disintegration is very small. They take it as established that a superheated liquid released to the atmosphere disintegrates into droplets in the size range 10–100 μm, citing the work of Bushnell and Gooderum just described.

The basic relations of the model for the depressurization zone are:

$$u_a = u_b + \frac{P_b - P_a}{u_b \rho_b} \quad [15.21.39]$$

$$A_a = \frac{A_b u_b \rho_b}{u_a \rho_a} \quad [15.21.40]$$

$$\rho_a = \frac{1}{x_a/\rho_g + (1 - x_a)/\rho_f} \quad [15.21.41]$$

$$h_o = h_f + x_a h_{fg} \quad [15.21.42]$$

where A is the cross-sectional area of the jet, h is the specific enthalpy of the jet, P is the pressure in the jet, u is the velocity of the jet, x is the vapour fraction, or quality, ρ is the density of the jet, subscript b denotes at the orifice, or break, and subscript a denotes the end of the depressurization zone. Subscripts f, fg, g and o denote the liquid, liquid-vapour transition, the vapour and stagnation conditions, respectively. The densities and specific enthalpies at the end of the zone are evaluated at atmospheric pressure.

For the entrainment zone the entrainment relation used is that of Ricou and Spalding (1961):

$$e \propto u\left(\frac{\rho}{\rho_\infty}\right)^{1/2} \quad [15.21.43a]$$

$$= E_o \rho_\infty u\left(\frac{\rho}{\rho_\infty}\right)^{1/2} \quad [15.21.43b]$$

where e is the entrainment rate, E_o is the entrainment coefficient and the subscript ∞ denotes atmospheric conditions.

The relations for the conditions at the entrainment zone are:

$$\frac{u}{u_a} = \frac{h - h_\infty}{h_o - h_\infty} \quad [15.21.44a]$$

$$= \frac{R_a}{R}\frac{\rho_a}{\rho} \quad [15.21.44b]$$

$$= \left[1 + 2E_o\left(\frac{\rho_\infty}{\rho_a}\right)^{1/2}\frac{z}{R_a}\right]^{-1} \quad [15.21.44c]$$

where R is the radius of the jet, z is the distance along the jet axis and h_∞ is the specific enthalpy of the gaseous phase evaluated at atmospheric temperature T_∞. Equation 15.21.44 is valid at the end of the entrainment zone; it should not be used to determine conditions part way through the zone.

The authors discuss the thermal effects within the entrainment zone, particularly the formation of vapour from evaporating liquid droplets and the condensation of vapour onto droplets, and refer to the work of Weimer, Faeth and Olson (1973) on the latter. They conclude that it is reasonable to proceed on the assumption that the liquid and vapour phases are at the normal boiling point. Then, for a release that is all liquid and is from a vessel at ambient temperature, the specific enthalpies may be taken as

$$h = h_g(T_{bp}) \quad [15.21.45]$$

$$h_o = h_f(T_\infty) \quad [15.21.46]$$

$$h_\infty = h_g(T_\infty) \quad [15.21.47]$$

where the subscript bp denotes boiling point.

Then, rearranging Equation 15.21.44 gives the following equations for the end of the entrainment zone

$$\frac{u_{tp}}{u_a} = \left[1 + 2E_o\left(\frac{\rho_\infty}{\rho_a}\right)^{1/2}\frac{z_{tp}}{R_a}\right]^{-1} \quad [15.21.48]$$

$$\frac{R_{tp}}{R_a} = \left(\frac{\rho_a}{\rho_\infty}\right)^{1/2}\left[1 + 2E_o\left(\frac{\rho_\infty}{\rho_a}\right)^{1/2}\frac{z_{tp}}{R_a}\right] \quad [15.21.49]$$

$$\frac{z_{tp}}{R_a} = \frac{1}{2E_o}\left(\frac{\rho_a}{\rho_\infty}\right)^{1/2}\left[\frac{h_o - h_\infty}{h_g(T_{bp}) - h_\infty} - 1\right] \quad [15.21.50]$$

where the subscript tp denotes two-phase.

Utilizing Equations 15.21.45–15.21.47, the last factor in Equation 15.21.50 is modified to give

$$\frac{z_{tp}}{R_a} = \frac{1}{2E_o}\left(\frac{\rho_a}{\rho_\infty}\right)^{1/2}\frac{(1 - x_a)h_{fg}}{c_{pg}(T_\infty - T_{bp})} \quad [15.21.51]$$

where c_{pg} is the specific heat of the gaseous phase.

As an illustration, consider the example given by the authors of an ammonia jet in one of the Desert Tortoise ammonia release trials, described by Goldwire (1986) and considered in more detail in Section 15.3. This example is summarized in Table 15.41.

15.22 Dense Gas Dispersion

The account given so far of gas dispersion has been confined to the dispersion of gases of neutral buoyancy, or passive dispersion. A large proportion of industrially important gases exhibit negative buoyancy. It is these gases particularly which are prominent in hazard assessment.

An account of the dispersion of dense, or heavy, gases is given in this and following sections. Section 15.23 deals with source terms; Section 15.24 with models and modelling; Section 15.25 with modified conventional models; Sections 15.26–15.28 with some principal box models; Sections 15.29–15.33 with some if-theory and other three-dimensional models; Section 15.34 with the *Workbook*; Section 15.35 with the DRIFT three-dimensional model; Section 15.36 with some other models; Sections 15.37 and 15.38 with field trials; Section 15.39 with physical modelling; Section 15.40 with terrain, obstructions and buildings; Section 15.41 with validation and comparison; Section 15.42 with particular gases; and Sections 15.43 and 15.44 with elevated plumes and an elevated plume model. Further aspects of dense gas dispersion are treated in Section 15.45 on concentration and concentration fluctuations; Sections 15.46 and 15.47 on flammable and toxic gas clouds; Section 15.48 on dispersion over short ranges; Section 15.49 on hazard ranges for dispersion; and Sections 15.53 and 15.54 on vapour cloud mitigation. Selected references on dense gas dispersion are given in Table 15.42.

15.22.1 Dense gas

Many of the more hazardous gases such as hydrocarbons, chlorine, ammonia and hydrogen fluoride, and oxygen, are capable of giving a gas cloud that is denser than air.

Table 15.41 *Illustrative calculation for a two-phase flashing jet of liquefied ammonia from pressure storage (after Fauske and Epstein, 1988) (Courtesy of Butterworth-Heinemann)*

A Scenario

Atmospheric pressure $P_\infty = 1.01 \times 10^5$ Pa
Density of ambient air $\rho_\infty = 1.1$ kg/m^3
Orifice diameter $d_b = 0.0945$ m
Storage temperature $T_o = 297$ K (24°C)
Storage pressure $P_o = 1.4 \times 10^6$ Pa
Discharge velocity $u_f = 22.7$ m/s
Pressure of jet at discharge conditions $P_b = 0.968 \times 10^6$ Pa
Density of jet at discharge conditions $\rho_b = 603$ kg/m^3
Density of gaseous ammonia at discharge conditions (boilingpoint, atmospheric pressure) $\rho_g = 0.89$ kg/m^3
Specific heat of liquid ammonia $c_{pf} = 4.46 \times 10^3$ J/kg K
Specific heat of gaseous ammonia $c_{pg} = 10^3$ J/kg K
Latent heat of vaporization of ammonia $h_{fg} = 1.37 \times 10^6$ J/kg
Normal boiling point of ammonia $T_{bp} = 240$ K (−33°C)
Entrainment coefficient $E_o = 0.116$

B Jet[a]

Quality at end of depressurization zone:

$$x_a = c_{pf}(T_o - T_{bp})/h_{fg} = 4.46 \times 10^6(297 - 240)/1.37 \times 10^6 = 0.19$$

Density of jet at end of depressurization zone:

$$\rho_a \approx \rho_g/x_a = 0.89/0.19 = 4.68 \text{ kg/m}^3$$

Velocity of the jet at end of depressurization zone:

$$u_a = u_b + (P_b - P_a)/u_b\rho_b = 22.7 + (0.968 \times 10^6 - 0.101 \times 10^6)/(22.7 \times 603) = 86 \text{ m/s}$$

Radius of jet at end of depressurization zone:

$$R_a = R_b\left(\frac{u_b\rho_b}{u_a\rho_a}\right)^{1/2} = \frac{0.0945}{2}\left(\frac{22.7 \times 603}{86 \times 4.68}\right)^{1/2} = 0.275 \text{ m}$$

Distance to end of two-phase jet zone:

$$z_{tp} = R_a\frac{1}{2E_o}\left(\frac{\rho_a}{\rho}\right)^{1/2}\frac{h_{fg}(1 - x_a)}{c_{pg}(T_\infty - T_{bp})} = 0.275\frac{1}{2 \times 0.116}\left(\frac{4.68}{1.1}\right)^{1/2}\frac{1.37 \times 10^6(1 - 0.19)}{10^3(306 - 240)} = 39.1 \text{ m}$$

Velocity at end of two-phase jet zone:

$$u_{tp} = u_a\left[1 + 2E_o\left(\frac{\rho_\infty}{\rho_a}\right)^{1/2}\frac{z_{tp}}{R_a}\right]^{-1} = 86\left[1 + 2 \times 0.116\left(\frac{1.1}{4.68}\right)^{1/2}\frac{39.1}{0.275}\right]^{-1} = 5.06 \text{ m/s}$$

Radius at end of two-phase jet zone:

$$R_{tp} = R_a\left(\frac{\rho_a}{\rho_\infty}\right)^{1/2}\left[1 + 2E_o\left(\frac{\rho_\infty}{\rho_a}\right)^{1/2}\frac{z_{tp}}{R_a}\right] = 0.275\left(\frac{4.68}{1.1}\right)^{1/2}\left[1 + 2 \times 0.116\left(\frac{1.1}{4.68}\right)^{1/2}\frac{39.1}{0.275}\right] = 9.6 \text{ m}$$

[a] The numerical values in this example have been revised after consultation with one of the authors (HKF).

Table 15.42 *Selected references on dense gas dispersion*

Howerton (n.d., 1969); Abbott (1961); Joyner and Durel (1962); J.S. Turner (1966); Hoult, Fay and Forney (1969); Feldbauer *et al.* (1972); Humbert-Basset and Montet (1972); MacArthur (1972); Yang and Meroney (1972); Bodurtha, Palmer and Walsh (1973); Hoot, Meroney and Peterka (1973); Simmons, Erdmann and Naft (1973, 1974); Battelle Columbus Laboratories (1974); Hoot and Meroney (1974); Kneebone and Prew (1974); Lutzke (1974); Buschmann (1975); Germeles and Drake (1975); Simmons and Erdmann (1975); Anon. (1976 LPB 10, p. 10); McQuaid (1976b, 1979a,b, 1980, 1982a,b, 1984a–c, 1985a); Havens (1977, 1980, 1982b, 1985, 1986, 1987, 1992); Kletz (1977i); US Congress, OTA (1977); HSE (1978b, 1981a); Slater (1978a); Britter (1979, 1980, 1982, 1988a,b); Gutsche, Ludwig and Vahrenholt (1979); Harvey (1979b); R.A Cox *et al.* (1980); Fiedler and Tangermann-Dlugi (1980); Flothmann and Nikodem (1980); Forster, Kramer and Schon (1980); Hartwig (1980a,b, 1983a,b, 1986a,b); Hartwig and Flothmann (1980); Kinnebrock (1980); Klauser (1980); McNaughton and Berkowitz (1980); Schnatz and Flothmann (1980); Bloom (1980); Fay (1980, 1984); Kaiser (1980, 1982a,b); Shell Research Ltd (1980); Dirkmaat (1981); Fay and Ranck (1981,1983); Jagger and Kaiser (1981); Jensen (1981, 1984); Snyder (1981); Anon. (1982f); Blackmore, Eyre and Summers (1982); Blackmore, Herman and Woodward (1982); Britter and Griffiths (1982); Farmer (1982 SRD R221); R.F. Griffiths and Kaiser (1982); Gunn (1982, 1984); N.C. Harris (1982, 1983, 1986); Hogan (1982); Jagger (1982, 1983); List (1982); Meroney (1982, 1984a,b, 1985, 1987a,b); Zeman (1982a,b, 1984); Astleford, Morrow and Buckingham (1983); Byggstoyl and Saetran (1983); Emblem and Fannelop (1983); Havens and Spicer (1984); Pikaar (1983, 1985); Schnatz, Kirsch and Heudorfer (1983); Anon. (1984q,y); Emblem, Krogstad and Fannelop (1984); Fanaki (1984); Hartwig, Schatz and Heudorfer (1984); Jacobsen and Fannelop (1984); Jensen and Mikkelsen (1984); A.G. Johnston (1984, 1985); Knox (1984); Webber (1984); Barrell and McQuaid (1985); Ermak and Chan (1985); Fay and Zemba (1985, 1986, 1987); Raj (1985); Spicer (1985); Alp *et al.* (1986); Bachlin and Plate (1986); Brighton (1986, 1988); Duijm *et al.* (1986); Fannelop and Zumsteg (1986); Heinhold *et al.* (1986); Heudorfer (1986); Layland, McNaughton and Bodmer (1986); Riou (1986); Schnatz (1986); M.T.E. Smith *et al.* (1986); Verhagen and Buytenen (1986); Bettis, Makhviladze and Nolan (1987); N.E. Cooke and Khandhadia (1987a,b); Emerson (1987a); S.R. Hanna (1987b); Jacobsen and Magnussen (1987); Raj, Venkataraman and Morris (1987); Redondo (1987); Schreurs and Mewis (1987); Schreurs, Mewis and Havens (1987); Webber and Wheatley (1987 SRD R437); Cave (1988); Doury (1988); C.D. Jones (1988); Mercer (1988); Shaver and Fornery (1988); Kakko (1989); Nielsen and Jensen (1989); Vergison, van Diest and Easier (1989); Askari *et al.* (1990); Chaineaux and Mavrathalassitis (1990); Cleaver and Edwards (1990); Matthias (1990, 1992); P.T. Roberts, Puttock and Blewitt (1990); Schulze (1990); Witlox (1990); J.L. Woodward (1990, 1993); Ayrault, Balint and Morel (1991); Ermak (1991); Huerzeler and Fannelop (1991); Mercer and Porter (1991); J.K.W. Davies (1992); Van Dop (1992); Anfossi *et al.* (1993); Cauffleld *et al.* (1993); Webber and Wren (1993 SRD R552)

Density effects, gravity currents
Penney and Thornhill (1952); Keulegan (1957); NBS (1957 Rep. 5482, 1958 Rep. 5831); Stoker (1957); Ellison and Turner (1959); Lofquist (1960); Middleton (1966); Benjamin (1968); Hoult (1972b); van Ulden (1974); Kantha, Phillips and Azad (1977); Britter and Simpson (1978); J.C.R. Hunt *et al.* (1978); Britter (1979); Fischer *et al.* (1979); Simpson and Britter (1979); Brighton (1980 SRD R444); Britter and Linden (1980); Huppert and Simpson (1980); Yih (1980); Beghin, Hopflnger and Britter (1981); Jagger (1982 SRD R238); Simpson (1982, 1987); Crapper (1984); J.C.R. Hunt, Rottman and Britter (1984); Kranenberg (1984); Rottman and Simpson (1984a,b); Stretch, Britter and Hunt (1984); Zeman (1984); Grundy and Rottman (1985); Stretch (1986); Britter and Snyder (1988); Carruthers and Hunt (1988); Darby and Mobbs (1988); J.C.R. Hunt, Stretch and Britter (1988); J.C. King (1988); Linden and Simpson (1988); McGuirk and Papadimitrou (1988)

Source terms
NRC (Appendix 28 *Source Terms*); HSE (1978b, 1981a); Rijnmond Public Authority (1982); Zeman (1982a,b); Mudan (1984a); Wheatley (1986); Fauske and Epstein (1987, 1988, 1989); C. Harris (1987); Webber and Wheatley (1987); Britter and McQuaid (1988); Puttock (1988a, 1989); Chikhliwala *et al.* (1989); Lannello *et al.* (1989); Kaiser (1989); J.L Woodward (1989a); Finch and Serth (1990); Matthias (1990, 1992); J. Singh, Cave and McBride (1990); McFarlane (1991); Webber (1991); Lantzy (1992); de Nevers (1992); Spadoni *et al.* (1992).
Release inside buildings: Brighton (1989 SRD R467); Raman (1993)

Heat transfer, thermodynamic effects
Andreiev, Neff and Meroney (1983); Meroney and Neff (1986); Ruff, Zumsteg and Fannelop (1988)

Buildings, obstacles, complex terrain
D.J. Hall, Barrett and Ralph (1976); Brighton (1978, 1986); Kothari and Meroney (1979, 1982); Raupach, Thorn and Edwards (1980); Kothari, Meroney and Neff (1981); Meroney (1981, 1992); Britter (1982, 1988a); Deaves (1983a, 1984, 1985, 1987a,b, 1989); Robins and Fackrell (1983); Chan and Ermak (1984); Chan, Rodean and Ermak (1984); Gunn (1984); Jensen (1984); de Nevers (1984b); Guldemond (1986); Krogstad and Pettersen (1986); McQuaid (1986); Riou and Saab (1986); Heinhold, Walker and Paine (1987); Britter and Snyder (1988); Britter and McQuaid (1988); Carissimo *et al.* (1989); Vergison, van Diest and Easier (1989); Briggs, Thompson and Snyder (1990); Deaves and Hall (1990); Snyder (1990); M. Nielsen (1991); Brighton *et al.* (1992 SRD R583); Jones *et al.* (1992 SRD R582); Kukkonen and Nikmo (1992); Nikmo and Kukkonen (1992); Webber, Jones and Martin (1992, 1993); Castro *et al.* (1993); S.J. Jones and Webber (1993); Duijm and Webber (1994); Perdikaris and Mayinger (1994)

Physical modelling, wind tunnels, water flumes
D.J. Hall, Barrett and Ralph (1976); Neff, Meroney and Cermak (1976); Meroney *et al.* (1977); BRE (1978 CP71/78); D.J. Hall (1979a,b); Isyumov and Tanaka (1979); Kothari and Meroney (1979, 1982); Meroney (1979b, 1981, 1982, 1985, 1986, 1987a,b); Meroney and Lohmeyer (1979, 1981, 1982, 1983, 1984); J.C.R. Hunt (1980); Meroney, lindley and Bowen (1980); Meroney and Neff (1980, 1981, 1984, 1985); T.B. Morrow (1980); Raupach, Thorn and Edwards (1980); Hansen (1981); Kothari, Meroney and Neff (1981); Lohmeyer, Meroney and Plate (1981); Neff and Meroney (1981, 1982); D.J. Hall, Hollis and Ishaq (1982, 1984); C.I. Bradley and Carpenter (1983); Cheah, Cleaver and Milward (1983a); Meroney *et al.* (1983); Wighus (1983); Builtjes and Guldemond (1984); Cheah *et al.* (1984); Morrow, Buckingham and Dodge (1984); M.E. Davies (1985); D.J. Hall and Waters (1985, 1989); van Heugten and Duijm (1985); Krogstad and Pettersen (1986); Riethmuller (1986); Schatzmann, Koenig and Lohmeyer (1986); Bachlin and Plate (1987); Knudsen and Krogstad (1987); R.L. Petersen and Ratcliff (1989); Blewitt *et al.* (1991); D.J. Hall, Kukadia *et al.* (1991); D.J. Hall, Waters *et al.* (1991); Moser *et al.* (1991); Seong-Hee Shin, Meroney and Williams (1991); ASME (1992 DSC 36); Heidorn *et al.* (1992); Havens, Walker and Spicer (1994); P.T. Roberts and Hall (1994)

Concentration fluctuations
Chatwin and Sullivan (1980); Chatwin (1982a,b, 1983, 1991); R.F. Griffiths and Megson (1982, 1984); Meroney and Lohmeyer (1983); Cam and Chatwin (1985); Misra (1985); Carn (1987); Mole and Chatwin (1987); Cam, Sherrell and Chatwin (1988)

Models
API (Appendix 28, 1986/16, 1987 Publ. 4459, 1989 Publ. 4491, 4492, DR 229, 1990 Publ. 4522, 4523, 1992 Publ. 4539, 4540, 4545–4547, 1993 Publ. 4559, 4577); Considine (1981); Blackmore, Herman and Woodward (1982); J.L. Woodward *et al.* (1982,1983); S.R. Hanna and Munger (1983); R.L. Lee *et al.* (1983); Ministry of Environment, Canada (1983, 1986); Scire and Lurmanis (1983); Grint (1984 SRD R315); Kunkel (1985); Whitacre *et al.* (1986); Havens, Spicer and Schreurs (1987a,b); Betts and Haroutunian (1988); Kaiser (1989); Nussey, Mercer and Clay (1990); Gudivaka and Kumar (1990); Zapert, Londergan and Thistle (1990); Goyal and Al-Jurashi(1991); S.R. Hanna, Strimaitis and Chang (1991a); Touma *et al.* (1991); S.R. Hanna *et al.* (1992); S.R. Hanna, Chang and Strimaitis (1993); Kumar, Luo and Bennett (1993); Brighton *et al.* (1994); S.R. Hanna (1994); Kinsman *et al.* (1994).
Eidsvik model: Eidsvik (1978, 1980, 1981a,b); Havens and Spicer (1983)
van Ulden model: van Ulden (1974, 1979, 1984, 1988); van Ulden and de Haan (1983)
BG/C&W model: R.A. Cox and Roe (1977); R.A. Cox and Carpenter (1980); C.I. Bradley *et al.* (1983); Carpenter *et al.* (1987)
TNO models: van den Berg (1978)
VKI models: Foussat (1981); van Dienst *et al.* (1986)
COBRA: Alp (1985); Alp and Mathias (1991)
DENZ, CRUNCH: Fryer and Kaiser (1979 SRD R152); Jagger (1983 SRD R229); Jagger (1985 SRD R277); Wheatley, Brighton and Prince (1986)
DISP2: Fielding, Preston and Sinclair (1986); Preston and Sinclair (1987)
SIGMET: England *et al.* (1978); Havens (1979, 1982a); Su and Patniak (1981); Havens and Spicer (1983); Havens, Spicer and Schreurs (1987a,b)
HEAVYGAS, SLUMP: Deaves (1985, 1987a, 1992)
MARIAH-II: Taft, Rhyne and Weston (1983); Havens, Schreurs and Spicer (1987); Havens, Spicer and Schreurs (1987a,b)
MERCURE-GL: Riou and Saab (1986); Riou (1987, 1988)

SLAB, FEM3: Chan, Gresho and Ermak (1981); Ermak, Chan *et al.* (1982); Zeman (1982a,b); Chan (1983); R.L Lee *et al.* (1983); D.L Morgan, Morris and Ermak (1983); Chan and Ermak (1984); Chan, Rodean and Ermak (1984); D.L. Morgan (1984); D.L. Morgan, Kansa and Morris (1984); Rodean *et al.* (1984); Leone, Rodean and Chan (1985); Ermak and Chan (1986, 1988); Rodean and Chan (1986); Chan, Ermak and Morris (1987); Chan, Rodean and Blewitt (1987); Havens, Spicer and Schreurs (1987a,b); Zapert, Londergan and Thistle (1990); S.R. Hanna, Strimatis and Chang (1991b); Touma *et al.* (1991)
HEGADAS: Te Riele (1977); Colenbrander (1980); J.L.Woodward *et al.* (1982); Colenbrander and Puttock (1983); Havens and Spicer (1983); Puttock (1987b,c, 1988a, 1989); Zapert, Londergan and Thistle (1990); S.R. Hanna, Strimatis and Chang (1991b); Moser *et al.* (1991)
HEGABOX: Puttock (1987b,c, 1988a); S.R. Hanna, Strimatis and Chang (1991a); Moser *et al.* (1991)
HGSYSTEM: McFarlane *et al.* (1990); Rees (1990); Witlox *et al.* (1990); McFarlane (1991); Puttock *et al.* (1991)
PLUME: McFarlane (1991)
ADREA: Andronopoulos *et al.* (1993); Statharas *et al.* (1993)
DEGADIS: Havens (1985, 1986, 1992); Havens and Spicer (1985); Spicer and Havens (1986, 1987); Spicer *et al.* (1986); Spicer, Havens and Kay (1987); Havens, Spicer and Guinnup (1989); Zapert, Londergan and Thistle (1990); Hanna, Strimatis and Chang (1991a); Havens *et al.* (1991); Moser *et al.* (1991); Touma *et al.* (1991)
CHARM: Fabrick (1982); Radian Corporation (1986); Zapert, Londergan and Thistle (1990); Hanna, Strimatis and Chang (1991a); HSE Workbook: McQuaid (1982b); Britter and McQuaid (1987, 1988)
DRIFT: Byren *et al.* (1992 SRD R553); Edwards (1992 SRD R563); Webber *et al.* (1992 SRD R586, R587); Webber and Wren (1993 SRD R552)

Experimental trials
AGA (1974/20–23); Buschman (1975); HSE (1978 RP 8); Puttock, Blackmore and Colenbrander (1982); Puttock and Colenbrander (1985a); Lewellen and Sykes (1986); Heinrich, Gerold and Wietfeldt (1988); Havens (1992).
AGA: Feldbauer *et al.* (1972); Drake, Harris and Reid (1973)
China Lake: Ermak *et al.* (1983)
Porton Down: Picknett (1978a–c, 1981); McQuaid (1979a,b); Anon. (1981J); D.J. Hall, Hollis and Ishaq (1982, 1984); Kaiser (1982b); Heudorfer (1986)
Maplin trials: Anon. (1982f); Puttock, Blackmore and Colenbrander (1982); Puttock, Colenbrander and Blackmore (1983, 1984); Colenbrander and Puttock (1984)
Nevada Test Site: Koopman and Thompson (1986); Koopman *et al.* (1986)
LLNL: Hogan (1982); Koopman, Ermak and Chan (1989)

Experimental trials: Thorney Island
McQuaid (1982b, 1984b,c, 1985a–c, 1987); HSE (1984 RP 24); Brighton (1985a, 1985 SRD R319, 1987); Brighton, Prince and Webber (1985); Cam and Chatwin (1985); CEC (1985 EUR 9933 EN, EUR 10029 EN); M.E. Davies and Singh (1985a,b); Deaves (1985); Gotaas (1985); R.F. Griffiths and Harper (1985); D.J. Hall and Waters (1985); N.C. Harris (1985); Hartwig (1985); van Heugten and Duijm (1985); D.R. Johnson (1985); Leek and Lowe (1985); Nussey, Davies and Mercer (1985); Pfenning and Cornwell (1985); Prince, Webber and Brighton (1985 SRD R318); Puttock (1985,1987a–c); Puttock and Colenbrander (1985b); Riethmuller (1985); Roebuck (1985); Rottman, Hunt and Mercer (1985); Rottman *et al.* (1985); Spicer and Havens (1985); Wheatley, Prince and Brighton (1985,1985 SRD R355); Wheatley, Brighton and Prince (1986); Brighton and Prince (1987); Cabrol, Roux and Lhomme (1987); Cam (1987); Carpenter *et al.* (1987); Chan, Ermak and Morris (1987); Cornwell and Pfenning (1987); J.K.W. Davies (1987); M.E. Davies and Inman (1987); Havens, Schreurs and Spicer (1987); Knudsen and Krogstad (1987); Mercer and Davies (1987); Mercer and Nussey (1987); Riou (1987, 1988); Sherrell (1987); van Ulden (1987); Wheatley and Prince (1987); Cam, Sherrell and Chatwin (1988); Carissimo *et al.* (1989); Andronopoulos *et al.* (1993)

Particular chemicals
Ammonia: HSE/SRD (HSE/SRD/WP13, 14, 16, 22 and unnumbered); W.L. Ball (1968b); Rohleder (1969); Comeau (1972); MacArthur (1972); J.D. Reed (1974); Lonsdale (1975); Luddeke (1975); HSE (1978b, 1981a); Kaiser and Walker (1978); Slater (1978a); R.F. Griffiths and Kaiser (1979 SRD R154, 1982); Haddock and Williams (1979); Kaiser (1979 SRD R150, 1980, 1981 LPB 38, 1982, 1989); Blanken (1980); Kaiser and Griffiths (1982); R.F. Griffiths and Megson (1984); Goldwire (1985,1986); Goldwire *et al.* (1985); Guldemond (1986); Koopman *et al.* (1986); Chan, Rodean and Blewitt (1987); Koopman, Ermak and Chan (1989); J. Singh and McBride (1990); S.R. Hanna, Strimaitis and Chang (1991a); Statharas *et al.* (1993)
Antiknock compounds: HSE/SRD (HSE/SRD/WP17)
Chlorine: McClure (1927); Ministry of Social Affairs (1975); R.F. Griffiths and Megson (1984); Riethmuller (1986); Wheatley (1986 SRD R357); Clough and Wheatley (1988 SRD R396); Vergison, van Dienst and Easier (1989); J. Singh and McBride (1990)
Hydrogen fluoride: Beckerdite, Powell and Adams (1968); Bosch and de Kayser (1983); Blewitt *et al.* (1987a,b); Chan, Rodean and Blewitt (1987); Chikhliwala and Hague (1987); Clough, Grist and Wheatley (1987); Schotte (1987, 1988); Koopman, Ermak and Chan (1989); Holve *et al.* (1990); Leone (1990); R.L. Petersen and Diener (1990); Blewitt *et al.* (1991); Fthenakis, Schatz and Zakkay (1991); S.R. Hanna, Strimaitis and Chang (1991a); Meroney (1991); Moser (1991); Puttock, MacFarlane, Prothero and Roberts *et al.* (1991); Antonello and Buzzi (1992); Schatz and Fthenakis (1994); Webber, Mercer and Jones (1994)
LNG: HSE/SRD (HSE/SRD/WP21); Fay (1973); AGA (1974/20–23,1978/27); Duffy, Gideon and Puttnam (1974); Drake and Puttnam (1975); Fay and Lewis (1975); Meroney, Cermak and Neff (1976); Neff, Meroney and Cermak (1976); Havens (1977, 1978, 1979, 1980,1982a); Meroney *et al.* (1977); England *et al.* (1978); Koopman, Bowman and Ermak (1980); Meroney and Neff (1980, 1981, 1984, 1985); Hogan, Ermak and Koopman (1981); Kothari, Meroney and Neff (1981); Neff and Meroney (1981, 1982); TNO (1981 Rep. 81–07020); Blackmore, Eyre and Summers (1982); Ermak *et al.* (1982); D.J. Hall, Hollis and Ishaq (1982); Hogan (1982); Koopman *et al.* (1982); Rodean (1982, 1984); Ermak *et al.* (1983); Goldwire *et al.* (1983); Havens and Spicer (1983); Meroney *et al.* (1983); Chan and Ermak (1984); D.L. Morgan *et al.* (1984); Rodean *et al.* (1984); Misra (1985); Havens, Spicer and Schreurs (1987a,b); Leone (1990); Havens *et al.* (1991); Seong-Hee Shin, Meroney and Williams (1991); Chan (1992)

Propane, LPG: Puttock, Colenbrander and Blackmore (1983); Wighus (1983); Meroney and Lohmeyer (1984)
Other gases: McRae *et al.* (1983); McRae (1986); Koopman *et al.* (1986)

Dispersion of aersosols
J.L. Woodward (1989)

Visibility of cloud
CCPS (1988/3); De Nevers (1992)

Mitigation sytems
R.W. Johnson *et al.* (1989); Hague (1992); Prugh (1992b); Buchlin (1994)
Vapour barriers, fences: R.L. Petersen and Diener (1990); Chan (1992)
Gas curtains: Rulkens *et al.* (1983)
Steam, curtains: Cairney and Cude (1971); Simpson (1974); Seifert, Maurer and Giesbrecht (1983); Sato (1989); Lopez *et al.* (1990); Earth (1992)
Water curtains: Rasbash and Stark (1962); Buschmann (1975); McQuaid (1975, 1976a, 1977, 1980, 1982b); Ministry of Social Affairs (1975); Eggleston, Herrera and Pish (1976); Heskestad, Kung and Todtenkopf (1976); Vincent *et al.* (1976a,b); J.W. Watts (1976); Benedict (1977); HSE (1978 TP1, 1978b, 1981a); van Doom and Smith (1980); Beresford (1981); Greenwood (1981); N.C. Harris (1981a); IChemE (1981/123); McQuaid and Fitzpatrick (1981, 1983); Moodie (1981, 1985); P.A.C. Moore and Rees (1981); J.M. Smith and Doom (1981); Zalosh (1981); McQuaid and Moodie (1982, 1983); Deaves (1983b); De Faveri *et al.* (1984); Kirby and Deroo (1984); Emblem and Madsen (1986); Blewitt *et al.* (1987b); NIOSH (1987/10); Fthenakis and Zakkay (1990); Holve *et al.* (1990); Lopez *et al.* (1990); Schatz and Koopman (1990); Fthenakis, Schatz and Zakkay (1991); Lopez, Lieto and Grollier-Baron (1991); Meroney (1991); Meroney and Seong-Hee Shin (1992); St Georges *et al.* (1992a,b); Fthenakis (1993); Fthenakis and Blewitt (1993); Ratcliff *et al.* (1993); Schatz and Fthenakis (1994)

Jets and plumes
Bodurtha (1961, 1980, 1988); Ooms (1972); J.L. Anderson, Parker and Benedict (1973); Bodurtha, Palmer and Walsh (1973); Hoot, Meroney and Peterka (1973); Ooms, Mahieu and Zelis (1974); Chu (1975); Meroney (1979b); Blooms (1980); Giesbrecht, Seifert and Leuckel (1983); Hirst (1984, 1986); Jagger and Edmundson (1984); Ooms and Duijm (1984); Emerson (1986a,b, 1989); Li Xiao-Yun, Leijdens and Ooms (1986); Tarn and Cowley (1989); J.L. Woodward (1989a); Epstein, Fauske and Hauser (1990); D.K. Cook (1991b); McFarlane (1991); Schatzmann, Snyder and Lawson (1993)

Hazard assessment
R.A. Cox and Roe (1977); Air Weather Service (1978); HSE (1978b, 1981a); Wu and Schroy (1979); Cornell and Church (1980); Doron and Asculai (1983); Barboza, Militana and Haymes (1986); Gebhart and Caldwell (1986); Hart (1986); Kasprak, Vigeant and McBride (1986); Layland, McNaughton and Bodmer (1986); Schewe and Carvitti (1986); Shea and Jelinek (1986); Costanza *et al.* (1987); Fauske and Epstein (1987); Nussey and Pape (1987); Paine, Smith and Egan (1987); Studer, Cooper and Doelp (1988); English and Waite (1989)

Accident simulation
M.P. Singh and Ghosh (1987); Fay (1988); Billeter and Fannelop (1989); M.P. Singh (1990); M.P. Singh, Kumari and Ghosh (1990)

Incident investigation
Vegetation damage: Benedict and Breen (1955); Hindawi (1970); Jacobson and Hill (1970); Booij (1979)

Whether or not a particular gas release forms a gas cloud that is denser than air depends on a number of factors. These are:

(1) the molecular weight of the gas;
(2) the temperature of the gas;
(3) the presence of liquid spray;
(4) the temperature and humidity of the air.

A gas cloud may be dense by virtue of the molecular weight of the gas released. However, even if the molecular weight of the gas is less than that of air, the gas cloud may be rendered dense by other factors. If the boiling point of the gas is low so that the gas cloud is cold, this may be sufficient to make the cloud dense.

The presence of liquid spray is another factor that can render the cloud dense. The effect of vaporization of the droplets of liquid is to remove heat from the gas and so cool it.

The density of the cloud is also affected by the humidity of the ambient air. The effect of the condensation of the droplets of water is to add heat to the gas. In general, the cloud will tend to have a higher density when mixed with dry air than with wet air.

The effect of molecular weight and temperature may be illustrated by considering the densities of gas clouds from releases of chlorine, methane and ammonia into dry air. The molecular weight of chlorine (71) is much greater than that of air (28.9) and thus gives a cloud heavier than air at ambient temperature. The cloud given by chlorine at its boiling point (−34°C) is even heavier.

Methane (mol. wt. 16) is much lighter than air at ambient temperature. But the cloud given by methane at its boiling point (−161°C) is heavier than air. Ammonia (mol. wt. 17) is much lighter than air at ambient temperature. The cloud given by ammonia at its boiling point (−33°C) is also lighter than air. But ammonia clouds tend to be denser than air due to presence of liquid spray.

There is now ample evidence, both from experiments and incidents, that releases of liquefied gas such as propane, LNG, ammonia, chlorine and hydrogen fluoride give rise to dense gas clouds.

As the gas cloud is diluted, the concentration, and the relative density, decrease and the mode of dispersion changes from dense gas dispersion to passive dispersion of a neutrally buoyant gas.

15.22.2 van Ulden's experiment

Experimental work on the dispersion of a heavy gas has been described by van Ulden (1974). Some results from this work are shown in Figure 15.76. Figures 15.76(a) and (b) show, respectively, the growth of the height and radius of the dense gas cloud from an instantaneous release at ground level. The first part of the curve in the former figure shows the initial sharp decrease in cloud height due to gravity slumping, followed by a gradual increase in height. The height is much less and the radius much greater than that predicted by the Gaussian model, which overestimates the height and underestimates the radius by factors of 5 and 2.5, respectively.

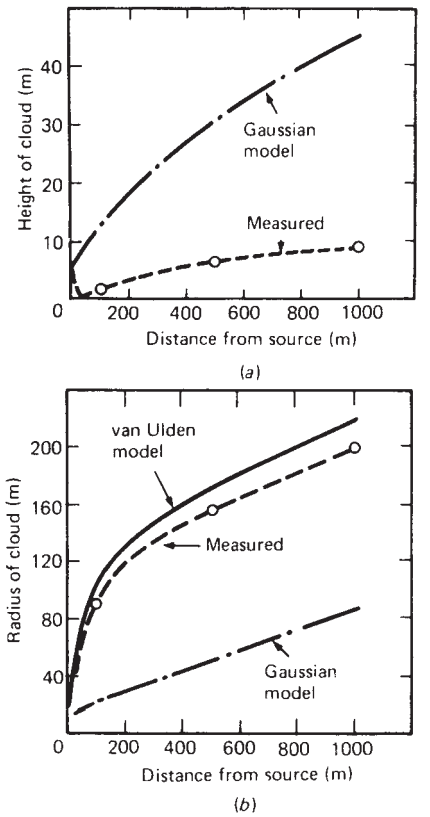


Figure 15.76 *Dutch Freon 12 trial on dense gas dispersion (van Ulden, 1974): (a) growth of height; (b) growth of radius (Courtesy of Elsevier Publishing Company)*

Van Ulden formulated a model for dense gas dispersion which was influential in the development of the topic. This is described in Section 15.26.

15.22.3 Experimental work

Experimental work bearing on dense gas dispersion includes not only field trials but also physical modelling in wind tunnels and water flumes, the latter being often on the laboratory scale. The work on field trials is described in Sections 15.37 and 15.38 and the physical modelling in Section 15.3(2). The laboratory experiments are referred to in discussion of the particular aspects to which they relate.

15.22.4 Dense gas behaviour

The behaviour of a dense gas may be described by considering the development of the gas cloud from the bursting of a vessel. The source term for this is usually modelled by assuming that air is entrained in a ratio of some 10–20:1 and that a cloud of unit aspect ratio is formed.

The behaviour of the cloud is influenced by gravity. Three stages may be distinguished:

(1) gravity slumping;
(2) gravity spreading;
(3) passive dispersion.

The flow is gravity driven in both the first two stages. The first stage is normally described as gravity slumping. The second stage is gravity-driven flow with stable stratification. The term 'gravity spreading' is applied sometimes to both the first two stages and sometimes only to the second stage; it is used here in the latter sense. The third stage is one of passive dispersion.

Gravity-driven flow is illustrated in Figure 15.77, which shows shadowgraphs taken in a water tunnel, these illustrate the intrusion of a more dense fluid into a less dense one on surfaces of different slopes. Features are the 'head' at the leading edge of the denser fluid and the mixing at the horizontal interface between the two fluids.

The density difference between the cloud and the atmosphere, or density excess, has four main effects. First, it imparts a strong horizontal velocity to the cloud. Second, it creates velocity shear. Third, it inhibits vertical mixing by atmospheric turbulence through the top of the cloud. Fourth, it affects the inertia of the cloud.

The inhibition of vertical mixing by atmospheric turbulence through the top of the cloud means that the mixing is less sensitive to the stability conditions. Vertical mixing still occurs, however, due to other forms of turbulence in the cloud. Moreover, the inhibition of mixing by atmospheric turbulence is counteracted by the creation of a large top surface area on the cloud due to gravity spreading.

If the ratio of the density difference to the density of the atmosphere, or reduced density, is small, an important approximation may be made. This is to neglect the effect of the density difference on the inertia. This is the Boussinescq approximation and it is widely used in dense gas dispersion modelling.

15.22.5 LNG spill study

Another piece of work which was influential in the development of the topic was the study for the US Coast Guard by Havens (1978) of the hazard range from a spill of 25,000 m^3 of LNG onto water. The work was a comparative study of the predictions of the distance to the lower flammability limit given by seven gas dispersion models. These predictions ranged from 0.75 up to 50 km. Reference to this study was made in Chapter 9 as an illustration of uncertainty in modelling. It is considered again in Section 15.41 in the context of validation of models.

15.23 Dispersion of Dense Gas: Source Terms

The source term can be critical for the modelling of the subsequent dispersion of a dense gas. It is therefore important that the source model should be realistic and complete. If the model for the source term is poor, the results of the whole dense gas dispersion estimate may be seriously in error.

15.23.1 Release scenarios

The modelling of release scenarios is assisted by an appropriate classification. Such classifications have been given by a number of workers, including Fryer and Kaiser (1979 SRD R152), Griffiths and Kaiser (1979 SRD R154) and Kaiser (1989).

The main concern is the modelling of the source term for a release of liquefied gas. The classification given for

liquefied gases is

(1) Pressurized release
  (a) small hole in vapour space,
  (b) large hole in vapour space – catastrophic failure,
  (c) intermediate-sized hole in vapour space,
  (d) hole in liquid space;
(2) Refrigerated release
  (a) spill onto land,
  (b) spill onto water;
(3) Jet release.

These cases are considered in turn for a dense gas.

15.23.2 Release from pressurized containment

For a pressurized liquefied gas, a release from a small hole in the vapour space (Case 1(a)) gives rise to a vapour jet which loses momentum and turns into a dense gas plume. This is considered further in Section 15.43.

A catastrophic failure of the vessel (Case 1(b)) results in the flash-off of a vapour fraction with the liquid falling to its normal boiling point. The vapour fraction is obtained by heat balance. A proportion of the residual liquid is also ejected as liquid droplets, or spray. The evidence is that in fact substantially all the residual liquid becomes airborne. Such a release generates considerable turbulence and results in the entrainment of large amounts of air. The liquid droplets in the cloud undergo partial evaporation with a further drop in their temperature. Thereafter the heat required for their further evaporation is taken from the gas cloud, which results in cooling of the cloud.

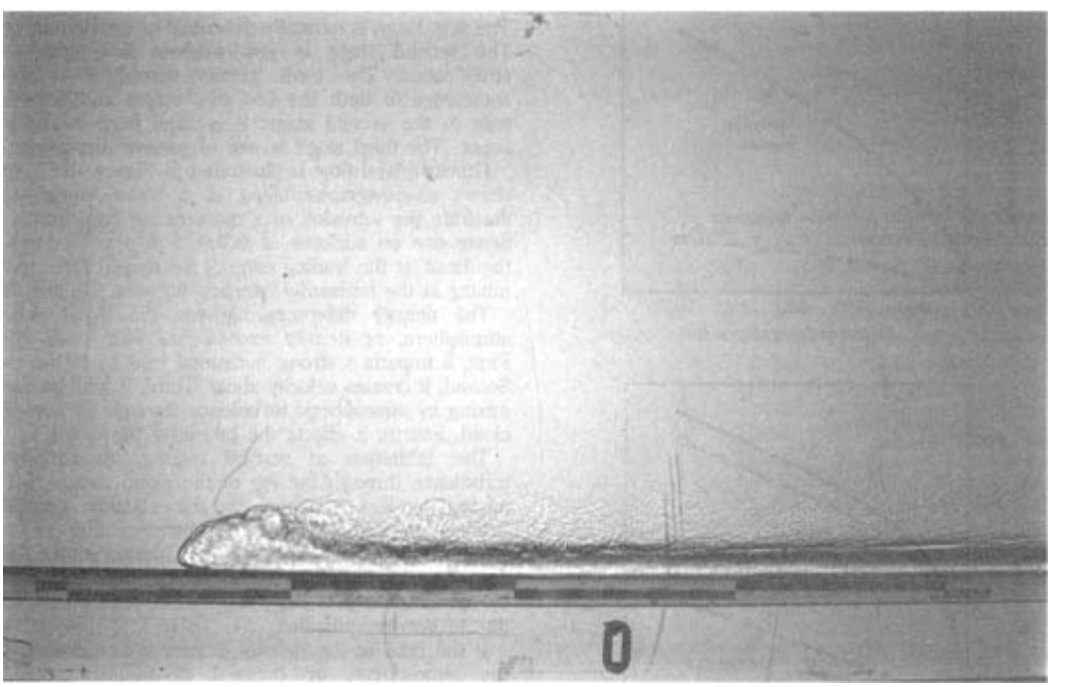
A release from a hole of intermediate size (Case 1(c)) may be presumed to give as spray a liquid fraction intermediate between the above two cases. Work bearing on this is described in Section 15.10. Some simple experiments by A.R. Edwards (1978) suggest that the liquid fraction which becomes airborne is a function of the ratio of the hole size to the vessel area. When this ratio reached about 0.01 the liquid fraction ejected became appreciable, whilst above a ratio of about 0.1 virtually all the liquid become airborne as spray. More detailed work is described in Section 15.10.

A hole in the liquid space (Case 1(d)) gives a two-phase flashing jet, as considered below.

15.23.3 Release from refrigerated containment

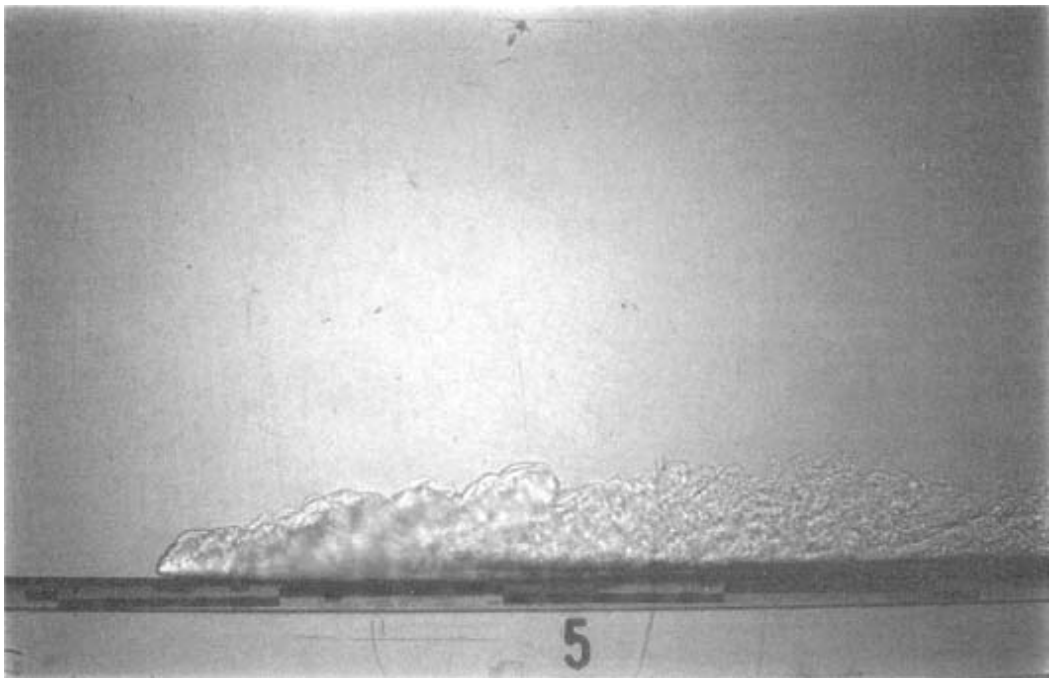
For a fully refrigerated liquefied gas, a spill onto land (Case 2(a)) results in a spreading, vaporizing pool. If the spill is into a bund, the size of the pool is constrained by the bund. Otherwise, the pool spreads until the liquid depth is so small that spreading ceases and break-up occurs. If the release is violent, there is a possibility that the wave created will spill over the edge of the bund.

The vaporization from the pool is a function of the area of the pool and of the rate of vaporization per unit area. The vaporization process is governed by the heat transfer from the surface to the liquid, which is initially high but rapidly falls off as the surface chills.

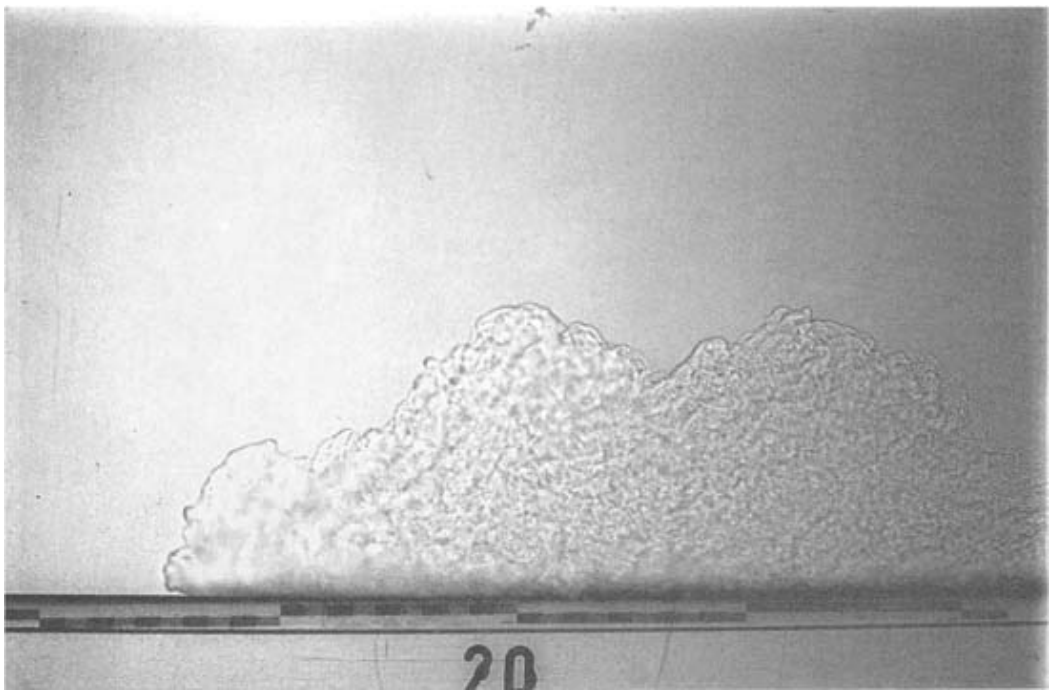


(a)

Figure 15.77 *Continued*



(b)



(c)

Figure 15.77 *Water tunnel modelling of the intrusion of a more dense fluid into a less dense one on flat and on sloping surface (Britter and Linden, 1980: (a) slope 0°; (b) slope 5°; (c) slope 20°. The entrainment increases with slope both into the head and into the flow behind it (Courtesy of Cambridge University Press)*

For a pool of fixed size filled rapidly, the pattern is one of very high vapour flow for a short initial period, lasting perhaps a minute, followed by rapid and then more gradual decline. For a spreading pool the vapour flow tends to pass through a maximum.

A spill onto water (Case 2(b)) again results in a pool spreading until the liquid depth becomes small and break-up occurs. The vaporization from the pool is a function of the area of pool and of the specific rate of vaporization. In this case, however, renewal of the water surface occurs and the heat transfer rate is constant and high. The vapour flow starts high and increases as the pool spreads, then falls off quite sharply as the pool evaporates.

Another possible scenario is an elevated jet release. In this case the liquid may well vaporize completely before it reaches the surface. Since the heat of vaporization is obtained from the entrained air rather than the surface, the resultant gas cloud is much colder.

15.23.4 Release from semi-refrigerated containment

For a semi-refrigerated liquefied gas, the scenarios are basically similar to those for the fully pressurized case.

The liquid is, however, at a lower pressure and a lower temperature. This may be expected to affect the proportion of the residual liquid which becomes airborne and the extent of rainout. The evidence is limited, but suggests that a semi-refrigerated release behaves broadly like a full refrigerated one. The main difference is that some, limited, degree of rainout may occur.

15.23.5 Two-phase jets

For a pressurized liquefied gas, a hole in the liquid space of a vessel or in a pipe gives a two-phase flashing jet. Accounts of such jets include those by Mudan (1984a), Wheatley (1987 SRD R410), Fauske and Epstein (1988), Webber and Kukkonen (1990) and Webber (1991).

The development of such a jet proceeds through three zones. The first is the depressurization, or flashing, zone in which the vapour and liquid droplets form. This extends several hole diameters and increases rapidly in diameter. The second zone is that of the two-phase momentum jet at atmospheric pressure into which air is entrained. The third zone starts where the jet loses momentum and other dispersion mechanisms take over.

The jet disintegrates into a spray of liquid droplets. These tend to remain airborne until they evaporate rather than to rain out.

Two-phase jets are considered in more detail in Section 15.21.

15.23.6 Initial density

The density of the gas cloud formed from the release depends on a number of factors. These include the density of the contaminant gas, the normal boiling point, the fraction of liquid present as droplets and the humidity of the ambient air. Typically, the density and temperature of the gas cloud is given as a function of the concentration of contaminant gas with the liquid fraction and humidity as parameters. The factors affecting the density of the gas cloud are discussed in general in Section 15.22 and, for particular gases, in Section 15.42.

15.23.7 Air entrainment

The mass of air entrained into the gas cloud is a crucial feature of the source model. There are available some estimates of the extent of entrainment for some of the scenarios just described.

For vaporization from a pool on land, the vapour is generally taken as pure vapour and the entrainment of air is modelled within the dense gas dispersion model.

For vaporization from a pool on water, the same approach appears often to be used. However, the turbulence generated by the boiling will cause some entrainment of air. Kaiser (1980) has estimated this as an entrainment within 5s of enough air to dilute the contaminant gas by a factor of 10.

For catastrophic failure of a pressurized containment vessel, estimates have been made by Fryer and Kaiser (1979 SRD R152) of the aspect ratio and of the mass of air entrained for ammonia. The gas cloud is assumed to form a cylinder. From field trials and incidents they suggest that the radius and height of this cloud be taken as equal and the mass ratio of air to contaminant gas as some 2 : 1 This applies to the failure of a vessel at a quite high pressure, with a correspondingly high degree of induced turbulence; the degree of entrainment may be expected to be rather less if the vessel pressure is lower.

The *Second Canvey Report* takes for the initial cylindrical gas cloud a value of the aspect ratio, or ratio of diameter to height, of unity and this value is adopted in the Workbook by Britter and McQuaid (1988).

Further discussion of such empirical estimates for catastrophic failure is given in Section 15.8, which also gives models of vessel failure from which alternative estimates of the quantity of air entrained may be made.

For two-phase flashing jets and for elevated jets the entraiment of air is part of the model for the jet. An account of these models is given in Section 15.21.

15.23.8 Liquid droplets

Another important aspect of the source term is the initial liquid fraction present in the gas cloud as spray, together with the extent to which this rains out and, if so, evaporates again. The methods of estimating the liquid fraction have been described briefly above and are dealt with in more detail in Section 15.10.

The liquid droplets tend not to rain out but rather to evaporate. The behaviour of liquid droplets in the gas cloud is considered in Section 15.2. If rainout does occur, the liquid in the resulting pool will evaporate and the contribution to the source term of this re-evaporation may be significant.

15.23.9 Matching to dispersion model

For the determination of the dispersion of the material released, the source model has to be matched to the dispersion model. The cases for which such matching is required include:

(1) vaporization from a liquid pool;
(2) catastrophic failure of a vessel;
(3) two-phase flashing jet;
(4) elevated jet.

Vaporization from a liquid pool appears at first sight to constitute a relatively simple source. However, both the area of and the rate of heat transfer to the pool are variable. Therefore either the vapour flow has to be treated as an idealized instantaneous or continuous release or the dense gas dispersion model has to be able to handle a

time-varying release. In addition, a gas blanket may form above the pool. A separate submodel of this gas blanket may be included in the dense gas dispersion model.

Catastrophic failure of a vessel is generally modelled by taking as the source term a cylindrical cloud of defined aspect ratio and containing a specified quantity of entrained air. It may then be treated by the dense gas dispersion model as an instantaneous release. A similar approach may be used for a release from an intermediate sized hole.

A two-phase flashing jet model may or may not be readily conformable with the dispersion model. Models of such jets are described in Section 15.21, including some which are designed explicitly to give a smooth transition to a dense gas dispersion model.

For an elevated jet, models have been developed that conform with dense gas dispersion models, but the two-phase aspect of such jets is not well developed. The models for an elevated jet give two main types of output. One type consists simply of the touchdown distance and the concentration at touchdown. The other gives the full profile of the touchdown plume, including dimensions, velocity and concentration. It is this latter type which gives the better match to a dense gas dispersion model. Both types of model for an elevated jet are described in Section 15.4. A jet would generally be expected to constitute a continuous release, unless the time is so short that this is not appropriate.

The matching of emission and vaporization models to dispersion models is treated in the CCPS *Workbook of Test Cases for Vapour Cloud Source Dispersion Models* (1989/8). This is described in Section 15.52.

15.23.10 LNG

Treatments of the source terms for specific gases are also available. Source terms for LNG have been discussed by Kaiser (1980) and Puttock (1987c, 1988a, 1989).

As stated above, for LNG spilled onto water evidence for field trials involving Refrigerant 12 suggests that the violent boiling results within about 5 s in the entrainment of some 10 times as much air. It is not known how this effect scales up.

LNG is not normally stored under pressure, but if it were the extent of air entrainment following catastrophic failure would be sufficient to dilute it close to its lower flammability limit.

An elevated jet release of LNG might well disintegrate and evaporate before it reached the surface.

15.23.11 Ammonia

Source terms for ammonia have been discussed by Kaiser and Walker (1978), Fryer and Kaiser (1979 SRD RR152), Griffiths and Kaiser (1979 SRD R154) and Kaiser (1980, 1989). They consider in particular the field trials with Refrigerant 12 and the ammonia release incidents at Potchefstroom in 1973 (Case History A65), Houston in 1976 (Case History A84), and Pensacola in 1977, and deduce for catastrophic failure of a vessel rules of thumb for aspect ratio and air entrainment, as mentioned above and described more fully in Section 15.8. The work of Wheatley (1986) on two-phase flashing jets is concerned specifically with ammonia.

15.24 Dispersion of Dense Gas: Models and Modelling

The mathematical modelling of dense gas dispersion is a complex subject with a large literature.

15.24.1 Types of model

There are three broad classes of model of dense gas dispersion:

(1) modified conventional models;
(2) box and slab models;
(3) K-theory and other three-dimensional models.

15.24.2 Modified conventional models

Once it was realized that some materials exhibit a degree of dense gas behaviour, the initial response was to attempt to modify existing models such as the Sutton and Pasquill–Gifford models, usually by making empirical adjustments to the diffusion parameter C or the dispersion coefficient u. This approach is described in Section 15.25. It was soon appreciated, however, that the behaviour of a dense gas is radically different from that of a neutrally buoyant gas and that a totally different approach is necessary.

15.24.3 Box models

A new generation of models, usually known as box models, was created. In the simple box model the gas cloud is assumed to be a pancake-shaped cloud with properties uniform in the crosswind and vertical directions. The model contains relations which describe the growth of the radius and height of an instantaneous release, or the crosswind width and height of a continuous release, and the entrainment of air at the top and edges of the cloud. The concentration in the cloud is obtained by mass balance. For an instantaneous release it is uniform in all three directions. For a continuous release it is uniform in the crosswind and vertical directions, but varies in the downwind direction.

The characteristic features of a typical box model are as follows. The cloud shape is determined by gravity-driven flow. Mixing inside the cloud is sufficiently rapid that the cloud has uniform concentration. Air entrainment velocities are specified as a function of cloud advection velocity, density difference and turbulence levels.

Although simple in concept, the box model actually places considerable demands on the modeller to specify correctly the various features just mentioned, such as cloud advection velocity and entrainment rates. In this respect it contrasts with the three-dimensional models described below, which largely take care of these aspects. In this sense, the apparent simplicity of the box model is deceptive. A box model contains a small number of adjustable parameters. These may be determined individually by experiment and confirmed by field trials.

The features of the box model for the investigation of dense gas dispersion have been described by McQuaid (1984a). A box model utilizes a top-hat concentration profile. McQuaid cites a number of other problems in fluid mechanics in which a similar 'black box' approach has been used, including the analysis of the boundary layer by Clauser (1954) and of plumes and of wakes by B.R. Morton, Taylor and Turner (1956) and B.R. Morton (1962).

A box model is based on the principle of similarity. For dense gas dispersion the conditions necessary for similarity are given by McQuaid as that the gas cloud is not so large as to alter the ambient atmosphere and that it is not subject to rapid change of depth.

McQuaid discusses the applicability of box models for the assessment of releases of flammable or toxic materials. He concludes that for toxic releases a box model gives concentrations which are generally sufficiently accurate, given the relatively high uncertainty in relations for toxic injury, but may be insufficiently accurate for some problems which arise in relation to flammability.

Box models are relatively simple, but have a number of drawbacks. One is that they are essentially limited to flat, unobstructed terrain and are not designed to handle terrain with slopes, obstructions, buildings or other special features. Another defect is the assumption of uniform concentration which may be inadequate for assessment of flammability and toxicity. A box model is sometimes termed a bulk property (BP) model.

Box models have been the dominant type of model used for dense gas dispersion and several such models are described below.

15.24.4 Advanced similarity models

Box models are simple similarity models which are based on assumptions about the shape of the gas cloud. A development from these is the advanced similarity models, which incorporate also assumptions about the concentration profile. The HEGADAS model, described below, is an advanced similarity model.

15.24.5 *K*-theory models

The limitations of box models have led to increasing use of the more fundamental if-theory models. An if-theory model consists of a set of equations for the conservation of mass, energy, momentum, and so on, together with boundary conditions. The model determines the variation of properties, velocity and concentration along the flow streamlines.

When the basic equations are averaged with respect to time certain second-order terms appear. The number of equations is less than the number of unknowns. It is therefore necessary to specify some of the unknowns in terms of the others. This is known as 'turbulence closure' and much work has been done on methods of effecting it. In an if-theory model the closure is a low order one. It is effected by making the gradient transfer assumption.

The model utilizes empirical relationships for the eddy diffusivities and eddy viscosities as a function of space, and sometimes also of stability category or Richardson number. Higher order closures are those in which additional equations are derived for the Reynolds stresses (e.g. $\overline{uw}$) and therefore also for the velocity concentration correlations (e.g. $\overline{wc}$). The new equations include third-order terms which in turn have to be modelled.

For undisturbed ambient flows if-theory models are reasonably satisfactory. But the presence of dense gas or obstructions renders them less so. In such cases the relations used for the eddy diffusivity K become inadequate, because they take insufficient account of local variations. In particular, the Reynolds analogy for the equivalence of mass, heat and momentum eddy diffusivities is not valid when the flow has stable density stratification.

The development of if-theory models was influenced by the need to obtain analytical solutions. This requirement meant that K had to be specified in a way compatible with this aim. The advent of computers has removed this constraint.

In some areas of work on turbulent diffusion the use of eddy diffusivities is regarded as out-dated and use is made of higher order closure models, if-theory models were in use before the recognition of the need for models specific to dense gas dispersion and a if-theory model, SIGMET, was in fact one of the first models applied to this problem. An if-theory model is sometimes termed a turbulence scheme model.

K-theory models are full three-dimensional models, but they may also be used in the two-dimensional mode, and in fact it is often sufficient to use them in this way.

Several of the models described below are if-theory models.

15.24.6 $\kappa-\epsilon$ Models

As just mentioned, the presence of a dense gas or of obstructions tends to render inadequate the relations normally used for the eddy diffusivity in a *K*-theory model.

The eddy diffusivity K is related to the turbulence energy (and the energy dissipation rate ϵ as follows:

$$K \propto \frac{\kappa^2}{\epsilon} \qquad [15.24.1]$$

The value of the eddy diffusivity is subject to local variations which are much more significant in the presence of dense gas or obstructions. A region of high density gradient tends to give low values of κ and thus, from Equation 15.24.1, very low values of K.

One way of overcoming this difficulty is to determine local values for κ and ϵ and then use them to obtain local values for K. This may be done by formulating the transport equations for κ and ϵ. This creates a two-equation $\kappa-\epsilon$ model. The parameters required for this $\kappa-\epsilon$ model are available and apply over a wide range of flows. This approach retains eddy diffusivity but allows it to vary locally.

$\kappa-\epsilon$ models are used extensively for the study of flows in regions of recirculation. One of the models described below, HEAVYGAS, is a $\kappa-\epsilon$ model.

15.24.7 Algebraic stress models

The $\kappa-\epsilon$ models just described still utilize the gradient transport relationship in regions where the diffusivities are very low and difficult to specify. They still retain the assumption that the eddy diffusivity is isotropic. It is known, however, that stability affects the different components of the Reynolds stresses in different ways.

A development that addresses this problem is the algebraic stress model. This replaces the gradient transport relation with equations which relate the various fluxes and stresses to the velocity and density gradients. This type of model is not, however, developed for dense gas dispersion.

15.24.8 Density difference

The treatment described below makes use of certain common relations and, before describing the principal models, it is convenient to give some of these relations. For the density intrusion represented by a dense gas spreading in ambient air

$$\Delta\rho = \rho - \rho_a \qquad [15.24.2]$$

$$\Delta = \frac{\Delta\rho}{\rho_a} \qquad [15.24.3]$$

$$g' = g\frac{\rho - \rho_a}{\rho_a} \quad [15.24.4a]$$

$$= g\Delta \quad [15.24.4b]$$

where $\Delta\rho$ and Δ are the absolute and reduced density differences between the gas cloud and the ambient air, g and g' are the absolute and reduced accelerations due to gravity, ρ is the density of the cloud and ρ_a is the density of the ambient air. The variable g' is generally referred to simply as the 'reduced gravity'.

An alternative reduced density difference is also used defined as

$$\Delta' = \frac{\Delta\rho}{\rho} \quad [15.24.5]$$

where Δ' is an alternative reduced density difference.

15.24.9 Wind velocity

The vertical wind velocity profile is frequently obtained from the empirical expression

$$u = u_r\left(\frac{z}{z_r}\right)^p \quad [15.24.6]$$

where u is the wind velocity, u_r is the wind velocity at the reference height z_r, z is the height, z_o is the roughness length and p is an index.

Use is made of the logarithmic vertical wind velocity profile:

$$u = \frac{u_*}{k}\ln\left(\frac{z}{z_r}\right) \quad [15.24.7]$$

where u is the friction velocity, z_o is the roughness length and k is the von Karman constant.

The logarithmic vertical wind velocity profile is also used in the modified form:

$$u = \frac{u_*}{k}\left[\ln\left(\frac{z+z_o}{z_o}\right) - \psi\left(\frac{z}{L}\right)\right] \quad [15.24.8]$$

where L is the Monin–Obukhov length and ψ is a profile function.

15.24.10 Heat transfer

Heat transfer from the ground to the cloud will, in general, have contributions from both natural and forced convection. For natural convection use is frequently made of the relation given by McAdams (1954) for heat transfer from an upwards-facing heated plate:

$$\mathrm{Nu} = 0.14(\mathrm{G}r\,\mathrm{Pr})^{1/3} \quad [15.24.9]$$

with

$$\mathrm{Nu} = \frac{hL}{k_f} \quad [15.24.10]$$

$$\mathrm{Gr} = \frac{L^3\rho_f\beta_f g\Delta T}{\mu_f} \quad [15.24.11]$$

$$\mathrm{Pr} = \frac{c_{pf}\mu_f}{k_f} \quad [15.24.12]$$

$$\beta_f = 1/T \quad [15.24.13]$$

where c_p is the specific heat, Gr is the Grashof number, h is the heat transfer coefficient, k is the thermal conductivity, L is a characteristic linear dimension, Nu is the Nusselt number, Pr is the Prandtl number, T is the absolute temperature, ΔT is the temperature difference for heat transfer, β is the coefficient of thermal expansion, μ is the viscosity, ρ is the density and the subscript f denotes film conditions. Then from Equation 15.24.9

$$h_{gr} = 0.14\left(\frac{\rho_f^2 k_f^3 g}{\mu_f^2}\frac{c_{pf}\mu_f}{k_f}\frac{\Delta T}{T}\right)^{1/3} \quad [15.24.14]$$

where the subscript gr denotes between the ground and the cloud.

For heat transfer by forced convection use is made of the relation given by Treybal (1955) for heat transfer from an upwards-facing heated plate:

$$j_H = \mathrm{St}_H\mathrm{Pr}^{2/3} = \frac{C_f}{2} \quad [15.24.15]$$

with

$$\mathrm{St}_H = \frac{k}{c_p G} \quad [15.24.16]$$

$$C_f = 2\left(\frac{u_*}{u}\right)^2 \quad [15.24.17]$$

where C_f is a friction factor, G is the mass velocity, j_H is the j factor for heat transfer, St_H is the Stanton number for heat transfer and u is the velocity of the cloud. Equation 15.24.15 can be rearranged to give, for the case considered,

$$h_{gr} = \left[\left(\frac{c_p\mu}{k}\right)^{-2/3}\left(\frac{u_*}{u}\right)^2\right]u\rho c_p \quad [15.24.18]$$

15.24.11 Density intrusion models

A dense fluid within a less dense fluid, such as a dense gas cloud in the atmosphere, represents a density intrusion which flows as a gravity current. The modelling of density intrusions and of the associated gravity-driven flow is a distinct area of work with applications in a number of fields. Reviews of gravity currents have been given by Benjamin (1968) and Simpson (1982). Gravity currents occur in many natural situations in the atmosphere and the ocean and they are relevant to industrial accidents such as oil spills and dense gas releases.

Work on gravity-driven flow includes the investigation of: the different phases of the flow (e.g. Huppert and Simpson, 1980); of the flow on a flat surface, and in particular the 'head' which develops at the leading edge (e.g. Benjamin, 1968) and the mixing which occurs (e.g. Britter and Simpson, 1978); of flow on slopes (e.g. Ellison and Turner, 1959; Britter and Linden, 1980; Beghin, Hopfinger and Britter, 1981); and of flow over and around obstacles (e.g. Rottman *et al.*, 1985).

The driving force of the gravity current is the buoyancy force. This is opposed by the inertial force, which is dominant initially, and the viscous force, which becomes dominant later. There is therefore an inertia-buoyancy phase and a viscous-buoyancy phase.

A model of gravity-driven flow which is increasingly utilized is the 'shallow water equations'. These are described in *Water Waves* (Stoker, 1957), Stratified Flows (Yih, 1980) and *Introduction to Water Waves* (Crapper, 1984). A derivation of the shallow water equations has been given by Penney and Thornhill (1952).

The non-linear shallow water equations are:

$$\frac{\partial h}{\partial t}+\frac{\partial(uh)}{\partial x}+n\frac{uh}{x}=0 \qquad [15.24.19]$$

$$\frac{\partial u}{\partial t}+u\frac{\partial u}{\partial x}+g'\frac{\partial h}{\partial x}=0 \qquad [15.24.20]$$

where g' is the reduced gravity, h is the height of the dense fluid, u is the velocity of the dense fluid, x is the distance and n is a symmetry index. For planar flow $n=0$, and for axisymmetric flow $n=1$.

From Bernouilli's equation, the velocity of the gravity-driven wave is

$$c=(g'h)^{1/2} \qquad [15.24.21]$$

where c is the velocity of the wave. Then, from Equations 15.24.19–15.24.21, for $n=0$

$$\frac{\partial c}{\partial t}+\frac{c}{2}\frac{\partial u}{\partial x}+u\frac{\partial c}{\partial x}=0 \qquad [15.24.22]$$

$$\frac{\partial u}{\partial t}+u\frac{\partial u}{\partial x}+2c\frac{\partial c}{\partial x}=0 \qquad [15.24.23]$$

15.24.12 Basic box model relations

The basic equations of the typical box model are:

$$\frac{\mathrm{d}R}{\mathrm{d}t}=c_{\mathrm{E}}(g'H)^{1/2} \qquad [15.24.24]$$

$$\frac{\mathrm{d}V}{\mathrm{d}t}=\pi R^2u_{\mathrm{e}}+2\pi RHw_{\mathrm{e}} \qquad [15.24.25]$$

where g' is the reduced gravity, H is the height of the cloud, R is the radius of the cloud, u_{e} is the top entrainment velocity, V is the volume of the cloud, w_{e} is the edge entrainment velocity and c_{E} is the damping coefficient.

Equation 15.24.24 may also be formulated in terms of the negative buoyancy B:

$$B=g'V \qquad [15.24.26a]$$

$$=g'(\pi R^2H) \qquad [15.24.26b]$$

Thus, from Equation 15.24.24 and 15.24.26b

$$\frac{\mathrm{d}R}{\mathrm{d}t}=c_{\mathrm{E}}\left(\frac{B}{\pi}\right)^{1/2}\frac{1}{R} \qquad [15.24.27]$$

15.24.13 Model development

Since the work on dense gas dispersion in the Netherlands in the early 1970s, notably the work of van Ulden, there has been a high level of interest and work on the subject, including mathematical modelling, physical modelling and field trials. Some early workers, such as the Bureau of Mines and Clancey, attempted to adapt passive dispersion models to dense gas dispersion, as described in Section 15.25. However, in view of the fundamentally different physical phenomena involved, this attempt came to be regarded as inappropriate, although the newer models often incorporate features of, and make transition to, passive dispersion models.

The next generation of models were box models. Of these, the models of van Ulden, of Cox and Roe (developed as the BG/C&W model) and the SRD models (DENZ and CRUNCH) are described in Sections 15.26–15.28, respectively. Even at this stage the box models did not have the field entirely to themselves. An early and influential if-theory model was SIGMET, which has already been referred to in connection with LNG spill study and which is described further in Section 15.29.

The more modern systems of models include: SLAB and FEM3; HEGADAS and HGSYSTEM; DEGADIS; and SLUMP and HEAVYGAS. These are described in Sections 15.30–15.33, respectively. Both advanced box models and three-dimensional models are represented here. A different type of modern model is the similarity model given in the Workbook and described in Section 15.34. In Section 15.35 an account is given of DRIFT, a model which develops but transcends the box model approach. Some other models are described in Section 15.36.

15.25 Dispersion of Dense Gas: Modified Conventional Models

15.25.1 Bureau of Mines model

Attempts were made in early work to modify the parameters in passive gas dispersion models to take into account heavy gas behaviour. An account is given, although the approach has now been largely superseded by other methods.

Thus, for example, for a neutral gas the vertical dispersion coefficient σ_z in the Pasquill–Gifford equations tends to be about half the value of the horizontal dispersion coefficient, but work at the Bureau of Mines (Burgess and Zabetakis, 1973 BM RI 7752) indicated that for a heavy gas

$$\sigma_z=0.2\sigma_y \qquad [15.25.1]$$

where σ_y and σ_z are the dispersion coefficients in the crosswind and vertical (y and z) directions, respectively. Equation 15.25.1 has been used by Burgess and Zabetakis to take into account the density effect in the gas cloud formed in the Port'Hudson explosion in 1970 (Case History A52).

15.25.2 Clancey model

V.J. Clancey (1976a) suggested that in Equation 15.16.25 the generalized diffusion parameter in the vertical direction C_z should be taken as

$$C_z=\tfrac{1}{2}C_x=\tfrac{1}{2}C_y \qquad [15.25.2]$$

where C_x, C_y and C_z are the generalized diffusion parameters in the downwind, crosswind and vertical (x, y and z) directions, respectively.

15.25.3 Germeles and Drake model

A modified Gaussian model was presented by Germeles and Drake (1975) to describe the dispersion of LNG vapour clouds. This model has also been described by Ermak, Chan *et al.* (1982).

The Germeles and Drake model for a continuous release contains elements both of a dense gas box model and a passive dispersion model. The source is assumed to be a cylindrical cloud with an initial radius R_i that of the pool and initial height H_i given by

$$H_i = 2R_i W_v/u \qquad [15.25.3]$$

The mass and heat content of the source are

$$m = \pi\rho R^2 H \qquad [15.25.4]$$

$$E = mc_p T \qquad [15.25.5]$$

where c_p is the specific heat of the gas in the source cloud, E is the heat in the source cloud, m is the mass of gas in the source cloud, T is the absolute temperature, u is the wind speed, W_v is the velocity of the vapour source, and ρ is the density. The value of W_v is some 250 times the liquid regression rate.

The development of the source cloud is as follows. For the rate of change of the radius use is made of Equation 15.24.24 and for that of the mass and heat content

$$\frac{dm}{dt} = \pi\rho_a R^2 u_e \qquad [15.25.6]$$

$$\frac{dE}{dt} = \pi\rho_a R^2 c_{pa} T_a u_e + \epsilon_v + \epsilon_w \qquad [15.25.7]$$

where u_e is the top entrainment velocity, ϵ_v is the heat released by the condensation and by freezing of the water vapour, ϵ_w is the surface heat flux and subscript a denotes air.

It is assumed that the release is from a finite line source of width L located at a virtual source a distance x_v upwind of the true source. Use is then made of a model of the Pasquill–Gifford type to model the dispersion. This gives for the concentration

$$c(x,y,z) = \frac{V}{(2\pi)^{1/2} u L \sigma_z} \exp\left(-\frac{z^2}{2\sigma_z^2}\right) \times \left\{ \mathrm{erf}\left[\frac{(L/2)-y}{2^{1/2}\sigma_v}\right] + \mathrm{erf}\left[\frac{(L/2)+y}{2^{1/2}\sigma_v}\right] \right\} \qquad [15.25.8]$$

where c is the volumetric concentration, L is the width of the source, $\dot{V}$ is the volumetric rate of release, and σ_y and σ_z are the dispersion coefficients in the crosswind and vertical directions, respectively. The values used for σ_y and σ_z are the regular Pasquill–Gifford values.

The source model is run until the radial velocity of the cloud is equal to the wind speed. The source length L is then set equal to the diameter $2R$ of the cloud and the virtual source distance x_v is found from the values of $\sigma_y(x_v)$ and $\sigma_z(x_v)$ required to make the concentration at the source centre, as given by Equation 15.25.8, equal to that in the source cloud. Equation 15.25.8 is then used with these parameters to determine the concentrations downwind.

Ermak, Chan *et al.* (1982) have compared the performance of the Germeles and Drake model with that of other models in relation to the Burro trials.

15.26 Dispersion of Dense Gas: Van Ulden Model

15.26.1 Van Ulden model

The experimental work of van Ulden (1974) which demonstrated the marked difference in behaviour between a neutrally buoyant gas and a dense gas has already been described. At the same time van Ulden also presented a theoretical model. The main model was for the dispersion of an instantaneous release of dense gas in still air, but a model for a continuous release with finite wind velocity was also outlined. Van Ulden has subsequently extended his model (van Ulden 1979, 1984, 1987, 1988; van Ulden and de Haan, 1983).

In van Ulden's original work the behaviour of the cloud is modelled as a two-stage process, in which spreading occurs in the first stage by gravity slumping and in the second by Gaussian dispersion. In the first stage the dispersion is treated as a dense fluid flow process but with air entrainment at the edge of the cloud.

The starting point of the model is the following equation for the movement of a front of dense fluid such as that resulting from a dam burst:

$$u_f = c_E(\Delta \cdot g H_f)^{1/2} \qquad [15.26.1]$$

with

$$\Delta = (\rho_1 - \rho_2)/\rho_1 \qquad [15.26.2]$$

where H_f is the height of the front, u_f is the velocity of the front, Δ is the reduced density difference, ρ_1 is the density of the fluid behind the wavefront, ρ_2 is the density of the fluid ahead of the wavefront and c_E is a slumping constant. Van Ulden states that experiment suggests that the constant C_E is approximately unity.

It is assumed that in the first stage the initial gas cloud is a cylinder of radius R, height $H(R)$ and volume $V(R)$ with a front moving at velocity $u_f(R)$ and with changing density $\rho(R)$. Then from the model just given

$$\frac{dR}{dt} = u_f \qquad [15.26.3]$$

$$= c_E(\Delta'_c \cdot gH)^{1/2} \qquad [15.26.4]$$

with

$$\Delta'_c = (\rho_c - \rho_a)/\rho_c \qquad [15.26.5]$$

where t is the time, Δ'_c is the reduced density difference of the cloud, ρ_a is the density of air and ρ_c is the density of the cloud. The volume V of the cloud is

$$V = \pi R^2 H \qquad [15.26.6]$$

Mixing at the front, or edge, of the cloud is assumed to take place at the rate

$$\frac{dV}{dt} = \gamma 2\pi RH \frac{dR}{dt} \qquad [15.26.7]$$

where γ is the edge entrainment coefficient. Solution of Equations 15.26.3–15.26.7 gives

$$V/V_o = (R/R_o)^{2\gamma} \quad [15.26.8]$$

$$H/H_o = (R/R_o)^{2\gamma-2} \quad [15.26.9]$$

$$\frac{dR}{dt} = \frac{c_E}{R}\left[\frac{gV_o/\pi}{V_o/V + \rho_a/(\rho_o - \rho_a)}\right]^{1/2} \quad [15.26.10]$$

$$\Delta = \left[1 + \frac{\rho_a V}{(\rho_o - \rho_a)V_o}\right]^{-1} \quad [15.26.11]$$

where the subscript o denotes time zero and hence the source.

Equation 15.26.10 reduces to

$$\frac{dR}{dt} = \frac{c_E}{R}\left[\frac{(\rho_o - \rho_a)gV_o}{\pi\rho_o}\right] \quad [15.26.12]$$

if the mixing at the front is negligible or if the term $(\rho_o - \rho_a)/\rho_a$ is small. Therefore Equation 15.26.12 is an adequate approximation in all circumstances. From Equation 15.26.12 the relation between the cloud radius and the time t is

$$R^2 - R_o^2 = 2c_E\left[\frac{(\rho_o - \rho_a)gV_o}{\pi\rho_o}\right]^{1/2} t \quad [15.26.13]$$

The transition from gravity spread to diffusional mixing is taken to occur at the point where the turbulent energy is equal to the average potential energy difference and hence where

$$2\rho_a u_*^2 = 1/2(\rho_c - \rho_a)gH \quad [15.26.14a]$$

$$= 1/2\rho_c u_f^2 \quad [15.26.14b]$$

The condition for transition with $\rho_e \approx \rho_a$ is then

$$u_f = 2u_* \quad [15.26.15]$$

Van Ulden uses the model just given to calculate the transition radius R_u and height H_u at which condition 15.26.15 applies and the position of the cloud and then applies an area source Gaussian dispersion model for the further determination of concentrations. The cloud radius and height obtained by Van Ulden for the experiment described earlier are shown in Figure 15.76. The fit is much superior to that given by the Gaussian model.

Van Ulden also gave a treatment of a continuous release. The mass flux across the cross-section of the plume at right angles to the wind direction is constant. The area of the cross-section is

$$S = 2LH \quad [15.26.16]$$

where L is the half-width of the plume and S is the area of the cross-section of the plume. For the source

$$S_o = 2L_oH_o \quad [15.26.17]$$

and

$$W_o = S_o u \quad [15.26.18]$$

where u is the mean wind speed and W_o is the volumetric flow from the source.

Then, by an argument similar to that for the instantaneous release,

$$S/S_o = (L/L_o)^{\gamma} \quad [15.26.19]$$

$$H/H_o = (L/L_o)^{\gamma-1} \quad [15.26.20]$$

$$u_y = \frac{c_E}{L^{1/2}}\left[\frac{gS_o/2}{S_o/S + \rho_a/(\rho_o - \rho_a)}\right]^{1/2} \quad [15.26.21]$$

$$\Delta_c' = \left[1 + \frac{\rho_a}{\rho_o - \rho_a}\left(\frac{L}{L_a}\right)^{\gamma}\right]^{-1} \quad [15.26.22]$$

where u_y is the velocity of the cloud in the crosswind direction.

For the particular case of no mixing ($\gamma = 0$) and hence constant reduced density ($\Delta_c' = \Delta_{co}'$)

$$u_y = \left(\frac{gS_o\Delta_{co}'}{2L}\right)^{1/2} \quad [15.26.23]$$

15.26.2 Critique of model

In subsequent work, van Ulden has described certain deficiencies in this model and in models by other workers, and has made modifications to his own model. Van Ulden and de Haan (1983) analyse the forces which determine the behaviour of an unsteady-state gravity current, notably the buoyant, viscous and inertial forces, and describe the viscous-buoyant and inertia-buoyant phases. They refer to the finding of Huppert and Simpson (1980) in work on flow of a dense fluid under a lighter fluid in a channel that the velocity of the gravity current is not solely a function of $(g'H)^{1/2}$ and that an important parameter is the fractional depth H/D, where D is the total depth of the channel.

Van Ulden (1984) gives a model for the particular case of two-dimensional flow in the inertia-buoyancy regime. In further critiques, van Ulden (1987, 1988) points out that Equation 15.26.4 is deficient in that it takes no account of the horizontal acceleration of the cloud from rest and therefore does not give conservation of momentum.

Various modellers have described air entrainment at the top and at the edge of the cloud by the relation

$$\frac{dV}{dt} = \pi R^2 u_e + 2\pi RHw_e \quad [15.26.24]$$

where u_e is the top entrainment velocity and w_e is the edge entrainment velocity. However, proportionality between u_e and u_f violates conservation of energy.

15.26.3 Van Ulden model 2

Van Ulden (1987, 1988) has presented a second model which corrects some of the weaknesses of the initial model just described. The model is again for an instantaneous release in still air.

The model consists of four simultaneous differential equations for the rate of change with time of the radius R, the volume V, the edge velocity u_f and the bulk turbulent kinetic energy T_E. It gives a more fundamental treatment in that the relations for u_f and T_E are based on conservation of momentum and of energy, respectively, and the velocity of entrainment u_e through the top surface of the cloud is

obtained from the bulk turbulent velocity $\bar{u}_t$ which itself is derived from the turbulent energy T_E.

The equations for the radius R and the volume V are

$$\frac{dR}{dt} = u_f \qquad [15.26.25]$$

$$\frac{dV}{dt} = \pi R^2 u_e \qquad [15.26.26]$$

For the edge velocity u_f, conservation of radial momentum gives

$$\frac{dM_{rd}}{dt} = F_s + F_d + F_a + F_v \qquad [15.26.27]$$

where F_a is the force due to the reaction of the ambient fluid to the outward radial acceleration of the cloud edge, F_d is the drag force on the cloud edge due to the presence of the quiescent ambient fluid, F_s is the static pressure force due to the negative buoyancy of the cloud, F_v is the force due to vertical acceleration in the cloud and the reaction of the ambient fluid to vertical acceleration of the cloud top and M_{rd} is the radial momentum integral of the cloud. This momentum budget yields a relation of the form

$$\frac{du_f}{dt} = f(g', H, R, u_f, u_e, \rho_c, \rho_a, \bar{\rho}_c, \Delta\bar{\rho}_c) \qquad [15.26.28]$$

where $\bar{\rho}_c$ is the mean density of the cloud and $\Delta\bar{\rho}_c$ is the mean density difference.

The relation for the bulk turbulent kinetic energy T_E is derived from conservation of the total energy in a large control volume containing the cloud and the secondary flows around it. Four types of energy are considered: I_E the internal heat, K_E the kinetic energy of the mean radial and vertical motions, P_E the potential energy and T_E the turbulent kinetic energy. Then

$$\frac{dP_E}{dt} = -G + B \qquad [15.26.29]$$

$$\frac{dK_E}{dt} = G - S \qquad [15.26.30]$$

$$\frac{dT_E}{dt} = S - B - D \qquad [15.26.31]$$

$$\frac{dI_E}{dt} = D \qquad [15.26.32]$$

where B is the rate of buoyant destruction of turbulent energy, which is the conversion of turbulent energy into potential energy by entrainment, D is the rate of dissipation of turbulent energy into internal heat, G is the rate at which gravity transforms potential energy into mean kinetic energy and S is the rate of shear production of turbulent energy. The relationship between these forms of energy is shown in Figure 15.78(a) and their variation with time is shown in Figure 15.78(b). Conservation of energy gives

$$\frac{d(I_E + K_E + P_E + T_E)}{dt} = 0 \qquad [15.26.33]$$

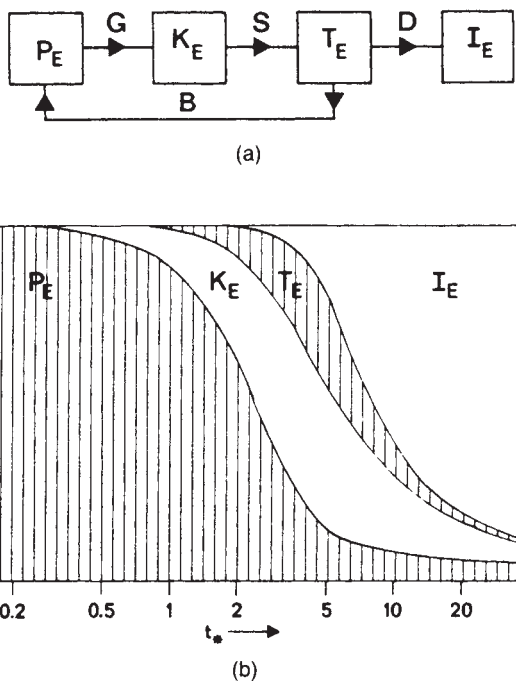


Figure 15.78 *van Ulden's second model of dense gas dispersion – components of energy balance (van Ulden, 1988): (a) relationship between components; (b) change of components with time, t^* is scaled time (Courtesy of Clarendon Press)*

This energy budget yields a relation of the form

$$\frac{dT_E}{dt} = f(g, H, R, u_f, \bar{u}_t, V, V_o, u_e, \rho_c, \rho_a, \bar{\rho}_c, \Delta\bar{\rho}_o, Ri_t) \quad [15.26.34]$$

where Ri_t is a bulk turbulent Richardson number and $\Delta\bar{\rho}_o$ is the mean initial density difference for the cloud. For air entrainment, edge entrainment is neglected and top entrainment is obtained using the entrainment model of Diedronks and Tennekes (1984):

$$u_e = \frac{c_1 \bar{u}_t}{c_t + Ri_t} \quad [15.26.35]$$

with

$$Ri_t = \frac{g\Delta\bar{\rho}_c H}{\bar{\rho}_c \bar{u}_t^2} \quad [15.26.36]$$

where c_1 and c_t are constants. The values of c_1 and c_t are 0.2 and 1.5, respectively.

The bulk turbulent velocity $\bar{u}_t$ is a function of the bulk turbulent kinetic energy T_E:

$$\bar{u}_t = (2T_E/\bar{\rho}_c V)^{1/2} \quad [15.26.37]$$

The average density $\bar{\rho}_c$ and density difference $\Delta\bar{\rho}_c$ of the cloud and average concentration C are

$$\bar{\rho}_c = \rho_a + \Delta\bar{\rho}_c \quad [15.26.38]$$

$$\Delta\rho = \Delta\bar{\rho}_o V_o/V \quad [15.26.39]$$

$$C = V_o/V \quad [15.26.40]$$

assuming $C_o = 1$.

The model itself assumes a uniform profile of concentration with height. Van Ulden states that, in general, the concentration may be described by a relation of the form

$$C(z)/\bar{C} = f(z/H) \quad [15.26.41]$$

where $\bar{C}$ is the mean concentration.

Any such relation should be consistent with conservation of mass:

$$\int_0^\infty f(z/H)\, d(z/H) = 1 \quad [15.26.42]$$

and with the definition of H, taken as

$$H = 2\int_0^\infty zC(z)\, dz \Big/ \int_0^\infty C(z)\, dz \quad [15.26.43]$$

Van Ulden quotes as a possible candidate the family of profiles

$$C(z)/\bar{C} = A\exp[-(Bz/H)^s] \quad [15.26.44]$$

with

$$A = 2s\Gamma(2/s)/[\Gamma(1/s)]^2 \quad [15.26.45]$$

$$B = 2\Gamma(2/3)/\Gamma(1/s) \quad [15.26.46]$$

where s is a profile shape factor and A and B are constants. In fitting his model to experimental results, he utilizes a shape factor $s = 1/2$, giving

$$C(z)/\bar{C} = 6\exp[-(12z/H)^{1/2}] \quad [15.26.47]$$

15.26.4 Extensions of De Nevers

De Nevers (1984b) has described a model of the type given by van Ulden and has extended it to the case of a continuous release and then to a comparison of instantaneous and continuous releases in windless conditions. The treatment is concerned with the short-term behaviour and ignores entrainment of air. Following van Ulden, for an instantaneous release

$$\frac{dR}{dt} = c_E(g'H)^{1/2} \quad [15.26.48]$$

$$V_o = \pi R_o^2 H_o \quad [15.26.49a]$$

$$= \pi R^2 H \quad [15.26.49b]$$

but with

$$g' = \frac{\rho_g - \rho_a}{\rho_a} \quad [15.26.50]$$

where g′ is the reduced gravity and subscript o denotes time zero. Then, combining Equations 15.26.48 and 15.26.49b

$$\frac{dR}{dt} = c_E\left(\frac{g'V_o}{\pi R^2}\right)^{1/2} \quad [15.26.51]$$

Integrating this equation with the initial condition

$$t = t_o; \quad R = R_o$$

and taking the initial aspect ratio as

$$R_o = H_o \quad [15.26.52]$$

yields

$$\frac{R^2}{2} = c_E\left(\frac{g'V_o}{\pi}\right)^{1/2} t + 1/2\left(\frac{V_o}{\pi}\right)^{2/3} \quad [15.26.53]$$

For a continuous release, Equations 15.26.48 and 15.26.49b are again applicable, but in addition

$$V_o = Qt \quad [15.26.54a]$$

$$= \pi R^2 H \quad [15.26.54b]$$

where Q is the volumetric rate of release. Then, combining Equations 15.26.48, 15.26.49b and 15.26.54a

$$\frac{dR}{dt} = c_E\left(\frac{g'Qt}{\pi R^2}\right)^{1/2} \quad [15.26.55]$$

Integrating this equation with the initial condition

$$t = t_o; \quad R = 0$$

yields

$$\frac{R^2}{2} = \frac{2c_E}{3}\left(\frac{g'Q}{\pi}\right)^{1/2} t^{3/2} \qquad [15.26.56]$$

There is a small transient when expansion by bulk flow from the source exceeds that due to gravity-driven flow, but this is so short it can be neglected.

From Equations 15.26.53 and 15.26.56 and setting $V_o = Qt$

$$\frac{R_i}{R_c} = \left[\frac{3}{2} + \frac{3Q^{1/6}}{4c_E(g')^{1/2}\pi^{1/6}t^{5/6}}\right]^{1/2} \qquad [15.26.57a]$$

$$= \left(\frac{3}{2}\right)^{1/2} \quad t \to \infty \qquad [15.26.57b]$$

where subscripts c and i denote continuous and instantaneous, respectively. The second term on the right-hand side of Equation 15.26.57a falls rapidly to zero, giving Equation 15.26.57b. From Equations 15.26.54b and 15.26.57b

$$\frac{H_i}{H_c} = \frac{2}{3} \qquad [15.26.58]$$

15.26.5 Validation and application

Van Ulden (1974) compared the performance of his first model against the Freon 12 experiment given in his paper, as described in Section 15.22 and shown in Figure 15.76. His work demonstrated that his model was much superior to the Gaussian model in predicting the radius and the height of the cloud, and stimulated work on dense gas dispersion.

15.27 Dispersion of Dense Gas: British Gas/Cremer and Warner Model

The work of van Ulden gave impetus to the development of a number of models of dense gas dispersion. One of the first of these was that by R.A. Cox and Roe (1977) of Cremer and Warner and British Gas, respectively. This model was further developed in treatments by R.A. Cox and Carpenter (1980), C.I. Bradley *et al.* (1983) and Carpenter *et al.* (1987), who refer to it as the British Gas/Cremer and Warner (BG/C&W) model.

15.27.1 Cox and Roe model

The model of R.A. Cox and Roe (1977) is for a continuous release. It follows the same approach as van Ulden in that the cloud is modelled as a sequence of rectangular crosswind slices each of uniform concentration and spreading laterally under gravity. The movement of the cloud edge is

$$\frac{dL}{dt} = (k_E g' H)^{1/2} \qquad [15.27.1]$$

where H is the height of the cloud, L is the half-width of the cloud, g' is the reduced gravity and k_E is a spreading constant. The value of the constant k_E is taken as unity, following van Ulden, although there is theoretical and some experimental basis for a value of 2.

For entrainment of air at the cloud edge, the approach followed is that of van Ulden:

$$Q_e = Hw_e \qquad [15.27.2]$$

with

$$w_e = \gamma\frac{dL}{dt} \qquad [15.27.3]$$

where Q_e is the volumetric flow of air entrained at the edge of the cloud per unit distance crosswind, w_e is the edge entrainment velocity and γ is an edge entrainment coefficient.

In this model account is also taken of entrainment of air at the top of the cloud:

$$Q_t = 2Lu_e \qquad [15.27.4]$$

where Q_t is the volumetric flow of air entrained at the top of the cloud per unit distance downwind and u_e is the top entrainment velocity. The rate of change of volume of the cloud is then

$$\frac{dV}{dt} = Q_t + Q_e \qquad [15.27.5]$$

where V is the volume of the cloud per unit distance downwind. For the top entrainment velocity u_e

$$u_e = \frac{\alpha u_1}{\mathrm{Ri}} \qquad [15.27.6]$$

with

$$\mathrm{Ri} = \frac{g'l}{u_1^2} \qquad [15.27.7]$$

where l is a turbulence length scale, Ri is a Richardson number, u_1 is the longitudinal turbulence velocity and α is a top entrainment coefficient. Equation 15.27.6 is valid for moderate values of Ri, but as Ri tends to zero the term (u_e/u_1) tends to a limiting small value.

The longitudinal turbulence velocity u_i may be expressed in the form

$$\frac{u_1}{u} = \frac{u_1}{u_*}\frac{u_*}{u} \qquad [15.27.8]$$

where u is the wind speed and u_* is the friction velocity. The ratio (u_1/u_*) has been shown by Monin (1962) to depend primarily on the stability condition. His results indicate the following approximate values:

Stability condition	u_1/u_*
Very stable	3.0
Neutral	2.4
Very unstable	1.6

The ratio (u_*/u) has been shown by O.G. Sutton (1953) to depend primarily on the surface roughness. A typical value for open terrain is 0.1. For the turbulence length scale l, use is made of the results of R.J. Taylor, Warner and Bacon (1970), which show that the parameter varies with the stability condition and the height H of the cloud. For the top entrainment coefficient α work in the literature suggests values ranging from 0.15 to 1.0. A value of 0.5 was obtained

by fitting the model to one of the American Gas Association tests for LNG dispersion.

The authors state that in the model the entrained air is assumed to mix adiabatically with the gas and that the effects of water vapour present in the air are taken into account, but give no further details.

15.27.2 Cox and Carpenter model

R.A. Cox and Carpenter (1980) extend the model of Cox and Roe to cover both continuous and instantaneous releases. The situations modelled are shown in Figure 15.79(a) and (b) for the instantaneous and continuous release cases, respectively. The models cover a continuous release in wind and an instantaneous release in still air or in wind, but not a continuous release in still air. The movement of the cloud edge for the two cases is

$$\frac{dL}{dt} = (k_E g' H)^{1/2} \quad \text{continuous release} \qquad [15.27.9a]$$

$$\frac{dR}{dt} = (k_E g' H)^{1/2} \quad \text{instantaneous release} \qquad [15.27.9b]$$

where R is the radius of the cloud. The value of the constant k_E is unity. The entrainment of air at the cloud edge is

$$Q_e = Hw_e \quad \text{continuous release} \qquad [15.27.10a]$$

$$Q_e = 2\pi RHw_e \quad \text{instantaneous release} \qquad [15.27.10b]$$

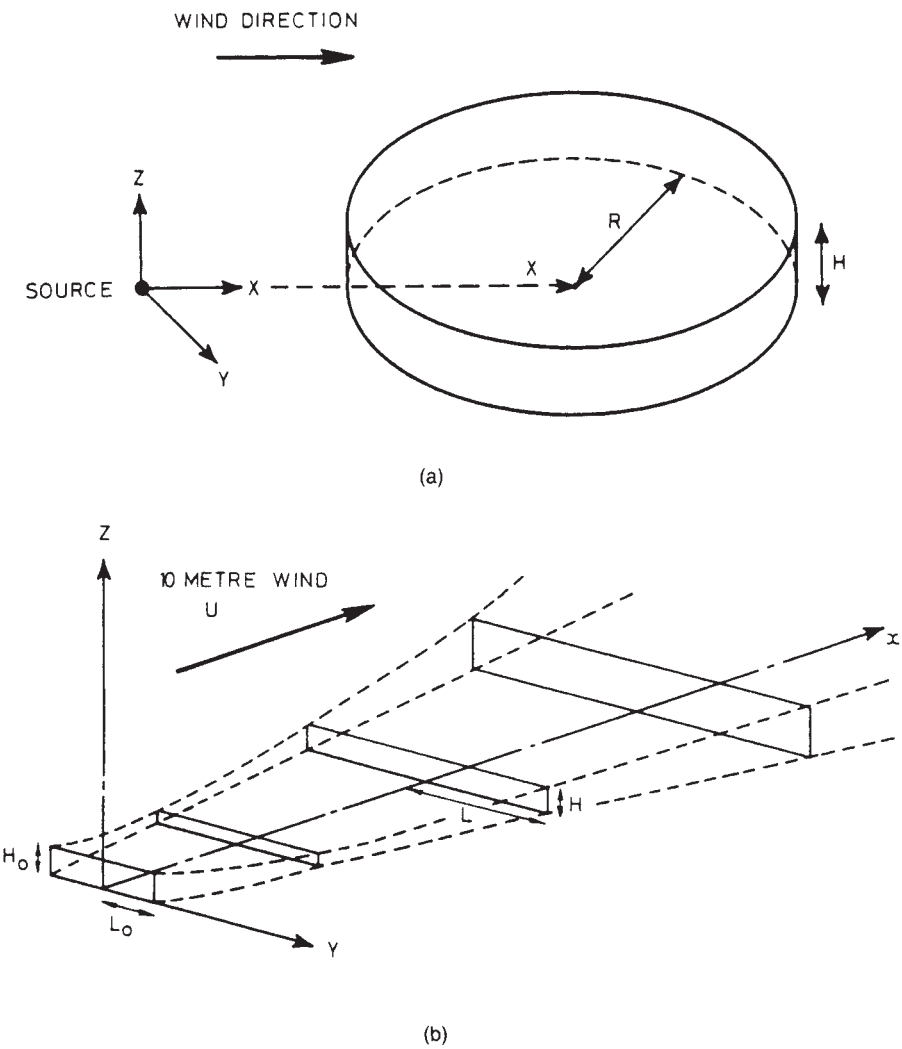


Figure 15.79 *Cox and Carpenter model for dense gas dispersion – idealized cloud shapes (R.A. Cox and Carpenter, 1980): (a) instantaneous release; (b) continuous release (Courtesy of Reidel Publishing Company)*

where Q_e is the volumetric flow of air entrained at the edge of the cloud, this being the total value for the instantaneous release case and the value per unit distance crosswind for the continuous release case. The edge entrainment velocity w_e is

$$w_e = \gamma \frac{dL}{dt} \quad \text{continuous release} \qquad [15.27.11a]$$

$$= \gamma \frac{dR}{dt} \quad \text{instantaneous release} \qquad [15.27.11b]$$

The entrainment of air at the cloud top is

$$Q_t = 2Lu_e \quad \text{continuous release} \qquad [15.27.12a]$$

$$Q_t = 2\pi R^2 u_e \quad \text{instantaneous release} \qquad [15.27.12b]$$

where Q_t is the volumetric flow of air entrained at the top of the cloud, this being the total value for the instantaneous release case and the value per unit distance downwind for the continuous release case.

The treatment of the entrainment velocity u_e at the top of the cloud is essentially that given by Cox and Roe. There is a limiting small value β to which the group (u_e/u_1) tends as Ri tends to zero. The values used for α, β and γ are discussed below.

The rate of change of volume of the cloud is

$$\frac{dV}{dt} = Q_t + Q_e \qquad [15.27.13]$$

where V is the volume of the cloud, this being the total value for the instantaneous release case and the value per unit distance downwind for the continuous release case.

A more detailed description is given of the heat balance used in the model. Vaporization of liquid spray, condensation of water vapour and heat transfer from the ground to the cloud are taken into account. If the source is not one which generates pure vapour but involves a flashing liquid it is assumed that the liquid flash-off is adiabatic, giving vapour and liquid spray. It is also assumed that half the liquid rains out but that this rainout revaporizes instantly. Thereafter the cloud is assumed to be at the saturated condition as long as liquid still remains. The cloud is assumed to be saturated with water.

For heat transfer from the ground by natural convection

$$Q_{gr} = h_{grn}(T_{gr} - T_c)^{4/3} \qquad [15.27.14]$$

and by forced convection

$$Q_{gr} = 0.5 C_f \rho_c c_{pc} u'(T_{gr} - T_c) \qquad [15.27.15]$$

where C_f is a friction factor, c_{pc} is the specific heat of the cloud, h_{grn} is the heat transfer coefficient between the ground and the cloud by natural convection, Q_{gr} is the heat flux from the ground to the cloud, T_c is the temperature of the cloud, T_{gr} is the temperature of the ground, u' is the magnitude of the vector sum of the slumping and wind velocities and ρ_c is the density of the cloud. The friction factor C_f is given by Equation 15.24.17. The value used for the heat flux Q_{gr} is the larger of the values obtained from Equation 15.27.14 for natural convection and Equation 15.27.15 for forced convection. The heat balance on the cloud is then

$$m_{vo}h_v(T_o) + m_{lo}h_l(T_o) + m_a h_a(T_a) + m_{wv}h_{wv}(T_a) + Q_{gr} = m_v h_v(T_c) + m_l h_l(T_c) + m_a h_a(T_c) + m_{wv}h_{wv}(T_c) + m_{wl}h_{wl}(T_c) \qquad [15.27.16]$$

where h is the specific enthalpy of a component, m_i is the mass of component i in the cloud, T_a is the temperature of the air and subscripts a, l, o, v, wl and wv denote air, liquid, source, vapour, liquid water and water vapour, respectively.

The model is extended in the region of passive dispersion. The transition from dense gas to passive dispersion is assumed to occur at the point where the rate of lateral spreading due to turbulence exceeds that due to gravity:

$$\frac{dL}{dt} = \frac{d\sigma_y}{dt} \quad \text{continuous release} \qquad [15.27.17a]$$

$$\frac{dR}{dt} = \frac{d\sigma_y}{dt} \quad \text{instantaneous release} \qquad [15.27.17b]$$

where σ is the dispersion coefficient and subscript y denotes crosswind.

Then from this point a continuous release is modelled using the Gaussian model for a finite line source:

$$\chi(x,y,0) = \frac{Q}{(2\pi)^{1/2}\sigma_z l_{vs} u}\left[\text{erf}\left(\frac{l_{vs}/2 - y}{2^{1/2}\sigma_y}\right) + \text{erf}\left(\frac{l_{vs}/2 + y}{2^{1/2}\sigma_y}\right)\right] \qquad [15.27.18]$$

where l_{vs} is the width of the virtual source, Q is the continuous mass rate of release and χ is the concentration (mass per unit volume).

The treatment for an instantaneous release is slightly more complex. The virtual source is represented as a set of 253 instantaneous point sources on a rectangular grid:

$$\chi(x,y,0) = \frac{2Q^* S^*}{253(2\pi)^{3/2}\sigma_y^2 \sigma_z} \qquad [15.27.19]$$

with

$$S^* = \sum_{n=1}^{253}\left\{-\frac{1}{2}\left[\frac{r(n)}{\sigma_y}\right]^2\right\} \qquad [15.27.20]$$

where Q^* is the mass released instantaneously and $r(n)$ is the distance downwind from the source n.

The dense phase model gives a uniform cross-sectional concentration profile, whereas the passive model gives a Gaussian concentration profile. The Gaussian model has only two degrees of freedom: the distance of the virtual source upstream of the matching point, and the width of the virtual source. The two cloud parameters selected for matching are the centre line concentration and the cloud width. It is assumed that at the matching point the cloud width is equal to the width at the virtual source plus $2\sigma_y$, where σ_y is the value at the matching point based on its distance from the virtual source.

The authors discuss the calibration of the top entrainment coefficient α, the limiting value β of the group u_e/u_1 and the edge entrainment coefficient γ, and give values of 0.1, 0.15 and 0.6, respectively.

15.27.3 Development of model

Development of the model of Cox and Carpenter has been described by C.I. Bradley *et al.* (1983). A deficiency of that model is the neglect of conservation of momentum and the assumption that the cloud travels at a constant speed equal to that of the wind.

For the cloud from an instantaneous release the rate of change of momentum in the frame of reference of the moving cloud is

$$\frac{\mathrm{d}(mu_c)}{\mathrm{d}t} = \dot{m}_e u_{av} + \dot{m}_t u_h + D - F \qquad [15.27.21]$$

where D is the drag force on the cloud, F is the friction force on the cloud, m is the total mass in the cloud, m_e is the mass of air entrained at the edge of the cloud, m_t is the mass of air entrained at the top of the cloud, u_{av} is the average wind speed over the cloud height, u_c is the velocity of the cloud and u_h is the wind speed at the cloud height H. The drag force D is

$$D = C_d \int_0^H R\rho_a[u(z) - u_c]|u(z) - u_c|\,\mathrm{d}z \qquad [15.27.22]$$

where C_d is a drag coefficient and $u(z)$ is the wind speed at height z. The value of the drag coefficient C_d is taken as 1.0. The friction force F is obtained by analogy with the shear stress τ in the atmospheric boundary layer

$$F = \tau\pi R^2 \qquad [15.27.23]$$

with

$$\tau = \left(\frac{u_*}{u_r}\right)^2 \rho_c u_c^2 \qquad [15.27.24]$$

where u_r is the wind speed at the reference height and τ is the shear stress. The reference height is 10 m. Then, from Equation 15.27.21 the acceleration of the cloud relative to a fixed point is

$$\frac{\mathrm{d}u_c}{\mathrm{d}t} = \frac{1}{\dot{m}}[\dot{m}_e(u_{av} - u_c) + \dot{m}_t(u_h - u_c) + D - F \qquad [15.27.25]$$

For the cloud from a continuous release there is no aerodynamic drag, since the main effect of this force is to reverse the upwind flow and give the plume its initial acceleration. There is, however, an additional term which allows for the interaction of one slice of the plume with another due to the variation of cloud dimensions and density as the plume is carried downwind. The rate of change of momentum is

$$\frac{\mathrm{d}u_c}{\mathrm{d}t} = \frac{1}{\dot{m}}\left\{\frac{\mathrm{d}\dot{m}_e}{\mathrm{d}t}(u_{av} - u_c) + \frac{\mathrm{d}\dot{m}_t}{\mathrm{d}t}(u_h - u_c) - 2\tau L u_c - g\frac{\mathrm{d}[LH^2(\rho_c - \rho_a)]}{\mathrm{d}t}\right\} \qquad [15.27.26]$$

A method is also described of handling a transient release which corresponds to neither of the two ideal cases, i.e. to neither a continuous nor an instantaneous release. A case in point is vaporization from a spill of a cryogenic liquid such as LNG. A suitable approach in such a case may be to model the release as an instantaneous release followed by a continuous release. If successively larger masses of vapour are considered, it is found that for a small amount m_1 the time t_1 for vaporization to occur is so short that the trailing edge of the cloud is still upwind of the source. For a large amount m_3, the time t_3 is so long that the trailing edge has moved downwind of the source. There is some intermediate mass m_2 and time t_2 such that the trailing edge is just on the source. This time t_2 is taken as that at which transition occurs. The instantaneous release model is used up to this time and the continuous release model thereafter.

At low wind speeds this method gives a large instantaneous release and the maximum travel distance to a given concentration is determined by this instantaneous part of the release. At high wind speeds and/or for small releases the maximum travel distance is determined by the continuous part of the release.

For very low wind speeds it can occur that the cloud is diluted below its lower flammability limit before it has moved away from the source. This is an indication that the model is inapplicable and it should not be used.

In a further treatment for an instantaneous release, Carpenter *et al.* (1987) express the average wind speed u_{av} over the cloud height as a function of the wind speed u_h at height H:

$$u_{av} = fu_h \qquad [15.27.27]$$

where f is the wind speed coefficient.

The authors present a further calibration of the parameters α, β, γ and f based on data from the Thorney Island Phase 1 tests, and give values of 0.08, 0.30, 0.65 and 0.55, respectively.

15.27.4 Validation and application

R.A. Cox and Roe (1977) compared predictions from their model with observations in the Matagordo Bay tests. R.A. Cox and Carpenter (1980) used the SS Gadila LNG spill trials to calibrate the parameters in their model. The resultant predicted cloud shape is shown in Figure 15.92(a). Carpenter *et al.* (1987) used the Thorney Island trials to calibrate the parameters in the BG/C&W model.

15.28 Dispersion of Dense Gas: DENZ and CRUNCH

Two models on somewhat similar lines have been developed by the Safety and Reliability Directorate (SRD). The model for an instantaneous release, DENZ, is described by Fryer and Kaiser (1979 SRD R152) and that for a continuous release, CRUNCH, by Jagger (1983 SRD R229). The two models are incorporated in the computer codes of the same name and have been widely used.

15.28.1 DENZ

Kaiser and Walker (1978) have described a model which was a forerunner of DENZ and applied it to releases of liquefied anhydrous ammonia.

DENZ is a model for an instantaneous release of a dense gas. It is described by Fryer and Kaiser (1979 SRD R152). The model is based on three simultaneous differential

equations for the radius R of the cloud, the mass m_a of air in the cloud and the temperature T_c of the cloud.

The cloud is assumed to be advected downwind at an advection velocity which corresponds to the mean wind velocity at the half-height of the cloud. This advection velocity is given by

$$u_c(t) = u_r \frac{\ln(H/2z_o)}{\ln(z_r/z_o)} \quad [15.28.1]$$

where $u_c(t)$ is the mean velocity of the cloud, u_r is the mean wind velocity at the reference height, z_o is the roughness length, z_r is the reference height and H is the height of the cloud. The reference height z_r is 10 m.

The rate of change of the downwind distance $x(t)$ of the centre of the cloud is equal to the advection velocity $u_c(f)$:

$$\frac{dx}{dt} = u_c(t) \quad [15.28.2]$$

For the radius R of the cloud

$$\frac{dR}{dt} = c_E(g'H)^{1/2} \quad [15.28.3]$$

The volume V is

$$V = \pi R^2 H \quad [15.28.4]$$

and c_E is the slumping coefficient.

Equation 15.28.3 is actually cast in the alternative form

$$\frac{dR^2}{dt} = 2c_E\left(\frac{g'V}{\pi}\right)^{1/2} \quad [15.28.5]$$

For the mass m_a of air entrained

$$\frac{dm_a}{dt} = \pi R^2 \rho_a u_e + 2\pi R H \rho_a w_e \quad [15.28.6]$$

The edge entrainment velocity w_e is

$$w_e = \gamma \frac{dR}{dt} \quad [15.28.7]$$

Following van Ulden (1974), the default value of the edge entrainment coefficient γ is taken as zero. Following R.A. Cox and Roe (1977), the top entrainment velocity u_e is obtained from Equation 15.27.6 using the methods given by these authors for relations for the group (u_1/u_*) and for the turbulence length scale l.

Heat transfer between the ground and the cloud is assumed to be by natural convection:

$$Q_{gr} = h_{gr}\Delta T_{gr} \quad [15.28.8]$$

with

$$\Delta T_{gr} = T_{gr} - T_c \quad [15.28.9]$$

$$h_{gr} = 0.418\frac{k_f}{L}Z^{1/4}\Delta T_{gr}^{1/4} \quad \text{laminar convection} \quad [15.28.10a]$$

$$= 0.146\frac{k_f}{L}Z^{1/3}\Delta T_{gr}^{1/3} \quad \text{turbulent convection} \quad [15.28.10b]$$

$$Z = \left(\frac{L^3\rho_f^2\beta_f g}{\mu_f^2}\Delta T_{gr}\frac{c_{pf}\mu_f}{k_f}\right)^{1/4} \quad [15.28.11]$$

and with convection turbulent if

$$3 \times 10^{10} > Z\Delta T_{gr} > 2 \times 10^7$$

where c_p is the specific heat, h_{gr} is the heat transfer coefficient between the ground and the cloud, k is the thermal conductivity of the cloud, L is a characteristic dimension of the cloud, Q_{gr} is the heat flux between the ground and the cloud, T_{gr} is the temperature of the ground, ΔT_{gr} is the temperature difference between the ground and the cloud, β is the coefficient of volumetric expansion, μ is the viscosity and subscript f denotes at film temperature $(=(T_c + T_{gr})/2)$.

Equation 15.28.8 gives the heat transfer between the ground and the cloud. Then for the temperature T_c of the cloud

$$\frac{dT_c}{dt} = \frac{m_a c_{pa}\Delta T_a + h_{gr}(\pi R^2)\Delta T_{gr}}{m_a c_{pa} + m_g c_{pg}} \quad [15.28.12]$$

with

$$\Delta T_a = T_a - T_c \quad [15.28.13]$$

where m_a is the mass of air, m_g is the mass of gas, ΔT_a is the temperature difference between the air and the cloud, and subscripts a, c and g denote the air, cloud and gas, respectively.

Use is also made of the relations

$$V = \frac{m_a + m_g}{\rho_c} \quad [15.28.14]$$

$$\rho_c = \frac{m_a + m_g}{(m_a/\rho_a) + (m_g/\rho_g)}\frac{T_a}{T_c} \quad [15.28.15]$$

For transition from dense gas dispersion to passive dispersion use is made of two alternative criteria. The first criterion is that transition occurs if the following two conditions are satisfied. The first condition is that the rate of increase of the radius due to gravity spreading is less than that due to atmospheric turbulence

$$\frac{dR}{dt} < 2.14\frac{d\sigma_y}{dt} \quad [15.28.16]$$

For the determination of the term $(d\sigma_y/dt)$ use is made of the treatment by Hosker (1974b):

$$\frac{d\sigma_y}{dt} = C^*\frac{dx}{dt} = C^* u_c \quad [15.28.17]$$

where u_c is the velocity of the cloud and C^* is a constant. The constant C^* is a function of the stability category and for categories A, B, C, D, E and F has the values 0.22, 0.16, 0.11, 0.08, 0.06 and 0.04, respectively. The second condition is that

$$u_e > u_l \quad [15.28.18]$$

where u_e is determined from Equation 15.27.6 and u_l is the longitudinal turbulence velocity.

The alternative criterion for transition is based on the density difference $\Delta\rho_c$ for the cloud:

$$\Delta\rho_c < \Delta\rho_r \quad [15.28.19]$$

where $\Delta\rho_r$ is a reference value. The default value of $\Delta\rho_r$ is $10^{-3}\,\mathrm{Kg/m^3}$.

Transition occurs at distance x_{tr} with cloud radius R_{tr} and height H_{tr}. Then assuming a Gaussian distribution the dispersion parameters are:

$$\sigma_{ytr} = R_{tr}/2.14 \quad [15.28.20]$$

$$\sigma_{xtr} = \sigma_{ytr} \quad [15.28.21]$$

$$\sigma_{ztr} = H_{tr}/2.14 \quad [15.28.22]$$

Beyond the transition point

$$\sigma_y^2(x) = \sigma_x^2(x) = \sigma_{ytr}^2 + \sigma_{yH}^2(x - x_{tr}) = (R/2.14)^2 \quad [15.28.23]$$

$$\sigma_z^2(x) = \sigma_{ztr}^2 + \sigma_{zH}^2(x - x_{tr}) = (H/2.14)^2 \quad [15.28.24]$$

where subscript H denotes the value given by the Hosker scheme.

The concentration distribution in the cloud is assumed to be Gaussian, even though this is not consistent with the gravity spreading treatment. The concentration is

$$X(x,y,z,t) = \frac{m_g}{2^{1/2}\pi^{3/2}\sigma_y^2\sigma_z}\exp\left\{-\frac{y^2 + [x - x(t)]^2}{2\sigma_y^2} - \frac{z^2}{2\sigma_z^2}\right\} \quad [15.28.25]$$

where $x(t)$ is the distance to the centre of the cloud at time t.

A simplified model is also given. The model has four stages: (1) formation of the source cylinder, (2) gravity slumping, (3) 'ground hugging' and (4) passive dispersion. Stage 1 involves the formation of the source cylinder. In Stage 2, this cylinder undergoes gravity slumping with little air entrainment; zero entrainment is assumed. The growth of the cloud radius R is given by Equation 15.28.3. The criterion for the end of this stage is that slumping terminates when the cloud height H is comparable to that of the roughness elements of the surface. In Stage 3, the growth of the cloud radius R is again given by Equation 15.28.3. The growth of the cloud height H is taken for all stability categories as one-third of that which would occur with dispersion by atmospheric turbulence for stability category F. The criterion for the end of this stage is that given by Equation 15.28.19. In Stage 4, passive dispersion applies.

Further developments of DENZ are described by Jagger (1985 SRD R277). It is shown by Jagger in this latter work that, on certain simplifying assumptions, it is possible to obtain a solution for the dense gas dispersion phase. Noting that

$$\Delta \cdot V = \Delta_o \cdot V_o \quad [15.28.26]$$

Equation 15.28.3 may be integrated to give

$$t^2 = R_o^2 + 2c_E A t \quad [15.28.27a]$$

with

$$A = \left(\frac{g'_o V_o}{\pi}\right)^{1/2} \quad [15.28.27b]$$

where Δ is the reduced density difference and the subscript o denotes the initial value. With minimal approximation, Equation 15.28.6 may be integrated and Equation 15.27.6 utilized to give the following solutions:

$$V = \{[B/(10 - C)][R^5 - R_o^5(R/R_o)^{C/2} + V_o^{1/2}(R/R_o)^{C/2}\}^2 \quad [15.28.28]$$

$$H = \{[B/10 - C][R^4 - R_o^4(R/R_o)^{C/2-1}/\pi^{1/2} + H_o^{1/2}(R/R_o)^{C/2-1}\}^2 \quad [15.28.29]$$

with

$$B = \alpha u_1^3 \pi^{1/2}/6A^3 c_E \quad [15.28.30]$$

$$C = 2\gamma \quad [15.28.31]$$

where B and C are parameters.

In windless conditions there is no top entrainment and $B = 0$, so that Equations 15.28.28 and 15.28.29 reduce to

$$V = V_o(R/R_o)^C \quad [15.28.32]$$

$$H = H_o(R/R_o)^{C-2} \quad [15.28.33]$$

15.28.2 CRUNCH

The CRUNCH model for an instantaneous release of a dense gas, described by Jagger (1983 SRD R229), is based on three simultaneous differential equations for the half-width L of the cloud, the mass m_a of air in the cloud and the temperature T_c of the cloud.

The cloud is assumed to be advected downwind at an advection velocity $\bar{u}(t)$ which corresponds to the mean wind velocity at the half-height of the cloud. This advection velocity is given by

$$u_c = u_r \frac{\ln(\dot{V}/4Lu_c z_o)}{\ln(z_r/z_o)} \quad [15.28.34]$$

where u_c is the mean velocity of the cloud, u_r is the mean wind velocity at the reference height, V is the volume of the cloud and z_r is the reference height. The reference height z_r is 10 m.

The rate of change in the downwind distance x is equal to the advection velocity u_c:

$$\frac{dx}{dt} = u_c \quad [15.28.35]$$

For the half-width L of the cloud

$$\frac{dL}{dt} = c_E(g'H)^{1/2} \quad [15.28.36]$$

The rate of change in the volume V is

$$\dot{V} = 2LHu_c \quad [15.28.37]$$

Equation 15.28.36 is recast, utilizing Equations 15.28.35 and 15.28.37, in terms of downwind distance x.

$$\frac{dL}{dx} = c_E \left(\frac{g' V}{2 L u_c^3} \right)^{1/2} \quad [15.28.38]$$

For the mass of air entrained per unit distance downwind

$$\frac{dm_a}{dt} = 2L\,dx\,\rho_a u_e + 2H\,dx\,\rho_a w_e \quad [15.28.39]$$

where m_a is the mass of air.

Equation 15.28.39 is recast in terms of x

$$\frac{dm_a}{dt} = 2L\rho_a u_e + 2H\rho_a w_e \quad [15.28.40]$$

The edge entrainment velocity w_e is

$$w_e = \gamma \frac{dL}{dt} \quad [15.28.41]$$

Following Cox and Roe, the top entrainment velocity u_e is obtained from Equation 15.27.6 using the methods given by these authors for the group (u_l/u_*) and for the turbulence length scale l. For the latter the following relation is quoted:

$$l = 5.88H^{0.48} \quad [15.28.42]$$

Equation 15.28.40 is recast, utilizing Equation 15.28.41, to maintain it as a function of x only:

$$\frac{d\dot{m}_a}{dx} = 2L\rho_a u_e + \gamma \frac{\dot{V}}{L} \rho_a \frac{dL}{dx} \quad [15.28.43]$$

Heat transfer between the ground and the cloud is treated as in DENZ. Then for the temperature T_c of the cloud

$$\frac{dT_c}{dx} = \frac{1}{\dot{m}_a c_{pa} + \dot{m}_g c_{pg}} \left[(T_a - T_c) c_{pa} \frac{d\dot{m}_a}{dx} + 2LQ_{gr} \right] \quad [15.28.44]$$

where $\dot{m}_g$ is the mass of gas.

Use is also made of the relations

$$\dot{m} = \dot{m}_a + \dot{m}_g \quad [15.28.45]$$

where $\dot{m}$ is the total mass in the cloud.

$$\dot{m} = 2LH\rho_c u_c \quad [15.28.46]$$

$$\dot{V} = \frac{T_c \dot{m}_a}{\rho_a T_a} + \frac{T_c \dot{m}_g}{\rho_g T_g} \quad [15.28.47]$$

$$\rho_c = \frac{\dot{m}_a + \dot{m}_g}{\dot{V}} \quad [15.28.48]$$

For transition from dense gas dispersion, use is made of two alternative criteria, which correspond to those in DENZ. For the first criterion the first condition is

$$\frac{dL}{dx} < 2.14 \frac{d\sigma_y}{dx} \quad [15.28.49]$$

and the second condition is that given in relation 15.28.18. The alternative criterion is that given in relation 15.28.19.

Transition occurs at downwind distance x_{tr} with cloud half-width L_{tr} and height H_{tr}. Then, assuming a Gaussian profile, the dispersion parameters are

$$\sigma_{ytr} = L_{tr}/2.14 \quad [15.28.50]$$

$$\sigma_{ytr} = H_{tr}/2.14 \quad [15.28.51]$$

For the dispersion beyond the transition point the approach used is to utilize two separate virtual sources at locations x_{vy} and x_{vz} for crosswind and vertical dispersion, respectively, as shown in Figure 15.80 where x_{vy} is upwind of the source, whilst x_{vz} is downwind of it. The determination of these two points is as follows. Use is made of the relations

$$\sigma_{yH}(X_{vy}) = \sigma_{ytr} \quad [15.28.52]$$

$$\sigma_{zH}(X_{vz}) = \sigma_{ztr} \quad [15.28.53]$$

where subscript H is the value given by the Hosker scheme. Since this scheme gives σ values which are a function of x, the solution is a trial-and-error one. Beyond the transition point the dispersion is determined using the virtual source at x_{vy} for the crosswind dispersion and the virtual source at x_{vz} for the vertical dispersion and with σ values from the Hosker scheme.

The concentration distribution in the cloud is assumed to be Gaussian. The concentration χ is

$$\chi(x,y,z) = \frac{\dot{m}_g}{\pi \sigma_y \sigma_z u_c} \exp\left[-\left(\frac{y^2}{2\sigma_y^2} + \frac{z^2}{2\sigma_z^2} \right) \right] \quad [15.28.54]$$

On certain simplifying assumptions, it is possible to obtain a solution for the dense gas dispersion phase. One case considered is that in which it is assumed that the advection velocity of the cloud is constant and that the cloud is at ambient temperature, so that heat effects can be neglected. For this case

$$\frac{dL}{dx} = A(Lu_c^3)^{-1/2} \quad [15.28.55]$$

$$\frac{d\dot{m}_a}{dx} = BL(\dot{m}_a + C) + \left[\gamma(\dot{m}_a + C)/L \frac{dL}{dx} \right] \quad [15.28.56]$$

with

$$A = c_E [g \dot{m}_g (1 - \rho_a/\rho_g)/2\rho_a]^{1/2} \quad [15.28.57]$$

$$B = 2\rho_a \alpha u_l^3 / g l \dot{m}_g (1 - \rho_a/\rho_g) \quad [15.28.58]$$

$$C = \frac{\dot{m}_g \rho_a}{\rho_g} \quad [15.28.59]$$

Integration of Equation 15.28.55 gives

$$L = X^{2/3} \quad [15.28.60]$$

with

$$X = L_o^{3/2} + A'x \quad [15.28.61]$$

$$A' = \tfrac{3}{2} A u_c^{-3/2} \quad [15.28.62]$$

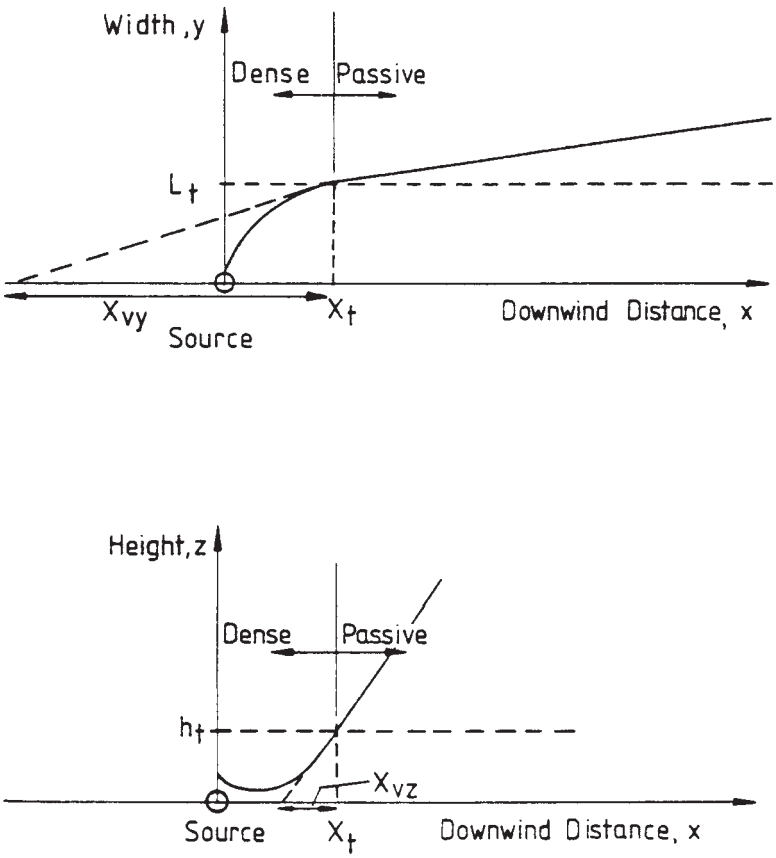


Figure 15.80 *CRUNCH model for dense gas disperion – transition from dense gas to passive dispersion (Dagger, 1983 SRD R229) h, X and subscript t in the figure are denoted in the text by H, x and subscript tr, respectively (Courtesy of the UKAEA Safety and Reliability Directorate)*

where L_o is the half-width of the cloud at the source. Substitution of Equation 15.28.60 in Equation 15.28.56 and integration gives

$$\dot{m}_a = C\{X^{(2/3)\gamma} \exp[3B(X^{5/3} - L_o^{5/2})/5A']/L_o^{\gamma} - 1\} \quad [15.28.63]$$

For short downwind distances Equation 15.28.63 reduces to

$$\dot{m}_a = \frac{CX^{(2/3)\gamma}}{L_o^{\gamma}} \quad [15.28.64]$$

A derivation is also given for the case where the advection velocity of the cloud is variable.

15.28.3 Validation and application

Kaiser and Walker (1978) have given a rough comparison of the predictions from their model with the observed clouds in the ammonia release incidents at Potchefstroom in 1973 and Houston in 1976; a further discussion has been given by Fryer and Kaiser (1979 SRD R152). Jagger (1985 SRD R277) has discussed the calibration of DENZ against the van Ulden trial and the Porton Down trials. Jagger (1983 SRD R229) has also compared predictions of CRUNCH for the cloud shape in the SS Gadila trials as shown in Figure 15.92(b).

DENZ and CRUNCH have been widely used. The Second *Canvey Report* gave hazard ranges computed from DENZ and more detailed relations for hazard ranges based on DENZ and CRUNCH have been given by Considine and Grint (1985), as described in Section 15.49. CRUNCH has been used by McQuaid and Fitzpatrick (1983) to model the dispersion of dense gas by a water spray barrier.

15.29 Dispersion of Dense Gas: SIGMET

Most of the early models were box models. Some of these have just been described. The early models also included, however, several if-theory models. Of these, the SIGMET model was particularly influential in the development of the subject.

15.29.1 SIGMET

SIGMETwas developed by Science Applications Inc. (SAI) for the US Coast Guard (USCG). It has been described by England *et al.* (1978), and evaluated by Havens, who also gives a description (Havens, 1982a).

The model is intended for investigating the dispersion of a large spill of LNG onto water. The starting point of the model is the set of hydrodynamic equations. In applying these to dense gas dispersion, where the cloud is wide but shallow, a simplification is made which eliminates the equation for the vertical velocity. The governing equations are

$$\frac{\partial(\pi u)}{\partial t}+\frac{\partial(u\pi u)}{\partial x}+\frac{\partial(v\pi u)}{\partial y}+\frac{\partial(\dot{\sigma}\pi u)}{\partial \sigma}+\left(\frac{\partial \phi}{\partial x}+\frac{\sigma}{\rho}\frac{\partial \pi}{\partial x}\right)=0 \quad [15.29.1]$$

$$\frac{\partial(\pi v)}{\partial t}+\frac{\partial(u\pi v)}{\partial x}+\frac{\partial(v\pi v)}{\partial y}+\frac{\partial(\dot{\sigma}\pi v)}{\partial \sigma}+\left(\frac{\partial \phi}{\partial y}+\frac{\sigma}{\rho}\frac{\partial \pi}{\partial y}\right)=0 \quad [15.29.2]$$

$$\frac{\partial(\pi h)}{\partial t}+\frac{\partial(u\pi h)}{\partial x}+\frac{\partial(v\pi h)}{\partial y}+\frac{\partial(\dot{\sigma}\pi h)}{\partial \sigma}+\frac{\pi\omega}{\rho}=0 \quad [15.29.3]$$

$$\frac{\partial(\pi c)}{\partial t}+\frac{\partial(u\pi c)}{\partial x}+\frac{\partial(v\pi c)}{\partial y}+\frac{\partial(\dot{\sigma}\pi c)}{\partial \sigma}=0 \quad [15.29.4]$$

$$\frac{\partial(\pi)}{\partial t}+\frac{\partial(u\pi)}{\partial x}+\frac{\partial(v\pi)}{\partial y}+\frac{\partial(\dot{\sigma}\pi)}{\partial \sigma}=0 \quad [15.29.5]$$

with

$$\sigma=\frac{p-p_t}{\pi} \quad [15.29.6]$$

$$\pi=p_s-p_t \quad [15.29.7]$$

$$\phi=gz \quad [15.29.8]$$

where c is the concentration (mass fraction), h is the specific enthalpy, p is the pressure at a given height, p_s is the pressure at the surface, p_t is the pressure at the top, T is the absolute temperature, ρ is the density, σ is a dimensionless pressure coordinate, ϕ is the geopotential height, w is the substantial pressure derivative, and u, v and ω are the components of the velocity in the alongwind, crosswind and vertical directions, respectively, σ is the substantial derivative in x, y, σ, t coordinates. The sigma coordinate takes the values $\sigma=0$ at the top and $\sigma=1$ at the surface.

The hydrostatic relation is

$$\frac{dz}{d\sigma}=-\frac{\pi}{g\rho} \quad [15.29.9]$$

The following supplementary equations are used:

$$h=[c_{pa}(1-c)+c_{pg}c]T+WL_o(1-c)f(T) \quad [15.29.10]$$

$$w=\pi\dot{\sigma}+\sigma\left(\frac{\partial \pi}{\partial t}+u\frac{\partial \pi}{\partial x}+v\frac{\partial \pi}{\partial x}\right) \quad [15.29.11]$$

where L_o is the latent heat of vaporization of water, W is the mass of water per unit mass of air, and the subscripts a and g denote air and gas, respectively.

These equations, which are the set given by England *et al.*, describe the fluid dynamic and thermodynamic processes but do not include the effects of turbulence. Corresponding equations incorporating the turbulence terms, including the eddy diffusivities, are given by Havens. He also gives a diagram showing the boundary conditions for solution of the model equations.

The eddy diffusivities required in the submodel for turbulent mass, momentum and energy transfer, as described by Havens, are obtained as follows.

For the horizontal eddy diffusivities the Reynolds analogy is assumed and the eddy diffusivities for turbulent momentum, mass and energy transfer are taken as equal and are denoted by K_h. The vertical diffusivities are likewise assumed equal and are denoted K_v. The relation for the vertical diffusion coefficient is

$$K_v=0.45\sigma_\epsilon ul \quad u\geq 1 \text{ m/s} \quad [15.29.12a]$$

$$=0.45\sigma_\epsilon l \quad u<1 \text{ m/s} \quad [15.29.12b]$$

where l is turbulence length scale and σ_ϵ is the standard deviation of the wind direction. Tabulated values of l and σ_ϵ are given by England *et al.* and a plot for K_h is given by Havens. The diffusion coefficient K_h is obtained from the vertical diffusion coefficient K_v using values of the ratio K_h/K_v. Havens gives for this ratio the values shown in Table 15.43, which evidently supersede the table of values given by England *et al.*

Other submodels are those for heat transfer and momentum transfer from the surface to the cloud. For heat transfer

$$q=U(T_s-T_c) \quad [15.29.13]$$

where q is the heat flux, T_c is the temperature of cloud, T_s is the temperature of the surface and U is the heat transfer coefficient. The value used for U is 20.4 W/m^2 K. For momentum transfer

$$\tau_o=C_d\rho u^2 \quad [15.29.14]$$

where C_d is the drag coefficient, u is the velocity and τ_o is the shear stress at the surface. The velocity u is that at 1 m height. The value of C_d is 0.001.

SIGMET incorporates a source submodel for the spillage of LNG on water. The source is assumed to be a cylindrical pool. The pool radius is determined from the density intrusion model given by Equation 15.24.21. The pool radius is allowed to grow, with a corresponding decrease in height, until a depth is reached at which break-up occurs. After pool break-up, the evaporation rate is determined by the empirical correlation of Feldbauer *et al.* (1972):

$$\dot{m}=\dot{m}_{max}\exp\left[\frac{0.04}{\rho_l H_{min}}(t-t_{max})\right] \quad [15.29.15]$$

where H_{min} is the height at break up, $\dot{m}$ is the mass rate of evaporation, $\dot{m}_{max}$ is the mass rate of evaporation at break-up, t is time, t_{max} is the time at break-up and ρ_l is the density of the liquid.

Table 15.43 *Ratio of horizontal to vertical diffusion coefficients (Havens, 1982a) (Courtesy of Elsevier Science Publishers)*

Stability category	K_h/K_v
D	1.0
E	10.0
F	25.0

15.29.2 Validation and application

England *et al.* (1978) give comparisons of the prediction of SIGMET with results of the American Gas Association LNG dispersion trials. They also use SIGMET to simulate an instantaneous spillage of 30,000 m^3 of LNG onto water.

An assessment of SIGMET has been carried out by Havens (1982a), who studied the somewhat similar case of a 25,000 m^3 LNG spill and performed a sensitivity analysis, investigating the effect of spill size, wind velocity and atmospheric stability, and made comparisons between the distance to the lower flammability limit for this dense gas and for a neutrally buoyant gas.

SIGMET, in the version SIGMET-N, was one of four models in a comparative evaluation of models by Havens and co-workers (Havens, 1986; Havens, Spicer and Schreurs, 1987), the other models being ZEPHYR, MARIAH-II and FEM3. SIGMET-N was discarded because the turbulent mixing model did not scale properly and because of the difficulty of controlling numerical 'diffusion'.

15.30 Dispersion of Dense Gas: SLAB and FEM3

A pair of models have been developed at the Lawrence Livermore National Laboratory (LLNL) by Chan, Ermak and coworkers (Ermak, Chan *et al.*, 1982; S.T. Chan, Rodean and Ermak, 1984; Ermak and Chan, 1986, 1988; S.T. Chan, Ermak and Morris, 1987). SLAB is an advanced similarity model and FEM3 a full three-dimensional model.

15.30.1 SLAB

SLAB was originally formulated by Zeman (1982a,b) and its development has been described by Ermak, Chan *et al.* (1982), D.L. Morgan, Kansa and Morris (1984) and Ermak and Chan (1986, 1988).

The SLAB model is for a continuous release. It is a slab model with properties averaged in the horizontal and vertical directions and is thus one dimensional. The model is based on a set of six simultaneous differential equations, for the conservation of total mass, conservation of the material released, conservation of momentum and conservation of energy. These equations are given by Ermak, Chan *et al.* (1982) as a set of six partial differential equations, in time t and downwind distance x, but subsequently by Ermak and Chan (1986) as six ordinary differential equations in x. The latter are

$$\frac{\mathrm{d}(Bhu_c\rho_c)}{\mathrm{d}x} = B_o u_o \rho_o + (Bu_e + hw_e)\rho_a \qquad [15.30.1]$$

$$\frac{\mathrm{d}(Bhu_c p_c \omega)}{\mathrm{d}x} = B_o u_o \rho_o \qquad [15.30.2]$$

$$\frac{\mathrm{d}(Bhu_c\rho_c c_{pc} T_c)}{\mathrm{d}x} = B_o u_o \rho_o c_{po} T_o + (Bu_e + hw_e)\rho_a c_{pa} T_a + Q_{gr} \qquad [15.30.3]$$

$$\frac{\mathrm{d}(Bhu_c^2\rho_c)}{\mathrm{d}x} = -\tfrac{1}{2}[Bh^2(\rho_c - \rho_a)]g + (Bu_e + hw_e)\rho_a u \qquad [15.30.4]$$

$$\frac{\mathrm{d}(Bhu_c u_y \rho_c)}{\mathrm{d}x} = h^2(\rho_c - \rho_a)g \qquad [15.30.5]$$

$$\frac{\mathrm{d}B}{\mathrm{d}x} = \frac{u_y + w_e}{u_c} \qquad [15.30.6]$$

where B is a cloud width parameter, c_p is the specific heat, h is a cloud height parameter, Q_{gr} is the heat flux between the ground and the cloud, T is the absolute temperature, u is the wind velocity, u_c is the velocity of the cloud in the downwind direction, u_e is the vertical entrainment velocity, u_o is the velocity of material at the source, u_y is the velocity of the cloud in the crosswind direction, w_e is the horizontal entrainment rate, ρ is the density, w is the mass fraction of material released and subscripts a, c and o denote the air, cloud and source, respectively.

The following supplementary equation is used:

$$\rho_c T_c = \frac{\rho_a T_a M_o}{M_o + (M_a - M_o)\omega} \qquad [15.30.7]$$

where M is molecular weight.

The vertical entrainment velocity u_e is taken as

$$u_e = \frac{2.7ku^*}{\phi(\mathrm{Ri})} \qquad [15.30.8]$$

where k is the von Karman constant and ((Ri) is the Monin–Obukhov profile function given by Dyer (1974).

The profile function ϕ is

$$\phi = 1 + 5\mathrm{Ri} \qquad \mathrm{Ri} > 0 \qquad [15.30.9a]$$

$$\phi = (1 - 16\mathrm{Ri})^{-p'} \qquad \mathrm{Ri} < 0 \qquad [15.30.9b]$$

where Ri is a Richardson number and p' is an index. The index p' is 1/4 for momentum and 1/2 for species and energy. The horizontal entrainment velocity w_e was given in the earlier versions (Ermak, Chan *et al.*, 1982) as

$$w_e = (1.8)^2(h/B)u_e \qquad [15.30.10]$$

where the term (h/B) implies that at low values of the height the horizontal entrainment rate is low but that it increases as the height increases. In the later version (Ermak and Chan, 1986, 1988) w_e is described as a function of the ground surface friction coefficient and of the Monin–Obukhov length.

The profile of the volumetric concentration C is represented as

$$C(x,y,z) = C(x)C_1(y)C_2(z) \qquad [15.30.11]$$

where C is the volumetric concentration and $C(x)$, $C_1(y)$, $C_2(z)$ are concentration functions. These functions are

$$C(x) = \frac{M_a\omega}{M_o + (M_a - M_o)\omega} \qquad [15.30.12]$$

$$C_1(y) = \frac{1}{4b}\left[\mathrm{erf}\left(\frac{y+b}{2^{1/2}\beta}\right) - \mathrm{erf}\left(\frac{y-b}{2^{1/2}\beta}\right)\right] \qquad [15.30.13]$$

$$C_2(z) = \frac{1}{h}\left(\frac{6}{h}\right)^{1/2}\exp\left(-\frac{3z^2}{2h^2}\right) \qquad [15.30.14]$$

with

$$B^2 = b^2 + 3\beta^2 \qquad [15.30.15]$$

where ω is the mass fraction and b and β are shape parameters. The variation of B with x is given by

Equation 15.30.6, and the variation of b with x is given by

$$\frac{db}{dx} = \frac{bu_y}{Bu_c} \quad [15.30.16]$$

The horizontal concentration profile is uniform when $\beta = 0$ and approaches a Gaussian one as $\beta \gg b$. The ratio of β to b remains constant under the influence of the horizontal velocity u_y. It is the horizontal entrainment rate w_e which causes an increase in β and results in a crosswind Gaussian profile.

The cloud shape parameters B, b and h are defined by Equations 15.30.15, 15.30.13 and 15.30.14, and are related to the velocities u_y, w_e and u_e by Equations 15.30.6, 15.30.16 and 15.30.2. The parameters B and h are related to the dispersion parameters as follows:

$$\sigma_y^2 = 3B^2 \quad [15.30.17]$$

$$\sigma_z^2 = 3h^2 \quad [15.30.18]$$

15.30.2 FEM3

Accounts of FEM3 have been given by Ermak, Chan *et al.* (1982), S.T. Chan and Ermak (1984), S.T. Chan, Rodean and Ermak (1984) and Ermak and Chan (1986, 1988).

The FEM3 model is also for a continuous release. It is a full three-dimensional model. The model is based on a set of four simultaneous differential equations, in terms of tensor quantities, for the conservation of total mass, conservation of the material released, conservation of momentum and conservation of energy. The equations are

$$\nabla \cdot (\rho_c \mathbf{u}) = 0 \quad [15.30.19]$$

$$\frac{\partial(\rho_c \mathbf{u})}{\partial t} + \rho_c \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \nabla \cdot (\rho_c \mathbf{K}^m \cdot \nabla \mathbf{u}) + (\rho_c - \rho_h)\mathbf{g} \quad [15.30.20]$$

$$\frac{\partial \theta}{\partial t} + \mathbf{u} \cdot \nabla \theta = \nabla \cdot (\mathbf{K}^\theta \cdot \nabla \theta) + \frac{c_{pg} - c_{pa}}{c_{pc}} (\mathbf{K}^\omega \cdot \nabla \omega) \cdot \nabla \theta + S \quad [15.30.21]$$

$$\frac{\partial \omega}{\partial t} + \mathbf{u} \cdot \nabla \omega = \nabla \cdot (\mathbf{K}^\omega \cdot \nabla \omega) \quad [15.30.22]$$

with

$$\mathbf{u} = (u, v, \omega) \quad [15.30.23]$$

$$\rho_c = \frac{M_g M_a P}{RT[M_g + (M_a - M_g)\omega]} \quad [15.30.24]$$

$$c_{pc} = c_{pa}(1 - \omega) + c_{pg}\omega \quad [15.30.25]$$

where p is the pressure deviation from an adiabatic atmosphere at rest with corresponding density ρ_h, P is the absolute pressure, S is the temperature source term (e.g. latent heat), θ is the potential temperature deviation from an adiabatic atmosphere, ω is the mass fraction of material released, $\mathbf{g}$ is the acceleration due to gravity, $\mathbf{K}^m$, $\mathbf{K}^\theta$ and $\mathbf{K}^\omega$ are the diagonal eddy diffusion tensors for the momentum, energy and mass fraction, respectively, $\mathbf{u}$ is a velocity tensor, and subscript $\mathbf{g}$ denotes material released. The numerical solution of these equations has been described by S.T. Chan, Rodean and Ermak (1984).

FEM3 is based on a generalized anelastic approximation, adapted from Ogura and Phillips (1962), which allows large density changes to be handled whilst precluding sound waves. The approximation is the use of Equation 15.30.19 instead of

$$\nabla \cdot (\rho_c \mathbf{u}) + \frac{\partial \rho_c}{\partial t} = 0 \quad [15.30.26]$$

In FEM3 turbulence is treated using the if-theory approach. The eddy diffusion tensors are associated with three diffusion coefficients, two horizontal and one vertical. The latter is particularly important. In the earlier versions (Ermak, Chan *et al.*, 1982) the vertical diffusion coefficient K_v was taken as

$$K_v = K_a(1 - \omega) + K_\rho \omega \quad [15.30.27]$$

where K_a is the ambient vertical diffusion coefficient, K_v is the vertical diffusion coefficient and K_ρ is a dense-layer diffusion coefficient. Two submodels were used for K_ρ, one based on a Richardson number and one on a mixing length.

In the later versions (Ermak and Chan, 1988) three submodels are given for the vertical diffusion coefficient. In the first submodel

$$K_v = \frac{k[(u_{*c}z)^2 + (\omega_{*c}h)^2]^{1/2}}{\phi(\mathrm{Ri})} \quad [15.30.28]$$

with

$$u_{*c} = u^*|u_c/u| \quad [15.30.29]$$

where u_* is the friction velocity, u_{*c} is the cloud friction velocity, w_{*c} is a cloud 'convection velocity' and ϕ(Ri) is the Monin–Obukhov profile function. The cloud convection velocity is a function of the temperature difference between the ground and the cloud.

The horizontal diffusion coefficient K_h is taken as

$$K_h = \frac{\beta^* k u_{*c} z}{\phi} \quad [15.30.30]$$

where β^* is an empirical coefficient. The value of β^* is taken as 6.5.

15.30.3 Validation and application

Ermak, Chan and coworkers (Ermak, Chan *et al.*, 1982; S.T. Chan, Rodean and Ermak, 1984; Ermak and Chan, 1986; Koopman, Ermak and Chan, 1989) compared predictions from SLAB and FEM3 with observations from the Burro trials. D.L. Morgan, Kansa and Morris (1984) have compared the predictions of SLAB with observations from the Burro and Coyote trials and Blewitt, Yohn and Ermak (1987) have compared its predictions with observations from the Goldfish trials. Touma *et al.* (1991) have compared the performance of this model with that of other models in relation to the Burro, Desert Tortoise and Goldfish trials.

15.31 Dispersion of Dense Gas: HEGADAS and Related Models

A series of models have been developed by Shell, leading to the model HEGADAS and then to the model system

HGSYSTEM. The first of these models was that of Te Riele (1977), which was followed by the model of Colenbrander (1980) and then HEGADAS itself. HEGADAS is complemented by the front-end model HEGABOX.

Another major model, DEGADIS, developed by Havens and coworkers is based on HEGADAS.

15.31.1 Te Riele model

The model described by Te Riele (1977) is for a continuous release. It is based on two simultaneous partial differential equations for conservation of mass and of momentum. The assumption is made that the take-up of material into the ambient flow field and the dispersion of material within this field are independent. Other assumptions are the Reynolds analogy and the Boussinesq approximation. The basic equations are:

$$\frac{\partial \rho u}{\partial x} = \frac{\partial}{\partial y}\left(K_y \frac{\partial \rho}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial \rho}{\partial z}\right) \qquad [15.31.1]$$

$$\frac{\partial \rho u^2}{\partial x} = \frac{\partial}{\partial y}\left(K_y \frac{\partial \rho u}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial \rho u}{\partial z}\right) \qquad [15.31.2]$$

where K is the eddy diffusion coefficient, u is the wind speed, ρ is the density of the cloud and subscripts x and y denote in the downwind and crosswind directions, respectively.

The assumption that the wind speed is independent of the take-up of material, the presence of the dense gas layer and the density gradients in the ambient flow field gives

$$\frac{\partial u}{\partial x} = \frac{\partial u}{\partial y} = 0 \qquad [15.31.3]$$

It can be shown from Equations 15.31.1–15.31.3 that

$$K_z = \frac{\rho_a \tau_o}{\rho^2}\left(\frac{\partial u}{\partial x}\right)^{-1} \qquad [15.31.4]$$

where τ_o is the shear stress acting on the upwind ground surface, and subscript a denotes air. Then from Equation 15.31.4 it is possible to derive the shear stress acting on the top of the plume, which gives

$$\tau_{gr} = \frac{\rho_a}{\rho_{gr}}\tau_o \qquad [15.31.5]$$

where ρ_{gr} is the density downwind and τ_{gr} is the shear stress acting on the downwind ground surface.

For the relation between density and concentration it is assumed that the ambient air and the dense gas are ideal gases with the same molecular specific heats and that equalization of temperature and density occur only through convection originating in atmospheric turbulence. Then

$$\frac{c}{\rho} = \frac{1}{\rho_a + (1 - \rho_a/\rho_g)} \qquad [15.31.6]$$

where c is the concentration (mass per unit volume) and subscript g denotes material released.

The prime purpose of the model is to determine concentrations downwind of an area source such as that from an evaporating pool of liquefied gas. This source is modelled as a rectangular area source of length L_s and half-width B_s and mass rate of release per unit area Q″. Figure 15.81 shows the general form of the model, in the later version HEGADAS.

For the concentration profile it is assumed that there is a middle part of half-width b in which the dispersion occurs in the vertical direction but not in the horizontal direction. The width of this middle part reduces due to mixing at the crosswind edges of the plume and thus decreases from a value of $2B$ at the source to zero at some point downwind. A concentration profile is assumed which in the vertical direction is Gaussian throughout but which in the crosswind direction has Gaussian features at the crosswind edges, but becomes fully Gaussian only when the middle part disappears:

$$\frac{c}{c_A} = \exp\left[-\left(\frac{z}{\sigma_z}\right)^s\right] \qquad |y| < b \qquad [15.31.7a]$$

$$\frac{c}{c_A} = \exp\left[-\left(\frac{|y| - b}{\sigma_y}\right)^r - \left(\frac{z}{\sigma_z}\right)^s\right] \qquad |y| \geq b \qquad [15.31.7b]$$

where c_A is the ground level concentration on the centre line, and r and s are shape factors for the crosswind and vertical concentration profiles, respectively.

This approach ensures a seamless transfer from the dense gas dispersion regime to the passive dispersion regime and avoids the need to define a transition point and to use separate models for the two regimes.

From Equations 15.31.1–15.31.4 and 15.31.6 the integral form of the mass and momentum balances can be derived:

$$\int_0^{y_{Ls}} \left[\frac{\partial}{\partial x}\left(\int_0^\infty cu\,dz\right)\right] dy = \left(\int_0^\infty K_y \frac{\partial c}{\partial y} dz\right)_{y=y_{Ls}} + \int_0^{y_{Ls}} Q\,dy \qquad [15.31.8]$$

$$\frac{d}{dx}\left(\int_0^\infty \int_0^\infty cu^2\,dy\,dx\right) = \int_0^\infty \frac{c_{gr}}{\rho_{gr}}\tau_o\,dy \qquad [15.31.9]$$

where the subscript gr denotes ground level.

Equation 15.31.8 is used with three different values of the limit y_{Ls}. These are:

Total mass balance: $y_{Ls} \to \infty$
Mass balance on middle part: $y_{Ls} < b$; $b > 0$
Mass balance for determination of σ: $y_{Ls} = b + 0.5(2)^{1/2}\sigma_y$

This therefore gives a set of four equations, the three versions of Equations 15.31.8 and 15.31.9, which are used to determine the four variables c_A, b, σ_y and σ_z.

The parameters necessary for this model include: the wind velocity u; the shape parameters r and s; the vertical eddy diffusion coefficient K_y; the upstream shear stress τ_o; and the mass rate of release per unit area Q″.

Wind velocity

For the wind velocity u use is made of the vertical wind velocity profile given in Equation 15.24.6 in the form

$$u = u_r\left(\frac{z}{z_r}\right)^{\alpha'} \qquad [15.31.10]$$

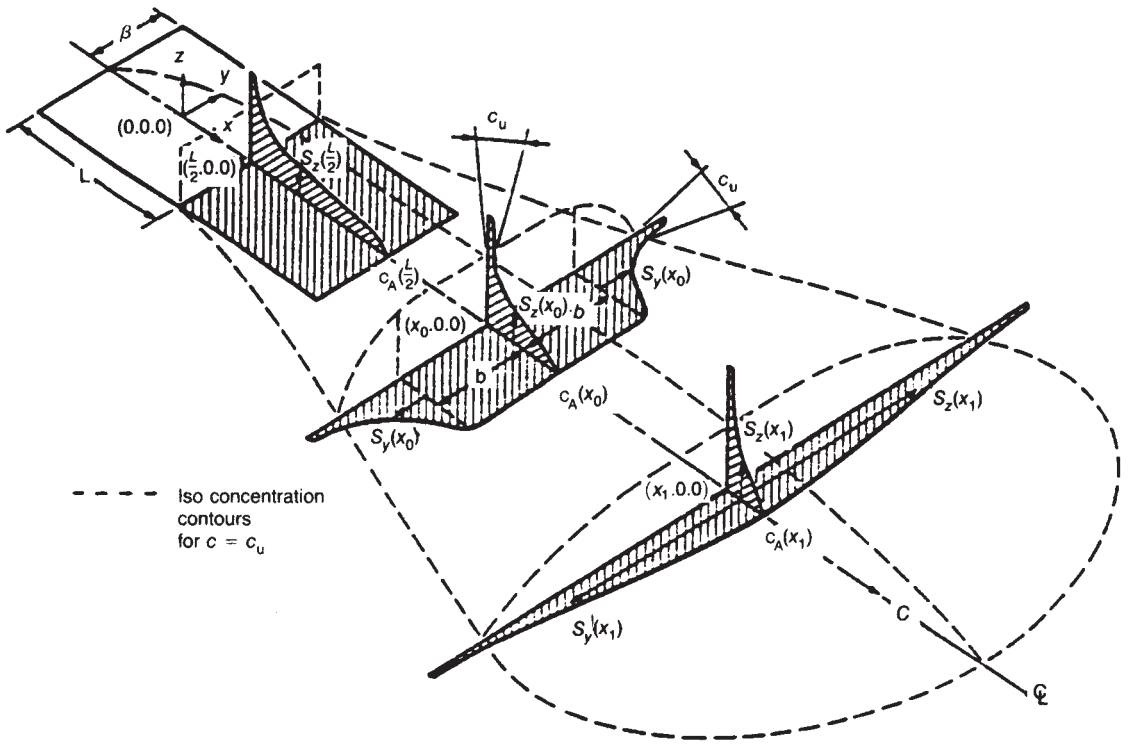


Figure 15.81 *HEGADAS model for dense gas dispersion – idealized cloud shapes (Puttock, 1987c) (Courtesy of the American Institute of Chemical Engineers)*

where u_r is the wind speed at reference height z_r and α' is an index. For the friction velocity use is made of Equation 15.24.7.

Shape parameters and eddy crosswind diffusivity

The parameters r, s and K_y are obtained by applying Equations 15.31.1, 15.31.4, 15.31.6 and 15.31.10 to the case of a point source with release of a neutrally buoyant gas ($b = 0$, $\rho = \rho_a$). This yields

$$r = 2 \qquad [15.31.11a]$$

$$s = 1 + 2\alpha \qquad [15.31.11b]$$

$$K_y = K_o^* \left(\frac{W_b}{B_s}\right)^{\gamma'} \left(\frac{z}{z_r}\right)^{\alpha'} \qquad [15.31.12]$$

with

$$K_o^* = \left[\frac{\delta'(\pi)^{1/2}}{2B_s}\right]^{1/\beta'} \frac{2B_s^2 u_r \beta'}{\pi} \qquad [15.31.13]$$

$$W_b = b + \frac{\pi^{1/2}}{2}\sigma_y \qquad [15.31.14]$$

$$\gamma' = 2 - 1/\beta' \qquad [15.31.15]$$

where K_o^* is the vertical eddy diffusion coefficient at reference height z_r acting on a concentration profile of width $2B$, W_b, is the half-width of the crosswind concentration profile, and β', γ and δ' are constants. The constants β' and δ' are obtained from the relation for the crosswind dispersion coefficient for a point source:

$$\sigma_y = \delta' x \beta' \qquad [15.31.16]$$

Table 15.44 gives the values of the shape parameter α' for the wind velocity profile given by Te Riele. The parameters β' and δ' are obtained from Equation 15.31.16, which corresponds in general form to a number of correlations for the crosswind dispersion coefficient.

Shear stress

For the shear stress τ_o the relation used is

$$\tau_o = 0.16 \frac{\rho_a u_r^2}{\ln^2(z_r/z_o)} \qquad [15.31.17]$$

where z_o is the roughness length.

Take-up flux

For the flux of material taken up into the ambient atmosphere, or take-up flux, Q″ there is a certain maximum value

Table 15.44 *Wind velocity profile shape parameter (after Te Riele, 1977) (Courtesy of DECHEMA)*

Stability category	*Shape parameter, α'*
A	0.02
B	0.05
C	0.09
D	0.14
E	0.20
F	0.28

Q''_{max}. This maximum value is obtained from Equation 15.31.5 which yields

$$\tau_{gr} = Q''_{max} \frac{\int_o^\infty cu\,dz}{\int_o^\infty c\,dz} \qquad [15.31.18]$$

Then the value of Q'' is given by

$$Q'' = Q''_o \quad Q''_{max} > Q''_o \qquad [15.31.19a]$$

$$= Q''_{max} \quad Q''_{max} \le Q''_o \qquad [15.31.19b]$$

where Q''_o is the mass flux of material from the source.

The model consists of Equations 15.31.8 and 15.31.9 with the supplementary Equations 15.31.6, 15.31.7 and 15.31.10–15.31.12 together with the three values of the integration limit y_{Ls}. It yields the four parameters c_A, b, σ_y and σ_z.

The dimensionless groups which govern dense gas dispersion are given as:

$$\alpha';\quad \gamma';\quad \frac{Q''L_s}{\rho_g u_r z_r};\quad \frac{\tau_o L_s}{\rho_g u_r^2 z_r};\quad \frac{K_o^* L_s}{B_s^2 u_r};\quad \frac{\rho_g}{\rho_a}$$

15.31.2 Colenbrander steady-state model

The further development of the Te Riele model has been described by Colenbrander (1980). The principal features which he describes are developments in: the source term; the treatment of the four parameters – centreline concentration c_A half-width of the middle part b, cross-wind dispersion parameter S_y and vertical dispersion parameter S_z; and in the criterion for transition to passive dispersion.

Source term

An evaporating pool may generate above itself a gas blanket. The condition for formation of such a gas blanket is that the rate of vapour evolution per unit area Q''_p exceeds the ambient take-up rate per unit area Q''_{max} of vapour. Where this is the case, the gas blanket grows until the area of the cloud is such that the rate of ambient take-up rate equals the rate of input into the cloud. If the rate of vapour evolution is less than the ambient take-up rate, a gas blanket does not form.

For the case where $Q''_p > Q''_{max}$, the ambient take-up rate Q'' is constrained to be

$$Q'' = Q''_{max} \qquad [15.31.20]$$

It is shown by a mass balance that

$$Q_{max} = \frac{\rho_E u_r S_z^{1+\alpha'}}{(1+\alpha')z_r^{\alpha'} L} \qquad [15.31.21]$$

where ρ_E is the density at emission conditions and S_z is evaluated at $x = 0.5L$. The length L and half-width B of the gas blanket are obtained from

$$Q''_p L_b B_p = Q''_{max} LB \qquad [15.31.22]$$

where B_p is half-width of the pool and L_p is the length of the pool. The centre line ground level concentration c_A is

$$c_A = \rho_E \qquad [15.31.23]$$

For the case where $Q''_p < Q''_{max,}$ the ambient take-up rate is

$$Q = Q''_p \qquad [15.31.24]$$

The length L and half-width B of the gas blanket are

$$L = L_P \qquad [15.31.25]$$

$$B = B_P \qquad [15.31.26]$$

The centre line ground level concentration c_A is obtained from the relation

$$Q''_p = \frac{c_A u_r S_z^{1+\alpha'}}{(1+\alpha')z_r^{\alpha'} L} \qquad [15.31.27]$$

where S_z is evaluated at $x = 0.5L$.

The foregoing applies to a rectangular source. It is convenient in dealing with the effective source constituted by a gas blanket to work in terms of a circular source. Assuming that the rectangle is a square, the radius R of this source is then

$$R = \frac{1}{\pi^{1/2}} L \qquad [15.31.28]$$

If there is a gas blanket, the radius $R_b(t)$ of the blanket is taken as having a minimum value $R_1(t)$ and as growing at the rate

$$\frac{dR_b(t)}{dt} = c_E[g' H_b(t)]^{1/2} \qquad [15.31.29]$$

where H_b is the height of the 100% gas blanket.

The value of $Q''_{max}(t)$ is obtained from the mass balance

$$\frac{d}{dt}(\pi R_b^2(t) H_b(t) \rho_E) = \pi R_1^2(t) Q''_p - R_b^2(t) Q''_{max}(t) \qquad [15.31.30]$$

For a spreading pool of radius Ri(t)

$$Q''_p = \frac{Q_p(t)}{\pi R_1^2(t)} \qquad [15.31.31]$$

where Q_p is the total mass rate of evaporation.

Vertical dispersion parameter

The vertical concentration distribution given by Equation 15.31.7a satisfies the two-dimensional diffusion equation

$$u\frac{\partial c}{\partial x} = \frac{\partial}{\partial z}\left(K_z \frac{\partial c}{\partial z}\right) \qquad [15.31.32]$$

with

$$K_z = \frac{ku_* z}{\phi(\mathrm{Ri}_*)} \quad [15.31.33]$$

$$\mathrm{Ri}_* = \frac{g' H_{\mathrm{eff}}}{u_*^2} \quad [15.31.34]$$

where H_{eff} is the effective height of the cloud, Ri_* is a Richardson number, k is the von Karman constant and $\phi(\mathrm{Ri}_*)$ is the Monin–Obukhov profile function.

Then from Equations 15.31.7a, 15.31.10, 15.31.32 and 15.31.33

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{S_z}{z_\mathrm{r}}\right)^{1+\alpha'} = \frac{k}{z_\mathrm{r}}\frac{u_*}{u_\mathrm{r}}\frac{(1+\alpha')^2}{\phi(\mathrm{Ri}_*)} \quad [15.31.35]$$

The ratio (u_*/u_r) is obtained from the logarithmic wind velocity profile Equation 15.24.7. Equation 15.31.35 describes the vertical growth of a plume for the two-dimensional case of a plume of constant width. It is generalized for a dense gas plume which spreads laterally to yield

$$\frac{\mathrm{d}}{\mathrm{d}x}\left[B_{\mathrm{eff}}\left(\frac{S_z}{z_\mathrm{r}}\right)\right]^{1+\alpha'} = \frac{k}{z_\mathrm{r}}\frac{u_*}{u_\mathrm{r}}\frac{(1+\alpha')^2 B_{\mathrm{eff}}}{\phi(\mathrm{Ri}_*)} \quad [15.31.36]$$

with

$$B_{\mathrm{eff}} = b + \frac{\pi^{1/2}}{2} S_y \quad [15.31.37]$$

where B_{eff} is the effective half-width of the plume.

Crosswind dispersion parameter

The crosswind concentration distribution given by Equation 15.31.7b with $z = 0$ satisfies the two-dimensional diffusion equation

$$u\frac{\partial c}{\partial x} = \frac{\partial}{\partial y}\left(K_y \frac{\partial c}{\partial y}\right) \quad [15.31.38]$$

with

$$K_y = K_\mathrm{o} u W_\mathrm{b}^{\gamma''} \quad [15.31.39]$$

where W_b, is the half-width of the cloud, K_o is a constant and γ'' is an index. Then, again from Equations 15.31.7b, 15.31.38 and 15.31.39,

$$S_y \frac{\mathrm{d}S_y}{\mathrm{d}x} = \frac{4\beta'}{\pi} W_\mathrm{b}^2 \left[\frac{\delta'(\pi/2)^{1/2}}{W_\mathrm{b}}\right]^{1/\beta'} \quad [15.31.40]$$

For $b = 0$, Equation 15.31.40 describes the lateral growth of a plume for the case of a plume where the width of the middle part is zero. In the generalization for a dense gas plume with a finite middle part, Equation 15.31.40 still applies but with finite b in Equation 15.31.37.

Width of middle part

The growth of the effective half-width B_{eff} is

$$\frac{\mathrm{d}B_{\mathrm{eff}}}{\mathrm{d}t} = c_\mathrm{E}(g' H_{\mathrm{eff}})^{1/2} \quad [15.31.41]$$

with

$$H_{\mathrm{eff}} = \frac{\Gamma(1/(1+\alpha'))}{1+\alpha'} S_z \quad [15.31.42]$$

$$\frac{\mathrm{d}B_{\mathrm{eff}}}{\mathrm{d}x} = \frac{1}{u_{\mathrm{eff}}}\frac{\mathrm{d}B_{\mathrm{eff}}}{\mathrm{d}t} \quad [15.31.43]$$

with

$$u_{\mathrm{eff}} = \frac{\int_0^\infty cu\,\mathrm{d}z}{\int_0^\infty c\,\mathrm{d}z} \quad [15.31.44]$$

$$u_\mathrm{r}\left(\frac{S_z}{z_\mathrm{r}}\right)^{\alpha'} \frac{1}{\Gamma(1/(1+\alpha'))} \quad [15.31.45]$$

where u_{eff} is the effective local cloud velocity.

The half-width b of the middle part is obtained from Equation 15.31.37 with B_{eff} obtained from Equation 15.31.43.

Centre-line concentration

For the centre-line concentration c_A the integral mass balance with substitution of the similarity profiles for c and u yields

$$c_\mathrm{A} = \frac{Q(1+\alpha')z_\mathrm{r}^{\alpha'}}{u_\mathrm{r} S_z^{1+\alpha'}(b + 0.5\pi^{1/2} S_y)} \quad [15.31.46]$$

The foregoing treatment does not allow for dispersion in the along-wind direction, which can be significant. In order to allow for this a correction is derived which when applied to the centreline ground level concentration c_A yields a concentration c'_A corrected for this effect.

Transition conditions

Transition to passive dispersion occurs when $b = 0$ at downwind distance x_{tr}. A virtual source is assumed to exist at x_v. The dispersion parameter S_y is

$$S_y = 2^{1/2}\delta'(x + x_\mathrm{v})^{\beta'} \quad [15.31.47]$$

The downwind distance x_v of the virtual source is obtained from Equation 15.31.47 by setting $x = x_{\mathrm{tr}}$. At transition

$$S_y = 2^{1/2}\sigma_y \quad [15.31.48]$$

15.31.3 Colenbrander quasi-steady-state model

Colenbrander has also described a method of accommodating within his model a transient release. The scenario of concern is the evaporation of a liquefied gas from a spreading pool. The author gives a source model which defines as a function of time both the rate of release $Q(t)$ and the radius of the pool $R(t)$.

He then applies to this source the concept of 'observers'. A series of observers is envisaged as passing over the source at fixed time intervals. A given observer i passes

over at a velocity $u_i(t)$ which is time dependent. The observer velocity increases with downwind distance and at a given distance χ the velocity of all observers is the same ($u_i(x) = u_{i+1}(x)$). It is implied in this that at a given time the velocity of observer i is greater than that of the succeeding observer ($u_i(t) > u_{i+1}(t)$). A detailed derivation of the velocity $u_i(t)$ of passage is given by the author.

There is then derived for each observer i a corresponding set of source parameters. If the times when observer i passes over the upwind and downwind edges of the source are t_{1i}, and t_{2i}, respectively, and if $x_i(t)$ is the location of the observer at time t, the local half-width $B'_{si}(t)$ is

$$B'_{si}(t) = [R^2(t) - x_i^2(t)]^{1/2} \qquad [15.31.49]$$

Then

$$A_{si} = \int_{t_u}^{t_{2i}} u_i(t) B'_{si}(t)\,\mathrm{d}t \qquad [15.31.50]$$

$$L_{si} = x_i(t_{2i}) - x_i(t_{1i}) \qquad [15.31.51]$$

$$B_{si} = A_{si}/L_{si} \qquad [15.31.52]$$

$$Q''_i B_{si} L_{si} = \int_{t_{1i}}^{t_{2i}} Q''_i(t) u_i(t) B'_{si}(t)\,\mathrm{d}t \qquad [15.31.53]$$

where for observer i, A_{si} is the half-area of the source, B_{si} is the half-width of the source, L_{si} the length of the source and Q''_i the average take-up flux.

Then for any specified time t_s the concentration distribution in the plume may be determined. At this time for observer i the location $x_i(t_s)$ is calculated and the plume parameters c_A, b, S_y and S_z are obtained as functions of this distance. A steady-state calculation is then performed, utilizing Equation 15.31.7, to obtain the concentration attributable to this observer. The calculation is repeated for all observers.

15.31.4 HEGADAS

As already described, HEGADAS is a development of the models of Te Riele (1977) and Colenbrander (1980). Accounts of this development have been given by Colenbrander and Puttock (1983, 1984) and Puttock (1987b,c, 1989). Further enhancements of the model have been described by Witlox (1991).

The basic HEGADAS model is for a continuous release of dense gas. The source is assumed to be an area source. The plume from this source is modelled as consisting of a middle part which has a uniform crosswind concentration and an outer part which has Gaussian features. The middle part initially constitutes the whole plume, but eventually disappears completely so that the plume assumes a fully Gaussian form. The development of the plume is illustrated in Figure 15.81. The model is a prime example of an advanced similarity model.

HEGADAS originally had two versions. The first, HEGADAS-S, is the steady-state model for a continuous release; this is the basic model just described. The other version, HEGADAS-T, is the quasi-steady-state model for a transient release, utilizing the Observer* concept.

In a subsequent version of the model, described by Colenbrander and Puttock (1983, 1984), enhancements were incorporated to take account of heat transfer between the ground, or water, surface and the cloud. The fifth version, HEGADAS-5, described by Witlox (1991), deals with interfacing with other source models and gives a model for vertical sources and an improved gas blanket model, and contains improved treatments of gravity spreading and of crosswind and along-wind dispersion and of time step selection. It also contains an HF thermodynamics model.

Witlox describes particularly the interface of HEGADAS-5 with the jet/plume model PLUME. Transition is taken as occurring when the jet/plume velocity is close to the wind velocity at centroid height and the air entrainment rate of the plume model is close to that of the dense gas model. There is also an advection criterion which stops the transition if the cloud becomes too buoyant. The PLUME model gives averaged values of the density, concentration, velocity and enthalpy. The matching of these variables between the two models is discussed in detail by the author.

The gas blanket model, as originally formulated, exhibited oscillatory behaviour and has been modified to correct this. A model is also given for a vertical source in terms of a breakpoint. Using this model, breakpoint data are specified for a series of times for the effective half-width and for any two of the following: the effective cloud height, the mass flow of gas and the centre line ground level concentration of gas.

The treatment of crosswind gravity spreading in HEGADAS-5 recognizes that gravity spreading undergoes a collapse beyond which the degree of gravity spreading is much reduced. This effect has been shown in wind tunnel work by R.L. Petersen and Ratcliff (1989) and is dealt with by P.T. Roberts, Puttock and Blewitt (1990). For the crosswind dispersion coefficient S_y use is made of an alternative formula for a_y due to Briggs.

The HEGADAS-5 model gives the four dependent variables: crosswind dispersion coefficient S_y, vertical dispersion coefficient S_z, effective half-width of cloud B_{eff} and centre line ground level concentration c_A. It contains five ordinary differential equations for the variables S_y, S_z, B_{eff}, H_e and y_{w3}, where H_e is the surface heat transfer and y_{w3} is the mole fraction of surface water vapour. The earlier versions of the program were sensitive to the choice of time interval for solution of the equations. HEGADAS-5 contains automatic time interval selection.

HEGADAS-5 incorporates a model of HF thermodynamics. This is described by Puttock *et al.* (1991a,b).

Vertical dispersion

In this later work the vertical dispersion is expressed in terms of the top entrainment velocity u_e:

$$u_e = \frac{(1+\alpha')k u_*}{\phi(\mathrm{Ri}_*)} \qquad [15.31.54]$$

with Ri_* defined by Equation 15.31.34.

Improved relations are also given for the Monin–Obukhov profile function $\phi(\mathrm{Ri}_*)$:

$$\phi(\mathrm{Ri}_*) = 0.74 + 0.25\mathrm{Ri}_*^{0.7} + 1.2\times10^{-7}\,\mathrm{Ri}_*^3 \quad \mathrm{Ri}_* \geq 0 \qquad [15.31.55a]$$

$$= \frac{0.74}{1 + 0.65|\mathrm{Ri}_*|^{0.6}} \quad \mathrm{Ri}_* < 0 \qquad [15.31.55b]$$

Equation 15.31.55a applies to stable conditions and is based on work by McQuaid (1976b) and Kranenburg (1984), and Equation 15.31.55b applies to unstable conditions and is based on fitting data from the Prairie Grass experiments.

Heat transfer

For heat transfer between the ground and the cloud, expressions are given for both the natural and forced convection cases. For natural convection the expression given for this heat flux Q_{gr} is

$$Q_{gr} = 0.14\left[\frac{\alpha_{Tc}^2 \beta_c g}{\nu_c}(\rho_c c_{pc})^3\right]^{1/3}(T_{gr} - T_c)^{4/3} \qquad [15.31.56]$$

with, for an ideal gas,

$$\beta_c = 1/T_c \qquad [15.31.57]$$

where C_f is a friction factor (=$(2u_*/u_c^2$, u_c is the velocity of the cloud, α_{Tc} is the thermal diffusivity of the cloud, β_c is the coefficient of volumetric expansion and ν_c is the kinematic viscosity of the cloud. For forced convection the heat flux is given as

$$Q_{gr} = 1/2\left(\frac{\alpha_{Tc}}{\nu_c}\right)^{2/3} C_f \rho c_{pc} u_c (T_{gr} - T_c) \qquad [15.31.58]$$

15.31.5 HEGABOX

HEGADAS models for a continuous release of dense gas the gravity spreading of the gas in the lateral direction. But for an instantaneous release, or for a non-instantaneous release in low wind, there is also strong gravity spreading along the direction of the wind. This aspect is taken care of by HEGABOX, which is used as a front-end addition to HEGADAS to cater for such cases. HEGABOX has been described by Puttock (1987c, 1988a).

In HEGABOX, the cloud from an instantaneous release is treated as a cylinder of uniform concentration. The gravity spreading and air entrainment are modelled as follows:

$$\frac{dR}{dt} = c_E (g' H)^{1/2} \qquad [15.31.59]$$

$$\frac{dV}{dt} = \pi R^2 u_e + 2\pi R H w_e \qquad [15.31.60]$$

The value of c_E is taken as 1.15.

For the edge entrainment velocity w_e

$$w_e = \gamma \frac{dr}{dt} \qquad [15.31.61]$$

where γ is the edge entrainment coefficient.

For the top entrainment velocity u_e

$$u_e = \frac{k u_{*I}}{\phi(\mathrm{Ri}_{*I})} \qquad [15.31.62]$$

with

$$u_{*I} = \frac{k u_B}{\ln(H/z_o) - 1} \qquad [15.31.63]$$

$$\phi(\mathrm{Ri}_{*I}) = (1 + 0.8\mathrm{Ri}_{*I})^{1/2} \qquad [15.31.64]$$

$$\mathrm{Ri}_{*I} = \frac{g' H}{u_{*I}^2} \qquad [15.31.65]$$

where u_B is a bulk cloud velocity and u_{*I} is an internal velocity scale. The internal velocity scale u_{*I} is chosen to be consistent with the uniform density assumed over the height of the cloud.

The bulk cloud velocity u_B is determined as follows. Strictly, this quantity should be obtained from conservation of momentum, but there are a number of aspects such as the effective velocity of the air entrained in the cloud, which are not well understood. The approach taken is therefore a semi-empirical one. The cloud acquires momentum from the entrainment of air passing over it. There is evidence that the effective air velocity u_A'seen' by the cloud bears a constant ratio to the average air velocity over the height H of the cloud and that this ratio is of the order of 0.7. Furthermore, the cloud must eventually accelerate to the velocity of the ambient air.

These features are taken into account by using the following relations:

$$u_B = f(u_A) \qquad [15.31.66]$$

$$u_A = \left(0.7 + \frac{0.3}{1 + \mathrm{Ri}_*}\right)\frac{1}{H}\int_0^H u(z)\,dz \qquad [15.31.67]$$

with

$$\mathrm{Ri}_* = \frac{g' H}{u_*^2} \qquad [15.31.68]$$

If HEGABOX is used as a front end for HEGADAS, transition is taken to occur at a transition value of Ri_I^*. This value is taken as 10.

At transition the cylindrical cloud is divided into slices with an observer at each slice, as shown in Figure 15.82. The parameters with which an observer starts are as follows. The half-width b of the middle part is equal to the cloud width at that point. The width parameter S_y is initially zero. The height parameter S_z is obtained from the height H. The centre line ground level concentration c_A is set equal to the uniform concentration c.

The transition from HEGABOX to HEGADAS is illustrated by the example shown in Figure 15.83.

15.31.6 HGSYSTEM

A set of models named HGSYSTEM has been developed, built around HEGADAS. These models were originally created specifically for releases of hydrogen fluoride and for this case the model system is called HFSYSTEM and the constituent models mainly bear the prefix HF. The models were subsequently generalized to give a set for an ideal gas. HGSYSTEM has been described in outline by Puttock *et al.* (1991a,b) and in detail by MacFarlane *et al.* (1990), Rees (1990) and Witlox *et al.* (1990). HFSYSTEM contains source models for an unpressurized source and for a pressurized source.

For an unpressurized source the model used is EVAP, which describes evaporation from a pool and which contains two options. The first models evaporation from a pool of fixed size or a spreading pool on land. Evaporation is assumed to be mass transfer limited. The second option models evaporation from a spreading pool on water. Evaporation is assumed to be heat transfer limited.

For a pressurized source at ground level the model used is HFSPILL. This gives the flow of a time-varying release of

gas, subcooled liquid or two-phase flashing liquid. The models used are of an accuracy matched to that of the models for the later dispersion phase.

For a pressurized release from an elevated source the model used is HFPLUME. This models the airborne, touchdown and slumping phases of the plume. An account of the generalized model PLUME is given in Section 15.44. Each of these three source models is designed to interface with HEGADAS.

As stated, the models in HFSYSTEM have been generalized to form the set of models for an ideal gas given in HGSYSTEM. This model system also contains an alternative model PGPLUME for passive dispersion. The models in HGSYSTEM are intended to give reasonable accuracy in the near field. One aim is to allow prediction of conditions both at the inlet and outlet of a mitigation system.

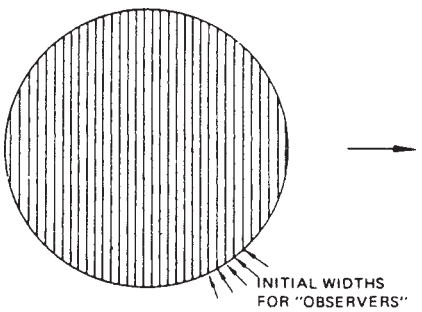


Figure 15.82 *HEGADAS model for dense gas dispersion – initial locations of Observers' (Puttock, 1987c) (Courtesy of the American Institute of Chemical Engineers)*

15.31.7 Validation and application

Te Riele (1977) compared predictions from his model with observations in the Bureau of Mines, van Ulden, and SS Gadila trials. The latter is shown in Figure 15.92(c). Colenbrander (1980) used the Matagordo Bay trials for comparison with predictions from his model.

Validations of the various versions of HEGADAS include comparison of predictions from the model with observations from the Maplin Sands trials by Colenbrander and Puttock (1983) and Puttock (1987c).

Puttock (1987c, 1988a) has compared predictions of HEGABOX/HEGADAS with observations from the Maplin Sands and Thorney Island Phase I trials.

J.L. Woodward *et al.* (1982) have compared the performance of HEGADAS with that of other models in relation to the Matagordo Bay and Porton Down trials, and S.R. Hanna, Strimaitis and Chang (1991b) its performance against other models for nine sets of trials, including the Porton Down, Maplin Sands, Thorney Island Phase I, Burro, Coyote, Desert Tortoise and Goldfish trials.

15.32 Dispersion of Dense Gas: DEGADIS

15.32.1 DEGADIS

As described above, the related model DEGADIS has been developed by Havens and coworkers (Havens, 1985, 1986; Spicer and Havens, 1986, 1987). DEGADIS is based on HEGADAS, but differs in several respects and, in particular, it incorporates its own source, vertical entrainment and heat transfer models. DEGADIS is for a continuous release but may be adapted to time-varying releases, and an instantaneous release, by treating these as a series of quasi-steady-state releases.

The source model used in DEGADIS has been described by Spicer and Havens (1986). It describes the transition by

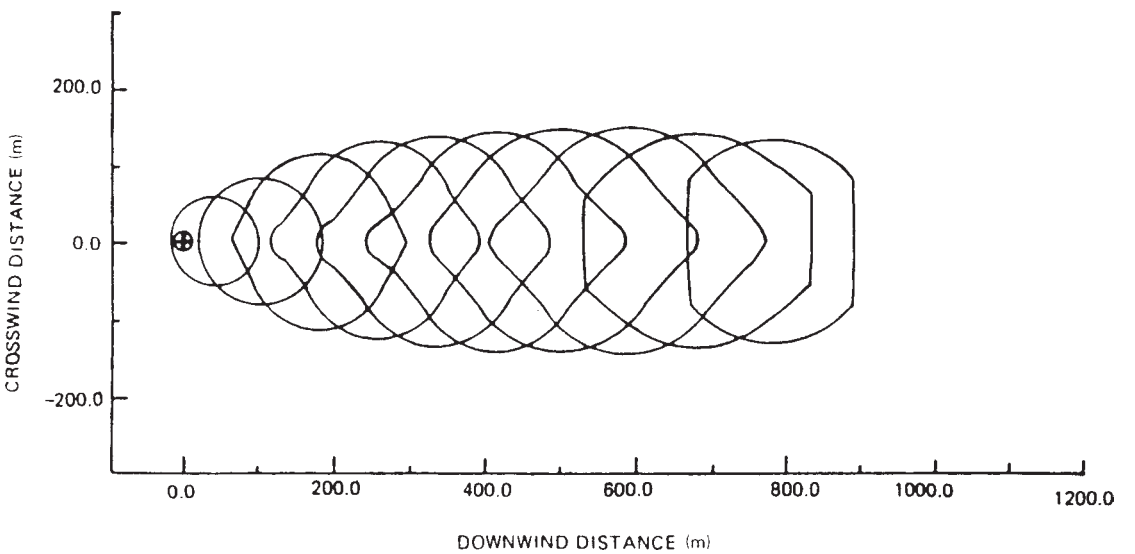


Figure 15.83 *HEGABOX/HEGADAS model for dense gas dispersion – prediction of combined model for cloud development for Thorney Island trial 14 (Puttock, 1987c), Contours are for 500 ppm ground level concentration shown at 20-s intervals from time of release; 20 and 40 s contours are from HEGABOX, remainder from HEGADAS (Courtesy of Reidel Publishing Company)*

gravity slumping from a cloud of high aspect ratio to one of low aspect ratio and to gravity spreading.

The source model includes the following treatment of heat transfer from the ground surface to the cloud. Relations are given for both natural convection and forced convection. For natural convection, use is made of Equation 15.24.14. The authors state that for the hydrocarbon gases methane and propane this equation can be written as

$$h_{gr} = 18\left[\left(\frac{\rho}{M}\right)^2 \Delta T\right]^{1/3} \qquad [15.32.1]$$

For heat transfer by forced convection, use is made of Equation 15.24.18. Then utilizing Equation 15.31.10 to give at height H

$$u = u_r\left(\frac{H}{z_r}\right)^{\alpha'} \qquad [15.32.2]$$

and taking $\mathrm{Pr} = 0.741$, Equation 15.32.1 yields

$$h_{gr} = \left[1.22\frac{u_*^2}{u_r}\left(\frac{z_r}{H}\right)^{\alpha'}\right]\rho c_p \qquad [15.32.3]$$

Another feature of DEGADIS is the correlation used for vertical dispersion in the stratified flow phase. The correlation is based on analysis of data obtained by McQuaid (1976b) in wind tunnel experiments and other data by Lofquist (1960) and Kantha, Phillips and Azad (1977) and is shown in Figure 15.84. The vertical entrainment velocity u_e is given by Equation 15.31.54 but with $\alpha' = 0$, so that

$$\frac{u_e}{u_*} = \frac{k}{\phi(\mathrm{Ri}_*)} \qquad [15.32.4]$$

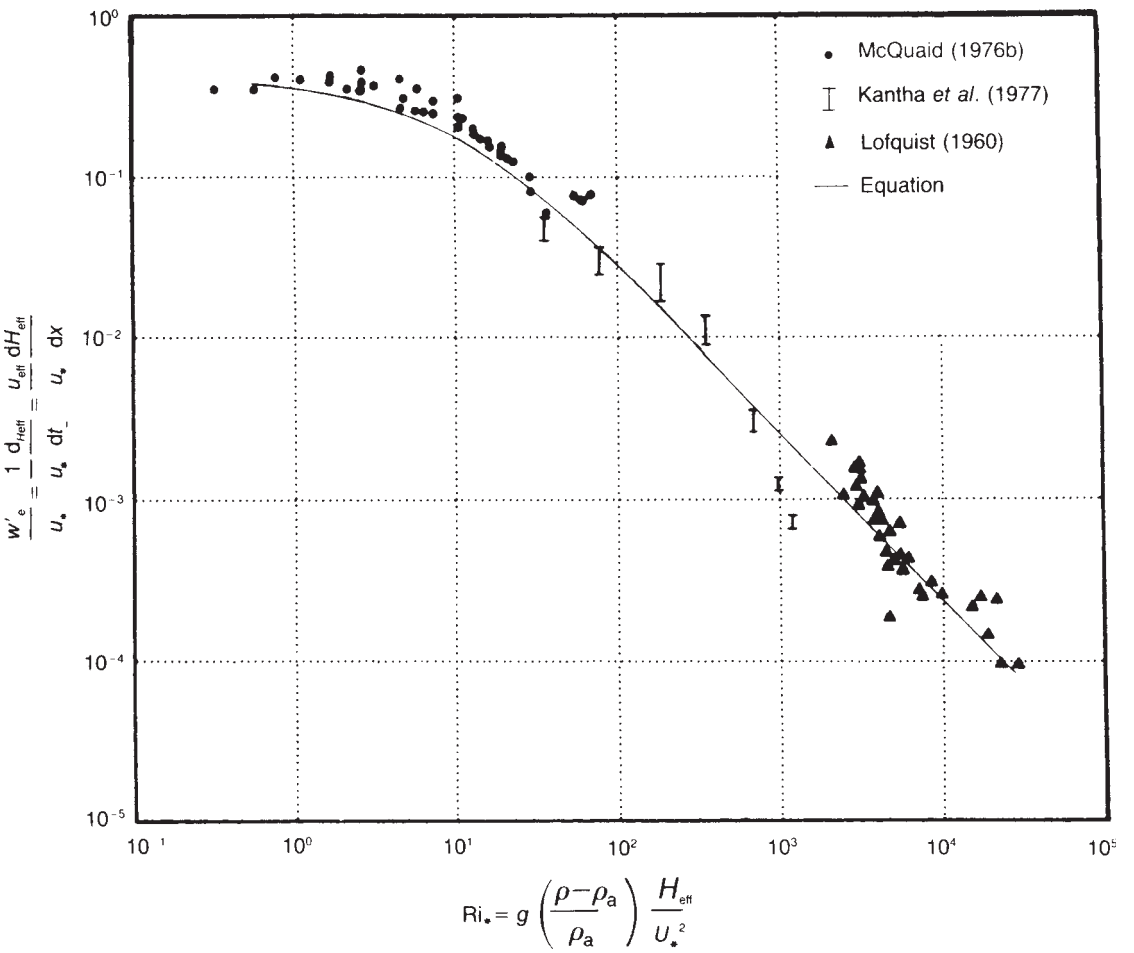


Figure 15.84 *Correlation of vertical entrainment velocity with bulk Richardson number (Spicer and Havens, 1986) (Courtesy of Elsevier Science Publishers)* H_{eff}*, height at which concentration is one-tenth of the maximum value;* u_{eff}*, effective advection velocity;* $w'_e = dH_{eff}/dt$

with the following alternative relation used for the profile function $\phi(\mathrm{Ri}_*)$:

$$\phi(\mathrm{Ri}_*) = 0.88 + 0.099\mathrm{Ri}_*^{1.04} + 1.4 \times 10^{-25}\mathrm{Ri}_*^{5.7} \quad \mathrm{Ri}_* \geq 0 \qquad [15.32.5a]$$

$$\frac{0.88}{1 + 0.65|\mathrm{Ri}_*|^{0.6}} \quad \mathrm{Ri}_* < 0 \qquad [15.32.5b]$$

where Ri_* is a modified Richardson number.

In later treatments by the authors (Spicer and Havens, 1987) the last term in Equation 15.32.5a is zero. The correlation has the properties that

$$\frac{u_e}{u_*} \rightarrow \frac{0.35}{0.88} = 0.4 \quad \mathrm{Ri}_* \rightarrow 0 \qquad [15.32.6a]$$

$$\propto \frac{1}{\mathrm{Ri}_*} \qquad \mathrm{Ri}_* \rightarrow \infty \qquad [15.32.6b]$$

taking the value of k for Equation 15.32.6a as 0.35. Equation 15.32.6a corresponds to the passive dispersion limit. Account is also taken of the enhancement of vertical mixing by the convective turbulence due to heat transfer.

15.32.2 Validation and application

Havens and co-workers (Spicer and Havens, 1985, 1986, 1987; Havens, 1986, 1992; Havens *et al.*, 1991) have compared predictions of DEGADIS with observations from the Matagordo Bay, Maplin Sands, Thorney Island Phase I, Burro, Coyote, Desert Tortoise, Eagle and Goldfish trials, and Blewitt, Yohn and Ermak (1987) have compared its predictions against the Goldfish trials. Touma *et al.* (1991) have compared the performance of the model with that of other models in relation to the Burro, Desert Tortoise and Goldfish trials, and S.R. Hanna, Strimaitis and Chang (1991b) have compared its performance against other models for nine sets of trials, including the Porton Down, Maplin Sands, Thorney Island Phase I, Burro, Coyote, Desert Tortoise and Goldfish trials.

15.33 Dispersion of Dense Gas: SLUMP and HEAVYGAS

Another pair of models are SLUMP and HEAVYGAS developed at WS Atkins. They have been described by Deaves (1983a,b, 1987a,b). SLUMP is a box model and HEAVYGAS an if-theory model with $\kappa-\epsilon$ modification.

15.33.1 SLUMP

SLUMP is described by Deaves (1987a), who refers to the equation set for box models formulated by Wheatley and Webber (1984 CEC EUR EN 9592) and deals particularly with the treatment in his model of slumping velocity, cloud advection and transition to passive dispersion.

15.33.2 HEAVYGAS

An account of HEAVYGAS has been given by Deaves (1983a). He has also described its subsequent development (Deaves, 1983b, 1984, 1985, 1987a,b, 1989b). The basic equations of the model are:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_j}(\rho u_j) = 0 \qquad [15.33.1]$$

$$\frac{\partial(\rho u_j)}{\partial t} + \frac{\partial}{\partial x_j}(\rho u_i u_j) = -\frac{\partial \rho}{\partial x_i} + \frac{\partial}{\partial x_j}\left(\mu \frac{\partial u_i}{\partial x_j}\right) + \Delta\rho g_i \qquad [15.33.2]$$

$$\frac{\partial \rho\phi}{\partial t} + \frac{\partial}{\partial x_j}(\rho u_j \phi) = \frac{\partial}{\partial x_j}\left(\Gamma_\phi \frac{\partial \phi}{\partial x_j}\right) + S_\phi \qquad [15.33.3]$$

where p is the pressure, t is the time, u is the velocity, x is the distance, μ is the viscosity, ρ is the density, ϕ is any scalar quantity and subscripts i and j denote the i and j directions, respectively. S_ϕ and Γ_ϕ are functions which vary with the quantity ϕ. Equation 15.33.3 is the general equation for any scalar quantity. Thus if it is used for concentration, $S_\phi = 0$ and Γ_ϕ is the eddy diffusion coefficient.

The model incorporates the $\kappa-\epsilon$ modification. The quantities κ and ϵ may be obtained from Equation 15.33.3 with γ adjusted to give the usual form of the $\kappa-\epsilon$ turbulence model equations and with γ either given as a function of κ and ϵ:

$$\Gamma_\phi = c_\phi \frac{\kappa^2}{\epsilon} \qquad [15.33.4]$$

where c_ϕ is a constant or defined in some other way such as a function of height for each stability category. The model is formulated in both two - and three-dimensional forms. The relative merits of the two forms has been discussed by Deaves (1987a). In essence, two-dimensional modelling is much simpler and is usually sufficient, but three-dimensional modelling may be required in special cases.

15.33.3 Validation and application

The predictions of HEAVYGAS have been compared with the results of Thorney Island Phase II trials 5 and 21 without and with a solid fence (Deaves, 1987a) and trial 29 with a single building (Deaves, 1984, 1985).

HEAVYGAS has been used to model a number of applications which exploit the ability of this type of model to deal with situations other than flat, unobstructed terrain. It has been used to model the dispersion of chlorine within a building (Deaves, 1983a) and the effect of water spray barriers on the dispersion of a plume of carbon dioxide (Deaves, 1983a,b, 1984). These studies are described in Sections 15.40 and 15.53, respectively.

It has also been applied to problems arising in safety cases (Deaves, 1987, 1989a,b). These include: the release of chlorine into and then from a building; the effect of individual buildings on hazard ranges for chlorine; and the effect of a whole plant site on hazard ranges for ammonia. Accounts of this work are given in Section 15.40.

15.34 Dispersion of Dense Gas: Workbook Model

A unified methodology for dense gas dispersion is given in the *Workbook on the Dispersion of Dense Gases* (Britter and McQuaid, 1988). The work was supported, though not necessarily endorsed, by the Health and Safety Executive and was closely associated with the Thorney Island trials.

15.34.1 Basic model

The basic model is a similarity relation and consists of a correlation of dimensionless groups. This relation is

$$\frac{C}{C_o} = f\left[\frac{x}{D}, \frac{y}{D}, \frac{z}{D}, \frac{tu_{ref}}{D}, \frac{q_o(t)}{u_{ref}D^2}\right.$$

$$\text{or } \frac{Q_o^{1/3}}{D}, \frac{u_{ref}^2}{gD}, \frac{\rho_o}{\rho_a}, \frac{z_o}{D}, \frac{l_i}{D}, G$$

$$\left.\text{or } \frac{Q_o^{1/3}}{D}, \text{ atmospheric stability}\right] \qquad [15.34.1]$$

where C is the volumetric concentration, C_o is the volumetric concentration of the initial release, D is a characteristic dimension of the source, g is the acceleration due to gravity, G is the source geometry, l_i is the length scale of the turbulence in the atmospheric boundary layer, $q_o(t)$ is the volumetric rate of release of material, Q_o is the volume of material released, u_{ref} is a characteristic mean velocity, ρ_a is the density of air, ρ_o is a characteristic density of the material released, and x, y and z are the distances in the downwind, crosswind and vertical directions, respectively.

The influence of some of the items in Equation 15.34.1 is relatively weak and in order to obtain a sufficient data set the following are disregarded: (l_i/D), (z_o/D), G and atmospheric stability. This then yields

$$\frac{C}{C_o} = f\left[\frac{x}{D}, \frac{y}{D}, \frac{z}{D}, \frac{tu_{ref}}{D}, \frac{q_o(t)}{u_{ref}D^2}\right] \quad \text{or} \quad \frac{Q_o^{1/3}}{D}, \frac{u_{ref}^2}{gD}, \frac{\rho_o}{\rho_a} \qquad [15.34.2]$$

15.34.2 Model for continuous release

For a continuous release the concentration of interest is the time mean concentration $\bar{C}$. From Equation 15.34.2

$$\frac{\bar{C}}{C_o} = f\left[\frac{x}{D}, \frac{y}{D}, \frac{z}{D}, \frac{q_o}{u_{ref}D^2}, \frac{u_{ref}^2}{gD}, \frac{\rho_o}{\rho_a}\right] \qquad [15.34.3]$$

For the maximum time mean concentration $\bar{C}_m$ on the centre line of the cloud

$$\frac{\bar{C}_m}{C_o} = f\left[\frac{x}{D}, \frac{q_o}{u_{ref}D^2}, \frac{u_{ref}^2}{gD}, \frac{\rho_o}{\rho_a}\right] \qquad [15.34.4]$$

Since the number of terms in Equation 15.34.4 is still too high for the data set available, two further approximations are called in aid. One is the Boussinesq approximation, in which the density variation is neglected in the inertial terms but is retained in the buoyancy terms. This means in effect that the problem is restricted to the case where formally $[(\rho_o-\rho_a)/\rho_a] \ll 1$ and, in practice, $[(\rho_o-\rho_a)/\rho_a] < 1$; the value of $[(\rho_o-\rho_a)/\rho_a]$ for the initial release tends to approximate to unity or less. The Boussinesq approximation allows the terms (u_{ref}^2/gD) and (ρ_o/ρ_a) to be replaced by (u_{ref}^2/g'_o) with

$$g'_o = \frac{g(\rho_o - \rho_a)}{\rho_a} \qquad [15.34.5]$$

where g'_o is the reduced gravity of the initial release.

The other approximation invoked is to neglect the characteristic dimension D of the source. D has progressively less effect as the distance x from the source increases, and becomes insignificant at about $x > 5D$.

With these simplifications, Equation 15.34.4 reduces to

$$\frac{\bar{C}_m}{C_o} = f\left[\frac{x}{(q_o/u_{ref})^{1/2}} \frac{g'_o q_o/u_{ref}^3}{(q_o/u_{ref})^{1/2}}\right] \qquad [15.34.6a]$$

$$= f\left[\frac{x}{(q_o/u_{ref})^{1/2}}\phi\right] \qquad [15.34.6b]$$

with

$$\phi = \left(\frac{g'^2_o q_o}{u_{ref}^5}\right)^{1/5} \qquad [15.34.7]$$

where ϕ is a stability parameter. The power 1/5 is introduced solely to give convenient numbers.

Equation 15.34.6b can be recast in the more useful form

$$\frac{x_n}{(q_o/u_{ref})^{1/2}} = f(\phi) \qquad [15.34.8]$$

where x_n is the distance at which the concentration is the fraction n of the initial concentration $\bar{C}_m/C_o$.

Downwind distance to a given concentration

The correlation of the data based on Equation 15.34.8 is shown in Figure 15.85(a). The correlation is intended to apply to the long-term average concentrations. It is based on both laboratory and full-scale trial data. Justifications of the correlation itself and of the limit of effectively passive dispersion are given in Appendices C and E of the report, respectively. The correlation is valid within the limits

$$0.002 \le \frac{\bar{C}_m}{C_o} \le 0.1; \quad 0 \le \phi \le 4$$

There are two useful relations which can be obtained from Figure 15.85(a). One is

$$\frac{x_n}{(q_o/u_{ref})^{1/2}} = A\phi^{-1/2} \quad \phi \ge 1 \qquad [15.34.9]$$

or

$$x = Aq_o^{0.4}(g'_o)^{-0.2} \qquad [15.34.10]$$

where A is given by Figure 15.85(b). This equation shows a quite strong dependence of the distance x to a particular concentration on source strength q_o. It also shows that the distance decreases as the stability parameter ϕ increases. The interpretation is that increased lateral spread more than compensates for the inhibition of vertical mixing. The other relation is

$$x = 17.5\left(\frac{\bar{C}_m}{C_o}\right)^{-1/2}\left(\frac{q_o}{u_{ref}}\right)^{1/2} \quad 0 < \phi < 3 \qquad [15.34.11]$$

Thus the distance depends only on the length scale $(q_o/u_{ref})^{1/2}$.

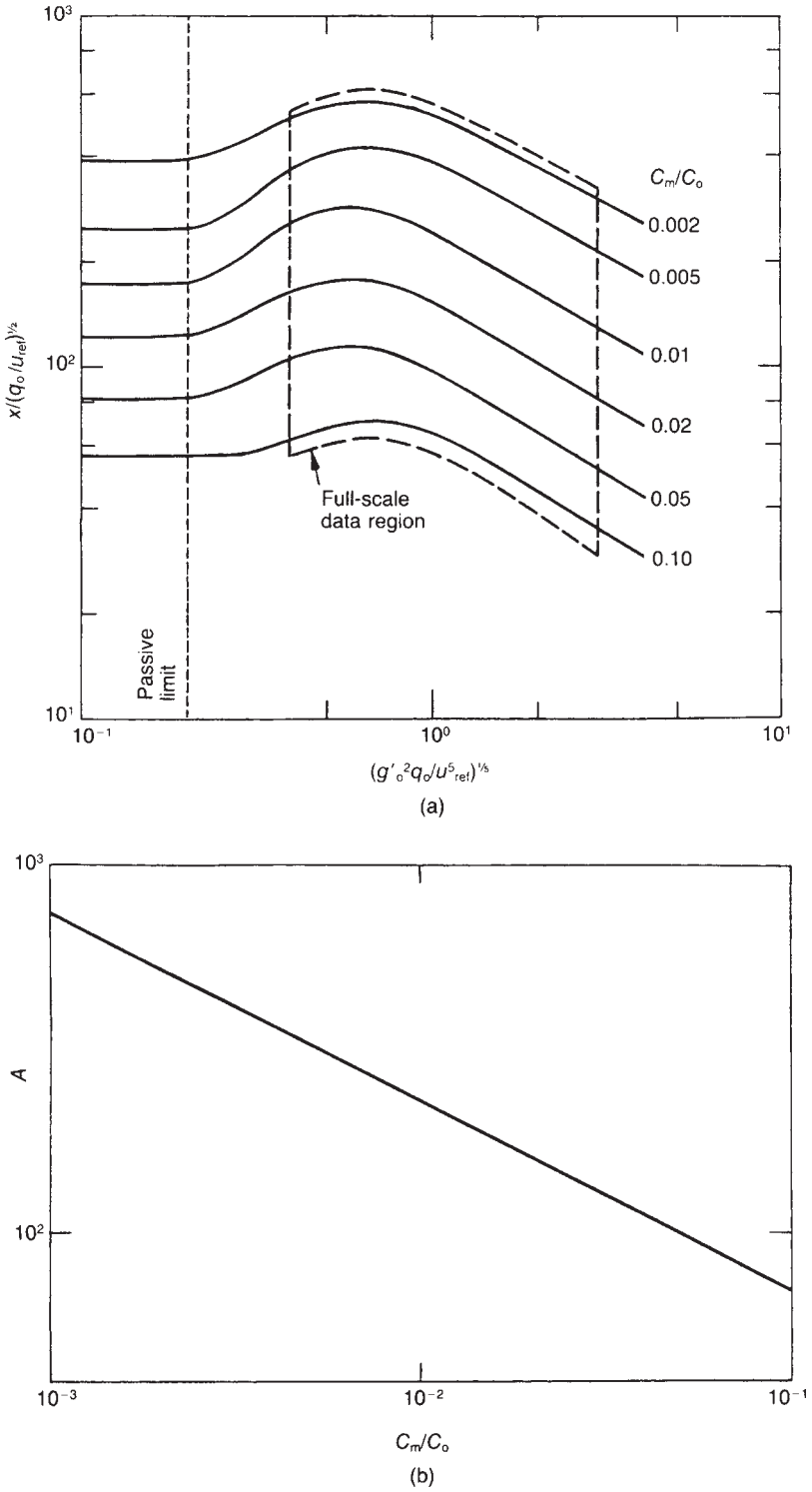


Figure 15.85 *Workbook method for dense gas dispersion – correlation for continuous release (Britter and McQuaid, 1988; reproduced by permission): (a) correlation; (b) parameter A*

For low concentrations outside the range of validity given, the suggestion made is that Equation 15.34.10 may be extrapolated, but still subject to the limits on ϕ.

Area bounded by a given concentration

A method is also given to obtain the area bounded by a given concentration. On the basis of modelling and experiment the dimensions of the cloud are found to be approximately as follows:

$$L_u = D/2 + 2l_b \qquad [15.34.12]$$

$$L_h = L_{ho} + 2.5l_b^{1/3}x^{2/3} \qquad [15.34.13]$$

with

$$l_b = \frac{q_o g'_o}{u_{ref}^3} \qquad [15.34.14]$$

$$L_{ho} = D + 8l_b \qquad [15.34.15]$$

where l_b is the buoyancy length scale, L_h is the half-width of the plume, L_{ho} is the half-width of the plume at the source and L_u is the upwind extent of the plume.

For the height of the plume, from conservation of mass

$$L_v = \frac{q_o}{u_{ref}L_h} \qquad [15.34.16]$$

where L_v is the height of the plume.

Equation 15.34.16 assumes that the concentration is homogenous throughput the plume. In fact, the concentration varies with height, but the exact vertical profile is uncertain and variable. There is experimental evidence that the bulk of the material is contained within a height of $2(q_o/u_{ref}L_h)$.

Since Equation 15.34.16 is unduly conservative, an alternative approach is also given. This is to locate, for the concentration of interest, the lateral boundaries of the cloud at the distance $(2/3)x_n$ and to join these boundary points with x_n, as shown in Figure 15.86.

15.34.3 Model for instantaneous release

For an instantaneous release the case considered is a source of unit aspect ratio. This allows the external length scale D to be equated with the internally set length scale $Q_o^{1/3}$.

Then, following an approach similar to that for the continuous case,

$$\frac{C_m}{C_o} = f\left(\frac{x}{Q_o^{1/3}}, \frac{u_{ref}^2/g'_o}{Q_o^{1/3}}\right) = f\left(\frac{x}{Q_o^{1/3}}, \psi\right) \qquad [15.34.17]$$

with

$$\psi = \left(\frac{g'_o Q_o^{1/3}}{u_{ref}^2}\right)^{1/2} \qquad [15.34.18]$$

where ψ is a stability parameter. Again the power 1/2 is used solely to give convenient numbers. Then,

$$\frac{x_n}{Q_o^{1/3}} = f(\psi) \qquad [15.34.19]$$

In this case, since $D = Q_o^{1/3}$, the assumption that the effect of D can be neglected is not necessary.

Downwind distance to a given concentration. The correlation based on Equation 15.34.19 is shown in Figure 15.87(a). The correlation is intended to apply to the ensemble average of the maximum short-time (0.6 s) mean concentrations. It is based on both laboratory and full-scale trial data. Justifications of the correlation itself and of the limit of effectively passive dispersion are given in Appendices D and E of the report, respectively. The correlation is valid within the limits

$$0.001 \le \frac{C_m}{C_o} \le 0.1; \quad 0.7 \le \psi \le 10$$

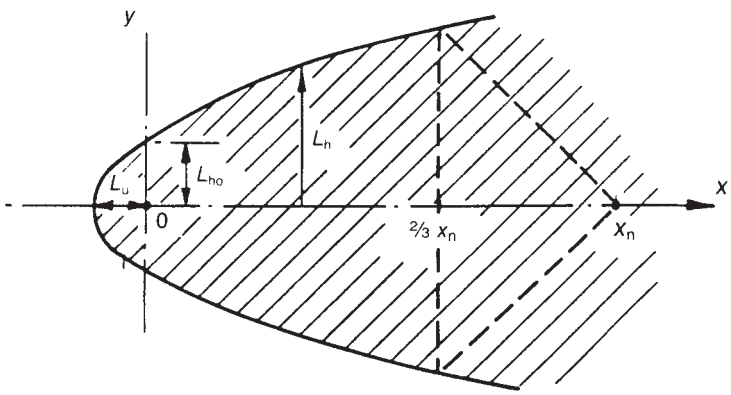
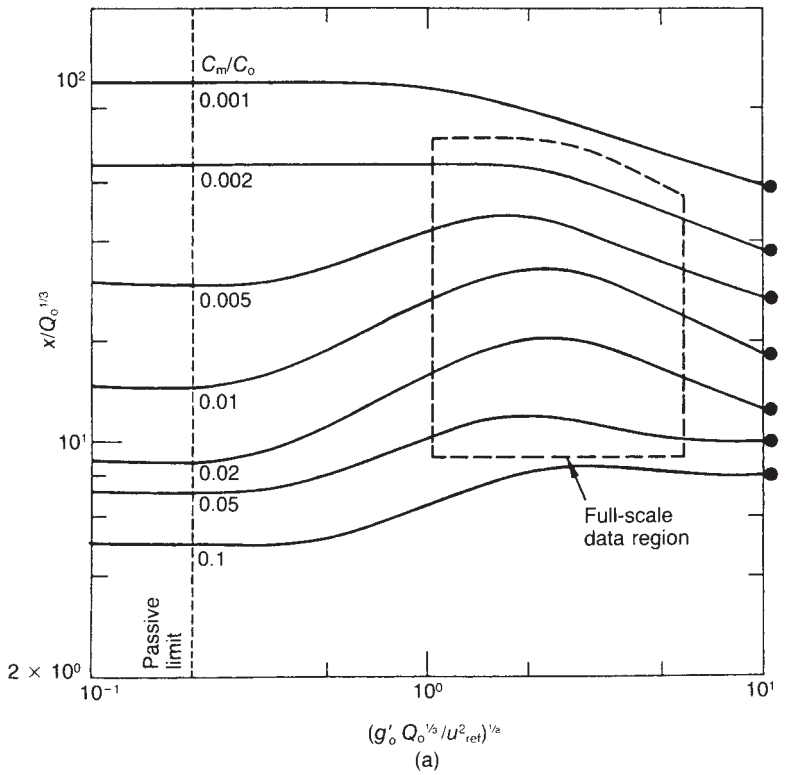


Figure 15.86 *Workbook method for dense gas dispersion – area covered by concentration contour for continuous release (Britter and McQuaid, 1988; reproduced with permission)*



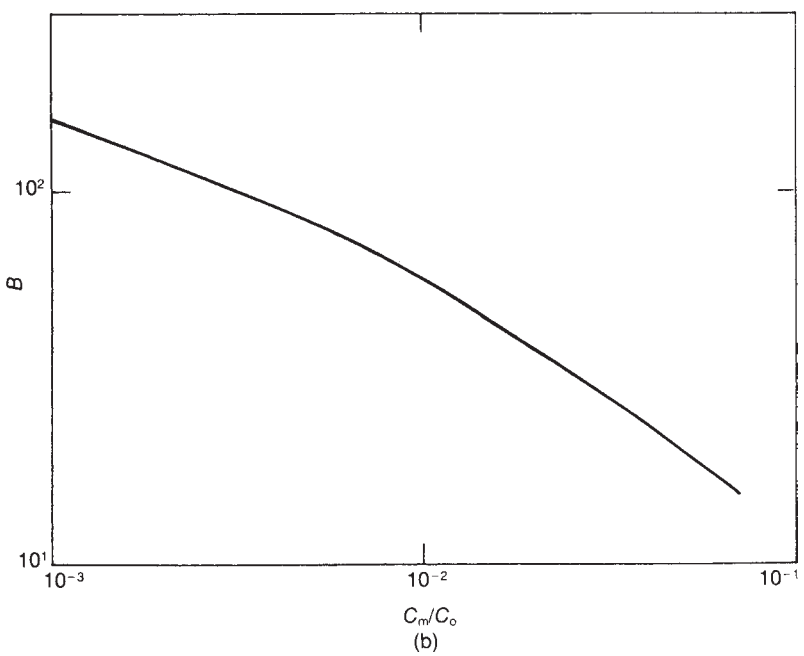


Figure 15.87 *Continued*

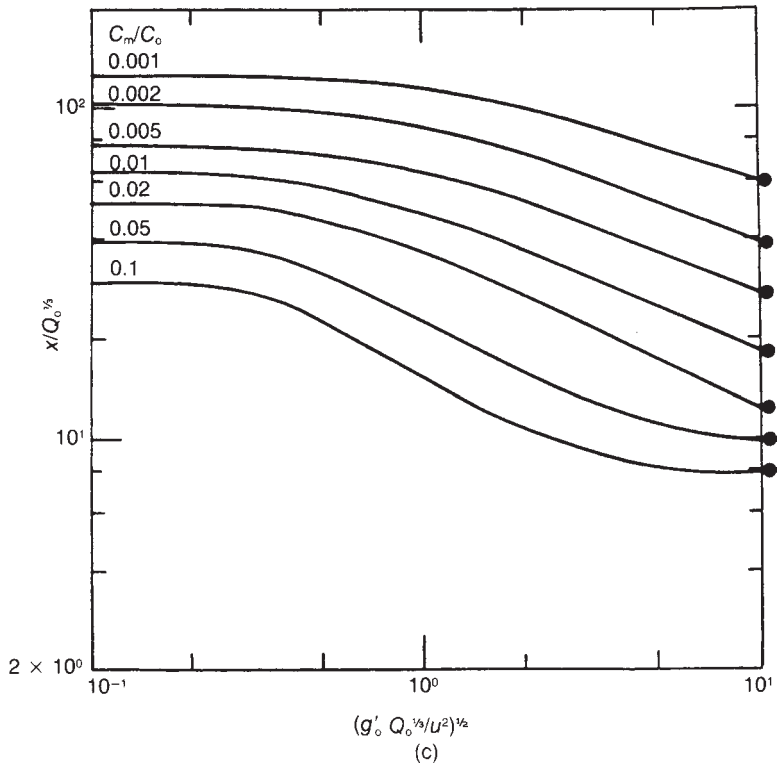


Figure 15.87 *Workbook method for dense gas dispersion – correlation for instantaneous release (Britter and McQuaid, 1988; reproduced with permission): (a) correlation; (b) parameter B; (c) correlation if initial dilution already taken into account*

There are again two useful relations which can be obtained from Figure 15.87(a). One is

$$\frac{x_n}{Q_o^{1/3}} = B\psi^{1/2} \quad 0.001 \leq \frac{C_m}{C_o} \leq 0.002;\ 2 \leq \psi \leq 10 \qquad [15.34.20]$$

or

$$x = BQ_o^{1/4} g_o'^{-1/4} u_{ref}^{1/2} \qquad [15.34.21]$$

where B is given by Figure 15.87(b). This equation shows a rather weaker dependence on source strength of the distance x to a given concentration compared with the continuous case. The other relation is

$$x = 2.8\left(\frac{C_m}{C_o}\right)^{-1/2} \quad 1 < \psi < 5 \qquad [15.34.22a]$$

$$= 1.8\left(\frac{C_m}{C_o}\right)^{-1/2} \quad \psi \to \infty \qquad [15.34.22b]$$

For low concentrations outside the range of validity given, the suggestion made is that Equation 15.34.21 may be extrapolated, but subject still to the limits on ψ.

For the case where there has already been significant dilution of the cloud and consequent cloud acceleration the *Workbook* proposes the modification shown Figure 15.87(c).

The *Workbook* also gives for an instantaneous release the correlation shown in Figure 15.88 obtained from the Thorney Island trials for $1 < \psi < 5$.

Area swept by a given concentration

For the area swept by a given concentration the method is as follows. A model is used which is based on gravity slumping

$$\frac{dR}{dt} = c_E (g'H)^{1/2} \qquad [15.34.23]$$

with

$$g' = \frac{g(\rho - \rho_a)}{\rho} \qquad [15.34.24]$$

where H is the height of the cloud, R is the radius of the cloud and C_E is the slumping constant. The value of the constant c_E is 1.07. By conservation of buoyancy

$$g'Q = g'_o Q_o \qquad [15.34.25]$$

Also

$$H = Q/\pi R^2 \qquad [15.34.26]$$

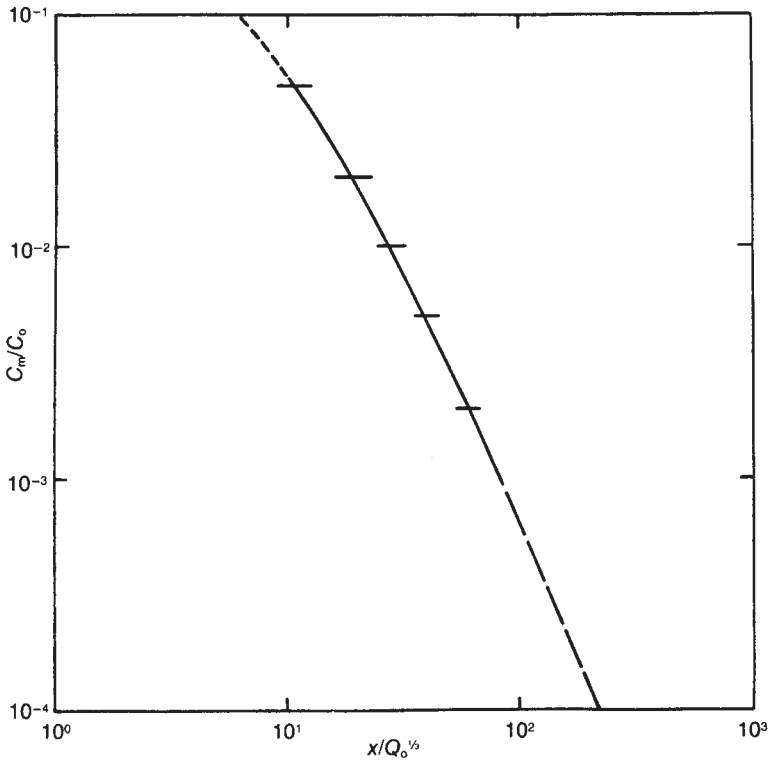


Figure 15.88 *Workbook method for dense gas dispersion—variation of maximum concentration with scaled distance, Thorney Island instantaneous release trials (see text) (Britter and McQuaid, 1988; reproduced with permission)*

where Q is the volume of the cloud. Integration of Equation 15.34.23 gives

$$R(t) = [R_o + 1.2(g'_o Q_o)^{1/2} t]^{1/2} \qquad [15.34.27]$$

where R_o is the initial radius. The advection velocity of the cloud is taken as $0.4u_{ref}$. At a distance x the arrival time t_a of the leading edge of the cloud is given by

$$x = 0.4u_{ref} t_a + R(t_a) \qquad [15.34.28]$$

and the departure time t_d of the trailing edge by

$$x = 0.4u_{ref} t_d + R(t_d) \qquad [15.34.29]$$

Now consider any time t_c between the arrival time t_a and the departure time t_d. For this time t_c the distance x_c of the leading edge is

$$x_c = 0.4u_{ref} t_c + R(t_c) \qquad [15.34.30]$$

where $x_c = x$, $t_c = t_a$ and $x_c > x$, $t_c > t_a$. Then for a given concentration C of interest, the value of x_c is obtained from the correlation given in Figure 15.87(a), or the equivalent equations, t_c is obtained from Equation 15.34.30 and the cloud half-width y_c is obtained from

$$y_c = R(t_c) \qquad [15.34.31]$$

The area required is a parabola enclosing the source and closed off at the downwind end by an arc of radius $R(t_c)$.

By conservation of mass, the cloud height H is

$$H = \frac{C_o Q_o}{\pi R^2 C} \qquad [15.34.32]$$

In practice, the bulk of the material is contained within twice this height.

15.34.4 Criterion for type of release

The criterion used to distinguish between a continuous and an instantaneous release is based on the group $(u_{ref} T_o/x)$ or, alternatively, $(u_* T_o/x)$.

An effectively continuous plume may be assumed if

$$\frac{u_{ref} T_o}{x} \geq 2.5 \qquad [15.34.33a]$$

or

$$\frac{u_* T_o}{x} \geq 0.15 \qquad [15.34.33b]$$

where u_* is the friction velocity. This criterion applies on the centre line of the cloud. Larger values apply off the centre line.

Relation 15.34.33 implies that the distance x at which the release can be regarded as continuous recedes closer to the source as the duration T_o of the release decreases. For distances greater than those given by relation 15.34.33, the assumption of a continuous source overestimates the concentration. An effectively instantaneous release may be assumed if

$$\frac{u_{ref}T_o}{x} < 0.6 \qquad [15.34.34a]$$

or

$$\frac{u_* T_o}{x} < 0.04 \qquad [15.34.34b]$$

In the region

$$0.6 \leq \frac{u_{ref}T_o}{x} \leq 2.5$$

the release is a transient one, being neither effectively continuous nor instantaneous.

15.34.5 Treatment of transient release

A transient release, as just defined, may be treated by considering it first as a quasi-continuous release and then as a quasi-instantaneous one. Taking first the quasi-continuous approach, a release of quantity Q_o over a release duration T_o has an effective release rate q_o. This release rate may be utilized in the continuous release correlation to obtain a value of the concentration. This approach neglects the effect of longitudinal dispersion and will overestimate the concentration. Alternatively, the release may be treated as a quasi-instantaneous one with quantity release Q_o. This approach will again give an overestimate of the concentration. The recommendation is then to take as the upper bound of concentration the lower of the two concentrations obtained by these two methods.

This treatment is based on the assumption that the material is transported downwind by the ambient velocity only. But such transport occurs also due to the buoyancy induced motion. For the ambient velocity the time scale is x/u_{ref} and for buoyancy-driven velocity it is $x^2/(g'_o Q_o)^{1/2}$. Then for an instantaneous release the additional criterion which must be met is

$$\frac{(g'_o Q_o)^{1/2} T_o}{x^2} \leq 0.6 \qquad [15.34.35]$$

By a similar argument for a continuous release the buoyancy-driven time scale is $x^{1/3}/(g'_o q_o)^{1/3}$ and the additional criterion is

$$\frac{(g'_o q_o)^{1/3} T_o}{x^{4/3}} \geq 2.5 \qquad [15.34.36]$$

As an illustration, consider the example given in the *Workbook*. This is the determination of the concentration ratio C_m/C_o at a distance of 200 m for a release of a total of 2000 m^3 of dense gas with initial reduced gravity 10 m/s^2 with a wind speed at reference height of 2 m/s for some release time T_o such that the release is truly neither instantaneous nor continuous. The procedure is as follows. First the release is treated as if it were an instantaneous one. For an instantaneous release $\psi = 5.6$ and $x/Q_o^{1/3} = 15.9$, so that from the correlation for an instantaneous release $C_m/C_o = 0.04$. Then the release is treated as a continuous one, with a release rate q_o of $2000/T_o$ m^3/s. A series of values of C_m/C_o are determined using the correlation for a continuous release. The results are shown in Figure 15.89. The figure also shows the limits determined from relations 15.34.35 and 15.34.36.

15.34.6 Criterion for effectively passive dispersion

The criterion used for effectively passive dispersion is for a continuous release

$$\left(\frac{g'_o q_o}{u_{ref}^3} \times \frac{1}{D}\right)^{1/3} \leq 0.15 \qquad [15.34.37]$$

and for an instantaneous release

$$\frac{(g'_o Q_o^{1/3})^{1/2}}{u_{ref}} = \frac{(g'_o Q_o/u_{ref}^2)^{1/2}}{Q_o^{1/3}} \leq 0.20 \qquad [15.34.38]$$

The justification of these criteria is given in Appendix A of the report.

For the case of an instantaneous release where the aspect ratio of the cloud is not unity, the suggestion made is that $Q_o^{1/3}$ be replaced by the initial height.

15.34.7 Thermodynamic and heat transfer effects

In the treatment so far described, it is assumed that the temperature of the release corresponds to ambient temperature, the relevant release temperature being that which pertains after the source effects have subsided and any aerosol has evaporated. If this is not the case, there are two additional effects, one thermodynamic and one of heat transfer, for which allowance needs to be made.

The first effect relates to the non-linear variation of temperature and density with volume fraction (or mole fraction) where the species have different molar specific heats. Considering the initial concentrations, the non-isothermal initial volume is V_o and the isothermal initial volume $V_o T_a/T_o$, where T_a and T_o are the absolute temperature of the air and the initial release, respectively, so that the isothermal concentration C_i and the non-isothermal concentration C_{ni} are

$$C_{ni} = \frac{V_o}{V_o + V_a} \qquad [15.34.39]$$

and

$$C_i = \frac{V_o T_a/T_o}{V_o T_a/T_o + V_a} \qquad [15.34.40]$$

where subscripts a, i and ni denote ambient, isothermal and non-isothermal, respectively. Hence

$$C_i = \frac{C_{ni}}{C_{ni}(1 - C_{ni})(T_a/T_o)} \qquad [15.34.41]$$

For example, for LNG at −162°C (111 K) and with ambient temperature of 17°C (290 K), a non-isothermal

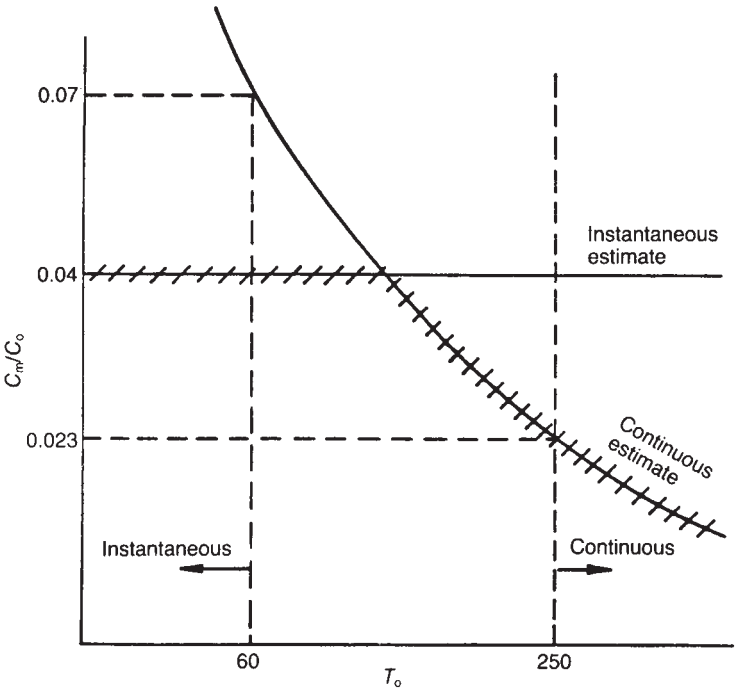


Figure 15.89 *Workbook method for dense gas dispersion – treatment for transient release (Britter and McQuaid, 1988; reproduced with permission)*

concentration of 0.05 in Equation 15.34.41 gives an isothermal concentration of 0.02.

The *Workbook* states that this effect is probably not significant for most hazardous materials, but it is for methane and hydrogen. It suggests that it be handled by determining the following two limiting cases (Cases A and B). For Case A the source density difference and volume, or volumetric flow, are used in the correlations. For Case A the density difference at the concentration of interest and the volume which satisfies mass conservation are obtained. A revised source density difference, source temperature and source volume, or volumetric flow, are then determined based on mass conservation, pure species at the source, adiabatic mixing and a constant molar specific heat equal to that of the ambient air, and used in the correlations.

These two limiting cases (A and B) are then compared. If the difference is small, the effect is unimportant. If it is neither large nor small, say a factor 2, the more pessimistic estimate is used. If it is large, say more than a factor of 2, further investigation may be warranted.

The second effect relates to heat transfer. This occurs by (a) air entrainment, (b) heat transfer at the surfaces of the cloud, particularly the lower surface and (c) latent heat exchange due to condensation and re-evaporation of water vapour. There is some uncertainty as to the effect of such heat transfer. Although it is usually assumed that it works to reduce the downwind extent of the cloud, it is not certain that this is universally the case; there may be parameter ranges where the reverse could be so, particularly if the sole effect of heat transfer is on density. This is a reflection of the uncertainty concerning the relative effects of inhibition of vertical mixing and of increase in the top area of the cloud. The authors' correlations suggest that this may vary with the stability condition.

This effect is handled in the *Workbook* by determining the following two limiting cases (Cases A and B). For Case A the source density difference and volume, or volumetric flow, are used in the correlations. For Case B the conditions of Case A are taken as the starting point. It is then assumed that heat addition at the source raises the cloud temperature to the ambient temperature. The revised source density difference and volume, or volumetric flow, obtained from this temperature are then used in the correlations. These two limiting cases (A and B) are then compared, the approach being identical to that used for the thermodynamic effect.

15.34.8 Concentration vertical profile

This basic method provides an estimate of the alongwind concentration profile but not of the crosswind or vertical concentration profiles and implies by default that the concentration is uniform in both these directions.

For crosswind concentration, the Thorney Island trials confirm that the assumption of uniform concentration is reasonable near the source where density effects are dominant. However, further from the source the cloud becomes diffuse at the edges. A criterion for the development of these diffuse edges has been given by Britter and Snyder (1988). This is the condition $(g'_m h)^{1/2} u^*$, where g'_m is the reduced gravity corresponding to the maximum concentration and h is a measure of plume height.

For a continuous release, the development of diffuse edges is due partly to true plume dilution and partly to meandering. For an instantaneous release, the equivalent to meandering is the difference between different members of an ensemble of trials at the same nominal conditions. It is necessary to decide whether the frame of reference is to be a fixed point one or a relative one such as that obtained by overlaying the centres of mass of the ensemble members.

For vertical concentration, the trials show clearly that the profile is not uniform. The variation of the vertical concentration can be represented by the relation

$$C \propto \exp(-z^n) \qquad [15.34.42]$$

In the Gaussian models used for passive dispersion the profile is normal with $n = 2$. A value of $n = \infty$ corresponds to a uniform distribution. The *Workbook* suggests that a more appropriate value of n is about 1.5. It also states that where density effects are strong, there is evidence pointing to a still smaller value of n.

In any event, there is in dense gas dispersion a very rapid change in concentration close to the surface. Implications of this are that it is necessary to exercise care in specifying a ground level concentration and that such a concentration may not be that most relevant to hazard assessment.

15.34.9 Dispersion at buildings and obstacles

The treatment of the effect of buildings and obstacles in the *Workbook* is limited to releases upwind and releases in the immediate lee. The *Workbook* treatment of these two cases is described in Section 15.40. Broadly, the effect of a building or obstacle on a release upwind is to reduce the concentration at a given distance. The evidence is that, even close to the face, the upwind concentration is not increased and that downwind it is significantly reduced.

15.34.10 Dispersion in complex terrain

The treatment of complex terrain in the *Workbook* is limited, but consideration is given to two bounding cases. One is where the topographical feature is large compared to the scale of the release and the other where it is small. If the feature is large relative to the scale of the release, the topography will tend to reduce locally at the source to a relatively simple feature, typically a slope.

If the feature is small relative to the scale of the release, the dense gas will tend to flow around it. For the case where the cloud or plume is very wide compared with the feature, the *Workbook* gives the following criterion for the cloud to flow over or around the feature:

Flow over crest of feature:

$$\frac{u^2}{g'h} \gg 2\left(\frac{h_c}{h} - 1\right)$$

Flow around feature:

$$\frac{u^2}{g'h} \ll 2\left(\frac{h_c}{h} - 1\right)$$

where h_c is the height of the crest.

15.34.11 Concentration and concentration fluctuations

The *Workbook* discusses concentration and its definition and use in models, including the *Workbook* correlations, and considers concentration fluctuations. The *Workbook* treatment of concentration is described in Section 15.45. The concentration used in the *Workbook* correlations is defined in Section 15.34.2 for a continuous release and in Section 15.34.3 for an instantaneous release. For a continuous release the concentration in the *Workbook* correlations is the long-term average, whilst for an instantaneous release it is the ensemble average of the maximum short-time (0.6 s) mean concentrations.

15.34.12 Validation and application

The *Workbook* includes a section on comparisons between, on the one hand, the predictions of its correlations and, on the other, observations from the field trials on LNG and liquefied propane at Maplin Sands, the Burro trials at the Nevada Test Site on LNG, the Thorney Island trials on Freon, and the chlorine trials at Lyme Bay, and the predictions of other models for these trials. The models include the following: the Germeles – Drake model; SLAB and FEM3; the BG/C&W model; HEGADAS; DEGADIS; a model by Wheatley *et al.* (1987 SRD R438); and a correlation by the Center for Chemical Process Safety (CCPS, 1987/2). Figure 15.90 shows a comparison given in the *Workbook* between the predictions of its correlation and those of DEGADIS for continuous releases of propane in the Maplin Sands trials. A comparison is also made between the prediction of the correlations and the observed cloud dimensions in the Potchefstroom incident (Lonsdale, 1975).

In estimating the distance to the LFL, the Workbook correlations were generally in good agreement. However, the correlations are essentially for gas clouds at ambient temperature and are not intended to handle very cold clouds such as those formed by LNG. The predictions for the Burro trials were conservative, even after utilizing the cold gas correction to the isothermal correlation.

15.35 Dispersion of Dense Gas: DRIFT and Related Models

A family of dense gas dispersion models based on a set of fundamental conservation equations has been developed by the SRD. The work is described in the following reports: *Mathematical Modelling of Two-phase Release Phenomena in Hazard Analysis* (Webber *et al.*, 1992 SRD R584), *Description of Ambient Atmospheric Conditions for the Computer Code DRIFT* (Byrne *et al.*, 1992 SRD R553), *A Differential Phase Equilibrium Model for Clouds, Plumes and Jets* (Webber and Wren, 1993 SRD R552), A *Model of a Dispersing Dense Gas Cloud and the Computer Implementation DRIFT.* I, *Near-instantaneous Releases* (Webber *et al.*, 1992 SRD R586) and *A Model of a Dispersing Dense Gas Cloud and the Computer Implementation DRIFT. II, Steady Continuous Releases* (Webber *et al.*, 1992 SRD R587). These reports may be summarized as

Source term	R584
Ambient atmospheric model	R553
Differential phase equilibrium model	R552
Integral dispersion model: near-instantaneous release	R586
Integral dispersion model: steady continuous release	R587

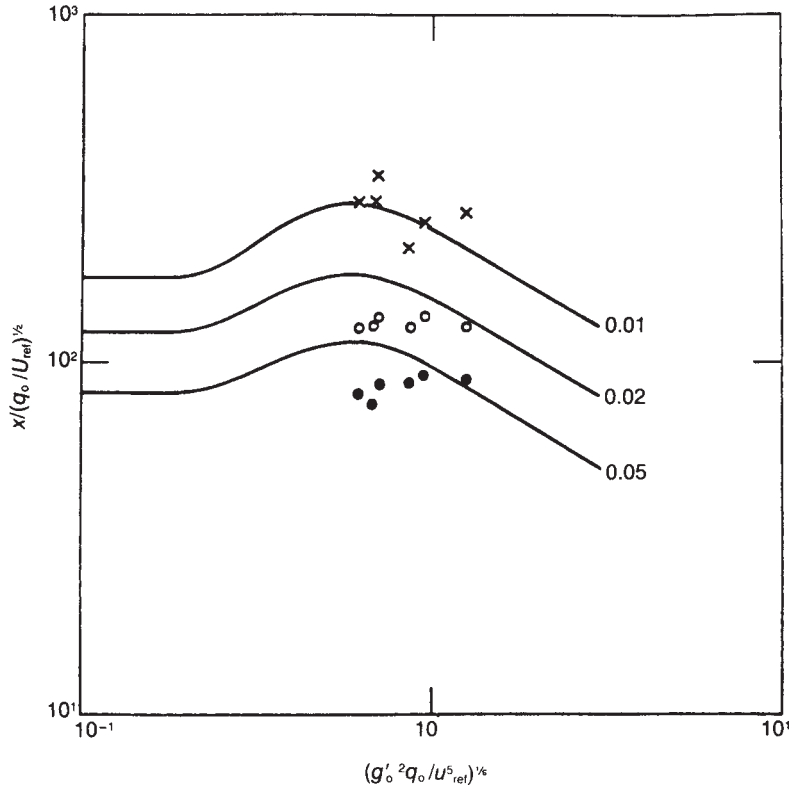


Figure 15.90 *Workbook method for dense gas dispersion—comparison of predictions of Workbook correlation with those of DEGADIS for Maplin Sands continuous propane spills (Britter and McQuaid, 1988; reproduced with permission)*

15.35.1 Source term model

The source term model is given in R584, which is in four parts: (1) modelling of two-phase jets; (2) modelling jets in ambient flow; (3) differential phase equilibrium model for clouds, plumes and jets and (4) dynamics of two-phase catastrophic releases. The third part is the same as R552.

15.35.2 Differential phase equilibrium model

The differential phase equilibrium model given in R552 is a simple two-phase model of the thermodynamics of the cloud. It provides a module which covers this aspect only and is intended to be used in combination with a set of fluid flow models which cover aspects such as the source term, air entrainment and deposition. The model can handle dry or moist air and contaminants which are immiscible with water or water soluble. The report includes a treatment of hydrogen fluoride in moist air.

15.35.3 Ambient atmospheric conditions model

The model for ambient atmospheric conditions described in R553 supplies the meteorological parameters required by the DRIFT model. The DRIFT model requires the following meteorological parameters: the roughness length z_o, the friction velocity u^* and the Monin–Obukhov length scale L_s (or rather the reciprocal $1/L_s$). The two latter quantities are obtained from the ambient atmospheric conditions model.

This model gives three schemes for determining $1/L_s$. The first is the Monin–Obukhov scheme itself and the other two schemes are named after Pasquill and Holtslag. In the Pasquill scheme use is made of the relationship given by Colder (1972) between z_o and $1/L_s$, which has been described in Section 15.12. The graph given in Figure 15.45 by Colder is fitted by the following equation:

$$1/L_s = (1/L_{ref})[\log_{10}(z_o/z_{ref})] \qquad [15.35.1]$$

where L_s is the length scale (m), z_o is the roughness length and L_{ref} (m) and z_{ref} (m) are the corresponding reference values. The two latter quantities are functions of the Pasquill stability class:

Pasquill stability category	L_{ref} (m)	z_{ref} (m)
A	33.162	1117
B	32.258	11.46
C	51.787	1.324
D	∞	–
E	−48.330	1.262
F	−31.325	19.36

The Holtslag scheme (Holtslag and van Ulden, 1983) involves the estimation of the sensible heat flux H, which is a function of the solar radiation and the albedo of the surface. The length scale L_s is obtained from Equation 15.12.46.

For al three schemes the friction velocity u^* is obtained from the wind speed at the height of interest using the similarity profile of Businger *et al.* (1971).

15.35.4 DRIFT: near-instantaneous release

The dense gas dispersion model itself is DRIFT (Dense Releases Involving Flammables or Toxics), an integrated model which is described in two reports: the near-instantaneous release version in R586 and the steady continuous release version in R587. The DRIFT models have similarities to the earlier SRD models DENZ and CRUNCH, but represent a significant advance on these. They incorporate both a more comprehensive thermodynamic module and improved models for the dispersion processes.

It is convenient to describe first the near-instantaneous model. The model uses the coordinate system (ξ, y, z) of Wheatley (1986 SRD R445), where y is the crosswind coordinate, z is the vertical coordinate and ξ is a coordinate described as the downwind coordinate relative to the skewed cloud axis. This allows for the case where the cloud is not a right cylinder but 'leans over'. The variable ξ is defined as

$$\xi = x' - \zeta(z - Z) \qquad [15.35.2]$$

with

$$x' = x - X \qquad [15.35.3]$$

where x (is a relative coordinate (m), X is the downwind coordinate of the cloud centre (m), Z is the vertical coordinate of the cloud centroid (m), ζ is a measure of the skewness of the cloud and ξ is a downwind coordinate relative to the skewed cloud axis (m).

A characteristic feature of the model is the way in which the air entrainment is modelled. Use is made of a general profile which comprehends both the top-hat and Gaussian approaches. This means that it is possible to dispense with arbitrary definitions of the cloud boundary, such as a concentration which is one-tenth that of the centre line concentration and that there is seamless transfer between the dense gas and passive gas dispersion regimes.

The concentration is expressed as

$$C = C_m F_h(\xi, y) F_v(z) \qquad [15.35.4]$$

with

$$F_h(\xi, y) = \exp\{-[(\xi/a_1)^2 + (y/a_z)^2]^{w/2}\} \qquad [15.35.5]$$

$$F_v(z) = \exp[-(z/a_3)^s] \qquad [15.35.6]$$

where C is the concentration, C_m is the ground level centre concentration and a_1, a_2, a_3, s and w are parameters.

The DRIFT model contains a model of the atmosphere with profiles of the wind speed and the diffusion coefficient and relationships for the moisture content. Essentially, the model may be regarded as a framework which takes care of the basic conservation relations and into which can be slotted models for the cloud dynamics and cloud thermodynamics. The former includes models for lateral spreading, air entrainment and vertical diffusion, downwind travel, and so on.

For the cloud thermodynamics there is a basic homogeneous equilibrium model. Models are also provided covering a number of additional options such as moist air, contaminant immiscible with or miscible in water and for ammonia and hydrogen fluoride. It will be apparent from this description that the model has the ability to accommodate new models both for cloud dynamics and cloud thermodynamics as these may be developed.

15.35.5 DRIFT: steady continuous release

The second DRIFT model, for a steady continuous release, which is described in R587, is essentially similar, but utilizes variables representing mass flux rather than mass, and so on. Apart from this the two versions, and the reports R586 and R587, are very similar.

15.35.6 Validation and application

Accounts of the application and validation of DRIFT do not as yet seem to have appeared.

15.36 Dispersion of Dense Gas: Some Other Models and Reviews

Several other models, or sets of models, and reviews of models merit brief mention. The field trials referred to in this account are described in Sections 15.37 and 15.38.

15.36.1 Eidsvik model

Another early and influential box model was that by Eidsvik (1979, 1980). The model utilizes the basic box model Equations 15.24.24 and 15.24.25. The vertical entrainment velocity is taken to be a function of a characteristic vertical turbulent velocity and the Richardson number.

15.36.2 Fay and Ranck model

Another box model frequently mentioned is that by Fay and Ranck (1983). This again uses the same two basic box model equations. The vertical entrainment velocity is taken as the product of the friction velocity and a function of the Richardson number.

15.36.3 TNO models

Several models for dense gas dispersion have been developed at TNO. One of these is the model described by van Buijtenen (1980). This models the dispersion as an initial phase of slumping without entrainment of air followed by a phase in which gas is 'picked off' into the air from the top of the cloud. Its subsequent dispersion is modelled as passive dispersion from a number of sources on the top of the cloud. A further account of TNO dense gas dispersion models is given by Verhagen and Buytenen (1986).

15.36.4 TRANSLOC

One of the early if-theory models for dense gas dispersion, SIGMET, has already been described. Another early if-theory model was TRANSLOC, produced at the Battelle Institute at Frankfurt, and described by Schnatz and Flothman (1980). Further information on TRANSLOC is given in the comparative review by Blackmore, Herman and Woodward (1982).

15.36.5 VKI models

The von Karman Institute (VKI) in Belgium has produced a number of models for dense gas dispersion. Early work was done by Foussat (1981). Van Dienst *et al.* (1986) have described subsequent work. Further development includes the BITC model referred to below.

15.36.6 BITC model

The Bureau International Technique du Chlore (BITC) and the VKI have developed a model for dense gas dispersion, with particular reference to chlorine. An account of the model is given by Vergison, van Dienst and Easier (1989). The BITC model is a three-dimensional one.

15.36.7 ZEPHYR

A further if-theory model is ZEPHYR, developed by Energy Resources Co. (ERCO) for Exxon Research and Engineering, as described by McBride (1981). The comparative review by Blackmore, Herman and Woodward (1982) gives further information on ZEPHYR. It is one of the models considered in the comparison of model predictions and results of the field trials at Matagordo Bay and Porton Down described by J.L. Woodward *et al.* (1982).

15.36.8 MARIAH and MARIAH-II

MARIAH is a if-theory model developed for Exxon Research and Engineering by Daygon-Ra. Descriptions have been given by Taft (1981) and Taft, Ryne and Weston (1983). MARIAH is one of the models included in the comparative review by Blackmore, Herman and Woodward (1982). The comparison given by J.L. Woodward *et al.* (1982) of model predictions with the results of the field trials at Matagordo Bay and Porton Down includes those of MARIAH.

Havens, Schreuers and Spicer (1987) have described an updated version, MARIAH-II, and given a comparison of its predictions with results of the Thorney Island field trials.

15.36.9 DENS20

DENS20 is an advanced slab model which has been described by Meroney (1984a). He gives comparisons of the prediction of the model with results both from wind tunnel experiments and from the Porton Down and Burro trials.

15.36.10 MERCURE-GL

The MERCURE-GL (GL = gaz lourd) model has been developed at Electricite de France (EOF) and described by Riou (1987, 1988) and Riou and Saab (1986). MERCURE-GL, which is a three-dimensional model, is a development of the non-hydrostatic model MERCURE (Caneffl *et al.*, 1985). The accounts by Riou (1987, 1988) and Riou and Saab (1986) include comparisons of model predictions with results of the Thorney Island trials.

15.36.11 DISP2

DISP2 is a pair of advanced box models, one for an instantaneous release and one for a continuous release, developed at ICI. Accounts have been given by Fielding, Preston and Sinclair (1986) and Preston and Sinclair (1987). The latter describe the calibration of the model against the results of the Thorney Island trials.

15.36.12 CCPS correlation

The CCPS (1987/2) has obtained expressions for the dilution ratio V/V_o, including the following relation obtained from dimensional analysis:

$$\frac{V}{V_o} = f\left(\frac{x}{V_o^{1/3}}\right) \qquad [15.36.1]$$

where V is the volume of the cloud and subscript o denotes initial. They obtain a fit to the Thorney Island Phase I instantaneous releases with the correlation

$$\frac{V}{V_o} = \left(\frac{x}{V_o^{1/3}}\right)^{1.5} \qquad [15.36.2]$$

or

$$\frac{C}{C_o} = \left(\frac{x}{V_o^{1/3}}\right)^{-1.5} \qquad [15.36.3]$$

where C is the volumetric concentration.

15.36.13 Reviews of model characteristics

A number of reviews have been published in which the characteristics, as opposed to performance, of dense gas dispersion models are compared. These include reviews by Blackmore, Herman and Woodward (1982), Webber (1983 SRD R243), Wheatley and Webber (1984 CEC EUR 9592 EN) and the CCPS (1987/2).

Characteristics typically considered in such reviews include:

(1) Source elevation: ground level, elevated.
(2) Source dimensions: point, line, area, spreading pool.
(3) Source type: jet, plume, evaporating pool.
(4) Type of release: instantaneous, continuous, transient.
(5) Meteorological conditions: wind speed, including calm conditions; stability conditions; atmospheric humidity.
(6) Topography: flat, sloping terrain; open, obstructed terrain.
(7) Type of model: modified Gaussian, box, if-theory, other.
(8) Submodels of model: gravity-driven flow; momentum relations; cloud advection; air entrainment; heat transfer.
(9) Model outputs: cloud width, height; concentration profiles vs downwind distance, crosswind distance, time.

Reviews of the performance of dense gas dispersion models are considered in Section 15.41.

15.36.14 Webber generalized box model

Webber (1983 SRD R243) has given a generalized box model in the form of a set of dimensionless equations. The basic box model equations, corresponding to Equations 15.24.24 and 15.24.25, are given as

$$\frac{d\hat{r}}{dt} = \frac{1}{2\hat{r}} \qquad [15.36.4]$$

$$\frac{d\hat{v}}{dt} = \frac{2\hat{v}}{\hat{r}}\left(\frac{u_E t_o}{R_o}\right) + \hat{r}^2\left(\frac{u_T t_o}{H_o}\right) \quad [15.36.5]$$

with

$$\hat{r} = R/R_o \quad [15.36.6]$$

$$\hat{h} = H/H_o \quad [15.36.7]$$

$$\hat{v} = V/V_o \quad [15.36.8]$$

$$\hat{t} = t/t_a \quad [15.36.9]$$

$$t_o = \frac{R_o}{2u_f(0)} \quad [15.36.10]$$

where H is the height of the cloud, R is the radius of the cloud, t is the time, t_o is an initial time scale, u_t is the cloud front velocity, V is the volume of the cloud, $\hat{h}$, $\hat{r}$, $\hat{t}$ and $\hat{v}$ are normalized values of H, R, t and V, respectively and o denotes initial.

Integration of Equation 15.36.4 gives

$$\hat{r} = (1 + \hat{t})^{1/2} \quad [15.36.11]$$

Dividing Equation 15.36.5 by Equation 15.36.4 yields

$$\frac{d\hat{v}}{d\hat{r}} = 2\alpha\hat{v}\hat{u}_E + 2\beta\hat{r}^3\hat{u}_T \quad [15.36.12]$$

with

$$\alpha = \frac{u_E}{u_f(0)} \quad [15.36.13a]$$

$$= 2t_o\frac{u_E(0)}{R_o} \quad [15.36.13b]$$

$$\beta = \frac{1}{2}\frac{u_T(0)}{2u_f(0)}\frac{R_o}{H_o} \quad [15.36.14a]$$

$$= t_o\frac{u_T(0)}{H_o} \quad [15.36.14b]$$

$$\hat{u}_E = \frac{u_E}{u_E(0)} \quad [15.36.15]$$

$$\hat{u}_T = \frac{u_T}{u_T(0)} \quad [15.36.16]$$

where u_E is the edge entrainment velocity, u_T is the top entrainment velocity, $\hat{u}_E$ and $\hat{u}_T$ are normalized values of u_E and u_T, respectively, and α and β are parameters. Webber then classifies models according to the dependency of $\hat{u}_E$ and $\hat{u}_T$ on $\hat{v}$.

15.37 Dispersion of Dense Gas: Field Trials

As already indicated, there have been a large number of field trials conducted on the dispersion of dense gases. Accounts of such field trials have been given by Puttock, Blackmore and Colenbrander (1982), McQuaid (1984b), Koopman, Ermak and Chan (1989) and Havens (1992), and also by Blackmore, Herman and Woodward (1982) and Koopman *et al.* (1986).

A summary of these trials is given in Table 15.45 and details of some of the principal trials are given in Table 15.46. Details of the Porton Down, Maplin Sands and Thorney Island trials are given separately below.

15.37.1 Early work

A series of experiments on dispersion of chlorine over water were carried out at Lyme Bay in 1927 (McClure, 1927). A summary of these trials has been given by Wheatley *et al.* (1988 SRD R438).

In 1967, some chlorine dispersion experiments were conducted at the Chemical Defence Establishment (CDE), Porton Down, for ICI and BP. Other than this, there appears to have been little work on dense gas dispersion prior to 1970.

In 1966–67, Air Products carried out experiments in which liquid oxygen was spilled into a bund and a steady continuous release maintained using a water spray and the oxygen concentration in the gas plume was measured (Lapin and Foster, 1967).

Some 18 experiments in which about 0.2 m^3 of LNG was spilled into a 2 m^2 bund with three types of surface were carried out in 1968 for the American Gas Association (AGA) by Thomson Ramo Woolridge (TRW) (Seargeant and Robinett, 1968). The vaporization rate decreased over the course of the experiment. Measurements were taken of the methane concentration in the plume. The correlation presented gives the concentration decreasing proportionately with downwind distance.

15.37.2 Bureau of Mines trials

The Bureau of Mines (BM) performed a series of trials in 1970–72 involving the vaporization and dispersion of LNG following spillage on water, as reported by Burgess and coworkers (Burgess, Murphy and Zabetakis, 1970 BM RI 7448, S 4105; Burgess, Biordi and Murphy, 1972 BM PMSRS 4177). In the 1970 work, some 51 trials were conducted in which LNG was spilled instantaneously on water and the pool spread and vaporization were measured; measurements of gas dispersion were not taken. Four trials were also carried out with continuous spillage of LNG and in these the gas dispersion was measured. The Pasquill–Gifford relations were used to model the dispersion, the data being correlated by taking the ratio σ_y/σ_z as 5, indicating a relatively flat cloud. A further 13 continuous spillage experiments were done in 1972, of which six were usable. The ratio σ_y/σ_z was again high.

15.37.3 Esso/API trials

In 1971, a series of spillages of LNG onto the sea were carried out in Matagordo Bay, Texas, by Esso under the auspices of the AGA (Feldbauer *et al.*, 1972). The concentration of methane in the cloud was measured. There were 10 smaller experiments of about 0.9 m^3 and seven larger ones of between 2.5 and 10.2 m^3; the former were virtually instantaneous and the latter nearly so. Again high values of the ratio a_y/a_z in the Pasquill–Gifford model were obtained. Downwind concentrations obtained in these tests are shown in Figure A7.3.

15.37.4 Gaz de France trials

A series of 40 experiments involving the instantaneous spillage of LNG into a bund were performed in 1972 at Nantes by Gaz de France to investigate vaporization, dispersion and combustion (Humbert-Basset and Montet, 1972). Most of the tests involved the spillage of 3 m^3 into bunds with areas 9–200 m^3. The vaporization rate decreased with time. There was also a test with a continuous release of 10 m^3/h.

Table 15.45 *Some field trials on dense gas dispersion*

Location	*Date*	*Gas*	*Code name*	*Organization*[a]	*References*
A Refrigerated liquefied gas					
California	1966–67	Oxygen		Air Products	Lapin and Foster (1967)
	1968	LNG		AGA/TRW	Seargeant and Robinett (1968)
Various	1970–72	LNG		Bureau of Mines	Burgess, Murphy and Zabetakis (1970 BM RI 4105); Burgess, Biordi and Murphy(1972 BM RI 4177)
Matagordo	1971	LNG		Esso/API	Feldbauer et al. (1972)
Bay Nantes	1972	LNG		Gaz de France	Humbert-Basset and Montet (1972)
SS *Gadila*	1973	LNG	*Gadila*	Shell	Kneebone and Prew (1974)
Capistrano	1974	LNG		AGA/Battelle	Duffy, Gideon and Putnam (1974)
China Lake	1978	LNG	Avocet	US DOE/LLNL	Koopman, Bowman and Ermak (1980)
China Lake	1980	LNG	Burro	US DOE/LLNL	Koopman *et al.* (1982)
China Lake	1981	LNG	Coyote	US DOE/LLNL	
Maplin Sands	1980	Propane, LNG		Shell/NMI	Puttock, Blackmore and Colenbrander (1982)
NTS[b]	1987	LNG	Falcon	US DOT, GRI/LLNL	T.C. Brown *et al.* (1989)
B Pressurized liquefied gas					
NTS[c]	1983	Ammonia	Desert Tortoise	USCG,TFI/LLNL	Goldwire (1985, 1986)
NTS[c]	1983	Nitrogen tetroxide	Eagle	USAF/LLNL	McRae *et al.* (1984); McRae (1986)
NTS	1986	Hydrogen fluoride	Goldfish	Amoco/LLNL	Blewitt,Yohn, Koopman and Brown (1987)
NTS	1988	Hydrogen fluoride	Hawk	HMAP	Diener (1991)
C Ambient pressure and temperature gas					
Netherlands	1973	Refrigerant 12		DGL	van Ulden (1974); Buschmann (1975)
Porton Down	1976–78	Refrigerant 12		HSE/CDE	Picknett (1981)
Thorney Island	1980–83	Refrigerant 12		HSE/NMI	McQuaid (1985b, 1987)

[a] AGA, American Gas Association; API, American Petroleum Institute; CDE, Chemical Defence Establishment, Porton Down; DGL, Directorate General of Labour, the Netherlands; GRI, Gas Research Institute; HMAP, Hydrogen Fluoride Mitigation and Assessment Program; HSE, Health and Safety Executive; LLNL, Lawrence livermore National Laboratory; NMI, National Maritime Institute; TFI, The Fertilizer Institute; TRW, Thomson Ramo Woolridge; USAF, US Air Force; USCG, US Coast Guard; US DOE, US Department of Energy; US DOT, US Department of Transportation.
[b] Nevada Test Site.
[c] Area of NTS known as Frenchman Flat.

These trials showed several features of interest. Following the spillage the vaporization was initially very rapid but then fell to a lower, plateau value. The initial visible cloud was observed to separate from the steady plume. The flammable region was always contained within the visible cloud. In a number of tests the cloud tended to lift off the ground in its later stages.

15.37.5 SS Gadila trials

In 1973, larger scale trials of spillage of LNG onto the sea were performed by Shell from the SS Gadila, a LNG carrier (Kneebone and Prew, 1974; Te Riele, 1977). The vessel was being commissioned and the purpose of the trials was to confirm recommended procedures for jettisoning cargo in an emergency. The study of gas dispersion was not a main intent, but photographs were taken of the cloud. There were six tests lasting some 10 min and involving releases of up to 200 m^3. The liquid was ejected from a nozzle at the stern 18 m above the water. It is believed that vaporization was complete before the jet reached the water surface. In two of the tests the ship was stationary and in the others it was moving at up to 10.5 knots. The wind speed at 30 m was 1.9–5.1 m/s with a stable atmosphere. The relative humidity was 80–85%.

Two trials, tests 4 and 6, have proved of particular interest. In test 4, the flow was 7.6 m/min (53.5 kg/s) of LNG with a wind speed of 5.1 m/s. The visible cloud was 1370 m long, although with considerable inhomogeneity beyond 1000 m. The plume had a maximum width of 300 m at 750 m downwind. Its height was about 8–10 m. This test is shown in Figure 15.91.

In test 6, the flow was 19.3 m^3/h (136.5 kg/s) with a wind speed of 3.9 m/s. The plume was more coherent and had a visible length of 2250 m, which was still increasing at the end of the test. It had a maximum continuous width of 550 m and a height of about 10–12 m. The outline of the plume is

Table 15.46 *Experimental conditions in some field trials on dense gas dispersion*

Trial	*Date*	*Gas*	*Surface*	*Topography*	*Release*				
					Type	*No*	*Volume* (m^3)	*Volumetric flow* (min^3/min)	*Duration* (min)
BM[a]	1970	LNG	Water		I[c]	51	0.04–0.5		
BM	1970	LNG	Water		C	4	0.2–0.3		
Esso/API[a]	1971	LNG	Sea		I	17	0.09–10.2		0.1–0.6
BM	1972	LNG	Water		C	13	0.2–1.3		≤10
Gaz de France	1972	LNG	Soil	Bund	I	40	≤3		
			Soil	Bund	C	1	0.16		4.5
Gadila	1973	LNG	Sea		C	6	27–198	2.7–19.8	10
Avocet	1978	LNG	Water			4	*c*.4.5	4	
Burro[b]	1980	LNG	Water			8	40	12–18	2.2–3.5
Coyote	1981	LNG	Water			15	3–28	6–19	0.2–2.3
Desert Tortoise	1983	Ammonia	Land			4	15–60	7.3–10.3	
Eagle	1983	Nitrogen tetroxide	Land			6	1.3–4.2	0.5–1.8	
Goldfish	1986	Hydrogen fluoride	Land						
Falcon	1987	LNG	Land	Fences			20–66		
Porton Down	See Table 15.47								
Maplin Sands	See Table 15.49								
Thorney Island	See Table 15.52								

Sources: Puttock, Blackmore and Colenbrander (1982); Koopman, Ermak and Chan (1989); Havens (1992); *inter alia*. See also text.
[a] API, Amerucan Petroleum Institute; BM, Bureau of Mines.
[b] See also Table 15.48.
[c] C, continuous; I, instantaneous.

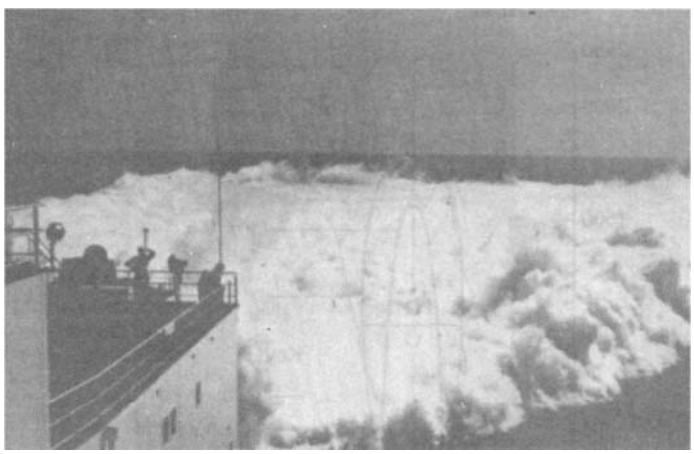
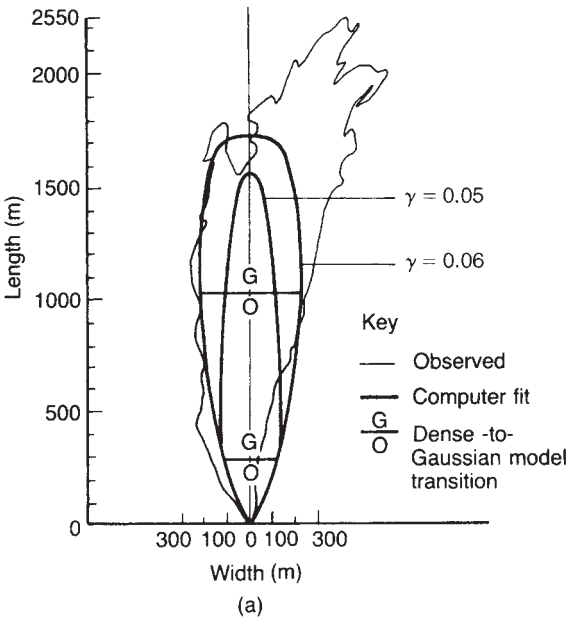


Figure 15.91 *SS Gadila trials on dense gas dispersion at sea – plume from continuous spill of LNG in trial 4 (Kneebone and Prew, 1974) (Courtesy of Gastech)*

shown in Figure 15.92, together with the predictions of the models of Cox and Carpenter, CRUNCH and Te Riele.

15.37.6 Dutch Freon 12 trial

The first trial involving the virtually instantaneous release of a dense gas at atmospheric pressure and temperature, as opposed to an evaporating liquefied gas, was conducted in 1973 by the Directorate General of Labour (DGL) of the Dutch Ministry of Social Affairs. This experiment has been described by van Ulden (1974) and Buschmann (1975), and also by Te Riele (1977). The release was 1000 kg of Freon 12 which has a relative density of 4.2. The wind speed at 10 m was 3 m/s and the stability was neutral.



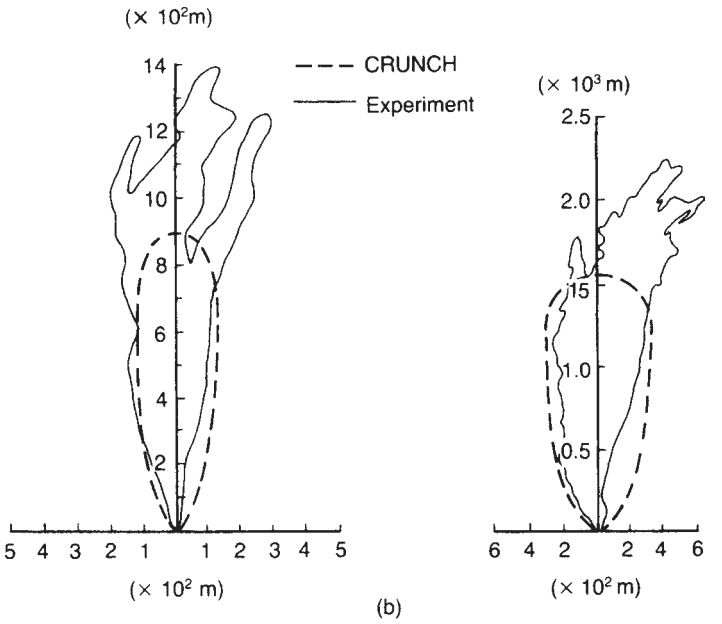


Figure 15.92 *Continued*

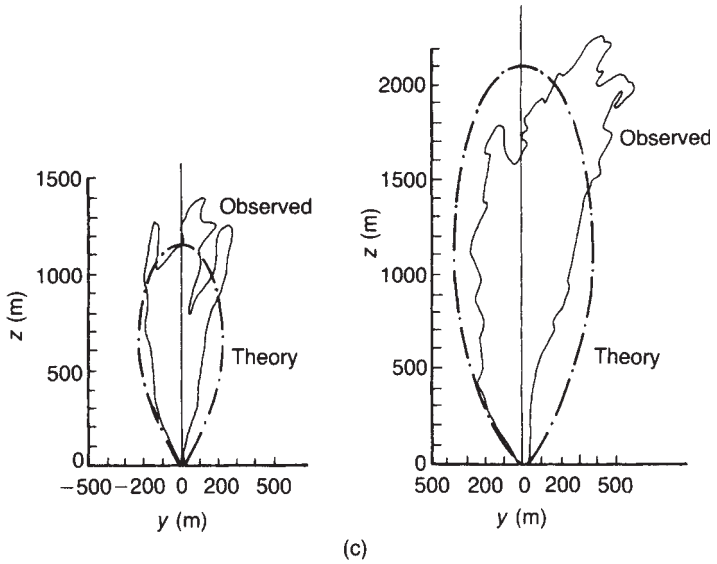


Figure 15.92 *SS Gadila trials on dense gas dispersion at sea—plume from continuous spill of LNG and comparison of observed cloud contour with model predictions of contour: (a) prediction of Cox and Carpenter model for trial 6 (R.A. Cox and Carpenter, 1980) Courtesy of Reidel Publishing Company); (b) prediction of CRUNCH for trials 4 and 6 (Jagger 1983 SRD R229) Courtesy of UKAEA Safety and Reliability Directorate); (c) prediction of te Riele model for trials 4 and 6 (te Riele, 1977) (Courtesy of DECHEMA)*

On release, there was rapid and intensive mixing with air and after some 5 s the estimated volume of the gas—air mixture was 2400 m^3. The shape of the cloud was roughly cylindrical with some elongation along the direction of the wind. Its height fell from an initial value of 5 m to a minimum of 0.2 m before increasing again, reaching 10 m at 1000 m downwind. Its radius increased rapidly with distance at first with the rate of increase then reducing.

The height and radius of the cloud are shown in Figure 15.76. The radius is much greater and the height much less than predicted for passive dispersion of a cloud of neutral buoyancy.

15.37.7 AGA/Battelle trials

In 1974, further experiments on the spillage of LNG into bunds were conducted near Capistrano, California, by Battelle Columbus Laboratories sponsored by the AGA (Duffy, Gideon and Puttnam, 1974). There were 42 trials, of which 14 involved ignition and 28 dispersion. Of the latter, 17 were with a 2 m bund, 9 with a 6 m bund and 2 with a 24 m bund. The test approximated an instantaneous spill, the release being made over 20—30 s. The results were marred by a tendency for the liquid to spill outside the bund. A correlation was derived for maximum downwind concentration in terms of bund area and wind velocity.

15.37.8 Porton Down trials

In 1976—78, a series of trials were conducted at the Chemical Defence Establishment for the HSE involving the virtually instantaneous release of a dense gas at atmospheric pressure and temperature. These have been described by Picknett (1981), and also by McQuaid (1979b).

Five sites were used: two flat with short grass, one flat with rough grass and two sloping with short grass. The source was a 40 m^3 collapsible tent. The gas released was a mixture of Refrigerant 12 and air, with relative densities varying from 1.03 to 4.2. Coloured smoke was also added to make the cloud more visible.

Selected experiments in the Porton trials are given in Table 15.47. The experiments were designed to yield pairs of trials which differed in one feature only and thus demonstrated the effect of that feature. Picknett gives tables of such trial pairs showing the effect of relative density, roughness length, ground slope and wind speed. Picknett describes the behaviour of the dense gas in these trials. The effect of density is seen in trial 8 which was conducted in still air. The cloud kept its original shape momentarily after the collapse of the tent and then gravity caused an accelerating flow downwards to the ground, followed by a billowing, outwards motion involving considerable mixing with air. The cloud then expanded as a horizontal disc but with a raised annular rim. This rim was highly turbulent and persisted for some seconds before the turbulence and the rim itself collapsed. These features are illustrated in Figure 15.93. There followed a phase in which the cloud height remained virtually constant, but the area of the cloud grew almost linearly, as shown in Figure 15.94.

The effect of wind, as in trial 36, was to cause the cloud to spread initially upwind somewhat and to assume downwind a horseshoe shape, as shown in Figure 15.95. At first the width exceeded the length, but this then reversed. Initially the cloud velocity was much less than the wind speed, but the cloud underwent a gradual acceleration.

The initial violent motion of the cloud caused rapid dilution. In trial 8 the gas concentration fell from an initial value of 30 to 3% in 6 s. In wind the rate of dilution was even higher.

The concentration of gas in the cloud initially was very inhomogeneous. In trial 8 in still air the concentration

Table 15.47 *Experimental conditions in some field trials on dense gas dispersion: Porton Down (after Picknett, 1981)*

Trial no.	*Initial density relative to air*	*Site*	*Roughness length* (mm)	*Wind speed* (m/s)	*Pasquill stability category*	*Comment*
6	1.7	Flat	2	2.8	C–D	
8	2.0	Flat	2	<0.5	F–G	Calm after release. Cloud remained in layer on ground for 20 min
10	2.5	Sloping	2	0.4	F	Calm allowed long period of gravity flow downhill
11	2.4	Sloping	2	2.0	F	
12	2.4	Flat	20	5.7	C	
15	2.0	Sloping	2	6.4	D	Dispersion in uphill wind
24	1.9	Flat	150	2.5	B	Dispersion over very long grass
29	4.2	Flat	2	4.3	C	Initially 100% dense vapour
36	1.5	Flat	10	4.7	C–D	
39	1.03	Flat	10	1.8	E–F	Initial density near neutral

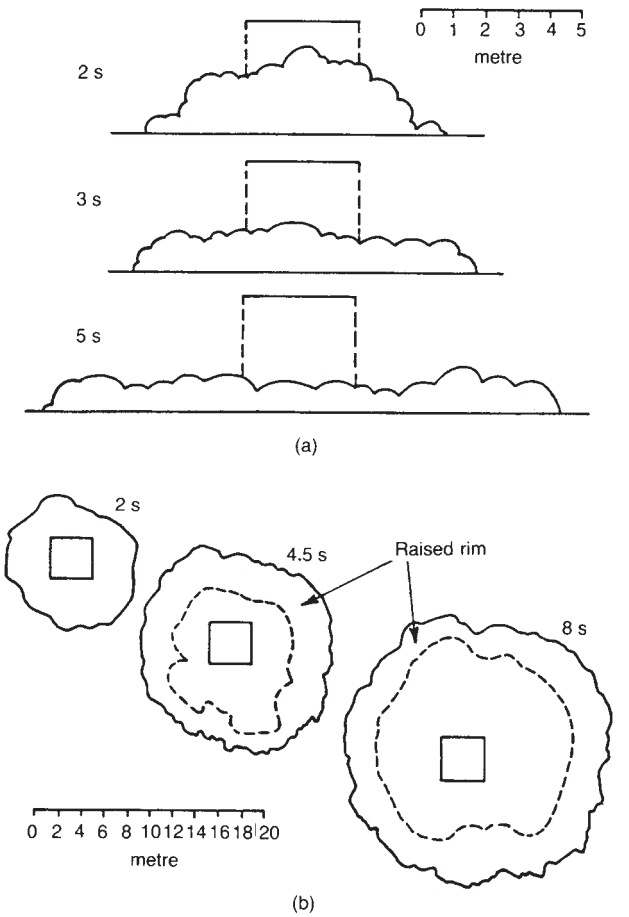


Figure 15.93 *Porton Down trials on dense gas dispersion with Refrigerant 12 – growth of cloud in trial 8–1 (Picknett, 1981): (a) elevation view; (b) plan view (Courtesy of Pergamon Press)*

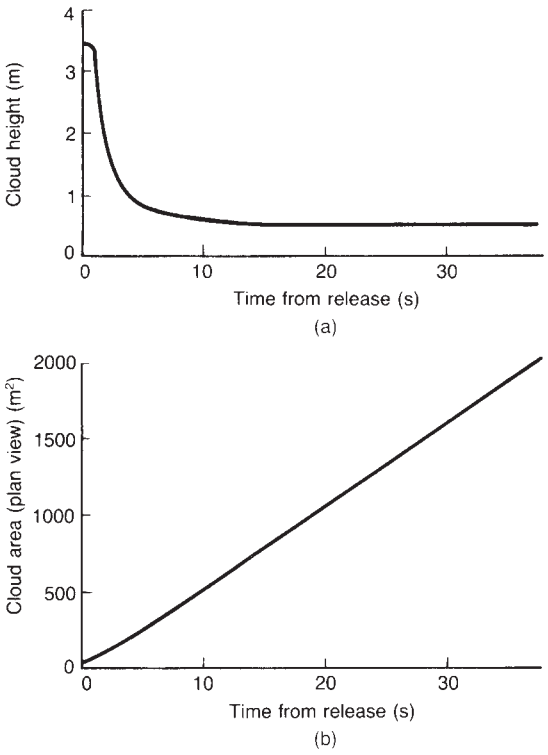


Figure 15.94 *Porton Down trials on dense gas dispersion with Refrigerant 12 – growth of cloud in trial 8–2 (Picknett, 1981) (Courtesy of Pergamon Press)*

measured near the ground fluctuated by a factor of 2 or more within 10 s. In trials 6 and 12 with wind the behaviour of the concentration varied with the measurement distance. In trial 6, at a point near the source the vertical concentration profile at 5 s was concave, but eventually a profile was established in which the concentration decreased monotonically with height, as shown in Figure 15.96(a). In trial 12, at a distance of 25 m the profile at 10 s was convex, but again in due course a monotonically decreasing profile was established, as shown in Figure 15.96(b).

The effect of slope was very large for a release in still air. In wind the effect was less marked. The main feature was that with wind blowing uphill and the cloud flowing downhill, the two opposing effects suppressed the formation of the raised rim and gave instead a tongue flowing along the ground and a reverse, uphill flow above the tongue. The cloud soon became dilute enough for the wind to carry it uphill.

15.37.9 China Lake trials: Avocet, Burro and Coyote series

The Naval Weapons Center (NWC) test facility at China Lake, California, has been the site of several series of dense gas dispersion trials. Accounts of the facility have been given by Ermak *et al.* (1983). Much of the work at this site has been sponsored by the Department of Energy (DoEn) and conducted by the Lawrence Livermore National Laboratory (LLNL).

The Avocet series was a set of four trials involving spillage onto water of some 4.5 m^3 of LNG over about 1 min. The main purpose of these trials, described by Koopman, Bowman and Ermak (1980), was the development of the test facility.

In 1980, the Burro series of trials was performed involving the continuous release onto water of up to 40 m^3 of LNG over periods up to 3.5 min. These tests are therefore classed as continuous releases. They have been described by Ermak, Chan *et al.* (1982) and Koopman *et al.* (1982). Selected trials are summarized in Table 15.48.

The experiments were well instrumented and obtained a fairly comprehensive set of measurements, including turbulence and concentration fluctuations in the plume.

Figure 15.97(a) shows the plume in Burro 8 after 30 s and Figure 15.97(b) the plume in Burro 6 after quasi-steady state had been reached. Analyses of the results of the Burro trials have been given by Koopman *et al.* (1982) and by Ermak, Chan *et al.* (1982). The latter have given comparisons of the results with predictions from the Germeles-Drake model and from SLAB and FEM3.

Further analyses have been reported by Koopman, Ermak and Chan (1989). Concentration contours in the Burro trial 8 are shown in Figure 15.98. Figure 15.98(a) gives the observed crosswind elevation view contours at a downwind distance of 140 m at 180 s. Figures 15.98(b) and (c) give the predictions of FEM3 for flat terrain and variable terrain, respectively. Figures 15.98(d) and (e) show the observed and predicted plan view contours.

The Burro tests were followed in 1981 by the Coyote series which were concerned primarily with rapid phase transition (KPT) and with ignition.

15.37.10 Maplin Sands trials

In 1980, a series of trials was carried out by Shell at Maplin Sands. Accounts of the work has been given by Puttock and coworkers (Puttock, Blackmore and Colenbrander, 1982; Puttock, Colenbrander and Blackmore, 1983, 1984; Colenbrander and Puttock, 1984).

Figure 15.99 shows the site used for the trials. The liquefied gases were released onto water from a pipeline terminating in a downwards-pointing pipe and measurements were taken by instruments located on pontoons placed in arcs around the release point.

Two series of trials were carried out, one with propane and one with LNG. The experiments were mainly continuous spills but, for both gases, some trials with instantaneous spills were conducted. A total of 34 trials were performed, of which 11 involved ignition. Table 15.49 gives details of some of the trials selected by the authors as providing results useful for dispersion work.

The propane trials with continuous spills, of which there were 11, have been described by Puttock, Colenbrander and Blackmore (1983). The two trials not shown in Table 15.49 are trial 42, an underwater release, and trial 50, an ignited release. Two experiments in particular are described. In trial 46 the wind speed was 8.1 m/s and in trial 54 3.8 m/s. Figure 15.100(a) and (b) show the corresponding comparisons between the outline of the observed plume and the contour predicted by HEGADAS.

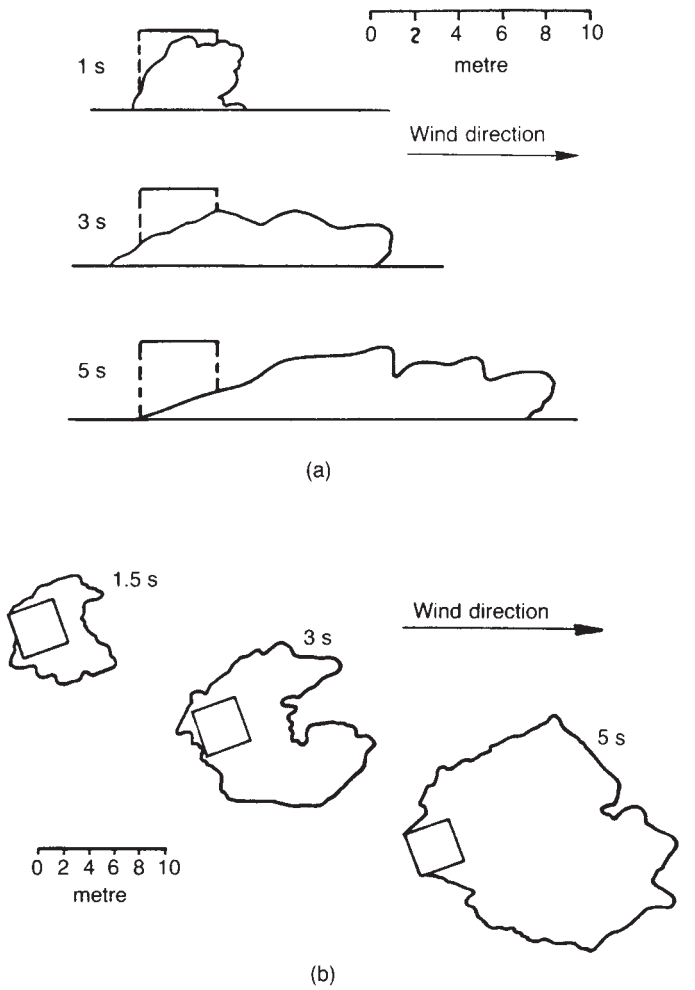


Figure 15.95 *Porton Down trials on dense gas dispersion with Refrigerant 12 – growth of cloud in trial 36 (Picknett, 1981): (a) elevation view; (b) plan view (Courtesy of Pergamon Press)*

An account of the three propane trials with instantaneous spillage has been given by Puttock, Blackmore and Colenbrander (1982). Trial 60 was performed with a very low wind speed of 1.2 m/s and gave an almost circular cloud. In trial 63 the wind speed was 3.5 m/s, and thus also fairly low. The cloud started off roughly circular and very shallow, then moved off with the wind, with a raised head around the edge, and growing in height as it moved.

The LNG trials have been described by Puttock, Blackmore and Colenbrander (1982), Puttock, Colenbrander and Blackmore (1984) and Puttock (1987c). There were 13 continuous spills, of which the authors describe three in particular: trials 15, 29 and 56. Figure 15.101 shows a comparison for the latter between the outline of the observed plume and the contour predicted by HEGADAS.

Of the instantaneous LNG spills, trials 22 and 23 were considered of particular value. The wind speed in these trials was 5 m/s and thus higher than in the propane instantaneous spills. Compared with the latter the cloud produced was very elongated and more like that from a continuous spill. Figure 15.102 shows the development of the cloud in trial 22 together with a comparison of the contour predicted by HEGADAS.

15.37.11 Thorney Island trials

The Thorney Island trials were a progression from the Porton Down trials and again involved release of a dense gas at atmospheric pressure and temperature. Most of the releases were instantaneous. The second series involved obstructions and a building. A third series was done with continuous releases. The Thorney Island trials are described in Section 15.38.

15.37.12 NTS trials: Desert Tortoise and Eagle series

The experimental work described so far has been concerned with dispersion of dense gases in general and of

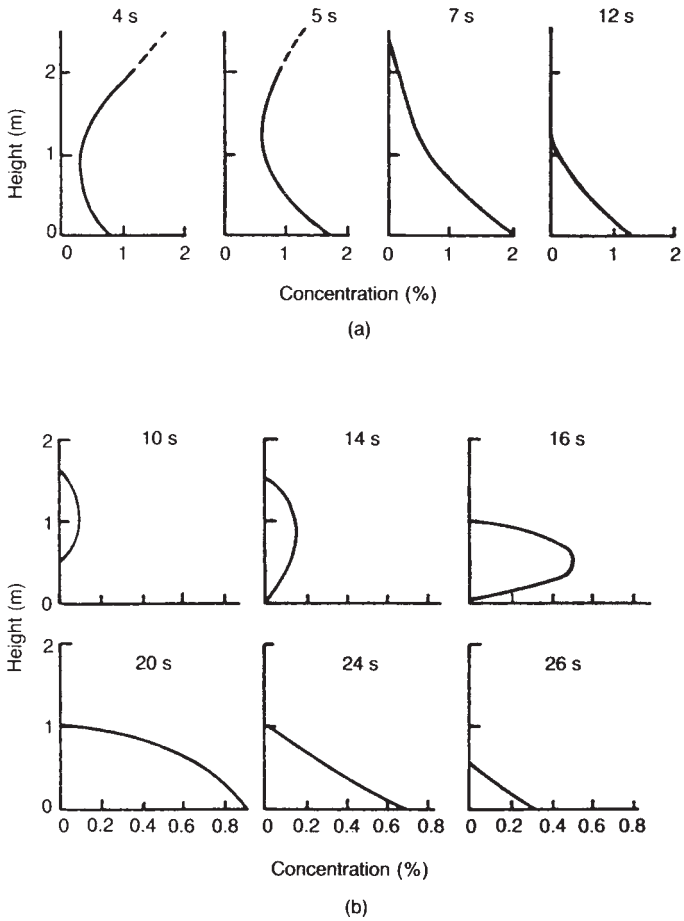


Figure 15.96 *Porton Down trials on dense gas dispersion with Refrigerant 12 – vertical concentration profiles in trials 6 and 12 (Picknett, 1981); (a) at point close to source in trial 6; (b) at 25 m downwind in trial 12 (Courtesy of Pergamon Press)*

Table 15.48 *Experimental conditions in some field trials on dense gas dispersion: China Lake, Burro series*

Trial no.	*Volume released* (m^3)	*Volumetric flow* (m^3/min)	*Duration*[a] (min)	*Wind speed* (m/s)	*Stability category*	*Bulk Richardson*[b] *no.*	*Travel*	
							Distance (m)	*Concentration* (%)
2	34.3	11.9	2.9	5.4	Unstable	−0.178		
3	34.0	12.2	2.8	5.4	C	−0.221	255	LFL
4	35.3	12.1	2.9	9.0	Slightly unstable	−0.054		
5	35.8	11.3	3.2	7.4	Slightly unstable	−0.079		
6	27.5	12.5	2.1	9.1	Slightly unstable	−0.044		
7	39.4	13.6	2.9	8.4	D	−0.018	200	LFL
8	28.4	16.0	1.8	1.8	E	+0.121	420	LFL
9	24.2	18.4	1.3	5.7	D	−0.014	325	LFL

Sources: Ermak, Chan *et al.* (1982); Koopman *et al.* (1982); Havens (1992).
[a] Calculated from volume and volumetric flow.
[b] Richardson no. at 2 m height.

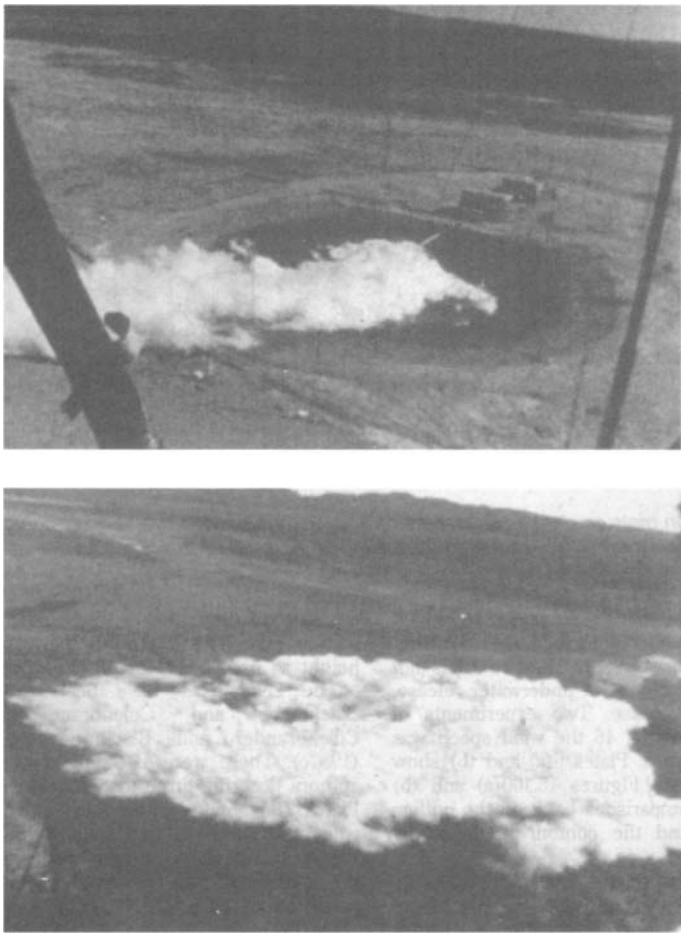


Figure 15.97 *Nevada Test Site trials, Burro series, on dense gas dispersion with LNG (Ermak, Chan et al., 1982): (a) plume in Burro trial 8 after 30 s; (b) plume in Burro trial 6 at quasi – steady state (Courtesy of Elsevier Science Publishers)*

hydrocarbons in particular. More recently, there has been growing interest in other hazardous materials, especially toxic liquefied gases.

Much of this work has been done at the Nevada Test Site (NTS). This site includes the area of Frenchman Flat which is the location of the Liquefied Gaseous Fuels Spill Test Facility (LGFSTF). This facility, and some of the test programmes conducted there, have been described by Leone (1990), and also by Koopman, Ermak and Chan (1989).

In 1983, the Desert Tortoise series of trials involving liquid ammonia were carried out at the NTS by the LLNL for the US Coast Guard and The Fertilizer Institute (TFI). These have been described by Goldwire (1986) and Koopman *et al.* (1986), and also by Koopman, Ermak and Chan (1989). A summary of the Desert Tortoise trials is given in Table 15.50. There were four trials, all approximating continuous spills. The accounts concentrate mainly on the largest release, trial 4. In this experiment 60 m^3 of liquid ammonia at 171 psia and 24°C was released at a rate of 9.5 m^3/min into air at 30.8°C and relative humidity 21% with a wind speed of 4.5 m/s and stability category E. The release was from a horizontal pipe 0.8 m above the ground surface and pointing downwind. The adiabatic flash was estimated to give 17% vapour and 83% spray.

Most of the ammonia remained airborne as vapour and spray but, in contrast to the smaller releases, a large pool of liquid formed and persisted for about 8 min. The pool temperature was measured as −52°C at 3 m and −63°C at 9 m downwind. Mass balances on the plume showed that the proportion of material released which passed the 100 m and 800 m arcs was about 70%; 30% was unaccounted for. At the 100 m point, small puffs of boiled-off vapour were seen on and off at least 1100 s after the start.

The jet persisted beyond the 100 m arc. The movement of the plume was dominated by the jet and dense gas features. At the 100 m arc the plume was about 70 m wide and

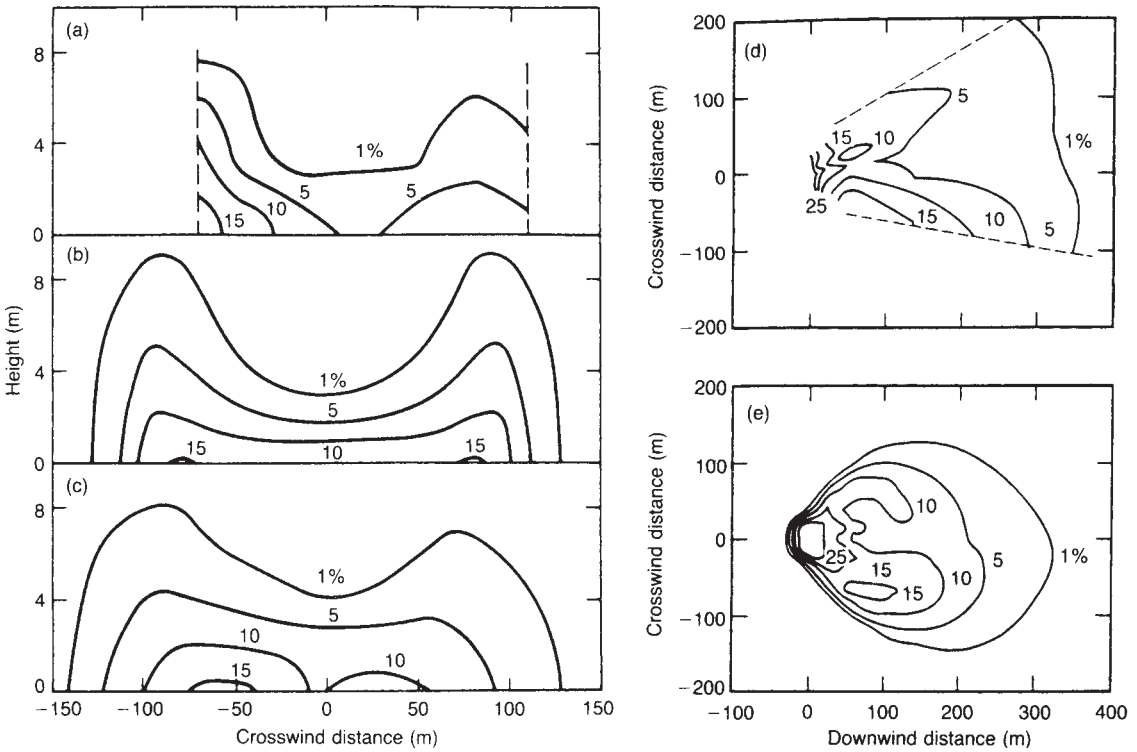


Figure 15.98 *Nevada Test Site trials, Burro series, on dense gas dispersion with LNG (Koopman, Ermak and Chan, 1989) – trial 8: (a) observed crosswind elevation view of concentration contours 140 m downwind after 180 s; (b) predictions of FEM3 of crosswind elevation view of concentration contours 140 m downwind after 180 s with flat terrain; (c) predictions of FEM3 of crosswind elevation view of concentration contours 140 m downwind after 180 s with variable terrain; (d) observed plan view of concentration contours at 1 m above ground level at 180 s; (e) predictions of FEM3 of plan view of concentration contours at 1 m above ground level at 180 s with variable terrain (Courtesy of Elsevier Science Publishers)*

generally less than 6 m high. At the 800 m arc the width had increased to about 400 m, but the height was still about 6 m. The ammonia fog persisted beyond 400 m.

The values given for the maximum gas concentrations vary slightly. Koopman *et al.* state that this concentration was 10% at 100 m, 1.6% at 800 m and 0.53% at 2800 m. The crosswind elevation of the concentration contours at the 800 m arc given by Goldwire is shown in Figure 15.103.

The boiling point of ammonia is −33.4°C. The temperature of the plume rose to −7°C at 100 m and to 23°C at 800 m, compared with the ambient air temperature of 32.8°C. The surface heat flux was determined as 2.2 kW/m^2.

The Eagle trial series, performed by LLNL for the US Air Force, involved spillages of nitrogen tetroxide and followed straight on from the Desert Tortoise series. It has been described by McRae and coworkers (McRae *et al.*, 1984; McRae, 1986).

15.37.13 NTS trials: Goldfish series

In 1986, the Goldfish series of trials involving liquid hydrogen fluoride was carried out at the Frenchman Flat area of the NTS for Amoco by LLNL and Amoco. An account of these has been given by Blewitt *et al.* (1987a), and also by Koopman, Ermak and Chan (1989).

A summary of the Goldfish trials is given in Table 15.51. There were six trials, all approximating continuous spills, three concerned with dispersion and three with water spray barriers. Of the former group, the first was an exploratory test. The main dispersion trials, therefore, were trials 2 and 3.

The liquid hydrogen fluoride was released as a horizontal jet. The adiabatic flash was estimated to give some 20% vapour and 80% spray, although the thermodynamics of hydrogen fluoride are complex. In none of these tests was any liquid collected in the spill pond. Special facilities were provided to give a capability to increase the humidity of the ambient air. These were located upwind and consisted of a large pond and of an array of nozzles half operating on steam and half on water spray.

Trial 2 was performed at low relative humidity, the dewpoint temperature being 1.1°C. In this experiment liquid hydrogen fluoride at 115 psig and 38°C was released at a rate of 175 US gal/min (0.011 m^3/s) into the ambient air at 36°C with a wind speed of 4.2 m/s and stability category D. The crosswind elevation of the concentration contours at 300 m at 54 s and 121 s are shown in Figure 15.104(a) and (b).

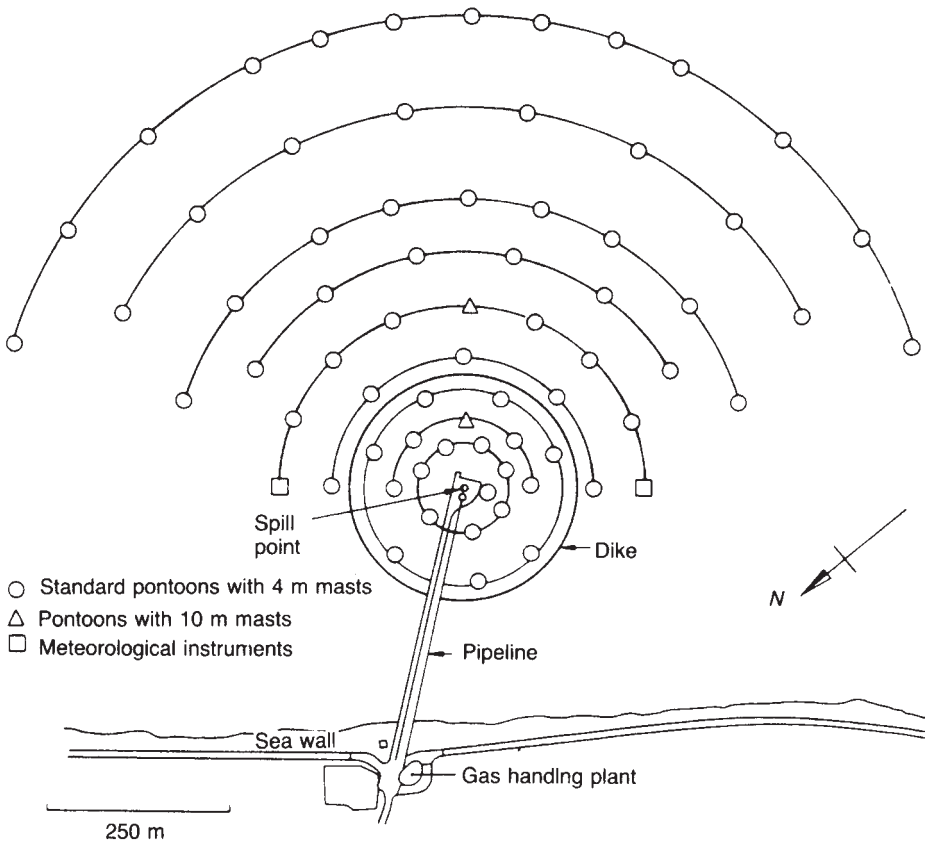


Figure 15.99 *Maplin Sands trials on dense gas dispersion – site layout (Puttock, Blackmore and Colenbrander, 1982) (Courtesy of Elsevier Science Publishers)*

Trial 3 differed in that the relative humidity was raised artificially to give a dewpoint temperature of 6.6°C. In this experiment the wind speed was 5.4 m/s and the air ambient was at 26.5°C, the other conditions being similar to those mentioned above for trial 2. The plume was visible at 400–500 m. The crosswind elevation concentration contours at 300 m at 113 and 225 s and at 1000 m at 292 and 358 s are shown in Figures 15.104(c)–(f).

The boiling point of hydrogen fluoride is 20°C. In trial 2 the temperature of the plume at 20 m downwind dropped within seconds to about −30°C below ambient temperature, then fell more gradually to about −45°C below over 350 s, whilst in trial 3 it fell sharply to about −48°C below and remained at about −45°C below again for about 350 s. In both trials the plume temperature then rose rapidly, stayed at about −10°C below until about 600 s and then rose to eliminate the temperature differential by about 700 s.

Trials 4–6 on water spray barriers are described in Section 15.53.

15.37.14 NTS trials: Hawk series

In 1988 another series of trials, the Hawk series, was carried out on hydrogen fluoride at the Nevada Test Site for the Industry Co-operative Hydrogen Fluoride Mitigation and Assessment Program (ICHMAP, or HMAP). These trials investigated not only dense gas dispersion but also the use of vapour barriers and water spray barriers. An account has been given by Diener (1991). The Goldfish trials caused some concern due to the ineffectiveness of a dike for containing a pressurized release and to the hazard ranges obtained.

The work included the development of a complete model system for emission, vaporization and dispersion of hydrogen fluoride. The HEGADAS model was selected for development as the basis of the system, HFSYSTEM, described in Section 15.31. The trials on vapour barriers and water spray barriers are described in Section 15.53.

15.38 Dispersion of Dense Gas: Thorney Island Trials

In 1982–84, the HSE organized a series of heavy gas dispersion trials (HGDTs) at Thorney Island. The trials were a major undertaking involving over a number of years the collection, processing and reconciliation of data from the trials and the comparison of the results with those from theoretical models and from physical modelling. They are described in Heavy Gas Dispersion Trials at Thorney Island (two volumes) by McQuaid (1985a, 1987).

The main trials were with instantaneous releases and were conducted in two series, Phases I and II. Phase I

Table 15.49 *Experimental conditions in some field trials on dense gas dispersion: Maplin Sands (after Puttock, Blackmore and Colenbrander, 1982) (Courtesy of Elsevier Science Publishers)*

Trial		*Volume released* (m^3)	*Volumetric flow* (m^3/min)	*Duration* (min)	*Wind speed* (m/s)	*Travel*		*Comments*
No.	*Type*					*Distance* (m)	*Concentration* (%)	
A	**Propane**[a]							
43	C		2.3	5.8	5.8			
45	C		4.6	6.8	2.2			Unusual atmospheric conditions
46	C		2.8	7.8	7.9	245	LFL	
47	C		3.9	4.5	5.2	340	LFL	
50	C		4.3	4.0	8.3			Ignited
51	C		5.6	3.7	7.8			Ignited
52	C		5.3	3.3	7			
54	C		2.3	5.0	3.6	400	LFL	
55	C		5.2	4.0	5.7			
60	I	27			1.2			
63	I	17			3.4			
B	**LNG**[b]							
12	C		1.0	10.7	2			Low and non-constant spill rate and wind
15	C		2.7	6.7	3.9	150	LFL	
29	C		3.5	5.4	5			
34	C		2.9	3.5	8.5			
35	C		3.8	4.5	10.0			
37	C		3.9	5.0	4.9			Highly buoyant cloud
39	C		4.5	2.3	4.5	130	LFL	Ignited
56	C		2.5	1.5	4.8	110	LFL	
22	I	10			5			Ignited
23	I	7			5			Momentary ignition

[a] Pasquill stability category quoted as D for trials 43, 46, 47, 50, 54; bulk Richardson number for all trials = 600.
[b] Pasquill stability category quoted as D for trials 29, 34, 35, 39, 56; bulk Richardson number for all trials = 40.

involved unobstructed releases over a flat surface, Phase II releases over a flat surface with obstructions. A short series of trials with continuous releases was also performed. In addition, the Thorney Island site was subsequently used by the US Coast Guard and Department of Transportation to conduct their own series of experiments, termed the Phase III series. A summary of the Thorney Island trials is given in Table 15.52.

15.38.1 Phase I trials

An account of the Phase I trials has been given by McQuaid (1984b,c, 1985b,c). The organization of the trials has been described by A.G. Johnston (1985) and McQuaid (1985b). Other accounts cover the following aspects: systems development and operations procedures (D.R. Johnson, 1985); the site geography and meteorology (M.E. Davies and Singh, 1985b); the gas sensor system (Leek and Lowe, 1985); the meteorological data (Puttock, 1987a); the determination of the cloud area and path from visual records (Brighton, Prince and Webber, 1985; Prince *et al.*, 1985 SRD R318); the determination of the cloud path from concentration measurements (Brighton, 1985 SRD R319); the computer processing of the visual records (Riethmuller, 1985); the cloud advection velocities (Wheatley and Prince, 1987); the effect of averaging time on the statistical properties of the sensor records (Nussey, Davies and Mercer, 1985); the mean concentration and variance (Cam, 1987); the area-averaged concentration, height scales and mass balances (Brighton, 1985a); the computer processing of the data for comparison with models (Pfennning and Cornwell, 1985); the presentation and availability of the data (Roebuck, 1985); and users' views of the data (N.C. Harris, 1985; Brighton, 1987). Critiques which discuss the contribution to dense gas dispersion modelling have been given by Hartwig (1985) and Puttock and Colenbrander (1985).

The aim of the Phase I trials was to obtain data which might be used to increase understanding of the mechanisms of dense gas dispersion and to validate models. The trials were designed with the needs of modellers very much in mind. Consideration was given to the requirements for the meteorological parameters and the parameters used in box and if-theory models. In particular, attention was given to the variables required to define stability and to characterize both Richardson number and Monin–Obukhov similarity, and thus in particular to wind speed, roughness length, friction velocity and sensible heat flux. These aspects are discussed by McQuaid (1985b).

The site was an airfield flat to within about 1 in 100. The layout of the site is shown in Figure 15.105. Some 250 instruments were deployed. The gas sensors were fixed to masts, the lowest level being located 0.4 m above ground and the highest levels being 4, 10 and 14.5 m in the near, mid and far fields, respectively. Photographic records were also

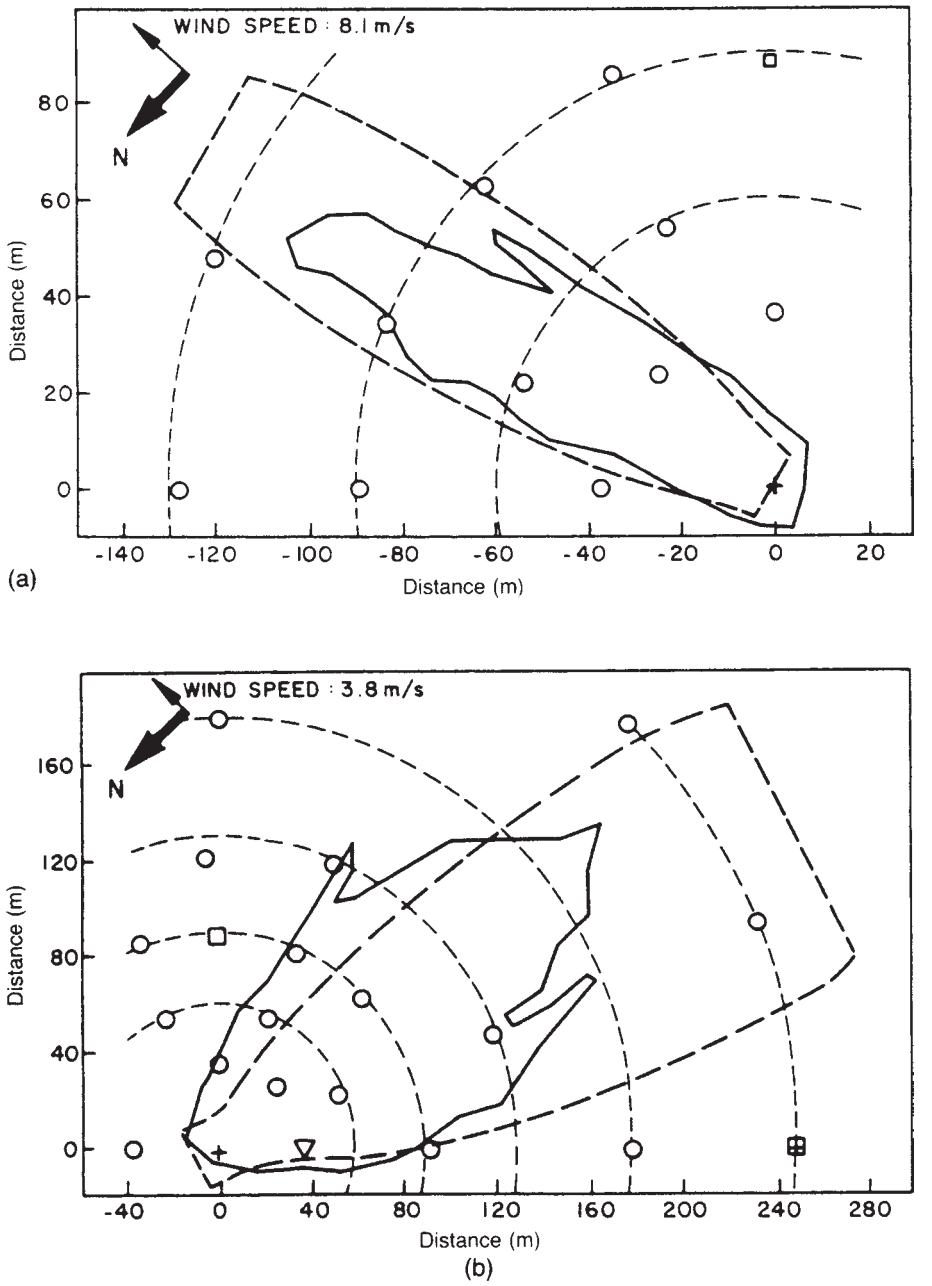


Figure 15.100 *Maplin Sands trials on dense gas dispersion – continuous spills of propane: comparison of observed plumes with limits of visible plumes predicted by HEGADAS (Puttock, Colenbrander and Blackmore, 1983). (a) Trial 46 (wind speed = 8.1 m/s); (b) trial 54 (wind speed 3.8 m/s) (Courtesy of Reidel Publishing Company)*

taken, the visibility of the cloud being enhanced by the use of cartridges of orange smoke.

The Phase I trials involved an instantaneous release of 2000 m^3 of a gas–nitrogen mixture. The gas used was Freon 12, the proportion being varied to give mixtures of different relative density up to 4.2. The container was a 12-sided container 14 m across by 13m high. The container was held up by rigging until the operation of a release mechanism which allowed it to fall to the ground.

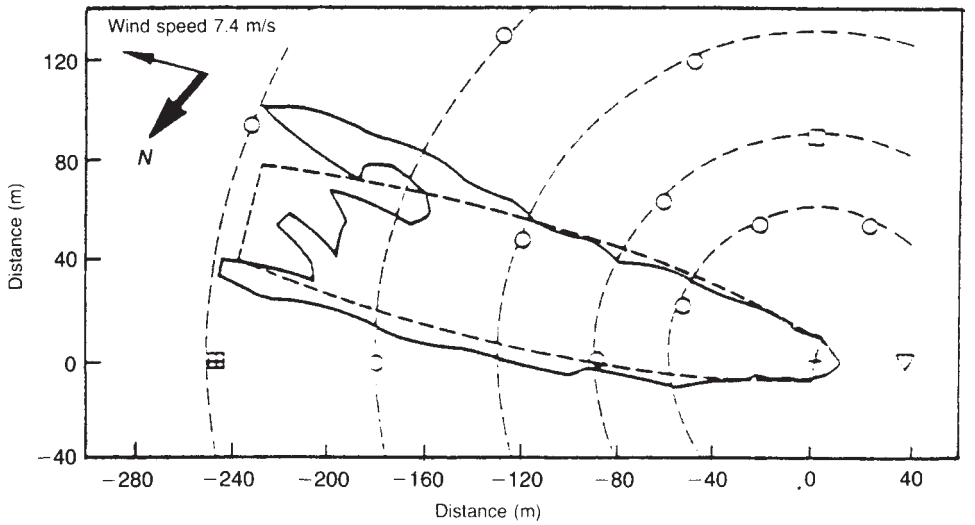


Figure 15.101 *Maplin Sands trials on dense gas dispersion – plume from continuous spill of LNG: Trial 29: comparison of observed plume with limits of visible plume predicted by HEGADAS (Puttock, Colenbrander and Blackmore, 1984) (Courtesy of the American Institute of Chemical Engineers)*

On release, the gas cloud slumped rapidly and spread out radially. There was some movement upwind until this was stopped by the wind. The cloud had a raised front and assumed the characteristic doughnut shape. It then travelled in this form for several hundred metres. Eventually a low-lying cloud formed which covered a large part of the site.

A total of 15 trials was performed, as shown in Table 15.52. In each trial measurements were taken of the concentration vs time profiles at the gas sensors within the cloud. These raw data have subsequently been processed to yield a variety of results. Plate 8 shows the development of the gas cloud in one of these trials. Figure 15.106 shows the peak concentration on the path of the cloud centroid in the Phase I trials.

15.38.2 Phase II trials

The Phase II trials have been described by M.E. Davies and Singh (1985a). The following aspects of the Phase II have been covered in other accounts: the overall properties of the clouds (Brighton and Prince, 1987); and a user's view of the data (Brighton, 1987).

The Phase II series was concerned with dense gas dispersion at obstructions. Three types of obstruction were used:

(1) solid fence;
(2) permeable screen;
(3) building cube.

Details of the Phase II trials are given in Table 15.52.

15.38.3 Phase II trials: solid fence

The solid fence consisted of tarpaulin sheets hung over scaffolding. The fence was 5 m high and was located on a 180° arc at 50 m from the source. Four trials were conducted with this configuration: trials 20–22 and 25.

In trial 25 there was complete blocking of the cloud by the fence, in trial 21 partial blocking and in trial 20 virtually no blocking. There was also appreciable blocking in trial 22 in which the cloud density was much higher.

The results of these trials were compared with Phase I trials carried out under similar conditions but without a fence. The fences affected the concentrations in the far field. Comparison of trial 20 with trial 19 exhibited a marked reduction in peak centreline concentration vs distance, with a several-fold reduction factor out to at least 500 m.

15.38.4 Phase II trials: permeable screens

The permeable screens consisted of military camouflage nets draped over scaffolding. The screens were 10 m high and were located on a 180° arc. Two trials were performed with this configuration: trial 23 with two rows of screens and trial 24 with four rows. The first row was located 50 m from the source, with the subsequent rows at intervals of 3.3 m.

The screens delayed the passage of the gas, and increased the height of the cloud, thus distributing the gas vertically, but they had little effect on peak ground level concentrations at the screens.

The screens affected the concentrations in the far field. Comparison of trial 23 with trial 19 showed a marked reduction in peak centreline concentration vs distance, with a several-fold reduction factor out to at least 500 m.

15.38.5 Phase II trials: building cube

The building cube was a single, isolated 9 m cube constructed of plastic sheets on a wooden frame. Four trials were performed with this configuration: trials 26–28 with the cube 50 m downwind of the source and trial 29 with it 27 m upwind.

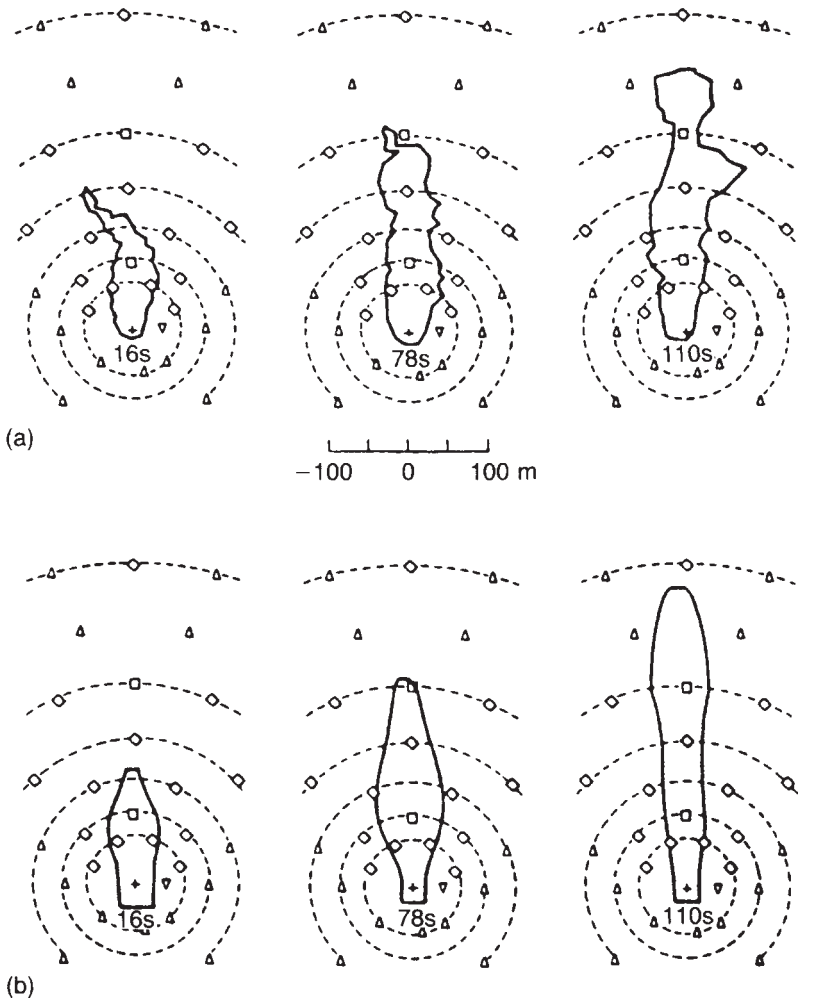


Figure 15.102 *Maplin Sands trials on dense gas dispersion – plume from instantaneous spill of LNG – trial 22 (Puttock, 1987c) (a) observed plume; (b) predictions by HEGADAS of 3% concentration contour, corresponding to visible limit (Courtesy of the American Institute of Chemical Engineers)*

Table 15.50 *Experimental conditions in some field trials on dense gas dispersion: Nevada Test Site, Desert Tortoise series (Goldwire, 1986; Koopman et al., 7986; Havens, 1992)*

Trial no.	*Volume released* (m^3)	*Volumetric flow* (m^3/min)	*Duration* (min)	*Wind speed* (m/s)	*Stability category*	*Travel*	
						Distance (m)	*Concentration* (%)
1	14.9	7.0	2.1	7.4	D		
2	43.8	10.3	4.3	5.7	D	100	9
						800	1.4
3	32.4	11.7	2.8	7.4	D	100	9
						800	1.6
						2400	0.22
4	60.3	9.5	6.4	4.5	E	100	10
						800	1.6
						2400	0.53

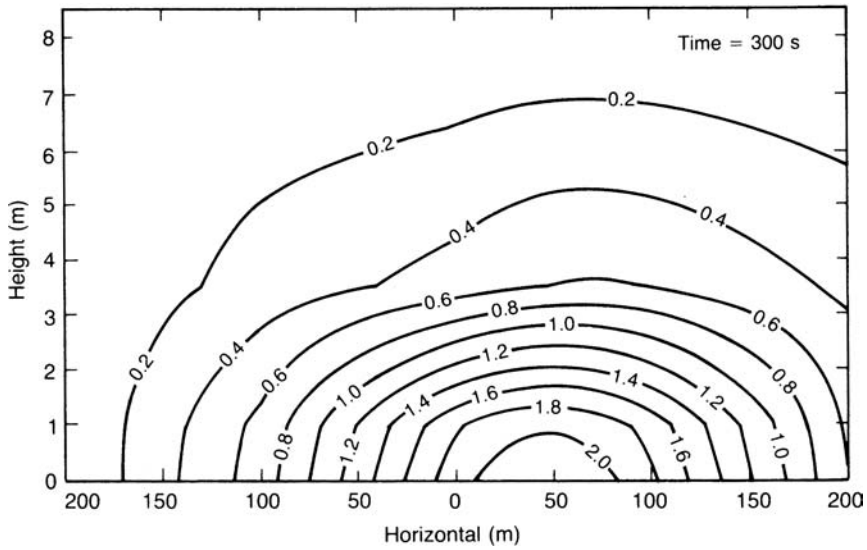


Figure 15.103 *Nevada Test Site trials, Desert Tortoise series, on dense gas dispersion with ammonia – trial 4: crosswind elevation view of concentration contours at 800 m arc (Goldwire, 1986) (Courtesy of the American Institute of Chemical Engineers)*

Table 15.51 *Experimental conditions in some field trials on dense gas dispersion: Nevada Test Site, Goldfish series (after Blewitt et al., 1987a) (Courtesy of the American Institute of Chemical Engineers)*

Trial no.	*Volume released* (m^3)	*Volumetric flow* (m^3/min)	*Duration* (min)	*Wind speed* (m/s)	*Stability category*	*Comments*
1	3.7	1.77	2.1	5.6	D	System check and dispersion test
2	4.0	0.66	6.0	4.2	D	Dispersion test
3	3.9	0.65	6.0	5.4	D	Dispersion test
4	3.6	0.255	14	6.8	D	Air/water mitigation test
5	2.0	0.123	16	3.8	C/D	Water spray (upflow) test
6	2.0	0.123	16	5.4	C/D	Water spray (downflow) test

The effect of wind speed on the promotion of mixing by the building was examined in trials 26 and 28. In the former trial the cloud passed around the building without much sign of mixing, whilst in the latter the enhancement of mixing by the building was more obvious.

Trial 27 tested the effect of a building located upwind of the source. The gravity front moving upwind was drawn into the wake of the building but the cloud did not pass around the sides.

15.38.6 Continuous release trials

A description of the continuous release trials has been given by McQuaid (1987). Accounts have also been given of the following aspects: the mass and flux balances (Mercer and Nussey, 1987); the turbulence records (Mercer and Davies, 1987); and a user's view of the data (Brighton, 1987). The aim of the trials was essentially similar to that for the instantaneous releases, i.e. to obtain data which might be used to increase understanding of the dispersion mechanisms and to validate models.

The gas used was a mixture of air and Freon 12 with a relative density of 2.0 in all trials. The source was designed to give a release with zero vertical momentum, the gas being released through an aperture in the ground with a cap above it. The release was at a rate of 5 m^3/s maintained for 400 s. Details of the continuous trials are given in Table 15.52. Three trials were conducted: trials 45–47.

The conditions for trials 45 and 47 were similar, except that the wind speeds were 2.1 and 1.5 m/s, respectively. In trial 45 at the higher wind speed the lateral spread was less and the downwind extent was greater than in trial 47.

The concentration vs time profiles showed that at 36 m downwind a steady-state profile existed for some 360 s, whereas at 250 m no steady profile was obtained. The shape of the concentration profile at 36 m was a sharp rise followed by a slow fall, whilst at 90 m there was a nearly symmetrical concentration rise and fall. With regard to the vertical concentration profile, at 36 m the concentration exhibited intermittency. The plume was characteristically very shallow, about 2 m high, and very broad, up to 300 m wide.

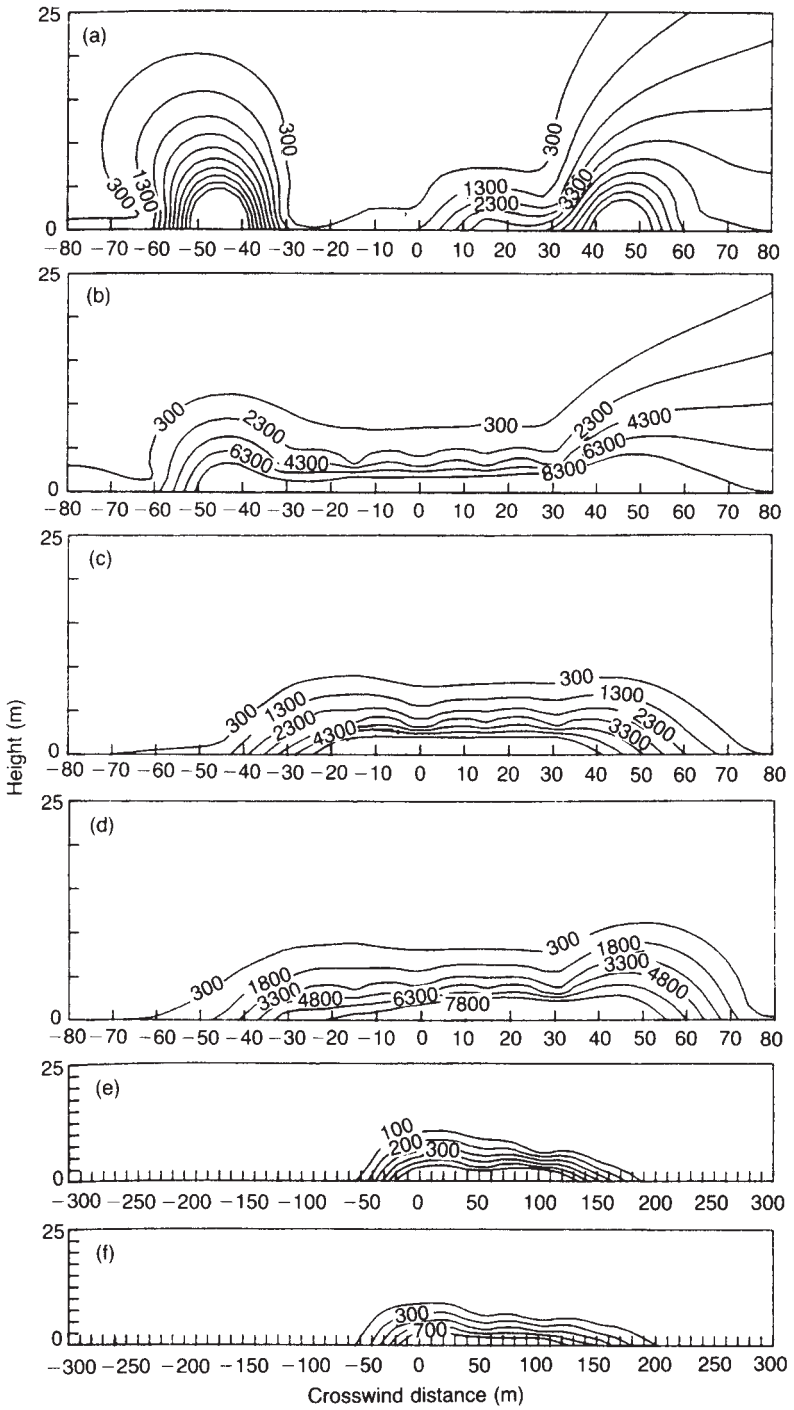


Figure 15.104 *Nevada Test Site trials, Goldfish series, on dense gas dispersion with hydrogen fluoride – crosswind elevation views of concentration contours for trials 2 and 3 (Blewitt et al., 1987a): (a) at 300 m downwind at 54 s in trial 2; (b) at 300 m downwind at 121 s in trial 2; (c) at 300 m at 113 s in trial 3; (d) at 300 m downwind at 113 s (sic) in trial 3; (e) at 1000 m downwind at 225 s in trial 3; and (f) at 1000 m downwind at 358 s in trial 3 (Courtesy of the American Institute of Chemical Engineers)*

Table 15.52 *Experimental conditions in some field trials on dense gas dispersion: Thorney Island*

Trial		*Volume released* (m^3)	*Volumetric flow* (m^3/min)	*Duration* (min)	*Relative density*	*Wind speed* (m/s)	*Stability category*	*Bulk Richardson no.*	*Comments*
No.	*Type*[a]								
005	I/1	1320			1.65	4.6	B		
006	I/1	1580			1.60	2.6	D/E	8.9	
007	I/1	2000			1.75	3.2	E	9.3	
008	I/1	2000			1.63	2.4	D	15.5	
009	I/1	2000			1.60	1.7	F	26.5	
010	I/1	2000			1.80	2.4	C	17.7	
011	I/1	2100			1.96	5.1	D	4.9	
012	I/1	1950			2.37	2.6	E	24.7	Flat unobstructed terrain
013	I/1	1950			2.00	7.5	D	2.2	
014	I/1	2000			1.76	6.8	C/D	2.1	
015	I/1	2100			1.41	5.4	C/D	2.1	
016	I/1	1580			1.68	4.8	D	3.0	
017	I/1	1700			4.20	5.3	D/E	12.5	
018	I/1	1700			1.87	5.3	D	1.7	
019	I/1	2100			2.12	6.6	D/E	3.5	
034	I/1	2110			1.8	1.4	F	60.4	
020	II/2	1920			1.92	5.7		3.5	5 m high, solid fence at 50 m
021	II/2	2050			2.02	3.9		8.8	5 m high, solid fence at 50 m
022	II/2	1400			4.17	5.9		8.1	5 m high, solid fence at 50 m
023	II/2	1960			1.80	5.8		3.0	Two rows of permeable screens, 10 m high
024	II/2	1925			2.03	6.8		2.7	Four rows of permeable screens, 10 m high
025	II/2	2000			1.95	1.4		61.8	5 m high, solid fence at 50 m
026	II/2	1970			2.00	1.9		34.8	9 m cube buliding, 50 m downwind
027	II/2	1700			4.17	2.2		71.0	9 m cube buliding, 50 m downwind
028	II/2	1850			2.00	9.0		1.5	9 m cube buiding, 50 m downwind
029	II/2	1950			2.00	5.6		4.0	9 m cube building, 50 m upwind
045	C/3	1972	260	7.6	2.0	2.1	E/F	380	Flat unobstructed terrain
046	C/3	1490	260	5.7	2.0	3.2	D	160	
047	C/3	1938	250	7.8	2.05	1.5	F	740	Flat unobstructed terrain
030	III/4	1603	260	6.2	1.4	4.3	E	0.2	Release inside fenced enclosure
033	III/4	1870	340	5.5	1.6	2.8	D/E	1.2	
036	III/4	1963	310	6.3	1.6	2.4	F/G	1.6	
037	III/4	1891	255	7.4	1.6	3.2	E	0.7	
038	III/3	1867	280	6.7	1.6	3.8	F	0.5	Flat unobstructed terrain
039	III/4	1808	350	5.2	1.4	5.8	D	0.1	Release inside fenced enclosure
040	III/4	1860	310	6.0	1.2	3.1	D	0.2	
042	III/4	1973	185	10.7	1.6	3.4	D	0.5	
043	III/4	1899	265	7.2	1.3	1.5	F	2.5	
049	III/4	1907	260	7.3	1.6	2.5	F	1.3	
050	III/4	1800	270	6.7	1.4	1.74	F	2.1	

Sources: McQuaid (1985b, 1987); M.E. Davies and Singh (1985a); M.E. Davies and Inman (1987).
[a] Phase C, continuous trials. Type: 1, instantaneous release, flat unobstructed terrain; 2, instantaneous release, flat obstructed terrain; 3, continuous release, flat unobstructed terrain; 4, continuous release, flat obstructed terrain.
[b] Nominal value.

15.38.7 Associated physical modelling

The programme of work associated with the Thorney Island trials included wind tunnel modelling. Preliminary wind tunnel experiments were conducted to screen the programme of trials and confirm that it was on the right lines. Following the trials comparisons were made with these simulations and with earlier ones conducted for the Porton trials. This work is described in Section 15.39.

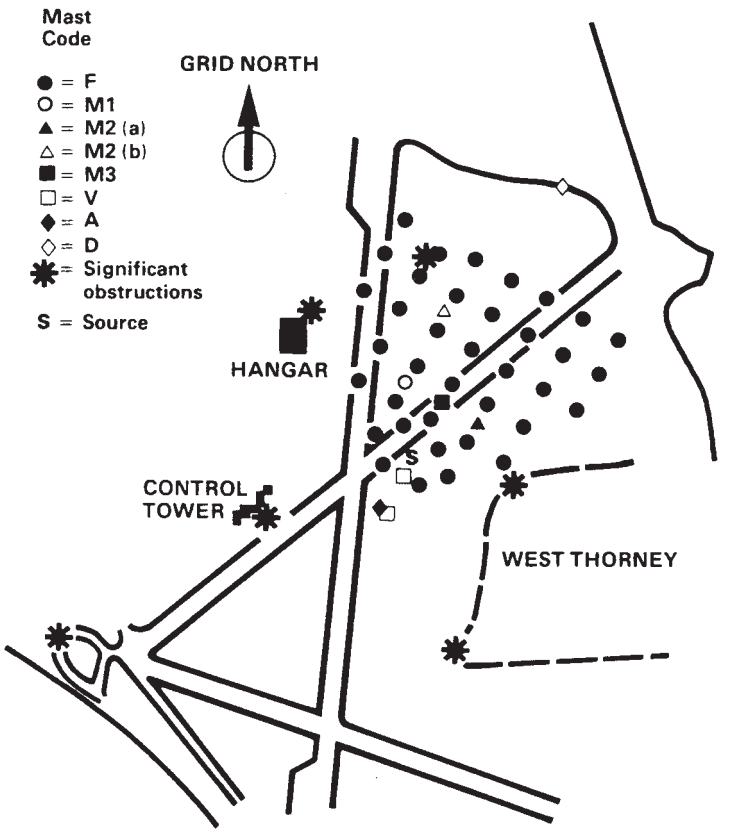


Figure 15.105 *Thorney Island trials on dense gas dispersion – site layout (McQuaid, 1985b) (Courtesy of Elsevier Science Publishers)*

15.38.8 Phase III trials

As described by M.E. Davies and Inman (1987), the Phase III trials involved releases with a 54 m × 26 m enclosure bounded by a 2.4 m vapour fence. They state that some 40 trials were performed.

15.38.9 Application to models

The Thorney Island trials, together with the analysis carried out on them, have provided a data set which has been extensively used for the determination of parameters in, and for the validation of, models. Reference to the use of these trials for both these purposes has already been made in the preceding sections. In particular, the trials have been used in the derivation of the *Workbook* correlations. The use of the Thorney Island data set in model validation is discussed further in Section 15.41.

15.39 Dispersion of Dense Gas: Physical Modelling

Another method of experimental investigation of dense gas dispersion is physical modelling, using mainly wind tunnels and water tunnels or flumes. Physical modelling makes it possible to perform dispersion experiments not only for flat unobstructed surfaces, but also with different ground slopes and other topographical features and with all kinds of obstructions, including fences and buildings, and even complete process plants, sites or terminals. It is also sufficiently economical to allow experiments to be repeated, either exactly or with minor variations.

The principal drawback is that it is not possible to scale so as to achieve complete similarity between the physical model and the scenario simulated, so that there is always a degree of distortion. However, the effects of such distortion are fairly well understood.

Accounts of physical modelling have been given by Snyder (1981), D.J. Hall, Hollis and Ishaq (1982), Meroney and Lohmeyer (1984), Meroney (1987a) and in the Workbook by Britter and McQuaid (1988).

15.39.1 Guidelines for physical modelling

Guidelines for physical modelling of dense gas dispersion have been given by Meroney (1987). They include guidance on formulation of the information to be obtained, the choice of modelling medium, the design of the experiments, the reporting of the experiments, the performance envelope within which experiments may be conducted and the scaling of the experiments.

The experiments should be matched to the information required. It may be required to determine the distance beyond which a hazardous concentration will not exist, or the distance at which the hazardous condition will occur more than a certain time with a certain probability.

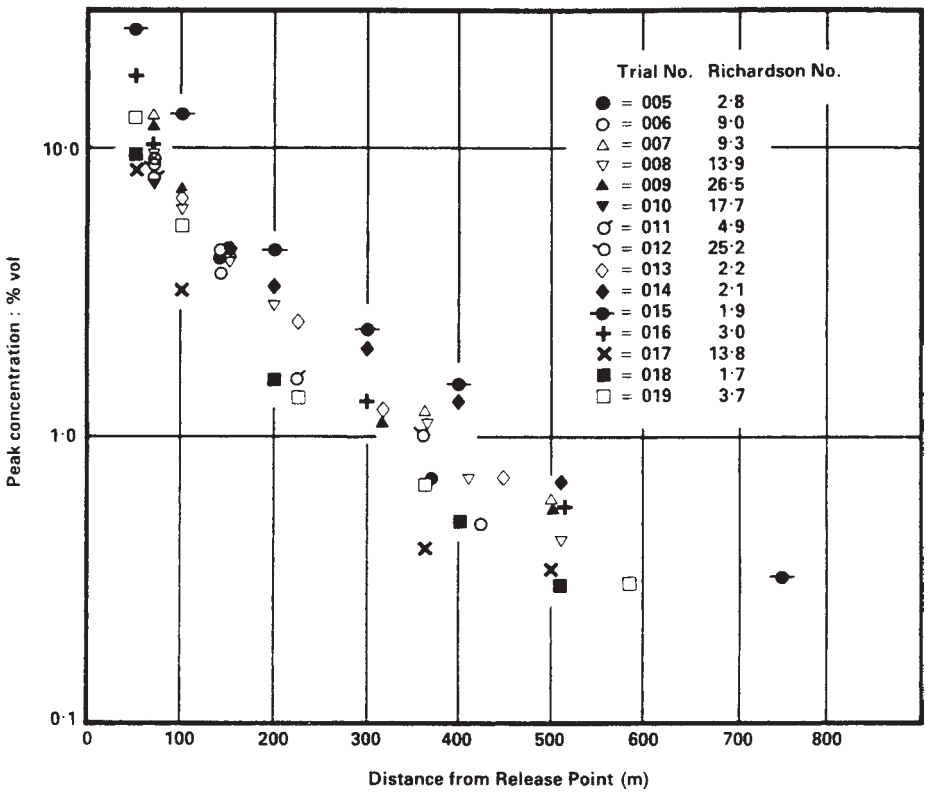


Figure 15.106 *Thorney Island trials on dense gas dispersion – peak concentrations on path of cloud centroid for instantaneous release trials (McQuaid, 1985b) (Courtesy of Elsevier Science Publishers)*

Or again, it may be required to determine the maximum concentration at a location near the source, or the concentration vs time profile at that location.

The information sought should be limited to what is really needed and overelaboration should be avoided. The data set specified should accord with what is realistically obtainable. It is useful to carry out preliminary experiments with a simple box model.

The modelling medium may be air or water. Broadly, water is often convenient for qualitative studies and visualization, but air is more often used for quantitative work. Air allows the use of a wide range of density ratios. Using heat it is comparatively easy to stratify. In theory, water should allow a Reynolds number some 16 times that of air, but in practice this advantage is not easily realized.

15.39.2 Wind tunnel facilities

A wind tunnel not only represents a major investment but also requires expertise in its use. It is therefore normal to contract work to an organization operating the wind tunnel with its own specialist team. A list of some of the principal wind tunnel facilities is given by Meroney (1987a).

15.39.3 Scaling for wind tunnel modelling

Physical modelling involves simulation of a full-scale situation by scaling down the dimensions in such a way as to retain similarity in the essential features.

Accounts of scaling for physical simulation include those given by Meroney (1979b, 1982), D.J. Hall, Hollis and Ishaq (1982), Cheah, Cleaver and Milward (1983a,b), Krogstad and Pettersen (1986), and Schatzmann, Koenig and Lohmeyer (1986) and the one given in the Workbook by Britter and McQuaid (1988).

The usual procedure is to list the relevant variables and then to derive from these the appropriate dimensionless groups. The number of dimensionless groups should be equal to the number of variables minus the number of dimensions. The lists of the variables given by different workers tends to vary slightly, in part because some list a variable only to disregard it, whilst others do not list it in the first place.

The conditions for similarity may be defined in stages. Thus, the *Workbook* defines first the requirements for the atmospheric boundary layer, then those for release of a gas with the same properties and temperature as air, and finally those for release of a dense gas. The variables commonly listed for similarity of the atmospheric boundary layer are

u characteristic velocity
L characteristic length scale
ρ density of atmosphere
μ viscosity of atmosphere
g acceleration due to gravity

The *Workbook* also includes

$\Delta\rho/\rho$ characteristic potential density difference due to atmospheric stability/instability
f Coriolis parameter

The dimensionless groups listed by the *Workbook* are:

$\mathrm{Re} = \dfrac{uL\rho}{\mu}$ Reynolds number

$\mathrm{Ri} = g\dfrac{\Delta\rho}{\rho}\dfrac{L}{u^2}$ Richardson number

$\mathrm{Ro} = \dfrac{u}{fL}$ Rossby number

This gives only three dimensionless groups, not the four which the rule quoted above would indicate. The explanation given in the Workbook is that the Boussinescq approximation has been made, so that the effect of $\Delta\rho/\rho$ on inertia is neglected but that on buoyancy is not.

Proceeding straight to the dense gas case, the further variables introduced in the *Workbook* are:

q_o volumetric release rate, or
Q_o volume released
ρ_a density of air
ρ_o density of source gas
x, y, z downwind, crosswind, vertical distance

The further dimensionless groups given are then:

$\dfrac{q_o}{uL^2}$ source number (continuous source), or

$\dfrac{Q_o}{L^3}$ source number (instantaneous source)

$\dfrac{\rho_o}{\rho_a}$ density ratio

$\mathrm{Fr} = \dfrac{u^2}{gL}$ Froude number

$\dfrac{x}{L}, \dfrac{y}{L}$ and $\dfrac{z}{L}$ dimensionless downwind, crosswind and vertical distance

If a degree of distortion is accepted, it is practice in modelling buoyant plumes to make the following approximations, which the *Workbook* tentatively proposes for dense plumes also. The Froude number and the density ratio may be combined using the Boussinesq approximation to give

$\dfrac{u^2}{g(\Delta\rho_o/\rho_a)L}$ densimetric Froude number

Similarly, the source number and density ratio may be combined to give

$\dfrac{\rho_o q_o^2}{\rho_a u^2 L^4}$ source momentum ratio

If the source momentum is negligible, this term may be replaced with the source number q_o/uL^2.

If the fine scale structure of the concentration field is to be preserved, the similarity of the Schmidt number Sc is relevant

$\mathrm{Sc} = \dfrac{v}{D}$ Schmidt number

where D is the diffusion coefficient and v is the kinematic viscosity.

This aspect may also be expressed in terms of the Peclet number Pe:

$\mathrm{Pe} = \dfrac{vL}{D}$ Peclet number

since

$\mathrm{Pe} = \mathrm{Re} \cdot \mathrm{Sc}$

If non-neutral temperature stratification is being modelled, the similarity of the Prandtl number Pr is relevant:

$\mathrm{Pr} = \dfrac{v}{k}$ Prandtl number

where k is the thermal conductivity.

Additional quantities mentioned by some workers include:

α ground slope
z_o roughness length
u^* friction velocity
μ_o viscosity of source gas

and additional dimensionless groups are

$\dfrac{z_o}{L}$ dimensionless roughness length

$\dfrac{u_*}{u}$ dimensionless friction velocity

The conditions for flow to be fully aerodynamically rough depend on the group $u_* z_o/v$. In other words, for such flow the role of the kinematic viscosity v is taken over by the group $u_* z_o/v$. The *Workbook* therefore defines a more relevant Reynolds number as

$\dfrac{uL}{u_* z_o}$ modified Reynolds number

It may be noted that this modified Reynolds number is the product of the reciprocals of the dimensionless roughness length and friction velocity just defined.

The source volumetric flow q_o is sometimes represented by the product $u_o A_o$, where u_o is the source velocity and A_o its area.

Turning to the application of these similarity criteria to the scaling problem, it is not possible to achieve similarity of all the relevant groups. Complete similarity is not attainable and some degree of distortion has to be accepted.

Some of the groups quoted are of secondary importance, and some are frequently not mentioned by modellers. Since the full scale and model fluids are generally both air, the Prandtl number is the same. Rossby number similarity is not attainable, but a limit can be set. The *Workbook* suggests that it would be reasonable to neglect rotational effects for $\mathrm{Ro} \geq 10$, but that a value of $\mathrm{Ro} \approx 1$ should be justified.

It is not possible to obtain Reynolds number similarity. However, since the properties of turbulent flow are independent of the Reynolds number provided it is large, the approach generally taken is to make the Reynolds number as large as practical.

The *Workbook* gives a detailed discussion of the setting of the Reynolds number. The essential requirement is similarity of the mean and turbulence velocity profiles and in practice the boundary layer is adjusted until this is achieved. It suggests that the condition $u_* k/\nu > 50$ gives Reynolds number independence, though for sharp-edged elements particularly $u_* k/\nu > 5$ may suffice. Since typically $z_o \approx 0.1$, these conditions are equivalent to $u_* k/\nu > 5$ and $u_* z_o/\nu > 2$, respectively.

As far as concerns Froude number similarity, this is often difficult to achieve because it tends to involve an air velocity that is too low to give stable flow. Generally the approach taken is to combine the density ratio and Froude number into a densimetric Froude number, as described above. The *Workbook* recommends that priority be given to achieving similarity of two groups, the densimetric Froude number and the source momentum ratio.

If the fine scale structure of the concentration field needs to be modelled, and molecular diffusion effects taken into account, the Schmidt number should be similar and the Reynolds number as large as possible. Failure to achieve adequate Reynolds number results in loss of fine scale structure and is not compensated by a correct Schmidt number.

Reports of physical modelling frequently discuss aspects of scaling, either in relation to the design of the experiments or in explanation of the results, and many of those quoted below include such discussions.

15.39.4 Wind tunnel performance envelope

There are a number of practical features which set a limit to the conditions under which a wind tunnel may be operated and to the applications for which it may be used. There are problems in achieving a steady low velocity. A velocity of 1 m/s is quoted as a practical lower limit, although velocities half this or less are sometimes used. This tends to be a major constraint.

Dense gas clouds are shallow but wide, and the width of the tunnel may be a constraint. The length of the tunnel can also constrain the concentrations which can be studied; there is usually little difficulty in obtaining concentrations down to typical flammability limit levels but it may not be possible to achieve concentrations at levels of interest for some toxic gases.

The use of a very small model can cause problems of spatial resolution. There is a practical limit to the fineness of size of measurement probes.

Attainment of a Reynolds number high enough to give correct wake flows can be a difficulty, particularly for smooth structures.

The performance envelope of a wind tunnel, with particular reference to LNG dispersion experiments, has been described by Meroney and Neff (1980) and Meroney (1987a).

15.39.5 Universal plume profile

An early wind tunnel study of dense gas dispersion was that by D.J. Hall, Barrett and Ralph (1976). These workers addressed the determination of the distance for the gas concentration to fall to 2% and expressed their results in the form of a universal plume, as shown in Figure 15.107. The plume is defined by the dimension D, which for a cloud boundary concentration of 2% is given by the empirical equation

$$D\left(\frac{u}{Q}\right)^{1/2} = 107 \qquad [15.39.1]$$

where Q is the volumetric release rate and u is the wind speed. The results apply only to a fully developed plume, which may take some hours to develop.

The work illustrated the fact that a dense gas forms a wide, very shallow plume with a strong resistance to vertical dispersion and that its behaviour is quite different from that of neutral buoyancy gas. The authors present calculations which show that for stable atmospheric conditions the travel distances given by passive dispersion models considerably exceed those obtained from their model.

15.39.6 Porton Down trials

A wind tunnel investigation of some of the Porton Down trials has been carried out by D.J. Hall, Hollis and Ishaq (1982, 1984). The aim of the work was to assess the applicability of wind tunnel modelling to dense gas dispersion.

Figures 15.108 and 15.109 show some of the results obtained for the Porton trials. Figure 15.108(a)–(c) give, respectively, the cloud width, the cloud arrival and departure times and the profile of the peak ground level concentration vs downwind distance for trial 37. Figure 15.109(a)–(d) show the concentration-time profiles at four points in this trial. The figure shows the profiles of the physical model tending to lead, and to be less smoothed than, the full-scale profiles.

Figure 15.109(e) shows the variability of the concentration-time profile in repeat runs at a single point in trial 52. The figure brings out the high degree of variability between individual runs and the desirability of performing enough runs to obtain a stable characterization of the concentration. Since such repeat runs are not practical in field trials, but are so in a wind tunnel; this is an important contribution of the latter. The authors give comparative photographs for the field trials and the wind tunnel. This format for presenting results has also been used in subsequent work by the authors and others

The authors also proposed a relationship between the distance to the 2% concentration level and the Richardson number. They investigated this further in relation to the Thorney Island trials, as discussed below.

15.39.7 Thorney Island trials

At the time when the above work was being done, the Thorney Island experiments were being designed and some additional, exploratory wind tunnel work was carried out to assist in this. Following the trials, the simulations done on the Porton trials and this further work for the Thorney Island trials were revisited. Several of the simulations were sufficiently closely matched to particular Thorney Island trials to allow comparisons to be made. These have been described by D.J. Hall and Waters (1985).

Figure 15.110 shows some of the results obtained for the Thorney Island trials. Figures 15.110(a)–(c) again give the cloud width, the cloud arrival and departure times and the profile of the peak ground level concentration vs distance,

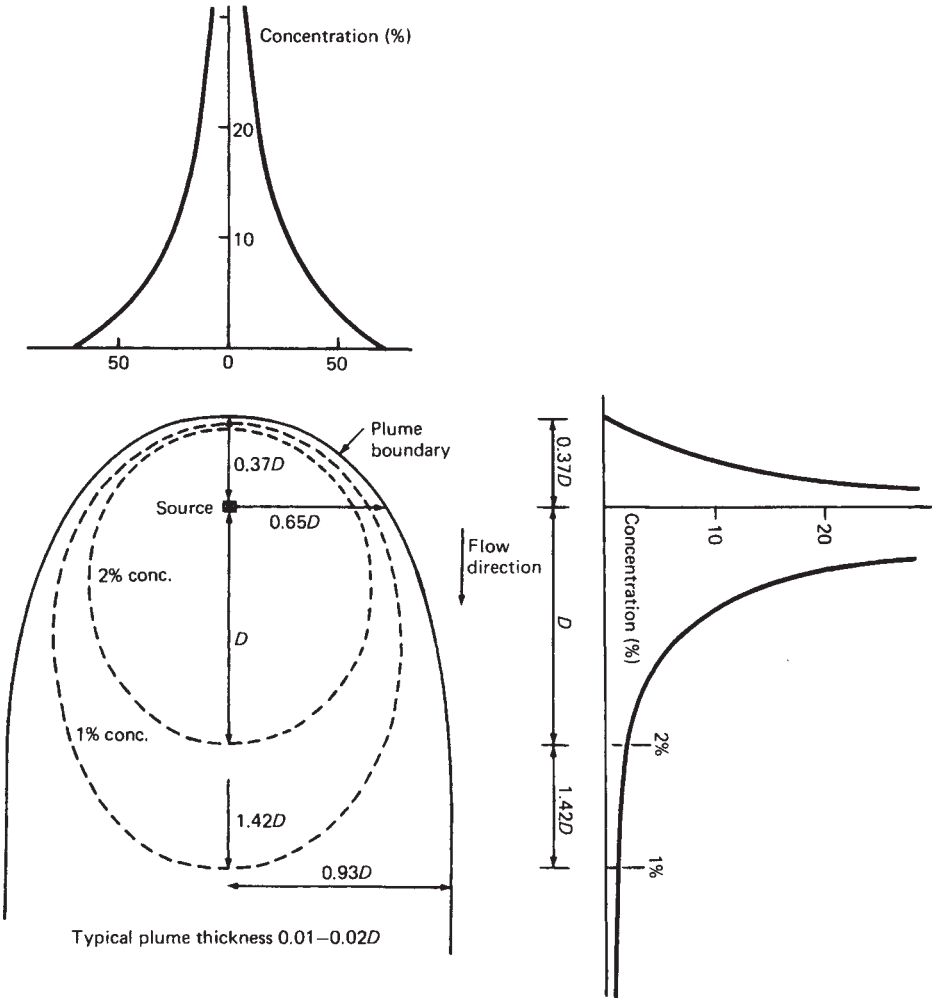


Figure 15.107 *Wind tunnel simulation of dense gas dispersion – universal plume profile (D.J. Hall, Barrett and Ralph, 1976) (Courtesy of Warren Spring Laboratory)*

respectively. Figure 15.111 shows the profile of concentration vs time at particular downwind locations. Figure 15.112 and Figure 15.113 show, respectively, plan and elevation views of the full-scale trial and of the wind tunnel model.

Figure 15.111 shows the profiles of the physical model tending in this case to lag, and to be more smooth than, the full-scale profiles. This contrasts with the results described above for Porton trial 37, where the reverse was the case. This 'persistence' of the concentration was the main discrepancy. The authors suggest that it may be explained in part by surface roughness present in the wind tunnel but not at full scale, and perhaps in part by the need to use a low wind speed of 0.4 m/s. Nevertheless, the concentrations obtained in the wind tunnel work were within a factor of 2 of those at full scale.

The authors also consider a correlation derived from their Porton simulations between the distance to a 2% concentration and the reciprocal of the Richardson number. This is shown in Figure 15.114. The distance is shown as having a maximum at $Ri \approx 3(1/Ri \approx 0.3)$. For high values of Ri the cloud is advected by the wind with relatively little dispersion. For lower values atmospheric turbulence increases dispersion above that obtained from gravity-driven flow. If valid, the relationship is of some interest, but it does not appear to be supported by the Thorney Island results.

M.E. Davies and Inman (1987) describe a programme of 86 simulations of the Thorney Island trials. They give numerous sample plots, particularly concentration-time profiles, concentration-distance correlations and plan view concentration contours.

Figure 15.115 shows photographs of full scale trials and wind tunnel simulations for instantaneous and continuous releases, in both cases without and with fences. The decay

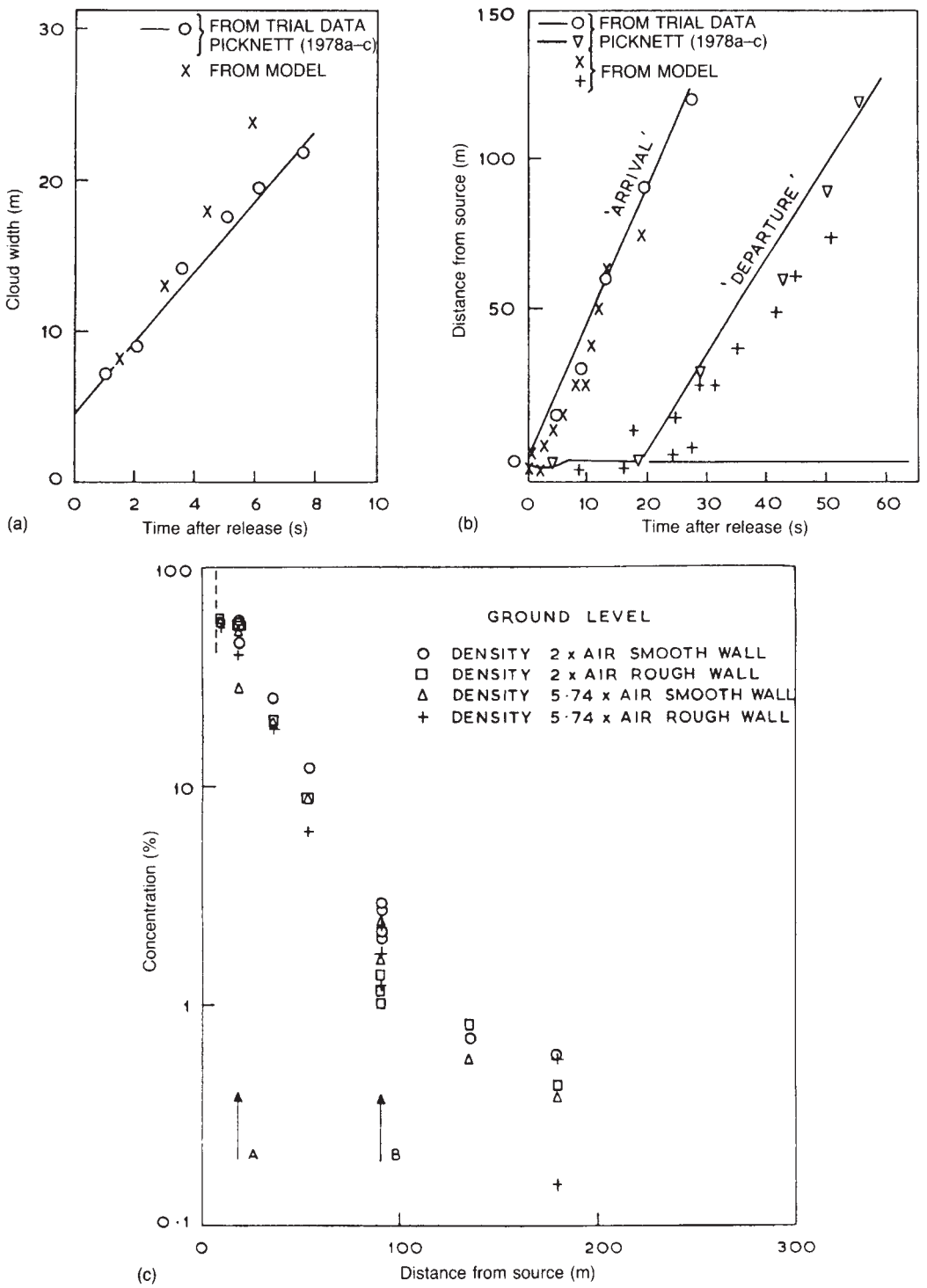


Figure 15.108 *Wind tunnel simulation of Porton Down trials on dense gas dispersion – comparison of observed and simulated features (D.J. Hall, Hollis and Ishaq, 1984): (a) cloud width in trial 37; (b) arrival and departure times in trial 37; (c) peak ground level concentration (Courtesy of Springer Verlag)*

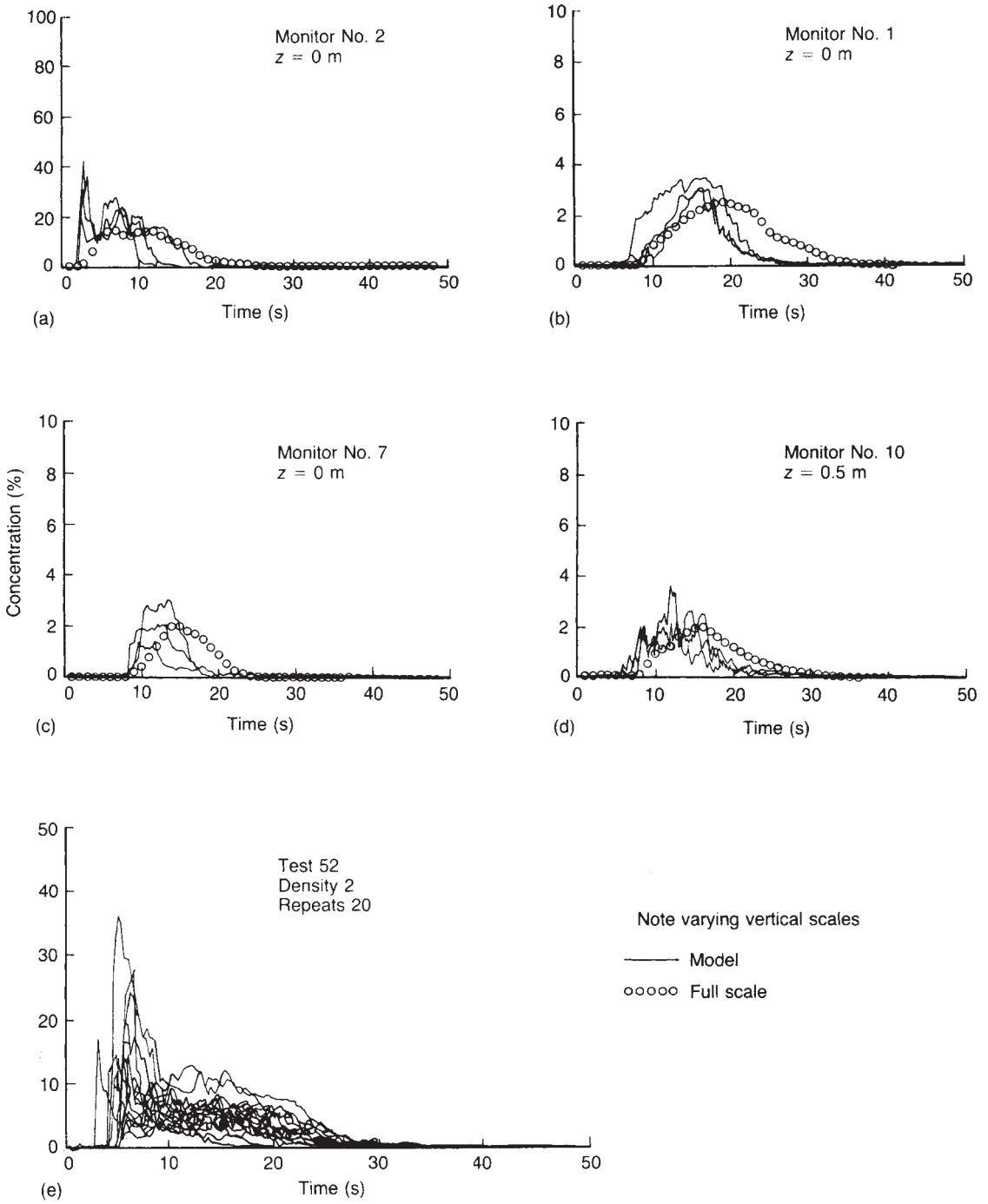


Figure 15.109 *Wind tunnel simulation of Porton Down trials on dense gas dispersion – comparison of observed and simulated features for trials 37 and 52 (D.J. Hall, Hollis and Ishaq, 1984): (a)–(d) concentration profiles at four points in trial 37; (e) variability of concentration profile in repeat simulation runs for trial 52 (Courtesy of Springer Verlag)*

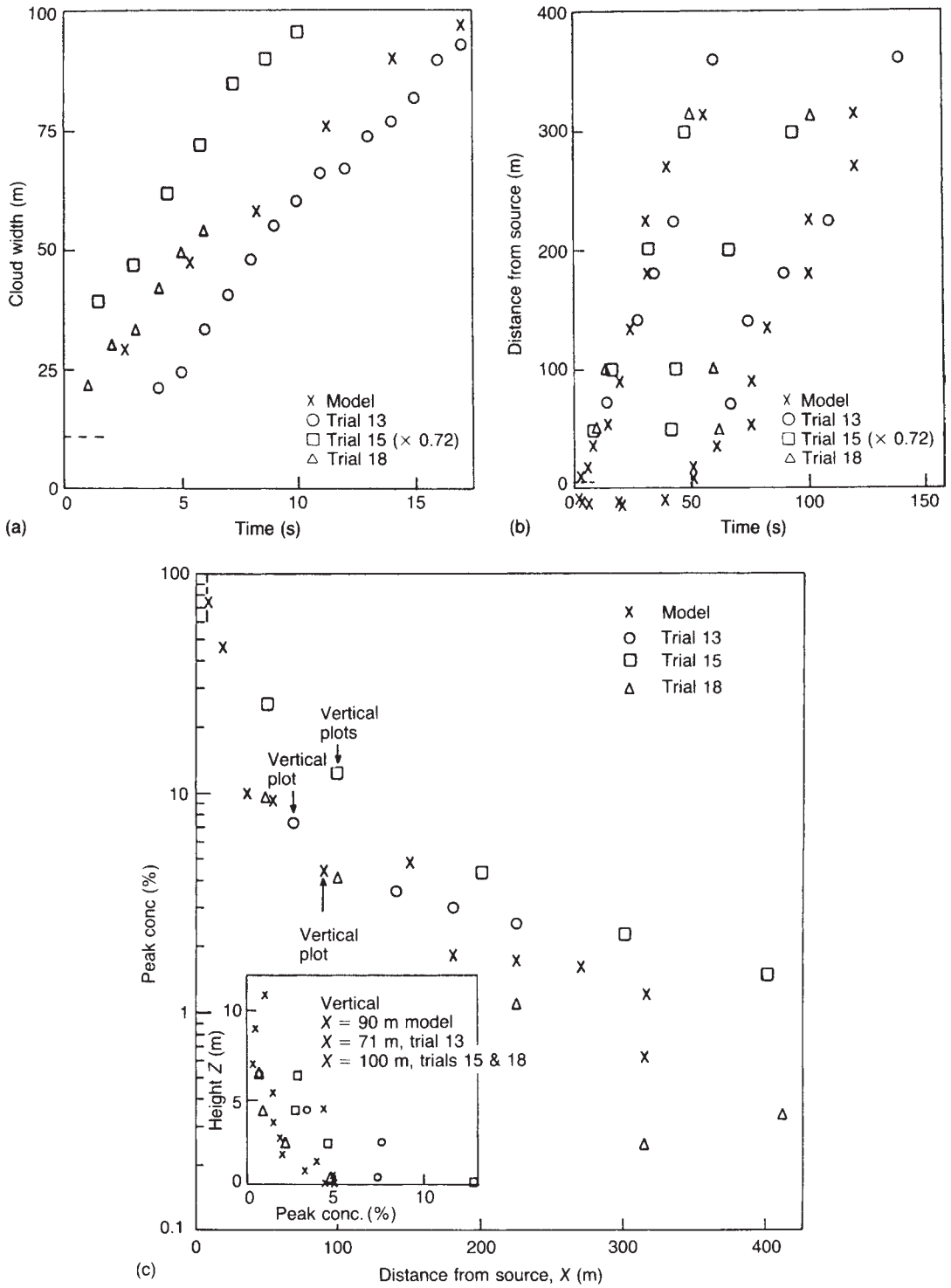


Figure 15.110 *Wind tunnel simulation of Thorney Island trials on dense gas dispersion – comparison of observed and simulated features for (D.J. Hall and Waters, 1985): (a) cloud width; (b) cloud travel time; (c) peak ground level concentration (Courtesy of Elsevier Science Publishers)*

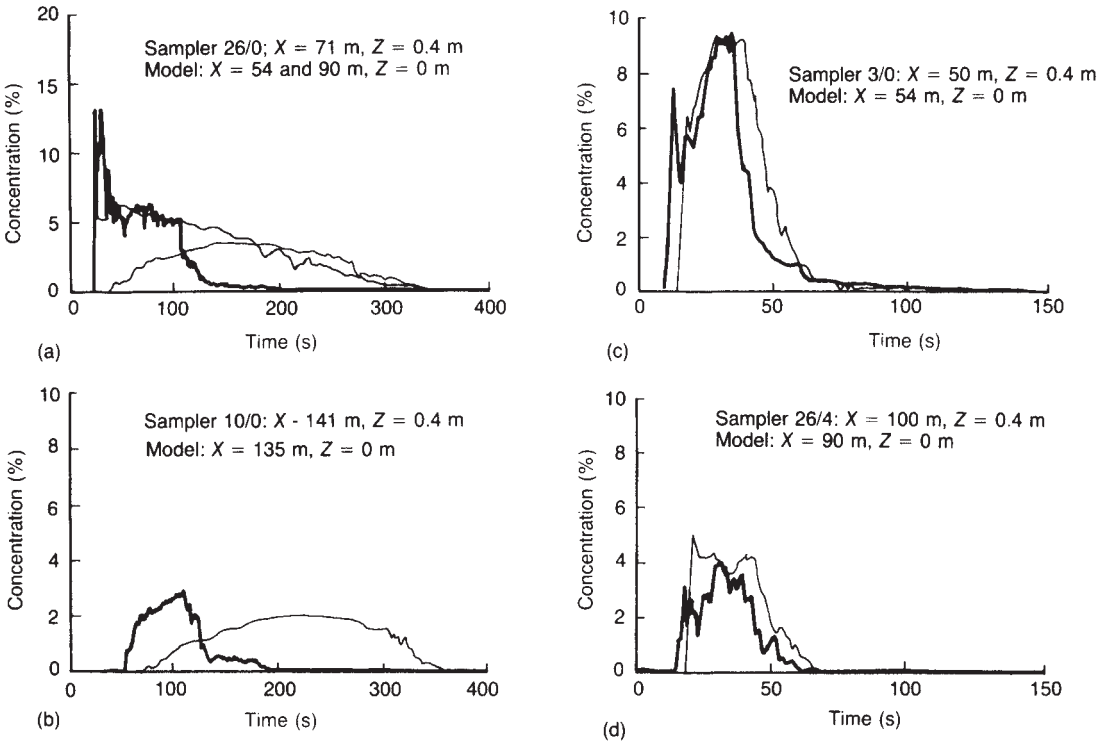


Figure 15.111 *Wind tunnel simulation of Thorney Island trials on dense gas dispersion – comparison of observed and simulated features: (a) and (b) concentration profiles at two points in trial 7; (c) and (d) concentration profiles at two points in trial 18 (D.J. Hall and Waters, 1985) – model; – trial samplers. Note the varying vertical scales (Courtesy of Elsevier Science Publishers)*

of peak concentration with distance for the continuous releases, without and with fences, is correlated in the form shown in Figure 15.116, after Meroney and Neff (1980). A buoyancy length scale $l/$, is defined as

$$l_b = \frac{g'Q}{u^3} \qquad [15.39.2]$$

and the further length scale l_q as

$$l_q = \left(\frac{Q}{u}\right)^{1/2} \qquad [15.39.3]$$

where Q is the volumetric release rate.

The plot gives

$$\frac{cul_b^2}{Q} \propto \left(\frac{x}{l_b}\right)^{-2} \qquad [15.39.4]$$

and hence

$$c \propto \left(\frac{x}{l_q}\right)^{-2} \qquad [15.39.5]$$

where c is the volumetric concentration.

The distance to the 2% concentration was investigated. It was found that the ratio of this distance in the model to that at full scale fell to about unity, though with some scatter. The authors suggest that the full scale distance may be estimated with 90% confidence as lying within the range delimited by a lower limit of half the model value and an upper limit of twice that value. The peak concentrations were found to be insensitive to the value of the Richardson number.

Several other workers have performed wind tunnel simulations of the Thorney Island trials. Figure 15.117 shows a computer graphics simulation of trial 8 by S.T. Chan, Ermak and Morris (1987); the computer simulation has the appearance of a wind tunnel simulation.

Van Heugten and Duijm (1985) investigated trial 8. They obtained reasonable agreement between the full-scale trials and wind tunnel model and between both of these and the TNO model described by van den Berg (1978).

Thorney Island trial 20, with a solid fence, has been simulated in a wind tunnel by Knudsen and Krogstad (1987). Again there was a tendency for the wind tunnel concentration profile to persist longer than that for the full-scale trial. The authors state that a possible explanation is the difference in Reynolds number and thus in the wake at the fence.

15.39.8 Ground slope

Physical modelling is particularly suited to investigation of the effects of terrain, obstructions and buildings. The

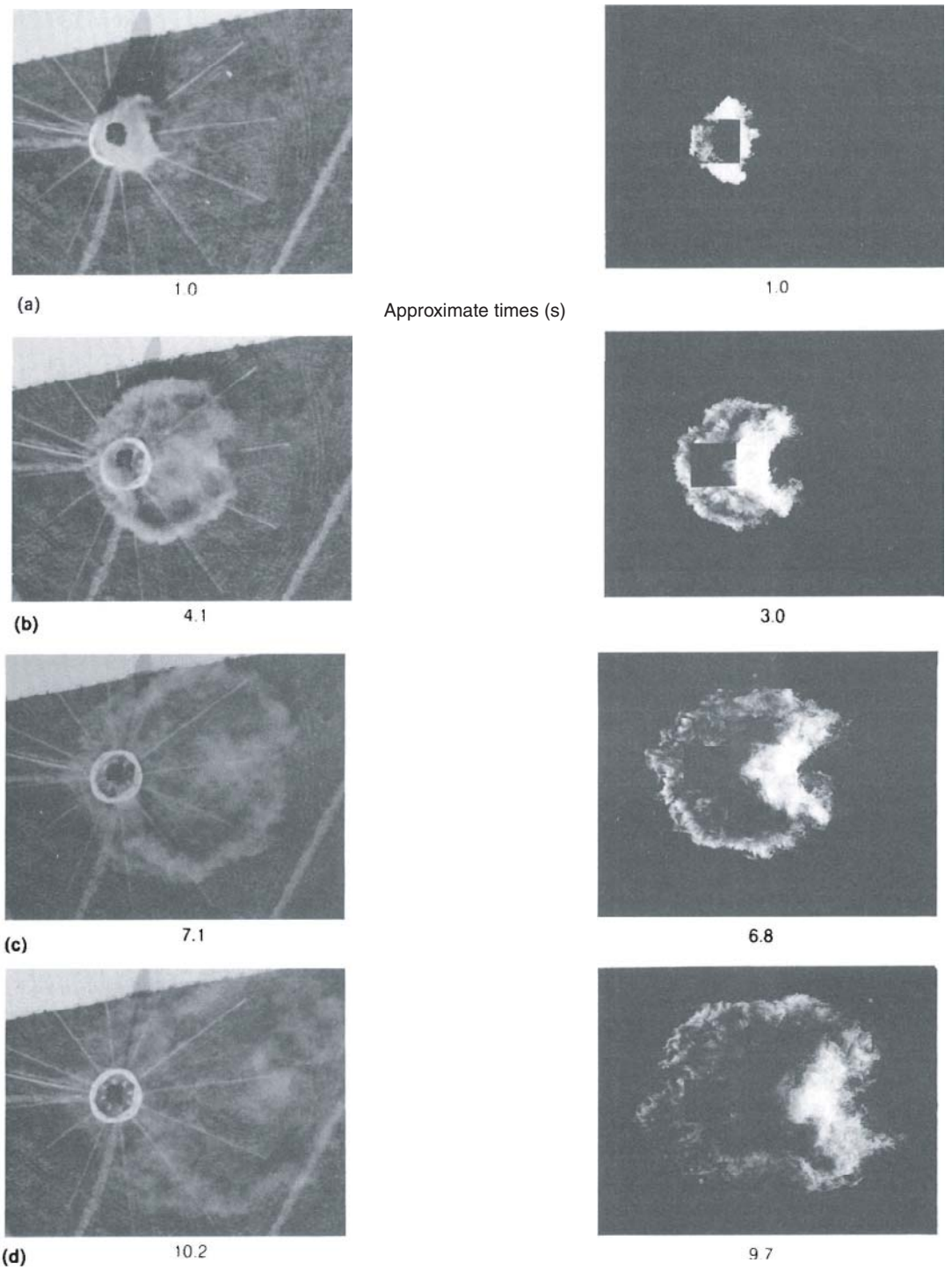


Figure 15.112 *Wind tunnel simulation of Thorney Island trials on dense gas dispersion – comparison of simulated and observed plan views of cloud in trial 13 (D.J. Hall and Waters, 1985): (a) both after 1.0 s; (b) observed after 4.1 s and simulated after 3.9 s; (c) observed after 7.1 and simulated after 6.8 s; (d) observed after 10.2 s and simulated after 9.7 s. All times are approximate (Courtesy of Elsevier Science Publishers)*

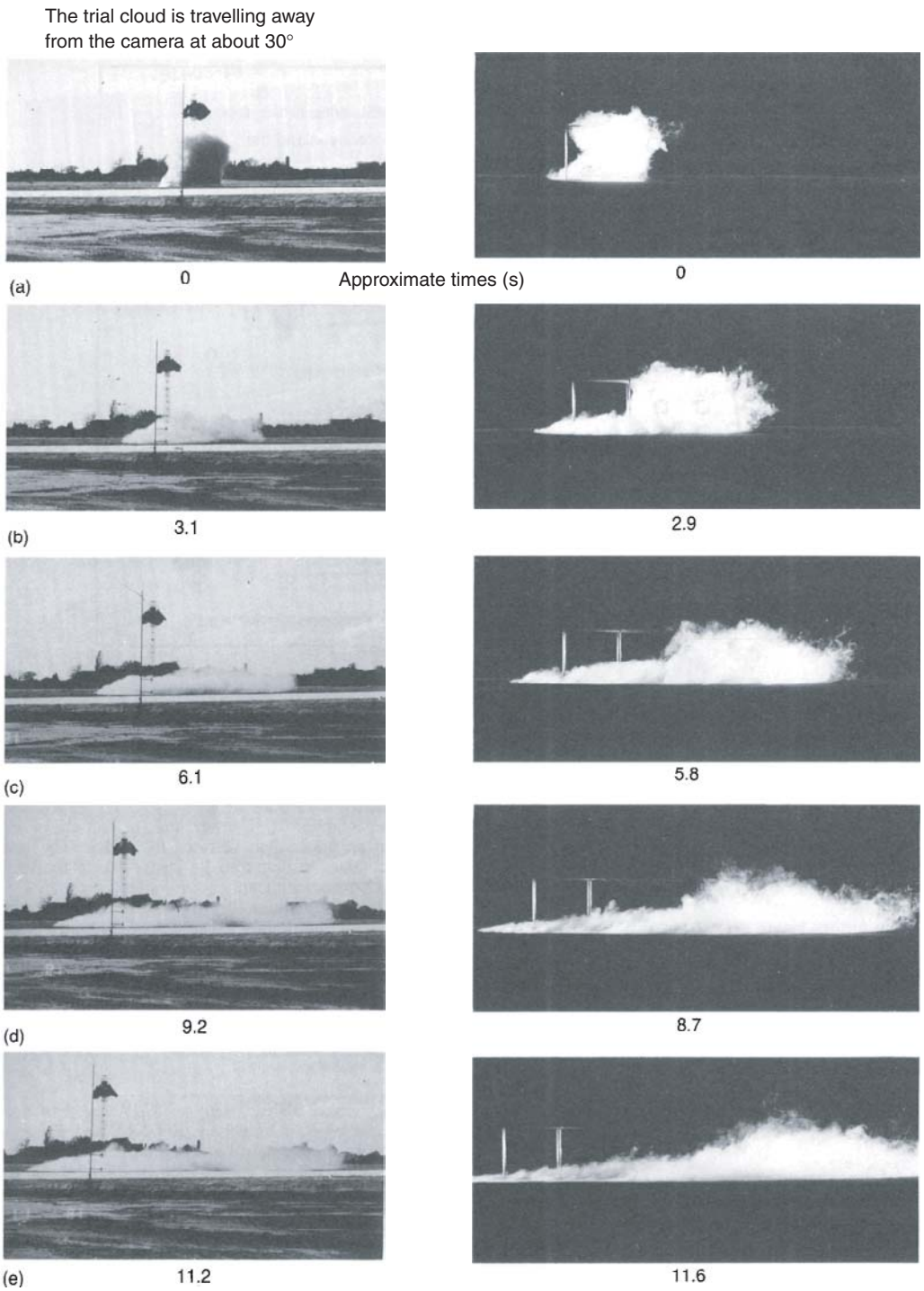


Figure 15.113 *Wind tunnel simulation of Thorney Island trials on dense gas dispersion – comparison of observed and simulated elevation views of cloud in trial 13 (D.J. Hall and Waters, 1985): (a) both at time zero; (b) observed after 3.1 s and simulated after 2.9 s; (c) observed after 6.1 s and simulated after 5.8 s; and (d) observed after 9.2 s and simulated after 8.7 s; (e) observed after 11.2 s and 11.6 s; all times approximate (Courtesy of Elsevier Science Publishers)*

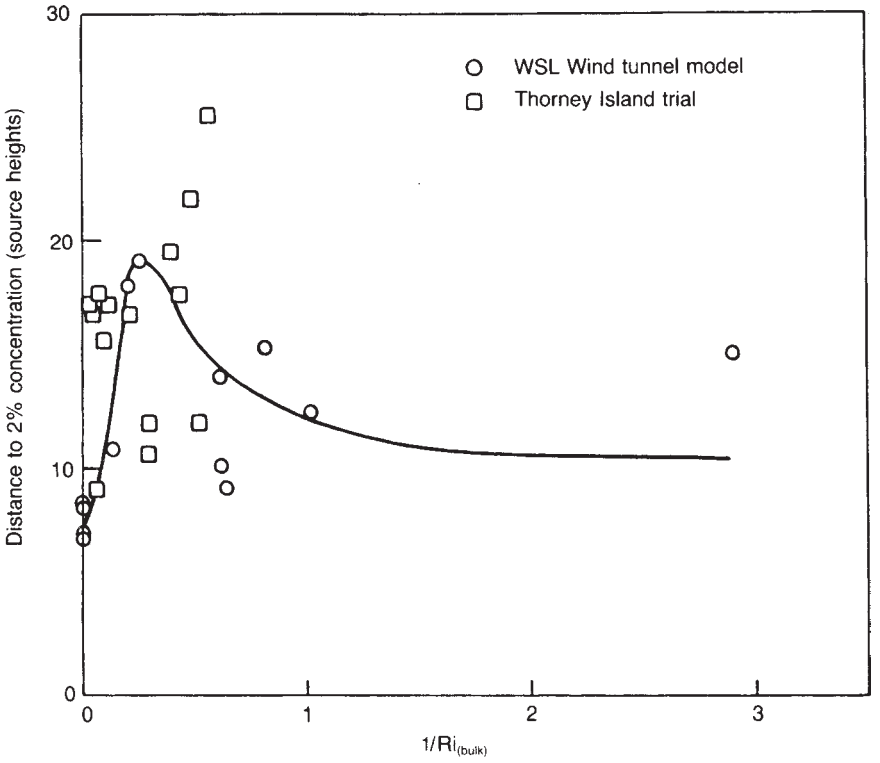


Figure 15.114 *Wind tunnel simulation of Thorney Island trials on dense gas dispersion – effect of bulk Richardson number on concentration downwind (D.J. Hall and Waters, 1985) (Courtesy of Elsevier Science Publishers)*

dispersion of dense gas on a slope was another feature investigated in the study by D.J. Hall, Barrett and Ralph (1976) already described. Some of their results for the universal profile on a slope are shown in Figure 15.118.

15.39.9 Obstructions and buildings

There have been several investigations of dense gas dispersion in the presence of obstructions and buildings. Cheah, Cleaver and Milward (1983a) have used a water tunnel to make an *ad hoc* study of the effect of a simple barrier on the dispersion of a dense gas plume. Their results give a clear illustration of the effect of the gravity-driven phase. The authors comment that Figure 15.119, which is a plot of mean concentration vs downstream distance (the distance being expressed in terms of the ratio of the distance to the source diameter and with the relative density as a parameter) shows that for the plumes of higher relative density (and Richardson number) there is an initial phase with gravity slumping but little entrainment followed by a further gravity-driven phase where entrainment does occur and that the slope of the curve in this latter phase is not the same as for passive dispersion, whilst for the plume of low relative density (and Richardson number) the slope in the second region progressively approximates that of a passive plume.

The work also indicated the effectiveness of a barrier in reducing the downstream concentration. Even with the least effective barrier distance the concentration downstream was reduced by an order of magnitude.

The dispersion of a dense gas plume around a building has been investigated by Krogstad and Pettersen (1986). The presence of the building caused a strong modification of the plume.

C.I. Bradley and Carpenter (1983) have described an assessment of physical modelling which included the comparison of results from such modelling with results from models for the dispersion of 1000 te of LNG spilled onto land at a tanker terminal and onto water at the terminal. Experiments were done using both a wind tunnel and a water flume.

They discuss the problem of scaling up in respect of the temperature of the gas. Heat transfer from the surface to the cloud has a greater influence at low wind speeds, but at higher wind speeds is less significant. They followed Neff and Meroney (1981) in taking the gas density as the source value, but restricted their study to higher wind speeds (>5 m/s).

Comparisons were made with results from the Germeles and Drake, Cox and Carpenter, Fryer and Kaiser, and ZEPHYR models. For the land spills a global roughness length of 0.2 m, corresponding to rough terrain, was used in the box models. The ZEPHYR model, being a if-theory model, modelled the effect of the structures directly.

Broadly, the distances to the extinction of the flammable plume in both the wind tunnel and water flume modelling were reduced by the presence of the terminal structures by a factor of about 2. Further, the dispersion of the land spill was dominated by the presence of the single tank from

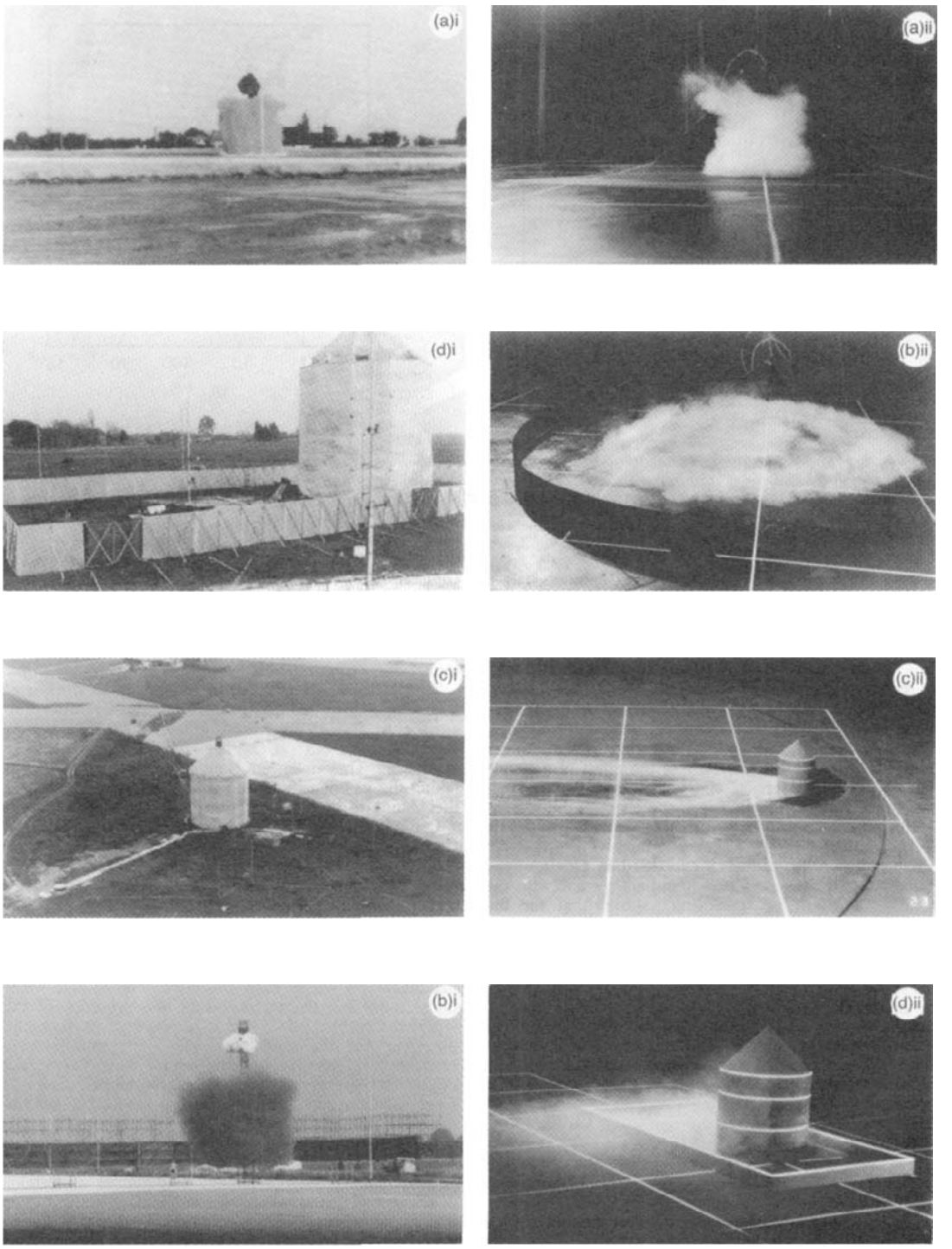


Figure 15.115 *Wind tunnel simulation of Thorney Island trials on dense gas dispersion – comparison of observed and simulated releases (M.E. Davies and Inman, 1987): (a) instantaneous release (Type 1); (b) instantaneous release with fence (Type 2); (c) continuous release (Type 3); (d) continuous release in fenced enclosure (Type 4) (Courtesy of Elsevier Science Publishers)*

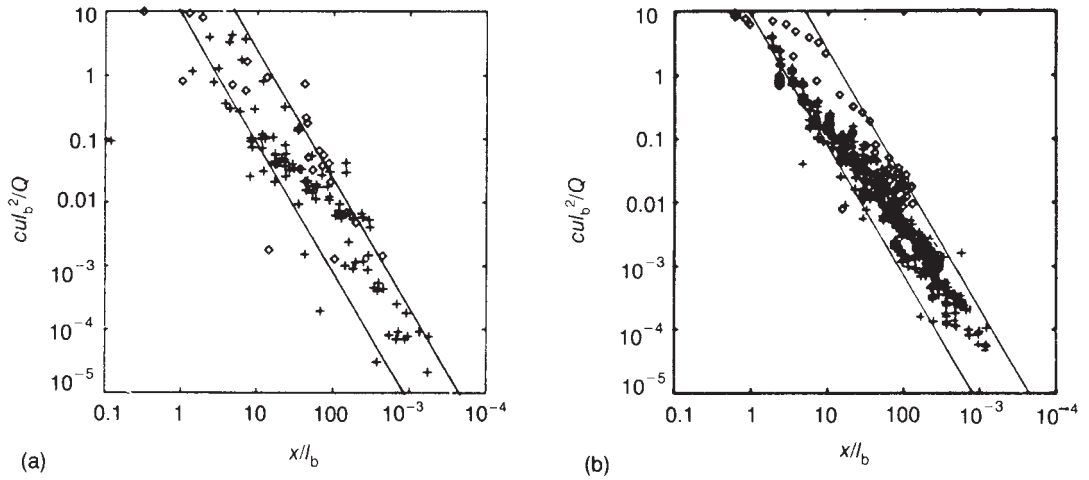


Figure 15.116 *Wind tunnel simulation of Thorney Island trials on dense gas dispersion—distance to 2% concentration (M.E. Davies and Inman, 1987): (a) observed; and (b) simulated. The solid lines represent the limits of data in the work of Meroney and Neff (1980) (Courtesy of Elsevier Science Publishers)*

which the spill originated. The models tended to give higher distances to cloud extinction than the physical modelling, but the distances generally agreed to within a factor of 2 and again showed the reduction caused by the terminal structures.

Guldemond (1986) performed wind tunnel simulations of releases of 15 ton of liquefied ammonia at release rates in the range 6.5–52 kg/s. Air entrainment was assumed such that the air/ammonia mass ratio at the source was 10 : 1 and that there was complete evaporation of the liquid spray formed. Figure 15.120(a) shows the model of the industrial site in the wind tunnel and Figure 15.120(b)–(e) show the plumes formed by a dense gas on flat terrain and on the industrial site and by neutral buoyancy gas on these two types of terrain, respectively.

On flat terrain for the neutral buoyancy gas the upwind dispersion was 10 m and the initial cloud width was 120 m. For the dense gas the values were 90 and 540 m, respectively. For the industrial site the corresponding figures for the neutral buoyancy gas were 60 and 250 m and for the dense gas 210 and 540 m.

The effect of different locations of the source within the industrial site was investigated. The location had a marked effect on the neutral buoyancy plume, which was strongly influenced by particular buildings. It had much less effect on the dense gas plume. Mixing of the dense gas plume was caused not only by atmospheric turbulence but was also strongly affected by mechanically induced turbulence due to the obstructions. The cloud tended to mix vertically up to the average height of the buildings.

The author gives concentration vs distance profiles and data on times to particular concentrations. Measurements were made at distances of 100, 400 and 450 m downwind. The concentrations at the first point were in the range 1000–3000 ppm, except for the very low release rate. Thereafter, the slope of concentration decay with distance on a log–log plot was about 1.7, which is characteristic of passive dispersion.

15.39.10 Concentration variability

As already mentioned, one of the strengths of wind tunnel modelling is that it furnishes an economical way of making a large number of repeat runs at the same nominal conditions. The variability in the concentration vs time profiles obtained in the simulation of the Porton trials by D.J. Hall, Hollis and Ishaq (1982, 1984) has already been described.

A systematic investigation of this variability in terms of the intensity of concentration fluctuations has been made by Meroney and Lohmeyer (1984). Their work is discussed in the context of concentration fluctuations in Section 15.45.

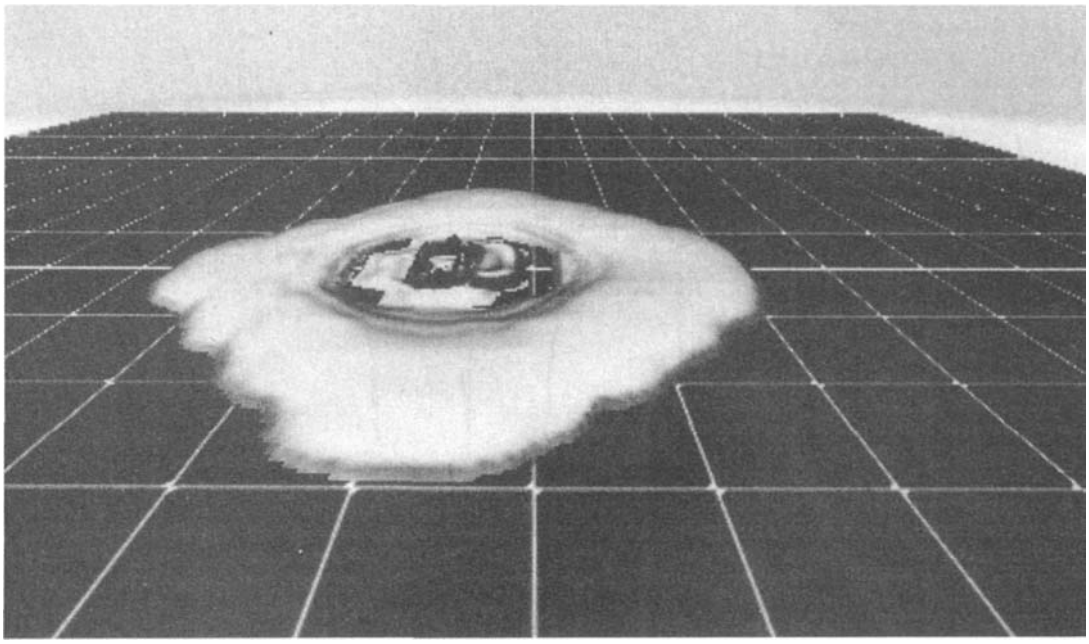
15.40 Dispersion of Dense Gas: Terrain, Obstructions and Buildings

The account of dense gas dispersion given so far has concentrated on dispersion over flat, unobstructed terrain. It is necessary now to consider more complex and obstructed terrain, including that containing buildings and obstructions. The corresponding treatment for passive dispersion is given in Section 15.17.

Some particular types of terrain which have been the subject of investigation include:

(1) slopes and ramps;
(2) fences and vapour barriers;
(3) water spray barrier and steam curtains;
(4) buildings – release upstream;
(5) buildings – release into wake;
(6) buildings – release inside;
(7) industrial sites;
(8) complex terrain.

The three principal approaches are the use of: (1) analytical models, (2) three-dimensional models and (3) physical modelling. The most versatile methods are three-dimensional models and physical modelling, but there is a growing body of analytical models for such features as



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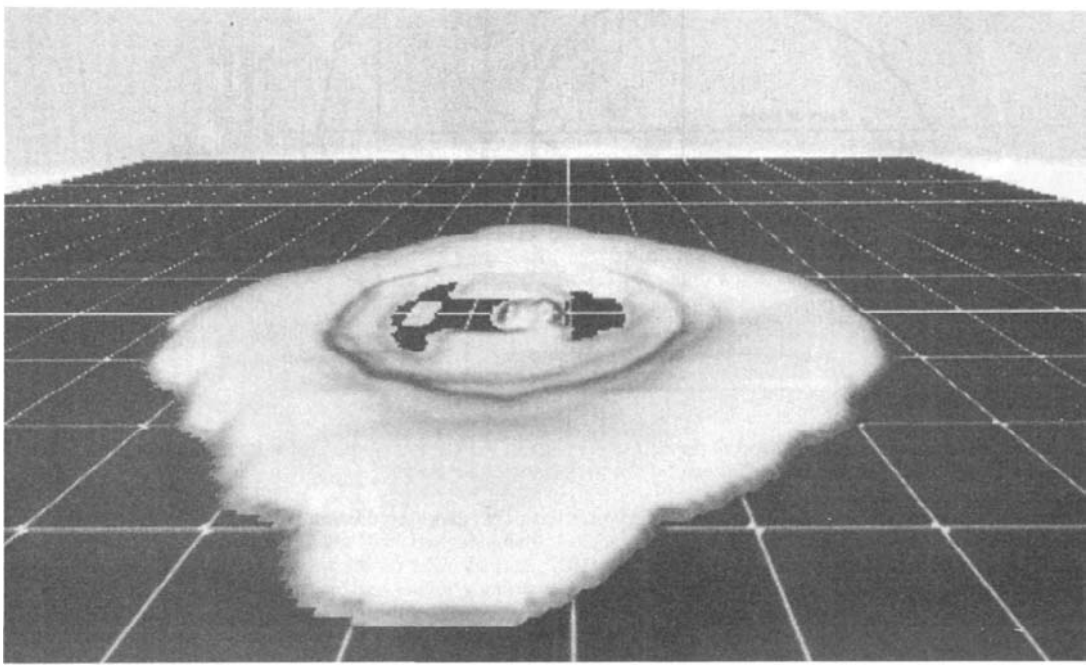


(b)

Figure 15.117 *Wind tunnel simulation of Thorney Island trials on dense gas dispersion – simulation of trial 9 (S.T. Chan, Ermak and Morris, 1987) (a) time 20 s; (b) time 30 s (Courtesy of Elsevier Science Publishers)*

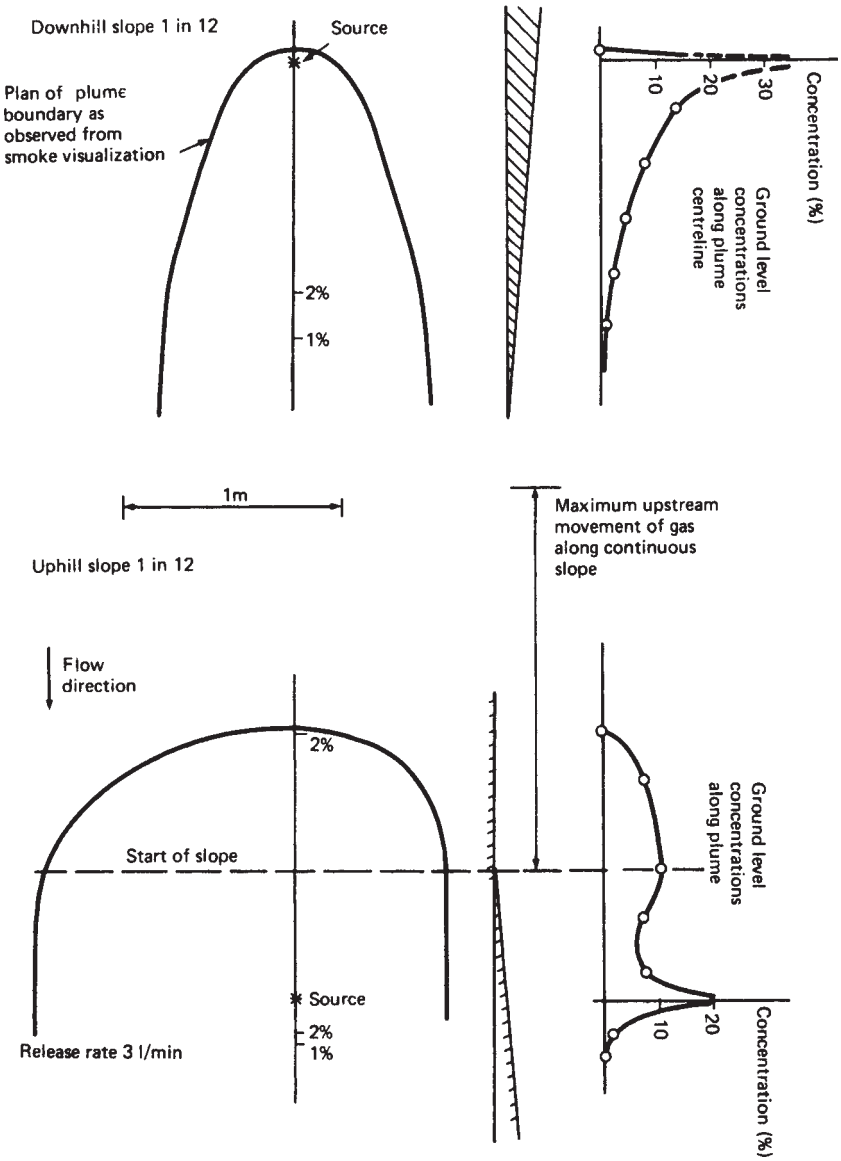


Figure 15.118 *Wind tunnel simulation of dense gas dispersion – universal plume profile for dispersion on a slope (D.J. Hall, Barrett and Ralph, 1976) (Courtesy of Warren Spring Laboratory)*

slopes and obstructions which generally draw on the theory of gravity-driven flow and which may be used alone or in combination with the other methods.

General discussions of the effect of more complex and obstructed terrain have been given by Britter and Griffiths (1982), Gunn (1984), McQuaid (1986) and Britter and McQuaid (1988).

15.40.1 Slopes and ramps

An account of the behaviour of a dense gas on a slope in the field trials at Porton Down has been given by Picknett (1978a), as described in Section 15.37. Analytical models of the dispersion of a dense gas on a slope have been given by several workers.

A gravity current flowing down a slope develops a characteristic thickening at the downhill edge, or 'head'. Ellison and Turner (1959) conducted an experimental and theoretical investigation of the gravity current on a slope. For the experiments they used salt water flowing down an inclined plane in pure water. They found that for the continuous current well behind the head the mean velocity is independent of distance, but that the thickness of the fluid layer

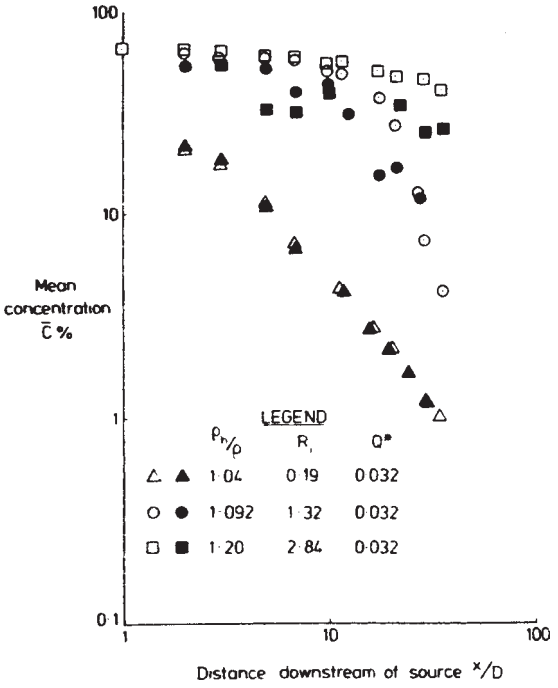


Figure 15.119 *Water tunnel simulation of dense gas dispersion at an obstacle – variation of mean concentration at ground level with distance for gas plumes of different density C̄, mean concentration; D, diameter of plume source; Q* non-dimensional plume spill rate; Ri, Richardson number; x, distance downstream of source; ρ, density of surrounding fluid; ρ_h, density of dense fluid (Cheah, Cleaver and Milward, 1983a) (Courtesy of the Institution of Chemical Engineers)*

increases at a constant rate due to entrainment. The density excess decreases, maintaining a constant buoyancy flux down the slope.

Another experimental and theoretical study is described by Britter and Linden (1980). The experiments again involved the flow of salt water in pure water down an inclined plane. These workers investigated particularly the head of the gravity current on a slope. They found that the behaviour of the head depends on the angle θ of the incline to the horizontal. For $\theta \gtrsim 5°$ the head has a constant velocity, for $\theta \lesssim 0.5°$ its velocity is strongly affected by friction and decreases with distance, whilst in the range $0.5° \lesssim \theta \lesssim 5°$ there is a perceptible but weaker frictional effect.

They also found that the velocity % of the front is proportional to the volumetric flow per unit width:

$$u_f \propto \left(g_o' Q\right)^{1/3} \qquad [15.40.1]$$

with

$$g_o' = 2g\frac{\rho_2 - \rho_1}{\rho_2 + \rho_1} \qquad [15.40.2]$$

where g_o' is a reduced gravity, Q is the volumetric flow per unit width, u_f is the velocity of the front, or head, ρ is the density and subscripts 1 and 2 denote less and more dense fluid, respectively. They obtain the relation

$$\frac{u_1}{\left(g_o' Q\right)^{1/3}} = S_2^{1/3}\left[\frac{\cos\theta}{\alpha} + \frac{\alpha\sin\theta}{2(E + C_D)} + \frac{\sin\theta}{(E + C_D)}\right]^{-2/3} \qquad [15.40.3]$$

with

$$\alpha = u_s/u \qquad [15.40.4]$$

$$E = \mathrm{d}h/\mathrm{d}x \qquad [15.40.5]$$

$$S_2 = \frac{\mathrm{Ri}_n \tan\theta - C_D}{1 + 0.5 S_1 \mathrm{Ri}_n} \qquad [15.40.6]$$

$$\mathrm{Ri}_n = \left(\frac{g' h\cos\theta}{u^2}\right)_n \qquad [15.40.7]$$

$$g' = g\frac{\rho - \rho_1}{\rho_1} \qquad [15.40.8]$$

where C_D is a drag coefficient due to stress at the lower surface, E is a dimensionless rate of entraiment, or entrainment coefficient, g' is a reduced gravity, h is the height of the following flow, u is the mean velocity of the following flow, u_s is the velocity on a defined streamline, x is the downhill distance, S_1 and S_2 are parameters, θ is the angle of incline (°), and subscript n denotes 'normal'. The numerical values of the parameters are typically as follows: $C_D < 0.02$; $0.1 \le S_1 \le 0.15$; $0.6 \le S_2 \le 0.9$; $\alpha \approx 1.2$. Ellison and Turner obtained typical values of $E = 0.001\theta$ and $S_2 = 0.75$.

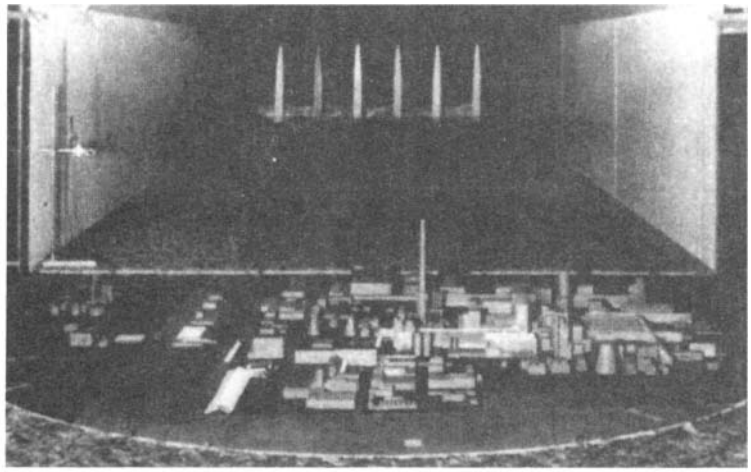
This value of the entrainment coefficient E should be valid for dense gases also, provided the density difference is not too large. For flow of a dense gas on slope there is a significant dilution which quite quickly produces a small density difference.

Britter and Linden found that for the velocity u_f of the head

$$\frac{u_f}{\left(g_o' Q\right)^{1/3}} = 1.5 \pm 0.2 \quad \theta \ge 5° \qquad [15.40.9]$$

The authors give expressions for the mean velocity u of the following flow for limiting cases. For large slopes ($\theta \ge 30°$) they obtain with a small density excess $u_f \approx 0.6u$ and with a large density excess $u_f \approx u$ as $\theta \to 90°$. For small slopes they quote the results of Middleton (1966) to the effect that at very small angles $u_f = u$ and that u_f/u decreases rapidly as θ increases.

De Nevers (1984a) has given a model based on a force balance in which the force in the downhill direction due to gravity, less buoyancy, is balanced by three forces acting in the uphill direction: the shear forces at ground surface and



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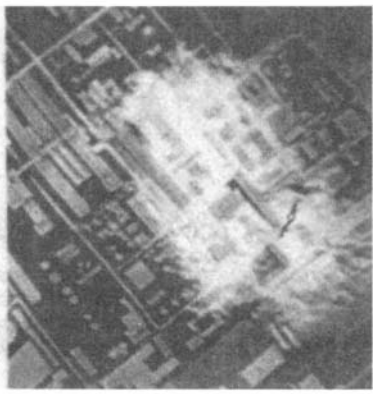

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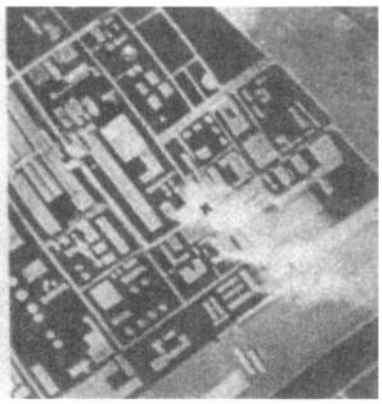


(e)

Figure 15.120 *Wind tunnel simulation of dense gas dispersion over an industrial site – continuous release of ammonia (Guldemond, 1986); (a) model in wind tunnel; (b) dense gas plume on flat terrain; (c) dense gas plume on industrial site; (d) neutral buoyancy gas plume on flat terrain; (e) neutral buoyancy plume on industrial site (Courtesy of the Institution of Chemical Engineers)*

at the top of the cloud, and the form force at the leading edge of the cloud. The force balance on a slope of angle θ is then

$$\pi R^2 H \rho_a g' \sin\theta = \pi R^2 \rho_g \frac{u^2}{2}(f_b + f_t) + 2RH\rho_a \frac{u^2}{2} C_D \quad [15.40.10]$$

and hence

$$u = \left[\frac{2\sin\theta}{(\rho_g/\rho_a)(f_b + f_t) + (2HC_D)/(\pi R)}\right](g'H)^{1/2} \quad [15.40.11]$$

where C_D is the form drag coefficient, f is the friction factor, g' is the reduced gravity, H is the height of the cloud, R is the radius of the cloud, u is the velocity downhill, ρ is the density, and subscripts a and g denote air and gas and b and t the bottom and top of the cloud, respectively.

De Nevers concludes that for even a modest slope the downhill velocity can be as large as the lateral velocity due to gravity spreading. The effect of a degree of slope in the Burro field trials has been investigated by Koopman, Ermak and Chan (1989) using FEM3, as described in Section 15.37.

The universal plume profile of a dense gas on a slope has been studied by D.J. Hall, Barrett and Ralph (1976). This work was described in Section 15.39. A model of the dispersion of a dense gas up a ramp has been given by Britter and Snyder (1988).

The effect of a slope in mitigating the dispersion of a dense gas from a source to an uphill target has been studied by Heinhold, Walker and Paine (1987) using both an analytical model and wind tunnel work. They start by quoting the work of Meroney *et al.* (1977) who carried out wind tunnel tests on the flow of dense gas on a slope with an uphill wind. After the initial gravity slumping, the flow of the gas is governed by the wind speed. There is a critical uphill wind speed below which the dense gas flows downhill and above which it flows uphill.

The authors model this situation as an energy balance between the potential energy which must be supplied to raise a plume element up the slope and the kinetic energy of the wind, and derive the relation

$$\frac{u^2}{2} = g\frac{z}{\theta}\frac{d\theta}{dz} + g'_o z \frac{A_o}{A_p} \quad [15.40.12]$$

with

$$g'_o = \frac{\rho_p - \rho_a}{\rho_p} \quad [15.40.13]$$

where A_o is the initial cross-plume area of the plume element, A_p is the final cross-plume area of the element, g'_o is the initial reduced gravity, u is the wind speed at ground level, z is the height from the source to the target, θ is the potential temperature, ρ is the density, and the subscript p denotes the plume. The left-hand side term is the kinetic energy. The first term on the right-hand side is the potential energy of the atmosphere, assuming constant lapse rate; this is zero for neutral conditions and a maximum for stable conditions. The second term on the right-hand side is the change in potential energy of the element. For a given density, and hence concentration, Equation 15.40.12 may be used to determine the height uphill which the plume can reach. The initial and final cross-plume areas were determined using the authors' own AIRTOX dense gas dispersion model.

Heinhold, Walker and Paine describe the application of this model to releases of liquefied ammonia, assuming complete evaporation of all liquid spray formed. Two release rates were studied, 10 and 100 kg/s. At the lower flow rate the plume became passive at 100 m. Only atmospheric stability inhibited dispersion uphill. At the higher flow rate the plume remained dense beyond 1000 m. In the latter case, the concentration at uphill locations decreased as the slope increased. For slopes of 50 : 1, 10 : 1, 5 : 1 and 2 : 1 the concentration was the following proportion of its value for flat terrain: 98, 90, 83 and 45% at 100 m; 86, 65, 35 and 20% at 200 m and 50, 28, 14 and 8% at 400 m uphill. The authors conclude that a slope can afford an appreciable degree of protection to a target uphill of a source. This is so not only for dense gas but also for passive dispersion.

Deaves (1987b) has described the treatment of the case of dense gas flowing over a river and encountering a river bank on the far side. For this use was made of the model of Rottman *et al.* (1985) for an obstacle, given below.

15.40.2 Fences and vapour barriers

One of the simplest obstacles to the dispersion of a dense gas is a fence, wall or similar barrier. This may be a feature which is already there, but in others a vapour barrier may be expressly erected to effect a reduction in downstream concentrations.

An account of the behaviour of a dense gas encountering a fence in the field trials at Thorney Island has been given by M.E. Davies and Singh (1987a), as described in Section 15.38. Field trials on dispersion of a dense gas at a fence have also been described by M. Nielsen (1991). A simple treatment of the effect of a fence has been given by Jensen (1984).

A model for the behaviour of a dense gas encountering an obstruction such as a fence or vapour barrier has been given by Rottman *et al.* (1985). The situation considered is shown in Figure 15.121(a). The model is based on the shallow water equations. At steady state, the governing equations are

$$\frac{\partial(uh)}{\partial x} = 0 \quad [15.40.14]$$

$$u\frac{\partial u}{\partial x} + g'\frac{\partial(h_w + h)}{\partial x} = 0 \quad [15.40.15]$$

with

$$g' = \frac{\rho - \rho_1}{\rho_1} \quad [15.40.16]$$

where g' is the reduced gravity, h is the height of the dense fluid layer, h_w is the height of the obstacle, u is the velocity of the fluid, ρ is the density of the fluid and subscript 1

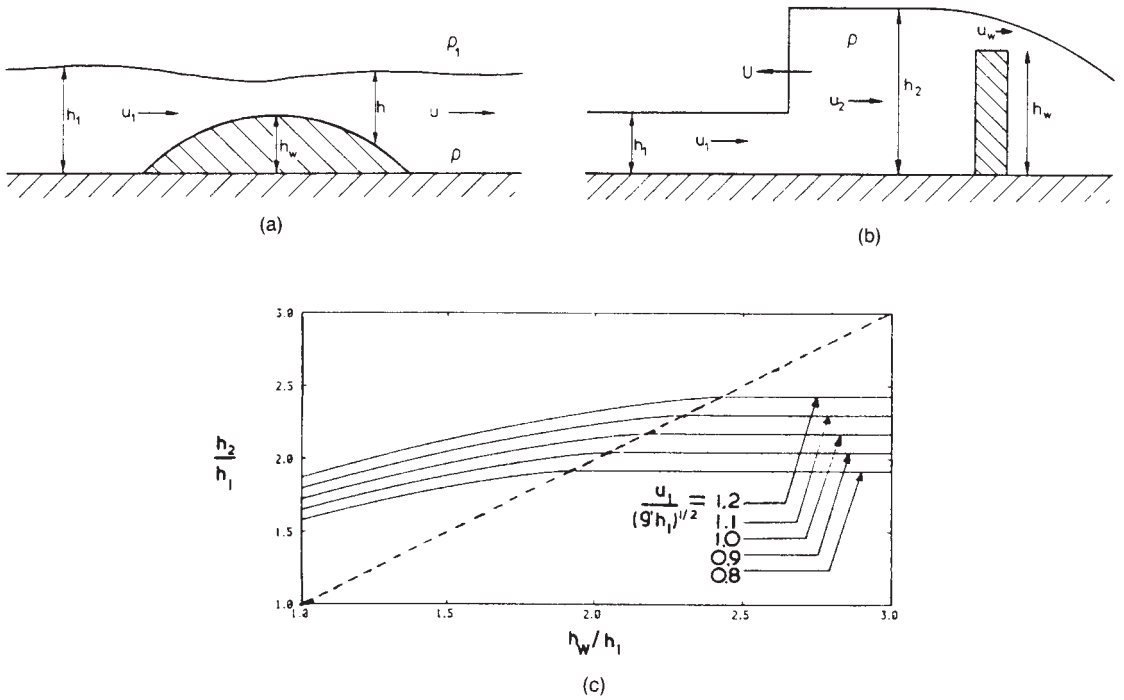


Figure 15.121 *Dispersion of dense gas over an obstacle (Rottman et al., 1985): (a) shallow two-layer flow over an obstacle; (b) shallow two-layer flow over a wall; and (c) solutions of shallow water equations for depth of fluid behind the hydraulic jump as function of wall height (Courtesy of Elsevier Science Publishers)*

denotes upstream. These equations are solved to give

$$uh = u_1 h_1 \qquad [15.40.17]$$

$$\frac{u^2}{2g'} + h + h_w = \frac{u_1^2}{2g'} + h_1 \qquad [15.40.18]$$

The regimes of interest are those of blocked flow and partially blocked flow. The equation of the boundary between these two regimes is

$$\frac{u_1^2}{g'h_1} + 1/2(H_2 - 1)^2\left(\frac{H_w + 1}{H_w}\right) \qquad [15.40.19]$$

with

$$H_w = \frac{h_w}{h_1} \qquad [15.40.20]$$

where H_w is a ratio of heights.

If the flow is completely blocked, the gas does not disperse downwind at all. The dispersion downwind for the case of partial blockage is obtained as follows. This situation is shown in Figure 15.121(b). Conservation of mass and momentum at the jump requires the conditions

$$(u_1 - U)h_1 = (u_2 - U)h_2 \qquad [15.40.21]$$

$$(u_1 - U)^2 = \frac{1}{2}(g'h_1)\frac{h_2}{h_1}\left(1 + \frac{h_2}{h_1}\right) \qquad [15.40.22]$$

and, assuming that flow over the obstacle is critical

$$u_w = (g'h)^{1/2} \qquad [15.40.23a]$$

with

$$\Delta h = h_2 - h_w \qquad [15.40.23b]$$

where Δh is the head difference, U is the velocity of the wave travelling upstream, u_w is the velocity over the obstacle, and subscript 2 is the fluid in the space between the upstream-moving wave and the obstacle.

By mass conservation Equation 15.40.23 can be expressed in terms of u_2 to give

$$u_2^2 = (g'h_2)\left(1 - \frac{h_w}{h_2}\right)^3 \qquad \frac{h_w}{h_2} < 1 \qquad [15.40.24a]$$

$$= 0 \qquad \frac{h_w}{h_2} > 1 \qquad [15.40.24b]$$

It can be shown that Equations 15.40.21, 15.40.22 and 15.40.24 yield for $h_w/h_2 < 1$

$$u_1 - (1 - H_b)U = (g'h_1)^{1/2}\left[H_b\left(1 - \frac{H_w}{H_b}\right)\right]^{3/2} \quad [15.40.25]$$

$$(u_1 - U)^2 = \frac{1}{2}(g'h_1)H_b(1 + H_b) \quad [15.40.26]$$

and for $h_w/h_2 \geq 1$

$$u_1 = (1 - H_b)U \quad [15.40.27]$$

$$U^3 = u_1U^2 - (g'h_1)^{1/2}U + 1/2(g'h_1)^{1/2}u_1 = 0 \quad [15.40.28]$$

with

$$H_b = \frac{h_2}{h_1} \quad [15.40.29]$$

where H_b is a ratio of heights.

Solutions of these equations are shown in Figure 15.121(c). The range $1.5 < h_2/h_1 < 2.5$ covers most cases of interest and as a rule-of-thumb $h_2/h_1 = 2$.

Release upstream of an obstacle such as a fence is one of the two main cases of more complex terrain treated in the *Workbook* by Britter and McQuaid (1988). The treatment is based on the work of Britter (1986 SRD R407). Using the Workbook notation given in Section 15.34, for a plume from a continuous release encountering a fence height H normal to the wind direction the height h of the plume in the absence of the fence is obtained from

$$C_g uh = C_o q_o^* \quad [15.40.30]$$

where C_g is the maximum volumetric concentration at ground level, C_o is the volumetric concentration of the initial release, h is the height of the cloud, q_o^* is the volumetric release rate per unit width and u is the mean velocity at the fence.

The following regimes are distinguished. For $u/(g'_o q_o^*)^{1/3} > 5$ and $H/h \leq 30$, the plume is not blocked by the fence. In the range $4.5 \leq H/h \leq 15$ the ground level concentration is as if the plume were not dense and

$$\frac{C}{C_o}\frac{uH}{q_o^*} = 1.7 \pm 0.3 \quad [15.40.31]$$

whilst in the range $3.5 \leq u/(g'_o q_o^*)^{1/3} \leq 5$

$$\frac{C}{C_o}\frac{uH}{q_o^*} = 2.2 \pm 0.4 \quad [15.40.32]$$

where C is the volumetric concentration.

For $h_{0.5}/H \geq 2$ and $u/(g'_o q_o^*)^{1/3} > 3.5$, where $h_{0.5}$ is the height at which the concentration is half the ground level value, the ground level concentration is little affected by the fence.

As far as concerns plume width, the relations given for the plume widths W_f and W_{nf} with and without a fence, respectively, are as follows. The ratio W_f/W_{nf} increases with increase in fence height:

$$\frac{W_f}{W_{nf}} = 3 \qquad \frac{h}{H} \approx 0.05 \quad [15.40.33a]$$

$$\frac{W_f}{W_{nf}} = 1.5 \quad \frac{h}{H} \approx 0.15 \quad [15.40.33b]$$

W_f/W_{nf} also increases weakly with $u/\left(g'_o q_o/W_{nf}\right)^{1/3}$.

The following relation for concentration in terms of fence width is also given:

$$\frac{C}{C_o}\frac{uHW_1}{q_o} = 2.1 \pm 0.3 \quad 0.04 < \frac{h}{H} < 0.2; \frac{u}{\left(g'_o q_o/W_{nf}\right)^{1/2}} \geq 4 \quad [15.40.34]$$

where q_o is the volumetric rate of release.

Meroney (1991) has described the use of models for the simulation of the effects of a fence on the dispersion of a dense gas. Carissimo *et al.* (1989) have described the use of MERCURE-GL to study the effect of a fence on dense gas dispersion. The water tunnel study by Cheah, Cleaver and Milward (1983a) of dense gas dispersion at a simple barrier has been described in Section 15.39.

15.40.3 Water spray barriers and steam curtains

Work on water spray barriers and steam curtains is described in Section 15.53. Accounts of the use of HEAVYGAS to simulate the effects of the water spray barrier used in the field trials described by Moodie (1981) have been given by Deaves (1983b, 1984). This work is described in Section 15.53. In the work just mentioned on dense gas dispersion at a fence, Meroney (1991) has also treated the case of a water spray barrier.

15.40.4 Buildings: release upstream

Another well defined obstacle to the dispersion of a dense gas is a single building or a defined sequence of buildings. The effect of a building on an upstream release is well treated for passive dispersion, but not so well for dense gas dispersion.

McQuaid (1987) has given an account of the behaviour of a dense gas encountering a building in the field trials at Thorney Island, as described in Section 15.38. A review of turbulent diffusion near buildings, including a treatment of dense gas dispersion, has been given by Meroney (1982). Krogstad and Pettersen (1986) used a wind tunnel to investigate the flow of a dense gas around a rectangular building. The effect of a sequence of rectangular buildings on the dispersion of a dense gas has been studied by Deaves (1989) using an adaptation of the model by Brighton for release into a building wake, described below.

15.40.5 Buildings: release into lee

Release into the immediate lee of a building is another topic where treatments are available for passive dispersion, but where there is less guidance for dense gas dispersion. This case is relevant, however, to a number of scenarios which may arise in practice. In particular, it applies to the case where a spillage occurs from a storage tank and then evaporates in the lee of the tank.

A model for the dispersion of a dense gas in the lee of a building has been given by Brighton (1986). He takes as his starting point the models for passive dispersion in a

building lee given by Vincent (1977, 1978) and Fackrell (1984b), which were described in Section 15.17. A dense gas will tend to reduce the turbulent mixing and, if the flow is large, to modify the mean wake flow, and a separate treatment is necessary.

He considers a rectangular building of height h, width w, length l and frontal area A

$$A = wh \qquad [15.40.35]$$

and a recirculation region, or wake, in the lee with height h, width w, length l_w, surface area S_w and volume V_w. The dimensionless wake length λ_w is defined as

$$\lambda_w - l_w/h \qquad [15.40.36]$$

The basis of the model is the existence of two layers, a lower and an upper layer, in the lee. It is assumed that air flows directly into the upper layer but not into the lower one:

$$F_A = \alpha_o S_w u \qquad [15.40.37]$$

where F_A is the flow of air into the wake, u is the wind speed and α_o is a constant. The concentration of contaminant C resulting from a source of strength Q in the lee is

$$C = Q/F_A \qquad [15.40.38]$$

Then from Equation 15.40.37

$$C = Q/\alpha_o S_w u \qquad [15.40.39]$$

The heights of the two layers are

$$\bar{h}_L = h_L/h \qquad [15.40.40]$$

$$\bar{h}_U = h_U/h \qquad [15.40.41]$$

$$h_L + h_U = h \qquad [15.40.42]$$

where h_L and h_U are the heights of the lower and upper layers, and $\bar{h}_L$ and $\bar{h}_U$ are the corresponding normalized values, respectively. Hence

$$\bar{h}_L + \bar{h}_U = 1 \qquad [15.40.43]$$

The treatment utilizes two main dimensionless parameters:

$$\bar{Q} = \frac{Q}{Au} \qquad [15.40.44]$$

$$B = \frac{g'_o Q}{u^3 w} \qquad [15.40.45]$$

with

$$g'_o = g\frac{\rho - \rho_a}{\rho_a} \qquad [15.40.46]$$

where B is the dimensionless buoyancy flux, g'_o is the reduced gravity at the source, $\bar{Q}$ is the dimensionless release rate, ρ is the density of the cloud and ρ_a is the density of air.

The flow from the lower to the upper layer F_{LU} is equal to that from the upper to the lower layer F_{UL} given that there is no air flow directly into the lower layer. These flows are taken as

$$F_{LU} = F_{UL} = \frac{\alpha_I \lambda_w}{\mathrm{Ri}} \qquad \mathrm{Ri} > \mathrm{Ri}_T \qquad [15.40.47a]$$

$$= \alpha_M \lambda_w \qquad \mathrm{Ri} < \mathrm{Ri}_T \qquad [15.40.47b]$$

where α_I and α_M are mixing coefficients. The Richardson number Ri is defined as

$$\mathrm{Ri} = \frac{(C_L - C_U)g'_o h}{u^2} \qquad [15.40.48]$$

which at the source becomes

$$\mathrm{Ri} = \frac{g'_o h}{u^2} \qquad [15.40.49]$$

The transition Richardson number Ri_T is

$$\mathrm{Ri}_T = \alpha_I/\alpha_M \qquad [15.40.50]$$

From analysis of the flows and concentrations in the wake, Brighton derives for one regime $\mathrm{Ri} \le \mathrm{Ri}_T$:

$$C_L = \frac{(\alpha_M \lambda_w + 0.7\bar{h}_U)\bar{Q}}{0.7\bar{h}_U \alpha_M \lambda_w + (\alpha_M \lambda_w + 0.7\bar{h}_U)\bar{Q}} \qquad [15.40.51]$$

$$C_U = \frac{\alpha_M \lambda_w C_L}{\alpha_M \lambda_w + 0.7\bar{h}_U} \qquad [15.40.52]$$

where C_L and C_U are the volumetric concentrations in the lower and upper layers, respectively. At the limit as $\bar{h}_L \to 0$ and $\bar{Q}_L \to 0$

$$\frac{C_U}{\bar{Q}} \to 1.4 \qquad [15.40.53]$$

whilst at the other limit as $\bar{h}_U \to 0$

$$C_L \to 1 \qquad [15.40.54]$$

This latter case corresponds to the situation where the source strength is so great that the gas released moves with a velocity comparable to the wind speed and occupies the whole of the wake region. For the other regime, with $\mathrm{Ri} > \mathrm{Ri}_T$:

$$C_L = 1 - \frac{\alpha_I \lambda_\omega}{B} \; B \ge \alpha_M \lambda_w \qquad [15.40.55]$$

$$C_U = \frac{\alpha_I \lambda_w}{0.7\bar{h}_U \mathrm{Ri}_o} \qquad [15.40.56]$$

where Ri_o is the initial Richardson number before mixing.

Brighton describes the matching of this model to unpublished experimental work by Britter. He takes for λ_w a value of 2.08, as given by Fackrell $\alpha_I \lambda_w$is taken as 0.036; and α_M as unity, although the influence of this parameter is weak.

This model gives as outputs the width, height and concentration at the end of the wake region. The inputs required for a dense gas dispersion model are these parameters plus the velocity. Brighton suggests matching may be achieved by retaining the width and concentration given by his wake model, but adjusting the height to give mass conservation. This will generally involve a reduction in the height; the plume contracts as it accelerates up to the wind speed.

If the buoyancy flux is large with $B \gg 1$, there is a tendency for the cloud at the source to spread upwind and sideways. For this condition Brighton quotes the relations obtained by Britter (1980):

$$S_U = \frac{1}{2}D + 2L_B \qquad [15.40.57]$$

$$S_L = \frac{1}{2}D + 4L_B \qquad [15.40.58]$$

with

$$L_B = \frac{g'_o Q}{u^3} \qquad [15.40.59]$$

where D is the diameter of the source orifice, L_B is the buoyancy length scale, S_L is the lateral spread of the cloud and S_U is the upwind spread of the cloud. This model has been used by Deaves (1987b, 1989), as described above, in modelling for safety cases.

Release into the lee of a building is the other main case treated by Britter and McQuaid (1988) in the Workbook. The treatment for a continuous release is based on the work of Britter (1982, 1986 SRD R407) on a square flat plate of side H normal to the direction of flow.

For the concentrations in the immediate lee, the following regions or limits are distinguished:

Region 1 $\quad \dfrac{g'_o q_o}{u^3 H} < 4 \times 10^{-3}$

Region 2 $\quad 4 \times 10^{-3} < \dfrac{g'_o q_o}{u^3 H} < 4 \times 10^{-2}$

Limit 3 $\quad \dfrac{g'_o q_o}{u^3 H} > 2 \times 10^{-1}$

Limit 4 $\quad \dfrac{g'_o q_o}{u^3 H} > 1$

where g'_o is the reduced gravity at the source, H is the height of the obstacle, q_o is the volumetric rate of release of material and u is the mean velocity at the obstacle height.

In region 1, the release rate is so low that the density of the release has virtually no effect on the concentration. In region 2, the lateral width of the plume is maintained within the recirculation zone in the immediate lee. At limit 3, there is some enhanced dilution in the immediate lee but the effect is weak. By limit 4, the effect of the obstacle has become negligible.

In both regions 1 and 2 by a distance of $x/H = 2$ the concentration is given by the relation

$$\frac{C}{C_o}\frac{uH^2}{q_o} \approx 1.5 \qquad [15.40.60]$$

where C is time mean ground level volumetric concentration and C_o is the volumetric concentration at the source.

These results apply for the condition (q_o/uH^2) or (q_o/uH^2) less than about 0.1, where q'_o is the volumetric rate of release per unit length. Further downwind, the effect of the density difference is liable to reassert itself. For concentrations further downwind, one approach is to work in terms of a new source with values of q_o and g'_o determined from the value of C.

15.40.6 Buildings: release inside

A release of gas may occur inside a building and then escape into the atmosphere. A study of this scenario has been made by Brighton (1986, 1989 SRD R468). The particular case of interest was a release of liquefied chlorine.

For a continuous release of gas into a space ventilated by air, the molar flow of gas is

$$\frac{q_G}{M_G} = \frac{N_G Q}{V} \qquad [15.40.61]$$

and that of air is

$$\frac{Q_A \rho_A}{M_A} = \frac{N_G Q}{V} \qquad [15.40.62]$$

where M is the molecular weight, N is the number of moles, Q is the volumetric flow, V is the volume of space, ρ is the density, and subscripts A and G denote air and gas, respectively. The variables Q and ρ without a subscript refer to the gas-air mixture.

The natural ventilation flow Q_A is given by the ventilation equation

$$Q_A = bA(\Delta P/\rho_A)^{1/2} \qquad [15.40.63]$$

where A is the area of the opening, ΔP is the pressure difference between the outside and the inside, and b is a constant. Equation 15.40.63 is an application of Bernouilli's equation and is a standard relation given in various ventilation codes such as BS 5925: 1980. The value of constant b is taken by Brighton as 0.88. The pressure drop is a function of the wind speed u:

$$P = \frac{1}{2}C\rho_A u^2 \qquad [15.40.64]$$

where C is a pressure coefficient. Values of C for cuboid buildings are tabulated in BS 5925: 1980. They are in the range 0.7–0.8 for an upwind face, −0.8 to −0.5 for the sides, and −0.4 to −0.1 for the lee.

The cases considered are (1) release under gravity alone and (2) release under the combined influence of gravity and wind. For the first case, Equation 15.40.63 is used for the air flow; Equation 15.40.64 is not used. For this case, the gas–air mixture flows out through an area at the bottom of the space and air flows in through an area at height h at the top of the space. The hydrostatic pressure is

$$= (\rho - \rho_A)gh \qquad [15.40.65]$$

where ρ is the density of the gas–air mixture and ρ_A is the density of air. The pressure at the top openings is

$$= P_o - P' \qquad [15.40.66]$$

and that at the bottom opening is the sum of these

$$= P_o - P' + (\rho - \rho_A)gh \quad [15.40.67]$$

where P is the pressure difference between atmospheric pressure and the internal pressure and P_o is the atmospheric pressure. Applying Equation 15.40.63 to the two areas, the inflow of air is

$$Q_A = bA_i(P'/\rho_A)^{1/2} \quad [15.40.68]$$

and the outflow of gas–air mixture is

$$Q = bA_o\left(-P'/\rho + \frac{\rho - \rho_o}{\rho}gh\right)^{1/2} \quad [15.40.69]$$

where A_i is the area for inflow and A_o is the area for outflow.

Eliminating P from Equations 15.40.68 and 15.40.69 and then utilizing Equations 15.40.61 and 15.40.62 yields

$$\tilde{q}_G = \tilde{N}_G\left(\frac{\rho/\rho_A - 1}{n^2\tilde{N}_G^2 + a^2\rho/\rho_A}\right)^{1/2} \quad [15.40.70]$$

with

$$\tilde{q}_G = \left(\frac{M_A q_G}{bM_G\rho_A A_i(gh)^{1/2}}\right) \quad [15.40.71]$$

$$\tilde{N}_G = \frac{N_G R T_A}{P_o V} \quad [15.40.72]$$

$$a = A_i/A_o \quad [15.40.73]$$

$$n = N_A/N_G \quad [15.40.74]$$

where a is the ratio of areas, n is the ratio of molar flows, $\tilde{N}_G$ is a dimensionless quantity, q_G is the flow of gas, $\tilde{q}_G$ is the dimensionless flow of gas, R is the universal gas constant and T_A is the absolute temperature of the air.

Treating the contents of the space as a mixture of perfect gases or a two-phase mixture with vapour fraction f

$$\tilde{N}_G = \frac{1}{1+f}\,\frac{T_A}{T} \quad [15.40.75]$$

where f is the vapour fraction and T is the absolute temperature of the gas–air mixture.

The time τ for the concentration of the gas to reach steady state if outflow is neglected is

$$\tau = \frac{M_G N_G}{q_G} \quad [15.40.76]$$

$$\frac{\bar{\tau} V}{bA_i(gh)^{1/2}} \quad [15.40.77]$$

with

$$\bar{\tau} = \frac{\tilde{N}_G}{\tilde{q}_G} \quad [15.40.78]$$

For this case n and $\bar{\tau}$ are shown in Figures 15.122(a) and (b), respectively.

For the second case, that of release under the combined influence of gravity and wind, use is made of both Equations 15.40.63 and 15.40.64. For this case, it is necessary to consider several different situations since, depending on the configuration, the ventilation flow may assist or oppose the gravity flow. This is illustrated in Figure 15.123. For Case (a) in Figure 15.123, the inlet opening is high up on the upwind face and above the outlet opening and hence the ventilation effect always assists the gravity effect. For Cases (b) and (c) the inlet opening is low down on the upwind face and below the outlet opening and hence the ventilation effect opposes the gravity effect. In Case (b) the ventilation effect is strong enough to overcome the gravity effect, whilst in Case (c) it is not. Case (a) is termed the 'co-operative combined' mode, whilst Cases (b) and (c) are termed the 'opposing combined' mode.

A Richardson number is defined as

$$\mathrm{Ri} = \frac{2gh}{(C_i - C_o)u^2} \quad [15.40.79]$$

where C_i is the pressure coefficient for the inflow opening and C_o is that for the outflow opening.

The point at which gravitational and wind effects are of equal importance is given by

$$\mathrm{Ri}^{-1} = \rho/\rho_A - 1 \quad [15.40.80]$$

Then, incorporating the additional pressure term from Equation 15.40.64 and proceeding as before yields

$$\tilde{q}_G = \tilde{N}_G\left(\frac{1 - \rho/\rho_A + \mathrm{Ri}^{-1}}{n^2\tilde{N}_G^2 + a^2\rho/\rho_A}\right)^{1/2}$$
$$\mathrm{Ri} < (\rho/\rho_A - 1)^{-1} \quad \text{(Case (b))} \quad [15.40.81a]$$

$$\tilde{q}_G = \tilde{N}_G\left[\frac{\rho/\rho_A - 1 - \mathrm{Ri}^{-1}}{n^2\tilde{N}_G^2 + (1/a^2)\rho/\rho_A}\right]^{1/2}$$
$$\mathrm{Ri} > (\rho/\rho_A - 1)^{-1} \quad \text{(Case (c))} \quad [15.40.81b]$$

For this case, n and $\bar{\tau}$ are shown in Figures 15.124(a) and (b), respectively. The plots have a rather peculiar shape. At values of $\tilde{q}_G$ below a critical value, there are three steady-state solutions, of which one is unstable. For the case of a space containing originally zero concentration of the gas, it is the higher value of η in Figure 15.124(a) which represents the eventual steady state. At values of $\tilde{q}_G$ above the critical value there is only one steady state.

Accounts of the use of this work in the modelling of dense gas dispersion for safety cases have been given by Deaves (1987b, 1989).

15.40.7 Industrial sites

There have been several studies of the effect on the behaviour of a dense gas when it disperses over an industrial site containing features such as process plants, storages or terminals.

C.I. Bradley and Carpenter (1983) have conducted an investigation of dense gas dispersion at a storage and

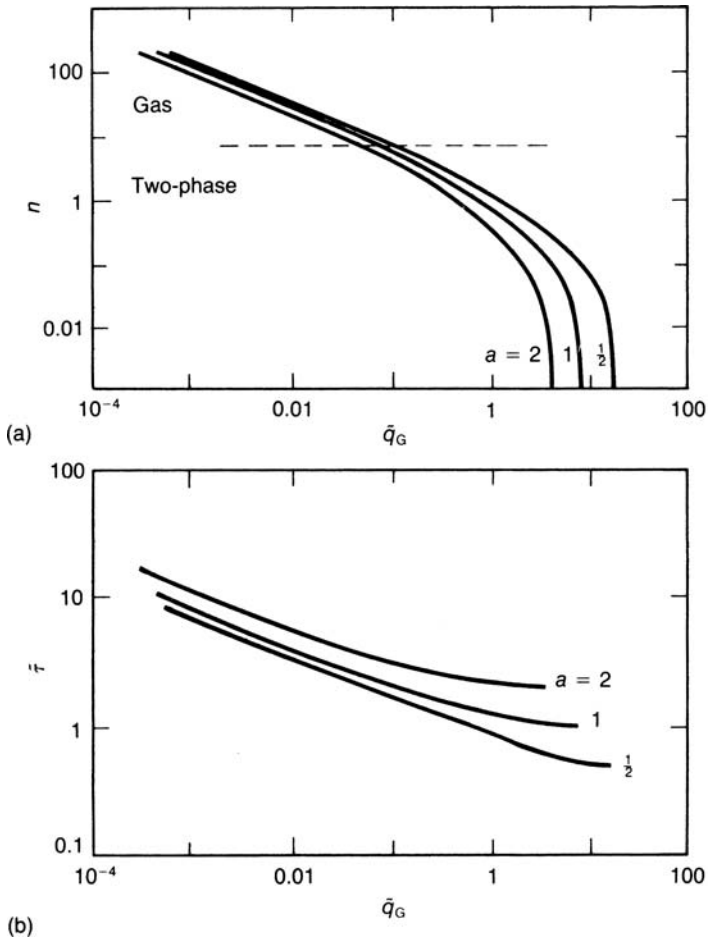


Figure 15.122 *Brighton model of release of gas inside a building – continuous release of chlorine under gravity alone (Brighton 1989, 3RD R468): (a) air/chlorine molar flow ratio; (b) dimensionless time (Courtesy of the UKAEA Safety and Reliability Directorate)*

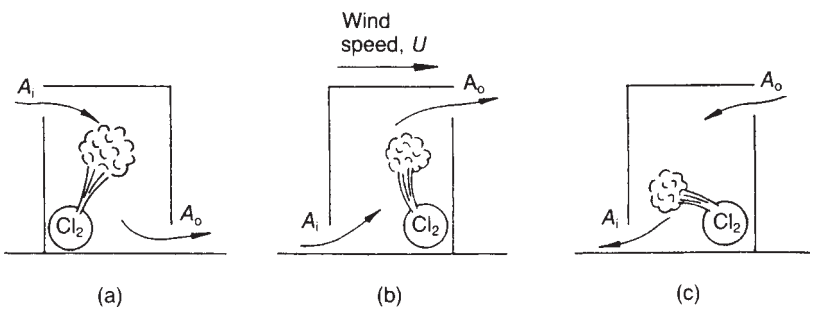


Figure 15.123 *Brighton model of release of gas inside a building – modes of release (Brighton 1989 SRD R468): (a) cooperative combined mode; (b) opposing combined mode* $Ri < (\rho/\rho_o - 1)^{-1}$*; (c) opposing combined mode* $Ri > (\rho/\rho_o - 1)^{-1}$ *(Courtesy of the UKAEA Safety and Reliability Directorate)*

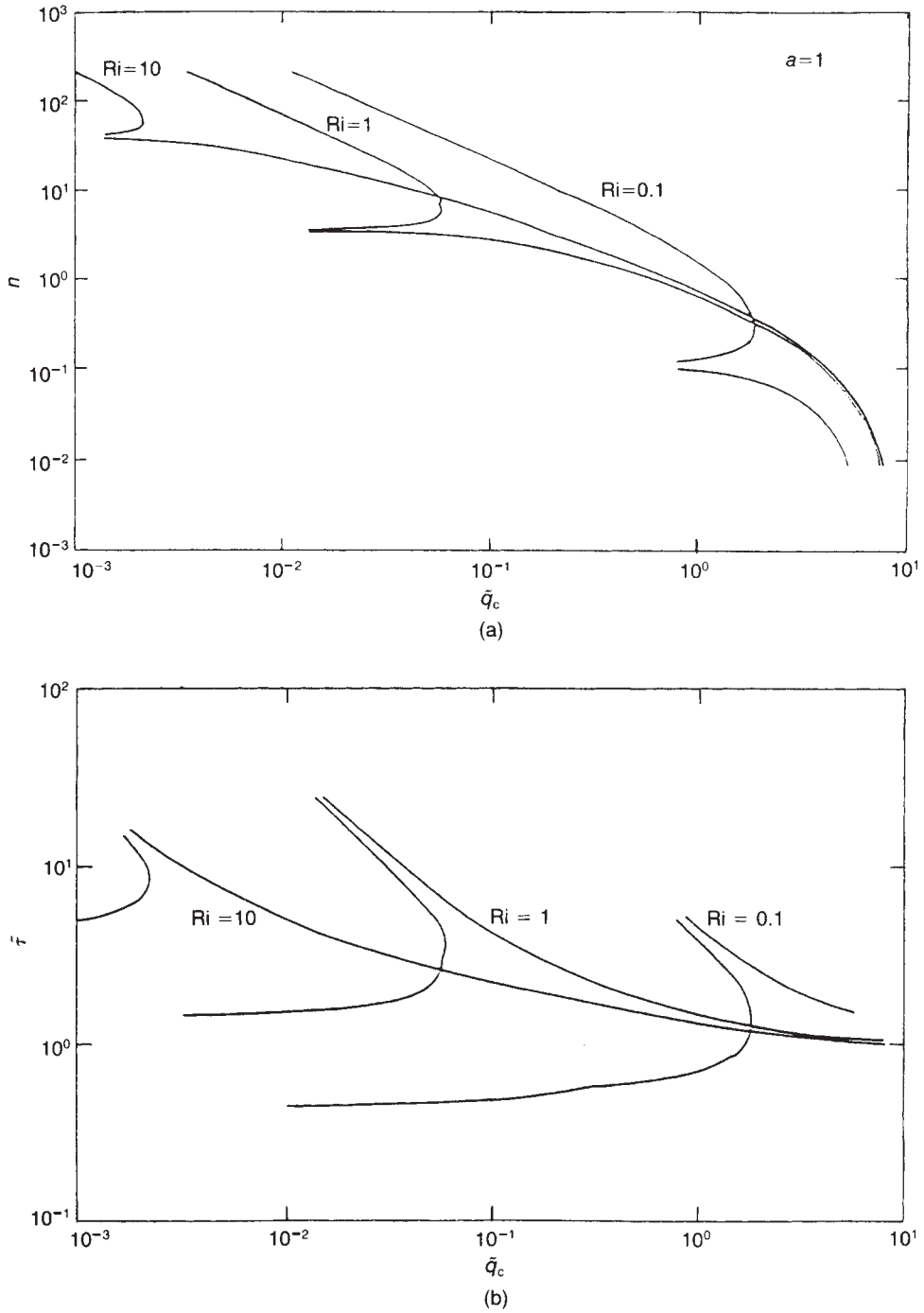


Figure 15.124 *Brighton model of release of gas inside a building – continuous release of chlorine in opposing combined mode with a = 1 (Brighton, 1989 3RD R468): (a) air/chlorine molar flow ratio n; and (b) dimensionless time (Courtesy of the UKAEA Safety and Reliability Directorate)*

terminal site using both ZEPHYR and wind tunnel modelling. This work is described in Section 15.39. An account is also given in the same section of the work of Guldemond (1986) on a wind tunnel study of dispersion of ammonia on an industrial site.

Deaves (1989), in the work on safety cases already mentioned, used HEAVYGAS to study dense gas dispersion over a works site. An account of this study is given in Section 15.33.

Both in the work of Bradley and Carpenter and in that of Deaves the presence of the industrial site caused a reduction in the hazard range compared with unobstructed ground. This reduction was typically of the order of 2, although this value should be regarded as no more than a pointer.

15.40.8 Complex terrain

Complex terrain such as hills and valleys appears not to have been investigated to any great extent in relation to dense gas dispersion. Such terrain is of practical importance for passive dispersion of pollutant gases where the contamination distances are typically some kilometres, but of less concern for dense gas dispersion where the hazard ranges tend to be shorter. Likewise, coastal regions and urban areas have not received much attention as far as dense gas dispersion is concerned.

15.41 Dispersion of Dense Gas: Validation and Comparison

In the account given so far of dense gas dispersion, the various models have been presented, often with some mention of comparisons made with experimental work, and physical modelling has been described, much of it simulating field trials.

The degree of scale-up between laboratory experiments (or even field trials) and incident scenarios, the differences in the definitions of concentration used and the variability of concentration between different realizations of an ensemble of experiments, the large number of models and the appreciable differences in the predictions which they give, and the variety of outputs which may be of interest, all underline the need for methods of evaluating models.

Model evaluation has been a live issue for passive dispersion, as described in Section 15.15. Approaches to validation of models of dense gas dispersion have been described by Fay (1980), Wheatley and Webber (1984 CEC EUR 9542 EN), Brighton (1987) and Mercer (1988).

15.41.1 Degree of scale-up

The degree of scale-up which is involved in going from even the largest field trials to the scenario of a major incident can be very large. For example, the Thorney Island trials involved 2000 m^3 of gas. The LNG spill studied by Havens (1978) involved 25,000 m^3 of LNG, equivalent to 6×10^6 m^3 of gas; this is a scale-up of over three orders of magnitude.

15.41.2 Differences between models

At the start of the Thorney Island trials the organizers invited modellers to submit for defined conditions and releases the profile of concentration with downwind distance which their models predict for a particular scenario. The results of this exercise are illustrated in Figure 15.125. The figure shows a high degree of variability between the models.

15.41.3 Differences in model outputs

There is large variety of outputs which have been used by authors of models in making comparisons with

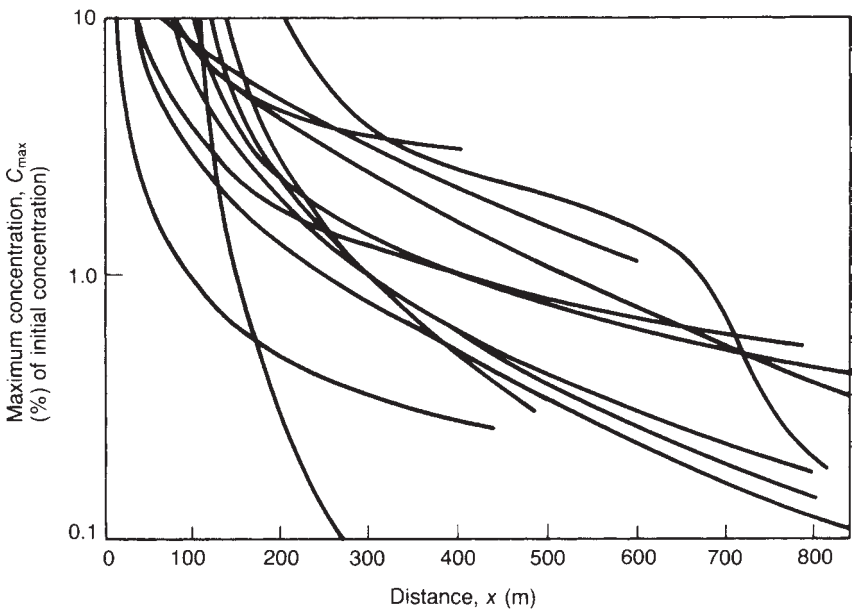


Figure 15.125 *Evaluation of models for dense gas dispersion – predictions of different models prior to the Thorney Island trials (McQuaid, 1984b) (Courtesy of Springer Verlag)*

experimental results. A review of these outputs has been given by Mercer. They include the concentrations

(1) bulk concentration as function of distance or time;
(2) peak concentration as function of distance or time;
(3) concentration at a given distance and time;

and

(4) cloud radius or height as a function of distance or time;
(5) location of cloud centre, leading edge or trailing edge, peak concentration as a function of time;
(6) maximum downwind extent of the lower flammability limit (LFL) or (1/2) LFL

Mercer gives details of comparisons made, showing there is little uniformity in the choice of outputs used for comparison.

15.41.4 Definition and determination of concentration

In large part, the problem of evaluation centres around that of defining the experimental concentrations and then obtaining experimentally stable values for these. One problem is that the values of the concentration obtained in a single trial vary with the sampling time. It is necessary that the sampling time be clearly defined both for the model and for the experiment.

Frequently, experimental results are reported using some kind of average concentration at a fixed location. Usually, for the plume from a continuous release the concentration used is a long-time average, whilst for the cloud from an instantaneous release it is a short-time average. Likewise, a model should include adequate definitions of the concentration to which the predictions are intended to apply. Such definitions are exemplified by those given in the Workbook. For a continuous release the correlations are for a concentration averaged over 10 min, whilst for a instantaneous release they are for the ensemble average of the maximum of 0.6 s mean concentrations.

A second problem is that there is a high degree of variability between the values of a concentration measured in experiments under the same nominal conditions. In principle, it is necessary to perform sufficient experiments to obtain a stable ensemble value. However, this is impractical with large field trials. Yet it is highly desirable that the predictions of models be compared with large-scale experiments.

A third problem is that the maximum concentration of a plume occurs on the centre line, but in relation to a fixed location this centre line may be continuously displaced due to plume meander. An alternative approach described by Puttock, Blackmore and Colenbrander (1982) is therefore to reconstruct from experimental measurements the variation of the location of the centre line with time and to utilize for comparison the concentrations on this reconstructed centre line.

A more detailed discussion of concentration is given in Section 15.45. The work described there, particularly that of Chatwin and co-workers, points to a fundamental approach in which the concentration is defined in terms of concentration probability contours.

15.41.5 Methods of evaluation

Some of the methods available for checking a model are described by Mercer. The predictions of the model may be compared with experimental work, either by the authors or by others. The data may also be compared with those from other models. The sensitivity of the predictions may be investigated. The variables and the dimensionless quantities used in the model may be examined. The constants in the submodels may be optimized by comparison with observation.

15.41.6 Comparison between models and experiments

Most authors of models have presented some comparison of predictions from their model with results of experimental work, ranging from laboratory-scale experiments to field trials. However, as just described, the problem of evaluation is a complex one, and such comparisons are frequently pointers rather than full validations.

A review of comparisons between models and experiments has been given by Mercer (1988). He defines a number of variables which are commonly compared (as described above), tabulates those which have been used in particular comparative studies and lists the data sets used in these studies. He comments that there is little commonality in the variables chosen for comparison and little justification given for the choice of experiments with which to make the comparison.

15.41.7 Comparison between models and experiments: some studies

Some mention of comparisons made between models and experiments has been made above in the accounts given of the individual models. In most cases, these are comparisons made by the authors themselves. There have also been a number of comparative studies involving a number of models and trial series. Reviews of studies involving comparison of models with experiments have been given by Blackmore, Herman and Woodward (1982) and the CCPS (1987/2).

The CCPS (1987/2) describes evaluation studies by a number of workers. Quantities compared include: cloud dimensions; concentration contours, both in plan and crosswind elevation views; concentration vs distance; and mean relative error.

J.L. Woodward *et al.* (1982, 1983) have compared the Germeles and Drake model, the Eidsvik model, HEGADAS, ZEPHYR and MARIAH with the Dutch Freon, Matagordo Bay and Porton Down trials. Quantities compared include cloud height, cloud concentration contour (for LFL), and the concentration vs time profile at a fixed point.

A comparison has been given by Havens, Spicer and Schreurs (1987a) of SIGMET-N, ZEPHYR, MARIAH-II and FEM3 with the Burro trials, the quantity compared being concentration vs distance.

Koopman, Ermak and Chan (1989) have described a comparison of the Gaussian model, SLAB, FEM3 and HEGADAS and the proprietary model CHARM with the Burro, Coyote, Desert Tortoise, Eagle, Goldfish, Falcon, Maplin Sands and Thorney Island trials. Quantities compared include: concentration contours, both in plan and crosswind elevation views; concentration vs distance; and cloud temperature vs distance.

S.R. Hanna, Strimaitis and Chang (1991b) have compared the Gaussian model, INPUFF, HEGADAS, DEGADIS and the Workbook model and the propriety models AIRTOX and CHARM with the results of the Burro, Coyote, Desert Tortoise, Goldfish, Porton Down, Maplin Sands and Thorney Island trials and also with the passive dispersion

Hanford and Prairie Grass trials. The quantities compared were the fractional bias and the normalized mean square error, evidently for the concentrations at different distances.

Touma *et al.* (1991) have compared SLAB, HEGADAS and DEGADIS and also AIRTOX and CHARM with the results of the Burro, Desert Tortoise and Goldfish trials, the quantity compared being concentration vs distance.

In some cases (e.g. CCPS, 1987/2) investigators have found the performance of the Gaussian model to be virtually as good as that of dense gas dispersion models, though this finding should be treated with caution.

15.41.8 Comparison between models and experiments: some problems

The use of data from field trials to validate models involves a number of problems. An account of these in the context of the Thorney Island trials has been given by Brighton (1987). He describes in detail the sources of error in the data obtained from such trials.

The data required depend on the type of model. The data yielded by a trial are a set of measurements of profiles of concentration vs time at each sensor within the cloud together with the parameters.

For a three-dimensional model the outputs are again concentration vs time profiles and thus comparison is relatively straightforward. A problem can arise, however, if the experimental measurements are taken very close to the ground. The grid size in the three-dimensional model may be too coarse to give an accurate prediction of these concentrations.

The comparison is more difficult for a box model. It is not a simple matter to extract from the experimental data the quantities required by modellers. The extent of the processing necessary to convert the Thorney Island results into a data set that conforms with the requirements of modellers was indicated in Section 15.38.

Quantities required are those such as mean concentration, cloud dimensions and advection velocity. Brighton gives examples of the differences in the estimates of these quantities given by different workers.

In view of the work involved in establishing the data sets required to conduct model evaluations, it is valuable, where the data permit it, to have an archive of data in standard format. S.R. Hanna, Strimaitis and Chang (1991b) describe the creation of such a modeller's data archive (MDA).

15.41.9 Comparison between different models: some studies

In addition to comparisons between predictions of models and results of experiments made by the authors of the particular model, comparisons have also been made between a number of models. A series of studies of the performance of available models has been carried out by Havens, starting with the LNG spill studies described in Section 15.22. Mention of some of the other comparisons made between models has been made in the accounts of the various models.

The CCPS Workbook of Test Coses for Vapor Cloud Source Dispersion Models (CCPS, 1990/8) gives results from a number of models, principally the Gaussian dispersion model, SPILLS, SLAB and DEGADIS, and thus gives a comparison of models in a set of typical hazard assessment applications.

15.41.10 Measures for evaluation

There have been, therefore, quite a large number of model evaluation studies. Most of these studies have relied on essentially *ad hoc* criteria of evaluation. One problem in developing evaluation criteria is to identify those parameters which are the best discriminators. Thus, for example, one of the main features which a model should predict is the degree of air entrainment. The cloud radius tends not to be a good discriminator for this. It is the height which is much more strongly affected by entrainment.

Another problem is the formulation of criteria which allow comparisons to be made between models. Here criteria such as cloud dimensions or concentration profiles may be abandoned in favour of statistical measures. There is no generally accepted set of measures for validating models, but several authors have developed particular methods.

Fay (1980) has utilized a scatter diagram technique in which for the variable of interest the experimental value is plotted against the model value. By normalizing the variable, the method can be extended to allow comparisons to be made between the experimental value and the values predicted by different models. One of the plots using a normalized variable given by Fay is shown in Figure 15.126.

Work on goodness-of-fit measures (GFMs) between area-averaged concentrations obtained in experiments and concentrations given by box models has been described by Wheatley, Prince and Brighton (1985).

S.R. Hanna, Strimaitis and Chang (1991b) have utilized two statistical measures: the fractional bias (FB) and the normalized mean square error (NMSE). They give a series of plots of FB vs NMSE, each showing the performance of a number of models for a particular series of trials.

In wind tunnel work there is evidence of a degree of uniformity in comparing results of field experiments and of physical modelling, in that several workers have adopted the practice of D.J. Hall, Hollis and Ishaq (1982, 1984) in utilizing cloud width, arrival and departure times, and concentration vs time profiles.

15.41.11 Extent of validation attainable

For gas dispersion modelling generally, it has to be recognized that there may be limits to the degree of agreement which can be expected between model predictions and experimental results. A discussion of the problem is given by Mercer (1988). In large part, it centres on the variability of concentrations just described. Mercer quotes the following statement by Lamb (1984) made in the context of air pollution and its regulation:

> The predictions even of a perfect model cannot be expected to agree with observations at all locations. Consequently, the goal of 'model validation' should be one of determining whether observed concentrations fall within the interval indicated by the model with the frequency indicated, and if not, whether the failure is attributable to sampling fluctuations or is due to failure of the hypotheses on which the model is based. From the standpoint of regulatory needs the utility of a model is measured partly by the width of the interval in which a majority of observations can be expected to fall.

For heavy gas dispersion specifically, the high degree of inertia of the cloud results in some reduction in the variability which would otherwise occur. Mercer suggests that

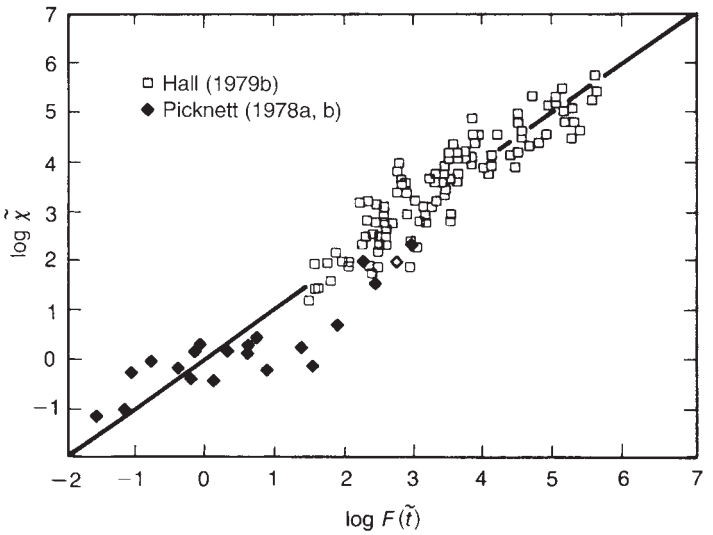


Figure 15.126 *Evaluation of models for dense gas dispersion – comparison of observed peak concentrations with those predicted by models τ, time of passage of peak concentration; $\tilde{\chi}$ peak cloud concentration. (Fay and Ranck, 1983) (Courtesy of Pergamon Press)*

a realistic expectation for a model may be that its predictions be accurate within a factor of 2–3.

In order to reduce the degree of uncertainty, the experimental work should cover a wide range of conditions and scales and should include repeat experiments, which may most conveniently be obtained by physical modelling.

15.41.12 Validation of models against Thorney Island trials: Phase I

Mention has already been made of the exercise carried out before the Thorney Island trials in which modellers were invited to submit predictions from their models. A large number of comparisons have been presented between the results of the Thorney Island Phase I trials and those from model simulations. Some of these comparisons are listed in Table 15.53.

15.41.13 Validation of models against Thorney Island trials: Phase II

The number of models which are capable of simulating dense gas dispersion over other than flat, unobstructed terrain is limited, and the number of comparisons between the results of the Thorney Island Phase II trials and those from model simulations is correspondingly smaller. Such comparisons have been given for SLUMP and HEAVYGAS by Deaves (1985, 1987a,b).

15.41.14 Comparison of physical models with Thorney Island trials

Comparisons have also been presented between the results of the Thorney Island trials and those from physical modelling, predominantly in wind tunnels. Mention has already been made of the exploratory work done by D.J. Hall, Hollis and Ishaq (1982, 1984) using a wind tunnel to assist in the design of the trials. Some of the trials conducted were sufficiently close to these pre-trial experiments to allow comparison to be made. These comparisons have been reported for trials 7, 11, 13, 15 and 18 by D.J. Hall and Waters (1985). Further comparisons include those for trial 8 by van Heugten and Duijm (1985) and for trial 20 by Knudsen and Krogstad (1987). A programme of wind tunnel simulations for all the Thorney Island trials has been described by M.E. Davies and Inman (1987).

15.42 Dispersion of Dense Gas: Particular Gases

So far the account given of dense gas dispersion has been a general one. It is now necessary to consider some gases of industrial interest for which the dense gas behaviour is governed by the specific characteristics of the gas. The gases considered are:

(1) propane;
(2) LNG;
(3) chlorine;
(4) ammonia;
(5) hydrogen fluoride.

The source terms for some of these gases are considered in Section 15.23. The validation of models against experimental work on, and the application of these models to simulations for, these gases are treated in the sections on the individual models, Sections 15.25–15.36. Mitigation of releases of the gases is dealt with in Sections 15.53 and 15.54.

The account in this section deals with the effect on the density of the gas cloud of the following factors:

(1) molecular weight;
(2) boiling point;
(3) chemical behaviour;
(4) atmospheric humidity;
(5) surface heat transfer;
(6) liquid spray.

Table 15.53 *Some comparisons made between results of Thorney Island Phase I trials and results of model simulations*

Model	*Authors*
van Ulden	van Ulden (1987)
BG/C&W	Carpenter *et al.* (1987); Cornwell and Pfenning (1987)
FEM3	S.T. Chan, Ermak and Morris (1987)
HEGADAS	Cornwell and Pfenning (1987)
HEGABOX/HEGADAS	Puttock (1987b)
DEGADIS	Spicer and Havens (1985, 1987)
Fay and Ranck	Sherrell (1987)
Eidsvik	Gotaas (1985); Cornwell and Pfenning (1987)
Picknett	Sherrell (1987)
Webber and Wheatley	Webber and Wheatley (1987)
CIGALE2	Cabrol, Roux and Lhomme (1987)
MARIAH II	Cornwell and Pfenning (1987); Havens, Schreurs and Spicer (1987)
MERCURE-GL	Riou (1987)
Jacobsen and Magnussen	Jacobsen and Magnussen (1987)

The modelling of the dispersion of these materials raises two questions: whether the gas cloud is dense immediately following the initial release; and, if so, how the cloud changes in density and whether it becomes buoyant. The main interest is in the behaviour of the gas cloud from release of a liquefied gas.

15.42.1 Propane

Propane has a molecular weight of 44. It is dense by virtue of its molecular weight. This is so whether the release is one of propane gas or liquefied propane.

The normal boiling point of propane is −42°C. If the release is one of liquefied propane, the low temperature makes the gas cloud initially somewhat more dense. In principle, heating up of the gas will render it less dense. However, the initial temperature difference between the gas at its boiling point, and the ambient features, the ground or water surface and the atmosphere, is not great and heat transfer to the gas does not play a major role. Any density changes due to temperature changes tend to be small.

The density of the gas cloud will also be affected by atmospheric humidity and by any liquid present as spray. The effect of these factors on the density of propane gas clouds does not appear to have been much studied, but some indication may be obtained from their effect on clouds of the other gases, as described below. Propane is generally modelled as a 'simple' dense gas.

15.42.2 LNG

The characteristics of the gas cloud from a release of LNG, mainly methane, have been described by Puttock (1987c). Broadly, LNG releases normally give rise to dense gas clouds. However, under conditions of very high atmospheric humidity the initial cloud may be buoyant, whilst in other cases the cloud, initially dense, may become buoyant with time due to surface heat transfer.

LNG is mainly liquefied methane and, as such, has a molecular weight of 16 and a normal boiling point of −161°C. Insofar as it behaves as a dense gas, it does so by virtue of factors other than its molecular weight. Of these the principal factor is temperature. The gas is sufficiently cold that on release it is dense.

The temperature difference between the cold gas and the ambient features is significant. Heat transfer from the atmosphere and from the surface is appreciable and can have a significant effect on the density. The gas may be heated up sufficiently that it becomes buoyant.

Another factor which affects the density of the gas cloud is the humidity. The cold gas causes condensation, and also freezing, to occur and the heat release consequent on these phase changes causes heating of the cloud. If the humidity is high, this can just cause the cloud to become buoyant.

Figure 15.127, from Puttock, gives relative density vs concentration curves for mixing of methane at its boiling point with air with relative humidity (RH) as parameter. They show that with dry air (RH = 0%) the gas cloud remains dense at all concentrations, whereas with wet air (RH = 100%) the cloud is slightly buoyant at lower concentrations.

The effect of the above variables is illustrated in the modelling work done on the Maplin Sands trials, described by Puttock. Using a version of the HEGADAS model in which surface heat transfer and atmospheric humidity were neglected gave downwind distances to the LFL which were large and exceeded those observed, whilst inclusion of these effects in the model reduced the distances appreciably and brought them closer to the observed values. This is illustrated in Figure 15.128 for trial 29, for which the wind speed was quite high (7.4 m/s). Comparative results for this and other trials are tabulated by Puttock.

Some accounts of work on mathematical modelling and physical modelling of LNG dispersion suggest that surface heat transfer can be neglected, except for low wind speed conditions. These results of Puttock indicate that failure to take it into account can lead to appreciable error.

The density of an LNG cloud will also be affected by any liquid spray which may be present. The source invariably considered for an LNG cloud is a spillage of the refrigerated liquid followed by evaporation of the liquid pool. By comparison with the quantity of spray generated by a typical flashing liquid jet, the quantity entrained in the vapour evolved will be small; it may be expected to be rather greater from a spillage on sea than from one on land. In any event, accounts of the density of gas clouds from LNG spillages tend to disregard the effect of liquid spray.

15.42.3 Chlorine

As a dense gas, chlorine has some of the features of propane. The molecular weight of chlorine is 71 so that it is dense by virtue of its molecular weight. This is so whether the release is one of chlorine gas or liquefied chlorine.

The normal boiling point of chlorine is −34°C. If the release is one of liquefied chlorine, the low temperature makes the gas somewhat more dense so that, in principle, heating up of the gas will render it less dense, but in practice heat transfer to the gas does not play a major role and any density changes due to temperature changes tend to be small.

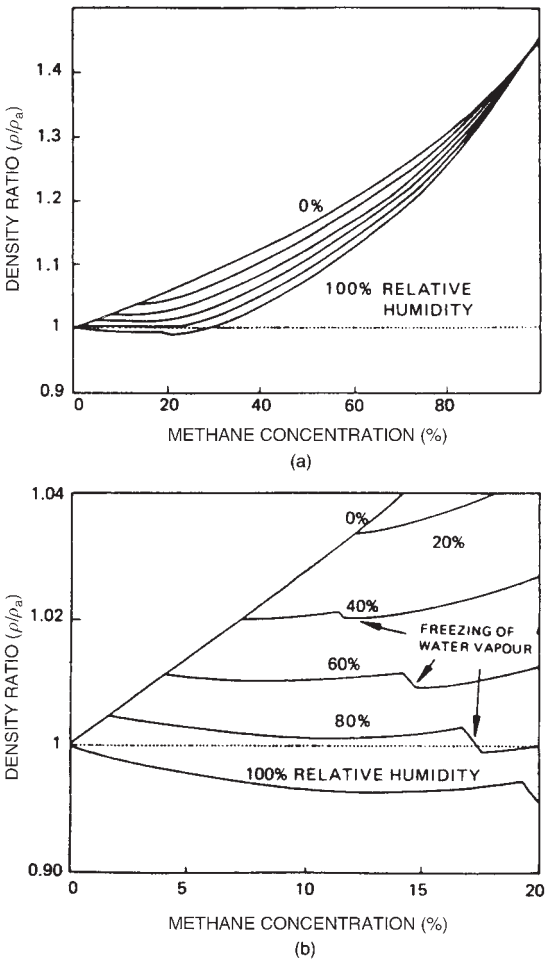


Figure 15.127 *Density of a methane–air mixture formed by release of LNG into the atmosphere (Puttock, 1987c): (a) main plot; and (b) enlargement of lower left-hand section of (a) (Courtesy of the American Institute of Chemical Engineers)*

With regard to atmospheric humidity and liquid spray, the points made above in relation to propane apply also to chlorine. Chlorine is another gas which tends to be modelled as a 'simple' dense gas.

15.42.4 Ammonia

The characteristics of the gas cloud from a release of anhydrous liquefied ammonia have been described by Haddock and Williams (1978 SRD R103, 1979) and Blanken (1980). Broadly, a release of liquid anhydrous ammonia normally gives rise to a dense gas cloud. The cloud will tend to be dense if the atmospheric humidity is low and/or the fraction of liquid spray is high. A cloud with little or no liquid spray in air with high humidity may be buoyant.

The molecular weight of ammonia is 17 and its normal boiling point is −33°C. Thus the molecular weight is not responsible for any dense gas behaviour. A systematic investigation of the factors governing the density of clouds of ammonia in air has been made by Haddock and Williams (1978 SRD R103, 1979). They consider chemical interactions, atmospheric humidity and liquid spray.

Possible chemical interactions with atmospheric air would appear to be formation of ammonium hydroxide (NH_4OH), ammonium bicarbonate (NH_4HCO_3) and ammonium carbonate ($(NH_4)_2CO_3$). The authors conclude that formation of these compounds directly from ammonia vapour, water vapour and carbon dioxide would be negligible, but that there would be dissolution of ammonia into water droplets formed due to cooling of the air by the cold ammonia gas and dissolution of carbon dioxide in these droplets. The effect of these processes on the density and temperature of the cloud would be minimal, but the effect on toxicity could be appreciable. Thus the volume of air required to convert a cloud of pure ammonia to one with an ammonia concentration of 2000 ppm contains enough carbon dioxide to reduce the concentration of free ammonia to about 1400 ppm.

A model of the thermodynamics of the NH_3–H_2O–air system is used to derive plots of the density and temperature of a cloud formed from the mixing of ammonia and air, as shown in Figure 15.129, whilst Figure 15.129(a) shows the temperature for the dry air case. Figure 15.129(b) shows a plot of the density vs the air/ammonia mass ratio with the liquid fraction f as the parameter, for ammonia initially at its boiling point, for dry air (RH = 0%) and Figure 15.129(c) that for wet air (RH = 100%).

The work showed that if there is no liquid spray, the density of the cloud, for dry or wet air, rises asymptotically to that of air, and therefore never exceeds that of air. If liquid spray is present, the cloud may be denser than air. There are limits to the liquid fraction below which the cloud density will not exceed that of air, the limits being different for dry and wet air. For dry air, this limit on the liquid fraction is about 8% and for wet air it is about 12%.

For wet air with liquid fractions of 12–16% the cloud is denser than air at low dilutions but less dense than air at high dilutions, whilst with liquid fractions of 16–20% it is denser than air at low dilutions and remains denser throughout the dilution process.

Haddock and Williams consider the behaviour of the ammonia droplets. Ammonia will evaporate from the droplets, causing their temperature to fall. Evaporation becomes mass and heat transfer limited. The presence of water vapour will not greatly affect this process. For droplets up to the upper limit of interest, about 100 μm the time scale for evaporation remains short relative to that for precipitation.

As far as concerns the behaviour of the droplets during the initial gravity slumping of the cloud, ammonia-air mixtures with mass ratios greater than 10 will not be significantly depleted of ammonia by precipitation of ammonia droplets. This applies even where the cloud height after slumping is quite low.

The broader aspects of an ammonia release, particularly dispersion, have been treated by Kaiser and Walker (1978), Griffiths and Kaiser (1979 SRD R154) and Kaiser and Griffiths (1982).

15.42.5 Hydrogen fluoride

The gas cloud characteristics for a release of liquefied anhydrous hydrogen fluoride (HF) have been described by Puttock *et al.* (1991). Broadly, releases of liquid HF may give

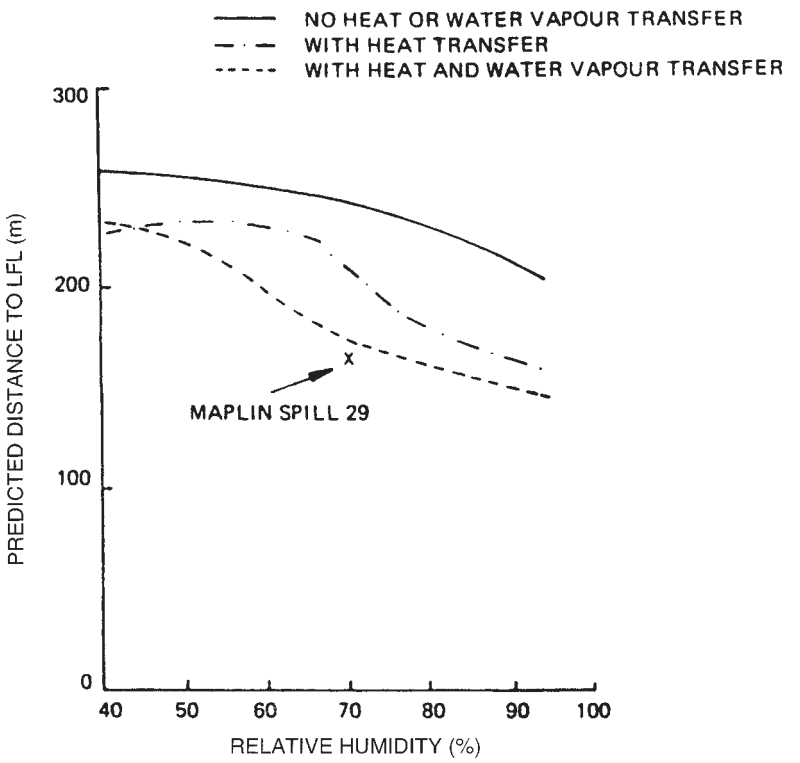


Figure 15.128 *Effect of heat transfer from surface on dense gas dispersion – predictions of HEGADAS for distance to the LFL for the Maplin Sands LNG spill trial 29 under three different assumptions (Puttock, 1987c) (Courtesy of the American Institute of Chemical Engineers)*

rise to gas clouds which are dense or buoyant; a large proportion will be dense. The cloud will tend to be dense if the atmospheric humidity is low and/or the fraction of liquid spray is high. A cloud with little or no liquid spray in air with high humidity may be buoyant.

The molecular weight of HF is 20 (as monomer) and its normal boiling point is 20°C. Dense gas behaviour is therefore attributable to factors other than molecular weight of the monomer.

HF differs from the other gases considered here in that it is subject to self-association and tends to form polymers of the general formula $(HF)_n$. Treatments of this feature in the context of dense gas dispersion have been given by Chikhliwala and Hague (1987), Clough, Grist and Wheatley (1987) and Schotte (1987).

Saturated vapour of HF has an apparent molecular weight of 78.2 at its normal boiling point. At 100°C, HF has a molecular weight of 49.1; at 300°C it is virtually monomolecular. Dilution of the gas cloud with air also results in a decrease in its apparent molecular weight. This associative behaviour, or oligomerization, of HF has been studied by a number of workers and various schemes have been proposed. For example, MacLean *et al.* (1962) give a monomer–dimer–hexamer model, and Beckerdite, Powell and Adams (1968) give a monomer–trimer–hexamer model.

Thus, in order to have a complete description of the behaviour of an HF cloud it is necessary to take account of self-association, atmospheric humidity and liquid fraction.

A model of HF fog formation is that proposed, and revised, by Schotte (1987, 1988). The model treats the self-association of HF and the formation of HF fog, or liquid $HF–H_2O$ droplets.

Another model of HF which takes into account self-association and atmospheric humidity has been described by Clough, Grist and Wheatley (1987); the model is entitled WETAFH. It comprises for self-association the monomer–dimer–hexamer model of MacLean *et al.*, which includes the chemical equilibrium relations, and a model for the equilibrium and thermodynamic relations of the HF–air–water system. The model shows that in moist air an $HF–H_2O$ liquid phase will generally form and that in some cases as much as 50% of the HF will be in this liquid phase. It is assumed that the liquid will be in the form of an aerosol. The density of the aerosol would be low, of the order of 0.05 kg/m^3. Provided the droplet size is not too large (<20 μm), the aerosol would be expected to persist for several hours. The authors give plots of cloud density and temperature vs concentration of HF, with relative humidity of the air as parameter.

A model which yields similar information and which is incorporated in HFSYSTEM has been described by Puttock, MacFarlane, Prothero, Roberts *et al.* (1991). The model is based on that of Schotte. Plots from this model are shown in Figure 15.130. This figure gives relative density and temperature curves with relative humidity as parameter for the mixing of HF and air, both initially at 25°C,

thus close to the boiling point of HF. They show that with dry air (RH = 0%) the gas cloud remains dense at all concentrations, whereas with saturated air (RH = 100%) the cloud is slightly buoyant at lower concentrations.

The effect of liquid present as spray is treated in the model given by Chikhliwala and Hague (1987). The authors refer to the method of Haddock and Williams for ammonia, and adopt a somewhat similar approach. They use the self-association model of Beckerdite, Powell and Adams and a model for the equilibrium and thermodynamic relations of the HF vapour-HF liquid system in dry air. Figure 15.131 gives plots of density and temperature vs the air/HF mass ratio with the liquid fraction as the parameter for the mixing of HF and air, the initial temperatures of the HF and of the air being 292.7 and 293 K, respectively.

Figure 15.132 gives the parameters for the condition where the liquid fraction just evaporates: the density D^*, the temperature T^* and the air/HF mass ratio R^*.

15.43 Dispersion of Dense Gas: Plumes from Elevated Sources

The treatment of dense gas dispersion given so far has been largely confined to releases from sources at ground level. It is now necessary to consider elevated releases. A review of work on the dispersion of an elevated plume of dense gas has been given by Ooms and Duijm (1984).

In this and the following section an account is given of some of the principal models for the dispersion of an elevated

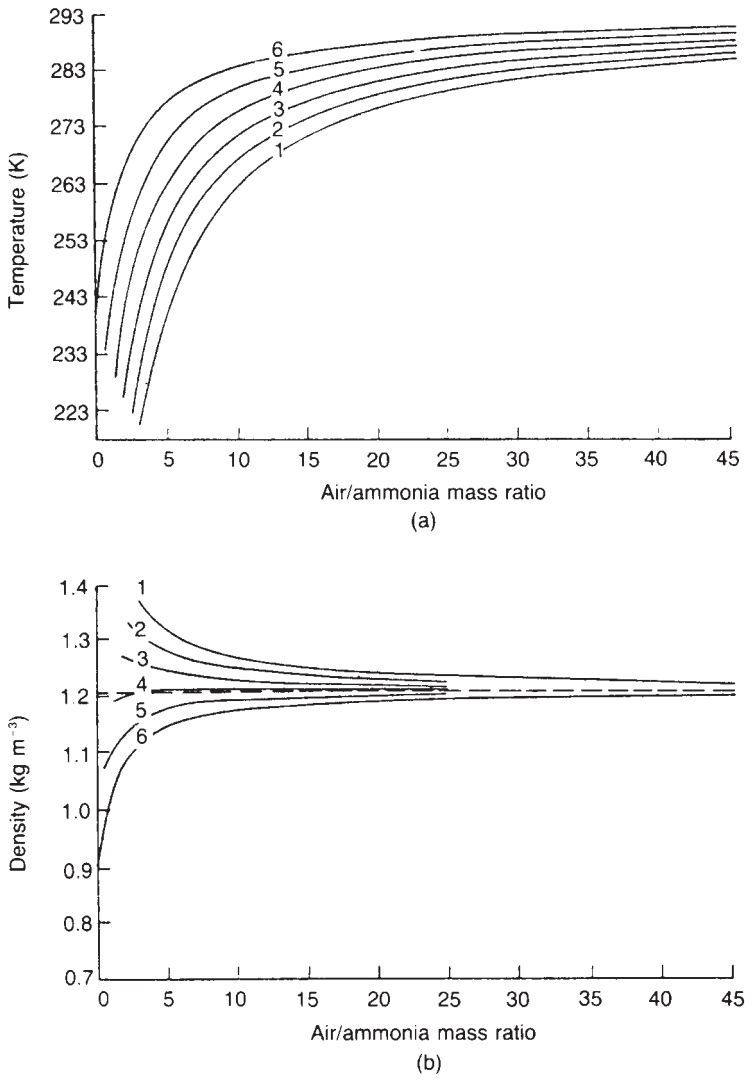


Figure 15.129 *continued*

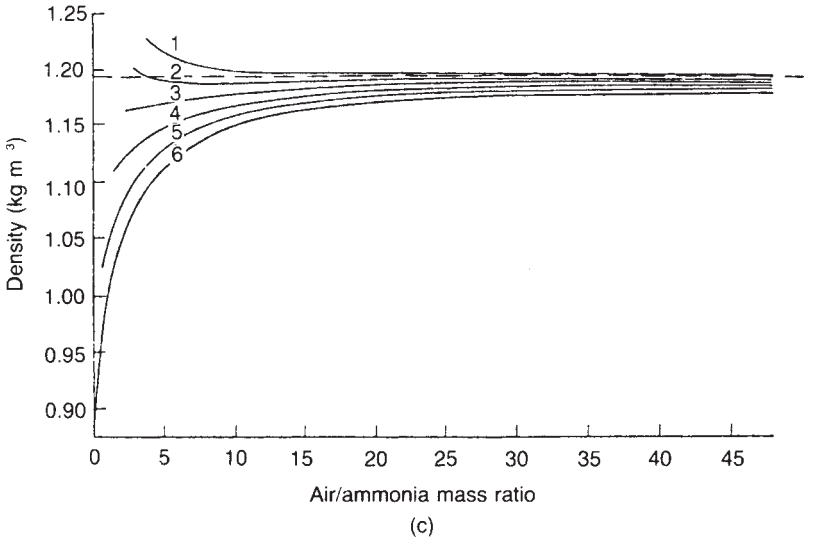


Figure 15.129 *Temperature and density of an ammonia–air mixture formed by release of ammonia into the atmosphere (after Haddock and Williams, 1978 3RD R103): (a) temperature for release into dry air; (b) density for release into dry air: and (c) density for release into wet air. (1) f = 20%; (2) f = 16%; (3) f = 12%; (4) f = 8%; (5) f = 4%; (6) f = 0, in all three plots (Courtesy of the UKAEA Safety and Reliability Directorate)*

release of a dense gas. A further discussion related to safe dispersion from reliefs and vents is given in Section 15.48.

15.43.1 Experimental work

Experimental work on dispersion of dense gas from an elevated source has been mainly by physical modelling. Bodurtha (1961, 1980, 1988), Hoehne and Luce (1970), Hoot, Meroney and Peterka (1973), Giesbrecht, Seifert and Leuckel (1983), Li Xiao Yun, Leidens and Ooms (1986) and Schatzmann, Snyder and Lawson (1993) used a wind tunnel; Holly and Grace (1972), J.L. Anderson, Parker and Benedict (1973), Chu (1975) and Badr (1984) used a water flume.

Bodurtha (1961) carried out wind tunnel experiments in which a photographic record was taken of a Freon 114–air mixture made visible with oil-fog smoke released from a stack. Measurements taken from the photographs include the maximum initial plume rise, distance to touchdown, velocity of plume descent and plume radius. Figure 15.133 shows the effect of the specific gravity of the gas on the behaviour of the plume.

The wind tunnel work of Hoot, Meroney and Peterka (1973) yielded data on, and correlations of, the maximum initial plume rise, distance to touchdown, and maximum concentrations, including those at maximum rise and at touchdown.

Work in the field has been reviewed by Schatzmann, Snyder and Lawson (1993). The main data sets are those of Bodurtha (1961) and Hoot, Meroney and Peterka (1973). The authors comment that the data of Bodurtha do not lend themselves to generalization and that those of Hoot, Meroney and Peterka are regarded as the most reliable and complete. However, the latter set has certain limitations. The experiments were performed in a laminar crossflow, whereas the real atmosphere is turbulent. The densimetric Froude numbers investigated did not cover the whole range of interest. The data of Bodurtha (1961) and Li Xiao Yun, Leidens and Ooms (1986) are also for laminar crossflow and low-to-medium Froude numbers. The work of Giesbrecht, Seifert and Leuckel (1983) does cover larger Froude numbers, but for quiescent atmospheres. The investigation which the authors report extends to a turbulent atmosphere and to higher Froude numbers.

Schatzmann, Snyder and Lawson found that a dense gas jet released into a turbulent atmosphere tended, by comparison with one released into a laminar atmosphere, to have a reduced rise height and an increased touchdown distance with lower concentrations both at the point of maximum rise and at touchdown.

The concentration of interest for a toxic release is generally much lower than that for a flammable release. The relative effect of atmospheric turbulence increases with distance from the release point. The authors suggest that, whereas it may not be overly conservative to neglect this factor for concentrations of interest in respect of their flammability, it appears essential to take it into account if a realistic estimate is to be obtained for toxic concentrations.

15.43.2 Ooms model

A model for dispersion of a dense gas plume from an elevated source which has been widely used is that described by Ooms (1972) and Ooms, Mahieu and Zelis (1974). Whereas previous models were based on the assumptions that the gas is of neutral density and that the plume velocity is equal to the wind speed, the Ooms model does not rely on these assumptions but gives a more realistic description of entrainment into and drag on the plume.

The model consists of a set of equations for conservation of mass, momentum and energy and for air entrainment of the general form

$$\frac{\mathrm{d}}{\mathrm{d}s}\int_0^{\sqrt{2}.b} \phi_i(r) 2\pi r \, \mathrm{d}r = \psi_i \qquad [15.43.1]$$

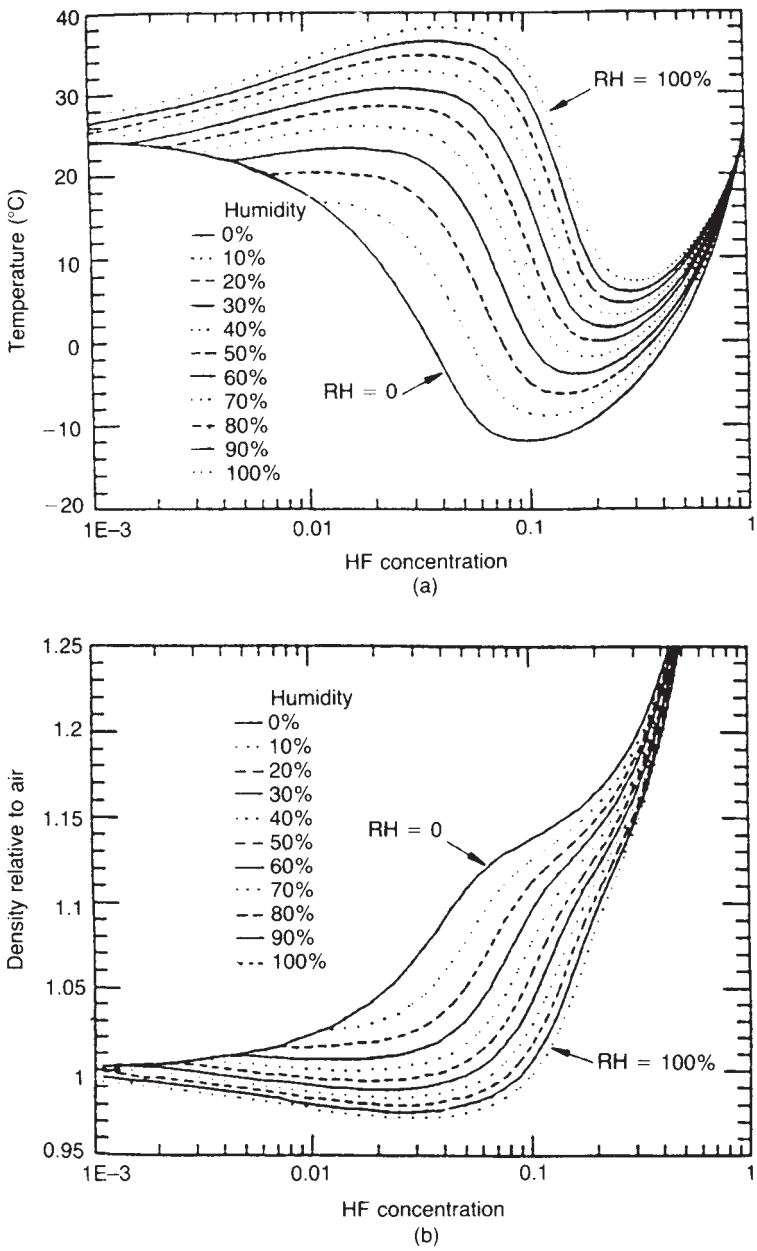


Figure 15.130 *Temperature and density of a hydrogen fluoride–air mixture formed by release of hydrogen fluoride into the atmosphere (Puttock, MacFarlane, Prothero, Roberts et al., 1991): (a) temperature for release into air of varying humidity; and (b) density for release into air of varying humidity (Courtesy of the American Institute of Chemical Engineers)*

where b is a characteristic width of the plume, r is the radius of the plume, s is the distance along the axis of the plume, π_i is a set of functions and ψ_i is a further set of functions.

The functions ϕ_i is given by the following relations for conservation of total mass, mass of contaminant, momentum in the horizontal direction, momentum in the vertical direction and energy, respectively:

$$\phi_i(r) = \rho u \qquad [15.43.2a]$$

$$= cu \qquad [15.43.2b]$$

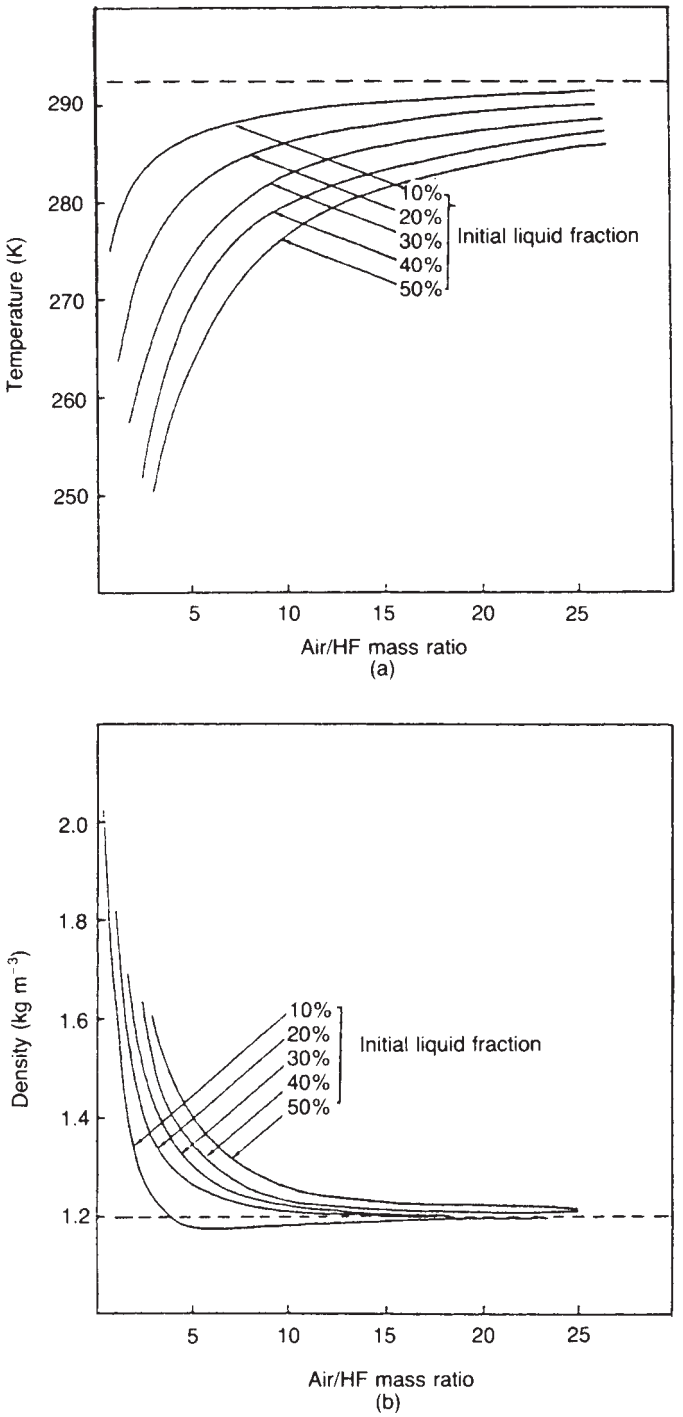


Figure 15.131 *Temperature and density of a hydrogen fluoride–air mixture formed by release of hydrogen fluoride into the atmosphere – 1 (Chikhliwala and Hague, 1987): (a) temperature for release with different liquid fractions; (b) density for release with different liquid fractions (Courtesy of the American Institute of Chemical Engineers)*

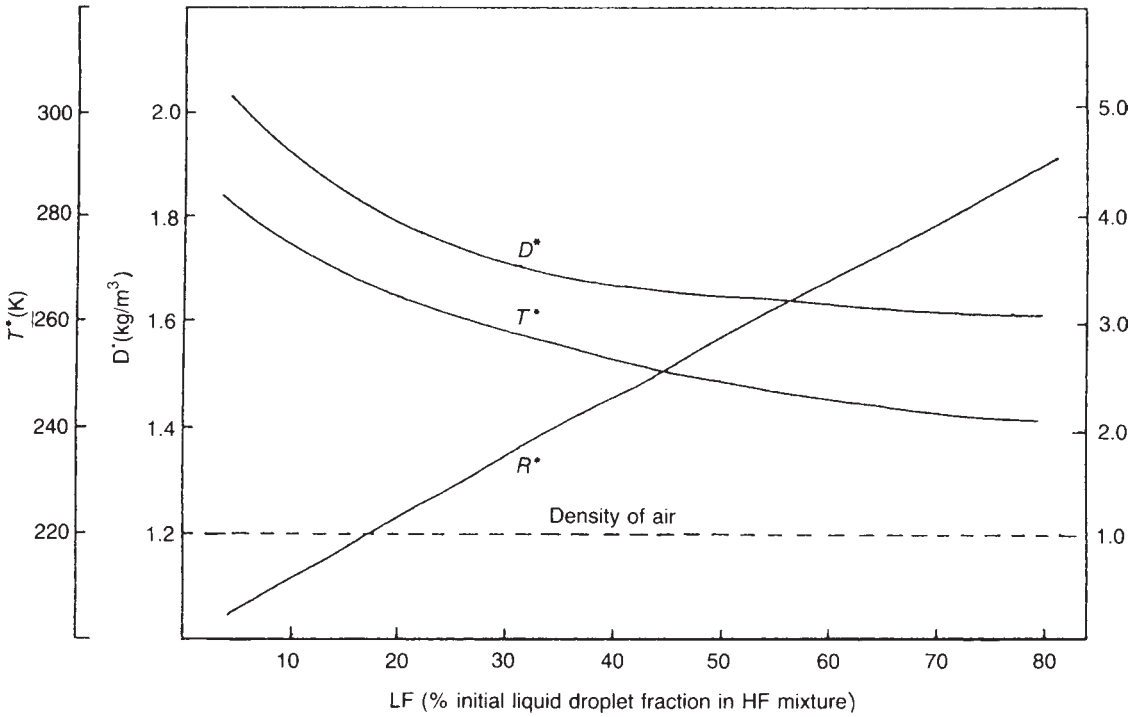


Figure 15.132 *Temperature and density of a hydrogen fluoride–air mixture formed by release of hydrogen fluoride into the atmosphere – 2 (Chikhliwala and Hague, 1987): parameters for condition where liquid fraction (LF) just evaporates. D* density; T, temperature and Ft*, air/HF mass ratio (Courtesy of the American Institute of Chemical Engineers)*

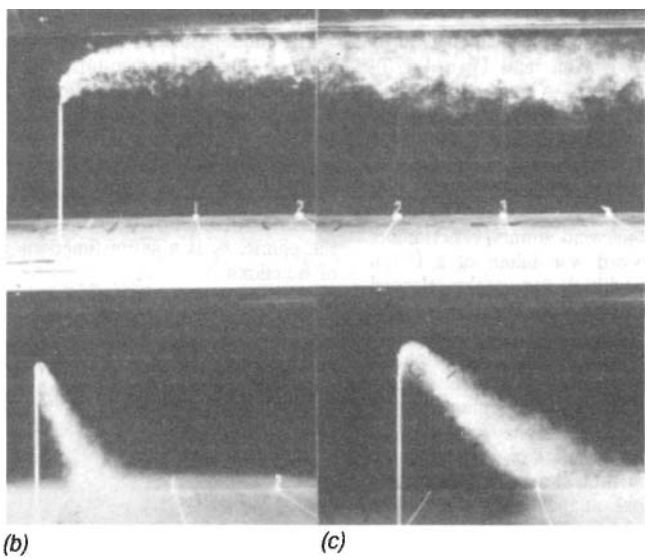


Figure 15.133 *Dispersion of dense gas from an elevated relief: wind tunnel tests (Bodurtha, 1961): Full scale conditions: stack diameter 610 mm, stack height 30.5 m, wind velocity 1.34 m/s, gas exit velocity 6.1 m/s: (a) gas specific gravity 1 (air); (b) gas specific gravity 5.15 and (c) gas specific gravity 1.52 (Courtesy of the Air Pollution Control Association)*

$$= \rho u^2 \cos\theta \quad [15.43.2c]$$

$$= \rho u^2 \sin\theta \quad [15.43.2d]$$

$$= \rho u\left(\frac{1}{\rho} - \frac{1}{\rho_{ao}}\right) \quad [15.43.2e]$$

where c is the concentration of the contaminant, u is the velocity along the axis of the plume, θ is the angle between the plume axis and the horizontal, ρ is the density of the plume and ρ_{ao} is the density of the atmosphere at the stack outlet.

The functions ψ_i are functions primarily of velocity and density.

For example, the relation used for the conservation of mass draws on the work of Albertson *et al.* (1950) and Abraham (n.d.) for entrainment into a turbulent jet and of Abraham (1970) for entrainment into a plume and is

$$\frac{\mathrm{d}}{\mathrm{d}s}\int_0^{\sqrt{2}.b} \rho u 2\pi r \,\mathrm{d}r = 2\pi b\rho_a[\alpha_1|u_*(s)| + \alpha_2 U_a|\sin\theta|\cos\theta + \alpha_3 u'] \quad [15.43.3]$$

where u' is the entrainment velocity due to atmospheric turbulence, U_a is the mean wind velocity, ρ_a is the density of the air and α_1, α_2 and α_3 are the entrainment coefficients for a free jet, a line thermal and due to turbulence, respectively. The values taken for the constants α_1, α_2 and α_3 are 0.057, 0.5 and 1.0, respectively. The set of equations represented by Equation 15.43.1 is integrated with respect to 5 numerically.

The model has been compared with various sets of experimental results and gives good agreement for the position of the plume axis. The Ooms model has been encoded for the US Coast Guard in the computer code ONDEK. For determination of the distances within which vented hydrocarbon releases may be assumed for design purposes to have fallen below the lower flammability limit, Ooms, Mahieu and Zelis give the relations shown in Figure 15.134(a).

They also give the illustrative example shown in Figure 15.134(b) for the discharge of butane from two different sized vents, one giving an exit velocity of 26.5 m/s and the other one of 41.5 m/s. For this heavy gas the lower outlet velocity leads to a much more rapid descent to ground level than does the higher velocity.

15.43.3 Hoot, Meroney and Peterka model

Another model is that given by Hoot, Meroney and Peterka (1973) (HMP model). This model too has found widespread

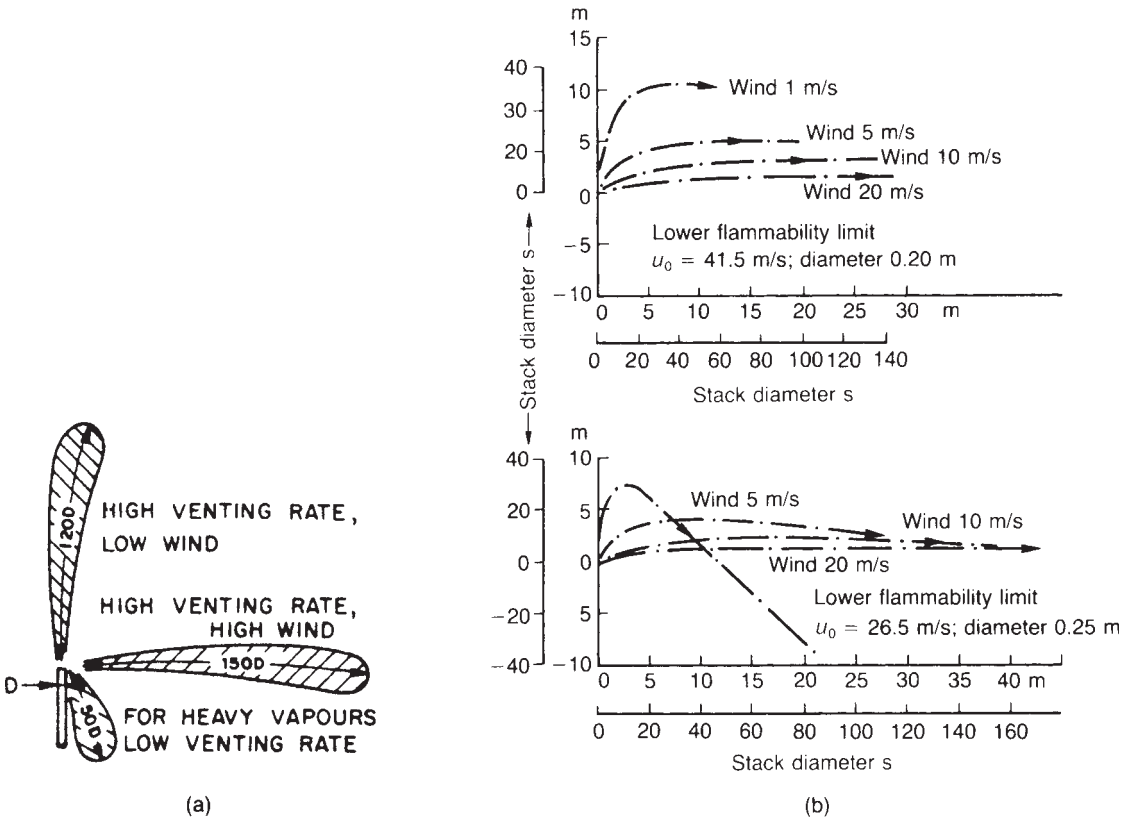


Figure 15.134 *Dispersion of dense gas from an elevated relief: (a) approximate distances for dispersion of hydrocarbons; (b) dispersion of butane vapour (Ooms, Mahieu and Zelis, 1974) (Courtesy of Elsevier Science Publishers)*

use. The basic equations of the model are those of conservation of mass, of horizontal and vertical momentum and of entrainment, and are as follows:

$$\frac{\mathrm{d}(R^2\rho_o u_s)}{\mathrm{d}s} = \rho_a \frac{\mathrm{d}(R^2 u_s)}{\mathrm{d}s} \quad [15.43.4]$$

$$\frac{\mathrm{d}(R^2\rho_o u_s^2 \cos\theta)}{\mathrm{d}s} = \rho_a u \frac{\mathrm{d}(R^2 u_s)}{\mathrm{d}s} \quad [15.43.5]$$

$$\frac{\mathrm{d}(R^2\rho_o u_s^2 \sin\theta)}{\mathrm{d}s} = (\rho_a - \rho_o)R^2 g \quad [15.43.6]$$

$$\frac{\mathrm{d}(R^2 u_s)}{\mathrm{d}s} = \alpha_1 R|u_s - u\cos\theta| + \alpha_2 Ru|\sin\theta| \quad [15.43.7]$$

where R is radius of the plume, s is the distance along the plume axis, u_s is the velocity along the plume axis, θ is the angle of the plume axis to the horizontal, ρ is the density of the plume, ρ_a is the density of the air, ρ_o is the density of the outlet gas and α_1 and α_2 are the entrainment coefficients. Values of α_1 and α_2 from wind tunnel work are 0.09 and 0.9, respectively.

The authors divide the plume path into three regions and solve the model Equations 15.43.4–15.43.7 analytically in each region. The HMP model is then as follows. For the initial plume rise

$$\frac{\Delta h}{2R_o} = 1.32\left(\frac{w_o}{u}\right)^{1/3}\left(\frac{\rho_o}{\rho_a}\right)^{1/3}\left[\frac{w_o^2}{2R_o g(\rho_o - \rho_a)/\rho_o}\right]^{1/3} \quad [15.43.8]$$

for the touchdown distance

$$\frac{x_{td}}{2R_o} = \left[\frac{w_o u}{2R_o g(\rho_o - \rho_a)/\rho_o}\right] + 0.56\left\{\left(\frac{\Delta h}{2R_o}\right)^3\left[\left(\frac{2 + h_s}{\Delta h}\right)^3 - 1\right]\right\}^{1/2} \times \left\{u^3/[2R_o w_o(\rho_o - \rho_a)/\rho_a]\right\}^{1/2} \quad [15.43.9]$$

and for the maximum concentration on the plume axis

$$\frac{C}{C_o} = 2.43\left(\frac{w_o}{u}\right)\left(\frac{h_s + 2\Delta h}{2R_o}\right)^{-1.95} \quad [15.43.10]$$

where C is the concentration, h_s is the height of the stack, Δh is the maximum initial plume rise, u is the wind speed, w is the velocity of the plume, x is the downwind distance, ρ is the density of the plume and subscripts a, m, o and td denote air, maximum, initial and touchdown, respectively.

The HMP model is one of the models given in the CCPS *Vapor Cloud Dispersion Model Guidelines* and is selected for use in the associated *Workbook*. As an illustration, consider the following example given in the *Workbook*. Butane is released from a stack internal diameter 0.75 m and height 5 m such that $h_s = 5$ m, $R_o = 0.375$ m, $u = 5$ m/s, $w_o = 12.7$ m/s, $\rho_a = 1.16$ kg/m^3 and $\rho_o = 2.67$ kg/m^3. The resultant values of the initial plume rise, the touchdown distance and the concentration ratio at the touchdown distance are, respectively, $\Delta h = 6$ m, $x_{td} = 57$ m and $C/C_o = 0.014$.

15.43.4 Jagger and Edmondson model

An alternative approach to the modelling of a heavy gas plume is that of Jagger and Edmondson (1984), who have developed from the basic conservation equations a set of asymptotic solutions. The model utilizes the following length scales

$$t_Q = \frac{Q}{M^{1/2}} \quad [15.43.11]$$

$$l_m = \frac{M^{3/4}}{B^{1/2}} \quad [15.43.12]$$

$$z_m = \frac{M^{1/2}}{U} \quad [15.43.13]$$

$$z_B = \frac{B}{U^3} \quad [15.43.14]$$

with

$$M = Qu_o \quad [15.43.15]$$

$$B = Qg' \quad [15.43.16]$$

$$g' = \frac{\rho - \rho_a}{\rho_a} g \quad [15.43.17]$$

where B is the initial buoyancy flux (m^4/s^3), g is the acceleration due to gravity (m/s^2), g' is the reduced gravity (m/s^2), M is the initial momentum flux (m^4/s^2), Q is the initial volumetric flow (m^3/s), u_o is the outlet velocity (m/s) and U is the wind speed (m/s).

The length l_Q is a function of the source and only influences flow near the source. l_m indicates the point of transition from momentum to buoyancy control. z_m and z_B indicate the influence of crossflow. For large values of z_m and z_B the jet is essentially vertical, while for small values it is bent over.

The method allows the calculation of the trajectory of the vertical co-ordinate z_s of the jet or plume axis and, in particular, of heights for the jet–plume transition and for the virtual source of the resultant effective plume.

For a vertical jet the relations given include:

$$\frac{\mathrm{d}z_s}{\mathrm{d}x} = \frac{w_{cl}}{u} \quad [15.43.18]$$

$$\frac{w_{cl}}{u} \approx \frac{z_m}{z_s} \quad [15.43.19]$$

where x, y and z are the distances in the downwind, crosswind and vertical directions (m), u, v and w are the components of the release velocity in the x, y and z directions (m), z_s is the coordinate of the jet axis (m) and the subscript cl denotes the centre line.

Then from Equations 15.43.18 and 15.43.19 the authors derive the following relation for the vertical coordinate of the axis:

$$\frac{z_s}{z_m} = A_1\left(\frac{x}{z_m}\right)^{1/2} \quad [15.43.20]$$

where A_1 is a constant. The value given for the constant A_1 is 2.0.

For the gas density the authors give

$$\theta = C_1 \frac{UBz_m}{Mgz_s} \quad [15.43.21]$$

with

$$\theta = \frac{\rho_a - \rho}{\rho_o} \quad [15.43.22]$$

where θ is a relative density difference, ρ is the density, C_1 is a constant and subscripts a and o denote atmosphere and initial gas, respectively. The value given for the constant C_1 is 2.4. The complete set of asymptotic formulae, and the corresponding values of the constants, given by Jagger and Edmondson are shown in Table 15.54.

The model is completed by the following additional relations. The maximum rise of the plume with weak crossflow is:

$$z_{max} = A_5 \frac{M^{3/4}}{B^{1/2}} \quad \frac{M^{1/2}}{B} U \ll 1 \quad [15.43.23]$$

and in strong crossflow conditions

$$z_{max} = A_6 \left(\frac{M^2}{BU}\right)^{1/3} \quad \frac{M^{1/2}}{B} U \gg 1 \quad [15.43.24]$$

where z_{max} is the maximum rise and A_5 and A_6 are constants. The value given for constants A_5 ands A_6 is about 2.0 for each.

It is convenient from this point for the purposes of exposition to introduce several quantities additional to those given in the original paper and to use a modified notation.

The distance of the virtual source of the jet below the stack outlet is given by

$$z_{vs} = \frac{d_o}{2\alpha} \quad [15.43.25]$$

where d_o is the diameter of the stack outlet (m), z_{vs} is the distance of the jet virtual source below the stack outlet (m) and α is an entrainment coefficient. The value given for α is 0.15.

The model also utilizes a second virtual source, that of the plume falling to earth. Use is made of two sets of coordinates. The first set is the horizontal and vertical coordinates (x_{je}, z_{je}) of the jet end point. The second set is the horizontal and vertical coordinates (x_{veff}, z_{veff}) of the plume virtual source. The second set of coordinates is obtained from the first by applying the distance corrections (Δx_v, Δz_v). The following equations apply:

$$z_{je} = h_s - z_{vs} + z_{max} \quad [15.43.26a]$$

$$x_{veff} = x_{je} + x_v \quad [15.43.26b]$$

$$z_{veff} = z_{je} + z_v \quad [15.43.26c]$$

$$x_{td} = \phi x'_{td} + x_{veff} \quad [15.43.27]$$

$$c = f(\theta) \quad [15.43.28]$$

where c is the concentration of the plume at touchdown (v/v), h_s is the height of the stack (m), x_{je} is the horizontal coordinate of the jet end point (m), x_{td} is the horizontal distance from the base of the stack at which touchdown occurs, or the touchdown distance (m), x'_{td} is an uncorrected touchdown distance (m), Δx_v is the horizontal distance between the jet end point and the plume virtual source (m), x_{veff} is the horizontal coordinate of the plume virtual source (m), z_{je} is the vertical coordinate of the jet end point (m), Δz_v is the vertical distance between the jet end point and the plume virtual source (m), z_{veff} is the vertical coordinate of the plume virtual source (m) and ϕ is a correction factor. The coordinates (x_{je}, x_{veff}, z_{je}, z_{veff} are measured from the base of the stack. x_{veff} may assume a negative value.

The correction factor ϕ is introduced to allow for the fact that the prior calculation applies to the centre line of the plume, whereas the touchdown distance at which a significant concentration occurs is that of the edge of the plume nearest the base of the stack. An empirical value of 0.85 is assigned to ϕ.

The application of the model to the case where there is wind is to determine by repeated use of the asymptotic formulae given in Table 15.54 first the coordinates of the jet end point, then those of the plume virtual source and finally the touchdown distance and concentration. The procedure is illustrated in the example given below.

Table 15.54 *Formulae and constants for asymptotic plume model (after Jagger and Edmondson, 1984) (Courtesy of the Institution of Chemical Engineers)*

A Formulae

Flow type	*Range of validity*	*(A)* w_{cl}	*(B)* z_s/z_m	*(C)* z_s/z_B	*(D)* $Mg\theta/UB$
Vertical jet	$z_s \ll z_m$	$\approx z_m/z_s$	$A_1(x/z_m)^{1/2}$		$C_1(z_m/z_s)^2$
Bent-over jet	$z_s \gg z_m$	$\approx (z_m/z_s)^2$	$A_2(x/z_m)^{1/3}$		$C_2(z_m/z_s)^2$
Vertical plume	$z_s \ll z_B$	$\approx (z_B/z_s)^{1/3}$	–	$A_3(x/z_B)^{3/4}$	$C_3(z_B/z_s)^{5/3}(z_m/z_B)^2$
Bent-over plume	$z_s \gg z_B$	$\approx (z_B/z_s)^{1/2}$	–	$A_4(x/z_B)^{2/3}$	$C_3(z_B/z_s)^2(z_m/z_B)^2$

B Constants

A_1	A_2	A_3	A_4	C_i	C_2	C_3	C_4
2.0	2.0	1.6	2.0	2.4	2.4	2.4	3.1

There is a separate treatment for calm conditions, or zero wind. For this case the method is to determine first the maximum rise of the plume. The plume is then envisioned as falling from this point to earth so that the plume fall distance is

$$z_{pf} = h_s - z_{vs} - z_{max} \quad [15.43.29]$$

where z_{pf} is the plume fall distance (m). The falling plume has a radius b and downward velocity w given by

$$b = \frac{6\alpha z}{5} \quad [15.43.30]$$

$$w = \frac{5}{6\alpha}\left(\frac{9\alpha B}{10\pi}\right)^{1/3} z^{-1/3} \quad [15.43.31]$$

and covers an area A_{pgr} and has a volumetric flow V_{pgr}, which are

$$A_{pgr} = \frac{\pi}{4} b^2 \quad [15.43.32a]$$

$$V_{pgr} = wA_{pgr} \quad [15.43.32b]$$

where A_{pgr} is the ground area centring on the base of the stack covered by the falling plume (m^2), b is the radius of the plume (m), V_{pgr} is the volumetric flow of the plume at ground level (m^3/s) and w is the vertical downwards velocity of the plume (m/s). The concentration is then obtained from

$$c = Q/V_{pgr} \quad [15.43.33]$$

The application of the model where there is a wind is as follows. The fluxes M and B, the wind speed U and the length scales l_m, l_Q, z_B and z_m are determined. The maximum height of the plume z_{max} is then obtained from Equation 15.43.24. The distance z_{vs} of the jet virtual source below the outlet is calculated from Equation 15.43.25.

The procedure involves first the determination of coordinates (x_{je}, z_{je}). The coordinate z_{je} is obtained from Equation 15.43.26a and the coordinate x_{je} from the relation given in Table 15.54 for a bent-over jet $z_s/z_m = A_2(x/z_m)^{1/3}$, setting $z_s = z_{max}$ and $x = x_{je}$. Next, an estimate is made of the distances (Δx_v, Δz_v). The first step is to obtain from the relation given in Table 15.54 for a bent-over jet the group $Mg\theta/UB = (z_m/z_s)^2$, setting $z_s = z_{max}$. Then the distance Δz_v is determined from the relation in Table 15.54 for a bent-over jet $Mg\theta/UB = C_4(z_B/z_s)^2(z_m/z_B)^2$, setting $z_s = \Delta z_v$. The distance Δx_v is calculated from the relation in Table 15.54 for a bent-over plume $z_s/z_B = A_4(x/z_B)^{2/3}$ setting $z_s = \Delta z_v$ and $x = \Delta x_v$. The coordinates (x_{veff}, z_{veff}) are then obtained from Equations 15.43.26b and 15.43.26c.

For the touchdown conditions, the uncorrected touchdown distance x'_{td} is obtained from the relation in Table 15.54 for a bent-over plume $z_s/z_B = A_4(x/z_B)^{2/3}$, setting $z_s = z_{veff}$ and $x = x'_{td}$. The corrected touchdown distance x_{td} is then calculated from Equation 15.43.27. The touchdown concentration is obtained from the relation in Table 15.54 for a bent-over plume $Mg\theta/UB = C_4(z_B/z_s)^2(z_m/z_B)^2$, setting $z_s =$ veff, which gives the relative density difference θ. For low concentrations the relation between the relative density difference θ and the volumetric concentration c is $c \approx [\theta(\rho_o - \rho_a)\rho_a]$.

For the case of calm conditions the model is applied as follows. The maximum rise of the plume z_{max} is obtained from Equation 15.43.23 and the plume fall distance from Equation 15.43.29. The touchdown radius b, velocity w, ground area A_{pgr}, volumetric flow V_{pgr} and concentration c are then determined from Equations 15.32.30–15.43.33.

Jagger and Edmondson give a set of illustrative examples of their method, in which they determine the touchdown distances and concentrations for a release of butane from an elevated pressure relief valve. The base conditions are

Height of vent $h_s = 30$m
Diameter of outlet $d_o = 0.2$ m
Mass flow of butane $= 7.1$ kg/s
Density of butane $= 2.54$ kg/m^3

Hence

Volumetric flow of butane $Q = 2.8$ m^3/s
Initial momentum flux $M = 255.6$ m$^4/s^2$
Initial buoyancy flux $B = 27.8$ m$^4/s^3$
Distance below outlet of jet virtual source $z_{vs} = 0.7$ m

Cases considered are calm conditions and wind speeds of 2 and 4 m/s. For these cases:

	Wind speed (m/s)		
	0	2	4
l_Q	0.18	0.18	0.18
l_B	12.1	12.1	12.1
z_m		8.0	4.0
z_B		3.5	0.4

For the case of a wind speed of 2 m/s, the method described yields

$z_{max} = 20.6$ m
$x_{je} = 17.1$ m; $z_{je} = 49.9$ m
$Mg\theta/UB = 0.36$
$\Delta x_v = 21.5$ m; $\Delta z_v = 23.5$ m
$x_{veff} = -4.4$ m; $z_{veff} = 73.4$ m
$x_{td} = 118.8$ m; $x_{td} = 96.6$ m
$\theta = 8.2 \times 10^{-4}$
$c(\approx 2\theta) = 0.00164$v/v $= 0.164\%$v/v

For the case of calm conditions

$z_{max} = 24.4$ m
$z_{pf} = 53.7$ m
$b = 9.7$ m; $A_{pgr} = 296$ m^2
$w = 1.56$ m/s; $V = 462$ m^3/s
$c = 0.0061$ v/v $= 0.061\%$ v/v

The touchdown conditions obtained for all three cases are:

	Wind speed (m/s)		
	0	2	4
Touchdown distance (from stack base) (m)	0	96.6	239
Touchdown concentration (v/v)	0.0061	0.0016	0.0011

(These values differ from those given in the original paper but have been checked with one of the authors (S.F.J.)).

15.43.5 Emerson models

Another model is that given by Emerson (1986a). The model is a modification of the Ooms model already described. The Emerson model differs from the Ooms model in several ways. One is that, whereas in the Ooms model the vertical component of the axial velocity tends to a constant value, in the Emerson model it is multiplied by the Gaussian term and therefore tends to zero. This obviates the need for the use of $2½b$ as the limit of integration. Another difference is in the selection of a more appropriate mass flow. This avoids problems with situations where the jet emission is in the upwind direction. The Emerson model is the basis of the computer code TECJET (Technica, 1987).

Emerson (1986b, 1989) has also given a further, separate model for a jet of dense gas undergoing transition to, and then dispersing as, a dense gas cloud. As already described, models for dense gas dispersion are sensitive to the source term used. It is the object of this model to provide an improved source term where the release occurs due to a jet, which is the usual situation.

The dispersion of the gas is assumed to occur in three phases, as shown in Figure 15.135. The first phase is a momentum jet, the second phase is a hybrid one in which slumping and transition occur and the third phase is a dense gas cloud. A box model approach is used in which the dimensions of the gas cloud are calculated and concentration within this envelope is assumed to be constant.

For the momentum jet phase Emerson quotes the work of Ricou and Spalding for the entrainment of air with distance along the jet axis and gives for a jet in still conditions the relation

$$Q_a = k_1(\rho_a I_o)^{1/2} \qquad [15.43.34]$$

where I_o is the momentum flux, Q_a is the entrainment flow and k_1 is a constant. The value of the constant k_1 is 0.282. Equation 15.43.34 is equivalent to Equation 15.20.13a of Ricou and Spalding.

Then, for a jet in windy conditions, Emerson assumes that Equation 15.43.34 can be modified to read

$$Q_a = k_1(\rho_a I_o)^{1/2} \frac{w - u_o}{v} \qquad [15.43.35]$$

where I_o is now the excess momentum flux, u_w is the wind speed and v is the velocity of the gas in the jet.

The jet is assumed to have a square cross-section. The rate of lateral growth is determined solely by the entrainment of air into the cloud. Transition to the second phase occurs when this rate of spreading falls below that which would occur due to gravitational slumping.

The second, hybrid phase combines features of both the preceding and the succeeding phases. It is assumed that the rate of air entrainment is as in the previous stage, but the rate of lateral spreading is based on dense gas behaviour. The relation used is

$$\frac{dR}{dt} = (k_2 g H \rho/\rho)^{1/2} \qquad [15.43.36]$$

where H is the height of the cloud, R is the half-width of the cloud, ρ is the density of the cloud, $\Delta\rho$ is the density difference between the cloud and the air and k_2 is a constant. The value of the constant k_2 is approximately unity. The height of the cloud in this second phase is obtained from the mass of air entrained in the jet and the resulting necessary cross-section.

In the third phase the dispersion is that of a dense gas cloud. This is described using the model of R.A. Cox and Carpenter (1980).

15.43.6 Woodward model

J.L. Woodward (1989a) has given a model for a release from an elevated source of a two-phase flashing fluid of pressurized liquefied gas, forming a jet of vapour and liquid droplets. The model is derived from that of Ooms, Mahieu and Zelis. The model is the basis of the computer code EJET.

15.43.7 Other models

There are several other models for dispersion of an elevated release of a dense gas. The Environmental Protection Agency (EPA) (1989a) has developed a relief valve screening model. Other models include those by Giesbrecht, Seifert and Leuckel (1983) and Havens and Spicer (1985).

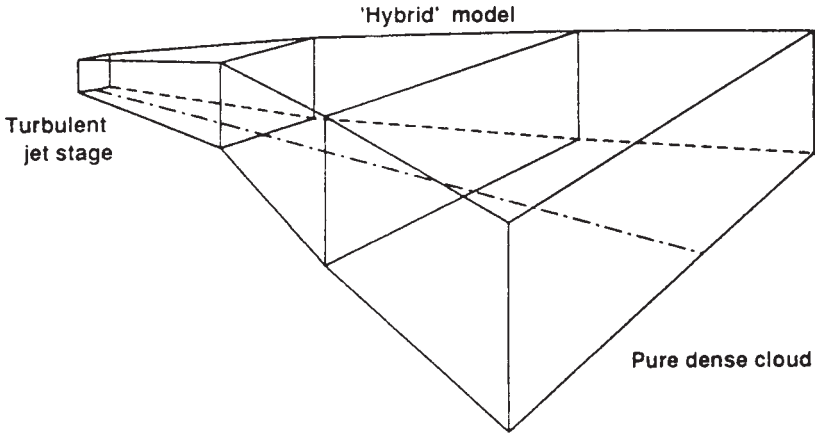


Figure 15.135 *Emerson model for dispersion of dense gas from elevated jets and plumes – idealized cloud shape (Emerson, 1986a) (Courtesy of the Clarendon Press)*

15.43.8 Criterion for dense gas dispersion

A criterion for deciding whether a dense gas treatment is necessary has been given by Fay and Zemba (1986) as follows:

$$\mathrm{Ri_o} \gg 1$$

with

$$\mathrm{Ri_o} = \frac{w_o D_o}{(u_*^3)} g = \frac{\rho_o - \rho_a}{\rho_a} \qquad [15.43.37]$$

where D is the diameter, w is the velocity of the plume, ρ is the density of the plume and the subscripts a and o denote air and initial, respectively. This criterion is adopted in the CCPS *Vapor Cloud Dispersion Model Guidelines*.

15.44 Dispersion of Dense Gas: Plumes from Elevated Sources – PLUME

A model for dispersion from a jet or plume has been developed by Shell as part of the HGSYSTEM package. This model, PLUME, is one of the front-end models for the main dispersion model, HEGADAS. It has been described by McFarlane (1991). PLUME is a generalization of a more specific model HFPLUME developed for the dispersion of hydrogen fluoride.

15.44.1 Plume development

The scenario modelled is that of a jet or plume issuing along the direction of the wind at an inclination to the horizontal. The plume is treated as passing through three stages:

(1) airborne plume;
(2) touchdown plume;
(3) slumping plume.

The plume geometry, coordinate system and control volume are shown in Figure 15.136.

The cross-section of the airborne plume is assumed to be circular. The touchdown regime starts when the circumference of the airborne plume touches the ground and it ends when the cross-section of the plume has become semi-circular. The slumping regime then begins and the cross-section becomes elliptical.

The coordinate system used is as follows. For the airborne plume the angle of inclination of the axis is ϕ, and the distance along the axis s and a point on the cross-section of that plume is given by the polar coordinates r and θ. For the plume in all regimes the centroid of the plume is located at distances x and z from the sources in the horizontal, vertical directions. For the touchdown and slumped plumes the height of the centre of the plume is z_c.

The core of the model is a complex set of integral equations which are then simplified to the sets of equations for the three regimes given below.

15.44.2 Airborne plume

The model for the airborne plume consists of the following set of six differential equations:

$$\frac{\mathrm{d}\dot{m}}{\mathrm{d}s} = \mathrm{Entr} \qquad [15.44.1]$$

$$\frac{\mathrm{d}\dot{P}_x}{\mathrm{d}s} = \mathbf{Drag} \cdot \mathbf{e}_x + \mathrm{Shear} \qquad [15.44.2]$$

$$\frac{\mathrm{d}\dot{P}_z}{\mathrm{d}s} = \mathbf{Drag} \cdot \mathbf{e}_z + \mathrm{Buoy} \qquad [15.44.3]$$

$$\frac{\mathrm{d}\dot{E}_x}{\mathrm{d}s} = \mathrm{Ener} \qquad [15.44.4]$$

$$\frac{\mathrm{d}x}{\mathrm{d}s} = \cos\phi \qquad [15.44.5]$$

$$\frac{\mathrm{d}z}{\mathrm{d}s} = \sin\phi \qquad [15.44.6]$$

where $\mathbf{e}_x$ is a unit vector in the horizontal, wind aligned direction, $\mathbf{e}_z$ is a unit vector in the vertical direction, $\dot{E}$ is the excess energy flux, $\dot{m}$ is the mass flux, $\dot{P}_x$ is the excess horizontal momentum flux, $\dot{P}_z$ is the excess vertical momentum flux and s is the distance along the axis of the plume.

The term 'Buoy' is the section averaged buoyancy force in the plume; '**Drag**' is the drag force acting on the plume as a result of vortex formation in the plume wake; 'Ener' is the change in energy in the plume resulting from vertical gradients of temperature and wind speed; 'Entr' is the entrainment rate for unit distance along the plume axis; and 'Shear' is the shear force associated with the vertical gradient of wind speed. Supplementary equations used are

$$A = \frac{\pi}{4} D^2 \qquad [15.44.7]$$

$$\dot{m} = A\rho u \qquad [15.44.8]$$

$$\dot{m}_g = Acu \qquad [15.44.9]$$

$$\dot{P}_x = \dot{m}(u\cos\phi - u_\infty) \qquad [15.44.10]$$

$$\dot{P}_z = \dot{m}\, u \sin\phi \qquad [15.44.11]$$

$$\dot{E} = \dot{m}\left[\left(h + \frac{1}{2}u^2\right) - \left(h_\infty + \frac{1}{2}u_\infty^2\right)\right] \qquad [15.44.12]$$

where A is the cross-sectional area of the plume, c is the concentration (mass per unit volume), D is the diameter of the plume, h is the specific enthalpy, ρ is the density, u is the mean flow velocity and subscripts g and ∞ denote material released and ambient conditions at centroid height, respectively.

15.44.3 Touchdown plume

Touchdown occurs when the plume envelope first touches the ground. The plume cross-section is then modelled as a circular segment, the centroid of which falls until the cross-section becomes a semi-circle, at which point the touchdown regime ends.

The model for the touchdown plume also consists of a set of six differential equations. These are Equations 15.44.1, 15.44.2 and 15.44.4–15.44.6 with:

$$\frac{\mathrm{d}\dot{P}_z}{\mathrm{d}s} = \mathbf{Drag} \cdot \mathbf{e}_z + \mathrm{Buoy} + \mathrm{Foot} \qquad [15.44.13]$$

where 'Foot' is a reactive pressure force function.

Supplementary equations used are Equations 15.44.8–15.44.12 and

$$A = \frac{D^2}{4}\left[\cos^{-1}(-\eta_c)(1-\eta_c)^{1/2}\right] \qquad [15.44.14]$$

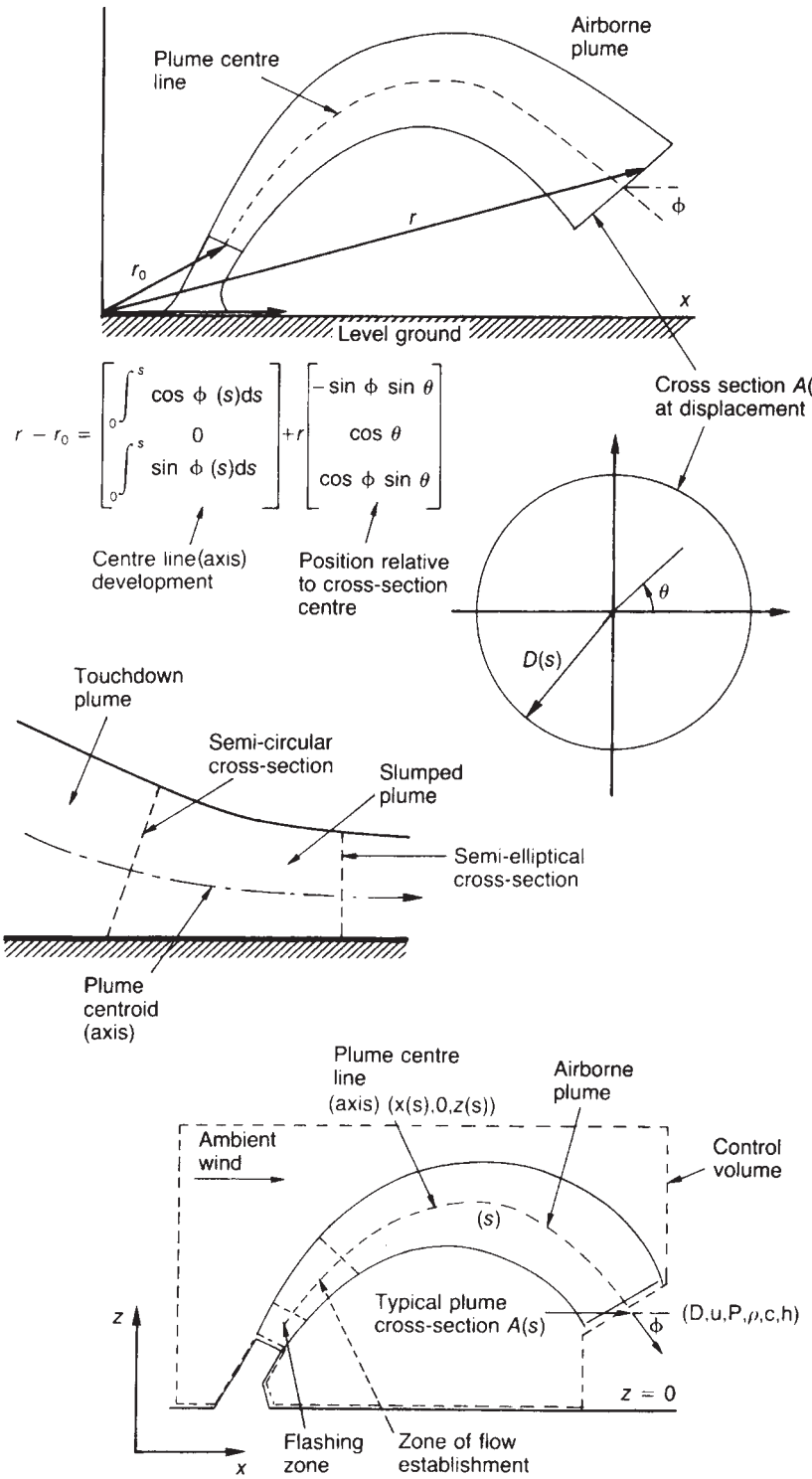


Figure 15.136 *PLUME model for dispersion of dense gas from elevated jets and plumes: plume geometry, coordinate system and control volume (McFarlane, 1991) (Courtesy of the American Institute of Chemical Engineers)*

$$\eta_c = \frac{\eta}{2\left(1+\left\{1-2/\left(3\left[\eta^2(1-\eta^2)(1-\eta^2)^{1/2}\right]\right)\right\}^{1/2}\right.} \quad [15.44.15]$$

$$\eta = \frac{2z}{D|\cos\phi|} \quad [15.44.16]$$

$$\eta_c = \frac{2z_c}{D|\cos\phi|} \quad [15.44.17]$$

where η is a parameter and subscript c denotes centre.

15.44.4 Slumped plume

The model for the slumped plume consists of the same set of six differential equations as for the touchdown plume. Supplementary equations used are Equations 15.44.8–15.44.12 and

$$A = \frac{e\pi}{8}D^2 \quad [15.44.18]$$

$$e = \frac{3\pi}{2}\frac{(z/D)}{|\cos\phi|} \quad [15.44.19]$$

where D is the length of the major axis of the ellipse and e is the eccentricity of the ellipse.

15.44.5 Buoyancy, shear and energy functions

For the airborne plume the buoyancy function 'Buoy' is

$$\text{Buoy} = A(\rho - \rho_g)g \quad [15.44.20]$$

This relation is valid, for expansion about the plume centroid, for the touchdown and slumped plume regimes also. The shear function 'Shear' is

$$\text{Shear} = \dot{m}\sin\phi\frac{du_\infty}{dz} \quad [15.44.21]$$

for all three regimes. The energy function 'Ener' is

$$\text{Ener} = \dot{m}\sin\phi\frac{d\left(h_\infty + 1/2u_\infty^2 + gz\right)}{dz} \quad [15.44.22]$$

15.44.6 Drag and pressure force functions

For the airborne plume the drag is airborne drag, which is not considered significant, and the drag function '**Drag**' is taken as zero. For the touchdown and for the slumped plume there is a ground surface drag, which is significant. For these latter regimes the drag function '**Drag**' is

$$\mathbf{Drag} = l\rho_\infty u_*^2\left[(\rho/\rho_\infty)^{1/2}(u/u_\infty)\cos\phi - 1\right] \times \left[(\rho/\rho_\infty)^{1/2}(u/u_\infty)\cos\phi + 1\right] \quad [15.44.23]$$

where l is the width of the 'footprint' of the plume and u_* is the friction velocity.

The value of the pressure force function 'Foot' is governed by the behaviour of the gravity current. At some point in the slumping regime the gravity current collapses. Before the point of collapse the spreading rate and the corresponding value of 'Foot' are

$$\frac{1}{2}\frac{dD}{ds} = (k/u)[gh(1-\rho_\infty/\rho)]^{1/2} \quad [15.44.24]$$

$$\text{Foot} = \left(\frac{3\pi^2}{32}\right)^3\frac{1}{k^2}l\rho u^2\left(\frac{1}{2}\frac{dD}{ds}\right)^2 \quad [15.44.25]$$

where k is the slumping coefficient. The value of k is taken as 1.15.

The criterion of collapse and the spreading rate after collapse are

$$(\rho_\infty/\rho)^{1/2}(D/h) > \frac{16}{3\kappa(\text{Ri}_*)^{1/2}\Phi(\text{Ri}_*)} \quad [15.44.26]$$

$$\frac{1}{2}\frac{dD}{ds} = \frac{\rho_\infty u_* h}{3\kappa C_D u D \text{Ri}_*\Phi(\text{Ri}_*)} \quad [15.44.27]$$

with

$$\Phi(\text{Ri}_*) = \frac{1}{(1-3\text{Ri}_*/5)^{1/2}} \quad \text{Ri}_* < 0 \quad [15.44.28a]$$

$$= 1 \quad 0 \le \text{Ri}_* < 189/80 \quad [15.44.28b]$$

$$= (10/17)\max\left[\text{Ri}_*/7, (1+4\text{Ri}_*/5)^{1/2}\right] \quad \text{Ri}_* > 189/80 \quad [15.44.28c]$$

$$\text{Ri}_* = \frac{gh(\rho/\rho_\infty - 1)}{u_*^2} \quad [15.44.29]$$

where h is the plume height, Ri_* is a bulk Richardson number, κ is the von Karman constant and $\Phi(\text{Ri}_*)$ is a heavy gas entrainment function. The value of 'Foot' after collapse is

$$\text{Foot} = \left(\frac{3\pi^2}{64}\right)^3\frac{3\kappa C_D}{\psi(\text{Ri}_*)}l_{lruu*}(D/z)\frac{dD}{ds} \quad [15.44.30]$$

for

$$(\rho_\infty/\rho)^{1/2}(D/z) > \frac{1024}{(9\pi^2)(\text{Ri}_*)^{1/2}\Phi(\text{Ri}_*)} \quad [15.44.31]$$

with

$$\text{Ri}_* = \frac{2gz(\rho/\rho_\infty - 1)}{u_*^2} \quad [15.44.32]$$

where C_D is an empirical spreading coefficient. The value of C_D is taken as 5.0.

15.44.7 Entrainment function

The entrainment function Entr is, in principle, the sum of the following entrainment mechanisms: jet entrainment, crosswind entrainment, gravity slumping entrainment, passive entrainment and heavy gas entrainment. The jet entrainment function Entr_{jet} is

$$\text{Entr}_{\text{jet}} = e_{\text{jet}}\eta_\rho L_{\text{fs}}\rho_\infty|u - u_\infty\cos\phi| \quad [15.44.33]$$

with

$$\eta_\rho = \frac{1+(4/3)(\rho/\rho_\infty - 1)}{1+(5/3)(\rho/\rho_\infty - 1)} \quad [15.44.34]$$

where e_{jet} is an entrainment coefficient and L_{fs} is the Monin–Obukhov length for a free surface, this latter being

the surface not bounded by the ground. The value of e_{jet} is taken as 0.08.

The crosswind entrainment function $Entr_{cw}$ is

$$Entr = e_{u,cr}\eta L_{fs}\rho_\infty u_\infty (u_\infty/u)^{1/2}|\sin\phi| \quad [15.44.35a]$$

with

$$\eta_\rho = 1 + e_{\rho,cr}\max[0, (\rho/\rho_\infty - 1)\sin\phi] \quad [15.44.35b]$$

where $e_{u,cr}$ and are $e_{\rho,cr}$ coefficients and η_ρ is a parameter. The values of $e_{u,cr}$ and $e_{\rho,cr}$ are 0.6 and 7.5, respectively.

The gravity slumping entrainment function $Entr_{gs}$ is, for the touchdown plume

$$Entr_{gs} = \left[1 - \frac{2z_c}{D|\cos\phi|}\right] e_{gs}\rho_\infty z u|\cos\phi|\frac{dD}{ds} \quad [15.44.36]$$

and for the slumped plume

$$Entr_{gs} = e_{gs}\rho_\infty z u|\cos\phi|\frac{dD}{ds} \quad [15.44.37]$$

where e_{gs} is a coefficient. A value of 0.85 is given for e_{gs}, but with some qualification.

The passive entrainment $Entr_{at}$ due to atmospheric turbulence is

$$Entr_{at} = (1 - 1/D)\pi e_{at}\rho_\infty \in^{1/3}\left(l_y^{4/3} + l_z^{4/3}\right) \quad [15.44.38]$$

with

$$l_y = \min[D/2, 0.88(z + z_o)(1 - 7.4\kappa\zeta/(1 - 5k\zeta)]$$
Stability categories A–C [15.44.39a]

$$= \min[D/2, 0.88(z + z_o)]$$
Stability category D [15.44.39b]

$$= \min[D/2, 0.88(z + z_o)(1 + 0.1\zeta)]$$
Stability categories E and F [15.44.39c]

$$l_z = \min[D/2, 0.88(z + z_o)(1 - 7.4\kappa\zeta/(1 - 5\kappa\zeta)]$$
Stability categories A–C [15.44.40a]

$$= \min[D/2, 0.88(z + z_o)]$$
Stability category D [15.44.40b]

$$= \min[D/2, 0.88(z + z_o)/(1 + 4\zeta)]$$
Stability categories E and F [15.44.40c]

$$\epsilon = (1 - 5\kappa\zeta)u_*^3/[\kappa(z + z_o)]$$
Stability categories A–C

$$= u_*^3/[\kappa(z + z_o)]$$
Stability category D [15.44.41b]

$$= (1 + 4\kappa)u_*^3/[\kappa(z + z_o)]$$
Stability categories E and F [15.44.41c]

$$\zeta = \frac{z + z_o}{L} \quad [15.44.42]$$

$$L = \frac{u_*^3}{\kappa(g/T_{gr}/u_* T^*)} \quad [15.44.43]$$

where e_{at} is a coefficient, l_y and l_z are the turbulent length scales in the horizontal and vertical directions, L is the Monin–Obukhov length, T_{gr} is the temperature of the ground, u_*T^* is the ground–air heat flux, ϵ is the dissipation rate of turbulent kinetic energy and is a parameter. The value of e_{at} is 1.0. The heavy gas entrainment $Entr_{hg}$ is

$$Entr_{hg} = \frac{1}{\Phi(Ri_*)} L_{fs}\kappa\rho_\infty u_* \quad [15.44.44]$$

with $\Phi(Ri_*)$ given by Equations 15.44.28 and 15.44.29, but with z substituted for h in the latter.

The jet entrainment and heavy gas entrainment each modify the level of turbulence and are not independent mechanisms. The combined contribution of these two effects is taken as the greater of the each of the two effects considered separately. Further, the contribution of each of the two effects is taken as proportional to the value of that effect divided by the sum of the values of the two effects. The passive entrainment and gravity slumping entrainment constitute another pair which interact and which are treated in a similar manner.

15.44.8 Atmospheric model

The plume behaviour is a function of the atmospheric conditions, and an atmospheric model is defined which includes the wind speed and temperature profiles and the Monin–Obukhov length. The wind speed profile is

$$= \frac{\kappa(z + z_o)}{u_*}\frac{du_\infty}{dz} = \psi_u(\zeta) \quad [15.44.45]$$

with

$$\psi_u(\zeta) = (1 - 22\zeta)^{-1/4} \quad \zeta < 0 \quad [15.44.46a]$$
$$= 1 + 6.9\zeta \quad \zeta \geq 0 \quad [15.44.46b]$$

The temperature profile is

$$\frac{\kappa(z + z_o)}{T^*}\frac{dT_{\infty pot}}{dz} = \psi_T(\zeta) \quad [15.44.47]$$

with

$$\psi_T(\zeta) = (1 - 13\zeta)^{1/2} \quad \zeta < 0 \quad [15.44.48a]$$
$$= 1 + 9.2\zeta \quad \zeta \geq 0 \quad [15.44.48b]$$

where the subscript pot denotes potential. The Monin–Obukhov length is

$$L = -10.99 z_o^{0.0993} \quad \text{Stability category A} \quad [15.44.49a]$$
$$= -13.44 z_o^{0.1631} \quad \text{Stability category B} \quad [15.44.49b]$$
$$= -113.5 z_o^{0.2946} \quad \text{Stability category C} \quad [15.44.49c]$$
$$= \infty \quad \text{Stability category D} \quad [15.44.49d]$$
$$= 125 z_o^{0.3090} \quad \text{Stability category E} \quad [15.44.49e]$$
$$= 26.12 z_o^{0.1667} \quad \text{Stability category F} \quad [15.44.49f]$$

15.45 Concentration and Concentration Fluctuations

The account of gas dispersion given so far has touched only lightly on the question of concentration and concentration

fluctuations and has dealt mainly with average concentration. It is now necessary to go into this more deeply.

Concentration fluctuations are relevant both to flammable and toxic gas releases. For flammable gas clouds, fluctuations may cause the gas concentration equivalent to the lower flammability limit to reach further than the boundary given by the mean value. For a toxic gas cloud, fluctuations may result in toxic effects associated with concentrations higher than the mean value.

Accounts of concentration fluctuations have been given by a number of authors, including Gosline (1952), Gifford (1960b), Long (1963), Slade (1968), Barry (1971), Ramsdell and Hinds (1971), Csanady (1973), Chatwin (1982b), C.D. Jones (1983), S.R. Hanna (1984), Ride (1984a,b) and J.K.W. Davies (1987, 1989).

It is convenient to deal primarily with the concentration in a plume from a continuous release, but that in a cloud from an instantaneous release is also considered.

15.45.1 Experimental studies and empirical features

It has been shown in experiments on plumes from a continuous point source by a number of workers that the instantaneous concentration measured at a fixed point fluctuates about the mean value and that the ratio of the maximum instantaneous value to the time mean value, or peak-to-mean ratio, can be quite large.

An account of experimental work on the peak-to-mean (P/M) ratio has been given by Gifford (1960b). He describes the results obtained by six previous workers. The ratio of the peak concentration P to the mean concentration M, or P/M, is a function of the ratio of the corresponding sampling times t_p and t_m from which these concentrations are derived. As shown in Figure 15.137 the P/M ratio tends to increase with increase in t_m/t_p, or decrease in t_p/t_m.

As Figure 15.137 indicates, the P/M ratio measured at ground level is appreciably greater for an elevated source than for one at ground level. This is illustrated also in Figure 15.138, which gives P/M as a function of distance. Gifford states that for measurements at ground level P/M can be expected to be about 1–5 for a ground level source but as much as 50–100 for an elevated source. Work by Ramsdell and Hinds (1971) has shown that the P/M ratio tends to be greater off the centre line.

Other workers have measured the proportion of time for which the concentration at a point is zero, or the intermittency. Work on concentrations in a plume by C.D. Jones (1983) has shown that the levels of intermittency can be very high, some 80–90%, with P/M ratios in the range 30–150.

Physical modelling using wind tunnels makes it possible to perform repeated experiments at the same nominal conditions. Figure 15.109(e) shows an ensemble of 21 concentration vs time profiles obtained by D.J. Hall, Hollis and Ishaq (1982) in wind tunnel work at Warren Spring Laboratory (WSL). The variability from one run to another is pronounced.

The intensity of the concentration fluctuations, defined below, is another widely used measure. An intensity value of zero corresponds to zero fluctuation. Figure 15.139 shows intensities obtained in wind tunnel work by Meroney and Lohmeyer (1984).

Such concentration fluctuations are not limited to gas clouds. Birch, Brown and Dodson (1980, 1981) have found large fluctuations in jets.

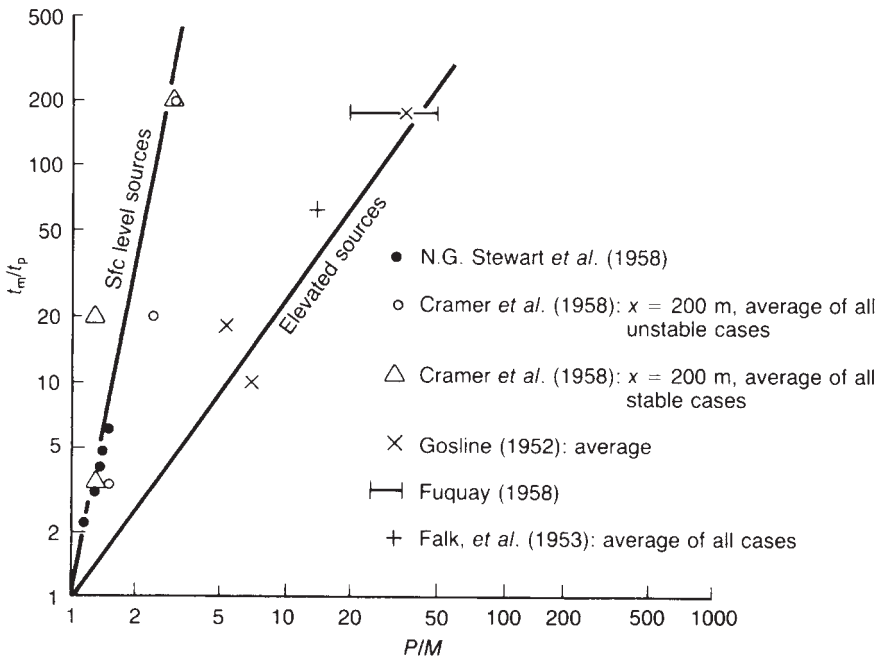


Figure 15.137 *Concentration fluctuations in a meandering plume: effect of mean sampling time t_m and peak sampling time t_p on the peak-to-mean concentration (Gifford, 1960b) (Courtesy of Pergamon Press)*

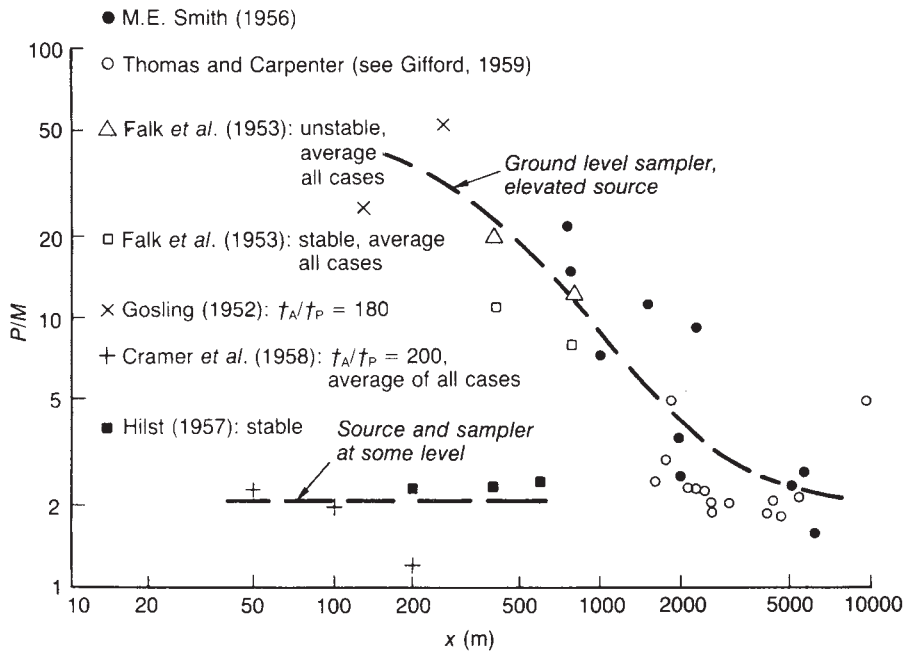


Figure 15.138 *Concentration fluctuations in a meandering plume: effect of distance (Gifford, 1960b) (Courtesy of Pergamon Press)*

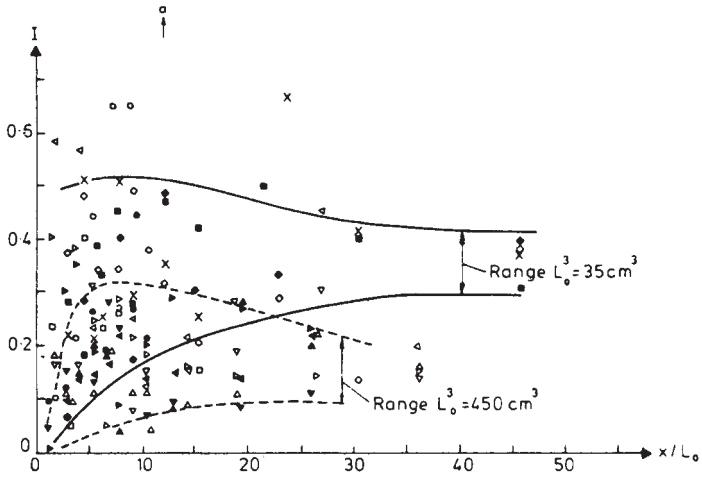


Figure 15.139 *Concentration fluctuations in gas dispersion—concentration fluctuation intensities measured in a wind tunnel (Meroney and Lohmeyer, 1984). Different symbols represent different release volumes, each being the result of at least five runs; I, intensity, L_O volume released; x, downstream distance (Courtesy of Kluwer Academic Publishers)*

15.45.2 Causes of concentration fluctuation

Fluctuations of concentration have a number of causes. One of these is meandering of the plume due to the variability of wind direction. But even without meander, concentration fluctuations occur due to the normal effects of turbulence.

15.45.3 Measures of concentration fluctuation

Concentration fluctuation may be characterized in a number of ways. These include

(1) peak-to-mean ratio;
(2) intermittency;

(3) intensity;
(4) distributional properties.

The peak-to-mean ratio is the ratio of the maximum instantaneous concentration to the time mean value:

$$\frac{P}{M} = \frac{C_{\max}}{\bar{C}} \qquad [15.45.1]$$

where $\bar{C}$ is the time mean concentration and $C_{\max}$ is the maximum instantaneous concentration.

Csanady (1973) introduced the concept of intermittency. The intermittency of concentration fluctuations, or simply intermittency, is the proportion of time during which the concentration is non-zero:

$$\gamma = \frac{t_s - t_p}{t_s} \qquad [15.45.2]$$

where t_p is the time during which the concentration is zero, t_s is the total sampling time and γ the intermittency. It should be noted that some authors define intermittency as the proportion of time during which the concentration is zero (i.e., the complement of the definition just given).

Two important statistical parameters of the concentration are the mean and the variance:

Mean: $\mu = \bar{C}$

Instantaneous deviation: $c = C - \bar{C}$

Standard deviation: $\sigma = (\bar{c}^2)^{1/2}$

The relative intensity i of concentration fluctuations, or simply intensity, is the ratio of the standard deviation to the mean of the concentration:

$$i = \left(\frac{\bar{c}^2}{\bar{C}}\right)^{1/2} \qquad [15.45.3]$$

The distributional properties are the distribution, and its parameters, which best describe the concentration fluctuations. The distribution most favoured is the log–normal distribution, which is characterized by the mean and log standard deviation. Alternatively, the mode may be used instead of the mean.

15.45.4 Time mean concentration

As discussed in Section 15.16, the mean concentration obtained by averaging over a particular sampling interval is a function of that interval. The correction used by D.B. Turner (1970) for this effect is

$$\frac{C}{C_r} = \left(\frac{t_r}{t}\right)^p \qquad [15.45.4]$$

where C is the concentration, t is the sampling time interval, p is an index and subscript r denotes reference. The value of p is between 0.17 and 0.2 where the sampling reference time t_r is of the order of 10 min and the other sampling time t is up to 2 h.

Another approach is that described by the CCPS (1987/2). On certain assumptions it can be shown that

$$\frac{\sigma^2(T)}{\sigma^2(0)} = 2\left\{\frac{T_1}{T}\left(1 - \frac{T_1}{T}\right)\left[1 - \exp\left(-\frac{T_1}{T}\right)\right]\right\} \qquad [15.45.5]$$

where T_1 is the integral time scale. They give for T_1 a typical value of 10 s.

Other approaches have been used as described by D.J. Wilson (1991a).

15.45.5 Models for concentration fluctuation

Most of the approaches used to model dispersion may also be applied to the modelling of concentration fluctuations. A review by S.R. Hanna (1984) describes Gaussian, gradient transfer, similarity, meandering plume and distribution function models.

15.45.6 Distribution function for concentration

The form of the distribution function of the instantaneous concentrations at a fixed point in a passive plume has been studied by several workers, including Barry (1971) and Csanady (1973).

As described above, since concentration is zero for a proportion of the time, Csanady introduced the concept of intermittency. The intermittency is close to unity on the centre line of the plume and to zero at the cloud edges.

Csanady adduces theoretical arguments that the distribution function for the non-zero concentrations should be log–normal. He also obtains the log–normal distribution for experimental results given by several authors. Figure 15.140 shows his plot of Gosline's results on log-probability paper, confirming the log–normal form for the concentration distribution.

Barry (1971) has found that the following exponential relation gives a good fit to experimental results:

$$P(C) = P(0)\exp\left(-P(0)\frac{C}{M}\right) \qquad [15.45.6]$$

where $P(0)$ and $P(C)$ are the probabilities that the concentration exceeds 0 and C, respectively, and C and M are

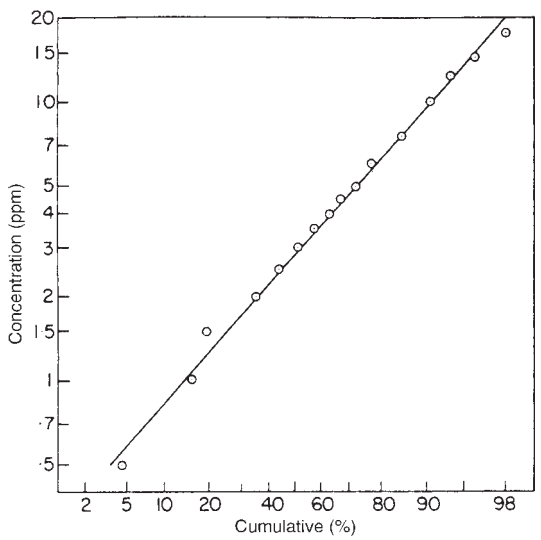


Figure 15.140 *Concentration fluctuations in a meandering plume: distribution function of concentrations (Csanady, 1973) (Courtesy of Reidel Publishing Company)*

the concentrations averaged over the peak sampling time t_p and the total sampling time t_m, respectively.

The form of the distribution function for concentration is also an issue in the work of Wilson, of Chatwin and of Davies, as described below.

15.45.7 Peak-to-mean concentration models

The distribution functions just described may be used as the basis for models of the peak-to-mean ratio.

Barry (1971) points out that the peak-to-mean ratio is simply a special case of the ratio of any short-lived concentration. By definition, the peak concentration is that which occurs only once. Hence the probability $P(P)$ of the peak value is

$$P(P) = t_p/t_m \qquad [15.45.7]$$

But from Equation 15.45.6

$$P(P) = P(0)\exp\left(-P(0)\frac{P}{M}\right) \qquad [15.45.8]$$

Then from equations 15.45.7 and 15.45.8

$$\frac{P}{M} = \frac{1}{P(0)}[1nP(0) - \ln(t_m/t_p)] \qquad [15.45.9]$$

Csanady gives the following approximate treatment of the case where the intermittency factor is unity and the concentration distribution is log–normal. This restriction on the intermittency factor implies that the plume does not meander. The probability density function of the concentration dF/dC is

$$\frac{dF}{dC} = \frac{1}{(2\pi)^{1/2}\sigma_1 C}\exp\left[-\frac{\ln(C/C_{med})}{2\sigma_1^2}\right] \qquad [15.45.10]$$

and the probability distribution function F is then

$$F = \frac{1}{2}\left\{1 + \mathrm{erf}\left[\frac{[\ln(C/C_{med})]}{2^{1/2}\sigma_1}\right]\right\} \qquad [15.45.11]$$

where C_{med} is the median concentration and σ is the logarithmic standard deviation. The mean concentration C_m is then

$$C_m = \int_0^1 C\frac{dF}{dC}dC \qquad [15.45.12a]$$

$$= C_{med}\exp(\sigma_1^2/2) \qquad [15.45.12b]$$

Then from Equation 15.45.11 the probability $P(=1-F)$ that a given peak concentration will not be exceeded is

$$P = 1 - \frac{1}{2}\left\{1 + \mathrm{erf}\left[\frac{\ln(C_p/C_{med})}{2^{1/2}\sigma_1}\right]\right\} \qquad [15.45.13]$$

and hence the peak concentration C_p is

$$C_p = C_{med}\exp\left[2^{1/2}\sigma_1\mathrm{erf}^{-1}(1-2P)\right] \qquad [15.45.14]$$

Then from Equations 15.45.12b and 15.45.14

$$\frac{C_p}{C_m} = \exp\left[2^{1/2}\sigma_1\mathrm{erf}^{-1}(1-2P) - \frac{\sigma_1^2}{2}\right] \qquad [15.45.15a]$$

$$= \frac{P}{M} \qquad [15.45.15b]$$

15.45.8 Gifford meandering plume model

As stated above, concentration fluctuations in a passive plume are due partly to turbulent movements and partly to meandering. The effect of these two influences is shown in Figure 15.141.

A model for a meandering plume has been given by Gifford (1960b). The basis of the model is Equation 15.16.41 for a release Q from a continuous point source at ground level. He treats the dispersion variance σ_y^2 as the sum of two parts: Y^2, the variance attributable to the fluctuations about the instantaneous centre line; and D_y^2, the variance

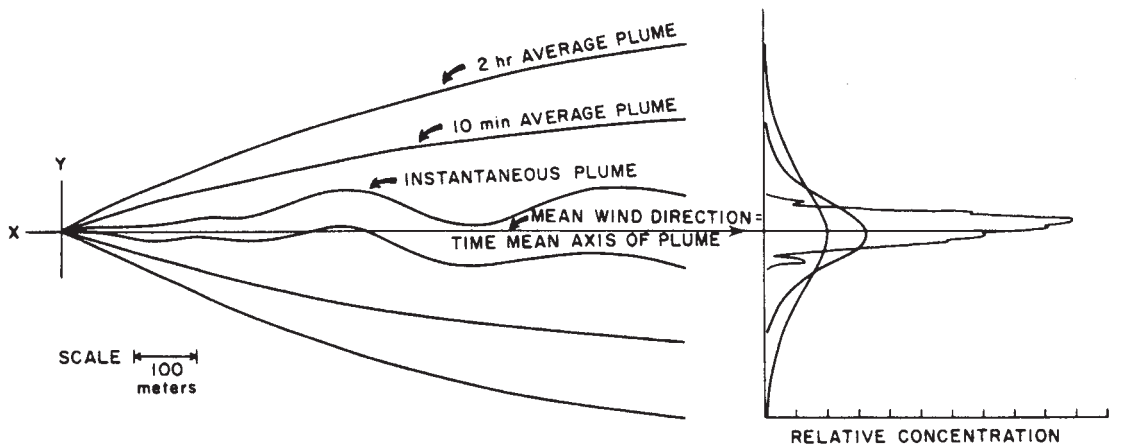


Figure 15.141 *Concentration fluctuations in a meandering plume: effect of combination of meandering and of turbulence (Slade, 1968)*

attributable to the meandering. Similarly, the variance σ_z^2 is taken as the sum of the fluctuation variance z^2 and the meandering variance D_z^2

$$\sigma_y^2 = Y^2 + D_y^2 \qquad [15.45.16a]$$

$$\sigma_z^2 = Z^2 + D_z^2 \qquad [15.45.16b]$$

From Equation 15.16.41 the mean concentration χ_m is then taken to be

$$\chi_m = \frac{Q}{2\pi u\left(Y^2 + D_y^2\right)^{1/2}\left(Z^2 + D_z^2\right)^{1/2}} \times \exp\left\{-\left[\frac{y^2}{2\left(Y^2 + D_y^2\right)} + \frac{z^2}{2\left(Z^2 + D_z^2\right)}\right]\right\} \qquad [15.45.17]$$

and the instantaneous concentration to be

$$\chi_i = \frac{Q}{2\pi u\left(Y^2Z^2\right)^{1/2}} \exp\left\{-\left[\frac{(y - D_y)^2}{2Y^2} + \frac{(z - D_z)^2}{2Z^2}\right]\right\} \qquad [15.45.18]$$

The peak value of the instantaneous concentration χ_p occurs at a point on the centre line of the instantaneous plume ($y = D_y$, $z = D_z$), and hence

$$\frac{\chi_p}{\chi_m} = \frac{\left(Y^2 + D_y^2\right)^{1/2}\left(Z^2 + D_z^2\right)^{1/2}}{\left(Y^2Z^2\right)^{1/2}} \times \exp\left\{\left[\frac{y^2}{2\left(Y^2 + D_y^2\right)} + \frac{z^2}{2\left(Z^2 + D_z^2\right)}\right]\right\} \qquad [15.45.19]$$

At ground level on the centre line ($y = z = 0$)

$$\frac{\chi_p}{\chi_m} = \frac{\left(Y^2 + D_y^2\right)^{1/2}\left(Z^2 + D_z^2\right)^{1/2}}{\left(Y^2Z^2\right)^{1/2}} \qquad [15.45.20a]$$

$$= \frac{P}{M} \qquad [15.45.20b]$$

If conditions are such that

$$Y^2 = Z^2 \qquad [15.45.21a]$$

and

$$D_y^2 = D_z^2 = D^2 \qquad [15.45.21b]$$

then

$$\frac{P}{M} = \frac{Y^2 + D^2}{Y^2} \qquad [15.45.22a]$$

$$= 1 + \frac{D^2}{Y^2} \qquad [15.45.22b]$$

But, at large distances, D^2 approaches a constant value, whereas Y^2 continues to grow, and hence

$$\frac{P}{M} \to 1 \qquad [15.45.23]$$

15.45.9 Ride model

A model for the intermittency effect in a passive plume has been given by Ride (1984b). The model envisages the cloud as a number of spheres of equal size and uniform concentration in a matrix with zero concentration between the spheres. It can be shown that the peak-to-mean concentration is

$$\frac{C^*}{\bar{C}} = \frac{1}{1 - \gamma} \qquad [15.45.24]$$

and that

$$\frac{C^*}{\bar{C}} = \left(\frac{\sigma}{\bar{C}}\right)^2 + 1 \qquad [15.45.25]$$

where C^* is the concentration in the sphere, $\bar{C}$ is the true mean concentration, γ is the intermittency and σ is the standard deviation of the instantaneous concentration. This author defines intermittency as the proportion of time the concentration is below a specified value.

If the maximum concentration which can occur over time τ is C_τ, the peak-to-mean ratio for this time is $C_\tau/\bar{C}$. In the limit, C_τ tends to C^* as τ tends to zero and to $\bar{C}$ as τ tends to infinity. The intermittency is then γ_τ.

Equation 15.45.25 holds for spheres of uniform size. Rodean (1982) has derived the more general relation

$$\frac{C_\tau}{\bar{C}} = k\left(\frac{\sigma}{\bar{C}}\right)^\lambda + 1 \qquad [15.45.26]$$

where k is a constant and λ is an index.

From the foregoing it is possible to derive the relation

$$\frac{C_\tau}{\bar{C}} = k\left(\frac{\sigma}{\bar{C}}\right)^\tau \psi^{\lambda/2} + 1 \qquad [15.45.27]$$

with

$$\frac{\sigma_\tau}{\bar{C}} = \frac{\sigma}{\bar{C}}\psi^{1/2} \qquad [15.45.28]$$

$$\psi = \left(\frac{\beta}{ut + \beta}\right) \qquad [15.45.29]$$

where β is a constant. From the data of C.D. Jones (1983), Ride (1984b) assigns the values: $k = 11$, $\lambda = 1.5$ and $\beta = 0.4x$. where x is the downwind distance. He gives for $C_\tau/\bar{C}$ a comparison of predicted values with observations made at short ranges by Jones.

In a further treatment, Ride (1984a) omits the factor ψ, equivalent to setting $\psi = 1$.

15.45.10 Wilson model

A model for the intensity of concentration fluctuations in a passive plume has been given by D.J. Wilson (1982). The concentration fluctuation c' is defined as

$$c' = c - \bar{c} \qquad [15.45.30]$$

where c is the concentration, c' is the concentration fluctuation about the mean and $\bar{c}$ is the mean concentration. The concentration variance is $\overline{c'^2}$.

The model is based on the Gaussian description of a plume:

$$\bar{c} = \frac{Q}{2\pi u_c \sigma_y \sigma_z} G_m F_m \qquad [15.45.31]$$

with

$$G_m = \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \qquad [15.45.32]$$

$$F_m = \exp\left[-\frac{1}{2}\left(\frac{z-h}{\sigma_z}\right)^2\right] + \exp\left[-\frac{1}{2}\left(\frac{z+h}{\sigma_z}\right)^2\right] \qquad [15.45.33]$$

where F_m is a height correction, G_m is a crosswind distance correction, h is the height of the source, Q is the mass rate of release and u_c is the advection velocity of the plume.

From the work of D.J. Wilson, Robins and Fackrell (1982), the concept of a variance source strength q is introduced

$$\overline{c'^2} = \left(\frac{q}{2\pi u_c \sigma_y \sigma_z}\right)^2 G_v F_v \qquad [15.45.34]$$

with

$$G_v = \frac{1}{2}\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y} - \phi\right)^2\right] + \frac{1}{2}\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y} + \phi\right)^2\right] \qquad [15.45.35]$$

$$F_v = \exp\left[-\frac{1}{2}\left(\frac{z-h_v}{\sigma_z}\right)^2\right] - \alpha\exp\left[-\frac{1}{2}\left(\frac{z+h_v}{\sigma_z}\right)^2\right] \qquad [15.45.36]$$

$$\frac{h_v}{\sigma_z} = \left[\left(\frac{h}{\sigma_z}\right)^2 + \phi^2\right]^{1/2} \qquad [15.45.37]$$

where F_v is a height correction, G_v is a crosswind distance correction, h_v is the effective height of the variance source, q is the variance source strength, α is the sink strength factor and ϕ is a location parameter for the variance source. The value of the parameter ϕ is 0.706. The variance source strength is given by the relation

$$\frac{q}{Q} = \frac{0.38\lambda}{\lambda^2 + \lambda_o^2} \qquad [15.45.38]$$

with

$$\lambda = \frac{(\sigma_y \sigma_z)^{1/2}}{H} \qquad [15.45.39]$$

$$\lambda_o = \frac{0.119d}{0.033z_e + d} \qquad [15.45.40]$$

$$z_e = h\exp\left[-\left(\frac{\sigma_z}{h}\right)^2\right] \qquad [15.45.41]$$

where d is the diameter of the source, H is the height of the neutrally stable atmospheric boundary layer, z_e is a scale height, λ is the normalized downwind distance and λ_o is the virtual origin of the variance source. The value of H is taken as 650 m. The intensity i is defined as

$$i = \left(\overline{c'^2}\right)^{1/2}/\bar{c} \qquad [15.45.42]$$

Hence from Equations 15.45.31–15.45.36 and 15.45.42

$$i = \left(\frac{q}{Q}\right)\frac{(G_v F_v)^{1/2}}{G_m F_m} \qquad [15.45.43]$$

The intensity just derived is the total intensity. Use is also made of the conditional intensity i_p based on the time when the concentration is non-zero.

A corresponding set of conditional concentrations is defined

$$c'_p = c - \bar{c}_p \qquad [15.45.44]$$

where c'_p is the conditional concentration fluctuation about the mean, $\bar{c}_p$ is the conditional mean concentration and subscript ρ refers to the time when the concentration is non-zero. The conditional concentration variance is c'^2_p. The conditional intensity i_p is

$$i_p = \frac{\left(\overline{c'^2_p}\right)^{1/2}}{\bar{c}_p} \qquad [15.45.45]$$

The ratio of the mean concentration to the conditional mean concentration is the intermittency γ

$$\gamma = \frac{\bar{c}}{\bar{c}_p} \qquad [15.45.46]$$

This author defines intermittency as the proportion of time the concentration is non-zero. Then from Equations 15.45.42 and 15.45.44–15.45.46

$$i^2 = \frac{i_p^2}{\gamma} + \frac{1-\gamma}{\gamma} \quad i_p > 0 \qquad [15.45.47]$$

$$i = \left[\frac{1-\gamma}{\gamma}\right]^{1/2} \quad i_p = 0 \qquad [15.45.48]$$

On certain assumptions it can be shown that the conditional intensity i_p is given by

$$i_p = i_{p\infty}\frac{\left[1 - \alpha\exp\left(-2h_v z/\sigma_z^2\right)\right]^{1/2}}{\left[1 + \exp\left(-2hz/\sigma_z^2\right)\right]} \qquad [15.45.49]$$

with

$$i_{p\infty} = \frac{q_p}{Q}\exp\left(-\phi^2/4\right) \qquad [15.45.50]$$

$$\frac{q_p}{Q} = \frac{0.38\lambda}{\lambda^2 + (0.119)^2} \qquad [15.45.51]$$

where $i_{p\infty}$ is the conditional intensity on the centre line with negligible surface interaction and q_p is the conditional variance source strength. The value of α is taken as 0.6. The results are sensitive to the value used for α.

From Equation 15.45.47 the intermittency γ is

$$\gamma = \frac{i_p^2 + 1}{i^2 + 1} \qquad [15.45.52]$$

The probability of exceeding a particular concentration c is then obtained using an appropriate distribution for the concentration c. The cumulative distribution function F_c for the concentration is

$$F_c = \int_o^c p(c)\,dc \qquad [15.45.53]$$

where p(c) is the probability density function for concentration. With intermittency this latter is

$$p(c) = (1-\gamma)\delta(c) + \gamma p_p(c) \qquad [15.45.54]$$

where $p_p(c)$ is the probability density function for conditional concentration. The delta function $\delta(c)$ is a spike at $c = 0$ and zero elsewhere with the further property that

$$\int_{-\infty}^{\infty} \delta(c)\,dc = 1 \qquad [15.45.55]$$

Hence from Equations 15.45.53–15.45.55

$$F_c = (1-\gamma) + \gamma \int_0^c p_p(c)\,dc \qquad [15.45.56]$$

For the log–normal distribution

$$p_p(c) = \frac{1}{(2\pi)^{1/2}\sigma_1 c} \exp\left[-\frac{\ln^2(c/c_{mp})}{2\sigma_1^2}\right] \qquad [15.45.57]$$

with

$$c_{mp} = \frac{\bar{c}_p}{\left(1 + i_p^2\right)^{1/2}} \qquad [15.45.58]$$

$$\sigma_1 = \left[\ln\left(1 + i_p^2\right)\right]^{1/2} \qquad [15.45.59]$$

Applying Equation 15.45.46, Equations 15.45.58 and 15.45.59 become

$$c_{mp} = \frac{\bar{c}}{\gamma[\gamma[1 + i^2]]^{1/2}} \qquad [15.45.60]$$

$$\sigma_1 = \left\{\ln\left[\gamma\left(1 + i^2\right)\right]\right\}^{1/2} \qquad [15.45.61]$$

Then from Equations 15.45.54, 15.45.56 and 15.45.57

$$F_c = (1-\gamma) + \frac{\gamma}{2}\left\{1 + \mathrm{erf}\left[\frac{\ln(c/c_{mp})}{2^{1/2}\sigma_1}\right]\right\} \qquad [15.45.62]$$

It is more convenient to work in terms not of the conditional median concentration c_{mp} but of the conditional mean concentration $\bar{c}_p$. The relation between them is

$$c_{mp} = \bar{c}_p \exp\left(-\sigma_1^2/2\right) \qquad [15.45.63]$$

Then from Equations 15.45.46 and 15.45.63 it can be shown that

$$\ln\left(\frac{c}{c_{mp}}\right) = \ln\left[\frac{\gamma c}{\bar{c}\exp\left(-\sigma_1^2/2\right)}\right] \qquad [15.45.64]$$

But from Equation 15.45.31 the relation between the mean concentration and the mean concentration $\bar{c}_o$ on the centre line is

$$\bar{c} = \bar{c}_o \exp\left(-y^2/2\sigma_y^2\right) \qquad [15.45.65]$$

Hence from Equations 15.45.62, 15.45.64 and 15.45.65

$$F_c = 1 - \gamma\left(1 - \frac{1}{2}\left\{1 + \mathrm{erf}\left[\frac{\ln(\gamma c/\bar{c}_o) + \left(y^2/2\sigma_y^2\right) + \left(\sigma_1^2/2\right)}{2^{1/2}\sigma_1}\right]\right\}\right) \qquad [15.45.66]$$

Equation 15.45.66 is the basic equation of the model, giving the distribution function of c as a function of the intensity i, the conditional intensity i_p and the intermittency γ.

Wilson also discusses the use of alternative distributions. The two distributions which are most appropriate for physical reasons are the log–normal and the exponential. The exponential distribution has advantages for high intermittency, but overall he favours the log–normal distribution.

For the exponential distribution the probability density function in terms of the conditional mean concentration is

$$p_p(c) = \frac{1}{\bar{c}_p}\exp(-c/\bar{c}_p) \qquad [15.45.67]$$

and that in terms of the mean concentration is

$$p_p(c) = \frac{\gamma}{\bar{c}}\exp(-c\gamma/\bar{c}) \qquad [15.45.68]$$

Then from Equation 15.45.56 and Equations 15.45.67 and 15.45.68

$$F_c = 1 - \gamma + \gamma[1 - \exp(-c/\bar{c}_p)] \qquad [15.45.69]$$

$$F_c = 1 - \gamma + \gamma[1 - \exp(-c\gamma/\bar{c})] \qquad [15.45.70]$$

This model has been developed in subsequent work by the authors and coworkers (D.J. Wilson and Simms, 1985; D.J. Wilson, 1991a).

The application of this model to toxic gas clouds is described in Section 15.47.

15.45.11 Concentration ensemble

Concentration measurements in one experiment represent a single realization of a potential ensemble of experiments. The WSL data set described above and shown in Figure 15.109(e) is an illustration of such an ensemble.

The importance of working in terms of the properties of the ensemble rather than of a single experiment has been brought out by Chatwin (1982b), and subsequently developed (Cam and Chatwin, 1985; Cam, 1987; Mole and Chatwin, 1987; Cam, Sherrel and Chatwin, 1988; Chatwin, 1991).

Chatwin (1982b) discusses the concentration $\Gamma(x, t)$ from a single experiment. The mean value of this concentration is $\bar{\Gamma}(x, t)$. The mean value for the ensemble $C(x, t)$ is defined as

$$C(x,t) = \lim_{n\to\infty}\left[\frac{1}{n}\sum_{r=1}^{n}\Gamma^{(r)}(x,t)\right] \qquad [15.45.71]$$

The concentration fluctuation $c(x, t)$ is then

$$c(x,t) = \Gamma(x,t) - C(x,t) \qquad [15.45.72]$$

This fluctuation has a mean value $\bar{c}(x, t) = 0$. The ensemble mean square fluctuation $\bar{c}^2(x, t)$ satisfies

$$\bar{c}^2(x,t) = \bar{\Gamma}^2(x,t) - C^2(x,t) \qquad [15.45.73]$$

The quantities $C(x, t)$ and $c^2(x, t)$ are the mean and variance of the ensemble, respectively.

In a given realization, there is a certain probability of a particular concentration $\Gamma(x, t)$. Let this concentration be $\theta = \Gamma(x, t)$. The ensemble may be characterized by a probability density function (PDF) $p(\theta, x, t)$. It is a property of the PDF that

$$\int_0^1 p(\theta,x,t)\,\mathrm{d}\theta = 1 \qquad [15.45.74a]$$

or for the case where air is entrained so that $\theta_{\max} < 1$

$$\int_0^{\theta_{\max}} p(\theta,x,t)\,\mathrm{d}\theta = 1 \qquad [15.45.74b]$$

The PDF is related to the mean and variance as follows:

$$C(x,t) = \int_0^1 \theta p(\theta,x,t)\,\mathrm{d}\theta \qquad [15.45.75]$$

$$\bar{c}^2(x,t) = \int_0^1 (\theta - C)^2 p(\theta,x,t)\,\mathrm{d}\theta \qquad [15.45.76]$$

The intensity i is

$$i = \frac{(\bar{c}^2(x,t))^{1/2}}{C(x,t)} \qquad [15.45.77]$$

If the PDF can be characterized by one of the standard distributions, such as the normal or log–normal distributions, the probability may be obtained analytically. Otherwise it must be obtained by numerical integration of the PDF. Thus if the PDF fits the normal distribution, then, for example, there is 90% confidence that the concentration θ lies between the limits $C(x,t) \pm 1.65[\bar{c}^2(x,t)]^{1/2}$.

A typical application of the PDF approach is the determination of the probability P that a concentration in a steady state cloud or jet will lie between the lower flammability limit θ_L and the upper flammability limit θ_U. Then

$$P = \int_{\theta_L}^{\theta_u} p(\theta,x)\,\mathrm{d}\theta \qquad [15.45.78]$$

Such an application is illustrated in the work of Birch, Brown and Dodson (1980) on the concentration fluctuations, and hence ignition probabilities, in methane jets. Figure 15.142(a) shows PDFs as a function of radial distance measured in such jets and Figure 15.142(b) shows the probability of ignition of the jets.

The experimental determination of a concentration ensemble from which statistical properties are to be derived requires considerable care. The experimental variables which can cause variability in concentration must be fully defined.

The properties of the ensemble are affected by the framework, absolute or relative, in which the measurements are made. If an absolute framework is chosen, the properties depend significantly on any feature which influences the motion of the cloud as a whole. This implies the need for a much larger number of experiments.

The relationships between the intermittency and the other quantities in this scheme have been given by Cam and Chatwin (1985). If the concentration θ is assumed to have only one of two values, θ_o or 0:

$$p(\theta,x,t) = \gamma(x,t)\delta(\theta - \theta_o) + [1 - \gamma(x,t)]\delta(\theta) \qquad [15.45.79]$$

where γ is the intermittency and δ is the delta function. These authors define intermittency as the proportion of time the concentration is non-zero. Then from Equation 15.45.79 and Equations 15.45.75 and 15.45.76 the mean and variance are

$$C(x,t) = \theta_o\gamma(x,t) \qquad [15.45.80]$$

$$\bar{c}^2(x,t) = \theta_o^2[\gamma(x,t) - \gamma^2(x,t)] \qquad [15.45.81]$$

Hence from Equations 15.45.77 and 15.45.81 the intensity is

$$i(x,t) = \left[\frac{\theta_o}{C(x,t)} - 1\right]^{1/2} \qquad [15.45.82a]$$

$$= \left[\frac{1}{\gamma(x,t) - 1}\right]^{1/2} \qquad [15.45.82b]$$

15.45.12 Concentrations for dense gas: intensity parameter

In an extension of this work, Cam (1987) has addressed the problem of concentration fluctuations in dense gas clouds. He defines an intensity parameter R which is the square of the intensity I so that

$$R(C) = \frac{\bar{c}^2(x,t)}{\bar{C}^2} \qquad [15.45.83]$$

Thorney Island trials 7–19 were analysed and empirical values of this intensity parameter were obtained as shown in Figure 15.143. It was found that $R(C)$ was constant for a substantial proportion of the total record of $C(t)$ and

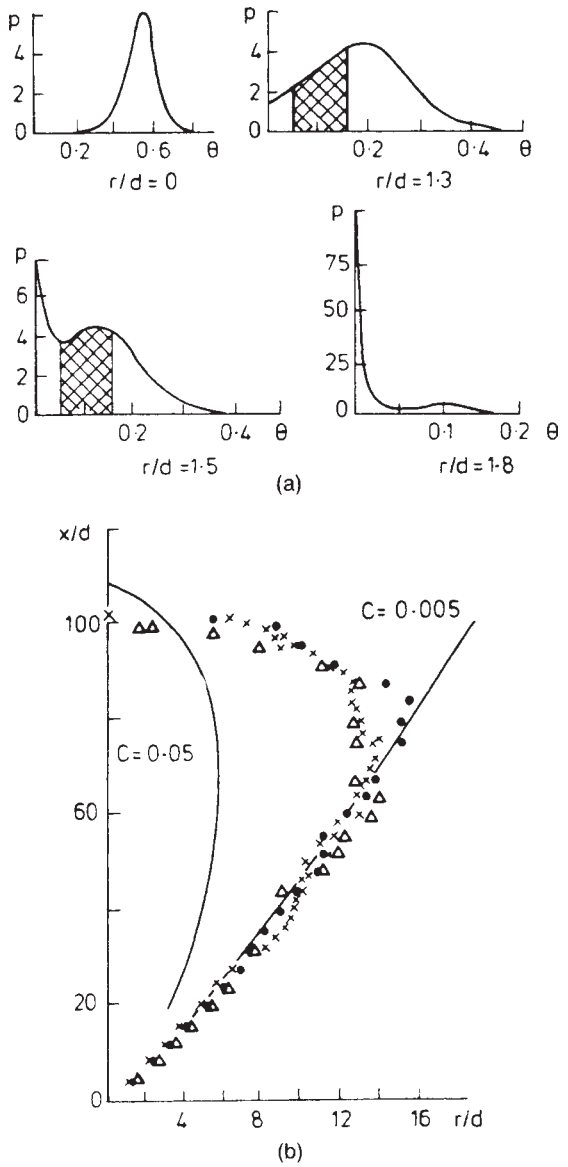


Figure 15.142 *Concentration fluctuations in gas dispersion – concentration and ignition probability in gas jets: (a) probability density functions of concentration in a methane jet (Birch et al., 1978) Courtesy of Cambridge University Press; (b) ignition probability in radial plane of a natural gas jet (Birch, Brown and Dodson, 1980; reproduced by permission) C, concentration; d, diameter; p, probability; r, radial distance; x, axial distance. In (b) measurements made at Reynolds number 12,500 (Δ), 16,700 (×) and 20,900 (•). Curve of measured ignition probabilities is different from that of the LFL (C = 0.05)*

constant over much of the area of the cloud, but there were also some substantial variations of $R(C)$ even at constant $\overline{C}$.

Carn quotes the following empirical relation, due to Chatwin (1982b), for the bound on $R(C)$:

$$R(C) = \epsilon(1/\overline{C} - 1) \qquad [15.45.84]$$

where ϵ is a constant. The suggested value of ϵ is 0.04. The behaviour of $R(C)$ was further investigated by obtaining an area-averaged value. This started at a peak of about 5, fell over some 30 s to about 1 and held this value for a period of 30–150 s and then rose to a plateau of about 4 some 160 s after the release.

15.45.13 Concentrations for dense gas: *Workbook*

The *Workbook* by Britter and McQuaid (1988) is primarily concerned with the provision of a method of estimating the mean concentrations in dense gas dispersion. It does,

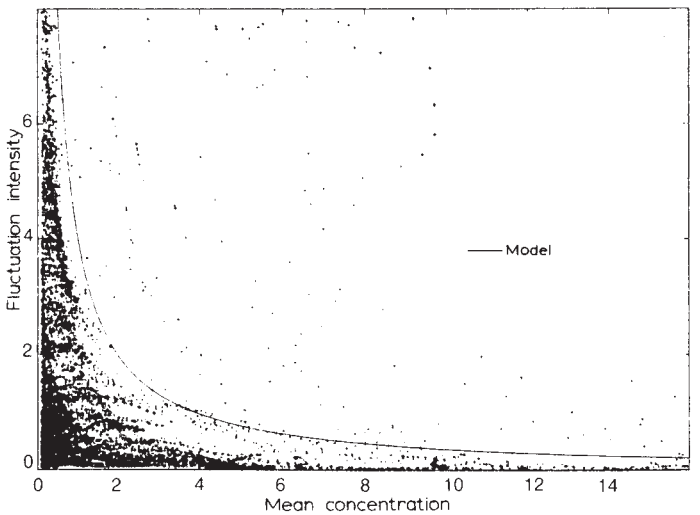


Figure 15.143 *Concentration fluctuations in gas dispersion – concentration fluctuation intensity factor for Thorney Island Phase 1 trials (Cam, 1987) (Courtesy of Elsevier Science Publishers)*

however, include a discussion of concentration fluctuations. It points out that, even for passive dispersion, there is uncertainty about the definition and quantification of concentration. The treatments available for dense gas dispersion are rudimentary.

It is possible, however, that for dense gas dispersion the problem may be simpler than for passive dispersion. The more deterministic nature of dense gas dispersion may result in smaller concentration fluctuations. Moreover, in dense gas dispersion the release is usually at ground level and the cloud remains near the ground. Work on passive dispersion has shown that fluctuations are less for ground level and near ground level releases.

15.45.14 Jets and plumes

The concentration fluctuations in jets have been measured by a number of workers. On the basis of this work Long (1963) has proposed that for the estimation of the maximum instantaneous concentration in a jet the value of the constants k_2k_3 to be used in Equation 15.20.8 should be 9 and 2, respectively, and that for the maximum instantaneous concentration in a plume the value of the constant k_4 to be used in Equation 15.20.96 should be 17; he does not propose a value for the constant k_5.

The work of Brown, Birch and Dodson (1980, 1981) on the probability density function approach to concentration fluctuations in jets has been described above.

15.46 Flammable Gas Clouds

It is often necessary to be able to estimate the mass of gas within the flammable range in a cloud from a flammable gas release. Workers who have studied this problem include Burgess *et al.* (1975), Eisenberg, Lynch and Breeding (1975), V.J. Clancey (1977c), van Buijtinen (1980) and J.G. Marshall (1977, 1980).

The treatments are mainly for jets and plumes at the point of release or for clouds with passive dispersion. The cases considered here are

(1) instantaneous source;
(2) continuous source;
(3) momentum jet;
(4) buoyant plume.

The flammable mass in a dense gas cloud is also discussed.

Approaches to dealing with the effect of concentration fluctuations on the determination of the flammable cloud are described.

15.46.1 Instantaneous source

A simple treatment for the mass of gas in the cloud from the instantaneous release of a neutral density gas has been given by V.J. Clancey (1977a), who uses the following equations derived from Equation 15.16.40 with Equation 15.14.5:

$$\chi = \frac{2Q^*}{(2\pi)^{3/2}\sigma^3}\exp\left(-\frac{1}{2}\frac{r^2}{\sigma^2}\right) \qquad [15.46.1]$$

$$\chi_{cc} = \frac{2Q^*}{(2\pi)^{3/2}\sigma^3} \qquad [15.46.2]$$

where Q^* is the mass released, r is the radial distance, σ is the dispersion coefficient, χ is the concentration and the subscript cc denotes the cloud centre.

The mass W of flammable gas between the radii r_1 and r_2 may then be calculated as

$$W = \int_{r_1}^{r_2} 2\pi r^2 \exp\left(-\frac{1}{2}\frac{r^2}{\sigma^2}\right)\mathrm{d}r \qquad [15.46.3]$$

where r_1 is the inner radius, r_2 is the outer radius and W is the mass of flammable gas. For $r_1 = 0$ and $r_2 = \infty$, Equation 15.46.3 gives $W = Q^*$.

The maximum quantity of flammable mixture, and hence the maximum hazard, occurs when the concentration χ_{cc} at the centre of the cloud equals the upper flammability limit χ_U:

$$\chi_U = \chi_{cc} \quad [15.46.4]$$

$$= \frac{2Q^*}{(2\pi)^{3/2}\sigma_m^2} \quad [15.46.5]$$

where σ_m is the value of σ at maximum hazard. The lower flammability limit χ_L and the radius r_L at which this occurs are given by the equations

$$\chi_L = \chi_U \exp\left(-\frac{1}{2}\frac{r_L^2}{\sigma_m^2}\right) \quad [15.46.6]$$

$$r_L = [2\sigma_m^2 \ln(\chi_U/\chi_L)]^{1/2} \quad [15.46.7]$$

The mass F of flammable gas between the flammability limits at maximum hazard is

$$F = \int_0^{r_L} 2\pi r^2 \chi_U \exp\left(-\frac{1}{2}\frac{r_L^2}{\sigma_m^2}\right) dr \quad [15.46.8]$$

The evaluation of Equation 15.46.8 is assisted by noting that it may be rewritten as

$$F = \int_0^{r_L} \frac{2Q^* r^2}{\sigma_m^2}\left[\frac{1}{\sigma_m(2\pi^{1/2})}\exp\left(-\frac{1}{2}\frac{r_L^2}{\sigma_m^2}\right)\right] dr \quad [15.46.9]$$

where the expression inside the square brackets is the Gaussian distribution.

This model indicates that the ratio χ_U/χ_L of the upper and lower flammability limits is an important quantity in determining the fraction of the cloud within the flammable range and thus available for combustion.

For a typical hydrocarbon the ratio of the upper to the lower flammability limit is in the range 4–6, so that the ratio of gas within the flammable range to the total gas in the cloud at maximum hazard is

$$F/Q^* \approx 2/3 \quad [15.46.10]$$

The growth of the cloud prior to this point may be determined from Equations 15.46.1–15.46.3. As a first approximation, however, the mass of gas within the flammable range may be taken as rising linearly from the initial value to the value at maximum hazard with a rapid fall-off thereafter.

A further treatment for an instantaneous release from a point source has been given by van Buijtenen (1980). Formulating his model in terms of mass and mass concentrations of gas, the starting point is the following relation for an instantaneous release from an elevated source, of height H, derived from Equations 15.16.40b and 15.16.43:

$$\chi(x,y,z,t) = \frac{Q^*}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z}\exp\left[-\frac{(x-ut)^2}{2\sigma_x^2}\right]\exp\left(\frac{-y^2}{2\sigma_y^2}\right) \times\left\{\exp\left[-\frac{(z-H)^2}{2\sigma_z^2}\right]+\exp\left[\frac{(z+H)^2}{2\sigma_z^2}\right]\right\} \quad [15.46.11]$$

Then from Equation 15.46.11 the fraction of gas between the flammability limits is

$$\frac{Q_e^*}{Q^*} = \mathrm{erf}\left[(\ln\chi_{cc}/\chi_L)^{1/2}\right] - \mathrm{erf}\left[(\ln\chi_{cc}/\chi_U)^{1/2}\right] - 2\frac{\chi_L}{(\pi)^{1/2}\chi_{cc}}\left[(\ln\chi_{cc}/\chi_L)^{1/2}\right] + \frac{2\chi U}{(\pi)^{1/2}\chi_{cc}}\left[\left(\ln\chi_{cc}/\chi_U^{1/2}\right)^{1/2}\right] \quad \chi_{cc} > \chi_U \quad [15.46.12a]$$

$$= \mathrm{erf}\left[(\ln\chi_{cc}/\chi_L)^{1/2}\right] - \frac{2\chi_L}{\pi^{1/2}\chi_{cc}}[(\ln\chi_{cc}/\chi_L)^{1/2}] \quad \chi_{cc} < \chi_U \quad [15.46.12b]$$

where Q^* is the mass of gas released and Q_e^* is the mass of gas within the flammable range. Equation 15.46.12 applies to a cloud completely free of the ground or, alternatively, to a cloud at ground level ($H = 0$).

The maximum value of the fraction Q_e^*/Q^* of gas within the flammable range is obtained by differentiating Equation (15.46.12a) with respect to χ_{cc} which gives

$$\ln\chi_{cc} = \frac{\chi_U^2\ln\chi_U - \chi_L^2\ln\chi_L}{\chi_U^2 - \chi_L^2} \quad [15.46.13]$$

Substituting for χ_{cc} from Equation 15.46.13 into Equation 15.46.12a gives

$$\left(\frac{Q_e^*}{Q^*}\right)_{max} = \mathrm{erf}\left(v_2^{1/2}\right) - \mathrm{erf}\left(v_1^{1/2}\right) - \frac{2\exp(-v_2)v_2^{1/2}}{\pi^{1/2}} + \frac{2\exp(-v_1)v_1^{1/2}}{\pi^{1/2}} \quad [15.46.14]$$

with

$$v = \chi_U/\chi_L \quad [15.46.15a]$$

$$v_1 = \ln(v)/(v^2-1) \quad [15.46.15b]$$

$$v_2 = v^2\ln(v)/(v^2-1) \quad [15.46.15c]$$

where the subscript max denotes the maximum value.

The influence of the ratio χ_U/χ_L of the flammability limits on the fraction Q_e^*/Q^* of gas between the flammability limits according to Equation 15.46.14 is shown in Figure 15.144.

The application of this model can be extended if necessary by the use of the virtual source method. Van Buijtenen also gives an equation for an instantaneous source of finite size.

The problem of the amount of gas available for combustion has also been considered by Eisenberg, Lynch and Breeding (1975). These authors list three assumptions which may be made about this quantity:

(1) all the fuel above the lower flammability limit;
(2) all the fuel between the upper and lower flammability limits;
(3) all the fuel between the upper and lower flammability limits for which oxygen is available.

The third assumption is the most accurate. For this latter case the mass of gas available for combustion is

$$W_F = \int_{V_{LS}} \chi\, dV + \int_{V_{SU}} \chi F(c)\, dV \quad [15.46.16]$$

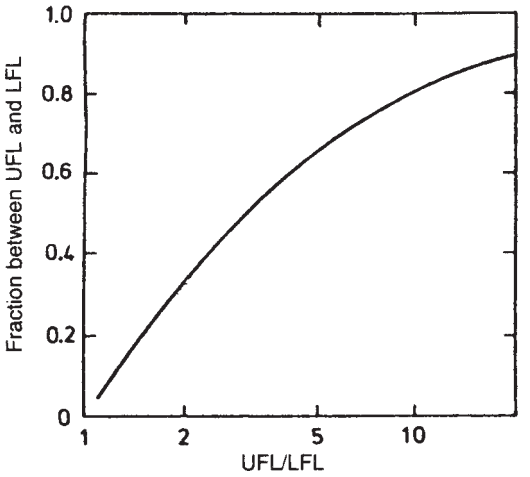


Figure 15.144 *Flammable gas clouds – effect of ratio of flammability limits on fraction of gas within flammable range for release from an instantaneous point source (van Buijtenen, 1980), LFL, lower flammability limit; UFL, upper flammability limit (Courtesy of Elsevier Science Publishers)*

where $F(c)$ is the weighting function giving the fraction of fuel present that enters into the combustion reaction, V_{LS} is the volume of the cloud between the lower flammability limit and the stoichiometric concentration (m^3), V_{SU} is the volume of the cloud between the stoichiometric concentration and the upper flammability limit (m^3) and W_F is the mass of fuel available for combustion (kg). The weighting function $F(c)$ is defined as

$$F(c) = \frac{n_c}{n_p} \qquad [15.46.17]$$

where n_c is the number of moles of fuel consumed and n_p is the number of moles of fuel present. Then if 1 mol of fuel reacts with L mol of oxygen

$$n_c = \frac{0.21 n_a}{L} \qquad [15.46.18]$$

where n_a is the number of moles of air in the rich mixture. Hence

$$F(c) = \frac{0.21}{L}\frac{n_a}{n_p} \qquad [15.46.19]$$

15.46.2 Continuous source

Van Buijtenen also gives a model for a continuous source, derived from Equation 15.16.43. In this case it is necessary to use a correlation for the crosswind and vertical dispersion coefficients. The relations used are

$$\sigma_y = ax^b \qquad [15.46.20a]$$

$$\sigma_z = cx^d \qquad [15.46.20b]$$

where a and c are constants and b and d are indices.

Then the ratio Q_e/Q of the mass of gas within the flammability limits to the mass of gas released is

$$\frac{Q_e}{Q} = \frac{b+d}{b+d+1}\frac{x_L - x_U}{u} \qquad [15.46.21]$$

where u is the wind speed, and x_L and x_U are the maximum distances to the lower and upper flammability limits, respectively. Equation 15.46.21 applies to a cloud completely free of the ground or, alternatively to a cloud at ground level.

An alternative formulation of Equation 15.46.21 may be obtained by substituting for x_L and x_U from Equation 15.16.43 in Equation 15.46.21 to obtain for a plume at ground level

$$\frac{Q_e}{Q} = \frac{b+d}{(b+d+1)u}\left(\frac{Q}{\pi uac}\right)^{1/(b+d)} \times \left[\left(\frac{1}{\chi_L}\right)^{1/(b+d)} - \left(\frac{1}{\chi_U}\right)^{1/(b+d)}\right] \qquad [15.46.22]$$

For a plume free of the ground the term πuac in Equation 15.46.22 is replaced by $2\pi uac$. If the concentration at the source is below the upper flammability limit χ_U, x_U in Equation 15.46.21 and the term in χ_U in Equation 15.46.22 are zero.

Values given by van Buijtenen of the parameters in Equation 15.46.20 for use in this model are shown in Table 15.55.

For typical values of the indices b and d, the rate of increase of the ratio Q_e/Q with Q exceeds a linear rate. The application of this model can be extended, if necessary, by the use of the virtual source method. This is discussed by van Buijtenen. A rather similar model for a continuous source has been given by J.G. Marshall (1980), who writes Equation 15.16.41 in the form

$$\chi(x,y,z) = \frac{\dot{m}_o}{\pi\sigma_y\sigma_z u}\exp\left[-\frac{1}{2}\left(\frac{y^2}{\sigma_y^2} + \frac{z^2}{\sigma_z^2}\right)\right] \qquad [15.46.23]$$

where $\dot{m}_o$ is the mass rate of release. Thus for the concentration on the center line at ground level ($y = z = 0$)

$$\chi(x,0,0) = \frac{\dot{m}_o}{\pi\sigma_y\sigma_z u} \qquad [15.46.24]$$

Use is made of the following correlation for the product of the crosswind and vertical dispersion coefficients

$$\sigma_y\sigma_z = Dx^f \qquad [15.46.25]$$

where D is a constant and f an index.

On the assumption that the crosswind isopleths are semi-elliptical in shape, substitution for $\sigma_y\sigma_z$ from Equation 15.46.25 in Equation 15.46.23 yields

$$Q_{FL} = \left(\frac{1}{\pi D}\right)^{1/f}\frac{f}{f+1}\left(\frac{\dot{m}_o}{u}\right)^{(f+1)/f}\left(\frac{1}{\chi_L^{1/f}} - \frac{1}{\chi_U^{1/f}}\right) \qquad [15.46.26]$$

where Q_{FL} is the mass of gas within the flammability limits. Values given by Marshall of the parameters in Equation 15.46.25 for use in this model are shown in Table 15.56.

15.46.3 Momentum jet

J.G. Marshall (1977) has also treated the cases of a flammable momentum jet and a buoyant plume. The basis of the

Table 15.55 *Meteorological parameters for van Buijtenen's equation (after van Buijtenen, 1980) (Courtesy of Elsevier Science Publishers)*

A Values of a and b

Pasquill stability category	*Parameters*	
	a	*b*
B	0.371	0.866
C	0.209	0.897
D	0.128	0.905
E	0.098	0.902
F	0.065	0.902

B Values of c, d, e

Pasquill stability category	*Distance* (m)				
	1–10	10–100	100–1000	1000–20,000	20,000–10^5
Values of c					
B	0.15	0.1202	0.0371	0.054	0.0644
C	0.15	0.0963	0.0992	0.0991	0.1221
D	0.15	0.0939	0.2066	0.9248	1.0935
E	0.15	0.0864	0.1975	2.3441	2.5144
F	0.15	0.0880	0.09842	6.5286	2.8745
Values of d					
B	0.8846	0.9807	1.1530	1.0997	1.0843
C	0.7533	0.9456	0.9289	0.9255	0.9031
D	0.6368	0.8403	0.7338	0.5474	0.5229
E	0.5643	0.8037	0.6865	0.4026	0.3576
F	0.4771	0.7085	0.7210	0.2593	0.3010
Values of e					
B	0	0	3.1914	2.5397	0
C	0	0	0.2444	1.7383	0
D	0	0	−1.3659	−9.0641	0
E	0	0	−1.1644	−16.3186	0
F	0	0	−0.3231	−25.1583	0

Table 15.56 *Meteorological parameters for Marshall's equation (after J.G. Marshall, 1980)*

Pasquill stability category	*Parameters*	
	D	f
A	3.06×10^{-3}	2.4
B	1.38×10^{-3}	1.9
C	8.9×10^{-3}	1.8
D	6.0×10^{-3}	1.7
E	3.88×10^{-3}	1.7
F	1.43×10^{-3}	1.7

model for a jet is the work of Long (1963). For a momentum jet the concentration in the jet is given by the equation

$$c(z,r) = \frac{k_1 d_o}{z} \frac{M_o T_a}{M_a T_o} \frac{\bar{M}}{M_o} \exp\left[-\left(\frac{k_2 r}{z}\right)^2\right] \qquad [15.46.27]$$

where c is the concentration (volume fraction), d_o is the effective diameter of the discharge (m), M is the molecular weight, $\bar{M}$ is the mean molecular weight of the gas mixture at an axial distance z, r is the radial distance from the axis (m), T is the absolute temperature (K), z is the axial length or vertical height (m), k_1 and k_2 are constants, and subscripts a denote air and o the original discharge.

Marshall states that d_o is the effective diameter of the jet after it has expanded to atmospheric pressure but before any entrainment has occurred. For a vent this will be the diameter of the vent, whereas for a plant failure it will be related to the effective 'hole' size and internal pressure.

The distance at which transition from jet to plume occurs is governed by the internal Froude number Fr:

$$Z_{tr} = k_3 \mathrm{Fr} d_o \qquad [15.46.28a]$$

$$= \frac{k_3 w_o d_o}{(g' d_o)^{1/2}} \qquad [15.46.28b]$$

with

$$g' = g \frac{M_a T_o - M_o T_a}{M_a T_o} \qquad [15.46.29]$$

where w is the velocity (m/s), k_3 is a constant and subscript tr denotes transition.

Equation 15.46.27 may be used to determine an axial length and may be integrated for volume and for quantity of flammable material. In order to simplify the integration Marshall assumes that $\bar{M}$ is equal to M_a. The effect of this simplification for a gas of lower molecular weight than air is to overestimate the axial distance at which the upper and lower limit concentrations are reached, the former more than the latter. For a gas of higher molecular weight than air the opposite is true. For most flammable gases the error in axial distance or quantity is much less than 20%.

The equations for the jet are then

$$z_L = \frac{k_1 d_o}{c_L}\left(\frac{M_a T_a}{M_o T_o}\right)^{1/2} \quad [15.46.30]$$

$$V_{FL} = \frac{\pi k_1^3}{9k_2^2}\left(\frac{M_a T_a}{M_o T_o}\right)^{3/2} d_o^3\left(\frac{1}{c_L^3} - \frac{1}{c_U^3}\right) \quad [15.46.31]$$

$$Q_{FL} = \frac{\pi k_1^3}{6k_2^2}\frac{273}{22.4}\left(\frac{M_a}{T_o}\right)^{3/2}\left(\frac{T_a}{M_o}\right)^{1/2} d_o^3\left(\frac{1}{c_L^2} - \frac{1}{c_U^2}\right) \quad [15.46.32]$$

where Q_{FL} is the mass of flammable material in the cloud between the flammability limits (kg), V_{FL} is the volume of the cloud between the flammability limits (m^3) and subscript L denotes the lower flammability limit and U the upper flammability limit.

The values of the constants used by Marshall are as follows. For k_1 and k_2, the values recommended by Long (1963) as giving the maximum instantaneous concentrations are 9 and 2, respectively. But these two constants are not independent. If the radial spread of velocity and concentration in the jet are the same

$$k_2 = (2)^{1/2} k_1 \quad [15.46.33]$$

Marshall uses values of 9 and 12.7 for k_1 and k_2, respectively. For k_3, values of 1.39 and 1.74 have been obtained by B.R. Morton (1959) and by J.S. Turner (1966) for the case where momentum and buoyancy forces are directly opposed. Marshall takes k_3 as 1.55, which is the mean of these two values.

For this model a comparison can be made between the length of the jet to the lower flammability limit and the length of the corresponding jet flame. The length of a turbulent jet flame has been given by Hawthorne, Weddell and Hottel (1949). Their equation is quoted in Chapter 16 as Equation 16.3.3. Rewriting this in Marshall's notation

$$z_F = \frac{5.3 d_o}{c_s}\left\{\frac{T_F}{\alpha T_o}\left[c_s + (1 - c_s)\left(\frac{M_a}{M_o}\right)\right]\right\}^{1/2} \quad [15.46.34]$$

where α is the ratio of the number of moles of unreacted and reacted gas and subscript F denotes the flame and s the stoichiometric mixture. Then, making the following assumptions,

$$T_o = T_a \quad [15.46.35a]$$

$$\frac{T_F}{\alpha T_o} \approx 8 \quad [15.46.35b]$$

$$c_s \approx 2c_L \quad [15.46.35c]$$

$$c_s(1 - c_s)\frac{M_a}{M_o} \approx \frac{M_a}{M_o} \quad [15.46.35d]$$

it can be shown from Equations 15.46.30 and 15.46.34 that

$$\frac{z_F}{z_L} = 0.83 \quad [15.46.36]$$

15.46.4 Buoyant plume

For the buoyant plume the basis of the model given by Marshall is the work of B.R. Morton, Taylor and Turner, (1956), Yih (1951) and Rouse, Yih and Humphreys (1952). The basic treatment is for neutral stability conditions, but other stability conditions are also taken into account, as described below.

For a buoyant plume the concentration in the plume is given by the equation

$$c(z,r)\frac{k_4 \dot{v}_o^{2/3}}{z^{5/3} g^{1/3}}\left(\frac{M_a T_o}{M_a T_o - M_o T_a}\right)^{1/3} \exp\left[-\left(\frac{k_5 r}{z}\right)^2\right] \quad [15.46.37]$$

where g is the acceleration due to gravity (m/s^2), $\dot{v}$ is the volumetric flow (m^3/s) and k_4 and k_5 are constants.

The equations for the length and volume of the flammable zone in the plume and for the mass of flammable gas in it are

$$z_L = \frac{k_4^{3/5} \dot{v}_o^{2/5}}{g^{1/5} c_L^{3/5}}\left(\frac{M_a T_o}{M_a T_o - M_o T_a}\right)^{1/5} \quad [15.46.38]$$

$$V_{FL} = \frac{5\pi k_4^{9/5} \dot{v}_o^{6/5}}{27 k_5^2 g^{3/5}}\left(\frac{M_a T_o}{M_a T_o - M_o T_a}\right)^{3/5}\left(\frac{1}{c_L^{9/5}} - \frac{1}{c_U^{9/5}}\right) \quad [15.46.39]$$

$$Q_{FL} = \frac{5\pi M_o k_4^{9/5} \dot{v}_o^{6/5}}{12 T_a k_5^2 g^{3/5}}\frac{273}{22.4} \times \left(\frac{M_a T_o}{M_a T_o - M_o T_a}\right)^{3/5}\left(\frac{1}{c_L^{4/5}} - \frac{1}{c_U^{4/5}}\right) \quad [15.46.40]$$

The dispersion is affected by three separate but related aspects of the atmospheric conditions. These are (1) the degree of turbulence, (2) the wind speed, and (3) the stability conditions.

These characteristics are not independent. Inversions in which the temperature increases with height occur more frequently in conditions of low turbulence and low wind speed. This is the combination of conditions least conducive to dispersion.

The effect of temperature gradient may be taken into account by using the parameter G:

$$G = \frac{g}{T_a}(dT_a/dz + \Gamma) \quad [15.46.41]$$

where Γ is the dry adiabatic lapse rate (= 0.0098°C/m). Equation 15.46.41 is related to the Richardson number.

It is not uncommon in the United Kingdom to have temperature gradients dT_a/dz of the order of 0.01°C/m, while gradients of 0.1°C/m are not unknown. The corresponding

values of the parameter Γ are:

dT_a/dz (°C/m)	G (s^{-2})
0 (isothermal)	0.000334
0.01	0.000674
0.1	0.00374

For an atmosphere in which the temperature gradient is greater than that of a neutral adiabatic atmosphere ($\Gamma > 0$) and in which these conditions continue sufficiently far upward, there will come a height at which the density of a plume of positive buoyancy equals that of the surrounding air. Marshall gives the following equation for the height of a plume based on the work of B.R. Morton, Taylor and Turner (1956):

$$z_{max} = \frac{k_6 \dot{v}_o^{1/4}}{G^{3/8}} \left(\frac{M_a T_o - M_o T_a}{M_a T_o} \right)^{1/4} \quad [15.46.42]$$

where k_6 is a constant.

Equation 15.46.42 sets a limit on the rise of the plume in stability conditions where the temperature increases with height. The plume height z_{max} calculated from Equation 15.46.42 may be compared with the height z_L at which the concentration reaches the lower flammability limit as given by Equation 15.46.38. If z_{max} is less than z_L, the plume does not rise sufficiently high to be diluted below the lower flammability limit.

The values of the constants used by Marshall are as follows. For k_4, the value recommended by Long as giving the maximum instantaneous concentration is 17, and this is used by Marshall. For k_5, Marshall assumes that the ratio k_5/k_4 is the same as for time mean values and thus obtains for k_5 a value of 13; for k_6 he uses the value of 6.65 given by B.R. Morton, Taylor and Turner (1956).

15.46.5 Comparative cloud sizes

J.G. Marshall (1977, 1980) has presented a number of illustrative calculations of the dimensions of and quantities of flammable material in clouds from a continuous source, a jet and a buoyant plume for hydrocarbon gases. J.G. Marshall (1980) gives the following summary of his equations.

Continuous source

$$Q_{FL} = \frac{0.321}{D^{0.59}} \frac{\dot{m}_o^{1.59}}{u^{1.59}} \left(\frac{1}{\chi_L^{0.59}} - \frac{1}{\chi_u^{0.59}} \right) \quad [15.46.43]$$

Equation 15.46.43 is obtained from Equation 15.46.26 with the value of the index f applicable to Pasquill stability categories D–F, which is 1.7.

Momentum jet

$$Q_{FL} = 3.4 \rho_a^{1.5} \left(\frac{\dot{m}_o}{w_o} \right)^{1.5} \left(\frac{1}{\chi_L^2} - \frac{1}{\chi_U^2} \right) \quad [15.46.44]$$

Buoyant plume

$$Q_{FL} = \frac{1.45 T_o^{1.8}}{T_a^{1.8}} \left(\frac{\rho_a^{0.6} \rho_o^{0.6} \dot{m}_o^{12}}{\Delta \rho_o^{0.6}} \right) \left(\frac{1}{\chi_L^{0.8}} - \frac{1}{\chi_U^{0.8}} \right) \quad [15.46.45]$$

with

$$\Delta \rho_o = \rho_a - \rho_o \quad [15.46.46]$$

where $\dot{m}_o$ is the mass rate of release (kg/s), u is the wind speed (m/s), $\Delta\rho_o$, is the density difference between air and the gas (kg/m^3) and χ is the concentration (kg/m^3).

The results shown in the table below were obtained by J.G. Marshall (1977) for jets of methane and ethylene at 288 K, from Equations 15.46.30 and 15.46.32:

	M_o	c_L (v/v)	c_U (v/v)	z_L/d_o	$\dot{m}/d_o^2$ (kg/m^2 s)	Q_{FL}/d_o^3 (kg/m^3)	z_F/z_L
CH_4	16	0.05	0.15	243	236	1388	0.83
C_2H_4	28	0.027	0.36	340	304	4020	0.73

For buoyant plumes of the same gases at the same temperature, from Equations 15.46.38 and 15.46.42:

	$\dot{m}$ (kg/s)	z_L (neutral atmosphere) (m)	z_{max} *(stable atmosphere)*	
			$G = 0.00034$ (m)	$G = 0.001$ (m)
CH_4	100	181	374	248
	1000	455	665	441
C_2H_4	100	346	175	116
	1000	870	311	206

Marshall also gives results for jets of ethane, propane and *n*-butane and at temperatures of 423 and 573 K.

For buoyant plumes the results show the relation between the maximum height attained by the plume z_{max} and the height required for dilution to the lower flammability limit z_L. For methane, which has a large positive buoyancy, $z_{max} > z_L$ approximately in all the cases considered. For ethylene, which has only a small positive buoyancy, $z_L > z_{max}$ in all the cases considered.

Both for jets and buoyant plumes the residence time is of interest as giving the lower limit for the time required for the flammable cloud to form. For the cases of jets considered by Marshall the residence times within the flammable envelope were in the range 2.5–11 s for mass flows of 100 kg/s and 8–24 s for mass flows of 1000 kg/s. For the cases of plumes the minimum residence times were 3 and 5 s for mass flows of 100–1000 kg/s, respectively. The results also show that emission rates of 100–1000 kg/s can give rise to vapour clouds containing at least 1 te of flammable material.

In a second study extending the comparison to a continuous source also, J.G. Marshall (1980) gives the emission rates necessary to produce clouds containing given amounts of gas as follows:

Type of release	*Emission rate* (kg/s) *to give cloud containing*	
	1000 kg	10,000 kg
Continuous source	6–100	25–440
Jet	13–110	50–600
Buoyant plume	16–110	100–700

He also gives the graphical comparison shown in Figure 15.145. In each of the three cases the critical parameter is different: for the continuous source in Figure 15.145(a) it is the stability category and wind speed u; for the jet in Figure 15.145(b) it is the pipe velocity w_o; and for the buoyant plume in Figure 15.145(c) it is the hydrocarbon species. In the case of the continuous source calculation assumes a hypothetical hydrocarbon with lower and upper flammability limits of 0.039 and 0.176 kg/m^3, respectively. In the case of the jet, which is for a typical lower paraffin, the

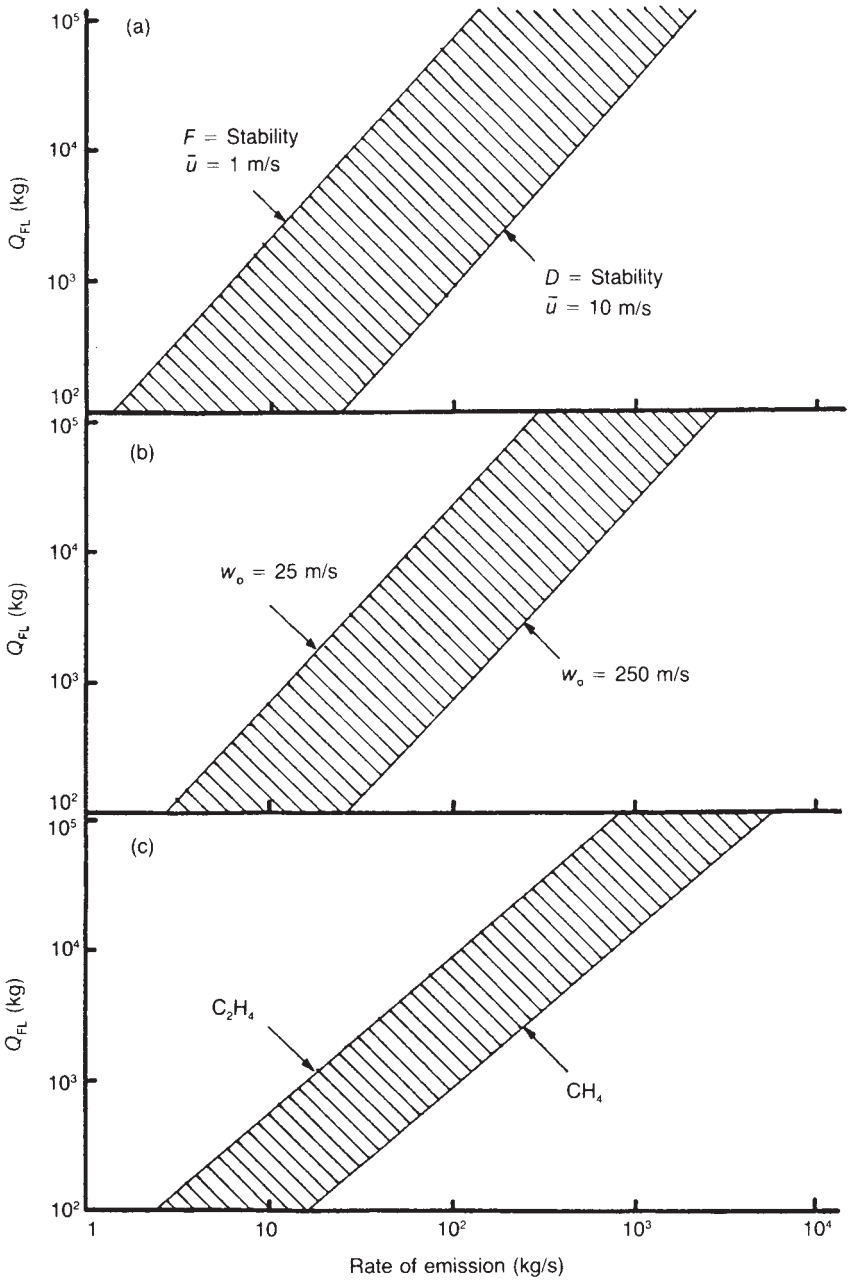


Figure 15.145 *Flammable gas clouds – mass of gas within flammable limits in gas cloud in some principal dispersion situations (J.G. Marshall, 1980): (a) passive gas dispersion; (b) jet dispersion; (c) plume dispersion. $\bar{u}$, mean wind speed; w_o, jet discharge velocity (Courtesy of the Institution of Chemical Engineers)*

lower pipe velocity is close to the limiting value below which jet dispersion would no longer be the controlling mechanism, while the upper velocity is close to the sonic velocity. In the case of the plume, methane has been taken as the most positively buoyant material likely to be of interest, other than hydrogen, while ethylene at 288 K represents the limiting gas density above which other modes of dispersion would predominate. This study indicates that in respect of the mass of gas within the flammable limits for a given size of release the three types of release appear remarkably similar.

15.46.6 Dense gas clouds

For dense gas clouds, the approach taken depends on the type of model used. A box model gives the cloud dimensions directly. The *Workbook* method gives correlations for the area within a given concentration.

15.46.7 Empirical relations

An empirical equation for the radius of a vapour cloud has been given in the Second Report of the Advisory Committee on Major Hazards (ACMH) (Harvey, 1979b):

$$R = 30M^{1/3} \qquad [15.46.47]$$

where M is the mass of vapour (te) and R is the radius of the cloud (m).

Equation 15.46.47 is based on the assumption that the ratio of the cloud radius to cloud height is 5 : 1. It appears to agree reasonably well with the estimated size of the clouds at Flixborough and at Beek. If it is assumed that the quantities released in these two incidents were 40 and 5.5 te, respectively, the cloud sizes as calculated from Equation 15.46.47 are 103 and 53 m, which compare with the estimated cloud sizes of 102 m (kidney-shaped cloud) (Sadee, Samuels and O'Brien, 1976–77) and of 50 m (Ministry of Social Affairs, 1976), respectively.

15.46.8 Concentration fluctuations

It has long been recognized that the effect of concentration fluctuations is to extend beyond the nominal mean lower flammability limit (LFL) concentration values the range and the area of the cloud which is susceptible to ignition.

Feldbauer *et al.* (1972) allowed for this by the use of an effective limit, replacing the LFL value by an effective value, which they took as the 0.5 LFL value. This approach has been widely utilized.

It has been suggested by Pikaar (1985) that the Maplin Sands vapour cloud fire tests indicate that for this purpose use may be made of a practical peak/mean concentration ratio of 1.4, which translates to a 0.7 LFL value. The account given by this author is discussed in more detail in Chapter 17.

More sophisticated approaches may be used, based on the modelling of concentration fluctuations, as described in Section 15.45. In the work of Birch, Brown and Dodson (1980, 1981) on ignition in jets, the relationship between the gas concentration and the occurrence of ignition is expressed as a probability distribution.

A discussion of the problem in the context of dense gas dispersion has been given by McQuaid (1984a). The deficiencies of applying averaging to turbulence phenomena have been discussed by Spalding (1983). For instance, the average obtained depends on the averaging time selected. There is no simple solution.

15.46.9 Cloud size estimation procedures

A number of companies have developed procedures for estimating the size of the flammable vapour cloud to be considered in plant design. Essentially these define the scenarios to be treated, such as the size and duration of the leak. Accounts of such procedures include those by Exxon (n.d.), Brasie (1976a), FMRC (1990) and Industrial Risk Insurers (IRI) (1990), and a review is given by the CCPS (1994/15).

The procedure of Brasie (1976a) for a continuous leak utilizes for the leak rate from a short nozzle or pipe the relation

$$W_{\mathrm{lr}} = 2343P^{0.7} \qquad [15.46.48]$$

where P is the operating pressure (bar) and W_{lr} is the mass flow per unit area (kg/m^2 s). The flow of vapour into the cloud is obtained from the flash fraction. The mass of vapour in the cloud above the LFL is a function of time. The maximum time is the time span for the cloud concentration to fall below the LFL. For this use is made of the relation

$$t = 516(W/Mf) \qquad [15.46.49]$$

where f is the lower flammability limit (%), M is the molecular weight, W is the mass flow (kg/s) and t is the time span (s).

The CCPS (1994/15) describes an unpublished procedure of Exxon (n.d.). This distinguishes between releases of (1) gas, (2) liquid and (3) two-phase or flashing liquid. For a gas release, the mass of vapour entering the cloud is taken as the lesser of (1) the total inventory or (2) the product of the flow and the time to stop the leak. For a liquid release, the quantity spilled is taken as the lesser of (1) the total inventory or (2) the product of the flow and the time to stop the leak. The mass of vapour entering the cloud is then taken as the product of the liquid evaporation rate and the time to find a likely source of ignition. For a liquid which is two-phase or flashing, the mass of vapour entering the cloud is the lesser of (1) the total inventory times twice the flash fraction or (2) the product of the rate of release and the time to stop the leak and twice the flash fraction.

The procedure of the Factory Mutual Research Corporation (FMRC, 1990) is oriented towards the estimation of the loss potential in insurance. In this method the credible releases are taken as: (1) 10-min releases from (a) the largest connection on the largest vessel or vessel train, (b) atmospheric or pressure storage, credit being given for the operation of excess flow valves, or (c) above-ground pipelines conveying material from a remote, large capacity source; and (2) the total inventory of mobile tanks, such as tank trucks or rail tank cars.

Another insurance-related procedure is that of the Industrial Risk Insurers (IRI, 1990). For the catastrophic loss potential, the mass released is based on the content of vessels or vessel trains, storage tanks and pipelines to storage. For the latter a guillotine fracture is assumed with a release duration of 30 min. No credit is allowed for shut-off valves between vessels. For the probable maximum loss potential, a credible release is determined, allowing for the operation of emergency shut-off and blowdown. The minimum release is the inventory of the largest process vessel and the maximum that of the largest train of vessels which are interconnected and not isolated.

15.47 Toxic Gas Clouds

The effect of exposure to a cloud of toxic gas is a function of the concentration–time profile and of the toxic characteristics of the gas. An account of the concentration behaviour of gas clouds was given in Section 15.45, whilst the toxic characteristics of gases are described in Chapter 18. This section describes the attempts made to marry these two features.

15.47.1 Toxic load and probit

As described in Chapter 18, the inhalation toxicity of a gas is characterized by the toxic load L which produces some defined toxic effect which is typically of the form

$$L = \int_0^T C^n \, dt \qquad [15.47.1a]$$

$$= C^n T \qquad [15.47.1b]$$

$$= \sum_{i=1}^{p} C_i^n t_i \qquad [15.47.1c]$$

where C is the concentration, L is the toxic load, t is the time, T is the time of exposure and n is an index.

The proportion of the exposed population which will suffer, or the probability that a single individual will suffer, this defined degree of injury is generally expressed in terms of a probit equation of the form

$$Y = k_1 + k_2 \ln L \qquad [15.47.2]$$

where Y is the probit and k_1 and k_2 are constants. The probability P of injury is a function of the probit Y. The use of probit equations is discussed in Chapter 9.

Equation 15.47.1 is the form typically taken by correlation of experimental work. There is usually little information on its applicability to combinations of values of (C,t) where C is high and t is short. There must therefore be doubt as to the appropriateness of applying it in a mechanistic way.

15.47.2 Intermittency and its effects

Griffiths and co-workers (R.F. Griffiths and Megson, 1984; R.F. Griffiths and Harper, 1985) have drawn attention to the implications of concentration intermittency when combined with the toxic load relation 15.47.1. The intermittency γ is defined as the fraction of time for which the concentration is zero:

$$\gamma = \frac{t_s - t_{pe}}{t_s} \qquad [15.47.3]$$

where γ is intermittency and subscripts pe and s denote exposure and sampling, respectively. These authors define intermittency as the proportion of time the concentration is zero. The average concentration $\bar{C}$ is

$$\bar{C} t_s = C_p t_{pe} \qquad [15.47.4]$$

where $\bar{C}$ is the average concentration and C_p is the concentration over time t_{pe}. Then from Equations 15.47.2–15.47.4

$$Y = k_1 + k_2 \ln \left[\left(\frac{1}{1-\gamma} \right)^{n-1} \bar{C}^n t_s \right] \qquad [15.47.5]$$

For the usual case of $n > 1$, the probit Y, and hence the probability P of injury, increase as the intermittency increases. The effect can be pronounced.

15.47.3 Ride model

The model given by Ride (1984b) for concentration fluctuations in a passive plume was described above. He has applied this model to the determination of toxic load.

From Equation 15.45.27, with $\psi = 1$

$$\frac{C_\tau}{\bar{C}} = k \left(\frac{\sigma_\tau}{\bar{C}} \right)^\lambda + 1 \qquad [15.47.6]$$

From this equation, with Equation 15.45.24

$$[k(\sigma_\tau/\bar{C})^\lambda + 1]^{-1} = 1 - \gamma_\tau \qquad [15.47.7]$$

Then for a receptor with response time τ Ride obtains from Equation 15.47.la for toxic load with Equations 15.47.6 and 15.47.7

$$L = C_\tau^n (1 - \gamma_\tau) T \qquad [15.47.8]$$

$$= \bar{C}^n T \omega \qquad [15.47.9]$$

with

$$\omega = [k(\sigma_\tau/C)^\lambda + 1]^{n-1} \qquad [15.47.10]$$

where ω is an enhancement factor which takes account of concentration fluctuations.

The enhancement factor ω is never less than unity and can be large. Table 15.57 given by Ride shows values of this factor obtained taking Jones' values of $k = 11$ and $\lambda = 1.5$ with values of n quoted in the literature for several gases and with postulated values of the intensity $\sigma_\tau/\bar{C}$ the values of $\sigma_\tau/\bar{C}$ from Jones' data are about 1–2.

15.47.4 Wilson model

The model of D.J. Wilson (1982) for concentration fluctuations in a passive plume and for the distribution function of the concentration was given in Section 15.45. If the relevant effect is toxic concentration rather than toxic load, that model may be applied as described by D.J. Wilson and Simms (1985). The model gives the distribution function for concentration and from this it is possible to determine the distribution function for the probability of fatality given such concentration fluctuations.

This is obtained by the authors as follows. The probability F_c that the concentration will not exceed a value c is given by Equation 15.45.66. Then the probability V_c that it will exceed this value is the complement:

$$V_c = 1 - F_c \qquad [15.47.11]$$

V_c is the probability of exceeding the concentration c over the exposure time T_e. Over some small time δt_I, the probability of exceeding c is $V\delta t$ and that of not exceeding it is $1 - V\delta t$. If the number of breaths over time T_e is N_b the probability $S(T_e)$ of not exceeding c, and thus of surviving, is

$$S(T_e) = (1 - VT_e/N_b)^{N_b}$$

$$= \exp(-VT_e) \quad N_\beta \to \infty \qquad [15.47.12]$$

If the effect is one of toxic load, an extension of the model is required, giving the distribution function of the toxic load as defined by Equation 15.47.1b. This extension has been discussed by D.J. Wilson and Simms (1985) and D.J. Wilson (1991b).

Table 15.57 *Effect of variations in concentration on toxic load (Ride, 1984a) (Courtesy of Elsevier Science Publishers)*

Intensity of fluctuations $\sigma_\tau/\bar{C}$	*Enhancement factor,* ω		
	HCN $n = 1.8$	*Ammonia* $n = 2.0$	*Chlorine* $n = 2.75$
0	1.0	1.0	1.0
1	7.2	12.0	77.4
2	16.1	32.1	433
5	47.3	124	4607

An illustration of the effect of concentration fluctuations has been given by D.J. Wilson (1991b) for the case of continuous release of hydrogen sulphide using a value of $n = 2.5$ in Equation 15.47.1a. Figure 15.146(a) shows the contours for the probability of fatality given by the mean toxic load, Figure 15.146(b) those for the median load and Figure 15.146(c) those for the 99% percentile.

15.47.5 Davies model

A model for the effective dosage based on concentration and dosage distributions obtained from concentration profiles for an ensemble have been given by J.K.W. Davies (1987, 1989a).

J.K.W. Davies (1987) starts from a consideration of the ensemble of 21 concentration profiles obtained in the work at Warren Spring Laboratory (WSL) by D.J. Hall, Hollis and Ishaq (1982) shown in Figure 15.147(a). Analysis of the WSL data for concentration C showed that at the 95% confidence level the mean $\mu(C)$ is constant over the period 2.4–4.4 s and the standard deviation $\sigma(C)$ is constant over the range 2.4–5.4 s, as shown in Figure 15.147(b) and (c),

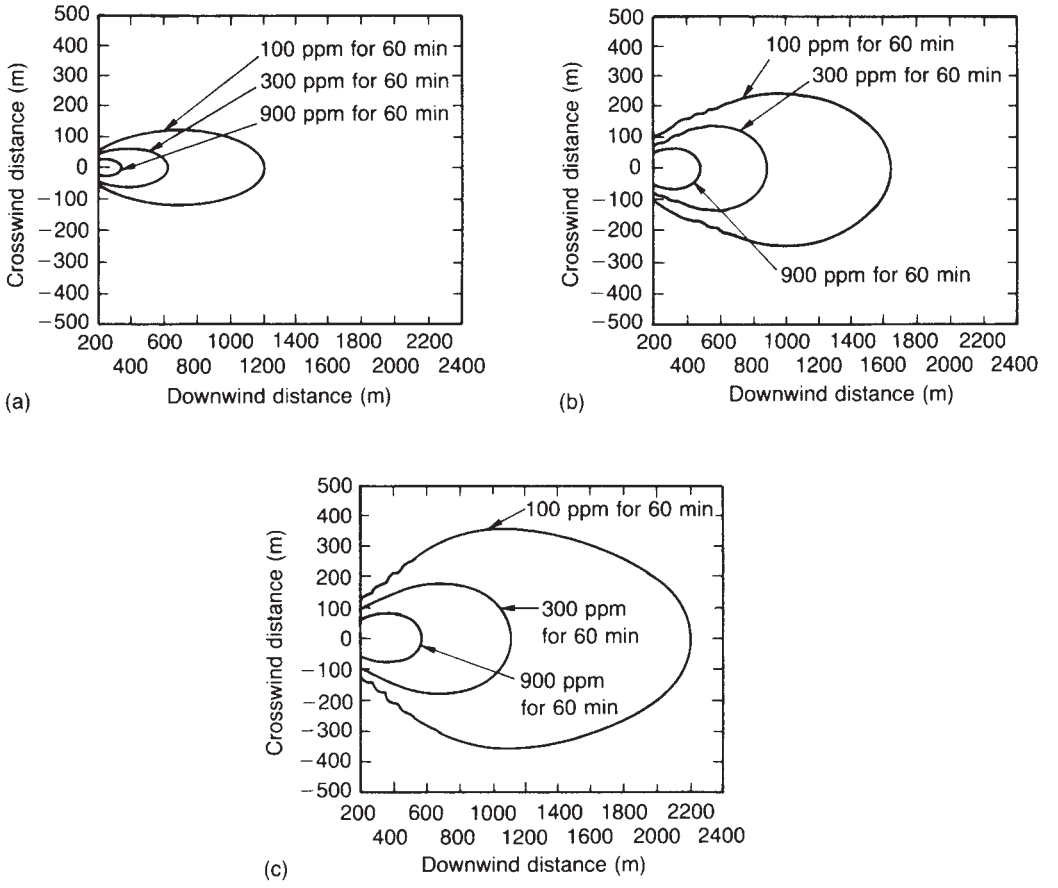


Figure 15.146 *Toxic gas clouds – contours of toxic load for a continuous release of hydrogen sulphide (D.J. Wilson, 1991a); (a) without concentration fluctuations; (b) with concentration fluctuations, median; (c) with concentration fluctuations, 99% percentile (Courtesy of the American Institute of Chemical Engineers)*

respectively. The variations of concentration at a given time between the members of the ensemble were fitted to various distributions. The distributions which best fitted the concentration varied over the time period, the log–normal distribution being the best for the critical period 1.7–2.7 s containing the concentration peak.

The distribution was also determined for dosage D, defined as

$$D(t) = \int_0^t C\,\mathrm{d}t \qquad [15.47.13a]$$

$$= Ct \qquad C = \text{constant} \qquad [15.47.13b]$$

and

$$D(t) = \int_0^t C^n\,\mathrm{d}t \qquad [15.47.14a]$$

$$= C^n t \qquad C = \text{constant} \qquad [15.47.14b]$$

where n is an index. In both cases the best fit was obtained using the log–normal distribution.

These findings have been applied by J.K.W. Davies (1989a) to devise a method of estimating the probability θ of fatality due to exposure to a toxic gas cloud. For this he utilizes the following alternative form of the probit relation. The probability θ of fatality is given by the distribution function ϕ:

$$\theta(D) = \phi(\delta) \qquad [15.47.15]$$

with

$$\delta = k\ln(D/D_{50}) \qquad [15.47.16]$$

where the dosage D is defined by Equation 15.47.14, D_{50} is the median fatal dosage, k is a constant and δ is a standardized log dose. The relation between Equations 15.47.28 and 15.47.15 is then

$$\phi^{-1}(\theta) = k\ln(D/D_{50}) \qquad [15.47.17a]$$

$$= -k\ln D_{50} + k\ln D \qquad [15.47.17b]$$

$$Y = \phi^{-1}(\theta) + 5 \qquad [15.47.18]$$

$$k_1 = 5 - k\ln D_{50}$$

$$k_2 = k$$

and

$$\phi(\theta) = (Y-5)^{-1} \qquad [15.47.19]$$

$$k = k_2 \qquad [15.47.20]$$

$$D_{50} = \exp\left(\frac{5-k_1}{k}\right) \qquad [15.47.21]$$

The model given by Davies is then as follows. The dose D is log-normally distributed. Thus, $\ln D$ is normally distributed:

$$\ln D = N[\ln \bar{D}, \sigma^2(\ln D)] \qquad [15.47.22]$$

where $N[\cdots]$ signifies the normal distribution and $\bar{D}$ is the mean dose. Then the standardized log dose δ, defined by

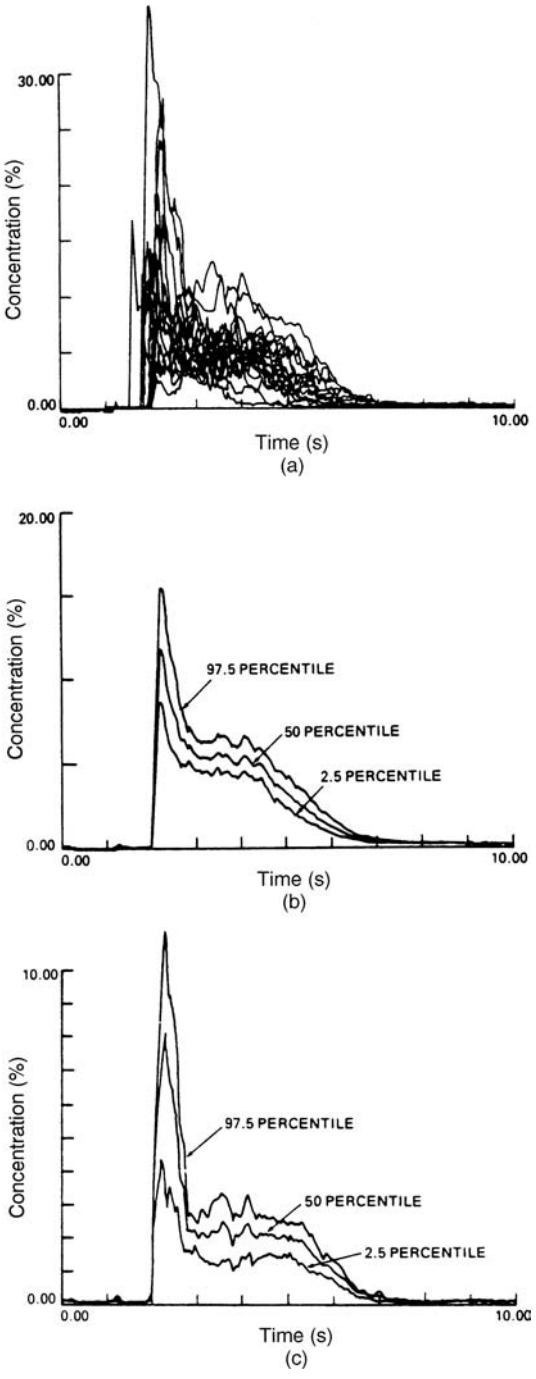


Figure 15.147 *Concentration fluctuations in gas dispersion – statistical parameters of a data set (J.K.W. Davies, 1987): (a) set of 21 concentration vs time traces obtained in repeat experiments in a wind tunnel (the WSL data set); (b) 95% confidence limits on mean concentration; (c) 95% confidence limits on ensemble standard deviation (Courtesy of Elsevier Science Publishers)*

equation [15.47.16], is also taken as normally distributed

$$\delta = N[\bar{\delta}, \sigma(\delta)] \quad [15.47.23]$$

with

$$\bar{\delta} = k \ln(\bar{D}/D_{50}) \quad [15.47.24]$$

$$\sigma^2(\bar{\delta}) = k^2 \ln(\ln D) \quad [15.47.25]$$

where $\bar{\delta}$ is the mean standardized log dose.

An effective dose D^* is defined as the dose which gives rise to the same mean number of fatalities as would be obtained by averaging the number of fatalities observed in successive realizations of the ensemble in which dose D is allowed to vary log–normally.

An effective standardized log dose δ^* is also introduced, defined as the standardized log dose which gives rise to the same mean number of fatalities as would be obtained by averaging the number of fatalities observed in successive realizations of the ensemble in which the standardized log dose δ is allowed to vary normally. It is defined as

$$\delta^* = k \ln(D^*/D_{50}) \quad [15.47.26]$$

An ideal gas dispersion model will produce for the standardized log dose a prediction $\bar{\delta}$ and the corresponding probability of fatality will be $\phi(\bar{\delta})$. The true probability of fatality is $\phi(\delta^*)$. The difference $\phi(\delta^*) - \phi(\bar{\delta})$ is a measure of the error in the prediction of fatality, even by an ideal model due to variations between members of the ensemble.

The equivalent standardized log dose δ^* may be determined by selecting values of δ from the normal distribution, calculating the corresponding values of the probability of fatality $\phi(\delta)$ and taking the mean value of this probability as $\phi(\delta^*)$. Table 15.58 (from Davies) shows the results of such a calculation.

The case of $\sigma(\delta) = 0$ corresponds to no concentration fluctuation, whilst $\sigma(\delta) = 1$ is typical of the value in the body of the cloud and $\sigma(\delta) \gg 1$ of values at the edges. For $\bar{D} > D_{50}$ the use of $\bar{\delta}$ instead of δ^* results in an overestimate of the probability of fatality, whilst for $\bar{D} < D_{50}$ it results in an underestimate. This misestimate is less than 10% in absolute terms for $\sigma(\delta) < 1$, but for $\sigma(\delta) > 1$ it becomes progressively greater, reaching a value of about 30% at $\sigma(\delta) = 5$.

An illustrative example is shown in Table 15.59. The case considered is the toxic effects 1000 m downwind of a 20 te release of chlorine in $D/3$ conditions. The index n is taken as 3.49, which is at the upper end of the range of published estimates. The effect of concentration fluctuations on toxic load is most marked towards the edges of the cloud.

15.48 Dispersion over Short Distances

It is necessary in some applications, particularly in relation to plant layout, to estimate dispersion over short distances.

15.48.1 Dispersion of passive plume

The relationships for passive dispersion are commonly used over relatively large distances, but the question of the range of his model was specifically considered by O.G. Sutton (1950). He describes experiments on the dispersion of a vertical jet of hot gas for which he obtained a value of the diffusion coefficient C. This value is similar to that obtained in the dispersion of smoke from a smoke generator over a distance of 100 m, provided that for comparability use is made in the latter case of the instantaneous rather than the time width of the plume. Sutton states:

> This leads to the striking conclusion that the same coefficient of diffusion is valid for the spread of smoke over hundreds of meters as for the mixing of a tiny column of hot air with the cold air of a laboratory.

The use of the Sutton model for estimation of dispersion in relation to hazard areas around vents has been treated by Long (1963), who devotes an appendix to the applicability of the model over short ranges. He discusses both the basic assumptions and the available experimental results. He reviews the assumptions systematically and finds no fundamental inapplicability for short ranges. In particular, the semi-angle of divergence of the roughly conical plume predicted using the values given by Sutton for the diffusion coefficient is about 10° and 16° in the vertical and horizontal directions, respectively, which compares well with semi-angles in the range 9–16° found for jets and plumes.

Table 15.58 *Effect of variations in dose between members of an ensemble on predicted fatality: $\phi(\delta^*) - \phi(\bar{\gamma})$ (J.K.W. Davies, 1989a) (Courtesy of Elsevier Science Publishers)*

$\sigma(\delta)$	$\phi(\delta^*) - \phi(\delta)$			
	δ			
	0	1	2	3
0	0	0	0	0
0.2	0	0	0	0
0.5	0	−0.03	−0.02	0
1	0	−0.08	−0.06	−0.02
2	0	−0.17	−0.17	−0.09
5	0	−0.20	−0.28	−0.29

Table 15.59 *Effect of variations in dose between members of an ensemble on predicted fatality: 20 te chlorine release[a] (J.K.W. Davies, 1989a) (Courtesy of Elsevier Science Publishers)*

Crosswind distance (m)	$\ln C^n t$	Y	δ	σ	$\phi(\delta)$	$\phi(\delta^*) - \phi(\delta)$
52	28.80	8	3	0.5	1	0
215	26.84	6.04	1.04	1	0.85	−0.08
235	26.32	5.52	0.52	1.2	0.70	−0.04
287	24.96	4.16	−0.84	2	0.20	−0.17

[a] Table relates to conditions 1000 m downwind of an instantaneous release of 20 te chlorine in $D/3$ conditions, assuming a source term in which 400 te of air is entrained. The cloud radius, defined as 10% of the centre line concentration, at this distance is 417 m.
[b] Toxicity parameters: $n = 3.49$; $k = 1$; $\ln D_{50} = 25.8$.

The only experimental work found by Long was that of Katan (1951). Using values of the Sutton coefficient based on a 3-min sampling time, Long found that the Sutton equations tend to overestimate the concentration somewhat.

15.48.2 Dispersion of dense gas plume

Some guidance on the dispersion of a dense gas plume over short ranges has been given by McQuaid (1980) in the context of the design of water spray barriers. He takes the plume as issuing at an angle of 35° and having a height of 1 m.

15.48.3 Dispersion from vents and reliefs

It is common practice in the process industries to discharge material to atmosphere. Intended discharges occur through chimneys, vents and relief devices. The treatment here is mainly confined to the problem of the safety of discharges occurring in an emergency, usually as a result of the operation of relief devices. Discharges to flare are discussed in Chapter 12 and disposal of material vented from chemical reactors in Chapters 12 and 17.

Recent years have seen a marked tightening up in the extent to which discharge to atmosphere is permissible and, although the situation varies as between countries, the trend is clear. Accounts of safe discharge include those given in the various editions of API RP 520 and RP 521 and by Long (1963), Loudon (1963), Bodurtha, Palmer and Walsh (1973) and Gerardu (1981). The topic is also frequently discussed by authors of models developed to assist with this problem.

An early review is that by Loudon (1963), who identifies the hazards arising from such a release as including, for flammable or toxic material

(1) hazardous concentration, particularly at ground level; and, for flammables
(2) vapour cloud explosion;
(3) jet flame.

Another hazard is flashback of flame into a vent.

For discharges, a distinction is to be made between those which have high momentum and/or buoyancy and those which do not. If the release has a high velocity, and thus high momentum, this promotes entrainment of air and dilution of the cloud. Another aspect is the height to which the material discharged travels before it starts to descend to the ground, the effective 'stack' height. This is increased if the release has high buoyancy and, for a discharge directed upwards, high momentum.

Safe discharge is generally addressed by a combination of engineering measures and hazard assessment. The former centre mainly on the height of the vent and on the velocity of the discharge, whilst the latter involves the use of suitable models to assess the hazards listed above.

Widespread use has been made of the equation in API RP 520 for the estimation of concentration of contaminant as a function of distance for use in high velocity discharge calculations based on the recommendations on discharge velocity. This equation is given in Chapter 12.

There are a considerable number of models for the estimation of the ground level concentration resulting from an elevated release. They include: the early models of Bosanquet (1935) and Bosanquet and Pearson (1936); O.G. Sutton (1952); the Pasquill model (Pasquill, 1961) and the Pasquill–Gifford model (Pasquill, 1961, 1962; Gifford, 1961); the model of Cude (1974b); and that of G.A. Briggs (1965, 1969). Other models have been developed to obtain the ground level concentration for elevated releases of a dense gas. Amongst these are the models of Hoot, Meroney and Peterka (1973), Bodurtha, Palmer and Walsh (1973), Ooms, Mahieu and Zelis (1974), Jagger and Edmondson (1984), Emerson (1986a), J.L. Woodward (1989a) and McFarlane (1991). Accounts of many of these models are given in Sections 15.20, 15.43 and 15.44.

The mass of gas from a discharge which is within the flammability limits and thus available to participate in a vapour cloud fire or explosion may be obtained from models of jets and plumes. There are also some models which specifically address this problem. These include the families of models given by Hess and co-workers (Hess and Stickel, 1970; Hess, Leuckel and Stoeckel, 1973), J.G. Marshall (1977, 1980), Palazzi *et al.* (1984) and Stock and co-workers (Stock and Geiger, 1984; Stock, 1987; Stock, Geiger and Giesbrecht, 1989). The effects of ignition may be estimated using models for vapour cloud fires or explosions, which are dealt with in Chapters 16 and 17, respectively.

Ignition of a sustained high momentum discharge gives a jet flame. Early models of jet flames developed for the assessment of such situations include those by Craven (1972, 1976) and Kovacs and Honti (1974). There are now a number of jet flame models, as described in Chapter 16.

Several authors have described sets of models used for the estimation of the hazards from discharges. They include Kovacs and Honti (1980) and Gerardu (1981). The models cover ground level concentration, jet flame radiation and vapour cloud overpressure.

Mention has already been made of the work of Katan (1951) on safe dispersion distances for aircraft fuelling. More recent work in this area has been described by Thorne (1986), who gives models for the plumes from circular, slot and elliptical vents. The results from these models show distances for dilution of the jet fuels below the LFL in the range 1.5–4 m.

15.48.4 ASME equation

A formula for plume rise from a momentum source widely used in design for safe discharge is that given by the American society of Mechanical Engineers (ASME, 1969/1). This is

$$h = D\left(\frac{v_s}{u}\right)^{1.4} \qquad [15.48.1]$$

where D is the internal diameter of the stack (m), Δh is the plume rise (m), v_s is the velocity of the stack gas (m/s) and u the wind speed at stack height (m/s).

The equation quoted for the maximum concentration at ground level is Equation 15.16.55. The applicability of the ASME equation is to a stack gas which is essentially of neutral density.

15.48.5 Bodurtha and Walsh method

An early method for safe discharge which applies to a dense gas mixture is that of Bodurtha and Walsh, described in Bodurtha, Palmer and Walsh (1973). Figure 15.133 shows photographs of the simulation of a dense gas plume in a wind tunnel obtained by these workers. The difference between the three tests lies in the density of the gas

discharged relative to that of air, the relative densities in Figures 15.133(a)–(c) being 1.0, 1.52 and 5.17, respectively.

On the basis of these admittedly limited tests, Bodurtha and Walsh obtained the following design equation:

$$h_s = 1.33ED^2 \qquad [15.48.2]$$

where D is the diameter of the vent tip (ft), E is the number of dilutions with air of the stack gas required to reduce its concentration to the lower flammability limit and h_s is the height of the vent above the exposure level (ft). As a design equation, the relation is conservative. The authors state their belief that it contains ample safety factors. They also say, however, that it is intended only for short period releases of dense gases.

15.48.6 Hanzevack method

Another experimentally based method is that by Hanzevack (1982), who conducted tests in which he measured the ground level concentration from elevated releases of both ambient and high density gas mixtures. He gives a model for the ground level concentration due to a continuous emission which is based on a modification of the ASME plume rise formula described in Section 15.48.4. The modification allows for differences in the density of the stack gas mixture and includes a constant to improve the fit to his experimental data.

The equations given by Hanzevack for the plume rise from a momentum source and for the maximum ground level concentration are

$$\Delta h = C_1 D\left(\frac{v_s}{u}\right)^{1.4}\left(\frac{\rho_a}{\rho_s}\right)^{1.4} \qquad [15.48.3]$$

and

$$\chi_{cr} = C_2\frac{Q}{h^{1.29}D^{0.71}v_s}\left(\frac{\rho_s}{\rho_a}\right) \qquad [15.48.4]$$

where D is the internal diameter of the stack (m), h is the height of the stack (m), Δh is the plume rise (m), Q is the mass rate of release (g/s), u is the wind speed (m/s), v_s is the stack gas outlet velocity (m/s), ρ is the density of the gas mixture (kg/m^3), χ_{cr} is the critical ground level concentration (μg/m^3) and subscripts a and s denote air and stack gas, respectively. The relations apply to a 1-h time-averaged concentration.

C_1 and C_2 are empirical constants obtained from the experimental data. In adjusting concentrations averaged over other time periods to the 1-hour average, use was made of Equation 15.16.45 with a value of the index p measured as 0.5.

For design, a more conservative approach is suggested with the two constants C_1 and C_2 replaced by constants C_3 and C_4, respectively. The values given for the four constants are:

	C_1	C_2	C_3	C_4
$\rho_s \le \rho_a$	6	0.012	3	0.02
$\rho_s > \rho_a$	2	0.027	1	0.044

The more conservative values thus incorporate a safety factor of about 2.

15.48.7 Method of de Faveri, Hanzevack and Delaney

Recognizing that in many instances the release of interest is not a continuous one, but a relatively short one, de Faveri, Hanzevack and Delaney (1982) have described an extension to Hanzevack's method which allows for this. The authors conducted experiments in which 10-min time-averaged concentrations were measured for (1) continuous releases and (2) 10-min releases, and obtained the ratio of the two time-averaged concentrations. This ratio should theoretically lie between 1 and 3. Their results indicate a ratio of approximately 2.

15.48.8 Bodurtha method

In addition to the method of Bodurtha and Walsh, described in Section 15.48.5, Bodurtha (1988) has also given another method for safe discharge of dense flammable gases.

The method is based on an adaptation of the Hoot, Meroney and Peterka (HMP) model. As discussed by Bodurtha (1980), the touchdown concentration passes through a maximum with stack gas outlet velocity, which the author terms the critical stack gas outlet velocity $v_{s,cr}$. The expression given by the author for this velocity is

$$v_{s,cr} = \frac{3.73D^{0.684}(\beta C_s/L)^{1.05}}{u^{0.368}A^{2.05}} \times 10^{-3} \qquad [15.48.5]$$

with

$$A = s^{0.67}/(s-1)^{0.33} \qquad [15.48.6]$$

$$s = M_w T_a/29T_s \qquad [15.48.7]$$

$$C_m = L/\beta \qquad [15.48.8]$$

where C_m is the maximum permissible value of the touchdown concentration of the contaminant (% v/v), C_s is the concentration of the contaminant in the stack gas (% v/v), D is the internal diameter of the stack (mm), L is the lower flammability limit (% v/v), M_w is the molecular weight of the stack gas mixture, s is the specific gravity of the stack gas mixture relative to air, T_a is the absolute temperature of the ambient air (K), T_s is the absolute temperature of the stack gas (K), u is the wind speed (m/s), v_s is the velocity of the stack gas (m/s), A is a parameter, β is the applicable peak/mean concentration ratio, and subscript cr denotes critical. The value of the touchdown concentration C_m passes through a maximum with specific gravity, this maximum occurring at a value of $s = 2$, and thus $A = 1.59$.

Substitution of the critical value $v_{s,cr}$ of the stack gas outlet velocity in the HMP model yields the following expression for the required height of the stack:

$$h_s = \frac{43.8D^{1.35}(\beta C_s/LA)^{1.05}}{u^{0.702}} \times 10^{-6} \qquad [15.48.9]$$

where h_s is the height of the stack (m).

The model is applicable to a release directed vertically upwards and only for stack gas specific gravity $s > 1.15$ and for stack gas outlet velocity v_s less than the choked, or sonic, value. The author suggests that for design purposes the value of the wind speed be taken as $u = 1$ m/s.

For the peak/mean concentration ratio ft Bodurtha quotes minimum and maximum values of 2.5 and 5, respectively, and states that the former is used in current

practice. This method is conservative in that the calculation of the required stack height is based on the critical value $v_{s,cr}$ of the stack outlet velocity, whereas use of the actual stack outlet velocity v_s will generally give a much lower stack height.

Bodurtha gives several sample calculations. As an illustration, consider the first of his examples. The problem is stated in terms of the following values of the variables:

$C_s = 100$ v/v; $L = 2.2\%$ v/v; $M_w = 44$; $T_a = 298$ K; $T_s = 298$ K; $u = 1$ m/s; $v_s = 152.3$ m/s; $\beta = 2.5$

Hence $s = 1.52$, $A = 1.64$, $v_{s,cr} = 8.6$ m/s and $h_s = 6.6$ m. The degree of conservatism is indicated by the fact that the actual velocity v_s is very much greater than the critical value $v_{s,cr}$.

15.49 Hazard Ranges for Dispersion

It is convenient for certain purposes, such as comparison of models or preliminary hazard assessment, to have simple expressions for the downwind extent of particular concentrations, such as lower flammability limits or toxic concentrations; in other words, for the hazard range.

The variables which enter into the simpler correlations are generally the concentration, the downwind distance, the mass rate of release and the wind speed, and the treatment here is confined to these.

15.49.1 Passive dispersion

For passive dispersion of an instantaneous release from a point source the relevant expression in the Pasquill-Gifford model is Equation 15.16.40b. Considering concentration at the centre of the cloud at ground level so that $x = ut$, $y = 0$ and $z = 0$, this equation reduces to

$$x \propto \frac{Q^*}{\sigma_x \sigma_y \sigma_z} \qquad [15.49.1]$$

From the correlations of Slade given in Table 15.31 and noting that it is usual to take $\sigma_x = \sigma_y$:

$$\sigma_x = \sigma_y \propto x^{0.92} \qquad [15.49.2a]$$

$$\sigma_z \propto x^{0.7} \qquad [15.49.2b]$$

Then relations 15.49.1 and 15.49.2 give for the hazard range x

$$x \propto Q^{*0.39} \qquad [15.49.3]$$

In this case the hazard range is a function of the mass released, but not of the wind speed.

For passive dispersion of a continuous release from a point source the relevant expression in the Pasquill–Gifford model is Equation 15.16.41. Considering concentration on the centre line at ground level so that $y = 0$ and $z = 0$ this equation reduces to

$$x \propto \frac{Q}{\sigma_y \sigma_z u} \qquad [15.49.4]$$

From the correlations given in Table 15.31

$$\sigma_y \propto x^{0.9} \qquad [15.49.5a]$$

$$\sigma_z \propto x^{0.85} \qquad [15.49.5b]$$

Then relations 15.49.4 and 15.49.5 give for the hazard range χ

$$x \propto \left(\frac{Q}{u}\right)^{0.57} \qquad [15.49.6]$$

In this case the hazard range is a function both of the mass rate of release and of the wind speed.

15.49.2 Dense gas dispersion

It is less easy to derive analytical expressions for the hazard range of a dense gas. One approach is to correlate results from a number of runs of a dense gas dispersion model. The *Second Canvey Report* gives for an instantaneous release the following correlation derived from DENZ for propane and butane:

$$R = kM^{0.4} \qquad [15.49.7]$$

where M is mass of release (te), R is the downwind range (km) and k is a constant. It also gives the following additional relations for distance (km): maximum width $= k_1 R$; distance to maximum width, $X = k_2 R$, and upwind range $= k_3 R$. The values of the constants are shown in Table 15.60.

A more detailed treatment on the same lines has been given by Considine and Grint (1985), who used DENZ and CRUNCH to obtain for propane and butane correlations for instantaneous and continuous releases, respectively. For a quasi-instantaneous release they give for any given distance or dimension L the relation

$$L = kM^n \qquad [15.49.8]$$

where L is a distance/dimension (m), M is the mass released (te), k is a constant and n is an index for the

Table 15.60 *Constants for correlation of downwind extent of flammability limits, and other cloud distances, for instantaneous releases of propane and butane (HSE, 1981a) (Courtesy of HM Stationery Office)*

Constant	*Propane*				*Butane*			
	LFL		*1/2 LFL*		*LFL*		*1/2 LFL*	
	D/5	*F*/2	*D*/5	*F*/2	*D*/5	*F*/2	*D*/5	*F*/2
k	0.12	0.17	0.14	0.21	0.10	0.14	0.12	0.16
k_1	0.8	1.2	0.8	1.2	1.0	1.6	1.0	1.5
k_2	0.5	0.4	0.4	0.4	0.4	1.2	0.4	0.2
k_3	0.1	0.25	0.1	0.3	0.2	0.6	0.2	0.6

Table 15.61 *Constants for downwind extent of flammability limits, and other cloud parameters, for instantaneous and continuous releases of propane and butane (Considine and Grint, 1985) (Courtesy of Gastech)*

A Dispersion of instantaneous release over land

Constants for	*Pressurized propane*		*Pressurized butane*		*Refrigerated propane*		*Refrigerated butane*	
	D/5	*F*/2	*D*/5	*F*/2	*D*/5	*F*/2	*D*/2	*F*/2
Value of k								
R_{LFL}	145.7	112.5	153.1	143.1	121.1	147.2	116.5	139.8
U	13.1	15.7	12.2	18.1	29.6	64.5	31	71.3
R_{UFL}	23.9	10.2	12.8	15	60.7	56.5	54.5	44.5
Y_{max}	29.7	32.1	35.5	41.7	49.6	92.4	50.2	96.9
h	5.6	4.2	4.8	2.1	3.0	0.94	3.12	1.33
Value of n								
R_{LFL}	0.294	0.248	0.319	0.273	0.383	0.408	0.386	0.415
U	0.356	0.374	0.375	0.374	0.364	0.351	0.363	0.346
R_{UFL}	0.241	0.226	0.382	0.239	0.392	0.423	0.393	0.442
Y_{max}	0.34	0.322	0.349	0.334	0.390	0.384	0.391	0.384
h	0.335	0.340	0.264	0.353	0.220	0.237	0.174	0.175

B Dispersion of instantaneous release over water (refrigerated gas)

Constants for	*k*				*n*			
	Propane		*Butane*		*Propane*		*Butane*	
	D/5	*F*/2	*D*/5	*F*/2	*D*/5	*F*/2	*D*/2	*F*/2
R_{LFL}	174.1	270.8	104.9	268.3	0.351	0.352	0.335	0.356
U	22.5	36	21.9	38.1	0.387	0.405	0.394	0.404
R_{UFL}	109.4	156	98.64	145.4	0.337	0.332	0.342	0.332
Y_{max}	49.8	91.9	50.2	92.2	0.389	0.385	0.390	0.385
h	1.4	0.843	1.94	0.683	0.313	0.277	0.269	0.276

C Dispersion of continuous release over land (pressurized and refrigerated gas

Constants for	*k*				*n*			
	Propane		*Butane*		*Propane*		*Butane*	
	D/5	*F*/2	*D*/5	*F*/2	*D*/5	*F*/2	*D*/2	*F*/2
R_{LFL}	12.1	44.2	11.23	41.9	0.557	0.571	0.582	0.574
R_{UFL}	6.25	15.8	5.53	12.9	0.553	0.486	0.553	0.481
h	0.51	0.34	0.46	0.29	0.327	0.323	0.329	0.330
k^*	1.85	5.47	2.1	6.0	0.159	0.145	0.149	0.142

D Dispersion of continuous release over water

Constants for	*k*				*n*			
	Propane		*Butane*		*Propane*		*Butane*	
	D/5	*F*/2	*D*/5	*F*/2	*D*/5	*F*/2	*D*/2	*F*/2
R_{LFL}	19.4	76.4	18.71	73.6	0.524	0.503	0.526	0.513
R_{UFL}	10.31	31.6	9.47	27.65	0.499	0.408	0.496	0.404
h	0.403	0.243	0.390	0.196	0.343	0.361	0.349	0.371
k^*	0.805	2.16	0.845	2.25	0.253	0.262	0.252	0.248

distance/dimension L. These parameters are given for the following dimensions: R_{LFL}, the downwind range to the LFL (m); R_{UFL} the downwind range to the UFL (m); U_{LFL}, the upwind range to the LFL (m); Y_{max}, the maximum crosswind range of the LFL (m); and h the height of the cloud (m).

The crosswind distance Y at any distance R downwind is given by

$$Y = Y_{max}\left\{1 - 4\frac{[R - (R_{LFL} - U_{LFL})/2]^2}{(R_{LFL} + U_{LFL})^2}\right\}^{1/2} \qquad [15.49.9]$$

For the cloud radius R_c at any downwind distance R

$$R_c = R_{LFL} - R \qquad R > R_{cr} \qquad [15.49.10]$$

$$R_c = [Y_1^2 + (R - X_1)^2]^{1/2} \qquad R < R_{cr} \qquad [15.49.11]$$

with

$$R_{cr} = R_{LFL} - \frac{2Y_{max}^2}{R_{LFL} + U_{LFL}} \qquad [15.49.12]$$

$$X_1 = \left[R - \frac{4Y_{max}^2(R_{LFL} - U_{LFL}}{2(R_{LFL} + U_{LFL})^2}\right] \Bigg/ \left[1 - \frac{4Y_{max}^2}{(R_{LFL} + U_{LFL})^2}\right] \qquad [15.49.13]$$

$$Y_1 = Y_{max}\left\{\frac{1 - 4[X_1 - (R_{LFL} - U_{LFL})/2]^2}{(R_{LFL} + U_{LFL})^2}\right\}^{1/2} \qquad [15.49.14]$$

where R is the downwind distance (m), R_c is the radius of the cloud (m), R_{cr} is a range transition criterion value (m), X_1 is a downwind dimension (m), Y is the crosswind distance (m) and Y_1 is a crosswind dimension (m).

For a continuously formed cloud the authors give for any given distance or dimension L the relation

$$L = k\dot{m}_v^n \qquad [15.49.15]$$

where L is a distance/dimension (m), $\dot{m}_v$ is the mass rate of release of vapour (kg/s), k is a constant and n is an index for the distance/dimension L. These parameters are given for the following dimensions: R_{UFL}, the downwind range to the LFL (m); R_{UFL}, the downwind range to the UFL (m); h, the height of the cloud (m); and k^*, a constant (defined below). Then for a downwind distance R the crosswind distance Y is

$$Y = k^* R^{2/3} \qquad [15.49.16]$$

The values of the constants are shown in Table 15.61. The flammable inventory of the cloud is

$$I = \frac{\dot{m}_v R_{LFL}}{u} \qquad [15.49.17]$$

where I is the inventory (kg) and u is the wind speed (m/s).

The authors also give guidance for the case of a flammable gas cloud where the release is neither truly instantaneous nor continuous, but transient. The procedure suggested is to evaluate R_{LFL} and the arrival time T_a from

$$T_a = R_{LFL}/u \qquad [15.49.18]$$

where T_a is the arrival time (s). The release is treated as continuous if $T_d > T_a/4$, where T_d is the duration of the release (s); otherwise the release is treated as an instantaneous one, based on the total mass released over the duration time.

Correlations obtained in this way are only as good as the model from which they are derived. The reliability of the hazard ranges predicted by dense gas dispersion models has been discussed in Section 15.41.

Explicit expressions for the downwind extent, or hazard range, are given in the *Workbook* by Britter and McQuaid (1988). For an instantaneous release Equation 15.34.21 gives for the downwind distance x

$$x \propto Q_o^{0.25} u_{ref}^{0.5} \qquad [15.49.19]$$

where Q_o is the volume released, u_{ref} is the wind speed at the reference height and x is the downwind distance. For a continuous release Equation 15.34.10 yields

$$x \propto q_o^{0.4} \qquad [15.49.20]$$

where q_o is the volumetric rate of release. In this case there is no dependence on wind speed. Further details, including the range of applicability of these equations, are given in Section 15.34.

15.50 Transformation and Removal Processes

There are various transformation and removal processes which a gaseous or particulate pollutant may undergo in the atmosphere. These may need to be considered in relation to acute accidental releases, although in general they are more relevant to long-term pollution. Accounts of these processes include those given by Chamberlain (1953), van der Hoven (1968), Csanady (1973), Hosker (1974), Gifford (1976a), Hales (1976) and S.R. Hanna, Briggs and Hosker (1982). Processes of transformation and removal include:

(1) chemical transformations;
(2) physical transformations;
(3) dry deposition
  (a) gravitational settling,
  (b) small particle deposition;
(4) wet deposition
  (a) rainout,
  (b) washout.

An account is now given of the models and parameters for these various processes.

15.50.1 Chemical transformations

Atmospheric reactions may occur in the gaseous or aqueous phase and may be conventional reactions or photochemical reactions. There is a large literature on atmospheric chemistry which includes Chemistry of the Atmosphere (McEwan and Phillips, 1975), Atmospheric Chemistry (Heicklen, 1976) and Atmospheric Chemistry (Meszaros, 1981). Information on conventional reactions is given in standard texts and information on photochemical reactions is given by Leighton (1961), Calvert and Pitts (1966) and Demerjian, Kerr and Calvert (1974). A review of atmospheric photochemical reactions is given by Hales (1976).

The decay of concentration due to chemical reaction is frequently modelled by a first order decay model:

$$\chi(t) = \chi(0)\exp(-t/\tau_c) \qquad [15.50.1]$$

where χ is the concentration of the pollutant and τ_c is a chemical decay time constant.

From Equation 15.50.1, the half-life $t_{1/2}$ of the concentration is

$$t_{1/2} = 0.693/\tau_c \qquad [15.50.2]$$

15.50.2 Physical transformations

Physical transformations are relevant principally to liquid particles, or aerosols. They include: nucleation, in which a

liquid particle is created by condensation of vapour; condensation, in which further vapour condenses onto an existing particle; and coagulation, in which particles come together to form a larger particle. Another relevant physical process is the absorption of soluble gas in water particles.

A case of particular relevance here is the behaviour of ammonia in humid air. A detailed discussion is given by Haddock and Williams (1978 SRD R103). An outline of their treatment of ammonia is presented in Section 15.42.

15.50.3 Dry deposition

In dry deposition of particles from a plume there are two distinct regimes. Deposition of larger particles is governed essentially by gravitational settling, while that of smaller particles is determined by turbulent motion.

Gravitational settling of the larger particles, say of radius >5 μm, is given by Stokes law, or modifications of it. Stokes law, for spherical particles, is

$$v_t = \frac{2r^2 g \rho_p}{9\mu} \qquad [15.50.3]$$

where r is the radius of the particle, v_t is the terminal velocity of the particle, μ is the viscosity of the air, and ρ_p is the density of the particle.

For particles of radius greater than about 10–30 μm, Stokes' law requires modification to take account of inertia and slip flow. Terminal velocities incorporating these corrections have been given by Hage (1964) for a particle of density 5 g/cm^3. Hage's work is described by van der Hoven (1968), and a plot derived from this work by S.R. Hanna, Briggs and Hosker (1982) is shown in Figure 15.148. For a particle of another density ρ_{p2} the corresponding value of the terminal velocity v_{t2} may be obtained from the standard value of the density ρ_{p1} and from the velocity v_{t1} as given by the figure using the approximate relation, based on Equation 15.50.3:

$$v_{t2} = v_{t1}\frac{\rho_{p2}}{\rho_{p1}} \qquad [15.50.4]$$

For a non-spherical particle, an equivalent radius r_e may be defined as

$$r_e = \left(\frac{3V_p}{4\pi}\right)^{1/3} \qquad [15.50.5]$$

where V_p is the volume of the particle. The terminal velocity v_{tn} of the particle may be estimated from the terminal velocity v_{ts} of a spherical particle with radius r equal to its equivalent radius r_e using an empirical dynamical shape factor α defined by

$$v_{tn} = v_{ts}/\alpha \qquad [15.50.6]$$

Values of the dynamical shape factor are given by Chamberlain (1975). For a cylinder with a 1 : 1 ratio of axes the value of the factor is 1.06 and for a ratio of 4 : 1 it is 1.32.

As stated above, the gravitational settling regime starts at a particle radius of about 5 μm, which corresponds to a terminal velocity of about 1 cm/s. There are a number of models for dry deposition and the appropriate model depends on the regime, and hence on the particle radius. For deposition of particles with a terminal velocity >100 cm/s, which corresponds to a radius of about 100 μm, it is suggested by van der Hoven that gravitational settling is so fast that it may be determined from the terminal velocity and the wind speed using a conventional ballistic approach.

For particles with terminal velocity in the range 1–100 cm/s the deposition rate ω is defined as

$$\omega = v_g \chi \qquad [15.50.7]$$

where v_g is the fall velocity.

The main model in this regime is the tilted plume model for an elevated source. In this model the height H of the source is modified with distance by the term xv_g/u as shown in Figure 15.149. Then the Sutton relation for a release from an elevated continuous point source given in Equation 15.16.29 may be modified to give

$$\chi = \frac{2Q}{\pi C_y C_z u x^{2-n}} \exp\left\{-x^{n-2}\left[\frac{y^2}{C_y^2} + \frac{(H - xv_g/u)^2}{C_z^2}\right]\right\} \qquad [15.50.8]$$

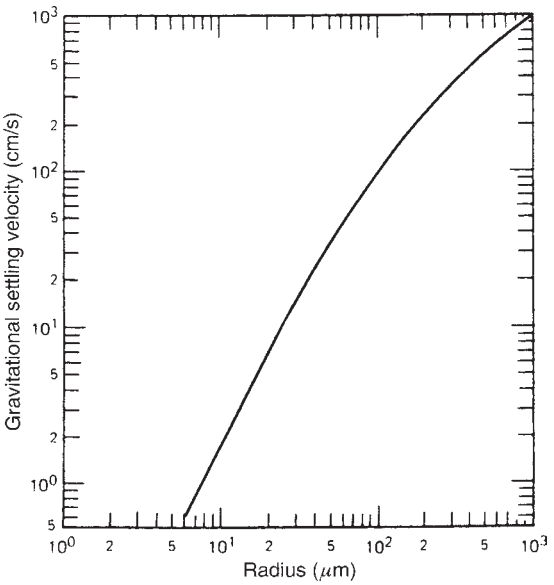


Figure 15.148 *Dry deposition from a dispersing cloud – gravitational settling speed of particles near earth's surface (S.R. Hanna, Briggs and Hosker, 1982). Particle density 5 g/cm^3*

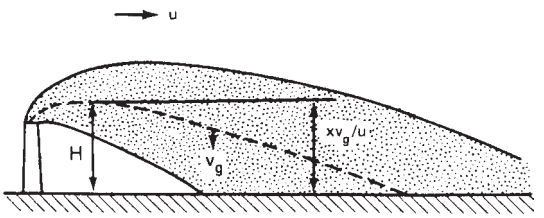


Figure 15.149 *Dry deposition from a dispersing cloud – tilted plume model (S.R. Hanna, Briggs and Hosker, 1982)*

The effect of depletion of the cloud may be taken into account by modifying Equation 15.50.7 by a depletion factor F, so that the deposition rate becomes

$$\omega = F v_g \chi \qquad [15.50.9]$$

This depletion factor has been given by Csanady (1955) as

$$F = 1 - \frac{1}{(1-n/2)(Hu/xv_g - 1) + 2} \qquad [15.50.10]$$

The tilted plume model is applicable only in the well-mixed boundary layer such as occurs in daytime adiabatic conditions.

For smaller particles with a terminal velocity of <1 cm/s, the deposition rate is defined in terms of the deposition velocity v_d:

$$\omega = v_d \chi \qquad [15.50.11]$$

Models available for the deposition of such particles are discussed by van der Hoven (1968). One is the model by Chamberlain (1953). For a ground level continuous point source this author modifies the Sutton relations to obtain for an initial source strength Q_o an effective source strength Q_x at distance x using the depletion term

$$\frac{Q_x}{Q_o} = \exp\left(-\frac{4v_d x^{n/2}}{nu\pi^{1/2}C_z}\right) \qquad [15.50.12]$$

This correction is then applied to Sutton's relation for a release from a ground level continuous point source given by Equation 15.16.27 to yield for the ground level concentration

$$\chi(x,y,0) = \frac{2Q_x}{\pi C_y C_z u x^{2-n}} \exp\left(-x^{n-2}\frac{y^2}{C_y^2}\right) \qquad [15.50.13]$$

and for the deposition rate from Equations 15.50.11 and 15.50.13

$$\omega = \frac{2Q_x v_d}{\pi u C_y C_z^{2-n}} \exp\left(-x^{n-2}\frac{x^{n-2}y^2}{C_y^2}\right) \qquad [15.50.14]$$

Chamberlain has also given a model for an elevated source.

An alternative model given by van der Hoven is derived from the Pasquill–Gifford equations. The depletion of the source is obtained as follows:

$$\frac{dQ_x}{dx} = \int_{-\infty}^{\infty} \omega \, dy = -\left(\frac{2}{\pi}\right)\frac{v_d Q_x}{u\sigma_z}\exp\left(-\frac{h^2}{2\sigma_z^2}\right) \qquad [15.50.15]$$

which on integration yields

$$\frac{Q_x}{Q_o} = \left[\exp\int_0^x \frac{dx}{\sigma_z \exp(h^2/\sigma_z^2)}\right]^{-(2/\pi)^{1/2}(v_d/u)} \qquad [15.50.17]$$

This correction is then applied to the Pasquill–Gifford equation for a release from an elevated continuous point source (Equation 15.16.43) to yield for the ground level concentration

$$\chi(x,y,0) = \frac{Q_x}{\pi\sigma_y\sigma_z u}\exp\left[-\left(\frac{y^2}{2\sigma_y^2}+\frac{h^2}{2\sigma_z^2}\right)\right] \qquad [15.50.18]$$

and for the deposition rate from Equations 15.50.11 and 15.50.18

$$\omega = \frac{Q_x v_d}{\pi\sigma_y\sigma_z u}\exp\left[-\left(\frac{y^2}{2\sigma_y^2}+\frac{h^2}{2\sigma_z^2}\right)\right] \qquad [15.50.19]$$

Evaluations of Equation 15.50.17 based on numerical integration have been made by van der Hoven (1968) for Pasquill categories A–F for a wind speed $u = 1$ m/s and a deposition velocity $v_d = 10^{-2}$ m/s. Figure 15.150 shows

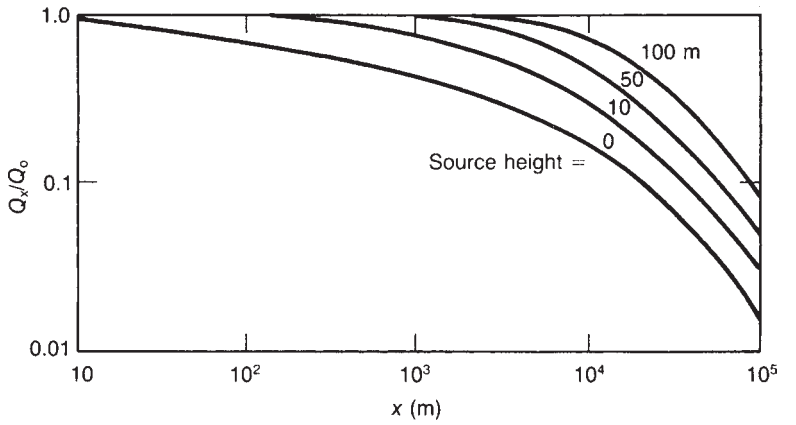


Figure 15.150 *Dry deposition from a dispersing cloud – effect of distance on source depletion fraction (van der Hoven, 1968). Weather conditions D/1; wind speed = 1 m/s; deposition velocity 10^{-2} m/s*

his plot for D conditions, while Table 15.62 summarizes the other plots in terms of the times at which Q_x falls to half its initial value of Q_o. For other wind speeds and deposition velocities use may be made of the relation

$$\left(\frac{Q_x}{Q_o}\right)_2 = \left(\frac{Q_x}{Q_o}\right)_1^{u_1 v_{d2}/u_2 v_{d1}} \quad [15.50.20]$$

where subscripts 1 and 2 refer to the standard conditions used by van der Hoven, as given in Figure 15.150, and to the conditions of interest, respectively.

Another model used for small particles is the partial reflection model of Overcamp (1976). The model is based on the Pasquill–Gifford relations and incorporates both the tilted plume approach to deal with the gravitational settling of larger particles and a reflection coefficient α which qualifies the 'image' term, or term containing $(z+h)$. The basic equation is

$$\chi(x,y,z) = \frac{Q}{2\pi\sigma_y\sigma_z u}\exp\left(-\frac{y^2}{2\sigma_y^2}\right) \times \left(\exp\left\{-\frac{[z-(h-v_t x/u)]^2}{2\sigma_z^2}\right\} + \alpha(x_G)\exp\left\{-\frac{[z+(h-v_t x/u)]^2}{2\sigma_z^2}\right\}\right) \quad [15.50.21]$$

where

$$\alpha(x) = 1 - \frac{2v_d}{v_t + v_d + (uh - v_t x)\sigma_z^{-1}(d\sigma_z/dx)} \quad [15.50.22]$$

and where x_G is obtained from the implicit equation

$$\left(h - \frac{v_t x_G}{u}\right)\frac{\sigma_z(x)}{\sigma_z(x_G)} = z + \left(h - \frac{v_t x}{u}\right) \quad [15.50.23]$$

Table 15.62 *Source depletion fraction Q_x/Q_o given by the van der Hoven model for dry deposition (after van der Hoven, 1968)*

Pasquill stability category	*Source height* (m)	*Distance* (m)			
		10	100	1000	10,000
A	0	0.90	0.82	0.75	
	10	1.0	0.96	0.90	
	100	1.0	1.0	1.0	
B	0	0.90	0.80	0.65	
	10	0.98	0.95	0.80	
	100	1.0	1.0	1.0	
C	0	0.90	0.70	0.60	0.45
	10	1.0	1.0	0.80	0.60
	100	1.0	1.0	1.0	0.80
E	0	0.90	0.60	0.15	0.012
	10	1.0	1.0	0.80	0.10
	100	1.0	1.0	1.0	0.80
F	0	0.90	0.65	0.40	0.07
	10	1.0	1.0	0.80	0.20
	100	1.0	1.0	1.0	0.80

Another model is the surface depletion model of Horst (1977).

A comparison of the models available has been made by Horst (1979), who found that in the near field the partial reflection model was reasonably accurate and easy to use, while in the far field the source depletion model performed better.

These models incorporate the deposition velocity which, as described below, is subject to considerable uncertainty and may be at least as great a source of error as inadequacies in a particular model.

15.50.4 Deposition velocity

Reviews of the deposition velocity, which include extensive data, have been given by McMahon and Denison (1979) and by Sehmel (1980). The deposition velocity is defined by Equation 15.50.11. It should be noted that the surface area for deposition implied in this equation is the normal ground surface area, not the actual vegetation surface, which can be much greater.

Sehmel lists a large number of variables which affect deposition velocity, divided into four categories: meteorology, surface, particle and gas. For particles of diameter >1 μm gravitational settling is dominant, while the movement of particles of diameter <0.1 μm is governed by Brownian motion. The deposition velocity tends to pass through a minimum with particle diameter and it may vary by two orders of magnitude. These effects are illustrated in Figure 15.151, which shows the variation of deposition velocity with particle diameter for grass surfaces.

Deposition velocity is applicable to gases also. Inert gases have almost negligible deposition velocity, say $10^{-4}-10^{-3}$cm/s, but chemically or biologically active gases tend to have a much larger deposition velocity, typically in the range 0.5–3 cm/s. Of interest in the present context are the deposition velocities of toxic gases. From data given by Sehmel, the ranges of deposition velocities of some typical toxic gases are as follows:

Gas	*Deposition velocity* (cm/s)
Cl_2	1.8–2.1
SO_2	0.04–7.5
HF	1.6–3.7
H_2S	0.015–0.38

Deposition velocity is affected very strongly by the surface on which deposition takes place. Again there are order of magnitude differences between different surfaces. Surfaces differ in the actual vegetation surface exposed. They also have different retention properties. Some deposition velocities for selected surfaces are shown in Figure 15.152.

Deposition velocity is also affected by wind speed, roughness length and friction velocity, but these effects are less readily characterized and are a matter of some debate.

A method for prediction of deposition velocity has been given by Sehmel and Hodgson (1978), but prediction remains subject to considerable uncertainty.

15.50.5 Wet deposition

In wet deposition due to rain, a distinction may in principle be made between scavenging within clouds (or rainout) and below clouds (or washout), but in practice these two are generally treated as a single process.

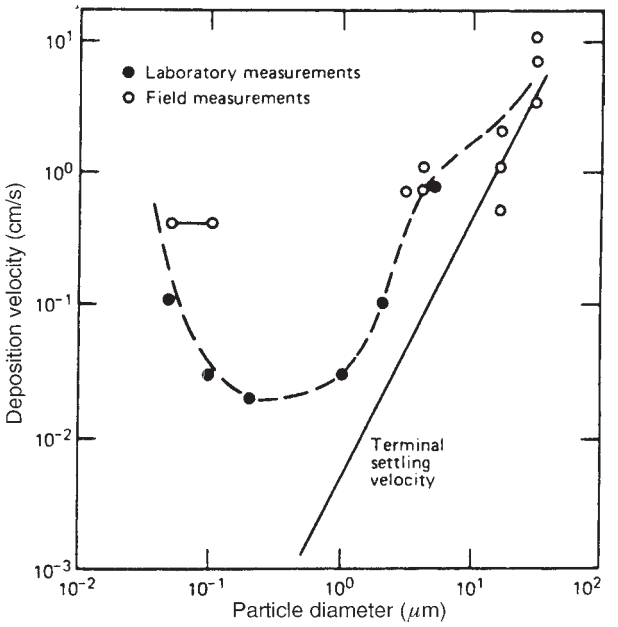


Figure 15.151 *Dry deposition from a dispersing cloud – effect of particle diameter on deposition velocity of particles to grass (McMahon and Denison, 1979) (Courtesy of Pergamon Press)*

Wet deposition of a pollutant is often treated empirically in terms of the washout ratio W_r:

$$W_r = k_o/\chi_o \qquad [15.50.24]$$

where χ is the concentration of pollutant in the air, k is the concentration of pollutant in the rainwater and subscript o denotes the reference height.

Use is also made of an alternative washout ratio W'_r

$$W'_r = \rho_a k'_o/\chi_o \qquad [15.50.25]$$

where k' is the concentration of pollutant in the rainwater and ρ_a is the density of air. The difference between k and k' is that the first has units of mass per unit volume and the second has units of mass per unit mass. The relation between the two washout ratios is:

$$W'_r = \rho_a W_r/\rho_w \qquad [15.50.26]$$

where ρ_w is the density of water. The flux of pollutant to the surface F_w is

$$F_w = k_o J_o \qquad [15.50.27]$$

where J_o is the equivalent rainfall rate. Hence from Equation 15.50.24

$$F_w = W_r \chi_o J_o \qquad [15.50.28]$$

A wet deposition velocity v_w may be defined

$$v_w = F_w/\chi_o \qquad [15.50.29a]$$

$$= W_r J_o \qquad [15.50.29b]$$

An alternative approach is that based on the washout coefficient, or scavenging coefficient Λ. The decay of the concentration of pollutant due to scavenging is frequently modelled by a first-order decay model

$$\chi(t) = \chi(0)\exp(-\Lambda t) \qquad [15.50.30]$$

It may readily be shown, by deriving Equation 15.50.8 from the unsteady-state mass balance, that the same washout coefficient may also be defined in terms of the relation between the interphase transport rate w and the concentration χ:

$$w = \Lambda\chi \qquad [15.50.31]$$

The flux of pollutant F_w through a wetted plume of height z_w is

$$F_w = \int_0^{z_w} w\,dz \qquad [15.50.32a]$$

$$= \int_0^{z_w} \Lambda\chi\,dz \qquad [15.50.32b]$$

For a Gaussian plume from a continuous point source the concentration χ may be obtained from Equation 15.16.41. Then, integrating this equation with respect to z from 0 to ∞, the effective concentration χ_e over the height z_w is

$$\chi_e = \frac{Q}{(2\pi)^{1/2}\sigma_y u z_w}\exp\left(-\frac{y^2}{2\sigma_y^2}\right) \qquad [15.50.33]$$

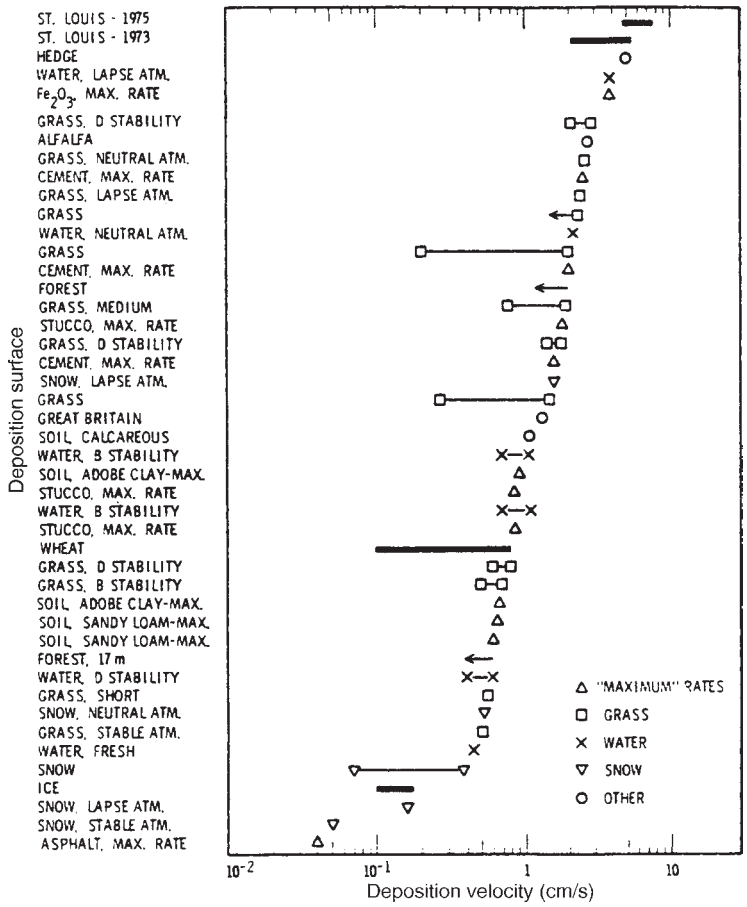


Figure 15.152 *Dry deposition from a dispersing cloud – effect of deposition surface on deposition velocity of sulfur dioxide (Sehmel, 1980) (Courtesy of Pergamon Press)*

Assuming constant Λ and substituting χ_e from Equation 15.50.33 for χ in Equation 15.50.32b gives

$$F_w = \frac{\Lambda Q}{(2\pi)^{1/2}\sigma_y u}\exp\left(\frac{y^2}{2\sigma_y^2}\right) \qquad [15.50.34]$$

On the centre line

$$F_w = \frac{\Lambda Q}{(2\pi)^{1/2}\sigma_y u} \qquad [15.50.35]$$

The use of a constant washout coefficient is a rather crude approximation. Strictly, it is applicable only to single size, or monodisperse, rain drops. Data on the washout coefficient for polydisperse systems have been given by Dana and Hales (1976).

It may be noted that for a polydisperse system the use of the geometric mean drop size tends appreciably to underestimate the washout coefficient. Another problem in the use of a constant washout coefficient concerns the absorption of gas in rain drops. If an absorbed gas does not undergo an irreversible reaction, it is liable to be desorbed as it passes through a zone of lower gas concentration.

15.50.6 Washout ratio and washout coefficient

The washout ratio W_r is an essentially empirical parameter. Data on the washout ratio have been given by McMahon and Denison (1979). The washout ratio tends to decrease with rainfall. As a rule of thumb, it halves for each order of magnitude increase in rainfall. The washout coefficient, or scavenging coefficient, Λ has been estimated theoretically for certain situations. The following relation has been given by Chamberlain (1953):

$$\Lambda = \int_0^{s_{max}} A_s N_s v_s E \, ds \qquad [15.50.36]$$

where A_s is the cross-sectional area of a drop of radius s, N_s is the number of drops per unit volume per unit time, v_s is the velocity of the drops and E is the collection efficiency and subscript max denotes maximum.

Chamberlain used Equation 15.50.36 to determine theoretical values of the washout coefficient as a function of the

velocity v_s and the rainfall, as shown in Figure 15.153. Experimental work by F.G. May (1958) on the washout of Lycopodium spores has shown good agreement with theory, as shown in Table 15.63.

The washout coefficient is a function of the physical and chemical characteristics and of the raindrop size distribution and the rainfall. In many cases where the system is not so well defined as that just described theoretical estimates may be less satisfactory. In such cases it is necessary to fall back on empirical values. Data on the washout coefficient have been given by McMahon and Denison (1979).

15.51 Infiltration into Buildings

In most toxic release scenarios, the major part of the population in the path of the gas cloud is likely to be indoors. The mitigating effect of such shelter can be appreciable. It is therefore necessary to be able to estimate the indoor concentrations. Discussions of air infiltration relevant to hazard assessment have been given in Meteorology and Atomic Energy (Slade, 1968) and the Rasmussen Report (AEC, 1975) and by Haastrup (1984) and P.C. Davies and Purdy (1986).

The degree of protection given by a building depends on the frequency of the air changes, or ventilation rate. The latter is a function of the construction and topographical situation of the building, of the wind speed and direction, of the difference between the outside and inside temperatures and of the number of doors and windows left open.

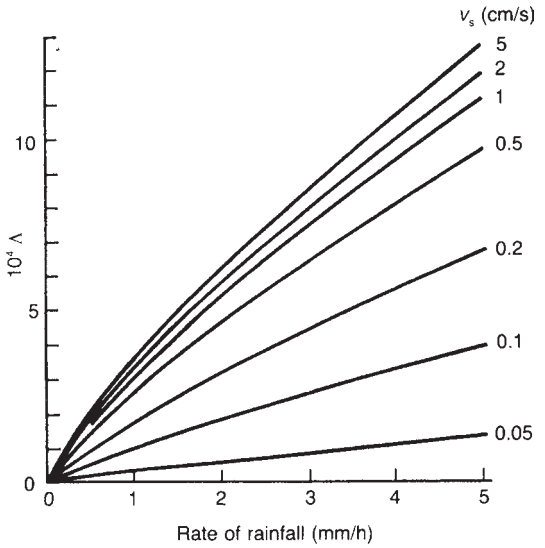


Figure 15.153 *Wet deposition from a dispersing cloud – effect of rate of rainfall on washout coefficient (Chamberlain, 1953) (Adapted from Deposition of Aerosols and Vapours in Rain, graph of A.C. Chamberlain (1955), the original graph being used by kind permission of AEA Technology)*

15.51.1 Models of infiltration

The infiltration of air into a building is usually modelled by assuming that the air in the building space is perfectly mixed so that

$$\frac{dc_i}{dt} = \lambda(c_o - c_i) \qquad [15.51.1]$$

where c is the concentration (various units), t is the time (h) and λ is the ventilation constant (h^{-1}) and subscripts i and o refer to indoor and outdoor, respectively. The ventilation constant is equal to the frequency of the air changes, is generally also referred to as the ventilation rate and is most often expressed as air changes per hour (ach). Imperfect mixing may be allowed for, as described below.

In the general case, where the outdoor concentration profile $c_o t$ is arbitrary, the indoor concentration is obtained from Equation 15.51.1 numerically.

For the case where the outdoor concentration profile, or forcing function, takes the form of a pulse, with

$$c_o(t < t_o) = c_o \qquad [15.51.2a]$$

$$c_o(t > t_o) = 0 \qquad [15.51.2b]$$

as shown in Figure 15.154(a), an analytical solution is available. If the outdoor concentration undergoes a step change from zero to c_o and then persists to time t_o, the rise of the indoor concentration is obtained by integrating Equation 15.51.1 to give

$$c_i = c_o[1 - \exp(-\lambda t_o)] \qquad [15.51.3]$$

Table 15.63 *Washout coefficient for Lycopodium spores (after May, 1958) (Courtesy of The Royal Meteorological Society)*

Type of rain	*Rate of rainfall* (mm /h)	*Wind velocity* (cm/s)	*Washout coefficient,* $\Lambda\ 10^{-4}$/s	
			Observed	*Theoretical*
Frontal	3.91	320	10.2	9.7
Frontal	1.12	543	4.2	3.6
Heavy frontal	14.1	845	30.8	26.8
Frontal	1.01	334	3.2	3.2
Continuous rain of showery type	3.64	332	8.9	9.2

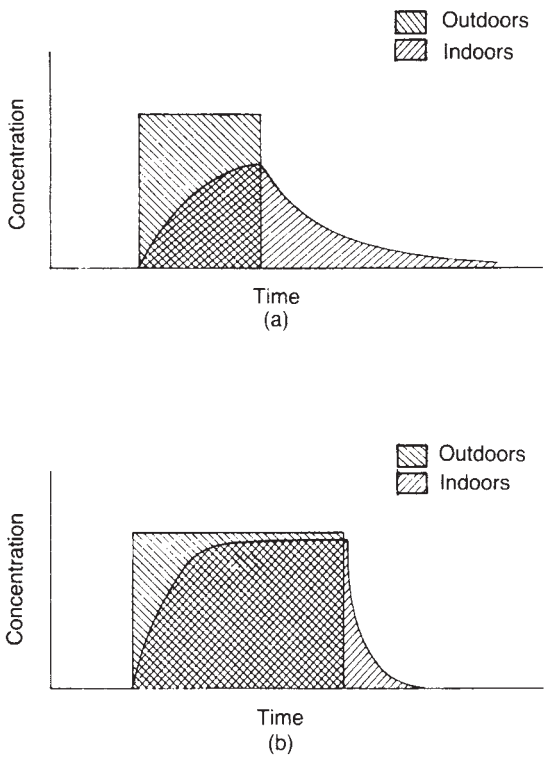


Figure 15.154 *Infiltration of gas into buildings – outdoor and indoor concentration profiles for a rectangular pulse forcing function (Pietersen, 1986c): (a) short pulse, low ventilation rate; and (b) long pulse, high ventilation rate*

If the outdoor concentration then falls to zero, the decay of the indoor concentration from its maximum value $c_i(t_o)$ is again obtained by integrating Equation 15.51.1:

$$c_i = c_i(t_o)\exp[-\lambda(t - t_o)] \quad [15.51.4]$$

$$= c_o[1 - \exp(-t_o)]\exp[-\lambda(t - t_o)] \quad [15.51.5]$$

This yields the concentration profile shown in Figure 15.154(b).

This rectangular pulse model may be used to obtain an approximate estimate of the indoor concentrations both for a puff from a nominally instantaneous release and for a plume from a short-duration continuous release. For a long-duration continuous release the appropriate model is a step forcing function and the indoor concentration is given by Equation 15.51.3.

In assessing the effect of a toxic gas, however, it is frequently necessary to work in terms of toxic dose or, more generally, toxic load rather than of concentration. The toxic dose is defined as

$$D = \int c\,\mathrm{d}t \quad [15.51.6]$$

and the toxic load is generally defined as

$$L = \int c^n\,\mathrm{d}t \quad [15.51.7]$$

where D is the toxic dose (units h) and L is the toxic load (units^n h).

It is shown below that for the pulse model the ratio of the indoor dose D_i to the outdoor dose D_o is unity. For the step model it is readily shown from Equation 15.51.3 that

$$\frac{D_i}{D_0} = 1 - \frac{1 - \exp(-\lambda t)}{\lambda t} \quad [15.51.8]$$

An extension of the pulse model in terms of toxic load has been given by Haastrup (1984), who has derived the following relations:

$$L_o = \int c_o^n\,\mathrm{d}t \quad [15.51.9]$$

$$L_i(t < t_o) = \int_o^{t_o} c_i^n\,\mathrm{d}t \quad [15.51.10a]$$

$$= c_o^n \int_o^{t_o} [1 - \exp(-\lambda t)]^n\,\mathrm{d}t \quad [15.51.10b]$$

$$L_i(t > t_o) = \int_{t_o}^{\infty} c_i^n\,\mathrm{d}t \quad [15.51.10c]$$

$$= c_o^n \frac{[1 - \exp(-\lambda t_o)]^n}{\lambda^n} \quad [15.51.10d]$$

The ratio R of the indoor to the outdoor toxic load is then

$$R = \frac{[1 - \exp(-\lambda t_o)]^n}{n\lambda t} + \frac{1}{t}\int_o^{t_o} [1 - \exp(-\lambda t)]^n\,\mathrm{d}t \quad [15.51.11]$$

It may be noted that if $n = 1$, Equation 15.51.11 simplifies to

$$R = \frac{D_i}{D_o} = 1 \quad [15.51.12]$$

For low values of the group λt_o it can be shown that

$$L_i(t > t_o) \gg L_i(t < t_o) \quad [15.51.13]$$

In other words, the total indoor load is dominated by the load during the decay period, or tail. For this case

$$\exp(-\lambda t) \approx 1 - \lambda t \quad \lambda t < 0.1 \quad [15.51.14]$$

Then

$$L_i \approx L_i(t > t_o) \quad [15.51.15]$$

and from Equations 15.51.10b and 15.51.14

$$L_i = \frac{c_o^n t_o^n \lambda^{n-1}}{n} \quad [15.51.16]$$

If the building space is not perfectly mixed, the effect of imperfect mixing may be taken into account in the model by substituting for the ventilation rate λ an effective ventilation rate λ'. The effective ventilation rate may be

determined by applying to the ventilation rate a mixing efficiency factor k:

$$\lambda' = k\lambda \qquad [15.51.17]$$

15.51.2 Ventilation rate

The ventilation of a building may be natural or mechanical. For the assessment of toxic hazard it is normally natural ventilation which is relevant. Information on ventilation is available from a number of sources. These include *Principles of Modern Building* (Building Research Establishment, 1959), the CIBS *Guide Part 1 A4 Air Infiltration* (Chartered Institute of Building Services, 1976) and BS 5925: 1991 *Code of Practice: Ventilation Principles and Designing for Natural Ventilation*.

The equations for air infiltration given by these sources have been reviewed by Brighton (1986). They are all based on following relation:

$$Q = k_1 A \left(\frac{\Delta p}{\rho_o}\right)^{1/2} \qquad [15.51.18]$$

where A is the area of the aperture (m^2), Δp is the pressure drop (N/m^2), Q is the volumetric flow of air (m^3/s), ρ_o is the density of the ambient air (kg/m^3) and k_1 is a constant. Equation 15.51.18 is based on Bernouilli's theorem and the constant is related to the contraction ratio of the emerging jet. For this constant k_1 Brighton gives a compromise value of 0.88.

Work on air infiltration into houses is done for a number of purposes. These include the comfort of the occupants, the safety of gas appliances and the saving of energy. In the latter case the emphasis is on eliminating infiltration, and work in this area illustrates the high degree of leak-tightness which can be achieved.

Studies of air infiltration into houses in Britain have been done at the Building Research Establishment (BRE). Work has been published by Dick (1949, 1950a,b), Dick and Thomas (1951), Brundrett (1977) and Warren and Webb (1980a,b).

Air infiltration is due to the existence of pressure difference between the outside and inside of the building and this pressure difference may be caused by wind or by air temperature, and hence air density, or buoyancy, difference. The ventilation rate due to wind effects may be expressed as

$$\lambda_w = k_2 u \qquad [15.51.19]$$

and that due to buoyancy effects as

$$\lambda_b = k_3 (\Delta T)^{1/2} \qquad [15.51.20]$$

where ΔT is the temperature difference between outdoors and indoors (°C), u is the wind speed (m/s), λ_b is the ventilation rate due to buoyancy (m^3/h), λ_w is the ventilation rate due to wind (m^3/h), and k_2 and k_3 are constants. Figure 15.155 shows data obtained by Dick and Thomas (1951) in work at the BRE on the effect of temperature difference and wind speed on ventilation rate.

In considering ventilation rate it is necessary to distinguish between closed houses and occupied houses, the

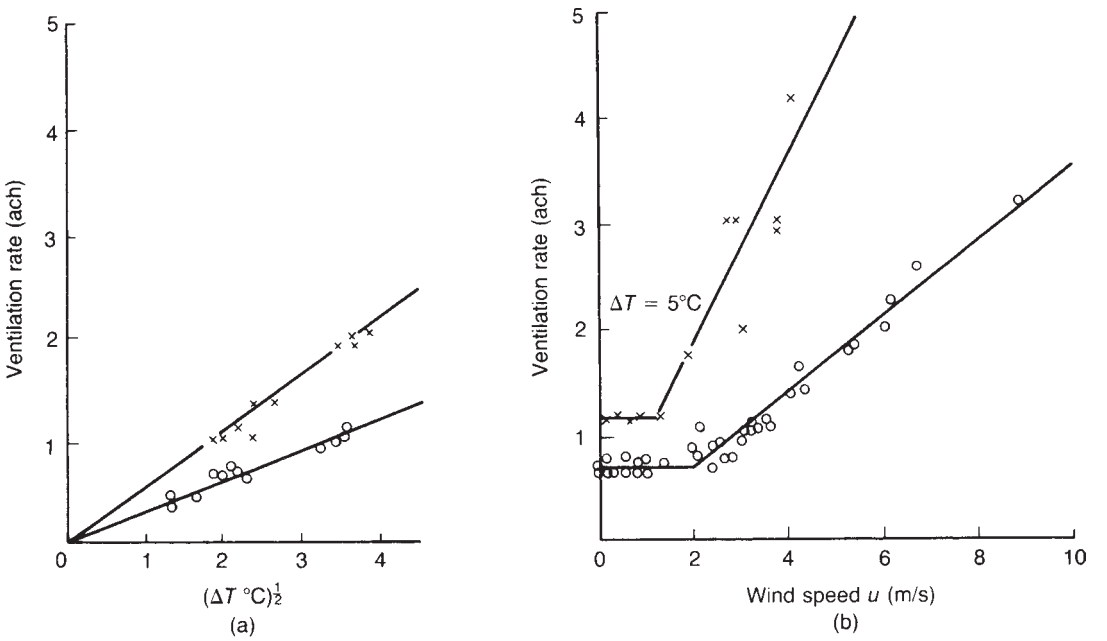


Figure 15.155 *Infiltration of gas into buildings – effect of buoyancy and wind on house ventilation rate (Dick and Thomas, 1951): (a) effect of buoyancy (temperature difference); (b) effect of wind speed, ○, house with no vents open; ×, house with three bedroom vents open. (Courtesy of the Chartered Institution of Building Services Engineers)*

difference being that the latter typically have some windows open. The BRE work includes correlations for the ventilation rate of a closed house as a function of wind speed. P.C. Davies and Purdy (1986) have presented versions of these equations modified so that the wind speed is that at the standard 10 m height. These are:

Exposed site

$$\lambda = 0.87 + 0.13u \qquad [15.51.21]$$

Sheltered site

$$\lambda = 0.88 \quad u < 4.2 \qquad [15.51.22a]$$

$$\lambda = 0.22u \quad u > 4.2 \qquad [15.51.22b]$$

Davies and Purdy give the following relation as the most recent BRE infiltration model:

$$\lambda = \lambda_s(k_4\Delta T^{1.2} + k_5 u^{2.4})^{0.5} \qquad [15.51.23]$$

where λ_s is the ventilation rate measured at standard conditions (h^{-1}) and k_4 and k_5 are constants.

The distribution of infiltration between the different apertures in the building has been investigated by Warren and Webb (1980b). For a typical house with a pressure difference of 50 Pa and an air infiltration rate of 3000 m^3/h they found the following distribution:

	Contribution to air infiltration	
	(m^3/h)	(%)
Windows and WC fan	940	31.3
Back door	280	9.3
Skirting boards	575	19.2
Lights, plugs, pipes, etc.	85	2.8
Other sources	1120	37.4

For occupied houses it is necessary to take into account the effect of open windows. The relation given by Dick and Thomas (1951) for houses with open windows is

$$\lambda = 0.87 + 0.13u + 0.23(n + 1.4m) + 0.05(n + 1.4m)u \qquad [15.51.24]$$

where m is the number of open casement windows and n is the number of open top-vent windows. Equation 15.51.24 is based on a study on an estate at Abbotts Langley. The following data were obtained on the number of windows open:

	Abbotts Langley	*Bucknalls Close*
Casement windows open, m	0.25	0.4
Vent windows open, n	1.75	3

Abbotts Langley is an exposed site and Bucknalls Close a sheltered one.

The number of windows open depends on a number of factors, including the degree of exposure, the season, the time of day, the wind speed, the outside temperature and the number of occupants. These factors are discussed in detail by Davies and Purdy. Many of the factors tend to cancel out. For example, the number of windows open on an exposed site tends to be less than on a sheltered site. Likewise, the number open in summer is greater than in winter, but the buoyancy effect is less.

Information on room ventilation rates from the work of Warren and Webb is given Table 15.64. The best estimates of whole house ventilation rates given by Davies and Purdy are shown in Table 15.65.

Data for air infiltration into British houses are not necessarily applicable in other countries. The ventilation rates for American houses are less and those for Swedish houses much less. Data given by Kronvall (1978) indicate that ventilation rates for Swedish houses are about a quarter those in Britain. Data on ventilation rates for buildings in the United States have been given by Handley and Barton (1973). The work of Handley and Barton also shows, however, that there is a wide range of ventilation rates. They found values from 0.07 to 3.0 air changes/h.

15.51.3 Hazard assessments

The mitigating effect of shelter is considered in the *First Convey Report* in Appendix 7 by Beattie, who quotes Equation 15.51.3 and suggests that a suitable value of the ventilation rate λ is 1 change/h for a modern building, but that this may rise to 2–3 changes/h if doors or windows are left ajar.

In the Rijnmond Report credit is taken for the effect of shelter using Equation 15.51.1. A ventilation rate of 2 changes/h is used, but it is stated that this could be as low as 1 or as high as 3.

Table 15.64 *Room ventilation rates[a] (after P.R. Warren and Webb, 1980b) (Courtesy of the Chartered Institute of Building Services Engineers)*

Room	*Room ventilation rate* (air changes/h)		
	Mean	*Minimum*	*Maximum*
Living room	0.89	0.24	1.64
Kitchen	1.43	0.43	3.50
Small bedroom (<15 m^3)	0.87	0.28	2.90[b]
Large bedroom (>15 m^3)	0.65	0.25	1.19
Bathroom	1.81	0.25	3.19

[a] Number of rooms in sample ranged from 14 to 29.
[b] This value corrected from one of 3.9 in the original paper (P.R. Warren, 1992).

Table 15.65 *Whole house ventilation rates (after P.C. Davies and Purdy, 1986) (Courtesy of the Institution of Chemical Engineers)*

	Ventilation (air changes/h)[a,b]			
	D/2.4	*D/4.3*	*D/6.7*	*F/2.4*
Closed house	1	1	1.5	1
Normal occupied house	2	2	3	2

[a] Best estimate.
[b] Values used by Pape and Nussey (1985) for these four stability category/wind speed combinations are 0.7, 1, 1.5 and 0.5 air changes/h, respectively.

15.52 Source and Dispersion Modelling: CCPS Guidelines

The CCPS has issued two publications giving practical guidance on emission and dispersion of hazardous materials. These are now described.

15.52.1 Guidelines for Use of Vapor Cloud Dispersion Models

The CCPS *Guidelines for the Use of Vapor Cloud Dispersion Models* (the CCPS *Vapor Cloud Dispersion Model Guidelines*) (1987/2) covers both emission and dispersion. The *Guidelines* give an overview of release scenarios, particularly pipe ruptures, vessel rupture and reactor venting, review the dominant phenomena of initial acceleration and dilution, buoyancy and atmospheric turbulence, and give a decision tree for handling the scenarios. A selection of release scenarios is given, and amplified in an appendix. The characteristics of routine and accidental releases are compared.

Models are given for the determination of emission flows. These include: two-phase flow; flow from tanks under liquid head as well as pressure; and flow from pipelines. Models for various types of jet are covered. Models for vaporization from pools include both heat and mass transfer limited cases and spreading pools. A critical review is given of pool vaporization models.

For gas dispersion, separate treatments are given for ground level and elevated releases. An overview is given of passive gas dispersion, including the Pasquill–Gifford model, the Pasquill stability categories and correlations for dispersion coefficients. The set of six models contained in the EPA UNAMAP6 system is outlined.

The variety in type and origin of dense gas dispersion models is described. The authors state that there are some 100 models, with 10 further models being created annually. Many existing models continue to undergo development and to acquire new features.

Dense gas dispersion is considered first in the absence of heat effects. The box model of van Ulden is outlined. The authors then derive for dense gas dispersion a number of simplified relations for cloud dimensions and concentration, and compare them with the Thorney Island trials data.

Accounts are then given of the thermodynamic and heat transfer phenomena and of correlations used for air entrainment. The three-dimensional models considered are FEM3 and MERCURE-GL. The review given of the criteria utilized by various workers for effectively passive dispersion brings out the large disparities in the criteria adopted. Physical modelling is described, particularly in respect of plume lift and complex terrain. The implications of concentration fluctuations are treated and the effect of sampling time and volume are discussed.

A review is given of some principal dispersion models, covering some 40 models and giving a tabulation of the characteristics of each model. Four models are described in more detail: AIRTOX, DEGADIS, FEM3 and INPUFF.

For elevated releases of dense gas the *Guidelines* give an overview of models for momentum jets and buoyant plumes. The use is described of an effective height in the Pasquill–Gifford model for handling plume rise and gas density. Momentum jet scenarios are classified and the model of D.J. Wilson (1979b) for a momentum jet from a pipeline is described. For plumes reference is made to the models of G.A. Briggs (1984) which are utilized in UNAMAP. An account is given of the models of Ooms, Mahieu and Zelis (1974) and of Hoot, Meroney and Peterka (1973). A criterion is given for effectively dense gas dispersion in an elevated release.

The *Guidelines* consider the extent to which models have been validated against field trials and the uncertainty in model estimates, and list some of the comparisons made between models and trials. They refer to the Environmental Protection Agency set of model evaluation procedures for passive dispersion and give a number of measures of performance.

The *Guidelines* give one of the few quantitative treatments of uncertainty in modelling. The sources of uncertainty considered are model physics, random variability and input data errors. A treatment is given of the effect on uncertainty of the number of model parameters.

15.52.2 Workbook of Test Cases for Vapor Cloud Source Dispersion Models

The CCPS *Vapor Cloud Dispersion Model Guidelines* are supplemented by the CCPS *Workbook on Test Cases for Vapor Cloud Source Dispersion Models* (the CCPS *Vapor Cloud Source Dispersion Model Workbook*) (1989/8). The *Workbook* gives a set of emission, pool vaporization and jet models, and describes methods of matching the output of these models with the input required by selected dispersion models. The principal models treated are: for emission, the Fauske–Epstein models for liquids, subcooled liquids and saturated liquids; for vaporization, the Fleischer model for an evaporating pool; for jets, the Briggs momentum jet model and the Hoot, Meroney and Peterka dense gas jet model; and for gas dispersion, the Pasquill–Gifford model, CAMEO, the Ooms model, SPILLS, SLAB and DEGADIS.

The criterion used to determine whether it is necessary to use for a continuous release a dense gas dispersion model

is $\mathrm{Ri} \gg 10$ with

$$\mathrm{Ri} = \frac{\pi}{4} g' \frac{u_o D}{u_*^2 u} \quad [15.52.1]$$

$$u_* \approx 0.065u \quad [15.52.2]$$

where D is the initial diameter of the plume, g' is the reduced gravity, u is the wind speed, u_o is the velocity of release and u_* is the ambient friction velocity. Five release scenarios are treated:

(1) continuous jet release of gaseous butane from a vent stack;
(2) continuous release of liquefied ammonia from a storage vessel
  (a) nozzle failure (liquid release),
  (b) line rupture (two-phase release);
(3) continuous jet release of high pressure carbon monoxide gas from a low level source;
(4) continuous two-phase release of liquefied chlorine from a storage vessel;
(5) continuous release of liquid acetone into a bund.

These are all continuous releases, the choice being deliberate, since the models for instantaneous or transient releases are subject to more uncertainty. Likewise, the first four cases were selected because the excess density is significant and it is necessary to use a dense gas dispersion model.

The *Workbook* gives detailed working for these five cases, with hand calculation of the sections on emission, vaporization, jet behaviour and interface to the dispersion model being followed by results of the gas dispersion computer codes. Several sample outputs are given from CAMEO, SPILLS, SLAB and DEGADIS.

15.53 Vapour Release Mitigation: Containment and Barriers

There are a number of methods of preventing or mitigating the dispersion of gases. They include the use of:

(1) bunds
(2) foam
(3) solid barriers
(4) fluid barriers
  (a) water spray barriers
  (b) steam curtains.

An account of the effect of some of these devices on gas dispersion is given in Section 15.40. The results of field trials and of physical modelling are given in Sections 15.37–15.39. Guidelines for vapour release mitigation have been given by Prugh (1985–, 1987b,c). The various methods of prevention and mitigation are now considered.

15.53.1 Bunds

The rate of evaporation of a spill, particularly that of a refrigerated liquefied gas, can be greatly reduced if the spill is contained within a bund. In turn, the evaporation from the bund may be much reduced by appropriate design. Two principal features are the geometry and the substrate of the bund. A bund around a storage tank is generally designed to contain the contents of the tank. A bund with a smaller floor area but higher walls presents a smaller surface to heat up and vaporize the liquid. The higher wall also acts as a barrier to the flow of the vapour.

The use of a suitable material for the substrate can greatly reduce the rate of heat transfer to the liquid. The relations for this heat transfer process are given in Section 15.10. From Equation 15.10.30 the rate of heat transfer is proportional to the heat transfer parameter $(k_s \rho_s c_s)^{1/2}$. Table 15.66 lists some values of this parameter for different substrates, as given by Dilwali and Mudan (1987). As the table indicates, there are differences of up to 16 in the values of the parameter. These authors describe a hazard assessment of the dispersion of the vapour from a spill of liquid chlorine into a bund. The study considered various designs of bund and showed that the distance to the concentration immediately dangerous to life and health could be reduced from 2.6 km for the base case to 320 m for an alternative design. Further, the provision of a bund facilitates the use in suitable cases of foam, which can effect a further large reduction in evaporation.

15.53.2 Foam

The use of foam is an effective means of reducing the rate of evaporation, where a suitable foam is available. Accounts of the testing of foams at facilities in 1986 at Pueblo, Colorado, and in 1988 at the Nevada Test Site (NTS) have been given by Dimaio, Norman and co-workers (Dimaio and Norman, 1988, 1990; Norman and Dimaio, 1989; Norman and Swihart, 1990).

Foams tested included: Hazmat 2, an acid resistant foam; ARAFFF, an alcohol resistant AFFF foam; and a fluoroprotein foam. Chemicals tested included bromine, chlorine, hydrogen fluoride, monomethylamine, phosphorous oxychloride, phosphorous pentachloride and sulphur dioxide. Using Hazmat 2 the proportional vapour suppressions achieved were as follows: bromine >95%; chlorine 67–82%; hydrogen fluoride 70–85%; sulfur dioxide >61%.

Foam acts by insulating the surface of the spill and preventing vaporization. Other modes of action include absorption of the vapour and scrubbing out of aerosol and particulate matter. Any foam used must be suitable for the application; the wrong foam can do more harm than good. A guide to the use of foam on hazardous materials has been published by Norman (1987). Likewise, water should only be used advisedly; incorrect use can make things worse.

Table 15.66 *Some values of the heat transfer parameter $(k_s \rho_s c_s)^{1/2}$ for different substrates (after Dilwali and Mudan, 1987) (Courtesy of the American Institute of Chemical Engineers)*

Material	*Heat transfer parameter* $(k_s \rho_s c_s)^{1/2}$ $(\mathrm{W\,s^{1/2}/m^2\,K})$
Soil (dry)	2570
Sand (dry)	2660
Sand (wet: 3% moisture)	2335
Uninsulated concrete	3750
Insulated concrete	230–440
Polyurethane	140
Other insulating materials	
Celofoam	99
Foamglass	74

Foam should be applied gently, possibly with continuous application or frequent reapplication. Personnel should be trained and should have suitable protective equipment, including self-contained breathing apparatus.

15.53.3 Solid barriers

A solid barrier such as a fence or wall can serve either to contain a gas cloud entirely or to effect an appreciable dilution. An impermeable barrier designed for this purpose and erected within the works is generally know as a vapour barrier. A barrier does not need to be impermeable to mitigate a gas release. A plantation of trees may provide a worthwhile degree of dilution of a gas cloud.

15.53.4 Vapour barriers: Hawk programme

As described in Section 15.37, two series of field trials have been conducted at the NTS on the mitigation of hydrogen fluoride releases. These trials were largely concerned with water spray barriers and are considered in Section 15.53.13. The second investigation, the Hawk programme, under the auspices of ICHMAP, also included a study of vapour barriers. An account of this work is given here.

The programme on vapour barriers included a review of the effectiveness of vapour barriers and wind tunnel tests on such barriers. The review concluded that, whilst a vapour barrier reduces the near field concentrations, in the far field this effect decays.

In the wind tunnel work, two types of configuration were tested. One consisted of vapour barriers or fences, with only partial enclosure of the gas cloud, and the other of vapour boxes, with complete enclosure. In addition, the effect of other types of plant obstacle was investigated.

The work demonstrated that the effect of a vapour barrier is extremely dependent on the nature of the release, the site where the release occurs and the barrier design. The results were expressed as the ratio of the concentration without a vapour barrier or box to the concentration with a barrier or box – the concentration reduction factor. Typically, concentration reduction factors were of the order of 2–10 in the near field, falling to factors of unity in the far field, but with the latter ranging up to 4.

There was concern that the use of a vapour box might aggravate the hazard of a vapour cloud explosion. Overpressure increases with cloud height; a vapour box increases the cloud height and may therefore be expected to increase the overpressure. The effect was investigated using the FLAGS explosion simulation code. This confirmed that the use of a vapour box does increase overpressure. This effect may be mitigated by reducing the height of the box or by installing vents in it, but the overpressure is still higher than without a box.

15.53.5 Vapour barriers: FENCE62

Meroney (1991) has described the use of a set of models with the generic title FENCE to simulate the behaviour of a dense gas cloud at a fence used as a vapour barrier, in particular FENCE62.

Models for the simulation of the dilution of a cloud of hydrogen fluoride are adaptations of the box model DENS62 and the slab model DENS23. For simulation of the effects of a vapour barrier the corresponding models are FENCE62 and FENCE23 and those for the effects of a water spray barrier are SPRAY62 and SPRAY23; SPRAY 65 is a modification of SPRAY62.

These models were used to simulate the Goldfish field trials on the dispersion by a fence of a continuous release of hydrogen fluoride. Figure 15.156(a) shows the effect of fence height on the height of the cloud and Figure 15.156(b) the effect on the downwind concentration. These effects decay so that by about 200 fence heights downwind they have largely disappeared.

The fence was found to be more effective in diluting the gas cloud if located near the source. For a fence placed within 400 m of the source, the dilution effects did not persist beyond about 1000 m. For a fence located 100 m from

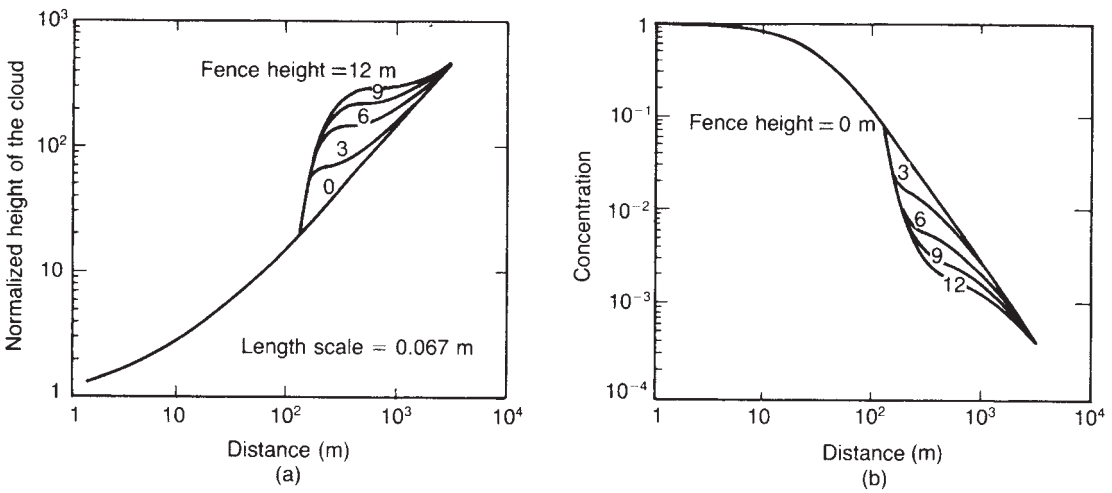


Figure 15.156 *Dispersion of dense gas at obstacles – predictions of FENCE62 for dispersion of hydrogen fluoride across barrier for Goldfish trial 1 (Meroney, 1991): (a) effect on plume height; (b) effect on centre line concentration (Courtesy of the American Institute of Chemical Engineers)*

the source there was little effect of wind speed in the range 1–8 m/s on either downwind cloud height or concentration.

15.53.6 Water spray barriers

A good deal of work has been done on the development of water spray barriers, or water curtains, as a means of mitigating the hazard from a gas release. The systems used include fixed water spray installations and mobile water spray monitors. Fixed installations are typically a set of spray nozzles several metres off the ground with the spray directed downwards. Such systems are used both in the open air and in buildings. A typical mobile monitor system is a set of spray nozzles inclined at an angle of approximately 45° to the horizontal. Water sprays and curtains are used mainly against flammable gases, but may be applied against toxic gases also.

A water spray directed vertically through a gas cloud will have a number of effects. These include:

(1) mechanical effects of acting as a barrier to the passage of gas, of imparting upward momentum to a gas or of dispersion and dilution by air entrainment;
(2) thermal effects by warming of cold gas;
(3) physico-chemical effects of absorption of gas, without or with chemical reaction.

A water spray barrier may be used for any of these purposes.

Where a water spray barrier is used, consideration should be given to the need for arrangements to drain away the water used, particularly if the application may be prolonged.

15.53.7 Water spray barriers: early work

An experimental investigation of the effectiveness of water sprays against gas clouds has been described by Eggleston, Herrera and Pish (1976). The experimental rig was a set of water spray nozzles mounted on a frame initially 15 ft high, later modified to 20 ft, and directed downwards. Clouds of ethylene and vinyl chloride monomer vapour were directed towards the spray system at ground level.

The water spray was effective as a vapour barrier in some experiments but not in others. The spray entrains air and pumps it down and horizontally outwards. If the velocity of this air exceeds that of the vapour cloud, the spray acts as a barrier, otherwise it does not. Thus vapour clouds with velocities of 3 and 9 mile/h were stopped by sprays with 100 psig nozzle pressure, but only the former was stopped when the nozzle pressure was reduced to 40 psig. The vapour tended to spread out at ground level in front of the spray, but did not go over the top.

The air entrainment rates obtained were in the range 87–213 ft^3/min air per US gal/min water with nozzle pressures in the range 20–90 psig. Total entrained air rates were in the range 1242–7107 ft^3/min. The velocity of the air pumped by the spray was low and the flow was therefore sensitive to any obstruction. In cases where the vapour cloud passed through the spray barrier there was still an appreciable dilution effect. The gases used are highly insoluble and the absorption effects were negligible.

The effect of the water spray on the ignition of a flammable vapour cloud and on the flame speed in the cloud was also investigated. It was found that the water spray did not prevent ignition occurring and that the flame speed actually increased, probably due to the greater turbulence.

Further experimental work on water sprays has been described by J.W. Watts (1976). Again the experimental rig was a set of nozzles mounted on a 20 ft high frame and directed downwards. Clouds of propane vapour were directed towards the spray system at ground level.

Some experiments were done in which ignition sources in the form of cans of burning gasoline were located on the far side of the sprays. In cases where the spray was not an effective barrier the vapour cloud ignited and the flame passed back through the spray.

Further experiments were carried out in a 13 ft high open rig with a single nozzle with the introduction of ethylene vapour through a pipe just below the nozzle. The flow of ethylene was increased until the concentration measured by gas detectors near the ground rose to just below the lower flammability limit. The maximum flow of ethylene controllable by the spray was 2609 lb/h with a calculated air entrainment rate of 23,600 ft^3/min.

Other experiments were done in which volumes of ethylene–air mixture held in polyethylene chambers were ignited by pentaerithrytol tetranitrate (PETN) and observations were made of the conditions under which deflagration and detonation were obtained. The volumes used were 500, 4000 and 10,000 ft^3. The authors state that given a sufficient charge of PETN detonation could be obtained, that the explosion yield was generally much higher with detonation than with deflagration, that the detonation limits were 5–10.5% and were thus narrower than the flammability limits, and that with a water spray in the chamber the strength of the PETN charge necessary to obtain detonation was considerably increased.

The effectiveness of water sprays in suppressing combustion in mists of heat transfer media, specifically Dowtherm A, has been investigated by Vincent *et al.* (1976a) in a 6.5 ft diameter spherical vessel. It was shown that combustion could be suppressed and it was tentatively concluded that, for such mist droplets, the mechanism was one of scrubbing rather than quenching.

Although in Watts' work water sprays were not effective in arresting the passage of flames, Brasie (1976b) has described work at the Bureau of Mines in which flames in gas clouds were quenched by the use of very high nozzle pressures in the range 1000–2000 psig, which give a much finer spray. In this case the mechanism was considered to be one of quenching, the distance between the drops being less than the quenching distance of the gas.

Experiments on the use of a water curtain generated by mobile monitors against a chlorine gas cloud have been described by the Ministry of Social Affairs (1975) in the Netherlands. A water curtain was successfully used to protect a small area against the gas cloud.

15.53.8 Water spray barriers: air entrainment

The design and application of a water spray barrier to entrain air into a gas cloud has been described in a series of studies by McQuaid. These include: the entrainment characteristics of a water spray barrier (McQuaid, 1975); the use of a water spray barrier to effect ventilation in mines (McQuaid, 1976a); the design of a water spray barrier to dilute flammable gas clouds (McQuaid, 1977); a comparative review of water spray barriers and steam curtains for dilution of flammable gas clouds (McQuaid, 1980); and the application to dense gas clouds. These aspects are described below.

An account of work on the entrainment of air by a water spray barrier has been given by McQuaid (1975), who has also described the application of this work to the design of water spray barriers for dispersion of gas clouds (McQuaid, 1977).

In order to dilute a gas cloud it is necessary to deliver air not only in sufficient quantity but also at a sufficient velocity. The relation for the flow of air Q_a and the air velocity V at the base of the cone of spray cone with base diameter D is

$$D = \left(\frac{4Q_a}{\pi V}\right)^{1/2} \qquad [15.53.1]$$

where D is diameter of the spray cone (m), Q_a is the volumetric flow of air (m^3/s) and V is the velocity of the entrained air (m/s).

McQuaid obtained the following correlation for entrainment of air into a spray nozzle:

$$\frac{Q_a}{Q_w} = f\left(\rho_w^{1/2}\frac{F_N}{D^2}\right) \qquad [15.53.2]$$

with

$$F_N = \frac{Q_w}{P_w^{1/2}} \qquad [15.53.3]$$

where F_N is the flow number of the nozzle ($(l/s)\cdot(kN/m^2)^{1/2}$), P_w is the pressure of water at the nozzle (kN/m^2) (gauge) Q_w is the volumetric flow of water (l/s) and ρ_w is the density of water (kg/m^3). This correlation is given in Figure 15.157(a). The ratio Q_a/Q_w is both a measure of the efficiency of the spray and a design parameter. It is given as a function of the water pressure and flow number in Figure 15.157(b). It should be noted that in other work different units are quoted for the nozzle flow number.

In the original work, this correlation was validated in small scale experiments with $D = 0.3$ m and $Q_w < 11$/s. McQuaid (1977) has compared values predicted by the correlation with results from the larger scale work of Rasbash and Stark (1962), Eggleston, Herrera and Pish (1976), J.W. Watts (1976), Heskestad, Kung and Todtenkopf (1976) and Beresford (1977).

For design, McQuaid takes an air velocity V of 6 m/s. Then, given a water pressure P_w, the number of nozzles n

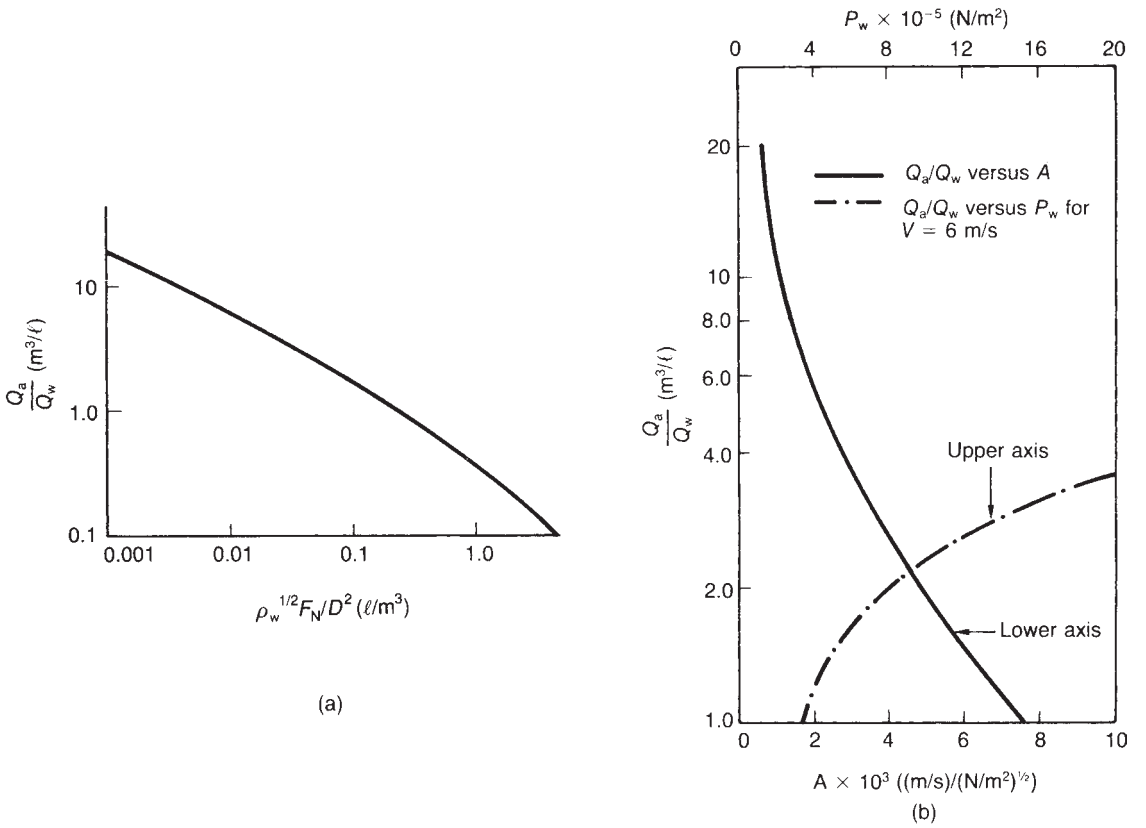


Figure 15.157 *Mitigation of gas dispersion by water spray barriers – water spray nozzle relationships (McQuaid, 1977): (a) and (b) air entrainment relationships. $A = \pi V/4P_w^{1/2}$ (Courtesy of HM Stationery Office)*

and the required total air flow nQ_a, the water flow Q_w and hence the flow number F of the nozzles may be determined. There is some latitude in the choice of the number of nozzles, since this does not affect the efficiency Q_a/Q_w.

15.53.9 Water spray barriers: illustrative example

An illustrative example of the design of a water spray barrier is given by McQuaid (1980). This example is summarized in Table 15.67. The problem considered is the design of a barrier for the dilution of a continuous release of ethylene gas escaping at a rate of 1 kg/s and forming a plume with an angle of 35° and a height of 1 m. The table also treats the case of a steam curtain, as described below.

15.53.10 Water spray barriers: Moore and Rees model

P.A.C. Moore and Rees (1981) have given a model, or rather a set of models, for the forced dispersion of gases by water or steam curtains. The model is applied by the authors to dilute gas plumes and to dense gas plumes. The situation considered is that shown in Figure 15.158.

Following Bosanquet (1957), the authors consider an elemental slice of the gas cloud

Table 15.67 *Illustrative calculation for a water spray barrier for dispersion of a dense gas plume (after McQuaid, 1980)*

A Scenario
Release of ethylene (MW = 28; LFL = 2.7%)
Mass rate of release from source = 1 kg/s
Angle of plume = 35°
Distance between source and barrier = 16 m
Width of plume at barrier = 10 m
Height of plume at barrier = 1 m
Gas loading at barrier = 1/10 = 0.1 kg/s m
B Water spray barrier
Water pressure = 700 kPa
Spacing between nozzles = 1.15 m
Height of nozzles = 2 m
Angle of spray cone = 60°
Distance from nozzle to top of plume = 2 − 1 = 1 m
Mass flow of air required = 0.1 × (29/28) × (1/0.027) = 3.8 kg/s m
Density of air = 1.2 kg/m^3
Diameter D of spray cone at plume top = 1.15 m
Volumetric flow of air required per unit length = 3.8/1.2 = 3.2 m^3/s m
Volumetric flow of air required per nozzle = 3.2D m^3/s = 3.2 × 1.15 m^3/s = 3.7 m^3/s
Velocity of entrained air at top of cloud = 6 m/s
Ratio Q_a/Q_w (from Figure 15.157) = 2 m^3/l
Water flow Q_w = 3.7/2 = 1.85 l/s
C Steam curtain
Mass flow of air required = 3.8 kg/s m
Steam flow S required (from Equation 15.53.26) = (0.1 × 2 × 3.8)/200 = 0.0385 kg/s m

$$\frac{d(\delta V)}{dt} = cSu \qquad [15.53.4]$$

where c is an entrainment parameter for the wind, S is the surface area of an elemental slice, u is the velocity of the gas and δV is the volume of the slice.

It is assumed that the cloud velocity u is equal to the wind speed w.

$$u = w \qquad [15.53.5]$$

Also

$$\frac{dx}{dt} = w \qquad [15.53.6]$$

where x is the distance along the plume.

The first model (model A) is for a downward pointing spray. The three regions (I–III) are considered in turn. For region I, the source has a volumetric rate of release Q. In time δt a volume $Q\delta t$ is emitted which at distance x is contained within the volume δV with radius r.

$$\delta V = \pi r^2 w \delta t \qquad [15.53.7]$$

The area S is

$$S = 2\pi r w \delta t \qquad [15.53.8]$$

By conservation of mass

$$Q\delta t = \pi r_o^2 w \delta t \qquad [15.53.9]$$

$$= C\pi r^2 w \delta t \qquad [15.53.10]$$

where C is the volumetric concentration and subscript o denotes the source. From Equations 15.53.4, 15.53.5, 15.53.7 and 15.53.8

$$\frac{d(r^2)}{dt} = 2crw \qquad [15.53.11]$$

Hence from Equations 15.53.6 and 15.53.11

$$\frac{dr}{dx} = c \qquad [15.53.12]$$

Integrating Equation 15.53.12 with respect to x over region I and at the boundary of the region

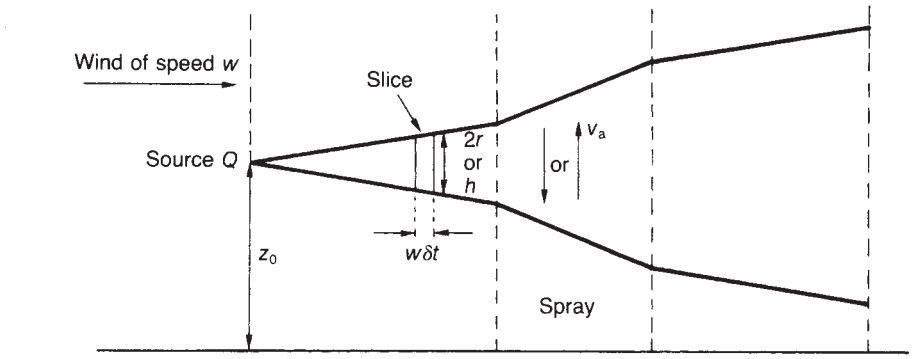
$$r = r_o + cx \qquad [15.53.13a]$$

$$r_1 = r_o + cx_1 \qquad [15.53.13b]$$

where subscript 1 denotes the end of region I. In region II

$$\frac{d(\delta V)}{dt} c \cdot 2\pi r w \delta t \cdot w + c_s \cdot 2\pi r w \delta t \cdot v_a \qquad [15.53.14]$$

where c_s is an entrainment parameter for the spray and v_a is the velocity of the air entrained in the spray. In this equation the first term on the right-hand side represents the entrainment of air by the wind and the second term



Distance	0	x_1	x_2	x
Radius of slice (A,B)	r_0	r_1	r_2	r
Height of slice (C)	h_0	h_1	h_2	h
Vertical velocity (A)	0	0	0	0
(B,C)	0	0	v_2	v

Region		I	II	III
Entrainment from:		Wind	Wind and spray	Wind
Width of slice (A)		$w\delta t$	$w\delta t$	$\dfrac{w\delta t}{\sqrt{v^2+w^2}\delta t}$
$\dfrac{1}{S}\bullet\dfrac{d(\delta V)}{dt}$	(B,C)	$w\delta t$	$w\delta t$	$\dfrac{cw}{c\sqrt{v^2+w^2}}$
	(A)	cw	$cw+c_s v_a$	
	(B,C)	cw	$cw+c_s v_a$	

Figure 15.158 *Mitigation of gas dispersion by water spray barriers – elevation view of dense gas cloud passing through a water spray barrier (P.A.C. Moore and Rees, 1981) (Courtesy of the Institution of Chemical Engineers)*

represents the entrainment by the spray. Proceeding as before yields

$$\frac{dr}{dx} = c + \frac{c_s v_a}{w} \qquad [15.53.15]$$

and integrating gives

$$r = r_1 + \left(c + \frac{c_s v_a}{w}\right)(x - x_1) \qquad [15.53.16a]$$

$$r_2 = r_1 + \left(c + \frac{c_s v_a}{w}\right)D \qquad [15.53.16b]$$

with

$$D = x_2 - x_1 \qquad [15.53.17]$$

where D is the width of the spray and subscript 2 denotes the end of region II. In region III, a similar procedure yields

$$r = r_o + \frac{c_s v_a D}{w} + cx \qquad [15.53.18]$$

From Equation 15.53.10

$$C = \frac{Q}{\pi r^2 w} \qquad [15.53.19]$$

The effectiveness of dilution is given in terms of a factor FD defined as the ratio

$$\mathrm{FD} = \frac{C_{ND}}{C_{FD}} \qquad [15.53.20]$$

where C_{ND} is the concentration with natural dilution, C_{FD} is the concentration with forced dispersion by the spray and FD is the forced dispersion effectiveness factor. For region III without spray Equation 15.53.13a applies. Then utilizing Equation 15.53.19 with Equation 15.53.13a to obtain C_{ND} and with Equation 15.53.18 to obtain C_{FD} in Equation 15.53.20:

$$\mathrm{FD} = \left[1 + \frac{c_s v_a D}{w(r_o + cx)}\right]^2 \qquad [15.53.21a]$$

$$= \left(1 + \frac{c_s v_a D}{cwx}\right)^2 \quad cx \gg r_o \qquad [15.53.21b]$$

Bosanquet gives a value of $c = 0.13$. The authors also derive from Katan's formula a value of $c = 0.14$.

The two other models (models B and C) are for an upward pointing spray. Taking model B, it is assumed that in region II the elemental slice gains a vertical velocity v in the spray and that in region III the horizontal velocity is given by

$$u = (w^2 + v^2)^{1/2} \qquad [15.53.22]$$

This model contains an additional equation for dv/dx. The result for FD is

$$\mathrm{FD} = \left(\frac{r_2}{r_1 + cx}\right)^2 \left\{\left[\left(\frac{v_2^2}{w^2}+1\right)^{1/2} + \frac{c(x-x_2)}{r_2}\right]^4 - \frac{v_2^2}{w^2}\left(\frac{v_2^2}{w^2}+1\right)\right\}^{1/2} \qquad [15.53.23]$$

Model C is similar but treats a cloud from a line source. Moore and Rees describe field trials conducted to validate their models using water spray barriers and steam curtains.

The trials included a continuous release of propane gas at 2 kg/min, a spill of some 60 kg of liquid propane and a continuous release of liquid propane at 10 kg/min. The barrier was generally located 1 m downwind of the source. The first of these three sources gave a propane concentration at the barrier of 10% and the other two concentrations of 100%. The concentration was measured at 15 m downwind. Other experiments were conducted with argon and sulphur hexafluoride at much lower flows and different downwind measurement distances. For downward-pointing nozzles the FD factors were in the range 1.1–3.3 and for upward-pointing nozzles they were in the range 2.5–6.3; the upward-pointing nozzles were more effective. The results of the experiments were used to obtain empirical values of c_s/c in the model and the predictions of the model were then compared with the results of the experiments.

15.53.11 Water spray barriers for dense gases: HSE field trials

Experimental work by the HSE on the dispersion of a dense gas plume from a continuous source has been described by Moodie (1981, 1985) and McQuaid and Moodie (1983). Three configurations of water spray barrier were used: sprays pointing vertically downward, sprays pointing downward but angled forward at 45° and sprays pointing vertically upward. The downward-pointing nozzles were at a height of 3 m and were spaced at 0.33 m intervals along a 17 m pipe; the upward-pointing nozzles were at the same interval on an 18 m long pipe. Solid cone, hollow cone and flat fan sprays were investigated. The distance between the barrier and the source was varied, one distance quoted being 5 m. The gas released was carbon dioxide at release rates of 2 and 4.2 kg/s in wind speeds of 0.6–11 m/s and with water consumptions at the barrier of 0.4–7.6 l/(sm). Wind speeds were measured at, and quoted for, 1.25 m.

Figure 15.159 shows the variation of the entrained air and of the concentration of carbon dioxide across the barrier. The results are correlated in terms of the momentum of the spray. Moodie (1985) defines a momentum flow number M_N as

$$M_N = KF_N \qquad [15.53.24]$$

where F_N is the flow number (l/(min bar$^{1/2}$)), M_N is the momentum flow number (N s/(s bar)) and K is a constant. The value of the constant K is 0.236. Use is also made of the momentum flow M of the barrier (N s/(s m)).

The results are presented as a concentration ratio CR, defined as the ratio of the concentration with the water sprays off to that with the sprays on. Figure 15.160 shows the variation of CR with wind speed with specific momentum as the parameter. Values of CR are mainly in the range 1–4. The ratio increases with the momentum of the spray and decreases with wind speed.

Compared with the sprays pointing vertically downwards, those angled at 45° showed no apparent improvement in performance, but the upwards-pointing sprays did, being some 17% more effective at a wind speed of 2 m/s.

For upwards-pointing barriers only, and for the range of parameters studied, the authors give the following correlation:

$$M = u_{1.25}^2[0.65 \exp(0.5CR) - 0.23]^2 \qquad [15.53.25]$$

where M is the specific momentum flow (N s/(s m)) and $u_{1.25}$ is the wind speed at 1.25 m height (m/s).

McQuaid and Moodie (1983) have reviewed the implications of this work for the design of a water spray barrier. The barrier should be located near the source, though not so near as to promote increased evaporation of any liquid pool. A barrier near the source gives a considerable reduction in gas in the first few tens of metres downwind, but this effect decays quite rapidly. It is most effective at low wind speeds (<3–4 m/s).

Water consumption at a water pressure of 700 kPa is about 1.6 l/(s m). A standard fire tender giving 60 l/s can thus supply a 35 m length of barrier.

15.53.12 Water spray barriers for dense gases: HSE modelling studies

McQuaid and Fitzpatrick (1981, 1983) of the HSE have described the modelling of the dispersion of a dense gas plume by a water spray barrier. One question addressed was the extent to which the effect of the water spray barrier falls off with downwind distance. For a dense gas cloud the

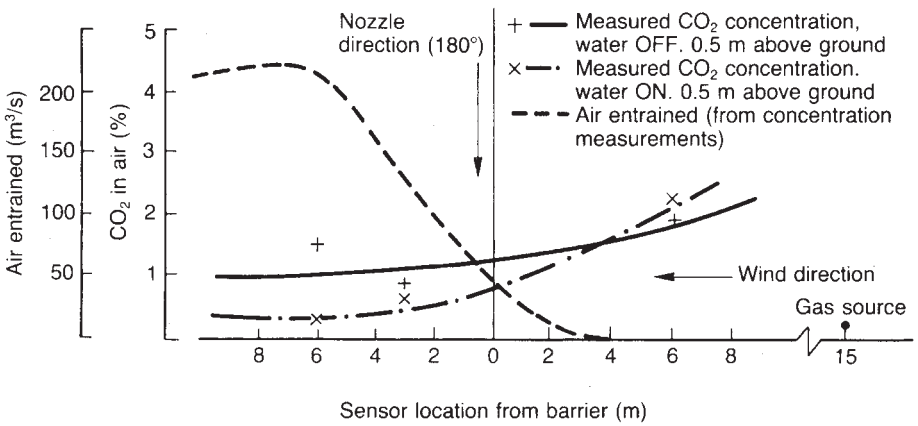


Figure 15.159 *Mitigation of gas dispersion by water spray barriers – variation of entrained air and concentration of carbon dioxide across barrier in HSE trials (Moodie, 1981) (Courtesy of the Institution of Chemical Engineers)*

effect of the density difference is to increase the area of the cloud top by lateral spreading, but to reduce vertical mixing. As far as concerns entrainment of air, the former effect tends to outweigh the latter so that the net effect is to increase entrainment and to shorten the length of the plume to a given concentration. A water spray barrier gives an addition of air and hence an immediate dilution, but it also gives a reduction of density and hence in lateral spread. Another question considered was the effect of the distance between the source and the barrier. If a barrier is close to the source it can be made smaller, but it will reduce the density of the cloud just at the point where this density is most effective in promoting entrainment.

The dispersion of a dense gas from a continuous release was modelled using CRUNCH. The experimental work showed that the entrained air mixes with the gas cloud within a distance roughly equal to the width of the spray. This effect was therefore modelled by assuming that the entrainment of the air at the barrier effects a change both in the geometry of the cloud and in its concentration. The plume modelled was a continuous release of 2 kg/s of carbon dioxide, representative of the sources used in the experiments of Moodie (1981). Some predictions given by the model are shown in Table 15.68 and Figure 15.161(a)–(d), which illustrate, respectively, the effect on plume height and concentration of the stability category, the wind speed, the downwind distance of the barrier and the specific air entrainment rate. The plume widths at the barrier vary, but it is assumed that they are not altered by passage through the barrier and that the only effect of this is to alter plume height. The results show that a water spray barrier gives a higher dilution if located close to the source, that a barrier with high specific air entrainment rates gives higher dilutions and that a barrier is particularly effective in stability category F conditions. The large air flows in this case are due to the large plume widths. The results also show that the effect of the barrier decays and that some distance downwind it disappears altogether.

As just described, the assumption in Figure 15.161(a)–(d) is that the effect of the barrier is to change the height of the plume but to leave its width unaltered. Figure 15.161(e) and (f) illustrate the results of the alternative assumption that it is the plume width which changes whilst the height remains unaltered. They show that it is

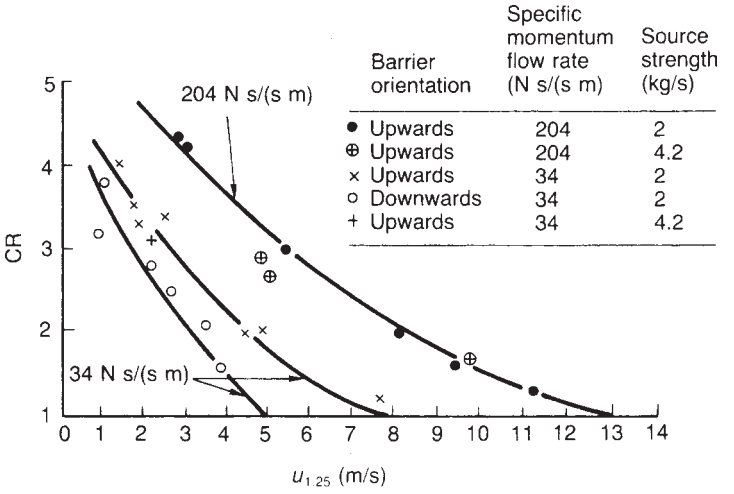


Figure 15.160 *Mitigation of gas dispersion by water spray barriers – effect of wind speed and specific momentum on concentration ratio (CR) for carbon dioxide in HSE trials (Moodie, 1985). Flat fan nozzles spaced 1 m apart each with momentum flow number $M_N = 4.9$ Ns/(s bar) (Courtesy of the Institution of Chemical Engineers)*

Table 15.68 *Predictions of CRUNCH of effect of water spray barrier on plume from continuous release of carbon dioxide (after McQuaid and Fitzpatrick, 1983). Air entrainment rate = 3.6 kg/s m (Courtesy of the Institution of Chemical Engineers)*

Barrier downwind distance (m)	*Pasquill stability category*	*Plume dimensions* (m)			*Airflow* (kg/s) *due to*	
		Width	*Height before barrier*	*Height after barrier*	*Plume entrainment*	*Spray barrier*
11	D	14.4	1.2	2.3	27	53
30	D	25.6	2.5	3.4	172	93
11	F	38.2	0.75	2.94	15	143
30	F	88.3	0.66	2.87	30	319

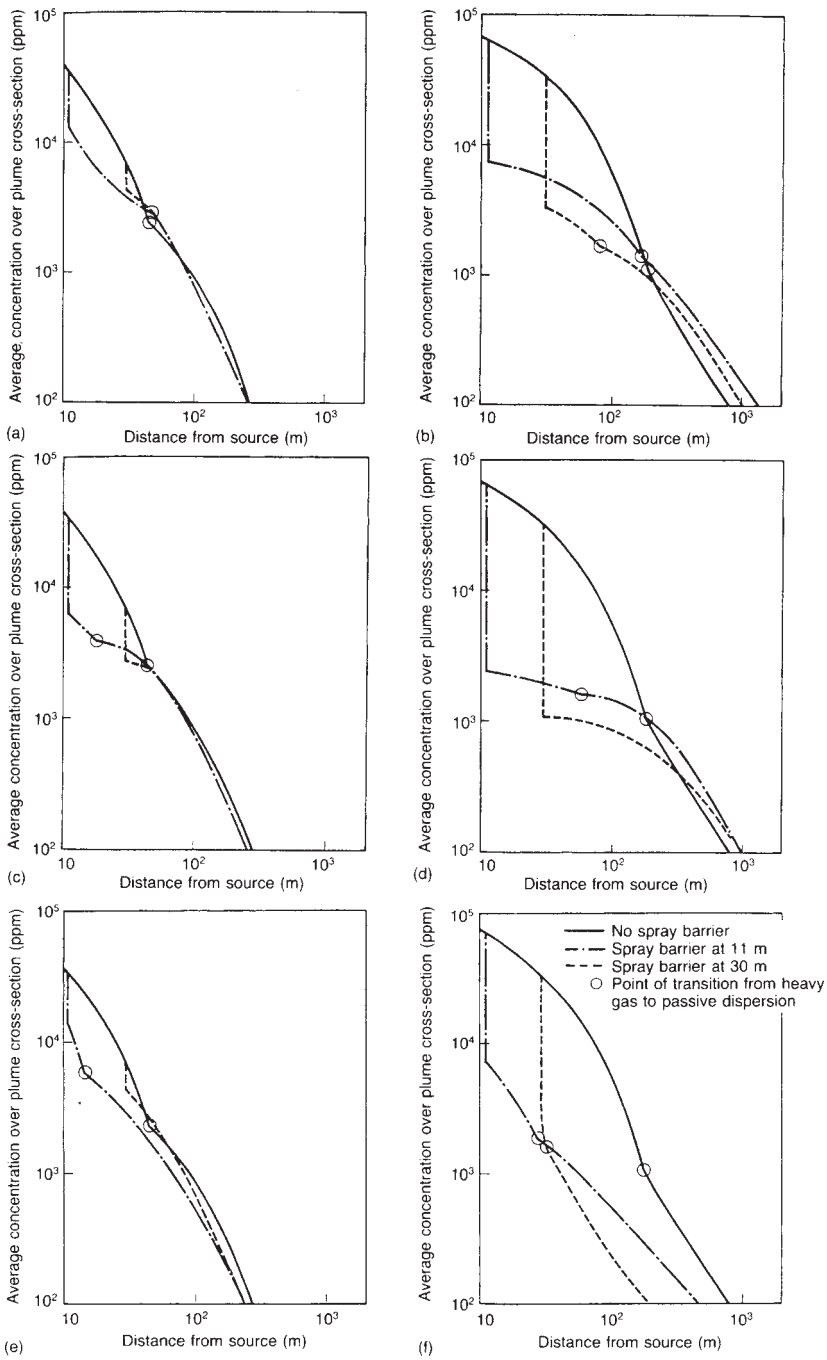


Figure 15.161 *Mitigation of gas dispersion by water spray barriers – predictions of CRUNCH for concentrations of carbon dioxide downwind of source for trials (McQuaid and Fitzpatrick, 1981): (a) air flow at barrier = 3.6 kg/s m, weather conditions D/4.3; (b) air flow at barrier = 3,6 kg/s m, weather conditions F/2; (c) air flow at barrier = 12 kg/s m, weather conditions D/4.3; (d) air flow at barrier = 12 kg/s m, weather conditions F/2; (e) air flow at barrier = 3,6 kg/ s m, weather conditions D/4.3; (f) air flow at barrier = 3.6 kg/s m, weather conditions F/2. Plume width maintained constant through barrier in (a)–(d) and plume height maintained constant in (e)–(f). The key to all six figures is given in graph (f) (Courtesy of the Institution of Chemical Engineers)*

much more effective to change the plume width. Quite how as a practical matter this may be effected is not obvious, but the general message is clear that any outward movement which can be imparted to the plume is highly beneficial.

These HSE field trials have also been modelled by Deaves (1983b, 1984) using HEAVYGAS. Figure 15.162 shows a comparison of the observed and predicted concentration profiles in one experiment. Other results from the model show that the gas, which had been hugging the ground, is lifted up and mixed by an upwind recirculation of the entrained air.

15.53.13 Water spray barriers for dense gases: Goldfish and Hawk trials

The Goldfish field trials at the NTS in 1986 on the dispersion of hydrogen fluoride included three trials involving the use of forced dispersion barriers. The main natural dispersion trials (trials 1–3) were described in Section 15.37 and the forced dispersion trials (trials 4–6) are described here. Accounts of these latter trials have been given by Blewitt, Yohn, Koopman and Brown (1987) and Blewitt, Yohn, Koopman, Brown and Hague (1987). The work constitutes an investigation of the case of dilution of a gas cloud due to absorption of the gas as well as entrainment of air into the cloud.

Trial 5 utilized an upwards-pointing water spray barrier and trial 6 a downwards-pointing one. A barrier with the water spray atomized by air was used in trial 4. The general conditions of the trials were described in Section 15.37. In trial 5 the flow of liquid hydrogen fluoride was 32.5 US gal/min with a wind speed of 3.8 m/s and stability category C/D, and trial 6 was essentially similar but with a wind speed of 5.4 m/s. The ambient temperature was 21°C in all three tests. In none of these three tests was any liquid collected on the spill pad.

The interpretation of trials 5 and 6 was complicated by shifts in wind direction during both trials, but the use of mass balances as well as concentration measurements allowed an estimate to be made of the proportion of hydrogen fluoride removed. The reduction in maximum hydrogen fluoride concentration 300 m downwind of the barrier was estimated as between 36 and 49%; the concentration at this point in trial 5 before the spray was turned on was 2028 ppm. The atomized water spray used in trial 4 was not effective in the form tested.

As already mentioned, a further set of field trials, the Hawk series, was performed at the NTS in 1988 under the auspices of ICHMAP. The gas dispersion aspect of these trials was considered in Section 15.37 and the vapour barrier work was described in Section 15.53.4. An account of the work on water spray barriers is given here.

A total of 87 trials were performed to investigate the effect of various parameters on the removal of hydrogen fluoride by a water spray barrier. The water/HF liquid volume ratio was found to be the dominant factor. Hydrogen fluoride removal efficiencies of 25 to >90% were achieved at water/HF liquid volume ratios of 6 : 1 to 40 : 1.

Of the other factors, the liquid droplet size also had some influence. Upward-pointing sprays were rather more effective than downward-pointing ones. The pressure and temperature of the hydrogen fluoride had little effect and the same applied to the atmospheric humidity and wind speed. Little difference was observed in removal efficiency of the spray as between hydrogen fluoride and alkylation unit acid.

Trials were done with the water augmented by various additives, including sodium bicarbonate, sodium hydroxide, calcium chloride and surfactant, but the only benefit was a marginal increase in removal efficiency when using sodium hydroxide.

It was found that fire monitors were virtually as effective in removing hydrogen fluoride as were fixed barriers. The best results were obtained using coarse droplets aimed directly at the release point from a short distance, as opposed to a wide angle fog or a jet directed from a distance. Tests were conducted to check on the risk of damage from jets from such monitors. The most severe of these involved a flow of 6000 US gal/min applied as a narrow jet at a distance of 7 ft from the target; damage was minimal.

15.53.14 Water spray barriers for dense gases: physical modelling

A wind tunnel investigation of the effect of water spray barriers on dense gas dispersion has been described by Blewitt *et al.* (1991). Tests were performed simulating continuous releases of hydrogen fluoride at flows in the range 11–96 kg/s and wind speeds in the range 3–10 m/s and with barrier configurations with water pressure 172 psi and flow 33,000 US gal/min with nozzle spacings of 0.46–1.83 m and orientations vertically downwards, angled, horizontal

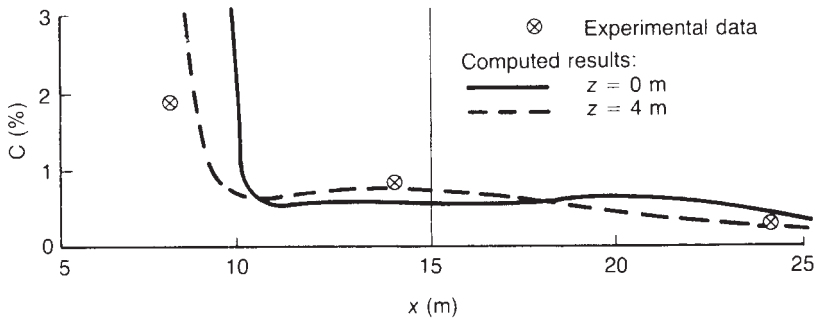


Figure 15.162 *Mitigation of gas dispersion by water spray barriers – predictions of HEAVYGAS for concentrations of carbon dioxide across barrier for HSE trials (Deaves, 1984). Nozzles pointing into wind and at an angle of 45° to horizontal. (Courtesy of Springer Verlag)*

and vertically upwards. The most effective dilution was good mixing with nozzles spaced as far apart as 1.83 m, the widest spacing studied. The authors discuss the principles of scaling water sprays in wind tunnel work.

15.53.15 Water spray barriers for dense gases: SPRAY65

The work of Meroney (1991) on the use of models of dense gas dispersion at vapour barriers was mentioned earlier. He has also reported work on models for dense gas dispersion at water spray barriers using the model SPRAY65.

This model was used to simulate the Goldfish field trials on the dispersion of a continuous release of hydrogen fluoride by a water spray barrier. Figure 15.163(a) shows for Goldfish trial 1 the effect of the water spray barrier location on the height of the cloud, and Figure 15.163(b) shows the effect on the downwind concentration. The water spray barrier is more effective in diluting the gas cloud if located near the source. The effects decay with distance and eventually disappear.

15.53.16 Water spray barriers: leak containment

The use of a water spray barrier by a works fire brigade to deal with escapes of gas has been described by Beresford (1981). The approach adopted is to hold the gas cloud inside a 'chimney' formed by a set of four mobile water spray barriers. These form a barrier to the passage of the gas, entrain air and dilute the gas, and impart to it upwards momentum so that it rises and disperses harmlessly. It is possible to see inside the chimney and for personnel to enter to effect valve isolation.

Two monitors are placed some 30 ft apart and arranged to give an inverted V some 40–50 ft above ground. At this point the water spray feathers and heavy drops fall to ground. Two fan-shaped sprays are set at right angles to the monitor curtains to give a vertical water curtain some 40 ft wide × 40 ft high. The overall effect is to surround the gas with an upward-moving wall of water so creating the chimney effect. The gas disperses some 50 ft or more above ground. The monitors are 250–1200 UK gal/min and the fan sprays 180–200 Ukgal/min devices and the water pressure used is 150 psig.

This technique is suitable for quite serious leaks but not for catastrophic failures. It may be used for flammable or toxic releases. It requires that the equipment be set up rapidly. Ignition of a flammable vapour cloud, for example, is liable to occur within 3–5 min of the start of the leak. It is necessary to consider the drainage of the water if application is likely to be prolonged.

Beresford gives examples of a number of escapes handled by this method. They include a leak of propylene from a 2 in. diameter drain line at 400 psig discharging at a rate of about 100 te/h which could not be isolated for several hours; one of ethylene gas from a flanged joint on a 14 in. diameter pipe at 500 psig which lasted some 50 minu; one of methane escaping at about 50 te/h for 30 min from a fracture on a 6 in. diameter pipe at 60 psig; and various other leaks of benzene, ethylene, ethylene oxide, naphtha and hydrocarbon solvents.

15.53.17 Water spray barriers: enclosed spaces

Work on the use of water sprays to promote entrainment into, or act as a barrier to, instantaneous and continuous leaks of gas in an enclosed space has been described by van Doom and Smith (van Doom and Smith, 1980; J.M. Smith and van Doom, 1981).

15.53.18 Steam curtains

A steam curtain is used as a permanent installation to contain and disperse leaks of flammable gas heavier than air. A steam curtain system has been described by Cairney and Cude (1971) and Simpson (1974).

The arrangement is that the plant is surrounded by a solid but lightly constructed wall. A horizontal steam pipe with a row of small holes is mounted near the top of the

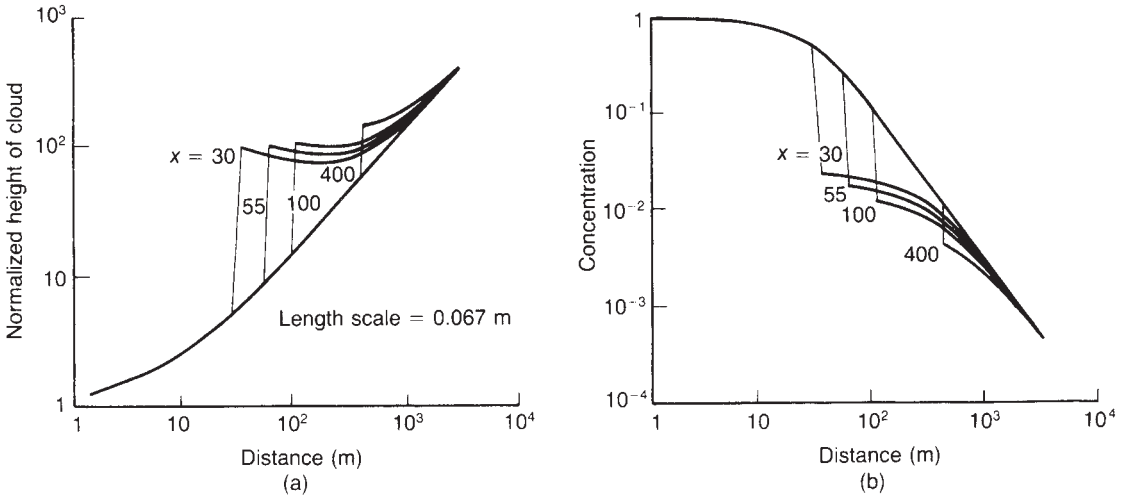


Figure 15.163 *Mitigation of gas dispersion by water spray barriers – predictions of SPRAY65 for dispersion of hydrogen fluoride across barrier for Goldfish trial 1 (Meroney, 1991): (a) effect on plume height; and (b) effect on centreline concentration, x is the downward distance of the water spray (m) (Courtesy of the American Institute of Chemical Engineers)*

wall. The pipe is divided into sections which are individually supplied with steam from distribution mains with remotely controlled, quick-acting valves. The associated monitoring of leaks is carried out by the flammable gas detector system, as described in Chapter 16. In the system described by the authors mentioned, Sieger diffusion-type detectors are used.

The wall constitutes an initial barrier to the cloud and thus serves both to provide a time delay during which the detection system can operate and to spread the gas along the length of the curtain. The relative spacing of the potential sources of escape, the detectors and the wall are chosen with these factors in mind. The wall is 1.5 m high, which is sufficient to check a heavy vapour cloud, but does not prevent dispersal of small leaks by natural air movement.

The steam pipe is designed so that the individual jets combine to form a planar jet which entrains sufficient air to dilute the vapour cloud below its lower flammability limit. The division of the pipe into sections allows steam to be supplied only to those sections near the leak. The activation of the system is controlled by the process operators.

The steam curtain was designed to dilute heavy flammable vapours. It is possible, in principle, to apply it to the dispersion of toxic gases, but in this case it is necessary to effect dilution to much lower concentrations.

The use of steam jets, particularly jets containing wet steam, can create a hazard of ignition by static electricity. Therefore particular care is taken that all pipework and other metal objects near the jets are properly earthed.

A method for the design of a steam curtain has been given by McQuaid (1980). The quantity of steam required is determined from the relation

$$S = \frac{G + 2Q_a}{200} \qquad [15.53.26]$$

where G is the mass flow of gas, Q_a is the mass flow of air and S is the mass flow of steam. The equation is based on conservation of momentum, a wind velocity of 2 m/s and a steam velocity equal to the velocity of sound in steam of 400 m/s. The illustrative example given in Table 15.67 also covers the case of a steam curtain.

P.A.C. Moore and Rees (1981), in the work already described, also conducted experiments on steam curtains and obtained empirical correlations for the FD value.

The generation of static electricity in steam curtains and in water curtains has been investigated by Napier (1974b). He concluded that a degree of static electricity hazard exists both with steam and with water curtains.

15.53.19 Water spray barriers vs steam curtains

Several authors have compared the use of water spray barriers and steam curtains. A detailed comparison of the two devices has been made by McQuaid (1980), as illustrated in Table 15.68. For the water spray barrier the water flow required is 1.6 kg/(s m) and the steam flow is 0.0385 kg/(s m). The ratio of the required mass of water to that of steam is therefore some 40 : 1.

P.A.C. Moore and Rees (1981) state that in their experimental work the FD value for steam curtains was less than 4, whereas for upwards-pointing water spray barriers it was in the range 4–16.

15.54 Vapour Cloud Mitigation: CCPS Guidelines

The CCPS has published guidance on the mitigation of vapour clouds and this is now described.

15.54.1 Guidelines for Vapor Release Mitigation

The CCPS *Guidelines for Vapor Release Mitigation* (the CCPS *Vapor Release Mitigation Guidelines*) (1988/4) cover a wide range of approaches to mitigation. Prugh (1985–, 1987b,c) has given a number of accounts of vapour release mitigation which foreshadow the Guidelines.

The main headings of the *Guidelines* may be summarized as

(1) Overview;
(2) Inherently safer design;
(3) Engineering design;
(4) Process safety management;
(5) Early vapour detection and warning;
(6) Cuntermeasures;
(7) On-site emergency response;
(8) Off-site emergency response;
(9) Selection of measures.

The interpretation of the concept of mitigation in the *Guidelines* is a broad one and covers both prevention and protection. It constitutes, but is more than, a comprehensive checklist of measures. Many of the topics listed above are dealt with in other parts of the present text. Table 15.69 gives an indication of the chapters or sections in which these topics are treated here.

The *Guidelines* give as a base case a system consisting of an unloading rail tank car, pump transfer, storage vessel, pump transfer and reactor. This system is then used throughout the text to illustrate the various points under consideration.

It starts with a discussion of the broad features of a vapour release: the forms which a release may take; the features of a flashing release; the causes of release; and the consequences of release. The different types of release are exemplified and categorized and an appendix is given which contains a checklist of release scenarios.

The principles of inherently safer design treated are: limitation of inventory; substitution of less hazardous materials; substitution of a less hazardous process; and siting. Consideration is given to both on-site and off-site exposure. There is an appendix on the properties of hazardous materials.

The contribution of engineering design is considered under the headings of plant integrity, process integrity, and emergency control. There is a fairly extensive treatment of the latter, dealing with emergency relief disposal, abort systems, isolation systems, material transfer, and spill containment. Emergency relief disposal covers active and passive scrubbers, stacks and flares, catchtanks, incinerators, and absorbers, adsorbers and condensers. There is an appendix on catchtank design and another on vendors of emergency equipment.

The treatment of management in the *Guidelines* concentrates on: operating procedures; training for emergencies; audits and inspections; equipment testing; maintenance programmes; plant and process modifications; methods of stopping a leak; and security.

Early warning is treated in terms of detectors for flammable and toxic gases, including their response time

Table 15.69 *Some principal topics treated in the CCPS Vapor Release Mitigation Guidelines and their treatment in this text*

	Chapter
1 Overview	
2 Inherently Safer Design	11
3 Engineering design	
3.1 Plant integrity	
3.1.1 Design practices	11, 12
3.1.2 Materials of construction	12
3.1.3 Inspection and testing (in construction)	12, 19
3.2 Process integrity	
3.2.1 Identification of process materials	20
3.2.2 Process operating limits	11, 20
3.2.3 Process control system	13
3.2.4 Pressure relief system	12
3.3 Emergency control	
3.3.1 Emergency relief disposal	11, 12
3.3.2 Emergency abort systems	12
3.3.3 Emergency isolation systems	12
3.3.4 Emergency material transfer	12
3.3.5 Spill control	15, 23
4 Process Safety Management	6
5 Early Vapour Detection and Warning	
5.1 Detectors and sensors	13, 16, 18
5.2 Detection by personnel	20
5.3 Alarm systems	13, 24
6 Countermeasures	
6.1 Vapour–liquid release	
6.2 Vapour release countermeasures	
6.2.1 Water sprays	15
6.2.2 Water curtains	15
6.2.3 Steam curtains	15
6.2.4 Air curtains	–
6.2.5 Deliberate ignition	17
6.2.6 Ignition source control	10, 16
6.3 Liquid release countermeasures	
6.3.1 Dilution	
6.3.2 Neutralization	
6.3.3 Covers	15, 16
6.3.4 Avoidance of spill aggravation	15, 16
7 On-site Emergency Response	24
8 Off-site Emergency Response	4, 24
9 Selection of Measures	9

and positioning, detection by personnel, and alarm systems.

Countermeasures against vapour releases are water sprays, water, steam and air curtains, deliberate ignition, and ignition source control, whilst those against liquid releases are dilution, neutralization, and liquid, foam and solid covers, together with the method of application and avoidance of actions which may aggravate vaporization.

On-site emergency response embraces: on-site communications; emergency shut-down equipment and procedures; site evacuation; havens; escape; personal protective equipment; medical treatment; and emergency plans, procedures, training and drills. There is an appendix on the capacity of a haven.

Off-site emergency response as such is not the direct responsibility of the company, and the account is confined to those aspects which are its responsibility: alerting systems; roles and lines of communication; and information to be communicated.

The approach described to the selection of mitigation measures is based on a formal system of hazard identification and assessment, by which the scenarios for loss of containment and potential Countermeasures are identified and the nature of the hazards and the effectiveness of the Countermeasures are assessed.

15.55 Fugitive Emissions

Process plants have numerous potential sources of leaks and, although the emission rate from any one source may be small, the cumulative effect of these leaks may be such as to require action. One effect of such emissions is to raise

the concentration of toxic chemicals in the plant and thus make it difficult to meet the workplace limit values set. Another effect is to increase the level of pollutants outside the plant. There is also a cost due to the loss of the chemicals.

Some of the emissions from the plant are attributable to particular sources or operations such as combustion and solvents handling, storage and terminal operations, process vents and stacks. The others are classed as fugitive emissions and consist of leaks from flanges, valves, pump and compressor seals, pressure relief valves, and so on.

An account of fugitive emissions is given in *Fugitive Emissions of Vapours from Process Equipment* by the British Occupational Hygiene Society (BOHS) (the *BOHS Guide*) (1984 TG3), *Health Hazard Control in the Chemical Process Industry* (Lipton and Lynch, 1987), *Fugitive Emissions and Controls* (Hesketh and Cross, 1983) and *Handbook of Health Hazard Control in the Chemical Process Industry* (Lipton and Lynch, 1994). There have been a number of publications by the Environmental Protection Agency (EPA) (1973, 1978a,b, 1982b, 1984c). Other accounts include those by Rosebrook (1977), Bierl and co-workers (Bierl *et al.*, 1977; Bierl, 1978, 1980; Bierl and Kremer, 1978), T.W. Hughes, Tierney and Khan (1979), M.J. Wallace (1979) and Wetherold *et al.* (1983). Selected references on fugitive emissions are given in Table 15.70.

Estimates of sources of emission in a typical refinery and in chemical plants are given in Tables 15.71 and 15.72, respectively.

15.55.1 Regulation of fugitive emissions

In the United States, early work on the control of fugitive emissions was the Los Angeles County project in 1958. Los Angeles has a particular problem of smog to which hydrocarbons are a main contributor.

A study was carried out of fugitive emissions in 11 refineries in the Los Angeles area in which measurements were made of the emission factors for various types of equipment. These constituted the original data for the compilations of emission factors produced by the EPA and were published as AP-42, which then became the basis for regulatory controls.

The EPA subsequently commissioned a number of studies, including in 1979 studies by the Radian Corporation and by Monsanto. The Radian project covered total emissions on refineries, but fugitive emissions received particular attention. The Monsanto project covered similar ground for chemical plants. The EPA has issued a number of documents giving emission factors.

The EPA has promulgated as amendments to the Clean Air Act 1970 regulations limiting fugitive emissions from refineries and chemical plants. These controls are concerned mainly with pollution rather than occupational exposure.

In the Federal Republic of Germany the Federal authorities maintain a register of emission factors (Bierl, 1980), which are used by the inspectorate of the States. In Nord Rhein-Westfalen, for example, these emission factors are incorporated in the local regulations.

In the United Kingdom, there is no specific requirement on emission factors as such. Fugitive emissions are regulated as an aspect of pollution and of the control of toxic concentrations in the workplace.

Table 15.70 *Selected references on fugitive emissions*

R.K. Palmer (1957); Anon. (1958); Steigerwald (1958); API (1959 Bull. 2513, 1962 Bull. 2516, 2518, 1967 Bull. 2522, 2533, 1980 Publ. 2517, 4322, 1981 Publ. 2514A, 1983 Publ. 2519); Schwaneke (1965, 1968, 1970); Chieffo and McLean (1968a,b); G.F. Bright (1972); Lfflis and Young (1975); Mack (1975); Radian Corporation (1975, 1979); Boland *et al.* (1976); Chicago Bridge and Iron Co. (1976b); Kremer (1976); Meteorological Research Inc. (1976); Burklin, Sugarek and Knapf (1977); Bierl *et al.* (1977); Jonker, Porter and Scott (1977a,b); Rosebrook (1977); Taback *et al.* (1977); Western Oil and Gas Association (1977); Zanker (1977); Bierl (1978, 1980); Bierl and Kremer (1978); Cavaseno (1978a); EPA (1978a,b, 1982b, 1984c, 1988a); Kittleman and Akell (1978); Monsanto Research Corporation (1978); Bochinski, Schoultz and Gideon (1979); Hesketh (1979); T.W. Hughes, Tierney and Kahn (1979); Hydroscience Inc. (1979); Morgester *et al.* (1979); M.J. Wallace (1979); Schroy (1979); Kenson and Hoffland (1980); Kunstmann (1980); Beckman and Gillmer (1981); Siegel (1981); Wetherold, Rosebrook and Tichenor (1981); Blackwood (1982); Freeburg and Aarni (1982); Gwyther (1982); Anon. (1983 LPB 49, p. 28); Cleaver (1983); Hanzevack, Anderson and Russell (1983); Harbert (1983, 1984); Hesketh and Cross (1983); Hess and Kittleman (1983); Kusnetz and Phillips (1983); Wetherold *et al.* (1983); Beckman (1984); BOHS (1984, 1987); Flanagan (1984); Goltz (1984); A. Jones (1984); R. Powell (1984); Rhoads, Cole and Norton (1984); Sivertsen (1984); Recio and Rhein (1985); Beckman and Holcomb (1986); CONCAWE (1986 2/86, 1987 87/52); Anon. (1987o); Berglund and Whipple (1987); lipton and Lynch (1987, 1994); Lipton (1989, 1990, 1992); Strachan *et al.* (1989); Early and Eidson (1990); J.C. Edwards and Bujac (1990); Kaufman *et al.* (1990); King (1990); Samdani (1990b); Surprenant (1990); Anon. (1991h,i,z); Adams (1991, 1992); Brestal *et al.* (1991); Gardner (1991); Jacob (1991b); Myerson (1991); Schaich (1991); Shiel, Siegel and Jones (1991); Stucker (1991); Bruere and Coenen (1992); CIA (1992 RC58); Crowley and Hart (1992); Gardner and Spock (1992); IBC (1992/96, 1993/108); Key (1992); Crowley (1993); Fruci (1993); Moretti and Mukhopadhy (1993); P.A. Ross (1993); Ruddy and Carroll (1993); Spock (1993); J.B. Wright (1993)

15.55.2 Measurement of fugitive emissions

The existence of a leak may be detected using the soap bubble method. However, this method is not generally regarded as suitable for quantitative measurement. The concentration at the point of leak may be used as a measure of the leak rate, but the values obtained are highly dependent on factors such as the size of leak, the wind conditions, the plant geometry, etc.

In the Radian study, the maximum concentration obtained around an emission source was termed the 'screening value.' The EPA has attempted to relate screening values to mass emission rates, but the correlation shows appreciable scatter.

The two principal methods of measuring emission rates both involve enclosing the source in a container. In the bag method the bag is placed around the source, air is passed through the bag and the outlet steady-state concentration of the chemical in the air stream is measured. In the box method there is no air flow and the measurement taken is

Table 15.71 *Estimated sources of emission in a refinery (Freeberg and Aarni, 1982) (Courtesy of the American Institute of Chemical Engineers)*

Source	*Proportion of total emissions* (%)
Combustion	2
Solvents, organics	2
Tanks	9
Bulk loading	2
Fugitive emissions	85
Total	100

Table 15.72 *Estimated sources of emission in chemical plants (British Occupational Hygiene Society, 1984 TG3)*

Source	*Proportion of total emissions* (%)
Waste disposal	2–5
Storage tanks, transport vents	8–10
Process vents, stacks	65–70
Fugitive emissions	15–20
Total	100

Table 15.73 *Fugitive emission sources in a hypothetical refinery (Environmental Protection Agency)*

Source	*Emission rate*	
	(lb/h)	(%)
Pump seals	60	48.7
Valves	305	4.0
Flanges	25	9.6
Compressor seals	29	4.6
Relief valves	21	7.7
Drains	48	3.4
API separators	138	22.0
Total	626	100

the rate of rise of concentration of the chemical in the air in the box.

15.55.3 Monitoring of fugitive emissions

The arrangements for monitoring emissions depend on the purpose of the monitoring. If the aim is to reduce pollution outside the works, periodic spot checks on emission sources may be sufficient. The control of toxic concentrations in the atmosphere of the workplace normally requires additional measures. In the latter case it is necessary to implement continuous sampling of the atmosphere. The data obtained by such sampling must then be interpreted statistically. A discussion of sampling and interpretation of sampled data is given in the BOHS *Guide*.

15.55.4 Emission factors for equipment

The contribution of the various sources of fugitive emissions to the total plant emission has been the subject of several studies. Table 15.73 shows the fugitive emission sources assigned in a hypothetical refinery in an EPA study. Table 15.74 gives the actual sources in the Monsanto study (T.W. Hughes, Tierney and Khan, 1979).

Information on emission factors is available from several sources. Mention has already been made of the Los Angeles County study and of the studies commissioned by the EPA. The California Resources Board has carried out a project involving six refineries to check the 1958 data. Rockwell International has carried out a study for the American Petroleum Institute on oil production operations.

Table 15.75 lists emission factors from the Los Angeles County project as given in the 1973 edition of the EPA publication AP-42. Tables 15.76 and 15.77 show emission factors obtained in the work by Radian (Wetherold, Rosebrook and Tichenor, 1981) and by Monsanto (T.W. Hughes, Tierney and Khan, 1979).

Work by Bierl (1978, 1980) at BASF is shown in Table 15.78. The literature values referred to in this table are those from earlier work by Schwaneke (1965, 1968, 1975). Bierl expresses his own measured values as percentages of these published ones.

A composite set of emission factors given by Schroy (1979), based mainly on those of AP42 and Bierl, are shown in Table 15.79.

The spread of emission rates is illustrated by the data for valves in light liquid service given by A.L. Jones (1984) and shown in Table 15.80.

Table 15.74 *Fugitive emission sources in four chemical plants (after T.W. Hughes, Tierney and Khan, 1979) (Courtesy of the American Institute of Chemical Engineers)*

Source	*Plant type*							
	Monochloro-benzene		*Butadiene*		*Dimethyl terephthalate*		*Ethylene oxide/glycol*	
	(ton/year)	(%)	(ton/year)	(%)	(ton/year)	(%)	(ton/year)	(%)
Pumps	1	3.1	96	8.6	8		2	
Valves	0.2	0.6	1000	90.0	?		?	
Flanges	29	91.0	0	0	?		?	
Other	1.7	5.3	16	1.4	7.9		8.6	
Total	31.9	100.0	1112	100.0				

The effect of maintenance on emission rates is shown in the data in Table 15.81 given by Kunstmann. In this a set of valves was selected at random and the leak rates were measured, the average value being 2.37 g/h. Some 80% of the total emission was attributable to the valves with leak rates greater than 2 g/h. The leak rates of these valves were reduced by maintenance and their leak rates were remeasured with the result that the average leak rate for all the valves was reduced to 0.44 g/h.

Table 15.75 *Emission factors in Los Angeles County project (AP-42) (after Environmental Protection Agency, 1973)*

Source	*Items inspected*	*Items tested*	*Emission rate* (g/h)
Pumps	473	75	79
Valves	9521	100	3.8
Flanges	326	129	0
Compressors	326	90	161
Relief valves	165	165	55

15.55.5 Emission losses from storage tanks

Losses from storage tanks have been the subject of a series of API bulletins, including:

API Bull. 2513: 1959 Evaporation Loss in the Petroleum Industry – Causes and Control (reaffirmed 1973)
API Bull. 2516: 1962 Evaporation Loss from Low Pressure Tanks
API Pub. 2517: 1980 Evaporation Loss from External Floating Roof Tanks
API Bull. 2518: 1962 Evaporation Loss from Fixed Roof Tanks
API Pub. 2519: 1983 Evaporation Loss from Internal Floating-roof Tanks

Table 15.76 *Emission factors in Radian project (Wetherold, Rosebrook and Tichenor, 1981)*

Source	*Emission rate* (g/h)		
	Mean	*95% confidence limits*	
		Lower	*Upper*
Pump seals			
Light liquid service	113	73	170
Heavy liquid service	20.9	8.6	50
Valves			
Gas/vapour service	26.8	14	49
Light liquid service	10.9	7.7	16
Heavy liquid service	0.23	0.1	0.68
Hydrogen service	8.16	3.2	20
Flanges	0.25	0.1	1.1
Compressor seals			
Hydrocarbon service	635	300	1300
Hydrogen service	49.9	20	100
Pressure relief valves	86.2	32	220
Drains	31.8	10	91
Open-ended lines	2.3	0.73	7.3

Table 15.77 *Emission factors in Monsanto project (after T.W. Hughes, Tierney and Khan, 1979) (Courtesy of the American Institute of Chemical Engineers)*

Source	*Emission rate by plant type* (g/h)[a]			
	Monochloro benzene	*Butadiene*	*Dimethyl terephthalate*	*Ethylene oxide/glycol*
Pump seals	7.7 (23)	63 (160)	3.3 (20)	13 (82)
Valves	0.05 (1.5)	17 (120)	1.5 (32)	0.07 (1.6)
Flanges	2.2 (82)	0	3.4 (110)	0.03 (1.0)
Compressor seals	–	54 (59)	–	5.9 (11)
Relief valves	–	5 (14)	0	0
Agitators	200 (200)	–	145 (218)	–
Drains	–	–	–	40 (68)
Sample valves	–	–	40 (91)	

[a] The figures given are average emission rates, those without parentheses being for all potential sources and those within parentheses being for significant sources.

Table 15.78 *Emission factors in BASF project (after Bierl, 1980)*

	Items tested	*Literature value* (g/h)	*Emission rates*	
			Measured value	
			(% of literature value)	(g/h)
Pumps (mechanical seals)	67	60	9	5.4
Valves				
General	1800	2.8	20	0.56
High pressure valves	400	2.8	18	0.50
Ball valves and stop-cocks	125	2.8	0.5	0.014
Flanges				
Gas service	5000	0.2 g/h m	2.5	0.005
Liquid service	600	2.0 g/h m	2.0	0.04
High pressure flanges	950	0.2 g/h m	4.8	0.01
Reciprocating compressors	13	104	12.5	13
Relief valves	50	55	1.1	0.61
Agitators (mechanical seals)	8	60	0.2	0.12

Table 15.79 *Some composite emission factors (after Schroy, 1979)*

Source	*Emission rate*[a] (g/h)
Flanges	
Gas service (10–20 bar)	0.02 g/h m
Liquid service (10–20 bar)	0.2 g/h m
High pressure (40–80 bar)	0.01 g/h m
Valves	
Gate and control valves	
10–20 bar	6
40–80 bar	0.1
Ball valves	0.015
Pressure relief valves	2.8
Pressure relief valve + bursting disc	0
Pumps and centrifugal compressors	
Packed seals	80
Single mechanical seals	
Process fluid flush	6
Water flush	0.02
Double mechanical seals	0
Reciprocating compressors	
Rod single packing	161
Rod double packing	13
Agitators	—[b]
Tanks:	
Floating roof	—[c]

[a] Emission rate is expressed as g/h per metre of outer flange circumference.

[b] Use packed or double mechanical seal data for pumps with the relation:

Loss for agitator = Loss for pump ($\times u/1.9$ where u is the face velocity (m/s).

[c] Loss 60% of value estimated from method given in API Bull. 2517.

Table 15.80 *Distribution of emission rates for valves in light liquid service (A.L. Jones, 1984) (Courtesy of the Institution of Chemical Engineers)*

No. of valves	*Emission rate* (g/h)
573	0
4	0.0076
10	0.021
14	0.056
28	0.152
40	0.414
58	1.125
50	3.06
52	8.32
46	22.6
20	61.4
12	167
4	454
2	1234

API Bull. 2521: 1966 Use of Pressure-Vacuum Vent Valves for Atmospheric Pressure Tanks to Reduce Evaporation Loss

API Bull. 2522: 1967 Comparative Test Methods for Evaluating Conservation Mechanisms for Evaporation Loss

API Bull. 2523: 1969 Petrochemical Evaporation Loss from Storage Tanks

These publications give equations for the estimation of evaporation losses.

Extensive work has been done on emissions from floating roof tanks. The background to this work is discussed by Zabaga (1980), by Hanzevack, Anderson and Russell (1983) and by Laverman (1984).

Table 15.81 *Effect of maintenance of emission rates of valves (after Kunstmann, 1980)(Courtesy of Elsevier Sequoia SA)*

A Valves before maintenance		
Valves tested		Emission rate (g/h)
No.	(%)	
31	79	0–2
6	16	2–10
2	5	10–50
0	0	>50
B Valves after maintenance		
36	92	0–2
3	8	2–10
0	0	10–50

15.55.6 Control of fugitive emissions

The information on emission factors given above indicates that for a given type of emission source there is a wide variability in emission rates but also that for almost all types the technology exists to reduce the emission rate to a low level. A detailed review of the methods of obtaining leak tight plant is given in the BOHS Guide. A further account is given by Bierl *et al.* (1977). The BOHS *Guide* describes the following types of seal:

(1) static seals
  (a) gasketed joints (full faced flanges, narrow faced flanges),
  (b) automatic face seals;
(2) dynamic seals
  (a) contact seals,
  (b) clearance seals (bushing seals, labyrinth seals);
(3) miscellaneous seals
  (a) O-rings,
  (b) flexible lip seals.

The *Guide* also gives a detailed account of packed glands (stuffing boxes) and mechanical seals.

For flanges, the *Guide* describes the elements of good practice necessary to reduce leakage. Its principal proposal for cases where high leak-tightness is required is the elimination of flanges by the use of all-welded pipe.

For valves, leakage of the rising stem may be reduced by the use of 100% graphite packing. For high leak-tightness use may be made of bellows-sealed or diaphragm-sealed valves. Bellows-sealed valves were developed for use in the nuclear industry. The *Guide* gives the following emission rates for rising stem valves:

	Emission rate (μg/s)
Regular packing	
<20 bar	100
>20 bar	2
100% graphite packing	
<20 bar	12
>20 bar	0.2

For pumps, the *Guide* gives the following emission rate index:

Seal type	*Shaft emission rate index*
Regular packing	100
Regular packing with lantern ring	10
100% Graphite packing	10
Single mechanical seal	1.2
Double mechanical seal	0.004

For bellows seal pumps, diaphragm pumps and canned pumps the index is zero. Details of the seal arrangements are given in the *Guide*. A further discussion of packed glands is given by Hoyle (1978).

For agitators, the *Guide* states that the pump data may also be used as a guide to the relative effectiveness of the different seal types. A discussion of agitator seals is given by Ramsey and Zoller (1976).

The sealing of centrifugal or reciprocating compressors is appreciably more difficult than the sealing of pumps. Labyrinth seals are commonly used on both types, but leakage rates are high, being typically 1–2% of the flow through the compressor. Carbon seals give lower leak rates, but for a more positive seal the *Guide* suggests oil film seals or mechanical seals with oil flush. A further discussion of centrifugal compressor seals is given by W.E. Nelson (1977).

15.55.7 Economics of emission control

Several studies have been published on the economics of emission losses and of control measures, including those by Kittleman and Akell (1978), Wetherold *et al.* (1983) and Rhoads, Cole and Norton (1984). The cost of control measures is also considered by Kunstmann (1980). These studies tend to be concerned with the costs of reducing leaks and with minimization of these costs rather than with savings obtained by leak elimination. The general conclusion is that effort should be concentrated on individual sources with a high leak rate, the outliers, and that thereafter the law of diminishing returns sets in strongly.

15.56 Leaks and Spillages

Leaks and spillages are main causes of fire and explosion in chemical plants. They may give rise to a local fire or explosion, a wider flash fire or a large vapour cloud explosion. Some of the situations which can give rise to leaks and spillages have been described by Kletz (1975b). They include:

(1) leaks from pump glands and seals;
(2) leaks from joints, valves and fittings;
(3) spillages from drain valves;
(4) spillages occurring during maintenance work;
(5) spillages from road and rail tankers.

Leaks have occurred not infrequently on pumps handling cold liquid ethylene. In some cases vapour clouds have been formed, while in others the leak has ignited, apparently due to static electricity.

On pumps handling C_3 and C_4 hydrocarbons at ambient temperature and moderate pressure there is little trouble

with seal leakages, but failures have occurred on high pressure injectors.

Joints, valves and fittings are common sources of leakage due to features such as loose bolts, ruptured gaskets, failed instrument connections.

Another fertile source of spillage is drain valves. Typically a drain valve blocks due to ice or hydrate formation, the blockage is cleared in some way, but it then proves impossible to shut the valve off.

The disaster at the Rhone Alps refinery at Feyzin in 1966 (Case History A38) began with blockage in a drain line from a propane storage sphere which was almost certainly caused by ice or hydrate. The drain line was a vertical pipe below the sphere and had two valves on it. The standing instruction was to drain by opening the top valve and controlling the flow with the lower one so that, if necessary, the former could be used to shut the flow off. But the operator in fact turned the bottom valve wide open and controlled draining from the top one. When this latter valve blocked, he opened it further, the blockage gave way and a jet of propane came out full bore through the 2 in. line, struck the ground, rebounded into the operator's face and knocked the handle off the valve. Attempts to replace the handle on the top valve or to shut the bottom one failed. There was a massive escape of propane, the vessel was engulfed by fire and 18 people were killed.

Maintenance work sometimes gives rise to spillages. This is usually the result of failure to ensure isolation of equipment. Isolation procedures are described in Chapter 21. Failures of connecting hoses on road and rail tankers at filling terminals are not unusual. These are discussed in Chapter 22.

The volume of vapour generated by a liquid spillage can be very large. Moreover, only a small percentage of vapour is needed to give a flammable mixture. Thus one volume of liquid can become 10,000 or more volumes of a flammable vapour–air mixture. Leaks of liquefied flammable gas (LFG) of different sizes are discussed in the ICI LFG Code (ICI/RoSPA 1970 IS/74).

Small leaks such as those from pump and valve glands or pipe joints are quite probable, but usually involve little risk, provided that the leak is discovered quickly, the gas is dispersed rapidly and there is no nearby source of ignition. Dispersion is assisted by ventilation and may be promoted by steam from a steam lance.

Medium leaks are defined as those large enough to go beyond the plant boundaries. The leak should be isolated if possible. Isolation by the use of hand valves near the leak may be hazardous and the use of remotely operated isolation valves is preferable if the latter are available. It may be noted that excess flow valves do not operate at lower leakage rates.

Attempts should also be made to disperse the leakage and to prevent it finding a source of ignition. Use may be made of steam curtains, if installed, or of mobile water curtains. A leak of LFG which is water soluble can be dealt with by diluting it with large amounts of water.

Major leaks are defined as those of 1 ton/h or more. The methods just described are appropriate, but a major leak usually gives rise to a large pool of liquid. There is typically a rapid flash-off of vapour followed by slower vaporization from the pool. It is necessary, therefore, to decide how the liquid is to be handled. One method is to assist vaporization and dispersion, another is to suppress vaporization and to dispose of the liquid. Vaporization may be suppressed by laying foam on the surface. In some cases the formation of an ice layer effects complete suppression.

Leaks are also discussed by J.R. Hughes (1970) who states that a leak of more than 1 UK gal/h (4.5 l/h) would be regarded as unusual on a modern pump seal and would not be allowed to continue, and that experiments on this size of leakage with motor gasoline have shown that in the open air the concentration of vapour produced is so small that a flammable concentration exists only within a few inches of the leakage point.

Hughes also describes experiments involving the spillage of two pints (1 l) of gasoline. In a light wind of 2 mile/h (3.2 km/h) the vapour cloud floated downwind and gave a flammable concentration near the ground at 20 ft (6 m) downwind, but at a few inches above ground the concentration was undetectable. For spillage near a low wall the distance at which the cloud gave a flammable concentration increased to 30 ft (9.1 m).

Leaks in confined spaces, such as an enclosed and poorly ventilated compressor or pump house, are another matter and can easily build up to flammable concentrations, giving rise in due course to a fire or explosion.

15.57 Notation

Bo	Bowen ratio
Fr	Froude number
Gr	Grashof number
Ma	Mach number
Nu	Nusselt number
Pe	Peclet number
Pr	Prandtl number
Re	Reynolds number
Ri	Richardson number
Ro	Rossby number
Sc	Schmidt number
Sh	Sherwood number
St	Stanton number
We	Weber number
c_p	specific heat
g	acceleration due to gravity
g'	reduced gravity
M	molecular weight
P	absolute pressure
R	universal gas constant
t	time
T	absolute temperature
γ	ratio of gas specific heats
Δ	reduced density
μ	viscosity
ρ	density
$\Delta\rho$	density difference

Superscript

·	time derivative

Subscripts

max	maximum
r or ref	reference

Note:

(a) Some of these variables have different local definitions, for example; P (probability), R (radius of cloud), T (time interval), γ (edge entrainment coefficient).

(b) There are different definitions of the reduced gravity g'.

Section 15.1

a	cross-sectional area of pipe
a_c	cross-sectional area of vena contractor
a_o	cross-sectional area of orifice
A	cross-sectional area of pipe or orifice; constant defined by Equation 15.1.62
B	constant defined by Equation 15.1.63
c	velocity of sound
C	effective coefficient of discharge
C_c	coefficient of contraction
C_{cv}	coefficient of contraction at vena contracta (external mouthpiece)
C_D	coefficient of discharge
C_v	coefficient of velocity
d	diameter of pipe or orifice
e	pipe roughness
f	friction factor
f_D	Darcy friction factor
f_F	Fanning friction factor
F	total frictional loss
F_c	frictional loss due to sudden contraction
F_f	frictional loss due to pipe
F_{ft}	frictional loss due to fittings
G	mass velocity
h	head
h_c	head loss due to contraction
h_{ft}	head loss due to fittings
H	enthalpy
k	expansion index
k_h	number of velocity heads
K	total number of velocity heads lost
K_e	number of velocity heads lost at entrance
K_f	number of velocity heads lost due to friction
K_{ft}	number of velocity heads lost due to fittings
l	distance along pipe, length of pipe
q	heat absorbed from surroundings
Q	total volumetric flow
R	shear stress at pipe wall (Equation 15.1.15)
R_o	shear stress at pipe wall (Equation 15.1.11)
S	entropy; perimeter of pipe (Equation 15.1.11)
u	velocity
u_c	velocity at vena contractor
v	specific volume
W	total mass flow
W_s	work done on surroundings, shaft work
x	mass fraction of vapour in wet vapour, or quality
z	vertical distance, height
Z	compressibility factor
γ	ratio of gas specific heats
η	pressure ratio
ϕ	friction factor

Subscripts

a	accelerational
c	critical
f	frictional
g	gravitational
l	liquid
v	vapour
1	intial, upstream, stagnation
2	final, downstream, outlet

Subsection 15.1.9

d	diameter of pipe (m)
G	mass velocity of gas (kg/m^2/s)
G^*	critical mass velocity of gas through an adiabatic nozzle (kg/m^2 s)
k	expansion index
L	length of pipe (m)
N	pipe resistance factor
p	absolute pressure (N/m^2)

Subsection 15.1.10

A	cross-section area of vessel at height h (m^2)
A_o	cross-sectional area of orifice (m^2)
C	constant defined by Equation 15.2.95
C_D	coefficient of discharge
D	diameter of cylinder (m)
g	acceleration due to gravity (m/s^2)
h	height of liquid above bottom of vessel (m)
h_o	height of orifice, or hole, above bottom of vessel (m)
h_p	equivalent liquid height (m)
H	height of vessel (m)
L	length of horizontal cylindrical vessel (m)
ΔP	pressure difference between liquid surface and atmosphere, imposed pressure (Pa)
Q	outflow through orifice (m^3/s)
t	time (s)
V	volume of vessel (m^3)
x	dimensional hole height
θ	half-angle of cone of vertical conical vessel (°)
ρ	density of liquid (kg/m)
τ	dimensionless drainage time

Section 15.2

A	cross-sectional area of pipe
C	parameter defined by Equation 15.2.47
C_D	coefficient of discharge
d	diameter of pipe
f	friction factor
F	friction loss
G	mass velocity
h	specific enthalpy
k	slip ratio
l	distance along pipe, length of pipe
n	polytropic index
dP_a/dl	pressure drop due to acceleration
dP_f/dl	pressure drop due to friction
$(dP_f/dl)_g$	pressure drop which would occur if gas phase were flowing alone in pipe

$(dP_f/dl)_{go}$	pressure drop which would occur if whole fluid were flowing alone in pipe
$(dP_f/dl)_l$	pressure drop which would occur if gas fluid were flowing as liquid in pipe
$(dP_f/dl)_{lo}$	pressure drop which would occur if whole fluid were flowing as liquid in pipe
dP_g/dl	pressure drop due to gravitational forces
Q	volumetric flow
R_o	shear stress at wall
S	perimeter of pipe
u	velocity
v	specific volume
W	mass flow
x	mass fraction of vapour, or quality
X	parameter defined by Equation 15.2.41
z	vertical distance, height
α	fraction of volume occupied by vapour, void fraction, or voidage; parameter defined by Equation 15.2.3
β	vapour phase volumetric flow fraction; parameter defined by Equation 15.2.4
Γ	parameter defined by Equation 15.2.42
η	critical pressure ratio
λ	parameter defined by Equation 15.2.1
σ	surface tension
ϕ	parameter used in Equations 15.2.40–15.2.43
ψ	parameter defined by Equation 15.2.2

Subscripts

a	air
c	critical
E	equilibrium
g	gas
go	gas only
h	homogeneous
l	liquid
lo	liquid only
L	all liquid condition
m	two-phase mixture
o	stagnation
s	two-phase
w	water

Section 15.3

A_a	cross-sectional area of aperture
A_p	cross-sectional area of pipe
c_l	specific heat of liquid
C	specific heat of liquid
C'_a	modified cavitation number
C_D	coefficient of discharge
C_{DM}	modified coefficient of discharge
d	diameter of pipe
f	friction factor
f^*	friction factor (two-phase flow)
f_m	average friction factor
F	flow correction factor
F'	friction loss
G	mass velocity
k	slip ratio
K	coefficient of discharge
l	distance along pipe, length of pipe
l_e	equilibrium, or relaxation, length
n	polytropic index
N	non-equilibrium parameter
P	absolute pressure
P^*	absolute effective downstream pressure
ΔP	pressure drop
P_a	absolute atmospheric pressure
P_c	absolute back pressure in choked flow
P_o	absolute stagnation pressure
P_v	absolute vapour pressure
R_g	fraction of cross-sectional area occupied by vapour
s	specific entropy
U	average velocity
v	specific volume
x	mass fraction of vapour, or quality
α	void fraction
β	parameter defined by Equation 15.3.12
ζ	parameter defined by Equation 15.3.34
η	parameter defined by Equation 15.3.16
ρ_l	density of liquid
ρ_m	average density

Subscripts

b	downstream
c	critical
E	equilibrium
ERM	equilibrium rate model
f	liquid
fg	transition from liquid to vapour
g	vapour
h	constant enthalpy
l	liquid
m	two-phase mixture
n	two-phase annular
t	throat

Section 15.4

C_f	specific heat of liquid
D	diameter of pipe
f	friction factor
Fi	flow inclination number
h	specific enthalpy
G	mass velocity
G^*	dimensionless mass velocity
G_o	mass velocity through nozzle
L	length of pipe
N	pipe resistance factor
s	specific entropy
v	specific volume
x	mass fraction of vapour, or quality
α	void fraction
η	pressure ratio
θ	angle between pipe axis and vertical

Subscripts

c	critical
f	liquid
fg	transition from liquid to vapour
lm	limiting
o	stagnation
r	reduced
s	saturation

Section 15.5

a	parameter defined by Equation 15.15.53
A	area of vent (m^2)
A_x	cross-sectional area of vessel (m^2)
C_0	distribution parameter
D	diameter of vessel (m)
F	geometric factor
h_{fg}	latent heat of vaporization (kJ/kg)
H	height of liquid (m)
H^*	dimensionless liquid height
H_{BL}	height of interface below which there is no vapour carryunder (m)
H_o	height of liquid without swell (m)
H_x	height of vessel (m)
j	total volume flux, or superficial velocity (m/s)
j_g	superficial velocity of gas (m/s)
j_{gl}	superficial velocity of gas phase relative to liquid phase, drift flux (m/s)
j_l	superficial velocity of liquid (m/s)
j_{lg}	superficial velocity of liquid phase relative to gas phase, drift flux (m/s)
$j_{g\infty}$	vapour superficial velocity (m/s)
J_o	dimensionless heat flux constant
L	length of vessel (m)
m	index
n	index
q	heat input per unit mass (kW/kg)
Q_{ex}	external heat input flux (kW/m^2)
S	volumetric source strength (m^3/s)
U	velocity (m/s)
U_c	downward liquid recirculating velocity (m/s)
U_g	area average velocity of gas (m/s)
U_l	area average velocity of liquid (m/s)
U_s	upward liquid superficial velocity (m/s)
U_∞	bubble rise velocity (m/s)
V_l	volume of liquid (m^3)
x_e	mass fraction of vapour at vent
z	vertical distance from bottom of vessel (m)
α	void fraction
α_o	initial void fraction, or freeboard
δ	thickness of boundary layer (m)
ϵ	geometric factor
ρ	parameter density (kg/m^3)
σ	surface tension (N/m)
ψ	dimensionless source strength, dimensionless velocity
Ω	ratio of vessel area to vent area

Superscript

$\bar{}$	average

Subscripts

c	continuous phase
g	gas
l	liquid
∞	rise

Section 15.6

See Section 15.4 plus

A	cross-sectional area of valve (m^2)
A_{in}	cross-sectional area of inlet pipe (m^2)
A_2	cross-sectional area of outlet pipe (m^2)
C_f	specific heat of liquid (J/kg K)
D_{in}	diameter of inlet pipe (m)
D_2	diameter of outlet pipe (m)
f	Fanning friction factor
g	acceleration due to gravity (m/s^2)
G	mass velocity ($kg/m^2 s$)
h	specific enthalpy (J/kg)
H	change in elevation (m)
K	valve discharge coefficient
L_2	length of outlet pipe (m)
L_{in}	length of inlet pipe (m)
ΔP_{in}	total pressure difference across inlet pipe (Pa)
P	absolute pressure
P_b	absolute back pressure at orifice (Pa)
P_c	absolute critical pressure (Pa)
P_o	absolute stagnation pressure in vessel (Pa)
P_s	absolute saturation pressure of liquid (Pa)
T	absolute temperature (K)
v	specific volume (m^3/kg)
$\bar{v}_{in}$	average specific volume in inlet pipe (m^3/kg)
W	mass flow (kg/s)
x	mass fraction of vapour, or quality
α	void fraction
η	pressure ratio defined by Equation 15.6.5
ρ	density (kg/m^3)
$\bar{w}$	parameter

Subscripts

act	actual
c	critical
f	liquid
fg	liquid–vapour transition
g	vapour
s	stagnation
req	required
s	saturation
1	upstream end of outlet line
2	downstream end of outlet line

Section 15.7

a	velocity of sound in gas at choke (m/s)
A	cross-sectional area of choke (m^2)
C_D	coefficient of discharge
H	enthalpy (J/kg)
P	absolute pressure (Pa)
P_{ms}	absolute pressure at which metastability is no longer supported (Pa)
P_s	absolute saturated vapour pressure of liquid (Pa)
P_x	absolute orifice pressure (Pa)
R	universal gas constant (kJ/mol K)
S	entropy (kJ/kg K)
T	absolute temperature (K)
T	absolute temperature upstream of orifice (K) (Equation (15.7.7)
T_c	absolute critical temperature of liquid (K)
V	volume of vessel (m^3)

W	mass flow from vessel (kg/s)
Π	depressurization rate (N/m^2 s)
ρ	density of gas (kg/m^3) (Equations 15.7.1–15.7.6); density (Equations 15.7.7 and 15.7.8)
σ	surface tension of liquid (N/m)

Subscripts

c	choke
d	downstream
g	gas
I	vessel
l	liquid
o	initial
s	isentropic
u	upstream

Section 15.8

Subsection 15.8.1

h	height of liquid in vessel
h_b	height reached by liquid on depressurization
h_0	initial height of liquid
h_v	height of vessel
ΔH_v	latent heat of vaporization
K	ratio of vent area to vessel cross-sectional area
m	mass
ΔT	superheat
δ	diameter of vapour nucleus
ρ	density
σ	surface tension

Subscripts

l	liquid
nb	nucleate boiling
o	initial
onb	onset of nuclear boiling
r	retained
sat	saturation value
v	vapour

Subsection 15.8.2

A_1	area of aperture
A_2	area of cloud perpendicular to direction of expansion at end of second stage (Hardee and Lee model)
c	constant
h	height of cloud; specific enthalpy (Equation 15.8.4)
r	radius, radial distance
s	specific entropy
u	velocity
V	volume of cloud
W	initial mass of fluid
ρ	density
ψ	momentum of cloud

Subscripts

a	air
d	dump
f	liquid
v	vapour
1, 2	initial and final states

Subsections 15.8.3 and 15.8.4

a	radius of initial cloud formed on completion of bursting process
c	concentration
l	mixing length
r	radial distance
u'	fluctuating velocity
V_g	effective volume of vapour
w	propagation velocity of cloud boundary
X_c	parameter characterizing mass fraction of gas in core
ϵ	eddy diffusion coefficient
τ	dimensionless time

Subscripts

c	core concentration
g	core radius
ign	within flammable limits
o	initial cloud

Subsection 15.8.5

c	concentration at transition
M	initial mass of liquid
N	transition criterion
r	distance
t_g	time to transition
t_v	volume of vapour released
w	radial velocity
α	momentum per unit mass
Δ	buoyancy term
ρ	density

Subscripts

a	air
v	vapour

Section 15.9

A	cross-sectional area of pipeline
d	diameter of pipeline
f	friction factor
f_D	Darcy friction factor
l	length of pipeline
m	mass flow from pipeline
N	correction factor
u	velocity
v	specific volume
W	mass hold-up in pipeline
Y	void fraction
z	distance along pipeline from rupture point
τ_1, τ_2	time constants
ϕ_g	parameter defined by Equation 15.9.14
ψ	parameter defined by Equation 15.9.7a

Subscripts

e	exit
f	liquid
fs	superficial value for liquid
g	vapour
i	two-phase interface

o	initial
s	sound

Section 15.10

Subsections 15.10.1–15.10.3

a	albedo
A_p	area of pool
C_{BM}	logarithmic mean concentration difference
C_T	total concentration
d	pool diameter or, more generally, characteristic length
D	diffusion coefficient
h	heat transfer coefficient
ΔH_v	latent heat of vaporization
j_h	j factor for heat transfer
j_m	j factor for mass transfer
k	thermal conductivity
k_m	mass transfer coefficient
m_v	mass vaporization rate per unit area
p	partial pressure
p°	vapour pressure
q	heat flow per unit area
q_{cd}	heat flow per unit area by conduction from ground to pool
q_{cn}	heat flow per unit area by convection from atmosphere to pool
q_r	net heat flow per unit area by radiation from pool
q_{ra}	heat flow per unit area by radiation from atmosphere to pool
q_{rI}	heat flow per unit area by radiation from pool to atmosphere
q_{rs}	heat flow per unit area by solar radiation to pool
q_v	heat required per unit area for vaporization
Q	total heat transferred per unit area
Re_x	point Reynolds number
u	velocity
w	mass of liquid
z	vertical distance down into soil
α	thermal diffusivity
ϵ	emissivity
θ	temperature above datum, or soil, temperature
λ	constant
σ	surface tension (Equation 15.10.4); Stefan–Boltzmann constant (Equations 15.10.35 and 15.10.36)
ϕ	fraction of liquid vaporized, flash fraction
ψ	solar constant

Subscripts

a	air, atmosphere
b	normal boiling point
d	drop
i	initial
l	liquid
o	initial
s	soil
v	vapour
∞	atmosphere beyond influence of pool

Equations 15.10.10 and 15.10.11:

k	constant
M_i	molecular weight of component i
M_{To}	initial mass of liquid
n_T	moles of liquid
p_{is}	vapour pressure of component i
x_{io}	initial mol fraction of component i in liquid

Subsection 15.10.4

a	constant defined by Equation 15.10.41
D	diffusion coefficient of vapour in air (cm^2/s)
E	evaporation rate (g/s)
f_1, f_2	parameters defined by Equations 15.10.45 and 15.10.46
k	von Karman constant
K	constant defined by Equation 15.5.39
K'	constant defined by Equation 15.5.40
M	molecular weight
n	diffusion index
p°	vapour pressure of liquid (dyn/cm^2)
r	radius of pool (cm)
R	universal gas constant (erg/gmol K)
T	absolute temperature (K)
u	wind speed (cm/s)
u_1	wind speed at height z_1 (cm/s)
x_0	downwind length of pool (cm)
y_0	crosswind width of pool (cm)
z	height (cm)
z_1	height at which wind speed u_1 is measured (cm)
λ	parameter (cm^2/s)
v	kinematic viscosity of air (cm^2/s)
χ_o	concentration (g/cm^3)

Equations 15.10.50 and 15.10.51
As for Subsection 15.10.4, but with SI units plus

a, a'	constants

Subsection 15.10.5

C_D	drag coefficient
u	wind speed
ρ_g	density of gas at 10 m from pool
ρ_{sg}	saturation density of gas at ambient conditions

Subsection 15.10.6

c	specific heat
C	constant
h	heat transfer coefficient
j_m	j factor for mass transfer
k	constant
k_m	mass transfer coefficient
N	mass transferred per unit area
p	partial pressure
q_{cn}	heat flow per unit area by convection from atmosphere to pool
u	wind speed
x	diameter of pool

Subscripts

a	air, atmosphere
l	liquid

v	vapour
∞	atmosphere beyond influence of pool

Subsection 15.10.7

c	constant
C	constant
C_L	constant (for land)
C_W	constant (for water)
f	constant
F	friction term
F_g	gravity force
F_i	inertia force
h	height of pool
r	radius of pool
s	shape factor
u	velocity of pool edge
V	volume of pool
β	shape factor
Δ	buoyancy term
ν	kinematic viscosity

Subscripts

l	liquid
w	water

Subsection 15.10.8

As Subsections 15.10.1–15.10.3 plus:

A_v	vaporization parameter

Equation 15.10.75

t	time (s)
υ	vaporization, or regression, rate of liquid surface (cm/s)

Subsection 15.10.9

As Subsections 15.10.1–15.10.3 plus

A	volume of liquid for instantaneous spill
k_3	constant
m	total mass vaporized
r	radial distance
v	vaporization, or regression, rate of liquid surface

Equations 15.10.77 and 15.10.78

E_i	mass vaporized per unit area within 1 min (g/cm^2)
E_s	steady-state mass vaporization rate per unit area (g/cm^2/s)
ΔH_v	latent heat of vaporization (cal/g)
k_1, k_2	constants

Equation 15.10.79

m_v	mass vaporization rate per unit area
q_w	heat flow per unit area from water to spill
ΔT	temperature difference between substrate and spill
β	coefficient of cubical expansion (Equation 15.10.79)
ν	kinematic viscosity

Subscript

w	water

Equation 15.10.80

m_v	mass vaporization rate per unit area (kg/m^2/s)
t	time (s)

Subsection 15.10.10

A	volume of liquid for instantaneous spill
A_p	area of pool
B	volumetric flow of liquid for continuous spill
ΔH_v	latent heat of vaporization
k	thermal conductivity
m	total mass vaporized
M_s	mass of spill liquid
r	radius of pool
v	vaporization, or regression, rate of liquid surface
V	volume of pool
X	surface roughness factor
α	thermal diffusivity
β_1	constant defined by Equation 15.10.102
β_2	constant defined by Equation 15.10.106
θ	parameter defined in Equation 15.10.98

Subscripts

b	normal boiling point
e	end of evaporation
o	initial
s	soil
1, 2	at time t_1, t_2

Subsections 15.10.11 and 15.10.12

A_o	area of confined spill
c	specific heat
ΔH_v	latent heat of vaporization
k	thermal conductivity
L	characteristic length
m_v	mass vaporization rate per unit area
q	heat flux per unit area
r	radial distance
S	parameter defined by Equation 15.10.114
t_{ch}	characteristic evaporation time
t_{cr}	time for transition from instantaneous to continuous spill, crossover time
t_o	time for spill to cover confined area
ΔT	temperature difference between liquid at distance r_1 and soil
v	vaporization, or regression, rate of liquid surface
V	volume of pool
V_c	volumetric flow of liquid into continuous spill
V_i	volume of liquid in instantaneous spill
α	thermal diffusivity
ξ	dimensionless maximum spread
τ	dimensionless time

Subscripts

e	end of evaporation
l	liquid

s	soil
sp	spill duration
1	value at radial distance r_1

Subsection 15.10.13

p	fraction which dissolves in water, partition coefficient
r_e	final evaporation radius (ft)
t_e	final evaporation time (s)
v	regression rate (ft/s)
V	volume spilled (US gal)
Δ	buoyancy term defined by Equation 15.10.63

Subsections 15.11–15.66

C_E	slumping coefficient
x, y, z	distances in downwind, crosswind, vertical directions
u	wind speed
u, v, w	wind velocity components in down wind, crosswind, vertical directions
u_*	friction velocity
x_i	mixed layer height
z_0	roughness length
Γ	dry adiabatic lapse rate
$\sigma_u, \sigma_v, \sigma_w$	standard deviations of wind velocity in downwind, crosswind, vertical directions
$\sigma_x, \sigma_y, \sigma_z$	standard deviations, or dispersion coefficients, in downwind, crosswind, vertical directions
χ	concentration (mass per unit volume)

Subscripts

a	air
cl	centreline
cr	critical
mgl	maximum ground level
tr	transition
x, y, z	in x, y, z directions

Section 15.11

h	height of cloud
p	index

Section 15.12

Subsection 15.12.4

f	Coriolis force
p	pressure
X, Y	accelerations in downwind, crosswind directions representative of forces not due to pressure and gravity
ϕ	latitude
ω	angular velocity of earth

Subsections 15.12.5–15.12.28 and 15.12.32–15.12.34

a	constant
c	constant
c_g	drag coefficient
c_p	specific heat of air
d	zero plane displacement, displacement height
E	vertical flux of water vapour, evaporation rate
f	Coriolis force
F_s	vertical flux
h^i	scale height of neutral atmospheric boundary layer
H	vertical heat flux, sensible heat flux
i_y, i_z	intensities of lateral, vertical turbulence
k	von Karman constant
K	coefficient of exchange, turbulent exchange coefficient
K_H	coefficient of exchange for heat, eddy thermal diffusivity
K_M	coefficient of exchange for momentum, eddy diffusivity for momentum, eddy viscosity
K_{Mo}	adiabatic value of K_M
K_w	coefficient of exchange for water vapour, eddy diffusivity
l	mixing length
L	Monin–Obukhov length
L_e	latent heat of vaporization
L_w	latent heat of water vapour
n	index
p	index (Subsection 15.12.8 and 15.12.25); absolute pressure (Subsection 15.12.13)
p_o	absolute pressure at surface
P_u	P value
P_θ	P value
q	concentration of water vapour, or specific humidity
Q_0	surface heat flux
Ri_B	bulk Richardson number
Ri_F	flux Richardson number
Ri_{mod}	modified Richardson number
s	environmental stability
S	non-dimensional windshear (Equation 15.12.25); mean quantity of property per unit mass of air (Equation 15.12.55)
S^*	scale parameter
T_o	absolute average temperature of mixed layer
u_g	geostrophic wind speed
U_R	wind speed ratio
u, v, w	wind speeds in downwind, crosswind, vertical directions
$\bar{v}, \bar{u}, \bar{w}$	mean wind speeds in downwind, crosswind, vertical directions
u', v', w'	wind speed fluctuations in downwind, cross–wind, vertical directions
$\overline{v'^2}, \overline{u'^2}, \overline{w'^2}$	variances of wind speed in downwind, crosswind, vertical directions
w^*	convective velocity
X	parameter defined by Equation 15.12.108
z	height
α	Monin–Obukhov coefficient
α_1, α_2	constants
β	ratio of specific heats of air; constant (Equation 15.12.49b)
ϵ	mean height of roughness elements (Subsection 15.12.12); eddy dissipation rate (Subsection 15.12.28)

θ	potential temperature
ζ	Monin–Obukhov parameter
μ	Kazanski–Monin parameter
ν	kinematic viscosity of air
ρ	density of air
$\Delta\rho$	density difference between cloud and air
σ_A	standard deviation of azimuth
σ_E	standard deviation of elevation
σ_θ	standard deviation of horizontal direction of wind
σ_ϕ	standard deviation of inclination to horizontal of wind
τ	mean momentum flux per unit area, Reynolds stress
ϕ_H	similarity factor for heat flux
ϕ_M	similarity factor for momentum flux
ϕ_s	similarity factor for property s
ϕ_W	similarity factor for water vapour flux

Subscripts

s	property specified
1, 2	at height 10 and 5 m, respectively

Equation 15.12.40

H	sensible heat flux (W/m^2)
S	incoming solar radiation (W/m^2)

Equation 15.12.80

p	index
t	sampling period

Equations 15.12.112–15.12.114

A, B	constants
Q_m	maximum surface heat flux
Z_{im}	maximum mixed layer height
τ	time after sunrise

Subsection 15.12.29

i	intensity of turbulence
r	radius of eddy
t_E	Eulerian time scale
t_L	Lagrangian time scale
β	ratio of Lagrangian to Eulerian time scales
ω	tangential velocity

Subsections 15.12.30 and 15.12.31

$R(x)$	correlation coefficient
$R(\tau)$	correlation coefficient
t	time
u	velocity
u'	component of velocity
x	distance
σ_x	standard deviation in downwind direction
τ	time

Subscripts

1, 2	points 1, 2

Sections 15.14 and 15.15

Subsection 15.14.1

K	diffusion coefficient (m^2/s)
K_x, K_y, K_z	diffusion coefficients in downwind, cross-wind, vertical directions (m^2/s)
r	radial distance (m)
t	time (s)
u, v, w	wind speeds in downwind, crosswind, vertical directions (m/s)
x, y, z	distances in downwind, crosswind, vertical directions (m)
χ	concentration (kg/m^3)

Subsection 15.14.5

D	diffusion coefficient, diffusivity
k	thermal conductivity
l	characteristic dimension
u	velocity
ν	kinematic viscosity

Section 15.16

Subsections 15.16.1, 15.16.2 and 15.16.5

As Subsection 15.14.1 plus

C	diffusion parameter ($m^{(1/2)n}$)
C_x, C_y, C_z	diffusion parameters in downwind, crosswind, vertical directions ($m^{(1/2)n}$)
h	height of source (m)
H	height of source (m)
K	diffusion coefficient (m^2/s)
K_0	modified Bessel function of second kind
n	diffusion index
p	index
Q	continuous mass rate of release (kg/s)
Q'	continuous mass rate of release per unit length (kg/ms)
Q^*	mass released instantaneously (kg)
y_o, z_o	cloud bondary in y, z directions (m)
$\sigma_x, \sigma_y, \sigma_z$	standard deviations, or dispersion coefficients, in downwind, cross wind, vertical directions (m)

Subsection 15.16.3

C	ground level concentration ($units/m^3$)
C_c	ground level concentration axis of plume for elevated source ($units/cm^3$)
C_0	ground level concentration axis of plume ($units/m^3$)
d	distance in downwind direction (km)
d'	half-distance for development of uniform vertical concentration profile (km)
F_1	stack correction factor
F_2	off-axis correction factor
h	vertical spread (m)
h'	limiting vertical spread (m)
H	height of stack (m)
Q	mass rate of release (units/min)
x	downwind distance (m)
u	mean wind speed (m/s)
β	deviation from axis (°)

θ	lateral spread (°)
σ_y	standard deviation of concentration in crosswind direction (m)
σ_θ	standard deviation of wind direction (°)
σ_ϕ	standard deviation of wind inclination (rad)
ϕ	wind inclination (rad)

Subsections 15.16.6– 15.16.8

As sections 15.16.1 –15.16.4 plus

D	dosage
D_{tid}	total integrated dosage
e	base of natural logarithms
L	load
n	index (Equation 15.16.67)

Subscripts

cb	cloud boundary
cc	cloud centre
ex	extinction

Subsection 15.16.9

C	volumetric concentration (v/v)
V_1	distance between first virtual source and actual source (m)
V_2	distance between second virtual source and actual source (m)
V	volume of gas released (m^3)
x	downwind distance (m)
x_b	distance between actual source and works boundary (m)
x_s	distance between actual source and point of interest (m)
x_{v1}	distance between first virtual source and works boundary (m)
x_{v2}	distance defined by Equation 15.16.72

Subsections 15.16.7 and 15.16.8

K	parameter
m, n	indices
t_e	time for total discharge or evaporation

Section 15.17

Subsection 15.17.1

Q_a	mass rate of release per unit area
Δx	incremental length
ξ_a	concentration above mixed layer height
ξ_b	concentration upwind of city, background concentration

Subsection 15.17.3

As Sections 15.16.1 –15.16.4 plus

a	radius of hill
D_y, D_z	parameter defined by Equations 15.17.5a and 15.17.5b
h	actual stack height
Δh	plume rise
h_e	equivalent stack height
h_0	effective stack height
h_1, h_2	height of hills 1 and 2
h_p	local height of plume
ζ	parameter defined by Equation 15.17.7
η	parameter defined by Equation 15.17.6
ψ	stream function

Subscripts

f	flat terrain
o	effective source height

Subsection 15.17.4

D_l	larger of dimensions height h and width w
D_s	smaller of dimensions height h and width w
h	height of building
h_s	height of source
l	alongwind length of building
R	scaling factor
w	crosswind width of building

Equations 15.17.11 –15.17.15

h_c	height of roof cavity
l_c	length of roof cavity
x	downwind distance
Z_{II}	upper boundary of high turbulence layer
Z_{III}	upper boundary of roof wake

Equations 15.17.6 and 15.17.17

A	characteristic area
A_v	vent area
K	dimensionless concentration
Q	mass rate of release
w_o	effluent velocity

Equations 15.17.18 and 15.17.19

h	actual stack height
h'	effective stack height after downwash
h_d	downwash
h_0	effective plume height

Equations 15.17.20 –15.17.22

A, B	parameters defined by Equations 15.17.21, 15.17.22
x_r, y_r, z_r	length, width, height of wake cavity

Equations 15.17.23 –15.17.26

A	cross-sectional area of building normal to wind
c	constant
D_A	atmospheric dilution factor
D_B	building dilution factor
D_{tot}	total dilution factor
Q	mass rate of release
x	downwind distance
σ_y, σ_z	dispersion coefficients in crosswind, vertical directions

Equations 15.17.27 –15.17.44

C	mean concentration
H	parameter defined by Equation (15.17.28)
k	constant
k_f	characteristic energy of free stream turbulence
l_f	characteristic length of free stream turbulence
Q	source strength
S	dimension of block

u	mainstream air velocity
V	volume of wake bubble
X	length of wake bubble
Λ	free stream turbulence parameter

Equations 15.17.33–15.17.44

A	frontal area of building
b	crosswind breadth of building
C_w	average concentration in near-wake region
F	flow out of wake
h	height of building
L_r	length of recirculation region
Q	source strength
S	surface area of near-wake region
t_r	residence time in near-wake region
u_h	wind speed at building height in undisturbed flow
V	volume of near-wake region
α	flux constant
β	wake shape parameter
λ_r	dimensionless length of recirculation region
τ_r	dimensionless residence time in recirculation region
χ_w	dimensionless average concentration in near-wake region

Section 15.18

H	height of 'lid'
Q	mass rate of release

Section 15.19

Subsection 15.19.1

As Subsections 15.16.1–15.16.4 plus

f_1, f_2	universal functions
$R(\tau)$	autocorrelation coefficient
t_L	Lagrangian time scale
T_i	dispersion time
T_y, T_z	time scales for lateral, vertical dispersion
δ	delta function
σ_θ	standard deviation of wind direction

Subsection 15.19.3

As Section 15.16.3 plus

d	distance
h	vertical spread
θ	lateral spread

Subsection 15.19.6

As Sections 15.16.1–15.16.4 plus

a, c, f, h	constants
b, d, g, j	indices
$F(z_0, x)$	roughness length correction factor
P	P value
T	duration of release (h)
u_{10}	wind speed at 10 m height (m/s)
σ_y	dispersion coefficient in crosswind direction (m)
σ_{yt}	turbulent diffusion term (m)
σ_{yw}	wind direction fluctuation term (m)
σ_θ	standard deviation of horizontal wind direction (rad)

Subsection 15.19.7

As Sections 15.16.1–15.16.4 plus

Equation 15.19.25

a, c	constants
b, d	indices

Equation 15.19.26

a, b, c	constants
σ	dispersion coefficient

Subsection 15.19.8

As Sections 15.16.1–15.16.4

Subsections 15.19.9–15.19.11

As Sections 15.16.1–15.16.4 plus:

p	index
R	reference distance
α, β	indices

Subsection 15.19.12

As Sections 15.16.1–15.16.4 plus

c_1, c_2, c_3	constants
ϵ	eddy dissipation rate
σ	dispersion coefficient
σ_o	initial size of puff

Subscripts

o	initial
plume	plume
puff	puff

Section 15.20

d_o	diameter of outlet
r_o	radius of outlet

Subscripts

e	exit
o	outlet

Subsections 15.20.2–15.20.3

u	velocity of gas

Equations 15.20.1–15.20.23

b_0	half-width of slot
c	volumetric concentration
d	width of slot
k	constant
k_1–k_7	constants
m	mass flow
M	momentum flux
r	radial distance
r_p	radius of pipe (for radial jet)
u	velocity of gas
w	wind speed
x	distance along axis of jet
β	half angle of jet
θ	air–fuel mass ratio

Subscripts

m	centre line, and hence maximum
tr	transition (from jet to plume)
x	mean value at axial distance x

x_o centre line
xr at axial distance x and radial distance r

Equations 15.20.24–15.20.37
D diameter
M mass flow
u velocity of gas

Subscripts
a atmospheric
E exit, or outlet
N nozzle, or outlet
s shock plane
v vessel

Equations 15.20.38–15.20.46
b_1–b_3 constants
d_{eq} equivalent diameter
j volumetric concentration
x distance along axis of jet
x' distance between virtual source and outlet
x'' distance defined by Equation 15.15.41
y radial distance
$\rho_{ga'}$ normalized density of gas at atmospheric conditions
$\rho_{go'}$ normalized density of gas at outlet
$\rho_{oeq'}$ normalized density of gas at equivalent diameter

Subscripts
m centre line, hence maximum
xy at point x, y

Equations 15.20.47–15.20.62
A cross-sectional area of flow
c_D coefficient of discharge
d diameter
k compressible eddy coefficient
k' eddy viscosity coefficient
m mass fraction
N pressure ratio
r radius
$r_{0.5}$ radius at which velocity is half centre line value
u velocity of gas
x_c dimensionless core length
z distance along axis of jet
z_b barrel length
z^* modified axial distance

Subscripts
eq equivalent
m centre line, hence maximum
v vessel

Subsection 15.20.4
a radius of outlet
c constant
d diameter of outlet
k constant representing air resistance
l height of outlet
x distance in horizontal direction
u horizontal velocity of liquid
z distance in vertical direction
Z breakup length
α angle between jet and horizontal (Equations 15.20.63–15.20.78); constant (Equations 15.20.79–15.20.86)
δ amplitude of disturbance
δ_o initial amplitude of disturbance
σ surface tension

Subsection 15.20.6
c volumetric concentration
F buoyancy flux
k_4 and k_5 constants
l characteristic length
M momentum flux
Q volumetric flow
r radial distance
u velocity of gas in jet or plume
x distance along axis
β coefficient of cubical expansion
$\Delta\rho_o$ density difference

Subscripts
lt transition (from laminar to turbulent)
xr at axial distance x and radial distance r

Subsection 15.20.7
As Sections 15.16.1–15.16.4

Subsection 15.20.8
C constant
F buoyancy flux
M momentum flux
u velocity of gas
z_{max} maximum plume rise

Subscripts
l ambient fluid

Subsection 15.20.9
A time parameter (defined by Equation (15.20.105))
D_c drag coefficient
$F_1(x_1)$ function expressing change in density of plume due to dilution by air
h_{pl} total effective height of plume
H height of outlet (m)
i rise of fall of plume at distance wt_1
J volumetric flow from outlet referred to ambient temperature (m^3/s)
k_1, k_6–kc_8 constants
l height of jet (above outlet)
m_a mass flow of air
m_l mass flow of gas-air mixture at distance l
m_o mass flow at outlet
M molecular weight of gas
M_a molecular weight of air
N volumetric flow from outlet
Q volumetric flow at outlet

p_a	concentration along axis at distance x (mole fraction)
p_{mgl}	maximum ground level concentration at distance x (mole fraction)
r	radial distance from axis
t_1	arbitrary chosen time interval
u	velocity of gas
u_b	buoyancy velocity
u_σ	velocity of plume along axis of falling plume from virtual source to ground
v	velocity at outlet
w	wind speed
x	downwind distance, downwind distance from virtual source
x_{max}	downwind distance from virtual source at which maximum rise of plume occurs
x_{mgl}	downwind distance to maximum ground level concentration
x_0	downwind distance of transition point from virtual source
x_1	downdwind distance from virtual source at which plume axis reaches ground
x_1	distance defined by Equation (15.20.106)
x_θ	distance from virtual source to point where plume reaches ground measured along axis of plume
z	vertical distance above transition point
z_{max}	maximum plume rise
θ	angle between axis of falling plume and horizontal
ρ_g	density of gas at outlet
ρ_l	mean density of gas–air mixture at distance l
ϕ	angle between axis and edge of plume, half-angle of plume
ψ	momentum flux in still air
ψ_w	momentum flux in windy conditions

Subscripts

g	gas at outlet
trw	transition in windy conditions
w	windy conditions

Subsection 15.20.10

C_1, C_2	constants
e	base of natural logarithms
F	buoyancy flux
h_e	effective stack height
h_s	stack height
Δh	plume rise (above stack outlet)
H	surface buoyancy flux
k	von Karman's constant
m	molecular weight
M	momentum flux
Q	mass rate of release
r	radius
s	environmental stability
s'	modified stability
S	ratio of effective area influenced by plume momentum to cross-sectional area of so-called thermal plume
u	wind speed
V	volumetric flow
w	velocity in vertical direction
w'	parameter defined by Equation (15.20.180)
z	vertical distance above stack outlet; height of jet or plume
z_{max}	maximum plume rise
α	constant
β	constant
ϵ	ambient eddy dissipation rate
η	constant
σ	dispersion coefficient

Subscripts

c	critical
eff	effective
en	environment
eno	initial environment
eq	equilibrium
fb	fallback
p	plume
po	initial plume

Section 15.21

Subsection 15.21.1

ϵ	constant

Subscripts

sat	saturation
sh	shattering

Subsection 15.21.2

A	cross-sectional area of jet
C	concentration (mass per unit volume)
G	mass flow in jet
R	radius of jet
u	velocity of jet
z	distance downstream from source
α	entrainment coefficient
β	half-angle of jet

Subscripts

d	end of deposition zone
∞	asymptotic value

Subsection 15.21.3

A	cross-sectional area of jet
B	buoyancy flux
C	concentration of contaminant
f	momentum flux
L	length scale
p	dimensionless variable defined by Equation 15.21.32
q	dimensionless variable defined by Equation 15.21.33
R	radius of jet
u	velocity of jet
u_E	entrainment velocity
U	velocity scale
x	downstream distance
α	entrainment coefficient
ϕ	ratio of density of jet to that of air

Subsection 15.21.4

A	cross-sectional area of jet
e	entrainment rate
E_o	entrainment coefficient
h	specific enthalpy
P	pressure in jet
R	radius of jet
u	velocity of jet
x	vapour fraction, or quality
z	distance along jet axis

Subscripts

a	at end of depressurization zone
b	at orifice
bp	boiling point
f	liquid
fg	liquid–vapour transition
g	vapour
o	stagnation conditions
tp	two-phase
∞	atmospheric conditions

Section 15.24

Subsections 15.24.6–15.24.9

k	van Karman constant
K	eddy diffusivity
L	Monin–Obukhov length
p	index
z	height
Δ	reduced density difference defined by Equation 15.24.3
Δ'	reduced density difference (alternative formulation, defined by Equation 15.24.5)
$\Delta\rho$	absolute density difference
ϵ	energy dissipation rate
κ	turbulence energy
ψ	profile function

Subsection 15.24.10

C_f	friction factor
G	mass velocity
h	heat transfer coefficient
j_H	j factor for heat transfer
k	thermal conductivity
L	characteristic dimension
St_h	Stanton number for heat transfer
ΔT	temperature difference for heat transfer
u	velocity of cloud
β	coefficient of thermal expansion

Subscripts

t	film
gr	between ground and cloud

Subsection 15.24.11

c	velocity of wave
h	height of dense fluid
n	symmetry index
u	velocity of dense fluid
x	distance

Subsection 15.24.12

B	negative buoyancy
H	height of cloud
R	radius of cloud
u_e	top entrainment velocity
V	volume of cloud
w_e	edge entrainment velocity

Section 15.25

As Sections 15.16.1–15.16.4 plus

c	volumetric concentration
c_p	specific heat of gas in source cloud
E	heat source in cloud
H	height of cloud
L	width of source
m	mass of gas in source cloud
R	radius of cloud
u_e	top entrainment velocity
V	volumetric rate of release
W_v	velocity of vapour source
x_v	distance of virtual source upwind of actual source
ϵ_v	heat released by condensation and freezing of water vapour
ϵ_w	surface heat flux

Subscript

i	initial

Section 15.26

A, B	constants
B	rate of buoyancy destruction of turbulent energy
c_1	constant
c_t	constant
C	volumetric concentration
D	rate of dissipation of turbulent energy into internal heat
F_a	force due to reaction of ambient fluid to outward radial acceleration of cloud edge
F_d	drag force on cloud edge due to presence of quiescent ambient fluid
F_s	static pressure force due to negative buoyancy of cloud
F_v	force due to vertical acceleration in cloud and reaction of ambient fluid
G	rate at which gravity transforms potential energy into mean kinetic energy
H	height of cloud
H_f	height of fluid front
I_E	internal heat
K_E	kinetic energy of mean radial and vertical motions
L	half-width of plume
M_{rd}	radial momentum integral of cloud
P_E	potential energy
Q	volumetric rate of release
R	radius of cloud
Ri_t	bulk turbulent Richardson number
s	profile shape parameter
S	cross-sectional area of plume from continuous release

	(Equations 15.26.19–15.26.18); rate of shear production of turbulent energy (Equations 15.26.30 and 15.26.31)
T_E	turbulent kinetic energy
u_e	top, or vertical, entrainment velocity
u_f	velocity of fluid front
u_y	cloud velocity in crosswind direction
u_t	bulk turbulent velocity
V	volume of cloud
w_e	edge, or horizontal, entrainment velocity
W_o	volumetric flow from source
γ	edge entrainment coefficient
Δ	reduced density difference
Δ'	reduced density difference for cloud
ρ_1, ρ_2	density of fluid behind, ahead of wavefront
$\bar{\rho}_c$	mean density of cloud
$\Delta\rho_c$	mean density difference of cloud
$\Delta\rho_o$	mean density difference of cloud

Superscript

$^-$	average

Subscripts

c	cloud
o	time zero, hence source
u	transition

Subsection 15.26.4

Subscripts

c	continuous
i	instantaneous

Section 15.27

C_d	drag coefficient
C_f	friction factor
c_{pc}	specific heat of cloud
D	drag force on cloud
f	wind speed coefficient
F	friction force
h	specific enthalpy
h_{grn}	heat transfer coefficient between ground and cloud by natural convection
H	height of cloud
k_E	spreading constant
l	turbulence length scale
l_{vs}	width of virtual source
L	half-width of cloud
m	total mass in cloud
m	mass of component in cloud (with subscript)
m_e	mass of air entrained at edge of cloud
m_t	mass of air entrained at top of cloud
Q	continuous mass rate of release
Q^*	mass released instantaneously
Q_e	volumetric flow of air entrained at edge of cloud (total value for instantaneous release; value per unit downwind distance for continuous release)
Q_{gr}	heat flux from ground to cloud
Q_t	volumetric flow of air entrained at top of cloud (total value for instantaneous release; value per unit downwind distance for continuous release)
$r(n)$	distance downwind from source η
R	radius of cloud
S^*	parameter defined by Equation 15.27.20
u'	magnitude of vector sum of slumping and wind velocities
u_{av}	average wind speed cloud height
u_c	velocity of cloud
u_e	top, or vertical, entrainment velocity
u_h	wind speed at cloud height H
u_r	wind speed at reference height (normally 10 m)
u_l	longitudinal turbulence velocity
V	volume of cloud per unit distance downwind (total value for instantaneous release; value per unit downwind distance for continuous release)
w_e	edge, or horizontal, entrainment velocity
α	top entrainment coefficient
β	limiting value of group (u_e/u_l)
γ	edge entrainment coefficient
σ	dispersion coefficient
τ	shear stress

Subscripts

c	cloud
gr	ground
l	liquid
o	source
v	vapour
wl	water liquid
wv	water vapour
y	crosswind

Section 15.28

C^*	constant
g_{gr}	heat transfer coefficient between ground and cloud
H	height of cloud
l	turbulence length scale
k	constant
k	thermal conductivity (with subscript)
m	total mass in cloud
m_a	mass of air
m_g	mass of gas
Q_{gr}	heat flux between ground and cloud
R	radius of cloud
ΔT_a	temperature difference between air and cloud
ΔT_{gr}	temperature difference between ground and cloud
u_c	velocity of cloud
u_e	top, or vertical, entrainment velocity
u_r	wind speed at reference height (normally 10 m)
u_l	longitudinal turbulence velocity
V	volume of cloud
w_e	edge, or horizontal, entrainment velocity

x_{vy}	distance downwind of virtual source for horizontal dispersion
x_{vz}	distance downwind of virtual source for vertical dispersion
X	parameter defined by Equation 15.28.61
z_r	reference height (normally 10 m)
Z	parameter defined by Equation 15.28.11
β	coefficient of volumetric expansion
γ	edge entrainment coefficient
Δ	reduced density difference
$\Delta\rho$	density difference

Subscripts

c	cloud
f	fluid film
g	gas, material release
gr	ground
H	Hosker scheme
o	initial
vy	virtual source for crosswind effects
vz	virtual source for vertical effects

Subsection 15.28.1

A, B, C	parameters
L	characteristic dimension of cloud

Subsection 15.28.2

A, B, C	parameters
A'	parameter defined by Equation 15.28.62
L	half-width of cloud

Section 15.29

c	concentration (mass fraction)
C_d	drag coefficient
h	specific enthalpy
H_{min}	height at breakup
K_h, K_v	horizontal, vertical eddy diffusivities
l	turbulence length scale
L_o	latent heat of water
$\dot{m}$	mass rate of evaporation
$\dot{m}_{min}$	mass rate of evaporation at breakup
p	pressure
p_s	pressure at surface
p_t	pressure at top
q	heat flux
t_{max}	time at breakup
U	heat transfer coefficient
W	mass of water vapour per unit mass of air
π	parameter defined by Equation 15.29.7
σ	dimensionless pressure coordinate
$\dot{\sigma}$	substantial derivative in x, y, σ, t coordinates
σ_ϵ	standard derivation of wind direction
τ_o	shear stress at surface
ϕ	geopotential height
ω	substantial pressure derivative

Subscripts

c	cloud
g	gas
l	liquid
s	surface

Section 15.30

b	cloud shape parameter
B	cloud width parameter
C	volumetric concentration
C_1, C_2	concentration functions
h	cloud height parameter
k	von Karman constant
K_a	ambient vertical diffusion coefficient
K_h	horizontal diffusion coefficient
K_v	vertical diffusion coefficient
K_ρ	dense-layer diffusion coefficient
K^m	eddy diffusion tensor for momentum
K^θ	eddy diffusion tensor for energy
K^ω	eddy diffusion tensor for mass fraction
Q_{gr}	heat flux between ground and cloud
p	pressure deviation from an adiabatic atmosphere at rest
ρ'	index
S	temperature source term
u_c	velocity of cloud
u_e	vertical entrainment velocity
u_o	velocity of material at source
u_y	velocity of cloud in crosswind direction
u_{*c}	cloud friction velocity
u	velocity tensor
w_e	horizontal entrainment velocity
w_{*c}	cloud 'convection velocity'
β	cloud shape parameter
β^*	constant
θ	potential temperature deviation from an adiabatic atmosphere
ρ_h	density corresponding to pressure p
ϕ	profile function
ω	mass fraction of material released

Subscripts

c	cloud
g	material released
o	source

Section 15.31

A_i	half-area of source for observer i
b	half-width of middle part
B	half-width of gas blanket
B_{eff}	effective half-width of plume
B_p	half-width of pool
B_s	half-width of source
B_{si}	half-width of source for observer i
B'_{si}	local half-width of source for observer I
c	concentration in mass per unit volume
c_A	ground level concentration on centre line
c'_A	corrected ground level concentration on centre line
c_{gr}	concentration at ground level
C_f	friction factor
H	height of cloud
H_b	height of 100% gas blanket
H_e	surface heat flux
H_{eff}	effective height of cloud
i	counter for observer i

k von Karman constant
K eddy diffusion coefficient
K_o constant
K_o^* vertical eddy diffusion coefficient at reference height z_r acting on concentration profile of width 2B
L length of gas blanket
L_p length of pool
L_s length of source
L_{si} length of source for observer i
Q_{gr} heat flux between ground and cloud
Q_p *total mass rate of evaporation*
Q'' *mass rate of take-up into atmosphere per unit area*
Q''_i mass rate of take-up into atmosphere per unit area for observer i
Q''_{max} mass rate of take-up into atmosphere per unit area
Q''_o mass rate of evaporation per unit area
Q''_p mass rate of evaporation per unit area
r shape factor for crosswind concentration profile
R radius of source
R_b radius of gas blanket
R_l radius of spreading pool
Ri_* Richardson number defined by Equation 15.31.34
Ri_{*I} internal Richardson number defined by Equation 15.31.65
s shape factor for vertical concentration profile
S dispersion parameter
t_s specified time
t_{1i}, t_{2i} times when observer i passes upwind, downwind edges of source
u wind speed; gas velocity (Equation 15.31.58)
u_e top entrainment velocity
u_{eff} effective local cloud velocity
u_A effective air velocity
u_B bulk cloud velocity
u_i velocity of observer i
u_{*I} internal velocity scale
w_e edge entrainment velocity
W_b half-width of concentration profile
x_i downwind distance of observer i at time t
x_{tr} downwind distance of transition point
x_v downwind distance of virtual source
y_{Ls} limit of integration of y
y_{w3} mole fraction of surface water vapour
α_T thermal diffusivity
α' index
β_c coefficient of volumetric expansion of cloud
β' constant
γ edge entrainment coefficient
γ' constant
δ' constant
ν kinematic viscosity
ρ_E density at emission conditions
ρ_{gr} density downwind
τ_{gr} shear stress acting on downwind ground surface
τ_o shear stress acting on upwind ground surface
ϕ profile function

Subscripts
c cloud
g material released
gr ground, ground level
i observer i

Section 15.32

As Section 15.24.10 and Section 15.31 plus
H height
k von Karman constant
Ri_* modified Richardson number
u_e vertical entrainment velocity
α index
ϕ profile function

Section 15.33

c_o constant or function
p pressure
S_o function
u velocity
x distance
Γ_o function
ϵ energy dissipation
κ turbulence energy
ϕ scalar quantity

Subscripts
i, j i, j direction

Section 15.34

A constant given in Figure 15.85(b)
B constant given in Figure 15.87(b)
C volumetric concentration
$\bar{C}_m$ maximum time mean volumetric concentration on the centre line
C_o volumetric concentration at initial release
D characteristic dimension of source
g'_m reduced gravity corresponding to maximum concentration
g_o reduced gravity of initial release
G source geometry
h measure of plume height
h_c height of crest
H height of cloud
l_b buoyancy length scale
l_i length scale of turbulence in the atmospheric boundary layer
L_h half-width of plume
L_{ho} half-width of plume at source
L_u upwind extent of plume
L_v height of plume
n fraction of initial concentration ($= \bar{C}_m/C_0$); index (Equation 15.34.42)
q_o volumetric rate of release
Q volume of cloud
Q_o volume of material released
R radius of cloud
R_o initial radius of cloud

t_a	arrival time of leading edge of cloud
t_c	time between arrival time t_a and departure time t_d
t_d	departure time of trailing edge of cloud
x_c	distance of leading edge
x_n	distance at which the fraction of initial concentration is n
y_c	half-width of cloud
u_{ref}	characteristic mean velocity
ρ_a	density of air
ρ_o	density characteristic of material released
ϕ	stability parameter
ψ	stability parameter

Subsections 15.34.4 and 15.34.5

T_o	duration of release

Subsection 15.34.7

T_a	absolute temperature of air
T_o	absolute temperature of initial volume
V_a	volume of air
V_o	non-isothermal initial volume

Subscripts

I	isothermal
ni	non-isothermal

Section 15.35

a_1–a_3	parameters
C	concentration
C_m	ground level centre concentration
F_h	parameter defined by Equation 15.35.5
F_v	parameter defined by Equation 15.35.6
L_s	Monin–Obukhov length scale
s	parameter
x'	relative coordinate
X	downwind coordinate of cloud centre
w	parameter
Z	vertical coordinate of cloud centroid
ζ	measure of skewness of cloud
ξ	downwind coordinate relative to skewed cloud

Section 15.36

C	volumetric concentration
$\hat{h}$	normalized height of cloud
H	height of cloud
$\hat{r}$	normalized radius of cloud
r	radius of cloud
$\hat{t}$	normalized time
t_o	initial time scale
u_E	edge entrainment velocity
u_f	cloud front velocity
u_T	top entrainment velocity
$\hat{v}$	normalized volume of cloud
V	volume of cloud
α	parameter defined by Equation 15.36.13a
β	parameter defined by Equation 15.36.14a

Superscript

Λ	normalized value

Subscript

o	initial

Section 15.39

A_o	area of source
D	diffusivity
f	Coriolis parameter
L	characteristic length scale
q_o	volumetric release rate
Q_o	volume released
u	characteristic velocity
u_o	source velocity
α	ground slope
κ	thermal conductivity
μ	viscosity of atmosphere
μ_o	viscosity of source gas
v	kinematic viscosity
ρ	density of atmosphere
ρ_a	density of air
ρ_o	density of source gas
$\Delta\rho/\rho$	potential density difference

Subscript

o	source gas

Subsection 15.39.5

D	plume dimension
Q	volumetric release rate

Subsection 15.39.7

c	volumetric concentration
l_b	buoyancy length scale
l_q	length scale
Q	volumetric release rate

Section 15.40

Equations 15.40.1–15.40.9

C_D	drag coefficient
E	entrainment coefficient
g'_o	reduced gravity
h	height of following flow
Q	volumetric flow per unit width
S_1, S_2	parameters
x	downhill distance
u	mean velocity of following flow
u_f	velocity of front
u_s	velocity on a defined streamline
α	parameter defined by Equation 15.40.4
θ	angle of incline to horizontal

Subscripts

n	normal
1, 2	less, more dense fluid

Equations 15.40.10 and 15.40.11

C_D	form drag coefficient
f	friction factor
H	height of cloud
R	radius of cloud
u	velocity downhill
θ	angle of slope

Subscripts

b	bottom of cloud
g	gas
t	top of cloud

Equations 15.40.12 and 15.40.13

A_o	initial cross plume area of plume element
A_p	final cross plume area of plume element
g'_o	initial reduced gravity
u	wind speed at ground level
z	height from source to target
θ	potential temperature

Subscript

p	plume

Subsection 15.40.2

As Section 15.34.4 plus

C_g	maximum volumetric concentration at ground level
C_o	volumetric concentration at initial release
h	height of dense fluid layer
Δh	head difference
h_w	height of obstacle
$h_{0.5}$	height at which concentration is half ground level value
H	height of fence
H_b	ratio of heights defined by Equation 15.40.29
H_w	ratio of heights defined by Equation 15.40.20
q_o	volumetric rate of release
q_o^*	volumetric release rate per unit width
u	velocity of fluid
u_w	velocity over obstacle
U	velocity of wave travelling upstream (hydraulic jump)
W	plume width

Subscripts

f	with fence
f	without fence
1	upstream
2	space between upstream moving wave and obstacle

Subsection 15.40.5

A	frontal area of building
B	dimensionless buoyancy flux
C_o	time mean ground level concentration
C_L	concentration in lower layer
C_o	volumetric concentration at source
C_U	concentration in upper layer
D	diameter of source orifice
F_A	flow of air into wake
F_{LU}	flow from lower layer to upper layer
F_{UL}	flow from upper layer to lower layer
g'_o	reduced gravity at source
h	height of building
h_L	height of lower layer
h_U	height of upper layer
h	dimensionless height of lower layer
h	dimensionless height of upper layer
H	height of obstacle
l	length of building
l_w	length of recirculation region, or wake
L_B	buoyance length scale
q_o	volumetric rate of release
q	volumetric rate of release per unit length
Q	release rate, source strength
$\bar{Q}$	dimensionless release rate
Ri_o	initial Richardson number before mixing
Ri_T	transition Richardson number
S_L	lateral spread of cloud
S_U	updwind spread of cloud
S_w	surface area of wake
u	wind speed; mean velocity at obstacle height

Equation 15.40.60

V_W	volume of wake
w	width of building
α_I	mixing coefficient
α_M	mixing coefficient
α_o	constant
α_W	dimensionless length of wake
ρ	density of cloud
ρ_a	density of air

Superscript

-	normalized

Subsection 15.40.6

a	ratio of areas defined by Equation 15.40.73
A	area of opening
A_i,	area for inflow
A_o	area for outflow
b	constant
C	pressure coefficient
C_i	pressure coefficient for inflow opening
C_o	pressure coefficient for oulflow opening
f	vapour fraction
h	height of inlet opening
n	ratio of molar flows
N	number of moles
$\bar{N}_G$	dimensionless quantity defined by Equation 15.40.72
P'	pressure drop between atmospheric pressure and internal pressure
ΔP	pressure difference between outside and inside
P_o	atmospheric pressure
q_G	flow of gas
$\bar{q}_\alpha$	dimensionless flow of gas
Q	volumetric flow
Q_A	volumetric air flow of air
T	absolute temperature of air–gas mixture
T_A	absolute temperature of air
u	wind speed
V	volume of space

τ	time for concentration of gas to reach steady state if outflow is neglected
$\bar{\tau}$	ratio defined by Equation 15.40.78

Subscripts

A	air
G	gas

Section 15.42

D^*	density of cloud
R^*	air/HF ratio of cloud
T^*	absolute temperature of cloud

Section 15.43

Subsection 15.43.2

b	characteristic width of plume
c	concentration
r	radius of plume
s	distance along axis of plume
u	velocity along axis of plume
u'	entrainment velocity
U_a	mean wind velocity
θ	angle between axis of plume and horizontal
ρ	density of plume
ρ_a	density of air
ρ_{ao}	density of atmosphere at stack outlet
$\alpha_1-\alpha_3$	entrainment coefficients
ϕ_i	set of functions defined by Equation 15.43.2
ψ_i	set of functions used in Equation 15.43.1

Subsection 15.43.3

C	concentration
Δh	maximum initial plume rise
h_s	height of stack
R	radius of plume
s	distance along plume axis
u_s	velocity along plume axis
w	velocity of plume
x	downwind distance
$\alpha_{1,2}$	entrainment coefficients
θ	angle of plume axis to horizontal

Subscripts

m	maximum
o	initial
td	touchdown

Subsection 15.43.4

A_1-A_6	constants
b	width of plume (m)
B	initial buoyancy flux (m^4/s^3)
C	constant
C_1-C_6	constants
d_o	diameter of outlet (m)
g	acceleration due to gravity (m/s^2)
g'	(reduced gravity (m/s^2)
h_s	stack height (m)
l_m	length scale, related to source (m)
l_Q	length scale, related to transition from momentum to buoyancy control (m)
m	ndex
M	initial momentum flux (m^4/s^2)
Q	initial volumetric flow (m^3/s)
u, v, w	wind velocities in downwind, crosswind, vertical directions (m/s)
u_o	outlet velocity (m/s)
U	wind speed (m/s)
w_*	entrainment velocity (m/s)
x, y, z	distances in horizontal, crosswind and vertical directions (m)
x_{TD}	horizontal distance from virtual source of final plume to touchdown point (m)
x^*_{TD}	horizontal distance from stack to touchdown point (m)
x_{tr}	horizontal distance from stack to jet transition point (m)
x_v	horizontal distance from stack to virtual source of final plume (m)
z_B	length scale, related to effect of crossflow on plume (m)
z_{effB}	effective stack height with strong crossflow (m)
z_{effv}	effective stack height with weak crossflow (m)
z_m	length scale, related to effect of crossflow on jet (m)
z_{max}	maximum rise (m)
z_s	vertical coordinate of jet or plume axis (m)
z_v	distance of virtual source of jet below stack outlet (m)
α	entrainment coefficient
θ	relative density difference

Subscripts

o	Source
v	virtual source

Subsection 15.43.5

H	height of cloud
I_o	momemtum flux (Equations 15.43.34); excess momentum flux (Equations 15.43.35)
k_1, k_2	constants
Q_a	flow of entrained air
R	half-width of cloud
u_w	wind speed
v	velocity of jet
$\Delta\rho$	density difference between cloud and air

Subsection 15.43.8

D	diameter
w	velocity of plume

Subscript

o	initial

Section 15.44

A	cross-sectional area of plume
Buoy	buoyancy function
c	concentration (mass per unit volume)
C_D	spreading coefficient

D	diameter of circle, major axis of ellipse
Drag	drag function
e	eccentricity of ellipse
e_{at}	coefficient
e_{gr}	coefficient
e_{jet}	entrainment coefficient
$e_{u,cr}$	coefficient
$e_{e,cr}$	coefficient
e_x, e_z	unit vector in horizontal (wind aligned), vertical direction
$\dot{E}$	excess energy flux
Ener	energy function
Entr	entrainment function
Foot	reactive pressure force function
h	plume height; specific enthalpy (Equation 15.44.12)
k	slumping coefficient
l	width of 'footprint' of plume
l_y, l_z	turbulence length scales in crosswind, vertical directions
L	Monin–Obukhov length
$\dot{m}$	mass flux
$\dot{P}_x$	excess horizontal momentum flux
$\dot{P}_z$	excess vertical momentum flux
r	polar radius coordinate of cross-section of airborne plume
Ri_*	bulk Richardson number
s	distance along axis of plume
Shear	shear force function
T_{gr}	absolute temperature of ground
T_*	u_*T_* = ground to air heat flux
u	mean flow velocity
x, z	horizontal, vertical distance of centroid
z_c	vertical distance of centre
ϵ	dissipation rate of turbulent kinetic energy
η	parameter defined by Equation 15.44.16
η_c	parameter defined by Equation 15.44.17
η_ρ	parameter defined by Equation 15.44.34
θ	polar angle coordinate of cross-section of airborne plume
ζ	parameter
κ	von Karman constant
ϕ	angle of inclination of airborne plume
$\Phi(\mathrm{Ri}_*)$	heavy gas entrainment function
ψ_T	temperature function
ψ_u	velocity function

Subscripts

at	atmospheric turbulence
c	centre
cw	crosswind
fs	free surface
g	material released
gs	gravity slumping
hg	heavy gas
jet	jet
pot	potential
∞	ambient conditions at centroid height

Section 15.45

M	mean value of concentration
P	peak value of concentration

Subsections 15.45.1–15.45.7

c	instantaneous deviation of concentration
$\bar{c}_2$	variance of concentration (see text)
c	concentration
C	mean concentration
C_{max}	maximum concentration
C_{med}	median concentration
C_p	peak concentration
$\bar{C}$	time mean concentration
$F(C)$	probability distribution function of concentration C
i	intensity
M	mean value of concentration
p	index
p	peak value of concentration
$P(C)$	probability that concentration exceeds C
t	sampling time
t_m	sampling time for mean value M
t_p	time during which concentration is non-zero (Equation 15.45.2); sampling time for peak value P (Equations 15.45.6–15.45.9)
t_s	total sampling time
T_I	integral time scale
γ	intermittency
μ	mean of concentration
σ	variance of concentration
σ_1	standard deviation (logarithmic)

Subsection 15.45.8

As Sections 15.16.1–15.16.4 plus

D_y, D_z	crosswind, vertical standard deviations attributable to meandering
Q	continuous mass rate of release
Y	crosswind standard deviations attributable to fluctuations about centre line
Z	crosswind standard deviations attributable to fluctuations

Subscripts

i	instantaneous
m	mean
p	peak

Subsection 15.45.9

C^*	concentration in sphere
C_τ	maximum concentration which can occur over time period τ
$\bar{C}$	time mean concentration
k	constant
x	downwind distance
β	constant
γ	intermittency
λ	index
σ	standard deviation of instantaneous concentration
τ	time period

ψ	parameter defined by Equation 15.45.29

Subscript

τ	limiting value

Subsection 15.45.10

As Subsections 15.16.1–15.16.4 plus

c	concentration
c'	concentration fluctuation about mean
$\bar{c}$	mean concentration
$\bar{c}'_2$	concentration variance
c_{mp}	condition median concentration
c_o	mean concentration on centre line
c'_p	conditional concentration fluctuation
$\bar{c}_p$	conditional mean concentration
c_{p2}	conditional concentration variance
d	diameter of source
F_c	cumulative distribution function for concentration
F_m	height correction
F_v	height correction
G_m	crosswind distance correction
G_v	crosswind distance correction
h	height of source
h_v	effective height of variance source
H	height of neutrally stable atmospheric boundary layer
i	intensity
i_p	conditional intensity
i_p	conditional intensity on centre line with negligible surface interaction
$p(c)$	probability density function for concentration
$p_p(c)$	probability density function for conditional concentration
q	variance source strength
q_p	conditional variance source strength
Q	mass rate of release
u_c	advection velocity of plume
z_e	scale height
α	sink strength
δ	delta function
γ	intermittency
λ	normalized downwind distance
λ_o	virtual origin of variance source
σ_1	standard deviation (log-normal)
ϕ	location parameter for variance source

Subscript

p	conditional

Subsection 15.45.11

$c(x, t)$	concentration fluctuation about mean
$\bar{c}(x, t)$	mean value of concentration fluctuations $c(x, t)$
$\bar{c}^2(x, t)$	variance defined by Equation 15.45.76
$C(x, t)$	mean value of ensemble of concentrations $\bar{\Gamma}(x, t)$
$\bar{C}$	mean concentration
i	intensity
I	intensity
$p(\theta, x, t)$	probability density function for θ
P	probability that concentration θ lies between lower and upper flammability limits
$R(C)$	intensity parameter
$\gamma(x, t)$	intermittency
$\Gamma(x, t)$	concentration from a single experiment
$\bar{\Gamma}(x, t)$	mean value of (x,t)
Δ	delta function
ϵ	constant
θ	(x, t) particular value of (x, t)
θ_L	lower limit of flammability
θ_0	limiting value of θ
θ_U	upper limit of flammability

Subsection 15.45.14

k_2–k_5	constants

Section 15.46

Subsection 15.46.1

As Sections 15.16.1–15.16.4 plus

F	mass of flammable gas at maximum hazard
H	height of source
Q^*	mass of gas released instantaneously
Q_e^*	mass of gas within flammable range
r	radial distance
v	ratio of upper to lower flammability limit
v_1, v_2	parameters defined by Equations 15.46.15b and 15.46.15c
W	mass of flammable gas
σ	dispersion coefficient

Subscripts

cc	cloud centre
L	lower flammability limit
m	at maximum hazard
U	upper flammability limit
1, 2	inner, outer

Equations 15.49.16–15.49.19

F_c	weighting function
L	number of moles of oxygen reacting with one mole of fuel
n_a	number of moles of air in rich mixture
n_c	number of moles of fuel consumed
n_p	number of moles of fuel present
V_{LS}	volume of cloud between lower flamm ability limit and stoichiometric concentration (m^3)
V_{SU}	volume of cloud between stoichiometric concentration and upper flammability limit (m^3)
W_F	mass of fuel available for combustion (kg)

Subsection 15.46.2

a, c	constants
b, d	indices
D	constant
f	index
m_o	mass rate of release
Q	mass of gas released
Q_e	mass of gas within flammability limits

Q_{FL}	mass of gas within flammability limits
x_L, x_U	distances to lower, upper flammability limits

Subsections 15.46.3–15.46.5

c	concentration (volume fraction)
d_o	effective diameter of discharge (m)
D	constant
f	index
g	acceleration due to gravity (m/s^2)
G	parameter defined by Equation 15.46.41
k_1–k_6	constants
$\dot{m}_o$	mass rate of release (kg/s)
M	molecular weight
$\bar{M}$	mean molecular weight of gas mixture at distance z
Q_{FL}	mass of flammable material in cloud between flammability limits (kg)
r	radial distance from axis (m)
T	absolute temperature (K)
u	wind speed (m/s)
$\dot{v}$	volumetric flow (m^3/s)
V_{FL}	volume of cloud between flammability limits (m^3)
w	velocity (m/s)
z	axial length or vertical height (m)
α	ratio of number of moles of unreacted and reacted gas
Γ	dry adiabatic lapse rate (°C/m)
$\Delta\rho_o$	density difference between gas and air
χ	concentration (kg/m^3)

Subscripts

F	flame
L	lower flammability limit
o	original discharge
s	stoichiometric mixture
U	upper flammability limit

Subsection 15.46.7

M	mass of vapour (t)
R	radius of cloud (m)

Subsection 15.46.9

f	lower flammability limit (%)
P	operating pressure (bar)
t	time span (s)
W	mass flow (kg/s)
W_{lr}	mass flow per unit area (kg/m^2)

Section 15.47

Subsections 15.47.1–15.47.3

C	concentration
C_p	concentration over time f_p
k_1, k_2	constants
L	toxic load
n	index
P	probability of injury
T	exposure time
Y	probit
γ	intermittency

Subscripts

pe	exposure
s	sampling

Equations 15.47.8-15.47.10

As	Subsection 15.45.9 plus
ω	enhancement factor

Subsection 15.47.4

c	concentration
F_c	probability that concentration will not exceed c
n	index
N_b	number of breaths
$S(T_e)$	probability that concentration will not exceed c over exposure time T_e
T_e	exposure time
V_c	probability that concentration will exceed c

Subsection 15.47.5

C	concentration
D	dosage
$\bar{D}$	mean dose
D^*	effective dose
D_{50}	median fatal dose
k	constant
k_1, k_2	constants
n	index
$N[]$	normal distribution
Y	probit
δ	standardized log dosei mean standardized log dose
δ^*	effective standardized log dose
θ	probability of fatality
$\mu(C)$	mean of concentration
$\sigma(C)$	standard deviation of concentration
ϕ	distribution function

Section 15.48

Subsection 15.48.4

D	internal diameter of stack (m)
Δh	plume rise (m)
u	wind speed (m/s)
v_s	velocity of stack gas (m/s)

Subsection 15.48.5

D	diameter of vent tip (ft)
E	number of dilutions to lower flammability limit
h_s	height of vent above exposure level (ft)

Subsection 15.48.6

C_1–C_4	constants
D	internal diameter of stack (m)
h	height of stack (m)
Δh	plume rise (m)
Q	mass rate of release (g/s)
u	wind speed (m/s)
v_s	stack gas outlet velocity (m/s)
ρ	density of gas mixture (kg/m^3)

χ	critical ground level concentration ($\mu g/m^3$)

Subscripts

s	stack gas

Subsection 15.48.8

A	parameter
C_m	maximum permissible value of touchdown concentration of contaminant (%v/v)
C_s	concentration of contaminant in stack gas (%v/v)
D	internal diameter of stack (mm)
h_s	height of stack (m)
L	lower flammability limit (%v/v)
M_w	molecular weight of stack gas mixture
s	stack gas specific gravity relative to air
T_a	absolute temperature of ambient air (K)
T_s	absolute temperature of stack gas (K)
u	wind speed (m/s)
v_s	velocity of stack gas (m/s)
β	peak/mean concentration ratio

Section 15.49

Subsection 15.49.1

As Sections 15.16.1–15.16.4

Subsection 15.49.2

Equation (15.49.7)

k	constant
k_1–k_3	constants
M	mass released (te)
R	downwind range (km)
X	distance to maximum width (km)

Equations 15.49.8–15.49.18

h	height of cloud (m)
k	constant
L	distance/dimension (m)
M	mass released (te)
n	index
R	downwind distance (m)
R_c	radius of cloud (m)
R_{cr}	range transition criterion (m)
R_{LFL}	downwind range to lower flammability limit (m)
R_{UFL}	downwind range to upper flammability limit (m)
X_1	downwind dimension (m)
Y	crosswind distance at downwind distance R (m)
Y_{max}	maximum crosswind range of lower flammability limit (m)
Y_1	crosswind dimension (m)
U_{LFL}	upwind range to lower flammability limit (m)

Equations 15.49.15–15.49.18

I	inventory (kg)
k	constant
k^*	constant
L	distance/dimension (m)
$\dot{m}_v$	mass rate of release of vapour (kg/s)
n	index
R	downwind distance (m)
T_a	arrival time (s)
T_d	duration of release (s)
u	wind speed (m/s)
Y	crosswind distance at downwind distance R (m)

Equations 15.49.19 and 15.49.20

q_o	volumetric rate of release
Q_o	volume released
x	downwind distance

Section 15.50

Subsections 15.50.1–15.50.3

As Sections 15.16.1–15.16.4 plus

F	depletion factor
H	height of source
Q_o	initial source strength
Q_x	effective source strength
r	radius of particle
r_e	equivalent radius
$t_{1/2}$	half-life of concentration
x_G	distance defined by implicit Equation 15.50.23
v_d	deposition velocity
v_g	fall velocity
v_t	terminal velocity of particle
V_p	volume of particle
α	dynamical shape factor (Equation 15.50.6); reflection coefficient (Equations 15.50.21 and 15.50.22)
μ	viscosity of air
ρ_p	density of particle
τ_c	chemical decay time constant
ω	deposition rate

Subscripts

n	non-spherical
s	spherical
1, 2	standard value, other value

Subsections 15.50.5 and 15.50.6

A_s	cross-sectional area of drop
E	collection efficiency
F_w	flux of pollutant to surface
J_o	equivalent rainfall rate
k	concentration of pollutant in rainwater (mass per unit volume)
k'	concentration of pollutant in rainwater (mass per unit mass)
N_s	number of drops
s	diameter of drop
v_w	wet deposition velocity
v_s	velocity of drop
w	interphase transport rate
W_r	washout ratio
W'_r	washout ratio (alternative formulation)
Z_W	height of wetted plume
Λ	washout coefficient, scavenging coefficient

ρ_a	density of air
ρ_w	density of water
χ	concentration of pollutant in air
χ_e	effective concentration over height of wetted plume

Subscripts

o	reference height
s	drop

Section 15.51

c	concentration (various units)
D	toxic dose (units h)
k	mixing efficiency factor
L	toxic load (units−h)
n	index
R	ratio of indoor to outdoor toxic loads
t	time (h)
t_o	duration of finite outdoor concentration (h)
λ	ventilation rate, ventilation constant (h^{-1})
λ'	effective ventilation rate (h^{-1})

Equation 15.51.18

A	area of aperture (m^2)
k_1	constant
Q	volumetric flow of air (m^3/s)
Δ_p	pressure drop (N/m^2)
ρ_o	density of ambient air (kg/m^3)

Equations 15.51.19−15.51.24

k_2−k_5	constants
m	number of open casement windows
n	number of open top-vent windows
ΔT	temperature difference between outdoors and indoors (°C)
u	wind speed (m/s)
λ	ventilation rate (h^{-1})
λ_b	ventilation rate due to buoyancy (m^3/h)
λ_s	ventilation rate measured at standard conditions (h^{-1})
λ_w	ventilation rate due to wind (m^3/h)

Subscripts

i	indoors
o	outdoors

Section 15.52

D	initial diameter of plume
u_o	velocity of release

Section 15.53

Subsection 15.53.1

As	Section 15.10.8

Subsection 15.53.8

D	diameter of spray cone (m)
F_N	flow number of nozzle (l/s). $(kN/m^2)^{1/2}$)
P_w	pressure of water at nozzle (kN/m^2) (gauge)
Q_a	volumetric flow of air (m^3/s)
Q_w	volumetric flow of water (l/s)
V	velocity of entrained air (m/s)

Subsection 15.53.10

c	entrainment parameter
c_s	entrainment parameter for spray
C	volumetric concentration
c_{FD}	concentration with forced dispersion
c_{ND}	concentration with natural dilution
D	width of spray
FD	forced dispersion effectiveness factor
Q	volumetric rate of release
r	radius of plume
S	surface area of elemental slice of plume
u	velocity of plume
v	vertical velocity in spray
v_a	velocity of air entrained in spary
δV	volume of elemental slice of plume
w	wind speed
x	downwind distance

Subscripts

o	source
1, 2	end of region I, II

Subsection 15.53.11

CR	concentration ration
F_N	flow number (1/ (min $bar^{1/2}$))
K	constant
M	specific momentum flow (m^2/s^3)
M_N	momentum flow number (N s/(s bar))
$u_{1.25}$	wind speed at 1.25 m height (m/s)

Subsection 15.53.18

G	mass flow of gas
Q_a	mass flow of air
S	mass flow of stream

16 FIRE

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The first of the major hazards in a process plant is fire. Fire in the process industries causes more serious accidents than explosion or toxic release, although the accidents in which the greatest loss of life and damage occur are generally caused by explosion. Fire is normally regarded as having a disaster potential less than explosion or toxic release. One of the worst explosion hazards, however, is usually considered to be that of an explosion of a vapour cloud that has drifted over a populated area, and in this case the difference in the number of casualties caused by a flash fire rather than an explosion in the cloud may be relatively small.

Fire is, therefore, a serious hazard. The Second *Report* of the Advisory Committee on Major Hazards (ACMH) (Harvey, 1979b) refers in particular to vapour cloud fires and to the description of fires given by V.C. Marshall (1977a):

> It can be said that such clouds will start to burn around their outer envelopes and will 'lift off' to form fireballs. Such fires are dangerous in the extreme. When formed of hydrocarbons, they are luminous and radiate heat which can cause fatal burns to bystanders and ignite wood and paper; for example, they have been known to set fire to the interior of office blocks. As fireballs rise they produce mushroom clouds, in the stalks of which are formed violent upward convection currents that can suck up and ignite debris, and scatter burning brands over a wide area. Such an occurrence can clearly cause damage far beyond the normal safety distance of what are termed conventional fires.

Vapour cloud, or flash fires and fireballs radiate intense heat that can be lethal. Another lethal effect is the depletion of oxygen in the atmosphere caused by a flash fire. Although the Flixborough disaster was primarily a vapour cloud explosion, a large flash fire in part of the cloud also accompanied the latter and this fire was responsible for some of the deaths that occurred. Flash fires can also do considerable damage to the plant. In buildings, fire is the main threat and can cause great damage as well as loss of life.

In the United Kingdom there are a number of bodies concerned with fire and fire protection. These include the fire services and organizations such as the British Fire Services Association, the professional institutions such as the Institution of Fire Engineers (IFE), the insurance organizations such as the Fire Offices Committee, the research establishments such as the Fire Research Station (FRS) and the educational institutions such as the Fire Protection Association (FPA) and the Department of Fire Engineering at Edinburgh University.

In the United States of America the relevant bodies include: in insurance, the National Board of Fire Underwriters, the Industrial Risk Insurers (IRI) (formerly the Factory Mutual Engineering Corporation (FMEC); in research, the Underwriters Laboratories (UL), the Bureau of Mines (BM) and the Combustion Institute; and in the formulation of codes and research, the National Fire Protection Association (NFPA).

There is a voluminous literature on fire and fire protection. Only a few selected items particularly relevant to process plants can be instanced here. These are *Safety in Petroleum Refining and Related Industries* (Armistead, 1959), *Chemical Fires and Chemicals at Fires* (IFE, 1962), *Fire Protection Handbook* (Vervalin, 1964a, 1973a), *Handbook of Industrial Loss Prevention* (FMEC, 1967), *A Guide to Fire Prevention in the Chemical Industry* (BCISC, 1968/7), *Storage and Handling of Petroleum Liquids: Practice and Law* (Q.R. Hughes, 1970), *Background Notes on Fire and its Control* (FPA, 1971/14), *Heat Transfer in Fires* (Blackshear, 1974), *Manual of Firemanship* (Home Office, 1974–), *An Introduction to Fire Dynamics* (Drysdale, 1985) and *Fire Protection Handbook* (NFPA, 2003).

Information on numerous aspects of fire and fire protection is given in the FPA *Compendium of Fire Safety Data Sheets* (1974–), which covers the following topics. Volume 1: (1) organization of fire safety and (2) management of fire risks. Volume 2: (3) industrial and process fire safety and (4) occupancy fire safety. Volume 3: (5) housekeeping and general fire precautions and (6) nature and behaviour of fire. Volume 4: (7) information sheets on hazardous materials. Volume 5: (8) fire protection equipment and systems, (9) security precautions and (10) arson. Volume 6: (11) design guides and (12) building products.

A relevant standard is BS 5908: 1990 *Code of Practice for Fire Precautions in Chemical Plant*. This contains the following sections:

(1) general;
(2) legal requirements;
(3) principles of initiation, spread and extinction of fire;
(4) site selection and layout;
(5) buildings and structures;
(6) storage and movement of materials;
(7) design of process plant;
(8) operation of process plant;
(9) maintenance of process plant;
(10) fire prevention;
(11) fire defence;
(12) works fire brigades;
(13) classification of fires and selection of extinguishing media;
(14) fixed fire fighting systems;
(15) portable and transportable appliances;
(16) organization of emergency procedures.

Most of these aspects are considered in the present chapter, but some are dealt with elsewhere, notably legal aspects, plant siting and layout, storage, maintenance and emergency procedures, which are treated in Chapters 3, 10, 22, 21 and 24, respectively.

US codes include the National Fire Codes of the NFPA. A selection of the codes relevant to process plant is given in Appendix 27.

Selected references on fire, prevention, protection and control are given in Tables 16.1 and 16.2, respectively. In addition, many of the publications listed in Appendices 27 and 28 are concerned with fire.

16.1 Fire

16.1.1 The combustion process

Fire (or combustion) is a chemical reaction in which a substance combines with oxygen and heat is released. Usually, fire occurs when a source of heat comes into contact with a combustible material. If a combustible liquid or solid is heated it evolves vapour and if the concentration of vapour is high enough, it forms a flammable mixture with oxygen in the air. If this flammable mixture is then heated further to its ignition point, combustion starts. Similarly, a

Table 16.1 *Selected references on fire*

FRS (Appendix 28); NRC (Appendix 28 *Fire, Fire Protection*); von Schwartz (1904–); McCarthy (1943); Smart (1947); Cameron (1948); Spiers (1950); Prentiss (1951); Bowden (1953); Spalding (1955); Wise and Agoston (1958); Simms, Hird and Wraigh (1960); B. Lewis and von Elbe (1961, 1987); FPA (1965 CFSD NB4, 1965/4, 1971/14, 1988 CFSD NB2, 1989 CFSD NB1); Risinger (1964a–f,hj); Vervalin (1964a, 1966, 1972a, 1973a,g, 1975a,f); F.A. Williams (1965); Zabetakis (1965); Waugh (1966); FMEC (1967); W.B. Howard (1970b); Custer (1972); de Ris, Kanury and Yuen (1973); Sylvia (1973); Home Office (1974– *Manual of Firemanship*); Ottoson (1974); Raj and Kalelkar (1974); Skramstad (1974); Wharry and Hirst (1974); Eisenberg, Lynch and Breeding (1975); AIChE (1976/69); Drysdale (1976b, 1985); Kletz (1976h, 1979a); Rasbash (1977a, 1979/80); Stull (1977); R. King and Magid (1979); Lock (1979); Solomon (1980); P.H. Thomas (1980); J.G. Marshall and Rutledge (1982); Pantony and Smith (1982); Tsuchiya (1982); ASME (1983/52); Hofinan (1983); Hottel (1984); BRE (1985 BR 60); Schultz (1985); Babrauskas (1986a); Kuo (1986); de Ris (1986); Harmathy and Mehaffey (1987); Emms (1988); Bagster and Pitblado (1989); ILO (1989); J.B. Moss (1989); Mudan (1989b); C.D. Woodward (1989); V.C. Marshall (1990b); Pineau *et al.* (1991); CPD (1992a,b); Carhart (1994) BS 5908: 1980

Fire statistics, fire costs (***see also*** **Table 2.1**)
BIA (annual report, 1975); Anon. (1960–61); Chandler (1969); BRE (1970–, UK Fire and Loss Statistics); CIA (1970/3); FRS (1972 Fire Res. Notes 910, 920, 1973 Fire Res. Notes 978, 981, 1974 Fire Res. Note 1011); H.D. Taylor and Redpath (1971); Vervalin (1972c, 1973d, 1974a, 1975c, 1976b, 1977, 1978a,b); Anon. (1974e,g,m); Tovey (1974); Duff (1975); Fry (1975); Redpath (1976); Rutstein (1979b); Rutstein and Clarke (1979); Beard (1981/82); Ramachandran (1982, 1988); Anon. (1983h)

Fire rating
UL (n.d./b); Dow Chemical Co. (1964, 1966a,b, 1976, 1980, 1987, 1994); Law (1991)

Fire properties of materials, fire tests (***see also*** **Tables 8.1, 11.1, 11.18, 16.3, 17.2 and 17.62**)
BRE (n.d./4–6, 1974 CP 91/74, 1975 CP 36/75); SMRE (Fire 1, 3, 6); Burgoyne and Richardson (1948); Burgess and Zabetakis (1962 BM RI 6099, 1964); IFE (1962, 1972); Madorsky (1964); Risinger (1964a,c,d,h); W.S. Wood (1965); Mansfield (1969); Hilado (1970, 1973); W.B. Howard (1970b); FPA (1971 /14, 15, 1974/22, 1986– CFSD H series NFPA (1972/9, 2000 NFPA 30, 2001/704, 1991/27, 1992 NFPA 49, 325M, 491M, 445); Woinsky (1972); DOT, CG (1974a,b); Rasbash (1975b); Groothuizen and Romijn (1976); Tewarson and Pion (1976); Kletz (1977i); Dokter (1985a); W.J. Bradford (1986a); Clarke (1986b); M.F. Henry (1986); UL (1986 UL 723); Walls (1986); Wharton (1990); BS 476: 1970–
Calorific value of wood: Goldfinger (1949); A.F. Roberts (1964, 1967b, 1971c); Allan, Cameron and Lambie (1966); Brenden (1967); Hsiang-Cheng Kung and Kalelkar (1973)
Oxygen index: Fenimore and Martin (1966); Abbott (1974)

Solids fires
F.R. Steward (1964, 1971); Kanury and Blackshear (1970); Havens *et al.* (1972); Kanury (1972a–c); Annamali and Durbetaki (1975); W.A. Gray (1979); Vovelle, Mellottee and Delbourgo (1982); Vovelle, Akrich and Delfau (1984); Wichman and Atreya (1987); Wichman and Agrawal (1991); Janssens (1991).

Crib and rack fires
FRS (Fire Res. Note 600); Fons, Clements and George (1963); P.H. Thomas, Simms and Wraight (1964, 1965); P.H. Thomas (1965b); Hsiang-Cheng Kung (1972); Hsiang-Cheng Kung and Kalelkar (1973); Hsiang-Cheng Kung and Hill (1975–); Delichatsios (1976); Emori and Saito (1983); Tewarson (1985); You and Kung (1985); Carrier, Fendell and Wolff (1991); Wolff, Carrier and Fendell (1991)

Free-burning fires, fire plumes
P.H. Thomas (1963); Emmons (1965); B.R. Morton (1965); P.H. Thomas, Baldwin and Heselden (1965); Huffman, Welker and Sliepcevich (1967); Block (1971); S.L. Lee and Otto (1975); G. Cox and Chitty (1980); Heskestad (1981, 1989); Kung and Stavrianidis (1982); Babrauskas (1986a); Zonato *et al.* (1993)
Large area fires: Muraszew, Fedele and Kuby (1979); T.Y. Palmer (1981); Carrier, Fendell and Feldman (1984); R.O. Weber (1989); Heskestad (1991); D.A. Carter (1992); Ghoniem *et al.* (1993); Fendell and Mitchell (1993); Weihs and Small (1993); Husain (1995)
Small area fires: Heikes, Ransohoff and Small (1990)
Subterranean fires: BRE (1989 IP3/98)

Metals fires
Steinberg, Wilson and Benz (1992); Classman (1993)

Propellant fires
Grumer *et al.* (1961)

Fires in buildings, warehouses
Kawagoe (1958); P.H. Thomas and Heselden (1962); FRS (1963 Fire Res. Tech. Pap. 5, 1966 Fire Res. Tech. Pap. 15, 1975 Fire Res. Note 1029); Kawagoe and Sekine (1963); P.H. Thomas (1963, 1973b, 1981a,b, 1982); P.H. Thomas *et al.* (1963); Roth (1964); Thomas and Hinckley (1964); P.H. Thomas, Simms and Wraight (1964, 1965); FMEC (1967); Waterman (1968); Law (1971, 1991); Langdon-Thomas (1967a,b, 1972); FPA (1970/9, 13, 1971/14, 1973/20, 21, 1982 CFSD FS 6017); P.H. Thomas and Law (1972, 1974); Butler, Martin and Wiersma (1973); BRE (1974 CP 30/74, CP 32/74, CP 43/74, 1978 CP 40/78); Hagglund, Jansson and Onnemark (1974); Rasbash (1974a, 1991); Croce (1975); Fang (1975); HSE (1975 TON 29); Prahl and Emmons (1975); Quintiere (1975, 1979, 1983); Petterson, Magnusson and Thor (1976); Rockett (1976); Ove Arup (1977); Theobald (1977); P.H. Thomas and Theobald (1977); Babrauskas and Williamson (1978); Bullen (1978); Quintiere, McCaffrey and Kashiwaga (1978); Bullen and Thomas (1979); Butcher and Parnell (1979); Emmons (1979); P.H. Thomas and Bullen (1979/80); Babrauskas (1981, 1986c); D.S. Baker (1981); McCaffrey, Quintiere and Harkleroad (1981); Siu (1982); Drysdale (1985); Lawson and Quintiere (1985); Steckler, Baum and Quintiere (1985); Beyler (1986); Budnick and Evans (1986); Budnick and Walton (1986); Shields and Silcock (1987); Anon. (1988 LPB 84); Ho, Siu and Apostolakis (1988); Jaluria and Kapoor (1988); Rabinkov (1988); Heskestad and Delichatsios (1989); Lockwood and Malalasekera (1989); Peacock and Bukowski (1990); Brandyberry and Apostolakis (1991a,b); Peacock and Babrauskas (1991); Babrauskas and Peacock (1992); N.R. Marshall and Morgan (1992); McCaughey and Fletcher (1993); Melinek (1993a); Pagella and de Faveri (1993);

Chamberlain (1994); Comitis, Glasser and Young (1994).
Warehouses: Barthelemy and Lamboley (1978); Isman (1978); G.T. Atkinson, Jagger and Kirk (1992); D.A. Carter (1992); G.T. Atkinson and Jagger (1994); Christiansen (1994); Smith-Hansen (1994)

Ventilated fires
Tewarson and Steciak (1983); Alvares, Foote and Pagni (1984); Chippett (1984); Mitler (1984)

Smoke
Hilado and Kosola (1977); Rasbash and Drysdale (1982); Fothergill (1984); Marchant (1984); Drysdale (1985); Heskestad (1986); Savilonis and Richards (1988); Gross (1991); Delichatsios (1993a); Ghoniem *et al.* (1993); Kandola and Morris (1994)

Brands from fires
Shao-Iin Lee and Hellman (1969, 1970)

Decomposition products of fires (***see also*** **Table 18.1**)
FRS (1972 Fire Res. Note 913, 947, 951, 1973 Fire Res. Note 966, 1975 Fire Res. Note 1025, 1976 Fire Res. Note 1048); Rasbash (1969b); Hilado (1970, 1973); FPA (1971/14, 1989 CFSD N3); BRE (1974 CP5/74, CP 11/74, CP12/74, CP 91/74, 1976 CP 22/76); Woolley and Raftery (1976); Hilado and Kosola (1977); Chisnall (1978); Einhorn and Grunnet (1978); Hilado, Cumming and Casey (1978); Hilado and Huttlinger (1980, 1981a,b); Herpol and Vandervelde (1981/82); Woolley and Fardell (1982); Landrock (1983); Kaplan and Hartzell (1984); Hartzell, Packham *et al.* (1985); Hartzell, Priest and Switzer (1985); Hartzell, Stacy *et al.* (1985); Alexeeff *et al.* (1986); Delumyea, Moore and Morgan (1986); Doe *et al.* (1986); Pollock, Campbell and Reid (1986); Tsuchiya and Nakaya (1986); Hartzell, Grand and Switzer (1987); M.T. Mills (1987); van Loo and Opschoor (1989); Hartzell (1989); CPD (1992b)
Warehouses: G.T. Atkinson, Jagger and Kirk (1992); D.A. Carter (1992); Smith-Hansen and Jorgensen (1993); G.T. Atkinson and Jagger (1994); Christiansen (1994); Smith-Hansen (1994)

Oil slick fires
Brzustowski and Twardus (1982)

Fires in process plants
H.R. Brown (1956 BM RI 5198); IFE (1962); Vervalin (1964a, 1973a); Zabetakis (1965); H.S. Robinson (1968); Hearfleld (1970, 1974); FPA (1971/14); Bland and Beddow (1974); Rasbash (1974b); Kletz (1978c, 1979a, 1988d); Kanury (1981); A.F. Roberts (1981/82); Considine, Grint and Holden (1982), BS 5908: 1980
Cable fires: FPA (1974a); Anon. (1980c); Anon. (1981 LPB 41, p. 5); B.F. Gray *et al.* (1990)
Duct fires: A.F. Roberts and Kennedy (1965); A.F. Roberts, Clough and Blackwell (1966); A.F. Roberts and Clough (1967a,b); de Ris (1970); A.F. Roberts (1971a); Wilde (1972); Church (1978); Lovachev (1978a); Anon. (1979 LPB 30, p. 55); C.K. Lee, Chaiken and Singer (1979); Hunter and Favin (1981); Brandeis and Bergman (1983); Newman and Tewarson (1983); Krupper (1991)
Flange fires: McFarland (1969)
Hydraulic accumulator fires: HSE (SIR 9)
Iron-chlorine fires: Anon. (1991 LPB 98, p. 25)
Lagging fires: P.H. Thomas and Bowes (1961b, 1967); Petkus (1963, 1964); Darling (1967); Lindner and Seibring (1967); Bowes and Langford (1968); Bowes (1974a, 1976); BRE (1974 CP 35/74); Gugan (1974a); Anon. (1977 LPB 17, p. 2); Buch and Filsinger (1985); Britton (1991); Craig (1993 LPB 110)
Pump fires: Kletz (1971); Fromm and Rail (1987b)
Transport: NFPA (2002/10)

Tank fires, including boilover, frothover
Burgoyne and Katan (1947); Burgoyne (1950, 1952); Laney (1963, 1964); Risinger (1964b,f); Herzog (1974); OIA (1974 Loss Inf. Bull. 400–2); Yumoto (1977); Brotz and Schonbucher (1978); Lois and Swithenbank (1979); Viergas, Campos and Oliviera (1984); Broekmann and Schecker (1992); Inamura, Saito and Tagavi (1992); Michaelis, Mavrothalassitis and Pinjeau (1992); Palmer (1992 LPB 106); Purdy, Pitblado and Bagster (1992)
Bitumen tank fires: Anon. (1991 LPB 102, p. 35)

Fires in liquids, leakages and spillages
Rasbash (1956, 1970a); Burgoyne, Roberts and Quinton (1968); Burgoyne and Roberts (1968a,b); Leroy and Johnson (1969); FPA (1971/14); Wilde and Curzon (1971); Stark (1972); A.F. Roberts (1975a); Kletz (1976b); Anon. (1980d,k); Crawley (1982); Toa and Kaviany (1991)

Fire models
Considine (1981); Simpson and Taylor (1984 SRD R276); Drysdale (1985); A.D. Davies (1987); Beard (1992a,b); P.H. Thomas (1992, 1993); Nam and Bill (1993)

Flames
NRC (Appendix 28 *Combustion*); Flamm and Mache (1917); Mache (1918); Bone and Townend (1927); Burke and Schumann (1928a,b); Bone and Newitt (1929); Jahn (1934); B. Lewis and von Elbe (1937, 1938, 1943, 1951, 1961, 1987); Jost (1939, 1946); Forsyth and Garside (1949); Hawthorne, Weddel and Hottel (1949); Hottel (1949, 1953); Hottel and Hawthorne (1949); Scholefield and Garside (1949); G.C. Williams, Hottel and Scurlock (1949); Wohl, Kapp and Gazley (1949); Thring (1952); Gaydon and Wolfhard (1953–); Gerstein (1953); Grove and Walsh (1953); Karlovitz (1953); Karlovitz *et al.* (1953); Wohl (1953); R. Friedman and Burke (1955); Grumer, Harris and Rowe (1956 BM RI 5225); Barnett and Hibbard (1957); Fristrom (1957); Spalding (1957a, 1963a, 1976); Berlad and Yang (1959); van Krevelen and Chermin (1959); Kydd (1959); Prudnikov (1959); Sundukov and Predvoditelev (1959); Zeldovitch and Barenblatt (1959); Westenberg and Favin (1960); Cekalin (1962); Menkes (1962); Potter, Heimel and Butler (1962); Yamazaki and Tsuji (1962); Markstein (1964); Fristrom and Westenberg (1965); Khitrin *et al.* (1965); H. Phillips (1965); Shchelkin and Troshin (1965); Wiebelt (1966); Essenhigh (1967); Gaydon (1967); J.N. Bradley (1969); Edmondson and Heap (1969); Gunther (1969); F. Powell (1969); Hearfield (1970); Emmons (1971); Werthenbach (1971a,b); Fox and Sarkar (1972); Ballal and Lefebvre (1973, 1975c); Chomiak (1973); H.B. Palmer and Beer (1973); Afgan and Beer (1974); Barnes and Fletcher (1974); R.O. Parker (1974); Eisenberg, Lynch and Breeding (1975); Kanury (1975); Modak (1975, 1978/79); Gugan (1976); Stambuleanu (1976); A. Williams (1976); G. Cox (1977); Classman (1977); Goodger (1977); Kaptein and Hermance (1977); Lockwood (1977); J.G. Marshall (1977); Lockwood and Syed (1979); Chandra and Davis (1980); Albini (1981); D. Bradley (1982); Buckmaster and Ludford (1982); Ishikawa (1982); Pong Chung and Smith (1982); Jeng, Chen and Feath (1982);

W.P. Jones and Whitelaw (1982); S.T. Lee and Tien (1982); Takahashi, Mizomoto and Ikai (1982); F.A. Williams (1982); Heskestad (1983a,b, 1984); Clavin (1984); Ramohalli, Jones and Bashar (1984); Hertzberg (1985); R.S. Levine (1985); Tune and Venart (1984/5a,b); Zukoski, Cetegen and Kubota (1985); Law (1989); Schefer, Namazian and Kelly (1989); Adiga *et al.* (1990); Carriere *et al.* (1991); Dixon-Lewis (1991); Kennel, Gottgens and Peters (1991); P.M. Thomas (1993)

Premixed flames
Burgess (1962 BM Bull. 604); S.B. Reed (1967, 1971); Vinckier and van Tiggelen (1968); Basu and Bhaduri (1972); N.J. Brown, Fristrom and Sawyer (1974–); Vance and Krier (1974); Lockwood (1977); Strehlow and Savage (1978); Bray, Champion and Libby (1989); Searby (1992); Duclos, Veynante and Poinsot (1993)

Diffusion flames
Wohl, Kapp and Gazley (1949); Barr (1953); H.N. Powell (1955); Sunavala, Hulse and Thring (1957); Schmitz (1967); Bilger (1975, 1976, 1977); Suris, Flankin and Shoring (1977); Kalghatgi (1981–); Chakravarty, Lockwood and Sinicropi (1984); Birch *et al.* (1988); Birch and Margrave (1989); Delichatsios and Orloff (1989); de Faveri *et al.* (1989); Chao, Law and Tien (1991)
Laminar diffusion flames: Burke and Schumann (1928a,b); Savage (1962)
Turbulent diffusion flames: F.R. Steward (1970); Brzustowski (1973); Kent and Bilger (1973); Chigier and Strokin (1974); Brzustowski, Collahalli and Sullivan (1975); Markstein (1976); Lockwood (1977); Tamanini (1977); Becker and Liang (1978); Becker and Yamazaki (1978); Pergament and Fishburne (1978); Heskestad (1983a); Nguyen and Pope (1984); Bilger (1989); Annaruma, Most and Joulain (1991); D.A. Smith and Cox (1992); Blake and McDonald (1993)
Turbulent jet diffusion flames: Baron (1954); Sunivala, Hulse and Thring (1957); Bilger (1976); Onuma and Ogasawara (1977); Peters and Williams (1983); Kalghatgi (1984); Pitts (1989); Delichatsios (1993b)
Buoyant diffusion flames! P.H. Thomas, Webster and Raftery (1961); Putnam and Grinberg (1965); P.H. Thomas, Baldwin and Heselden (1965); Masliyah and Steward (1969); Steward (1970); Delichatsios and Orloff (1985)
Flame regime intermediate between premixed and diffusion conditions: Talley (1992)

Radiant heat transfer, fire spread
BRE (n.d./2–4, 1974 CP 29/74, CP 72/74); FRS (Appendix 28, F3, F4, Fire Res. Special Rep. 2, 1961 F1, 1963 Fire Res. Tech. Pap. 5, 1966 F6, F8, 1972 Fire Res. Note 921); Lawson and Simms (1952a,b); McAdams (1954); Eckert and Drake (1959); Kreith (1962); Sparrow (1962); Sparrow and Cess (1966, 1978); Law (1969); Hearfield (1970, 1974); FPA (1971/14); Langdon-Thomas (1972); Siegel and Howell (1972, 1991); Sirignano (1972); P.H. Thomas and Law (1972, 1974); Blackshear (1974); L.E. Brown, Wesson and Welker (1974a,b, 1975); Fernandez-Pello and Williams (1974, 1977); W.A. Gray and Muller (1974); Kovacs and Honti (1974); Alpert (1975); Eisenberg, Lynch and Breeding (1975); Feng, Williams and Kassoy (1975); Craven (1976); Groothuizen and Romijn (1976); Klootwijk (1976); Nakakuki (1976); Rasbash (1976c); R.B. Robertson (1976b); Feng and Sirignano (1977); Straitz and O'Leary (1977); Yumoto (1977); HSE (1978b); Modak (1979); D.C. Bull *et al.* (1980); Carrier, Fendell and Feldmann (1980); F.R.S. Clark (1981); Anon. (1984 LPB 56, p. 11); Harmathy (1985); Modest (1993)
Flame radiation: Hottel and Mangelsdorf (1935); Hottel and Smith (1935); Hottel and Egbert (1941, 1942); Daly and Sutherland (1949); Hottel, Williams and Satterfleld (1949); Cassel, liebman and Mock (1957); Foster and McGrath (1960); D.K. Edwards (1963); Siddall and MacGrath (1963); Echigo, Nishiwaki and Hirata (1967); Hottel and Saroflm (1967); R.K. Smith (1967); Tien (1968); Beer and Howarth (1969); Dalzell and Saroflm (1969); Godridge and Hammond (1969); Masliyah and Steward (1969); Sato *et al.* (1969); Dalzell, Williams and Hottel (1970); Leckner (1971, 1972); Lowes and Newall (1971); J.M. Jones and Rosenfeld (1972); Thring and Lowes (1972); Felske and Tien (1973, 1974a,b); C.S. Kelly (1973); N.K. King (1973); Cess (1974); Markstein (1974, 1976, 1977, 1985, 1989); P.B. Taylor and Foster (1974, 1975); C.K. Lee (1975); W.A. Gray, Kilham and Muller (1976); Yuen and Tien (1977); Fishburne and Pergament (1979); Orloff, Modak and Markstein (1979); de Ris (1979); Wagner (1979); Calcote (1981); Ganapathy (1981); Grosshandler and Modak (1981); Orloff (1981); Vervisch, Puechberty and Mohamed (1981); Becker and Liang (1982); Tien and Lee (1982); Coppalle and Vervisch (1983); Frenklach, Taki and Matula (1983); Vervisch and Coppalle (1983); Gill and Olson (1984); Brosmer and Tien (1986); Raparotte and Brzustowski (1986); E.B. Cohen and Taylor (1987); MHAP (1988 LPB 82); Mudan (1989b); Hamins *et al.* (1991); Orloff, de Ris and Delichatsios (1992)
Radiant heat factor: A.F. Roberts (1981/82); Hymes (1983 SRD R275)
Soot: Mie (1908); Arthur and Napier (1955); Schalla and McDonald (1955); Tesner, Robinovitch and Rafalkes (1962); A. Thomas (1962); Yagi and lino (1962); Bonne, Homann and Wagner (1965); Narasimhan and Foster (1965); Homann (1967); Kunugi and Jinno (1967); McLintock (1968); Fenimore and Jones (1969); J.B. Howard (1969); Columbo and Thring (1972); Feugier (1972); Wersborg, Howard and Williams (1973); Muller-Dethlefs and Schlader (1976); Becker and Yamzaki (1977); Prado *et al.* (1977); Orloff, Modak and Markstein (1979); Wagner (1979); Classman and Yaccarino (1981); S.C. Lee and Tien (1981); Pong Chung and Smith (1982); Sen and Ludford (1982); Homan (1983); Santoro, Semerjian and Dobbins (1983); Senkan, Robinson and Gupta (1983); Takahashi and Classman (1984); Hirschler (1985); Kent and Wagner (1985); K.Y. Lee, Zhong and Tien (1985); R.S. Levine (1985); Markstein (1985, 1989); Pagni and Okoh (1985); Santoro and Semerjian (1985); Delumyea *et al.* (1986); Kent and Honnery (1987, 1991); Classman (1989); Giilder (1989); McCaffrey and Harkleroad (1989); Megaridis and Dobbins (1989); J.B. Moss (1989); Honneiy and Kent (1990, 1992); I.M. Kennedy, Kollman and Chen (1990); Leung, Lmstedt and Jones (1991); C.D. Stewart, Syed and Moss (1991); Syed, Stewart and Moss (1991); Fairweather *et al.* (1992); Smedley, Williams and Bartle (1992); Coppalle and Joyeux (1993); Chamberlain (1994)
View factor: Hottel (1930, 1931, 1954); Hamilton and Morgan (1952); McGuire (1953); McAdams (1954); Coulson and Richardson (1955–, 1977–); Rogers and Mayhew (1957); Eckert and Drake (1959); Bird, Stewart and Lightfoot (1960); Chandrasekhar (1960); C.O. Bennett and Myers (1962); Sparrow (1962); Sparrow, Miller and Johnson (1962); Dunkle (1963); Kourganoff (1963); Feingold (1966); Sparrow and Cess (1966, 1978); Hottel and Sarofim (1967); Grier (1969); Rein, Sliepcevich and Welker (1970); Chung and Sumitra (1972); Merriam (1972); Siegel and Howell

(1972); Ozisik (1973); Raj and Kalelkar (1974); Minning (1977); Becker (1980a,b); Chung and Naraghi (1981); Howell (1982); Mecklenburgh (1985); Tune and Venart (1984/85a,b); Crocker and Napier (1986, 1988a,b); Napier and Roopchand (1986); Mudan (1987, 1989b); Wong and Steward (1988); B.C. Davis and Bagster (1989–); Bagster and Davies (1990); Beard *et al.* (1993); CPD (1992a); CCPS (1994/15)
Atmospheric transmissivity: R.O. Parker (1974); Glasstone and Dolan (1980); Horvath (1981); Lihou and Maund (1982); Hymes (1983 SRD R275); Considine (1984 SRD R297); Simpson (1984 SRD R304); Babrauskas (1986b); R.C. Henry (1987); V.C. Marshall (1987); Wayne (1991); CPD (1992a) CCPS (1994/15)

Flames on pools, pool fires
Rasbash (1956); Blinov and Khudiakov (1957); Hottel (1958); Rasbash, Rogowski and Stark (1960); Burgess, Strasser and Grumer (1961); Fons (1961); Magnus (1961); Welker and Sliepcevich (1965, 1966); Agoston (1962); Burgess and Grumer (1962); Burgess and Zabetakis (1962 BM RI 6099); Spalding (1962); P.H. Thomas (1963); P.H. Thomas, Pickard and Wraight (1963); Pipkin and Sliepcevich (1964); Akita and Yumoto (1965); Atallah (1965); Welker, Pipkin and Sliepcevich (1965); Corlett and Fu (1966); A.F. Roberts (1966, 1971b); Corlett (1968, 1970); Classman and Hansel (1968); Canfield and Russell (1969); Classman, Hansel and Eklund (1969); Huffman, Welker and Sliepcevich (1969); Masliyah and Steward (1969); B.D. Wood and Blackshear (1969); Hearfield (1970); ICI/RoSPA (1970 IS/74); Murad *et al.* (1970); Akita and Fujiwara (1971); Hillstrom (1971); Torrance (1971); B.D. Wood, Blackshear and Eckert (1971); Yumoto (1971b); Chetty and Voinov (1972); A.R. Hall (1972); de Ris and Orloff (1972); Hertzberg (1973); C.S. Kelly (1973); Nakakuki (1973, 1974a,b, 1976); A.F. Roberts and Quince (1973); Dayan and Tien (1974); Duffy, Gideon and Puttnam (1974); Fu (1974); P. Nash (1974a); Dehn (1975); Escudier (1975); Hirano and Kinoshita (1975); Craven (1976); Dow Chemical Co. (1976); MITI (1976); Brotz, Schonbucher and Schable (1977); Modak (1977, 1981); Modak and Croce (1977); Yumoto, Takahashi and Handa (1977); Alger *et al.* (1979); NASA (1979); Raj, Moussa and Aravamudan (1979a,b); Anon. (1980d,k); Classman and Dryer (1980/81); Mizner (1981); Mizner and Eyre (1982); Dinenno (1982); Hsiang-Cheng Kung and Stavrianidis (1982); Kletz (1982h); Moorhouse (1982); Moorhouse and Pritchard (1982); Orloff and de Ris (1982); Pantony and Smith (1982); Sher (1982); Babrauskas (1983, 1986b); Cline and Koenig (1983); Mudan (1984c, 1989b); Santo and Delichatsios (1984); Shinotake, Koda and Akita (1985); Webber (1985 SRD R325); Croce and Mudan (1986); Crocker and Napier (1986); Frank and Moieni (1986); Uguccioni and Messina (1986); Brosmer and Tien (1987); Delichatsios (1987, 1988, 1993a,b); Fischer, Hardouin-Duparc and Grosshandler (1987); Nishio and Machida (1987); Fischer (1988); Koseki and Yumoto (1988); Adiga *et al.* (1989); Bagster and Pitblado (1989); Bouhafld, Vantelon, Soudil *et al.* (1989); Bouhafid, Vantelon, Joulain *et al.* (1989); Fischer and Grosshandler (1989); Koseki (1989); Koseki and Hayasaka (1989); J.B. Moss (1989); Schneider and Kent (1989); Seung Wook Back and Chan Lee (1989); Arpaci and Selamet (1991); Holen, Brostrom and Magnussen (1991); Koseki and Mulholland (1991); Pineau *et al.* (1991); Ditali, Rovati and Rubino (1992); Hayasaki, Koseki and Toshiro (1992); Inamura, Saito and Tagavi (1992); Klassen *et al.* (1992); Lautkaski (1992); Mangialavori and Rubino (1992); Schonbucher, Gock and Fiala (1992); Cetegen and Ahmed (1993)
LNG fires: HSE/SRD (HSE/SRD/WP 34); Welker, Wesson and Sliepcevich (1969); Hoult (1972a); Atallah and Raj (1973); Fay (1973); May and McQueen (1973); Welker (1973, 1982); Opschoor (1975a,b); Raj and Atallah (1975); Stannard (1977); Raj, Moussa and Aravamulan (1979); Schneider (1980); Blackmore, Eyre and Summers (1982); Ermak, Koopman *et al.* (1982); Mizner and Eyre (1982); Croce, Mudan and Wiersma (1986); Napier and Roopchand (1986); Rosenblatt and Hassig (1986); A.D. Johnson (1992)
LPG fires: Rasbash (1979/80); Blackmore, Eyre and Summers (1982); Mizner and Eyre (1982)
Pool fires on water: A.D. Little (1979); Mizner and Eyre (1983); Arai, Saito and Altenkirch (1990); Alramadhan, Arpaci and Selamet (1991)
Pool fires in enclosures: Tatem *et al.* (1986)
Fires on wicks: Burgoyne, Roberts and Quinton (1968); Toa and Kaviany (1991)

Trench fires
Welker (1965); Alger and Capener (1972); Gollahalli and Sullivan (1974); Mudan and Croce (1984); Croce, Mudan and Wiersma (1986); D.A. Smith (1992)

Fire engulfment, including directed jets
Chichelli and Bonilla (1945–); L.H. Russell and Canfield (1973); C. Anderson *et al.* (1974); Charles (1974); Charles and Norris (1974); Borgnes (1979a,b); Borgnes and Karlsen (1979); Birk and Oosthuize (1982); J.M. Wright and Fryer (1982); Heitner, Trautmanis and Morrissey (1983a,b); Hunt *et al.* (1983 SRD R240); A.F. Roberts, Cutler and Billinge (1983); Solberg and Borgnes (1983); Sousa and Venart (1983); Nylund (1984); Droste *et al.* (1984); Schulz-Forberg, Droste and Charlett (1984); Venart *et al.* (1984); Tune and Venart (1984/85a); Grolmes and Epstein (1985); Moodie, Billinge and Cutler (1985); Siddle (1986); Aydemir *et al.* (1988); Bainbridge and Keltner (1988); Beynon *et al.* (1988); Birk (1988, 1989); Droste and Schoen (1988); Moodie (1988); Moodie *et al.* (1988); Ramskill (1988); Venart *et al.* (1988); Venart *et al.* (1989); Dancer (1990); Hadjisophocleous, Sousa and Venart (1990); Tanaka *et al.* (1990); Bennet *et al.* (1991); Cowley and Pritchard (1991); Crespo *et al.* (1991); Verheif and Duijm (1991); Giselle and Krause (1992); Hernandez and Crespo (1992); Duijm (1994)
Fireballs, BLEVEs (*see also* Table 17.36)
Gayle and Bransford (1965); van Nice and Carpenter (1965); R.W. High (1968); Bader, Donaldson and Hardee (1971); Patterson *et al.* (1972); Hardee and Lee (1973, 1975, 1977–78); MLTI (1976); Fay and Lewis (1977); Hasegawa and Sato (1977, 1978); V.C. Marshall (1977a, 1987); Maurer *et al.* (1977); Hardee, Lee and Benedick (1978); HSE (1978b, 1981a); A. Baker (1979); Fay, Desgroseillers and Lewis (1979); Harvey (1979b); R.C. Reid (1979); Appleyard (1980); Gillette (1980); Mallory (1980); Aravamudan and Desgroseillers (1981); Kletz (1981n); A.F. Roberts (1981a,b, 1981/82, 1982); Considine, Grint and Holden (1982); Crawley (1982); Moorhouse and Pritchard (1982); Williamson and Mann (1981); Lihou and Maund (1982); Pantony and Smith (1982); Ursenbach (1983); Martinsen (1984); D.L.M. Hunt and Ramskffl (1985); Kohler (1985); Pietersen (1985); Tune and Venart (1984/5a,b); Blything (1986); Hirst (1986); Roper *et al.* (1986); Bagster and Pitblado (1989); J.B. Moss (1989); Buckmaster, Joulin and Ronney (1991); Pineau *et al.* (1991); Satyanarayana, Borah and Rao (1991); Buckmaster,

Gessman and Ronney (1992); Buckmaster and Joulin (1993); Buckmaster, Smooke and Giovangigli (1993); Prugh (1994)

Vapour cloud fires, flash fires
Kletz (1971); Eisenberg, Lynch and Breeding (1975); Fay and Lewis (1975, 1977); Raj and Emmons (1975); A.D. Little (1979); Hogan (1982); Rodean *et al.* (1984); Roper, Arno and Jaggers (1991); Seshadri, Berlad and Tangirala (1992); CCPS (1994/15)

Jet flames
Hawthorne, Weddell and Hottel (1949); Hottel and Hawthorne (1949); Hottel (1953); Thring and Newby (1953); Goldburg and Sin-I Cheng (1965); Chervinsky and Manheimer-Timnat (1969); Hoehne, Luce and Miga (1970); Guruz *et al.* (1974); Lockwood and Naguib (1975); Becker and Yamazaki (1978); Becker (1980a,b); Kalghatgi (1983); Peters and Williams (1983); Hirst (1984, 1986); Sonju and Hustad (1984); Tune and Venart (1984/85b); Delichatsios and Orloff (1985); de Faveri *et al.* (1985); Hustad and Sonju (1986); McCaffrery and Evans (1986); M.T.E. Smith *et al.* (1986); Beychok (1987b); Chamberlain (1987, 1989); D.K. Cook, Fairweather, Hammonds and Hughes (1987); D.K. Cook, Fairweather, Hammonds and O'Brien (1987); Delichatsios (1987, 1993a); Leahey and Schroeder (1987); Crocker and Napier (1988b); Bagster and Pitblado (1989); Birch *et al.* (1989); Greenberg (1989); Grint (1989); Loing and Yip (1989); J.B. Moss (1989); Mudan (1989b); Tarn and Cowley (1989); Turns and Lovett (1989); J. Cook, Bahrami and Whitehouse (1990); Damiano (1990); R.W. Davis *et al.* (1990); D.A. Carter (1991); D.K. Cook (1991a); Cowley and Pritchard (1991); Fairweather *et al.* (1991); Peters and Gottgens (1991); Arnaud *et al.* (1992); Fairweather, Jones and Linstedt (1992); GollahaUe, Khanna and Prabhu (1992); Vfflermaux and Durox (1992); API (1990 RP 521); Coppalle and Joyeux (1993); Sivathanu and Gore (1993); Duijm (1994); A.D. Johnson, Brightwell and Carsley (1994); C.R. Kaplan *et al.* (1994)

Mist and spray fires
Godsave (1953); Burgoyne and Cohen (1954); J.A. Browning and Krall (1955); Hottel, Williams and Simpson (1955); Kobayasi (1955); Agoston, Wise and Rosser (1957); Bolt and Saad (1957); J.A. Browning, Tyler and Krall (1957); Eraser (1957); Kumagai (1957); F.A. Williams (1959); Reichenbach, Squires and Penner (1962); Rosser (1967); Aldred and Williams (1966); Eisenklam and Arunachalam (1966); Eisenklam, Arunachalam and Weston (1967); Faeth (1967, 1977, 1979, 1983); Polymeropoulos and Peskin (1969); Sioui and Roblee (1969); Lemott, Peskin and Levine (1971); Law and Williams (1972); Mizutani and Nakajima (1973); A. Williams (1973, 1976, 1990); Polymeropoulos (1974, 1984); Kapila, Ludford and Buckmaster (1975); Hayashi and Kumagai (1975); Law (1975); Miyasaki and Mizutani (1975); Polymeropoulos and Das (1975); Yuen and Chen (1976); Sangiovanni and Kesten (1977); Ballal and Lefebvre (1978, 1979, 1981a,b, 1983a,b); Anon. (1980h); Briffa (1981); K.N. Palmer (1983); Yule, Ereaut and Ungut (1983); Pindera and Brzustowski (1984); Sichel and Palinaswamy (1985); Polymeropoulos and Peskin (1989); P.J. Bowen and Shirvffl (1994a,b)

Flames on flares
Ludwig *et al.* (1968); Becker (1980a,b); de Faveri *et al.* (1985); Beychok (1987b); Chamberlain (1987); O.K. Cook *et al.* (1987); D.K. Cook *et al.* (1987); A.D. Johnson, Brightwell and Carsley (1994)

Flames on pipelines
Hoff (1983); Hirst (1984); Chamberlain (1987); D.A. Carter (1991)

Effect of fire on materials, buildings
Kashiwagi (1974, 1976, 1979a,b, 1981); C.S. Kelley (1975); Hymes (1984); J.L. Bryan (1986); Rasbash, Drysdale and Deepak (1986); van Loo and Opschoor (1989); Opschoor, van Loo and Pasman (1992).
Ignition and combustion of wood, cellulose: Bamford, Crank and Malan (1946); Hopkins (1952); E.K. Lawrence (1952); Lawson and Simms (1952a,b); Stout (1952); Garden (1953, 1959); C.C. Williams (1953); Hottel and Williams (1955); S. Martin (1956, 1964, 1965); Akita (1959); Simms (1960, 1961, 1962, 1963); Courteney (1962); A.F. Roberts and Clough (1963); Blackshear and Murty (1965); Weatherford and Sheppard (1965); Lipska (1966); Weatherford and Valtierra (1966); Koohyar (1967); Murty and Blackshear (1967); A.F. Roberts (1967a, 1971d); Simms and Law (1967); Rasbash and Langford (1968); Deverall and Lai (1969); Kosdon, Williams and Buman (1969); A.F. Roberts (1970); W.K. Smith and King (1970); Wesson (1970); Alvares and Martin (1971); Garg and Steward (1971); Panton and Rittmann (1971); Wesson, Welker and Sliepcevich (1971); Kanury (1972a–c); Kashiwagi (1974, 1979a,b, 1980, 1981); Ndubizu and Durbetaki (1978); EPRI (1979b, 1981a); Gelderblom (1980); Vovelle, Mellotee and Delbourgo (1982); Yoshizawa and Kubota (1982); Cullis *et al.* (1983a,b); Wichman and Atreya (1987); Janssens (1991)
Ignition of flammable liquids: Burgoyne and Roberts (1968a); Burgoyne, Roberts and Quinton (1968); Sirignano and Classman (1970); A.F. Roberts and Quince (1973); Kashiwagi (1980); Dorofeev *et al.* (1993)

Flame spread
Kinbari, Endo and Sega (1966); Baldwin (1968); de Ris (1969); Magee and McAlevy (1971); Kanury (1972a); W.J. Parker (1972); Akita (1973); Fernandez-Pello and Williams (1974, 1977); Hirano, Noreikis and Waterman (1974); Alvares (1975); Kashiwagi (1976); Fernandez-Pello (1977a,b, 1984); R. Friedman (1977); F.A. Williams (1977); Hirano and Tazawa (1978); Annamalai and Sibulkin (1979a,b); Fernandez-Pello and Mao (1981); Quintiere (1981); Fernandez-Pello and Hirano (1983); Ray and Classman (1983); Anon. (1984 LPB 56, p. 11); Alpert and Ward (1984); Delichatsios (1985); Drysdale (1985); Takeno and Hirano (1989); Mekki *et al.* (1991); Mitler (1991); Drysdale and Macmfflan (1992); Hirano and Sato (1993)
Flame spread over liquids: Sirignano and Classman (1970); Drysdale (1985); Burgoyne and Roberts (1968a,b); Burgoyne, Roberts and Quinton (1968); MacKinven, Hensel and Classman (1970); Welker, Wesson and Sliepkevich (1971); Torrance and Mahajan (1975); Suzuki and Hirano (1982); Murphy (1985); Hirano and Suzuki (1993)
Flame spread over oil-soaked ground: Ishida (1986, 1988, 1992)

Effect of fire on people
Williams *et al.* (n.d.); Bigelow *et al.* (1945); Henriques (1947); Moritz and Henriques (1947); J.P. Bull and Squire (1949); Buettner (1950, 1951a,b, 1952, 1957); Hardy, Wolff and Goodell (1952); Benjamin (1953); Elder and Strong (1953); Hardy, Jacobs and Meixner (1953); J.P. Bull and Fisher (1954); Hinshaw (1957); Stoll and Greene (1958, 1959); Mixter (1959); Glasstone (1962); Mehta and Wong (1967);

Schlapowksy (1967); Stoll and Quanta (1969, 1971); Graves (1970); J.P. Bull (1971); White (1971); Arnold *et al.* (1973); Denison and Tonkins (1967); Mehta, Wong and Williams (1973); Wulff (1973); Wulff *et al.* (1973); I.F.K Muir and Barclay (1974); Wulff and Durbetaki (1974); Eisenberg, Lynch and Breeding (1975); Lawson and Rasbash (1976); Hardee and Lee (1977/78); Seader and Einhorn (1977); Einhorn and Grunnet (1978); HSE (1978b, 1981a); Artz, Moncrief and Pruit (1979); Carson (1981); Pantony (1981); Williamson and Mann (1981); Crawley (1982); J.W.L. Davies (1982); Hummell (1982); Mecklenburgh (1982, 1985); Anon. (1983e); Hymes (1983 SRD R275, 1984); Kemble (1983); Pietersen (1985); Sutherland (1985); J.L. Bryan (1986); W. Clark and Fromm (1987); Goldin (1987); J.C. Lawrence and Bull (1988); Mudan (1989b); API (1990 RP 521); Boydell (1990 SRD R536); McCarthy (1990); Salisbury (1990); J.C. Lawrence (1991); Pineau *et al.* (1991); CPD (1992b); Opschoor, van Loo and Pasman (1992); CCPS (1994/15); Lees (1994a); Shoemaker (1995) BS 5980: 1980

Hazard assessment
ASTM (1982 STP 762); Budnick (1986); F.B. Clarke (1986a); J.R. Hall (1986); Milke (1986); J.M. Watts (1986); H.E. Nelson (1987); MHAP (1988 LPB 82); FPA (1990 CFSD FPDG 7); Ramachandran (1990c); J.R. Hall and Sekizawa (1991); G.T. Atkinson, Jagger and Kirk (1992); Melinek (1993c); Williamson and Dembsey (1993)

Table 16.2 *Selected references on fire prevention, protection and control*

FIA (n.d.); FPA (Appendix 28, CFSD OR series, 1964/2, 1965/3, 1968/5, 1969/7, 8, 1971/14, 1972/18, 1974/26, 1975 S10, 1979 CFSD FS 6013, 1988 CFDS GP5, 1989 CFSD FS 6011, FS 6012, 1990 CFSD FS 6014); FRS (Appendix 28, 1973 Fire Res. Note 963); IRI (n.d./1, 2, 4, 1964/5, 1966/7); MCA (SG-13, SG-17); NFPA (Appendix 27, 28, 1976/17, 2002/19, 1986/19, 1988/22, 20031989/24, 2002/26, 1991/27, 2003 NFPA 1); NRC (Appendix28 *Fire, Fire Protection*); UL (Appendix 27); Ashton (1961); Bahme (1961); Risinger (1962); Vervalin (1962, 1964a, 1966, 1972a, 1973a,g, 1975a, 1985a); R.V. Wright (1962); Bateman (1963); Webb (1963); Bluhm (1964a); Dow Chemical Co. (1964, 1966a,b, 1976, 1980, 1987, 1994); Lindemann and Whitehorn (1965); FMEC (1967); Aubrecht, Lindemann and Schreiber (1968); BCISC (1968/7); Leeah (1968); P. Nash (1969); Newall (1969); Rasbash (1969a, 1970b, 1974a,b, 1976a, 1977a, 1980a,c); Watkins (1969); Way (1969); Hearfleld (1970); HSE (1970 HSW Bklt 10); J.R. Hughes (1970); ICI/RoSPA (1970 IS/74, 1975 IS/107); Constance (1971a); Klaassen (1971); Kletz (1971, 1972a, 1974e, 1975d); Strother-Smith (1971); Underwood (1971–); Birchler (1972); Lockwood (1973a); Ackroyd (1974); Emmons (1974, 1990); Home Office (1974–, *Manual of Firemanship*); Hoy-Petersen (1974); R.B. Robertson (1974a,b, 1976a,b); Unwin, Robins and Page (1974); Drewitt (1975); PITB (1975/6); Clayton (1976); J.M. Rees (1976); Spiers (1976); ASTM (1977 STP 614, 1985 STP 882); N.T. Freeman (1977); Monroy and Majul (1977); H. West and Brown (1977); Coleman (1978); Beard (1979); R. King and Magid (1979); Planer (1979); IP (1980 Eur. MCSP R 2, 1981 MCSP R 1, 1987 MCSP Pt 9, 1993 MCSP R 19); Anon. (1981q); Beaumont (1981); Chandnani (1981); Hilado and Huttlinger (1981a); Anon. (1982 LPB 43, p. 1); Benedetti (1982); W.S. Wood (1982a); Anon. (1983d); Besnard (1983); R.S. Levine and Pagni (1983); New (1983); API (1984 RP 2001, 1991 RP 2003); British Gas (1984 BGC/PS/SFP1); Prugh (1985–); Soden (1985); Cote (1986); Cote and Lmvffle (1986); Haessler (1986); Anon. (1987 LPB 74, p. 17); Burke and Finucane (1988 SRD R428); Quintiere (1988); Ramachandran (1988); Haverstad (1989); Hirst (1989); NSW Government (1989a); Pastorini *et al.* (1989); Tuhtar (1989); Barnfield and Hay (1990); Ellinor (1990); Renowden and Woolhead (1990); Becker and Hertel (1991); Clerehugh (1991); Hirano (1993); C.J. King (1993); Shelley (1993) BS (Appendix 27 *Fire Protection*)

Fire risk management
FPA (CFSD MR series); ASTM (1982 STP 762); NFPA (2002 NFPA 550); Alexander (1992b); C.J. King and Alexander (1992); C.J. King (1993)

Buildings
BRE (Appendix 28, 1974 CP 72/74, 1975 CP 37/75); FPA (n.d., CFSD B and CFSD series, 1971/14, 1973/20, 21, 1974/24); FRS (Appendix 28); Langdon-Thomas (1967a,b, 1972); Dahms (1964); ASTM (1967, 1979 STP 685); ISO (1968); Cutmore (1972); Malhotra (1972, 1977, 1984a,b); Binns, Nelson and Thompson (1973); G.M.E. Cooke (1974, 1975); ASCE (1975/4); Harmathy (1977); Raes (1977); Quintiere, Macaffrey and Kashiwagi (1978); Lecornu (1980); BRE (1982 IP22/82, 1984 IP15/84, 1989 IP21/89); Diysdale (1985); Kendik (1986); Shields and Silcock (1987); Gross (1991); BS 476: 1970, BS 5306: 1976–, BS 5588: 1978–
Time-temperature curves: Hinkley (1984); Shipp (1984); Harmathy and Sultan (1988)
Fire resistance: Ministry of Works (1946); BRE (1975 CP37/75); Home Office (1975 Manual of Firemanship Bk 8); Janss and Minne (1981/82); Malhotra (1984a,b); Gehri (1985); Odeen (1985); K.J. Schwartz and lie (1985); American Insurance Services Group (1986); Anchor, Malhotra and Parkiss (1986); Jacobsen (1986); UL (1986 UL 263); Choi 1987); Cullington (1987); Harmathy and Oleskiewicz (1987); Harmathy and Sultan (1988); Pettersson (1988); NFPA (1999 NFPA 251, 2002/262, 2001 NFPA 258, 1995 NFPA 220, 1992/29, 2001 NFPA 80A, 2003 NFPA 259); G. Butcher (1991); Hosser, Dorn and Richter (1994)
Fire resistance of steel: FPA (n.d.); FRS (1966 Fire Res. Tech. Paper 15); UL (1981 UL 1709); Klingsch (1981/82); Wickstrom (1981/82); Witteveen and Twilt (1981/82); American Iron and Steel Constructors (1983); European Convention for Constructional Steelwork (1985); Wickstrom (1985); Barnfield (1986); Franssen and Bruls (1986); Anderberg (1988); G.M.E. Cooke (1988); Gandhi (1988); Kirby and Preston (1988); Rubert and Schaumann (1988); Twilt (1988); Melinek (1989); Schneider (1990); Burgess, Olawale and Plannk (1992); Franssen and Dotreppe (1992); Tomecek and Milke (1993)
Fire resistance of concrete: Schneider (1988); O'Meagher and Bennetts (1991); Sullivan and Sharshan (1992)
Fire resistance of glass: FPA (CFSD B series); Howe (1989); Klein (1990); Jackman (1993); Joshi and Pagni (1994)
Oil soaked floors: FPA (1973 S4, 1983 CFSD GP 10)
Piped services: FPA (1973/21, 1982 CFSD FS 6017)
Fire ventilation, smoke control: ASHRAE (n.d./1); IRI (n.d./3); FRS (1964 Fire Res. Tech. Pap. 10, 1965 F5); Leach and Bloomfield (1973, 1974 BRE CP 36/74); Gerhardt (1982); BRE (1984 IP21/84, IP22/84); Marchant (1984); Drysdale

(1985); Hinkley (1986); NFPA (2000 NFPA 92A, 2000 NFPA 92B); FPA (1989 CFSD FS 6018, 1990 CFSD FRDG 3); Wighus and Medland (1989); Wild (1989)
Fire venting and sprinklers: Naidus (1981a); Heselden (1982); Holt (1982); Hinkley *et al.* (1992)
Floors: FPA (CFSD FPDG 14, 1974/24, 1990 CFSD GP 11); NFPA (1999 NFPA 80)
Fire dampers: Baines (1988 LPB 84); UL (1989 555); Cullen (1990)
Emergency lighting: C. Watts (1984); BS 5266: 1981–

Handling of flammable materials
MCA (SG-3); Bahme (1961, 1972); FPA (1964/1, 1970/12, 1971/14, 1974 S5, 1987 CFSD FS 6028); Orey (1973); NFPA (1991 NFPA 49, 325M, 491M, 1991/27, 2000 NFPA 30); HSE (1978 HS(G) 3); Bradford (1986b)
Handling cylinders: Carver *et al.* (1977); CGA (1983 SB-3, 1985 SB-10, 1990 P-1, SB-4)

Plant layout (*see also* Table 10.2)
Landy (1964a–c); Seppa (1964); FPA (1971/14); Hearfield (1970); Atallah and Allan (1971); Simpson (1971); Day and Moorhouse (1973); Mecklenburgh (1973, 1976, 1982, 1985); R.B. Robertson (1974a,b, 1976a,b); Klootwijk (1976); Anon. (1982j); Martinsen, Johnson and Millsap (1989); Gore Willse and Smith (1993)

Warehouses
FPA (1970/9, 13, 1972/17, 19); FRS (1972 Fire Res. Note 914, 916, 944, 1977 Fire Res. Note 1068); P. Nash (1972a, 1977a); BRE (1974 CP 68/74, 1988 IP5/88); Home Office (1974/10); Bridge (1977); R.A. Young and Nash (1977); Parnell (1979); Anon. (1980t); Baldovinetti (1983); Field (1985); Mackintosh (1988 LPB 84); Murrell (1988); Johnston (1989 LPB 85); Palmer (1989 LPB 86); Murrell and Field (1990); NFPA (1991 NFPA 231C)

Electrical protection, hazardous area classification
ICI (n.d.a); IEC (n.d.); Illuminating Engineering Society (n.d.); IEE (1971 Conf. Publ. 74, 1975 Conf. Publ. 134, 1982 Conf. Publ. 218, Control Ser. 17, 1988 Conf. Publ. 296); MCA (SG-19); Post Office (n.d.); SMRE (Elec. Hazards 1–7); Swann (1957, 1959); EEUA (1959 Doc. 9, 1969 Doc. 32); R.W. Scott (1961, 1964); IRI (1965/6); R.Y. Levine (1965a,b, 1968a,b, 1972a, 1983); Magison (1966, 1975, 1978); Burgoyne (1967b, 1969, 1971); ICI/RoSPA (1970 IS/74, 1972 IS/91); Arnaud (1971); Bartels (1971a, 1975a,c, 1977–); Bartels and Howes (1971); Cockram (1971); W. Cooper (1971); Cowen, Godsmark and Goodwin (1971); Dreier and Engel (1971); FPA (1971/14); Gehm and Bittner (1971); Heidelberg (1971); Lord (1971); MacCarthy (1971); J. Nixon (1971); Palles-Clark and James (1971); Steen (1971); Wheatley (1971); Short (1972, 1982, 1985); API (1973 RP 500B, 1982 RP 500A, 1984 RP 500C, 1991 RP 500); Schon (1973, 1977); Arnaud and Jordan (1975); Bartels and Day (1975); Buschart (1975); Chubb, Pollard and Butterworth (1975); Ellis (1975); N.C. Harris (1975); Nailen (1975); Rogowski (1975); Towle (1975a); Rees (1976); IBC (1981/9, 1991/81); Marshall (1981 LPB 39); J.T. Woods (1981); D.R. Brown and Gregory (1982); Bryce, Ramsey and Seaton (1982); B.D. Cooper (1982); Gwyther (1982); Hay (1982); O'Shea (1982, 1985); Palles-Clark (1982); Peck and Palles-Clark (1982); Shevchenko *et al.* (1982); Summers-Smith (1982); British Gas (1983 BGC/PS/DAT12, 1986 BGC/PS/SHA1); Boon (1983); Bryce and Robertson (1983); Calder and Magison (1983); Joshi (1983); ISA (1984 S12.12, 1987 RP 12.6, 1988 S12.10); Pankowski (1984); Mecklenburgh (1985, 1986); Ashmore (1987a,b); IMechE (1987/92); H. Kramer (1987); NFPA (1999/20, 1997 NFPA 497, 2002 NFPA 70, 1999/35); A.W. Cox, Lees and Ang (1990); IP (1990 MCSP Pt 15, 1991 MCSP Pt 1); Ahern (1991); AGA (1992/17); BS (Appendix 27 *Hazardous Area Classification*, *HBC*), BS 4683: 1971–, BS 5345: 1977–, BS 5501: 1977–
Dusts: ICI/RoSPA (1972 IS/91); EEUA (1973 Doc. 47D)
Safeguarding: EECS (SFA 3009, 1992 EECG2); Riddlestone (1967, 1975, 1979); Engel and Wickboldt (1975); Macmfflan (1975, 1982); HSE (1984 HS(G) 22)

Flameproofing, explosion proofing
Ministry of Power (n.d.a); NCB (n.d.a); SMRE (Elec. Hazards 2, 3, 7); UL (1951); IEE (1962 Conf. Publ. 3); Gelfer *et al.* (1964); Northrup (1964); Carhart (1968); House (1968a); Bartels (1971b, 1975b); Eastwood (1971); H. Phillips (1971a,b, 1972b, 1973, 1984); Lunn and Phillips (1973); Davison and Lord (1974); Fleisig (1975); Maekawa (1975); Sansom and Gust (1975); Maekawa, Takeichi and Kato (1978); Maekawa and Takeichi (1979); Shevchenko *et al.* (1982); Cleare (1991) BS 229: 1957; BS 4683: 1971; BS 5501: R 5: 1977; BS 5345: R 3: 1979

Intrinsic safety
BASEEFA (SFA 3012, 1970 SFA 3004); EECS (SEA 3012); Ministry of Power (n.d.b); NCB (n.d.b); SMRE (Elec. Hazards 1, 1968 Res. Rep. 256); Barlow (1963); Burgoyne (1965c); Hickes (1968, 1969, 1972); Redding (1969, 1971a,b, 1972); A.E. Turner (1969); Weismantel (1969b); Cartwright and Widginton (1971); Hickes and Brown (1971); Kheradmand-Fard (1971); Deloney (1972); Deuschle and Tiffany (1973); Krigman and Redding (1974); Weatherhead (1977); Hutcheon (1981); Calder (1982); Garside (1982); Bartels (1983); Bass (1984); Magison (1984); Beevers (1986); Tortoishell (1986); ISA (1987 RP 12.6) BS 5345: Pt 4: 1977; BS 5501: Pt 7: 1977; BS 5501: Pt 9: 1982

Purging, pressurization
ICI/RoSPA (1972 IS/91); Ecker, James and Toensing (1974); Hinds (1975); Rogerson (1982); E.G. Butcher and Moss (1991); C. Campbell (1991–); NFPA (1998 NFPA 496)
BS 5501: Pt 3: 1977; BS 5345: Pt 5: 1983

Instrumentation
Magison (1966, 1975, 1978, 1984); Redding (1971a,b, 1972, 1975); Towle (1975b); Bossert (1976); Foxboro Co. (1980); Hutcheon (1981); Garside (1982); Macmfflan (1982); Corrigan (1990)

Portable apparatus
EEUA (1958 Doc.4); IGasE (1970/9); UL (1992 UL 781)

Diesels
Lloyds Register (n.d.); HSE (1977g); ICI (1977); Oil Companies Materials Association (1977); BP Trading Ltd (1980); EEMUA (1983 Publ. 107)

Electrical surface heating
ICI/RoSPA (1972 IS/91); Angel (1975); Dobie, Cunningham and Reid (1976); UL (1990 UL 130)

Inerting
Hotchkiss and Weber (1953); P.A.F. White and Smith (1962); Funk (1963); Husa (1964); Penland (1967); Rosenberg (1968); H.A. Price and McAllister (1970); Kletz (1971, 1984 LPB 56); Kurz (1973); Loeb (1974); Craven (1975); Gammell (1976); Simon (1976); Corlett, Stone and Williams (1980);

Polytechnic Inst. (1980); Schwarz (1980); Depaola and Messina (1984); Halpern, Nyce and Wrenn (1986); Wrenn (1986); Tufano (1992)

Lightning protection
Baatz (1977); Golde (1977a,b); Gumley, Invernizzo and Khaled (1977); Rusck (1977); Saraoja (1977); FMEC (1987 LPB 73); UL (1988 UL 96)

Jet flame protection
Ranz and Marshall (1952); Yuen and Chen (1978); van der Schaaf (1986); Lev (1991); Shirvill (1992)

Fire detection and alarm
FPA (1971/14, 1989 CFSD PE 1, 1991 CFSD FPDG 6); FRS (1970 Fire Res. Note 810, 1971 Fire Res. Note 899, 1972 Fire Res. Note 932, 1974 Fire Res. Symp. 6, 1977 Fire Res. Note 1063); Rasbash (1972); J.L Bryan (1974); M.J. Miller (1974); BRE (1975 CP 29/75, CP 32/75); Haessler (1975); NFPA (2003/14, 2002 NFPA 72, 2001/36, 1994/38); P. Nash and Theobald (1976a,b); Benarie (1977); R.G. Bright (1977); Rutstein (1979a); Anon. (1980g); Street, Williams and Alexander (1980); Cullis and Firth (1981); R. Phillips (1981); Bearman (1983); Frost (1983); R.W. Murray and O'Neill (1983); Scheidweiler (1983); von Tomkewitsch (1983); Finucane (1984 LPB 59); Gupta (1985); Gupta and Dharmadhikari (1985); Musselwhite (1985); O'Shea (1985); Todd (1985); Vaughn (1986); Atallah and Guzman (1987); Combley (1987); Northey (1988); Bellamy (1989); Drake (1989); Medlam (1990); Ramachandran (1991)
Gas, smoke and fire detectors: BASEEFA (SFA 3007); SMRE (Gas Detectors 1–11); UL (Appendix 27, 1985 UL 217, 268A, 1987 UL 521, 1988 UL 268); Schall (1962); R.L. Swift (1963); Steel (1971); FRS (1972 Fire Res. Note 938, 1973 Fire Res. Note 957); Firth, Jones and Jones (1973, 1974); HSE (1973 TON 45, 1980 EC 3, EC 4, 1987 CS 1); Smith (1973); Steen (1973); Verdin (1973); Bossart (1974); Johanson (1974, 1976); Allan and Schiff (1975); Associated Octel Co. (1975 Bull. 13); Riley (1975); Anon. (1976l); BRE (1976 CP 50/76); Dailey (1976); Herrick (1976); P. Nash and Theobald (1976a,b); K.N. Palmer (1976a,c); Weiby and Dickinson (1976); Anon. (1977h); Kletz (1977i); Gowar (1978); Kunz and Thalman (1978); St John (1978); Anon. (1979f,g); Bond (1979); H.N. Nelson (1979); Schaeffer (1980); Snee (1980); Cullis and Firth (1981); Mannon (1981); C. Martin (1981); Boccio (1982); Sonley (1982); Heitman (1983); Middleton (1983); Ricca (1983); Beyler (1984); Larsen (1984); British Gas (1986 Comm. 1298); ISA (1986 S12.13.1, 1987 RP 12.13 R II); Penny (1986); Anon. (1987m,x); EEMUA (1988 Publ. 155); Cholin (1989a,b); Grover (1990); Mowrer (1990); NFPA (2002 NPFA 72); API (1991 Publ. 2031); Ishii *et al.* (1991); Okayama (1991); Ramachandran (1991); A.J. Rogers (1991); Smithies, Burry and Spearpoint (1991); Bjb'rkman, Kokkala and Ahola (1992); Buckland (1992); Varey (1992a); Wffley (1992); BS (Appendix 27 EN series), BS 5445: 1977–
Fire alarm: Fire Offices Committee (n.d.b); EEUA (1972 Doc. 45D, 1975 Doc. 46D)

Fire insulation, fireproofing
Steverding and Nieberlein (1965); Waldman (1967); Way and Hilado (1968); Boult, Gamadia and Napier (1972); Boult and Napier (1972); Heselden, Theobald and Bedford (1972); Law (1972, 1991); Castle (1974); Cooke (1974, 1975, 1988); Feldman (1974); Kayser (1974); McMillan (1974); Montle and Mayhan (1974); O'Rourke (1974); Schwab and Lawler (1974); Hildenbrand (1975); Rains (1975, 1977); Warren and Corona (1975); Kbotwijk (1976); Florence (1977); Kawaller (1977, 1980); Castle (1979); Anon. (1980 LPB 31, p. 5); Modak and Orloff (1980); Melinek (1989); Barry (1991); Shirvffl (1992)
Fire resistance: SMRE (Fire 1, 6); Parnell (1977); Duffy (1983); Corona (1984); Berhinig (1985); Buck and Belason (1985); Dilliberto and Gratzol (1985); Rains (1985); Gustaferro and Lin (1986); Castle and Castle (1987); Lathom, Kirby and Thomson (1987); Melinek and Thomas (1987); API (1988 Publ. 2218)
Intumescent coatings, seals: O'Rourke (1974); R. James (1988); Gfflon (1989); Droste (1992); Hulin (1993)

Fire water systems
L.T. Wright (1962, 1964); R. Wilson (1964a,b); FPA (1971/14, 1988 PE 7, 1989 PE 8, 1990 PE 6); Orey (1972c); Sylvia (1972b,c); W.S. Thompson (1972, 1973); FRS (1973 Fire Res. Note 959); Woodard (1973); R.B. Robertson (1974a,b, 1976a,b); Unwin, Robins and Page (1974); Kfootwijk (1976); Theobald (1981, 1984); Hodge (1985); Hodnett (1986d); NFPA (2002 NFPA 291, 2003 NFPA 14, 2002 NFPA 1961, 2003 NFPA 14, 2003/1962, 1998/1963)
Fire pumps: UL (1988 UL 1478; 1991 UL 1247); NFPA (1999 NFPA 20) BS 5041: 1974– BS 5306: 1976–; BS 750: 1984; BS 5908: 1990

Water sprinklers and sprays
FPA (PE 10, 1970/11, 1971/14, 1985 PE 13, 1989 PE 9, 11, 12); Nickerson (1954); Rasbash and Rogowski (1957); Rasbash and Stark (1960, 1962); Rasbash, Rogowski and Stark (1960); C.M. Wood (1961); Rasbash (1962); NFPA (1964/3, 2001/15, 1987 NFPA ISA, 2001 NFPA 15, 2002/17A, 1995/18, 2002/25, 2002 NFPA 13, 2002/37, 39); Chaillot (1966); O'Dogherty, Nash and Young (1966); FMEC (1967); Fire Offices Committee (1968); Charney (1969); FRS (1971 Fire Res. Note 899, 1972 Fire Res. Notes 914, 916, 1974 Fire Res. Note 1003); Kalelkar (1971); Association Nationale pour la Protection centre l'Incendie (1972); P. Nash (1972a, 1973a, 1974a,b, 1975a,b, 1976, 1990); W.S. Thompson (1972, 1973); Arscott, Street and Twamley (1973); Bray (1973, 1980); BRE (1975 CP 29/75, CP 42/75, CP 67/75, CP 77/75, CP 78/75, CP 79/75, 1976 CP 52/76, 1977 CP 9/77); Leworthy (1975); P. Nash and Theobald (1976a,b, 1976 BRE CP 50/76, 1988 IP5/88); P. Nash and Young (1976); Tamanini (1976); Beyler (1977); FMEC (1977, 1986 LPB 71); Ashfleld (1979, 1993); Hems (1979, 1983); Rieschl (1979); Anon. (1980t); Barris and Conte-Russian (1980); Bray (1980); Cresswell (1980); Kitson and Guy (1980); Nicholls (1981); R. Young (1981); Crowley (1982); IRI(1982); Pignato (1983); Wass (1983); Anon. (1984k); Angelini (1984); Watson (1984); Billinge, Moodie and Beckett (1986); Hodnett (1986a–c); Mullhaupt (1986); API (1987 Publ. 2030); Theobald (1987a,b); Murrell (1988); Theobald, Westley and Whitbread (1988); Thorne, Theobald and Melinek (1988); W.S. Wood (1988); Yao (1988); Lev and Strachan (1989a,b); McCaffrey (1989); Vasey (1989); Chow and Fong (1991); FMRC (1991); Lev (1991); Melinek (1993b); Jackman and Nolan (1994)

Steam systems
Steam curtains: Cairney and Cude (1971); Simpson (1971)
Steam snuffing: Runes and Kaminsky (1965, 1973); Muller-Dethlefs and Schlader (1976)

Fire extinguishing agents and systems
Guise and Zeratsky (1965, 1982); FMEC (1967); Charney (1969); Hearfleld (1970); J.R. Hughes (1970); NFPA (1970/6); Harpur (1971); Haessler (1973); Anon. (1974d); J.L. Bryan

(1974); Anon. (1978 LPB 22, p. 107); Rushbrook (1979); Riley (1983); Fuchs (1984); HSE (1984 GS 16); Webster (1984); Welker, Martinsen and Johnson (1986); Sharma, Lai and Singh (1987); Ewing *et al.* (1989a); Scheinson, Penner-Hahn and Indritz (1989); Simmonds (1993) BS 5306: 1976–
Water: Ashill (1966b); G. Clarke (1978); Corlett and Williams (1979); Heskestad (1980); Fritz and Jack (1983); Hodnett (1986a)
Foam: Burgoyne (1949a); Burgoyne, Katan and Richardson (1949a); Bikerman *et al.* (1953); Perri (1953); Bartkowiak, Lambiris and Zabetakis (1959); Hird and Fippes (1960); Burgoyne and Steel (1962); UL (1963); Jensen (1964); Vervalin (1964b,d); Meldrum and Williams (1965); Ashffl (1966); G. Nash (1966); Hearfleld (1970); Hird, Rodrigues and Smith (1970); J.R. Hughes (1970); J.R. Williams (1970); FRS (1972 Fire Res. Note 925, 1973 Fire Res. Note 980, 993, 1974 Fire Res. Note 1007); Meldrum (1972, 1982); Sylvia (1972e); P. Nash (1973b, 1984); Corrie (1974, 1977); E.M. Evans and Whittle (1974); Anon. (1975c); BRE (1975 CP 25/75, CP 42/75, 1976 CP 74/76, 1978 CP15/78); Anon. (1976b); Burford (1976); Elliott and Chiesa (1976); MITI (1976); Gillespie and Dimaio (1977); Klunick (1977); P. Nash and Whittle (1978); Woodman *et al.* (1978); L.E. Brown and Romine (1979, 1981); Chiesa (1980); Lev (1981b); Murphy (1981); Anon. (1983k); Boughen (1983); Dimaio and Lange (1984); Dimaio, Lange and Cone (1984); J.L. Evans (1985, 1988); SKUM (1986); Lockwood (1986); Briggs and Webb (1988); NFPA (2002 NFPA 11, 1999/11A, 2003/16, 1990 NFPA 11C, 2003 NFPA 16); Tabar (1989); Harker (1990); Waters (1990 LPB 91); M. Clarke (1992); Anon. (1993d); Howells (1993, 1993 LPB 114) BS 5306: Pt 6: 1988–
Inert gas, including carbon dioxide: McGuire (1964); Atallah and Wohl (1965); Williamson (1986); Bryant (1991); NFPA (2000 NFPA 12)
Solid carbon dioxide: Burgoyne, Katan and Richardson (1949b)
Dry chemicals: Fire Control Engineering Co. (n.d.); Dolan (1957); McCamy, Shoub and Lee (1957); Lafitte and Bouchet (1959); T.G. Lee and Robertson (1960); UL (1963); Dewitte, Vrebosch and van Tiggelen (1964); Tuve (1964); Vervalin (1964e); Laffitte *et al.* (1965); Meldrum and Williams (1965); Anon. (1966b); W.E. Wilson, O'Donovan and Fristrom (1969); BirchaU (1970); Dodding, Simmons and Stephens (1970); Emmrich (1971); Wesson (1972); Woolhouse and Sayers (1973); Schweinfurth (1974); Anon. (1975b); Iya, Wollowitz and Kaskan (1975); McHale (1975); Spence and McHale (1975); Stauffer (1975); MITI (1976); Morikawa (1976); Dixon-Lewis and Simpson (1977); Russell (1977); Vanpee and Shirodkar (1979); Mitani (1981, 1982, 1983); Boughen (1982); Mitani and Niioka (1982); Haessler (1986); Ewing *et al.* (1989b); NFPA (2002 NFPA 17) BS 5306: Pt 7: 1988
Particulate materials: Sharma *et al.* (1992)
Vaporizing liquids, halons: Burgoyne and Richardson (1949a); Belles and O'Neal (1957); Garner *et al.* (1957); Rasbash (1968); Homann and Poss (1972); Sylvia (1972d); Tatem, Gann and Carhart (1973a,b); Anon. (1974–); Hirst (1974a,b); NFPA (2002/13, 1990 NFPA 12B, 1997 NFPA 12A); Gann (1976); Williamson (1976); FRS (1977 Fire Res. Note 1073); Gann *et al.* (1978); P.F. Thorne (1978b,c); Wiersma (1978); Boughen (1979); Peterson (1979); Anon. (1981t); Tucker, Drysdale and Rasbash (1981); Peissard (1982); Westbrook (1982c); Capper (1983); Mitani (1983); C.C. Grant (1985); D.W. Moore (1986) BS 5306: Pt 5: 1982–
Alternatives to halons, clean agents: Molina and Rowland (1974); Anon. (1991g); G. Taylor (1991); Senecal (1992a,b); B. Ward (1992); Hough (1993); McKay (1993); NFPA (2000 NFPA 2001)
Gels: Ishida and Iwami (1984)
***Combustible metal agents*:** McCormick and Schmitt (1974); Prokopovitsh (1986)
Fixed equipment: Anon. (1974–); Schweinfurth (1974); Anon. (1975b,c); Stauffer (1975); Burford (1976); Rasbash (1976a); P. Nash (1977b); Boughen (1982, 1983); J.L Evans (1985); FPA (1990 PE 6)
Halon systems: Williamson (1976); Wiersma (1978); Boughen (1979); Anon. (1981t); Forrester (1982); Peissard (1982); C.C. Grant (1985); Hoskins (1985); R.J. Martin, Shepherd and Hamlin (1986); Goodall (1988); Genge (1989); Sreeves (1989); Whiteley (1989); Boyce (1990)
Mobile and portable equipment: Fire Offices Committee (n.d.a); Guccione (1961); Lockwood (1965, 1973b); BRE (1975 CP 82/75); P. Nash (1969, 1975a, 1991); R. Russell (1977); M.E. Petersen (1986a,b); FPA (1988 CFSD PE 3, 1990 CFSD PE 4); NFPA (2002 NFPA 10) BS 5423: 1987
Fire points: FPA (1974 S6, 1988 CFSD PE 2)

Fire protection of particular activities, equipment
Air compressors: Duguid (1965)
Bin storage: Field and Murrell (1988)
Cables: IRI (1965/6); F.E. Baker and Shepherd (1971); Kirkham (1987); Annemaier and Graf (1988); Woolhead (1989, 1990)
Computers: IRI (1971/8); Bray (1973); Pucill (1973); Mottershead (1977); NFPA (2003 NFC 75)
Control systems: Castle (1984)
Crushing and grinding equipment: FPA (CFSD FS 6033)
Dip tanks, heat treatment baths: HSE (1971 HSW Bklt 27); Orey (1972b); FPA (1974 S8)
Documentation, records: FPA (1974 S7); NFPA (2000 NFPA 232)
Drum stores: Delichatsios (1982); Mikloucich and Noronha (1982); Rogerson (1982); Capizzani (1985)
Electrical equipment: FPA (1968/6, 1974/25, 1990 CFSD FS 6014); NFPA (2002 NFPA 70B, 2002 NFPA 79, 2002 NFPA 70)
Gas and vacuum systems: NFPA (1993 NFPA 99C)
Heat transfer systems: Fuhr (1992)
Hydraulic oil systems: FPA (1976 CFSD FS 6016)
***Incinerators*:** FPA (S3, 1987 CFSD GP 9)
Oil burners: FPA (1989 CFSD FS 6042)
Pilot plants: Capraro and Strickland (1989)
Pneumatic conveying: NFPA (1990 NFPA 650)
Power stations: NFPA (2000 NFPA 850)
Reciprocating compressors: FPA (CFSD FS 6034)
Valves: Arant (1981); Choquette (1984); Symalla (1984); Varey (1988)
Turbines: NFPA (2002 NFPA 37)
Vaporizers: Bowman and Perkins (1990)
Vessels and tanks: Pettit (1945); Hird, Rodrigues and Smith (1970); Kletz (1971, 1974e, 1975d, 1977d,k, 1986g); Bray (1964, 1966); Thomas and Law (1965 FRS Fire Res. Note 609); Anon. (1966d); Chaillot (1966); FPA (1966); Warren (1966); Hearfield (1970); J.R. Hughes (1970); ICI/RoSPA (1970 IS/74); Vervalin (1973f); van Eijndhoven, Nieuwenhuizen and Wally (1974); Nash and Young (1975 BRE CP 42/75); Kaefer (1977); Peyton (1984); Smith (1984); I. Williams (1984); B.M. Lee (1989); Droste (1992); Meiers and Jarman (1993); M. Wilson (1993)
Construction activities: NFPA (2000 NFPA 241)
Transport: NFPA (Appendix 27, 1973/10); Fitch (1986);

Keller, Kerlin and Loeser (1986); McGinley (1986)
Jetties: Dicker and Ramsey (1983)
Waste disposal activities: FPA (1971/15)

Oxygen enriched atmospheres
HSE (1984 HSE 8); NFPA (1999 NFPA 53)

Fire security, arson prevention
FPA (CFSD AR, MR, SEC series, 1972/16, 19, 1989 CFSD OR 7); NFPA (1986 NFPA 602, 2000 NFPA 601)

Fire fighting
FPA (CFDS FPDG 5); Rasbash and Stark (1960); Risinger (1964b,c,e–g); Zeratsky (1964); O'Dogherty (1965); NFPA (1966-/4, 1972/8, 2002/11, 2003/16, 1995/18); Guise (1967, 1975, 1976); Methner (1968); Home Office (1972/9, 1974– *Manual of Firemanship*, 1974/10); HSE (1970 HSW Bklt 10); J.R. Hughes (1970); Rawill (1971); Stark (1972, 1976); Sylvia (1972b); W.E. Clark (1974); PLTB (1975/6); Clayton (1976); Hodnick (1976); Lawson and Rasbash (1976); Brennan and Stow (1977); Austin (1979); Ishida and Iwama (1984); P.F. Johnson (1986); Hem and Saunders (1986); Purington (1986); Rosenhah (1986); P.O. Davis and Dotson (1987); Nazario (1988); E. Meyer (1989); Gore, Evans and McCaffrey (1991); A. Evans (1994) BS (Appendix 27 *Fire Protection, Hoses and Hose Couplings*), BS 5041: 1974–; BS 5274: 1985; BS 3165: 1986; BS 3169: 1986; BS 336: 1989
Liquid fires: Rasbash and Rogowski (1957); Rasbash (1960); Rasbash and Stark (1960, 1962); Sylvia (1972b,e); P. Nash (1973b, 1974b); Corrie (1974); Capper (1985)
Dilution of water-soluble liquids: Thorne (1978a)
LNG fires: Petersen, Morizumi and Carpenter (1968); Welker, Wesson and Sliepcevich (1969); Welker and Sliepcevich (1970); Walls (1971, 1973); Wesson, Welker and Brown (1972, 1975); Wesson *et al.* (1973a,b); Welker, Wesson and Brown (1974); Guise (1975, 1976); H.H. West, Brown and Welker (1975); Bellus, Vincent *et al.* (1977); Wesson and Associates (1977); L.E. Brown and Romine (1979, 1981); Boughen (1980); Lev (1981a, b); Lee (1989)
LPG fires: Martinsen (1982); Williams (1984); Blomquist (1988); B.M. Lee (1989)
Tank fires: Risinger (1964b,f,g); J.R. Hughes (1970); Stillman (1971); E.M. Evans and Whittle (1974); Herzog (1974, 1979); Mahley (1975); NFPA (2003/16); P. Nash and Whittle (1978); Kletz (1982 LPB 47); B.M. Lee (1989); API (1991 Publ. 2021)
Metal, metal powder fires: Reuillon *et al.* (1977); NFPA (2002 NFPA 484); Sharma, Lai and Singh (1987); Varshney, Kumar and Sharma (1990); Cardillo and Nebuloni (1992); Sharma, Varshney and Kumar (1993)
Sulfur fires: NFPA (2001 NFPA 655)
Wood fires: Tamanini (1976)
Transport fires: W. Ward (1978); Home Office (1985, *Manual of Firemanship* Bk 4)
Water curtains: Rielsch (1979); Stephenson and Coward (1987); Maini and Stephenson (1989); Coppalle, Nedel and Bauer (1993)
Thermal image aids: Blatte (1985); Treliving (1985)
Fire fighting hazards: OSHA (n.d./l); Lathrop (1977)
Gas cylinders: CGA (1990 SB-4)
Breathing apparatus: NFPA (2002 NFPA 1404)
Protective clothing: Abbott and Schulman (1976); Holcombe (1981); Anon. (1982/83); NFPA (1951/2001, 1971/2000, 1976/2000, 1977/1998, 1994/2001, 1999/2003) BS (Appendix 27 *Personal Protection*), BS 1547: 1969; BS 3791: 1970; BS 4667: 1974–
Radiation control: NFPA (1960/2)
Smokehoods: B. Brown (1989)
Fire services (*see also* Table 24.1)
Home Office (1974– *Manual of Firemanship*); FPA (1988 CFSD OR 2, 1990 CFSD OR 1)
Fire communications: NFPA (1221/2002)
Occupational fire services: FPA (CFSD MR 11, 1989 CFSD MR 14)

Human behaviour in fires
Wood (1972 FRS Fire Res. Note 953); J.L Bryan (1976, 1978); Carmack (1976); Canter (1980, 1980/81); Jin (1981); Ikeda (1982); Keating (1982); Tong (1983); Wardlaw (1983); Paulsen (1984); BRE (1985 BR 61, IP20/85); E.G. Butcher (1985); Ramachandran (1990a)

Fire response, evacuation
J.M. Watts (1987); FPA (1990 CFSD MR 7); NFPA (1990 NFPA 902M, 2002/1561, 2002 NFPA 471–473)

Fire training
FPA (CFSD M 10, 1974/23, 1987 CFSD M 12, 1989 CFSD M 9); API (1966); B. Martin (1966); NFPA (1968/5, 2000 NFPA 1410); Anon. (1973b); Bruce and Diggle (1974); Long (1975); PITB (1975/6); Vervalin (1975d,e); N. Anderson (1991)

Fire inspection, checklists
Landy (1964a–c); FPA (1965/3); API (1971 Refinery Inspection Guide Ch. 20); NFPA (1994/41)

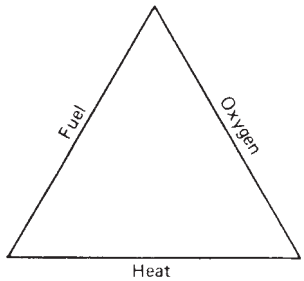

Figure 16.1 *The fire triangle*

combustible gas or vapour mixture burns if it is heated to a sufficiently high temperature.

Thus there are three conditions essential for a fire: (1) fuel, (2) oxygen and (3) heat. These three conditions are often represented as the fire triangle shown in Figure 16.1. If one of the conditions is missing, fire does not occur; if one of them is removed, fire is extinguished.

Normally, the heat required is initially supplied by an external source and then provided by the combustion process itself. The amount of heat needed to cause ignition depends on the form of the substance. A gas or vapour may be ignited by a spark or small flame, while a solid may require a more intense heat source.

Ignition of a combustible gas or vapour mixture may occur in two ways. In the first, the energy for ignition is supplied by a local source such as a spark or small flame at a point within the mixture, as shown in Figure 16.2(a). In the second, the bulk gas mixture is heated up to its ignition temperature, as shown in Figure 16.2 (b).

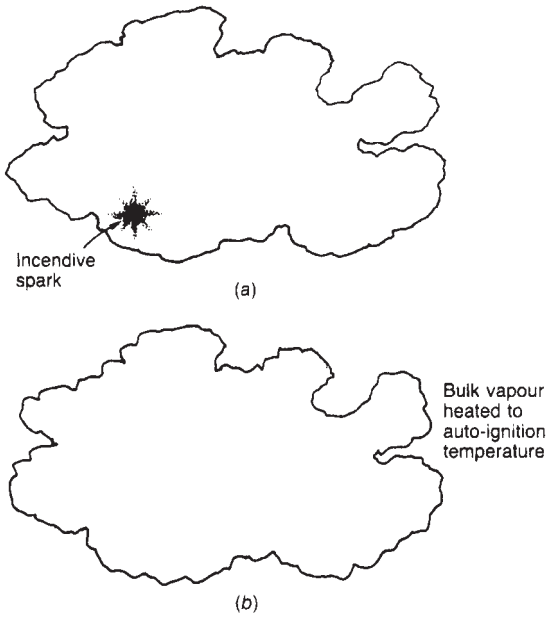

Figure 16.2 *Ignition of a flammable mixture: (a) local ignition and (b) bulk gas ignition*

The three conditions of the fire triangle indicate how fires may be fought. The first method is to cut off the fuel. This is particularly relevant for fires caused by leaks at a process plant. The second method is to remove heat. Putting water on the fire usually does this. The third method is to stop the supply of oxygen. This may be affected in various ways, including the use of foam or inert gas.

Fire is sustained only if there is a net release of heat. The heat comes from the combustion of fuel. If this fuel is liquid or solid, it must first be vaporized. With liquids or solids, fire usually involves a process of positive feedback. The heat evolved by the fire causes the vaporization of an increasing amount of fuel and the fire spreads.

Development of the fire depends on the situation of the fuel. This is commonly illustrated by considering the difference in modes of burning of a lighted match held upwards or downwards. Thus, the stacking of material in closely spaced vertical piles in a warehouse may tend to encourage fire spread.

Fire needs to be supported by the ignition source until it is self-sustaining. For this, duration may be more important than temperature. Thermite bombs, which reach about 1650°C for 15–20 s, have been found less effective in starting fires than napalm, which reaches about 1100°C for 10–15 min.

Different parts of a fire have different heat balances. In some parts, particularly near the edge of the fire, the heat balance may be only just positive. It is sometimes good sense, therefore, to direct fire extinguishant to those parts of the fire and attack it at its weakest points.

It is not necessarily essential to remove all the oxygen in order to extinguish a fire. Reducing the oxygen concentration below 12–16% can generally put out liquid fires. Solids fires may require a greater reduction of oxygen concentration – below about 5% for surface smoldering and as low as about 2% for deep-seated smoldering.

16.1.2 Fire growth and spread

Fire normally grows and spreads by direct burning, which results from impingement of the flame on combustible materials, by heat transfer or by travel of the burning material.

The three main modes of heat transfer are (1) conduction, (2) convection and (3) radiation. All these modes are significant in heat transfer from fires. Conduction is important particularly in allowing heat to pass through a solid barrier and ignite material on the other side.

Most of the heat transfer from fires, however, is by convection and radiation. It is estimated that in most fires, some 75% of the heat emanates by convection. The hot products of combustion rising from a fire typically have a temperature in the range of 800–1200°C and a density a quarter that of air. On open plant much of the heat is dissipated into the atmosphere, but in buildings it is transferred to the ceiling.

Radiation is the other main mode of heat transfer. Although it usually accounts for a smaller proportion of the heat issuing from the fire, radiated heat is transferred directly to nearby objects, does not go preferentially upwards and crosses open spaces. For these reasons it is generally the most significant mode of transfer on open plant.

An account of the modes of heat transfer is given in *Heat Transfer in Fire* (Blackshear, 1974). Radiant heat transfer is treated in *Thermal Radiation Heat Transfer* (Siegel and Howell, 1991).

The other way in which fire spreads is by travel of bulk materials, such as burning liquids or solid brands. With fires in buildings particularly, a stage is generally reached when the materials have been heated up to the point where they produce flammable vapours. The rapid spread of fire which occurs at this point is called 'flashover'.

16.1.3 Classification of fires

There are several classification systems for fires. In the United Kingdom, the BS classification is given in BS EN2: 1992 *Classification of Fires*. This classification is:

Class A	Fires involving solid materials, usually of an organic nature, in which combustion takes place with the formation of glowing embers.
Class B	Fires involving liquids or liquefiable solids.
Class C	Fires involving gases.
Class D	Fires involving metals.

BS EN2: 1992 replaces BS 4547: 1972.

In the United states, the NFPA classification is given in the NFPA Codes. NFPA 10: 2002 contains the following classification:

Class A	Fires in ordinary combustible materials, such as wood, cloth, paper, rubber and many plastics
Class B	Fires in flammable or combustible liquids, oils, greases, tars, oil-based paints, solvents, lacquers, alcohols and flammable gases.
Class C	Fires that involve energized electrical equipment.
Class D	Fires in combustible metals, such as magnesium, titanium, zirconium, sodium, lithium and potassium.

Class K Fires in cooking appliances that involve combustible cooking media (vegetable or animal oils and fats).

This classification has obvious relevance to the extinguishing medium to be used. For a Class C fire, when electrical equipment is de-energized, extinguishers for Class A and B fires may be used.

Fires are also classified by size. The classification recommended by the Central Fire Brigades Advisory Council and given in the *Manual of Firemanship* by the Home Office (1974–) is:

Major fire	>20 jets
Large fire	8–19 jets
Medium fire	3–7 jets
Small fire	1–2 jets, or >3 hose reels
Minor fire	1–2 hose reels, or hand extinguishers

The classifications of combustible and flammable liquids given in Chapter 10 are also relevant.

16.1.4 Classification of fires: process industries

With regard to fires in the process industries specifically, fires may be classified broadly into the following categories:

(1) vapour cloud fires
  (a) fires with no explosion,
  (b) fires resulting from explosion,
  (c) fires resulting in explosion;
(2) fireballs;
(3) jet flames;
(4) liquid fires
  (a) pool fires,
  (b) running liquid fires;
(5) solids fires
  (a) fires of solid materials,
  (b) dust fires;
(6) warehouse fires;
(7) fires associated with oxygen.

Many major fires are vapour cloud fires. It is convenient to term the three categories of vapour cloud fire, or flash fire, as

Type 1	Fires with no explosion.
Type 2	Fires resulting from explosions.
Type 3	Fires resulting in explosions.

16.2 Flammability of Gases and Vapours

Combustion of a flammable gas–air mixture occurs if the composition of the mixture lies in the flammable range and the conditions exist for ignition. As already mentioned, ignition may result from either (1) bulk gas temperature rise or (2) local ignition.

The combustion of the mixture occurs if the bulk gas is heated up to its auto-ignition temperature (AIT) Alternatively, combustion occurs if there is a source of ignition that has sufficient energy to ignite the applied mixture.

Accounts of flammability characteristics and collections of flammability data are given in *Limits of Flammability of Gases and Vapours* (Coward and Jones, 1952 BM Bull. 503) and *Flammability Characteristics of Combustible Gases and Vapours* (Zabetakis, 1965 BM Bull. 627). A further description of flammability characteristics is given by Burgoyne (1965a). Flammability data are also given in the *Handbook of Industrial Loss Prevention* (FMEC, 1967) and the ICI *Electrical Installations in Flammable Atmospheres Code* (ICI/RoSPA, 1972 IS/91).

The discussion of flammability characteristics given below assumes, unless otherwise stated, that the flammable gas mixture is with air and that the pressure and temperature conditions are the initial values. Selected references on flammability and ignition characteristics are given in Table 16.3.

16.2.1 Flammability limits

A flammable gas burns in air only over a limited range of composition. Below a certain concentration of the flammable gas, the lower flammability limit (LFL), the mixture is too 'lean'; while above a certain concentration, the upper

Table 16.3 *Selected references on flammability and ignition characteristics*

SMRE (Fire 3); Factory Mutual Insurance Co. (1940); NFPA (1972/9, 2000 NFPA 30, 2001/704, 1991 NFPA 49, 325M, 491M, 1991/27); FPA (1974/22); Cruice (1986); Gerlach (1987); Bond (1991) BS (Appendix 27 *Test Methods*)

Flammability

Affens (1968); Affens, Carhart and McLaren (1977); Bajpai (1980)

Flammability limits

Mallard and Le Chatelier (1883); Le Chatelier (1891); Le Chatelier and Boudouard (1898); Burgess and Wheeler (1911); Coward and Brinsley (1914); A.G. White (1922, 1924); G.W. Jones (1928, 1937, 1938); Goldmann (1929); G.W. Jones *et al.* (1935 BM RI 3278); Hsieh and Townend (1939b); Zeldovich (1941); Drozdov and Zeldovich (1943); G.W. Jones *et al.* (1945 BM RI 3826); Burgoyne (1948, 1949a); Egerton and Fowling (1948); Matson and Dufour (1950); UL (1950); Fenn (1951); B. Lewis and von Elbe (1951, 1961, 1987); Zabetakis, Scott and Jones (1951); Coward and Jones (1952 BM Bull. 503); Egerton and Thabet (1952); Spakowski (1952); Burgoyne and Neale (1953a,b); Egerton (1953); Simon, Belles and Spakowski (1953); Zabetakis and Jones (1953); Zabetakis and Richmond (1953); Burgoyne and Hirsch (1954); Umland (1954); J.A. Browning and Krall (1955); Wolfson and Dunn (1956); Delbourgo and Laffitte (1957); Linnett and Simpson (1957); Meyer (1957); Spalding (1957d); Dalmai (1958); Dixon-Lewis and Isles (1959, 1961); Zabetakis, Lambiris and Scott (1959); Bartkowiak and Zabetakis (1960 BM RI 5610); Berlad (1961); Kuchta *et al.* (1961 BM RI 5877); Monger, Sello and Lehwalder (1961); K.N. Palmer and Tonkin (1961); Buckley and Husa (1962); Kuchta, Lambiris and Zabetakis (1962 BM RI 5992); Pusch and Wagner (1962); van Tiggelen and Burger (1964); G.S. Scott (1965 BM RI 6659); Zabetakis (1965 BM *Bull.* 627); Craven and Foster (1966); FMEC (1967); D.J. Miller and Webb (1967); Prugh (1967); Yang and Gray (1967); Kuchta *et al.* (1968); Burgess (1969); W.B. Howard (1970a); Rozlovsky (1970); Furno *et al.* (1971); Lovachev (1971, 1979); Lu, Dabora and Nicholls (1971); Steen (1971, 1974); Grove, Patel and Webster (1972); Homann and Poss (1972); Andrews and Bradley (1973b); Gerstein and Stine (1973); Halstead, Prothero and Quinn (1973); Lovachev *et al.* (1973);

Tien (1973); Halstead, Pye and Quinn (1974); Burgess and Hertzberg (1975); Sorenson, Savage and Strehlow (1975); Hertzberg (1976 BM RI 8127); Meadows (1976); Crescitelli *et al.* (1977); G.F.P. Harris and MacDermott (1977); Hilado and Cumming (1977, 1979); Viallon (1977); FPA (1978 Fire Res. Note 1078); Jarosinski and Strehlow (1978); Nettleton (1978a, 1979, 1980b); D.C. Bull (1979); Macek (1979); Yamaoka and Tsuji (1979); Ale, Burning and Koenders (1980); Mitani (1980); P. Roberts, Smith and Ward (1980); Buckmaster and Mikolaitis (1982); Crescitelli *et al.* (1982); Hertzberg (1982, 1985); Zalosh (1982); Kanury (1983); von Lavante and Strehlow (1983); Palazzi *et al.* (1984); ASTM (1985 E681); Peters and Smooke (1985); M.S. High (1987); Hustad and Sonju (1988); Kletz (1988a); Tarn and Ludford (1988); Wierzba, Karim and Cheng (1988); Wierzba, Harris and Karim (1990); Ishizuka (1991); Lakshimisha, Paul and Mukunda (1991); Law and Egolfopoulos (1991, 1992); Seaton (1991); Conrad *et al.* (1992); Hansel, Mitchell and Klotz (1992); Gibbon, Wainwright and Rogers (1994)

Effect of diluents: Burgoyne and Williams-Leir (1948a,b); Egerton (1953); Mellish and Linnett (1953); Atalla and Wohl (1965); Zabetakis (1965 BM Bull. 627); Hirst and Booth (1977); Crescitelli, Russo and Tufano (1979b); Mitani (1981); Hirst and Savage (1981/82); P. Roberts and Smith (1983); Plett (1984); Lihou (1993)

Oxygen concentration: Denison *et al.* (1968); Huggett (1973); Nguyen and Branch (1987); Subramanian and Cangelosi (1989)

Oxygen-enriched atmospheres: ASTM (1983 STP 812); HSE (1984 HSE 8); NFPA (1990 NFPA 53M)

Flammability of mists

Burgoyne (1949b, 1963); Burgoyne and Cohen (1954); J.A. Browning and Krall (1955); Hayashi *et al.* (1981)

Flammability of liquids

Burgoyone and Williams-Leir (1949); Anon. (1973c); Steen (1974)

Flashpoint, fire point

FRS (Fire Res. Note 1022); BDH (1962); Johnston (1974); Lenoir (1975); Li and Moore (1977); Lance, Barnard and Hooyman (1979); Loader (1981); Kanury (1983); ASTM (1984 E502, 1990 D92, D93); Riazi and Daubert (1987); Nakano, Hirai and Hayashi (1990); Bothe and Brandes (1992) BS 6664: 1986-; BS 2000: Pt 35: 1993

Vapour pressure: T.E. Jordan (1954)

Autoignition temperature, spontaneous ignition temperature

Townend and Madelkar (1933); Le Chatelier (1937); Silver (1937); Matson and Dufour (1950); UL (1950); J.L Jackson (1951); Coward and Jones (1952 BM Bull. 503); Setchkin (1954); Zabetakis, Furno and Jones (1954); Riddlestone (1958); Vanpee and Wolfhard (1959); Affens, Johnson and Carhart (1961); Zabetakis, Scott and Kennedy (1962 BM RI 6112); Kuchta, Cato and Zabetakis (1964); Kuchta, Bartkowiak and Zabetakis (1965 BM RI 6654); J.A. MacDonald and White (1965); Ashmore and Preston (1967); FMEC (1967); B.F. Gray (1970); Hilado and Clark (1972a,b); Affens and Carhart (1974); Beerbouwer (1974); Santon (1976); Halstead, Kirsch and Quinn (1977); Stull (1977); D.J. Lewis (1980a); Cudahy and Troxler (1983); FPA (1984 CFSD NB 5); C. Robinson and Smith (1984); Ashmore and Blumson (1987 LPB 75); Snee (1988 LPB 81); Conti and Hertzberg (1989); Oberhagemann and Schecker (1989); S.M. Richardson, Saville and Griffiths (1990); J.F. Griffiths *et al.* (1991); Egolf and Jure (1992); J.F. Griffiths *et al.* (1992); Lakshimisha *et al.* (1992); J.F. Griffiths (1993); J.F. Griffiths, Halford-Maw and Rose (1993)

Liquid ignition temperature

N.J. Thompson (1929); Setchkin (1954); Malychuk and Gollahalli (1987)

Ignition energy

Blanc *et al.* (1947, 1949); Fenn (1951); Swett (1955, 1956, 1957); Brokaw and Gerstein (1957); Riddlestone (1957); Litchfleld (1960 BM RI 5671); Ashman and Buchler (1961); Rae, Singh and Danson (1964); Slack and Woodhead (1966); FMEC (1967); Bartels and Howes (1971); de Soete (1971); Moorhouse, Williams and Maddison (1974); Ballal and Lefebvre (1975b); Bartels (1975a); Rao and Lefebvre (1976); Halm (1979); CMI (1980 CMI 803301–1); H. Kramer (1987); Sloane and Schoene (1989); Frendi and Sibulkin (1990); Glor and Siwek (1992); Chin-Shu Wang and Sibulkin (1993)

Burning velocity

Gouy (1879); Payman and Wheeler (1922); Fiock and Marvin (1937a,b); Zeldovitch and Frank-Kamenetsky (1938); Fiock *et al.* (1940); Tanford (1947); Tanford and Pease (1947); Culshaw and Garside (1949); M.E. Harris *et al.* (1949); Linnett and Hoare (1949, 1951); Strickland-Constable (1949); Gerstein, Levine and Wong (1950); Coward and Jones (1952 BM Bull. 503); Dugger and Simon (1953); Linnett (1953); Manton, von Elbe and Lewis (1953); Egerton and Lefebvre (1954); J.A. Browning and Krall (1955); Bundy and Strong (1955); Fiock (1955); D.G. Martin (1956); Spalding (1956, 1957a–c); Brokaw and Gerstein (1957); Gilbert (1957); Golovina and Fyodorov (1957); D. Smith and Agnew (1957); Eschenbach and Agnew (1958); Gibbs and Calcote (1959); O'Donovan and Rallis (1959); Schotte and Vaags (1959a,b); Spalding and Yumlu (1959); Strauss and Edse (1959); Agnew and Graiff (1961); Raezer (1961); Yang (1961); Dugger (1962); Kuehl (1962); Raezer and Olsen (1962); Rallis, Garforth and Steinz (1965); Andrews and Gray (1964); Armitage and Gray (1965); Lefebvre and Reid (1966); Yumlu (1967a,b, 1968); Fells and Rutherford (1969); Palm-Leis and Strehlow (1969); Edmondson and Heap (1970, 1971); D. Bradley and Hundy (1971); S.B. Reed (1971); Spalding, Stephenson and Taylor (1971); Andrews and Bradley (1972a,b, 1973a); Peschel and Fetting (1972); Simmons and Wright (1972); Halstead, Prothero and Quinn (1973); P.L Stephenson and Taylor (1973); Halstead, Pye and Quinn (1974); Nair and Gupta (1974); Putnam (1974); Muller-Dethlefs and Schlader (1976); Garforth and Rallis (1978); Sriramulu, Padiyar and Shet (1978); Putnam, Ball and Levy (1980); Agrawal (1981); Dixon-Lewis and Islam (1982); Gulder (1982); Liu and MacFarlane (1983); Tufano, Crescitelli and Russo (1983); Ronney and Wachman (1985); Yamaoka and Tsuji (1985); Lijima and Takeno (1986); Yu, Law and Wu (1986); P.G. Hill and Hung (1988); Gottgens, Mauss and Peters (1992); Sher and Ozdor (1992); Koroll, Kumar and Bowles (1993) *Turbulent burning velocity*: Damkb'hler (1940); Shchelkin (1943); Bellinger and Williams (1949); D.T. Williams and Bellinger (1949); Karlovitz, Denniston and Wells (1951); Wohl *et al.* (1953); Wohl (1955); Wohl and Shore (1955); J.M. Richardson (1956); Richmond, Singer *et al.* (1957); Fine (1958); Shetinkov (1959); Kozachenko (1962); Lefebvre and Reid (1966); Vinckier and van Tiggelen (1968); Palm-Leis and Strehlow (1969); Sanematsu (1969a,b); Annand (1970); Bhaduri (1970); Mizutani (1972); Andrews, Bradley and

Lwakabamba (1975a,b); Abdel-Gayed and Bradley (1977, 1982); Gokalp (1980); Abdel-Gayed, Bradley and Lawes (1987); Sivashinsky (1988); Liu and Lenze (1989); Catlin and Linstedt (1991); D. Bradley, Lau and Lawes (1992); D. Bradley, Gaskell and Gu (1994)

Quenching
Blanc *et al.* (1947); R. Friedman (1949); M.E. Harris *et al.* (1949); Wohl (1953); Loison, Chaineaux and Delclaux (1954); Berlad and Potter (1955); Brokaw and Gerstein (1957); Potter and Berlad (1957); Singer and von Elbe (1957); Anagnostou and Potter (1959); Wolfhard and Bruszak (1959 BM RI 5457, 1960); Potter (1960); Pusch and Wagner (1962); Kydd and Foss (1964); Grove (1966, 1967); Rosser, Inami and Wise (1966); H. Phillips (1971a, b, 1981a); Rozlovski and Zakaznov (1971); E.C. Woodward and Drew (1971); FRS (1973 Fire Res. Notes 973, 990, 1974 Fire Res. Note 1018); Lunn and Phillips (1973); Nair and Gupta (1973); Ryason and Hirsch (1974); Ballal and Lefebvre (1975a, 1977, 1978, 1979); Maekawa (1975); Buckmaster (1976); F.A. Williams (1976b); Jarosinski and Strehlow (1978); Maekawa, Takeichi and Kato (1978); Maekawa and Takeichi (1979); Strehlow, Nichols *et al.* (1979); P. Roberts, Smith and Ward (1980); Chomiak and Jarosinski (1982); Lunn (1982a,b, 1984a); Jarosinski (1983); Dickie and Lunn (1984); Mendoza, Smolensky and Straitz (1993)

Calorific value
FMEC (1967); Association Nationale pour la Protection centre l'Incendie (1972)

Flame temperature
Loomis and Perrott (1928); G.W. Jones, Lewis and Seaman (1931, 1932); G.W. Jones *et al.* (1931); Ministry of Power (1944); Fehling and Leser (1949); Winternitz (1949); Huff, Gordon and Morrell (1951); B. Lewis and von Elbe (1951, 1961, 1987); Thring (1952); Gaydon and Wolfhard (1953); Bundy and Strong (1955); General Electric Co. (1955); Kaskan (1957); Zabetakis, Lambiris and Scott (1959); Berenblut and Downes (1960); Gay *et al.* (1961); Zeleznik and Gordon (1968); Gordon and McBride (1971, 1976); Stall and Prophet (1971); Svehla and McBride (1973); Eisenberg, Lynch and Breeding (1975); J.G. Marshall and Rutledge (1982); Vancini (1982); Chang and Rhee (1983); Rhee and Chang (1985)
Gas specific heats: W.D.M. Bryant (1933); Spencer and Justice (1934); Justi and Liider (1935); Justi (1938); Spencer and Flannagan (1942); Dodge (1944); Spencer (1945); Hougen and Watson (1947); Prothero (1969); Vancini (1982); Barnard and Bradley (1985); Yaws, Ni and Chang (1988)

Mists and sprays
Haber and Wolff (1923); Burgoyne (1963); Mizutani (1972b); Mizutani and Nishimoto (1972); J.T. Bryant (1975); S.J. Cook, Cullis and Good (1977); Hayashi, Kumagai and Sakai (1977); Nettleton (1978a, 1987); Ballal (1983a,b)

Thermodynamic properties (*see also* Table 11.1)
Westenberg (1957); M.K. Martin and Heywood (1977)

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flammability limit (UFL), it is too 'rich'. The concentrations between these limits constitute the flammable range. The LFLs and UFLs are also sometimes called, respectively, the lower and upper explosive limits (LELs and UELs). They are distinct from the detonability limits.

In general, the most flammable mixture corresponds approximately, but not exactly, to the stoichiometric mixture for combustion. It is frequently found that the concentrations at the LFLs and UFLs are roughly one-half and twice that of the stoichiometric mixture, respectively.

Flammability limits are affected by pressure, temperature, direction of flame propagation, gravitational field and surroundings. The limits are determined experimentally and the precise values obtained depend, therefore, on the particular test method.

Although there is no universally used equipment, one which has been utilized for the measurement of many flammability limit data is the BM apparatus, which is described by Coward and Jones (1952 BM Bull. 503) and which consists of a cylindrical tube 5 cm diameter and 1.5 m high. The tube is closed at the top but open at the bottom. Gas–air mixtures of different compositions are placed in the tube and a small ignition source is applied at the bottom. The lower and upper limit concentrations at which the flame initiated by the source of ignition just travels the full length of the tube are then determined.

The test is normally carried out with the mixture at atmospheric pressure and temperature and with upward flame propagation, but other conditions can be investigated such as different pressures and temperatures, downward flame propagation and/or addition of inert gases. Table 16.4 shows flammability limits of selected substances. It also gives other flammability characteristics that are described below.

For many organic substances the LFL, expressed in mass per unit volume, lies within a relatively narrow range. Burgoyne (1963) quotes data that show the limits as lying mainly in the range 0.04–0.10 g/l (or oz/ft^3). More specifically, he states that for saturated hydrocarbons the LFL is of the order of 0.045 g/l (oz/ft^3). For unsaturated hydrocarbons it is less and for oxygenated hydrocarbons it is more.

Flammability limits are affected by pressure. Normal variations of atmospheric pressure do not have any appreciable effect on flammability limits. The effect of larger pressure changes is not simple or uniform, but is specific to each mixture. A decrease in pressure below atmospheric can narrow the flammable range by raising the LFL and reducing the UFL until the two limits coincide and the mixture becomes non-flammable. This effect is illustrated for methane in Figure 16.3.

Conversely, an increase in pressure above atmospheric can widen the flammable range by reducing the LFL and raising the UFL. This effect is shown in Figure 16.4 for natural gas. It may be noted that the effect is more marked on the upper than on the LFL. In the case of higher hydrocarbons, increase in pressure causes an abnormal increase in the UFL with the creation of a region of cool flames (Hsieh and Townend, 1939b). Cool flames are considered further below. However, an increase in pressure does not always widen the flammable range; in some cases it can narrow it.

Flammability limits are also affected by temperature. An increase in temperature tends to widen the flammable range. This effect is shown for methane in Figure 16.5. The variation of the LFL of methane with temperature is illustrated in Figure 16.6. The limit values obtained experimentally fall fairly close to a straight line that passes through the lower limit at 25°C and through zero at the flame temperature of 1225°C.

Table 16.4 *Flammability limits, AITs and flashpoints of selected substances in air at atmospheric pressure*

	Flammability limit (%v/v)		*Auto-ignition temperature* (°C)	*Flashpoint* (°C)	
	Lower	*Upper*		*Closed cup*	*Open cup*
Acetone	2.6	13	465	−18	−9
Acetylene	2.5	100	305	–	–
Ammonia	15	28	651[a]	–	–
Benzene	1.4[a]	8.0[a]	562[a]	−11	–
-Butane	1.8	8.4	405	−60	–
Carbon disulfide	1.3	50	90	−30	–
Cabon monoxide	12.5	74	–		
Cyclohexane	1.3	7.8	245	−20	–
Ethane	3.0	12.4	515	−135	–
Ethylene	2.7	36	490	−121	–
Ethylene dichloride	6.2[a]	15.9[a]	413[a]	13	18
Ethylene oxide	3[a]	100[a]	429[a]	–	−20
Hydrogen	4.0	75	400	–	–
Methane	5.0	15.0	540	–	–
Propane	2.1	9.5	450	< −104	–
Propylene	2.4	11	460	−108	–
Styrene	1.1[a]	6.1[a]	490[a]	32	38
Toluene	1.3[a]	7.0[a]	536[a]	4	7
Vinyl chloride	4[a]	22[a]	472[a]	–	−78

Sources: Flammability limits: Zabetakis (1965 BM Bull. 627), except as given in footnote. AIT: Zabetakis (1965 BM Bull. 627), except as given in footnote. Flash points: FMEC (1967).
[a] FMEC (1967).

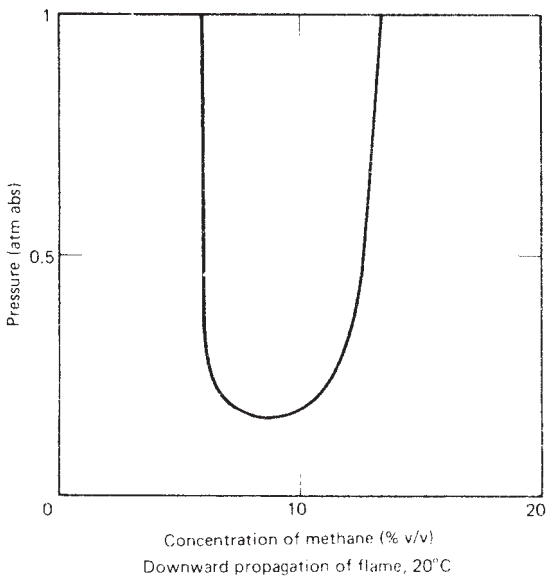


Figure 16.3 *Effect of pressure on flammability limits of methane in air (Coward and Jones, 1952 BM Bull. 503) (Courtesy of the Bureau of Mines)*

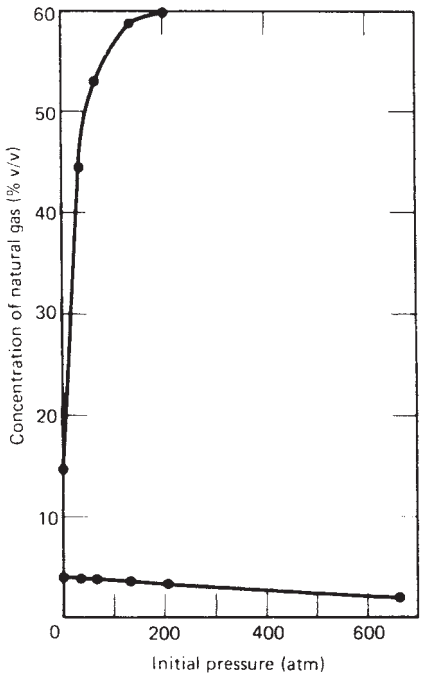


Figure 16.4 *Effect of pressure on inflammability limits of natural gas in air (Zabetakis, 1965 BM Bull. 627) (Courtesy of the Bureau of Mines)*

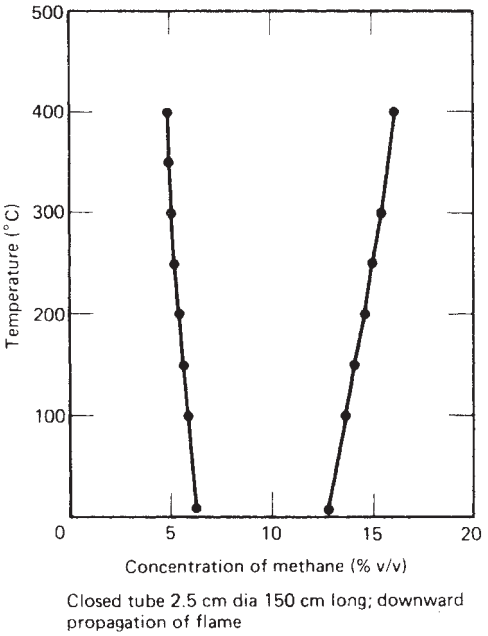


Figure 16.5 *Effect of temperature on flammability limits of methane in air (Coward and Jones, 1952 BM Bull. 503) (Courtesy of the Bureau of Mines)*

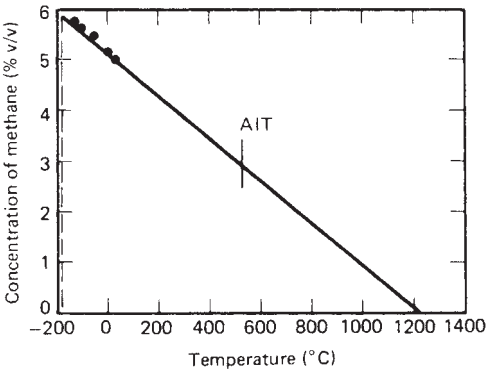


Figure 16.6 *Effect of temperature on low flammability limit of methane in air (Zabetakis, 1965 BM Bull. 627) (Courtesy of the Bureau of Mines)*

Similar results are obtained for the effect of temperature on the LFLs of other lower paraffinic hydrocarbons. For these the approximate flame temperature can be taken as 1300°C. Then for the first 10 members of the series from methane to decane

$$\frac{L_t}{L_{25}} = 1 - \frac{t - 25}{1300 - 25} \qquad [16.2.1]$$

where L_t is the LFL at t°C (% v/v), L_{25} is LFL at 25°C (% v/v) and t is the temperature (°C).

The data may also be fairly well correlated by the modified Burgess–Wheeler law, suggested by Zabetakis, Lambiris and Scott (1959):

$$\frac{L_t}{L_{25}} = 1 - \frac{0.75(t - 25)}{\Delta H_c} \qquad [16.2.2]$$

where ΔH_c is the net heat of combustion (kcal/mol). Likewise the modified Burgess–Wheeler law may correlate the effect of temperature on the UFL of these hydrocarbons, in the absence of cool flames:

$$\frac{U_t}{U_{25}} = 1 - \frac{0.75(t - 25)}{\Delta H_c} \qquad [16.2.3]$$

where U_t is the UFL at t°C (% v/v), and U_{25} is the UFL at 25°C (% v/v).

The variation of flammability limits with temperature was studied by Bodurtha (1980), who obtained for the substances studied a value of 0.0008/°C both for the fractional decrease with temperature of the LFL and for the fractional increase with temperature of the UFL.

A more recent study of the effect of pressure and temperature on flammability limits is that of Gibbon, Wainwright and Rogers (1994), who investigated a limited number of solvents. Their work confirmed that an increase in temperature causes a decrease in the LFL and an increase in the UFL. They also found that the UFL increased with increase in pressure. Unexpectedly, the LFL also increased with increase in pressure.

In sum, the effect of pressure on the flammability limits is much less predictable than that of temperature. In particular, increase in pressure causes in some cases a decrease in the LFL and in others an increase.

It has been demonstrated that flammability limit measurements can be complicated by surface and vapour phase reactions that occur above the AIT. It has been shown, for example, that methane–air mixtures containing up to 5% v/v methane burn readily at 1000°C. The experiments were conducted with methane concentrations as low as 0.5% v/v (Burgoyne and Hirsch, 1954).

Flammability limits are also affected by the addition of an inert gas such as nitrogen, carbon dioxide or steam. This effect is shown for methane in Figure 16.7. Minimum inert gas contents for suppression of flammability of selected substances in air are shown in Table 16.5. In general, carbon dioxide causes a greater narrowing of the flammable range than does nitrogen. For many flammable gas–air systems, the mixtures can be rendered non-flammable by the addition of about 30% of carbon dioxide or about 40% of nitrogen.

The flammability limits described are those for mixtures of a flammable gas in air. There are also flammability limits for combustion in pure oxygen. In general, the LFL of a gas is almost the same in oxygen as in air, but the UFL is much greater in oxygen than in air. The flammable range in oxygen is thus wider than it is in air. The applicability of flammability limits is not confined, however, to air and oxygen. There are flammability limits for substances that burn in chlorine.

Flammability limits for a fuel mixture that contains several flammable gases may be calculated from the equation of Le Chatelier (1891). For the lower limit

$$L = \frac{1}{\sum_{i=0}^{n} (y_i / L_i)} \qquad [16.2.4a]$$

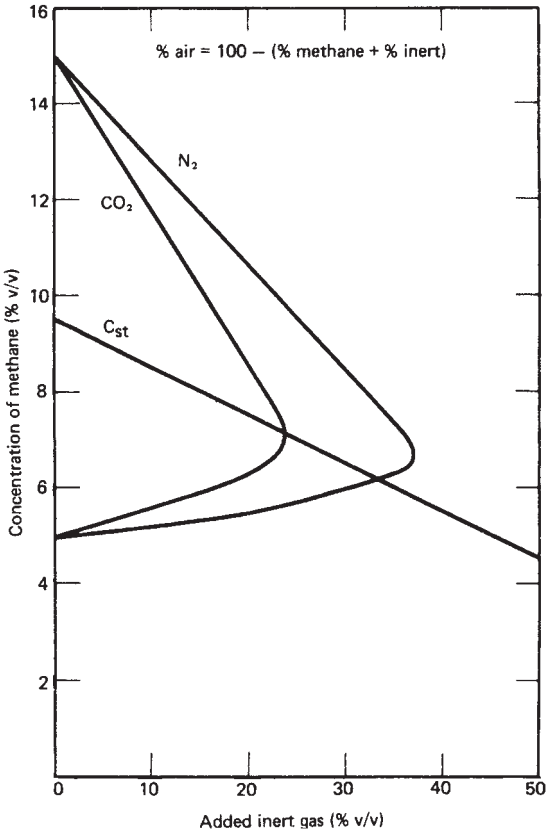


Figure 16.7 *Effect of inert gases on flammability limits of methane in air (Zabetakis, 1965 BM Bull, 627) (Courtesy of the Bureau of Mines)*

where L is the LFL of air-free fuel (%v/v), L_i the LFL of fuel component i (%v/v) and y_t is the concentration of fuel component i (mole fraction). For the upper limit

$$U = \frac{1}{\sum_{i=0}^{n} (y_i/U_i)} \qquad [16.2.4b]$$

where U is the UFL of air-free fuel (%v/v), and U_i, the UFL of fuel component i (%v/v).

Le Chatelier's equation is an empirical one and it is not universally applicable. Its limitations are discussed by Coward and Jones (1952 BM Bull. 503, p. 6). Further information on and examples of the calculation of the flammability limits of fuel mixtures are given in BS 5345: Part 1: 1976.

It is necessary to exercise care in using flammability limit data, since the limit may vary with pressure, temperature and other conditions. The LFL required to determine the amount of flammable gas–air mixture resulting from a plant leak can probably be obtained quite readily, because usually the data are available for ambient conditions and the accuracy called for is not high, but that required to maintain the concentration of a flammable gas–oxygen mixture entering a reactor just below the flammable range under other pressure and temperature conditions needs greater consideration, because the data may not be available so readily for these other conditions, but they must be accurate.

Table 16.5 *Minimum inert gas content for suppression of flammability of selected substances in air (after Burgoyne, 1965a) (Courtesy of the Institution of Marine Engineers)*

	Nitrogen (% v/v)	*Carbon dioxide* (% v/v)
Methane	38	24
Ethane	46	33
Propane	43	30
n-Butane	41	28
n-Pentane	43	29
n-Hexane	42	29
Ethylene	50	41
Propylene	43	30
Benzene	45	32

16.2.2 Ignition temperature

If the temperature of a flammable gas–air mixture is raised in a uniformly heated apparatus, it eventually reaches a value at which combustion occurs in the bulk gas. For the range of flammable mixtures there is a mixture composition that has the lowest ignition temperature. This is the minimum spontaneous ignition temperature (SIT) or auto-ignition temperature (AIT).

The AIT for the first 10 paraffinic hydrocarbons are as follows (Zabetakis, 1965 BM Bull. 627):

	AIT (°C)		*AIT* (°C)
Methane	537	*n*-Hexane	223
Ethane	515	*n*-Heptane	223
Propane	466	*n*-Octane	220
n-Butane	405	*n*-Nonane	206
n-Pentane	258	*n*-Decane	208

It may be noted that there is a break between the AIT for *n*-butane and that for *n*-pentane and that the rate of decrease of these temperatures after *n*-pentane is low. Some substances have quite low AITs. The AIT of carbon disulfide, for example, is 90°C.

The AIT temperature is a property that is particularly liable to variations caused by the nature of hot surfaces. The values normally quoted are obtained in laboratory apparatus with clean surfaces. The AIT may be reduced by as much as 100–200°C for surfaces that are lagged or are contaminated by dust.

Auto-ignition temperatures of selected substances are given in Table 16.4.

16.2.3 Ignition time delay

Ignition of a flammable mixture raised to or above the temperature at which spontaneous ignition occurs is not instantaneous; there is a finite time delay before ignition

takes place. This time delay decreases as the ignition temperature increases and the reduction has been correlated by Semenov (1959) using the equation

$$\ln \tau = \frac{k_1 E}{T} + k_2 \qquad [16.2.5]$$

where E is the apparent activation energy, T is the absolute temperature, τ is the time delay before ignition, and k_1 and k_2 are constants. The time delay may be as little as a fraction of a second at higher temperatures or several minutes close to the AIT.

This effect may be of significance in flow systems where the fluid is a flammable mixture that comes in contact with a hot surface above the AIT, but for a short time only.

16.2.4 Flashpoint

The flashpoint of a flammable liquid is the temperature at which the vapour pressure of the substance is such as to give a concentration of vapour in the air that corresponds to the LFL.

There are two methods of measuring flashpoint, the closed cup test and the open cup test. Some standard test methods are:

Closed cup	Pensky Martens	ASTM D 93–61 BS 2839: 1969
	Tagliabue	ASTM D 56–61
Open cup	Cleveland	ASTM D 92–57

The open cup flashpoint is usually a few degrees higher than the closed cup flashpoint. The relationships between vapour pressure, flammability limits, flashpoint and AIT are illustrated in Figure 16.8.

A liquid that has a flashpoint below ambient temperature and can thus give rise to flammable mixtures under ambient conditions is generally considered more hazardous than one with a higher flashpoint. The flashpoint is a main parameter, therefore, in hazard classification of liquids and in government regulations based on these. Thus, in aviation there has been movement to replace fuel JP4 with JP1. The former is akin to petroleum and has a low flashpoint, while the latter is more like kerosene and has a higher flashpoint, which is therefore safer.

Obviously, however, a higher flashpoint liquid also becomes more hazardous if it is heated up to a temperature above its flashpoint. The flashpoints of selected substances are given in Table 16.4.

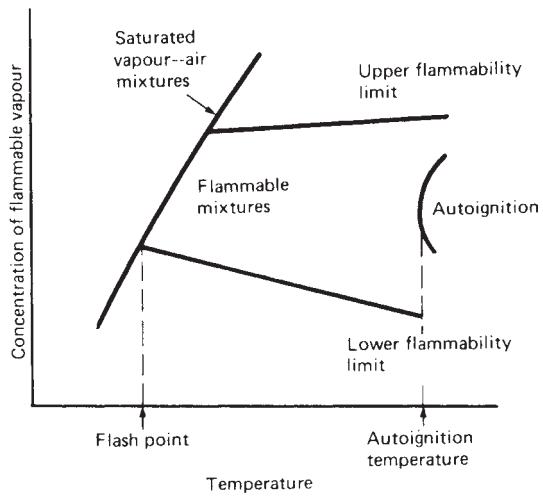


Figure 16.8 *Relationships between vapour pressure, flammability limits, flashpoint and auto-ignition temperature (after Zabetakis, 1965 BM Bull. 627) (Courtesy of the Bureau of Mines)*

16.2.5 Fire point

The fire point of a flammable liquid is the lowest temperature at which the liquid, when placed in an open container, will give off sufficient vapour to continue to burn once ignited. The fire point is usually a few degrees above the open cup flashpoint.

16.2.6 Ignition energy

If a flammable gas–air mixture is to be ignited by a local source of ignition, however, it is not sufficient (as it is with auto-ignition) to raise a volume of the mixture to a certain temperature for a certain time. There is also a minimum volume of mixture so treated that is required in order to give rise to a continuing flame through the rest of the mixture. It has been shown, for example, that to ignite a methane–air mixture in a cold container by means of a hot patch an area of 18 mm^2 is required at 1000–1100°C (Rae, Singh and Danson, 1964). There is in effect an ignition energy requirement.

Similarly, ignition of a flammable gas–air mixture by a local source of ignition by electrical discharge occurs only if the latter possesses a certain energy. The variation of ignition energy with composition is shown for hydrogen and for methane in Figure 16.9.

There is a minimum ignition energy (MIE), which usually occurs close to the stoichiometric mixture. Minimum ignition energies (MIEs) for selected substances are shown in Table 16.6.

16.2.7 Burning velocity

The burning velocity affects the rate of combustion of a flammable mixture. The burning velocity is a property of the mixture. It is in effect the velocity at which a gaseous fuel–air mixture issuing from a burner burns back on to the burner. The burning velocity of a fuel–air mixture is usually determined by measurement of a premixed bunsen burner flame in the laminar region. The burning velocity S_u is obtained by dividing the volumetric gas flow V by the area A of the flame front cone:

$$S_u = V/A \qquad [16.2.6]$$

Alternatively, the burning velocity may be obtained from the velocity u of the gas and the half-angle α of the apex of the flame front cone:

$$S_u = u \sin \alpha \qquad [16.2.7]$$

If the flame front cone has radius r, height h and slant height l, the area A of the cone surface and the area A' of the

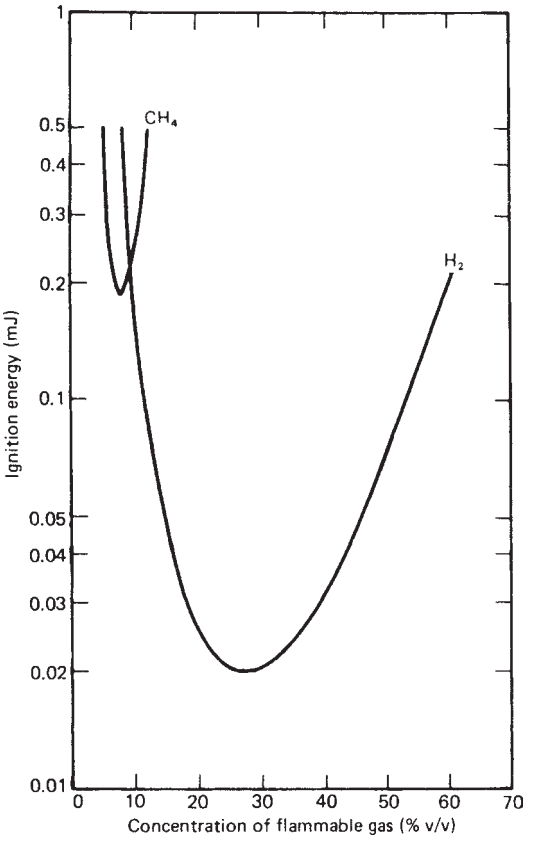


Figure 16.9 *Effect of mixture composition on electrical ignition energy of methane and of hydrogen in air (Factory Mutual Engineering Corporation, 1967)*

cone triangular cross-section are, respectively

$$A = \pi r l \qquad [16.2.8a]$$

$$= \pi r\left(r^2 + h^2\right)^{1/2} \qquad [16.2.8b]$$

$$A' = rh \qquad [16.2.9]$$

Also

$$A = \pi A' l / h \qquad [16.2.10]$$

The gas velocity u is

$$u = \frac{V}{\pi r^2} \qquad [16.2.11]$$

The flame front is usually not a perfect cone and, in consequence, the equations just quoted are subject to errors of varying size. The choice of equations for the calculation of burning velocity is discussed by B. Lewis and von Elbe (1961) and by Fells and Rutherford (1969). The maximum burning velocity obtained at atmospheric pressure and temperature is referred to as the maximum fundamental burning velocity.

Table 16.6 *Minimum ignition energies for selected substances in air*

	Minimum ignition energy (mJ)
Carbon disulfide	0.01–0.02
Hydrogen	0.019
Acetylene	0.02
Methane	0.29
Ethane	0.24
Propane	0.25
n-Butane	0.25
n-Hexane	0.25
Ethylene	0.12
Benzene	0.22
Ammonia	up to >100

Sources: Burgoyne (1965a); FMEC (1967).

Burning velocities for methane in air and in oxygen are shown in Figure 16.10. In general, burning velocities for paraffinic hydrocarbons range from a few centimetres per second near the flammability limits up to about 45 cm/s near the stoichiometric mixture. For these hydrocarbons in oxygen the corresponding values are about 125 and 425 cm/s, respectively.

Burning velocities are affected by pressure and temperature. The effect of pressure changes is variable. A decrease in the burning velocity of stoichiometric methane–air mixtures has been found with increasing pressure in the range 0.5–20 atm, but with stoichiometric methane–oxygen mixtures an increase in pressure in the range 0.2–2 atm gave an increase in burning velocity.

The effect of temperature on burning velocity is more consistent and is sometimes described by the equation

$$S_u = A + BT^n \qquad [16.2.12]$$

where T is the absolute temperature, A and B are constants and n is an index. A value of 2.0 for the index n has been found for some paraffinic hydrocarbons (Zabetakis, 1965 BM Bull. 627, p. 43). Maximum fundamental burning velocities of selected substances in air and in oxygen are given in Table 16.7.

The actual flame speed in combustion of a flammable mixture is greater, and sometimes very much greater, than the burning velocity. Whereas the burning velocity is a property of the mixture only, the flame speed depends on other factors such as turbulence and pressure waves. If detonation occurs, the flame speed is greater by orders of magnitude than the burning velocity.

16.2.8 Adiabatic flame temperature

The heat radiated by combustion of a flammable mixture depends on the flame temperature, the theoretical maximum value of which is the adiabatic flame temperature. The adiabatic flame temperature is the temperature attained by combustion under adiabatic conditions. It is normally determined for the stoichiometric mixture and values quoted generally refer to this unless otherwise stated.

The adiabatic flame temperature can be calculated, but for an accurate calculation this is not entirely

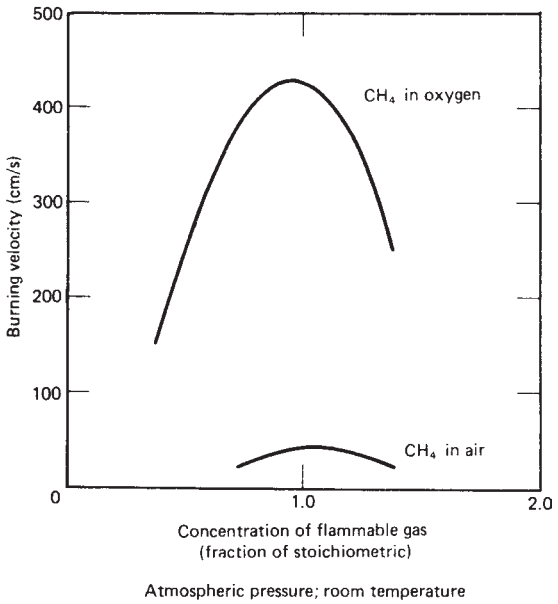


Figure 16.10 *Effect of mixture composition on burning velocity of methane in air and in oxygen (Zabetakis, 1965 BM Bull. 627) (Courtesy of the Bureau of Mines)*

Table 16.7 *Maximum fundamental burning velocities of selected substances in air and in oxygen*

	Maximum fundamental burning velocity,[a] S_u	
	(cm/s)	(ft/s)
In air		
Methane	36.4[b]	1.2
Ethane	40.1	–
Propane	45[b]	1.5
n-Butane	40.5	1.3
n-Hexane	38.5	1.3
Ethylene	68.8[b]	2.3
Town gas[c]	–	3.7
Acetylene	173	5.8
Hydrogen	320	11.0
Benzene	40.7[b]	–
In oxygen		
Methane	393[d]	–
Propane	390	–
Ethylene	550	–
Acetylene	1140	–
Hydrogen	1175	–

[a] The values given in the first column (cm/s) are those of Fiock (1955) and in the second column (ft/s) those of the HSE (1965 HSW Bklt 34). The values quoted from Fiock are for initial pressure atmospheric and initial temperature room temperature and, in most cases, dry gas, and generally are selected from several values listed.
[b] Some higher values are also listed by Fiock.
[c] For town gas containing 63% H_2.
[d] For stoichiometric mixture.

straightforward. Accounts of calculation methods are given by Hoil pen. Watson and Rasyatz (1954–). W.A. Grav. Kilham and Mffller (1976), Barnard and Bradley (1985), Drysdale (1985) and Kuo (1986).

The adiabatic flame temperature may be determined for constant pressure or constant volume conditions. The value normally quoted is for the former. For this case the enthalpy balance is

$$\Delta H_2 + \Delta H_1 + \Delta H_c = 0 \qquad [16.2.13]$$

or

$$\Delta H_2 + \Delta H_1 + (-\Delta H_c) \qquad [16.2.14]$$

with

$$\Delta H_1 = \sum_{i=1}^{r} n_i \int_{T_1}^{T_0} c_{pi}(T)\,\mathrm{d}T \qquad [16.2.15]$$

$$= c_{pmr}(T_0 - T_1) \qquad [16.2.16]$$

$$\Delta H_2 = \sum_{i=1}^{p} n_i \int_{T_0}^{T_2} c_{pi}(T)\,\mathrm{d}T \qquad [16.2.17]$$

$$= c_{pmp}(T_2 - T_0) \qquad [16.2.18]$$

where c_p is the specific heat at constant pressure of component i (kJ/kmol°C), c_{pm} is the mean specific heat over the range of interest (kJ/kmol°C), ΔH_c is the heat of combustion (kJ/mol of fuel), ΔH_1 is the enthalpy change between states 1 and 0 (kJ/kmol of fuel), ΔH_2 is the enthalpy change between states 1 and 2 (kJ/kmol of fuel), n is the number of moles per mole of fuel, p is the number of products, r is the number of reactants and subscripts i, p and r denote component i, products and reactants, and 0, 1 and 2 denote the standard state, initial state and final state, respectively.

The specific heat c_{pi} of a reactant or product is a function of the temperature T. It is commonly represented in the form

$$c_{pi} = a_i + b_i T + c_i T^2 + d_i T^3 \qquad [16.2.19]$$

where a_i (kJ/kmol°C), b_i (kJ/kmol°C K), c_i (kJ/kmol°C K^2) and d_i (kJ/kmol°C K^3) are constants.

Then from Equations 16.2.17–16.2.19 the mean specific heat of product i is

$$c_{pmi} = \frac{\left(a_i T + b_i T^2/2 + c_i T^3/3 + d_i T^4/4\right)_{T_0}^{T_2}}{T_2 - T_0} \qquad [16.2.20]$$

and the mean specific heat of the product mixture is

$$c_{pmp} = \sum_{i=1}^{p} n_i c_{pmi} \qquad [16.2.21]$$

If necessary, equations similar to Equations 16.2.20 and 16.2.21, derived from Equations 16.2.15 and 16.2.19, may be used to obtain c_{pmr}, but generally the initial temperature T_1 is close to the standard temperature T_0 so that a point value of c_{pmr} may be used. If in fact $T_1 = T_0$, then $\Delta H_1 = 0$.

Table 16.8 gives values of the constants in Equation 16.2.19 for the determination of point values of the specific

Table 16.8 *Constants for specific heat at constant pressure (Barnard and Bradley, 1985) (Courtesy of Chapman and Hall)*

Species	*Constant*[a]				*Valid over temperature range* (K)
	a	$10^2 b$	$10^5 c$	$10^9 d$	
H_2	29.09	− 0.1916	0.4000	− 0.870	273–1800
O_2	25.46	1.519	− 0.7150	1.311	273–1800
N_2	27.32	0.6226	− 0.0950	–	273–3800
CO	28.14	0.1674	0.5368	− 2.220	273–1800
CO_2	22.24	5.977	− 3.499	7.464	273–1800
H_2O	32.22	0.1920	1.054	− 3.594	273–1800
CH_4	19.87	5.021	1.286	− 11.00	273–1500
C_2H_2	21.80	9.208	− 6.523	18.20	273–1500
C_2H_4	3.95	15.63	− 8.339	17.66	273–1500
C_2H_6	6.895	17.25	6.402	7.280	273–1500
C_3H_8	− 4.042	30.46	− 15.71	31.71	273–1500
C_6H_6	− 39.19	48.44	− 31.55	77.57	273–1500
CH_3OH	19.04	9.146	− 1.218	− 8.033	273–1000
NH_3	27.55	2.563	0.9900	− 6.686	273–1500
NO	27.03	0.9866	0.3223	0.3652	273–3800
SO_2	25.76	5.791	− 3.809	8.606	273–1800

[a] Constants in the equation $c_p = a + bT + cT^2 + dT^3$, where c_p is the specific heat (kJ/kmol °C) and T is the absolute temperature (K).

Table 16.9 *Mean specific heats (kJ/kmol °C) at a constant pressure (after Hougen, Watson and Ragatz, 1954–)*

Final temperature, t (°C)	*Mean specific heat* (kJ/kmol °C)			
	O_2	N_2	CO_2	H_2O
2000	35.27	33.47	54.85	43.67
2100	35.42	33.61	55.14	44.05
2200	35.55	33.72	55.43	44.42

[a] Mean specific heat over the temperature interval 0°C to t °C. Values based on data for zero pressure given by the authors and based on those of Wagman (1953).

heats c_p. Table 16.9 gives values of the mean specific heat c_{pm} over the interval 0°C to t °C.

In the foregoing the implicit assumption is that the products of combustion are those given by the simple stoichiometric equation, which for hydrocarbons yields only CO_2 and H_2O. In fact, for flame temperatures above about 1370°C dissociation of the products of combustion occurs. At adiabatic flame temperatures, dissociation and ionization absorb a significant amount of energy and result in an appreciable lowering of the temperature of the flame. This is illustrated in Table 16.10, which shows that for propane the values obtained for the adiabatic flame temperature are 2219 K using a comprehensive set of equilibriums, 2232 K using a simplified set and 2324 K considering only the formation of CO_2 and H_2O.

Calculations of the adiabatic flame temperature allowing for dissociation are complex. A computer program that performs such calculations has been described by Gordon and McBride (1971, 1976). An account of its use is given by Kuo (1986).

Table 16.11 gives some theoretical and experimental values of flame temperature quoted by B. Lewis and von Elbe (1987) and Siegel and Howell (1991). The theoretical values given in the table are adiabatic flame temperatures at constant pressure. Details of the experimental temperatures are given in the footnote to the table. Lewis and von Elbe state that the experimental flame temperatures were probably influenced somewhat by heat loss and other factors, but that the error is small; Siegel and Howell describe the experimental values as 'maximum temperatures'.

16.2.9 Degree of flammability

Comparisons are often made between the flammability either of different substances or of different mixtures of the same substance in air. There is no single parameter that defines flammability, but some that are relevant are (1) the flashpoint, (2) the flammability limits, (3) the AIT, (4) the ignition energy and (5) the burning velocity.

The flashpoint of a substance is often treated as the principal index of flammability, a substance being regarded as highly flammable if it has a low flashpoint. The other flammability characteristics are also important, however. The flammability of the substance is increased by wide flammability limits and by a low minimum AIT, low MIE and a high maximum burning velocity.

The mixtures that have the lowest AITand ignition energy and the highest burning velocity, tend to occur near to, but normally not exactly at, the stoichiometric composition.

16.2.10 Quenching effects

Flame propagation is suppressed if the flammable mixture is held in a narrow space. Thus there is a minimum diameter for apparatus used for determination of flammability limits such that below this diameter the flammable range measured is narrower and inaccurate. Ultimately, if the space is sufficiently narrow, flame propagation is suppressed completely. The largest diameter as which flame propagation is suppressed is known as the quenching diameter. For an aperture of slot-like cross-section there is a critical slot width.

Table 16.10 *Complete thermodynamic treatment of adiabatic flame temperature of propane in air (Barnard and Bradley, 1985) (Courtesy of Chapman and Hall)*

Species	*Concentration* (mole fraction)			
	Constant pressure			*Constant volume*
	Case 1	*Case 2*	*Case 3*	
CO_2	0.1004	0.1003	0.1111	0.0914
H_2O	0.1423	0.1439	0.1481	0.1374
N_2	0.7341	0.7347	0.7407	0.7276
CO	0.0099	0.0100		0.0182
H_2	0.0032	0.0033		0.0053
O_2	0.0048	0.0055		0.0075
NO	0.0020	0.0022		0.0052
CH_2O	$<10^{-5}$			$<10^{-5}$
C_2H_4	$<10^{-5}$			$<10^{-5}$
C_3H_6	$<10^{-5}$			$<10^{-5}$
N_2O	$<10^{-5}$			$<10^{-5}$
CHO	$<10^{-5}$			$<10^{-5}$
CH_3	$<10^{-5}$			$<10^{-5}$
C_2H_5	$<10^{-5}$			$<10^{-5}$
i-C_3H_7	$<10^{-5}$			$<10^{-5}$
H	0.0035			0.0009
O	0.0020			0.0008
N	$<10^{-5}$			$<10^{-5}$
OH	0.0027			0.0058
HO_2	$<10^{-5}$			$<10^{-5}$
Final temperature (K)	2219	2232	2324	2587

[a] Calculations are for a stoichiometric mixture. Case 1 refers to calculations based on a comprehensive set of equilibriums, Case 2 to calculations using a smaller set of equilibriums, and Case 3 to calculations made considering only the formation of CO_2 and H_2O.

Table 16.11 *Adiabatic flame temperatures of selected substances in air at atmospheric pressure*

	Theoretical[a] (K)		*Experimental* (K)	
	Complete combustion	*With dissociation and ionization*	1[a]	2[b]
Methane	2285	2191	2148	2158
Ethane	2338	2222	2168	2173
Propane	2629	2240	2198	2203
n-Butane	2357	2246	2168	2178
Ethylene	2523	2345	2248	2253
Propylene	2453	2323	2208	2213
Acetylene	2859			2598
Benzene	2484			
Carbon monoxide	2615			
Hydrogen	2490			2318

[a] Given by Siegel and Howell (1991), quoting Barnett and Hibbard (1957) and Gaydon and Wolfhard (1960). Values for combustion in dry air at 298 K.
[b] Given by B. Lewis and von Elbe (1987), quoting Loomis and Perrott (1928), G.W. Jones, Lewis and Seaman (1931) and G.W. Jones *et al.* (1931). See text.

The term 'quenching distance' is used sometimes as a general term covering both quenching diameter and critical slot width and sometimes meaning the latter only. An account of quenching distances is given by Potter (1960). He gives the following empirical relation between quenching diameter D_o and critical slot width $D_\parallel$:

$$D_\parallel = 0.65 D_o \qquad [16.2.22]$$

He also discusses the effect of pressure and temperature on these variables.

There is a maximum experimental safe gap (MESG) that avoids the transmission of an explosion occurring within a container to a flammable mixture outside the container. The MESG is measured in a standard apparatus. One apparatus consists of a spherical vessel with the gap between a pair of flat equatorial flanges, the breadth of the gap being 1 in. A value of less than 1 in. causes a decrease in the MESG, but a greater value has no effect. An account of maximum safe gaps is given by Lunn and Phillips (1973).

Critical slot widths and MESGs for selected substances in air are given in Table 16.12. It is emphasized that these values relate to a stationary flame. If the gas flow is in the direction of flame propagation, a smaller gap is needed to quench the flame and, conversely, if the gas flow is in the opposite direction, a larger gap will effect quenching. If the gas velocity is high enough, a condition can occur in which a flame propagating against the flow is stabilized at a constriction and causes local overheating.

For some substances, notably acetylene, carbon disulfide and hydrogen, the quenching diameters and distances are very small. These quenching effects are important in the design of flameproof equipment and of flame arresters.

Table 16.12 *Critical slot widths and maximum experimental safe gaps for selected substances in air*

	Critical slot width[a,b] (mm)	*Maximum experimental safe gap*[b,c] (mm)
Acetone	–	1.01
Acetylene	0.52	0.37[d]
Ammonia	–	3.18
Benzene	1.87	0.99
n-Butane	–	1.07[e]
Carbon disulfide	0.55	0.20
Carbon monoxide	–	0.91[d]
Cyclohexane	3.0	0.94
Ethane	–	0.91
Ethylene	1.25	0.65
Ethylene dichloride	–	1.82
Ethylene oxide	1.18	0.59
Hydrogen	0.50	0.20
Methane	2.16	1.14
n-Pentane	2.07	0.89[e]
Propane	1.75	0.92
Propylene	–	0.91
Vinyl chloride	–	0.96

Sources: Critical slot width: Potter (1960). Maximum experimental safe gap: Lunn and Phillips (1973), except as given in footnotes.
[a] Critical slot widths are for stoichiometric mixtures and are corrected where necessary to atmospheric pressure and 25°C.
[b] Where several values of critical slot width or maximum experimental safe gap are given in original reference, the value quoted here is the smallest.
[c] Maximum experimental safe gaps are corrected where necessary to atmospheric pressure and 20°C.
[d] Data for acetylene and carbon monoxide should be interpreted with care. For acetylene under certain ill-defined circumstances external ignitions have been reported at flange gaps too small to measure. For carbon monoxide data are for moist (not saturated) gas. Addition of moisture greatly increases the burning velocity of carbon monoxide.
[e] Burgoyne (1965a). Maximum experimental safe gap at atmospheric pressure.

16.2.11 Flammability in oxygen

The flammability of a substance depends strongly on the partial pressure of oxygen in the atmosphere. The oxygen concentration affects both the flammability limits and the other flammability parameters. In general, increasing oxygen content alters the LFL only slightly, but its effect on the UFL is marked. Figure 16.11 illustrates the effect of oxygen concentration on the flammability limits of methane–oxygen–nitrogen mixtures. Conversely, there is a minimum oxygen content to support combustion. For the system shown in Figure 16.11 this is approximately 12%. Increasing the oxygen content reduces the ignition energy and the quenching distance of methane–oxygen–nitrogen mixtures as shown in Figures 16.12 and 16.13, respectively. Again the effect is a marked one.

The increase in burning velocity of methane when air is replaced by oxygen was illustrated in Figure 16.10.

16.2.12 Uncertainty in data

It has already been emphasized that there is frequently some uncertainty in the data available for design. The point is illustrated by the data on flammability characteristics

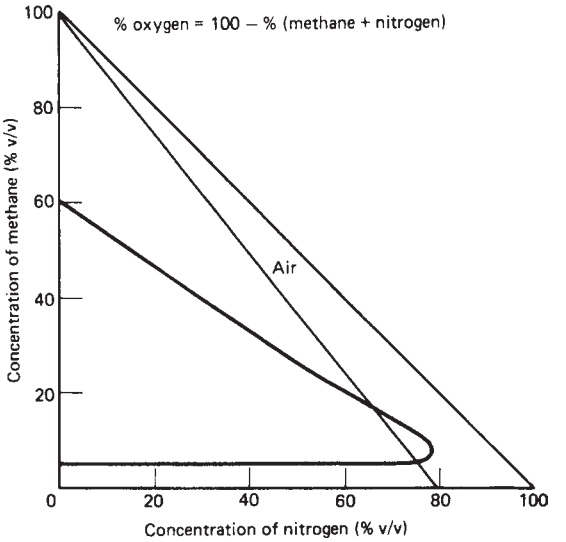


Figure 16.11 *Effect of mixture composition on burning velocity of methane in air and in oxygen (Zabetakis, 1965 BM Bull. 627) (Courtesy of the Bureau of Mines)*

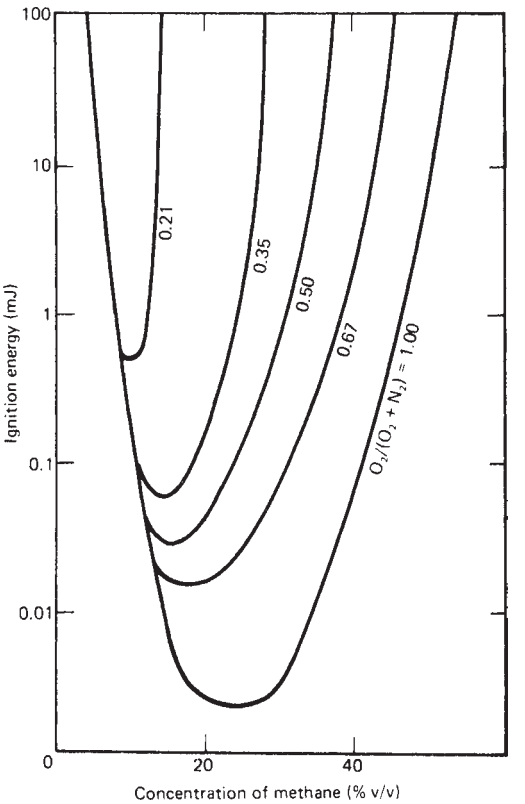


Figure 16.12 *Minimum spark ignition energies in methane–oxygen–nitrogen mextures at 1 atm pressure (B. Lewis and von Elbe, 1961) (Courtesy of Academic Press)*

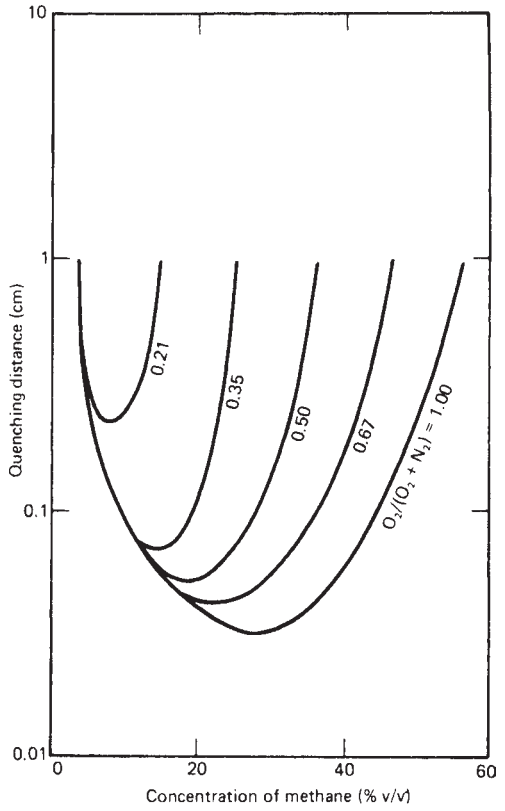


Figure 16.13 *Quenching distances in methand–oxygen–nitrogen mixtures at 1 atm pressure (B. Lewis and von Elbe 1961) (Courtesy of Academic Press)*

given in Table 16.13. The LFL of ethylene–air mixtures at atmospheric pressure and temperature is generally taken as 2.7%, as indicated in the table, and it is not regarded as particularly uncertain. But as the figures show, previous values differ from this by a factor as high as 1.22. On the other hand, the MIE of ammonia–air mixtures at atmospheric pressure and temperature appears still to be subject to some uncertainty. The situation is similar for the AIT of acetone, methanol and methylethyl ketone mixtures with air at atmospheric pressure.

16.3 Combustion Phenomena

The use of the flammability characteristics just described is a simplification of rather complex combustion phenomena, which for engineering purposes it is necessary to make. It is convenient at this point, therefore, to indicate some of this combustion background, both as a commentary on the flammability characteristics just described and as an introduction to the subsequent sections on flames and fires.

Accounts of basic combustion are given in *The Science of Flames and Furnaces* (Thring, 1952), *Flames, Their Structure, Radiation and Temperature* (Gaydon and Wolfhard, 1953–), *Some Fundamentals of Combustion* (Spalding, 1955), *Combustion, Flames and Explosions of Gases* (B. Lewis and von Elbe, 1961, 1987), *Combustion Theory* (F.A. Williams, 1965), *Fundamentals of Combustion* (Strehlow, 1968a), *Flames and Combustion Phenomena* (G.N. Bradley, 1969), *Flame and Combustion* (Barnard and Bradley, 1985), *An Introduction to Fire Dynamics* (Drysdale, 1985), *Principles of Combustion* (Kuo, 1986) and *Combustion of Liquid Fuel Sprays* (A. Williams, 1990).

Selected references on combustion phenomena are given in Table 16.14. Some topics in combustion research relevant to loss prevention are shown in Table 16.15.

In this section the following aspects of combustion are reviewed:

(1) flame propagation;
(2) diffusion and premixed flames;
(3) premixed flame flashback and blowoff;
(4) diffusion flame characteristics;
(5) flame stretch and wrinkling;
(6) reaction kinetics and transport processes;
(7) thermal explosion theory;
(8) flammability limits;
(9) ignition phenomena;
(10) burning velocity;
(11) quenching effects;
(12) cool flames;
(13) combustion in tubes.

Some of the reviews are essentially historical, illustrating the development of the basic concepts.

16.3.1 Flame propagation

A useful starting point for consideration of combustion is the propagation of the flame as an adiabatic planar combustion wave, as shown in Figure 16.14. At the front of the combustion zone the temperature is that of the burnt gas T_b. From this maximum value the temperature then falls off. Within the wave there is a plane at temperature T_1 where transition occurs from a heat source to a heat sink in that the heat supplied by the reaction now falls below the heat lost to the unburnt gas behind. The temperature then falls further until it reaches the temperature T_u of the unburnt gas behind the wave. The first part of the combustion zone, in front of T_1, is the reaction zone and the second part, behind T_1, the preheat zone.

In many practical situations the flame front is not planar. In particular, a small spherical flame has a divergent flame front and undergoes stretch, as described below. However, as the spherical flame becomes larger, the flame front may be approximated by a planar front.

Although it is convenient to start with the model of the adiabatic planar combustion wave, it has often been the case in combustion theory that progress has only been made when this model is abandoned and real, but more complex, situations are considered. Thus, B. Lewis and von Elbe (1961) state:

> The use of the adiabatic plane wave equations for general theoretical deductions of flame behaviour is futile

Table 16.13 *Variability of experimental data on flammability characteristics in air*

Property	*Mixture*	*Value* (% v/v)	*Reference*
Lower flammability limit (upwards propagation of flame)	Ethylene–air[a]	2.75	Jones *et al.* (1935 BM RI 3278)
		3.2	Burgoyne and Williams-Leir (1948a)
		3.3	Chapman (1921)
		(mJ)	
Minimum ignition energy	Ammonia–air[b]	40	Magison (1966)
		60	Magison (1966)
		<90	G.F.P. Harris and MacDermott (1977)
		170	G.F.P. Harris and MacDermott (1977)
		680	Buckley and Husa (1962)
		(°C)	
Auto-ignition temperature	Acetone–air[c]	465	Zabetakis (1965 BM Bull. 627)
		600	Marsden (1963)
	Methanol–air[c]	385	Zabetakis (1965 BM Bull. 627)
		470	Marsden (1963)
	Methylethyl[c] ketone–air	404	Hilado and Clark (1972a)
		550	Marsden (1963)

[a] The value given by Zabetakis (1965 BM Bull. 627) and in the ICI *Electrical Installations Code* (ICI/RoSPA 1972 IS/91) is 2.7%.
[b] These differences are discussed by G.F.P. Harris and MacDermott (1977).
[c] These differences have been noted by Santon (1977).

Table 16.14 *Selected references on combustion, pre-flame and ignition phenomena, slow oxidation and cool flames and flame propagation*

Perkin (1882); Lotka (1920); Penning (1926); J.White (1927); Payman (1928); Prettre, Dumanois and Lafitte (1930); Norrish (1935); Pease (1935, 1937); Ubbelohde (1935, 1936); Norrish and Foord (1936); Coward and Payman (1937); von Elbe and Lewis (1937a,b); Newitt (1937); Newitt and Thornes (1937); Townend (1937); Hsieh and Townend (1939a–c); Townend and Hsieh (1939); B. Lewis and von Elbe (1947); Boord (1949); Henkel, Hummel and Spaulding (1949); Henkel, Spaulding and Hirschfelder (1949); Hirschfelder and Curtiss (1949); Prettre (1949); Reynolds and Gerstein (1949); Spence and Townend (1949); Jost (1950); Fenn (1951); Grove and Walsh (1953); J.E. Johnson, Crellin and Carhart (1953, 1954); Schmidt, Steinecke and Neubert (1953); G.K. Adams and Scrivener (1955); Bardwell (1955); Bawn and Skirrow (1955); Dugger,Weast and Heimel (1955); Foresti (1955); Grumer (1955); Newitt (1955); Burgoyne and Weinberg (1956); Barnett and Hibbard (1957); von Karman (1957); Lucquin and Laffltte (1957); W.W. Robertson and Matsen (1957); Tipper (1957); D.H. Allen *et al.* (1959); Berlad and Yang (1959, 1960); Ferguson and Yokley (1959); Goldenberg and Pelevin (1959); Mullins and Penner (1959); Salooja (1960, 1961, 1964a,b, 1966, 1967, 1968a,b); Wolfhard and Bruszak (1960); Barnard and Hawtin (1961); Yang (1962); Hirschfelder (1963); Seakins and Hinshelwood (1963); Rhein (1964); Yao and Ruof (1964); Agnew and Agnew (1965); Barnard and Ibberson (1965); Bonner and Tipper (1965a,b); Sueyasu and Hikita (1965); Adler and Zaturska (1966); Fish (1966, 1968); Melvin (1966, 1969a,b); Ashmore (1967); Ashmore and Preston (1967); Barnard and Kirschner (1967); Hoare, Ting-Man Li and Walsh (1967); Knox (1967a,b); Barnard and Sankey (1968); Bell, Skirrow and Tipper (1968); M.H. Friedman (1968); J.F. Griffiths, Skirrow and Tipper (1968–); Howe and Ting-Man Li (1968); Neiman and Gal (1968); Barnard and Watts (1969, 1972); Fish *et al.* (1969); B.F. Gray (1969a,b); Bowman (1970); Fine, Gray and Macinven (1970); R. Hughes and Simmons (1970); Korman (1970); Perche, Perez and Lucquin (1970, 1971); Dechaux, Flament and Lucquin (1971); Drysdale (1971); Halstead, Prothero and Quinn (1971, 1973); Knox and Kinnear (1971); Leyer and Manson (1971); Meyer and Oppenheim (1971a,b); Burgess and Laughlin (1972); Crossley *et al.* (1972); Lucquin and Antonik (1972); H. Phillips (1972a, 1973); Tse (1972); Barnard and Harwood (1973a,b, 1974); Berlad (1973); Dehn (1973); Luckett and Pollard (1973); Feay and Bowen (1973); R. Hughes and Prodan (1973); Vovelle and Delbourgo (1973); McKay *et al.* (1975); F.W.Williams, Indritz and Sheinson (1975); D.C. Bull, Pye and Quinn (1976); Caprio, Insola and Lignola (1977); Hirano *et al.* (1977); Bilger (1979); Dechaux and Delfosse (1979); Maly and Vogel (1979); Affens and Sheinson (1980); Coffee (1980,1982b); Kolodner and Pratt (1980); d'Onofrio (1980); Abdel-Gayed and Bradley (1981); Coffee (1981 LPB 81); Snee (1981 LPB 81); Hoffmann-Berling, Giinther and Leuckel (1982); Rhee (1982); F.A Williams (1982, 1992); G. Freeman and Lefebvre (1984); Ronney (1985); Chakir *et al.* (1989); Wilk *et al.* (1989); Xiao-Jing Wang (1989); Sloane (1990a,b, 1992); Borghese *et al.* (1991); P.P. Gray (1991); B.F. Gray, Merkin and Griffiths (1991); Leclerc-Battin *et al.* (1991); Pitt, Clements and Topham (1991); Battin-Leclerc *et al.* (1992); D. Bradley (1992); B.F. Gray, Little and Wake (1992); Miles and Gouldin (1992); Trevino and Mendez (1992); Sloane and Ronney (1993); Vanpee (1993)

Chemical reaction kinetics

Kassel (1937); Dugleux and Freling (1955); von Elbe (1955); Hoare and Walsh (1955); Levy (1955); Ubbelohde *et al.* (1955); Vanpee and Grard (1955); Giddings and Hirschfelder (1957); W.G. Parker (1958); Szabo (1959); Baulch *et al.* (1973); Jensen and Jones (1978); Lovachev (1981); Westbrook and Dryer (1981); Kaufman (1982); Golden and Larson (1985); Wolfrum (1985); R.D. Levine (1989); Stewart, Rothem and Golden (1989); Troe (1989); Hai Wang and Frenklach (1991)

Kinetic schemes: Dixon-Lewis (1955); W.W. Robertson *et al.* (1955); Westbrook, Hellwig and Anderson (1955); Knox (1959, 1967a); Minkoff and Tipper (1962); Ashmore, Dainton and Sugden (1967); Smoot, Hecker and Williams (1976); Dryer and Schug (1982); J.A. Miller *et al.* (1982); Westbrook and Pitz (1984); Warnatz (1985); Hwang *et al.* (1987); Yetter, Dryer and Rabitz (1991)

> because the model is unrealistically restricted by the specification of one-dimensional, adiabatic propagation in an infinite medium for an infinite time. For one thing, the model does not yield limits of inflammability as they are known to the experimenter. (p. 210)

An important feature in combustion work is the flow regime. In particular, there is a distinction between a flame propagating in a stagnant gas and in a flowing gas. Another distinction is that between laminar and turbulent flow. Flammability characteristics such as the ignition energy or burning velocity are affected by the flow regime.

16.3.2 Diffusion and premixed flames

A fundamental distinction is made between (1) premixed flames and (2) diffusion flames. In a premixed flame the air for combustion is mixed with the fuel gas before it issues from the orifice, while in a diffusion flame gas or liquid leaving the orifice is pure fuel and the air for combustion has to diffuse to it from the surrounding atmosphere. Both types of flame may be produced on a bunsen burner, a premixed flame being obtained by opening the primary air inlet and a diffusion flame by closing it.

With a premixed flame the rate of burning is limited by reaction kinetics, while, in principle, with a diffusion flame the rate limiting mechanism is diffusion. At high turbulence in a diffusion flame, however, kinetics and diffusion may be of roughly equal importance.

Another distinction in flames is that between (1) laminar flames and (2) turbulent flames. The criterion for transition from the laminar to the turbulent regime in a flame is the Reynolds number. The relevant Reynolds number, however, is that of the flame, which is actually several times less than that of the cold gas leaving the tube, because the gas viscosity at the flame temperature is that much greater.

16.3.3 Premixed flame flashback and blow-off

The behaviour of a premixed flame burning on a tube or similar burner is a function of the concentration of the fuel and of the gas velocity. Aspects of particular interest are flashback, blow-off, lift and blow-out of the flame. These features have been studied for flames of butane–air mixture by Wohl, Kapp and Gazley (1949) and are shown in Figure 16.15. In region A a stable flame can exist only at the burner port and in region B only lifted off the port. In region C the flame may be stable either on the port or lifted off it. In region D flashback can occur down the burner pipe.

The limits for flashback, blow-off and lift are determined by the velocity gradients at the boundary of the flame. In the flame the gas velocity is opposed by the axial component of the burning velocity. Flashback occurs under conditions where the gas velocity is low relative to the

Table 16.15 *Some topics in combustion research relevant to loss prevention*

- Chemical kinetics of combustion
- Combustion initiation and propagation
  - Flammability limits
  - Ignition phenomena
    - Spontaneous ignition
    - Spark ignition
    - Hot wire ignition
    - Hot surface ignition
    - Hot gas ignition
    - Hot particle ignition
    - Compression ignition, shock heating
    - Induction period
  - Flame propagation
  - Slow oxidation, cool flames
  - Quenching effects
    - Burning velocity
    - Measurement methods
    - Turbulence effects
- Detonation
  - Properties of detonation wave
  - Detonation limits
  - Detonation cell structure
  - Transition from deflagration to detonation
  - Detonation in tubes
  - Detonation in vapour clouds
- Flames
  - Premixed flames
  - Diffusion flames
  - Flame stability, flashback, blowoff
  - Flame stretch and wrinkling
  - Flame emissivity
    - Emissivity of CO_2, H_2O
    - Emissivity of sooty flames
    - Soot formation and properties
  - Inerting
  - Inhibition
  - Flame spread
    - Flame spread over solid surfaces
    - Flame spread over liquid pools
  - Ignition and burning of wood and cellulose
    - Calorific value of wood
    - Thermal radiation levels for spontaneous and pilot ignition
    - Burning of wood
    - Wood crib fires
- Duct fires
- Pool fires
  - Flame dimensions
  - Flame emissivity
  - Heat transfer to pool
  - Regression rate
- Large fires
- Vapour cloud fires and explosions
- Mist and spray combustion and explosion
  - Burning of single drops
  - Burning of mist/spray clouds
- Dust fires and explosions
  - Dust explosibility limits
  - Dust cloud explosions
  - Smoldering dust fires
- Self-heating, thermal explosion
- Building fires

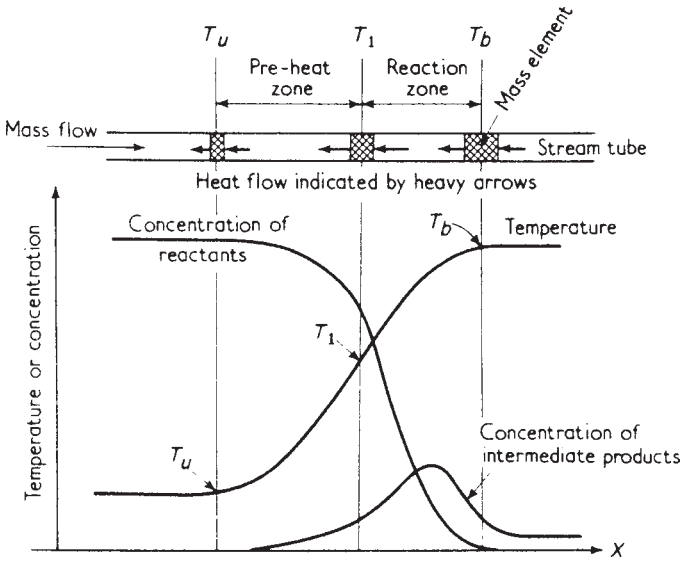


Figure 16.14 *Scheme of a planar combustion wave (B. Lewis and von Elbe, 1961) (Courtesy of Academic Press)*

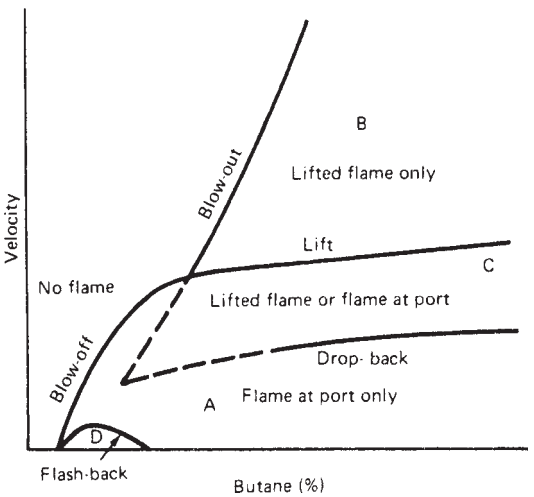


Figure 16.15 *Scheme of characteristic regions of flame stability for a premixed flame (after Wohl, Kapp and Gazley, 1949) (Courtesy of the Combustion Institute)*

burning velocity. Blow-off at lower fuel concentration and lift at high fuel concentrations occur where the gas velocity is high relative to the burning velocity. The lift curve is an extension of the blow-off curve. The limits for blow-out and drop back of a lifted flame are not determined by the boundary velocity gradients and their shapes are specific for each burner diameter.

For laminar flow, from the Poiseuille equation the boundary velocity gradient g is

$$g = 4V/\pi r^3 \qquad [16.3.1]$$

where r is the distance from the centre of the tube to the boundary of the stream and V is the volumetric flow of gas. The critical boundary velocity gradient for flashback g_F may be obtained from Equation 16.3.1 using the volumetric flow for flashback V_F. Likewise, the critical boundary velocity gradient for blow-off g_B may be obtained using the volumetric flow for blow-off V_B.

Data on critical velocity gradients for flashback and for blow-off have been given by M.E. Harris *et al.* (1949).

16.3.4 Diffusion flame characteristics

The behaviour of a diffusion flame is a function of the fuel velocity. As aspect of particular interest is the dimensions of the flame. This is illustrated in Figure 16.16, which is based on the work of Hottel and Hawthorne (1949) and a further interpretation by Gugan (1976). In the laminar regime the flame length is approximately proportional to the velocity, while in the turbulent regime it is independent of velocity. Turbulence spreads from the flame tip downwards. As velocity increases there are successively a region where the flame may be on the port or lifted, a region where only a lifted flame occurs and a point beyond which there is blow-off.

There are a number of correlations for the dimensions of a diffusion flame. The simple equation given by Jost (1946) for flame length is

$$L = \frac{d^2 u}{4D} \qquad [16.3.2]$$

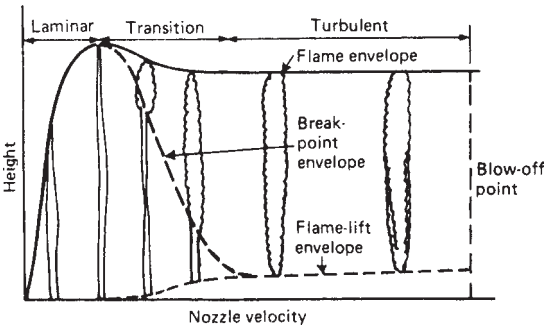


Figure 16.16 *Scheme of characteristic regions of flame stability for a diffusion flame (after Hottel and Hawthorne, 1949; Gugan, 1976) (Courtesy of the Combustion Institute and the Institution of Chemical Engineers)*

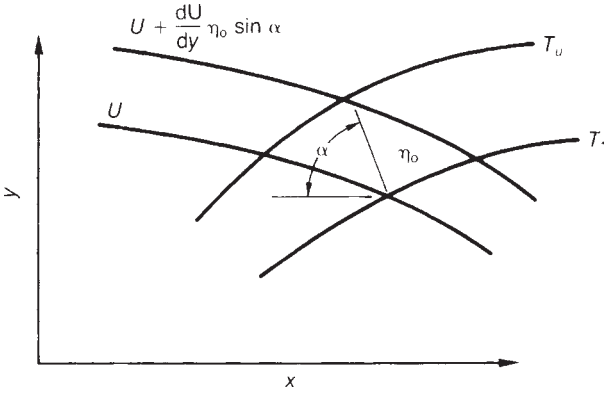


Figure 16.17 *Scheme of stretch of combustion wave in a flow field (after B. Lewis and von Elbe, 1961) (Courtesy of Academic Press)*

where d is the diameter of the pipe (m), D is the diffusion coefficient (m^2/s), L is the flame length (m), and u is the fuel velocity (m/s).

For the laminar regime the diffusion coefficient D may be taken as the molecular diffusion coefficient D_m, which is a constant with respect to velocity. The flame length in this regime is thus proportional to velocity. But for the turbulent regime, D may be taken as the eddy diffusion coefficient D_e, which is proportional to the velocity u. The flame length in this regime is thus independent of velocity.

For the turbulent regime an equation commonly used to predict flame length is that of Hawthorne, Weddell and Hottel (1949):

$$L = \frac{5.3D}{C_t}\left\{\frac{T_f}{\alpha_t T_n}\left[C_t + (1 - C_t)\frac{M_s}{M_n}\right]\right\}^{1/2} \qquad [16.3.3]$$

where C_t is the concentration of fuel in the stoichiometric mixture (mole fraction), D is the diameter of the pipe (m), L is the flame length (m), M_n is the molecular weight of the fuel, M_s is the molecular weight of the surrounding fluid (normally air), T_f is the absolute adiabatic flame temperature (K), T_n is the absolute temperature of fuel in the pipe (K), and α_t is the ratio of the number of moles of unreacted and reacted gas in the stoichiometric mixture.

The shape of the flame envisaged in this treatment is an inverted cone with the apex at the orifice such that

$$\frac{L}{D} = 5.3\frac{W}{D} \qquad [16.3.4]$$

where W is the diameter at the top of the flame (m).

Another equation for the diameter of the flame is given by Baron (1954):

$$Z = 0.29x[\ln(L/x)]^{1/2} \qquad [16.3.5a]$$

and

$$Z_{max} = 0.12L \quad \text{at} \quad x = 0.61L \qquad [16.3.5b]$$

where x is the axial distance (m), Z is the flame diameter (m) and the subscript max denotes the maximum.

16.3.5 Flame stretch and wrinkling

Two properties of the laminar combustion wave which are of particular importance in combustion theory are flame stretch and flame wrinkling. If a combustion wave enters a flow field where there are significant changes of velocity over a distance comparable with the width η_o of the wave, significant stretching of the flame occurs. If a flow line of velocity U intersects the T_1 surface of the wave, as shown in Figure 16.17, the velocity of the flow line at a distance η_o along the line normal to this surface at the point of intersection is $U + (dU/dy)\,\eta_o \sin\alpha$. The ratio of the mass flows normal to this surface over the distance η_o is $1 + (dU/dy)(\eta_o/U)\sin\alpha$ and where the flow velocity is much greater than the burning velocity this reduces to $1 + (dU/dy)(\eta_o/U)$. The fractional increase, or stretch, is thus

$$\frac{dU}{dy}\frac{\eta_o}{U} = K \qquad [16.3.6]$$

where K is the Karlovitz number, which is thus a measure of the flame stretch.

The parameter η_o may be obtained from the heat balance in the combustion wave:

$$c_p \rho_u S_u (T_1 - T_u) = k\left(\frac{dT}{dx}\right)_1 \qquad [16.3.7]$$

The distance η_o is taken as

$$\eta_o = (T_1 - T_u)/(dT/dx)_1 \qquad [16.3.8]$$

Then from Equations 16.3.7 and 16.3.8

$$\eta_o = k/c_p \rho_u S_u \qquad [16.3.9]$$

where c_p is the specific heat, S_u is the fundamental burning velocity, ρ is the density, k is a constant and the subscript u denotes unburnt gas.

If the flame stretch is sufficiently great, the flame is quenched. The Karlovitz number K, as a measure of flame stretch, is therefore also a criterion of quenching.

The Karlovitz number K may also be defined in terms of the critical velocity gradient for blow-off. The definition is

$$K = g_B \eta_o / S_u \quad [16.3.10]$$

The flame stretch concept may also be applied to a spherical combustion wave in stagnant gas. If a sphere diameter d of burnt gas exists with an unburnt outer shell thickness η_o, the ratio of the surface areas after and before combustion of this shell is

$$= \frac{\pi(d + 2\eta_o \rho_u/\rho_b)^2}{\pi d^2} \quad [16.3.11]$$

$$\approx 1 + 4\eta_o \rho_u / d\rho_b \quad [16.3.12]$$

The fractional flame stretch is then

$$K = 4\eta_o \rho_u / d\rho_b \quad [16.3.13]$$

Critical values of K for spark ignition are given by B. Lewis and von Elbe (1961) and lie mainly in the range 0.5–1.5.

If in the combustion wave of a stoichiometrically unbalanced mixture the diffusivity of the deficient component substantially exceeds that of the excess component, the gas mixture entering the wave stratifies so that there are alternate increases and decreases in the burning velocity. The wave becomes wrinkled and exhibits a cellular structure.

16.3.6 Reaction kinetics and transport processes

Chemical reaction and transport processes govern at the most fundamental level the process of combustion. There are available reaction kinetic schemes for the reaction of many of the main compounds of interest. Certain reactions have proved of particular interest to investigators. For example, Semenov (1935) discusses the reactions of oxygen with hydrogen, carbon monoxide and hydrocarbons and of hydrogen with chlorine and bromine. B. Lewis and von Elbe (1961) also discuss the reactions of oxygen with hydrogen, carbon monoxide and hydrocarbons and those in the H_2–CO–O_2 system. The reactions in the hydrogen–bromine systems have been of particular interest, as discussed by Lovachev *et al.* (1973).

16.3.7 Thermal explosion theory

Many problems in combustion involve the self-heating of a reactive mass in a defined volume. The theory that deals with this, thermal explosion theory, or simply thermal theory, is therefore important in combustion and has numerous applications.

The concept of thermal explosion derives from Van't Hoff (1884), who identified the condition for thermal ignition as one in which no equilibrium between the reacting system and its surroundings can exist. This was developed qualitatively by Le Chatelier (1937), who characterized the problem as one in which the variation of heat production is a curve and that of heat loss is a straight line, as illustrated in Figure 16.18. A quantitative treatment of thermal explosion theory was described in *Chemical Kinetics and Chain Reactions* by Semenov (1935), and developed by Semenov, Frank-Kamenetsky and Zeldovich (e.g. Zeldovich and Frank-Kamentsky, 1938; Frank-Kamenetsky, 1939a,b; Semenov, 1940). Accounts of thermal explosion theory are given in *Diffusion and Heat Exchange in Chemical Kinetics* (Frank-Kamenetsky, 1955) and *Selfheating: Evaluating and*

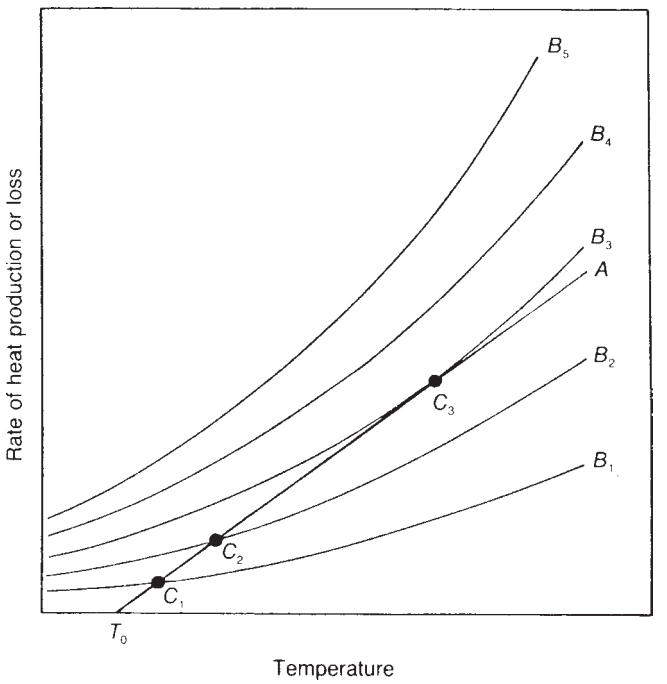


Figure 16.18 *Heat generation by and removal from a chemical reaction (after Semenov, 1935; Knox, 1967a)*

Controlling the Hazards (Bowes, 1984) and by P. Gray and Lee (1967b) and Merzhanov and Averson (1971).

The basic concepts of thermal explosion theory are as follows. For a mass subject to an exothermic reaction the unsteady-state heat balance is

$$c\rho\frac{\partial T}{\partial t} = k\nabla^2 T + Q \qquad [16.3.14a]$$

$$= k\left[\frac{d^2T}{dx^2} + \frac{d^2T}{dy^2} + \frac{d^2T}{dz^2}\right] + Q \qquad [16.3.14b]$$

with

$$Q = Q'\rho A \exp(-E/RT) \qquad [16.3.15]$$

where A is the pre-exponential factor, c is the specific heat of the reacting mass, E is the activation energy, k is the thermal conductivity, Q is the heat released per unit volume, Q' is the heat of reaction per unit mass, t is the time, T is the absolute temperature, x, y and z are the distances from the centre of the hot spot in the x, y and z directions, respectively, ρ is the density and ∇^2 the Laplacian operator with respect to the distance x.

The exponential term in Equation 16.3.15 may be approximated as follows:

$$\exp(-E/RT) \approx \exp\{-(E/RT_o)[1-(T-T_o)/T_o]\} \qquad [16.3.16]$$

$$= \exp\{-(E/RT_o)\exp\{(E/RT_o^2)(T-T_o)\}\} \qquad [16.3.17]$$

where T_o is the initial temperature.

A dimensionless parameter θ is defined as

$$\theta = \frac{E}{RT_o^2}(T - T_o) \qquad [16.3.18]$$

Substituting from Equation 16.3.18 in Equation 16.3.17 gives

$$\exp(-E/RT) = \exp(-E/RT_o)\exp\theta \qquad [16.3.19]$$

Another dimensionless parameter δ is defined as

$$\delta = \frac{Q'\rho A r^2}{k}\frac{E}{RT_o^2}\exp(-E/RT_o) \qquad [16.3.20]$$

where r is the semi-thickness or radius of the reacting volume.

Then, defining two further dimensionless parameters

$$\zeta = x/r \qquad [16.3.21]$$

$$\tau = \frac{kt}{c\rho r^2} \qquad [16.3.22]$$

Equation 16.3.14 becomes, in dimensionless form,

$$\frac{d\theta}{d\tau} = \nabla^2\theta + \delta\exp\theta \qquad [16.3.23]$$

where ∇^2 is now the Laplacian operator with respect to ζ.

From Equation 16.3.14 the following equation for the temperature may be obtained for particular geometries:

$$c\rho\frac{dT}{dt} = k\left[\frac{d^2T}{dx^2} + \frac{m}{x}\frac{dT}{dx}\right] + Q \qquad [16.3.24]$$

or, in dimensionless form,

$$\frac{d\theta}{d\tau} = \frac{d^2\theta}{d\zeta^2} + \frac{m}{\zeta}\frac{d\theta}{d\zeta} + \delta\exp\theta \qquad [16.3.25]$$

where $m = 0$, 1 or 2 for a slab, cylinder or sphere, respectively.

There are numerous assumptions that may be made concerning the geometry, the boundary conditions, the physical properties and the reaction kinetics of the thermal explosion problem and there are numerous applications of the theory. This has given rise to a large literature.

The application of the thermal explosion model to combustion problems is considered in this section, while its application to self-heating of solid materials is discussed in Section 16.6.

16.3.8 Flammability limits

It is convenient for design purposes to define flammability limits, but the question of whether such flammability limits are a fundamental physicochemical property has been the subject of some debate. Reviews of the fundamentals of flammability limits have been given by Egerton (1953), B. Lewis and von Elbe (1961), Lovachev *et al.* (1973), Lovachev (1979) and Macek (1979).

The determination of practical flammability limits is usually effected using the BM apparatus as described by Coward and Jones (1952 BM Bull. 503). In this apparatus it is found that the lower limit concentration is lower and the upper limit concentration is higher for upward than for downward propagation. Since for design purposes it is desirable to use the wider limits, Coward and Jones recommend the use of the flammability limits for upward propagation.

In his review, Egerton states three conditions that a satisfactory theory of flammability limits should meet. It should predict (a) the existence of a lower limit, (b) the value of the lower limit concentration and (c) the value of the burning velocity at the lower limit. He discusses the relation between the flammability limit and the flame temperature attained at the limit.

Egerton and Fowling (1948) have drawn attention to the relationship that exists, given complete combustion, between the lower and upper limits if a limit mixture requires a certain concentration of fuel to provide the temperature necessary for flame propagation. Provided allowance is made for the different specific heats of the two mixtures; the upper limit might then be estimated from the lower one. This approach is applicable only if combustion is complete. This is not the case for hydrocarbon–air mixtures.

For the UFL Egerton and Fowling found the principal determining factor to be the heat of combustion per mole of mixture. Egerton states that the direction of propagation is important because of the effect of convection. The upward propagating flame is assisted by convection.

It is desirable to have some more fundamental method of measuring flammability limits than the standard tube method. Such a method is the flat flame method described by Egerton and Thabet (1952). This method appears better suited to the provision of fundamental data than the standard method, although it is not suggested that it should replace the latter for practical determinations. Egerton (1953) presents data on the different limit flame temperatures obtained by the standard tube and flat flame methods, as shown in Table 16.16. The temperature given by the latter is lower and more constant.

Spalding (1957d) has presented a theory of flammability limits. He argues that a theory, which is capable of predicting the existence of a limit of flammability, needs to take account of heat loss. The novel feature of his theory is that it allows for heat loss by radiation. The theory for the laminar one-dimensional flame is thus brought into line with the theoretical treatments of other types of flame, each of which exhibits a zone of stable operation limited on one side by chemical kinetics and on the other by heat loss to the surroundings. The theory is not dependent on any particular assumptions about the dependence of the reaction rate on concentration and temperature, other than that the dependence of the rate should be steeper than that for the heat transfer. Spalding found that at the flammability limit there is a small but finite burning velocity. In addition, he showed that there exist two burning velocities, of which only the upper one is stable in normal circumstances.

Other workers who have given theories of flammability limits based on heat radiation include Zeldovich (1941) and Rozlovsky (1970). Later workers have tended to argue that the heat radiation theory is difficult to reconcile with experimental phenomena. The work of Egerton and Fowling (1948), showing that heat radiation loss is small, is often quoted.

The contrasting views on flammability limits are described by Dixon-Lewis and Isles (1959). Although the limits are often treated as fundamental properties, they state that the limits obtained experimentally are essentially convection or quenching limits, depending on the conditions.

In their review of flammability limits, B. Lewis and von Elbe (1961) emphasize that, despite the theoretical problems, the experimentally determined limits have proved to be reliable for practical purposes. They state that there is no solution to the theoretical problem of flammability limits in terms of adiabatic one-dimensional propagation. Spalding's model represents the only feasible approach in terms of one-dimensional propagation, but the attribution of heat loss to radiation is not regarded as satisfactory by experimentalists, who prefer to believe that heat absorption by the unburned gas is the important effect.

Lewis and von Elbe illustrate the effect of the direction of propagation by the data shown in Table 16.17. They refer to the work of Linnett and Simpson (1957), who draw attention to the role of convection. Evidently, convection currents are generated which are capable of quenching the flame. Such convectional quenching implies that heat is transferred to the unburned gas.

Lewis and von Elbe suggest that the mechanism of such quenching may be flame stretching. Stretching leads to extinction if the stretch exceeds a critical value of the Karlovitz number. The latter is inversely proportional to the burning velocity. Thus flames with low burning velocity, such as occur at the flammability limit, are particularly susceptible to stretch and hence extinction. These effects accord with the existence of narrow limits for downward propagation of the flame, since flame stretch is greater for downward propagation.

Table 16.16 *Flammability limits: lean limit flame temperatures from standard tube and flat flame methods (after Egerton, 1953) (Courtesy of the Combustion Institute)*

Gas	*Lower limit* (%)	*Flame temperature* (°C)	
		Tube method	*Flat flame method*
Methane	5.26	1254	1222
Propane	3.10	1383	1200
n-Butane	1.93	1445	1233
n-Pentane	1.62	1485	1158
n-Heptane	1.26	1569	1228

Table 16.17 *Flammability limits: the effect of the direction of flame propagation (B. Lewis and von Elbe, 1987; after A.G. White, 1922, 1924) (Courtesy of Academic Press)*

Mixture	*Direction of propagation*	*Fuel concentration* (%)		*Stoichiometric fraction ratio*	
		Lower	*Upper*	*Lower*	*Upper*
Methane–air	Upwards	5.35	14.85	0.54	1.7
	Horizontal	5.40	13.95	0.54	1.6
	Downwards	5.95	13.35	0.60	1.5
Ethane–air	Upwards	3.12	14.95	0.54	2.9
	Horizontal	3.15	12.85	0.54	2.5
	Downwards	3.26	10.15	0.56	1.9
Pentane–air	Upwards	1.42	8.0	0.55	3.3
	Horizontal	1.44	7.45	0.56	3.1
	Downwards	1.48	4.64	0.57	1.9
Benzene–air	Upwards	1.45	7.45	0.53	2.9
	Horizontal	1.46	6.65	0.53	2.6
	Downwards	1.48	5.55	0.54	2.1

They also discuss the susceptibility of the flammability limits to diffusional stratification. Experiments by Coward and Brinsley (1914) in hydrogen–air mixtures with 4.1–10% hydrogen show that some hydrogen remains unburned. This effect has been explained by Goldmann and co-workers (Goldmann, 1929) as being due to diffusional stratification. Such stratification leads to local differences in concentrations and to locally increased burning velocities.

Lewis and von Elbe also mention that, according to the work of Markstein, upward flame propagation tends to promote cell formation. Cell formation, and Markstein's theory, is discussed below.

A further discussion of preferential diffusion is given by Furno *et al.* (1971). Coward and Jones (1952 BM Bull. 503) describe work on hydrogen–air mixtures in which burning is propagated upward by the buoyancy of individual flamelets and explain this by preferential diffusion. When the deficient reactant, in this case hydrogen, is the faster diffusing one, a flame zone concave to the burned gas will be enriched in this reactant. In downward propagation flame surfaces of small curvature are opposed by buoyancy, and the lean limit concentration is thus higher.

Furno *et al.* refer to the quantitative treatment of preferential diffusion given by Spalding (1955). He observed that the concentrations most easily ignited by electrostatic spark ignition were 0.9 and 1.8 stoichiometric ratios for methanol–air and heptane–air mixtures, respectively, and that the ratio of these two figures is close to the ratio $(D_o/D_f)^{1/2}$ where D_f and D_o are the diffusivities of the fuel and oxygen, respectively. Spalding suggests that the actual fuel–oxygen ratio in the developing flame kernel is stoichiometric. Furno *et al.* extend this argument and suggest that the ratio of the limits for upward and downward propagation may be given by this group also. They state that the data available to verify this hypothesis are sparse, but quote the results shown in Table 16.18.

Table 16.18 *Stoichiometric ratios*[a] *of most easily ignited mixtures and of limit mixtures in upward and downwards propagation (after Furno et al., 1971) (Courtesy of the Combustion Institute)*

Mixture	$(D_o/D_f)^{1/2}$[b]	*Optimum ratio for ignition*	*Ratio of upwards to downwards propagation limit*
			Upper limit
Methane–air	0.96	0.9	1.02
Ethane–air	1.29	1.2	1.24
Propane–air	1.44	1.3	1.43
Butane–air	1.55	1.5	1.41
Pentane–air	1.63	–	1.72
Hexane–air	1.70	1.7	–
Heptane–air	1.78	1.8	–
Benzene–air	1.52	–	1.46
			Lower limit
Hydrogen–air	0.54	–	0.46
Methane–air	0.96	0.9	0.92

[a] Fuel concentration/stoichiometric fuel concentration.
[b] D_f, diffusivity of fuel; D_o, diffusivity of oxygen.

Furno *et al.* also discuss the limit temperatures. It would be helpful if the rich limit temperature could be taken to be the same as the lean limit temperature. This would be equivalent to saying that in heavy hydrocarbon–air mixtures downward propagation reaches its limit at a stoichiometric ratio of about 1.9.

Several reviews of flammability limits have been given by Lovachev and co-workers (Lovachev, 1971, 1979; Lovachev *et al.*, 1973). Like earlier reviewers, Lovachev (1971) states that a theory based on radiant heat loss does not account for the experimental phenomena and prefers to explain flame extinction as due to heat loss into the unburned gas due to convection flows.

Lovachev *et al.* (1973) emphasize the role of convection. They state that agreement exists that convection is the reason for the difference between upward and downward propagation, but not on the mechanisms involved. They refer to three proposed mechanisms: Drozdov and Zeldovich (1943) have suggested unequal flame speeds and heat transfer; Linnett and Simpson (1957) have suggested differences in the flame surface; and B. Lewis and von Elbe (1961) have suggested flame stretching.

They quote a relation, derived by Lovachev (1971), for the flame velocity at the flammability limit. They discuss the question of whether the upward or downward propagation limit is more appropriately regarded as the true flammability limit. They acknowledge the practical reasons why Coward and Jones adopted the upward propagation limit, but opt for the downward propagation limit as the more fundamental.

They state that for hydrocarbon–air mixtures the lean limit flame temperature is approximately constant. Different experimental methods give different values, those obtained by the flat flame method being the lowest quoted. They draw attention to the results of Gibbs and Calcote (1959), who found that for such mixtures the flame speeds are similar. This suggests that the heat release and the flame temperature should also be similar.

Lovachev (1979) outlines the various factors that influence the measured flammability limits, which he terms the ignition scheme. He states that the flammability limits determined in a large chamber of volume 8 m^3 are wider than those given by the standard tube method. Thus there are some compounds which are classed as flammable by the former method, but which would be classed as non-flammable by tests conducted in the latter one. He describes experiments showing the buoyant deformation of the flame kernel in large confinements. The illustrations given show a transition from a sphere to a vertically oblated sphere with an inflection at its based, somewhat kidney-shaped.

Lovachev also describes the effect of turbulence on flammability limits and quotes several pieces of work that illustrate this. These include work by K.N. Palmer and Tonkin (1961) on propane–air mixtures in horizontal tubes. At flow velocities of 0.5 m/s the limits widened, but with a four-fold increase they narrowed again. He states that the experimental studies carried out on turbulence effects have been done with tubes that are too narrow and ignition sources that are too weak. He points out that flammability limits given in handbooks are for non-turbulent conditions, but that in practice turbulence effects are not negligible.

Macek (1979) discusses the concept that extinction occurs when the burning velocity is so low that it is overcome by the dissipation processes and refers to the

accounts of these processes by Burgess (1969) and Burgess and Hertzberg (1975).

The effect of pressure on flammability limits is discussed by Egerton (1953), B. Lewis and von Elbe (1961) and Lovachev *et al.* (1973).

The temperature effect on flammability limits is discussed by Egerton (1953) and Lovachev *et al.* (1973).

Other aspects of flammability limits include the effect of additives and of inhibitors. Additives are discussed by B. Lewis and von Elbe (1961), and inhibitors are considered by Lovachev *et al.* (1973) and Lovachev (1979).

Further aspects of flammability limits are considered in Sections 16.3.10 on burning velocity and 16.3.11 on quenching.

16.3.9 Ignition phenomena

Ignition of a flammable mixture be effected either by raising the temperature of the bulk gas until it ignites spontaneously or by local ignition of a part of the gas. The modes of ignition considered here are principally:

(1) auto-ignition;
(2) local ignition;
  (a) spark ignition,
  (b) hot surface ignition,
  (c) friction and impact ignition,
  (d) hot gas jet ignition,
  (e) hot particle ignition,
  (f) flame torch and jet ignition,
  (g) compression ignition.

Auto-ignition

Auto-ignition, or spontaneous ignition, is of practical interest not only in relation to hazards, but also in combustion systems such as gas engines and turbines. Auto-ignition, though simple in concept, needs careful definition. A definition of such ignition has been given by Sage and Weinberg (1959), who state that if the temperature of an infinite volume of reactants at constant pressure is raised instantaneously and homogeneously above some critical value and maintained there, an explosion will occur homogeneously throughout the volume, thus forestalling flame propagation. As these authors point out, available AIT data are based on experiments far removed from the conditions of this definition. Under the conditions described ignition can occur even if the concentration of the gas mixture is outside the normal flammability limits. These limits constrain flame propagation, but in this case the ignition occurs homogeneously throughout the mixture and propagation is not involved.

Measurement of the AIT is usually carried out by heating the flammable gas mixture in a spherical vessel. With this method there is found to be an effect of the surface/volume ratio, the AIT decreasing as the vessel volume increases. This effect was observed by Setchkin (1954) and has been found by other workers.

A method of measurement that matches more closely their definition of the AIT has been described by Sage and Weinberg (1959). The method is a two-stage one. A series of experiments is conducted in which, in the first stage, the flammable gas mixture is brought to a temperature somewhat below the ignition temperature and, in the second stage, a small quantity of energy is added which ignites the gas. The AIT is found by extrapolation of these results to determine that temperature for which no additional energy is required.

The application of thermal theory to spontaneous ignition has been discussed by several workers, including P. Gray and Harper (1959a,b), Kuchta, Barkowiak and Zabetakis (1965) and Cullis and Foster (1973). For a spherical vessel with ignition at the the relation between the vessel radius r and the absolute ignition temperature T is, to a first approximation,

$$\ln r \propto 1/T \qquad [16.3.26]$$

It has been shown for a large number of fuels that if the AIT is plotted against vessel volume the lines pass through a single point, as shown in Figure 16.19 (Coffee (1982b), based on work by Beerbouwer (1974)).

A comparison of the values of the ignition temperature obtained in work using heated vessels (auto-ignition), hot wires and hot gas jets has been made by Kuchta, Cato and Zabetakis (1964). Their results are shown in Table 16.19. The values of the ignition temperature obtained with the Pyrex Erlenmeyer flask are appreciably lower than the other values.

The variation of ignition temperature with heat source dimensions has been discussed by Kuchta, Bartkowiak and Zabetakis (1965). They state that thermal theory predicts that the ignition temperature varies inversely with the logarithm of the heat source size, as in relation 16.3.26. While this behaviour was observed for one material studied (engine oil) over the whole range of surface areas, the other hydrocarbons tested exhibited in large vessels an ignition temperature appreciably lower than that predicted by this equation.

The variability of values of the AIT given in the literature has already been mentioned. This is illustrated by the values for methane quoted by C. Robinson and Smith (1984), which range from 537°C to 748°C. They state that the convention is to quote the lowest value found in the literature, but in the case of methane they could not determine the origin of the widely quoted value of 537°C and give the value of 601°C determined by themselves as the lowest of those for which experimental details are available. The AIT of mixtures has been studied by Cullis and Foster (1974). They found that for the binary mixture studied (*n*-decane and 2,2,5-trimethylhexane) the ignition tendency is controlled largely by the more ignitable component. It was necessary to go to nearly 50% of the less ignitable component before the ignition temperature started to rise appreciably.

Ignition delay time

In spontaneous ignition there is an induction period, or ignition delay, before ignition occurs. This delay is of interest both theoretically in relation to reaction kinetics and practically in relation to ignition in combustion systems. The ignition delay may be as little as a fraction of a second at higher temperatures, or several minutes close to the AIT.

Ignition delay decreases with increasing temperature. Semenov (1959) has given the following relation:

$$\ln \tau = \frac{k_1 E}{T} + k_2 \qquad [16.3.27]$$

where E is the apparent activation energy, τ is the time delay and k_1 and k_2 are constants.

Ignition delay has been studied by many other workers, including Brokaw and Jackson (1955), Ashmore and Levitt

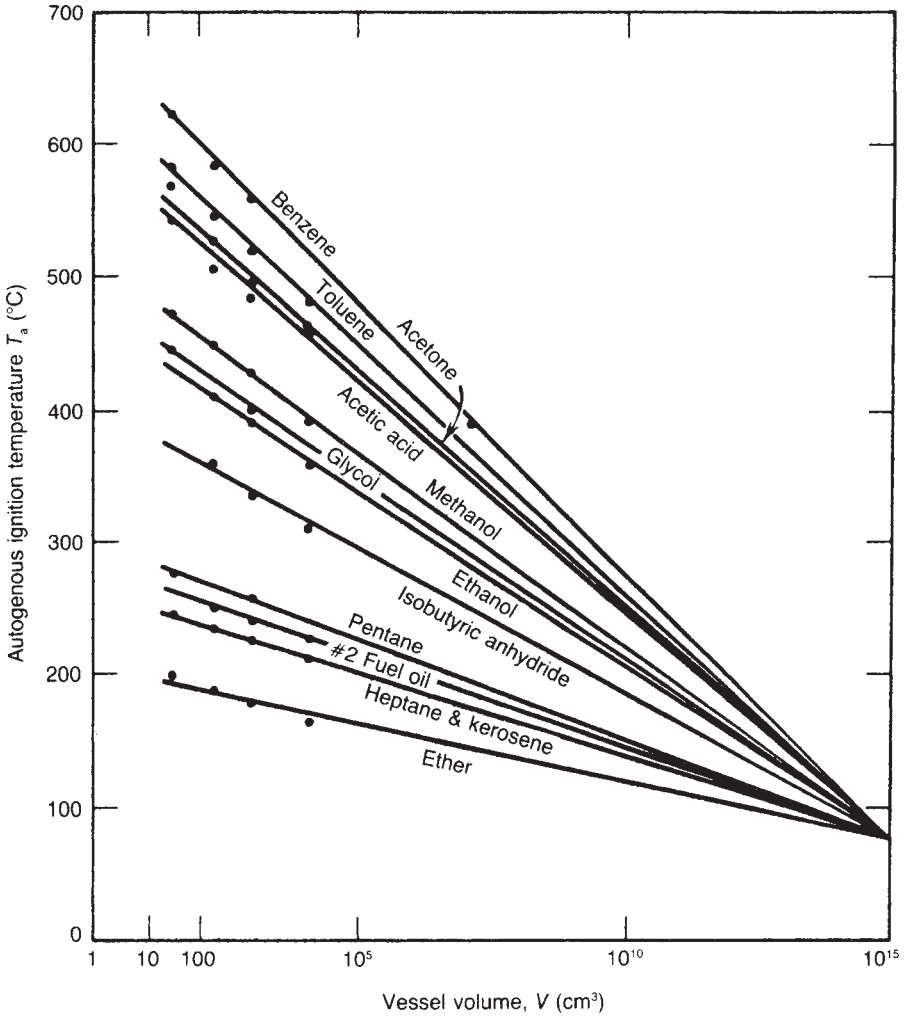


Figure 16.19 *Effect of vessel volume on the auto-ignition temperature (Reproduced with permission from Safety and Accident Prevention in Chemical Operations. 2nd ed., by H.H. Fawcett and W.S. Wood, ©, 1982, John Wiley and Sons Inc.)*

(1959), P. Gray and Harper (1959a,b), Voevodsky (1959) and Bascombe (1967). For propane–air mixtures with flowing gas, Brokaw and Jackson found the following variations of ignition delay with oxygen concentration and pressure p:

$$\frac{1}{\tau} \propto [O_2]^{1/4} \qquad [16.3.28]$$

$$\propto \ln p \qquad [16.3.29]$$

but did not find a constant activation energy relation with temperature.

Spark ignition

Turning to local ignition, it is convenient first to consider spark ignition. Here the ignition energy is determined by using the spark between two electrodes to ignite the flammable gas mixture. Apart from its implications for hazards, spark ignition has long been of practical interest for combustion in car engines and jet engines. A more recent aspect is lean burn engines for cars.

The results obtained for spark ignition energy are critically dependent on the electrode and spark arrangements. In early work this was not fully appreciated. In particular, the electrodes were usually too close together so that quenching occurred and the results obtained were too high.

It was suggested in early work, such as that of B.W. Bradford and Finch (1937), that there was a specifically electrical effect involving excitation of reactant molecules, but this suggestion was rejected by von Elbe (1953) in favour of a thermal effect.

A model of spark ignition has been developed by von Elbe and Lewis (1949) and von Elbe (1953) and is described

Table 16.19 *Ignition temperatures of flammable gas mixtures with different heated surface areas (Kuchta, Cato and Zabetakis, 1964) (Courtesy of Combustion and Flame)*

Substance	*Ignition temperature* (°C)			
	Pyrex Erlenmeyer flask[a] (2.2 cm radius, 13 cm long)	*Cylindrical Pyrex vessel* (0.5 cm radius, 15 cm long)	*Inconel wire* (0.5 cm radius, 5 cm long)	*Air jet*[b] (0.5 cm radius, >10 cm long)
Methane	537	745	–	1040[c]
Ethane	515	580	–	840[c]
n-Butane	405	630	–	910[c]
n-Hexane	234	605	670	765
n-Octane	220	585	660	755
n-Decane	208	585	650	750
Benzene	562	685	–	1020[d]
Hydrogen	554	635	–	640[c]

[a] Minimum AIT values obtained in a 200 cm^3 Erlenmeyer flask equivalent cylinder radius 2.2 cm.
[b] Hot air jet injected into fuel–air mixture, except as noted by footnotes (c) and (d).
[c] Hot air jet injected into fuel only.
[d] Hot nitrogen jet injected into fuel–air mixture.

by B. Lewis and von Elbe (1961). In simple terms, the argument is that the volume heated needs to exceed a certain critical size, otherwise the temperature gradient is too great and heat is lost too fast for combustion to be sustained. There is a MIE needed to overcome quenching by the unburnt gas.

More formally, the theory envisages a preheat zone and a reaction zone. A heat balance is taken between a plane x in the combustion wave and the plane b where combustion is complete and, assuming that the heat transferred by mass diffusion is less than that transferred by heat conduction, the enthalpy per unit mass within the wave is larger than that at the boundary b of the burnt gas or that at the boundary u of the unburnt gas, the two latter being equal. Thus there is a wave of thermal energy, or excess enthalpy, travelling with the combustion wave. It is this excess enthalpy which ensures that the temperature gradient is such that heat flow into the preheat zone balances the heat liberated in the reaction zone. When a flame grows spherically, the combustion wave requires from some external source a continuous supply of excess enthalpy in proportion to the growth of its surface, until the wave has effectively become a planar one. On this theory, the MIE is equal to the excess enthalpy requirement of the minimum flame.

Von Elbe defines the MIE H in terms of the excess enthalpy per unit area h and the critical diameter d at which the flame can propagate unaided:

$$H = \pi d^2 h \qquad [16.3.30]$$

There are a number of models of spark ignition, including those of Fenn (1951), Khitrin and Goldenburg (1957), Mayer (1957), Swett (1957), Penner and Muffins (1959), Rose and Priede (1959a,b), Ballal and Lefebvre (1975a), Adelman (1981), Maly (1981) and Sher and Refael (1982). Adelman gives a review of spark ignition models.

Fenn (1951) derives the critical diameter of the spark kernel by equating the heat released in the volume of the kernel to that transferred across its surface. The MIE H is then

$$H = \frac{K\pi d^3 c_p \rho}{6}(T_f - T_o) \qquad [16.3.31]$$

where T_f is the absolute adiabatic flame temperature and K is a constant. He states that the value of K is probably less than unity.

The model of Khitrin and Goldenberg (1957) is based on the thermal theory. Swett (1957) used long duration discharges and his treatment assumes that only part of this energy contributes to the ignition.

Ballal and Lefebvre (1975a) consider a spark kernel of the shape shown in Figure 16.20. It is assumed in this model that the heat release occurs only within the flame front, rather than throughout the whole kernel volume. The criterion for ignition is that the width d_c of the kernel is just equal to twice the width δ_L (laminar) or δ_T (turbulent regime) of the flame zone:

$$d_c = 2\delta_L \quad \text{Laminar regime} \qquad [16.3.32a]$$

$$= 2\delta_T \quad \text{Turbulent regime} \qquad [16.3.32b]$$

The authors give correlations for d_c for stagnant gas conditions and for laminar and turbulent flow regimes. For the stagnant gas condition

$$d_c = \frac{2k}{c_p \rho S_L} \qquad [16.3.33]$$

where S_L is the laminar burning velocity.

The model given by Adelman (1981) takes account not only of the heat balance on the spark kernel but also of the rate of growth of the kernel. Adelman states that spark kernels with the same spark energy input show identical growth in inert and combustible mixtures up to the critical point and that it is the spark discharge itself rather than combustion, which is responsible for kernel growth up to this point.

In his review Adelman relates the critical diameter of the spark kernel to the flame thickness δ_L and gives

$$\delta_L \approx \frac{k}{c\rho S_L} \qquad [16.3.34a]$$

$$= \frac{\alpha}{S_L} \qquad [16.3.34b]$$

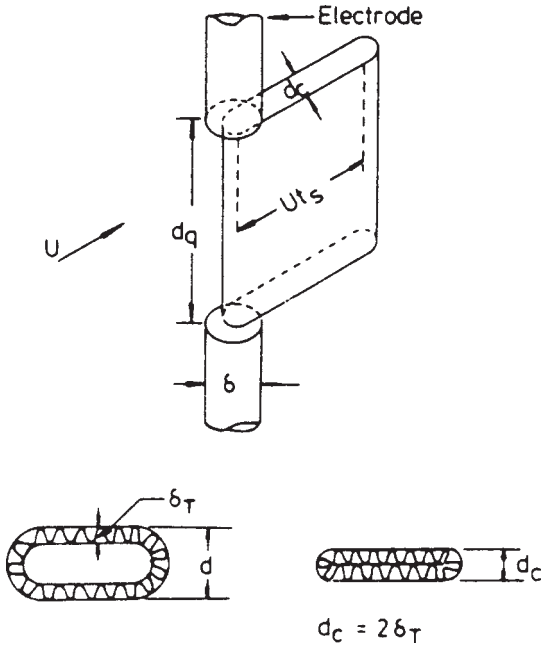


Figure 16.20 *Idealized model for the formation of a spark kernel (Ballal and Lefebvre, 1975a). d_q quenching distance; t_s spark duration; U, flow velocity (Courtesy of the Combustion Institute)*

where $\alpha(=k/c_p\rho)$ is the thermal diffusivity. He defines a characteristic flame dimension l_L as the value of the group α/S_L at ambient conditions and states that the flame thickness is about $10\,l_L$. Critical radii tend to be of the order $5\,l_L - 8\,l_L$ and thus about 0.5–0.8 of the flame thickness.

Maly (1981) distinguishes three modes of spark discharge – breakdown, arc and glow – and gives an ignition model. He emphasizes the importance of the breakdown mode. He states that ignition depends not so much on the total energy supplied but rather on high energy density deposition over a short time.

Minimum ignition energy

Work on measurement of ignition energy for spark ignition includes that of Blanc *et al.* (1947, 1949) and Moorhouse, Williams and Maddison (1974). The former determined ignition energies of hydrocarbon–oxygen–nitrogen mixtures over a range of concentrations, while the latter determined MIEs energies.

The problems in making such measurements have been discussed by a number of investigators. Rose and Priede (1959a) state that MIEs obtained by Lewis and von Elbe are some 1/100 of those obtained in early work in which the electrodes were too close together so that quenching could occur. Moorhouse, Williams and Maddison (1974) state that to obtain reproducible results they found it necessary to recondition the electrodes after about 15 trials.

Moorhouse, Williams and Maddison discuss the effect on the MIE of molecular structure.

The effect of turbulence on the MIE has been investigated by de Soete (1971). He states that turbulence causes an increase in the MIE, due mainly to an increase in flame front thickness, but also to a decrease in the fraction of energy that is effective.

Another study of the effect of turbulence is that of Ballal and Lefebvre (1975a). They state that the overriding effect of turbulence is heat loss by diffusion. They found that the MIE increases with increase in velocity and in turbulence intensity.

The effect of pressure and temperature on the MIE E is correlated by Moorhouse, Williams and Maddison (1974) as follows:

$$E = AP^{\alpha}T^{\beta} \qquad [16.3.35]$$

where P is the absolute pressure, T is the absolute temperature, A is a constant and α and β are indices. The values of the indices α and β were approximately 2 and -2, respectively.

Measurements of hot wire ignition energies have been made by number of workers, including Stout and Jones (1949). Different combinations of excitation current and time were used and the ignition energy was found to increase as the current was decreased and the time increased. A linear relation between the MIE and excitation time t was found:

$$E = A + Bt \qquad [16.3.36]$$

Hot surface ignition

Another mode of local ignition is contact with a hot surface. The AIT sets a lower limit to the temperature at which a hot surface may cause ignition, but it has long been known that in most situations of practical interest the hot surface temperature required to cause ignition is considerably higher than the AIT.

Interest has therefore centered on the difference between the hot surface ignition temperature and the AIT, or temperature excess. Research has shown that this temperature excess is a function of the material, area and geometry of the hot surface, of the gas and gas concentration, and the fluid flow and heat transfer conditions.

Some gases that have been widely used in work on hot surface ignition include methane, propane, butane and pentane. The AITs of these gases are 595, 470, 360 and 285°C, respectively.

Guest (1930 BM Tech. Pap. 475) investigated the ignition temperature of methane–air mixtures using various hot surface materials and areas up to 108 mm, and obtained values of 897–1420°C.

The effect of the area of the hot surface has been studied by Rae, Singh and Danson (1964), who exposed a methane–air mixture to hot surfaces of different size. Some typical results are shown in Figure 16.21. The work on hot particles by Silver (1937) and Paterson (1939–), described below, shows a similar decrease of the temperature excess as the hot surface area increases.

The effect of gas velocity has been studied by Mullen, Fenn and Irby (1949), who were concerned with the ignition of gas flowing past heated rods at high velocity as in a jet engine. Working with pentane–air mixtures, they found that the temperature excess increased with gas velocity.

Gas velocity has also been investigated by Goodall and Ingle (1967), who studied the ignition of kerosene in a wind

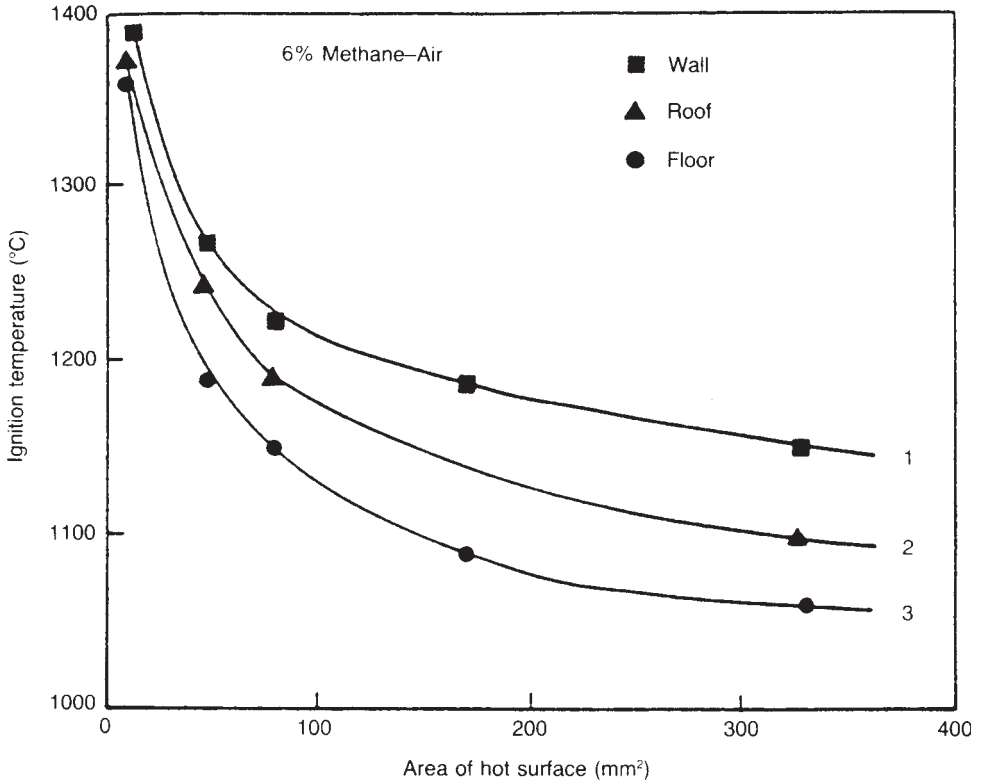


Figure 16.21 *Hot surface ignition temperature: effect of hot surface area on ignition temperature (Laurendeau, 1982; after Rae, Singh and Danson, 1964) (Courtesy of Combustion and Flame)*

tunnel. The hot surface temperature required to cause ignition in the experiments was as follows:

Gas velocity (m/s)	*Surface temperature for ignition* (°C)
0.3	405
1.5	660
3.0	775

The AIT of kerosene is given as 208–257°C, depending on the method of measurement

A number of workers have studied ignition of a flammable gas–air mixture on a vertical plate. A criterion widely used in this work has been the van't Hoff criterion that ignition occurs when the temperature gradient normal to the hot surface at some point becomes zero. Investigations have been done under forced convection by Toong (1957) and under natural convection by Ono *et al.* (1976).

L.D. Chen and Faeth (1981a) found that the zero temperature gradient condition is not always the appropriate one, that the lume above the hot surface influences ignition and needs to be taken into account, and that near limiting conditions there needs to be a substantial distance above the surface for the deflagration wave to develop so that quenching surfaces may suppress the deflagration.

Sharma and Sirignano (1969, 1970) have studied other geometries. Bull and co-workers have conducted an extensive investigation of the parameters influencing hot surface ignition.

Hot surface ignition is essentially a two-stage process, with initiation of a cool flame in the first stage followed by 'hof ignition'. A distinction is made between ignition and propagation. Propagation is confined between the flammability limits, but auto-ignition is not so bounded. In constant volume tests substantial, rapid pressure rises have been obtained with very rich mixtures.

Bull has conducted experiments using a parallel plate reactor (D.C. Bull and Quinn, 1975; D.C. Bull, 1977). In this apparatus the hot surface is placed above a cold surface so as to limit heat transfer to the conduction mode. Studies were conducted on propane, butane and hexane, and ignition diagrams for these gases obtained. The absolute results depended on the design of the apparatus, but certain trends emerged. A typical ignition diagram is shown in Figure 16.22. The figure shows the effect of the surface temperature. Another result of this work is to demonstrate that if there is even a modest temperature gradient normal

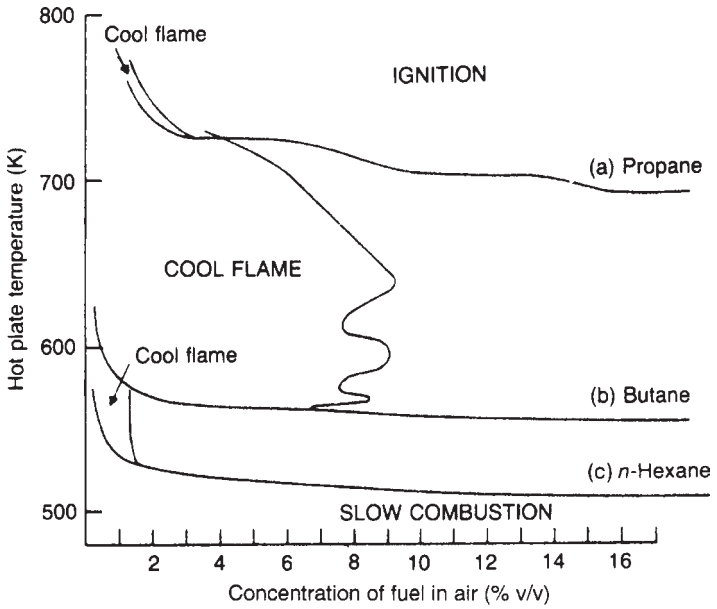


Figure 16.22 *Hot surface ignition temperature: ignition temperature boundaries for selected fuel-air mixtures in a parallel plate reactor (D.C. Bull, 1977). Plate separation 50 mm 'hot' and 'cold' plates at the same temperature – see text (Courtesy of DECHEMA)*

to the hot surface, a much higher temperature excess is required for ignition.

D.C. Bull, Cairnie *et al.* (1980) have also described research directed at understanding of the influence of fluid flow on hot surface ignition. Experiments were done on ignition by a hot vertical plate under laminar flow conditions. These conditions are favourable for experimentation and modelling and also approximate to the practical cases of a hot vertical surface or a hot large diameter pipe. The work showed that as the gas flows over the vertical surface it undergoes self-heating. Figure 16.23 gives the results obtained for a non-reacting gas and for a reacting gas.

The authors found that their initial model with reaction kinetics based on the Arrhenius equation was deficient. It predicted thermal runaway when the van't Hoff criterion of zero temperature gradient is satisfied, but this did not fit the experimental results. A second, more complex model, based on the acetaldehyde kinetics model, described below, was more successful. Figure 16.24 shows some predictions given by this latter model. Bull and Grant (D.C. Bull and Grant, 1975; D.C. Bull, 1977) have investigated ignition by a hot horizontal pipe, using two concentric pipes. They found that there was a region of high temperature gradient at the hot inner pipe, then a region of nearly constant temperature, then a cool region at the cold outer pipe. Ignition occurred in the region of nearly constant temperature. They derived a model, correlating their results in terms of the ratio of the pipe diameters, the Rayleigh number and the temperature across the annular gap.

Work was also done to investigate ignition by a hot exhaust pipe in the open air. The model showed that for ignition to occur there would need to be a very high temperature excess with high convective flows and ignition in the wake of the pipe. Under these conditions the residence time in the hot region may be less than the induction time.

Work on the development of a model for hot surface ignition has been described by Harrison and Cairnie and co-workers (A.J. Harrison and Cairnie, 1988; A.J. Harrison *et al.*, 1988). These authors have developed a chemical reaction model for the hot surface ignition of acetaldehyde–air mixtures. The full model is a 20-reaction model, but has been simplified successively to 8-, 5- and 2-species models. Some success has been achieved in describing the initiation of cool flame behaviour for hot vertical plate and continuous stirred tank reactor configurations. Below about 500°C, the ignition process depends critically on a build up of intermediate compounds. This indicates that the one-step ignition model often used is inappropriate.

Bartknecht (1988) has described work on ignition by steel pins heated by rubbing against a steel wheel. The pins were 6 and 8 mm in diameter with heated surfaces of area 2.9 and 4.0 cm^2, respectively. The lowest temperatures that he reports for ignition are 1248°C for methane and propane, and 1169°C for butane.

Work on ignition by heated rods has been described by Adomeit (1965), who investigated, in particular, ignition delay.

Friction and impact ignition

If one body strikes another, ignition may occur by impact or friction. In either case the ignition occurs as a result of a rise in surface temperature. If one body strikes another normal to its surface, there is impact but little friction. Impact causes a surface temperature rise in two ways (Bowden and Tabor, 1954). Kinetic energy is converted to heat. This causes a surface temperature rise, which may

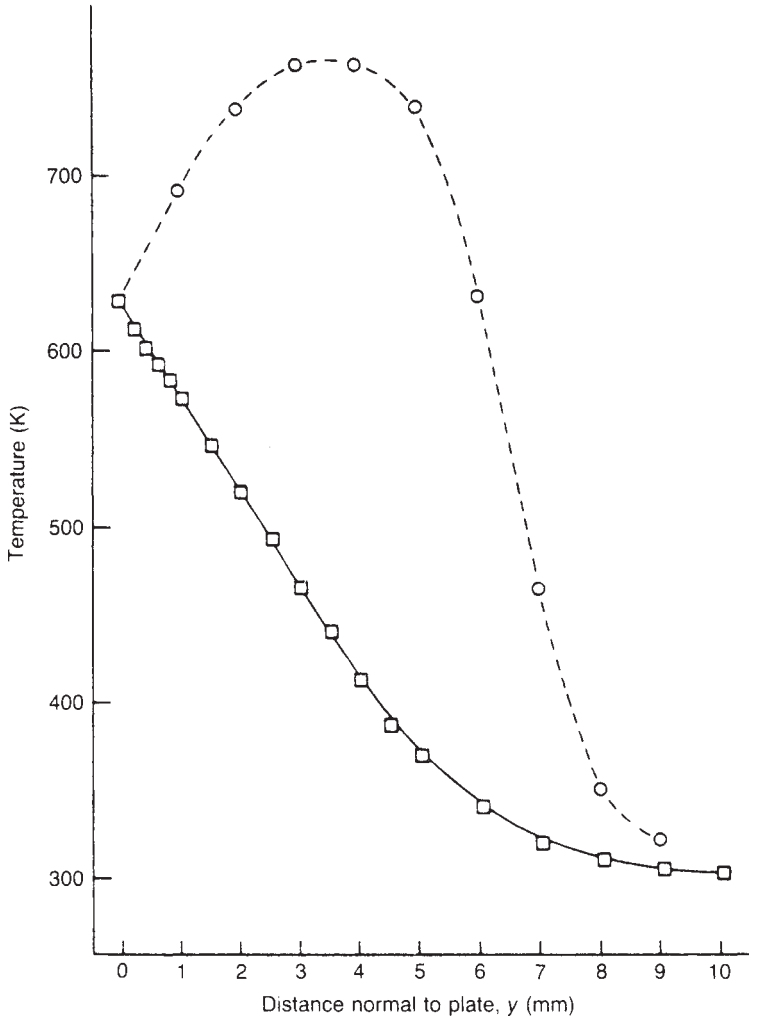


Figure 16.23 *Hot surface ignition temperature: boundary layer temperature profiles (D.C. Bull et al., 1980). (□) experimental values for air (non-reacting flow); (○) experimental values for 7.1% diethyl ether–mixture (reacting flow); and (--) theoretical values for air. Plate temperature 623 K; distance up plate 0.1 m. (Reproduced with permission)*

lead to exothermic oxidation of the surface resulting in a further temperature rise. The second of these effects tends to predominate.

The surface temperature rise depends on the oxidation characteristics and the thermal conductivity and does not simply correlate with the energy of impact. The heat generated by oxidation is highest for easily oxidizable metals such as iron and aluminium. The heat of oxidation of iron is several times that of copper and its thermal conductivity is less; the surface temperature rise of iron exceeds that of copper.

If one body is pressed against the surface of another and made to move, there is friction and this causes a surface temperature rise. If the first body strikes the second at an angle, there is a combination of impact and friction, which is described as frictional impact.

It has long been known that striking rusty steel covered with aluminium paint may produce incendive sparks. The effect is due to a chemical reaction, known as the thermite reaction. In this reaction the temperature can reach 3000°C. Following a study in 1941 by the Safety in Mines Research Board, which showed that no sparks were obtained unless the steel surface was rusty and that the effect varied with the type of paint, work was done by Kingman, Coleman and Rogowski (1952) to define more closely the conditions under which this effect occurs. Using both ferrous and non-ferrous strikers, they confirmed that sparks occurred only if rust was present. They found that no oil bound paint gave sparks unless the specimen had been preheated to at least 150°C. Cellulose nitrate paints, however, gave sparks after preheating to 100°C. In an appended note, HM Senior Chemical Inspector of Factories stated that the earlier report had given rise to exaggerated fears and that aluminium

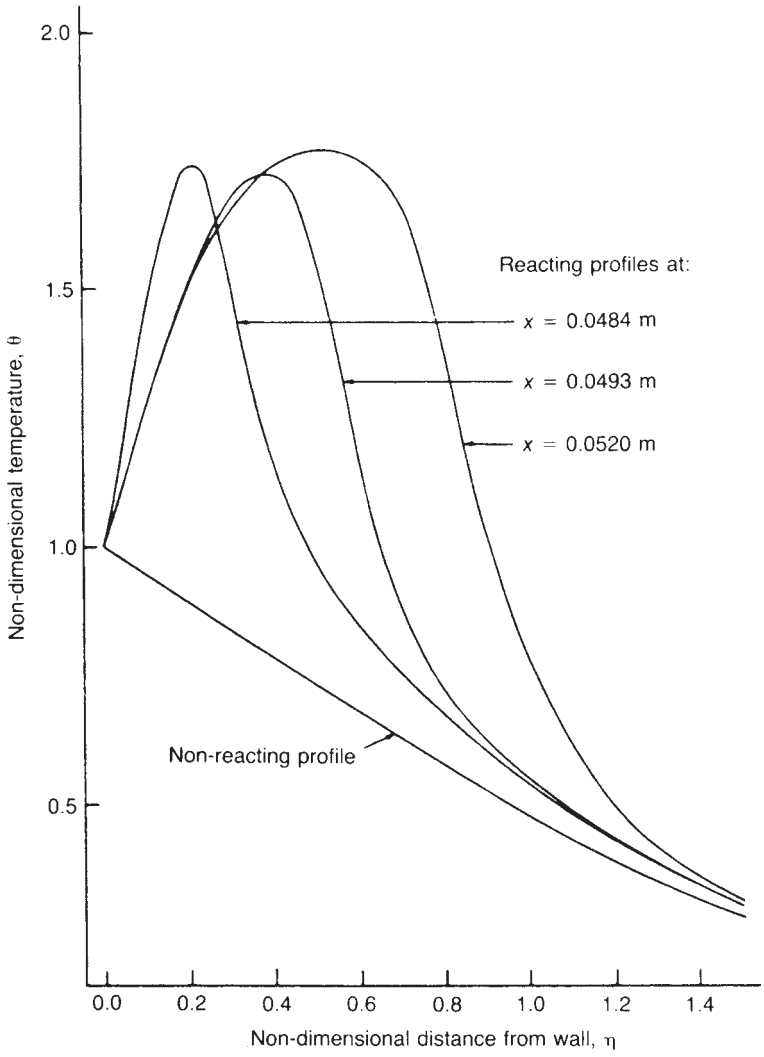


Figure 16.24 *Hot surface ignition temperature: theoretical boundary layer temperature profiles in a parallel plate reactor.* $\theta = (T - T_\infty)/\Delta T$; $\eta = [(g\Delta T^2\rho_\infty)/(4T_\infty\mu_\infty^2)]^{1/4}\frac{1}{x}\int^y \frac{\rho}{\rho_\infty}\,dy$ *(D.C. Bull et al., 1980). Reproduced with permission*

paint could be used in hazardous areas provided cellulose nitrate based paints were avoided and that no aluminium paint, whatever its base, should be used if it was likely to be heated to 150°C. A review of ignition by friction and impact has been given by F. Powell (1969), with particular reference to ignition of firedamp in coal mines. He states that frictional heating, usually by coal cutting machines, is the largest single cause of ignition in British mines. With regard to surface temperature rise he states that impact normal to the surface tends to give a relatively small surface temperature rise, that sliding friction gives surface temperatures sometimes approaching the melting points of the two materials and that frictional impact sometimes gives surface temperatures equal to the melting points. He reviews impact or rubbing between rocks, impact or sliding of metals on rocks, impact or rubbing between metals, and grinding and drilling operations.

In a study of impact of metals on metals, Titman and Wynn (1954) ignited methane–air mixtures with steel balls shot at steel and aluminium targets. Burgess and Wheeler (1929) were able to ignite methane–air mixtures with a steel locomotive wheel rubbing on steel rails, but only by using a shield to concentrate the sparks.

Powell describes extensive work in which ignition of mainly methane–air mixtures has been obtained by the impact of light alloys such as aluminium. In most cases ignition was by the thermite reaction. It is characteristic of light alloys that they tend to give a smear on rusty steel. Even if ignition does not occur at the time, a glancing blow from a hard object at some later time may produce the

thermite reaction and cause ignition. For this reason the use of light alloys in British mines is severely restricted. However, ignitions have been obtained with light alloys where neither rust nor steel were involved. W.G. Thomas (1962) ignited methane–air mixtures by shooting aluminium pellets at clean steel targets. In an investigation of an explosion in a ship's tank, Rae (1965) obtained ignitions of methane–air mixtures by dropping brass onto partly consumed magnesium anodes.

Ignition by the frictional impact of steel on rock has been studied by Blickensderfer (1975) in connection with ignition by coal-cutting machines. In severe impact a smear of molten metal is deposited on the rock. Most of the impact energy is converted to heat at the interface. This hot smear has the potential to ignite methane–air mixtures. In experimental work in which a metal object representing a cutting tool was secured to a flywheel and made to impact on rock, it was found that the impact energy had little effect on the probability of ignition, but that the impact speed had a strong effect. Hot streak temperatures of 1400°C were obtained. The effect of an increase in the impact speed was to increase the area rather than the temperature of the hot surface. This work includes a model of hot smear ignition.

Ignition of methane–air mixtures has been obtained by both ferrous and non-ferrous metals striking against quartzite materials, such as sandstone or concrete containing sand. This work is relevant to the use of 'non-sparking' tools.

Hot gas jet ignition

Ignition of flammable gas–air mixtures by jets of hot gas has been studied by Wolfhard and Vanpee (1959) to determine the degree of hazard of ignition of methane in coal mines from hot spent gases from the detonation of an explosive charge.

Ignition temperatures for a hot jet of air entering a cold, pure fuel are shown in Table 16.20 and those for a hot jet of nitrogen entering an ethylene–air mixture at an optimum concentration (close to stoichiometric) for ignition are shown in Table 16.21.

Table 16.20 *Hot gas jet ignition: ignition temperatures of a hot air jet entering a cold, pure fuel (Wolfhard and Vanpee, 1959) (Courtesy of the Combustion Institute)*

Fuel	*Ignition temperature* (°C)
Methane	1190
Ethane	945
Propane	1010
n-Butane	1025
Ethylene	875
Propylene	1060
iso-Butylene	1070
Acetylene	755
Carbon monoxide (commercial)	765
Hydrogen	670

Table 16.21 *Hot gas jet ignition: ignition temperatures for a hot jet of nitrogen entering an ethylene–air mixture of optimum concentration (close to stoichiometric) for ignition (Wolfhard and Vanpee, 1959) (Courtesy of the Combustion Institute)*

Jet flow (cm^3/s)	*Maximum temperature within jet* (°C)
25	1020
35	1035
50	1040
70	1050
100	1100
130	1140

Hot particle ignition

Investigations of the ignition of flammable gas–air mixtures by hot particles have been conducted by Silver (1937) and Paterson (1939–). Hot particles are another potential source of ignition in the use of blasting explosives in coal mines.

Silver carried out experiments in which hot particles were injected into flammable gas–air mixtures. The gases were coal gas, pentane and hydrogen and the particles quartz and platinum. The particle velocities were in the range 2–5 m/s. The particle temperature necessary to give ignition decreased as the particle diameter increased. Figure 16.25 shows some results obtained for the effect of particle diameter on the particle temperature required for ignition.

Paterson extended this work, using a wider range of gases and materials and particle velocities up to 65 m/s. Some results showing the effect of particle velocity and diameter on the particle temperature required for ignition are shown in Figure 16.26. Paterson's work shows that for small particles and for high particle velocities the surface temperatures required for ignition are very high.

A model for ignition by a hot inert particle has been described by Su, Homan and Sirignano (1979). Sharma and Sirignano (1970) have given a model for ignition by a hot projectile.

Flame torch and jet ignition

Flame torch ignition of a flowing flammable gas mixture is important in combustion systems. The work of Mullen, Fenn and Irby (1949) has already been mentioned. Work on this topic has also been done by Wang *et al.* (1981). Ignition of a vapour cloud by a flame jet has been studied by Mackay *et al.* (1988) in the context of vapour cloud explosions. These are described in Chapter 17.

Compression ignition

If a mixture of flammable gas and air is compressed, the resultant temperature rise may take the mixture into the temperature range in which auto-ignition occurs. This effect is exhibited in the diesel engine and is sometimes known as the diesel effect.

There is a considerable body of work on compression ignition, coming from several sources. Compression ignition is another of the modes of ignition studied in relation to ignition of firedamp in coal mines. Ignition by the pressure wave from a blasting explosive has been investigated by W.C.F. Shepherd (1949).

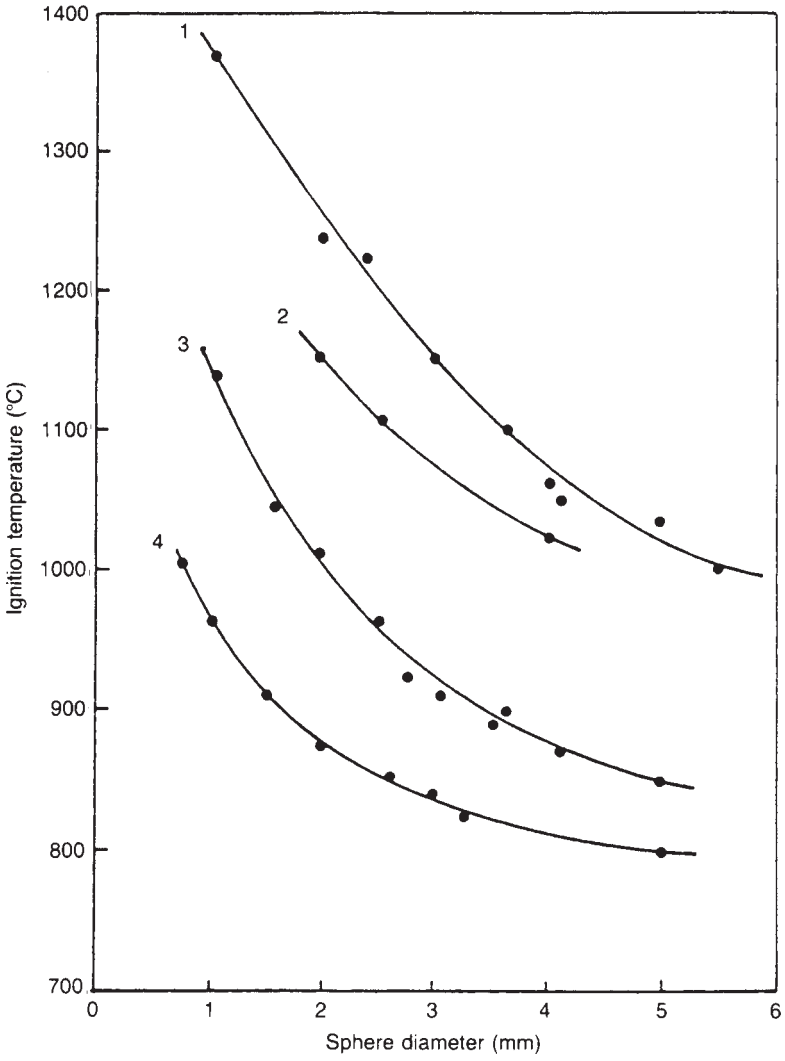


Figure 16.25 *Hot surface ignition temperature: effect of particle diameter on the particle temperature required for ignition of fuel–air mixtures by a hot particle travelling through the mixture (Laurendeau, 1982; after Silver, 1937; and Paterson, 1939–) 1, 3% pentane at ≈4 m/s; 2, 3% pentane at ≈1, 2 m/s; 3, 10% coal gas at ≈1.2 m/s (Courtesy of Combustion and Flame)*

Another motivation for research on compression ignition is the study of fast chemical reactions. Compression is a convenient method of effecting the very rapid translation of a reaction mixture into the temperature range of interest. The technique has been described by Jost (1949). According to Jost, for hydrocarbon–air mixtures over the temperature range of interest the value of the ratio of specific heats 7 is about 1.3. He also states that the variation with hydrocarbon concentration is not negligible.

A major aspect of research on combustion is the behaviour of shock waves, and ignition by shock waves is one aspect of this. Such work has been described by J.W. Meyer and Oppenheim (1971b), Vermeer, Meyer and Oppenheim (1972) and Eubank *et al.* (1981). Regimes of weak and strong ignition and ignition time delay are features that have been particularly investigated.

Research into internal combustion engines and diesel engines is another source of work on compression ignition. Work on compression ignition, and 'knock', in internal combustion engines is illustrated by the work of Halstead *et al.* (1975). There are also some studies of compression ignition of particularly sensitive chemicals such as those by Beeley, Griffiths and Gray (1980) on isopropyl nitrate and J.F. Griffiths and Perche (1981) on ethylene oxide (EO).

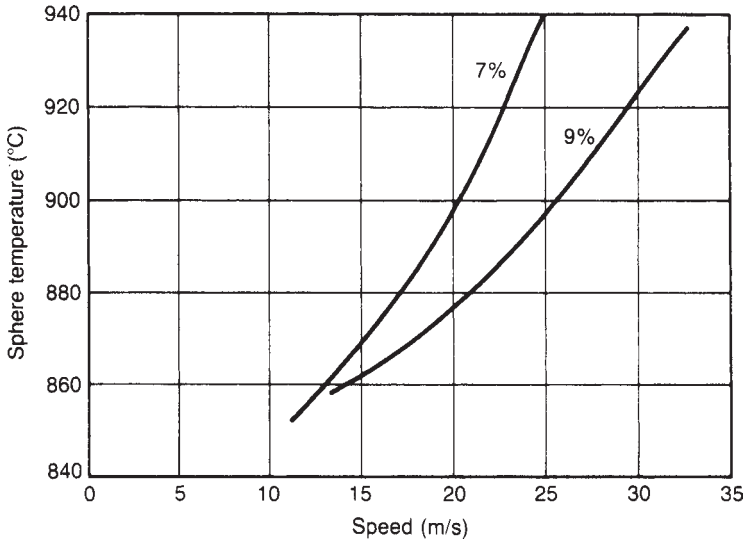


Figure 16.26 *Hot surface ignition temperature: the effect of particle velocity on particle temperature for the ignition of fuel-air mixtures by a hot particle travelling through the mixture (after Paterson, 1939–). Parameter of curves is concentration of coal gas in air (% v/v) (Courtesy of the Philosophical Magazine)*

Ignition in compression is a form of auto-ignition. The comment made earlier is therefore applicable, that, given a homogeneous mixture, ignition may occur outside the normal flammability limits, since these apply essentially to propagation of the flame.

16.3.10 Burning velocity

It is usual to distinguish between flame speed, which is the actual speed of the flame front in a given situation, and burning velocity, which is a property, or at any rate a quasi-property, of the flammable gas mixture. Definition of the burning velocity is not, however, straightforward, Linnett (1953) states that it seems impossible to define a burning velocity which is equally applicable to both planar and spherical flames and will have the same value for both cases, but suggests that the best approach is to use a value obtained by dividing a suitable flame area into a volumetric flow rate. It has been shown by Spalding and Yumlu (1959) that there are in fact two burning velocities, the higher value normally being the stable one.

There are a number of methods available for the measurement of burning velocity. These are reviewed by Linnett (1953) and by Andrews and Bradley (1972b). They include:

(1) propagating flame methods
  (a) soap bubble,
  (b) bomb,
  (c) tube,
  (d) flame kernel;
(2) cylindrical burner
  (a) cone angle,
  (b) total area;
(3) nozzle burner
  (a) cone angle,
  (b) total area.

With the cylindrical burner and nozzle burner methods measurement may be based on luminous flame, shadow or schlieren techniques.

A model for a spherical flame is given in Chapter 17. Other early models, including those by Semenov (1940), Tanford and Pease (1947) and Manson (1949), are reviewed by Dugger and Simon (1953). Further rather more complex models have been given by Yang (1961) and by Spalding, Stephenson and Taylor (1971).

Near the limits of flammability there is a minimum burning velocity to sustain combustion. This minimum burning velocity is influenced by natural convection. It has been suggested by Simmons and Wright (1972) that the following equation, derived by R.M. Davies and Taylor (1950) for the rise of an air bubble up a tube through a denser fluid, may be applied to the rise of a bubble of hot gas through a flammable gas mixture: $^1/_2$

$$v_o = 0.464(gr)^{1/2} \qquad [16.3.37]$$

where g is the acceleration due to gravity (cm/s^2), r is the radius of the tube (cm) and v_o is the velocity of the bubble (cm/s).

The effects of pressure and temperature on burning velocity have been the subject of several studies including those by Andrews and Bradley (1972a, 1973a), Halstead, Pye and Quinn (1974), Gulder (1982) and Lijima and Takeno (1986).

For methane, Andrews and Bradley (1972a, 1973) found that the burning velocity decreases with increasing pressure according to the relation

$$S_u \propto p^{-m} \qquad [16.3.38]$$

where $m = 0.5$. A similar relation was obtained by Gülder (1982) for methanol, ethanol and iso-octane with values

of m of the order of 0.2. On the other hand, for hydrogen, Lijima and Takeno (1986) report an increase in burning velocity with pressure.

Burning velocity is generally reported to increase with temperature. Gülder (1982) found the relation

$$S_u \propto T^n \qquad [16.3.39]$$

where $n = 1.75$ for methanol and ethanol and $n = 1.56$ for *iso*-octane. Andrews and Bradley (1972a) obtained for methane the relation

$$S_u = 10 + 0.000371 T_u^2 \qquad [16.3.40]$$

where S_u is the burning velocity (cm/s) and T is the absolute temperature of the unburned gas. Lijima and Takeno (1986) obtained similarly strongly positive correlations of burning velocity with temperature for both methane and hydrogen.

The effect of physical and chemical properties on burning velocity has been studied by Golovina and Fyodorov (1957). The effect on burning velocity of the recirculation of the products of combustion has been investigated by Putnam (1974).

The variability in the values of burning velocity given in the literature is discussed by Andrews and Bradley (1972b). For methane they quote values ranging from 31 to 50 cm/s and the variation is as great for most of the other gases considered.

Relations for the burning velocity of mixtures have been given by Payman and Wheeler (1922) and Spalding (1956). The Payman and Wheeler rule is

$$S_{u,m} = \sum S_{u,i} y_i \qquad [16.3.41]$$

where y is the mole fraction in the fuel–oxidant mixture and subscripts i and m denote component i and the mixture, respectively.

Spalding's treatment is based on the concept that the sole effect of mixing two fuel–air mixtures is to alter the flame temperature to a common value. In the simplified form given by Yumlu (1967a), the Spalding rule is

$$S_{u,m}^2 = \sum S_{u,i}^2 \alpha_i \qquad [16.3.42]$$

where α is the ratio of the mass of fuel i and the corresponding amount of oxidant to the total mass of fuel and oxidant.

The burning velocity so far considered is the laminar burning velocity S_L. The burning velocity is increased by turbulence and it is necessary to consider also the turbulent burning velocity S_T.

The definition of burning velocity becomes more difficult if the conditions are turbulent. The definition is usually given in terms of the flame surface, but this surface is difficult to specify. A rigorous definition of turbulent burning velocity has been given by J.M. Richardson (1956). Its application has been discussed by Palm-Leis and Strehlow (1969).

Measurement of the turbulent burning velocity has usually been carried out utilizing a modification of the burner method used for laminar burning velocity. The method of flame propagation in a vessel has also been used.

There are a number of correlations and models of turbulent burning velocity. Most of these involve parameters for the turbulence due to the gas flow such as the axial component of turbulence u' and the radial component v'. Turbulence generated by the flame is also taken into account in some treatments.

Treatments of turbulent burning velocity have been reviewed by B. Lewis and von Elbe (1961). The first model was that by Damköhler (1940), who suggested that the flame front is strongly distorted by turbulence and that under these conditions for a stable flame the burning velocity must exceed not only the average velocity U but also the velocity $U + u'$. This leads to the relation

$$S_T \propto u' \qquad [16.3.43]$$

In this model S_T is independent of S_L. Shchelkin (1943) modified the Damköhler model by assuming that the distortions of the flame front are cone shaped. Then from geometrical considerations he obtains

$$\frac{S_T}{S_L} = [1 + (2u'/S_L)^2]^{1/2} \qquad [16.3.44]$$

The model is a crude one, and in recognition of this the 2 in Equation 16.3.44 may be replaced by an undetermined number B of the order of unity. Equation 16.3.44 reduces to relation 16.3.43 for large values of $(u'/S_L)^2$

Thus, according to these theories, under conditions of high turbulence the turbulent burning velocity S_T should be independent of the fuel gas. Work by D.T. Williams and Bellinger (1949) has shown, however, that this is not so.

Karlovitz, Denniston and Wells (1951) have developed a model that addresses this problem. The model is based on the concept of an undulated flame front and yields the relations

$$\frac{S_T}{S_L} = 1 + \frac{S_t}{S_L} \qquad [16.3.45]$$

with

$$S_t = \left(2 S_L u' \left\{1 - \frac{S_L}{u'}[1 - \exp(-u'/S_L)]\right\}\right)^{1/2} \qquad [16.3.46]$$

where S_t is the average velocity of displacement of the turbulent wave. At low turbulence, Equation 16.3.46 reduces to

$$\frac{S_T}{S_L} = 1 + \frac{u'}{S_L} \quad 1 < \frac{u'}{S_L} \qquad [16.3.47]$$

and at high turbulence it reduces to

$$\frac{S_T}{S_L} = 1 + \left(\frac{2u'}{S_L}\right)^{1/2} \quad \frac{u'}{S_L} > 1 \qquad [16.3.48]$$

In this model, therefore, the turbulent burning velocity remains dependent on the laminar burning velocity, even at high turbulence.

In their work, D.T. Williams and Bellinger (1949) obtained the correlation

$$u_t = 0.1761\ u_n d^{0.2564} \mathrm{Re}^{0.238} \quad 3000 < \mathrm{Re} < 35{,}000 \qquad [16.3.49]$$

where d is the burner diameter (cm), u_n is the laminar burning velocity (cm/s) and u_t is the turbulent burning velocity (cm/s).

Fine (1958) describes two models for the effect of turbulence on burning velocity. One treatment is based on the effect of turbulence in inducing flame wrinkling and gives

$$\frac{S_T}{S_L} = f(u'/S_L) \qquad [16.3.50]$$

The other model involves the effect of turbulence on thickening of the reaction zone. Fine applied these models in an attempt to determine by studying the effect of pressure whether the Reynolds number is the proper correlator, but the results were inconclusive. Correlations of the turbulent burning velocity have been given by a number of workers. Thus Kozachenko (1962) gives a relation of the form

$$S_T = S_L + \phi_1 \qquad [16.3.51]$$

and Gökalp (1980) one of the form

$$S_T = S_L + \phi_2 \qquad [16.3.52]$$

where ϕ_1 and ϕ_2 are functions of turbulence.

An extensive program of work on the turbulent burning velocity has been undertaken by Bradley and co-workers. Andrews, Bradley and Lwakabamba (1975a) obtained a graphical correlation of turbulent burning velocity in terms of the unburnt gas Reynolds number defined as

$$R_\lambda = u'\lambda/v \qquad [16.3.53]$$

where u' is the root mean square (rms) turbulent velocity, λ is the Taylor microscale and v is the kinematic viscosity. On the assumption that $u'/U = 0.05$ this Reynolds number is given approximately by the relation

$$R_\lambda = (\mathrm{Re} - 2500)^{1/2} \qquad [16.3.54]$$

Abdel-Gayed and Bradley (1977) present a further graphical correlation. For high turbulence they give the relation

$$\frac{u_t}{u_l} = 3.788 R_\lambda^{0.238} \quad R_\lambda > 100;\ u_1/u' \to 0 \qquad [16.3.55]$$

where u_1 and u_t are the laminar and turbulent burning velocities, respectively. Further work is reported by Abdel-Gayed and Bradley (1987), who also give details of the correlations found by previous workers.

Continuing this investigation, Bradley, Lau and Lawes (1992) give the correlation shown in Figure 16.27. They use an integral length scale of turbulence L such that

$$\frac{\lambda^2}{L} = \frac{Av}{u'} \qquad [16.3.56]$$

with a turbulent Reynolds number $\mathrm{Re_L}$ defined by

$$\mathrm{Re_L} = \frac{u'L}{v} \qquad [16.3.57]$$

where A is a constant. Then for the parameter group $K\mathrm{Le}$ in Figure 16.27 they give for the Karlovitz flame stretch factor K the relation

$$K = 0.157\left(\frac{u'}{u_1}\right)^2 \mathrm{Re_L}^{-1/2} \qquad [16.3.58]$$

in which the value of A has been taken as 40.4, while the Lewis number Le is defined as

$$\mathrm{Le} = \frac{k}{c_p \rho D} \qquad [16.3.59]$$

where c_p is the specific heat of the gas, D is the diffusion coefficient of the deficient reactant, k is the thermal conductivity of the gas and ρ is the density of the gas. They also give the following limited-range relation:

$$\frac{u_t}{u'_k} = 0.88(K\mathrm{Le})^{-0.3} \quad 0.01 < K\mathrm{Le} < 0.63 \qquad [16.3.60]$$

The correlation given makes use of the rms turbulent velocity u' and the effective rms turbulent velocity acting on the flame u'_k. Although in this work use was made of measured values, where necessary Abdel-Gayed and Bradley (1977) also used the relation

$$\frac{u'}{U} = 0.1676\ \mathrm{Re}^{-0.119} \qquad [16.3.61]$$

With regard to u'_k this velocity is given mainly in terms of the ratio u'_k The treatment, described in detail by Abdel-Gayed and Bradley (1987), is complex, but at high turbulence the value of the ratio tends to unity.

The effect of pressure on turbulent burning velocity has been studied by Fine (1958), as already mentioned. He obtained for propane and hydrogen the relation

$$\frac{S_T}{S_L} \propto P^n \qquad [16.3.62]$$

where n is approximately 0.3.

Selected values of the turbulent burning velocity of various fuels are given by Abdel-Gayed and Bradley (1977).

Burning velocity is closely related to quenching distance, as described in the next section.

16.3.11 Quenching effects

Flame propagation may be extinguished by quenching. Such quenching may be due to heat loss to unburnt gas or to a solid surface. Quenching is closely related to several of the other properties already discussed. Explanations for the existence of flammability limits invoke quenching. There is a close inverse relation between burning velocity and quenching.

Quenching is of practical interest in a number of ways. The stabilization of flames on burners is related to quenching. The quenching effect is utilized in equipment designed to stop the passage of flame, such as flameproof motors and flame arresters. The occurrence of unreacted fuel in car exhaust may be attributable to quenching.

For quenching in a gap between surfaces use is often made of the quenching distance d_q. This is sometimes used as a general term covering both the quenching diameter d_o and the critical slot width $d_{||}$ and sometimes means only the latter.

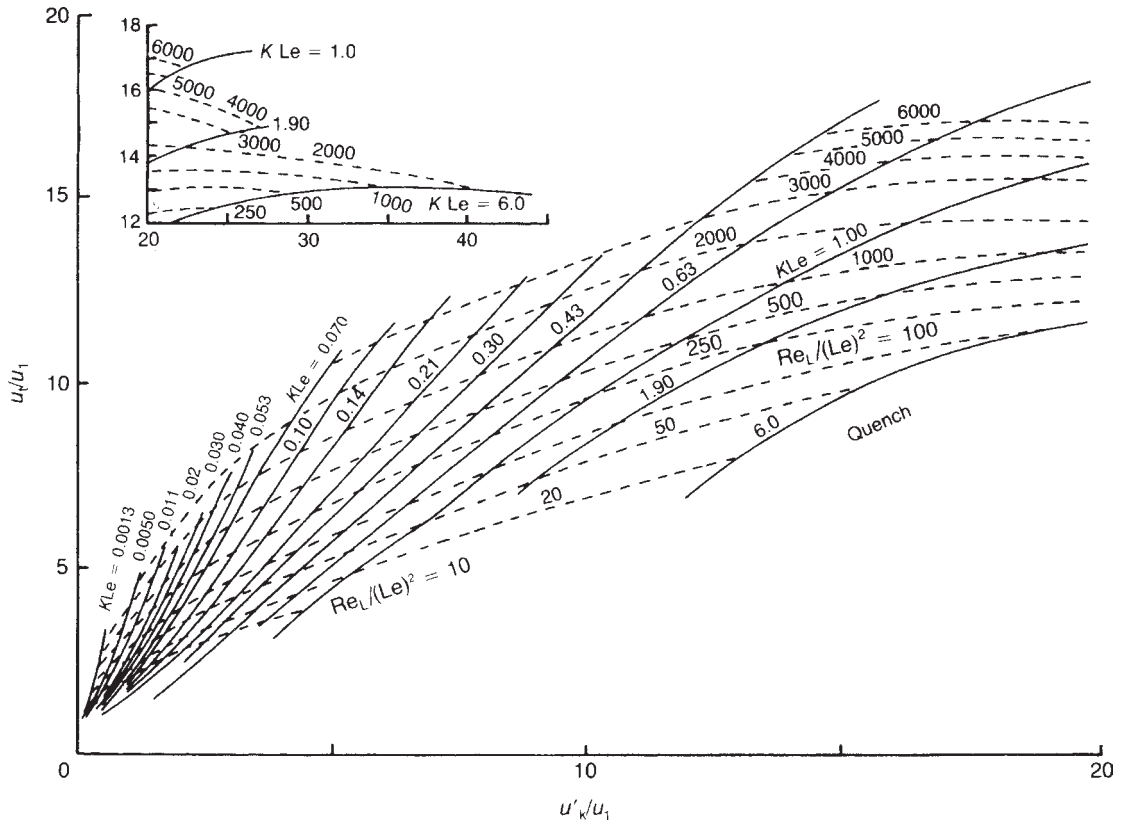


Figure 16.27 *Correlation for turbulent burning velocity (D. Bradley, Lau and Lawes, 1992) (Courtesy of The Royal Society)*

Potter (1960) gives the relation between the quenching diameter d_o and the critical slot width $d_{||}$ as

$$d_{||} = 0.65 d_o \qquad [16.3.63]$$

A third quenching parameter is the depth of penetration of quenching d_p. This is defined as the ratio of the burning velocity to the critical boundary velocity gradient for flashback:

$$d_p = S_u / g_F \qquad [16.3.64]$$

The variation of these three quantities for flammable mixtures of natural gas and air is shown in Figure 16.28. The quenching diameter is the greatest dimension and the depth of penetration of quenching is the smallest.

Measurement of the quenching distance may be made by a number of methods. Reviews of these methods have been given by R. Friedman (1949) and Anagnostou and Potter (1959). Methods include those based on measurement of

(1) flame blow-off and stability;
(2) the critical distance between parallel plates;
(3) the critical tube diameter.

Extensive measurements of quenching distance have been made by Blanc, *et al.* (1949). There are a number of models and correlations for quenching distance. Drawing on earlier work by Mallard and Le Chatelier (1883), R. Friedman (1949) derived a quenching equation. Equating the heat generated to the heat lost to the walls, he obtained for the critical value of the quenching distance x

$$x = \frac{k}{S_u c_{pu}} \left[\frac{1}{f} \frac{(T_f - T_i)}{(T_i - T_o)} \right]^{1/2} \qquad [16.3.65]$$

where c_{pu} is the specific heat of the unburnt gas, f is a geometrical factor of the order of unity, k is the thermal conductivity of the gas, T_f is the absolute flame temperature, T_i is the absolute ignition temperature and T_o is the absolute temperature of the unburned gas.

Some theories of quenching involve the Peclet number Pe defined as

$$\mathrm{Pe} = S_u d_q / \alpha_u \qquad [16.3.66]$$

with

$$\alpha_u = k_u / \rho_u c_u \qquad [16.3.67]$$

where α is the thermal diffusivity and subscript u denotes the unburned gas.

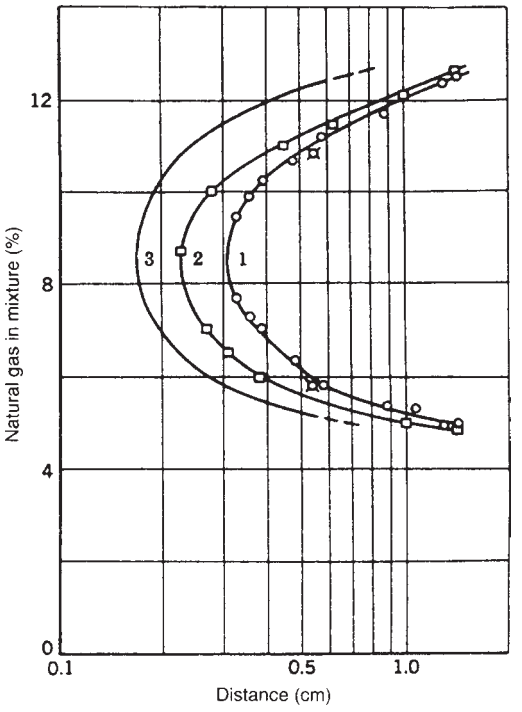


Figure 16.28 *Quenching parameters of burner wall for natural gas–air mixtures (B. Lewis and von Elbe, 1961) 1, quenching diameter d_0; 2, quenching distance $d_{||}$; 3 depth of penetration, d_p (Courtesy of Academic Press)*

Equations 16.3.66 and 16.3.67 imply a constant value of the burning velocity-quenching product, which is also used by Potter and Berlad (1957).

$$\frac{d_q}{S_u} = \text{Constant} \qquad [16.3.68]$$

Ballal and Lefbvre (1977) have attempted to correlate the quenching distance for turbulent flow conditions using

$$d_q = \frac{\text{Pe}\alpha}{S_u} = A \qquad [16.3.69]$$

where A is a constant, but found that it was necessary to modify this relation and proposed instead

$$d_q = A + 13\text{Pr}^{-0.05}(u'/S_L)^{0.5} \qquad [16.3.70]$$

Kydd and Foss (1964) emphasize the influence on quenching of three-dimensional effects.

Several investigators have studied the effect on quenching distance of gap length. R. Friedman (1949) states that the quenching distance appears to depend not on gap length but on gap width only. On the other hand, Maekawa (1975) obtained for quenching in rectangular channels the relation

$$d_q = k_1 L \exp(-k_2 L) + k_3 L \qquad [16.3.71]$$

where L is the gap length and k_1 to k_3 are constants.

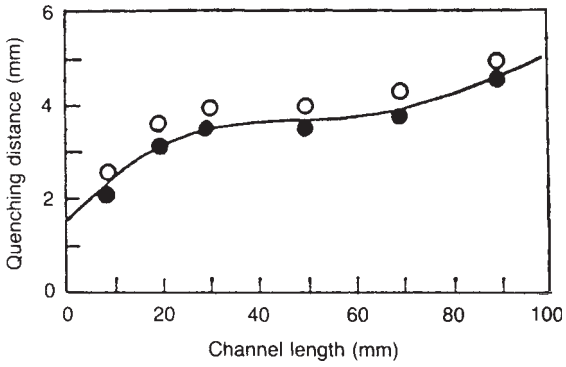


Figure 16.29 *Quenching distance in a rectangular duct (Maekawa, 1975) (Courtesy of Combustion Science and Technology)*

Some results from this work are shown in Figure 16.29.

Mention should also be made of experiments by Wolfhard and Bruszak (1960) in which they investigated the propagation of flame down narrow tubes between two chambers. In experiments with methane the flame did not propagate through tubes of diameter less than 3 mm. But ignition could still occur in the outer chamber due to the jet of hot gases. Whether ignition did in fact occur depended on the properties of the jet. Very short channels were more effective in preventing ignition than were 10 mm long ones.

The effect of pressure on quenching distance has been studied by several workers including Brokaw and Gerstein (1957), Potter (1960) and Ballal and Lefebvre (1975a). The quenching distance increases with decreasing pressure.

Potter (1960) states that the quenching distance is approximately inversely proportional to pressure:

$$d_q \propto P^{-1} \qquad [16.3.72]$$

This relation is in fact implied in the use of the Peclet number.

Practical quenching criteria such as the MESG were discussed in Section 16.2.

16.3.12 Cool flames

Certain compounds are capable of slow oxidation at mixture concentrations outside the normal flammability limits and at temperatures lower than those pertaining in normal combustion. Cool flames are of practical interest for several reasons. Much of the work done has been concerned with knock in internal combustion engines and also in jet engines. They are also of interest in relation to hydrocarbon oxidation in chemical reactors.

Cool flames were discovered by Sir Humphrey Davy and were studied by Perkin (1882), who found that they could be obtained with a wide variety of compounds, including hydrocarbons, alcohols and aldehydes. They were most easily demonstrated with diethyl ether and acetaldehyde. They were effectively rediscovered by Prettre, Dumanois and Lafitte (1930) and Townend and Mandlekar (1933).

Townend and co-workers carried out a series of studies on cool flames. The characteristics of such flames are illustrated by the work of Hsieh and Townend (1939a–c). The concentration region within which cool flames occur is

illustrated by the results for hexane–air mixtures obtained by Hsieh and Townend (1939b), as shown in Figure 16.30(a). They state:

> Reference to the results at 1500°C shows that at pressures up to 4.1 atm there was only one range of inflammable mixtures, viz. that for normal flames. This was at first unaffected by increase in initial pressure, the lower limit being lower by about 0.3% and the higher limit raised by about 1% of hexane at pressure up to 4 atm. At a pressure of 4.1 atm a cool flame range was located with mixtures of composition between 11 and 22% of hexane, the normal range at the same pressure extending over mixtures of hexane content between 1.2 and 7.0%. The 'normal' and 'cool' flame ranges were thus separated by a range of non-flammable mixtures containing between 7 and 11% of hexane. At pressures higher than 4.8 atm the two ranges of inflammability became superposed so that at, 6.5 atm, mixtures containing between 1 and 14.5% of hexane were capable of propagating 'normal' flames and those between 14.5 and 32% 'cool' flames.

Hsieh and Townend (1939a) also investigated the ignition of cool flames both by spontaneous ignition and by hot wire ignition, in order to establish that the cool flame process is the same in both modes. Their results for ether–air mixtures are shown in Figure 16.30(b).

The results of cool flame experiments may also be presented as an ignition diagram in which the regions of the different modes of combustion are shown on a plot of temperature vs. pressure for a given mixture composition. An ignition diagram for a propane-oxygen mixture given by Newitt and Thornes (1937) is shown in Figure 16.31. Ignition diagrams for a number of compounds have been given by Townend (1937). A characteristic feature of an ignition diagram is the peninsular region. Apart from its practical significance, the diagram provides a test of theories for cool flames.

Cool flames are associated with a negative temperature coefficient for the overall combustion over a limited range of temperature, as illustrated by the data shown in Figure 16.32 for the reaction rate of propane and oxygen obtained by Seakins and Hinshelwood (1963). The negative temperature coefficient is discussed by Knox, who interprets it as evidence of a fundamental change from one reaction mechanism to another.

Interpretations of cool flames in terms of the reaction kinetics have been undertaken by a large number of workers. Reviews are given by von Elbe and Lewis (1937a), Ashmore (1967) and Knox (1967a).

Von Elbe and Lewis (1937b) review the theories of Norrish and Foord (1936), Ubbelohde (1935, 1936), Jost, von Muffling and Rohrmann (1936), Pease (1935), Semenov (1935) and von Elbe and Lewis (1937a). They discuss the role of unbranched and branched chain reactions and of the intermediate aldehydes and peroxides formed.

Thermal and isothermal theories of cool flames have been proposed by Semenov (1935) and are discussed by Ashmore (1967). In the thermal theory, which applies both to unbranched and branched chain reactions, a rapid increase in reaction rate occurs as a result of self-heating, while in the isothermal theory, which applies to branched chain reactions only, the reaction rate increases as a result of exponential growth in the chain centres at the end of an isotherm induction period.

A series of investigations of pre-flame and ignition behaviour and of cool flames has been carried out by Barnard and co-workers (e.g. Barnard and Ibberson, 1965 Barnard and Kirschner, 1967; Barnard and Sankey, 1968; Barnard and Watts, 1972; Barnard and Harwood, 1973a) and by Salooja (1966, 1967, 1968a,b).

A feature of cool flames is the occurrence of multiple flames, one after the other. Coffee (1982b) quotes observation of up to 11 cool flame zones.

The periodicity of cool flames is another feature that is of theoretical interest. Attempts have been made to apply to cool flames the theory developed by Lotka (1920) for essentially biological phenomena, which for certain conditions predicts oscillations in the concentration of intermediate species. This aspect is discussed by B.F. Gray and Yang (1969). Cool flames exhibit an ignition delay, or induction period. Studies of ignition delay in cool flames include those of J.E. Johnson, Crellin and Carhart (1954), Fish (1968) and Barnard and Watts (1972). Fish obtained for the variation of ignition delay with pressure the relation

$$\tau = kP^{-n} + c \qquad [16.3.73]$$

where P is the absolute pressure, τ is the ignition delay, c and k are constants and n is an index.

Cool flames result in rises in pressure and temperature, but these are more modest than with normal combustion. Correlations for pressure and temperature effects are given by Fish (1968) and by Luckett and Pollard (1973). For the pressure rise Fish found

$$\Delta P_{cf} = kP_o^m \qquad [16.3.74]$$

where P_o is the absolute initial pressure, ΔP_{cf} is the pressure rise for a cool flame, k is a constant and m is an index. The value of the index m was $1 < m < 2$.

The temperature rise was found by Fish to be a function of the oxygen concentration of the mixture. For low oxygen concentrations the rise in temperature corresponded closely to the rise in pressure, assuming the ideal gas law.

Cool flames in mixtures have been studied by Salooja (1968b). He found that for binary mixtures two different types of behaviour could be distinguished: those cases for which the ignition tendency is (1) intermediate between those of the two compounds and (2) even greater than that of the more ignitable component.

The features of cool flames have been compared with those of normal flames by Coffee (1982b) as follows:

	Normal flames	*Cool flames*
ΔT_{cf}	800–2000°C	1–200°C
P_{if}/P_o	6–10 (confined spaces)	Low (<2)
Products	CO_2, H_2O	CO, CH_2O

P_{cf}, absolute final pressure of cool flame; P_o, absolute initial pressure; ΔT_{cf}, temperature rise for cool flame.

16.3.13 Combustion in tubes

The behaviour of flames in tubes has been extensively studied. Early work was carried out by Mallard and Le Chatelier (1883) and by Wheeler and co-workers, the latter including the work by Mason and Wheeler (1917, 1920a–c), Chapman and Wheeler (1926, 1927), Ellis (1928), Ellis and

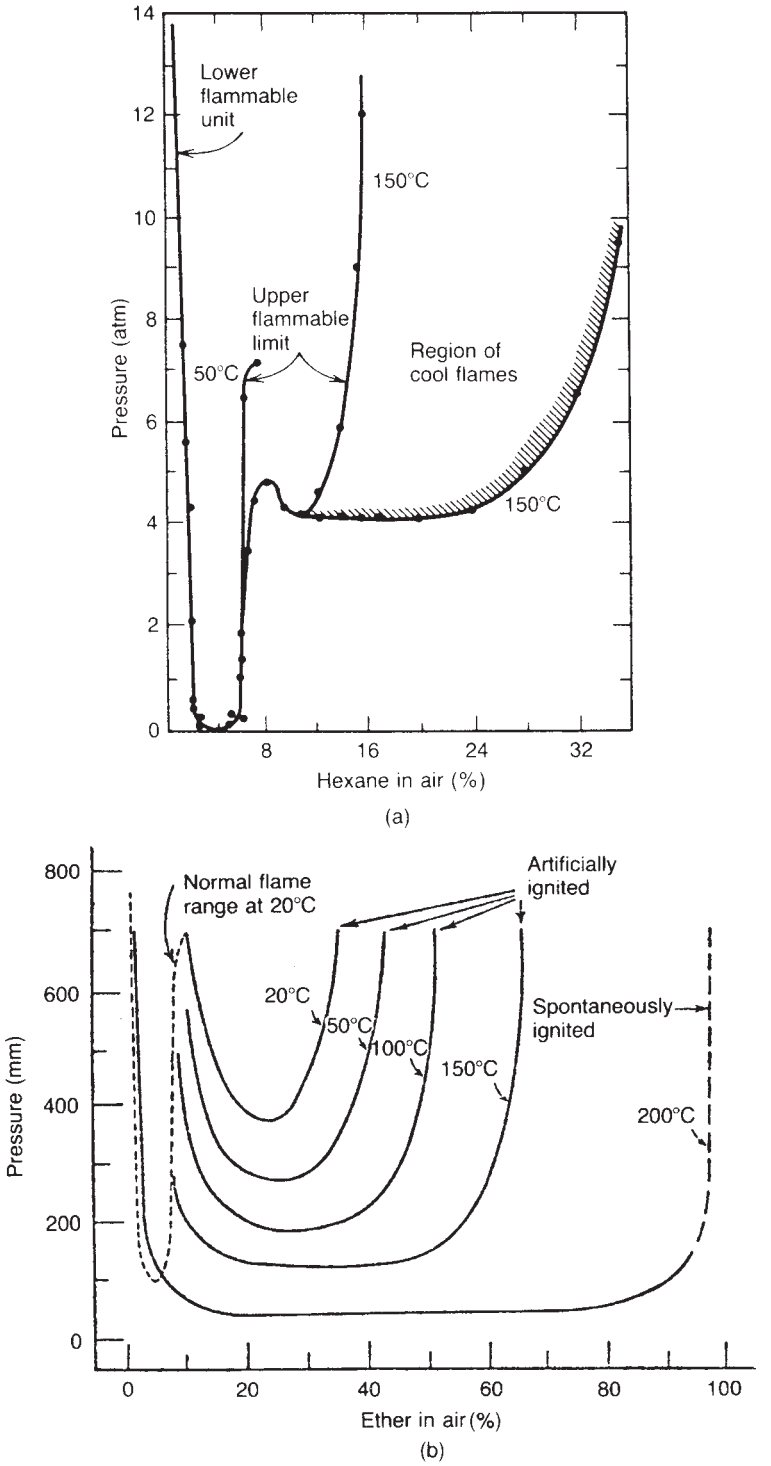


Figure 16.30 *Effect of pressure on cool flame ranges: (a) cool flames of hexane–air mixtures (after Hsieh and Townend, 1939b); and (b) cool flames of ether–air mixtures (after Hsieh and Townend, 1939a). Latter shows ignition both by ignition source and by bulk gas ignition (Courtesy of the Chemical Society)*

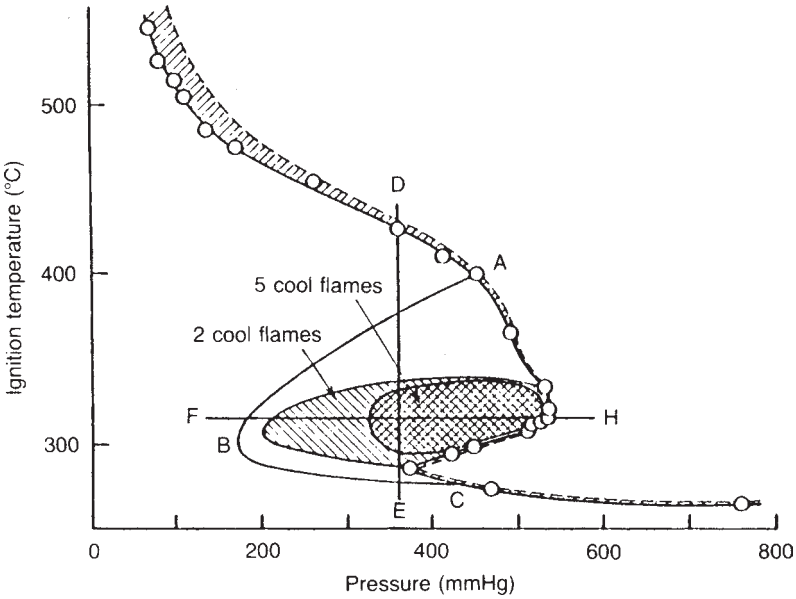


Figure 16.31 *Ignition diagram for equimolar concentration of propane and oxygen, showing effect of pressure on ignition temperature and cool flame ranges (Knox, 1967a; Newitt and Thornes, 1937) (Courtesy of Cambridge University Press)*

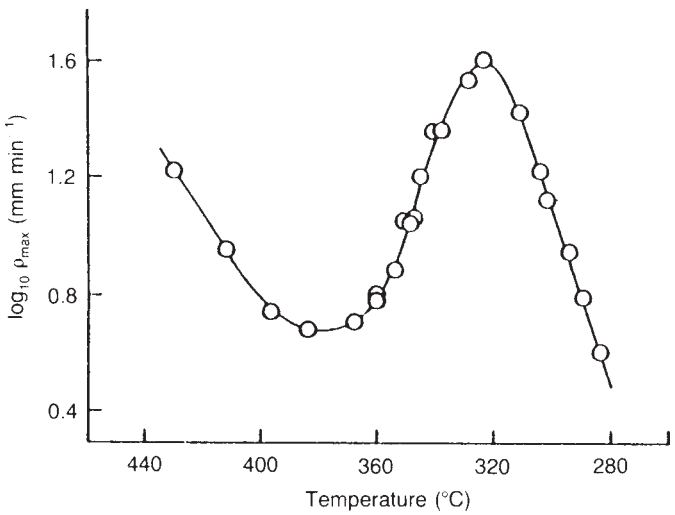


Figure 16.32 *Effect of temperature on reaction rate for oxidation of propane, illustrating negative temperature coefficient (Knox, 1967a; after Seakins and Hinshelwood, 1963) P_{max} maximum pressure (mmHg) (Courtesy of Cambridge University Press)*

Wheeler (1925, 1928a,b), Kirby and Wheeler (1931a,b) and H. Robinson and Wheeler (1933).

Much work on combustion in tubes has dealt with detonation, and with the transition from deflagration to detonation; this is considered in Chapter 17. There is also, however, a body of work which is concerned with the more general aspects of combustion in tubes, including tubes containing obstacles, in respect of features such as vibratory oscillations, flame acceleration, pressure rise and so on.

Such work includes *Non-Steady Flame Propagation* by Markstein (1964) and that by M.W. Evans *et al.* (1949), Schmidt, Steinicke and Neubert (1953), Guenoche (1964), Leyer and Manson (1971), Andrews, Herath and Phylaktou (1990) and Phylaktou, Andrews and Herath (1990).

The latter authors have reviewed some of the findings of this work. They consider four cases: Case 1, a tube open at one end with ignition at the open end; Case 2, a tube open at one end with ignition at the closed end; Case 3, a tube open at both ends; and Case 4, a tube closed at both ends.

Case 1 appears to provide the simplest propagation conditions and has been the most widely investigated. After a short initial phase, the flame propagates for some distance at a fairly constant velocity. This phase is sufficiently prolonged to permit measurement of the burning velocity. As the flame progresses, there begin vibrations of the combustion surface that can turn into violent oscillations. Towards the end of the tube the flame velocity falls rapidly to a roughly constant value.

In Case 2 the flame accelerates rapidly and develops violent vibrations. In the work of Mason and Wheeler (1920a,b), using a long tube, this resulted in extinction of the flame.

In Case 3 the behaviour of the flame is somewhat similar to that in Case 1, with a short initial phase followed by propagation at a higher velocity, since the unburned gas can be pushed out of the open end. In this phase there is a slight acceleration. Vibration begins and the velocity increases, either with smooth acceleration or with oscillations.

In Case 4 with ignition at one end it was found by Kirby and Wheeler (1931b) that initially the flame accelerated rapidly, then decelerated and travelled at a comparatively low speed until it approached the far end, when it accelerated somewhat. The time of attainment of maximum pressure coincided with that of the arrival of the flame at this end.

Phylaktou, Andrews and Herath (1990) describe experiments on the Case 4 configuration using a pipe with a length/diameter (L/D) ratio of 21.6 with a wide range of gas concentrations and a variety of gases. All gases exhibited two distinct regimes: vibratory near the stoichiometric concentration and non-vibratory near the limits of flammability. In the near-limit mixtures the flame speeds were higher than those in the stoichiometric mixtures, and the initial rates of pressure rise were high. For the near stoichiometric mixtures vibration was found to enhance the rate of pressure rise.

Further accounts of combustion in pipes, and also in vessels, as well as treatment of detonation are given in Chapter 17.

16.4 Flammability of Aerosols

It is also relevant to consider the combustion of aerosols such as fogs, mists and sprays. Such aerosols may be produced by condensation of a saturated vapour or by atomization of liquid by mechanical forces. The former may be referred to as a condensed fog or mist and the latter as a mechanical spray. Normally in a condensed mist the diameter of most of the drops is less than 10 μm, while in a mechanical spray it is greater than 100 μm.

Accounts of the combustion of aerosols, particularly liquid sprays, include *Combustion of Liquid Fuel Sprays* (A. Williams, 1990) and those by F.A. Williams (1959), Faeth (1977, 1979, 1983) and Kuo (1986).

A large proportion of work in this field is directed towards the combustion of atomized fuels at burners in furnaces and boilers. Some of the work deals with the combustion of single droplets of fuel, and some deals with the combustion of an aerosol cloud.

16.4.1 Combustion of aerosols

A suspension of finely divided droplets of flammable liquid in air can give a flammable mixture which has many of the characteristics of a flammable gas–air mixture and which can burn or explode. The combustion of aerosols has been the subject of a series of studies by Burgoyne and co-workers (Burgoyne and Richardson, 1949b; Burgoyne and Cohen, 1954; Burgoyne, Newitt and Thomas, 1954; Burgoyne, 1957, 1963).

In classic experiments using aerosols of tetrahydronaphthalene, or tetralin, with droplets of closely controlled diameter in the range 7–55 μm, Burgoyne and Cohen (1954) found that below a droplet diameter of 10 μm, the aerosol behaved like a vapour in respect of the LFL and the burning velocity. With a droplet diameter above 40 μm, the behaviour of the aerosol was different. The droplets were observed to burn individually in their own air envelopes, one burning droplet igniting the next.

If the droplet size, and hence the distance between droplets, exceeds a critical value, the flame does not propagate. The critical distance is of the same order of magnitude as the radius of the sphere of air required for the combustion of a droplet.

Coarser aerosols are capable of sustaining a flame at substantially lower fuel–air ratios than fine aerosols and vapours. The difference lies in the ability of the droplets to move in relation to the ambient air. Coarse particles are responsive to acceleration and move randomly, and thus communicate flame more readily.

Burgoyne's work has also shown that the burning velocity and the quantity of inert gas required for the suppression of flammability in aerosols with small droplet diameters are those of the equivalent vapour–air mixture.

In addition to this work on the conditions for combustion to occur in an aerosol, there have been other studies that have investigated the behaviour and shape of the flame in a droplet cloud. The studies include those by J.A. Browning and Krall (1955), J.A. Browning, Tyler and Krall (1957), Reichenbach, Squires and Penner (1962), Rosser (1967), Mizutani and Nishimoto (1972), Mizutani and Nakajima (1973), Polymeropolous (1974, 1984), Hayashi and Kumagai (1975), Polymeropoulos and Das (1975) and Ballal and Lefebvre (1978, 1979, 1981a).

Another aspect of the combustion of aerosols, which has been actively investigated, is ignition and extinction. Work on this topic has been described by Polymeropoulos and Peskin (1969), Kapila, Ludford and Buckmaster (1975), Law (1975) and Pindera and Brzustowski (1984).

The explosion of aerosols of flammable liquids is considered in Chapter 17.

16.4.2 Burning of single droplets

The combustion of the individual liquid droplets of an aerosol has been the subject of a good deal of work, particularly in relation to spray combustion in gas turbines and rockets.

Work on this topic includes that by Godsave (1953), Hottel, Williams and Simpson (1955), Kobayasi (1955), Agoston, Wise and Rosser (1957), Bolt and Saad (1957), Wise and Agoston (1958), Aldred and Williams (1966), Eisenklam and Arulachanam (1966), Faeth (1967), Sioui and Roblee (1969) and Yule, Ereaut and Ungut (1983). Reviews are given by A. Williams (1973, 1990).

Research in this area includes work on: the formation of droplets by atomization and other mechanisms, and the size distribution and velocities of the droplets produced;

the evaporation of and the drag on the droplets; and the mass burning rate of the droplets.

The mass burning rate $\dot{m}_F$ of a liquid droplet is

$$\dot{m}_f = -\frac{d}{dt}\left(\frac{\pi}{6} d_L^3 \rho_L\right) \quad [16.4.1]$$

where d_L is the diameter of the droplet and ρ_L is the density of the liquid. This equation can be rearranged to give

$$-\frac{d}{dt}(d_L)^2 = \frac{4\dot{m}_F}{\pi d_L \rho_L} \quad [16.4.2]$$

It is found experimentally that

$$-\frac{d}{dt}(d_L)^2 = K \quad [16.4.3]$$

where the constant K is known as the burning constant. This constant is therefore

$$K = \frac{4\dot{m}_F}{\pi d_L \rho_L} \quad [16.4.4]$$

There are a number of correlations of the burning constant, predominantly for conditions of forced convection, as in spray combustion. One of the most widely used is that of Wise and Agoston (1958).

16.4.3 Flammability limits

Burgoyne and co-workers, as described above have studied the flammability limits of the aerosols of flammable liquids. Burgyone (1963) quotes early work by Haber and Wolff (1923), who obtained for the LFL the results shown in Table 16.22.

As already described, Burgoyne and Cohen (1954) found in their studies on tetralin a difference in behaviour between aerosols with a droplet diameter d_L less than 10 μm and those with a droplet diameter more than 40 μm. The LFLs were found to be 46 mg fuel/l of aerosol for $d_L < 10$ μm and 18 mg fuel/l of aerosol for $d_L > 40$ μm; for intermediate diameters the LFLs change linearly between these two concentrations.

For aerosols in which the droplet diameter is less than 10 μm the LFL of the liquid and vapour suspension is virtually the same as that of the substance wholly in vapour form at the somewhat higher temperature necessary for vaporization. Above a droplet diameter of 10 μm the lower limit of flammability decreases as the drop diameter increases.

Above a droplet diameter of 20 μm another phenomenon was identified as significant, namely the rate of sedimentation of the droplet. For this effect Burgoyne (1963) gives the following treatment. He defines a flame front concentration C_f that is related to the volumetric concentration C_v as follows:

$$\frac{C_f}{C_v} = \frac{V_f + V_a + V_s}{V_f + V_a} \quad [16.4.5]$$

where C_f is the volumetric flame front concentration, C_v is the volumetric concentration, V_a is the downward velocity of the air, V_f is the upward velocity of the flame through the suspension and V_s is the sedimentation velocity of the drops relative to the air.

The LFL concentrations obtained by experiment were close to the flame front concentrations as defined by Equation 16.4.5. In some experiments with larger drop diameters the LFL measured was less than one-tenth of that for the equivalent vapour–air mixture. The burning velocity and the quantity of inert gas required for the suppression of flammability are also affected by large drop sizes.

In general, for flammable aerosols in air, it is found that for small droplet diameters the LFLs, measured as mass of fuel per unit volume of aerosol, are similar to those for vapour–air mixtures. Some values of the LFLs of vapours are quoted by Burgoyne (1963). For most of the substances which he lists the LFLs of the vapour lies in the range 0.04–0.10 g/l (or oz/ft^3). Further details are given in Section 16.2.

16.4.4 Minimum ignition energy

A method of obtaining the MIE of a dust cloud, which is also applicable to a vapour and an aerosol has been given by Ballal (1983b). Ballal has correlated MIEs for a number of mixtures of gases, vapours, liquid droplets and dusts with air at atmospheric pressure, the size of the liquid and solid particles being of the order of 50 μm. The correlation is in terms of the Spalding mass transfer number B:

$$B = \frac{q_{st}H + c_{pa}(T_g - T_b)}{L + c_p(T_b - T_s)} \quad [16.4.6]$$

where c_p is the specific heat of the fuel, c_{pa} is the specific heat of air, H is the heat of combustion, L is the latent heat of vaporization, q is the mass ratio of fuel to air, and subscripts b, g, s and st denote the boiling point of the fuel, gas, the surface of the fuel and stoichiometric, respectively.

Figure 16.33 (a) gives an approximate relation between the MIE E_{min} and B for homogeneous and two-phase mixtures of the type described. For a more accurate estimate Ballal gives the MIE E_{min} as a function of the quenching diameter d_q:

$$E_{min} = \pi C_p \rho_a \Delta T d_q^3 \quad [16.4.7]$$

Table 16.22 *Lower flammability limits of some vapours and mists in air (after Haber and Wolff, 1923)*

	Temperature (°F)	*Mist concentration* (oz/ft^3)	*Temperature* (°F)	*Vapour concentration* (oz/ft^3)
Petroleum 356–428°F	75	0.044	140	0.043
Tetralin	84	0.0409	212	0.0416
Quinoline	97	0.0662	230	0.064

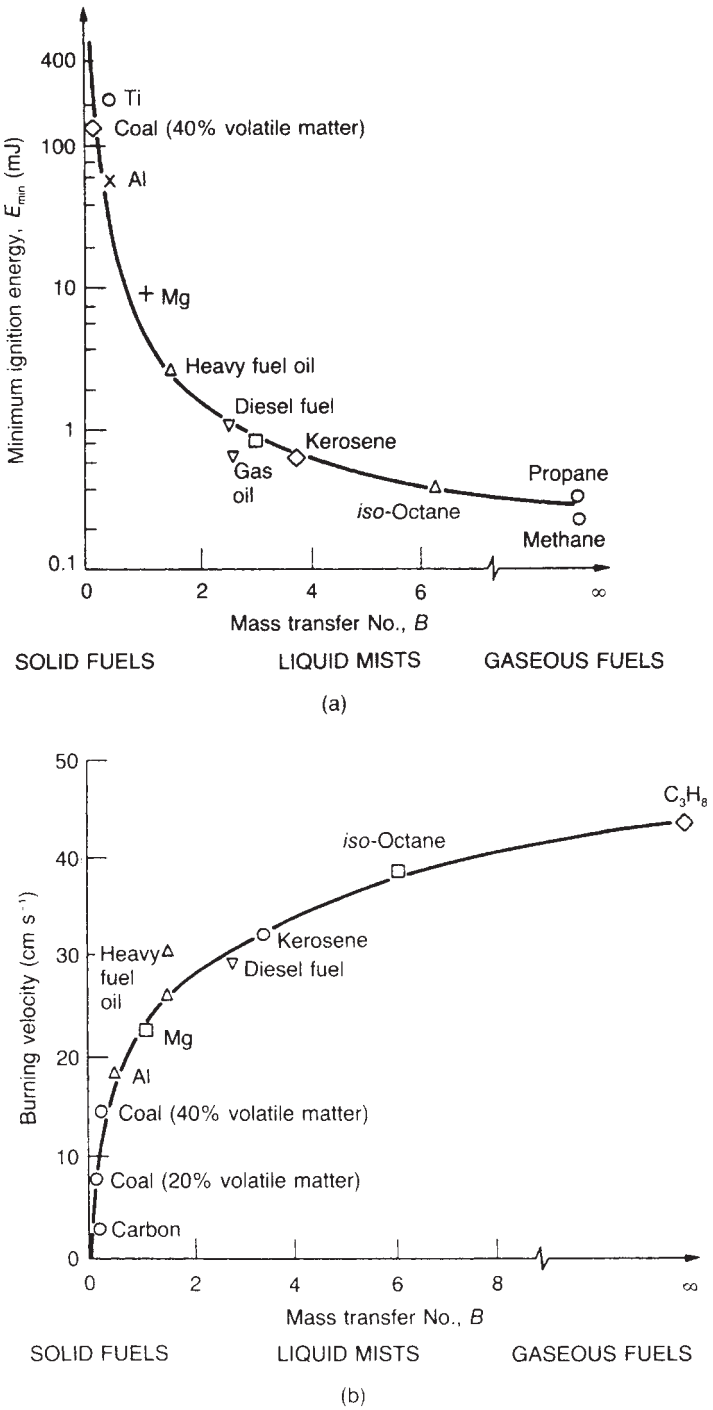


Figure 16.33 *Some properties of mixtures of air with flammable vapours, aerosols or dusts: (a) minimum ignition energy (after Ballal, 1983b) (Courtesy of Combustion and Flame); and (b) fundamental burning velocity (after Ballal, 1983a) (Courtesy of the Combustion Institute)*

with

$$d_q = (8\alpha)^{\frac{1}{2}} \left\{ \left[\frac{C_3^3 \rho_p D_{32}^2}{8 C_1 f^2 (k/c_p) \phi \ln(1+B)} + \frac{12.5\alpha}{S_u^2} \right]^{-1} - \frac{9 q C_1^2 \epsilon \sigma T_p^4}{c_p \rho_p C_3^3 f D_{32} \Delta T_{st}} \right\} \quad [16.4.8]$$

where c_{pg} is the specific heat of the gas, C_1 is the ratio of the surface mean area to the Sauter mean diameter, C_3 is the ratio of the volume mean diameter to the Sauter mean diameter, D_{32} is the Sauter mean diameter, f is the swelling factor of the fuel, k is the thermal conductivity of the fuel, S_u is the laminar burning velocity, α is the thermal diffusivity of the particle, ϵ is the emissivity of the particle, ρ is the density, ΔT is the temperature difference, σ is the Stefan–Boltzman constant, ϕ is the equivalence ratio and subscript p denotes fuel.

16.4.5 Burning velocity

Ballal (1983a) has also given a method of obtaining the laminar burning velocity of a dust cloud, which is also applicable to a vapour and an aerosol. Figure 16.33(b) gives an approximate relation between laminar burning velocity S_u and B for homogeneous and two-phase mixtures. For a more accurate estimate Ballal gives the laminar burning velocity as a function of the thickness δ_r of the reaction zone:

$$S_u = \frac{\alpha \Delta T_r}{\delta_r \Delta T_{pr}} \quad [16.4.9]$$

with

$$\delta_r = \alpha_g^{0.5} \left\{ \left[\frac{C_3^3 \rho_f D_{32}^2}{8 f^2 C_1 (c_p/k)_g \phi \ln(1+B)} + \frac{\alpha \Delta T_r}{S_g^2 \Delta T_{pr}} \right]^{-1} - \frac{9 q C_1^2 \epsilon \sigma T_p^4}{c_{pg} \rho_f C_3^3 f D_{32} \Delta T_r} \right\}^{-0.5} \quad [16.4.10]$$

where c_{pg} is the specific heat of the gas, S_g is the laminar burning velocity of the gases liberated from the particles, α_g is the thermal diffusivity of the gas, and subscripts f, g, pr and r denote the fuel, gas, pre-reaction zone and reaction zone, respectively.

These correlations of Ballal are subject to a number of qualifications, as discussed by the author and by Nettleton (1987), who nevertheless concludes that the approach is applicable to many practical situations. Nettleton quotes some typical ranges of the laminar burning velocity S_u in air. These are: $0.05 < S_u < 0.2$ m/s for particulate suspensions; $0.2 < S_u < 0.35$ m/s for fogs; $0.3 < S_u < 0.4$ m/s for hybrid fog and vapour; and $S_u < 0.5$ m/s for mixtures with gas or vapour. For stoichiometric mixtures of acetylene or hydrogen in air, $S_u > 1.0$ m/s. For the estimation of turbulent burning velocity, Nettleton quotes Equation 16.3.45 as one in common use.

16.4.6 Chemical decomposition

If a condensed mist is formed from the saturated vapour of a liquid hydrocarbon of high boiling point, prolonged contact with a source of heat can result in the formation of cracking products such as hydrogen or acetylene, which reduce the LFL and increase the burning velocity and the quantity of inert gas required for the suppression of flammability.

16.5 Ignition sources

Selected references on ignition sources are given in Table 16.23.

Table 16.23 *Selected references on ignition and ignition sources*

D.J. Lewis (n.d.); SMRB (Pap. 74); von Elbe and Lewis (1949); von Elbe (1953); Khitrin and Goldenberg (1957); H.E. Rose and Priede (1959a); F. Powell (1960); Risinger and Vervalin (1964); SMRE (1965 Res. Rep. 231); FMEC (1967); FPA (1971/14); J.F. Griffiths, Gray and Gray (1971); Page and Gardner (1971); Dehn (1972); KN. Palmer (1973a, 1976b); Dixon-Lewis and Shepherd (1975); Eisenberg, Lynch and Breeding (1975); Japan Gas Association (1976); Kletz (1971); Birch, Brown and Dodson (1981); IBC (1981/9, 19, 1982/36, 1991/81); Dold and Clarke (1985); Fordham Cooper (1986); Vilyunov and Zarko (1989); Bond (1991)

Ignition induction period, time delay
SMRB (1925 Pap. 9); Mullins (1949); Brokaw and Jackson (1955); Ashmore and Levitt (1959); P. Gray and Harper (1959a,b); R.E. Miller (1959); Voevodsky (1959); Salooja (1961); Melvin (1966); Bascombe (1967); Burcat, Scheller and Lifschitz (1971); Drysdale (1971); Bowes (1984); Freeman and Lefebvre (1984)

Spontaneous ignition
Khitrin and Goldberg (1957); Sage and Weinberg (1959); Sokolik (1960); J.A. Macdonald and White (1965); Melvin (1966); Goodman, Gray and Jones (1972); Cullis and Foster (1973, 1974); Anon. (1982 LPB 47, p. 15); Bowes (1984); Reid, Robinson and Smith (1985); Gandhi and Kanury (1988)

Compression ignition, shock ignition
Falk (1906, 1907); Dixon (1910); Dixon, Bradshaw and Campbell (1914); Dixon and Crofts (1914); Tizard and Pye (1922); Dixon, Harwood and Higgins (1926); Payman and Titman (1935); SMRB (1935 Pap. 93); Wheeler (1935b); Payman and Shepherd (1937, 1946); Jost (1949); W.C.F. Shepherd (1949); M.H. Friedman (1963a,b); Borisov, Kogarko and Lyubimov (1968); J.W. Meyer and Oppenheim (1971b); Vermeer, Meyer and Oppenheim (1972); Halstead *et al.* (1975); Anon. (1978 LPB 19, p. 24); Beeley, Griffiths and Gray (1980); Eubank *et al.* (1981); J.F. Griffiths and Perche (1981)

Chemical ignition
Bretherick (1979)

Friction and impact
SMRE (Appendix 28 *Research Reports*, Frictional Ignition 2–5); SMRB (1928 Pap. 46, 1929 Pap. 54, 1930 Pap. 62, 1931 Pap. 70); Burgess and Wheeler (1929); Bowden, Stoke and Tudor (1947); Bowden (1949); Archard (1952); Calcote *et al.* (1952); Bowden and Tabor (1954); Bowden and Thomas (1954); Titman and Wynn (1954); Titman (1955/56); Rae (1961); M.H. Friedman (1963a,b); Downing (1964); N. Gibson, Lloyd and Perry (1967); F. Powell (1969, 1978);

Cutler (1974, 1978); Blickensderfer (1975); Andersen (1979); HSE (1980 FI 2); Billinge (1981); Gomez, Wake and Gray (1985); Bartknecht (1988)
Hand tools, non-sparking tools: Anfenger and Johnson (1941); API (1956, 1980 PSD 2214, 1989 Publ. 2214); Bernstein and Young (1960); Anon. (1962e); DSIR (1963); Fischer (1965); Riddlestone and Bartels (1965); F. Powell (1969); Bartels (1970); FPA (1975 Sll, 1989 CFSD FS 6029)

Electrical discharges and sparks
Coward, Cooper and Jacobs (1914); Thornton (1914a,b, 1915a,b); Wheeler (1920, 1924); Bradford and Finch (1937); Landau (1937a,b); Blanc *et al.* (1947); Llewellyn (1947–48); Blanc *et al.* (1949); H. Morris (1949); Fenn (1951); Calcote *et al.* (1952); Laffltte and Delbourgo (1953); Olsen, Gayhart and Edmondson (1953); Swett (1955, 1956, 1957); H.E. Rose and Priede (1959b); Berz (1961); SMRE (1966 Res. Rep. 240); Johnsson, Strid and Johansson (1972); Kumagai, Sakai and Yasugahira (1972); Kono, Kumagai and Sakai (1976); Adelman (1981); Ballal and Lefebvre (1981b); Maly (1981); Sher and Rafael (1982); Fiumara and Avella (1983); FPA (1984 CFSD NB 6); H. Kramer (1987); Ko, Anderson and Arpaci (1991); Ko, Arpaci and Anderson (1991)
Flashlights: API (1983 Publ. 2212)
Telephones: API (1974 PSD 2213)

Hot wires
J.H.T. Roberts (1913); Thornton (1919); SMRB (1927 Pap. 36); Stout and Jones (1949); Kumagai and Kimura (1957); Ashman and Buchler (1961); Detz (1976)

Hot surfaces
Mason and Wheeler (1922, 1924); Coward and Guest (1927); Guest (1930 BM Tech. Pap. 475); Naylor and Wheeler (1931, 1933); Landau (1937a,b); Mullen, Fenn and Irby (1949); Dooley (1957); Husa and Runes (1963); Kuchta, Cato and Zabetakis (1964); SMRE (1964 Res. Rep. 224); Adomeit (1965); Kuchta, Bartowiak and Zabetakis (1965); Goodall and Ingle (1967); Sharma and Sirignano (1969, 1970); Bartels (1971a); Alkidas and Durbetaki (1973); KN. Palmer (1973a); Angel (1975); D.C. Bull and Grant (1975); D.C. Bull and Quinn (1975); Thiyagarajan and Hermance (1975); Ono *et al.* (1976); D.C. Bull (1977); Law (1978); Law and Law (1979); API (1980 PSD 2216, 1991 Publ. 2216); Chen and Faeth (1981a); Trevino and Sen (1981); Laurendeau (1982); Laurendeau and Caron (1982); F. Powell (1984); Leiber (1985); Bartknecht (1988); A.J. Harrison and Cairnie (1988); A.J. Harrison *et al.* (1988); Bothe and Steen (1989); Kumar (1989); Giesbrecht *et al.* (1992)

Hot gases
Muffins (1953); Wolfhard (1958); Wolfhard and Vanpee (1959); Vanpee and Bruszak (1973 BM RI 6293); Fink and Vanpee (1975)

Hot particles
Silver (1937); Paterson (1939–); SMRE (1956 Res. Rep. 129); Tolson (1972); Su, Homan and Sirignano (1979); Yu-Pen Su and Sirignano (1981); F. Powell (1984); Hills *et al.* (1992)

Hot projectiles
Sharma and Sirignano (1970)

Flame torches and jets
FPA (CFSD GP 4); Wang *et al.* (1981); Mackay *et al.* (1988)

Smoking
FPA (1989 CFSD GP 8)

Diesel engines
HSE (1986 PM 58); Sokolov (1989)

Lightning
Golde (1977a); W.R. Lee (1977); Anon. (1987q); NFPA (2000 NFPA 780)

Hygroscopic combustible materials
P. Gray and Wake (1990)

Sodium
Yuasa (1985)

Metal oxides
Meguerian and Radowsky (1967)

Welding (*see* Table 21.1)

RF ignition
Jordan and Balmain (1968); Anon. (1978 LPB 23, p. 147); Excell and Howson (1978); HSE (1978a, 1979f, 1983 GS 21); A. Hall and Burstow (1980); A. Hall and Loveland (1980); ERA (1981, 1982); Burstow *et al.* (1981); Howson, Excell and Butcher (1981); Maddocks and Jackson (1981); S.J.J. Robertson and Loveland (1981); Rosenfeld *et al.* (1981); Bergman (1982); Mannon and Johnson (1982); Widginton (1982); Excell and Maddocks (1984); P. Knight and Robson (1984); Harrold (1992 SRD R579)

Laser ignition
Hills *et al.* (1992)

Arson
FPA (CFSD AR series, 1972/19); J. Kennedy (1962); NFPA (1971/7); Broodo, Gilmore and Armstrong (1976); French (1979); Hanson (1980); Carson and Mumford (1986 LPB 70)

Piloted ignition
Tzeng, Atreya and Wichman (1990)

Ignition of gas clouds, jets
M.T.E. Smith *et al.* (1986); Gustafson and Mudan (1987)

Ignition of sprays
Aggarwal and Cha (1988); Capp (1988); Aggarwal (1989); Bergeron and Hallett (1989a,b)

Ignition models
English and Waite (1989); A.W. Cox, Lees and Ang (1990)

Some potential ignition sources on process plants include the following:

(1) flames;
(2) hot work;
(3) hot surfaces;
(4) hot particles;
(5) friction and impact;
(6) chemical energy;
(7) hot materials and gases;
(8) reactive, unstable and pyrophoric materials;
(9) engines;
(10) vehicles;
(11) lightning;
(12) radio frequency (RF) emissions;
(13) smoking;

(14) arson and sabotage;
(15) self-heating;
(16) static electricity;
(17) electrical equipment.

Each of the above sources can cause ignition of a flammable gas–air mixture outside the plant.

Insofar as they can occur inside the plant, these sources can also cause ignition of a flammable gas–air mixture inside it. In addition, ignition of a flammable gas–air mixture inside the plant may occur due to:

(18) autoignition
(19) compression effects.

Table 16.24 gives a more detailed breakdown of these ignition sources.

These ignition sources are discussed in this section, with the exception of self-heating, static electricity and electrical equipment, which are considered in Sections 16.6, 16.7 and 16.8, respectively. Information on the most frequent sources of ignition was given in Table 2.11.

The modelling of ignition sources for the purpose of hazard assessment is considered in Section 16.10.

Many potential sources of ignition are associated with activities. These need to be controlled by a permit-to-work system. This aspect is discussed in Chapter 21.

The area of flammable hazards should be fenced off and strict security enforced on persons entering the area. In particular, matches and cigarette lighters should be given up on entry. Equipment brought into the area should be suitable for use within it.

16.5.1 Flames

The flames of burners in fired heaters and furnaces, including boiler houses, may be sources of ignition on process plants. The source of ignition for the explosion at Flixborough may well have been burner flames on the hydrogen plant. The flame at a flare stack may be another source of ignition. Such flames cannot be eliminated. It is necessary, therefore, to take suitable measures such as care in location and use of trip systems.

Burning operations such as solid waste disposal and rubbish bonfires may act as sources of ignition. The risk from these activities should be reduced by suitable location and operational control.

Smoldering material may act as a source of ignition. In welding operations it is necessary to ensure that no smoldering materials such as oil-soaked rags have been left behind.

Small process fires of various kinds may constitute a source of ignition for a larger fire. The small fires include pump fires and flange fires; these are dealt with in Section 16.11.

Dead grass may catch fire by the rays of the sun and should be eliminated from areas where ignition sources are not permitted. Sodium chlorate is not suitable for such weed killing, since it is a powerful oxidant and is thus itself a hazard.

16.5.2 Hot work

Hot work, such as welding, cutting and grinding activities, is a potential source of ignition. In welding, for example, this applies not only to the welding flame or arc, but also to material ignited by the welding.

Table 16.24 *Some ignition sources on process plants*

A General	
Flames	Flare: elevated or ground level flare; full flare or pilot condition; incinerator
	Furnace: natural or forced draught furnace
	Fired heater
	Boiler
	Laboratory heater: bunsen burner; furnace
	Personnel heater: solid fuel or electrical fire
	Burning operations: burning rubbish; burning during demolition
	Firing: explosion for demolition; other explosives
	Warning flare: hazard warning flare; fog warning detonator
	Accidental fire
	Hot material: brand; hot particles
Hot work	Welding: arc welding; oxyacetylene welding
	Cutting: oxyacetylene cutting
	Grinding
	Hot tapping
Hot surface	General: vessel and pipework
	Machinery: engines; turbines; exhausts
	Laboratory equipment: hot plate; oven
	Hot particles: soot
Friction and impact	Impact: hand tool; power tool; boot stud; loosening of caked material; moving vehicle
	Rubbing: belt, conveyor, roller; brake, clutch on machinery; skidding of road or rail tanker
Hot material or gas	Discharged material: hot ash from boiler; used catalyst; hot process material
	Hot gas
Pyrophoric, reactive and unstable materials Engines	Ingestion of flammable: petrol, diesel or gas engine mixture
	Chemical effects
	Friction and impact: thermite reaction (see above)
	Instrument: catalytic element
Smoking	Means of lighting: matches; lighter
	Item smoked: cigarette; cigar; pipe
Vehicles	General vehicles: petrol, diesel or electrically driven
	Crane
	Forklift truck
	Helicopter
	Aircraft
Atmospherics	Lightning
Radio frequency transmission	See Subsection 16.5.12

Arson, sabotage	Fire Explosion
Compression	Ingestion of flammable mixture: compressor; high speed blower
Mechanical rupture	Spark associated with rupture giving rise to release
Self-heating	Dust layer Oil soaked lagging See also Section 16.6
Static electricity	See Section 16.7
Electrical	Machinery: motors, alternators, dynamos, converters Fixed equipment: contact devices such as switches, relays, contactors Fixed equipment—failures: failure of protective equipment; failure causing arcing Insulator: arcing across spark gaps at high voltage insulators Wiring: loose connection; poor joint; damaged wiring Cable: broken cable; damaged cable; water ingress Batteries: connecting up damaged battery Instrument Heating tape Lighting Fault current conductor: poor joint Portable equipment: meter; radio; TV; camera; hearing aid Ground movement: sparking due to ground movement such as earthquake or subsidence

B Internal

Auto-ignition[a]	
Compression	Pump: compression by pumping against closed valve Hammer blow: compression by hammer blow in pipeline Liquid slug: compression by liquid slug Air bubbles: compression of air bubbles in liquid
Reactive, unstable material	Pyrophoric material Incompatible material: material which reacts with material of construction
Catalytic material	
Hot material	Hot catalyst; hot dust; hot gas
Hot surface	External hot work Rotating machinery: ingestion of tramp metal Distressed machinery: hot bearings; hot particles Lamp: damaged wander lamp
Electrical	Heater – failure: failure causing overheating
Self-heating	See Section 16.6
Static electricity	See Section 16.7

[a] A flammable mixture can undergo a combustion reaction outside the normal flammability limits. These limits apply essentially to propagation rather than ignition as such.

Hot work accounts for an appreciable proportion of ignition incidents. In the vast majority of cases the material ignited is in the equipment being worked on. It is relatively rare for hot work to be the source of ignition of a vapour cloud.

It is necessary to exercise close control of hot work by training, supervision and use of a permit system.

16.5.3 Hot surfaces

Surfaces of plant equipment are frequently hot and some may be potential ignition sources. Hot surfaces include:

(1) hot process equipment;
(2) distressed machinery.

Much process equipment operates at high temperature. Although the equipment is usually lagged, there may be some surfaces, which could be a source of ignition.

Machinery in distress, such as a pump with a faulty bearing, may run hot and this hot spot is a potential source of ignition.

Traditionally, the AIT was taken as the limiting temperature above which a hot surface might ignite a gas mixture. Codes for HAC have tended to quote AITs as hot surface temperature limits.

It has long been appreciated, however, that there is a difference between the hot surface temperature that will ignite a flammable gas–air mixture and the AIT. This temperature excess depends on the conditions. Relevant factors include the fuel and fuel concentration, the material, area and geometry of the surface, and the fluid flow and heat transfer conditions.

Hot surface ignition has been the subject of a good deal of work and details are given in Section 16.3. This work consistently shows that an appreciable temperature excess is necessary for ignition to occur. It also demonstrates that the temperature excess required increases as the hot surface area decreases. The necessary temperature excess also increases as the gas velocity increases. One effect of increasing the gas velocity is to reduce the residence time of the gas and this may then fall below the ignition induction period.

Industrially oriented work by Husa and Runes (1963) indicated that for hot surfaces in the open air a temperature excess of several hundred degrees was required to give ignition. The systems investigated were, however, not well defined by the standards of more recent work.

Practical guidance is given in API Publ. 2216: 1991 *Ignition Risk of Hydrocarbon Vapors by Hot Surfaces in Open Air.* This draws attention to the work of Hilado and Clark (1972b) and Goodall and Ingle (1967) on the effects on ignition of the induction time and of gas velocity, respectively, and the work of Husa and Runes. It states that as a rule of thumb, and based on open air tests, ignition by a hot

surface should not be assumed unless the surface temperature is at least 200°C above the normally accepted minimum ignition temperature.

A hot surface is a potential ignition source inside as well as outside the plant. The rule of thumb just quoted is not intended to apply in this case, although induction time and gas velocity are again relevant factors.

16.5.4 Hot particles

Another form of hot surface is a hot particle. A hot particle that is common on plant is soot from burners or from a flare. Hot soot from chimneys may be a source of ignition. It is a particularly important potential source of ignition on ships.

16.5.5 Friction and impact

Impact, friction and frictional impact can be a source of ignition for a flammable gas–air mixture. A review has been given by F. Powell (1969). An account of some of the fundamental phenomena is given in Section 16.3.

Essentially, incendive sparks caused by impact and friction are due to the generation of a surface hot spot. A falling object can give an incendive spark. The temperature rise may correlate only weakly with the kinetic energy but can be sufficient to cause ignition. It is normal to adopt procedures to prevent damage to the plant by falling objects. However, dropping of objects can occur which may not be controlled by these measures such as drums, hand tools, etc.

Ignition by a falling object is likely to be most serious in a space that already contains a flammable atmosphere. Objects such as tank washing machines or cathodic protection anodes in ships' cargo tanks illustrate this. Cigarette lighter flints can also cause a mechanical spark if the lighter is dropped.

One situation that is liable to cause ignition in frictional impact is where rusty steel with an aluminium smear is hit by a hard object. Under these conditions the thermite reaction occurs. This reaction, which can reach a temperature of 3000°C, is an effective ignition source. The source of the aluminium may be aluminium paint or the impacting object itself.

Work by Kingman, Coleman and Rogowski (1952) has shown that oil bound paints do not give sparks unless preheated to 150°C. Subject to avoidance of such heating, therefore, such paints may be used on steel in hazardous areas.

The striking of quartzite materials, including concrete containing sand, by a metal tool is another situation liable to give incendive sparks. A report by the Department of Scientific and Industrial Research (DSIR) (1963) gives details of fires attributed to frictional sparks, most of which involved various metals and concrete or stone.

An aspect that has received a good deal of attention over the years is the use of 'non-sparking tools'. Materials used in such tools characteristically do not readily oxidize and have high thermal conductivity.

Reviews of the use of non-sparking tools have been given by F. Powell (1969) and Cross and Fairer (1982). Essentially, some investigators have concluded that regular steel tools are no more hazardous than non-sparking tools, while others believe there is a benefit to safety in the use of non-sparking tools. Anfenger and Johnson (1941) performed experiments on the incendivity of sparks produced by steel on a grinding wheel, which ignited carbon disulfide but not petrol vapour.

On the basis of this work and practical experience the American Petroleum Institute (API) in *Sparks from Hand Tools* (1956) concluded that there is no significant increase in safety from the use of non-sparking tools. API Publ. 2214: 1989 *Spark Ignition Properties of Hand Tools* states that nothing essentially new has been learned since the 1956 publication and that the fire records of more and more companies which have never used, or have ceased to use, non-sparking tools amply confirm the position then taken. Non-sparking hand tools are discussed further in Chapter 21.

Other workers such as those at the DSIR (1963) and Riddlestone and Bartels (1965) draw attention to ignitions caused by the striking of metals on concrete or stone and point out that it is in this situation that the ignition risk is significant, and that metals used in non-sparking tools are also liable to give ignition in this case. For this rather different reason they conclude that non-sparking tools offer little benefit.

Another point that detracts from the potential benefit of non-sparking tools is that they tend to be soft, so that hard particles can become embedded in the tool.

Other workers have seen a benefit in the use of non-sparking tools. On the basis of impact and grinding experiments Fischer (1965) recommends the use of steel tools for work where there may be Class I gases, but not where there may be Class II gases.

Certain gases such as hydrogen, acetylene and carbon disulfide are particularly sensitive to ignition by impact and friction. If such a gas is present, there is a potential ignition risk in the use of any tool. Non-sparking tools are considered further in Chapter 21.

A study of ignitions by impact, friction and frictional impact has been made by Billinge (1981). He classifies these ignitions as due to impact, rubbing or cutting and grinding, and as high, medium or low energy. The individual incidents are shown in Table 16.25 and the analysis of these incidents is given in Table 16.26.

16.5.6 Chemical energy

There are several forms of chemical energy that may give ignition. They include (1) the thermite reaction, (2) reactive, unstable and pyrophoric materials and (3) catalytic instruments. The thermite reaction is obtained from aluminium smears on rusty steel, as described above. Reactive, unstable and pyrophoric materials are considered below.

Some instruments contain catalytic elements, which measure the temperature rise resulting from combustion of a flammable gas. Generally, these instruments (such as flammable gas detectors) are intended to operate in hazardous areas and are therefore designed so that they should not act as an ignition source.

16.5.7 Hot materials and gases

Hot materials such as hot ash, hot used catalyst or hot process material, and hot gases may, in principle, act as ignition sources. Generally, however, operations involving such hot materials are excluded from hazardous areas and they do not figure as a significant ignition source.

Table 16.25 *Some incidents involving friction and impact ignition relevant to the process industries in the period 1958–78 (after Billinge, 1981): details of incidents (Courtesy of Fire Prevention Science and Technology)*

A Gases and vapours

Fuel	*Cause*	*Classification*
Group IIA		
Petrol	Spark from hammer; hammer on steel clasp; shoe nail on concrete floor; boot nail on concrete floor; dropped tool or steel tipped boot on concrete floor; dropped tool on floor; screwdriver punched through drum lid	Low energy impact
	Falling drum; dropped can of petrol on floor; impact between drums; impact between car and petrol pump; impact between cars	Medium energy
	Sparking from brakes of rail tank wagon	Medium energy Rubbing
	Collision between ships	High energy impact
	Skidding overturned road tanker (×3); barge ripped open by bridge fender	High energy rubbing
Jet fuel	Tanker scraped lock wall	
Crude oil vapour	Magnesium anode impact; pipeline coupling falling onto ship's deck	Medium energy impact
	Collision between ships	High energy impact
Oil vapour	Defective pump	Medium energy rubbing
	Ferrous metal in aluminium polishing and grinding machine	Medium energy cutting and grinding
LPG	Steel cylinders with aluminium smears	Low energy impact
	Crashing rail wagons	High energy impact
Liquefied butane	Crashing road tanker	High energy impact
Propane	Valve knocked off gas tank	Medium energy impact
	Impact of aluminium wrench on pipe joint	Low energy impact
Pentane	Metal object in chopping machine	Medium energy impact
Benzene	Collapsing metalwork	Medium energy impact
Natural gas	Tool dropped down oil well	Medium energy impact
	Mechanical shovel fractured gas main	High energy impact
Methanol	Impact between nozzle and wall	Medium energy impact
	Tramp metal in grinding process	Medium energy cutting and grinding
	Belt rubbing on copper tube	Medium energy rubbing
Ethanol	Friction in centrifuge	Medium energy rubbing
	Impact between digger and center cone of centrifuge	Medium energy impact
	Grindstone sparks	Medium energy cutting and grinding
Hexane/ethanol	Friction in centrifuge	Medium energy rubbing
Isopropanol	Impact of drum on ground	Medium energy impact
Acetone	Impact of drum on ground	Medium energy impact
Acrylic paint solvent	Defective extractor motor fan	Medium energy rubbing
Mixed solvent vapours	Truck ran over drum of solvent	Medium energy rubbing
	Impact between drum or lighter and floor	Medium energy impact
Ethyl chloride	Impact between metal ditch covers	Medium energy impact
Vinyl acetate	Impact between filling nozzle and loading aperture	Medium energy impact
Group IIB		Low energy impact
Ethylene	Unscrewing valve from pipe	Medium energy
	Sparks from bursting tire	cutting and grinding
Coke oven gas	Collapsing shelf holding gas meter	Medium energy impact
Group IIC		
Hydrogen	Hammer hitting bolts on steam line; spark between cylinder cap and tool	Low energy impact Medium energy cutting and grinding
	Drilling pipe; abrasive cutting and grinding of pipe	
Acetylene	Moving or opening drum of carbide; cylinder fell from lorry; feed cone dropped into hopper of carbide	Medium energy impact

Table 16.25 *(continued)*

	Sparks from grinding process	Medium energy cutting and grinding
Carbon disulfide	Impact between brass rod and caked material	Low energy impact
Various vapours and solvents	Gear wheels not properly meshed; friction in centrifuge; falling metalwork; dismantling metalwork; agitator fell into mixing tank	Medium energy impact
	Cellulose film rubbing on roller	Medium energy rubbing
	Cutting pipe with (mechanical) hacksaw	Medium energy cutting and grinding
B Powders and dusts		
Foodstuffs		
Grain dust	Nut, bolt or stone in suction pipe; metal object in hopper machine	Low energy impact
	Impact of pulley with wall; foreign body in mill	Medium energy impact
Sugar dust	Wood screw fell into mill	Medium energy impact
	Elevator buckets rubbing on guides	Medium energy rubbing
Peppercorn dust	Foreign body in mill	Medium energy impact
Flour dust	Overheated bearing (×3); overheated motor	Medium energy rubbing
Flour and grain dust	Overheated pulley and belt drive	Medium energy rubbing
Corn dust	Friction between belt drive and pulley guard	Medium energy rubbing
Organic chemicals		
Organic powder	Foreign body in mill	Medium energy impact
Niacin dust	Bolt in mill	Medium energy impact
Phenolic molding powder	Spark from unknown agent	Medium energy impact
	Spark from grinding machine	Medium energy cutting and grinding
Cellulose nitrate dust	Chipping concrete with air hammer	Medium energy impact
Dinitrosopentamethylene tetramine	Impact of fork lift truck with fibre container	Medium energy impact
Diazonium salt	Hammering wedges	Low energy impact
Sodium picramate	Impact of drum on floor	Medium energy impact
Inorganic chemicals		
Giant gel 40% dope/sulfur	Aluminium tamp punch on steel grating bars	Low energy impact
Ammonium perchlorate	Scraping with spatula	Low energy impact
	Spatula left in mixer	Medium energy rubbing
	Friction from beryllium cutting knives	Medium energy cutting and grinding
Thermite	Cleaning edge runner mill	Low energy impact
Aluminium powder	Steel tool on rusty lid of container	Low energy impact
Sulfur	Mechanical shovel striking metal deck; mechanical impact of crane grab with bulkhead; metal grabs striking ships structure; frictional spark from crane grab; mechanical shovel hitting side of ship's hold; steel tub falling into ship's hold	Medium energy impact Medium energy impact
Windproof matches	Carton of matches fell 2 m	
Rocket propellant	Metal–metal contact in mixer	Medium energy rubbing
Pyrotechnic mixture	Metal–metal contact in mixer	Medium energy rubbing
Zirconium dust	Sparks from grinding steel	Medium energy cutting and grinding
Powder	Hopper fell and impacted tram car	Medium energy impact
Oil mist	Overheated pump	Medium energy rubbing

Table 16.26 *Some incidents involving friction and impact ignition relevant to the process industries in the period 1958–78 (after Billinge, 1981): analysis of incidents (Courtesy of Fire Prevention Science and Technology)*

	No. of incidents	
	Gases and vapours	*Powders and dusts*
Low energy: impact	13	7
Medium energy: impact	27	19
rubbing	8	11
cutting and grinding	8	3
High energy:		
impact	5	–
rubbing	5	–
Total low energy	13	7
Total medium energy	43	33
Total high energy	10	–
Total impact	45	26
Total rubbing	13	11
Total cutting and grinding	8	3
Overall total	66	40

16.5.8 Reactive, unstable and pyrophoric materials

Reactive, unstable or pyrophoric materials may act as an ignition source by undergoing an exothermic reaction so that they become hot. In some cases the material requires air for this reaction to take place, in others it does not.

The most commonly mentioned pyrophoric material is pyrophoric iron sulfide. This is formed from reaction of hydrogen sulfide in crude oil in steel equipment. If conditions are dry and warm, the scale may glow red and act as a source of ignition. Pyrophoric iron sulfide should be damped down and removed from the equipment. No attempt should be made to scrape it away before it has been dampened.

A reactive, unstable or pyrophoric material is a potential ignition source inside as well as outside the plant.

16.5.9 Engines

Engines on process plants are another ignition source and tend to figure significantly.

One type of engine in use for a variety of purposes is the diesel engine. Guidance on the use of diesel engines in relation to hazardous areas is given in a number of codes. One is *Guidelines on Protection of Diesel Engines for Hazardous Zone 2 Areas* (Lloyd's Register, n.d.). Another is *Recommendation for the Protection of Diesel Engines Operation in Hazardous Areas* (Oil Companies Materials Association, 1977).

A discussion of diesel engines in this context has been given by Sokolov (1989), who considers the various potential ignition sources on the engine and the steps that can be taken to prevent ignition by these sources.

One potential ignition source on a diesel engine is the hot gas. Exhaust gas temperatures can be as high as 500°C. Ignition by hot exhaust gas involves turbulent stream ignition, which can occur at a temperature less than the average temperature of the gas mixture. A safety factor is therefore required. Codes typically recommend that the temperature of the exhaust gas should not exceed 0.6–0.8 of the AIT of any flammable gas that may be present. Sokolov quotes the following:

Gas	*Ignition temperature* (°C)	*Safe exhaust gas temperature* (°C)
Methane	595	396
Propane	470	313
Natural gas	482–650	320
Condensate	275	183

Another important part of the engine is the induction and exhaust systems. These systems are designed to avoid detonation but to handle deflagration. There are minimum design pressures which tend to lie in the range 8–10 bar, that for the United Kingdom being 10 bar and that for the United States 8.6 bar. Induction and exhaust systems are provided with flame arresters; exhausts are provided with spark arresters.

Crank cases are another feature of a diesel engine that requires protection.

The preferred start-up arrangements for the engine in a hazardous area are pneumatic, hydraulic or manual rather than electrical.

Diesel engines are generally equipped with shut-down devices and alarms activated by overspeed and by failures of the various subsystems. Depending on the application, the device may act to cut off the fuel or to shut off the air intake and effect gradual gas path deflection.

16.5.10 Vehicles

A chemical plant may contain at any given time considerable numbers of vehicles. These vehicles are potential sources of ignition. Instances have occurred in which vehicles have had their fuel supply switched off, but have continued to run by drawing in, as fuel, flammable gas from an enveloping gas cloud. The ignition source of the flammable vapour cloud in the Feyzin disaster in 1966 was identified as a car passing on a nearby road (Case History A38). It is necessary, therefore, to exclude ordinary vehicles from hazardous areas and to ensure that those that are allowed in cannot constitute an ignition source.

Vehicles that are required for use on process plant include cranes and forklift trucks. Various methods have been devised to render vehicles safe for use in hazardous areas and these are covered in the relevant codes.

16.5.11 Lightning

Lightning is another potential ignition source on process plants. Information on lightning and on lightning protection is given in *Installation of Lightning Protection Systems* (NFPA 780) and *Lightning* (Golde, 1977a).

Lightning has traditionally been a significant ignition source for storage tank fires. A major incident of this kind occurred at Beaumont, Texas, in 1970 (Case History A46).

Guidance on lightning protection is given in BS 6651: 1985 *Code of Practice for Protection of Structures against Lightning*.

16.5.12 Radio frequency transmissions

The possibility exists that RF transmissions from strong sources such as large military transmitters may act as an ignition source on process plants. This has been recognized for some time as instanced by the existence of a British

Standard BS 4992: 1974 *Guide to Protection Against Ignition and Detonation Initiated by Radio Frequency.*

A situation where concern was expressed about such possible interaction arose in Britain in the late 1970s in respect of the transmitter at Crimond operated by the Royal Navy and located about 4 miles from the natural gas terminal at St Fergus. The naval transmitter responded by reducing its power output.

Studies of this hazard were undertaken by a number of workers (A. Hall and Burstow, 1980; A. Hall and Loveland, 1980; Burstow *et al*., 1981; Howson, Excell and Butcher, 1981; Rosenfeld *et al*., 1981) and the Health and Safety Executive (HSE) published two reports: *Assessment of the Hazard from Radio Frequency Ignition at the Shell and Esso Sites at Braefoot Bay and Moss Morran, Fife* (HSE, 1978a) and *Report of the Steering Committee on Radio Frequency Ignition Hazards at St Fergus, Scotland* (HSE, 19790).

The British Standard guidance was revised and issued as BS 6656: 1986 *Prevention of Inadvertent Ignition of Flammable Atmospheres by Radio-frequency Ignition*, and revised again in 1991.

The conditions for RF ignition of a flammable mixture to occur are (1) electromagnetic radiation of sufficient intensity, (2) a structure capable of acting as a receiving aerial and (3) a mechanism for creating an incendive spark.

The transmitter may be fixed or mobile. Mobile transmitters include vehicles, ships and aircraft. The standard give details of typical transmitter frequency ranges and power outputs. Transmission may be continuous wave (CW) or modulated. The latter includes pulsed radar.

The degree of hazard depends on the frequency of the transmission. The hazardous range of interest is 15 kHz to 35 GHz. There is little hazard at frequencies below 15 kHz. For frequencies below 30 MHz the most efficient receiver is the loop configuration. At higher frequencies all structures are large compared with the wavelength. A part of a structure may behave as an efficient aerial and is then treated as a long dipole. An aerial can concentrate the power in a particular direction and is said to have gain in that direction.

The structures primarily considered in BS 6656: 1991 are loop-type structures and vertical structures. Some typical loop-type structures are illustrated in Figure 16.34. A loop structure has maximum efficiency and is self-resonant when its internal perimeter is about half one wavelength, but structures with a smaller perimeter can be brought to resonance if there is a discontinuity with stray capacitance across it. Cranes are particularly efficient receivers in this context and require particular attention.

For any potential discontinuity in the structure it is possible to determine the maximum extractable power given (1) the structure perimeter, (2) the transmission frequency and (3) the incident field strength.

Vertical structures include vents, flares and columns. Free-standing structures of this kind are not classed as among the more efficient receivers, since even a concrete base has a low impedance path to ground. They can generally be disregarded, except where the vertical structure is part of a loop.

An RF discharge occurs most readily when two surfaces are drawn apart, thus giving a break-spark. Discharges across a fixed gap are not considered to be a significant problem. It is activities such as maintenance and handling and phenomena such as flexing and vibration of pipe work or thermal expansion of structures, which are liable to give rise to an incendive discharge.

The factor determining RF ignition is the thermal initiation time. For times less than this ignition is governed by the discharge energy, and for times greater than this it is governed by its power. The thermal initiation times are approximately 100 μs for methane and ethylene and 20 μs for hydrogen, which are representative of the Class IIA, IIB and IIC gases, respectively. The standard gives ignition criteria for continuous transmissions and for pulsed radar transmissions.

The potential RF ignition hazard exists only in a few locations. There are few reported incidents of such ignition. BS 6656: 1991 adopts a graded approach to assessment of the hazard. An initial assessment is used for screening and a full assessment is undertaken only if a potential hazard is found to exist.

The initial assessment is based on the search areas given in Table 16.27 and proceeds as follows. The search area around the plant is determined from the table. If there is no transmitter within the search area, there is no hazard. If there is a transmitter with the search area, a check is made as to whether the plant is within the vulnerable zone of the transmitter. The standard gives information on the vulnerable zones for various types of transmitter. If the plant is within the vulnerable zone of a transmitter, a full assessment should be undertaken.

BS 6656: 1991 gives the procedures for a full assessment, including: a flow chart for a theoretical assessment and one for an assessment based on plant measurements; methods of taking measurements; methods of performing the calculations; and worked examples.

If a hazard exists, the principal countermeasures are (1) bonding, (2) insulating, (3) reducing the RF efficiency of structures and (4) de-tuning of structures. Typical applications where bonding might be used are where thermal expansion may result in intermittent contacts and across a pair of flanges prior to their parting in maintenance work. Bonding to ground is not suitable. Insulation may sometimes be used where bonding is impractical; it is a possible solution for intermittent contact by thermal expansion. The RF efficiency of a structure may be reduced at the design stage by altering the internal perimeter. Other measures for reducing efficiency include breaking the loop into smaller sections by the use of conductors and covering the entire area of the loop with a sheet of metallic mesh bonded to the structure at points around the perimeter. If there is one major transmission frequency causing the problem and other measures are not practical, it may be possible to detune the structure by connecting to it reactive components.

Special cases considered in the standard include cranes, mobile and portable transmitters, ships and offshore platforms. The Orford Ness transmitter is accorded special treatment.

16.5.13 Smoking

Smoking and smoking materials are potential sources of ignition. Ignition may be caused by a cigarette, cigar or pipe or by the matches or lighter used to light it. A cigarette itself may not be hot enough to ignite a flammable gas–air mixture, but a match is a more effective ignition source.

It is normal to prohibit smoking in a hazardous area and to require that matches or lighters be given up on entry to that area. The 'no smoking' rule may well be disregarded, however, if no alternative arrangements for smoking are

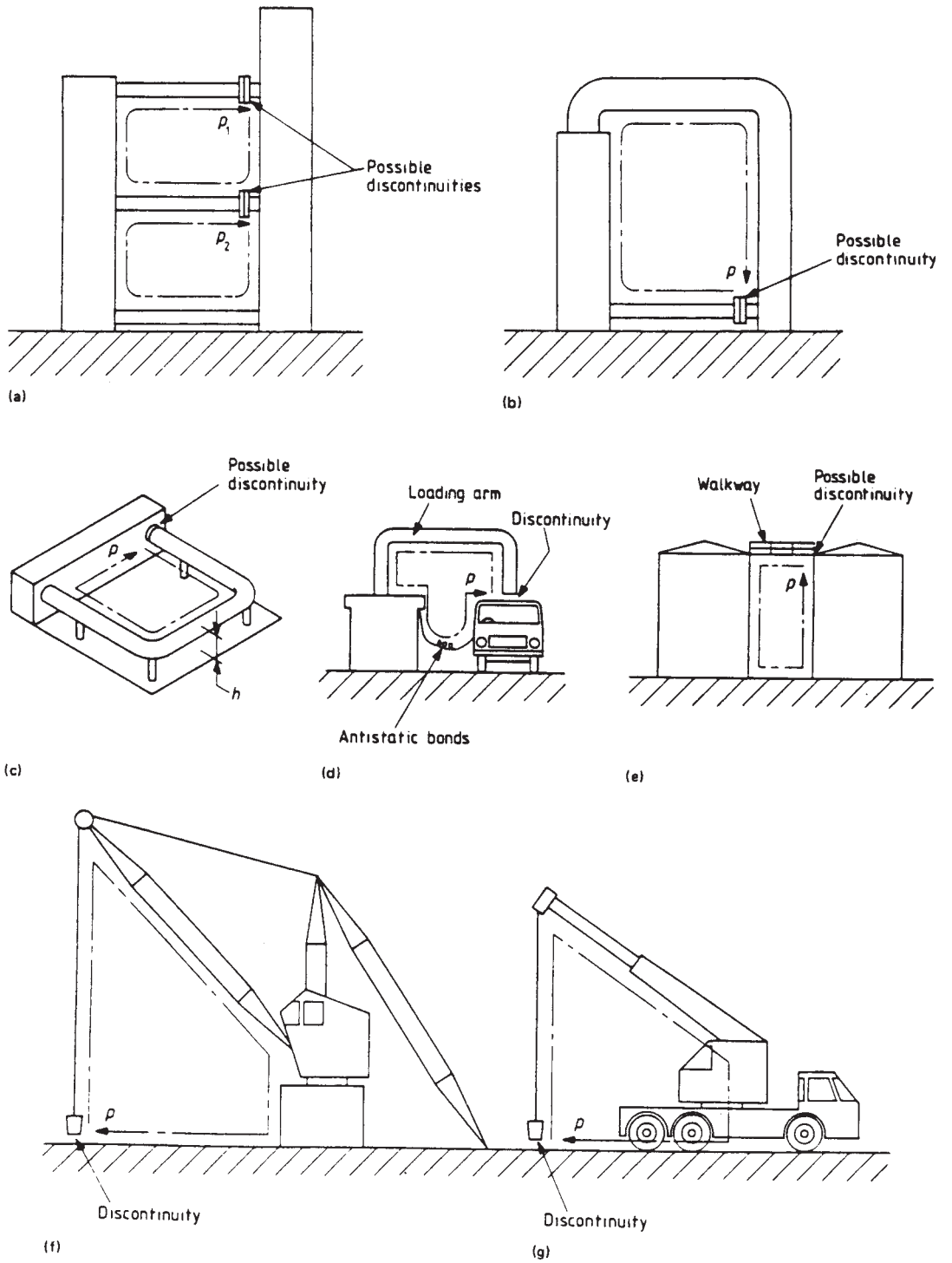


Figure 16.34 *Some typical loop-type structures for RF ignition (BS 6656: 1991): (a) loop formed by columns and pipes; (b) loop formed by columns and pipes; (c) horizontal loop; (d) tanker loading facility; (e) storage tanks; (f) fixed crane; and (g) mobile crane, h, Height of loops; p, internal perimeter of loop (Courtesy of the British Standards Institution)*

Table 16.27 *Maximum radius of search area (m) for initial assessment of an RF ignition hazard*[a] *(BS 6656: 1991) (Courtesy of the British Standards Institution)*

Gas group	*Maximum radius* (m)	
	All loop structures of inside perimeter ≤40 m and horizontal loops of height ≤5 m	*All other loop structures*
I or IIA	4,100	11,500
IIB	5,200	14,200
IIC	6,500	17,500

[a] Table does not apply to locations to the seaward side of Orford Ness, Suffolk.

provided. It is regarded as desirable, therefore, to provide a room where it is safe to smoke, though whether this is done is likely to depend increasingly on general company policy with regard to smoking.

16.5.14 Arson and sabotage

A source of ignition, which cannot be ruled out, is arson. Information on the frequency of arson as a source of ignition was given in Table 2.11. While arson is probably a less important cause of fires in the process industry than of fires generally, it should nevertheless be considered. Security in relation to arson is discussed in Chapter 20.

16.5.15 Autoignition

Strictly, ignition of a bulk flammable gas–air mixture by heating the mixture to its AIT is the alternative to ignition by a local ignition source. It is convenient, however, to deal with it at this point.

Heating of the bulk gas–air mixture outside the plant will occur by contact with a hot surface, as described above. Autoignition as such may therefore be regarded as a form of ignition, which occurs inside the plant.

The autoignition may occur inside the plant at essentially atmospheric pressure or at some higher pressure. If, however, the heating occurs due to compression, the phenomenon is one of compression ignition, which is described below.

16.5.16 Compression effects

A mixture of flammable gas and air may be heated to its AIT by compression. This effect is often referred to as the diesel effect. There are a number of conditions in process plant that can give rise to such compression.

Compression ignition is described in Section 16.3. The point was made there that, given a homogeneous mixture, such autoignition is not restricted to the normal flammability range.

Compression of a mixture of flammable gas and air may be caused by pumping against a closed valve, by water hammer in a pipeline or by a liquid slug travelling down a line.

A case history involving compression ignition in which a mixture of flammable gas and air was compressed by a pump pumping against a closed valve is described by Anon. (LPB 19 1978, p. 24). The pump had a nominal head of 30 m. Subsequent tests showed that pressure oscillations occurred in the trapped gas, which were up to eight times higher than the equilibrium head of the pump.

Another form of compression ignition can occur due to compression of air bubbles in a flammable liquid. The temperature rise inside such bubbles can be high.

16.6 Self-heating

Self-heating, or spontaneous combustion, of a solid material is generally a process of slow oxidation. Material undergoing self-heating may act as a source of ignition or it may give rise to a fire or explosion. The topic of thermal explosion and self-heating has many ramifications beyond the self-heating of solid materials. These other aspects are considered in Section 16.3.

Early work on self-heating was done by Frank-Kamenetsky (1955) and by Semenov (1935). P.M. Thomas and Bowes, both separately and together, have published a series of treatments (e.g. P.M. Thomas, 1958; P.M. Thomas and Bowes, 1961a, 1967; Bowes, 1976). The subject has been reviewed in *Self-heating* (Bowes, 1984) and by P. Gray and Lee (1967b). Application of the theory to process plant problems has been discussed by Bowes (1976).

Selected references on self-heating are given in Table 16.28.

16.6.1 Self-heating in industrial processes

Materials in process, storage or transport may undergo self-heating. The self-heating is due to the exothermic reaction of slow oxidation of the material. If conditions are critical, this self-heating results in ignition. Examples are materials handled in process equipment such as driers, materials stored in piles in warehouses or in the open, or materials transported in large containers as in ships. A well-known example is the spontaneous combustion of coal stored in piles on the ground.

In some cases the hazard is intensified by the fact that the material enters the storage relatively hot. This can occur, for example, with material that has just been passed through a drier.

Unstable materials may also undergo an exothermic reaction so that self-heating occurs.

Self-heating is liable to occur in oil-soaked lagging. In this case it is the oil, which undergoes oxidation. Self-heating may also occur in dust layers. In both cases the smoldering material may then act as an ignition source.

Self-heating can also occur in oil rags left on steam pipes, in dirty cotton waste put in a boiler suit pocket, or in damp clothing stowed away in a locker.

The substance that undergoes reaction must be reactive and may be bulk solid such as coal or a reactive substance on a substrate such as oil-soaked lagging.

16.6.2 Self-heating incidents

Most incidents due to self-heating arise in the kind of situations just described. Usually they do not have dramatic consequences. This is not always so, however.

In 1987, a severe explosion and fireball occurred at the BP Chemicals EO plant at Antwerp (Case History A115). The cause of the explosion was identified as the decomposition of EO in the purification column. It was concluded that the most probable cause of the explosion was a leak of EO into the insulation of the column, leading to self-heating which ignited the escaping EO.

In 1989, the BASF EO plant at Antwerp suffered two severe explosions, each accompanied by a fireball (Case History A122). The first explosion occurred in a column

Table 16.28 *Selected references on thermal explosion, self-heating and spontaneous combustion*

Mackey (1895, 1896); Semenov (1928, 1935,1940, 1942, 1959); Frank-Kamenetsky (1939a,b, 1942, 1945, 1955); Zeldovitch (1939); Gordon (1948); Rideal and Robertson (1948); N.D.Mitchell (1951); A. Thomas (1951); Chambre (1952); Bowes (1954, 1962, 1968,1969, 1972,1974a,b, 1976, 1984); Hicks (1954); Mullins (1955); Enig (1956, 1966); Enig, Shanks and Southworth (1956); Khitrin and Goldenberg (1957); P.M. Thomas (1958, 1960,1961, 1965a, 1972, 1973a, 1984); Cook (1959); P. Gray and Harper (1959a,b); Kinabara and Akita (1960); Zinn and Mader (1960); Parks (1961); P.M. Thomas and Bowes (1961a,b, 1967); Bowes and Townshend (1962); Gross and Amster (1962); Zinn (1962); Boddington (1963); M.H. Friedman (1963a,b, 1967, 1968); Merzhanov, Barzykin and Gontovskaya (1963); Adler and Enig (1964); Wake and Walker (1964); Clemmow and Huffington (1965); P. Gray and Lee (1965, 1967a,b); Steggerda (1965); Bowes and Thomas (1966); van Geel (1966); Merzhanov (1966, 1967); Merzhanov and Dubovitsky (1966); B.F. Gray and Yang (1967); Gugan (1967, 1974a); Tyler and Wesley (1967); Bowes and Langford (1968); B.F. Gray (1969a,b, 1973–); P. Gray, Lee and MacDonald (1969); Rosser and Rajapakse (1969); Boddington and Gray (1970); Boddington, Gray and Harvey (1971a,b); Merzhanov and Averson (1971); Wake (1971, 1973); Birkby, Brown and Street (1972); FRS (1972 Fire Res. Note 937); Goodman, Gray and Jones (1972); B.F. Gray and Sherrington (1972); Hardee, Lee and Donaldson (1972); Hermance (1973); Wake and Rayner (1973); Shouman, Donaldson and Tsao (1974); Zaturska (1974, 1975,1978, 1980,1981, 1983,1984); Kassoy and Poland (1975); Shouman and Donaldson (1975, 1977); MacDermott (1976); P. Gray and Sherrington (1977); Kerns (1977 BM 1C 8757); Takeno (1977); Adler (1978, 1983, 1987); BRE (1978 CP12/78, 1982 IP6/82, 1984 SO 41); Anthony and Greaney (1979); Boddington, Gray and Robinson (1979); Gill, Donaldson and Shouman (1979–); Kordylewski (1979, 1980); Naujokas (1979, 1985); Brogli (1980); Brogli *et al.* (1980); Drysdale (1980); Takemo and Sato (1980); M.M. Baum (1981); Beever (1981); Boddington, Gray and Scott (1981); Gill, Shouman and Donaldson (1981); B.F. Gray and Jones (1981); Kordylewski and Krajewski (1981, 1985); Lawn, Street and Baum (1981); Tyler and Jones (1981); Boddington, Chang-Gen Feng and Gray (1982); Egeiban *et al.* (1982); Poland, Hindash and Kassoy (1982); Zaturska and Banks (1982, 1990); Adler and Bowes (1983); B.F. Gray and Wake (1984, 1988); Lermant and Yip (1984–); Vega and linan (1984); Gomez, Wake and Gray (1985); B.F. Gray and Scott (1985); Greenway and Spence (1985); Griffiths, Hasko and Tong (1985); Winters and Cliffe (1985); Adler (1987); Snee 1987, 1989); Brooks, Balakotaiah and Luss (1988); Ahmed, Fisher and Janeshek (1989); de Faveri, Zonato *et al.* (1989); P. Gray and Griffiths (1989); Kassoy, Kapila and Stewart (1989); Kotoyori (1989a, 1993); Babushok, Goldshtein and Sobolev (1990); Benin, Kossoi and Sharikov (1990); McIntosh and Tolputt (1990); Britton (1991); Gorelov and Sobolev (1991); J.F. Griffiths and Kordylewski (1992a,b); Schliephake, Giesbrecht and Loffler (1992); Uehara and Seino (1992); Davie, Nolan and Tucker (1993); H. Martin and Ruppert (1993); Vaughan and Mancini (1993); El-Sayed (1994)

separating EO and acetaldehyde. The investigation found that a small leak of EO had probably led to an accumulation of auto-oxidizable polyethylene glycols in the insulation of the column. Self-heating occurred in the insulation. Although the heat released would not have been enough to cause decomposition of the EO flowing past on the inside of the column, it was concluded that decomposition occurred at a section of pipe work where the gas was stagnant.

16.6.3 Self-heating process

If self-heating occurs, the occurrence of a thermal explosion depends on the heat balance in the solid. The heat balance is illustrated in Figure 16.35 (after Semenov). The rate of heat release is a function of the temperature as shown in curve A. Over the lower temperature range the reaction is rate limited and the reaction rate, and hence the heat released, rises rapidly. The rise is often governed by an exponential relation, and in particular by the Arrhenius equation. Over the higher temperature range the rate becomes diffusion limited and increases only weakly with temperature, so that the reaction rate and the heat released then increase relatively slowly.

The heat removed is approximately proportional to the temperature difference between the solid mass, or pile, and the surrounding medium. A series of lines can be drawn corresponding to different effective heat transfer coefficients. Line Bl is tangential to curve A at point 1. For the

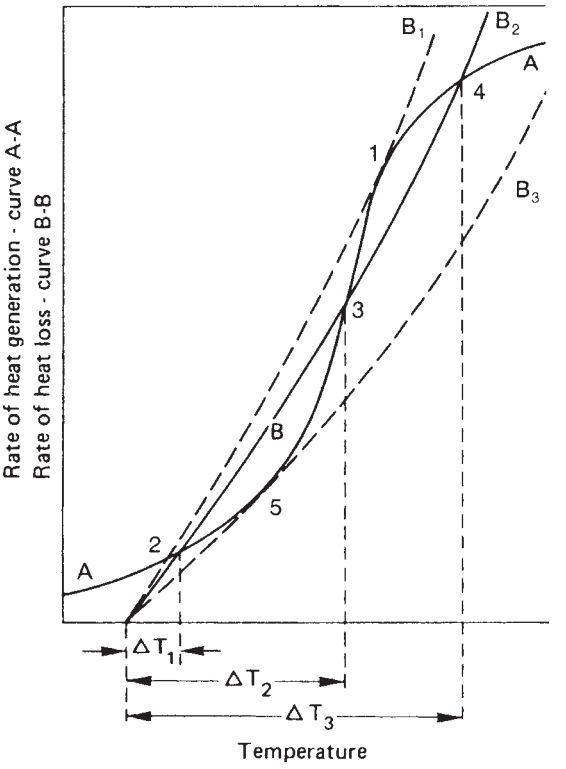


Figure 16.35 *Heat balance in a body undergoing self-heating (Bowes, 1984) (Courtesy of HM Stationery Office. © All rights reserved).*

condition where the heat transfer is greater than this, the heat removed will always be greater than heat released and no thermal explosion will occur. Line B3 is tangential to curve A at point 5. For any condition where heat transfer is less than this, the heat removed will always be less than the heat released and thermal explosion will occur. Line B2 represents the intermediate case. It crosses curve A at the three points 2, 3 and 4, which each constitute a steady state. Points 2 and 4 are stable steady states in that if there is a small increase in the temperature difference AT, the heat removed is greater than that released and the system returns to the steady state point. Point 3, however, is an unstable steady state in that if there is a small increase in AT the heat removed is less than that released so that the system will tend move up curve A to the stable steady state at point 4. Conversely, if there is a small decrease in AT the system will tend to move down curve A to point 2.

It is also instructive to consider the effect of the size of the solid mass and the temperature difference AT between the center of the mass and the surroundings as shown in Figure 16.36. There are two critical dimensions (r_1 and r_2) and four regions (A–D). There are two curves 1 and 2, which typically correspond to moderate heating and smoldering combustion. If the dimension of the solid mass is less than r_1 and the initial temperature difference is in region A, the temperature difference will move to the value on curve 1 corresponding to the value of r. If the dimension is greater than r_1 and the initial temperature difference is in region B, the temperature difference will move to curve 2. If the dimension lies between r_1 and r_2 and the initial temperature difference is in region B or C, there are two possibilities. If the temperature difference tends towards a value within region C, it will move to curve 1. If it tends towards region B, it will move to curve 2. If the dimension lies between r_1 and r_2 and the initial temperature difference is in region A, the temperature difference will move to curve 1, unless an additional heat source shifts it to curve 2. If the dimension is greater than r_2 and the initial temperature difference is in region D, the temperature difference will move to curve 2.

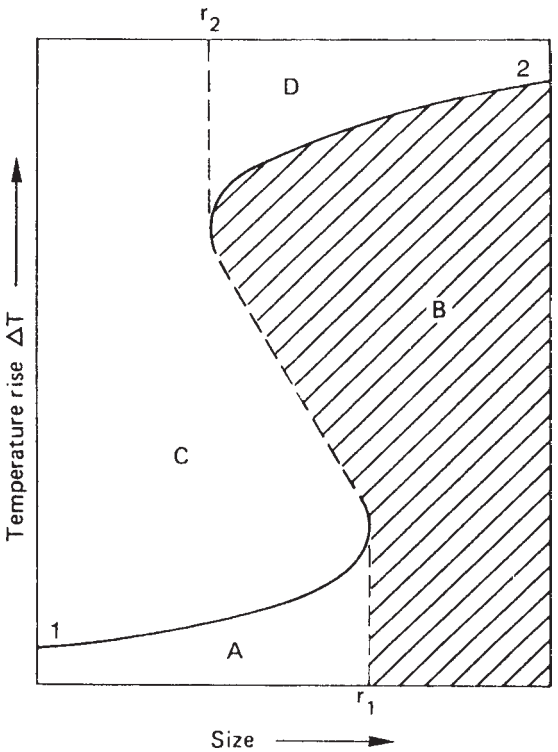


Figure 16.36 *Steady states in a body undergoing self-heating (Bowes, 1984) (Courtesy of HM Stationery Office, ©, All rights reserved)*

These considerations bring out the importance of the size of the pile. If the size of the pile is small, the system will tend to move towards curve 1, and if the pile is large the system will tend to move toward curve 2.

16.6.4 Elementary relations of self-heating

The basic equation for self-heating is

$$\rho c \frac{\partial T}{\partial t} = k\nabla^2 T + Q \qquad [16.6.1]$$

with

$$Q = Q'\rho A \exp(-E/RT) \qquad [16.6.2]$$

where A is the pre-exponential factor, c is the specific heat, E is the activation energy, k is the thermal conductivity, Q is the heat released by the reaction per unit volume, Q' is the heat of reaction per unit mass, R is the universal gas constant, T is the temperature and ρ is the density.

For the three principal centrisymmetric shapes of interest – the slab, cylinder and sphere – Equation 16.6.1 becomes, in rectangular co-ordinates in one dimension,

$$\rho c \frac{\partial T}{\partial t} = k\left(\frac{\partial^2 T}{\partial x^2} + \frac{j}{x}\frac{\partial T}{\partial x}\right) + Q'\rho A \exp(-E/RT) \qquad [16.6.3]$$

with

$j = 0$ Plane slab
$j = 1$ Cylinder
$j = 2$ Sphere

where x is the distance from the centre of the body.

The heat transfer at the surface is characterized by an overall heat transfer coefficient h such that

$$-k\frac{\partial T}{\partial t} = h(T_s - T_a) \qquad [16.6.4]$$

with

$$h = h_c + h_r \qquad [16.6.5]$$

where h is the heat transfer coefficient at the surface, h_c is the heat transfer coefficient for convection and h_r is the heat transfer coefficient for radiation.

The following dimensionless quantities are defined. The dimensionless distance z is

$$z = x/r \qquad [16.6.6]$$

where r is the half-width or radius, or characteristic length, and z is the dimensionless distance.
The dimensionless time τ is

$$\tau = \frac{kt}{\rho c r^2} \quad [16.6.7]$$

The dimensionless parameter ϵ is

$$\epsilon = RT_a/E \quad [16.6.8]$$

where T_a is the air absolute temperature.

The dimensionless temperature difference θ is

$$\theta = \frac{E}{RT_a^2}(T - T_a) \quad [16.6.9]$$

The dimensionless ignition parameter δ is

$$\delta = \frac{E}{RT_a^2}\frac{r^2}{k}Q'\rho A \exp(-E/RT_a) \quad [16.6.10]$$

Frank-Kamenetsky introduced the approximation

$$-\frac{E}{RT} \approx -\frac{E}{RT_a} + \frac{\theta}{1+\epsilon\theta} \quad E/RT_a \leq 1 \quad [16.6.11a]$$

$$\approx -\frac{E}{RT_a} + \theta \quad \epsilon \leq 1 \quad [16.6.11b]$$

Then, utilizing Equations 16.6.6–16.6.11, Equation 16.6.3 becomes, in dimensionless form,

$$\frac{\partial\theta}{\partial\tau} = \frac{\partial^2\theta}{\partial z^2} + \frac{j}{z}\frac{\partial\theta}{\partial z} + \delta \exp[\theta/(1+\epsilon\theta)] \quad [16.6.12a]$$

$$\frac{\partial\theta}{\partial\tau} = \frac{\partial^2\theta}{\partial z^2} + \frac{j}{z}\frac{\partial\theta}{\partial z} + \delta \exp\theta \quad \epsilon \ll 1 \quad [16.6.12b]$$

and Equation 16.6.4 becomes

$$\frac{\partial\theta}{\partial z} = -\alpha\theta_s \quad [16.6.13]$$

with

$$\alpha = hr/k \quad [16.6.14]$$

where α is the Biot number.

Equation 16.6.12 is the basic dimensionless equation of self-heating, as formulated by Frank-Kamenetsky. The parameter <5 is the Frank-Kamenetsky parameter.

Use is also made of the following further dimension-less temperature differences:

$$\theta_s = \frac{E}{RT_a^2}(T_s - T_a) \quad [16.6.15]$$

$$\theta_o = \frac{E}{RT_a^2}(T_o - T_a) \quad [16.6.16]$$

where subscripts o and s denote the centre of the body and the surface, respectively. At steady state Equation 16.6.12 becomes

$$\frac{\partial^2\theta}{\partial z^2} + \frac{j}{z}\frac{\partial}{\partial z} = -\delta\exp\theta \quad [16.6.17]$$

Equation 16.6.17 is the Poisson–Boltzmann equation.

The principal sets of boundary conditions that are used with Equations 16.6.12 and 16.6.17 are:

(1) surface exposed to air – surface heat transfer coefficient finite;
(2) surface exposed to air – surface heat transfer coefficient zero;
(3) surface exposed to air – surface heat transfer coefficient infinite;
(4) one surface against a hot body – constant temperatureat hot face;
(5) one surface against a hot body – constant heat flux at hot face.

The second boundary condition is referred to as the Semenov condition and the third as the Frank-Kamenetsky condition.

16.6.5 Model for a symmetrical slab

One principal configuration is the symmetrical slab. For the steady-state condition the temperature profile for self-heating is as shown in Figure 16.37(a). From Equation 16.6.17, setting $j = 0$

$$\frac{d^2\theta}{dz^2} = -\delta\exp\theta \quad [16.6.18]$$

Assuming a finite surface heat transfer coefficient, the boundary conditions are

$$z = 0; \frac{d\theta}{dz} = 0 \quad [16.6.19a]$$

$$z = \pm 1; \frac{d\theta}{dz} = -\alpha\theta_s \quad [16.6.19b]$$

The general solution of Equation 16.6.18 is

$$\theta = \ln C_2 - 2\ln\cosh\left[z(\delta C_2/2)^{1/2} + C_1\right] \quad [16.6.20]$$

Differentiating Equation 16.6.20 and utilizing boundary condition 16.6.19a,

$$C_1 = 0 \quad [16.6.21a]$$

and

$$C_2 = \exp\theta_0 \quad [16.6.21b]$$

Utilizing boundary condition 16.6.19b

$$2D\tanh D = \alpha\theta_s \quad [16.6.22]$$

with

$$D = \left(\frac{\delta\exp\theta_o}{2}\right)^{1/2} \quad [16.6.23]$$

Eliminating θ_s from Equations 16.6.20 and 16.6.22

$$\ln\delta = \ln\frac{2D^2}{\cosh^2 D} - 2D\frac{\tanh D}{\alpha} \quad [16.6.24]$$

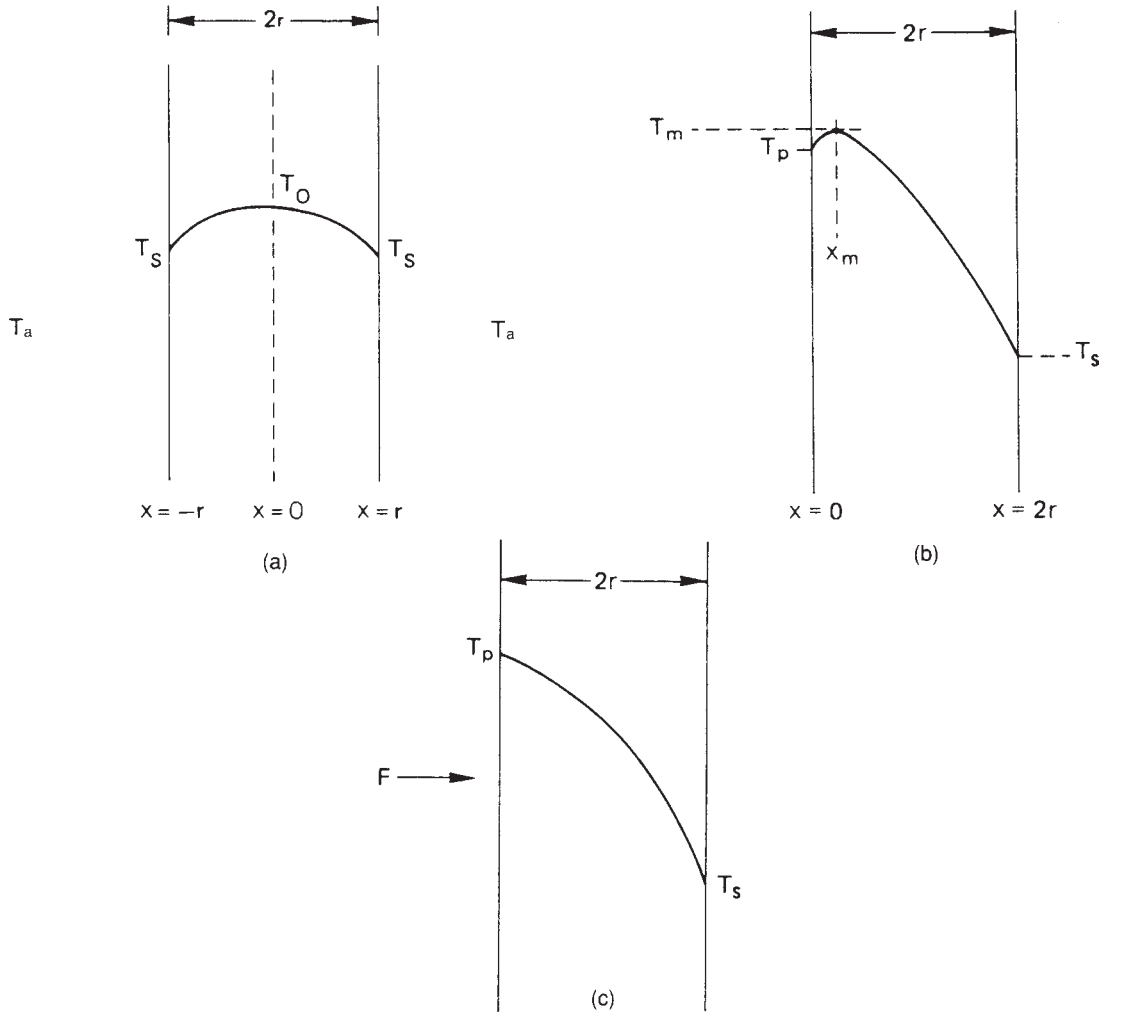


Figure 16.37 *Steady-state temperature profiles in a slab undergoing self-heating: (a) symmetrical slab; (b) asymmetrical slab with constant temperature at a hot face; and (c) asymmetrical slab with constant heat flux at hot face*

16.6.6 Characteristics of symmetrical slab model

It is instructive to consider the characteristics of the slab model. For low values of heat transfer at the surface, and hence of α, Equations 16.6.20–16.6.24 imply that

$$\theta_o \to \theta_s \quad \text{and} \quad \delta \to 0 \qquad \alpha \to 0$$

From Equations 16.6.22 and 16.6.24

$$\frac{(2\delta)^{1/2}\sinh\left[(\delta\exp(\theta_o)/2)^{1/2}\right]}{\alpha} = \theta_s\exp(-\theta_s/2) \qquad [16.6.25]$$

In the region $0<\alpha<1$, $0<\delta<1$, $\theta_o \approx \delta_s$, Equation 16.6.25 reduces to

$$\delta/\alpha = \theta_s\exp(-\theta_s) \qquad [16.6.26]$$

Equation 16.6.26 implies that for a given value of α the parameter δ passes through a maximum with θ_s and has this maximum at $\theta_s = 1$. This value of δ is the critical value δ_c:

$$\delta_c = \alpha/e \qquad [16.6.27]$$

For values of δ less than δ_c there exist steady-state temperature distributions that satisfy Equation 16.6.26, but for values that exceed δ_c there are no such steady states and thermal explosion occurs.

At the other extreme, as α becomes very high Equation 16.6.24 reduces to

$$\ln\delta = \ln\frac{2D^2}{\cosh^2 D} \qquad [16.6.28]$$

Equation 16.6.28 also implies that δ passes through a maximum with D. This maximum occurs at

$$D = \coth D = 1.2 \qquad [16.6.29]$$

which gives a value for δ_c of 0.88.

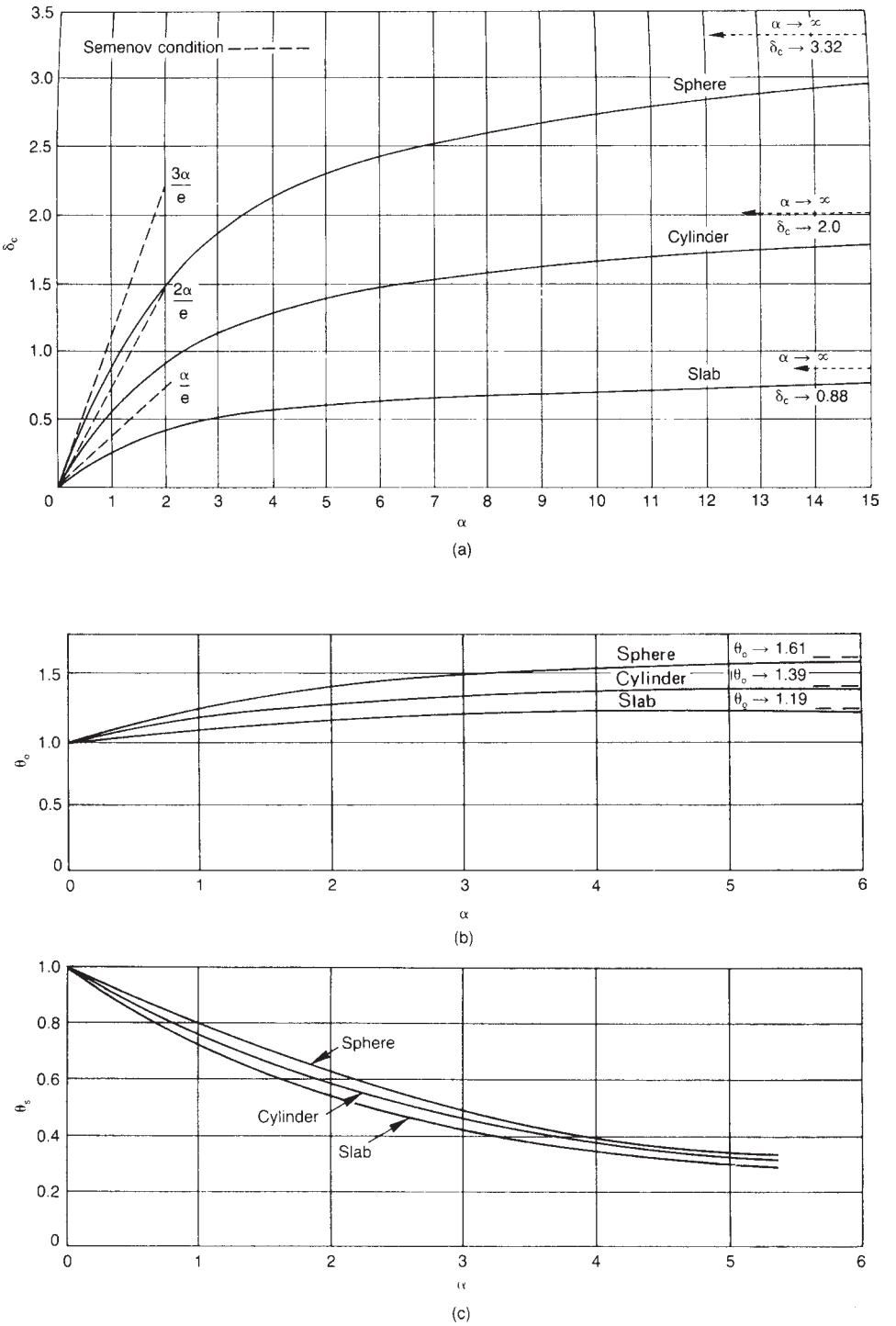


Figure 16.38 *Parameters governing self-heating without reactant consumption for three principal centrisymmetric shapes (P. H. Thomas, 1958): (a) critical values δ_c of the self-heating parameter (b) critical values of the dimensionless temperature θ_o at the centre and (c) critical values of the dimensionless surface temperature θ_s (Courtesy of the Faraday Society)*

Values of δ_c, θ and θ_s for a slab over the whole range of α have been obtained by P.M. Thomas (1958) and are shown in Figure 16.38. The figure also gives the corresponding values for a cylinder and a sphere. The limiting values are:

	$\alpha \to 0$		$\alpha \to \infty$	
	δ_c	θ_o	δ_c	θ_o
Plane slab	α/e	1	0.88	1.19
Cylinder	$2(\alpha/e)$	1	2.00	1.39
Sphere	$3(\alpha/e)$	1	3.32	1.61

16.6.7 Model for a cylinder

Another principal configuration is the infinite cylinder. From Equation 16.6.17, setting $j = 1$

$$\frac{d^2\theta}{\delta z^2} + \frac{1}{z}\frac{d\theta}{dz} = -\delta \exp\theta \qquad [16.6.30]$$

Assuming a finite heat transfer coefficient, the boundary conditions are those given in Equation 16.6.19.
The general solution is

$$\theta = \ln\left[\frac{8B}{\delta(1+Bz^2)^2}\right] \qquad [16.6.31]$$

where B is a constant of integration. Then from boundary condition 16.6.19b

$$\ln\delta = \ln\left[\frac{8B}{(B+1)^2}\right] - \frac{4B}{\alpha(B+1)} \qquad [16.6.32]$$

The maximum value of δ occurs at

$$\alpha = \frac{4B_c}{1-B_c^2} \qquad [16.6.33]$$

where the subscript c denotes critical.

Then, utilizing this value of α, the parameters δ_c and θ_s may be obtained from Equations 16.6.31 and 16.6.32.

16.6.8 General model for slab, cylinder and sphere

A general steady-state model for the symmetrical slab, cylinder and sphere may be obtained from Equation 16.6.17. The further approximation is introduced:

$$(j+1)\beta\theta \approx \delta \exp\theta \qquad [16.6.34]$$

where β is an effective heat transfer coefficient. There is no simple relation for β, but

$$\beta \approx \alpha \quad \alpha \ll 1 \qquad [16.6.35]$$

Then, utilizing Equation 16.6.34 in Equation 16.6.17

$$\frac{d^2\theta}{\delta z^2} + \frac{j}{z}\frac{d\theta}{dz} = -(1+j)\beta\theta \qquad [16.6.36]$$

It can be shown that

$$\beta = c_1^2 \quad \text{Plane slab} \qquad [16.6.37a]$$

$$= \frac{c_2^2}{2} \quad \text{Cylinder} \qquad [16.6.37b]$$

$$= \frac{c_3^2}{3} \quad \text{Sphere} \qquad [16.6.37c]$$

where c_1 is the first root of

$$c_n \tan c_n = \alpha \qquad [16.6.38a]$$

c_2 is the first root of

$$c_n J_1(c_n) = \alpha J_0(c_n) \qquad [16.6.38b]$$

and c_3 is a solution of

$$c_n \coth c_n + \alpha - 1 = 0 \qquad [16.6.38c]$$

where J_0 and J_1 are Bessel functions of the first kind and of order zero and one, respectively. The parameter δ has a maximum at $\theta = 1$ so that

$$\delta_c = \frac{(j+1)\beta}{e} \qquad [16.6.39]$$

16.6.9 Model for an asymmetrical slab

Returning to the slab, an alternative situation is one face against a hot body and one exposed to the atmosphere. For this case, in addition to the heat transfer at the surface exposed to the atmosphere, it is necessary to consider different conditions at the hot face. One assumption is that there is a constant temperature at the hot face; another is that there is a constant heat flux at the hot face. The steady state temperature profiles for these two cases are shown in Figures 16.37 (b) and (c), respectively. For the asymmetrical slab the dimensionless ignition parameter is defined as

$$\delta = \frac{E}{RT_p^2}\frac{r^2}{k}Q'\rho A \exp\left(-E/RT_p\right) \qquad [16.6.40]$$

and the dimensionless temperature difference as

$$\theta = \frac{E}{RT_p^2}(T - T_p) \qquad [16.6.41]$$

The relevant equation is Equation 16.6.18 and the general solution is Equation 16.6.20 and in addition

$$\frac{d\theta}{dz} = -(2\delta C_2)^{\frac{1}{2}} \tanh\left[z(\delta C_2/2)^{1/2} + C_1\right] \qquad [16.6.42]$$

The case considered here is that where the hot face is at a constant temperature and the surface of the other face is at a much lower temperature. For this case the boundary conditions are

$$z = 0; \quad \theta = 0 \qquad [16.6.43a]$$

$$z = 2; \quad \theta = \theta_s \qquad [16.6.43b]$$

Then from boundary condition 16.6.43a

$$C_1 = \pm\cosh^{-1}\left(C_2^{1/2}\right) \qquad [16.6.44a]$$

$$C_2 = \exp\theta_m \qquad [16.6.44b]$$

where subscript m denotes maximum.

From boundary condition 16.6.43b

$$(2\delta)^{1/2} = \frac{\cosh^{-1}\left[\exp(\theta_m/2) \pm \cosh^{-1}[\exp(\theta_m/2)\cdot\exp(-\theta_s/2)\right]}{\exp(\theta_m/2)} \qquad [16.6.45]$$

Given that the temperature of the surface is much less than that of the hot face, so that $\theta_s < 0$, it can be shown that $z_m \to 0$ and $\theta_m \to 0$, and that

$$(2\delta)^{1/2} = \cosh^{-1}\left[\exp(-\theta_s/2)\right] \quad [16.6.46]$$

For large $|\theta_s|$ Equation 16.6.46 provides a good estimate of δ_c so that

$$\delta_c = \frac{(2\ln 2 - \theta_s)^2}{8} \quad [16.6.47a]$$

$$= \frac{(1.4 - \theta_s)^2}{8} \quad [16.6.47b]$$

Equation 16.6.47 is a good approximation for $|\theta_s|$ values as low as 8.

This argument suggests that for large θ_s it is permissible to adopt the approximation used by Zeldovitch and Semenov that the maximum temperature occurs at the hot face. Physically this means that the hot face is a perfect insulator instead of a perfect conductor of infinite thermal capacity.

The boundary conditions at the hot face then become

$$z = 0; \quad \theta = 0 \quad [16.6.48a]$$

$$z = 0; \quad \frac{d\theta}{dz} = 0 \quad [16.6.48b]$$

There is now only one steady-state temperature profile, which is the critical one. With these boundary conditions

$$C_1 = 0 \quad [16.6.49a]$$

$$C_2 = 1 \quad [16.6.49b]$$

which gives Equation 16.6.47.

An alternative derivation in terms of the ambient temperature utilizes the boundary condition

$$z = 2; \frac{d\theta}{dz} = -\alpha(\theta_s - \theta_a) \quad [16.6.50]$$

with

$$\theta_a = \frac{E}{RT_p^2}(T_a - T_p) \quad [16.6.51]$$

and yields for $\theta_a < 0$ and large $|\theta_a|$

$$(2\delta_c)^{1/2}\tanh\left[(2\delta_c)^{1/2}\right] + 2\alpha\ln\left\{\cosh\left[(2\delta_c)^{1/2}\right]\right\} = -\alpha\theta_a \quad [16.6.52]$$

For $\delta_c > 5$, Equation 16.6.52 simplifies to

$$\delta_c \approx \frac{1}{2}\left(\frac{\alpha}{1+2\alpha}\right)^2(1.4 - \theta_a)^2 \quad [16.6.53]$$

Equation 16.6.53 gives results of accuracy comparable to those of Equation 16.6.47 and simplifies to that equation as $\alpha \to \infty$.

For the assumption that the hot face is a perfect insulator, Equation 16.6.53 is valid for all values of α, but as an approximation to the more realistic case it fails at $\alpha = 0$.

16.6.10 Model for a hollow cylinder

Another important asymmetrical case is that of the hollow cylinder with the inner face at a constant hot temperature. For this case the dimensionless distances are defined as

$$Z = r/r_1 \quad [16.6.54a]$$

$$z = r_1/r_1 = 1 \quad \text{Inner face} \quad [16.6.54b]$$

$$z = r_2/r_1 = z_s \quad \text{Outer face} \quad [16.6.54c]$$

The dimensionless temperature difference θ is defined by Equation 16.6.41 and the dimensionless ignition parameter as

$$\delta = \frac{E}{RT_p^2}\frac{r_i^2}{k}Q'\rho A\exp(-E/RT_p) \quad [16.6.55]$$

The relevant equation is Equation 16.6.30 and the general solution is

$$\theta = \ln\left[\frac{2F^2Gz^{F-2}}{\delta(1+Gz^F)^2}\right] \quad [16.6.56]$$

where F and G are constants of integration.

The boundary conditions are

$$z = 1; \quad \theta = 0 \quad [16.6.57a]$$

$$z = 1; \quad \frac{d\theta}{dz} = 0 \quad [16.6.57b]$$

$$z = z_s; \quad \theta = \theta_s \quad [16.6.57c]$$

From boundary condition 16.6.57b

$$F\frac{1-G}{1+G} = 2 \quad [16.6.58]$$

From Equations 16.6.56 and 16.6.58

$$\delta_c = \frac{8G}{(1-G)^2} \quad 0 < G < 1 \quad [16.6.59]$$

From Equation 16.6.56 and boundary condition 16.6.57c

$$\theta_s = \ln\left[\frac{2F^2Gz_s^{F-2}}{\delta_c(1+Gz_s^F)^2}\right] \quad [16.6.60]$$

For the critical ignition parameter δ_c^* expressed in terms of the half thickness of the cylinder wall is

$$\delta_c^* = \delta_c\left(\frac{z_s - 1}{z}\right)^2 \quad [16.6.61]$$

For a solid cylinder $F = 2$ and Equation 16.6.56 then reduces to Equation 16.6.31.

The model for the hollow cylinder may be applied to the problem of the self-heating of lagging on a pipe. The maximum, or critical, thickness of lagging to avoid self-heating may be calculated as follows. Calculate δ from Equation 16.6.55, assume that this is the critical value of δ ($\delta = \delta_c$), and calculate G and then F from Equations 16.6.58 and 16.6.59. Then assume a normalized outer radius z_s and

calculate θ_s from Equation 16.6.60. If θ_s differs from that specified, assume a fresh value of z_s and recalculate.

Some illustrative calculations have been made by Gugan (1974a) and are summarized in Table 16.29. The results show that if the pipe temperature is increased, the thickness of lagging needs to be decreased in order to avoid self-heating. Thus the relation between pipe temperature and lagging thickness is the reverse of that required for heat insulation.

16.6.11 Critical parameters

The parameter is given by Equation 16.6.10, which may be written as

$$\delta = \frac{E}{RT_a^2}\frac{r^2}{k}Q(T_a) \qquad [16.6.62]$$

For a slab, Equation 16.6.62 may be rewritten utilizing Equation 16.6.14 and

$$\frac{V}{S} = r \qquad [16.6.63]$$

as

$$\delta = \frac{E}{RT_a^2}\frac{\alpha}{h}\frac{V}{S}Q(T_a) \qquad [16.6.64]$$

Further, since

$$\theta_o = \frac{E}{RT_a^2}(T_o - T_a) \qquad [16.6.65]$$

$$\delta = \theta_o \frac{r}{k}\frac{V}{S}\frac{Q(T_a)}{(T_o - T_a)} \qquad [16.6.66]$$

Table 16.29 *Illustrative calculation of the critical thickness of lagging to avoid self-heating (after Gugan, 1974a) (Courtesy of the Institution of Chemical Engineers)*

Parameters assumed	
$Q' = 2000$ cal/g	$r_i = 5.08$ cm
$\rho = 0.03$ g/cm^3	$E = 6000$ cal/mol
$A = 0.04$ s^{-1}	$R = 1.987$ cal/mol K
$k = 10^{-4}$ cal/cm s°C	
$T_s \not> 313$ K	
$T_p = 473$ K Case 1	
573 K Case 2	
Calculation results	
Case 1:	
$\delta_c = 14.1$	
$G = 0.479$	
$F = 5.68$	
$\theta_s = -2.21$	$T_s = 309$ K
$z_s = 1.75$	$r_s = 8.6$ cm
Case 2:	
$\delta_c = 29.3$	
G = 0.596	
F = 7.91	
$\theta_s = -2.48$	$T_s = 304$ K
$z_s = 1.55$	$r_s = 7.8$ cm

or

$$\delta = \theta_o \frac{\alpha}{h}\frac{V}{S}\frac{Q(T_a)}{(T_o - T_a)} \qquad [16.6.67]$$

Equation 16.6.67 can be extended to the other geometries by the generalization

$$\delta = (j+1)\theta_o \frac{r}{k}\frac{V}{S}\frac{Q(T_a)}{(T_o - T_a)} \qquad [16.6.68]$$

since

$$\frac{V}{S} = \frac{r}{2} \quad \text{Cylinder} \qquad [16.6.69a]$$

$$\frac{V}{S} = \frac{r}{3} \quad \text{Sphere} \qquad [16.6.69b]$$

or generally for the three principal symmetrical shapes

$$\frac{Sr}{V} = 1 + j \qquad [16.6.70]$$

These equations show that for these geometries the value of δ is a function of the surface/volume ratio S/V.

The relation between δ_c and S/V is illustrated in the table given in Section 16.6.6. As $\alpha \to 0$, δ_c is exactly proportional to S/V; while as $\alpha \to \infty$, δ_c lies within 10% of S/V.

There are a number of methods available for the estimation of the critical parameters δ_c and θ_o. One approximate analytical method has been developed by Boddington, Gray and Harvey (1971b). This method is based on the application of Equation 16.6.17 to any centrisymmetric convex body. The parameters are expressed in terms of an average radius R_o and of the shape factor j and procedures are given for determining these. At criticality, the following relations hold:

$$\delta_c(r) = \delta_c(R_o)\frac{r^2}{R_o^2} \qquad [16.6.71]$$

$$\theta_o = 2\ln[(j+7)/4] \qquad [16.6.72]$$

with

$$\delta_c(R_o) = 3F(j) \qquad [16.6.73]$$

$$F(j) = \frac{2j+6}{j+7} \qquad [16.6.74]$$

For the three principal symmetrical shapes the shape parameter has its usual values (0, 1 or 2) and

$$\frac{r^2}{R_o^2} = \frac{j+1}{3} \qquad [16.6.75]$$

Another approximate analytical method has been given by Hardee, Lee and Donaldson (1972). Other methods include expansion about the maximum temperature and use of a step function. Numerical solutions have also been obtained. In particular, results for the principal geometries have been given by Enig and co-workers (Enig, 1956; Enig, Shanks and Southworth, 1956). Results for some of the principal cases are summarized in Table 16.30.

The self-heating parameter δ is a function of the parameters of the reaction and solid mass and of the ambient temperature. There exists, therefore, a critical value of

Table 16.30 *Selected critical values of the ignition parameter δ_c and the center temperature θ_o without reactant consumption for centrisymmetric shapes*

Shape	*Dimension*	ϵ	α	δ_c	θ_o	*Method*[a]	*Reference*
Plane/slab, infinite	Thickness $2r$	0	0	α/e	1	FK	P.M. Thomas (1958)
		0	∞	0.88	1.19	FK	P.M. Thomas (1958)
		0	∞	0.86	1.119	BGH[a]	Boddington, Gray and Harvey (1971b)
		0.02	∞	0.90	1.24	Numerical	Enig, Shanks and Southworth (1956)
		0.06	∞	0.94	1.37	Numerical	Enig, Shanks and Southworth (1956)
Cylinder, infinite	Radius r	0	0	$2\alpha/e$	1	FK	P.M. Thomas (1958)
		0	∞	2.00	1.39	FK	P.M. Thomas (1958)
		0	∞	2.00	1.39	BGH	Boddington, Gray and Harvey (1971b)
		0.02	∞	2.04	1.45	Numerical	Enig, Shanks and Southworth (1956)
		0.06	∞	2.15	1.61	Numerical	Enig, Shanks and Southworth (1956)
Sphere	Radius r	0	0	$3\alpha/e$	1	FK	P.M. Thomas (1958)
		0	∞	3.32	1.61	FK	P.M. Thomas (1958)
		0	∞	3.33	1.62	BGH	Boddington, Gray and Harvey (1971b)
		0.02	∞	3.40	1.68	Numerical	Enig, Shanks and Southworth (1956)
		0.06	∞	3.57	1.87	Numerical	Enig, Shanks and Southworth (1956)
Cube	Side $2r$	0	–[b]	2.52	1.89	Numerical	Parks (1961)[c]
		0.02	–	2.58		Numerical	Parks (1961)
		0.06	–	2.68		Numerical	Parks (1961)
Right cylinder	Radius r, height $2d$; $p = r/d$	0	∞	See formula in footnote[d]			
Cuboid[e]	Sides $2a$, $2b$, $2c$ $p = b/a$; $q = c/a$	0	∞	See formula in footnote[f]			

[a] BGH, Boddington, Gray and Harvey method; FK, Frank–Kamenetsky formulation.
[b] Values of δ_c quoted are those given by Bowes (1984). The corresponding values of α are not given, but Parks gives results for the range $\alpha = 20-100$.
[c] Corrected by Boddington, Gray and Harvey (1971b) and quoted by Bowes (1984).
[d] Bowes gives the relation: $\delta_c \approx 2.0 + 0.84p^2$.
[e] Also referred to as a rectangular brick.
[f] Bowes gives the relation: $\delta_c \approx 2.0 + 0.84(1 + l/p^2 + l/q^2)$.

the ambient temperature that gives a critical value δ_c for the self-heating parameter. As the parameter $\alpha \to \infty$ there is a corresponding critical value of the surface temperature.

16.6.12 Oxidative self-heating

The self-heating reaction is usually, though not invariably, an oxidative one. Then the reaction will typically be governed by the reaction kinetics relation and by the diffusion of oxygen from the atmosphere.

There is relatively little information on the oxidation reactions which occur in self-heating. Models of the reaction frequently assume that it is first order with respect to oxygen concentration with a reaction index $n = 1$. For a number of reactions studied the value of the index n is about 0.7. Others are zero order over a wide range of oxygen concentrations. It is usual to assume that the Arrhenius equation applies, but Bowes warns that it is not always appropriate.

For oxidative self-heating it can be shown by a steady-state analysis that at critical conditions the value of the dimensionless temperature difference θ_o is given by

$$(1 + \epsilon\theta_o)^2\left[1 + (n-1)\frac{\theta_o}{\xi}\right] = \theta_o\left(1 - \frac{\theta_o}{\xi}\right) \qquad [16.6.76]$$

with

$$\theta_o = \frac{E}{RT_a}(T_o - T_a) \qquad [16.6.77]$$

$$\xi = \frac{E}{RT_a}\frac{Q^* D_p C_o}{k} \qquad [16.6.78]$$

where C_o is the concentration of oxygen in the atmosphere, D_p is the diffusion coefficient of oxygen in the pores, n is the index of the concentration term, Q^* is a modified heat release per unit mass, T_o is the temperature at the centre, θ_o

is the dimensionless temperature difference at the centre and ξ is a parameter.

16.6.13 Effect of water

Organic materials tend to be hygroscopic and commonly contain some 10–20% water as a condensed phase. Water can have a strong effect on self-heating but its effect is somewhat complex. Reviews have been given by Walker (1967) and Bowes (1984). Some of the effects are chemical. Water increases the rate of oxidation of many materials. In some cases, however, there can be an inhibiting effect.

Other effects are physical. Water has a high latent heat of vaporization and a correspondingly high heat of adsorption. During self-heating it vaporizes in the hotter regions and condenses again in the cooler regions. The net effect is an appreciable increase in the rate of heat transfer. The presence of water thus increases the effective thermal conductivity of the material. The increase may be by an order of magnitude.

The increase in temperature in the hotter region is retarded by the presence of water as vaporization takes place. The effect usually occurs at temperatures in the range 60–90°C, which is generally well below the temperature at which thermal ignition occurs. Thus this effect tends to manifest itself as an increase in the induction time.

If the vaporization of water occurs fairly uniformly over the temperature range as the material undergoes self-heating, the effect is to reduce the effective heat of reaction. In some cases this may result in the suppression of thermal ignition. This effect is seen in the case of 'overdried' materials. If a material is dried down to a very low water content, the reduction in the effective heat of reaction just described is no longer operative, and the material becomes more prone to thermal ignition.

There is also another effect of water on overdried material. When the material is first exposed to the atmosphere, water is adsorbed and heat is released. This may cause a temperature rise in cool material or may delay a temperature fall in hot material. In either case the base temperature from which any self-heating process starts is increased.

16.6.14 Unsteady-state model

The treatment of self-heating given so far has been based on the assumption of steady state. There are a number of situations in which this assumption breaks down and for which it is necessary to adopt an unsteady-state approach. These include:

(1) reactant consumption;
(2) induction period;
(3) autocatalytic reactions;
(4) hot spots and hot materials;
(5) high ambient temperature;
(6) varying ambient temperature.

The basic equation for self-heating is the unsteady-state Equation 16.6.1 with Equation 16.6.2. This latter equation may be modified to make explicit the dependence on reactant consumption, and then takes the form of Equation 16.6.81.

Consideration is now given to some of the principal aspects of the unsteady state, namely reactant consumption, induction period, autocatalytic reactions, and hot spots and hot materials.

16.6.15 Reactant consumption

In general the reaction equation will be of the form

$$\frac{dC}{dt} = -C^n A \exp(-E/RT) \quad [16.6.79a]$$

$$\frac{dC}{dt} = -\psi(C) A \exp(-E/RT) \quad [16.6.79b]$$

with

$$\psi(C) = C^n \quad [16.6.80]$$

Then Equation 16.6.2 becomes

$$Q = C^n Q'' A \exp(-E/RT) \quad [16.6.81a]$$

$$= \psi(C) Q'' A \exp(-E/RT) \quad [16.6.81b]$$

where C is the concentration of oxygen, Q'' is the modified heat released per unit volume, ψ is a concentration function and n is an index. Then Equation 16.6.3 becomes

$$\rho c \frac{\partial T}{\partial t} = k\left(\frac{\partial^2 T}{\partial x^2} + \frac{j}{x}\frac{\partial T}{\partial x}\right) + C^n Q'' A'' \exp(-E/RT) \quad [16.6.82]$$

Introducing the dimensionless concentration

$$\omega = C/C_o \quad [16.6.83]$$

where C_o is the concentration of oxygen in the ambient air and ω is the dimensionless concentration, and an alternative form of the dimensionless ignition parameter

$$\delta = \frac{E}{RT_a}\frac{r^2}{k} C_o^n Q'' A \exp(-E/RT_a) \quad [16.6.84]$$

Equation 16.6.82 becomes

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial z^2} + \frac{j}{z}\frac{\partial \theta}{\partial z} + \delta \omega^n \exp[\theta/(1+\epsilon\theta)] \quad [16.6.85]$$

and Equation 16.6.79 becomes

$$\frac{d\omega}{d\tau} = -\frac{\delta}{B}\omega^n \exp[\theta/(1+\epsilon\theta)] \quad [16.6.86]$$

with

$$B = \frac{E}{RT_a^2}\frac{C_o Q''}{\rho c} \quad [16.6.87]$$

where B is a dimensionless parameter. The parameter B may be interpreted as a dimensionless adiabatic temperature rise.

For the three principal symmetrical shapes and for general case of finite α the usual boundary conditions for Equation 16.6.85 are

$$z = 0; \quad \frac{d\theta}{dz} = 0 \quad [16.6.88a]$$

$$z = 1; \quad \frac{d\theta}{dz} = -\alpha\theta_s \quad [16.6.88b]$$

and the initial conditions are

$$\tau = 0; \quad \theta = 0; \quad \omega = 1 \qquad [16.6.89]$$

The behaviour of a self-heating mass may be characterized in terms of the parameters B and δ as shown in Figure 16.39. For large values of B, shown in Figure 16.39(a), the profiles of θ are sensitive to δ and there is a value of δ at which there is a relatively sharp transition to thermal explosion. For small values of B, shown in Figure 16.39(b), the profiles of θ are less sensitive, thermal explosion is less well defined and may not occur at all.

It is possible to derive a relation for the critical value as a function of B and n. Let $\delta(B)$ be the initial value δ and $\delta_c(\infty)$ be the critical value of δ at the end of the induction period for $B = \infty$. Then it can be shown that

$$\delta_c(B, n) = \frac{\delta_c(\infty)}{1 - 2.7(n/B)^{2/3}} \qquad [16.6.90a]$$

$$\delta_c(B, n) = \delta_c(\infty)(1 + 2.7(n/B)^{2/3}) \quad B \to \infty \qquad [16.6.90b]$$

The effect of reactant consumption has been studied, particularly for the three principal symmetrical shapes. Results for the centri-symmetric shapes obtained by Tyler and Wesley (1967) using numerical integration are shown in Table 16.31.

16.6.16 Induction period

It is possible to define a number of induction periods. One period of particular interest is the total time from the initiation of a situation leading to thermal explosion to the explosion itself. It is this induction period, which is considered here.

A treatment of the induction period, assuming no reactant consumption, has been given by Zinn and Mader (1960), who performed numerical integration of Equation 16.6.12 for the following case. A body at initial temperature T_i has its surface suddenly raised to a temperature T_s, which exceeds the critical value T_c for thermal explosion. They defined a dimensionless induction period τ_i such that

$$\tau_i = \frac{kt_i}{\rho c r^2} \qquad [16.6.91]$$

where t_i is the induction period and τ_i is the dimensionless induction period. They obtained for the three principal symmetrical shapes the results shown in Figure 16.40. The induction period decreases as the surface temperature increases.

If the surface temperature is raised to one greatly in excess of the critical value, the temperature rise in the solid occurs near the surface rather than at the centre. Zinn and Mader examined this situation also and obtained for the case of a 1 in. sphere of cyclotrimethylene trinitramine, or RDX explosive the results shown in Figure 16.41. It has been

Table 16.31 *Selected critical values of the ignition parameter δ_c with reactant consumption for centrisymmetric shapes (after Tyler and Wesley, 1967) (Courtesy of the Combustion Institute)*

n	B	*Cylinder*			*Sphere*		
		$\epsilon = 0$	0.025	0.05	$\epsilon = 0$	0.025	0.05
0	–	2.000	2.057	2.119	3.322	3.420	3.527
1	1000	2.052	2.113	2.180	3.405	3.510	3.626
1	100	2.248	2.328	2.417	3.722	3.859	4.013
1	25	2.729	2.860	3.010	4.491	4.713	4.965
2	1000	2.082	2.145	2.215	3.453	3.563	3.684
2	100	2.403	2.498	2.606	3.971	4.134	4.321
2	25	3.255	3.443	3.651	5.309	5.610	5.937

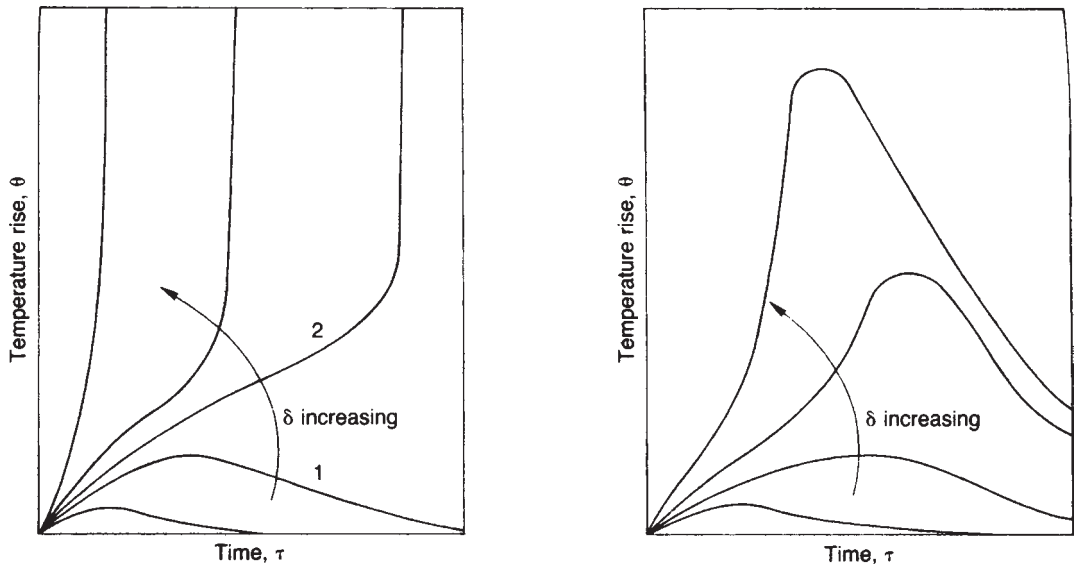


Figure 16.39 *Effect of parameters governing self-heating with reactant consumption (Bowes, 1984). (a) Large B; differences between curves 1 and 2 can result from small changes in δ. (b) Small B; differences between curves can result from large changes in δ (Courtesy of HM Stationery Office. © All rights reserved)*

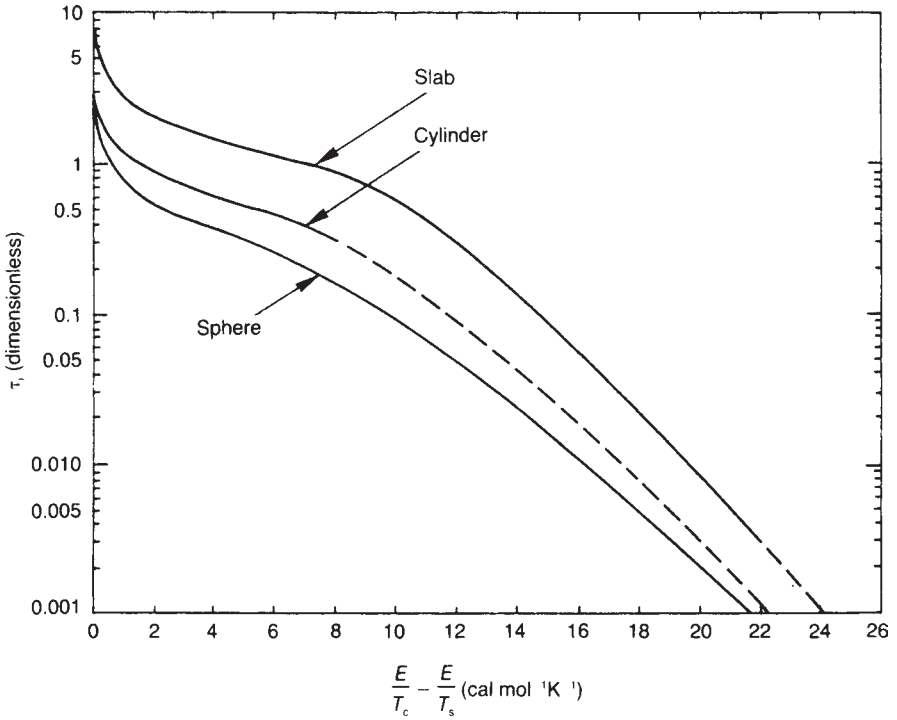


Figure 16.40 *Induction period for self-heating without reactant consumption for three principal centrisymmetric shapes (Zinn and Mader, 1960). Initial temperature $T_o = 298$ K ($< T_c$) (Courtesy of the Journal of Applied Physics)*

shown that the values of for the transition from a central to an annular explosion are approximately as follows:

	δ
Plane slab	9.25
Cylinder	12.25
Sphere	14.25

16.6.17 Autocatalytic reactions

In some cases the self-heating reaction is an autocatalytic one. For this case the reaction may be expressed as

$$\frac{d\phi}{dt} = k(\phi^* + \phi)(1 - \phi) \qquad [16.6.92]$$

where ϕ is the fractional conversion and ϕ^* is the small fractional conversion necessary to initiate the reaction. A quantity χ may be defined as

$$\chi = \frac{\delta}{(1+j)\alpha} \qquad [16.6.93]$$

where χ may be interpreted broadly as the ratio of the rate of heat generation to the rate of heat loss. The critical condition for thermal ignition is

$$\chi = \frac{4}{(1+\phi^*)^2 e} \qquad [16.6.94a]$$

$$\approx \frac{4}{e} \qquad [16.6.94b]$$

and the value of the critical ignition parameter δ_c is

$$\delta_c = \frac{4}{(1+\phi^*)^2} \frac{(1+j)\alpha}{e} \qquad [16.6.95]$$

16.6.18 Thermal explosions of the second kind

As already described, there exist both stable and unstable steady states. A thermal explosion of the second kind involves passage through an unstable steady state. This situation can occur where there is an additional heat source or where there are certain initial conditions. A typical additional heat source might be a wander lamp left lying in a pile of material in a silo. Another form of additional heat source is a parallel reaction. The situation involving initial conditions of particular interest are those relating to hot spots, which are now considered.

16.6.19 Hot spots and hot materials

The topic of hot spots includes the following cases:

(1) reactive hot spots,
(2) inert hot spots and
(3) hot materials.

A hot spot is a limited volume in a mass of reactive material, which is at a temperature above that of the material. The hot spot may be reactive or inert. A hot material in this context is one in which the whole mass of the material is above ambient temperature. It may be

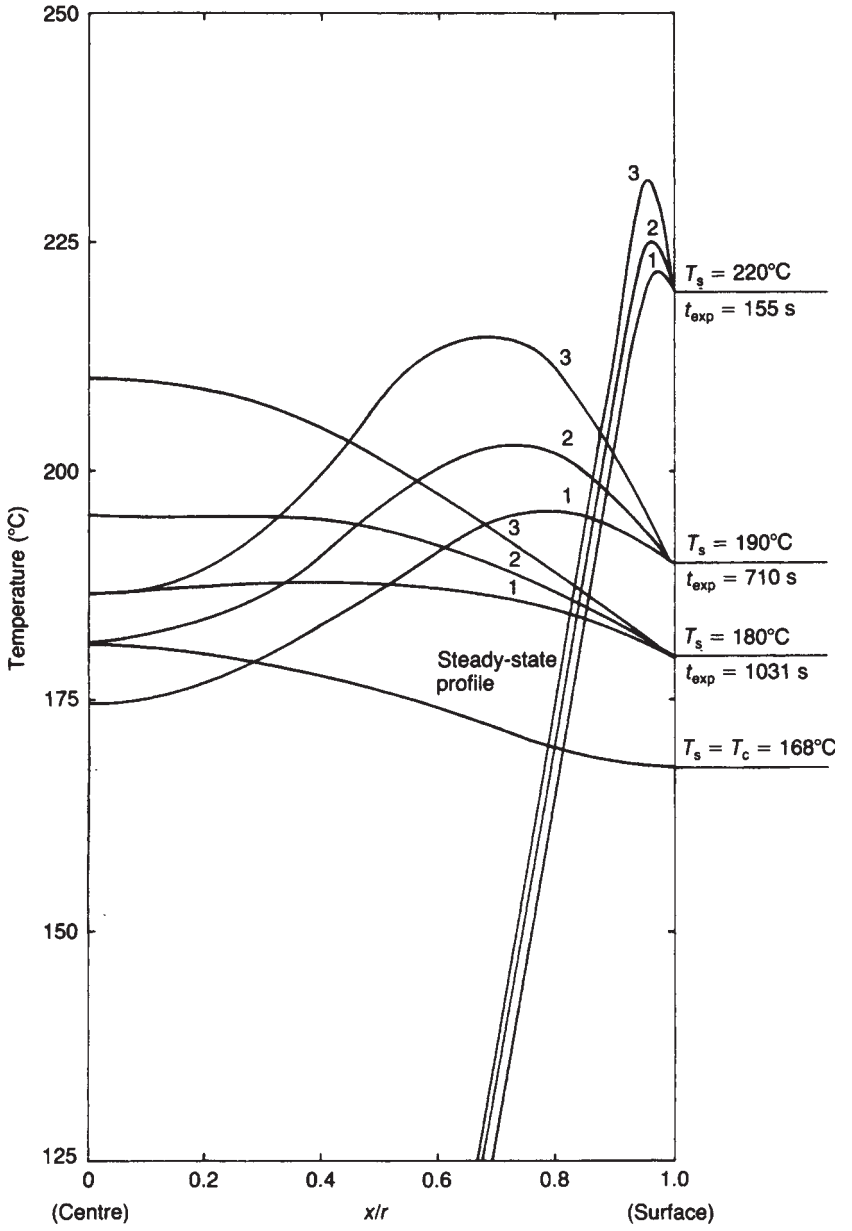


Figure 16.41 *Temperature profiles for a 1 in. sphere of RDX at times close to the end of the induction period (Zinn and Mader, 1960): (1) fraction of time to explosion 0.9; (2) fraction of time to explosion 0.95; (3) fraction of time to explosion 0.98. Initial temperature 25° C. The steady-state temperature profile at the critical temperature T_c is also shown (Courtesy of the Journal of Applied Physics)*

regarded as a form of reactive hot spot in which the hot region extends to the whole mass. The temperature profiles in a hot spot with a 'square' initial temperature distribution are shown in Figure 16.42. The initial temperature profile is given by outline A. An inert hot spot will lose heat to the surrounding medium and the temperature distribution in the early period may then be expected to take a form such as that shown in curve B. A reactive hot spot, however, will generate some heat and, assuming this is appreciable, its temperature distribution in the early period may be expected to take a form such as that shown by curve C.

For a reactive hot spot it has been shown by P.H. Thomas (1973a) that

$$\delta_c \approx \theta_o \psi'(\tau) \qquad [16.6.96]$$

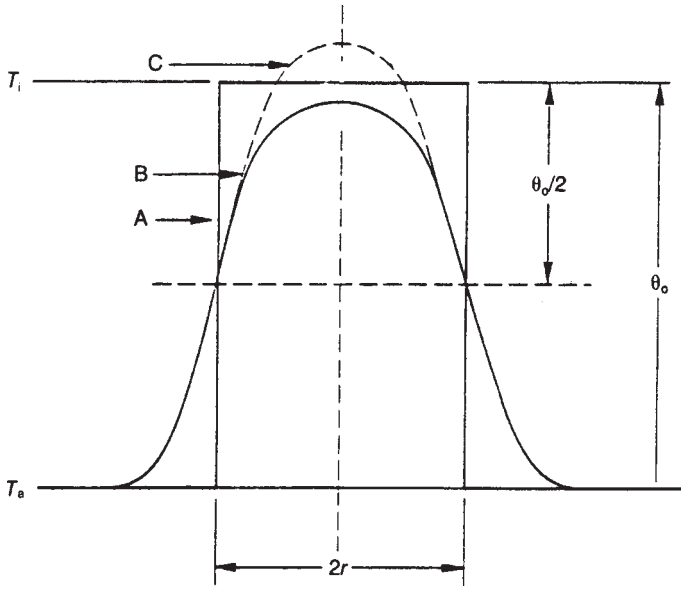


Figure 16.42 *Temperature profiles for a hot spot: A, initial temperature profile of hot spot, reactive or inert; B typical early temperature profile for inert hot spot; and C, typical early temperature profile for reactive hot spot*

with

$$\tau = 1/\delta_c \qquad [16.6.97]$$

where the parameters are defined in terms of the initial temperature T_i of the hot spot so that

$$\delta_c = \frac{E}{RT_i^2}\frac{r^2}{k}Q'\rho A\exp(-E/RT_i) \qquad [16.6.98]$$

$$\theta_i = \frac{E}{RT_i^2}(T_i - T_{im}) \qquad [16.6.99]$$

$$\psi = \frac{T_i - T}{T_i - T_{im}} \qquad [16.6.100]$$

$$\psi' = \frac{d\psi}{d\tau} \qquad [16.6.101]$$

where T_i is the initial temperature of the hot spot, T_{im} is the initial temperature of the medium, θ_i is the initial value of θ in the hot spot and τ is the dimensionless time.

Of particular interest is the solution of Equations 16.6.96–16.6.101 for hot material, where in effect the hot spot extends through the whole mass. In applying these equations use is made of the fact that in the early stages of cooling of an inert hot spot the temperature profiles all tend to intersect at a temperature $\theta_o/2$ as shown in Figure 16.42. Then the value of θ_o used in the treatments for hot materials is one-half of the value of θ_i as given by Equation 16.6.99.

Then for the case where $\alpha \to \infty$, P.H. Thomas (1972) has shown that

$$\psi'(\tau) \approx \frac{\exp(-1/4\tau)}{2\pi^{1/2}\tau^{3/2}} \quad \text{Plane slab} \qquad [16.6.102]$$

$$\psi'(\tau) \approx \frac{\exp(-1/4\tau)}{4\pi^{1/2}\tau^{3/2}} \quad \text{Sphere} \qquad [16.6.103]$$

$$\psi'(\tau) \approx \frac{3\exp(-1/4\tau)}{2\pi^{1/2}\tau^{3/2}}[\mathrm{erf}(1/2\tau^{1/2})]^2 \quad \text{Cube} \qquad [16.6.104]$$

For this case the value of δ_c is obtained from Equation 16.6.96 utilizing Equations 16.6.102–16.6.104. At the other extreme, for $\alpha \to 0$ it can be shown that

$$\psi = 1 - \exp(-\alpha S r\tau/V) \qquad [16.6.105]$$

Then, differentiating Equation 16.6.105 and utilizing Equation 16.6.70 for the three principal symmetrical shapes it is readily shown that

$$\delta_c = \alpha(1+j)\theta_o\exp[-\alpha(1+j)/\delta_c] \qquad [16.6.106a]$$

$$\delta_c \approx \alpha(1+j)\theta_o \quad \theta_o \gg 1; \delta_c \gg 1 \qquad [16.6.106b]$$

Treatments for the inert hot spot tend to be more complex.

16.6.20 Determination of model parameters

The self-heating properties of a porous solid may be characterized in terms of (1) the minimum ignition temperature, (2) the critical characteristic length, (3) the surface heat transfer coefficient and (4) the induction period.

The minimum ignition temperature may be obtained by exposing a body of the material in a defined shape to a series of successively higher temperatures using calorimetric methods and determining the temperature which is just high enough for ignition to occur.

For the critical characteristic length use is made of Equation 16.6.10 with the ignition parameter taken as the critical value δ_c and rearranged to give

$$\ln\left(\frac{\delta_c T_a^2}{r^2}\right) = M - \frac{P}{T_a} \qquad [16.6.107]$$

with

$$M = \ln(Q'\rho AE/Rk) \qquad [16.6.108]$$

$$P = E/R \qquad [16.6.109]$$

where R is the universal gas constant, T_a is the absolute temperature of the air and M and P are parameters.

Then if experiments are conducted with a range of slabs of different sizes and different surface temperatures, pairs of values of r and T_a are obtained. A plot of $\ln(\delta_c T_a^2/r^2)$ vs $1/T_a$ then gives the values of M and P.

Such experiments are in fact usually done using cubes rather than slabs. For a cube, δ_c is 2.6 so that the relation between the critical characteristic length for a cube r_{cb} and for a slab r_{sb} is

$$r_{sb} = r_{cb}(0.88/2.6)^{1/2} \qquad [16.6.110]$$

The commonly used test for the determination of the self-heating parameters M and P is to heat up a cube of the material in an oven under standard conditions and to measure the temperatures in the cube.

For the surface heat transfer coefficient, and hence the Biot number, use is made of Equation 16.6.5. The heat transfer coefficient for convection depends on the shape of the body and on whether the convection is natural or forced. For the case of natural convection and for a small sphere

$$\mathrm{Nu} \approx 2.0 + 0.6\,\mathrm{Pr}^{0.33}\mathrm{Gr}^{0.25} \qquad [16.6.111a]$$

For air, for which $\mathrm{Pr} \approx 0.7$, Equation 16.6.111a can be approximated by

$$\mathrm{Nu} \approx 2.0 + 0.6(\mathrm{Pr\,Gr})^{0.25} \qquad [16.6.111b]$$

$$= 2.0 + 0.6(\mathrm{Ra})^{0.25} \qquad [16.6.111c]$$

with

$$\mathrm{Nu} = \frac{\mathrm{d}h_c}{k_f} \qquad [16.6.112]$$

$$\mathrm{Pr} = \frac{v}{\alpha_f} \qquad [16.6.113]$$

$$\mathrm{Gr} = \frac{gad^3\Delta T}{v^2} \qquad [16.6.114]$$

$$\mathrm{Ra} = \frac{g}{v\alpha_f} d^3 \frac{\Delta T}{T} \qquad [16.6.115]$$

$$a = 1/T \qquad [16.6.116]$$

where a is the volume coefficient of expansion, d is the diameter of the sphere, k_f is the thermal conductivity of the fluid, ΔT is the difference between the surface temperature and the ambient temperature ($T_s - T_a$), is the thermal diffusivity of the fluid and v is the kinematic viscosity of the fluid. Gr, Nu, Pr and Ra are the Grashof, Nusselt, Prandtl and Rayleigh numbers, respectively.

Then from Equations 16.6.111c, 16.6.112 and 16.6.115

$$h_c = \frac{k_f}{d}(2.0 + 0.6\,\mathrm{Ra}^{0.25}) \qquad [16.6.117]$$

The first term in the brackets in Equation 16.6.117 represents film conduction and the second term represents convection. The heat transferred by radiation q is

$$q = \frac{\epsilon_1\epsilon_2}{\epsilon_1 + \epsilon_2 - \epsilon_1\epsilon_2}\sigma(T_s^4 - T_a^4) \qquad [16.6.118]$$

where ϵ_1 is the emissivity of the surface and ϵ_2 is that of the surroundings.

Differentiating Equation 16.6.118 with respect to T_a, and linearizing

$$\frac{\mathrm{d}q}{\mathrm{d}T_a} = 4\frac{\epsilon_1\epsilon_2}{\epsilon_1 + \epsilon_2 - \epsilon_1\epsilon_2}\sigma T_a^3 \qquad [16.6.119a]$$

$$= h_r \qquad [16.6.119b]$$

As an approximation, the values of ϵ_1 and ϵ_2 in Equation 16.6.119a may be taken as unity. Bowes gives the following values for a sphere:

r (mm)	0.6 $\mathrm{Ra}^{0.25}$	h_c (W/m^2 K)	h_r (W/m^2 K)	α	δ_c
1.6	0.87	39	47	2.7	1.80
25.4	8.2	7.1	21	14.1	2.90
279	54	3.2	12.6	88	3.24

In Equation 16.6.117 for the convection heat transfer coefficient the dominant term is the film term at the smaller diameters and the convection term at the larger diameters.

The induction period may be determined by experiment. The results of a number of experiments follow the relation

$$t_i \propto r^2 \qquad [16.6.120]$$

Alternatively, the induction period may be estimated from Figure 16.40.

A material liable to self-heating is often a powder and its self-heating properties therefore depend on the particle size distribution. Experimental determinations of self-heating parameters are valid only for similar material.

16.6.21 Precautions against self-heating

Prevention of self-heating depends on recognition of the hazard, design features, and good housekeeping and adherence to procedures.

If a material may be liable to self-heating, tests may be done to determine first whether this is the case, and, if so, the critical size. Bowes gives the following broad rules of thumb for liability to self-heating in terms of the critical dimension r_c:

$r_c \geq 40$ m Material not liable to self-heating

$r_c \leqslant 10$ m Material liable to self-heating

Materials leaving the process hot can be cooled before being sent to storage. Self-heating of materials in storage and transport can be prevented by using smaller containers and/or by remixing the material periodically. Where oxidative self-heating is involved, measures can be taken to reduce the oxygen content of the ambient gas. One approach is the use of atmosphere control and, in particular, of inerting. Another method is the use of an oxygen barrier such as plastic liners inside paper bags. Polyethylene has been successfully used to prevent self-heating. It is not, however, a totally effective oxygen barrier and may be of limited use for more reactive materials.

Factors that tend to increase safety include the presence of antioxidants and the limitation of the residence time. Conversely, the safety margin is reduced if there is a loss of antioxidants that are normally present or a rise in the residence time above the normal value.

Some materials, such as freshly made activated carbon, heat up appreciably during the first 24 hours after manufacture. The processes involved are probably sorption and oxidation of the most reactive sites. Such materials can be 'weathered' by allowing the material to stand for a period in separate, freshly filled bags.

Self-heating of lagging can be minimized by measures to prevent leaks and by use of suitable lagging thicknesses.

Special measures are required to deal with situations where there is a possibility of a leak such as the EO leaks described in Section 16.6.2. Measures proposed following the investigation of these incidents include avoidance of dead leg pipework and other stagnant zones, reduction of the number of flanges and other possible leak points, measures to ensure leak-tight construction, use of non-absorbent lagging material if possible, inerting of regions at risk, provision of leak detection devices and regular testing for leak tightness and regular inspection for leaked materials. Large flanges may be installed without fire insulation but protected by sprinkler systems instead. The insulation used may be of the two-layer type with an inner material of close cell structure, such as cellular glass, and an outer layer of fire resistant material, with a vapour barrier between to prevent ingress of water and chlorides.

Good housekeeping can reduce self-heating caused by items such as waste rags or dust layers.

16.7 Static Electricity

Static electricity is an important source of ignition in process plants. There have been many apparently mysterious explosions the cause of which was eventually traced to static electricity. On the other hand there has been some tendency in investigations to attribute to static electricity ignitions for which no other cause could be found, even though the positive evidence for static was weak.

There is now much more information available both on the nature and on the prevention of static electricity. But despite this it remains a phenomenon which is often not well understood or appreciated. It is for this reason that a separate section is devoted here to static electricity rather than because it is a statistically dominant source of ignition.

Static electricity is a potential source of ignition wherever there is a flammable mixture of gas or of powder or dust. Accounts of static electricity are given in *Electrostatics in the Petroleum Industry* (Klinkenberg and van der Minne, 1958), *Handbuch der Raumexplosionen* (Freytag, 1965), *Handbook of Industrial Loss Prevention* (FMEC, 1967), *Electrostatic Hazards* (Haase, 1977), *Dust Explosions* (Cross and Fairer, 1982), *Electrostatics* (Cross, 1987), *Electrostatic Hazards and Powder Handling* (Glor, 1988) and *Understanding and Controlling Static Electricity* (Luttgens and Glor, 1989) and by R.V. Wright (1964), J.C. Howard (1964), N. Gibson (1969), J.R. Hughes (1970), Napier (1971) and K.N. Palmer (1973a).

The relevant British Standard is BS 5958: 1991 *Code of Practice for Control of Undesirable Static Electricity* Part 1: 1991 *General Considerations* and Part 2: 1991 *Recommendations for Particular Industrial Situations*. In the USA, NFPA 77: 2000 *Static Electricity* applies.

Selected references on static electricity are given in Table 16.32.

16.7.1 Static electricity in industrial processes

The industrial situations in which undesired static charges are generated are largely those in which two surfaces move

Table 16.32 *Selected references on static electricity*

Pauthenier and Moreau-Hanot (1932); Guest (1938 BM Bull. 638); Smythe (1939); Silsbee (1942); Ktinkenberg and Mooy (1948); NFPA (1950); Cooper (1953a,b); P.H.S. Henry (1953, 1971b); Swann (1953); Bustin, Culbertson and Schleckser (1957); J.C. Howard (1958, 1959, 1964); Klinkenberg (1957, 1959, 1964b, 1967c, 1971); Klinkenberg and van der Minne (1958); McGuire (1958); Saletan (1959a,b); Trevana (1961); Anon. (1962a); Schon (1962a,b, 1965, 1967, 1968); Department of Labor (1963); L. Wright and Ginsburgh (1963, 1964); R.V. Wright (1964); Freytag (1965); Owens (1965); Durand (1966); Eichel (1967); Harper (1967a,b); Herzog (1967); Rees (1967); J.R. Hughes (1970); N. Gibson (1969, 1971, 1983, 1986a, 1990b); Hearfleld (1970); Mahley (1971, 1972); Napier (1971); A.D. Moore (1973); K.N. Palmer (1973a); Strawson (1973); Napier and Rossell (1974); Anon. (1975 LPB 2, p. 1); Barreto (1975); Chubb, Pollard and Butterworth (1975); Horvath and Bertha (1975); Pesetsky and Fisher (1975); PITB (1975 Safety Training Guide 2); Rivera (1975); J.F. Wagner (1975); Bright (1977); Haase (1977); R. King and Magid (1979); Wada, Perlman and Kokado (1979); J.T. Leonard (1981); Cross and Fairer (1982); IBC (1982/29, 1983/43, 1991/80); Ramage, Swithendy and Ross (1982); Bustin and Dukek (1983); Anon. (1986J); Crowley (1986); Cross (1987); Pay (1987 LPB 78); Sproston (1987); Kalisvaart (1988 LPB 79); Liittgens and Glor (1989); Hearn (1991); Britton (1992); Cartwright (1992); Dean *et al.* (1992); Pratt (1993, 1994 LPB 120) BS 5958: 1991–

Prevention

NFPA (1950); Klinkenberg and van der Minne (1958); Shell Chemical Co. (1963); Aron (1964); Beach (1964–); Valko and Tesoro (1964); FMEC (1967); Mallinson (1969); ICI/RoSPA (1970 IS/74); Warren, Lange and Rhynard (1974); Lovstrand (1975); Jowett (1976); J.T. Leonard (1976); G.J. Butterworth (1979a); Denbow and Bright (1979); Felici and Larigaldie (1980); IP (1981 NCSP Pt 3); Cross and Fairer (1982); API (1984 RP 2001, 1991 RP 2003); N. Gibson (1986a); Cross (1987); Kletz (1987d); Luderer (1987); Cartwright (1988); Expert Commission for Safety in the Swiss Chemical Industry (1988); Glor (1988); Mancini (1988); NFPA (2000 NFPA 77); Liittgens and Glor (1989); Taillet *et al.* (1992) BS 5958: 1991–

Earthing, grounding (see Table 10.2)

Fundamental phenomena

Helmholtz (1879); Lenard (1882); Gouy (1910); Chapman (1913); Stern (1924); Peek (1929); Gemant (1933, 1962); Bikerman (1947); Frohlich (1949); Butler (1951); Rutgers and de Smet (1952); Meek and Graggs (1953); Klinkenberg (1957, 1964b, 1967c, 1970); Rutgers, de Smet and Myer (1957); Klinkenberg and van der Minne (1958); Pauthenier (1961); Gavis and Hoelscher (1964); D.K. Davies (1967); Douwes and van der Waarden (1967); M.D.Foster (1967); Gavis (1969); Parsons (1971a); Battocletti (1976); Pohl (1978); Gibbings (1979)

Electrical fields

E. Weber (1950, 1965); Friedlander and Reed (1953); Harries (1953); Meek and Graggs (1953); A.D.Moore (1954); W.E. Rogers (1954); Klinkenberg and van der Minne (1958); Moon and Spencer (1961); Vellenga (1961); Carruthers and Wigley (1962); Heidelberg (1970b); Dakin *et al.* (1974); Penman and Fraser (1983)

Electrostatic charging
Coehn (1898); Russel (1909); Loeb (1945, 1958); Holm (1952); Vick (1953); Wagener (1956); Kragelski and Demkin (1960); Harper (1967a,b); D.K Davies (1970); Gibbings, Saluja and Mackey (1971); Krupp (1971); Bertein (1973); Chives, Mitchel and Rowe (1974); Haenen (1976); Coste and Pechery (1977); Postnikov (1978); Jonassen, Hansson and Nielsen (1979); Cross (1987); Owens (1988); Liittgens and Glor (1989)

Electrostatic discharge
Heidelberg (1959, 1967,1970a); line, Rhodes and Gilmer (1959); Litchfield and Blanc (1959 BM RI 5461); Berz (1961); D.V.Harris, Karel and Ludwig (1961); Bruinzeel (1963); Muller-Hillebrand (1963); N. Gibson and Lloyd (1965); Loeb (1965); J.T. Leonard and Carhart (1967); J.F. Hughes *et al.* (1973); Bertein (1975, 1977); Dorsey (1976); Haig and Bright (1977); J.K. Johnson (1977); Goldman and Goldman (1978); Sigmond (1978); Berta and Gastanek (1979); H. Kramer and Asano (1979); Kalkert and Schecker (1980); Strnad (1980); Glor (1981, 1984, 1988); Guoxiang Li and Wang Changying (1981); Loveland (1981); Lovstrand (1981); Britton and Williams (1982); HSE (1982 OP 5); H.R. Edwards and Underwood (1984); Cross (1987); Glor *et al.* (1987); Maurer *et al.* (1987); Liittgens and Glor (1989); G.M.Williams and Pratt (1990)

Liquid conductivity
Klinkenberg and van der Minne (1958); Schb'n (1962a,b, 1965); Douwes and van der Waraden (1967); Klinkenberg (1967a); H. Kramer and Schon (1973, 1975); P.I. Mason (1975); Rees (1975); J.T. Leonard (1976)

Liquid flow in pipes
Mackeown and Wouk (1942); Cooper (1953a); Boumanns (1957); Hampel and Luther (1957); Klinkenberg and van der Minne (1958); Schuringa and Luttik (1960); Gavis and Koszman (1961); Carruthers and Marsh (1962); Gavis (1964, 1967a,b, 1972); Koszman and Gavis (1962a,b); Schon (1962a, 1965); Klinkenberg (1964a,b, 1967b,c, 1971); Vellenga and Klinkenberg (1965); Gibbings and Hignett (1966); Gibbings (1967); N. Gibson and Lloyd (1967, 1970a,b); Schon and Masuda (1967, 1969); Goodfellow and Graydon (1968a,b); J.T. Leonard and Carhart (1970); N. Gibson (1971); Schon and Kramer (1971); Lauer and Antal (1972); Cross, Haig and Cetronio (1977); Touchard (1978); Touchard and Dumarque (1978); P.I. Mason and Rees (1981); Walmsley and Woodford (1981a,b); Abedian and Sonin (1982); Walmsley (1982, 1983a-c); Britton and Smith (1988); Pratt *et al.* (1989); Watanabe *et al.* (1991)
Ball valves: N. Gibson and Lloyd (1975); Kletz (1989e)
Filters: Cooper (1953a); Schon (1965); Gavis and Wagner (1967, 1968); Masuda and Schon (1967); N. Gibson (1969, 1979); J.T. Leonard and Carhart (1970); Huber and Sonin (1975)

Liquid droplets, bubbles, etc.
Lenard (1882); Raleigh (1882); Iribane and Mason (1967); Jonas and Mason (1968); Levin and Hobbs (1971); Schweitzer and Hanson (1971); Vos (1971); Vos, Ramakers and van de Weerd (1974); Napier and Rossell (1977); Felici (1979); H. Kramer (1981); Castle and Inculet (1991)

Liquid droplet settling
von Smoluchowski (1921); Klinkenberg and van der Minne (1958)

Liquid agitation
Vos *et al.* (1974); H. Kramer (1981)

Liquid aerosols, mists and sprays
C.N. Davies (1966); N. Gibson (1971); J.F. Hughes *et al.* (1973); Napier and Rossell (1973); Bassett (1975); Jennings (1975); J.T. Leonard and Clark (1975); G.J. Butterworth and Dowling (1981); Castle, Inculet and Littlewood (1983); Astbury (1991)
Fire extinguishers, including carbon dioxide: Heidelberg, Nabert and Schb'n (1958a,b); Haessler (1963); Schon and Masuda (1969); Cockram (1971); J.T. Leonard and Clark (1977); Butterworth (1979b); Anon. (1980J); Collocot, Morgan and Morrow (1980); V.T. Morgan, Collocott and Morrow (1981)
Steam, including steam curtains: Napier (1974a); Anon. (1978 LPB 21, p. 81)

Liquid foams
Howells (1993 LPB 114)

Behavior of chemicals
Ethyl acetate: Bond (1994 LPB 119)

Tanks, vessels, including filling
Heidelberg and Schon (1961); VeUenga (1961); Carruthers and Wigley (1962); Bruinzeel (1963); Bustin, Koszman and Tobye (1964); Vellenga and Klinkenberg (1965); M.D. Foster (1967); J.T. Leonard and Carhart (1967); Tinson (1967); Bulkley and Ginsburgh (1968); Schon and Masuda (1969); H. Kramer and Schon (1973, 1975); Diserens, Smith and Bright (1975); Asano, Kramer and Schon (1977); Bright and Haig (1977); P. Lees *et al.* (1981); G.J. Butterworth and Brown (1982); Matsubara (1991); Pratt (1992)

Road and rail tankers, including filling
OIA (Publ.711); D.V. Harris, Karel and Ludwig (1961); Herzog, Ballard and Hartung (1961, 1964); L Wright and Ginsburgh (1963); Holdsworth, van der Minne and VeUenga (1964); Bulkley and Ginsburgh (1968); Mahley and Warren (1968); Lyle and Strawson (1971, 1972, 1973); H. Kramer and Schon (1973, 1975); Strawson and Lyle (1975a,b); H. Kramer, Asano and Schon (1977); Rees (1981); Anon. (1990 LPB 95, p. 5)

Intermediate bulk containers
Ebadat and Cartwright (1991a,b); Britton (1993); Dahn, Kushani and Reyes (1994)

Drums
Pesetsky and Fisher (1975); Britton and Smith (1988); Rosenthal (1988)

Tankers, including tank cleaning
Holdsworth *et al.* (1962); Bustin (1963, 1973–74); Rees (1971); van der Meer (1971); Smit (1971); Vos (1971); van de Weerd (1971, 1972,1975); J.F. Hughes *et al.* (1973); A.W. Bright and Hughes (1975); H.R. Edwards (1983); J.S. Mills and Haighton (1983); J.S. Mills and Oldham (1983); M.R.O. Jones and Bond (1984, 1985); Anon. (1994 LPB 118, p. 14)

Powders and dusts
Boyle and Llewellyn (1950a,b); Mfflller-Hildebrand (1963); N. Gibson (1969, 1970, 1972, 1973b); Lapple (1970); Ramackers (1970); Eden (1971,1972); A.W. Bright (1977); Blythe and Reddish (1979); Lloyd (1979); Anon. (1980 LPB 35, p. 1); Boschung and Glor (1980); Napier (1983); Glor (1984, 1985, 1987, 1988); Maurer (1984); T.B. Jones (1987); Ebadat (1991, 1993); Wolfson Electrostatic Unit (1991); Britton (1993)

Powder flow in pipes: Cole, Baum and Mobbs (1969–70); van de Weerd (1974); Masuda, Komatsu and Lenora (1976); Boschung and Glor (1980); Napier (1983); Touchard *et al.* (1987); Bond (1989 LPB 88); Dahn (1992) Silos: J.F. Hughes *et al.* (1975); Blythe and Reddish (1979); Maurer (1979); Britton (1988); Glor (1988)

Containment and containment materials
Keller and Hoelscher (1957); Heidelberg and Schon (1960); Heidelberg (1970a,b, 1971); N. Gibson and Harper (1981a)

Belts, conveyors
Bulgin (1945); Hubbard (1967, 1971a); Cunningham (1970); Javadi and Napier (1974)

Human body
Bulgin (1945); P.S.H. Henry (1971a); L.G. Wilson and Cavanagh (1972); Movilliat and Monomakoff (1977); N. Wilson (1977, 1979, 1983); Greason (1979); Movilliat and Giltaire (1979); Tolson (1980); R.W. Johnson (1981); Berkey, Pratt and Williams (1988); Bailey, Smallwood and Tomita (1991)

Humidity
Small, Brooksbank and Thornton (1931)

Aircraft systems
Winter (1962); Bruinzeel (1963); D.V. Harris, Karel and Ludwig (1967); Tinson (1967)

Measurements
M.D. Foster and Marsh (1964); Beck *et al.* (1971); Cross (1987); Liittgens and Glor (1989)

relative to each other, with initial contact followed by subsequent separation. When the surfaces are separated, one body tends to be left with a positive charge and the other with a negative charge. If the bodies are good conductors of electricity, the charge moves quite freely and both bodies are effectively restored to their original uncharged state through the last points of contact at separation. But if one or both of the bodies are poor conductors, the charge does not flow freely and both bodies retain charge after separation.

There are many industrial processes that involve surface contact, movement and separation of poorly conducting materials. These processes may be classified in terms of: the phases involved, for example, gas-solid; the general type of system, for example, dusts and powders; or the particular type of process or equipment, for example, pneumatic conveying. Some systems in the process industries where static effects are important are listed, by the phases involved, in Table 16.33. The treatment given below is based on the general type of system. The hazard of static electricity occurs in the process industry in: fluid handling operations such as pipeline flow, settling of drops, agitation, filling of storage tanks, filling of tankers; powder and dust and powder handling operations such as grinding, sieving and pneumatic conveying; in sprays and mists such as in steam cleaning and steam leaks; moving equipment such as conveyor belts and bucket elevators; and the human body.

There are also industrial processes in which static electricity is exploited. They include electrostatic gas filtration and electrostatic spray coating. An account of these processes, which are of minimal interest here, is given by Cross (1987).

Table 16.33 *Some systems in the process industries where static electricity effects are important*

System	
Liquid–solid	Flow of liquid through pipes, filters
	Splash filling of tanks
Liquid–liquid	Mixing of immiscible liquids
	Settling of drops of one liquid through another
Gas–liquid	Cleaning with wet steam
	Spraying with water
	Leakage of wet steam
Gas–solid	Pneumatic conveying
	Fluidized beds
Solid–solid	Belt drives
	Conveyor belts
	Reeling of paper or plastics
	Human body

Static electricity is essentially a phenomenon of low current but high voltage. A low conductivity liquid flowing through a pipeline can generate charge at a rate of 10^{-8}–10^{-4} A. A powder coming out of a grinding mill can carry charge at a rate of 10^{-8}–10^{-4} A. At a charging rate of 10^{-6} A the potential of a container insulated from ground can rise at a rate of 1000 V/s. Potentials of 10,000 V or more are readily obtained in this way.

Objects that can become charged include process materials, process plant and the human body. As long as any of these can remain charged, the electrostatic hazard is not eliminated.

The static charge may discharge causing an incendive spark or it may give a less hazardous corona discharge or may leak away to ground. Sparks from good conductors are more incendive than are those from poor conductors.

The hazard of static electricity may be estimated by comparing the energy of an electrostatic charge with the MIE of flammable gas mixtures and powder or dust suspensions.

Static electricity is a complex phenomenon and it is emphasized that only an outline treatment is given here.

16.7.2 Static ignition incidents

In the past there has often been a tendency in incident investigation where the ignition source could not be identified to ascribe ignition to static electricity. Static is now much better understood and this practice is now less common.

In 1954, a large storage tank at the Shell refinery at Pernis in the Netherlands exploded 40 min after the start of pumping of tops naphtha into straight-run naphtha. The fire was quickly put out. Next day a further attempt was made to blend the materials and again an explosion occurred 40 min after the start of pumping. The cause of these incidents was determined as static charging of the liquid flowing into the tank and incendive discharge in the tank. These incidents led to a major program of work by Shell on static electricity.

An explosion occurred in 1956 on the *Esso Paterson* during loading at Baytown, Texas, the ignition being attributed to static electricity.

In 1969, severe explosions occurred on three of Shell's very large crude carriers (VLCCs): the *Marpesa*, which

sank, the *Mactra* and the *King Haakon VII*. In all three cases tanks were being cleaned by washing with high pressure water jets, and static electricity generated by the process was identified as the ignition source. Following this set of incidents Shell initiated an extensive program of work on static electricity in tanker cleaning.

Explosions due to static ignition occur from time to time in the filling of liquid containers, whether storage tanks, road and rail tanks or drums, with hydrocarbon and other flammable liquids.

Explosions have also occurred due to generation of static charge by the discharge of carbon dioxide fire protection systems. Such a discharge caused an explosion in a large storage tank at Biburg in Germany in 1953, which killed 29 people. Another incident involving a carbon dioxide discharge occurred in 1966 on the tanker *Alva Cape*.

The majority of incidents have occurred in grounded containers. Grounding alone does not eliminate the hazard of static electricity.

These incidents are sufficient to indicate the importance of static electricity as an ignition source. Further incidents attributed to static electricity are described in Case Histories B36, B56 and B61.

16.7.3 Some basic relations

In work on static electricity it is often necessary to distinguish between the potential ϕ at a point and the potential difference, or voltage, V between two points. Where one point is grounded and the other is not, the potential and the voltage are the same.

Some of the fundamental relations of static electricity are as follows.

Ohm's law

Ohm's law states that

$$V = IR \qquad [16.7.1]$$

where I is the current (A), R is the resistance (Ω), and V is the potential difference, or voltage (V).

Definitions

The following relations are effectively definitions:

$$R = \frac{V}{I} \qquad [16.7.2]$$

$$G = \frac{1}{R} \qquad [16.7.3]$$

$$\rho = \frac{RA}{l} \qquad [16.7.4]$$

$$\kappa = l/\rho \qquad [16.7.5]$$

$$C = \frac{q}{V} \qquad [16.7.6]$$

$$\sigma = \frac{q}{A} \qquad [16.7.7]$$

$$s = \frac{q}{V_{cn}} \qquad [16.7.8]$$

$$\epsilon = \frac{\epsilon_a}{\epsilon_o} \qquad [16.7.9]$$

where A is the area (m^2), C is the capacitance (F), G is the conductance (S), l is the length (m), q is the charge (C), s the space charge density (C/m^3), V_{cn} is the volume of the containment (m^3), ϵ is the relative permittivity, or dielectric constant, ϵ_a is the absolute permittivity (F/m), ϵ_o is the permittivity of free space (F/m), κ is the conductivity (S/m), ρ is the volume resistivity (Ω m) and σ is the surface charge density (C/m^2). The volume resistivity ρ is frequently referred to simply as the resistivity.

Field strength and force

The field strength E is defined as

$$E = -\frac{dV}{dx} \qquad [16.7.10]$$

or

$$E = -\frac{V}{x} \qquad [16.7.11]$$

where E is field strength (V/m) and x is the distance (m). Frequently the negative sign in Equation 16.7.11 is dropped, since it is only the magnitude of the voltage or field strength that is of interest.

The force F_e on a body due to the charge on it and to the field in which it is placed is

$$F_e = qE \qquad [16.7.12]$$

where F_e is force (N). For a gravitational field

$$mg = qE \qquad [16.7.13]$$

where g is the acceleration due to gravity (m/s^2) and m is the mass of the body (kg).

Charge, energy and work

The charge accumulated on a body charged by a current is

$$\frac{dq}{dt} = I \qquad [16.7.14]$$

The energy W on a charged body is

$$\frac{dW}{dq} = V \qquad [16.7.15]$$

$$= \frac{q}{C} \qquad [16.7.16]$$

where W is work, or energy (J).

Then, integrating Equation 16.7.16,

$$W = \frac{1}{2}\frac{q^2}{C} \qquad [16.7.17]$$

$$= \frac{1}{2}qV \qquad [16.7.18]$$

$$= \frac{1}{2}CV^2 \qquad [16.7.19]$$

Equation 16.7.19 also gives the energy of discharge when there is discharge of the full charge on a charged body. If there is a partial discharge from potential V_1 to potential V_2, the energy of discharge is

$$W = \frac{1}{2}C(V_1^2 - V_2^2) \qquad [16.7.20]$$

Surface charge density and displacement
The surface charge density a is proportional to the field-strength E. For a unidirectional field

$$\sigma \propto E \quad [16.7.21a]$$
$$= \epsilon_a E \quad [16.7.21b]$$
$$= \epsilon\epsilon_o E \quad [16.7.22]$$

For a bidirectional field

$$\sigma = \epsilon_1\epsilon_o E_1 + \epsilon_2\epsilon_o E_2 \quad [16.7.23]$$

where subscripts 1 and 2 denote the two fields.

Another quantity that is used is the displacement D which is defined as

$$|D| = \sigma \quad [16.7.24]$$

Then

$$D \propto E \quad [16.7.25a]$$
$$= \epsilon_a E \quad [16.7.25b]$$
$$= \epsilon\epsilon_o E \quad [16.7.26]$$

where D is the displacement (C/m^2).

Time constant
The time constant for charging and discharge of a liquid is

$$\tau = \frac{\epsilon\epsilon_o}{\kappa} \quad [16.7.27]$$
$$= \epsilon\epsilon_o\rho \quad [16.7.28]$$

where τ is the time constant (s).

16.7.4 Laws of Coulomb, Gauss and Poisson

Coulomb's law
It was shown by Coulomb that the force between two charged bodies is proportional to each of the charges on the two bodies and inversely proportional to the square of the distance between them. In electrostatic units:

$$F_e = \frac{qq'}{x^2} \quad [16.7.29]$$

where q is the charge on one of the bodies (C), q' is the charge on the other body (C) and x is the distance between them (m). In SI units

$$F_e = \frac{qq'}{4\pi\epsilon\epsilon_o x^2} \quad [16.7.30]$$

where F_e is the force (N), q is the charge on one of the bodies (C), and q' is the charge on the other body (C).

Coulomb's law was originally derived by experiment, but has subsequently been demonstrated theoretically.

It follows from Equations 16.7.12 and 16.7.30 that

$$E = \frac{q'}{4\pi\epsilon\epsilon_o x^2} \quad [16.7.31]$$

Gauss' law
Gauss' law may be stated as

$$\nabla D = s \quad [16.7.32]$$

which in Cartesian co-ordinates becomes

$$\frac{\partial V}{\partial x} + \frac{\partial V}{\partial y} + \frac{\partial V}{\partial z} = s \quad [16.7.33]$$

where x, y and z are the spatial co-ordinates (m). It may also be written for a cloud surface S as

$$\int D\,dS = \sum q \quad [16.7.34]$$

or, from Equations 16.7.26 and 16.7.34,

$$\int E\,dS = \frac{\sum q}{\epsilon\epsilon_o} \quad [16.7.35]$$

or for constant E

$$ES = \frac{\sum q}{\epsilon\epsilon_o} \quad [16.7.36]$$

Whereas Coulomb's law applies to a point source, Gauss' law is more widely applicable. It is used particularly to estimate capacitance and charge, given the limiting breakdown field strength of air. Several applications of Gauss' law are given below.

Poisson's law
Poisson's law, or equation, is

$$\nabla^2 V = -\frac{s}{\epsilon\epsilon_o} \quad [16.7.37]$$

which in Cartesian co-ordinates becomes

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = -\frac{s}{\epsilon\epsilon_o} \quad [16.7.38]$$

In general, applications of Poisson's equation tend to be relatively complex and often involve numerical solution. However, some applications of the equation are given below.

The laws of Coulomb, Gauss and Poisson are all formulations of the same physical law. They relate the charge, the potential and the field strength.

16.7.5 Charge

The charge on a body is expressed as the total charge q, the surface charge density σ or the space charge density s.

Sphere (uniform surface charge density)
For a sphere with uniform space charge density the charge is

$$q = 4\pi a^2\sigma \quad [16.7.39]$$

where a is the radius of the sphere (m).

Sphere (uniform space charge density)
For a sphere with uniform space charge density the charge is

$$q = \frac{4}{3}\pi a^3 s \qquad [16.7.40]$$

Cylinder (uniform space charge density)
For a cylinder with uniform space charge density the charge per unit length is

$$q = \pi r^2 s \qquad [16.7.41]$$

Maximum surface charge
From Gauss' law, as given by Equation 16.7.36, and from Equation 16.7.22, the maximum surface charge on an insulating surface is

$$\sigma_{max} = \epsilon\epsilon_o E_b$$
$$= 2.64 \times 10^{-5}\ \mathrm{C/m^2}$$

where E_b is the breakdown field strength (V/m)

16.7.6 Capacitance

Given the charge on a body, the field strength, potential and capacitance may be obtained from Equations 16.7.6, 16.7.11 and 16.7.22. In this section the general approach to the determination of the capacitance of a system is illustrated for the cases of parallel plates and an isolated sphere and expressions are given for the capacitance of some other common systems. The capacitance of some common objects is also given. Field strengths are treated in the following section.

Parallel plates
For the capacitance of two parallel plates, Equation 16.7.22 yields

$$q = \epsilon\epsilon_o AE \qquad [16.7.42]$$

and Equation 16.7.10 yields

$$V = Ex \qquad [16.7.43]$$

where A is the area of each plate (m^2) and x is the distance between the plates (m). Combining Equations 16.7.42 and 16.7.43

$$q = CV \qquad [16.7.44]$$

with

$$C = \frac{\epsilon\epsilon_o A}{x} \qquad [16.7.45]$$

Isolated sphere
For the capacitance of an isolated sphere, Equation 16.7.22 yields

$$q = 4\pi r^2 \epsilon\epsilon_o E \qquad [16.7.46]$$

and Equation 16.7.10 yields

$$V = -\int_{\infty}^{a} E\,\mathrm{d}r \qquad [16.7.47]$$

where r is the radial distance (m).

Hence, substituting for E in Equation 16.7.47 and integrating gives

$$q = CV \qquad [16.7.48]$$

with

$$C = 4\pi\epsilon\epsilon_o a \qquad [16.7.49]$$

Concentric spheres
The capacitance of two concentric spheres is

$$C = 4\pi\epsilon\epsilon_o \frac{ab}{b-a} \qquad [16.7.50]$$

where a and b are the radii of the smaller and larger spheres (m), respectively.

Sphere and plane
The capacitance of a sphere adjacent to a plane is

$$C = 4\pi\epsilon\epsilon_o a[\psi + 0.5\ln(2a/z)] \qquad [16.7.51]$$

where z is the distance from the nearest point on the sphere to the plane (m) and ψ is Euler's constant. The value of Euler's constant is 0.577.

This system was originally studied by Russel (1909) and is treated by Cross (1987).

Coaxial cylinders
The capacitance of two coaxial cylinders is

$$C = \frac{\epsilon\epsilon_o 2\pi l}{\ln(r_2/r_1)} \qquad [16.7.52]$$

where l is the length of the cylinders (m) and r_1 and r_2 are the radii of the inner and outer cylinders (m), respectively.

Parallel cylinders
The capacitance of two parallel cylinders is

$$C = \frac{\pi\epsilon\epsilon_o l}{\ln\left[\dfrac{a + (a^2 - r^2)^{\frac{1}{2}}}{r}\right]} \qquad [16.7.53]$$

where a is the half-distance between the axes of the cylinders (m) and r is the radius of each cylinder (m).

Common objects
The capacitance of some common objects is given in Table 16.34.

16.7.7 Field strength and breakdown

Permittivity
The permittivity of a substance or medium is generally expressed in terms of its relation to the permittivity of free space. The relative permittivity, or dielectric constant, ϵ of a substance is the ratio of the absolute permittivity of that substance ϵ_a to the permittivity ϵ_o of free space, as given by Equation 16.7.9. Another notation that is quite widely used is to denote the absolute permittivity of a substance as ϵ and the relative permittivity as ϵ_r. The permittivity ϵ_o of free space is

$$\epsilon_o = 8.55 \times 10^{-12}\ \mathrm{F/m}$$

Table 16.34 *The capacitance of some selected objects*[a]

Object	*Capacitance*[b] (pF)
Single bolt	1
Tools	5
Small metal item (scoop, hose nozzle)	10–20
Flange (100 mm nominal)	12 (10–15)
Shovel	20
Small container (bucket, 50 l drum)	20 (10–100)
Medium container (250–500 l)	30–300
General plant item[c]	100–1000
Road tanker	1000
Human body	200 (100–300)

[a] *Sources*: N. Gibson (1969); BS 5958: Part 1: 1980; Expert Commission (1988); Glor (1988); Luttgens and Glor (1989).
[b] Approximate values.
[c] Item immediately surrounded by grounded structure.

The relative permittivity, or dielectric constant, of air is about 1, that of hydrocarbons about 2, and that of water about 80.

Parallel plates
From Equation 16.7.42 the field strength between two parallel plates with one at potential V and the other at zero potential is

$$E = \frac{q}{\epsilon\epsilon_o A} \qquad [16.7.54]$$

where A is the area of each plate (m^2).

Isolated sphere
From Equation 16.7.46 the field strength at the surface of an isolated sphere is

$$E = \frac{q}{4\pi\epsilon\epsilon_o a^2} \qquad [16.7.55]$$

where a is the radius of the sphere (m).

Infinite parallel plates (uniform space charge density)
The maximum field strength between two infinite parallel plates with a uniform charge density between them and with both at zero potential occurs at the boundary and is

$$E = \frac{sx}{\epsilon\epsilon_o} \qquad [16.7.56]$$

where x is the half-distance between the plates (m).

Sphere (uniform space charge density)
The maximum field strength in a sphere with a uniform space charge density and with zero potential at the boundary is

$$E = \frac{sa}{3\epsilon\epsilon_o} \qquad [16.7.57]$$

where a is the radius of the sphere (m).

This equation is often applied to systems that approximate a sphere such as a cubic storage tank.

For a sphere with a uniform space charge density exerting fields both inside and outside the sphere the field strengths are

$$E = \left(\frac{s}{3\epsilon\epsilon_o}\right) r \quad r \le a \qquad [16.7.58a]$$

$$E = \frac{s}{3\epsilon\epsilon_o}\frac{a^3}{r^2} \quad r > a \qquad [16.7.58b]$$

where r is the radial distance (m).

It can be shown by Gauss' law that the field strength outside a sphere is the same if the total charge q is (1) concentrated at one point, (2) uniformly distributed in space in the sphere and (3) uniformly distributed over the surface of the sphere.

The relation between the field strength and the potential on a sphere is as follows. From Equation 16.7.10, for the sphere

$$V = \int_a^\infty E\, dr \qquad [16.7.59]$$

Then from Equations 16.7.40, 16.7.58 and 16.7.59

$$E = V/a \qquad [16.7.60]$$

Cylinder (uniform space charge density)
The maximum field strength in an infinite cylinder with a uniform space charge density and with zero potential at the boundary is

$$E = \frac{sr_c}{2\epsilon\epsilon_o} \qquad [16.7.61]$$

where r_c is the radius of the cylinder (m). This equation is often applied to pipes.

For a cylinder with a uniform space charge density exerting fields both inside and outside the cylinder the fields' strengths are

$$E = \left(\frac{s}{2\epsilon\epsilon_o}\right) r \quad r \le r_c \qquad [16.7.62a]$$

$$E = \frac{s}{2\epsilon\epsilon_o}\frac{r_c^2}{r} \quad r \ge r_c \qquad [16.7.62b]$$

Coaxial cylinders (uniform space charge density)
The field strengths at the surfaces of the inner and outer cylinders in a system of two coaxial cylinders with a uniform charge density in the space between them are, respectively

$$E_i = \frac{sr_o}{4\epsilon\epsilon_o}\left[2\beta + \frac{1-B^2}{B\ln B}\right] \qquad [16.7.63]$$

$$E_o = \frac{sr_o}{4\epsilon\epsilon_o}\left[2 + \frac{1-B^2}{B\ln B}\right] \qquad [16.7.64]$$

with

$$B = r_i/r_o \qquad [16.7.65]$$

where E_i and E_o are the field strengths at the surfaces of the inner and outer cylinders (V/m) and r_i and r_o are the radii of the inner and outer cylinders (m). If $r_i \ll r_o$

$$E_i = \frac{sr_o}{4\epsilon\epsilon_o}\frac{1}{B\ln B} \quad [16.7.66]$$

$$E_o = \frac{sr_o}{2\epsilon\epsilon_o} \quad [16.7.67]$$

These equations have been applied to the case of a cable hanging inside a storage tank.

Tanks fully and partially filled

A detailed treatment of the field strengths in fully and partially filled tanks is given by Hinkenberg and van der Minne (1958) and further treatments are described below.

Field breakdown

The breakdown field strength E_b of air at atmospheric pressure is usually given as

$$E_b = 3 \times 10^6\,\text{V/m} = 3000\,\text{kV/m} = 3\,\text{MV/m}$$

In fact, the breakdown field strength is a function of the electrode gap. Klinkenberg and Van der Minne give the following data for the critical field strength between large parallel electrodes in air at atmospheric pressure:

Electrode gap (mm)	*Critical field strength* (kV/m)
0.6	5220
10	3150
100	2650
Large gap	2240

Figure 16.43 gives the breakdown field strength in air over a somewhat wider range.

According to a relationship usually known as Paschen's law, the breakdown field strength is a function of the product Pl of the pressure P and the gap l, where P is pressure (bar) and l is gap width (m). Figure 16.44 shows the breakdown voltage V for air as a function of Pl. For values of $Pl > 10^{-3}$ bar m, this graph is consistent with a constant breakdown field strength of 3000 kV/m.

16.7.8 Electrostatic charging

The conditions for a significant accumulation of electrostatic charge are that there occurs some process, which generates the charge, and that any process of charge dissipation is sufficiently slow.

There are a number of mechanisms by which an electrostatic charge can build up. The mechanisms of principal interest here are (1) contact and separation, (2) induction, (3) double layer separation and (4) charge sharing. Other mechanisms include (5) corona charging, (6) diffusion charging, and (7) particle capture.

Most accounts of the generation of static electricity begin with a discussion of the electrostatic phenomena involved in the contact and separation of surfaces, in the first instance solid surfaces. If two different materials are rubbed together, so that there is first contact and then separation of their surfaces, charges build up on the surfaces of the two materials, one material having a charge of one polarity and the other a charge of opposite polarity.

Modern theory, stemming from work on solid-state physics, treats electrostatic phenomena in terms of electron transfer. If the temperature of a surface is high enough, electrons are emitted from it. This emission is characterized by the electron work function. The work function is lower in conducting materials and higher in insulating ones.

If the surfaces of two different materials at the same temperature are brought into contact, electron transfer occurs. The material with the lower work function is the donor and that with the higher work function the acceptor. Electrons migrate from the former to the latter, so that the acceptor acquires a negative charge and the donor a positive one. At equilibrium the potential difference due to the difference in the two work functions is equal to that due to the charge transfer. The proportion of electrons transferred is very small, at most eight in a million.

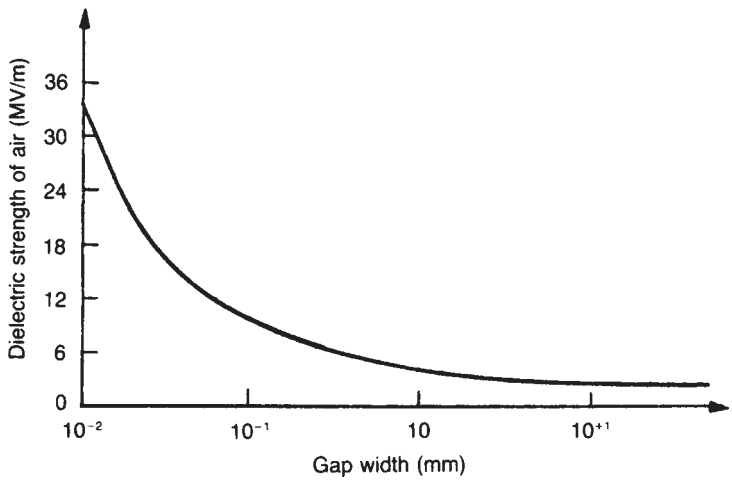


Figure 16.43 *Dielectric strength of air (Glor, 1988): effect of gap width (Courtesy of Research Studies Press)*

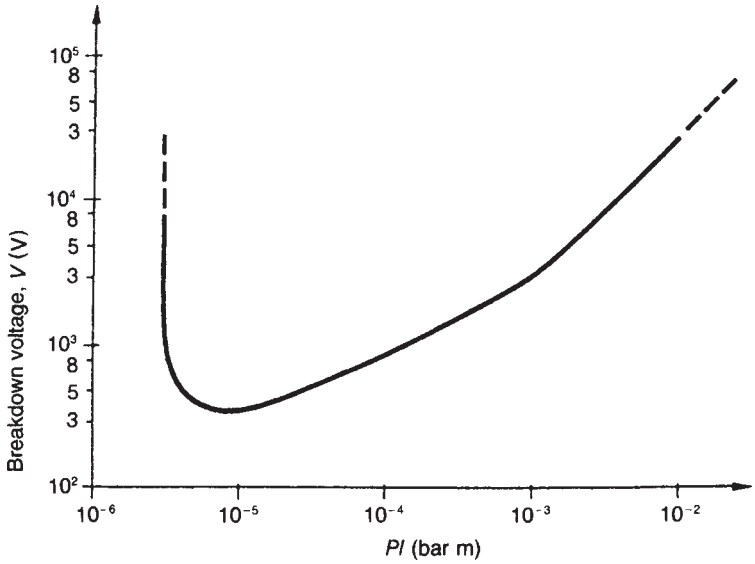


Figure 16.44 *Dielectric strength of air (Glor, 1988): the effect of group Pl (Courtesy of Research Studies Press)*

If the two surfaces are then separated, charge separation also occurs. Provided charge dissipation is limited, one material retains a negative charge and the other a positive charge. The two processes of contact and separation comprise the process of charge generation.

Charge is also generated between two surfaces of the same material at different temperatures.

The nature of the charges depends on the permittivity of the two materials. According to Coehn's (1898) laws':

(1) the body with the higher permittivity has the positive charge;
(2) the magnitude of the charge is a function of the difference in the permittivities of the two materials.

These laws' are, however, controversial. For one thing, as just stated, charge generation can occur between surfaces of the same material.

Materials may be ranked in a triboelectric series. Charge generation is larger for two materials far apart in the series. However, there is no standard triboelectric series, different versions being given by different authorities. Before separation the distance between the surfaces will be very small, of the order of 10^{-9} m. After separation the capacitance is greatly decreased due to the large increase in the distance between the surfaces. The charge remains constant. The voltage is therefore greatly increased ($q = CV$). The energy is also greatly increased ($W = qV/2$). Energy is supplied to the system as work done in moving the two charges apart.

The model just given is a highly simplified one. In particular, it is based exclusively on electron transfer and takes no account of ion transfer. There are some phenomena that are more readily explained by ion transfer. For example, glass may acquire a negative or a positive charge, depending on whether it has previously been in contact with acid or with alkali. An account of ion transfer is given by Cross (1987).

In discussing charging by contact and separation, Cross draws a distinction between contact and friction charging and states that the failure to distinguish between them has been the cause of much confusion. Friction charging can occur even between identical materials. It is probably a surface temperature effect.

However, some workers prefer to avoid the terms 'contact' and 'friction' altogether. There is no dispute that actual charge accumulation happens when separation occurs, and to this extent the term 'separation charging' may be preferred. Liittgens and Glor (1989) argue that 'friction charging' is also a misnomer in that charge accumulation has nothing to do with friction *per se*, but is an effect of surface temperature.

Some of the factors which influence the magnitude of charge accumulation in separation charging include (1) the temperature of the surfaces, (2) the permittivity, (3) the number and density of contact points, (4) the electrical conductivity, (5) the speed of separation and (6) changes in the condition of the materials.

The temperature of the surfaces is a fundamental factor determining the extent of electron transfer.

Coehn's laws, as already discussed, describe the effect of permittivity.

The number and density of contact points depends on the force on the two surfaces. Work on a series of metals and polymers has been done by Haenen (1976), who obtained the relation

$$q \propto F_c^n \qquad [16.7.68]$$

where F_c is the force (N/m^2), q is the charge generated (C) and n is an index. The value of n was in the range 0.3–1.0.

The higher the conductivity of the materials, the greater the extent to which any charge generated is neutralized.

If both bodies are poor conductors, both will become charged. Of one body is a good conductor and grounded, the charge on that body will flow to ground. If one body is a good conductor but not grounded, the charge will distribute itself over the body. In this way a considerable charge may build up.

The speed of separation is another factor governing the extent of charge neutralization. The higher the speed of separation, the less time there is available for charge neutralization to occur.

Physical changes in the condition of the materials, such as expansion and compression, must have some effect, but are not well documented. Another important mechanism of charging is induction. Induction charging occurs only where the body is a conductor. If a body that is an isolated conductor is placed in an electrical field, charges of different polarity are induced on opposite sides. If then a grounded electrode touches, or even approaches close to, this body, the charges close to the electrode flow away, leaving the body with a charge of opposite sign.

This effect may be illustrated by the situation shown in Figure 16.45. In Figure 16.45(a) the man, wearing nonconducting footwear approaches a positively charged conveyor belt. A negative charge is induced on the upper part of his body on the side nearer the belt, and a positive charge on the lower part. In Figure 16.45(b) he touches a grounded point on the conveyor and the negative charge leaks to ground. In Figure 16.45(c) he is left with a positive charge, which equalizes over his body.

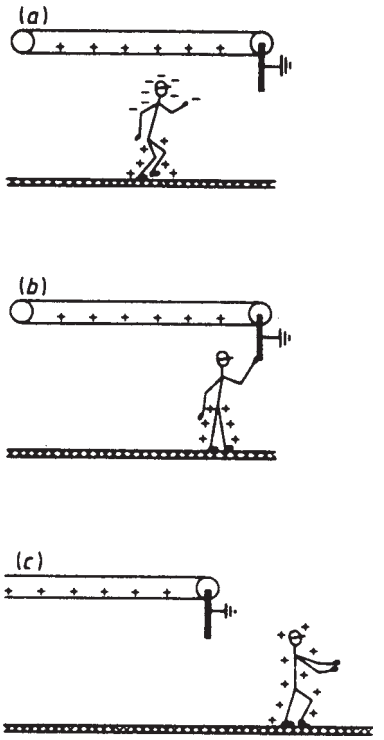


Figure 16.45 *Inductive charging of the human body (Cross, 1987): (a) the charge separates in the field due to the charged belt; (b) the charge from top of the body flows to ground; and (c) the body is left with a net charge (Courtesy of Adam Hilger)*

Liquids also can be charged by induction. A charging mechanism that is particularly important for liquids is double layer separation. If an ionic substance is dissolved in a liquid of high dielectric constant, the ions are dissociated and in an electrical field they move in opposite directions. An example of such a situation is sodium chloride ions in water. At an interface such as a pipe wall ions of one charge will be held strongly, while those of the other charge will be held less strongly and will form a diffuse layer. For a liquid with conductivity as high as that of water, the diffuse layer will be only a few molecules thick. Liquids such as hydrocarbons, however, also contain some ions. For these liquids, which have much lower conductivity, the diffuse layer will be much thicker.

There are a number of models of the double layer, as shown in Figure 16.46. The original model was that of Helmholtz (1879). In the Helmholtz model, shown in Figure 16.46(a), the layer of counter ions is compact, in the Guoy-Chapman model (Guoy 1910, 1917; Chapman, 1913), shown

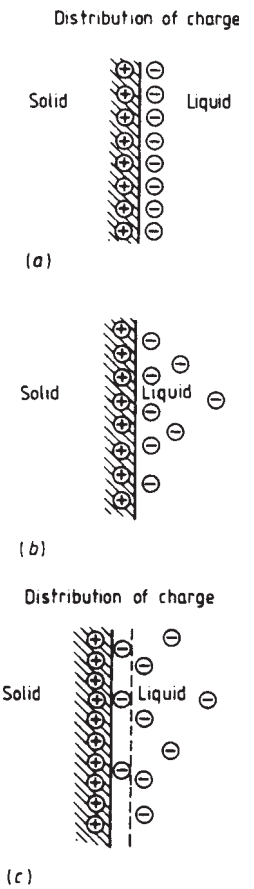


Figure 16.46 *Double layer at a solid-liquid interface (Cross, 1987): (a) Helmholtz model; (b) Gouy-Chapman model; and (c) stem model (Courtesy of Adam Hilger)*

in Figure 16.46(b) the layer is more diffuse, while in the Stern model (Stern, 1924), shown in Figure 16.46(c), the layer of counter ions partly compact and partly diffuse. If the liquid moves through the pipe, the diffuse layer moves with the liquid and charge separation occurs.

Some of the factors that influence the magnitude of charge accumulation in liquid double layer separation include (1) permittivity, (2) electrical conductivity and (3) speed of separation. The effects of these variables are discussed below.

Charge accumulation over time is not necessarily a simple monotonic process. There are three principal patterns of charge accumulation, as shown in Figure 16.47. The charge may either (1) rise to a maximum and stay there, (2) rise to a maximum and then stabilize at a lower plateau, or (3) rise to a maximum, fall to zero and then stabilize at a plateau of opposite sign.

The time taken to reach the maximum value may be characterized by the half-life, which is a function of the materials.

Charge sharing occurs when two bodies, at least one of which is charged, come into contact and charge passes from one to the other. It is relevant particularly to mists and dusts.

Corona charging can be used to create a defined charge on a body for experimental purposes. An account is given by Cross (1987).

Diffusion charging of particles occurs as a result of collisions between particles and ions in a gas. Particle capture, particularly the capture of small particles by larger ones, is another mechanism of charging.

In certain situations it is possible to calculate the limiting charge density. The limiting factor is the charge, which gives an electric field strength equal to the breakdown field strength of air. Gauss' law, given below, may be used to determine the limiting surface charge densities and also the limiting volume charge densities.

Little has been said so far about the polarity of the charge. This is important in some applications, as described below.

Processes in which charge separation occurs include: (1) flow of liquids, (2) transfer of liquids, (3) size reduction, (4) transfer of powders, (5) reeling processes and (6) rotation of belts.

16.7.9 Electrostatic charge accumulation, retention and relaxation

The charging processes described lead to an accumulation of charge in the system. In the general case this input of charge is balanced by an output. This output may take various forms. Charge may be carried away in material leaving the system or it may leak away to ground. The equivalent electrical diagram such as that shown in Figure 16.48 commonly represents this situation.

One common case is where the charging current on an object is balanced by the leakage current so that the system is at steady state. Then the voltage V of the object is then related to the charging current I and the resistance R to ground by Equation 16.7.1 (Ohm's law).

This situation is relevant to grounding. If the charging current is known, it is possible to ensure that the voltage does not exceed a specified limit by ensuring a suitable resistance to ground. The limit on the voltage is generally set in order to avoid an incendive spark. The limiting factor may be the need to avoid a field strength, which causes breakdown or the need to avoid an accumulation of energy that equals the MIE of the flammable mixture. The energy accumulated also depends on the capacitance of the object. Table 16.35 gives typical electrostatic potentials and spark energies quoted for charged objects.

Another common case is where material undergoes a transition from a situation where it was being charged to one where the charging reduces or ceases. It is then able to dissipate this charge, usually by leakage to a containment and so to ground. This process is known as relaxation. It is relevant particularly to liquids. Where a liquid has acquired a charge, arrangements may be made to allow the charge to relax. In a flow system these take the form of providing residence time, while in a storage or tanker system they involve allowing time to elapse before operations are undertaken.

Some of the relations commonly used for the charging and discharge of a system are as follows.

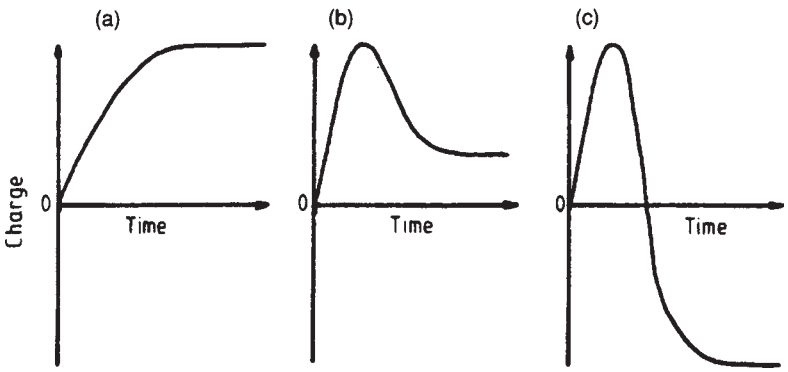


Figure 16.47 *A streaming current in a liquid flowing in a pipe (Cross, 1987; aftter Coste and Pechery, 1977): (a) monotonic rise; (b) initial peak followed by a fall to a plateau; and (c) initial peak followed by a fall to a plateau, with reversal of sign (Courtesy of Adam Hilger)*

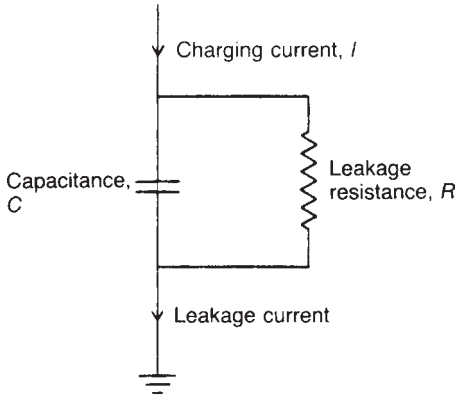


Figure 16.48 *Equivalent electrical circuit for an electrostatically charged conductor (BS 6958: Part 1: 1980) (Courtesy of the British Standards Institution)*

Table 16.35 *Typical electrostatic potentials and spark energies of selected objects*

	Potential (kV)	*Spark energy* (mJ)
Flange	10	0.5
Shovel	15	2
Drum	20	40
Road tanker	15	100
Human body	10	10
Flange on a glass line with toluene flowing in it	≤15	
Flange on a steam ejector	≤15	
Transmission belt (speed 3–15 m/s)	≤80	
Surface of liquid fuel in large container which has been filled rapidly	≤100	

Sources: Britton and Smith (1988); Expert Commission (1988); Glor (1988).

Charging of a condenser

The relations for the charging of, and discharge from, a simple resistance–capacitance (RC) circuit provide the basis for analysis of more complex systems. For the charging of such a circuit

$$\frac{dq}{dt} = I \qquad [16.7.69]$$

$$I = \frac{1}{R}(V_o - V) \qquad [16.7.70]$$

From Equations 16.7.6, 16.7.69 and 16.7.70 the unsteady-state charge balance on the capacitance gives

$$\tau\frac{dV}{dt} = V_o - V \qquad [16.7.71]$$

with

$$\tau = RC \qquad [16.7.72]$$

Integrating Equation 16.7.71

$$V = V_o[1 - \exp(-t/\tau)] \qquad [16.7.73]$$

Multiplying Equation 16.7.73 by C and applying Equation 16.7.6

$$q = q_o[1 - \exp(-t/\tau)] \qquad [16.7.74]$$

Differentiating Equation 16.7.74 and utilizing Equation 16.7.69

$$I = I_o \exp\,(-t/\tau) \qquad [16.7.75]$$

where I_o is the current at the start of charging (A), q_o is the charge equivalent to the impressed voltage, or the charge at the end of charging (C), and V_o is the voltage across the circuit, or the voltage at the start of charging (V).

Discharge of a condenser

For the discharge of the circuit the unsteady-state charge balance is, from Equations 16.7.1, 16.7.6 and 16.7.69

$$\tau\frac{dV}{dt} = -V \qquad [16.7.76]$$

Integrating Equation 16.7.76

$$V = V_o \exp(-t/\tau) \qquad [16.7.77]$$

Multiplying Equation 16.7.77 by C and applying Equation 16.7.6

$$q = q_o \exp(-t/\tau) \qquad [16.7.78]$$

Differentiating Equation 16.7.78 and utilizing Equation 16.7.69

$$I = I_o \exp\,(-t/\tau) \qquad [16.7.79]$$

Charging of a tank

For the charging of a tank into which liquid is being pumped, from Equation 16.7.4

$$R = \frac{\rho h}{A} \qquad [16.7.80a]$$

$$R = \frac{h}{\kappa A} \qquad [16.7.80b]$$

where h is the height of liquid in the tank (m). The relationships for the time constant τ are given by Equations 16.7.27, 16.7.72 and 16.7.80.

The initial and final charges in the tank contents are $q = 0$ and $q = q_o$. The initial rate of change of charge is the charge current in the liquid entering the tank, or streaming current I_o:

$$\left(\frac{dq}{dt}\right)_{t=0} = I_o \qquad [16.7.81]$$

The unsteady-state charge balance on the tank is

$$\tau\frac{dq}{dt} = q_o - q \qquad [16.7.82]$$

From Equations 16.7.81 and 16.7.82

$$q_o = I_o \tau \qquad [16.7.83]$$

Integration of Equation 16.7.82 gives, for tank charging, Equation 16.7.74.

Relaxation of a tank

Equation 16.7.78 is applicable for the relaxation of charge in a liquid in a tank into which pumping has just stopped. The rate of decay in this case may be defined in terms of the relaxation time τ or of the charge half-life $t_{1/2}$. The relationship between the two is

$$\frac{t_{1/2}}{\tau} = \ln 2 = 0.693 \qquad [16.7.84]$$

where $t_{1/2}$ is the half-life (s). The charge decays during relaxation to 50% of its original value in 0.69τ, 37% in $1\,\tau$ and 5% in $3\,\tau$.

16.7.10 Electrostatic discharge

When an electrostatic charge has accumulated, it may discharge either by leaking away, usually to ground, or by a specific mode of discharge. There are a number of mechanisms by which an electrostatic charge can discharge. Those of principal interest here are (1) spark discharge, (2) brush discharge, (3) corona discharge, (4) propagating brush discharge and (5) bulking brush discharge.

A corona discharge can cause ignition of a flammable gas mixture but its incendivity is borderline; it is sometimes stated to be non-incendive to flammable gases or dusts. Essentially it is incendive only to gases with very low MIEs such as hydrogen and carbon disulfide. The other modes of discharge can be incendive, except that it has not been demonstrated that a brush discharge can ignite dusts.

A corona discharge occurs over a longer time than a spark discharge and may give a faint glow and a sound of hissing.

Streaming currents for substances such as petroleum products are of the order of 10^{-6}–10^{-5} A. Corona currents can be much larger. The existence of a corona may therefore dissipate the charge due to the streaming current and lead to a lower steady-state electrostatic potential.

In discussion of discharges it is usual to speak of the bodies the surfaces of which act as points of discharge as electrodes. In this sense the human body may act as an electrode.

A spark discharge is one that occurs between two conductors isolated from each other and involves two electrodes. Typically one of the conductors is isolated from ground and the other is grounded. Spark discharges are also called capacitor discharges, since any system of two conductors isolated from each other is effectively a capacitor. A spark discharge can occur between a fixed isolated object and a grounded object. Alternatively, one or even both of the objects may be moving.

If the resistance between the origin of the spark and all other points on the conductor is less than about $10^6\,\Omega$, a spark discharge can occur. The resistance above that such a discharge will not occur cannot be stated with any precision.

The value of the breakdown electric field strength usually quoted for air is that applicable to two parallel plates. If the surfaces are not parallel, the breakdown field strength can be lower. There are numerous industrial situations in which there are two objects in combination which constitute a capacitor and which therefore may have the potential for a spark discharge.

A spark discharge occurs in a fraction of a second and gives a short, sharp, crackling sound.

A brush discharge is one that occurs on a single electrode and the discharge ends in space. The electrode is a grounded conductor. A charged insulator or a charged conductor may create the electric field. Most accounts of brush discharges deal mainly with the former.

Some industrial situations in which a brush discharge can occur are as follows. The grounded conductor may be a fixed metal object, a sampling device or the human body. The charged object may be a plastic pipe, a drum or a bag, a conveyor belt, a flowing liquid or a powder or a cloud of spray or dust.

Where the second object, like the first, is a conductor, a spark discharge is also possible, and brush and spark discharges may be in competition. The nature of the discharge depends on the shape of the objects.

A corona discharge is similar to a brush discharge but occurs where the electrode is more pointed. The radius of curvature limits quoted are >5–50 mm for a brush discharge and <1 mm for a corona discharge. A corona discharge may persist over a long period.

There are a number of situations in which a propagating brush discharge may occur. These are where there is (1) a non-conducting film suspended parallel to a conductor, (2) a non-conducting film on a conductor, or (3) a non-conductor. The situation may be explained by reference to Figure 16.49, where Figure 16.49(a) shows an isolated

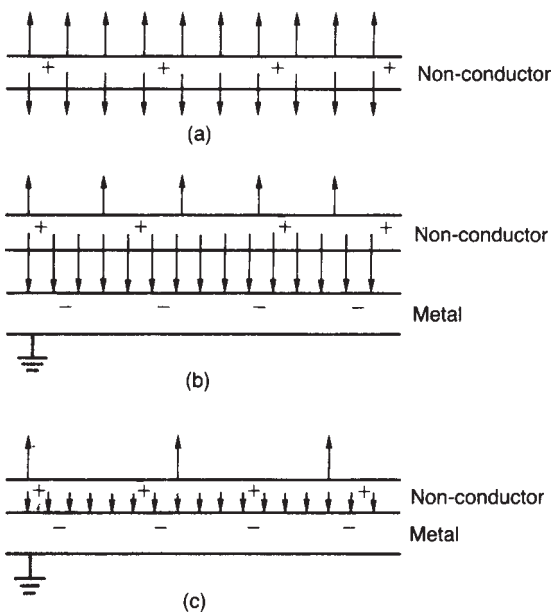


Figure 16.49 *Electric field strength due to an electrically charged sheet (BS 6958: Part 1 1980): (a) isolated sheet; (b) sheet adjacent to a metal plate grounded on the opposite side; and (c) sheet backed by an grounded metal plate (Courtesy of the British Standards Institution)*

non-conducting film in free space and Figures 16.49(b) and (c) show the first two cases mentioned; the third case is similar to the second as far as the field is concerned. The strength of the electric fields is proportional to the density of the arrows. For the isolated film in free space the breakdown field strength of air sets a limit on the surface charge density. For case 1 the presence of the grounded conductor causes a redistribution of the field so that much of it is directed towards the conductor. In this situation a much higher charge density can be accommodated before field breakdown occurs. For case 2 even greater redirection occurs and an even greater charge density can be accommodated. Case 3 is similar to case 2 except that now there is a single non-conducting object.

A propagating brush discharge can occur if there is a short circuit between the insulating film and the conductor or, in case 3, between one side and the other of the non-conductor. One way in which this can occur is if the film is perforated by mechanical damage. Alternatively, if an electrode approaches the non-conducting surface the field may be altered so that a brush discharge occurs on the electrode; the central channel may extend to that surface and damage it. In either case the change in direction of the field gives a very high field strength across the surface and ionization occurs, so that the whole non-conducting surface then discharges into the original channel.

A suitable colouring powder may be used to effect visualization of the discharge patterns on the insulator surface. These patterns are characteristic and are called lichtenberg figures. Propagating brush discharges are referred to as Lichtenberg discharges.

Propagating brush discharges have also been reported on insulating film not backed by a conductor. Although propagating brush discharges have traditionally been explained in terms of a non-conducting film adjacent to or on a conducting surface, the more important practical case is that of a non-conducting envelope such as a pipe or container.

Some industrial situations in which a propagating brush discharge can occur include: the flow of a low conductivity liquid or a powder through a pipe or into a container which is either non-conducting or has an insulating internal coating, and rotation of a conveyor belt with a conductive coating on one side.

A bulking brush discharge is a type of brush discharge that can occur on a heap of powder in a silo. Non-conductive, relatively coarse powders are the most susceptible. The discharge spreads over the surface of the powder, starting at the wall and moving to the centre.

Reference should also be made to lightning-like discharges. These have been observed in the ash and dust clouds over volcanoes and at one time it was supposed that such discharges might occur in industrial operations. There is, however, no evidence of this.

The four types of discharge described, other than bulking brush discharge and lightning discharge, are shown in Figure 16.50.

16.7.11 Liquids

Charge generation

Static electricity effects in liquids may usefully be considered in terms of the classical theory of the electrical double layer at an interface. This has been described by Stern as comprising two parts: a compact or Helmholtz layer near the interface and a diffuse or Guoy layer extending further into the liquid.

According to this model, if a liquid such as oil is at rest and in contact with another immiscible liquid such as water or with a solid such as a container wall, there builds up in that liquid an electrical double layer. This electrical double layer may be represented in convenient, though oversimplified, form as one layer of positive ions and one of negative ions. The phenomenon is illustrated schematically in Figures 16.51(a) and (b) for these two cases. There is no significance in the fact that the ions nearest the interface are positive; they could equally well be negative.

If, in the system described, the oil is a poor conductor and there is a relative movement between the surface of the oil and that of the water or of the container, the ions closest to the interface tend to adhere to it so that the oil loses some ions of one particular sign and thus becomes electrostatically charged. Situations in which such charge separation may occur are the pipeline flow of an oil, the settling of water droplets through an oil and the splashing of oil droplets onto the side of a tank, as illustrated in Figures 16.51(c) and (d), (e) and (f), and (g) and (h), respectively.

The classical electrochemical models describe some of the situations mentioned. The equations are useful at least as a guide to the factors that are important. In some cases they have been further developed to give relations more applicable to industrial situations.

The extent of charge separation is dependent on the resistivity of the liquid. If its resistivity is low, charge separation is easy, but so is charge recombination through the liquid, while if its resistivity is so high as to be effectively infinite, no charge separation occurs. If the liquid has high resistivity, however, there may be appreciable charge separation without immediate recombination. It is the handling of high resistivity liquids, therefore, which tends to generate static electricity. Examples of low resistivity liquids are water, ethanol and crude oil, and examples of high resistivity liquids are gasoline, kerosene, naphtha, benzene and other white oils.

Charge discharge

A hazard occurs with a liquid if charge is able to accumulate and if this charge undergoes rapid discharge rather than gradual dissipation. This hazard depends to a large extent on the container in which the liquid is held. Broadly, such containers are (1) containers made of conducting material and grounded, (2) containers made of conducting material and insulated from ground and (3) containers made of non-conducting material.

In process plants the container is usually made of metal and is grounded. If the liquid has low conductivity, it is possible for a large charge to accumulate in the container. The relaxation time for dissipation of the charge may be long. A discharge may occur between the liquid and the grounded container. Thus, in this situation, grounding of the container is not sufficient to eliminate the hazard. The comment has already been made that the majority of ignition incidents have occurred in grounded containers.

It is easier for charge recombination to occur if one, or both, of the two oppositely charged objects is pointed. Thus any metal object which protrudes into a tank and which is electrically connected to it acts as a path for the discharge current. Such an object is known as a 'grounded probe'. Objects that can act as grounded probes include dipsticks and ullage tapes, tank washing machines and metallic objects floating on the liquid surface.

An activity that causes particular risk of discharge is level gauging. If a man standing on a tank inserts a

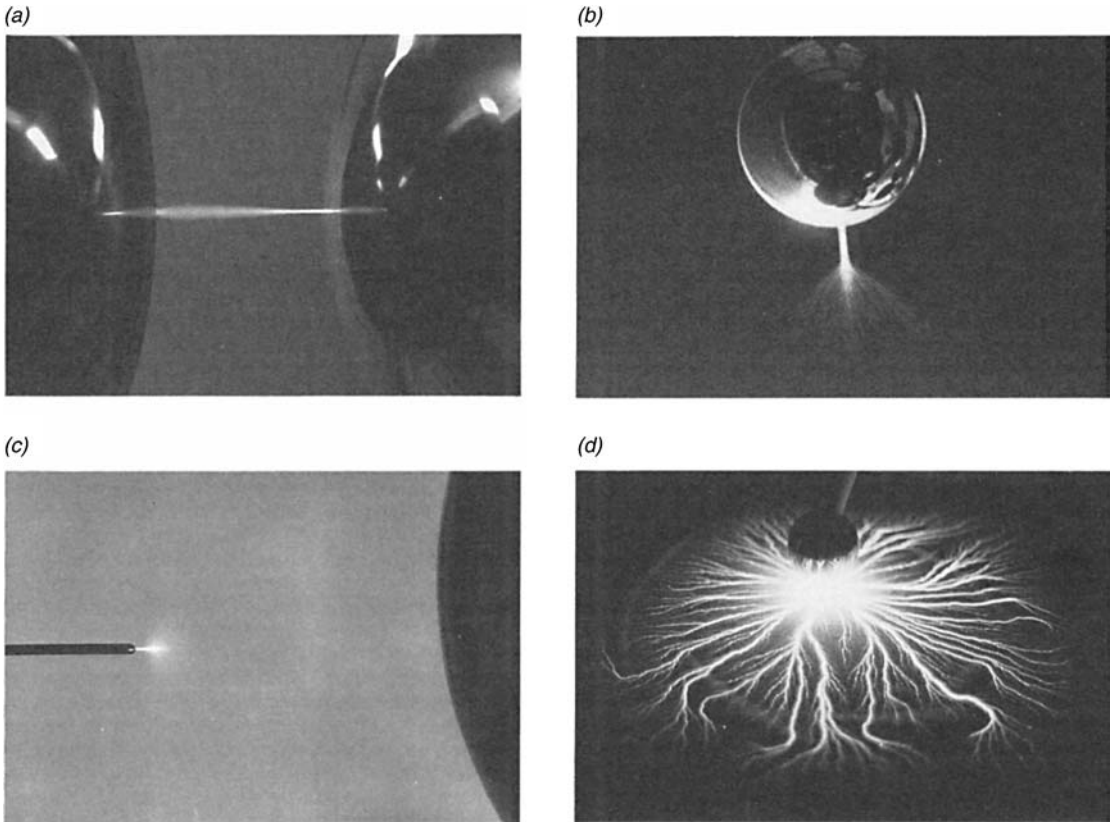


Figure 16.50 *Four types of electrostatic discharge (Lüttgens and Glor, 1989): (a) spark discharge; (b) brush discharge; (c) corona discharge; and (d) propagating brush discharge (Courtesy of Expert Verlag)*

conducting ullage tape into the liquid in the tank and the liquid is charged, a discharge may occur between the liquid and the tape. This may happen in two ways. If the tape is connected to ground via the man, or otherwise, it can act as a grounded probe. Alternatively, if it is insulated from ground but inserted in the liquid there may be a discharge across to the grounded tank.

A container may be made of metal but insulated from ground. In this case a large charge may accumulate in the liquid and on the container. Then if a path to ground is created there may be a discharge.

A similarly large charge may accumulate in a liquid held in a container made of insulating material, and again discharge may take place if a path to ground occurs.

Another configuration which gives rise to the possibility of discharge is that of an isolated conductor. The conductor may become charged and then give a discharge. Isolated conductors in plant may occur not only in vessels but also in pipework. A section of non-conductive material in metal pipework may constitute an isolated conductor.

If the charged object is a good conductor, it may be treated in the conventional way as an electrical capacitance. The energy available for discharge is given by Equation 16.7.19. The energies calculated in this way may be compared with the MIEs of flammable gas mixtures and of dust suspensions (as described in Section 16.2 and Chapter 17, respectively) in order to determine the probability that a spark discharge may have sufficient energy to cause ignition.

If the charged object is a poor conductor, no similar calculation of the energy available to produce a spark is possible, because the charge is generally not uniformly distributed and the resistance to its flow is high.

16.7.12 Some electrolytic relations

The model of a hydrocarbon electrolyte which is most often used in work on static electricity is that of a binary, monovalent electrolyte. For such an electrolyte some basic relations are as follows. The number of charges z is

$$z = |z_+| = |z_-| \qquad [16.7.85]$$

where z is the number of elementary charges per particle.

The ionic mobility u is assumed to be

$$u = u_+ = -u_- \qquad [16.7.86]$$

where u is the ionic mobility (m^2/Vs). The ionic velocity v is

$$v = uE \qquad [16.7.87]$$

where v is the ionic velocity (m/s).

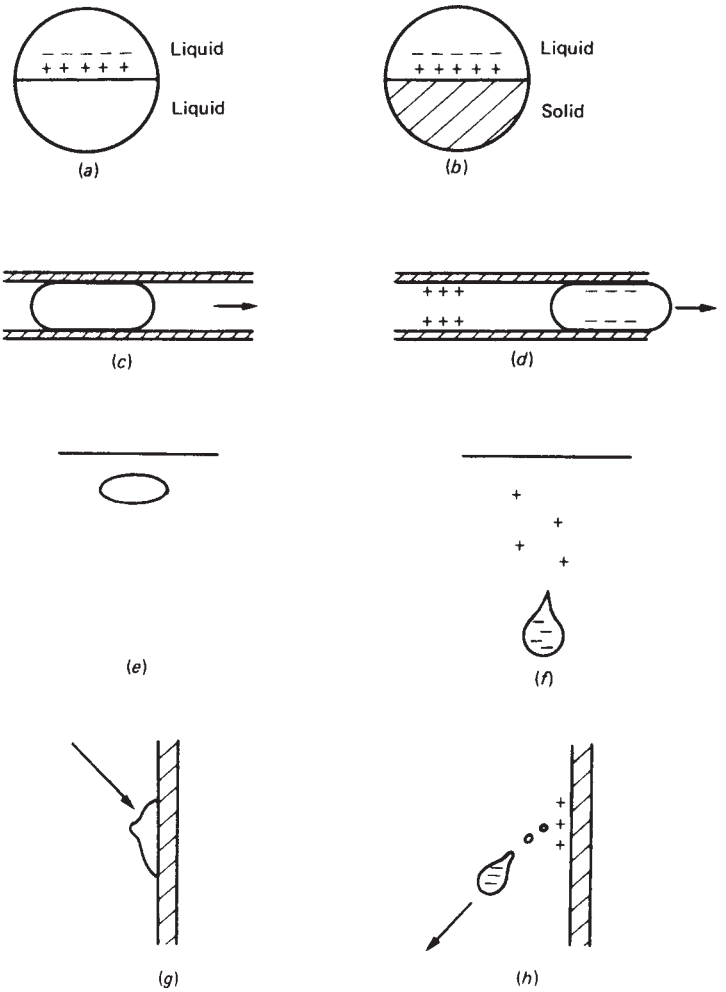


Figure 16.51 *Generation of static electricity in liquid systems: (a) electrical double layer at a liquid–liquid interface; (b) electrical double layer at a liquid–solid interface; (c, d) charge separation as oil flows through a pipeline; (e, f) charge separation as a water drop falls through oil; and (g, h) charge separation as oil spashes onto a tank wall*

The charge flux j for each ionic species with concentration n is

$$j = z\frac{n}{N}Fv \qquad [16.7.88]$$

$$j = z\frac{n}{N}FuE \qquad [16.7.89]$$

where F is the charge per kilomole equivalent (C/kmol), j is the charge flux (A/m^2), n is the number of ions per unit volume (ions/m^3), and N is the number of molecules per kilomole (molecules/kmol). F is Faraday's constant ($= 9.65 \times 10^7$) and N is Avogadro's number ($= 6.02 \times 10^{26}$).

The concentration c of each ionic species is

$$c = \frac{n}{N} \qquad [16.7.90]$$

The force F_e due to the electric field is

$$F_e = zeE \qquad [16.7.91]$$

where e is the charge on a proton (C) ($= 1.6 \times 10^{-19}$) and F_e is force (VAs/m). The electric charge is given by

$$ne = cF \qquad [16.7.92]$$

The total concentration of ions is

$$c_+ + c_- = 2c \qquad [16.7.93]$$

The current density J is

$$J = 2nvze \qquad [16.7.94]$$

$$= 2cvzF \quad [16.7.95]$$

$$= 2cuzFE \quad [16.7.96]$$

$$= \kappa E \quad [16.7.97]$$

with

$$\kappa = 2nuze \quad [16.7.98]$$

$$= 2cuzF \quad [16.7.99]$$

where J is the current density (A/m^2). In terms of the ionic concentrations, the conductivity is

$$\kappa = (c_+ - +c_-)uF \quad [16.7.100]$$

where c_+ is the concentration of positive ions ($kmol/m^3$) and c_- is the concentration of negative ions ($kmol/m^3$). The space charge density is

$$s = (c_+ - c_-)F \quad [16.7.101]$$

The relation between the ionic velocity and the diffusion coefficient is

$$D_m = \frac{kTu}{ze} \quad [16.7.102]$$

where D_m is the molecular diffusion coefficient (m^2/s), k is Boltzmann's constant ($kg\,m^2/s^2K$) and T is the absolute temperature (K).

The relation between the concentration and the conductivity is

$$\kappa_\pm = \frac{c_\pm z^2F^2D_m}{RT} \quad [16.7.103]$$

$$\kappa = \kappa_+ + \kappa_- \quad [16.7.104]$$

$$\kappa = \frac{(c_+ + c_-)z^2F^2D_m}{RT} \quad [16.7.105]$$

$$\kappa = \frac{2cz^2F^2D_m}{RT} \quad [16.7.106]$$

where R is the universal gas constant (kJ/kmol K).

For a liquid from which all the ions of one sign have been removed, Equations 16.7.100 and 16.7.101 become

$$\kappa = cuF \quad [16.7.107]$$

$$s = cF \quad [16.7.108]$$

The thickness δ of the double layer is derived as follows. It has been shown by Debye and Huckel that

$$\delta = \left(\frac{\epsilon\epsilon_o kT}{2nz^2e^2}\right)^{1/2} \quad [16.7.109]$$

where k is the Boltzmann constant (J/K) and δ is the thickness of the double layer (m).

From Equations 16.7.98, 16.7.102 and 16.7.109 it can be shown that

$$\delta = (D_m\tau)^{1/2} \quad [16.7.110]$$

The surface charge density σ at the electrical double layer is given by

$$\sigma = \frac{\epsilon\epsilon_o V_d}{\delta} \quad [16.7.111]$$

where V_d is the potential difference across the double layer (V).

Another important parameter is the zeta potential. This is the potential at the plane of slip between the surface and a liquid moving across it. The zeta potential is

$$\zeta = \frac{\eta u}{\epsilon\epsilon_o} \quad [16.7.112]$$

or

$$\zeta = \frac{\eta v}{\epsilon\epsilon_o E} \quad [16.7.113]$$

where ζ is the zeta potential (V) and η is the viscosity of the liquid (kg/m s).

16.7.13 Liquid conductivity

The electrical conductivity of a liquid is due to the presence of ions. This is true for hydrocarbons as well as for aqueous solutions. Addition of ions increases the conductivity and removal of ions decreases it.

It has been found by a number of investigators that the electrical conductivity of hydrocarbon liquids is not a true constant but may vary. It is therefore usual to speak of a 'rest' conductivity, which is the intrinsic property, and an 'effective' conductivity, which depends on the conditions.

Douwes and van der Waarden (1967) showed that when the dc electrical conductivity of hydrocarbons was measured under different conditions so that there were different decay times, extrapolation back to zero time gave conductivities equal to each other and equal to the ac conductivity. They concluded that it was this zero time dc conductivity, which is the intrinsic property.

A discussion of fundamental aspects of liquid conductivity has been given by Klinkenberg (1967a).

According to Schön (1967), the effective conductivity κ_e and rest conductivity κ_r (S/m) may vary by a factor of 10. In general, the difference increases as the charge density increases.

Britton and Smith (1988) give relations for the effect of charge density on the conductivity and for the effect of temperature on the effective conductivity. They quote the work of H. Kramer and Schön (1973) on the effect of charge density:

$$\kappa_e = k_1 + k_2 s \quad [16.7.114]$$

where k_1 and k_2 are constants. The constant k_2 is positive for liquids with low rest conductivity (<1 pS/m) and negative for liquids with a higher rest conductivity. Kramer and Schön obtained a maximum value of 4 for the ratio κ_r/κ_e. For the effect of temperature Britton and Smith quote an equation of P.I. Mason (1975):

$$\log_{10}(\kappa_2/\kappa_1) = k_3(T_2 - T_1) \quad [16.7.115]$$

where k_3 is a constant and subscripts 1 and 2 refer to states 1 and 2, respectively. For liquids such as kerosene, the value

of the constant k_3 is about $0.015°C^{-1}$. H. Kramer and Schön (1975) give some experimental data showing the effective conductivity to be, on average, half the rest value. W.D. Rees (1975) reports measurements in which the effective conductivity varied between one-tenth and one-half of the rest value.

The above relations also indicate that for low conductivity liquids the effective conductivity is greater than the rest value. This is important, because the relaxation times for low conductivity liquids are long and any feature that reduces them is helpful. Thus Vellenga and Klinkenberg (1965) have derived a model of charge relaxation in a liquid in which the assumption is that the conductivity is proportional to the charge density and which gives a hyperbolic rather than an exponential decay. Another model has been given by M.D. Foster (1967).

The range of conductivities that occur in practice is very wide. According to Klinkenberg and van der Minne (1958), the conductivity of a crude oil may be 10^7 times that of a light fraction. There tend to be large differences between the conductivity of pure and commercial chemicals. For example, the conductivity of pure heptane has been given as 0.03 pS/m and that of the commercial product as 10–100 pS/m.

The electrical conductivity, dielectric constant and relaxation time of selected liquids are shown in Table 16.36. Relaxation times vary from very small fractions of a second for some crude oils up to minutes or even hours for some highly purified products.

One broad classification of liquid conductivity (Expert Commission, 1988) is that liquids with a conductivity of less than 10^{-8} S/m are classed as non-conductive and those with a conductivity exceeding this are classed as conductive. Examples quoted of non-conductive liquids are aliphatic and aromatic hydrocarbons, ethers and methane derivatives, and examples of conductive liquids are hydrocarbons with polar groups, alcohols, aldehydes, ketones, acids, esters (except those of higher acids), nitriles, amides, amines and nitro compounds.

Two liquid conductivities that are commonly taken as demarcation values are 1 pS/m and 50 pS/m. A conductivity less than 1 pS/m is commonly classed as very low and one in the range 1–50 pS/m as low. The conductivity criterion of 50 pS/m appears to derive in large part from the work at Shell (e.g. Klinkenberg and van der Minne, 1958). It is quoted as a demarcation value in codes such as NFPA 77: 1988 and BS 5958: 1991.

The greatest danger occurs where the liquid conductivity is in the intermediate range, that is, not so low that there is little charge generation and not so high that charge equalization is very rapid. Figure 16.52 illustrates the zone of particular hazard.

Mention is made in the literature of the possibility of prostatic agents and of 'hot fluids', but usually only in passing.

A note on the units of conductivity/resistivity is given in the notation at the end of this chapter.

16.7.14 Liquid flow in pipes

One of the most important situations in which static electricity may be generated by a liquid is in flow through a pipe into a receiver such as a storage tank or a road or rail tanker. The flow of liquid results in a charging, or streaming, current that then transports charge into the receiver.

Factors that affect the charge generation in liquid flow in pipes include the pipe diameter and material, the liquid viscosity and electrical conductivity, and the liquid velocity. Impurities, including water, are also important. Figure 16.53, from Leonard and Carhart (1970), illustrates the variation of charging current with conductivity.

The charge generated by a liquid flowing in a pipe is greatly increased if the liquid contains water. An increase in the charge generated by a factor of up to 50 is quoted by Klinkenberg and van der Minne (1958). Many accidents attributed to static electricity have involved wet liquids.

Charge generation by liquid flow in pipes has been modelled by a number of workers and some success has been achieved in explaining theoretically the charging currents generated in small diameter pipes, but there has

Table 16.36 *Electrical conductivity, dielectric constant and relaxation time of selected liquids*

A Electrical conductivity, dielectric constant and relaxation time

	Electrical conductivity (S/m)	*Dielectric constant*	*Relaxation time* (s)
Highly purified hydrocarbons	10^{-15}	2	1.8×10^4
White products	$10^{-13} - 10^{-10}$	2	$1.8 \times 10^{-1} - 10^2$
Crude oil	$10^{-9} - 10^{-7}$	2	$1.8 \times 10^{-4} - 1.8 \times 10^{-2}$
Demineralized water	10^{-5}	80	7.1×10^{-5}

B Dielectric constant

Hexane	1.9
Heptane	2.0
Benzene	2.3
Toluene	2.4
Cyclohexane	2.0
Ethyl ether	4.3
Acetone	21.0
Methanol	33.7
Ethanol	25.7

Sources: Klinkenberg and van der Minne (1958); Eichel (1967); Napier (1971).

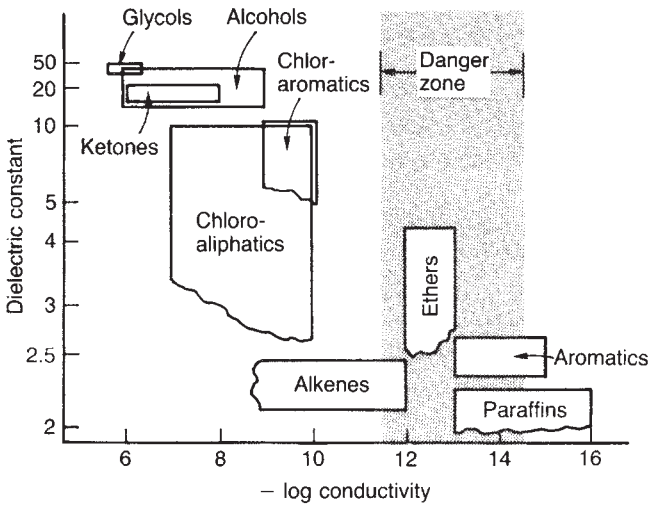


Figure 16.52 *Liquid electrical conductivity (Saletan, 1959b): conductivity ranges of selected liquids (Courtesy of Chemical Engineering)*

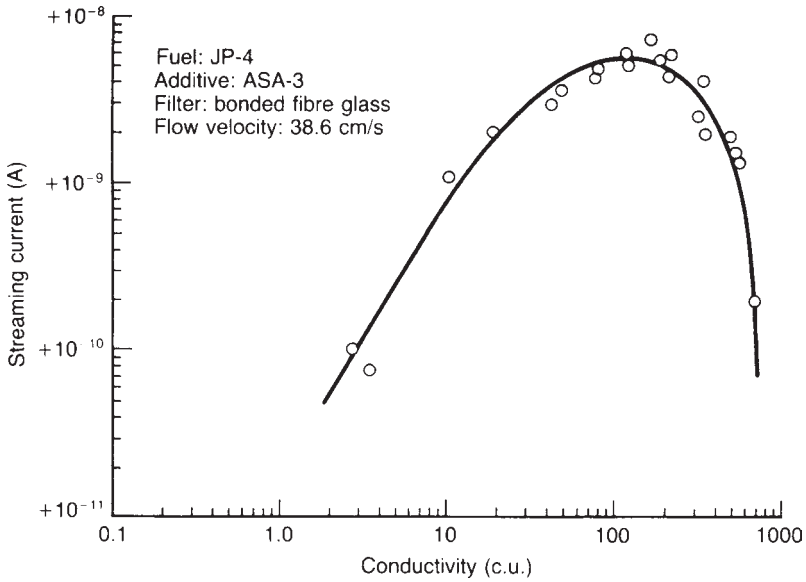


Figure 16.53 *Streaming current for liquid flow in a pipe (Leonard and Carhart, 1970): effect of liquid electrical conductivity (Courtesy of the Journal of Colloid and interface Science)*

been less success with large pipes and for these it is necessary to rely on empirical correlations. Empirical correlations are generally of the form

$$I \propto u^m d^n \qquad [16.7.116]$$

where d is the pipe diameter (m), I is the streaming current (A), u is the velocity of the liquid (m/s) and m and n are indices.

Most of the work on liquid flow in pipes refers to metal pipes, but there is a limited amount of work on non-conducting pipes. Obstructions in the pipe may cause appreciable charge generation. Filters are the main case in point, but other items such as ball valves have also received attention.

16.7.15 Early models

Early theories of charge generation by a liquid flowing in a pipe were given by W.F. Cooper (1953a) and Boumanns

(1957). In Boumanns' theory charge is generated as the flow of liquid entrains ions from the double layer. But this mechanism, while capable of giving a transient, does not fully explain the existence of a steady-state current. Boumanns therefore introduced the concept of a 'wall current'.

Another early model was that of Schön, given in unpublished work quoted by Hampel and Luther (1957). This work is also referred to by Klinkenberg and van der Minne (1958).

16.7.16 Klinkenberg and van der Minne model

A model for the streaming current and the streaming potential for the flow of liquid in a pipe has been given by Klinkenberg and van der Minne (1958). The assumptions of the model are that (1) the electrical double layer is thin compared with the pipe diameter, (2) this layer is also thin compared with the laminar sublayer, (3) the streaming current is independent of the pipe length, and (4) the shear stress is constant throughout the electrical double layer. The charging current I is

$$I = \pi d_p \int s v \mathrm{d}x \qquad [16.7.117]$$

where d_p is the pipe diameter (m) and x is the distance from the pipe wall (m). The shear stress τ_s in the electrical double layer is

$$\tau_s = \eta \frac{\mathrm{d}v}{\mathrm{d}x} \qquad [16.7.118]$$

where η is the viscosity of the liquid (kg/m s) and τ_s is the shear stress (N/m^2). Then, since the shear stress is assumed constant throughout the layer,

$$\tau_{so} = \frac{\eta v}{x} \qquad [16.7.119]$$

where τ_{so} is the shear stress at the wall (N/m^2).

Applying Poisson's equation, Equation 16.7.38, in one dimension

$$s = -\epsilon\epsilon_o \frac{\mathrm{d}^2 V}{\mathrm{d}x^2} \qquad [16.7.120]$$

Hence from Equations 16.7.117–16.7.120

$$I = -\frac{\pi d_p \tau_{so} \epsilon\epsilon_o}{\eta} \int x \frac{\mathrm{d}^2 V}{\mathrm{d}x^2} \mathrm{d}x \qquad [16.7.121]$$

Integrating Equation 16.7.121 between the wall ($x = 0$) and the plane where the potential gradient is zero ($\mathrm{d}V/\mathrm{d}x = 0$)

$$I = -\frac{\pi d_p \tau_{so} \epsilon\epsilon_o}{\eta} \left(x \frac{\mathrm{d}V}{\mathrm{d}x} - \int \frac{\mathrm{d}V}{\mathrm{d}x} \mathrm{d}x \right)_{x=0}^{\mathrm{d}V/\mathrm{d}x = 0} \qquad [16.7.122]$$

For the limit just given the first term in the integration in Equation 16.7.122 is zero. The second term may be replaced by the zeta potential. Hence

$$I = -\frac{\pi d_p \tau_{so} \epsilon\epsilon_o \zeta}{\eta} \qquad [16.7.123]$$

Eliminating the shear stress by using a force balance which introduces the pressure drop

$$\pi d_p l \tau_{so} = A_p \Delta P \qquad [16.7.124]$$

where A_p is the pipe cross-sectional area (m^2), l is the pipe length (m) and ΔP is the pressure drop (N/m^2). Hence from Equations 16.7.123 and 16.7.124

$$I = -\frac{A_p}{l} \frac{\epsilon\epsilon_o \zeta}{\eta} \Delta P \qquad [16.7.125]$$

The streaming potential V_s is obtained by equating the streaming current to minus the leakage current through the liquid in the pipe:

$$I = -\frac{V_s}{R_p} \qquad [16.7.126]$$

where R_p is the resistance of the liquid in the pipe (Ω) and V_s is the streaming potential (V). Then from Equations 16.7.4, 16.7.5 and 16.7.126

$$I = -\frac{A_p \kappa}{l} V_s \qquad [16.7.127]$$

Equating Equations 16.7.125 and 16.7.127 yields

$$V_s = \frac{\epsilon\epsilon_o \zeta}{\kappa\eta} \Delta P \qquad [16.7.128]$$

16.7.17 Koszman and Gavis model

Another theoretical model, or rather suite of models, is that of Koszman and Gavis (Gavis and Koszman, 1961; Koszman and Gavis, 1962a,b). They postulate that electrolytic oxidation-reduction reactions can occur in hydrocarbons, that in effect a cell reaction occurs in the pipe, and that the current flow is associated with this reaction. With current flow, concentration polarization will occur. They thus avoid the need to assume a wall current of unspecified origin. The current is explicitly described as a diffusion current due to the concentration polarization. The Koszman and Gavis models are given in cgs units and these units are retained for these models here.

The first model derived is for a low conductivity liquid. The mechanisms of charge transport are diffusion, convection and electrical conduction. The basic equation for charge transport, or current, is

$$I = -D_m \nabla q - \kappa \nabla \phi + v q \qquad [16.7.129]$$

where D_m is the diffusion coefficient (cm^2/s), I is the streaming current (A), q is the charge (C), v is the local velocity (cm/s), κ is the electrical conductivity of the liquid (Ω^{-1} cm^{-1}) and ϕ is the potential (V). The solution of the charging current equation is

$$I = \frac{2\pi r_p u D_m \tau F (c_o - c_s)}{\delta_m n_t} [1 - \exp(-L/u\tau)] \qquad [16.7.130]$$

where c_o is the concentration of the discharging ion in the bulk fluid (mol/cm^3), c_s is the concentration of the discharging ion at the pipe wall (mol/cm^3), F is Faraday's constant ($= 96{,}500$ C/mol), L is the length of tube (cm), n_t is the transference number, r_p is the pipe radius (cm), u is the average velocity (cm/s), δ_m is the thickness of the diffusion layer (cm) and τ the relaxation time (s).

The total transport of charge across the diffusion layer includes normal conduction transport under the influence

of the potential difference between the tube and the bulk liquid, and it is therefore necessary to include the transference number n_t of the ions of charge opposite to those being discharged.

The thickness of the diffusion layer is given by

$$\delta_m = 2r_p/\mathrm{Nu} \qquad [16.7.131]$$

Then from Equations 16.7.106, 16.7.130 and 16.7.131

$$I = I_\infty[1 - \exp(-L/u\tau)] \qquad [16.7.132]$$

with

$$I_\infty = \frac{\pi\epsilon\epsilon_0 RTu}{2n_t F}\mathrm{Nu}(1 - c_s/c_o) \qquad [16.7.133]$$

From the correlation for the Nusselt number Nu

$$\mathrm{Nu} = 0.0223\ \mathrm{Re}^{7/8}\mathrm{Sc}^{1/4} \qquad [16.7.134]$$

with

$$\mathrm{Re} = \frac{(2r_p)u}{v} \qquad [16.7.135]$$

where v is the kinematic viscosity (cm^2/s). Then from Equations 16.7.133 and 16.7.134

$$I_\infty = \frac{0.035\epsilon\epsilon_0 RTu}{n_t F}\,\mathrm{Re}^{7/8}\,\mathrm{Sc}^{1/4}(1 - c_s/c_o) \qquad [16.7.136]$$

Sc is the Schmidt number.

The concentration c_s should be sensitive to the surface materials, but since these are found to have only a small effect it is possible to assume $c_s \ll c_o$.

As described below, Equation 16.7.132 has had some success in describing the current generation in hydrocarbon liquids of low conductivity, but not for high conductivity hydrocarbon liquids. Koszman and Gavis utilizing the model of Klinkenberg and Van der Minne have therefore extended the treatment. Starting with Equation 16.7.123, and introducing the Reynolds number

$$\mathrm{Re} = \frac{ud_p\rho_1}{\eta} \qquad [16.7.137]$$

where η is the viscosity of the liquid (g/cm s) and ρ_1 is the density of the liquid (g/cm^3), the friction factor f

$$f = \frac{\tau_{so}}{2\rho_1 u^2} \qquad [16.7.138]$$

and the correlation for the friction factor

$$f = 0.079\ \mathrm{Re}^{-0.25} \qquad [16.7.139]$$

yields

$$I = 0.04\pi\epsilon\epsilon_o\ \mathrm{Re}^{3/4}u\zeta \qquad [16.7.140]$$

The authors then write Equation 16.7.140 as

$$I = \frac{0.02\pi r_p\kappa\zeta}{G} \qquad [16.7.141]$$

with

$$G = \frac{4r_p^2}{\mathrm{Re}^{7/8}\tau v} \qquad [16.7.142]$$

From Equation 16.7.141 they derive

$$I = \frac{0.04I_\infty\,\mathrm{Re}^{-1/8}\,\mathrm{Sc}^{-1/2}}{G^{1/2}} \qquad [16.7.143]$$

where I_∞ is given by Equation 16.7.133.

The high conductivity model of Equation 16.7.141 does not include a term, which corrects for pipe length comparable to that in Equation 16.7.132, because the relaxation time is so short that the equilibrium current is reached in a very short distance.

The Koszman and Gavis model for low conductivity is Equations 16.7.132 and 16.7.133, and that for high conductivity is Equations 16.7.141 and 16.7.142.

Some features of the low conductivity model are:

$$I = f(\kappa) \quad \text{Short pipes} \qquad [16.7.144a]$$

$$I_\infty \neq f(\kappa) \quad \text{Long pipes} \qquad [16.7.144b]$$

$$I_\infty \propto u^{1\frac{7}{8}} \qquad [16.7.145]$$

$$I_\infty \propto (2a)^{7/8} \qquad [16.7.146]$$

Koszman and Gavis performed experiments to study the charge generation in small diameter pipes. The experiments confirmed relations 16.7.144–16.7.146. They then plotted the group $(I_\infty/u^{1\frac{7}{8}}(2a)^{7/8})$ against G, as shown in curve A of Figure 16.54. The graph shows that in the low conductivity region the group $(I_\infty/u^{1\frac{7}{8}}(2a)^{7/8})$ is independent of G, as predicted by theory. This held for a wide range of liquid electrical conductivities, liquid velocities and a rather smaller range of pipe diameters and materials. The main exception was platinum pipes, which gave a much higher current generation, as shown in curve B of Figure 16.54. The authors attributed this to a surface roughness effect.

The low conductivity model is not applicable, however, in the high conductivity region. Its range of applicability is for values of $\log_{10}G < -5$. For higher conductivities the current predicted is higher than that observed. At high conductivities the high conductivity model, Equation 16.7.141, was used. It gave the predicted values shown in curves C and D of Figure 16.54. The two curves are for the two extreme values of the Reynolds number used (2100 and 45,000).

N. Gibson (1971) has cast the Koszman and Gavis model in the form

$$Y = Kf(G) \qquad [16.7.147]$$

with

$$Y = \frac{I_\infty}{u^{1.88}d^{0.88}} \qquad [16.7.148]$$

$$G = \frac{d^2}{\mathrm{Re}^{1.75}\tau v} \qquad [16.7.149]$$

$$K = \frac{0.35RT\epsilon\epsilon_o}{n_t F_v^{0.88}}\mathrm{Sc}^{0.25}f(C)$$

where f(C) is a concentration function.

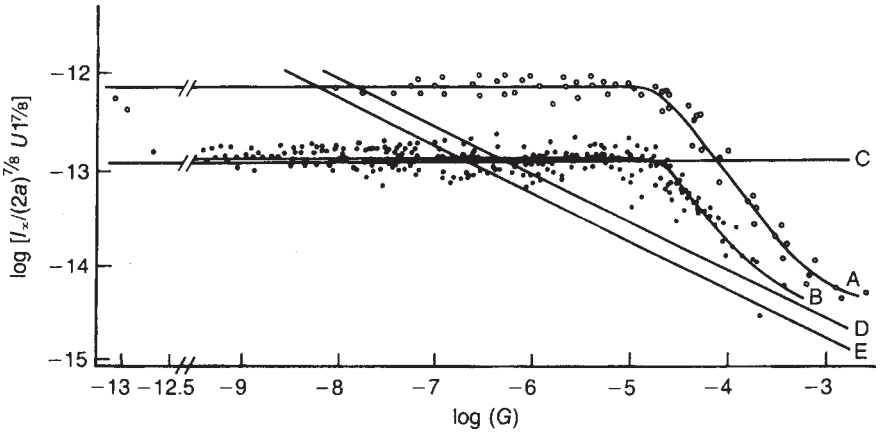


Figure 16.54 *Streaming current for liquid flow in a pipe (Koszman and Gavis, 1962b): A, B experimental curves for platinum, stainless steel tubes respectively. C, theoretical line for low conductivity liquids; D, theoretical line for high conductivity liquids, Re = 2100; and E, theoretical line for high conductivity liquids, $R_e = 45\,000$ (Courtesy of Chemical Engineering Science)*

Equation 16.7.147 applies to liquids of all conductivities. For the case of liquids of low conductivity in turbulent flow

$$f(G) = 1 \qquad [16.7.151]$$

The model of Equation 16.7.147 gives exponents for the pipe diameter d and the liquid velocity u, which may be compared with values obtained in empirical correlations.

16.7.18 Schön model

Schön (1965) carried out experiments using pipe diameters in the range 2.5–20 cm and 'motor spirit' (resistivity $10^{-14} - 10^{-11}\ \Omega$cm) and obtained the correlation

$$I_\infty = \beta(ur)^n \qquad [16.7.152]$$

where r is the pipe radius (cm), u is the liquid velocity (cm/s), β is a constant and n is an index. The value of n was in the range 1.8–2.0. The author states that the experimental scatter was such that a value of 2 may be taken for n. For this value of n the constant $\beta = 1.5 \times 10^{-13}$.

Equation 16.7.152 has been given by Klinkenberg (1967c) in SI units:

$$I_\infty = Cu^2d^2 \qquad [16.7.153]$$

where d is the pipe diameter (m), u is the liquid velocity (m/s) and C is a constant. The value of the constant C is given as $3.75 \times 10^{-6}\ \mathrm{As^2/m^4}$.

Schon states that Equation 16.7.152 is intended to give an upper limit. It has been widely quoted in the literature and thus evidently is widely used.

A critique of Equation 16.7.152 has been given by Britton and Smith (1988), who indicate that it is not conservative in all cases and propose a revised value of C of $2.5 \times 10^{-5}\ \mathrm{As^2/m^4}$.

16.7.19 Gibson and Lloyd model

Another set of experiments are those of N. Gibson and Lloyd (1967, 1970b), who utilized pipe diameters in the range 1.62–10.9 cm with toluene and toluene with ASA additive as a conductivity modifier.

They found that the Koszman and Gavis model broke down for these larger pipe diameters. They correlated their results using the equation

$$I_\infty = ku^m d^n \qquad [16.7.154]$$

where d is the diameter of the pipe (cm), u is the velocity of the fluid in the pipe (cm/s), k is a constant and m and n are indices. The indices m and n were somewhat variable, as was the constant, but N. Gibson (1971) has given Equation 16.7.154 as

$$I_\infty = ku^{2.4}d^{1.6} \qquad [16.7.155]$$

and the values of k given by N. Gibson and Lloyd (1970b) are then of the order of 10^{-14}.

The variability of the indices is taken into account in the alternative equation given by N. Gibson and Lloyd (1967) as follows:

$$I = 2.24 \times 10^{-11} d^{1.8} u^{1.45} + 0.01d \exp(0.4 \log_{10} d \log_{10} u) \qquad [16.7.156]$$

where d is the pipe diameter (cm) and u is the liquid velocity (cm/s).* Equation 16.7.156 is another equation which is often quoted.

N. Gibson and Lloyd (1970a) also studied the effect of contamination on charge generation. They found that the presence of contaminant in the toluene could affect the charge generated, but that the values of the streaming current never exceeded those of pure toluene by a factor of more than 10. They attributed this effect to the influence of the contaminant on the electrical conductivity of the liquid.

*In the original paper, and in the first edition of this book, a negative sign incorrectly preceded the index of d in Equation 16.7.156.

16.7.20 Other models

There are a number of other models for the charging current in liquid flow through pipes. They include those by Gibbings (1967) and Gibbings and Hignett (Gibbings and Hignett, 1966; Hignett and Gibbings 1968), Goodfellow and SGraydon (1968a,b), Walmsley (1982, 1983a–c) and Walmsley and Woodford (1981a,b), and Abedian and Sonin (1982).

16.7.21 Liquid flow in non-conducting pipes

Most of the work done on streaming currents has been for metal pipes, but a small amount of work has been done on non-conducting, or insulating, pipes. In this context a non-conducting pipe is one made of a material such as glass, rubber or plastic. However, the point is often made that these materials can conduct the very low currents, which occur in static electrification.

Work using 12 mm diameter polyethylene pipe with kerosene has been described by N. Gibson (1971). The main difference compared with results for metal pipes was that for a low conductivity liquid (resistivity 10^{10}–10^{12} Ω cm) the streaming current passed through a transient, decreasing with time to a constant value. For a high conductivity liquid the current was constant with time, as is the case for liquids of all conductivities in metal tubes. This decrease of current was attributed to the fact that the charge, which separates to the pipe surface, is unable to migrate along it sufficiently fast and impedes charge separation.

Work on the electrification of xylene in a glass pipe has been described by Cross, Haig and Cetronio (1977). These workers found a number of features that had a marked effect. There were high charge levels at bends and constrictions compared with straight pipe. Current flowing to metal flanges and to metal bands placed around the pipe varied both in magnitude and polarity. The state of the pipe surface was difficult to control and had a strong effect. For example, baking the pipe at 400°C effected a change in polarity.

16.7.22 Carruthers and Marsh model

Carruthers and Marsh (1962) have developed a model for the streaming current that is applicable to both conducting and insulating pipes. The model was developed as part of a study of the fuelling of aircraft where a filter in the pipe is liable to generate a large amount of charge. The model assumes that the liquid entering the system is already charged and deals with its subsequent behaviour. It does no itself provide an estimate of the streaming current in the liquid entering the pipe. The simple model initially used was

$$I_o = I_i \exp(-t/\tau) + I_p[1 - \exp(-t/\tau) \qquad [16.7.157]$$

where I_i is the current entering the pipe (A), I_p is the current generated in the pipe (A), I_o is the current leaving the pipe (A) and t is the residence time in the pipe (s).

This model proved inadequate, however, and the following more complex model was developed. A conductance ratio B was defined as

$$B = \frac{\text{Conductance per unit length of liquid in pipe}}{\text{Conductance per unit length of liquid in pipe} + \text{pipe wall}} \qquad [16.7.158]$$

so that

$$B = 0 \quad \text{Conducting pipe} \qquad [16.7.159a]$$

$$B = 1 \quad \text{Insulating pipe} \qquad [16.7.159b]$$

Then the general expression derived is

$$I = [I_i e^{-\lambda} + I_p(1 - e^{-\lambda}) + B(I_i - I_p)\left[\left(\frac{1 - e^{-\lambda}}{\lambda}\right) - e^{-\lambda}\right] \qquad [16.7.160a]$$

with

$$\lambda = t/\tau \qquad [16.7.160b]$$

For the two extreme cases

$$I_o = I_i f(\lambda) + I_p[1 - f(\lambda)] \qquad [16.7.161]$$

with, for conducting pipe

$$f(\lambda) = e^{-\lambda} \quad B = 0 \qquad [16.7.162a]$$

and for insulating pipe

$$f(\lambda) = \frac{1 - e^{-\lambda}}{\lambda} \quad B = 1 \qquad [16.7.162b]$$

where f is the fraction of the charge unrelaxed.

The authors conducted experiments with 0.47 cm diameter pipe and *iso*-octane. Some of their results are shown in Figure 16.55. Figure 16.55(a) gives experimental data for copper pipe and Figure 16.55(b) data for PTFE pipe. They regarded these results as reasonable confirmation of the model.

Larger scale experiments using a 2.5 in. rubber hose were also performed and here the performance of the model using a rest conductivity was less good. However, the fit improved when an effective conductivity some 13 times lower than the rest value was used.

16.7.23 Liquid flow through filters and ball valves

Obstruction and filters in pipes can cause considerable increases in charge generation. Filters, in particular, can be prolific charge generators. For example, H. Kramer and Schön (1975) quote charge densities as high as 1000 C/m^3 obtained at filters. N. Gibson (1969) states that the current generated by a filter can be as high as 10^{-6}–10^{-5} A.

Factors that affect the charge generation at a filter include the porosity and pore diameter, the electrical conductivity of the liquid, and the superficial velocity of the liquid.

Experimental investigations of charge generation in filters include those of Gavis and Wagner (1967), Masuda and Schön (1967), Leonard and Carhart (1970) and Huber and Sonin (1975). The latter workers also give a model for the charge generation. The filters used by these various investigators were somewhat different and the original work should be consulted for the correlations obtained. The model of Carruthers and Marsh for the relaxation of charge after a charge generator such as a filter has already been described.

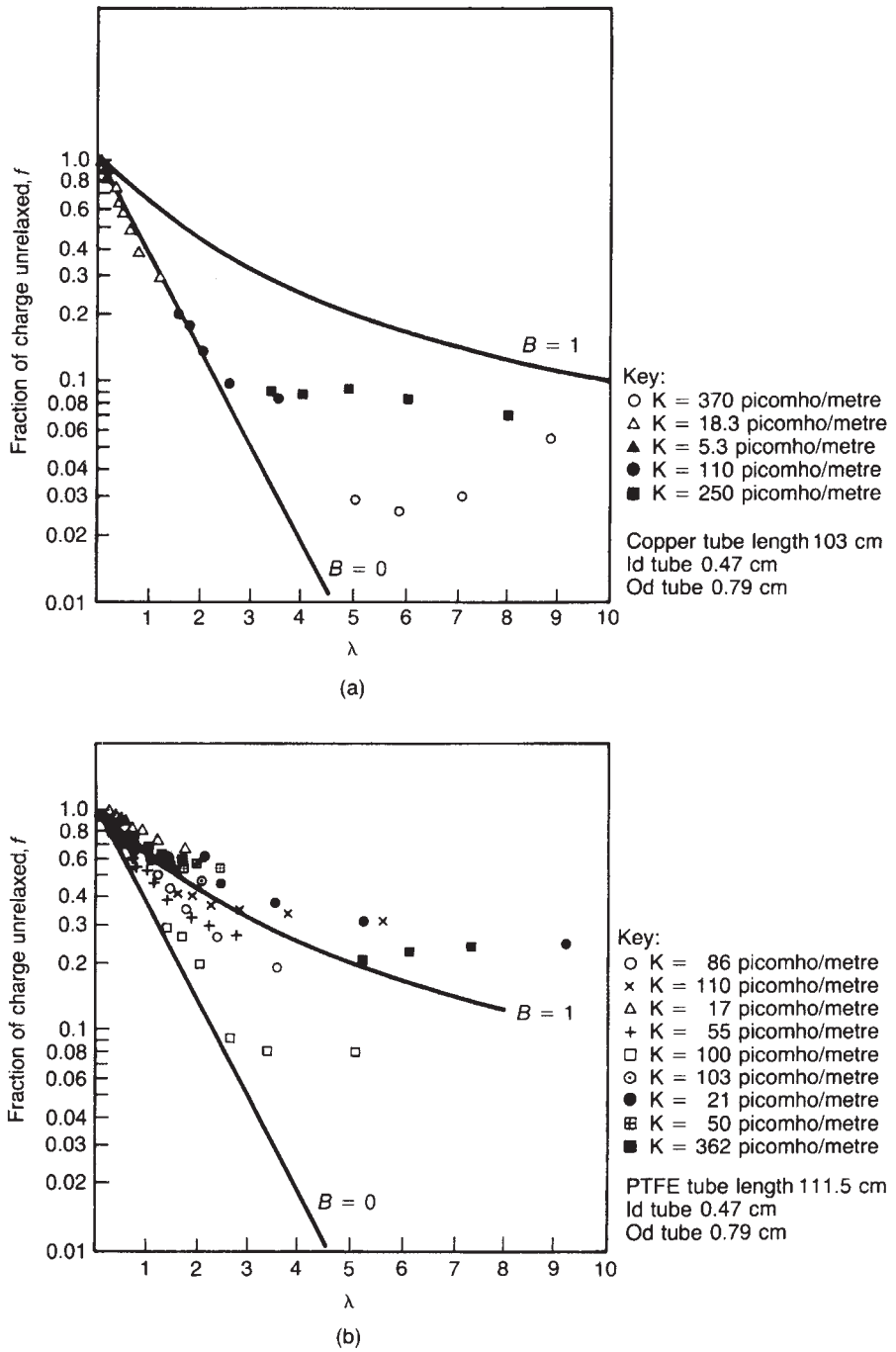


Figure 16.55 *Streaming current for liquid flow in a pipe (Carruthers and Marsh, 1962): non-conducting pipe: (a) charge relaxation in a copper pipe; and (b) in a PTFE pipe (Courtesy of the Institute of Petroleum)*

Work on charge generation in ball valves has been carried out by N. Gibson and Lloyd (1975). They performed experiments in a 10.9 cm stainless steel pipe with a 4 in. bore stainless steel ball valve with toluene and with toluene + water. Parameters investigated were the liquid velocity, the water content in the range 0–5% v/v and the fractional opening of the valve. Charge densities in the liquid increased with liquid velocity and with water content, the latter increase being marked for water contents above 0.1–0.2% v/v. Of the openings investigated, a fractional opening of 0.13 gave the highest charge generation. The highest charge density obtained in the work was 623 C/m^3 at a liquid velocity of 10 m/s with a water content of 5% v/v and a fractional opening of 0.13.

In addition to the effect such charging may have on a liquid flowing into a receiver, there is also a hazard of an incendive discharge at the valve itself. Gibson and Lloyd state that incidents have occurred where the valve body has been insulated by PTFE support rings and packing, and discharges have been observed during the flow of liquid. The capacitance of ball valves in the range 2–20 cm has been measured as 2–150 pF and the resistance to ground in the range 10^8–10^{14} Ω. The authors take a potential of 1 kV as the minimum likely to give an incendive spark, and use a MIE of 0.2 mJ. They are then able to compute the charging current required to give an incendive spark for different values of the valve capacitance, resistance to ground and potential using Equations 16.7.1, 16.7.6 and 16.7.19.

16.7.24 Liquid droplet settling

Klinkenberg and van der Minne (1958) have also given a treatment for liquid droplet settling, based on earlier work by von Smoluchowski (1921). For the settling of a drop of immiscible liquid, such as water, or of a solid particle, the downwards-acting force in an electric field is

$$F_e = \frac{4}{3}\pi a^3 g\Delta\rho + qE \qquad [16.7.163]$$

The upwards-acting force is

$$F_e = 6\pi\eta a u \qquad [16.7.164]$$

where a is the diameter of the liquid droplet (m), u is the settling velocity (m/s) and $\Delta\rho$ is the density difference between the droplet and the continuous liquid phase (kg/m^3). Following Stokes' law, and equating these two forces

$$u = \frac{\frac{4}{3}\pi a^3 g\Delta\rho + qE}{6\pi\eta a} \qquad [16.7.165]$$

The current caused by the transported charge is the sum of that from the falling droplets ($un_d q$) and that from conduction (κE). At equilibrium there is no net current and hence

$$un_d q + \kappa E = 0 \qquad [16.7.166]$$

where n_d is the number of droplets per unit volume (droplets/m^3) and q is the charge on a droplet (C). But

$$n_d = \frac{X}{4/3\pi a^3} \qquad [16.7.167]$$

where X is the volume fraction of the dispersed phase (v/v). From Equations 16.7.165–16.7.167

$$E = -\frac{qXg\Delta\rho}{6\pi\eta a\kappa\alpha} \qquad [16.7.168]$$

with

$$\alpha = 1 + \frac{n_d q^2}{6\pi\eta a\kappa} \qquad [16.7.169]$$

Also, the settling velocity is

$$u = \frac{2a^2 g\Delta\rho}{9\eta a} \qquad [16.7.170]$$

$$= \frac{u_{st}}{\alpha} \qquad [16.7.171]$$

where u_{st} is the Stokes velocity (m/s) and α is a correction factor.

Equation 16.7.168 contains the charge term q which is generally not known. It is more convenient to reformulate it in terms of the zeta potential, which can be estimated. From Equations 16.7.6 and 16.7.47

$$q = 4\pi\epsilon\epsilon_o a\zeta \qquad [16.7.172]$$

Hence from Equations 16.7.168 and 16.7.172

$$E = -\frac{2}{3}\frac{\epsilon\epsilon_o}{\kappa}\frac{Xg\Delta\rho\zeta}{\alpha\eta} \qquad [16.7.173]$$

with

$$\alpha = 1 + \frac{2X_\kappa}{\eta}\left(\frac{\epsilon\epsilon_o\zeta}{\kappa a}\right)^2 \qquad [16.7.174]$$

The settling potential gradient V_{set} is equal to the field strength E. The charge q_{ves} in the vessel is

$$q_{ves} = n_d q V_{ves} \qquad [16.7.175]$$

where q_{ves} is the charge in the vessel (C), V_{set} is the settling potential gradient (V/m) and V_{ves} is the volume of the vessel (m^3).

The foregoing gives the field strength in the liquid. The field strength in the vapour space may be obtained by equating the potential differences so that

$$E_v = \frac{Eh_1}{H - h_1} \qquad [16.7.176]$$

where E_v is the field strength in the vapour space (V/m), h_1 is the height of liquid in the tank (m) and H is the height of the tank (m).

As an illustration, consider the estimate made by Howells (1993 LPB 114) for the settling of droplets of water from a foam blanket injected onto the top of a hydrocarbon fuel in a floating roof storage tank, as described in Section 16.28. He uses the following values of the parameters: $\epsilon = 2$, typical of hydrocarbons; $\epsilon_o = 8.85 \times 10^{-12}$ F/m; $\Delta\rho = 300$ kg/m^3, typical for the density difference between water and hydrocarbons; $\zeta = 0.04$ V, typically in the range 0.01–0.1 V;

$\eta = 5 \times 10^{-4}$ Ns/m^2, typical of hydrocarbons; $\kappa = 0.1$ pS/m, typical of a very low conductivity product; $\alpha = 1$, constant dependent on particle size, which can be taken as unity for particles over a few hundred microns diameter; and $g = 9.81$ m/s. The value of X is obtained on the assumptions that a 0.3 m blanket of foam with an expansion ratio of 5 and a 25% drainage time is applied to the surface and that the foam breaks down into 750 μm droplets; this gives $X = 2.7 \times 10^{-4}$. Equation 16.7.173 then yields an electric field of 9 kV/m. Applied to a tank filled with liquid to a depth of 3 m grounded at the bottom, the liquid surface potential obtained is 27 kV.

16.7.25 Liquid sprays and mists

Another situation that can give rise to the generation of static charge is the break-up of a liquid to form a spray or mist. This can occur in two main ways: (1) discharge through an orifice, or (2) splashing against a surface.

The charge on a liquid droplet resides on the surface and exerts an outward force, which is countered by surface tension. There is thus an upper limit to the amount of charge on a droplet, which was determined by Lord Rayleigh (1882), and is known as the Rayleigh limit. This may be written as

$$q = (64\pi^2 \epsilon \epsilon_o \gamma a^3)^{1/2} \qquad [16.7.177]$$

or

$$\left(\frac{q}{m}\right)_{max} = \left(\frac{36\epsilon\epsilon_o\gamma}{a^3\rho_l}\right)^{1/2} \qquad [16.7.178]$$

with

$$m = \frac{4\pi a^3 \rho_l}{3} \qquad [16.7.179]$$

where a is the radius of the droplet (m), m is the mass of the droplet (kg), q is the charge (C), γ the surface tension of the liquid (N/m), ρ_l is the density of the liquid (kg/m^3) and the subscript max denotes the maximum. The Rayleigh limit is higher than the Gauss limit.

If a droplet is charged to the Rayleigh limit it disrupts. Work by Schweizer and Hanson (1971) on *n*-octanol showed that such a droplet then forms one particle with some 95% of the mass and some 77% of the charge, and a number of other, much smaller particles.

N. Gibson (1971) has reported work on the electrification of kerosene and of kerosene with 5% water released as a jet from a 3 mm pipe. Some results of this work are shown in Figure 16.56. The presence of relatively small amounts of water produced a 1000-fold increase in the space charge density.

Napier and Rossell (1973) studied the charge in a spray from a jet of xylene from a 0.25 mm tube. Space charge densities of 0.6×10^{-3} C/m^3 were measured. They comment that the conductivity of the liquid may have been increased by small amounts of water (up to 0.1%), oxidation products and dissolved metals.

After separation the liquid droplets retain their charge until they settle out or until a discharge occurs. A mist containing enough energy to give an incendive spark can be created by a high-pressure jet, but the conditions under which discharge occurs are not well defined. Discharges

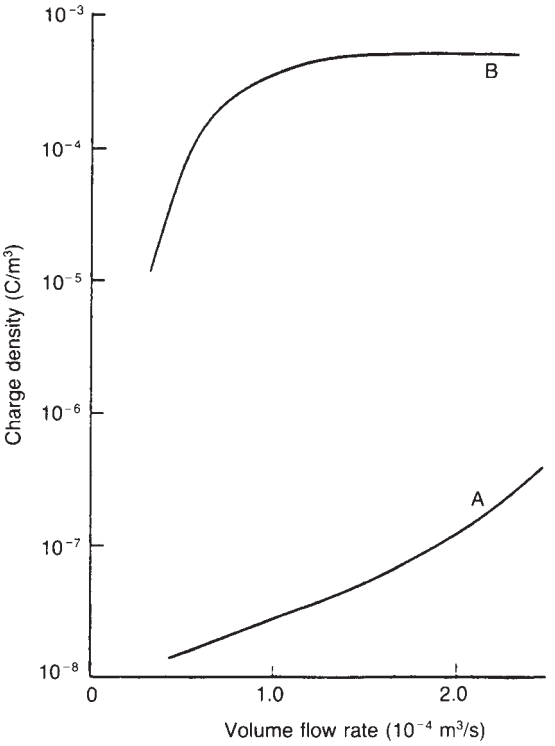


Figure 16.56 *Charge generated in a liquid jet (N. Gibson, 1971): A, kerosene; B, kerosene plus 5% water (Courtesy of the Institute of Physics)*

observed have tended to be of the non-incendive corona type rather than spark discharges.

N. Gibson (1971) has given a simple model that treats the mist as a sphere containing uniformly sized droplets. The maximum field strength occurs at the periphery of the sphere and is

$$E_{max} = \frac{s a_{ms}}{3\epsilon_{ms}\epsilon_o} \qquad [16.7.180]$$

while the total energy of such a spherical mist cloud isolated in space is

$$W = \frac{2\pi s^2 a^5 ms}{9\epsilon_o}\left(\frac{1}{\epsilon_{ms}} + \frac{1}{\epsilon_{ar}}\right) \qquad [16.7.181]$$

where a_{ms} is the radius of the mist cloud (m), E is the field strength at the edge of the cloud (V/m), s is the space charge density of the mist (C/m^3), W is the energy in the cloud (J), ϵ_{ar} is the dielectric constant of air and ϵ_{ms} is the dielectric constant of the mist.

Another situation that can occur is where the jet impinges on a conducting object insulated from ground. A charge may accumulate on the object and then give a discharge.

These electrostatic effects occur when steam is let down from a high pressure so that it comes out wet from the orifice, as with a leak on a steam main. The principal hazard with such a leak is generally that presented by a conducting object insulated from ground.

An electrostatic charge can accumulate in droplets in steam. There is a static electricity hazard, therefore, when steam is used for cleaning or purging of equipment that has contained flammables.

Similarly, charge generation can occur when a vapour, such as propane, containing some small liquid droplets is let down through a jet.

Charge is also generated when a gas containing solid particles issues from an orifice. Thus a carbon dioxide jet being directed from a fire extinguisher into a vessel containing a flammable atmosphere may contain small particles of solid carbon dioxide and may generate enough charge to ignite the mixture.

The splashing of liquid falling onto, or directed against, a surface also results is charge generation. This has been studied by Iribane and Mason (1967), Jonas and Mason (1968), Levin and Hobbs (1971) and Vos (1971).

Levin and Hobbs showed that the main charging mechanism is disruption of the double layer at the liquid-air interface. Most of the charge is associated with the ejection of droplets of some 20 μm diameter from the liquid surface.

Vos obtained for aqueous solutions the following relation for the charging current

$$I = c^* u^2 \qquad [16.7.182]$$

where c^* is the charging tendency (As^2/m^2), I is the charging current (A) and u is the velocity of the jet impinging on the surface (m/s).

16.7.26 Liquid agitation

The agitation of liquids can generate charges of the same order of magnitude as charging by liquid flow in a pipe. Vos *et al.* (1974) have described work undertaken following several fires involving agitation to effect the dissolution of epoxy resin in xylene. With epoxy resin flakes of 0.3–4 mm and with a liquid conductivity of 50 pS/m, the charge density increased from below 30 $\mu C/m^3$ at a stirrer speed of 250 rpm to 450 $\mu C/m^3$ at a speed of about 1250 rpm. Increasing the conductivity to 2000 pS/m led to a reduction in charge density to 10 $\mu C/m^3$. The charge density decreased with increase in temperature to an extent that could not be accounted for simply by the effect of temperature on conductivity. Further studies of agitation charging have been described by H. Kramer (1981). Blowing gas through the liquid may also effect agitation. This also is liable to generate charge. Static electricity is also generated by splash filling of tanks.

16.7.27 Liquid storage tanks

Charge accumulation and relaxation are particularly important in relation to the filling of liquid storage tanks and of road and rail tankers. The storage tank problem has a number of different aspects: charge accumulation and relaxation; field strengths and potentials; and the generation of sparks, particularly incendive sparks. Some of the work in this field has been associated with the fueling of aircraft.

16.7.28 Klinkenberg and van der Minne model

Klinkenberg and van der Minne (1958) have given a number of expressions for the electric field strength in storage tanks. For a full spherical tank, Equation 16.7.57 is applicable and they also suggest its use for tanks that are cubic in shape. For long shallow tanks they refer to Equation 16.7.56.

For a partially full tank with a uniform charge density in the liquid but otherwise no liquid surface charge and zero charge density in the vapour space, they give the following relation for the field strength in the vapour space

$$E_v = \frac{s h_l^2}{2\epsilon_o(\epsilon_v h_l + \epsilon_l h_v)} \qquad [16.7.183]$$

where E_v is the field strength in the vapour space (V/m), h_l is the depth of liquid (m), h_v is the height of the vapour space (m), ϵ_l is the dielectric constant of the liquid and ϵ_v, is the dielectric constant of the vapour.

16.7.29 Vellenga model

Vellenga (1961) obtained a model for the electric field strength inside a rectangular tank. He assumes that the charge is uniformly distributed and that the dielectric constant of the liquid and of the vapour are the same, the difference between them being in practice a factor of about 2. He obtained for the general case the expression

$$E_\gamma = \frac{1}{2}\frac{sc}{\epsilon\epsilon_o}\left[w^2 - \sum_{n=1}^{n=\infty} A_n(\cos \pi n w - 1)\cos \pi n \gamma\right] \quad \gamma > w \qquad [16.7.184]$$

with

$$A_n = \frac{4}{\pi^2}\frac{1}{n^2 \cosh(n\pi/2\beta)} + \frac{16}{\pi^3}\sum_{m=1}^{m=\infty} \sin(m\pi/2)/[mp^2 \cosh(p\pi/2\alpha)] \qquad [16.7.185]$$

$$\alpha = c/a \qquad [16.7.186]$$

$$\beta = c/b \qquad [16.7.187]$$

where a, b and c are the length, width and height of the tank (m), respectively, E_γ is the field strength at the fraction of the tank height γ (V/m), w is the fraction of the height filled with liquid, α and β are shape parameters, and γ is the fraction of the tank height at which the field strength is measured.

For the particular case of a tank whose height is small relative to its lateral dimensions, Vellenga obtains

$$E = \frac{1}{2}\frac{scw^2}{\epsilon\epsilon_o} \qquad [16.7.188]$$

16.7.30 Carruthers and Wigley model

Carruthers and Wigley (1962) developed a model for the field strength and potential in a partially filled rectangular metal storage tank filled with uniformly charged liquid. They then extended this model to give the fields produced by a charge on the surface of the liquid and in the mist in the vapour space above it.

The space charge density s is given by

$$s = \frac{I_o \tau}{V_{ves} t} \quad t \gg \tau \qquad [16.7.189]$$

where I_o is the current entering the tank (A), t is the time of filling (s) and V_{ves} is the volume of the liquid in the tank (m^3).

For a point in the vapour space with the co-ordinate *x, y, z* as measured from the top of the tank, the approximate field strength in the z direction E_z is

$$E_z = \frac{16s}{\epsilon_o \pi^3 (1/a^2 + 1/b^2)^{1/2}} \times \frac{(\cosh\ \beta d - 1)\cosh\ \beta z \sin(\pi x/a)\sin(\pi y/b)}{\epsilon_v \cosh\ \beta p \sinh\ \beta d + \sinh\ \beta p \cosh\ \beta d} \quad [16.7.190]$$

with

$$\beta = \pi^2 \left(\frac{1}{a^2} + \frac{1}{b^2}\right) \quad [16.7.191]$$

where a is the length of the tank (m), b is the width of the tank (m), d is the height of the liquid (m), p is the height of the vapour space (m), ϵ_l is the dielectric constant of the liquid and ϵ_v is the dielectric constant of the vapour.

The authors also derive the space charge densities and field strengths for any mist existing in the vapour space in the tank. They consider two cases: (1) a tank filled with mist and (2) a tank half filled with liquid and half with mist. In this treatment they assume a cubical tank of length a. For the first case the field strength is at a maximum at the centre of each wall and is

$$E_{mf} = \frac{64}{3}\frac{a s_{mf}}{\epsilon\epsilon_o \pi^4} \quad [16.7.192a]$$

$$E_{mf} = 6.79\frac{a s_{mf}}{\epsilon\epsilon_o \pi^3} \quad [16.7.192b]$$

where E_{mf} is the maximum field strength with the tank full of mist and s_{mf} is the space charge density with the tank full of mist. For the second case, from Equation 16.7.190 and setting $d = p = a/2$, the maximum field strength in the vapour space is

$$E_{mh} = 2.84\frac{a s_{mh}}{\epsilon\epsilon_o \pi^3} \quad [16.7.193]$$

where E_{mh} is the maximum field strength in the vapour space with the tank half full of liquid (V/m) and s_{mh} is the space charge density with the tank half full of liquid (C/m^3).

It can then be shown that in some circumstances a charged mist may produce a field strength of the same order as that of a charged liquid. Thus, assuming that in the first case all the liquid entering the tank in a time equal to the relaxation time τ forms a mist, the space charge density is

$$s_{mf} = \frac{I_o \tau}{a^3} \quad [16.7.194]$$

while in the second case the space charge density is

$$s_{mh} = \frac{2I_o \tau}{a^3} \quad [16.7.195]$$

From Equations 16.7.192 and 16.7.194 for the first case and Equations 16.7.193 and 16.7.195 for the second, the maximum field strengths are, respectively,

$$E_{mf} = 6.79\frac{I_o \tau}{\epsilon\epsilon_o \pi^3 a^2} \quad t = \tau \quad [16.7.196]$$

and

$$E_{mh} = 5.68\frac{I_o \tau}{\epsilon\epsilon_o \pi^3 a^2} \quad t \gg \tau \quad [16.7.197]$$

16.7.31 Vellenga and Klinkenberg model

As already mentioned, there is frequently an appreciable difference between the effective and rest conductivities of the liquid. One consequence of this is that during the relaxation of charge in a liquid following the filling of a tank, the relaxation time constant, given by Equation 16.7.27, is not in fact constant and the decay of the charge does not then follow the exponential decay given by Equation 16.7.78.

Vellenga and Klinkenberg (1965) have derived an alternative expression for charge decay based on the assumption that the conductivity of the liquid is proportional to the charge density. Considering a small element of volume V with space charge density s and hence a charge Vs, application of Gauss law, Equation 16.7.34, gives

$$\int D_n \mathrm{d}A = sV \quad [16.7.198]$$

where D_n is the component of D normal to an element of surface $\mathrm{d}A$. The rate of loss of charge from $\mathrm{d}A$ is the current density J_n, and that from the whole element is the current density J. Then from Equations 16.7.26, 16.7.27, 16.7.97 and 16.7.198

$$\frac{1}{\tau}\int D_n \mathrm{d}A = -\frac{\mathrm{d}(sV)}{\mathrm{d}t} \quad [16.7.199]$$

Integrating Equation 16.7.199 gives

$$\frac{\mathrm{d}s}{\mathrm{d}t} = -\frac{s}{\tau} \quad [16.7.200]$$

Taking the limiting case where all the ions of one sign are removed, as described in Section 16.7.12, and substituting from Equations 16.7.107 and 16.7.108 in Equation 16.7.200

$$\frac{\mathrm{d}s}{\mathrm{d}t} = -\frac{us^2}{\epsilon_o \epsilon} \quad [16.7.201]$$

Integrating Equation 16.7.201 yields

$$s = \frac{s_o}{1 + t/\tau_o} \quad [16.7.202]$$

where s_o is the initial charge density and τ_o is the initial relaxation time.

Equation 16.7.202 is a hyperbolic equation and the authors describe it as the hyperbolic law of relaxation. Another hyperbolic decay model is that of M.D. Foster (1967). A number of workers have reported decay of charge in tanks, which approximates more closely to the hyperbolic than to the exponential law.

16.7.32 Kramer and Schön model

H. Kramer and Schön (1975) have carried out a series of fundamental studies of the static electricity hazard in storage tanks, including the charging current entering the tank, the distribution of charge in the liquid, the field strength in the liquid and in the vapour space and the effect of bodies which distort this field, the incendivity of sparks produced and development of rules for tank filling.

With regard to the charge distribution, the authors postulate that the charge is not uniformly distributed within the liquid but is concentrated in a charge cloud. They estimate the volume of this charge cloud as

$$V_e = Q\tau \qquad [16.7.203]$$

where Q is the volumetric flow of liquid (m^3/s) and V_e is the volume of the charge cloud (m^3), this volume being that at the surface of which the charge density has decayed to $1/e$ of its original value. This model is based on laminar flow. For turbulent flow the cloud would be somewhat larger.

Kramer and Schön made measurements in a 15 m^3 tank, near the fill pipe outlet and at the far end of the tank, of the relative field strength, or field strength divided by total charge in the tank, at different filling rates, and plotted the relative field strengths at these two points vs the volume of the charge cloud. Whereas the relative field strength at the fill pipe was virtually constant, that at the far side of the tank was constant at high charge cloud volumes but fell off rapidly for charge cloud volumes below 2 m^3. The authors suggest that these results indicate that the effective charge cloud volume was some five times the nominal value given by Equation 16.7.203.

A further detailed study of the space charge cloud is given by Schön and Masuda (1969) and Schön and Kramer (1971).

H. Kramer and Schön (1975) then discuss the problem of field strength. They comment that the model of Carruthers and Wigley may not be applicable to large tanks containing high conductivity liquids. In any event, features such as the fill pipe distort the field, and this is crucial.

They treat the fill pipe as a cylindrical object. For such a configuration the relation between the potential and the field strength is

$$\phi_{max} = Er_1 \ln(r_2/r_1) \qquad [16.7.204]$$

where r_1 and r_2 are the radii of the inner and outer cylinders (m) and ϕ_{max} is the maximum potential in the center of the tank in the absence of the fill pipe (V). The inner cylinder is the radius of the fill pipe and the outer one may be equated with a suitable lateral dimension of the tank.

They measured the field strength at the fill pipe in a large tank and a tank truck as

$$E = 7.5 \times 19^9 q \qquad \text{Large tank} \qquad [16.7.205a]$$

$$E = 30 \times 10^9 q \qquad \text{Tank truck compartment} \qquad [16.7.205b]$$

where q is the charge (C).

Then from Equation 16.7.204 they obtained the maximum potential ϕ_{max} as

$$\phi_{max} = 1.9 \times 10^9 q \qquad \text{Large tank} \qquad [16.7.206a]$$

$$\phi_{max} = 5.0 \times 10^9 q \qquad \text{Tank truck compartment} \qquad [16.7.206b]$$

The smaller tank therefore had the higher maximum potential. The authors state that the Carruthers and Wigley model gives the maximum potential as inversely proportional to the diagonal of the mid-height cross-sectional area, and that their results confirm this.

They then consider the incendivity of discharges. For an incendive discharge there is a critical radius of curvature below which an incendive spark is unlikely. This radius is about 5 mm. For small radii of curvature above this value

$$E_e r = 35{,}000 \quad 5 \times 10^{-3} \leq r \leq 12 \times 10^{-3} \qquad [16.7.207]$$

where E_e is the field strength for the onset of incendive discharge (V/m) and r is the radius of curvature (m). For larger radii

$$E = 3{,}000{,}000 \quad r > 12 \times 10^{-3} \qquad [16.7.208]$$

With a small probe the potential distribution in the vicinity of the probe is changed only locally. The undisturbed potential ϕ at the probe determines the field strength E at the surface of the probe according to the relation

$$Er \approx \phi \qquad [16.7.209]$$

Then from Equations 16.7.207–16.7.209 an incendive spark is unlikely as long as the maximum potential in the vapour space is kept below 35 kV.

Kramer and Schön consider two limiting cases: (1) a tank with a probe and (2) a tank with a fill pipe only. These two cases correspond, therefore, to field strengths for the onset of an incendive discharge of 35 kV and 3000 kV, respectively.

For the first case, from relations 16.7.207–16.7.209 and taking account of the empirical factor of 0.6 for the maximum potential

$$0.6\,\phi_{max} \leq 35{,}000 \qquad [16.7.210]$$

The streaming current entering the tank and the total charge in the tank are

$$I_o = \frac{\pi d^2 u s_o \epsilon \epsilon_o}{4\kappa_e} \qquad [16.7.211]$$

$$q = I_o \epsilon \epsilon_o / \kappa_e \qquad [16.7.212]$$

where d is the diameter of the fill pipe (m), I_o is the charging current in the liquid entering the tank (A), s_o is the charge density of that liquid (C/m^3), u is the liquid velocity (m/s) and κ_e is the effective conductivity of the liquid (S/m). Then from Equations 16.7.206 and 16.7.210–16.7.212

$$\frac{s_o u d^2}{\kappa_e} \leq 2.2 \times 10^6 \qquad \text{Large tank} \qquad [16.7.213a]$$

and

$$\frac{s_o u d^2}{\kappa_e} \leq 0.83 \times 10^6 \quad \text{Tank truck compartment} \qquad [16.7.213b]$$

For the second case

$$E_e \approx 3{,}000{,}000 \qquad [16.7.214]$$

and assuming that the field strength at the fill pipe is

$$E \propto 1/d \qquad [16.7.215]$$

Equations 16.7.205, 16.7.211, 16.7.212 and 16.7.214 yield

$$\frac{s_o u d}{\kappa_e} \leq 1.2 \times 10^8 \quad \text{Large tank} \qquad [16.7.216a]$$

$$\frac{s_o u d}{\kappa_e} \leq 0.6 \times 10^8 \quad \text{Tank truck compartment} \qquad [16.7.216b]$$

The relationship between the effective conductivity and the rest conductivity proposed by the authors in this context is

$$\kappa_e = \kappa_r/2 \qquad [16.7.217]$$

From these relations the authors give the limiting filling criteria shown in the table at the bottom of the page.

Where, for a container of lateral dimensions a and b, L is the length of the diagonal, calculated from $L = (a^2 + b^2)^{1/2}$.

The relation for other tank sizes utilizes scaling based on the diagonal of the mid-height-cross-sectional area. These are limiting criteria that do not include a safety factor. The authors also quote the following German safety rule:

$$u^2 d \leq 0.64 \qquad [16.7.218]$$

For liquids with very low conductivities the treatment described may be too restrictive. The streaming current is likely to be lower and may not reach its steady-state value. The authors state that experimental evidence suggests that a limiting rest conductivity of 0.8 pS/m may be applied.

This treatment is applicable only to conditions where there are no generators of unusually large amounts of charge, such as a liquid velocity above 7 m/s, water in the liquid or a filter in the inlet pipe. Also the treatment applies to tank sizes up to those of a tank car. For larger tanks the assumption of a uniform charge density breaks down, because the effective relaxation volume is small compared with the tank volume.

and a probe. They concluded that the latter was the principal hazard.

These authors developed the concept that the approach of a grounded probe can cause a very high charge to build up on the liquid surface. A system composed of a liquid surface and a probe is a capacitor. Capacitance is inversely proportional to separation. Therefore as the probe approaches the liquid surface, or rather as the liquid surface during filling approaches the probe, with the charge initially being constant, the liquid surface potential at the point near the probe will drop according to Equation 16.7.6. The difference in liquid surface potentials thus created will cause the charge to move in order to equalize the potentials. They carried out experimental work and found that at lower flow rates there was little difference in potential between a point near the probe and one some distance away, so that there was a degree of charge concentration, but that at higher flow rates a potential difference developed and the charge concentration was less; they attributed this latter condition to the increased turbulence.

They found that the design of the fill pipe had a marked effect on its capacitance. The pipe capacitance decreased linearly with the separation between the pipe and the liquid surface up to a separation of 0.1 in. The lowest separation at which capacitances were measured was 0.02 in. but capacitance values were extrapolated back to a separation of 0.0025 in. The pipe design with the lowest capacitance at 0.0025 in. was one with a 45° slant end, with a capacitance of 140 pF. Other designs were, in ascending order of capacitance, an open pipe end, a T deflector and a cone deflector, the latter having the highest capacitance at 470 pF. The liquid surface potentials measured in this work were up to 10 kV.

Mahley and Warren (1968) carried out an investigation in which the effect of the following parameters was studied: (1) fill tube design, (2) liquid velocity, (3) compartment height, (4) fill tube height, (5) liquid conductivity, (6) liquid wetness, (7) air bleed and (8) filter.

They found that the design of the fill tube had a marked effect on the potential of the liquid surface. The lowest potential was obtained with the 45° slant end pipe. The ranking of the other devices was generally, in ascending order of potential, an open pipe end, a T deflector and a cone deflector.

Drop heights of <2, 30 and 60 in. were used. The difference in liquid surface potential between the first two drop heights was minimal, but use of a 60 in. drop height gave much higher potentials.

The liquid surface potential increased with liquid velocity, with water content and with the use of a filter. The increase in potential with liquid velocity was more than proportional and the magnitudes were much higher for fill tube designs other than the slant end one. The increase in potential when a filter was used was large.

Filling condition			*Projections permitted*
Tank truck	*Rail tank car*	*Other tanks*[a]	
$u^2 d \leq 6.2 \times 10^{12} \kappa_r$	$u^2 d \leq 12.4 \times 10^{12} \kappa_r$		Fill pipe only; outlet fully covered by liquid
$ud \leq 0.29 \times 10^6 \kappa_r$	$ud \leq 0.47 \times 10^6 \kappa_r$	$ud \leq = 0.17 \kappa_r^{1/2} L^{1/2}$	Projections of all kinds permitted

[a] Where, for a container of lateral dimensions a and b, L is the length of the diagonal, calculated from $L = (a^2 + b^2)^{1/2}$.

16.7.33 Road and rail tankers

As described in Section 16.7.2, a large proportion of the incidents attributed to ignition by static electricity have involved road tankers and rail tank cars. The work of H. Kramer and Schön (1975) on tanks in general and road and rail tankers in particular was described in Section 16.7.32.

An early study of the static ignition hazard in filling road tankers was made by Herzog, Ballard and Hartung (1961). They considered three paths for a discharge: (1) between two points on the liquid surface, (2) between the liquid surface and the tank wall and (3) between the liquid surface

The effect of liquid conductivity was somewhat complex. The conductivity range studied was 2.5–100 cu (pS/m). In this range, use of a conductivity additive caused the liquid surface potential to decrease with the resultant increases in liquid conductivity. But the results for undoped liquid did not show this regular variation. A liquid with 16 cu gave a higher potential than one with 2.5 cu.

The effect of an air bleed, which might occur due to equipment malfunction upstream, was simulated using a nitrogen bleed, but this appeared to have a minimal effect on the liquid surface potential.

The account of this work just given is necessarily simplified. There was considerable interaction between the different variables, with mutually enhancing or reducing effects.

The liquid surface potentials measured in this work were up to almost 50 kV, the latter value being obtained-with a liquid conductivity of 16 cu, a liquid velocity of 30 ft/s, a fill tube with cone deflector and a drop height of 60 in.

Tank truck loading has been studied by Ginsburgh and co-workers (L. Wright and Ginsburgh, 1963; Bulkley and Ginsburgh, 1968) with special reference to charge relaxation and discharge incendivity.

L. Wright and Ginsburgh (1963) investigated discharges. They present a model that shows that the controlling features of the discharge are the potential of the liquid surface and the geometry of the probe. They report experiments on discharges induced by applying power between a liquid surface and a probe, including a 3 in. diameter vertical pipe, a vertical plate and a horizontal plate. For the pipe the potentials for onset of a discharge were 25 kV at a separation of 0.5 in. and 50 kV at one of 1 in. When power was applied the liquid rose towards the probe, and for separations of less than 0.5 in. it touched the probe.

Bulkley and Ginsburgh (1968) continued this work on discharges. The MIE normally quoted, say >0.25 mJ for hydrocarbons, applies only to a spark gap of optimal shape and separation and to a near-stoichiometric mixture. They suggest that, in practice, the energy required to give an incendive spark is at least an order of magnitude greater.

The spark between a liquid surface and a probe is quite different from that between two metal electrodes. Although concentrated at the probe, it branches over a relatively large part of the liquid surface.

The authors state that most of the sparks obtained in the work of Wright and Ginsburgh did not possess enough energy to be incendive. For an incendive spark to occur the liquid surface potential must exceed 20 kV, which requires a charge density of 30 $\mu C/m^3$. They propose that a charge density of 15 $\mu C/m^3$, incorporating a safety factor of 2, be taken as the safety limit.

Bulkley and Ginsburgh point out that over the years, oil products have become much purer so that their conductivity is much less, with corresponding increases in relaxation times from seconds to minutes. One consequence of this is that the residence time of typically 30 s in tanks, provided to allow relaxation, is no longer adequate.

16.7.34 Strawson and Lyle model

Strawson and Lyle (Lyle and Strawson, 1971, 1972, 1973; Strawson and Lyle 1975a,b) have reported an extensive program of work by Shell on the safe loading of road and rail tankers.

Lyle and Strawson (1971) conducted experiments in which they studied discharges between a charged liquid surface and a fill pipe when a tank is filled with charged fuel. The fuel was gas oil with a conductivity of 2–7 pS/m. The locus of the liquid inlet charge density limit curve for onset of discharge ranged from an inlet liquid charge density of about 200 $\mu C/m^3$ at low liquid inlet velocities down to less than 20 $\mu C/m^3$ at high velocities. The discharge energies were determined to be about 0.005 mJ.

A separate experiment was conducted to determine the energy in an incendive discharge between a liquid surface and a probe. The liquid used was kerosene with a propane–air mixture in the vapour space around the probe. Liquid entering the tank was given a high charge by passing it through a filter. The energy required to achieve ignition was 4.7 mJ. This compares with the normal MIE of 0.2 mJ.

In an extension of this work, Strawson and Lyle (1975b) performed experiments in three metal tanks of 1.2, 2.3 and 5 m^3 volume and with overhead and bottom filling pipes. They investigated the conditions for discharge between the liquid surface and the fill pipe or a gauge marker. They developed a model for the discharge conditions. In addition to determining the locus of the liquid inlet charge density limit curve for the onset of discharge as a function of liquid inlet velocity for a fixed tank length, they also obtained both experimentally and theoretically the locus of that curve as a function of tank length for a fixed liquid inlet velocity. The locus passed through a minimum for a tank length of about 2 m. For this tank length the authors determined the limiting liquid inlet charge density as 20 $\mu C/m^3$.

The authors state that no sparks were obtained with liquids with conductivities greater than 4 pS/m.

Strawson and Lyle went on to consider the parameters that might be taken as the basis of safety, the field strength and the potential. In particular they discuss the criterion of field strength at the filling tube used by Kramer and Schb'n (Schön and Kramer, 1971; H. Kramer and Schön, 1975). This model is based on a charge distribution in the liquid around the fill pipe. They argue that the charge distribution is more likely to be relatively uniform. At the high filling rates, which are of prime interest, turbulence will tend to equalize the charge density. Moreover, Kramer and Schön have shown that for a low conductivity liquid the charge density is uniform even in large tanks.

The alternative is to use the potential of the liquid surface. Strawson and Lyle conclude that this is the better criterion. They assume that the charge is uniformly distributed and define the relevant potential as that existing in the absence of any protrusion. Various limiting values of this potential have been proposed. Mahley and Warren (1968) have proposed 1 kV, based apparently on the work of Herzog, Ballard and Hartung (1961), but the authors regard this as too low. They refer to the value given by Kramer and Schön of 35 kV. They state that in their own work the minimum potential for incendive discharge was 45 kV, and propose this as the limit value.

A model was developed for the potential of the liquid surface that gives

$$\phi \propto s_t\, f\,(\text{tank dimension, liquid depth}) \qquad [16.7.219]$$

where s_t is the space charge density in the liquid in the tank (C/m^3) and ϕ is the potential of the liquid surface (V).

The charge density in the tank is in turn related to that in the liquid entering the tank according to the relation

$$s_t = \frac{s_o Q \tau}{V_{ves}}[1 - \exp(-t/\tau)] \qquad [16.7.220]$$

where Q is the volumetric flow of the liquid entering the tank (m^3/s), s_o is the space charge density of the liquid entering the tank (C/m^3), and V_{ves} is the volume of liquid in the tank (m^3).

From Equations 16.7.219 and 16.7.220, the authors derive their guideline for safe filling conditions:

$$ud \leq \left[\frac{\kappa u}{s_o} f(L)\right]^{1/2} \qquad [16.7.221]$$

where d is the fill pipe diameter (m), L is the length of the tank (m), s_o is the inlet charge density ($\mu C/m^3$), u is the liquid inlet velocity (m/s), κ is the liquid conductivity (pS/m) and k is a constant.

In subsequent work, Strawson and Lyle (1975a) obtained limiting values of the group $s_o/\kappa u$. Their results are shown inFigure 16.57, which gives the following limits:

$s_o/\kappa u$ ($\mu C/s(pS\ m^3)^{-1}$)	
≤ 1.8	Tests at filling stations
≤ 3.3	Experiments
≤ 12.5	Experiments with partially blocked filter

Also shown in Figure 16.57 are the limit lines given by the model of Schön (1962a) for charge generation in a pipe, which are a function of the residence time in the pipe, and hence of the pipe length. From this work Strawson and Lyle propose a limiting value for the group $s_o/\kappa u$ of 12.5.

Using this limit value in Equation 16.7.221 together with appropriate values of $kf(L)$, the authors obtain the following guidelines for safe filling:

Filling mode	*Tank length*			
	≤ 2 m		>2 m	
	$kf(L)$	ud	$kf(L)$	ud
Top filling	3.1	≤ 0.50	$3.1\,(L/2)^{1/2}$	$0.50\,(L/2)^{1/2}$
Bottom filling	1.6	≤ 0.36	$1.6\,(L/2)^{1/2}$	$0.36\,(L/2)^{1/2}$

The criteria for bottom filling allow for a central protrusion from the roof. In addition, a further overall limit is imposed to limit the field created by the jet:

$$ud \leq 0.77 \qquad [16.7.222]$$

This treatment contains a number of assumptions, which are therefore the conditions for its applicability. Three of these are: that the charge distribution in the liquid is uniform; that the charge generation due to splashing can be neglected; and that any charge density transient at start-up can be neglected. The authors regard these criteria as being confirmed experimentally. With regard to the conductivity of the liquid, it is assumed that the ratio of the effective to the rest conductivity is the same as in the experiments and that the inlet liquid charge density is proportional to the liquid conductivity. Further restrictions are the absence of high charge generation conditions, specifically water in the liquid or a filter in the pipe, and absence of insulated conductors in the system or tank.

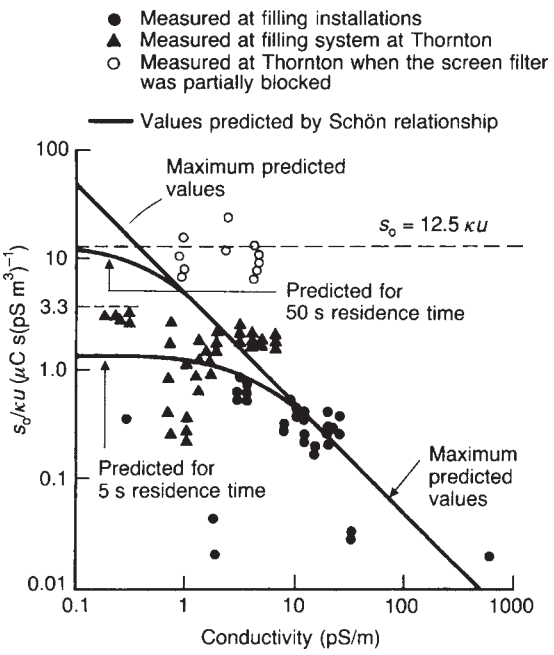


Figure 16.57 *Charge generated at filling stations (Strawson and Lyle, 1975a) (Courtesy of the Institution of Electrical Engineers)*

16.7.35 Kramer and Schön model

The work of Kramer and Schon on the filling of tanks in general and of road and rail tankers in particular, was described in Section 16.7.32. This work provides another set of guidelines for tanker filling.

16.7.36 Rees model

Another extensive program of work on the safe loading of road and rail tankers is that carried out by BP, as described by W.D. Rees (1981). Rees describes experimental work on discharges between a charged liquid surface and a metal probe. In this work it proved relatively easy to obtain discharges, which would ignite a propane–air mixture with negatively charged liquids at liquid surface potentials as low as 25 kV, but ignition did not occur with positively charged liquids even at potentials as high as 80 kV. It was found that a charge transfer in the discharge of at least 75 nC was required for ignition. The shape and dimensions of the probe affected ignition. The shape most favourable to ignition was a sphere, then a hemisphere and then a rod.

Using a 28 mm sphere with the most ignitable propane–air mixture the probability of ignition was close to unity, provided the charge transfer exceeded 75 nC.

Rees summarizes the principal guidelines for safe filling as follows. The criterion of the Physikalische Technische Bundesanstalt (PTB) is

$$ud < 0.38 \qquad [16.7.223]$$

The Shell criteria are

$$ud < 0.50 \qquad [16.7.224]$$

and

$$s_o/\kappa u < 12.5(\mu C\ s(pS\ m^3)^{-1}) \qquad [16.7.225]$$

The criterion given by Equation 16.7.224 is criticized insofar as the work described on incendive discharges has shown that critical values of the group $s_o/\kappa u$ can be less than 12.5. The critical values depend on the pipe diameter, the liquid conductivity and the liquid inlet velocity; values down to 2.4 are quoted.

Rees refers to four incidents that have occurred in Canada with a loading limit $ud < 0.5$, and two in Germany with a loading limit $ud < 0.37$.

Rees states the BP view that it is not possible to determine a loading velocity that is completely safe, but that it can be said that reducing the velocity reduces the risk. The PTB guideline is preferred and, in order to avoid proliferation of guidelines, is the one adopted.

However, he also puts forward for discussion the following proposals for loading limits:

Liquid conductivity (pS/m)	*Loading rate, ud*
$\kappa \geq 10$	$\leq$3500 l/min
$5 \leq \kappa \leq 10$	$\leq$0.5
$\kappa < 5$	$\leq$0.38

16.7.37 Oil and chemical tankers

As described in Section 16.7.2, some of the most serious incidents attributed to ignition by static electricity have involved oil tankers. An early study of the problem is that of Bustin (1963). Following the *Esso Paterson* explosion in 1956 the company adopted a set of safety rules to reduce the static ignition hazard. The investigation described was to assess the effectiveness of these safety rules.

Bustin considers the following conditions: (1) loading of product, (2) steam cleaning, (3) water washing, and (4) ventilation.

He describes an extensive series of tests on the loading of tankers. Charge densities of up to 0.2 $\mu C/m^3$, liquid surface potentials of 10 kV and field strengths of 4 kV/m were calculated from these tests. The author states that while at these potentials discharge would not occur to normal tank internals, it might well to a pointed probe. He therefore lays emphasis on ensuring that there are no grounded probes or insulated conductors.

The cleaning of tanks using steam has been associated with a number of explosions. Tests by BP some years previously showed that if the steam-cleaning machine was not grounded, or lost its ground connection, a high potential could build up on it and, in the event of a discharge, the spark was likely to incendive. Isolated conductors in particular are a hazard in this respect. With regard to the steam cloud itself, faint discharges were detected. The highest field strength determined was 60,000 V/m, which indicates that a volume of steam equivalent to a sphere some 1.25 m diameter would need to discharge to give an incendiary spark. The author states that steam cleaning is to be avoided; in fact it is frequently banned. The main method of cleaning tanks is water washing. The author regards this as safe.

Rapid ventilation may be used for gas freeing. But there was concern that charge generation could occur due to the presence of rust particles or fuel droplets in the air. Tests were performed in which the conditions in a ventilation pipe were measured. At 510 cfm of air, an air velocity of 170 ft/s and a dust loading of 0.016 lb/ft^3 the charging current was 5×10^{-6} A and the calculated field strength at the pipe wall was 50 kV/m. This was considered close to the region where discharges might occur, though not necessarily incendive ones. In fact even abnormally high dust loadings did not lead to ignition unless an insulated conductor was present.

Bustin states that neither water washing nor ventilation necessarily ensure the elimination of a flammable mixture.

Following the three tanker explosions in 1969, a major program of work was undertaken by Shell. Some of the results were described in a set of papers by van der Meer (1971), van der Weerd (1971), Smit (1971) and Vos (1971).

The work described by van de Weerd (1971) was concerned with water washing. A typical washing machine operates at 10 bar giving 180 m^3/h of water with a jet velocity of 40 m/s. The jet diameter is 4 cm at the nozzle increasing to 1–3 m at the wall. Quite large amounts of air are entrained. The mist formed has a density of about 1 g/m^3. Mist formed by impact at the wall is charged.

The factors studied were (1) number and type of washing devices, (2) jet velocity, (3) water temperature, (4) type of water, (5) impurities, (6) wall conditions and (7) tank size. It was found that the number of water guns had relatively little effect. The type of water, the water temperature and impurities in the water and presence of crude oil or sludge on the wall affected the sign and magnitude of the charge, but in an unpredictable way.

In a series of tests on water washing of tanks a typical value obtained for the charge density of the mist was 3×10^{-8} C/m^3. For a 12 m-radius tank in the absence of a protrusion this translates using Equation 16.7.57 to a field strength of 13.5 V/m. The field strength at a probe comprising a 2.5 cm cylinder was calculated to be 600 kV/m. The maximum field strength measured was 400 kV/m and the maximum space potential was estimated as 40 kV.

Experiments were conducted to investigate discharges and their incendivity. Tests are described in which a 28 mm hemispherical probe was inserted into a steam mist with a maximum space potential of 36 kV and a field strength of 330 kV/m. Discharges were obtained and were measured as groups of pulses. The discharges were of relatively long duration, some tens of milliseconds, which contrasts with a duration for metal to metal discharges of about 10^{-7} s. The energy dissipation in the first millisecond at this potential was some 0.04 mJ. The author comments that such energy dissipation may be a better measure of incendivity than energy accumulation.

The charging of insulated conductors inside a tank was also studied. The charging mechanisms include charge induction, charge transfer from mist droplets, and corona charging. It was found that with a space potential of 30 kV a cord lowered by a man standing insulated on the deck charged up to about half the space potential within seconds once his resistance to ground exceeded $10^{10}\Omega$. A man wearing normal footwear on a well-painted deck would have a resistance to ground in excess of this.

In another study a 13 mm diameter rod was dropped through a mist with a maximum space potential of 37 kV and the rod acquired a charge of some 2×10^{-7} C. Laboratory tests showed that such an object could have given an incendive spark.

Smit (1971) describes models for potential distribution developed in support of this work, and Vos (1971) describes work on the generation of a charged mist by an impacting jet, as already described.

J.F. Hughes *et al.* (1973) give an account of related work on water mists. One study dealt with periodic discharges at a probe that were found to be associated with the departure of a water droplet from the probe. These were corona discharges and were not incendive to a propane–air mixture. Another phenomenon investigated was a slug of water falling through the cloud. Slugs of water were made to fall on a trajectory spaced 0.1–0.4 cm from a grounded probe. The discharges obtained were incendive.

A number of mechanisms for incendive discharges in water washing were investigated by van de Weerd (1975), in particular discharges from a falling water slug. Washing machines can give water slugs some 4 cm diameter by 50 cm long. The maximum space potential during tank washing is at least 30 kV. Work was done to determine the fraction of the energy of the charge induced on the slug, which participates in the discharge when the slug approaches a protrusion on the tank, and this fraction was estimated as 0.2–0.4. Taking a figure of 0.2 gives a discharge energy of 1.5 mJ. This compares with a minimum ignition energy of some 0.5 mJ for a hydrocarbon–air mixture in this situation, van de Weerd concludes that such discharges are incendive.

H.R. Edwards (1983) addresses the rather different matter of chemical tankers. The background was a proposal to extend to chemical tankers the Safety of life at Sea (SOLAS) regulations which are applicable to oil tankers. There is a problem with this in that inerting by combustion products is not acceptable for chemicals, while the use of nitrogen is expensive.

He describes trials on five chemical tankers in respect of loading, steam cleaning and water washing. It was found that the liquid electrical conductivities were relatively high, being in the range 20–80 pS/m. These are the conductivities of the industrial chemicals as loaded. For example, Analar quality benzene has a conductivity of 0.8 pS/m, but the conductivity for benzene loaded in the trials was 40 pS/m. The highest value measured for the liquid surface potential was 3.4 kV for benzene. The Carruthers and Wigley model was used to confirm that the liquid surface potential would not give rise to incendive sparks.

In steam cleaning tests the maximum space potential in the steam mist in smaller tanks of 300 m^3 was about 4 kV, but tanks above 1000 m^3 gave potentials above 10 kV, the maximum recorded value being 18 kV.

Edwards details the procedures used in water washing. He gives data on the maximum space potentials in the water mist. Except for esters, the maximum space potential was 7.9 kV. For esters it exceeded 10 kV in several cases, the highest value being 11.7 kV for ethyl acetate. As already described, some of the space potentials given by Edwards are based on his model. He refers to 10 kV as the safety criterion. He lists a number of factors that suggest that, in practice, there is a safety margin. One is the safety margin in the 10 kV criterion itself. Another is the fact that chemical tankers use smaller washing machines, which tend to give smaller water slugs. He suggests that for these the hazard threshold is closer to 15 kV. Another factor is that the maximum space potential is near the centre of the vapour space, which is not the location of protrusions.

The problem of a falling water slug has been investigated further by M.R.O. Jones and Bond (1984, 1985), in the context of chemical tankers. The situation envisaged is a slug falling from the jet of the washing machine and approaching a grounded wall. The authors refer to work by Bustin (1973–74) on the size of water slugs from washing machine jets. They state that the hazardous conditions are often taken to be a space potential of at least 10 kV near the washgun and a slug of at least 0.5 m, but that there is no firm foundation for this.

Jones and Bond refer to the empirical finding of van der Weerd that the effective ignition energy required for a discharge between a water slug and a metal conductor is about twice that for a metal-to-metal discharge. They describe a model for the limiting hazardous conditions in terms of the tank centre space potential (TCSP) and the slug length. They compare their model with data given by H.R. Edwards (1983) on space potential in chemical tankers, described below. The crude data need to be converted to give the TCSP using a suitable model. In their initial work Jones and Bond accept Edwards' model for the calculation of the TCSP, but in the second paper replace this with their own model. The highest TCSP in the test data set is calculated to be some 20 kV. The initial treatment revealed no case in which the safety margin between the observed potential and the hazard threshold value was exceeded, but in some cases the difference was small, whereas in the revised treatment it is considerably larger.

Jones and Bond give a number of recommendations for the conduct of water washing of tanks, including limits on the number of washing machines and the water supply pressure.

J.S. Mills and Haighton (1983) have studied the charging of tanks by the flue gas used for inerting. The charge is generated in the boiler and carried by soot particles. Charge dissipation occurs by drift of soot particles to the walls and by corona discharge. The purpose of the work was to determine whether incendive discharges could be produced and to study the decay of the charge. Tests were done in which discharges from a charged cloud to a projection were simulated by discharges from an electrode. An electrode with a 25 mm diameter tip gave ignition most easily. The lowest space potential at which this electrode would give ignition was estimated as 70 kV. In subsequent shipboard trials the maximum space potential obtained was about 55 kV. The time for decay to 10 kV was about 5.5 h. It was concluded that the maximum space potentials were not such as to give incendive brush discharges, but that spark discharges from isolated conductors were a possibility and more stringent measures should be taken to exclude these.

J.S. Mills and Oldham (1983) review the hazard of static ignition in tankers. They quote the potentials required to

give an incendive brush discharge as 45 kV for a liquid surface potential and 70 kV for the space potential of a mist, both these potentials being negative. They refer to work that has shown mist space positive potentials of 40 kV in open cycle washing and 120 kV in closed cycle washing. These authors also discuss the static hazards of the use of glass reinforced plastic (GRP) pipes in tankers.

16.7.38 Discharges incendive in gas and liquid systems

As far as concerns ignition by an electrostatic discharge, what matters is the incendivity of the discharge. Non-incendive discharges can in some cases be helpful in dissipating charge that might otherwise participate in an incendive discharge. For a discharge to be incendive, a minimum voltage and a minimum energy are required. It is usually reckoned that for a spark discharge from a conducting object into a flammable mixture the minimum voltage is 1000 V, or 1kV.

As far as the energy of the discharge is concerned, the incendivity of the discharge is generally assessed by comparing the energy of the discharge with the MIE of the flammable mixture. For a flammable gas or vapour mixture this is the MIE of the gas. For hydrocarbons the figure most often quoted is that for a propane–air mixture which is given as 0.2 mJ. The figure appears to derive in the first instance from Lewis and von Elbe. This MIE is that measured for a spark discharge at metal electrodes. It is effectively a minimum figure.

Certain substances have a lower MIE. Hydrogen and carbon disulfide are the gases generally mentioned in this context. The MIE of carbon disulfide is 0.009 mJ and that of hydrogen is about 0.011 mJ. Substances with such low MIEs are therefore treated as sensitive substances.

In order to assess the incendivity of a discharge, therefore, it is necessary to know any minimum potential required, the energy of the discharge and the efficiency of that energy in effecting ignition relative to the energy in the spark discharge between the metal electrodes used in the measurement of MIEs. For a spark discharge various values are given for the minimum potential, but these often incorporate a safety factor. One commonly quoted value of this kind is 100 V. Britton and Smith (1988) give a value of 1000 V, or 1 kV, which they relate to the minimum gap required to avoid quenching.

The energy in a spark discharge depends on the potential and on the capacitance of the conductor. The energy is therefore variable, but there are many situations that will give an incendive spark discharge. For a brush discharge a minimum potential is not usually quoted, but may be obtained from field breakdown considerations.

With regard to the energy of a brush discharge use is made of the equivalent energy as proposed by N. Gibson and Lloyd (1965). If a flammable gas has a given MIE and a brush discharge is just able to ignite the appropriate mixture for that gas, the discharge is said to have an equivalent energy equal to the MIE value. Glor quotes values of the equivalent energy of brush discharges in the range 1–3.6 mJ and gives a theoretical treatment for a particular configuration that gives an actual energy of 4 mJ.

A brush discharge is incendive to most flammable gases. A series of studies on brush discharges has been made by Heidelberg (1959, 1967, 1970a).

For a propagating brush discharge there is a minimum voltage across the non-conducting layer for breakdown to occur. This is shown in Figure 16.58 (Maurer *et al.*, 1987). For

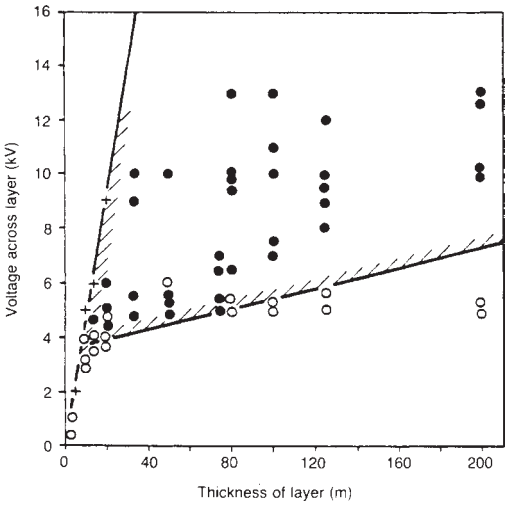


Figure 16.58 *Voltage across dielectric layers for generating a propagating brush discharge: (●) Propagating brush discharges; (O) no propagating brush discharges; (+) breakdown voltage (Maurer et al., 1987) (Courtesy of the Institute of Physics)*

layers of about 10 μm the minimum voltage is 4 kV, this value rising to 8 kV for layers of about 200 μm.

Other conditions governing propagating brush discharges have been determined by Heidelberg (1967, 1970a), who found that such discharges occur only if the surface charge density exceeds $2.7 \times 10^{-4} \mathrm{C/m^2}$ and that they do not occur if the non-conducting layer is more than 8 mm thick.

The energy in a propagating brush discharge is very high. It depends essentially on the participating area and the surface charge density. The high energies in propagating discharges may be explained as follows. As explained in Section 16.7.5, the normal maximum surface charge density, given that the permittivity of free space is $\epsilon_0 = 8.85 \times 10^{-12}$ F/m, the dielectric strength of air is $\epsilon = 1$ and the breakdown field strength of air is $E_b = 3 \times 10^6$ V/m, is given by Equation 16.7.22 as 2.64×10^{-5} C/m^2. For a configuration capable of giving a propagating brush discharge the relevant quantity to replace the breakdown field strength ϵ_b is the dielectric strength. Then for a typical non-conducting material of dielectric strength 2.7×10^7 V/m and dielectric constant 2–4, the maximum surface charge density becomes 5×10^{-4} C/m^2. This is nearly 20 times the previous figure. A propagating brush discharge is incendive to most flammable gases.

The energy in the four main types of discharge and their incendivity to gases and dusts is illustrated in Figure 16.59 (Glor, 1988).

As described in Sections 16.7.27–16.7.39, investigations of liquid storage tanks, road and rail tankers and oil and chemical tankers have often included studies of the incendivity of discharges in these systems. In addition, there has been some work specifically directed to this topic.

In the context of aircraft fuelling, Bruinzeel (1963) carried out experiments on discharges during the filling of a liquid storage tank with kerosene. The tank was $4 \times 1 \times 0.75$ m divided into four compartments. Discharges were

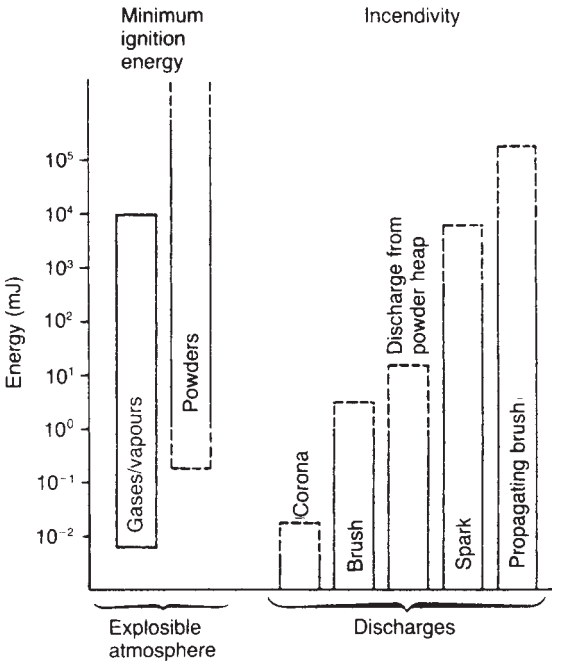


Figure 16.59 *Energy of five types of electrostatic discharge (Glor, 1988) (Courtesy of Research Studies Press)*

observed between the liquid surface and the fill pipe before its submersion, between the liquid surface and the roof even at a low liquid level, and between the liquid surface and a probe. The discharges occurred most frequently during filling when the liquid level was below one-quarter to one-third full and after it was three-quarters full. The liquid charge when discharges occurred was, with few exceptions, negative.

As found by other workers also, discharges occurred at average field strengths of the order of 400–500 kV/m, although the local field strength at some point must have reached 3000 kV/m. The author quotes, however, the view of Heidelberg and Schb'n that hazardous discharges might occur at an average field strength as low as 100 kV/m.

Typical results were for a liquid with a conductivity of 3–4 pS/m, a discharge gap of 0.2 m, a charging current of 12–18 μA and a liquid surface potential of 100 kV a discharge energy of 160–500 mJ with more than half being transferred within 0.2–0.3 μs. It was estimated that the charge in the tank was typically 12–18 μC and that in the discharge 1–5 μC. The ignition of a flammable gas mixture was demonstrated.

Leonard and Carhart (1967) carried out work on discharges between the liquid surface of JP4 and JP5 fuels and electrodes of different configurations. These were a needle, a 60° point and $\frac{1}{4}$, $\frac{1}{2}$ and 1 in. sphere electrodes. The characteristics of the discharges between these electrodes and a metal plate were also studied.

The needle and 60° point electrodes gave mainly corona discharges, but the latter also gave spark discharges. The 60° point and small spherical electrodes gave spark discharges at small gaps, but otherwise gave corona discharges. The large spherical electrodes gave pre-breakdown streamers, which never made the transition to filamentary sparks. These streamers occurred at a frequency of about 100/min and had a duration some 7 times longer than that of filamentary sparks of the same energy.

It was found that for comparable conditions with the lin. spherical electrode the discharges between the electrode and the metal plate had 30–40 times as much energy as those between the electrode and the liquid surface. For the latter case the highest energies, up to 2.3 mJ, were obtained with the lin. electrode. The discharges studied were not incendive to JP4.

Summarizing the work on incendive discharges in liquid storage tanks and in road and rail tankers, the principal conditions for which there have been proposed limiting values below which discharges are not incendive are the liquid surface charge and the maximum vapour space potential. For these conditions the value quoted may be either the technical limit at which the discharge is just incendive, or a safety limit that is intended to incorporate a safety margin. Bulkley and Ginsburgh (1968) proposed for the technical limit 20 kV and for the safety limit 10 kV. A much lower figure of IkV was suggested for the latter limit by Mahley and Warren (1968). Subsequent workers have regarded this as too low. The technical limit has been proposed as 45 kV by Strawson and Lyle (1975b) and as 25 kV by W.D. Rees (1981). H. Kramer and Schön (1975) have proposed 35 kV as the technical limit on the maximum vapour space potential.

As far as concerns tanker water washing, a technical limit for the maximum vapor space potential of below 37 kV emerges from the work of van de Weerd (1971), while one of 70 kV has been given by J.S. Mills and Oldham (1983). The safety limit on the maximum vapour space potential is taken as 10 kV by H.R. Edwards (1983) and by M.R.O. Jones and Bond (1984, 1985).

16.7.39 Powders and dusts

The problem of ignition by static electricity in powder handling has some similarities with that in handling liquids, but there are also some important differences.

The powder may be handled as a dust suspension or a settled powder, and often as both.

The charging tendency of a powder is difficult to predict, but it tends to be high. It is also difficult to modify. Options that can be used with liquids may not be available. There is limited scope for reducing the velocity in pneumatic conveying. There is also limited scope for dosing with an additive to increase conductivity.

In the settled state particularly, a powder has a high bulk density and its volume charge density tends to be correspondingly high.

Prediction of the charging tendency is made difficult by a number of factors, including the particle diameter and size distribution, impurities, the water content, and the speed of separation.

The extent of charging of a powder depends on its volume resistivity. Charging is to be expected at a resistivity of $10^8\Omega$m and above. The resistivity of most organic powders exceeds this value.

Some data on the electrical volume resistivity of powders are given in Table 16.37. Figure 16.60 (N. Gibson, 1971) show the distribution of the resistivities of organic powder products.

Table 16.37 *Electrical volume and surface resistivity of selected solid materials*

A Volume and surface resistivity[a]

	Volume resistivity[b] (Ω m)	*Surface resistivity*[c] (Ω)
Plastics, overall range	10^6–10^{15}	10^8–10^{17}
PVC, unplasticized	10^{12}–10^{13}	10^{13}–10^{14}
PVC, plasticized	10^9–10^{12}	10^{10}–10^{13}
Polyethylene, high density	10^{14}	10^{14}–10^{15}
Polyethylene, low density	10^{15}	10^{14}–10^{15}
Polypropylene	10^{15}	10^{14}–10^{15}

B Surface resistivity of glass: effect of relative humidity[d]

Relative humidity (%)	*Relative surface resistivity*
100	1
80	4
70	30
60	800
50	30,000
40	6,000,000

[a] *Source*: Lüttgens and Glor (1989).
[b] Manufacturer's specification.
[c] Literature values.
[d] *Source*: W.F. Cooper (1953b), quoting Smail, Brooksbank and Thornton (1931).

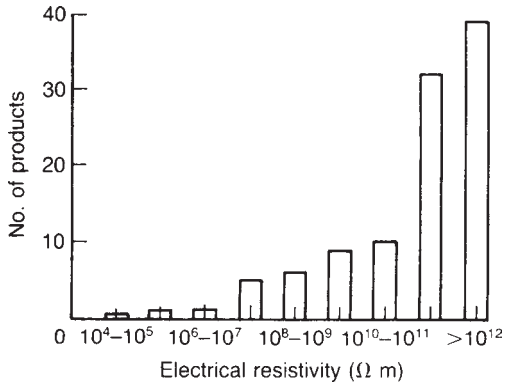


Figure 16.60 *Electrical volume resistivity of powders (N. Gibson, 1979) (Courtesy of Filtration and Separation)*

Given that the resistivity of the powder is sufficiently high for it to exhibit charging, the charging tendency depends more on the operations to which the powder is subjected than on the powder properties. Operations in which charging occurs include micronizing, grinding, sieving, gas filtration, pneumatic conveying and mechanical transfer.

The electrostatic charges generated in powders by these operations are typically as follows (N. Gibson, 1969):

	Charge (C/lb)
Micronizing	10^{-7}–10^{-3}
Grinding	10^{-7}–10^{-6}
Scroll feed transfer	10^{-8}–10^{-6}
Pouring	10^{-9}–10^{-7}
Sieving	10^{-11}–10^{-9}

The charge per particle increases, but less than proportionately, with increasing particle diameter. Thus the charge per unit mass must decrease. This is in line with the data just given.

The charge density on a powder is commonly expressed either as the volume charge density or the mass charge density. The relation between the two is

$$\frac{q}{m} = \frac{s}{\rho_e} \qquad [16.7.226]$$

where q is the charge on a particle (C), m is the mass of the particle (kg), s is the volume charge density (C/m^3) and ρ_e is the effective density (kg/m^3 air). The ratio q/m is also the mass charge density of the powder (C/kg). The effective density is that of the dust cloud or settled powder, as the case may be, and in the latter case it is the bulk density. The charge on a particle is then

$$q = \pi d^2 \sigma \qquad [16.7.227]$$

and the mass is

$$m = \frac{\pi}{6} d_d^3 \rho_s \qquad [16.7.228]$$

where d_d is the particle diameter (m) and ρ_s is the density of the particle (kg/m^3). Hence from Equations 16.7.227 and 16.7.228

$$\frac{q}{m} = \frac{6\sigma}{d_p \rho_s} \qquad [16.7.229]$$

The maximum charge on the particle in free space is determined by the maximum surface charge density.

As an illustration, consider a powder with a material density of 1000 kg/m^3 and a limiting surface charge density in free space of 2.7×10^{-5} C/m^2. Then for particle

diameters of 10^{-2} and 10^{-6} m Equation 16.7.229 gives mass charge densities of 1.6×10^{-5} and 2×10^{-1} C/kg, respectively.

Dust may be in suspension or deposited. There is very little information on the occurrence of discharge between particles in suspension, but it cannot be ruled out. With a deposited dust there is a relaxation of the charge similar to that in a liquid. If the dust has a high resistivity, the relaxation time may be hours or even days. Discharges from deposited dusts are often coronas.

In much equipment handling dusts a flammable atmosphere does not exist during normal operation, because the dust suspension is above its upper flammability limit. But a flammable suspension is more likely to occur during transient conditions such as start-up and shut-down.

The principal hazard in dust-handling equipment is that presented by a container or other object made of conducting material but insulated from ground. There are certain factors that tend to reduce the probability of electrostatic ignition in equipment handling dust suspensions. One is that the dust suspensions tend to have high MIEs. A second is that discharge is frequently by a corona. The hazard of static electricity in dusts is discussed by K.N. Palmer (1973a).

16.7.40 Powder flow in pipes

The charging current for the flow of particles in a pipe, in other words in pneumatic conveying, has not been studied as extensively as that for liquids. The most common approach appears to be to estimate the maximum theoretical charge on the particles and to express the experimental results in terms of the fraction of this maximum charge attained.

The maximum charge on a particle in flow in a pipe differs from the maximum charge in free space. The maximum space charge density is obtained from Equation 16.7.61 and is inserted in Equation 16.7.229 to give the maximum charge on a particle q/m, or mass charge density.

As an illustration, consider the example given by J.F. Hughes and Bright (1979) for which the pipe radius is 0.05 m and the particle density is 0.95×10^3 kg/m^3. Then, utilizing the usual values for the permittivity of air and the breakdown field strength, Equation 16.7.61 gives a space charge density of about 1.06 C/m^3 and Equation 16.7.229 gives a mass charge density of about 1.12×10^{-6} C/kg. Furthermore, by equating the mass charge density q/m in Equations 16.7.226 and 16.7.229, and utilizing Equations 16.7.22 and 16.7.61, the condition for the equality of the maximum mass charge densities in free space and in a pipe is obtained:

$$\frac{d_d \rho_s}{3 r_p \rho_e} = 1 \qquad [16.7.230]$$

Several workers have obtained experimentally determined values of mass charge densities, and hence charging currents, which are close to the theoretical maximum. For example, J.F. Hughes and Bright (1979) report mass charge densities of $0.8-3.4 \times 10^{-6}$ C/kg for the case described above, for which the theoretical value was 1.12 C/kg. On the other hand, Boschung and Glor (1980) obtained the results shown in Figure 16.61, where the experimental mass charge densities are about one-tenth of the theoretical values.

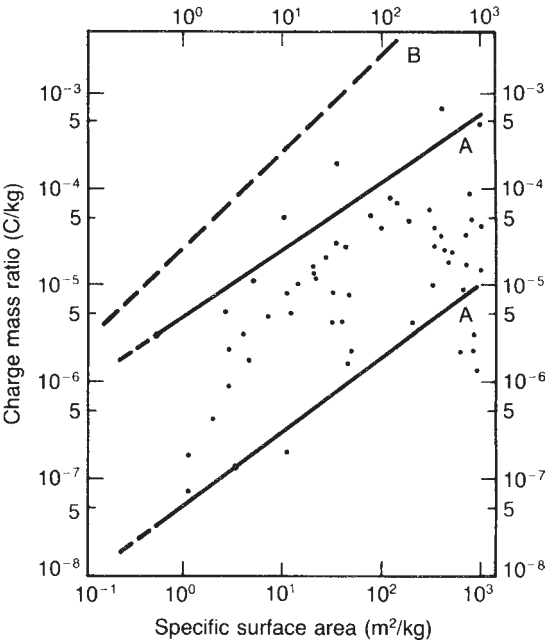


Figure 16.61 *Mass charge densities in powder flow in a pipe (Boschung and Glor, 1980): A, general trend of experimental data; and B, maximum values from a theoretical model (Courtesy of the Journal of Electrostatics)*

16.7.41 Powder storage silos

As with liquid storage tanks, so with powder silos there is a problem of charge accumulation and relaxation. The heap of powder in a silo tends to have a high volume resistivity and a high mass charge density. Such a powder will therefore retain a large charge over a long period. Relaxation of the charge may take days or even weeks.

The main hazard in such a situation is a discharge. The envelope of conditions that can give a discharge is determined by two limiting factors. The field must be strong enough to give field breakdown but not so strong that it prevents a charged particle from settling under gravity. Glor (1984) has utilized these two limitations to derive a simple model, which gives the envelope for discharges shown in Figure 16.62. This model leads to the conclusion that discharges are to be expected only for rather coarse powders, having particle diameters in the range 1–10 mm.

16.7.42 Discharges incendive in powder and dust systems

The incendivity of discharges for flammable gases was described in Section 16.7.10. The incendivity of a discharge for dusts may be determined by comparing the effective energy of the discharge with the MIE of the dust. The MIEs of dusts are given in Chapter 17 but, broadly, dusts typically have an MIE in the range 1–10 mJ.

A spark discharge may be incendive to dusts, depending on its energy.

A brush discharge is not regarded as incendive to dusts. According to Glor, there is no known case of ignition of a dust by a brush discharge. In practice it is difficult in handling powders to avoid brush discharges.

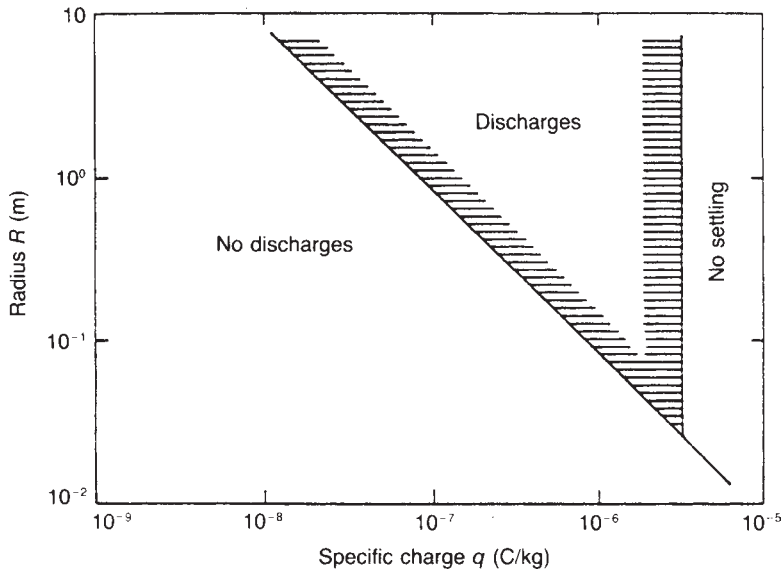


Figure 16.62 *Region for brush discharges on a settled powder in a silo: spherical heap of radius R (Glor, 1984) (Courtesy of the Journal of Electrostatics)*

A propagating brush discharge has very high energy and is incendive to most dusts.

With powders it is also necessary to consider another type of discharge, that is a bulking brush discharge in a silo. A discussion of the conditions under which such a discharge is most likely to occur has been given by Glor (1988). The conditions are a high bulk resistivity ($>10^{10}$ Ωm) and relatively large particle size (diameter >1 mm). The energy release in a bulking brush discharge is estimated to be of the order of 10 mJ and this is sufficiently high to be incendive to many dusts.

16.7.43 Drums and small containers

As mentioned earlier, explosions due to static ignition also occur in the filling of drums. Treatments of this problem include those by Pesetsky and Fisher (1975), Britton and Smith (1988) and Rosenthal (1988).

An incident is described by Pesetsky and Fisher involving an explosion during the filling with toluene of a 55 US gal steel drum that was not grounded. The drum was lined with a 5 mil (1 mil = 0.001 in.) non-conductive epoxy coating. Tests showed that when an ungrounded steel drum was filled with toluene, discharges between the steel drum and a grounded probe regularly caused ignition. It was also found that insertion of a 3 ft section of plastic pipe into the filling line increased the charging current by a factor of 23. It was estimated that under the test conditions the capacitance of the drum was about 100 pF, while the potential was measured as 8700 V, giving an energy of 3.6 mJ. In other tests in which a plastic drum and a plastic filling pipe were substituted, both the drum and the liquid reached a potential of 87,000 V, that is a value 10 times as high, but incendive discharges were not obtained between an grounded probe and the liquid surface. The authors refer, however, to work by Bruinzeel (1963) on tank filling, using a liquid with conductivity some 20 times less than toluene, in which incendive discharges were obtained from the liquid surface.

Britton and Smith (1988) describe an extensive investigation of drum explosions, following an incident in which an explosion occurred in a lined drum that was grounded. A review of all available incidents showed that in all cases low conductivity liquids (<50 pS/m) were involved. The authors conclude, however, that in certain situations a conductive liquid may give an incendive discharge. While it is true that for a grounded drum, unlined or with a lining of negligible resistance, an incendive discharge requires a low conductivity liquid, with a lined drum it may occur with either a conductive or a low conductivity liquid.

In at least one case reviewed the drum was grounded and the ignition occurred due to brush discharge between the liquid surface and the filling lance tip. It is this type of incendive discharge in particular that the authors address.

Such a discharge has a relatively low energy and ignition occurs only over a limited range of concentration. This cuts both ways. On the one hand it greatly reduces the risk of an explosion, but on the other it means that the fact that an explosion has not occurred to date is no guarantee that it will not do so.

The risk of static ignition depends on a number of factors, including the grounding, the drum, the liquid conductivity, the filling arrangements and the fill pipe. With regard to grounding, the authors state that to obtain an incendive discharge a potential of 1000 V is required. Allowing a safety factor of 10, the potential should be limited to 100 V. The charging current rarely exceeds 10^{-4} A. Thus it is sufficient that the resistance to ground does not exceed 1 MΩ.

One measure is to reduce the resistance of the lining. Some drum linings have a significant electrical resistance, while others do not. Polyethylene, for example, is essentially a perfect insulator. On the other hand, drum coatings of the epoxy or phenolic types have very low resistance.

Another approach is to address the charge generation and relaxation. Some features are prolific charge generators. The authors state that a high charging current can be generated not only by a filter but also by a hose with an internal grounding spiral. In their work, such a hose gave a charging current much greater than that of a smooth bore hose and within an order of magnitude of that produced by a microfilter.

Britton and Smith refer to recommendations on relaxation of the charge. It is normally advised that three time constants be provided for the liquid between a filter and the drum. Of the then current guides, API RP 2003 gives a relaxation time of 30 seconds for liquids with a conductivity less than 50 pS/m, and BS 5958: 1991 gives a relaxation time of 3 time constants for liquids with conductivities down to 2 pS/m combined with a global relaxation time of 100 s for liquids with lower conductivity.

The design of the fill pipe is also important. The dip pipe should have the largest practicable diameter and should have a pointed end; a rounded end is to be avoided.

The authors present electrostatic models for drums in support of the assessment of the risk of incendive discharge.

Dahn, Kashani and Reyes (1994) describe the problem of control of the static electricity hazard in the use of flexible intermediate bulk containers (FIBCs) for powders. They point out the hazard of attempting to solve the problem by utilizing grounded exterior bag surfaces. This tends to increase the likelihood of a propagating brush discharge. Further, if the grounding is lost and the static charge is high, there is potential for an incendive discharge.

They describe their preferred approach, the elements of which are to estimate the static charging rate, the charge dissipation rate, the field strength and the discharge strength. The charging rate is determined by a test in which the powder is passed down an inclined chute into a metal bucket container where the charge is measured. Tests are also done using an ASTM method to determine the surface and volume resistivities so that the charge dissipation may be estimated.

For the field strength in the container they use Equation 16.7.58a. As an illustration, they give a calculation of the field strength for the case of a container of radius 0.807 m, with a charge density of 38.53×10^{-6} C/m^3 and utilizing the permittivity of air of 8.83×10^{-12} C/V m. The resultant field strength is 1171 kV/m.

They also give calculations of the energy in a propagating brush discharge.

16.7.44 Moving machinery

Static electricity is generated by the relative movement of surfaces in machinery. In particular, conveyor belts and reeled material tend to accumulate a large electrostatic charge.

The voltages generated by a conveyor belt are often compared with those generated by a van de Graaff generator. Typically such a generator might have a potential of 100 kV with a current of several microamps, but values of up to 50 kV and several milliamps have been quoted.

Cross (1981) has described experiments on two conveyor belts, one an insulating belt and one an antistatic belt, in which the effect of humidity was measured. At zero absolute humidity the potential on the insulating belt reached 110 kV, while that on the antistatic belt was about 6 kV. Bucket elevators also can build up an appreciable charge.

16.7.45 Human body

The human body can become electrostatically charged and can be the source of an incendive spark. The human body has a low volume resistivity and thus acts as a conductor. Charging can occur by contact charging, by induction or by charge sharing. Some activities which can cause charging are walking, rubbing, removing clothing, pouring liquids and powders, and touching charged objects. The maximum potential of the body is of the order of 50 kV, the limitation being leakage and sparking. It is not uncommon for the body to be at some 10 kV. The capacitance of the body is in the range 100–300 pF, say 200 pF. Then at a potential of 10 kV, from Equation 16.7.19 the energy of a discharge from the body is some 10 mJ.

Discharge from the body is therefore capable of giving a spark incendive to a flammable gas mixture. Removal of clothing can also give an incendive spark. BS 5958 : 1991 recommends precautions against incendive discharge for the body for flammable mixtures with MIEs < 100 mJ. Discharge from clothing is reckoned to be incendive only to sensitive mixtures.

The main precaution against sparks from the human body is grounding. The charging current which occurs as a result of manual activities generally does not exceed 10^{-6} A. Then, applying the $100/I$ criterion gives a required resistance to ground of not more than 10^8 Ω. There are also two other relevant criteria. For avoidance of uncomfortable shocks the resistance to ground should not exceed 10^9 Ω. For protection against mains voltage it should not exceed 5×10^4 Ω. In BS 5958 Part 1: 1991 a resistance to ground for personnel of 10 represents good practice in most applications, but the standard allows one of up to 10^6 Ω in certain cases.

In order to achieve this degree of grounding it is necessary to consider both footwear and flooring. BS 5958: 1991 gives requirements for the two main types of footwear used: antistatic footwear and conducting footwear. It also states that leather footwear usually has a sufficiently low resistance, except when very dry.

BS 2050: 1978 gives requirements for flooring materials and BS 3187: 1991 gives requirements for laid floors, but only of the conductive type. A conductive type floor is not suitable if protection is required against mains voltage. It is sometimes permissible to provide a limited area of low resistance flooring such as a metal plate.

16.7.46 Containments

The effect of the containment has been referred to a number of times in the preceding sections. It is now considered in more detail. Containment materials are classed as conductive or non-conductive. BS 5958: 1991 defines a non-conductive, or high resistivity, material as one with volume and surface resistivities of 10^{12} Ωm and 10^{12} Ω, respectively. In process containments the principal conductive materials are metals and the principal non-conductive materials are plastics. Some data on the electrical volume and surface resistivities of solid materials are given in Table 16.37. In addition, use is also made of non-metallic conductive materials, essentially plastics modified to increase their conductivity.

Some principal containments and containment materials are given in Table 16.38, based broadly on the distinctions made in BS 5958. Most are self-explanatory, but several require further comment. Where the container is non-conducting, there may be the possibility of a discharge

Table 16.38 *Some containments and containment materials*

Metal container for liquids
Non-conducting container for liquids
Metal container for liquids with fixed non-metallic coating
Metal container for liquids with outer non-metallic coating/jacket
Metal pipes for gases and liquids
Metal container for powders
Non-conducting container for powders
Container for powders with liner:
Metal container with conductive liner
Metal container with non-conductive liner
Non-conductive container with non-conductive liner

from its external surface. Some metal containers have an internal non-conductive coating. This creates the possibility that charge from repeated filling or rubbing is retained on the coating. Metal containers may also have an external non-conductive coating or jacket. There is then the possibility of a discharge from the external surface of the container. Another possible effect where there is a non-conductive outer surface, whether that of the main container or of a coating, is that metallic objects on this surface may constitute isolated conductors. Any situation where there may be a discharge from the container is relevant if the container is in a classified hazardous area.

Some containers for dry powders have removable liners. Broadly, BS 5958: 1991 treats a metal container with a conductive liner as an unlined metal container and a non-conductive container with a non-conductive liner as an unlined non-conductive container. It recommends against the use of a non-conductive liner with a metal container or of a conductive liner with a non-conductive container, and recommends additional precautions where such mixed systems have to be used.

16.7.47 Precautions against static electricity

Static electricity can act as a source of ignition giving rise to a fire or explosion only under the following conditions:

(1) a flammable atmosphere exists;
(2) an electrostatic charge is generated, accumulates and produces an electric field strength which exceeds the critical value for breakdown;
(3) the resultant incendive discharge has an energy greater than the minimum ignition energy of the flammable atmosphere.

Thus precautions against static electricity aim to eliminate one or more of the above factors. These precautions tend to be based, therefore, on the following approaches:

(1) elimination of a flammable atmosphere;
(2) control of charge generation;
(3) control of charge accumulation;
(4) minimization of incendive discharge.

It is a general principle in handling flammable materials to make avoidance of a flammable atmosphere the first line of defence where this is practical. It is necessary also to try to eliminate sources of ignition, but it is much more difficult to do this reliably.

Since electrostatic charge builds up both on process materials and on process plant, it is not sufficient simply to ensure that charge is drained away from plant by measures such as grounding. It is essential to deal also with the charge on the material being handled.

In the handling of liquids the precautions used may include the following:

(1) elimination of flammable mixtures;
(2) bonding and grounding;
(3) modification of liquid conductivity;
(4) limitation of flow velocity;
(5) minimization of charge generation by –
  (a) immiscible liquids,
  (b) filters, valves;
(6) avoidance of splashing and settling;
(7) avoidance of grounded probes;
(8) grounding of personnel;
(9) measures associated with low conductivity containers;
(10) provision of relaxation time.

The elimination of a flammable mixture is used particularly for liquid storage tanks and for tank cleaning on tankers.

Bonding and grounding are discussed in Section 16.7.48.

The modification of liquid conductivity was developed particularly by Shell, and the Shell additive ASA 3 is widely used for conductivity modification. Modification of liquid conductivity has been discussed by Klinkenberg and van der Minne (1958). The liquid conductivities recommended in order to keep charge separation below a safe level are 50 and 500 pS/m for pipeline velocities below and above 7 m/s, respectively.

Thus some products, such as crude oil, have a sufficiently high conductivity to render them safe, while others, such as light distillates, do not. It is possible, however, to modify the conductivity of the latter by the use of a very small amount of a suitable additive. Additives are usually a combination of divalent or polyvalent metal salt of an acid such as carboxylic or sulphonic acid and a suitable electrolyte that imparts a conductivity of about 10,000 pS/m in a 0.1% solution in benzene. Thus concentrations of 0.6 and 6 ppm of additive Shell ASA 3 raise the conductivity of such products to about 200–300 and 1000 pS/m, respectively.

The charging current in the pipeline flow of liquids is of the order of 10^{-10}–10^{-7}A. This current is approximately proportional to the square of the velocity. Keeping the velocity down can, therefore, reduce charge generation. A limit on pipeline velocities of 7 and 1 m/s, respectively, for liquids without and with an immiscible component has been recommended by Klinkenberg and van der Minne (1958). The much lower limit for liquids with an immiscible component, such as free water, is due to the fact that in such liquids the rate of charge generation can be up to 50 times greater.

Filters generally require special precautions. Since the streaming current generated in a filter is proportional to the flow rate rather than the square of the flow rate, as with a pipe, the limitation of liquid velocity is rather less effective for filters. The usual approach is to allow a relaxation time by providing an adequate length of pipe between the

filter and the tank. This is more difficult to do, however, for high purity products with long relaxation times.

For liquid storage in a tank of non-conductive material or in a tank of non-conductive material with an embedded metal grid not in contact with the liquid, BS 5958:1991 recommends the use of an grounding plate of area

$$A_{ep} = 0.04\, V_t \qquad [16.7.231]$$

where A_{ep} is the area of the grounding plate (m^2) and V_t is the volume of the tank (m^3).

Although they are generally less prolific generators than filters, valves and other constrictions can also give substantial increases in charging.

Tank filling arrangements should avoid free fall and splash filling of liquids. Inlets should reach to the bottom of the tank or, preferably, should enter at the bottom of the tank and be submerged.

Grounded probes in tanks should be avoided as far as is practicable, as should isolated conductors.

There should be suitable arrangements for level gauging. The hazard is reduced if antistatic additives are used and if an adequate relaxation time is allowed. Level measuring equipment, which is used where there is an electrostatic hazard, includes non-conducting ullage tapes and permanently fixed and grounded sounding pipes extending to within a few centimeters of the tank bottom. Detailed discussions of the precautions associated with level gauging are given by J.R. Hughes (1970) and Page and Gardner (1971).

Settling of immiscible liquids, such as water droplets in oil, should be avoided as far as possible.

A liquid storage tank made of a non-conductive material may be provided with a grounded metal grid on or just below the surface throughout the material. If this conducting grid covers the inner surface of the tank and is thus in contact with the liquid, this provides a ground for the liquid.

Precautions against the charging of the human body take the form of special footwear and flooring. There are two types of product available: antistatic and conductive. Both prevent accumulation of electrostatic charge, but whereas the former gives protection against electrical mains failure, the latter does not and should only be used where there is other protection against such failure. There are a number of British Standards on antistatic and conductive footwear and flooring. Since the resistance of these products can change, it is important that it be monitored regularly; instruments are available to do this.

The hazard involved in using non-conducting containers may be dealt with by limiting the container size. Some maximum sizes for non-conducting plastic containers have been suggested by Heidelberg and Schön (1960) as follows:

	Maximum container size (l)
Liquids with low ignition energy	1
Liquids with flashpoint <21°C	2–5
Liquids with flashpoint >21°C	60

As already indicated, both conducting and non-conducting containers present static electricity hazards and applications need to be considered individually.

The precautions required in the handling of dusts and powders are somewhat similar to those for liquid handling. Principal measures again include elimination of flammable suspensions, bonding and grounding of plant, and grounding of personnel. Antistatic additives, which modify dust resistivity, are not well developed. Measures such as humidification and ionization are used, but have limitations. Non-metallic containers for sensitive dusts should have low resistance. Detailed information on the precautions for dust handling is given by K.N. Palmer (1973a).

The electrostatic hazard from steam leaks is that a nearby conductor insulated from ground becomes charged. An example of such a conductor is wire netting around lagging. Insulated conductors should be avoided in situations where they could become a hazard.

Steam used for purging or cleaning can cause charge generation. Again it is necessary to consider both the plant and the fluid. The risk of ungrounded pipelines and charge accumulation on these is reduced if the lines used are fixed rather than portable apparatus. Keeping the flow velocity down should minimize charge generation in the steam. Grounded probes should be avoided so that the probability of a discharge is reduced.

Carbon dioxide should not be used for the rapid inerting of flammable atmospheres, since it can generate static electricity and so act as an ignition source.

The accumulation of electrostatic charge on moving machinery can be prevented in some cases by grounding the machinery. Objects such as conveyor belts and transmission belts, however, may also accumulate charge and this is not prevented by normal grounding arrangements. The usual solution is to modify the conductivity of the belt material by the incorporation of additives during manufacturing or by the use of a dressing in operation.

The reduction of the resistance of materials is a widely used approach and there are British Standard specifications for low resistance polymeric materials not only for flooring, footwear and belts, as already mentioned, but also for sheeting, hose, tires and wheels.

Electrostatic eliminators based on ionization are used to prevent charge accumulation in applications such as reeling operations. The charge is either drained to ground through the ionized air or is directly neutralized by ions from the air. Air can be ionized by heat, high voltage, ultraviolet light or radioactivity. Not all types of electrostatic eliminator are suitable for flammable atmospheres. Flames are sometimes used, for example, as ionizers on printing presses.

Devices that have pointed surfaces and are electrically energized are another type of ionizer. If flammable mixtures can be present, however, it is necessary to ensure that the electrical equipment is not itself a source of ignition.

Another method of ionization uses a radioactive source. This type of equipment is of limited applicability, because it is only suitable where charging rates are low. It is used, however, in the paper and textile industries. It is necessary with such devices to take the usual precautions for a radioactive hazard.

Since a pointed object will ionize air near a charged object, it is also possible to use devices rather like wire brushes as induction collectors. There is in this case no electrical energization.

The relative humidity in the atmosphere has a considerable influence on the incidence of electrostatic hazards. In general, most fires attributed to static electricity occur

indoors in winter when the relative humidity is below about 30%. If the relative humidity is kept above 60–70%, the electrostatic charge tends to drain away. This is largely a surface electrical conductivity effect. The change in surface conductivity with relative humidity can be dramatic. For plate glass there is a 1000-fold increase in surface conductivity between 20% and 50% relative humidity.

16.7.48 Precautions against static electricity: grounding and bonding

Grounding and bonding comprise one of the principal methods of providing protection against static electricity. Bonding involves making an electrical connection between two conducting objects and ground. The effect of bonding is to maintain the two objects connected at the same potential and that of grounding is to drain away to ground the charge on the object connected. Grounding and bonding systems are also required to give protection against electrical systems and against lightning, but the systems considered here relate only to static electricity.

The purpose of grounding and bonding is to prevent an incendive discharge. The conditions for an incendive discharge to occur are that the field strength reaches the breakdown value and that the energy in the discharge equals the relevant ignition energy.

A potential of at least 300 V is normally considered necessary for an incendive discharge, but since a potential of 100 V has been considered hazardous in explosives manufacture, the latter figure is generally taken as the limit value. Applying Equation 16.7.1 (Ohm's law) gives the criterion that the resistance should not exceed $100/I$. Charging currents vary in the range 10^{-11}–10^{-4} A. Taking the worst case of a charging current of 10^{-4} A yields the criterion resistance to ground of $10^6\ \Omega$. Taking a more realistic value of 10^{-6} A for the charging current yields a resistance to ground of $10^8\ \Omega$.

As a practical matter it is usually recommended that for conducting equipment, such as a metal, the resistance to ground should not exceed 10 Ω. The reason for this is that the equipment might contain certain high resistance features such as paint, grease and oil, corrosion and rust, which could increase in resistance and negate the required grounding if the resistance were set at, say, $10^6\ \Omega$. The value recommended in BS 5958: 1991 is 10 Ω; this has the advantage of being the same as the value prescribed for lightning protection.

Different requirements for grounding are given in BS 5958 for equipment made of non-conducting material and of conductive or antistatic materials. For plant built in non-conducting material, isolated conductors are of particular concern. It is frequently recommended that all isolated conductors be grounded. BS 5958 questions this philosophy and proposes instead an approach based essentially on hazard assessment, taking into account the probability that the item will be charged, that it will give an incendive spark and that a flammable mixture will be present. For equipment made of conductive or antistatic material, BS 5958 recommends a resistance to ground not greater than $100/I$. This will tend give a resistance in the range 10^4–$10^8\ \Omega$. The general recommendation is for $10^6\ \Omega$, but a higher resistance, which still meets the $100/I$ criterion, is acceptable.

General grounding requirements are discussed in BS 5958: Part 1: 1991. These include a table summarizing the requirements. Further guidance on detailed requirements for particular situations is given in BS 5958: Part 2: 1991.

Grounding is usually achieved by means of copper strips or wire attached to a special point on the object to be grounded. Bonding across flanged joints to ensure better electrical continuity than that through the bolts has been widely practiced, but many companies have satisfied themselves by tests that this is not necessary and have discontinued the practice.

A good grounding system also requires that it be recognizable as such and that it be checked periodically and after maintenance operations.

Grounding of the human body and the use of appropriate footwear and floors are described in Section 16.7.45.

16.7.49 Precautions against static electricity: BS 5958

BS 5958: Parts 1 and 2: 1991 gives very detailed recommendations for precautions against static electricity, with those for particular situations being given in Part 2. Table 16.39 lists the principal contents of Part 2.

Some of the precautions for handling liquids recommended in BS 5958: Part 2: 1991 are summarized in Table 16.40. For liquid storage tanks made of metal, a flammable atmosphere may be eliminated by reduction of the vapour space by using a floating roof, or by some form of atmosphere control such as inerting. The tank should be grounded. Splash filling should be avoided. Filling may be by a top or bottom fill pipe. A top fill pipe should extend close to the bottom of the tank. There should be a limitation of the liquid velocity during filling. Measures should be taken to avoid excessive charge in the liquid entering the tank. An adequate relaxation time should be allowed before operations such as gauging and sampling are carried out. Measures should be taken to avoid discharge between the liquid in the tank and the tank itself during such operations.

The standard discourages the use of non-conductive liquid storage tanks and recommends that specialist advice be taken before installing one. The precautions recommended for metal storage tanks apply, but in addition it is preferable that the liquid itself should be grounded and, for a classified hazardous area, the effect of an external discharge should be considered.

The recommendations for metal road and rail tanks are broadly similar, but additional measures are specified concerning filling hoses.

For barge and ship loading BS 5958: 1991 gives recommendations on atmosphere control, grounding, fill pipes and liquid filling velocity.

Some of the limitations on liquid velocity for operations involving filling with liquids, as given in BS 5958: 1991, are summarized in Table 16.41. For small liquid containers the Standard recommends for metal containers grounding of the container and a limitation of the liquid velocity during filling. For non-conductive containers consideration needs to be given to the hazardous area classification. The container itself can be considered a Zone 1 area if either a flammable liquid is being handled or if a flammable atmosphere may be present in normal operation. A non-conductive container should be used only if the risk of ignition is acceptably low, which may be a matter for expert guidance. With non-conductive containers in classified hazardous areas consideration needs to be given also to external discharge. This applies whether or not the liquid is flammable.

Table 16.39 *Principal contents of BS 5958: Part 2: 1991*

Larger containers
3. Fixed metal tanks for the storage of liquids
4. Fixed non-metallic tanks for the storage of liquids sited partially or wholly above ground
5. Fixed non-metallic tanks for the storage of liquids sited completely below ground
7. Metal road/rail tanks for liquids
8. Non-metallic road/rail tanks for liquids
13. Ships (tankers) and barges
17. Metal containers and tanks for the storage and transport of liquids, with a fixed internal non-metallic coating
18. Metal containers for liquids with outer non-metallic coatings or jackets

Smaller containers
11. Small metal containers for liquids
12. Small non-metallic containers for liquids
21. Containers for powders
22. Flexible intermediate bulk containers
23. Removable non-metallic liners in containers for solvent wet materials or powders

Equipment and processes
9. Installation for the transfer of liquids to and from road and rail vehicles
10. Liquid/liquid and solid/liquid blending and mixing
16. Fine particle filters and water separators
19. Pipelines for liquids and gases
20. Pneumatic conveying systems
33. Vacuum filters
34. Centrifuges
35. Flaker
36. Dust collectors

Operations
6. Gauging and sampling of tanks
14. Tank cleaning with high-pressure water jets or steam
24. Manual addition of powders to flammable liquids
25. Release of gases and vapours

The standard also gives precautions for filling containers with high resistivity powders. These may be summarized as follows. A distinction is made between metal containers of volume $\leq 65\ m^3$ or non-metallic containers of $5\ m^3$ and larger ones, and between powders which give rise to flammable mixtures with a minimum ignition energy MIE of ≤ 25 mJ and those with an MIE of >25 mJ. It may be noted that for metal containers the volume delimitation just quoted is an increase from one of $5\ m^3$ in the 1983 edition, reflecting a growth in knowledge. For metal containers, if the container volume is $\leq 65\ m^3$ and the MIE is >25 mJ, the measures recommended are to ground the container and any filling pipe. However, if there is a possibility that a flammable atmosphere such as a dust cloud with an MIE of ≤ 100 mJ could occur, personnel should also be grounded. For the same size container, if the MIE is ≤ 25 mJ, there should be grounding of equipment and personnel and, in addition, consideration should be given to charge rate limitation and explosion prevention and protection; these comprise a set of measures which in this context it is convenient to refer to as 'explosion protection'. If the metal container is $>65\ m^3$, there should be grounding of equipment and personnel and, unless incendive discharges can be ruled out, consideration should be given to explosion protection. Moving on to non-metallic containers to be filled with dry powders, if the container volume is $\leq 5\ m^3$ and the MIE is >25 mJ, the measures recommended are to ground the container and any filling pipe. It should also be established that the rate of charge input is insufficient to promote propagating brush discharges. However, if there is a possibility that a dust cloud with an MIE of ≤ 100 mJ could occur, personnel should also be grounded. For the same size container, if the MIE is ≤ 25 mJ, there should be grounding of equipment and personnel and, unless incendive discharges can be ruled out, consideration should be given to explosion protection. For the same size container, if the MIE is <25 mJ and there is a possibility of propagating brush discharges, there should be grounding of equipment and personnel and, unless incendive discharges can be ruled out, consideration should be given to explosion protection; in addition, grounded rods should be inserted into the container to assist relaxation of charge from the powder. If the non-metallic container is >5 m, for which the probability of incendive discharge from a dust cloud is as yet unknown, there should be grounding of equipment and personnel and, unless it can be shown that incendive discharges will occur neither from the bulk powder nor the dust cloud, consideration should be given to explosion protection; if there is a possibility of propagating brush discharges, consideration should be given to the use of grounded rods.

The Standard deals with the use of removable non-metallic liners in containers for solvent wet materials or dry powders. The effect of such a liner depends on whether it is used in a metal or in a non-conductive container. If the liner is used in a metal container, it may insulate the material being handled from ground via the metal and it may itself become charged, with the possibility of a propagating brush discharge. The standard strongly recommends that the liner be conductive with a surface resistivity not exceeding $10^{11}\ \Omega$. The precautions applicable to the equivalent unlined container should be taken. A liner with a higher resistivity should be used in a metal container only where this is essential, in which case expert advice is required. The precautions recommended by the standard for the case of a non-metallic liner in a non-conductive container are the same as those for a non-conductive container alone. The use of conductive liners in non-conductive containers is not recommended but, if practiced, such liners should be grounded. In almost all cases an essential precaution is that removal of the liner from the container, with the attendant risk of sparking, should be avoided in the presence of a flammable mixture.

Another type of container is the FIBC used for powders. Typically, such containers are made of polypropylene fabric or some similar heavy-duty material. Some have conducting thread woven into them. The variety of FIBCs, and the lack of data on their performance, is such that the standard gives only very general advice and recommends expert consultation. It does, however, state the basic principle that if an FIBC is made of a conducting material it should be grounded.

Table 16.40 *Some precautions against static electricity given in BS 5958: Part 2: 1991 – precautions for selected containments and equipment and operations involving liquids*

Configuration/operation	*Containment material*	*Precautions*
1. Liquid storage tank	Metal	Vapour space reduction/atmosphere control Liquid conductivity Grounding of tank Avoidance of splash filling, fill pipe arrangements Liquid velocity Charge generators Relaxation time Gauging and sampling
2. Liquid storage tank	Non-conductor	As (1) plus: limitation on use, grounding of liquid, hazardous areas
3. Road/rail tanker	Metal	As (1) plus: hoses
	Non-conductor	As (2) plus: hoses
4. Liquid/liquid and liquid/solid-blending		Atmosphere control Grounding Agitator power
5. Small containers for liquids	Metal	Grounding Liquid velocity
6. Small containers for liquids	Non-conductor	As (5) plus: hazardous areas
7. Ships and barges: loading		Atmosphere control Grounding Fill pipe Liquid velocity
8. Ships and barges: tank cleaning		Atmosphere control Grounding

For liquid–liquid and liquid–solid blending, measures recommended in the Standard include atmosphere control, grounding of the container and limitation of agitator power.

The Standard also deals with a number of operations. One of these is gauging and sampling. Such operations are commonly carried out on storage tanks. The gauging and sampling equipment should be made of a conducting material such as a metal or of wood or natural fibre. The resistivity of wood and natural fibre is such that they do not become highly charged or give incendive sparks. Use should not be made of metal chains or of synthetic polymers, which have high resistivity. All metallic parts on gauging and sampling equipment should be grounded, by connection to the grounded tank if it is a metal one or direct to ground if the tank is a non-conductive one. For liquids with conductivities of $\leq$50 pS/m, gauging and sampling operations should not be carried out during any charge generating operation, including filling, and after filling not until the lapse of a prescribed relaxation time. The relaxation times recommended are at least 30 min if the filling liquid has a separate water phase and a period of, say, 10 min if it does not. After any mixing operation the gauging and sampling should be deferred until the components have settled. After a cleaning operation that has generated a charged mist, gauging and sampling should be delayed until the mist has settled, which may take some hours. If the liquid conductivity is >50 pS/m, gauging and sampling may be done at any time. Also, the foregoing restrictions on when gauging can be performed do not apply if it is done using fixed gauging equipment or through a fixed, grounded pipe extending to the bottom of the tank. Gauging and sampling should not be undertaken during adverse weather conditions such as thunderstorms or snow or hail storms.

Another operation considered is the manual addition of powders to flammable liquids. The flammable vapour should be contained within the receiving vessel, and dust cloud formation should be strictly controlled. The container being emptied should preferably be of metal or other conductive material and should be grounded. A paper sack can be grounded by contact with the grounded plant. Emptying from non-conductive containers is not generally recommended. The standard also gives precautions to be taken if there is a liner in the container being emptied, these precautions being similar to those described above in relation to the filling of lined containers. The receiving vessel and chutes should preferably be of metal or other conductive material and should be grounded. The Standard recommends against the use of non-conductive materials for such equipment. The risk of incendive discharge by the powder as it enters the receiver is assessed as generally low unless the chute is longer than 3 m or the powder has high resistivity, in which case expert advice is in order. For a liquid in the receiving vessel with a conductivity of >50 pS/m, it is sufficient to ensure that the liquid is grounded, either by contact with the grounded metal vessel or, if the vessel has a non-conductive lining, by a special ground point at the base of the receiver. If the liquid conductivity is $\leq$50 pS/m, and it cannot be reduced below this by a conductivity

Table 16.41 *Some precautions against static electricity given in BS 5958: Part 2: 1991 – some limitations on liquid velocity for operations involving filling with liquids*

Configuration/operation	*Liquid conductivity* (pS/m)	*Liquid velocity*[a] (m/s)
1. Liquid storage tank filling	≤50	≤7 General limit ≤1 Until fill pipe submerged ≤1 If immiscible phase present
	>50	No limitation
2. Road or rail tanker loading	≤50	Lower of (a) $u \leq 7$ (b) $ud \leq N^b$ ≤1 If immiscible phase present
3. Small container filling	≤50	≤1 If immiscible phase present
	>50	No limitation
4. Ship or barge loading	≤50	≤1 Until fill pipe submerged ≤1 If immiscible phase present
	>50	No limitation

[a] These are the liquid velocity limits given for metal containers.
[b] N is a constant with a value of 0.5 m^2/s for liquid conductivities of >5 pS/m. The Standard states that the value to be applied for liquid conductivities of ≤5 pS/m is a matter for debate and quotes values of 0.38 and 0.5 m^2/s as having been accepted, but it also states that in the United Kingdom the value used is 0.5 m^2/s.

modifier, expert advice should be sought. An alternative basis of safety can be the elimination of a flammable atmosphere, but in this case it should be appreciated that air can enter with the powder. It may be necessary to monitor the oxygen content.

The Standard emphasizes that in operations generally, it should be ensured that the human body does not present an ignition risk.

The foregoing summary is no more than a sample from the detailed recommendations made in the Standard on a wide range of situations.

16.7.50 Precautions against static electricity: NFPA 77

In the United States the relevant standard is NFPA 77: 2000 *Static Electricity*. Its recommendations agree in broad outline with, but differ in some details from, those just described.

The precautions given for the handling of liquids include avoidance of entrained water and gas, avoidance of splash filling and gas bubbling, limitation of flow velocity, location of the fill pipe near the bottom of the container and provision of relaxation time.

The code gives detailed arrangements for a number of specific situations, including filling of storage tanks, road tankers, rail tank cars, small containers and drums.

Where bottom loading of road tankers is used, the code recommends limitation of the flow velocity or use of splash deflectors to prevent upward spraying.

It draws attention to the particular hazard of hydrogen containing small particles of oxide from the inside of containments. In this contaminated state the gas will generate charge. Its MIE is very low.

16.7.51 Precautions against static electricity: Expert Commission

Another set of recommendations on static electricity are those of the Expert Commission for Safety in the Swiss Chemical Industry (1988). The following account summarizes some of the principal points.

The report gives guidance on a number of specific situations. For the handling of liquids, these include (1) liquid transfer through pipes and hoses, (2) liquid filling or emptying of small containers and drums under gravity, (3) liquid transfer by drum pumps, (4) liquid filling of agitated vessels, (5) operations at the open access port of an agitated vessel, (6) liquid filling of large glass vessels, (7) loading and unloading of road and rail tankers and (8) transfer and filtration of suspensions on filters and centrifuges close to the flashpoint.

Guidance is also given on the handling of powders. Separate consideration is given to the handling of powders without and with flammable vapours. Specific situations considered include (1) 'open' charging of powder into flammable liquids, (2) discharging of solids containing flammable liquids from filtration apparatus, (3) charging and emptying of containers, (4) pneumatic conveying, (5) charging of powders into silos, (6) spray and fluidized bed drying and (7) ventilation, extraction and dust aspiration systems. For each situation the report rehearses the hazards and describes precautions. It gives a large number of diagrams showing in detail the configurations recommended.

For liquid transfer through pipes and hoses, the hazards are those already described. Precautions include exclusion of impurities such as water or dust, operation with the pipe full, limitation of the flow velocity and care with charge generators such as filters. Guidance is given on velocity limits for partially full pipes and for pipes conveying slurries of crystals, and on hose selection.

For liquid filling or emptying of small containers and drums under gravity, the hazards depend on whether the container is conductive or non-conductive, as described above. Precautions include taking the fill pipe close to the bottom of the container, and grounding of the container and fill pipe and of personnel. Liquids containing an immiscible component should be charged only into conducting containers. For liquids at a temperature less than 5°C below the flashpoint a table is given for the selection of a suitable type of container.

For liquid transfer by drum pumps, the hazards are charging of the liquid and sparking between the drum pump and the container. Precautions are to connect the drum pump both to the container being emptied and to that being charged and to ground it. The connectors should be permanently fixed to the drum pump so that it is clear that the connections need to be made. The connecting points should not be the openings of the drum or the container, as these are the very points where a flammable mixture is most likely to be present.

For liquid filling of agitated vessels, the situation particularly envisaged is the charging of a liquid using compressed air or inert gas, where the hazards are charging by turbulence and the creation of brush discharges between the liquid surface and internal fittings. Precautions include bottom filling or taking a top fill pipe close to the bottom, limitation of charging velocity, avoidance of discharging by 'blowing off with air, and use of nitrogen blanketing. Guidance is also given on the alternative procedure of charging under vacuum and on special precautions for enameled vessels.

For operations at the open access port of an agitated vessel, the hazard is sparking between the liquid surface of the reaction mass and an approaching metal object, or between the port flange and a conducting object in contact with the liquid. Precautions include avoidance of sampling through open ports or, if this cannot be avoided, the use of non-conductive sampling devices and the observance of a relaxation time.

For liquid filling of large glass vessels, the hazards are charging of the liquid and the vessel by turbulence and sparking between conductive items. Precautions include grounding of metal parts, limitation of flow velocity and inerting. Guidance is given on the alternative procedure of charging under vacuum.

For loading and unloading of road and rail tankers, the hazards are charging of the liquid, the vehicle and even the driver when leaving the cab, and sparking between conductive items. Precautions include a connection between the vehicle and the fixed tank at the terminal and the use of conductive hoses and footwear.

For the transfer and filtration of suspensions on filters and centrifuges at temperatures less than 5°C below the flashpoint, the hazard is charge generation during the filtration or centrifugation so that the filter cake or isolated conductors become charged, and sparking between these and conductive items. Precautions include grounding and inerting.

For powders, the report distinguishes between powders without and with flammable vapours. It takes the dividing line as 1% flammable solvent; powders with less than this can be considered as essentially solvent free. For solvent-free powders the hazard is charging of large metal parts and sparking from these. Precautions include the grounding of such parts. Provided the solvent-free status of the powder is assured, the construction material of containments such as drums or pipes is not restricted. Containers with plastic liners are acceptable.

For powders that are handled in the presence of a flammable vapour, are wet with flammable solvent or are charged into flammable solvent, the report gives the following guidance. The hazards include charging not only of metal parts but also of the powder and of sparking from metal parts. There is a particular hazard of brush discharges. A large proportion of incidents due to static electricity occur with such systems. Precautions include grounding and inerting. For powders containing flammable solvents only grounded containers should be used.

Powders containing flammable solvents should not be poured from non-conductive containers or bags or through non-conductive ducts into a charging vessel. Nor should powders be poured into a vessel containing a flammable solvent from non-conductive containers or non-conductive ducts.

For the open charging of powder into flammable liquids, three cases are distinguished: Case A, non-combustible or high MIE powders; Case B1, open charging of powders into precharged solvent; and Case B2, open charging of solvent-wet solids into an empty container. Guidance is given for each of these cases.

For discharging of solids containing flammable liquids from filtration apparatus, including centrifuges, the hazard is charging of the filter cake, filter cloth and metal parts and sparking to conductive items. In some cases dust formation has been observed with solvent contents up to 10%. Precautions include conductive filters, discharging using grounded chutes and containers, non-conductive shovels, local exhaust ventilation and inerting. Non-conductive filters should be withdrawn slowly.

For charging and emptying of containers with powders containing flammable liquids, the hazard is charging and sparking to a conductive item or brush discharges. Precautions include the use of grounded, metal containers and the avoidance of non-conductive containers or non-conductive linings.

For pneumatic conveying, the hazards are charging of the pipe and of the powder, charge accumulation in silos and sparking between metal parts. Precautions include the use of grounded, metal pipes. If plastic piping is used, the flanges should be plastic also or, if metal, grounded. Before discharge into a silo, the charge on powder can be reduced by first passing the powder through a grounded, metal cyclone.

For the charging of powders into silos, the hazard is as described above. In principle, a large, charged dust cloud could be created and could discharge, though the report states that no such cases are known. Precautions include the avoidance of internal insulating coatings, the use of conducting paints and the exclusion of tramp metal.

For spray and fluidized bed drying, the hazard is charging of metal parts and of the powder, and sparking. The high-speed movement and the very dry atmosphere are conducive to high charge generation. Precautions include grounding and inerting.

For ventilation, extraction and dust aspiration systems, the hazard is charging of dust deposits and sparking. Precautions are the use of grounded metal rather than plastic ducting, the avoidance of sections of plastic duct or, if this is unavoidable, the use of bridging connections across such sections.

16.8 Electrical Equipment

Electrical equipment is widely used in process plant and may be a source of ignition unless close control is exercised.

In the United Kingdom the relevant legislation is as follows. For the premises to which it applies, the Factories Act 1961, Section 31, deals with hazard from flammable and explosive materials, but the main statutory requirements governing electrical apparatus are those given in the Electricity at Work Regulations 1989, which apply to all places

of work. Regulation 6, on adverse or hazardous environments, states that:

> Electrical equipment which may reasonably/foreseeably be exposed to – (a) mechanical damage; (b) the effects of weather, natural hazards, temperature or pressure; (c) the effects of wet, dirty, dusty or corrosive conditions; or (d) any flammable or explosive substance, including dusts, vapors or gases, shall be of such construction or as necessary protected as to prevent, so far as is reasonably practicable, danger arising from such exposure.

In addition, the Highly Flammable Liquids and Liquefied Petroleum Gases Regulations 1972 state in Regulation 9.1: 'No means likely to ignite vapor from highly flammable liquids shall be present when a dangerous concentration of vapors from highly flammable liquids may be reasonably expected to be present.' In general, these regulations apply to premises where the Factories Act applies. A highly flammable liquid is one that has a flashpoint below 32°C and supports combustion under specified test conditions.

The Petroleum (Consolidation) Act 1928 is also relevant in cases where petroleum spirit and certain other materials are kept.

The use of electrical apparatus in flammable atmospheres is a topic in which there is active development of standards and codes of practice. In consequence, there is a continuously changing situation and a rather large number of codes, which may contain contradictory provisions.

Some important British Standards on electrical protection are given in Table 16.42.

The relations between these standards are as follows. BS 5345: 1977– gives the overall philosophy of the use of electrical apparatus in flammable atmospheres. It supersedes the older code BS CP 1003: 1964–, which is obsolescent and is retained only for use with existing plants. BS 5345: Part 1 covers general recommendations and Part 2 covers hazardous area classification.

The principles and specific methods of safeguarding are dealt with in BS 4683: 1971–BS 5501: 1977– and BS 5345: Parts 3–8.

There are several other relevant UK codes. Of particular importance are the Institute of Petroleum (IP) *Area Classification Code for Petroleum Installations* (the IP *Area Classification Code*) (1990 MCSP Pt 15) and the *Electrical Safety Code* (1991 MCSP Pt 1). Another, older code is the ICI *Electrical Installations in Flammable Atmospheres Code* (the ICI *Electrical Installations Code*) (ICI/RoSPA 1972 IS/91).

US codes include NFPA 70: 2002 *National Electrical Code* and API RP 540: 1991 *Recommended Practice for Electrical Installations in Petroleum Processing Plants*.

The international standard in this field is the International Electrotechnical Commission (IEC) *Publication 79, Electrical Apparatus for Explosive Gas Atmospheres*.

Codes and standards for HAC, as distinct from safeguarding, are given in the next section.

Organizations in the UK, which are engaged in work in this field, include the Electrical Research Association (ERA) and the Electrical Equipment Certification Service (EECS).

16.8.1 Hazardous area classification

The basis for the control of electrical equipment to prevent its acting as a source of ignition is the classification of plant according to the degree of hazard. Originally this procedure was commonly termed the 'electrical area classification', but it is now known by the more comprehensive term HAC, or classification of hazardous locations (CHL).

The definitions originally used in the United Kingdom for area classification and given in BS CP 1003: 1964– are based on divisions:

Division 0	An area or enclosed space within which any flammable or explosive substance, whether gas, vapour or volatile liquid, is continuously present in a concentration within the lower and upper limits of flammability.
Division 1	An area within which any flammable or explosive substance, whether gas, vapour or volatile liquid, is processed, handled or stored, and where during normal operations an explosive or ignitable concentration is likely to occur in sufficient quantity to produce a hazard.
Division 2	An area within which any flammable or explosive substance, whether gas, vapour or volatile liquid, although processed or stored, is so well under control that the production (or release) of an explosive or ignitable concentration in sufficient quantity to constitute a hazard is only likely to occur under abnormal conditions.

These definitions have been replaced in BS 5501: Part 1: 1977 and BS 5345: Part 1: 1989 with the international definitions of the IEC which are in terms of zones:

Zone 0	A zone in which an explosive gas air mixture is continuously present or present for long periods.
Zone 1	A zone in which an explosive gas–air mixture is likely to occur in normal operation.
Zone 2	A zone in which an explosive gas–air mixture is not likely to occur in normal operation and if it occurs will only exist for a short time.
Non-hazardous	An area in which an explosive gas–air mixture is not expected to be present in quantities such as to require special precautions for the construction and use of electrical apparatus.

The IP *Area Classification Code* also makes use of the following fluid categories:

Fluid Category A	A flammable liquid that, on release, would vaporize rapidly and substantially.
Fluid Category B	A flammable liquid, not in Category A, but at a temperature sufficient for boiling to occur on release.
Fluid Category C	A flammable liquid, not in Categories A and B, but which can, on release, be at a temperature above its flashpoint, or form a flammable mist.
Fluid Category G	A flammable gas or vaopur.

The code gives further guidance on assignment to Category A.

Table 16.42 *Selected British Standards on electrical protection*

BS CP 1003: 1964–	Electrical apparatus and associated equipment for use in explosive atmospheres of gas or vapour other than mining applications (obsolescent)[a]
	Part 1: 1964 Choice, installation and maintenance of flameproof equipment and intrinsically-safe equipment
	Part 2: 1966 Methods of meeting the explosion hazard other than by use of flameproof or intrinsically-safe equipment
	Part 3: 1967 Division 2 areas
BS 5345: 1977–	Code of practice for the selection, installation and maintenance of electrical apparatus for use in potentially explosive atmospheres (other than mining applications or explosive processing and manufacture)
	Part 1: 1989 General recommendations
	Part 2: 1983 Classification of hazardous areas
	Part 3: 1979 Installation and maintenance requirements for electrical apparatus with type of protection 'd'. Flameproof enclosure
	Part 4: 1977 Installation and maintenance requirements for electrical apparatus with type of protection 'i'. Intrinsically safe electrical apparatus and systems
	Part 5: 1983 Installation and maintenance requirements for electrical apparatus protected by pressurization 'p' and by continuous dilution, and for pressurized rooms
	Part 6: 1978 Recommendations for type of protection 'e'. Increased safety
	Part 7: 1979 Installation and maintenance requirements for electrical apparatus with type of protection N
	Part 8: 1979 Installation and maintenance requirements for electrical apparatus with type of protection 's'. Special protection
BS 229: 1957	Specification. Flameproof enclosure of electrical apparatus (obsolescent)
BS 4137: 1967	Guide to the selection of electrical equipment for use in Division 2 areas (obsolescent)
BS 1259: 1958	Intrinsically safe electrical apparatus and circuits for use in explosive atmospheres (obsolescent)
BS CP 1013: 1965	Grounding
BS 4683: 1971–	Specification for electrical apparatus for explosive atmospheres
	Part 1: 1971 Classification of maximum surface temperatures
	Part 2: 1971 The construction and testing of flameproof enclosures of electrical apparatus
	Part 3: 1972 Type of protection N (withdrawn)
	Part 4: 1973 Type of protection 'e' (obsolescent)
BS 5501: 1977	Electrical apparatus for potentially explosive atmospheres
	Part 1: 1977 General requirements
	Part 2: 1977 Oil immersion 'o'
	Part 3: 1977 Pressurized apparatus 'p'
	Part 4: 1977 Powder filling 'q'
	Part 5: 1977 Flameproof enclosure 'd'
	Part 6: 1977 Increased safety 'e'
	Part 7: 1977 Intrinsic safety 'i'
	Part 8: 1988 Encapsulation 'm'
	Part 9: 1982 Specification for intrinsically safe electrical systems 'i'
BS 6941: 1988	Specification for electrical apparatus for explosive atmospheres with type of protection N

[a] Obsolescent. Replaced by BS 5345:1977–, but retained temporarily as a reference guide for existing plants.
[b] Obsolescent.

In the USA, NFPA 70: 2002 gives in Article 500 the following classification of hazardous locations:

Class I in which the combustible material is a gas or vapour.
Class II in which the combustible material is a dust.
Class III in which the combustible material is a fibre or flying material.

Each class is divided into Division 1 and Division 2, the distinction between the two being based on the frequency with which the substance may be present in the atmosphere.

The CHLs given in API RP 500: 1991 is essentially the same as that in NFPA 70, but with some change of wording:

Class I A location in which flammable gases or vapours are, or may be, present in the air in quantities sufficient to produce explosive or ignitable mixtures.

Division 1 A location is a location (1) in which ignitable concentration of flammable gases or vapours exist under normal operating conditions; (2) in which ignitable concentrations of such gases or vapours may exist frequently because of repair or maintenance operations or leakage; or (3) in which breakdown or faulty operation of equipment or processes might release ignitable concentrations of flammable gases or vapours, *and* might also cause simultaneous failure of

electrical equipment that could become a source of ignition. Division 2 location is a location (1) in which volatile flammable liquids or flammable gases are handled, processed or used, but in which the liquids, vapours or gases normally will be confined within closed containers or closed systems from which they escape only in case of accidental rupture or breakdown of such containers or systems, or in case of abnormal operation of equipment; (2) in which ignitable concentrations of gases and vapours normally are prevented by positive ventilation, and that might become ignitable through failure or abnormal operation of the ventilating equipment; or (3) that are adjacent to a Class I, Division 1 location (and not separated by a tight–tight barrier), and to which ignitable concentrations of gases or vapours might occasionally be communicated unless such communication is prevented by adequate positive-pressure ventilation from a source of clean air, and effective safeguards against ventilation failure are provided.

NFPA 497 M: 1997 gives a grouping of atmospheric mixtures. API RP 500 gives the following partial listing:

Group A Atmospheres containing acetylene.
Group B Atmospheres such as butadiene, EO, propylene oxide, acrolein, or hydrogen (or gases or vapours equivalent in hazard to hydrogen, such as certain manufactured gases).
Group C Atmospheres such as cyclopropane, ethyl ether, ethylene, hydrogen sulfide or gases or vapours of equivalent hazard.
Group D Atmospheres such as acetone, alcohol, ammonia, benzene, butane, gasoline, hexane, lacquer solvent vapours, methane, naphtha, natural gas, propane or gases or vapours of equivalent hazard.

16.8.2 Safeguarding of equipment

There are a number of methods available for the safeguarding of electrical equipment so that it is suitable for use in a hazardous area, but it is a fundamental principle that electrical equipment should not be located in a hazardous area if it is practical to site it elsewhere. The methods of safeguarding traditionally used in the United Kingdom are listed in the ICI *Electrical Installations Code* as:

(1) segregation;
(2) flameproof enclosures;
(3) intrinsically safe systems;
(4) approved apparatus and apparatus with type of protection 's';
(5) pressurizing and purging;
(6) apparatus with type of protection 'N';
(7) Division 2 approved apparatus;
(8) apparatus with type of protection 'e';
(9) non-sparking apparatus and totally enclosed apparatus;
(10) apparatus for use in dust risks.

The *Code* discusses these methods and their application.

Reference is made to normally sparking, non-sparking and totally enclosed apparatus. The ICI *Code* describes these as follows. Normally sparking apparatus is that which in normal operation produces sparks, arcs or surface temperatures capable of igniting the flammable atmosphere. Non-sparking apparatus is that which in normal operation does not produce such sources of ignition, although it may do so as a result of electrical or mechanical failure. It includes Division 2 approved apparatus and apparatus with type of protection N. Examples of non-sparking apparatus include cage motors and solenoid valves.

Totally enclosed apparatus is that contained in an enclosure, which renders the risk of entry of a flammable atmosphere small. Total enclosure is applied to lamp fittings. It may also be applied to non-sparking apparatus as an additional safeguard. An example of the latter is a totally enclosed cage motor.

The principle of segregation is the use of a fire-resistant impermeable barrier to create a lower risk zone or non-hazardous area where electrical equipment suitable for a lower classification can be used. An example is the use of a non-sparking motor in a Zone 2 area to drive a pump in a Zone 1 area, the two machines being connected by a shaft that passes through a gas-tight gland in a wall separating the two zones.

The methods of protection given above are now supplemented by a number of newer methods.

The British Standards governing safeguarding of electrical apparatus are principally BS 4683: 1971–, BS 5501: 1977– and BS 5345: Part 1: 1989. BS 229: 1957 also applies, but is obsolescent.

The certification of equipment is performed by the EECS. This body is the successor to the former British Approvals Service for Electrical Equipment in Flammable Atmospheres (BASEEFA). Guidance on the system operated by the EECS is given in EECG2 *Electrical Equipment Certification Guide* (1992). The EECS inherited from BASEEFA a system of SFA standards. As far as concerns the 'types of protection' described below, this system is now essentially obsolete, although some limited use is made of SFA 3009 for special protection 's' and of SFA 3102 for intrinsic safety 'i'.

The overall procedure for selecting electrical apparatus for flammable atmospheres is described in BS 5345: Part 1: 1989. The selection is made by establishing the zone type in which the apparatus is to be used and then selecting the appropriate apparatus on the basis of:

(1) temperature classification;
(2) apparatus group;
(3) environmental conditions.

There is a maximum surface temperature of the equipment, which should not be exceeded. This corresponds to the ignition temperature of the gases or vapours involved. The relation between the apparatus Class T and the maximum surface temperature are given in BS 5345: Part 1: 1989 as follows:

Class	*Maximum surface temperature* (°C)
T1	450
T2	300
T3	200
T4	135
T5	100
T6	85

Apparatus is grouped according to the properties of the gases or vapours involved. BS 5345: Part 1: 1989 divides apparatus into: Group I, apparatus for mines susceptible to firedamp; and Group II, apparatus for places with potentially explosive atmosphere, other than mines susceptible to firedamp. In the present context it is only Group II that is of interest. This is itself is divided into subgroups.

BS 5345: Part 1: 1989 lists the following relationships between representative gases and the group and subgroup classifications:

Representative gas	BS 55 01[a]	BS 4683	BS 229	BS 1259
Methane	I[b]	I[b]	I	1
Propane	IIA	IIA	II	2c
Ethylene	IIB	IIB	II	2d
Hydrogen	IIC	IIC	IV	2e
Acetylene	IIC	Not allocated	IV	2f
Carbon disulfide	IIC	Not allocated	IV	2f

[a] Reference is to the then current edition of these standards.
[b] For underground mining applications.

For BS 229 the entries refer to the former gas groups and for BS 1259 to the former apparatus class.

BS 5345: Part 1: 1989 gives data on the flammability characteristics of the common industrial gases. Most gases and vapours are classified in BS 5345: Part 1 as Group IIA.

The allocation to apparatus subgroup in BS 5345: Part 1: 1989 is on the basis of the MESG and/or minimum igniting current (MIC).

These apparatus groups and subgroups and the method of allocation follow broadly that given in BS 5501: Part 1: 1977. For flameproof enclosures the criterion is the MESG, which is related to the subdivision as follows:

	MESG (mm)
Subdivision A	>0.9
Subdivision B	0.5–0.9
Subdivision C	<0.5

The MESG was described in Section 16.2. For intrinsically safe apparatus the criterion is the MIC ratio, which is related to the subdivision as follows:

	MIC
Subdivision A	>0.8
Subdivision B	0.45–0.8
Subdivision C	<0.45

The MIC is the ratio of the MIC for the gas or vapour to that for laboratory methane. A gas or vapour is assigned to a subdivision on the basis either of its MESG, of its MIC ratio, or both.

The methods of safeguarding recognized in BS 5345: Part 1: 1989 are shown in Table 16.43, which gives the definitions for each type of protection and cross-references to other standards. Similar, but in some cases not identical definitions, are given in BS 4683: 1971– and BS 5501: 1977.

Type of protection 'd' is a flameproof enclosure. The principle of a flameproof enclosure is that an explosion may occur in the enclosure, but a flame does not then travel back through any opening. There are maximum permissible dimensions for an opening in a flameproof enclosure. The opening needs to be of sufficient length and construction to prevent the passage of flame. MESGs were discussed in Section 16.2. The equipment should be sufficiently robust to withstand an occasional explosion without distorting, otherwise the dimensions of the gap may increase above the safe level. Alteration of the internals of a flameproof enclosure is not allowed because of the possible hazard of pressure piling.

Where a flameproof enclosure is exposed to wet weather it should be weatherproof. Weatherproofing is normally effected by the use of gasketed joints additional to and separate from the flame paths. For other apparatus suitable grease or tape is usually used. Protection against corrosion is also necessary in some applications.

Flameproof enclosures are classified by T Class and by apparatus subgroup. The main example of flameproof enclosures is the casing of flameproof electric motors.

Type of protection 'i' is intrinsically safe apparatus or system. The principle of intrinsic safety is that there is insufficient energy in the system to given incendive sparking or heating effects.

Two categories of intrinsically safe system are recognized in BS 5345: Part 4: 1977– ia, suitable for use in hazardous areas including Zone 0; and ib, suitable for use in hazardous areas excluding Zone 0.

In an intrinsically safe system it is necessary to take precautions to ensure that the power source of the system cannot release unsafe amounts of energy in the hazardous area and also that power from other sources cannot invade the system. There are thus requirements for insulation, grounding, screening, etc.

There are two main types of intrinsically safe system. One has some parts in the hazardous area, but the power supply is in the non-hazardous area. With this method it is necessary not only that the equipments in both areas be intrinsically safe but also that they be matched so that the system also is intrinsically safe. The power supply should be such as not to overload the current-limiting devices. Where the power supply is from the mains, it is usually necessary to use an inviolate transformer. Current limitation is then effected by inviolate resistors. Alternatively, barrier units may be used to limit both voltage and current.

The other system has all parts in the hazardous area and has its own power supply such as a battery. This type of system may be a fixed installation or a portable apparatus. In the former case it should again be intrinsically safe as a system.

It is particularly important with an intrinsically safe system that the system is not used outside the scope of the certification. Intrinsically safe systems are classified by T Class and by apparatus subgroup.

Since the minimum ignition energy of flammable mixtures is very small, this method of safeguarding is applicable only to low power systems, in particular instrumentation. Examples of intrinsically safe systems include instrument systems and portable gas detectors. Further information is given in *Intrinsic Safety* by Redding (1971a).

Table 16.43 *Types of electrical protection in BS 5345: 1989 (Reproduced by permission of the British Standards Institution)*

Type of protection	*Title*	*Description*
d	Flameproof enclosure	A method of protection where the enclosure for electrical apparatus will withstand an internal explosion of the flammable gas or vapour (for which it is designed) that may enter it, without suffering damage and without communicating the internal flame to the explosive atmosphere for which it is designed, through any joints or structural openings in the enclosure
i	Intrinsically safe apparatus or system	A protection technique based upon the restriction of electrical energy within apparatus and in the interconnecting wiring, exposed to a potentially explosive atmosphere, to a level below that which can cause ignition by either sparking or heating effects. Because of the method by which intrinsic safety is achieved it is necessary that not only the electrical apparatus exposed to the potentially explosive atmosphere, but also other (associated) electrical apparatus with which it is interconnected, is suitably constructed.
p	Pressurization, continuous dilution and pressurized rooms	A method of protection using the pressure of a protective gas to prevent the ingress of an explosive atmosphere to a space that may contain a source of ignition and, where necessary, using continuous dilution of an atmosphere within a space that contains a source of emission of gas, which may form an explosive atmosphere
e	Increased safety	A method of protection by which additional measures are applied to an electrical apparatus to give increased security against the possibility of excessive temperatures and of the occurrence of arcs and sparks during the service life of the apparatus. It applies only to an electrical apparatus, no parts of which produce sparks or arcs or exceed the limiting temperature[a] in normal service
N	Type of protection N	A type of protection applied to an electrical apparatus such that, in normal operation, it is not capable of igniting a surrounding explosive atmosphere, and a fault capable of causing ignition is not likely to occur
s	Special protection	A concept for those types of electrical apparatus that, by their nature, do not comply with the constructional or other requirements specified for apparatus with established types of protection, but that nevertheless can be shown, where necessary by test, to be suitable for use in hazardous areas in prescribed zones
o	Oil immersion	A method of protection where electrical apparatus is made safe by oil immersion in the sense that an explosive atmosphere above the oil or outside the enclosure will not be ignited
q	Powder/sand filling	A method of protection where the enclosure of electrical apparatus is filled with a mass of granular material such that, if an arc occurs, the arc will not be liable to ignite the outer flammable atmosphere
m	Encapsulation	A type of protection in which parts that could ignite an explosive atmosphere by either sparking or heating are enclosed in a compound in such a way that this explosive atmosphere cannot be ignited

[a] Limiting temperature is defined in BS 5345: Part 6: 1976.

Type of protection 'p' is pressurization, continuous dilution and purging. Pressurizing and purging are used to control the atmosphere in a room or apparatus. Such control allows the safe use of electrical apparatus which otherwise would be hazardous.

In pressurizing, a positive pressure of air or inert gas is maintained in the enclosure so that the flammable material cannot enter. In purging, a flow of air or inert gas is maintained through the enclosure so that a flammable atmosphere does not form. Sometimes a combination of pressurization and purging may be employed.

Mechanical ventilation may be used for pressurization and purging. In the latter case the ventilation may be a forced or induced draught. Alternatively, an air or gas supply may be used.

Air is a suitable pressurizing medium and is generally preferable to inert gas, because it does not constitute an asphyxiation hazard. For purging, inert gas provides a higher degree of protection against flammability hazard and is suitable for small enclosures, but air is preferable for large enclosures and rooms on account of the asphyxiation hazard. The source of air or inert gas should be free of

flammables and should be reliable. It may be necessary to clean and/or dry the air or inert gas.

It is recommended in BS 5501: Part 3: 1977 that the minimum overpressure in a pressurized enclosure should be 0.5 m bar.

The ICI *Code* states that pressurizing is not suitable for Zone 0. For Zone 1 with normally sparking apparatus there should be a pressure failure interlock and alarm. The interlock should disconnect the electrical supply on failure of pressure, except where this could create a hazardous condition, in which case other precautions are necessary. For Zone 1 with non-sparking apparatus and for Zone 2 with normally sparking apparatus there should be a pressure alarm. The action to be taken on failure of purging requires consideration of the particular circumstances.

Further details of pressurizing and purging, including monitoring systems, room and enclosure design, piping and ducting design and auxiliary apparatus are given in BS 5345: Part 5: 1983 and in the ICI *Code*.

> Examples of enclosures, which may be pressurized with air or inert gas, are a totally enclosed motor and an instrument cubicle. Also a control room is often fitted with double doors, forming an air lock, and pressurized with air. Examples of enclosures that may be purged or pressurized/purged are rooms or instrument cubicles containing instruments analyzing flammable gas.

Type of protection N is defined in terms of the degree of protection achieved rather than of the particular means by which this is done. The general characteristics of such apparatus are that under normal operation it does not produce an arc or spark except where the latter occurs in an enclosed break device, has insufficient energy to cause ignition of a flammable atmosphere or occurs in a hermetically sealed device and does not develop a surface temperature capable of igniting a flammable atmosphere.

Apparatus with type of protection N complies with another British Standard that specifies this type of protection, e.g. BS 5000: Part 16: 1985 for motors.

Guidance on the construction and testing for type of protection N is given in BS 6981: 1988.

Before the introduction of type of protection N, apparatus could be submitted to HM Factories Inspectorate (HMFI) for approval for use in Division 2 applications, the basis of examination being BS 4137: 1967 *Guide to the Selection of Electrical Equipment for Use in Division 2 Areas*. If an apparatus was considered suitable for use in a Division 2 area, HMFI issued a letter to this effect and the apparatus was then commonly referred to as 'Division 2 approved'.

Type of protection 'e' is again defined in terms of the degree of protection achieved. It has features in common with type of protection N, but is more stringent. Apparatus with type of protection 'e' complies with BS 5501: Part 6: 1977.

Special protection 's' deals with 'approved' apparatus. This is equipment for which there is no specific British Standard. It is covered instead by the approval system.

'Approved' apparatus is that which has been approved for use in flammable atmospheres by HMFI. This approval system operated up to 1969, the list of approved equipment being given in HMSO *Form F931 Intrinsically Safe and 'Approved' Electrical Apparatus*. This was subsequently superseded by certification as special protection 's' in accordance first with BASEEFA *Certification Standard SFA 3009* and then with the EECS certification system. Apparatus with type of protection 's' is classified by T Class and by apparatus subgroup. Examples of approved equipment include compressed air-driven generator and lamp sets, and battery handlamps.

Before the introduction of 'Division 2 approved' apparatus and apparatus with type of protection N, use was made in Division 2 areas of non-sparking apparatus and of totally enclosed apparatus.

There are three other types of protection recognized in BS 5345: Part 1: 1989. These are oil immersion V, powder/sand filling 'q' and encapsulation 'm'. Compounds used for encapsulation include thermosetting, thermoplastic and elastomeric compounds.

There is much less guidance on dust risks, but some is given in the ICI *Code*. For dusts the most widely used method of safeguarding is a combination of (1) enclosure of apparatus and (2) elimination of hot surfaces.

The apparatus is enclosed so as to limit the amount of dust that can come in contact with sources of ignition and it is designed so that in normal operation its surface temperature does not exceed the ignition temperature of the dust in cloud or layer form. Other methods that may be used with dust risks include segregation, intrinsically safe systems and pressurizing or purging.

There are certain general precautions that should be taken with all the methods of safeguarding described. Apparatus should be used only for the purpose for which it has been designed and certified. It should not be altered by modification. It should not be allowed to deteriorate due to weather or corrosion. It should be properly maintained.

BS 5345: Part 1: 1989 gives a scheme for the selection of apparatus and systems, as shown in Table 16.44. Intrinsic safety is applied in all zones, but the type used should be suitable for the zone. The same applies to special protection's'. The principal application of flameproof enclosures is in Zone 1. Pressurization and purging is applicable in Zones 1 and 2. Of the methods involving enhanced safety, type of protection 'e' is suitable for Zones 1 and 2, while type of protection N is suitable for Zone 2.

Other aspects of electrical systems in flammable atmospheres include: the installation of electrical equipment, particularly cabling; the inspection and maintenance of equipment; and electronic instrumentation. These are treated in detail in BS 4683: 1971–, BS 5501: 1977 and the ICI *Code*.

16.8.3 Electrical surface heating

The methods of safeguarding described above have been developed primarily for equipment such as electric motors and electronic instruments in which heating is undesirable. Their application to apparatus the prime purpose of which is heating requires separate treatment.

Electrical surface heating (ESH) is widely used in process plants and constitutes another potential source of ignition.

Types of heater used include (1) flexible heaters (fabric, braid, mesh), (2) heating cable, (3) panel heaters and (4) parallel circuitry heaters. The latter are often purpose made and may be in panel, mantle or jacket form.

An account of the design of electrical surface heaters for use in hazardous areas has been given by Dobie, Cunningham and Reid (1976). Their approach to safeguarding is to design the apparatus so that for a given workpiece surface temperature (e.g. pipe temperature) the maximum linear

Table 16.44 *Selection of methods of safeguarding electric apparatus in hazardous areas in BS 5345: 1989 (Reproduced by permission of the British Standards Institution)*

Zone	*Type of protection*	*Part of BS 5345*
0	'ia' Intrinsically safe apparatus or system	4
	's' Special protection (specifically certified for use in Zone 0)	8
1	Any explosion protection suitable for Zone 0 and:	
	'd' Flammable enclosure	3
	'ib' Intrinsically safe apparatus or system	4
	'p' Pressurization, continuous dilution and pressurized rooms	5
	'e' Increased safety	6
	's' Special protection	8
2	Any explosion protection suitable for Zones 0 or 1 and:	
	N[a] Type of protection N[b]	7
	'o' Oil-immersion	9[c]
	'q' Sandfilling[d]	9[c]

[a] Alternatively, apparatus that in normal operation is not capable of producing ignition capable arcs, sparks or surface temperatures may also be acceptable for use in Zone 2 where it has been assessed by persons who should:
(a) be familiar with the requirements of any relevant standards and codes of practice and their current interpretations;
(b) have access to all information necessary to carry out the assessment;
(c) where necessary, utilize similar test apparatus and test procedures to those used by recognized testing stations.
[b] Whereas in BS 6941 the type of protection is known as type N, in IEC publication 79 15 it is designated type 'n';
[c] In preparation.
[d] The use of apparatus with type of protection 'q' in Zone 1 is under consideration.

power loading (W/m) cannot give an element surface temperature in excess of the ignition temperature of the flammable atmospheres as given in BS 4683: Part 1: 1971. The equipment is also designed so as not to give rise to hazards from arcs and sparks.

Guidance on EHS devices, including their use in hazardous areas, is given in BS 6351 *Electrical Surface Heating*, of which Part 1: 1983 deals with specification, Part 2: 1983 deals with design and Part 3: 1983 deals with installation, testing and maintenance. Part 1 requires that an ESH device for use in a hazardous area should *inter alia:* (1) comply with type of protection 'e', N, 'd', 's', 'm' or 'p'; (2) be assigned a temperature classification; (3) be given a type test to establish the maximum surface temperature; and (4) comply with respect to the terminations and markings with specified in British Standards. Procedures are given for type testing, a distinction being made between ESH devices that have self-limiting characteristics and those that do not.

BS 6351: Part 2: 1983 sets certain minimum safety requirements for all ESH devices. It gives a system of service categories with a two-digit code, the first digit indicating the probability of the presence of water and the second the risk of mechanical damage. 0 denotes no risk, 1 low risk and 2 high risk: thus, for example, a coding of 00 denotes no risk in both categories and one of 22 high risk in both categories. The principal requirements referred to are (1) overcurrent protection, (2) residual current protection with trip indication, (3) means of isolation and (4) overtemperature limitation. Overcurrent protection and means of isolation are required for all ESH devices. For types of protection N and 'e' all four requirements apply.

Part 3 states isolation and permit-to-work requirements.

Further recommendations for ESH are given in the ICI *Electrical Installations Code.*

16.9 Hazardous Area Classification

The exclusion of sources of ignition is effected on process plant by a system of HAC. The principles of HAC have been outlined in Chapter 10 in relation to plant layout. In this section consideration is given to the application of these principles.

Hazardous area classification is the subject of a number of codes and standards. These include BS 5345 *Code of Practice for the Selection, Installation and Maintenance of Apparatus for Use in Potentially Explosive Atmospheres (Other than Mining Applications or Explosive Processing and Manufacture*), including Part 1: 1989 *General Recommendations* and, in particular, Part 2: 1983 (1990) *Classification of Hazardous Areas*. Other relevant British Standards have been given in Section 16.8. Influential codes have been those of the successive IP codes and the ICI *Electrical Installations in Flammable Atmospheres Code* (the ICI *Electrical Installations Code*) (ICI/RoSPA 1972 IS/91). The current IP code is *Area Classification Code for Petroleum Installations* (the IP *Area Classification Code*) (1990 MCSP 15).

In the USA, NFPA codes include NFPA 70: 2002 *National Electrical Code*, NFPA 497: 1997 *Classification of Flammable Liquids, Gases, or Vapors and of Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas*. API RP 500: 1991 *Recommended Practice for Classification of Locations for Electrical Installations at Petroleum Facilities* consolidates previous separate codes (RP 500A, 500B and 500C).

Other accounts of HAC include *Classification of Hazardous Locations* (A.W. Cox, Lees and Ang, 1990) and those by Swann (1957, 1959), Levine (1965a,b, 1968a,b, 1972a, 1983), Magison (1966, 1975, 1978), Burgoyne (1967b, 1969, 1971), Bartels (1971a, 1975a,c, 1977–), O'Shea (1982), Palles-Clark (1982), Peck and Palles-Clark (1982), Fordham Cooper (1986) and Mecklenburgh (1986).

Electrical safety and HAC has been the subject of a series of symposia by the IEE (1971, 1975, 1982, 1988 Conf. Publs 74, 134, 218 and 296, respectively; 1982 Coll. Dig 82/26).

Traditionally, HAC has centred around electrical equipment and has been the province of electrical engineers. Electric motors, instruments and other electrical equipment have to be present on plant, but may constitute potential sources of ignition. It is necessary, therefore, to assess the ignition risk and to match the equipment to it. This has been done by a system of area classification.

As already described, however, there are many other potential ignition sources on plant and a more balanced approach is called for. The modern approach to HAC involves the control of all sources of ignition and deals not

only with design but also with activities such as operation and maintenance. There is a tendency for chemical engineers to be much more involved.

16.9.1 Hazardous area classification systems

The HAC system currently applicable in the United Kingdom is that of the IEC and is outlined in Chapter 10 and in Section 16.8 where accounts are given of the system of zones used (Zone 0, Zone 1 and Zone 2) together with definitions of these zones.

In the United States, two principal systems are those of the NFPA and the API, which are also described in Section 16.8.

16.9.2 ICI Electrical Installations Code

The ICI *Electrical Installations in Flammable Atmospheres Code* (the ICI *Electrical Installations Code*) (ICI/RoSPA 1972 IS/91) describes the two basic methods of HAC: (1) the generalized method and (2) the source of hazard method. It remains a principal guide for the latter. Classification of electrical areas is not an exact science and inevitably involves a degree of judgment. There are, however, a number of guidelines available.

The terms 'normal' and 'abnormal' require some interpretation. Normal conditions should be taken to be not ideal but real conditions as they actually exist, taking into account the precautions that are taken on a well-run plant. Abnormal conditions should be read to refer not to catastrophic accidents such as a major equipment rupture but to events that are generally non-catastrophic such as a pump gland or pipe gasket failure.

The stages of the classification process are (1) identification of the hazard, (2) assessment of the hazard, and (3) delineation of the zone. The classification should be comprehensive. An area where flammable materials are not to be handled is non-hazardous, but this status should be formally established.

A basic distinction is between (1) well-ventilated locations and (2) poorly ventilated locations. Ventilation is here interpreted in a broad sense and covers the whole question of the dispersion of vapours and liquids from leaks and spillages. Thus it is necessary to consider how much flammable material may escape, whether an escape is continuous or not, whether it is lighter or heavier than air, whether there may be jet effects, whether the liquid may travel outside the area on the surface of water on the ground or in drains or pipe trenches, and what the influence of the plant topography is.

There are two basic approaches to area classification. These are (1) the generalized method and (2) the source of hazard method. The generalized method is the older and involves making a judgment on the appropriate classification for a fairly large area of plant.

The ICI *Code* gives guidance for both the generalized and source of hazard methods. For the former a Zone 0 classification is necessary for locations such as vapour spaces in closed storage tanks or closed process vessels in which a flammable atmosphere may exist continuously or for long periods and immediately above an open tank or vessel containing a flammable liquid. Locations where in normal operation there may be release of flammable materials sufficient to cause a hazard either from relief valves or vents designed to make such release or from other sources such as vessels, pumps or pipes, should be classified as Zone 1. Classification as Zone 2 is acceptable provided that there are no releases in normal operation of flammable materials sufficient to cause a hazard, that relief valves and vents release flammable materials only under abnormal conditions and that the area is well drained and ventilated so that any abnormal occurrence of a flammable atmosphere is rapidly dispersed.

The *Code* states that it is characteristic of the generalized method that it gives a large Zone 1. The typical pattern is as follows. An area somewhat larger than that occupied by the process equipment is classified as either Zone 1 or Zone 2. If it is Zone 1, it may or may not be surrounded by a Zone 2. There may be isolated Zones 0 within a Zone 1 or a Zone 2.

While this blanket application of a Zone 1 classification is in itself conservative, it is also expensive, and there may be a tendency, which should be guarded against, to ignore a few high hazard points and classify as Zone 2 an area that should be Zone 1.

The source of hazard method is the newer approach and involves identifying, assessing and delineating affected areas for individual sources of hazard. The latter are classified according to the expected frequency and period of release of flammable materials. The classification together with the suggested quantitative guidelines is as tabulated below:

Source of hazard	*Period of release*	*Frequency* (hazards/year)
0 (Continuous)	Long periods	>1000
1 (Primary)	Frequent or if infrequent persistent	10–1000
2 (Secondary)	Infrequent and of short duration	<10

The characteristic area classification yielded by the source of hazard method is predominantly Zone 2 with small isolated Zones 1. Zones 0 may also occur in either Zones 1 or Zones 2.

In a well-ventilated situation the extent of the zone is determined essentially in both methods by the distance at which it is judged that the flammable atmosphere will fall below its LFL.

In a poorly ventilated situation it is necessary to pay particular attention to the following aspects:

(1) sources of hazard which are continuous should be avoided or provided with special ventilation;
(2) each room in a building should be given separate consideration for possible sources of hazard;
(3) mobile sources of hazard should be taken into account;
(4) spillage hazards associated with portable or transportable vessels or open handling of liquids should be taken into account.

For a room which does not contain a source of hazard the classification depends on the probability of flammable materials entering the room and on the ventilation and may be Zone 1, Zone 2 or non-hazardous. In general, mechanical ventilation may be used as a means of modifying the classification for an enclosed space.

The extent of a zone in a poorly ventilated situation is again determined for both methods essentially by the dilution of the flammable atmosphere below its flammability

limit. In confined situations, however, even the source of hazard method tends frequently to lead to Zone 1 classifications, so that there is less difference between the two methods in this case.

Some area classifications are illustrated in Figures 16.63 and 16.64. Figure 16.63(a) shows a classification for a reciprocating or centrifugal compressor handling a gas lighter than air (e.g. hydrogen or fuel gas) in a building with open sides and ventilation. There is a Zone 1 around the compressor. For a reciprocating compressor this Zone 1 is a sphere of 0.5 m radius all round the gland, cylinder, and frequently operated drain points or vents, and for a centrifugal compressor it is a sphere of 0.5 m radius all round the seal and a sphere of 1 m radius around the seal-oil tank cover and vent and around seal-oil traps. Figure 16.63(b) shows a classification for a reciprocating or centrifugal compressor handling a gas that is heavier than air (e.g. ethylene or propylene refrigerants). The Zones 1 are the same as for the previous case. Figures 16.64(a) and (b) show, respectively, classifications for a fixed roof and a floating roof storage tank for a flammable liquid with a flashpoint below 32°C.

The ICI *Code* also deals with area classification for flammable dusts. The basic principles of classification are similar to those for flammable gases and liquids, but it is recognized that the behaviour of dusts is generally rather less predictable.

The definition of the zones in the ICI *Code* includes dusts and has already been given. In this case the source of hazard method is less useful and the generalized method is usually more appropriate.

Since dust presents a hazard in layer as well as in cloud form, it is necessary, irrespective of the area classification, to ensure that any surface on which dust can settle is below the ignition temperature of the dust in layer form. In exceptional cases where a surface temperature higher than the ignition temperature of the dust is required for process reasons, the equipment should be designed and operated so as to prevent the accumulation of dust on its surface and the formation of dust clouds.

16.9.3 IP Area Classification Code

The IP *Area Classification Code for Petroleum Installations* (the IP *Area Classification Code*) (1990 MCSP Pt 15) is written for petroleum installations, but the principles are of wider applicability. The code utilizes the IP classification of fluids given in Chapter 10 and the British Standard classification of hazardous locations and IP grouping of atmospheric mixtures given in Section 16.8. The principal contents of the code are listed in Table 16.45 and its application is shown in Figure 16.65.

The code emphasizes that HAC is not intended to deal with catastrophic events, but with more commonly occurring releases. In the design of new plant, or in plant modification, HAC should be carried out before the design and layout are finalized, and reviewed again on completion of the design.

The code describes two methods of HAC: (1) the method of direct example and (2) the point source method.

Information required

The information required for the conduct of HAC includes (1) the classification of the fluid(s), (2) the flow diagram, (3) the piping and instrument diagram, (4) the plant layout, (5) the equipment features, including operation and (6) the ventilation.

Classification of petroleum fluids

Petroleum fluids are classified by flashpoint. The code gives in Appendix A details of the IP classification by flashpoint. This classification system is described in Chapter 10. Fluids are classed as Class 0 (LPG); Class I; Class 11(1) or 11(2); Class III(l) or 111(2); and Unclassified.

A further, supplementary classification by fluid category, utilized in the point source method, is given in the code in Appendix B. This categorization has been described in Section 16.8.

General approach

The general approach, described in the Chapters 1 and 2 of the IP *Code*, is to identify the sources and grades of release, and then to assign the appropriate zones. The grades of release are defined as:

Continuous grade release	A release that is continuous or nearly so, or that occurs for short periods that occur frequently
Primary grade release	A release that is likely to occur periodically or occasionally in normal operation
Secondary grade release	A release that is unlikely to occur in normal operation and, in any event, will do so only infrequently and for short periods

The grade of release reflects the frequency and duration of the release.

The *Code* gives the following rule of thumb to assist in the assignment of the grade of release. A release should be treated as continuous if it is likely to be present for more than 1000 h/year, as primary if present for more than 10 but less than 1000 h/year and as secondary if present for less than 10 h/year.

For open-air conditions, there is a direct relation between the grade of release and the type of zone to which it gives rise, the continuous grade corresponding to Zone 0, the primary grade to Zone 1 and the secondary grade to Zone 2. However, this relationship applies only where the ventilation corresponds to unrestricted open locations with good natural ventilation. Poor ventilation may require the use of a more stringent zone, while very good ventilation may allow a relaxation to a less stringent one. There are certain guiding principles that govern HAC.

Where a number of fluids are handled, as in storage and loading/unloading facilities, the classification should be based on the most volatile.

The identification of sources of continuous and primary grade releases, and the delineation of Zones 0 and 1, should be as complete as possible. Many plant areas are designated as Zone 2. Particular attention should be given to sources of secondary grade releases at the edge of the plant, since these will tend to define the extent of the Zone 2. In some cases it is not practical to determine a blanket Zone 2 and the secondary grade sources, or groups of sources, must then be addressed individually. A Zone 1 area will often be surrounded in practice by a Zone 2 area, but there is no general requirement for this. Within a hazardous area,

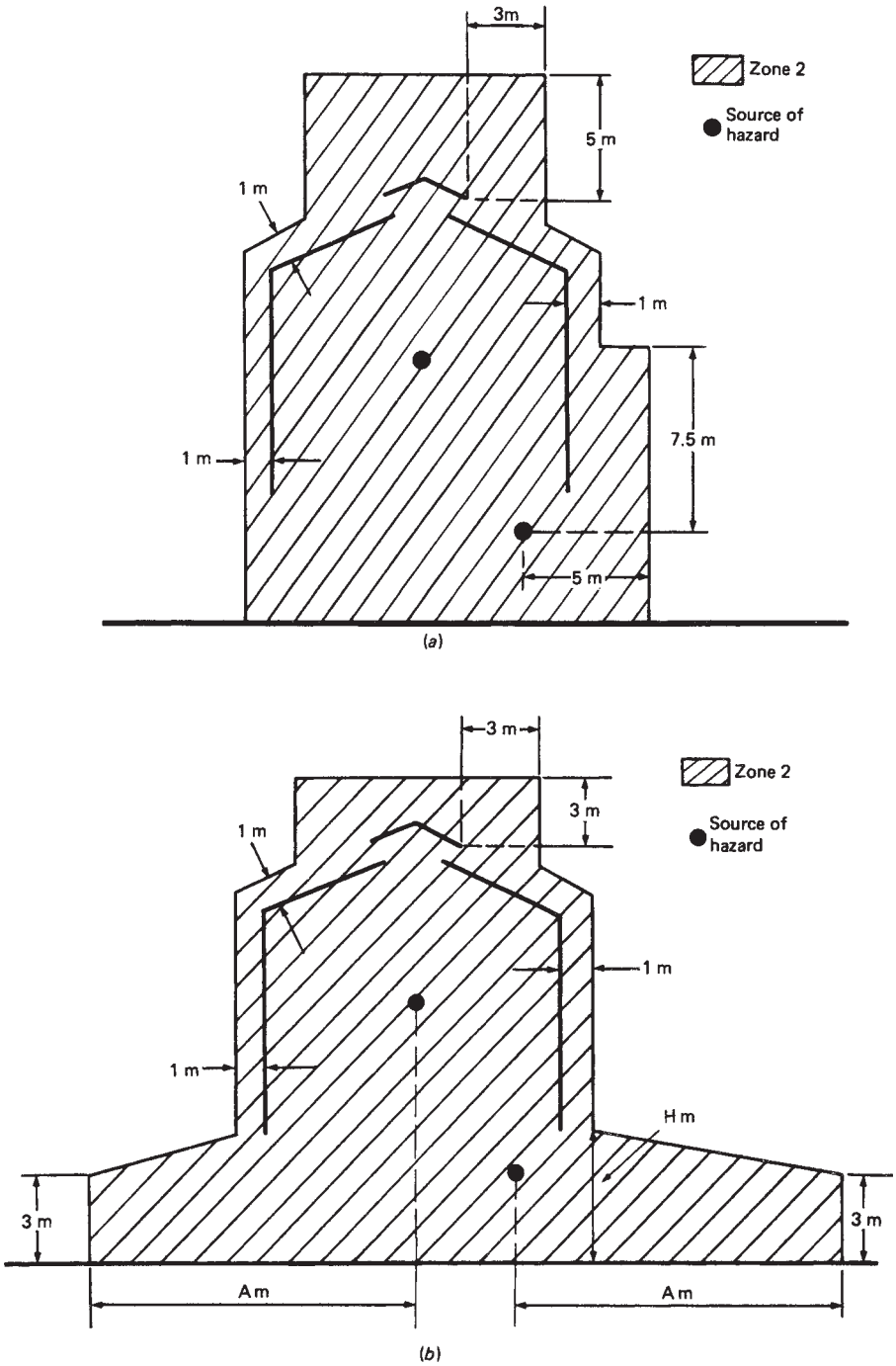


Figure 16.63 *Hazardous area classification – ICI Electrical Installations Code (Imperial Chemical Industries Ltd, ICI/RoSPA 1972 IS/91; reproduced with permission): zoning for a reciprocating or centrifugal compressor handling flammable gas in building with open sides and roof ventilation: (a) compressor handling a lighter than air gas; (b) compressor handling a heavier than air gas. Extent of Zone 2: for gases heavier than air, up to 30* bar*, up to 100* °C *(e.g. ethylene and propylene refrigerants), A is 15* m*; for supercritical ethylene, up to 100* bar*, A is 30* m*; dimension H is 3* m *or height of the wall opening, whichever is the greater*

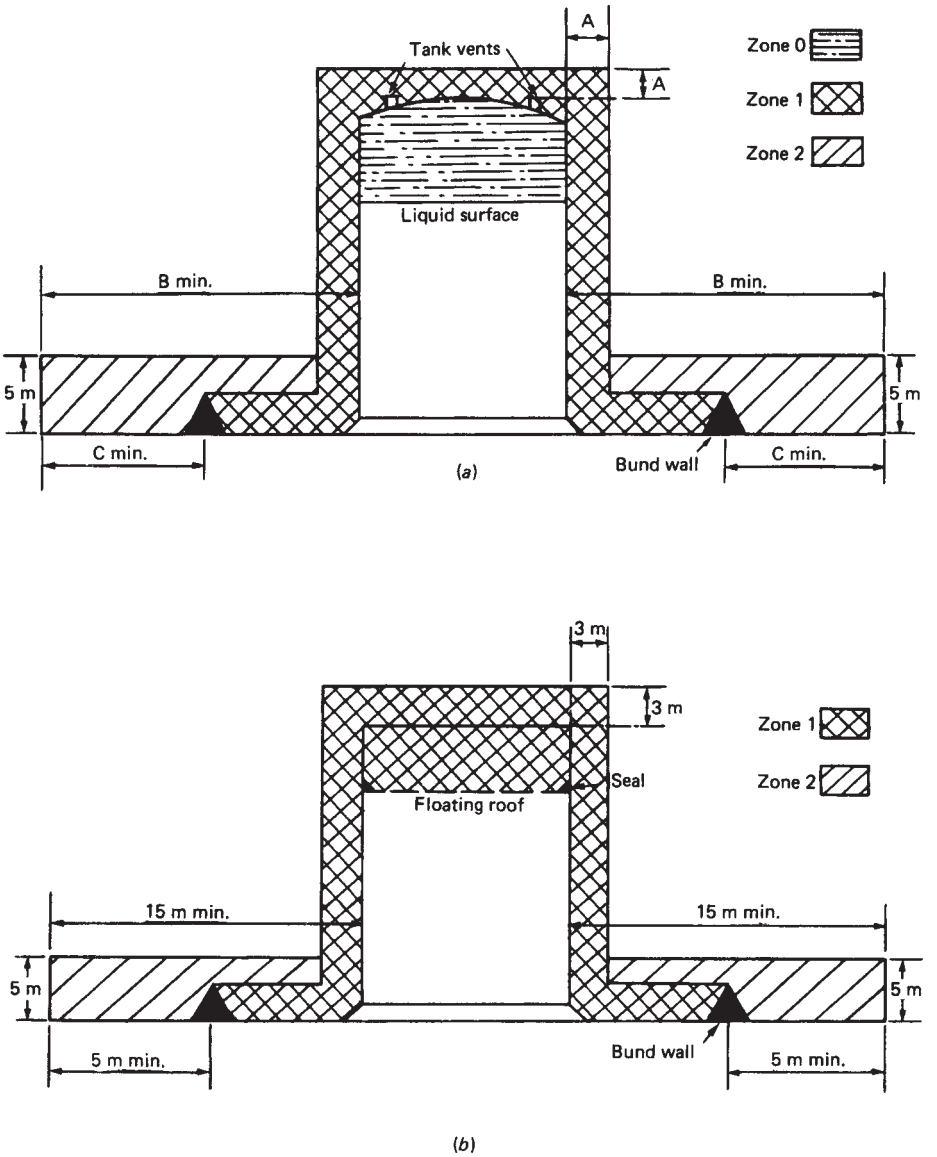


Figure 16.64 *Hazardous area classification – ICI Electrical Installations Code (Imperial Chemical Industries Ltd, ICI/RoSPA 1972 IS/91; reproduced with permission): zoning for a storage tank holding a flammable liquid with flash point below 32°C: (a) fixed roof tank; (b) floating roof tank. Extent of Zones 1 and 2: for a tank with capacity greater than 50* m^3*, A is 3 m and for a tank with smaller capacity A is 1.5* m*; Zone 2 extends Bm minimum from the tank side and C m minimum from the bund. For a tank with capacity greater than 100* m^3 *B and C are 15 and 5* m *respectively; for a tank with a capacity between 50* m^3 *smaller distances may be appropriate*

the designation of small areas as non-hazardous should be avoided. HAC is not sufficiently precise to warrant this.

Classification by method of direct example

The basic method of classification, the method of direct example, is described in Chapter 3 of the IP *Code*.

There are on petroleum installations some arrangements of equipment, which are so common that it is possible to give exemplars of the zonings to be used. The zoning of the relevant exemplar is applicable to an installation that does not differ significantly from it. Differences that may be significant may be associated with the fluid, the type of equipment, the operating conditions, the plant layout

Table 16.45 *Principal contents of the IP Area Classification Code (IP, 1990 MCSP Pt 15)*

1. Introduction
2. The technique of HAC
3. The classification of storage tankage, bulk loading and unloading by road and rail, petroleum jetties, and bulk distribution and marketing facilities by the method of direct example
4. The classification of drilling rigs and other equipment systems used in well operations and production wellhead areas
5. Alternative procedure for classification of an upstream or downstream petroleum sector facility by consideration of the individual point source
6. Variation in ventilation conditions
7. Application to the selection and location of electrical facilities
8. Application to the control and location of ignition sources other than electrical

and/or the ventilation. If a significant difference exists, use should be made of the point source method.

For this method examples are given for Classes I, II(2) and III(2) for: (1) storage tanks, both fixed and floating roof, in the open, (2) road tanker loading, (3) road tanker discharge, (4) rail car loading, (5) marine facilities and jetties, (6) drum filling in the open, (7) filling and service stations and (8) certain bulk pressurized liquefied petroleum gas (LPG) installations.

Figure 16.66 shows the zoning recommended in the code for four storage tank configurations. Figure 16.66(a) is a cone or dome roof tank; Figure 16.66(b) a floating roof tank; Figure 16.66(c) a cone roof tank with an outer protective wall; and Figure 16.66(d) a floating roof tank with an outer protective wall.

Chapter 4 of the code extends the method of direct example by giving exemplars for drilling rigs and other petroleum production systems.

Classification by point source method

The alternative method of classification, the point source method, is described in Chapter 5 of the IP *Code*.

The process plant will generally consist of a Zone 2 area with Zone 1, and occasionally Zone 0, areas within this. The point source method is applied to potential sources of release to determine for each whether it should be assigned a Zone 1 or Zone 0 envelope and whether it affects the boundary of the Zone 2 area.

The method involves identifying for each point source (1) the grade of release and (2) the extent of the hazard zone, or hazard radius.

The grade of release determines the zone to be assigned: Zone 0 for continuous grade, Zone 1 for primary and Zone 0 for secondary for open air conditions, with adjustment of the severity of the zone for poor or very good ventilation.

The extent of the hazard zone is determined by the mass released and the fraction forming a gas or vapour cloud and by the conditions, which affect the dispersal of the cloud that is its buoyancy and the ventilation at that location. The hazard zone is characterized in terms of the hazard radius. The hazard radius of a source is defined as 'the largest horizontal extent of the hazardous area which is generated by the source when situated in an open area'. The *Code* gives guidance in Appendix C on the assessment of buoyancy and in Appendix D on the derivation of the hazard radius.

The *Code* treats a number of common types of point source, including the following: (1) pumps, (2) compressors, (3) piping systems, (4) drains and liquid sample points, (5) process and instrument vents, (6) liquid pools due to spillage, (7) sumps, interceptors and separators, (8) pig receivers and launchers and (9) surface water drainage systems.

The general approach taken is illustrated by the following examples. For pumps, for the case where the pump can be treated as a single point source, the hazard radius (m) is given as:

Fluid category	*Standard pump*	*High integrity pump*
A	30	7.5
B	15	3
C	7.5[a]	3

[a] For clean fluids, e.g. finished products which are pumped from atmospheric storage at rates not exceeding 100 m^3/h, the hazard radius may be reduced to 3 m.

For drains and liquid sample points the hazard radius (m) is:

Fluid category	*Diameter*[a] (mm)			
	3	6	12	25
A	7.5	15	30	—[b]
B	3	7.5	15	30
C	0.3	1.5	1.5	3

[a] Diameter of smallest item on drain or sample line, i.e. line, valve or restrictor.
[b] The size of release is greater than is normally considered in HAC, the hazard radius being greater than 30 m.

Elimination or modification of sources

As far as practical, features that pose problems in HAC should be eliminated or mitigated by changes in plant layout. In particular, (1) continuous or primary grades releases in less ventilated conditions should be avoided and (2) the creation of sheltered areas by obstructions should be minimized.

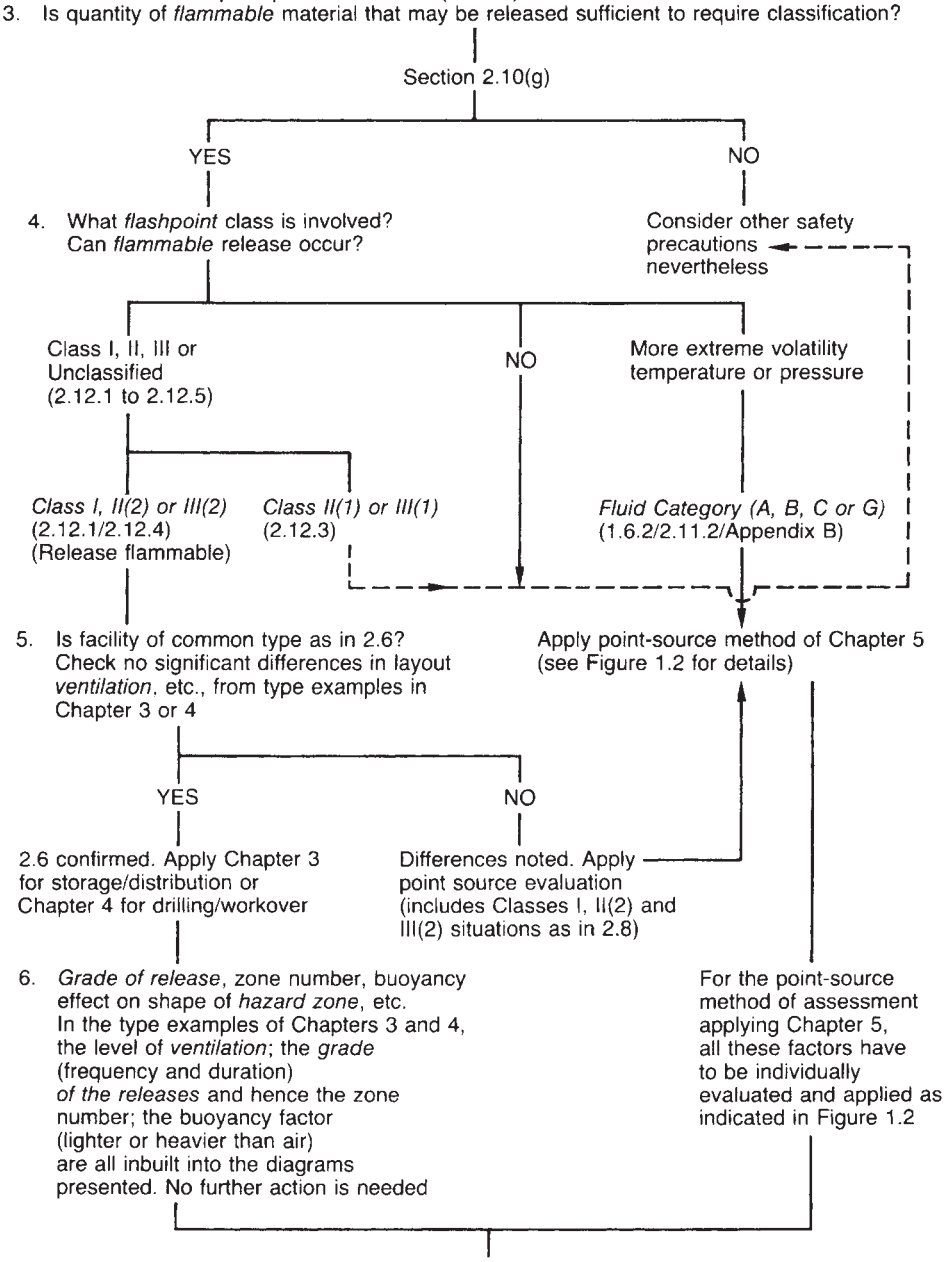
Ventilation

As the foregoing treatment indicates, ventilation affects the extent of the hazard zone. For artificial ventilation it may also affect the severity of the zone.

The IP *Code* takes as it starting point the types of ventilation given in IEC 79-10, which are (1) natural ventilation, (2) general artificial ventilation and (3) local artificial ventilation. IEC 79-10 recognizes two situations in which natural ventilation occurs. These are (1) open locations typical of process plant located outside and (2) open buildings in which the size and positioning of the openings is such as to give an equivalent degree of ventilation.

The IP *Code* treats ventilation in terms of the following situations: (1) 'open areas', (2) less ventilated conditions, which include (2a) sheltered areas and (2b) enclosed areas. The *Code* gives detailed guidance on what can be considered an open area. Essentially this is an open situation, which for

1. Familiarize concepts/definitions of *area classification* in Chapter 1 (1.1 to 1.9).
2. Define installation/plant/process sections (2.2/2.3).
3. Is quantity of *flammable* material that may be released sufficient to require classification?



7. Final stages for completion of the area classification. In all cases, having evaluated the extent of the *hazard zone* and its zone number, Chapter 7 must be used to select the appropriate *type of protection* for electrical equipment, and also its *apparatus subgroup* and *temperature class* (2.13). These should be incorporated in the final *area classification* records or drawings.

   In making this selection, the question of whether there is an *internal release* should be assessed in accordance with Appendix F, 7.5(b) and 7.6(c) to determine whether it is the *internal release* or the external zone assessment that will govern the ultimate *type of protection* requirement.
8. For non-electrical *sources of ignition* see Chapter 8.

Figure 16.65 *Hazardous area classification – IP Area Classification Code (IP, 1990 MCSP Pt 15): decision tree for application of the code (Courtesy of the Institute of Petroleum; reproduced with permission)*

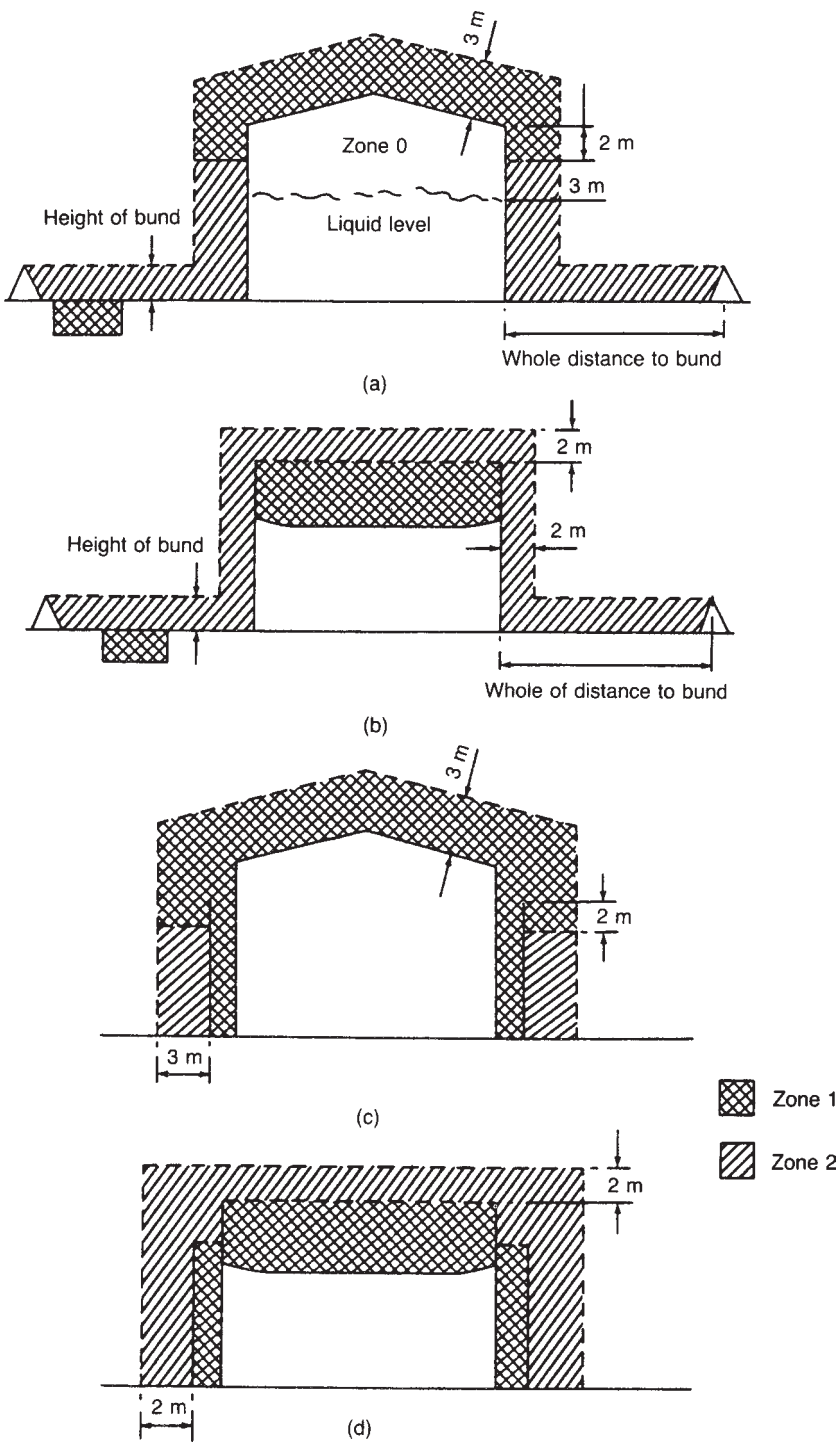


Figure 16.66 *Hazardous area classification – IP Area Classification Code (IP, 1990 MCSP Pt 15): zoning for storage tanks for Class I, II(2) and III(2) flammable liquids, (a) Cone or dome roof tank; (b) floating roof tank; (c) cone roof tank with outer protective wall; and (d) floating roof tank with outer protective wall. See Code for notes and qualifications (Courtesy of the Institute of Petroleum; reproduced with permission)*

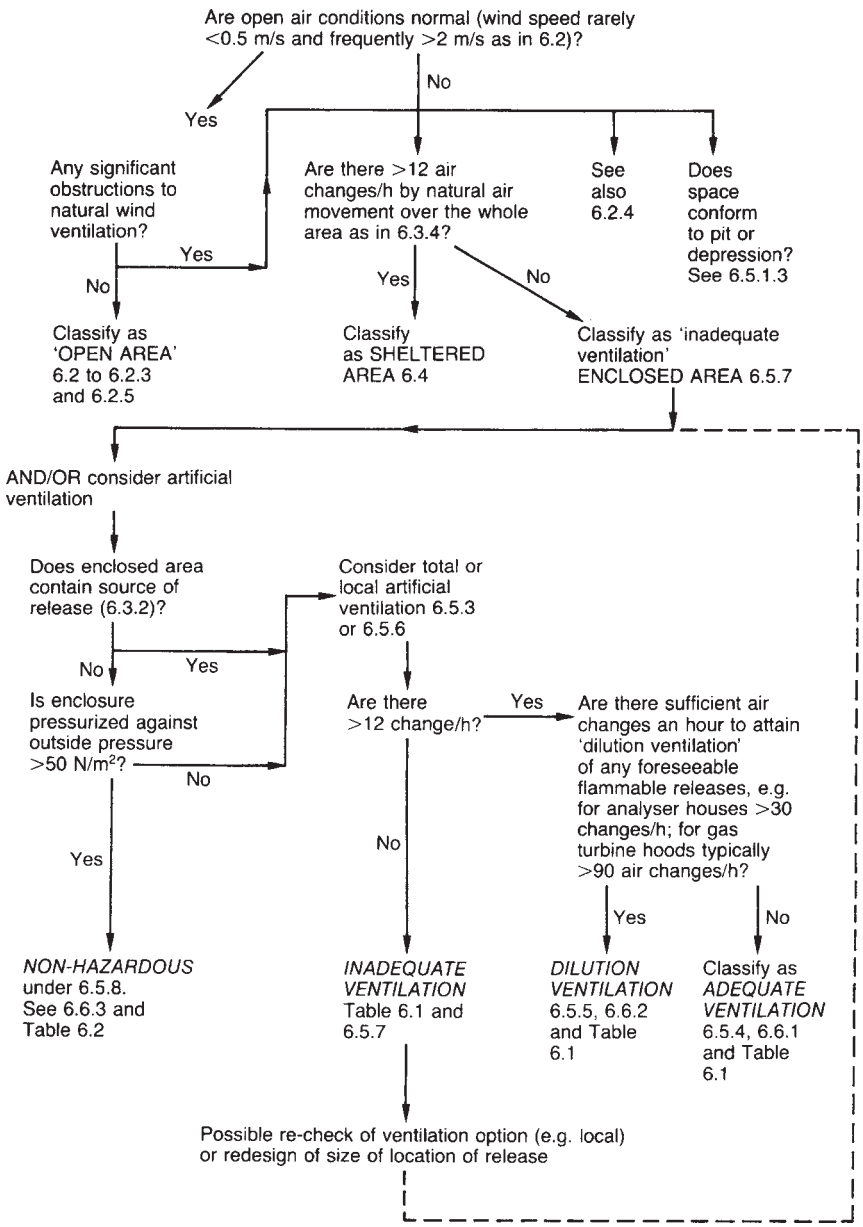


Figure 16.67 *Hazardous area classification – IP Area Classification Code (IP, 1990 MCSP Pt 15): decision tree for ventilation. This figure applies to facilities not covered in Chapters 3 and 4 of the code (Courtesy of the Institute of Petroleum; reproduced with permission)*

land-based locations means that the wind velocity is rarely less than 0.5 m/s and is frequently greater than 2 m/s.

With regard to less ventilated conditions, it distinguishes between locations where the sheltered or enclosed area itself contains a source of release and those where it merely abuts an area containing, or lies within the hazard zone of, such a source. In both cases the severity of the zoning depends on the degree of ventilation. For less ventilated conditions, the *Code* utilizes the concept of 'adequate ventilation', defined as: 'the achievement of a uniform ventilation rate of at least twelve air changes an hour with no stagnant areas'.

If a less ventilated location has adequate ventilation through natural ventilation, it may be treated as a sheltered area. Otherwise, it must be treated as an enclosed area. Guidance on the classification of sheltered areas, with natural ventilation, is given in the *Code, which* also describes a number of examples.

An enclosed area is one that in the absence of artificial ventilation has inadequate ventilation. The *Code* gives guidance on the classification of enclosed areas, utilizing the distinction between those with and those without an internal source of release.

An enclosed area requires artificial ventilation, which the *Code* treats in terms of the following three categories: (1) 'adequate' ventilation, (2) dilution ventilation and (3) overpressure ventilation.

The *Code* distinguishes between adequate ventilation and dilution ventilation. As already stated, adequate ventilation exists if there is an assurance of at least 12 air changes per hour. It is not related to the size of any potential release that may occur. If there is a release, adequate ventilation may not be sufficient to prevent the build-up of a flammable atmosphere, but on termination of the release it will be sufficient to prevent the persistence of such an atmosphere.

Dilution ventilation, by contrast, is intended to prevent a release giving rise to a flammable atmosphere and is therefore a function of the size of the potential release. It should be such that even immediately after a release the area can be considered as non-hazardous. The design criterion is that the flammable concentration should not rise above 20% of the LFL.

In some cases, particularly where there is a source of release in a large area, local artificial ventilation, typically utilizing a hood, may be used either to obtain local dilution ventilation or to restrict the extent of a Zone 1 area.

Another form of ventilation is pressurization, or overpressure ventilation. In this method an overpressure is maintained in the space so that flammable gas is excluded. The *Code* recommends an overpressure of at least 5 mm WG (50 Pa). This form of ventilation is not used where there is a source of release inside the enclosed area.

Figure 16.67 shows the decision tree given in the *Code* for the determination of ventilation.

Where artificial ventilation is provided for an enclosed area, consideration should be given to possible stagnant areas. Where these exist, possible countermeasures may include additional ventilation and gas detectors. It is necessary to consider what precautions should be taken to deal with the possibility of loss of artificial ventilation. The appropriate measures will depend on the particular situation. They may be aimed at reducing the frequency of failure, such as the installation of stand-by fans with separate power supplies and/or mitigating its consequences, such as the provision of gas detectors.

Selection and location of electrical equipment

The IP *Code* deals in Chapter 7 with the selection and location of electrical equipment, covering much the same ground as Section 16.8. The table showing the types of protection available has already been given in the previous section as Table 16.43.

The *Code* makes a distinction between electrical apparatus without and that with potential for internal release of flammable material. Certain types of instrument come into the latter category. Guidance on such apparatus is given in Appendix F of the *Code*.

Control of non-electrical ignition sources

Chapter 8 of the IP *Code* deals with the control and location of ignition sources other than electrical equipment. A hazardous area should preferably contain no fixed sources of ignition and close control should be exercised over any mobile ignition sources. In respect of mobile ignition sources, the *Code* deals mainly with permit-to-work systems and with the use of gas detectors.

Specific ignition sources the control of which is considered in the code include (1) hot surfaces, (2) furnaces and fired heaters, (3) combustion engines, (4) turbines, (5) road and rail traffic and (6) flares. Consideration is also given to pyrophoric and electrostatic hazards and air intakes.

16.9.4 API RP 500

The approach described in API RP 500: 1991 is broadly similar to the method of direct example just described. The code utilizes the NFPA classification of fluids given in Chapter 10 and the NFPA classification of hazardous locations and grouping of atmospheric mixtures given in Section 16.8. It distinguishes between outdoor and enclosed locations.

The *Code* gives exemplars of zoning in Section A for petroleum refineries; in Section B for production facilities, on land and offshore; and in Appendix C for petroleum pipelines.

The criterion given in the *Code* for 'adequate ventilation' is 6 air changes per hour. Appendices A–C of the *Code* deal with ventilation. They treat, respectively, (1) ventilation of an enclosed area by natural means, (2) ventilation for fugitive emissions and (3) development of ventilation criteria.

16.9.5 Quantification in hazardous area classification

The methods used in the codes just described are based essentially on industry experience supplemented by estimates of the frequency and range of releases. An indication that traditional approaches have tended to yield disparate results is given in Figure 16.68 (A.W. Cox, Lees and Ang, 1990). The figure shows the zoning recommendations of selected codes for certain common items.

One approach to hazardous area classification is: to identify particular types of source of release; to assign to each source a typical release rate, or set of rates; to assign to each release rate a frequency; to estimate the range of the release; and to use this release range to determine, for purposes of zoning, a hazard range. The estimation of frequency and the determination of the hazard range may be a matter of judgement.

This basic approach may be applied in one of two ways. One is to perform the whole exercise afresh for each source of release on each occasion that such a source is encountered in the design. The other, and more practical, way is to do the assessment once and for all and then to produce guidelines.

Approaches on these lines evidently inform some of the methods used in the codes just described, such as the source of hazard method of the ICI *Electrical Installations Code* and the point source method of the IP *Area Classification Code*.

A method based on the examination of individual leak sources has the advantage that it forces the engineer to identify these sources and to examine them more closely. It takes full account of the properties of the fluids and the operating conditions. It allows for engineering features designed to reduce the risk. It should give greater reassurance that the zone distances are right. On the other hand, there is a view that this approach can lead to much effort for little return, the end result often being little different from that obtained using a more general approach.

Hazardous area classification has not to date been based on any formal quantitative risk assessment. There have been different views on whether or not this is necessary. In any event, in this particular field quantification has proved difficult. Foremost among the problems is the lack of data on the basic frequency and size distribution of leaks for different potential sources. Uncertainties in modelling have been another significant factor.

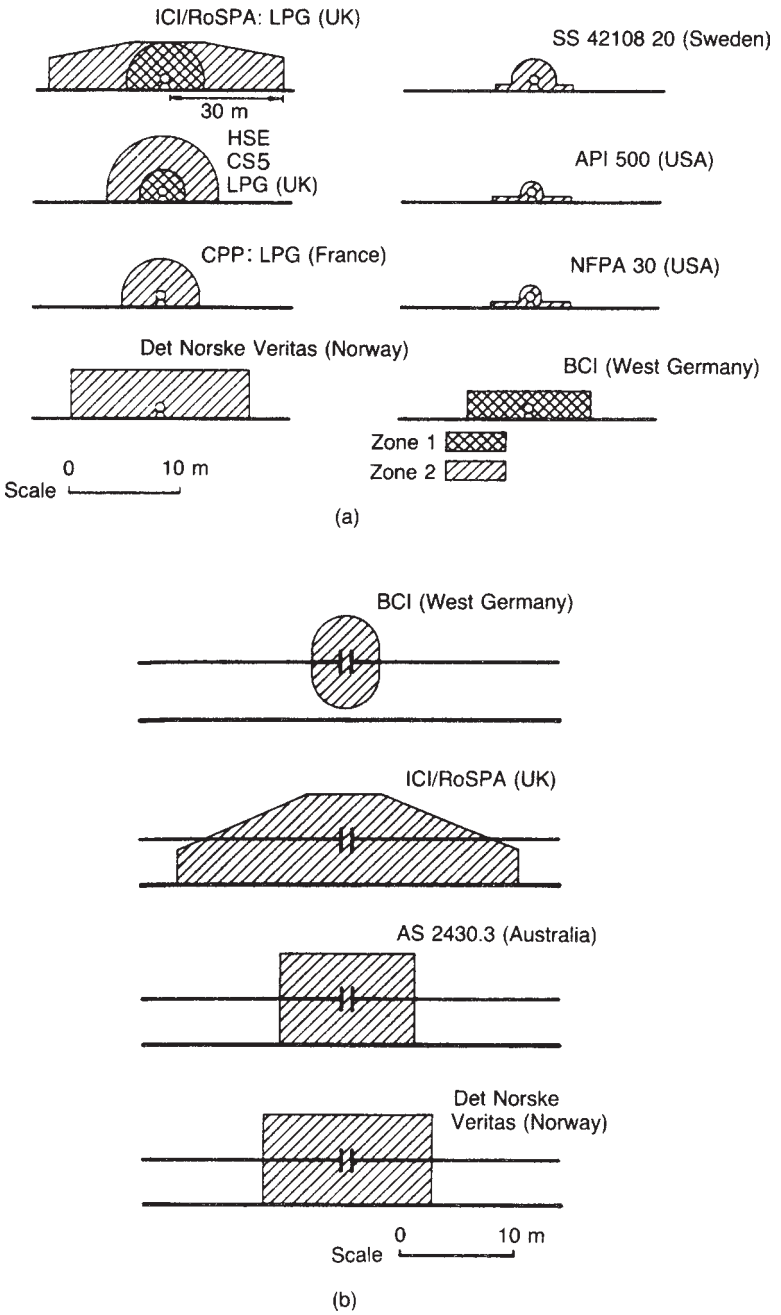
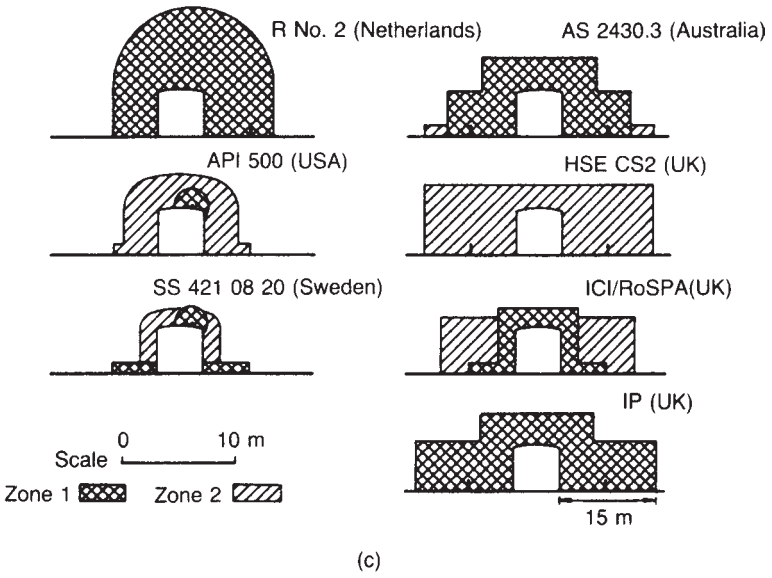


Figure 16.68 *Hazardous area classification: zone distances given by selected codes (A.W. Cox, Lees and Ang, 1990): (a) zone distances for pumps for LPG; (b) zone distances for flanges of pipework handling LPG; and (c) zone distances for storage tanks (Courtesy of the Institution of Chemical Engineers)*



(c)

Figure 16.68 *continued*

Several parties have addressed the modeling aspect. In the mid-1980s, a draft appendix to BS 5345 was produced which contained a collection of models for use in hazardous area classification, but this did not see the light of day. A discussion of such models has been given light of day. A discussion of such models has been given by O'Shea (1982). Another set of models area those given for plan layout by Mecklenburgh (1985), as described in Chapter 10. A set of models for natural gas is given in the British Gas in-house code BGC/PS/SHA1.

Research in support of a more quantitative approach has been described in *Classification of Hazardous Areas* A.W. Cox, Lees and Ang (1990). This work involved the development and refinement of estimates of (1) the frequency and size distribution of leak s from typical leak sources, (2) the probability of ignition of the release and (3) the probability of explosion given ignition. An account of this ignition model is given in the next section. The authors state that the provision of these data provides the basis for the development of guidance based on quantitative risk assessment. They suggest that quantitative guidance might be formulated by exploring representative scenarios of release on plant layouts incorporating typical equipment, and sources of release, using a three-dimensional computer-aided design (CAD) plant layout code, utilizing the data on release frequency and size and ignition on which the ignition model is based, together with other data such as the probability of exposure of personnel.

16.10 Ignition Models

It is frequently necessary in hazard assessment to estimate the probability of ignition and of explosion if a leak occurs. There is therefore a requirement both for ignition models and for data from which to determine the parameters in such models. This is, however, an area where there is relatively little guidance available.

Information relevant to the modelling of ignition sources has been given in *Classification of Hazardous Areas*, the study by A.W. Cox, Lees and Ang (1990) already mentioned. This work includes a model for leaks of flammable fluids and for their ignition and explosion.

16.10.1 Modes of ignition

Ignition of a leak may occur either at the point of leak or at some distance from it. The cause of ignition may be the leak event itself or an ignition source. These distinctions may be illustrated by the following examples. A leak may occur at a pump seal which has failed due to a bearing failure and the hot bearing may ignite the leak. A leak may occur due to equipment rupture and the rupture may give a spark which ignites the leak. A leak may generate static electricity which then gives an incendive spark and ignites the leak. All these cases are treated here as ignitions by the leak event itself, regardless of how close to point of leak ignition occurs.

It is usually convenient to consider a limited number of specific sources and to treat the large number of other potential ignition sources as background sources. A specific ignition source may be present continuously or only intermittently.

From the foregoing, the modes of ignition may be classified as follows:

(1) event ignition;
(2) specific ignition source
    (a) continous,
    (b) intermittent;
(3) background ignition.

It may also be helpful to distinguish between those ignition sources on which action is practical when a gas alarm occurs and those for which it is not.

16.10.2 Distribution of ignition sources

Some data on the distribution of ignition sources onshore are given in Table 16.46 These data are from a survey by Cox, Lees and Ang of incidents reported to the Health and Safety Executive (HSE).

Information on ignition sources offshore has been given by Sofyanos (1981) and by Forsth (1981a,b,1983). Table 16.47 shows data given by Forsth (1983) for the Gulf of Mexico (GoM) and for the Norwegian North Sea (NNS). The number of accidents considered was 326 in the GoM over the period 1956–82 and 133 in NNS over an unspecified period.

16.10.3 Probability of ignition

The information available on the probability of ignition is mostly in the form of expert estimates. In the context of vapour cloud explosions, Kletz (1977j) states that on polyethylene plants the leaks are mostly very small and that about one leak in 10,000 ignities, due probably to good jet mixing with air. He also states that on a series of plants handling a hot mixture of hydrogen and hydrocarbons about one leak in 30 ignites. He argues that the probability of ignition increases with the size of leak and suggest that for large leaks (>10 ton) the probability of ignition is greater than 1 in 10 and perhaps as high as 1 in 2.

R.L. Browning (1969c) has given a set of estimates of the relative probabilities of ignition. For ignition under conditions of no obvioius source of ignition and with explosion-proof electrical equipment he gives the following probabilities of ignition:

	Relative probability of ignition
Massive LPG release	10^{-1}
Flammable liquid with flashpoint below 110°F or with temperature above flashpoint	10^{-2}
Flammable liquid with flashpoint 110–200°F	10^{-3}

Elsewhere R.L. Browning (1980) gives a table of probabilities which are evidently absolute probabilities. The table includes an estimate of the probability of ignition of flammable gas–liquid spills of 10^{-2}–10^{-1}.

The First *Canvey Report* (HSE, 1978b) gives for LNG vapour clouds:

	Probability of ignition
Limited releases	10^{-1}
Large releases	1

Table 16.46 *Ignition sources in fire and explosion survey of national case histories (A.W. Cox, Less and Ang, 1990) (Courtesy of the Institution of Chemical Engineers)*

	No. of incidents	*Proportion of incidents* (%)	
		Unadjusted	*Adjusted*[a]
Flame:			
General	8	9.3	16.7
LPG fired equipment	2	2.3	4.1
Hot surfaces	10	11.6	20.8
Friction	4	4.7	8.4
Electrical	8	9.3	16.7
Hot particles	3	3.5	6.3
Static electricity	6	7.0	12.5
Smoking	–	–	–
Autoignition	7	8.1	14.5
Unknown	38	44.2	–
Total	86	100.0	100.0

[a] Adjusted figures are based on eliminating the unknown category and redistributing the known ignition sources in their original relative proportions.

Table 16.47 *Ignition sources for fires and explosions on offshore platforms in the Gulf of Mexico 1956–81 and the Norwegian North Sea (A.W. Cox, Lees and Ang, 1990; after Forsth, 1983) (Courtesy of the Institution of Chemical Engineers)*

	Proporation of incidents[a] (%)			
	NNS		*GoM*	
	Unadjusted	*Adjusted*	*Unadjusted*	*Adjusted*
Welding/cutting/grinding	18	–	59	–
Engines and exhausts	34	50.7	4	14.3
Sparks	4	6.0	1	3.6
Electrical	16	23.9	9	32.0
Hot surfaces[b]	0	0	6	21.4
Self-ignition	1	1.5	1.5	5.4
Cigarette, lighter, match	1	1.5	1.5	5.5
Other	11	16.4	5	17.9
Unknown, not reported	17	–	12	–
Total		100		100

GoM, Gulf of Mexico; NNS, Norwegian North Sea.

[a] Adjusted figures are based on eliminating the hot work and unknown categories and redistributing the known ignition sources in their original relative proportions.

[b] Other than engines and exhausts.

The Second *Canvey Report* (HSE, 1981a) gives the following 'judgment' values for ignition on site:

Ignition sources	*Probability of ignition*
None	0.1
Very few	0.2
Few	0.5
Many	0.9

For offshore locations, Dahl *et al.* (1983) have analysed ignition data for gas and oil blowouts, which may be regarded as massive releases. The data are shown in Table 16.48, Section A. They cover both drilling rigs and production platforms. The overall probability of ignition of blowouts is similar for the two cases.

Cox, Lees and Ang draw on the foregoing to make estimates of the probability of ignition, They define a minor leak as one <1 kg/s and take for this an average leak flow of 0.5 kg/s. They define a massive leak as one >50 kg/s and take for this an average leak flow of 100 kg/s. They estimate the probability of ignition of a minor leak of either gas or liquid as 0.01, that of a massive leak of gas as 0.03 and that of a massive leak of liquid as 0.08. From these estimates they derive those given in Table 16.49 and Figure 16.69.

16.10.4 Probability of explosion

The information available on the probability of explosion is also mostly in the form of expert estimates. In his account of vapour cloud exlosions, Kletz (1977j) has also given estimates of the probability of explosion. He quotes the following figures:

Frequency of serious vapour cloud fires = 5/year
Frequency of serious vapour cloud explosions = 0.5/year

and derives from these for a large vapour cloud

Probability of explosion given ignition = 0.1

He also gives estimates which are evidently for the probability of explosion given leak. These are a probability >0.1 for a large vapour cloud (>10 ton) and 0.0001–0.01 for a medium vapour cloud (1 ton or less).

The First *Canvey Report* gives for a refinery

Probability fo explosion, given major fire = 0.5

and for large LNG vapour clouds

	Probability of explosion given ignition
Large vapour clouds	1
Smaller clouds of gases other than methane	0.1
Smaller clouds of methane	0.01

For offshore locations, Dahl *et al.* (1983) have analysed blowouts as shown in Table 16.48, Section B.

Sofyanos (1981) has given for fires and explosion s in the Gulf of Mexico the data shown in Table 16.50.

For the estimation of the probability of explosion, Cox, Lees and Ang use for massive leaks the value of 0.3 given by Dahl *et al.* for blowouts and for minor leaks the value of 0.04 given by Sofyanos for Category V leaks. From these estimates they derive those given in Table 16.51 and Figure 16.70.

Table 16.48 *Probability of ignition and of explosion for offshore blowouts (A.W. Cox, Lees and Ang, 1990; after Dahl et al., 1983) (Courtesy of the Institution of Chemical Engineers)*

A Probability of ignition

Blowout fluid	*No. of blowouts*	*No. of ignitions*	*Probability of ignition*
Gas	123	35	0.3
Oil	12	1	0.08

B Probability of explosion, given ignition

Blowout fluid	*No. of blowouts*	*No. of ignitions*	*No. of explosions*	*Probability of explosion given ignition*
Gas	123	35	12	0.34
Oil	12	1	0	0

Table 16.49 *Estimates of probability of ignition for leaks of flammable fluids (A.W. Cox, Lees and Ang, 1990) (Courtesy of the Institution of Chemical Engineers)*

Leak (kg/s)	*Probability of ignition*	
	Gas	*Liquid*
Minor (<1)	0.01	0.01
Major (1–50)	0.07	0.03
Massive (>50)	0.3	0.08

16.10.5 Distribution of leaks

In order to model the occurrence of fire and explosion on a plant it is also necessary to have information on the frequency of leaks. Table 16.52 gives the estimates of leak frequency used by Cox, Lees and Ang.

16.10.6 Cox, Lees and Ang model

The approach taken by Cox, Lees and Ang is to define an equivalent standard plant and to make for this plant estimates of the frequency of leaks of flammable gas and liquid and of ignitions and explosions. The inventory of equipment in the equivalent standard plant (ESP) is list in Table 16.53.

These various data sets are then combined to give a model, described by the authors as a fire and explosion model, but referred to here as an ignition model. From the inventory of equipment on the ESP and the generic estimates of leak frequency the frequency of leaks on the plant is obtained. The frequency of fire and explosions is then obtained from the ignition and explosion probabilities shown in Figures 16.69 and 16.70.

The data in Tables 16.52 and 16.53 and Figures 16.69 and 16.70 used in the model were initially obtained as independent estimates, but were then adjusted to give a better fit to the historical data such as the frequency of plant fires and

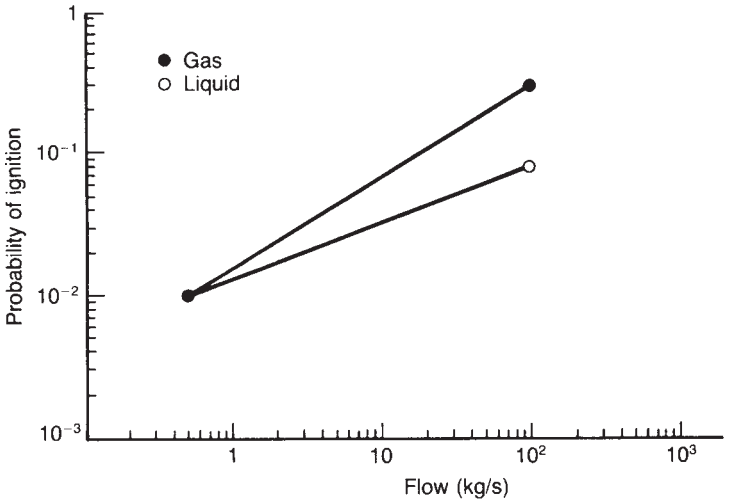


Figure 16.69 *Estimated probability of ignition for leaks of gas or liquid (A.W. Cox, Lees and Ang, 1990). (–) Initial estimates, which were used unaltered in the ignition model – see text (Courtesy of the Institution of Chemical Engineers)*

Table 16.50 *Probability of explosion given ignition for blowouts in the Gulf of Mexico (A.W. Cox, Lees and Ang, 1990; after Sofyanis, 1981) (Reproduced by permission of the Institution of Chemcial Engineers)*

Damage category[a]	*No. of incidents with fire and explosion*	*No. of incidents with explosion only*	*Probability of explosion given ignition*
I	9	5	0.55
II	13	3	0.23
III	33	6	0.18
IV	128	22	0.18
V	143	6	0.042
Total	326	42	0.13[b]

[a] The damage categories are in decreasing order of severity, Category I being loss of platform and Category V being an incident of no consequence.
[b] Weighted average.

vapour cloud explosions. For the leak frequency the original estimates are shown in Table 16.52 in brackets. No adjustment was made to the ignition probabilities given in Table 16.49 and Figure 16.69, but the explosion probabilities given in Table 16.51 and Figure 16.70 were adjusted to:

Leak (kg/s)	*Probability of explosion given ignition*
Minor (<1)	0.025
Massive (>50)	0.25

If, therefore, the estimate of the probability of explosion is based on the outcome from the model the model rather than on those derived in Subsection 16.10.4, the values given by the dotted line in Figure 16.70 apply.

Some results obtained by running the model for the equivalent standard plant are given Table 16.54. Leak, fire and explosion frequencies are given in Section A of the table by leak source and in Section B by fluid phase. The authors give comparisons of these results with

Table 16.51 *Estimates of probability of explosion given ignition for leaks of flammable gas (A.W. Cox, Lees and Ang, 1990) (Courtesy of the Institution of Chemical Engineers)*

Leak (kg/s)	*Probability of given ignition*
Minor (<1)	0.04
Major (1–50)	0.12
Massive (>50)	0.3

historical data on fires and vapour cloud explosions, both overall and by leak source and fluid phase.

The purpose of the model as developed by the authors is to provide a check on the estimates of leak frequency. The conventional approach in hazard assessment is to make estimate of frequency and to derive confidence limits on these estimates. For leaks, however, the data appeared to be too sparse to permit this approach. The problem was therefore tackled in a different way. The estimates of leak size distribution and frequency were used to make, for a typical plant, estimates not only of the overall frequency of

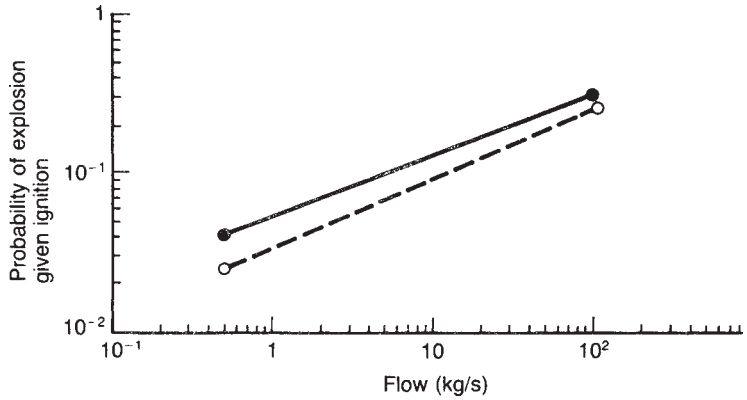


Figure 16.70 *Estimated probability of explosion given ignition for leaks of gas (A.W. Cox, Less and Ang, 1990): (–) Initial estimate; and (- -) estimate used in the ignition model – see text (Courtesy of the Institution of Chemical Engineers)*

Table 16.52 *Estimates*[a] *of leak frequency used in ignition model (A.W. Cox, Lees and Ang, 1990) (Courtesy of the Institution of Chemical Engineers)*

A Pipework: leak frequency (leaks/m yr)

	Pipe diameter (m)			
	0.025	0.050	0.100	0.300
Rupture leak	0.005 (0.01)	0.005 (0.01)	0.0015 (0.003)	0.0005 (0.001)
Major leak	0.05 (0.1)	0.05 (0.1)	0.015 (0.06)	0.005 (0.03)
Minor leak	0.5 (1)	0.5 (1)	0.15 (0.3)	0.05 (0.1)

B Flanges (all pipe diameters): leak frequency (leaks/yr)

Major leak	0.3 (1)
Minor leak	3 (10)

C Valves: leak frequency (leaks/yr)

	Pipe diameter (m)			
	0.025	0.050	0.100	0.300
Rupture leak	0.01 (0.1)	0.01 (0.1)	0.01 (0.1)	0.005 (0.1)
Major leak	0.1 (1)	0.1 (1)	0.1 (1)	0.05 (1)
Minor leak	1 (10)	1 (10)	1 (10)	0.5 (10)

D Pumps (all pipe diameters): leak frequency (leaks/yr)

Rupture leak	0.3 (0.3)
Major leak	3 (3)
Minor leak	30 (30)

E Small bore connections: leak frequency (leaks/yr)

Pipe diameter = 0.01 m

Rupture leak	1 (5)
Major leak	10 (50)

[a] All values to be multiplied by 10^{-4}.

fire and explosion but also of leaks by leak size, by fluid phase and by leak source, and hence of the distribution of leaks by size, fluid phase and leak source. Thus the model may be tested in terms not only of the final results but also of a numbers of intermediate results. For example, not only should the overall frequency of explosions accord with historical values, but so should the distribution of explosions by leak source. The totality of such comparisons

Table 16.53 *Inventory of leak sources on equivalent standard plant used in ignition model (A.W. Cox, Lees and Ang, 1990) (Courtesy of the Institution of Chemical Engineers)*

A Pipework, flanged joints, valves

Pipe diameter (mm)	*Pipe length*		*Flanged joints*	*Valves*	*Proportion on gas* (%)
	(m)	(%)			
15	525	3.5	100	120	0
20	90	0.6	200	100	0
25	3,000	20.0	600	500	0
40	2,100	14.0	420	200	5
50	2,100	14.0	650	300	8
80	3,300	22.0	530	140	8
100	1,050	7.0	160	60	8
150	1,050	7.0	120	40	8
200	600	4.0	100	18	10
250	300	2.0	55	10	20
300	150	1.0	30	5	20
350	45	0.3	5	2	20
400	525	3.5	20	3	20
450	45	0.3	5	–	20
500	120	0.8	5	2	20
Total	15,000		3,000	1,500	

B Pumps

No. of pumps = 25

Table 16.54 *Leak, fire and explosion frequencies obtained using the ignition model (A.W. Cox, Lees and Ang, 1990) (Courtesy of the Institution of Chemical Engineers)*

A By leak source

Flow (kg/s)	<1	1–50	>50	*Total*	*Proportion* (%)
Leak frequency (leaks/plant year)					
Pipework	0.422	0.115	0.00318	0.540	21.2
Flanges	0.910	0.080	0	0.990	38.9
Valves	0.130	0.340	0.00037	0.164	6.4
Pumps	0.045	0.038	0.00030	0.083	3.3
Small bore connections	0.711	0.060	0	0.770	30.2
Total	2.22	0.33	0.0038	2.55	
Proportion (%)	87.0	12.8	0.15		
Fire frequency [a] *(fires/plant year)*					
Pipework	42.7	31.3	5.82	80.0	25.9
Flanges	91.0	16.3	0	107	34.8
Valves	13.2	9.21	0.741	23.1	7.5
Pumps	4.50	9.02	0.504	14.0	4.5
Small bore connections	71.1	13.1	0	84.2	27.3
Total	222	79	7	308	
Proportion (%)	72.1	25.6	2.3		
Explosion frequency[a] *(explosions/plant year)*					
Pipework	0.431	1.42	1.10	2.95	48.0
Flanges	0.753	0.418	0	1.17	19.1
Valves	0.128	0.427	0.151	0.705	11.5
Pumps	0.027	0.281	0.090	0.398	6.5
Small bore connections	0.630	0.362	0	0.991	15.0
Total	1.90	2.90	1.34	6.14	
Proportion (%)	30.9	47.3	21.8		

Table 16.54 *(continued)*

B By fluid phase

Flow (kg/s)	<1	1–50	>50	*Total*	*Proportion* (%)
Leak frequency (leaks/plant year)					
Liquid	0.930	0.164	0.00184	1.10	43.0
Gas	0.285	0.00494	0.000026	0.29	11.4
Two-phase	1.00	0.157	0.00200	1.16	45.6
Total	2.22	0.326	0.0039	2.55	
Proportion (%)	87.0	12.8	0.15		
Fire frequency[a] *(fires/plant-year)*					
Liquid	93.0	32.4	1.46	127	41.1
Gas	28.6	1.7	0.077	30	9.8
Two-phase	101	44.9	5.53	151	49.1
Total	222	79	7.1	309	
Proportion (%)	72.0	25.6	2.3		
Explosion frequency[a] *(explosions/plant year)*					
Gas	0.248	0.137	0.019	0.404	6.6
Two-phase	1.65	2.77	1.32	5.74	93.4
Total	1.90	2.90	1.34	6.14	
Proportion (%)	30.9	47.3	21.8		

[a] All values to be multiplied by 10^{-4}.

constitutes a relatively robust cross-check. It is this conceptual approach which is the main value of the model.

16.10.7 Models utilizing dispersion relations

The model just described utilizes the overall probability of ignition expressed as a function of the leak flow. The characterization of ignition probability may be extended by modeling the physical basis for the relation between it and the leak flow.

Some features which such a model should possess are given by Cox, Lees and Ang as follows:

(1) the effect of the fluid phase, gas or liquid, should be taken into account;
(2) the probability of ignition for an unprotected location should increase as the leak flow increases;
(3) there should be a finite probability of event ignition which allows for the failure to achieve perfect protection even within the designated zones, and this probability also should increase as the leak flow increases;
(4) there should be a finite probability of event ignition;
(5) the estimated probability of ignition should be the sum of (3) and (4) over the range covered by zoning and of (2) and (4) over the range not so covered.

The overall probability of ignition and the probability of event ignition estimated from the model should both be in broad agreement with that observed.

The leak flow determines the distance, and hence the area covered or volume encompassed by the leak. This area or volume may be obtained using suitable emission and dispersion relations. A model for the probability of ignition may then be constructed in which the probability is a function of the area or volume, depending on the situation considered.

One outcome of such an approach is the speculative model shown in Figure 16.71. Lone A gives the estimated probability of ignition given a normal, partial degree of protection against ignition and corresponds to the line given in Figure 16.69. Lines B and C represent the component parts of line A, line C being the part due to event ignition and line B that due to ignition sources, both specific and background. Line D gives the estimated probability of ignition assuming no protection. Line E illustrates a possible actual curve for ignition probability.

Critical features of such a model are the probabilities of event ignition and the slope of the lines derived on the one hand from estimates of overall probability of ignition and on the other from the dispersion models.

16.10.8 Models with specific ignition sources

The matter can be taken further by expressing the overall probability of ignition as a function of the contributions of the various ignition sources. For this purpose it is convenient to utilize the classification given in Section 16.10.1 and to write the overall probability of ignition P as a function of the probability P_a of ignition by the event itself, or event ignition, of the probability P_b of ignition by a specific ignition source, and of the probability P_c of ignition by one of the background ignition sources, or background ignition:

$$P = f(P_a, P_b, P_c) \qquad [16.10.1]$$

The overall probability of ignition is then

$$P = P_a + P_b + P_c - P_aP_b - P_aP_c - P_bP_c + P_aP_bP_c \qquad [16.10.2a]$$

$$= P_a + P_b + P_c \quad P_a, P_b, P_c \ll 1 \qquad [16.10.2b]$$

The probability P_b of ignition by specific ignition sources is

$$P_b = 1 - \prod_{i=1}^{n} (1 - P_{b;i}) \qquad [16.10.3a]$$

$$P_b = \sum_{i=1}^{n} P_{b;i} \qquad P_{b;i} \ll 1 \qquad [16.10.3b]$$

where $P_{b;i}$ is the probability of ignition by ignition source i.

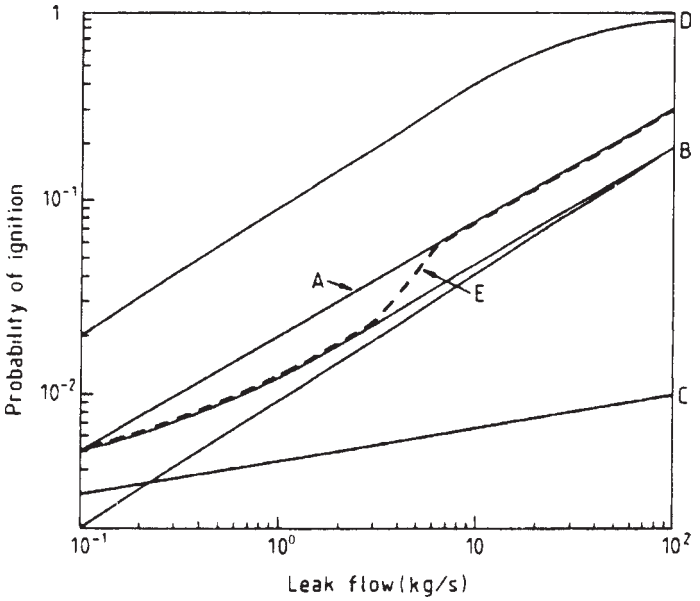


Figure 16.71 *Speculative model for the probability of ignition of leaks of flammable gas (after A.W. Cox, Lees and Ang, 1990) (Courtesy of the Institution of Chemical Engineers)*

For a specific ignition source the probability of ignition is

$$P_{b;i} = P_{b;i;1}P_{b;i;2}P_{b;i;3}P_{b;i;4} \quad [16.10.4]$$

where $P_{b;i;1}$ is the probability that the source is present, $P_{b;i;2}$ is the probability that the flammable region of the gas cloud reaches the source, $P_{b;i;3}$ is the probability that the source, if active, is able to ignite the gas, and $P_{b;i;4}$ is the probability that the source is active.

The probability $P_{b;i;1}$ depends on the plant configuration and zoning practices under consideration. Probability $P_{b;i;2}$ may be estimated using dispersion relations. Probability $P_{b;i;3}$ allows for the strength of the ignition source in relation to the strength required to ignite the cloud. Probability $P_{b;i;4}$ allows for the fact that the ignition source may be intermittent. The last two depend on the type of ignition source.

The model can accommodate different sets of specific ignition sources. From Tables 16.46 and 16.47 and from general considerations a suitable set might be

(1) flames;
(2) hot work;
(3) hot surfaces;
(4) electrical;
(5) engines, motors;
(6) human activity.

In making this selection, allowance has been made for the possibility of action when a gas alarm occurs. An engine may be shut-down, but a hot exhaust will remain hot for a period. Broadly speaking, the items in this set on which action may be taken are hot work, engines and motors and human activity.

For the probability P_a of event ignition the offshore data given in Table 16.47 suggest an overall value of about 1–5%, say 3%. It may be expected that this probability will be higher for a large leak than for a small one.

Insofar as a model of this kind gives more detailed information about the specific ignition sources and their characteristics, it provides a basis not only for hazard assessment but also for taking action to reduce the probability of ignition.

16.10.9 Models in hazard assessment systems

Hazard assessment systems often include an ignition model. Other ignition models have been given in specific hazard assessments. Most of these models relate to ignition sources which might ignite a vapour cloud drifting beyond the plant boundary.

In the Vulnerability model described by Eisenberg, Lynch and Breeding (1975), the occurrence of ignition is determined as follows. It is assumed that an ignition source is located at the centre of each population cell and that ignition occurs if a flammable mixture reaches such an ignition source. The type of ignition source is specified for each cell by the user, the two types giving fire or explosion, respectively.

The handling of ignition sources in the SAFETI package has been described by Ale and Whitehouse (1986) and Pitblado and Nalpanis (1989). As for population, a 100 m × 100 m grid is used, and ignition sources are located inside each grid. Point, line or areas sources may be specified. Each source has two attributes: the probability that it is active and the probability that it is effective. Day and night are treated as separate cases.

A somewhat different approach is used in the short-cut classical method (SCM) described by R.A. Cox and Comer (1982). There the probability P of ignition is assigned

specified values at regular intervals of distance dr and is thus specified as a function of the direction θ and the distance $r\,(=i\mathrm{d}r)$

$$P = f(\theta, r) \qquad [16.10.5]$$

Another approach, described by English and Waite (1989), is to assume a constant density μ of ignition sources. The probability increment δP of ignition for a sector of semi-angle θ_s at distance r is then

$$\delta P = \mu r \tan\theta_s \mathrm{d}r \qquad [16.10.6]$$

and the probability P of ignition by the time a distance r has been reached is

$$P = 1 - \exp(-\theta_s \mu r^2) \qquad [16.10.7]$$

The treatment of ignition sources in the *Rijnmond Report* is described in Appendix 8.

16.11 Fire in Process Plant

Fires in process plant are a serious hazard to both life and property. It is essential, therefore, to understand the ways in which fire can occur and develop.

Normally, fire occurs as a result of a leakage or spillage of fluid from the plant. Larger leaks may occur due to the failure of a vessel, pipe or pump, and smaller ones from flanges, sample and drain points and other small bore connections.

Combustion of material which has leaked from a plant may take a number of forms. A leak of gas or liquid may be ignited at the point of issue so that it behaves like a flame on a burner. In some circumstances this flame may be directed like a blow torch at another part of the plant.

If the leak gives rise to a gas or vapour cloud which grows for a period before it is ignited, the resultant effect may be either a vapour cloud, a flash fire, or a vapour cloud explosion. Vapour cloud explosions are considered in Chapter 17.

In a flash fire the gas cloud burns, but does not explode. A typical flash fire may cause quite extensive damage, particularly to vulnerable items such as electric cabling, but may leave the main plant equipment relatively unharmed. However, a flash fire does cause a sudden depletion of oxygen, and this effect can be lethal to personnel.

If the leak forms a liquid pool on the ground, this may ignite and burn. The flame may be substantial and may do damage by direct impingement or by radiation.

If the release results from fire engulfment of a vessel, a fireball may be formed.

Prevention of fire in process plant is primarily a matter of preventing leaks and avoiding sources of ignition.

In addition to fires arising from leakage in general, there are certain characteristic types of fire on process plant. These include (1) pump fires, (2) flange fires, (3) lagging fires, (4) duct fires, (5) cable tray fires, and (6) storage tank fires. These various types of fire are now discussed.

16.11.1 Pump fires

Pumps tend to leak at the gland or the seal and the leakage frequently ignites causing a fire. Pump fires have been discussed by Kletz (1975b), who describes a number of incidents involving leakage and/or fire from seals on cold duty pumps on olefin separation plants. He quotes three cases of leaks from cold ethylene pumps. In one there was a leakage over 20 min of some 3 ton of vapour which formed a cloud, but blew away without igniting. In the other two there was ignition at the pump. The cause of ignition may have been static electricity. In both instances there was a jet of vapour containing liquid droplets. With C3 and C4 hydrocarbons at moderate pressure and ambient temperature, however, there are far fewer pump seal leak fires.

Table 16.55 *Estimated frequency of pump fires (after Kletz, 1971) (Courtesy of the Institution of Chemical Engineers)*

Material in pump	*Estimated frequency of fires* (fires/pump-year)
LPG below ambient temperature	$>10^{-3}$
Material above autoignition temperature	$>10^{-3}$
Flammable material well above ambient temperature (e.g. petrol at 70°C, gas oil at 150°C)	$<10^{-3}$ $>10^{-4}$
LPG at ambient temperature	$<0.33\times10^{-3}$ $>0.33\times10^{-4}$
Petrol or similar materials at or near ambient temperature	$<10^{-4}$ $>10^{-5}$
Gas oil or similar materials below their flashpoints	$<10^{-5}$

Kletz (1971) has also provided estimates made by experts of the frequency of fires on pumps with different duties. These estimates are given in Table 16.55.

These accounts of pump fires are given by Kletz in the context of the use of emergency isolation valves to prevent a serious leak at the pump. The provision of such isolation arrangements is one of the principal means of mitigating pump fires. An alternative approach is to improve the mechanical reliability of the pump. The use of double mechanical seals, for example, greatly reduces the frequency of seal failure.

A fire at a pump can do considerable damage. It is important, therefore, to assess the effect of a fire on equipment above the pump. In some fires the damage has been much reduced by a concrete floor above the pump alley.

Electrical and instrument cabling is particularly liable to be damaged by a pump fire. If such cabling is put out of action, the plant may be down for a much longer period than is required to deal with the fire itself. Methods are available for giving such cabling a 15-min protection against fire, but they involve additional expense.

The provision of protection against pump fires is a good illustration of the loss prevention approach. The need for measures such as improved pump reliability, an emergency isolation valve or protected cabling, should be assessed by considering for each case the frequency and consequences of a pump fire.

16.11.2 Flange fires

Pipe flanges tend to leak and sometimes the leakage is ignited so that there is a fire.

An account of flange fires and their prevention has been given by McFarland (1969). Leakage at flanges is induced

mainly by temperature transients which put elements of the flange assembly under stress and may cause them to yield.

Figure 16.72 shows this effect for a normal gasketed joint. The joint is shown in Figure 16.72(a) as new, in Figure 16.72(b) during the passage of hot fluid when the temperature of the inside of the pipe is hotter than that of the outside and causes differential expansion, and in Figure 16.72(c) after the transient has caused yielding of the flanges an/or bolts and compression in the gasket.

A lens ring joint of the type which is self-tightening under pressure is illustrated in Figure 16.73. Figure 16.73(a) shows the joint as new and Figure 16.73(b) shows it after a sudden reduction in temperature has caused the joint ring to suffer radial strain and leak. Figures 16.73(c) and (d) indicate two possible solutions, the use of an insulating pad between the joint ring and the pipe bore, and the provision of a more massive flange.

Figures 16.74(a) and (b) show two other methods of improving the leak-tightness of an existing flanged joint: using longer bolts with sleeves and with Belleville washers, respectively. In the latter case it is necessary to ensure that the washers cannot lose temper due to high temperatures.

The main alternative hypothesis advanced to explain the Flixborough disaster involved a flange fire. The elbow of an 8 in. line showed evidence of having been subjected to a directed flame. It was suggested that a gasket blew on a non-return valve inside a lagging box near to the elbow and gave rise to an annular leak and off-port flame directed at the elbow.

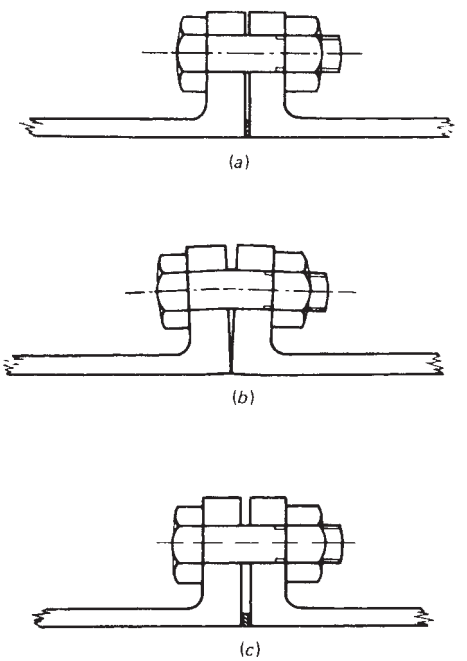


Figure 16.72 *A normal gasketed joint (after McFarland, 1969): (a) as new; (b) a hot fluid puts pipe under stress and causes bolts and flanges to yield; (c) when the fluid temperature falls, leakage can occur (Courtesy of the American Institute of Chemical Engineers)*

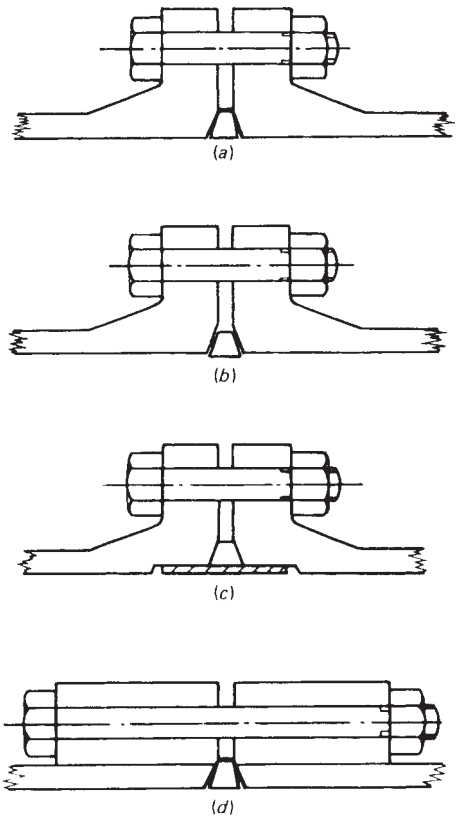


Figure 16.73 *A lens ring joint (after McFarland, 1969): (a) as new; (b) if there is a sudden temperature reduction the joint ring can suffer radial strain and leak; (c) addition of an insulating panel between the joint ring and the pipe bore reduces leakage; (d) use of more massive flanges gives better resistance to stress (Courtesy of the American Institute of Chemical Engineers)*

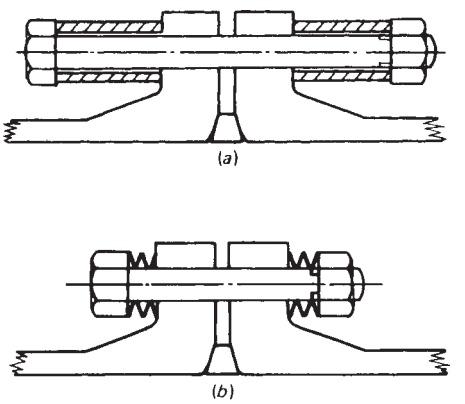


Figure 16.74 *Modification of existing joints (after McFarland, 1969): (a) use of longer bolts and sleeves; (b) use of Belleville washers (Courtesy of the American Institute of Chemical Engineers)*

16.11.3 Lagging fires

Lagging on plant equipment frequently becomes impregnated with oils and other liquids. If the lagging is hot, self-heating and ignition may occur, leading to a lagging fire.

In one small refinery the number of lagging fires in the period 1958–61 ranged from 14 to 21 per year (Petkus, 1964).

Lagging fires have been investigated by P.H. Thomas, Bowes and co-workers (e.g. P.H. Thomas, 1958; P.H. Thomas and Bowes, 1961a, 1967; Bowes and Langford, 1968; Bowes, 1974a, 1976) and by Gugan (1974a, 1976).

A lagging fire is essentially a self-heating phenomenon. Self-heating was discussed in Section 16.6. The design of insulation systems to minimize lagging fires has been considered in Chapter 12.

The conditions for a lagging fire to occur are that there should be sufficient fuel, oxygen and heat. Factors relevant to the occurrence of a fire are (1) oil, (2) leak, (3) insulation material, (4) insulation sealing, and (5) insulation geometry and temperature.

The most important factor in a lagging fire is the oil itself. For significant self-heating to occur the oil needs to be involatile (a volatile oil vaporizes too easily). An intrinsically reactive unsaturated oil is more prone to self-heating than is a saturated mineral oil, but any combustible involatile oil may self-heat.

Some liquids are described as 'fire resistant'. Of these, some, such as chlorinated paraffins and phosphate esters, are intrinsically fire resistant, but others, such as liquids dosed with antioxidant or hydraulic fluids containing water, are not, and may become combustible again if they suffer preferential loss of the antioxidant or water, respectively, in the warm lagging.

The amount of oil which gives the maximum ignition sensitivity in the more porous insulating media is estimated by Gugan (1974a) as about 6–12% v/v (equivalent to about 150 = 300% w/w).

A continuous leak is not necessarily the most favourable to self-heating. If a suitable concentration of oil can only be maintained by a continuous flow, the oil is too volatile; and if there is a continuous flow of involatile oil, it is likely to oversaturate the lagging.

Typical leakage points which may cause a lagging fire are pumps, flanged joints, and sample and drain points.

The material of insulation is another factor in determining self-heating, although it is generally less important than the nature of the oil. A good insulating material has a low thermal conductivity based on a porous structure of low density. It is precisely these features which favour self-heating. The important aspects for self-heating are the extent to which the material provides surface area on which the oil is exposed, allows air to diffuse in and prevents heat from being conducted away.

The insulation material may have some inhibiting or catalytic effect on self-heating in some systems. Bowes (1974a) quotes a difference in the minimum pipe temperature of 24°C for the ignition of oil in two different lagging materials.

Frequently the main insulating material is covered with an impervious cement finish or sealing material. This greatly reduces the extent to which oxygen can diffuse into the insulation.

The temperature which can be attained in the lagging depends on its geometry and on the pipe temperature. In some cases it is possible to estimate the lagging temperature resulting from self-heating by using theoretical methods in combination with suitable experimental tests, as described in Section 16.6.

There are a number of precautions which can be taken against lagging fires. One is to prevent the lagging becoming soaked with oil. This means primarily a high standard of operation and maintenance to avoid leaks. But, in addition, measures may be adopted such as not lagging flanged joints and protecting lagging at sample points with sheet metal collars.

As discussed earlier, the maximum temperature which is attained in self-heating depends on the thickness of the lagging. A thick lagging gives good heat insulation, but also favours self-heating. A compromise is necessary, therefore, between these two factors.

Methods of making the lagging surface impervious to air include the use of a cement finish, bituminous coating material or aluminium foil. If such sealing is used, it is necessary to ensure that the sealing is maintained, particularly at the ends of the lagging.

Another approach is to use not the usual type of insulating material but other insulation such as foam glass or crimped aluminium sheeting. Foam glass is relatively brittle and requires additional care. It is more expensive, although the price differential appears to be narrowing. Aluminium sheeting is another alternative, although it is not a particularly good insulation. It has been suggested that the use of aluminium introduces the hazard of aluminium–iron smear ignition.

On some plants with high risk and difficult self-heating problems, the approach adopted is to do without insulation altogether. In such cases expanded metal 'stand-offs' may be used to protect personnel from the hot pipework.

A lagging fire is usually detected by the evolution of smoke or other fumes. Such fumes are in fact the most satisfactory means of detection insofar as they precede incandescence as well as accompany it. It is usually a matter of chance, however, whether self-heating is detected before a fire has developed.

The use of temperature sensitive paints has been suggested as a means of detection, but this is not likely to be particularly effective since the lagging surface temperature is not a very reliable indicator of self-heating.

The hazard from a lagging fire may be that of flames issuing from the lagging. But frequently the worst hazard occurs when the lagging is opened up to remove the smouldering material. The fire may then grow, sometimes very strongly, particularly if it has been deprived of air previously.

Flames from a lagging fire should normally be extinguished with small quantities of water. Water should also be available to extinguish fire when smouldering lagging is removed. Fire extinguishing agents which do not contain water are generally less effective, because of the high risk of re-ignition. Regard should be paid, however, to any hazard which the use of water may involve, such as that associated with electrical equipment. Any lagging which might re-ignite should be removed to a safe place. Further precautions may be required if the lagging contains asbestos material or evolves toxic fumes.

Accidents involving lagging fires are described in Case Histories A115 and A122.

16.11.4 Duct and cable fires

Ducts of various kinds are common in process plants and buildings. They include ducts used for (1) the conveyance of fluids, (2) extraction and other ventilation, (3) pipes and (4) electrical cables.

Such ducts may have walls which are combustible and/or may/contain combustible materials. In ordinary ventilation systems the duct walls may be plastic. In fume extraction systems combustible deposits may build up on the duct walls. Cable and pipe coverings may be combustible. Other sources of combustible material include leaks from pipes and debris left in the duct.

In many ducts air flow occurs due to forced ventilation, which is used not only in the ventilation and extraction systems, but also to dilute leaks in ducts carrying pipes. In other cases air flow may occur in fire conditions due to the flue effect.

If combustible material in a duct is ignited, fire growth can be rapid, because the heat does not escape as readily as in an open fire and much of it serves to preheat surfaces further down the duct, making the fire much more severe and causing combustion of materials which would not normally make much contribution to a fire.

Accounts of duct fires include those by A.F. Roberts (1969/70) and Anon. (1979 LPB 30, p. 155). Investigations have been carried out by Roberts and co-workers (A.F. Roberts and Clough, 1967a,b; A.F. Roberts, 1969/70, 1971a). These have included experimental work on fires in ducts with walls of wood and of polyurethane.

Roberts has given a model of duct fires in which, as shown in Figure 16.75 important parameters are the length L of the flame zone and the velocity V of the advance of the leading edge of the flame. From these the dimensionless parameters L^* and V^* may be defined as

$$L^* = \frac{4CfLB\rho_f}{V_A \rho_A D} \qquad [16.11.1]$$

$$V^* = \frac{4CfVd\rho_f}{V_A \rho_A D} \qquad [16.11.2]$$

where B is the rate of penetration of burning into the fuel bed, C is the mass of air required for the complete combustion of unit mass of fuel, d is the depth of fuel bed consumed by the fire, D is the duct diameter, f is the fraction of surface covered by the lining, V_A is the velocity of the air, ρ_A, is the density of the air and ρ_f is the density of the fuel bed.

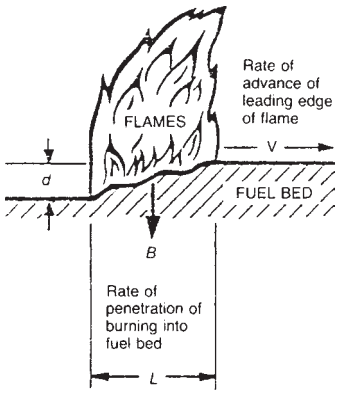


Figure 16.75 *Flame spread in a duct fire (A.F. Roberts, 1969/70) (Courtesy of HM Stationery Office.© All rights reserved)*

An important distinction is between oxygen-rich and fuel-rich fires. The parameter L^* is effectively a fuel/air ratio so that the conditions for such fires are that for $L^*<1$ the fire is oxygen rich, while for $L^*>1$ it is fuel rich.

A fuel rich fire is the more serious hazard, There is a greater rate of flame advance and heat release, the combustion gases still contain a large proportion of flammable material and they are also toxic. In a fuel rich fire the flame advances some 10 times as rapidly as in an oxygen-rich fire. Potentially combustible materials arc subject to prolonged preheating by flames and combustion products at 1000–1300°C. At a fuel/air ratio of 3, two-thirds of the material vaporized or pyrolysed is still unreacted. The combustion gases contain a large proportion of carbon monoxide. Evidence indicates that fuel-rich combustion is favoured by narrow ducts, high air velocities, high fuel loading, the presence of obstructions and large ignition sources.

In an established duct fire, the transition from oxygen-rich to fuel-rich conditions tends to increase the hazard. Reduction of the air flow may thus actually make things worse. Since the combustion gases leaving the duct may still be highly flammable, they present the hazard of further fire and explosion. These gases also contain large amounts of smoke and toxic gas, which are not only hazardous, but also tend to hamper severely attempts to fight the fire.

Work by C.K. Lee, Chaiken and Singer (1979) on duct fires with forced ventilation indicates that the fire can cause an appreciable increase in the flow resistance of the duct and can even lead to flow reversal.

Much of the interest in duct fires relates to fire in coal mine roadways, where wood is used as a lining. Work on such fires has been done by Roberts and co-workers (A.F. Roberts and Kennedy, 1965; A.F. Roberts, Clough and Blackwell, 1966; A.F. Roberts and Clough, 1967a,b) and by de Ris (de Ris, 1970; A.F. Roberts, 1971a).

These studies indicate that in modelling duct fires with infinitely thick walls there is need for care in making the assumption of a steady state. Roberts comments that a fully developed duct fire would be a highly elongated phenomenon and suggests that the full length of the fire, from the start of the burnt out zone to the end of the preheating zone, might be of the order of 370 times the duct diameter.

Another point highlighted by this work is the uncertainty surrounding the value of the heat of vaporization H_{vap} of wood, which extends not only to the magnitude but even to the sign.

There are a number of precautions which may be taken against duct fires. Good housekeeping can reduce the amount of combustible material in the duct. Fire detectors may be provided to give early warning. Fire stops may be installed to prevent fire spread. The duct may be designed to allow access for firefighting. Fire protection systems of various kinds are available. Proper working practices may be enforced by the use of a permit-to-work system.

As stated earlier, a case history of a duct fire is given by Anon. (1979 LPB 30, p. 155). Other case histories include those of cable tray fires as described below.

A type of duct fire which is of particular concern in process plants is cable tray fires. This problem has been discussed by the FPA (1974a) and by Anon. (1980 LPB 41, p. 5).

This is an important matter, because damage to cable systems often results in a long outage.

The widespread use of electric motors in process plants has led to a proliferation of motor control centres and large electric power and control cable runs. In a large proportion of cases it is not practical to use metal conduits and cables are run in open metal troughs.

A single cable may not burn very readily, but a number of cables will often burn vigorously, particularly in a vertical duct which is favourable to fire spread. Once heated up cables may not need a flame to ignite them. Rubber covered cables can be ignited by hot air or radiant heat.

PVC insulated cables present a particular problem. They burn well and readily spread fire in vertical ducts, with the plastic melting and releasing burning droplets. The PVC also decomposes to give large quantities of hydrogen chloride gas which is toxic and renders corrosive the water used in firefighting. In one power station fire about a third of the damage was attributed to this cause.

Where power and control cables are mixed, short circuits can occur from high current lines to lines which are not rated for such currents.

Cable ducts form a means by which fire may spread. This is especially serious where the cable ducts lead to a vulnerable point such as a control room.

Ignition in several cable fires has been assisted by an oil leak from machinery which has entered the cable duct through an unsealed opening.

Damage to cables may disable the emergency system, including the telephones required to summon assistance. In one incident notification of the fire brigade was delayed because the telephone circuits had failed.

There are a number of precautions which may be taken against cable fires. Cables may be segregated from other services and the different types of cable, particularly power and instrument cables, may be segregated. The criticality of all cable runs should be assessed and an appropriate degree of protection provided for each. The hazard of fire spread through cable ducts to vulnerable points should be minimized.

Fire protection for petrochemical plants and oil platforms has been discussed by Corona (1984) who states that a fire protection system for cabling should be based on a hydrocarbon pool fire at not less than 1800°F (980°C), should maintain the cable temperature within operating limits, which on ordinary PVC cables is usually below 300°F (149°C), and should do this for a time period long enough for emergency operation of equipment, which might be of the order of 20 min. Another time period often quoted for cable protection in petrochemical plants is 15 min.

Use may be made of fire resistant cabling. If reliance is placed on such fire resistance, it is important to select the right cable. This is partly a matter of specifying the degree of fire resistance required and partly one of assessing whether a given cable meets this specification. Several workers have emphasized that any tests conducted should be on a sufficiently large scale as to be realistic.

The problem of fire testing of cables and of standard fires for such tests is discussed by Schultz (1986). He describes the protection of cables using a ceramic-refractory blanket held by steel bands.

Spillage of oil into the cable duct may be minimized by sealing the cable holes. Protection against the spread of fire through the duct may be provided by fire stops. The design of such stops is discussed by Anon. (1980 LPB 41, p. 5).

Smoke detection devices may be used to give early warning. The cable duct may be designed to give access for firefighting with a maximum distance between access points. Points may be provided to receive high expansion foam from mobile generators.

Use is also made of sprinklers and other fixed fire protection systems. The application of such protection to electrical cables is a specialist matter.

Protection against cable fires is required during construction as well as during operation. There have been several serious cable fires during the construction phase.

Accounts of case histories of cable fires have been given by the FPA (1974a) and by Anon. (1980 LPB 41, p. 5).

16.11.5 Storage tank fires

Storage tank fires are not infrequent in process plant and other sites. The quantities of material involved, and consequently the losses, tend to be large. The problem is discussed in *Fire Protection Manual for HydrocarbonProcessing Plants* (Vervalin, 1964a, 1973a), in *Tank Fires* (OIA, 1974 Loss Inf. Bull. 400–1) and by a number of other authors (e.g. Burgoyne, 1950; Kletz, 1971).

Storage is discussed in Chapter 22, where the main types of storage tank are described. The larger storage tanks are atmospheric tanks of the fixed roof or floating roof types. The main materials held in atmospheric storage tanks are flammable liquids.

The scale of the fire/explosion on a storage tank installation can be very large. A single 'jumbo' storage tank in the petroleum industry may have a capacity of 500,000 barrels or more. In many tank fires more than one tank is involved.

The frequency of fires/explosions in fixed roof tanks containing volatile hydrocarbons has been estimated by Kletz (1971) as once in 833 tank-years. The estimated frequency for tanks holding non-hydrocarbons is one-tenth of this value. Comparable data for floating roof tanks are not given.

It is also apparent that, in addition to accidents involving fire/explosion, there are also near misses in which, for example, tanks are buckled but do not rupture.

In some cases there is a fire/explosion of a flammable mixture in the vapour space of the tank. In others a vapour cloud forms outside the tank and the ignites. Other cases are fire following liquid slopover or liquid spillage due to tank rupture.

One of the most frequent causes of tank fires/explosions is overfilling of the tank. This is usually due to defects in operating procedures, failure of instrumentation and/or operator error. Failure of ancillary equipment, such as pumps, and strikes of lightning are other common causes.

If there is an initial explosion which blows the tank roof off, a fire may be established in the tank and may burn there without spreading.

If there is a spillage of liquid into the bund around the tank, due to overfilling, a vapour cloud may form, find a source of ignition, and flash back. This may ignite the liquid leaving the tank and/or that in the bund.

If there is a spillage of liquid in the bund from ancillary equipment, such as a pump, and the spillage again ignites, a general fire may occur. Initially at least there may be no fire in the tank.

Once a fire is established, it frequently causes failures which feed the fire. Thus a fire on equipment such as pumps or pipework within the bund can cause a pipe failure which then results in spillage of the tank contents into the bund.

Experience shows that pipework exposed to a strong fire in a bund usually fails within about 10–15 min. and heat radiation from a tank fire may cause other nearby tanks to fail.

There are a number of measures which can be taken to reduce the risk of tank fires. Much can be done by good plant layout. There should be generous spacing between tanks to reduce the risk from radiant heat. Tanks should be provided with water spray systems which drench them in water and keep them cool. To some extent there is a trade-off which can be made between these two measures.

Frequently the fire engulfs all tanks in the bund. It is highly desirable, therefore to have a separate bund for each tank, particularly for large tanks.

Pipework inside bunds should be kept to a minimum with as few flanges, valves and other fittings as possible. Pipework can be buried, but then tends to corrode. Pumps should be installed outside bunds, both because they are sources of leakage and of ignition, and because they are often needed to fight the fire by pumping out the tank.

Measures should be taken to prevent overfilling of the tank. A high level alarm is normally a minimum requirement and often a high level trip is desirable. This instrumentation should be backed up by appropriate operating procedures.

If a fire occurs in a tank, the water sprays should be activated to protect the other nearby tanks. It is often appropriate to pump down to a suitable receiver the tank which is on fire, but it should be borne in mind that in the later stages of this operation the liquid may be very hot and may create a hazard at the receiver.

Tank fires are fought with water and/or foam. The quantities required are very large. It is essential, therefore, that the fire water mains be adequately sized, both for the fire pumps and for the drench water sprays. The tank farm should not be a backwater in this respect. Similarly, there should be a substantial storage of foam.

A tank fire can be difficult to fight for several reasons. The conditions favour the formation of vapour clouds. Metal surfaces become and remain very hot. In consequence, there is frequently flashback of fire to an area where it had appeared to have been extinguished.

Some atmospheric storage tanks contain refrigerated liquefied flammable gas. There is much less experience, however, with fires on such tanks.

Liquefied flammable gases are also stored in pressure vessels. Again, at a pressure storage vessel overfilling is one of the most frequent causes of fire. A fire which develops around a storage vessel containing a liquid under pressure can cause the pressure in the vessel to build up so that there is an explosion.

It is normal practice to provide a pressure relief valve on such vessels and it is essential for it to be properly designed and maintained, although this does not fully protect against the hazard. If the vessel is overheated, it. may rupture even though the relief valve has operated. The occurrence of boiling liquid expanding vapour explosions (BI.EVEs) on pressure storage vessels is described in Chapter 17.

Measures should be taken to minimize fire and explosion on pressure storage vessels. The ground underneath the vessel should be sloped away to prevent accumulation of flammable liquid. There should be water sprays and/or fireproof thermal insulation to give protection against fire exposure and there should be safeguards against overfilling.

16.11.6 Major fire events

In addition to the various types of process plant fire just described, there are a number of major fire events to which process plants are vulnerable. These are (1) vapour cloud fires, (2) fireballs, (3) pool fires, (4) jet flames and (5) engulfing fires. These are described in Sections 16.14, 16.15, 16.17, 16.19 and 16.20, respectively.

16.11.7 CCPS Fire and Explosion Model Guidelines

Guidance on the modelling of such major fire events is given in the CCPS *Guidelines for Evaluating the Characteristics of Vapor Cloud Explosions, Flash Fires and BLEVEs* (1994/15) (the CCPS *Fire and Explosion Model Guidelines*).

The *Guidelines* deal with (1) vapour cloud, or flash, fires, (2) vapour cloud explosions and (3) BLEVEs. They also cover (4) fireballs, which are treated as an aspect of BLEVEs. For each of the three phenomena the *Guidelines* outline basic physical concepts, experimental work and available models and correlations for the phenomena themselves and for damage and injury, and give sample problems. They also contain a set of case histories.

Vapour cloud fires and fireballs are treated here in Sections 16.14 and 16.15, respectively and vapour cloud explosions and BLEVEs are discussed in Chapter 17.

16.12 Flames

An important factor in the consideration of both the causes and the effects of fires/explosions in process plants is the behaviour of flames. The study of combustion and flames is a specialist matter and only a few selected features are mentioned here. It is emphasized, however, that this discipline makes a very large contribution to loss prevention.

Accounts of combustion and flames are given in *Flames* (Gaydon and Wolfhard, 1953–) and *Combustion, Flames and Explosion of Gases* (B. Lewis and von Elbe, 1961), in the other texts quoted in Section 16.3 and in the series *International Symposia on Combustion* (Combustion Institute, 1928–).

Certain aspects of the behaviour of flames inside plant have already been considered. These include flames in vessels, flames in pipes and cool flames, which were discussed in Section 16.3. The present section is concerned with flames in the open.

Flames outside the plant include those of:

(1) flash fires;
(2) pool fires;
(3) fireballs;
(4) flares;
(5) jet flames;
(6) fire engulfed vessels.

These are considered in the following sections.

In general, a complete model of a flame will include information on:

(1) flame shape and dimensions;
(2) heat release rate;
(3) fraction of heat radiated;
(4) flame temperature;
(5) flame emissivity;
(6) surface emissive power;
(7) view factor.

However, it is often not necessary to have full information on all of these. If the flame can be treated as a point source,

it may be characterized by the heat release rate and the fraction of heat radiated and the simple point source view factor used. The other methods require the flame dimensions and may utilize a more accurate view factor. There are three approaches. One is to use the flame dimensions in combination with the heat release rate and the fraction of heat radiated, which together, in effect, give the surface emission. Another is to use the flame dimensions in combination with the flame temperature and flame emissivity, which together again give the surface emission. The third is to use the flame dimensions and the surface emissive power.

16.13 Radiant Heat Transfer

In many process plant fires the dominant mode of heat transfer is radiation. An account is given here of radiant heat transfer relevant in the present context, but it is emphasized that this is no more than an outline treatment of a rather complex topic. Standard texts on radiant heat transfer include *Radiation Heat Transfer* (Sparrow and Cess, 1966, 1978), *Thermal Radiation Heat Transfer* (Siegel and Howell, 1991) and *Radiative Heat Transfer* (Modest, 1993), and, for process plant, *Heat Transmission* (McAdams, 1954) and *Process Heat Transfer* (D.Q. Kern, 1950).

16.13.1 Thermal radiation

Radiant energy may be conceived as being transmitted either as electromagnetic waves or as photons. It travels at the speed of light and may be characterized either by its frequency v or by its wavelength λ, which are related by the equation

$$c = \lambda v \qquad [16.13.1]$$

with

$$c = c_o/n \qquad [16.13.2]$$

where c is the velocity of light, n is the refractive index and the subscript o refers to vacuum conditions.

The electromagnetic spectrum ranges from γ-rays (wavelength $\approx 10^{-12}$ m) to radio waves (wavelength $\approx 10 - 10^2$ m). The range of wavelengths for thermal radiation is approximately 0.3–50 μm. As shown in Figure 16.76, this range spans the infrared and visible ranges and part of the ultraviolet range.

16.13.2 Black body radiation

It has been shown by Planck from thermodynamic considerations that there is a maximum amount of radiant energy of a given frequency which can be emitted at a given temperature. An object which emits this quantity is termed a black body and the quantity itself the monochromatic, or spectral, emissive power for black body radiation. The fundamental form of Planck's law is

$$e_{bv} = \frac{2\pi h v^3 n^2}{c_o^2[\exp(hv/kT) - 1]} \qquad [16.13.3]$$

where e_{bv} is the monochromatic emissive power for a black body, h is Planck's constant and k is Boltzmann's constant.

On the assumption that the refractive index is independent of frequency

$$v = c_o/n\lambda \qquad [16.13.4]$$

Equation 16.13.3 may be reformulated in terms of the wavelength λ using the relation

$$e_{bv}\,dv = -e_{b\lambda}\,d\lambda \qquad [16.13.5]$$

which yields the equation

$$e_{b\lambda} = \frac{2\pi h c_o^2}{n^2\lambda^5[\exp(hc_o/n\lambda kT) - 1]} \qquad [16.13.6]$$

or

$$e_{b\lambda} = \frac{c_1}{n^2\lambda^5[\exp(c_2/n\lambda T) - 1]} \qquad [16.13.7]$$

with

$$c_1 = 2\pi h c_o^2 \qquad [16.13.8a]$$

$$c_2 = hc_o/k \qquad [16.13.8b]$$

Equation 16.13.7 may be further recast in the form

$$\frac{e_{b\lambda}}{\sigma n^3 T^5} = \frac{c_1/\sigma}{(n\lambda T)^5[\exp(c_2/n\lambda T) - 1]} \qquad [16.13.9]$$

where σ is the Stefan–Boltzmann constant. The quantity on the right-hand side of Equation 16.13.9 is a function solely of $n\lambda T$. The form of this function is shown in Figure 16.77.

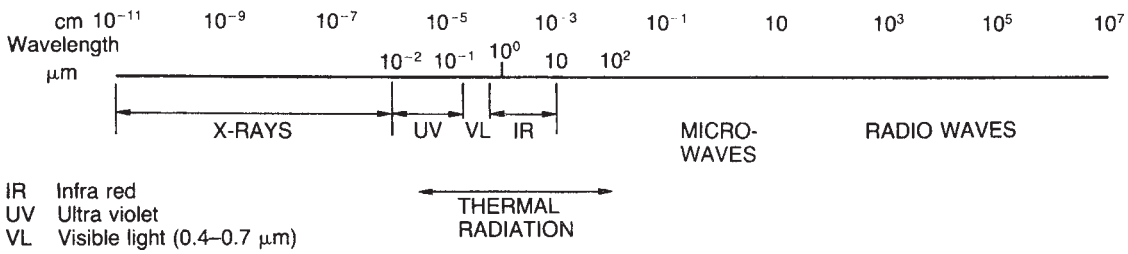


Figure 16.76 *The electromagnetic spectrum*

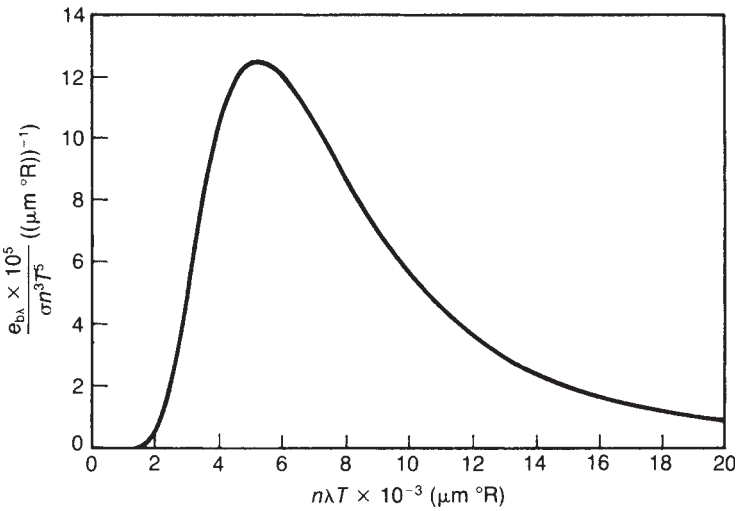


Figure 16.77 *Emissive power of a black body (Sparrow and Cess, 1978) (Courtesy of Brooks/Cole Publishers)*

The principal black body radiation constants are:

Speed of light in vacuum $c_o = 2.9979 \times 10^8$ m/s
Planck's constant $h = 6.626 \times 10^{-34}$ J s
Boltzmann's constant $k = 1.381 \times 10^{-23}$ J/K
Stefan–Boltzmann constant $\sigma = 5.6705 \times 10^{-8}$ W/m^2 K^4
First radiation constant $c_1 = 3.472 \times 10^{-16}$ W m^2
Second radiation constant $c_2 = 0.01439$ m K

The total emissive power of a black body is thus

$$e_b = \int_0^\infty e_{bv}\, dv \qquad [16.13.10]$$

Then from Equation 16.13.3

$$e_b = n^2 \frac{(2\pi k^4) T^4}{c_o^2 h^3} \int_0^\infty \frac{x^3}{e^x - 1} dx \qquad [16.13.11]$$

$$= n^2 \frac{(2\pi k^4) T^4}{c_o^2 h^3} \frac{\pi}{15} \qquad [16.13.12]$$

$$= n^2 \sigma T^4 \qquad [16.13.13]$$

Equation 16.13.13 is the Stefan–Boltzmann equation.

The refractive index n in Equation 16.13.13 is conventionally taken as unity. This is the value in most practical applications involving transmission of radiation through a gas. The equation then reduces to

$$e_b = \sigma T^4 \qquad [16.13.14]$$

16.13.3 Non-black and gray body radiation

For a non-black body the monochromatic emissive power e_λ is

$$e_\lambda = \epsilon_\lambda e_{b\lambda} \qquad [16.13.15]$$

where ϵ_λ is the monochromatic hemispherical emissivity.

It is also necessary to consider the absorption of radiation. If radiation incident on the surface is H_λ, the amount absorbed is $\alpha_\lambda H_\lambda$ and that reflected is $\rho_\lambda H_\lambda$, where α_λ is the monochromatic hemispherical absorptivity and ρ_λ the monochromatic hemispherical reflectivity. For an opaque surface

$$\alpha_\lambda + \rho_\lambda = 1 \qquad [16.13.16]$$

It has been shown that for a system in thermodynamic equilibrium that

$$\epsilon_\lambda = \alpha_\lambda \qquad [16.13.17]$$

Equation 16.13.17 is Kirchhoff's law.

For a black body ϵ_λ is unity and so therefore is α_λ. Thus a black body is also a perfect absorber as well as a perfect emitter of radiation.

The total emissive power e of a non-black body is

$$e = \int_0^\infty e_\lambda\, d\lambda \qquad [16.13.18a]$$

$$= \int_0^\infty \epsilon_\lambda e_{b\lambda}\, d\lambda \qquad [16.13.18b]$$

The overall emissivity ϵ is

$$\epsilon = e/e_b \qquad [16.13.19]$$

$$= \frac{\int_0^\infty \epsilon_\lambda e_{b\lambda}\, d\lambda}{\int_0^\infty e_{b\lambda} d\lambda} \qquad [16.13.20]$$

$$\alpha = \frac{\int_0^\infty \alpha_\lambda H_\lambda\, d_\lambda}{\int_0^\infty H_\lambda\, d\lambda} \qquad [16.13.21]$$

where H_λ is the hemispherically incident radiation per unit area per unit time.

The emissivity ϵ is a function of the surface. The absorptivity α, on the other hand, is a function not only of the surface but also of the nature of the incident radiation.

There are several cases for which a simple relation between ϵ and α applies. The most important of these is the

gray body. For a gray body ϵ_λ and α_λ are independent of wavelength λ and hence

$$\epsilon_\lambda = \epsilon \quad [16.13.22]$$

$$\alpha_\lambda = \alpha \quad [16.13.23]$$

Then from Kirchhoff's law as given in Equation 16.13.17

$$\alpha = \epsilon \quad [16.13.24]$$

In engineering applications the gray body assumption is frequently made.

Other cases where a simple relation holds between ϵ and α are described by Sparrow and Cess (1966, 1978).

For gray body radiation from an opaque material

$$\alpha + \rho = 1 \quad [16.13.25]$$

From Equations 16.13.14 and 16.13.19 the emissive power of a gray body is

$$\mathrm{e} = \epsilon\sigma T^4 \quad [16.13.26]$$

The total radiation from a gray body is given by the radiosity B, which is the sum of the radiation emitted by the surface and that reflected from it

$$B = \epsilon\sigma T^4 + \rho H \quad [16.13.27]$$

Radiation from a surface may be uniform in all directions or it may be directional. The two situations are termed diffuse and specular radiation, respectively. Surfaces of interest in engineering applications usually approximate to diffuse surfaces and the assumption is usually made that the radiation is diffuse.

In general, a surface tends to be diffuse at short wavelengths and specular at long wavelengths. Roughness increases the diffuseness of the surface.

16.13.4 Participating media

The radiation transmitted may be affected by the medium through which it passes. Radiation can suffer attenuation due to absorption and scattering. A medium which causes such attenuation is termed a participating medium.

Most monatomic and diatomic gases are non-participating media, except when at high temperature and/or when dissociated. Dry air is therefore also effectively a non-participating medium, but air containing water and air or gas containing water and carbon dioxide are participating media.

The attenuation of the radiation with distance x may be expressed by the relation

$$I_\lambda = I_{o\lambda} \exp(-\beta_\lambda x) \quad [16.13.28]$$

with

$$\beta_\lambda = \kappa_\lambda + \gamma_\lambda \quad [16.13.29]$$

where I_λ is the monochromatic radiation intensity, $I_{o\lambda}$ is the initial monochromatic radiation intensity, β_λ is the monochromatic extinction coefficient, κ_λ is the monochromatic absorption coefficient and γ_λ is the monochromatic scattering coefficient.

An overall absorption coefficient κ may be defined by the relation

$$k = \frac{\int_0^\infty \kappa_\lambda \int_{4\pi} I_\lambda \mathrm{d}\omega \mathrm{d}\lambda}{\int_{4\pi} I \mathrm{d}\omega} \quad [16.13.30]$$

and a similar relation applies for the overall scattering coefficient γ.

16.13.5 Radiant exchange

The intensity of radiation i from a radiation source, as shown in Figure 16.78, is

$$i = \frac{\mathrm{d}\Phi}{\mathrm{d}\omega \cos\theta} \quad [16.13.31]$$

where Φ is the radiant flux contained within the solid angle $\mathrm{d}\omega$ and θ is the angle between the direction of this flux and the normal. For uniform, or diffuse, radiation

$$i = \Phi/\pi \quad [16.13.32]$$

A similar expression applies for radiosity

$$i = B/\pi \quad [16.13.33]$$

For the general situation of an arbitrary configuration with radiant transfer between two differential surfaces $\mathrm{d}A_i$ and $\mathrm{d}A_j$, as shown in Figure 16.79, the treatment is as follows. Noting that r is the distance between the surfaces and that $\mathrm{d}\omega$ is the solid angle subtended by $\mathrm{d}A_j$ when viewed from $\mathrm{d}A_i$ and that it is given by

$$\mathrm{d}\omega = \mathrm{d}A_j \cos\beta_j / r^2 \quad [16.13.34]$$

and that from Equation 16.13.33

$$i_i = B_i/\pi \quad [16.13.35]$$

the radiation leaving $\mathrm{d}A_i$ in the direction of $\mathrm{d}A_j$ may be expressed as

$$= i_i \, \mathrm{d}A_i \cos\beta_i \, \mathrm{d}\omega \quad [16.13.36]$$

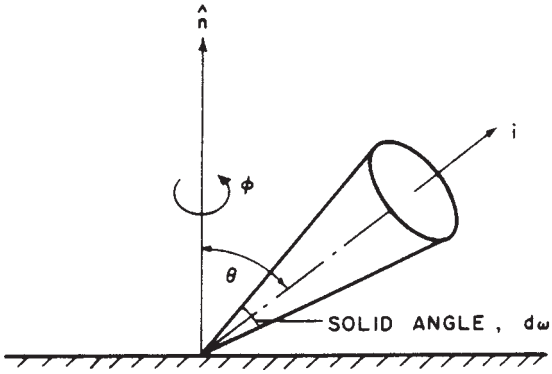


Figure 16.78 *Intensity of radiation (Sparrow and Cess, 1978) (Courtesy of Brooks/Cole Publishers)*

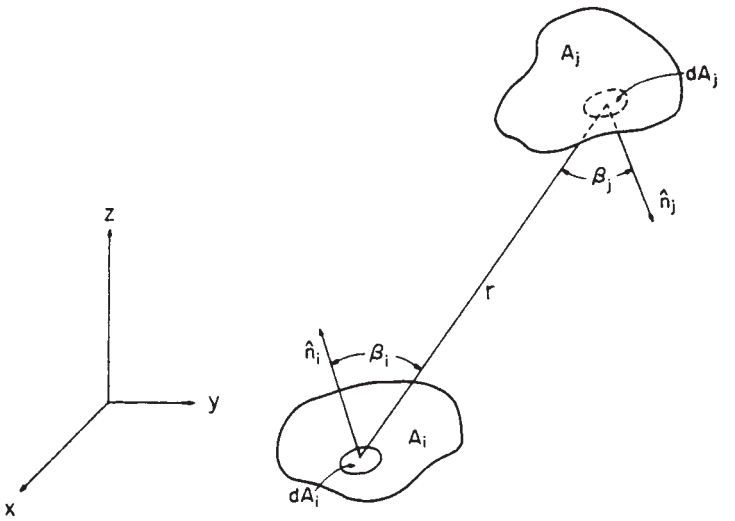


Figure 16.79 *Radiant interchange between two differential surfaces (Sparrow and Cess, 1978) (Courtesy of Brooks/ Cole Publishers)*

or as

$$= B_i \cos\beta_i \cos\beta_j \, dA_i \, dA_j / \pi r^2 \qquad [16.13.37]$$

An angle factor $dF_{dA_i - dA_j}$ may be defined as the fraction of the radiation $B_i \, dA_i$ which is incident on dA_j. Then

$$dF_{dA_i - dA_j} = \cos\beta_i \cos\beta_j dA_j / \pi r^2 \qquad [16.13.38]$$

Similarly, an angle factor $F_{A_1 - A_2}$ may be defined for the radiation from finite surface A_1 to finite surface A_2. Angle factors are discussed in greater detail below.

It should be noted that such angle factors only take account of radiation from a source to a target and not of radiation back from the target to the source. In the applications of interest here, however, the latter is usually negligible.

Where it is necessary to consider radiation back from the target, an emissivity factor F_ϵ may be introduced. Then the product of the angle factor F_A and the emissivity factor F_ϵ is the overall interchange factor F_o

$$F_o = F_A F_\epsilon \qquad [16.13.39]$$

The application of these factors is described below.

There are a number of configurations which occur in engineering and for which simple solutions of the radiant flux are available. One is the case where a body with arbitrary radiation properties and at temperature T_1 is located inside a completely enclosed space with wall temperature T_2 such that black body radiation obtains. Then the net radiant heat transfer is

$$Q = A(\epsilon\sigma T_1^4 - \alpha\sigma T_2^4) \qquad [16.13.40]$$

For gray body conditions, Equation 16.13.40 reduces to

$$Q = A\epsilon\sigma(T_1^4 - T_2^4) \qquad [16.13.41]$$

Another case is where radiation occurs between black bodies consisting of two large parallel planes 1 and 2. For this case

$$Q = A\sigma(T_1^4 - T_2^4) \qquad [16.13.42]$$

For gray body conditions, following D.Q. Kern (1950), the radiant heat fluxes are

	Hot plane 1	*Cold plane 2*
Radiated	$e_1(=\epsilon_1\sigma T_1^4)$	$e_2(=\epsilon_2\sigma T_2^4)$
Returned	$e_1(1-\epsilon_2)$	$e_2(1-\epsilon_1)$
Radiated	$e_1(1-\epsilon_2)\,(1-\epsilon_1)$	$e_2(1-\epsilon_1)\,(1-\epsilon_2)$
Returned	$e_1(1-\epsilon_2)\,(1-\epsilon_1)\,(1-\epsilon_2)$	$e_2(1-\epsilon_1)\,(1-\epsilon_2)\,(1-\epsilon_1)$

Summation of these terms ε for the net radiant flux gives a series whose solution is

$$Q = A\frac{1}{(1/\epsilon_1) + (1/\epsilon_2) - 1}\sigma(T_1^4 - T_2^4) \qquad [16.13.43]$$

which reduces to Equation 16.13.42 for $\epsilon_1 = \epsilon_2 = 1$.

Equations 16.13.41 and 16.13.43 may be reformulated in terms of the angle and emissivity factors to give

$$Q = AF_A F_\epsilon \sigma(T_1^4 - T_2^4) \qquad [16.13.44]$$

where for Equation 16.13.41 $F_A = 1$ and $F_\epsilon = \epsilon$, and for Equation 16.13.43 $F_A = 1$ and

$$F_\epsilon = \frac{1}{(1/\epsilon_1) + (1/\epsilon_2) - 1} \qquad [16.13.45]$$

16.13.6 Heat radiation

The main application of radiant heat transfer in the present context is the estimation of the heat radiated from flames in accident conditions. Accounts of flame radiation are given in the standard texts on radiant heat transfer. A review relevant to process plant fires has been made by Considine (1984 SRD R297).

The radiant heat flux emitted by a flame in such a situation is given by the relation

$$E = \epsilon\sigma T^4 \qquad [16.13.46]$$

$$= \frac{Q_r}{A_f} \qquad [16.13.47]$$

with

$$Q_r = F_r Q_c \qquad [16.13.48]$$

where A_f is the surface area of the flame, E its surface emissive power, F_r the fraction of het released which is radiated, Q_c the total heat released by combustion and Q_r the total heat radiated.

The heat received by the target is

$$I = \alpha\tau FE \qquad [16.13.49]$$

where F is the view factor, $I\alpha\tau$ the heat radition intensity received by the target and τ is the atmospheric transmissivity.

These equations are used in conjunction with relations for the geometrty of the flame and for the heat radiated per unit area of the flame surface.

There are alternative approaches to the estimation of the heat radiated Q_r. One is to work in terms of the flame temperature and emissivity. Another is to use empirical values of the surface emissivity of the flame envelope. A third is to calculate the total heat generated and to apply an factor F_r for the franction of heat radiated.

16.13.7 Heat radiation: flame emissivity

If the first, and most fundamental, of these approaches is adopted, it is necessary to estimate the emissivity of the flame. The emissivity of a flame depends on the type of fuel and on the nature of the combustion. The heat radiated from a flame is emitted by gases, in particular the products of combustion CO_2, H_2O, N_2, CO and O_2 and by carbon particles, or soot. The former are band emitters while the later emit over a continuous range. A flame in which the radiation is emitted solely from the gaseous constituents is termed non-luminous and one in which there is soot is termed luminous.

CO_2 and H_2O

The principal gaseous contributors to flame emissivity are carbon dioxide and water vapour. The emissivity ϵ_g of a non-luminous flame may be estimated from that of these gases using the relation

$$\epsilon_g = \epsilon_c + \epsilon_w - \Delta\epsilon \qquad [16.13.50]$$

where ϵ_c and ϵ_w are the emissivities of CO_2 and H_2O, respectively, and $\Delta\epsilon$ is a correction term which allows for the overlap between the bands for these two gases.

Flame emissivity is required for many furnace calculations and there is a standard method of estimating it. The method is as follows. The emissivity for each gas species is a function of the partial product path length

$$e_c = f(p_c L) \qquad [16.13.51a]$$

$$\epsilon_w = f(p_w L) \qquad [16.13.51b]$$

where L is the mean path length, p_c is the partial pressure of CO_2 and p_w is the partial pressure of H_2O.

In process calculations, it is necessary to make a correction to the partial pressure path length products for carbon dioxide and water if the total pressure is other than atmospheric. Plots for the correction factors C_c and C_w are given in standard texts. These corrections are not required for flames at atmospheric pressure, which are those of prime interest here. The mean beam length L is considered below.

The correction term $\Delta\epsilon$ is a function of the ratio of the partial pressure of water to the sum that of the two gases

$$\Delta\epsilon = f\left(\frac{p_w}{p_c + p_w}\right) \qquad [16.13.52]$$

Graphs for the determination of the two gas emissivities ϵ_w and ϵ_c and the correction $\Delta\epsilon$ given by Hottel (1954), from the experiments of Hottel and Mangelsdorf (1935) and Hottel and Smith (1935) for carbon dioxide and the correlation of Hottel and Egbert (1942) on water vapour are shown in Figure 16.80.

Soot

An account of the properties of soot and of its occurrence in different types of flame is given by H.G. Wagner (1979). Soot usually forms in flames in the temperature range 1000–2500°C. The total amount of soot is only a small fraction of the carbon present. Theoretically, from the stoichiometry for a hydrocarbon, soot formation should start when the carbon/oxygen ratio (C/O) reaches unity, but in practice it starts around $C/O \approx 0.5$. In work on gaseous diffusion flames on burners it has been found that the soot concentration is a maximum along the axis, where measurements by Kunugi and Jinno (1967) gave concentrations of 3×10^2 particles/cm^3, or 10^{-7}–10^{-6} g/cm^3. In their classic work on turbulent diffusion flames, Dalzell, Williams and Hottel (1970) found axial concentrations of soot of 10^{-6}g/cm^3.

The characterization of the emissivity of soot is somewhat complex. The emissivity is a function of the wavelength, and the following expression has been, suggested

$$\epsilon_{s\lambda} = k_1/\lambda^{k_2} \qquad [16.13.53]$$

where $\epsilon_{s\lambda}$ is the emissivity of soot at wavelength λ, and k_1 and k_2 are constants. The value of the constant k_2 is of the order of unity.

As described by Markstein (1974), highly sooty flames satisfy gray gas models. This implies that the radiation is concentrated in a relatively narrow waveband, which in turn indicates that the emitting soot particles are distributed over a narrow temperature range.

A relation widely quoted for the emissivity of soot from non-gray analysis is

$$\epsilon_s = 1 - \frac{15}{\pi^4}\psi^{(3)}(1 + X) \qquad [16.13.54]$$

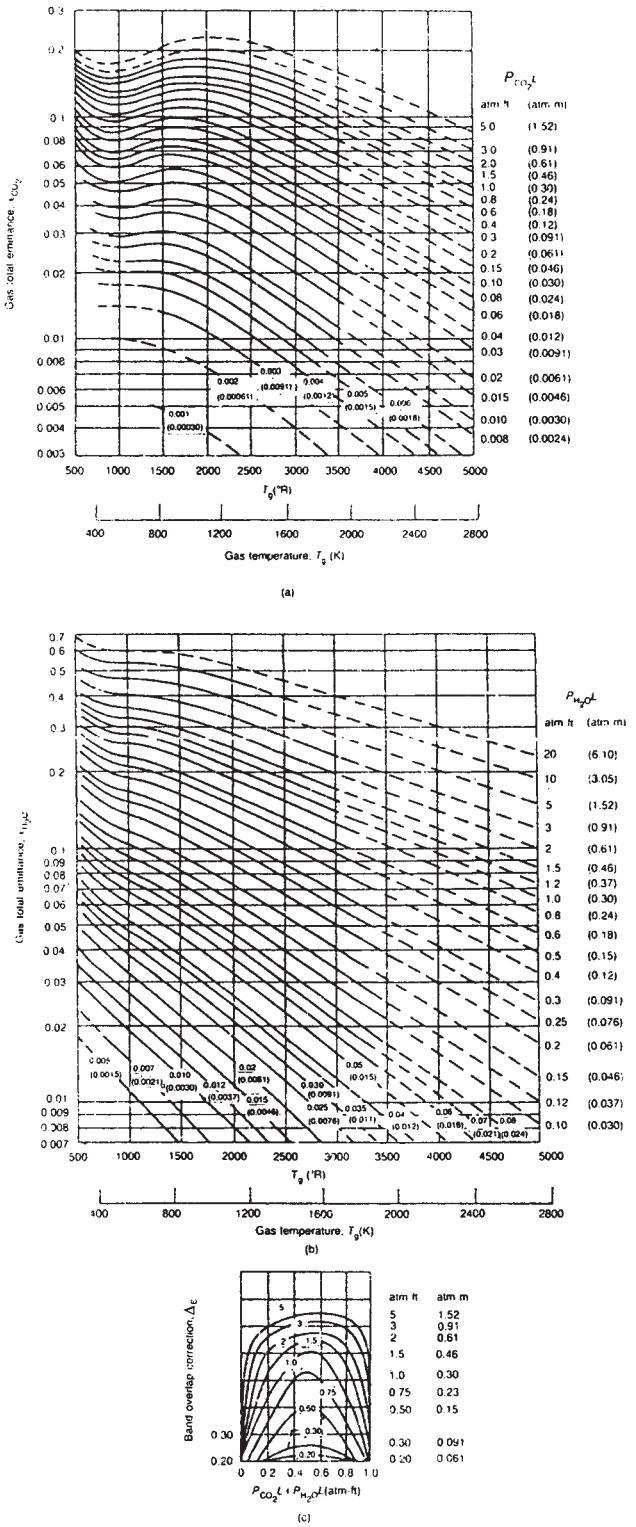


Figure 16.80 *Emissivity of carbon dioxide and water vapour (Siegel and Howell, 1991): (a) carbon dioxide; (b) water vapour and (c) overlap correction term (Courtesy of Hemisphere Publishing Corporation)*

with

$$X = \frac{cLT}{c_2} \qquad [16.13.55]$$

$$c = 36\pi f_v \frac{n^2 k}{[n^2 - (nk)^2 + 2]^2 + 4(nk)^2} \qquad [16.13.56]$$

where c is the effective soot concentration (volume fraction), f_v is the volume fraction of soot particles, L is the path length, T is the absolute temperature, X is a parameter and $\psi^{(3)}$ is the pentagamma function; c_2 is the Planck second constant, and k and n are the infrared-average optical constants of soot particles. The penta-gamma function is given by Abramowitz and Stegun (1974).

It has been shown by Dalzell and Sarofim (1969) that an alternative, and more convenient, equation which gives results similar to Equation 16.13.54 is

$$\epsilon_s = 1 - \frac{1}{(1+Y)^4} \qquad [16.13.57]$$

with

$$Y = \frac{k_3 CLT}{c_2} \qquad [16.13.58]$$

where C is the volume fraction of soot particles, Y is a parameter and k_3 is a constant. The value of the constant k_3 is discussed by Siegel and Howell who use a value $k_3 = 5.0$ in some of their calculations.

A method for the emissivity of soot has been given by Yuen and Tien (1977) based on a gray analysis. They take

$$\epsilon_s = 1 - \exp(-\kappa L) \qquad [16.13.59]$$

with

$$\kappa = 3.6\frac{cT}{c_2} \qquad [16.13.60]$$

where T_m is the mean absolute temperature of the flame and κ is a parameter. The constant 3.6 is that required to ensure that Equation 16.13.59 yields results similar to those given by Equation 16.13.54.

These authors give a tabulation of values of these variables for a number of gaseous fuels, which includes:

Gas	*C/H*	c	κ (cm^{-1})	T_m (K)
Methane	0.25	2.00×10^{-5}	0.0645	1289
Ethane	0.33	1.60×10^{-5}	0.0639	1590
Propane	0.38	3.41×10^{-5}	0.1332	1561
n-Butane	0.40	3.12×10^{-5}	0.1259	1612
Ethylene	0.50	2.76×10^{-5}	0.1192	1722
Propylene	0.50	6.46×10^{-5}	0.2407	1490

Combined CO_2, H_2O and soot

For the emissivity ϵ_m of a gray gas containing CO_2, H_2O and soot, Yuen and Tien use the method just described for the emissivity ϵ_s of soot together with the relation

$$\epsilon_m = \epsilon_s + \epsilon_g(1 - \epsilon_s) \qquad [16.13.61]$$

A method for the estimation of the emissivity of a gray gas containing CO_2, H_2O and soot, i.e. a gas–soot mixture, has been described by P.B. Taylor and Foster (1974, 1975). These authors express the emissivity ϵ_m of such a mixture as

$$\epsilon_m = \sum_{n=1}^{3} a_{m,n}[1 - \exp(-K_{m,n}L)] \qquad [16.13.62]$$

with

$$K_{m,n} = \exp(q_{1,n} + q_{2,n}c) \qquad c > 0.0005 \qquad [16.13.63]$$

except that

$$K_{m,1} = 0.09 + 500c \qquad c \le 0.0005 \qquad [16.13.64]$$

and with

$$a_{m,n} = r_{1,n} + r_{2,n}T \qquad n = 1 \text{ or } 2 \qquad [16.13.65]$$

$$a_{m,n} = 1 - (a_{m,1} + a_{m,2}) \qquad n = 3 \qquad [16.13.66]$$

where c is the concentration of soot (kg/m^3), L is the path length (m) and T is the absolute temperature (K); $a_{m,n}$ is a weighting coefficient, $K_{m,n}$ is an absorption coefficient and $q_{1,n}$, $q_{2,n}$, $r_{1,n}$ and $r_{2,n}$ are coefficients; subscript m denotes a mixture and n denotes the component of the mixture.

These relations are applicable to the combustion of oil ($p_w/p_c = 1$) and gas ($p_w/p_c = 2$) at atmospheric pressure with $p_c = 0.1$ atm over the temperature range 1400–2400 K for path lengths between 0.01 and 10 m.

The values given for the coefficients are:

	$p_w/p_c = 1$		$p_w/p_c = 2$	
n	$q_{1,n}$	$q_{2,n}$	$q_{1,n}$	$q_{2,n}$
1	−1.252	558.55	−1.274	590.82
2	−0.221	665.38	−0.233	672.04
3	2.608	839.62	2.452	692.61

and

Soot concentration, c (kg/m^3)	n	$p_w/p_c = 1$		$p_w/p_c = 2$	
		$r_{1,n}$	$r_{2,n}$	$r_{1,n}$	$r_{2,n}$
0.0001	1	0.8119	−0.0000355	0.7191	−0.0000336
	2	0.0280	0.0001013	0.0804	0.0001131
0.0005	1	0.5478	−0.0001869	0.6123	−0.0002489
	2	0.3846	0.0002071	0.2688	0.0002901
0.001	1	0.5478	−0.0001869	0.6123	−0.0002489
	2	0.3846	0.0002071	0.2688	0.0002901

Further values are given by the authors.

Mean beam length

In his treatment of radiant heat transfer Hottel (1954) introduced the concept of the mean beam path length L, generally known as the mean beam length or path length, as a means of taking into account the geometry of the situation considered. He states: 'The mean beam length L may be thought of as the radius of a gas hemisphere which will radiate to unit area at the center of its base the same as

the average radiation, over A, from the actual gas mass', where A is the area of interest.

A distinction, amplified below, is made between flames which are optically thick and those which are optically thin. If the flame is optically thin, and thus $p_g L \approx 0$, the corresponding mean beam length L_o is equal to four times the mean hydraulic radius

$$L_o = 4V/A \qquad [16.13.67]$$

where A is the area of the enclosure, L_o is the mean beam length for the optically thin condition, p_g is the partial pressure of the radiating gases and V is the volume of the enclosure.

Thus, for example, for a sphere

$$L_o = \frac{4\pi D^3/6}{\pi D^2} = \frac{2}{3}D \qquad [16.13.68]$$

where D is the diameter of the sphere. For a long, thin cylinder

$$L_o = \frac{4\pi D^2/4}{\pi D} = D \qquad [16.13.69]$$

where D is the diameter of the cylinder.

For a gas which is optically thick, Equation 16.13.67 is modified to give

$$L = C_{bl} L_o \qquad [16.13.70]$$

where C_{bl} is a beam length correction factor. It is found that, as good approximation,

$$C_{bl} \approx 0.9 \qquad [16.13.71]$$

Then from Equations 16.13.67, 16.13.70 and 16.13.71

$$L \approx 0.9\frac{4V}{A} \qquad [16.13.72]$$

Following Hottel's original tabulation, values of the mean beam length L_o and of the beam length correction factor C_{bl}, more accurate than that of Equation 16.13.71, are listed for various geometries by Siegel and Howell (1991). Their results include:

System geometry	*Optical thickness tending to zero, L_o*	*Finite optical thickness, L*	*Correction factor, C_{bl}*
1. Sphere radiating to its surface	$2D/3$	$0.65D$	0.97
2. Cylinder with a height equal to twice its diameter radiating to the entire surface	$0.8D$	$0.73D$	0.91
3. Cube radiating to a face	$2X/3$	$0.6X$	0.90

where D is the diameter of the sphere or cylinder and X is the length of a side of the cube.

Optical thickness

Another aspect of effective flame emissivity is the extinction of radiation within the flame itself. The ratio of the heat radiated E to the heat radiated under black body conditions E_b is

$$\frac{E}{E_b} = 1 - \exp(-\beta L) \qquad [16.13.73]$$

where β is an effective extinction coefficient and the subscript b denotes a black body. If the product βL is large, the flame is said to be optically thick and, conversely, if $\beta L \to 0$ the flame is said to be optically thin.

For a flame where the optical thickness depends only on the partial pressure p_g of the radiating gases, the condition for optical thinness may be stated as $p_g L \to 0$.

Hydrocarbon flames

The flames of some hydrocarbons, such as natural gas, contain relatively little soot, whereas those of other hydrocarbons, such as kerosene, contain much larger amounts. In consequence, with natural gas, for paths through the flame which in this context are short, say 5 m in length, the radiation exhibits a background level due to soot emission with superimposed peaks due to gaseous emission. As the path length increases so does the.contribution of the soot, until at a path length of 10–20 m the emission spectrum becomes that of a black body.

Approximations

Frequently use is simply made of a point estimate of flame emissivity. A smoky flame is often assumed to be a black body radiator and thus to, have an emissivity of unity. Values of emissivity of 0.9–1.0 are commonly used for such flames. LPG is a typical material which gives a smoky flame. LNG, on the other hand, tends to give a less smoky flame, but also a wider range of emissivities.

16.13.8 Heat radiation: fraction radiated

If the alternative approach is adopted of applying a radiant heat factor R, it is necessary to have appropriate values of this factor. Hymes (1983 SRD R275) has quoted the following values given by Roberts:

Type of flame	*Radiant heat factor*
Flare and jet flames	0.2
Pool fires	0.3
Fireballs from vessels bursting below relief valve pressure	0.3
Fireballs from vessels bursting above relief valve pressure	0.4

In general, the fraction of heat radiated depends on the efficiency of combustion and the soot formation and on the heat lost by convection to the entrained air. Some flame models include correlations in which the fraction of heat radiated is a function of the operating conditions.

Further discussion of flame emissivity, the radiant heat factor and the generalized heat flux is given in the sections below on specific types of flame.

16.13.9 Atmospheric transmissivity

As described above, appreciable attenuation may occur when radiation is transmitted from a source to a target through the atmosphere. Accounts of gas transmissivity have been given by D.Q. Kern (1950) and McAdams (1954). These are concerned primarily with radiant transfer in process plant items such as furnaces.

Treatments of atmospheric transmissivity have been given by Glasstone (1962) and Glasstone and Dolan (1980), Raj *et al.* (1979), Simpson (1984 SRD R304), V.C. Marshall (1987), Wayne (1991) and the Committee for the Prevention of Disasters (CPD) (1992a). Other accounts of radiant heat transmission which include estimation of atmospheric transmissivity include those by R.O. Parker (1974), Lihou and Maund (1982) and Hymes (1983 SRD R275).

Attenuation of radiation in the atmosphere is due to absorption and scattering. The constituents of the atmosphere responsible for such attenuation are water vapour and carbon dioxide. Absorption of radiation is a function of the number of absorbing molecules in the path, while scattering is a function of the number and the size of the droplets.

Glasstone and Dolan (1980) state that, in general, the atmospheric transmissivity τ for estimation of the thermal radiation received by a target from a nuclear bomb explosion is a complex function which depends on the absorption, scattering and distance. For attenuation due only to absorption in a uniform atmosphere they give

$$\tau = \exp(-\kappa x) \qquad [16.13.74]$$

where x is the distance to the target and κ is the absorption coefficient. They also utilize this equation for the attenuation due to both absorption and scattering, but state that due to the latter κ, now an attenuation coefficient, is then not constant with distance x.

They give the following relations between atmospheric condition and visibility:

Atmospheric condition	*Visibility* (km)
Exceptionally clear	280
Very clear	50
Clear	20
Light haze	10
Haze	4
Thin fog	2
Light to thick fog	≤ 1

and the following values relating the attenuation coefficient κ to the visibility:

Visibility (km)	κ (km^{-1})
80	0.03
40	0.1
20	0.2

A number of workers have utilized Equation 16.13.74 with suitable values of the attenuation coefficient. Lihou and Maund have used values ranging from 0.4 km^{-1} for a clear day to 1.0 km^{-1} for a hazy day with an average of 0.7 km^{-1}. Hymes has used values of 0, 0.4, 1.0 and 2.0 km^{-1} for conditions ranging from zero absorption to foggy or smoky atmospheres. Simpson quotes values from Glasstone (1962) of 0.4, 1.0 and 2.01 km^{-1} for visual ranges of 10, 5 and 2 km, respectively.

A more fundamental treatment has been given by Simpson (1984 SRD R304). This SRD method involves the separate computation of the transmissivities based on absorption and on scattering and each of these transmissivities is calculated for a set of discrete 'windows' spanning the range of wavelengths. The overall atmospheric transmissivity is then obtained as the product of the transmissivities based on absorption and on scattering.

For the transmissivity based on absorption the approach followed is based on the transmission windows method of Elder and Strong (1953) and is as follows. The water absorption bands occur at wavelength $\lambda = 1.1, 1.38, 1.87, 2.7$ and 6.0 μm and the carbon dioxide bands at 2.7, 4.3 and 14.5 μm. The wavelength spectrum from 0.72 to 15.0 μm is divided into 8 windows, as shown in Table 16.56 separated by the water and carbon dioxide bands.

For a given window i the transmissivity based on absorption τ_{ai} is determined from the equations

$$\tau_{ai} = \exp(-A_i w^{1/2}) \qquad w < w_i \qquad [16.13.75a]$$

$$\tau_{ai} = k_i (w_i/w)^{\beta_i} \qquad w > w_i \qquad [16.13.75b]$$

where w is the concentration of water in the atmosphere (pr mm), w_i is the value of w which causes absorption in window i to go from weak band to strong band absorption (pr mm), and A_i, k_i and β_i, are constants. The units for water content refer to precipitable water (pr mm). Equation 16.13.75 is based on curve fitting of the plots given by Elder and Strong and on extensions by Simpson. Values of the parameters are given in Table 16.57.

For scattering transmissivity an empirical approach is taken. This transmissivity is given by the relation

$$\tau_{si} = \exp[-\beta(\lambda_i)x] \qquad [16.13.76]$$

where x is the path length and $\beta(\lambda_i)$ is the scattering coefficient for window i.

The scattering coefficient $\beta(\lambda_i)$ is reiated to the meteorological, or visible, range V. The meteorological range may be defined by the contrast between the sky and a distant black target. Taking a value of 2% contrast gives the relation

$$V = \frac{1.0}{0.02}\,\frac{1}{\beta n} \qquad [16.13.77]$$

Table 16.56 *Window limits for estimation of atmospheric transmissivity (Simpson, 1984 SRD R304) (Courtesy of the UKAEA Safety and Reliability Directorate)*

Window no.	*Window boundaries,* λ (=m)
I	0.72–0.94
II	0.94–1.13
III	1.13–1.38
IV	1.38–1.90
V	1.90–2.70
VI	2.70–4.30
VII	4.30–6.0
VIII	6.0–15.0

Table 16.57 *Parameters for estimating the absorption effects on atmospheric transmissivity (Simpson, 1984 SRD R304) (Courtesy of the UKAEA Safety and Reliability Directorate)*

Window no.	A_i	k_i	b_i	w_i
I	0.0305	0.800	0.112	54
II	0.0363	0.765	0.134	54
III	0.1303	0.830	0.093	2.0
IV	0.2110	0.802	0.111	1.1
V	0.3500	0.814	0.1035	0.35
VI	0.3730	0.827	0.095	0.26
VII	0.9310	0.679	0.194	0.18
VIII	0.5980	0.784	0.122	0.165
I–VIII	0.2110	0.855	0.815	0.6

where n is the refractive index of the scattering particles. Following standard practice in evaluating the visual range at $\lambda = 0.55$ μm

$$\beta = 3.91/V \quad \lambda = 0.55 \qquad [16.13.78]$$

A widely used expression relating the scattering coefficient β to the wavelength λ is

$$\beta = A\lambda^{-q} \qquad [16.13.79]$$

where A is a constant and q is an index.

Then from Equations 16.13.76–16.13.79

$$\tau_{si} = \exp\left[-\frac{3.91}{V}\left(\frac{\lambda_i}{0.55}\right)^{-q} x\right] \qquad [16.13.80]$$

The value most often proposed for q is 1.3, but on exceptionally clear days it can be as high as 1.6 and for days in which haze reduces the visible range below 6 km a good estimate may be made from the relation

$$q = 0.585\ V^{1/3} \qquad [16.13.81]$$

The total transmissivity τ_{T_i} for window i is the product of the transmissivities based on absorption and on scattering:

$$\tau_{T_i} = \tau_{ai}\tau_{si} \qquad [16.13.82]$$

The radiation transmitted is then determined as follows. From the theoretical black body radiation spectrum a discrete black body radiation spectrum is derived with the radiation in each window i at a constant value. The discrete spectrum of transmitted radiation is then calculated by multiplying the theoretical values by the total transmissivity τ_{T_i} for each window i. The procedure is illustrated in Figure 16.81.

If desired, the overall transmissivily τ may then be determined as the ratio of the total radiation transmitted to the total black body radiation.

Values of the overall atmospheric transmissivity τ have been tabulated by Simpson. He considers black body flame temperatures of 1000, 1150, 1300, 1450 and 1600 K, ambient air temperatures of 0, 15 and 30°C, relative humidities of 10, 30, 70 and 100%, visual ranges of 2, 5, 10 and 20 km and actual ranges of from 5 m to 10 km. Some of the

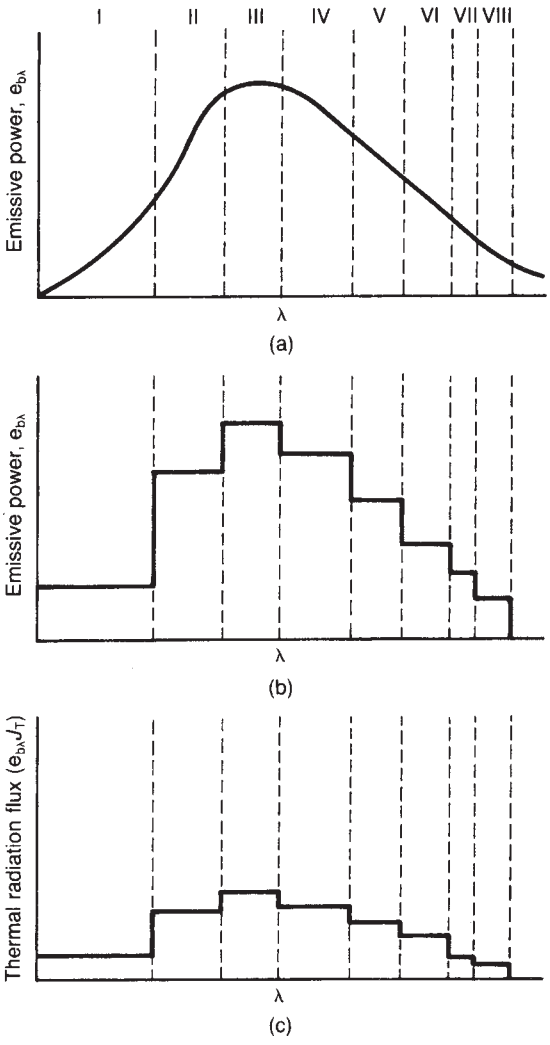


Figure 16.81 *Estimation of radiation transmitted through the atmosphere: (a) theoretical black body radiation spectrum; (b) black body radiation spectrum produced using the procedure outlined; (c) example of the effect of atmospheric transmission on the radiation spectrum (Simpson 1984 SRD R304). J_T thermal radiation flux (unattenuated) (Courtesy of the UKAEA Safety and Reliability Directorate)*

meteorological data for the United Kingdom given by Simpson are shown in Table 16.58. Values of the atmospheric transmissivity τ obtained by Simpson for some typical meteorological conditions are given in Table 16.59.

Simpson gives comparisons of results obtained with the SRD method with those obtained from the methods of Glasstone, Raj *et al.* and TNO. The Glasstone method gives higher values of the atmospheric transmissivity, which Simpson attributes primarily to the fact that the method neglects absorption. The agreement with the Raj method is better, though the latter gives higher values at the longer

Table 16.58 *Some meteorological data for the United Kingdom relevant to the estimation of atmospheric transmissivity (after Simpson, 1984 SRD R304) (Courtesy of the UKAEA Safety and Reliability Directorate)*

A Maximum air temperatures[a]

Temperature range (°C)	*Relative frequency* (%)
<0	0.7
0.5–5.0	8.8
5.5–10.00	23.5
10.5–15.0	25.6
15.5–20.00	24.0
20.5–25.00	14.0
25.5–30.00	3.2
>30.0	0.2

B Relative humidity (RH) as a function of air temperature[b]

Temperature (°F)	*Relative frequency of RH* (%)						
	40–49	50–59	60–69	70–79	80–89	90–100	*Total*
54.0–57.9	–	–	–	–	0.6	1.6	2.2
58.0–61.9	–	0.3	1.9	3.5	3.5	5.2	14.4
62.0–65.9	0.4	2.3	6.5	13.0	8.1	5.2	35.5
66.0–69.9	0.6	7.5	8.1	7.1	2.9	0.3	26.5
70.0–73.9	0.3	3.2	4.5	6.1	–	–	14.1
74.0–77.9	–	1.9	2.9	0.3	–	–	5.1
78.0–81.9	–	1.6	0.3	–	–	–	1.9
82.0–85.9	–	0.3	–	–	–	–	0.3
Total	1.3	17.1	24.2	30.0	15.1	12.3	100.0

[a] Kew, 1914–40.
[b] Calshot, July 1931–40.

distances, which Simpson attributes to the fact that the method neglects scattering. There is good agreement with the TNO method for the conditions where comparison can be made, but the SRD method is more comprehensive in that it takes into account the visual range.

A number of other treatments and expressions for atmospheric attenuation have been listed by Bagster and Pitblado (1989) and Satyanarayana, Borah and Rao (1991) as follows:

$$\tau = 1.382 - 0.135\log_{10}(p_w x) \quad \text{TNO (1979 } \textit{YellowBook}\text{)} \quad [16.13.83]$$

$$\tau = 2.02(p_w x)^{-0.09} \quad \text{TNO revised} \quad [16.13.84]$$

$$\tau = 1 - 0.058\ \ln x \quad \text{Major Hazards Assessment Unit} \quad [16.13.85]$$

where p_w is the partial pressure of water vapour (Pa) and x is the distance (m).

Wayne (1991) has given the following empirical method for the estimation of atmospheric transmissivity. The flame is assumed to be a black or gray body at a temperature of 1500 K, which is chosen as an average value lying between mat of a propane fire and that of an LNG fire. His equation is

$$\tau = 1.006 - 0.01171[\log_{10}X(H_2O)] - 0.02368[\log_{10}X(H_2O)]^2 - 0.03188[\log_{10}X(CO_2)] + 0.001164[\log_{10}X(CO_2)]^2 \quad [16.13.86]$$

Table 16.59 *Some typical values of atmospheric transmissivity as a function of visual range (Simpson, 1984 SRD R 304) (Courtesy of the UKAEA Safety and Reliability Directorate)*

Visual range (km)	*Range* (m)	
	100	5000
1	0.581	0.003
2	0.631	0.046
3	0.656	0.115
4	0.662	0.176
5	0.665	0.224
10	0.665	0.341
50	0.421	–
100	0.426	–
500	0.426	–

with

$$X(CO_2) = L\frac{273}{T} \quad [16.13.87]$$

$$X(H_2O) = R_H L S_{mm}\left(\frac{288.651}{T}\right) \quad [16.13.88]$$

where L is the path length (m), is the fractional relative humidity, S_{mm} is the saturated vapour pressure of water at temperature T (mmHg), T is the atmospheric temperature (K),

$X(CO_2)$ is a function representing the amount of carbon dioxide in the path (m) and $X(H_2O)$ is a corresponding function for water vapour (μm). $X(H_2O)$ is actually defined as the thickness of the uniform liquid layer which would be obtained by notionally condensing the water vapour in an absorbing path of unit cross-sectional area onto its base. $X(H_2O)$ must not exceed a minimum value, assigned as 1 μm, which corresponds to a 10 m path through an atmosphere with $T = 253$ K and $R_H = 0.10$.

Another set of relations is that given by V.C. Marshall (1987), as described in Section 16.15.

16.13.10 Target absorptivity

The fraction of the incident radiant heat which the target absorbs depends on its absorptivity. As already described, absorptivity is closed related to emissivity. An account of the radiation properties of surfaces is given by Sparrow and Cess (1978).

Emissivity is generally tabulated as a property of the material. It should be borne in mind that it is dependent both on the surface condition and on the temperature. The emissivity of many materials has been tabulated by Hottel (McAdams, 1954). Hottel's table includes the following emissivities for steel:

Mild steel (after cleaning)	0.20–0.32
Rolled sheet steel	0.66
Rough steel plate	0.94–0.97

Numerous other tabulations are available.

In most flame radiation applications it is assumed that the absorptivity of a target is equal to the emissivity.

16.13.11 View factor

The treatment of radiant heat transfer from a source to a target is based on the concepts of the enclosure and of the angle factor. Estimation of the radiation incident on a surface requires that account be taken of the radiation arriving on that surface from all directions. In order to do this use is made of the concept of an enclosure for each surface of which the radiation properties and thermal state are defined. An enclosure is not necessarily bounded by solid surfaces; some surfaces may be open.

The other concept is that of the angle factor, also variously known as the shape, geometrical, configuration or view factor. Accounts of angle factors, or view factors, include those given by Hottel (1954), Hamilton and Morgan (1952), McGuire (1953), Sparrow and Cess (1978), Howell (1982) and Siegel and Howell (1991).

An expression for the angle factor between two differential surfaces dA_i and dA_j has been given in Equation 16.13.38 and is

$$dF_{dA_i-dA_j} = \cos\beta_i \cos\beta_j \, dA_j/\pi r^2 \qquad [16.13.89]$$

Similarly

$$dF_{dA_j-dA_i} = \cos\beta_j \cos\beta_i \, dA_i/\pi r^2 \qquad [16.13.90]$$

Hence from Equations 16.13.89 and 16.13.90

$$dA_i \, dF_{dA_i-dA_j} = dA_j \, dF_{dA_j-dA_i} \qquad [16.13.91]$$

Equation 16.13.91 is one of three reciprocity rules. The other two are

$$A_i dF_{dA_i-dA_j} = dA_j \, dF_{dA_j-dA_i} \qquad [16.13.92]$$

and

$$A_i F_{A_i-A_j} = A_j F_{A_j-A_i} \qquad [16.13.93]$$

A further property of angle factors which follows from the principle of energy conservation is

$$\sum_{j=1}^{N} F_{A_i-A_j} = 1 \qquad [16.13.94]$$

where N is the number of surfaces in the enclosure.

There are a number of methods for the derivation of angle factors. They include:

(1) direct integration;
(2) contour integration:
(3) short-cut methods
  (a) angle factor algebra,
  (b) elongated surfaces,
  (c) string method.

Angle factors have been derived for a large number of standard configurations. There are a number of tabulations available, including those of Hamilton and Morgan (1952), McGuire (1953), Stannard (1977), Sparrow and Cess (1978), Howell (1982) and Siegel and Howell (1991).

It is usual to give for each case the configuration diagram together with the governing equation. Angle factor algebra may be applied to derive an angle factor for a non-standard case from that for a standard case. As an illustration consider the derivation of the angle factor $F_{A_1-A_4}$ for the system shown in Figure 16.82. Applying the principle of energy conservation

$$A_1 F_{A_1-A_4} = A_{12} F_{A_{12}-A_4} - A_2 F_{A_2-A_4} \qquad [16.13.95]$$

where

$$A_{12} = A_1 + A_2 \qquad [16.13.96]$$

Applying the principle further

$$A_{12} F_{A_{12}-A_4} = A_{12} F_{A_{12}-A_{34}} - A_{12} F_{A_{12}-A_3} \qquad [16.13.97]$$

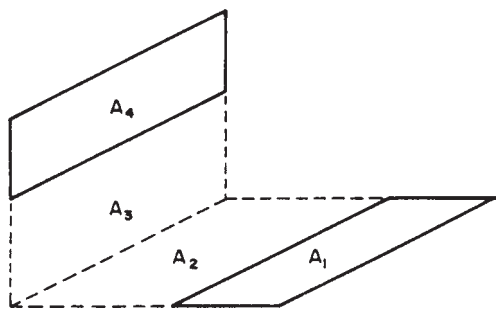


Figure 16.82 *Configuration for illustrative example of angle factor algebra (Sparrow and Cess, 1978) (Courtesy of Brooks/Cole Publishers)*

where

$$A_{34} = A_3 + A_4 \qquad [16.13.98]$$

and hence

$$A_2F_{A_2-A_4} = A_2F_{A_2-A_{34}} - A_2F_{A_2-A_3} \qquad [16.13.99]$$

Substituting from Equations 16.13.97 and 16.13.99 in Equation 16.13.95 yields

$$F_{A_1-A_4} = \frac{1}{A_1}(A_{12}F_{A_{12}-A_{34}} + A_2F_{A_2-A_3} - A_{12}F_{A_{12}-A_3} - A_2F_{A_2-A_{34}}) \qquad [16.13.100]$$

All the angle factors on the right-hand side of Equation 16.13.100 are obtainable from the single standard case of two adjacent surfaces at right angles to each other.

Treatments of view factors specifically oriented to process plant problems include those by Crocker and Napier (1986, 1988a,b) and B.C. Davis and Bagster (1989–).

An common situation is radiation from a source, which can be treated as a point source. In this case the radiation at a spherical surface is

$$E = \frac{Q_r}{4\pi r^2} \qquad [16.13.101]$$

where r is the radius of the spherical surface. Then, for simplicity, neglecting the absorptivity of the target and the atmospheric transmissivity, the heat radiation intensity received by the target is

$$I = \frac{FQ_r}{4\pi l^2} \qquad [16.13.102]$$

where l is the slant distance from the point source to the target.

Then from Equations 16.13.101 and 16.13.102, with Equation 16.13.49 the view factor for this case is

$$F \approx \frac{r^2}{l^2} \qquad [16.13.103a]$$

$$F \approx \frac{r^2}{x^2} \quad x \approx 1 \gg r \qquad [16.13.103b]$$

where l is the slant distance and x is the ground distance from the point source to the target.

An important class of flame is elevated flames such as flares and fireballs. These are frequently treated as point sources using Equations 16.13.101–16.13.103.

The view factor is affected by the orientation of the target. The implicit assumption in Equations 16.13.102 and 16.13.103 is that the surface of the target is normal to the line connecting it with the point source. For heat radiation from an elevated point source to a small, or differential, target, a correction is required if the target is, say, vertical or horizontal. For a target which is vertical, so that the line between the point source and the target makes an angle θ with the horizontal, the correction factor to be applied to the view factor is $\cos\theta$. For a target which is horizontal, so that the line between the point source and the target makes an angle ϕ with the vertical, the correction factor is $\cos\phi$. Then, since $\theta + \phi = 90°$, $\cos\phi = \sin\theta$. Hence for these two cases, from Equation 16.13.103

$$F = \frac{r^2}{x^2}\cos\theta \qquad \text{Vertical target} \qquad [16.13.104]$$

$$F = \frac{r^2}{x^2}\sin\theta \qquad \text{Horizontal target} \qquad [16.13.105]$$

Equations for view factors are often expressed not in terms of the angle θ but of the lengths of the two sides of the relevant triangle.

The expressions just given apply to differential elements, or, in practice, small objects. This is generally taken to include the human body. Larger objects, such as storage tanks, are finite surfaces.

For the purposes of determining a view factor, there are a number of different ways of treating a flame. They include treatment as (1) a single point source, (2) multiple point sources, (3) an equivalent radiator or (4) a solid flame. The equivalent radiator (ER) model treats the flame as a two-dimensional surface. For example, the flame on a pool fire is represented as a vertical rectangle. In the solid flame (SF) model the flame is treated as a three-dimensional solid body. For example, the pool fire flame is represented as a vertical cylinder. The point source (PS) and multiple point source (MPS) models are self-explanatory.

Table 16.60 gives references to certain standard view factors listed by Siegel and Howell (1991) which may be of use in work on radiant heat transfer in process plants. Relations for view factors for fireballs, pool fires, flares and jet flames are given in Sections 16.15 and 16.17–16.19, respectively.

16.14 Vapour Cloud Fires

A vapour cloud fire, or flash fire, occurs when a vapour cloud forms from a leak and is ignited, but without creation of significant overpressure. If such overpressure occurs, the event is a vapour cloud explosion (VCE) rather than a vapour cloud fire (VCF).

16.14.1 vapour cloud fire incidents

Release of flammable vapour from a process plant followed by ignition is a not uncommon occurrence. If the ignition is prompt, the cloud may be modest in size, but if the cloud has time to spread over an appreciable part of the site and is then ignited, a major vapour cloud fire may result. This occurs in only a very small proportion of ignited releases.

Large and destructive vapour cloud fires occurred at Port Newark, New Jersey, in 1951 and at Mexico City, Mexico, in 1984. These and other incidents are described in Section 16.38 and Appendix 4.

16.14.2 Experimental studies

Early experimental work on the combustion of vapour clouds from spills on land has been described by Raj (1977) and work at China Lake in 1978 on spills on water has been described by A.D. Little (1979).

Large-scale tests involving vapour cloud fires from spills of refrigerated liquefied gas on water have been conducted in association with other tests concerned with

Table 16.60 *Some standard view factors that are potentially useful in process radiant heat transfer work*

Configuration	*Reference*[a]
Circular discs	
1. Plane differential element parallel with element:	
1a. Normal to element passes through centre of disc	18
1b. Normal to element does not pass through centre of disc	19
1c. Planes containing element and disc intersect at 90°	20
2. One disc to another parallel disc with centres of both discs along the same axis	23
Right circular cylinders	
3. Plane differential element to cylinder of finite height with normal to element passing through one end of the cylinder and perpendicular to the cylinder axis	26
4. Infinitely long line source to parallel infinitely long cylinder	28
5. Infinitely long plane of finite width to parallel infinitely long cylinder	27
6. Infinitely long cylinder to second infinitely long cylinder of same diameter	30
7. Two concentric cylinders of infinite length	31
8. Two concentric cylinders of finite length	32
Spheres	
9. Spherical point source to sphere	35
10. Plane differential element to sphere	
10a. Normal to element passes through centre of sphere	36
10b. Tangent to element passes through centre of sphere	37
11. Sphere to disc with normal to centre of disc passing through centre of sphere	38
12. Two concentric spheres	41

[a] References are to Siegel and Howell (1991), Appendix C.

heavy gas dispersion. The vapour cloud dispersion and fire tests at Maplin Sands have been described by Blackmore, Eyre and Summers (1982) and Hirst and Eyre (1983), and those at China Lake in 1980–81 have been described by Ermak *et al.* (1983). An account of the dispersion tests has already been given in Chapter 15.

The Maplin Sands trials involved the spillage onto the sea, dispersion and, in some cases, combustion of liquefied natural gas (LNG) and refrigerated liquid propane. Both quasi-instantaneous and continuous releases were made. In the trials involving combustion, seven were with LNG and four were with propane. Plate 9 shows the progress of Trial 27 at Maplin.

Ignition was effected by spark igniters located on certain pontoons. In two of the LNG tests flame failure occurred soon after ignition. Moreover, infrared measurements indicated that in several tests, both with LNG and with propane, at least one and sometimes two ignitions were followed by flame failure before the bulk of the cloud ignited. These latter failures were not visible to the eye. Flame failure was attributed to inhomogeneities of the concentration in the cloud.

The instantaneous and continuous releases differed in that, whereas in the latter a pool of liquefied gas was created which gave in effect a pool fire also, in the former there was no pool fire.

The combustion of the vapour cloud involved first burning of the pre-mixed part and then diffusive burning of the fuel-rich part. The flame in the pre-mixed burning did not propagate quickly across the top of the cloud, but remained as a 'wall of fire'.

Expansion of the combustion products was principally in the vertical direction. The unburnt gas was not pushed ahead of the flame front to any significant extent. Where a pool fire occurred, the height of the flame was appreciably greater.

The vapour clouds were made visible by the associated water fog. In the case of the LNG clouds the contour of the lower flammability limit (LFL) lay within that of the fog, and combustion was entirely within the visible fog; some of the visible cloud remained unburned. For the propane clouds the LFL contour lay outside the fog and combustion took place in part outside it.

The flame speeds measured during the combustion were relatively low, and far removed from the figure of 150 m/s often quoted as necessary for the generation of appreciable overpressure. For LNG in Test 27 the flame speed averaged 4 m/s with a maximum of 10 m/s, whilst for pronane in Test 51 the corresponding figures were 12 and 20 m/s, respectively.

Pressure deviations measured during the combustion were a maximum of 0.8 mbar for LNG and 0.4 mbar for propane. The maximum deviations were underpressures, the overpressures being rather less. The form of the decay of the overpressure was that the overpressure was inversely proportional to the distance.

With regard to thermal radiation, the surface emissive power of the cloud fires was measured as 173 kW/m^2 for both LNG and propane. For the pool fires the values obtained were 203 kW/m^2 for LNG but 43 kW/m^2 for propane. The authors suggest that a value of 200 kW/m^2 may be representative for larger vapour cloud fires and for LNG pool fires. The lower value for propane pool fires is in accordance with results for pool fires of propane on land, as described below.

The account of the combustion tests in the Coyote trials described by Ermak *et al.* (1983) gives broad confirmation of these findings. The tests involved 40 m^3 spills of LNG onto water. Again the flame velocities were modest. They lay in the range 11.9–18.9 m/s for wind speeds of 4.6–10.0 m/s, the values of the flame speed less the wind speed being 6.4–12.9 m/s. The flame velocities appeared to be high near the ignition source, whether a flare or a jet, and fell off rapidly. There was no indication of significant flame acceleration. The flame heights were somewhat higher than in the Maplin tests.

16.14.3 Empirical features

The foregoing description indicates some of the empirical features of a vapour cloud fire. A further account is given by Crawley (1982). The conditions favouring a vapour cloud fire are a prolonged release in conditions of poor dispersion.

Two main types of flame behaviour have been assumed. Raj and Emmons (1975) conceive the burning as a 'wall of fire', whilst Fay and Lewis (1977) propose the formation of

a fireball by the rising thermal. No fireball effect is mentioned in connection with the tests just described. The wall of fire mode occurs in the combustion of the fuel-rich portion. Overall, the combustion is usually not especially rapid or violent, the flame progressing through the cloud at a speed of several metres per second.

Strictly, a vapour cloud combustion which generates overpressure has to be classed as a vapour cloud explosion. In practice, the latter term tends to be reserved for cases where the explosion causes significant destruction. For vapour cloud fires, the overpressures vary from the imperceptible up to those which may cause some window damage.

A vapour cloud fire may cover a wide area, perhaps some thousands of square metres. It results in scorching and depletion of oxygen, with potential for injury and damage. It may initiate BLEVEs and other releases of flammable material which then feed the fire. It also deposits soot.

16.14.4 Modelling of vapour cloud fires

The hazard from a vapour cloud fire is usually assessed by considering dispersion of the vapour cloud and ignition of this cloud and making some relatively simple assumption concerning the effects inside and outside the cloud.

In many assessments no explicit model of a vapour cloud fire has been utilized. Instead it has been assumed that: the contours of the burning cloud are those of the lower flammability limit concentration; persons inside the cloud suffer a denned degree of injury, generally a fatal injury; and those outside the cloud are subject to a level of thermal radiation based on an assumed surface emissive power at the edge of the burning cloud.

16.14.5 Eisenberg, Lynch and Breeding model

An early model for a flash fire is the Vulnerability model by Eisenberg, Lynch and Breeding (1975). The vapour cloud is assumed to be a half ellipsoid with volume V_r and area A_r given by the equations

$$V_r = \frac{2\pi}{3}\sigma_x\sigma_y\sigma_z(r_l^3 - r_u^3) \qquad [16.14.1]$$

$$A_r = \frac{2\pi}{3}(\sigma_x^2 + \sigma_y^2 + \sigma_z^2)(r_l^2 + r_u^2) \qquad [16.14.2]$$

with

$$r_l = 2\ln\left[\frac{2m}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z k_l}\right]^{1/2} \qquad [16.14.3]$$

$$r_u = 2\ln\left[\frac{2m}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z k_u}\right]^{1/2} \qquad [16.14.4]$$

where A_r is the area of radiation of the hot gas layer (m^2), k_l is the concentration at the lower explosive limit (kg/m^3), k_u is the concentration at the upper explosive limit (kg/m^3), m is the total mass of vapour released (kg), r_l is a parameter of the cloud at the lower explosive limit, r_u is a parameter of the cloud at the upper explosive limit, V_r is the volume of the hot gas layer (m^3), and σ_x, σ_y and σ_z are dispersion coefficients in the downwind, crosswind and vertical (x, y and z) directions, respectively (m).

The heat loss q from the gas is predominantly by radiation, so that

$$q \approx A_r\sigma(\epsilon_g T_g^4 - \epsilon_a T_a^4) \qquad [16.14.5]$$

where q is the heat loss by radiation (W), T_a is the absolute temperature of the environment (K), T_g is the absolute temperature of the hot gas (K), ϵ_a is the emissivity of the environment, ϵ_g is the emissivity of the hot gas and ϵ is the Stefan-Boltzmann constant ($= 5.67 \times 10^{-8}\ W/m^2K^4$).

The layer of radiating gas may be expected to be some tens or even hundreds of meters thick. Under these conditions the gas emissivity does not change much with layer thickness or temperature and has a value of about 0.5. The authors replace Equation 16.14.5 by the approximate relation

$$q \approx A_r\sigma(T_g^4 - T_a^4) \qquad [16.14.6]$$

The gas emissivity of unity in Equation 16.14.6 includes an allowance for the other modes of heat transfer.

The heat loss is also given by

$$q = -c_p\rho V_r\frac{dT_g}{dt} \qquad [16.14.7]$$

where c_p is the specific heat of the hot gas layer (J/ kg K), the time (s) and ρ is the density of the hot gas layer (kg/m^3). The hot gas layer is nearly always mostly air.

Equating the heat flows in Equations 16.14.6 and 16.14.7 gives

$$\frac{dT_g}{dt} = -k(T_g^4 - T_a^4) \qquad [16.14.8]$$

with

$$k = \frac{A_r\sigma}{c_p\rho V_r} \qquad [16.14.9]$$

Equation 16.14.8 has the solution

$$t = \frac{1}{2kT_a^3}\left\{\left[\tan^{-1}\left(\frac{T_g}{T_a}\right) - \frac{1}{2}\ln\left(\frac{T_g - T_a}{T_g + T_a}\right)\right] - \left[\tan^{-1}\left(\frac{T_{gi}}{T_a}\right) - \frac{1}{2}\ln\left(\frac{T_{gi} - T_a}{T_{gi} + T_a}\right)\right]\right. \qquad [16.14.10]$$

where subscript i denotes the initial value.

Equation 16.14.10 may be rewritten in terms of the half-life $t_{1/2}$ of the fire, or the time at which

$$T_g = \frac{T_{gi} + T_a}{2} \qquad [16.14.11]$$

Then

$$t_{1/2} = \frac{1}{2kT_a^3}\left[\tan^{-1}\left(\frac{\beta+1}{2}\right) - \tan^{-1}\beta - \frac{1}{2}\ln\left(\frac{\beta+1}{\beta+3}\right)\right] \qquad [16.14.12a]$$

or, in the equivalent form given by the authors,

$$t_{1/2} = \frac{1}{2kT_a^3}\left[\tan^{-1}(1/\beta) - \tan^{-1}\left(\frac{2}{\beta+1}\right) - \frac{1}{2}\ln\left(\frac{\beta+1}{\beta+3}\right)\right] \qquad [16.14.12b]$$

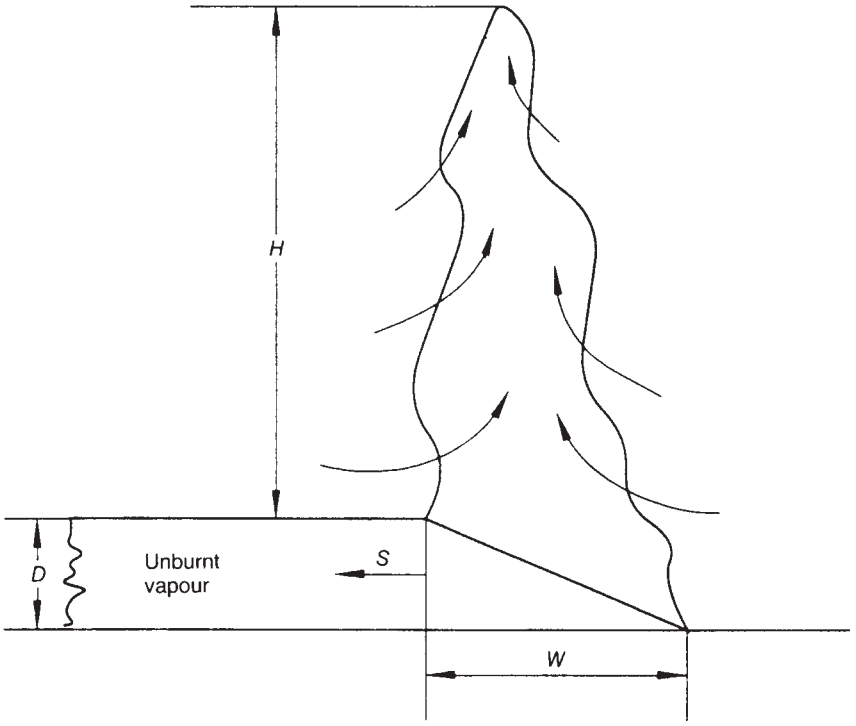


Figure 16.83 *Flame at the edge of a burning vapour cloud (after Raj and Emmons, 1975; CCPS, 1994/15) (Reproduced by permission of the American Institute of Chemical Engineers)*

with

$$\beta = T_{gi}/T_a \qquad [16.14.13]$$

where $t_{1/2}$ is the half-life of the flash fire (s).

The effective thermal radiation intensity is given by

$$I_r = \sigma(T_g^4 - T_a^4) \qquad [16.14.14]$$

where I_r is the effective thermal radiation intensity of the flash fire (W/m^2).

The effective time duration t_{eff} is

$$t_{eff} = 3t_{1/2} \qquad [16.14.15]$$

where t_{eff} is the effective time duration of the flash fire (s). The initial value of the absolute temperature of the hot gas T_{gi} is taken as the adiabatic flame temperature.

16.14.6 Raj and Emmons model

Another flash fire model is that of Raj and Emmons (1975). This model takes into account the speed of the flame propagating through the cloud. The assumptions made are that during the combustion of a vapour cloud there is a turbulent flame front propagating into the unburned cloud at a constant velocity which is roughly proportional to the wind speed, and that at high gas concentrations there is a tall flame plume at the edge of the unburned cloud.

This model is represented in Figure 16.83 in which a flame front is propagating at constant velocity S into an unburned cloud of depth D with a flame base of width W and a flame height H above the top of the cloud.

The treatment of flame height is based on the pool fire model of F.R. Steward (1964). The observed height of such flames is approximately twice that of the base ($H/W = 2$). Application of the conservation equations gives a relation between the flame height and the upward velocity of the gases. Then from a mass balance on the triangle formed by the flame and the base, a relation may be derived between the flame height H and the flame speed S.

This treatment forms the basis of the semi-empirical equation given by Raj and Emmons for the flame height of a flash fire:

$$H = 20D\left[\frac{S^2}{gD}\left(\frac{\rho_o}{\rho_a}\right)^2 \frac{wr^2}{(1-w)^3}\right]^{1/3} \qquad [16.14.16]$$

with

$$S = 2.3U_w \qquad [16.14.17]$$

where D is the cloud depth (m), g is the acceleration due to gravity (m/s^2), H is the visible flame height (m), r is the stoichiometric air–fuel mass ratio, S is the flame speed, or 'burning speed' (m/s), U_w is the wind speed (m/s), w is a

parameter, ρ_a is the density of air (kg/m^3) and ρ_o is the density of the fuelair mixture (kg/m^3).

The parameter w represents the inverse of the volumetric expansion due to combustion in the plume and is strongly dependent on the composition of the cloud. For a cloud of pure vapour, $w \approx 1/9$, assuming the vapour is hydrocarbon, whilst for a cloud of stoichiometric composition or leaner, $w = 0$.

The application of the relation for w given by Raj and Emmons is somewhat complex. As described below, the Center for Chemical Process Safety (CCPS) has developed an alternative and more straightforward equation.

The expression for the flame speed S is derived by Raj and Emmons from a limited number of experimental observations.

The heat flux incident on a receptor may be estimated from Equation 16.13.49.

16.14.7 CCPS model

The set of hazard models given in the CCPS *Fire and Explosion Model Guidelines* (1994/15) includes a model for flash fires. The model is essentially that of Raj and Emmons with a modification of the expression for the parameter w. For this the CCPS gives

$$w = 0 \quad \phi \leq \phi_{st} \qquad [16.14.18a]$$

$$w = \frac{\phi - \phi_{st}}{\alpha(1 - \phi_{st})} \quad \phi > \phi_{st} \qquad [16.14.18b]$$

where α is the constant pressure expansion ratio for stoichiometric combustion, ϕ is the volumetric concentration of fuel (v/v) and the subscript st denotes stoichiometric. For hydrocarbons the value of α is typically about 8.

In applying the model for the estimation of thermal radiation the CCPS propose the use of the following two assumptions: (1) during the propagation of the flash fire, the cloud is stationary and is fixed and homogeneous in composition; and (2) the time-dependent flame surface is a plane cross-section moving through the cloud at the flame speed.

16.14.8 Considine and Grint model

Considine and Grint (1985) have given a model for a flash fire in the form of graphs of the distance to particular levels of fatal injury. This model is described in Section 16.39.

16.15 Fireballs

Another significant fire hazard is that from fireballs. Accounts of fireballs include those by Gayle and Bransford (1965), R.W. High (1968), Hardee and Lee (1973), Strehlow and Baker (1976), Fay and Lewis (1977), V.C. Marshall (1977a, 1987), Hardee, Lee and Benedick (1978), Hasegawa and Sato (1977, 1978), Fay, Desgroseillers and Lewis (1979), Williamson and Mann (1981), A.F. Roberts (1981/82, 1982), Crawley (1982), Lihou and Maund (1982), Moorhouse and Pritchard (1982), W.E. Baker *et al.* (1983), Pietersen (1985), Jaggers *et al.* (1986), Roper *et al.* (1986), D.M. Johnson and Pritchard (1991) and the CCPS (1994/15).

Most treatments of fireballs relate to liquefied gas. Here a distinction needs to be made between a fireball resulting from the bursting of a pressure vessel and one resulting from the formation of a vapour cloud. In the first case the bursting may occur under fire conditions and be part of a BLEVE or it may occur in the absence of fire. Momentum forces predominate if a fireball is formed from the bursting of a vessel, and buoyancy forces predominate in one formed from a vapour cloud.

There are two other types of event which may give rise to a 'fireball'. One is the ignition of a release on a liquefied gas pipeline, where the jet flame is preceded by a fireball in which unignited gas is burned. The other is an eruption in hot oil giving rise to a release of burning vapour. This is exemplified by the event that occurs when water is added to burning fat in a chip pan. Eruptions of burning vapour have occurred in some storage tank fires.

An instance has also occurred of a congested fireball following rupture and release of the flammable contents of a reactor into a building.

The type of fireball of particular interest, however, is that which occurs as part of a BLEVE and it is this type which is mainly treated here.

A quite different type of fireball is that associated with the explosion of a propellant or high explosive. Such fireballs are discussed in the next section.

Some studies on fireballs are given in Table 16.61.

16.15.1 Fireball incidents

Incidents involving fireballs are not uncommon. They usually occur as pan of a BLEVE when a vessel ruptures after it has been engulfed in fire or has been subjected to a directed flame. The vessels principally liable to such conditions are storage vessels, rail tank cars and road tankers.

Fireball incidents are generally associated with BLEVE incidents. BLEVEs are considered in Chapter 17, which contains in Table 17.37 a list of incidents involving fireballs with and without BLEVE.

A massive BLEVE fireball occurred at Crescent City, Illinois, in 1970 with an estimated diameter of 150–200 m (Case History A50). Other major BLEVE fireball inti-dents include those at Houston, Texas, in 1971 (Case History A53), Lynchburg, Virginia, in 1972 (Case Histoiy A59), Kingman, Arizona, in 1973 (Case History A63), Oneonta, New York, and West St Paul, Minnesota, in 1974, and Belt, Montana, in 1976. The estimated diameters of the fireballs at Houston, Kingman and Belt were 300 m. The disaster at Mexico City in 1985, described in Appendix 4, involved a series of fireballs from BLEVEs. Other fireball incidents have occurred at Eagle Pass, Texas, in 1975, Goldona, Virginia, in 1977, and Donnellson, Iowa (Case History A91) and Lewisville, Arkansas, in 1978. The estimated diameter of the fireball at Donnellson was 610 m and of those at Goldonna and Lewisville 320 and 310 m, respectively.

16.15.2. Experimental studies

Experimental research on fireballs has taken three main forms treating fireballs generated by: (1) explosives and propellants, (2) gas-filled bubbles and balloons and (3) containers undergoing BLEVE.

Early experimental investigations of fireballs were concerned with fireballs from propellants. Gayle and Bransford (1965) obtained data from 47 tests and incidents with the mass of combined propellant (fuel + oxidizer) in the range 10–250,000 lb.

A correlation for the diameter of the fireball of the propellant of the Saturn rocket of NASA, based on tests, has been given by R.W. High (1968).

Taking first small scale tests, Fay and Lewis (1977) studied the fireball from hydrocarbon fuels held initially,

Table 16.61 *Some studies of fireballs*

Experimental study on fireballs of propellants	Gayle and Bransford (1965)
Theoretical study of fireballs of rocket propellants	R.W. High (1968)
Theoretical study of fireballs of propellants	Bader, Donaldson and Hardee (1971)
Theoretical study of fireballs from bursting vessels	Hardee and Lee (1973, 1975)
Experimental and theoretical study of fireballs from a stationary vapour cloud	Fay and Lewis (1977) Fay, Desgroseilliers and Lewis (1979)
Theoretical study of LNG fireballs	Hardee, Lee and Benedick (1978)
Experimental and theoretical study of fireballs following liquid flash-off	Hasegawa and Sato (1977, 1978)
Experimental and theoretical study of fireballs from bursting vessels	Maurer *et al.* (1977) Giesbrecht *et al.* (1980)
Review of experimental and theoretical work on fireballs and of case histories and assessment of hazard	V.C. Marshall (1977a, 1987) A. Baker (1979)
Experimental study on fireballs Review of experimental and theoretical work on fireballs and correlation of principal features of fireball behaviour	A.F. Roberts (1981/82, 1982) Lihou and Maund (1982)
Experimental and theoretical study of fireballs Review of experimental and theoretical work on fireballs	Moorhouse and Pritchard (1982)
Theoretical study of fireballs	Jaggers *et al.* (1986); Roper *et al.* (1986)
Experimental study of BLEVEs, including fireballs	D.M. Johnson and Pritchard (1991)

inside soap bubbles with volumes in the range 20–190 cm^3. Hasegawa and Sato (1977) carried out a series of 22 tests on fireballs of *n*-pentane held in glass spheres with a fuel mass in the range 3.1–6.2 kg. These authors also performed a further series of 32 tests on fireballs with a fuel mass in the range 3.1–31.0 kg. Hardee, Lee and Benedick (1978) have described tests on fireballs of pure and pre-mixed methane held in balloons and polyethylene bags, with quantities in the range 0.1–10 kg. A.F. Roberts (1981/82) reports two unpublished tests by A. Baker (1979) with a fuel mass of the order of 10 kg. Lihou and Maund (1982) have described experiments on fireballs from hydrocarbons in bubbles with a fuel mass in the range 0.07–6 g.

Of the larger scale tests, most have been associated with BLEVEs. C. Anderson *et al.* (1975) have described a test on a fully loaded 125 m^3 rail tank car which was made to suffer a BLEVE. A single fireball experiment with a fuel mass of 452 kg has been described by Maurer *et al.* (1977) and Giesbrecht *et al.* (1980). In the work at Bundesanstalt für Materialprüfung (BAM) on fire engulfed vessels, described by Schulz-Forberg, Droste and Charlett (1984), Droste and Schoen (1988) and Schoen, Probst and Droste (1989), several of the vessels were taken to the point of a BLEVE. Other larger scale experiments on BLEVEs have been reported by D.M. Johnson and Pritchard (1991). In this work the mass of fuel involved was of the order of 1–2 te.

16.15.3 Empirical features

A fireball from the bursting of a pressure vessel containing liquefied gas is observed to pass through a number of fairly well-defined phases.

The development of a full-scale fireball is captured in the National Fire Protection Association (NFPA) film on BLEVEs. Crawley (1982) has described the development based on a frame-by-frame analysis of this film. The fireball passes through three phases: (1) growth, (2) steady burning and (3) burnout. The growth phase may be divided into two intervals, each of about 1 s duration. In the first interval the flame boundary is bright with yellowish-white flames indicating a flame temperature of about 1300°C. The fireball grows to about half its final diameter. Calculation indicates that fuel droplets of less than 4–5 mm diameter would vapoirize. This would give good mixing with air at the droplet scale. There would also be good bulk mixing.

In the second interval of the growth phase, the fireball grows to its final volume, but about 10% of the surface is dark and sooty with the rest being white, yellowish-orange or light red, indicating flame temperatures in the range 900–1300°C, with an estimated effective flame temperature of 110–1200°C.

In the second phase, which lasts some 10 s, the fireball, which is now roughly spherical, is no longer growing. At the start of this phase it begins to lift off. It rises and changes to the familiar mushroom-shape. The estimated effective flame temperature is 1100–1200°C.

In the third phase, which lasts some 5 s, the fireball remains the same size, but the flame become less sooty and more translucent.

Figure 16.84 illustrates the typical development of a fireball as a function of time.

The experimental work has also yielded useful information on aspects such as the fraction of the fuel which participates in the fireball, the fireball diameter and duration, the fraction of heat of combustion which is radiated, and the surface emissive power of the fireball. These aspects are discussed below.

16.15.4 Modelling of fireballs

The modelling of fireballs covers the following aspects: (1) the fireball regime, (2) the mass of fuel in the fireball, (3) the fireball development and timescales, (4) the fireball diameter and duration, (5) the heat radiated and (6) the view factor.

The treatment of the heat radiated from a fireball is a good illustration of the different approaches which may be taken to the modelling of fires in process plants. Specifically, there are three different ways of determining the heat radiated. One is to assume that it is a given fraction of the heat released. Another is to assume a given value for the heat radiated from the flame surface, or surface emissive power.

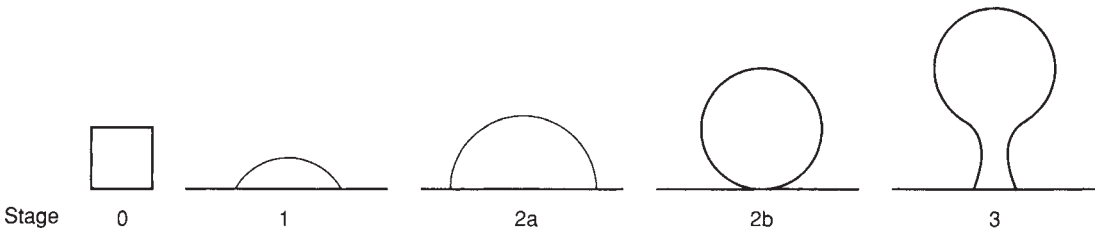


Figure 16.84 *Development of a typical fireball from a source at ground level*

The third is to estimate the heat radiated from the flame properties, such as flame temperature and emissivity.

Models of fireballs are of two broad types: correlations of diameter and duration time, and fundamental models.

In order to maintain some consistency with the notation of the original authors, the symbols M and W are both used for mass.

16.15.5 Fireball regimes

As stated earlier, there are two basic scenarios for the fireball of a liquefied gas. The case of prime interest is a fireball resulting from the bursting of a pressure vessel. The other case is a fireball from the burning of a stationary vapour cloud at atmospheric pressure.

These two situations constitute quite different regimes. The duration times for these are: for the bursting vessel where momentum forces dominate

$$t_d \propto M^{1/3} \qquad [16.15.1]$$

and for a vapour cloud where buoyancy forces dominate

$$t_d \propto M^{1/6} \qquad [16.15.2]$$

where M is the mass of fuel (kg) and t_d is the duration time (s).

For the situation where initially there is high momentum, a change of regime occurs as the momentum declines and gravity slumping begins.

The case of prime interest here is the bursting of a vessel, but that of a stationary vapour cloud is also treated in Subsections 16.15.17 and 16.15.18.

16.15.6 Mass of fuel

The mass of fuel in the fireball depends on the fraction of fuel which flashes off and on the further fraction which forms liquid spray.

For propane the relation between the theoretical adiabatic flash fraction and the liquid temperature and vapour pressure is shown in Figure 16.85 (A.F. Roberts, 1981/82). The 35% flash fraction occurs at 21°C and the 50% flash faction at 45°C.

Hasegawa and Sato (1977) found that when the theoretical adiabatic flash fraction reaches 35% virtually all the liquid released burns as a fireball.

From this, A.F. Roberts (1982) derives the relalions

$$f = \frac{M}{M_r} = 0 \quad \phi = 0 \qquad [16.15.3a]$$

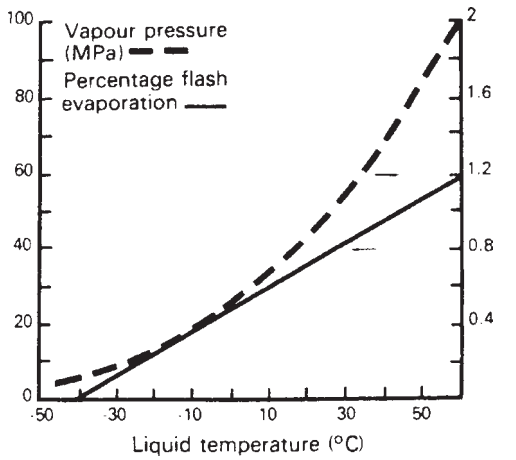


Figure 16.85 *Relation between the theoretical adiabatic flash fraction and temperature and vapour pressure prior to rupture for a fireball (A.F. Roberts, 1981/82). (Reproduced by permission of the Fire Safety Journal)*

$$f = 1 \quad \phi \geq 0.35 \qquad [16.15.3b]$$

where f is the fraction of fuel released entering the fireball, M is the mass of fuel in the fireball (kg), M_r is the mass of liquid released (kg) and ϕ is the fraction of liquid vaporized. Hence by linear interpolation

$$f = \frac{\phi}{0.35} \qquad 0 < \phi < 0.35 \qquad [16.15.3c]$$

This treatment is broadly equivalent to the rule of thumb commonly used for fireballs that the fraction of the fuel released which participates in the fireball is three times the flash fraction. This is the method used by the CCPS (1994/15) to determine the mass of fuel in the fireball.

Both the equations and the rule of thumb just quoted evidently derive from the Hasegawa and Sato's work. An essentially similar approach is taken in the treatment given by V.C. Marshall (1987), as described in Subsection 16.15.20, except that he makes a distinction between summer and winter conditions. Another commonly used, and conservative, approach is to assume that all the fuel released enters the fireball.

16.15.7 Fireball development and timescales

A fireball is of relatively short duration, but it passes in its life cycle through several distinct stages which need to be

carefully defined if confusion is to be avoided. A discussion of these stages and of the associated time scales is given by A.F. Roberts (1981/82).

He distinguishes three distinct stages of fireball development. Stage 1 involves the rapid mixing of the fuel with air and rapid combustion of the fuel and is dominated by the initial momentum of release. In Stage 2, the residual fuel is mixed with air already in the cloud or entrained into it and is burned; this stage is more affected by buoyancy and combustion effects and less by the initial momentum. In Stage 3, with combustion essentially complete the fireball rises due to buoyancy, entraining further air and cooling; in this stage the size may be increasing or decreasing depending on the relative rates of air entrainment and of heat loss. These stages of development are illustrated for a small fireball in Figure 16.86.

Roberts defines five timescales. The time t_a is the duration of combustion in a system dominated by initial momentum effects. The time t_b is the duration of combustion in a system dominated by buoyancy effects, and t_c is the duration of combustion in a system dominated by deflagration effects; these are alternatives to time t_a. The time t_d is that at which visible radiation from the fireball ceases. The time t_e is that at which fireball lift-off occurs. Of the three combustion times, that of prime concern here is t_a which is that applicable to a fireball following bursting of a vessel.

16.15.8 Fireball diameter and duration

Fundamental models of fireballs are given below. The most widely used models, however, are essentially correlations of fireball diameter and duration time, of which there are a considerable number.

Various workers have correlated fireball diameter using a relation of the form

$$D = k_1 M^{n_1} \qquad [16.15.4]$$

where D is the diameter of the fireball (m), k_1 is a constant and n_1 is an index.

An early correlation of fireball diameter is that of R.W. High (1968), who gives

$$D = 9.82\ W^{0.320} \qquad [16.15.5a]$$

where D is the diameter of the fireball (ft) and W is the mass of propellant (fuel + oxidizer) (lb). Roberts converts this equation to

$$D = 2.95\ W^{0.320} \qquad [16.15.5b]$$

where D is the fireball diameter (m) and W is the mass of propellant (kg).

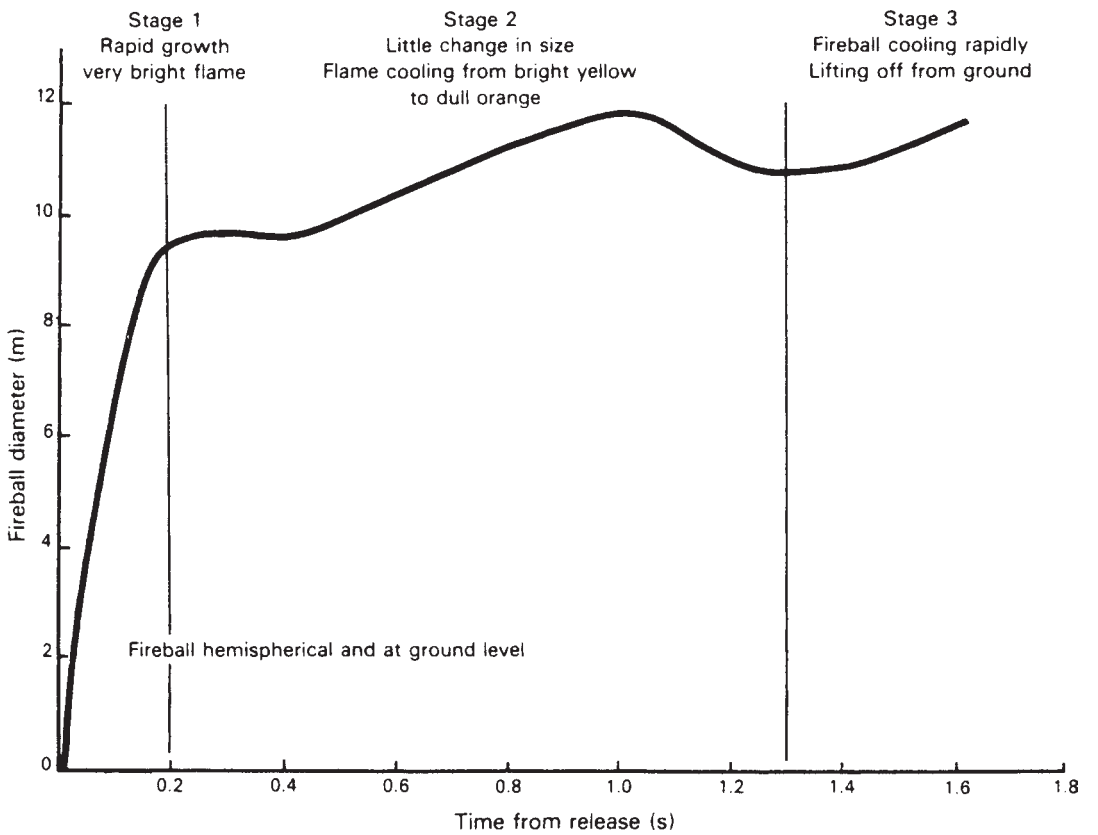


Figure 16.86 *Timescales for the development of a small fireball (A.F. Roberts, 1981/82). (Reproduced by permission of the Fire Safety Journal)*

Hasegawa and Sato (1978) give for their definitive correlation following their second series of tests

$$D = 5.25\,M^{0.314} \qquad [16.15.6]$$

The available experimental data on, and correlations for, fireball diameters have been reviewed by A.F. Roberts (1981/82) who obtained for hydrocarbons the following relation:

$$D = 5.8\,M^{1/3} \qquad [16.15.7]$$

This is now probably the mostly widely used correlation for fireball diameter.

Most correlations of the duration time t_d are of the form

$$t_d = k_2\,M^{n_2} \qquad [16.15.8]$$

where k_2 is a constant and n_2 is an index.

An early equation for duration time is that of R.W. High (1968) who gives the following equation for the persistence time

$$d = 0.232\,W^{0.320} \qquad [16.15.9a]$$

where d is the persistence time (s) and W is the mass of propellant (lb). Roberts converts this to the equivalent relation

$$t_d = 0.49\,M^{0.320} \qquad [16.15.9b]$$

Hasegawa and Sato give equations for the duration time of their first set of experiments with smaller fireballs ($M < 6.1$ kg) and for the combined sets of experiments with smaller and larger fireballs. The exponents in their equations are 0.097 and 0.181, respectively.

These two sets of correlations reflect, therefore, the difference in the exponent discussed in Subsection 16.15.5.

Here it is the fireball from the bursting of a vessel which is of prime interest. From a review of the experimental data and correlations for duration time, Roberts obtains

$$t_d = 0.45\,M^{1/3} \qquad [16.15.10]$$

Equation 16.15.10 is not applicable, however, to larger masses, where the regime is dominated by buoyancy rather than momentum. These different regimes have been described in Subsection 16.15.5 and are treated again in the model of Jaggers, Roper et al. in Subsection 16.15.18. In the buoyancy-dominated regime, the index of M is approximately 1/6 rather than 1/3 as in the momentum dominated regime. The Major Hazards Assessment Panel (MHAP) (1988 LPB 82) has therefore proposed the following modification:

$$t_d = 0.45\,M^{1/3} \quad M < 30{,}000 \qquad [16.15.11]$$

$$t_d = 2.6\,M^{1/6} \quad M > 30{,}000 \qquad [16.15.12]$$

Pietersen (1985) gives for LPG fireballs the correlations

$$D = 6.48\,M^{0.333} \qquad [16.15.13]$$

$$t_d = 0.852\,M^{0.26} \qquad [16.15.14]$$

A summary of correlations of fireball diameter and duration time is given in Table 16.62. Further compar isons of such correlations are given by Bagster and Pitblado (1989), Satyanarayana, Borah and Rao (1991) and the CCPS (1994/15).

16.15.9 Heat radiated

There are three methods of estimating the heat radiated by a fireball. These are based on (1) the heat evolved and radiated, (2) the surface emissive power and (3) the flame temperature and emissivity.

The heat evolved may be obtained from the heat of combustion of the fuel.

For the fraction of heat radiated Roberts states that the work of Hasegawa and Sato suggests a value of the order of 0.25. He also proposes the following relation based on the results of these workers:

$$F_r = 0.27\,P^{0.32} \qquad 1.35 \le P \qquad [16.15.15]$$

where F_r is the fraction of heat radiated and P is the vapour pressure at the moment of release (MPa). He states that extrapolation up to $P = 6$ MPa, about the highest pressure of interest, gives $F_r = 0.48$. A more refined treatment by Roberts is described below.

Another rule of thumb for the fraction of heat radiated is that given by Hymes (1983, SRD R275) which is that the fraction of heated radiated for a vessel bursting below the set pressure of the pressure relief valve may be taken as 0.3 and that for one bursting above this pressure as 0.4.

Table 16.62 *Some correlations of fireball diameter and duration time for hydrocarbons*[a]

Diameter D (m)	*Duration time,* t_d (s)	*Material*	*Reference*
$5.55\,M^{0.333}$	–	Propane	Hardee and Lee (1973)
$6.36\,M^{0.325}$	$2.57\,M^{0.167}$	Hydrocarbons	Fay and Lewis (1977); Hardee, Lee and Benedick (1978)
$5.25\,M^{0.314}$	$1.07\,M^{0.181}$	*n*-Pentane	Hasegawa and Sato[b] (1978)
$5.8\,M^{0.333}$	$0.45\,M^{0.333}$	Hydrocarbons	A.F. Roberts (1981/82, 1982)
$5.88\,M^{0.333}$	$1.09\,M^{0.167}$	Propane	Williamson and Mann (1981)
$5.72\,M^{0.303}$	$0.45\,M^{0.333}$	Butane	Lihou and Maund (1982)
$5.33\,M^{0.327}$	$0.923\,M^{0.303}$	Hydrocarbons	Moorhouse and Pritchard (1982)
$6.48\,M^{0.325}$	$0.852\,M^{0.26}$	LPG	Pietersen (1985)
$5.5\,M^{0.333}$	$0.38\,M^{0.033}$	Hydrocarbons	V.C. Marshall (1987)

[a] *Sources*: Lihou and Maund (1982); Bagster and Pitblado (1989); Satyanarayana, Borah and Rao (1991); and original papers.
[b] These authors' earlier correlation (1977) was $D = 5.28\,M^{0.277}$.

A commonly used value for the fraction of heat radiated from a fireball is 0.3.

Several workers have quoted values of the surface emissive power. Estimates made by Roberts of the heat flux at the surface of the fireballs in the work of Hasegawa and Sato are in the range 141–l96 kW/m^2 with individual values up to 450 kW/m^2. A review of the surface emissive power of fireballs by Moorhouse and Pritchard (1982) concludes that the realistic range is 150–300 kW/m^2. In large-scale experiments on BLEVEs, D.M. Johnson and Pritchard (1991) obtained surface emissive powers in the range 250–350 kW/m^2. Considine, Grint and Holden (1982) use a value of 350 kW/m^2 for hazard assessment. These figures are appreciably higher than those for pool fires.

Based on the work of Roberts, the MHAP give the following relation for surface emissive power:

$$E = 235\,P^{0.39} \quad P \leq 2 \qquad [16.15.16]$$

where E is the surface emissive power (kW/m^2) and P is the pressure (MPa). The limit on pressure given is equivalent to a limit on the surface emissive power of 308 kW/m^2.

A surface emissive power commonly used for fireballs is 350 kW/m^2.

The fraction of heat radiated is used in conjunction with the point source model of a fireball and the surface emissive power is used in conjunction with the solid flame model. The two quantities are not independent but are linked via the surface area of the fireball. Given a fireball diameter, and hence a surface area, a particular value of the surface emissive power implies a corresponding value of the fraction of heat radiated.

With regard to fireball temperature, Roberts states that the values which he derives for the surface emissive power in the work of Hasegawa and Sato, just mentioned, are in the range consistent with flame temperatures of 1000–l400°C, a flame emissivity of unity, and 50–100% excess air. As described in Subsection 16.15.3, Crawley (1982) has used film of an actual fireball to obtain estimates of effective flame temperature of the order of 1100–1200°C.

The proportionalities between the diameter D, the duration time t_d and the mass of fuel M given in Subsection 16.15.8 have an important consequence. The heat generation is proportional to the mass M of the fireball, the heat loss per unit time is proportional to the surface area A, the heat loss at a given fraction of the duration time is proportional to the product At_d, the surface area A is proportional to $M^{2/3}$ and the duration time t_d is proportional to $M^{1/3}$. It follows, according to this model, that for a given fuel the heat radiation and temperature at a given fraction of the duration time are the same for all masses of fuel, or, in other words, that there is a single heat radiation and temperature profile.

16.15.10 Fireball scenarios

Before considering the view factor it is necessary to say something about the scenarios usually considered in the modelling of thermal radiation from a fireball. The approach commonly taken is to assume that the fireball is a sphere with its base just touching the ground and that its diameter and duration are given by one of the sets of correlations just described.

A target close to the fireball may be engulfed by it and it is of interest to know the furthest distance at which engulfment occurs. For this purpose there are two fireball geometries which may be used. One is that of a fireball which is essentially spherical but slightly settled on the ground. This corresponds to the shape of the fireball over most of its life and the engulfment distance approximates to the radius of the fireball. The other geometry is that of a hemispherical fireball. This corresponds to the shape of the fireball during its initial expansion and the engulfment distance then approximates to the radius of this hemispherical fireball, being greater than the spherical case by a factor of about 1.25 ($2^{1/3}$). The period of engulfment in the hemispherical fireball is much shorter.

In the near field estimates of the thermal radiation from a fireball are subject to some inaccuracy.

The set of view factors available for fireballs covers both the near and far fields and includes view factors for targets beneath an elevated fireball. The more complex expressions for the view factor are those applicable to such near field situations.

16.15.11 View factor

For a spherical fireball the thermal radiation intensity at the surface is

$$E = \frac{Q_r}{4\pi r^2} \qquad [16.15.17]$$

where E is the surface emissive power, Q_r is the heat radiated and r is the radius of the fireball.

The heat received I by a target normal to the surface of the fireball is

$$I = \alpha\tau F E \qquad [16.15.18]$$

$$= \frac{\alpha\tau F Q_r}{4\pi r^2} \qquad [16.15.19]$$

$$= \frac{\alpha\tau Q_r}{4\pi l^2} \qquad [16.15.20]$$

where l is the distance between the centre of the fireball and the target, α is the absorptivity of the target and τ is the atmospheric transmissivity. Hence from Equations 16.15.19 and 16.15.20 the view factor F for such a target is

$$F = \frac{r^2}{l^2} \qquad [16.15.21]$$

A set of view factors for fireballs covering other situations has been given by the CCPS (1994/15). For a horizontal surface at a ground distance x the view factor is

$$F = \frac{r^2 h}{(x^2 + h^2)^{3/2}} \qquad [16.15.22]$$

where h is the height of the centre of the fireball *($h \geq r$)* and x is the distance from the point directly beneath the centre of the fireball and the target, or the ground distance.

The corresponding expression for a vertical surface is limited to the case where the surface is not directly beneath the fireball:

$$F = \frac{r^2 x}{(x^2 + h^2)^{3/2}} \quad x > r \qquad [16.15.23]$$

In the far field *($x \approx l \gg h$)* Equation 16.15.23 reduces to Equation 16.15.21.

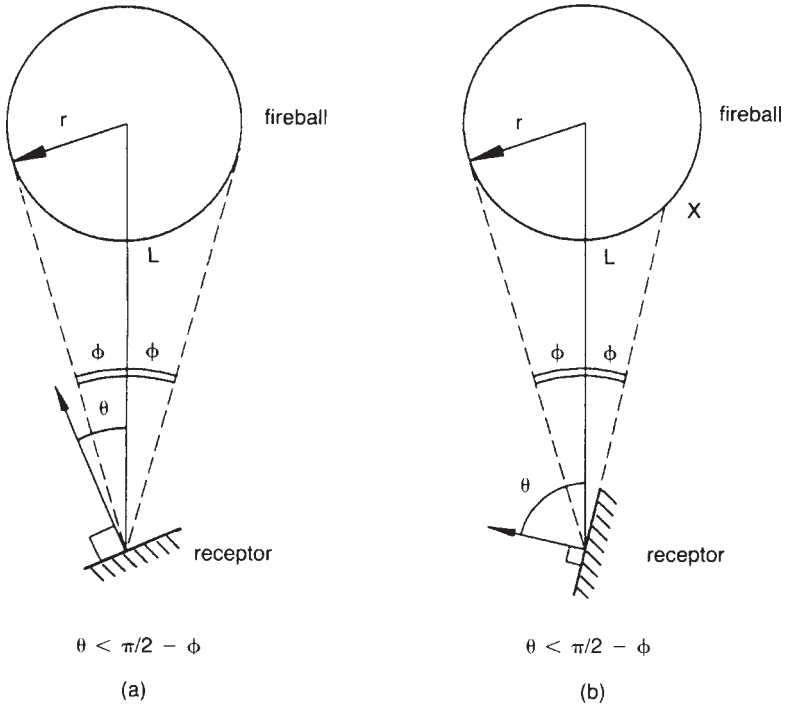


Figure 16.87 *View factor for fireballs (after CCPS, 1994/15): (a) the target 'sees' the whole fireball; and (b) the target 'sees' only part of the fireball (Courtesy of the American Institute of Chemical Engineers)*

For the case where the surface is beneath the fireball expressions exist both for a vertical surface and for a surface of any inclination. The latter is given here as being the more general case. Here two situations have to be considered, as shown in Figure 16.87. In Figure 16.87(a) the target 'sees' the whole fireball, whilst in Figure 16.87(b) it does not, the part of the fireball marked × being out of sight The expressions for the view factor in these two separate cases are

$$F = \frac{r^2}{l^2}\cos\theta \quad \theta \le \frac{\pi}{2} - \phi \qquad [16.15.24]$$

$$F = \frac{1}{2} - \frac{1}{\pi}\sin^{-1}\left[\frac{(l^2 - r^2)^{1/2}}{l\sin\theta}\right] + \frac{r^2}{\pi l^2}\cos\theta \times \cos^{-1}\left[-\frac{(l^2 - r^2)^{1/2}}{r}\cos\theta\right] - \frac{1}{\pi l^2}(l^2 - r^2)^{1/2}(r^2 - l^2\cos^2\theta)^{1/2} \quad \theta > \frac{\pi}{2} - \phi \qquad [16.15.25]$$

The case to which these latter equations apply is a rather special one and, as indicated above, near field estimates are subject to some inaccuracy.

Crocker and Napier (1988a) have given relations for the view factor for a spherical fireball just touching the ground for the three cases of (1) a large vertical target, (2) a differential vertical target and (3) a differential horizontal target. Their expressions are equivalent, respectively, to Equation 16.15.21, or Equation 16.13.103; Equation 16.13.104; and Equation 16.13.105. These authors also treat the case of an elevated fireball.

16.15.12 Point source model

One of the simplest practical models for a fireball is the point source model. For this model the heat received by the target is

$$I = \frac{\alpha\tau F_r Q}{4\pi l^2} \qquad [16.15.26]$$

where Q is the heat release rate (kW).

Hymes (1983 SRD R275) has given a version of this model which effectively incorporates a combustion rate and an allowance for the effect on this of the mass of fuel. Introducing the term α to put the model on the same basis as the previous equation gives

$$I = \frac{2.2\alpha\tau F_r \Delta H_c M^{0.67}}{4\pi l^2} \qquad [16.15.27]$$

where ΔH_c is the heat oc combustion (kJ/kg).

16.15.13 Solid flame model

The other main alternative for practical use is the solid flame model

$$I = \alpha\tau F E \qquad [16.15.28]$$

16.15.14 Fireball modelling

Fireball models in the form of correlations of diameter and duration time have already been described. There are also a number of more fundamental models. Such models include those by Bader, Donaldson and Hardee (1971), Hardee and Lee (1973), Fay and Lewis (1977), Hardee, Lee and Benedick (1978), A.F. Roberts (1981/82, 1982), Williamson and Mann (1981), Lihou and Maund (1982), Jaggers *et al.* (1986), Roper *et al.* (1986) and V.C. Marshall (1987). Some of these models are now described.

16.15.15 Bader, Donaldson and Hardee model

An early fundamental model of a fireball is that by Bader, Donaldson and Hardee (1971). The model is for the fireball of a propellant such as the Saturn fireball. The fireball is assumed to be a homogeneous, isothermal body, which is spherical throughout. Other assumptions are that the rate of addition of propellant is constant, that no air enters the fireball either during or after the reaction period, that all the propellant participates in the reaction, and that the fireball radiates as a black body. For simplicity, it is assumed that the burnout and lift-off times coincide.

For a high temperature fireball such that the difference $\Delta\rho$ between the density of the air ρ_a and the density of the fireball gas ρ is approximated by $\Delta\rho \approx \rho$, the buoyancy force is

$$F_B = \frac{4}{3}\pi r^3 \rho g \qquad [16.15.29]$$

and the fluid resistance force of the fireball gas is

$$F_R = \frac{2}{3}\pi r^3 \rho \left[\frac{2}{r}\left(\frac{dr}{dt}\right)^2 - \frac{d^2r}{dt^2}\right] \qquad [16.15.30]$$

where F_B is the buoyancy force (N/m^2), F_R is the resistance force (N/m^2), g is the acceleration due to gravity (m/s^2), r is the radius of the fireball (m), ρ is the density of the fireball (kg/m^3) and t is time (s). Equating these two equations yields

$$\frac{d^2r}{dt^2} - \frac{2}{r}\left(\frac{dr}{dt}\right)^2 + 2g = 0 \qquad [16.15.31]$$

In this equation the first term is the inertia term and the second the added mass term due to the displacement of air by the gaseous products. The solution of Equation 16.15.31 is

$$r = \frac{g}{3}t^2 \qquad [16.15.32]$$

The radius of the fireball at burnout, and on lift-off, is

$$r_b = \left(\frac{3}{4\pi\rho}\right)^{1/3} W_b^{1/3} \qquad [16.15.33]$$

where r_b is the radius of the fireball at burnout (ft), W_b is the mass of propellant, and therefore of the fireball, at burnout (lb) and ρ is the density of the fireball gas (lb/ft^3). Taking a value of $\rho = 0.0055\ lb/ft^3$ yields

$$r_b = 3.51 W_b^{1/3} \qquad [16.15.34]$$

Combining Equations 16.15.32 and 16.15.33 gives for the burnout time

$$t_b = 0.572\, W_b^{1/6} \qquad [16.15.35a]$$

$$\approx 0.6\, W_b^{1/6} \qquad [16.15.35b]$$

where t_b is the burnout time (s).

For the growth of the fireball

$$R = W/t \qquad [16.15.36]$$

$$= W_b/t_b \qquad [16.15.37]$$

where R is the rate of addition of propellant (lb/s), W is the mass of the fireball (lb), t is time (s) and the subscript b denotes burnout.

From Equations 16.15.35b and 16.15.37

$$R = \frac{5}{3}W_b^{5/6} \qquad [16.15.38]$$

The radius of the fireball may then be written as

$$r = \left(\frac{3Rt}{4\pi\rho}\right)^{1/3} \qquad [16.15.39]$$

where r is the radius of the fireball and ρ is its density. Utilizing Equation 16.15.38

$$r = \left(\frac{5W_b^{5/6}}{4\pi\rho}\right)^{1/2} t^{1/3} \qquad [16.15.40]$$

16.15.16 Hardee and Lee model

Another early fireball model is that by Hardee and Lee (1973). This model applies to the fireball following the rupture of a vessel containing a liquefied flammable gas. The assumptions made reflect those of the model of Bader, Donaldson and Hardee, with the changes necessary to treat the case in hand. It is assumed that a vapour cloud grows into which the rate of addition of fuel is assumed to be constant. Ignition occurs when the mixture is stoichiometric. The fireball is homogeneous, isothermal and spherical. Other assumptions are that all the available fuel is burned, that the fireball radiates as a black body, and that the burnout and lift-off times coincide. The model given is similar to that of Bader. Donaldson and Hardee and includes Equations 16.15.33, 16.15.35b, 16.15.38 and 16.15.40.

The authors obtain for a propane fireball a relation equivalent in SI units to

$$D = 5.55 M^{1/3} \qquad [16.15.41]$$

where D is the diameter of the fireball (m) and M is the mass of fuel (kg).

This model has been further developed by Hardee, Lee and Benedick (1978), who apply it to a fireball of LNG. Equation 16.15.35b may be rewritten in SI units as

$$t_b = 0.684\, W_b^{1/6} \qquad [16.15.42]$$

and then as

$$t_b = 0.684(W_b/W_f)^{1/6} W_f^{1/6} \quad [16.15.43]$$

where t_b is the burnout time (s), W_b is the mass of the fireball, including air, at burnout (kg), W_f is the mass of fuel (kg). For a stoichiometric mixture of methane and air $W_b/W_f = 18.3$. Substituting this value in Equation 16.15.43 yields

$$t_b = 1.11\, W_f^{1/6} \quad [16.15.44]$$

Further, taking the density ρ as $0.160\,kg/m^3$ and the value of W_b/W_f as 18.3, and utilizing Equation 16.15.44 in Equation 16.15.40 yields

$$r = 3.12\, W_f^{1/2} \quad [16.15.45]$$

where r is the radius of the fireball (m).

The resulting correlations for fireball diameter and duration time are therefore

$$D = 6.24\, M^{0.333} \quad [16.15.46]$$

$$t_b = 1.11 M^{0.167} \quad [16.15.47]$$

A critique of this model of an LNG fireball has been given by Gillette (1980), who makes detailed criticisms of the model itself and suggests that for LNG the occurrence of 'fireballs' is a speculation.

16.15.17 Fay and Lewis model

The model by Fay and Lewis (1977) is applicable to the quite different situation of a fireball formed from a compact, stationary cloud of pure fuel vapour ignited at the edge. In this scenario, the combustion products move upwards, promoting mixing with the air. When the volume of these products becomes comparable with the initial volume of the vapour, the mixture of fuel, air and products begins to rise, burning more vigorously as it accelerates, consuming virtually all the fuel.

In modelling the combustion, it is assumed that the volume of the unburned vapour is negligible compared with that of the products. Thus, for example, the volume of the products of the stoichiometric, adiabalic combustion of methane is 83 times that of the fuel vapour.

The authors state that it can be shown by dimensional analysis that the following proportionalities hold;

$$r_p \propto g t^2 \quad [16.15.48]$$

$$r_p \propto V_f^{1/3} \quad [16.15.49]$$

$$z_p \propto V_f^{1/3} \quad [16.15.50]$$

$$t_p \propto V_f^{1/6}/g^{1/2} \quad [16.15.51]$$

where r is the radius of the cloud, t is the time, V_f is the volume of the initial cloud of fuel, z is the height of the centre of the cloud and subscript p denotes the products.

The growth of the cloud is modelled drawing on the entrainment hypothesis of B.R. Morton, Taylor and Turner (1956). The volumetric rate of growth is taken as being proportional to the product of the local surface area and the local rise velocity:

$$\frac{d}{dt}\left(\frac{4}{3}\pi r^3\right) = \beta 4\pi r^2 \frac{dz}{dt} \quad [16.15.52]$$

where, β is the entrainment coefficient. The order of magnitude of β is one.

Integrating Equation 16.15.52 with the boundary conditions $r = 0; z = 0$ yields

$$r = \beta z \quad [16.15.53]$$

Hence

$$z = \frac{1}{\beta}\left(\frac{3V}{4\pi}\right)^{1/3} \quad [16.15.54]$$

Equating the forces of buoyancy and of the rate of change of vertical momentum

$$\frac{d}{dt}\left[\frac{4}{3}\pi r^3 \rho_p \left(\frac{dz}{dt}\right)\right] = \frac{4}{3}\pi r^3 g(\rho_a - \rho_p) \quad [16.15.55]$$

where ρ_a is the density of air.

Utilizing Equation 16.15.52 in the integration of Equation 16.15.55 gives

$$r = \frac{g\beta}{14}\left(\frac{\rho_a - \rho_p}{\rho_p}\right) t^2 \quad [16.15.56]$$

Hence

$$t = \left[\frac{14\rho_p}{g\beta(\rho_a - \rho_p)}\right]^{1/2} \left(\frac{3V}{4\pi}\right)^{1/6} \quad [16.15.57]$$

where V is the volume of the fireball.

The radius r, height z and duration t have their maximum values when the cloud volume V equals the volume V_p of the combustion products. For a hydrocarbon C_nH_m

$$V_p = \left[\frac{m\phi + 4.762(4n + m)}{4\phi}\right]\left(\frac{T_p}{t_r}\right) V_f \quad [16.15.58]$$

where T_p is the absolute temperature of the products, T_r is that of the reactants, V_f is the volume of the fuel, V_p is that of the products and ϕ is the equivalence ratio.

The authors treat β and ϕ as parameters to be determined. From soap bubble experiments they obtain for the entrainment coefficient an average value of β = 0.285. Tliis is in reasonable agreement with the values given by Morton, Taylor and Turner. For the equivalence ratio the average value is ϕ = 0.217, which corresponds to about 4.5 times the stoichiometric amount of air.

16.15.18 Jaggers, Roper *et al.* model

Studies of the conditions under which the buoyancy and momentum regimes apply have been described by Jaggers, Roper and co-workers (Jaggers *et al.*, 1986; Roper *et al.*, 1986).

Jaggers *et al.* (1986) give a set of relations based on dimensional analysis. For the case where the release velocity is low and buoyancy forces dominate those of momentum, they obtain

$$t_b \propto \frac{1}{g^{1/2}}\left(\frac{M}{\rho_a}\right)^{1/6} \quad [16.15.59]$$

whilst for the other limiting case where the release velocity is high and momentum forces dominate those of buoyancy

$$t_b g^{1/2}\left(\frac{\rho_a}{M}\right)^{1/6} \propto \frac{g^{1/2}}{v_o}\left(\frac{\rho_a}{M}\right)^{-1/6} \quad [16.15.60]$$

Hence

$$t_b \propto \frac{1}{v_o}\left(\frac{M}{\rho_a}\right)^{1/3} \quad [16.15.61]$$

where M is the mass of fuel, t_b is the burning time, v_o is the mean release velocity and ρ_a is the density of air. The mean release velocity v_o is defined as the ratio of the initial momentum of the release to the mass of fuel released.

16.15.19 Roberts model

The fireball model which is most widely used is probably that of A.F. Roberts (1981/82, 1982). The model comprises both fundamental and correlation models and covers the whole range of features of practical interest.

Fireball development

Roberts takes as his starting point for fireball growth the model by Hardee and Lee (1973). From this he obtains for a hemispherical fireball

$$r = \left(\frac{4\alpha M t}{\pi \rho_a}\right)^{1/4} \quad [16.15.62]$$

$$\frac{dr}{dt} = \left(\frac{\alpha M}{64\pi\rho_a}\right)^{1/4} t^{-3/4} \quad [16.15.63]$$

$$V = \frac{2\pi}{3}\left(\frac{4\alpha M t}{\pi\rho_a}\right)^{3/4} \quad [16.15.64]$$

where M is the mass of fuel released (kg), r is the cloud radius (m), t is the time (s), V is the cloud volume (m^3), α is the momentum per unit mass (m/s) and ρ_a is the density of air (kg/m^3).

The concentration of the fuel may be determined from the mass released M and from the volume V of the cloud.

The term α is a function of the vapour pressure of the liquid in the vessel prior to failure. For a vapour pressure less than the atmospheric pressure, $\alpha = 0$. For propane at 28°C and a vapour pressure of 1 MPa, $\alpha = 220$ m/s.

For propane, the cloud volume given by Equation 16.15.64 may be written as

$$V = 118(Mt)^{3/4} \quad [16.15.65]$$

Since for propane at the lower flammability limit the volume of the cloud is approximately $30M$, the lime t' required for the cloud to fall below the lower flammability limit (s) is

$$t' = \frac{35}{\alpha}M^{1/3} \quad [16.15.66]$$

Some typical values for this time are

M (kg)	α (m/s)	t' (s)
1,000	220	1.6
100,000	220	7.4

The time t_g required for the transition from a regime dominated by momentum effects to one dominated by gravitational slumping is derived by Roberts from the work of Jagger and Kaiser (1981). The criterion given for transition is

$$N = \frac{gr\Delta\rho}{\rho_a(dr/dt)^2} = 1 \quad [16.15.67]$$

where $\Delta\rho$ ($=\rho_v - \rho_a$) is the density difference between of the vapour and the air (kg/m^3).

For the Hardee and Lee model

$$N = g\frac{(\rho_v - \rho_a)}{\rho_v}\frac{6t}{\alpha} \quad [16.15.68]$$

Then for $N = 1$

$$t_g = \frac{\rho_v}{6g(\rho_v - \rho_a)}\alpha \quad [16.15.69]$$

where t_g is the time to the transition from control by momentum to control by gravity slumping (s).

For propane from Equation 16.15.68 and with $N = 1$

$$t_g = 0.05\alpha \quad [16.15.70]$$

Fireball volume and diameter

For the fireball volume and diameter Roberts gives the following treatment. The volume V of the fireball at the mean temperature T_f is

$$V = \frac{M_a + M_f}{\rho_f} \quad [16.15.71]$$

$$= \frac{(M_a + M_f)T_f}{\rho_o T_o} \quad [16.15.72]$$

and the enthalpy H is

$$H = c(M_a + M_f)(T_f - T_o) \quad [16.15.73]$$

where c is the specific heat (kJ/kg K), H is the enthalpy rise of the fireball (kJ), M_a is the mass of air in the fireball (kg), M_f is the mass of fuel in the fireball (kg), T_f is the absolute mean temperature of the fireball (K), T_o is the absolute initial temperature of the reactants (K), ρ_f is the density of the products at temperature T_f (kg/m^3) and is the density of the products at temperature T_o (kg/m^3).

Then from Equations 16.15.72 and 16.15.73

$$V = \frac{M_a + M_f}{\rho_o}\left[1 + \frac{H}{T_o c(M_a + M_f)}\right] \quad [16.15.74]$$

and hence

$$D = \left\{\frac{6}{\pi}\left[1 + \frac{H}{T_o c(M_a + M_f)}\right]\frac{M_a/M_f + 1}{\rho_o}\right\}^{1/3} M_f^{1/3} \quad [16.15.75]$$

where D is the diameter of the fireball (m).

Different relations are required for the enthalpy H, depending on whether the mixture is fuel or oxygen rich. If R is the value of the ratio M_a/M_f for the stoichiometric mixture, then

$$H = \frac{\eta M_a Q}{R} \qquad \frac{M_a}{M_f} < R \text{ (fuel rich)} \qquad [16.15.76a]$$

$$H = \eta M_f Q \qquad \frac{M_a}{M_f} > R \text{ (oxygen rich)} \qquad [16.15.76b]$$

where Q is the heat of combustion (kJ/kg) and η the thermal efficiency. The thermal efficiency η takes account of heat losses during growth to the maximum diameter and losses due to unburned fuel.

Roberts uses Equation 16.15.75 to explore the effect of the air/fuel ratio parameter M_a/RM_f and the thermal efficiency η on the constant k_1 in Equation 16.15.4 for fireball diameter. The value of this constant is 5.8 for $M_a/RM_f = 1$ and $\eta = 1$ and it is relatively insensitive to M_a/RM_f over the range 0.8–3.0 and to η over the range 0.75–1.0.

Duration time

Roberts, argues that the behaviour of larger fireballs ($M > 5$ kg) appears to differ from that of smaller ones, and obtains for larger fireballs only the relation

$$t_d = 0.83\, M^{0.316} \qquad [16.15.77]$$

where t_d is the duration time (s).

The experimental correlations for duration time t_d therefore lie between Equation 16.15.10 and the relation

$$t_d = 0.90\, M^{1/3} \qquad [16.15.78]$$

The data of Baker also lie between the lines given by Equations 16.15.10 and 16.15.78. The relation recommended by Roberts for the duration time t_d is Equation 16.15.10.

For the lift-off time t_e Roberts quotes the equation given by Hardee and Lee

$$t_e = 1.1\, M^{1/6} \qquad [16.15.79]$$

where t_e is the lift-off time (s). Lift-off is determined by buoyancy effects and the exponent of 1/6 is well established for such effects.

The exponent of $\frac{1}{6}$ in Equation 16.15.79 for lift-off time t_e compares with that of $\frac{1}{3}$ in Equation 16.15.10 for the duration time t_d. Thus the lift-off time t_e may be less or greater than the duration time t_d. Roberts quotes the following typical figures obtained from these equations:

M (kg)	t_d(s)	t_e(s)
200	2.6	2.6
50,000	16	6.7

Thus for smaller fireballs combustion will tend to be complete before lift-off occurs, while for larger ones lift-off will tend to occur while combustion is still taking place. It is the duration time t_d which is used to characterize the period during which the fireball radiates heat.

Heat radiated

In the model given by Roberts for heat radiation from the fireball, it is assumed that such radiation occurs as a square wave pulse of duration t_d. The basic equation for heat radiation is

$$Q_r = \frac{F_r M \Delta H_c}{t_d} \qquad [16.15.80]$$

where ΔH_c is the heat of combustion (kJ/kg), F_r is the fraction of heat radiated and Q_r is the heat radiation rate (kW).

The intensity of thermal radiation at a target, neglecting target absorptivity and atmospheric transmissivity effects, is then

$$I = \frac{Q_r}{4\pi l^2} \qquad [16.15.81]$$

where I is the radiation intensity received by a target perpendicular to the direction of radiation (kW/m^2) and l is the distance from the centre of the fireball to the target (m). The relation between the term $(1/4\pi l^2)$ in Equation 16.15.81 and the view factor is given in Subsection 16.15.11.

Roberts' treatment of the fraction F_r of heat radiated has already been described, but for completeness is restated here. He quotes values in the range 0.2–0.4 as typical of both pool fires and fireballs. He also analyses the data of Hasegawa and Sato (1978), shown in Figure 16.88, and derives from these a relation between the heat radiation factor and the vapour pressure prior to rupture

$$F_r = 0.27\, P^{0.32} \qquad [16.15.82]$$

where F_r is the fraction of heat radiated and P is the vapour pressure just prior to rupture (MPa).

Equation 16.15.82 is thus derived for data with vapour pressures up to 1.3 MPa, but Roberts suggests it may be extrapolated up to 6 MPa at which pressure the value of F_r is 0.48.

Summary

Roberts' model for a fireball from a bursting vessel may be summarized as follows. The mass of fuel in the fireball is given by Equation 16.15.3, the diameter of the fireball by Equation 16.15.7, the duration time of the fireball by Equation 16.15.10, the fraction of heat radiated by Equation 16.15.82, the total heat radiated by Equation 16.15.80, and the thermal radiation received by the target (neglecting the target absorptivity and atmospheric transmissivity effects) by Equation 16.15.81.

16.15.20 Marshall model

Another model which is readily applied to practical situations is that by V.C. Marshall (1987). This model is based essentially on correlations for diameter and duration time, but again deals with the other features of practical interest.

The model may be summarized as follows. For the mass of fuel in the fireball

$$M = 2\phi M_s \quad \text{Winter} \qquad [16.15.83a]$$

$$M = 3\phi M_s \quad \text{Summer} \qquad [16.15.83b]$$

where M is the mass of fuel entering the fireball (te), M_s is the mass of fuel in the vessel (te) and ϕ is the theoretical adiabatic flash fraction (TAFF).

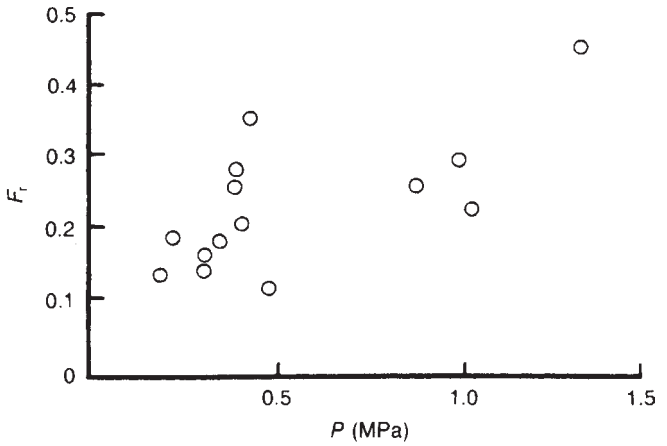


Figure 16.88 *Relation between the fraction of heat radiated and the vapour pressure prior to rupture for a fireball (A.F. Roberts, 1981/82). Data from Hasegawa and Sato (1978); 6.2 kg of pentane in each test (Reproduced by permissionof the Fire Safety Journal)*

The radius and duration time of the fireball are

$$R_{FB} = 27.5\,M^{1/3} \quad [16.15.84]$$

$$D_{FB} = 3.8\,M^{1/3} \quad [16.15.85]$$

where D_{FB} is the duration time of the fireball (s) and R_{FB} is its radius (m).

The heat released and fraction of heat radiated are

$$E_T = HM \quad [16.15.86]$$

where E_T is the heat released (J) and H is the heat of combustion (J/te). The fraction F_r of heat radiated is taken as 0.3.

The radiative power and radiative power density are then

$$P_{FB} = E_T F_R / D_{FB} \quad [16.15.87]$$

$$P_D = P_{FB} / V_{FB} \quad [16.15.88]$$

where P_D is the radiative power density (W/m^3), P_{FB} is the radiative power (W) and V_{FB} is the volume of the fireball (m^3).

The thermal radiation intensity is

$$I_T = \frac{P_{FB}}{4\pi R_T^2} \quad [16.15.89]$$

where I_T is the unattenuated thermal radiation at the radius where the target is located (W/m^3) and R_T is the distance from the centre of the fireball to the target (m). The effective surface temperature is

$$T_e = \left[\frac{E_T F_R}{\sigma D_{FB}(4\pi R_{FB}^2)}\right]^{1/4} \quad [16.15.90]$$

where T_e effective fireball temperature (K) and σ is the Stefan–Boltzmann constant.

The atmospheric attenuation is given by

$$\tau = X - 0.12 \log_{10} R_T \quad [16.15.91]$$

where τ is the atmospheric transmissivity and X is a parameter. The values of X are 1.0, 0.96 and 0.92 for relative humidities of 0.2, 0.5 and 1.0, respectively.

The thermal radiation received by the target is then

$$I_{TA} = \tau I_T \quad [16.15.92]$$

where I_{TA} is the thermal radiation received by the target, taking account of attenuation by the atmosphere (W/m^2).

Taking for hydrocarbons a heat of ombustion of 47 MJ/kg yields

$$E_T = 47 \times 10^9\,M \quad [16.15.93]$$

$$P_{FB} = 1.24 \times 10^{10} F_r M^{2/3} \quad [16.15.94]$$

$$I_T = 2.94 \times 10^8\,M^{2/3}/R_T^2 \quad [16.15.95]$$

As an illustration, consider the example given by Marshall of the fireball from a release of 20 te of propane. Then

$M = 20$ te
$H = 47 \times 10^9$ J/te
$R_{FB} = 74.6$ m
$D_{FB} = 10.3$ s
$E_T = 9.4 \times 10^{11}$ J
$F_R = 0.3$
$P_{FB} = 2.73 \times 10^{10}$ W
$I_T = 2.17 \times 10^9/R_T^2$

16.15.21 CCPS method

A model for a fireball was given in the CCPS *QRA Guidelines* (1989/5). A summary of this model has been published by Prugh (1994). A more recent model is that included in the

CCPS *Fire and Explosion Model Guidelines* (1994/5), where it is included as part of the treatment of BLEVEs.

The method covers the following features: (1) the mass of fuel participating in the fireball, (2) the diameter and duration of the fireball, (3) point source and solid flame models of the fireball, (4) the surface emissive power of the fireball, (5) the view factor and (6) the atmospheric transmissivity.

The mass of fuel in the fireball is taken as three times the flash fraction or, if this figure exceeds unity, the mass released. For the fireball diameter and duration, use is made of Roberts' equations (Equations 16.15.7 and 16.15.11 or 16.15.12).

Both point source and solid flame models are used. For the point source method use is made of Hymes' Equation 16.15.2. For the solid flame method Equation 16.15.28 is used in conjunction with a surface emissive power of 350 kW/m^2.

The view factors are those attributed to the CCPS in Subsection 16.15.11, especially Equation 16.15.23.

The atmospheric transmissivity is taken in the sample problem as unity, although several relationships are given for it.

The *Guidelines* give a sample problem involving BLEVE of a tank truck containing propane, for which two treatments are presented, one using the point source model and the other using the solid flame model.

16.15.22 Congested fireballs

A type of fireball which somewhat resembles one arising from a BLEVE is that which can occur following sudden rupture of a vessel, such as a reactor, with release of flammable contents and immediate ignition. An instance of this is given by Cates (1992), who terms the incident which he describes a 'congested fireball'. Since such an event gives an appreciable overpressure, it is considered in Chapter 17.

16.15.23 Fireballs on pipelines

An account of a fireball and a subsequent jet flame resulting from the rupture of a pipeline containing liquefied propane has been given by Hirst (1984, 1986). The photographs show at −10 s an unignited cylindrical cloud, at 1 s partial ignition, at 3 s a mushroom cloud and at 8 s an elongated jet flame. This work is described in IE. more detail in Section 16.19.

16.16 Fireballs from Explosives

The models just given are for fireballs of hydrocarbons. There may also be a requirement for a model of the fireball from a condensed phase explosive. There is a limited amount of information available on the fireballs from solid and liquid propellants and from high explosives. Accounts of work in this area are given by Jarrett (1952), Gayle and Bransford (1965), Rakaczky (1975), Stull (1977), Mallory (1980), Kovar *et al.* (1982), W.E. Baker *et al.* (1983) and Gilbert, Lees and Stilly (1994d).

16.16.1 Fireball incidents

Not surprisingly, data on the features of fireballs in incidents involving the explosion of high explosives are sparse. An exception is the explosion which occurred in Peterborough in the United Kingdom in 1989 on a truck carrying commercial explosives. According to the report by the HSE (1990c) the load was essentially nitroglycerine-based explosives with a total mass of some 800 kg. From the fact that one fireman was engulfed in flames at a distance of 18 m and another suffered slight burns at 25 m, the fireball diameter was taken as approximately 36 m.

16.16.2 Experimental studies

The experimental studies of main relevance here are the relatively large-scale tests done by Jarrett (1952) on fireballs from solid propellants and by Gayle and Bransford (1965) on fireballs from liquid propellants. This work is described below. There are also a number i of laboratory studies such as those by Mallory (1980) and Kovar *et al.* (1982).

16.16.3 Empirical features

Fireballs from high explosives tend to be of shorter duration than those of hydrocarbons for a given mass. Further, the mass involved in accidents tends to be less. Generally, therefore, the duration time of the fireball is short. The fireball diameter also appears to be less than for the same mass of hydrocarbons. On the other hand, the fireball temperatures are appreciably higher, particularly in the early stages.

16.16.4 Fireballs of munitions

For munitions fireballs, W.E. Baker *et al.* (1983) quote the following model by Rakaczky (1975). For the diameter

$$D = 3.76\, M^{0.325} \qquad [16.16.1]$$

and for the duration time

$$t_d = 0.258\, M^{0.349} \qquad [16.16.2]$$

where D is the diameter of the fireball (m), M is the mass of chemicals (kg) and t_d is the duration time (s).

Baker *et al.* state that these relations were obtained by fitting data from the literature, but no limits of applicability are given and the equations should be used with caution.

16.16.5 Fireballs of solid propellants

An investigation of the fireball from solid propellants has been described by Jarrett (1952). The work was done in connection with the storage of explosives. Its purpose was to determine the maximum extent of flame travel at ground level when a store of propellant explodes. Experiments were conducted with quantities of cordite in the range 50−175,000 lb.

For the flame radius at ground level, correlations were obtained which may be written as

$$D = 0.906\, M^{0.38} \quad \text{Peripheral ignition} \qquad [16.16.3]$$

$$D = 0.906\, M^{0.44} \quad \text{Central ignition} \qquad [16.16.4]$$

16.16.6 Fireballs of liquid propellants

In another early study, Gayle and Bransford (1965) described an investigation of the fireballs from liquid propellants and from high explosives, based on a literature survey and measurements taken from photographs in experimental work. The propellents considered were RP-1/LOX, LH_2/LOX, RP-1/LH_2/LOX and N_2O_4/UDMH-hydrazine (LH_2, liquid hydrogen; LOX, liquid oxygen). These liquid propellants are therefore strictly bipropellants incorporating their own oxidizer for combustion. The high explosive tests are considered further below.

Gayle and Bransford comment that the fireball diameters for the liquid propellants were governed almost exclusively by the mass involved. The diameters effectively obeyed the cube root law.

They state further that there was little difference in the diameters of the fireballs from the liquid bipropellants and from high explosives. They give separate equations for the diameter of the fireball for individual liquid bipropellants and the following equation for the combination of liquid bipropeliants and high explosives:

$$d = 9.56\ W^{0.325} \qquad [16.16.5]$$

where d is the diameter of the fireball (ft) and W is the mass of material (fuel + oxidizer) (lb). In SI units

$$D = 3.77\ M^{0.325} \qquad [16.16.6]$$

The duration times of the fireballs were relatively variable. These authors attribute this partly to variations in photographic variables and partly to the difficulty of defining the end of the visible fireball in an unambiguous manner. For the combined set of liquid bipropeliants *V.* they give for the duration time:

$$t_d = 0.196\ W^{0.349} \qquad [16.16.7]$$

where W is the mass of material (fuel + oxidizer) (lb). In SI units

$$t_d = 0.258\ M^{0.349} \qquad [16.16.8]$$

where M is the mass of material (fuel + oxidizer) (kg).

The duration times of the high explosive fireballs were appreciably shorter, but no correlation is given.

For liquid bipropellants, R.W. High (1968) has given the following model:

$$d = 0.82\ W^{0.320} \qquad [16.16.9]$$

$$t_d = 0.232\ W^{0.320} \qquad [16.16.10]$$

where W is the mass of bipropellant (lb). In SI units

$$D = 3.86\ M^{0.320} \qquad [16.16.11]$$

$$t_d = 0.299\ M^{0.320} \qquad [16.16.12]$$

High gives graphs showing experimental data for the diameter and duration time of a number of liquid bipropeliants together with his correlation lines. The data cover the range $10-10^5$ kg.

Fireballs from liquid propellants are one of the hazards reviewed in the *Hazards of Chemical Rockets and Propellants Handbook* (Jensen, 1972). The authors quote Equations 16.16.6 and 16.16.8 from the work of Gayle and Bransford and give some additional results, as described below.

They make the point that the firebaH can be very asymmetrical. The Titan test with 100,000 lb of RP-1/LOX gave maximum horizontal dimensions of 800–1000 ft, whereas the equivalent diameter from Equation 16.16.5 is some 400 ft.

They describe work on fireballs in Project Pyro and quote the following equations for the duration time of experiments done with 25,000 lb of liquid bipropellants:

$$t_d = 0.113\ W^{0.333} \qquad \mathrm{RP-1/LOX} \qquad [16.16.13]$$

$$t_d = 0.077\ W^{0.333} \qquad \mathrm{LH_2/LOX} \qquad [16.16.14]$$

They also describe further work on fireballs of propellant ANB-3226, which has a mass fraction of 69% oxidizer and 15% aluminium, in Project Sophy and give tabulated data.

There are several points of interest in the data given. The ratio of the maximum height of the fireball to its maximum diameter is an indication of the extent to which it undergoes a transition from hemispherical to spherical shape. This ratio is in the range 1.5–2.4. In other words, in most cases the fireball grows to a nearly spherical shape. The times to maximum diameter and to maximum height, and the ratio of these to the duration time are also significant. The ratio of the time to maximum height to the time to maximum diameter is generally of the order of 3, but can vary between 1.5 and nearly 10. If the ratio of the time to maximum diameter to the duration time is considered, this tends to be small, typically in the range 0.03–0.15.

16.16.7 Fireballs of high explosives

There is relatively little in the literature by way of models for high explosive fireballs. The high explosive experiments of Gayle and Bransford (1965), mentioned earlier, consisted of some 14 explosions involving TNT, Composition C-4 and pentolite. For the fireballs from these explosions they obtained the following equation:

$$d = 8.50\ W^{0.341} \qquad [16.16.15]$$

where d is the diameter (ft) and W is the mass of explosive (lb). The quantities of explosive were in the range $3-10^6$ lb. In SI units

$$D = 3.3\ M^{0.341} \qquad [16.16.16]$$

As stated above, Gayle and Bransford did not give a correlation for the duration time of a high explosive fireball. They give some limited data which indicate that for a mass of explosive of 23 kg the duration time obtained was 0.23 s.

Stull (1977) quotes for TNT the following model:

$$d = 0.5\ W^{0.333} \qquad [16.16.17]$$

$$t_d = 0.23\ W^{0.333} \qquad [16.16.18]$$

He gives for these correlations two separate sources: for fireball diameter, the work of van Dolah and Burgess (1968); and for the fireball duration, that of Strehlow and Baker (1975).

Not all the models quoted are original. High quotes the work of Gayle, prior to publication of the report by Gayle and Bransford, and his model, although not the same as that of the latter authors, appears to be based on some of their data. The model given by Rakaczky appears to be the one by Gayle and Bransford. The model of Stull also is very similar to that by Gayle and Bransford.

16.16.8 Fireball temperature

According to W.E. Baker *et al.* (1983), typical fireball temperatures are

Hydrocarbons	1350 K
Solid propellants	2500 K
Liquid propellants	3600 K
High explosives	5000 K

These authors suggest that the Rakaczky model is probably applicable to fireballs with temperatures of 2500 K. They also state that a temperature of 2500 K is typical of gun propellant fireballs. Gilbert, Silly and Lees infer that Rakaczky's model applies to gun propellant rather than liquid propellant or high explosive fireballs.

The temperatures of fireballs of liquid bipropellants are discussed by R.W. High (1968). He gives as typical a temperature of 2400 K. He also quotes computed values of 2690 and 2610 K, assuming unity and estimated emissivities, respectively. The *Rocket and Propellants Handbook* (Jensen, 1972) quotes temperatures of 2300 K obtained in Project Pyro for liquid bipropellants.

The temperatures given by Baker *et al.* for propellants and high explosives appear high.

16.16.9 Gilbert, Lees and Scilly model

A model for the fireball from a high explosive has been given by Gilbert, Lees and Scilly (1995d). The model is based partly on theoretical and partly on empirical considerations.

The combustion processes in the fireball pass through two stages: (1) detonation and (2) combustion of the detonation products. The first stage is very rapid.

The growth of the fireball passes through several all stages: (1) expansion following detonation; (2a) growth to the maximum diameter as a hemisphere; (2b) formation of a sphere at ground level, lift-off and rise to maximum height as a sphere and (3) persistence at this height as a sphere until cooled.

Following detonation, air is entrained in the fireball. For oxygen deficient explosives, this air provides the oxygen required for secondary combustion of the products. The air contributes to the growth of the fireball.

It is assumed in the model that the time t_c to complete combustion is equal to the time t_s for the fireball to form the maximum size hemisphere on the ground. In other words, the end of Stage 2 of the combustion processes is taken as the end of Stage 2a of the growth process.

The model consists of relations for the diameter and the duration time of the fireball and for the profile of shape and temperature with time, and has three stages. In Stage 1 the detonation reaction occurs and gives the gaseous detonation products without admixture of air. In Stage 2 the detonation products undergo complete combustion with entrained air, except that for oxygen deficient explosives some solid carbon survives, the amount being a function of the extent of the deficiency. In Stage 3 the air entrainment decreases gradually to zero and the fireball cools. The model gives the diameter of the fireball and its temperature from the end of the detonation stage onwards.

The differences in the diameters of the fireballs in the hemispherical and spherical stages are not large. The temperatures range from approximately 2000–4200 K at the end of Stage 1 to 1150–2500 K in Stage 2.

In the overall model, the relations for the diameter and the duration time are based on the empirical models described above. The relation for the diameter is cross-checked with the heat balance model. The relations given in the model for the diameter and duration time of the fireball of a high explosive are

$$D = 3.5\, M^{0.333} \qquad [16.16.19]$$

$$t_d = 0.3\, M^{0.333} \qquad [16.16.20]$$

Equation 16.16.19 is applicable to any high explosive. Equation 16.16.20 is specific to explosives similar in oxygen balance to TNT.

For the profile of the shape and temperature the approach taken is as follows. The time required for the fireball to reach its maximum diameter is a small fraction of the total duration time. The authors define a time t_s at which the shape of the fireball changes from the maximum diameter hemisphere to a sphere, still at ground level:

$$t_s = \phi t_d \qquad [16.16.21]$$

where ϕ is a fraction. They use a value for ϕ of 0.25.

The temperature profile of the fireball is obtained from a heat balance model. In this model the detonation is taken as virtually instantaneous and the adiabatic flame temperature is determined. For an explosive which is oxygen deficient it is assumed that the rate of release of the remaining energy and the rate of entrainment of air are constant from time zero to time t_s. At time t_s combustion ceases, although air continues to be entrained at a linearly diminishing rate falling to zero at t_d. The temperature at the termination of the fireball T_f is taken as 1150 K.

The authors give for four explosives the generalized temperature profiles shown in Figure 16.89. These profiles are expressed as functions of the duration time calculated from Equation 16.16.20. This equation applies to TNT, and for this explosive the duration time is used directly. For the other explosives, an effective duration may be obtained from the graphs using a suitable value of the termination temperature T_f, taken as 1150 K.

As stated earlier, it is an implication of the values of the indices in the pair of Equations 16.16.19 and 16.16.20 that for a given explosive the temperature and thermal radiation at a given fraction of the duration time are the same for all masses of explosive.

The authors note that in the example which they give for a fireball of TNT that the fraction of heat radiated over the duration time is about 0.44.

A comparison between the diameter of the fireball in the Peterborough incident with that predicted by the model, as given in Equation 16.16.19, gives a predicted value of 33 m (spherical) or 40 m (hemispherical) compared with an apparent observed value of 36 m.

16.17 Pool Fires

A pool fire occurs when a flammable liquid spills onto the ground and is ignited. A fire in a liquid storage tank is also a form of pool fire, as is a trench fire. A pool fire may also occur on the surface of flammable liquid spilled onto water.

There is a considerable literature on pool fires, including the work of Burgoyne and Katan (1947), Rasbash, Rogowski and Stark (1956), Blinov and s Khudiakov (1957), Hottel (1959), Burgess and Zabetakis (1962 BM RI 6099), Welker and Sliepecevich (1965). P.M. Thomas (1963), P.H. Thomas, Pickard and Wraight (1963), A.F. Roberts (1966, 1971b), Werthenbach (1971a,b, 1973), Yumofo (1971b), A.R. Hall (1972, 1973), de Ris and Orloff (1972), L.E. Brown, Wesson and Welker (1974a, b, 1975), Seeger (1974), Escudier (1975), Modak (1977, 1978, 1981), Raj, Moussa and Aravamudan (1979a,b), de Ris (1979), Orloff (1980), Mizner (1981), Mizner and Eyre (1982, 1983). Moorhouse (1982), Moorhouse and Pritchard (1982), Orloff and de Ris (1982), Babrauskas (1983, 1986b), Heskestad (1983a), Hirst and Eyre (1983),

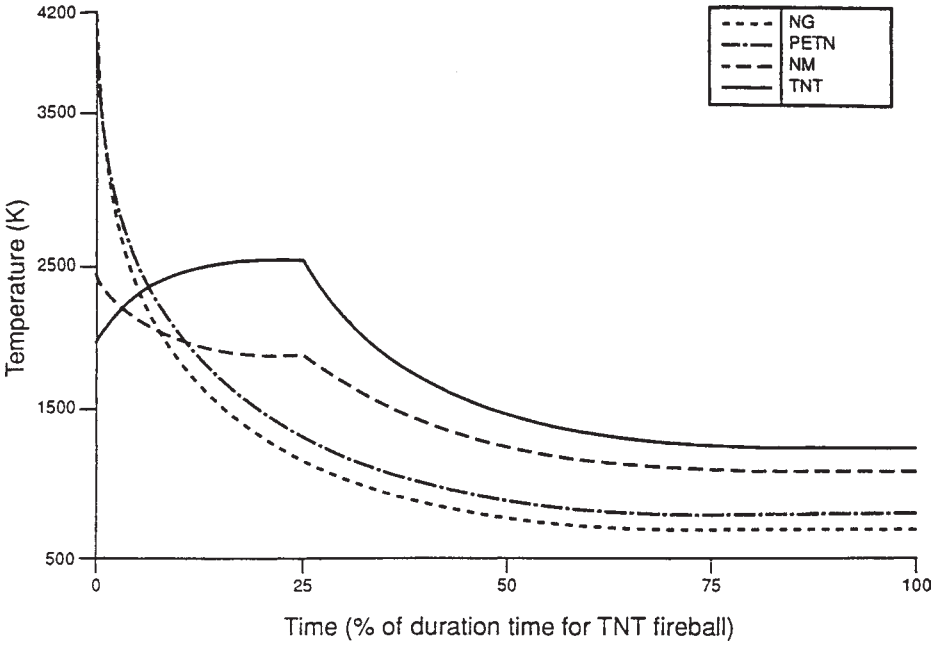


Figure 16.89 *Estimated temperatures of the fireballs of four explosives (Gilbert, Lees and Scilly, 1994e) NG, nitroglycerin; NM, nitromethane; PETN, pentaerythrito! tetranitrate; TNT, trinitrotoluene*

Considine (1984 SRD R297), Mudan (1984c), and Crocker and T. Napier (1986).

Some studies of pool fires are given in Table 16.63. Most work on pool fires deals with circular pools. A particular type of circular pool fire is the storage tank fire, which is considered in Subsection 16.17.1. A non-circular pool fire is a slot fire, which is treated in Subsection 16.17.15.

16.17.1 Experimental studies

There is a considerable experimental literature related to pool fires. Apart from the large number of publications on pool fires themselves, there are many relevant studies on flames such as those on combustion processes in, and heat radiation from, flames.

Much of the early work was done on relatively small diameter pool fires. Subsequent studies indicate that the effect of pool diameter is important and that it is preferable to carry out studies on large pool fires.

This initial work tended to be concerned with the determination of the liquid burning rate, of heat transfer to the liquid surface and of the fraction of heat radiated. Experimental studies on these aspects were conducted by Rasbash, Rogowski and Stark (1956) and by Blinov and Khudiakov (1957).

The work of Blinov and Khudiakov covered a wide range of pool diameters. Hottel (1959) analysed their data to show that, as the diameter of pool fire is increased, there is progression from a laminar to a transition and finally to a turbulent regime.

Burgess and Zabetakis (1962 BM RI 6099) carried out experiments on small pool fires to determine the liquid burning rate and fraction of heat radiated.

Yumoto (1971b) has done experiments to study the relative contribution of radiation and convection to heat transfer to the liquid surface in large pool fires.

Large-scale tests on pool fires of LNG have been undertaken as an American Gas Association (AGA) project as described by L.E. Brown, Wesson and Welker (1975), who give correlations for the liquid burning rate and the heat radiated.

Experiments on pool fires of aviation fuels have been done by Fu (1972).

Large-scale tests on pool fires of ethylene have been performed as part of the experiments done by the Ministry of International Trade and Industry (MITI), (1976) described earlier.

Modak (1981) has reported experiments on pool fires of polymethylmethacrylate (PMMA). Tests on large pool fires of LPG and LNG have been described by Mizner and Eyre (1982).

There is also a number of studies of fires in storage tanks. These include the work of Burgoyne and Katan (1947), Werthenbach (1971a,b, 1973), Seeger (1974), Lois and Swithenbank (1979) and Kobori, Handa and Yumoto (1981).

Investigations have also been carried out of fires on spills of flammable liquids on water, particularly for LNG. Closely related to these are tests on the spread of liquids on water. Experimental studies of the spreading of LNG on water have been done by Burgess, Murphy and Zabetakis (1970 BM RI 7448). A model of fire on a spill of LNG has been derived from this work by Burgess, Biordi and Murphy (1972 BM PMSRC 4177).

Large-scale tests of the spreading of spills and of fire on spills of LNG on water have been carried out as part of the Liquefied Gaseous Fuels (LGF) Spill Effects program by

Table 16.63 *Some studies of pool fires*

A General	
Experimental study of pool fires, including liquid burning rate and flame height	Rasbash, Rogowski and Stark (1956); Blinov and Khudiakov (1957)
Analysis of experimental work on pool fires, including combustion regimes, heat transfer to liquid surface, liquid burning rate and flame height	Hottel (1959)
Relation for flame height	P.H. Thomas (1963)
Relation for flame tilt	Welker and Sliepcevich (1966)
Review of pool fire relations and models	Atallah and Allan (1971)
Experimental study of heat transfer to liquid surface	Yumoto (1971b)
Experimental study of pool fires	Fu (1972)
Experimental study of pool fires of LNG	May and McQueen (1973)
Theoretical study of heat radiation from pool fires, including fraction of heat radiated and relative contribution of luminous and non-luminous radiation	Sibulkin (1973)
Review of relations and models for pool fires, including liquid burning rates	Burgess and Hertzberg (1974)
Experimental study of pool fires, including liquid burning and heat radiation	L.E. Brown, Wesson and Weiker (1975); Mizner (1981)
Theoretical model of a pool fire	Modak (1977)
Experimental study of pool fires, including heat transfer to liquid surface and heat radiation	Modak (1981)
Experimental study of pool fires of LPG and LNG	Mizner and Eyre (1982)
Equations for pool fires, including flame length, tilt and drag	Moorhouse (1982)
Review of relations and models for pool fires	Moorhouse and Pritchard (1982)
Review of relations and models for pool fires	Dinenno (1982)
Relation for liquid burning rate	Babrauskas (1983)
Review of relations and models for pool fires	Considine (1984 SRD R297)
Review of relations and models for pool fires	Mudan (1984c)
Theoretical model of a pool fire	Tune and Venart (1984/85a)
Theoretical model of a pool fire	Babrauskas (1986b)
B Head radiation	
Model of heat radiation from soot, CO_2 and H_2O in hydrocarbon flames	P.B. Taylor and Forster (1974, 1975)
Theoretical study of heat radiation from soot, CO_2 and H_2O in hydrocarbon laminar diffusion flames	Modak (1975, 1979)
Model of heat radiation from hydrocarbon flames	Considine (1984 SRD R297)
C Storage tank fires	
Experimental study of heat wave in tank fires	Burgoyne and Katan (1947)
Review of relations and models for tank fires	Atallah and Allan (1971)
Experimental and theoretical study of tank fires	Werthenbach (1971a,b, 1973)
Experimental study of tank fires, including view factor	Seeger (1974)
Experimental study of fire spread between tanks	Kobori, Handa and Yumoto (1981)
Review of relations and models for tank fires, including view factor	Crocker and Napier (1986)
D Fire on spills on water	
Experimental study of spreading of LNG on water	Burgess, Murphy and Zabetakis (1970)
Theoretical model of fire on LNG spill on water	Burgess, Biordi and Zabetakis (1972)
Theoretical model of fire on LNG spill on water	Raj and Kalelkar (1973)
Theoretical model of fire on LNG spill on water	Stannard (1977)
Review of models of LNG fires, including fire on LNG spill on water, vapour cloud fire and fireballs	Schneider (1980)
Experimental study of fire on propane and LNG spills on water	Mizner and Eyre (1983)

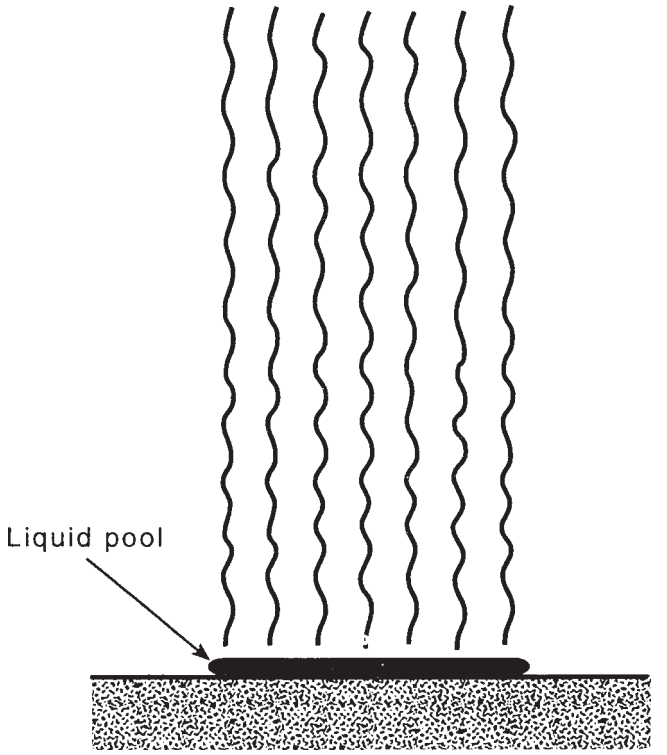


Figure 16.90 *A typical pool fire*

the Lawrence Livermore National Laboratory (LLNL) at the Naval Weapons Center, China Lake, California. The work has been described by Hogan, Ermak and Koopman (1981).

Other large-scale tests on fire on spills of propane and LNG have been done by Shell at Maplin Sands as described by Blackmore, Eyre and Summers (1982) and Mizner and Eyre (1983).

Figure 16.90 shows a typical pool fire.

16.17.2 Empirical features

A pool fire is a complicated phenomenon and the theoretical treatment is correspondingly complex. It is appropriate, therefore, to describe first some of the empirical features of pool fires.

A pool fire burns with a flame which is often taken to be a cylinder with a height twice the pool diameter. In still air the flame is vertical, but in wind it tilts. Wind also causes the base of the flame to extend beyond the downwind edge of the pool, thus exhibiting flame drag. With some pool fires blowout can occur at a wind speed of about 5 m/s.

The characteristics of a pool fire depend on the pool diameter. The liquid burning rate increases with diameter until for large diameters it reaches a fixed value. The heat radiated from the flame behaves similarly.

Some fuels, such as LNG, burn with a relatively clear flame, while others, such as kerosene and LPG, give a smoky flame. The extent of the smoke affects the heat radiation.

The fraction of heat radiated by a pool fire usually lies in the range 0.2–0.4.

A few fuels do not burn stably but at a certain temperature exhibit boilover.

16.17.3 Modelling of pool fires

The modelling of pool fires covers the following aspects: (1) flame geometry, (2) liquid burning rate, (3) flame characteristics, (4) heat radiated and (5) view factor.

The approach to modelling the heat radiated from a pool fire is broadly similar to that taken for fireballs. Again, there are three different ways of determining the heat radiated: (1) the use of a value of the fraction of the heat radiated; (2) the use of a value for the surface emissivity; and (3) the estimation from the flame properties such as flame temperature and emissivity.

Reviews of pool fire models have been given by several authors, including de Ris (1979), Considine (1984 SRD R297), Mudan (1984c) and Cracker and Napier (1986).

16.17.4 Fire regimes

As just mentioned, Hottel (1958) analysed the work of Blinov and Khudiakov and showed that as the pan diameter increases the fire regime changes from laminar to turbulent. He gave the graph shown in Figure 16.91, in which burning velocity and flame height are plotted against pan diameter.

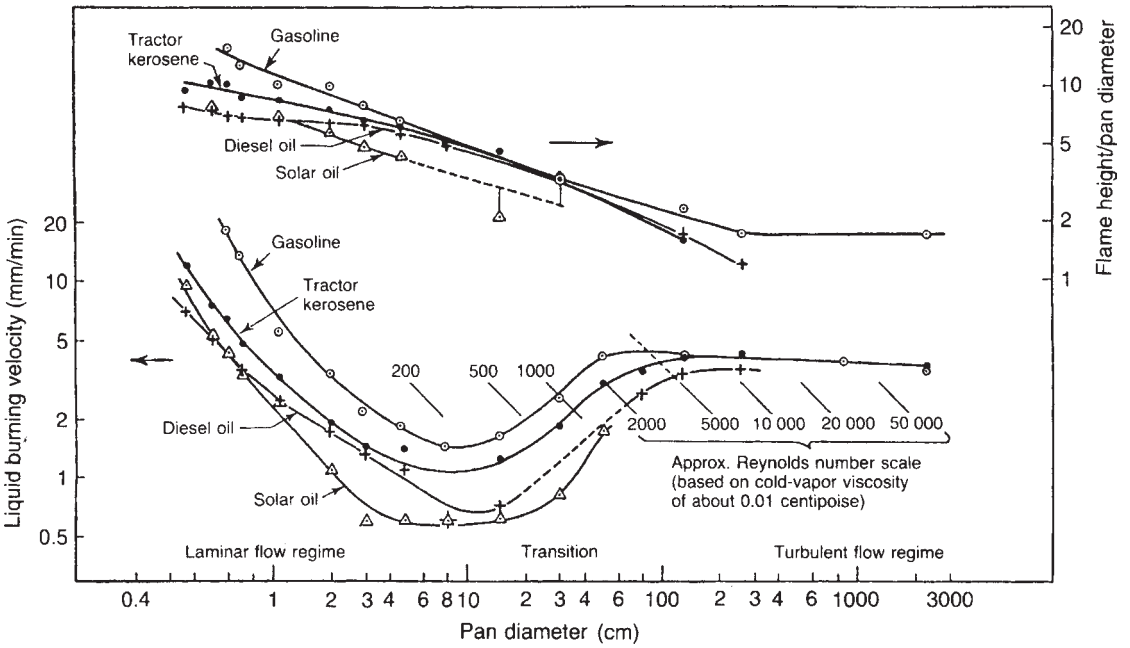


Figure 16.91 *Liquid burning rate and flame height as function of fire regime in pool fires (after Hottel, 1958; reproduced with permission)*

He defined a Reynolds number based on the vapour phase and related it to the parameters of the liquid phase as follows:

$$\mathrm{Re} = \frac{u_g d \rho_g}{\mu_g} \qquad [16.17.1a]$$

$$= \frac{u_l d \rho_l}{\mu_g} \qquad [16.17.1b]$$

where d is the pan diameter, u is the velocity, μ is the viscosity, ρ is the density and subscripts g and l refer to the vapour and liquid phases, respectively. The vapour phase Reynolds number was calculated using the cold gas values. The liquid velocity u_l is the liquid burning velocity v. Since the Reynolds number is proportional to the product vd, the lines of constant Reynolds number lie across the plot in Figure 16.91 from top left to bottom right with a slope of −1, as shown.

At a Reynolds number of about 20 the regime is laminar and the burning velocity decreases with increasing pan diameter. In the transition regime between Reynolds numbers of 20 and 200, the burning velocity first decreases, then increases and finally levels off with increase in pan diameter. Above Reynolds numbers of 500 the regime is turbulent and the burning velocity remains constant with increasing pan diameter. The pan diameter at which the regime becomes turbulent is about 1 m.

The flame height decreases with increasing pan diameter in the laminar and transition regimes and then remains constant with pan diameter in the turbulent regime.

16.17.5 Flame geometry

The flame on a pool fire has often been assumed to be an upright cylinder, as shown in Figure 16.90, with a length L twice the diameter D. An L/D ratio of 2 is used, for example, by Hearfield (1970) and R.B. Robertson (1976b). The work of Blinov and Khudiakov (1957) described above and shown in Figure 16.91 includes measurements of this ratio. It can be seen that for large diameters the value obtained is approximately 2.

Alternatively, the flame may be assumed to have a conical shape, but this assumption is less common and, unless otherwise stated, it is assumed in the following that the flame is treated as a cylinder.

An equation for flame length in still air has been given by P.H. Thomas (1963). This is

$$\frac{L}{D} = 42\left[\frac{m}{\rho_a (gD)^{1/2}}\right]^{0.6} \qquad [16.17.2]$$

where D is the flame diameter (m), g is the acceleration due to gravity (m/s^2), L is the flame height (m), m is the mass burning rate (kg/m^{2}s) and ρ_a the density of the ambient air (kg/m^3). Equation 16.17.2 is based on experiments on wood crib fires.

Steward (1970) has given a similar equation which takes into account the properties of the fuel.

Another expression for flame length is that of Heskestad (1983a). The basic relation is

$$\frac{L}{D} = f(N) \qquad [16.17.3]$$

where

$$N = \left[\frac{c_p T_o}{g\rho_a^2(\Delta H_c/r_s)^3}\right]\frac{Q^2}{D^2} \qquad [16.17.4]$$

where c_p is the specific heat of air (kJ/kg K), ΔH_c is the heat of combustion of the fuel (kJ/kg), N is a dimensionless group, Q is the total heat release rate (kW), r_s is the stoichiometric air to volatiles mass ration, T_o is the absolute temperature of the ambient air (K) and ρ_a is the density of the ambient air (kg/m^3).

The air/volatiles ratio r_s for a fuel $C_\alpha H_\beta O_\gamma$ burning in air is

$$r_s = 137.9\frac{\alpha + \beta/4 - \gamma/2}{12\alpha + \beta + 16\gamma} \qquad [16.17.5]$$

Heskestad has shown theoretically that for large values of N

$$\frac{L}{D} \propto N^{1/5} \qquad [16.17.6]$$

and has correlated experimental data with the relation

$$\frac{L}{D} = -1.02 + 15.6N^{1/5} \qquad [16.17.7]$$

The flame length in storage tank fires has been studied by Werthenbach (1971a,b, 1973). He gives an analysis, the point of departure of which is the ratio of the buoyancy to the momentum forces as given by the Archimedes number Ar:

$$\mathrm{Ar} = \frac{gD}{u^2}\frac{\Delta\rho}{\rho} \qquad [16.17.8]$$

where g is the acceleration due to gravity (m/s^2), u is the vapour velocity (m/s), ρ is the density of the vapour (kg/m^3) and $\Delta\rho$ is the difference between the density of the vapour and that of air (kg/m^3). Werthenbach correlates his results in terms of the Froude number Fr:

$$\frac{L}{D} = A\ \mathrm{Fr}^{0.2} \qquad [16.17.9]$$

with

$$\mathrm{Fr} = \frac{u^2}{gD^2} \qquad [16.17.10]$$

where A is a constant characteristic of the fuel. Values obtained for A were 29 for methane and natural gas and 40 for propane and gasoline. The vapour velocities were of the order of 0.75–1.0 cm/s. The author comments that these values are much lower that those in burner flames and that an attempt to apply the correlation for such flames to those on pool fires may be misleading.

Wind has several effects on the flame: it causes it to tilt, alters its length and extends it along the ground on the downwind side.

P.H. Thomas (1963) has provided an equation for flame length for a tilted flame also. This is

$$\frac{L}{D} = 55\left[\frac{m}{\rho_a(gD)^{1/2}}\right]^{0.67}(u^*)^{-0.21} \qquad [16.17.11]$$

with

$$u^* = u/u_c \qquad [16.17.12]$$

$$u_c = \left(\frac{gmD}{\rho_a}\right)^{1/3} \qquad [16.17.13]$$

where u is the wind velocity (m/s), u_c is a characteristic velocity (m/s) and u^* is a dimensionless wind velocity. The basis of Equation 16.17.11 is again experiments on fires on wood cribs.

The AGA (1973) has given an equation of the same general form as Equation 16.17.11, but with different parameters:

$$\frac{L}{D} = \left[\frac{m}{\rho_a(gD)^{1/2}}\right]^{-0.19}(u^*)^{0.06} \qquad [16.17.14]$$

Equation 16.17.14 therefore exhibits behaviour different from that of the Thomas equation 16.17.11.

Moorhouse (1982) has made correlations of available data which yield

$$\frac{L}{D} = 6.2\left[\frac{m}{\rho_a(gD)^{1/2}}\right]^{0.254}(u_{10}^*)^{-0.044} \quad \text{Cylindrical flame} \qquad [16.17.15a]$$

$$\frac{L}{D} = 4.7\left[\frac{m}{\rho_a(gD)^{1/2}}\right]^{0.2104}(u_{10}^*)^{-0.1144} \quad \text{Conical flame} \qquad [16.17.15b]$$

with

$$u_{10}^* = u_{10}/u_c \qquad [16.17.16]$$

where u_{10} is the wind speed at a height of 10 m and u_{10}^* is the dimensionless wind speed at that height. These equations are valid for wind speeds $u_{10} > u_c$, while for wind speeds $u_{10} < u_c$ the dimensionless wind speed term is taken as unity.

Considine (1984 SRD R297) gives an analysis in which it is shown that, given certain assumptions, the use of a constant fraction of heat radiated implies a constant L/D ratio.

Thomas has also provided an equation for flame tilt

$$\cos\theta = 0.7(u^*)^{-0.49} \qquad [16.17.17]$$

where θ is the angle of tilt from the vertical (rad). The basis of Equation 16.17.17 is again experiments on wood crib fires.

The AGA (1973) has given an equation of the same form

$$\cos\theta = (u^*)^{-0.5} \qquad [16.17.18]$$

This equation is based on tests on large LNG fires.

Another correlation for flame tilt is that of Welker and Sliepcevich (1965)

$$\frac{\tan\theta}{\cos\theta} = 3.2\left(\frac{Du\rho_a}{\mu_a}\right)^{0.07}\left(\frac{u^2}{Dg}\right)^{0.7}\left(\frac{\rho_g}{\rho_a}\right)^{-0.6} \qquad [16.17.19]$$

where μ_a is the viscosity of air (kg/m s), and ρ_g is the density of the fuel vapour at the normal boiling point (kg/m^3).

Equation 16.17.19 is based on experiments on small pool fires.

Moorhouse (1982) has correlated the available data to obtain equations of the form given by Thomas and of that given Welker and Sliepcevich. These are, respectively,

$$\cos\theta = 0.86(u_{10}^*)^{-0.250} \quad \text{Cylindrical flame} \quad [16.17.20a]$$

$$\cos\theta = 0.87(u_{10}^*)^{-0.272} \quad \text{Conical flame} \quad [16.17.20b]$$

and

$$\frac{\tan\theta}{\cos\theta} = 1.19\left(\frac{Du\rho_a}{\mu_a}\right)^{0.050}\left(\frac{u^2}{Dg}\right)^{0.399} \quad \text{Cylindrical flame} \quad [16.17.21a]$$

$$\frac{\tan\theta}{\cos\theta} = 3.0\left(\frac{Du\rho_a}{\mu_a}\right)^{0.011}\left(\frac{u^2}{Dg}\right)^{0.422} \quad \text{Conical flame} \quad [16.17.21b]$$

For flame drag, Welker and Sliepcevich (1966) give the following equation

$$\frac{D'}{D} = 2.1\left(\frac{u^2}{Dg}\right)^{0.21}\left(\frac{\rho_g}{\rho_a}\right)^{0.48} \quad [16.17.22]$$

where D' is the elongated flame base (m). The experimental basis of Equation 16.17.22 is wind tunnel tests on small pool fires.

Moorhouse (1982) has correlated the available data to obtain the equations

$$\frac{D'}{D} = 1.5\left(\frac{u^2}{Dg}\right)^{0.069} \quad \text{Cylindrical flame} \quad [16.17.23a]$$

$$\frac{D'}{D_w} = 1.6\left(\frac{u^2}{Dg}\right)^{0.061} \quad \text{Conical flame} \quad [16.17.23b]$$

where D_w is the maximum pool dimension in the direction of the wind (m).

16.17.6 Liquid burning rate

The review by Hottel (1959) of the work of Blinov and Khudiakov includes a simple analysis of the heat q transferred from the flame to the pool, which may be written as

$$q = q_c + q_r + q_{rim} \quad [16.17.24]$$

where q_c is the heat transferred to the pool by conduction, q_r is the heat transferred by radiation and q_{rim} is the heat transferred by the pan rim. The heats transferred by convection and by radiation are

$$q_c = \frac{\pi}{4}d^2U(T_f - T_b) \quad [16.17.25]$$

$$q_r = \frac{\pi}{4}d^2\sigma F(T_f^4 - T_b^4)[1 - \exp(-kd)] \quad [16.17.26]$$

where d is the pool diameter, F is the view factor, k is the extinction coefficient, T_b is the absolute temperature of the burning liquid surface, T_f is the absolute temperature of the flame, U is the heat transfer coefficient and σ is the Stefan–Boltzmann constant. He considers heat transfer to a gasoline pool assuming $F = 0.25$, $T_f = 1100$ K and $U = 1$ BTU/ft^{2}h.

For small pans q_{rim} will be large and the liquid burning rate will be high. For large pans q_{rim} will be negligible, q_c will be constant and q_r will be dominant with large kd and hence a large and constant value of the term $[1 - \exp(-kd)]$. For intermediate size pans q_{rim} will again be negligible, but q_r will not be so large due to the thinness of the flame. Hence the liquid burning rate will pass through a minimum for intermediate pan diameters. This analysis agrees with the experimental results shown in Figure 16.91.

An equation for the regression rate of a burning liquid surface under windless conditions has been given by Burgess and Zabetakis (1962 BM RI 6099) as follows:

$$v = v_\infty[1 - \exp(-k_1 d)] \quad [16.17.27]$$

$$v_\infty = k_2\left(\frac{-\Delta H_c}{\Delta H_v}\right) \quad [16.17.28]$$

where d is the diameter of the pool (cm), ΔH_c is the net heat of combustion (negative) (kJ/kmol), ΔH_v is the total heat of vaporization (kJ/kmol), v is the liquid burning rate (cm/min), v_∞ is the liquid burning rate for a pool of infinite diameter (cm/min), and k_1, k_2 are constants ($k_2 = 0.0076$).

Liquid burning rate parameters for Equation 16.17.27 for selected substances are given in Table 16.64. For LNG the maximum liquid burning rate given in Table 16.64 is 0.66 cm/min, but in further experimental work at Bruceton and Lake Charles described by these authors considerably higher values were obtained. In one experiment the burning rate was 1.16 cm/min.

Equation 16.17.27 also be written in the form

$$m = m_\infty\ [1 - \exp(-k_1 d)] \quad [16.17.29]$$

$$m_\infty = v_\infty \rho_l \quad [16.17.30]$$

where m is the mass liquid burning rate (kg/m^2 s), m_∞ is the mass burning rate for a pool of infinite diameter (kg/m^2 s) and ρ_l the liquid density (kg/m^3).

Brown, Wesson and Welker used Equation 16.17.29 to correlate the mass burning rate for large LNG fires in the AGA tests. In British Units they give for the parameters m_∞ a value of 0.6 (in./min) and k_1 a value of 0.2 (ft^{-1}).

Work on the heat transfer from the flame to the liquid pool has been reviewed by Yumoto (1971b). This work was limited to smal-scale fires. He decribes experimental work on fires in pools up to 3 m diameter in which measurements were made of the relative contribution of convective and radiant heat transfer. As shown in Figure 16.92 the contribution of convection falls and that of radiation rises as the pool diameter increases, until both contributions reach a constant value.

Sibulkin (1973) discusses the ratio q_r/q_c. He assumes in his analysis that q_c is constant and that

$$q_r \propto \epsilon \quad [16.17.31]$$

where ϵ is the flame emissivity. He gives for the latter

$$\epsilon = 1 - \exp(-k_3 L_m) \quad [16.17.32]$$

where L_m is the mean beam length and k_3 is a constant. But for pools of intermediate diameter

$$\epsilon \propto L_m^{1/2} \quad [16.17.33]$$

$$L_m \propto D \quad [16.17.34]$$

Hence

$$\epsilon \propto D^{1/2} \quad [16.17.35]$$

$$\frac{q_r}{q_c} \propto D^{1/2} \quad [16.17.36]$$

For large diameter pools $\epsilon = 1$, and hence

$$\frac{q_r}{q_c} \propto \text{Constant} \quad [16.17.37]$$

An extensive review of liquid burning rates is given by A.R. Hall (1973), who considers among other things the effects of (1) the fuel, (2) fuel mixtures, (3) fuel containing dispersed water, (4) the liquid surface temperature, (5) the liquid temperature distribution, (6) the pool diameter, (7) the heat transfer from the flame to the liquid and (8) the wind speed.

Table 16.64 *Parameters for liquid burning rate on pools of selected substances (Burgess and Zabetakis, 1962 BM RI 6099) (Courtesy of the Bureau of Mines)*

	v_∞ (cm/min)	k_1 (cm^{-1})
Hydrogen	1.4[a]	0.07[a]
Butane	0.79	0.027
Hexane	0.73	0.019
Benzene	0.60	0.026
Methanol	0.17	0.046
LNG	0.66[b]	0.03[b]

[a] Uncertain value.
[b] Value calculated.

Work on the burning rates of fuels of solid plastics has been reviewed by de Ris (1979) in the context of pool fires. He tabulated for the fuels including polymethylmethacrylate (PMMA), polypropylene (PP) and polystyrene (PS) a large number of potentially relevant variables and found that the actual volumetric heat release rate appears to be independent of the fuel. He explained this by the fact that the heat released per unit mass of oxygen consumed is essentially the same for most organic fuels, despite incomplete combustion, whilst the rate of oxygen consumption is controlled by the overall rate of turbulent mixing, which is driven by temperature differences that are generally insensitive to the fuel.

Babrauskas (1983, 1986b) distinguishes the following burning modes of pool fires:

Pool diameter (m)	*Burning mode*
<0.05	Convective, laminar
<0.2	Convective, turbulent
0.2–1.0	Radiative, optically thin
>1.0	Radiative, optically thick

and uses the relations

$$m = m_\infty[1 - \exp(-k\beta D)] \quad [16.17.38]$$

with

$$m_\infty = \frac{\sigma T_f^4}{\Delta h_g} \quad [16.17.39]$$

where Δh_g is the total heat of gasification (kJ/kg), k is an absorption–extinction coefficient (m^{-1}), T_f is the absolute temperature of the effective equivalent gray gas (K) and β is a mean beam length corrector. He discusses whether the mean beam length corrector β can be derived, and concludes that it cannot. He gives tabulations of m_∞ and $(k\beta)$ from work on large pool fires reported by some 20 authors. These data are given in Table 16.65.

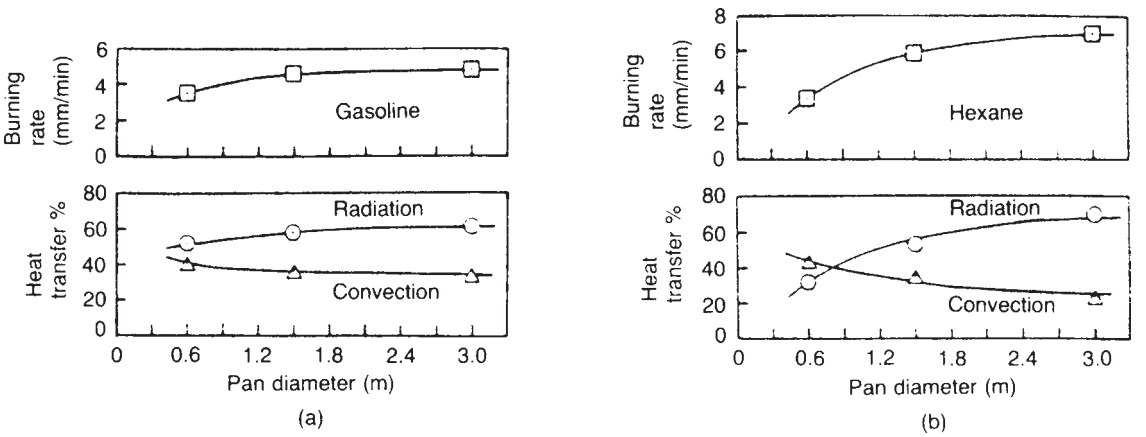


Figure 16.92 *Liquid burning rate and heat transfer to the liquid surface in large pool fires (after Yumoto, 1971b): (a) gasoline fire; (b) hexane fire (Courtesy of Combustion and Flame)*

Table 16.65 *Pool fire parameters for selected substances (after Babrauskas, 1983) (Courtesy of Fire Technology)*

Material	ρ_l (kg/m^3)	m_∞ (kg/m^{2}s)	$k\beta$ (m^{-1})	χ_r
H_2 (liquid)	700	0.169	6.1	0.25
LNG (mostly CH_4)	415	0.078	1.1	0.16–0.23
LPG (mostly C_3H_6)	585	0.099	1.4	0.26
Butane	573	0.078	2.7	0.27–0.30
Hexane	650	0.074	1.9	0.20–0.40
Heptane	675	0.101	1.1	
Methanol	796	0.017		0.17–0.20
Ethanol	794	0.015		0.20
Benzene	874	0.085	2.7	0.14–0.38
Xylenes	870	0.090	1.4	
Acetone	791	0.041	1.9	
Diethyl ether	714	0.085	0.7	
Gasoline	740	0.055	2.1	0.18
Kerosene	820	0.039	3.5	
JP-4	760	0.051	3.6	0.35
JP-5	810	0.054	1.6	
Transformer oil (hydrocarbon)	760	0.039	0.7	
Fuel oil (heavy)	940–1000	0.035	1.7	
Crude oil	830–880	0.022–0.045	2.8	0.18

Babrauskas (1986b) also addresses some of the factors affecting the liquid burning rate, including (1) pool diameter, (2) lip effects and (3) wind speed.

For very large pool fires with diameters greater than 5–10 m, there is some evidence of a slight decrease in burning rate. This is presumably due to poor mixing with air. Babrauskas suggests that this effect is unlikely to reduce the burning rate by more than 20%.

Effects of lip, or freeboard, on large pool fires involve all three modes of heat transfer. A lip can affect the temperature distribution in the wall of a storage tank and hence heat transfer by conduction. It can promote turbulence and enhance heat transfer by convection. It tends to make the flame more stable and emissive, thus increasing heat transfer by radiation. Babrauskas quotes the following work of Orloff (1981), on fires of one fuel, PMMA, on the effect of the ratio d/D of the freeboard height to the pool diameter on the ratio ϕ_{br} of the liquid burning rate to it base value with no lip:

d/D	ϕ_{br}
0	1.0
0.07	1.6
0.2	2.0
>0.2	Slow decrease

With regard to wind speed there is some work showing an increase in burning rate and other work indicating a decrease. Relevant studies include those of Blinov and Khudiakov (1957) and Lois and Swithenbank (1978).

Some spot values of the liquid burning rate are as follows. In the experiments of Blinov and Khudiakov on gasoline, kerosene, diesel oil and solar oil, the liquid burning rate in the turbulent regime was 0.5 cm/min. In one of the large-scale tests on the pool burning of ethylene conducted by MITI (1976) a liquid burning rate of 0.88 cm/min was obtained. Values of liquid burning rate are given in the ICI *LFG Code* (ICI/RoSPA 1970 IS/74) and by Hearfield (1970) and R.B. Robertson (1976b) and liquid burning rate is treated in Chapter 22 in relation to heat radiation from fires to storage tanks.

A liquid burning rate of 0.75–1.0 cm/min is quoted in the fourth edition of the Dow *Guide* (Dow Chemical Company, 1976). This value is given in relation to the fireproofing of structures as part of the 'Recommended Minimum Fire Prevention and Protection Features', which do not appear as such in later editions.

16.17.7 Flame characteristics

Important characteristics of the flame on a pool fire are the nature of the flame, its temperature and its emissivity.

Some flammable liquids burn with a relatively clear flame, while others give a more smoky flame. The difference is well illustrated by the work of Mizner and Eyre (1982) on LNG and LPG pool fires. The LPG flames were smoky, the LNG flames much less so. Figure 16.93 illustrates the difference. The presence of carbon particles in the flames has several effects. One is that the soot enhances the emissivity of the flame. Another is that smoke may shroud the flame from the target.

Several authors refer to a flame temperature of 1100 K. This is the typical value taken by Hottel (1959). Craven (1976) also mentions this figure, but states that this is not necessarily the maximum value which may be attained. Some data on pool fire flame temperatures given by Babrauskas are shown in Table 16.65 and further data on flame temperature and surface emissive power given by Mudan (1984c) are shown in Table 16.66. Further information on flame temperatures is given in relation to engulfing fires in Section 16.20.

As far as emissivity is concerned, pool fires of most hydrocarbon fuels become optically thick when the diameter reaches about 3 m. For such fires it is often stated that the emissivity of the flame may be taken as unity. More refined estimates of flame emissivity may be made using the relations given in Section 16.13.

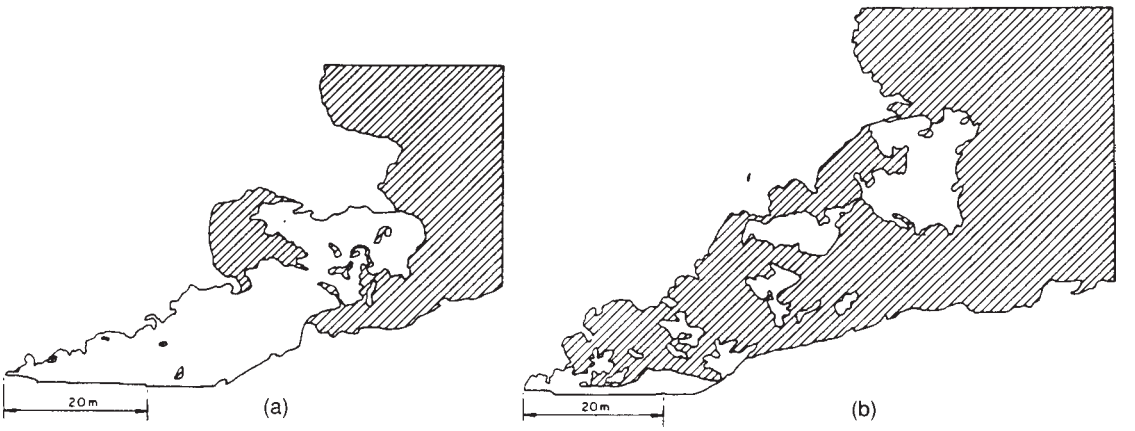


Figure 16.93 *Smokiness of flames in large pool fires (after Mizner and Eyre, 1982): (a) LNG fire; (b) LPG fire (Courtesy of the Institution of Chemical Engineers)*

Table 16.66 *Some data on the measured flame temperature and surface emissive power of flames of flames on pool fires (Mudan, 1984c)(Courtesy of Progress in Energy and Combustion Science)*

Material	*Pool fire dimensions* (m)	*Flame radiation temperature* (K)	*Surface emissive power* (kW/m^2)	*Reference*
LNG on water	8.5–15	1500	210–280	Raj, Moussa and Aravamudan (1979b)
LNG on land	20	–	150–220	Mizner and Eyre (1982)
LPG on land	20	–	48	Mizner and Eyer (1982)
Pentane	1.0		61	Modak (1978)
Ethylene	2.5		130	Modak (1978)
Gasoline	1.0–10	1240	60–130 (max)	Hägglund and Persson (1976)
Kerosene	30–80	1600	10–25 (av.)	Japan Institute for Safety Engineering (1982)
JP-4	5.8	1200		NASA (1979)
JP-5	1.0–30		30–50	Modak (1978)

The conditions which give rise to smokiness in the flame are also given in Section 16.13. If the flame is smoky, the unobscured parts of the flame will emit radiation to the target, while the obscured parts will not.

A method of taking account of obscuration of the flame has been given by Considine (1984 SRD R297). He divides the flame into unobscured section with a surface emissive power q and obscured sections with 'blooms' of radiation where the average emissive power is 0.3 q. From photographs of flames the relative proportion of unobscured flame varied from about 30% for fires a few metres in diameter to zero for flames 50 m or more in diameter. He analyses the following three cases:

(1) flame radiating continuously over entire height;
(2) flame radiating 30% continuously, 70% in blooms;
(3) flame radiating in blooms over entire height.

He suggests that for flames in the range 5–25 m diameter the bottom 30% be taken as radiating continuously and the rest radiating in blooms, and that flames >25 m diameter be taken as radiating in blooms over their entire height. The view factor for such a flame is considered below.

16.17.8 Heat radiated

There are three methods of estimating the heat radiated by a pool fire. These are based on:

(1) heat evolved and radiated;
(2) surface emissive power;
(3) flame temperature and emissivity.

The heat evolved in the flame may be determined from the liquid burning rate. The heat radiated from the flame is then usually calculated as a fraction of the heat evolved by using an empirical factor. Some data on this radiant heat factor have been given by Burgess and Zabetakis in the work already described and are shown in Table 16.67. They suggest that the fraction of heated radiated generally does not exceed half that evolved.

It is stated by Roberts that the fraction of heat radiated both by fireballs and pool fires is typically in the range 0.2–0.4. He suggests a value of 0.3 for this radiant heat factor.

Large pool fires are affected by smoke blockage. The following data of Hägglund and Persson (1976) for the

Table 16.67 *Fraction of heat radiated from flames burning on liquid pools (Burgess and Zabetakis, 1962 BM RI 6099) (Courtesy of the Bureau of Mines)*

	Pool diameter (cm)	*Heat radiated* (fraction)
Hydrogen	33	0.25
Butane	76	0.27
Benzene	122	0.36
Methanol	122	0.17
LNG	76	0.23

effect of pool diameter on the fraction of heat radiated in JP-4 fuel fires is quoted by Babrauskas:

Pool diameter (m)	*Fraction of heat radiated*
1.0	0.35
1.5	0.39
2.0	0.34
3.0	0.31
5.0	0.16
10.0	0.10

He states, however, that similar information is not available for other fuels and suggests that a conservative estimate can be obtained by disregarding smoke blockage.

The intensity of heat radiation may then be calculated by dividing the heat radiated by the area of the flame envelope.

The second method is to use directly information on the heat radiation intensity, or emissive power, of the flame surface. Values of surface emissive power of hydrocarbon fires have been reviewed by P. Nash (1974a). He lists values of heat fluxes, extrapolated from experimental fires of different sizes, in the range 30–189 kW/m^2.

In the context of safety distances, a value of 170 kW/m^2 has been suggested by law (1969). This aspect has also been discussed by Craven (1976), who concludes that the value of 170 kW/m^2 given by Law provides a realistic initial estimate.

Further data on surface emissive power are given by Mudan (1984c). His tabulated values are given in Table 16.66; he also gives other values in the text.

There are wide differences in surface emissive power, depending on the smokiness of the flame. Mizner and Eyre (1982) obtained in their work surface emissive powers of 35 kW/m^2 for kerosene, 48 kW/m^2 for LPG but 153 kW/m^2 for LNG.

Reviewing work on pool fires on land and water, Moorhouse and Pritchard (1982) conclude that for large pool fires of hydrocarbons, excluding liquefied gases, the surface emissive power is unlikely to exceed 60 kW/m^2 and state that for such fires the value of 170 kW/m^2 often quoted is based on small scale tests and is not appropriate.

With regard to pool fires of LNG, small fires clearly burn with a particularly clean flame. Evidence of soot formation is found only when the pool diameter reaches about 10 m or when most of the fuel has been consumed and the proportion of higher hydrocarbons is rising rapidly. Optical thickness is approached only when the flame is some meters wide. Moorhouse and Pritchard quote for pool fires of LNG the surface emissivities of the order of 200 kW/m^2 obtained by Raj, Moussa and Aravamudan (1979a).

Values of the surface emissive power for pool fires on water obtained in the experiments on the dispersion and burning of vapour clouds at Maplin Sands have been given by Blackmore, Eyre and Summers (1982), Hirst and Eyre (1983) and Mizner and Eyre (1983). This work has been described in Section 16.14. Pool fires formed on the liquefied gas spilled on the sea. The surface emissive power for these pool fires, as opposed to the vapour cloud fire, were 203 kW/m^2 for LNG and 43 kW/m^2 for propane. The authors suggest a value of 200 kW/m^2 as being representative for LNG pool fires.

Further indications of surface emissive power are provided in the work on engulfing fires described in Section 16.20.

L.E. Brown, Wesson and Welker (1975), in the work on LNG fires described earlier, have derived for such fires the following equation for surface emissive power:

$$q = q_\infty[1 - \exp(k_4 d)] \qquad [16.17.40]$$

where d is the diameter of the fire (ft), q is the heat flux from the surface (BTu/h ft^2), q_∞ the heat flux from the surface of a 'large' fire (BTU/h ft^2) and k_4 a constant (ft^{-1}). The values given for the parameter q_∞ is and the constant k_4 are 45,000 and 0.055, respectively.

Mudan (1984c) suggests that for hazard assessment the surface emissive power be taken as a weighted value for the unobscured and obscured portions of the flame. For example, for a flame comprising 20% luminous spots and with 80% obscured by smoke

$$q = 0.2 \times 130 + 0.8 \times 20 = 42 \text{ kW/m}^2$$

Similarly, Considine (1984 SRD R297) proposes that for hydrocarbons, but not LNG, the surface emissive power of the flame be taken as 120 kW/m^2 over the part radiating continuously and as $0.3 \times 120 = 36$ kW/m^2 over the part radiating in blooms.

A further discussion of the intensity of heat radiation is given in the ICI *LFG Code* and is described in Chapter 22 in relation to heat radiation from fires to storage vessels.

The third method is to determine the heat radiated from the temperature and emissivity of the flame. The heat radiated is

$$E = \epsilon\sigma T_f^4 \qquad [16.17.41]$$

where E is the surface emissive power (kW/m^2). The heat so radiated may be assumed to come either from a point source or from the flame surface. The estimation of the emissivity ϵ is discussed in Section 16.13.

In order to determine the heat incident on a target it is necessary to take into account the target absorptivity, the atmospheric transmissivity and the view factor. The determination of the latter is now considered.

16.17.9 View factor

The targets for heat radiated form a pool fire include both the liquid surface and objects outside the flame. There are therefore two different types of view factor relevant to relevant to pool fires.

As mentioned earlier, Hottel (1959) has used for the view factor of the liquid pool a value of 0.25.

For an object outside the flame there are several different treatments. For heat radiation from a flame treated as a vertical or tilted cylinder to a target the three principal models are:

(1) point source model;
(2) solid flame model;
(3) equivalent radiator model.

These models and their application have been described by Crocker and Napier (1986).

For a point source the radiation at a surface a distance r from the source is

$$E = \frac{Q_r}{4\pi r^2} \qquad [16.17.42]$$

and the radiation incident on the target is

$$I = \alpha\tau \frac{FQ_r}{4\pi l_s^2} \qquad [16.17.43]$$

where E is the surface emissive power (kW/m^2), F is the view factor, I is the thermal radiation intensity (kW/m^2), Q_r is the heat radiated (kW), r is a surface radius (m), l_s is the slant distance between the source and the target (m), α is the absorptivity of the target and τ is the transmissivity of the atmosphere.

Then from Equation 16.17.42 and 16.17.43 for a point source with a target surface normal to the line joining it to the source, as given in Equation 16.13.100

$$F = \frac{r^2}{l_s^2} \qquad [16.17.44]$$

The expressions for vertical and horizontal targets are given by Equations 16.13.101 and 16.13.102.

The geometry of this model is shown both for pool fires and for storage tanks in Figure 16.94. This approach has been used by a number of workers (e.g. Hearfield, 1970) for pool and tank fires. The point source model is not accurate for a target close to the flame and for this situation other methods should be used.

Of the more accurate methods, the more widely used appears to be the solid flame model. Methods for the calculation of the view factor for a vertical cylinder have been described by Hamilton and Morgan (1952) and Sparrow, Miller and Jonsson (1962), and for a tilted cylinder by Rein, Sliepcevich and Welker (1970), Merriam (1972) and Raj and Kalelkar (1974). A collection of view factors is given by Howell (1982).

For a vertical cylinder with a target with a vertical surface, as shown in Figure 16.95(a), the view factor given by Hamilton and Morgan (1952) (Howell, configuration B-29) is

$$F = \frac{1}{\pi X}\tan^{-1}\left[\frac{L}{(X^2-1)^{1/2}}\right] + \frac{L}{\pi}\left(\frac{(A-2X)}{X(AB)^{1/2}} \times \tan^{-1}\left\{\frac{[A(X-1)]^{1/2}}{[B(X+1)]^{1/2}}\right\} - \frac{1}{X}\tan^{-1}\left[\frac{(X-1)^{1/2}}{(X+1)^{1/2}}\right]\right) \qquad [16.17.45]$$

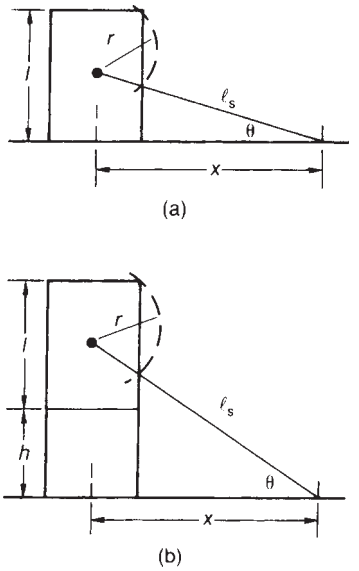


Figure 16.94 *View factor for pool and tank fires – point source model: (a) pool fire; (b) tank fire*

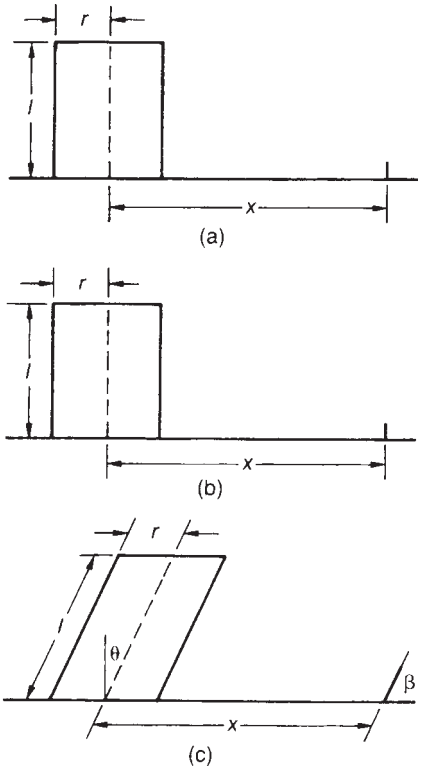


Figure 16.95 *View factor for pool fires – solid flame model: (a) vertical cylindrical flame, vertical target; (b) vertical cylindrical flame, horizontal target; (c) tilted cylindrical flame, angled target*

with

$$L = l/r \quad [16.17.46a]$$

$$X = x/r \quad [16.17.46b]$$

$$A = (X+1)^2 + L^2 \quad [16.17.46c]$$

$$B = (X-1)^2 + L^2 \quad [16.17.46d]$$

where r is the radius of the cylinder.

For a vertical cylinder with a target with a horizontal surface, as shown in Figure 16.95(b), the view factor given by Sparrow, Miller and Jonsson (1962) (Howell, configuration B-27) is

$$F = \frac{1}{2\pi}\cos^{-1}R + \frac{1}{\pi}\left\{\tan^{-1}\left[\frac{R}{(1-R^2)^{1/2}}\right] - \frac{(1+L^2-R^2)}{X} \times \tan^{-1}\left[\frac{X\tan(0.5\cos^{-1}R)}{1+L^2+R^2-2R}\right]\right\} \quad [16.17.47]$$

with

$$R = r/x \quad [16.17.48a]$$

$$L = l/x \quad [16.17.48b]$$

$$X = [(1+L^2+R^2)^2 - 4R^2]^{1/2} \quad [16.17.48c]$$

For a vertical cylinder, an expression based on the more approximate subtended solid angle method has been given by Stannard (1977)

$$F = \frac{2}{\pi}\sin^{-1}(r/x)\sin\{\tan^{-1}[l/(x-r)]\} \quad [16.17.49]$$

For a tilted cylinder with a circular base tilted at an angle θ to the horizontal and with the target having a surface at an angle β to the horizontal, as shown in Figure 16.95(c), the view factor has been given by Mudan (1984c), following work by Raj and Kalelkar (1974), and is

$$F = \frac{1}{\pi}[(\cos\beta\sin\theta - \sin\beta\cos\theta)(A_1\cos\phi + LA_2) + \cos\beta(A_3 - A_4)] \quad [16.17.50]$$

with

$$L = l/r \quad [16.17.51a]$$

$$X = x/r \quad [16.17.51b]$$

$$\phi = \sin^{-1}(1/X) \quad [16.17.51c]$$

$$A_1 = \frac{1}{B_1}\left\{\tan^{-1}\left[\frac{L-(X-1/X)\sin\theta}{B_1}\right] + \tan^{-1}\left[\frac{(X-1/X)\sin\theta}{B_1}\right]\right\} \quad [16.17.51d]$$

$$B_1 = [(X^2-1)\cos^2\theta + (1-1/X^2)\sin^2\theta]^{1/2} \quad [16.17.51e]$$

$$A_2 = \int_0^{\pi/2} f(v)\mathrm{d}v \quad [16.17.51f]$$

$$f(v) = \frac{\sin v}{(1+L^2+X^2-2XL\sin\theta) + 2(L\sin\theta - X)\sin v} \quad [16.17.51g]$$

$$A_3 = \int_0^{\pi/2} \frac{(X\sin v - 1)\ \mathrm{d}v}{(1+X^2-2X\sin v)} \quad [16.17.51h]$$

$$A_4 = \int_0^{\pi/2} \frac{(X\sin v - 1)\ dv}{[(1+L^2+X^2-2L\sin\theta) + 2(L\sin\theta - X)\sin v]} \quad [16.17.51i]$$

For a tilted cylinder with a target with a vertical surface ($\beta = 90°$), Equation 16.17.50 reduces to

$$F = \frac{1}{\pi}\cos\theta(A_1\cos\phi + LA_2) \quad [16.17.52]$$

Stannard has given an expression based on the subtended solid angle method for a tilted cylinder also

$$F = \frac{2}{\pi}\sin^{-1}\left[\frac{r}{r+(x-r)\cos\theta}\right] \times \left\{\sin\theta + \sin\tan^{-1}\left[\left(\frac{1}{(x-r)\cos\theta}\right) - \tan\theta\right]\right\} \quad [16.17.53]$$

The third approach is the equivalent radiator method. For a vertical cylinder the view factor has been given by Hamilton and Morgan (1952). For a target with vertical surface as shown in Figure 16.96(a) the view factor for a half-radiator is

$$F = \frac{1}{2\pi}\left\{\frac{R}{(1+R^2)^{1/2}}\tan^{-1}\left[\frac{L}{(1+R^2)^{1/2}}\right] + \frac{L}{(1+L^2)^{1/2}} \times \tan^{-1}\left[\frac{R}{(1+L^2)^{1/2}}\right]\right\} \quad [16.17.54]$$

and for a target with a horizontal surface as shown in Figure 16.96(b) the view factor for a half-radiator is

$$F = \frac{1}{2\pi}\left\{\tan^{-1}R - \frac{1}{(1+L^2)^{1/2}}\tan^{-1}\left[\frac{2}{(1+L^2)^{1/2}}\right]\right\} \quad [16.17.55]$$

with

$$R = r/x \quad [16.17.56a]$$

$$L = l/x \quad [16.17.56b]$$

Since the view factors given by Equations 16.17.54 and 16.17.55 are for half the radiator surface, they must be doubled to give the full view factors.

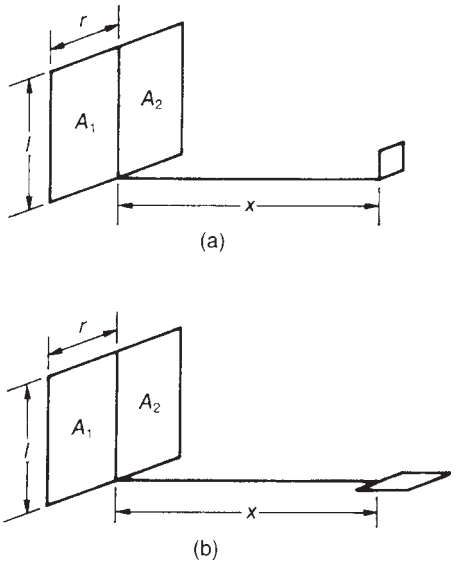


Figure 16.96 *View factor for pool fires – equivalent radiator model: (a) vertical cylindrical flame, vertical target and (b) vertical cylindrical flame, horizontal target*

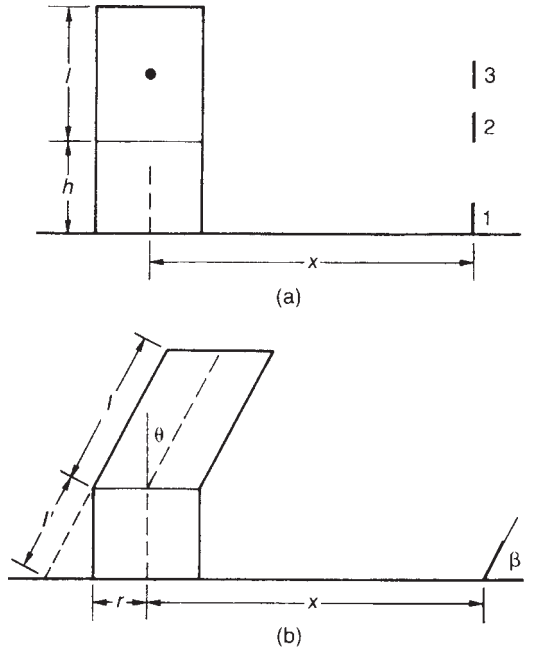


Figure 16.97 *View factor for tank fires – solid flame model: (a) vertical cylindrical flame, vertical target; and (b) tilted cylindrical flame, angled target*

The maximum view factor F_m is the geometric mean of the view factor F_v for a vertical surface and the view factor F_h for a horizontal surface:

$$F_m = (F_v + F_h)^{1/2} \quad [16.17.57]$$

The application of the view factors just given to tank fires has been discussed by Crocker and Napier (1986). For a vertical flame and for targets with vertical surfaces three possible configurations are shown in Figure 16.97(a). Using the solid flame model for target 2 on a level with the base of the flame, the view factor for a vertical flame may be used as it is. For target 3 on a level with the centre of the flame the view factor for a vertical flame may again be used, but the value is doubled to take account of the two halves of the falme. For target 1 the view factor may be obtained as follows:

$$F = F[(l + h), x] - F[h, x] \quad [16.17.58]$$

This view factor is therefore the difference between view factors. A similar approach may be used for view factors based on the equivalent radiator model.

For a tilted flame with a target at ground level with a surface at an angle β to the horizontal, the configuration is as shown in Figure 16.97(b). Using the solid flame model given in Equation 16.17.50 the view factor is

$$F = F[(l + l'), x'] - F[l', x'] \quad [16.17.59]$$

Further expressions for more complex situations are given by Crocker and Napier.

A set of graphs for the view factors for pool fires of LPG are given in the IP *LPG Code*. Figure 16.98 (a) shows a vertical cylindrical flame and Figure 16.98(b) the corresponding maximum view factor, whilst Figure 16.99(a) shows a tilted cylindrical flame and Figure 16.99(b) the maximum view factor for a cylindrical flame with an angle of tilt of 30°.

The view factor for a flame partially obscured by smoke is given by Considine (1984 SRD R297). He also gives the view factor where there is obstruction by an obstacle.

16.17.10 Pool fire models

A review of pool fire models has been given by Mudan (1984c) who describes the principal elements of pool fire models, but does not present a preferred selection. An earlier review by de Ris (1979) concentrates particularly on flame emissivity.

There are a number of Models of pool fires including those by R.O. Parker (1974), Modak (1977), Mizner and Eyre (1982), Moorhouse (1982), Ndubuzu *et al.* (1983), Considine (1984 SRD R297), Tunc and Venart (1984/85a) and Babrauskas (1986b).

R.O. Parker (1974) describes a pool fire model said to give satisfactory results in accident investigation.

Modak (1977) has described a relatively complex, model consisting of a fairly large set of equations. The model is capable of determining the heat radiation to the liquid surface and to objects outside the flame. Another relatively complex model is that by Ndubuzu *et al.* (1983).

Considine (1984 SRD R297) proposes the use of the Thomas equation for flame height, the method for surface emissive power which takes account of smoke obscuration and appropriate view factors and atmospheric transmissivity.

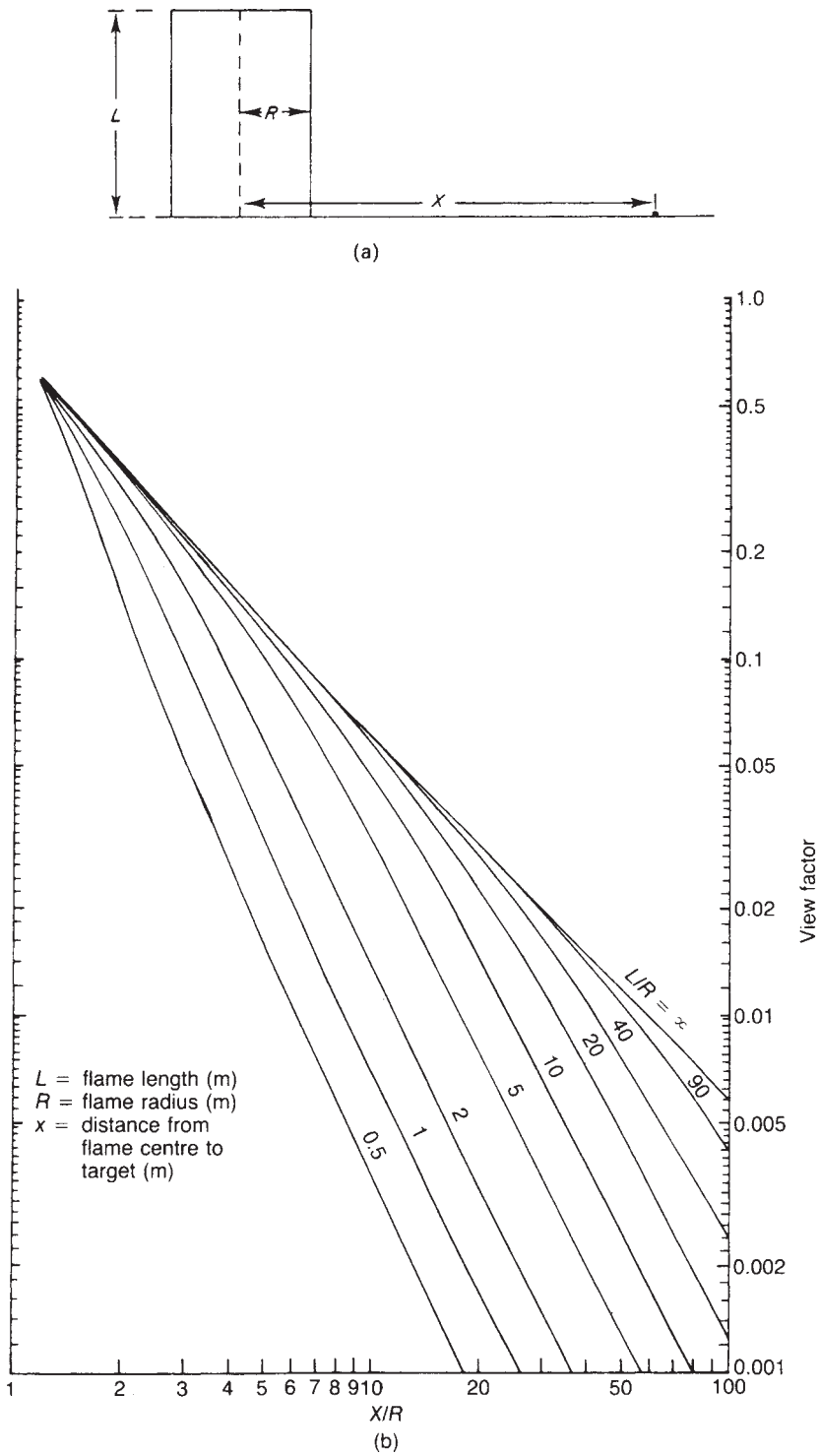


Figure 16.98 *View factor for pool fires: vertical cylinder – IP LPG Storage Code (Institute of Petroleum, 1987 MCSP Pt 9). (a) Flame and (b) view factor (Courtesy of the Institute of Petroleum)*

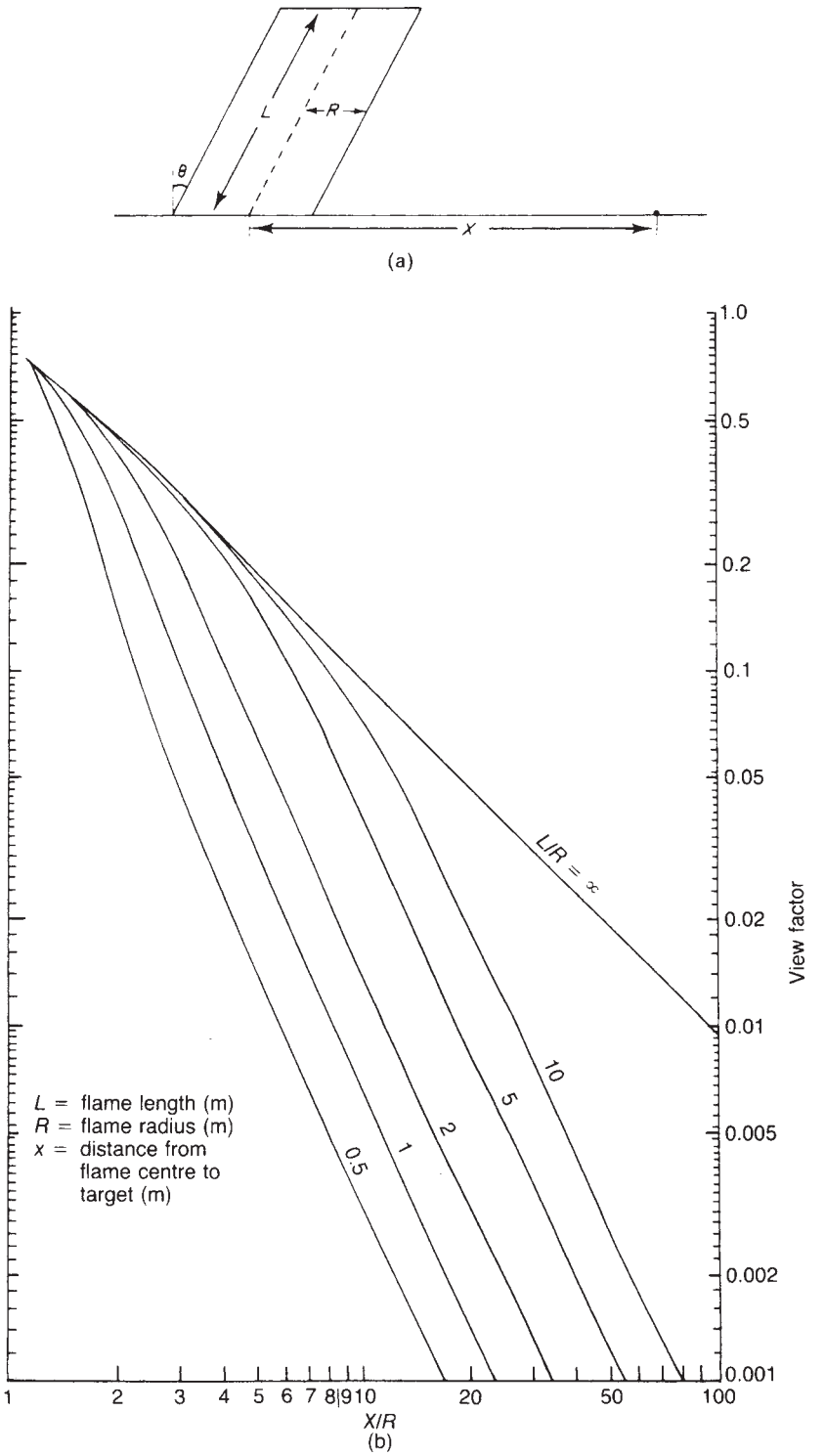


Figure 16.99 *View factor for pool fires: tilted cylinder – IP LPG Storage Code (Institute of Petroleum, 1987 MCSP Pt 9): (a) Flame and (b) view factor. Angle of title 30° (Courtesy of the Institute of Petroleum)*

Tunc and Venart (1984/85a) have given a model of the same general type intended for the estimation of the heat radiated to a cylindrical object, such as a rail tank car, inside the flame.

Some of the other models mentioned are now described.

16.17.11 Mizner and Eyre model

Mizner and Eyre (1982) review the relations available for a pool fire. In particular, they quote for the length of flame Equation 16.17.2 and for the angle of tilt Equation 16.17.19. Their preferred values for the surface emissive power are given in Subsection 16.17.8.

16.17.12 Moorhouse model

The set of original correlations given by Moorhouse (1982) and Moorhouse and Pritchard (1982) constitute another pool fire model. These authors emphasize that the flame may have a conical rather than cylindrical shape. Their model contains pairs of relations, one for a cylindrical and one for a conical flame. These are: for the length of flame, Equations 16.17.15a and 16.17.15b; for the angle of tilt, Equations 16.17.20a and 16.17.20b, or Equations 16.17.21a and 16.17.21b; and for flame drag, Equations 16.17.23a and 16.17.23b. Surface emissive powers are given in Subsection 16.17.8.

16.17.13. Babrauskas model

Another pool fire model is that given by Babrauskas (1986b). The model uses the author's treatment of liquid burning rates described in Subsection 16.17.6.

With regard to flame geometry Babrauskas argues that, given the approximation involved in treating the flame as a cylinder with uniform diameter, refined methods for flame height are not justified. In his model the flame is represented as a cylinder with diameter D and height h, For a target on the ground at distance l the following quantities are defined:

$$H = h/D \qquad [16.17.60]$$

$$L = l/D \qquad [16.17.61]$$

where D is the pool diameter (m), h is the height of the flame (m) and l is the distance from its centre to the target (m). For a flame with diameter $D > 0.1$ m it is sufficient to take $H = 1.5$.

The heat radiated by the flame is expressed in terms of the radiative power P where

$$P = \chi_r \Delta h_c m \left(\frac{\pi D^2}{4}\right) \qquad [16.17.62]$$

where Δh_c is the heat of combustion (kJ/kg), m is the mass burning rate (kg/m^{2}s), P is the radiative power (kW) and x_r is the fraction of heat radiated.

The radiative power can also be expressed for the far field as

$$P = 4\pi l^2 q_i \qquad L > 4 \qquad [16.17.63]$$

where q_i is the thermal radiation incident on the target (kW/m^2). Hence from Equations 16.17.62 and 16.17.63

$$q_i = \frac{\chi_r \Delta h_c m}{16L^2} \qquad L > 4 \qquad [16.17.64]$$

For the near field a more accurate estimate of the thermal radiation is

$$q_i = F \epsilon_f \sigma T_f^4 \qquad 1/2 < L < 4 \qquad [16.17.65]$$

where F is the view factor, T_f is the absolute flame temperature (K) and ϵ_f is the emissivity of the flame.

For the view factor F a suitable approximation is

$$F \approx H/\pi L^2 \qquad [16.17.66]$$

Then from Equations 16.17.64–16.17.66

$$\epsilon_f \sigma T_f^4 = \frac{\pi \chi_r \Delta h_c m}{16H} \qquad [16.17.67]$$

which for $H = 1.5$ and for $D \to \infty$ reduces to

$$(\epsilon_f \sigma T_f^4)_\infty = 0.131 \chi_r \Delta h_c m_\infty \qquad [16.17.68]$$

Combining Equations 16.17.38, 16.17.64, 16.17.65 and 16.17.68 yields the relations for thermal radiation

$$q_i = \frac{\chi_r \Delta h_c m_\infty}{16L^2}[1 - \exp(-k\beta D)] \qquad L > 4 \qquad [16.17.69]$$

$$q_i = F(0.131 \chi_r \Delta h_c) m_\infty [1 - \exp(-k\beta D)] \qquad \frac{1}{2} < L < 4 \qquad [16.17.70]$$

where k is the extinction coefficient (m^{-1}) and β is the mean beam length corrector.

For the fractuion of heat radiated Babrauskas refers to the data of Hägglund and Persson (1976) quoted in Table 16.65.

16.17.14 Storage tank fires

A type of pool fire which is of special interest is a storage tank fire. Such fires are usually treated as pool fires. The differences are that the liquid surface, and hence the base of the flame, is elevated and that it is surrounded by a metal wall. Another important feature is that the targets of interest usually include other storage tanks. This means that the targets may be close to the flame and that it may be necessary to consider targets at levels other than ground level and heat transfer by modes other than radiation.

Burgoyne and Katan (1947) conducted experiments on the heat wave moving through the liquid in a tank fire.

Tank fire experiments have been carried out at the Forschungsstelle für Brandschutztechnik described by Werthenbach (1971, 1971a,b, 1973) and Seeger (1974). Tank diameters up to 2 m were used. Agreement between theoretical estimates of heat radiated based on Equations 16.17.41 and 16.17.42 was obtained using a flame temperature and emissivity of 900°C and 0.9, respectively.

Seeger also investigated numerically the view factor for a vertical cylindrical flame on a tank to a target with a vertical surface on a level with the base of the flame. The effect on the view factor of altering the height of the flame or of moving the target to a level halfway up the flame was slight.

Lois and Swithenbank (1979) have used wind tunnel experiments to study fire in an array of tanks. Features considered include the effect of wind on the flame and the interaction of the wind with the tank array.

Kobori, Handa and Yumoto (1981) have studied the interactions between a tank that is on fire and a neighbouring tank that is not on fire, including heat transfer to the unignited tank by convection as well as radiation, formation of vapour in the unignited tank, induction into the fire of the vapour from that by the air drawn into flame, and flashback to the unignited tank.

Crocker and Napier (1986) have reviewed the main elements of pool fire models as they apply to tank fires, have listed the applicable view factors and have considered the implications for storage tank layout.

16.17.15 Slot fires

Another type of pool fire is the slot, trench or channel fire. Such a fire may occur on a spill of flammable liquid which has entered a trench or channel of any kind. A characteristic feature is that there is a high aspect ratio. One situation in which this type of fire may occur is the burning of a liquid spill directed to a high aspect ratio catchment area.

Slot fires are discussed briefly by Moorhouse and Pritchard (1982). One approach is to treat the fire as a series of individual pool fires and then apply the relations for circular pools. This approach appears to fit the results of small-scale experiments described by Welker (1965) and Gollahalli and Sullivan (1974). Further, data reported by Alger and Capener (1972) on the burning rates of large-scale fires of JP-5 on a pool of aspect ratio greater than 2 are consistent with those from circular pool fires. Moorhouse (1982) states that the work on LNG pool fires which he describes included some limited tests on LNG fires with an aspect ratio of 1 to 2.5.

Work on trench fires of LNG with aspect ratios up to 30 has been conducted by Mudan and Corce (1984) and is summarized by Mudan (1989b). The work indicates that in such fires the flame height is influenced more by the width than by the length of the trench and that the flame geometry is more sensitive to wind conditions than is the case in fires on circular pools.

Mudan and Croce obtained for LNG the following correlations for flame height, angle of tilt and flame drag:

$$\frac{H}{W} = 2.2 \qquad \mathrm{Fr}' \geq 0.25 \qquad [16.17.71a]$$

$$\frac{H}{W} = 0.88(\mathrm{Fr}')^{-0.65} \qquad 0.1 < \mathrm{Fr}' < 0.25 \qquad [16.17.71b]$$

$$\frac{H}{W} = 4.0 \qquad \mathrm{Fr}' < 0.1 \qquad [16.17.71c]$$

$$\cos\theta = 0.56 \qquad \mathrm{Fr}' > 0.25 \qquad [16.17.72a]$$

$$\cos\theta = 0.36\,(\mathrm{Fr}')^{-0.32} \qquad 0.042 < \mathrm{Fr}' < 0.25 \qquad [16.17.72b]$$

$$\cos\theta = 1 \qquad \mathrm{Fr}' < 0.042 \qquad [16.17.72c]$$

$$\frac{W'}{W} = 3.5 \qquad \mathrm{Fr}' > 0.25 \qquad [16.17.73a]$$

$$\frac{W'}{W} = 23.3\,(\mathrm{Fr}')^{1.37} \qquad 0.1 < \mathrm{Fr}' < 0.25 \qquad [16.17.73b]$$

$$\frac{W'}{W} = 1 \qquad \mathrm{Fr}' < 0.1 \qquad [16.17.73c]$$

with

$$\mathrm{Fr}' = u_w/2(gW)^{1/2} \qquad [16.17.74]$$

where Fr′ is a modified Froude number, g is the acceleration due to gravity (m/s^2), H is the length pf the flame, u_w is the wind speed (m/s), W is the width of the trench (m), W' is the extended width of the flame base (m) and θ is the angle of tilt (°). For calm conditions, where the value of Fr′ is very low, the flame geometry depends only on the trench width. For values of Fr′ which are higher but still less than about 0.25, the flame length decreases but the angle of tilt and flame drag increase with wind speed. For still higher values of Fr′ the flame geometry is independent of wind speed. The correlations are not strictly applicable where the wind direction is parallel to the axis of the trench.

The application of these relations to liquid fuels other than LNG is uncertain.

16.18 Flares

A jet flame occurs when flammable gas issuing from a pipe or other orifice is ignited and burns on the orifice. Historically, treatments of such flames have been concerned mainly with flames which are there by design, such as the flames on burners and flares. It is convenient, therefore, to start by considering flares.

The fundamentals of combustion in flares have been studied by Brzustowski and co-workers (e.g. Bzrustowski, 1973, 1977; Brzustowski and Sommer, 1973; Bzruztowski *et al.*, 1975) and by others.

16.18.1 Experimental studies

There is vast literature on flames. Discussion here is limited to some of the studies which have been concerned specifically with flare systems. Some of the studies on flares are tabulated in Section 16.19.

Conventionally, flares have been designed to give a flame which is vertical in still air. The use of flares on offshore oil production platforms, where helicopter access is necessary, has prompted the development of flares with an inclined flame. The models developed for inclined flares are relevant to jet flames arising from accidents.

A series of experimental studies of flares has been reported by Brzustowski and co-workers. The correlations obtained by Brzustowski and Sommer (1973) are the basis of the more elaborate flare model given in API RP 521, as described below.

Various workers have found that the API methods tend to overpredict the incident heat radiation. The need for tighter design of flares offshore, where space is limited, has given an incentive to obtain improved methods.

Experiments on flares have been conducted by Shell and are described by Chamberlain (1987). Ranges of some of the parameters in these trials were as follows: gas molecular weight 16–44; pipe diameter 0.006–1.07 m; Mach number 0.06–0.9; gas exit velocity 14–554 m/s; and wind speed 2.7–13 m/s. This work is the basis of the Chamberlain flare model given below

Chamberlain's work has been extended in the model by A.D. Johnson, Brightwell and Carsley (1994), also described below. This work was on natural gas. The ranges of some of the parameters were: pipe diameter 0.02–0.152 m; gas mass flow 2.8–8.4 kg/s; and wind speed 0.3–6.9 m/s.

Other experiments have been carried out by British Gas, as described by D.K. Cook, Fairweather, Hammonds and Hughes (1987). The experiments were on natural gas and the flows were both subsonic and sonic. Ranges of some of the other parameters in these trials were as follows: pipe diameter 0.051–0.59 m; gas exit velocity 89–402 m/s; and wind speed 1.0–13 m/s.

16.18.2 Hajeck and Ludwig model

An equation which has been widely used for the determination of the thermal radiation from a flame on a flare stack is that of Hajek and Ludwig (1960)

$$I = \frac{F_r Q}{4\pi r^2} \qquad [16.18.1]$$

where F_r is the fraction of heat released which is radiated, I is the radiation intensity on the target (kW/m^2), Q is the net heat release rate (kW) and r is the radius from the centre of the flame (m).

Combustion in the flare is a complex process. In Equation 16.18.1 this complexity is subsumed in the factor F_r. This factor has traditionally been taken as a property of the fuel only. It has been shown, however, that the F_r factor is discussed by Brzustowski (1977). and by Straitz *et al.* (1977) Some values of the fraction F_r of heat radiated are given in Table 16.68.

For the determination of radiation expsoure, the current version of API RP 521 gives Equation 16.81.1 in the form

$$D = \left(\frac{\tau F_r Q}{4\pi K}\right)^{1/2} \qquad [16.18.2]$$

where D is the distance from the centre of the flame to the target (m) K is the allowable radiation (kW/m^2) and τ is the atmospheric transmissivity.

Table 16.68 *Fraction of heat radiated by a flare*

A Fraction of heat release F_r: overall values

Gas	*F*	*Reference*
Methane	0.16	Brzustowski and Sommer (1973)
Propane	0.33	Kent (1964)
Butane	0.30	Brzustowski and Somer (1973)
Ethylene	0.38	Brzustowski and Sommer (1973)

B Fraction of heat release F_r: values as function of burner diameter[a]

Gas	*Burner diameter* (cm)	F_r (%)
Hydrogen	8.4	0.16
	20.3	0.15
	40.6	0.17
Butane	8.4	0.29
	20.3	0.28
	40.6	0.30
Methane	8.4	0.15
Natural gas	20.3	0.19
	40.6	0.23

[a] Zabetakis and Burgess (1961 BM RI 5707); quoted in API RPI 521: 1990. Also Burgess and Zabetakis (1962 BM RI 6099).

16.18.3 API RP 521 models

Flare models which have been widely used are those given in the successive aditions of API RP 521 *Guide for Pressure-relieving and Depressuring Systems*. API RP 521: 1990 gives two models. The first is described as a simplified approach. The second is based on the method of Brzustowski and Sommer (1973).

The simplified model is as follows. The Mach number Ma at the flare tip is

$$\mathrm{Ma} = 11.61 \times 10^{-2} \frac{W}{Pd^2}\left(\frac{T}{kM}\right)^{1/2} \qquad [16.18.3]$$

where d is the flare diameter (m), k is the ratio of the specific heats of the gas, M is the molecular weight of the gas, P is the absolute pressure just inside the flare tip (kPa), T is the absolute temperature of the gas (K) and W is the mass flow of gas (kg/s).

The flare diameter is determined by setting a suitable value of the Mach number. The *Guide* gives as examples values of 0.2 and 0.5.

The length of the flame is a function of the heat release and is determined from Figure 16.100.

The distortion of the flame caused by the wind velocity is defined in terms of the horizontal deviation $\sum \Delta x$ and the vertical deviation $\sum \Delta y$ of the flame tip and is a function of the ratio of the velocity at the flare tip u_j to the wind velocity u_∞. The flare tip exit velocity u_j is obtained as

$$u_j = \frac{V}{\pi d^2/4} \qquad [16.18.4]$$

or as

$$u_j = \mathrm{Ma}\ u_s \qquad [16.18.5]$$

with

$$u_s = 91.2\left(\frac{kT_j}{M_j}\right)^{1/2} \qquad [16.18.6]$$

where u_j is the exit velocity of the gas at the flare tip (m/s) , u_s is the velocity of sound (m/s) , u_∞ is the velocity of the wind (m/s), V is the volumetric flow of gas (m^3/s) and subscript j denotes the flare tip exit. The co-ordinates of the flame tip are determined using Figure 16.101.

This method does not give an explicit relation for the intensity of heat radiation on a target, but use may be made of Equation 16.18.2.

16.18.4 Brzustowski and Sommer model

In the second method given in API RP 521, the Brzustowski and Sommer model, the flare diameter is determined in the same manner by using Equation 16.18.3. The centre of the flame is then determined as follows. The horizontal distance x_c and the vertical distance y_c from the flare tip to the centre of the flame are

$$x_c = f(\bar{C}_L, d_j R) \qquad [16.18.7]$$

$$y_c = f(\bar{C}_L, d_j R) \qquad [16.18.8]$$

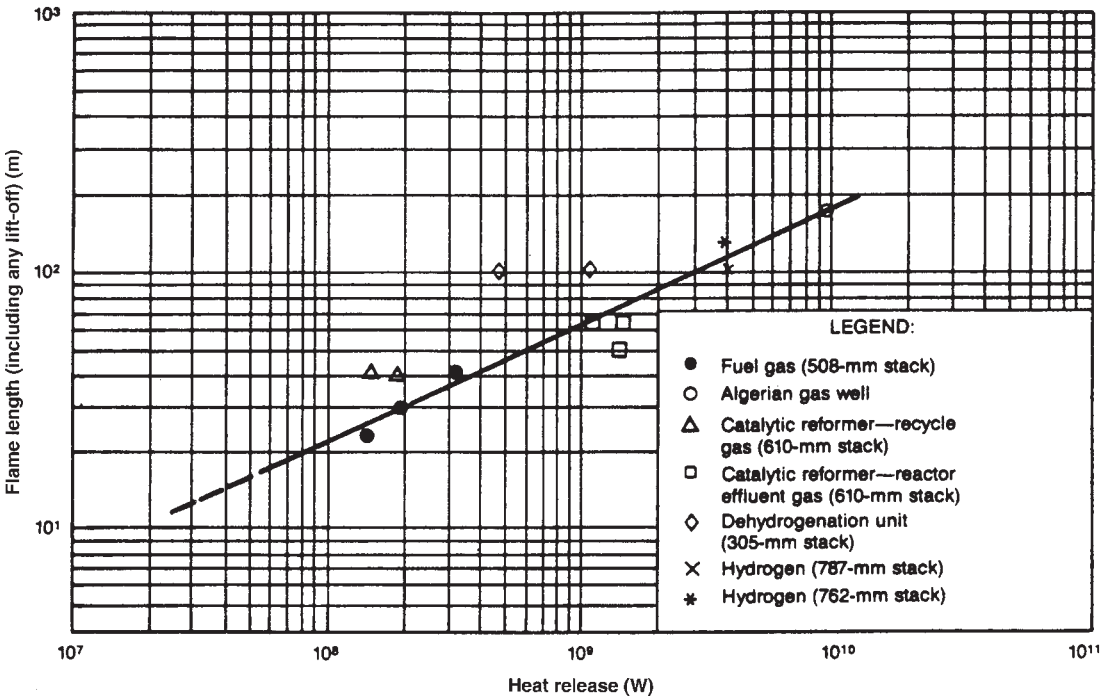


Figure 16.100 *Flare flames: flame length (API RP 521: 1990; reproduced with permission). (Multiple points indicate separate observations or different assumptions of heat content)*

with

$$\bar{C}_L = C_L \frac{u_j}{u_\infty} \frac{M_j}{29} \qquad [16.18.9]$$

$$R = \frac{u_j}{u_\infty} \left(\frac{T_\infty M_j}{T_j} \right)^{1/2} \qquad [16.18.10]$$

where C_L is the lower explosive limit (volume fraction), R is a parameter, T_∞ is the absolute temperature of the air (K), x_c and y_c are the horizontal and vertical distances of the flame centre from the flame tip (m) and $\bar{C}_L$ is a modified lower explosive limit (volume fraction). The coordinates of the flame centre are determined using Figure 16.102.

Equation 16.18.2 is used to determine the intensity of heat radiation incident on a target.

16.18.5 de Faveri *et al.* model

Another flare model is that by de Faveri *et al.* (1985). These workers performed wind tunnel experiments on small 'flares' in a wind and obtained correlations for various features of the flare such as the downwind position of the flame tip and the axis of the flame.

This model has been discussed by Crocker and Napier (1988b) in relation to multiple point source modelling of flare radiation.

16.18.6 Chamberlain model

The flare model given by Chamberlain (1987) of Shell is based on the flame shown in Figure 16.103. The geometric components of the model are (1) the effective diameter of the source D_s (2) the length of the flame in still air L_o, (3) the length of the flame in the pertaining conditions L, (4) the angle between the axis of the orifice and that of the flame α, (5) the lift-off distance of the frustrum of the flame b, (6) the length of the frustrum R_L, (7) the width of the base of the frustrum W_1, (8) the width of the top of the frustrum W_2 and (9) the area of the flame A.

The parameters which define the model geometry are determined as functions of the velocity ratio R

$$R = v/u_j \qquad [16.18.11]$$

where u is the gas velocity (m/s) , v is the wind velocity (m/s) and subscript j denotes the expanded jet.

The model equations are as follows. As described in Chapter 15, use is made of D_s for the source. For unchoked flow

$$D_s = d_o \left(\frac{\rho_j}{\rho_a} \right)^{1/2} \qquad [16.18.12]$$

with

$$\rho_j = \rho_g^o \frac{273}{T_j} \qquad [16.18.13]$$

where d_o is the throat diameter of an imagined flow nozzle (m), D_s is the effective diameter of the source (m), T_j is the temperature of the gas in the expanded jet (K), ρ_a is the

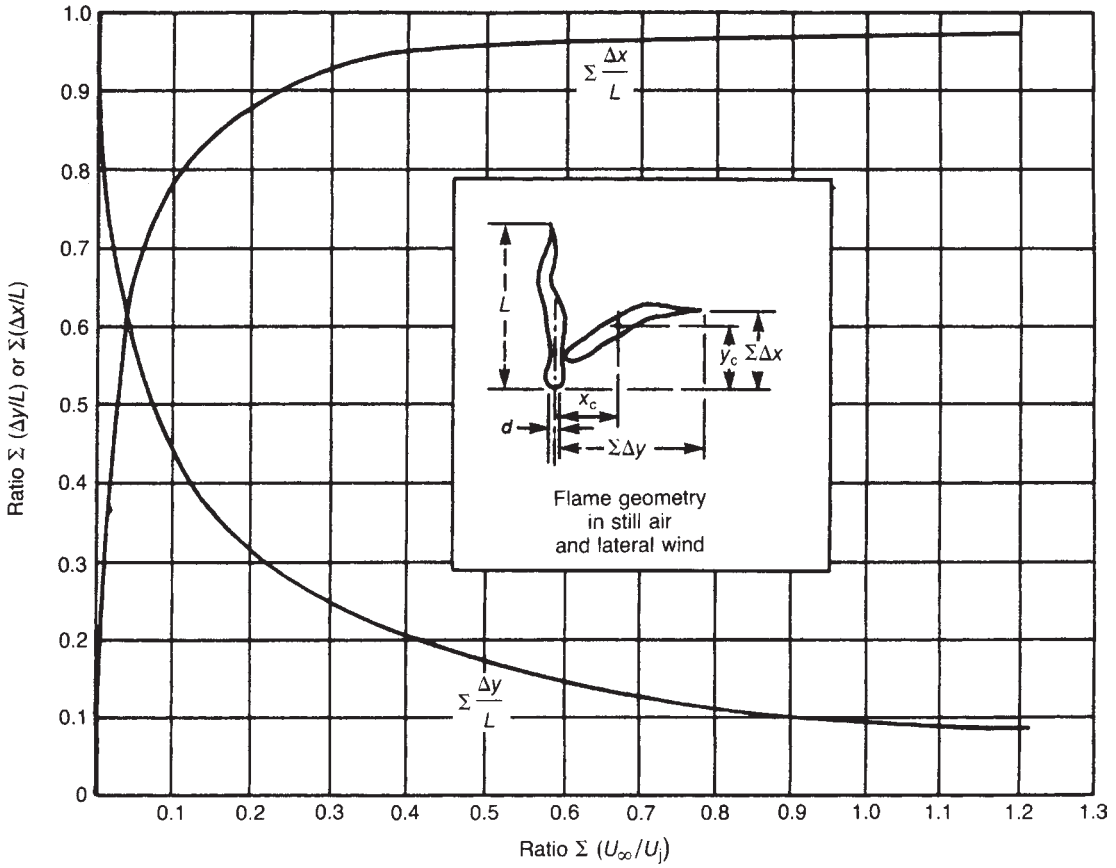


Figure 16.101 *Flare flames: distortion due to wind (API RP 521: 1990; reproduced with permission). U_∞, Lateral wind velocity; U_j exit gas velocity from the stack*

density of air (kg/m^3), ρ_g^o is the density of the gas under standard conditions (kg/m^3) and ρ_j is the density of the gas in the expanded jet (kg/m^3). For choked flow the jet expands to atmospheric pressure at a plane downstream of the exit hole, the plane then acting as a virtual source of diameter d_j. Then

$$D_s = d_j\left(\frac{\rho_j}{\rho_a}\right)^{1/2} \qquad [16.18.14]$$

with

$$d_j = \left(\frac{4\dot{m}}{\pi u_j \rho_j}\right)^{1/2} \qquad [16.18.15a]$$

$$= \frac{4\dot{m}}{\pi P_o \mathrm{Ma}_j}\left(\frac{R_c T_j}{\gamma M_k}\right)^{1/2} \qquad [16.18.15b]$$

where d_j is the diameter of the virtual source (m), $\dot{m}$ is the mass flow of gas (kg/s), M_k is the kilogram molecular weight of the gas (kg/mol), Ma_j is the Mach number of the expanded jet, P_o is the absolute atmospheric pressure (N/m^2), R_c is the universal gas constant (J/kmolK), u_j is the velocity of the gas in the expanded jet (m/s) and γ is the ratio of the specific heats of the gas.

For the length L_{Bo} of the flame in still air the implicit equation of Kalghatgi (1984) is used:

$$\Psi(L_{Bo}) = 0.2 + 0.024\xi(L_{Bo}) \qquad [16.18.16]$$

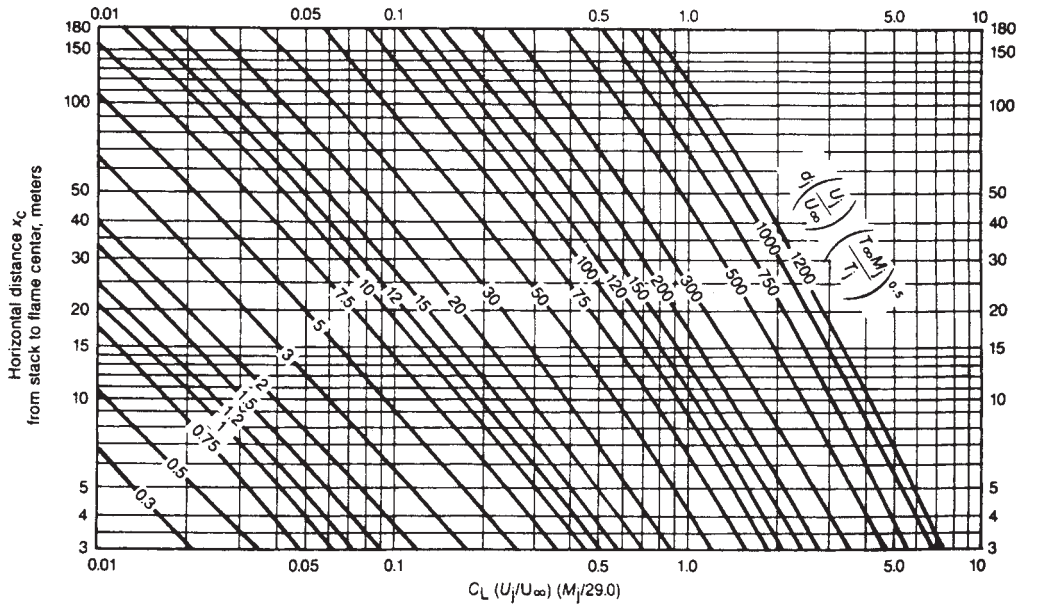
with

$$\Psi(L_{Bo}) = \left(\frac{D_s \beta}{L_{Bo} W}\right)^{2/3} \qquad [16.18.17]$$

$$\xi(L_{Bo}) = \left(\frac{g}{D_s^2 u_j^2}\right)^{1/3} L_{Bo} \qquad [16.18.18]$$

$$\beta = \left(\frac{M_a T_1}{M_p T_a}\right)^{1/2} \qquad [16.18.19]$$

where g is the acceleration due to gravity (m/s^2), L_{Bo} is the length of the flame in still air (m), M is the molecular weight of the gas, T is the absolute temperature (K), u is the velocity



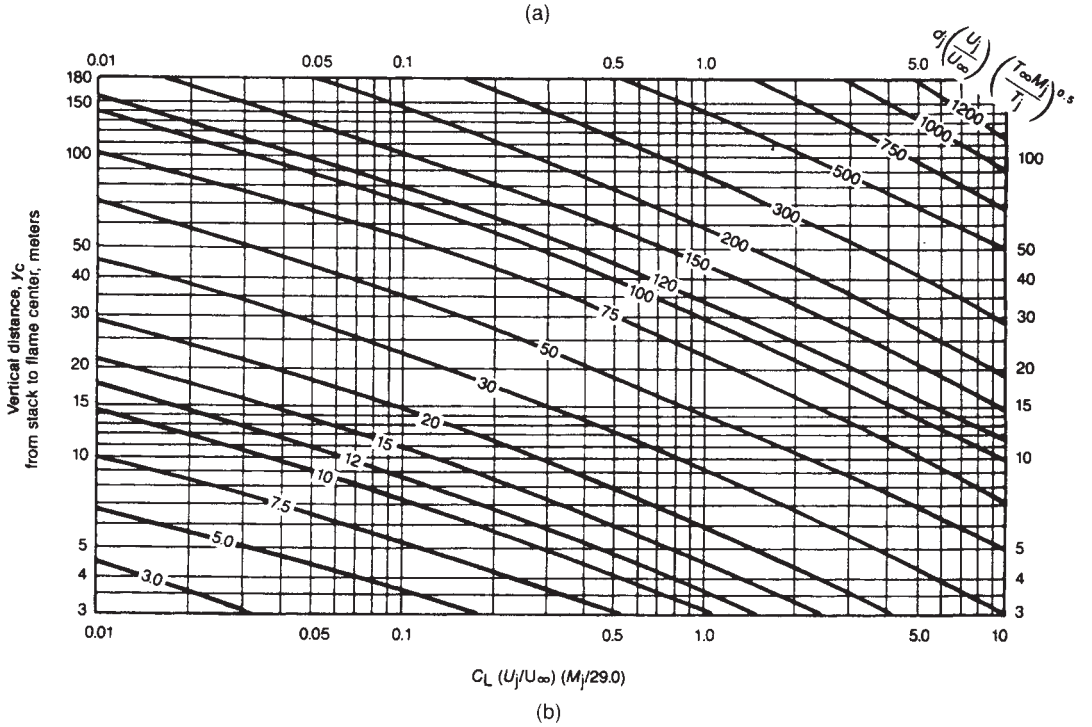


Figure 16.102 *Flare flames: location of flame centre (API RP 521: 1990; reproduced with permission): (a) Horizontal distance x_c of the flame centre from the orifice and (b) vertical distance (m) of the flame centre from the orifice. C_L, lower explosive limit; y_c, volume fraction; d_j, inside diameter of flare tip (m); M_j, molecular weight of the gas; T_j, temperature of the gas (K); T_∞, temperature of the air (K); U_j, gas exit velocity (m/s); U_∞, average wind velocity (m/s)*

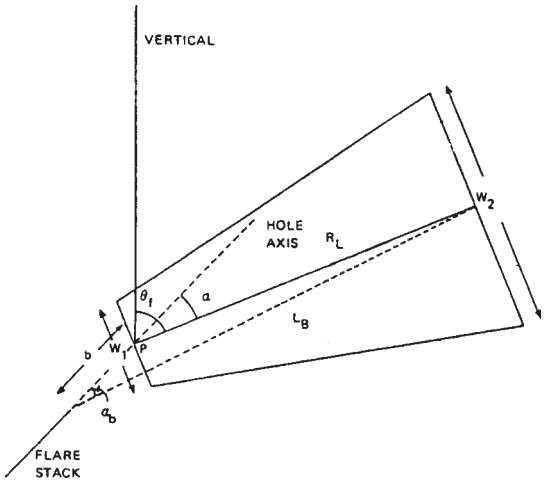


Figure 16.103 *Flare flames: flame dimensions for Chamberlain model (Chamberlain, 1987). (Note that point P is always at the intersection of the hole and frustrum axes) (Courtesy of the Institution of Chemical Engineers)*

of gas, W is the mass fraction of the fuel in a stoichiometric mixture with air, and ξ is the Richardson number based on the flame length in still air. The subscript a denotes air, j the conditions in the expanded jet, p the mean product value and 1 adiabatic combustion conditions.

For a paraffin of molecular weight M the mass fraction W of fuel in a stoichiometric mixture with air is

$$W = \frac{M}{15.816M + 39.5} \qquad [16.18.20]$$

Typical conditions of $M_a \approx 29.0$, $M_p \approx 28$, $T_a \approx 288$ K and $T_1 = 2250$ K yield $\beta \approx 2.85$.

For a tilted jet, in which the hole axis is in the wind direction and at an angle θ_j to the horizontal, it has been shown by laboratory experiments that the flame length reduces as the jet is tilted into the wind, that is as θ_j. increases, because the air entrainment coefficient increases. A linear relation holds between L_B/D_s and θ_j. Then for the actual length L_B of the flame

$$\frac{L_B}{D_s} = 163 - 0.64\theta_j \qquad [16.18.21a]$$

or

$$L_B = 105.4D_s[1 - 6.07 \times 10^{-3}(\theta_j - 90)] \qquad [16.18.21b]$$

On the assumption that L_B scales similarly with θ_j for all wind speeds and directions, the general correlation for L_B is

$$L_B = L_{Bo}[0.51\exp(-0.4v) + 0.49][1 - 6.07 \times 10^{-3}(\theta_{jv} - 90)] \qquad [16.18.22]$$

where θ_j is the angle between the hole axis and the horizontal (°) and θ_{jv} is the angle between the hole axis and the wind vector in the plane containing the hole axis, the flame axis and the wind vector (°).

For the angle α between the axis of the orifice and that of the flame

$$\alpha = \frac{1}{\xi(L_{Bo})}\{8000R + \xi(L_{Bo})(\theta_{jv} - 90)[1 - \exp(-25.6R)]\}$$
$$R < 0.05 \qquad [16.18.23a]$$

$$\alpha = \frac{1}{\xi(L_{Bo})}\{1726(R - 0.026)^{1/2} + 134 + \xi(L_{Bo})(\theta_{jv} - 90) \times [1 - \exp(-25.6R)] \quad R > 0.05 \qquad [16.18.23b]$$

where α is the angle between the hole axis and the flame axis (°).

For the lift-off distance b of the frustrum of the flame, by geometry

$$b = L_B\frac{\sin(\alpha - \alpha_b)}{\sin\alpha} \qquad [16.18.24a]$$

or

$$b = L_B\frac{\sin K\alpha}{\sin\alpha} \qquad [16.18.24b]$$

with

$$K = \frac{\alpha - \alpha_b}{\alpha} \qquad [16.18.25]$$

where b is the lift-off height (m) and α_b is the angle between the hole axis and the line joining the top of the flame to the centre of the hole (°).

K was correlated as follows:

$$K = 0.185\exp(-20R) + 0.015 \quad 0.005 < R < 3 \qquad [16.18.26]$$

For $\alpha = 0°$ or 180°

$$b = KL_B \qquad [16.18.27]$$

For the length R_L of the frustrum, by geometry

$$R_L = (L_B^2 - b^2\sin^2\alpha)^{1/2} - b\cos\alpha \qquad [16.18.28]$$

For the width W_1 of the base of the frustrum the following correlation was obtained:

$$W_1 = D_s[13.5\exp(-6R) + 1.5] \times \left\{1 - \left[1 - \frac{1}{15}\left(\frac{\rho_a}{\rho_j}\right)^{1/2}\right]\exp(-70\xi(D_s)CR)\right\} \qquad [16.18.29]$$

with

$$C = 1000\exp(-100R) + 0.8 \qquad [16.18.30]$$

$$\xi(D_s) = \left(\frac{g}{D_s^2u_j^2}\right)^{1/3}D_s \qquad [16.18.31]$$

where W_1 is the width of the frustrum base (m).

For the width of the top of the frustrum W_2, the correlation obtained was

$$W_2 = L_B[0.18\exp(-1.5R) + 0.31][1 - 0.47\exp(-25R)] \quad [16.18.32]$$

where W_2 is the width of the frustrum top (m).

For the surface area A of the flame, including the two end discs, by geometry

$$A = \frac{\pi}{4}(W_1^2 + W_2^2) + \frac{\pi}{2}(W_1 + W_2)\left[R_L^2 + \left(\frac{W_2 - W_1}{2}\right)^2\right]^{1/2} \quad [16.18.33]$$

where A is the surface area of the flame (m^2).

The surface emissive power of the flame is then

$$E = \frac{F_r Q}{A} \quad [16.18.34]$$

where F_r is the fraction of heat radiated, E is the surface emissive power (kW/m^2) and Q is the net heat release rate (kW).

The fraction F_r of heat radiated was found to correlate with gas velocity u_j as follows:

$$F_r = 0.21\exp(-0.00323u_j) + 0.11 \quad [16.18.35]$$

The radiation incident on a target is then

$$I = \tau FE \quad [16.18.36]$$

where F is the view factor, I is the radiation incident on the target (kW/m^2) and τ is the atmospheric transmissivity.

A version of the Chamberlain model incorporated in the computer code SAFETI has been described by J Cook, Bahrami and Whitehouse (1990).

16.18.7 Johnson, Brightwell and Carsley model

A.D. Johnson, Brightwell and Carsley (1994) have described a model for a jet flame of natural gas issuing horizontally, which is an extension of the flare model of Chamberlain (1987), already described. The model was developed in conjunction with large-scale tests on natural gas flames.

As in the original model, the flame is represented as the frustrum of a cone with the maximum width at the end furthest from the origin. For the flame shape the treatment is as follows. The momentum flux of the expanded jet is

$$G = \frac{\pi\rho_j u_j^2 d_j^2}{4} \quad [16.18.37]$$

where d_j is the diameter of the expanded jet (m), G is the initial momentum flux of the expanded jet (N), u_j is the velocity of the expanded jet (m/s) and ρ_j is the density of the expanded jet (kg/m^3). The parameters d_j, u_j and ρ_j are as defined by Chamberlain.

A Richardson number $\xi(L)$ is defined as

$$\xi(L) = \left(\frac{\pi\rho_a g}{4G}\right)^{1/3} L \quad [16.18.38]$$

where g is the acceleration due to gravity (m/s^2), L is a characteristic length (m) and ρ_a is the density of air (kg/m^3).

The length scale L is the length over which the buoyancy force acts and is taken as the flame length L_{bo} for a vertical flame in still air. The value of L_{bo} is given by a correlation derived by Khalhatgi (1984). L_{bo} is obtained as the solution of the equations

$$\Psi = 0.2 + 0.024\xi(L_{bo}) \quad [16.18.39]$$

with

$$\Psi = \left(\frac{2.85D_s}{L_{bo}W}\right)^{2/3} \quad [16.18.40]$$

where D_s is the effective source diameter (m), L_{bo} is the flame length in still air (m), W is the mass fraction of the fuel in a stoichiometric mixture with air and Ψ is a parameter. The effective source diameter is the throat diameter of an imaginary nozzle from which air at ambient density issues with the same mass flow and momentum as the fuel:

$$D_s = d_j\left(\frac{\rho_j}{\rho_a}\right)^{1/2} \quad [16.18.41]$$

The authors indicate that range of validity of the relation for L_{bo} is $2 < \xi(L_{bo}) < 20$.

The flame shape is defined relative to the x, y and z co-ordinates, where x, y and z are the distances in the release direction, the vertical direction and the crosswind direction, respectively. The position of the flame is determined by the relative effects of the initial jet momentum flux and the wind momentum fluxes in the x, or release, direction and in the z direction, perpendicular to the flame. The balance of these momentum fluxes is characterized by the two parameters

$$\Omega_x = \left(\frac{\pi\rho_a}{4G}\right)^{1/2} L_{bo}u_a \quad [16.18.42]$$

$$\Omega_z = \left(\frac{\pi\rho_a}{4G}\right)^{1/2} L_{bo}w_a \quad [16.18.43]$$

where u_a is the wind speed in the release direction (m/s), w_a is the wind speed perpendicular to the release (m/s) and Ω_x and Ω_z are parameters.

The end of the flame frustrum is correlated by a term defining the end of the flame in still air multiplied by a term allowing for the effect of the wind. It was found experimentally that a croswind had little effect on the position of the flame in the x direction so that the influence of the parameter Ω_z could be neglected. Then for the Ω_x position of the flame X

$$\frac{X}{L_{bo}} = f(\xi)[1 + r(\xi)\Omega_x] \quad [16.18.44]$$

with

$$f(\xi) = 0.55 + (1 - 0.55)\exp(-0.168\xi) \qquad \xi < 5.11 \quad [16.18.45a]$$

$$f(\xi) = 0.55 + (1 - 0.55)\exp[-0.168\xi - 0.3(\xi - 5.11)^2] \qquad \xi > 5.11 \quad [16.18.45b]$$

$$r(\xi) = 0 \qquad \xi < 3 \quad [16.18.46a]$$

$$r(\xi) = 0.82\{1 - \exp[-0.5(\xi - 3.3)]\} \qquad \xi > 3 \quad [16.18.46b]$$

where f and r are parameters. A limit is placed on the x position by setting a maximum value of X/L_{bo} of 1.0. Similarly, for the y position of the flame Y

$$\frac{Y}{L_{bo}} = h(\xi)[1 - c(\xi)\Omega_x] \quad [16.18.47]$$

with

$$h(\xi) = (1 + 1/\xi)^{-8.78} \quad [16.18.48]$$

$$c(\xi) = 0.02\xi \quad [16.18.49]$$

The y position is confined within the range $0 < Y/L_{bo} < 1.0$.

The maximum diameter of the flame, at the point furthest from the origin, is given by the correlation

$$\frac{W_2}{Lb_{xy}} = -0.004 + 0.0396\xi - \Omega_x(0.0094 + 9.5 \times 10^{-7}\xi^5) \quad [16.18.50]$$

with

$$Lb_{xy} = (X^2 + Y^2)^{1/2} \quad [16.18.51]$$

where W_2 is the maximum diameter of the flame (m) and Lb_{xy} is a parameter (m). For a realistic flame shape, W_2 must be greater than W_1 and less than Lb_{xy}.

The lift-off distance of the flame is

$$b = 0.141(G\rho_a)^{1/2} \quad [16.18.52]$$

where b is the lift-off distance (m). The minimum diameter of the flame is

$$\frac{W_1}{b} = -0.18 + 0.081\xi \quad [16.18.53]$$

where W_1 is the minimum diameter of the flame (m). The flame cannot become narrower than the forced convection limit and W_1/b has a minimum value of 0.12.

The z position of the flame is given by the correlation

$$\frac{Z}{X - b} = 0.178\Omega_z \quad [16.18.54]$$

This completes the model for the flame shape. For the thermal radiation, the surface emissive power is given by

$$S = S_\infty[1 - \exp(-kL)] \quad [16.18.55]$$

with

$$S_\infty = \frac{F_{s\infty}Q}{A} \quad [16.18.56]$$

where A is the total surface area of the flame (m^2), $F_{s\infty}$ is the fraction of heat radiated for flames which emit black body radiation, k is a gray gas absorption coefficient (m^{-1}), L is a length representing the emitting path length (m), Q is the net heat release rate (kW), S is the surface emissive power (kW/m^2) and S_∞ is the black body surface emissive power (kW/m^2). The value of k was found to be 0.4 m^{-1}, whilst $F_{s\infty}$ was correlated as follows:

$$F_{s\infty} = 0.21\exp(-0.00323u_j) + 0.14 \quad [16.18.57]$$

The thermal radiation on the target is then

$$q = (F_{sd}S_{sd} + F_{en}S_{en})\tau \quad [16.18.58]$$

where F is the view factor, q is the thermal radiation incident on the target (kW/m^2) and τ is the atmospheric transmissivity. Subscripts en and sd denote the end and the side of the flame, respectively.

Figure 16.104 shows a set of comparisons between the results obtained with the model and those obtained from the experimental tests for four standard trial conditions B–E.

16.18.8 Cook *et al.* model

A model for a flare of natural gas has been given by D.K. Cook *et al.* (1987). This model also is relatively complex.

16.19 Jet Flames

There is a wide variety of situations in which a jet flame, or ejected flame, can occur in the process industries, either by design or by accident. The principal situations in which flames occur by design are in burners and flares. Flames on burners are not treated here. Those on flares have been considered in Section 16.18.

Ejection of flammable fluid from a vessel, pipe or pipe flange can give rise to a jet flame if the material ignites. An intermediate situation, and one which particularly concerns the designer, is where the jet flame results from ignition of flammable material vented from a pressure relief valve.

Scenarios involving jet flames are not easy to handle, since a large jet flame may have a substantial 'reach', sometimes up to 50 m or more.

Jet flames have been involved in a number of accidents. Perhaps the most dramatic were the large jet flames from the gas riser on the Piper Alpha oil platform, as described in Appendix 19. In other cases jet flames from pressure relief valves have caused adjacent vessels to overheat and burst, giving a boiling liquid expanding vapour explosion, or BLEVE. Such was the case at Mexico City, as described in Appendix 4.

16.19.1 Experimental studies

Much of the early experimental work relevant to jetflames was concerned with flares. An account of this work was given in Section 16.18. There is now, however, a growing interest in the jet flame in its own right.

Table 16.69 lists some studies on flares and on jet flames. Investigations of the combustion of large-scale jet releases of liquefied flammable gas have been undertaken by Shell, BP and British Gas, both separately and in co-operation.

The work done covers a variety of jet flames, including flames of natural gas and of LPG. Representative accounts of work using natural gas are those by Chamberlain (1987) and AD. Johnson, Brightwell and Carsley (1994) at Shell, and by D.K. Cook *et al.* (1987) at British Gas.

Accounts of work on jet flames of LPG at Shell and British Gas have been given by Hirst (1984) and Tam and

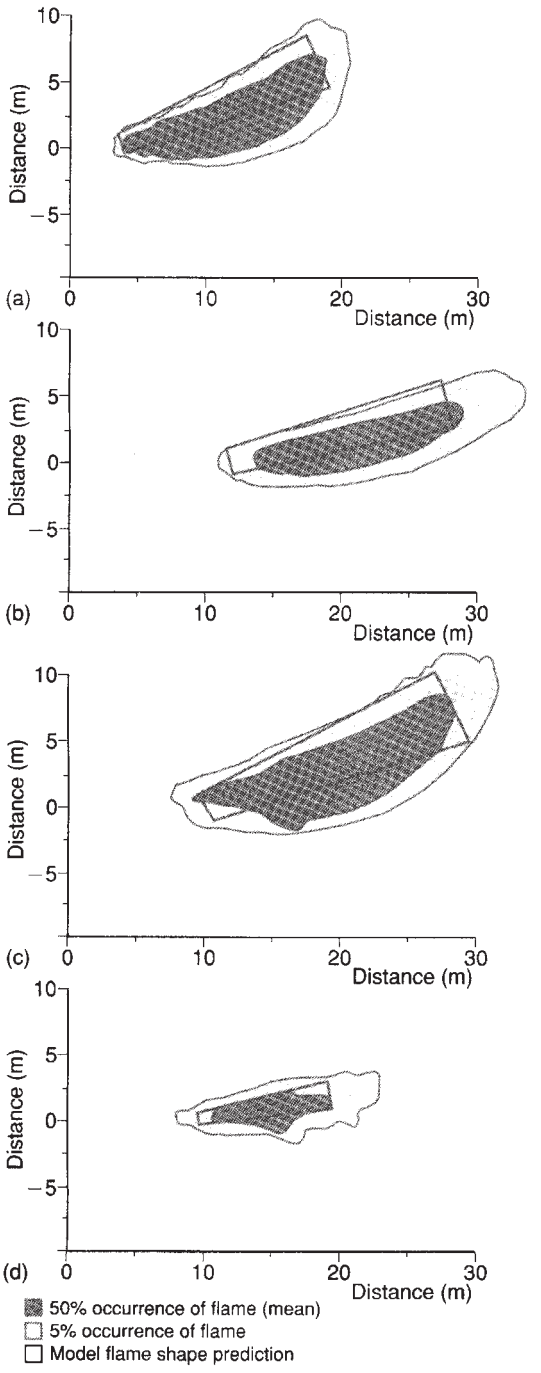


Figure 16.104 *Flare flames: flame dimensions for the model of Johnson, Brightwell and Carsley. Comparison between model predictions and experimental results (A.D. Johnson, Brightwell and Carsley, 1994): (a) Test 1040, Type B; (b) Test 1033, Type D; (c) Test 1083 Type C and (d) Test 1089, Type E*

Cowley (1989). The work on flames formed part of a study of emission and gas dispersion of jets as well as of combustion.

Hirst (1984) describes experiments using liquefied propane. Tests were carried out using orifices ranging from 9 to 52 mm in diameter and pressures from about 6 to 20 bar. Both vertical and horizontal releases were studied.

A series of tests were done with vertical releases. The liquid rose in a strongly divergent cone bending with the wind. The cone angle was typically 30° for the plume but up to 90° in the flash region. The releases usually reached a steady state before ignition. The visible clouds at ignition were large, extending up to 45 m vertically and 70 m downwind. In most cases a fireball formed and in several tests rose to 100 m; the most fully developed fireballs occurred at low wind speeds.

The overpressures generated by the flames were also measured. The maximum observed overpressures fell from some 3 mbar at 20 m from the release point to about 0.8 mbar at 100 m.

Other tests were done with horizontal releases. One of features measured in these trials was the distance reached by the flame. Figure 16.105 gives for a 5 mm diameter pipe the relation between the mass flow and the impingement distance of the flame.

One of the trials shows a 35 m long jet flame from a full bore release of 7.9 kg/s from a 50 mm pipe at a pressure of 13 barg. The combustion energy was 365 MW. The maximum surface emissive power was 250 kW/m^2 and occurred 25 m from the release point and just before the flame underwent transition from the momentum-dominated to the buoyancy-dominated condition.

However, for such full bore discharges the heat radiation within the flame was complex and steady heat fluxes were mainly in the range 50–220 kW/m^2 and depended on the discharge conditions and the target distance. The maximum temperature occurred at a distance of 4 m and had a value of 1570 K.

The problem of heat radiation from a flame on a pressure relief valve on a rail tank car onto the surface of the latter has been studied by Tunc and Venart (1984/85b). Experiments were conducted on ignited releases from pressure relief valves on tank cars.

16.19.2 Empirical features

A jet flame resulting from the ignition of a leak of flammable fluid at the leak aperture is a diffusion flame. The basic characteristics of such a flame have been outlined in Section 16.12.

At low velocities the flame is generally attached to the point of release, but at higher velocities it becomes detached, the distance between the orifice and the flame increasing with velocity so that it may become unstable and lift off, thus being extinguished. If, however, the flame impinges on an obstruction, this may serve to stabilize it.

As already stated, jet flames can have a considerable reach. The flame impingement distance can be up to 50 m or more. The reach is sometimes expressed in terms of the ratio of the flame length to the orifice diameter, and values of this l/d ratio in excess of 300 are quoted.

Generally, the length of a jet flame over the range of practical interest is approximately proportional to the square root of the mass flow. This is the implication of the API correlation for the flame length on a flare and of

Table 16.69 *Some studies on flares and on jet flames*

A Studies of flares	
Experimental studies of heat radiation	Studies referenced in API RP 521: 1990
Experimental and theoretical studies of flare dimensions and heat radiation	Brzustowski and Sommer (1973)
Experimental and theoretical studies of flare characteristics	de Faveri *et al.* (1985)
Theoretical model of flare dimensions and heat radiation	Chamberlain (1987)
Experimental and theoretical studies of flare dimensions and heat radiation	D.K. Cook Fairweather, Hammonds and Hughes (1987); D.K. Cook, Fairweather, Hankinson and O'Brien (1987) D.K. Cook (1991a,b)
Experimental and theoretical studies of flare dimensions and heat radiation	A.D. Johnson, Brightwell and Carsley (1994)
B Studies of jet flames	
Theoretical model of jet flame dimensions	Burke and Schuman (1928a,b)
Theoretical model of jet flame dimensions	Hawthorne, Weddell and Hottell (1949)
Theoretical model of jet flame dimensions and heat radiation	Craven (1972, 1976)
Experimental studies of jet flames of LPG	Hirst (1984)
Experimental and theoretical studies of jet flame dimensions and heat radiation	Sonju and Hustad (1984); Hustad and Sonju (1986)
Experimental and theoretical study of jet flames on rail tank cars	Tunc and Venart (1984/85b)
Empirical model of jet flame dimensions and hazard range	Considine and Grint (1985)
Empirical model of jet flame dimensions and heat radiation	Clay *et al.* (1988); Grint (1989)
Experimental studies of jet flames of LPG	Tam and Cowley (1989)
Theoretical model of gas pipeline jet flame heat radiation	D.A. Carter (1991)

the work on propane jet flames just described. It is also implied in a number of models.

The graph given in Figure 16.105 is fitted approximately by the relation

$$l_i \approx 6m^{0.5} \qquad 0 < m < 50 \qquad [16.19.1]$$

where l_i is the impingement distance (m) and m is the mass flow (kg/s).

The fraction of heat radiated by a jet flame is a function of the fuel, being less for hydrogen and methane than for propane. It tends to increase and reach a maximum as the orifice diameter increases. It usually lies in the range 0.15–0.3.

For diffusion flames in general the flame temperatures have been discussed by Gugan (1976). He quotes values of some 1600°C for laminar diffusion flames and 2000°C for turbulent diffusion flames, the heat release in the latter being an order of magnitude greater. The maximum flame temperature in a gas jet flame is of the order of 2000°C.

The maximum flame temperatures observed in the work on jet flames of liquefied propane were of the order of 1300°C. Further, in this work on liquefied propane the values of the surface emissive power up to 250 kW/m^2 were observed, but these are spot values and do not occur over the whole flame.

16.19.3 Modelling of jet flames

By comparison with fireballs and pool fires, with jet flames the number of possible scenarios to be considered is much greater. The case mainly treated is that of a vertical flame on an upward pointing jet, In calm conditions or in wind. Another case occurs where the jet points upwards not vertically but at an angle. In this case there may be a variety of wind directions, confluent with, opposed to or across the jet. A third case is the horizontal jet, for which again the wind direction may be confluent, opposed or across.

Different workers have assumed different geometries for the jet. These include a cone (e.g. Craven, 1972), a cylinder (e.g. Croce and Mudan, 1986) and a frustrum (e.g. Chamberlain, 1987). One consequence of this is that there is no generally applicable view factor and that the view factor to be used has to be developed for the particular geometry, except in so far as the point source method is applicable.

A model of a jet flame was formulated by Burke and Schumann (1928a,b) and was later taken up by Savage (1962). Another early model is that of Hawthorne, Weddell and Hottel (1949). Work on the modelling of jet flames has been done by Craven (1972), Bilger (1975, 1976, 1977, 1979, 1989), MITI (1976), H.A. Becker and Liang (1978, 1982), R. Becker (1980a,b), Kalghati (1981–1983, 1984), de Faveri, Fumarola and co-workers (Fumarola *et al.*, 1983; de Faveri *et al.*, 1985), Peters and co-workers (Peters and Williams,

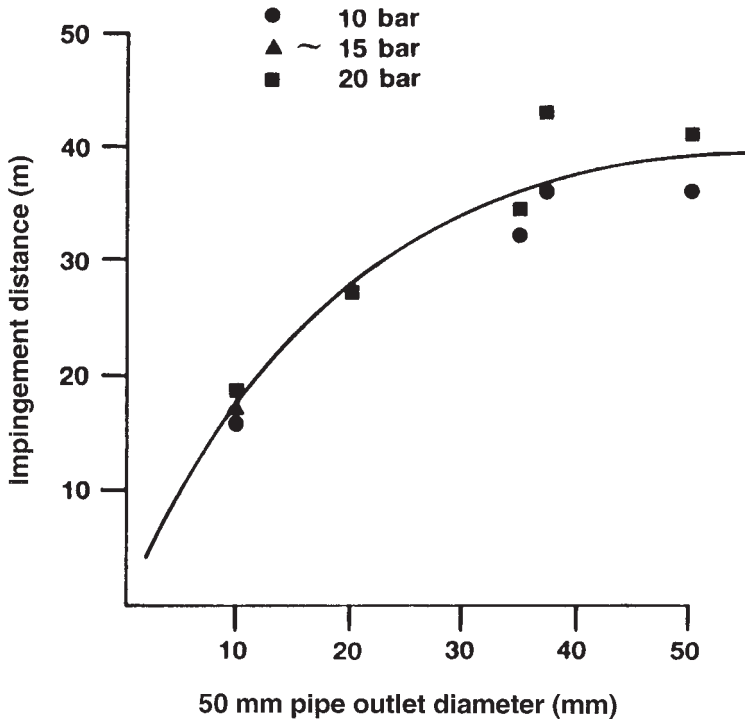


Figure 16.105 *Jet flames: flame impingement distance vs mass flow for propane (Tam and Cowley, 1989) (Courtesy of Gastech)*

1983; Peters and Göttgens, 1991), Hustad and Sonju (Sonju and Hustad, 1984; Hustad and Sonju, 1986), Croce and Mudan (1986) and Duijm (1994).

Work at Shell includes that by Chamberlain (1987) and A.D. Johnson, Brightwell and Carsley (1994).

Birch and co-workers at British Gas have conducted a series of studies on unignited and ignited jets (Birch *et al.*, 1978, 1984, 1988, 1989). Also at British Gas, D.K. Cook, Fairweather and co-workers have modelled natural gas flares (D.K. Cook, Fairweather, Hammonds and Hughes, 1987; D.K. Cook, Fairweather, Hankinson and O'Brien, 1987; D.K. Cook, 1991a,b; Fairweather *et al.*, 1991; Fairweather, Jones and Linstedt, 1992).

Models used by the HSE have been described by Clay *et al.* (1988), Grint (1989) and D.A. Carter (1991).

The set of models of fire events given by Considine and Grint (1985) includes one for a jet flame.

Many jet flame models derive from work on the modelling of flares, and most models are for jet flames of gas, particularly natural gas. There are also a few models for jet flames of a flashing liquid such as LPG.

Models for jet flames of LPG include those given by Clay *et al.* (1988), Grint (1989) and J. Cook, Bahrami and Whitehouse (1990).

Some of the principal jet flame models are now described.

16.19.4 Hawthorne, Weddell and Hottel model

One of the first models of a jet flame was that given by Hawthorne, Weddell and Hottel (1949). They envisage the flame as an inverted cone with the apex on the orifice. The equations for the length of the flame and for the diameter at the top of the cone have been given above as Equations 16.3.3 and 16.3.4, respectively.

16.19.5 Bzrustowski and Sommer model

The model of Brzustowski and Sommer (1973), which is given in API RP 521 as an alternative to the simplified API method for flare design and has been described in Section 16.18, is also used as a model for a jet flame.

16.19.6 Craven model

A model of a jet flame developed for the purpose of designing of emergency relief vents has been described by Craven (1972). He gives the following method of estimating the heat flux incident on a target near the flame.

The flame model considered is shown in Figure 16.106. The dimensions of the flame are estimated using the correlation of Hawthorne, Weddell and Hottel given in Equations 16.3.3 and 16.3.4. The flame temperature is assumed to be 2300 K, a value which is equal to or somewhat greater than adiabatic flame temperature for most hydrocarbons. The emissivity of the flame is taken as unity. The radiant heat flux E is then

$$E = \epsilon \sigma T^4 \qquad [16.19.2]$$

where E is the radiant heat flux (W/cm^2), T is the absolute temperature of the flame (K), ϵ is the emissivity of the

flame, and σ is the Stefan–Boltzmann constant. The emissivity is assumed to be unity, so that for a flame temperature of 2300 K

$$E = 160 \text{ W/cm}^2 = 1600 \text{ KW/m}^2$$

The heat flux and view factors for targets at points X, Y and Z in Figure 16.106 are considered. At point X, which is directly beneath the vent, the emissivity may be taken as unity. For a horizontal target at this point the flame is viewed as a disc and the view factor F_X (Howell, 1982–configuration B-11) is

$$F_X = \frac{r^2}{(l+h)^2 + r^2} \qquad [16.19.3]$$

where h is the height of the vent orifice (m), l is the length of the flame (m) and r is the radius of the flame at its tip (m).

For radiation at point Z the flame is treated as a rectangular radiator ABCD with an emissivity of unity. For

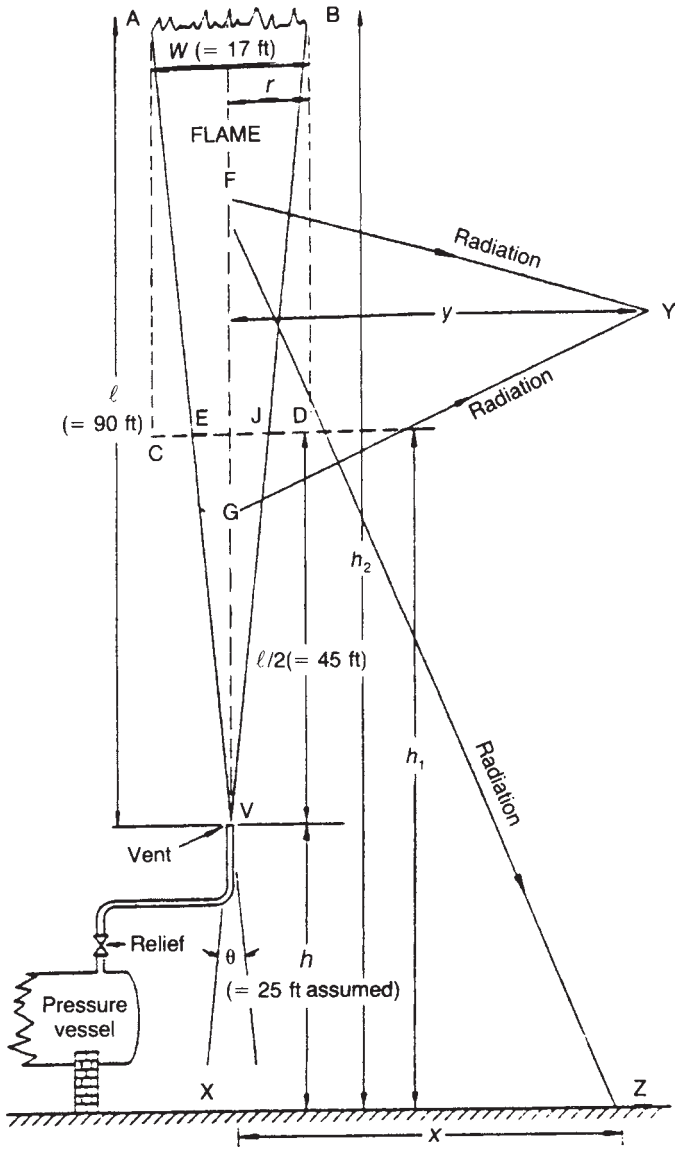


Figure 16.106 *Jet flames: flame dimensions for the Craven model (after Craven, 1972) (Courtesy of the Institution of Chemical Engineers)*

a horizontal target at this point the configuration factor F_Z is

$$F_Z = \frac{xr}{\pi}\left[\frac{1}{(h_1^2 + x^2)} - \frac{1}{(h_2^2 + x^2)}\right] \quad [16.19.4]$$

with

$$h_1 = h + l/2 \quad [16.19.5a]$$

$$h_2 = h + l \quad [16.19.5b]$$

where h_1 is the distance from the ground to the bottom of the radiator ABCD (m), h_2 is the distance from the ground to the top of the radiator (m) and x is the distance between points X and Z (m). The value of the view factor F_Z passes through a maximum as x increases.

The radiation at point Y is more difficult to determine, but an estimate may be made as follows. At this point part of the radiation comes from the thin part of the flame. In this case the area of the radiator ABEJ is approximated by $^3/_4\,rl$ and the view factor F_Y is given very approximately by the expression

$$F_Y \approx \frac{rl}{\pi y^2} \quad [16.19.6]$$

with

$$y \approx 10 D_{max} \quad [16.19.7]$$

where D_{max} is the maximum cone diameter (m) and y is the horizontal distance to the axis of the flame (m).

Craven points out that, whilst the above treatment applies to the highly turbulent flame occurring during the main discharge, a different situation occurs as this discharge subsides. In this stage there may exist for a short period a flame which is much less turbulent. Such a flame will tend to be larger but its temperature will be much less and the net effect is that the heat radiated is also less.

He also draws attention to the strong forces which can be exerted by a jet reaction when material under pressure is vented, and to the possibility that if the vent supports are inadequate, the vent pipe, and hence the flame, may be deflected from the vertical.

The method described is not intended to be used for flames on flare stacks, which are not highly turbulent and are therefore cooler.

Craven (1976) has compared estimates made by his method with observations given by R.O. Parker (1974) based on the ignition of an accidental discharge of natural gas. The results of the comparison of predicted and observed thermal radiation fluxes to targets side-on to the turbulent flame brush are given in Table 16.70.

The method given by Craven is essentially intended for design rather than for hazard assessment. In particular, the value assumed for the flame temperature is at the upper end of the range that is likely to occur in practice.

Table 16.70 *Thermal radiation from a flame on a vent: comparison of predicted and observed radiation fluxes to side-on targets (Craven, 1976) (Courtesy of the Institution of Chemical Engineers)*

Distance ratio[a]	*Heat radiation flux* (W/cm^2)	
	Predicted[b]	*Observed*[c]
3.3	9.0	7.0
6.67	2.3	2.8
10	1.0	1.37
13.3	0.6	0.8
16.7	0.4	0.51

[a] Ratio of the distance from the flame to the target to the flame diameter.
[b] Predicted using the method of Craven (1972), as described in the text.
[c] Observed data given by R.O. Parker (1974).

16.19.7 Hustad and Sonju model

Another jet flame model is that of Hustad and Sonju (Sonju and Hustad, 1984; Hustad and Sonju, 1986). Following earlier work by Suris, Flankin and Shoring (1977), Hustad and Sonju correlate the flame dimension in terms of the Froude number Fr. Their equations are

$$\frac{H}{d} = A\ \mathrm{Fr}^m \quad [16.19.8]$$

$$\frac{D}{d} = B\,\mathrm{Fr}^m \quad [16.19.9]$$

with

$$\mathrm{Fr} = \frac{u^2}{gd} \quad [16.19.10]$$

where d is the diameter of the orifice (m), D is the diameter of the flame (m), g is the acceleration due to gravity (m/s^2), H is the height of the flame (m), u is the gas velocity at the nozzle exit (m/s) , A and B are constants and m is an index.

For vertical flames they obtained values of A of 21 for methane and 27 for propane, and values of B of 2.5 for methane and 4 for propane. For both gases the value of m in both equations was 0.2 for $\mathrm{Fr} < 10^5$, but zero for $\mathrm{Fr} > 10^5$. Thus for both gases the value of the ratio H/D was constant, being 8.4 for methane and 6.75 for propane.

For horizontal flames of propane Equations 16.19.8 and 16.19.9 again applied. For Equation 16.19.8 the values of the constant just given were again applicable, but for Equation 16.19.9 the values of B and m were 10 and 0.156, respectively.

The height H^* over which the flame radiates heat is given as

$$H^* = H - h \quad [16.19.11]$$

with

$$\frac{h}{d} = C\left(\frac{d}{u}\right)^{-1} \quad [16.19.12]$$

where h is the lift-off height (m), H^* is the flame radiation height (m) and C is a constant. The value of the constant C is $3.6 \times 10^{-3}\ s^{-1}$.

For the fraction of heat radiated, Hustad and Sonju give

$$F = 4.74Q^{-0.2} + 11.6Q^{0.4} \qquad 1 < Q < 7 \quad [16.19.13]$$

where F is the fraction of heat radiated and Q is the heat release rate (MW).

Thus, for example, for propane at heat release rates of 1 and 7 MW the fractions of heat radiated are 0.163 and 0.285, respectively.

16.19.8 Chamberlain model and Johnson, Brightwell and Carsley model

The flare models of Chamberlain (1987) and A.D. Johnson, Brightwell and Carsley, described in Section 16.18, also have application as models for a jet flame in an accident. The latter model is for a horizontal flame, which is the orientation of most interest in that context.

16.19.9 Cook, Bahrami and Whitehouse model

J. Cook, Bahrami and Whitehouse (1990) have described the jet flame models incorporated in the computer code SAFETI. There are two such models.

The first model is described as based on the API RP 521 jet flame model. The relations given are

$$L = 0.00326[\dot{m}(-\Delta H_c)]^{0.478} \qquad [16.19.14]$$

$$R_s = 0.29s[\log_{10}(L/s)]^{0.5} \qquad [16.19.15]$$

where $(-\Delta H_c)$ is the heat of combustion (J/kg), L is the length of the flame (m), $\dot{m}$ is the mass flow (kg/s), R_s is the radius of the flame at distance s (m) along the centre line (m).

It is assumed that the jet is emitted either vertically upwards or horizontally downwind. For a vertical jet which may be bent over by the wind, the trajectory is constructed using the API prescription according to the equation

$$\frac{dz}{dx} = \frac{1.6\pi D_j u_j}{u_w}\left(\frac{1}{s} - \frac{1}{L}\right) \qquad [16.19.16]$$

where D_j is the diameter of the jet (m), u_j is the velocity of the jet (m/s), u_w is the wind velocity (m/s) and x and z are the distances in the horizontal and vertical directions (m). Then the trajectory of the centre line of the jet flame is

$$x(s) = \int_0^s \frac{ds'}{\left[1 + (dz/dx)^2\right]^{0.5}} \qquad [16.19.17]$$

$$z(s) = \int_0^s \frac{ds'}{\left[1 + (dx/dz)^2\right]^{0.5}} \qquad [16.19.18]$$

The other jet flame model used is the Chamberlain model.

16.19.10 Carter model

A model for the thermal radiation incident on a target from a jet flame on a gas pipeline has been given by D.A. Carter (1991).

The flame assumed is as shown in Figure 16.107. Its dimensions are based on its state 30 s after release. Carter states that the model of the flame itself is based on that of Chamerlain, but otherwise gives no details.

The flame is treated as a multiple source radiator. For each source in the flame the relation for the thermal radiation is

$$q = \frac{F_r(-\Delta H_c)\dot{m}\tau}{4\pi x^2} \qquad [16.19.19]$$

with

$$\tau = 1 - 0.0565 \ln x \qquad [16.19.20]$$

where F_r is the fraction of heat radiated, $(-\Delta H_c)$ is the heat of combustion (kJ/kg), $\dot{m}$ is the mass flow (kg/s), q is the heat incident on the target (kW/m^2), x is the distance from the source to the target (m) and τ is the atmospheric transmissivity.

The flame model is embodied in the computer code SHELF and the heat radiation model in the code MAJESTIC.

As an illustration of the model, consider the example given by Carter. The problem is the determination of the heat radiation contours for a release of ethylene from a 9 in. pipeline at 100 bar with a mass flow of 43.7 kg/s. The flame length is 39 m and the flame tilt from vertical 11.5°. The heat of combustion is 4.771×10^4 kJ/kg and the fraction of heat radiated is 0.1284. Then from Equation 16.19.19 the contours of incident heat are as shown in Figure 16.108.

16.19.11 MITI model

Turning now to models for jet flames of flashing liquids, an equation for the length of a diffusion flame on the surface of an oil storage tank as a function of the Froude number has been given by Werthenbach (1971a,b, 1973). This equation has been adapted by the MITI (1976) for the jet flame formed if liquefied flammable gas blows a bursting disc and then ignites:

$$q = 0.0006785L^{2.5} \qquad [16.19.21]$$

where L is the flame length (m) and q is the fuel flow (kg/s). The use of this equation to correlate the length of ejected flames from fire engulfed vessels is discussed below.

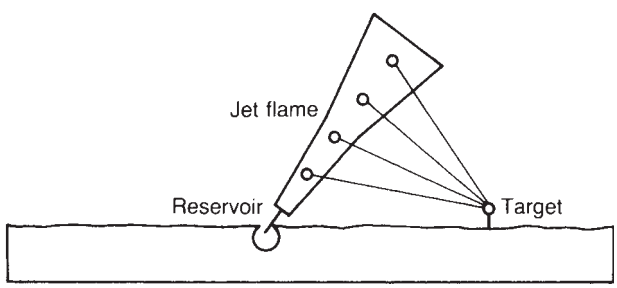


Figure 16.107 *Jet flames: flame dimensions for the Carter model of gas pipeline release (D.A. Carter, 1991) (Courtesy of Butterworth-Heinemann)*

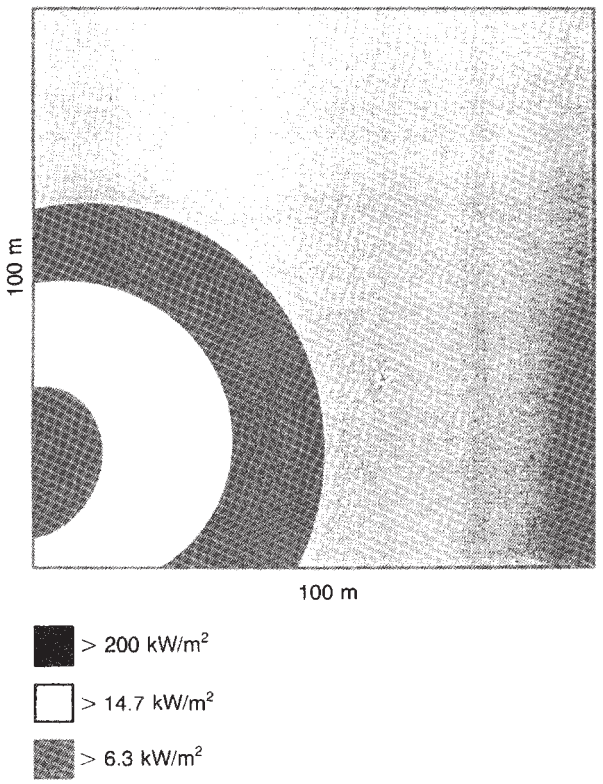


Figure 16.108 *Jet flames: heat radiation contours for illustrative example of flame from gas pipeline release (D.A. Carter, 1991). A > 200 kW/m²; B > 14.7 kW/m² and C > 6.3 kW/m² (Courtesy of Butterworth-Heinemann)*

16.19.12 Considine and Grint model

Considine and Grint (1985) have derived a model for a jet flame based on the work of the MITI (1976) on liquid ethylene.The flame is assumed to be conical. The model equations are

$$L = 9.1\dot{m}^{0.5} \quad [16.19.22]$$

$$W = 0.25L \quad [16.19.23]$$

where L is the length of the flame (m), $\dot{m}$ is the mass flow (kg/s), and W is the half-width of the flame tip (m).

This model also includes relations for the hazard range of the flame. These are given in Section 16.39.

16.19.13 Clay *et al.* model

Clay *et al.* (1988) describe a set of models used by the HSE for hazard assessment, one of which is for a jet flame of LPG.

The flame length is given as

$$F = \frac{(H_c m)^{0.444}}{161.66} \quad [16.19.24]$$

where F is the flame length (m), H_c is the heat of combustion (J/kg) and m is the mass flow (kg/s).

The flame is modelled as a point source radiator with heat radiated from a point located 4/5 of the flame length from the origin. For the thermal radiation the relation used is

$$q = \frac{fH_c m\tau \times 10^{-3}}{4\pi x^2} \quad [16.19.25]$$

with

$$\tau = 1 - 0.0565 \ln x \quad [16.19.26]$$

where f is the fraction of heat radiated, q is the thermal radiation received by the target (kW/m^2), x is the distance between the source and the target (m) and τ is the atmospheric transmissivity.

Graphs for the flame length and thermal radiation from a jet flame of LPG are given by Grint (1989) and appear to give results similar to those obtained with this model.

16.19.14 Modified Cook, Bahrami and Whitehouse model

J. Cook, Bahrami and Whitehouse (1990) state that for jet flames from a liquid or from a two-phase liquid–vapour mixture Chamberlain's model can be adapted by the following modification of the effective source diameter:

$$D_s = D_j \frac{(\rho_j \rho_v)^{1/2}}{\rho_a} \quad [16.19.27]$$

and the lift-off distance b modified as follows:

$$b = 0.015L \qquad [16.19.28]$$

where ρ_v is the density of the vapour (kg/m^3).

16.19.15 Tunc and Venart model

The problem of heat radiation from a flame on a pressure relief valve on a rail tank car onto the surface of the latter has been studied by Tunc and Venart (1984/85b). Vertical and tilted flames are considered. The flame is modelled as a radiating surface rather than a point source. The view factor for a tilted flame is given.

16.19.16 View factors

In some applications it is sufficient to treat the jet flame as a point source radiator. In other cases it may be necessary to use a more accurate view factor. For a view factor based on the point source method use may be made of Equations 16.13.101–16.13.103.

View factors for some of the jet flame models just described have been given by Crocker and Napier (1988a). For the model by Hawthorne, Weddel and Hottel (1949) of a vertical flame, Crocker and Napier refer to the work of Tunc and Venart (1984/85b), who treat the flame as conical, and quote for the view factor F in this case the following integral equations given by Becker (1980a):

$$F = \frac{2}{\pi}\int_h^{h+L} \frac{[x\sin\psi + (z\tan\alpha - r_f)\psi]r_f z}{(x^2+z^2)^2}\,dz \qquad [16.19.29]$$

Horizontal target

$$F = \frac{2}{\pi}\int_h^{h+L} \frac{(x - r_f)r_f[x\sin\psi + (z\tan\alpha - r_f)\psi]}{(x^2+z^2)^2}\,dz$$

Vertical target [16.19.30]

where h is the height of the jet above the ground (including any lift-off), L is the visible length of the flame, $r_f(z)$ is the radius of the flame at height z, x is the distance between the axis of the jet and the target, z is the height of the flame differential element, α is the half-angle of the flame and $\psi(z)$ is the angular position of the flame differential element.

In the model of Chamberlain (1987) for a flare, the jet flame is treated as a frustrum with the widest end furthest from the jet exit, as shown in Figure 16.103. For this case Crocker and Napier give the following expressions by Croce and Mudan (1986), in which the flame is treated as equivalent to a cylinder with diameter D_e and length L:

$$D_e = 2\frac{(W_1+W_2)^{1/2}}{L}[L^2 + (W_2 - W_1)]^{1/4} \qquad [16.19.31]$$

$$L = \frac{L_{BV}\sin\alpha_B}{\sin(90-\alpha_B)\sin(180-\theta)} \qquad [16.19.32]$$

where the notation is as defined in Subsection 16.18.6 and Figure 16.103, except that L_{BV} is the height of the centre of the flame tip above the level of the jet exit (m) and α_B is the angle between the vertical and the line joining the jet exit and the centre of the flame tip (°). In general, the angle α_B is not equal to the angle α_B as defined in Figure 16.103, although the two become the same for a vertical jet. The view factor for this equivalent tilted cylinder is then obtained using the standard view factors for a tilted cylinder, as described in Section 16.17.

Crocker and Napier also give the results of a numerical investigation of the values of the radiation intensity on a target for a propane jet flame burning at a vent, as obtained for vertical and tilted flames using for the vertical flame the model of Hawthorne, Weddell and Hottel and the Becker relations, and for the tilted flame a point source treatment based on the model of Brzustowksi and Sommer, a multiple point source treatment based on the model of de Faveri *et al.* and the solid flame model of Chamberlain with the Croce and Mudan view factor. They select the latter as the preferred model for a tilted flame.

A treatment of the view factor for a jet flame is also given in the IP *LPG Storage Code*. To the extent that a jet flame may be characterized as a cylinder, view factors for cylinders may be used. The *Code* gives view factors for vertical and tilted cylinders with target levels above and below.

16.19.17 Application of models

The model of Hawthorne, Weddell and Hottel was used in some early work. For example, Gugan (1976), in a discussion of the release at Flixborough, expressed the view that whilst this model had not been verified for large-scale situations, there was no fundamental reason why it should not apply, and stated that use of the model to correlate incidents had not revealed any defect.

The model of Considine and Grint of SRD has been widely used by the HSE and others in hazard assessment work. The model is given in the CCPS *QRA Guidelines* (1989/5).

The Chamberlain model has been used by Shell for the study of possible impingement of jet flames from gas risers on the accommodation modules of oil production platforms, as described by Chamberlain (1989) at the Piper Alpha Inquiry.

The IP *LPG Storage Code* recommends for a jet flame of LPG the use of the Brzustowski and Sommer point source model provided that: (a) the target is at least one flame length away; (b) the fraction of heat radiated is taken as 0.38 for exit velocities up to Mach 0.5 and 0.22 up to Mach 0.9; (c) allowance is made for attenuation due to atmospheric transmittance and (d) the code calculation methods are used. The flame length is taken as twice the distance from the flame centre to the point of discharge.

For the case where the target is less than one flame length away, the *Code* refers to the treatment of Chamberlain, whilst stating that this is not universally accepted.

16.19.18 Enclosed jet flames

The work just described relates to jet flames in the open. In some instances, a jet flame may occur within an enclosure. This case is of particular relevance to ignited releases in offshore modules.

Work on this aspect has been described by Chamberlain (1994). The experiments were conducted in an enclosure 8 m long × 3.54 m wide × 3.91 m high. The enclosure contained a cylindrical target 0.27 m in diameter, and thermocouples, radiometers and total heat flux gauges were located on the target and the enclosure walls. Propane was

released both as a vapour, in the subsonic and sonic flow regimes, and as a liquid at a flow which averaged 0.21–0.3 kg/s. Both vertical and horizontal nozzle orientations were used. Some trials were conducted with full end wall opening and others with partial wall opening (2.5 m × 2 m); one trial condition involved a partially open roof. Measurements were also made of the composition, particularly the carbon monoxide concentration, of the combustion products and of the size of and thermal radiation from the external flame from the enclosure.

The situation investigated is strongly similar to the compartment fires which have been much studied in work on fires in buildings, as described in Section 16.36. In the ventilation-controlled conditions which occur in a compartment the hot combustion products flow out through the top of the aperture and cold air flows in through the bottom, with a relatively well-defined boundary between the two. This has led to the three zone model of a compartment fire, the three zones being the fire plume itself and the hot and cold gas zones. The air flow in such a fire is normally modelled in terms of the ventilation factor $AH^{1/2}$, where A is the area of the ventilation opening (m^2) and H is its height (m).

However, a jet flame in an enclosure differs from the pool fire case in at least two important respects. One is the much greater degree of mixing and the other the absence of 'flashover'.

Some of the findings from these tests were as follows. For ventilation-controlled fires with vertical apertures it took about 10 min to reach steady-state conditions. The boundary between the hot and cold layers occurred about halfway up the opening. The gas temperature in the upper layer was remarkably uniform and could reach about 1200°C.

In addition to the heat effects on the wall and the contents of the enclosure, other hazards are the thermal radiation from the external flame and the generation of smoke and carbon monoxide.

In some tests using propane gas from a vertical nozzle the heat flux at the impingement area on the roof reached over 300 KW/m^2, rising to this value as radiation from the walls came into play.

For the external flame the maximum vertical and horizontal extents measured were 6 and 3 m , respectively, for a trial using liquid propane, though two trials using propane gas gave comparable values of 5 and 3 m, respectively; there was no external flame in the two trials with full wall opening.

It is the flame stoichiometry which governs the production of soot and carbon monoxide. This stoichiometry is a function of the fuel flow, the jet momentum and the vent opening. The experiments showed that the parameter $0.5AH^{1/2}$ tends to give an overestimate of the air flow. The author advises against its use for the determination of flame stoichiometry.

Jet flames which were fuel rich gave much higher yields of soot and of carbon monoxide and larger external flames.

When ventilation-controlled, roof ventilated jet flames were found to be unstable and to self-extinguish. With this geometry a stable two-way flow of air and combustion products is not established.

16.20 Engulfing Fires

The engulfment of vessels in fire may occur in various ways and the problem has been studied from several different angles. Important distinctions relate to the container, which may be a fixed tank or vessel or pipework or a transport container, and to the fire, which may be a pool fire or a directed flame.

There have been a number of experiments on rail tank cars and on fixed storage vessels engulfed in fire, and various models have been developed for heat transfer to such vessels, for the response of the temperatures and pressures in the vessel, for pressure relief of the vessel and for bursting of the vessel. Some studies of engulfing fires are given in Table 16.71.

16.20.1 Heat absorbed

Relations for the heat absorbed by a vessel from a pool fire are given in API RP 520: 1976 *Recommended Practice for Design and Installation of Pressure Relieving Systems in Refineries* and API Std 2000: 1982 *Venting Atmospheric and Low-pressure Storage Tanks*. It is convenient to consider first the relationships given in these publications and then the subsequent changes.

Table 16.71 *Some studies of engulfing fires*

Derivation of formulae for heat absorbed by a vessel exposed to fire	API RP 520: 1976; API Std 2000: 1982
Experiment on fire engulfment of a full-scale rail tank car vessel containing LPG	C. Anderson *et al.* (1974); Charles (1974)
Discussion of heat absorbed in fire engulfment	Craven (1976)
Experiments on fire engulfment of 1/5 scale rail tank car vessels containing LPG	Appleyard (1980)
Experiments on fire engulfment of small- and full-scale vessels containing LPG	A.F. Roberts, Cutler and Billinge (1983); Moodie, Billinge and Cutler (1985)
Theoretical studies of temperatures and pressures in vessels and pipes containing gas or liquid engulfed by fire	Solberg and Borgnes (1983)
Theoretical studies of temperatures and pressures in a vessel filled with gas engulfed by fire	Nylund (1984)
Theoretical models for heat transfer from pool fires and jet fires (relief valve flare) to a horizontal cylinder	Tunc and Venart (1984/85a,b)
Theoretical model of temperatures and pressures in a vessel containing liquid engulfed by fire	D.L.M. Hunt and Ramskill (1985)

The two documents mentioned give for the heat absorbed by the wetted surface area expressions of the engulfing general form

$$Q = kA^n \quad [16.20.1]$$

where A is the wetted surface area, Q is the heat absorbed, k is a constant and n is an index.

For the estimation of the heat absorbed for purposes of determining relief requirements, API RP 520 gives the equation

$$Q = 21{,}000\ FA^{0.82} \quad [16.20.2]$$

where A is the wetted area (ft^2), F is an environment factor and Q is the heat absorbed (BTU/h).

API RP 520 contains an appendix (Appendix A) in which the origin of Equation 16.20.2 is explained. It is based on tests carried out in 1925 by Standard Oil of California. The tests were conducted on a small tank and were intended to give guidance on relief sizing for tank trucks. The tests indicated the maximum heat absorption rate to be expected in the worst case. There were also available data on cases where tanks had survived fire exposures. The available data were plotted by Stroop on log–log paper as a curve. This curve was intended to give guidance for small tanks and, by extrapolation, for tanks with wetted areas up to 10,000 ft^2. It was subsequently observed by Maker that the data could be represented by a straight line and he proposed the equation

$$q = 48{,}000\ A^{-1/3} \quad [16.20.3]$$

where q is the heat absorbed per unit area (BTU/h ft^2) and A is the wetted area (ft^2). Equation 16.20.3 became known as the Stroop–Maker formula and was applied not only to atmospheric storage tanks but also to pressure vessels.

Another set of equations developed during the Second World War are the formulae of the Petroleum Administration for War (PAW). These are

$$q = 16{,}000\ A^{-0.18} \quad [16.20.4]$$

$$Q = 16{,}000\ A^{0.82} \quad [16.20.5]$$

The Stroop–Maker and PAW formula have been widely used in the petroleum industry.

API RP 520 gives a plot comparing the PAW and API fonnulae given here as Equations 16.20.2 and 16.20.5, respectively, with various additional data points obtained from tests carried out during the period 1925–1950. Some of the tests represent the worst conditions likely to occur, since they were delayed until calm conditions prevailed and plentiful fuel supplies were used.

API Std 2000 quotes Equation 16.20.2 for use in determining the venting requirements of atmospheric and low Pressure storage tanks for wetted areas greater than 2800 ft^2. It also gives tables for determining the venting requirements for wetted areas less than this. It is explained in an appendix (Appendix B) that the tables are based on the following equations:

$$Q = 20{,}000\ A \qquad 20 < A < 200 \quad [16.20.6a]$$

$$Q = 199{,}300\ A^{0.566} \qquad 200 < A < 1000 \quad [16.20.6b]$$

$$Q = 963{,}400\ A^{0.338} \qquad 1000 < A < 2800 \quad [16.20.6c]$$

The method used in earlier versions of API Std 2000 was to assume a constant value of heat absorbed ($q = 6000$ BTU/h ft^2), but tests conducted in 1961 on a horizontal tank led to a revision and development of the equations just quoted.

A discussion of the heat absorbed by a vessel in an engulfing fire has been given by Craven (1976). He suggests that if a well-developed fire radiates heat at a given rate, then it could be argued that an object engulfed in a fire should receive heat at the same rate, since the view factor is unity. A large fire can radiate heat at a rate of some 17 W/cm^2 (170 kW/m^2). In tests on small tanks the heat input rates recorded are, on average, about 11 W/cm^2 (110 kW/m^2), while for large tanks they rarely exceed 7 W/cm^2 (70 kW/m^2). The exponents in Equations 16.20.1, as given in Table 16.72, reflect this falling off in heat absorption with size. Craven argues, however, that there is no theoretical justification for an exponent less than unity and that in certain circumstances a vessel might receive a heat input nearer 17 W/cm^2 (170 kW/m^2). For the latter case he gives the equation

$$Q = 54{,}000\ A \quad [16.20.7]$$

where A is the wetted area (ft^2) and Q is the heat absorbed (BTU/h).

Figure 16.109 (Crawley and Scott, 1984) shows a comparison of the PAW and API formulae and some of the data points given in API RP 520.

Table 16.72 *Parameters for use in the equations given in API RP 520 and API Std 2000 for the heat absorbed in fire engulfment*

	Wetted area, A		*Heat absorbed, Q*		*Conditions*
	(ft^2)	(m^2)	(BTU/h)	(kW)	
API RP 520: 1990			$21{,}000\ A^{0.82}$	$43.1\ A^{0.82}$	–[a]
			$34{,}500\ A^{0.82}$	$70.8\ A^{0.82}$	–[b]
API Std 2000: 1992	20–200	1.86–18.6	$20{,}000\ A$	$6.31\ A$	
	200–1000	18.6–92.9	$199{,}300\ A^{0.566}$	$224.1\ A^{0.566}$	
	1000–2800	92.9–260	$963{,}400\ A^{0.338}$	$632.0\ A^{0.338}$	
	>2800	>260	$21{,}000\ A^{0.82}$	$43.1\ A^{0.82}$	

[a] Drainage and fire fighting equipment adequate.
[b] Drainage and fire fighting equipment inadequate

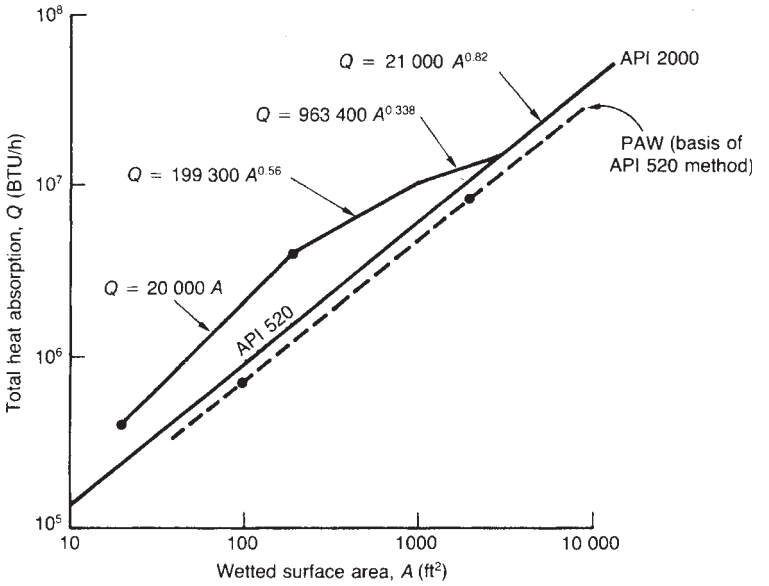


Figure 16.109 *Comparison of the equations given by the API for the heat absorbed by a tank or vessel in a fire (Crawley and Scott, 1984) (Courtesy of the Institution of Chemical Engineers)*

The history of the API RP 520 treatment of heat absorption is discussed by Heller (1983).

API RP 520: Part 1: 1990 gives in Appendix *D* two equations for the heat absorbed, which differ in that they are based on the adequacy of drainage and fire protection. The first is Equation 16.20.2 and the second the equation

$$Q = 34{,}500\, FA^{0.82} \qquad [16.20.8]$$

Equation 16.20.2 is to be applied where adequate drainage and fire-fighting equipment exist and Equation 16.20.8 where they do not.

The API recommendations are therefore as follows. API RP 520: 1990 and API Std 2000: 1992 recommend the use of Equation 16.20.1 with the constants shown in Table 16.72.

It should be borne in mind that the API RP 520 equations are given for the purpose of plant design rather than hazard assessment.

Further information on the heat absorbed is given below in relation to particular studies of engulfing fires.

16.20.2 General studies of engulfing fires

A series of theoretical studies of the effect of engulfing fires on vessels and pipework with and without insulation has been carried out by Borgnes, Solberg and coworkers, as reported by Solberg and Borgnes (1983). The work was done using the Det norske Veritas (DnV)computer program NV613 for the determination of temperature profiles.

The heat absorbed in an engulfing fire is not well defined, but at the flame surface a heat flux of about 150 kW/m^2 seems to be a reasonable value. Inside the flame the heat flux would be higher; how much higher is uncertain, but perhaps by some 50–100 kW/m^2. There is also a convective heat flux. For pool fires a heat flux of 30–40 kW/m^2 is a conservative estimate, but for jet fires it may be appreciably higher. The approach taken is therefore as follows. Heat transfer is assumed to be by radiation only, with the object engulfed in the flame so that the view factor is unity. The flame temperature of the engulfing fire is assumed to be 1525 K with the flame emissivity and target absorbtivity both taken as unity. The justification for the latter is that in such a fire the metal would soon be covered with a deposit of carbon. For an object at an initial temperature of 400 K the initial heat flux under these conditions is 310 kW/m^2.

The temperature at which steel suffers serious loss of strength, or the critical steel temperature, is taken as 675 K.

The base case is a considered 2 m diameter vessel with 20 mm wall thickness and 50 mm mineral wool insulation, containing gaseous propane at an initial temperature of 400 K and at pressures of 5, 20 and 80 bar. Figure 16.110(a) shows the wall temperatures attained for different gas pressures after different time periods. For an uninsulated vessel the critical steel temperature is reached within a few minutes. For an insulated vessel at 5 bar pressure the time to critical steel temperature is less than 1.5 h, while for one at 80 bar pressure the steel reaches a temperature of 610 K after 2 h.

Figure 16.110(b) shows, for a 0.2 m diameter uninsulated pipe, the times to different wall temperatures/or stagnant and flowing methane gas at 5 and 80 bar pressure. Figure 16.110(c) shows, for uninsulated and insulated pipe of the same diameter, the wall temperature response for stagnant and flowing liquid methane at an initial temperature of 110 K.

Figure 16.110(d) shows the wall temperature and gas pressure responses for 2 and 10 m uninsulated horizontal vessels partly filled with liquid propane, with fill ratios of 0.625 and 0.88. Figure 16.110(e) shows the corresponding responses for insulated vessels. For the latter case the temperature profile in the vessel wall is shown in Figure 16.110(f). This very steep temperature gradient may give rise to severe stresses in the vessel shell.

The authors also describe work on other aspects, such as the effect of defects in the insulation and unevenness in water sprays.

16.20.3 Vessels filled with gas

A theoretical study of the effect of an engulfing fire on a vessel filled with methane has been made by Nylund (1984).

The vessel considered was 13 m long × 3 m diameter with a wall thickness of 53 mm, a working temperature of 300 k and a pressure of 8.2 MPa.

Pool and jet fires were investigated. The flame temperature for both fires was assumed to be 1500 k. The convective heat transfer coefficient was taken as 28 W/m^2 K for the pool fire and as 250 W/m^2 K for the jet fire. A model is given for vessel rupture as a function of vessel temperature and pressure and wall thickness.

Some of the results obtained by Nylund are shown in Figue 16.111. Figure 16.111(a) shows the time response of the gas temperature, the gas pressure and the rupture pressure for a jet fire, for a jet with an effective diameter of 1 m. The rupture pressure does not fall below the gas pressure. Figure 16.111(b) shows the response for a jet fire with a jet having an effective diameter of 4 m. In this case the rupture pressure does fall below the gas pressure, so the vessel would rupture. Rupture is predicted for jet fires with jets having an effective diameter of 2, 3 and 4 m for which the pressure crossovers occur at about 7.5, 7 and 5 min respectively. Figure 16.111(c) shows the response for a pool fire. In this case not only does the rupture pressure fall, but the gas pressure rises appreciably so that rupture occurs in somewhat less than 5 min.

Nylund also discusses pressure relief and depressurization. In both types of fire rupture can occur within 5 min. For neither type does a pressure relief valve provide real protection. In the case of the jet fire the rupture occurs at gas pressures well below the relief valve set pressure. In the pool fire case the gas pressure does reach the set pressure, but the relief valve capacity is insufficient to vent the pressure quickly enough.

Depressurization is capable of providing protection. Figure 16.111(d) illustrates a successful depressurization.

16.20.4 Vessels part filled with liquid

There have been several experimental investigations of the response of vessels containing liquefied flammable gas to an engulfing fire.

A test on fire engulfment of a 64 te LPG rail tank car has been described by C. Anderson *et al.* (1974) and Charles (1974). Measurements were made of the heat flux from the fire, of the vessel wall temperatures in the liquid and vapour spaces and the relief valve flare. The relief valve opened at 1.96 MPa and remained open. The vessel ruptured after some 24.5 min, propelling 63 fragments, some for considerable distances. The pressure at failure was 24.1 bar and the wall temperature near the point where failure occurred had a maximum value of 650°C. The temperatures of and heat fluxes from the pool fire and the relief valve torch are given in Table 16.73.

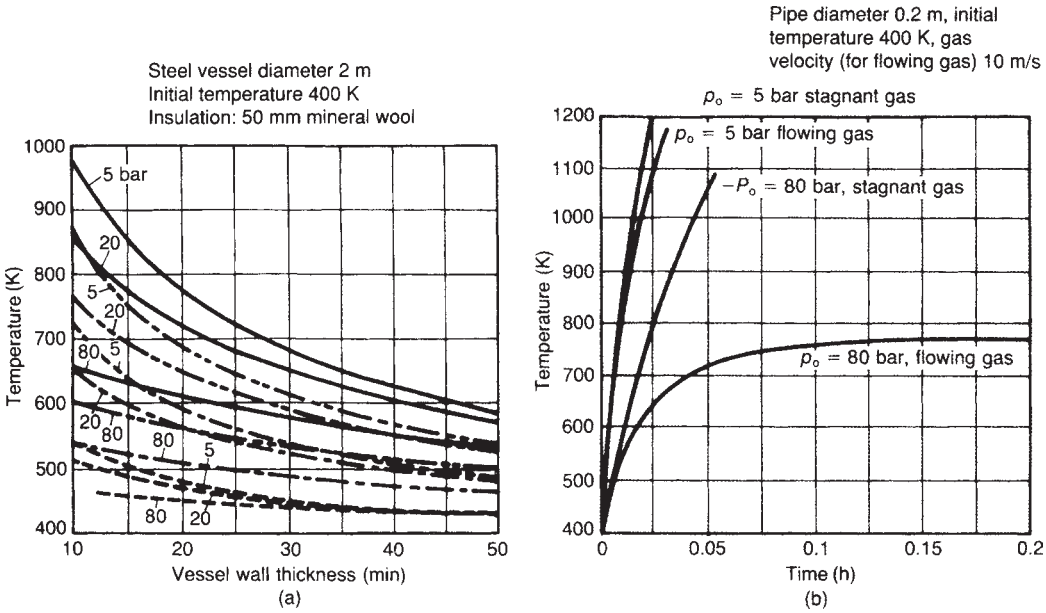


Figure 16.110 *Theoretical predictions of the temperatures and pressures in vessels and pipes containing gas and liquids engulfed in a fire (after Solberg and Borgnes, 1983). (a) temperature rise of the outside of the vessel wall for vessel filled with propane gas; (b) temperature rise of the pipe wall (uninsulated) for pipe filled with stagnant and flowing methane gas; (c) temperature rise of the pipe wall (uninsulated and insulated) for pipe filled with stagnant and flowing liquid methane; (d) maximum outside vessel wasll temperature and pressure in uninsulated vessel for vessel partly filled with liquid propane; (e) maximum vessel wall temperature and pressure in insulated vessel partly filled with liquid propane; (f) temperature profile of insulated vessel wall for vessel partly filled with liquid propane. (Courtesy of the American Institute of Chemical Engineers)*

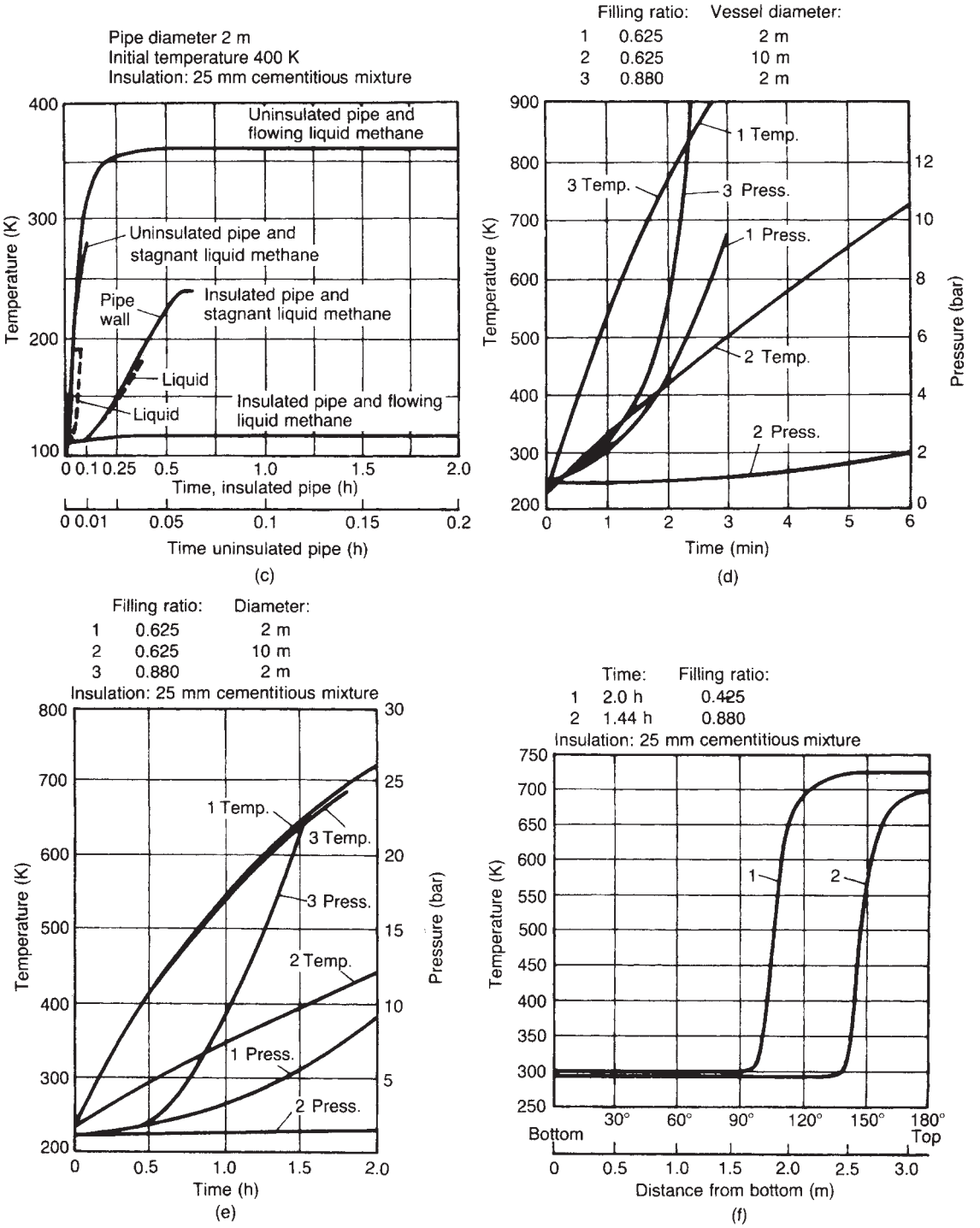


Figure 16.110 *continued*

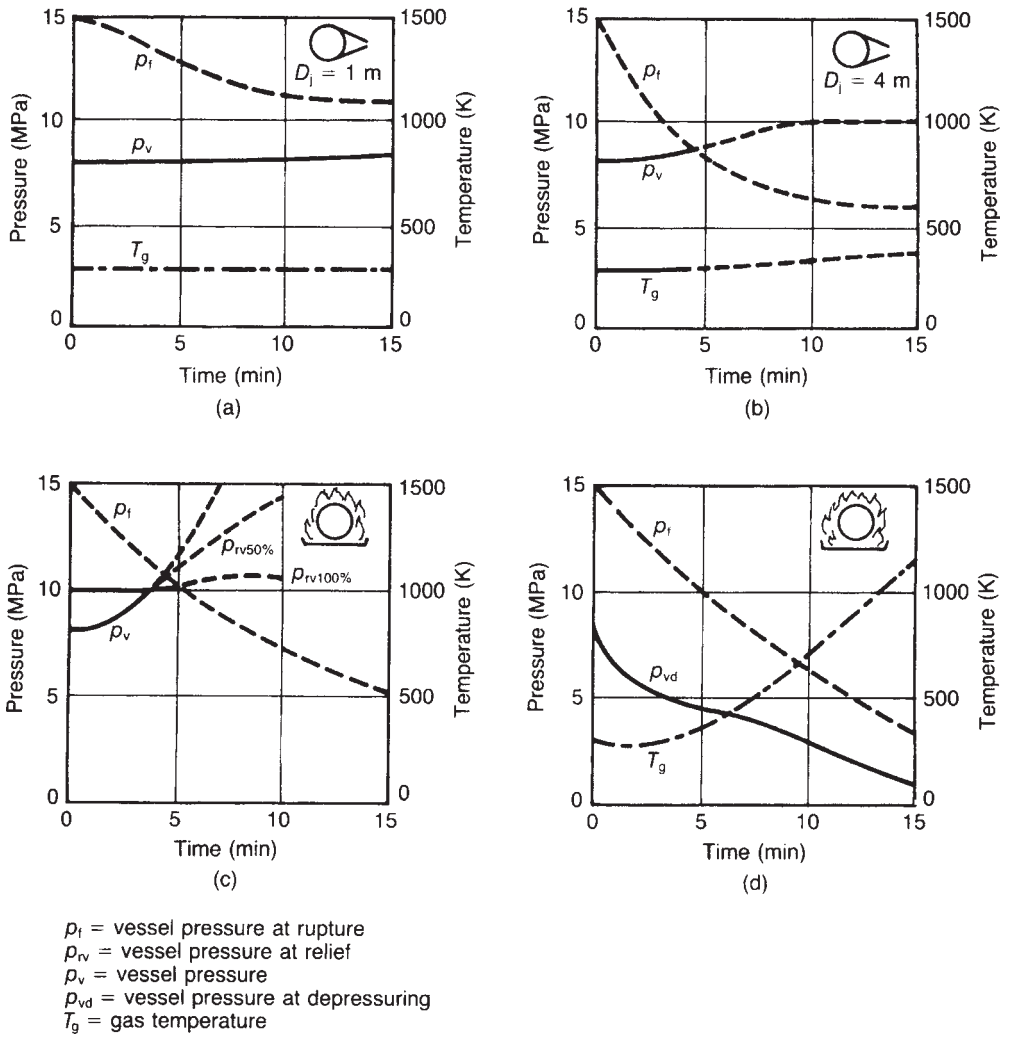


Figure 16.111 *Theoretical predictions of the temperatures and pressures in vessels filled with gas (after Nylund, 1984): (a) impingement of jet flame-1 m diameter; (b) impingement of jet flame 4 m diameter; (c) engulfing fire; (d) engulfing fire with depressurization (Courtesy of the Institution of Chemical Engineers)*

A series of tests on vessels for rail tank cars have been carried out at 1/5 scale by Appleyard (1980). One objective of these tests was to investigate the effectiveness of the internal thermal radiation protection Explosive.

These and other tests have been reviewed by Tunc and Venart (1984/85b) and by Moodie, Billinge and Cutler (1985).

Models for radiant heat transfer to a horizontal cylindrical vessel from (1) an engulfing fire and (2) a relief valve flare have been given by Tunc and Venart (1984/85a,b).

Large-scale tests on the effect of fire around a liquid ethylene storage vessel have been carried out as part of the experiments by the MITI (1976) described earlier.

In one test, a storage vessel with vacuum perlite insulation fitted, with a 25 cm diameter bursting disc and containing 718.5 kg of liquid ethylene was subjected to a flame from LPG burners for 15 min with the water sprays on and then for 15 min with the sprays off. The total quantity of LPG consumed in the fire was 80 kg and the total heat released was estimated as 960,000 kcal. The pressure in the vapour space in the vessel remained at about 1.0 kg/cm^2 g throughout the test.

In another test the insulating vacuum of the vessel was broken and part of the perlite at the base of the vessel was removed. The vessel was subjected to a pool fire of kerosene which engulfed it. The water spray was not used on the vessel. The total quantity of heat released by the kerosene fire was estimated as 34,496,000 kcal. The bursting disc blew when the vapour pressure reached 8.3 kg/cm^2 g, which occurred 34 min after ignition.

When the disc blew, some 620 kg of ethylene was ejected as a vapour–liquid mixture within about 6.5 s. The material ignited and gave a large flame which lasted about 8–9 s and

Table 16.73 *Temperatures and heat fluxes in a full scale fire engulfment test on a rail tank car (Tunc and Venart, 1984/85b; after Charles, 1974)(Courtesy of the Fire Safety Journal)*

Time (min)	*Recorded heat flux* (kW/m^2)	*Temperature* (°C)		*Heat flux* (kW/m^2)	
		Fire	*Torch*	*Fire*	*Torch*
5.0–11.5	90.12	871	1120	60.28	171.8
11.5–15.0	68.7	816	1040	49.4	134.28
15.0–24.5	29.65	802	1090	46.94	159.22
Maximum reading (6.5 min)	104.8	871	1180	60.28	203.4

was about 100 m long. The actual length of the flame agreed well with the value of 105 m calculated from Equation 16.19.21 assuming that 620 kg was released over 8 s.

Part of the flame formed a fireball. The diameter and duration of the fireball were calculated from the NASA formula (Equations 16.16.5 and 16.16.7). The total mass of the combustion reactants was taken to include the air required Jor combustion, so that 28 kg of ethylene require 96 kg of oxygen, making a total mass of 124 kg. The observed fireball had a diameter of 40 m and persisted for about 3 s. According to Equations 16.16.5 and 16.16.7 this corresponds to about 324 kg of ethylene. Thus on the basis of this calculation about half the mass of ethylene ejected was involved in the fireball.

Two series of tests on horizontal cylindrical vessels partly filled with liquid and engulfed in a pit fire have been carried out by the HSE. In the first series, described by A.F. Roberts, Cutler and Billinge (1983), 5001 vessels were used. A preliminary set of tests was done with vessels containing water; the main tests were then done with LPG.

In the tests using water the vapour space heated up rapidly and caused boiling at the water surface at 4 min. The bulk water began to boil after 8 min. Between 4 and 8 min the boiling reduced the temperature of the vapour but not that of the wall in the vapour space. After 8 min it reduced both these temperatures.

The heat balance on the wall was expressed as

$$\rho c d \frac{\mathrm{d}T_1}{\mathrm{d}T} = Q - \epsilon\sigma T_1^4 - \sigma \mathrm{F} T_1^4 \qquad [16.20.9]$$

where the second and third terms on the right-hand side represent the heat radiated externally and that radiated internally, respectively. The equation is solved to give

$$\frac{4Qt}{\rho c d T_\mathrm{A}} = \ln\left(\frac{T_A + T_1}{T_\mathrm{A} - T_1}\right) - \ln\left(\frac{T_\mathrm{A} + T_0}{T_\mathrm{A} - T_0}\right)$$

$$+ 2\tan^{-1}\left(\frac{T_1}{T_\mathrm{A}}\right) - 2\tan^{-1}\left(\frac{T_0}{T_\mathrm{A}}\right) \qquad [16.20.10]$$

with

$$T_A = \left[\frac{Q}{\sigma(\epsilon + F)}\right]^{1/4} \qquad [16.20.11]$$

where c is the specific heat of the wall metal, d is the thickness of the metal wall, F is a factor (explained below), Q is the heat absorbed per unit area, T_A is the asymptotic value of T_1, T_0 is the initial value of the wall temperature, T_1 is the value of the wall temperature at time t, ϵ is the emissivity of the external surface of the wall, ρ is the density of the metal and σ is the Stefan–Boltzmann constant. The factor F includes the emissivity of the internal surface of the wall, the absorptivity of the water surface and the view factor from the wall to the water surface.

Equation 16.20.10 was used to obtain estimates of the heat absorbed Q and of the factor F from the wall temperature data. The heat absorbed was estimated to have an average value of 134 kW/m^2 and the factor F a value of 0.055, which is consistent with a wall emissivity of unity, a water surface absorptivity of 0.09 and the view factor of $2/\pi$. The estimated average flame temperature was 1100°C.

The calculated equilibrium conditions for the unwetted upper part of the vessel were a wall temperature of 950°C, a total heat transfer from the fire of 134 kW/m^2, re-radiation from the vessel to the atmosphere of 127 kW/m^2 and internal radiation to the liquid layer 7 kw/m^2. For the wetted lower part of the vessel the total heat transfer was estimated as 124 kW/m^2, giving an overall average heat flux of 130 kW/m^2.

The main set of ten trials were then conducted using propane, one with an uninsulated vessel and nine with insulated vessels. A feature of these trials was the behaviour of the pressure relief valves. The valves were set to open at 1.7 MPa, but in fact opened at pressures in the range 0.7–1.8 MPa, due probably either to weakening of the spring or damage to the valve seat from the effects of the fire.

In the water tests the boiling regime was nucleate boiling. In the propane tests the regime was film boiling in most cases, although nucleate boiling did occur. Figure 16.112(a) illustrates film boiling in which the wall temperature in the liquid space is close to that in the vapour space, while Figure 16.112(b) shows nucleate boiling when the liquid space wall temperature is much lower. The occurrence of film boiling, and the associated poor heat transfer, therefore renders the walls vulnerable to thermal weakening.

In the second series of fire engulfment tests by the HSE, described by Moodie, Billinge and Cutler (1985) the tanks used were 1/4 and 1 the uninsulated vessels part filled with propane. Five tests were carried out, two with 1/4 te vessels and three with 1 te vessels. In one of the former tests the pressure relief valve failed, so that there were four successful tests. Plate 13 shows a test in which the pressure relief valve is operating, giving a large jet flame.

The vessels were instrumented for the measurement of temperatures in the tank wall, the vapour space and the liquid, as shown in Figure 16.113.

In these larger-scale tests the fire was deficient in oxygen and gave a yellow, smoky flame. The flame temperatures

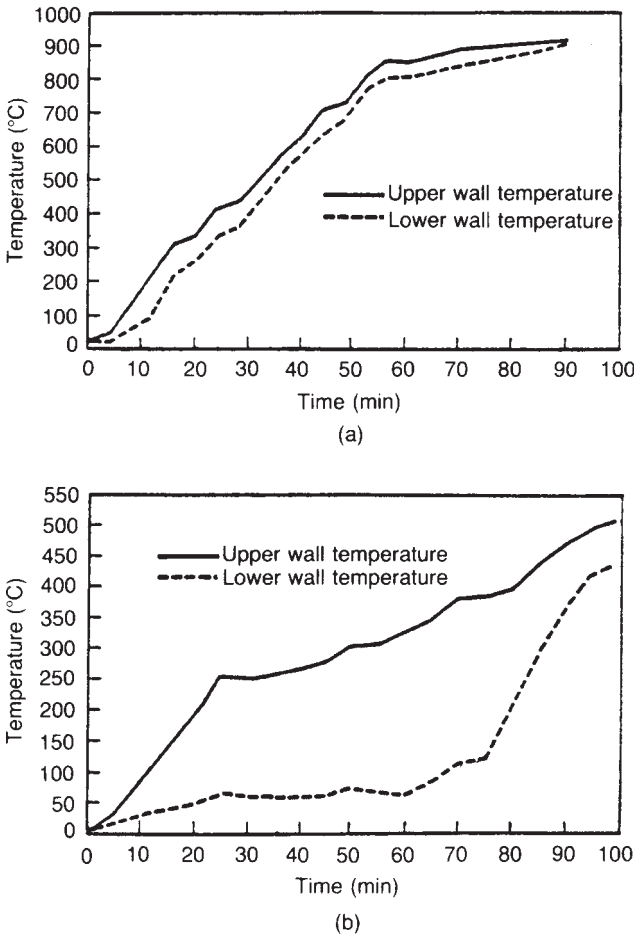


Figure 16.112 *Temperatures in a 500 l vessel part filled with propane engulfed in fire (A.F. Roberts, Cutlerand Billinge, 1983): (a) typical film boiling; (b) typical nucleate boiling (Courtesy of the Institution of Chemical Engineers)*

were 900–950°C with a maximum of 1000°C. The maximum wall temperatures recorded were in the range 600–800°C, which is consistent with a flame emissivity of 0.56.

The experimental conditions and heat fluxes are summarized in Table 16.74.

Thus in the successful 1/4 te tank test the average heat flux before venting into the propane was estimated as 73 kW/m^2 and that into the tank wall as 24 kW/m^2 giving a total of 97 kW/m^2. During venting the heat flux into the propane was 80 kW/m^2.

The four successful tests, one with the 1/4 te tank and three with the 1 te tank, showed a similar pattern. The wall temperature of the vapour space rose almost linearly, while the wall temperature of the liquid space rose to a plateau, levelled out and then rose again. When the pressure relief valve opened giving a nearly constant pressure the liquid wall temperature settled just above the corresponding boiling point, until the wall became exposed due to evaporation of the liquid. Figure 16.114(a) shows for the successful 1/4 te test the temperatures of the walls in the liquid an vapour spaces and Figure 16.114(b) shows the temperatures of the vapour and liquid.

The behaviour of the wall temperature in the liquid space in these tests points to nucleate rather than film boiling, and estimates of the heat flux indicate that the high heat fluxes necessary for film boiling did not occur.

In all the successful tests the internal pressure rose to the relief valve set pressure within 3–5 min. The relief valves cycled at least twice, then remained open venting the pressure down eventually to atmospheric pressure. This behaviour was attributed to weakening of the springs or damage to the seats due to the fire. Although the vessel walls would be weakened by the high temperatures experienced, at no time did the internal pressure have a value which would have been likely to cause rupture.

One of the tests on the 1/4 te tank with 40% fill was unsuccessful in that the relief valve, after opening correctly, failed to do so subsequently. The vessel ruptured at an internal pressure of 35 bar and maximum wall temperature of 600°C.

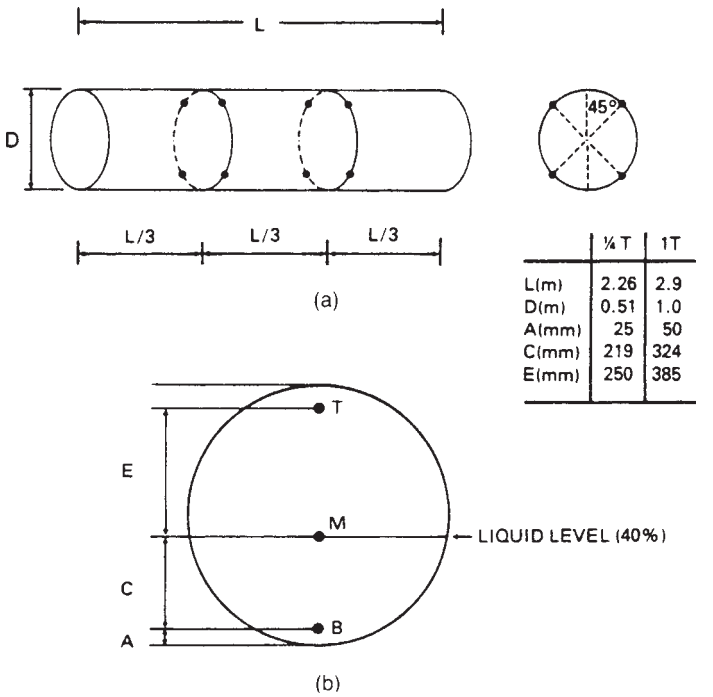


Figure 16.113 *Temperature measurement arrangements in fire engulfment tests on 1/4 and 1 te vessels part filled with propane (Moodie, Billinge and Cutler, 1985); (a) positions of the wall thermocouples; (b) positions of the internal thermocouples (Courtesy of the Institution Engineers).*

Table 16.74 *Experimental conditions and heat fluxes in fire engulfment tests on vessels containing propane (after Moodie, Billinge and Cutler, 1985) (Courtesy of the Institution of Chemical Engineers)*

Test	*Tank size* (te)			
	1/4	1/4	1	1
Degree of fill (%)	40	80	40	20
Mass of liquid (kg)	100	870	420	160
Volume of liquid (m^3)	185	1635	789	308
Tank pressure (bar)	5.5	6.1	4.1	4.1
Ambient temperature (°C)	5	14	−3	−3
Surface areas (m^2):				
Total	3.8	10.4	10.4	10.4
Wetted	1.68	6.28	4.32	3.02
Average heat flux (kW/m^2):				
To propane before venting	73	84	59	33
To walls before venting	24	34	16	28
To propane during early stages of venting	85	50	54	76

Metallurgical examination revealed no indication of failure due to cracks and was consistent with failure by hoop stress in the wall. The authors suggest that the burst pressure may therefore be calculated from thick-walled cylinder theory and give the equation

$$P_b = \frac{2}{3^{1/2}} \sigma_y A \ln K \qquad [16.20.12]$$

with

$$A = 2 - \sigma_u/\sigma_y \qquad 0 < T < 700 \qquad [16.20.13a]$$

$$A = 1 \qquad T > 700 \qquad [16.20.13b]$$

where K is the ratio of the outside to the inside diameter, P_b is the burst pressure, T is the metal temperature (°C), σ_u is the ultimate tensile strength and σ_y is the yield strength, both as measured at temperature T.

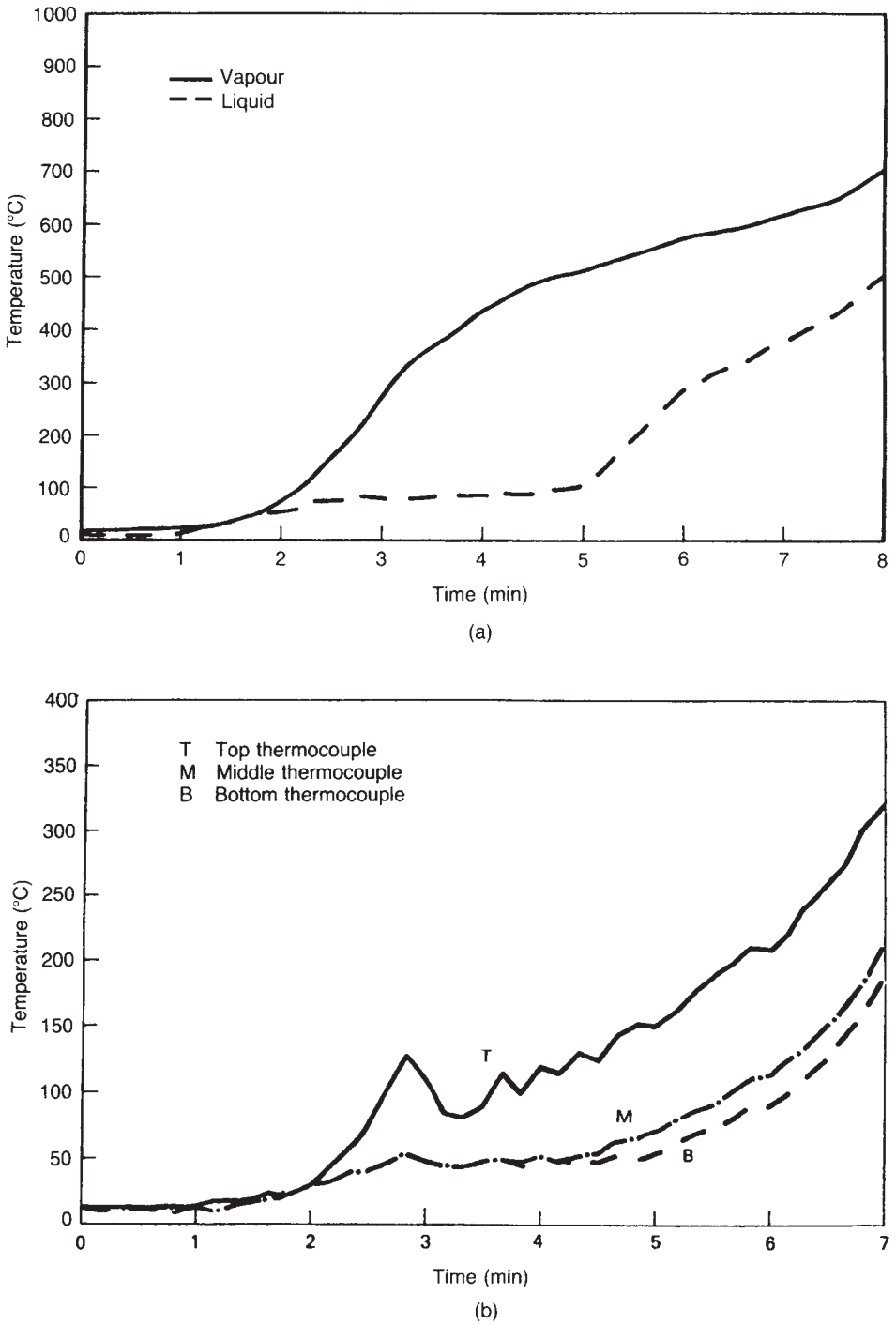


Figure 16.114 *Temperatures in the $^1/_4$ te vessel part filled with propane engulfed in fire (Moodie, Billinge and Cutler, 1985): (a) temperatures of walls in liquid and vapour spaces; (b) temperatures of vapour and liquid (Courtesy of the Institution of Chemical Engineers)*

If the wall temperature in this test is taken as 600°C, the burst pressure calculated by Equation 16.20.12 is 38 bar, which is within 8% of the observed value. Moreover, application of Equation 16.20.12 to data given by C. Anderson *et al.* (1974) and Droste *et al.* (1984) predicts all the burst pressures with an error of less than 18%. The authors also discuss the implications of the work for the pressure relief of vessels engulfed in fire.

In association with these tests a theoretical model for the behaviour of a vessel engulfed in fire has been developed by D.L.M. Hunt and Ramskill (1985). Figure 16.115 shows the heat flows taken into account in the model.

Some predictions given by the model for one of the 5001 vessels in the first HSE series of tests are compared with the observed values in Figure 16.116. Figure 16.111(a) shows the wall temperatures of the vapour and liquid spaces and Figures 16.116(b) and (c) the temperatures of the vapour and liquid, respectively.

16.20.5 Jet flame attack

There is relatively little available data on the effect on equipment of jet flame attack, as opposed to pool fire engulfment, but the EC currently has in hand a major

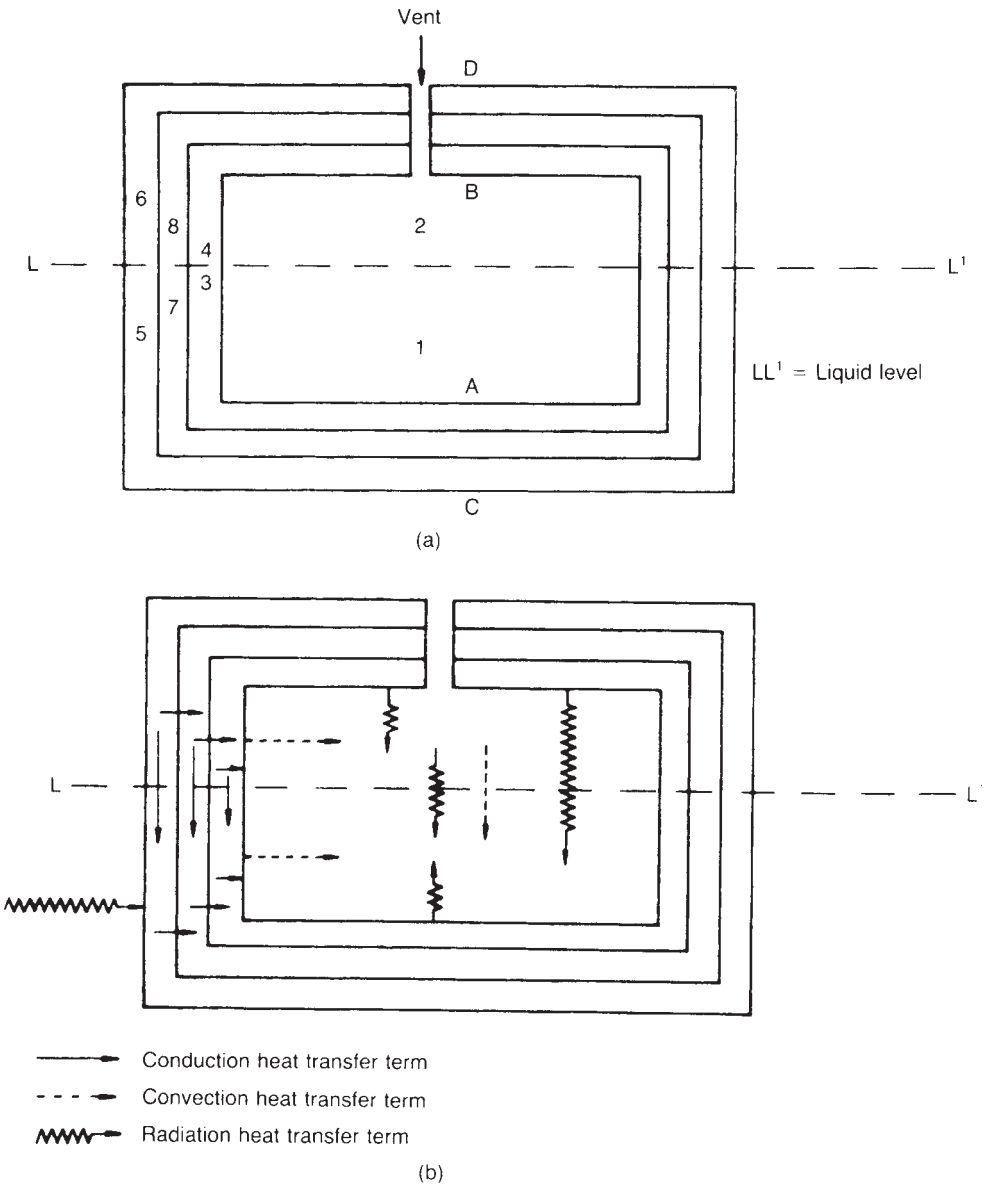


Figure 16.115 *Heat flows in the theoretical model of heat transfer in a vessel engulfed in fire (D.L.M Hunt and Ramskill, 1985): (a) the tank node scheme; (b) heat transfer within the tank (Courtesy of the Institution of Chemical Engineers)*

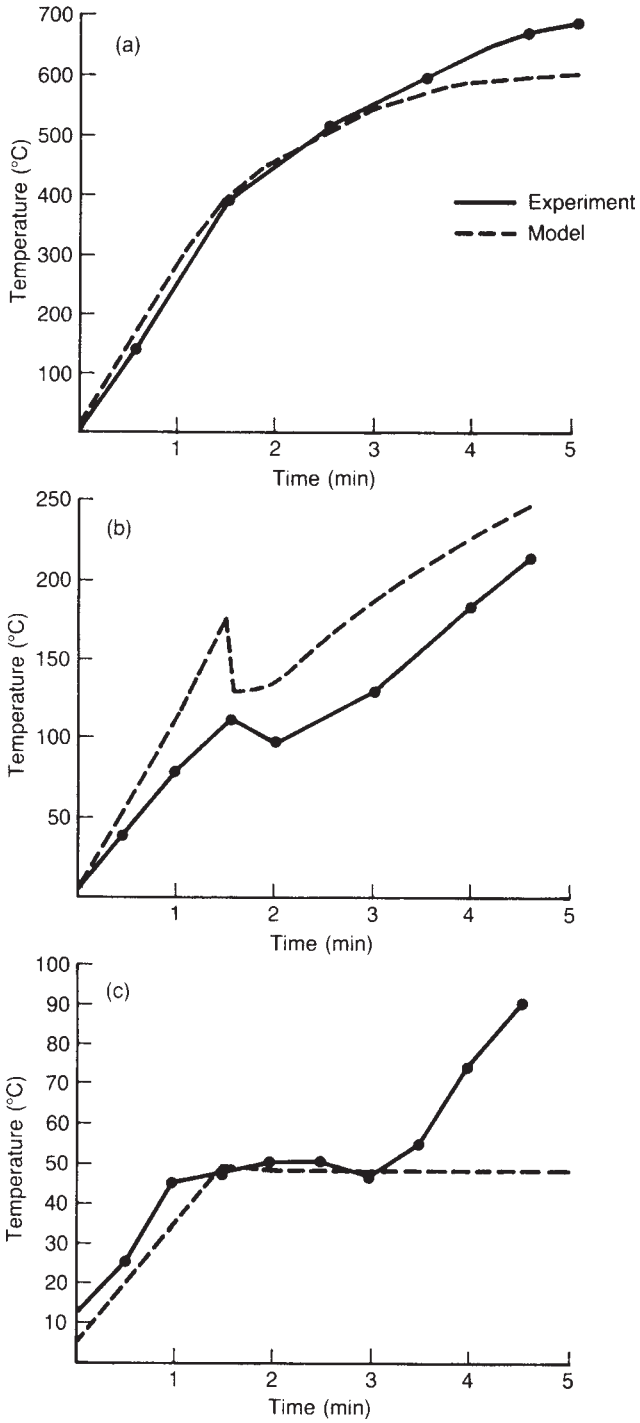


Figure 16.116 *Theoretical predictions of the temperatures in a 500 l vessel part filled with propane engulfed in fire (DLM. Hunt and Ramskill, 1985): (a) Outer wall (vapour space) temperature; (b) vapour temperature; (c) liquid temperature (Courtesy of the Institution of Chemical Engineers)*

programme of work on this, an account of which is given by Duijm (1994). The objectives of the programme are (1) the modelling of unobstructed jet fires, (2) the modelling of obstructed jet fires, (3) the modelling of the thermal response of pressure vessels, (4) the assessment of mitigation techniques and (5) the modelling of the failure modes of the pressure vessels.

For unobstructed single-phase jet flames the work involves the development of the models incorporated in the UMPFIRE and TORCIA codes, as described by Crespo *et al.* (1991) and Bennett *et al.* (1991), with extension of the treatment to two-phase jet flames. For obstructed jet flames a distinction is made between small targets engulfed by the flame and large targets. For the latter the heat flux distribution can be very non-uniform and can thus create thermal stresses. The heat fluxes shown in the figures given by Duijm vary between 40 and 300 kW/m^2. Techniques such as CFD (Hernandez and Crespo, 1992) and wind tunnel tests (Verheij and Duijm, 1991) are used to model the heat transfer. The principal mitigation techniques investigated are insulation and water sprays.

The cooling of vessels subject to an impinging jet flame is considered in Section 16.27.

16.21 Effects of Fire: Damage

Fire causes damage to property and injury to people. The statistics of fire damage and injury have been considered in Chapter 2. The modelling of fire damage is treated in this section and that of fire injury in the following one.

Broadly, fire may be treated terms of ignition, steady- and unsteady-state combustion, an extinction, and of flame spread, both over surfaces and within buildings. An account of these aspects is given in *An Introduction of Fire Dynamics* (Drysdale, 1985).

In this section the treatment is confined to (1) the ignition of liquids, (2) the ignition of wood and (3) the spread of flame.

16.21.1 Ignition of liquids

The susceptibility of a flammable liquid to ignition is related to the flashpoint. For high flashpoint liquids, the firepoint is also relevant. The flashpoint and firepoint of a liquid, and the methods of determination, have been discussed in Section 16.2. The firepoint is the temperature at which the liquid not just ignites but also supports a flame and it is therefore a higher temperature than the flashpoint. Essentially, the flashpoint may be obtained by experiment using closed cup or open cup methods, or by calculation as the temperature at which the vapour pressure reaches the lower flammability limit. Data on the flashpoint are available for a large number of substances. The firepoint is determined experimentally. Information on the firepoint of liquids is relatively sparse.

It was found in the work of A.F. Roberts and Quince (1973) that for a flame to be sustained on the surface of the liquid, it is necessary for the vapour concentration to be above the stoichiometric value. An apparent exception is alcohols for which the flashpoint and firepoint measured using spark ignition are the same. The maintenance of the flame on a liquid surface has been interpreted by Rasbash (1975b) in terms of the flame heat balance.

Traditionally, a liquid has been classed as highly flammable if it has a low flashpoint. Essentially the criterion value used in a particular country reflects the summer temperatures in that country. In the United Kingdom, the value taken has been a temperature of less than 32°C as measured by the Abel closed cup test. For a low flashpoint liquid the hazard is that a flammable mixture will form above the liquid surface and will be ignited.

If the temperature of the liquid is high enough a vapour cloud may form. The evaporation and dispersion of such a cloud has been dealt with in Chapter 15. Vapour cloud fires have been considered in Section 16.14.

For a high flashpoint liquid to be ignited it must be heated above its firepoint. This may occur due to the play of a flame on the surface of the liquid. It has been shown by Sirignano and Glassman (1970) that if such flame impingement occurs, a surface tension effect occurs and convection currents are set up which have the effect of cooling the volume of liquid which is being heated. The liquid pool will eventually ignite but, as shown by Burgoyne and Roberts (1968a), only after the transfer of a substantial amount of heat.

Ignition of a high flashpoint liquid occurs much more readily, however, if there exists at the surface of the liquid a wick. This may take the form of a porous material such as a cloth. The liquid layer held in such a wick is too thin for the heat to dissipate and there is a rapid increase in the local temperature. The effect has been studied by Burgoyne, Roberts and Quinton (1968).

16.21.2 Ignition of solids

In the ignition of combustible solids it is usual to distinguish between (1) spontaneous, or unpiloted, ignition and (2) piloted ignition. With spontaneous ignition, also termed unpiloted ignition or autoignition, ignition occurs when the material has been heated up to the point where not only does it evolve vapours of volatile material but it is not enough to ignite these vapours. With piloted ignition, by contrast, ignition of these vapours is by the pilot flame.

A further distinction may be made between the case where the pilot flame actually impinges on the surface of the solid and that where it does not. Simms (1962) refers to these situations as (1) piloted ignition (in the more restricted sense) and (2) surface ignition. This terminology is adopted here.

In this section consideration is restricted to the ignition of wood. This is the solid combustible material principally studied and it is also that of prime interest on process plants.

16.21.3 Ignition of wood

A classic study of the ignition of wood by thermal radiation is that described by Lawson and Simms (1952a,b), who subjected samples of dry wood to thermal radiation from a heated panel, with and without a pilot flame playing half an inch from the surface of the sample.

They first obtained for various kinds of wood critical values I_o of the thermal radiation intensity I below which ignition does not occur even at long exposure times. The woods used included oak, mahogany, red cedar and whitewood. For the minimum thermal radiation intensity for spontaneous ignition I_s they obtained the range of values 0.57–0.66 cal/cm^2 s with an average of about 0.62 cal/cm^2 s, and for the minimum thermal radiation intensity for piloted ignition I_p they obtained the range 0.30–0.36 cal/cm^2 s with an average of about 0.35 cal/cm^2 s. They also studied fibre insulation board, for which the critical values were 0.57 and 0.15 cal/cm^2 s for spontaneous and for piloted ignition, respectively.

For thermal radiation intensities above these threshold values they obtained the following relations. For piloted ignition*

$$(I - I_p)t_i^{2/3} = A \qquad [16.21.1]$$

with

$$A = 0.025 \times 10^6(k\rho s + 68 \times 10^{-6}) \qquad [16.21.2]$$

where A is a parameter (cal^2/cm^4(°C)^2 s), I is the thermal radiation intensity (cal/cm^2 s), I_p is the minimum thermal radiation intensity for piloted ignition (cal/cm^2 s), k is the thermal conductivity of the wood (cal/cm^2 s (°C/cm)), s is the specific heat of the wood (cal/g°C), t_i is the ignition time (s) and ρ is the density of the wood (g/cm^3).

For spontaneous ignition they obtained*

$$(I - I_s)t_i^{4/5} = B \qquad [16.21.3]$$

with

$$B = 0.05 \times 10^6(k\rho s + 35 \times 10^{-6}) \qquad [16.21.4]$$

where B is a parameter (cal^2/cm^4(°C)^2/s) and I_s is the minimum thermal radiation intensity for spontaneous ignition (cal/cm^2 s).

On the assumption that surface cooling occurs, there should be an effect of the thermal inertia $k\rho s$ (cal^2/cm^4 (°C)^2 s). This is the case, in that the parameters A and B are found to be linear functions of this quantity. Values of ρ, s and k for a number of materials are given in texts on heat transfer such as that by Carslaw and Jaeger (1959).

Thus for oak the relations between thermal radiation intensity and exposure times for ignition were approximately as follows:

Ignition time, t_i (s)	*Thermal radiation intensity* (cal/cm^2 s)	
	Piloted ignition, I_p	*Spontaneous ignition*, I_s
5	1.45	
10	1.10	1.40
25	0.77	1.05
50	0.65	0.86
100	0.52	

From this work a minimum thermal radiation intensity for ignition of wood of 0.3 cal/cm^2 s (12 kW/m^2) has been used for building design. This figure was given, for example, in the Scottish Building Regulations 1971.

Further work by Simms and co-workers (Simms, 1960, 1961, 1962, 1963; Simms and Law, 1967) has shown that it is possible to determine for a given wood a minimum surface temperature for ignition.

* In the first edition of the book SI versions of Equations [16.21.1] and [16.21.3] given by Eisenberg, Lynch and Breeding (1975) were quoted which are incorrect, evidently due to an error in the conversion. The latter work gives incorrect dimensions for the thermal conductivity k, as do the original authors, which may be the explanation.

Simms and co-workers have also developed a number of models for ignition of a thin slab and of a semi-infinite solid by radiant heat. One standard heat transfer relation applicable to a semi-infinite solid is quoted by Drysdale (1985) as follows:

$$\frac{\theta_s}{\theta_\infty} = 1 - \exp(\beta^2)\ \text{erfc}\ (\beta) \qquad [16.21.5]$$

with

$$\theta_s = T_s - T_o \qquad [16.21.6]$$

$$\theta_\infty = T_\infty - T_o \qquad [16.21.7]$$

$$\beta = \frac{ht^{1/2}}{(k\rho c)^{1/2}} \qquad [16.21.8]$$

where h is a heat transfer coefficient for convection (cal/cm^2 s°C), t is the time (s), T is the surface temperature for ignition (K), T_o is the initial surface temperature (K), T_∞ is the surface temperature for ignition at infinite time (K), β is a parameter, θ_s is the surface temperature difference for ignition (°C) and θ_∞ is the surface temperature difference for ignition at infinite time (°C).

The parameter β is known as the cooling modulus. It may be written in the alternative form

$$\beta = \frac{h(\alpha_h t)^{1/2}}{k} \qquad [16.21.9]$$

where α_h is the thermal diffusivity (cm^2/s).

It may also be expressed in terms of the dimensionless groups

$$\beta = \text{BiFo}^{1/2} \qquad [16.21.10]$$

with

$$\text{Bi} = \left(\frac{hL}{k}\right) \qquad [16.21.11]$$

$$\text{Fo} = \left(\frac{\alpha_h t}{L^2}\right) \qquad [16.21.12]$$

where L is a linear dimension, Bi is the Biot number and Fo is the Fourier number.

It has been shown by Simms (1963) that Equation 16.21.5 may be reformulated as follows. The surface temperature difference θ_∞ is related to the thermal radiation intensity I:

$$h\theta_\infty = \alpha I \qquad [16.21.13]$$

where α is the absorptivity.

Then from Equations 16.21.5 and 16.21.13

$$\theta_s = \frac{\alpha I}{h}[1 - \exp(\beta^2)\ \text{erfc}\ (\beta)] \qquad [16.21.14]$$

which Simms recasts as

$$\gamma = \beta[1 - \exp(\beta^2)\ \text{erfc}\ (\beta)]^{-1} \qquad [16.21.15]$$

with

$$\gamma = \frac{\alpha I t}{\rho c(\alpha_h t)^{1/2}\theta_s} \qquad [16.21.16]$$

where γ is a parameter known as the energy modulus.

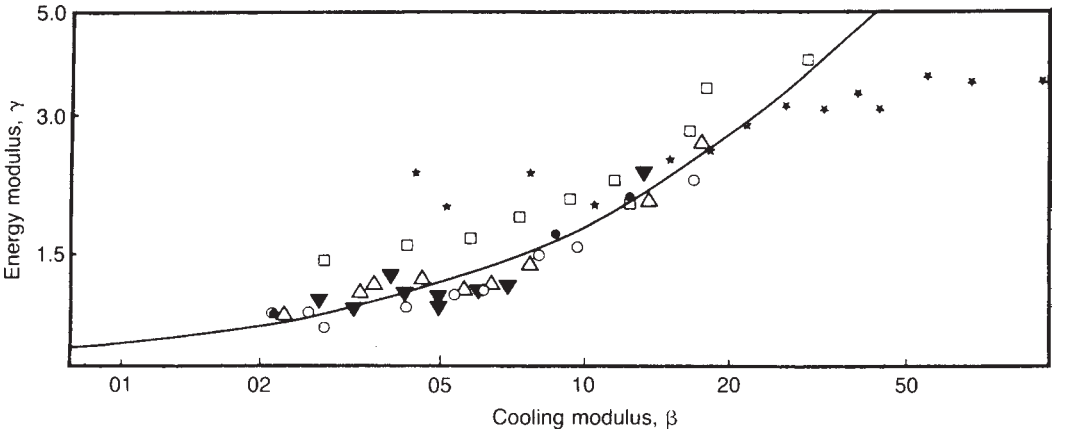


Figure 16.117 *Ignition of wood by thermal radiation: energy vs cooling modulus correlation (Simms, 1963): $\theta_s = 30°C$; $h = 33$ W/m^2 K; (∗) fibre insulation board; (□)cedar; (△) freijo; (○) mahogany; (•) oak (▼) iriko. The cure is that given by Equation 16.21.15. (Courtesy of Combustion and Flame)*

Simms obtained for various woods the relation between the energy modulus γ and the cooling modulus β shown in Figure 16.117.

Another form of the model given by Simms and Law (1967) is

$$\frac{It}{\rho c(kt)^{1/2}\theta_s} = \frac{\beta}{1 - \exp(\beta^2)\ \text{erfc}\ (\beta)} \qquad [16.21.17]$$

These authors term the heat transfer coefficient, given above by the symbol h, the Newtonian cooling coefficient, but the two are identical. They also give values for the coefficient for various temperature differences.

The work of Simms and others has shown that for a given wood it is also possible to correlate results in terms of the minimum ignition temperatures for spontaneous ignition, pilot ignition, and surface ignition. These temperatures are discussed by Simms (1962) and Simms and Law (1967). For piloted ignition without flame contact the results obtained tend to depend on the precise positioning of the flame, though they are reproducible for a given configuration.

Further, for spontaneous ignition, woods exhibit a common minimum ignition temperature of about 545°C. This does not apply, however, at very low rates of heating such that the volatile matter becomes exhausted without ever igniting. Likewise, there is a common minimum ignition temperature for piloted ignition of about 380°C. Taking an initial temperature of 20°C, these two minimum ignition temperatures correspond respectively to minimum ignition temperature differences θ_s of about 525°C and 360°C.

The relation between the minimum thermal radiation intensity I_o and the minimum temperature difference θ_s for ignition is

$$I_o = h\theta_s \qquad [16.21.18]$$

Thus, for example, for piloted ignition Simms and Law give a value of h of 8.6×10^{-4} cal/cm^2 s °C. Then for $\theta_s = 360$°C, $I_o = 0.31$ cal/cm^2 s.

The results described were obtained in carefully controlled experiments using dry wood samples with specified characteristics. It is known that there are effects of thermal inertia, water content, wood grain, etc., and surface absorptivity.

A material with low thermal inertia ignites more readily than one with high inertia. This effect is taken into account in the correlations given above.

The effect of water content has been studied by Simms and Law (1967). Water content influences ignition in several ways. It affects the thermal inertia of the wood through its effects on the individual properties, namely density, specific heat and thermal conductivity. In addition, it affects the overall heat transfer in two ways: heat transfer by molecular diffusion of water; and vaporization of water, which cools the hot zone, and condensation, which heats the cooler zones.

The water content of the wood increases the minimum ignition energy, the minimum thermal radiation intensity and the ignition time for both spontaneous ignition and piloted ignition without contact. But for the latter it becomes significant only at water contents of 40% or more. A water content of 60% doubles the minimum thermal intensity for piloted ignition.

The properties of the wood itself affect thermal radiation ignition. These include the cut end, the direction of the grain and any knots. One effect of grain is on thermal conductivity. Another is on the flow of volatile matter.

The absorptivity of the wood increases as charring occurs.

With regard to the thermal radiation incident on the wood, it has been shown by Kashiwagi (1979a) that there can be a significant attenuation due to the volatile matter issuing from it.

Further work on ignition of wood has been described by Wesson, Welker and Sliepcevich (1971). They use a correlation of the form

$$t_i = k_1 \rho^{n_1} (\alpha I)^{n_2} \text{erf}[L/2(\alpha_h t)^{1/2}]^{n_3} \qquad [16.21.19]$$

where L is the thickness of the slab (cm), k_1 is a constant and n_1–n_3 are indices. For wood $\alpha_h \approx 1.5 \times 10^{-3}$ cm^2/s and for the wood samples used $L \approx 2$ cm. Using these values in Equation 16.21.19 the term $\text{erf}\,[L/2(\alpha_h t_i)^{1/2}]$ is approximately unity for $t < 700$ s. From experiments on a number of woods

the authors obtained values of the constant in Equation 16.21.19 to yield

$$t_i = 35\rho^{0.9}(\alpha I)^{-2.8} \qquad [16.21.20]$$

A comparison of the minimum ignition temperature for heat transfer by radiation and convection has been made by Kanury (1972a), who quotes the following approximate values:

Heat transfer mode	*Minimum ignition temperature* (°C)	
	Piloted ignition	*Spontaneous ignition*
Radiation	300–410	600
Convection	450	490

16.21.4 Flame spread

The growth of fire is frequently governed, particularly in the early stages, by flame spread over the surface of solids or liquids. Flame spread itself is considered at this point. The spread of fire through buildings is discussed in Section 16.36.

Accounts of flame spread include those given by P.H. Thomas, Simms and Wraight (1964, 1965), Burgoyne, Roberts and Quinton (1968), de Ris (1969), MacKinven, Hensel and Glassman (1970), Sirignano and Glassman (1970), Magee and McAlevy (1971), W.J. Parker (1972), Fernandez-Pello and Williams (1974), R. Friedman (1977). F.A. Williams (1977), Quintiere (1981), Suzuki and Hirano (1982), Ray and Glassman (1983), Drysdale (1985) and Ishida (1986, 1988).

The two situations considered here are flame spread across (1) a liquid surface and (2) a solid surface. In both cases the spreading flame has two effects: it serves as a source of heat and it causes pilot ignition.

In work on flame spread across a combustible liquid surface a distinction is made between a liquid which is below the fire point and one which is above it. If the liquid is below the fire point, it has first to be heated up. As described above, work by Sirignano and Glassman (1970) has demonstrated the role of surface tension effects in the circulation flows set up in the bulk liquid. Further work includes that by MacKinven, Hensel and Glassman (1970) on the effect of pool depth and width.

If the liquid is above its fire point, the flame spread is governed by flame propagation through the flammable mixture above the liquid surface. It has been found by Burgoyne and Roberts (1968a) that for a stoichiometric mixture the apparent rate of spread reaches a limiting value of some 4–5 times the fundamental burning velocity.

Work on flame spread over ground soaked with fuel has been described by Ishida (1986, 1988).

Flame spread over solid surfaces is a function of (1) the orientation and geometry of the surface, (2) the direction of propagation, (3) the thickness of the combustible material, (4) the properties of the material and (5) the environment factors.

The behaviour of a flame on a vertical surface differs from that of one on a horizontal surface. The direction of propagation also makes a radical difference. Flame spread is most rapid when propagation is upwards on a vertical surface. These differences are largely accounted for by differences in the extent to which the flame preheats the solid.

The rate of upward flame spread on a vertical surface tends to increase exponentially. It can be characterized by the time taken for the rate of spread to double, or the doubling time, as described by Alpert and Ward (1984).

For thin layers of combustible solid, the rate of flame spread has been shown by experiment and theory to be inversely proportional to the thickness of the bed. Relevant work has been described by Magee and McAlevy (1971) and Fernandez-Pello and Williams (1974).

The rate of flame spread is also a function of the thermal properties of the material. The precise relations depend on the thickness of the surface. A critical thickness exists which is

$$\tau_{cr} = (\alpha_h L/V)^{1/2} \qquad [16.21.21]$$

where L is the 'heating length', V is the rate of flame spread, α_h is the thermal diffusivity of the material and τ_{cr} is the critical thickness. The heating length is the length of solid over which the material is heated to its fire point. It can be shown that for thin surfaces $(\tau < \tau_{cr})V \propto (\rho c \tau)^{-1}$ and for thick surfaces $(\tau > \tau_{cr})V \propto (k\rho c)^{-1}$, where c is the specific heat, k is the thermal conductivity, ρ is the density of the material and τ is the thickness. Further, since the thermal conductivity k is approximately proportional to the density, in this latter case $V \propto \rho^{-2}$. Thus the rate of flame spread over the surface of a low density material can be very rapid.

The geometry of the surface also affects flame spread. There have been a number of studies of features such as width and edge effects.

Flame spread is also influenced by environmental factors, including the initial temperature of the fuel, the air velocity over the surface, the imposed thermal radiation and an oxygen enriched atmosphere.

Thermal radiation can cause a marked enhancement of the rate of flame spread, as evidenced by the work of Alvares (1975), Kashiwagi (1976), Fernandez-Pello (1977 a,b), Hirano and Tazawa (1978) and Quintiere (1981) and others.

The effect of air velocity on flame spread depends on the direction of air flow. If the air flow is in the same direction as the flame spread, an increase in air velocity tends to increase the rate of spread, whilst if it is in the opposing direction the effect depends on the magnitude of the air velocity. A low air velocity tends to enhance the rate of flame spread but a high one tends to reduce it. Whichever of the two directions the air flow has, there will come a point at which a very high velocity results in flame extinction, or blow-off.

The spread of flame across surfaces has been modelled by a number of workers. F.A. Williams (1977) gives the so-called 'fundamental equation of fire spread'

$$\rho V \Delta H = \dot{q} \qquad [16.21.22]$$

where ΔH is the enthalpy change per unit mass in raising the material to its fire point, $\dot{q}$ is the rate of heat transfer across the surface, V is the rate of flame spread and ρ is the density of the fuel.

The rather different problem of flame spread through open fuel beds has been studied by P.H. Thomas, Simms and Wraight (1964, 1965), who conducted a classic set of experiments on wooden cribs. Their results have been applied by other workers to a variety of fire situations.

In practical cases some factors which are of particular importance in determining flame spread over a solid surface are the thickness and composition of the surface, the imposed thermal radiation and the air movement over the surface.

16.21.5 Thermal radiation limits

Thermal radiation limits are quoted in a number of codes and standards and in numerous papers. Many limits are given for the purposes of plant design and layout. Some are relevant to hazard assessment. Generally, such sets of limits include both limits related to damage and others related to injury. It is convenient, therefore, to defer consideration of such limits to the next section.

16.22 Effects of Fire: Injury

There is a requirement in hazard assessment for relationships which permit heat radiation intensity to be translated into the equivalent burn injury. Correlations for both fatal and non-fatal burn injury have been derived in the Vulnerability model by Eisenberg, Lynch and Breeding (1975). A detailed review and additional information have been given by Hymes (1983 SRD R275). Further correlations are given in the *Green Book* (CPD, 1992b).

16.22.1 Sources of thermal radiation

The effect of thermal radiation on man depends very much on the source of radiation and it is therefore necessary to specify this. One source of thermal radiation which is of long-standing interest is a flare and some of the earliest thermal radiation limits relate to flares.

Another source of thermal radiation which has received increasing attention is a fireball, typically as part of a BLEVE. A fireball is well defined relative to most other types of fire to which people may be exposed and it is one of the fire hazards most likely to give rise to a large number of serious injuries.

16.22.2 Experimental studies

Experimental work on injury from thermal radiation has been done on humans and on animals. The use of human subjects is limited to the lower levels of pain and injury.

Henriques (1947) carried out experiments in reddening and blistering in man exposed to thermal radiation. Buettner (1951b) performed experimental work on man in which skin temperature and pain threshold were measured. Experiments on man were also conducted by Stoll and Greene (1959) to investigate skin temperature and thresholds of pain and blistering.

Experimental work on rats exposed to thermal radiation by NML, Brooklyn, and on rats exposed to direct flame contact by NADC, Johnsville, quoted by Stoll and Chianta (1971), provides a basis for comparing burn injury by these two modes.

Hinshaw (1957) at the University of Rochester investigated the thermal radiation intensities required to produce second and third degree burns in pigs. Experiments on swine burn have also been performed by Hardee and Lee (1977/78).

Tests on the response of fabrics to thermal radiation have been done by Wulff and co-workers (Wulff, 1973; Wulff *et al.*, 1973; Wulff and Durbetaki, 1974), and work on heat transfer from burning clothing to the wearer has been done by Williams *et al.* (n.d.) at MIT and by Arnold *et al.* (1973) at the Gillette Research Institute.

16.22.3 Skin properties

Human skin consists of two layers, the epidermis and the dermis. It ranges in thickness from some 5 mm on the back to some 0.5 mm on the eyelids. The area of skin on the average man is some 1.8 m^2. The distribution of skin surface area is considered in Section 16.22.10.

16.22.4 Pathology of burns

Accounts of burns and burn treatment are given in *Burns and Their Treatment* (I.K. Muir and Barclay, 1974), *Burns: a Team Approach* (Artz, Moncrief and Pruit, 1979), *Clinical Burn Therapy* (Hummel, 1982), *Physiological Responses to Burn Injury* (J.W.L. Davies), *Burn Mortality* (W. Clark and Fromm, 1987), *Plastic Surgery* (Goldin, 1987) and *Plastic Surgery* (McCarthy, 1990). Treatments of burn injuries of particular relevance here are those by Glasstone (1962) and Hymes (1983 SRD R275).

The effects of incident heat radiation are, in order of increasing severity:

Burn type	*Criterion*
First degree	Persistent redness
Second degree:	
Moderate	Some blistering
Deep	Full blistering
Third degree	Charring

A first degree burn involves the epidermis. There is reddening but no blistering. A second degree burn may be superficial or deep. The former affects the epidermis and part of the dermis and involves some blistering, but with damage to the surface layers only. The latter penetrates further into the dermis and damages it more severely. A third degree burn destroys both the epidermis and the dermis.

The terms second and third degree burn have largely given way to characterization in terms of the depth of burn, reference being made to full depth and other burns.

16.22.5 Skin temperature

Burn injury correlates closely with skin temperature. Pain is experienced at a temperature of 44°C and above this temperature injury occurs.

Relations for the unsteady-state temperature profile of the skin suddenly exposed to a source of heat radiation have been given by Buettner (1951a) and by Stoll and Chianta (1971). The simplest of these is the equation given by Buettner for a non-penetrating constant source of thermal radiation.

$$T_s - T_o = \frac{2Qt^{1/2}}{(\pi k \rho c)^{1/2}} \qquad [16.22.1]$$

where for the skin c is the specific heat, k is the thermal conductivity, Q is the net heat absorbed, t is the time, T_o is the initial temperature throughout, T_s is the surface temperature and ρ is the density.

The thermal response is governed by the thermal inertia ($k\rho c$). Measurements of the thermal inertia were made by Stoll and Greene (1959), who found that it varied strongly with the thermal radiation intensity.

Stoll and co-workers (Stoll and Greene, 1959; Stoll and Chianta, 1971) have studied the temperature at the basal

layer of skin, which is about 80 μm (0.08 mm) below the surface. They found that damage occurs at temperatures above 44°C.

The temperature profile of skin at 80 μm subjected to thermal radiation sufficient to cause blistering given by these workers is shown in Figure 16.118(a). They give a model for the degree of tissue damage W due to heat radiation. Part of the damage occurs during the cooling period after the heat source is removed.

The rate of injury above 44°C increases very rapidly indeed with temperature. The relation given by Stoll and Chianta is shown in Figure 16.118(b). There is an approximate trebling of the rate of injury for each 1°C temperature rise. Thus the injury rate at 50°C is some 100 times that at 44–55°C.

Stoll and Chianta describe work on burn in rats. The responses of rats to thermal radiation and to flame contact have been studied by NML, Brooklyn, and by NADC, Johnsville, respectively. Figure 16.118(c) gives a comparison of the two sets of results which shows that the responses are virtually identical. These results indicate that the dose–response relation is similar for thermal radiation and for flame contact. The results are usually regarded as applicable to man also.

16.22.6 Injury factor

Inquiry due to exposure to a short but strong pulse of thermal radiation may be correlated in several ways. The most convenient is to take the injury factor as the thermal dose which is the product of the thermal radiation intensity and time. The level of thermal radiation for a particular effect is often correlated in terms of the thermal dose.

It is found, however, that this somewhat understates the effect of very high intensities of thermal radiation and that better correlation is obtained if these are more highly weighted. The empirical correlation for the injury factor which best fits the data is

$$tI^n = \text{Constant} \qquad [16.22.2]$$

where I is the intensity of thermal radiation (W/m^2), t is the time (s) and n is an index.

As described below, Equation 16.22.2 has been given by Eisenberg, Lynch and Breeding (1975) for the correlation of data on burn fatalities with a value of the index $n = 4/3 = 1.33$. For non-fatal burn injuries these authors use the slightly different exponent $n = 1.15$. It has been proposed by Hymes that the data for fatal and non-fatal injury are adequately correlated using a value of $n = 1.33$ for both.

The term $tI^{4/3}$ is referred to here as the thermal load L to distinguish it from the thermal dose $D = tI$. It is conventional to express the thermal radiation intensity in kW/m^2 but to use in probit equations an intensity expressed in W/m^2. Since this latter practice gives rise to thermal loads which are large numbers, it is convenient to define also an alternative thermal load L'. These quantities are thus defined as follows:

$$D = tI \qquad [16.22.3]$$

$$L = tI^{4/3} \qquad [16.22.4]$$

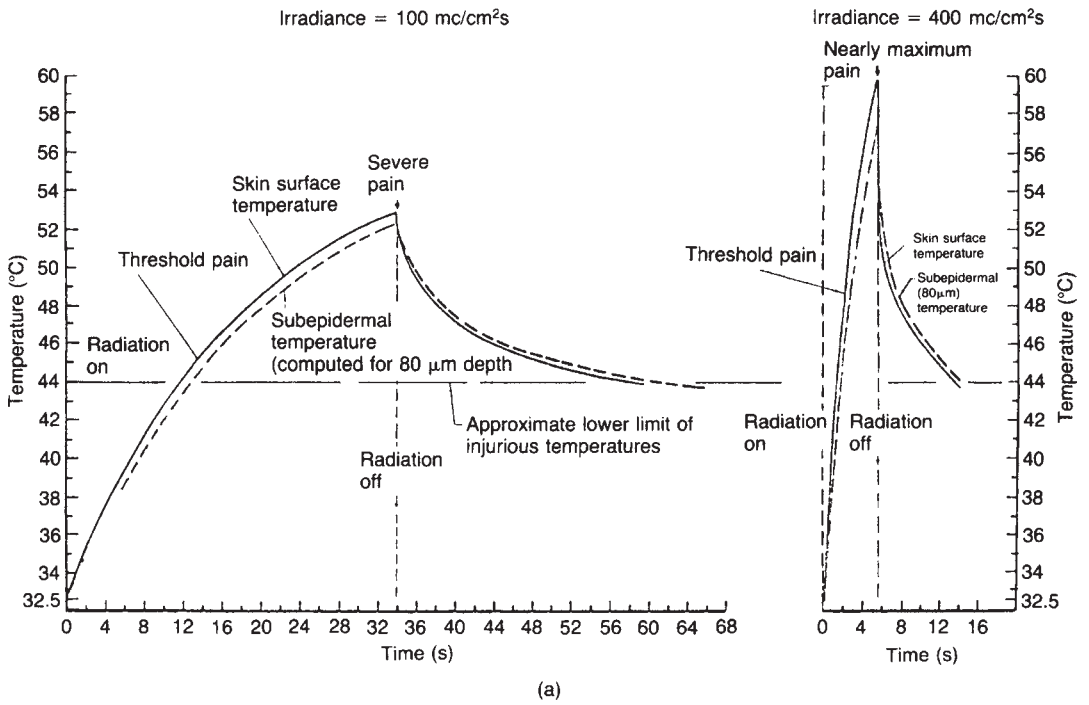


Figure 16.118 *Effect of heat on skin (Stoll and Chianta, 1971): (a) heating and cooling of skin exposed to heat radiation*

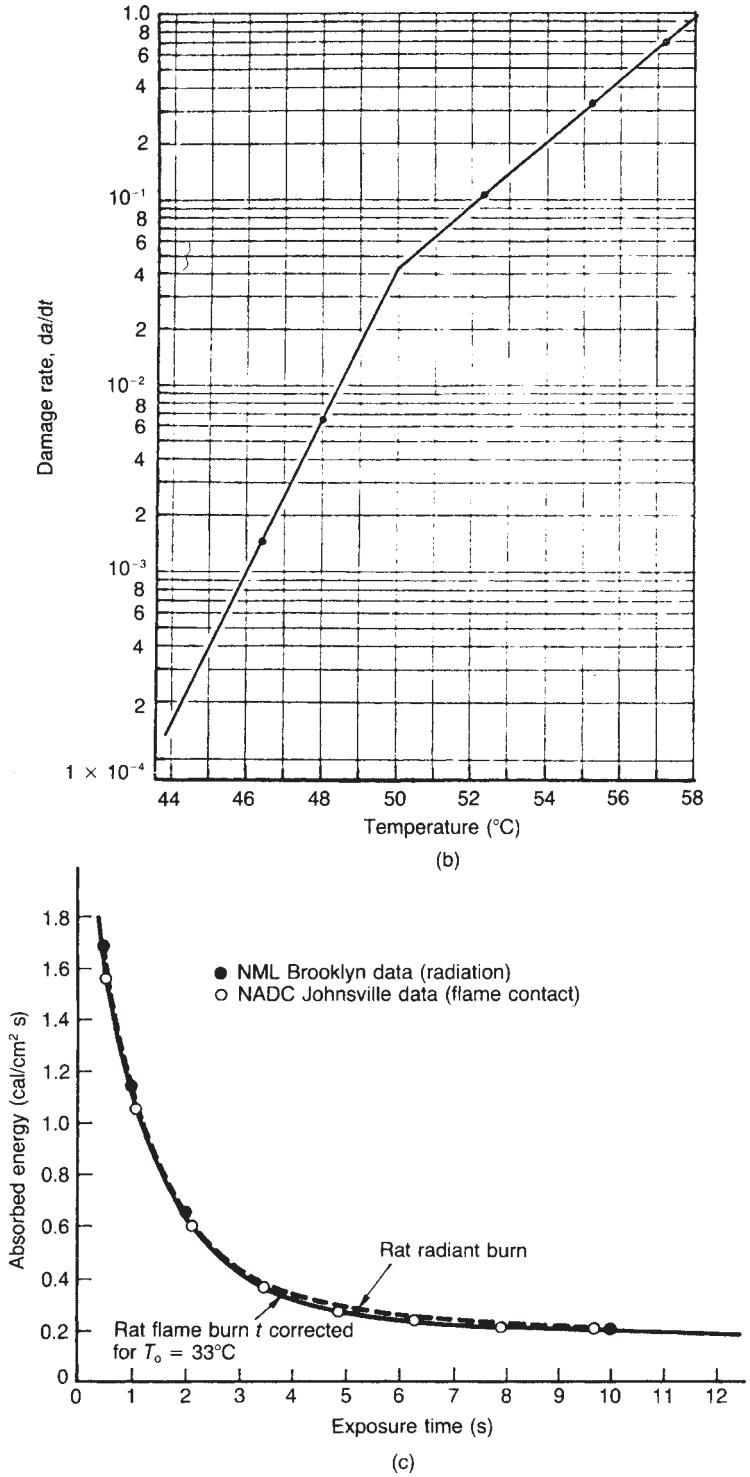


Figure 16.118 continued *(b) rate of damage to skin exposed to heat radiation; and (c) burn injury to rats exposed to heat radiation and to flame contact (Courtesy of the New York Academy of Sciences)*

where D is the thermal dose (kJ/m^2), I is the thermal radiation intensity (kW/m^2), L is the thermal load (s (kW/m^2)$^{4/3}$) and t is the exposure time (s). Further

$$L' = tI^{4/3}/10^4 \qquad [16.22.5]$$

where I is the thermal radiation intensity (W/m^2) and L' is the thermal load ((s (W/m^2)$^{4/3}$)/10^4).

16.22.7 Pain and blister thresholds

A number of workers have correlated thresholds of pain and blistering. Table 16.75 shows some limits for pain and injury given in the literature, in terms of thermal radiation intensity in Section A and of thermal dose in Section B.

Table 16.76, Section A, shows the results obtained for the time to the threshold of pain in man by Buettner (1961b), and by Stoll and Green (1959). Figure 16.119(a) (Mudan, 1984c) is a plot of data reported by these and other workers.

The threshold of pain may also be expressed in terms of the thermal load. Values given by Hymes based on the work of Stoll and Greene are shown in Table 16.76, Section C. Hymes gives as the approximate threshold of pain a value of 92 s (W/m^2)$^{4/3}$/10^4.

Results for the time to the threshold of blistering in man by Stoll and Greene are shown in Table 16.76, Section B, whilst a plot by Mudan of these and other data is given in Figure 16.119(b).

16.22.8 Second and third degree burns

Several workers have investigated the degree of exposure of pigs to levels of thermal radiation which cause second and third degree burns. In work by Hinshaw (1957) at the University of Rochester, pigs were subjected to thermal radiation exposures of 210, 420 and 670 kJ/m^2 for periods of 0.5, 1, 3, 5, 10 and 30s.

At high thermal radiation intensities the heat is sufficient to vaporize the tissue fluids, an effect known as ablation. The burn injury occurring in these circumstances is termed a 'steam bleb'. Histological examination in these experiments showed that the thermal radiation was sufficiently intense in some tests to cause steam 'bleb' formation and mitigation of the tissue damage.

The data have been analysed by Hymes who has derived the results given in Table 16.77 correlated in terms of the heat injury factor. From these data Hymes estimates the threshold for steam bleb formation as a thermal load of some 4000–4500 s (W/m^2)$^{4/3}$/10^4. This is a very high level of thermal radiation which, according to the relations for fatality given below, would be lethal in some 90% of cases. It is therefore thermal radiation intensity below the level of steam bleb formation which is of prime interest.

The depth of skin burn in Hinshaw's experiments at thermal radiation intensities below those which cause steam bleb has been correlated by Hymes, as shown in Figure 16.120(a). He takes the burn depths for the threshold of second degree burns and the onset of third degree burns

Table 16.75 *Some limits for pain and injury from thermal radiation*

A Thermal radiation intensity

Thermal radiation intensity (kW/m^2)		*Reference*
1.5	Threshold of pain	Atallah and Allan (1971)
2.1	Level at which pain is felt after 1 min	
1	Level just tolerable to a clothed man	HSE (1978b)
8	Level which causes death within minutes	
4.7	Threshold of pain. Average time to experience pain, 14.5 s	Crocker and Napier (1986)

B Thermal dose

Thermal dose (kJ/m^2)		*Reference*[a]
40	Second degree burns	Williamson and Mann (1981)[a]
125	Third degree burns	
65	Threshold of pain	Rijnmond Public Authority (1982)
125	First degree burns	
250	Second degree burns	
375	Third degree burns	
c. 100	Threshold of blistering	Crossthwaite (1984)[a]
200	Blistering	
700	50% fatality	
65	Threshold of pain, no reddening or blistering of skin	BS 5908: 1990
125	First degree burns	
200	Onset of serious injury	
250	Second degree burns	
375	Third degree burns	

[a] For thermal radiation from a fireball.

Table 16.76 *Times to pain and blister thresholds*

A Time to threshold of pain: thermal radiation intensity

Authors	*Thermal radiation intensity* (kW/m^2)	*Time* (s)
Stoll and Greene (1959)[a]	4.2	13.5
	5.2	10.1
	6.3	7.8
	8.4	5.5
	12.6	2.9
	16.8	2.2
Buettner (1951b)[b]	3.7	20
	6.2	10
	9.7	5
	18	2
API RP 521: 1990	1.74	60
	2.33	40
	2.90	30
	4.73	16
	6.94	9
	9.46	6
	11.67	4
	19.87	2

B Time to threshold of blistering: thermal radiation intensity

Authors	*Thermal radiation intensity* (kW/m^2)	*Time* (s)
Stoll and Greene (1959)	4.2	33.8
	6.3	20.8
	8.4	13.4
12.6	7.8	
16.8	5.6	

C Time to threshold of pain: thermal load

Authors	*Thermal load,* $tI^{4/3}$ $(s(W/m^2)^{4/3}/10^4)$	*Time* (s)
Hymes (1983 SRD R275)	86	13.0
	88	10.0
	90	8.0
	91	5.5
	103	3.0

[a] Time to threshold of pain.
[b] Time to unbearable pain.

as 0.1 and 2 mm, respectively. The corresponding thermal loads are approximately 1200 and 2600 s $(W/m^2)^{4/3}/10^4$, respectively.

Swine burn experiments have also been done by Hardee and Lee (1977/78), who have derived from their results considerably lower values for the levels of heat radiation intensity for given degrees of injury. According to Hymes, the reinterpretation of this work does not support these lower values.

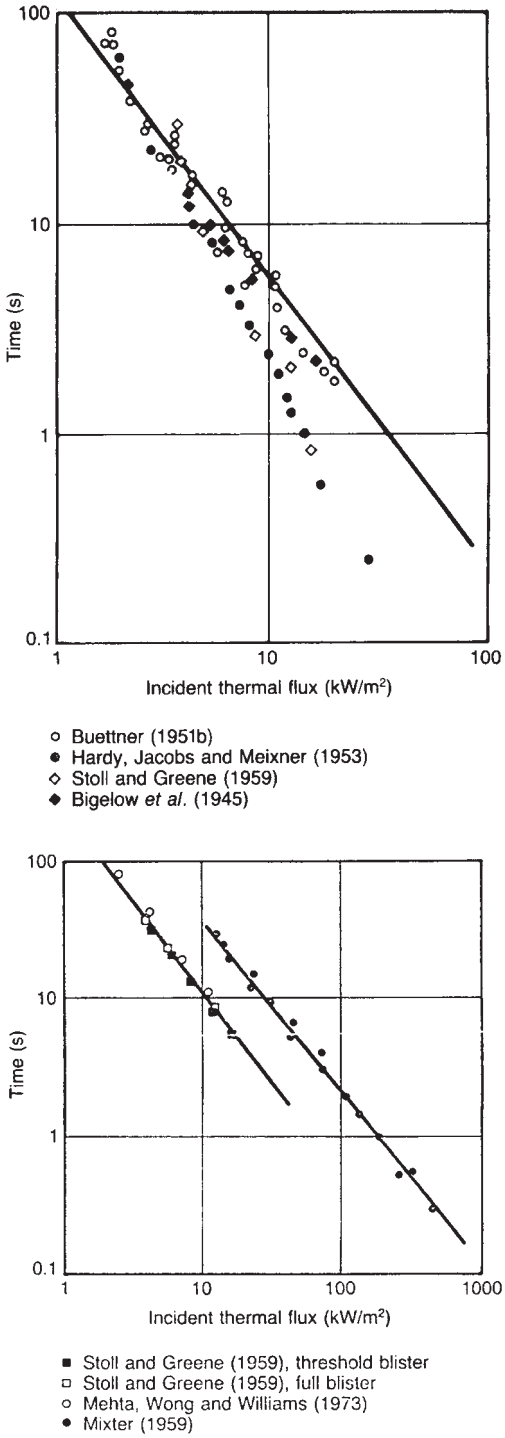


Figure 16.119 *Time to threshold effects of heat radiation (Mudan, 1984c): (a) threshold of pain; and (b) threshold of blistering (Courtesy of Progress in Energy and Combustion Science)*

Table 16.77 *Second and third degree burn injury to pigs exposed to thermal radiation (after Hymes, 1983 SRD R275) (Courtesy of the UKAEA Safety and Reliability Directorate)*

Thermal dose (kJ/m^2)	*Time* (s)	*Thermal load* $(s\,(W/m^2)^{4/3}/10^4)$	*Thermal damage* (mm)	*Steam bleb*
210	0.5	1570	0.17	No
	1	1240	0.16	No
	3	860	None	No
	5	730	None	No
	30	400	None	No
420	0.3	4680	0.49	Yes
	3	2170	0.72	No
	10	1450	0.45	No
670	0.5	7385	0.9	Yes
	1	5860	1.1	Yes
	3	4065	1.4	Sometimes
	5	3430	1.6	No
	10	2720	1.6	No
	30	1890	1.1	No

As described above, work has been done at MIT and at the Gillette Research Institute on the heat transferred from burning clothing to the wearer.

Figure 16.120(b) shows the relation between depth of skin burn and thermal load from these sources as given by Hymes.

Another source of information on second and third degree burns is data on burn victims from the nuclear weapons dropped on Japan, which are given by Glasstone (1962).

16.22.9 Human response to fire events

Human response to a fire event depends on (1) the nature of the event and (2) the awareness of the person.

The event primarily considered in relation to burn injury is a fireball. Another sudden event may be a rapid growth in the size of a flare. Other types of event such as a pool fire are generally considered to occur more gradually and to allow more time for escape, though this may not always be so. It is the fireball hazard which is primarily considered by Hymes and Marshall, and also here.

Accounts of burn injury such as those by Hymes and in the *Green Book* quote a human response time of 5 s. The application of this reaction time to a fireball scenario is that the person faces the fireball for 5 s and then turns his back and seeks to escape.

In an analysis of human exposure to a BLEVE, in the context of a discussion of the disaster at San Carlos, Hymes considers two situations. In Situation 1 with the lift-off time less than the reaction time, the first phase involves frontal exposure for the 5 s reaction time. The person then turns his back and seeks to escape. During this escape the fireball passes through three further phases: further growth at ground level, shrinkage just prior to lift-off, and rise. In Situation 2, the lift-off time equals the reaction time, so that there is no phase of further growth at ground level; otherwise the scenario is similar, with the period of frontal exposure again being 5 s.

In practice, human behaviour tends to be more complex. Hymes gives an account of the BLEVE at the Lowell Gas Company at Tewkesbury, Massachusetts, in 1972. One comment quoted contains two relevant points. The firefighters seem to have had 'momentary warning' of the impending BLEVE. Since the front of their clothing was not burned but the back was, they appear to have turned their backs very promptly, but since their faces were burned, it is believed that they tended to look round to see what was happening.

16.22.10 Protection by clothing

The degree of protection offered by clothing depends on the fraction of the body which is so protected. Data on the fraction of the body area represented by the different parts of the body are given in the *Green Book*. An extract from this tabulation, giving the fraction of body area (%) for the parts of the body most likely to be exposed, is as follows:

Fraction of body area (%)						
Part of body	*Age group* (years)					
	1	1–4	5–9	10–14	15	*Adult*
Head	19	17	13	11	9	7
Neck	2	2	2	2	2	2
Hands (each)	2.5	2.5	2.5	2.5	2.5	2.5
Lower arms (each)	3	3	3	3	3	3
Upper arms (each)	4	4	4	4	4	4
Lower legs (each)	5	5	5.5	6	6.5	7
Upper legs (each)	5.5	6.5	8	8.5	9	9.5

The *Green Book* takes for the Dutch population a maximum value of the body surface exposed of 20% in normal conditions.

From the above data the following estimates of the fractions of body area (%) exposed for an adult may be obtained:

	Fraction of body area (%)		
	Front	*Back*	*Total*
Head	4	3	7
Neck	1	1	2
Hands	2.5	2.5	5
Lower arms	3	3	6
Total	10.5	9.5	20

If the thermal radiation is so intense as to ignite the clothing, a different situation pertains. This is considered in Subsection 16.22.13. A detailed discussion of the protection afforded by clothing is given by Hymes.

16.22.11 Protection by buildings

The degree of protection afforded by a building to a person within it depends on the location of that person. In many cases this will be such that the building affords complete protection. Persons in buildings are liable to be exposed, however, to thermal radiation through glass windows. A person aware of an event outside may well move to view it through a window.

Figure 16.121 from Hymes shows the transmissivity of window glass for thermal radiation from sources up to 1200°C.

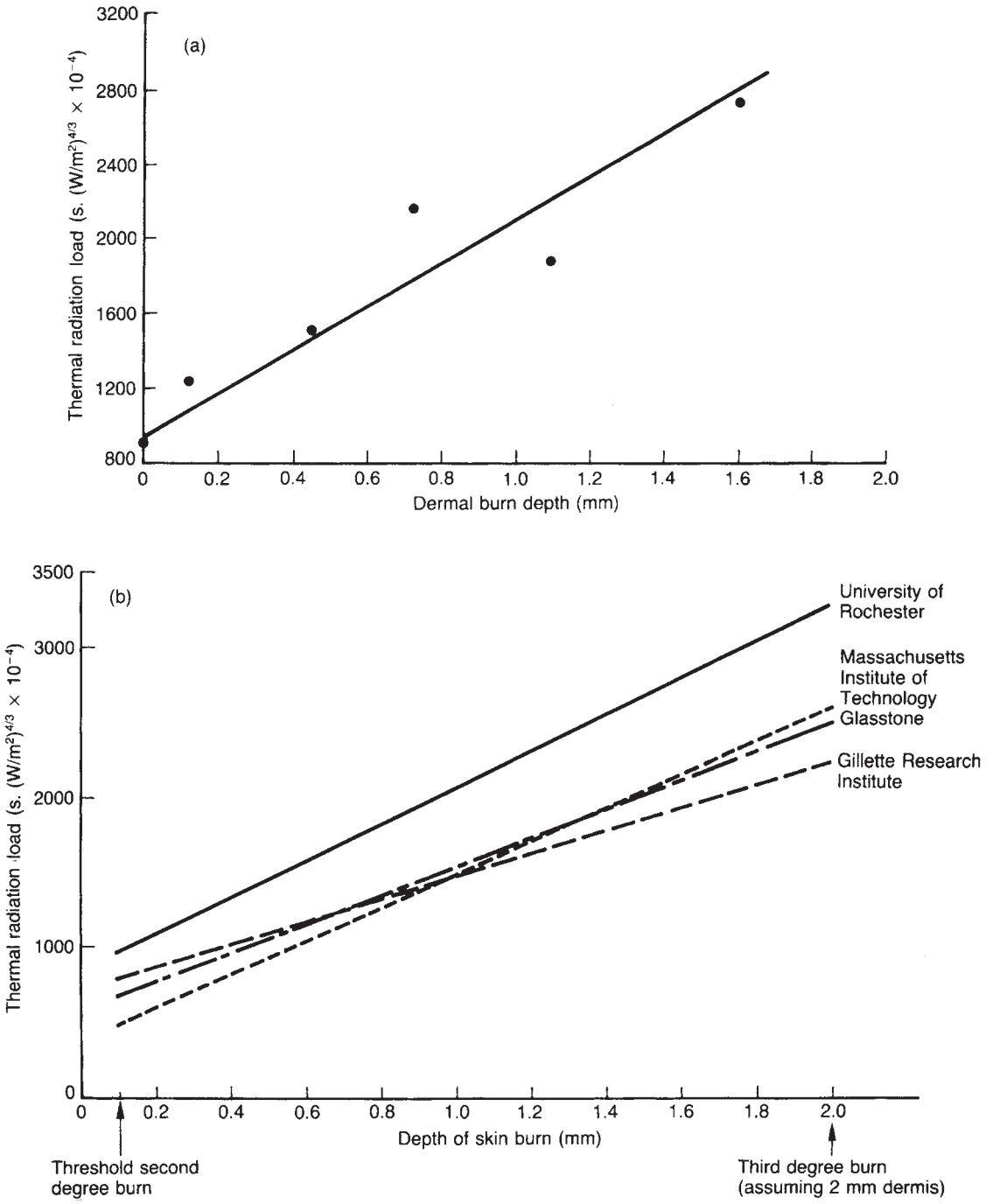


Figure 16.120 *Depth of skin burn due to heat radiation (Hymes, 1983 SRD R275): (a) sub-'steam bleb' burns in pigs obtained at University of Rochester by Hinshaw; and (b) comparison with results of other workers (Courtesy of the UKAEA Safety and Reliability Directorate)*

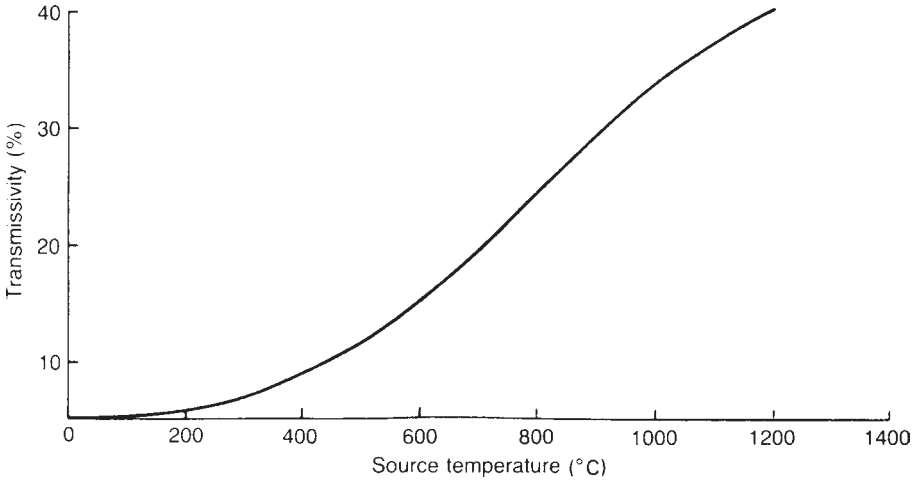


Figure 16.121 *Transmissivity of ordinary window glass for heat radiation (Hymes, 1983 SRD R275) (Courtesy of the UKAEA Safety and Reliability Directorate)*

16.22.12 Effective radiation intensity

In estimating burn injury it is important to utilize an appropriate value of the thermal radiation. The effective intensity is determined by the atmospheric transmissivity and the geometry of the body as presented to the radiation source. The attenuation due to the atmosphere has been discussed in Section 16.13 and is not considered further here.

The importance of the geometry of the body has been emphasized by V.C. Marshall (1987). There is a tendency in hazard assessments to treat the whole of the exposed area of the body as subject to the radiation nominally incident at the particular point. If the body is treated as a thin object, the ratio of the surface to the projected area is approximately 2. If it is treated as a long cylinder, the ratio is π. For a sphere the ratio is 4. The three-dimensional nature of the body is therefore significant. The thermal radiation incident on the exposed area is appreciably less than that calculated as falling on the projected area.

A related aspect is that with a three-dimensional body the angle of incidence of the radiation varies from 90° to close to zero. Typically, the view factor used takes account of the angle of incidence in two dimensions, but not three.

16.22.13 Ignition of clothing

The protection afforded by clothing is limited by the fact that at thermal radiation intensities within the range of interest here it is prone to ignite. A distinction needs to be made between everyday clothing and fire fighters' suits; the latter are naturally designed to resist ignition. It is primarily everyday clothing which is considered here.

For clothing subject to thermal radiation, there is also a distinction to be made between spontaneous and piloted ignition. A similar distinction is made for ignition of wood by thermal radiation, as described in the previous section. Whilst spontaneous ignition may be regarded as the base case, Hymes suggests that in certain scenarios, notably a BLEVE, the probability of piloted ignition, for example, by burning paper or leaves, is quite high.

As already stated, work on ignition of fabrics has been carried out by Wulff and co-workers. From this work Hymes has given relations for the determination of the times to unpiloted and to piloted ignition together with tables of parameters for common fabrics.

For spontaneous ignition times are correlated by Hymes using the relation

$$tI^n = \text{Constant} \qquad [16.22.6]$$

where I is the thermal radiation intensity (W/m^2), t is the time (s) and n is index. The values quoted for n lie in the range 1.16–3.22.

Using this equation, Hymes gives for one fabric subject to a thermal radiation intensity of 198 kW/m^2 the following estimate of the induction time for ignition.

$$t = \frac{2.87 \times 10^{18}}{(198,000)^{3.44}} = 1.7 \text{ s}$$

For piloted ignition the approach is slightly different. In this case the time is taken as that required to heat the fabric from its initial temperature to its piloted ignition temperature:

$$t_p = \frac{SC(T_p - T_o)}{aW} \qquad [16.22.7]$$

where a is the absorptivity of the fabric, C its specific heat (J/g°C) and S its density (g/cm^2), t_p is the time to piloted ignition (s), T_o is the initial temperature of the fabric (°C), T_p is the piloted ignition emperature (°C)and W is the incident heat radiation (W/cm^2). It should be noted that the density is defined in terms of the mass per unit thickness. Values of the piloted ignition temperawre and other properties of the fabric are tabulated by Hymes.

He gives as an example a fabric subjected to a thermal radiation intensity of 198 KW/m^2, hence $W = 19.8$ W/cm^2,

with the properties $a = 0.19$, $C = 1.35$ J/g°C; $S = 0.024$ g/cm^2, and at conditions $T_o = 14$°C and $T_p = 334$°C, yielding $t_p = 2.75$ s.

Hymes states that for thermal radiation intensities greater than 75 kW/m^2 most clothing will undergo spontaneous ignition within about 5 s. Under conditions such as a BLEVE, piloted ignition is probable and the time to ignition will tend to be even shorter.

The *Green Book* refers to the work of Hymes and proposes for the ignition of clothing the following threshold relation

$$tI^2 = D_s \qquad [16.22.8]$$

where D_s is the clothing ignition load (s(KW/m^2)^2), I is the thermal radiation intensity (kW/m^2) and t is the time (s). It states that the value of D_s lies approximately in the range 2.5×10^4 and 4.5×10^4 s (kW/m^2)^2.

Ignition of clothing has two main effects. One is that it distracts the wearer. He May well stop running and try to douse the flames, with effects not only on the speed of escape but also on the orientation of the body.

The other effect is to cause injury from burning clothing. For the heat released by the burning of clothing, Hymes quotes the following figures for typical clothing such as cotton. The heat of combustion lies in the range 5–20 kJ/g Which translates to 1–4 J/mm^2 of fabric. When the clothing burns there is transfer of some 15–50% of the heat of combustion. The thermal does received would then be of the order of 105–356 kJ/m^2. He also refers to the medical adage that 'one square centimetre of burnt skin'.

Mortality from burning clothing is discussed in the next subsection.

16.22.14 Mortality from burns

Information of the mortality in persons admitted to hospital with burn injuries has been given in a series of papers spanning some 40 years by Bull, Lawrence and co-workers, the first being that of J.P. Bull and Squire (1949) and the most recent that of J.C. Lawrence (1991), the intermediate publications being those of J.P. Bull and Fisher (1954) and J.P. Bull (1971).

Table 16.78 from J.C. Lawrence (1991) shows the mortality among persons admitted with burns or scalds as a function of fraction of the body exposed and of age group. The total number of cases in the 7-year survey period was 3044.

Analysis of the data given by Lawrence indicates the following breakdown of causes of burn injury in the admissions trated:

	Proportion (%)	
	Admissions	*Fatalities*
Building fires	3	16
Flammable liquids	10	21
Space heating	8	19
Electrical fire/flashover	~20	
Chemicals	~20	
Explosions, molten metal	~25	
Hot objects, chemicals and molten fats	14	low
Other		
Total	100	

Table 16.78 *Mortality in cases admitted to hospital with burn and scald injuries as a function of body area exposed and age group (J.C. Lawrence, 1991) (Courtesy of the Fire Safety Journal)*

Body area burned (%)	*Age* (years)																	
	0–4	5–9	10–14	15–19	20–24	25–29	30–34	35–39	40–44	45–49	50–54	55–59	60–64	65–69	70–74	75–79	80–84	85+
93+	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
88–92	0.9	0.9	0.9	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
83–87	0.8	0.8	0.9	0.9	0.9	1	1	1	1	1	1	1	1	1	1	1	1	1
78–82	0.8	0.8	0.8	0.8	0.9	0.9	0.9	1	1	1	1	1	1	1	1	1	1	1
73–77	0.7	0.7	0.7	0.8	0.8	0.8	0.9	0.9	0.9	1	1	1	1	1	1	1	1	1
68–72	0.6	0.6	0.6	0.7	0.7	0.8	0.8	0.8	0.9	0.9	1	1	1	1	1	1	1	1
63–67	0.5	0.5	0.5	0.6	0.6	0.7	0.7	0.8	0.8	0.9	0.9	1	1	1	1	1	1	1
58–62	0.3	0.4	0.4	0.5	0.5	0.6	0.6	0.7	0.7	0.8	0.9	0.9	1	1	1	1	1	1
53–57	0.2	0.3	0.3	0.4	0.4	0.5	0.5	0.6	0.6	0.7	0.8	0.9	1	1	1	1	1	1
48–52	0.2	0.2	0.2	0.3	0.3	0.4	0.4	0.5	0.5	0.6	0.7	0.8	0.9	1	1	1	1	1
43–47	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.4	0.4	0.5	0.5	0.7	0.9	1	1	1	1	1
38–42	0	0.1	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.4	0.4	0.6	0.8	0.9	1	1	1	1
33–37	0	0	0	0.1	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.5	0.7	0.9	1	1	1	1
28–32	0	0	0	0	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.3	0.5	0.8	0.9	1	1	1
23–27	0	0	0	0	0	0	0	0.1	0.1	0.1	0.2	0.2	0.4	0.6	0.8	0.9	0.9	1
18–22	0	0	0	0	0	0	0	0	0	0.1	0.1	0.1	0.3	0.5	0.7	0.8	0.8	0.9
13–17	0	0	0	0	0	0	0	0	0	0	0	0.1	0.1	0.3	0.5	0.6	0.6	0.7
8–12	0	0	0	0	0	0	0	0	0	0	0	0	0.1	0.2	0.3	0.4	0.4	0.4
3–7	0	0	0	0	0	0	0	0	0	0	0	0	0	0.1	0.1	0.1	0.2	0.2
0–2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.1	0.1

The proportion of burn victims who die without ever being admitted is not stated, but it is probably small. An appreciable fraction of such cases is likely to be victims of building fires who have died from both smoke and burns. Table 16.78 takes account of vulnerable groups, the elderly being particularly at risk from this mode of injury.

Burn injury is an area where there have been great improvements in medical treatment over the years. One aspect of this mentioned by Craven (1976) is the improvement in survival rates since 1965 due to silver nitrate prophylaxis.

Lawrence states that over the 40-year period up to 1991 deaths attributable to burns and scalds have halved. Since the situation reported by Bull in 1971, mortality has decreased by 19%. The data given in the table therefore take account of the effects of modem medical treatment.

Work is available by Arnold *et at.* (1973) on the degree of incapacitation as a function of the fraction of body area burned. Graphs from this work are given by Hymes.

With regard to fatal injury from ignited clothing, in a survey of five American hospitals by Schlapowsky (1967) of 179 people admitted to hospital suffering from burns from clothing, almost 40% had second degree burns or worse, requiring extensive surgery and skin grafts; 16% had third degree burns.

In his survey, Lawrence states that there were 248 cases of ignition of ordinary clothing, excluding those involving flammable liquids, of whom 46 died, giving a mortality of 18.5%.

16.22.15 Eisenberg, Lynch and Breeding models

An early set of relations for thern1al injury were those given in the Vulnerability model by Eisenberg, Lynch and Breeding (1975). For fatal injury, these authors utilize an adaptation of data given by C.S.White (1971) for the thermal injuries caused by nuclear weapons dropped on Japan. The data of the latter author for thermal radiation are based on the weapon yield. Using a formula given by Glasstone (1962) for the relationship between weapon yield and pulse duration, Eisenberg, Lynch and Breeding convert the original data to thermal radiation intensities over a defined pulse. The figures obtained are summarized in Section A of Table 16.79.

From analysis of these data the authors obtain the data shown in the first four columns of Section B of Table 16.79. Further analysis indicated that the form of the causative factor, in this case a thermal load, should be the $I^{4/3}$, which is confirmed by the relative constancy of the three sets of figures for 1, 50 and 99%mortality in the last column of Section B. The profit equation derived by these authors is then

$$Y = -14.9 + 2.56 \ln\left(tI^{4/3} \times 10^{-4}\right) \qquad [16.22.9]$$

where I is the thermal radiation intensity (W/m2), t is the time of exposure (s) and Y is the profit.

Since Equation 16.22.9 is based on burn injuries to people going about their normal affairs, it applies to persons who are clothed.

The same equation is applied by these authors to burn injury both from flash fires and pool fires. In their model system the values of thermal radiation intensity and of time are for flash fires the effective values and for pool fires the actual values.

Eisenberg, Lynch and Breeding also give the following relation for the threshold of burns, or first degree burns, obtained from the values in Table 16.79:

$$tI^{1.15} = 550 \times 10^3 \qquad [16.22.10]$$

16.22.16 Hymes models

The review of burn injury given by Hymes, which has already been extensively quoted, does not include any new model as such. For fatal injury Hymes utilizes Equation 16.22.9 of Eisenberg, Lynch and Breeding. He also gives a number of thermal injury effects which ar1fa.bk summarized in Table 16.80.

The work of Hymes covers most of the relevant aspects of burn injury, including clothing ignition, thresholds of pain and blistering, and burn fatalities.

Some of the heat radiation limits and dos−response relations given by Hymes are shown in Figure 16.122, and others are given in the tables in Subsection 16.22.20.

16.22.17 *Green Book* models

A set of relations for thermal injury are given in the *Green Book*. For fatal injury, use is made of an adaptation of Equation 16.22.9 by Eisenberg, Lynch and Breeding. The modification is based on the fact that thermal radiation from nuclear weapons is in the UV range, whereas that from hydrocarbons is in the IR range.

Two relations are given, one for persons unprotected by clothing and one for those so protected. These are:

$$Y = -36.38 + 2.65 \ln\left(tI^{4/3}\right) \quad \text{Unprotected} \qquad [16.22.11]$$

$$Y = -37.23 + 2.56 \ln\left(tI^{4/3}\right) \quad \text{Protected} \qquad [16.22.12]$$

where I is the thermal radiation intensity (W/m^2) and t is the time of exposure (s).

The *Green Book* also gives relations for non-fatal injury. For first degree burns

$$Y = -39.83 + 3.02 \ln\left(tI^{4/3}\right) \qquad [16.22.13]$$

and for second degree burns

$$Y = -43.14 + 3.02 \ln(tI^{4/3}) \qquad [16.22.14]$$

16.22.18 Lees model

Another model for injury by thermal radiation has been developed by Lees (1994a). The model is essentially a set of relationships which may be combined in various ways depending on the scenario modelled and which have been utilized by the author to produce a relation for fatal injury from a sudden heat release such as a fireball, subject to defined assumptions.

The causative factor is taken as the thermal load $L' = tI^{4/3}$ ([s$(W/m^2)^{4/3}$]/10^4).

For the severity of the burn injury use is made of the relation given in Figure 16.120(a) of Hymes between thermal load and burn depth δ, which is equivalent to

$$\delta = 8.85 \times 10^{-4}(L' - 920) \qquad [16.22.15]$$

For the relationship between burn injury and mortality the data of J.C. Lawrence (1991) given in Table 16.78 are utilized.

The fraction of the body exposed depends on the scenario considered. The base case is taken as an adult wearing light clothing such that the head, neck, hands and lower arms are exposed. From the data given in Subsection 16.22.10, it can

Table 16.79 *Estimated relations between thermal radiation intensity and burn injury (after Eisenberg, Lynch and Breeding, 1975)*

A Nuclear weapons: effects and thermal injury

Thermal radiation intensity (cal/cm^2 s)			
Weapon yield	20 kt	1 Mt	20 Mt
Pulse duration	1.43	10.1	45.2
Thermal injury			
First degree burn	1.75	0.297	0.0886
Second degree burn	3.14	0.643	0.221
Lightly clothed (summer)			
Few, if any, injuries	1.75	0.297	0.0886
Significant injury threshold	2.80	0.594	0.210
Lethality			
Threshold	3.50	0.792	0.243
Near 50%	6.30	1.385	0.442
Near 0%	14.0	3.07	0.952

B Thermal radiation intensity and mortality

Mortality %	*Duration* (s)	*Thermal radiation intensity*		*Thermal load,* $tI^{4/3}$ (s (W/m^2)$^{4/3}$)
		(cal/cm^2 s)	(W/m^2)	
1	1.43	3.50	146×10^3	1099×10^4
1	10.1	0.792	33.1×10^3	1073×10^4
1	45.2	0.243	10.2×10^3	1000×10^4
50	1.43	6.30	263.6×10^3	2471×10^4
50	10.1	1.385	57.95×10^3	2264×10^4
50	45.2	0.442	18.5×10^3	2210×10^4
99	1.43	14.0	586×10^3	7008×10^4
99	10.1	3.07	128×10^3	6546×10^4
99	45.2	0.952	39.8×10^3	6149×10^4

be seen that the fraction exposed is about 10.5% at the front and 9.5% at the back. The total bare skin, or nominal exposed, area is taken as 20%. The corresponding grouping in Table 16.78 is an exposed fraction of 18–22%.

The population considered is that in the age range 10–69 years (12 groups). Then for 18–22% exposure the average mortality P_{ma} given burn injury is

$$P_{ma} = \frac{(0.1 \times 3) + 0.3 + 0.5}{12} = 0.09$$

Table 16.80 obviously applies to a wide range of burn depths. Since it is desirable to be able to reflect the severity of burns: a particular burn depth δ_a is selected as that corresponding to the average mortality P_{ma} of 0.09 just quoted.

It is reasonable to assume that most burns treated are the less severe end of the range of burn depths. For the case just considered the burn depth corresponding to the average mortality $P_{ma} = 0.09$ is taken as $\delta_a = 0.25$ mm, which from Equation 16.22.15 corresponds to a thermal load $L'_a = 1200$ (W/m^2)$^{4/3}$ s/10^{-4}. This thermal load corresponds to the value for second degree burns given in Table 16.80. The thermal load at which the burn depth and the mortality are zero is given by Equation 16.22.15 as 920 s (W/m^2)$^{4/3}$/10^4. Then, by linear interpolation between these two points of burn depth vs thermal load, full depth burn with $\delta = 2.0$ occurs at a thermal load L'_a of 3200 s (W/m^2)$^{4/3}$/10^4. Similarly, linear extrapolation gives at this thermal load a mortality P_m of 0.64. By further linear extrapolation, $P_m = 1.0$ occurs at a thermal load L' of 4500 s (W/m^2)$^{4/3}$/10^4 and an extrapolated, or notional, 'burn depth' δ of 3.17.

Table 16.80 *Some limits and dose–response relations for heat radiation (after Hymes, 1983 SRD R275) (Courtesy of the UKAEA Safety and Reliability Directorate)*

Thermal load (s(W/m^2)$^{4/3}$/10^4)	*Effect*
210–700[a]	Threshold of blistering
1200[b]	Second degree burn
2600[c]	Third degree burn
1060[d]	1% mortality
2300[d]	50% mortality
1100–4000	Piloted ignition of clothing
3000–10,000	Unpiloted ignition clothing

[a] There is evidence for a region of constant injury between these limits.
[b] Second degree burns with a burn depth of 0.1 mm. This value is approximately the same as that for 50% mortality. Burn depth increase linearly up to a thermal load value of 2600.
[c] Third degree burns with a burn depth of 2 mm. This value is approximately the same as that for 50% mortality.
[d] Values based on the profit equation of Eisenberg, Lynch and Breeding (1975).

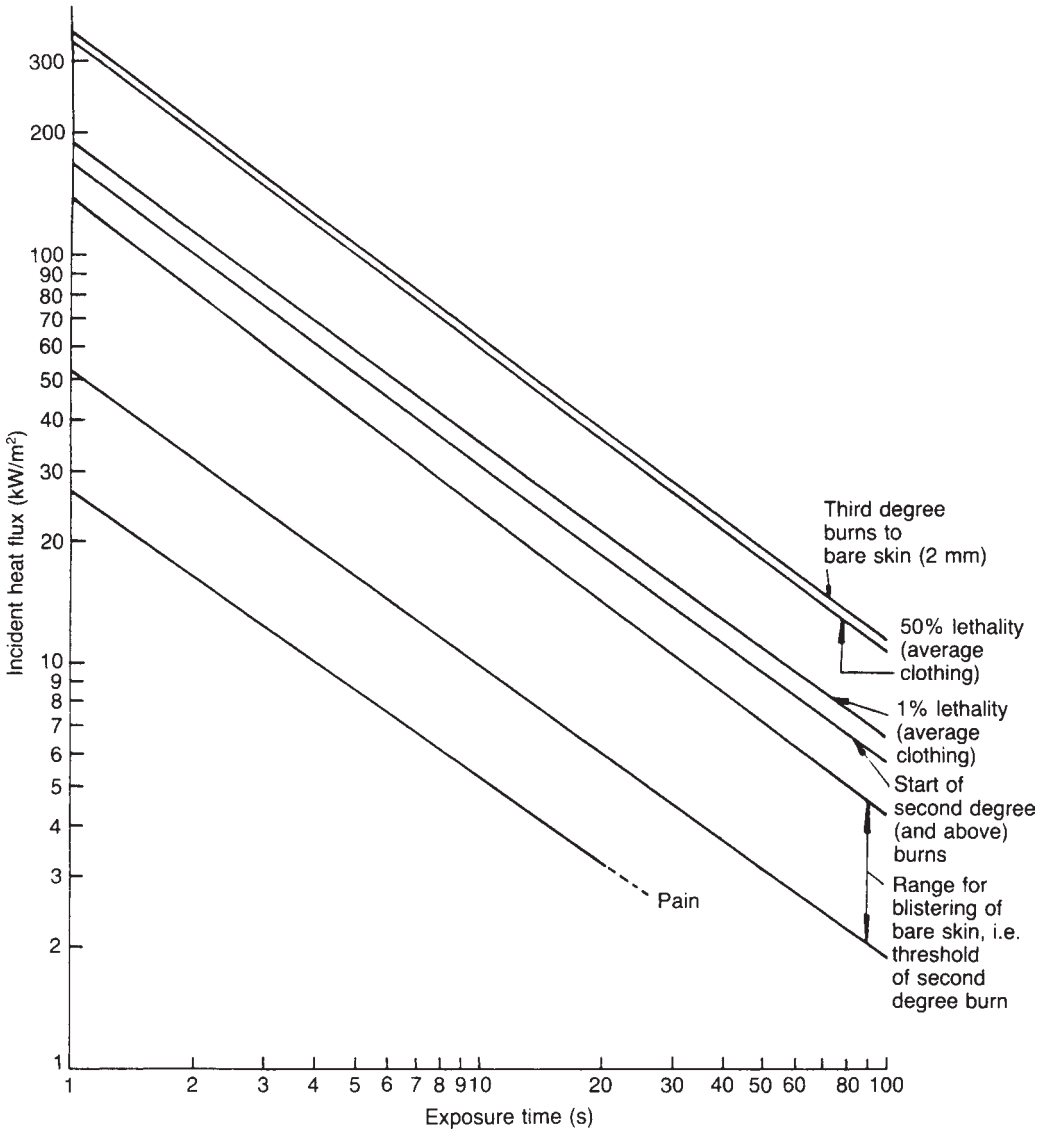


Figure 16.122 *Time to various levels of burn discomfort and injury due to heat radiation (Hymes, 1983.SRD R275) (Courtesy of the UKAEA Safety and Reliability Directorate)*

The relations between thermal load, burn depth and mortality in this model are then:

Thermal load, L' (s $(W/m^2)^{4/3}/10^4$)	*Burn depth,* δ (mm)	*Mortality,* P_m
920	0	0
1200	0.25 $(=\delta_a)$	0.09 $(=P_a)$
3200	2.0	0.64
4500	3.17 (notional)	1.0

The variation of the mortality P_m with burn δ depth may expressed in terms of the average burn depth δ_a using the relations

$$\delta_1 = \frac{\delta - \delta_l}{\delta_a - \delta_l} \quad \delta < \delta_a \qquad [16.22.16]$$

$$\delta_2 = \frac{\delta - \delta_a}{\delta_u - \delta_a} \quad \delta > \delta_a \qquad [16.22.17]$$

where δ is the burn depth (mm) and subscripts a, l, u, 1 and 2 denote average, lower, upper, first coefficient and second coefficient, respectively. The mortality P_m is then

obtained as

$$P_m = \delta_1 P_{ma} \qquad \delta < \delta_a \qquad [16.22.18]$$

$$P_m = P_{ma} + \delta_2(1 - P_{ma}) \qquad \delta > \delta_a \qquad [16.22.19]$$

The thermal radiation intensity used is the value incident on the person after atmospheric attenuation.

The exposure of the person to this radiation depends his behaviour. One model of response is that he faces event for the response time of 5 s and then turns his back and runs away. However, as described in Subsection 16.22.9, there is evidence, on the one hand, of shorter response times but, on the other, of a tendency to turn round to look at the event. From the data given above the fraction of the body exposed when facing the event is greater than that exposed when the back is turned to it, but the difference is not great. The base case adopted is, therefore, that, at least until any clothing ignition, the front and back are equally exposed.

At this stage there are a number of corrections which might be applied. One is for the three-dimensional effect discussed in Subsection 16.22.12. Another is for the angle of incidence of the radiant heat on the body surface. In the base case a single factor ϕ of 0.5 is used, which takes account of the fact that only about half the bare skin is exposed to the thermal radiation at a given time. This factor is applied to the time t in the thermal load expression, which thus becomes $\phi t I^{4/3}$ so that a given thermal load applied to half the exposed surface over a given time interval t is treated as equivalent to half that load applied to the whole exposed surface over the same time interval.

For clothing ignition correlations have been developed using different 'thermal loads'. One of those used by Hymes is the regular thermal load $tI^{4/3}$ and it is this which is utilized. With respect to the load at which clothing ignition occurs, the value adopted corresponds to the middle value of the range of 'load' given in the *Green Book*. Thus from Equation 16.22.8

$$tI^2 = 3.5 \times 10^4 \, \mathrm{s(kW/m^2)^2}$$

which for a 5 s pulse gives an intensity $I = 84$ kW/m^2 and a thermal load

$$L' = tI^{4/3} \approx 1800 \, \mathrm{s(W/m^2)^{4/3}}/10^4$$

Clothing ignition is taken in the model as resulting in the doubling of the effective exposed area. Following such ignition, therefore, this area is taken as the nominal exposed area. Thus from this point the factor ϕ has a value of unity.

Table 16.81 shows for this model the burn depth and the mortality as a function of the thermal load. The profit equation for fatal injury obtained from these data is

$$Y = -10.7 + 1.99 \ln L' \qquad [16.22.20]$$

where L' is the thermal load ($[\mathrm{s\,(W/m^2)^{4/3}}]/10^4$).

This profit equation is based on the mortality values given in Table 16.81, except the last value of 1.0. A described above, in the model a thermal load of 4500 is taken as corresponding to a mortality of unity. Therefore the probit equation is used only up to a mortality of 70%, and the following relations are used thereafter:

$$P_m = 0.70 + 0.0003(L' - 3500) \qquad L' < 4500 \qquad [16.22.21a]$$

$$P_m = 1.0 \qquad L' > 4500 \qquad [16.22.21b]$$

Table 16.81 *Lees model for burn injury from a sudden fire event such as a fireball (Lees, 1994a): mortality as a function of thermal load (Courtesy of the Institution of Chemical Engineers)*

Thermal load, L' ($[\mathrm{s\ (W/m^2)^{4/3}}]/10^4$])	*Burn depth, δ* (mm)	*Mortality*, P_m (%)	*Mortality (Eisenberg)* (%)
1000	0.07	0.025	0.015
1200	0.25	0.09	0.04
1400	0.42	0.14	0.09
1600	0.60	0.20	0.16
1800	0.78	0.26	0.24
2000	0.96	0.31	0.33
2500	1.4	0.45	0.55
3000	1.84	0.59	0.73
3200	2.00	0.64	0.78
4500	3.17 (notional)	1.0	0.95

Also shown in Table 16.81 for comparison are the mortalities predicted by Equation 16.22.9 of Eisenberg, Lynch and Breeding. Apart from those at very high thermal loads, the values are not greatly different. The difference between the method of these authors and that of Lees lies in the treatment of the effective exposed area.

In Section 16.15 an account has been given of the 16 fireball model by V.G. Marshall (1987). Table 16.82 illustrates the application of Lees' model to the case of the 20 te fireball considered by this author. For this fireball the spherical radius is 75 m, the hemispherical radius 95 m, the duration 10.3 s and the crude thermal radiation intensity $2.17 \times 10^9/x^2$ W/m^2, where x is the distance from the centre of the fireball to the target (m). In the calculation underlying the data in Table 16.82, use was made of the atmospheric attenuation factors given by Marshall and the fireball duration time was rounded to 10 s. Also shown in the table are the predictions of mortality from the Eisenberg probit applied to the unadjusted thermal loads for the full duration time of 10 s. In his discussion of the rotational factor, Marshall suggests that whereas the Eisenberg probit gives for a such a fireball a distance of 170 m to 50% mortality, experience of incidents indicates this is much too far, and he tentatively suggests that the distance of about 90 m given by assuming rotation through 360° is closer to reality. From the table, Lees' model gives a distance of 125 m.

Lees states that his model, whilst not intended to be conservative and whilst less so than the Eisenberg relation, may nevertheless still be so.

16.22.19 Prugh model

A model for burn injury from exposure to a fireball has been given by Prugh (1994). He presents a summary of data on burn injury, which for fatality draws on the work of Eisenberg, Lynch and Breeding (1975), Lees (1980b), A.F. Roberts (1982) and the Society of Fire Protection Engineers (1988 NFPA/22). From these data he derives the

Table 16.82 *Lees model for burn injury from a sudden fire event such as a fireball (Lees; 1994a): illustrative example of mortality from a 20 te LPG fireball (Courtesy of the Institution of Chemical Engineers)*

A Physical conditions

Distance (m)	*Thermal radiation intensity* (kW/m^2)		*Thermal load factor, L′/t* $((W/m^2)^{4/3}/10^4)$	*Time to ignition, t* (s)	*Thermal load* (s $(W/m^2)^{4/3}/10^4$)		
	Crude, I	*Attenuated,* I_e			*Before ignition*	*After ignition*	*Total, L′*
75[a]	390						
95[b]	240	173	964	3.73	1800	6044	7844
105	197	142	738	4.89	1800	3771	5571
115	164	118	577	6.24	1800	2169	3969
125	139	97	444	8.11	1800	839	2639
135	119	83	361	9.97	1800	54	1854
145	103	72	298	N	(1490)	N/A	1490

B Thermal injury

Distance (m)	*Clothing ignition*	*Mortality* P_m (%)	*Mortality* (Eisenberg) (%)
75[a]	Y	1.0	1.0
95[b]	Y	1.0	1.0
105	Y	1.0	1.0
115	Y	0.84	0.99
125	Y	0.49	0.95
135	Y	0.23	0.86
145	N	0.12	0.72

[a] Radius of spherical fireball.
[b] Radius of hemispherical fireball.

following correlation for the probability P of fatality:

$$P = \{1 + [1 - \exp\{-5.3[\ln(E/53)]^2\}]^{0.5}\} \times [1 - 2(E/53)] \quad [16.22.22]$$

where E is the thermal dose (J/m^2). He presents a graphical comparison of this equation with the two *Green Book* relationships for unprotected and protected exposure, which shows that the mortalities predicted by his correlation are appreciably lower.

With regard to the extent of the burns and to medical treatment, Prugh gives a graph of mortality vs fraction of the body with third degree burns, based on the data of J.W. Davies (1982), but states that such treatment is presumably already taken into account in the basic mortality data which he uses.

Combining the fireball model and the injury relationships, Prugh derives for a propane fireball a graphical correlation for mortality, which is a function of the mass of fuel and the distance of the person exposed. He also gives equations, which are considered in Section 16.39.

16.22.20 Thermal radiation limit

There are a number of empirical limits of thermal radiation which have traditionally been used in plant design. Other limits are quoted in work on hazard assessment. Some of these limits are quoted in Table 16.83.

16.23 Fire Protection of Process Plant

In general, fire prevention and protection measures constitute either (1) passive prevention and protection or (2) active protection.

Reference has already been made to some principal publications on fire in relation to process plants, but it is appropriate to refer here to *Practical Fire Protection* (Underwood, 1971–) and *Underwood's Practical Fire Protection* (Hirst; 1989), *Fire Protection Manual for Hydrocarbon Processing Plants* (Vervalin, 1964a, 1973a), *Storage and Handling of Petroleum Liquids: Practice and Law* (J.R. Hughes, 1970), to the NFPA codes and to BS 5908: 1990 *Code of Practice for Fire Precautions in the Chemical and Allied Industries*.

16.23.1 Passive fire protection

Passive prevention and protection comprises measures which are taken in order to prevent a fire occurring and to limit its spread. Measures of active protection comprise fixed and mobile fire fighting systems and emergency arrangements.

As a broad generalization, passive fire protection has the great advantage that it is very much less dependent on the intervention of protective devices or of humans, both of which are liable to fail, and is therefore that much less vulnerable to management failings.

One of the principal passive fire protection measures is fireproofing. In general this has the advantages just mentioned. But it also brings with it the risk that corrosion may occur under the fireproof coating and may be difficult to detect. Another problem with fireproofing is the fact that it may not withstand the action of the powerful water jets used in fire fighting.

Insofar as management has some control over both these features – the avoidance of corrosion and of loss of coating by water jets – they illustrate the fact that even the use of

Table 16.83 *Some limits for thermal radiation*

A Design guidance: IP *LPG Storage Code* 1987

See Table 22.8

B Design guidance: API RP 510: 1990

Thermal radiation intensity (kW/m^2)	*Limit*
15.6	Intensity on structures where operators are unlikely to be performing and where shelter is available
9.5	Intensity at design flare release at locations to which people have access and where exposure would be limited to a few seconds for escape
6.3	Intensity in areas where emergency actions lasting up to 1 min may be required without shielding but with protective clothing
4.7	Intensity in areas where emergency actions lasting up to several minutes may be required without shielding but with protective clothing
1.6	Intensity at design flare release at locations where people are continuously exposed

C Design guidance: Kletz (1980h)

Thermal radiation intensity (kW/m^2)	*Limit*
38	Intensity on storage tanks
12.5	Intensity on wood or plastics[a]
5	Intensity on people performing emergency operations

D Design and assessment guidance – BS 5980: 1990[b]

Thermal radiation intensity (kW/m^2)	*Limit*
37.5	Intensity at which damage is caused to process equipment
25	Intensity at which non-piloted ignition of wood occurs
12.5	Intensity at which piloted ignition of wood occurs
4.5	Intensity sufficient to cause pain to personnel unable to reach cover in 20 s, though blistering of skin (first degree burns) unlikely
1.6	Intensity insufficient to cause discomfort for long exposures

E Design and assessment guidance: Mecklenburgh (1985)

Thermal radiation intensity (kW/m^2)	*Limit*
14	Intensity which normal buildings should be designed to withstand
10–12	Intensity at which vegetation ignites
6	Intensity tolerable to escaping personnel
3	Intensity tolerable in infrequent emergency situations of up to 30 min duration
1.5	Intensity safe for stationery personnel and members of the public

F Assessment guidance: Dinenno (1982)

Thermal radiation intensity (kW/m^2)	*Limit*
30	Spontaneous ignition of wood
15	Piloted ignition of wood
20	Ignition of No. 2 fuel oil in 40 s[c]
10	Ignition of No. 2 fuel oil in 120 s[c]
18–20	Cable insulation degrades[d]
12	Plastic melts[e]
37.5	Equipment damage[f]
9	Equipment damage[f]

[a] Kletz comments that the implication of this limits that large storage tanks need to be located at least 200 m from public roads.
[b] BS 5908: 1990 also gives a thermal dose of 600–1800 kJ/m^2 from a fireball as a criterion for the starting of secondary fires.
[c] EPRI (1981a).
[d] EPRI (1979b).
[e] Gelderblom (1980).
[f] Di Nenno comments that there is significant variation in the thresholds for equipment damage. He gives the source of the value of 37.5 kW/m^2 as Gelderblom (1980), and treats the value of 9.5 kW/m^2 given by Tan (1967a), in relation to flare system design, as conservative.

passive fire protection measures does not avoid the need for good management.

The optimum solution to the fire protection problem is normally a combination of passive and active measures. Often passive fire protection can limit fire spread and can 'buy time' in which the firefighting resources can be mobilized.

16.23.2 Active fire protection

Active fire protection measures are also provided in the basic plant design, but are effective only when activated in response to a fire. Elements of active fire protection are:

(1) fire warning systems;
(2) fire detection systems;
(3) firefighting agents;
(4) fire water supply system;
(5) fixed firefighting systems;
(6) mobile firefighting systems.

Item (1) of these measures is described in Chapter 24 and item (4) in Chapter 10, while the other items are dealt with below.

16.23.3 Fire detection and alarm

The initiation of active fire protection measures, whether fixed systems or mobile firefighting systems, depends on the fire detection and alarm arrangements.

Accounts of fire detection and alarm are given by Fry and Eveleigh (1975 BRE CP 32/75) and P. Nash and Young (1975 BRE CP 29/75). Treatments of water sprinkler and water spray systems also frequently deal with detection systems.

Relevant codes and standards are the NFPA 72 series, particularly NFPA 72E: 1990 *Automatic Fire Detectors*, BS 5445: 1977 – *Components of Automatic Fire Detection Systems*, BS 5839: 1988 – *Fire Detection and Alarm Systems for Buildings* and, until recently, BS 6020: 1981 – *Instruments for the Detection of Combustible Gases*, now superseded by the series BS EN 50054–50058 which has the general title *Electrical Apparatus for the Detection and Measurement of Combustible Gases*.

When a fire occurs, two things which are of prime importance are to ensure the safety of personnel and the prompt initiation of action to deal with the fire. The most effective way of ensuring rapid action is generally the use of an automatic system. But in situations where personnel may be present the arrangements need to ensure that they are not put at risk by the action of the automatic system.

There are several different types of system for the detection of leakage and/or fire. They may be classified according to whether they detect (1) leakage, (2) flame, (3) heat or (4) smoke. These systems and the devices used are listed in Table 16.84.

In general, it is preferable to detect a leakage in its initial stages and before it ignites. On the other hand, some types of fire, such as lagging fires, are not preceded by readily detectable leakage.

The alternative is to detect the fire itself. This is done most rapidly by flame detection. Detection of the heat and smoke from the fire is possible only after it has developed to some extent.

Some important characteristics of detection systems are:

(1) area covered;
(2) response time;
(3) reliability
    (a) fail-to-danger faults,
    (b) fail-safe faults (spurious alarms);
(4) cost.

The area covered by a detection device is important, because a small coverage leads to a complex and expensive system. The reliability is also important both in respect of fail-to-danger faults and of fail-safe faults which cause spurious alarms.

Detection of abnormal conditions, including leakage and fire, is a basic function of the process operator. He is capable of detecting such conditions by all the modes described and gives wide coverage with high reliability and low cost. His great disadvantage is that he may not respond rapidly enough, not only in making the initial detection but also in initiating firefighting action.

Instrument detection systems are therefore widely used. In many cases they are part of a fully automatic system which triggers protective devices such as steam curtains, or releases firefighting agents. In other cases, however, the function of the detection system is limited to providing an alarm signal to the operator, which he then has to interpret. There are several reasons for not always making the system fully automatic. One is that detection systems are liable to give spurious alarms; another is that it is not always easy to define in advance precisely what is required. It is often difficult, for example, in an automatic water spray system to avoid wasting water in cooling plant where this is not really necessary. This is important, because the quantities of water required for water sprays are large.

Table 16.84 *Some detection systems for fire protection*

Basis of detection	*Detector*
All modes	Humans
Leakage	Flammable gas detector
Flame	Infrared detector
	Ultraviolet detector
Heat	Temperature measuring instrument
	Quartz bulb detector
	Gun cotton bridge and wire
	Fusible link and wire
	Temperature sensitive resistor
	Air line
Smoke	Smoke detector

The most widely used type of system is the combustible gas detection method. Descriptions are given by several authors (e.g. Bossart, 1974; Dailey; 1976; Johnson, 1976). There are two main types of combustible gas detection. One consists of a number of devices which sample the atmosphere at different points and pass the sample back to a common analyser. Typical sample pipe velocities are 3 m/s and sampling rates 10–30 s per point.

There are a variety of instruments available for combustible gas analysis, based on the measurement of the heat produced by a catalytic reaction, radiant energy, absorption, ionization phenomena, electrochemical effects, colorimetric effects and gas chromatography. Details are given by Dailey.

A single instrument system is, in general, most appropriate where the analyser itself is very complex and expensive and where some time delay is acceptable. These characteristics appear to make it more suitable for detecting toxic gases which pose a long-term hazard, but less so for detecting flammable gases, where the analytical instruments are comparatively simple but fast response is important. Common analyser systems have in fact been subject to severe criticism by some users (e.g. Kletz, 1976i) as being excessively slow in response and liable to faults such as blockage.

The other system, which is preferred by such users, utilizes an individual catalytic diffusion type detector at each detection point. Generally, a combustible gas detector is installed and calibrated for one particular hydrocarbon gas, but will respond to others. The instrument scale is usually calibrated as 0–100%of the lower explosive limit (LEL). The output of a detector calibrated on propane will read some 20% high on methane and some 20% low on propylene.

Catalytic detectors are susceptible to poisoning. In particular, silicone grease and silicone rubber sealants have been found harmful. Combustible gas detector

instruments should be regularly serviced. Portable detectors should be checked before use.

There tends to be some trade-off between the speed of response and the number of spurious signals obtained. It is suggested by Johanson that the specification for response time is generally too tight and that an allowance of a few seconds delay reduces the number of false alarms.

There are various approaches to laying out the detection points. Generally, it is desirable to have detectors around the periphery. Other detectors are then sited according to principles such as uniform coverage, location at leak sources, location between leak and ignition sources.

The optimum height of the sample point depends on the density of the gas. Johanson suggests installation at $1\frac{1}{2}$ and 6–8 ft heavy and light gases, respectively. It is also necessary to take into account depressions, roofed areas and other pockets.

A combustible gas leakage detection system may be used to provide alarm signals in the control room or to initiate protective action by water sprays or by a steam curtain.

Detection of a flame is done by infrared or ultraviolet detecting instruments. The response time of the former is generally about 10 s, while with the latter it is almost zero. The reliability of these relatively complex instruments is a problem, particularly, although not exclusively, because they tend to give frequent false alarms, but there has been considerable improvement in this aspect. The instruments are also comparatively expensive. Again a flame detection system may be used to give alarm signals or to trigger water sprays.

There are a number of devices which detect heat. They include temperature measuring instruments, quartz bulbs, and devices which explode, melt or change characteristics when exposed to fire. The latter include guncotton bridges and wire, fusible links and wire, air lines which melt through and resistors which change resistance. Measuring instruments can be used to furnish alarm signals or to set off water sprays, but the other devices are generally used for the latter purpose. Thus a simple detection system might be based on an air line which can be melted through by a fire so that the air pressure in the line falls, allowing the drench valve on apply the water spray system to open.

A quartz bulb detector figured prominently in the Flixborough inquiry (R.J. Parker, 1975, pp. 20–26, especially paragraphs 137, 156, 157 and 160, and figure 8). According to the 8 in. pipe hypothesis, a fire occurred at a non-return valve in a lagging box. There was believed to be a quartz bulb some 12 in. above the top of the valve and some 18 in. to the east which was set to actuate a water spray system at a temperature of 68°C or above. It was a matter of dispute whether there could have been a fire at the lagging box without activation of this detector. Proponents of the 8 in. pipe hypothesis argued that either there was no quartz bulb or that it did not operate. Calculations were done which were said to show that heat radiation from the assumed flame would not be enough to trigger the detector and that heat radiation from the pipework would be necessary to do this. The assessors considered, however, that if the hypothesis were correct the sensor would have been triggered by other flames and radiating surfaces present. In any event, the water spray system apparently did not operate. These points are of some importance, because they bear on the effectiveness of detector systems. Further discussion of the matter is given by J.I. Cox (1976b).

Another method of detecting fire is by smoke detectors. These are widely used in buildings, but appear likely to be less effective for fires on open plant.

16.23.4 Emergency material transfer

It is necessary to have arrangements so that in the event of fire it is possible to transfer flammable material away from the parts of the plant affected. Provision of a relief header leading to a vent stack or flare stack allows vapour to be vented safely from pressure vessels. The removal of liquid from a pressure vessel may be catered for by facilities for blowdown to a suitable receiver. Similarly, pumps may be installed on atmospheric storage tanks to allow liquid to be transferred out.

16.23.5 Dow Fire and Explosion Index

The Dow Fire and Explosion Index given in the Dow *Guide* has been described in Chapter 8, where the method of calculating the index was outlined. The purpose of the index is to assist in the selection of preventive and protective features.

The following set of preventive and protective features are listed in the Fourth Edition of the *Guide* (Dow Chemical Company, 1976): (1) basic preventive and protective features and (2) recommended minimum preventive and protective features. The latter features are not given as such in the later editions, but the Fifth Edition introduces loss control credits, which cover similar ground, and also an engineer's checklist. Table 16.85 lists the basic preventive and protective features given in the Seventh Edition (Dow Chemical Company, 1994) and Table 16.86 lists the headings of the recommended minimum preventive and protective features in the Fourth Edition.

The features shown in Table 16.85 should always be provided, irrespective of the degree of hazard. If they are not, the hazard will be greater than that calculated by the index. Many of them apply in any plant, regardless of whether it contains flammable materials.

It should be noted that the codes and electrical area classification mentioned in Table 16.85 are those applicable in the United States.

Table 16.86 lists headings of the features which should always be considered where a fire or explosion hazard exists. The detailed measures under these headings are described in the *Guide*. The features are intended to reduce the magnitude and/or the probability of the loss. The need for a particular feature depends on the nature of the hazard.

The Dow Fire and Explosion Index is widely used as an aid to the selection of fire preventive and protective features, and is therefore a relatively well-proven method. Nevertheless, it is a generalized method and, if used, it should be supplemented by specific hazard identification and assessment studies which may reveal the need for other preventive and protective features.

16.24 Passive Fire Protection

The previous section has given an account of the general nature and purpose of passive fire protection. In this section specific passive fire protection measures are considered.

Table 16.85 *Dow Guide: Basic Preventive and Protective Features(Seventh Edition) (Dow Chemical Company, 1994; reproduced with permission)*

A	Adequate water supply for fire protection, This is determined by multiplying the water demand by the length of time for which the worst possible fire can be expected to last. The supply deemed adequate will vary with different authorities and may range from enough for a 2-h fire to enough for one lasting 8 h
B	Structural design of vessels, piping, structural steel, etc.
C	Overpressure relief devices
D	Corrosion resistance and/or allowances
E	Segregation of reactive materials in process lines and equipment
F	Electrical equipment grounding
G	Safe location of auxiliary electrical gear (transformers, breakers, etc.)
H	Normal protection against utility loss (alternate electrical feeder, spare instrument air compressor, etc.)
I	Compliance with various applicable codes (ASME, ASTM, ANSI, Building Codes, Fire Codes, etc.)
J	Fail-safe instrumentation
K	Access to area for emergency vehicles and exits for personal evacuation
L	Drainage to handle probable spills safely, plus firefighting water from hose nozzles and sprinkler heads and/or chemicals
M	Insulation of hot surfaces that heat to within 80% of the autoignition temperature of any flammable in the area
N	Adherence to the National Electrical Code, The Code should be followed except where variances have been requested/approved
O	Limitation of glass devices and expansion joints in flammable and hazardous service, Such devices are not permitted unless absolutely essential. Where used, they must be registered and approved by the production manager and installed in accordance with Dow standards and specifications
P	Building and equipment layout. Separation of high-hazard area must be recognized especially as it relates to both property and interruption of business. Separation of tanks must be at least in accordance with NFPA 30
Q	Protection of pipe racks and instrument cable trays as well as their supports from exposure to fire
R	Provision of accessible battery limit block valves
S	Cooling tower loss prevention and protection
T	Protection of fired equipment against accidental explosion and resultant fire
U	Electrical classification. Division 2 electrical equipment will be required for outside flammable liquid handling where congestion is minimal and natural ventilation, is unobstructed, Division 1 equipment is required only for special chemicals and/ or special building or process handling conditions or where ventilation is inadequate
V	Process control rooms shall be isolated by 1 fire walls from process control laboratories and/or electrical switchgear and transformers
W	A process review shall determine a need for reactive
X	A hazard and operability (hazop) review is recommended in high hazard areas

Table 16.86 *Dow Guide: Minimum Preventive and Protective Features (Fourth Edition) (Dow Chemical Company, 1976) – these features are listed in the Guide which gives a detailed description of them*

1	Fireproofing
2	Water spray protection of equipment and area
3	Foan or filming agents
4	Monitor guns
5	Dump, blowdown or spill contrl
6	Combustible gas monitors
7	Diking for storage tanks
8	Buried tanks
9	Foam on tanks
10	Remote manual Control
11	Special instrumentation
12	Fire Walls and barrier walls/cubicles
13	Building ventilation
14	Dust explosion control
15	Open explosin structure
16	Emergency relief venting for buildings

Measures of fire prevention and passive fire protection are built into the basic plant layout and design. They include such aspects as:

(1) elimination of fires
  (a) leaks and spillages,
  (b) sources of ignition;
(2) emergency material transfer
  (a) pressure relief and flaring,
  (b) blowdown,
  (c) dumping;
(3) fire spread limitation;
(4) fire protective insulation
  (a) fire resistant thermal insulation,
  (b) fire insulation;
(5) storage tank layout.

Of these measures, items (1) and (2) have been dealt with already in this chapter and item (5) is considered in Chapters 10 and 22. The Other items are described below.

16.24.1 Fire spread limitation

There are certain plant configurations which assist fire spread, By avoiding or modifying these configurations, fire spread may be limited.

Two examples given by Klootwijk (1976) are shown in Figure 16.123. In a fire a chimney effect can develop in the space between a table top and a tall equipment or structure as illustrated in Figure 16.123(a). Such an effect tends to increase damage and to extend it to a higher level. Where a potential chimney cannot be avoided, it may be appropriate to install a water spray system to control fire in the area.

A chimney effect can also occur between a table top and the bottom of a large column. In this case the opening should be closed off with a support skirt, as shown in Figure 16.123(b).

Another way in which fire can spread is by the flow of a burning liquid. The plant layout with regard to this aspect should be carefully considered, It is normal practice to put bunds around storage tanks. But there may be other situations which can give rise to liquid flow, Drains, sewers

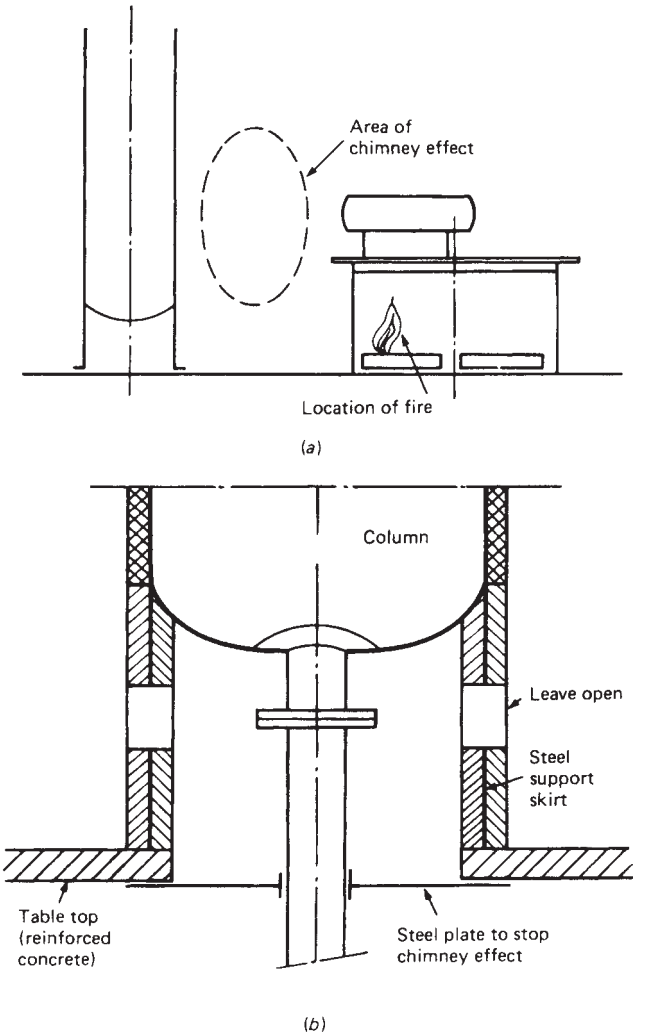


Figure 16.123 *Fire spread and its limitation (Klootwijk, 1976): (a) chimney effect between table top and a tall structure; (b) elimination of the chimney effect between a table top and the bottom of a column by use of a steel support skirt*

and pipe trenches are features which are particularly liable to aggravate this hazard.

16.24.2 Fire resistant thermal insulation

Many items of equipment are fitted with thermal insulation. This is to be distinguished from fire insulation proper. Nevertheless, provided it is of the right type, thermal insulation can provide a degree of fire protection. Much process plant is thermal insulated, as are low temperature storage tanks.

The fire resistant properties of regular thermal insulation are considered in Chapter 12. The fire protection offered by such insulation on storage tanks is discussed in Chapter 22.

16.24.3 Fire insulation

Some form of structural protection against fire, in the form of fire insulation or fireproofing, is normally provided for supporting members, and also for vessels and pipe work. A general account of fireproofing has been given by Waldman (1967).

Factors which need to be taken into account in considering such fireproofing include:

(1) protection criteria
  (a) type of structure,
  (b) height of structure,
  (c) degree of protection;
(2) fireproofing system.

There are differences of practice in the types of structure which are fireproofed. The main emphasis is generally on the protection of supporting members. Fireproofing is sometimes limited to supports of major items such as large columns or vessels, but it is often extended to supports of

other items, such as heat exchangers and pipework. In some cases it is applied to the vessels and pipework themselves.

The main object of fireproofing is to prevent the failure in a fire of items containing flammable material which can feed the fire. Fireproofing may not be needed, therefore, for items with a small inventory, unless failure could lead to large loss of containment from some other source.

The height above grade, or ground level, to which the protection extends is also variable. Most fires do not reach much more than 10 m above grade, although there have been instances of damage at heights of 30 m or more. It is suggested Waldman that fireproofing should extend to 35 ft (10m) above grade.

It is also necessary to decide on the degree of protection required. A common criterion is that the steel member should not reach a temperature greater than 1000°F (538°C) under specified fire conditions.

In deciding on the degree of protection required for fireproofing, allowance may be made for other fire protection features, such as water sprays. It is the whole fire protection system which matters. In general, the aim should be to prevent a fire occurring at all near a vulnerable structure. It is better to provide drainage to take the flammable liquid away.

A fireproofing system normally consists of a bulk insulation material which gives protection against fire. This bulk fire insulation may be clad with aluminium, galvanized or stainless steel sheet. Such fire insulation should be distinguished from conventional insulation which is used to reduce heat transfer between the plant and the atmosphere. Such insulation mayor may not have fire resistant properties. Materials which are widely used as the bulk fire insulation include (1) concrete and (2) magnesium oxychloride cement. Concrete is often used in the form of lightweight aggregate concrete, or vermiculite cement.

Protection against fire may also be obtained by the use of a mastic, which may be asphaltic or vinyl acrylic. Mastics are used to fireproof not only plant but also conventional insulations.

Some materials used as the bulk fire insulation have special fire resistant properties. Magnesium oxychloride, for example, contains water of crystallization, which takes up heat when it is driven off. Similarly, some coating materials have properties which increase their effectiveness in fireproofing. Intumescent mastics swell in fire by a factor of 5–10 and this gives increased insulation.

Some features of a fireproofing system include:

(1) insulation properties;
(2) mechanical strength;
(3) corrosion
    (a) substructure,
    (b) reinforcing;
(4) water penetration;
(5) flexibility;
(6) weight;
(7) ease of installation;
(8) cost.

Fireproofing should provide sufficiently effective insulation to keep the temperature of the structural member to be protected below a specified temperature under defined fire conditions. It has been suggested by Kayser (1974) that the ideal system will hold the substrate below 1000°F (538°C) for 1½ h while its surface is exposed continuously to a temperature of 1800°F (982°C). The maximum substrate temperature of 1000°F is that widely quoted, but the maximum period of protection is generally less. Thus Waldman suggests, for example, that in order to allow for spray failure protection is required for 1 h. This time period is also quoted by other workers, as described below.

The mechanical strength of the fireproofing should be sufficient to offer reasonable resistance to damage both from normal plant activities and from water from fire hoses.

The bulk fire insulation should not be corrosive to the substrate or to the reinforcing material. The substrate should be made clean and rust free before the insulation is put on.

It is essential that water should not be allowed to penetrate the insulation and corrode the substrate or the reinforcing material. Corrosion of the steel structural members is difficult to detect, but could have serious results. The coating or cladding used should therefore offer complete protection, particularly at horizontal surfaces where water may get in.

The insulation should be able to accommodate, without cracking, the expansion and contraction of the structure protected. Other desirable features are light weight, ease of application and low cost.

A fireproofing system which is widely used is concrete with galvanized steel sheet cladding (Klootwijk, 1976). Vermiculite cement and magnesium oxychloride cements are also much utilized.

Some illustrations of fireproofing of structural supports are shown in Figure 16.124.

16.24.4 Tests for fire insulation

There is frequently a requirement to test a proposed fireproofing system. Unfortunately, there is no standard test appropriate to structural elements in a flammable liquid fire, which is the typical situation in process plant. Many experimenters have resorted, therefore, to the ASTM E-119 standard time–temperature test, which was devised for building fires. The test involves maintaining the element in a standard fire in which the temperature rises along the standard curve shown in Figure 16.125, curve 1. The criterion of success is the ability of the element to carry out its original function, in this case fireproofing. The ASTM E-119 test is discussed further in Section 16.36 in relation to its original application to fires in buildings. Most workers have used as the criterion of success the ability of fireproofing to keep the temperature of the steel protected below 1000°F (538°C) for a period of 1 h.

It has long been recognized that the ASTM curve tends to underestimate the temperatures which occur in fires of hydrocarbons. An early proposal for a higher temperature relation was made by Waldman (1967), who gave two alternative curves.

The unsatisfactory nature of the ASTM E-119 test in this application has been demonstrated by Castle (1974). He emphasizes that in order to assure similarity of test conditions it is necessary to use not only the same temperature but also the same heat fluxes. He presents experimental results which illustrate this point. He also discusses the alternative pool and pit fire tests and states that a pit fire test is generally a more severe one than the ASTM E-119 test.

Since then several other time–temperature curves have gained currency. Two of these are shown in Figure 16.125. Curve 2 is that of the Norwegian Petroleum Directorate (NPD). Curve 3 is generally known as the 'Mobil curve'.

The use of a standard time–temperature curve for hydrocarbon fires leads to an H rating, as opposed to the A rating obtained by using a curve suitable for building fires.

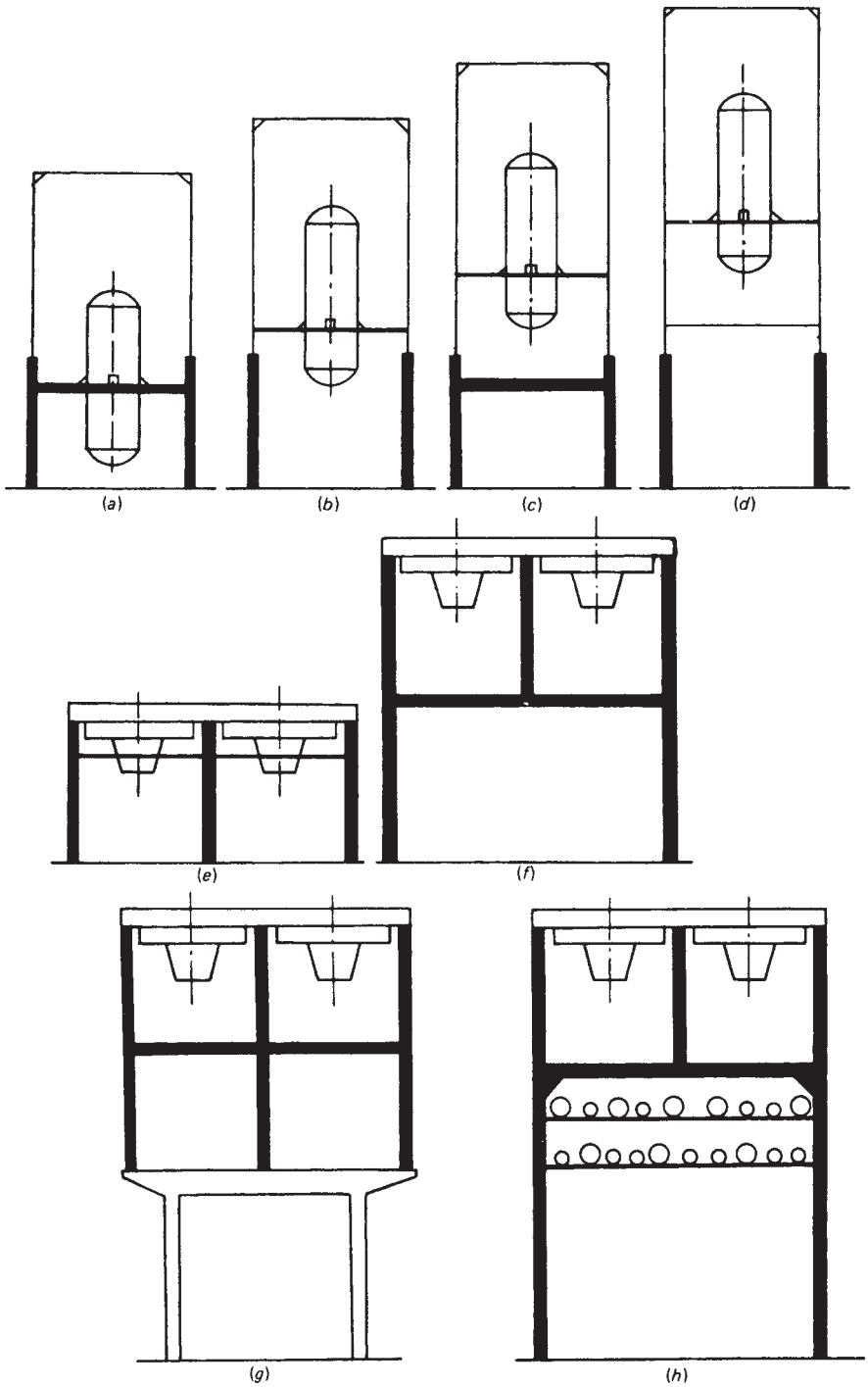


Figure 16.124 *Fireproofing of structural supports (Klootwijk, 1976): (a–d) supporting structure of small storage vessel; (e–g) supporting structure of fin-fan cooler and (h) supporting structure of fin-fan cooler and overhead pipe track*

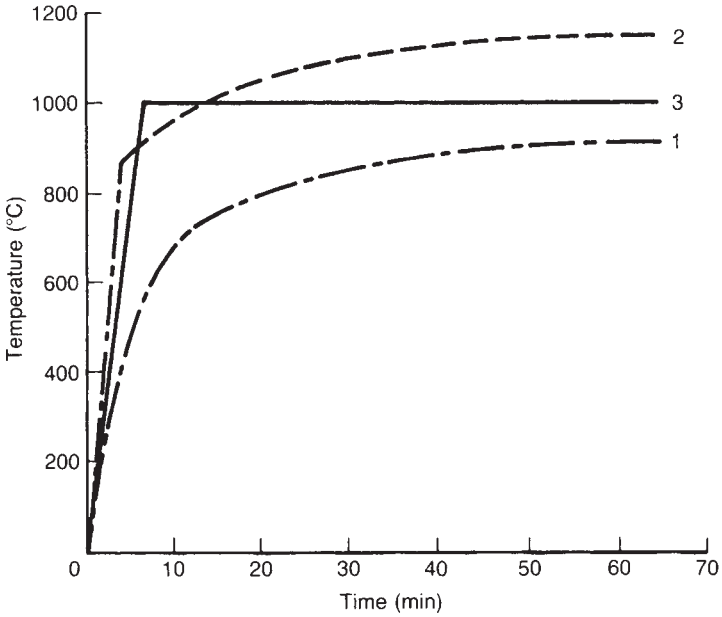


Figure 16.125 *Some time–temperature curves for fires in process plant. Curve 1, ASTM E 119–1988; Curve 2, Norwegian Petroleum Directorate; Curve 3, 'Mobil' curve (after Cullen, 1990)*

Another test which is utilized is the ASTM-84 surface burning test, in which a standard fire is used to evaluate the rate of flame spread across the surface of the element. The later is rated on a scale on which the points 0 and 100 correspond to asbestos cement and redwood, respectively. An index above 25 is generally regarded as unsatisfactory for fireproofing. The use of this test is described by Feldman (1974).

Much equipment and pipework is provided with insulation which serves primarily to conserve heat or cold in the process. Such insulation is different from that used for fireproofing. But it is important to know what degree of protection against fire it offers.

Experiments on insulations commonly used for pipework have been described by McMillan (1974). The test exposed five insulated pipes of 3 in. diameter to a flame area of approximately 30 ft^2 at temperatures corresponding to the ASTM E-119 time–temperature curve. The minimum fire resistance considered acceptable was taken as maintenance of the pipe temperature below 1000°F (538°C) for 1 h.

Systems which met this criterion almost exactly included: a 1 in. calcium silicate insulation with a 10 mil (1 mil = 0.001 in.) stainless steel jacket; a 2 in. ceramic foam insulation with vinyl acrylic mastic or asphaltic mastic coating or 10 mil cladding of aluminium or stainless steel; and a 3 in. rigid polyurethane foam insulation with 10 mil vinyl coated steel cladding.

The behaviour of polyurethane foam insulation in fire has been a subject of some controversy. There are a number of different types of polyurethane foam. In a fire, some foams melt, some char, some both melt and char, and some char and rupture, leaving gaps. According to McMillan, however, a suitable polyurethane foam can give good fire resistance. Detailed experimental work on the behaviour of polyurethane foams in fires is described by Boult, Gamadia and Napier (1972) and by Boult and Napier (1972).

Fireproofing is discussed in the ICI *LFG Code* (ICI/RoSPA 1970 IS/74). For pressurized storage vessels the code suggests that one suitable form of fireproofing is vermiculite cement. For the 2 h protection which is commonly provided, the minimum thickness of vermiculite cement required is 2 in. For refrigerated storage vessels the convenstional insulations are cork, polyurethane and perlite powder. The Code discusses the degree of fire resistance offered by these materials and suggests that an additional fireproof finish may be required to give 2 h fire resistance.

16.24.5 Reactive fire resistant coatings

A quite different method of fireproofing is the use some form of a reactive coating. Accounts of reactive coatings include those by Feldman (1974), O'Rourke (1974), Kawaller (1980), R. James (1988), Gillon (1989) and Droste (1992).

Reactive coating are of three main types: (1) magnesium oxychloride, (2) intumescent coatings and (3) subliming coatings.

Magnesium oxychloride exposed to fire undergoes loss of its combined water so that a porous matrix is formed. It gives a light, hard covering that is resistant to impact, abrasion and weather and provides good fire resistance. A proper formulation should be used; home-made ones can be unsatisfactory. It does, however, have some drawbacks. One is that it requires metal lath reinforcement, another that it is somewhat corrosive so that the equipment needs to be protected, and a third that it tends to lack adhesion and requires a good 'key'.

Intumescent coatings were first used as paint to retard surface spread of flame. They were so successful that a fire

resistant coating was developed. In a fire an intumescent coating releases cooling gases and leaves a residue of thick insulating foam. Tests show that a $\frac{1}{4}$ in. layer can give a 1-h protection. Langer periods of protection can be obtained using thicker layers with reinforcement.

With a subliming compound the principle of operation is that the coating sublimes so that as long as material remains on the surface the temperature of sublimation is not exceeded. The technique was initially developed for aerospace work. Thus subliming coating ThermoLag 330 has been used to protect the structure holding the Saturn rocket at blastoff when temperatures reach 3000°F (1649°C). The coating material itself is expensive, but is relatively cheap to apply.

The use of subliming coating is described by Feldman (1974). He quotes tests conducted on steel beams in an alcohol pit fire with exposure of 1800°F (982°C) for 2 h. An unprotected beam reached a temperature of 1000°F (538°C) in 10 min, whereas a beam protected by subliming coating rose to a maximum temperature of only 500°F (260°C) over the whole period.

Droste (1992) describes two full-scale tests on a 3.6 m^3 LPG vessel protected in one test by the subliming coating ThermoLag 440 and in the other by the intumescent coating Chartek III. The tests demonstrated satisfactory performance of both cotings for full fire engulfment over 90 min.

Reactive coatings are lightweight and durable. The applications where they are most likely to be economic are those where alternative softer materials are less suitable. Some practicalities of the use of reactive materials are discussed by Kawaller (1980).

16.24.6 Fire protection of steelwork

Turning to the passive fire protection of particular plant features, protection of structural steelwork is of some importance. Accounts of the fire protection of steelwork include those by Kayser (1974), Klootwijk (1976), Buck and Belason (1985), Latham, Kirby and Thomson (1987), Melinek and Thomas (1987), G.M.E. Cooke (1988) and Melinek (1980).

From standard tests information is available on the time for steel configurations, either uninsulated or with insulation arrangements, to reach a given temperature (e.g. Franssen and Bruls, 1986; API RP 520: 1990). A commonly used criterion temperature is 550°C.

Design guidance for fire protection of steelwork is given in *Designing Fire Protection for Steel Columns* (American Iron and Steel Institute, 1980), *Fire Protection for Structural Steel in Buildings* (CONSTRADO, 1983) (the *Yellow Book*) and *Design Manual on the European Recommendations for the Fire Safety of Steel Structures* (ECCS, 1985) and by Law (1972, 1991), Barnfield (1986) and Melinek (1980).

There are a number of models for predicting the times required to attain particular temperatures for insulated steelwork in a fire, including those by the European Convention for Constructional Steelwork (ECCS) (1985) and the National Research Council or Canada (NRCC) and by Wickström (1981/82, 1985) and Melinek (1980).

In estimating these times it is also necessary to define the nature of the fire to which the steelwork might be exposed.

16.24.7 Fire resistant valves

Valves are another type of equipment for which good fire resistance is highly desirable. Fire resistant, or fire safe, valves are available. Accounts of fire resistant valves are given by J.B. Wright (1981) and Cory and Riccioli (1985).

Relevant standards are API Std 589: 1993 *Fire Test for Evaluation of Valve Stem Packing*, API Spec. 6FA: 1994 *Specification for Fire Test for Valves* and BS 6755: *Testing of Valves*, Part 2: 1987 *Specification for Fire-Type Testing Requirements*, which replaces the earlier BS 5146: 1974–.

Interest centres particularly on the fire resistance of ball valves.

Among the features listed by J.B. Wright (1981) as being evaluated in tests are: operability whilst hot, leakage behaviour in a rapidly controlled fire and in a more prolonged one, and ability to withstand/relieve cavity pressure build-up.

16.25 Fire Fighting Agents

16.25.1 Types of firefighting agent

The main types of firefighting agent are (1) water, (2) foam, (3) vaporizing liquids, (4) dry powders, (5) inert gases and (6) other agents.

Accounts of firefighting agents are given in the *Manual of Firemanship* (Home Office, 1974–) and by Guise and Zeratsky (1965, 1982), the Factory Mutual Engineering Corporation (FMEC) (1967), J.R. Hughes (1970), Hearfield (1970), Harpur (1971), the Petroleum Industry Training Board (PITB) (1975/6), Riley (1983), Fuchs (1984), Welker, Martinsen and Johnson (1986), and Scheinson, Penner-Hahn and Indritz (1989) as well as the various contributors to the NFPA *Handbook* referred to below.

The principal firefighting agents are discussed in Sections 16.26–16.33.

16.25.2 Mechanism of fire extinguishment

Firefighting agents have several different mechanisms of operation. These include:

(1) cooling of flame;
(2) reduction of fuel
  (a) cooling of liquid,
  (b) dilution of liquid,
  (c) emulsification of liquid,
  (d) blanketing of liquid;
(3) reduction of oxygen;
(4) interference with combustion reaction.

The flame may be cooled to render it unstable. The supply of fuel to the flame may be reduced by cooling the liquid, by diluting or emulsifying it and so reducing the partial pressure of the vapour, or by blanketing the liquid with some inert material. The partial pressure of oxygen at the flame may be reduced by diluting the atmosphere with inert gas. The combustion reaction may be disrupted by the use of an agent which interferes with the combustion chain reaction.

16.25.3 Hazards of firefighting agents

There are a number of hazards in the use of firefighting agents. They are associated primarily with (1) discharge of the agent, (2) incompatibility between the agent and the material on fire, (3) an electric shock from high voltage equipment and (4) toxic and asphyxiant effects from the agent or its breakdown products.

A treatment of the toxic and asphyxiant hazards is given in GS 16 *Gaseous Fire Extinguishing Systems: Precautions for Toxic and Asphyxiating Hazards* (HSF, 1994). This deals

with the hazards associated with systems using inert gases such as carbon dioxide and nitrogen and those using vaporizing liquids such as halons.

These hazards and the precautions to be take against them are considered in more detail in the following sections. Further discussion of the precautions advised in GS 16 is deferred to Sections 16.30 and 16.31 so that an account can first be given of the basic methods.

16.25.4 Methods of delivery

The principal methods of delivery of firefighting agents are, in broad terms, (1) fixed systems, (2) mobile systems and (3) portable systems. Fixed systems encompass both fixed systems consisting of nozzles and feeder pipework and fixed monitors. The following sections give a more detailed discussion of these different types of delivery system.

16.25.5 Application of agents

For fire extinguishment or control agents such as water, foam and dry chemicals are generally applied directly to the burning liquid surface, and fixed systems are arranged to do this.

For agents such as dry chemicals, inert gases and vaporizing liquids, two widely used fixed systems are:

(1) total flooding system;
(2) local application system.

A manual method applicable to the first two of these is the use of a

(3) hand held hose line.

A total flooding system is used to protect a space which is essentially enclosed, whilst a local application system is used for a particular hazard such as an open tank. A hand held hose line is used to direct a jet of the agent at the fire.

Medium and high expansion foams may also be used in total flooding and local application systems.

16.25.6 Compatibility of agents

The compatibility of firefighting agents has two distinct aspects: (1) compatibility with the material and/or a fire of the material and (2) compatibility with other agents.

Some firefighting agents are incompatible with some chemicals. Information on this aspect is given in *Dangerous Substances. Guidance on Dealing with Fires and Spillages* (Home Office, 1972/4), in *Hazardous Loads* (IEF, 1972), *Fire Protection Guide to Hazardous Materials* (NFPA, 1991/27) and by various authors in the NFPA *Handbook*, as described below.

The most widely used firefighting agent is water, but it is not suitable in all cases. For example, water reacts with aluminium alkyls, usually with some violence. In some cases the incompatibility is with the fire of the material rather than with the material as such. For example, water is not incompatible with bulk titanium, but it is unsuitable for a titanium fire. Water is not generally an appropriate agent for fires of alkali metals, sodium chlorate or sodium peroxide. Chemicals which are incompatible with water may generally be expected to be incompatible with water-based foam, particularly the low expansion variety.

It is important that full information is available on the proper agents for fighting fires with the chemicals used in the process, that the right agents are selected and are available on the plant, and that personnel understand the nature of the agents and their use.

The other type of incompatibility is that exhibited between two different agents. It is often desirable to use two agents, either together or in quick succession. An example is the use of dry chemicals to knock down a fire and then of foam to blanket the liquid and prevent reignition. In such applications the agents must be compatible. This aspect is discussed further below in relation to specific agents. Examples of work on the compatibility of foams and dry chemicals are the accounts by Hird and Fippes (1690), the Underwriters Laboratories (1963) and Jensen (1964).

16.25.7 Selection of agents

In firefighting there is no single aim, and the selection of firefighting agents reflects this. An agent may be required to effect (1) extinguishment, (2) control or (3) exposure protection.

For fire extinguishment or control, the first consideration is usally given to water. Water is cheap and generally readily available. It is non-toxic and does not give rise in fire to toxic products. It has a large capacity to absorb heat, whether as sensible or latent heat. It vaporizes to give some 1700 times its own volume of steam, which acts as an inert vapour. Water is therefore particularly useful in fires where high cooling capacity is needed such as those involving solid materials and high flashpoint liquids, and where it is necessary to cool hot metal to prevent flashback.

There are some disadvantages, however, in the use of water. Since water has a higher density than most flammable liquids, it does not generally float on the surface of a burning liquid and so blanket it. Instead it often displaces the liquid from any depression, bund or equipment containing it and may thus cause burning liquid to spread out.

Its effectiveness against liquid fires depends on the type of liquid. This is discussed in more detail below. It is sufficient to note here that with some liquids water is not a very efficient extinguishant.

There are some liquids where the use of water can be positively hazardous. This may be the case where there is an undesirable reaction between the liquid and the water so that an explosive or toxic hazard is created. This aspect has been discussed above.

Where the liquid is a refrigerated liquefied gas, the use of water for firefighting is generally discouraged except for very small fires, since it has the effect of increasing the vaporization of the liquid. Further discussions of the use of water with LNG and with LFG fires are given in Section 16.35.

Water conducts electricity in the solid stream condition and water jets should not be used against electrical fires. This aspect is discussed further in Section 16.34.

Water is a relatively ineffective agent on a weight basis and is not very attractive for self-contained mobile, and particularly portable, equipment. This characteristic is less significant for use in fixed systems, where the quantities used are large.

Fire extinguishment by blanketing may be achieved using foam. Foam is frequently the most effective agent for fire on liquids in spillages, bunds and storage tanks. Foam is essentially expanded water and, apart from its density, has the general characteristics of water. It is just as unsuitable as water for fighting fires involving electrical

equipment or substances which have undesirable reactions with water. The uses and limitations of foam are considered in Section 16.28. There are a number of different types of foam, each with its characteristic uses.

The other principal agents are dry chemicals, vaporizating liquids and inert gases. Their uses and limitations are treated below.

It should be appreciated that where use is made of agents which are available in limited amounts only, it is essential to kill the whole fire first time. The supply of dry chemicals, for example, is usually sufficient to last only some tens of seconds. Unless the fire is completely extinguished, it is likely to reignite. On the other hand, foam forms a relatively long-lived blanket on the liquid and thus prevents reignition. This ability to hinder reignition makes foam an especially useful firefighting agent.

It is necessary to establish that the firefighting agent selected is capable of extinguishing a fire on the particular chemical concerned and this may require that tests be conducted. As already mentioned, tests may be needed to check the effectiveness of foam; they may also be necessary to verify that of vaporizing liquids or dry powders.

In selecting a firefighting agent, regard should be given to hazards to personnel. This aspect of selection is discussed in GS 16.

16.26 Fire Protection Using Water: Extinguishment and Control

Water is used in several distinct ways to fight fire. These are:

(1) extinguishment of fire;
(2) control of fire;
(3) fire exposure protection;
(4) fire and explosion prevention.

The third application is discussed in the next section and the others in this section.

Fire protection using water is treated in the NFPA *Handbook* by Hodnett (1986e). Two principal codes are NFPA 13: 1991 *Installation of Sprinkler Systems* and NFPA 15: 1990 *Water Fixed Systems*.

16.26.1 Water as a firefighting agent

Some general characteristics of water as a firefighting agent have been outlined in the previous section. Further aspects are considred here, particularly in relation to fires of flammable liquids.

Water is much the most widely used firefighting agent. The majority of fires which occur are fires in buildings or fires of other solid materials, and for these the most suitable agent is generally water. But water is also important as an agent for fighting fires, including liquid fires, in process plant.

It is most effective against fires of high flashpoint liquids. The principal mechanism is the cooling of the liquid so that its vaporization is reduced. The cooling effect is strong, because water has a high latent heat. With fires of low flashpoint liquids, however, it becomes more difficult using water to achieve a sufficient reduction in the vaporization.

Another important mechanism by which water extinguishes liquid fires is vaporization to form steam, which blankets the fire and cuts off the oxygen.

In fires of particular liquids other mechanisms may be involved. If the liquid is miscible with water (e.g. ethylene oxide), addition of water reduces the vapour concentration. A similar result is obtained if the water added forms an emulsion on the surface of the liquid. If the liquid is denser than water (e.g. carbon disulfide), water floats on the surface and prevents vaporization altogether.

On the other hand, if the liquid has a low boiling point, and particularly if it is a refrigerated liquefied gas, the effect of adding water is not to take heat away from the liquid as latent heat of vaporization of water, but to put heat in as sensible heat of cooling of water, and thus to increase the vaporization of the liquid.

The water used to fight a fire may be large in volume and is liable to become contaminated. Its removal can pose a serious problem. This may well be a factor in the deciding whether water is the appropriate agent to use.

The hazards associated with the use of water for certain types of fire are discussed in Subsection 16.26.3.

16.26.2 Extinguishment of liquid fires

Work has been done by Rasbash and co-workers on the extinction of liquid fires (e.g. Rasbash and Rogowski, 1957; Rasbash and Stark, 1960, 1962; Rasbash, Rogowski and Stark, 1960; Rasbash, 1962). The work has been reviewed in relation to water spray systems by P. Nash (1947b). For this purpose flammable liquids may be divided into three classes, depending on the mechanism of extinction:

(1) liquids not miscible with water and with a fire point $>45°C$;
(2) liquids miscible with water and therefore capable of having their fire point raised above 45°C by the addition of water;
(3) liquids not miscible with water and with a fire point $<45°C$.

The first class of liquid may be extinguished by heat transfer from it to water drops which penetrate its surface until its temperature falls below the fire point. Such liquids include heavy fuel oil, diesel oil, gas oil, and, as a borderline case, kerosene.

The water drops must enter the liquid in sufficient quantity despite the updraught of the flames and the evaporation of the spray in the flames. Factors which assist in achieving this are positioning of the spray near the liquid surface, high spray impetus and large liquid drop size. The impetus of the spray depends on the reaction of the nozzle and the width of the spray.

Figure 16.126 shows the results of some experiments of kerosene burning in a 30 cm diameter vessel with downward application of the spray (Rasbash, 1962). The ratio of the water actually penetrating the liquid surface to that expected to do so from geometrical considerations varied from about 10% to about 60%, depending on the thrust of the air current and the drop size of the spray. It was found that a mass median drop size above 0.4 mm is necessary to penetrate the flames effectively, but that at a drop size of about 0.8 mm the penetration becomes nearly independent of impetus and that above this size there begins to be a problem with splash fires caused by the larger drops splashing liquid from the surface so that burning continues even after the average liquid temperature has fallen below the fire point.

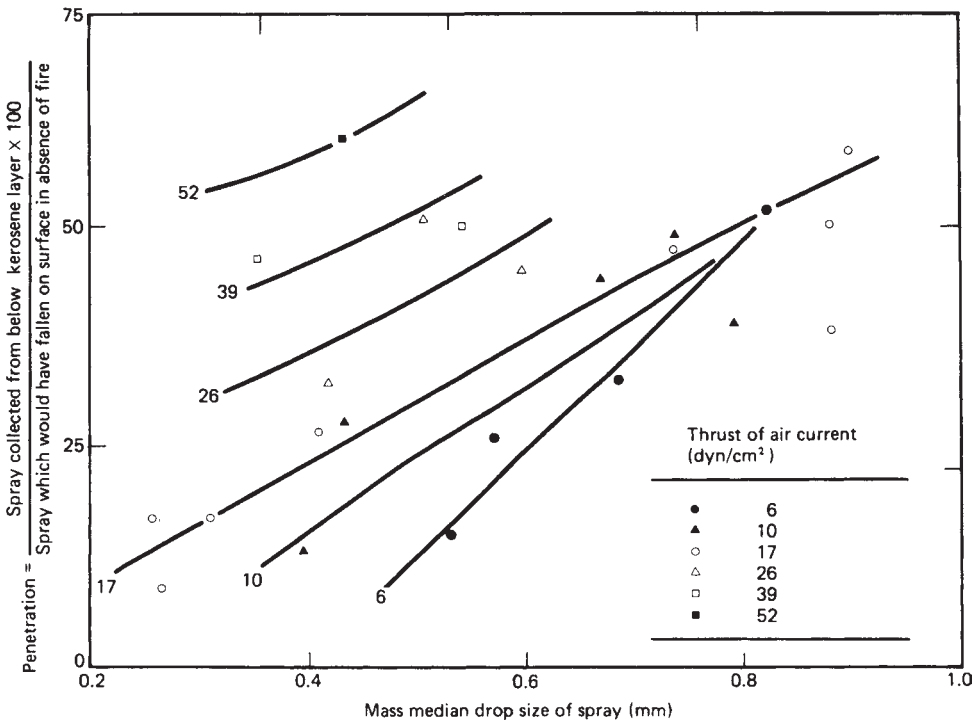


Figure 16.126 *Effect of the mass median drop size on the penetration of a water spray into a flammable liquid surface (Rasbash, 1962): kerosene fire, 30 cm diameter; downward application of spray; pressure at spray nozzle 0.35–2.1 bar (5–30 lbf/in.^{2}); flow rate to fuel surface in absence of fire 0.4–1.2 g/cm^2 min (Courtesy of the National Academy of Sciences)*

The work demonstrated that extinction can be achieved by application of water above a critical rate which is given by the equation

$$R_c = k_1 \frac{D^{n_1}}{\Delta T^{n_2}} \qquad [16.26.1]$$

where D is the mass median drop size (mm), R_c is the critical rate of water application (l/min), ΔT is the difference between the water temperature and the liquid fire point (°C), k_1 is a constant, and n_1 and n_2 are indices.

In practice it is necessary for the value of ΔT to be at least 40°C if the critical rate is not to be excessive. The indices n_1 and n_2 are approximately unity. The constant k_1 is a function of the flammable liquid, the area of the fire and the time for which the fire has already been burning. For a tray of gas oil of 8 ft diameter which has burned for 5 min before spray application, the value of k_1 was approximately 1140.

The time taken to extinguish the fire at rates of water application above the critical value is given by the equation

$$t = 5.2 \times 10^5 \frac{D^{0.85}}{R^{0.67} \Delta T^{1.67}} \qquad [16.26.2]$$

where R is the rate of water application (l/m^2 s) and t is the time to extinguish the fire (s).

Water spray systems for this liquid class typically use rates of water application in the range 0.16–1.2 l/m^2 s (9.6–72 l/m^2 min). High velocity nozzles are used with nozzle pressures of 2.75 bar (40 psig) or above and with a conical spray. The desirable mass median drop size is an even distribution in the range 0.4–0.8 mm and the drops should have a velocity sufficient to penetrate the liquid surface.

When a deep pool of liquid in this class in burning, it may form after a period a 'hot zone' and water below the surface may then boil and cause a 'slopover', thus spreading the fire. This can heppen, for example, with fuel oil which has been burning in depth for 15–30 min. It is necessary, therefore, to try to detect and extinguish fires before a hot zone occurs.

The second class of liquid may be extinguished by diluting the surface layer with water until the fire point of the mixture is raised sufficiently to cause extinction. Typical liquids are ethanol and acetone.

Although in this case the basic requirement for extinction is rather simple, there are certain problems. It is not always easy to tell when extinction has been achieved, since flames may continue to burn at some point and may be difficult to detect due to their low luminosity. Even if the fire is extinguished, the liquid remains flammable unless the whole bulk is diluted, and this may not be easy to achieve without spreading the spillage. Acetone, for example, requires a dilution of some 30 : 1.

The mass median drop size for a water spray for this liquid class should be less than 0.4 mm.

Liquids which are only partially miscible with water and have a low fire point are difficult to extinguish with water

and generally their fires can only be controlled. Such liquids include ether and methyl ethyl ketone.

For water spray systems for such partially miscible liquids rates of water application in the range 0.12–0.30 l/m^2 s (7.2–18 l/m^2 min) are normally required with nozzle pressures of 1.4 bar (20 psig) or above.

The third class of liquid may be extinguished by cooling the flame by heat transfer to the water droplets falling through it. Such liquids include petrol and, again as a borderline case, kerosene. It has been estimated that to cool a kerosene flame to extinction it is necessary to remove about 0.1 cal/cm^3 s if extinction is solely by steam formation and about 0.7 cal/cm^3 s if it is entirely by cooling. Thus the rate of heat removal to achieve extinction is of the order of 0.1–1 cal/cm^3 s, depending on the conditions.

The drop size required depends on several factors. In general, the extinction time falls sharply as drop size is reduced. With some liquids such as petrol it is essential that the drops penetrate to the lower part of the flames. There can be some 'sputtering' at the liquid surface, however, in the early stages of extinction if the drop size is too small. A mass median drop size of about 0.3 mm is usually suitable. Medium velocity nozzles of the open or closed type are used.

Additional cooling is obtained from air entrained with the spray. This effect is increased by the use of high nozzle pressures and drop velocities.

Water sprays are also used to deal with certain electrical fires, as described in Section 16.34.

16.26.3 Hazards associated with water

Although water is the most common firefighting agent, there are certain cases where it use is hazardous. One such case is where the material is incompatible with water, as discussed in the previous section. Another is where the fire is incompatible with water. This applies to in particular to metal fires, which are considered in Section 16.34.

The use of water on live electrical equipment involves the hazard of electrical shock. The extent to which water can be used with electrical fires is discussed in Section 16.34.

Also, as already mentioned, the use of water in large quantities and contamination of this water can pose a problem of disposal. Uncontrolled release of such water can cause damage to the environment.

16.26.4 Delivery systems for water

Water is delivered to the fire mainly either by fixed systems such as water sprinkler and water spray systems and fixed water monitors or by mobile systems such as fire hoses. Little use is made of water in portable systems.

Fixed water systems are used both indoors and outdoors. Indoors, widespread use is made of water sprinkler systems. Water spray systems may also be used indoors. Outside water spray systems and fixed water monitors predominate.

16.26.5 Applications of fire extinguishment or control

For most fire protection applications water is the agent of choice.

Fixed water sprinkler systems are used to protect indoor areas. Fixed water spray systems are used indoors to protect specific equipment such as grinding mills or conveyors.

Outdoors, fixed water spray systems are used to protect vulnerable items, loading and unloading facilities, including jetties, and storage vessels. Fixed water monitors are also provided for tank farms and jetties.

Except where it is unsuitable, water is the main agent used in mobile equipment by the works and public fire services for fighting fire wherever it occurs.

16.26.6 Fixed water sprinkler systems

Fixed water delivery systems are widely used in process occupancies. Fixed water sprinkler systems are used for fire extinguishment by delivering specified quantities of water over the protected area, mainly in buildings and warehouses. Fixed water spray systems are used for fire extinguishment or control by delivering specified quantities of water spray, characterized by the nozzle used, onto the protected equipment or area.

There is a considerable literature on fixed water sprinklers systems. It includes treatments by O'Dogherty, Nash and Young (1966), the Fire Offices Committee (1968), Kalelkar (1971), P. Nash (1972a, 1973a, 1976, 1975a,b, 1975 BRE CP 79/75, 1977a,b, 1990), Nash, Bridge and Young (1974 BRE CP68/74), Leworthy (1975), Nash and Young (1975 BRE CP29/75, CP67/75, CP52/76, CP77/75, CP78/75), Rogers (1977 BRE CP9/77), Nicholls (1981), R. Young (1981), Theobald (1987a,b), Yao (1988), FMRC (1991) and Melinek (1993b).

Fire protection by fixed water sprinkler systems is treated in the NFPA *Handbook* by several authors, notably Hodnett who deals with automatic sprinklers (1986a), automatic sprinkler systems (1986b) and water supplies for sprinkler systems (1986d).

Relvant NFPA codes are NFPA 13: 1991 *Installation of Sprinkler Systems*, NFPA 13A: 1987 *Inspection, Testing and Maintenance of Sprinkler Systems*, NFPA 16: 1991 *Deluge Foam–Water Sprinler and Spray Systems* and NFPA 16A: 1988 *Installation of Closed-Head Foam–Water Sprinkler Systems*. Other NFPA publications on sprinklers include *Automatic Sprinkler and Standpipe Systems* (1990/25), *Automatic Sprinkler Systems Handbook* (1994/37) and *Installation of Sprinkler Systems* (1994/39). The relevant British Standard is BS 5306 *Fire Extinguishing Installations and Equipment on Premises*, Part 2: 1990 *Specification for Sprinkler Systems*.

NFPA 13 is a large code, covering the use of sprinklers generally rather than in the process industries.

The elements of a fixed water sprinkler system include the sprinkler alarms, the sprinkler heads, the water distribution pipework, the valves and other fittings, and the water supply system and disposal arrangements.

The NFPA gives a classification of occupancies relevant to sprinkler systems. Those with moderate or substantial amounts of flammable liquid fall into the group Extra Hazard (Group 2).

A sprinkler system needs to respond rapidly so that the fire is extinguished before it can take hold. The time response of the sprinkler head is therefore crucial. Traditionally sprinkler heads have been classed according to the temperature at which they respond (e.g. 68°C). For fast response it is the time constant which matters. Fast response sprinklers are discussed by P. Nash (1972a), Watson (1984), Field (1985), Murrell (1988) and Mullhaupt (1986).

The use of sprinkler systems as fire sensors is considered by Nash and Theobald (1976 BRE CP50/76).

A sprinker system needs to be designed so that each head is supplied with the intended water pressure. The hydraulics of sprinklers are treated in *Hydraulics of Fire Protection Systems* (FMEC, 1977) and *Sprinkler Hydraulics* (Wass, 1983) and by Nickerson (1954), C.M. Wood (1961), Beyler

(1977), Ashfield (1979), Barris and Conte-Russian (1980), Bray (1980), Cresswell (1980), Kitson and Guy (1980) and Crowley (1982).

One way of achieving a uniform distribution of water in a sprinkler system is the use of a balanced system in which this uniformity is assured by the similarity of the pipework from the source to the individual sprinkler heads. For a system which it not balanced in this way it is necessary to ensure uniform distribution by calculating the pressure drops between the source and the individual heads.

16.26.7 Fixed water spray systems

As just indicated, fixed water spray systems are distinguished by the fact that the spray is characteristic of the type of nozzle used.

Accounts of fixed water spray system are given by Rasbash and co-workers, as already described, and by P. Nash (1974b), Hems (1979, 1983), Fritz and Jack (1983), Angelini (1984), Lev and Strachan (1989a,b), McCaffrey (1989), Chow and Fong (1991) and Jackman and Nolan (1994).

Fire protection by fixed water spray systems is treated in the NFPA *Handbook* by Hodnett (1986c).

Relevent codes and standards are NFPA 15: 1990 *Water Spray Fixed Systems* and NFPA 16: 1991 *Deluge Foam–Water Sprinkler and Spray Systems*.

The elements of a fixed water spray system include the fire detection and alarm system, the spray nozzles, the water distribution pipework, the valves and other fittings, and the water supply system and disposal arrangements.

16.26.8 Fixed water monitors

For fire risks involving large quantities of flammable liquid, notably tank farms and jetties, fixed water monitors are generally provided. These monitors are generally dual purpose devices which can be used to project water or foam.

16.26.9 Water rates for extinguishment or control

Recommended water rates for the extinguishment or control of fire are given in the various codes and standards. Those recommended by the NFPA probably have the greatest currency. NFPA 15 distinguishes the four types of application, listed at the beginning of this section, and gives for each type a recommended approach.

NFPA water rates for fire extinguishment

For fire extinguishment, NFPA 15 states that water rates should be based on tests or experience. It gives a general, or default, range of water rates which applies to the protected surface for most combustible solids and flammable liquids. This is 0.2–0.5 USgal/ft^2 min (8.1–20.4 l/m^2 min).

NFPA water rates for control of burning

For control of burning, NFPA 15 states that the water rate on the probable surface of the spill should not be less than 0.5 USgal/ft^2 min (20.4 l/m^2 min).

Control rather than extinguishment of the fire implies that the water flow needs to be maintained. NFPA 15 requires that the system function at full effectiveness until there has been time for the flammable material to be consumed, for the leak to be shut off, for the assembly of repair forces, etc.

NFPA water rates for exposure protection

For exposure protection, or cooling, the water rates recommended in NFPA 15 vary according to the item protected. They are considered in the next section.

NFPA water rates for fire and explosion prevention

For fire and explosion protection NFPA 15 simply states that the water rate should be based on tests or experience.

Critique of NFPA recommended water rates

A critique of water rates traditionally recommended has been given by Fritz and Jack (1983). They take as their starting point the then current edition of NFPA 15 and deal both with water rates for extinguishment or cooling and rates for exposure protection.

They refer in particular to work at the Rubber Reserve Company in the 1940s on horizontal cylindrical vessels containing fuel (gasoline, butane and butadiene–butylenes mixtures) and engulfed in fire.

Fritz and Jack discuss the work of Rasbash and co-workers on fire extinguishment described above. They draw attention to the influence of the water nozzle and spray characteristics on the water rates needed for extinguishment and to the fact that these characteristics are not specified in the NFPA codes. They consider the water rate required to effect extinguishment based on a heat balance model in which the total heat released by combustion goes to evaporate the water. They obtain from this a water rate of 2.5 USgal/ft^2 min. On this basis they suggest that a water rate of 0.5 USgal/ft^2 min is no more than cosmetic. They also discuss the water rate for exposure protection, as discussed in the next section.

16.26.10 Fire water supply systems

The amount of water needed for firefighting and cooling presents a considerable problem. Aspects where better understanding may lead to less onerous requirements include the heat flux from liquid fires, the reflectivity and wetability of tank surfaces, and methods of applying the water to the surfaces.

Water spray systems both for firefighting and for cooling may be of two types. In a wet system the pipes are kept full of water under pressure, whereas in a dry system these pipes are normally empty and are filled by the opening of a master valve only when the system is to be activated. A dry system should be used where there is risk of freezing. It is therefore this type of system which is most suitable for process plants, particularly in the open. The pipework in a dry system needs to be arranged to allow complete drainage.

There should be a secure water supply to the water spray system. This aspect is discussed in Chapter 10 in relation to plant layout.

There are a number of ways in which a water spray system can be rendered ineffective. One of these is freezing up, as just mentioned. Another is leaving valves closed, particularly after maintenance. The latter occurrence needs to be guarded against by specific procedures.

In addition, it is not uncommon for a water spray system to be knocked out by an explosion. The Fourth Edition of the Dow *Guide* (Dow Chemical Company, 1976) states that where an explosion hazard exists, it is a recommended minimum prevention and protection feature that water spray piping of $2\frac{1}{2}$ in. diameter or above be welded or flanged, not threaded.

16.26.11 Fire water disposal systems

As already indicated, the disposal of fire water, particularly contaminated water, can be a serious problem, which it is sufficient here to highlight. As an aspect of plant layout, fire water disposal is treated in Chapter 10. A method of alleviating this problem which merits mention here,

however, is the use of foam to obtain a given degree of fire extinguishment or control with a smaller water usage.

16.27 Fire Protection Using Water: Exposure Protection

In the foregoing section an account has been given of the use of water to extinguish or control a fire. In this section consideration is given to its use for exposure protection by cooling of equipment exposed to fire.

Accounts of fire exposure protection are given by Pettit (1945), Chaillot (1966), P. Nash (1973b, 1974a), Fritz and Jack (1983), Billings, Moodie and Beckett (1986), Lev and Strachan (1989b), Lev (1991) and Meiers and Jarman (1993).

As indicated above, a relevant code for exposure protection using water is NFPA 15.

16.27.1 Delivery systems for water

The means of delivery of water for cooling are broadly similar to those used for extinguishment. Water is delivered to the protected surface by fixed systems such as fixed water spray systems and fixed water monitors or by mobile systems such as fire hoses.

16.27.2 Applications of water cooling

Essentially, exposure protection is provided for large flammable gas or liquid inventories which are liable to be exposed to a fire. For the most part such inventories occur in storage tanks and vessels, though protection may also be provided for certain process vessels and for road and rail tankers.

The purpose of providing such protection is to cool the metal and so prevent loss of strength. It is normal to provide the tank or vessel with pressure relief but, even if the relief operators, it will not prevent failure if the wall temperature is allowed to rise too high.

16.27.3 Water rates for cooling

NFPA water rates for cooling

For exposure protection by cooling, NFPA 15 treats the following cases: vessels, structures and miscellaneous equipment, transformation and belt conveyors.

For vessels, the code states that the rules given assume that there is a relieving capacity based on a maximum allowable heat input of 6000 BTU/ft^2 h (18.9 kW/m^2). If there is no such relief, the water rates should be increased accordingly.

For a vertical or inclined vessel surface the water rate should not be less than 0.25 USgal/ft^2 min (10.2 l/m^2 min) of exposed uninsulated surface. Where on such a surface rundown is assumed, the vertical distance between nozzles should not exceed 12 ft (3.7 m). The horizontal extremities of the spray patterns should at least meet.

For a vertical vessel the bottom and top surfaces should be completely covered by directed water sprays with a water rate of 0.25 USgal/ft^2 min (10.2 l/m^2 min) of exposed uninsulated surface. On the bottom surface the horizontal extremities of the spray patterns should at least meet.

The surfaces below the equator of a spherical or horizontal cylindrical vessel cannot be considered to be wetted by rundown.

The code also gives various other provisions.

The structures and equipment considered are primarily horizontal and vertical structural steel members, pipework and pipe racks, and cable trays and cable runs. Water rates are given for each of these.

Critique of NFPA recommended water rates

Mention has already been made of the critique by Fritz and Jack (1983) of the water rates recommended in NFPA 15 for fire extinguishment or control. These authors also review the NFPA recommendations on water rates for exposure protection.

The background to these recommended rates is work on heat fluxes to vessels engulfed in fire, such as the tests listed in API RP 520: 1990 and earlier editions, which include the Rubber Reserve Company tests mentioned in the previous section.

In this case the authors base their estimate of the cooling water requirement on a heat removal rate of 20,000 BTU/ft^2 h, effected by a rise in water temperature to a few degrees above the boiling point. On this basis they obtain an estimate of 0.04 USgal/ft^2 h for the required water rate. They suggest that the NFPA recommended value of 0.25 USgal/ft^2 h is higher than it need it.

Thus Fritz and Jack's critique of the NFPA water rates recommended is that for fire extinguishment they are too low, but that for exposure protection they are too high.

Other Recommneded Water Rates

For the exposure protection of storage tanks containing low fire point liquids a rate of water application over the surface of the tank of 0.2 UKgal/ft^2 min (0.16 l/m^2) is recommended by P.H. Thomas and Law (1965 FRS Fire Res. Note 609).

The Fourth Edition of the Dow *Guide* (Dow Chemical Company, 1976) gives as a recommended minimum fire prevention and protection feature exposure protection a rate of 0.2–0.35 USgal/ft^2 min (0.14–0.24 l/m^2 s) for directional sprays. The later editions give water rates as part of the loss control credits, but these refer to indoor sprinkler applications.

For the exposure protection of LFG vessels the ICI *LFG Code* (ICI/RoSPA 1970 IS/74) recommends a rate of 0.20 UKgal/ft^2 min (0.16 l/m^2 s), but allows a reduced rate if certain precautions are taken. This is discussed more fully in Chapter 22.

16.27.4 Cooling of tank exposed to a pool fire

A tank exposed to fire, including an engulfing fire, may be cooled by applying water. The water rates recommended have just been described. At these water rates the total water requirements may be very large. The requirements for exposure protection generally greatly exceed those for extinction of fire.

This generalized requirement is not difficult to meet for small tanks, but becomes much more onerous for large ones. Thus, based on this criterion, the water requirement for an 80 m diameter tank is of the order of 150 t/min. The power required to lift and distribute the water is large also, being about 1 MW.

The water needed for exposure protection is greatly reduced if application is restricted to the tank roof and ullage sections. Figure 16.127, given by P. Nash (1973b, 1974a), illustrates this difference. The curves are based on the water rates recommended in the then current edition of NPFA 15, which were 0.25 USgal/ft^2 min. Curves A1 and B1 give, respectively, the water requirements for extinction and exposure with coverage of the whole tank and with coverage of the roof and ullage sections only. Curves A2 and B2 give the corresponding water requirements for exposure only.

A further discussion of the use of water sprays for protection against fire exposure is given in relation to storage in Chapter 22.

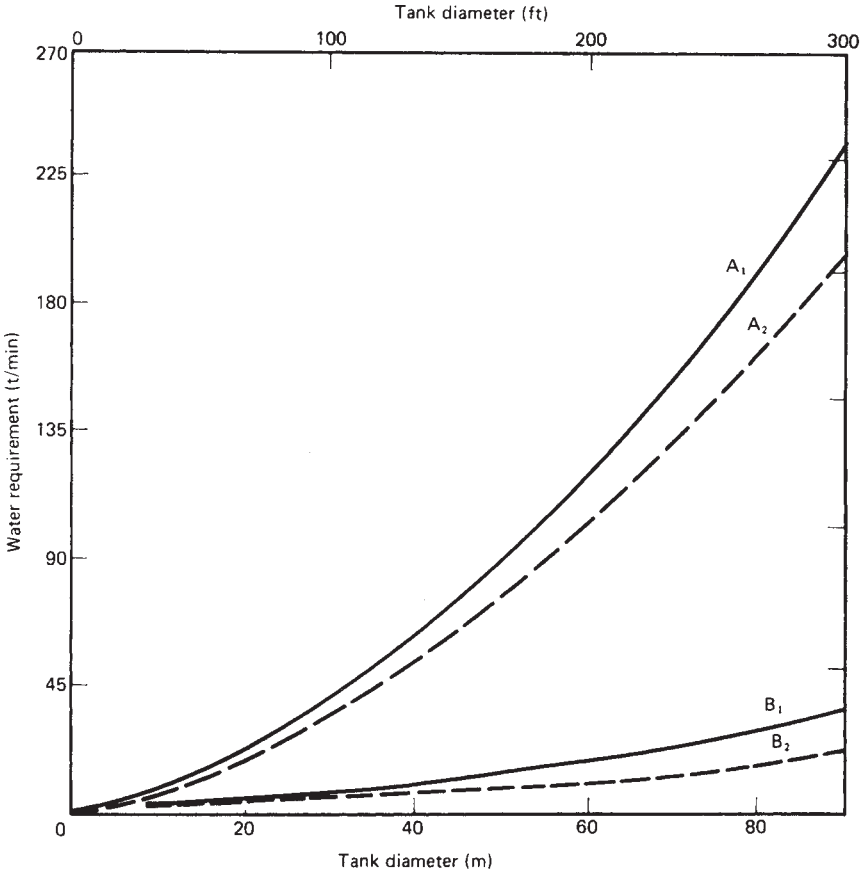


Figure 16.127 *Water requirements for protection against exposure to fire and for extinction of fire for a storage tank (P. Nash, 1974a): A_1, NFPA 15 – extinction and exposure;A_2, NFPA 15 – exposure only; B_1, 'economial' requirement – extinction and exposure; B_2, 'economical' requirement – exposure only (Reproduced by permission of HM Stationery Office. Copyright. All rights reserved)*

16.27.5 Cooling of vessel exposed to an impinging jet flame

A rather different, and stringent, fire protection requirement arises where a jet flame impinges directly on a target. This problem has been studied by Lev and Strachan (1989b) and Lev (1991).

The surface of a vessel exposed to a jet flame is likely to rise to a temperature of over 100°C very rapidly. A continuous film of water over the metal surface is capable of intercepting radiant heat, but as the heat flux is increased the protection so afforded is gradually lost as the water film thins and then disintegrates.

A model for a water spray system to protect against jet flames has been described by Lev (1991). It has three main elements which model: (1) the three-dimensional droplet trajectory, (2) the in-flight evaporation loss and (3) the heat transfer between the cooling water and the metal surface.

For the droplet trajectory, the equation of motion of a droplet moving through a parallel gas stream is written as

$$m_d \frac{dv}{dt} = C_d \rho_g (U - v)(|U - v|) \frac{A}{8} - m_d g \qquad [16.27.1]$$

where A is the surface area of the droplet (m^2), C_d is the drag coefficient, g is the acceleration due to gravity (m/s^2), m_d is the mass of the droplet (kg), t is the time (s), U is the gas velocity (m/s), v is the droplet velocity (m/s) and ρ_g is the gas density (kg/m^3).

The drag coefficient is taken as given by the following relations for a non-evaporating droplet, the correction for evaporation being small:

$$C_d = 24/\mathrm{Re} \quad \mathrm{Re} < 2 \quad \text{Stokes regime} \qquad [16.27.2]$$

$$C_d = 10/(\mathrm{Re})^{1/2} \quad 2 < \mathrm{Re} < 500 \quad \text{Intermediate regime} \qquad [16.27.3]$$

$$C_d = 0.44 \quad \mathrm{Re} > 500 \quad \text{Newton's regime} \qquad [16.27.4]$$

with

$$\mathrm{Re} = \frac{D(|U - v|)}{v} \qquad [16.27.5]$$

where D is the droplet diameter (m) and ν is the gas kinematic viscosity (m^2/s).

For the in-flight evaporation loss, use is made of the correlation of Ranz and Marshall (1952), with the correction for high stream temperatures given by Yuen and Chen (1978):

$$\mathrm{Nu}(1+B) = 2 + 0.6\,\mathrm{Re}^{0.5}\mathrm{Pr}^{0.33} \qquad [16.27.6]$$

with

$$B = (h_s - h_d)/L \qquad [16.27.7]$$

where B is a mass transfer number, h_d is the surface enthalpy of the droplet (J/kg), h_s is the free stream enthalpy (J/kg) and L is the latent heat of evaporation of the droplet (J/kg). The properties are evaluated at the film temperature.

Since the work of Yuen and Chen was done using streams of hot air, it is necessary also to introduce a term for absorbed radiant heat:

$$M_r = cQA\delta t/L \qquad [16.27.8]$$

where c is an absorption coefficient, M_r is the rate of evaporation loss due to thermal radiation (kg/s), Q is the heat flux to the droplets (W/m^2) and δt is the time of exposure of the droplet (s).

For the heat transfer between the cooling water and the surface, the relation used is that of Yao and Choi (1987):

$$Q = 29.5 \times 10^{-4} G^{0.76} \qquad [16.27.9]$$

where G is the liquid mass flux (kg/m^2 s) and Q is the heat flux between the water and the surface (W/m^2).

Information on the flame temperature and surface emissive power in jet flames has been reviewed by Lev (1991). A study by Blything (1983 SRD R263) quotes a flame temperature of about 1300°C and heat fluxes of about 300–400 kW/m^2. Work on jet flames by Cowley and co-workers (Cowley, 1989; Tam and Cowley, 1989; Cowley and Pritchard 1991) on several different configurations has shown heat fluxes in the range 50–250 kW/m^2.

The model described was used to obtain results relevant to spray system design. These showed that the heat transfer passes through a marked maximum with surface temperature, this maximum occurring around 140–150°C. Thus the water mass flux to remove the heat from an incident heat flux of 250 kW/m^2 was 12 kg/m^2 min at 150°C but 50 kg/m^2 min at 300°C. Due to instabilities, maintenance of conditions where the lower water rate is sufficient is dubious. Lev recommends, therefore, a design cooling water rate of some 60–120 kg/m^2 min.

In order to deliver this cooling water under conditions where there is likely to be in-flight evaporation and crossflow losses, the droplets need to be large and to be projected at high velocity. Lev presents results from the model showing the fraction of water droplets reaching the target as a function of crossflow velocity and droplet diameter. Droplets of less then 0.5 mm diameter are vulnerable and a droplet size of more than 1 mm diameter should be aimed for.

Typical medium velocity (MV) nozzles tend to produce a high proportion of droplets less than 0.5 mm in diameter. They appear less suitable that high velocity (HV) nozzles. Alternative modes of water delivery are hand-held monitors and fixed monitors. Suitable HV nozzles mounted less than 1 m from the target are capable of delivering the 60–120 kg/m^2 min required. There are hand-held monitors which from a distance of 16 m can deliver water at a rate of 120 kg/m^2 min, wetting an area of 6 m^2.

The method just described is applicable to impining jet flames of LPG with stream temperatures of 500–1300°C and stream velocities up to 40 m/s with radiative heat fluxes of 50–250 kW/m^2 and for metal surface temperatures of 150–300°C.

16.27.6 Fixed water cooling systems

Exposure protection is effected using fixed water spray systems. Proper cooling requires that water be applied such that the whole surface protected is wetted by the water rate specified. The spray nozzles should be located so that the extremities of the spray pattern at least meet, and for wetting below a vessel equator reliance should not be placed on rundown. More detailed requirements have been given in the previous section.

The relevant codes, notably NFPA 15, have been discussed in the previous section.

16.28 Fire Protection Using Foam

A prime alternative to water, particularly for large fires, is foam. Accounts of foam are given by Burgoyne (1949a), Burgoyne, Katan and Richardson (1949a), the American Chemical Society (ACS) (1956), Burgoyne and Steel (1962), Vervalin (1964b,d), Meldrum and Williams (1965), Ashill (1966b), G. Nash (1966), Hearfield (1970), Hird, Rodrigues and Smith (1970), Meldrum (1972, 1982), P. Nash (1973b), Corrie (1974, 1975 BRE CP25/75), Nash and Young (1975 BRE CP42/75), Burford (1976), Gillespie and Dimaio (1977), Murphy (1981), Boughen (1983), J.L. Evans (1985, 1988), SKUM (1986), A.A. Briggs and Webb (1988), Tabar (1989), Waters (1990 LPB 91) and M. Clarke (1992). Fire protection using foam is treated in the NFPA *Handbook* by Lockwood (1986).

Relevant codes and standards are NFPA 11: 1988 *Low Expansion Foam and Combined Agent Systems*, NFPA 11A: 1988 *Medium and High Expansion Foam Systems*, NFPA 16: 1991 *Deluge Foam–Water Sprinkler and Spray System*, NFPA 16A: 1988 *Installations of Closed Head Foam–Water Sprinkler Systems*, NFPA 11C: 1990 *Mobile Foam Apparatus* and BS 5306: 1976– *Fire Extinguishing Installations and Equipment on Premises*, Part 6: Foam, Section 6.1: 1988 *Specification for Low Expansion Foams* and Section 6.2: 1989 *Specification for Medium and High Expansion Foams*.

16.28.1 Mechanisms of fire extinguishment

Foams are widely used against liquid fires. Initially the foam acts as a blanketing agent and then, as the water drains from the foam, as a cooling agent.

16.28.2 Types of foam

Foams are water based and come in several kinds. These include:

(1) chemical foam;
(2) protein-based mechanIcal foam
    (a) standard, low expansion foam,

(b) high expansion foam,
(c) medium expansion foam;
(3) special foams
(a) fluorochemical foam,
(b) fluoroprotein foam;
(4) detergent foam;

There is now a large family of foams of different types and applications. One broad distinction is made on the basis of the viscosity of the foam. The blanket formed by the more viscous type is resistant to rupture by flame, but the less viscous type flows more readily over a liquid surface. Other relevant properties of foams are their resistance to oil and alcohols.

Chemical foam
Chemical foam is produced by reacting aqueous solutions of sodium bicarbonate and aluminium sulfate in the presence of a foam stabilizer. The reaction generates carbon dioxide, which both forms foam and ejects the mixture from the apparatus. This type of foam may be regarded as obsolete, its use long having been almost entirely confined to mobile and portable equipment.

Protein, or mechanical, foam (P)
Mechanical foam is generated by mechanical aeration of aqueous solutions of certain chemicals, which usually have a protein base. One type is based, for example, on blood hydrolysed by caustic soda. Standard foam is made by introducing the foam compound into the water in the hose to give a 3–6% aqueous solution and then mixing the solution with air in an ejector nozzle to give an approximately 10 : 1 expansion. This type of foam is the most widely used both for fixed and mobile apparatus. Such standard low expansion foam is very cheap.

High expansion foam is generally similar to standard foam but has an approximately 1000:1 expansion. This type of foam contains little water so that it acts almost entirely by blanketing rather than by cooling. It is very light and is easily blown away, and is thus more suitable for fires in containers such as tanks or ships' holds than for those in open situations such as in a bund.

Medium expansion foam is again generally similar to standard foam, but has an approximately 100–150 : 1 expansion. This type of foam is also light, but is not so easily blown away as high expansion foam.

Both medium and high expansion foams have a good three-dimensional extinction capability and can be used against fires on piles of materials such as rubber.

A disadvantage of protein foams is that if the foam blanket is broken the liquid may re-ignite and burn back the blanket. Low expansion foam, however, has reasonably good heat and 'burnback' resistance.

Fluorochemical, or light water, foam
Agents have been developed to overcome this problem. One type is fluorochemical foam. This includes 'light water' foam, which contains a straight-chain fluorocarbon surface active agent. This has the effect that as the water drains from the foam it spreads in a thin film over the liquid and seals it. Even if the film is disturbed by agitation, it reforms rapidly. Light water foam behaves differently, however, on different liquids, and it is not universally effective. The cost of light water foam is high.

Fluoroprotein foam (FP)
Another agent which works in a similar manner is fluoroprotein foam, which contains a branched chain fluorocarbon. It is therefore a candidate where good burnback resistance is needed. It is less expensive and appears in many cases to be more effective than light water foam. Fluoroprotein foam is less prone to pick up oil particles when passed through oil. This 'fuel-shedding' property is useful in subsurface foam injection on storage tanks. This type of foam tends to have good compatibility with dry chemicals.

Synthetic detergent foam (S)
Synthetic detergent foam is generated by mechanical aeration of aqueous solutions containing 2–3% of detergent. This foam is less stable than protein-based foam. The most effective method of usage appears to be massive application is a knockout attack. Detergent foam has enjoyed some popularity, the attraction being that it is cheaper even than protein foam.

Aqueous film forming foam (AFFF)
AFFF has low viscosity and spreads easily over a liquid fires. Another useful property of AFFF is that does not need elaborate foaming devices and can be utilized in many water sprinkler and spray systems.

Film forming fluoroprotein foam (FFFP)
FFFP foam is another type of foam which has low viscosity and good spreading properties and can be used in many water spray systems. FFFP foam tends to drain rapidly and is therefore less reliable in maintaining a foam blanket.

Alcohol resistant (AR) foam
Regular air foams do not perform well on liquids which are of the polar solvent type, notably alcohols. For these AR foams have been developed. The first generation of AR foams were not entirely satisfactory, but effective foams have been developed. One type of AR foam is polymeric alcohol resistant AFFF.

Low temperature foams
Foams have been developmed for use at low ambient temperatures; one quoted temperature for such foams is −29°C. These foams come in both protein and AFFF types.

16.28.3 Properties of foam

A foam for firefighting should possess certain general properties, which include (1) expansion, (2) cohesion, (3) stability, (4) fluidity, (5) fuel resistance and (6) heat resistance.

Clearly, the foam must have an appreciable expansion ratio, its bubbles must cohere together and form a blanket, it must retain its water and remain stable, it must flow freely over the liquid surface and around any obstacles, it must not pick up so much fuel that it is itself liable to burn and it must resist the heat of flames on the liquid. Foams for use on alcohols must also be alcohol resistant.

Three quantitative criteria for foam are (1) the expansion, (2) the fluidity and (3) the drainage time. Expansion is measured by the expansion ratio.

A measure of fluidity is the shear stress. A shear stress in the range 150–200 dyn/cm^2, measured on a torsional viscometer, is typical of a good foam.

The drainage of liquid out of the foam is usually expressed as the '25% drainage rate', which is the time in minutes for 25% of the total liquid content to drain away under standard conditions. For a good foam this drainage time is typically 2–5 min.

Foam can be affected by the quality of the water used. A study by Dimaio and Lange (1984) detected deleterious effects from contaminants such as corrosion inhibitors, anti-fouling agents, etc. In general, however, such effects were found to be much weaker if high application rates were used.

Compatibility with other firefighting agents is another important property of foams. This aspect has been discussed above and is considered further below.

16.28.4 Tests for foam

There are a number of standard tests to evaluate the performance of foam in extinguishing fire. Standard tests include the Underwriters Laboratories and Det norske Veritas (DnV) tests and those specified in the MIL Specification MIL-F.24385, the draft ISO/DP 7203 and, in the United Kingdom, Defence Standards 42–21, 42–22, 42–24 and BS 6535: Part 6: 1988–. Such tests are discussed by J.L. Evans (1988) who compares the performance of different foams in different tests.

Tests may be required to establish the effectiveness of a foam in a particular application. Details of the conduct of tests to select a foam for methylisobutyl ketone (MIBK) have been given by Corrie (1974).

16.28.5 Hazards associated with foam

Foam is water based and, to this extent, hazards associated with water apply to foam also. They include increased vaporization of low boiling liquids, reaction with incompatible materials and electric shock from live wihe incompatible materials and electric shock from live electrical equipment.

Another hazard is rupture of the foam blanket and burnback, which may put firefighters at risk.

Hazard can arise from the use of a foam on a liquid at a temperature of 100°C or above. The formation of steam can cause a four-fold expansion of the foam with slopover of the burning liquid.

In the case of the medium and high expansion foams used to fill spaces, there is the hazard of asphyxiation.

16.28.6 Hazards associated with foam: static electricity

Another hazard is ignition of hydrocarbons in a storage tank roof by static electricity from foam injection, as described by Howells (1993 LPB 114). This author describes several incidents in which ignition of volatile refined products in a floating roof storage tank appears to have been caused by foam injection. He suggests two possible modes of charge generation: (1) the settling of water droplets through the hydrocarbon liquid and (2) the streaming current of the foam mixture leaving the nozzle.

Using Equation 16.7.173, Howells obtains for the case of a tank filled to a depth of 3 m with the bottom earthed, an estimated liquid surface potential of 27 kV, a value which has been shown in work on road tankers to be hazardous. He suggests that an even higher potential may occur if the foam jet is applied directly to the liquid surface so that the concentration of foam in the fuel is orders of magnitude higher than that used in this calculation.

With regard to the second mechanism, aqueous foam systems, has a high conductivity and any charge generated at the nozzle would be quickly dissipated back to the branch pipe or the tank walls. However, if charged foam enters the liquid the charge could be retained. The streaming current of foam of foam is not readily calculable, so experimental work was undertaken. At the time of writing this work was inconclusive.

16.28.7 Delivery systems for foam

Foams is delivered to the fire by means essentially similar to those used for water. The means used are mainly fixed systems such as foam–water spray systems and fixed foam–water monitors or mobile foam–water systems such as fire hoses. Little use is made of foam in portable devices.

The delivery of foam involves three stages: (1) proportioning of the foam concentrate, (2) foam generation and (3) foam distribution. There are a number of methods for the proportioning of the foam concentrate.

The devices for the generation of the foam are incorporated in the devices used for its distribution, as just described. The basic method of generation is aspiration of air into the foam.

A detailed account of methods of proportioning and distribution is given by Lockwood (1986).

16.28.8 Applications of foam

Fire extinction by blanketing may be achieved using foam. Low expansion foam is mainly used to prevent, extinguish or control fires in storage tank tops and bunds and on spills.

Foam should be used only if it is compatible with the hazardous liquid. In particular, foam is essentially expanded water and, apart from its density, has the general characteristics of water. It is just as unsuitable as water for fighting fires involving electrical equipment or substances which have undesirable reactions with water.

Other conditions for the use of foam are that the liquid surface be horizontal and that the temperature of the liquid be not too high. The liquid temperature should be below the boiling point. If the liquid temperature is below the boiling point but above 100°C, water in the foam will turn to steam, which can result in a very large expansion of the foam.

There are optimum rates of application of foam. For low expansion foam with an expansion ratio of 8 : 1 an application rate of 0.1 USgal/ft^2 will give 0.8 USgal/ft^2 min of foam. Foam application rates are discussed by Lockwood (1986). The foam should be applied gently.

Medium and high expansion foams are used to prevent, extinguish or control fire in spaces such as ships' holds. Application systems for these foams comprise both (1) total flooding systems and (2) local application systems.

16.28.9 Fixed foam systems

For low expansion foam, one type of fixed foam system is the foam–water deluge system. Another type of system is the foam–water monitor. Fixed foam systems are used for fire prevention, extinguishment and control in bunds or on spills.

Relevant codes are NFPA 11 for low expansion systems, NFPA 11A for medium and high expansion systems, NFPA 16 for deluge foam–water sprinkler and spray systems and NFPA 16A for closed head foam–water sprinkler systems.

The fighting of a major fire requires a very large quantity of foam. An example quoted by G. Nash (1966) is a requirement of 300×5 UKgal drums for a 30 min foam

attack on a single 150 ft diameter oil storage tank. The supply, and disposal, of such a large number of drums in an area congested with fire appliances and hoses constitutes a major problem. He describes the alternative of providing a piped supply of foam concentrate.

16.28.10 Fixed foam systems for storage tanks

A particularly important application of foam is the protection of storage tanks. A variety of systems are used. Accounts of foam systems for storage tanks are given by E.M. Evans and Whittle (1974), P. Nash and Whittle (1978), Lockwood (1986) and SKUM (1986). A relevant code is NFPA 11.

For fixed roof tanks some principal arrangements are foam chambers, internal tank distributors and subsurface foam injection. Foam chambers are installed at intervals on the outside near the top of the tank wall, providing an over-the-top foam generation (OFG). An alternative is internal distributors fitted inside the tank.

Application of foam at the top of the tank poses several problems. If the fire is initiated by an explosion, this may well also disable the foam system. The upward flow of air caused by the fire may interfere with the distribution of the foam. In a large tank the foam may not reach the centre.

Subsurface foam injection is designed to counter these difficulties. Foam is injected under pressure up through the liquid in the tank. Injection may be through the product pipe or a dedicated line, Mobile foam trucks may be used to provide the foam supply.

Floating roof tanks may be open top or closed. They have a good fire record so that foam systems are generally not required, with one exception, This is the need to cater for rim fires which can occur on either type. An open-type floating roof tank may be protected by a fixed foam system which pours foam into the annulus formed by the tank wall and a foam dam. A closed floating roof tank may be protected using a top injection system similar to those used in fixed roof tanks. Subsurface foam injection is not generally used for floating roof tanks since a tilted or sunken roof can cause poor foam distribution.

16.28.11 Mobile foam systems

Foam trucks are the principal mobile mode of delivery for foam. The trucks are typically purpose built twin agent trucks with a capability of delivering dry chemicals also.

Relevant codes are NFPA 1901 which covers basic water systems with a foam option, and NFPA 11C which covers foam trucks.

Foam trucks carry a supply of foam concentrate and delivery hoses and can be equipped with telescopic booms of articulated towers. They have low clearances to allow passage under pipe bridges. A combined agent truck might typically carry AFFF and dry chemical. Monitor capacities are of the order of 500–1000 USgal/min.

There are a variety of mobile devices that can be used to apply foam to the top of a storage tank which is on fire. They include mobile foam monitors and foam towers. There are a number of problems in using a foam monitor for this purpose, such as crosswinds and fire updrafts, and a significant proportion can be wasted. Lockwood advises making an allowance of 60% above the desired application rate to allow for such factors.

16.28.12 Vapour suppression by foam

Fire control and extinguishment is not the only use of foam. Another important application is the suppression of vaporization from toxic liquid spills. This use of foam is treated in ASTM-F-1129-88 *Standard Guide for Using Aqueous Foams to Control the Vapor Hazard from Immiscible Volatile Liquids*. Vapour suppression using foam is discussed in Chapters 15 and 18.

16.29 Fire Protection Using Dry Chemicals

An alternative to water or water-based foam is dry chemicals, or dry powders. Accounts of dry chemicals include those by T.G. Lee and Robertson (1960), Vervalin (1964e), Laffitte *et al.* (1965), Emmrich (1971), Wesson (1972), Woolhouse and Sayers (1973), Schweinfurth (1974), Stauffer (1975), MITI (1976) and Ewing *et al.* (1989a,b). Fire protection using dry chemicals is treated in the NFPA *Handbook* by Haessler (1986).

Relevant codes and standards are NFPA 17: 1990 *Dry Chemical Extinguishing Systems* and BS 6535: 1989– *Fire Extinguishing Media*, Part 3: 1989 *Specification for Powder*.

The use of dry chemicals has been developed particularly in Germany, wher some large fixed and mobile systems have been used. Since with dry chemicals it is essential to apply enough agent to extinguish the fire outright, their use on large fires requires the availability of large quantities.

16.29.1 Mechanisms of fire extinguishment

The principal mechanism by which dry chemicals act against fire is to cause chain termination of the combustion reactions. There are several other less significant mechanisms. The bicarbonate chemicals release carbon dioxide in an endothermic reaction. To some extent the gas evolved blankets the liquid and the gas evolution reaction has a cooling effect, whilst the particle cloud reduces the heat transfer between the flame and the liquid surface.

Treatments of the inhibition mechanisms and general theory of dry chemicals are given by Laffitte *et al.* (1965), Laffitte and Bouchet (1959), Dewitte, Vrebosch and van Tiggelen (1964), Birchall (1970), Iya, Wohowitz and Kaskan (1975), McHale (1975), Spence and McHale (1975), Vanpee and Shirodkar (1975), Mitani (1981, 1982, 1983) and Mitani and Niioka (1982).

The combustion chain reactions are broken by adsorption on solid surfaces. Thus for a given material a large powder specific surface enhances the effectiveness. Haessler (1986) states that best results are obtained with a particle size range of 10–75 μm with a median size of 20–25 μm.

16.29.2 Types of dry chemical

Some basic dry chemicals are (1) sodium bicarbonate (standard dry chemical), (2) potassium bicarbonate, (3) potassium chloride, (4) urea potassium bicarbonate (5) monoammonium phosphate. There are also the formulations (6) general purpose powder (ABC) and (7) Monnex powder.

Standard dry chemical consists principally (over 90%) of sodium bicarbonate with additives to improve fluidity, non-caking and water repellent characteristics. Potassium bicarbonate formulation, however, are also used and are about $1\frac{1}{2}$–2 times as effective as those with the sodium bicarbonate base.

General purpose powder is a mixture of ammonium dihydrogen phosphate, diammonium hydrogen phosphate and ammonium sulfate.

Monnex is a potassium alkali based material. The particles disintegrate in contact with the flames and thus give a greatly enhanced surface area. Its effectiveness is about 5–6 times that of standard dry chemical.

16.29.3 Properties of dry chemicals

Dry chemical formulations may be ranked in respect of their effectiveness in extinguishing fires according to their performance in test. This performance is a function both of the chemical composition and the particle size.

Some types of dry chemical based on sodium or potassium bicarbonate are not compatible with foam. The dry chemical, and particularly the additives, tend to break down the foam bubbles. However, foam-compatible forms for dry chemical are also available.

In storage, dry chemicals are stable at normal and low temperatures but deteriorate at high temperature. Haessler quotes an upper temperature for storage of 120°C. Different dry chemicals should be segregated. Mixing of alkali and acid agents can result in release of carbon dioxide, and incidents have occurred where extinguishers have exploded.

16.29.4 Hazards associated with dry chemicals

One hazard from the use of dry chemicals is that due to the sudden release of the agent. Another hazard is unexpected reignition. The main toxic hazards following the use of dry chemicals will generally be those due to the combustion process. Dry chemicals themselves are non-toxic.

16.29.5 Delivery systems for dry chemicals

Dry chemicals are delivered to the fire mainly by fixed systems, from cylinders or by mobile systems. They are also on of the agents used in portable extinguishers. Delivery from cylinders is by hand held hose line.

16.29.6 Applications of dry chemicals

Dry chemicals are used to extinguish fire. They are utilized on class A fires (combustible materials), Class B fires (flammable liquids) and Class C fires (electrical equipment) in the NFPA classification. With regard to the latter, dry chemicals tend to be somewhat corrosive and to insulate contact surfaces. They are not suitable, therefore, for fires in delicate electrical equipment but can be used on fire of equipment such as transformers and circuit breakers.

Dry chemicals are an extremely versatile type of agent. They are low hazard and non-toxic. They can deal with a wide range of fires. They find application to extinguishment of large outdoor fires, to protection of spaces indoors and in portable extinguishers.

A dry chemical agent acts by extinguishing the fire in a single shot. In this it can be extremely effective. It is necessary, however, to use sufficient powder to ensure that the flame is completely extinguished. Otherwise once the powder is exhausted reignition is liable to occur. A dry chemical has little cooling effect and does not leave behind an inert atmosphere.

There are also other potential causes of reignition when a dry chemical is used. Vapours from a flammable liquid may be reignited by a hot surface, a combustible solid may be reignited by smouldering material and an electrical fire may reignite due to continued arcing.

If the fire is one in a combustible material and there is no reason why water should not be used, it may be advisable to use follow up with water to complete the extinguishment of the fire.

16.29.7 Fixed dry chemical systems

Fixed dry chemical systems may be (1) total flooding systems or (2) local application systems. A fixed system may be supplemented by hand held hose lines from cylinders.

16.30 Fire Protection Using Vaporizing Liquids

Another type of firefighting agent is the vaporizing liquid. Accounts of vaporizing liquids include *Halogenated Fire suppressants* (Gann, 1976) and those by Burgoyne and Richardson (1949a), Rasbash (1968), Hirst (1974a,b), Boughen (1979, 1982), Forrester (1982), Peissard (1982), Capper (1983), C.C. Grant (1985), Hoskins (1985), R.J. Martin, Shepherd and Hamlin (1986), Goodall (1988), Boyce (1990) and Senecal (1992a,b). Fire protection using vaporizing liquids is treated in the NFPA *Handbook* by D.W. Moore (1986).

Relevant codes and standards are NFPA 12A: 1992 *Halon 1301 Fire Extinguishing Systems*, NFPA 12B: 1990 *Halon 1211 Fire Extinguishing Systems*, NFPA 2001: *Clean Agent Fire Extinguishing Systems*, BS 5306: 1976– *Fire Extinguishing Installations and Equipment on Premises*, Part 5: 1982– *Halon Systems* and BS 6535: 1989– *Fire Extinguishing Media*, Part 2: 1989– and *Halons*, Section 2.1: 1989 *Specification for Halon 1211 and Halon 1301* and Section 2.2: 1989 *Code of Practice of Safe Handling and Transfer Procedures*.

16.30.1 Mechanisms of fire extinguishment

Vaporizing liquids act against fire by essentially the same two mechanisms of interruption of the chain reactions and of blanketing. Treatments of the inhibition mechanisms and general theory of vaporizing liquids are given by Belles and O'Neil (1975), Spence and McHale (1965), W.E. Wilson, O'Donovan and fristrom (1969), Dixon-Lewis and Simpson (1977), P.F. Thorne (1978b), Westbrook (1982c) and Mitani (1983).

16.30.2 Types of vaporizing liquid

The substances used as vaporizing liquids are halogenated hydrocarbons. They include the following classes: halon (H), hydrofluorocarbon (HFC), hydrochlorofluorocarbon (HCFC) and perfluorocarbon (PFC). The halons contain bromine and the perfluorocarbons contain fluorine as the only halogen.

Prominent halons are:

Halon 1211 Bromochlorodifluoromethane (BCF) CF_2ClBr
Halon 1301 Bromotrifluoromethane (BTM) CF_3Br

HCFCs include:

HCFC-22 Chlorodifluoromethane $CHClF_2$
HCFC-124 Chlorotetrafluoroethane C_2HF_4Cl

Vaporizing liquids are available which are much more effective extinguishants than carbon dioxide. Table 16.87 shows the relative effectiveness of various vaporizing liquids in extinguishing a hexane test fire (Hearfield, 1970). Whereas a concentration of 28% was required for carbon dioxide, the concentrations required with the vaporizing liquids were as shown in the table.

One of the most efficient extinguishing agents is Halon 1301. The relative fire extinguishing capability of other vaporizing liquids may be expressed in terms of the relative mass extinguishing efficiency (RMEE), defined as the ration of the mass extinguishing concentration of the agent

Table 16.87 *Extinction of hexane test fire by vaporizing liquids (after Hearfield, 1970)*

		Hexane fire extinction (%v/v)
Bromochlorodifluoromethane (BCF)	$CBrClF_2$	5.2
Dibromodifluoromethane	CBr_2F_2	3.6
Trifluoromethyl bromide	CF_3Br	4.2
Chlorobromomethane	CH_2ClBr	6.4
Methyl bromide	CH_3Br	7.7
Carbon tetrachloride	CCl_4	9.9

to that of Halon 1301 in a standard test. One such standard test is the ICI cup burner test.

Halon 1211, or bromochlorodifluoromethane (BCF), is now the principal vaporizing liquid. A comparison at 20°C of Halon 1211 with carbon dioxide shows that the specific gravities relative to air are 6.35 and 1.52 and the vapour pressures 2.61 and 57.2 bar, respectively. Thus BCF gives a better blanketing action and does not require such high strength containers.

Halon 1211 is a very effective extinguishing agent for flammable liquid and electrical fires. It is electrically non-conducting. Its cooling capacity, however, is low (latent heat 134 kJ/kg). It is capable, therefore, of dealing with a small solids fire but not with a large one.

Most Halon 1211 and Halon 1301 systems are of the total flooding type used to protect an enclosed space. The concept is that the halon is injected into the space and develops an approximately uniform concentration capable of extinguishing a fire anywhere in the enclosure. The alternative method of deployment of halon systems in local application in which the jet of halon is directed at the seat of the fire.

It is usually desirable to follow up the extinction of fire by Halon 1211 with water of foam cooling. This does not apply, however, to electrical fires or to situations where electrical equipment is near the seat of the fire.

16.30.3 Properties of vaporizing liquids

Vaporizing liquids may be ranked in respect of their effectiveness in extinguishing fires according to their performance in tests. There are numerous tabulations of relative effectiveness in particular tests.

Properties of a vaporizing liquid which bear on its effectiveness as a fire fithting agent include (1) chemical action, (2) vapour pressure and (3) density.

The ability to arrest combustion by interfering with the chain reactions is obviously a prime property.

The vapour pressure is significant in several respects. It determines the ability of the agent to discharge under its own pressure, the extent to which the flow in the pipework is two-phase and the behaviour of jet.

The density of the agent affects the mixing in the space into which is it discharged.

Compatibility with foams is another relevant property of vaporizing liquids.

In storage, early vaporizing liquids tended to give rise to corrosion problems. Halon 1301 and Halon 1211 have little corrosive action, provided that free water is not present.

16.30.4 Hazards associated with vaporizing liquids

There are certain toxic hazards associated with the use of vaporizing liquids. These include the toxic effects of (1) the agent, (2) the breakdown products of the agent and (3) the combustion products of the fire.

The first vaporizing liquid used was carbon tetrachloride, which is toxic. It was superseded by methyl bromide, which is highly toxic. Dibromofluoromethane is a convulsant. Chlorobromomethane is moderately toxic and produces narcosis. Bromochlorodifluoromethane (BCF) has a low acute toxicity. Bromotrifluoromethane (BTM) has an even lower acute toxicity, but also a very low boiling point (−58°C), so that contact can cause freezing of the skin and eyes by evaporation.

Vaporizing liquids give rise to decomposition products in fires. Halon 1211 yields the products hydrogen chloride, hydrogen bromide and hydrogen fluoride, which are extremely irritating to the eyes, nose and throat.

D.W. Moore (1986) gives the following approximate lethal concentrations of the natural vapour and of the decomposed vapour for a 15 min exposure:

	Lethal concentration (ppm)	
	Natural vapour	*Decomposed vapour*
Methyl bromide	5,900	9,600
Bromochlorodifluoromethane	324,000	7,650
Bromotrifluoromethane	832,000	14,000

The toxicity of the combustion products of the fire is another significant factor in firefighting using vaporizing liquids.

16.30.5 Delivery systems for vaporizing liquids

Vaporizing liquids are delivered to the fire mainly by fixed systems. They are the agents used in portable extinguishers. Vaporizing liquids are less suitable for delivery from cylinders by hand held hose line or from mobile equipment. In addition, vaporizing liquids are used in fixed systems to suppress combustion inside plant.

16.30.6 Applications of vaporizing liquids

Vaporizing liquids are used to extinguish fires. They are utilized for this purpose in enclosed spaces, and in portable extinguishers. They are also used to suppress incipient combustion inside plant.

16.30.7 Fixed vaporizing liquid systems

Fixed vaporizing liquid systems may be (1) total flooding systems or (2) local application systems.

The hydraulics of some vaporizing liquid systems may involve two-phase flow. Although Halon 1211 can usually be treated as a single liquid phase in the pipework, Halon 1301, which exists as a single liquid phase in storage, begins to vaporize as it travels down the pipe. The flow characteristics of halon systems are discussed by Williamson (1976) and Wiersma (1978). Computer programs for halon hydraulics have been developed by suppliers.

Halon systems tend to be subject to corrosion. The problem is discussed by Peissard (1982).

16.30.8 Vapour retention tests

A feature of interest for a space protected by a halon system is the retention time of the halon. A method for the

determination of this has been developed by the NFPA based on its Enclosure Integrity Test. In this integrity, or pressure, test, portable fan equipment is used to create a pressure difference between the protected volume and the surrounding space. Measurements are made from which the effective leakage area of the enclosure can be estimated. This is then used to calculate the halon retention time. Vapour retention tests are discussed by Genge (1989), Sreeves (1989) and Whiteley (1989).

16.30.9 Precautions

As stated earlier, guidance on the precautions to be taken to counter the toxic and asphyxiation hazards of halon and of inert gas extinguishing systems is given in GS 16. There are a number of general precautions to be taken with any gaseous extinguishing system. If the system is an automatic one activated by rapid response fire detectors, two separate detection signals should be provided in order to reduce the frequency of false activations. The space protected should be provided with warning signs at all entrances. There should be an indication as to whether the system is set for manual or automatic activation.

If the system is a manually activated one, the release devices should be so located such that the person operating the device is not at risk from the fire or the discharge of the agent. For a total flooding system, activation of the system should be accompanied by an audible alarm distinct from the fire alarm. The entrances should have continuous warning signs which remain on until the space has been certified as fit to re-enter. There should be suitable escape routes. The space should be provided with adequate means of ventilation after a fire and/or discharge of the agent.

The installation should be covered by a safe system of work. The system should be subject to regular inspection by a competent person. GS 16 states that such an inspection should be done not less than twice a year and should result in an inspection report. It also details the precautions to be taken during maintenance. One measure required is the provision of a means of isolating the agent storage tank for maintenance or other circumstances where normal escape might be difficult.

GS 16 gives guidance on the selection of the agent and the system. The choice should have regard to the hazards to personnel. A local application system tends to involve less risk of personnel being trapped and may be preferable in some circumstance. If a total flooding system is used, the volume of the space protected should be kept to a minimum and the design should avoid excessive concentrations of the agent.

Account should be taken of the possibility that discharge of the agent may raise a dust cloud, with the attendant risk of a dust explosion.

With regard to the precautions which relate specifically to the agent, for a total flooding system using Halon 1211 the system should ensure that discharge does not occur whilst personnel are present. For a local application system for Halon 1211 the requirement is to design so that there is no foreseeable risk of a hazardous concentration being produced.

For Halon 1301 the precautions required are related to the concentration of the agent which may be attained. GS 16 states that, provided the concentration of this halon will not exceed 6%, and subject to certain other qualifications, an automatic total flooding system may be used to protect a normally occupied space. The space should be evacuated before the concentration of Halon 1301 exceeds 6%. It may be appropriate to incorporate a short time delay and predischarge alarm, but in order to ensure rapid response to the fire, the delay should not usually exceed 30 s.

16.30.10 Halon phase-out

The discovery by Molina and Rowland (1974) that chlorine can act as a catalyst for the conversion of ozone to molecular oxygen in the upper atmosphere initiated a growing concern for the state of the ozone layer. It was subsequently shown that halons have a particularly damaging effect.

This has led to the Montreal Protocol on Substances that Deplete the Ozone Layer, 1987, which lays down a programme for the phasing out of halons. Amendments to the treaty have been made at meetings in 1990 and in November 1992. Accounts of the Montreal Protocol and its implications for halon systems are given by Senecal (1992a,b), Hough (1993) and Simmonds (1993). The halons discussed are primarily Halon 1211 and Halon 1301. The original Montreal Protocol provides that the production of halons be reduced to 50% of the 1986 level by 1994 and to 0% by 1999.

With regard to the continued use of existing halon systems and to the recycling of halons for use in such systems, national policies vary. Germany has banned the use of halon firefighting systems. According to Simmonds, in the absence of a suitable halon destruction technology, it is current policy not to dismantle the systems or return them to the suppliers but to let them remain on site capped off.

In the United States, it is government policy to permit continued use of existing systems and the recycling of halons for use in such systems.

The United Kingdom also is evidently moving towards a policy of permitting continued use of existing systems, as evidenced by the HSE draft guidance on *Gaseous Fire Extinguishing Systems*.

Amendments to the Montreal Protocol also cover HCFCs, the production of which is to be frozen at 1989 levels and phased out by 2030, or possibly earlier.

16.30.11 Halon replacement and clean agents

The demise of the use of halons has led to a search for alternatives. These alternatives include both other vaporizing liquids and agents other than vaporizing liquids. Alternatives to halons have been reviewed by the Halons Technical Options Committee (G. Taylor, 1991) of the UN Environment Programme (UNEP). Other accounts of alternatives include those by Senecal (1992a,b), Hough (1993), McKay (1993) and Simmonds (1993). NFPA 2001: 1994 deals with clean agent alternatives to halons.

A review of vaporizing liquids used or proposed for use as fire extinguishing agents is given by Senecal (1992b), who covers HCFCs, HFCs and PFCs as well as CO_2, with a comparative tabulation of relevant properties and a detailed discussion of each agent.

Hough (1993) also reviews alternatives, but ranges more widely, from designing out of the need, through other vaporizing liquids, notably HCFCs, to foam, dry powder and fogging systems.

An account of work on the later has been given by McKay (1993). Building on research on burner nozzle technology, a fine water spray system has been developed which uses water droplets in the diameter range 80–200 μm and is

claimed to be a highly effective suppressant alternative to halons.

16.31 Fire Protection Using Inert Gas

The last of the principal firefighting agents is inert gas. Here a distinction needs to be made between the use of inerting of equipment to prevent internal fire or explosion, as described in Chapter 17, and the use of inert gas to extinguish fire, which is considered here.

Accounts of the use of inert gas for fire extinguishment include those by Burgoyne, Katan and Richardson (1949b), McGuire (1864) and Bryant (1991). Fire protection using inert gas is treated in the NFPA *Handbook* by P.F. Johnson (1986) and, for carbon dioxide, by Williamson (1986).

Relevant codes and standards are NFPA 12: 1993 *Carbon Dioxide Extinguishing Systems* and BS 5306: 1976– *Fire Extinguishing Installations and Equipment on Premises*, Part 4: 1986 *Specification for Carbon Dioxide Systems* and BS 7273: *Code of Practice for the Operation of Fire Protection Measures*, Part 1: 1990 *Electrical Actuation of Gaseous Total Flooding Extinguishing Systems*.

16.31.1 Mechanisms of fire extinguishment

Extinguishment of fire by an inert gas is effected by reducing the concentrations both of the fuel and of oxygen. Design of an inert gas system is based on reducing the concentration of oxygen below that which will support combustion. A further, more recently favoured, mechanism is the reduction of the flame temperature below that necessary for combustion – the thermal ballast effect.

Inert gas also has a cooling effect. A large mass flow of gas over a liquid surface can be beneficial in preventing ignition when the discharge ceases and the liquid again comes in contact with air.

These latter mechanisms indicate that it is desirable that the inert gas have a high heat capacity.

16.31.2 Types of inert gas

The principal individual inert gases used in fire protection applications are carbon dioxide and nitrogen. Use is also made of inert gas mixture formulations.

16.31.3 Properties of inert gas

Properties of an inert gas relevant to its use fire protection include (1) its density, (2) its vapour pressure, (3) the minimum concentration required for extinguishment and (4) its gas specific heat.

The density of the gas affects both its 'throw' and its subsequent flow.

The vapour pressure is relevant to the ability of the gas itself to provide the pressure necessary for discharge. An advantage of carbon dioxide, for example, is that its vapour pressure at room temperature is high enough to give satisfactory discharge.

The minimum concentration for extinguishment sets the lower limit of concentration of inert gas to be used. Information on this minimum concentration has been given by Coward and Jones (1952 BM Bull. 503), and has been widely reproduced. Values for carbon dioxide are tabulated by Williamson (1986).

As just indicated, a high gas specific heat is beneficial in that it enhances the thermal ballast and cooling effects of the inert gas. This is one of the advantages of carbon dioxide with its high heat capacity.

16.31.4 Hazards associated with inert gas

The two principal inert gases used are carbon dioxide and nitrogen. Carbon dioxide is mildly toxic, but the main hazard with both gases is hat of asphyxiation. This hazard is present in all fire situations, but insofar as the extinguishment of fire requires high concentrations of inert gas the hazard is enhanced.

The density of the gas is relevant to the asphyxiation hazard; the density of nitrogen is close to that of air, whilst that of carbon dioxide is appreciably greater, so that it may accumulate in low lying spaces.

16.31.5 Delivery systems for inert gas

Inert gases are delivered to the fire by fixed systems, but not normally by mobile systems. The inert gas carbon dioxide is one of the agents used is portable extinguishers. In some cases hand held hose liens from cylinders are used to supplement a fixed delivery system.

16.31.6 Applications of inert gas

Inert gases are used to extinguish fires. They are utilized for this purpoe in enclosed spaces, and in portable extinguishers.

16.31.7 Fixed inert gas systems

Inert gases are used in (1) total flooding systems, (2) local applicaton systems and (3) hand held hose lines.

In a total flooding system the inert gas is injected into an enclosure in sufficient quantity to ensure the minimum concentration for extinguishment.

In a local application system a jet of inert gas is directed at the surface protected, which is typically a tank surface but may also include the adjacent floor area. There is a minimum discharge time for effective extinguishment, that recommended for carbon dioxide being 30 s.

For carbon dioxide, hand held hose lines from cylinders are also used.

16.31.8 Precautions

The precautions given in GS 16 for halon and inert gas extinguishing systems have been outlined in the previous section. Those for an inert gas are broadly similar to those for Halon 1211. The essential requirement is to ensure that operation of the system does not expose personnel to hazardous concentrations. For a total flooding system this means that the arrangement should prevent the system from operating when personnel are present, whilst for a local application system the requirement is to design so that there is no foreseeable risk of a hazardous concentration being produced.

16.32 Fire Protection Using Special Methods

In addition to the methods just described, there are also several special methods of fighting fires. They include the use of (1) solids and powders, (2) wet water or wet water foam and (3) combined agent systems. Fire protection using such special methods is treated in the NFPA *Handbook* by P.F. Johnson (1986).

16.32.1 Solids and powders

In addition to dry chemicals, use is also made of various kinds of dry powder, sand and other solid materials. One group of solid agents comprises those used for metal fires, for example, talc, soda ash and graphite.

Another solid agent is glass granules used for the control of LNG bund fires (Lev, 1981). The granules are stores within the bund and, when an LNG spill occurs, they float to the top. The mechanism of action is reduction of the radiation from the flame to the surface and thus of the evaporation of the fuel.

A third solid agent is carbon microspheres used for extinguishment of metal fires (McCormick and Schmitt, 1974).

Treatments of the extinguishment mechanisms of dry powders, including inert particulates, are given by Dolan (1957), McCamy, Shoub and Lee (1957), Morikawa (1976) and G. Russell (1977).

The provision of sand buckets for dealing with small fires has long been common practice on process plant. Sand is also used for diking in, and thus containing, liquid spillages.

16.32.2 Wet water and wet water foam

A second special method is the use of wetting agents to modify the properties of water, thus producing 'wet water'. A relevant code is NFPA 18: 1990 *Wetting Agents*.

In this context a wetting agent is one which, when added to water, effects a substantial change in its surface tension, thus increasing its ability to penetrate and spread. The wetting agent may also impart emulsifying and foaming characteristics.

The use of a wetting agent makes the water more 'effective' so that less is needed. This is of particular value in firefighting where water is in short supply. A typical application is to forest fires.

If the wetting agent has suitable foaming qualities, a wet water foam is produced.

Fixed water sprinkler and water spray systems, as described in NFPA 13 and NPFA 15, may be designed to operate on wet water.

16.32.3 Combined agent systems

A third special method is the use of a combination of agents. An early application of the combined agents technique was the use during World War II of a combination of carbon dioxide and foam to attack a spill of aviation fuel from an aircraft and so rescue the aircrew.

Some agent combination used are (1) water and foam, (2) carbon dioxide and foam and (3) certain dry chemicals and foam. Thus foam is prominent as one of the agents in such combinations.

In some cases the agents are applied simultaneously, in others they are used in rapid succession. A typical case of the application of a dry chemical and foam combination might be to extinguish fire on a flammable liquid by a large but short discharge of dry chemical and then to blanket the liquid with foam to prevent reignition.

16.33 Fire Protection Using Portable Extinguishers

So far only passing reference has been made to portable fire extinguishers. These are, however, another important resource for fire protection. Accounts of portable fire extinguishers are given by Guccione (1961), Guise and Zeratsky (1965, 1982) and P. Nash (1969, 1991). Fire protection using portable fire extinguishers is treated in the NFPA *Handbook* by M.E. Petersen (1986a,b).

Relevant codes and standards are NFPA 10: 1990 *Portable Fire Extinguishers* and BS 5423: 1987 *Specification for Portable Fire Extinguishers* with its associated standard BS 6643: 1985– *Recharging Fire Extinguishers*. There are also a number of Underwriters Laboratories (UL) standards.

It is a fundamental principle of firefighting that a fire should be hit hard and quickly, preferably before it has a chance to take hold. Usually the time which elapses before the fire brigade arrives is measures in minutes, even tens of minutes, and by then the fire may be well developed. For some hazardous items prompt response can best be achieved by an automatic fire protection system. For others, portable fire extinguishers provide the necessary means.

Conditions for success in the use of portable fire extinguishers are that the fire be small, that extinguishers be accessible, that they be of the right type, that they operate when activated and that personnel capable of using them are present.

These conditions have a number of implications. The potential sources of fire need to be idenftified and extinguishers with appropriate agents located at suitable points. The selection and maintenance of the extinguishers should take account of any potential unrevealed failure. Personnel should be trained in their use.

Fires of combustible materials (NFPA Class A), flammable liquids (Class B), electrical equipment (Class C) and metals (Class D) can all be dealt with by the use of suitably chosen portable fire extinguishers.

Principal agents used in portable fire extinguishers are (1) water, (2) foam, (3) carbon dioxide, (4) dry chemicals, (5) vaporizing liquids and (6) dry powders. Broadly, water is used on Class A fires and foam (AFFF) on Class B fires. Carbon dioxide and suitable dry chemicals and vaporizing liquids (Halon 1211) are used on fires of Classes A–C and dry powder is used on Class D fires. Some dry chemicals are suitable for fire Classes B and C and others for Classes A–C. A detailed tabulation of agents and their applications is given by M.E. Petersen (1986b).

There are several different principles of operation of a portable fire extinguisher. For water and foam extinguishers the three traditional types have been: (1) stored pressure, (2) pump tank and (3) inverting. In a stored pressure type the agent is expelled by an expellant gas held in the same chamber. In a pump tank type expulsion of the agent is effected by pressure generated by operation of the hand pump. The inverting type has been obsolete for some years; manufacture in the United States ceased in 1969. The agents used only in this type, soda acid and foam, have also become obsolete.

Other portable extinguishers utilize (1) stored pressure, (2) cartridge or (3) self-expulsion methods. As just explained, in the stored pressure type, the agent and expellant gas are held in the same chamber, whilst in the cartridge type the expellant is held in a separate cartridge. Dry chemical extinguishers use both stored pressure and cartridge methods. Halon 1211 extinguishers tend to use stored pressure. In carbon dioxide extinguishers the agent is self-expelling.

16.34 Fire Protection Applications

Firefighting applications in process plant may be classified according to the material on fire or according to the plant and storage protected. The applications considered here are, by material, (1) combustible solids fires, (2) flammable liquid fires, (3) electrical fires and (4) metal fires and, by plant or storage (1) storage tanks and (2) warehouses.

16.34.1 Combustible solids fires

A type of fire common in all occupancies is a combustible solids fire (NFPA Class A). In the process industries

combustible solids occur in bulk and powder forms both in process and in storage. Process operations which typically involve combustible solids include dust handing plant, conveyors and packaging plant. Storage sites such as silos and warehouses may contain large quantities of combustible solids.

There are a number of NFPA codes covering particular solid materials. They include NFPA 43A (oxidizers), NFPA 43B (organic peroxides), NFPA 490 (ammonium nitrate), NFPA 654 (powders and dusts) and NFPA 655 (sulfur). Other NFPA codes for metals are given in Subsection 16.34.4.

Fixed fire protection systems are provided in selected cases. The design options depend on the situation. For example, a total flooding design is practical only if the solids are being handled in an enclosure and it will not endanger personnel.

Where solids are handled indoors, regard should be had to the potential difficulties of fighting the fire once it has taken hold and is producing large volumes of smoke. It may be only minutes before entry into the building becomes impossible. This implies that any fixed fire protection system should respond rapidly and strongly.

The fire protection of warehouses is considered further in Subsection 16.34.7.

16.34.2 Flammable liquid fires

Another type of fire common in the process industries particularly is a flammable liquids fire (NFPA Class B). Process industry activities involve the processing and storage of a wide variety of flammable liquids. Storages may contain large quantities of flammable liquids.

Fixed fire protection systems are provided for process operations and areas vulnerable to releases and spills, for loading and unloading facilities and, above all, for storage tanks and vessels. Storage tanks are commonly provided with a bund. It is therefore necessary to protect not only against a fire in the tank itself but also against one in the bund.

The fire protection of storage tanks in general is considered further in Subsection 16.34.6. Further accounts of the protection of particular types of storage tank such as LPG, LNG and ammonia tanks are given in Chapter 22.

16.34.3 Electrical fires

There are also certain special types of fire that require treatment, once of which is the electrical fire (NFPA Class C). If electrical equipment is involved in a fire on a process plant, this is generally due to an explosion at the equipment itself or to a spread of a fire from the rest of the plant. If there is a fire at a piece of live electrical equipment, it is usually appropriate to de-energize the equipment, unless there are good reasons for not doing so.

In respect of fire, electrical equipment may be divided into (1) equipment which has exposed contacts and (2) equipment such as transformers and circuit breakers.

Among the agents used on electrical fires are water, dry chemicals, vaporizing liquids and inert gases, but not all agents are suitable for every type of electrical fire.

Water as a continuous jet conducts electricity and should not be used in this form on electrical fires. In the form of spray, however, this hazard is much less and is generally negligible (O'Dogherty, 1965).

Some electrical equipment is protected using a fixed water spray system. Water sprays are used, for example, to protect against fires in oil cooled electrical equipment such as transformers, Such a fire is generally the result of an electrical breakdown which causes an explosion. Such mixed fires of hot oil and hot metal are difficult to handle. Typically the oil is being pumped over metal surfaces which become hot and sustain the fire. It is important, therefore, to ensure that such situations are detected and dealt with as early as possible, The protection of such electrical equipment with water sprays is a specialist matter. It is discussed by P. Nash (1974a).

Fixed systems for the protection of electrical equipment tend to use dry chemicals of carbon dioxide. As already stated, the former is not suitable for equipment with exposed contacts which are liable to suffer adhesion and corrosion. Fires of electrical equipment are mainly fought using portable carbon dioxide or dry chemical extinguishers.

16.34.4 Metal fires

Another type of fire which requires special treatment is metal fires (NFPA Class D). Accounts of metal fires and methods of dealing with them are given by Reuillon *et al.* (1977), Sharma, Lal and Singh (1987), Varshney, Kumar and Sharma (1990), Cardillo and nebuloni (1992) and Sharma, Varshney and Kumar (1993). Metal fires are treated in the NFPA *Handbook* by Prokopovitsh (1986) and by P.F. Johnson (1986).

The NFPA codes on the storage of certain metals are of some relevance. These are NFPA 48 (magnesium), NFPA 481 (titanium) and NFPA 482 (zirconium).

Metal fires involve a number of hazards. Characteristic hazards are (1) extremely high temperatures, (2) steam explosion and (3) hydrogen explosion, as well as the usual hazards of (4) toxic combustion products and (5) oxygen depletion.

Extinguishment of a metal fire is not always achievable and it may be necessary to settle for control of the fire. The agent used should be matched to the metal: an agent suitable for dealing with a fire of one metal may be quite unsuitable for that of another. Water should not be used on a sodium fire, and a vaporizing liquid should not be used on a magnesium fire. That said, there are some powder agents which are suitable for fires of several metals, as described below.

Combustible metal extinguishing agents are classified according to whether they are (1) approved or (2) proprietary. Approved agents are those proprietary agents which are tested and approved by organizations such as the UL. There are also proprietary agents and non-proprietary agents.

Prominent proprietary agents are Pyrex G1 powder, which is a coke powder with an organic phosphate additive. Metalguard powder has a similar formulation. Another agent is Met-L-X powder, which has a sodium chloride base, again with additives. Prokopovitsh gives a tabulation of the comparative capabilities of G1 and Met-L-X powders in dealing with fires of a number of metals, including aluminium, magnesium, sodium, potassium, titanium, zirconium and lithium. He also discusses the use of other proprietary agents and of non-proprietary agents such as talc powder, soda ash, salt and sand.

16.34.5 Storage tanks

Turning to the fire protection of particular plant and storage, protection of storage tanks is a prominent theme. Accounts of fire protection of storage tanks and bunds are

given by A.H. Warren (1966), Hearfield (1970), J.R. Hughes (1970), Vervalin (1973f). P. Nash and Young (1975 BRE CP42/75), Peyton (1984) and M. Wilson (1993) Fire protection of storage tanks is treated in the NFPA *Handbook* for flammable liquids by M.F. Henry (1986) and for chemicals by Bradford (1986b).

Relevant codes and standards for storage tanks, including low temperature storages, are NFPA 30: 1990, API Std 620: 1990 and API Std 650: 1993, and BS 799: 1972–, BS 2654: 1989, Bs 4741: 1971 and BS 5387: 1976. There are also codes for the Storage of particular chemicals such as NFPA 43A: 1990, which covers liquid oxidizers.

Fire protection of a storage tank needs to address several different scenarios: (1) a fire near to the tank, (2) a fire in the top of the tank and (3) a fire in the bund. There are therefore requirements for exposure protection by cooling of the tank and for fire extinguishments and control in the tank itself, in the bund and of a liquid spill outside the bund.

Among the facilities which may be provided for the fire protection of a storage tank are (1) fire resistant thermal insulation or fire insulation, (2) a fixed water system for cooling, (3) a fixed foam system for the tank top, (4) a fixed foam system for the bund, (5) fixed water/foam monitors and (6) mobile water/foam monitors, There may also be a role for fixed water spray systems for the extinguishments and control of liquid spills.

Foam systems for storage tanks have been discussed in section 16.28. A further account of fire protection of storage tanks is given in Chapter 22. Firefighting on storage tanks is discussed in the next section.

16.34.6 Storage vessels

The fire protection of storage vessels, particularly those containing liquefied flammable gas, is equally important. Accounts of the fire protection of storage vessels are given by Petitit (1945), Bray (1964, 1966), Chaillot (1966), the FPA (1966), ICI/RoSPA (1970 IS/74), Eijnhoven, Nieuwenhuizen and Wally (1974), I. Williams (1984) and B.M. Lee (1989). Fire protection of storage vessels for LFG is treated in the NFPA *Handbook* by walls (1986).

Relevant codes and standards for storage vessels for LFG are NFPA 54: 1992, NFPA 58: 1992, NFPA 50: 1990, NFPA 59A: 1990, the ASME *Boiler and Pressure Vessel Code*, Section VIII and BS 5500: 1991. NFPA 50: 1990 covers liquid oxygen and NFPA 50A: 1989 and NFPA 50B cover gaseous and liquid hydrogen, respectively.

Among the facilities which may be provided for the fire protection of a storage vessel are (1) drainage, including sloped ground, (2) fire resistant thermal insulation or fire insulation, (3) a fixed water system for cooling and (4) depressuring facilities.

A further account of the fire protection of storage vessels is given in Chapter 22.

16.34.7 Warehouses

Warehouses are another type of storage which contain large quantities of combustible material. The account here is limited to fire protection systems; a fuller account of warehouses, including prevention of fire, is given in Chapter 22.

Accounts of fire protection of warehouses include those by P. Nash (1972a, 1977), P. Nash, Bridge and Young (1974 BRE CP68/74), Bridge (1977), Young and Nash (1977), Parnell (1979), Field (1985), Murrell (1988) and Murrell and Field (1990).

Much of the work described by these authors was conducted at the Fire research Station, with one programme in the mid-1970s (e.g. FRS, 1972 Fire Res. Note 914, 916, 944; P. Nash, 1977) and another in the mid-1980s (e.g. Field, 1985; Murrell, 1988).

A relevant code is NFPA 231C: 1991 *Rack storage of Materials*.

The fire problem is particularly acute in automated high bay, or high rack, warehouses. The FRS work has shown that in such situations fire develops rapidly, with flames propagating upwards, mainly in the flues between adjacent pallets. The fire typically reaches the top of the rack within 2 min. It becomes virtually impossible to fight the fire by conventional means.

The earlier FRS programme also showed that conventional sprinklers with glass bulbs set to operate at 68° C do not respond quickly enough to counter the fire before it gains hold. An alternative system was developed in which the bays are zoned with setsof sprinklers dedicated to a zone and actuated by a fire detection wire 'laced' through the racking. This system was criticized as being too complex and liable to false alarms and was not taken up by industry.

The later programme, described by Field (1985), concentracted on the response of the sprinkler head. A solder-link sprinkler was identified which proved satisfactory. For a single localized ignition source the sprinkler system operated to extinguish the fire with a maximum water volume of 350 UKgal.

16.35 Firefighting in Process Plant

The foregoing account has described some of the passive measures used to prevent fire and to protect against it and some of the agents and equipment available for active measures of actual firefighting. It is now necessary to discuss some of the general principles underlying fire fighting in process plants, bearing in mind the wide variety of types of fire which may be encountered.

General accounts of firefighting are given in *Manual of Firemanship* (Home Office, 1974–), *Fire fighting in Factories* (HSE, 1970 HSW Bklt 10) and *Fire Attack, Fire Service Communications for Fire Attack and The Extinguishment of Fire* (NFPA, 1966/4, 1972/8, 1974/11). Firefighting in the process industries and with chemicals is discussed in *Fire Protection Manual for Hydrocarbon Processing Plants* (Vervalin, 1964a, 1973a) and the *Fire Training Manual* (PITB, 1975/6) and by several other authors, particularly Risinger (1964b,c,f,g).

In most firefighting operations on process plant it is necessary not only to fight the fire but also to protect the vessels exposed to it. This second activity is just as important as the first.

A fundamental principle of firefighting is to attack the fire at as early a stage as possible and to hit it hard. Once a fire is well established and has heated up large quantities of metal and liquids, it becomes much more difficult to contain it and prevent it growing. There are a number of case histories, described in Appendix 1, which illustrate the problems of firefighting in process plants.

16.35.1 Liquid fires

There are two important distinctions to be made in considering firefighting of burning liquids. One is that between (1) contained fires and (2) uncontained fires.

A liquid fire is contained if the liquid is held in a well-defined container such as a storage tank, bund or deep depression. In other situations, such as spillages or pools, the liquid fire is uncontained. In some cases it may even be flowing.

The other distinction is between fire of (1) high flashpoint liquids and (2) low flashpoint liquids. A liquid with high flashpoint can generally be extinguished by cooling with water, whereas one with a low flashpoint usually needs to be blanketed by foam or dry chemicals.

Contained fires of either high or low flashpoint liquids can normally be extinguished by foam. Fires of contained high flashpoint liquids can alternatively be extinguished by cooling with water.

With a highflash point product, such as refined oil, the rise in liquid temperature is generally confined to a layer of about 2 in. (5 cm) below the liquid surface, even when the liquid has been burning for a long time. In consequence, when water or foam is added, the heat in the liquid is generally not sufficient to cause an oil–water slopover, unless the surface is very close to the top of the container.

The fact that the bulk oil remains relatively cold means that it also possible to cool the surface layer by agitating the oil. This may be done, for example, by directing a fire water jet down into the liquid.

It sometimes occurs that a high flashpoint liquid is contaminated by error with some low flashpoint material. Usually the amount of contaminant does not exceed 5%. In such cases the more volatile material tends to burn off in the early stages of the fire, leaving an essentially high flashpoint liquid again.

With uncontained fires the first step is generally not to extinguish the fire but to cut off the flow of liquid from the containment. If such a fire is merely extinguished without cutting off the flow of fuel, there is a serious risk that it will re-ignite and cause a much larger fire or possibly an explosion. It is difficult to overemphasize the importance of this point. To quote Risinger (1964g): 'It is more important to know when not to put a fire out than to know the details of actual extinguishments.' With low flashpoint liquids the risks include that of a vapour cloud explosion.

Often the flow of liquid may be stopped by shutting off an emergency isolation valve. It is good practice that such valves should have remote operation for just this situation. Where it is necessary to approach the fire in order to close a valve, a water fog may be used to provide a shield from the heat.

Another device which may be adopted where a flammable liquid which has a density below that of water is flowing from a pipe connected to the bottom of a tank, is to inject water into the tank and so replace the liquid flowing through the pipe with water.

An uncontained fire of a high flashpoint liquid can generally be extinguished by the use of water. For a fire on a low flashpoint liquid, foam or dry chemicals should normally be used.

Often where dry chemicals are used, it is necessary to use water also. Although the former are effective in putting out the fire, there is generally a high risk of re-ignition from the metal which has been heated by the fire. Typically, it is necessary to apply water to cool this metal, then use dry chemicals to extinguish the fire, and then apply water to cool the liquid.

With dry chemicals the quantity which can be used and therefore the time of application are both strictly limited, the latter being generally of the order of some tens of seconds. It is essential, therefore, to put the fire out in the initial attack.

In some cases there are simultaneous contained and uncontained fires. A typical example is burning petroleum liquid flowing over the side of a storage tank. In such a case the procedure is to put out the uncontained fire first. If this is done, the uncontained part does not readily re-ignite because the more volatile components have already been burned off in the tank, whereas if the converse approach is taken, the spillage does tend to be re-ignited by flame travel over the liquid surface.

It is not always either practical or desirable to extinguish a liquid fire. It is generally impractical, for example, to extinguish a very large fire of LPG in an open container or spillage. Moreover, even if it were, extinction of the fire would create the risk of a vapour cloud explosion.

The procedure in such cases, therefore, is to cut off the flow of liquid to the fire, to cool the container and other exposed surfaces and to seek not to put out the fire itself but to control it. It is particularly important to cool the surface of tanks above the liquid level. If the fire is causing any blowtorch effect, the area affected by this should also be cooled.

The use of large quantities of water, or to a lesser extent foam, involves the hazard of spreading the fire by displacing and/or floating the burning liquid. This hazard should be borne in mind in firefighting operations.

Further information is given by Risinger (1964g).

16.35.2 LFG fires

Fires of liquefied flammable gas (LFG) are often fought using dry chemicals or foam, or both in combination. Although the extinction of fire is generally desirable, it may not always be appropriate or possible. It is nevertheless a worthwhile objective to control the fire and so reduce the heat radiation from it.

Large-scale tests on the effectiveness of foam and of dry powder on fires have been carried out as part of the experiments by MITI (1976), described earlier. In one test liquid ethylene was poured into a 3 m diameter bund with a wire netting cover and ignited. An attempt was then made to extinguish the flame using high expansion foam with an expansion ratio of 500 from fixed foam generators with a combined output of 200 m^3/min. The first foam generator was started 2 min after ignition and the second 1 min later. The rate of application of foam was 7.07 m^3/m^2 min. The foam brought the fire about 50% under control within about $3\frac{1}{2}$ min after ignition, and 80% under control just over 6 min after ignition. Thereafter the effectiveness of control remained unaltered. It was concluded that liquid ethylene fires can be kept under control using high expansion foam.

In another test the fire extinguishing agent used was dry powder of ammonium phosphate discharged from two vehicles near the bund. An initial discharge of dry powder for 7 s was observed to extinguish the fire, but a second discharge of 4 s was applied to make sure. The rate of discharge was 45 kg/s to an area of 20 m^2 and, assuming that 50–80% of the powder covered this area, the rate of application was 1.3–1.8 kg/m^2 s. This compares with a slightly higher rate of 2.4 kg/m^2 s reported from other Japanese work.

16.35.3 LNG fires

As already described, the quantities of LNG held in storage are very large. A fire on a large LNG spillage radiates

intense heat and can do extensive damage. The behaviour of LNG fires was discussed in Sections 16.11 and 16.17.

As stated above, firefighting will often be conducted with the aim of controlling rather than extinguishing the fire. The control of LNG fires has been the subject of investigations over a period of time and in a number of countries. Early work by Burgoyne and Richardson (1948) showed that foam forms a frozen blanket on burning liquid methane, leaving only small tears which can be readily extinguished with dry chemicals.

Small LNG fires can in fact be extinguished by most firefighting agents. Thus water, foam, dry chemicals, vaporizing liquids and carbon dioxide are all effective on fires sufficiently small to allow the whole area of the fire to be extinguished simultaneously.

With larger LNG fires the problem is more difficult. The feasibility of extinguishing large LNG fires has been a matter of doubt. Walls (1973), for example, states: 'Foams and water will not extinguish LNG fires.'

Dry chemicals can extinguish an LNG fire, but only if extinction is complete in the short application period, which is difficult to achieve. He continues: 'An LNG fire extinguishing system should be considered essentially as a fringe benefit which will be nice if it works but which a plant had better be able to do without.'

The limitation of the effects of LNG fires is described by Wesson *et al.* (1973a) as follows:

> Water has long been considered the prime – if not the only – agent suitable for controlling LNG fires. Water curtains and direct contact water sprays protect exposed structures until fire intensity is tolerable. However, for major LNG spills or tank fires the rate of water application required is unrealistic (30,000–50,000 gpm) if several proximate exposures require simultaneous protection from the high radiant heat fluxes, which can reach 10,000 BTU/h ft^2.

The control of LNG fires by agents such as foam or dry chemicals has thus contined to appear attractive.

Work at Lake Cahrles, Louisiana, in a 1961 on the extinction of LNG fires has been reported by Burgess and Zabetakis (1962 BM RI 6099). Tests were done using dry chemicals. The surface area of the burning liquid pools was 400 ft^2. Extinction was achieved using sodium and potassium bicarbonates at application rates of 0.14 lb/ft^2 s. In one test extinction was achieved in 3 s at this rate of application.

More recently an extensive series of tests on the extinction of large LNG fires conducted by the University Engineers has been sponsored by the American Gas Association (AGA) and has been reported by Wesson and co-workers. The control of LNG fires using foam is described by Wesson, Welker and Brown (1972) and Wesson *et al.* (1973a). Twelve tests were conducted, of which eleven were concerned with vaporization behaviour. The surface areas of the burning pools were in the range 400–1200 ft^2. The fire conditions were steady state with an evaporation rate of approximately 0.5 in./min from the spillage surface. It was found that high expansion foam was effective in bringing the fire under control and thus reducing heat radiation, although in the majority of cases the fire was not actually extinguished, and that a foam with an expansion ratio of 500 : 1 was the most suitable. The foam quickly froze in open cellular form at the foam–LNG interface, and was light enough to float on the LNG, but had sufficient structural strength to support several feet of additional foam without collapsing. A fire control time was defined as the time for the heat flux sensors to reach a new, reduced reading after initial application of the foam and while the foam was still being applied. Using a high quality foam with a 500 : 1 expansion ration, a fire control time of 120 s was achieved with a foam application rate of 8 cfm/ft^2. Reduction in heat radiation up to 97% were measured at a distance of about one fire diameter from the fire edge.

Wesson *et al.* (1973) also report work on the extinction of LNG fires using dry chemicals. The fire sizes were in the range 200–1200 ft^2. The dry chemical application rates and extinction times obtained for a 1200 ft^2 fire are given in Table 16.88. The work described applies to steady-state LNG fires with an evaporation rate of not more than 0.5 in./min. Immediately after a spillage the vaporization of LNG is very rapid. Even 1 min after the initial spillage and ignition, the evaporation rate could be 1 in/min on average dry soil, which is twice the long-term burning rate due only to heat transfer by flame radiation to the liquid surface.

The effectiveness of the firefighting agents depends on the fire conditions, including the weather, the ground and the process plant. The foregoing account should be regarded, therefore, only as a guide. Further details are given in the original paper.

16.35.4 Storage tank fires

The occurrence of storage tank fires was discussed in Section 16.11 and the pool fire characteristics of such fire Section 16.17. A fire in a storage tank which has lost its roof may be dealt with in two ways. One is to try to extinguish it; the other is to let it burn itself out. Such a fire is normally extinguished by the use of water or foam. The blanketing action of the latter is particularly effective against fires in open storage tanks.

There is a risk, however, that the addition of water or foam may cause a slopover of oil–water mixture. This can occur if there is a deep layer of hot oil at the burning liquid surface. Such a layer tends to develop in a crude oil but not in a refined one. The depth of the layer is greater after the fire has been burning some time. The hazard to slopover may be detected by such methods as the addition of small

Table 16.88 *Application rates for extinction of LNG fires by dry powders (after Wesson et al., 1973b)*

	Threshold rate		*Optimum rate*	
	Application rate (lb/ft^2 s)	*Extinction time* (s)	*Application rate* (lb/ft^2 s)	*Extinction time* (s)
Sodium bicarbonate (SB)	0.012	18	0.0192	9.0
Potassium bicarbonate (PB)	0.007	30	0.0125	8.2
Urea–potassium bicarbonate (U–PBP)	0.00275	25	0.00417	10.9

amounts of water to one edge of the tank or the use of a strip of water to one edge of the tank or the use of a strip of heat sensitive paint down the side of the tank. Methods of reducing the hazard include mixing the hot oil in the tank with cold oil, by pumping the liquid out and in again, or by using only small quantities of water or foam until frothing subsides. Alternatively, the fire may simple be allowed to burn itself out. Often it is possible to pump out most of the liquid in the tank to another receiver so that the scale and duration of the fire are much reduced.

As described in Section 16.17, in a storage tank fire a heat wave moves down through the liquid. The fire is sustained by a zone of liquid at the top which is at a higher temperature than the rest of the contents. This fact can be exploited to control a tank fire by agitating the liquid with air. The method is described by P.F. Johnson (1986).

Other fires at storage tanks include a fire or a liquid spillage at the base of the tank. In this case it is generally appropriate to attempt to extinguish the liquid fire or to run the burning liquid off while cooling the tank to prevent its overheating.

In general, the fighting of storage tank fires involved not only extinction of the fire itself but also protection of other exposed tanks. Suitable water application rates are given in Section 16.27.

Storage tank fires are discussed by Risinger (1964b, f).

16.35.5 Fog nozzles

There is a wide variety of nozzles which can be fitted to fire hoses. Accounts of such nozzles are given by Purington (1986) and Rosenhahn (1986).

In certain situations the requirement is not so much to project water onto the fire as to permit the firefighters to advance towards the fire. This might be the case, for example, where an attempt is to be made to shut a valve. In such cases use may be made of a fog nozzle, which is more fit for this purpose than a regular hose nozzle.

16.35.6 Water curtains

A technique which finds application in certain situations involving a leak or fire of a flammable material is the use of a water curtain. One application of a water curtain is to disperse a leak of flammable vapour, before it can ignite. This has been described by Beresford (1981) and is considered in Chapter 15. Although not strictly a firefighting measure, the deployment of a such water curtain is likely to be the responsibility of the works fire service and to be made in a fire situation.

Another use of water curtains is to attenuate the thermal radiation from a fire. Accounts are given by Stephenson and Coward (1987), Maini and Stephenson (1989) and Coppalle, Nedelka and Bauer (1993). The first two sets of authors describe a project to explore the use of water curtains to protect the crew of a tanker as they make their way to lifeboats during a shipboard fire. The design basis fires and heat fluxes are described by Stephenson and Coward and the modelling of and full scale experimental work on the water curtain is described by Maini and Stephenson.

The issues to be determined were the stability of the curtain and its capability to attenuate thermal radiation. The aim was to design a curtain some 5 m high which would remain stable in a 6 m/s wind. The modelling showed that heat attenuation is effected by a curtain of small droplets, which thus has a large total surface area, falling at low velocity. Work on curtain stability showed that to obtain a stable curtain it was better to use narrow angle nozzles rather than wide angle nozzles. With the former the droplets leave with a high initial velocity and then decelerate so that the velocity becomes such lower. There was relatively little difficulty in obtaining stability in the initial zone of 2–3 m, but below this the curtain can become unstable. It was found that in order to achieve a stable curtain it was necessary to obtain a sufficient momentum flow, where

$$\text{Momentum flow} = \text{Mass flow} \times \text{Exit velocity}$$

and that for the nozzles used a minimum value of the momentum flow was some 60 Ns/s. Given a momentum flow in excess of this value, narrow angle nozzles provided a stable curtain.

Work on attenuation of thermal radiation was performed using fires with surface emissive powers of the order of 50 kW/m^2. It should that in order to obtain adequate attenuation in the upper zone it was necessary to deploy, in addition, wide angle nozzles. One arrangement which gave good performance was narrow angle nazzles spaced at 1 m intervals with two wide angle nozzles in each interval. With this arrangement attenuation was effected in the upper zone by the small slow droplets from the wide angle nozzles and in the lower zone by the small, slowed droplets from the narrow angle nozzles. The fractional attenuations obtained ranged from 30% to 70%, being an approximately linear function of the optical thickness. Models were developed for the behaviour of the water curtain with respect to both stability and attenuation; the results for the latter show close agreement with the experimental values.

Commenting on this work, the authors state that the essential requirement for such a water curtain is the combination of high momentum flow with small droplet size. The design which they favour is one with narrow and wide angle nozzles. They refer to the need for a water supply at a pressure of at least 5 barg. They indicate that the curtain should be stable in winds up to 6 m/s but not in very high winds.

16.35.7 Hazards to fire fighters

Firefighting is always a hazardous task, but this is particularly so on a process plant. Some of the hazards encountered are:

(1) heat and flames;
(2) falling structures and brands;
(3) flashback;
(4) explosion;
(5) toxic fumes;
(6) asphyxiating fumes;
(7) refrigerated liquids;
(8) chemical hazards;
(9) hazards due to firefighting activities
    (a) spread of burning liquids,
    (b) slopover due to foam,
    (c) fumes from vaporizing liquids,
    (d) discharge of dry chemicals.

Many process plant fires involve liquids. These are difficult to extinguish and tend re-ignite, particularly if there are areas of hot metal. There is a danger, therefore, that flashback of the fire may occur.

Fires often cause explosions in vessels, particularly those containing liquids. It is standard practice to cool vessels with water to lessen the chance of their rupturing or exploding, but nevertheless explosions do occur. Process plants also contain many other objects which may explode.

Large quantities of toxic fumes are frequently involved in fires. They may come not only from process materials but also from lagging and from firefighting agents. In particular, hydrogen chloride and other acid gases are often produced.

Some materials produce more insidious fumes. For example, the fumes of toluene diisocyanate not only cause euphoria and lead firemen to undertake rash actions but also attack the nervous system and can lead to permanent disability. Outright asphyxiation due to lack of oxygen is another hazard in such fires.

Some liquid spillages involve refrigerated liquefied gases. Contact with these can cause freezing of and injury to parts of the body.

Fire causes loss of containment of other chemicals, such as corrosive substances, which constitute further hazards to personnel.

Some of the hazards arise from the firefighting activities. The use of water may cause burning hydrocarbon liquids to spread, particularly into drains. The addition of foam to a tank where the fire has formed a hot zone can cause slopover. The fumes from vaporizing liquids tend to be highly toxic. The high velocity discharge of dry chemicals can cause injury.

Although local authority firemen should be generally familiar with the hazards of process plants in their area though training and exercises, it is important for them to be fully informed of the particular hazards presented by a fire which they are called on to fight.

16.35.8 Planning and training

It is essential to plan for emergencies and fires and to train personnel in emergency procedures and firefighting. A detailed account of emergency planning is given in Chapter 24. This includes devising scenarios of accidents and conducting full-scale emergency and firefighting exercises.

The *Fire Training Manual* of the Petroleum Industry Training Board (PITB) (1975/6) givers guidance on training for firefighting related specifically to process plant fires.

16.36 Fire and Fire Protection in Buildings

The most serious fires, with respect both to loss of life and to damage, are those which occur in buildings. Although fire in buildings does not have the same relative significance for process plant, it is still important, because there are many plants which need to be housed in buildings and there are on virtually all sites a range of other buildings from laboratories, workshops and offices, to stores and warehouses.

Accounts of fire and fire protection in buildings are given in *Fire Safety in Buildings. Principles and Practice* (Langdon-Thomas, 1972), *Handbook of Industrial Loss Prevention* (FMEC, 1967), *Fire protection Handbook* (NFPA, 1991/28) and *Background Notes on Fire and its control* (FPA, 1971/14). Further information is available in the publications of the FPA and NEPA, some of which are given in Appendix 28.

The problem of fire in buildings falls under three main headings: (1) hazard to life, (2) hazard of damage to the building and (3) hazard of exposure of nearby buildings. Fire protection of buildings, as of plants, is based on a combination of passive measurers such as structural design, and active ones, such as firefighting systems.

16.36.1 Fire load

The maximum size of fire which can develop in a building depends on the amount of material available for combustion.

The severity of a fire in a building is a function of the material available for combustion. In a classic study, described below, Ingberg (1928) put forward the concept of 'fire load' as the determinant of the severity of a fire.

The fire load is the total heat which can be generated by the combustible material within the building. It is the product of the mass of material and its heat of combustion, or calorific value. The fire load density is the heat per unit area of floor which can be generated. Alternatively, the fire load density may be expressed as the equivalent mass of wood per unit area of floor. A discussion of fire load is given by Langdon-Thomas (1972).

Fire load density has been classified as follow (this table assumes a calorific value of 8000 BTU/lb for wood):

	Fire load density		*Typical occupations*
	(lb/ft^2)	(BTU/ft^2)	
Low	12.5	$<1 \times 10^5$	Dwellings, offices
Medium	12.5–25	$1–2 \times 10^5$	Factories
High	25–50	$2–4 \times 10^5$	Warehouses

Langdon–Thomas comments that it is preferable to estimate the fire load density for the particular building under study. Generalized estimates are available but appear to vary widely.

The calorific values of some common materials, as given by the FPA (1971/14), are shown in Table 16.89. Further data are given in the Association National pour la Protection centre l'Incendie (1972).

16.36.2 The time–temperature curve

It has been shown that under standard conditions there is a close relationship between the time for which a building fire burns and the temperature which it attains. This was first demonstrated in 1928 by Ingberg (1928), who carried out a series of test burns in an experimental building at the National Bureau of Standards (NBS). Similar work has been done by other investigators and has led to the development of a number of standard time–temperature curves.

Table 16.89 *Calorific value of some common materials (Fire Protection Association, 1971/14)*

	(kJ/kg)
Paper	15,600–18,100
Cotton	16,750
Woods	17,500–21,000
Coals	20,000–30,000
Wool	20,700
Rubber	≈40,000
Petroleum products	43,000–48,000

A standard time–temperature curve which has been widely used is that of ASTM E-119 which has changed relatively little over the years. There is also a British Standard curve, given formerly in BS 476: Part 8: 1972 and now in Part 20: 1987.

The BS 476: Part 20: 1987 curve is defined by the following equation:

$$T = 345\log_{10}(8t + 1) + 20 \quad t < 360 \qquad [16.36.1]$$

where t is the time (min) and T is the temperature (°C) The ASTM E-119 curve is defined as a set of time–temperature values. These are given below together with values of the BS 476: Part 20: 1987 curve calculated from Equation 16.36.1:

Time (min)	*Temperature* (°C)	
	ASTM E-119	*BS 476: Part 20: 1987*
5	538	576
10	704	678
30	843	842
60	927	945
120	1010	1049
240	1093	1153
360	–	1214
>480	1260	

The ASTM and BS time–temperature curves are shown in Figure 16.128.

A fire at 900°C appears cherry red, one at 1100°C orange, and one above 1400°C white. Building fires generally look orange or yellow, which suggests a temperature in the range 1100–1200°C. This has been confirmed in practice.

The area under the time–temperature curve corresponds effectively to the fire load density. The greater the fire load density, the longer the duration of the fire and the higher its temperature.

The standard time–temperature curves are widely used for the testing of structural components for fire grading. The component is put in a furnace and the temperature of the furnace is controlled to follow the curve. There is, however, a view that a test based on heat flux might be more satisfactory.

16.36.3 Fire severity

The fire load was used by Ingberg (1928) to define the severity of a potential fire. The time–temperature profile of a real fire exhibits a rapid rise to a maximum value, followed by a gentler decline. The fuel consumed is related to the area under the curve. The profile thus differs from that of a standard time–temperature curve.

The proposition put forward by Ingberg is that two fires should be regarded as of equal severity if the area under the time–temperature curve, above a certain datum temperature, is equal, a concept which has become known as the 'equal area hypothesis'.

The relationship given by Ingberg between fire load and fire severity may be expressed as:

Combustible content (kg/m^2 of wood equivalent)	*Thermal equivalent* (GJ/m^2)	*Standard fire duration* (h)
49	0.90	1
73	1.34	1.5
98	1.80	2
146	2.69	3
195	3.59	4.5
244	4.49	6
293	5.39	7.5

Here the thermal equivalent is based on the floor area and on a heat of combustion of wood of 18.4 MJ/kg.

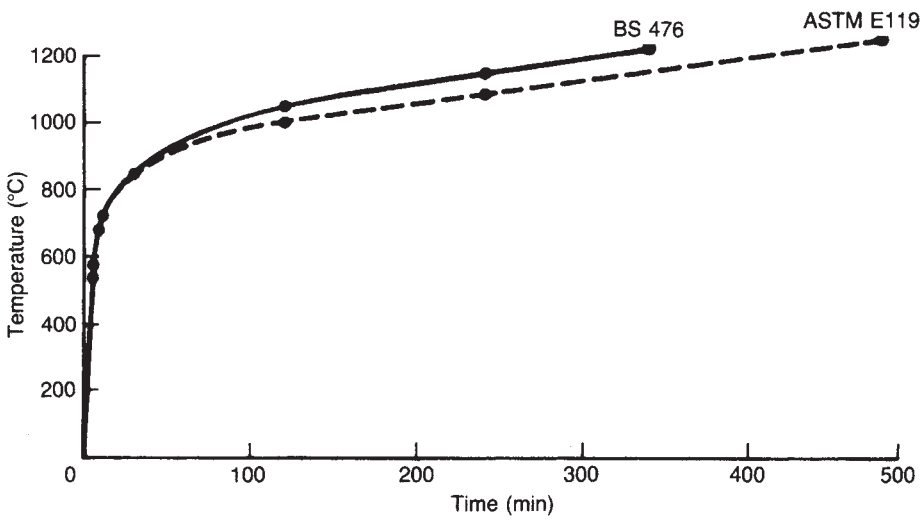


Figure 16.128 *Standard time–temperature curves for building fires. ASTM E119: 1988; BS 476: Part 20: 1987*

16.36.4 Fire grading of buildings

A scheme for the fire grading of buildings in the United Kingdom which is based essentially on the concepts of fire load and the time–temperature curve was proposed in *Fire Grading of Buildings*, Part I, *General Principles and Structural Precautions* (Ministry of Works, 1946). An outline of this system is given in Table 16.90. Buildings of Types 1 and 2 have steel frames with concrete protection, brick walls and reinforced concrete or equivalent resistance floors. In Types 4 and 5 the buildings have load-bearing brick walls, timber floors and roofs, and fire-retardant roof covering; ordinary houses are of this type. A Type 6 building is made of incombustible material, such as corrugated iron or asbestos cement. A Type 7 building is one of combustible material such as wood. Although the system was never adopted as such, it illustrates some general principles of fire grading.

A different approach to fire grading is that developed by law (1971), who investigated the relation between fire severity and fire resistance. In this work a real fire was modelled as having a temperature equal to its peak temperature maintained for a period equal to the ratio $M_f/\dot{m}$, where $\dot{m}$ is the rate of mass loss and M_f is the total mass of combustible material. Fire resistance of insulated columns was investigated using unsteady-state heat transfer models to determine the time to failure. The following relation was obtained:

$$t_f = k_f \frac{M_f}{(A_W A_T)^{1/2}} \qquad [16.36.2]$$

where A_T is the total area of the internal surface, excluding ventilation openings (m^2), A_W is the area of the ventilation openings (doors, windows) (m^2), M_f is the total combustible load (kg of wood equivalent), t_f is the effective fire resistance time, or fire grading (min), and k_f is a constant. With the units quoted, the value of the constant k_f is approximately unity.

Table 16.90 *Minimum fire resistance requirement for types of construction (after Ministry of Works, 1946)*

Grading of construction		*Minimum fire resistance*[a] (h)
Type 1	Incombustible fire resisting construction Fully protected in relation to high fire loads, e.g. warehouses	4
Type 2	Incombustible fire resisting construction Fully protected in relation to moderate fire loads, e.g. shops and factories	2
Type 3	Incombustible fire resisting construction Fully protected in relation to low fire loads, e.g. offices and residential buildings	1
Type 4	Fire resisting construction but not necessarily incombustible and may therefore include timber floors and timber roof construction. Partially protected only in relation to all fire loads	½
Type 5	Externally protected construction Fire resisting incombustible external walls, non-fire resisting internal construction	–
Type 6	Non-fire-resisting construction Incombustible	–
Type 7	Non-fire-resisting construction Combustible	–

[a] This refers to floors and roofs and to columns and beams supporting them. Walls and columns and beams supporting them have a minimum fire resistance equal to or greater than this.

16.36.5 Fire growth in buildings

Ignition is important not only in the initiation of fire but also for its spread. After the fire has started, its growth depends on the ease with which further combustible material is ignited.

Solid materials do not have a well-defined ignition temperature, but they tend to ignite at relatively low temperatures. The ignition temperature for wood, for example, is generally taken as about 200°C. But if wood is left in contact with a hot surface such as a steam pipe for a long period, it can undergo chemical changes so that it ignites at a much lower temperature. The maximum temperature at which wood can be safely exposed for a long period has been given as 65°C (FPA 1971/14).

Once ignition has occurred, the immediate growth of the fire is affected by the form of the nearby materials. Here the surface area of the materials is important:

	Surface area (cm^2/g)
Tinder	>20
Kindling	2–20
Bulk fuel	<2

The fire then grows by heat transfer and flame spread.

All three heat transfer modes (convection, conduction and radiation) contribute to fire growth. Convection within the space where the fire has started is important initially; so is conduction along burning objects. As the fire grows, convection to the ceilings and conduction through the wall become significant. When the fire is well developed and temperatures are high, the contribution of radiation becomes important.

Fire spread can be considered as occurring in three ways: (1) flame spread across combustible surfaces, (2) fire spread through a continuous fuel bed and (3) fire spread through a discontinuous fuel bed.

Flame spread across a combustible surface differs somewhat according to whether it is vertical or horizontal. Spread is more rapid in the vertical direction, because the surface is preheated by convection. However, in both cases flames can spread very quickly.

Fire spread through a continuous fuel bed requires little explanation except that this description includes spread between any types of object which can act as a fuel, including whole buildings. The fuel bed is effectively continuous if the flames pass right through it.

With a discontinuous bed, by contrast, it is necessary for the fire to spread by one of the modes of heat transfer and to

cause ignition by heating other objects to their ignition temperature without the aid of direct flame contact.

16.36.6 Flashover

If a fire takes hold in a compartment, a point is reached when the fire is no longer localized, but spreads throughout the whole space. There is sudden propagation of flame through the unburned gas below the ceiling and all the combustible surfaces become involved in the fire. This condition is known as 'flashover'.

In this situation the rate limiting feature frequently is no longer the fuel but the air supply. If the air supply is suddenly increased, as by the cracking of windows, the opening of a door or other means, there will be a sudden increase in the rate of burning.

With flashover, the fire is fully developed. Flashover is discussed further in Section 16.36.10.

16.36.7 Fire spread through buildings

The spread of fire through a building depends on a number of factors. Staircases, lift shafts and open corridors encourage the rapid spread of flames. Features such as gaps in walls where pipes pass through or doors left open allow flames to bypass enclosing elements which are intended to be a barrier to fire. Fire spread is also strongly influenced by the surfaces in the building. Some surfaces support a very rapid passage of flame.

16.36.8 Fire spread from buildings

Fire spread from a building across an open space is generally almost entirely by radiation, although there may sometimes be a contribution from convection and there may also be flying brands. Usually the object is heated by radiation to a temperature at which it is ignited by a small brand or spark. This is known as pilot ignition. Such pilot ignition of dry unpainted wood in the open can be obtained if the heat flux onto it is about 12.6 kW/m^2. A lower value is sufficient to ignite the wood in a closed room.

A method of calculating the heat radiation from the windows of a burning building has been developed by Law (1963 FRS Fire Res. Tech. Pap. 5) and has been used in conjunction with fire resistance data to determine suitable separation distances between buildings. The method is described in the original paper and in an explanatory memorandum to the Building Regulations 1965.

The amount of heat radiated from a building is a function of the area radiating heat and of the heat flux per unit area. The assumption that there is fire at all windows is a conservative one, particularly for larger buildings. The additional radiation from flames outside the windows is not generally significant.

The upper limit of the intensity of heat radiation from a fire in a room of a building can generally be taken as 168 kW/m^2, but a lower value applies for lower fire load densities (Langdon-Thomas, 1972).

The spread of fire between buildings depends on the distance between them, the sizes and angles of the radiating surfaces, the contents of the buildings and the construction of the buildings. The contents of the burning building determine the temperature reached and the extent to which flying brands are produced, and the materials of walls and roofs of the two buildings determine the extent to which the burning building radiates heat and produces brands and the extent to which the exposed building is vulnerable to them.

16.36.9 Effects of fire in buildings

Fire in a building presents three hazards to life: (1) toxic gas, (2) smoke and (3) heat.

People may be overcome or may be burned. Most people who die in fires do so in the early stages of the outbreak, not infrequently before the alarm has been raised. Usually they are killed by toxic gases which arrive before the fire itself reaches that part of the building. Others are overcome by toxic gas or become trapped and then die in the fire itself.

Toxic gases produced by building fires are principally the normal products of combustion, that is, carbon monoxide and carbon dioxide. The amount of carbon monoxide produced is increased if the air supply to the fire is limited. Carbon monoxide has almost the same density as air and so spreads easily through the building. It is odourless, and so is not readily detected. At a concentration of 1.3% it causes unconsciousness after a few breaths.

Carbon dioxide is also toxic, but in building fires acts mainly as an asphyxiant. A concentration of about 9% is generally enough to cause unconsciousness within a few minutes.

Other more toxic gases may be produced by the combustion of materials such as plastics and rubber. These include hydrogen chloride, sulfur dioxide, hydrogen cyanide and phosgene.

Smoke has the effect of reducing visibility and hindering both escape and rescue. The quantity of smoke generated is greater if the air supply is restricted and the burning material is wet.

It is often the case that smoke rising up a staircase causes people trying to escape to turn back, even though the route is actually passable. It is a prime function of fire doors, therefore, to prevent the spread of smoke. It is desirable that people in the building understand these points.

The damage done to the building by fire is due partly to the fire itself and partly to smoke and water. Some estimates of fire damage attribute more than half to water damage.

16.36.10 Modelling of building fires

Some progress has been made in the modelling of fires in buildings. Accounts of the modelling of building fires are given by Drysdale (1985), Babrauskas (1986c), Budnick and Evans (1986), Budnick and Walton (1986) and Law (1991).

Most modelling has been directed to the characterization of the fire in a compartment. There are also some models of other aspects such as fire spread along corridors.

A compartment fire may (1) burn out, (2) self-extinguish due to lack of air or (3) progress to flashover.

'Flashover' has been used with a number of meanings, as reviewed by P.H. Thomas (1982). There are three in common use: (1) transition from a localized fire to a conflagration involving all the fuel surfaces in the enclosure; (2) transition from fuel to ventilation controlled burning and (3) sudden propagation of flame through the unburnt volatiles collected under the ceiling.

The modelling of a compartment fire proceeds broadly along the following lines. The fire load in and ventilation conditions of the compartment are determined. In the pre-flashover stage, the fire is modelled first under 'free burn' conditions. As the fire grows, a transition may occur from the regime of free burning to one of ventilation controlled burning. Prior to flashover, the features of interest include (1) the fire regime, (2) the rates of mass loss and heat release, (3) the upper gas temperature and (4) the radiant heat flux.

Determination of these variables permits an estimate to be made of the possibility that flashover will occur. There are a number of criteria for flashover, which utilize (1) the upper gas temperature, (2) the radiant heat flux and (3) the heat release rate. These variables are, of course, related. The various equations involve time in some way, and hence provide a means of estimating the time to flashover, assuming that it does occur.

For the post-flashover stage, the features of interest are (1) the rates of mass loss and heat release and (2) the compartment temperature. Principal purposes of the modelling of compartment fires include determining whether flashover will occur, the time to flashover and the temperature profile after flashover.

Programmes of experimental work which have provided data for workers in the field include the Home Fire Project (Croce, 1975) and the project of the Conseil Internationale du Batiment (CIB) (Heselden and Melinek, 1975 FRS Fire Res. Note 1029).

16.36.11 Models of pre-flashover compartment fire

In the pre-flashover stage, the mass loss rate is at first relatively low. The fire regime is one of fuel controlled burning. As the fire grows, the quantity of air required increases markedly, and the regime becomes one of ventilation controlled burning.

The mass loss rate in the initial, free burning stage necessarily depends on the particular scenario, but the work of P.H. Thomas, Simms and Wraight (1964, 1965) on the modelling of crib fires provides one approach.

An equation for the mass loss rate under conditions of ventilation controlled burning has been given by Kawagoe (1958):

$$\dot{m} = k_v A_W H^{1/2} \qquad [16.36.3]$$

where A_W is the area of the ventilation opening (m^2), H is its height (m), $\dot{m}$ is the mass burning rate (kg/s) and k_v is a constant ($kg/m^{3/2}$ s). The term $A_W H^{1/2}$ is referred to as the 'ventilation factor'. The value given for k is 0.09, which is often rounded to 0.1. In another widely used form of the equation, $\dot{m}$ is expressed in kg/min and k_v has the value 6.

The heat release rate is

$$\dot{q} = \dot{m}\Delta H_c \qquad [16.36.4]$$

where ΔH_c is the heat of combustion (kJ/kg) and $\dot{q}$ is the heat release rate (kW).

A number of equations have been given for the estimation of the upper gas temperature in pre-flashover conditions. One is that by Quintiere (1983), quoted by Babrauskas (1986c). The temperature is a function of, among other things, the heat release rate, the ventilation conditions and time.

Another model, described by Drysdale (1985), has been given by McCaffrey, Quintiere and Harkleroad (1981).

P.H. Thomas (1974) and Ove Arup (1977) have developed a model, quoted by Budnick and Evans (1986) and Law (1991), which allows for limitation by fire load. It is

$$T_u = T_o + \frac{6000}{\eta^{1/2}}[1 - \exp(-0.1\eta)][1 - \exp(-0.5\tau)] \qquad [16.36.5]$$

with

$$\eta = \frac{A_T}{A_W H^{1/2}} \qquad [16.36.6]$$

$$\tau = \frac{L}{(A_W A_T)^{1/2}} \qquad [16.36.7]$$

where L is the mass of fuel (kg), η is a ventilation term ($m^{-1/2}$) and τ a fire load term (kg/m^2).

The radiant heat flux from the fire to the compartment boundaries is typically obtained by determining the radiative power of the flame and estimating the thermal radiation intensity as that at the surface of a hemisphere.

There are a number of criteria for flashover in a compartment fire. One takes the form of a limiting value of the upper gas temperature. Hagglund, Jansson and Onnermark (1974) and Fang (1975) obtained in their work a value of 600°C. Other workers such as Lawson and Quintiere (1985) use 500°C. Another criterion is the radiant heat flux to the floor of the compartment. Work by Waterman (1968) indicates a critical value of 20 kW/m^2. Also relevant is that in his work flashover did not occur below a mass loss rate of 40 g/s.

Since the upper gas temperature is related to the heat release rate, the flashover criterion can also be expressed in terms of a limiting heat release. One such relation, based on a flashover temperature of 600°C and enclosures with materials having a density similar to that of gypsum board, is

$$\dot{q}_{fo} = 378 A_W H^{1/2} + 7.8 A_T \qquad [16.36.8]$$

where $\dot{q}_{fo}$ is the heat release rate at flashover (kW). Another such equation is that by Lawson and Quintiere (1985).

16.36.12 Models of post-flashover compartment fire

Flashover results in a rapid rise in temperature, possibly up to 1100°C.

There are a number of models of the post-flashover compartment fire. It is usually assumed that the atmosphere in the compartment is perfectly mixed. The models differ in two main ways. One is in the terms which are included in the heat balance. The other is in the estimation of the individual terms, and particularly the rates of mass loss and hence heat release.

Models for this stage include those by Kawagoe and Sekine (1963), Pettersson, Magnussson and Thor (1976), Babrauskas and Williamson (1978) and Babrauskas (1981). Expositions of these models have been given by Drysdale (1985) and Babrauskas (1986c).

The general nature of the models is illustrated in the account given by the latter author, who describes his own model (Babrauskas, 1981) for the post-flashover upper gas temperature in a compartment fire:

$$T_u = T_o + (T^* - T_o)\theta_1\theta_2\theta_3\theta_4\theta_5 \qquad [16.36.9]$$

where T_o is the ambient temperature (K), T_u is the upper gas temperature (K), T^* is an empirical constant, and θ_1, θ_2, θ_3, θ_4 and θ_5 are factors which allow respectively for (1) the burning rate stoichiometry, (2) the steady-state heat loss through the wall, (3) the transient heat loss through the wall, (4) the effect of the height of the opening and (5) the combustion efficiency.

A determining factor in such models is the expression used for the mass loss rate. As described above, there are two distinct regimes. At low ventilation rates the mass loss

rate is ventilation controlled, whilst at high ventilation rates it is fuel controlled.

Under ventilation controlled conditions, the expression commonly used for the mass loss rate is that by Kawagoe, given above as Equation 16.36.3. The range of validity of this equation, however, is restricted. Its limitations are discussed by Drysdale. Work by Bullen (1978) points to a family of curves of the same general form as Equation 16.36.3, but with different values of the constant and hence with different slopes. In other words the group $(\dot{m}/A_W H^{1/2})$ is not a constant. Rather it is a function of factors such as the heat of gasification of the volatiles and the heat flux to the burning surface.

If the ventilation is increased, there comes a point at which the regime becomes fuel controlled. However, fuel control is appreciably more complex. The predominant factor is the geometry of the fuel, and above all its surface area. For this regime, therefore, there is no single criterion for transition and no single expression for the mass loss rate.

There exist methods, such as that by Harmathy (1972), for the determination of the transition from ventilation to fuel control. The application of this criterion is discussed by Drysdale, who shows that there is appreciable scatter.

In view of the variety of mass loss rates within the fuel control regime, the most widely applicable approach would appear to be to estimate the values of the mass loss rate using a correlation for each of the two regimes and to identify the transition point in this way. There is no generally applicable relation for the estimation of the mass loss rate $\dot{m}$. Bullen and Thomas (1979) have obtained a correlation which includes some of the important variables. It may be expressed as

$$\dot{m} \approx IA_f/L_v \qquad [16.36.10]$$

where A_f is the surface area of the fuel (m^2), I is the thermal radiation intensity (kW/m^2) and L_v is the heat of gasification of the volatiles (kJ/kg).

Babrauskas (1986c) treats this aspect by utilizing for both regimes expressions for the burning rate stoichiometry factor θ_1 which are a function of the ratio ϕ of the actual mass loss rate to that at stoichiometric air flow. Separate expressions are used for the fuel-rich and fuel-lean regimes, in other words for ventilation control and for fuel control.

Treatments of a fully developed compartment fire frequently use Equation 16.36.3, which is applicable to the ventilation controlled regime.

16.36.13 Models of flame projection

Flame projected from an opening may cause fire to spread to the storey above. It may impinge on an object outside and is in any event a source of radiant heat.

Flame projection has been correlated by P.H. Thomas and Law (1972) who obtained the equation

$$z + H = 12.8(\dot{m}/B)^{2/3} \qquad [16.36.11]$$

where

$$x/H = 0.454/n^{0.53} \qquad [16.36.12]$$

$$n = 2B/H \qquad [16.36.13]$$

where B is the width of the window (m), H is its height (m), n is a shape factor, x is the horizontal reach of the flame (m) and z is the height of the flame up above the soffit, or top, of the window (m). Thus $(z + H)$ is the height of the flame above the base of the window.

16.36.14 Models of fire spread

The spread of fire from a compartment into other parts of a building has received less attention. Quintiere (1979) has reviewed work on this aspect.

Tests in which fires were lit in buildings due for demolition indicate that the volume of the fire tends to grow exponentially.

A particular aspect which has been studied is fire spread from a room into a corridor. Work on this has been described by Quintiere, McCaffrey and Kashiwagi (1978).

Another route for the spread of flames is through an opening and up to the next storey. Work on this indicates that such spread is influenced by the shape factor $(2B/H)$, where B is the width of the opening and H is the height. For narrow windows and thus small values of this group, flame spread may occur with only a relatively small projection, whereas for wide windows a greater projection is required.

16.36.15 Models of detector response

A quite different type of fire model is that used to, investigate the response of temperature measuring devices used for fire detection. An account of such models is given by Budnick and Evans (1986).

16.36.16 Models of smoke

The agent responsible for the majority of deaths in building fires is smoke. The treatment of the production and movement of smoke in such fires is therefore a significant aspect.

Smoke is produced by smouldering fires and by flaming combustion, but the types of smoke are very different. Smouldering tends to produce an oily smoke and flaming produces solid particles. Smoke generally contains unburned carbon and toxic gases. The carbon particles in smoke are the result of incomplete combustion, as is carbon monoxide. Other gases, such as hydrogen chloride or phosgene, may also be present, depending on the materials burned. Features of smoke which relevant here are that it reduces visibility and that it is toxic.

Characterization of the yield and composition of smoke is difficult due to the wide variety of materials that become involved and the range of conditions that are prevalent in fires. From the practical viewpoint, the significant feature is the rate of production of smoke, which is governed by the burning rate. The use of a suitable model for the smoke production rate permits the determination of the rate of smoke extraction required to prevent the layer of the hot smoke under the ceiling exceeding a certain depth.

One method of estimating of the rate of smoke production is to infer it from the rate of air entrainment. P.H. Thomas *et al.* (1963) have described a model based on this approach. Another model on these lines is that by Butcher and Parnell (1979).

The movement of smoke is governed by buoyancy and air movement effects. The fire itself generates hot gases and creates buoyancy effects, whilst the smoke itself has a temperature in excess of that of the atmosphere, creating a stack effect. Natural and forced ventilation are responsible for the air movement.

16.36.17 Computer models

A number of computer codes have been developed incorporating models of fires in buildings. An account is given by Budnick and Walton (1986). These computer models are of two main types: (1) enclosure fire models and (2) special purpose models.

Enclosure fire models include not only deterministic models but also probabilistic ones. A large proportion of the former are zone models in which the enclosure is divided into control volumes, or zones, and the conditions in each zone are simulated. Typically the enclosure might be divided into a lower and an upper zone. Probabilistic models deal with the transitions between different stages in the development of a fire, often using techniques such as Markov models.

There are also a number of special purpose models which address topics such as detector actuation, smoke control, structural response and evacuation.

Tabulations of the codes available are given by Budnick and Walton.

16.36.18 Fire protection by structure

The objectives of fire protection by means of the structural design of buildings are to (1) limit fire spread between buildings, (2) limit fire spread within buildings, (3) facilitate escape, (4) facilitate firefighting and (5) limit water damage.

The Building Regulations 1976, particularly Part E, contain requirements which deal *inter alia* with: restriction of the spread of flame; provision of compartment walls and floors; fire resistance of elements of the structure, floors and doors; fire protection of penetrations, cavities and shafts; and means of escape. These requirements cover both materials and construction. Other requirements are designed to limit fire spread between buildings and deal with distances between other buildings and boundaries and with the construction and combustibility of external walls and roofs.

These regulations were revoked by the Building Regulations 1985, which are much less detailed (31 pages as opposed to 295), though they retain in Schedule 1 certain minimum requirements. The provisions of the earlier regulations retain value as an indication of good practice.

The material and component properties which are important are indicated by the tests specified in BS 476: 1970– *Fire Tests on Building Materials and Structures*. These include:

Part 3: 1975	*External Fire Exposure Roof Test*
Part 4: 1970	*Non-combustibility Test for Materials*
Part 5: 1979	*Method of Test for Ignitability*
Part 6: 1989	*Method of Test for Fire Propagation for Products*
Part 7: 1987	*Method of Classification of the Surface Spread of Flame of Products*
Part 8: 1972	*Test Methods and Criteria for the Fire Resistance of Elements of Building Construction* (obsolescent, replaced by Parts 20–23)
Part 13: 1987	*Method of Measuring the Ignitability of Products Subjected to Thermal Irradiance*
Part 20: 1987	*Method for Determination of the Fire Resistance of Elements of Construction (General Principles)*
Part 21: 1987	*Methods for Determination of the Fire Resistance of Load-bearing Elements of Construction*
Part 24: 1987	*Method for Determination of the Fire Resistance of Ventilation Ducts*
Part 32: *1987*	*Guide to Full Scale Fire Tests within Buildings*

BS 476: Part 8: 1972 is obsolescent, being replaced by BS 476: Parts 20–23: 1987, which cover, respectively, (1) general principles, (2) load-bearing elements, (3) non-loading bearing elements and (4) certain special components.

The constructional features which are relevant to fire protection include:

(1) compartmental construction;
(2) fire resistance;
(3) limitation of openings;
(4) partitions and linings;
(5) roofs;
(6) vents;
(7) escape routes.

Compartments are spaces in buildings which are enclosed by fire-resistant walls and floors, and have all openings protected by fire-resistant construction. The object of compartmentation is to confine a fire to the compartment where it originates and to control the movement of flames, smoke and heat.

The maximum size of compartment is usually set by consideration of hazard to life and of ease of firefighting. The size should be kept to a minimum consistent with the basic purpose of the building.

The fire resistance of the floors and walls should be capable of containing the most severe and prolonged fire which is likely to occur. The nature of such a fire depends on the likely contents of the compartment.

The openings between compartments should be minimal. In some explosives factories openings are virtually eliminated. But, in general, openings are acceptable, provided appropriate precautions are taken. All openings should be protected with fire-resisting doors or shutters. All vertical shafts such as staircases, lifts and hoists should have fire-resistant walls and fire-protected openings. All unnecessary openings should be closed, including those around services and pipework.

Linings for walls and ceilings should be of non-combustible material or should have low flame spread characteristics.

Roofs should be constructed so that fire does not spread either internally beneath the roof or externally over it. Flame spread beneath the roof is reduced by the use of incombustible or low flame spread materials and partitioning, and that above the roof is reduced by the use of incombustible materials and partition walls.

Vents should be provided for the release of hot gases and smoke. These control the spread of fire and smoke and assist firefighting. The design of vents depends on the type of building.

The Building Regulations 1976, Regulation E5, specify minimum periods of fire resistance which are a function of the type and size of building and the part of the building. The required minimum periods do not exceed 2 h, except for basements in large buildings and forlarge storage buildings.

16.36.19 Fire protection by sprinklers

As already mentioned in Section 16.26, the installation of fixed water sprinkler systems has proved very effective and is wholeheartedly supported by the insurance companies. Sprinkler systems for buildings are usually automatic, with a detection system which actuates the sprinklers and sounds the fire alarm.

Detection is usually based on heat or smoke. Heat sensitive detectors are dealt with in BS 5445: Part 5: 1977.

Sprinkler heads are usually arranged to cover an area not exceeding 12 m^2 per head. The amount of water required depends on the risk protected. For storage, for example, water requirements in the range 0.041–0.514 l/m^2 s have been determined, the latter being for high stacked, closely packed materials in which water penetrates with difficulty (O'Dogherty, Nash and Young, 1966).

In a large proportion of cases where a sprinkler installation has not been effective in protecting a building, this has been due to the fact that it was disabled in some way. Often the main system valve was closed. It is necessary, therefore, to have specific procedures to prevent this.

16.36.20 Smoke control

Smoke control may be applied to a space where smoke from a fire may occur and also to escape routes. Methods of smoke control include removal by venting and exclusion by maintaining a positive pressure.

The design of a smoke venting system has been treated by P.H. Thomas *et al.* (1963), P.M. Thomas and Hinckley (1964) and Butcher and Parnell (1979). Relevant factors are the height of the space, the size of the design fire, the type of roof and the pressure at the roof. A positive pressure on the roof will reduce and may negate the effectiveness of a vent. The spread of smoke under the roof may be limited by installing smoke curtains hanging down from it.

The use of smoke vents has certain drawbacks. One danger is that venting may hinder the operation of smoke detectors. Another problem is that venting of the smoke at a high level requires a compensating introduction of air at a low level, which may exacerbate the fire. Each case needs to be considered on it merits.

An escape route may be protected from smoke by the use of closed doors, by applying positive pressure and/or by venting the smoke from the space where it is being produced. Where reliance is placed on closed doors, it must be ensured by means of suitable measures, including training, that they remain closed in fire conditions. Where positive pressurization is used, air locks may be required to ensure that an adequate pressure is maintained.

16.36.21 Other fire precautions

Other fire precautions which should be taken in buildings include the following:

(1) fire alarm system;
(2) escape routes;
(3) firefighting equipment;
(4) fire notices;
(5) fire drills.

The building should be provided with a fire alarm system which can be heard in all parts of the building and which is tested regularly. There should be clearly marked escape routes from all parts of the building. Firefighting equipment such as portable fire extinguishers and hoses should be provided, as appropriate. The fire extinguishers used should be suitable for the types of fire which are likely to occur. Notices on the procedures to be followed should be prominently posted. Fire drills should be practised regularly.

16.37 Fire Protection in Transport

The account so far has dealt with the fire protection of fixed installations. It is also necessary to give brief consideration to fire protection, and firefighting, in transport. The consideration here is confined to road, rail and marine transport.

In large part, the fire hazard in road, rail and marine transport is addressed by measures to prevent accidents and to ensure appropriate design and maintenance.

The principles of fighting fires arising from transport accidents are, in general, no different from those for buildings, but two aspects are of particular importance. These are the wide variety of chemicals which are carried and the relative lack of familiarity of the local authority fire services with these chemicals.

A considerable effort has been made, therefore, to furnish information to the fire services in advance about the hazards of chemicals which they may encounter. *Dangerous Substances. Guidance on Dealing with Fires and Spillages* (Home Office, 1972/4) and *Hazardous Loads* (IFE, 1972) provide some information on this aspect.

Transport aspects are discussed in more detail in Chapter 23.

16.37.1 Road transport

Accounts of fire protection and firefighting in road transport are given in *Transportation Fire Hazards* (NFPA, 1973/10), *Hazardous Materials Response Handbook* (NFPA, 1992/30) and by Stillman (1971) and Ward (1978). Fire protection in road transport is treated in the NFPA *Handbook* by McGinley (1986).

Relevant codes for road transport are NFPA 385: 1990 *Tank Vehicles for Flammable and Combustible Liquids*, NFPA 1901: 1985 *Automotive Fire Apparatus*, NFPA 512: 1990 *Truck Fire Protection* and NFPA 513: 1990 *Motor Freight Terminals*, and, for explosive materials NFPA 495: 1992 *Explosive Materials Code* and NFPA 498: 1992 *Explosives Motor Vehicles Terminals*.

Firefighting in road transport needs to be seen as one aspect of the wider topic of handling the emergency. With regard to firefighting proper, principal points are prompt action in using portable extinguishers, alerting of the fire services, alerting of the public and discouragement of spectators. The firefighting agents used should be compatible with the materials constituting the load.

Where a road tanker contains LPG, a notable hazard of a fire is that of a BLEVE.

16.37.2 Rail transport

An account of fire protection and firefighting in rail transport is given in *Manual of Firemanship*, Book 5, *Incidents Involving Aircraft, Shipping and Railways* (Home Office, 1985). Fire protection in rail transport is treated in the NFPA *Handbook* by Fitch (1986).

Fire arrangements for rail transport are not well served with national codes, the matter tending to be left to the carrier. As with road tankers, a fire on an LPG rail tank car involves the hazard of BLEVE. The risk of such an event is much increased if there are a number of such tank cars, perhaps with a flame from the pressure relief valve of one playing on another.

16.37.3 Marine transport

Accounts of fire protection and firefighting in marine transport are given in *Fire Aboard* (Rushbrook, 1979), *Manual of Firemanship*, Book 5 (Home Office, 1985), already referred to, and by Tanner (1976), Wynne (1986) and McKenna (1989). Fire protection in marine transport is treated in the NFPA *Handbook* by Keller, Kerlin and Loeser (1986).

Fire control is an important feature of the fighting capability of a warship. An account is given by Dimmer (1986).

A relevant code is NFPA 306: 1993 *Control of Gas Hazards on Vessels*. Other codes and standards, notably the IMO codes, are detailed in Chapter 23.

The much larger storages of flammable materials in marine transport provide more scope for, and necessitate, fire protection arrangements more similar to those used in fixed installations.

Fire protection measures include the use of inerting and operational procedures to counter static electricity.

The fire protection arrangements on chemical tankers and gas carriers and the application of water sprinkler, mechanical foam, vaporizing liquid and carbon dioxide systems are discussed by Keller, Kerlin and Loeser (1986).

Another aspect of fire protection in marine transport is that relating to jetties. Accounts are given by Dicker and Ramsey (1983) and Gebhardt (1989).

Ship fire protection is considered in more detail in Chapter 23.

16.38 Fire Hazard

The types of fire typical of the process industries are those described above. The hazard of a large industrial fire may be assessed by consideration of the historical record of such fires and their effects and/or of assumed scenarios using appropriate frequency estimates and hazard and effects models.

The process industries also suffer the more common types of fire such as fires in warehouses and in buildings. Both types of fire may cause extensive damage and the latter may give rise to a high death toll.

16.38.1 Historical experience

Fire constitutes the largest proportion of major accidents involving property damage which have occurred in the process industries. However, most accidents involving large loss of life involve explosions. Frequently large fires are associated with explosions, either causing the fire or resulting from it.

A classification of fires in the process industries has been given in Section 16.1. The main headings are (1) vapour cloud fires, (2) fireballs, (3) jet flames, (4) liquid fires, (5) solids fires, (6) warehouse fires and (7) fires associated with oxygen. These various types of fire are now considered, except for jet flames and solid fires.

In Section 16.1 vapour cloud fires are classified as: Type 1, fire with no explosion; Type 2, fire resulting from explosion; and Type 3, fire resulting in explosion.

Taking these three types of fire in turn, it is not easy to identify major fires without explosion, partly because such a fire does usually result in some explosions, notably BLEVEs, and partly because even if no explosion has occurred, this is generally not stated in the account given. Major fires on large sites therefore tend to involve explosions. Major fires on cross-country pipelines which do not involve explosions are relatively more frequent for the simple reason that targets vulnerable to a BLEVE are generally absent.

Thus a Type 1 fire occurred on an NGL pipeline at Austin, Texas, in 1973 (Case History A62), The fire engulfed and killed people in the vapour rich zone formed before ignition occurred and then burned back to the pipeline; there were six deaths.

With respect to Type 2 vapour cloud fires, such fires often occur following the explosive rupture of a vessel and release of its contents. One such fire was that at the campsite at San Carlos, Spain in 1978, described in Appendix 16, which resulted from the rupture of a passing road tanker and caused some 216 deaths.

It is common for the aftermath of a large vapour cloud explosion to involve extensive fires, particularly in the storage area of the site. Cases in point are those at refinery at Lake Charles, Louisiana, in 1967 (Case History A40) and at the chemical works at Flixborough, UK, in 1974, described in Appendix 2, which burned for 2 weeks and 1 week, respectively. The fires on Piper Alpha following the gas explosion in C Module were Type 2 fires.

An explosion characteristic of Type 2 vapour cloud fires is the BLEVE. Outstanding examples are the vapour cloud fire at Port Newark, New Jersey, 1951, in which more than 70 horizontal bullet tanks on site were destroyed (Case History A19), and that at Mexico City, Mexico, 1984, described in Appendix 4, in which the entire storage area was destroyed, with some 15 explosions being recorded over a $1\frac{1}{2}$ h period.

Turning to fireballs, these are generally associated with the BLEVE of a vessel containing liquefied gas, but a type of fireball occurs also on oil storage tanks. A large proportion of fireballs recorded have been on transport: pipelines, road tankers and, above all, rail tank cars.

Fireballs at fixed installations include those occurring during the BLEVEs at Feyzin, France, 1966 (Case History A38), West St Paul, Minnesota, 1974, and Mexico City, Mexico, 1984, described in Appendix 4.

Fireballs on rail tank cars occurred in the BLEVEs of: propane at Crescent City, Illinois, 1970 (Case History A50); VCM at Houston, Texas, 1971 (Case History A53); propane at Kingman, Arizona, 1973 (Case History A63); and LPG at Belt, Montana, 1976. A fireball on a road tanker is exemplified by the propane fireball at Lynchburg, Virginia, 1972 (Case History A59). The radii of these fireballs have been estimated at 75–100, 150, 150, 150 and 60 m, respectively. An even larger fireball occurred on an LPG pipeline at Donnellson, Iowa, 1978, with an estimated radius of 305 m (Case History A91).

A type of liquid pool fire which figures prominently among the large losses is the tank fire. A prominent example is the fire on a 66 ft high × 256 ft diameter oil storage tank which occurred in the refinery at Milford as: Haven, UK, 1983 (Case History A106).

A major running liquid fire involving oil froth occurred at the refinery at Signal Hill, California, 1958 (Case History A26). The oil froth eventually covered some 27 acres, causing extensive damage and the loss of two lives. In 1970, in the refinery at Beaumont, Texas, lightning struck a 40 ft high × 60 ft diameter oil tank, causing a massive release of oil which spread to create a fire involving 16 nearby undiked tanks (Case History A46).

There have also been major running liquid fires involving LNG and LPG. The fire at Cleveland, Ohio, 1944, followed the rupture of an LNG storage tank which discharged its entire contents over the plant and the nearby urban area (Case History A12). The LNG ignited and a major fire ensued. Some of the LNG flowed as liquid down storm sewers where it mixed with air, with consequent explosions. The death toll was 128.

The release of a massive wave of liquid propane at the gas plant at Umm Said, Qatar, 1977, was, at least he primarily, a liquid fire (Case History A88).

Warehouse fires constitute another category. These a can involve large loss, though the death toll is usually not great.

Examples are two warehouse fires in Britain, at Renfrew in 1977 (Case History A85) and at Salford in he 1982, both of which involved explosions of stored sodium at chlorate.

An example of a fire associated with an oxygen release is that at Brooklyn, New York, 1970, when the vessel of for a road tanker ruptured violently, releasing liquid oxygen (Case History A48). A number of fires broke out as the oxygen came into contact combustible materials, and two people were killed.

There are also fires that occur during construction, maintenance and decommissioning operations. The Staten Island fire in 1973, in which 40 died, occurred in an empty LNG storage tank on which men were working (Case History A67). The tank was insulated with he polyurethane foam with an aluminium–polyester lining. It was this insulation which was the main seat of the fire.

The historical record indicates that large death tolls from process fires are relatively infrequent compared with those from explosions. However, it should be emphasized that, overall, process fires are responsible for a large proportion of fatalities and damage in the process industries.

16.38.2 Hazard assessment

Hazard assessment of fire on process plant generally involves: the development of a set of scenarios for fire, principally by release and ignition, and of the associated event trees; an estimation of the frequency/probability of the initial events and of the events in the branches in the event trees from a mixture of historical data and synthesis of values; and modelling of the outcome events in the event tree, including both physical events all and damage/injury.

A hazard assessment involves, in principle, the formulation of a set of scenarios and a full assessment of the frequency and consequences of the events. An assessment which is confined either to the estimation of the frequency of the events or to the modelling of the consequences is a partial one. Hazard assessments may be generic or may relate to specific hazardous situations.

Overviews of generic process plant fire scenarios have been given for LPG by Rasbash (1979/80) and for LNG by Napier and Roopchand (1986). Essentially, the principal scenarios involve various modes of release of vapour and liquid, including rupture of pressure vessels and storage tanks and releases from pipework, hoses, pumps, and so on.

A large proportion of such releases will give rise to a vapour cloud. The assessment of this cloud involves: the modelling of cloud formation and of mixing with air during the initial release; any liquid flashing and evaporation; the dispersion of the cloud and the mass of fuel within the flammable limits; the ignition of the cloud; and the development of any overpressure. If the event gives no overpressure, it is a vapour cloud, or flash fire.

A jet, or torch, fire and an engulfing fire tend to be of interest primarily as events which may cause a vessel to suffer a BLEVE. Likewise, a fireball on a vessel are generally considered as part of the BLEVE event. Separate treatment is given to a flame on, or fireball from, a pipeline.

Some principal types of model used for the hazard assessment of fires on process plants are those for (1) vapour cloud fires, (2) fireballs, (3) jet flames, (4) pool fires (5) engulfing fires and (6) pipeline fires. Accounts of some of the models available have been given above.

An early, essentially representative, hazard assessment of fire is that given in the vulnerability model by Eisenberg, Lynch and Breeding (1975), who studied among other things the area affected by a flammable vapour cloud and the lethality of flash fires from such a cloud. The events of principal interest which they consider are marine spillages of 20,750, 83 and 0.8 t of LNG on water with drifting of the vapour cloud towards populated areas. For gas dispersion they use a modification of the Pasquill–Gifford model. For ignition of the cloud they assume that an ignition source is located at the centre of each population cell and that ignition occurs if a flammable mixture reaches such an ignition source. The type of ignition source is specified for each cell by the user, the two types giving fire or explosion, respectively. For thermal injury they utilize their own probit equation, as described in Section 16.22. The populations at risk are defined in terms of the cell model already described. Some results obtained are as tabulated below:

LNG spillage (t)	*Wind direction towards* (°)	*Ignition*		*Fatalities*	
		Time of travel (min)	*Distance travelled* (km)	*Explosion*	*Flash fire*
20,750	50	4.2	1.01	984	
20,750	53	4.2	1.01	1238	534
83	50	5.6	1.35	921	617
83	53	No ignition			

Both explosions and flash fires are considered. The results are sensitive to the location of the population cells relative to the wind direction, so that for the cases considered the flash fire casualties for the 83 ton release were actually greater than those for the 20,750 ton one. For the 83 ton release with flash fire the effective thermal radiation intensity and time duration were 124 kW/m^2 and 0.08 min, respectively, and 58% of the people in the cell affected were killed.

The First *Canvey Report* (HSE, 1978b) included assessments of: the hazard at the specific installations at Canvey from oil spillage over the bund at storages; a vapour cloud fire from the British Gas LNG storage; and vapour cloud fires from several LPG storages. These assessments were refined in the second report (HSE, 1981a). An account of this work is given in Appendix 7.

The *Rijnmond Report* (Rijnmond Public Authority, 1982) gives hazard assessments for storages at Rijnmond of acrylonitrile, propylene and LNG. It considers vapour cloud fires, fireballs, jet flames and pool fires. An account of this work is given in Appendix 8.

The hazard assessments of BLEVEs by Drysdale and, David (1979/80), Blything and Reeves (1988 SRD R488) and Selway (1988 SRD R492) include extensive treatment of fire events which could cause a BLEVE.

A general account of hazard assessment for warehouses is described by G.T. Atkinson, Jagger and Kirk 1992).

16.39 Hazard Range of Fire

The hazard range of a fire depends on the type of fire concerned. Fires other than a vapour cloud, or flash fire occur at a fixed point, and therefore the range of the fire is essentially determined by radiant heat transfer. The intensity of thermal radiation from a fire decays according to the inverse square law. For a flash fire, it is also necessary to take into account the movement of the cloud, which is likely then to be the dominant factor.

A set of relations for the hazard range of fire from LPG has been given by Considine and Grint (1985). Their treatment is based on combining models for various types of fire or flame with injury relations. The injury relations used are those of Hymes (1983 SRD R275). These give the 1% and 50% lethality levels as a function of thermal toad. The relations cover flash fires, fireballs, pool fires and jet flames.

16.39.1 Vapour cloud fires

The relations given by Considine and Grint for the hazard range of a flash fire are based on their relations for dense gas dispersion, which are given in Chapter 15. These are used to determine the distance to the lower flammability limit (LFL) and the flammable mass in the cloud.

The authors derive their results for a flash fire from a flash fire code in which the flame is assumed to travel radially away from the ignition source. The thermal load at a given location is then evaluated numerically. They present the results for a quasi-instantaneous release as the plots shown in Figure 16.129. Two pairs of graphs are given, one pair, those shown in Figure 16.129(a,b), for a cloud with concentrations between the upper flammability limit (UFL) and the LFL and another pair, shown in Figure 16.129(c,d) for a cloud with concentrations above the UFL. Figure 16.129(a,b) give the hazard ranges for 1% and 50% lethality for the first type of cloud and Figure 16.129(c) and give the corresponding hazard ranges for the second type. Both types of cloud will burn: the first has the potential to give a vapour cloud explosion, whilst the second will burn by diffusion.

For a quasi-continuous release, the authors state that the envelopes for 1% and 50% lethality do not cover an area significantly different from that covered by the flammable plume and suggest that engulfment in the burning plume be taken as the basis for evaluating fatality.

16.39.2 Fireballs

For fireballs, Considine and Grint use the model of A.F. Roberts (1981/82) described in Section 16.15. The lethality relations are then

$$\left.\begin{aligned} r_{50} &= 22t^{0.379}M^{0.307} \\ r_1 &= 30t^{0.366}M^{0.306} \end{aligned}\right\} \quad 10 < M < 3000; \quad [16.39.1]$$

$$10 < t < 300;\ t < t_d \quad [16.39.2]$$

with

$$t_d = 4.5M^{0.33} \quad [16.39.3]$$

where M is the mass of LPG (te), r is the distance to a given lethality (m), t is the exposure time (s), t_d is the duration time (s) and subscripts 1 and 50 denote 1% and 50% lethality, respectively. The distances r are measured from the centre of the release. The maximum exposure time is limited to the duration time of the fireball.

The CCPS *QRA Guidelines* (1989/5) give the hazard distance for a fireball as

$$r_{50} = 38.9M_T^{0.432} \quad [16.39.4]$$

where M_T is the mass of fuel (ton) and r is the distance to 50% lethality (m).

Another set of hazard distances are those given for a propane fireball by Prugh (1994), as described in Section 16.22:

$$r_{50} = 38M_T^{0.46} \quad [16.39.5]$$

where M_T is the mass of fuel (ton) and r is the distance to 50% lethality (m). He draws attention to the similarity between his model and that of the CCPS.

Prugh also gives the following relations for lethal distance

$$r_{01} = 5.0W_T^{0.46} \quad [16.39.6]$$

$$r_{50} = 3.6W_T^{0.46} \quad [16.39.7]$$

$$r_{99} = 2.5W_T^{0.46} \quad [16.39.8]$$

where r is the distance to the given lethality (ft) and it W_T is the mass of fuel (lb), and for second degree burns

$$r_{50} = 5.3W_T^{0.46} \quad [16.39.9]$$

and first degree burns

$$r_{50} = 3.6W_T^{0.46} \quad [16.39.10]$$

where now r is the distance to the given degree of injury (ft).

16.39.3 Pool fires

For pool fires, the model used by Considine and Grint is that by Considine (1984 SRD R297) described in Section 16.17. The treatment does not take into account flame tilt or trailing, and therefore is limited to conditions with little or no wind. Hazard range relations are given for the case of an unhanded quasi-instantaneous spill with immediate ignition and with a spreading, burning pool. The relations are

$$r_{50} = 16.1M^{0.38} \quad [16.39.11]$$

$$r_1 = 21.7M^{0.38} \quad [16.39.12]$$

The distances r are measured from the centre of the pool. The exposure time is assumed to be equal to the total burning time, and therefore does not appear explicitly in the correlations.

16.39.4 Jet flames

For jet flames of LPG, the model used by considine and Grint is

$$L = 9.1\dot{m}^{0.5} \quad [16.39.13]$$

$$W = 0.25L \quad [16.39.14]$$

Where L is the length of the flame (m). $\dot{m}$ is the mass release flow (kg/s) and W is the half-width of the flame at the flame tip (m).

Two sets of hazard range relations are given, one for persons end on and one for those side on to the flame. The end on relations are

$$\left.\begin{aligned} r_{50} &= 16t^{0.4}\dot{m}^{0.47} \\ r_1 &= 2.8t^{0.38}\dot{m}^{0.47} \end{aligned}\right\} \quad 1 < \dot{m} < 3000; \quad [16.39.15]$$

$$10 < t < 300 \quad [16.39.16]$$

where r is the distance from the edge of the flame for a given

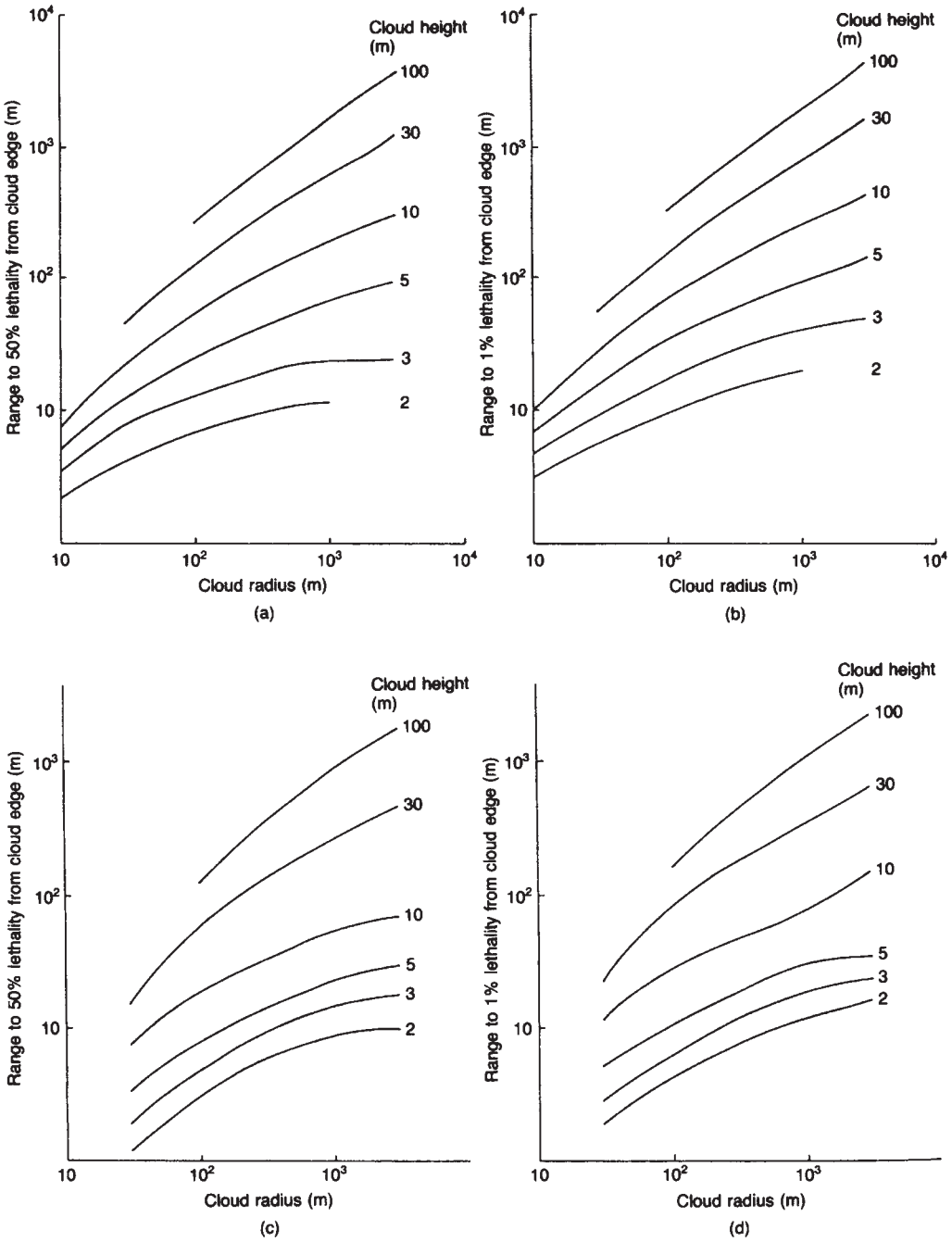


Figure 16.129 *Hazard ranges of flash fires (Considine and Grint, 1985): (a) vapour clouds with concentrations above the upper flammability limit, 50% lethality; (b) vapour clouds with concentrations above the upper flammability limits, 1% lethality; (c) vapour clouds with concentrations between the upper and lower flammability limits, 50% lethality; and (d) vapour clouds with concentrations between the upper and lower flammability limits, 1% lethality (Courtesy of Gastech)*

lethality (m). The side on relations are

$$r_{50} = 1.9t^{0.4}\dot{m}^{0.47} \quad \left.\begin{array}{l} 1 < \dot{m} < 3000; \\ 10 < t < 300; \end{array}\right. \quad [16.39.17]$$

$$r_1 = 2.8t^{0.38}\dot{m}^{0.47} \quad r > W \quad [16.39.18]$$

where r is the distance from the axis of the flame for a given lethality (m).

16.40 Notation

Ar	Archimedes number
Bi	Biot number
Fo	Fourier number
Fr	Froude number
Le	Lewis number
Nu	Nusselt number
Re	Reynolds number
Pe	Peclet number
Pr	Prandtl number
g	acceleration due to gravity
P	absolute pressure
R	universal gas constant
t	time
T	absolute temperature
ρ	density
σ	Stefan–Boltzmann constant

Subscript

max	maximum

Section 16.2

Subsections 16.2.1–16.2.7

A	area of flame front cone; constant (Equation 16.2.12)
A'	area defined by Equation 16.2.9
B	constant
E	apparent activation energy
h	height of flame front cone
ΔH_c	net heat of combustion (kcal/mol)
k_1, k_2	constants
l	slant height of flame front cone
L	lower flammability limit (%v/v)
n	index
r	radius of flame front cone
S_u	burning velocity
t	temperature (°C)
u	velocity of gas
U	upper flammability limit (%v/v)
V	volumetric flow of gas
y	concentration of fuel component i (mole fraction)
α	half-angle of apex of flame front cone
τ	time delay before ignition

Subscripts

i	fuel component i
t	at temperature t
25	at 25°C

Subsection 16.2.8

a_i	constant for component i
b_i	constant for component i
c_i	constant for component i
d_i	constant for component i
c_{pi}	specific heat at constant pressure of component i
c_{pm}	mean specific heat over range specified
c_{pmp}	mean specific heat of products
C_{pmr}	mean specific heat of reactants
ΔH_c	heat of combustion
ΔH_1	enthalpy change between states 0 and 1
ΔH_2	enthalpy change between states 1 and 2
n	number of moles per mole of fuel
p	number of products
r	number of reactants

Subscripts

i	component i
o	standard state
p	products
r	reactants
1, 2	initial, final state

Subsection 16.2.9

D_o	quenching diameter
$D_{\|\|}$	critical slot width

Section 16.3

Subsection 16.3.3

g	boundry velocity gradient
r	diameter of tube
V	volumetric flow gas

Subscripts

B	blow-off
F	flashback

Subsection 16.3.4

Equation 16.3.2

d	diameter of pipe (m)
D	diffusion coefficient (m^2/s)
L	flame length (m)
u	fuel velocity (m/s)

Equation 16.3.3–16.3.5

C_t	concentration of fuel in stoichiometric mixture (mold fraction)
D	diameter of pipe (m)
L	flame length (m)
M_n	molecular weight of fuel
M_s	molecular weight of surrounding fluid (normally air)
T_f	absolute adiabatic flame temperature (K)
T_n	absolute temperature of fuel in pipe (K)
W	diamter at top of flame (m)
x	axial distance (m)
Z	flame diameter (m)
α_t	ratio of number of mole of unreacted and reacted gas in stoichiometric mixture

Subsection 16.3.5

c_p	specific heat of gas at constant pressure
g_B	critical velocity gradient for blow-off
k	constant
K	Karlovitz number

S_u burning velocity
T_u absolute temperature of unburned gas
T_1 absolute temperature defined by Figure 16.17
U flow line velocity
x, y coordinates defined by Figure 16.17
η_o width of wave

Equations 16.3.11–16.3.13
d diameter of sphere
η_o thickness of unburnt outer shell

Subscripts
b burnt
u unburnt

Subsection 16.3.5
A pre-exponential factor
c specific heat of reading mass
E activation energy
k thermal conductivity
m number defining geometry of reaction volume
Q heat released per unit volume
Q' heat of reaction per unit mass
r semi-thickness or radius of reacting volume
x, y, z distances in x, y, z directions

δ dimensionless parameter defined by Equation 16.3.20
η dimensionless parameter defined by Equation 16.3.18
ζ dimensionless parameter defined by Equation 16.3.21
τ dimensionless parameter defined by Equation 16.3.22

Subscript
o initial

Subsection 16.3.9
c_p specific heat of gas at constant pressure
S burning velocity

Equations 16.3.27–16.3.29
E apparent activation energy
k_1, k_2 constants
p pressure
r radius of vessel

τ ignition time delay

Equations 16.3.30 and 16.3.31
d critical diameter
h excess enthalpy
H minimum ignition energy
K constant
T_f absolute adiabatic flame temperature
T_o absolute temperature of unhurried gas mixture ahead of the flame front
ρ density of gas mixture

Equations 16.3.32–16.3.34
d_c width of spark kernel
k thermal conductivity of gas
l characteristic flame dimension

α thermal diffusivity of gas
δ width of flame zone
ρ density of gas

Subscripts
L laminar
T turbulent

Equations 16.3.35 and 16.3.36
A constant (Equation 16.3.25)
A, B constant (Equation 16.3.36)
E minimum ignition energy
t excitation time
α index
β index

Subsection 16.3.10
Equation 16.3.37
g acceleration due to gravity (cm/s^2)
r radius of tube
v_o velocity of bubble (cm/s)

Equations 16.3.38–16.3.48 and 16.3.50–16.3.52
B constant
m, n indices
S_t average velocity of displacement of turbulent wave
S_u burning velocity
u' axial component of turbulence
v' radial component of turbulence
U average velocity
y mol fraction
α_i ratio of mass of fuel component i + corresponding amount of oxidant to total mass of fuel + oxidant
ϕ_1, ϕ_2 functions of turbulence

Equation 16.3.40
S_u burning velocity (cm/s)
T_u absolute temperature of unburned gas (K)

Subscripts
i component i
L laminar
m mixture
T turbulent

Equation 16.3.49
d burner diameter (cm)
u_n laminar burning velocity (cm/s)
u_t turbulent burning velocity (cm/s)

Equations 16.3.53–16.3.62
A constant
c_p specific heat of gas
D diffusion coefficient of deficient reactant
k thermal conductivity of gas
K Karlovitz flame stretch factor
L integral length scale of turbulence
n index
R_L turbulent Reynolds number
R_λ unburnt gas Reynolds number
u' r.m.s. turbulent velocity

u_l laminar burning velocity
u_t turbulent burning velocity
u_k' effective r.m.s. turbulent velocity acting on Flame
U average velocity
λ Taylor miscoscale
ν kinematic viscosity

Section 16.3.11
A constant
c specific heat of unburned gas
d quenching diameter
d_o quenching diameter
d_p depth of penetration of quenching
d_q quenching distance
$d_{||}$ critical slot width
f geometrical factor
g_F critical boundary velocity for flashback
k thermal conductivity of gas
k_1–k_3 constants
L gap length
S_L laminar burning velocity
S_u burning velocity
T_f absolute flame temperature
T_i absolute ignition temperature
T_o absolute temperature of unburned gas
u' r.m.s. turbulent velocity
x half-width of slot
α thermal diffusivity

Subscript
u unburned

Subsection 16.3.12
c constant
k constant
m, n indices
P_{cf} absolute final pressure for cool flame
ΔP_{cf} pressure rise for cool flame
P_o initial pressure
ΔT_{cf} temperature rise for cool flame
τ ignition delay

Section 16.4

Subsection 16.4.2
d_L diameter of droplet
K burning constant
$\dot{m}_F$ mass burning rate of droplet
ρ_L density of liquid

Subsection 16.4.3
C_f flame front volumetric concentration
C_v volumetric concentration
V_a downward velocity of air
V_f upward velocity of flame through suspension
V_s sedimentation velocity of drops relative to air

Subsections 16.4.4 and 16.4.5
B Spalding mass transfer number
c_p specific heat of fuel
c_{pa} specific heat of air
c_{pg} specific heat of gas
C_1 ratio of surface mean area to Sauter mean diameter
C_3 ratio of volume mean diameter to Sauter mean diameter
d_q quenching diameter
D_{32} Sauter mean diameter
E_{min} minimum ignition energy
f swelling factor of fuel
H heat of combustion
k thermal conductivity of fuel
L latent heat of vaporization
q mass ratio of fuel to air
S_g laminar burning velocity of gases liberated from particles
S_u laminar burning velocity
ΔT temperature difference
α thermal diffusivity of particle
α_g thermal diffusivity of gases
δ_r thickness of reaction zone
ϵ emissivity of particle
ρ density
ϕ equivalence ratio

Subscripts
b boiling point of fuel
f fuel
g gas
p fuel
pr pre-reaction zone
r reaction zone
s surface of fuel
st stoichiometric

Section 16.6
a volume coefficint of expansion
A pre-exponential term
B constant (Equations 16.6.31–16.6.33 only); dimensionless parameter (Equations 16.6.86–16.6.90 only)
c specific heat of material
c_1–c_3 roots, solutions of equations
C concentration of oxygen
C_o concentration of oxygen in air
C_1, C_2 constants
d diameter of sphere
D constant
D_p diffusion coefficient in pores
E activation energy
F constant
G constant
h surface heat transfer coefficient
h_c convection heat transfer coefficient
h_r radiation heat transfer coefficient
j shape index, or factor (= 0 for slab; =1 for cylinder; = 2 for sphere)
k thermal conductivity
M parameter defined by Equation 16.6.108
n index
P parameter defined by Equation 16.6.109
q heat transferred by radiation
Q heat released by reaction per unit volume
$Q(T_a)$ modified heat released by reaction per unit volume

Q'	heat released by reaction per unit mass
Q''	modified heat released by reaction per unit volume
Q^*	modified heat released by reaction per unit mass
r	radial distance, half-width
r_1	inner radius of cylinder
r_2	outer radius of cylinder
R	gas constant
R_o	average radius
S	surface area
t	time
T	temperature
ΔT	temperature difference
V	volume
x	horizontal distance
z	dimensionless distance
α	Biot number
β	effective heat transfer coefficient
δ	dimesionless ignition parameter
δ_c	critical ignition parameter
δ^*	modified critical ignition parameter
ϵ	dimensionless parameter
ϵ_1	emissivity of surface
ϵ_2	emissivity of surroundings
θ	dimensionless temperature difference
ν	kinematic viscosity
ρ	density of material
τ	dimensionless time
ξ	dimensionless parameter defined by Equation 16.6.78
χ	dimensionless parameter defind by Equation 16.6.93
ϕ	fractional conversion
ϕ^*	small fractional conversion necessary to initiate autocatalytic reaction
ψ	fractional temperature defined by Equation 16.6.100
$\psi(C)$	concentration function defined by Equation 16.6.80
ψ'	derivative of ψ with respect to τ
ω	dimensionless concentration

Subscripts

a	ambient
c	critical value
cb	critical value for cube
f	fluid
i	induction, initial value
im	initial value for medium
o	centre
p	hot face
s	surface
sb	critical value for slab

Section 16.7

a	radius of sphere (m); half distance between axes of two parallel cylinders (m) (Equation 16.7.53 only); length of tank (m) (Equations 16.7.184–16.7.187, 16.7.190 and 16.7.191 only)
A	area (m^2)
A_n	parameter defined by Equation 16.7.185
A_p	cross-sectional area of pipe (m^2)
b	radius of sphere (m); width of tank (m) (Equations 16.7.184–16.7.187, 16.7.190 and 16.7.191 only)
B	parameter defined by Equation 16.7.65; parameter defined by Equation 16.7.185
c	concentration of ions ($kmol/m^3$); height of tank (m) (Equations 16.7.184–16.7.187 only)
c	constant
c_o	concentration of ions in the bulk fluid ($kmol/m^3$)
c_s	concentration of ions at the pipe wall ($kmol/m^3$)
c^*	charging tendency (As/m^2)
C	capacitance (F)
d	diameter (m)
d_d	diameter of droplet, particle (m)
d_p	diameter of pipe (m)
D	displacement (C/m^2)
D_m	molecular diffusion coefficient (m^2/s)
e	charge on proton (C) ($=1.6 \times 10^{-19}$)
E	field strength (V/m)
E_b	breakdown field strength (V/m)
E_e	field strength for onset of incendive discharge (V/m)
E_i	field strength at surface of inner cylinder (V/m)
E_{mf}	maximum field strength with tank full of liquid (V/m)
E_{mh}	maximum field strength with tank half full of liquid (V/m)
E_o	field strength at surface of outer cylinder (V/m)
E_v	field strength in vapour space of tank (V/m)
E_z	field strength at distance z below roof of tank (V/m)
E_γ	field strength at fraction γ of tank height (V/m)
f	friction factor
f	fraction of charge unrelaxed (Equations 16.7.161–16.7.162 only)
F	Faraday's constant (C/kmol) ($=9.65 \times 10^7$)
F_c	field applied in contact between surfaces (N)
F_e	force (VAs/m)
g	acceleration due to gravity (m/s^2)
G	parameter defined by Equation 16.7.142; conductance (S) (Equation [16.7.3] only)
h	height of liquid in tank (m)
h_l	height of liquid in tank (m)
h_v	height of vapour in tank (m)
H	height of tank (m)
I	current (A)
I_i	current at inlet of pipe (A)
I_{lk}	leakage current (A)
I_o	current at outlet of pipe, at inlet of tank (A)
I_∞	streaming current in infinitely long pipe (A)
j	charge flux (A/m^2)
J	current density (A/m^2)
k	Boltzmann constant (J/K) ($=1.38 \times 10^{-23}$); constant (Equation 16.7.221 only)
l	length (m)
L	length of tank (m)
m	mass (kg)
n	number of ions per unit volume (ions/ m^3)
n_d	number of droplets per unit volume (droplets/ m^3)
n_t	transference number
N	Avogadro's constant (molecules/kmol) ($=6.02 \times 10^{26}$)
p	height of vapour space (m)
P	pressure (N/m^2)
ΔP	pressure drop (N/m^2)
q	charge (C)
q'	charge (on second body) (C)

q_o charge in equilibrium with initial voltage (C) (charging); initial charge (C) (discharging)
Q volumetric flow (m^3/s)
r radial distance (m); (with subscript) radius (m)
r_c radius of cylinder (m)
r_i radius of inner cylinder (m)
r_o radius of outer cylinder (m)
r_p radius of pipe (m)
R universal gas constant (VC/mol K)
R resistance (Ω); gas constant (Equations 16.7.103–16.7.106 and 16.7.133–16.7.136 only)
R_p resistance of liquid in pipe (Ω)
s space charge density (C/m^3)
s_m mass charge density (C/kg)
s_{mf} space charge density with tank half full of liquid (C/m^3)
s_{ms} space charge density with tank full of mist (C/m^3)
s_o space charge density of liquid entering tank (C/m^3); initial space charge density (Equation 16.6.202 only) (C/m^3)
s_t space charge density of liquid in tank (C/m^3)
S surface area (m^2)
t time (s)
$t_{1/2}$ half-life (s)
T absolute temperature (K)
u liquid velocity (m/s); ionic mobility ($m^2/V\,s$) (Equations 16.7.85–16.7.113)
u_{st} Stokes' velocity (m/s)
v ionic velocity (m/s)
V potential difference, potential above earth, voltage (V)
V_{cn} volume of containment (m^3)
V_d potential difference across double layer (V)
V_e volume of charge cloud (m^3)
V_o initial voltage (V)
V_s streaming potential (V)
V_{set} settling potential gradient (V/m)
V_{ves} volume of vessel (m^3)
w fraction of height of tank filled with liquid
W energy, work (J)
x distance (m); half-distance between parallel plates (m) (Equation 16.7.56 only)
x, y, z spatial coordinates (m)
X volume fraction of dispersed phase (v/v)
Y parameter defined by Equation 16.7.148
z number of elementary charges per particle
α shape parameter defined by Equation 16.7.186; parameter defined by Equation 16.7.169
β shape parameter defined by Equation 16.7.152; parameter defined by Equation 16.7.187; parameter defined by Equation 16.7.191
γ surface tension (N/m); fraction of tank height at which field strength is measured (Equation 16.7.184 only)
δ thickness of double layer (m)
δ_m thickness of diffusion layer (m)
ϵ relative permittivity, dielectric constant
ϵ_a absolute permittivity (F/m)
ϵ_{ar} relative permittivity of air
ϵ_o permittivity of free space (F/m) ($=8.85 \times 10^{-12}$)
η viscosity (kg/m s)
ζ zeta potential (V)
κ conductivity ($S/m = \Omega^{-1}\,m^{-1}$)
κ_e effective conductivity (S/m)
κ_r rest conductivity (S/m)
λ parameter defined by Equation 16.7.160
ν kinematic viscosity (m^2/s)
ρ volume resistivity, resistivity (Ω m)
ρ_e effective density of dust cloud or settled powder (kg/m^3)
ρ_l density of liquid (kg/m^3)
ρ_s density of particle material (kg/m^3)
$\Delta\rho$ density difference between droplet and continuous liquid phase (kg/m^3)
σ surface charge density (C/m^3)
τ relaxation time, relaxation time constant (s)
τ_o initial relaxation time (s)
τ_s shear stress (N/m^2)
τ_{so} shear stress at wall (N/m^2)
ϕ potential (V)
ψ Euler's constant (=0.577)

Subscripts
d droplet, particle
fp fill pipe
l liquid
lk leakage
ms mist
p pipe
t tank
v vapour
ves vessel
∞ infinitely long pipe

Units
Units in this section are SI, as given above, with the following exceptions:
Equations 16.7.123–16.7.150, 16.7.152, 16.7.154–16.7.156: cgs units
Subsections 16.7.34 and 16.7.36: units defined locally
For resistivity
$ohm^{-1} = \Omega^{-1} = mho = S$
Units of surface resistivity: Ω
Units of volume resistivity: Ω m
cu = conductivity units (pS/m)

Section 16.10

P probability of ignition
P_a probability of ignition by event itself
P_b probability of ignition by a specific ignition source
$P_{b,i}$ probability of ignition by a ignition source i
$P_{b,i,1}$ probability that ignition source i is present
$P_{b,i,2}$ probability that flammable region of gas cloud reaches ignition source i
$P_{b,i,3}$ probability that ignition source i if active is able to ignite gas
$P_{b,i,4}$ probability that ignition source i is active
P_c probability of ignition by a background ignition source
r distance
θ direction
θ_s semi-angle of sector
μ density of ignition source

Subscript
i ith ignition source

Section 16.11

B rate of penetration of burning into fuel bed
C mass of air required for complete combustion of unit mass of fuel
d depth of fuel bed consumed by fire
D duct diameter
f fraction of surface covered by lining
L length of flame zone
L^* dimensionless parameter defined by Equation 16.11.1
V velocity of advance of leading edge of flame
V^* dimensionless parameter defined by Equation 16.11.2
V_A velocity of air

ρ_A density of air
ρ_f density of fuel bed

Section 16.13

A area
A constant in Equation 16.13.59
A_i constant in Equation 16.13.55a
B radiosity
c velocity of sound
c_o velocity of sound in vacuum
C_c correction factor for emissivity of carbon dioxide
C_w correction factor for emissivity of water vapour
e emissive power
F_A angle factor
F_{A_1-A2} angle factor between surface A_1 and surface A_2
F_o interchange factor
F_ϵ emissivity factor
h Planck's constant
H incident radiation
i intensity of radiation
I intensity of radiation
I_o intensity of radiation at surface of source
J_T thermal radiation flux (unattenuated)
k Boltzmann constant
k_i constant in Equation 16.13.55
k_1, k_2 constants in Equation 16.13.52
L mean path length
n refractive index
P_{CO_2} partial pressure of carbon dioxide
P_{H_2O} partial pressure of water vapour
r distance
R radiant heat factor
V visual range
w concentration of water in atmosphere (pr mm) (pr = precipitative water; see text)
w_i concentration of water in atmosphere which causes absorption in window i to go from weak band to strong band absorption (pr mm)
x path length in flame
X path length outside flame

α absorptivity
β extinction coefficient
β_i constant in Equation 16.13.55b
γ scattering coefficient
ϵ_{CO_2} emissivity of carbon dioxide
ϵ_{H_2O} emissivity of water vapour
$\Delta\epsilon$ emissivity correction
Φ radiant heat flux
θ angle
κ absorption coefficient
λ wavelength
ν wave frequency
ρ reflectivity
τ transmissivity
τ_{ai} transmissivity based on absorption in window i
τ_{si} transmissivity based on scattering in window i
τ_{Ti} total transmissivity in window i
ω solid angle

Subscripts
b black body
i, j for surfaces i, j
s source
t target
λ for wavelength λ
ν for wave frequency ν

Section 16.14

Subsection 16.14.5

A_r area of radiation of hot gas layer (m^2)
c_p specific heat of hot gas layer (J/kg K)
I_r effective thermal radiation intensity (W/m^2)
k parameter defined by Equation 16.14.9
k_l concentration at lower explosive limit (kg/m^3)
k_u concentration at upper explosive limit (kg/m^3)
m total mass of vapour released
q heat loss by radiation (W)
r_l parameter of cloud at lower explosive limit
r_u parameter of cloud at lower explosive limit
t time (s)
t_{eff} effective duration of fire (s)
$t_{1/2}$ half-life of fire (s)
T_a absolute temperature of environment (K)
T_g absolute temperature of hot gas (K)
V_r volume of hot gas layer (m^3)
x, y, z distance in downwind, crosswind, vertical directions (m)
β parameter defined by Equation 16.14.13
ϵ_a emissivity of environment
ϵ_g emissivity of hot gas
ρ density of hot gas layer (kg/m^3)
σ Stefan–Boltzmann constant ($W/m^2\,K^4$)
$\sigma_x, \sigma_y, \sigma_z$ dispersion coefficients in downwind, crosswind, vertical directions (m)

Subscript
i initial

Subsections 16.14.6 and 16.14.7

D cloud depth (m)
H visible flame height (m)
r stoichiometric air–fuel mass ratio
S flame speed (m/s)
U_w wind speed (m/s)

w parameter
W width of pool fire
α constant pressure expansion ratio for stoichiometric combustion
ρ_a density of air (kg/m^3)
ρ_o density of fuel–air mixture (kg/m^3)
ϕ Volumetric concentration of fuel (v/v)

Subscript
st stoichiometric

Section 16.15

Subsections 16.15.5–16.15.9
D diameter of fireball (m)
f fraction of fuel released entering fireball
k_1, k_2 constants
M mass of fuel (kg)
M_r mass of liquid released (kg)
n_1, n_2 indices
t_a duration of combustion in system dominated by initial momentum effects (s)
t_b duration of combustion in system dominated by buoyancy effects (s)
t_c duration of combustion in system dominated by deflagration effects (s)
t_d duration time of fireball (s)
t_e time at which lift-off occurs (s)
ϕ fraction of liquid vaporized

Equation 16.15.9a
d persistence time (s)
W mass of propellant (lb)

Equation 16.15.15
P absoluter pressure at moment of release (Mpa)

Equation 16.15.16
E surface emissive power (kW/m^2)
P absolute pressure (MPa)

Subsections 16.15.11–16.15.13
E surface emissive power
F view factor
h height of center of fireball
ΔH_c heat of combustion (kJ/kg)
I heat received by target
l distance between center of fireball and target
Q heat release rate (kW)
Q_r heat rediated
r radius of fireball
x distance from point directly beneath centre of fireball and target, or ground distance
α absorptivity of target
τ atmospheric transmissivity
θ, ϕ angles defined in Figure 16.87

Subsection 16.15.15
F_B buoyancy force (N/m^2)
F_R fluid resistance force (N/m^2)
g acceleration due to gravity (m/s^2)
r radius of fireball (m)
t time (s)
t_b burnout time
ρ density of fireball (kg/m^3)

Equations 16.15.33–16.15.40
r radius of fireball (ft)
r_b radius of fireball at burnout (ft)
R rate of addition of propellant (lb/s)
t times (s)
W mass of fireball (lb)
W_b mass of propellant, and fireball, at burnout (lb)
ρ_b density of fireball at burnout (lb/ft^3)

Subscript
b burnout

Subsection 16.15.16
D diameter of fireball (m)
M mass of fuel (kg)
r radius of fireball (m)
t_b duration time of fireball (s)
W_b mass of fireball, including air, at burnout (kg)
W_f mass of fuel (kg)

Subsection 16.15.17
r radius of cloud
t time
V_f volume of initial cloud of fuel
z height of center of cloud
β entrainment coefficient
ρ_a density of air
ϕ equivalence ratio

Subscripts
p products
r reactants

Subsection 16.15.18
M mass of fuel
t_b burning time
v_o mean release velocity
ρ_a density of air

Subsection 16.15.19
c specific heat (kJ/kg °C)
D diameter of fireball (m)
f flash fraction
F_r fraction of heat radiated, heat radiation factor
g acceleration due to gravity (m/s^2)
H enthalpy of fireball (kJ)
ΔH_c heat of combustion (kJ/kg)
I heat radiation intensity received by target (kW/m^2)
l distance from centre of fireball to target (m)
M mass of fuel released (kg)
M_a mass of air in fireball (kg)
M_f mass of fuel in fireball (kg)
N parameter governing transition from control by momentum to control by gravity slumping
P vapour pressure (MPa)
Q heat of combustion (kJ/kg)

Q_r heat radiation rate (kW)
r radius of cloud (m)
R stoichiometric value of M_a/M_f
t time (s)
t' time for cloud to fall below lower flammability limit (s)
t_d duration time of fireball (s)
t_e lift-off time (s)
t_g time to transition from control by momentum to control by gravity slumping (s)
T_f absolute mean temperature of fireball (K)
T_o absolute temperature of initial reactants (K)
V volume of cloud (m^3)

α momentum per unit mass (m/s)
η thermal efficiency
$\Delta\rho$ density difference between vapour and air (kg/m^3)
ρ_a density of air (kg/m^3)
ρ_f density of products at temperature T_f (kg/m^3)
ρ_o density of products at temperature T_o (kg/m^3).
ρ_v density of vapour (kg/m^3)

Subsection 16.15.20

D_{FB} duration time of fireball (s)
E_T heat released (J)
F_R fraction of heat radiated
H heat of combustion (J/kg)
I_T unattenuated thermal radiation at radius of target (W/m^2)
I_{TA} thermal radiation at radius of target, taking account of atmospheric attenuation (W/m^2)
M mass of fuel in fireball (te)
M_s mass of fuel in vessel (te)
P_D radiative power density (W/m^3)
P_{FB} radiative power (W)
R_{FB} radius of fireball (m)
R_T distance from centre of fireball to target (m)
T_e effective absolute fireball temperature (K)
V_{FB} volume of fireball (m^3)
X parameter

σ Stefan–Boltzmann constant (W/m^2K^4)
τ atmospheric transmissivity
ϕ theoretical adiabatic flash fraction

Section 16.16

Subsections 16.16.4 and 16.16.5

D diameter of fireball (m)
M mass of chemicals (kg)
t_d duration time of fireball (s)

Subsection 16.16.6

d diameter of fireball (ft)
D diameter of fireball (m)
M mass of material (fuel + oxidizer) in fireball (kg)
t_d duration time of fireball (s)
W mass of material (fuel + oxidizer) in fireball (lb)

Subsection 16.16.7

d diameter of fireball (ft)
D diameter of fireball (m)
M mass of explosive (kg)
t_d duration time of fireball (s)
W mass of explosive (lb)

Subsection 16.16.9

D diameter of fireball (m)
M mass of explosive (kg)
t_c time to complete combustion (s)
t_d duration time of fireball (s)
t_s time for transition from hemispherical to spherical shape (s)
T_f absolute temperature of fireball at termination

ϕ parameter defined by Equation 16.16.21

Section 16.17

Subsection 16.17.4

d pan diameter
u velocity
v liquid burning velocity

μ viscosity
ρ density

Subscripts

g gas
l liquid

Subsection 16.17.5

c_p specific heat of air (kJ/kg)
D flame diameter (m)
D' elongated flame base (m)
D_w maximum pool dimension in direction of wind (m)
g acceleration due to gravity (m/s^2)
ΔH_c heat of combustion of fuel (kJ/kg)
L flame height (m)
m mass burning rate ($kg/m^2\,s$)
N dimensionless parameter defined by Equation [16.17.4]
Q total heat release rate (kW)
r_s stoichiometric mass air to volatiles ratio
T_o absolute temperature of ambient air (K)
u wind speed (m/s)
u^* dimensionless wind speed
u_c characteristic wind speed (m/s)
u_{10} wind speed at height of 10 m (m/s)
u^*_{10} dimensionless wind speed at height of 10 m
α, β, γ number of carbon, hydrogen, oxygen atoms in fuel molecule
θ angle of tilt from vertical (rad)
μ_a viscosity of air (kg/m s)
ρ_a density of ambient air (kg/m^3)
ρ_g density of fuel vapour at normal boiling point (kg/m^3)

Equations 16.17.5 and 16.17.6

A constant
u vapour velocity (m/s)
ρ density of vapour (kg/m^3)
$\Delta\rho$ density difference between vapour and air (kg/m^3)

Subsection 16.17.6

d pool diameter
F view factor
k extinction coefficient

q heat transferred from flame to pool
q_c heat transferred from flame to pool by conduction
q_r heat transferred from flame to pool by radiation
q_{rim} heat transferred from flame to pool by pan rim
T_b absolute temperature of burning liquid surface
T_r absolute temperature of flame
U heat transfer coefficient

Equations 16.17.27 and 16.17.28
ΔH_c net heat of combustion (kJ/kmol)
ΔH_v latent heat of vaporization (kJ/kmol)
k_1, k_2 constants
v liquid burning rate (cm/min)
v_∞ liquid burning rate for pool of infinite diameter (cm/min)

Equations 16.17.29 and 16.17.30
m mass burning rate ($kg/m^2 s$)
m_∞ mass liquid burning rate for pool of infinite diameter ($kg/m^2 s$)
ϵ flame emissivity
ρ_l density of liquid (kg/m^3)

Equations 16.17.31–16.17.39
Δh_g total heat of gasification (kJ/kg)
k absorption–extinction coefficient
k_3 constant
L_m mean beam length
m mass burning rate ($kg/m^2 s$)
m_∞ mass liquid burning rate for pool of infinite diameter ($kg/m^2 s$)
T_f absolute temperature of effective equivalent gray gas (K)
β mean beam length corrector
ϵ flame emissivity

Subsection 16.17.8

Equation 16.17.40
d diameter of fire (ft)
k_4 constant
q heat flux from surface ($BTU/ft^2 h$)
q_∞ heat flux from surface of 'large' fire ($BTU/ft^2 h$)

Equation 16.17.41
E surface emissive power (kW/m^2)
T_f absolute temperature of flame (K)
ϵ emissivity of flame

Subsection 16.17.9

A, B parameters defined by Equations 16.17.46c and 16.17.46d, respectively
$A_1 - A_4$ parameters defined by Equations 16.17.51d, 16.17.51f, 16.17.51h and 16.17.51i, respectively
B_1 parameter defined by Equation 16.17.51e
E surface emissive power (kW/m^2)
$f(v)$ parameter defined by Equation 16.17.51g
F view factor
h height of tank
I heat radiation incident on target (kW/m^2)
l, l' distances defined by Figures 16.94.95 and 97
l_s slant distance between heat source and target
L parameter defined by Equations 16.17.46a, 16.17.48b, 16.17.51a, 16.17.58b
Q_r heat radiation rate (kW)
r radius of surface (m)
R parameter defined by Equations 16.17.44a and 16.17.56a
x ground distance between source and target (m)
X parameter defined by Equations 16.17.46b, 16.17.48c and 16.17.51b

α absorptivity
β angle of target surface to horizontal
θ angle of tilt of cylinder
τ atmospheric transmissivity
ϕ parameter defined by Equation 16.17.51c

Subscripts
h horizontal surface
m maximum
v vertical surface

Subsection 16.17.13

D diameter of cylinder
F view factor
h height of flame (m)
Δh_c heat of combustion (kJ/kg)
H dimensionless flame height
k extinction coefficient
l distance from centre of flame to target (m)
L dimensionless distance to target
m mass burning rate ($kg/m^2 s$)
P radiative power (kW)
q_i thermal radiation incident on target (kW/m^2)
T_f absolute temperature of flame (K)

β mean beam length corrector
ϵ_f emissivity of flame
χ_r fraction of heat radiated

Subscript
∞ pool of infinite diameter

Subsection 16.17.15

Fr′ modified Froude number
g acceleration due to gravity (m/s^2)
H length of flame (m)
u_w wind speed (m/s)
W width of trench (m)
W' extended width of flame base (m)

θ angle of tilt of flame (°)

Section 16.18

Subsections 16.18.2–16.18.4

C_L lower explosive limit (v/v)
$\bar{C}_L$ modified lower explosive limit (v/v)
d flare diameter (m)
D distance from centre of flame to target (m)
F_r fraction of heat radiated
I heat radiation intensity incident on target (kW/m^2)
k ratio of specific heats of gas
K allowable heat radiation incident on target (kW/m^2)

M molecular weight of gas
P pressure just inside flare tip (kPa)
Q net heat release rate (kW)
r radius from centre of flame (m)
R parameter defined by Equation 16.18.10
T absolute temperature of gas (K)
u_j exit velocity of gas at flare tip (m/s)
u_s velocity of sound (m/s)
u_∞ wind velocity (m/s)
V volumetric flow of gas (m^3/s)
W mass flow of gas (kg/s)
$\Sigma\Delta x$ horizontal deviation of flame (m)
x_c horizontal distance from flare tip to centre of flame (m)
$\Sigma\Delta y$ vertical deviation of flame (m)
y_c vertical distance from flare tip to center of flame (m)
τ atmospheric transmissivity

Subscript
j flare tip

Subsection 16.18.6
A surface area of flame (m^2)
b lift-off distance of flame frustrum (m)
C parameter defined by Equation 16.18.30
d_j diameter of virtual source (m)
d_o throat diameter of imagined flow nozzle (m)
D_s etIective diameter of source (m)
E surface emissive power (kW/m^2)
F view factor
F_r fraction of heat radiated
g acceleration due to gravity (m/s^2)
I heat radiation incident on target (kW/m^3)
K parameter defined by Equation 16.18.25
L_B length of flame (m)
L_{Bo} length of flame in still air (m)
$\dot{m}$ mass flow of gas (kg/s)
M molecular weight
M_k kilogram molecular weight of gas (kg/mol)
P_o atmospheric pressure (N/m^2)
Q neat heat release rate (kW)
R velocity ratio
R_c gas constant (J/mol K)
R_L length of flame frustrum (m)
T absolute temperature (K)
T_j absolute temperature of gas in expanded jet (K)
W mass fraction of fuel in stoichiometric mixture with air
W_1 width of base of flame frustrum (m)
W_2 width of top of flame frustrum (m)
u gas velocity (m/s)
u_j velocity of gas in expanded jet (m/s)
v wind velocity (m/s)
α angle between hole axis and flame axis (°)
α_b angle between hole axis and line joining tip of flame to centre of hole plane (°)
β parameter defined by Equation 16.18.19
γ ratio of gas specific heats
θ_j angle of flame to horizontal (°)
θ_{jv} angle between hole axis and wind vector in plane containing hole axis, flame axis and wind vector (°)
ρ_a density of air (kg/m^3)
$\rho_g{}^o$ density of gas at standard conditions (kg/m^3)
ρ_j density of gas in expanded jet (kg/m^3)
ξ Richardson number based on flame length in still air
τ atmospheric transmissivity
Ψ parameter defined by Equation 16.18.17

Subscripts
a air
j expanded jet
p mean product value
l adiabatic combustion conditions

Subsection 16.18.7
A total surface area of flame (m^2)
b lift-off distance (m)
$c(\xi)$ parameter defined by Equation 16.18.49
d_j diameter of expanded jet (m)
D_s effective source diameter (m)
$f(\xi)$ diameter defined by Equation 16.18.45
F view factor
$F_{s\infty}$ fraction of heat radiated for flames which emit black body radiation
g acceleration due to gravity (m/s^2)
G initial momentum flux of expanded jet (N)
$h(\xi)$ parameter defined by Equation 16.18.48
k gray gas absorption coefficient (m^{-1})
L characteristic length (m) (Equation 16.18.38); length representing emitting path length (Equation 16.18.55)
Lb_{xy} parameter defined by Equation 16.18.51
L_{bo} length of vertical flame in still air (m)
q heat radiation incident on target (kW/m^2)
Q net heat release rate (kW)
$r(\xi)$ parameter defined by Equation 16.18.46
S surface emissive power (kW/m^2)
S_∞ black body surface emissive power (kW/m^2)
u_a wind speed in release direction (m/s)
u_j velocity of expanded jet (m/s)
w_a wind speed perpendicular to release (m/s)
W mass fraction of fuel in stoichiometric mixture with air
W_1 maximum diameter of flame (m)
W_2 minimum diameter of flame (m)
x, y, z distances in release, vertical, crosswind directions (m)
X, Y, Z x, y, z positions of flame
ρ_a density of air (kg/m^3)
ρ_j density of expanded jet (kg/m^3)
τ atmospheric transmissivity
ξ Richardson number
Ψ parameter defined by Equation 16.18.40
Ω_x, Ω_y parameters defined by Equations 16.18.42 and 16.18.43

Subscripts
a air
en end of flame
j expanded jet
sd side of flame

Section 16.19

Subsection 16.19.2
l_i impingement distance (m)
m mass flow (kg/s)

Subsection 16.19.6

D_{max} maximum cone diameter (m)
F_x, F_y, F_z view factors defined by Equations 16.19.3, 16.19.4 and 16.19.6
h height of vent orifice (m)
h_1 distance from ground to bottom of flame radiator (m)
h_2 distance from ground to top of flame radiator (m)
I radiant heat flux (W/m^2)
l length of flame (m)
r radius of flame at tip (M)
T absolute temperature of flame (K)
x, y distances defined in Figure 16.106 (m)
ϵ emissivity of flame

Subsection 16.19.7

A, B, C constants
d diameter of orifice (m)
D diameter of flame (m)
F fraction of heat radiated
g acceleration due to gravity (m/s^2)
h lift-off height (m)
H height of flame (m)
H^* flame radiation height (m)
m index
Q heat release rate (MW)
u gas velocity at nozzle exit (m/s)

Subsection 16.19.9

D_j diameter of jet (m)
ΔH_c heat of combustion (J/kg)
L length of flame (m)
$\dot{m}$ mass flow (kg/s)
R_s radius of flame at distance s (m)
s distance along centre line (m)
u_j velocity of jet (m/s)
u_w wind velocity (m/s)
x, z distances in horizontal, vertical directions (m)

Subsection 16.19.10

F fraction of heat radiated
ΔH_c heat of combustion (kJ/kg)
$\dot{m}$ mass flow (kg/s)
q heat radiation incident on target (kW/m^2)
x distance from source to target (m)
τ atmospheric transmissivity

Subsection 16.19.11

L flame length (m)
q fuel flow (kg/s)

Subsection 16.19.2

L length of flame (m)
$\dot{m}$ mass flow (kg/s)
W half-width of flame at tip (m)

Subsection 16.19.13

f fraction of heat radiated
F flame length (m)
H_c heat of combustion (J/kg)
m mass flow (kg/s)
q heat radiation incident on target (kW/m^2)
x distance between source and target (m)
τ atmospheric transmissivity

Subsection 16.19.14

As Subsection 16.18.6 plus
b modified lift-off distance
D_j jet diameter (m)
D_s effective source diameter (m)
L flame length (m)
ρ_a density of air (kg/m^3)
ρ_j initial density at jet (kg/m^3)
ρ_v density of vapour (kg/m^3)

Subsection 16.19.16

F view factor
h height of jet above ground including any lift-off
L visible length of flame
r_f radius of flame at height z
x distance between axis of jet and target
z height of flame differential element
α half-angle of flame
ψ angular position of flame differential element

Equations 16.19.31 and 16.19.32
As Subsection 16.18.6 plus
D_c diameter of cylinder equivalent to flame
L length of cylinder equivalent to flame
L_{BV} height of centre of flame tip above level of jet exit
α_B angle between vertical and line joining jet exit and centre of flame tip
θ angle between vertical and flame axis

Subsection 16.19.18

A area of ventilation opening (m^2)
H height of ventilation opening (m)

Section 16.20

Subsection 16.20.1

A wetted surface area
k constant
n index
Q heat absorbed

Equations 16.20.2–16.20.8
A wetted surface area (ft^2)
q heat absorbed per unit area ($BTU/ft^2\,h$)
Q heat absorbed (BTU/h)

Subsection 16.20.4

c specific heat of wall metal
d thickness of wall metal
F parameter (see text)
Q heat absorbed per unit area
t time
T_A asymptotic value of T_1
T_o absolute initial wall temperature
T_1 absolute wall temperature at time t
ϵ emissivity of external surface of wall
ρ density of wall metal
σ Stefan–Boltzmann constant

Equations 16.20.12 and 16.20.13
A parameter defined by Equation 16.20.13
K ratio of outside to inside diameter of wall
P_b burst pressure
T wall temperature (°C)
σ_u ultimate tensile strength or wall metal
σ_y yield strength of wall metal

Section 16.21

Subsection 16.21.3
I thermal radiation intensity (cal/cm^2 s)
k thermal conductivity of wood (cal/cm^2 s (°C/cm))
t_i ignition time (s)

α thermal diffusivity (cm^2/s)
ρ density of wood (g/cm^2)

Equations 16.21.1–16.21.4
A parameter defined by Equation 16.21.2 (cal^2/cm^4 (°C)^2)
B parameter defined by Equation 16.21.4 (cal^2/cm^4 (°C)^2)
I_p minimum thermal radiation intensity for piloted ignition (cal/cm^2 s)
I_s minimum thermal radiation intensity for spontaneous ignition (cal/cm^2 s)
s specific heat of wood (cal/g °C)

Equations 16.21.5–6.21.18
c specific heat of wood (cal/g °C)
h heat transfer coefficient for convection (cal/cm^2 s °C)
I_o minimum thermal radiation intensity (cal/cm^2 s)
L linear dimension (cm)
t time (s)
T_o absolute initial temperature (K)
T_s absolute surface temperature for ignition (K)
T_∞ absolute surface temperature for ignition at infinite time (K)
β cooling modulus
γ energy modulus
θ_s absolute surface temperature difference for ignition (°C)
θ_∞ absolute surface temperature difference for ignition at infinite time (°C)

Equations 16.21.19 and 16.21.20
k_1 constant
L thickness of slab (cm)
n_1–n_3 indices

Subsection 16.21.4
c specific heat of material
ΔH enthalpy change per unit mass in raising material to its firepoint
k thermal conductivity of material
L 'heating length'
$\dot{q}$ rate of heat transfer across surface
V rate of flame spread

α thermal diffusivity of material
ρ density of material
τ thickness
τ_{cr} critical thickness

Section 16.22

Subsection 16.22.5
c specific heat of skin
k thermal conductivity of skin
Q net heat absorbed
T_o initial temperature of skin
T_s surface temperature of skin

ρ density of skin

Subsection 16.22.6
Equation 16.22.2
I thermal radiation intensity (W/m^2)
n index
t time (s)

Equations 16.22.3 and 16.22.4
D thermal dose (kJ/m^2)
I thermal radiation intensity (kW/m^2)
L thermal load ((s kW/m^2)$^{4/3}$)
L' thermal load ([s (W/m^2)$^{4/3}$]/10^4)
t exposure time (s)

Equation 16.22.5
I thermal radiation intensity (W/m^2)
L' thermal load ([s (W/m^2)$^{4/3}$]/10^4)
t exposure time (s)

Subsection 16.22.13
Equation 16.22.6
I thermal radiation intensity (W/m^2)
n index
t time (s)

Equation 16.22.7
a absorptivity of fabric
C specific heat of fabric (J/g °C)
S density of fabric (g/cm^2)
t_p time to piloted ignition (s)
T_o initial temperature of fabric (°C)
T_p piloted ignition temperature (°C)
W incident heat radiation (W/cm^2)

Equation 16.22.8
D_s clothing ignition load (s (kW/m^2)^2)
I thermal radiation intensity (kW/m^2)
t time (s)

Subsections 16.22.15 and 16.22.17
I thermal radiation intensity (W/m^2)
t time of exposure (s)
Y probit

Subsection 16.22.18
L' thermal load ([s ([W/m^2)$^{4/3}$]/10^4)
P_m mortality
P_{ma} average mortality
Y probit

δ burn depth (m)
δ_a burn depth corresponding to average mortality (mm)

Subscripts
a average
l upper
u lower
1 first coefficient
2 second coefficient

Section 16.26
D mass median drop size (mm)
k_1 constant
n_1, n_2 indices
R rate of water application (l/m^2 s)
R_c critical rate of water application (l/min)
t time to extinguish fire (s)
ΔT difference between water temperature and liquid fire point (°C)

Section 16.27
A surface area of droplet (m^2)
B mass transfer number
c absorption coefficient
C_d drag coefficient
D droplet diameter (m)
g acceleration due to gravity (m/s^2)
G liquid mass flux (kg/m^2 s)
h_d surface enthalpy of droplet (J/kg)
h_s free stream enthalpy (J/kg)
L latent heat of evaporation of droplet (J/kg)
m_d mass of droplet (kg)
M_r rate of evaporation loss due to thermal radiation (kg/s)
Q heat flux droplets (W/m^2) (Equation 16.27.8); heat flux between water and surface (W/m^2) (Equation 16.27.9)
t time (s)
δt time of exposure of droplet (s)
U gas velocity (m/s)
v droplet velocity (m/s)
ν gas kinematic viscosity (m^2/s)
ρ_g gas density (kg/m^3)

Section 16.36
t time (min)
T temperature (°C)

Subsection 16.36.4
A_T total surface area of walls and ceilings, excluding ventilation openings (m^2)
A_W area of ventilation openings, including doors and windows (m^2)
k_f constant
M_f total mass of combustible material (kg of wood equivalent)
$\dot{m}$ mass burning rate (kg/min)
t_f effective fire resistance time (min)

Subsection 16.36.11
Equations 16.36.3–16.36.4
A_W area of ventilation opening (m^2)
H height of ventilation opening (m)
ΔH_c heat of combustion (kJ/kg)
k_v constant (kg/m$^{3/2}$ s)
$\dot{m}$ mass burning rate (kg/s)
$\dot{q}$ heat release rate (kW)

Equations 16.36.5–16.36.8
A_T total area of enclosure, excluding ventilation openings (m^2)
A_W area of ventilation openings (m^2)
h height of opening (m)
L mass of fuel (kg)
$\dot{q}_{fo}$ heat release rate at flashover (kW)
T_o ambient temperature (°C)
T_u upper limit air temperature (°C)
η ventilation parameter (m$^{-1/2}$)
τ fire load parameter (kg/m^2)

Subsection 16.36.12
A_f surface area of fuel (m^2)
I thermal radiation intensity (kW/m^2)
L_v heat of gasification of volatiles (kJ/kg)
$\dot{m}$ mass burning rate (kg/s)
T^* constant
T_o absolute ambient temperature (K)
T_u absolute upper gas temperature (K)
θ_1–θ_5 modification factors (see text)

Subsection 16.36.13
B width of window (m)
H height of window (m)
$\dot{m}$ mass burning rate (kg/s)
n shape factor defined by Equation 16.36.13
x horizontal reach of flame (m)
z height of flame above top of window (m)

Section 16.39
L length of flame (m)
$\dot{m}$ mass release flow (kg/s)
M mass of LPG (te)
r distance of specified lethality (m)
t exposure time (s)
t_d duration time (s)
W half-width of flame at flame tip (m)

Subscripts
1 1% lethality
50 50% lethality

Lees' Loss Prevention in the Process Industries

VOLUME 2

Hazard Identification, Assessment and Control

THIRD EDITION

Edited by
SAM MANNAN

Lee's Loss Prevention in the Process Industries

Volume 2

This book is dedicated to

Herbert Douglas Lees (1860–1944), gas engineer;
Frank Priestman Lees (1890–1916), gas engineer;
Herbert Douglas Lees (1897–1955), gas engineer;
David John Lees (1936–), agricultural engineer;
Frank Lyman MacCallum (1893–1955), mining engineer and missionary;
Vivien Clare Lees (1960–), plastic and hand surgeon;
Harry Douglas Lees (1962–), restaurateur
and their families

'They do not preach that their God will rouse them a little before
the nuts work loose.
They do not teach that His Pity allows them to drop their job when
they dam'-well choose.
As in the thronged and the lighted ways, so in the dark and the
desert they stand,
Wary and watchful all their days that their brethren's days may be
long in the land.'

Rudyard Kipling (The Sons of Martha, 1907)

Wo einer kommt and saget an,
Er hat es allen recht getan,
So bitten wir diesen lieben Herrn,
Er wöll uns solche Kunste auch lehrn

(Whoever is able to say to us
'I have done everything right',
We beg that honest gentleman
To show us how it is done)

Inscription over the 'Zwischenbau' adjoining the Rathaus in Brandenburg-on-the-Haven
(quoted by Prince B.H.M. von Bulow in *Memoirs*, 1932)

If the honeye that the bees gather out of so manye floure of herbes . . . that are growing in other

mennis medowes . . . may justly be called the bees' honeye . . . so maye I call it that I have . . .

gathered of manye good autores . . . my booke.

William Turner (quoted by A. Scott-James in *The Language of the Garden: A Personal Anthology*)

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Lee's Loss Prevention in the Process Industries

Hazard Identification, Assessment and Control

Volume 2

Third edition

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Elsevier Butterworth–Heinemann
200 Wheeler Road, Burlington, MA 01803, USA
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Library of Congress Cataloging-in-Publication Data
Lee's loss prevention in the process industries. – 3rd ed. / edited by Sam Mannan.
p. cm.
Rev. ed. of: Loss prevention in the process industries / Frank P. Lees. 2nd ed. 1996.
Includes bibliographical references and indexes.
ISBN 0-7506-7555-1 (casebound, set : alk. paper) 1. Petroleum chemicals industry–Great Britain–Safety measures. 2. Petroleum chemicals industry–United States–Safety measures. I. Title: Loss prevention in the process industries. II. Mannan, Sam. III. Lees, Frank P. Loss Prevention in the process industries.
TP690.6.L43 2005
660′.2804–dc22

2004018498

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from British Library

Set ISBN: 0-7506-7555-1
Volume 1 ISBN: 0-7506-7857-7
Volume 2 ISBN: 0-7506-7858-5
Volume 3 ISBN: 0-7506-7589-3

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04 05 06 07 08 09 10 10 9 8 7 6 5 4 3 2 1

Printed in the United States of America

Preface to Third Edition

The first edition of this book appeared in 1980, at the end of a decade of rapid growth and development in loss prevention. In the preface to the second edition, Frank P. Lees wrote, "After another decade and a half the subject is more mature, although development continues apace. In preparing this second edition it has been even more difficult than before to decide what to put in and what to leave out." Frank Lees' statement in 1996 rings even truer today, another eight years later in 2004. Industrial advances and technology changes coupled with recent events have made it essential to focus on new topics while keeping a complete grasp of all of older technologies and learnings as well. Safety programs today must also consider issues such as chemical reactivity hazards, safety instrumented systems, and layer of protection analysis. In the post 9-11 world, process safety and loss prevention must also include consideration of issues related to chemical security and resilient engineering systems.

The history of safety regulations in the United States can be traced back to the year before the beginning of the twentieth century. The River and Harbor Act, the first known federal legislation relevant to safety was promulgated in 1899. Since then, the total number of legislations has steadily increased. In addition to the federal government, local entities such as the state, county, and cities have also promulgated regulations and ordnances, which impose safety requirements on process facilities. Varying degrees of similar legislative action has also occurred in the rest of the world. These legislation were all promulgated in response to some event, demographic changes, as well as changes in the industry. Also, as our understanding of the hazards associated with industrial processes developed, procedures and practices were put in place to limit or eliminate the damage. Government programs and industry initiatives spurred improvements in the science and technology needed for the recognition of hazards and associated risks.

Management systems have been put in place to implement regulations and industry practices. Government regulations will continue to be a significant driver for safety programs. As such, one of the main objectives of these management systems is to ensure compliance. However, it is also quite clear that profitability is directly related to safety and loss prevention. Thus the management systems for safety are intricately tied into the operational management.

The industrial revolution brought prosperity and along with it the use of hazardous processes and complex technologies. Growing economies and global competition has led to more complex processes involving the use of hazardous chemicals, exotic chemistry, and extreme operating conditions. As a result, a fundamental understanding of the hazards and associated risks is essential. Process safety and risk management requires the application of the basic sciences and a systematic approach. Recent advances, such as overpressure protection alternatives and reactive chemistry allow safer design and operation of processes.

In the multiple barriers concept, plants are designed with several layers so that an incident would require the failure of several systems. Another novel approach to process safety and risk management is to consider various actions in a descending hierarchical order. Inherently safer design consideration should be first in the hierarchy followed by prevention systems, mitigation, and response. The success of these systems is dependent on the fundamental understanding of the process and the associated hazards. Chronic as well as catastrophic consequences resulting from toxic and flammable substances can be reduced and/or eliminated through appropriate design and operating practices.

Managing safety is no easy task, but it makes bottomline sense. There is a direct payoff in savings on a company workers' compensation insurance, whose premiums are partly based on the number of claims paid for job injuries. The indirect benefits are far larger, for safe plants tend to be well run in general and more productive. The recipe for safety is remarkably consistent from industry to industry. It starts with sustained support of top management followed by implementation of appropriate programs and practices that institutionalize safety as a culture as compared to add-on procedures. The ingraining of safety as second nature in day-to-day activities requires a paradigm shift and can only be accomplished when safety is viewed as an integral and comprehensive part of any activity as compared to being a stand-alone or add-on activity.

This third edition of ***Loss Prevention in the Process Industries*** represents a combination of appropriate revisions of the essential compilations put together by Frank P. Lees, along with several new chapters and additions on new areas that deserve attention and discussion. The third edition includes five new chapters and three new appendices. The five new chapters address incident investigation, inherently safer design, reactive chemicals, safety instrumented systems, and chemical security. The three new appendices address process safety management regulation in the United States, risk management program regulation in the United States, and incident databases.

The chapter on incident investigation provides a summary of incident investigation procedures that can be used not only to determine causes of incidents but also provides a primer on capturing and integrating lessons learned from incident investigations into design, operations, maintenance, and response programs. Chemical process incidents can be accompanied by significant consequences, both in terms of human life and in financial impact. Many major chemical process incidents are the result of a complex scenario involving simultaneous failures of multiple safeguards. A robust system for incident investigation is usually necessary to determine and understand the causes, as well as implement measures to prevent a repeat event. This chapter is intended to provide an overview of incident investigation by addressing major concepts, principles, and characteristics of effective incident investigations of chemical process events. The focus is on incidents pertaining to chemical processes and their associated hazards, and the associated investigation techniques appropriate for complex systems and scenarios. This chapter is based on

best practices for incident investigation, and those common concepts (i.e., tools, techniques, definitions) included in root cause investigation methodologies currently in the public domain in use in the process industry. It is not the intention to provide a stand-alone investigation methodology/guideline, nor address internal or proprietary investigation methodologies.

The chapter on inherently safer design addresses options and issues that can be considered with regard to the design and operation of plants. Inherently safer design is a philosophy that focuses on elimination of hazards or reduction of the magnitude of hazards rather than the control of hazards. Many of the concepts of inherently safer design have been applied by engineers in a wide variety of technologies for many years, without recognizing the common approach. In the late 1970s, in the wake of many large incidents in the chemical industry, Trevor Kletz recognized the common philosophies of hazard elimination and hazard reduction, gave the philosophy the name "inherently safer design," and developed a specific set of approaches to help engineers in the chemical process industries to design inherently safer processes and plants. Trevor realized that increased expectations for safety, from companies, regulatory bodies, and society in general, combined with the increased potential damage from incidents in the larger plants being built to meet increased demand and global markets, resulted in increased complexity and cost for the safety systems required to satisfy these demands. Furthermore, while hazard control systems can be made highly reliable, they can never be perfect and will always have some failure probability. While this probability can be made very small, there is always some chance that all safety systems will fail simultaneously and the result would be a large incident. Also, the hazard management systems require ongoing maintenance, as well as management and operator training, for the life of the plant. This results in ongoing costs, and the potential for future deterioration of the safety systems. Deteriorated systems will have reduced reliability, increasing the potential for a catastrophic accident. Trevor Kletz suggested that in many cases, a simpler, cheaper, and safer plant could be designed by focusing on the basic technology, eliminating or significantly reducing hazards, and therefore the need to manage them.

The chapter on reactive chemicals provides an overview of this critical issue and provides guidance on management systems as well as experimental and theoretical methods for analyses of chemical reactivity hazards. Serious incidents arising from uncontrolled reactivity have taken place since the inception of the chemical industry. The human toll of such incidents has been staggering. In recent decades, greater recognition and resources have been directed toward preventing and mitigating such occurrences. A number of incidents have been so severe as to prompt regulatory initiatives to force better management of reactivity. It is prudent for any company, organization, or other group to scrutinize the chemicals being handled and implement measures to limit the risk of a major reactive hazards event. A sampling of incidents that have substantially heightened concerns regarding reactive hazards in the general public, in governmental agencies, and in industry includes:

- The 1976 ICMESA incident in Seveso, Italy in which an uncontrolled chemical reaction generated pressure resulting in relief venting of a highly toxic dioxane into the neighboring villages and countryside.
- The 1984 Union Carbide incident in Bhopal, India in which methyl isocyanate was contacted with water, generating highly toxic cyanide gas and leading to thousands of fatalities.
- The 1994 Napp Technology incident in Lodi, New Jersey in which an uncontrolled reaction involving gold ore processing led to the deaths of five firefighters.
- The 1999 Concept Sciences incident in Allentown, Pennsylvania in which an explosion arising from a process concentrating hydroxylamine resulted in five fatalities. Another event involving purified hydroxylamine took place in a Nissin Chemical plant in Gunma Prefecture, Japan in 2000 and led to four fatalities.
- The 2001 TotalFinaElf incident in Toulouse, France in which ammonium nitrate being processed for nitrogen fertilizers exploded leading to 30 fatalities.

These events, as well as numerous others, have influenced the perception and approach to reactive hazards.

The chapter on safety instrumented systems addresses systems and procedures that need to be in place with regard to this area of safety and instrumentation. In many processes, technical or manufacturing issues limit the engineer's capability to design an inherently safer process. Further, there is generally a point where the required capital investment is disproportional to the additional risk reduction provided by the process modification. In other words, the derived safety benefit is too low relative to the economic investment. When this occurs, protection layers or safeguards must be provided to prevent or mitigate the process risk. A Safety Instrumented System (SIS) is a protection layer, which shuts down the plant, or part of it, if a hazardous condition is detected. Throughout the years, SIS have also been known as Emergency Shutdown Systems (ESD, ESS), Safety Shutdown Systems (SSD), Safety Interlock Systems (SIS), Safety Critical Systems (SCS), Safety Protection Systems (SPS), Protective Instrumented Systems (PIS), interlocks, and trip systems. Regardless of what the SIS may be called, the essential characteristic of the SIS is that it is composed of instruments, which detect that process variables are exceeding preset limits, a logic solver, which processes this information and makes decisions, and final control elements, which take necessary action on the process to achieve a safe state.

The chapter on chemical security deals with this new and critical element of the management of a process facility following the events of September 11, 2001. Security management is required for protecting the assets (including employees) of the facility, maintaining the ongoing integrity of the operation, and preserving value of the investment. Process security and process safety have many parallels and make use of many common programs and systems for achieving their ends. Process security requires a management systems approach to develop a comprehensive security program, which shares many common elements to process safety management.

The new appendix on process safety management regulation in the United States provides a summary of this regulatory requirement. The fourteen elements of the OSHA Process Safety Management (PSM) regulation (*29 CFR 1910.119*) were published in the U.S. Federal Register on February 24, 1992. The objective of the regulation is to

prevent or minimize the consequences of catastrophic releases of toxic, reactive, flammable, or explosive chemicals. The regulation requires a comprehensive management program: a holistic approach that integrates technologies, procedures, and management practices. The process safety management regulation applies to processes that involve certain specified chemicals at or above threshold quantities, processes that involve flammable liquids or gases on-site in one location, in quantities of 10,000 pounds or more (subject to few exceptions), and processes that involve the manufacture of explosives and pyrotechnics. Hydrocarbon fuels, which may be excluded if used solely as a fuel, are included if the fuel is part of a process covered by this regulation. In addition, the regulation does not apply to retail facilities, oil or gas well drilling or servicing operations, or normally unoccupied remote facilities.

The new appendix on risk management program regulation in the United States provides a summary of this regulatory requirement administered by the U.S. Environmental Protection Agency. In 1996, EPA promulgated the regulation for ***Risk Management Programs for Chemical Accident Release Prevention*** (40 CFR 68). This federal regulation was mandated by section 112(r) of the Clean Air Act Amendments of 1990. The regulation requires regulated facilities to develop and implement appropriate risk management programs to minimize the frequency and severity of chemical plant accidents. In keeping with regulatory trends, EPA required a performance-based approach towards compliance with the risk management program regulation. The EPA regulation also requires regulated facilities to develop a Risk Management Plan (RMP). The RMP includes a description of the hazard assessment, prevention program, and the emergency response program. Facilities submit the RMP to the EPA and subsequently is made available to governmental agencies, the state emergency response commission, the local emergency planning committees, and communicated to the public.

The new appendix on incident databases addresses compilations of incident databases that can used for improving safety programs, developing trends, performance measures, and metrics. Incident prevention and mitigation of consequences is the focus of a number of industry programs regulatory initiatives. As part of these programs and regulations, accident history data are often collected. There are two basic types of information. One is a database consisting of standardized fields of data usually for a large number of incidents. The second are more detailed reports of individual incidents. Analysis of these incident history databases can provide insight into incident prevention needs. While the analysis and conclusions obtained from the incident database are often limited by the shortcomings of the databases themselves, the fact remains that incident history databases are very useful and can be a powerful tool in focusing risk reduction efforts. The conclusions can be used to identify systematically the greatest risks to allow prioritization of efforts to improve process safety. At the plant level this might entail identifying certain processes, types of equipment, chemicals, operations and other factors most commonly associated with incidents. Databases that cover a very large number of facilities are likely to reveal trends and patterns that no one company or facility could determine from their own experience. Statistical knowledge of the likelihood of the release of certain types of chemicals could help emergency responders, state emergency response commissions, and local emergency planning committees determine the most likely and most serious chemical releases in their areas and plan appropriate chemical accident responses. Incident databases may also help identify technologies and practices to prevent chemical accidents, or the need to develop them. For example, the data could indicate that inspection and preventive maintenance of equipment and instruments should become more thorough or more frequent.

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College Station,
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2004

Preface to Second Edition

The first edition of this book appeared in 1980, at the end of a decade of rapid growth and development in loss prevention. After another decade and a half the subject is more mature, although development continues apace. In preparing this second edition it has been even more difficult than before to decide what to put in and what to leave out.

The importance of loss prevention has been underlined by a number of disasters. Those at San Carlos, Mexico City, Bhopal and Pasadena are perhaps the best known, but there have been several others with death tolls exceeding 100. There have also been major incidents in related areas, such as those on the Piper Alpha oil platform and at the nuclear power stations at Three Mile Island and Chernobyl.

Apart from the human tragedy, it has become clear that a major accident can seriously damage even a large international company and may even threaten its existence, rendering it liable to severe damages and vulnerable to takeover.

Accidents in the process industries have given impetus to the creation of regulatory controls. In the UK the Advisory Committee on Major Hazards made its third and final report in 1983. At the same time the European Community was developing its own controls which appeared as the EC Directive on Major Accident Hazards. The resulting UK legislation is the NIHHS Regulations 1982 and the CIMAH Regulations 1984. Other members of the EC have brought in their own legislation to implement the Directive. There have been corresponding developments in planning controls.

An important tool for decision-making on hazards is hazard assessment. The application of quantitative methods has played a crucial role in the development of loss prevention, but there has been lively debate on the proper application of such assessment, and particularly on the estimation and evaluation of the risk to the public.

Hazard assessment involves the assessment both of the frequency and of the consequences of hazardous events. In frequency estimation progress has been made in the collection of data and creation of data banks and in fault tree synthesis and analysis, including computer aids. In consequence assessment there has been a high level of activity in developing physical models for emission, vaporization and gas dispersion, particularly dense gas dispersion; for pool fires, fireballs, jet flames and engulfing fires; for vapour cloud explosions; and for boiling liquid expanding vapour explosions (BLEVEs). Work has also been done on injury models for thermal radiation, explosion overpressure and toxic concentration, on models of the density and other characteristics of the exposed population, and on shelter and escape.

Some of these topics require experimental work on a large scale and involving international cooperation. Large scale tests have been carried out at several sites on dense gas dispersion and on vapour cloud fires and explosions. Another major cooperative research programme has been that of DIERS on venting of chemical reactors.

The basic approach developed for fixed installations on shore has also been increasingly applied in other fields. For transport in the UK the *Transport Hazards Report* of the Advisory Committee on Dangerous Substances represents an important landmark. Another application is in the offshore oil and gas industry, for which the report on the Piper Alpha disaster, the *Cullen Report*, constitutes a watershed.

As elsewhere in engineering, computers are in widespread use in the design of process plants, where computer aided design (CAD) covers physical properties, flowsheeting, piping and instrument diagrams, unit operations and plant layout. There is increasing use of computers for failure data retrieval and analysis, reliability and availability studies, fault tree synthesis and analysis and consequence modelling, while more elusive safety expertise is being captured by computer-based expert systems.

The subject of this book is the process industries, but the process aspects of related industries, notably nuclear power and oil and gas platforms are briefly touched on. The process industries themselves are continually changing. In the last decade one of the main changes has been increased emphasis on products such as pharmaceuticals and agrochemicals made by batch processes, which have their own particular hazards.

All this knowledge is of little use unless it reaches the right people. The institutions which educate the engineers who will be responsible for the design and operation of plants handling hazardous materials have a duty to make their students aware of the hazards and at least to make a start in gaining competence in handling them.

I would like again to thank for their encouragement the heads of the Department of Chemical Engineering at Loughborough, Professors D.C. Freshwater, B.W. Brooks and M. Streat; our Industrial Professors T.A. Kletz and H.A. Duxbury and Visiting Professor S.M. Richardson; my colleagues, past and present, in the Plant Engineering Group, Mr R.J. Aird, Dr P.K. Andow, Dr M.L. Ang, Dr P.W.H. Chung, Dr D.W. Edwards, Dr P. Rice and Dr A.G. Rushton – I owe a particular debt to the latter; the members of the ACMH, chaired by Professor B.H. Harvey; the sometime directors of Technica Ltd, Dr D.H. Slater, Mr P. Charsley, Dr P.J. Comer, Dr R.A. Cox, Mr T. Gjerstad, Dr M.A.F. Pyman, Mr C.G. Ramsay, Mr M.A. Seaman and Dr R. Whitehouse; the members of the IChemE Loss Prevention Panel; the IChemE's former Loss Prevention Officer, Mr B.M. Hancock; the members of the IChemE Loss Prevention Study Group and of the Register of Safety Professionals; the editorial staff of the IChemE, in particular Mr B. Brammer; numerous members of the Health and Safety Executive, especially Dr A.C. Barrell, Mr J. Barton, Dr D.A. Carter, Mr K. Cassidy, Mr P.J. Crossthwaite, Dr N.W. Hurst, Dr S.F. Jagger, Dr J. McQuaid, Dr K. Moodie, Dr C. Nussey, Dr R.P. Pape, Dr A.F. Roberts and Dr N.F. Scilly; workers at the Safety and Reliability Directorate, particularly Dr A.T.D. Butland, Mr I. Hymes, Dr D.W. Phillips and Dr D.M. Webber; staff at Shell Thornton Research Centre, including Dr D.C. Bull and Dr A.C. Chamberlain; staff at British Gas, including Dr J.D. Andrews, Dr M.J. Harris, Mr H. Hopkins, Dr J.M. Morgan and Dr D.J. Smith; staff at the Ministry of

Defence, Explosives Storage and Transport Committee, including Mr M.A. Gould, Mr J. Henderson and Mr P. Stone; and colleagues who have taught on post-experience courses at Loughborough, in particular Dr C.D. Jones, Dr D.J. Lewis and Mr J. Madden; BP International and Mr R. Malpas for allowing me to spend a period of study leave with the company in 1985–86 and Mr F.D.H. Moysen, Mr G. Hately, Mr M. Hough, Mr R. Fearon and others in the Central Safety Group and in Engineering Department; the Honourable Lord Cullen, my fellow Technical Assessors on the Piper Alpha Inquiry, Mr B. Appleton and Mr G.M. Ford and the Cremer and Warner team at the inquiry, in particular Mr G. Kenney and Mr R. Sylvester-Evans; other professional colleagues Dr L.J. Bellamy, Professor B.A. Buffham, Dr D.A. Crowl, Mr T.J. Gilbert, Mr D.O. Hagon, Dr D.J. Hall, Mr K.M. Hill, Professor T.M. Husband, Mr M. Kneale, Dr V.C. Marshall, Dr M.L. Preston, Dr J. Rasmussen, Dr J.R. Roach, Dr J.R. Taylor, Dr V.M. Trbojevic, Mr H.M. Tweeddale, Dr G.L. Wells and Dr A.J. Wilday; my research colleagues Dr C.P. Murphy, Mrs J.I. Petts, Dr D.J. Sherwin, Mr R.M.J. Withers and Dr H. Zerkani; my research students Mr M. Aldersey, Mr D.C. Arulanantham, Dr A. Bunn, Dr M.A. Cox, Dr P.A. Davies, Dr S.M. Gilbert, Mr P. Heino, Dr A. Hunt, Dr B.E. Kelly, Dr G.P.S. Marrs, Dr J.S. Mullhi, Dr J.C. Parmar, Mr B. Poblete, Dr A. Shafaghi and Dr A.J. Trenchard as well as colleagues' research students Mr E.J. Broomfield, Mr R. Goodwin, Mr M.J. Jefferson, Dr F.D. Larkin, Mr S.A. McCoy, Dr K. Plamping, Mr J. Soutter, Dr P. Thorpe and Mr S.J. Wakeman; the office staff of the Department, Mrs E.M. Barradell, Mr D.M. Blake, Miss H.J. Bryers and Miss Y. Kosar; the staff of the University Library, in particular Miss S.F. Pilkington; and my wife Elizabeth, whose contribution has been many-faceted and in scale with this book.

FRANK P. LEES
Loughborough,
1994

Preface to First Edition

Within the past ten or fifteen years the chemical and petroleum industries have undergone considerable changes. Process conditions such as pressure and temperature have become more severe. The concentration of stored energy has increased. Plants have grown in size and are often single-stream. Storage has been reduced and interlinking with other plants has increased. The response of the process is often faster. The plant contains very large items of equipment. The scale of possible fire, explosion or toxic release has grown and so has the area which might be affected by such events, especially outside the works boundary.

These factors have greatly increased the potential for loss both in human and in economic terms. This is clear both from the increasing concern of the industry and its insurers and from the historical loss statistics.

The industry has always paid much attention to safety and has a relatively good record. But with the growing scale and complexity involved in modern plants the danger of serious large-scale incidents has been a source of increasing concern and the adequacy of existing procedures has been subjected to an increasingly critical examination.

Developments in other related areas have also had an influence. During the period considered there has been growing public concern about the various forms of pollution, including gaseous and liquid effluents and solid wastes and noise.

It is against this background that the loss prevention approach has developed. It is characteristic of this approach that it is primarily concerned with the problems caused by the depth of technology involved in modern processes and that it adopts essentially an engineering approach to them. As far as possible both the hazards and the protection are evaluated quantitatively.

The clear recognition by senior management of the importance of the loss prevention problem has been crucial to these developments. Progress has been made because management has been prepared to assign to this work many senior and capable personnel and to allocate the other resources necessary.

The management system is fundamental to loss prevention. This involves a clear management structure with well defined line and advisory responsibilities staffed by competent people. It requires the use of appropriate procedures, codes of practice and standards in the design and operation of plant. It provides for the identification, evaluation and reduction of hazards through all stages of a project from research to operation. It includes planning for emergencies.

The development of loss prevention can be clearly traced through the literature. In 1960 the Institution of Chemical Engineers held the first of a periodic series of symposia on *Chemical Process Hazards with Special Reference to Plant Design*. The Dow Chemical Company published its *Process Safety Manual* in 1964. The American Institute of Chemical Engineers started in 1967 an annual series of symposia on Loss Prevention. The European Federation of Chemical Engineers' symposium on *Major Loss Prevention in the Process Industries* at Newcastle in 1971 and the Federation's symposium on *Loss Prevention and Safety Promotion in the Process Industries* (Buschmann, 1974) at Delft are further milestones.

Another indicator is the creation in 1973 by the Institution of Chemical Engineers Engineering Practice Committee of a Loss Prevention Panel under the chairmanship of Mr T.A. Kantyka.

In the United Kingdom the Health and Safety at Work etc. Act 1974 has given further impetus to loss prevention. The philosophy of the *Robens Report* (1972), which is embodied in the Act, is that of self-regulation by industry. It is the responsibility of industry to take all reasonable measures to assure safety. This philosophy is particularly appropriate to complex technological systems and the Act provides a flexible framework for the development of the loss prevention approach.

The disaster at Flixborough in 1974 has proved a turning point. This event has led to a much more widespread and intense concern with the loss prevention problem. It has also caused the government to set up in 1975 an Advisory Committee on Major Hazards. This committee has made far-reaching recommendations for the identification and control of major hazard installations.

It will be apparent that loss prevention differs somewhat from safety as traditionally conceived in the process industries. The essential difference is the much greater engineering content in loss prevention.

This is illustrated by the relative effectiveness of inspection in different processes. In fairly simple plants much can be done to improve safety by visual inspection. This approach is not adequate, however, for the more technological aspects of complex processes.

For the reasons given above loss prevention is currently a somewhat fashionable subject. It is as well to emphasize, therefore, that much of it is not new, but has been developed over many years by engineers whose patient work in an often apparently unrewarding but vital field is the mark of true professionalism.

It is appropriate to emphasize, moreover, that accidents arising from relatively mundane situations and activities are still responsible for many more deaths and injuries than those due to advanced technology.

Nevertheless, loss prevention has developed in response to the growth of a new problem, the hazard of high technology processes, and it does have a distinctive approach and some novel techniques. Particularly characteristic are the emphasis on matching the management system to the depth of technology in the installation, the techniques developed for identifying hazards, the principle and methods of quantifying hazards, the application of reliability assessment, the practice of planning for emergencies and the critique of traditional practices or existing codes, standards or regulations where these are outdated by technological change.

There is an enormous, indeed intimidating, literature on safety and loss prevention. In addition to the symposia already referred to, mention may be made of the *Handbook of Safety and Accident Prevention in Chemical Operations* by Fawcett and Wood (1965); the *Handbook of Industrial Loss*

Prevention by the Factory Mutual Engineering Corporation (1967); and the Industrial Safety Handbook by Handley (1969, 1977). These publications, which are by multiple authors, are invaluable source material.

There is a need, however, in the author's view for a balanced and integrated textbook on loss prevention in the process industries which presents the basic elements of the subject, which covers the recent period of intense development and which gives a reasonably comprehensive bibliography. The present book is an attempt to meet this need.

The book is based on lectures given to undergraduate and postgraduate students at Loughborough over a period of years and the author gladly acknowledges their contribution.

Loss prevention is a wide and rapidly developing field and is therefore not an easy subject for a book. Nevertheless, it is precisely for these reasons that the engineer needs the assistance of a textbook and that the attempt has been considered justified.

The structure of the book is as follows. Chapter 1 deals with the background to the historical development of loss prevention, the problem of large, single-stream plants, and the differences between loss prevention and conventional safety, and between loss prevention and total loss control; Chapter 2 with hazard, accident and loss, including historical statistics; Chapter 3 with the legislation and legal background; Chapter 4 with the control of major hazards; Chapter 5 with economic and insurance aspects; Chapter 6 with management systems, including management structure, competent persons, systems and procedures, standards and codes of practice, documentation and auditing arrangements; Chapter 7 with reliability engineering, including its application in the process industries; Chapter 8 with the spectrum of techniques for identifying hazards from research through to operation; Chapter 9 with the assessment of hazards, including the question of acceptable risk; Chapter 10 with the siting and layout of plant; Chapter 11 with process design, including application of principles such as limitation of inventory, consideration of known hazards associated with chemical reactors, unit processes, unit operations and equipments, operating conditions, utilities, particular chemicals and particular processes and plants, and checking of operational deviations; Chapter 12 with pressure system design, including properties of materials, design of pressure vessels and pipework, pressure vessel standards and codes, equipment such as heat exchangers, fired heaters and rotating machinery, pressure relief and blowdown arrangements, and failure in pressure systems; Chapter 13 with design of instrumentation and control systems, including regular instrumentation, process computers and protective systems; Chapter 14 with human factors in process control, process operators, computer aids and human error; Chapter 15 with loss of containment and dispersion of material; Chapter 16 with fire, flammability characteristics, ignition sources, flames and particular types of process fire, effects of fire and fire prevention, protection and control; Chapter 17 with explosion, explosives, explosion energy, particular types of process explosion such as confined explosions, unconfined vapour cloud explosions and dust explosions, effects of explosion and explosion prevention, protection and relief; Chapter 18 with toxicity of chemicals, toxic release and effects of toxic release; Chapter 19 with commissioning and inspection of plant; Chapter 20 with plant operation; Chapter 21 with plant maintenance and modification; Chapter 22 with storage; Chapter 23 with transport, particularly by road, rail and pipeline; Chapter 24 with emergency planning both for works and transport emergencies; Chapter 25 with various aspects of personal safety such as occupational health and industrial hygiene, dust and radiation hazards, machinery and electrical hazards, protective clothing and equipment, and rescue and first aid; Chapter 26 with accident research; Chapter 27 with feedback of information and learning from accidents; Chapter 28 with safety systems, including the roles of safety managers and safety committees and representatives. There are appendices on Flixborough, Seveso, case histories, standards and codes, institutional publications, information sources, laboratories and pilot plants, pollution and noise, failure and event data, Canvey, model licence conditions for certain hazardous plants, and units and unit coversions.

Many of the matters dealt with, such as pressure vessels or process control, are major subject areas in their own right. It is stressed, therefore, that the treatment given is strictly limited to loss prevention aspects. The emphasis is on deviations and faults which may give rise to loss.

In engineering in general and in loss prevention in particular there is a conflict between the demand for a statement of basic principles and that for detailed instructions. In general, the first of these approaches has been adopted, but the latter is extremely important in safety, and a considerable amount of detailed material is given and references are provided to further material.

The book is intended as a contribution to the academic education of professional chemical and other engineers. Both educational and professional institutions have long recognized the importance of education in safety. But until recently the rather qualitative, and indeed often exhortatory, nature of the subject frequently seemed to present difficulties in teaching at degree level. The recent quantitative development of the subject goes far towards removing these objections and to integrating it more closely with other topics such as engineering design.

In other words, loss prevention is capable of development as a subject presenting intellectual challenge. This is all to the good, but a note of caution is appropriate. It remains true that safety and loss prevention depend primarily on the hard and usually unglamorous work of engineers with a strong sense of responsibility, and it is important that this central fact should not be obscured.

For this reason the book does not attempt to select particular topics merely because a quantitative treatment is possible or to give such a treatment as an academic exercise. The subject is too important for such an approach. Rather the aim has been to give a balanced treatment of the different aspects and a lead in to further reading.

It is also hoped that the book will be useful to practising engineers in providing an orientation and entry to unfamiliar areas. It is emphasized, however, that in this subject above all others, the specialized texts should be consulted for detailed design work.

Certain topics which are often associated with loss prevention, for example included in loss prevention symposia, have not been treated in detail. These include, for example, pollution and noise. The book does not attempt to deal in detail with total loss control, but a brief account of this is given.

The treatment of loss prevention given is based mainly on the chemical, petrochemical and petroleum industries,

but much of it is relevant to other process industries, such as electrical power generation (conventional and nuclear), iron and steel, gas, cement, glass, paper and food.

The book is written from the viewpoint of the United Kingdom and, where differences exist within the UK, of England. This point is relevant mainly to legislation.

Reference is made to a large number of procedures and techniques. These do not all have the same status. Some are well established and perhaps incorporated in standards or codes of practice. Others are more tentative. As far as possible the attempt has been made to give some indication of the extent to which particular items are generally accepted.

There are probably also some instances where there is a degree of contradiction between two approaches given. In particular, this may occur where one is based on engineering principles and the other on relatively arbitrary rules-of-thumb.

The book does not attempt to follow standards and codes of practice in drawing a distinction between the words *should, shall* and *must* in recommending particular practices and generally uses only the former. The distinction is important, however, in standards and codes of practice and it is described in Appendix 4[a].

An explanation of some of the terms used is in order at this point. Unfortunately there is at present no accepted terminology in this field. In general, the problems considered are those of loss, either of life or property. The term *hazard* is used to describe the object or situation which constitutes the threat of such loss. The consequences which might occur if the threat is realized are the *hazard potential*. Associated with the hazard there is a risk, which is the probability of the loss occurring. Such a risk is expressed as a *probability* or as a *frequency*. Probability is expressed as a number in the range 0 to 1 and is dimensionless; frequency is expressed in terms of events per unit time, or sometimes in other units such as events per cycle or per occasion. Rate is also used as an alternative to frequency and has the same units.

The analysis of hazards involves qualitative *hazard identification* and quantitative hazard assessment. The latter term is used to describe both the assessment of hazard potential and of risk. The assessment of risk only is described as *risk assessment*.

In accident statistics the term *Fatal Accident Frequency Rate* (FAFR) has some currency. The last two terms are tautologous and the quantity is here referred to as *Fatal Accident Rate* (FAR).

Further treatments of terminology in this field are given by BS 4200: 1967, by Green and Bourne (1962), by the Council for Science and Society (1977) and by Harvey (1979b).

Notation is defined for the particular chapter at the point where the symbols first occur. In general, a consistent notation is used, but well established equations from standards, codes and elsewhere are usually given in the original notation. A consolidated list of the notation is given at the end of chapters in which a large number of symbols is used.

The units used are in principle SI, but the exceptions are fairly numerous. These exceptions are dimensional equations, equations in standards and codes, and other equations and data given by other workers where conversion has seemed undesirable for some reason. In cases of conversion from a round number it is often not clear what degree of rounding off is appropriate. In cases of description of particular situations it appears pedantic to make the conversion where a writer has referred, for example, to a 1 inch pipe.

Notes on some of the units used are given in Appendix 12[a]. For convenience a unit conversion table is included in this appendix. Numerical values given by other authors are generally quoted without change and numerical values arising from conversion of the units of data given by other authors are sometimes quoted with an additional significant figure in order to avoid excessive rounding of values.

Some cost data are quoted in the book. These are given in pounds or US dollars for the year quoted.

A particular feature of the book is a fairly extensive bibliography of some 5000 references. These references are consolidated at the end of the book rather than at the end of chapters, because many items are referred to in a number of chapters. Lists of selected references on particular topics are given in table form in the relevant chapters.

Certain institutions, however, have a rather large number of publications which it is more convenient to treat in a different manner. These are tabulated in Appendices 4[a] and 5[a], which contain some 2000 references. There is a cross-reference to the institution in the main reference list.

In many cases institutions and other organizations are referred to by their initials. In all cases the first reference in the book gives the full title of the organization. The initials may also be looked up in the Author Index, which gives the full title.

A reference is normally given by quoting the author and, in brackets, the date, e.g. Kletz (1971). Publications by the same author in the same year are denoted by letters of the alphabet a, b, c, etc., e.g. Allen (1977a), while publications by authors of the same surname and in the same year are indicated for convenience by an asterisk against the year in the list of references. In addition, the author's initials are given in the main text in cases where there may still be ambiguity. Where a date has not been determined this is indicated as n.d.

In the case of institutional publications listed in Appendices 4[a] and 5[a] the reference is given by quoting the institution and, in brackets, the date, the publication series, e.g. HSE (1965 HSW Bklt 34) or the item number, e.g. IChemE (1971 Item 7). For institutional publications with a named author the reference is generally given by quoting the author and, in brackets, the initials of the institution, the date and the publication series or item number, e.g. Eames (UKAEA 1965 Item 4).

The field of loss prevention is currently subject to very rapid change. In particular, there is a continuous evolution of standards and codes of practice and legislation. It is important, therefore, that the reader should make any necessary checks on changes which may have occurred.

I would like to thank for their encouragement in this project Professor D.C. Freshwater and the publishers, and to acknowledge the work of many authors which I have used directly or indirectly, particularly that of Dr J.H. Burgoyne and of Professor T.A. Kletz. I have learned much from my colleagues on the Loss Prevention Panel of the Institution of Chemical Engineers, in particular Mr T.A. Kantyka and Mr F. Hearfield, and on the Advisory Committee on Major Hazards, especially the chairman Professor B.H. Harvey, the secretary Mr H.E. Lewis, my fellow group chairmen

[a]Appendices 4, 5 and 12 in the first edition correspond to Appendices 27, 28 and 30, respectively, in this second edition.

Professor F.R. Farmer and Professor J.L.M. Morrison and the members of Group 2, Mr K. Briscoe, Dr J.H. Burgoyne, Mr E.J. Challis, Mr S. Hope, Mr M.A. McTaggart, Professor J.F. Richardson, Mr J.R.H. Schenkel, Mr R. Sheath and Mr M.J. Turner, and also from my university colleagues Dr P.K. Andow, Mr R.J. Aird and Dr D.J. Sherwin and students Dr S.N. Anyakora, Dr B. Bellingham, Mr C.A. Marpegan and Dr G.A. Martin-Solis. I am much indebted to Professor T.A. Kletz for his criticisms and suggestions on the text. My thanks are due also to the Institution of Plant Engineers, which has supported plant engineering activities at Loughborough, to the Leverhulme Trust which awarded a Research Fellowship to study *Loss Prevention in the Process Industries* and to the Science Research Council, which has supported some of my own work in this area. I have received invaluable help with the references from Mrs C.M. Lincoln, Mrs W. Davison, Mrs P. Graham, Mr R. Rhodes and Mrs M.A. Rowlatt, with the typing from Mrs E.M. Barradell, Mrs P. Jackson and, in particular, Mrs J. Astley, and with the production from Mr R.L. Pearson and Mr T. Mould. As always in these matters the responsibility for the final text is mine alone.

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Loughborough,
1979

Acknowledgements

Many have helped with the long and tedious production process for this 3rd edition of ***Frank P. Lees Loss Prevention in the Process Industries***. However, I would be seriously remiss if I did not start with Frank P. Lees himself. I have always had great respect and admiration for Frank Lees, the engineer and the educator. After Frank passed away, and late in 2002, our mutual friend, Roy Sanders contacted me with a request from Frank's publisher to take up the job of editing the next version. I had no idea of the enormity of the task and Frank's accomplishment. I must say that this experience has truly humbled me and has given me a new respect and new appreciation for Frank Lees' knowledge, grasp, and mastery of the subject of safety and loss prevention. I am honored and privileged to be the editor of the 3rd edition of ***Frank P. Lees Loss Prevention in the Process Industries***. I have tried to maintain Frank's high standards and appreciate the help that many others have given me, but ultimately any *faux pas* or mistakes in the 3rd edition are all mine.

I want to thank all the people who have helped revise and update the chapters that were carried over from the 2nd edition. In this respect, I would like to mention A.A. Aldeeb, J.A. Alderman, P.C. Berwanger, C.A. Brown, S. Chervin, J. Cowling, W.F. Early, M. Gentile, J.P. Gupta, J.A. Havens, D.C. Hendershot, N. Keren, K. Krishna, S.H. Landis, M.E. Levin, P.N. Lodal, M.E. Livingston, S. Mohindra, D.A. Moore, T.M. O'Connor, S.W. Ostrowski, M. Paradise, J.A. Philley, W.J. Rogers, R.E. Sanders, S.R. Saraf, M.E Sawyer, R.L. Smith, T.O. Spicer, A.E. Summers, Y. Wang, H.H. West, J.L. Woodward, and J. Zanoni. Special thanks go to individuals who helped with the new chapters and appendices: J.A. Philley for the incident investigation chapter; J.P. Gupta and D.C. Hendershot for the inherently safer design chapter; S. Chervin, M.E. Levin, and W.J. Rogers for the reactive chemicals chapter; A.E. Summers for the safety instrumented systems chapter, D.A. Moore for the chemical security chapter and T.M. O'Connor for the new appendix on incident databases.

I also want to thank those who helped with research, literature review, galley proofing, and many other jobs without which such a project is never complete. I would like to specifically mention S. Anand, L.O. Cisneros-Trevino, W. Kowhakul, Y.-S. Liu, Y. Qiao, V. Raghunathan, S. Rajaraman, J. Suardin, M. Vidal, C. Wei, C. Zhang, and Y. Zhou. I would like to make specific mention of K.L. Potucek and L.J. Littlefield who undertook the painful task of converting the pdf files of the 2nd edition to Word format. I would like to thank M.A. Cass and D.K. Startz for administrative support and keeping things going through the long haul.

I would also like to take this opportunity to thank two individuals who have provided more than moral support and encouragement. They are Trevor Kletz and Mike O'Connor. First, I have appreciated Trevor's support for our work at the Mary Kay O'Connor Process Safety Center. I also want to thank him for his pioneering leadership in many areas of process safety. Trevor is really a giant in this field, and as Roy Sanders likes to say, "Trevor does cast a long shadow in the field of process safety." I am proud to have Trevor's friendship and his support. I also want to take this opportunity to thank Mike O'Connor. He has converted his personal tragedy into an opportunity to integrate process safety into education, research, and service activities at universities. He has been a true friend and supporter of the mission and goals of the Center.

I also want to thank Mrs. Elizabeth Lees for being kind, gracious, and helpful throughout this process. I am especially grateful for her hospitality and help during my visit to Loughborough to look through Frank's notes and books.

I am grateful to my mother for her love and everything she has done for me and continues to do. I am indebted to my father for having taught me the desire for learning. He was a humble man who truly believed that, "If you stop learning, you must already be dead." I would also like to thank my wife, Afroza, and our daughters, Joya and Rumki, for their love and support. Quite often a project of this magnitude causes the personal and family life to suffer and my wife and daughters have borne the brunt of it. I appreciate their understanding.

I am sure I have failed to mention everybody who has helped me with the many facets of this project. To them I apologize and want to assure them the oversight is not intended. To everyone who has helped put this 3rd edition together, I extend my heartfelt thanks and warmest gratitude again. I must say that you have helped in a noble cause, spread the word and disseminate information that will, we hope and pray, lead to a safer industry and society.

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2004

Terminology

Attention is drawn to the availability in the literature of a number of glossaries and other aids to terminology. Some British Standard glossaries are given in Appendix 27 and other glossaries are listed in Table 1.1.

Notation

In each chapter a given symbol is defined at the point where it is first introduced. The definition may be repeated if there has been a significant gap since it was last used. The definitions are summarized in the notation given at the end of the chapter. The notation is global to the chapter unless redefined for a section. Similarly, it is global to a section unless redefined for a subsection and global to a subsection unless redefined for a set of equations or a single equation. Where appropriate, the units are given, otherwise a consistent system of units should be used, SI being the preferred system. Generally the units of constants are not given; where this is the case it should not be assumed that a constant is dimensionless.

Use of References

The main list of references is given in the section entitled References, towards the end of the book. There are three other locations where references are to be found. These are Appendix 27 on standards and codes; Appendix 28 on institutional publications; and in the section entitled Loss Prevention Bulletin which follows the References.

The basic method of referencing an author is by surname and date, e.g. Beranek (1960). Where there would otherwise be ambiguity, or where there are numerous references to the same surname, e.g. Jones, the first author's initials are included, e.g. A. Jones (1984). Further guidance on names is given at the head of the section References.

References in Appendices 27 and 28 are by institution or author. Some items in these appendices have a code number assigned by the institution itself, e.g. API (1990 Publ. 421), but where such a code number is lacking, use is generally made of an item number separated from the date by a slash, e.g. IChemE (1971/13). Thus typical entries are

API Std 2000: 1992	a standard, found in Appendix 27 under American Petroleum Institute
API (1990 Publ. 421)	an institutional publication, found in Appendix 28 under American Petroleum Institute
HSE (1990 HS(G) 51)	an institutional publication, found in Appendix 28 under Health and Safety Executive, Guidance Booklets, HS(G) series
Coward and Jones (1952 BM Bull. 503)	an institutional publication, found in Appendix 28 under Bureau of Mines, Bulletins

Institutional acronyms are given in the section Acronyms which precedes the Author Index.

There are several points of detail which require mention concerning Appendix 28. (1) The first part of the appendix contains publications of a number of institutions and the second part those of the Nuclear Regulatory Commission. (2) The Fire Protection Association publications include a number of series which are collected in the *Compendium of Fire Safety Data* (CFSD). A typical reference to this is FPA (1989 CFSD FS 6011). (3) The entries for the Health and Safety Executive are quite extensive and care may be needed in locating the relevant series. (4) The publications of the Safety and Reliability Directorate appear under the UK Atomic Energy Authority, Safety and Reliability Directorate. A typical reference is Ramskill and Hunt (1987 SRD R354). These publications are immediately preceded by the publications of other bodies related to the UKAEA, such as the Health and Safety Branch, the Systems Reliability Service and the National Centre for Systems Reliability.

References to authors in the IChemE *Loss Prevention Bulletin* are in the style Eddershaw (1989 LPB 88), which refers to issue 88 of the bulletin.

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The second of the major hazards is explosion. Explosion in the process industries causes fewer serious accidents than fire but more than toxic release. When it does occur, however, it often inflicts greater loss of life and damage than fire. Explosion is usually regarded as having a disaster potential greater than that of fire but less than that of toxic release.

The *First Report of the Advisory Committee on Major Hazards* (ACMH) (Harvey, 1976) states

> In the case of flammable materials, the greatest threat arises from the sudden massive escape of those volatile liquids, or gases, which could produce a large cloud of flammable, possibly explosive, vapour. If the cloud were ignited, the effects of combustion would depend on many factors including wind speeds and the extent to which the cloud is diluted with air. The worst consequence could be large numbers of casualties and wholesale damage on site and beyond its boundaries. Nevertheless where combustion has taken place it has generally been on or in the immediate vicinity of the site. An important feature of this threat is the small time interval between the initial escape and the fire or explosion, which could be less than a minute.

The Flixborough disaster was primarily due to a vapour cloud explosion. It was this explosion which caused most of the casualties.

There is a considerable literature on explosions. Much of the information relates to chemical or nuclear explosions and to military applications. Reference can be made here only to a few selected texts. These are *Explosions, Their Anatomy and Destructiveness* (C.S. Robinson, 1944), *Explosion and Combustion Processes in Gases* (Jost, 1946), *Supersonic Flow and Shock Waves* (Courant and Friedrichs, 1948), *The Science of High Explosives* (M.A. Cook, 1958), *Combustion, Flames and Explosions of Gases* (B. Lewis and von Elbe, 1961, 1987), *The Effects of Nuclear Weapons* (Glasstone, 1962; Glasstone and Dolan, 1980), *Explosive Shocks in Air* (Kinney, 1962; Kinney and Graham, 1985), *Explosions in Air* (W.E. Baker, 1973) and *Explosion Hazards and Evaluation* (W.E. Baker *et al.*, 1983).

Selected references on explosion are given in Table 17.1 and on detonation in Table 17.2.

Table 17.1 *Selected references on explosion (see also Tables 17.2, 17.29, 17.36 and 17.61)*

Explosion, deflagration, detonation
D.J. Lewis (n.d.); Ministry of Defence, ESTC (n.d.); von Schwartz (1904–); Jouguet (1905, 1917); Chapman (1921); Kratz and Rosencranz (1922); F.W. Stevens (1928); Coward and Hersey (1935 BM RI 3274); Milne-Thompson (1938–, 1947–); C.S. Robinson (1944); Kirkwood and Brinkley (1945); Jost (1946); G.I. Taylor (1946); Brinkley and Kirkwood (1947, 1949, 1961); Smart (1947); Courant and Friederichs (1948); Doering and Burkhardt (1949); Bowden and Yoffe (1952); Zabetakis and Jones (1955); Burgoyne (1956); K.N. Palmer (1956); Glasstone (1957, 1962, 1964); Randall *et al.* (1957); Emmons (1958); Ghormley (1958); Brinkley and Lewis (1959); Penner and Mullins (1959); Pipkin (1959); Rinehart (1959); Anon. (1960a); M.W. Evans and Ablow (1961); B. Lewis and von Elbe (1961, 1987); J.K. Wright (1961); J.N. Bradley (1962); Kinney (1962, 1968); Ginsburgh and Bulkley (1963, 1964); Yakovlev (1963); Jacobs (1964); Jacobs, Blunk and Scheineman (1964); Markstein (1964); Muzzall (1964); Oswatitsch (1965); Zabetakis (1965); Fordham (1966); Kogarko, Adushkin and Lyamin (1966); Laderman (1966); Soloukhin (1966, 1969); Urtiew and Oppenheim (1965, 1966, 1967, 1968); Craven and Greig (1967); P. Gray and Lee (1967a,b); Liepman and Roshko (1967); Burgess *et al.* (1968 BM RI 7196); E. Cohen (1968); D.L. Jones (1968, 1970); Lutzsky and Lehto (1968); Munday, Ubbelohde and Wood (1968); H.S. Robinson (1968); Strehlow (1968a,b); van Dolah (1969b); Nagy, Conn and Verakis (1969 BM RI 7279); van Dolah and Burgess (1968); Ubbelohde and Munday (1969); Pawel *et al.* (1970); Rasbash (1969c, 1970a, 1976a,b); Furno *et al.* (1971); Gruschka (1971); Klaassen (1971); Munday (1971b); Nagy *et al.* (1971 BM RI 7507); Panton (1971); Cubbage and Marshall (1972, 1973, 1974); Alexander and Taylor (1973a,b); W.E. Baker (1973); W.E. Baker, Westine and Dodge (1973); Grein (1973); Guill (1973); Hatfield (1973); Sadee (1973a,b); Bartknecht (1974a, 1980, 1981a); Hess, Hoffmann and Stoeckel (1974); W.G. High (1974, 1976); NFPA (1974/12); Perlee, Fuller and Saul (1974 BM RI 7839); Raj and Kalelkar (1974); Sivashinsky (1974); W.E. Baker *et al.* (1975); Eisenberg, Lynch and Breeding (1975); Groothuizen and Pasman (1975); Kanury (1975); Kassoy (1975); Swisdak (1975); MLTI (1976); Strehlow and Baker (1975, 1976); AIChE (1976/69); J.W. Watts (1976); Fiumara (1977); Kletz (1977c, 1977–78); Leiber (1977); V.C. Marshall (1977a,b,d, 1987,1990b); Stull (1977); W.E. Baker *et al.* (1978); HSE (1978b, 1981a); R. King and Magid (1979); Pohto (1979); Bartknecht *et al.* (1980); Bodurtha (1980); Yallop (1980); Croft (1980/81); J.G. Marshall and Rutledge (1982); Mecklenburgh (1982, 1985); Pantony and Smith (1982); Ramsay, Sylvester-Evans and English (1982); Solberg (1982a,b); Zeeuwen (1982); W.E. Baker *et al.* (1983); Anon. (1984qq); J.R. Bowen *et al.* (1984a,b); J.F. Clarke and Kassoy (1984); Kinney and Graham (1985); Cruice (1986); Fordham Cooper (1986); Pasman and Wagner (1986); C.K. Chan and Greig (1989); FPA (1989 CFSD FS 6011); ILO (1989); Teodorczyk, Lee and Knystautas (1989); Lazari, Burley and Al-Hassani (1991); Makhviladze and Rogatykh (1991); Pineau *et al.* (1991); D.C. Bull (1992); CPD (1992a,b); Opschoor, van Loo and Pasman (1992); Lefebvre *et al.* (1993); Tang and Baker (1998, 1999); Baker *et al.* (1997); Tang, Baker and Cao (1996)

Explosion energy (*see also* Tables 17.29 and 17.36)
Girdhar and Aurora (1977); Hardesty and Kennedy (1977); Kinney and Graham (1985); Crowl (1991, 1992a); CCPS (1994/15)
Gas-filled vessels: Erode (1955, 1957, 1959); Kinney (1962); Kiwan (1970a,b, 1971); W.E. Baker (1973); Strehlow and Ricker (1976); Pohto (1979); Polentz (1980); Aslanov and Golinsky (1989); Crowl (1992a); CCPS (1994/15)

Explosion scaling
Hopkinson (1915); C.J.M. van Wingerden (1989b); Catlin and Johnson (1992)

Flame acceleration, deflagration to detonation transition (DDT) (*see also* Table 17.29)
Markstein (1957); Thibault *et al.* (1982); Lee, ICnystautas and Freeman (1984); Stock, Schildknecth and Geier (1984); S.B. Murray and Lee (1984); Peraldi, ICnystautas and Lee (1986); Nettleton (1987); Lindstedt and Michels (1989); Moen *et al.* (1989); C.K Chan, Lau and Radford (1991)

Pipes, tubes: M.W. Evans *et al.* (1949); Holzapfel and Schon (1965); Craven and Greig (1967); Leyer and Manson (1971); Moen, Murray *et al.* (1982); Rinnan (1982); J.F. Clarke and Kassoy (1984); Picone *et al.* (1984); Taki and Fujiwara (1984); Lee, ICnystautas and Chan (1985); Dunn-Rankin, Barr and Sawyer (1986); Ungiit and Shuff (1989); Dupre *et al.* (1991); Phylaktou, Andrews and Herath (1990); C.K Chan, Lau and Radford (1991); Phylaktou and Andrews (1991a,b); Phylaktou, Foley and Andrews (1993); CCPS (1994/15)
Enclosures, modules: Urtiew (1981); Moen (1982a); Hjertager *et al.* (1984); J.R. Harris and Wickens (1989); Hjertager (1991); K. van Wingerden, Visser and Pasman (1991)
Vapour clouds: Urtiew (1982a); H.G. Wagner (1982); Nettleton (1987); CCPS (1994/15)

Combustion in pipes
Mason and Wheeler (1917, 1920a–c); Chapman and Wheeler (1926, 1927); Penning (1926); de C.O.C. Ellis and Wheeler (1925, 1928a,b); Kirby and Wheeler (1931a,b); H. Robinson and Wheeler (1933); D.T. Williams and Bellinger (1949); Guenoche (1964); Gugan (1974b); Dorge, Pangritz and Wagner (1981); Moen, Lee *et al.* (1982); Hjertager (1984); J.H.S. Lee, ICnystautas and Chan (1985); Hjertager, Bjorkhaug and Fuhre (1988); Hjertager, Fuhre and Bjorkhaug (1988a)

Combustion in partially confined spaces
Abou-Arab, Erayet and Kamel (1991)
Parallel plates: Moen, Donate, ICnystautas and Lee (1980); Moen, Donate, ICnystautas, Lee and Wagner (1980); C.J.M. van Wingerden and Zeeuwen (1983); Hjertager (1984); C.J.M. van Wingerden (1984, 1989c)
Channels: Urtiew (1981); C. Chan, Moen and Lee (1983); Elsworth, Eyre and Wayne (1983); Sherman *et al.* (1985); P.H. Taylor (1986)

Spherical and cylindrical explosions (*see also* Tables 17.13 and 17.29)
Cousins and Cotton (1951a,b); Crouch *et al.* (1952); Vance and Krier (1974); Frankel and Sivashinsky (1983)

Explosions in vessels (*see also* Table 17.13)
Creech (1940); G.F.P. Harris and Briscoe (1967); Perlee, Fuller and Saul (1974 BM RI 7839); Sibulkin (1980); S.R. Moore and Weinberg (1981); Grewer and Klais (1987); Rota *et al.* (1987); Phylaktou, Andrews and Herath (1990); Phylaktou and Andrews (1991b, 1993); Checkel and Thomas (1994); Phylaktou, Andrews and Liu (1994)
Spherical geometry, spherical vessels: Flamm and Mache (1917); Mache (1918); Grumer, Cook and Kubala (1959); Spalding (1960); Spalding and Jain (1961); Spalding, Jain and Samain (1961); Raezer (1961); Pliickebaum, Strauss and Edse (1964); G.F.P. Harris (1967); Nagy, Conn and Verakis (1969 BM RI 7279); D. Bradley and Mitcheson (1976); Groff (1982); Kumar, Tamm and Harrison (1983); McCann, Thomas and Edwards (1985); Champion *et al.* (1986); Hjertager, Bjorkhaug and Fuhre (1988); Cant and Bray (1989); A.A. Evans (1989, 1990, 1991, 1992a,b); Tanaka (1989); Canu *et al.* (1990)
Cylindrical geometry, cylindrical vessels: Jain and Ebenzer (1966); Vance and Krier (1974); Starke and Roth (1986, 1989); Andrews, Herath and Phylaktou (1990)

Pressure piling
Beyling (1906); Grice and Wheeler (1929); Coward and Wheeler (1934); Gleim and March (1952 BM RI 4904); T.A.J. Brown (1959); K.C. Brown and Curzon (1963); Heinrich (1975); J. Singh (1977, 1984, 1994a); Bartknecht (1981a); Boyd *et al.* (1981); Fitt (1981a,b); Zeeuwen (1981); Phylaktou and Andrews (1993)

Other enhanced pressure effects
Kordylewski and Wach (1986, 1988)

Explosions in enclosures, modules
Rasbash (1976b,d); DnV (1979 79-0483); Hirano (1984); Hjertager *et al.* (1984); Hjertager (1986, 1991, 1993); Hjertger, Bjorkhaug and Fuhre (1988); Catlin (1991); Takahashi *et al.* (1991); Catlin and Johnson (1992); Hjertager, Solberg and Nymoen (1992); Phylaktou *et al.* (1992); Catlin, Manos and Tite (1993); Samuels (1993); Phylaktou, Andrews and Liu (1994); K. van Wingerden, Pedersen and Wilkins (1994)

Explosions in buildings
Astbury *et al.* (1970); Cubbage and Moppett (1970); FRS (1971 Fire Res. Note 847, 1974 Fire Res. Note 984, 985); Fry (1971); Astbury, West and Hodgkinson (1972, 1973); Astbury and Vaughan (1972); W.B. Howard (1972); BRE (1973 CP 11/73, 1974 BR9, CP 45/74, 1976 CP 24/76); Bartknecht (1981a); Buckland (1980); Zalosh (1980a); R.J. Harris (1983); Cleaver, Marshall and Linden (1994); Woodward, Thomas (2000)
Ronan Point: H. Griffiths, Pugsley and Saunders (1968)

Bursting vessels
Boyer *et al.* (1958); M.P. Friedman (1961); Garrison (1975); Leslie and Birk (1991); Gelfand *et al.* (1992); Crowl (1999); Baker, Tang, Cao (1996)

Vented explosions
Hjertager (1982a,b, 1986, 1991); P.H. Taylor (1986); Hjertager, Fuhre and Bjorkhaug (1988a,b); Bakke *et al.* (1989); van den Berg, van Wingerden and Verhagen (1989); P.H. Taylor and Bimson (1989); C.J.M. van Wingerden (1989c); Tamanini and Chaffee (1992)
CLICHE: Catlin (1990); Tamanini (1990, 1995, 1996a,b); Tamanini and Valiulis (1996)
FLACS: Hjertager (1982a); Bakke, Bjerketvedt and Bjorkhaug (1990)

Explosive loads
ACDS (1991); Gilbert, Lees and Scffly (1994a–c)

Particular types of explosion
Adsorbers: Anon. (1986 LPB 69, p. 25); CCPS (1993/13)
Air plants: Rotzler *et al.* (1960); Matthews (1961); G.T. Wright (1961); Lang (1962, 1965); Rendos (1963); Boyne (1966)
Air systems, oil films: Mallow (1964a,b); Thoenes 1964; Sichel, Rao and Nicholls (1971); Burgoyne and Craven (1973); Fowle (1973)
Ammonium nitrate: Commentz *et al.* (1921); Kintz, Jones and Carpenter (1948 BM RI 4245); National Board of Fire Underwriters (1948); Hainer (1955); Sykes, Johnson and Hainer (1963); Sykes *et al.* (1963); van Dolah *et al.* (1966 BMI 6747, RI 6773); HSE (1978b); Heemskerk and Schuurman (1989); ACDS (1991)
Asphalt, bitumen tanks: Anon. (1986 LPB 71, p. 71); Trumbore, Williamson and Wolfsberger (1991); Davie, Nolan and Hoban (1993, 1994); Davie, Nolan and Tucker (1993)
Boilers: Ostroot (1976b); Hewison (1983); G.D. Davis (1987); Bond (1990 LPB 93)
Centrifuges: Butterwick (1976); Funke (1976); Lindley (1987)
Chlorine systems: Eichelberger, Smura and Bergenn (1961); Johnsen and Yahnke (1962, 1973); Dokter (1985a,b); Tabata, Kodama and Kotoyori (1987); Bafflou *et al.* (1992)

Compressors: Gibbs (1960); Perlee and Zabetakis (1963 BM RI 8187); Walton (1963); W.L. Ball (1964); Schmitt (1964); Strelzoff (1964); Thoenes (1964); J.A. Rogers (1965); Armistead (1973); Burgoyne and Craven (1973); Fowle (1973); Prentice, Smith and Virtue (1974); HSE (1978b); Anon. (1979 LPB 26, p. 51); Kolodner (1980)
Cooling systems: Mansfield (1990 LPB 94)
Crankcase: Burgoyne, Newitt and Thomas (1954); Burgoyne and Newitt (1955); Mansfield (1956); Freestone, Roberts and Thomas (1965); Rushbrook (1979)
Diesel engines: Anon. (1970d)
Distillation systems: Carrara (1973); Fire Journal Staff (1973a); Freeman and McReady (1971); Jarvis (1971); Keister, Pesetsky and Clark (1971); Griffith and Keister (1973); Kotoyori *et al.* (1976); Kroger (1979)
Driers: K.N. Palmer (1973a); Reay (1977); Bartknecht (1981a); Abbott (1990); Schoofs (1992); Anon. (1994 LPB 119, p. 5)
Drums and small tanks: HSE (1970 Bklt 32); Pinsky, Vickery and Freeman (1990); Anon. (LPB 103, p. 31)
Electrical: Benjaminsen and van Wiechen (1968); Fordham Cooper (1986); Bartels (1990)
Ethylene: Martinet (1984); Vanderwater (1989)
Ethylene oxide systems: Troyan and Levine (1968); Ogawa, Miyake and Matsuo (1992)
Extruders: Anon. (1986 LPB 71, p. 31); Carter (1987 LPB 73); Anon. (1989 LPB 87, p. 3)
Flare systems: Bluhm (1964b); Kilby (1968)
Furnaces: P. Peterson (1967); Kletz (1972c); Ostroot (1972, 1976b); Durrant and Lansing (1976); Anon. (1992 LPB 108, p. 17)
Gas distribution system (public supply): DoEn (1977b); Buckland (1980); R.J. Harris (1983)
Heat exchangers: Zabetakis (1960 BM RI 5645); Bohlken (1961); Mesloh (1964); Lang (1965); Anon. (1987 LPB 74, p. 15); Anon. (1987 LPB 75, p. 22); Cullen (1990)
Hydraulic accumulators: Pratt (1986)
Hydrogen: Kolodner (1980); Anon. (1984x); Nordmo and Emblem (1989); Tamanini *et al.* (1989)
Incinerators: Anon. (1988 LPB 81, p. 17, 1990 LPB 92, p. 29)
Liquefied natural gas: Anon. (1972f); HSE (1978b); ACDS (1991)
Liquefied petroleum gas: HSE (1978b); Rasbash (1979/80); ACDS (1991)
Low temperature fluids: Burgoyne (1965b)
Lubricants: Anon. (1960c); Burgoyne and Craven (1973); Hasegawa (1992)
Mist and spray: Haber and Wolff (1923); Burgoyne and Richardson (1949b); Burgoyne (1957); Eichhorn (1964); J.R. Bowen *et al.* (1971); Vincent and Howard (1976); Vincent *et al.* (1976a,b); Gubin and Sichel (1977); Nettleton (1977b, 1987); Bar-or, Sichel and Nicholls (1981, 1982); Dabora (1982); Sichel (1982a,b); Sichel and Palaniswamy (1985); Bothe, Brandes and Redeker (1986)
Molten metal: Genco and Lemmon (1970)
Molten metal-water: C.F. Epstein (1961); Lipsett (1966); Brauer, Green and Mesler (1968); Flory, Paoli and Mesler (1969); Konway, Mead and Page (1975); HSE (1977/8); Vaughan (1980 SRD R177)
Nitrogen systems: Conklin (1961); Sanders and Nordop (1963); J.A. Rogers (1965); Anon. (1979 LPB 29, p. 151)
Piping: J.B. Smith (1949); Ringer (1985); Anon. (1989 LPB 88, p. 13)
Pollution control equipment: K.N. Palmer (1973a); Bodurtha (1976)
Pumps: Anon. (1987 LPB 74, p. 23)
Rail tank cars: Vanderwater (1989)
Ships: Burgoyne (1965a); Page and Gardner (1971); V.J. Clancey (1981); Blything and Edmonson (1984 SRD R292); ACDS (1991)
Spray driers: Masters (1972–, 1979); N. Gibson and Schofield (1977); Bartknecht (1981a)
Storage tank 'pops': Anon. (1988 LPB 82, p. 12); Kletz (1988 LPB 83)
Superheat: D.L. Katz (1972); R. King (1975a–c, 1976a,b, 1977); R.W. King (1976); Porteous and Blander (1975); Reid (1976)
Tanks, including storage tanks: Kletz (1971); Leiber (1980); HSE (1981 SHW 2125); McDaniel (1986); Anon. (1987 LPB 73, p. 9)
Vaporizers: Wright (1961)
Vent flashback: Burgoyne (1986a); W.B. Howard (1992a,b)
'Blameless' or 'physical' explosions, LNG/water explosions, rapid phase transition explosions, steam explosions
Witte, Cox and Bouvier (1970); D.L. Katz and Sliepcevich (1971); Enger and Hartman (1972a); D.L. Katz (1972); W. Nelson (1973a,b); Yang (1973); Opschoor (1974); Porteous and Blander (1975); Porteous and Reid (1976); Reid (1976, 1978); AGA (1977/26); Dincer, Drake and Reid (1977); Briscoe and Vaughan (1978 SRD R131); Witte and Cox (1978); Hogan (1982); Fauske and Henry (1983); McRae (1983); Ogiso, Fujita and Uehara (1986); Ogiso, Takagi and Katagawa (1986); D.C. Bull and Strachan (1992); Fletcher and Theofanous (1994)

Table 17.2 *Selected references on detonation*

B. Lewis and Friauf (1930); C. Campbell, Littler and Whitworth (1932); Payman and Titman (1935); Zeldovich (1940); von Neumann (1942); Doring (1943); Brinkley and Kirkwood (1947, 1949); Ubbelohde (1949, 1953); Berets, Greene and Kistiakowsky (1950); G.I. Taylor (1950); Fay (1952, 1962); R. Friedman (1953); Hirschfelder, Curtiss and Campbell (1953); Manson and Ferri (1953); Oppenheim (1953, 1969); Chester (1954); Gerstein, Carlson and Hill (1954); Weir and Morrison (1954); Zeldovich, Kogarko and Semenov (1956); Chisnell (1957); Adams and Pack (1959); Brinkley and Lewis (1959); M.A. Cook, Pack and Gey (1959); D.H. Edwards, Williams and Breeze (1959); Eisen, Gross and Rivlin (1960); Zeldovitch and Kompaneets (1960); Brinkley and Kirkwood (1961); M.W. Evans and Ablow (1961); Gvozdeva (1961); Randall and Ginsburgh (1961); Sommers (1961); Wehner and Phillips (1962); Boddington (1963); Freiwald and Koch (1963); Litchfield, Hay and Forshey (1963); Oppenheim and Rosciszewski (1963); Spalding (1963b); H.G. Wagner (1963); Mitrovanov and Soloukhin (1964); Monger *et al.* (1964); Dabora, Nicholls and Morrison (1965); J.J. Lee, Lee and Shanfield (1965); Strehlow and Fernandes (1965); Urtiew and Oppenheim (1965, 1966, 1967, 1968); Litchfield and Hay (1966 BM RI 6840, 1967 BM RI 7061); de Malherb *et al.* (1966); Solouokhin (1966, 1969); Strehlow, Crocker and Cusey (1967); Strehlow *et al.* (1967); Skinner *et al.* (1968); Strehlow (1968, 1971); Zeldovich and Raiza (1968); Brinkley and Seely (1969); E.L. Lee and Hornig (1969); Lundstrom and Oppenheim (1969); Strehlow and Bffler (1969); Strehlow and Engle (1969); Trezek and Balcerzak (1969); Ubbelohde and Munday (1969); Zajac and Oppenheim

(1969); J.W. Meyer, Urtiew and Oppenheim (1970); Pawel *et al.* (1970); Nagaishi, Yoneda and Hikita (1971); Panton (1971); Vasilev, Gavrilenko and Topchian (1972); Carlson (1973); Whitham (1974); Fry and Nicholls (1975); J.H. Lee, Knystautas and Guirao (1975, 1982); Sloan and Nettleton (1975, 1978); Takai, Yoneda and Hikita (1975); D.C. Bull *et al.* (1976); Chiu and Lee (1976); Knystautas and Lee (1976); J.H. Lee and Ramamurtha (1976); Matsui and Lee (1976,1979); J.H.S. Lee (1977, 1980); J.H. Lee and Matsui (1977); Benedick (1979); D.C. Bull, Elsworth and Hooper (1979a,b); D.H. Edwards, Thomas and Nettleton (1979,1983); Fickett and Davis (1979); Knystautas *et al.* (1979); Mader (1979); van der Molen and Nicholls (1979); Nicholls *et al.* (1979); R. Atkinson, Bull and Shuff (1980); Moen *et al.* (1980); Sibulkin (1980); Bowers *et al.* (1981); Edwards *et al.* (1981); Eidelman and Burcat (1981); Moen *et al.* (1981); Oran *et al.* (1981); Urtiew and Tarver (1981); Wolanski *et al.* (1981); Abouseif and Toong (1982a,b, 1986); D.C. Bull *et al.* (1982); Burcat and Hasson (1982); Dabora (1982); Damamme (1982); Eidelman (1982); Guirao *et al.* (1982); Knystautas, Lee and Guirao (1982); Logan and Bdzil (1982); Moen, Lee *et al.* (1982); Moen, Murray *et al.* (1982); Oran *et al.* (1982); Tarver (1982); Westbrook (1982a,b); Westbrook and Urtiew (1982); J.R. Bowers *et al.* (1983); Elsworth and Eyre (1984); Elsworth, Shuff and Ungut (1984); Kailasanath and Oran (1984); Ohyagi, Yoshihashi and Harigaya (1984); Vandermeiren and van Tiggelen (1984); Westbrook, Pitz and Urtiew (1984); Kailasanath *et al.* (1985); Kuznetsov and Kopotev (1985); Moen, Bjerketvedt *et al.* (1985); Moen, Ward *et al.* (1985); Presles *et al.* (1985); Moen, Sulmistras *et al.* (1986); Weinberg (1986); Huang Zhong-Wei and Xu Bin (1987); Nettleton (1987); Linstedt and Michels (1988); Zerillief Z. (1988); Bauer *et al.* (1989); Knystautas *et al.* (1989); Moen *et al.* (1989); G.O. Thomas, Sutton and Edwards (1991); Bourlioux and Majda (1992); He and Clavin (1992); Lefebvre *et al.* (1993); Moen (1993)

17.1 Explosion

17.1.1 The explosion process

An explosion is a sudden and violent release of energy. The violence of the explosion depends on the rate at which energy is released. The energy stored in a car tyre, for example, is capable of causing an explosive burst, but it can be dissipated by gradual release.

There are several kinds of energy which may be released in an explosion. Three basic types are (1) physical energy, (2) chemical energy and (3) nuclear energy.

Physical energy may take such forms as pressure energy in gases, strain energy in metals or electrical energy. Examples of the violent release of physical energy are the explosion of a vessel due to high gas pressure and the sudden rupture of a vessel due to brittle fracture. Another important physical form is thermal energy. In particular, superheat in a liquid under pressure causes flashing off of the liquid if it is let down to atmospheric pressure. However, this is generally important in creating the conditions for an explosion rather than as a source of energy for the explosion itself.

Chemical energy derives from a chemical reaction. Examples of the violent release of chemical energy are explosion of a vessel due to combustion of flammable gas, and explosion of a reactor caused by decomposition of reaction products in a runaway chemical reaction.

Chemical explosions are either (1) uniform explosions or (2) propagating explosions. An explosion in a vessel tends to be a uniform explosion, while an explosion in a long pipe gives a propagating explosion.

Nuclear energy is not considered here. In the present context, it is chemical explosions, and in particular explosions resulting from combustion of flammable gas, that are of prime interest.

17.1.2 Deflagration and detonation

Explosions from combustion of flammable gas are of two kinds: (1) deflagration and (2) detonation.

In a deflagration the flammable mixture burns at subsonic speeds. For hydrocarbon–air mixtures the deflagration velocity is typically of the order of 300 m/s.

A detonation is quite different. In a detonation the flame front travels as a shock wave followed closely by a combustion wave which releases the energy to sustain the shock wave. At steady state the detonation front reaches a velocity equal to the velocity of sound in the hot products of combustion; this is much greater than the velocity of sound in the unburnt mixture. For hydrocarbon–air mixtures the detonation velocity is typically of the order of 2000–3000 m/s. For comparison the velocity of sound in air at 0°C is 330 m/s.

A detonation generates greater pressures and is more destructive than a deflagration. Whereas the peak pressure caused by the deflagration of a hydrocarbon–air mix-air mixture in a closed vessel is of the order of 8 bar, a detonation may give a peak pressure of the order of 20 bar.

A deflagration may turn into a detonation, particularly when travelling down a long pipe. Where a transition from deflagration to detonation is occurring, the detonation velocity can temporarily exceed the steady-state detonation velocity in so-called 'over driven' condition. Deflagration and detonation are discussed further in Sections 17.2, 17.5 and 17.6.

17.1.3 Process industries explosions: explosions vs fires

Some data on 83 large loss fires/explosions over a 5-year period have been given by W.H. Doyle (1969) , and were reproduced in Table 2.14. These data have been expressed by Kletz (1977k) in terms of the proportion of fires and of explosions of different types:

	Proportion (%)
Explosions inside equipment because air got in	11
Explosions inside equipment because of runway reactions or explosive decomposition	23
Explosions outside equipment but inside buildings	24
Explosions in the open	3
Vessels bursting (due to corrosion, overheating or overpressure)	7
Fires	32
Total	100

17.1.4 Process industries explosions: classification of explosions

Explosions in the process industries include the following types:

(1) physical explosions
  (a) mechanical failure of pressure system (within design envelope),
  (b) overpressure of pressure system,
  (c) underpressure of pressure system,
  (d) overtemperature of pressure system,
  (e) undertemperature of pressure system;
(2) condensed phase explosions
  (a) high explosives,
  (b) ammonium nitrate,
  (c) organic peroxides,
  (d) sodium chlorate;
(5) vapour cloud explosions (VCEs);
(6) boiling liquid expanding vapour explosions (BLEVEs);
(7) confined explosions with reaction
  (a) explosion involving vapour combustion,
  (b) reactor explosions,
  (c) other explosions involving liquid phase reactions;
(8) vapour escapes into, and explosions in, buildings (VEEBs);
(9) dust explosions.

17.2 Detonation

A particularly severe form of explosion occurs when an explosive substance detonates. Detonation can occur in liquid and solid explosives, in explosive gas mixtures and in vapour clouds. These aspects of detonation are considered in Sections 17.3, 17.6 and 17.28.

Accounts of detonation, and of shock waves, are given in *Supersonic Flow and Shock Waves* (Courant and Friederichs, 1948), *Theory of Detonation* (Zeldovich and Kompaneets, 1960), *Shock Waves in Chemistry and Physics* (G.N. Bradley, 1962), *Gas Dynamics of Combustion* (Shchelkin and Troshin, 1965), *Shock Waves and Detonations in Gases* (Soloukhin, 1966), *Fundamentals of Combustion* (Strehlow, 1968a), *Detonation* (Fickett and Davis, 1979), *Unconfined Vapour Cloud Explosions* (Gugan, 1979), *The Effects of Nuclear Weapons* (Glasstone and Dolan, 1980), *Explosive Shocks in Air* (Kinney and Graham, 1985), *Principles of Combustion* (Kuo, 1986), *Combustion, Flames and Explosions* of Gases (B. Lewis and von Elbe, 1987) and *Gaseous Detonations* (Nettleton, 1987).

The origins of work on detonations are to be found in explosion disasters, notably in coal mines, and in the mathematical theory of shock waves. Studies by Riemann showed that even starting from smooth initial conditions the movement of compressible gases can lead to formation of discontinuities with a sudden rise in pressure and temperature. The thermodynamics of shock waves were investigated by Hugoniot (1887–89). The extension to reactive systems then led to the detonation theory of Chapman (1899) and of Jouguet (1905) .

The Chapman–Jouguet (CJ) equations, however, were consistent with a number of final states. The choice of final state was made by these workers on the basis of a minimum velocity criterion. Their studies provided a working model which in certain features gave good agreement with experiment and held the field for some 40 years.

A further advance came with the concept of the initiation of combustion by a shock wave travelling ahead of the reaction zone, proposed independently by Zeldovich (1940), von Neumann (1942) and Db'ring (1943). This theory takes into account the finite rate of the chemical reactions.

Later work has shown, however, that the Zeldovitch–von Neumann–Doring (ZND) model is unstable for the case where the reactions are strongly temperature dependent. There still exists, therefore, no comprehensive theory of detonations. Another aspect of interest here is the transition from deflagration to detonation, to which a particular contribution has been made by Shchelkin (Shchelkin and Troshin, 1965).

Much work on detonation utilizes mixtures of fuel with oxygen rather than air. Hence, care should be exercised in reading the literature to check the oxidant to which a particular statement or correlation is applicable.

Selected references on detonation are given in Table 17.2, and on detonability characteristics in Table 17.3.

17.2.1 Detonation waves

In a detonation, a detonation wave passes through the explosive substance. This detonation wave has certain well-defined properties. These are now considered.

The detonation wave may develop by a process of transition. This transition may be illustrated by considering the combustion in a tube of a flammable gas–air mixture which is initially at constant pressure. If ignition occurs and energy is released at one end of the tube, the burnt gases expand. The deflagration front moves at a flame speed which is the sum of the burning velocity and the velocity of the burnt gases. If the flame speed is low enough, the combustion continues at essentially constant pressure, but if the flame speed is sufficiently high for momentum changes to exercise a significant effect, pressure disturbances are created. In this latter case the flame front accelerates and travels as a combustion wave preceded by a shock wave. Further acceleration of the flame front may cause the deflagration to turn into a detonation. The detonation wave then travels with a velocity greater than that of sound in the unburnt gas.

Table 17.3 *Selected references on detonability characteristics*

Explosibility, flammability (*see Tables* 8.1, 16.3 and 17.62)
Detonation limits and velocity (also cell size, critical tube diameter, critical initation energy)
Hirschfelder, Curtiss and Campbell (1953); Ghormley (1958); Belles (1959); Shchelkin (1959); B. Lewis and von Elbe (1961); Burgess *et al.* (1968 BM RI 7196); Benedick, Kennedy and Morosin (1970); Michels, Munday and Ubbelohde (1970); Benedick, Morosin and Kennedy (1971); Munday (1971b); Carlson (1973); Nolan (1973); Strehlow (1973b); J.W. Watts (1976); Borisov and Loban (1977); J.H. Lee and Matsui (1977); Nettleton (1978a, 1979, 1980a,b, 1987); Moen *et al.* (1981); J.H.S. Lee, Knystautas and Guirao (1982); Bauer, Brochet and Presles (1984); Kailasanath and Oran (1984); Vandermeiren and van Tiggelen (1984); Knystautas *et al.* (1984); Bauer, Presles and Heuze (1986); Michels and Rashidi (1992); Rashidi and Michels (1992)

17.2.2 Unidimensional models

Analysis of the behaviour of shock waves with and without reaction was for many years conducted mainly in terms of models in one dimension. Although the deficiencies of these unidimensional models are now recognized, they have been very successful in describing some important properties of the waves.

17.2.3 Non-reactive shock wave Rankin–Hugoniot conditions

It is convenient to consider first the unidimensional model of a planar shock wave in a non-reactive medium. Conventionally, the model is derived for a shock wave acting like a piston compressing the gases before the wave front. It is expressed first with a coordinate system moving with the wavefront as stated by Lewis and von Elbe (1987, p. 535) . The basic equations are

$$G = \frac{u_1}{v_1} = \frac{u_2}{v_2} \quad \text{conservation of mass flux} \quad [17.2.1]$$

$$p_1 + \frac{u_1^2}{v_1} = p_2 + \frac{u_2^2}{v_2} \quad \text{conservation of momentum} \quad [17.2.2]$$

$$h_1 + \frac{1}{2}u_1^2 = h_2 + \frac{1}{2}u_2^2 \quad \text{conservation of energy} \quad [17.2.3]$$

with

$$h = e + pv \quad [17.2.4]$$

$$pv = RT \quad [17.2.5]$$

$$v = 1/\rho \quad [17.2.6]$$

where e is the specific internal energy of the gas, h is its specific enthalpy, p is the pressure, u is the velocity of the gas, v is its specific volume, T is its absolute temperature, ρ is its density and the subscripts 1 and 2 refer to the gas entering and leaving the shock wave, respectively. From Equations 17.2.1–17.2.4

$$\Delta h = h_2 - h_1 = \frac{1}{2}(p_2 - p_1)(v_1 + v_2) \quad [17.2.7]$$

$$\Delta e = e_2 - e_1 = \frac{1}{2}(p_2 + p_1)(v_1 - v_2) \quad [17.2.8]$$

Equations 17.2.7 and 17.2.8 comprise the Rankine–Hugoniot (R–H) equation which replaces the integral $\int_{v_1}^{v_2} P\,\mathrm{d}V$ of isentropic compression. It can be shown, taking a perfect gas for example, that for the same volume change, Equation 17.2.8 will lead to a larger Δe and therefore a higher temperature than isentropic compression provides. For a very small volume change the RH equation reduces to $\mathrm{d}E = -P\,\mathrm{d}V$ which is valid for piston velocities up to the velocity of sound. When the piston velocity becomes on the order of magnitude of molecular velocities, the degradation of the kinetic energy of the piston into random molecular motion, that is, thermal energy, makes a significant additional contribution to the increase of internal energy of the compressed gas.

Other useful relations are, from Equations 17.2.1, 17.2.2 and 17.2.6,

$$(\rho_1 u_1)^2 = \frac{p_2 - p_1}{v_1 - v_2} \quad [17.2.9]$$

and from this equation and Equation 17.2.6

$$u_1 = v_1\left(\frac{p_2 - p_1}{v_1 - v_2}\right)^{1/2} \quad [17.2.10]$$

The internal energy change Δe is

$$\Delta e = e_2 - e_1 \quad [17.2.11]$$

$$= \bar{c}_v(T_2 - T_1) \quad [17.2.12]$$

where $\bar{c}_v$ is the mean specific heat at constant volume. The particle velocity is w

$$w = u_1 - u_2 \quad [17.2.13]$$

and it may be written, utilizing Equations 17.2.1 and 17.2.10, as

$$w = (v_1 - v_2)\left(\frac{p_2 - p_1}{v_1 - v_2}\right)^{1/2} \quad [17.2.14]$$

Another parameter of interest is the 'impulse force' i_f, which is a measure of the pressure exerted by the shock wave as it strikes an obstacle. The velocity heads pressure (kinetic energy) exerted is $\rho_2 w^2$. Then, substituting for this term using Equations 17.2.6 and 17.2.14 and adding the static term $(p_2 - p_1)$, the net pressure i is

$$i_f = \frac{v_1}{v_2}(p_2 - p_1) \quad [17.2.15a]$$

The impulse force should be distinguished from the impulse, i, which has units of force times the duration the force is applied, which also equals a change in momentum. The value of i from a blast wave is the area under the positive overpressure portion of the blast wave. For a detonation wave, the positive pressure portion is well approximated as a triangle with a peak pressure p_2 and a plateau pressure p_3:

$$i = \frac{v_1}{v_2}(p_2 - p_1) \quad [17.2.15b]$$

For the case where the coordinates of the system are with respect to a fixed frame of reference, rather than moving with the shock wave, the velocity of the shock wave is

$$D = V_1 + u_1 \quad [17.2.16]$$

where D is the velocity of the shock wave and V_1 is the velocity of the gas entering the shock wave, both in the fixed frame of reference. But since for the unburned gas $V_1 = 0$,

$$D = u_1 \quad [17.2.17]$$

The two coordinate systems are discussed by Kuo (1986) and B. Lewis and von Elbe (1987, p. 535).

From Equations 17.2.10 and 17.2.17

$$D = v_1\left(\frac{p_2 - p_1}{v_1 - v_2}\right)^{1/2} \quad [17.2.18]$$

Values of the shock wave parameters for air calculated by Becker (1922) are shown in Table 17.4.

For the case of detonation, in which a reaction occurs in the shock wave and the energy conservation equation is augmented by a heat input term, as discussed below, D becomes the detonation velocity.

17.2.4 Rankin–Hugoniot curves for ideal gases

The R–H equations show the relation between the initial and final states for a given change of enthalpy across the shock front. For an ideal gas with a constant ratio of specific heats 7, Equation 17.2.7 may be reformulated as

$$\frac{\gamma}{\gamma-1}(p_2v_2-p_1v_1)=\frac{1}{2}(p_2-p_1)(v_1+v_2) \qquad [17.2.19]$$

Table 17.4 *Some shock wave parameters for air (after Becker, 1922)*

p_2/p_1	v_1/v_2	D (m/s)	w (m/s)	T_2 *shock wave* (K)	T_2 *adiabatic compression* (K)	i/p_1
2	1.63	452	175	336	330	1.63
5	2.84	698	452	482	426	11.4
10	3.88	978	725	705	515	34.9
100	7.06	3020	2590	3860	950	699

Equation 17.2.19 (Nettleton) yields in the p–v plane a curve which is a rectangular hyperbole. Such a curve is known as an R–H curve. Various forms of the curve are shown in Figure 17.1. Figure 17.1(a) shows for comparison an R–H curve and a curve for an isentropic process $pv^{\gamma}=$ constant. Equation 17.2.9 gives a line between a pair of points on the R–H curve which is known as a Rayleigh line. Figure 17.1(a) also shows such a line.

On the assumption that there is no change in the molecular weight or ratio of specific heats of the gas, Equations 17.2.1–17.2.3, 17.2.5 and 17.2.6 yield

$$\frac{p_2}{p_1}=\frac{2\gamma\mathrm{Ma}_s^2-(\gamma-1)}{\gamma+1} \qquad [17.2.20]$$

$$\frac{\rho_2}{\rho_1}=\frac{(\gamma+1)\mathrm{Ma}_s^2}{(\gamma-1)\mathrm{Ma}_s^2+2} \qquad [17.2.21]$$

$$\frac{T_2}{T_1}=\frac{\left[\gamma\mathrm{Ma}_s^2-(\gamma-1)/2\right]\left[((\gamma-1)/2)\mathrm{Ma}_s^2+1\right]}{((\gamma+1)/2)\mathrm{Ma}_s^2} \qquad [17.2.22]$$

with

$$\mathrm{Ma}_s=u_1/a_1 \qquad [17.2.23]$$

where a is the velocity of sound, Ma is the Mach number and the subscript s is the shock wave.

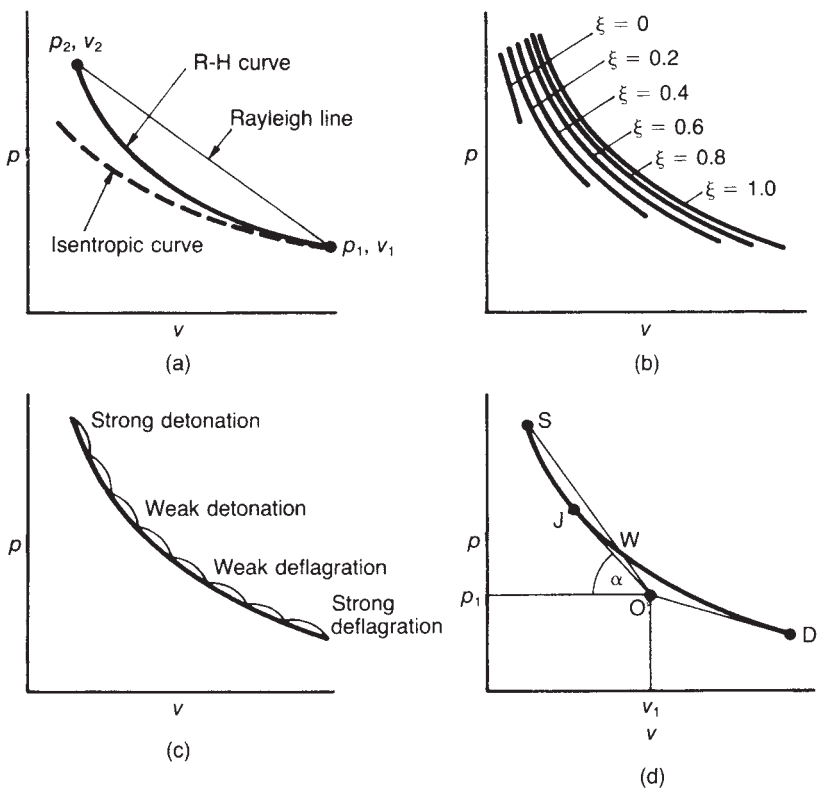

Figure 17.1 *Rankin–Hugoniot diagram: (a) R–H curve, isentropic curve and Rayleigh line; (b) family of R–H curves for different fractions ξ of completion of reaction; (c) detonation and deflagration regions of the R–H curve; and (d) the Chapman–Jouget state*

A detailed discussion of the properties of the R–H curve is given by Kuo (1986).

17.2.5 Reactive shock wave

Moving on to modelling of a planar shock wave in a reactive medium, or detonation wave, the introduction of a heat input term q into Equation 17.2.7 gives

$$h_2 - h_1 - q = \frac{1}{2}(p_2 - p_1)(v_1 + v_2) \qquad [17.2.24]$$

where q is the energy addition per unit mass, or specific energy input, in the flow behind the shock front. As before, Equation 17.2.24 can be rewritten in the alternative form

$$\frac{\gamma}{\gamma - 1}(p_1 v_1 - p_2 v_2) - q = \frac{1}{2}(p_2 - p_1)(v_1 + v_2) \qquad [17.2.25]$$

As shown in Figure 17.1(b), this equation gives a family of R–H curves for $q = 0$ and a family of R–H curves for various fractions of completion of the combustion reaction, ξ. At $\xi = 1$, the full value of q is released, so these curves also represent fractions of q as ξq.

17.2.6 Chapman–Jouguet model

The CJ model explains why detonations for a given fuel travel at a constant velocity. Equation 17.2.24 is the basis of the CJ model. Equation 17.2.25 is an alternative form for ideal gases.

Figure 17.1(c) shows the regions of the R–H curve for a finite value of q. There are two broad regions. The first, where $p_2 > p_1$ and $v_2 < v_1$, is the region of detonation with a compression wave and the second, where $p_2 < p_1$ and $v_2 < v_1$, is the region of deflagration with a rarefaction wave. The combustion conditions along the curve pass from strong detonation, through weak detonation, then weak deflagration, to strong deflagration.

The CJ equation has not one but a set of solutions. The solution to which its authors came, namely that the velocity of the shock front is the minimum consistent with the conservation laws, is embodied in the CJ hypothesis that

$$a + u_2 = u_1 \qquad [17.2.26]$$

The CJ hypothesis may be explained by reference to Figure 17.1(d). The initial state of the gas is represented by the point O. Three possible final states are shown at S, W and J together with the lines OWS and OJ, the latter being the line of the tangent from O. In the region of S the sum of the velocity of sound and that of the gas exceeds the velocity of the front ($a + u_2 > u_1$) so that any rarefaction occurring in the flow behind the front tends to overtake and weaken it, and thus this state is unstable. The velocity of the front tends towards point J. In the region of W the sum of the velocity of sound and that of the gas is less than the velocity of the wave ($a + u_2 < u_1$) so that any energy release occurring in the flow behind the front is not available to sustain it, and thus this state also is unstable. Again the velocity of the front tends towards point J. Hence J is the only stable state in the detonation region. It can also be shown that in the deflagration region the only stable state is D, where the line OD is that of the tangent from O. Points J and D are known as the upper and lower CJ points.

The angle α of the line OJ is given by $\tan \alpha = (p_2 - p_1)/(v_1 - v_2)$ and from Equation 17.2.9

$$u_1 = v_1 \left(\frac{p_2 - p_1}{v_1 - v_2}\right)^{1/2} = v_1 (\tan \alpha)^{1/2} \qquad [17.2.27]$$

In this model the pressure p_2, the velocity u_1 and the Mach number Ma_1 are frequently referred to as the CJ pressure p_{CJ}, the CJ velocity u_{CJ} or D_{CJ} and the CJ Mach number $\mathrm{Ma}_{\mathrm{CJ}}$.

More detailed accounts of the full CJ model equations are given by B. Lewis and von Elbe (1987, p. 538) and Kuo (1986). The latter also gives a calculation scheme for the determination of the CJ parameters.

Work by von Neumann (1942) showed that at the instant when the front arrives there is a sharp, higher pressure, the von Neumann spike.

The shock wave profile yielded by the CJ model is illustrated in Figure 17.2. The shock wave travels as a sharp front. At the instant when the front arrives there occurs the von Neumann spike (point A). Very close to this in time is a lower pressure peak at the CJ plane (point B). Following this the pressure decays to a plateau value (point C).

There are a number of relations which may be used to obtain approximate estimates of the CJ parameters. A very simple equation is the Zeldovich approximation (Zeldovich and Kompaneets, 1960) relating the CJ pressure p_2 to the pressure p_{v} of constant volume combustion:

$$p_{\mathrm{CJ}} \approx 2p_{\mathrm{v}} \qquad [17.2.28]$$

Another equation for the CJ pressure is that given by Weir and Morrison (1954):

$$\frac{p_{\mathrm{CJ}}}{p_1} = \frac{1 + \gamma_1 \mathrm{Ma}_{\mathrm{CJ}}}{1 + \gamma_2} \qquad [17.2.29]$$

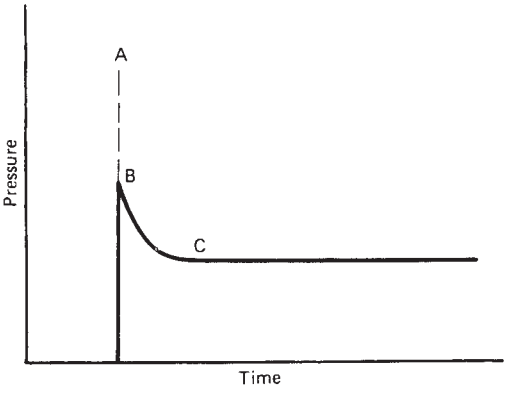

Figure 17.2 *Detonation front in a pipe: A, von Neumann spike; B, CJ peak; C, plateau pressure*

The following approximate equations are given by Nettleton (1987):

$$p_2 \approx \frac{2q(\gamma_2 - 1)}{v_1} \quad [17.2.30]$$

$$\frac{\rho_2}{\rho_1} \approx \frac{\gamma_1 + 1}{\gamma_1} \quad [17.2.31]$$

$$u_1 \approx [2q(\gamma_2^2 - 1)]^{1/2} \quad [17.2.32]$$

These relations are applicable for $Ma_{CJ} \geq 4$, which for systems of interest is generally the case.

Some data of Strehlow on the specific heat input and ratio of specific heats γ for stoichiometric mixtures of various fuels for use in CJ model calculations are given by W.E. Baker *et al.* (1983). The data for ethylene are a specific heat input of 3.834 MJ/kg of the mixture and a ratio of specific heats of 1.188. The CJ pressure, temperature and velocity quoted, obtained from relations given by these authors rather than from those quoted above, are 18.63 bar, 2929 K and 1822 m/s, respectively.

The behaviour of detonation waves from combustion of hydrocarbon gases has been investigated by Burgess *et al.* (1968 BM RI 7196) in experiments in pipes of up to 24 in. diameter. An illustration of a detonation in a stoichiometric acetylene–air mixture is described in detail. The von Neumann spike pressure is 34 atm with an ignition delay time of 10^{-6} s. The decay from the von Neumann spike pressure to the CJ, or detonation, pressure of 19 atm occurs in about 10^{-5} s, giving an impulse of $(34 + 19)/2 \times 14.7 \times 10^{-5} = 4 \times 10^{-3}$ psi. The von Neumann spike is described as too fast to detect by instrumentation, but the CJ peak is detectable. The decay from the CJ pressure to the plateau pressure of 6.7 atm occurs in about 8.5 ms, giving an impulse of about 1.6 psi s.

The experiments confirmed the Zeldovich approximation. Also, the experimental plateau pressure p_{pl} was about 40% of the CJ pressure:

$$p_{pl} \approx 0.4 p_{CJ} \quad [17.2.33]$$

Equations are given for the calculation of the plateau pressure.

The CJ model has proved relatively successful in predicting the detonation pressure, density and velocity in readily detonable mixtures in straight pipes.

Comparisons based on experimental data obtained by B. Lewis and Friauf (1930) for mixtures of hydrogen, oxygen and other gases have been widely quoted. Other work includes that of Berets, Greene and Kistiakowsky (1950) and that of D.G. Edwards, Williams and Breeze (1959). For a 2:1 mixture of hydrogen and oxygen the latter obtained the following values of the detonation parameters:

Pressure (atm)		*Velocity* (m/s)	
Observed	*CJ model*	*Observed*	*CJ model*
18.6	18.6	2825	2853

The observed pressure was the average pressure over 20–80 μs.

17.2.7 Zeldovich–von Neumann–Doring model

A weakness of the CJ model is the assumption that the chemical reaction which is the source of the heat release is infinitely fast. A further advance came with the development of a model which takes account of the finite rate of reaction, and of heat release. The model was formulated independently by Zeldovitch (1940), von Neumann (1942) and Döring (1943), and is known as the ZND model. In this model there is no reaction immediately behind the shock wave and there is an incubation period before the reaction begins. The fractional completion of the reaction is characterized by the parameter ξ, and there is therefore a family of R–H curves for values of ξ between 0 and 1 as in Figure 17.1(b).

The ZND model is more realistic and provides a firmer basis for the development of unidimensional models. One particular use is in predicting the pressure–time profile of the detonation, including the von Neuman spike. Considerable effort was expended from 1950 to 1970 to test the validity of the ZND model. While ZND corrected values were most frequently below the CJ value, they were occasionally larger (Brochet, Manson; Roye and Struck 1963). However, the discrepancies between theory and experiment are less than 1%, which is adequate for engineering predictions.

17.2.8 Taylor expansion wave

The product gases behind the CJ plane expand isentropically and accelerate, so that there is a distribution of particle velocities. This distribution was investigated by G.I. Taylor (1950). The Taylor expansion wave theory provides predictions for the velocity decay behind the CJ wave front.

17.2.9 Deflagration and detonation

Deflagrations are defined by $u_1/a_1 < 1$; for detonations $u_1/a_1 > 1$. Some typical characteristics of deflagrations and detonations have been listed by R. Friedman (1953):

Characteristic ratio	*Deflagration*	*Detonation*
u_1/a_1	0.0001–0.03	5–10
u_2/u_1	4–6 (acceleration)	0.4–0.7 (deceleration)
p_2/p_1	0.98 (slight expansion)	13–55 (compression)
T_2/T_1	4–16 (heat addition)	8–21 (heat addition)
p_2/p_1	0.06–0.25	1.7–2.6

17.2.10 Detonation wave structure

The account of detonation waves which has just been given is a simplified one. In particular, it does not take account of the unsteady and multidimensional features of such waves. In some cases, the detonation wave exhibits behaviour which results in pressures higher than those predicted by unidimensional theories. A case in point is spinning detonation fronts. In certain media the detonation front passing down a tube exhibits a stable spin. A spinning detonation front may be characterized in terms of the wavelength λ of the spin, or ratio of the pitch p of the spin to the diameter d of the tube:

$$\lambda = p/d \quad [17.2.34]$$

It has been shown by Fay (1952) that

$$\frac{p}{d} = \frac{\pi(\gamma_o + 1)}{\gamma_o k_n} \quad [17.2.35]$$

where γ_o is the ratio of specific heats of the detonation products and k_n is a Bessel function derivative. The values of γ_o range between 1.2 and 1.4 and k_n has the value 1.841. Equation 17.2.35 may be reformulated as

$$\frac{p}{d} = \frac{\pi d}{a_o k_n} \qquad [17.2.36]$$

where a_o is the velocity of sound in the burned gas.

Experimental evidence indicates that in a spinning front, local pressure ratios occur which are in excess of those predicted by unidimensional theories. Pressure ratios as high as 160 have been obtained in some work.

Another, related behaviour is that of galloping detonation fronts. These show regular oscillations in the velocity of the leading front. The phenomenon appears to be an extension of that of spin occurring in mixtures too close to the limit of detonability for a single transverse front to be supported. The regular peak velocities can exceed the CJ velocity by up to 35%, and the peak pressures shows a similar enhancement. The overdriven phase can persist over the relatively extended length of 0.1 m.

In marginally detonable mixtures, detonations are multidimensional. Several different types of front have been identified. They include equilibrium fronts, which have both constant time-averaged properties and a regularly recurring structure; other fronts which have the first but not the second of these features and transient fronts.

The spinning detonation front is now regarded as a limiting form of multidimensional front. The leading front consists of a number of bulges formed by Mach stems. There are a number of transverse waves orthogonal to the leading front which start at the depressions between the bulges and which reflect from each other and from the walls. There are reaction zones at the leading front and at the transverse waves.

17.2.11 Detonation wave cells

A gas detonation possesses a three-dimensional structure made up of 'cells', a regular pattern of diamond shapes. A good deal of work has been done to characterize these cells and to relate to them the principal features of detonations.

Experimentally the cell structure may be studied from soot patterns formed on smoked foil on the inner surface of the tube. It is found that typically for a cell

$$S \approx 0.6 L_c \qquad [17.2.37]$$

where L_c is the length of the cell and S its width.

Related variables are the induction zone length L_i and the induction time τ_i. The induction zone length is the distance between the shock front and the reaction zone front and the induction time the interval between the passage of these two fronts, the relation between the two is

$$L_i = \tau_i \, \mathrm{Ma}_s \, a_o \qquad [17.2.38]$$

where a_o is the speed of sound in the mixture and Ma_s the Mach number of the shock wave.

With regard to the form of the relation between L_c and L_i, work by Vasiliev, Gavrilenko and Topchian (1972), and others, on fuel–oxygen mixtures indicates that

$$L_c = 10 n L_i \quad 5 \leq n \leq 10 \qquad [17.2.39]$$

in other words, $50L_i \leq L_c \leq 100L_i$, where n is a constant. Nettleton (1987) describes the use of hydrocarbon–oxygen mixtures of the value

$$L_c \approx 50 L_i \qquad [17.2.40]$$

and of hydrocarbon–air mixtures, except acetylene, of the value

$$L_c \approx 15 L_i \qquad [17.2.41]$$

The induction length L_i increases as tube diameter increases. Nikuradse (1933) has shown that in pipe explosions the distance to the establishment of fully developed turbulence is about 60 diameters. A similar proportionality to diameter might be expected for the induction length. The question is discussed by Lewis and von Elbe (1987). The evidence is that the proportionality holds in some cases but not in others.

The cell width S is equivalent to the spacing of the transverse waves. For this spacing, Nettleton (1987) gives the following estimates for mixtures at atmospheric pressure: 1–10 mm for near stoichiometric fuel–oxygen mixtures; 10–100 mm for near stoichiometric fuel–air mixtures and 0.1–1.0 m for lean fuel–air mixtures.

The cell length L_c is related to the critical diameter d_c for transmission of a detonation in a tube, and also across an abrupt expansion. Detonations do not develop in a tube of diameter less than d_c, where d_c depends on fuel composition. In a classic study, Zeldovich, Kogarko and Semenov (1956) found that $d_c/L_i =$ constant for all the gases which they tested.

Further work on this feature has been done by Gvozdeva (1961) and Mitrovanov and Soloukhin (1964). Using acetylene–oxygen mixtures, the latter obtained the relationships

$$d_c = 13S \quad \text{circular tubes} \qquad [17.2.42a]$$

$$d_c = 10S \quad \text{planar channels} \qquad [17.2.42b]$$

Additional work includes that of D.H. Edwards, Thomas and Nettleton (1979), who have shown that the two results are equivalent and suggested that they are of general applicability to detonations.

D.C. Bull *et al.* (1982) have studied the cell length, and the factors influencing it, for a number of gases. For stoichiometric mixtures with air at atmospheric pressure they give the following values of L_c: methane 310 mm, ethane 54 mm, propane 46 mm, *n*-butane 54 mm, acetylene 9.2 mm, ethylene 24 mm and hydrogen 10 mm.

These authors also discuss the relevance of cell size. A planar detonation wave cannot propagate in a channel of width substantially smaller than the half-width of a cell. This feature is relevant to the quenching of detonations.

In the transition from a planar to a spherical detonation wave at an abrupt expansion there is a critical number of cell widths in the planar front to sustain the detonation. For a circular tube this number is 13.

Equation 17.2.42a is a statement of this fact. This feature also is relevant to quenching.

There is a close connection between the cell size and the critical energy E_c for initiation of a spherical detonation. Thus, Zeldovich, Kogarko and Semenov (1956) give the relation

$$E_c \propto \Delta^3 \qquad [17.2.43]$$

where Δ is an induction length, which is related to the cell size.

In the transition from deflagration to detonation there is some indication that the critical turbulent length scales may be of the same order as detonation cell lengths and that systems of different reactivity have a rank order similar to that for cell sizes.

17.2.12 Detonability characteristics

The detonability of fuel–air mixtures is characterized in terms of detonability limits and ignition sources.

There has been some debate about the existence of detonation limits separate from flammability limits, as illustrated in the following comment by Burgess *et al.* (1968 BM RI 7196): 'A consensus has gradually developed that almost any gas mixture that is flammable is also detonable if initiated with a sufficiently strong ignition source'. However, the existence of separate detonability limits is now recognized.

Compilations of data on the flammability of fuels generally do not include detonation limits, although a considerable amount of data are available scattered in the literature.

There are certain features which cast a degree of uncertainty over detonation limits. One is the phenomenon of cool flames. Another is the existence of compounds which are capable of detonation in the absence of an oxidant. Further, a distinction is made in respect of detonation between confined and unconfined situations. Separate detonation limits are quoted for these two situations.

For detonation limits for confined situations measurements are made in tubes. Accounts of such work include those of Michels, Munday and Ubbelohde (1970) and Borisov and Loban (1977). The measurement of detonation limits in unconfined gas clouds is more difficult.

Features of such work have included the use of a containment such as a balloon, a very high energy ignition source and oxygen-enriched mixtures, the results being extrapolated back to the composition of air. Work in this area has been described by Benedick, Kennedy and Morosin (1970) and D. C. Bull, Elsworth and Hooper (1979a,b).

Table 17.5 from Nettleton (1980b) gives detonation limits for a number of fuels in air for confined and unconfined situations. The author's original table gives limits for a large number of compounds and also the limits for mixtures with oxygen. In general, the detonation limits of a particular fuel are narrower than its flammability limits, with the exception of compounds which can detonate in the absence of an oxidant.

There are a number of compounds which can detonate in the absence of an oxidant. One such substance is gaseous acetylene, and extensive precautions are necessary when handling it industrially. Other self-decomposing chemicals include ethylene at pressures in excess of 7 MPa, hydrogen peroxide and ozone. Information on such compounds is given by Bretherick (1985).

Nettleton suggests that any self-decomposing compound should be considered as possibly capable of detonation, but also adds that there is no well-established example of unconfined detonation of a self-decomposing substance.

In view of the relative paucity of data on detonation limits, it is attractive to be able to derive them from the flammability limits. Some correlations have been given by Nettleton (1987, p. 77) for both confined and unconfined detonations. For a number of fuels, which include alkanes and alkenes, he gives the following relations for the lower and upper limits of detonation in a confined situation. Define ϕ as the fuel–air ratio and the subscripts l, st and u to denote the lower limit, stoichiometric and upper limit, respectively. For mixtures with air

$$\log_{10}\phi_{\mathrm{l}} = 1.08\log_{10}\phi_{\mathrm{st}} - 0.84 \qquad [17.2.44]$$

$$\log_{10}\phi_{\mathrm{u}} = 1.06\log_{10}\phi_{\mathrm{st}} + 0.64 \qquad [17.2.45]$$

and for mixtures with oxygen

$$\log_{10}\phi_{\mathrm{l}} = 0.60\log_{10}\phi_{\mathrm{st}} - 0.78 \qquad [17.2.46]$$

$$\log_{10}\phi_{\mathrm{u}} = 1.13\log_{10}\phi_{\mathrm{st}} - 0.56 \qquad [17.2.47]$$

The stoichiometric mixture is defined in terms of water and carbon dioxide as the products. For unconfined situations there is a single correlation for mixtures with air or with oxygen. This is

$$\log_{10}\phi_{\mathrm{l}} = 0.51\log_{10}\phi_{\mathrm{st}} - 0.81 \qquad [17.2.48]$$

$$\log_{10}\phi_{\mathrm{u}} = 1.17\log_{10}\phi_{\mathrm{st}} + 0.60 \qquad [17.2.49]$$

These correlations do not apply to acetylene, for which the detonation limits are wider. Another approach to the

Table 17.5 *Some data on detonation limits in mixtures with air for confined and unconfined situations (after Nettleton, 1980b) (Courtesy of Fire Prevention Science and Technology)*

Compound	*Detonation limits* (%)				*Flammability limits* (%)	
	Confined tube		*Unconfined*		*Lower*	*Upper*
	Lower	*Upper*	*Lower*	*Upper*		
C_2H_6	2.87	12.20	4.0	9.2	3.0	12.4
C_3H_8	2.57	7.37	3.0	7.0	2.1	9.5
C_4H_{10}	1.98	6.18	2.5	5.2	1.8	8.4
n-C_8H_{18}	1.45	2.85			0.95	
C_2H_4	3.32	14.70			2.70	36.0
C_3H_6	3.55	10.40	3.5	8.5	2.4	11.0
C_2H_2	4.20	50.0			2.5	80.0
C_6H_6	1.60	5.55			1.3	7.9
C_2H_5OH	5.1	9.8			3.3	19.0
H_2	18.3	58.9			4.0	75.0

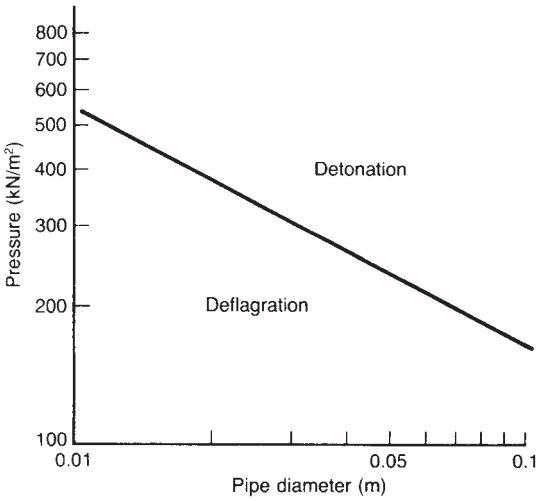

Figure 17.3 *Effect of pipe diameter and pressure on detonability of pure acetylene (after Sargent, 1957)*

prediction of detonation limits is in terms of homologous series.

There is relatively little information available on the influence of initial pressure and initial temperature on detonation limits, in confined situations. The general effect of an increase in initial pressure is to widen the detonation limits, and the same applies to an increase in initial temperature. The widening is more marked for the upper limit.

For acetylene, however, there exists a good deal of information on the effect of initial pressure. For this gas there is a pipe diameter below which only deflagration occurs, but above which detonation is possible, and this diameter is a function of the initial pressure. The correlation for this, which has been widely used in plant design, is shown in Figure 17.3. There is less information on the effect of initial temperature on acetylene, but at temperatures much in excess of 100°C there are likely to be present decomposition products which will affect the detonation limits.

The influence of additives, whether inert gases such as nitrogen or chemically active additives such as halohydrocarbons, presents a complex picture. The general effect of a diluent such as nitrogen is to narrow the detonation limits, particularly the upper limit. The amount of diluent required to suppress detonation tends to be large, but falls off sharply for mixtures close to the detonation limits. With regard to chemically active additives, the action of such additives may be rather specific, and there is some evidence, for example, that an additive effective as a fire extinguishant may not suppress a detonation.

The foregoing account has been concerned with the limits of detonation. However, whereas a mixture close to stoichiometric is, comparatively, readily detonable, one at the limits of detonation is only marginally detonable.

17.2.13 Initiation of detonation waves

The modes of initiation of a detonation differ somewhat from the modes of initiation of a deflagration. In both cases the process may be initiated by a suitable ignition source, but in the case of detonation other important mechanisms to be considered are initiation of a detonation by shock waves and acceleration of a deflagrative combustion into a detonation. It is also necessary to consider the distinction already made between confined and unconfined situations.

A further relevant distinction is that between readily detonable and marginally detonable mixtures. It is by no means clear that the mechanisms of detonation in readily detonable media are those operating in marginally detonable media.

In addition, there is some evidence that detonation may be a stochastic process (Terao, 1977).

In treating detonation by an ignition source, it is usual to speak of strong and weak sources. The terms are convenient but often not well defined. Nettleton (1987) treats as strong those ignition sources which produce a shock or blast wave of velocity greater than the CJ velocity, associated particularly with marginally detonable media and with unconfined systems. These strong ignition sources can range in strength from <10 J from sparks up to some 50 kJ from high explosives.

There is a considerable literature on the initiation of detonations in confined systems, but a large variety of methods have been used, and the interpretation of the findings is not straightforward. A greater degree of uniformity is now obtained by the adoption of standard methods, notably that of Zeldovitch and Kompaneets (1960). In this method a readily detonable mixture and a driving mixture are held in a tube separated by a diaphragm, which is removed seconds before detonation is initiated in the driving mixture. This technique allows the parameters of the driving mixture such as composition and initial pressure to be varied and the effect of the strength of the triggering wave to be investigated. The technique has been adapted to the study of unconfined detonations using an expansion nozzle.

Dealing first with initiation by ignition sources, for confined systems the quantity of interest is the minimum ignition energy for detonation. In principle, this is measured as a spark energy. However, data on this parameter are sparse and generally there is no alternative but to resort to the value of the regular minimum ignition energy (MIE), that for ignition of a flammable mixture.

A large amount of work has been done on initiation of detonation in unconfined vapour clouds by ignition sources such as sparks and high explosives. Here, the ignition energy for detonation is generally expressed as the critical energy E_c for a spherical detonation. The critical energy E_c varies with the concentration of the fuel and has a minimum value E_c^*.

Work on spark initiation of detonation of unconfined clouds has shown that, as in similar work on ignition of flammable mixtures, the results obtained depend on factors such as the spark gap width and efficiency and the rate of energy deposition.

With regard to the strength of the explosive ignition source necessary to induce detonation, work by Bach, Knystautas and Lee (1971) has shown that for direct initiation of spherical detonation waves the rate of deposition of energy into the gas is critical. Reviewing this work, Strehlow (1973b) suggests that charge geometry is probably very important and that this factor may account for the apparent discrepancies in the quantities of explosive required to initiate detonation in the work which he quotes.

In considering the initiation of detonation in an unconfined cloud, the mechanism by which this occurs is of some

relevance. It is now believed that when initiation occurs by a source with relatively low energy such as an electrical spark or 10 g of high explosive, the velocity of the initial blast wave decays below the CJ value before significant chemical reaction occurs in the flow, and there may be a propagation as quasi-steady-state velocity before acceleration sets in again and leads to detonation. For the size of charge quoted, the distance over which this overall process occurs is of the order of 10 cm. For larger charges the distance is correspondingly greater, and may thus be appreciable.

Critical energies for initiation of spherical detonation have been obtained by a number of workers. Reviewing these, Nettleton (1987) quotes in particular data given by Carlson (1973) for mixtures of fuel and oxygen. The fuel concentrations in the most readily detonable mixtures lie in the range 20–40% and the values of the critical energy E_c obtained range over two orders of magnitude from <0.11 J for acetylene to 12.5 J for acetaldehyde. He comments that the chemical nature of the fuel strongly influences detonability but that the effect is more complex than one of simple bond strength.

The critical energy E_c for detonation in a spherical cloud is related to the critical diameter d_c for transmission of a detonation from a tube across an abrupt enlargement of area as described below. The determination of d_c therefore provides a means of estimating E_c. Matsui and Lee (1979) use the relation

$$E_c = \frac{\pi p_D u_D}{24 C_D} d_c^3 \qquad [17.2.50]$$

where a is the velocity of sound, p is the absolute pressure and u is the particle velocity and the subscript D denotes the detonation, or CJ, state.

These authors also give a detonation hazard parameter D_H, which they define as

$$D_H = \frac{E_c^*(\text{fuel})}{E_c^*(\text{acetylene})} \qquad [17.2.51]$$

where E_c^* is the minimum critical energy determined.

Work on the critical energy for detonation of fuel–air mixtures using high explosives has been described by D.C. Bull, Elsworth and Hooper (1979a). Figure 17.4 shows their results for the initiation of detonation in mixtures of ethane and air using charges of tetryl. As the graph shows, the mass m of explosive required to give initiation increases rapidly as the ratio of fuel concentration to stoichiometric ratio ϕ diverges from the value for minimum critical energy.

A second mode of initiation of detonation in confined systems is by shock waves. This is amenable to study in shock tubes, and is thus a relatively well-defined situation and has been widely investigated. A shock wave entering a flammable mixture compresses and heats it, typically creating hot spots. The mechanisms involved in the transition to detonation have been elucidated by Oppenheim and coworkers (Urtiew and Oppenheim, 1966, 1968; Lundstrom and Oppenheim, 1969), who found that intense reaction occurs in the highly turbulent region between the leading shock front and the flame, in effect an 'explosion within an explosion', so that the compression fronts created overtake and merge with the leading front, forming a detonation wave.

The third mode of initiation is acceleration of deflagration up to detonation, or 'run up'. Consideration is given first to the general phenomenon and then to run-up distances in confined and unconfined situations.

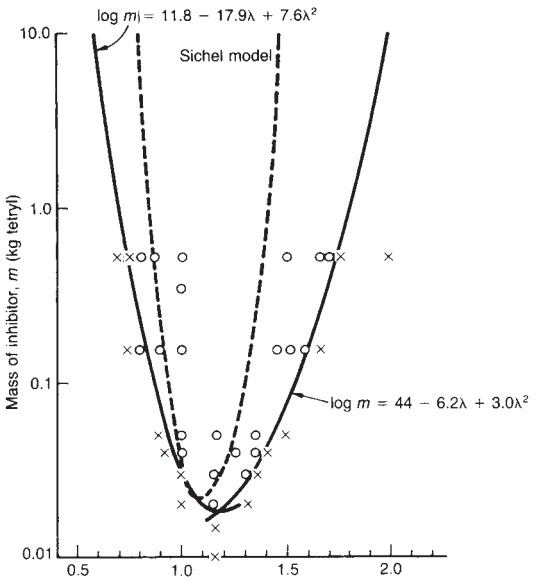

Figure 17.4 *Energy for initiation of explosion in ethane–air mixtures (D.C. Bull, Elsworth and Hooper, 1979a) (Courtesy of the Combustion Institute)*

17.2.14 Deflagration to detonation transition

The deflagration to detonation transition (DDT) has been the subject of a considerable amount of work.

Considering first conditions in confined systems, elucidation of the mechanisms of the DDT in tubes owes much to the work of Oppenheim and co-workers. Accounts include those of Laderman, Urtiew and Oppenheim (1963), Urtiew and Oppenheim (1965, 1966, 1967) and Lundstrom and Oppenheim (1969).

If a flammable mixture is ignited at the open end of a pipe with the other end closed and if the pipe is of sufficiently small diameter for the flow of the unburned gas to be stabilized by viscous drag at the wall, the flame does not accelerate. Outside this laminar steady-state regime, however, the propagation of the flame is always self-accelerating.

The flame acceleration is caused by a number of factors. As the flame moves down the pipe, the turbulent boundary layer grows until it occupies the whole cross-section of the pipe, so that there is a growth in turbulence. As the flame elongates, there is an increase in flame area. The flame creates pressure waves. There is precompression and preheating of the unburned gas ahead of the flame. Shock waves form and a turbulent flame brush is created. At some point, burnout of this turbulent flame brush occurs which intensifies the shock waves. These processes can be sufficient to cause the shock waves to coalesce and form a shock front and for this then to escalate into a detonation.

Another mechanism which can cause the DDT is the impact of a shock wave on the accelerating flame. Studies have been conducted by Markstein (1957) on the effect of the impact of a shock wave meeting a laminar flame head-on. These showed that a rarefaction wave travelled back

through the unburned gas and a jet of unburned gas developed which penetrated deeply into the burned gas. The shear between the burned and unburned gas resulted in extreme turbulence and a massive increase in the burning rate. Such an effect may occur when a shock wave travels ahead of the flame and is then reflected back into it.

The sequence of events in the DDT is summarized by Kuo (1986) as follows: (1) an accelerating laminar flame, with flame wrinkling and compression waves; (2) formation of a shock front; (3) creation of a turbulent flame brush; (4) onset of an explosion within an explosion, with transverse waves; (5) development of a spherical shock behind the shock front; (6) interactions of the transverse waves with the shock front, retonation wave and reaction zone and (7) establishment of a steady wave, leading to a shock–deflagration ensemble, or detonation.

Kuo distinguishes four modes of transition, classified according to the location of the explosion within an explosion. Since generation of any particular pattern depends on minute inhomogeneities, the detailed sequence of events in the DDT is not reproducible.

17.2.15 Run-up distances in confined situations

There is a good deal of information on run-up distances for particular mixtures and pipes, but a general correlation has been lacking.

An attempt to remedy this deficiency has been made by Nettleton (1987, p. 119), in terms of the distance X_s between the origin of the flame and the position at which shock is produced. He gives for this

$$X_s = \beta(\gamma + 1)X_f \qquad [17.2.52]$$

with

$$X_f = \frac{2c^2}{(\gamma + 1)^2 \beta^2 g_f} \qquad [17.2.53]$$

$$g_f = f(\varepsilon S_u) \qquad [17.2.54]$$

where c is the speed of sound in the uncompressed gas, g_f is the acceleration of the flame, S_u is the maximum fundamental burning velocity, X_f is the distance from the origin of the flame to its position at the time at which the shock first forms, X_s is the distance from the origin to the position at which the shock is produced, β is the ratio of the velocity of the flow just ahead of the flame to that of the flame, γ is the ratio of specific heats of the reactants and c is the expansion ratio. The value used for β is 0.9.

Nettleton gives a number of graphs comparing predictions of the distance X_s for shock formation with experimental values of the run-up distance X_d. The curves given by the model appear to have the general shape of, but do not always coincide with, the experimental ones. Specifically, the model predicts correctly the marked increase in run-up distance near the detonation limits.

It is suggested by Nettleton that if use is made of a run-up distance determined experimentally, this should be divided by a safety factor of 2 to allow for possible differences between the pipe used in the experiments and that on the plant. With regard to the factors which influence the run-up distance, one of the most important is pipe diameter. Here, there are a number of features which influence run-up but which vary with diameter. Thus, for example, in larger pipes the effect of viscous drag will be less but the surface roughness may be greater. It is clear from experiments that the run-up distance increases as the diameter increases, but the precise form of the relationship obtained varies. Nettleton quotes three sets of results, one in pipes of diameter $d \leq 102$ mm showing $X_d \propto d^{0.44}$, one in pipes of $d \leq 51$ mm showing $X_d \propto d^{0.5}$ and one with $X_d \propto d^{1.25}$, but states that there is general agreement that for large pipes $X_d \propto d$.

Another factor which affects the run-up distance is the surface roughness of the pipe. Essentially, any feature which promotes turbulence will tend to reduce the run-up distance. Such features include internal welds and bellows.

There is relatively little information available on the influence on run-up distances of initial pressure, initial temperature or additives. However, evidence confirms that run-up distance decreases with increasing pressure with $X_d \propto pm$ where $-0.4 < m < -0.8$ except for materials that decompose in the absence of oxygen.

Attention is drawn by Nettleton to the fact that where pressure piling may occur, the probability of occurrence increases with the induction distance.

17.2.16 Run-up distances in unconfined situations

Turning now to acceleration of deflagration to detonation in unconfined systems, it is appropriate at this juncture to point out that the occurrence of a detonation in a vapour cloud which is truly unconfined has been a matter of some debate. The nature of, and models for, vapour cloud explosions are discussed in Section 17.28. Here, consideration is confined to the process of flame acceleration in the cloud. This is closely linked to the question of the minimum size of cloud for a detonation to occur.

A model for the direct formation of a spherical detonation has been given by J.H.S. Lee and Moen (1980). This is the shock wave amplified coherent energy release (SWACER). The energy from the ignition source is assumed to create a gradient of temperature and of active species such that as the wave expands, each successive shell has a different induction time. Where there exists a suitable relation between this gradient and that of the decaying blast, the reaction zone couples to the leading front and a detonation wave forms.

There are certain features of combustion in a vapour cloud in the open which have been identified as possibly capable of promoting flame acceleration. One is heat radiation from the burning part of the cloud. It has been shown experimentally that heat flux can be such as to heat up incombustible particles ahead of the flame front so that they become ignition sources. Another is inhomogeneities in the cloud.

More importantly the interaction of flame fronts with plant structure is widely recognized as the key factor in flame acceleration to destructive deflagrations or detonations. This is treated in Section 17.2.19. It is also of interest to know whether there is a minimum diameter d_{min} of a vapour cloud to support a detonation. Nettleton (1987) states that experience of deflagration in vapour clouds indicates that $d_{min} \geq 50$ m.

Moen, Donate *et al.* (1981), in work directed to the measurement of detonation limits, have studied the effect of tube diameter on the fuel concentration at the limit of detonability, which they take as the occurrence of single-head spin. They give results showing for ethylene–air mixtures the variation of the tube diameter for the transition from multiheaded detonation to single-head spin. They take the

cell length L_c as proportional to the tube diameter, and express the correlation in terms of cell length also.

They then equate the above diameter to the critical diameter d_c and propose that this be taken as an indication of the minimum cloud diameter d_{min} for detonation. Thus for the stoichiometric concentration of 6.5% ethylene, they obtain $L_c = 46$ mm and, using Equations 17.2.37 and 17.2.42a, $S = 28$ mm and $d_c = 359$ mm $= 0.36$ m. Similarly for a 3% concentration they obtain $L_c = 0.9$ m, $S = 0.54$ m and $d_c = 7$ m.

17.2.17 Interaction between detonation and confinement

The foregoing has given an account of the general behaviour of detonations, essentially in tubes. It is now necessary to consider the interaction of a detonation wave with confinements in general.

There is no comprehensive theory for the interaction of a detonation wave with a confinement of arbitrary geometry. It is possible that a deterministic theory may be precluded by the stochastic properties already referred to.

The pressure profiles occurring in confined detonations have a number of characteristic features. The pressures generated exhibit wide variations in magnitude and duration. Anomalously high pressures can be generated by reinitiation of combustion in previously quenched regions of the gas.

Treatments of the interaction between a detonation wave and its confinement are mainly for non-reactive shock waves. Two principal theoretical descriptions are the two-shock theory and the method based on the work of Chester (1954), Chisnell (1957) and Whitham (1974), known as Chester–Chisnell–Whitham (CCW) analysis.

In general, theory in its current state is not able to predict peak local pressures or pressures on confining surfaces, but is helpful in understanding how interaction with confinements can result in fronts with properties different from those predicted by unidimensional models.

Models of a number of standard cases occurring with a confined detonation wave are treated by Nettleton (1987), using mainly CCW theory. These cases include (1) diffraction of a shock wave at an isolated wall, (2) normal reflection of a shock wave, (3) transmission of a detonation wave through an abrupt expansion and (4) propagation of a detonation through a bend or junction.

For diffraction at an isolated wall, the situation considered is a shock wave travelling parallel to a horizontal surface and then encountering another surface, or wall, at an angle θ_w to the horizontal. At some critical angle θ_{cr} there occurs transition to regular reflection. Three cases are treated: case 1, a wall at a negative angle with $\theta_w < 0$; case 2, a wall at a positive angle less than the critical, hence $0 < \theta_w < \theta_{cr}$, and case 3, a wall at a positive angle greater than critical but less than perpendicular, hence $\theta_{cr} < \theta_w < 90°$.

Normal reflection of a detonation wave may occur in various configurations. These include reflection at a sharp 90° bend and at the wall of a spherical vessel. Essentially, the situation is that the use of unidimensional theory tends to overpredict the pressures generated, but that multidimensional theory is difficult to apply.

The transmission of a detonation wave through an abrupt expansion is a case of some importance. It constitutes a symmetrical, and therefore relatively simple, instance of a change from a planar front to a curved one and involves progression of the detonation from the pipe into a hemispherical detonation. It is therefore relevant to the critical diameter d_c of the pipe for the establishment of a hemispherical detonation and thus to the quenching of detonations and to the critical energy for the initiation of hemispherical detonations.

Nettleton gives a treatment of this case involving a combination of CCW analysis and Shchelkin (1959) instability theory.

He also describes a number of theoretical approaches to the derivation of a relation between the critical diameter d_c for quenching and the critical energy E_c for spherical detonation. Sloan and Nettleton (1975) have studied the case of a planar non-reactive shock wave emerging from a nozzle into a large space. Within the decaying shock envelope there exists a truncated cone, the front edge of which is travelling at the velocity of the incident front and which does work on the surrounding gas. A similar situation pertains for a detonation emerging from the nozzle. This case has been treated by Urtiew and Tarver (1981), who equate the work done with the critical energy. The work done W is

$$W = \int_0^{t_c} p u_{CJ} A_t \, dt \qquad [17.2.55]$$

where A_t is the area of truncation, p the pressure of the planar detonation, t_c the time at which the heads of the expansion fan cross the axis of symmetry and u_{CJ} the gas velocity behind the CJ front. But

$$t_c = \frac{L_c}{S} \frac{(d_c - d_o)/2}{D_{CJ}} \qquad [17.2.56]$$

where d is a diameter of the nozzle, D_{CJ} is the CJ velocity, L_c is the length of a detonation cell, S is the width of the cell and the subscripts c and o denote critical and actual, respectively. Then, integrating Equation 17.2.55 using Equation 17.2.56 and noting that for spherical symmetry $E_c = 2W$

$$E_c = \frac{\pi p_{CJ} u_{CJ}}{4 D_{CJ}} \frac{L_c}{S} \left(\frac{d_c}{d_o} - 1 \right)^3 \qquad [17.2.57]$$

Equation 17.2.57 gives a relationship between the critical diameter d_c and the critical energy E_c. It has been shown by Nettleton (1987) that the equation gives a good fit to the data for mixtures of hydrocarbons with air and with oxygen obtained by Matsui and Lee (1979).

The propagation of a detonation through a bend is another case which is important but which has received rather less attention. There has been some success with CCW analysis of the early stages of the propagation of non-reactive shock waves round the bend, but rather less in the later stages as the process becomes more complicated due to interactions of wave systems set up at opposing walls.

Where the shock wave is in a reactive medium, the situation is yet more complex. Experimental work on detonation entering bends by Edwards, Nettleton and coworkers (D.H. Edwards *et al.*, 1981; D.H. Edwards, Thomas and Nettleton, 1983) has shown that steady detonation is re-established, but the distances at which re-establishment occurs and the locations of pressures higher than the CJ pressure depend on the configuration. Figure 17.5 by D.H. Edwards *et al.* (1981) shows a sketch

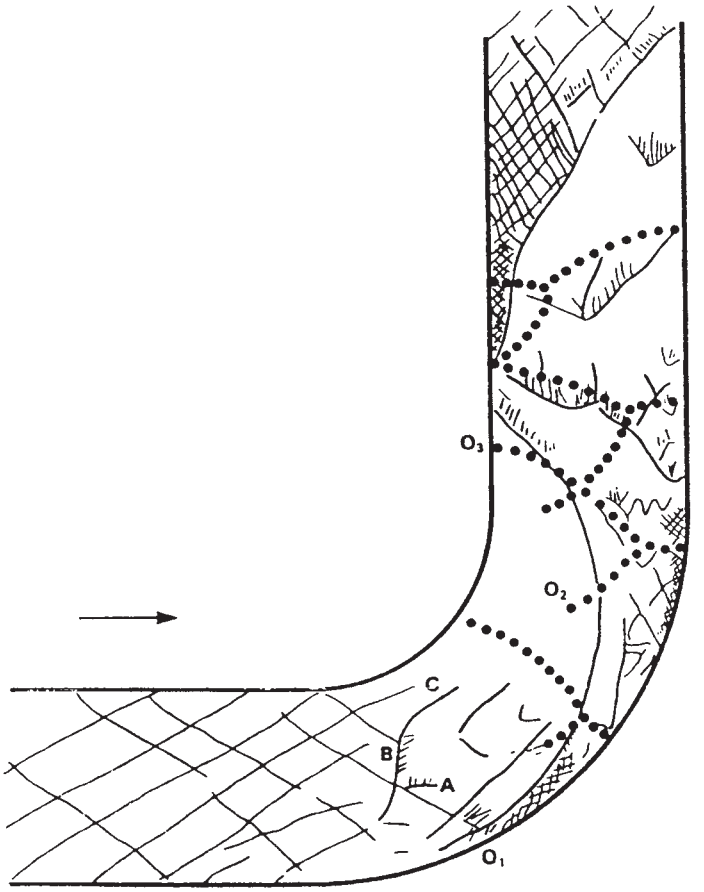

Figure 17.5 *Sketch of a smoke foil record of re-establishment of detonation in a sharp bend (D. H. Edwards et al., 1981). Steady front formed some diameters downstream of bend, following reflection of triple point, trajectory $O_1O_2O_3$ at inner wait . . . , shock profile in reactive medium (Courtesy of Archivum Combustions)*

from this work of a smoke-foil record of the re-establishment of a detonation in a sharp bend.

The patterns on, and damage to, the inner surface of such bends are characteristic, and thus in incident investigation may provide evidence of the occurrence of a detonation.

In addition to the interaction of a detonation wave with a confining envelope, the detonation wave may also interact with an adjacent gaseous medium. Some situations of interest are those where the adjacent medium is (1) an inert gas, (2) a gas mixture of uniformly decreasing concentration and (3) a gas mixture with concentration variations. The first case is relevant to any use of devices containing inert gas for the suppression of detonations. The other two cases have relevance to possible detonations in vapour clouds, which will in general have both concentration gradients and pockets of high and low concentration. Nettleton (1987) gives an account of some research findings which bear on these phenomena.

In the absence of an adequate treatment of the interaction between the detonation wave and its confinement, the common practice of comparing predicted pressures and static strength is likely to continue.

17.2.18 Damage caused by detonation to confinement

The treatment of the damage caused by detonations differs depending on whether the detonation is confined or unconfined. The effects of explosions in the open, whether fast deflagrations or detonations, are considered in Sections 17.31–17.42. The account here is limited to confined detonations.

The general effects of confined detonations are evident from the explosions which have occurred inside plant over the years. A review has been given by Strehlow and Baker (1976). Accounts of some of these incidents are given in Appendix 1.

One classic case is the explosion at Whiting, Indiana, in 1955 described by Jacobs *et al.* (1957) and Randall *et al.* (1957) (Case History A22).

Generally, the amount of information which can be gleaned from an incident of detonation inside plant is limited, because crucial items of data are missing.

Two general points on damage caused by detonations may be noted. One is that the evidence indicates that the damage done by a dynamic loading is no greater than that which would be expected from the corresponding static

loading. The other is that ductility appears to have little effect on the dynamic bursting pressure.

The present state of knowledge does not permit a fundamental prediction of the damage to plant by a detonation occurring in it. As already described, there is no comprehensive theory to support the reliable estimation of the pressures generated in complex plant. Further, understanding of the mechanisms and modes of damage caused by confined detonations is imperfect.

Some general guidance is provided by the work which has been done to determine the effective pressures generated in a detonation. C. Campbell, Littler and Whitworth (1932) carried out experiments in which a copper disc at the end of a tube was sheared by a detonation in the tube. They found that the pressure at which failure occurred was close to the CJ pressure. In other words, it was less than the pressure spike and still less than the reflected pressure.

Approaches to the prediction of the pressures occurring in a detonation have been described above. Then, given an estimate of this pressure, an attempt may be made to estimate the damage either from theoretical models or experimental correlations.

It can be shown that the force exerted by a suddenly applied load of a duration much longer than the time constant of the object impacted can be up to twice that produced by the corresponding load slowly applied. This provides a general theoretical indication of the force which a detonation may be expected to exert.

The behaviour of the wall of a pipe as a detonation passes along it has been modelled in terms of the acceleration, velocity and deformation, both elastic and plastic, of the wall. Some simplified models are given by Nettleton (1987), drawing on work such as that of Randall and Ginsburgh (1961) and de Malherbe *et al.* (1966).

17.2.19 Effect of congestion on explosions

The effect of turbulence and turbulence-generating obstacles and structure can be a dominant factor in determining the flame speed and peak overpressure in a deflagration. Rasbash *et al.* (1976e) suggest that for indoor explosions, the turbulent flame speed is typically 1.5–5 times the laminar flame speed. For enclosures of a room or laboratory size, where turbulence is developed by furniture or similar objects, they suggest a factor of 1.5. For large enclosures where explosions propagate through large openings connecting parts of the structure, a factor of 5 is likely and appropriate. With a high-pressure jet discharging indoors, the authors advise that a turbulence factor might be as high as 8 or 10.

For outdoor or partially confined deflagrations, empirical estimation methods developed by Baker *et al.* (1994, 1997) and the multienergy method by van den Berg (1985) and van Wingerdon *et al.* (1989) apply a similar factor to account for congestion. These factors range over three orders of magnitude to predict the peak overpressure. Risk-planning studies usually incorporate a detailed determination of the congestion and turbulence-inducing structure in a plant setting. These effects are discussed further in Section 17.28.4.

17.3 Explosives

Although the properties, manufacture, handling, storage and transport of high explosives are outside the scope of this book, it is necessary to make some brief mention of them.

Accounts of explosives are given in *Explosives, Their Anatomy and Destructiveness* (C.S. Robinson, 1944), *The Science of High Explosives* (M.A. Cook, 1958), *Prevention of and Protection against Accidental Explosion of Fuel and Other Hazardous Mixtures* (E. Cohen, 1968) and *Detonics of High Explosives* (Johansson and Persson, 1970).

Explosives are relevant to loss prevention in two areas in particular. These are (1) estimation of effects of explosions and (2) control of manufacture, handling, storage and transport of explosive materials.

Many of the data available on explosions and their effects and many of the methods of estimating these effects relate to explosives. In particular, the methods developed for calculating the effects of explosions are based mainly on the high explosive trinitrotoluene (TNT).

The hazard of explosives has long been recognized, and an approach has been developed for their control. Some aspects of this approach are applicable in the chemical industry also.

Selected references on explosives are given in Table 17.6.

Table 17.6 *Selected references on explosives*

MoD, ESTC (n.d.); Upmann (1878); Berthelot (1892); Assheton (1930); Thomson (1941); Read (1942); T.L. Davis (1943); M. Meyer (1943); Lothrop and Handrick (1949); E. Fisher (1950, 1953a,b); Jarrett (1952, 1968); J. Taylor (1952); H. Watts (1954); Johansson, Persson and Selberg (1957); M.A. Cook (1958, 1960); Home Office (1958/7, 1972/3); Tomlinson (1958); US Army, Ordnance Corps (1958, 1960); Federoff (1960); ICI (1961); Deb, Evans and Yoffe (1962); M.H. Friedman (1963a,b); Langefors and Kihlstrom (1963); Urbanski (1964–, 1983); Freytag (1965); Lenz (1965); D. Levine and Boyars (1965); D. Price and Wehner (1965); Fordham (1966, 1980); Gould (1966); Ornellas, Carpenter and Gunn (1966); Department of the Army (1967); Ornellas (1967, 1968); R.F. Fletcher (1968); Kamlet and Jacobs (1968); Napadensky (1968); Roylance (1968); W.I. Taylor (1968); Wieberson *et al.* (1968); Dremin (1969); Fauquignon and Cheret (1969); Johansson and Persson (1970); Porzel (1972, 1974, 1980); R. Meyer (1973, 1977); Woolfolk and Ablow (1973); Darling (1974); Filler (1974); Lovold (1974); Sablon (1976); R.L. Allen (1977a); Gregory (1977); C.M. Anderson and Pakulak (1978); HSE (1978b); Medard (1979); Dupont Co. (1980); Short *et al.* (1981); Kuo and Summerfeld (1983); Urbanski (1983); C. Tayler (1986a); Yinon and Zitrin (1987); Ijsselstein and van Steen (1988); J.H. Johnson et al. (1988); Doherty *et al.* (1989); Ho and Fong (1989); Ho, Fong and Hamshere (1989); E. Meyer (1989); de Yong and Campanella (1989); Meyers and Shanley (1990); Moran (1992); NFPA (1992 NFPA 495); Twisdale *et al.* (1992); P.A. Davies (1993); Kohler (1993)

Initiation of explosives

Bowden (1949, 1953); Bowden, Stoke and Tudor (1947); Bowden *et al.* (1947); Bowden and Yoffe (1949, 1952, 1958); A.J.B. Robertson (1949); Kistiakowsky (1949); Bowden and Tabor (1954); Bowden and Thomas (1954); Johansson, Persson and Selberg (1957); Johansson, Lundborg and Sjolin (1962); Rindner (1968); Chaudhri (1976); Berger (1977); W.H. Andersen (1979); Bauer (1982); Bless (1982);

Erikson (1982); Nellis, Seaman and Graham (1982); Vantine, Chan and Erickson (1982); Vorthman (1982); Ho (1992); P.A. Davies (1993); Raha and Chhabra (1993)
Sympathetic detonation: van Dolah (1966 BM RI 6903)

Explosives testing (*see* Table 8.1)
Fireballs from explosives: Jarrett (1952); Gayle and Bransford (1965); Rakackzy (1975); Stull (1977); Kovar *et al.* (1982); W.E. Baker *et al.* (1983); Gilbert, Lees and Scffly (1994e)
Fireballs from nuclear weapons: Glasstone (1962); Telleref Z. (1968); Ramsey (1983)

Munitions, weapons
MoD, ESTC (n.d); Rohne (1895); Gurney (1943, 1944, 1946); Christopherson (1946); Mott (1947); Dunn and Stern (1952); E. Fisher (1953); Tomlinson (1958); G.I. Taylor (1963a,b); Lenz (1965); Pollard and Arnold (1966); Department of the Army (1967); I.G. Henry (1967); Held (1968, 1979, 1990, 1991); Roylance (1968); Draper and Watson (1970); Filler (1974); Karpp and Predebon (1974); SIPRI (1978); Kamlet and Finger (1979); G.E. Jones, Kennedy and Bertholf (1980); Grady (1982a,b); C.E. Anderson, Predebon and Karpp (1985); E. Hirsch (1986); Massa (1987); McCleskey (1988a–c, 1992); Burman (1989); Helwig, Klee and Hubner (1989); Jagusch (1989); Naz (1989)

17.3.1 Explosions of high explosives

In an explosion caused by a high explosive the rate of energy release is particularly rapid, and the explosion has high shattering power, or 'brisance'.

A high explosive produces, therefore, a quite distinct type of explosion. The shock wave from such an explosion has a very short duration time. Differences in the types of explosion are a weakness in the application of correlations based on explosions of high explosives to other explosion situations.

Nevertheless, the TNT equivalent model is widely used in explosion calculations for estimating the effects of explosion on process plant.

17.3.2 Scaling laws

The effects of the explosion of a high explosive are generally determined using a scaling law. A principal parameter which characterizes an explosion is its overpressure. The overpressure generated by the explosion of a explosive is discussed in detail in Section 17.25. It is shown there that overpressure p^o is a function of scaled distance z.

$$p^o = f(z) \qquad [17.3.1]$$

with

$$z = \frac{r}{W^{1/3}} \qquad [17.3.2]$$

where p^o is the peak overpressure, r is the distance, W is the mass of explosive and z is the scaled distance. Equation 17.3.2 implies that for a given overpressure the distance is related to the mass of explosive by a cube root law:

$$r \propto W^{1/3} \qquad [17.3.3]$$

Damage done by the explosion of an explosive has been correlated mainly by insurance companies in terms of damage circles within which defined degrees of damage occur. The radius R of such a damage circle is related to the mass W of explosive approximately by a cube root law:

$$R \propto W^{1/3} \qquad [17.3.4]$$

Another effect of an explosion of a high explosive is the formation of a crater. A cube root law applies to the relation between the radius r_c of the crater and the mass W of explosive:

$$r_c \propto W^{1/3} \qquad [17.3.5]$$

In the storage of explosives the limit of distance between one store of explosive and the next is set by the risk of sympathetic detonation. A mean detonation distance r_{50} can be defined at which there is a 50% chance of sympathetic detonation occurring. It is found that this mean detonation distance 750 is also related to the mass W of explosive by a cube root law:

$$r_{50} \propto W^{1/3} \qquad [17.3.6]$$

17.3.3 Housing damage

A scaling relation for blast damage to housing has been given by Jarrett (1968):

$$R = \frac{kW^{1/3}}{\left[1 + \left(\frac{7000}{W}\right)^2\right]} \qquad [17.3.7]$$

where R is the distance (ft), W the mass of explosive (lb) and k a constant. The constant k defines the degree of damage which may be expected to the average British dwelling house. It is based on the analysis of damage in 24 well-documented explosions and in wartime bombing. The following categories of damage are defined:

		k
A	Almost complete demolition	9.5
B	50–75% external brickwork destroyed or rendered unsafe and requiring demolition	14
Cb	Houses uninhabitable – partial or total collapse of roof, partial demolition of one or two external walls, severe damage to Load-bearing partitions requiring replacement	24
Ca	Not exceeding minor structural damage, and partitions and joinerywrenched from fittings	70
D	Remaining inhabitable after repair – some damage to ceilings and tiling, more than 10% window glass broken	140

For damage to process buildings, the Center for Chemical Process Safety (CCPS) of the American Institute of Chemical Engineers (AIChE) defines the following levels (1996).

Level	*Building Damage*
1 Minor	Onset of visible damage. Repairs are only needed for cosmetic reasons. Building is reusable following an explosion
2A Moderate	Localized building damage. Building performs function and can be used: however, major repairs are required to restore integrity of structural envelope. Total cost of repairs is moderate
2B Moderate	Widespread building damage. Building cannot be used until major repairs are completed. Total cost of repairs is significant, approaching replacement cost of building
3 Major	Building has lost structural integrity and may collapse due to environmental conditions (i.e. wind, snow or rain). Total cost of repairs exceeds replacement cost of building
4 Collapse	Building fails completely. Repair is not feasible

17.3.4 Quantity–distance relations

In the handling of explosives separation distances are governed by quantity–distance relations. An account of the quantity–distance relations used in Britain has been given by Jarrett (1968).

The principal explosion effects of the different categories of explosive are:

Category X: missiles and slight blast effects, projected ammunition;
Category Y: radiant heat;
Category Z: missiles and major blast effects, cratering, earth shock;
Category ZZ: major blast effects, cratering, earth shock.

The quantity–distance relations are used for (1) storage distances, (2) process building distances, and (3) public building and traffic distances. The process building distances are also known as intraline distances.

The storage of explosives involves the hazard of explosion of the stored material. Explosives tend to be sensitive to shock. They also tend to deteriorate in storage. In particular, there is the hazard of sympathetic detonation of one store of explosives by another adjacent store.

Although sympathetic detonation is important, it is not the only explosion effect which has to be taken into account. Other effects include flame spread, heat radiation, missiles and blast. Jarrett quotes a number of quantity–distance relationships of the general form

$$R = kW^n \qquad [17.3.8]$$

where R is the distance, W is the mass of explosive, k is a constant and n is an index. The index n lies in the range $\frac{1}{3}$–$\frac{1}{2}$.

For storage distances for category Z explosive in shells filled with RDX/TNT explosive the basis of separation is sympathetic detonation. For this case Jarrett gives the relation

$$R = 12W^{1/3} \qquad [17.3.9]$$

where R is the distance (ft) and W the mass of explosive (lb).

For intraline and public buildings distances for category Y explosive the basis of separation is heat radiation. For these cases the relations given by Jarrett are, respectively,

$$R = 8W^{1/3} \qquad [17.3.10]$$

and

$$R = 3.2W^{1/2}, \quad W < 10{,}000 \qquad [17.3.11a]$$

$$R = 16W^{1/3}, \quad W > 10{,}000 \qquad [17.3.11b]$$

For intraline and public building distances for category Z explosive the basis of separation is blast effects. The relevant relation is Equation 17.3.7.

17.3.5 Sympathetic detonation

Explosives are normally stored in separate stacks with a separation distance between each stack so as to reduce the probability of detonation of one stack as a result of detonation of an adjacent one. The effect is known as sympathetic detonation.

A model for the propagation of an explosion by sympathetic detonation has been described by Masso and Rudd (1968). The blast effect B is assumed to be given by the relation

$$B = \frac{kW^{n_1}}{r^{n_2}} \qquad [17.3.12]$$

where B is the blast effect, r is the distance, W is the mass of explosive, k is a constant and n_1 and n_2 are indices. The probability p of further detonation of the pressure-sensitive material is taken as

$$p = B/B^* \qquad [17.3.13]$$

where B^* is the blast effect required for certainty of detonation. Then, a general model for propagation of detonation is

$$p = 0, \quad p' < T \qquad [17.3.14a]$$

$$p = p', \quad T < p' < 1 \qquad [17.3.14b]$$

$$p = 1, \quad \text{otherwise} \qquad [17.3.14c]$$

with

$$p' = \frac{kW^{n_1}}{B^* r^{n_2}} \qquad [17.3.15]$$

where T is the threshold of p′ below which no propagation occurs.

The simplest model described by the authors consists of a linear array of explosive components in n sites. The probability that the detonation reaches the jth site but does not continue to the $(j+1)$th site is as follows. The component of the initiating site detonates with certainty. The

probabilities of detonation of components in the second, third and jth sites are $p, p^2, \ldots, p^{j-1}$. If the component at the jth site has detonated, the probability that the component at the $(j+1)$th site does not detonate is $(1-p)$. This yields the following relation for $P(j)$, the probability that j sites are involved in the detonation chain:

$$P(j) = (1-p)p^{j-1}, \quad 1 \leq j \leq (n-1) \qquad [17.3.16a]$$

$$P(j) = p^{j-1}, \quad j = n \qquad [17.3.16b]$$

Various more complex models are also given by these authors.

17.3.6 Controls on explosives

The explosives industry has no choice but to exercise the most stringent controls to prevent explosions. Some of the basic principles which are applied in the management of hazards in the industry have been described by R.L. Allen (1977a). There is an emphasis on formal systems and procedures. Defects in the management system include:

> A defective management hierarchy... Inadequate establishments... Separation of responsibilities from authority, and inadequate delegation arrangements.... Inadequate design specifications or failures to meet or to sustain specifications for plants, materials and equipments.
>
> Inadequate operating procedures and standing orders.... Defective cataloguing and marking of equipment stores and spares....
>
> Failure to separate the inspection function from the production function....
>
> Poor inspection arrangements and inadequate powers of inspectorates....
>
> Production requirements being permitted to over-ride safety needs....

The measures necessary include:

> The philosophy for risk management must accord with the principle that, in spite of all precautions, accidents are inevitable. Hence the effects of a maximum credible accidents at one location must be constrained to avoid escalating consequences at neighbouring locations.... Siting of plants and processes must be satisfactory in relation to the maximum credible accident.... Inspectorates must have delegated authority – without reference to higher management echelons – to shut down hazardous operations following any failure pending thorough evaluation....
>
> No repairs or modifications to hazardous plants must be authorized unless all materials and methods employed comply with stated specifications.... Components crucial for safety must be designed so that malassembly during production or after maintenance and inspection is not possible....
>
> All faults, accidents and significant incidents must be recorded and fed back without fail or delay to the Inspectorate....

A fuller checklist is given by Allen.

R.L. Allen (1977b) also discusses the relevance of these principles to the chemical industry, and to Flixborough in particular. He suggests that the probability of such accidents can be greatly reduced if the chemical industry uses these well-proved methods. The principles are essentially those described elsewhere in this book.

In addition to these basic management aspects, the special precautions necessary in the manufacture and storage of explosives are instructive in relation to process plant hazards. Here, some basic principles are (1) minimization of inventory, (2) minimization of exposure, (3) use of blast walls and (4) separation by distance.

In explosives manufacture and storage the scale of the potential accident is reduced by minimizing the inventory of material and the number of people. The application of these concepts to process plant is discussed in Chapters 11 and 20.

Much use is made in the explosives industry of blast walls, cubicles and barricades. An account of their design has been given by Callahan (1968).

The only completely reliable protection with explosives, however, is distance. It is normal practice, therefore, to allow generous distances in both manufacture and storage. The principle of separation is applicable to process plant also, as described in Chapter 10, although it should be added that it does not necessarily follow that it is economically justifiable to require separation to be such as to give absolute protection.

There is much to learn from the explosives industry in managing the hazards on process plant, but, as always, methods developed for a similar, but not identical, problem need to be adapted to the needs of the process industries.

17.4 Explosion Energy

As already stated, an explosion is a sudden and violent release of energy. Discussions of explosion energy are given in the *High Pressure Safety Code* (B.C. Cox and Saville, 1975) and by Kinney (1962), Kinney and Graham (1985), Burgess *et al.* (1968 BM RI 7196), Eisenberg, Lynch and Breeding (1975), W.E. Baker *et al.* (1983), Crowl (1991, 1992a,c) and the (1994/15).

The energy released in an explosion on a process plant is normally one of the following: (1) chemical energy, (2) fluid expansion energy and/or (3) vessel strain energy.

The distribution of energy between the blast wave and missiles and any crater formation needs also to be considered as does the effect of the height above ground at which the explosion occurs.

17.4.1 Chemical energy

In considering the energy release in a chemical explosion, it is convenient to consider first condensed phase explosives, or high explosives, and then flammable gases and liquids.

The energy release in a chemical explosion is a function of the nature and state of the reactants and of the products. In general, the explosion products are not well defined. As the gas mixture cools, the chemical equilibrium shifts and the transient products disappear.

A condensed phase explosive contains its own oxygen so that it can explode even in the absence of air. It is conventional to assume certain nominal products of explosion. Explosives may be classified on the basis of nominal oxygen distribution. An oxygen-rich explosive has excess oxygen and the nominal products contain molecular oxygen and incombustible gases such as CO_2 and H_2O. An oxygen deficient explosive gives combustible gases such as CO and H_2 among the nominal products. The actual gases generated by explosives contain a mixture of all these products.

A flammable organic gas or vapour which explodes in excess air is normally assumed to yield incombustible gases such as CO_2 and H_2O. The same applies to a condensed phase explosive which undergoes combustion in excess air. Accurate distribution of products can be predicted using chemical equilibrium programs such as the one developed for rocket exhausts by NASA (McBride and Gordon, 1991).

The quantities which characterize a high explosive are discussed by Kinney and Graham (1985). Those of interest here are (1) the energy of explosion, (2) the heat of explosion and (3) the heat of combustion.

The energy in an explosion is of two different kinds: (1) thermal energy and (2) work energy. That part of the energy transferred due to temperature difference is termed the heat of explosion.

The differences between the heat of explosion, the energy of explosion and the heat of combustion may be explained by reference to the methods by which they are measured for an explosive, as described by Kinney and Graham. The heat of combustion is determined by causing the substance to burn in air in a bomb calorimeter and measuring the heat evolved.

The heat of explosion is determined in a similar manner, but using inert gas instead of air. The substance is placed in a bomb calorimeter, air is replaced with inert gas, the substance is initiated and the heat evolved is measured.

Measurement of the energy of explosion is carried out by encasing the substance in a heavy sheath of metallic gold. The explosion flings the gold casing against the bomb wall, where it gives up its kinetic energy as heat, so that in this case the heat measured now includes this energy as well as that transferred by temperature difference.

The relative magnitude of these quantities may be illustrated by considering the values for TNT as given by Kinney and Graham (1985): heat of combustion = 15,132 J/g, energy of explosion = 4850 J/g, heat of explosion = 2710 J/g.

The heat of explosion corresponds to the internal energy change for the explosion ΔE. In order to estimate the effects of an explosion it is necessary to know the energy of explosion. This is the work energy, or work. This work is done by the expansion of the gas and is given by

$$W = -\int_1^2 P \, \mathrm{d}V \qquad [17.4.1]$$

where P is the absolute pressure, V is the volume and W is the work of expansion. This is the energy transferred in the explosion as work done on the blast wave and missiles. The integral of Equation 17.4.1 is difficult to evaluate, and it is more convenient to work directly in terms of the initial and final values of the thermodynamic properties. The quantity generally used is the Helmholtz free energy change ΔA:

$$-\int_1^2 P \, \mathrm{d}V \approx \Delta A \qquad [17.4.2]$$

Treatments of the relationship between the work and the Helmholtz free energy change are given by Kiefer, Kinney and Stuart (1954) and W.J. Moore (1962).

The actual energy released in an explosion tends to be somewhat less than the Helmholtz free energy change. One reason is that the process is not reversible. Another is that the products of combustion of the explosion are usually at a temperature higher than ambient.

Often, data are not available on the Helmholtz free energy change for a compound, but are available for the Gibbs free energy change. For many substances, including hydrocarbons, the difference is not great and the error involved in using the Gibbs instead of the Helmholtz free energy is small.

The following thermodynamic relations, which apply to a reversible process at constant temperature and pressure, are useful in explosion calculations. For absolute quantities

$$H = E + PV \qquad [17.4.3]$$

$$A = E - TS \qquad [17.4.4]$$

For isothermal change in a system

$$\Delta H = \Delta E + \Delta(PV) \qquad [17.4.5]$$

$$\Delta A = \Delta E - T\Delta S \qquad [17.4.6]$$

$$\Delta F = \Delta H - T\Delta S \qquad [17.4.7]$$

where ΔA is the Helmholtz free energy change, ΔE is the internal energy change, ΔF is the Gibbs free energy change, ΔH is the enthalpy change, ΔS is the entropy change and T is the absolute temperature.

The energy of explosion is usually calculated at standard conditions of 25°C and atmospheric pressure.

The internal energy change for the explosion reaction is

$$\Delta E = \left(\Delta E_f^{\circ}\right)_{\mathrm{p}} - \left(\Delta E_f^{\circ}\right)_{\mathrm{r}} \qquad [17.4.8]$$

where the superscript o denotes the standard state and the subscript f the formation value, p the products and r the reactants. The enthalpy change for the reaction is

$$\Delta H = \left(\Delta H_f^{\circ}\right)_{\mathrm{p}} - \left(\Delta H_f^{\circ}\right)_{\mathrm{r}} \qquad [17.4.9]$$

The entropy change for the explosion reaction, or entropy of explosion, is

$$\Delta S = (S)_{\mathrm{p}} - (S)_{\mathrm{r}} \qquad [17.4.10]$$

The Helmholtz free energy change ΔA for the explosion reaction is given by Equation 17.4.6, or alternatively by

$$\Delta A = (\Delta A_f)_{\mathrm{p}} - (\Delta A_f)_{\mathrm{r}} \qquad [17.4.11]$$

For the entropy and Helmholtz free energy per mole of the reactants and products, assuming ideal gases,

$$S = S^{\circ} - R \ln p \qquad [17.4.12]$$

$$A = A^{\circ} + RT \ln p \qquad [17.4.13]$$

where R is the universal gas constant. For liquids and solids, the second term on the right-hand side of Equations 17.4.12 and 17.4.13 is negligible.

The Helmholtz free energy change may be calculated from thermodynamic data in several ways. One is to calculate ΔE from Equation 17.4.8 and ΔS from Equation 17.4.10

using Equation 17.4.12 to obtain S, and then to calculate ΔA from Equation 17.4.6. Alternatively, ΔA may be calculated from Equation 17.4.11, using Equation 17.4.13 to obtain ΔA_f.

The entropy term $T\Delta S$ is significant where there is a large difference between the number of moles of the reactants and of the products. This is the case for condensed phase explosives, but usually not for flammable gases and vapours. Where the change in the number of moles is not significant

$$\Delta A \approx \Delta E \qquad [17.4.14]$$

the enthalpy change may also be written as

$$\Delta H = \Delta E + \Delta nRT \qquad [17.4.15]$$

where Δn is the change in the number of moles. Where the change in the number of moles is not significant

$$\Delta H \approx \Delta E \qquad [17.4.16]$$

Thus, for explosions of flammable gases and vapours it is often possible to make certain approximations which simplify the task of obtaining the necessary data on thermodynamic properties.

For the explosive combustion of hydrocarbon clouds the method generally used is to determine the enthalpy change ΔH, which is usually obtained from the heat of combustion ΔH_c, and to apply to this an 'explosion efficiency', or yield factor, as discussed below.

The enthalpy change of the reaction ΔH may be calculated from the standard enthalpies of formation using Equation 17.4.9. Alternatively, it may be obtained from the heat of combustion.

If the heat of combustion is that of a gas and if the final water product is also gaseous, then the enthalpy change for the reaction is equal to the heat of combustion. Generally, however, the heat of combustion is given for a final water product which is a liquid. In this case the standard heat of combustion with liquid water product ΔH^o_{clw} should be corrected by a term which allows for the latent heat of vaporization of water ΔH_{vw}, to give the standard heat of combustion with water product as vapour ΔH^o_{cvw}.

$$\Delta H^o_{cvw} = \Delta H^o_{clw} + n_w \Delta H_{vw} \qquad [17.4.17]$$

where ΔH_{cvw} is the heat of combustion with the final water product as vapour, ΔH_{clw} is the heat of combustion with the final water product as liquid, ΔH_{vw} is the latent heat of vaporization of water and n_w is the number of moles of water. This correction is usually of the order of 5–10% for hydrocarbons.

Sometimes the heat of combustion is given for a liquid rather than a gas. In this case the standard heat of combustion for a liquid ΔH^o_{cl} should be corrected by a term which allows for the latent heat of vaporization of the liquid ΔH_v to give the standard heat of combustion for the vapour:

$$\Delta H^o_{cv} = \Delta H^o_{cl} - \Delta H_v \qquad [17.4.18]$$

where ΔH_{cl} is the heat of combustion with initial reactant as liquid, ΔH_{cv} the heat of combustion with initial reactant as vapour and ΔH_v the latent heat of vaporization.

As an illustration of the calculation of the energy of explosion of an explosive, consider the calculation of the energy of explosion of TNT in the absence of air. Following Kinney (1962) the explosion reaction is assumed to be

$$C_7H_5O_6N_3 \rightarrow C + 6CO + 2.5H_2 + 1.5N_2 \qquad [17.4.19]$$

The thermodynamic data are

	ΔE^o_f (kcal/mol)	S° (cal/mol K)
$C_7H_5O_6N_3$	−13.0	65
C	0	1.361
CO	−26.722	47.301
H_2	0	31.211
N_2	0	45.767

The molecular weight of TNT is 227.

Then, the internal energy of explosion from Equation 17.4.8 is

$$\begin{aligned}\Delta E &= (\Delta E^o_f)_p - (\Delta E^o_f)_r \\ &= \{(1 \times 0) + [6 \times (-26.722)] + (2.5 \times 0) \\ &\quad + (1.5 \times 0)\} - [1 \times (-13.0)] \\ &= -147.3 \text{ kcal/mol} \\ &= -147{,}300 \text{ cal/mol} \\ &= -147{,}000/227 \\ &= -649 \text{ cal/g of TNT}\end{aligned}$$

The entropy of explosion from Equations 17.4.10 and 17.4.12 is

$$\Delta S = (S^o - R \ln p)_p - (S^o)_r$$

The entropy of mixing terms is:

	p	$-R \ln p$
CO	0.6	1.016
H_2	0.25	2.753
N_2	0.15	3.767

Then, the entropy of explosion is

$$\begin{aligned}\Delta S &= \{(1 \times 1.361) + [6 \times (47.301 + 1.016)] \\ &\quad + [2.5 \times (31.211 + 2.753)] \\ &\quad + [1.5 \times (45.767 + 3.767)]\} - (1 \times 65) \\ &= 385.5 \text{ cal/mol K}\end{aligned}$$

Hence, the energy of explosion from Equation 17.4.6 is given by

$$\begin{aligned}\Delta A &= \Delta E - T\Delta S \\ &= -147{,}300 - (298 \times 385.5) \\ &= -262{,}180 \text{ cal/mol} \\ &= -262{,}180/227 \\ &= -1155 \text{ cal/g of TNT}\end{aligned}$$

The experimental value of the energy of explosion of TNT is quoted by Kinney as 1120 cal/g. Kinney gives an

alternative calculation which utilizes instead Equations 17.4.11 and 17.4.13, but gives an identical result.

Other values of the energy of explosion of TNT have been discussed by Burgess *et al.* (1968 BM RI 7196).

An alternative explosion reaction without air given by Ornellas (1967) is

$$C_7H_5O_6N_3 \rightarrow 3.7C + 2CO + 1.3CO_2 + 0.1CH_4 + 0.5H_2 + 1.6H_2O + 1.3N_2 + 0.2NH_3 \quad [17.4.20]$$

For this reaction the energy of explosion given is 1093 cal/g.

If the combustion of TNT takes place in the presence of excess air, the conventional explosion reaction is

$$C_7H_5O_6N_3 + O_2(\text{excess}) \rightarrow 7CO_2 + 2.5H_2O + 1.5N_2 \quad [17.4.21]$$

For this reaction the energy of explosion, or rather combustion, given is 3600 cal/g.

The energy of explosion of TNT is widely utilized as a reference value. The energy used is normally that for explosion in the absence of air. The value of this energy of explosion which is used here is 1120 cal/g of TNT, as given by Kinney.

As an illustration of the calculation of the enthalpy change in the explosion of a flammable gas, consider the calculation of that for an acetylene–air mixture. The explosion reaction is assumed to be

$$C_2H_2 + 2.5O_2 \rightarrow 2CO_2 + H_2O \quad [17.4.22]$$

The thermodynamic data are

	ΔH_f° (kcal/mol)
C_2H_2	54.194
O_2	0
CO_2	−94.052
H_2O (g)	−57.798

Then, the enthalpy change for the explosion from Equation 17.4.9 is

$$\begin{aligned}\Delta H &= (\Delta H_f^\circ)_p - (\Delta H_f^\circ)_r \\ &= \{[2 \times (-94.052)] + [(1 \times (-57.798)]\} \\ &\quad - [(1 \times 54.194) + (2.5 \times 0)] \\ &= -300.096 \text{ kcal/mol}\end{aligned}$$

Alternatively, the heat of combustion may be used. The standard heat of combustion of acetylene is

$$\Delta H_{clw}^\circ = -310.615 \text{ kcal/mol}$$

This value is for acetylene gas, so no correction is required for the state of the reactant, but the value assumes that the final water product is liquid. The latent heat of water is

$$\Delta H_{vw} = 9.7 \text{ kcal/mol}$$

Hence the corrected standard heat of combustion of acetylene is

$$\begin{aligned}\Delta H_{cvw}^\circ &= -310.615 + 9.7 \\ &= -300.915 \text{ kcal/mol}\end{aligned}$$

ΔH is then equal to this value of ΔH_c° and agrees well with that calculated earlier.

These methods of calculating the energy of explosion of flammable gases and vapours are those which are normally used for industrial explosion calculations.

The foregoing methods assume that the hot product gases are cooled back to standard conditions. The effect on the enthalpy change in the explosion of assuming other termination conditions is illustrated by the calculations given by Burgess *et al.* (1968 BM RI7196) for the combustion of a stoichiometric acetylene–air mixture. Some cases are considered in Table 17.7. For the bomb calorimeter the final mixture composition is CO_2 16.1%, H_2O 8.1% and N_2 75.8%, but for the other cases there are other products present such as CO, H_2, O, H and OH.

Calculations of this kind are relevant to the estimation of the energy available in explosion processes in process plant and pipelines.

There are available extensive tabulations of thermodynamic properties at standard conditions (25°C, atmospheric pressure). Tabulations of thermodynamic properties are given in National Bureau of Standards (NBS) Circular 461 Selected Values of Properties for Hydrocarbons (1947), NBS Circular 500 Selected Values of Chemical Thermodynamic Properties (1952) and NBS Circular 270-3 Selected Values of Chemical Thermodynamic Properties (1969), in the *NBS JANAF Thermochemical Tables* (Stull and Prophet, 1971) and in American Petroleum Institute (API) Research Project 44 Selected Values of Hydrocarbons and Related Compounds (Rossini, 1952; C.C. Williams, 1975). Thermodynamic properties of explosives are listed by Kinney (1962) and Kinney and Graham (1985).

Thermodynamic properties may also be estimated by theoretical methods, which are generally based on group contributions. A number of methods are described by Reid and Sherwood (1958, 1966), Reid, Prausnitz and Sherwood (1977) and Reid, Prausnitz and Poling (1987).

Table 17.7 *Characteristics of four combustion processes for acetylene in air*[a,b] *(after Burgess et al., 1968 BM RI 7196)*

	Final pressure (atm)	*Final temperature* (K)	$-\Delta H$ (cal/g of initial mixture)
Bomb calorimeter	1	298	842
Open flame	1	2537	692
Constant volume explosion	9.78	2918	630
Detonation	19.56	3230	550

[a] The legend to the authors' table refers to 'stoichiometric acetylene–air'.

[b] The original table gives the heat released in terms of the enthalpy change (−ΔH), as shown here. The heat released at constant pressure, as in the open flame case, is an enthalpy change, that released at constant volume, as in the bomb combustion cases, is an internal energy change.

Thermodynamic properties of selected substances are given in Table 17.8.

17.4.2 Gas expansion energy

Explosions can also be caused by gas or liquid under high pressure. The energy released in an explosive expansion of a compressed gas is again given by Equation 17.4.1.

Considering an ideal gas, for 1 mol of the gas, the limiting value of the energy of explosion, assuming an ideal gas and isothermal expansion, is

$$W = \int_1^2 P \, \mathrm{d}V \approx T\Delta S = RT \, \ln(P_1/P_2) \qquad [17.4.23]$$

where the subscript 1 denotes the initial state and 2 the final state.

Assuming isentropic expansion, the limiting value of the energy of explosion is

$$W = \frac{P_1V_1 - P_2V_2}{\gamma - 1} \qquad [17.4.24]$$

or eliminating V_2 using $PV^\gamma = \text{constant}$

$$W = \frac{P_1V_1}{\gamma - 1}\left[1 - \left(\frac{P_2}{P_1}\right)^{(1-\gamma)/\gamma}\right] \qquad [17.4.25]$$

where γ is the ratio of the gas specific heats.

17.4.3 Liquid expansion energy

The energy released in an explosive expansion of a liquid is

$$U_\mathrm{l} = \frac{1}{2}\beta P^2 V \qquad [17.4.26]$$

where U_l is the liquid strain energy, V is the volume of the vessel and β is the bulk modulus of the liquid.

17.4.4 Vessel metal strain energy

The elastic strain energy in a cylindrical vessel neglecting the ends is given by Manning and Labrow (1971) as

$$U_\mathrm{m} = \frac{P^2V}{2E}\left[\frac{3(1-2\nu) + 2K^2(1+\nu)}{K^2 - 1}\right] \qquad [17.4.27]$$

where E is Young's modulus, K is the diameter ratio, U_m is the metal strain energy and ν is Poisson's ratio. The elastic strain energy of the metal is usually small compared with the chemical and fluid expansion energies.

17.4.5 Vessel burst energy: ideal gas

For the energy of explosion in the bursting of a vessel containing fluid under pressure, it is necessary to distinguish between cases where the fluid can be treated as an ideal gas and those where it cannot.

Taking the ideal gas case first, there are a number of treatments available. Accounts include those of Erode (1955, 1959), Kinney (1962), W.E. Baker (1973), Adamczyk (1976), Strehlow and Ricker (1976), W.E. Baker *et al.* (1983), the CCPS (1994/15) and Crowl (1999).

The literature reveals a variety of approaches based on different treatments of the thermodynamics. The two most widely used relations appear to be those of Erode (1959) and of W.E. Baker (1973).

In the treatment given by Erode (1959) the energy of explosion is the energy required to raise the pressure of the gas at constant volume from atmospheric pressure to the initial, or burst, pressure. It is thus the difference in the

Table 17.8 *Thermodynamic properties of selected substances*

	State	ΔE_f° (kcal/mol)	ΔH_f° (kcal/mol)	ΔA_f° (kcal/mol)	ΔF_f° (kcal/mol)	S° (cal/mol k)	$\Delta E_f^\circ a$ (kcal/mol)
C (graphite)	s	0	0	0	0	1.3609	−94.052
CO	g	−26.722	−26.416	−33.104	−32.808	47.301	−67.636
CO_2	g	−94.052	−94.052	−94.260	−94.260	51.061	–
H_2	g	0	0	0	0	31.211	−68.317
H_2O	g	−57.502	−57.798	−56.339	−54.636	45.106	–
N_2	g	0	0	0	0	45.767	–
O_2	g	0	0	0	0	49.003	–
Cl_2	g	0	0	0	0	53.286	–
Acetylene	g		54.194		50.000	47.997	−310.615
Benzene	g		19.820		30.989	64.34	−789.08
n-Butane	g		−30.15		−4.10	74.12	−687.982
Cyclohexane	g		−29.43		7.59	71.28	−936.88[b]
Ethane	g		−20.236		−7.860	54.85	−372.820
Ethylene	g		12.496		16.282	52.45	−337.234
Methane	g		−17.889		−12.140	44.50	−212.798
Propane	g		−24.820		−5.614	64.51	−530.605
Propylene	g		4.879		14.990	63.80	−491.987
Styrene	g		35.22		51.10	82.48	–
Toluene	g		11.950		29.228	76.42	−943.58
TNT	s	−13.0				65	

[a] Final products CO_2 (g), H_2O (l).
[b] Heat of combustion value is for liquid.
Notes: g, gas; l, liquid; s, solid.
Sources: First eigtht items and last item, all properties except ΔH_c°: Kinney (1962). Other etems, ΔH_f°, ΔF_f°, S°: C.C.Williams (1975). All items, ΔH_c°: Washburn (1926); Rossini (1952); Perry (1950) (quoted by Hougen, Watson and Ragatz, 1954).

internal energies of the gas at the initial and final pressures. The internal energy is

$$E = \frac{PV}{\gamma - 1} \qquad [17.4.28]$$

where E is the internal energy, P is the absolute pressure in the vessel and V is the volume of the vessel. Brode's equation is

$$E_{Br} = \frac{(P_1 - P_o)V}{\gamma_1 - 1} \qquad [17.4.29]$$

where E_{Br} is Brode's energy of explosion, P is the absolute pressure, V is the volume of the vessel and the subscripts 1 and o denote 'initial vessel' and 'atmospheric', respectively.

The treatment of W.E. Baker (1973) is based on the work done on the surroundings in an isentropic expansion. Baker's equation is

$$E_{Ba} = \frac{P_1V_1 - P_oV_2}{\gamma_1 - 1} \qquad [17.4.30]$$

where E_{Ba} is Baker's energy of explosion and the subscripts 1 and 2 denote the initial and final conditions. For an isentropic expansion (PV^{γ} =constant). Equation 17.4.30 can be written as

$$E_{Ba} = \frac{P_1V_1}{\gamma_1 - 1}\left[1 - \left(\frac{P_o}{P_1}\right)^{(\gamma-1)/\gamma}\right] \qquad [17.4.31]$$

A third relation for the energy of explosion is that given by Kinney (1962). This is based on work done in isothermal expansion and is

$$E_{Ki} = nRT \ln(P_1/P_o) \qquad [17.4.32]$$

where E_{Ki} is Kinney's energy of explosion and n is the number of moles.

Other expressions for the energy of explosion include those of Adamczyk (1976) and Aslanov and Golinsky (1989).

Aslanov and Golinsky (1989) extend Baker's approach to take into account the internal energy of the air displaced by the expanding gas. Their expression, which contains an additional term to allow for this effect, is

$$E_{AG} = \frac{P_1V_1 - P_oV_2}{\gamma_1 - 1} + \frac{P_o(V_2 - V_1)}{\gamma_o - 1} \qquad [17.4.33]$$

where E_{AG} is the Aslanov–Golinsky energy of explosion. Comparisons of the expressions for energy of explosion have been given by Strehlow and Ricker (1976) and the CCPS (1994/15). The former define a scaling radius

$$R_o = \left(\frac{E}{P_o}\right)^{1/3} \qquad [17.4.34]$$

where R_o is the scaling radius (m).

They then compare the results given by the equations for the energy of explosion of Erode, Baker and Kinney at a given actual distance r_o and dimensionless distance R_o/r_o as shown in Figure 17.6(a). At higher pressure ratios the results given by the Kinney equation diverge from those

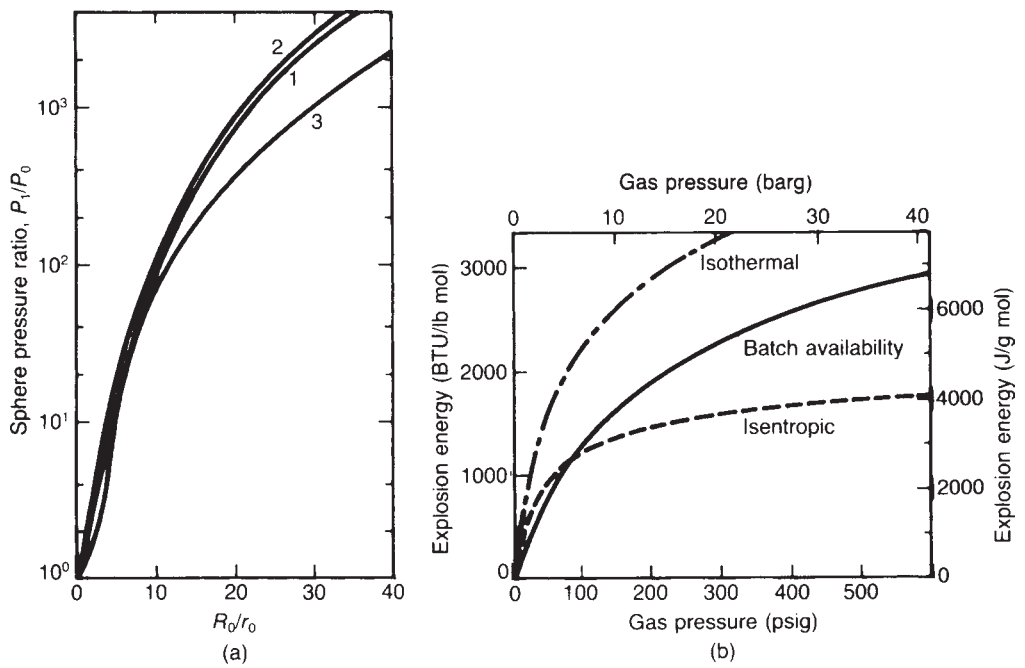

Figure 17.6 *Energy of explosion in a vessel burst (a) Comparison by Strehlow and Ricker (1976): curve 1, model of Srode (1955), curve 2, model of W.E. Baker (1953); and curve 3, model of Kinney (1962) (Courtesy of the American Institute of Chemical Engineers). (b) Comparison by Crowl (1992a) (Courtesy of Butterworth–Heinemann)*

given by the other equations. They recommend the use of the Erode equation.

The CCPS (1994/15) give plots of the ratio of the energies of explosion given by Baker, by Adamczyk and by Aslanov and Golinksy to that given by Erode. This comparison indicates that the values yielded by the other expressions tend to those of the Erode equation at higher pressures, but there is a considerable divergence at lower pressures. For the latter they state that the ratio of values obtained from the different models is as high as 4. In the method given for vessel bursts the CCPS uses the Erode equation.

The preferred method for the estimation of the explosion energy of gas-filled vessels appears to be that of Erode. The main alternative is that of Baker. The method of Kinney considerably overestimates the explosion energy.

The following version of the Erode equation in terms of TNT equivalence has been given in the *Second Canvey Report* (HSE, 1981a):

$$E = 1.43 \times 10^{-6} \frac{(P_1 - P_o)V}{\gamma^{-1}} \qquad [17.4.35]$$

where E is the explosion energy (te of TNT), P_1 the initial pressure in the vessel (kPa), P_o is the pressure of the surroundings (kPa) and V is the volume of the vessel (m^3).

As an illustration, consider the energy of explosion of 1 kmol of air at 100 bar and 20°C. The volume V of the gas is

$$\begin{aligned} V &= znRT/P \\ &= 0.970 \times 10^3 \times 8.314 \times 293/(100 \times 10^5) \\ &= 0.236 \text{ m}^3 \end{aligned}$$

with the compressibility factor, z, by the Peng–Robinson equation of state = 0.970. Using the Erode Equation 17.4.29, the explosion energy E_{ex} is

$$\begin{aligned} E_{ex} &= [(100-1) \times 10^5 \times 0.236]/(1.4-1) \\ &= 0.584 \times 10^7 \text{ J} \\ &= 5.84 \times 10^3 \text{ kJ} \\ &= 1.39 \times 10^6 \text{ cal} \end{aligned}$$

The energy in this explosion is thus equivalent to the following quantity of TNT:

$$\begin{aligned} &= \frac{1.39 \times 10^6}{1120} \\ &= 1243 \text{ g of TNT} \end{aligned}$$

The distribution of this energy is discussed below.

17.4.6 Vessel burst energy: non-ideal gas, vapour, flashing liquid

For the energy of explosion in the bursting of a vessel containing fluid under pressure which is not an ideal gas but a non-ideal gas, vapour or flashing liquid, the foregoing approach is not suitable.

In this case the energy of explosion is obtained as the difference in the internal energy between the initial and final states assuming an isentropic expansion, using suitable thermodynamic diagrams or tables.

Since it is the specific internal energy e which is of interest and since thermodynamic data tend to be given in terms of specific enthalpy, use may be made of the relation

$$h = e + pv \qquad [17.4.36]$$

where e is the specific internal energy, h is the specific enthalpy, p is the absolute pressure and v is the specific volume.

The initial condition of the fluid is defined in terms of the variables P_1, v_1, S_1 and H_1 and the final condition in terms of the variables P_2, v_2, S_2 and H_2, where S is the specific entropy and the subscripts 1 and 2 denote the initial and final states. An isentropic expansion is performed from P_2 to P_1, where the latter equals atmospheric pressure P_o, so that

$$S_2 = S_1 \qquad [17.4.37]$$

The enthalpy change $(h_1 - h_2)$ is obtained, and from this the internal energy change $(e_1 - e_2)$ using Equation 17.4.36. Then

$$E_{ex} = n(E_1 - E_2) \qquad [17.4.38]$$

where E_{ex} is the energy of explosion and n the number of moles.

For expansion of a vapour there are several different cases which may arise. The fluid may be (1) a vapour superheated in both states, (2) a vapour wet in both states or (3) a vapour superheated in state 1 but wet in state 2.

The vapour mass fraction may be expressed as

$$x = \frac{\phi - \phi_f}{\phi_g - \phi_f} \qquad [17.4.39]$$

where ϕ is a variable, and the subscripts f and g denote saturated liquid and saturated vapour, respectively. In this equation the variable ϕ may be replaced by s, e or h, depending on the thermodynamic path (s = constant entropy, etc.).

The following equation given by the CCPS is useful in interpolating in thermodynamic tables:

$$e_2 = (1-x)h_f + xh_g - (1-x)p_0v_f - xp_0v_g \qquad [17.4.40]$$

The CCPS gives data on the work of expansion for a limited set of fluids, namely ammonia, carbon dioxide, ethane, isobutane, nitrogen, oxygen and propane.

17.4.7 Energy distribution in an explosion

The energy distribution in an explosion is shown schematically in Figure 17.7. Only a fraction of the total energy in the explosion appears in the blast wave or the missiles. Some is dissipated as radiation and thermal energy. Other energy appears as potential and kinetic energy, in the explosion products and, eventually, in the fragments.

17.4.8 Energy distribution in a vessel burst explosion

For vessel rupture the effects of an explosion with a given energy release depend on the way in which the energy is distributed.

The total energy E_s in a system is the sum of the chemical energy E_1, the fluid expansion energy E_2 and the vessel strain energy E_3:

$$E_s = E_1 + E_2 + E_3 \qquad [17.4.41]$$

For a catastrophic or near-catastrophic failure of a vessel the *High Pressure Safety Code* gives the energy distribution shown in Table 17.9. The energy in the shock, or blast, wave

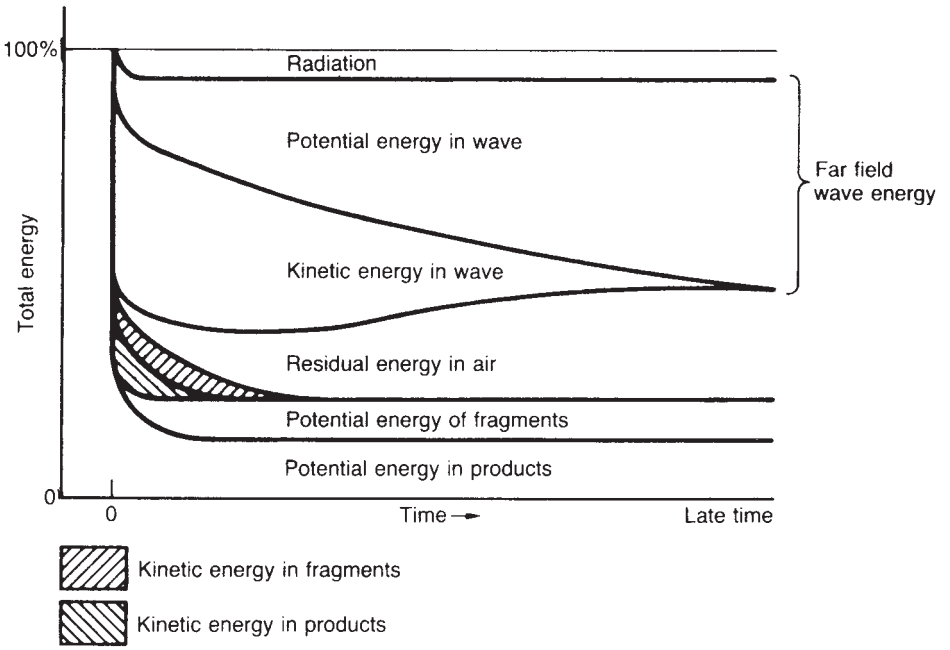

Figure 17.7 *Schematic energy distribution in a chemical explosion (after Strehlow and Baker, 1976; Stull, 1977)*

Table 17.9 *Approximate distribution energy of explosion of a bursting vessel (after B.G. Cox and Seville, 1975)*

	Shock wave energy	*Fragment kinetic energy*
Complete shattering of vessel due to brittle failure	$0.8E_s$	$0.2E_s$
Ejection of a major vessel section such as an end closure of a short, large bore vessel	$0.4E_s$	$0.6E_s$

is given for this case as between 40% and 80% of the explosion energy. A value of 50% is often used. The energy in the fragments is given for the case considered as between 20% and 80%.

The explosion energy in vessel rupture and its partition between blast and missiles is discussed further in Section 17.27. The energy imparted to missiles in also considered in Section 17.34.

17.4.9 Energy of a vapour cloud explosion: yield factor

In a vapour cloud explosion the energy in the blast wave is generally only a small fraction of the energy theoretically available from the combustion of all the material in the cloud. The ratio of the actual energy in the explosion to that theoretically available is variously termed the 'explosion efficiency', 'yield factor' or simply 'yield'.

This ratio is referred to here as the yield factor, or yield, and has a value less than unity. It is to be distinguished from the yield ratio, described in the next subsection.

If it is assumed that all the flammable material in the cloud is available for combustion, the combustion energy theoretically available is the product of the total mass of flammable material and the heat of combustion. This gives a 'gross' efficiency. On this basis, explosion efficiencies are typically 1–10%.

Typically, however, only the part of the cloud which is within the flammable range is considered giving rise to a 'net' efficiency.

Often, the fraction of mass in the flammable range is up to an order of magnitude less than the total cloud. Consequently, explosion efficiencies calculated on this basis tend to be as much as an order of magnitude greater than those based on combustion of the whole cloud.

The energy of vapour cloud explosions is discussed further in Section 17.28.

17.4.10 Blast energy of ground level explosion: yield ratio

A large proportion of explosions of interest in process plants occur at ground level. For such an explosion the ground forms a barrier to the explosion. For an explosion at ground level the blast wave has a strength that corresponds to an apparent energy of explosion which exceeds that for a free-air explosion by a yield ratio lying between 1 and 2. In other words, for a ground level explosion the apparent energy to be used in the correlations for the blast wave parameters is multiplied by the yield ratio, typically 2.

In general, the yield ratio is determined by two factors. These are:

(1) explosion symmetry;
(2) crater formation.

A free-air explosion has spherical symmetry, whilst a ground level explosion with three degrees of freedom to expand has hemispherical symmetry. On the basis of

symmetry alone, the apparent energy in the blast wave from a ground level explosion will be twice that in the blast wave from a free-air explosion. In other words, the yield ratio of the ground level explosion will be 2.

If, however, energy is expended in crater formation the yield ratio will be less. This is typically the case with ground level explosions of condensed phase explosives. Thus, for example, yield ratios for TNT explosions at or near ground level frequently lie in the range 1.5–2. A typical value of the yield ratio for high explosives at ground level is 1.8.

On the other hand, vapour cloud explosions tend not to give a crater. There was no crater formed, for example, at Flixborough. Thus, for a vapour cloud explosion at ground level the yield ratio approaches.

As already described, the effective energy release in a vapour cloud explosion is only a small fraction of the total energy theoretically available and the ratio of these two energies is expressed as an explosion efficiency. If an explosion efficiency is utilized, it should be used in conjunction with the same yield ratio as was used in its original derivation. Frequently this yield ratio is not stated, but it appears in many cases to be unity.

For an explosion such as the bursting of a pressure vessel due to high gas pressure at ground level the explosion energy absorbed by the ground is generally smaller than for a condensed phase explosion. Again the value of the yield ratio lies nearer to 2.

It is not always clear what assumption should be made concerning the yield ratio, and it may be necessary to exercise judgement. For the calculation of the maximum peak overpressure from an explosion the conservative assumption is a yield ratio of 2.

The term 'yield ratio' is used in work on condensed phase explosives (e.g. Kinney and Graham, 1985) and is therefore retained here, despite its similarity to the yield factor described in the previous subsection. The yield ratio has a value greater than unity. However, where only symmetry and not cratering is in question, use is also made here of the alternative term 'symmetry factor'. This is identical to the yield ratio if cratering is disregarded and has a value greater than unity.

These considerations relate solely to the method of estimating the energy imparted to the blast wave. The actual energy of explosion remains the same whether the explosion is in free air or at ground level. In particular, the energy imparted to fragments is unaffected.

In some cases, equations for energy of explosion are quoted with a factor of 2 already incorporated. These equations are solely for use in estimating the blast wave parameters.

17.4.11 Energy of explosion from thermodynamic availability

As indicated, the energy of explosion obtained from the Helmholtz free energy change is an approximation. Its use has been criticized by Crowl (1991) on the grounds that it applies to a constant temperature process, whereas in a real explosion the initial state of the substance may be at some higher temperature and/or pressure.

Accounts of the concept of availability are given by Keenan (1941) and Vogler and Weissman (1988). It has been applied by Crowl to the energy of explosion in general and in particular to explosions associated with combustion of gases (Crowl, 1991, 1992a) and with vessel bursts (Crowl, 1992a,c).

The treatment here is confined to its application to the estimation of the energy of explosion in the cases of a vessel burst explosion and a chemical explosion Crowl (1992a).

For a vessel burst the explosion energy is the change in batch availability. Assuming ideal gas behaviour,

$$\Delta B = -R\left[T_a \ln\left(\frac{P_1}{P_a}\right) - T_1\left(1 - \frac{P_a}{P_1}\right)\right] - C_p\left[T_a \ln\left(\frac{T_2}{T_1}\right) - (T_2 - T_1)\right] \quad [17.4.42]$$

where ΔB is the change in batch availability (kcal/mol), C_p is the specific heat at constant pressure (kcal/mol K), P is the absolute pressure (Pa), R is the universal gas constant (kcal/molK), T is the absolute temperature (K) and the subscripts a, 1 and 2 denote ambient, initial state and final state, respectively.

For the case where the initial and final temperatures are equal to the ambient temperature ($T_1 = T_2 = T_a$), Equation 17.4.42 reduces to

$$\Delta B = -RT_a\left[\ln\left(\frac{P_1}{P_a}\right) - \left(1 - \frac{P_a}{P_1}\right)\right] \quad [17.4.43]$$

Crowl compares the energy of explosion in a vessel burst, obtained from the isentropic and isothermal expansion treatments of Baker and of Kinney, given above as Equations 17.4.31 and 17.4.32, with his values from his method, in Figure 17.6(b). The graph indicates that compared with the thermodynamic availability method the isentropic expansion method generally underestimates the energy of explosion, whilst the isothermal expansion method always overestimates it. In an isentropic expansion the final temperature is in fact not the ambient temperature but a much lower temperature. He advises against the use of the isentropic expansion method for the determination of the energy of explosion in vessel bursts.

As an illustration, consider the case given by Crowl. This is the determination of the energy of explosion of a cylinder containing 45.4 kg of nitrogen at 1.53×10^4 kPa at 298 K with an ambient pressure of 100 kPa. The mass of gas is thus 1.621 kgmol (45.5/28). Then, from Equation 17.4.43

$$\Delta B = -2.39 \text{ kcal/mol} = -1621 \times 2.39 = -3870 \text{ kcal}$$

For a chemical explosion the explosion energy is the change in batch availability. For the energy change where the initial conditions of a gas/air mixture are ambient temperature and pressure,

$$\Delta B = (B)_{pr} - (B)_r \quad [17.4.44]$$

where

$$B = \sum_{i=1}^{m} n_i(\phi_{oi} + RT_a \ln x_i) \quad [17.4.45]$$

where B is the batch availability (kcal/mol), n_i is the number of moles of species i, m is the number of species, x_i is the mole fraction of species i, ϕ_o is the standard batch

availability (kcal/mol) and subscripts pr and r denote the products and reactants, respectively.

If the gas/air mixture is at a pressure other than ambient, the batch availability of the reactants is adjusted by the addition of the term

$$\delta B = nRT_a\left[\ln\left(\frac{P_1}{P_a}\right) - \left(1 - \frac{P_a}{P_1}\right)\right] \qquad [17.4.46]$$

For the special case of explosion of a substance in stoichiometric combustion in pure oxygen at standard temperature and pressure the energy of explosion is simply the batch availability ϕ_o of the substance.

Two cases of chemical explosion given by Crowl are considered by way of illustration. The first is the calculation of the energy of explosion for the stoichiometric combustion of methane in air:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O\ (g)$$

The energy of explosion is obtained from Equation 17.4.44 using Equation 17.4.45 for the batch availability B. Considering 1 mol of methane:

Initial state

Species	*Moles,* n_i	*Mole fraction,* x_i	*Standard availability*		*Batch availability*
			ϕ_{oi} (cal/mol)	$RT_a \ln x_i$	B (cal/mol)
CH_4	1.00	0.0951	195,500	−1,393	194,107
O_2	2.00	0.1901	0	−983	−1,966
N_2	7.52	0.7148	0	−199	−1,496
Total	10.52				190,645

and

Final state

Species	*Moles,* n_i	*Mole fraction,* x_i	*Standard availability*		*Batch availability*
			ϕ_{oi} (cal/mol)	$RT_a \ln x_i$ (cal/mol)	B (cal/mol)
CO_2	1.00	0.0951	0	−1,393	−1,393
H_2O	2.00	0.1901	2,054	−983	2,142
N_2	7.52	0.7148	0	−199	−1,496
Total	10.52				−747

Then,

$$\Delta B = (-747) - (190,645)$$
$$= -191,392 \text{ cal/mol of methane}$$

The second case is the energy of explosion of a mixture of 85% methane and 15% oxygen initially at 1 atm and 298 K. The stoichiometry for the combustion products is as follows: CH_4 77.5%, O_2 0%, CO_2 7.5% and H_2O 15%. Proceeding as before and considering 1 mol of mixture,

Initial state

Species	*Moles,* n_i	*Mole fraction,* x_i	*Standard availability*		*Batch availability*
			ϕ_{oi} (cal/mol)	$RT_a \ln x_i$ (cal/mol)	B (cal/mol)
CH_4	0.85	0.85	195,500	−96.2	166,096
O_2	0.15	0.15	0	−1,123	−168
Total	1.00				165,925

and

Final state

Species	*Moles,* n_i	*Mole fraction,* x_i	*Standard availability*		*Batch availability*
			ϕ_{oi} (cal/mol)	$RT_a \ln x_i$ (cal/mol)	B (cal/mol)
CH_4	0.775	0.775	195,500	150.7	151,396
O_2	0	0	0		
CO_2	0.075	0.075	0	−1,535	−115
H_2	0.15	0.15	2,054	−1,123	−140
Total	1.000				151,141

Further, from Equation 17.4.46

$\delta B = 830$ cal

Then,

$$\Delta B = (151,374) - (165,925 + 830)$$
$$= -15,381 \text{ cal/mol of mixture}$$

Crowl states that the energy of explosion computed using the thermodynamic availability method is always less than that obtained from the heat of combustion method. For stoichiometric mixtures the difference is of the order of 5–10%, but for other conditions such as non-stoichiometric mixtures and higher initial pressure and temperature the difference can be substantial.

The application of the method requires the use of data on the standard availability, which is not one of the thermodynamic quantities normally listed. Crowl (1992a) provides a table of standard availabilities for quite a large number of substances.

The following values are given for the standard availability of some common gases at standard conditions (1 atm, 298 K) and final state (H_2O (l)):

Substance	*Standard availability,* ϕ_o (kcal/mol)
Methance	195.5
Ethane	350.73
Propane	503.93
n-Butane	656.74
Ethylene	318.18
Propylene	467.81
Acetylene	295.21
Hydrogen	56.69
O_2 (g)	0
CO_2 (g)	0
H_2O (l)	0

17.5 Deflagration inside Plant

The explosion of a flammable mixture in a process vessel or pipework may be a deflagration or a detonation. These two types of explosion differ fundamentally and require different countermeasures. Both types, but particularly detonation, can be very destructive.

The conditions for a deflagration to occur are that the gas mixture is within the flammable range and that there is a source of ignition or that the mixture is heated to its autoignition temperature.

The conditions for a detonation to occur are similar except that in this case the mixture should be within the detonable range. If the source of ignition is sufficiently strong, detonation may be initiated directly. Alternatively, a deflagration may undergo transition to a detonation. This transition occurs in pipelines but is most unlikely to occur in vessels.

17.5.1 Sources of ignition

The sources of ignition usually considered are those outside the process plant, but ignition sources can occur inside vessels and pipework also. These include:

(1) flames and hot surfaces;
(2) sparks;
(3) chemicals
  (a) unstable compounds,
  (b) reactive compounds and catalysts,
  (c) pyrophoric iron sulphide;
(4) static electricity;
(5) compression.

This list is sufficient to show that there is no shortage of possible ignition sources inside the plant. The wide variety of conditions which can cause ignition is illustrated by the fact that compressed air at 60 psig striking a suitably shaped depression in the end of a piece of wood can ignite the latter (W.G. High, 1976).

If a flammable mixture may be present, precautions should be taken to eliminate all ignition sources. But it is prudent to assume that, despite these efforts, a source of ignition will at some time occur.

Ignition can also occur if the flammable mixture is heated to its autoignition temperature.

17.5.2 Deflagration in vessels

For a deflagration at constant volume in a sphere the maximum explosion pressure is

$$\frac{P_2}{P_1} = E \qquad [17.5.1]$$

with

$$E = \frac{n_2 T_2}{n_1 T_1} \qquad [17.5.2a]$$

$$= \frac{M_1 T_2}{M_2 T_1} \qquad [17.5.2b]$$

where E is the expansion ratio, M is the molecular weight of the gas mixture, n is the number of moles in the gas mixture, P is the absolute pressure, T is the absolute temperature and the subscripts 1 and 2 denote the initial and final states, respectively.

For deflagration of hydrocarbons the ratio of the maximum explosion pressure to the initial pressure is quoted as being approximately 8 for hydrocarbon–air mixtures and 16 for hydrocarbon–oxygen mixtures (Zabetakis, 1965 BM Bull. 627; W.G. High, 1976). These values apply for initial pressures in the range 1–40 bar, for initial temperatures in the range 0–300°C and for relatively small volumes of a few cubic metres.

However, as described in Section 17.7, the values quoted for the final pressure attained in deflagration in a closed vessel are often underestimated due to the use of constant pressure rather than constant volume assumptions. On the correct basis of constant volume combustion, for hydrocarbon–air mixtures the ratio of the maximum explosion pressure to the initial pressure is approximately as follows:

$$\frac{P_2}{P_1} \approx 10 \qquad [17.5.3]$$

This is the order of pressure rise in deflagrative combustion, for example, in the results given in Table 17.7.

For conventionally designed pressure vessels the bursting pressure P_b is of the order of

$$\frac{P_b}{P_1} \approx 4 - 5 \qquad [17.5.4]$$

Hence in the absence of explosion relief the deflagration of a hydrocarbon–air mixture is easily capable of bursting a pressure vessel.

If the explosion relief is to be effective, it must act within a period which is generally much less than 1 s. Methods of explosion relief are available which do this and are discussed in Section 17.12.

17.5.3 Pressure piling

If an explosion occurs in a compartmented system in which there are separate but interconnected spaces, a situation can arise in which the pressure developed by the explosion in one space causes a pressure rise in the unburnt gas in an interconnected space, so that the enhanced pressure in the latter becomes the starting pressure for a further explosion. This effect is known as pressure piling, or cascading.

The type of system geometry in which pressure piling is liable to occur is illustrated in Figure 17.8(a). If the initial explosion occurs in space A, this may cause pressure piling in space B. If the final pressure in A is ζ times the initial pressure, a simplified argument would suggest that the final pressure in B might in the worst conceivable case be two times the initial pressure in both spaces.

An account of pressure piling has been given by Fitt (1981a,b). The phenomenon of pressure piling was first detected by Beyling (1906) in work on flameproof electrical equipment and has subsequently been studied by a number of workers. Table 17.10 lists some of the experimental work done on pressure piling.

Fitt distinguishes between studies done on compartmented tube systems and linked tube systems, as shown in Figures 17.8(a) and (b), respectively. He also points out that there are two separate effects, which he calls flame front projection (FFP) and peak pressure enhancement (PPE).

The first causes a very rapid rise of pressure, the second an enhanced final pressure.

Fitt states that in compartmented systems, pressure piling is observed with low compartment volume ratios (v_1/v_2) and high connecting orifice-to-enclosure diameter ratios, whereas in link tube systems a volume ratio of at least 5 : 1 appears to be required for peak pressure enhancement. He suggests that there is a mechanism of pressure piling in compartmented systems which is suppressed in link tube systems.

The enhancement of pressure is limited by the fact that the total pressure volume energy cannot exceed that which would arise in an uncompartmented enclosure. If pressure piling occurs in one space, the maximum pressure in the remaining space must be reduced. At some stage the pressure differential will cause back venting, which lowers the peak value.

For hydrocarbon–air mixtures the maximum pressure obtained in combustion is at least eight times the initial pressure. Thus, taking a peak pressure enhancement factor of 4, the maximum pressure obtained with pressure piling would be of the order of 30. Pressure piling can therefore give a very large increase in the maximum pressure rise in the plant.

With regard to design to avoid pressure piling, Fitt states that in link tube systems the peak pressure enhancement is unlikely to exceed a factor of 4. This is the maximum enhancement obtained in the experiments given in Table 17.10. The peak pressure enhancement in compartmented tube systems is less predictable, and such systems should be avoided. Pressure piling may be significant not only in the main process plant but in other equipment also. As already mentioned, much of the work on pressure piling has been concerned with flameproof equipment. This aspect is considered further in Chapter 16.

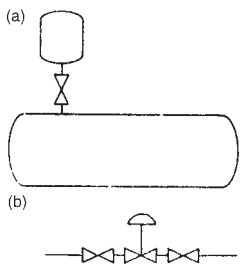

Figure 17.8 *Plant configuration to illustrate pressure pilling: (a) compartmented tube system and (b) linked tube system*

17.5.4 Deflagration in pipes

Whereas in a vessel, deflagration results in a pressure rise which is uniform throughout the vessel, this is not so in a pipe, where the explosion velocity and explosion pressure can change along the length of the pipe.

An account of deflagration in pipes has been given by Bartknecht (1981a). He defines three cases:

Case 1: pipe open at one end, ignition at open end;
Case 2: pipe open at one end, ignition at closed end;
Case 3: pipe closed at both ends.

In order to understand the phenomena involved, it is necessary to consider all three cases. The explosion velocity is given by the relation

$$u_{ex} = \phi u_n + u_d \qquad [17.5.5]$$

Table 17.10 *Some experiments on pressure piling (after Fitt, 1981a)*

Worker(s)	*Apparatus*		*Compartment volume ratio*
Beyling (1906)	Compartmented pipe		2
Beyling (1906)	Linktube		11.7
Grice and Wheeler (1929)	Link tube		12 and 16.7
Coward and Wheeler (1934)	Compartmented pipe		Many compartments
Gleim and March (BM 1952 RI 4908)	Compartmented pipe		1.0–7.0
T.A.J. Brown (1959)	Link tube		13.5
J. Singh (1977)	Link tube		5.0–32.0
Bartknecht (1981a)	Link tube		5.0
	Larger compartment diameter or side (cm)	*Conneting passage diameter* (cm)	*Maximum observed peak pressure enhancement ratio*
Beyling (1906)	33.5	3.0	1.3
Beyling (1906)	33.5	2.0	2.3
Grice and Wheeler (1929)	45.8[a] and 50	2.5	2.0
Coward and Wheeler (1934)	30.6	2.5	Not studied[b]
Gleim and March (BM 1952 RI 4908)	30.6[a]	5.1–25.4	4.0
T.A.J. Brown (1959)	15.2	0.6–2.5	4.0
J. Singh (1977)	30.5	1.3–5.1	3.7
Bartknecht (1981a)			3.1

[a] Square section.
[b] Flame front projection.

where u_d is the displacement velocity, u_{ex} is the explosion velocity, u_n the normal burning velocity and ϕ the ratio of the area of the flame front to the cross-sectional area of the pipe. The displacement velocity u_d is the velocity of the unburned mixture, and the explosion velocity is the visible flame velocity. The equation applies to all three cases, but for that of an open pipe with ignition at the open end the displacement velocity is zero. For ignition at the closed end (case 2) it is high, being some 80–90% of the explosion velocity. In this latter case only part of the gas mixture, theoretically 1/7, is burned within the pipe, the rest being ejected from the open end and burned outside. The high displacement velocity also results in much higher turbulence, a higher flame front area and a higher value of ϕ, in this latter case.

For an open pipe with ignition at the closed end with large diameter pipes ($\geq$400 mm) the explosion velocity exhibits an approximately linear increase along the length of the pipe. With smaller diameter pipes this continuous increase is no longer observed. As the pipe diameter is decreased, a critical diameter is reached at which the flame propagation no longer occurs.

For an open pipe with ignition at the closed end the explosion pressure P_{ex} increases linearly with the logarithm of explosion velocity, as shown in line 1 of Figure 17.9(a). This effect is independent of pipe diameter.

Thus, in the case of a 1600 mm diameter pipe, 10 m long, open at one end, Bartknecht quotes, for ignition at the open end, values of u_{ex} and P_{ex} of 4 m/s and 0.02 bar and, for ignition at the closed end, values of 150 m/s and 0.2 bar, respectively.

If the flow is highly turbulent and if the pipe is long enough, the explosion velocity can reach a value such that detonation, or quasi-detonation, occurs. The reference to quasi-detonation applies particularly to methane. It is difficult to cause methane to detonate, and although it exhibits detonation-like behaviour, the flame front and shock wave can separate, whereas in a normal detonation they are coupled.

Table 17.11 shows the pipe lengths required for run-up to detonation for the three gases methane, propane and hydrogen with flame jet ignition in pipes of 100, 200 and 400 mm diameter. Section 17.2.15 treats run-up distance for weaker ignitions.

Turning to the case of a pipe closed at both ends (case 3), and considering first a quiescent gas mixture, experimental results given by Bartknecht show that the explosion velocity initially increases along the length of the pipe due to a high displacement velocity, but since the gas is confined, the displacement velocity and the explosion velocity then decrease. For gases such as methane and propane, the net effect is to cause the explosion velocity to pass through a maximum, and for the value of that maximum to be less than that attained in an open pipe with ignition at the closed end. There is in effect a braking action. Hydrogen constitutes an exception: the explosion velocity is the same in both configurations and does not pass through a maximum.

If the gas mixture is turbulent, however, there is no such braking action. In this case in a pipe closed at both ends all three gases will run up to detonation, or quasi-detonation. The distance required to do this is longer than for a pipe with one end open, but is less than 30 m.

For a pipe closed at both ends, the explosion pressure again increases linearly with the explosion velocity, but since all the gas is burned the explosion pressure is several bar higher than for the open pipe case, as shown in line 2 in Figure 17.9(a).

The pressures developed in detonation, or quasi-detonation, of the three gases mentioned in pipes of 100 and 200 mm diameter with flame jet ignition are shown in Table 17.12. There are several points worthy of note. The pressures tend to be higher in the small diameter pipe. The pressures on the end flange P_{pf} are some three times those on the pipe wall P_{pw}. And the pressures given by hydrogen are less than those given by the other two gases.

Considering the simple case of a flame accelerating down a pipe closed at the end distant from the ignition source, the pressure in the gas ahead of the flame may rise due not only to a shock wave close to the flame front but possibly also due to a shock wave reflected from the end of the pipe. It is estimated by Nettleton (1987) that the pressure in the unburned gas may rise by a factor of 2–5.

A separate but related phenomenon is wave interactions associated with the advancing detonation wave. An example is the retonation wave in a pipe closed at the end where ignition occurs. This retonation wave is created at the same time as the detonation wave itself. It travels back through the burned gas, is reflected and then travels forwards again and, since the velocity of sound in the burned gas is much higher than in the unburned gas, overtakes the detonation wave. The latter thus becomes overdriven for a short distance, before it becomes attenuated by the Taylor expansion effect.

17.5.5 Plant design

The hazard of an explosion should in general be minimized by avoiding flammable gas–air mixtures inside a plant. It is bad practice to rely solely on elimination of sources of ignition.

If the hazard of a deflagrative explosion nevertheless exists, the possible design policies include (1) design for full explosion pressure, (2) use of explosion suppression or relief, and (3) the use of blast cubicles.

It is sometimes appropriate to design the plant to withstand the maximum pressure generated by the explosion. Often, however, this is not an attractive solution. Except for single vessels, the pressure piling effect creates the risk of rather higher maximum pressures. This approach is liable, therefore, to be expensive.

An alternative and more widely used method is to prevent overpressure of the containment by the use of explosion suppression or relief. This is discussed in more detail in Section 17.12.

In some cases the plant may be enclosed within a blast resistant cubicle. Total enclosure is normally practical for energy releases up to about 5 kg TNT equivalent. For greater energy releases a vented cubicle may be used, but tends to require an appreciable area of ground to avoid blast wave and missile effects.

It is more difficult to design for a detonative explosion. A detonation generates much higher explosion pressures. Explosion suppression and relief methods are not normally effective against a detonation. Usually, the only safe policy is to seek to avoid this type of explosion.

Direct initiation of detonation in ordinary flammable gas–air mixtures is generally improbable. Avoidance of detonation depends mainly, therefore, on elimination of conditions under which transition from deflagration to detonation can occur in equipment such as pipelines.

Where a significant explosion hazard exists, the possible consequences of explosion should be reviewed.

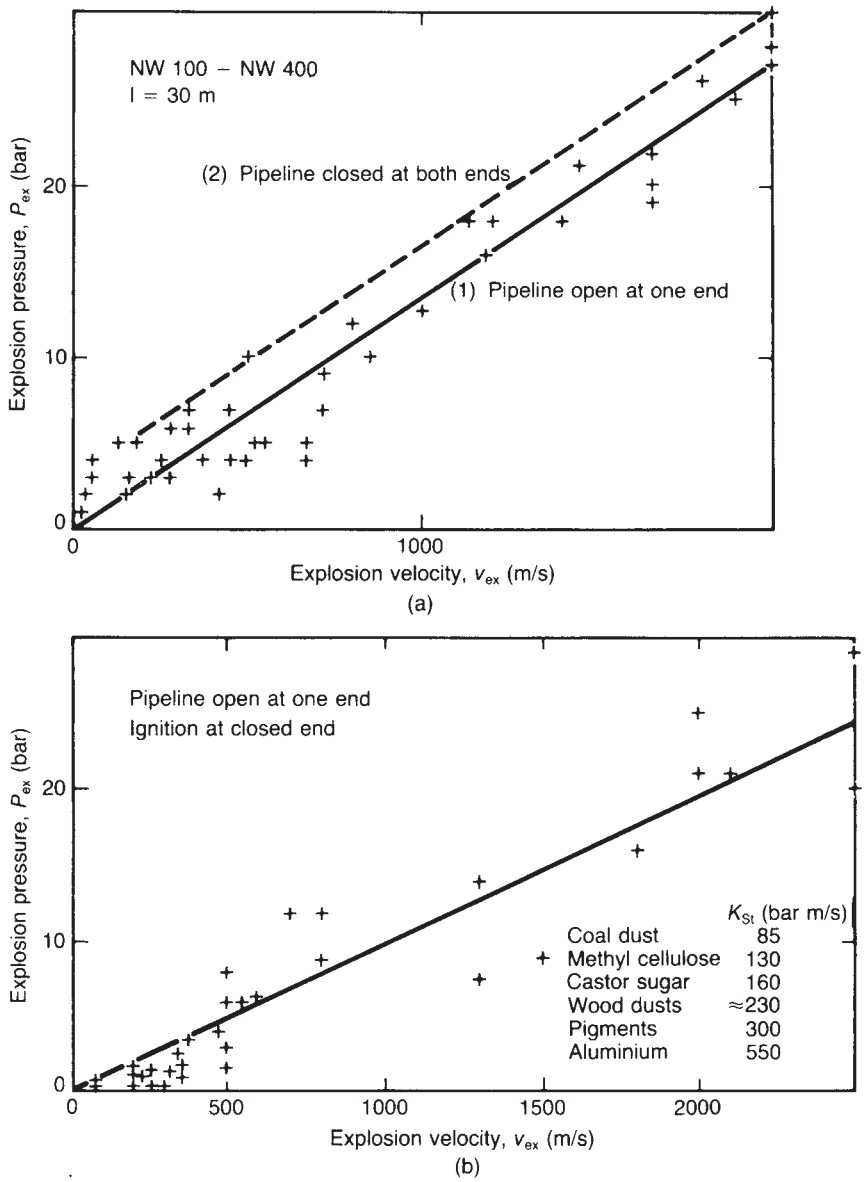

Figure 17.9 *Explosion pressure in pipes (after Bartknecht, 1981a). (a) Flammable gas: line 1, flammable gas in a pipe of diameter 100–400 mm and length 30 m open at one end; line 2, flammable gas in a pipe of the same dimensions closed at both end. (b) Flammable dusts: dusts with K_{st} values of 85–550 bar m/s in a pipe of diameter 400 mm length 40 mm open at one end with ignition at the closed end (Courtesy of Elsevier Science)*

17.6 Detonation inside Vessels and Pipes

Detonation of a flammable gas–air mixture may occur by direct initiation of detonation by a powerful ignition source or by transition from deflagration.

The transition from deflagration to detonation requires a strong acceleration of the flame front. It occurs in pipelines but is very improbable in vessels. The transition from deflagration to detonation is a complex process. The properties of the detonation, however, are fairly well defined and depend essentially on the properties and condition of the unburnt gas.

17.6.1 Detonation in vessels

A general account of the pressures which may be generated by detonation inside a plant has been given in Section 17.2. In practical terms, the peak pressure ratio P_2/P_1 resulting from a detonation of a hydrocarbon–air mixture in a

Table 17.11 *Pipe lengths (m) for acceleration to detonation (after Bartknecht, 1981a) (Courtesy of Springer-Verlag)*

Gas	*Pipe diameter* (mm)		
	100	200	400
Methane	12.5	18.5	>30
Propane	12.5	17.5	22.5
Hydrogen	7.5	12.5	12.5

Table 17.12 *Some pressures (bar) in a pipeline closed at both ends following a detonation, or quasi-detonation (after Bartknecht, 1981a) (Courtesy of Springer-Verlag)*

Gas	*Pipe diameter,* 100 mm		*Pipe diameter,* 200 mm	
	P_{pw}	P_{pf}	P_{pw}	P_{pf}
Methane	32	100	25	80
Propane	35	95	25	75
Hydrogen	23	56	23	40

containment such as a vessel is about 20:

$$\frac{P_2}{P_1} \approx 20 \qquad [17.6.1]$$

This is the order of pressure rise, for example, in the experiment reported in Table 17.7.

17.6.2 Detonation in pipes

The transition from deflagration to detonation was discussed in Sections 17.2 and 17.5, where information was given on the run-up length to detonation and on the pressures exerted both on the pipe wall and on the end flange.

Accounts of detonation in pipes have been given by a number of workers, including Craven and Greig (1967), Munday (1971b) and Bartknecht (1981a).

Craven and Greig describe experimental work on the pressure generated by the detonation of ammonia–nitrous oxide mixtures in 3 and 4 in. pipes initially at atmospheric pressure. Determinations were made of the incident pressure and of the reflected pressure. The latter was determined from the distortion suffered by test plates bolted to the end of the pipe. It was found that the velocity, the incident pressure and the reflected pressure all rose rapidly with distance from the ignition source to a peak value and then fell to a lower, plateau value. Thus, the transition from deflagration to detonation was associated with high but unstable velocities and pressures. In the 3 in. pipe with a 50 : 50 ammonia–nitrous oxide mixture the incident pressure peak and plateau values were about 1250 and 370 psi, and the reflected pressure peak and plateau values were about 4800 and 1100 psi, respectively.

The effects of detonation in a pipe system vary. In some cases damage is confined to blank ends and sudden changes of direction. In other cases the pipe may be ripped open from end to end.

17.6.3 Pressure piling

The phenomenon of pressure piling has been discussed in Section 17.5.

17.6.4 Plant design

Essentially, the preferred approach in plant design to the hazard of detonation in vessels and pipes is prevention rather than protection.

Where an estimate is to be made of the ability of a plant to withstand detonation, the approach generally adopted is to use a unidimensional method such as the CJ model. Such models work reasonably well in the simple case of a readily detonable mixture in straight pipe. In any event, there is a lack of a more comprehensive treatment adapted to design.

The traditional approach has been to compare the pressures obtained from a unidimensional model with the static pressures which the plant can withstand. Some of the weaknesses of this approach have been described in Section 17.2. The pressures predicted by unidimensional models are well below those produced by real detonation waves. The method does not take into account the difference between rapidly and slowly applied loads nor the interaction between the shape of the pressure profile and the response time of the confining structure.

The pressures predicted for detonations inside plant tend to be so high that containment is impractical except for certain limited cases such as straight pipes which are of small diameter and/or are open-ended.

However, from an assessment of the limited experimental evidence, Nettleton (1987) concludes that the traditional approach just described appears to be a safe one. The tests were conducted, conservatively, with stoichiometric mixtures for which the detonation pressures are relatively predictable.

With regard to mechanical design, the velocity of an elastic wave in a metal usually exceeds the detonation velocity. This points to separate treatment of the arrivals of the elastic wave and of the detonation wave itself.

In designing against explosions, an approach usually considered is to accept a degree of plastic deformation. A discussion of the planned deformation approach and of the practical problems in implementing it is given by Nettleton (1987). Essentially, it is limited to the early stages of flame acceleration. Nettleton also gives guidance on the local strengthening of plant at vulnerable points.

17.6.5 Protection against detonation

Where protection against detonation is to be provided, the preferred approach is to intervene in the processes leading to detonation early rather than late.

Attention is drawn first to the various features which tend to promote flame acceleration, and hence detonation. Minimization of these features therefore assists in inhibiting the development of a detonation. To the extent practical, it is desirable to keep pipelines small in diameter and short; to minimize bends and junctions and to avoid abrupt changes of cross-section and turbulence promoters.

For protection, the following strategies are described by Nettleton (1987): (1) inhibition of flames of normal burning velocity, (2) venting in the early stages of an explosion, (3) quenching of flame–shock complexes, (4) suppression of a detonation, and (5) mitigation of the effects of a detonation.

Methods for the inhibition of a flame at an early stage are described in Chapter 16. Two basic methods are the use of flame arresters and flame inhibitors.

Flame arresters are described in Section 17.11. The point to be made here is that although an arrester can be effective in the early stages of flame acceleration, siting is critical

since there is a danger that in the later stages of a detonation it may act rather as a turbulence generator.

The other method is inhibition of the flame by injection of a chemical. Essentially, this involves detection of the flame followed by injection of the inhibitor. At the low flame speeds in the early stage of flame acceleration, there is ample time for detection and injection. This case is taken by Nettleton to illustrate this is a gas mixture with a burning velocity of about 1 m/s and expansion ratio of about 10, giving a flame speed of about 10 m/s, for which a separation between detector and injection point of 5 m would give an available time of 0.5 s.

In the early stage of an explosion, venting may be an option. The venting of explosion in vessels and pipelines is discussed in Sections 17.12 and 17.13, respectively.

It may be possible in some cases to seek to quench the flame–shock complex just before it has become a fully developed detonation. The methods are broadly similar to those used at the earlier stages of flame acceleration, but the available time is drastically reduced; consequently, this approach is much less widely used. Two examples of such quenching given by Nettleton are the use of packed bed arresters developed for acetylene pipelines in Germany, and widely utilized elsewhere, and the use in coal mines of limestone dust which is dislodged by the flame–shock complex itself.

The suppression of a fully developed detonation may be effected by the use of a suitable combination of an abrupt expansion and a flame arrester. As described earlier, there exists a critical pipe diameter below which a detonation is not transmitted across an abrupt expansion, and this may be exploited to quench the detonation. Work on the quenching of detonations in town gas using a combination of abrupt expansion and flame arrester has been described by Cubbage (1963).

An alternative method of suppression is the use of water sprays, which may be used in conjunction with an abrupt expansion or without an expansion. The work of Gerstein, Carlson and Hill (1954) has shown that it is possible to stop a detonation using water sprays alone.

17.6.6 Some limitations

There are two principal mechanisms which create pressures which exceed those predicted by the unidimensional models and against which it is difficult to design. One is the pressure piling and wave interaction effects described above which occur during the development of the detonation wave. The other, which applies to the detonation condition itself, arises from instabilities in the combustion behind the leading front. The effects are enhanced in marginally detonable mixtures and by interactions with the confinement.

17.7 Explosions in Closed Vessels

The deflagration of a flammable gas mixture in a closed vessel is important in itself and in relation to venting of the vessel. It is closely related to the combustion of a flammable dust mixture in a vessel. Quantification requires the measurement of flame speed and burning velocity. The two parameters of main interest in explosion in a closed vessel are the maximum pressure P_m and the rate of pressure rise, particularly the maximum rate $(dP/dt)_{max}$.

17.7.1 Energy release and final conditions

As described in Section 17.5, for a deflagration at constant volume, in a sphere, the maximum explosion pressure is

$$\frac{P_2}{P_1} = \frac{n_2 T_2}{n_1 T_1} \qquad [17.7.1]$$

where n is the number of moles in the gas mixture, P is the absolute pressure, T is the absolute temperature and the subscripts 1 and 2 denote the initial and final state, respectively. The determination of the maximum pressure therefore involves the calculation of the final temperature.

Combustion in a closed vessel is a constant volume process. The heat of reaction and the gas specific heats applicable to it are those at constant volume. The relevant thermodynamic quantity is the internal energy. Thus, the final temperature should be obtained by equating the internal energy of the products to the internal energy of the reactants and the heat of reaction at constant volume.

The computation of the final temperature is frequently done making the incorrect assumption of constant pressure conditions. The problem is discussed by S.M. Richardson, Saville and Griffiths (1990). It is a common, but incorrect, practice to take the final temperature as the adiabatic flame temperature. This is incorrect because the adiabatic flame temperature is a constant pressure quantity. The constant volume flame temperature is appreciably higher.

The aforementioned authors give an example which illustrates the extent of the error. For a stoichiometric mixture of propane and air, which contains 3.98% propane, at initial conditions of pressure 1 bara and temperature 290 K (17°C), the calculated final conditions for adiabatic constant volume combustion are pressure 10.2 bara and temperature 2850 K (2577°C). This compares with values quoted in the literature of final pressure 7.6 bara and temperature 2198 K (1925°C).

The authors state that the difference between the heat of reaction at constant volume and that at constant pressure is not great. The main source of error lies in the difference between the gas specific heat at constant volume and that at constant pressure.

Thus, in constant volume combustion both the final temperature and the final pressure are considerably higher than for combustion at constant pressure.

17.7.2 Experimental studies

There have been a large number of experimental studies of combustion in vessels, both closed and vented. Many of these have been concerned with the venting process, but the proportion of the total work done on closed vessels is appreciable.

Research on combustion in closed vessels has been undertaken for a number of purposes, of which three may be mentioned here. One is the determination of burning velocity. Burning velocity and its measurement have been discussed in Chapter 16. Some models incorporating burning velocity which may be used for its determination are described in this section. Experimental work related to burning velocity includes that of Fiock and Marvin (1937a,b), Fiock *et al.* (1940), Manton, von Elbe and Lewis (1953) and Eschenbach and Agnew (1958).

The second area of work is the investigation of the various factors which influence explosion development in

a closed vessel. Here, particular mention needs to be made of the extensive programme of work undertaken at the Bureau of Mines (BM), an account of which is given by Nagy and Verakis (1983). It is illustrated by the work of Nagy *et al.* (1971 BM RI 7507) on the effect of variables such as initial pressure, initial temperature and vessel size and shape. Other work includes that of Kratz and Rosecrans (1922), Ellis and Wheeler (1925, 1928b), Fenning (1926), Rallis, Garforth and Steinz (1965) and G.F.P. Harris (1967).

The third area is studies of detonation, as opposed to deflagration. The BM is again well represented in work in this area, by investigations such as that of Burgess *et al.* (1968 BM RI 7196). Other work includes that of Manson and Ferri (1953) and Pliickebaum, Strauss and Edse (1964).

An account of the findings concerning the effects of the various influencing factors investigated in this work is given below.

One particular outcome of the experimental work may be mentioned at this point. When the flame front reaches a certain radius there is a marked increase in its velocity. At this point the ratio of the pressure to the initial pressure P/P_o becomes strongly influenced by the expansion ratio E.

Plate 15, from the work of R.J. Harris (1983), shows the development of the flame within a vessel with the latter stages influenced by the presence of a vent.

17.7.3 Factors influencing closed vessel explosions

The maximum pressure and the rate of pressure rise in a closed vessel explosion are affected by a number of factors. These are discussed by Bartknecht (1981a), R.J. Harris (1983), Nagy and Verakis (1983) and Lunn (1984b, 1992). They include:

(1) vessel size and shape;
(2) fuel;
(3) fuel–air ratio;
(4) vessel fractional fill;
(5) initial pressure;
(6) initial temperature;
(7) initial turbulence;
(8) ignition source.

A factor which may affect both explosion parameters is heat transfer from the flame and the hot gas to the vessel wall. This can be significant if the vessel has a high aspect, or length/diameter, ratio or if the combustion is relatively slow.

The vessel shape to which most treatments apply is a compact vessel with a length/diameter ratio not exceeding 3. For a compact vessel, maximum pressure is theoretically independent of vessel size and shape if heat transfer is neglected. In practice, maximum pressures tend to show some scatter, but this is random. Maximum pressure may be less than theoretical if the mixture is slow burning. Mixtures close to the lower explosibility limit tend to burn relatively slowly. The rate of pressure rise depends on vessel size and shape. The effect of vessel volume is illustrated in Figure 17.10.

In one series of tests it was found that for cubical, rectangular and spherical vessels the rate of pressure rise was proportional to the ratio of the vessel surface S to its volume V. If the vessel shape is such as to promote heat transfer, the rate of pressure rise is reduced.

In an elongated vessel the flame front travels along the axis compressing the unburned gas. The rate of pressure rise is increased compared with that in a more compact

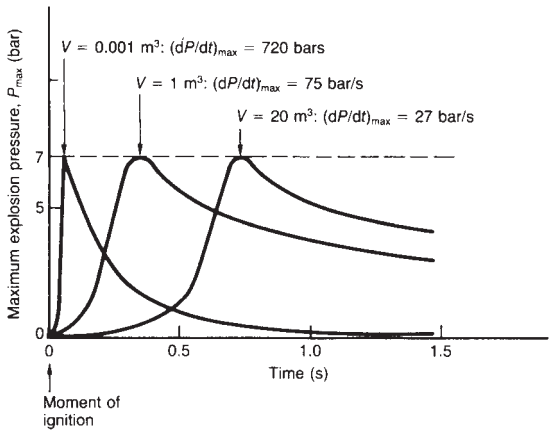

Figure 17.10 *Explosions in closed vessels: effect of vessel volume (Bartknecht, 1981a). Propane at stoleniometric concentration (Courtesy of Elsevier Science)*

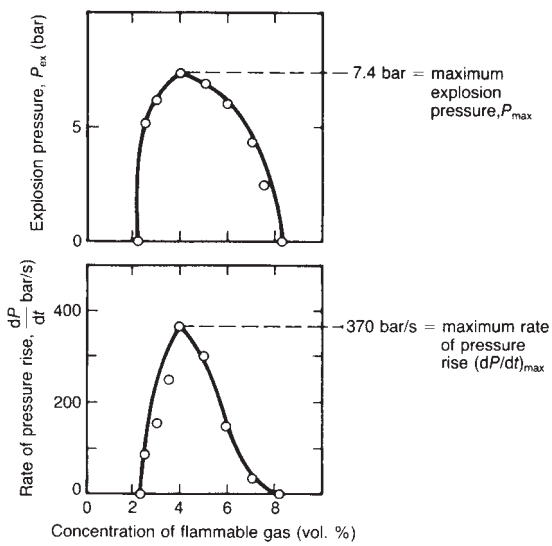

Figure 17.11 *Explosions in closed vessels: effect of gas concentration (Bartknecht, 1981a) (Courtesy of Springer-Verlag)*

vessel. The maximum pressure, though, tends to be less. However, for initial pressures greater than atmospheric, both parameters are enhanced by elongation, as described below.

If the initial pressure is atmospheric, most fuels give a maximum explosion pressure of 8–9 bara.

Both the maximum pressure and rate of pressure rise have maximum values at a fuel concentration close to the stoichiometric value, and decrease as the concentration moves away from this towards the explosibility limits. The effect is shown in Figure 17.11.

If the vessel is only partially filled by the fuel–air mixture, the maximum pressure varies in an approximately linear manner with the fractional fill.

In compact vessels over a limited range of initial pressure the maximum pressure increases linearly with the initial pressure. The rate of rise of pressure is a function of the initial pressure. One set of relations for this are those of Nagy and Verakis which are given below.

In elongated vessels the effect of initial pressure is different, as shown in Figure 17.12, smaller for a spherical vessel and larger for an elongated one. At atmospheric pressure the maximum explosion pressure in the larger vessel is slightly less than that in the smaller one, but at higher initial pressures it is much greater. The maximum rate of pressure rise should be less in the larger vessel, but it is actually higher.

The initial temperature affects the maximum pressure, the rate of pressure rise and the final temperature. The maximum pressure decrease as the initial temperature increases is due to the decrease in density of the fuel–air mixture. The following equation has been used to fit some experimental results

$$\frac{P_m}{P_o} = k_1 + \frac{k_2}{T_o} \qquad [17.7.2]$$

where P is the absolute pressure and T is the absolute temperature, the subscripts m and o denote maximum and initial, respectively, and k_1 and k_2 are constants. The rate of pressure rise is essentially independent of the initial temperature, because there are two opposing effects, the lower expansion ratio and the faster burning rate. The final temperature T_e increases linearly with the initial temperature:

$$T_e = k_3 + k_4 T_o \qquad [17.7.3]$$

where k_3 and k_4 are constants.

For compact vessels the initial turbulence has only a slight effect on the maximum pressure, but has a strong effect on the rate of pressure rise. This is illustrated in Figure 17.13. Turbulence increases the flame speed. Nagy and Verakis describe experiments on methane–air mixtures where turbulence was created by injecting the fuel–air mixture. In the concentration range 8–12% the effective burning velocity increased by a factor of 5. This factor is generally known as the coefficient of turbulence α. At lower concentrations a value of 8 was obtained for α. For elongated vessels initial turbulence can affect the maximum pressure.

Scheuermann (1994) has described work on the modelling of turbulence relevant to explosions of gas or dust in closed or vented vessels. He correlates the ratio of the laminar and turbulent burning velocities in terms of the velocity component u'.

In a spherical vessel the location of the ignition source has a slight effect on the maximum pressure, but a marked effect on the rate of pressure rise. The rate of pressure rise is greatest for central ignition. The rate of pressure rise increases with the strength of the ignition source.

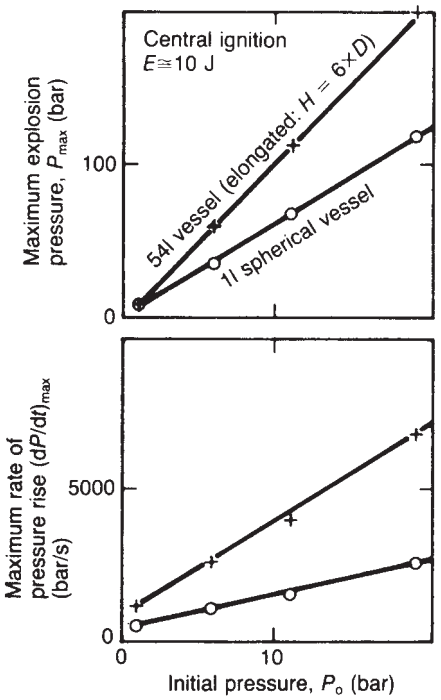

Figure 17.12 *Explosions in closed vessels: effect of initial pressure (Bartknecht, 1981a): methane in a 1 l spherical vessel and in a 54 l elongated vessel (HID = 6) (Courtesy of Springer-Verlag)*

17.7.4 Modelling of closed vessel explosions

The principal case considered is deflagration in a closed spherical vessel. Treatments of the problem typically produce relations for the pressure P, the rate of change of pressure (dP/dt), the radius r_b of the burned gas core, the rate of change of this radius (dr_b/dt) and the burning velocity S_u.

17.7.5 Elementary relations

These treatments make use of certain common relations and before describing the principal models it is convenient

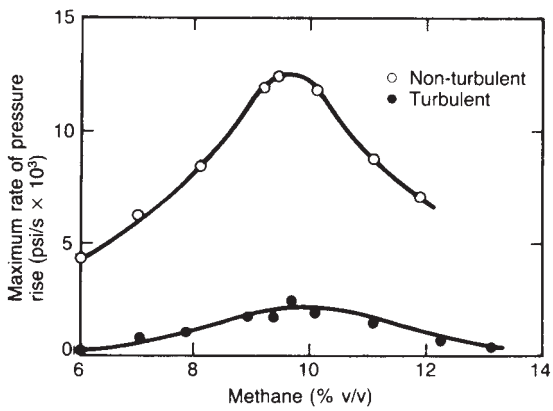

Figure 17.13 *Explosions in closed vessels: effect of initial turbulence (Nagy and Verakis, 1983)*

to give some of these relations. For combustion of a flammable gas mixture in a spherical vessel

$$V_o = V_u + V_b \quad [17.7.4]$$

$$m_o = m_u + m_b = m_u n_u + m_b n_b \quad [17.4.5]$$

$$m_o = V_o \rho_o \quad [17.7.6]$$

$$m_u = V_u \rho_u \quad [17.7.7]$$

$$m_b = V_b \rho_b \quad [17.7.8]$$

$$n_u = \frac{m_u}{M_u} \quad [17.7.9]$$

$$n_b = \frac{m_b}{M_b} \quad [17.7.10]$$

$$dV_b = -dV_u \quad [17.7.11]$$

$$dm_b = -dm_u \quad [17.7.12]$$

$$V_o = \frac{4\pi R_o^3}{3} \quad [17.7.13]$$

$$V_i = \frac{4\pi r_i^3}{3} \quad [17.7.14]$$

$$V_b = \frac{4\pi r_b^3}{3} \quad [17.7.15]$$

$$n = \frac{m_b}{m_o} \quad [17.7.16]$$

$$1 - n = \frac{m_u}{m_o} \quad [17.7.17]$$

$$n = \frac{V_i}{V_o} = \frac{r_i^3}{R_o^3} \quad [17.7.18]$$

$$\frac{dn_b}{dt} = -\frac{m_u}{m_b}\frac{dn_u}{dt} \quad [17.7.19]$$

Since some authors work in mass terms and others in molar terms, the gas laws are needed in both forms. For mass specific volume v and molar specific volume ν

$$Pv = \frac{RT}{M} \quad [17.7.20]$$

$$= R_g T \quad [17.7.21]$$

$$R_g = \frac{R}{M} \quad [17.7.22]$$

$$P\nu = RT \quad [17.7.23]$$

For the total volume V

$$PV = \frac{mRT}{M} \quad [17.7.23]$$

$$PV = mR_g T \quad [17.7.24]$$

$$PV = n_j RT \quad [17.7.25]$$

and specifically

$$PV_o = n_o RT \quad [17.7.26]$$

$$PV_u = n_u RT_u \quad [17.7.27]$$

$$PV_b = n_b RT_b \quad [17.7.28]$$

$$\rho = \frac{1}{v} \quad [17.7.29]$$

For the compression of gas

$$Pv^\gamma = \text{ constant} \quad [17.7.30]$$

$$P\rho^{-\gamma} = \text{constant} \quad [17.7.31]$$

$$TP^{(1-\gamma)/\gamma} = \text{constant} \quad [17.7.32]$$

$$RTP^{(1-\gamma)/\gamma} = \text{constant} = F \quad [17.7.33]$$

$$PV^{1/\gamma} = \text{constant} = F \quad [17.7.34]$$

For a spherical flame front

$$A_n = 4\pi r_b^2 \quad [17.7.35]$$

$$\frac{dV_b}{dr_b} = A_f \quad [17.7.36]$$

$$\frac{dm_b}{dt} = A_f \rho_u S_u \quad [17.7.37]$$

$$\frac{dr_b}{dt} = S_f \quad [17.7.38]$$

$$S_f = u_u + S_u \quad [17.7.39]$$

$$S_f = E S_u \quad [17.7.40]$$

$$E = \frac{\rho_u}{\rho_b} = \frac{n_b}{n_u}\frac{T_b}{T_i} \quad [17.7.41a]$$

where a is the radius of the spherical vessel, A_f is the area of the flame front, E is the expansion ratio, m is the mass of gas, M is the molecular weight, η is the fractional degree of combustion, n (with subscript) is the number of moles of gas, P is the absolute pressure, r is the radius, R is the universal gas constant, R_g is the mass basis gas constant, S_f is the flame speed, S_u is the burning velocity, t is time, T is the absolute temperature, m_u is the velocity of the unburned gas into the flame front, v is the specific mass volume of the gas, V is the total volume, γ is the ratio of gas specific heats, ν is the specific molar volume of the gas, ρ is the mass density and the subscripts b, o and u denote burned, initial and unburned, respectively. V_0 is the volume of the vessel and m_0 the mass of gas in the vessel. The subscript i refers to the initial state of the burned gas and j to any gas state. The area A_n is the ideal (geometric) area normal to the flame direction. The actual flame area of the wrinkle and folding flame front, A_f, is a multiple α (where $\alpha > 1$) of A_n. Expanding the definition of the expansion ration, E, Equation 17.7.41 using Equation 17.7.7 and 17.7.8:

$$E = \frac{m_u}{V_u}\frac{V_b}{m_b} \quad [17.7.41b]$$

Substituting for volume from the ideal gas law, Equation 17.7.23

$$\frac{V_b}{V_u} = \frac{m_b}{m_u}\frac{T_b}{T_u}\frac{M_u}{M_b}\frac{P_o}{P_b} \qquad [17.7.41c]$$

gives

$$E = \frac{M_u}{M_b}\frac{T_b}{T_u}\frac{P_o}{P_b} \qquad [17.7.41d]$$

In an unconfined explosion, approximated by a vented enclosed explosion, the pressure ratio P_o/P_b is approximately unity and E is approximately:

$$E \cong \frac{M_u}{M_b}\frac{T_b}{T_u} \qquad [17.7.41e]$$

The molecular weights of burned and unburned gases are constant, as are the initial temperature and adiabatic flame temperature, so the expansion ratio is constant in a constant pressure explosion.

Use is also made of the approximations

$$r_b = S_f t \qquad [17.7.42]$$

$$E^2(E-1) \cong E^3 \qquad [17.7.43]$$

17.7.6 Zabetakis model

Zabetakis (1965 BM Bull. 627) has given the following equation for the pressure rise resulting from combustion in a closed spherical vessel:

$$\frac{\Delta P}{P_o} = \frac{K S_u^3 t^3}{V} \qquad [17.7.44]$$

with

$$\Delta P = P - P_o \qquad [17.7.45]$$

where K is a constant. Hence,

$$\frac{P}{P_o} = 1 + \frac{K S_u^3 t^3}{V} \qquad [17.7.46]$$

According to Nagy and Verakis, Equation 17.7.44 is in the first instance an empirical one, but both they and other workers have derived it theoretically, as described below. Differentiating Equation 17.7.46 gives

$$\frac{dP}{dt} = \frac{3KP_o S_u^3 t^2}{V} \qquad [17.7.47]$$

For a given explosion pressure $t \propto V^{1/3}$ and hence

$$\left(\frac{dP}{dt}\right) V^{1/3} = \text{constant} \qquad [17.7.48a]$$

$$= K_G \qquad [17.7.48b]$$

Equations 17.7.48 are usually applied to $(dP/dt)_{max}$ but are strictly applicable only where (dP/dt) is measured at the same pressure in each volume.

17.7.7 Flamm and Mache model

In one of the earliest treatments of the problem, Flamm and Mache (1917) derived the equation

$$1 - n = \frac{RT_o}{RT_u(\gamma_b - \gamma_u)/(\gamma_u - 1) + K(\gamma_b - 1)}\frac{P_e - P}{P_o} \qquad [17.7.49]$$

where K is a constant and the subscript e denotes the end.

17.7.8 Flock and Marvin model

Fiock and Marvin (1937a,b) derived the following equation for the burning velocity:

$$S_u = \frac{dr_b}{dt} - \frac{a^3 - r_b^3}{3P\gamma_u r_b^2}\frac{dP}{dt} \qquad [17.7.50]$$

17.7.9 Lewis and von Elbe model

Another early treatment was that of B. Lewis and von Elbe (1951) (also Manton, von Elbe and Lewis, 1953). Starting with Equation 17.7.33 and the relation

$$V_o = \frac{R}{P}\left(n_e \int_0^n T_{bP}\, dn + n_o T_u (1-n)\right) \qquad [17.7.51]$$

where T_{bP} is the absolute temperature corresponding to pressure P, they derive Equation 17.7.49 of Flamm and Mache.

Then, from Equation 17.7.49 for $n = 0$, $T_u = T_o$ and $P = P_o$ and noting that for practical cases

$$RT_o(\gamma_b - \gamma_u)/(\gamma_u - 1) << K(\gamma_b - 1) \qquad [17.7.52]$$

they derive the following approximation

$$n = \frac{P - P_o}{P_e - P_o} \qquad [17.7.53]$$

Equation 17.7.53 is often used in the differential form

$$\frac{dn}{dt} = \frac{1}{P_e - P_o}\frac{dP}{dt} \qquad [17.7.54]$$

For the burned gas core they define two radii: r_i the radium before ignition of the gas and r_b the radius after expansion. Then utilizing Equation 17.7.19 for the radius before expansion

$$r_i = a\left(\frac{P - P_o}{P_e - P_o}\right)^{1/3} \qquad [17.7.55]$$

and utilizing Equations 17.7.17 and 17.7.27 for the radius after expansion

$$V_u = \frac{n_o R T_u (1-n)}{P} \qquad [17.7.56]$$

$$r_b = a\left(1 - \frac{P_o T_u}{P T_o}(1-n)\right)^{1/3} \qquad [17.7.57]$$

$$r_b = a\left[1 - \frac{P_o T_u}{P T_o}\left(\frac{P_e - P}{P_e - P_o}\right)\right]^{1/3} \qquad [17.7.58]$$

with

$$T_u = T_o\left(\frac{P}{P_o}\right)^{(\gamma_u - 1)/\gamma_u} \qquad [17.7.59]$$

For the burning velocity, the volume of an element of the shell of the burned gas core before expansion is

$$4\pi r_i^2\, dr_i \qquad [17.7.60]$$

at P_i and T_i, and the volume after expansion is

$$4\pi r_i^2\, dr_i \left(\frac{T_u P_o}{T_o P}\right) \qquad [17.7.61]$$

But this volume is also equal to

$$4\pi r_b^2 S_u \, dt \qquad [17.7.62]$$

Equating Equations 17.7.61 and 17.7.62 and applying Equation 17.7.59

$$S_u = \left(\frac{r_i}{r_b}\right)^2 \left(\frac{P_o}{P}\right)^{1/\gamma_u} \frac{dr_i}{dt} \qquad [17.7.63]$$

17.7.10 O'Donovan and Rallis model

The following treatment by O'Donovan and Rallis (1959) supplements those of the last two sets of workers. From Equations 17.7.17, 17.7.24 and 17.7.32

$$V_u = V_o(1-n)\left(\frac{P_o}{P}\right)^{1/\gamma_u} \qquad [17.7.64]$$

From Equations 17.7.15 and 17.7.64

$$V_b = V_o\left[1-(1-n)\left(\frac{P_o}{P}\right)^{1/\gamma_u}\right] \qquad [17.7.65]$$

$$r_b = a\left[1-(1-n)\left(\frac{P_o}{P}\right)^{1/\gamma_u}\right]^{1/3} \qquad [17.7.66]$$

or rearranging Equation 17.7.66

$$n = 1-\left(1-\frac{r_b^3}{a^3}\right)\left(\frac{P_o}{P}\right)^{1/\gamma_u} \qquad [17.7.67]$$

Equating the volume rate of change of the unburned gas passing through the flame front with that of the unburned gas in its actual state of adibiatic compression

$$4\pi r_b^2 S_u = 4\pi r_i^2 \left(\frac{dr_i}{dt}\right)\left(\frac{T_u P_o}{T_o P}\right) \qquad [17.7.68]$$

Hence

$$S_u = \frac{dr_i}{dt}\left(\frac{r_i}{r_b}\right)^2 \left(\frac{P_o}{P}\right)^{1/\gamma_u} \qquad [17.7.69]$$

Also from Equation 17.7.19

$$\frac{dn}{dt} = \frac{3r_i^2}{a^3}\frac{dr_i}{dt} \qquad [17.7.70]$$

From Equations 17.7.69 and 17.7.70

$$S_u = \frac{a^3}{3r_b^2}\left(\frac{P_o}{P}\right)^{1/r_u}\frac{dn}{dt} \qquad [17.7.71]$$

Then noting that in Equation 17.7.67 both r_b and P are functions of time and differentiating n in that equation with respect to t and substituting for dn/dt in Equation 17.7.71 gives Equation 17.7.50 of Fiock and Marvin.

17.7.11 Nagy and Verakis model

Nagy and Verakis (1983) give treatments for both ideal gas and adiabatic expansion. Their starting point is the rate of production of the burned mass. Assuming $M_b = M_u$,

$$\frac{dn_b}{dt} = \frac{\alpha A_t S_u P}{RT_u} \qquad [17.7.72]$$

where α is a flame area factor which allows for the difference between the nominal area of the flame front and the actual area, which is higher due to flame wrinkling. Also

$$\frac{M_b}{M_u}\frac{T_u}{T_b} = \frac{P_o}{P_e} \qquad [17.7.73]$$

From Equations 17.7.27 and 17.7.28, differentiating with respect to t and assuming $M_b = M_u$ so that $dn_u/dt = -dn_b/dt$

$$V\frac{dP}{dt} = \frac{dn_b}{dt}(RT_b - RT_u) \qquad [17.7.74]$$

From Equations 17.7.72–17.7.74

$$\frac{dP}{dt} = \frac{\alpha A_f S_u P(P_e - P_o)}{VP_o} \qquad [17.7.75]$$

In order to integrate Equation 17.7.75 it is necessary to express A_f as a function of P. From Equations 17.7.15 and 17.7.35

$$A_f = 4_\pi\left(\frac{3V_b}{4\pi}\right)^{2/3} \qquad [17.7.76]$$

and from Equations 17.7.5, 17.7.9, 17.7.10, 17.7.27 and 17.7.28 and again assuming $M_b = M_u$ so that $n_0 = n_u + n_b$

$$V_b = V\frac{1-P_o/P}{1-P_o/P_e} \qquad [17.7.77]$$

From Equations 17.7.75, 17.7.76 and 17.7.77

$$\frac{dP}{dt} = \frac{\alpha S_u P_e^{2/3}}{VP_o}(P_e - P_o)^{1/3}(1-P_o/P)^{2/3}P \qquad [17.7.78]$$

Integration of Equation 17.7.78 is difficult, but an approximate solution over a limited range is

$$P = P_o + (P_e - P_o)\left(\frac{P_e}{P_o}\right)^2\left(\frac{\alpha S_u t}{3V}\right)^3, \quad P_o \le P \le 2P_o \qquad [17.7.79]$$

Equation 17.7.79 is similar to Equation 17.7.46 of Zabetakis. Equating the two equations gives the value of the constant K in the latter equation as

$$K = \frac{4}{3}\frac{\pi}{P_o}(P_e - P_o)\left(\frac{P_e}{P_o}\right)^2 \qquad [17.7.80]$$

The authors also treat the adiabatic case, which leads to rather complex relationships.

17.7.12 Model of Perlee, Fuller and Saul

Perlee, Fuller and Saul (1974 BM RI 7839) have derived Equation 17.7.46 and have determined the value of the constant K. Differentiating Equation 17.7.27 with respect to n_b and Equation 17.7.28 with respect to n_b

$$V_u\,dP + P\,dV_u = RT_u\,dn_u + Rn_u\,dT_u \qquad [17.7.81]$$

$$V_b\,dP + P\,dV_b = RT_b\,dn_b + Rn_b\,dT_b \qquad [17.7.82]$$

Hence

$$dP[V_o(1-\alpha_u) + V_b(\alpha_u - \alpha_b)] = -R\left[T_b - T_u\left(\frac{M_b}{M_u}\right)\right]dn_u \qquad [17.7.83]$$

with

$$\alpha_u = \frac{\gamma_u - 1}{\gamma_u} \quad [17.7.84]$$

$$\alpha_b = \frac{\gamma_b - 1}{\gamma_b} \quad [17.7.85]$$

But from Equations 17.7.9, 17.7.12, 17.7.35 and 17.7.37

$$\frac{dn_u}{dt} = -4\pi r_b^2 \frac{\rho_u S_u}{M_u} \quad [17.7.86]$$

Then from Equations 17.7.83 and 17.7.86

$$\frac{dP}{dt} = \frac{3\gamma_u P(E-1)S_u r_b^2}{a^3 + r_b^3\left(\frac{\gamma_u}{\gamma_b} - 1\right)} \quad [17.7.87]$$

with E as defined by Equation 17.7.41 or alternatively

$$E = \frac{M_u T_b}{M_b T_u} \quad [17.7.88]$$

then from Equations 17.7.40, 17.7.42 and 17.7.87

$$\frac{d\ln P}{dt} = \frac{3\gamma_u P(E-1)}{a}\left(\frac{S_u E t}{a}\right)^2 S_u \quad [17.7.89]$$

Integrating Equation 17.7.89

$$\ln\left(\frac{P}{P_o}\right) = \gamma_u E^2(E-1)\left(\frac{S_u}{a}\right)^3 t^3 \quad [17.7.90]$$

Introducing the approximation

$$\ln\left(\frac{P_o + \Delta P}{P_o}\right) \approx \frac{\Delta P}{P_o} \quad [17.7.91]$$

$$\frac{\Delta P}{P_o} = \gamma_u E^2(E-1)\left(\frac{S_u}{a}\right)^3 t^3 \quad [17.7.92]$$

$$= \frac{K S_u^3 t^3}{V} \quad [17.7.93]$$

with

$$K = \frac{4}{3}\pi E^2(E-1)\gamma_u \quad [17.7.94]$$

17.7.13 Harris model

An alternative relation for the rate of pressure rise is derived by R.J. Harris (1983). From Equations 17.7.8 and 17.7.37 where r_s is the radius of the vessel

$$V_b\frac{d\rho_b}{dt} + \rho_b\frac{dV_b}{dt} = A_f\rho_u S_u \quad [17.7.95]$$

$$\frac{dV_b}{dt} = \frac{dV_b}{dr_b}\frac{dr_b}{dt} = 4\pi r_b^2\frac{dr_b}{dt} = A_n S_f \quad [17.7.96]$$

Then from Equations 17.7.36, 17.7.38, and 17.7.95

$$V_b\frac{d\rho_b}{dt} + \rho_b A_n S_f = A_f\rho_u S_u \quad [17.7.97]$$

But initially dP/dt is small and so is $d\rho_b/dt$. Hence Equation 17.7.97 reduces to

$$S_f = \alpha\left(\frac{\rho_u}{\rho_b}\right)S_u \quad [17.7.98]$$

$$= \alpha E S_u \quad [17.7.99]$$

which relates the flame speed to the burning velocity. The coefficient of turbulence, α, relates A_f to A_n.

Initially, when the pressure rise is low, it is possible to make the assumption that T_u and T_b are constant, termed by the author the isothermal assumption. Then differentiating Equations 17.7.27 and 17.7.28 and adding the resulting equations and utilizing Equation 17.7.4 and 17.7.12 gives

$$V\frac{dP}{dt} = \left(\frac{RT_b}{M_b} - \frac{RT_u}{M_u}\right)\frac{dm_b}{dt} \quad [17.7.100]$$

From Equations 17.7.7, 17.7.37, 17.7.27, 17.7.98 and 17.7.100

$$V\frac{dP}{dt} = A_f P(E-1)S_u \quad [17.7.101]$$

From Equations 17.7.35, 17.7.40, 17.7.42 and 17.7.101

$$\frac{dP}{dt} = \frac{4\pi P S_u^3 E^2(E-1)t^2}{V} \quad [17.7.102]$$

Integrating Equation 17.7.102

$$\frac{P}{P_o} = \exp\left(\frac{4\pi E^2(E-1)(\alpha S_u t)^3}{3V}\right) \quad [17.7.103]$$

For a spherical vessel of radius a:

$$\frac{P}{P_o} = \exp\left(\frac{E^2(E-1)}{r_s^3}(\alpha S_u t)^3\right) \quad [17.7.104]$$

17.7.14 Bradley and Mitcheson model

D. Bradley and Mitcheson (1976) derive what they call a universal expression for the rate of pressure rise. From Equations 17.7.8, 17.7.12, 17.7.35 and 17.7.37 they obtain for the unburned gas

$$\frac{d[(r_s^3 - r_b^3)\rho_u]}{dt} = -3r_b^2\rho_u S_u \quad [17.7.105]$$

and for the burned gas

$$\frac{d(r_b^3\rho_b)}{dt} = 3r_b^2\rho_u S_u \quad [17.7.106]$$

From Equations 17.7.31 and 17.7.105 it can be shown that

$$\frac{dP}{dt} = \frac{3r_b^2\gamma_u P}{r_s^3 - r_b^3}\left(\frac{dr_b}{dt} - S_u\right) \quad [17.7.107]$$

which can be rearranged to give Equation 17.7.50 of Fiock and Marvin (1937a,b).

From Equations 17.7.4, 17.7.5, 17.7.7, 17.7.12, 17.7.27, 17.7.31, 17.7.35 and 17.7.37 Bradley and Mitcheson derive

$$\frac{dP}{dt} = \frac{3S_u\rho_u}{r_s\rho_o}(P_e - P_o)\left[1 - \left(\frac{P_o}{P}\right)^{1/\gamma_u}\frac{P_e - P}{P_e - P_o}\right]^{2/3} \quad [17.7.108]$$

They also give Equation 17.7.108 in dimensionless universal equation.

17.7.15 Morton and Nettleton model

Morton and Nettleton (1977) give the following treatment. Consider an element of the burned gas shell of inner radius r and outer radius $r + \delta r$. If the shell is moving with velocity $u(r)$, then after time δt the inner radius is equal to

$$r + u\,dt \quad [17.7.109]$$

and the outer radius is equal to

$$r + \delta r + \left(u + \frac{\mathrm{d}u}{\mathrm{d}r}\delta r\right)\mathrm{d}t \qquad [17.7.110]$$

The initial volume of the element is

$$V = 4\pi r^2\ \delta r \qquad [17.7.111]$$

After time dt the area of the shell is

$$4\pi(r + u\ \mathrm{d}t)^2 \qquad [17.7.112]$$

and the thickness is

$$\left\{r + \delta r\left[u + \left(\frac{\mathrm{d}u}{\mathrm{d}r}\delta r\right)\right]\mathrm{d}t\right\} - (r + u\ \mathrm{d}t) \qquad [17.7.113a]$$

or

$$\delta r\left(1 + \frac{\mathrm{d}u}{\mathrm{d}r}\mathrm{d}t\right) \qquad [17.7.113b]$$

Subtracting the initial volume given by Equation 17.7.111 from the volume after the time increment dt given by Equations 17.7.112 and 17.7.113 gives

$$\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{\mathrm{d}u}{\mathrm{d}r} + \frac{2u}{r^2} \qquad [17.7.114]$$

By logarithmic differentiation of Equation 17.7.30

$$\frac{1}{P}\frac{\mathrm{d}P}{\mathrm{d}t} = -\gamma\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}t} \qquad [17.7.115]$$

Hence, from Equations 17.7.114 and 17.7.115

$$\frac{1}{P}\frac{\mathrm{d}P}{\mathrm{d}t} = -\gamma\left(\frac{\mathrm{d}u}{\mathrm{d}r} + \frac{2u}{r}\right) \qquad [17.7.116]$$

Integrating Equation 17.7.116 with the boundary conditions

$$r = a; \quad u_1 = 0 \qquad [17.7.117a]$$

$$r = 0; \quad u_2 = 0 \qquad [17.7.117b]$$

where the subscripts 1 and 2 denote unburned gas and burned gas, respectively, gives

$$u_1 = \frac{1}{3\gamma_1 P}\left(\frac{a^3 - r^3}{r^2}\right)\frac{\mathrm{d}P}{\mathrm{d}t} \qquad [17.7.118]$$

$$u_2 = \frac{-r}{3\gamma_2 P}\frac{\mathrm{d}P}{\mathrm{d}t} \qquad [17.7.119]$$

Now consider a stationary flame front with a flow of unburned mixture into the front and of burned mixture away from the front. By conservation of mass

$$u_1 - u_2 = (E - 1)S_\mathrm{u} \qquad [17.7.120]$$

From the definition of burning velocity S_u

$$\frac{\mathrm{d}r}{\mathrm{d}t} = u_1 + S_\mathrm{u} \qquad [17.7.121]$$

From Equations 17.7.118 and 17.7.121

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{3\gamma_1 P r^2}{a^3 - r^3}\left(\frac{\mathrm{d}r}{\mathrm{d}t} - S_\mathrm{u}\right) \qquad [17.7.122]$$

From Equations 17.7.118–17.7.120

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{3\gamma_1 P r^2 S_\mathrm{u}(E - 1)}{a^3 - (1 + \gamma_1/\gamma_2)r^3} \qquad [17.7.123]$$

Equating Equations 17.7.122 and 17.7.123 gives

$$\frac{\mathrm{d}r}{\mathrm{d}t} = \frac{ES_\mathrm{u}[a^3 - (1 + \gamma_1/E\gamma_2)r^3}{[a^3 - (1 - \gamma_1/\gamma_2)r^3} \qquad [17.7.124]$$

Then, from Equations 17.7.123 and 17.7.124

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \left(\frac{E - 1}{E}\right)\frac{3\gamma_1 P r^2}{[a^3 - (1 - \gamma/E\gamma_2)r^3]}\frac{\mathrm{d}r}{\mathrm{d}t} \qquad [17.7.125]$$

Integrating Equation 17.7.125 with the boundary condition

$$r = 0; \quad P = P_\mathrm{o} \qquad [17.7.126]$$

gives

$$\frac{P}{P_\mathrm{o}} = \left(\frac{a^3}{a^3 - (1 - \gamma_1/E\gamma_2)r^3}\right)^{\gamma_1(E-1)/(E-\gamma_1/\gamma_2)} \qquad [17.7.127]$$

The authors point out that their model is not formulated in terms of the rate of flame spread. It gives the maximum pressure as a function of the expansion ratio, but not explicitly of the burning velocity. However, the expansion ratio increases with burning velocity, since it increases with flame temperature, which in turn increases with burning velocity.

17.7.16 Fairweather and Vasey model

The Fairweather and Vassey model (1982) develops a full treatment of a transient explosion in a totally confined or vented enclosure. It treats spherical, cubical or rectangular enclosures. The authors'treatment of venting and transient pressure build-up with incomplete venting typifies an approach generally adapted subsequently (for example Yao, 1974). Although the model is thorough, it is not yet suitable as a basis for explosion vent sizing because it depends on an empirical treatment of flame speed and flame acceleration (Harris, 1983, p. 77).

The treatment by Fairweather and Vasey (1982) makes allowance for two features not usually taken into account. One is the fact that due to the existence of dissociation reactions the polytropic assumption, though valid for the unburned gas, is not valid for the burned gas. The other is heat loss to the vessel by radiation. They give the heat balance

$$m_\mathrm{u}U_\mathrm{u} + m_\mathrm{b}U_\mathrm{b} - Q = m_\mathrm{o}C_\mathrm{n} - m_\mathrm{u}C_\mathrm{n} \qquad [17.1.128]$$

with

$$U_\mathrm{u} = \frac{R(T_\mathrm{u} - T_\mathrm{o})}{(\gamma_\mathrm{u} - 1)M_\mathrm{u}} \qquad [17.7.129]$$

$$U_\mathrm{b} = h_\mathrm{b} - \frac{R(T_\mathrm{b} - T_\mathrm{o})}{M_\mathrm{b}} \qquad [17.7.130a]$$

where C_n is the calorific value of the mixture, h is the enthalpy, Q is the thermal energy lost from the burned products and U is the internal energy.

The heat loss, Q, is found by assuming that the gases and the surface of the vessel are grey bodies. The rate of heat loss as given by Hottel and Sarofim (1967) is:

$$\frac{dQ}{dt} = \frac{a_g A_b \sigma (T_b^4 - T_u^4)}{\left[\frac{a_g}{E_b} + \frac{A_b}{A_u}\left(\frac{1}{E_u} - 1\right)\right]} \quad [17.7.130b]$$

with

$$a_g = \frac{E_b^2}{2E_b - E_w} \quad [17.7.130c]$$

where E_b, E_u, and E_w are the emissivities of the burned gases, the unburned gases and the wall respectively and σ is the Stephan Boltzman constant. Equation 17.7.131 is integrated numerically and the heat balance Equation 17.7.128 is solved implicitly for the burned gas temperature, T_B.

The vent rate of burned and unburned gas is found from the ideal gas venting equations. At low pressure (when venting is adequate), P/P_o is less than the choke pressure ratio:

$$\frac{P}{P_o} < \left[\frac{1+\gamma}{2}\right]^{\gamma/\gamma-1} \quad [17.7.130d]$$

and venting flow m_v (split between burned, m_{bv} and unburned gases, m_{uv}) is subsonic and:

$$\frac{dm_v}{dt} = C_D A_V \left\{ \left[\frac{2\gamma P\rho}{\gamma - 1}\right] \left[\frac{P_o}{P}\right]^{2/\gamma} \left[1 - \left(\frac{P_o}{P}\right)^{(\gamma-1)/\gamma}\right] \right\}^{0.5} \quad [17.7.130e]$$

In the event that venting area is inadequate and the pressure in the enclosure exceeds the choke pressure; flow is sonic and:

$$\frac{dm_v}{dt} = C_D A_V \left\{ \gamma P\rho \left[\frac{\gamma+1}{2}\right] \frac{(1+\gamma)}{(1-\gamma)} \right\}^{0.5} \quad [17.7.130f]$$

The mass remaining in the enclosures at any time is:

$$m_u + m_b = m_o - (m_{uv} + m_{bv}) \quad [17.7.130g]$$

The pressure in the vessel is assumed equal for the burned and unburned gases. The pressure of the unburned gases is compressed isentropically from its original volume using:

$$V_u = V_o \frac{m_u}{m_o} \left(\frac{P}{P_o}\right)^{1/\gamma_u} \quad [17.7.130h]$$

$$\left(\frac{P}{P_o}\right)^{1/\gamma_u} = \frac{V_o}{V_u}\frac{m_u}{m_o} \quad [17.12.152]$$

The model is completed using the ideal gas equation of state 17.7.23 for the burned and unburned gases.

In order to determine the mass burning rate, the model must calculate the flame area, A_f, from the volume of burnt gas at each time step. Inside a rectangular box enclosure, when the spherical flame reaches the enclosure walls, the volume takes the form of a sphere minus truncated spherical caps. Once the flame reaches an enclosure edge where the walls join, the flame may be assumed to expand in cylindrical symmetry. This approach was used also by Chappell (1973) who maintained the flame radius constant at the point where the geometry changes. This procedure leads to a discontinuity in the pressure profile. This discontinuity need not occur if the burned volume is kept constant instead of the flame radius.

Treating the flame geometry as a truncated sphere allows finding the area burned and unburned gases passing the vent area. This is used to find the relative vent volume of burned and unburned gases.

17.7.17 Singh model

The foregoing models are for spherical vessels. A treatment which covers cylindrical geometries also has been given by J. Singh (1988b). From Equations 17.7.7, 17.7.12 and 17.7.37

$$\frac{dP}{dt} = -A_f S_u \left(\frac{dV_u}{dP} + \frac{V_u}{\rho_u}\frac{d\rho_u}{dP}\right)^{-1} \quad [17.7.131]$$

By logarithmic differentiation of Equation 17.7.31

$$\frac{d\rho}{dP} = \frac{\rho}{\gamma P} \quad [17.7.132]$$

Hence from Equations 17.7.131 and 17.7.132

$$\frac{dP}{dt} = -A_f S_u \left(\frac{V_u}{\gamma_u P} + \frac{dV_u}{dP}\right)^{-1} \quad [17.7.133]$$

Equations 17.7.6, 17.7.7, 17.7.17 and 17.7.31, writing the latter in the form

$$\frac{\rho_o}{\rho_u} = \left(\frac{P_o}{P}\right)^a \quad [17.7.134]$$

with

$$a = \frac{1}{\gamma_u} \quad [17.7.135]$$

yield

$$V_u = V_o(1-n)\left(\frac{P_o}{P}\right)^a \quad [17.7.136]$$

Differentiating Equation 17.7.136 with respect to P and combining the result with Equation 17.7.133 gives

$$\frac{dP}{dt} = \frac{A_f S_u}{V_o}\left(\frac{P_o}{P}\right)^{-a}\left(\frac{dn}{dP}\right)^{-1} \quad [17.7.137]$$

In order to solve Equation 17.7.137 it is necessary to have a relation between P and n. A simple approach is to use Equations 17.7.4, 17.7.6, 17.7.8 and 17.7.16, which gives

$$V_u = V_o(1 - n/\alpha) \quad [17.7.138]$$

with

$$\alpha = \rho_b/\rho_o \quad [17.7.139]$$

Then, from Equations 17.7.136 and 17.7.138

$$n = \alpha\left(\frac{(P/P_o)^a - 1}{\alpha(P/P_o)^a - \alpha}\right) \quad [17.7.140]$$

There remains, however, a difficulty in that ρ_b, and hence a, varies throughout the burnt gas region. Again, it is necessary to adopt a simplified approach. From Equations 17.7.23b for the burnt gas

$$\rho_b = \left(\frac{\bar{M}_b P}{R\bar{T}_b}\right) \quad [17.7.141]$$

and for gas at the end of combustion

$$\rho_e = \left(\frac{\bar{M}_e P_e}{R\bar{T}_e}\right) \quad [17.7.142]$$

where $\bar{M}$ is the mean molecular weight.

Hence from Equation 17.7.139 and noting that for a closed volume $\rho_b = \rho_e$

$$\alpha = \left(\frac{\bar{M}_b \bar{T}_e P}{\bar{M}_e \bar{T}_b P_e}\right) \quad [17.7.143]$$

One simplification of Equation 17.7.143, where $\bar{M}_b \simeq \bar{M}_e$, is

$$\alpha = \left(\frac{\bar{T}_e P}{\bar{T}_b P_e}\right) \quad [17.7.144]$$

In fact the values of n obtained from Equation 17.7.144 differ only slightly from those obtained from the further simplification

$$\alpha \cong \frac{P}{P_e} \quad [17.7.145]$$

Then, from Equations 17.7.140 and 17.7.145

$$n = \left(\frac{P}{P_e}\right)\left(\frac{(P/P_o)^a - 1}{(P/P_o)^a - (P/P_e)}\right) \quad [17.7.146]$$

So far the treatment is general with respect to vessel geometry. For a specific geometry it is necessary to characterize the area of the flame front A_f. Consider first combustion in a spherical vessel. For this case

$$\left(\frac{r_b}{r_s}\right)^3 = \left(\frac{V_b}{V_o}\right) \quad [17.7.147]$$

Combining Equations 17.7.4, 17.7.136 and 17.7.147

$$r_b = r_s\left[1 - (1-n)\left(\frac{P_o}{P}\right)^a\right]^{1/3} \quad [17.7.148]$$

From Equation 17.7.137

$$S_u = \frac{V_o}{A_f}\left(\frac{P_o}{P}\right)^a \left(\frac{dn}{dP}\right)\left(\frac{dP}{dt}\right) \quad [17.7.149]$$

Then, from Equations 17.7.148 and 17.7.149

$$S_u = \frac{r_s (P_o/P)^a}{3[1-(1-n)(P_o/P)^a]^{2/3}}\left(\frac{dn}{dP}\right)\left(\frac{dP}{dt}\right) \quad [17.7.150]$$

For combustion in a cylindrical vessel Singh considers a vessel length L and radius r_c, where $L > r_c$. He distinguishes between central ignition and end ignition, and for each of these cases takes a two-stage approach. For combustion in a cylindrical vessel with central ignition he gives the following treatment. Initially, the flame expands symmetrically in all directions. When the radius r_b, of the flame is approximately equal to the radius r_c of the vessel, the flames begins to distort. It is assumed that the flame front then separates into two parts and that these two parts of the flame front then travel as two hemispherical shells of radius r_c in opposite directions until they reach the ends of the cylinder. For the first stage of this process substituting for n from Equation 17.7.146 into Equation 17.7.150 gives

$$\frac{d\bar{P}}{d\bar{t}} = G_1 P^{-a}\left\{1 - \bar{P}^{-a}\left[1 - \frac{\bar{P}}{\bar{P}_e}\left(\frac{\bar{P}^a - 1}{\bar{P}^a - \bar{P}/\bar{P}_e}\right)\right]\right\}^{2/3}\left(\frac{dn}{d\bar{P}}\right)^{-1} \quad [17.7.151]$$

and

$$\frac{dn}{d\bar{P}} = \left[\left(\frac{\bar{P}}{\bar{P}_e}\right)\frac{a(\bar{P} - \bar{P}/\bar{P}_e)\bar{P}^{(a-1)} - (\bar{P}^a - 1)(a\bar{P}^{(a-1)} - 1/\bar{P}_e}{(\bar{P}^a - \bar{P}/\bar{P}_e)^2}\right] + \left[\frac{1}{\bar{P}_e}\left(\frac{\bar{P}^{-a} - 1}{\bar{P}^a - \bar{P}/\bar{P}_e}\right)\right] \quad [17.7.152]$$

with

$$\bar{P} = \frac{P}{P_o} \quad [17.7.153]$$

$$\bar{P}_e = \frac{P_e}{P_o} \quad [17.7.154]$$

$$\bar{t} = \frac{tS_u}{r_s} \quad [17.7.155]$$

$$G_1 = 3 \quad [17.7.156]$$

where the overbar denotes 'dimensionless'. Transition from the first stage to the second stage occurs at pressure $\bar{P}_x$ such that

$$r_b = G_2 r_s\left(\frac{\bar{P}_x^a - 1}{\bar{P}_x^a - \bar{P}_x/\bar{P}_e}\right)^{1/3} \quad [17.7.157a]$$

$$= r_c \quad [17.7.157b]$$

with

$$G_2 = 1 \quad [17.7.158]$$

where now r_s is the radius of the sphere equal in volume to the cylinder. Hence

$$r_s = \left(\frac{3r_c^2 L}{4}\right)^{1/3} \quad [17.7.159]$$

For the second stage the total flame area is

$$A_f = 4\pi r_c^2 \quad [17.7.160]$$

Also

$$V_o = \pi r_c^2 L \quad [17.7.161]$$

Then, from Equations 17.7.53, 17.7.137, 17.7.160 and 17.7.161

$$\frac{dP}{dt} = \frac{4S_u}{L}(P_e - P_o)\left(\frac{P_o}{P}\right)^{-a} \quad [17.7.162]$$

Integrating Equation 17.7.162 gives

$$\bar{t} = \frac{(L/r_s)\bar{P}^{(1-a)}}{G_3(\bar{P}_e - 1)(1-a)} + \frac{S_u K_1}{r_s} \quad [17.7.163]$$

with

$$G_3 = 4 \quad [17.7.164]$$

for central ignition. The constant K_1 satisfies the condition that transition occurs at time $\bar{t}_x$ where the latter is obtained from Equation 17.7.151. The treatment for a cylindrical vessel with end ignition is similar. In this case

$$\left(\frac{r_b}{r_s}\right)^3 = \left(\frac{2V_b}{V_o}\right) \quad [17.7.165]$$

and hence

$$r_b = 2^{1/3} r_s \left[1 - (1-n)\left(\frac{P_o}{P}\right)^a\right]^{1/3} \quad [17.7.166]$$

Equations 17.7.151 and 17.7.157 apply but with

$$G_1 = 3/2^{1/3} \quad [17.7.167]$$

$$G_2 = 2^{1/3} \quad [17.7.168]$$

For the second stage the total area of the flame is

$$A_f = 2\pi r_c^2 \quad [17.7.169]$$

Hence

$$\frac{dP}{dt} = \frac{2S_u}{L}(P_e - P_o)\left(\frac{P_o}{P}\right)^{-a} \quad [17.7.170]$$

For transition, Equation 17.7.163 applies but with

$$G_3 = 2 \quad [17.7.171]$$

17.8 Explosions in Buildings

Many process plants are in buildings. It is also necessary, therefore, to consider explosions occurring inside buildings.

A leak of flammable gas or liquid may create a flammable atmosphere inside a building and give rise to an explosion. Such leaks may occur from plant processing flammable fluids, from activities involving such fluids or from fuel gas supplies. In enclosed conditions, dispersion of the leaked gas is poor and the hazard is therefore much enhanced.

An area of prime concern in respect of explosions in buildings is the hazard of gas explosions in dwellings, and much of the work done relates to this. An account is given in *Gas Explosions in Buildings and Heating Plant* (R.J. Harris, 1983).

17.8.1 Building explosion incidents

Statistical information on the hazard of explosions in buildings has been given by F. Morton (1970), Mainstone (1973 BRE CP 11/73, 1974 BRE BR9, 1983 BRE CP 2/83) and Taylor and Alexander (1974 BRE CP 45/74).

A number of case histories of building explosions have been described by Mainstone (1976 BRE CP 24/76). One of the most severe building explosions was that at Ronan Point in 1968, which was the subject of an official report (H. Griffiths *et al.,* 1968).

Analyses of the factors bearing on gas explosions in buildings have been given by Mainstone (1973 BRE CP 11/73, 1976 BRE CP 24/76) and Taylor and Alexander (1974 BRE CP 45/74).

17.8.2 Ventilation of buildings

Movement of air in a building may be due to natural or forced draught ventilation. Natural draught ventilation may be either thermal driven or wind driven. In the former case the movement of air is caused by the temperature difference between the inside and the outside of the building, while in the latter it is caused by the pressure of the wind on the side of the building.

General guidance on natural ventilation is given in BS 5925: 1991 *Code of Practice: Ventilation Principles and Designing for Natural Ventilation*. Typical natural ventilation rates are in the range 0.5–3 air changes per hour.

Guidance on ventilation in relation to flammable and toxic gases is given by Leach and Bloomfield (1973, 1974 BRE CP 36/74).

For forced draught ventilation, guidance is given in BS 5720: 1979 *Code of Practice for Mechanical Ventilation and Air Conditioning in Buildings*. Forced draught ventilation is provided by fans. With forced draught ventilation rates can be not only higher but more dependable.

Human comfort sets a limit to the ventilation rate which can be used under normal conditions. A typical rule of thumb is that the upper limit of the air velocity for comfort is about 0.5 m/s.

There is no reason, however, why the ventilation rate should be limited to a low level in an emergency. In such a situation additional ventilation may be brought into play.

A more detailed discussion of ventilation is given in Chapter 10.

17.8.3 Gas accumulation and mixing in buildings

If a leak occurs, the part of the enclosure which is affected depends on the density of the gas, the height of the leak source and the ventilation pattern. The normal ventilation pattern is upward flow. Harris describes experimental work which shows that with this ventilation pattern for a gas with a density lighter than air, such as methane, a high gas concentration tends to build up in the space above the leak source. This situation is illustrated in Figure 17.14.

If the ventilation pattern is downward flow, which is rather unusual, this situation no longer pertains, and high gas concentration can occur below the leak source.

For a gas with a density heavier than air with an upward ventilation pattern the buoyancy and the ventilation act in oppositive directions, and in this case a high concentration will tend to build up in the whole space.

Thus, for the normal arrangement of upward flow ventilation the space liable to have a high gas concentration should be taken as the space above the leak for a light gas and as the whole space for other gases.

For practical purposes, the space liable to have a high concentration may be assumed to be perfectly mixed, and the gas concentration in the space may be determined from the equation for a single, perfectly mixed stage, which may be written for this case as

$$\tau \frac{dC}{dt} = C_i - C \quad [17.8.1]$$

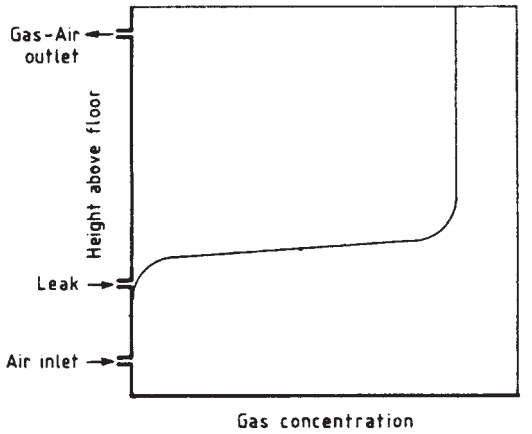

Figure 17.14 *Concentration from a leak of gas lighter than air under conditions of upward ventilation (after R. J. Harris, 1983) (courtesy of British Gas)*

with

$$C_i = Q_g/Q \quad [17.8.2]$$

$$Q = Q_g + Q_a \quad [17.8.3]$$

$$\tau = V/Q \quad [17.8.4]$$

where C is the volumetric concentration in the space, C_i is an effective inlet volumetric concentration defined by Equation 17.8.2, Q is the total volumetric flow rate, Q_a is the volumetric flow of air, Q_g is the volumetric flow of contaminant gas, t is the time, V is the volume of the space and τ is the volume/throughput ratio, or time constant.

Then for an increase in concentration starting from the time of release

$$\frac{C}{C_i} = 1 - \exp\left(-\frac{t}{\tau}\right) \quad [17.8.5]$$

and for a decrease in concentration starting from cessation of the release with a concentration C_o at that time

$$\frac{C}{C_o} = \exp\left(-\frac{t}{\tau}\right) \quad [17.8.6]$$

In this latter case the value of Q to be used in Equation 17.8.3 is $Q = Q_a$, since $Q_g = 0$.

17.8.4 Some structural features of buildings

Much of the work done on explosions in closed containments applies to vessels. There are some significant differences between vessels and buildings.

A building is generally rectangular in shape and the volume enclosed is relatively large. The increase in size and in aspect ratio compared with a vessel can create difficulties in scaling up correlations developed for small compact vessels. Moreover, phenomena which are relatively insignificant on the smaller scale can become important on the larger one.

The space in a building tends to contain obstructions. There are usually multiple compartments which are connected to each other. The presence of obstacles will tend to increase turbulence. So also will the existence of multiple compartments, since gas flowing through open internal doorways will generate turbulence.

The building itself is generally not very strong. An explosion pressure of 7 N/m^2 (1 psi) is often quoted as that at which a typical brick building may be destroyed. On the other hand, a normal building will have walls which contain weaker members which will fail and in so doing provide vents so that the explosion pressure does not rise as high as it otherwise would.

The static pressures at which certain building components fail have been given by Rasbash (1969c) and Astbury *et al.* (1970) and are quoted by Lunn (1984b). Some typical values are:

	Failure pressure (kN/m^2)
Windows (normal)	3–4.6
Windows (strained)	1, or even 0.2
Chipboard (19 mm)	7
Brick wall (114 mm)	Survived at 23, destroyed at 35
Brick wall (228 mm)	Survived at 70, destroyed at 105

It has been suggested by Buckland (1980) that the explosion pressure should not exceed 21 kN/m^2 if the building is to avoid serious damage.

Another relevant feature is the natural period of the building. Rasbash (1969c) quotes a value of 40 ms as a typical natural period for the slabs and floors of a building. W.B. Howard and Karabinis (1980) give further details of natural periods. See also *TNO Green Book* (1989, p. 34). Structural damage to buildings from explosions is considered in more detail in Section 17.32.

17.8.5 Gas explosions in buildings

Some features of gas explosions in buildings have been discussed by Rasbash (1969c). The maximum unvented pressure created in an unvented building by the explosion of the most explosive gas mixture is of the order of 7 bar. A 30 m^3 room requires about 2.5 kg of fuel to give such a mixture. The energy of this fuel is equivalent to some 20 kg of TNT.

The pressure from such an explosion will build up relatively gradually, giving a duration of several hundred milliseconds compared with about 1 ms for a condensed phase explosion. Rasbash quotes for a vented explosion with low turbulence a typical duration of 300 ms. But he also gives for the explosion of the most explosive mixture of town gas with high turbulence a duration in the range 20–150 ms.

An account of experimental work on venting of gas explosions in buildings has been given by W.B. Howard and Karabinis (1980, 1982). They state that the durations of the explosions were in the range 40–150 ms. Experimental pressure–time profiles showed that the pressure impulse is well approximated by a triangle with equal rise and decay times.

17.8.6 Modelling of gas explosions in buildings

The pressure in deflagrations in a closed system was considered in Section 17.7. The treatment given there is applicable in broad outline to an explosion in a building, but, as

indicated above, there are some important differences. The model of R.J. Harris (1983) described in that section is for explosion in a building, and gives the pressure and rate of pressure rise during the initial stages of the explosion.

Most of the models available for explosions in buildings are for vented explosions. These are considered in Section 17.14. One of these is the model of Runes (1971, 1972). The Runes equation is intended for the design of explosion relief for a building. It has been used, however, by W.B. Howard (1972) to estimate the explosion effects in an explosion incident in a building with open vents.

17.8.7 Condensed phase explosions in buildings

Experiments in which TNT charges were detonated inside a chamber have been described by Weibull (1968). The work was done to develop a nuclear blast simulator in which it would be possible to obtain arbitrary values of peak pressure and duration of the blast wave. The chambers used were provided with a variable vent opening.

Weibull states that in this system the peak pressure would be determined mainly by the mass of the explosive and the duration mainly by the area of the vent opening.

The pressure measured showed several very high initial spikes of very short duration which were reckoned to have minimal effect on the heavy walls of the chamber. The pressure, which had a long duration relative to the period of the walls, was taken as the blast load acting on them. The area of the vent opening had insignificant effect on the smoothed peak pressure. This pressure was given by the equation

$$p = K(m/V)^a \qquad [17.8.7]$$

where p is the peak pressure (bar), m is the mass of explosive (kg), V is the volume of the chamber (m^3), K is a constant and a is an index. The value of K is 22.5 and that of a is 0.72. Further information on pressures in enclosures estimated as a function of a TNT equivalent charge is given in Section 17.26 in the context of design of barriers.

17.9 Explosions in Large Enclosures

The type of large enclosure which is envisaged here is exemplified by an offshore module. It is with such enclosures that the account given in this section is primarily concerned.

An offshore module tends to have a high aspect, or length/diameter ratio, and to contain a number of obstructions in the form of equipment and pipework.

The overpressure generated in the combustion of a vapour cloud is due to two effects. One contribution to the overpressure comes from the production of a large quantity of hot burned gas, the volume production. The other is due to the effect of the flame speed. The overpressure which might occur due to the volume production would be up to about 8 bar, whereas the overpressure due to the flame speed effect might have any value up to that associated with a detonation.

Much work has been done on the development of explosion overpressures in vapour clouds. This work has shown that in the part of the cloud that is free of obstacles the flame speed is relatively low. If the flame passes first through a region which is unobstructed, then through one which is obstructed and finally through one which is unobstructed, the flame accelerates on entering the obstructed region and decelerates on leaving it. The flame speed in the obstructed space can reach quite high values.

Merc X (1992, 1998) conducted experiments in which two congested areas, each 2 m wide, are separated by an open, uncongested area of width 0.5, 1 and 2 m. He found that if mostly small-sized piping creates the turbulence, the decay is rapid and the flame speed reaches a low level within a few metres. Otherwise, more than 3–5 m may be needed for the flame speed to slow to non-damaging levels.

17.9.1 Experimental studies

Work on the generation of overpressures in vapour clouds has been done primarily in connection with the explosion of vapour clouds in the open. This work is described in Section 17.28. Most accounts of explosion in semi-confined spaces derive from, or are closely related to, this work.

An account of the experiments to determine the overpressures which might be generated in an offshore module was given by Vasey (1989) in evidence to the Piper Alpha Inquiry. The experimental rig used consisted of an enclosure 46.5 m long, 5 m wide and 4 m high with one end consisting of a confined section, a long box, with an open end, and then an open section, a gallery enclosed only by transparent polyethylene sheet to contain the gas mixture. Obstacle array supports were located every 1.5 m along both the confined and the open sections. The obstacles consisted of 3 m lengths of 0.18 m pipes or 0.18 m wide planks. The flame speed was sufficiently high so that venting to the side through the sheet did not occur and high overpressures were attained.

Work was done using both natural gas–air and propane–air mixtures. With a natural gas mixture a flame speed of 500 m/s was obtained and the overpressure was several bar. With a propane mixture the flame accelerated to detonation, and the overpressure, both measured and calculated, was about 18 bar.

17.9.2 Simulation models

Several models have been developed to simulate the development of an explosion in a semi-confined space such as an offshore module.

The FLACS model of the Christian Michelsen Institute (CMI) is a computational fluid dynamics (CFD) model which solves the fundamental equations of fluid flow taking account of turbulence and combustion. The three-dimensional Navier–Stokes equations, suitably amplified to include the effects of turbulence and combustion, are cast in discrete form, employing a finite volume technique, and are solved implicitly. Turbulence is modelled in terms of eddy viscosity, and combustion in terms of turbulent, mixing-limited reaction. The space modelled is divided into a grid of 'boxes' of volume 1 m^3. Normal assumptions are that the flammable gas cloud is a quiescent homogeneous stoichiometric mixture so that the effects of any concentration differences within the gas cloud, any ventilation air flow or a continuing leak source are neglected. Ignition is modelled as a weak ignition source by assuming that at time 0 half of the flammable mixture in one of the boxes has undergone combustion so that the temperature of the gas in the box is correspondingly increased. Accounts of the model have been given by Hjertager (1982a) and by Bakke, Bjerkevedt and Bjorkhaug (1990).

The CLICHE model of British Gas is based on a spherical flame front. It was originally intended for use in simulating explosions in vessels with a high degree of confinement and

low flame speeds, but has been extended to allow simulation of different geometries and flow conditions. It has been used to investigate flame acceleration through obstacles and the generation of overpressures much higher than those for which it was originally intended. An account of the model has been given by Catlin (1990).

CFD modelling is discussed further in Section 17.28 in relation to vapour cloud explosions.

17.9.3 Computer codes

There are several computer codes based on simulation models of the type just described.

These codes include FLACS at the CMI (Bakke, Bjerkevedt and Bjorkhaug, 1990), EXSIM (Hjertager *et al.*, 1994), CLICHE at British Gas (Catlin, 1990) and, at the TNO, BLAST (van den Berg, 1980) and REAGAS (van de Berg, 1989).

The FLACS suite of codes comprises a front end program CASD which captures details of the structure of the module and the equipment in it, a program which processes this information into a form in which it can be utilized by the main program, the FLACS code proper.

The FLACS code has been validated by comparison of the results of code simulations with measurements made in experiments on explosions in scale models of modules with 1 : 33 and 1 : 5 scale. The overpressures predicted by the code lie within ±30% of those in the model experiments with perhaps 1 case in 20 lying outside this range, corresponding to a confidence level of some 95%. The variability of the model experiments themselves is of the same order.

The FLACS code was used at the Piper Alpha Inquiry to investigate the overpressures which would have resulted from an explosion in one of the modules, as described in Appendix 19. Results from CLICHE were also given in evidence.

Plate 28 illustrates typical output from the FLACS code, showing the contours of the unburnt fuel, the burnt combustion products and the overpressures and the wind velocity vectors.

17.10 Explosion Prevention

Prevention of gas and vapour explosions in general depends on (1) avoidance of flammable mixtures and (2) elimination of sources of ignition. These general requirements for explosion prevention have already been discussed.

For plant, or closed, systems an important method of eliminating flammable mixtures which merits further consideration is (3) atmosphere control. This is discussed below.

Other aspects of explosion prevention which have already been discussed include avoidance of runaway chemical reactions and excessive fluid pressures.

Selected references on explosion prevention, protection and relief are given in Table 17.13.

17.10.1 Atmosphere control

The hazard of explosion can be much reduced by control of the atmosphere to render it non-flammable. This control is often effected by the use of an inert gas.

The atmosphere control of process plant has been discussed by Craven (1975). An account of inerting in tankers has been given by Halvorsen (1975).

Table 17.13 *Selected references on explosion prevention, protection and relief*

SMRE (Explosion 4); J.H.F. Smith (1956): Maisey (1957); Ghormley (1958); Burgoyne (1961); Grabowski (1964); Adcock and Weldon (1967a); Charney (1967); Allan and Athens (1968); Bartknecht (1968, 1974a, 1981a); Callahan (1968); E. Cohen (1968); Jarrett (1968); Constance (1971b); Conrad (1973); Donat (1977b); Grein (1973); K.N. Palmer (1973a); Franke *et al.* (1975); Funke (1976); R.L. Allen (1977a); Carver *et al.* (1977); Glatt (1977); Rogowski (1977); Schampel and Steen (1977); Ray (1978); P.E. Moore (1982a,b, 1990); IBC (1983/41, 1984/47, 49 Pt 1); Haessler (1986); Huff (1988); Nazario (1988); I. Swift (1988c); FPA (1989 CFSD FS 6012); Haverstad (1989); Tuhtar (1989); Vodyanik (1990); NFPA (1992 NFPA 69, 1994 NFPA 68)
CCPS guidelines: Huff (1992)

Flame arresters
FRS (n.d., Fire Res. Note 1037, 1967 Fire Res. Note 658, 1972 Fire Res. Notes 931, 945, 1973 Fire Res. Notes 964, 974); Radier (1939); Egerton, Everett and Moore (1953); Cubbage (1959, 1963); K.N. Palmer (1959, 1960); Joint Fire Research Organization (1960); Quinton (1962); K.N. Palmer and Tonkin (1963); HSE (1965 HSW Bklt 34); Litchfield (1965); K.N. Palmer and Rogowski (1967); Leineman (1970); H. Phillips (1972b); J.P. Davies, Palmer and Rogowski (1973); Barton, Carver and Roberts (1974); W.B. Howard, Rodehorst and Small (1975); Rogowski (1975, 1980); BRE (1978/8); R.P. Wilson and Flessner (1979); Worrell (1979); Amal Ltd (1980); Borger *et al.* (1980); HSE (1980 HS(G) 11); Peter (1980); Anon. (1981 LPB 41, p. 13); Bjorklund, Kshida and Flessner (1982); W.B. Howard (1982, 1988 LPB 79, 1992a,b); Kletz (1982c); Thorne (1982); Broschka *et al.* (1983); O.W. Johnson (1983); Lietze (1983); IMC (1984); UL (1984 UL 525); Lunn and Przybylski (1985); H. Phillips and Pritchard (1986); Wilkie (1987b); Fellensiek *et al.* (1987); Stalder (1987); Watson (1988 LPB 79); Overhoff *et al.* (1989); Babkin, Korzhavin and Bunev (1991); Piotrowski (1991); Roussakis and Lapp (1991); Capp (1992, 1994); S.P. Cooper *et al.* (1992); Rubach, Schecker and Onken (1992); Bishop and Knittel (1993); Mendoza, Smolensky and Straitz (1993); Siwek and Wegmuller (1993); G.O. Thomas and Oakley (1993 BS 7244: 1990)

Explosion protection
Grabowski (1958, 1968); Rentsch (1971); Yasuhara, Kita and Hiki (1978); Woods and Speechly (1979); Maisey (1980); J.M. Wilson and Tyrer (1980); Kirby (1985a); Altorfer (1992); Cadeddu *et al.* (1992); S.P. Cooper and Moore (1993); BS (Appendix 27 Explosion Protection)
Pipes: HSE (1965 HSW Bklt 34); Flessner and Bjorklund (1980, 1981); Bartknecht (1981a); O.W. Johnson (1983); Steen and Schampel (1983); Chatrathi (1992b,c)
Buildings: K.N. Palmer and Tonkin (1980); C.J.M. van Wingerden and Zeeuwen (1983); Mercx, van Wingerden and Pasman (1992)
Jetties: Dicker and Ramsey (1983)

Design against explosion
Grein (1973); Guill (1973)

Explosion containment
Bartknecht (1981a); Donat (1982); Noronha, Merry and Reid (1982); Kirby (1985a); Kirby and Siwek (1986); Wilday (1991)

Explosion prevention by inerting
Penland (1967); Kletz (1971); Craven (1975); Halvorsen (1975); O'Shea (1983); Blakey and Orlando (1984)

Explosion isolation
Chatrathi (1991); Chatrathi and Degood (1991)

Explosion suppression
Merewood (1958); Laflte and Boucher (1959); Hammond (1961); Grabowski (1964, 1965); Graviner (Colnbrook) Ltd (1966); Charney and Lawler (1967); Charney (1969); FPA (1974 CFSD FS 6015); P.E. Moore (1979b, 1981, 1982b, 1984, 1986, 1990); J. Singh (1979c); Maisey (1980); S.R. Moore and Weinberg (1981); Westbrook (1982c); Hertzberg *et al.* (1985); P.E. Moore and Bartknecht (1986); P.E. Moore and Cooper (1993)

Explosion suppression in modules, including water sprays
G.O. Thomas, Edwards and Edwards (1990); G.O. Thomas, Jones and Edwards (1991); A. Jones and Thomas (1992, 1993); Catlin *et al.* (1993)

Explosion venting
G.W. Jones, Harris and Beattie (1933 BM Tech. Pap. 553); Bonyun (1935, 1945); Creech (1941); Murphy (1944a,b); H. Brown (1946); Coffee, Raymond and Crouch (1950); Benson and Burgoyne (1951); Cousins and Cotton (1951a,b); Cubbage and Simmonds (1955a–c, 1957a–c); Gas Council (1955 GC 23,1957 GC 43); Schmidt, Haberle and Recklinghausen (1955); FRS (1956 Fire Res. Note 248); Burgoyne and Wilson (1957,1960); Grumer, Cook and Kubala (1959); Rasbash and Rogowski (1960a,b); Simmonds and Cubbage (1960); Spalding (1960); Westenberg and Favin (1960); D.S. Davis (1961); Raezer (1961); Spalding and Jain (1961); Spalding, Jain and Samain (1961); Block (1962); Munday (1963,1974); Philpott (1963); Rogowski and Rasbash (1963); Salter, Fike and Hansen (1963); W.H. Doyle (1964); Pliickenbaum, Strauss and Edse (1964); Maisey (1965); Heinrich (1966,1974); Charney (1967); Grein and Donat (1967); G.F.P. Harris (1967); G.F.P. Harris and Briscoe (1967); Woods and Thornton (1967); Bartknecht (1968, 1972b, 1974a, 1975,1977a, 1981a); FMRC (1969/1, 1973/ 2); Yao *et al.* (1969); Walker (1970); Decker (1971); R.L. Miller and Howard (1971); Donat (1971a,b, 1973a–c, 1977a,b); Cubbage and Marshall (1973, 1974); Institution of Gas Engineers (1973 Comm. 926); W.W. Russell (1973); Butlin and Tonkin (1974 FRS Fire Res. Note 1019); W.B. Howard and Russell (1974); Yao (1974, 1982); Nettleton (1975, 1978b); D. Bradley and Mitcheson (1976,1978); Guirao, Bach and Lee (1976); Sapko, Furno and Kuchta (1976 BM RI 8176); Anthony (1977b, 1977–78); Chappell (1977); Fiumara (1977); N. Gibson (1977); Hattwig (1977); M.R. Marshall (1977); V.M. Morton and Nettleton (1977); Crescitelli, Russo and Tufano (1979a, 1980); J.G. Marshall (1979); Monk and Davis (1979); Rust (1979); J. Singh (1979b, 1984, 1988a,b, 1989); O.K. Burchett (1980); Hattwig (1980); HSE (1980 HS(G) 11); Solberg, Skramstad and Pappas (1980); Zalosh (1980b, 1982); Solberg, Pappas and Skramstad (1981); Tufano, Crescitelli and Russo (1981); Fairweather and Vasey (1982); Hirano (1982, 1984); J.H.S. Lee and Guirao (1982b); Noronha, Merry and Reid (1982); Porter (1982); Fearnley and Nettleton (1983); J.H.S. Lee (1983a); I. Swift (1983, 1984, 1988a,b, 1989); Thorne, Rogowski and Field (1983); Chippett (1984); Cummings *et al.* (1984); Eckhoff *et al.* (1984); LleweUyn (1984); Hart (1985); McCann, Thomas and Edwards (1985); Champion *et al.* (1986); M.G. Cooper, Fairweather and Tite (1986); Degood (1986); M. Epstein, Swift and Fauske (1986); D.J. Lewis (1986a); Seifert and Giesbrecht (1986); Simpson (1986); Starke and Roth (1986, 1989); I. Swift, Batz and Degoode (1986); Schwab (1987); I. Swift and Epstein (1987); de Groot and Heemskerk (1989); Kumar, Dewit and Greig (1989); M. Epstein et al. (1990); Itagaki, Miyake and Ogawea (1990); Phylaktou, Andrews and Herath (1990); W.E. Baker, White and Hokanson (1991); Cates and Samuels (1991); Degood and Chatrathi (1991); Makhviladze and Phillipov (1991); Rota *et al.* (1991); Santon *et al.* (1991); Chathrathi (1992a); K. Bell and Morris (1992); Chaineaux and Danin (1992); Haaverstad (1992); Mercx, van Wingerden and Pasman (1992, 1993): Parry (1992); Rota *et al.* (1992); Skouloudis (1992); Wu and Swithenbank (1992); Anon. (1994a); Scheuermann (1994); NFPA (1994 NFPA 68).
Module venting: Committee for Explosion Research (1958); Hirano (1982); Hjertager (1982a); Moen (1982a); Solberg (1982a); P.F. Thorne (1982)
Effects in outside vent system, acoustic coupling and instabilities: Wiekema, Pasman and Groothuizen (1977); K.N. Palmer and Tonkin (1980); Zeeuwen (1982); Kordylewski and Wach (1986, 1988); A.J. Harrison and Eyre (1987b); I. Swift (1988c); C.J.M. van Wingerden and Zeeuwen (1988); Frolov, Gelfand and Tsyganov (1990); Tamanini and Chaffee (1992a,b); Ural (1993)

Reactor venting
Tangren, Dodge and Seifert (1949); Gasche (1956); Block (1962); Sestak (1965); Boyle (1967); Harmon and Martin (1970); Schlegel (1972); W.B. Howard (1973); Huff (1973, 1977a,b, 1982a,b, 1984a,b, 1985, 1987, 1988, 1990, 1992); Duxbury (1976, 1979a,b, 1980); W.E. Baker, Esparza and Kulesz (1977); Kneale and Binns (1977); Gartner, Giesbrecht and Leuckel (1978, 1980); BPF (1979); IChemE (1979/117); Karmarkar (1979); V.C. Marshall and Cockram (1979); Minors (1979); J. Singh (1979a, 1988a, 1989,1990a,b, 1992a); Townsend and Pantony (1979); Booth *et al.* (1980); Fauske *et al.* (1980); de Groot, Groothuizen and Verhoeff (1980); Mejdell (1980); Mayinger (1981); Friedel and Lohr (1982); Solberg, Pappas and Skramstad (1982); Friedel and Purps (1983, 1984a,b); Steen and Schample (1983); Barton and Nolan (1984); Binns and Barrett (1984); Harmon and Stuper (1984); Quinn, Weir and Hoppe (1984); P.W. Thomas (1984); I. Swift (1985); Giesbrecht and Seifert (1986); Schulz and Schoft (1986); Duxbury and Wilday (1987, 1989, 1990); Friedel and Kissner (1988); Nolan and Proctor (1988); First and Huff (1989); D.P. Mason (1989); Tharmalingam (1989a); Wilday (1989, 1989 LPB 89); Banerjee, Prandini and Patroncini (1990); Gustin (1990); Oster, Bell and Koltowski (1990); Sumapathala, Venart and Steward (1990a,b); H.G. Fisher (1991); Skouloudis and Kottowski (1991); K Bell, Morris and Oster (1993); Friedel and Schmidt (1993); Duffield and Nijsing (1994); Goetz and Sawrey (1994); Snee and Hare (1994); Waldram (1994).
Particular reactions: Crowley and Block (1989); J. Singh (1992a, 1994); Gustin *et al.* (1993); Whitmore, Cutler and Gladwell (1994); Yue, Sharkey and Leung (1994)
Reactor venting: DIERS
Fauske, Grolmes and Henry (1983); I. Swift, Fauske and Grolmes (1983); Fauske (1983, 1984a–c, 1985a, 1987a,b, 1988a, 1989a, 1990); I. Swift (1984); Anon. (1985g); Fauske, Grolmes and Leung (1984); Fauske and Leung (1985); H.G. Fisher (1985, 1986, 1989, 1991); Grolmes and Leung

(1985); Grolmes, Leung and Fauske (1985, 1989); Klein (1986); Leung (1986b, 1987, 1992b); Leung, Fauske and Fisher (1986); Noronha (1986); N. Gibson, Maddison and Rogers (1987); Leung and Fauske (1987); Wilday (1987); Leung and Epstein (1988); J. Singh (1988a); M. Epstein, Fauske and Hauser (1989); Fauske, Clare and Creed (1989); Fauske, Grolmes and Clare (1989); Gustin (1989b); Leung, Creed and Fisher (1989); Leung and Fisher (1989); Leung, Stepaniak and Cantrell (1989); Noronha, Seyler and Torres (1989); Skouloudis *et al.* (1989); Creed and Fauske (1990); M. Epstein *et al.* (1990); Kirch, Magee and Stuper (1990); Skouloudis, Bell and Kotowski (1990); Friedel and Wehmeier (1991); Grossel (1991); DIERS (1992); Prugh (1992d); C.M. Sheppard (1992, 1993, 1994); Grolmes and Yue (1993)

Reaction forces
Faber (1982); Porter (1982); Beveridge (1984); Huff (1990); Parry (1992)

Disposal of vented material
Kneale (1984, 1989); Faukse (1986a, 1990, 1992); Grossel (1986, 1990b); Muschelknautz and Mayinger (1986, 1990); Keiter (1989, 1992); Fauske and Grolmes (1992); Friedel, Schmidt and Wehmeier (1992); Hermann, Schecker and Schoft (1992); Parry (1992); Rupert, Muschelknautz and Klug (1992); J. Singh (1992b); Spatz, Drees and Schoft (1992); Lindsay and Rogers (1994)

Building venting
FRS (Fire Res. Note 820, 1969 Fire Res. Note 759, 760, 1975 Fire Res. Note 1026); Rasbash (1969c); Astbury *et al.* (1970); Mainstone (1971); Runes (1971, 1972); Astbury, West and Hodgkinson (1972, 1973); Dragosavic (1972a,b, 1973); W.B. Howard (1972, 1980); Butlin (1975 FRS Fire Res. Note 1026); Naidus (1976,1981a,b); Rasbash, Drysdale and Kemp (1976); Anthony (1977/78); W.B. Howard and Karabinis (1980, 1982); Cummings *et al.* (1984); NFPA (1994 NFPA 68)

In general, the use of atmosphere control is a much more reliable method than the elimination of sources of ignition, which is very difficult to achieve. Craven comments:

> The elimination of ignition sources is often promoted as an alternative to atmosphere control to prevent explosions. There are few situations in the process industries today in which this philosophy can be seriously defended.
>
> Only in the simplest situations – such as isolated liquid storage – can the elimination of ignition sources seriously compete with atmosphere control as the first line of defence.

For an atmosphere which may contain flammable gas, air and inert gas, Craven distinguishes four regions. These are:

Region I: flammable mixture;
Region II: fuel-lean mixture;
Region III: oxygen-deficient mixture;
Region IV: fuel-rich mixture.

The atmosphere is non-flammable in all but the first of these regions. Atmosphere control is often effected by the use of inert gas, but this is not the only option. In some cases it is more appropriate to operate in the fuel-rich region.

Some operations and equipments in which atmosphere control is practised are (1) reactors, (2) storage tanks, (3) head tanks, (4) centrifuges, (5) driers, and (6) pneumatic conveyors.

Generally, in an oxidation reactor the off-gas is deficient in oxygen. The oxygen concentration is usually analysed, and action is taken if it rises. This action may be to shut off an air or oxygen feed to the reactor or to inject inert gases.

Such trip systems are required to act very rapidly, and time delays can be a problem. There may also be difficulties in gas sampling due to vapour drops or solid particles. In some cases, therefore, other measurements, such as reactor temperature, may be used to complement the oxygen measurement by giving advanced warning of abnormal conditions.

Storage tanks containing flammable liquids are often blanketed with inert gas. The quantity of inert gas required can be large due to the movements of the liquid surface. An economical system is the use of breather vacuum valves which admit inert gas only when the liquid level falls.

The effectiveness of inerting in reducing the probability of storage tank fire/explosion has been discussed by Kletz (1971).

Inert gas blanketing is also frequently provided in constant head tanks for flammable liquids. Difficulties are often experienced, however, in maintaining an inert atmosphere in a head tank fitted with an overflow, because the return pipe from the overflow tank tends to act as an air entrainment pump. This problem can be eliminated by fitting suitable gas balance lines.

An inert atmosphere is necessary in centrifuges handling flammable liquids as described in Chapter 11. Again, the consumption of inert gas may be high due to air ingress during operation, but the use of gas balance lines can effect appreciable reductions.

The provision of inert atmospheres in dust-handling plant is considered in Section 17.46. The quantity of inert gas used must not be excessive if inerting is to be economic. It is important, therefore, to seek to minimize inert gas consumption.

For a perfectly mixed system the concentration changes effected by a ventilating air or purge gas flow are given by the equation

$$\frac{c}{c_o} = \exp\left(-\frac{QT}{V}\right) \qquad [17.10.1]$$

where c is the volumetric concentration of the component in the system atmosphere, Q is the volumetric flow of gas through the vessel, t is the time, V is the volume of the vessel and the subscript o denotes the initial value. Equation 17.10.1 may be rewritten as

$$\log_{10}\left(\frac{c}{c_o}\right) = -\frac{E}{2.3} \qquad [17.10.2]$$

with

$$E = Qt/V \qquad [17.10.3]$$

where E is the number of changes of atmosphere. Thus, the concentration of a component in the system atmosphere can be reduced by a factor of 10 by 2.3 changes and by a factor of 100 by 4.6 changes.

Purging can be effected more economically, however, if the flow regime is plug flow rather than perfect mixing. Plug flow can often be achieved if the vessel is one with

a very high aspect ratio, such as a tall column or a pipeline. Other situations which allow plug flow are buoyant displacement with a cold gas and gravitational displacement of a heavy vapour.

If the density difference between the atmosphere to be purged and the purge gas is small, turbulent mixing is usually achieved. For a simple vessel such as a storage tank without baffles, Craven states that such mixing should be enhanced by the use of gas jets directed across the tank with final velocities in the remote corners of 300 ft/min. He gives the following equation for the nozzle velocity required to give an air velocity of 300 ft/min along the jet axis in the remote corners

$$\frac{u_o}{u_x} = \frac{1}{K}\frac{X}{D} \qquad [17.10.4]$$

where D is the diameter of the jet orifice (ft), u_o is the nozzle velocity (ft/min), u_x is the required velocity (ft/min) (=300), X is the distance from the jet to the most remote corner (ft) and K is a constant (=6).

17.11 Explosion Protection

Explosion protection and relief include the following aspects:

(1) containment;
(2) separation;
(3) flame arresters;
(4) automatic isolation;
(5) automatic explosion suppression;
(6) explosion venting of vessels;
(7) explosion venting of pipes and ducts;
(8) explosion relief of buildings;
(9) explosion relief of large enclosures;
(10) venting of chemical reactors.

Deflagration and detonation inside plants has been discussed in Sections 17.5 and 17.6, and explosion in closed vessels specifically in Section 17.7.

Protection by containment of the explosion is a potential design option, but as discussed in Section 17.5, it is usually not practicable except for small-scale plants.

Another method of containment is the use of blast walls and barricades, and of blast cubicles. The design of such blast protection is described in the *High Pressure Safety Code* (B.C. Cox and Saville, 1975) and by W.G. High (1967) and CaUahan (1968).

Separation as a method of protection is discussed in relation to plant siting and layout in Chapter 10 and in relation to storage in Chapter 22. It is also considered in Section 17.3 in terms of the quantity–distance relations used for storage of explosives.

Methods of explosion protection and relief are described in *Dust Explosions and Fires* (K.N. Palmer, 1973a) and *Explosions* (Bartknecht, 1981a). Health and Safety Executive (HSE) guidance is given in *Guide to the Use of Flame Arresters and Explosion Reliefs* (the HSE *Explosion Relief Guide*) (1965 HSW Bklt 34). Relevant US codes are NFPA 69: 1992 *Explosion Prevention Systems* and NFPA 68: 1994 *Deflagration Venting.*

Selected references on explosion prevention, protection and relief are given in Table 17.13.

17.11.1 Flame arresters

A flame arrester, or flame trap, is a device used to prevent the passage of a flame along a pipe or duct.

A flame arrester is generally an assembly of narrow passages through which gas or vapour can flow, but which are too small to allow the passage of flame.

Typical applications of flame arresters are on vents of storage tanks containing flammable liquids, on pipe systems supplying fuel gas to burners, on certain pipelines conveying flammable gases within the plant and on flare stacks. Flame arresters are also used on exhausts of engines working in atmospheres with a flammability hazard and on crankcases of small engines.

Accounts of flame arresters include those given in the *CCPS Guidelines* book by Grossell (2001), in the HSE *Explosion Relief Guide* (1965 HSW Bklt 34) and by H. Phillips (1972b), Barton, Carver and Roberts (1974), W.B. Howard, Rodehorst and Small (1975), W.B. Howard (1982, 1992a,b), Kletz (1982c), Thorne (1982), Lunn and Przybylski (1985), H. Phillips and Pritchard (1986), Capp (1992, 1994) and G.O. Thomas and Oakley (1993).

An extensive programme of work on flame arresters was conducted in the 1960s by the Joint Fire Research Organization (JFRO) at the Fire Research Station at Borehamwood. Accounts of this work have been given by K.N. Palmer and co-workers (e.g. K.N. Palmer and Tonkin, 1963; K.N. Palmer and Rogowski, 1967; J.P. Davies, Palmer and Rogowski, 1973; Rogowski, 1980).

The United Kingdom has had certain long-standing but limited legal requirements for the use of flame arresters, on diesel engines in mines and on equipment using acetylene above 0.62 barg. Their use is recommended in codes.

17.11.2 Flame arresters: modes of combustion

In general, combustion may take the form of a deflagration or a detonation. The characteristics of these two forms of combustion have been described above.

A deflagration has a flame speed of 3–500 m/s and generates overpressures of 8–11 bara. A detonation has flame speeds of 500–2000 m/s and overpressures of 11–100 + bara.

Flame arresters are generally distinguished as end-of-line or in-line arresters. An end-of-line arrester is designed to prevent the passage of a deflagration from the downstream to the upstream side.

An in-line arrester should be able to stop either a deflagration or a detonation passing in either direction. Although it is often assumed that detonation presents the more difficult duty, this is not necessarily so. Some detonations are overdriven (meaning the flame speed temporarily exceeds the coustic speed), and if this is a possibility the arrester needs to be able to handle this form of detonation.

Definition of the nature of the flame with which an arrester may have to cope is difficult, so that in principle it may be necessary to allow for both deflagration and detonation, possibly including overdriven detonation.

It should be appreciated that even if a flame arrester prevents the passage of the detonation flame, it does not stop the detonation shock wave.

17.11.3 Flame arresters: types of arrester

The types of flame arrester used are described in the *HSE Guide* and FPA FS 6012 in Grossell (2001) and by H. Phillips

and Pritchard (1986) and W.B. Howard (1992a)., Grossell defines three types of arrester:

Type 1 arresters with multiple small channels;
Type 2 hydraulic devices;
Type 3 velocity flame stoppers.

Some principal type 1 flame arresters are

(1) sheet metal arresters
  (a) planar sheet metal arresters,
  (b) cylindrical sheet metal arresters (crimped ribbon arresters);
(2) perforated plate arresters;
(3) perforated block arresters;
(4) sintered arresters;
(5) expanded metal arresters;
(6) parallel plate arresters;
(7) wire gauze arresters;
(8) wire pack arresters;
(9) packed bed arresters.

Figure 17.15 illustrates some of these types of arrester.

The operation of a type 1 arrester is generally treated in terms of the mechanism of quenching and heat loss. These are a large part of the story, but not the whole, as discussed by H. Phillips and Pritchard (1986).

Desirable properties of a flame arrester are high free cross-sectional area available for flow, low resistance to flow and freedom from blockage; a high capacity to absorb the heat of the flame and the ability to withstand mechanical shock, including explosion.

Sheet metal arresters are of two main types. The planar type consists of thin, planar sheets with corrugations or protuberances stacked in a block. The cylindrical type is constructed by winding a thin corrugated metal ribbon to form a cylindrical assembly. This type is also known as a crimped ribbon arrester.

Crimped ribbon arresters are an important type of arrester and are available in a range of designs. These arresters have about 80% free cross-sectional area, can be manufactured to close tolerances, are robust enough to withstand mechanical and thermal shock and can be made to quench violent explosions.

Wire gauze arresters have a lower free area, which with fine gauzes is less than 50%. They also tend to be less effective and less robust. They have a limited ability to quench flame and are not suitable for violent explosions. A limited enhancement of arrester effectiveness can be obtained by using a number of wire gauze arresters in series as a combined pack.

Perforated plate arresters have a lower free area than gauzes, but higher heat capacity and greater mechanical robustness than wire gauzes, but they are little more effective and again are not suitable for violent explosions.

Perforated metal blocks can also be used as arresters.

Sintered arresters again have a low free area and high flow resistance. Their main use is on flammable gas detectors and on welding equipment.

Parallel, or stacked, plate arresters have a low free area and high flow resistance, but can be designed to quench violent explosions. They are used particularly on the exhausts of internal combustion engines.

Wire pack arresters are made by compressing a pack of wire which has been knitted or assembled at random. This type of arrester tends not to have very reproducible characteristics.

Packed bed arresters are vertical containers fitted with pebbles, Raschig or Pall rings or similar packings. The packing may be irrigated with water or oil. The size of the

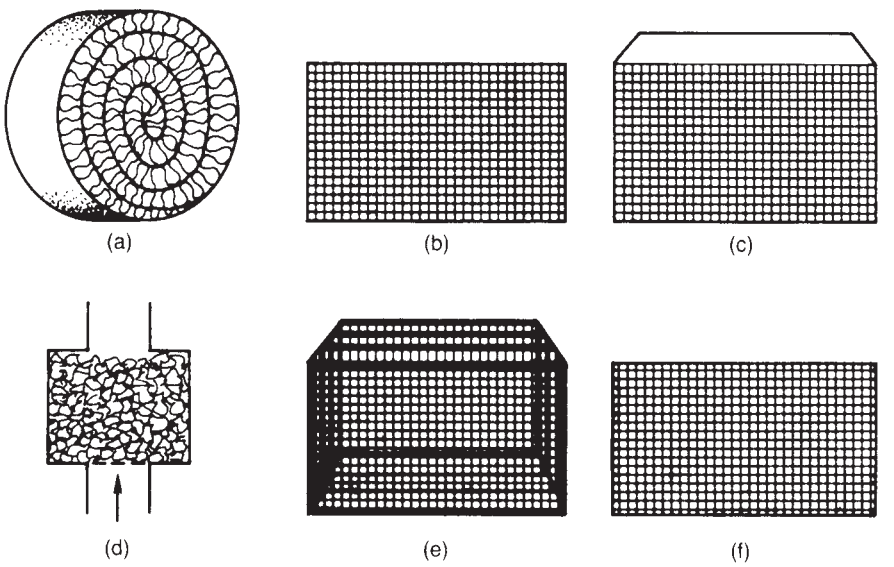

Figure 17.15 *Some type of flame arrester (after Fire Protection Association, 1989 FS 6012): (a) crimpled ribbon arrester; (b) perforated metal sheet; (c) perforated metal block; (d) box of pebbles or ceramic rings; (e) wire gauzes; and (f) construction of a gauze arrester*

passages is not well defined. This type of arrester has high flow resistance. Such an arrester can quench a violent explosion, but movement of packing due to such an explosion can result in arrester failure. A more detailed account of packed bed arresters is given by W.B. Howard (1992a).

The design of a flame arrester depends on the combustion properties of the flammable mixture and on the function and location of the arrester.

The size of the aperture through the arrester is determined by the quenching distance of the flammable mixture. Quenching distances have been discussed in Chapter 16. The diameter of the aperture of an arrester should be smaller than the quenching diameter by at least 50%. The performance of an arrester is affected by the temperature. The quenching distance increases as the temperature increases. It is approximately inversely proportional to the square root of the absolute temperature.

In general, such flame arresters are cheap, can be easily installed and are readily replaced if damaged. They do present some problems, however, due to their fine structure. These include high pressure drop and blockage. They are not suitable, therefore, in dusty or polymerizing gases. The maintenance of an arrester is relatively simple, but it is essential that it should not be neglected if the device is to function properly when required.

17.11.4 Flame arresters: hydraulic devices

Hydraulic, or liquid seal, arresters contain a liquid, usually water, which serves to break up the gas stream into bubbles and so prevents passage of the flame. This type of arrester operates on a quite different principle from that of the other types described. The arrester is effective only if the liquid level is maintained and the gas flow is kept within the range in which it is broken into bubbles.

Hydraulic arresters exist which are reported to be effective in preventing flame propagation in both directions. Tests to establish this on a particular arrester design have been described by Flessner and Bjorklund (1981).

A particular kind of hydraulic arrester is the linde hydraulic valve developed for acetylene duty. This is described by Flessner and Bjorklund (1981).

Hydraulic arresters are discussed further by W.B. Howard (1992a), with comments on the extent to which the various kinds of arrester are in general use.

17.11.5 Flame arresters: velocity flame stoppers

A velocity flame stopper is an arrester used in end-of-line applications. Its function is to prevent a flame passing from the downstream to the upstream side.

It operates on a quite different principle from other types of arrester. This principle is to ensure that the velocity of the upstream gas passing through the arrester is sufficiently high to prevent a flame propagating through the arrester from the downstream side.

The velocity flame stopper is discussed by W.B. Howard (1992a). For the velocity necessary to prevent flashback through apertures larger than those which would give quenching, Howard quotes the equation of Hajek and Ludwig (1960):

$$u_T = 0.2015 g_L D \qquad [17.11.1]$$

where D is the internal diameter of the pipe (m), g_L is the laminar velocity gradient (m/s)/m and u_T the turbulent flashback velocity (m/s). The parameter g_L is also termed the critical boundary velocity gradient. This parameter is a function of the gas and of its concentration. It tends to have a maximum value at a concentration somewhat above the stoichiometric. The following maximum values are based on the work of Grumer, Harris and Rowe (1956 BM RI 5225):

Gas	*Maximum laminar velocity gradient,* g_L (s^{-1})
Methane	400
Ethane	650
Propane	600
Ethylene	1,500
Propylen	700
Hydrogen	10,000

Howard recommends that for normal design the minimum velocity through the holes of a velocity flame stopper should be four times the turbulent flashback velocity given by Equation 17.11.1.

A velocity flame stopper is effective only as long as there is a sufficient gas flow through it. Ensuring a reliable gas flow may not be a simple matter, and in such cases a regular flame arrester may be a more attractive alternative.

Velocity flame stoppers are used particularly on certain gas flows to furnaces.

17.11.6 Flame arresters: conservation vents

Storage tanks are commonly provided with conservation vents to allow them to 'breathe'. Over the years there has been some debate as to whether it is necessary to incorporate a flame arrester in such a vent. The question is discussed in Chapter 22. The view has emerged that a conservation vent acts, in effect, as a velocity flame stopper and that a separate flame arrester is not necessary.

17.11.7 Flame arresters: critical flame speed

It was shown by Palmer at the Fire Research Station (FRS) that a crucial variable in the performance of flame arresters is the flame velocity incident on the arrester, or critical flame speed. The critical flame speed is discussed by H. Phillips and Pritchard (1986), drawing largely on the FRS work on propane–air mixtures at atmospheric pressure. A simple model based on heat abstraction from the flame yields the following relation:

$$u = 0.95 \frac{nyp_o}{p} \qquad [17.11.2]$$

where n is the number of apertures per unit area of arrester surface (cm^{-2}), p is the explosion pressure at the arrester, p_o is atmospheric pressure, u is the flame speed at the arrester (m/s) and y is the thickness of the arrester elements (cm). This equation includes the term (p_o/p), which takes into account the explosion pressure. The authors state that for the system considered this equation gave reasonable agreement, with a number of qualifications, including the facts that it applies only to crimped ribbon arresters of

a particular design and to propane–air mixtures. They also quote the following empirical equation:

$$u = 0.38\frac{ay}{d^2} \qquad [17.11.3]$$

where a is the fractional free area of the arrester, d is the diameter of the apertures (cm), u is the flame speed at the arrester (m/s) and y is the thickness of the arrester elements (cm). This equation applies to crimped ribbon, wire gauze and perforated plate arresters. For the former, d is taken as the hydraulic mean diameter. The equation does not taken into account the explosion pressure and is therefore limited to applications where the pressure does not rise substantially above atmospheric; the authors instance a short length of straight pipe.

17.11.8 Flame arresters: minimum effective safe gap

The selection of flame arresters is largely based on the minimum effective safe gap (MESG) of the fuel. This is defined as the smallest gap between parallel metal surfaces that will not allow propagation of an ignition. The theory of suppression by narrow gaps is discussed by Phillips (1972). Compilations of MESG are provided by the National Academy of Sciences report to the US Coast Guard (1975), the National Materials Advisory Board (1982), NFPA 497 (1997) and Britton (2000).

The purpose of MESG measurement is to specify the degree of integrity required for 'explosion proof' electrical equipment. See NFPA 70 (2002), National Electrical Code (NEC) and NFPA 497 (1997). A classification of flame arrester specifications was introduced into the *US National Electrical Code* (NEC) Article 500 in 1935, in four groups, A, B, C, D, ranging from Class D suitable for relatively unreactive fuels to Class A suitable for very reactive fuels. The four fuel groups 'complemented the design of electrical equipment used in hazardous (classified) locations and were defined based on the level of hazard associated with explosion pressures of specific atmospheres and the likelihood that the effects of that explosion could be transmitted outside the enclosure' (NFPA 497). The typical materials for each group as defined in the NEC are listed below.

Flame arrester class	*Typical materials*	*Upper limit defining material*	*US Coast Guard*	*MESG* (mm), *Westerberg apparatus*	*NFPA 497*
D	Acetone[a]		1.02	n/a	1.02
D		Propane	0.90	0.92	0.97
C	Diethyl Ether		0.86	0.30	0.83
C		Ethylene	0.71	0.69	0.65
B	Hydrogen		0.10	0.08	0.28
A	Acetylene		<0.02	0.08	0.25

[a] Naphtha, gasoline, petroleum, alcohols, acetone, lacquers, solvent vapours, natural gas.

Differences in measured values of MESG arise between measurement devices. The values listed above are from Britton (2000), who discusses the reasons for differences, as does Phillips (1981).

Considerable use has been made of the MESG for key compounds to separate chemicals into the groups. There is some variability in the choice of the 'border material'. For example, the National Materials Advisory Board originally selected gasoline to define the border between Classes C and D. Gasoline has an MESG by the Westerberg apparatus of 0.74 mm (0.029 in.), but is a poorly defined mixture and MESG measurements of gasolines vary. Propane has since become the NEC border material for Groups C and D. Ethylene is currently the NEC border material for Groups C and B. However, the US Coast Guard's demarcation between Groups C and D is 0.90 mm and is inconsistent with the NEC demarcation of only 0.75 mm. The NFPA 497 has 'grandfathered' certain gases under their original NEC groupings. For example, diethyl ether continues to be listed as NEC Group C even though it would be NEC Group D based on its listed MESG (0.83 mm using the IEC apparatus). Britton (2000) has suggested revisions in the present grouping system.

The 1997 revision of NFPA 497 provides an equation for estimating the MESG of mixtures (Breisch, 2000). The equation is described as a 'form of Le Chatelier's equation' although there is a distinct difference in application with respect to the treatment of inert components.

17.11.9 Flame arresters: applications and requirements

The duty which the arrester performs depends on the nature of the system and on the location of the arrester.

One basic distinction is between (1) end-of-line and (2) in-line arresters. The typical application of an end-of-line arrester is on the vent of an atmospheric storage tank. The function of such an arrester is primarily to stop a flame arising from ignition of vapour vented. The flame is thus of low speed and at atmospheric pressure.

In-line arresters are used in plant pipework and the demands placed on them are much more severe and varied. They may have to deal not only with deflagrations but also with detonations.

Some of the differences in application which arise from the location of the arrester and of the ignition source are discussed in the HSE *Guide*, which distinguishes the following three standard situations: (1) ignition at the open end of a duct, (2) ignition at the closed end of a duct, and (3) ignition near the arrester. These situations are shown in Figure 17.16.

Another minor distinction is between a stationary and a flowing mixture. Consider first a stationary mixture. If ignition occurs at the open end of the duct, the arrester is required only to quench the flash of flame. This requires absorbing the heat from the hot gases. If ignition occurs at the closed end of the duct, the arrester must quench the flame and withstand the pressure created by combustion within the duct, some cooling of the hot gases occurs by the duct walls.

Now consider a flowing mixture. Assume that in Figure 17.16 the flow is from left to right. If ignition occurs in the open end and the gas velocity is high, the flame may be swept out of the duct or may stabilize on the end of the duct or at a restriction in the duct. In either case the arrester is unaffected. But if the gas velocity is low, the flame will stabilize on the arrester. If ignition occurs at the closed end of the duct or near the arrester, the flame may again stabilize on the arrester and eventually allow a temperature and ignition breakthrough.

Thus, if a flame arrester is installed in a system in which the gas mixture is flowing, there is a risk of stabilization of the flame and overheating of the arrester. It is necessary, therefore, to arrange for this condition to be detected and for the gas flow to be shut off when it occurs.

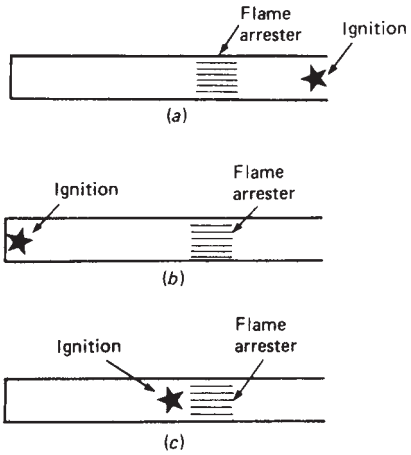

Figure 17.16 *Ignition situations relevant to the design of flame arresters (after Health and Safety Executive, 1965 HSW Bkk 34): (a) ignition at open end of duct; (b) ignition at closed end of duct; and (c) ignition near arrester (Courtesy HM Stationery Office)*

The function which a flame arrester is required to perform therefore varies. In some cases it is required only to prevent simple flashback, but in others, where hot gases may be forced through it or where flame may stabilize on or near the arrester, it must also be capable of absorbing a considerable quantity of heat. For the latter duties it is necessary not only that the arrester have apertures smaller than the quenching diameter but also that it have sufficient mass and suitable material of construction to absorb heat.

In many applications a flame may arrive at the arrester from either direction and the arrester needs to be capable of stopping the flame in both cases.

17.11.10 Flame arresters: HSE *Guide*

It is convenient at this juncture to consider the guidance on flame arresters given by the HSE *Explosion Relief Guide*. This guide is based on the work in the 1950s and in 1960 at the FRS. Unless otherwise stated, it applies to gas mixtures at atmospheric pressure.

For crimped metal, wire gauze and perforated plate arresters the following equation is given in the HSE *Guide* for the calculation of the maximum flame speed for a deflagration at atmospheric pressure which can be quenched by an arrester:

$$u = 0.5\frac{ay}{d^2} \qquad [17.11.4]$$

where a is the fractional free area, d is the diameter of the aperture (in.), u is the flame speed (ft/s) and y is the thickness of the arrester (in.).

Equation 17.11.4 is applicable to deflagration but not to detonation. The value of the flame speed u includes a safety factor which takes account of experimental scatter. For non-circular apertures the equivalent hydraulic diameter should be used.

For crimped metal arresters, the equivalent diameter for a right angle isosceles triangle is 0.83 times the crimp height. The thickness of a crimped metal arrester should be at least 0.5 in. For a wire gauze arrester, Equation 17.11.4 applies only to a single layer of gauze. For a single layer of gauze the thickness y is twice the wire diameter.

An increase in allowable flame speed of about 20% of the original value may be obtained for each additional layer up to a maximum of 5, but further increase gives no additional advantage.

For detonations, only crimped metal arresters are considered by the HSE *Guide*. It quotes the following equation for the maximum flame speed obtained by Cubbage (1959) for the stoppage of town gas–air mixture detonations by arresters with crimp height of 0.017 in.:

$$y = 1.3u^{1/5} - 4.4 \qquad [17.11.5]$$

The HSE *Guide* emphasizes the limited amount of work then available on the arrest of detonations.

The use of these equations requires data on flame speeds. Flame speed is a function not only of the flammable mixture but also of the system geometry. In particular, there exists a 'run-up' length over which there is a considerable acceleration of flame speed. The HSE *Guide* gives data on flame speed for several gas–air mixtures as a function of the run-up length in straight smooth pipes of up to 12 in. diameter.

For propane–air mixtures, the flame speeds given for run-up lengths of 1, 5, 10 and 35 ft are 16, 230, 330 and 330 ft/s, respectively, for ignition near the open end of the pipe, and 110, 380, 420 and 490 ft/s, respectively, for ignition near the closed end of the pipe. For other run-up distances the higher neighbouring flame speed value should be used.

These flame speeds for propane are typical of saturated hydrocarbons. There are, however, a number of substances, for example, ethylene, which have higher flame speeds.

The HSE *Guide* also recommends that for certain substances, for example, hydrogen, and for all substances in pipe lengths greater than 35 ft, detonations giving pressures up to 500 psig should be assumed.

For propane–air mixtures, the detonation velocity is about 5800 ft/s. For town gas–air mixtures it is about 7000 ft/s. The HSE *Guide* gives the following equation for detonation velocity:

$$u = 300[(\gamma^2 - 1)Q]^{1/2} \qquad [17.11.6]$$

where Q is the heat of detonation (cal/g) of the gas mixture, u is the detonation velocity (ft/s), and γ is the ratio of specific heats of the gas mixture at the combustion temperature.

Equations 17.11.5 and 17.11.6 apply to gas mixtures at atmospheric temperature and pressure. At higher pressures flame speed is not greatly affected, but the volumetric heat release increases in proportion to absolute pressure. The effect of higher temperature is more complex. An increase in temperature raises the burning velocity but reduces the volumetric heat release.

If the flammable gas is mixed not with air but with oxygen or even oxygen-enriched air, there is a strong possibility of detonation. Such mixtures can give detonation velocities up to 12,000 ft/s and detonation pressures up to 1,000 psig.

The basic design options are to keep the pipe length below 35 ft or to design for detonation. The former option includes the use of explosion relief vents to eliminate pipe runs of more than 35 ft.

If the pipe is not a straight smooth duct, but contains bends or obstacles, much higher flame speeds may be reached. A single right angle bend can cause a substantial increase in flame speed. In such cases it is necessary to use explosion relief much more liberally or to design for detonation.

17.11.11 Flame arresters: environment

As described above, flame arresters differ in their applications. Arresters also differ considerably in the environment in which they are required to function, particularly in-line arresters but also end-of-line arresters.

In discussing the environment of a flame arrester, H. Phillips and Pritchard (1986) consider (1) the upstream volume, (2) the arrester matrix, and (3) the downstream volume. They define these regions in terms of the direction of flame propagation, which is not necessarily that of gas flow. This terminology is followed here, but in this section only.

The ignition source is by definition located in the upstream volume. The properties of the flame arriving at the arrester are determined by conditions in this space. These include the pressure, temperature and gas mixture composition. They also include the shape of the space, the run-up distance and, of great importance, features that affect the flow into the arrester. The authors cite cowls on end-of-line arresters and bends and obstacles in the pipework upstream of an in-line arrester.

Even if the arrester stops the flame from passing through, the hot gases leaving the arrester may reignite. Whether they do so depends on the conditions in the downstream volume. Reignition is governed by the balance between the heat generated by reaction of the hot gases leaving the arrester and the cooling due to mixing with cool gas or air. This mixing will depend on features tending to promote turbulence in the downstream space.

17.11.12 Flame arresters: testing

An account of British practice in the testing of flame arresters is given by H. Phillips and Pritchard (1986).

They classify tests into (1) tests on end-of-line arresters, (2) deflagration tests on in-line arresters, (3) detonation tests on in-line arresters and (4) endurance burning tests. A similar account of US practice is given by the US Coast Guard.

One issue in the testing of arresters is definition of the conditions for which the arrester is to be tested. An arrester at a particular location may be required to deal with a number of different flame conditions.

Another issue is the selection of test gas mixtures which are representative of other mixtures of interest to the designer. One approach to this is to utilize the gas groups as defined in the standards on hazardous area classification, described in Chapter 16 or the US Coast Guard classification.

A third issue is the definition of the 'worst case' conditions.

The test conditions for end-of-line arresters typically involve low flame speeds and atmospheric pressure. Use is made of the hazardous area classification (HAC) gas groups, except for endurance burning.

The deflagration testing of in-line arresters is complicated by the fact that performance depends not only on flame speed but also on pressure. A typical test sequence is to increase the run-up distance in lengths of straight pipe and determine the flame speed at which failure occurs. This procedure does not, however, take account of pressure, and experience indicates that it is not necessarily sufficient to use a safety factor based solely on the relation between run-up distance and flame speed at atmospheric pressure. In view of these problems, the authors recommend that an arrester be tested under conditions which approximate as closely as possible those under which it is to be used.

The detonation testing of in-line arrester is usually based on a steady-state detonation, with CJ velocity. This does not allow for the possibility that the detonation may be overdriven. In a practical application it may be uncertain whether an overdriven detonation could occur. The authors emphasize that an in-line arrester should be tested for both deflagration and detonation conditions. It should not be assumed that if the arrester is satisfactory for detonation, it will be so for deflagration also, since cases have occurred where this was not the case.

With regard to overdriven detonations, they state that it is uncertain whether flame arresters are effective against such detonations.

The arrester should be tested for its ability to stop a flame travelling from either direction.

A flame arrester must also pass an endurance burning test to ensure that it will not fail if a flame becomes stabilized on it. In this test the gas mixture is adjusted to obtain a maximum value for the flame temperature and the endurance period of the arrester is then determined. Flashback of the flame should not occur during the test when the gas is turned off.

For this type of test the use of the HAC gas groups, based on the maximum experimental safe gap (MESG) and the minimum igniting current (MIC), is unsatisfactory. The authors discuss alternative approaches.

The testing of arresters is also discussed by W.B. Howard (1992a). He instances the case of a flame arrester which was found to be satisfactory for detonations of mixtures of air with propane but not with propylene, despite the fact that the fundamental burning velocities of these two gases are comparable, being 46 and 52 cm/s, respectively. The MESG for propane and propylene are, respectively, 0.97 and 0.91 mm (NFPA 97, Britton, 2000).

The test procedures for in-line arresters utilize straight pipes. In practical applications the pipework is likely to contain features such as bends and valves.

Both sets of authors emphasize the unsatisfactory state of the art in the testing of flame arresters. There are a large number of arrester designs and a wide range of applications, with variations in system geometry, gas mixtures and ignition sources. There is a paucity of published scientific work on which general design methods might be based. The message is therefore that if there is doubt as to the suitability of an arrester in a particular application, tests should be conducted which simulate as closely as possible the set of worst case conditions in that application.

17.11.13 Flame arresters: codes and standards

Flame arresters are the subject of a number of codes and standards in different countries. These are reviewed by H. Phillips and Pritchard (1986), W.B. Howard (1992a) and Britton (2000).

In the United Kingdom BS 7244: 1990 covers the testing of arresters, as described in the next subsection. In the United States the Underwriters Laboratories standard UL 525-1984 deals with construction and testing. Germany

has legally backed standards on the same aspects, as described by Leineman (1970).

The International Maritime Organization (IMO) also has requirements for flame arresters (1984 MSC Circ. 373).

The testing of flame arresters is covered by BS 7244: 1990 Specification for Flame Arresters for General Use. The standard requires that an arrester withstand a fixed number of flame and detonation tests without flame propagating through the arrester.

An account of the practicalities of testing against this standard is given by G.O. Thomas and Oakley (1993).

17.11.14 Flame arresters: design features

There are a number of design features which are crucial to the effectiveness of a flame arrester. These relate to (1) mechanical strength, (2) flame endurance, (3) instrumentation, and (4) blockage avoidance.

For an in-line application, the arrester, its housing and the adjacent pipework should be able to withstand the shock from a detonation. This is a prime requirement in the selection of the type of arrester to be used.

The arrester element itself needs to have adequate mechanical strength. Use may be made of additional strengthening in the form of reinforcing grids across both faces of the arrester.

One expedient which is sometimes used to reduce the impact on the arrester is to set the arrester in a holder of enlarged cross-section. It has been found in practice that this does not always provide the degree of reduction of impact expected.

Another measure taken by some manufacturers is the provision of baffles to break up the detonation wave as it approaches the arrester, but there is little published on the performance of these devices.

An in-line arrester generally presents an appreciable resistance to flow. Data on pressure drop through arresters have been correlated by Quinton (1962).

Both end-of-line and in-line arresters are subject to blockage. Both types are vulnerable to dust and corrosion products. An end-of-line arrester may also suffer blockage from sand, fibres and crystallized or polymerized vapours. There may also be more exotic forms of blockage such as birds nests.

Some protection may be afforded by the use of a screen on an end-of-line arrester or a filter for an in-line arrester.

An arrester, whether end-of-line or in-line, should be able to withstand a flame stabilized on it. An endurance burning test may be required to confirm this.

The instrumentation of arresters is discussed in the following section.

In some installations the end-of-line arrester is heated to prevent blockage by condensed products. Where this is done it should be confirmed, by tests if necessary, that the arrester operates satisfactorily at the higher temperature.

With an end-of-line flame arrester there may be a risk to the plant from impingement of the flame.

A short vent pipe is sometimes used to prevent this. W.B. Howard (1992a) recommends that the arrester should be no more than five pipe diameters from the end of the pipe.

17.11.15 Flame arresters: instrumentation

An in-line flame arrester should be provided with instrumentation which will give an alarm to signal the presence of a flame and to take any appropriate protective action.

A common arrangement is two temperature sensors, one on each side of the arrester and close to it. The sensors should have rapid response and the trip level should be low enough to ensure effective protective action. If the sensors are sufficiently accurate, their response sequence can also indicate in which direction the flame has travelled.

The protective action might consist of the operation of fast-response isolation valves. It is desirable to detect the presence of flame on an end-of-line arrester also, again using temperature sensors.

17.11.16 Flame arresters: inspection and maintenance

As a protective device, a flame arrester should be entered in the inspection schedule and inspected at suitable intervals.

It should have pressure tappings either side to allow the pressure drop across it to be measured. There should be adequate access to allow this to be done and to permit removal if necessary.

In general, a blocked arrester should be cleaned by blowing air or steam through it or by washing. It should not be cleaned, however, in any way which is liable to enlarge the apertures, such as rodding out.

17.11.17 Flame arresters: alternatives to arresters

It should not be assumed that a flame arrester is necessarily the right solution. Depending on the situation, it may be preferable to consider an alternative approach such as the use of automatic isolation or explosion suppression.

These alternatives are now briefly considered. They find application particularly in protection against dust explosions and a fuller account is given in Section 17.47.

17.11.18 Automatic isolation

In some systems, the passage of an explosion from one section to another may be prevented by automatic high speed isolation. An account of this method is given in FPA FS 6012: 1989 *Flammable Liquids and Gases: Explosion Control* and NFPAI2A (1997).

A typical installation is illustrated in Figure 17.17. Very rapid detection and valve closure are necessary.

The design of such a system requires information on the rate of pressure rise caused by the expected explosion. This information is also required for the design of automatic explosion suppression systems and is discussed below in relation to the latter. From the data on the rate of pressure rise a suitable high speed detector can be chosen. The shut-off valve must also operate very quickly. One method of achieving rapid closure is the use of explosives.

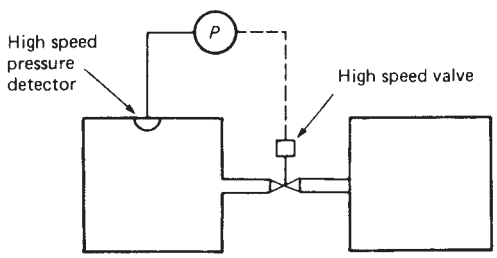

Figure 17.17 *System for automatic isolation installed in a pipe*

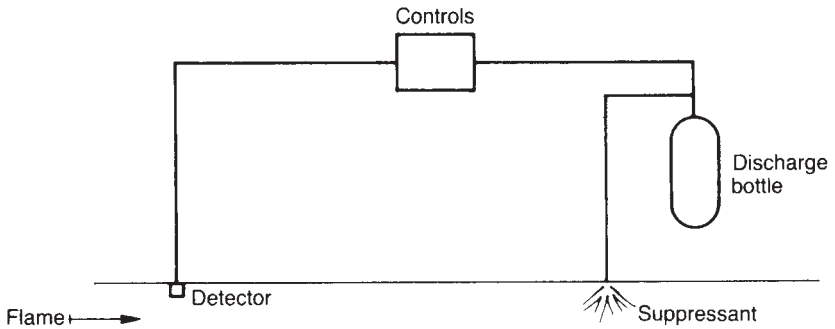

Figure 17.18 *System for automatic explosion suppression installed in a pipe*

Isolation protects only the section isolated and not the section in which the explosion occurs. The application of automatic high speed isolation appears to be fairly limited.

17.11.19 Automatic explosion suppression

A developing explosion may be detected and suppressed using an automatic high speed suppression system.

Accounts of automatic explosion suppression are given in FPA FS 6012: 1989 and FS 6015: 1974 *Explosible Dusts, Flammable Liquids and Gases: Explosion Suppression* and by Grabowski (1965) and K.N. Palmer (1973a).

A typical explosion suppression system in a pipe is illustrated in Figure 17.18.

An explosion suppression system for a vessel, and the principles of operation of such a system, are shown in Figure 17.19. Again, very rapid detection and suppression are required.

The basic data for the design of an explosion suppression system are given by the explosion pressure curve for the gas. A typical curve is shown in Figure 17.20 as curve 1.

This information is used to estimate the required response time of the detector and of the suppressant in order to limit the explosion pressure to a specified value. The pressure response typically obtained with explosion suppression is shown in curve 2 of Figure 17.20.

Broadly, the rate of rise of pressure follows the cube law given in Equation 17.7.48, as described in Section 17.6, but factors such as vessel geometry and turbulence effects make prediction difficult.

The main suppressants used to be halons such as bromochlorodifluoromethane and chlorobromomethane. Now, with environment restraints on the use of chlorofluorocarbon substitutes are used, as discussed in NFPAI2A (1997). The quantity of liquid agent commonly specified is 2.14 l/m^3 of protected space. The suppressant is discharged by an electrically fired detonator within 1 ms of the closure of the detonator contacts.

The size and shape of vessel to which explosion suppression can be effectively applied is not unlimited. FS 6015: 1974 stated that explosion suppression is applicable to vessels with a volume of up to 115 m^3 and for flammable gas mixtures for which the maximum explosion pressure is generated in not less than 40 ms.

Developments in technology have tended to expand these limits, as described in relation to dusts in Section 17.47.

With an automatic explosion suppression system operating, the maximum pressure of the suppressed explosion is typically reached in about 10 ms.

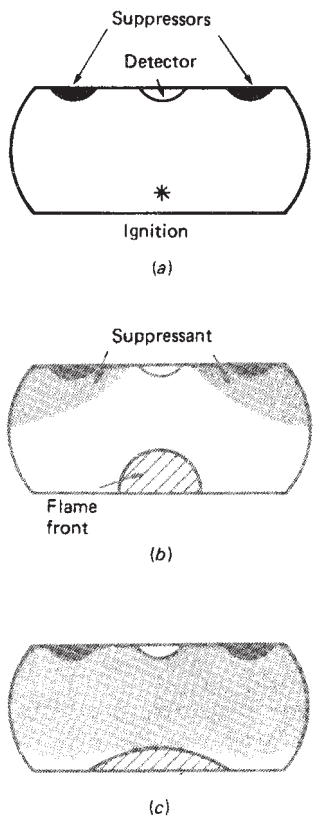

Figure 17.19 *System for automatic suppression of an explosion in a vessel (after Fire Protection Association, 1974 FS 6015): (a) initial ignition; (b) suppressors activated; and (c) suppression nearly complete*

A potential disadvantage of automatic explosion suppression is the risk of spurious trips. This has not proved sufficiently serious, however, to discourage its use.

Automatic explosion suppression systems are widely used.

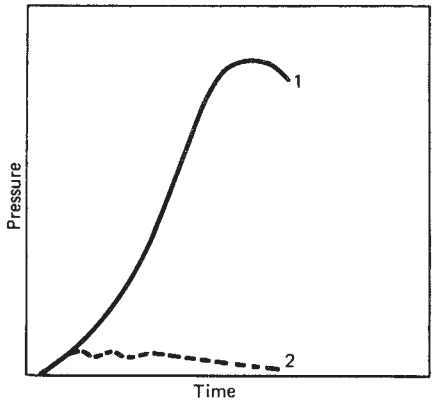

Figure 17.20 *Typical explosion pressure curves for an automatic suppression system: curve 1, explosion pressure in absence of suppression; cure 2, explosion pressure with suppression operating*

17.11.20 Explosion relief and venting

A quite different approach is to relieve the explosion by venting. Explosion venting is applied to (1) vessels, (2) pipes and ducts, (3) buildings, (4) large enclosures, (5) reactors and (6) storage vessels.

If this option is adopted, it is necessary to consider not only the venting itself, but also the disposal of the material vented, which may not be a trivial problem.

Explosion relief of vessels is treated in Section 17.12, of pipes and ducts in Section 17.13, of buildings in Section 17.14, of large enclosures in Section 17.15 and of reactors in Sections 17.16–17.23.

17.12 Explosion Venting of Vessels

One of the options for the protection of a vessel against a gas explosion is the use of explosion venting, also referred to as explosion relief.

Accounts of explosion venting are given in *Explosions* (Bartknecht, 1981a), *Development and Control of Dust Explosions* (Nagy and Verakis, 1983), *Gas Explosions in Buildings and Heating Plants* (R.J. Harris, 1983) and *Venting Gas and Dust Explosions – A Review* (Lunn, 1984b, 1992). All of these except the book by Harris also deal with dust explosions.

Explosion venting is also dealt with in NFPA 68: 2002 *Deflagration Venting*.

The notation used in explosion venting is particularly liable to cause confusion. The term 'maximum explosion pressure' refers generally to a closed, or unvented, explosion, but occasionally it refers to a vented explosion. Pressure is defined sometimes as an absolute pressure, sometimes as a gauge pressure and sometimes as a pressure in excess of the initial pressure. Explosion venting of vessels is a topic in which there are a large number of empirical equations in particular sets of units. Some equations are quoted here in their original form in British units, but generally the use of SI units is preferred. However, with the latter, unless otherwise stated, where units are given, the common practice of giving pressure in kilopascals has been followed. In some subsections equations are given without units, and in these cases any consistent set of units is applicable. Further information on the units used is given in the Notation.

In the account given here, the maximum pressure in a vented system is referred to as the reduced pressure, P_{red}.

The definition of reduced pressure P_{red} as absolute or gauge is not always clearly stated in the original papers and sometimes has to be inferred.

17.12.1 Factors influencing explosion venting

The various factors which influence the maximum pressure and the rate of rise of pressure in an explosion in a closed vessel were described in Section 17.7. They are relevant to vented explosions also.

One factor which assumes particular significance for a vented explosion is the location of the ignition source. Different models have been developed for vented explosions with different locations of the ignition source, as described below.

17.12.2 Experimental studies of venting

There have been a number of experimental studies of explosion venting. Some of the principal studies are listed in Table 17.14.

Early work on explosion relief was done by Cousins and Cotton (1951a,b), who studied a range of containers with L/D ratios varying from 1.41 to 22.1. The relief was a bursting disc. The gases used were propane and hydrogen.

Another early study was carried out at the Midlands Research Station (MRS) of the Gas Council by Cubbage and Simmonds (Cubbage and Simmons, 1955a,b; Simmonds and Cubbage, 1960). Their work was concerned with the explosion venting of industrial drying ovens. The experiments were done on ovens which were approximately cubical and with a variety of vent conditions. The principal gas used was town gas. The pressure profile resulting from an explosion with explosion relief was of the form shown in Figure 17.21. The initial pressure peak at A was followed by a second, higher peak at B

Other experimental studies which have yielded data sets against which correlations can be tested include those of Burgoyne and Wilson (1960), G.F.P. Harris and Briscoe (1967), Yao and co-workers (Yao *et al.*, 1969; Yao, 1974) and Zalosh (1980b).

Experimental studies on larger containments which are often referred to in relation to explosion venting of vessels include those of the Committee for Explosion Research (1958) in Sweden, Dragosavic (1973), Solberg, Pappas and Skramstad (1980, 1981) and Buckland (1980).

17.12.3 Phases of vented explosion

A vented explosion passes through three phases: the initial confined explosion phase, the vent removal phase and the venting phase.

The pressure–time profiles obtained in venting experiments may exhibit as many as three peaks, although in many cases one or more of these peaks is absent or runs into another peak. Explanations of this multiple-peak behaviour have been given by Anthony (1977/78), R.J. Harris (1983) and Lunn (1984b).

The first peak occurs when the vent opens. The magnitude of this peak is a function of the vent opening pressure P_v and the vent inertia w.

The second peak is associated with an increase in the rate of combustion as the burned gas core grows. The magnitude of this peak is a function of two factors. One is

Table 17.14 *Explosion venting of vessels: some experimental studies*

Investigator(s)	*Vessel or enclosure*			
	Type and dimensions (m)	*Volume* (m^3)	*Relief*	*Gas mixture*
Cousins and Cotton (1951a)	(1) Drum, 0.59 diam. × 0.84; L/D 1.41	0.215		Propane, hydrogen
	(2) Tank, 0.36 diam. × 0.823 length; L/D 2.3	0.085		
	(3) Vessel, 0.305 diam. × 0.469 height	0.032		
	(4) Pipe, 0.28 diam. × 6.22 length	0.40		
Cubbage and Simmonds (1955a–c)	Cubical drying ovens	≤14	Vent	Town gas, methane
Burgoyne and Wilson (1960)	Cylindrical chamber, 1.27 diam.	1.7, 5.7	Bursting disc	Pentane
G.F.P. Harris and Briscoe (1967)	Vessel, 1.37 diam. × 1.45 length	1.7		
Yao *et al.* (1969); Yao (1974)	(1) Cubical chamber, 0.91 × 0.91 × 0.91	0.765	Open vent	Propane, hydrogen
	(2) Cylindrical chamber, 0.91 diam. × 0.91 length	0.786	Bursting diaphragm	
	(3) Cylindrical chamber, 0.91 diam. × 2.74 length	2.36		
Zalosh (1980b)	Rectangular enclosures:		Vent	Methane, propane, ethylene
	(1) 0.92 × 0.61 × 0.31	0.17		
	(2) 0.56 × 0.56 × 0.56	0.18		
	(3) 0.71 × 0.71 × 0.37	0.19		
	(4) 1.47 × 0.91 × 0.43	0.58		
	(5) 1.80 × 2.00 × 3.10	11.2		
	(6) 5.40 × 2.00 × 3.10	33.5		

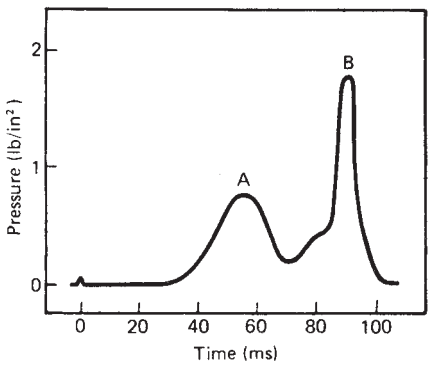

Figure 17.21 *Explosion venting of vessels: typical explosion pressure curve obtained in explosion venting of an enclosure in work of Cubbage and Simmonds (1960) (courtesy of the Institution of Chemical Engineers)*

the features which may give an enhanced combustion rate. These include shear turbulence and stretching of the flame towards the vent. The other factor is the flow resistance, which depends on the vent size and on any vent ducting.

The third peak is associated with the venting of burned gas. When the burned gas starts to vent, the volumetric flow increases markedly, since the burned gas density is much less than that of the unburned gas.

The first peak may be weak or absent if the vent is an open one. It tends to be large if the vent opening pressure or vent inertia is high. But if the vent area is small so that there is little vent outflow before the second peak arrives, the first peak merges into the second one. This may also occur if the vent opening pressure is sufficiently high.

The second peak may be weak if the rate of combustion is slow or the vent area large. Conversely it is large if the rate of combustion is high and the vent area is small. In the former case the second peak may merge into the first one.

In the later stages of venting the explosion may exhibit various types of oscillatory behaviour as evidenced by the pressure trace.

Some typical pressure profiles are illustrated in Figure 17.22. Other examples of the multiple peaks obtained in explosion venting are given in Section 17.15.

Another feature of the venting process is the effect of the vent pressure on the combustion process. For a vessel with a relatively low vent area, if the vent pressure is set at a low value, the explosion pressure tends to exceed the vent pressure. The phenomenon has been studied by G.F.P. Harris and Briscoe (1967), who attribute it to a large increase in the flame area when the vent is opened. This is illustrated in Figure 17.23.

17.12.4 Oscillatory behaviour

Pressure–time profiles of a vented explosion often show marked oscillatory behaviour in the later stages. The significance of this is that combustion oscillations can greatly increase the combustion rate, particularly in the later stages, and can result in higher pressures. The effect becomes relatively more important as the scale increases, but it may not be negligible even for vessels. Oscillation in explosion venting was described by Zalosh (1980b), who

obtained high, delayed, oscillatory second peaks in the pressure–time profile using propane.

Oscillatory behaviour in explosion venting of a spherical vessel with a vent tube attached has been investigated by Kordylewski and Wach (1988).

One type of oscillatory behaviour is that due to acoustic oscillation. For an acoustic oscillation Kordylewski and Wach used the relation

$$f_a \approx \frac{c\lambda_1}{2\pi r_s} \qquad [17.12.1]$$

where c is the speed of sound in the medium, f_a is the frequency of the oscillation, r_s is the radius of the spherical vessel and λ_1 is a constant. The value of λ_1 is 4.4934.

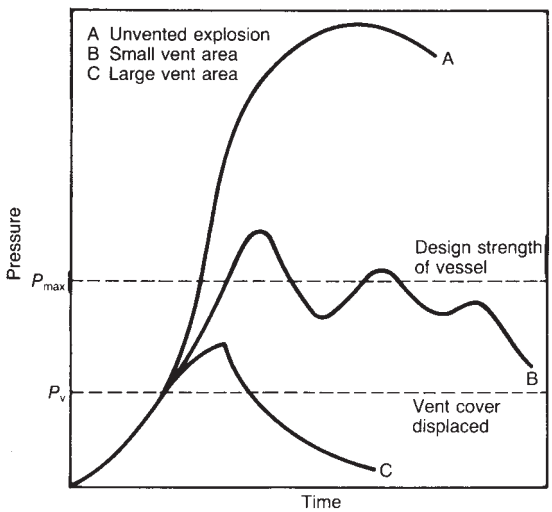

Figure 17.22 *Explosion venting of vessels: generalized explosion pressure curves for closed and vented vessels (Field, 1982; reproduced by permission of Elsevier Science Publishers)*

Formulae for this and other geometries are given in *Formulas for Natural Frequency and Mode Shape* (Blevins, 1979).

Another type of oscillatory behaviour is that due to Helmholtz oscillation. For Helmholtz oscillation Kordylewski and Wach used the relation

$$f_H = \frac{c}{2\pi}\left(\frac{A_v}{L + \alpha V}\right)^{1/2} \qquad [17.12.2]$$

with

$$a = 0.255D \qquad [17.12.3]$$

where A_v is the vent area, D is the duct diameter, f_H is the frequency of Helmholtz oscillation, L is the length of the duct, V is the volume of the vessel and α is a correction factor.

The occurrence and strength of combustion oscillations depend on the concentration of the gas mixture. Thus, in the work of Zalosh (1980b) just described, oscillations were observed for propane concentrations only in the range 5.0–5.5%.

The oscillations tend to be more marked just on the fuel-rich side of the stoichiometric ratio. C.J.M. van Wingerden (1989c) found, using 9.5 and 10% methane–air mixtures, that whilst the former was the stoichiometric concentration it was the latter which was more sensitive to oscillatory combustion.

17.12.5 Empirical and semi-empirical methods

As already indicated, the venting of an explosion is a complex process. It is therefore difficult to model theoretically. This has led to the development of a number of empirical and semi-empirical methods and scaling laws.

17.12.6 Vent ratio and vent coefficient

Work on explosion venting makes frequent use of two quantities, the vent ratio and the vent coefficient. The vent ratio f is defined as the ratio of the vent area A_v to the volume vented V:

$$f = A_v/V \qquad [17.12.4]$$

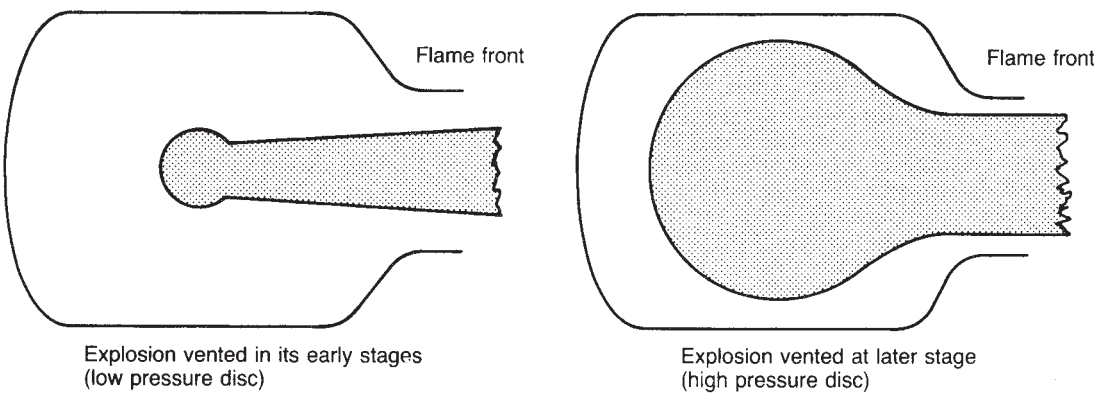

Figure 17.23 *Explosion venting of vessels: distortion of flame front on opening of vent (G.F.P. Harris and Briscoe, 1967) (Courtesy of the Combustion institute)*

The vent coefficient K is defined as

$$K = A_c/A_v \qquad [17.12.5]$$

with

$$A_c = L_1 L_2 \qquad [17.12.6]$$

where A_c is the area of the smallest cross-section of the enclosure (m^2), A_v is the vent area (m^2), L_1 and L_2, for a rectangular enclosure, are the dimensions of the two smallest sides (m).

The vent coefficient is therefore dimensionless, but the vent ratio is not.

These two quantities are discussed further below, particularly in relation to scaling methods.

17.12.7 Rasbash method

An early equation for the reduced pressure P_{red} in a vented explosion, or vented explosion pressure, was that of Rasbash (1969c), who gave the following equation for the maximum pressure in a vented explosion in a building:

$$P_{red} = 1.5P_v + 0.5K \qquad [17.12.7]$$

with

$$K = A_c/A_v \qquad [17.12.8]$$

where A_c is the area of the smallest cross-section of the enclosure (ft^2), A_v is the total area of combustion vents (ft^2), K is the venting ratio, P_{red} is the reduced pressure, or maximum pressure reached during the venting of combustion (gauge) ($lb_f/in.^2$) and P_v is the pressure within the building space at which the vent opens (gauge) ($lb_f/in.^2$). In SI units these equations become

$$P_{red} = 1.5P_v + 3.5K \qquad [17.12.9]$$

where P_{red} is the reduced pressure (gauge) (kPa) and P_v is the pressure within the building space at which the vent opens (gauge) (kPa).

Rasbash stated that Equation 17.12.9 was based on a collation of information on experimental work on venting using particularly propane and referred to work on explosion relief of ducts (Rasbash and Rogowski, 1960b).

There are a number of restrictions on the use of Equation 17.12.9. They may be summarized as

$$L/D \leq 3; \quad 1 \leq K \leq 5; \quad w \leq 24; \quad P_v \leq 7 \qquad [17.12.10]$$

where w is the inertia of the vent (kg/m^2). In addition, the pressure should be virtually exhausted after the vent has moved a few millimetres.

Equation 17.12.9 applies to propane. For natural gas and for town gas which contains 60% H_2, the pressures reached are, respectively, about 0.8 and 2.5 times that given by Equation 17.12.9 (Mainstone, 1971).

If the flammable mixture is turbulent when ignited or becomes turbulent during the combustion, pressures considerably higher than those given in Equation 17.12.9 may be generated.

In subsequent work, Rasbash, Drysdale and Kemp (1976) modified Equation 17.12.9 to include a term for the vent inertia

$$P_{red} = AP_v + P_I + BK \qquad [17.12.11]$$

with

$$P_I = \frac{0.20Kw + 1.17}{V^{1/3}} \qquad [17.12.12]$$

$$w = W_v/A_v \qquad [17.12.13]$$

where P_I is the back pressure due to the inertia of the vent (gauge) (kPa), w is the inertia of the vent (kg/m^2) and W_v is the mass of the vent cover (kg). The values of the constants given are 1–1.5 kPa for A and 2.5 kPa for B; the value commonly used for A is 1.5.

The authors then generalize Equation 17.12.11 to make it applicable to other flammable gases:

$$P_{red} = 1.5P_v + S_u(P_I + 2.5K)/0.45 \qquad [17.12.14]$$

where S_u is the maximum fundamental burning velocity (m/s). The constant 0.45 represents the maximum fundamental burning velocity of propane.

Finally, Rasbash, Drysdale and Kemp introduce a turbulence factor f so that Equation 17.12.14 becomes

$$P_{red} = 1.5P_v + fS_u(P_I + 2.5K)/0.45 \qquad [17.12.15]$$

They suggest for f a value of 1.5 for a single room, but modify this considerably for certain conditions. For a situation where the explosion propagates from one room to another they propose for f a value of 5, and for a high pressure leak of liquid petroleum gas (LPG) values of 8 or even 10.

For comparison with equations derived by other workers it is helpful to combine Equations 17.12.11 and 17.12.12, to give

$$P_{red} = 1.5P_v + \frac{0.20KwS_u}{0.45V^{1/3}} + \frac{1.17S_u}{0.45V^{1/3}} + \frac{2.5S_uK}{0.45} \qquad [17.12.16]$$

The relative importance of the terms in Equation 17.12.16 may vary. If P_v is high, P_{red} approximates to it, whilst if P_v is low, P_{red} may be appreciably higher than P_v. If K is low (high A_v), P_{red} approximates to P_v whilst if K is high, P_{red} may again be higher than P_v.

Equation 17.12.11 has been widely used for the explosion relief of buildings. It is considered further in Section 17.14.

17.12.8 Cubbage and Simmons method

The pressure profile obtained by Cubbage and Simmonds in their work on drying ovens was described above. The relation obtained by these authors for the first pressure peak (peak A in Figure 17.21) is

$$P_1 = \frac{0.437KwS_u}{V^{1/3}} + \frac{2.817S_u}{V^{1/3}} \qquad [17.12.17]$$

and that for the second peak (peak B in Figure 17.21) is

$$P_2 = 5.8S_uK \qquad [17.12.18]$$

where K is the vent coefficient, P_1 and P_2 are, respectively, the first and second pressure peaks (gauge) (kPa), S_u is the maximum fundamental burning velocity (m/s), V is the volume of the vessel (m^3) and w is the inertia of the vent (kg/m^2).

In contrast to Rasbash's method, Cubbage and Simmonds's method is based on separate equations for the two pressure peaks. The first of their equations depends only on the inertia w of the vent panel, the second only on the vent coefficient K, whilst the vent opening pressure P_v does not appear.

17.12.9 Runes method

In contrast to the two empirical correlations just described, the equation given by Runes (1972) for the vent area of a large container or building has some theoretical basis. It is based on equating the volume production rate and the volumetric vent outflow. The volume production rate is

$$Q_m = A_m u_f (E - 1) \qquad [17.12.19]$$

with

$$A_m = \pi L_1 L_2 \qquad [17.12.20]$$

where A_m is the maximum area of the flame front (ft^2), E is the expansion ratio, L_1 and L_2, are the two smallest dimensions of the enclosure (ft), Q_m is the rate of volume production (ft^3/s) and u_f is the flame speed (ft/s). The volumetric vent outflow is

$$Q_v = Y C_d A_v (2g \times 144 \Delta P/\rho)^{1/2} \qquad [17.12.21]$$

where C_d is the coefficient of discharge, g is the acceleration due to gravity (ft/s^2), ΔP is the vented explosion pressure (gauge) ($lb_f/in.^2$), equivalent to P_{red}, Q_v is the volumetric vent outflow (ft^3/s), Y is a constant which takes account of the expansion of the gas as it discharges and ρ is the density of the gas (lb/ft^3). The value of C_d is 0.6, and Y is usually unity.

Runes takes $Y = 1$, $C_d = 0.6$, $g = 32.2$ and $\rho = 0.085$, and obtains

$$Q_v = 200 A_v \Delta P^{1/2} \qquad [17.12.22]$$

(Equation 17.12.22 is obtained from Equation 17.12.21 by substituting the numerical values given by Runes. He actually gives not Equation 17.12.21 but one in which the right-hand side is $Y C_d A_v 2g(144\Delta P)^{1/2}/\rho$, but this is evidently a typographical error. This error has caused some confusion in the expressions quoted in the literature for the Runes constant C, described below.) Then, from Equations 17.12.19, 17.12.20 and 17.12.22

$$A_v = \frac{\pi L_1 L_2 u_f (E - 1)}{200 \Delta P^{1/2}} \qquad [17.12.23]$$

$$= \frac{C L_1 L_2}{\Delta P^{1/2}} \qquad [17.12.24]$$

with

$$C = \frac{\pi u_f (E - 1)}{200} \qquad [17.12.25]$$

where C is a constant.

The value of the constant C is discussed in more detail in Section 17.14 on explosion venting of buildings. Runes himself did not assign a value to the constant, though from Equation 17.12.25 $C = 0.108 u_f$. As described in Section 17.14, W.B. Howard (1972) assigned a value to C of 1.2 by inserting the value for propane of $u_f = 11$ ft/s. However, in the same paper Howard also made his own calibration of the constant based on an incident involving ethanol for which he took $u_f = 24$ ft/s and thus obtained a value of $C = 2.6$ ($1.2 \times 24/11$).

The constant C is best regarded as an empirical one which allows for the actual flame speed under the conditions of turbulence in the enclosure. NFPA 68: 1978 gives for C in British units for use in Equation 17.12.24 a value of 2.6 for gases such as propane and other gases with a similar burning velocity. A higher value is recommended for gases with a higher burning velocity. The suggested value for ethylene is 4 and that for hydrogen 6.4.

In SI units Equation 17.12.24 is

$$A_v = C \frac{L_1 L_2}{\Delta P^{1/2}} \qquad [17.12.26]$$

where A_v is the necessary building vent area (m^2), L_1 is the smallest dimension of the rectangular building enclosure to be vented (m), L_2 is the second smallest dimension of that building (m), P is the maximum internal building pressure (gauge) (kPa) and C is a constant.

NFPA 68: 1978 gives for C in metric units for use in Equation 17.12.26 a value of 6.8 for gases such as propane and others gases with a similar burning velocity, whilst the suggested value for ethylene is 10.5 and that for hydrogen is 17.

Equation 17.12.26 has been widely used for the explosion relief of buildings. It is considered further in Section 17.14. NFPA 68: 1994 gives a relationship similar to Equation 17.12.26; this is described in Section 17.14.

17.12.10 Decker method

The method described by Decker (1971) is based on somewhat similar considerations to that of Runes. The approach is again to equate the volume production rate and the volumetric vent outflow;

$$Q_v = \frac{dP}{dt} \frac{V}{P_v} \qquad [17.12.27]$$

$$= V/t \qquad [17.12.28]$$

where P is the pressure ($lb_f/in.^2$), P_v is the vent pressure ($lb_f/in.^2$), Q_v is the volumetric vent outflow (ft^3/s), t is time (s) and V is the volume of the vessel (ft^3). For the vent area he then obtains

$$A_v = k \frac{dP}{dt} V \left(\frac{\bar{M}}{T}\right)^{1/2} \frac{1}{P_v} \qquad [17.12.29]$$

where A_v is the vent area (ft^2), $\bar{M}$ is the mean molecular weight of the gas, T is the absolute temperature of the burnt gases (°R) and k is a constant. The temperature T of the burnt gases is of the order of 3600°R. The treatment by Lowenstein (1958) is rather similar. The value of the constant k is 1/132.

17.12.11 Dragosavic method

Dragosavic (1973) has given equations for the first and second peak pressures in explosions in rooms in dwellings. For the first peak pressure

$$P_1 = P_v + C \quad [17.12.30]$$

and for the second peak pressure

$$P_2 = AP_v + B/f^2 + C \quad [17.12.31]$$

with

$$f = A_v/V \quad [17.12.32]$$

where P_1 and P_2 are, respectively, the first and second peak pressures (gauge) (kPa), P_v is the vent opening pressure (kPa), f is a vent ratio (m^{-1}) and A, B and C are constants. The values of A, B and C for natural gas–air mixtures are 0.5, 0.04 and 3.0 kPa, respectively. Equation 17.12.30 applies to enclosures with open and closed vents. Equation 17.12.31 represents an envelope of the experimental values and therefore overestimates the second peak pressure.

17.12.12 Cubbage and Marshall method

Cubbage and Marshall (1973) have obtained the relation

$$P_{red} = P_v + 2.44(KwS_u^2/V^{1/3}) \quad [17.12.33]$$

where K is the venting coefficient, P_{red} is the reduced pressure (gauge) (kPa), P_v is the vent opening pressure (gauge) (kPa), S_u is the maximum fundamental burning velocity (m/s), V is the volume of the vessel (m^3) and w is the inertia of the vent (kg/m^2).

17.12.13 Other methods

The following further equations for explosion venting are quoted by Lunn. Rasbash has given the two equations

$$P_{red} = P_v + 7.76S_uK \quad [17.12.34]$$

$$P_{red} = (P_v + 7.76K)S_uK \quad [17.12.35]$$

where K is the venting coefficient, P_{red} is the reduced pressure (gauge) (kPa), P_v is the vent opening pressure (gauge) (kPa) and S_u is the fundamental burning velocity (m/s).

Burgoyne and Wilson (1960) have given the following equation for their work on pentane–air systems:

$$P_{red} = 68 \log_{10}(K) - 28.6 \quad [17.12.36]$$

where K is the venting coefficient and P_{red} is the reduced pressure (gauge) ($lb_f/in.^2$).

17.12.14 Scaling methods

Empirical equations have the limitation that they cannot be used with confidence outside the range of experimental data on which they are based. An alternative empirical approach is the use of scaling laws validated over a wide range of experimental conditions.

There are two principal methods based on scaling laws which are used for gas explosion venting: the vent ratio method and the vent coefficient method. Traditionally, in Britain the vent coefficient method has been used for venting of gas explosions and the vent ratio method for venting of dust explosions, but there is no logical basis for this.

17.12.15 Vent ratio method

The vent ratio f is defined as

$$f = A_v/V \quad [17.12.37]$$

where A_v is the vent area, f is the vent ratio and V is the volume of the enclosure.

The simple application of the vent ratio method is the use of a constant vent ratio.

It is found in practice that in scaling up from small scale tests, the use of a constant vent ratio tends to overestimate the vent area required. The following alternative treatment given by Lunn addresses this problem. The relationship between the rate of pressure rise and the volume of the vessel is given by the cube root law (17.7.48)

$$\frac{dP}{dt} V^{1/3} = \text{constant} = K_G \quad [17.12.38]$$

Following an approach similar to that of the Decker method, as given in Equation 17.12.29, but using P_{red} rather than P_v, the volumetric venting flow Q_v, and hence the vent area required, is

$$A_v \propto \frac{dP}{dt}\frac{V}{P_{red}} \quad [17.12.39]$$

Hence, for the vent ratio

$$fV^{1/3} = \text{constant} \quad [17.12.40]$$

This approach implies that the cube root law is applicable to vented vessels also. It is the basis of the Bartknecht nomograph method described below

A common method of characterizing the vent area required is to plot the reduced explosion pressure as a function of vent ratio. Numerous such plots are given by Lunn.

17.12.16 Vent coefficient method

The vent coefficient K is defined as

$$K = A_c/A_v \quad [17.12.41]$$

with

$$A_c = L_1/L_2 \quad [17.12.42]$$

where A_c is the area of the smallest cross-section of the enclosure, K is the vent coefficient and L_1 and L_2 are the two smallest dimensions of the enclosure.

For a cubical enclosure of volume V if $L_1 = L_2 = (\pi/6)^{1/3}$, $D = 0.80D$

$$A_c = V^{2/3} \quad [17.12.43a]$$

$$L_1L_2 = V^{2/3} \quad [17.12.43b]$$

The following treatment by Lunn gives the relation between the vent coefficient and the reduced pressure. Again, following Decker and using Equation 17.12.29 with P_{red} together with Equations 17.12.38, 17.12.41 and 17.12.43

$$P_{red} \propto K \quad [17.12.44]$$

The characteristics of the vent ratio and vent coefficient methods have been explored by N. Gibson and Harris

(1976), as shown in Figure 17.24. Their experimental results for pentane, and also those for class St 2 dusts, are well fitted using the vent coefficient with $K = 3$. Also shown are curves for various vent ratios. The two methods exhibit an increasing divergence in the predicted vent areas as the vessel volume increases.

A critique of vent coefficient scaling has been given by Zalosh (1980b). He carried out experiments with a range of containment volumes from 0.17 to 33.5 m^3, and found that such scaling is valid for volumes up to 12 m^3 but that for larger volumes the relationship breaks down due apparently to effects related to flame speed.

17.12.17 The K_G method

The K_G method developed by Bartknecht is based on the cube root law given in Equation 17.12.38. The cube root law in terms of the maximum rate of pressure rise is

$$\left(\frac{dP}{dt}\right)_{max} V^{1/3} = K_G \qquad [17.12.45]$$

and in terms of the rate of pressure rise with venting

$$\left(\frac{dP}{dt}\right)_{P_{red}} V^{1/3} = K_G \qquad [17.12.46]$$

Thus, for the same reduced pressure the vent ratio f also follows the cube root law

$$fV^{1/3} = \text{constant} \qquad [17.12.47]$$

As described by Bartknecht (1981a), Donat and Bartknecht have carried out extensive experimental work on vented explosions using the Ciba–Geigy 20 l sphere. They apply the cube root law of Equation 17.12.45 and determine the value A_v for values of the gas factor K_G, the vent opening pressure P_{stat} and the reduced explosion pressure P_{red}.

The results of their work are given in the form of a series of nomographs for the determination of the vent area A_v for particular values of the vessel volume V, the initial pressure P_o and the vent explosion pressure P_{red}. Each nomograph is for a particular value of K_G degree of initial turbulence and strength of ignition source. For gases the values given for K_G are as follows:

	K_G (bar m/s)
Methane	55
Propane	75
Coke gas	140
Hydrogen	550

For solvents the value used is that for propane. The nomographs give the vent area A_v as

$$A_v = f(V, K_G, P_{stat}, P_{red}) \qquad [17.12.48]$$

where P_{red} is the reduced pressure and P_{stat} the vent opening pressure and V is the volume of the vessel.

The derivation of these nomographs has been described by Lunn, Brookes and Nicol (1988) and in NFPA 68: 1994, and is discussed further in Section 17.48.

There is a separate nomograph for each of the four gases mentioned. The vent opening pressure P_{stat} is given as a parameter. The three values of P_{stat} are 0.1, 0.2 and 0.5 barg. The range of values of P_{red} is 0.2–2.0 barg.

The nomographs are valid within a limited range of conditions. They are for a quiescent mixture and a weak

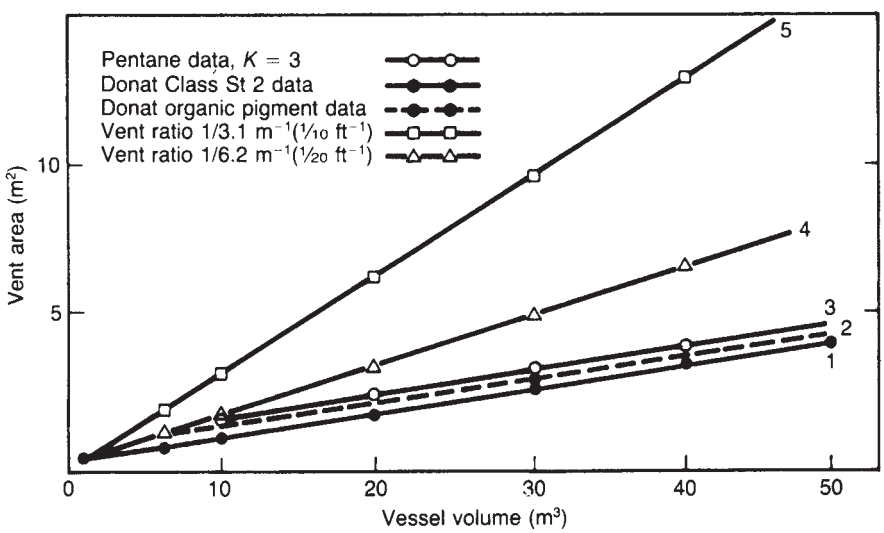

Figure 17.24 *Explosion venting of vessels: some vent ratio and vent coefficient predictions (N. Gibson and Harris, 1976): (1) Donat's results for St 2 dust; (2) Donat's results for organic pigment; (3) results for pentane with vent coefficient $K = 3$; (4) vent ratio 1/6.2 m^2/m^3; and (5) vent ratio 1/3.1 m^2/m^3. Maximum pressure rise 48 kPa and vent rupture pressure 7–14 kPa (courtesy of the American Institute of Chemical Engineers)*

ignition source (10 J). Their use is not recommended for $V > 1000\ m^3$, $P_{stat} < 0.1$ barg and $P_{red} < 0.2$ or > 2.0 barg.

Experiments have shown that above a reduced pressure P_{red} of 2.0 barg, a well-defined correlation of P_{red} cannot be obtained, which is the reason for the upper limit in the nomographs.

The K_G nomograph method was adopted in NFPA 68: 1988, and the nomographs in Figure 17.25 are those given in the 1994 version NFPA 68.

The use of the nomographs is illustrated in Figure 17.26. For a vessel of volume V, enter on the right-hand graph, move up to the desired value of the reduced pressure P_{red}, move left on the left-hand graph to the desired value of the vent opening pressure P_{stat} and then move down to the required vent area A_v.

The vent area given by the nomographs is illustrated in Figure 17.27 for a 1 m^3 vessel with a vent opening pressure $P_{stat} = 0.1$ barg.

The nomographs may be used for other gases by interpolation of the K_G values. They may be used for stronger ignition sources if the K_G value for the gas with that ignition source is known.

In Bartknecht's method, if the mixture is not quiescent, the effect of turbulence must be taken into account. The information available on this is limited. But for large vent area A_v and low reduced pressure P_{red} ($\leq$2 bara) turbulence has little effect and the nomographs may be used as they stand. For small A_v and high P_{red} (>2 bara) A_v should be increased by a correction term ΔA_v, where

$$\Delta A_v = 0.08 V^{2/3} \qquad [17.12.49]$$

Bartknecht states that this treatment is applicable only to methane, propane and solvent vapours and for $P_{stat} \leq 0.1$ barg. This correction is not accepted yet by NFPA 68.

The initial, or operating, pressure on which the nomographs are based is 1 bara, but they may be used without correction up to a value of 1.2 bara. Data outside this range were not available when the nomographs were formulated, but Bartknecht states that for higher operating pressures it should be assumed that for a given vent area the reduced explosion pressure is proportional to the operating pressure.

An equation equivalent to the Bartknecht nomographs has been given by Simpson (1986). His equation is

$$A_v = a V^b \exp(c P_{stat}) P_{red}^d \qquad [17.12.50]$$

where the units are A_v (m^2), P_{red} (barg), P_{stat} (barg) and V (m^3). The range of validity of the equation is

$$1 \leq V \leq 1000; \quad 0.1 \leq P_{stat} \leq 0.5; \quad P_{stat} + 0.1 \leq P_{red} \leq 2$$

Values of the constants in Equation 17.12.50 are given in Table 17.15. Equation 17.12.50 is quoted in NFPA 68: 1994.

17.12.18 Experimental studies of venting relations

A review of experimental studies comparing the predictions of empirical and semi-empirical equations with experimental results is given by Lunn.

The equations recommended by Lunn as the most versatile are Equation 17.12.11 of Rasbash and Equations 17.12.17 and 17.12.18 of Cubbage and Simmonds. The Runes equation (Equation 17.12.22) contains the constant C, which is too dependent on the particular conditions from which it was derived. The Decker equation (Equation 17.12.29) gives upper limits of P_{red} which are often reasonable but in other cases are overestimates. The Dragosavic equations (Equations 17.12.30 and 17.12.31) are limited to methane–air mixtures, and the Burgoyne and Wilson equation (Equation 17.12.36) to pentane–air mixtures. Rasbash's other equations (Equations 17.12.34 and 17.12.35) are limited to low turbulence, and of the two relations Equation 17.12.34 is superior to Equation 17.12.35 in all cases. The Cubbage and Marshall equation (Equation 17.12.33) is limited to methane–air mixtures as the dependency on the square of the burning velocity tends to give overestimates of P_{red} for gases with high burning velocity.

17.12.19 Modelling of explosion venting

The modelling of combustion in an unvented vessel was described in Section 17.7. Models have also been developed on similar lines for combustion in vented vessels.

17.12.20 Vent outflow equations

The outflow from a vented vessel may be subsonic or sonic. Equations for both types of flow were given in Chapter 15. As the absolute pressure P in the vessel increases relative to atmospheric pressure P_a the ratio η ($= P_a/P$) decreases. When this ratio falls below a critical value $\eta_c (= 2/(\gamma+1)^{\gamma/(\gamma+1)})$ sonic flow occurs. The mass outflow per unit area G_v from the vessel is then

$$G_v = C_d f_v \qquad [17.12.51]$$

with

$$f_v = f_{v1} \qquad [17.12.52]$$

$$f_{v1} = f_{vsb1} \quad \text{subsonic flow} \qquad [17.12.53a]$$

$$= f_{vs1} \quad \text{sonic flow} \qquad [17.12.53b]$$

$$f_{vsb1} = \left\{ 2P\rho \frac{\gamma}{\gamma - 1} \left[\left(\frac{P_a}{P} \right)^{2/\gamma} - \left(\frac{P_a}{P} \right)^{(\gamma+1)/\gamma} \right] \right\}^{1/2} \qquad [17.12.54]$$

subsonic flow

$$f_{vs1} = \left[P\rho\gamma \left(\frac{2}{\gamma + 1} \right)^{(\gamma+1)/(\gamma-1)} \right]^{1/2} \quad \text{sonic flow} \qquad [17.12.55]$$

where C_d is the coefficient of discharge, γ is the ratio of gas specific heats and ρ is the density of the gas. An alternative form of these equations utilized in some models is

$$f_v = (P\rho\gamma)^{1/2} f_{v2} \qquad [17.12.56]$$

$$f_{v2} = f_{vsb2} \quad \text{subsonic flow} \qquad [17.12.57a]$$

$$= f_{vs2} \quad \text{sonic flow} \qquad [17.12.57b]$$

with

$$f_{vsb2} = \frac{f_{vbs1}}{(P\rho\gamma)^{1/2}} \quad \text{subsonic flow} \qquad [17.12.58]$$

$$f_{vs2} = \frac{f_{vs1}}{(P\rho\gamma)^{1/2}} \quad \text{sonic flow} \qquad [17.12.59]$$

For common gases such as air ($\gamma = 1.4$) the value of η_c is about 0.5.

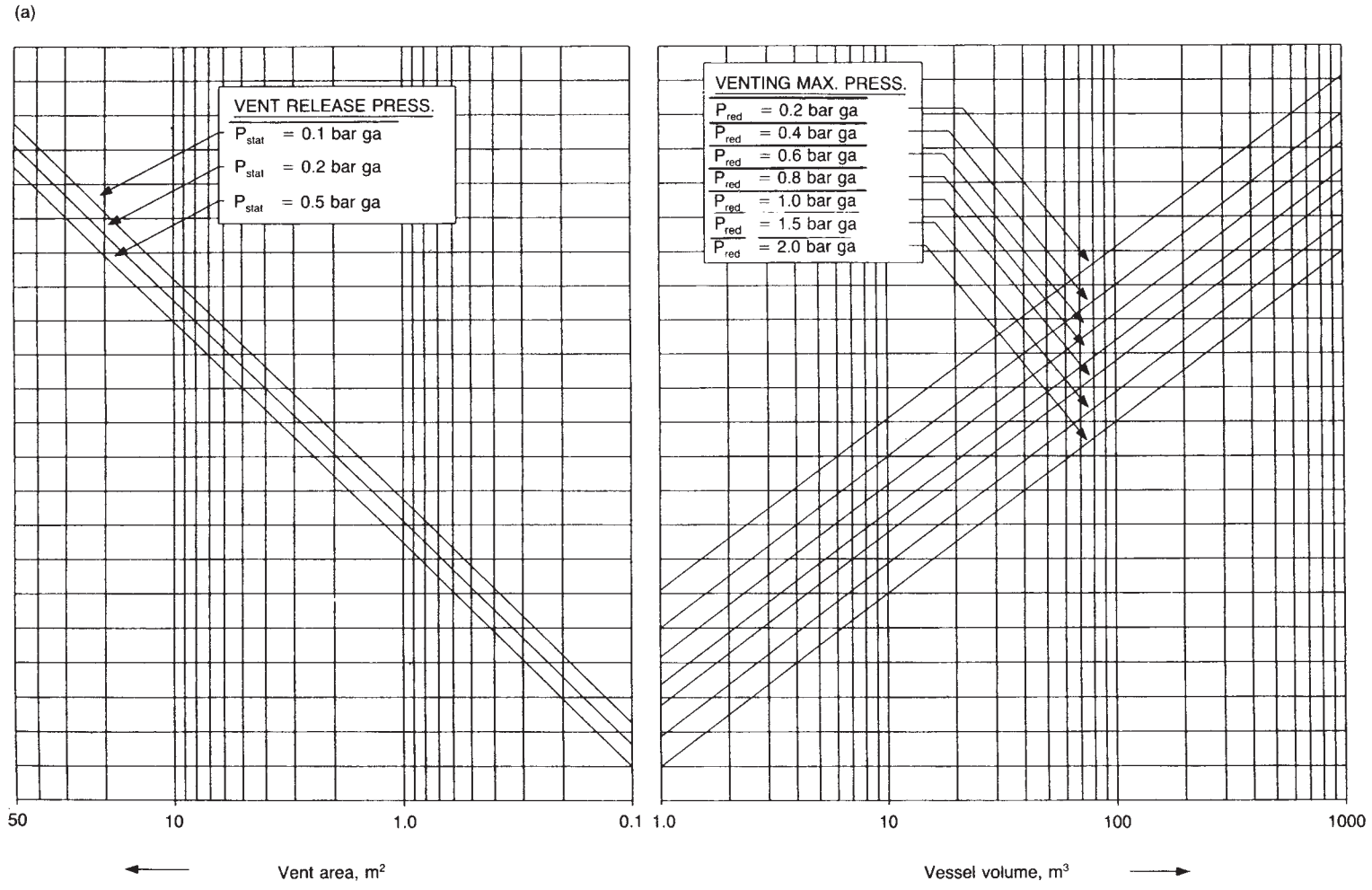

Figure 17.25 *Explosion venting of vessels: nomographs for vent area (NFPA 68: 1994) (a) methane, (b) propane, (c) coke gas, and (d) hydrogen. See text for details (reproduced with permission from NFPA 68 Deflagration Venting, Copyright © 1994, National Fire Protection Association, Quincy, MA 02269). Note: This reprinted material is not the complete and official position of the National Fire Protection Association on the referenced subject which is represented only by the standard in its entirety)*

(b)

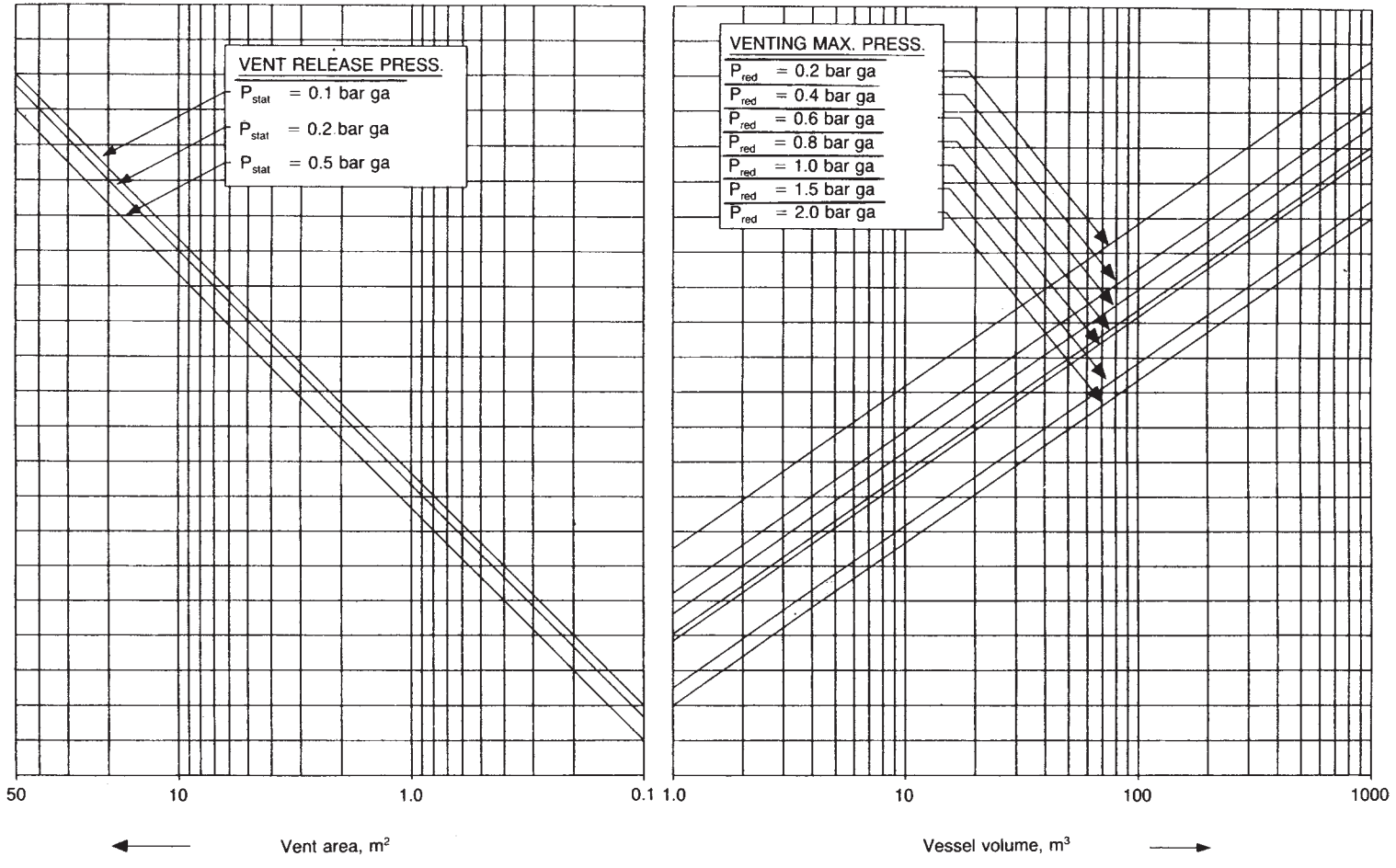

Figure 17.25 *Continued*

(c)

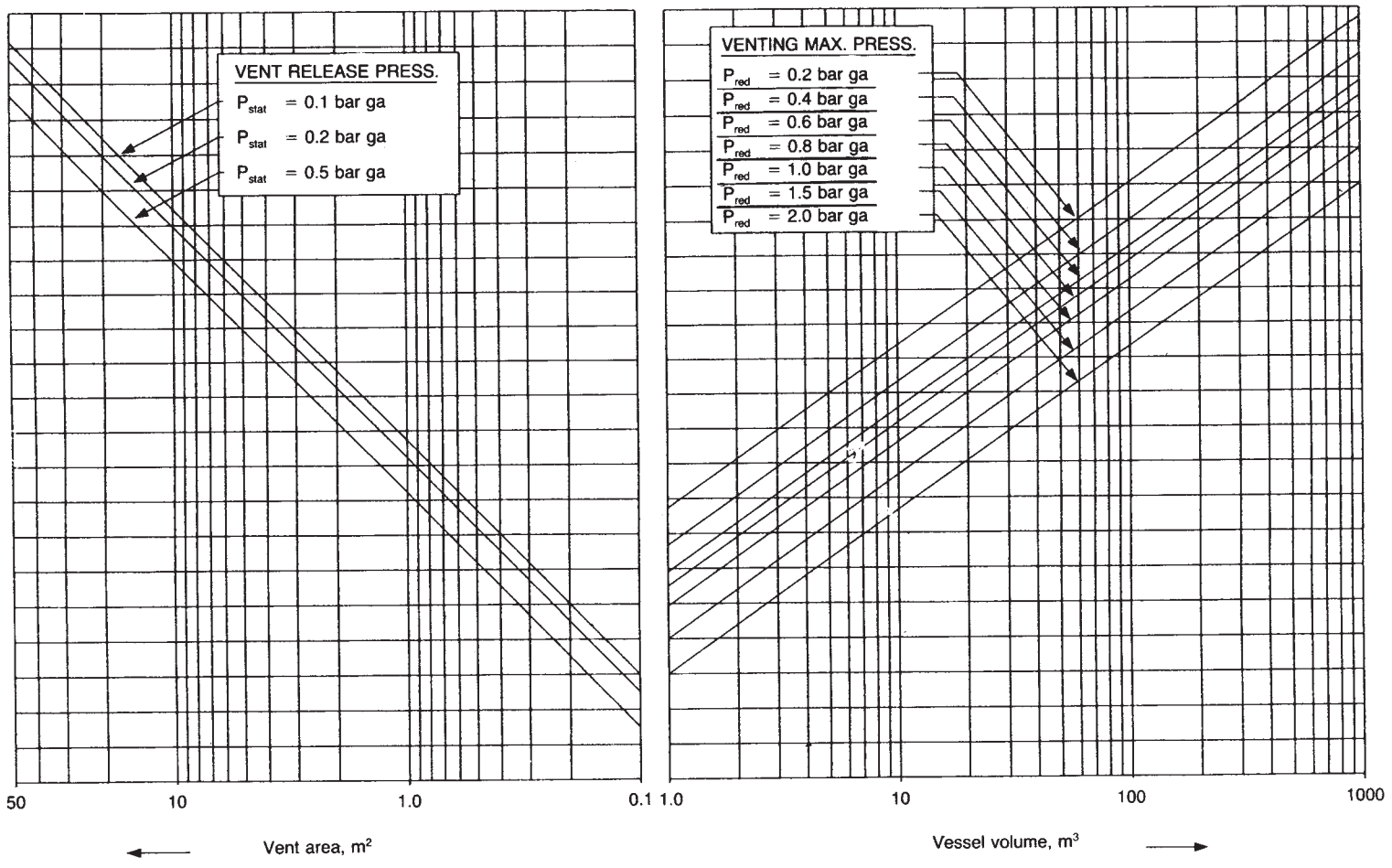

Figure 17.25 *Continued*

(d)

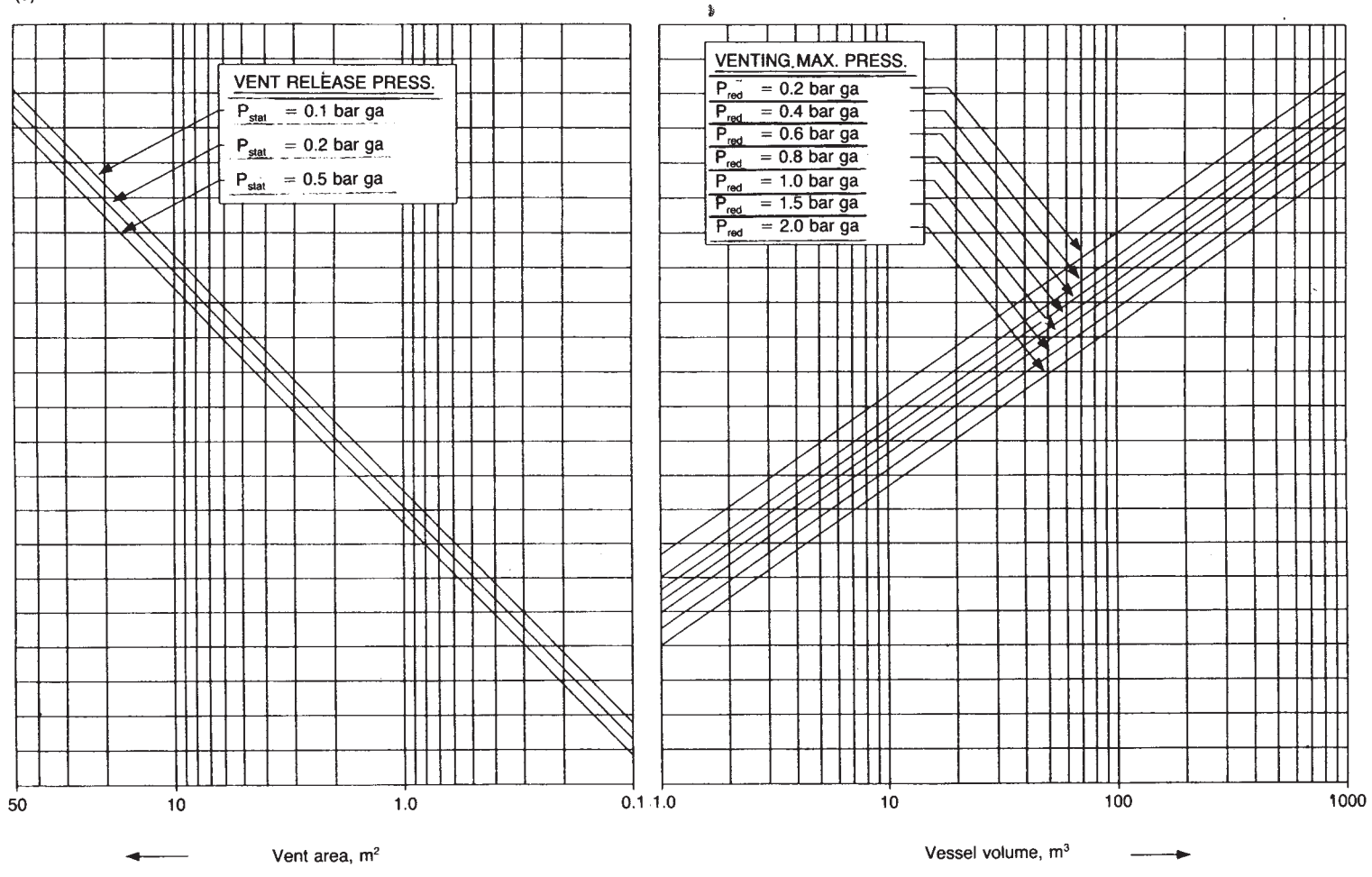

Figure 17.25 *Continued*

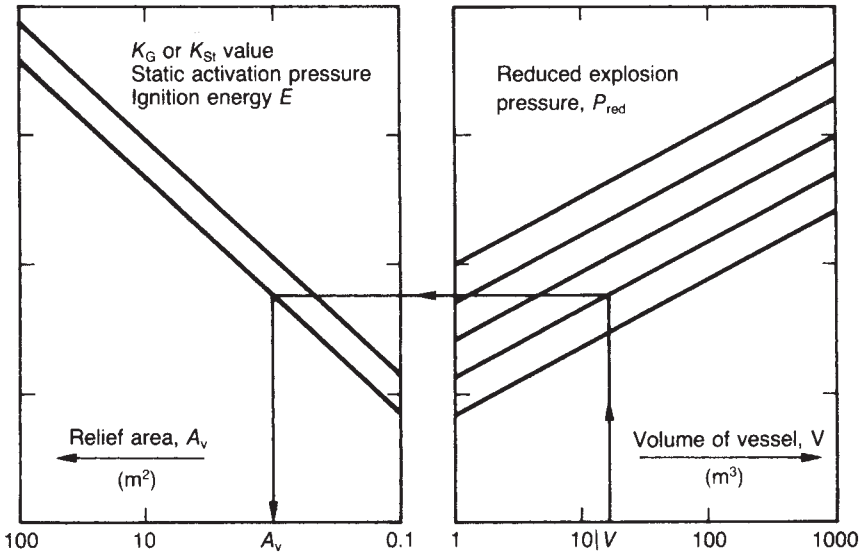

Figure 17.26 *Explosion venting of vessels: nomographs for vent area – use of nomograph (Bartknecht, 1981a) (Courtesy of Springer-Verlag)*

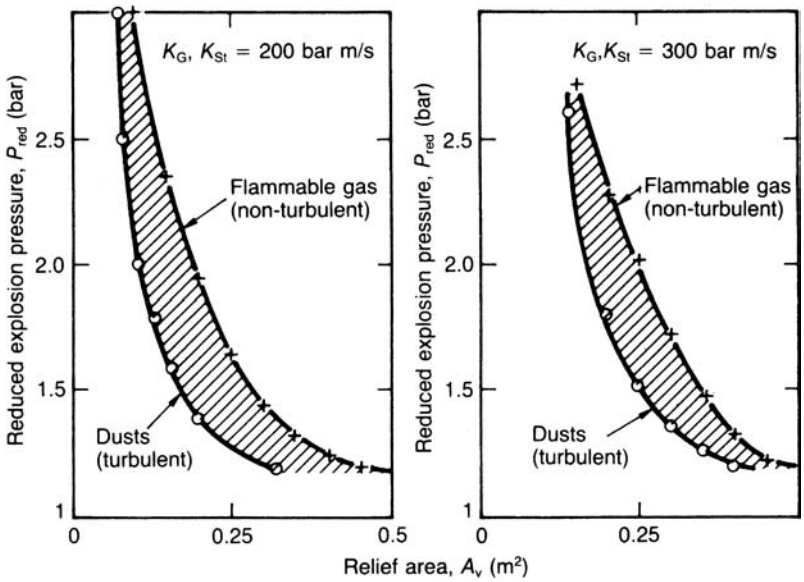

Figure 17.27 *Explosion venting of vessels: vent area recommendations for 1 m^3 vessel with P_{stat} = 0.1 barg (Bartknecht, 1981a): (a) K_G, K_{St} = 200 bar m/s and (b) K_G, K_{St} = 300 bar m/s (Courtesy of Springer-Verlag)*

Two other vent outflow relations which are sometimes used for small pressure drops in the subsonic flow range, for which near-isothermal conditions apply, are

$$f_v = f_{v3} \qquad [17.12.60]$$

or

$$f_v = f_{v4} \qquad [17.12.61]$$

with

$$f_{v3} = [2\rho_o(P - P_a)]^{1/2} \qquad [17.12.62]$$

$$f_{v4} = [2\rho_a P_a \ln(P/P_a)]^{1/2} \qquad [17.12.63]$$

where ρ_a is the density of the gas at atmospheric pressure.

Table 17.15 *Explosion venting of vessels: values of parameters for an equation equivalent to the Bartknecht nomographs (after Simpson, 1986) (Courtesy of American Institute of Chemical Engineers)*

Gas	*Parameter*			
	a	*b*	*c*	*d*
Methane	0.105	0.770	1.23	−0.823
Propane	0.148	0.703	0.942	−0.671
Coke gas	0.150	0.695	1.38	−0.707
Hydrogen	0.279	0.680	0.755	−0.393

17.12.21 Benson and Burgoyne model

In an early treatment of the problem, Benson and Burgoyne (1951) gave the following model for combustion venting of a spherical vessel. From Equation 17.7.15 the rate of increase of the volume V_b, of the burned gas expanding as a sphere of radius r_b is

$$\frac{dV_b}{dt} = 4\pi r_b^2 \frac{dr_b}{dt} \qquad [17.12.64]$$

The flame speed is

$$\frac{dr_b}{dt} = \frac{EW}{\rho_u} \qquad [17.12.65]$$

where E is the expansion ratio defined by Equation 17.7.41, W is the mass rate of combustion and ρ_u the density of the unburned gas. It is pointed out by Lunn that according to Bradley and Mitcheson E in Equation 17.12.65 and the following equations should be replaced by $E-1$. Hence, from Equations 17.12.64 and 17.12.65

$$\frac{dV_b}{dt} = \frac{4\pi r_b^2 W(E-1)}{\rho_u} \qquad [17.12.66]$$

The rate of increase of the burned volume is at a maximum when $r_b = r_v$, the radius of the vessel, so that

$$\left(\frac{dV_b}{dt}\right)_{max} = \frac{4\pi r_v^2 W(E-1)}{\rho_u} \qquad [17.12.67]$$

The volumetric vent flow Q_v at the venting pressure P_{red} through a vent area A_v is

$$Q_v = \frac{C_d A_v f_v}{\rho_u} \qquad [17.12.68]$$

Then, equating the maximum rate of increase of the burned volume given by Equation 17.12.67 with the volumetric vent outflow in Equation 17.12.68

$$A_v = \frac{4\pi r_v^2 W(E-1)}{C_d f_v} \qquad [17.12.69]$$

The density of the unburned gas ρ_u is obtained assuming adiabatic compression:

$$\rho_u = \rho_o \left(\frac{P_{red}}{P_o}\right)^{1/\gamma} \qquad [17.12.70]$$

17.12.22 Yao model

A numerical model for explosion venting of vessels has been given by Yao and co-workers (Yao *et al.*, 1969; Yao, 1974). The method is intended for venting of low pressure explosions.

The explosions are characterized by a pressure–time profile with two peaks. The model can be made to fit these two peaks fairly well, but to do so requires the use of a turbulence correction factor χ, which allows for effects which enhance the burning velocity or the flame area and is in effect a parameter that can be tuned to fit the experimental results.

Yao (1974) defines a venting parameter a such that

$$\alpha = \frac{(2C_d A_v a)^{1/2}}{S_u V}\left(\frac{P_o}{\rho_{uo}}\right)^{1/2}\left(\frac{\rho_{bo}}{\rho_{uo}}\right)^{7/6} \qquad [17.12.71]$$

and a venting area parameter G,

$$G = aA_v/V \qquad [17.12.72]$$

where a is a characteristic length (which for a spherical vessel is the radius), ρ_{bo} is the density of the burned gas at the initial pressure and ρ_{uo} is the density of the unburned gas at the initial pressure.

Then for a given maximum explosion pressure ΔP_m

$$\alpha \propto G \qquad [17.12.73]$$

and for varying maximum explosion pressure

$$\Delta P_m = f(\alpha) \qquad [17.12.74]$$

Yao gives plots of ΔP_m for the second peak as a function of α showing both experimental and theoretical results.

17.12.23 Bradley and Mitcheson method

D. Bradley and Mitcheson (1978) have given two models for combustion venting of a spherical vessel, one an analytical model and the other a numerical, or computer, model. They treat both subsonic and sonic flow and both venting of unburned gas and venting of burned gas.

They define the following parameters:

$$\bar{A} = \frac{C_d A_v}{A_s} \qquad [17.12.75]$$

$$\bar{S} = \frac{S_v}{a_v}\left(\frac{\rho_{uv}}{\rho_{bv}} - 1\right) \qquad [17.12.76]$$

$$\bar{S}_o = \frac{S_o}{a_{uo}}\left(\frac{\rho_{uo}}{\rho_{bo}} - 1\right) \qquad [17.12.77]$$

with

$$a_{uo} = (P_o \gamma_u / \rho_{uo})^{1/2} \qquad [17.12.78]$$

where a is the velocity of sound, $\bar{A}$ is the vent area ratio, A_s is the surface area of the spherical vessel, A_v is the vent area, C_d is the coefficient of discharge, P is the pressure, S is the burning velocity, ρ is the gas density, the subscripts b, o, u and v denote burned, initial, unburned and at vent conditions, respectively, and an overbar denotes dimensionless.

The authors state that on the assumption that the initial pressure in the vessel and the external pressure are equal, it can be shown that

$$\frac{\bar{S}}{\bar{A}} \geq f_{v2} \qquad [17.12.79]$$

The vent area A_v is that which is just sufficient to vent the volume of gas.

Bradley and Mitcheson give the following volume balance on the gas. The volumetric rate of increase of burned gas is

$$= S_v A_s \frac{\rho_{uv}}{\rho_{bv}} \qquad [17.12.80]$$

The volumetric rate of decrease of unburned gas is

$$= S_v A_s \qquad [17.12.81]$$

Hence, the net rate of increase of gas volume is

$$= S_v A_s \left(\frac{\rho_{uv}}{\rho_{bv}} - 1\right) \qquad [17.12.82]$$

The mass rate of venting is

$$\frac{dm_v}{dt} = C_d A_v (P_v \rho_{uv} \gamma)^{1/2} f_{v2} \qquad [17.12.83]$$

where m_v is the mass vented and P_v the pressure at the vent. Although not given by Bradley and Mitcheson, the further steps in the derivation are evidently as follows. The volumetric rate of venting is

$$\frac{dV_v}{dt} = C_d A_v \left(\frac{P\gamma}{\rho_{uv}}\right)^{1/2} f_{v2} \qquad [17.12.84]$$

where V_v is the volume vented. But

$$\left(\frac{P_v \gamma}{\rho_{uv}}\right)^{1/2} = a_v \qquad [17.12.85]$$

where a_v is the velocity of sound at the vent conditions. Then, equating the net rate of increase of gas volume given by Equation 17.12.82 with the volumetric rate of venting given by Equation 17.12.84 together with Equation 17.12.85 yields the relation given in Equation 17.12.79 but with an equality. These authors also give the relation

$$\frac{\bar{A}}{\bar{S}_o} \geq f_{v2} \zeta \qquad [17.12.86]$$

with

$$\zeta_u = \frac{S_v(\rho_{uv}/\rho_{bv} - 1)}{S_o(\rho_{uo}/\rho_{bo} - 1)} \left(\frac{P_a}{P_v}\right)^{(\gamma_u - 1)/2\gamma_u} \qquad [17.12.87]$$

for the venting of unburned gas and

$$\zeta_b = \zeta_u \left(\frac{\gamma_u \rho_{bv}}{\gamma_b \rho_{uv}}\right)^{1/2} \qquad [17.12.88]$$

for the venting of burned gas, where ζ is the vent flow coefficient. The value of γ in the term f_{v2} in Equation 17.12.86 should also be the appropriate one for unburned or burned gas as the case may be.

17.12.24 Rust model

Rust (1979) has derived the following model for explosion venting of a spherical vessel:

$$V_{fl} = 4/3\,\pi r^3 \qquad [17.12.89]$$

with

$$r = ut \qquad [17.12.90]$$

and

$$V_t = EV_{fl} \qquad [17.12.91]$$

with

$$E = P_{max}/P_o \qquad [17.12.92]$$

$$= V_f/V \qquad [17.12.93]$$

$$\frac{P}{P_o} = \frac{V_t}{V} \qquad [17.12.94]$$

where E is the expansion ratio, P is the absolute pressure, P_{max} is the absolute maximum pressure of the unvented explosion, P_o is the absolute initial pressure, r is the radius of the burned gas before expansion, t is time, u is the velocity of the flame front, V is the volume of the sphere, V_f is the volume of burned gas after expansion at the end of combustion, V_{fl} is the volume of burned gas before expansion and V_t is the volume of burned gas after expansion. Then, from Equations 17.12.89–17.12.92

$$V_t = 4/3\,\pi u^3 t^3 \frac{V_f}{V} \qquad [17.12.95]$$

$$= 4/3\,\pi u^3 t^3 \frac{P_{max}}{P_o} \qquad [17.12.96]$$

But from Equations 17.12.92, 17.12.93 and 17.12.94

$$\frac{P}{V_t} = \frac{P_{max}}{V_f} \qquad [17.12.97]$$

Then, from Equations 17.12.95 and 17.12.97

$$P = 4/3\,\pi u^3 t^3 \frac{P_{max}}{V} \qquad [17.12.98]$$

Hence

$$P = \frac{Kt^3}{V} \qquad [17.12.99]$$

with

$$K = 4/3\,\pi u^3 P_{max} \qquad [17.12.100]$$

From Equation 17.12.99

$$t = \frac{(PV)^{1/3}}{K^{1/3}} \qquad [17.12.101]$$

and from Equations 17.12.96 and 17.12.100

$$V_t = Kt^3/P_o \qquad [17.12.102]$$

Equating the volume production rate dV_t/dt with the vent outflow Q_v

$$Q_v = \frac{dV_t}{dt} \qquad [17.12.103]$$

differentiating Equation 17.12.102 with respect to t and substituting for t from Equation 17.12.101 gives

$$Q_v = \frac{3(PV)^{2/3}K^{1/3}}{P_o} \qquad [17.12.104]$$

For the volumetric vent outflow Rust uses the relation for subsonic flow

$$Q \propto A_v \Delta P^{1/2} \qquad [17.12.105]$$

where ΔP is the pressure difference. Rust sets P in Equation 17.12.104 equal to P_{max} to give a maximum flow requirement and ΔP in Equation 17.12.105 equal to the reduced explosion gauge pressure P_{red} and introduces a shape factor F to take account of non-spherical vessels, defined as

$$F = A_F/A_S \qquad [17.12.106]$$

where A_F is the largest spherical surface in the enclosure and A_S the surface area of the sphere having the same volume as the enclosure. Then, from Equations 17.12.104 and 17.12.105 the vent area is

$$A_v = \frac{kF(P_{max}V)^{2/3}K^{1/3}}{P_{red}^{1/2}} \qquad [17.12.107]$$

where P_{red} is the reduced pressure (gauge) and k a constant.

In British units, A_v (ft^2), k($lb_f ft/s^3$), P_{max}(lb_f/ft^2), P_{red} (lb_f/ft^2) and V(ft^3), the value of k is 8.35 x 10^{-5}.

17.12.25 Nagy and Verakis model

Nagy and Verakis (1983) have derived models for the following cases:

(1) venting of cylinder
  (a) ignition at closed end,
  (b) ignition at vent end,
  (c) ignition at center;
(2) venting of sphere
  (a) ignition at centre.

The gas laws are used in the form

$$P_oV = n_oRT_u \qquad [17.12.108]$$
$$P_mV = n_oRT_b \qquad [17.12.109]$$
$$PV_b = n_bRT_b \qquad [17.12.110]$$
$$P(V - V_b) = n_uRT_u \qquad [17.12.111]$$

where n is the number of moles (lb mol), P is the absolute pressure ($lb_f/in.^2$), R is the universal gas constant (lb ft^3/ $in.^2$ mol °R), T is the absolute temperature (°R) and V is the volume (ft^3) and the subscripts b, m, o and u denote burned, final, initial and unburned. Also, from Equations 17.12.108 and 17.12.109

$$\frac{T_b - T_u}{T_u} = \frac{P_m - P_o}{P_o} \qquad [17.12.112]$$

For the vent gas outflow the authors use the following equations:

$$\frac{dn_e}{dt} = \frac{k_{v1}A_v}{T^{1/2}}(P - P_o)^{1/2} \quad \text{subsonic flow} \qquad [17.12.113]$$

and

$$\frac{dn_e}{dt} = \frac{k_{v2}A_v}{T^{1/2}}P \quad \text{sonic flow} \qquad [17.12.114]$$

where A_v is the vent area (ft^2), P_o is the atmospheric pressure ($lb_f/in.^2$), k_{v1} (mol $in.°R^{1/2}/lb^{1/2}ft^2s$) and k_{v2} (mol $in.°R^{1/2}/lb^{1/2}ft^2s$) are constants and the subscript e denotes the end of combustion. The values of the constants in these units are $k_{v1} = 20.6$ and $k_{v2} = 2.63$. These values incorporate a mean molecular weight for the vented gas, the value used being that of air ($M = 29$). The mass balance is

$$\frac{dn_u}{dt} + \frac{dn_b}{dt} + \frac{dn_e}{dt} = 0 \qquad [17.12.115]$$

The rate of pressure rise is obtained by differentiating Equations 17.12.110 and 17.12.111 with respect to f and adding them to give

$$\frac{dP}{dt} = \frac{1}{V}\left(\frac{dn_u}{dt}RT_u + \frac{dn_b}{dt}RT_b\right) \qquad [17.12.116]$$

Then, combining Equations 17.12.115 and 17.12.116 gives

$$\frac{dP}{dt} = \frac{1}{V}\left[\frac{dn_b}{dt}R(T_b - T_u) - \frac{dn_e}{dt}RT_u\right] \qquad [17.12.117]$$

The rate of burned gas production is

$$\frac{dn_b}{dt} = -\frac{\alpha APS_u}{RT_u} \qquad [17.12.118]$$

where A is the area of the flame front (ft^2), S_u is the burning velocity (ft/s) and α is the coefficient of turbulence.

The treatment for the individual cases, which is for an open vent, is then as follows. The case of subsonic flow is considered first.

Venting of cylinder, ignition at closed end

For venting of a cylinder with ignition at the closed end, Equations 17.12.113, 17.12.117 and 17.12.118 yield

$$\frac{dP}{dt} = \frac{\alpha PS_u}{L}\left(\frac{P_m - P_o}{P_o}\right) - \frac{RT_uk_{v1}(A_v/V)}{T_u^{1/2}}(P - P_o)^{1/2} \qquad [17.12.119]$$

where L is the length of the cylinder (ft).

Setting $dP/dt = 0$ for the vent condition and also setting P as the vent pressure P_{red} and rearranging gives

$$\frac{P_{red}}{(P_{red} - P_o)^{1/2}} = \frac{RT_uk_{v1}P_oL(A_v/V)}{T_u^{1/2}\alpha S_u(P_m - P_o)} \qquad [17.12.120]$$

Equation 17.12.120 is sometimes referred to as the Pittsburgh method. For venting of burned gas the term $T_b^{1/2}$ replaces $T_u^{1/2}$, in the denominator of the term on the right–hand side to give

$$\frac{P_{red}}{(P_{red}-P_o)^{1/2}} = \frac{RT_u k_{v1} P_o L(A_v/V)}{T_b^{1/2}\alpha S_u (P_m - P_o)} \quad [17.12.121]$$

Venting of cylinder, ignition at vent end

Venting of a cylinder with ignition at the vent end differs in that burned gas is vented from the start so that

$$\frac{dn_b}{dt} = \frac{\alpha A P S_u}{RT_u} - \frac{k_{v1}A_v}{T_b^{1/2}}(P-P_o)^{1/2} \quad [17.12.122a]$$

$$\frac{dn_e}{dt} = \frac{k_{v1}A_v}{T_b^{1/2}}(P-P_o)^{1/2} \quad [17.12.122b]$$

and hence

$$\frac{dP}{dt} = \frac{\alpha P S_u}{L}\left(\frac{P_m - P_o}{P_o}\right) - \frac{RT_b k_{v1}(A_v/V)}{T_b^{1/2}}(P-P_o)^{1/2} \quad [17.12.123]$$

Venting of cylinder, ignition at centre

Venting of a cylinder with ignition at the centre is rather more complex in that there are two flame fronts travelling out from the centre. For the rate of rise of pressure P_1 on the closed end side

$$\frac{dP_1}{dt} = \frac{\alpha P_1 S_u}{L}\left(\frac{P_m - P_o}{P_o}\right) - \frac{RT_u k_{v1}(A_v/V)}{T_u^{1/2}}(P_1 - P_o)^{1/2} \quad [17.12.124]$$

and for the rate of rise of the pressure P_2 on the vent end side

$$\frac{dP_2}{dt} = \frac{\alpha P_2 S_u}{L}\left(\frac{P_m - P_o}{P_o}\right) - \frac{RT_u k_{v1}(A_v/V)}{T_b^{1/2}}(P_2 - P_o)^{1/2} \quad [17.12.125]$$

Summing these two rates of pressure rise gives

$$\frac{dP}{dt} = \frac{2\alpha P S_u}{L}\left(\frac{P_m - P_o}{P_o}\right) - R\left(T_u^{1/2} + \frac{T_u}{T_b^{1/2}}\right)k_{v1}(A_v/V)(P-P_o)^{1/2} \quad [17.12.126]$$

Venting of sphere, ignition at centre

It might be thought that venting of a sphere is a simple case, but this is not so, since the flame front distorts as the gas flows through the vent. The rate of rise of the pressure is considered in two stages. For the period before the burned gas reaches the vent

$$\frac{dP}{dt} = \frac{\alpha P A S_u}{V}\left(\frac{P_m - P_o}{P_o}\right) - \frac{RT_u k_{v1}(A_v/V)}{T_u^{1/2}}(P-P_o)^{1/2} \quad [17.12.127]$$

and for the period after $T_b^{1/2}$ replaces $T_u^{1/2}$ in the denominator of the second term on the right-hand side.

The relations for sonic flow may be obtained in a similar manner using Equation 17.12.114.

Summarizing the various cases, Nagy and Verakis state that the most representative relationship for venting is Equation 17.12.121 for the venting of a cylinder with ignition at the closed end. It is that equation which is referred to by Lunn as the Pittsburgh method.

Effect of vent opening pressure

The effect of the vent opening pressure P_v has been allowed for by Nagy and Verakis by modifying Equation 17.12.121 to give

$$\frac{P_{red} + \Delta P_v}{(P_{red}-P_o)^{1/2}} = \frac{RT_u k_{v1} P_o L(A_v/V)}{T_b^{1/2}\alpha S_u (P_m - P_o)} \quad [17.12.128]$$

where ΔP_v is the overpressure at which the vent opens ($lb_f/in.^2$ g).

17.12.26 Singh method

J. Singh (1979b, 1988b) has described a method of vent sizing based on the venting parameter (A/S_o) of Bradley and Mitcheson described above.

These latter workers defined a maximum pressure rise ΔP_m above the initial pressure and gave a number of plots of ΔP_m vs $(\bar{A}/\bar{S}_o)$ The plot given by Singh is shown in Figure 17.28. The full lines represent sets of data reported by various workers, the dashed lines approximate upper and lower limits on these data. The change of slope in the lines is due to the transition from subsonic to sonic flow as the pressure rises.

The equations given by Singh for the two sets of lines are as follows. The basic equation is

$$\Delta P_m = k(\bar{A}/\bar{S}_o)^{-n} \quad [17.12.129]$$

with for the upper limit lines

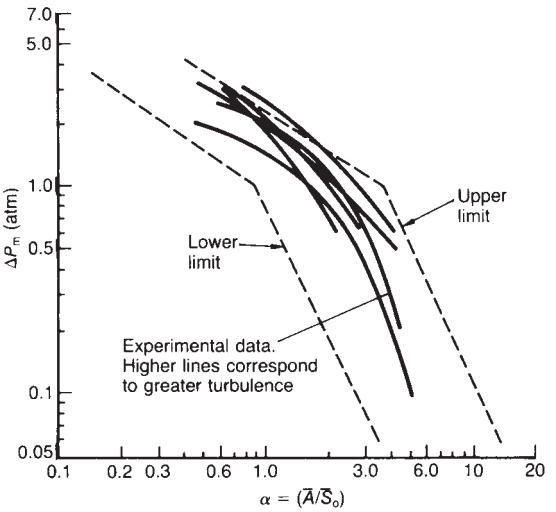

Figure 17.28 *Explosion venting of vessels: effect of normalized vent ratio on maximum pressure rise (J. Singh, 1979b) (Courtesy of Chemical Engineering)*

$k = 12.32, \quad n = 2, \quad \Delta P_m \leq 1$

$k = 2.4, \quad n = 0.7, \quad \Delta P_m > 1$

and for the lower limit lines

$k = 0.77, \quad n = 2, \quad \Delta P_m \leq 1$

$k = 0.91, \quad n = 0.7, \quad \Delta P_m > 1$

where $\bar{A}$ is the dimensionless vent area, ΔP_m is the maximum pressure rise (atm), $\bar{S}_o$ is the dimensionless burning velocity at the initial conditions and k is a constant.

The lower limit lines correspond to situations with essentially zero turbulence. If the burning velocity term in the venting parameter is adjusted to allow for an enhancement of burning velocity by turbulence by a factor of about 4 the upper limit lines are obtained. In other words, the difference in the two sets of lines is mainly due to turbulence.

The burning velocity term of the venting parameter is defined in Equation 17.12.77. The density ratio term may be approximated by the relation

$$\frac{\rho_{uo}}{\rho_{bo}} = \frac{T_{fo}}{T_{uo}} \qquad [17.12.130]$$

where T_f is the adiabatic flame temperature (K), ρ is the density of the gas (kg/m^3) and the subscripts b, o and u denote burned, initial and unburned, respectively. The density ratio tends to lie in the range 7.5–8.5 for most fuels.

J. Singh (1988b) has extended his treatment to non-spherical vessels. From Equation 17.7.137 the rate of pressure rise dP/dt is proportional to the area A_f of the flame front. The following areas apply to different vessel geometries:

$$A_f = 4\pi r_s^2 \quad \text{sphere} \qquad [17.12.131a]$$

$$= A_s \qquad [17.12.131b]$$

$$A_f = 4\pi r_c^2 \quad \text{long cylinder with central ignition} \qquad [17.12.132a]$$

$$= 4A_x \qquad [17.12.132b]$$

$$A_f = 4\pi r_c^2 \quad \text{long cylinder with end ignition} \qquad [17.12.133a]$$

$$= 2A_x \qquad [17.12.133b]$$

where A_f is the area of the flame front (m^2), A_s is the surface area of the sphere (m^2), A_x is the cross-sectional area of the cylinder (m^2), r_c is the radius of the cylinder (m) and r_s is the radius of the sphere (m).

Singh's method is to treat A_s in the venting parameter as equivalent to A_f and to adjust it for non-spherical vessels according to the above relations.

The results of the method are illustrated in Table 17.16.

17.12.27 Method of Epstein, Swift and Fauske

Epstein, Swift and Fauske (1986) have developed a model for explosion venting of a spherical vessel on the following lines. The mass balance is

$$\frac{dm_u}{dt} + \frac{dm_b}{dt} + \frac{dm_e}{dt} = 0 \qquad [17.12.134]$$

The mass production of burned gas is

$$\frac{dm_b}{dt} = 4\pi r_b^2 \rho_u \phi S_u \qquad [17.12.135]$$

Table 17.16 *Explosion venting of vessels: overpressures (pressure above vent opening pressure, ΔP_m) in non-spherical vessels using Singh's method (after J. Singh, 1988b) (Courtesy of Butterworth–Heinemann)*

Vent area (m^2)	*Experimental* (bar)	*Theoritical* (bar)	
		Unmodified[a]	*Modified*[b]
0.2	0.048	1.85	0.054
0.1	0.24	3.01	0.22
0.067	0.37	4.0	0.48
0.02	1.22	9.31	1.81

[a] Calculated using Equation 17.12.129, unmodified.
[b] Calculated using Equation 17.12.129, modified by using Equation 17.12.132 or 17.12.133.

and the mass vent outflow is

$$\frac{dm_e}{dt} = A_v G_v \qquad [17.12.136]$$

where ϕ is a turbulence correction factor. The densities of the unburned and burned gas are

$$\frac{\rho_u}{\rho_{uo}} = \left(\frac{P}{P_o}\right)^{1/\gamma_b} \qquad [17.12.137]$$

$$\frac{\rho_b}{\rho_{bo}} = \left(\frac{P}{P_o}\right)^{1/\gamma_b} \qquad [17.12.138]$$

The volume of the closed vessel is

$$V = \frac{m_u}{\rho_u} + \frac{m_b}{\rho_b} \qquad [17.12.139]$$

Then substituting for ρ_u and ρ_b from Equations 17.12.137 and 17.12.138 in Equation 17.12.139 and then differentiating the latter with respect to t, eliminating dm_u/dt and dm_b/dt using Equations 17.12.135 and 17.12.136, solving for dP/dt, setting $\gamma_u = \gamma_b$ and applying Equation 17.12.139 again yields

$$\frac{V}{\gamma_b}\frac{d \ln P}{dt} = 4\pi r_b^2 \left(\frac{\rho_u}{\rho_b} - 1\right)\phi S_u - \frac{A_v G_v}{\rho_u} \qquad [17.12.140]$$

Combining Equations 17.12.135 and 17.12.138, differentiating with respect to time and combining the result with Equation 17.12.140 to eliminate dP/dt yields

$$4\pi r_b^2 \frac{dr_b}{dt} = 4\pi r_b^2 \left[\left(\frac{\rho_u}{\rho_b}\right)\phi S_u - \frac{r_b}{3V}\right]\left[4\pi r_b^2 \left(\frac{\rho_u}{\rho_b} - 1\right)\phi S_u - \frac{A_v G_u}{\rho_u}\right] \qquad [17.12.141]$$

Dividing Equation 17.12.140 by Equation 17.12.141 gives

$$\frac{1}{\gamma_b}\frac{d \ln P}{dt} = \frac{B(\rho_u/\rho_b - 1)Z^{2/3} - 1}{B[\rho_u/\rho_b - (\rho_u/\rho_b - 1)Z]Z^{2/3} + Z} \qquad [17.12.142]$$

with

$$B = \frac{\rho_u \phi S_u A_s}{A_v G_v} \qquad [17.12.143]$$

and

$$Z = \frac{4\pi r_b^3}{3V} \qquad [17.12.144]$$

where B is a dimensionless burning number and Z a dimensionless burned volume. For sonic flow Epstein, Swift and Fauske use

$$G_v = (2P\rho_u)^{1/2} \qquad [17.12.145]$$

Making a number of additional assumptions the authors derive

$$\frac{P_f}{P_o} = \frac{P_{max}}{P_o}\left(\frac{\lambda + B}{1 + B}\right)^{\gamma_b} \qquad [17.12.146]$$

with

$$\lambda = \frac{(P_{set}/P_o)^{1/\gamma_b} - 1}{(P_{max}/P_o)^{1/\gamma_b} - 1} \qquad [17.12.147]$$

where P_{set} is the vent opening pressure and λ is a dimensionless vent opening pressure.

The vent area A_v may be obtained from the burning number B defined by Equation 17.12.143.

The model contains a number of approximations. The authors compared their results with results given from the computer model of Bradley and Mitcheson and obtained a good fit, leading them to conclude that the approximations were justified.

This model has been extended by Swift and Epstein (1987) for subsonic flow. For subsonic flow they use

$$G_v = C_d[2P\rho_u(1 - (P_a/P)]^{1/2} \qquad [17.12.148]$$

where P_a is atmospheric pressure. They derive an equation equivalent to Equation 17.12.146 for sonic conditions as

$$\frac{P_f}{P_a} = 1 + \left[\left(\frac{P_{max}}{P_o}\right)^{1/\gamma_b} - 1\right]^2 B^2 \qquad [17.12.149]$$

where P_f is the absolute final pressure of the vented explosion, or the reduced pressure.

Then rearranging Equation 17.12.149 and substituting for B from Equation 17.12.143 gives

$$A_v = \frac{A_s\rho_u\phi S_u}{C_d G_v}\frac{[(P_{max}/P_o)^{1/\gamma_b} - 1]}{(P_f/P_o - 1)^{1/2}} \qquad [17.12.150]$$

17.12.28 Other models

Morton and Nettleton's model for explosion in a closed vessel was described in Section 17.7. The model may be used to determine the vent opening pressure for a given proportion of burned gas in the total gas vented.

As an illustrative example, consider the plot of the pressure ratio P/P_o vs the radius ratio r/a shown in Figure 17.29. From this figure a spherical vessel of 5 m radius (520 m^3) with a vent designed to open at 1 barg ($P/P_o = 2$) will have a value of r/a of 0.77. Hence, the volume of unburned gas will be 280 m^3 and that of burned gas 240 m^3 at the start of venting.

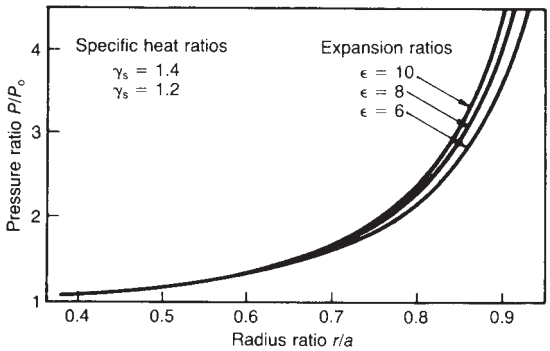

Figure 17.29 *Explosion venting of vessels: variation of pressure with flame radius in a spherical vessel (V.M. Morton and Nettleton, 1977) (Courtesy of the Combustion Institute)*

The model of Fairweather and Vasey (1982) for explosion in a closed vessel was described in Section 17.7. The treatment given by these authors also extends to explosion venting. The mass production of burned gas is given by Equation 17.7.37. The mass vent outflow of gas is obtained from Equation 17.12.51. The mass of unburned gas is given by

$$m_u + m_b = m_o - m_e \qquad [17.12.151]$$

The volume of unburned gas is obtained assuming adiabatic compression of the initial gas:

$$V_u = V_o\frac{m_u}{m_o}\left(\frac{P}{P_o}\right)^{-1/\gamma_b} \qquad [17.12.152]$$

The volume of burned gas is obtained from Equation 17.7.4. The temperatures of the unburned and burned gases are obtained from Equations 17.7.9, 17.7.10, 17.7.27 and 17.7.28.

17.12.29 Elongated vessels

Vessels which have a length/diameter (L/D) ratio of 3 or less may be regarded as compact, those with an L/D greater than that as elongated.

For L/D ratios greater than 6, the usual practice is to install one vent for each section divided lengthwise to lengths L_i such that each L_i/D is approximately 3.

In their early studies of venting, Cousins and Cotton (1951a) investigated a range of L/D ratios from 1.41 to 22.1. The systems which they studied are given in Table 17.14.

They did experiments with 5% propane–air and 40% hydrogen–air mixtures, with open vents and with initial pressures of 0, 15 and 45 psig and measured the maximum pressure of the vented explosion. They expressed their results in terms of plots of this maximum pressure against the vent ratio. Some of the results are shown in Figure 17.30. They show that there is a reasonable correlation with vent ratio across the L/D range investigated.

The work of Singh, described above, also covers elongated vessels with an L/D ratio up to 30.

Further treatment of venting of high L/D containers is given in Section 17.13 on the explosion venting of pipes and ducts.

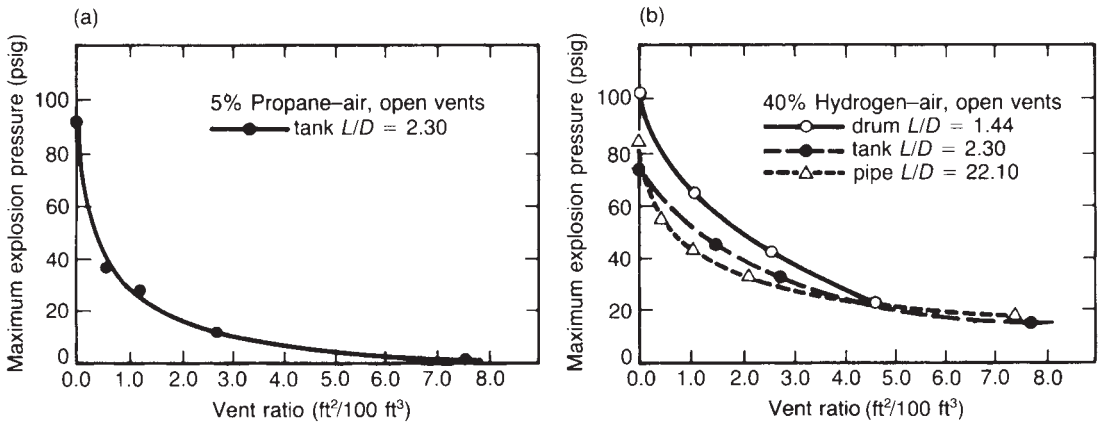

Figure 17.30 *Explosion venting of vessels: effect of vessel aspect ratio on maximum explosion pressure (Cousins and Cotton, 1951a): (a) 5% propane–air mixture in a tank (L/D = 2.30) and (b) 40% hydrogen–air mixture in a drum (L/D = 1.44), tank (L/D = 2.30), and pipe (L/D = 22.1) (Courtesy of Chemical Engineering)*

17.12.30 Critique of available methods

The methods available for the prediction of the vented explosion pressure have been reviewed by Lunn. Of the empirical methods, his preferred methods are those of Cubbage and Simmonds and of Rasbash.

For the Cubbage and Simmonds method to be applicable it is necessary that the vent opening pressure should not exceed 7 kPa and that the vent panel have a low inertia. For these conditions the second peak equation of these authors gives good results. For finite vent opening pressure the results are not so good, since the method does not take vent opening pressure into account.

For finite vent opening pressures up to 7 kPa Lunn states that the first three terms of the Rasbash equation give good results for the first peak.

For high vent opening pressures, Lunn recommends the use of the data given by Cousins and Cotton or the Bartknecht K_G method for good results.

Lunn states that the methods of Cubbage and Marshall, Runes, Decker, Dragosavic and Burgoyne and Wilson are not recommended for general use.

Of the theoretical methods which he reviews, that of Bradley and Mitcheson gives an upper bound.

17.12.31 Venting phenomena

If the vent is an open one, venting will result in the emergence of flame. The flame may be substantial. C.J.M. van Wingerden (1989c) has reported a jet flame 18 m long.

If the vent has a duct, there is potential for unburned gas to undergo further combustion in the duct, possibly resulting in overpressure in the duct. The ducting needs to be designed to avoid this.

17.12.32 Reaction force due to venting

Venting causes a back reaction on the vessel. The determination of this force may be approached by considering the flow from the vessel or the pressure in the vessel.

A fundamental treatment based on the flow is given by Duncan, Thorn and Young (1960) and by Leung (2002). The mass vent flow from the vessel is $A_v \rho u$, the mass vented in time t is $A_v \rho u t$, its momentum is $A_v \rho u^2 t$ and the rate of change of momentum is $A_v \rho u^2$. The force is equal to the rate of change of momentum thus

$$F_r = A_v \rho u^2 \qquad [17.12.153]$$

where A_v, is the vent area, F_r is the force due to back reaction, t is the time, u is the velocity of the fluid and ρ is the density of the fluid.

Alternatively, the force may be obtained from the maximum pressure P_{red} in the vessel during venting.

The reaction force has also been measured in tests. NFPA 68: 1994 gives the following empirical equation for the reaction force, applicable only to enclosures without ducts:

$$F_r = 1.2 A_v P_{red} \qquad [17.12.154]$$

where A_v is the vent area (in.^{2}), F_r is the reaction force (lb$_f$) and P_{red} is the reduced pressure (gauge) (lb$_f$/in.^{2}).

NFPA 68 states that the reaction force can be considered as equivalent to a force applied at the geometric centre of the vent. It warns, however, against assuming that the forces on two opposing vents will cancel out, since one vent may open before the other.

It further states that equivalent static force on the structure supporting the vented enclosure is given by Equation 17.12.154 but with the constant 1.2 replaced by 0.62.

Back reaction forces due to venting are also discussed in Chapter 12.

17.12.33 Vent ducting effects

It has been found that the presence of a vent duct can have a marked effect on the maximum pressure in a vented explosion.

Figure 17.31 is a graph from the work of Pineau, Giltaire and Dangreux (1978), showing the pressure in the vessel and in the duct as a function of duct length for a 10 m^3 vented vessel.

Typically, the maximum pressure rises rapidly with the initial increase in the length of the tube and then reaches a plateau or increases or decreases at a much slower rate. This effect was described by Sagalova and Resnick (1962) for dust explosions and has been observed by Kordylewski and Wach (1986, 1988) for gas.

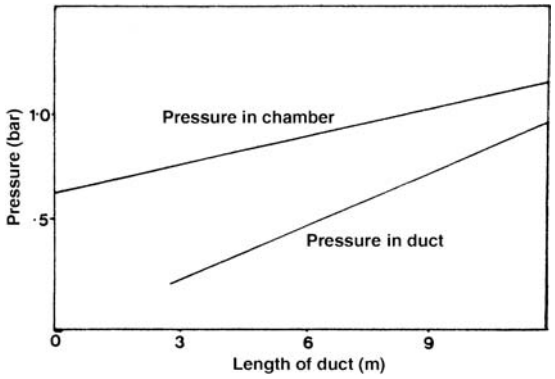

Figure 17.31 *Explosion venting of vessels: effect of vent duct on pressure in a 10 m³ vessel (Cross and Farrer, 1982; after Pineau, Giltaire and Dangreaux, 1978)*

The latter conducted experiments using a 22 l vessel with vents and vent tubes of 21, 25 and 35 mm diameter. The gas used was town gas. They were unable to account for the increase in the maximum pressure by the flow resistance of the duct and instead considered turbulence, secondary explosions, acoustic oscillations and Helmholtz oscillations to be responsible. They found that acoustic oscillations can increase the maximum overpressure by 203 times for tube length in the range 0–20 diameters.

17.12.34 Vent design

Design of a vent system based on a vent panel includes consideration of the following features: (1) reduced explosion pressure, (2) vent opening pressure, (3) vent area, (4) vent distribution, (5) vent opening, and (6) vent panel.

The reduced explosion pressure for a vented explosion will be determined by the mechanical strength of the containment. Explosion venting is used for low-strength as well as high-strength equipment.

The vent opening pressure also needs to be set before the vent area can be calculated. The values of the vent opening pressure P_{stat} to which the Bartknecht nomographs apply are $0.1 \leq P_{stat} \leq 0.5$ barg.

The distribution of the vent area determined is generally not critical for vessels, though it may be more important for buildings and modules.

The time of opening of the vent can affect the pressure developed. A sudden opening, such as occurs with a bursting disc, tends to increase turbulence. A smooth opening is desirable to minimize turbulence.

The design of the vent panel itself is important.

17.12.35 Vent panel design

Some features which need to be taken into account in the design of the vent panel itself are (1) panel material, (2) panel inertia, (3) relieving fasteners, (4) panel restraint system, (5) guarding, and (6) maintainability.

Detailed guidance on vent panel design is given in the *HSE Guide* and in NFPA 68: 1994.

The guidance given by W.B. Howard and Karabinis (1980) for vent panels for explosion venting of buildings is outlined in Section 17.14.

17.12.36 Vent panel dynamics

The static pressure required to move a vent panel slowly may be quite low, but the pressure needed to impart a high acceleration to the panel so that it moves rapidly may be much higher. Thus

$$F = Ma \qquad [17.12.155]$$

and hence dividing by the area A of the panel

$$P = wa \qquad [17.12.156]$$

with

$$w = M/A \qquad [17.12.157]$$

where a is the acceleration of the panel, F is the force on the panel, M is the mass of the panel, P is the pressure and w is the weight per unit area of the panel.

An analysis of vent panel dynamics has been given by Rust (1979). He considers the following five situations:

(1) Panel moves by translation; vertical panel; horizontal translation.
(2) Panel moves by translation; horizontal panel; vertical translation.
(3) Panel hinged along width; vertical panel; horizontal rotation.
(4) Panel hinged along width; horizontal panel; vertical rotation against gravity.
(5) Panel hinged along width; horizontal panel; vertical rotation with gravity.

Figure 17.32 illustrates cases (1) and (3).

For a panel of width W and length L which moves by translation a distance S to give a peripheral area WL equal to the vent area A_v the peripheral area is $2S(W+L)$. Equating these two areas

$$S = \frac{WL}{2(W+L)} \qquad [17.12.158]$$

At pressure P the acceleration a of the panel is

$$a = PA_v/M \qquad [17.12.159]$$

where M is the mass of the panel. From Equations 17.12.99 and 17.12.159

$$a = \frac{Kt^3A_v}{VM} \qquad [17.12.160]$$

Integrating Equation 17.12.160 to obtain the velocity v attained by the panel with the initial condition $t = t_v$, $v = 0$, where t_v is the time of start of venting, and integrating again to obtain the distance s travelled by the panel with the initial condition $t = t_v$, $s = 0$, substituting at $t = t_v$ pressure $P = P_v$, the vent opening pressure, and defining a panel 'density' D,

$$D = Mg/A_v \qquad [17.12.161]$$

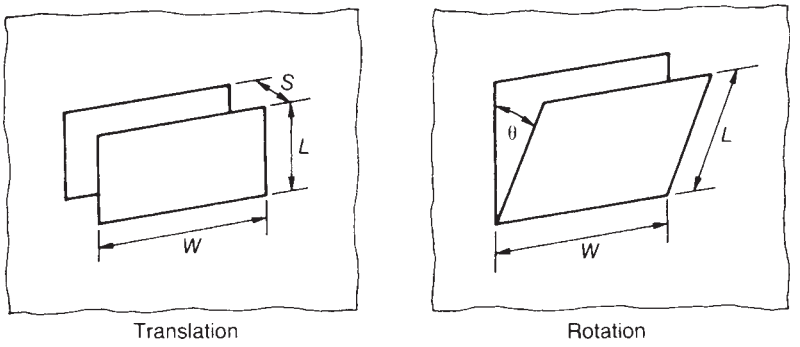

Figure 17.32 *Explosion venting of vessels: movement of vent panels for release of gas (Rust, 1979) (Courtesy of Chemical Engineering)*

where g is the acceleration due to gravity, yields

$$S = g\left(\frac{V}{K}\right)^{2/3}\frac{C}{D} \qquad [17.12.162]$$

with

$$C = \frac{P^{5/3}}{20} - \frac{P_v^{4/3}P^{1/3}}{3} + \frac{P_v^{5/3}}{5} \qquad [17.12.163]$$

where P is the pressure (gauge) (lb_f/ft^2) and P_v is the vent opening pressure (gauge) (lb_f/ft^2). Relations for the other cases are derived in a similar manner. For cases of rotation, the angle θ to give the vent area is

$$\theta = \frac{W}{W+L} \qquad [17.12.164]$$

and an additional constant E is obtained,

$$E = \frac{P^{2/3}}{2} - P_v^{1/3}P^{1/3} + \frac{P^{2/3}}{2} \qquad [17.12.165]$$

Table 17.17 summarizes Rust's equations for vent panel dynamics. In his worked example, in Equations 17.12.163 and 17.12.165 Rust uses a corrected vent opening pressure $P'_v = (P_v + D)$, where D is the 'density' of the vent panel (lb/ft^2) and P'_v is the corrected vent opening pressure (gauge) (lb_f/ft^2), instead of P_v.

Table 17.17 *Explosion venting of vessels: equations for vent panel dynamics given by Rust (after Rust, 1979) (Courtesy of Chemical Engineering)*

Horizontal translation	$s = g\left(\frac{V}{K}\right)^{2/3}\frac{C}{D}$
Horizontal rotation	$\theta = \frac{3g}{2L}\left(\frac{V}{K}\right)^{2/3}\frac{C}{D}$
Vertical translation upward	$s = g\left(\frac{V}{K}\right)^{2/3}\left(\frac{C}{D} - E\right)$
Vertical rotation against gravity	$\theta = \frac{3g}{2L}\left(\frac{V}{K}\right)^{2/3}\left(\frac{C}{D} - E\right)$
Vertical rotation with gravity	$\theta = \frac{3g}{2L}\left(\frac{V}{K}\right)^{2/3}\left(\frac{C}{D} + E\right)$

17.12.37 Vent details

Guidance on details of vents for enclosures, both buildings and equipment, is given in NFPA 68: 1994. The vents considered are (1) open or unobstructed vents and (2) closed or sealed vents.

Open vents are applicable to buildings rather than equipment. With a building it is often not practical to have a completely open aperture, but there are various arrangements which can provide good vents. They include louvres, open roof vents and hangar-type doors which can be moved to one side when an operation which may need to be vented is in progress.

Closed vents may be used for either buildings or equipment. Features which can constitute a vent closure for a building or room include a door, window, movable sash, roof or wall panel or skylight. On equipment a vent closure may take the form of a charging door or inspection port, a dedicated venting device or a diaphragm. Diaphragm materials described include paper, cloth, plastic and metal. The diaphragm may be provided with a cutter.

17.12.38 Vent duct design

The effect of a vent duct on the reduced explosion pressure has already been mentioned. There is available guidance to assist in allowing for this effect.

Correlations due to Bartknecht are shown in Figures 17.33 and 17.34. Figure 17.33, given originally by Bartknecht (1981a), gives the relationship between the reduced explosion pressure with the duct and that without a duct. There are two lines, the parameter being the duct length. Figure 17.34 gives a further correlation for the same relationship, but in this case the parameter is the gas velocity.

Both correlations were given in NPFA 68: 1988, but only the first is retained in NFPA 68: 1994.

17.12.39 Safe discharge

Explosion venting gives rise to three effects: a pressure wave, and discharges of flame and unburned material. All three effects need to be handled safely.

If the material discharged is sufficiently toxic, this may invalidate the venting option.

17.13 Explosion Venting of Ducts and Pipes

In general, where combustion of a flammable gas mixture occurs in a duct or pipe, there is a possibility that if the duct

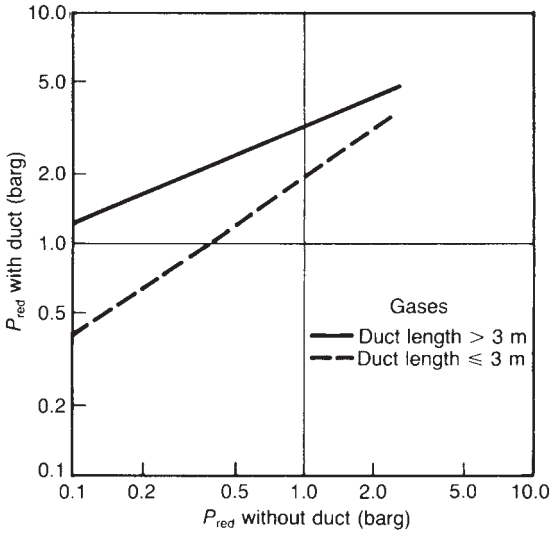

Figure 17.33 *Explosion venting of vessels: effect of length of vent duct on reduced pressure (NFPA 68: 1994). See text for details (reproduced with permission from NFPA 68 Deflagration Venting, © 1994, National Fire Protection Association, Quincy, MA 02269). See note to Figure 17.25*

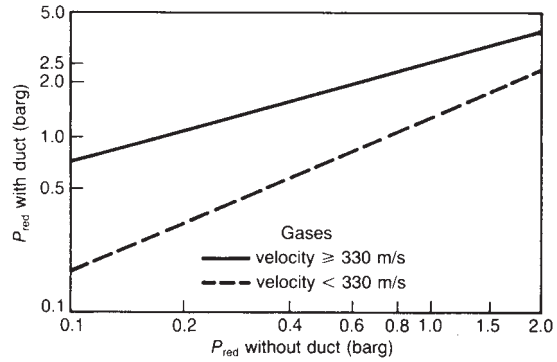

Figure 17.34 *Explosion venting of vessels: effect of velocity in vent duct on reduced pressure (NFPA 68: 1994). See text for details (reproduced with permission from NFPA 68 Deflagration Venting, © 1994, National Fire Protection Association, Quincy, MA 02269). See note to Figure 17.25*

is long enough the flame front will accelerate to the point where the deflagration turns into a detonation. Detonation is considered in Section 17.6 and is not considered further in this section, which deals with the explosion venting of deflagrations.

The venting of elongated vessels was described in Section 17.12. The methods given there cover the venting of containers with length/diameter (L/D) ratios up to 30.

Accounts of explosion venting of ducts are given in the *Guide to the Use of Flame Arresters and Explosion Reliefs* (HSE, 1965 HSW Bklt 34), *Explosions* (Bartknecht, 1981a), *Venting Gas and Dust Explosions* (Lunn, 1984b) and in NFPA 68: 1994 *Deflagration Venting*.

17.13.1 Experimental studies

The design methods for explosion relief of ducts have tended to draw heavily on experimental work at the JFRO by Rasbash and Rogowski (Rasbash and Rogowski, 1960a,b; Rogowski and Rasbash, 1963).

The duct dimensions used in the experiments were from 3 in. (76 mm) and 6 in. (152 mm) diameter to 12 in. (305 mm) square section and from 6 to 30 ft (1.8–9 m) long. Most of the experiments were done using propane–air and pentane–air mixtures.

The results of the work are summarized by Lunn (1984b) as follows. For a base case in which a single open vent was located at one end of a straight, unobstructed duct with the ignition source either 15 cm from the closed end or a quarter of the way along the duct and with the most explosive concentration of the gas–air mixture, the vented explosion pressure P_{red} at any position along the duct was proportional to the ratio of the vent area to the cross-sectional area of the duct, or vent coefficient, K, the constant of proportionality ranging from 5.6 to 12.6 for the conditions $6 < L/D < 30$ and $2 < K < 32$. For a vent coefficient K of unity, the maximum explosion pressure P_{max} was proportional to L/D, the constant of proportionality being 0.49 for the conditions $6 < L/D < 48$. The pressure and proportionality constants in the relations just described are in SI units (kPa). Lower vented explosion pressures were obtained when the ignition source was located near the vent or when a given vent area was provided by distributing a number of small vents along the duct.

More recent work is that described by Bartknecht (1981a). The account given by Bartknecht of explosions, both deflagrations and detonations, was summarized in Section 17.5. His recommendations for protection of pipes, which are a combination of containment and relief, are described below.

Work on combustion in pipes has drawn attention to several distinguishing phenomena which are relevant to the design of explosion venting for such systems. If a flammable mixture is ignited in a vessel and then enters an attached pipe, the flame front at the point of entry is fully developed and turbulent. It propagates much more strongly than one arising from spark ignition in the pipe itself.

A flame front travelling down a pipe tends to accelerate, with possible run-up to detonation. In addition, turbulence promoters such as bends and valves can cause sudden accelerations of the flame front.

If a flame front travels down an inadequately vented pipe and then enters a vessel containing a flammable mixture, it does so as a jet flame which constitutes a massive ignition source, which can cause a violent explosion in the vessel.

17.13.2 *HSE Guide* method

The methods given in the *HSE Guide* are based on the work of Rasbash and Rogowski just described. Essentially, the same methods were used in NFPA 68: 1978, which was superseded by a revision in 1988. Since the methods in the revision of NFPA 68 are a development from this work,

although the link is no longer so clear, the *HSE Guide* method is described first.

Unless otherwise stated, *HSE Guide* methods are applicable to gas mixtures at atmospheric pressure. They are applicable to ducts with an L/D ratio of 6 or more. Other methods are available for vessels with an L/D ratio of 3 or less. For containers with an L/D ratio greater than 3 but less than 6 the use of methods for vessels with an L/D ratio of 3 or less is increasingly conservative as the L/D ratio approaches 6.

In designing explosion vents for ducts the following cases are distinguished:

(1) Gas velocity < 10 ft/s
  (a) straight unobstructed ducts with $L/D < 30$,
  (b) straight unobstructed ducts with $L/D > 30$,
  (c) ducts containing obstacles;
(2) Gas velocity 10–60 ft/s
  (a) unobstructed ducts,
  (b) ducts containing obstacles.

The design of vent areas is essentially based on the relations between the maximum pressure P and the vent coefficient K.

If the gas is stationary or has a velocity less than 10 ft/s, the duct is straight and unobstructed and the L/D ratio is less than 30, only one relief opening is generally sufficient. The maximum pressure is given by the equation

$$P = k_1 \frac{L}{D} + k_2 K \qquad [17.13.1]$$

where D is the diameter of the duct (ft), K is the ratio of the cross-sectional area of the duct to the vent area, or vent coefficient, L is the length of the duct (ft), P is the maximum pressure ($lb_f/in.^2$) and k_1 and k_2 are constants. The values of the constant k_1 and k_2 are:

K	k_1	k_2
1	0.07	0
1–2	0.035	0.9
2–23	0	1.8

If a single vent is used, it should be placed as near as possible to the most probable location of the ignition source, but if this latter is uncertain, the vent should be placed near the centre of the duct.

For this vent system, a vent weighing not more than 2 lb/ft^2 and held by springs or magnets is suitable. An alternative relief is a bursting disc designed to burst at a pressure one half of the maximum pressure given in Equation 17.13.1.

If the gas has a velocity less than 10 ft/s and the duct is straight and unobstructed, but the L/D ratio is greater than 30, it is necessary to have more than one relief opening. The maximum pressure is given by the equation

$$P = k_3 \frac{L_1}{D} + k_4 \qquad [17.13.2]$$

where L_1 is the distance between relief openings (ft) and k_3 and k_4 are constants. The values of the constants k_3 and k_4 and the maximum value of the distance between relief openings L_{1max} (ft) are:

K	L_{1max} (diameters)	k_3	k_4
1	60	0.04	0
2	30	0.06	0.1
4	20	0.07	0.2
8	15	0.08	0.3

The open end of a long duct may be regarded as an explosion relief opening. In this context an open end is an end leading without restriction to atmosphere or to a vessel which is itself provided with explosion reliefs or to a room of volume 200 times greater than that of the duct. For such an open end $K = 1$.

If the end of a duct is not open or if it may be regarded as restricted, an explosion relief should be located as near as possible to the end. For this vent system also, vents weighing not more than 2 lb/ft^2 of vent area and held by springs or magnets are suitable.

If at a gas velocity of less than 10 ft/s the duct contains obstacles or features such as sharp right angle elbows or tees, the maximum pressure resulting from an explosion is greatly increased. An obstacle blocking only 5% of the cross-sectional area of the duct can increase the maximum pressure by a factor of 2–3, whilst an orifice blocking 30% of the duct area can increase the pressure by a factor of 10.

Any bend sharper than a long, sweeping, smooth bend and any obstruction blocking more than 5% of the cross-sectional area of the duct should be regarded as an obstacle.

If there is a long straight duct connected to an obstacle, then to reduce the maximum pressure to 2 $lb_f/in.^2$, explosion relief openings of size $K = 1$ should be located as near as possible to the obstacle and at 6 diameters on either side of it. Thereafter, the straight unobstructed section of the duct may be treated in the usual way.

For a vent system around an obstacle, a vent weighing not more than 3 lb/ft^2 and held by springs or magnets is suitable.

If the gas has a velocity of 10–60 ft/s and the duct is straight and unobstructed, the explosion relief openings required to limit the maximum pressure resulting from an explosion to 2 lb_f/in^2. are as follows:

D (ft)	L_1/D	K
≤1.5	12	1
–	6	2
1.5–2.5	9	1
–	5	2

For this vent system, the weight of vents depends on the velocity of the gas. For gas velocities of 25 and of 25–60 ft/s, the vents should weigh not more than 10 and 5 lb/ft^2, respectively. The vents may be held by springs or magnets.

If at a gas velocity of 10–60 ft/s the duct contains obstacles, additional explosion relief openings are required. If there is a long straight duct connected to an obstacle, explosion reliefs of size $K = 1$ should be located at 3 diameters on either side of the obstacle and again at 6 diameters on either side of it. Thereafter, the straight

unobstructed section of the duct may be treated in the usual way.

For this case, the maximum duct diameter for which information was available is 1.5 ft.

For this vent system, the weight of the six vents nearest the obstacle again depends on the velocity of the gas. For gas velocities below 25 and of 25–60 ft/s, the vents should weigh not more than 3 and l.5 lb/ft^2, respectively. The vents may be held by springs or magnets.

For gases other than propane, the maximum pressure may be calculated from the maximum pressure for propane using the relation

$$P_2 = \frac{S_u^2}{2.2} P_1 \qquad [17.13.3]$$

where P_1 is the maximum pressure resulting from an explosion for propane (lb_f/in^2.), P_2 is the maximum pressure resulting from an explosion for a gas other than propane ($lb_f/in.^2$) and S_u is the maximum fundamental burning velocity of the gas other than propane (ft/s). The value of 2.2 derives from the square of the maximum fundamental burning velocity of propane, which is 1.5 ft/s.

Alternatively, for a given maximum pressure the distance between neighbouring vents L_1 may be calculated using the relation

$$L_2 = \frac{2.2}{S_u^2} L_1 \qquad [17.13.4]$$

where L_1 is the distance between relief openings for propane (ft) and L_2 is the distance between relief openings for a gas other than propane (ft).

Vent closures should be designed so that a degree of deterioration or lack of maintenance does not cause the design maximum pressure resulting from the explosion to be exceeded. Closures should be robust and leak-tight. Methods of holding vent closures include springs, magnets and hinges. Further details of vent closure are given in the *HSE Guide*.

It is pointed out by Lunn (1984b) that the experimental data on which these recommendations are based are sparse. He suggests that the maximum pressure correlates as well with vent ratio A_v/V as with vent coefficient K. Figure 17.35 shows the data given by Lunn for vented ducts in support of this argument.

He is also critical of the use of Equation 17.13.3 to extrapolate from propane to other gases. Figure 17.35 shows a curve for the maximum pressure in hydrogen–air mixtures calculated from Equation 17.13.3 which differs appreciably from the experimental curve also shown in the figure.

On the basis of the work of Cousins and Cotton (1951a) he suggests as an alternative that if explosion pressures for a particular gas have been measured in a compact enclosure, then for a duct with $L/D < 30$ and with the same vent ratio these pressures represent upper bounds on the pressures likely to occur in the duct.

17.13.3 Bartknecht method

Bartknecht states that experience has shown that explosions may cause considerable damage in pipes even if reliefs are installed.

He suggests that the effectiveness of such reliefs is doubtful, that if they are used they need to be installed every 1–2 m and that such a design is suitable only for use on pipes which are outdoors.

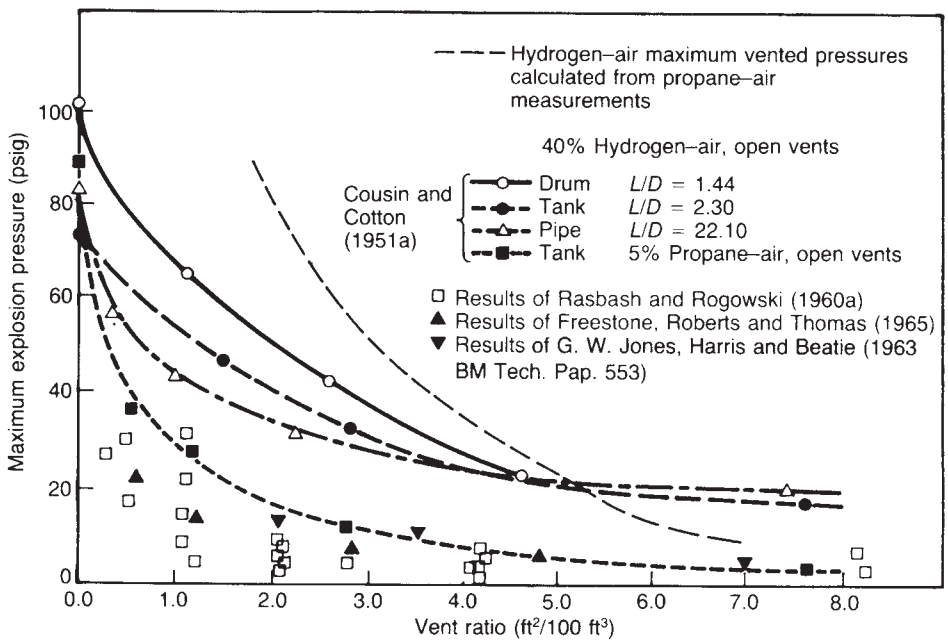

Figure 17.35 *Explosion venting of ducts and pipes: maximum explosion pressure in vessels of different aspect ratios (Lunn, 1984b) (Courtesy of the Institution of Chemical Engineers)*

He recommends instead that the pipe should be designed to contain the explosion, which means in practice that it should have a design pressure of at least 10 bar. Such a pipe will withstand even the very high but very short peak pressures associated with detonations.

In this design approach, reliefs are still required but are limited to handling the much higher pressures which occur at end flanges or bends. These must be provided with vents if they are not to be destroyed.

The venting must occur along the axis of the pipe. Relief which is based on flow at right angles to the axis gives much higher pressures for deflagrations and is quite ineffective for detonations. Further, the whole cross-sectional area of the pipe must be utilized for the vent.

As described in Section 17.5, the explosion velocity and explosion pressure developed in a pipe open at one end tend to be higher than in a closed pipe. It follows that if the vent opens too soon, it may aggravate the situation. Therefore, the vent opening pressure should be set sufficiently high to prevent the development of excessive explosion pressure.

One way of achieving this is to use an activated vent in which the explosion pressure is detected by a suitable sensor which causes the vent to open.

Relief devices which can be used include bursting discs and vent doors. The latter have the advantage that they seal the vent opening after effecting relief. However, relief of a pipe is a more demanding duty for a vent door and experience shows that it is not easy to get a suitable design. Many of those tested have either blown off or failed to reseat to give a tight closure.

Another device which might in principle be used is the spring-loaded valve. The explosion pressure forces the valve cover outwards against the force of the springs and the gas vents through the annulus so formed. However, there has been a problem in obtaining a satisfactory design of valve.

17.13.4 NFPA 68 method

As already mentioned, the method of explosion venting for ducts given in NFPA 68: 1988 and 1994 differs from that given in the 1978 edition, which essentially followed the *HSE Guide*.

The method given in NFPA 68: 1994 which is described here is that for the explosion venting of pipes, ducts and elongated vessels operating at or near atmospheric pressure. The pressure is given in the code in terms of the reduced pressure P_{red}, which is expressed as a gauge pressure. The treatment applies to pipes in which the reduced pressure P_{red} is limited to 0.2 barg.

For ducts of non-circular cross-section, the relevant diameter is taken as the hydraulic mean diameter.

Two basic situations are distinguished: (1) a pipe with a single vent consisting of an open end and (2) a pipe with multiple vents.

NFPA 68 gives several graphs to assist in the design of vents for the relief of deflagrations in pipes. The figures apply to flow in smooth, straight pipes. Some are applicable only to propane, but a formula is given which permits them to be applied to certain other gases also, as described below. They are also applicable to dusts, but with restrictions on the St class.

Figure 17.36 is used to determine the maximum allowable length of smooth, straight pipe or vessel which is closed at one end and vented at the other. If the L/D ratio is greater than that shown, there is a risk of detonation. The graph is applicable to propane and to dusts, a distinction being made between dusts with $K_{st} \leq 200$ and $K_{st} > 200$.

Figure 17.37 gives the reduced pressure P_{red} for deflagration of propane in a pipe with a single vent at one end and with an initial velocity <2 m/s.

Figure 17.38 gives the reduced pressure for deflagration of gases and dusts in a pipe with multiple vents for an initial velocity <2 m/s. The limits for gas are a burning velocity ≤ 1.3 times that of propane and for dusts $K_{st} \leq 300$.

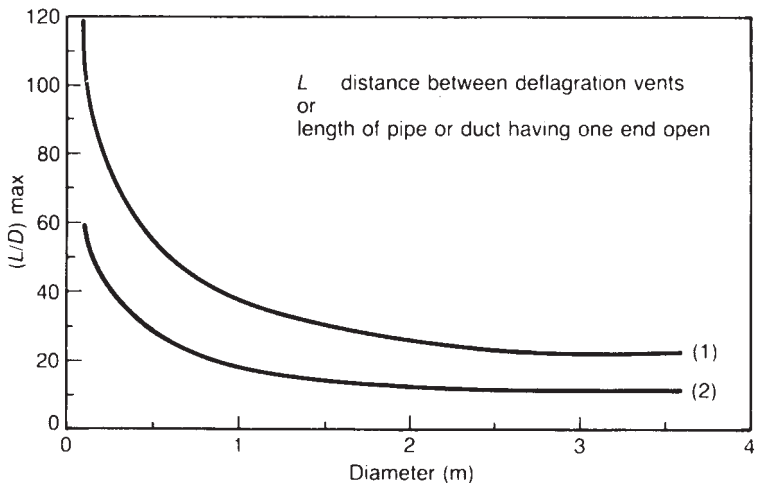

Figure 17.36 *Explosion venting of ducts and pipes: maximum allowable length of a pipe vented at one end, or maximum allowable distance between vents, for gases and dusts (NPFA 68: 1994): (1) dusts with $K_{st} \leq 200$ bar m/s and (2) propane, dust with $K_{st} > 200$ bar m/s. See text for details (reproduced with permission from NPFA 68 Deflagration Venting, © 1994, National Fire Protection Association, Quincy, MA 02269). See note to Figure 17.25*

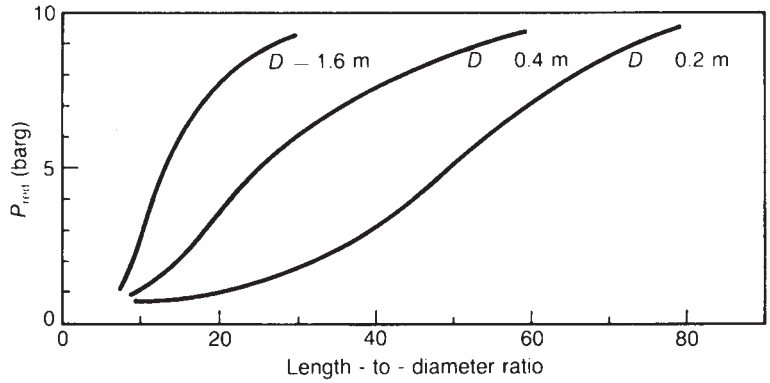

Figure 17.37 *Explosion venting of ducts and pipes: reduced explosion pressure in deflagration of propane–air mixtures in a smooth, straight pipe or duct closed at one end (NPFA 68: 1994). Initial flow velocity <2 m/s. See text for details (reproduced with permission from NFPA 68 Deflagration Venting, © 1994, National Fire Protection Association, Quincy, MA 02269). See note to Figure 17.25*

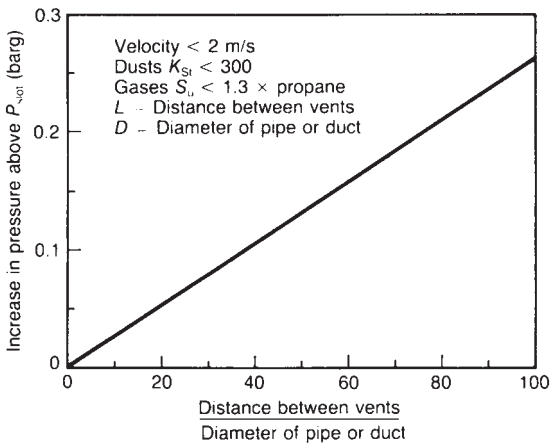

Figure 17.38 *Explosion venting of ducts and pipes: reduced explosion pressure in pipe with multiple vents for deflagration of gases and dusts (NPFA 68: 1994). Initial flow velocity<2 m/s, gas burning velocity≤ 1.3 × burning velocity of propane, dust $K_{st} \leq 300$ bar m/s. See text for details (reproduced with permission from NFPA 68 Deflagration Venting, 1994, National Fire Protection Association, Quincy, MA 02269). See note to Figure 17.25*

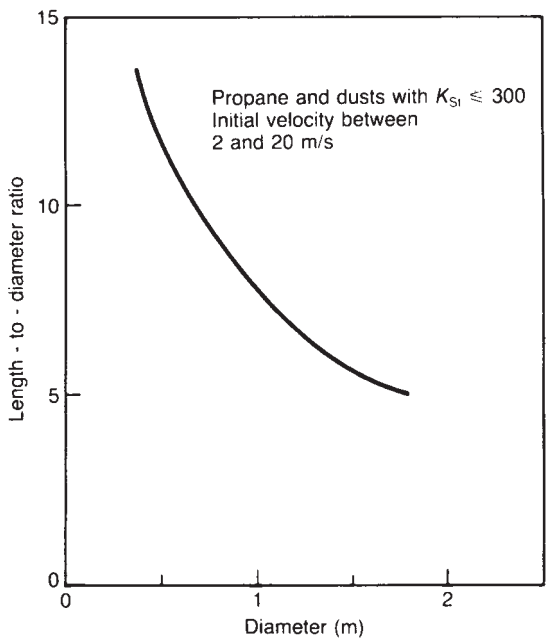

Figure 17.39 *Explosion venting of ducts and pipes: vent spacing to prevent reduced explosion pressure exceeding 0.2 barg for deflagration of gases and dusts (NPFA 68: 1994). Initial flow velocity between 2 and 20 m/s; propane gas, dust $K_{st} \leq 300$ bar m/s. See text for details (reproduced with permission from NFPA 68 Deflagration Venting, © 1994, National Fire Protection Association, Quincy, MA 02269). See note to Figure 17.25*

Figure 17.39 gives the spacing of multiple vents for the particular case where, for deflagration of gases and dusts, it is required to limit the reduced pressure to 0.2 bar and where the initial velocity is in the range 2–20 m/s. The limits for gas are a burning velocity $\leq$1.3 times that of propane and for dusts $K_{st} \leq 300$.

For gases other than propane which have a burning velocity not exceeding 1.3 times that of propane the following formulae are given:

$$L_x = \left(\frac{S_p}{S_x}\right)^2 L_p \qquad [17.13.5]$$

$$P_{red,x} = \left(\frac{S_x}{S_p}\right)^2 P_{red,p} \qquad [17.13.6]$$

where L is the maximum distance between vents, P_{red} is the reduced pressure, S is the maximum fundamental burning

velocity and the subscripts p and x denote propane and the gas in question.

When the initial velocity exceeds 20 m/s, the gas burning velocity exceeds 1.3 times that of propane or the dust K_{st} value exceeds 300, the distance between vents should not exceed 1–2 m.

Further, for gases, there is additional guidance in respect of obstacles, which include an elbow, tee, flow splitter, orifice or valve, or any feature which blocks more than 5% of the cross-sectional area of the pipe. In such cases in designing for a reduced pressure of $\leq$0.2 bar, there should be placed on each side of the obstacle two vents, at distances from the obstacle of 3 and 6 diameters. If the design is for a reduced pressure >0.2 bar, it is sufficient to use on each side of the obstacle one vent at a distance of 3 diameters from it. The code states that there is insufficient information to allow corresponding guidance to be given for dusts.

With regard to the vents, the total vent area at each location should be at least equal to the cross-sectional area of the pipe. This area may be provided by one or more vents. For an individual vent, an area exceeding the cross-sectional area of the pipe is not effective in further reducing the pressure of a deflagration.

The release pressure of the vents should be set as far below the reduced pressure P_{red} as practical, but in any event should not exceed half the reduced pressure. The mass of the vent closures should not exceed 2.5 lb/ft^2.

NFPA 68 gives a number of worked examples illustrating the application of the above guidance. These include an example involving the specification of the vents on a drier system consisting of the drier itself and a dust collector.

17.14 Explosion Relief of Buildings

An account was given in Section 17.8 of explosions in buildings. In this section explosion relief of such buildings is considered. The relief of dust explosions in buildings is considered in Section 17.48.

Accounts of explosion relief of buildings are given in *Gas Explosions in Buildings and Heating Plants* (R.J. Harris, 1983) and *Venting Gas and Dust Explosions* (Lunn, 1984b) and by Rasbash (1969c), Runes (1972) and W.B. Howard (1972). A relevant code is NPFA 68: 1994 *Deflagration Venting*.

A building is usually too weak to withstand a high explosion pressure and may be blown apart by a sustained pressure of 1 psig (0.07 bar) or even less. Nevertheless, for buildings containing flammable materials it is often appropriate to provide explosion venting. This gives the building a degree of protection against explosions resulting from such causes as leaks and spillages.

Explosion relief of buildings may be regarded as intermediate between explosion relief of vessels and explosion relief of large enclosures such as offshore modules.

17.14.1 Relief by failure of weak components

Most buildings have a number of weaker components such as windows and doors which will fail at a lower pressure than the main structure and to this extent will act as vents.

The designer may take advantage of this fact to provide at least part of the vent area in the form of regular openings with the components deliberately designed to fail at pressures which make them an integral part of the total venting arrangements.

17.14.2 Experimental studies

There have been a number of experimental studies of explosion venting of buildings and large enclosures. Some of the principal studies are listed in Table 17.18.

Reviews on work on explosion relief of buildings have been given by Rasbash (1969c), Butlin (1975 FRS Fire Res. Note 1026) and R.J. Harris (1983).

Early work on explosion relief of a large enclosure of 200 m^3 was carried out by the Committee for Explosion Research (1958) in Sweden. This work is described in Section 17.15. It was particularly valuable in that it was an early contribution and was done on a large scale so that it has provided evidence on scale-up and on phenomena of large scale.

Work at Potters Marston on the characteristics of and damage done by vented explosions in buildings has been described by Astbury *et al.* (1970) and Astbury, West and Hodgkinson (1972, 1973).

Table 17.18 *Explosion venting of buildings and modules: some experimental studies*

Investigator(s)	*Vessel or enclosure*			
	Type and dimensions (m)	*Volume* (m^3)	*Relief*	*Gas mixture*
Committee for Explosion Research (1958)	Rectangular enclosure, 8.8 × 5.8 × 3.7–4.15 height	199		
Dragosavic (1973)	Rectangular enclosure, 4 × 3 × 2.6	20.8	Vents	Methane
Solberg, Pappas and Skramstad (1980, 1981)	Rectangular enclosure, 4 × 3.5 × 2.5	35	Open vents	Propane
W.B. Howard and Karabinis (1980)	Rectangular building	81		Propane
Buckland (1980)	Rectangular enclosure, 3.7 × 3.0 × 2.4 height		Vents	Natural gas
A.J. Harrison and Eyre (1986, 1987a,b)	Rectangular enclosure, 5.92 × 2.38 × 2.16	30.4	Open vents?	Natural gas equivalent, propane
C.J.M. van Wingerden (1989c)	Rectangular enclosure, 4.0 × 3.7 × 2.6	38.5	Open vents?	Methane

Dragosavic (1972a,b, 1973) has described work at TNO, and has given an equation correlating the results, as described in Section 17.12.

Following an explosion incident in a process plant building, reported earlier by W.B. Howard (1972), explosion relief experiments were performed by W.B. Howard and Karabinis (1980, 1982) on a test building $5.5 \times 4.5 \times 3$ m high. The building contained obstacles to simulate process plant equipment. The tests provided information on potential for structural damage, on explosion venting, and particularly on the Runes constant, and on vent system design.

17.14.3 Empirical and semi-empirical methods

The methods available for the explosion relief of buildings are essentially a subset of those already given for explosion venting of vessels.

Two methods which have been widely used are those of Rasbash (1969c) and Runes (1972). Both methods were in fact developed in the first instance for the relief of buildings.

The methods preferred by R.J. Harris (1983) are those of Cubbage and Simmonds (Cubbage and Simmonds 1955a–c; Simmonds and Cubbage 1960) and Cubbage and Marshall (1973). Harris gives a theoretical model for the initial rate of pressure rise and initial pressure in an explosion in a building, but not for a vented explosion in a building; for the latter he refers to the model of Fairweather and Vasey (1982). These methods have all been developed by British Gas and thus may be considered to constitute a coherent set of methods for this problem.

17.14.4 Rasbash method

An equation for the maximum pressure in a vented explosion in a building has been given by Rasbash (1969c). This equation has been described in Section 17.12.

In the form given by Rasbash, Drysdale and Kemp (1976) the equation is

$$P_{\text{red}} = 1.5P_{\text{v}} + fS_{\text{u}}(P_{\text{I}} + 2.5K)/0.45 \qquad [17.14.1]$$

with

$$P_{\text{I}} = \frac{0.20Kw + 1.17}{V^{1/3}} \qquad [17.14.2]$$

$$K = A_{\text{c}}/A_{\text{v}} \qquad [17.14.3]$$

where A_{c} is the smallest cross-sectional area of the building space (m^2), A_{v} is the total area of combustion vents (m^2), f is a turbulence factor, if is the venting ratio, P_{I} is the back pressure due to inertia of the vent (gauge) (kPa), P_{red} is the maximum pressure reached during the venting of combustion, or reduced pressure (kPa), P_{v} is the pressure within the building space at which the vent opens (gauge) (kPa), S_{u} is the maximum fundamental burning velocity of the gas (m/s), V is the volume of the enclosure (m^3) and w is the inertia of the vent (kg/m^2).

A fuller account of Equation 17.14.1, including details of the parameters and range of validity, is given in Section 17.12.

Equation 17.14.1 has been widely used for the explosion relief of buildings.

17.14.5 Runes method

Another equation which has been widely used for the explosion relief of buildings is that of Runes (1972). This equation also has been described in Section 17.12. The Runes equation is

$$A_{\text{v}} \frac{CL_1L_2}{\Delta P^{1/2}} \qquad [17.14.4]$$

with

$$C = \frac{\pi u_f (E-1)}{200} \qquad [17.14.5]$$

where A_{v} is the vent area (ft^2), E is the expansion ratio, L_1 and L_2 are the two smallest dimensions of the building (ft), ΔP is the vented explosion overpressure ($\text{lb}_\text{f}/\text{in.}^2$), u_{f} is the flame speed (ft/s), ρ is the density of the gas (lb/ft^3) and C is a constant ($(\text{lb}_\text{f}/\text{in.}^2)^{1/2}$. Runes did not actually give a value of the constant C beyond that which can be calculated for specific cases using Equation 17.14.4.

Runes considered that his equation gives conservative but reasonable vent areas. He presented several worked examples showing that by comparison with the then current version of NFPA 68 his equation gave reasonable values and avoided the more extreme vent areas which the latter sometimes gave. He also gave a comparison with the results of the Bromma explosion venting tests.

Following an explosion incident, W.B. Howard (1972) made proposals for modification of the Runes equation. The explosion occurred in a building which contained process plant equipment and had an area of 5335 ft^2 of open windows and of weak components which would act as vents. The end wall was estimated to be able to withstand a static pressure of 7 kPa. This wall was blown off, some portions falling as integral sections, but not forming missiles. Part of the side walls were also blown out and the other end wall was cracked.

Howard first took one of Runes's examples and substituted numerical values to obtain for the case of a gas mixture with a nominal flame speed u_{f} of 11 ft/s the equation

$$A_{\text{v}} = \frac{1.2L_1L_2}{\Delta P^{1/2}} \qquad [17.14.6]$$

thus giving by comparison with Equation 17.14.4 a Runes constant of 1.2. He substituted the values of A_{v} and ΔP for the explosion incident, and obtained for the flame speed u_{f} a value of 24 ft/s. Then, taking the ratio of the two flame speeds (24/11) he proposed that the value of the Runes constant be increased to 2.6 ($1.2 \times 24/11$), in effect calibrating the Runes constant from this incident.

In SI units Equation 17.14.4 becomes

$$A_{\text{v}} = C \frac{L_1L_2}{P^{1/2}} \qquad [17.14.7]$$

where A_{v} is the vent area (m^2), L_1 is the smallest dimension of the rectangular building enclosure to be vented (m), L_2 is the second smallest dimension of that building (m), P is the maximum internal building pressure (kPa) and C is a constant. The maximum internal building pressure P is that which can be withstood by the weakest building member which it is desired should not vent or break.

Equation 17.14.7 is believed to apply to buildings with a nominal length/width, or L/D, ratio up to 3. In a rectangular building where L_1 and L_2 are unequal, D should be taken as $(L_1L_2)^{1/2}$. For a building in which the L/D ratio is greater than 3, the space should be divided into units each of which has an L/D ratio of not more than 3.

The basis of the Runes constant has been explained in Section 17.12. It is discussed by Lunn (1984), who regards it as conservative. The value of the constant was obtained by Howard. The flame speed originally used by Runes was 3.35 m/s for propane–air, whereas that quoted by Howard for ethanol–air is 7.31 m/s, which introduces a factor of 2.2 on Runes' original formulation.

NFPA 68: 1978 gives for C a value in metric units of 6.8 for gases such as propane and others with a similar burning velocity, but a higher value for gases with a higher burning velocity. The suggested value for ethylene is 10.5 and that for hydrogen is 17.

17.14.6 Harris methods

The method used by R.J. Harris (1983) is based on the Cubbage and Simmonds equations given earlier as Equations 17.12.17 and 17.12.18,

$$P_1 = \frac{(4.3Kw + 28)S_u}{V^{1/3}} \qquad [17.14.8]$$

$$P_2 = 58S_u fK \qquad [17.14.9]$$

with

$$K = A_s/A_v \qquad [17.14.10]$$

where A_s is the area of the side of the enclosure (m^2), A_v is the vent area (m^2), K is the venting ratio, P_1 is the first peak pressure (mbar), P_2 is the second peak pressure (mbar), S_u is the burning velocity (m/s) and V is the volume of the enclosure (m^3).

Harris also utilizes the Cubbage and Marshall equation given earlier as Equation 17.12.33,

$$P_m = P_v + 23\frac{Kw(fS_u)^2}{V^{1/3}} \qquad [17.14.11]$$

with

$$P_v = a/A_v \qquad [17.14.12]$$

where P_m is the maximum pressure reached during venting (mbar), P_v is the pressure at which the vent opens (mbar), S_u is the maximum fundamental burning velocity of the gas (m/s) and w is the inertia of the vent (kg/m^2). The constant a is numerically equivalent to the failure pressure of a panel of unit area.

As an illustration of the use of these two equations, Harris gives the example of the calculation of the explosion relief for a furnace $5 \times 5 \times 5 \times 5$ m fired by natural gas with a limit of 3 m^2 on the size of any one vent panel. The maximum pressure rise is to be limited to 250 mbar, and the panel inertia is 10 kg/m^2. The burning velocity is taken as 0.45 m/s, the turbulence factor as 3, and the constant a is 40.

Then, by the method of Cubbage and Simmonds, taking the maximum pressure as that occurring in the second pressure peak as given by Equation 17.14.9

$$A_v = \frac{58 \times (3 \times 0.45) \times 5^2}{250}$$
$$= 7.83 \text{ m}^2$$
$$K = 5^2/7.83$$
$$= 3.2$$

This indicates the need for three panels.

For the method of Cubbage and Marshall, Harris recast Equation 17.14.11 in the following forms. For a relief panel in the side with the largest cross-section:

$$A_v = \frac{1}{P_m}\left[a + 23A_s wf^2 S_u^2/V^{1/3}\right]; \quad K = \frac{A_s}{A_v}$$

and for panels on any other side

$$A_v = \frac{1}{P_m}\left[a + 23V^{1/3} wf^2 S_u^2\right]; \quad k = \frac{V^{2/3}}{A_v}$$

$$A_v = \frac{1}{250}[40 + 23 \times (5^2)^{1/3} \times 10 \times (3 \times 0.45)^2] = 8.5$$

$$K = (5^3)^{2/3}/8.5 = 2.9$$

This again indicates the need for three panels.

17.14.7 NPFA68 method

Explosion relief of buildings is treated in NFPA 68: 2002. The approach adopted has evolved over the years. That used in the 1974 edition was to calculate the vent area A_v using both the Rasbash and the Runes equations and to take the larger of the two areas. The 1978 edition gave only the Runes equation.

For the venting of low strength enclosures, including buildings, NFPA 68: 2002 gives the following equation:

$$A_v = C\frac{A_s}{P_{red}^{1/2}}, \quad P_{red} \leq 0.1 \qquad [17.14.13]$$

where A_s is the internal surface area of the enclosure (m^2), A_v is the vent area (m^2), P_{re} is the maximum internal overpresssure which can be withstood by the weakest structural element not intended to fail (bar) and C is a venting constant ($bar^{1/2}$).

For the venting constant the code gives in metric units a value of 0.045 $bar^{1/2}$ for gases which have a fundamental burning velocity less than 1.3 times that of propane. The value of the constant for methane is 0.037 $bar^{1/2}$.

NFPA 68: 1994 gives an illustrative example of the use of Equation 17.14.13 involving a building of fairly complex shape.

17.14.8 Relief of multiple compartments

It is possible that the leak of flammable gas enters more than one compartment of the building and that an explosion in one compartment may propagate to another. An event in which explosions propagate in this way is known as a cascade explosion.

There are several factors which may cause the pressure in the second compartment to be higher than that in the first. The explosion in the first compartment may cause compression of, and turbulence in, the gas in the second compartment.

Cubbage and Marshall (1973) performed experiments using two interconnected rooms each of which had a volume of 28 m^3. They derived the following equation for the vented explosion pressure P_2 in the second compartment following ignition:

$$P_2 = (k_2 P_1 + k_2 P_1^2)^{0.5} \qquad [17.14.14]$$

with

$$k_1 = \frac{V_2}{V_1}\left(46(Kw)_{2av}\frac{S_u^2}{V_2^{0.33}}\right) \quad [17.14.15]$$

$$k_2 = \frac{V_2}{V_1}\frac{K_2}{K_{12}} \quad [17.14.16]$$

where K_1, K_{12} and K_2 are the vent coefficients for compartment 1, between compartments 1 and 2 and for compartment 2, $(Kw)_{2av}$ is the average value of Kw for compartment 2, P_1 and P_2 are the vented explosion pressures of compartment 1 and of compartment 2 (mbar), V_1 and V_2 are the volumes compartment 1 and compartment 2 (m^3), respectively and k_1 and k_2 are constants.

The experiments were done with large vent openings. It is uncertain how far the results can be extrapolated. Harris recommends against their general use.

17.14.9 Vent design

It is preferable that the vent areas should be located on different walls of the building rather than concentrated all on one wall.

Vent panels for buildings should have the lowest practicable inertia. The release pressure for a vent panel should be as low as possible relative to the expected wind pressures. An appropriate value is usually in the range 1–1.5 kPa.

A vent panel should be restrained by a device such as a hinge or chain to prevent it flying off the building if it does open. Consideration should be given to the space into which the panel is to open.

Materials which shatter into pointed fragments should not be used for vent panels. In particular, asbestos cement-type board is unsuitable.

It may be necessary to provide railings along the edge of the floor near a vent panel to prevent people accidentally knocking the panel open and falling out.

An account of the guidance in NFPA 68 on design of vents for enclosures generally, including buildings, has been given in Section 17.12.

17.15 Explosion Relief of Large Enclosures

An account was given in Section 17.9 of explosion in a large enclosure such as an offshore module. In this section explosion relief of such an enclosure is considered.

17.15.1 Relief by structural collapse

Explosion relief of a large enclosure may occur in two ways. The relief may take place exclusively through vent apertures which already exist and which are intended as vents or it may also take place through apertures which are created by the explosion itself. In the latter case the extent of the relief opening will depend on the degree of structural collapse and hence on the strength of the explosion.

Such relief may be investigated using one of the computer codes for simulation of a semi-confined explosion. In this case it will usually be necessary to adopt an iterative procedure, calculating initially the strength of the explosion without structural collapse, determining the degree of collapse for this maximum strength explosion and gradually adjusting the strength of the explosion and the degree of structural collapse until a match is obtained.

17.15.2 Experimental studies

Experiments on large vented explosions using a steel module of dimension $2.5 \times 3.5 \times 4$ m, and hence 35 m^3 volume, were performed by Solberg, Pappas and Skramstad (1981). Vent openings extended all the way along the front wall and could be varied in steps of 0.25 m^2. A propane–air mixture was used.

Tests were done with the ignition source at three different locations: at the centre of the module, at the vent opening and at the rear wall. In all cases the overpressure gave two peaks. Typical overpressure traces are shown in Figure 17.40.

With central ignition the overpressure rose until the hot burned gas began to flow through the vent. The volumetric flow then increased, the density of the gas being less. The pressure rise was arrested. This effect also inhibited the backward propagation of the flame front towards the rear wall. The arrest of this flame front created just the conditions which favour Taylor instability. Under these conditions the flame front breaks up into a large number of fronts propagating in many directions. There is a massive increase in the rate of combustion and a large increase in the overpressure. This is illustrated in Figure 17.41.

This phenomenon was not limited to the case of central ignition. It occurred with ignition at the vent opening also. For Taylor instability a major part of the flame must be able to propagate away from the vent opening, but the distance between the ignition source and the opening is not important.

With the ignition source at the rear wall the course of the explosion was different. In this case there was less scope for Taylor instability. However, there was still a strong second peak. This was thought to be due probably to the shear between the high-velocity burned gas and the low-velocity unburned gas and the consequent enhancement of turbulence at the flame front. This is illustrated in Figure 17.42.

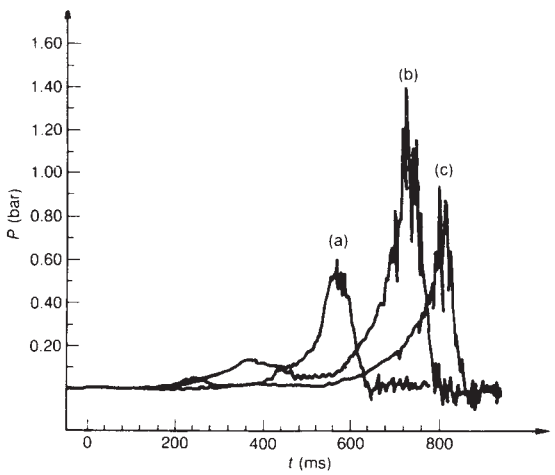

Figure 17.40 *Explosion venting of large enclosures: profiles of overpressure for explosions with different locations of the ignition source – 1: (a) rear wall ignition, (b) central ignition, and (c) front wall ignition (Solberg, Pappas and Skramstad, 1981). P, pressure; t, time (Courtesy of the Combustion Institute)*

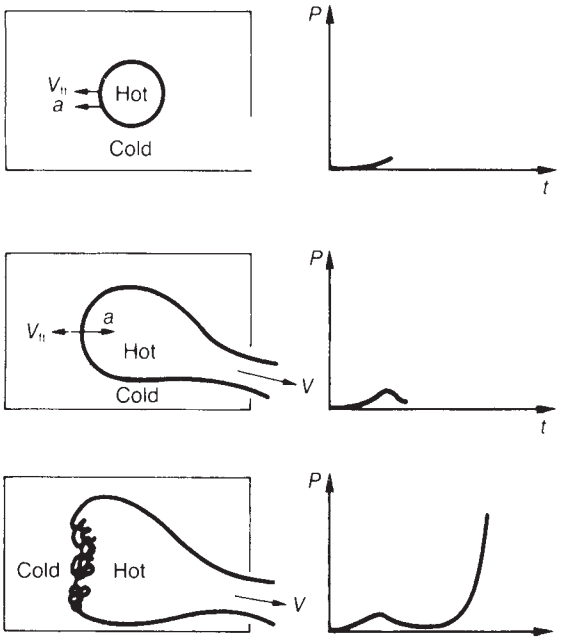

Figure 17.41 *Explosion venting of large enclosures: development of a vented explosion with central ignition showing Taylor instability (schematic) (Solberg, Pappas and Skramstad, 1981). P, pressure; t, time (Courtesy of the Combustion Institute)*

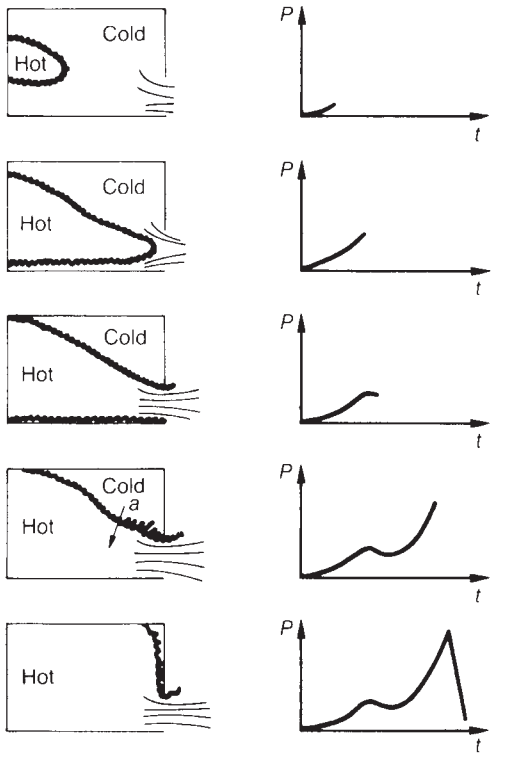

Figure 17.42 *Explosion venting of large enclosures: development of a vented explosion with rear wall ignition (schematic) (Solberg, Pappas and Skramstad, 1981). P, pressure; t, time (Courtesy of the Combustion Institute)*

The authors also explored the validity of vent coefficient scaling ($A_v/V^{2/3} = \text{constant}$). They found that for large volumes such scaling was not valid and was not conservative. They concluded that whereas combustion in small volumes is characterized by a small, spherical flame front, in larger volumes combustion instabilities dominate.

Experiments on generation of overpressures in vapour clouds have been described by A.J. Harrison and Eyre (1986, 1987a,b). This work included investigation of the ignition of a vapour cloud by a jet flame issuing from a vented chamber. In this work it was observed that when unburned gas displaced from the chamber was ignited by the emerging flame, there occurred a rapid combustion of the displaced gas, near spherical in form and located a few metres from the vent opening. They termed this an 'external explosion'. They noted that a similar phenomenon had been reported by Solberg, Pappas and Skramstad (1980).

Overpressure traces showing the external explosion are given in Figure 17.43. Figure 17.43(a) shows the overpressure at the rear wall of the chamber and Figure 17.43(b) that just outside the chamber. The peak caused by the external explosion occurs first.

The blast wave from the external explosion is shown in Figure 17.44. The overpressure is constant for some distance from the vent opening to a virtual centre and then falls off, the decay being proportional to the reciprocal of the distance from that centre.

C.J.M. van Wingerden (1989c) has reported experiments to investigate the various effects which may enhance the overpressures obtained in large vented explosions. He lists

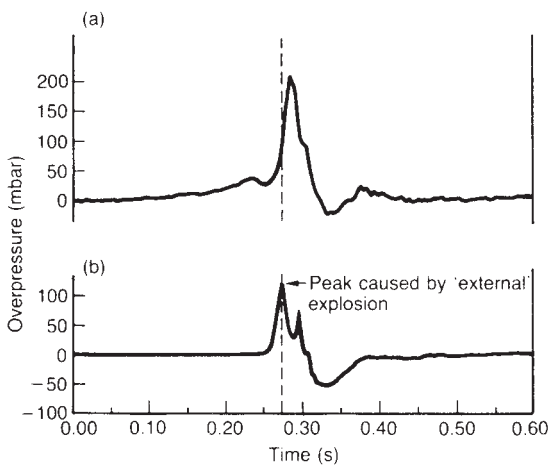

Figure 17.43 *Explosion venting of large enclosures: profiles of overpressure inside and outside the enclosure showing effect of external explosion: (a) overpressure at rear wall and (b) overpressure just outside enclosure (A.J. Harrison and Eyre, 1986; reproduced with permission)*

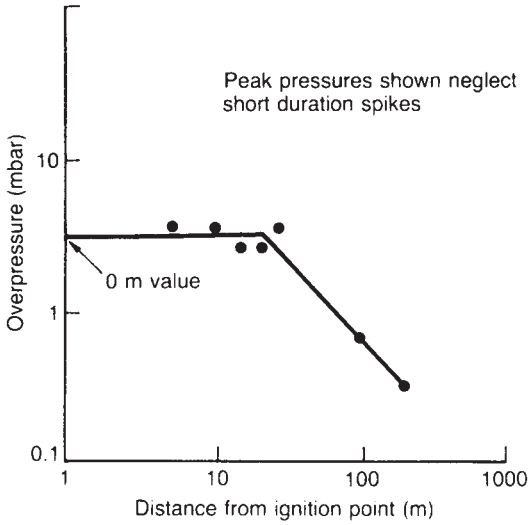

Figure 17.44 *Explosion venting of large enclosures: decay of overpressure outside enclosure (A.J. Harrison and Eyre, 1987a) (Courtesy of Combustion Science Technology)*

as possible enhancing mechanisms shear turbulence, oscillatory combustion and Taylor instability.

The tests were performed using a chamber $2.6 \times 3.7 \times 4.0$ m, and hence a volume of 38.5 m^3, and methane–air mixtures. Features investigated included vent area, vent shape, ignition source location, effect of an obstacle and gas concentration.

The overpressure traces obtained had two peaks. Van Wingerden attributes the first to opening of the vent cover and the second, which was generally larger than the first, to oscillatory combustion. An acoustic wave generated during the combustion process enhances combustion and creates higher overpressures. A frequency analysis showed a maximum at a frequency of 120 Hz, corresponding to the fundamental mode of the chamber with the wave standing between the two side walls. The repeatability of this mechanism was low, however, and the overpressures obtained varied by a factor of nearly 2.

An external explosion occurred and had the effect of making the pressure peaks rather sharp.

Overpressures measured with vent areas <5.2 m^2 were low, but high overpressures were obtained with vent areas >5.2 m^2. No explanation was found for this anomalous effect. Vent shape and vent opening pressure had little effect. There was a wide scatter of overpressures for different vent opening pressures.

The location of the ignition source affected the overpressure traces but had little influence on the maximum overpressures obtained. Central ignition and ignition at the vent opening gave a maximum overpressure due to oscillatory combustion, whilst rear wall ignition gave a maximum overpressure due to the external explosion.

Tests were done with a single obstacle which, depending on its orientation blocked 12 or 23% of the cross-section of the chamber. With this configuration, overpressure traces with three peaks were obtained. Van Wingerden attributes the first to the opening of the vent, the third to oscillatory combustion and the second to turbulent combustion in the wake of the obstacle proceeding outside the enclosure. This second peak increased as the distance between the ignition source and the obstacle increased. The peak was at a maximum when this distance was large.

Gas concentrations used were 9.5 and 10% methane–air mixtures. Oscillatory behaviour was obtained more readily with the latter and this was used in most of the work.

The venting of the explosion gave rise to long flame jets, up to 18 m in length.

The overpressure due to the blast wave outside the chamber was also measured. There were two pressure peaks, the first due to the external explosion and the second due to the internal explosion. With central ignition the two peaks were comparable, whilst with rear wall ignition the external explosion effect was dominant. Essentially, the strength of the blast wave depended on the external explosion. The overpressure was constant for some distance from the vent opening and then decayed inversely with the distance as seen in Figure 17.44.

A review of the experimental evidence on the overpressures which might occur due to an explosion in a vented module was given to the Piper Alpha Inquiry by Chamberlain (1989). He drew attention to the complexity of the phenomena involved and illustrated this by reference to the overpressure traces shown in Figure 17.45. Figure 17.45(a) is for a case with central ignition and exhibits five peaks: peak 1 at vent panel rupture, peak 2 at flame emergence from the vent, peak 3 at the moment of external explosion, peak 4 due to Helmholtz oscillations and peak 5 due to acoustic coupling oscillations. The maximum peak pressure is at peak 5 at about 200 mbar. Figure 17.45(b) is for rear wall ignition. With ignition near the wall the oscillations are severely damped and peaks 2 or 3 dominate. In this particular case, the maximum peak pressure is at peak 3 at about 550 mbar.

17.15.3 Influencing factors

Some of the factors which influence the severity of a large vented explosion have been described by Chamberlain (1989). They include the fuel, the fuel/air ratio, the initial turbulence, the location of the ignition source, the size of the enclosure, the degree of obstruction and the vent area. The severity is increased if the fuel is a reactive one and if the fuel–air mixture is near stoichiometric. Initial turbulence will enhance the severity, but the effect is not readily quantifiable. The location of the ignition source has a strong effect. For a space with only one vent, locating the ignition source furthest from the vent will tend to give the highest overpressures. The severity tends to increase with the volume of the enclosure and to decrease with the vent area.

Obstacles tend to have a very strong effect on the severity of the explosion. The effect depends on the number, dimensions and profile of the obstacles and on the resultant blockage ratio. Considering an obstructed region of grid arrays, the overpressure increases exponentially with the number of arrays. For obstacle dimensions a worst case diameter of between 5 and 25 cm has been observed in experiments. The effect of an obstacle having a sharp profile is about twice that of one with the same cross-section but with a rounded profile. The overpressure increases exponentially with blockage ratio. As far as the scale of the

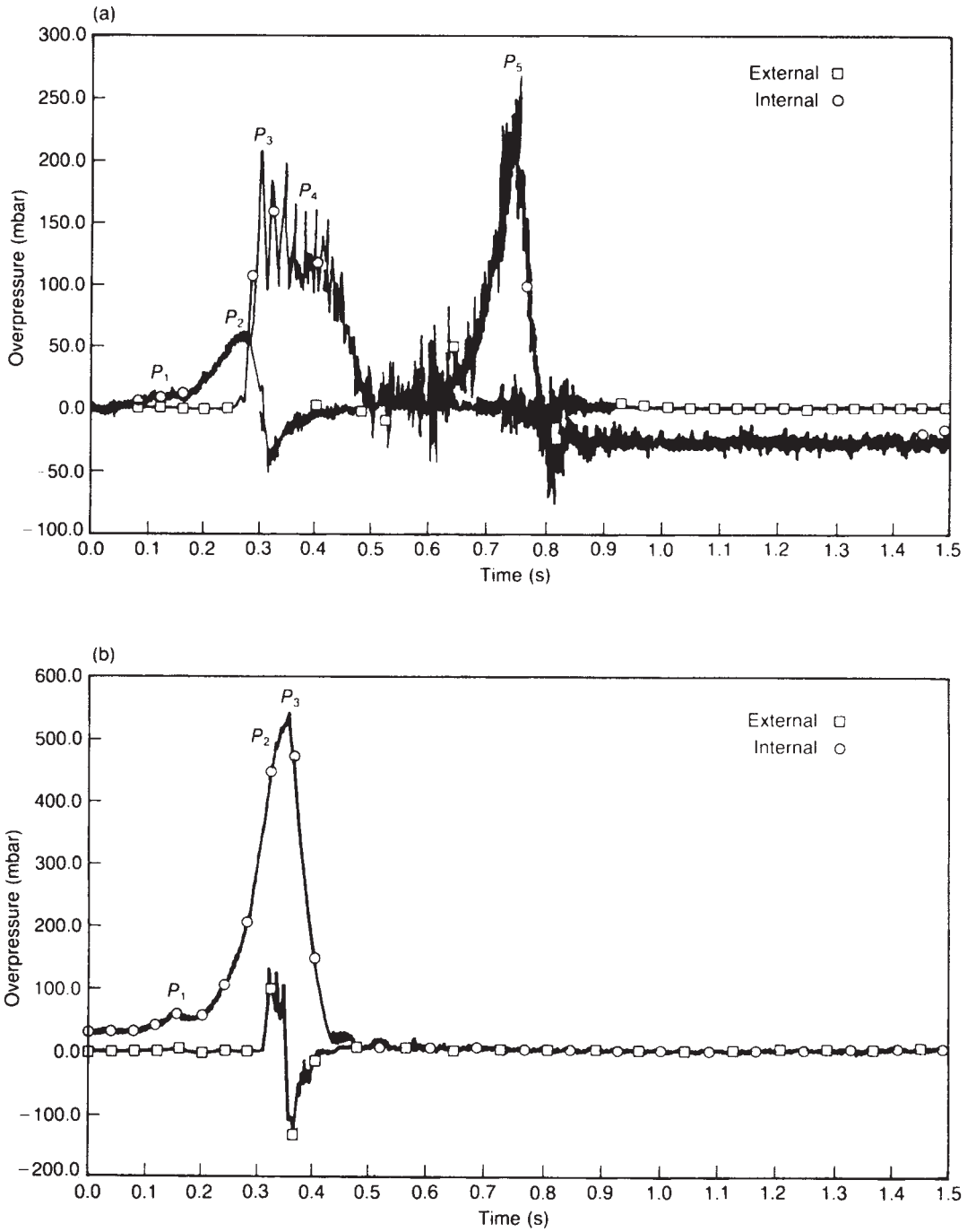

Figure 17.45 *Explosion venting of large enclosures: profiles of overpressure for explosions with different locations of the ignition source −2 (Chamberlain, 1991; after A.J. Harrison and Eyre, 1987b) (Courtesy of the Institution of Chemical Engineers)*

obstacles is concerned, large scale obstacles have a considerably smaller effect than corresponding configurations of small scale obstacles.

The initial temperature has only slight influence as does the strength of the ignition source, leaving aside flame jet ignition.

17.15.4 External explosion

The occurrence of an external explosion has already been mentioned. The effect has been discussed by Chamberlain (1989).

The external explosion occurs because the advancing flame front expels unburned fuel from the vent. The external flow has a large and strong coherent structure and entrains a considerable quantity of air. When the flame emerges it constitutes a strong ignition source for this external flammable cloud and the external explosion can be severe. Its magnitude depends on the mass of fuel expelled, which in turn depends on the location of the ignition source. If all the fuel in the internal space is consumed before the flame reaches the vent, an external explosion will not occur. The external explosion will be weakened if the gas cloud is displaced far from the vent or if it is strongly diluted with air.

The influence of the external explosion on the internal overpressures is negligible where the latter exceeds 1 bar. At lower internal overpressures, however, the external explosion can have a marked effect. The larger the vent area and the lower the internal overpressure, the larger the relative contribution of the external explosion. Thus, the external explosion is a factor which works against the attempt to limit the internal overpressures. There is some evidence that the importance of the external explosion increases with scale.

17.15.5 Computer codes

The computer codes available for the simulation of an explosion in a semi-confined enclosure were described in Section 17.9. These codes may be used, as there indicated, to investigate the course of an explosion with little or no venting, but their main application is to study situations in which there is appreciable venting.

There also exist codes designed specifically for venting calculations. One of these is the VENTEX code of Shell. This incorporates a semi-empirical model based on extensive experimentation. The code is used mainly for preliminary screening to investigate the effect of different parameters prior to use of more fundamental models. The VENTEX code calculates first the overpressure in an empty enclosure at the instant when the flame reaches the vent, then the amplifying effect of obstacles and finally the effects of the external explosion.

17.15.6 Design methods

There is no full satisfactory fundamental method of predicting the overpressure from an explosion in a large vented enclosure. The available empirical equations are of limited use. They have usually been derived for empty vessels and tend not to take into account complicating factors such as internal obstacles or external explosions.

More useful are computer codes and model experiments. The former include the fundamental models incorporated in computer codes such as FLACS and CLICHE and the semi-empirical models of codes such as VENTEX. The use of the large CFD codes tends to be expensive.

Scale model experiments provide an alternative, or complement, to computer codes. This approach also is expensive.

Both computer codes and model experiments tend to involve a degree of extrapolation. It needs to be borne in mind that some phenomena become more significant as scale increases.

17.16 Venting of Reactors

The reactors which are considered here are liquid-phase reactors, essentially those capable of an exothermic reaction runaway.

It has long been the practice to protect such reactors against overpressure by the use of some form of relief such as a bursting disc or pressure relief valve. The overpressure protection of reactors was described in Chapter 11.

In this section an account is given of methods of sizing the vent for a reactor. Methods have progressed from early empirical correlations to methods based on various types of model, both simplified analytical models and full unsteady-state models embodied in computer codes.

One point is worth emphasizing at the outset. This is that in reactor venting it is the volumetric flow which is important.

The need for adequate vent sizing methods is evidenced by a number of incidents of reactor overpressure which have been attributed to the undersizing of the reactor vent.

Vent sizing of reactors is a complex and specialist matter. The account given here is no more than an overview.

17.16.1 Venting scenarios

The vent system for a reactor should be designed for the worst case scenario which is reasonably foreseeable. The scenarios considered should include fire engulfment as well as reaction runaway.

17.16.2 FIA method

An early method of vent sizing was the Factory Insurance Association (FIA) method, described by Sestak (1965). The method is an empirical one in which vent area is plotted as a function of reactor volume and reaction class. The graphical relations may be represented by the following approximate equation:

$$A = KV^{0.92} \qquad [17.16.1]$$

where A is the vent area (in.^{2}), V is the reactor capacity (US gal) and k is a constant. The constant k has the approximate values 0.0056, 0.021 and 0.095 ($V \leq 10{,}000$) for exothermic reactions, categories A–D, with very low, low and moderately high heat releases, and 0.48 ($V \leq 4000$) for reactions with extraordinarily high heat releases. The value of k of 0.0056 is also used for endothermic reactions. The vent areas are given not as single lines but as bands of approximately $\pm 50\%$ about the values given by Equation 17.16.1.

The FIA method is relatively simple to apply and has been widely used. Examples of its use have been given by Harmon and Martin (1970).

A number of authors have discussed the method, including Duxbury (1976, 1980) and Fauske (1984a,b).

Fauske (1984b) has given the quantification of the FIA chart shown in Figure 17.46. This interpretation is based on the equation given by Fauske for the vent area of a vapour

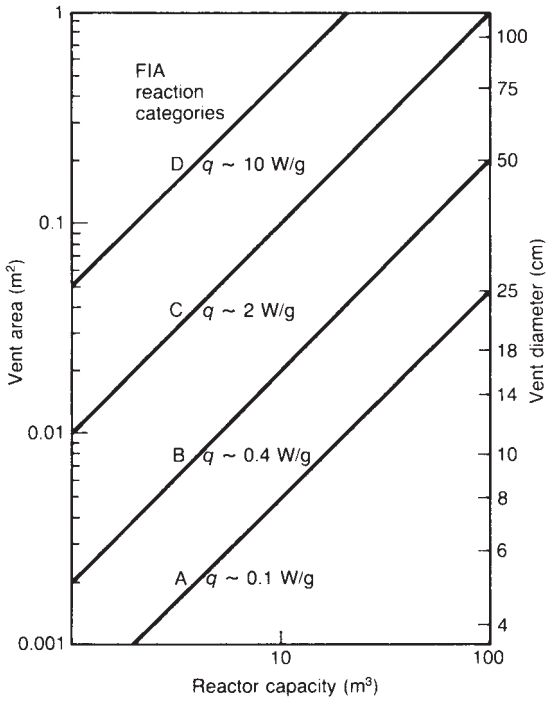

Figure 17.46 *Venting of chemical reactors: interpretation of FIA vent sizing method (Fauske, 1984b); q, energy release rate (Courtesy of the American Institute of Chemical Engineers)*

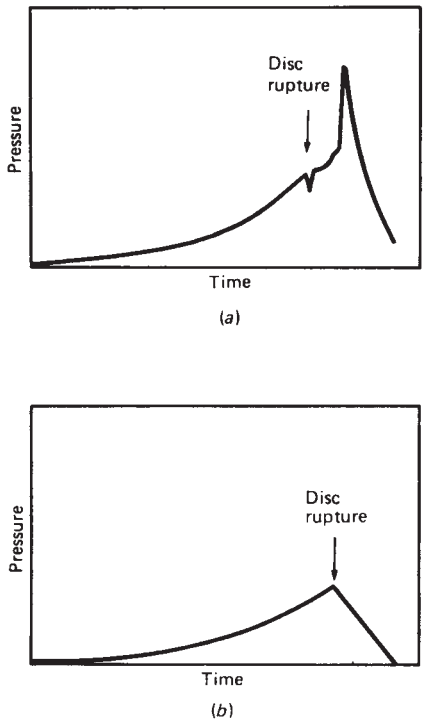

Figure 17.47 *Venting of chemical reactors: typical pressure curves for a runaway reaction (after Harmon and Martin, 1970): (a) vent area inadequate; (b) vent area adequate (Courtesy of the American Institute of Chemical Engineers)*

pressure system, given below as Equation 17.19.3, with properties of water ($\rho_1 = 1000$ kg/m^3, $C = 4.18$ kJ/kg K and $T = 373$ K) and for an overpressure of 20%. The heat release rate q for the reaction categories A–D is quantified as shown in the figure.

Industrial Risk Insurers (IRI), the successor to FIA, withdrew the FIA method from its engineering procedures in the 1970s and recommended the use of other methods (Davenport, 1977c).

17.16.3 Monsanto correlation

Another simple method of vent sizing is the Monsanto correlation (W.B. Howard, 1973). This method is one of those included in a review given by Fauske (1984a). The correlation is used for sizing vents for runaway phenol–formaldehyde reactions. It is

$$D = 0.3V^{1/2} \qquad [17.16.2]$$

where D is the diameter of the vent (in.) and V is the volume of the reaction mass (US gal). The correlation is applicable for a self-heat rate of the order of 6.5°C/min and a set pressure of 15–16 psia. This implies a horizontal vent line to prevent build-up of static pressure due to liquid head.

17.16.4 Vent flow

The venting of a liquid-phase reactor is generally treated by determining (1) the flow of material which must be vented to prevent excessive overpressure and (2) the vent area required to effect this discharge.

The problem is complicated by the fact that it is difficult to predict whether the fluid discharged will be (1) a vapour, (2) a liquid or (3) a two-phase vapour-liquid mixture. Methods have been developed based on each of these assumptions. In general, the assumption of a single phase yields a simpler treatment, but the assumption of two-phase flow is more realistic.

It has often been observed that in practice the fluid vented from a reactor is not a vapour, but is either a liquid or a vapour-liquid mixture. Descriptions of incidents in which the charge was vented as either a liquid or a vapour–liquid mixture are given by Boyle (1967), Harmon and Martin (1970), Huff (1973, 1977a) and Duxbury (1976).

The general shape of the pressure curve for the venting of a runaway reaction as given by Harmon and Martin (1970) is shown in Figure 17.47. Figure 17.47(a) shows the curve for a runaway polymerization of ethyl acrylate with a vent of inadequate area and Figure 17.47(b) that for a runaway polymerization of methyl methacrylate with an adequate vent area.

17.16.5 All vapour venting method

An approach to reactor venting which has frequently been adopted is that based on venting of the vapour from the boiling liquid reaction mass. This involves calculating the maximum allowable liquid temperature, which is related by

the vapour pressure to the maximum allowable pressure, and then determining the rate of reaction and of heat generation at this temperature, the rate of vapour evolution and hence the flow of vapour to be generated. The vent area is then

$$A = W/G \qquad [17.16.3]$$

with

$$W = \frac{r(-\Delta H_r)V}{\Delta H_v} \qquad [17.16.4]$$

where A is the vent area (m^2), G is the mass flux (kg/m^2s), ΔH_r is the heat of reaction (negative for exothermic reaction) (kJ/kg), ΔH_v is the latent heat of vaporization (kJ/kg), r is the rate of reaction (kg/m^3s), V is the volume of the reaction mass (m^3) and W is the mass flow (kg/s).

The vent mass flux G is determined by standard methods for vapour flow.

17.16.6 All liquid venting method

As mentioned above, however, it is known that in some cases the fluid is vented as a liquid or a vapour–liquid mixture.

An alternative approach, therefore, is to size the vent on the basis of discharging the whole reaction mass as a liquid. The required flow is calculated from the rate of reaction and of heat generation at the maximum liquid temperature and the time required to heat the reaction mass to this temperature.

Then

$$W = m_o/\Delta t \qquad [17.16.5]$$

with

$$\Delta t = \frac{m_o C \Delta T}{r(-\Delta H_r)V} \qquad [17.16.6]$$

where C is the specific heat of the reaction mass (kJ/kg K), m_o is the initial mass in the vessel, or the reaction mass (kg), Δt is the time interval to the maximum allowable pressure (s) and ΔT is the temperature difference at equilibrium between the initial pressure and the maximum allowable pressure (K).

The vent area is again determined from Equation 17.16.3. The vent mass flux G is determined by standard methods for liquid flow.

It is found that in some cases the all vapour venting method gives the larger area and in others the all liquid venting method does.

17.16.7 Boyle method

A method based on the all liquid venting approach has been described by Boyle (1967). The method given by Boyle is based on the pressure–time curve for the reactor. This may be obtained from the reaction rate or by experiment. Effectively, the method separates the calculation of the vent area from that of the vent flow. The latter is determined from the time for the reactor pressure to rise to the maximum allowable pressure. The former is estimated using the pressure in the reactor at the relief point.

A statement of the Boyle model has been given by Leung (1986b) as follows:

$$W = \frac{m_o}{\Delta t_p} \qquad [17.16.7]$$

where Δt_p is the emptying time (s).

Leung also refers to the relation given by Fauske (1984b) for the emptying time

$$\Delta t_p = \frac{\Delta T}{(dT/dt)_s} \qquad [17.16.8]$$

where ΔT is the temperature rise corresponding to the overpressure ΔP (°C) and $(dT/dt)_s$ is the self-heat rate at the set pressure (°C/s).

Boyle recommends that the vent area be calculated by both the all vapour venting and the all liquid venting methods, that the larger area be used and that a factor of safety of 2–3 be applied to the area so obtained.

A critique of Boyle's method is given by Duxbury (1980). In general, provided the flow is single phase the method tends to give vent sizes on the high side and thus to be conservative.

There is evidence from the work of Harmon and Martin (1970) that Boyle's method may underestimate the vent areas for larger reaction vessels. It gives for such vessels vent areas which are in some cases considerably less than those obtained by the FIA method. Further evidence is given by Huff (1973, 1977a).

The method given by Boyle is not conservative for situations in which two-phase flow occurs. It is still possible, however, to use the first part of the method to calculate the flow to be vented, but to use two-phase flow methods for the vent sizing.

A modified Boyle method which takes account of two-phase flow has been described by Duxbury (1976). The two-phase flow calculations are performed using a fluid flow code.

17.16.8 Huff method

A method of vent sizing based on a much more comprehensive reactor model, including reaction kinetics and two-phase flow relations and embodied in a computer code, has been described by Huff (1973).

Huff also gives a comparison of the different methods of calculating vent sizes for liquid-phase reactors. For the case which he considers the two-phase flow model is more conservative that the FIA method or the all vapour venting and all liquid venting methods.

This model has undergone further development as described by Huff (1977a,b, 1982a,b, 1984a).

One version of this model (Huff 1977a,b, 1982a,b) has come to be known as the pseudo-steady-state model (e.g. Duxbury and Wilday, 1989).

Duxbury (1980) describes this model as a two-phase venting method for reactions in which pressure and temperature peak simultaneously. Huff states that it is conservative for reactions in which pressure peaks first.

A statement of the Huff model has been given by Leung (1986b) as follows:

$$W = \frac{m_o}{\tau_t} - \frac{\beta}{2\tau_t^2}\left[\left(1 + \frac{4m_o\tau_t}{\beta}\right)^{1/2} - 1\right] \qquad [17.16.9]$$

with

$$\beta = \frac{h_{fg} V}{q_m v_{fg}} \quad [17.16.10]$$

$$\tau_t = \Delta t_p + \frac{h_{fg}}{q_m}(x_m - x_o) \quad [17.16.11]$$

$$x_m = \frac{V/m_m - v_f}{v_{fg}} \quad [17.16.12]$$

$$m_m = m_o - W_{\tau t} \quad [17.16.13]$$

where h_{fg} is the latent heat of vaporization (kJ/kg), m is the reaction mass in the vessel (kg), q is the heat release rate per unit mass (kW/kg), x is the mass fraction of vapour, or quality, v_f is the specific volume of the liquid (m^3/kg), v_{fg} is the specific volume change between the vapour and liquid phases (m^3/kg), β is a parameter, τ_t is the turnaround time for temperature (s) and the subscripts m and o denote peak and initial pressure (or temperature), respectively.

17.16.9 BPF method

Another full unsteady-state model is that developed for phenolic resin reactors by the British Plastics Federation (BPF) and described by Booth *et al.* (1980).

17.16.10 Scale-up methods

An alternative approach to the vent sizing of liquid phase reactors is scale-up from experimental tests. Such extrapolation is valid, however, only if similarity exists between the test and full-scale systems.

Some of the conditions which must be met before similarity can be assumed are listed by Duxbury (1976). Thus, for polymerization reactions he suggests that the basis for scaling up, though not for scaling down, might be a constant ratio of vent area to reactor volume. This accords quite well with the FIA method in which vent area increases with reactor volume to the power 0.92.

17.16.11 ICI methods

Reviews of methods of vent sizing used in ICI have been given by Duxbury (1976, 1980) and by Duxbury and Wilday (1987, 1989, 1990). An account of the ICI scheme is given in Section 17.21.

17.16.12 Reaction parameters

As already indicated, there are a number of reactor parameters which are relevant to reactor venting. They include: P_s, set pressure (Pa); $(dT/dt)_s$ self-heat rate, at set pressure (°C/s); Q_g, volumetric gas evolution rate (m^3/s); Q_v, volumetric vapour evolution rate (m^3/s).

17.16.13 Source term

The flow entering the vent may be a homogeneous vapour–liquid equilibrium mixture or, if vapour disengagement occurs, a vapour. The size of vent required is different for the two cases.

When the reactor pressure is reduced due to venting, the liquid becomes superheated and vapour bubbles are formed, causing liquid swell. Unless vapour disengagement occurs, a two-phase mixture will enter the vent. Vapour disengagement does tend to occur in non-foamy system, though not in foamy ones.

Definition of the source term for the flow entering the vent is therefore of some importance. This is considered in Chapter 15 by a so-called coupling equation.

17.16.14 Relief devices

The relief devices normally used for venting of liquid-phase reactors are bursting discs or pressure relief valves.

It is necessary to allow for two-phase flow through these devices. This is dealt with in Chapter 15.

17.16.15 Relief disposal

The material vented must be disposed of safely. Relief disposal is considered in Sections 17.22 and 17.23.

17.16.16 Containment

In certain cases, as discussed by Duxbury (1976), containment of a possible runaway reaction may be an attractive alternative to venting. This may be so, for example, if the peak pressure attainable is close to the working pressure or if it is less than the minimum design pressure for a vessel of that size or if there are special venting problems such as blockage of the vent lines.

The application of this concept to reactors has been developed by Wilday (1991). An account is given in Chapter 12.

17.16.17 Instrumented systems

Another design option for reactor venting is the use of an instrumentation and control system designed to ensure that overpressure does not occur and thus to eliminate the need for venting. This approach is discussed in Chapters 11–13.

17.16.18 Design conservatism

It is generally desirable in design to adopt a conservative approach, but in reactor venting, care is needed in defining what this means. A low mass velocity through the vent is conservative with regard to determination of the vent area. But it is not conservative with respect to pressure drops in the system, reaction forces caused by the venting or load on the relief system.

17.17 Venting of Reactors and Vessels: DIERS

17.17.1 DIERS

It was recognized towards the end of the 1970s that understanding of reactor relief was deficient and that methods of vent sizing were inadequate and a major international cooperative project, DIERS, was initiated to remedy this. This project is now described.

17.17.2 DIERS project

A major project on reactor venting was undertaken during the mid-1980s by the Design Institute for Emergency Relief Systems (DIERS) of the American Institute of Chemical Engineers (AIChE) with sponsorship from a large international group of companies. The main contractor was Fauske and Associates Inc., and results from the project and its aftermath have been the subject of a series of publications by Fauske and co-workers, notably Epstein, Grolmes, Leung and Swift. Overviews of the project have been given by H.G. Fisher (1985, 1991).

The work is described in the *DIERS Project Manual*, which gives an overview and contains chapters on the following aspects: vapour disengagement; relief system flow;

large scale tests; high viscosity flashing flow; mechanical design, containment and disposal; bench-scale apparatus and the SAFIRE computer code.

Some principal elements of the work are given in the Technology Summary. This deals with the behaviour of the vapour in the vessel and with vapour–liquid flow in the vent line and gives emergency relief system (ERS) design methods. It also deals with fire relief of storage vessels.

The DIERS project involved an extensive investigation of the behaviour of the fluid venting through the vent line. It included study of the vapour disengagement in the vessel and of the fluid flow through the vent. The work showed that there are different types of reaction systems and that the behaviour of these systems is different. A major finding was that the flow at the vent tends to be a two-phase vapour–liquid flow. Methods of ERS design were developed for the different systems. These included simplified methods, a computer model and a scale-up method. A bench-scale apparatus was designed capable of determining the principal design parameters.

There is a DIERS Users Group which is described by H.G. Fisher (1989). A newsletter of the group has been carried in Plant/Operations Progress.

17.17.3 Influencing factors

The overall venting behaviour of reaction system depends on a number of factors. They include (1) reaction regime, (2) vapour disengagement, (3) fluid viscosity and (4) vent line length. It is necessary to allow for these factors in design, and in particular to take them into account in scale-up from bench scale to full scale.

17.17.4 Reaction regimes

The different types of reaction system, or reaction regimes, distinguished in the work are

(1) vapour-generating system;
(2) gas-generating system;
(3) hybrid system.

A vapour-generating system is one in which the total pressure is the system vapour pressure. In other words, the system contains one or more high vapour pressure components. When the vent opens, tempering of the reaction occurs due to the cooling associated with the latent heat of vaporization. Such a system is also referred to as a high vapour pressure, or vapour pressure, system or a tempered system.

In a gas-generating system, by contrast, there is no high vapour pressure component, and the total pressure is that of the gaseous components. The reaction is not tempered and its course is essentially independent of the venting process. Such a system is also referred to as a gassy system or a non-tempered system.

The intermediate case is that of a hybrid system, and its behaviour is intermediate between that of a pure vapour pressure system and a pure gassy system. A degree of tempering occurs.

17.17.5 Vessel behaviour

The nature of the fluid which enters the vent depends on the flow regime in the vessel when the vent opens, and the vessel is depressurized. There are two flow regimes, the bubbly, or foaming, regime and the churn turbulent regime. In the former there is little vapour disengagement and the vapour–liquid mixture entering the vent line is essentially the same as that in the vessel itself. In the latter regime there is significant vapour disengagement.

Methods exist which allow an estimate to be made for vapour disengagement in systems with pure substances, but not in reacting systems.

In practice, therefore, for venting of a reaction mass it is generally necessary to fall back on the default assumption that there is no vapour disengagement and that the fluid entering the vent is a homogeneous two-phase vapour–liquid mixture.

A considerable amount of work was done, however, to increase understanding of liquid swell and vapour disengagement. An account of these aspects is given in Chapter 15.

17.17.6 Bench-scale equipment: apparatus

As already indicated, it is sometimes preferable to base the vent design on experimental tests. There are, however, certain pitfalls in scale-up from bench to full scale. A suitable design of test apparatus provides a safeguard against these. The design of such apparatus was another task undertaken in the DIERS project.

A low heat capacity test cell was designed with a capacity of 120 ml and a ϕ factor of about 1.05. As stated in Chapter 11, the ϕ factor is the ratio of the heat capacity of the sample plus cell to that of the sample alone, and a value close to unity means that the temperature rise measured is close to the actual temperature rise of the sample. This equipment is generally referred to as the bench-scale apparatus and is also known as the vent sizing Package (VSP). This apparatus is shown in Figure 17.48. It has been described by Fauske and Leung (1985) and Fauske (1988a).

Another apparatus, distinct from the VSP and developed later, is the reactive system screening tool (RSST), described

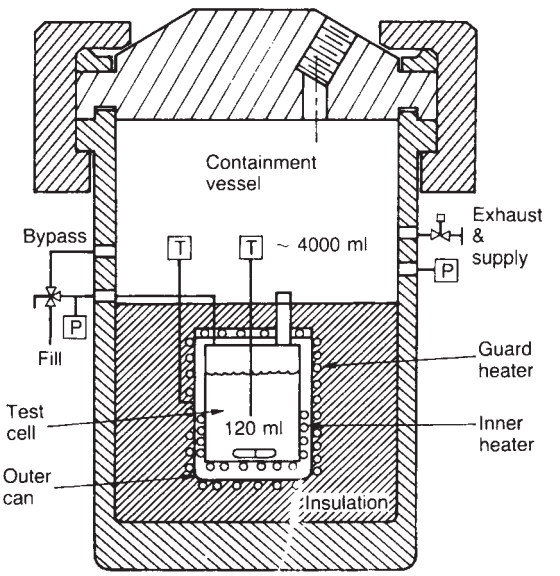

Figure 17.48 *Venting of chemical reactors: Vent Sizing Package (Fauske and Leung, 1985) (Courtesy of the American Institute of Chemical Engineers)*

by Creed and Fauske (1990). The RSST is a test cell with a capacity of about 10 ml and a ϕ factor of about 1.04. The authors state that the ease of use approaches that of DSC and the accuracy that of the VSP. The RSST may be used for the measurement of the rate of temperature rise, and hence the energy release rate in a vapour pressure system, or to determine the rate of pressure rise, and hence the gas evolution rate in a gassy system. It may also be used for direct scale-up.

17.17.6 Bench-scale equipment: application

For a vapour pressure system, it is necessary for vent sizing to know the rate of temperature rise, or self-heat rate, and hence the energy release rate. This may be measured using the VSP.

In addition, if the reaction mixture is highly viscous and the vent flow likely to be laminar, the apparatus may be used to determine the vent flow.

For a gassy system, the information required is the rate of pressure rise and hence the peak gas evolution rate. The VSP may be used to measure this. It may also be used to obtain the vent flow, though generally gassy systems are not particularly viscous.

These reaction parameters are then used in the appropriate vent sizing relationships.

Alternatively, the VSP may also be used to carry out direct scale-up.

The application of the bench scale equipment, and the relationships with which it is used, are described further in Section 17.19.

17.17.7 Vent flow models

A number of models for vent flow were developed by DIERS. These are given in the Technology Summary and have been described in papers by Fauske and co-workers. An account of these models is given in Section 17.18.

17.17.8 Vent area

DIERS developed methods for the sizing of vents for vapour pressure, gassy and hybrid systems. These are outlined in the Technology Summary and described by Fauske and co-workers. Section 17.19 gives an account of these methods.

In some cases it may be possible to use vent sizing correlations without resort to experimentation, but in other cases experimental work is essential.

17.17.9 Scale-up

The bench-scale equipment may be used to determine the vent area by vent area/reaction mass scaling using direct scaling relationships. This approach is to be distinguished from the use of the apparatus to determine parameters such as self-heat rate or gas evolution rate which are then utilized in vent sizing equations which require these parameters.

17.17.10 Numerical model

The DIERS project also involved the development of a numerical model of the venting of a reactor based on a full set of differential equations for the reaction kinetics and thermal and fluid flow effects. The model is essentially an unsteady-state heat balance with supporting equations. This model is referred to as the integral model and is the basis of the computer code SAFIRE described below. An account of the model has been given by Grolmes and Leung (1985).

17.17.11 SAFIRE code

The integral model is the core feature of the computer program SAFIRE (System Analysis for Integrated Relief Evaluation) developed as part of the project. This has been described by Grolmes and Leung (1985).

The program requires as input, data on the physical and thermodynamic properties of the mixture, the reaction stoichiometry and kinetics, the vessel and vent line geometry and selection of the flow model assumptions.

The vessel geometries handled are a vertical cylinder, a horizontal cylinder and a sphere. The vent entry location can be at the top or bottom of the vessel. The vent may be an effectively frictionless nozzle, a nozzle fitted with a safety relief valve or a vent line in which friction is significant. The latter may have a single segment, two segments with a change of cross-section or three segments with a safety relief valve followed by a change in cross-section.

Vessel flow regimes incorporated are all vapour, all liquid, homogeneous mixture and partial disengagement regimes. Vent line flow models are as follows. There are both all vapour flow and all liquid flow models. Nozzle models include the ERM, the homogeneous equilibrium flashing model and the frozen homogeneous model. For long vent lines the models are the homogeneous equilibrium model and the slip equilibrium model.

The program may be run in three modes: pre-relief, post-relief or combined.

The authors describe the use of the code to simulate a number of experimental tests on styrene and ethylbenzene.

17.17.12 Experimental tests

The DIERS programme included a series of experimental tests, both at laboratory scale and on a larger scale. An account of the larger scale tests in Phase III of the project has been given by Grolmes, Leung and Fauske (1985).

The test vessels used were a 32 l vessel and a 2200 l vessel. The latter had a 12,000 l catchtank.

A set of 70 tests were performed, including 25 with the larger vessel. Water was used in 15 tests with the smaller vessel and 20 tests with the larger one. Using ethylbenzene, four tests were performed in the smaller vessel and none in the larger, whilst using styrene 16 tests were done in the smaller vessel and five in the larger.

The configurations studied included both top and bottom vent locations and both nozzles and long vent lines.

The systems tested were all vapour pressure systems. The principal feature investigated in the tests was vapour disengagement. The work showed that vapour disengagement and the associated churn turbulent regime were confined to non-foaming and non-viscous systems.

17.17.13 Non-Arrhenius behaviour

The low heat capacity test cell was used to investigate a number of systems. One of the effects observed is noteworthy.

As described by Fauske (1985a), tests were performed on a 50/50 mixture of zinc peroxide/zinc oxide at two different heating rates. The test at the lower heating rate obeyed the classic Arrhenius relation between temperature and reaction rate as evidenced by the pressure rise, that at the higher heating rate did not, but gave a much sharper pressure rise, presumably due to a hot spot.

17.18 Venting of Reactors and Vessels: Vent Flow

A general account of two-phase flow models was given in Chapter 15. The account given here is confined to those models used for the venting of reactors and storage vessels.

There are a number of relations used in the DIERS work for the mass flux of fluid flowing out of the vent and down the vent line. Accounts are given by Fauske (1984b,c, 1985a), Grolmes and Leung (1985) and Leung (1986b) and in the Technology Summary.

Leung (1986b) has reviewed flow models for venting of a vapour pressure, or tempered, system. He considers frictionless flow and a short vent line ($L/D < 50$). The models include:

(1) the non-flashing liquid flow;
(2) the homogeneous equilibrium model;
(3) the equilibrium rate model;
(4) the homogeneous non-equilibrium model;
(5) the slip equilibrium model.

For a simple orifice in the side of a vessel the outflow may be determined by treating the fluid as a non-flashing liquid.

For other cases the homogeneous equilibrium model (HEM) is generally the most appropriate. It gives lower flows over the entire two-phase region and is to this extent conservative for ERS design. However, it is realistic rather than overly conservative and agrees well with experimental data. The original HEM model is somewhat complex and requires extensive thermodynamic data, but a more convenient version requiring only stagnation properties has been developed by Leung (1986a).

An alternative model is the equilibrium rate model (ERM) of Fauske (1985b), who has developed the model to deal with a number of different situations.

For the all-liquid inlet condition, Leung has given a version of his approximate HEM model which is similar in form to the ERM model, as described below.

The equilibrium condition is closely approached for pipes longer than 0.1 m. Where the vent line is shorter than this, the homogeneous non-equilibrium model of R.E. Henry and Fauske (1971), the HFM model, may be used to estimate the flow.

Leung also discusses the use of the slip equilibrium model (SEM) of F.J. Moody (1965).

Some of the principal flow models are now described. An account of those used in the DIERS work is given in the Technology Summary.

17.18.1 Vapour pressure systems

A family of flow models for venting of vapour pressure systems has been described by Fauske (1984a,b, 1985a,b) in the context of DIERS, in particular the ERM. The base case is choked non-equilibrium flashing frictionless flow. For this case Fauske gives

$$G \approx \frac{h_{fg}}{v_{fg}} \left(\frac{1}{NTC} \right)^{1/2} \qquad [17.18.1]$$

with the dimensionless quantity N:

$$N \approx \frac{h_{fg}^2}{2\Delta P\, \rho_l K^2 v_{fg}^2 TC} + 10L \qquad [17.18.2]$$

where K is the discharge coefficient, L is the length of the vent pipe (m), ΔP is the total available pressure drop (Pa), T is the absolute temperature (K), ρ_l is the density of the liquid (kg/m^3) and N is a non-equilibrium parameter. For a sharp-edged orifice K is 0.61 and C is the system heat capacity.

For no vent line ($L = 0$) Equation 17.18.1 reduces to

$$G = K(2\Delta P_{\rho l})^{1/2} \qquad [17.18.3]$$

For a vent line long enough for equilibrium conditions to apply ($L \geq 0.1$ m) the parameter N is unity, and Equation 17.18.1 becomes

$$G = \frac{h_{fg}}{v_{fg}} \left(\frac{1}{TC} \right)^{1/2} \qquad [17.18.4]$$

There is an alternative formulation of Equation 17.18.4 based on the relation between vapour pressure P and temperature T:

$$G = \frac{dP}{dT} \left(\frac{T}{C} \right)^{1/2} \qquad [17.18.5]$$

Equation 17.18.5 implies

$$\left(\frac{dP}{dT} \right)^2 \frac{T}{C} = \left(\frac{h_{fg}}{v_{fg}} \right)^2 \frac{1}{TC} \qquad [17.18.6]$$

Equations 17.18.4 and 17.18.5 are the ERM. For venting the rate of change of pressure with temperature is $\Delta P/\Delta T$. In Fauske's work for this model the mass flux is frequently written as G_{ERM} so that

$$G_{ERM} = \frac{\Delta P}{\Delta T} \left(\frac{T}{C} \right)^{1/2} \qquad [17.18.7]$$

where ΔP is the overpressure (Pa) and ΔT is the temperature rise corresponding to overpressure ΔP (°C). Further, it is assumed in the model that the flow is turbulent. Where this aspect is emphasized the mass velocity is written as G_T so that

$$G_T = \frac{\Delta P}{\Delta T} \left(\frac{T}{C} \right)^{1/2} \qquad [17.18.8]$$

Equation 17.18.8 is used where there is homogeneous equilibrium flow, there is a moderate overpressure (≈20%) and the flow is turbulent.

Normally the vent line will be long enough for equilibrium flow to be assured. For the case where there is a very short vent line ($0 < L < 0.1$ m), the mass flow may be obtained by interpolation between Equations 17.18.3 and 17.18.8.

For a long vent line Fauske (1989a) introduces into Equation 17.18.8 a correction factor F to give

$$G_T = F \frac{\Delta P}{\Delta T} \left(\frac{T}{C} \right)^{1/2} \qquad [17.18.9]$$

with

$$F = f(L/D) \qquad [17.18.10]$$

where D is the diameter of the vent line (m) and F is a correction factor for vent line length.

The flow correction factor F is a function of the length/diameter ratio L/D. Slightly different correlations have been given in different papers. That currently used for

vapour pressure systems is that given by Fauske, Grolmes and Clare (1989), and is:

L/D	F
0	1.0
50	0.8
100	0.7
200	0.6
300	0.55
400	0.5

The original values of F were 0.85, 0.75, 0.65 and 0.55 at L/D ratios of 50, 100, 200 and 400, respectively (Fauske, 1989a).

If the flow is highly viscous, it may be laminar. The relation given by Fauske (1987b, 1989a) for the mass velocity G_L for this case is

$$G_L \approx \left(\frac{h_{fg}}{v_{fg}}\right)^2 \frac{1}{TC}\frac{1}{32\mu} D \frac{D}{L} \quad [17.18.11]$$

$$= \left(\frac{dP}{dT}\right)^2 \frac{T}{C}\frac{1}{32\mu} D \frac{D}{L} \quad [17.18.12]$$

where D is the diameter of the vent line (m) and μ is the viscosity (kg/ms).

In practice the liquid viscosity for the reaction mixture is generally not known. In this case, therefore, the bench-scale apparatus may be used to determine the mass flow. Relations for this case are given by Fauske (1989a) in terms of the required vent diameter and are therefore described in Section 17.19.

17.18.2 Gassy systems

For gassy systems one DIERS approach is to utilize the bench-scale apparatus to determine the flow.

Leung and Fauske (1987) have used for such systems the method of Tangren, Dodge and Seifert (1949). Leung (1992b) has also given a method of his own.

Fauske (1985a) gives as a reasonable upper bound for the mass velocity the relation

$$G = [2(P_s - P_a)\rho_l(1-\alpha)]^{1/2} \quad [17.18.13]$$

where P_a is the atmospheric pressure (Pa), P_s is the set pressure (Pa) and α is the initial vapour fraction. Equation 17.18.13 is suitable for use where some overestimation of flow may be acceptable such as in sizing of the relief equipment.

17.18.3 Hybrid systems

For hybrid systems there is again no entirely satisfactory flow relation, and one DIERS approach is to utilize the bench-scale apparatus to determine the flow.

For a hybrid system Fauske (1985b) gives the following approximate relations:

$$G \approx (2P_{g\rho_l} + G_{ERM}^2)^{1/2} \quad [17.18.14]$$

with

$$G_{ERM} \approx \frac{P_v}{P}\frac{dP}{dT}\left(\frac{T}{C}\right)^{1/2} \quad [17.18.15]$$

$$P = P_v + P_g \quad [17.18.16]$$

where P_g is the partial pressure of the gas (Pa) and P_v is the partial pressure of the vapour (Pa).

17.18.4 Storage vessels

For flow of a flashing liquid from the liquid space of a storage vessel, Fauske (1985b) distinguishes between a saturated liquid and a subcooled liquid. For a saturated liquid he gives

$$G = 0.6[2(P_o - P_a)\rho_l]^{1/2}, \quad L = 0 \quad [17.18.17]$$

$$G_{ERM} = \frac{\Delta P}{\Delta T}\left(\frac{T}{C}\right)^{1/2}, \quad L > 0.1\ \text{m} \quad [17.18.18]$$

where P_o is the absolute stagnation pressure (Pa). For a subcooled liquid Fauske gives

$$G = 0.6[2(P_o - P_a)\rho_l]^{1/2}, \quad L = 0 \quad [17.18.19]$$

$$G = [2(P_o - P(T_o))\rho_l + G_{ERM}^2]^{1/2}, \quad L > 0.1\ \text{m} \quad [17.18.20]$$

where T_o is the absolute stagnation temperature (K).

17.18.5 Vapour pressure systems: homogeneous equilibrium model

The family of flow relations given above is that of Fauske and the principal model is the ERM. An alternative model for equilibrium flow is the HEM.

This model has been formulated in convenient form by Leung (1986b), who gives the following relations. For the high and low quality regions, respectively, the equations are

$$\frac{G}{(P/v)^{1/2}} = \frac{0.66}{\omega^{0.39}}, \quad \omega < 4.0 \quad [17.18.21a]$$

$$\frac{G}{(P/v)^{1/2}} = \frac{0.6055 + 0.1356\ln\omega - 0.0131(\ln\omega)^2}{\omega^{0.5}}, \quad \omega \geq 4.0 \quad [17.18.21b]$$

with

$$\omega = \frac{xv_{fg}}{v} + \frac{CTP}{v}\left(\frac{v_{fg}}{h_{fg}}\right)^2 \quad [17.18.22]$$

$$v = v_f + xv_{fg} \quad [17.18.23]$$

where P is the pressure (Pa), v is the specific volume of the mixture (m^3/kg) and ω is the critical flow scaling parameter.

For an all liquid inlet flow, Equation 17.18.21 may be approximated by

$$G \approx 0.9\frac{h_{fg}}{v_{fg}}\left(\frac{1}{TC}\right)^{1/2} \quad [17.18.24]$$

This equation is similar in form to Equation 17.18.4 except for the factor 0.9. The flow given by it is termed by Grolmes and Leung (1984) the limiting flow.

Leung (1986b) has given a set of models for vent sizing for vapour pressure systems, which is described in Section 17.20. These models are independent of the expression used for the mass velocity G, but the flow model quoted in that account is the HEM as just outlined.

17.19 Venting of Reactors and Vessels: Vent Sizing

Some of the methods available for vent sizing prior to the DIERS project were described in Section 17.16. An account is now given of methods developed in DIERS.

The bench-scale apparatus used in some of the methods is described in Section 17.17.

17.19.1 Vapour pressure systems

For a vapour pressure system, it is necessary to know the self-heat rate. One option for obtaining this is the use of the bench-scale apparatus. But it may be possible to determine it without resort to experiment.

Given the self-heat rate, the following simplified method has been described by Fauske (1984b) for the vent area:

$$A = \frac{V_\rho}{G\Delta t_v} \qquad [17.19.1]$$

with

$$\Delta t_v = \frac{\Delta TC}{q_s} \qquad [17.19.2]$$

where q_s is the energy release rate at the set pressure (kW/kg), Δt_v is the venting time (s) and ρ is the density of the reaction mass (kg/m^3).

Combining Equations 17.19.1 and 17.19.2 with Equation 17.18.7 gives

$$A = V_\rho (TC)^{-1/2} \frac{q_s}{\Delta P} \qquad [17.19.3]$$

Equations 17.18.7 and 17.19.3 are based on the assumption that the flow in the vent line is homogeneous equilibrium flow and that it is turbulent and intended for use where there is a modest overpressure in the range 10–30%, say 20%.

For a frictionless vent line, Equation 17.19.3 predicts a vent area larger by a factor of less than 2 than that given by the integral model, assuming homogeneous vessel behaviour and homogeneous equilibrium flow.

The mass flow is relatively insensitive to the length/diameter ratio L/D. It varies by less than a factor of 2 for L/D up to 400. Most vent lines are 5–10 m in length.

17.19.2 Vapour pressure systems: high viscosity systems

For a high viscosity system, the flow in the vent line is likely to be laminar. The bench-scale apparatus may be used to determine an actual flow. Then, as described by Fauske (1989), the diameter of the full scale vent line may be obtained from the relations

$$D_L = D_T \quad G_o(D_T/D_o) \geq G_T \qquad [17.19.4a]$$

$$\approx \left(D_T^2 D_o \frac{G_T}{G_o}\right)^{1/3} \quad G_o(D_T/D_o) < G_T \qquad [17.19.4b]$$

where D_L is the diameter of the full scale vent line for laminar flow (m), D_o is the diameter of the vent line in the bench-scale apparatus (m), D_T is the diameter of the full-scale vent line for turbulent flow (m), G_o is the mass velocity in the bench-scale apparatus (kg/m^{2}s), G_T is the mass velocity at full scale in turbulent flow (kg/m^{2}s).

According to the Technology Summary, viscous effects on level swell are generally not important if the liquid viscosity is below 100 kPa s.

17.19.3 Vapour pressure systems: Fauske nomograph

For a vapour pressure system, a generalized vent sizing nomograph based on Equation 17.19.3 was published in 1984 by Fauske (1984a). A revised nomograph, given below, was published in 1988.

This initial nomograph was based on the assumptions of turbulent flow and a modest overpressure.

Fauske (1984a) has compared the nomograph method with some of the earlier methods of vent sizing described above. He considers three different duties, one for the Monsanto method, one for the BPF and Huff methods, and one for the SAFIRE method. His results may be summarized as follows:

Method	*Vent area* (m^2) *from:*	
	Method named	*Nomograph*
Monsanto	Area = 0.0125 m^2/1000 kg	Area = 0.012 m^2/1000 kg
BPF	Area = 0.026 m^2/1000 kg	Area = 0.0145 m^2/1000 kg
Huff code	Diameter = 33.7 cm	Diameter 34 cm
SAFIRE code	Diameter = 15.8 cm ($L/D \approx 100$) = 18 cm ($L/D \approx 400$)	Diameter $\approx$ 18.5 cm

17.19.4 Vapour pressure systems: revised Fauske nomograph

A revised method for vapour pressure systems, and an associated nomograph, have been given by Fauske, Grolmes and Clare (1989). The relation given for the vent area is

$$A = \frac{5}{2} \frac{Q_v}{F(TC)^{1/2} P_s} \frac{\alpha_d - \alpha_o}{1 - \alpha_o} \qquad [17.19.5]$$

where α is the void fraction and the subscripts d and o denote the disengagement and initial, or freeboard, value, respectively.

The flow reduction factor F used in Equation 17.19.5 is given in Table 17.19, column 1.

Figure 17.49 is a nomograph based on Equation 17.19.5. The nomograph is for the following conditions: C = 2500 J/kg K, T = 400, α_d = 1 and L/D = 0. It is therefore applicable to the case of no vapour disengagement.

17.19.5 Vapour pressure systems: extended method for vapour disengagement

As described by Grolmes, Leung and Fauske (1983), interpretation of the DIERS data has shown that during two-phase venting relatively large deviations in the equilibrium between the vapour and the liquid may exist.

The implications are discussed by Fauske (1989a). It is virtually impossible to predict the vapour/liquid ratio entering the vent line. The absence of equilibrium means that following actuation of the relief the temperature continues to rise, but without a corresponding overpressure. In

due course a 'turnaround', or 'turnover', of temperature occurs.

Fauske states that in most practical systems there is likely to be only modest superheating (10–20°C) and that temperature turnaround should be assured before the onset of vapour disengagement. The rate of loss of reaction mass can be assumed to be largely independent of the vapour/liquid ratio of the mixture entering the vent line.

On these assumptions, an extension of the method was developed which takes into account vapour disengagement, as described by Fauske (1987a,b). The extension requires information on the self-heat rate. The relation given for the vent area, assuming turbulent flow, is

$$A = \frac{1}{2}\frac{m_o(dT/dt)_s(\alpha_d - \alpha_o)}{F(T/C)^{1/2}\Delta P(1-\alpha_o)}, \quad 0.1 \le \frac{\Delta P}{P_s} \le 0.3 \qquad [17.19.6]$$

where ΔP is the overpressure (Pa).

The loss of reaction mass at time of turnaround, given by Fauske (1988a, 1989a), is

$$G \approx \frac{1}{A\Delta t_v} m_o \frac{\alpha_d - \alpha_o}{1-\alpha_o} \qquad [17.19.7]$$

where Δt_v is the time to temperature turnaround (s), given by

$$\Delta t_v \approx \frac{2\Delta T}{(dT/dt_s)} \qquad [17.19.8]$$

Table 17.19 *Venting Chemical reactors: flow reduction factor F in Fauske vent sizing correlations (Fauske, Grolmes and Clare, 1989) (Courtesy of American Institute of Chemical Engineers)*

L/D	*All vapour flow* I	*Vapour pressure system, two-phase flashing flow* II	*Gassy system, two-phase non-flashing flow* III
0	1.0	1.0	1.0
50	0.8	0.8	0.71
100	0.7	0.7	0.58
150	0.65	0.65	0.50
200	0.60	0.60	0.45
250	0.58	0.58	0.41
300	0.55	0.55	0.38
350	0.52	0.52	0.35
400	0.50	0.50	0.33

17.19.6 Gassy systems

For gassy systems, it is necessary to know the peak gas generation rate. It is usually necessary to use the bench-scale apparatus to obtain this.

Then, as given in the Technology Summary (Equation 2.4) the vent area is

$$A = \frac{Q_g(1-\alpha)\rho_l}{G} \qquad [17.19.9]$$

$$= \frac{Q_g m}{GV} \qquad [17.19.10]$$

where m is the mass of mixture in the vessel (kg) and Q_g is the peak volumetric gas evolution rate (m^3/s).

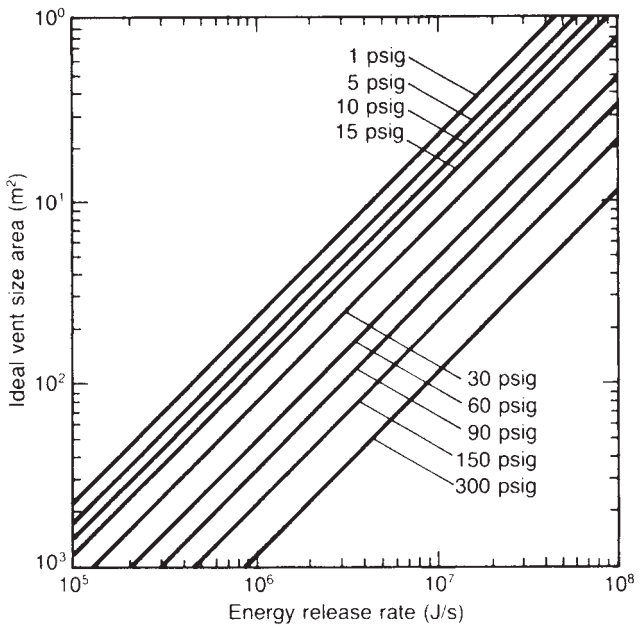

Figure 17.49 *Venting of chemical reactors: nomograph for vent sizing for a vapour pressure system (Fauske, Gmimes and Clare, 1989) (Courtesy of the American Institute of Chemical Engineers)*

17.19.7 Gassy systems: Fauske nomograph

A method for gassy systems, and an associated nomograph, have been given by Fauske, Grolmes and Clare (1989). The relation given for the vent area is

$$A = \left(\frac{1}{2}\right)^{1/2} \frac{Q_g}{F} \left(\frac{\rho_l}{P - P_a}\right)^{1/2} \qquad [17.19.11]$$

where P is the absolute pressure (Pa) and P_a is the absolute atmospheric pressure (Pa). (In the authors' paper the term $P - P_a$ is written as P where the latter is a gauge pressure.)

The flow reduction factor F for use in Equation 17.19.11 is given in Table 17.19, column 3.

Figure 17.50 is a nomograph based on Equation 17.19.11. The nomograph is for the following conditions: $\rho_l = 1000\ \text{kg/m}^3$ and $L/D = 0$.

17.19.8 Hybrid systems

For hybrid systems, the situation is more complex. The behaviour of the system depends on whether it is tempered or non-tempered.

Untempered hybrid systems have generally to be treated as gassy systems.

A relation for the vent area at initiation of homogeneous two-phase venting, reflecting the worst case, is given in the Technology Summary (Equation 2.5) as follows:

$$A = \frac{(Q_g + Q_v)_{\rho_l}(1 - \alpha)}{G} \qquad [17.19.12]$$

where Q_g is the peak volumetric gas evolution rate (m^3/s) and Q_v is the peak volumetric vapour evolution rate (m^3/s).

Tempered hybrid systems may be treated as tempered systems, provided it is assured that the system really is tempered and will continue to be so until the reaction is complete.

Effective tempering can occur well before the peak volume generation rate.

Leung and Fauske (1987) have described the application of Leung's method to a tempered hybrid system.

17.19.9 Bench-scale equipment

As already described, the bench-scale equipment may be used in three different ways: (1) to determine the required flow, (2) to determine the parameters for the calculation of flow, and (3) to effect direct scale-up.

There are certain pitfalls in the use of bench-scale apparatus. These are described in the accounts given by Fauske and co-workers together with the precautions necessary to avoid them (Fauske, 1984a, 1985a).

The inaccuracies due to high thermal inertia, or ϕ value, are minimized in the DIERS apparatus by its design.

The viscosity of the reaction mass is often not known and the possibility may exist that the vent flow will be not turbulent but laminar. This can be checked by measuring the vent flow in the bench-scale test.

An important feature for both vapour pressure and gassy systems is the effect of reactor height, since the superficial velocity is a function of height and is therefore much larger at the full scale than at bench-scale.

There is a possibility that with vapour pressure systems the volumetric vent flow may be high at bench-scale because the flow is all vapour rather than two-phase and/or because it is non-equilibrium due to insufficient relaxation length.

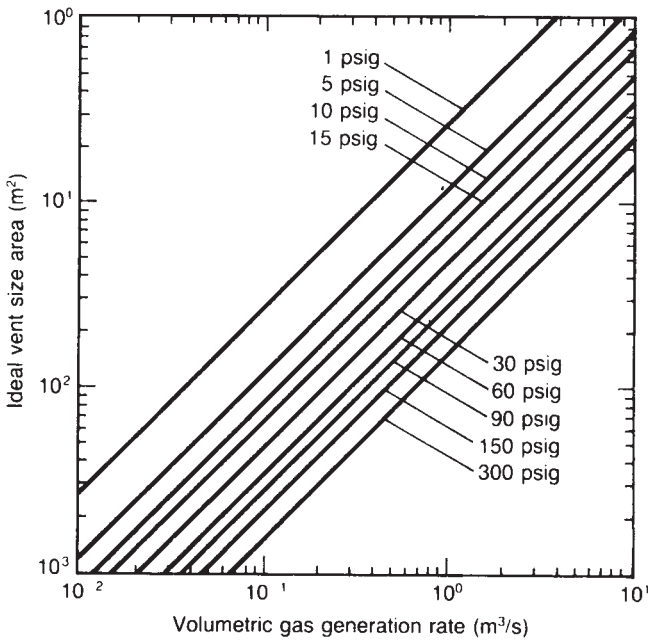

Figure 17.50 *Venting of chemical reactors: nomograph for vent sizing for a gassy system (Fauske, Grolmes and Clare, 1989) (Courtesy of the American Institute of Chemical Engineers)*

With a vapour pressure or hybrid tempered system it is necessary to ensure that the system remains tempered throughout by running the reaction to term. It is also necessary to confirm that there are no further reaction exotherms.

17.19.10 Direct scale-up

A method for direct scale-up from the bench-scale apparatus, applicable only to vapour pressure systems, has been described by Fauske (1984c). An experiment is performed with bottom venting and with a vent line long enough to ensure equilibrium flow ($L > 0.1$ m) and the adiabatic rise time Δt_A and vessel emptying time Δt_E are determined. The vent area of the full scale reactor is then obtained as

$$A_{LS} = A_T \frac{\Delta t_E}{\Delta t_A} \frac{V_{LS}}{V_T} \qquad [17.19.13]$$

where A is the vent area (m^2), Δt_A is the measured adiabatic rise time (s), Δt_E is the measured vessel emptying time (s) and the subscripts LS and T denote large scale and test, respectively.

For gassy systems Fauske (1985a) states that use of top venting on the bench-scale apparatus and direct scale-up on a vent area/reactor volume basis is suitable.

17.19.11 Validation

The DIERS project and the subsequent work have included a number of validation exercises.

The Technology Summary describes the validation of the method for vapour pressure systems against incidents described by Burchett (1980) and a large-scale styrene/ethylbenzene test.

The Burchett incidents involved runaways of chloroprene reactions. The first was in a 11,355 litre vessel with a 0.010 m bursting disc set at 0.3 MPa and an equivalent-sized vent pipe, which vented safely. The second incident was in a 7570 litre vessel with a bursting disc of the same size, but set at 0.61 MPa, which resulted in vessel rupture. On the assumption of churn turbulent flow it is predicted that both vessels should vent safely, whilst on the assumption of homogeneous venting (homogeneous vessel behaviour and homogeneous equilibrium vent flow), the prediction is that the first vessel would vent safely but that the second would not, which is what happened.

These incidents are also treated by Fauske (1984c).

The method for vapour pressure systems has also been compared by Fauske (1984a) with the results from a number of methods, as described in Section 17.19.2.

Test data for some 55 systems, tempered and non-tempered, have been given by Leung and Fauske (1987). They give comparisons with the vent area predicted by the FIA method.

Fauske (1989a) gives some experimental data obtained on both bench-scale and large scale equipment, as shown in Table 17.20. The table shows the measured mass velocities together with the values obtained by calculation from Equation 17.18.12 and by scale-up.

Kirch, Magee and Stuper (1990) compare the DIERS method with a method used by their company based on scale-up using a constant ratio of the vent area to the charge volume.

17.19.12 Illustrative examples

A variety of illustrative examples are given in the Technology Summary and by Fauske and co-workers.

The main examples in the Technology Summary are in Appendix D, which gives calculations for determination of the flow regime into the vent and of the mass velocity with homogeneous flow and with partial vapour disengagement for a nozzle vent and for a long line vent.

Leung (1986b) gives two examples: one is the styrene polymerization described by Huff (1982b) and the other a phenolic reaction described by the BPF (1979) and Booth *et al.* (1980).

Leung and Fauske (1987) deal with the following types of system: type Ia, a vapour pressure, tempered system; type Ib, a gassy tempered system and type II a non-tempered system. These are illustrated by a phenol–formaldehyde reaction, a hydrogen peroxide reaction and a hypothetical gassy reaction, respectively. They give illustrative examples for all three cases.

Examples illustrating the application of the methods to check existing plant are given by Fauske (1988a), who deals with a vapour pressure system for three cases: (1) without vapour disengagement, (2) with disengagement, and (3) check for potential viscosity effect (none found).

Fauske and Leung (1985) describe a study of the reaction runaway for an 80% styrene/20% ethylbenzene reaction which combines elements of validation and illustration. This system is a vapour pressure system and is foamy. The mass velocity was calculated from Equation 17.18.5, which requires no experimental data. The vent area was obtained from the model of Leung, Equation 17.20.18 with its supporting Equation 17.20.19, described below. This requires the self-heat rates at the set and turnaround temperatures. The bench-scale apparatus was used to obtain these self-heat rates. It was also used to check the mass velocity determined from Equation 17.18.5. This agreed within 10%

Table 17.20 *Venting of chemical reactors: some experimental data, bench-scale and large scale, on the venting of runaway reactions of polystyrene/ethylbenzene (Fauske, 1989a) (Courtesy of American Institute of Chemical Engineers)*

Vent diameter (m)	*Vent length/ vent diameter*	*Stagnation conditions*				*Mass velocity* (kg/m^2s)		
		Pressure (Pa)	*Temperature* (K)	$\Delta P/\Delta T$ (Pa/°C)	*Viscosity* (kg/ms)	*Measured*	*Calculated*[a]	*Scaled up*
0.0525	100	5.8×10^5	498	11.35×10^5	0.45	1296	974	1258
0.0525	175	5.3×10^5	493	10.58×10^5	0.50	407	496	452
0.00457	100	5.1×10^5	480	10.14×10^5	0.55	71	55	
0.00457	175	5.03×10^5	490	10.14×10^5	0.55	33	31	

[a] Equation 17.18.12.

Table 17.21 *Venting of chemical reactors: illustrative calculation of vent sizing for reactor with vapour pressure system (after Fauske and Leung, 1985) (Courtesy of American Institute of Chemical Engineers)*

A Scenario

Liquid specific head $C = 2520$ kJ/kg K
Initial reaction mass $m_o = 5000$ kg
Reactor volume $V = 7.78\ m^3$
Set pressure $P_s = 5.15 \times 10^5$ Pa
Set temperature $T_s = 491$ K
$dP/dT = 8246$ Pa/K
$(dT/dt)_s = 0.25°C/s$
$(dT/dt)_m = 0.33°C/s$
Mass velocity $G = 3640\ kg/m^2$, s

B Vent sizing

Using Equation 17.20.19:

$$q = \tfrac{1}{2}2520(0.25 + 0.33) = 0.735\ kW/kg$$

Using Equation 17.20.18

$$A = \frac{5000 \times 735}{3640\left[([7.78/5000](491 \times 8546)^{1/2} + (2520 \times 11.6)^{1/2}\right]^2} = 0.016\ m^2$$

confirming the validity of Equation 17.18.5 which assumes turbulent flow.

Estimates of vent size were made for a range of overpressures using Equation 17.20.18. Estimates were also made using SAFIRE. There was excellent agreement between the two.

Table 17.21 shows the calculations given by the authors for the vent area using Equation 17.20.18 for this case.

In addition, a kinetic model for this reaction, given by Husain and Hamilec (1978), was used to predict the temperature and pressure profiles of the reaction. The predictions agreed well with the profiles measured in the bench-scale apparatus.

17.19.13 Safety factors

Whatever method of vent sizing is used, a safety factor should be applied, having regard to the accuracy of the method itself and of the data used.

There is relatively little guidance given on this by Fauske and co-workers or by DIERS, but the problem has been discussed by Duxbury and Wilday (1990). These authors describe several methods for vent sizing and mention certain safety factors. The safety factor to be applied is specific to the particular method and in each case the safety factor should be applied before a choice is made between the methods.

Safety factors are discussed further in Section 17.21 and Appendix 13.

17.20 Venting of Reactors and Vessels: Leung Model

Another model for vent sizing both of reactors and of storage vessels which has found wide acceptance has been given by Leung (1986b).

The model gives relations for vent sizing. The equations for vent area contain the vent flow mass velocity, but the model may be regarded as independent of the vent flow correlation used. The author does, however, state his own homogeneous equilibrium model (Leung, 1986a).

The model applies to vapour pressure systems, which give the tempering effect. It includes relations for the following cases:

(1) reactors
  (a) homogeneous venting,
  (b) all vapour or all liquid venting;
(2) storage vessels
  (a) homogeneous venting,
  (b) all vapour or all liquid venting.

The basic relations of the model and the treatments of these cases are now described.

17.20.1 Elementary relations

The unsteady-state mass and energy balances for the vessel, reactor or storage vessel are

$$\frac{d(\rho V)}{dt} = -W \qquad [17.20.1]$$

$$\frac{d(\rho V u)}{dt} = Q - W\left(u_1 + \frac{P}{\rho_1}\right) \qquad [17.20.2]$$

where P is the absolute pressure, Q is the heat generation or input rate, T is the absolute temperature, u is the specific internal energy, V is the volume of the vessel, W is the mass flow from the vessel, ρ is the density and the subscript 1 denotes vent inlet. Combining Equations 17.20.1 and 17.20.2 leads to

$$\rho V \frac{du}{dt} = Q - W\left(u_1 - u + \frac{P}{\rho_1}\right) \qquad [17.20.3]$$

But

$$m = \rho V \qquad [17.20.4]$$

$$\rho = 1/v \qquad [17.20.5]$$

$$v = v_f + x v_{fg} \qquad [17.20.6]$$

$$u = u_f + x u_{fg} \qquad [17.20.7]$$

$$h = u + Pv \qquad [17.20.8]$$

where h is the specific enthalpy, h_{fg} is the latent heat of vaporization, m is the mass of material in the vessel, x is the mass fraction of the vapour, or quality, and the subscript f denotes liquid and fg liquid–vapour transition. Then, from Equations 17.20.3 and 17.20.4–17.20.8

$$m\left(\frac{du_f}{dT} + x\frac{du_{fg}}{dT}\right)\frac{dT}{dt} = Q - W[(x_1 - x)u_{fg} + Pv_1] - m u_{fg}\frac{dx}{dt} \qquad [17.20.9]$$

Noting that $dV/dt = 0$, Equation 17.20.1 may be expressed as

$$\frac{dm}{dt} = -w \qquad [17.20.10]$$

With constant phase properties Equation 17.20.10 becomes

$$\frac{dx}{dt} = \frac{Wv}{mv_{fg}} \quad [17.20.11]$$

For an ideal gas and a nearly full vessel a practical approximation is obtained by reformulating the left-hand side of Equation 17.20.9 to give

$$mx\left\{(C_{pg} - R) + (1-x)\left[C_{pf} - T\left(\frac{dv_f}{dT}\right)\left(\frac{dP}{dT}\right)\right]\right\}\frac{dT}{dt} = Q - W[(x_1 - x)u_{fg} + P_{V_1}] - mu_{fg}\frac{dx}{dt} \quad [17.20.12]$$

where C_{pf} is the specific heat at constant pressure of the liquid, C_{pg} is the specific heat at constant pressure of the vapour and R is the gas constant. Then, from Equations 17.20.11 and 17.20.12

$$mC\frac{dT}{dt} = Q - Wh_{fg}\left(x_1 + \frac{v_f}{v_{fg}}\right) \quad [17.20.13]$$

where C is the specific heat at constant volume of the liquid, the assumption being made that $C_{pf} \approx C_{vf} \approx C$.

Equation 17.20.13 is used to derive expressions for the vent area for the specific cases.

The vent area is given by the relation

$$W = GA \quad [17.20.14]$$

where A is the area of the vent and G is the mass velocity of the vent flow.

17.20.2 Reactor venting: homogeneous venting

For a reactor with homogeneous venting

$$x_1 = x \quad [17.20.15]$$

$$v_1 = v = V/m \quad [17.20.16]$$

Hence, Equation 17.20.13 becomes

$$mC\frac{dt}{dt} = mq - GA\frac{V}{m}\frac{h_{fg}}{v_{fg}} \quad [17.20.17]$$

where q is the heat release rate per unit mass.

On certain assumptions and utilizing Equations 17.20.1 and 17.20.14, Equation 17.20.17 can be integrated to yield

$$A = \frac{m_o q}{G\left[\left(\frac{V}{m_o}\frac{h_{fg}}{v_{fg}}\right)^{1/2} + (C\Delta T)^{1/2}\right]^2} \quad [17.20.18]$$

with arbitrary average

$$q = \frac{1}{2}C\left[\left(\frac{dT}{dt}\right)_s + \left(\frac{dT}{dt}\right)_m\right] \quad [17.20.19]$$

where m_o is the initial mass in the vessel and the subscripts m and s denote peak pressure or temperature and relief set pressure, respectively. For zero overpressure, Equation 17.20.18 reduces to

$$A_o = \frac{m_o q_s v_{fg}}{Gvh_{fg}} \quad [17.20.20]$$

where A_o is the area of the vent for zero overpressure.

17.20.3 Reactor venting: all vapour or all liquid venting

For a reactor with all vapour or all liquid venting

$$v_i = v_g \quad \text{all vapour venting} \quad [17.20.21]$$

$$= v_f \quad \text{all liquid venting} \quad [17.20.22]$$

where the subscript i denotes phase (either g or f). Hence Equation 17.20.13 becomes

$$mC\frac{dT}{dt} = mq - GAv_i\frac{h_{fg}}{v_{fg}} \quad [17.20.23]$$

This equation can be integrated to give

$$T_m - T_s = \frac{m_o q}{GAC}\left(1 - \frac{A}{A_o}\right) + \frac{v_i h_{fg}}{v_{fg}C}\ln\left(\frac{A}{A_o}\right) \quad [17.20.24]$$

with

$$A_o = \frac{m_o q_s v_{fg}}{Gv_i h_{fg}} \quad [17.20.25]$$

For zero overpressure, Equation 17.20.24 reduces to the correct limit with $A = A_o$.

17.20.4 Storage vessel venting: homogeneous venting

For a storage vessel with homogeneous venting

$$Q = Q_T \quad [17.20.26]$$

where Q_T is the total heat input. Hence, Equation 17.20.13 becomes

$$mC\frac{dT}{dt} = Q_T - GA\frac{V}{m}\frac{h_{fg}}{v_{fg}} \quad [17.20.27]$$

This equation can be integrated to give

$$T_m - T_s = \frac{Q_T}{GAC}\left[\ln\left(\frac{m_o}{V}\frac{Q_T}{GA}\frac{v_{fg}}{h_{fg}}\right) - 1\right] + \frac{Vh_{fg}}{m_o C v_{fg}} \quad [17.20.28]$$

For zero overpressure, Equation 17.20.28 reduces to the correct limit

$$A_o = \frac{Q_T m_o v_{fg}}{GVh_{fg}} \quad [17.20.29]$$

A comparison of the reactor and storage vessel cases may be made by setting $Q_T = m_o q$ and $v = V/m_o$. Equations 17.20.20 and 17.20.29 are then equivalent.

Leung refers to the work of Forest (1985), who has given a relationship which is equivalent to, but differs slightly

in form from, Equation 17.20.29 and which has found application to the fire exposure of storage vessels.

17.20.5 Storage vessel venting: all vapour or all liquid venting

For a storage vessel with all vapour or all liquid venting, utilizing again $v_i = v_g$ and $v_i = v_f$ for the two cases, respectively, Equation 17.20.13 becomes

$$mC\frac{dT}{dt} = Q_T - GAv_i\frac{h_{fg}}{v_{fg}} \qquad [17.20.30]$$

For all vapour venting, it is assumed that the design is for no overpressure. The right-hand side of Equation 17.20.30 is set to zero to yield

$$A_o = \frac{Q_T v_{fg}}{G v_g h_{fg}} \qquad [17.20.31]$$

For all liquid venting, it is assumed that temperature turnaround occurs at a point where the vessel contains 10% of its initial inventory. Equation 17.20.30 can then be integrated to yield

$$A = \frac{Q_T}{G\left(v_f\frac{h_{fg}}{v_{fg}} + \frac{C\Delta T}{e}\right)} \qquad [17.20.32]$$

where e is the base of natural logarithms (= 2.303). For zero overpressure, Equation 17.20.32 reduces to

$$A_o = \frac{Q_T v_{fg}}{G_{v_g} h_{fg}} \qquad [17.20.33]$$

17.20.6 Illustrative examples

Leung gives illustrations of the effect of these different assumptions on the vent areas required for venting of reactors and storage vessels. His results are shown in Figure 17.51. Figure 17.51(a) shows an example for a reactor with a phenolic reaction and Figure 17.51(b) one for an LPG storage vessel.

17.21 Venting of Reactors and Vessels: ICI Scheme

Accounts of the approach to vent sizing for reactors used in ICI have been given by Duxbury and Wilday (1987, 1989, 1990). These provide a useful insight into the way in which one company has integrated the DIERS methods with other methods. The description given here is based unless otherwise stated on the most recent paper. The basic notation is the same as that used in Section 17.20.

17.21.1 Set pressure and overpressure

An effective, or redefined, set pressure is defined as the pressure at which the relief device is known to be fully open. For a bursting disc this will correspond to the nominal set pressure plus any tolerances or to the maximum specified bursting pressure. For a safety valve the redefined set pressure will often be 10% above the nominal set pressure. Similarly, an effective, or redefined, overpressure is defined as the difference between the redefined set pressure and the maximum pressure attained during the venting process. These definitions differ from those in some standards, including the British Standards, but are implicit in much of the DIERS work.

17.21.2 Vent sizing methods

Duxbury and Wilday (1989) give a list of vent sizing methods. This list is given in Table 17.22. All the methods, except method M, may, in appropriate circumstances, be applicable to vapour pressure systems.

17.21.3 Vent flow

The methods used for estimation of vent flow described by Duxbury and Wilday (1990) are those applicable to vapour pressure systems. Use is made of the ERM given in Equations 17.18.4 and 17.18.5 where it is applicable. Where it is not applicable, a fluid flow code is utilized.

If venting is through a safety valve, it is usually sized using the ERM, but where the pipework is significant, a fluid flow code is used to check pressure drops upstream and downstream. If venting is through a bursting disc the vent line flow correction factor provided for use with the ERM model is used for preliminary estimates, but since it is applicable only to a vent line with constant diameter and no static head changes, the final calculation is done using the fluid flow code.

17.21.4 Vapour pressure systems

For vapour pressure systems, use is made of Leung's method, as given in Equation 17.20.18. The assumption of homogeneous equilibrium flow is safe and generally realistic and the method gives a safe and usually acceptable vent size.

An alternative and sometimes more convenient formulation of Equation 17.20.18,

$$A = \frac{m_o q}{G\left[\left(\frac{V}{m_o}T_m\left(\frac{dP}{dT}\right)_m\right)^{1/2} + (C\Delta T)^{1/2}\right]^2} \qquad [17.21.1]$$

where subscript m denotes the mean value between the set pressure (as redefined) and the maximum allowable pressure.

The authors term this the Leung long-form equation (method J).

Where it is suitable, use is also made of Fauske's method for vapour pressure systems. This is the enhanced method which takes account of vapour disengagement, as given in Equation 17.19.6 (method K).

The Fauske method is used in conjunction with the Leung method. In the first instance it provides a check. If the two methods are significantly different, the calculations are reviewed. A significantly smaller answer from the Fauske method would not be accepted without rechecking the conditions for applicability and checking that the vent is large enough for all vapour venting.

Appropriate safety factors are then applied for each method. One safety factor is associated with the uncertainties in the data. If 'safe' values have been used, this safety factor is taken as unity. Another safety factor is associated with uncertainties in the vent flow calculation. Typically, this safety factor is in the range 1–2 on flow, or area, the larger values being typical for two-phase flow in long lines. A detailed treatment of safety factors by Duxbury is given in Appendix 13.

The vent sizes from the two methods so obtained are then compared. The final vent size is taken as the smaller of the two.

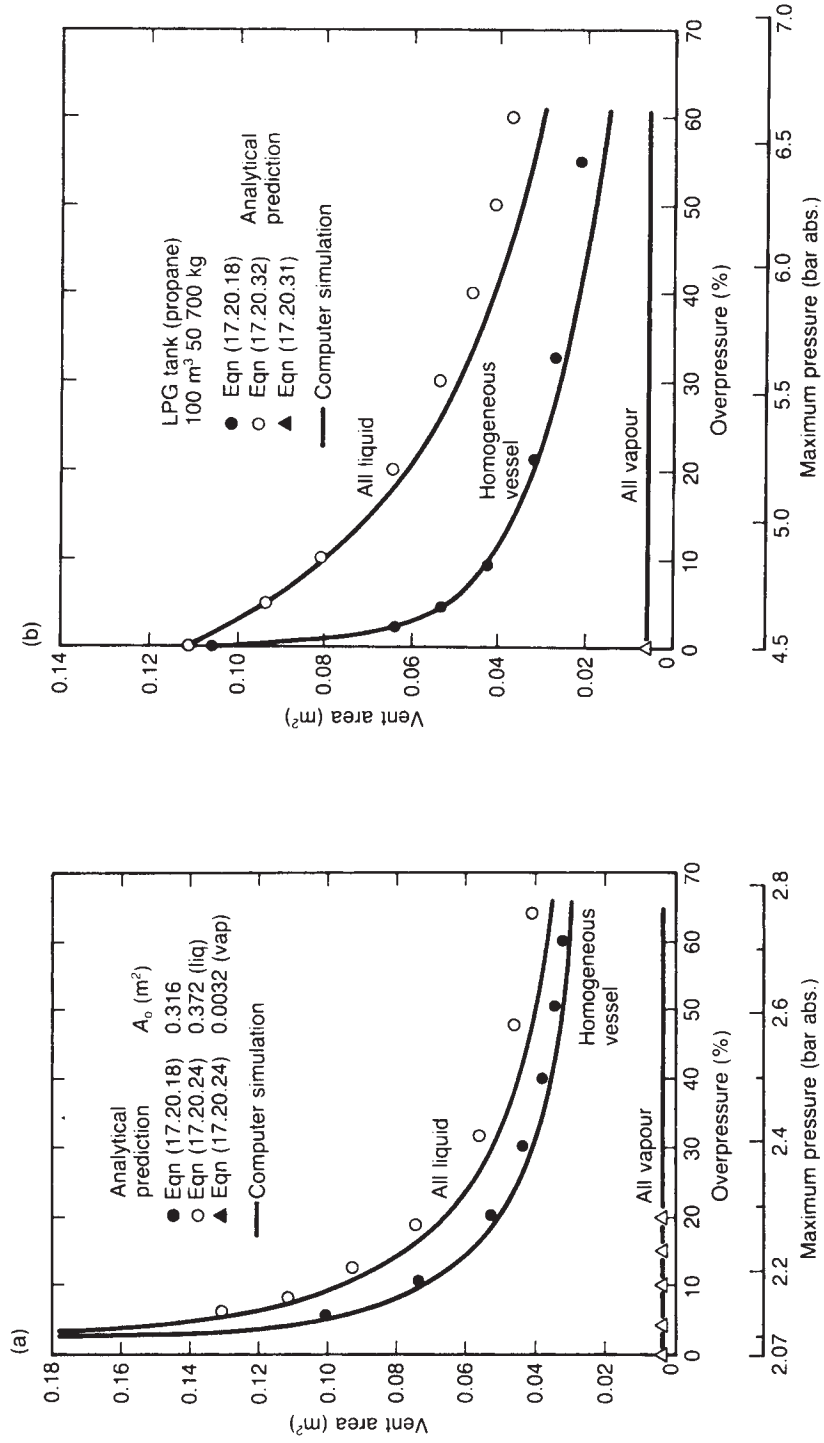

Figure 17.51 *Venting of chemical reactors: effect of vent fluid phase on vent area (Leung, 1986b): (a) phenolic reaction and (b) propane storage vessel (Courtesy of the American Institute of Chemical Engineers)*

Table 17.22 *Venting of chemical reactors: some vent sizing methods (after Duxbury and Wilday, 1989) (Courtesy of American Institute of Chemical Engineers)*

		Reference
A	All gas/vapour venting	Duxbury (1980)
B	Two-phase venting to maintain pressure constant	Duxbury (1980); Duxbury and Wilday (1989)
C	Modified Boyle method	Boyle (1967); Duxbury (1980)
D	Vent area/vessel volume scale-up	Duxbury (1980)
E	Full dynamic simulation	Duxbury (1980); Huff (1984a); Grolmes and Leung (1985); Klein (1986)
F	Huff's pseudo-steady-state method	Duxbury (1980)
G	Fauske short-form equation	Fauske (1984a)
H	Fauske nomograph	Fauske (1984b)
J	Leung long-form equation	Fauske and Leung (1985); Leung (1986b); Leung and Fauske (1987)
K	Fauske revised method	Fauske (1987a,b)
L	Fauske revised nomograph for tempered systems	Fauske, Grolmes and Clare (1988)
M	Fauske nomograph for gassy/untempered systems	Fauske, Grolmes and Clare (1988)
N	Leung's method taking account of disengagement	Leung (1987)
P	Wilday's method for homogeneous venting until disengagement	Duxbury and wilday (1989)
Q	Wilday's method for homogeneous venting at high overpressure	Duxbury and Wilday (1989)

This hand calculation method is generally both convenient and sufficient. The main effort required is associated with definition of the worst case conditions and gathering of data rather than with the vent sizing as such. Other methods are used only if both methods are judged to be inapplicable or if the vent size obtained is unacceptably large.

Before applying either method it is necessary to review its applicability.

The DIERS documentation states that Leung's method is limited to effective overpressures of 0–50%. It tends in fact to overestimate the vent size for higher overpressures. In order to permit integration, the model assumes constant various quantities such as physical and thermodynamic properties, heat evolution rate and vent capacity per unit area. The values of the parameters at the set pressure and maximum allowable pressure may be compared in order to assess the error and the extent to which the model may tend to oversize the vent.

The Fauske method is based on the ERM with a correction factor for vent line length. It is limited to overpressures in the range 10–30% and to turbulent flow.

In most cases the Fauske method is used without taking vapour disengagement into account and thus with α_d set equal to unity.

For those cases where credit is to be taken for vapour disengagement, it is necessary to perform the following check. The Fauske method is regarded as potentially unsafe if early vapour disengagement occurs, which in this context means disengagement occurring before the pressure would otherwise have turned around during two-phase venting. The method is therefore used only if disengagement would have occurred after the turnaround. Duxbury and Wilday (1989) have derived the following criterion which must be satisfied for safe use of the method:

$$q < \frac{GAh_{fg}v_f^2}{Vv_{fg}(1-\alpha_d)^2} \qquad [17.21.2]$$

where α_d is the void fraction at disengagement.

17.21.5 Vapour pressure systems: enhancements of Wilday

Duxbury and Wilday (1989) describe two enhancements to the Leung method (method J) for vapour pressure systems developed by Wilday.

The first of these (method P) is for the case where there is vapour disengagement part-way through the venting, with two-phase flow in the early part and all vapour flow in the later part and, further, the disengagement occurs before the pressure would have turned around during homogeneous venting. It is based on an adaptation of Leung's model. The following additional equations may be written:

$$m = V(1-\alpha)/v_f \qquad [17.21.3]$$

and, neglecting the vapour phase mass,

$$m_o = V(1-\alpha_o)/v_f \qquad [17.21.4]$$

where α is the void fraction and α_o is the initial void fraction.

Then, combining Equations 17.20.1 and 17.20.17 of Leung and Equations 17.21.3 and 17.21.4 gives

$$A = \frac{qV(\alpha-\alpha_o)}{Gv_f\left(\dfrac{h_{fg}v_{fg}(\alpha-\alpha_o)}{v_{fg}(1-\alpha_o)(1-\alpha)} + C\Delta T\right)} \qquad [17.21.5]$$

This method is valid only if vapour disengagement occurs before the point at which pressure turnaround would have occurred in homogeneous venting. Otherwise it gives too small a vent area and is unsafe. Before pressure turnaround the rate of temperature rise dT/dt in a vapour pressure system is positive, and hence from Equation 17.20.17

$$mq > GA\frac{V}{m}\frac{h_{fg}}{v_{fg}} \qquad [17.21.6]$$

which with Equation 17.21.3 gives the criterion

$$q > \frac{GAh_{fg}v_f^2}{Vv_{fg}(1-\alpha_d)^2} \qquad [17.21.7]$$

The second method given by Wilday (method Q) is based on Leung's model for homogeneous venting (method J). The assumption underlying this model is that the physical properties, heat release rate and mass velocity are constant. Wilday's method involves dividing the available pressure range into stages in which it is more reasonable to assume these quantities constant. Again, criteria are given for the applicability of the method.

17.21.6 Gassy systems

For gassy systems, the principal method of vent sizing is based on maintaining the pressure constant.

The vent is sized so that the two-phase volumetric flow at the maximum allowable pressure exceeds the peak volumetric gas generation rate at that pressure. The vent sizing equation given is Equation 17.19.9. An appropriate safety factor should then be applied as described in Section 17.21.4.

Use of the Fauske nomograph for gassy systems, Figure 17.50, would be limited to making preliminary estimates. Mention is also made of the treatment of gassy systems by Leung and Fauske (1987).

For gassy systems, use may also be made of direct scale-up, which may well give a smaller vent area due to early loss of reactant. Alternatively, the vent may be sized by simulation using a numerical model. Again, for the reason just given, this may give a smaller vent.

A note of caution is sounded in that for gassy systems it may be unsafe to make the assumption of homogeneous two-phase venting. This assumption gives the maximum rate of emptying the reactor. If some disengagement occurs, liquid will remain in the reactor and the peak gas generation rate may be reached. A larger vent may then be required than for the relatively low gas generation rate occurring earlier in the relief process.

17.21.7 Hybrid systems

For hybrid systems, the appropriate method depends on whether the reaction is tempered. For tempered hybrid systems, it is first necessary to check that the reaction will remain tempered throughout. Reference is made to the treatment of such systems by Leung and Fauske (1987).

Untempered hybrid systems usually have to be treated as gassy systems. Use would be made of Equation 17.19.9 provided the vent size obtained is not excessive. The flow Q_g to be used in that equation is the total volumetric evolution of both gas and vapour.

17.21.8 Illustrative examples

The illustrative examples of vent sizing for a vapour pressure system and a gassy system given by Duxbury and Wilday (1990) are summarized in Table 17.23.

17.22 Venting of Reactors: Relief Disposal

17.22.1 General considerations

The problem of reactor relief does not stop with the venting. There remains the question of the disposal of the vented materials, which is often not trivial. The engineering of relief disposal is therefore a topic in its own right. An account is given by Kneale (1984).

The legal requirement is that any venting should be to 'a safe place'. Discharge to atmosphere may meet this requirement, but such discharge is increasingly constrained.

The options for disposal are (1) discharge and dispersion, (2) destruction, and (3) containment.

A full definition of the relief requirements is as important for the design of the disposal system as for that of the relief device itself. Cases which should be considered include cooling failure during normal reaction, runaway of reaction for other reasons, explosion due to runaway or thermal instability, fire, overpressure by gas and overfilling by liquid.

The relieving process may be violent, and all equipment connected to the relief device, however remotely, should be designed for the hydraulic and mechanical forces released. This includes not only the inlet and outlet lines to the device but vessel and line supports, foundations and foundation bolts, and building structures.

Some common causes of deficiencies in relief disposal systems include failure to allow for (1) the presence of another phase, (2) the presence of fine particles, and (3) variation in emission with time.

A general strategy for relief disposal is shown in Figures 17.52 and 17.53. Liquid and solid are to be treated or contained and treated later, whilst liquid is contained and treated later.

Gas should be discharged to atmosphere only if it can be dependably diluted below any flammable and/or toxic limits which have to be met. Relations for the dispersion of such discharges are given in Chapter 15.

A study by Gerardu (1981) concluded that it is often simpler and safer to vent a pressure relief valve directly to the atmosphere, provided the hazard of ignition is allowed for.

It should be appreciated, however, that emergency discharge from a reactor is a transient process and that towards the end of this process the discharge will lose momentum and will tend to slump. This stage may well be the most hazardous, but also the most difficult to model.

Vents for the discharge of flammable gas to the atmosphere may be equipped with flame arresters, but where it is considered that the maintenance of such arresters cannot be guaranteed, they are often omitted.

Gas relieved is often sent to flare. The efficiency of destruction of combustible gas in a flare can be high; studies have shown combustion efficiencies well in excess of 99% (B.C. Davis, 1983). An alternative means of dealing with gas is scrubbing. A major factor in the choice of system is whether the scrubber has the function of handling a normal process gas stream or of treating the emergency vent gas only. In the latter case the options are to run with liquid constantly circulating or to start up automatically when venting starts. The cost of continuous circulation can be high, but it is not usual to rely on automatic start-up. Problems which can occur with scrubbers are boiling due to the high heat load imposed by the vent gas and carryover of spray.

Another option for handling the vented material is containment in a separate containment vessel, or catchtank. If the vent stream contains liquid or solid this is the appropriate design. Systems vary widely in complexity depending on the duty.

Table 17.23 *Venting of chemical reactors: illustrative calculations of vent size for reactors with (A) a vapour pressure system and (B) a hybrid system treated as a gassy system (after Duxbury and Wilday, 1990) (Courtesy of Institution of Chemical Engineers)*

A Example of vapour pressure system

	Reactor pressure (bara)		
	3.2	4.2	*Average*
Bubble point temperature (°C)	110	120.5	115.3
Liquid density (kg/m^3)	847	835	841
Vapour density (kg/m^3)	3.75	4.62	4.19
Liquid specific heat (J/kg K)	1960	1960	1960
Latent heat (J/kg)	6.749×40^5	6.630×10^5	6.690×10^5
dP/dT (Pa/K)	8300	9500	
v_{fg} (m^3/kg)	0.2655	0.2153	0.2404
Heat release rate (W/kg)	1150	1660	1405

Reactor volume = 2.1 m^3
Reaction mass = 1500 kg
Vessel design pressure = 2.86 barg
Bursting disc pressure[a] = 3.20 bara
Vent line length/diameter = 200

Maximum allowable pressure = $1.1 \times 2.86 = 3.15$ barg = 4.16 bara
Allowable overpressure = $4.16 - 3.20 = 0.96$ bar

For mass velocity at 3.2 bara, using Equation 17.18.9 with a correction factor $F = 0.65$:

$$G = 0.65 \times 8300 \times \left(\frac{383}{1960}\right)^{1/2} = 2385\,\text{kg/m}^2\,\text{s}$$

Alternatively, using Equation 17.18.4:

$$G = 0.65 \times \frac{6.749 \times 10^5}{0.2655}\left(\frac{1}{1960 \times 383}\right)^{1/2} = 1907\,\text{kg/m}^2\,\text{s}$$

Since the difference between these two estimates is appreciable, a rigorous fluid flow method was used to obtain the following estimate:

$G = 2264\,\text{kg/m}^2\,\text{s}$

A similar calculation for the mass flux at 4.16 bara gave

$G = 2688\,\text{kg/m}^2\,\text{s}$

The average of these two mass fluxes is:

$G = (2264 + 2688)/2 = 2476\,\text{kg/m}^2\,\text{s}$

Applying a safety factor of 2 on mass flux:

$G = 2476/2 = 1238\,\text{kg/m}^2\,\text{s}$

Allowable temperature rise $\Delta T = 120.5 - 110 = 10.5$ K

(1) Using Leung's method, Equation 17.20.18:

$$A = \frac{1500 \times 1405}{1238\left[\left(\dfrac{2.1 \times 6.690 \times 10^5}{1500 \times 0.2404}\right)^{0.5} + (1960 \times 10.50)^{0.5}\right]^2} = 0.04\,\text{m}^2; \quad D_v = 0.226\,\text{m}$$

Alternatively, using Equation 17.21.1:

$$\left(\frac{dP}{dT}\right)_m = \frac{(4.16 - 3.2) \times 10^5}{120.5 - 110} = 9143\,\text{Pa/K}$$

$$A = \frac{1500 \times 1405}{1238\left[\left(\dfrac{2.1 \times 388 \times 9143}{1500}\right)^{0.5} + (1960 \times 10.50)^{0.5}\right]^2} = 0.0372\,\text{m}^2; \quad D_v = 0.218\,\text{m}$$

Table 17.23 *(continued)*

(2) Using Fauske's method, Equation 17.19.6; assume no vapour disengagement so that $\alpha_D = 1$

$$\left(\frac{dT}{dt}\right)_s = \left(\frac{q_m}{C_m}\right)_s = \frac{1150}{1960} = 0.587 \text{ K/s}$$

For vent line $L/D = 200$ with a correction factor $F = 0.65$

$$A = \frac{1}{2} \frac{1500 \times 0.587}{0.65(383/1960)^{1/2} \times 0.96 \times 10^5} \frac{(1-\alpha_o)}{(1-\alpha_o)} = 0.016 \text{ m}^2$$

Applying a safety factor of 2 on vent area:

$A = 2 \times 0.016 = 0.032 \text{ m}^2$; $D_v = 0.202$ m

The difference between the vent area given by Leung's method and that given by Fauske's method, after application of the safety factor of 2, is some 20%.

B Example of hybrid system treated as gassy system

Molecular weight of liquid	65
Liquid density at 95°C (kg/m^3)	800
Latent heat (J/kg)	2.76×10^5
Heat release rate (W/kg)	53
Temperature for peak reaction rate (°C)	95
Peak gas evolution rate (l/kg s)[b]	0.146
Reactor volume (m^3)	5.0
Reaction mass (kg)	3200
Maximum allowable pressure (bara)	4.8

From a separate calculation, the mass velocity, including the safety factor, is found to be 2400 kg/m^2 s:

$$\text{Vapour evolution rate} = \frac{3200 \times 53}{2.76 \times 10^5} = 0.614 \text{ kg/s}$$

Volumetric vapour evolution rate at 4.8 bara and 95°C:

$$= \frac{0.614}{65} \times 22.4 \times \frac{368}{273} \times \frac{1.013}{4.8} = 0.06 \text{ m}^3/\text{s}$$

Volumetric gas evolution rate at 4.8 bara and 95°C:

$$= 0.146 \times 10^{-3} \times 3200 \times \frac{368}{298} \times \frac{1.013}{4.8} = 0.122 \text{ m}^3/\text{s}$$

Liquid volume in reactor $= 3200/800 = 4.0 \text{ m}^3$

Void fraction $\alpha = (5.0 - 4.0)/5.0 = 0.2$

Using Equation 17.19.9:

$$A = \frac{(0.060 + 0.122) \times 800(1 - 0.2)}{2400} = 0.0485 \text{ m}^2; \quad D_v = 0.249 \text{ m}$$

[a] Maximum specified bursting pressure.
[b] Volume (l) measured at atmospheric pressure and 25°C.

Apart from the cost, some problems which arise with containment are (1) reaction forces, (2) undetected leakage, (3) testing, and (4) plugging of lines.

The reaction forces affect the containment vessel as they do the whole system. A leak occurring undetected across the relief system may fill the containment. Testing of the system requires careful thought.

A review of reaction forces has been given by Woods and Thornton (1967) and Leung (2002).

Studies have also been made on particular configurations. The forces on a system consisting of a reactor and a containment vessel separated by a bursting disc have been analysed by Porter (1982), and the interactive effects of bursting discs in a relief manifold by Beveridge and Jones (1984).

Relief venting can give rise to appreciable noise. Sonic flow across a pressure relief device is a very efficient noise generator. The tall vertical stack frequently used for dispersion tends to broadcast noise. Work by Shearer (1969) has shown that at a distance of 200 ft from a vent the noise level in decibels for a wide range of vent flows can be approximated by 25 $\log_{10} V$, where V is the volumetric discharge (scfh).

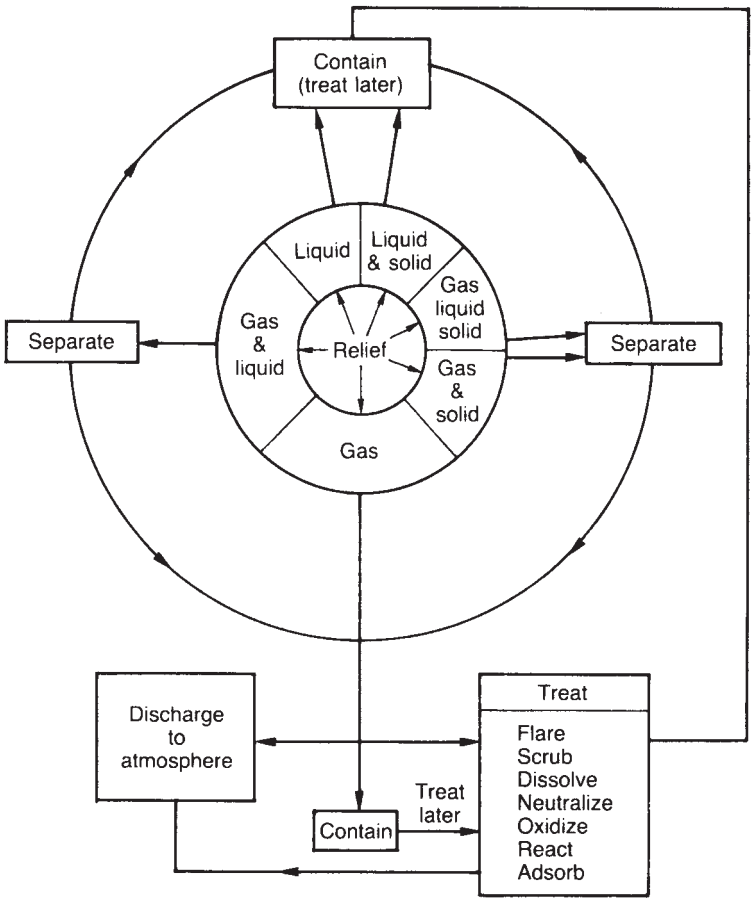

Figure 17.52 *Venting of chemical reactors: a taxonomy for relief disposal (Kneale, 1984) (Courtesy of the Institution of Chemical Engineers)*

This was confirmed experimentally for a range of flows from 1 to 3000 scfh regardless of the initial pressure and temperature. See also Perry and Green (1997 pp. 8–74).

In view of the problems associated with venting, the alternative of containment within the reactor vessel should be considered. Kneale suggests that if vacuum collapse may occur, the vessel should preferably be designed for full vacuum. As far as concerns overpressure he proposes that the vessel design criterion should depend on the expected frequency of overpressure. If overpressure is expected to be a very rare event (say once in 100–10,000 years) the vessel may be designed for overstress beyond the yield point but within the bursting strength, whereas if it is expected more frequently (say once in 10–100 years), a stronger design is appropriate.

Kneale describes a number of incidents arising from reactor venting.

17.22.2 Two-phase relief flows

As already described, there has been growing appreciation, further stimulated by the DIERS work, that it is generally necessary that the relief disposal system for a reactor be capable of handling a two-phase vapour–liquid mixture.

Discussions of the implications of the need to dispose of two-phase mixtures and proposals for dealing with the problem have been given by Fauske (1986a, 1987b), H.G. Fisher (1991) and Fauske and Grolmes (1992).

In particular, more guidance has become available on knockout and catchment facilities.

17.22.3 Knockout drums and catchtanks

Treatments of the design of knockout drums and catchtanks are given in API RP 521: 1990, by the BPF (1979) and by Grossel (1986, 1990b). Further references are given in API RP 521 and in Fthenakis (1993, Chapter 14).

API RP 521 gives a method for the sizing of a knockout drum which has been widely used. The basis is the provision of a cross-sectional area sufficient to ensure that the liquid droplets are not entrained in the vapour. The relation given is

$$u_d = 1.15\left(\frac{gd(\rho_l - \rho_v)}{C\rho_v}\right)^{1/2} \qquad [17.22.1]$$

where d is the particle diameter (m), g is the acceleration due to gravity (m/s^2), u_d is the dropout velocity (m/s), ρ_l is

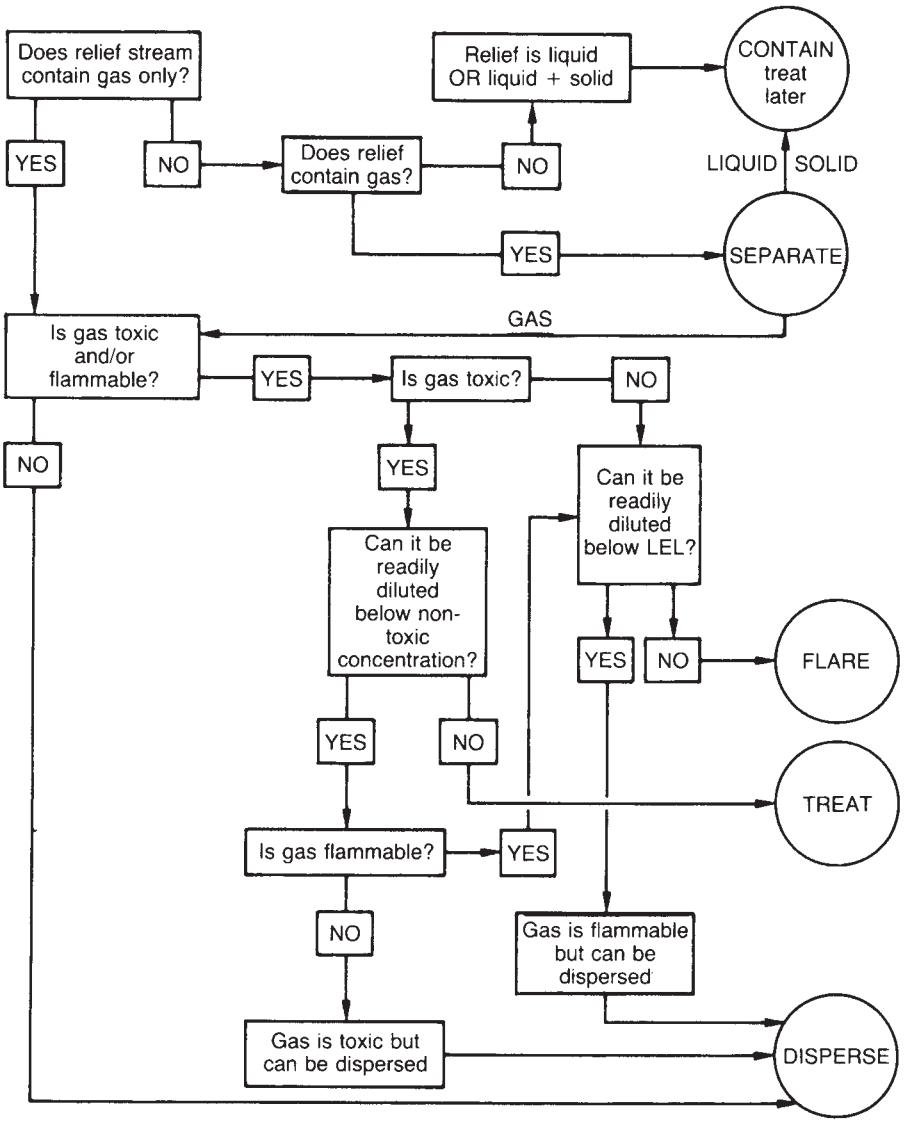

Figure 17.53 *Venting of chemical reactors: decision tree for relief disposal (Kneale, 1984). LEL, lower explosive limit (Courtesy of the Institution of Chemical Engineers)*

the density of the liquid (kg/m^3), ρ_v is the density of the vapour (kg/m^3) and C is the drag coefficient.

The drag coefficient C is given by Figure 17.54 in which

$$C(\mathrm{Re})^2 = 0.13 \times 10^8 \frac{\rho_v d^3(\rho_l - \rho_v)}{\mu^2} \qquad [17.22.2]$$

where μ is the viscosity of the gas (cP).

The selection and design of knockout drums and catchtanks has been described by Grossel (1986). There are a number of reasons why such devices may be needed. In a large proportion of cases the fluid entering the relief disposal system is a two-phase mixture, so that it is necessary to separate the vapour from the liquid, and the liquid is hot and flammable, toxic and/or corrosive.

Grossel describes the following types of knockout and catchtank systems: (1) horizontal drum plus catchtank, typical of a refinery or petrochemical plant where space is not restricted; (2) cyclone separator plus catchtank, typical of chemical plant with less space available; (3) cyclone separator with integral catchtank, capable of handling a large vapour flow; (4) open tank; (5) quencher knockout drum/catchtank; (6) multi-input knockout drum/catchtank, with connections from a group of reactors; and (7) cyclone knockout drum. The first two of these systems are shown in Figure 17.55.

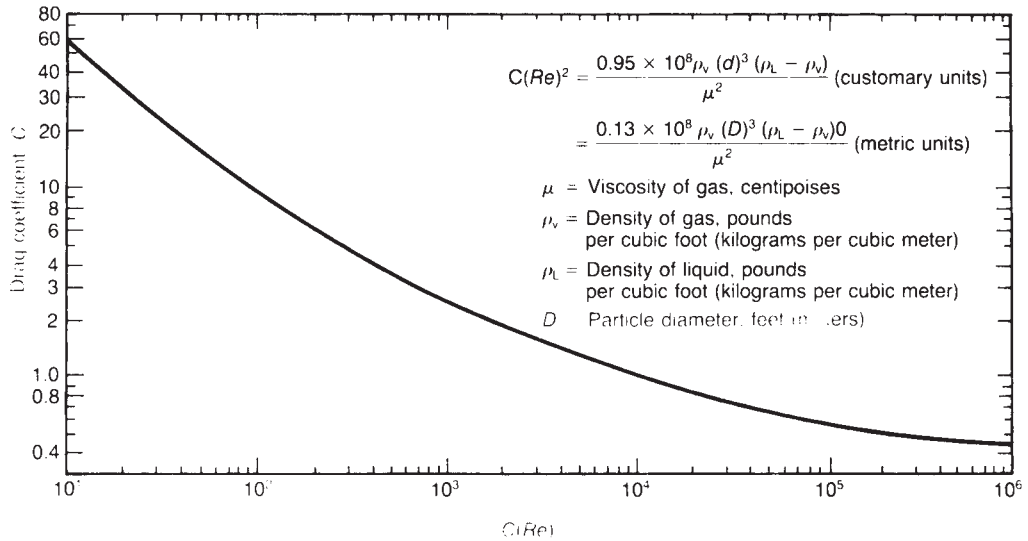

Figure 17.54 *Venting of chemical reactors: drag coefficient for knockout drum design (API RP 521: 1990) (Courtesy of the American Petroleum Institute)*

The open tank system may be used where the relief fluid contains an explosive mixture which it is judged better to release direct to atmosphere than to contain. The quencher knockout drum/catchtank system is used to condense out condensable vapour.

Principal factors in the design of such systems are a volume sufficient to hold the liquid and, for non-cyclone systems, a cross-sectional area sufficient to prevent liquid entrainment.

Expressions are given for the allowable vapour velocity u of the general form

$$u = k\left(\frac{\rho_l - \rho_v}{\rho_v}\right)^{1/2} \qquad [17.22.3]$$

where k is a constant.

For cyclone separators the design requirement may diverge somewhat from that for conventional applications. For a high flow, short duration emergency relief, some mist may be tolerable in the outlet, and a high vapour velocity may be acceptable.

For quench tanks critical features are the suppression pool and quencher arm. The quench liquid should be compatible with the reaction mass to be quenched. The quantity of quench liquid in the pool should be sized so that its temperature rise after condensation of the condensable vapour does not exceed a suitable value. Grossel gives two further rules-of-thumb for the quench fluid. One is that the quantity should be some 2–3 times by volume that of the reaction mass and the other that the exit temperature of the vapour leaving the pool should be at least 10°C below its saturation temperature.

The design of the quench arm is also important. The device is prone to water hammer. Grossel gives several rules-of-thumb for this feature also. One is the limitation of the size of the holes to 1/4 in., since high hole velocities are desirable and large holes may result in water hammer. The other is that the hole area should be at least as great as the cross-sectional area of the inlet pipe from the relief device.

The relief pipework should be as short and as straight as possible. An account of the design of such piping has been given by Chambard (1980).

Consideration should be given to the pressure drop through the relief disposal train and its effect on the back-pressure at the reactor vent.

Guidance is also given by Grossel on mechanical design of the catchtank. He suggests a minimum design pressure of 50 psig. The tank should be able to withstand a deflagration without rupture, though it may deform. Some companies use a design pressure of 125–150 psig.

The blowdown loads should be taken into account. Operation of a relief device creates reaction and impact forces. The reaction vessel is subject to reaction force and impact force due to slugs. Both reactor vessel and piping are affected by fluid acceleration wave forces. A quasi-steady state jet force occurs at the containment vessel.

Further, a quencher vessel is subject to impact force, condensation vibrations and final water hammer. The impact force is due to the impact of the fluid. The final water hammer occurs at the end of blowdown, when, if the reactor has been vented through a bursting disc, condensation can lead to a high flow back into the vent line and reactor vessel.

Grossel states that the catchtank should itself be provided with a bursting disc relieving into the catch-tank vent line to handle continued reaction and fire engulfment, but also that this device is not necessary if its size turns out to be less than that of the aforementioned vent line.

Another design of separator is the vortex separator of Muschelknautz and Mayinger (1986, 1990) described in the CCPS *Guidelines for Vapor Release Mitigation* (1988/4). This separator may be mounted directly above the reactor and may be used to separate the liquid from the vapour prior to the relief device.

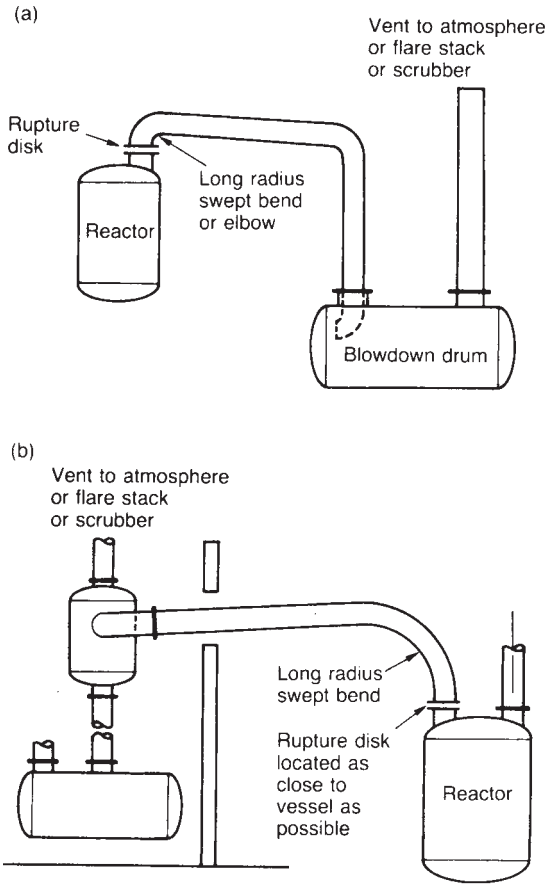

Figure 17.55 *Venting of chemical reactors: blowdown systems (Grossel, 1986): (a) horizontal blowdown drum and (b) knockout drum with separate catchtank (Courtesy of the American Institute of Chemical Engineers)*

17.22.4 Quench systems

The handling of a two-phase mixture in the relief disposal system poses a number of potential problems which have been discussed by Fauske (1986a).

The typical relief train consists of a separator, a scrubber and a flare. A two-phase relief requires a separator, but the typical system has these defects: (1) the relief is liable to be foamy and difficult to separate; (2) the size of the separator is often larger than that of the reactor; (3) the potential may exist for reaction runaway in the separator; and (4) the instantaneous flow may be very high and the flow of scrubbing fluid needs to be correspondingly high.

The method of disposal which Fauske favours to overcome these difficulties is the use of a suitable quench system. This should quench the vapour so that scrubber and/or flare are eliminated, apart from any arrangements needed to deal with small amounts of non-condensables. The selection of the quench fluid is critical, particularly if the reaction mixture has potential for explosive decomposition.

17.23 Venting of Reactors: CCPS Work

The CCPS has done work with a view to providing guidance on relief disposal. An outline of draft *Guidelines for Effective Handling of Emergency Release Effluents* has been given by Huff (1992). He describes a methodology for characterizing and handling the relief flow.

The purpose of the guidelines is to provide sufficient information to allow the non-specialist to do the design of the relief disposal system in more than nine cases out of 10 and to be able to identify those which need to be handled by a specialist. Such cases are typically systems which are chemically reactive, contain fractionating multicomponent systems or fluids near their critical point or involve relief from distributed systems such as long pipe heaters.

The main heads of the guidelines may be summarized as:

(1) relief scenarios;
(2) characterization of flow from protected system;
(3) applicable standards and codes;
(4) relief devices;
(5) flow through relief devices;
(6) installation of relief devices;
(7) disposal scenarios;
(8) disposal strategies;
(9) characterization of flow in relief system.

Guidance is given on the formulation of the relief scenarios and identification of a credible worst case. The problem of scenarios with a high degree of uncertainty is highlighted. Approaches to reducing the relief requirement, such as elimination of aggravating features and the use of alternatives to relief, are described. A checklist is given of events for which relief may be required.

Events in the protected system which may need relief include for non-reactive fluids shut-in pipework and thermal expansion, excess of heating or lack of cooling, and fire exposure, and for reactive fluids runaway reactions.

The characterization of the flow to be handled concentrates particularly on two-phase flow. The mixture vented may be two-phase or it may be superheated so that it becomes two-phase in the relief system. During venting, two-phase flow may stop and start. Information is provided on fluid properties, including mixture properties and phase equilibrium.

The terminology and requirements of standards and codes relevant to relief are summarized, both in respect of the relief pressures and the relief devices. The relief devices recognized in the American National Standards Institute (ANSI) system are described. Guidance is given on sizing and on sources of data. Auxiliary components are also described such as block and diverting valves, bleed system components and non-bleed relief monitors.

The guidelines deal with the selection of relief devices, calculation of the flow through relief devices, sizing of the associated pipework and definition of the flow through the relief disposal system. Methods are given for the calculation of the flow through relief devices, both nozzles and piping, starting with the fundamental equations and following through with working forms of these equations. Devices dealt with include gas safety valves, liquid relief valves, low pressure devices, bursting discs and open vents. Fluids considered include compressible gases and vapours, subcooled liquids, two-phase gas–liquid mixtures and two-phase flashing vapour–liquid mixtures.

The installation of relief devices is treated, including pressure drops in the pipework, provisions to ensure drainage and prevent freezing, static head and siphoning for low pressure devices and backflow from header connections. Mechanical aspects are also considered, including reaction forces.

Guidance is given on the formulation of the disposal scenarios and identification of a credible worst case, which need not necessarily be the same as the worst case for relief. The potential for vent flows in each phase should be considered and a worst case identified for each phase. The maximum flows and volume to be handled should be determined.

The strategies for relief disposal and the various options are described.

The characterization of the flow in the relief system is considered, including volatility, foaming behaviour and state of aggregation of phases.

17.24 Venting of Storage Vessels

It is necessary to protect storage vessels against overpressure and this is done by fitting vents. Principal sources of overpressure are operational deviations and fire, but there are numerous other sources, as described in Chapter 20. The fire protection of storage vessels is discussed in Chapter 16.

Fire is not the sole potential source of heat input to a storage vessel. Many chemicals held in storage have the potential to undergo exothermic reaction. Any external heat source, including fire, may act as an initiator. Addition of water may be another. This effect should be taken account of in considering the venting requirements for storage.

17.24.1 Fire behaviour of atmospheric storage tanks

Work on the fire behaviour and on vent sizing for storage vessels has been described by Fauske, Epstein, Grolmes and Leung (1986) and Fauske (1987a).

Vent sizing for atmospheric storage tanks has traditionally been based on all vapour flow. The aim of the study was to check whether this approach is adequate. The implication of the need to consider two-phase flow would be a large increase in vent size. As a first approximation the increase in vent area required would be of the order of the square root of the ratio of the vapour and liquid densities $(\rho_g/\rho_l)^{1/2}$.

This concern was addressed in an extension of the DIERS project. The work is described in Chapter 15. It was concluded that liquid swell in an externally heated storage tank is essentially limited to the boiling two-phase boundary layer and that for a non-foaming liquid all vapour venting would appear adequate, provided the tank is not completely filled with liquid.

However, for an atmospheric storage tank, it is necessary to avoid entrainment of liquid in the vapour vented. The relation given for the vent area is

$$A = \frac{Q_T}{h_{fg}\rho_g u} \qquad [17.24.1]$$

where A is the area of the vent, h_{fg} is the latent heat of vaporization, Q_T is the total heat input to the tank and u is the velocity of vapour through vent.

The limiting value of the velocity u in Equation 17.24.1 for an atmospheric storage tank is the entrainment velocity u_E:

$$u = u_E \qquad [17.24.2]$$

The relation given for the entrainment velocity is that of Kutateladze (1972):

$$u_E \approx 3.0\left(\frac{\sigma g \rho_l}{\rho_g^2}\right)^{1/4} \qquad [17.24.3]$$

where g is the acceleration due to gravity, ρ_l is the density of the liquid and σ is the surface tension of the liquid.

Fauske (1987a) states that a safety factor of 2 on the vent area determined from Equations 17.24.1–17.24.3 should be adequate even for a foamy liquid.

A criterion for the onset of liquid entrainment in a storage vessel exposed to fire has been given by Epstein, Fauske and Mauser (1989). They consider a hemispherical surface centred on a vent at the centre of the top of a vertical cylindrical vessel. The velocity across this surface is

$$u_s = \frac{1}{2}\left(\frac{a}{s}\right)^2 u_o \qquad [17.24.4]$$

where a is the radius of the vent, s is the radius of the hemisphere, u_s is the velocity across the hemispherical surface and u_o is the velocity up the vent. Onset of entrainment occurs when the velocity u_s attains a critical value u_{scr} at the height $h = s$. Then, from Equation 17.24.4

$$h = a\left(\frac{u_o}{2u_{scr}}\right)^{1/2} \qquad [17.24.5]$$

The authors state that this work indicates that rather small freeboard volumes can be tolerated without the occurrence of two-phase venting.

For vessels which can withstand substantially higher pressures, the approach given by Fauske is to take the velocity u in Equation 17.24.1 as

$$u \approx 2\Delta P/\rho_g \qquad [17.24.6]$$

where ΔP is the pressure drop through the vent system. He states that a factor of 2 on the vent area determined from Equations 17.24.1 and 17.24.6 is generally consistent with a modest overpressure of some 10–30% above the relief pressure even for a foamy liquid.

Further relationships for the vent area for storage vessels with non-foamy liquid have been given by Fauske, Grolmes and Clare (1989). For an atmospheric storage tank

$$A = \frac{Q_v}{3Fh_{fg}[\sigma g(\rho_l - \rho_g)]^{1/4}\rho_g^{1/2}} \qquad [17.24.7]$$

where F is the flow reduction factor and Q_v is the energy release rate. This equation is based on all vapour flow with no entrained liquid.

For a storage vessel capable of withstanding substantially higher pressure

$$A = \frac{Q_v(R_m T)^{1/2}}{0.62Fh_{fg}P_s} \qquad [17.24.8]$$

where P_s is the absolute set pressure, R_m is the mass basis gas constant and T is the absolute temperature. This equation is based on all vapour critical flow.

Fauske, Grolmes and Clare (1989) describe an approach to vent sizing for storage tanks based on relating the external heating rate to an equivalent self-heat rate and give a graph for checking uninsulated and insulated vessels.

17.24.2 Designs for protection of storage vessels

Fauske (1988b, 1989b) has described a number of designs for the protection of atmospheric storage tanks and pressure storage vessels against fire and the hazard of BLEVE.

For atmospheric storage tanks, two designs are given, both involving double wall construction. In one design the intermediate space is filled with water. In the other design there is an air space with facility to inject heating or cooling medium through the space.

For pressure storage vessels, the vessels considered are spheres and there are again two design proposals. The first has an internal spherical baffle so that on fire engulfment the liquid swell would occur in the annulus between the outer wall and the baffle, with liquid being 'pumped' from the bottom to the top of the baffle and then falling down into the centre of the vessel while the vapour is vented. In the other design there is a double wall construction with the vessel held inside a tank, the intermediate space being filled with water.

17.25 Explosive Shock in Air

One of the main effects of an explosion is the creation of a shock wave, or blast wave. This blast wave generates overpressures which may injure people and damage equipment and buildings.

Accounts of explosive shock in air are given in *The Effects of Nuclear Weapons* (Glasstone, 1962) and its later edition (Glasstone and Dolan, 1980), *Explosive Shocks in Air* (Kinney, 1962) and its later edition (Kinney and Graham, 1985), *Explosions in Air* (W.E. Baker, 1973) and *Explosion Hazard and Evaluation* (W.E. Baker *et al.*, 1983).

The situation of prime interest here is that of a chemical explosion at the ground surface and it is this which is mainly considered.

The description given of the explosion is based, unless otherwise stated, on an explosion of high explosive such as TNT.

17.25.1 The blast wave

An explosion in air is accompanied by a very rapid rise in pressure and by the formation of a shock wave. An account of the phenomena involved is given by Glasstone (1962).

The shape of the pressure profile near the centre depends on the type of explosion involved. The initial shape differs for explosions of high explosives, nuclear weapons and flammable vapour clouds.

The initial pressure profile for nuclear explosions is probably the most readily defined. The pressure at the edge of the fireball is approximately twice that at the centre.

With detonations the shock wave travels outwards with the higher pressure parts moving at higher velocities. After it has travelled some distance the shock wave reaches a constant limiting velocity which is greater than the velocity of sound in the air, or in the unburnt gas in the case of a vapour cloud. The shock wave has a profile in which the pressure rises sharply to a peak value and then gradually tails off. As the shock wave travels outwards the peak pressure at the shock front falls.

At some distance from the explosion centre the region of positive pressure, or overpressure, in the shock wave is followed by a region of negative pressure, or underpressure. The underpressure is quite weak and does not exceed about 4 psi.

An idealized representation of the blast wave is given in Figure 17.56. This shows the pressure pulse as a function of distance from the explosion centre with time as the parameter. The shock wave reaches points A,B,C and D at times 1, 2, 3 and 4, respectively, and at these times its pressure profile is as illustrated. The shape of the curve at point A is not shown, since it depends on the type of explosion. As the wave moves outwards, however, the influence of the nature of the explosion declines and the wave establishes a profile which is common to all types of explosion. The curves at points B–D and times 2–4 show the decrease in peak overpressure. The curve at point D and time 4 shows both positive and negative pressures.

The variation of overpressure with time at such a point is illustrated in Figures 17.57(a) and (b). Important parameters are the peak overpressure p°, the arrival time t_a, the duration time t_d, which is the duration of the positive phase, and the decay parameter a, which defines the shape of the decay curve in the positive phase. For a deflagration the rising pressure is gradual and for a detonation it is abrupt.

The peak overpressure p° is more correctly described as the peak side-on overpressure or peak incident overpressure, in order to distinguish it from other peak overpressures such as the peak reflected overpressure described below. The peak side-on overpressure is the peak overpressure occurring at the side of a structure being passed by the blast wave.

There are several equations which are used to describe the positive phase of the overpressure decay curve of Figure 17.57. A widely used one is the modified Friedlander equation (Kinney, 1962)

$$p = p^\circ(1 - t/t_d \exp(-\alpha t/t_d) \qquad [17.15.1]$$

where p is overpressure, p° is the peak overpressure, t is the time, t_d is the duration time and α is the decay parameter. Another common equation applicable at or below about

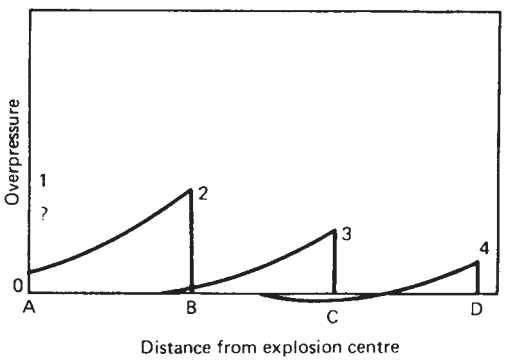

Figure 17.56 *Idealized representation of development of detonation blast waves*

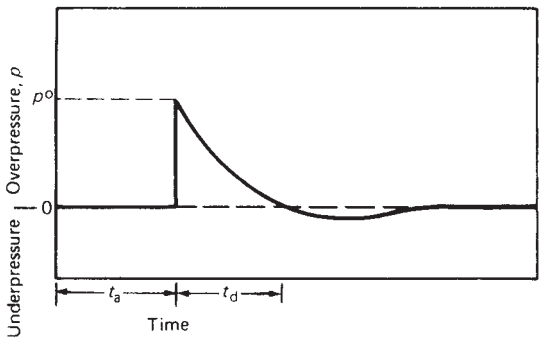

Figure 17.57 *Variation of overpressure from a blast wave with time at a fixed point*

l0 psi is Equation 17.25.1 with the decay parameter set equal to unity. Information on the decay of overpressure is given by Glasstone (1962, p. 124).

Other important properties of the blast wave, described by Glasstone (1962), are the shock velocity, the particle velocity, or peak wind velocity, behind the shock wave, the peak dynamic pressure and the peak reflected overpressure. The shock velocity is given by

$$U = c_o\left(1 + \frac{\gamma+1}{2\gamma}\frac{p^\circ}{p_a}\right)^{1/2} \qquad [17.25.2a]$$

where c_o is the velocity of sound in air, p_a is the absolute ambient pressure (ahead of the shock front), U is the shock velocity and γ is the ratio of specific heats of air. For air $\gamma = 1.4$ and hence

$$U = c_o\left(1 + \frac{6p^\circ}{7p_a}\right)^{1/2} \qquad [17.25.2b]$$

The particle velocity is given by

$$u = \frac{c_o p^\circ}{\gamma p_a}\left(1 + \frac{\gamma+1}{2\gamma}\frac{p^\circ}{p_a}\right)^{-1/2} \qquad [17.25.3a]$$

where u is the particle velocity. For $\gamma = 1.4$

$$u = \frac{5c_o p^o}{7p_a} + \left(1 + \frac{6p^o}{7p_a}\right)^{-1/2} \qquad [17.25.3b]$$

The peak dynamic pressure q° is defined as

$$q^o = \frac{1}{2}\rho u^2 \qquad [17.25.4]$$

where q° is the peak dynamic pressure and ρ is the density of air (behind the shock front). This can be shown to be

$$q^o = \frac{p^{o2}}{2\gamma p_a + (\gamma-1)p^o} \qquad [17.25.5a]$$

For $\gamma = 1.4$

$$q^o = \frac{5}{27}\frac{p^{o2}}{p_a + p^o} \qquad [17.25.5b]$$

The peak reflected overpressure p_r^o, which occurs if the blast wave strikes a flat surface at normal incidence, is

$$p_r^o = 2p^o + (\gamma+1)q^o \qquad [17.25.6a]$$

For $\gamma = 1.4$

$$p_r^o = 2p^o + 2.4q^o \qquad [17.25.6b]$$

Then, substituting for q° from Equation 17.25.5b

$$p_r^o = 2p^o\left(\frac{7p_a + 4p^o}{7p_a + p^o}\right) \qquad [17.25.7]$$

As stated earlier, the distinction between the peak incident overpressure, or simply the peak overpressure, p° and the peak reflected overpressure p_r^o is important, and it should always be made clear which overpressure is being referred to.

The peak dynamic pressure is less than the peak overpressure at low values of these two pressures, but greater at higher values. Equation 17.25.5b shows that the cross-over point is about 70 psi (4.83 bar).

The peak reflected overpressure is shown by Equation 17.25.6b to approach a value of twice the peak overpressure for weak shocks in which the peak dynamic pressure is negligible, but to approach a value of eight times the peak overpressure for strong shocks in which the peak dynamic pressure is dominant.

This maximum factor of 8 by which the peak reflected pressure exceeds the peak overpressure is frequently quoted. It depends, however, on the validity of the assumptions underlying Equation 17.25.6b.

17.25.2 Blast scaling

The characteristics of the blast wave produced by an explosion are generally determined by the application of scaling laws.

As described in Section 17.3 in relation to explosives, there are a number of scaling laws which relate explosion effects such as overpressure, damage circle radius, crater radius and sympathetic detonation distance.

For the blast wave from an explosion the scaling relation which is much the most widely used is the 'cube root' law, which was first enunciated by Hopkinson (1915). This law states that when two charges of the same explosive and geometry but of different size are detonated in the same atmosphere, self-similar shock waves are produced at the same scaled distances. The scaled distance is defined as

$$z = \frac{r}{W^{1/3}} \qquad [17.25.8]$$

where r is the distance, W is the mass of explosive and z is the scaled distance. It should be noted that the Hopkinson scaled distance is not dimensionless.

Strictly, the relevant scaling variable is the energy E rather than the mass of explosive W, but for a particular explosive it is usual to assume that the energy released is proportional to the mass of explosive.

The cube root index in the scaling law is related to the fact that energy is deposited into a spherical, or hemispherical, region, the volume of which varies with the cube of the radius. Other scaling laws are described by W.E. Baker (1973).

Another parameter which may be used in blast scaling is the yield factor λ, which is defined as

$$\lambda = \left(\frac{W}{W_o}\right)^{1/3} \quad [17.25.9]$$

and the subscript o denotes the reference value.

Since from Equation 17.25.8 self-similar shock effects occur at the same scaled distance

$$z = \frac{r_o}{W_o^{1/3}} = \frac{r}{W^{1/3}} \quad [17.25.10]$$

or, introducing the yield factor from Equation 17.25.9,

$$r = \lambda r_o \quad [17.25.11]$$

where r_o is the reference distance.

If in Equation 17.25.9, $W_o = 1$, then λ is numerically equal to $W^{1/3}$; and Equation 17.25.11 reduces to Equation 17.25.8 with r_o numerically equal to z.

The application of the Hopkinson scaling laws to the principal blast parameters is now considered.

17.25.3 Peak overpressure

An important parameter of the blast wave is the peak side-on overpressure p^o. The scaling relation for this parameter is

$$p^o = f(z) \quad [17.25.12]$$

Equation 17.25.12 states that a given peak overpressure occurs at a given scaled distance.

This scaling law implies, for example, that for a given peak overpressure an increase in the mass of explosive by a factor of 1000 corresponds to an increase in the distance from the explosion by a factor of 10.

The decay of the peak overpressure is given by Equation 17.25.1.

The peak overpressure is frequently presented in the form of the ratio

$$p_s = \frac{p^o}{p_a} \quad [17.25.13]$$

where p_a is the ambient pressure and p_s is the scaled pressure.

17.25.4 Arrival and duration time

Blast scaling applies to the time parameters arrival time and duration time. The Hopkinson scaled time τ is defined as

$$\tau = \frac{t}{W^{1/3}} \quad [17.25.14]$$

where t is the time and τ is the scaled time. It should be noted that scaled time is not dimensionless. Then, from Equation 17.25.14

$$\tau = \frac{t_o}{W_o^{1/3}} \quad [17.25.15]$$

where t_o is a reference time. The scaled arrival time and the scaled duration time are thus

$$\tau_a = \frac{t_a}{W^{1/3}} \quad [17.25.16]$$

and

$$\tau_d = \frac{t_d}{W^{1/3}} \quad [17.25.17]$$

where t_a is the arrival time, τ_a is the scaled arrival time and τ_d the scaled duration time.

In terms of the yield factor λ

$$t = \lambda t_o \quad [17.25.18]$$

where t_a is a reference time.

17.25.5 Dynamic pressure

Another important parameter of the blast is the peak dynamic pressure q°. This is defined by Equation 17.25.4 and may be obtained from Equation 17.25.5.

Information on the decay of the dynamic pressure is given by Glasstone (1962).

17.25.6 Overpressure impulse

Further important parameters of the blast are the overpressure and dynamic impulses. The positive phase overpressure impulse, overpressure impulse, or simply impulse, i_p is the integral of the overpressure during the positive phase:

$$i_p = \int_0^{t_d} p \, dt \quad [17.25.19]$$

Substituting Equation 17.25.1 in Equation 17.25.19 gives

$$i_p = p^o t_d \left(\frac{1}{\alpha} - \frac{1}{\alpha^2}[1 - \exp(-\alpha)]\right) \quad [17.25.20]$$

The simplifying assumption is sometimes made that the impulse takes the form of a triangle. In this case it may be approximated by

$$i_p \approx 1/2 p^o t_d \quad [17.25.21]$$

The overpressure impulse i_p is another parameter of the blast wave to which scaling is applied. The Hopkinson scaled impulse i_s is defined as

$$i_s = \frac{i_p}{W^{1/3}} p^o t_d \quad [17.25.22]$$

17.25.7 Dynamic pressure impulse

The dynamic pressure impulse i_q is

$$i_q = \int_0^{t_d} q \, dt \quad [17.25.23]$$

As for the overpressure impulse, it is often assumed that the dynamic pressure impulse takes the form of a triangle so that it may be approximated by

$$i_q \approx 1/2q^o t_q \qquad [17.25.24]$$

Information on the impulse and duration time for the dynamic pressure is not as readily available as for the corresponding parameters for overpressure. The following empirical relation is given for the dynamic pressure impulse by Richmond and Fletcher (1971):

$$\ln R = \frac{5.4054 + 1.1067 \ln W - \ln i_q}{2.3201} \qquad [17.25.25]$$

where i_q is the dynamic pressure impulse (psi s), R is the distance (ft) and W is the mass of explosive (lb) as TNT equivalent.

17.25.8 Air bursts

So far the account given of the blast wave is a general one, and no distinction has been made between a burst occurring in free air and one occurring on the ground surface.

If the explosion is an air burst, or an explosion which occurs at some height above ground level, the behaviour of the shock waves on reaching the ground surface is rather more complex. The situation may be explained by reference to Figure 17.58. As shown in Figures 17.58(a) and (b), the incident shock I strikes the ground and gives rise to a reflected shock wave R. The reflected shock wave passes through an atmosphere which has already been heated and compressed by the incident wave. It therefore travels faster and tends to overtake the incident wave. Where this happens, the two waves fuse at the triple point T and form a Mach system M below this point, as shown in Figure 17.58(c). The Mach stem is a shock front similar to that generated by ground level explosions.

For moderate heights the Mach stems forms at a distance from the ground which is approximately equal to the height of the explosion (Glasstone, 1962, figure 3.67a).

17.26 Condensed Phase Explosions

An explosion of a high explosive is referred to as a condensed phase explosion. The explosive which serves as the reference standard is TNT.

In this section consideration is given primarily to the characteristics of the explosion itself. The effects of the explosion are considered in detail later. However, an account is first given of some incidents involving high explosives.

17.26.1 Condensed phase explosion incidents

Condensed phase explosions include explosions of munitions, commercial explosives and ammonium nitrate. An account of early accidental condensed phase explosions is given in *History of Explosions* (Assheton, 1930). Some further incidents are detailed in *Darkest Hours* (Q.R. Nash, 1976) and *Handbuch Störfalle* (Kier and Mffller, 1983). Apart from this, information has to be sought mainly in the accounts of individual explosions. Incident data are also available from the Explosions Incidents Data Service (EIDAS) data bank of the Safety and Reliability Directorate (SRD).

Appendix 1 includes a section devoted to accidental condensed phase explosions. Some principal explosions are given in Table 17.24, with incidents involving munitions and commercial explosives listed in Section A and those involving ammonium nitrate in Section B. Further information on these incidents is given in Table A1.2 in Appendix 1. The criteria for inclusion of condensed phase explosion incidents in both these tables is that the incident is a major one, that it is of technical interest and/or that it is frequently referenced. The tables give only a small sample of the condensed phase explosions which have occurred.

In the early years of the chemical industry, many of the worst incidents involved condensed phase explosives, including ammonium nitrate.

Incidents involving munitions and commercial explosives include the explosion of the munition ship Mont Blanc in the harbour at Halifax, Nova Scotia, in 1917, in which 1963 people were killed (Case History A3). Within a radius of about three quarters of a mile, destruction was almost complete. It was estimated that 95% of the glass in the city was broken.

Also in 1917 there was an explosion at a munitions works in Silvertown, London, and another, less well-known, explosion at a chemical works at Ashton, Manchester (Case Histories A4 and A2, respectively).

In 1989 there was an explosion of a load of commercial explosives on a road vehicle at Peterborough in the United Kingdom (Case History A125). This incident has significance for the transport of explosives.

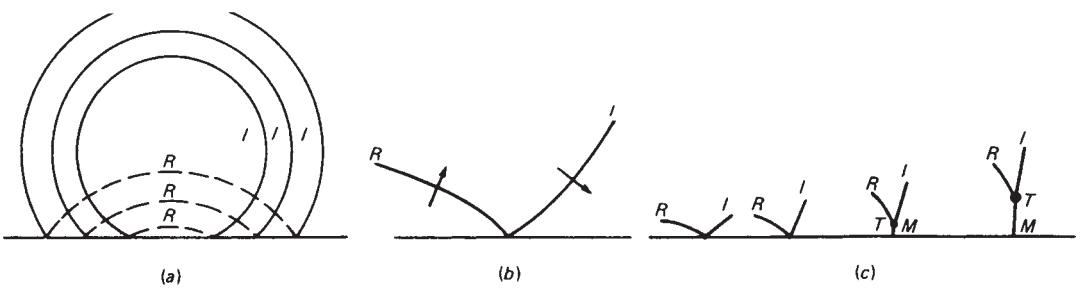

Figure 17.58 *Blast waves produced by an air burst: (a) development of blast wave; (b) incident and reflected waves; and (c) development of Mach stem. I, incident wave; R, reflected wave; M, Mach stem; T, triple point*

Table 17.24 *Some condensed phase explosion incidents*

Date	*Location*	*Explosive*[a]	*Plant/transport*	*Deaths/injuries*
A Munitions and commercial explosives				
1913	Mexico city	Dynamite	Road vehicle	41+, ≈100i
1917	Ashton, UK			
	Halifax, Nova Scotia	Munitions	Ship	1963d, ≈8000i
	Silvertown, UK	TNT	Munitions works	69d, 426i
1944	Fauld,UK	Munitions	Munitions store	68d, 22i
1956	Cali, Columbia	Munitions, dynamite	Seven road vehicles	≈1200d
1971	Waco, GA	Explosives	Road vehicle	5d, 33i
1985	Checotah, OK	Munitions	Road vehicle	0d, 49i
1989	Peterborough, UK	Explosives	Road vehicle	1d, 107i
1990	Meerut, India	Explosives	Road vehicle	50d
1991	Thung Maproah, Thailand	Dynamite	Road vehicle	123d
B Ammonium nitrate				
1918	Morgan, NJ			64d
1921	Oppau, Germany		Chemicals works	561d
1942	Tessenderloo, Belgium			>100d
1944	Bombay Docks, India		Ship	>350d, 1800i
1947	Brest, France		Ship	21d
1947	Texas City, TX		Two ships	552d, ≈3000i

[a] Only the main item of the load is given. In some cases there were other items such as detonators, boosters, etc.

Turning to ammonium nitrate, the explosion at Oppau in 1921 resulted from the use of blasting powder to break up stored piles of the material (Case History A5). It created a crater 250 ft in diameter and 50 ft deep, destroyed hundreds of houses and killed 561 people.

The explosions at Texas City in 1947 occurred in two ships, the Grandcamp and the High Flyer, both of which were carrying ammonium nitrate (Case History A16). They damaged thousands of buildings, hurled missiles several miles and killed 552 people. The fires burned for nearly a week.

17.26.2 TNT explosion model

The blast characteristics of a TNT explosion are important in their own right and are also sometimes used in modelling other types of explosion. There is available much more information on explosions of explosives, particularly TNT, than for other cases.

Sources of information on the blast characteristics from the explosion of TNT charges include *Structural Defence* (Christopherson, 1946), *The Effects of Nuclear Weapons* (Glasstone, 1962; Glasstone and Dolan, 1980), *Explosive Shock in Air* (Kinney, 1962; Kinney and Graham, 1985), *Hazards of Chemical Rockets and Propellants Handbook* (Jensen, 1972), *Explosions in Air* (W.E. Baker, 1973) and *Explosion Hazard and Evaluation* (W.E. Baker *et al*., 1983) and work by Hoffman and Mills (1956), Goodman (1960), Kingery and Pannill (1964), Kingery (1966), Swisdak (1975) and Kingery and Bulmash (1984).

In principle, the blast characteristics of a TNT explosion depend on the mass and shape of the charge and also on the point(s) of ignition.

For a TNT explosion the two standard types of reference data are those for explosions from a point source and from a spherical charge. The blast parameters for the two explosions are slightly different. For overpressure, for example, the initial effect of a finite charge size is to reduce the overpressure very close to the charge relative to that from a point source. This effect holds for a distance of some five charge diameters. At greater distances, however, the overpressure from a spherical charge is greater, being approximately equivalent to that from a point source with one-third greater energy release.

Other features which affect the blast characteristics include the location relative to sea level and the meteorological conditions.

There is a degree of scatter in the experimental results for condensed phase explosions, including TNT explosions. W.E. Baker *et al*. (1983, figures 2 and 3) give for high explosives a plot of peak overpressure vs scaled distance for which the highest and lowest curves of peak overpressure differ in parts by almost an order of magnitude. The most recent data on the plot was from W.E. Baker (1973). On the other hand, work on the measurement of peak overpressure from TNT explosions has continued, and it is to be expected that the more recent results are more accurate.

The two reference standards for data on a TNT explosion are a free air burst (where the blast wave is not affected by interaction with the ground), which has spherical symmetry, and a surface burst, which has hemispherical symmetry.

The principal parameters of the blast wave from a TNT explosion are the peak side-on overpressure p°, the impulse of the positive phase i, the duration of the positive phase t_d and the arrival time t_a. Values of these parameters may be presented in scaled or unscaled form. The scaled forms are those given in Equations 17.25.13, 17.25.22, 17.25.17 and

17.25.16, respectively. Thus, the unscaled and scaled forms of the parameters in SI units are:

	Unscaled	*Scaled*
Peak overpressure	p°(Pa)	$p_s = p^\circ/p_a(-)$
Impulse	i_p (Pa s)	$i_s = i_p/W^{1/3}$(Pa s/kg$^{1/3}$)
Duration time	t_d (s)	$\tau_d = t_d/W^{1/3}$ (s/kg$^{1/3}$)
Arrival time	t_a (s)	$\tau_a = t_a/W^{1/3}$ (s/kg$^{1/3}$)

where p_a is atmospheric pressure (Pa) and W is the mass of explosive (kg).

Values for TNT explosion parameters which appear to have gained general acceptance are those determined at the Ballistics Research Laboratory, Aberdeen Proving Ground, Maryland, by Kingery and co-workers (Kingery and Pannill, 1964; Kingery, 1966). A review of the data from this and other work has been made by Kingery and Bulmash (1984), who give data and correlations both for free air bursts and surface bursts.

Figure 17.59(a) is a plot of the four parameters mentioned for a free-air burst (spherical symmetry) based on the data of Kingery and Bulmash. The graph is plotted in terms of the scaled parameters p_s, i_s, τ_d and τ_a. Figure 17.59(b) is the corresponding plot for a surface burst (hemispherical symmetry), again from Kingery and Bulmash.

Other widely used values for TNT explosions are those of W.E. Baker *et al.* (1983) and Kinney and Graham (1985). Baker *et al.* give a graph (their figure 2.45) for free-air bursts which is broadly similar to Figure 17.59(a), but which also includes several other parameters. Kinney and Graham give a graph for peak overpressure and data in tabular form for all four parameters treated here.

Work quoted by Kingery and Bulmash includes that of Goodman (1960), Kingery (1966), W.E. Baker (1973), Swisdak (1975) and Reisler, Pettit and Kennedy (1976, 1977), and that quoted by Kinney and Graham includes that of Hoffman and Mills (1956), Goodman (1960), Keefer *et al.* (1966) and Kingery (1966).

Table 17.25 shows a comparison of the values for free-air bursts by Kingery and Bulmash with those of Kinney and Graham.

As an illustration of the use of the Figure 17.59, consider the determination from Figure 17.59(a) for a free-air burst of the values of the peak overpressure p° and the impulse i_p for a charge weight W of 8 kg of TNT at a distance of 10 m with ambient pressure 1.01×10^5 Pa. Then

$$
\begin{aligned}
z &= 10/8^{1/3}\\
&= 5\,\text{m/kg}^{1/3}\\
p_s &= 0.31\\
p^\circ &= p_s \times p_a\\
&= 0.31 \times 1.01 \times 10^5\\
&= 0.313 \times 10^5\,\text{Pa}\\
i_s &= 3.6 \times 10^{-4}\,\text{Pa s kg}^{1/3}\\
i_p &= i_s \times W^{1/3}\\
&= 3.6 \times 10^{-4} \times 8^{1/3}\\
&= 7.2 \times 10^{-4}\,\text{Pa s}
\end{aligned}
$$

The original graphs given by Kingery and Bulmash are plots showing the unscaled parameters p°, i_p, t_d and t_a for an explosion involving 1 kg of TNT ($W = 1$). The graphs given in Figure 17.59 are the same plots but with the parameters shown as scaled.

Also shown on the full curve in Figure 17.59(a) are the effects on the peak overpressure, in the far field of surface temperature inversion, labeled 1, and unstable atmosphere, z. Under surface temperature inversion conditions there can be a two- or three-fold increase in peak overpressure.

The variation of the blast parameters may also be expressed in the form of equations. Kingery and Bulmash use for the peak overpressure p°, impulse i_p, duration time t_d and arrival time t_s of a 1 kg explosion of TNT correlations of the following form. For a given parameter ϕ the relations are

$$U = a + b \log_{10} z \qquad [17.26.1]$$

$$\log_{10} \phi = \sum_{i-0}^{n} c_i U_i \qquad [17.26.2]$$

The values of the constants in these equations given by these authors are shown in Table 17.26. In these equations the units of the parameters are as shown in the table.

Kinney and Graham have given their values of the peak overpressure, impulse and duration time from an explosion of 1 kg of TNT in the form of network equations. In SI units for the scaled peak overpressure p_s

$$p_s = \frac{808[1 + (z/4.50)^2]}{[1 + (z/0.048)^2]^{1/2}[1 + (z/0.32)^2]^{1/2}[1 + (z/1.35)^2]^{1/2}} \qquad [17.26.3]$$

for the impulse

$$i_p = \frac{0.067[1 + (z/0.23)^4]^{1/2}}{z^2[1 + (z/1.55)^3]^{1/2}} \qquad [17.26.4]$$

and for the scaled duration time

$$\frac{t_d}{W^{1/3}} = \frac{980[1 + (z/0.54)^{10}]}{[1 + (z/0.02)^3][1 + (z + 0.74)^6][1 + (z/6.9)^2]^{1/2}} \qquad [17.26.5]$$

where p_s is the scaled peak overpressure, i_p is the impulse (bar ms), t_d is the duration time (ms), W is the mass of explosive (kg) and z is the scaled distance (m/kg$^{1/3}$).

It has already been mentioned that the blast parameters for a surface burst (hemispherical symmetry) can be obtained from those for a free-air burst (spherical symmetry) by using in the relations for the latter a charge weight suitably modified to account for the concentration of energy into the hemisphere rather than the sphere. The presumption is that this yield ratio, or symmetry factor, should be 2, and it is this value which is commonly used.

Table 17.27 gives a comparison between values of the peak overpressure, impulse and duration time for a surface burst calculated directly from the surface burst model and values calculated from the free-air burst model using a

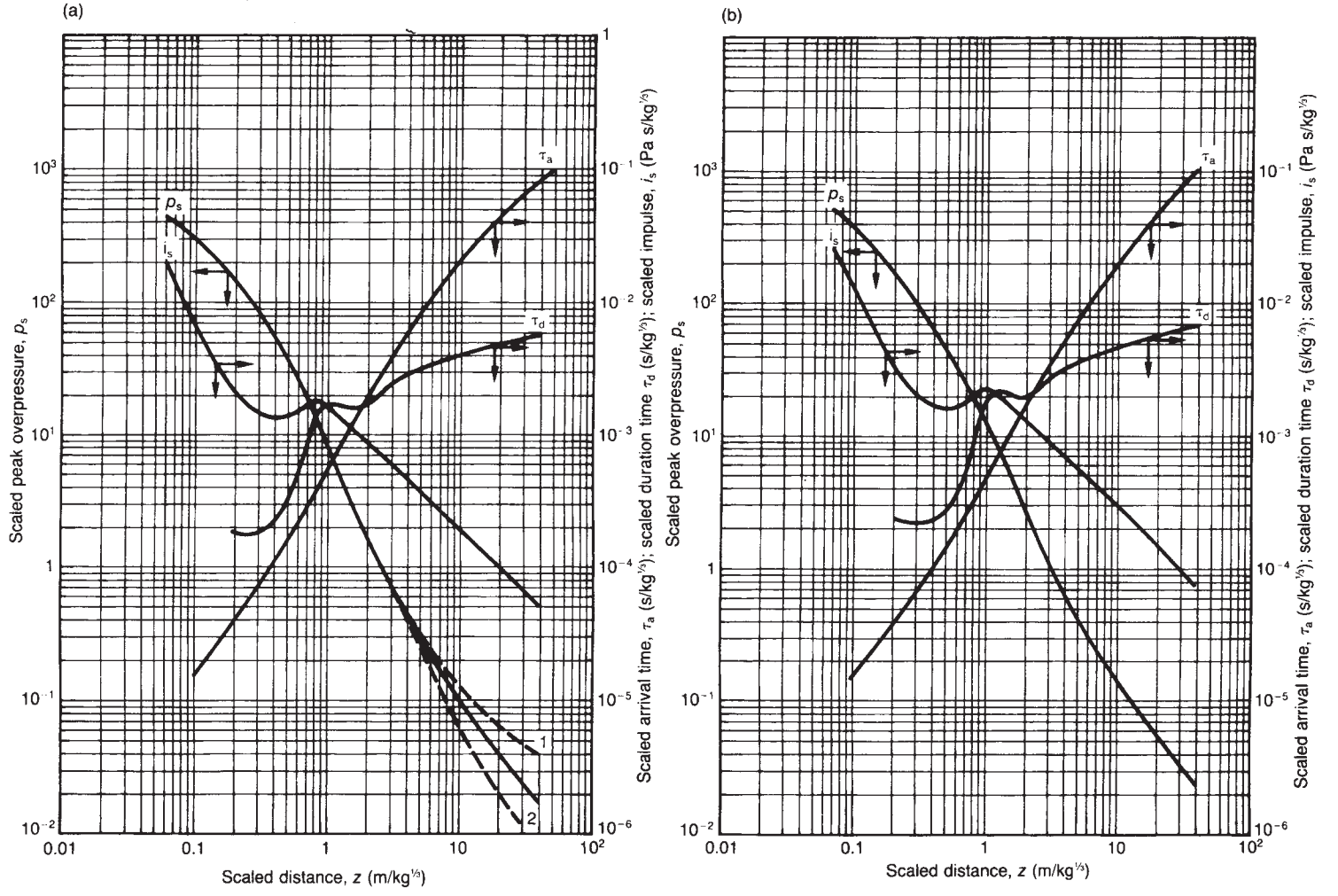

Figure 17.59 *Some side-on blast parameters for a TNT explosion (after Kingery and Bulmash, 1985): (a) free air burst (spherical symmetry and (b) surface burst (hemispherical symmetry)*

Table 17.25 *Some values*[a] *of the side-on blast parameters for a free-air explosion of TNT*

Scaled distance, z ($m/kg^{1/3}$)	*Peak overpressure,* p° (Pa)		*Impulse,* i_p (Pa s)		*Duration time,* t_d (s)	
	K&B	*K&G*	*K&B*	*K&G*	*K&B*	*K&G*
0.5	38.8×10^5	39.0×10^5	1.41×10^2	1.07×10^2	3.20×10^{-4}	0.84×10^{-4}
1.0	9.35×10^5	9.83×10^5	1.75×10^2	1.02×10^2	1.79×10^{-3}	0.52×10^{-3}
5	0.313×10^5	0.285×10^5	4.06×10^1	3×10^1	3.33×10^{-3}	2.47×10^{-3}
10	0.111×10^5	0.097×10^5	2.11×10^1	1.51×10^1	4.20×10^{-3}	3.47×10^{-3}
40	0.017×10^5	0.021×10^5	5.30	4.0	6.16×10^{-3}	4.15×10^{-3}

[a] K&B, Kingery and Bulmash (1985); K&G, Kinney and Graham (1985).

Table 17.26 *Constants in correlations of side-on blast parameters for an explosion of TNT of Kingery and Bulmash*

Range constant		*Parameter*			
		p° (kPa)	i_p (kPa ms)	t_d (ms)	t_a (ms)
A	**Free air burst**				
1		$0.0531 \le z \le 40$	$0.0531 \le z \le 0.792$	$0.147 \le z \le 0.888$	$0.0531 \le z \le 40$
2		–	$0.792 \le z \le 40$	$0.888 \le z \le 2.28$	–
3		–	–	$2.28 \le z \le 40$	–
1	a	−0.214 362 789 151	2.347 239 213 54	2.263 672 684 96	−0.253 273 111 999
2		–	−1.753 056 603 15	−1.333 612 067 14	–
3		–	–	−3.130 058 053 46	–
1	b	1.350 342 499 93	3.242 990 664 75	5.115 885 543 05	1.374 070 437 77
2		–	2.306 292 318 03	9.299 628 861 1	–
3		–	–	3.152 472 536 4	–
1	c_o	2.611 368 669	2.388 305 167 57	−0.686 608 550 419	0.072 070 778 763 7
2		–	1.551 972 271 15	0.230 318 410 78	–
3		–	–	0.621 036 276 475	–
1	c_1	−1.690 128 013 9	−0.443 749 377 691	−0.164 953 518 069	1.364 568 712 14
2		–	0.404 632 920 88	−0.029 794 426 896 9	–
3		–	–	0.096 703 199 555 2	–
1	c_2	0.008 049 735 919 51	0.168 825 414 684	0.127 788 499 497	−0.057 003 569 278 4
2		–	0.014 272 194 608 2	0.030 632 954 294 1	–
3		–	–	−0.008 013 020 596 67	–
1	c_3	0.336 743 114 941	0.034 813 803 030 8	0.002 91 430 135 946	−0.182 832 224 796
2		–	0.009 123 663 166 17	0.018 340 557 407 4	–
3		–	–	0.004 827 057 797 32	–
1	c_4	−0.005 162 263 513 34	−0.010 435 192 824	0.001 879 574 492 27	0.011 885 143 601 4
2		–	−0.000 675 068 140 4	−0.017 396 466 628 6	–
3		–	–	0.001 875 872 722 87	–
1	c_5	−0.080 922 861 988 8	–	0.017 341 396 254 3	0.043 264 868 762 7
2		–	−0.008 008 637 189 01	−0.001 063 219 635 76	–
3		–	–	0.002 467 385 093 21	–
1	c_6	−0.004 785 072 667 47	–	0.002 697 397 580 43	−0.000 799 736 783 4
2		–	0.003 148 195 159 31	0.005 620 600 312 8	–
3		–	–	−0.000 841 116 668	–
1	c_7	0.007 930 304 722 42	–	−0.003 619 765 027 98	−0.004 360 735 550 33
2		–	0.001 520 447 833 82	0.000 161 821 749 9	–
3		–	–	0.000 619 329 105 2	–
1	c_8	0.000 768 446 973 5	–	−0.001 009 265 779 34	–
2		–	0.000 747 026 589 9	−0.000 686 018 894 4	–
3		–	–	–	–

Table 17.26 (*continued*)

B	Surface burst				
1		$-0.0674 \leq z \leq 40$	$0.0674 \leq z \leq 0.955$	$0.178 \leq z \leq 1.01$	$0.0674 \leq z \leq 40$
2		–	$0.995 \leq z \leq 40$	$1.01 \leq z \leq 2.78$	–
3		–	–	$2.78 \leq z \leq 40$	–
1	a	−0.214 362 789 151	2.067 619 08721	1.929 461 540 68	0.202 425 716 178
2		–	−1.947 088 467 47	−2.124 925 252 16	
3		–	–	−3.536 262 180 91	–
1	b	1.350 342 499 93	3.076 032 966 6	5.250 991 939 25	1.377 842 236 35
2		–	2.406 977 454 06	9.299 628 861 1	–
3		–	–	3.463 497 455 71	–
1	c_0	2.780 769 165 77	2.524 556 209 25	−0.614 227 603 559	0.059 163 428 804 6
2		–	1.672 816 458 63	0.315 409 245 784	–
3		–	–	0.686 906 642 409	–
1	c_1	1.695 898 874 1	−0.502 992 763 686	0.130 143 717 675	1.357 064 962 58
2		–	0.384 519 026 965	−0.029 794 426 897 6	–
3		–	–	0.093 303 530 400 9	–
1	c_2	−0.154 159 376 846	0.171 335 645 235	0.134 872 511 954	0.052 492 798 645
2		–	−0.026 081 670 630 1	0.030 632 954 288	–
3		–	–	−0.000 584 942 088 3	–
1	c_3	0.514 060 730 593	0.045 017 696 305 1	0.039 157 427 690 6	−0.196 563 954 086
2		–	0.005 957 987 538 22	0.018 340 557 408 6	–
3		–	–	−0.002 268 849 950 13	–
1	c_4	0.098 853 436 527 4	−0.011 896 462 640 2	−0.004 759 336 647 02	−0.060 177 005 228 8
2		–	0.014 544 526 107	−0.017 396 466 621 1	–
3		–	–	−0.002 959 085 915 05	–
1	c_5	−0.293 912 623 038	–	−0.004 281 445 980 08	0.069 636 027 089 1
2		–	−0.006 632 893 347 34	0.001 063 219 636 33	–
3		–	–	0.001 480 298 689 29	–
1	c_6	−0.026 811 234 501 9	–	–	0.021 529 749 009 2
2		–	−0.002 841 893 272 04	0.005 620 600 309 77	–
3		–	–	–	–
1	c_7	0.109 097 496 421	–	–	−0.016 165 893 078 5
2		–	0.001 364 481 622 7	0.000 161 821 749 9	–
3		–	–	–	–
1	c_8	0.001 628 467 563 11	–	–	−0.002 325 319 702 94
2		–	–	−0.000 686 018 894 4	
3		–	–	–	–
1	c_9	−0.021 463 103 024 2	–	–	0.001 477 520 675 24
2		–	–	–	–
3		–	–	–	–
1	c_{10}	0.000 145 672 338 2	–	–	–
2		–	–	–	–
3		–	–	–	–
1	c_{11}	0.001 678 477 522 66	–	–	–
2		–	–	–	–
3		–	–	–	–

Table 17.27 *Comparison of the side-on blast parameters for a surface explosion calculated (1) from a surface explosion relation and (2) from a free-air explosion relation*

Scaled distance, z ($m/kg^{1/3}$)	*Hemispherical model*			*Scaled distance, z* ($m/kg^{1/3}$)	*Spherical model using yield factor of 2*		
	p^o (Pa)	i_p (Pa s)	t_d (s)		p^o (Pa)	i_p (Pa s)	t_d (s)
0.5	48.7×10^5	1.66×10^2	2.81×10^{-4}	0.4	57.4×10^5	1.73×10^2	2.87×10^{-4}
2.5	1.72×10^5	1.09×10^2	2.36×10^{-3}	2	1.95×10^5	1.16×10^2	2.33×10^{-3}
5	0.432×10^5	5.93×10^1	3.79×10^{-3}	4	0.465×10^5	6.27×10^1	3.86×10^{-3}

yield ratio of 2, based on the Kingery and Bulmash data for these two cases. Thus, in using the free-air burst model, the modified charge weight used is $2W$, which introduces a correction factor of $2^{1/3}$ ($= 1.26$). The scaled distance to be used for the free-air burst case is therefore that for the surface burst case divided by 1.26. The scaled parameters are then obtained. No further correction is required for the peak overpressure, which is scaled not by charge weight but by ambient pressure, but for the two parameters for which charge weight (or rather its cube root) is the scaling factor, the impulse and the duration time, the scaled values are multiplied by 1.26 to convert them to the unscaled values.

17.26.3 TNT explosion model: methods of Baker *et al.*

Work on the correlation of blast parameters which is frequently utilized is that of W.E. Baker *et al.* (1983). Some discussion of their treatment is therefore necessary.

Using Hopkinson scaling Equation 17.25.8 the authors present TNT graphs for (1) side-on blast parameters, (2) normally reflected blast parameters and (3) additional side-on blast parameters (their figures 2-45, 2-46 and 2-47, respectively). These graphs cover a large number of blast parameters and a wide range of scaled distance.

In the second method or energy scaling described earlier in W.E. Baker *et al.* (1975), the scaled distance is expressed as

$$\bar{R} = r\left(\frac{p_o}{E_{ex}}\right)^{1/3} \qquad [17.26.6]$$

where E_{ex} is the explosion energy (J), p_o is the absolute pressure of the ambient air (Pa), r is the distance (m) and $\bar{R}$ is the scaled distance. The scaled overpressure is defined as

$$\bar{P}_s = \frac{p_s}{p_o} - 1 \qquad [17.26.7]$$

where p_s is the absolute peak side-on pressure (Pa) and $\bar{P}_s$ is the scaled peak side-on overpressure. The scaled impulse is defined as

$$\bar{I} = \frac{i_s a_o}{P_o^{2/3} E_{ex}^{1/3}} \qquad [17.26.8]$$

where a_o is the speed of sound in the gas (m/s), i_s is the side-on impulse (Pa s) and $\bar{I}$ is the scaled side-on impulse.

Figures 17.60 and 17.61 show the curves for scaled peak side-on overpressure and scaled impulse given by W.E. Baker *et al.* (1975) for pentolite.

The actual peak side-on overpressure $\bar{P}_s$ and side-on impulse $\bar{T}$ are then obtained from Equations 17.26.7 and 17.26.8.

This second method, utilizing Equations 17.27.7–17.27.9, is also that used by Baker and co-workers for the treatment of vessel burst explosions and vapour cloud explosions, as described in Sections 17.27 and 17.28, respectively.

17.26.4 TNT equivalent model

In the absence of models for other types of explosion, such as vessel burst or vapour cloud explosion, it has frequently been the practice to model such explosions by estimating the energy of the explosion, calculating the TNT equivalent and then treating the explosion as if it were one from a TNT charge, a TNT equivalent model.

For example, the TNT equivalent model was used by Brasie and Simpson (1968) in an investigation of vapour cloud explosions.

However, the characteristics of the blast from the explosion of a TNT charge are significantly different from those given by other explosions. The pressure developed by a TNT explosion confined within the boundaries of the charge is of the order of half a million bar, which is very much higher than that within a bursting vessel or vapour cloud.

Comparing the profile of the peak overpressure from a TNT explosion with that from a vapour cloud explosion, in the near field the peak overpressure of the TNT explosion is higher, in the far field it is less. One consequence of this is that the use of the TNT equivalent model is not conservative in the far field.

The duration time of a TNT explosion is relatively short. This contrasts with a vapour cloud explosion, for which the duration time, and hence the impulse, is longer. This is another feature which is not conservative in the use of the TNT equivalent model.

A further discussion of the application of the TNT equivalent model to vapour cloud explosions is given in Section 17.28.

17.27 Vessel Burst Explosions

Turning now to types of explosion more typical of process plant, consideration is given first to vessel bursts in which the energy of explosion derives from the pressure in the vessel and the explosion is essentially physical rather than chemical.

17.27.1 Experimental studies

Only a small amount of experimental work on the bursting of gas-filled vessels is reported in the literature. Boyer *et al.* (1958) performed tests on the bursting of small gas-filled

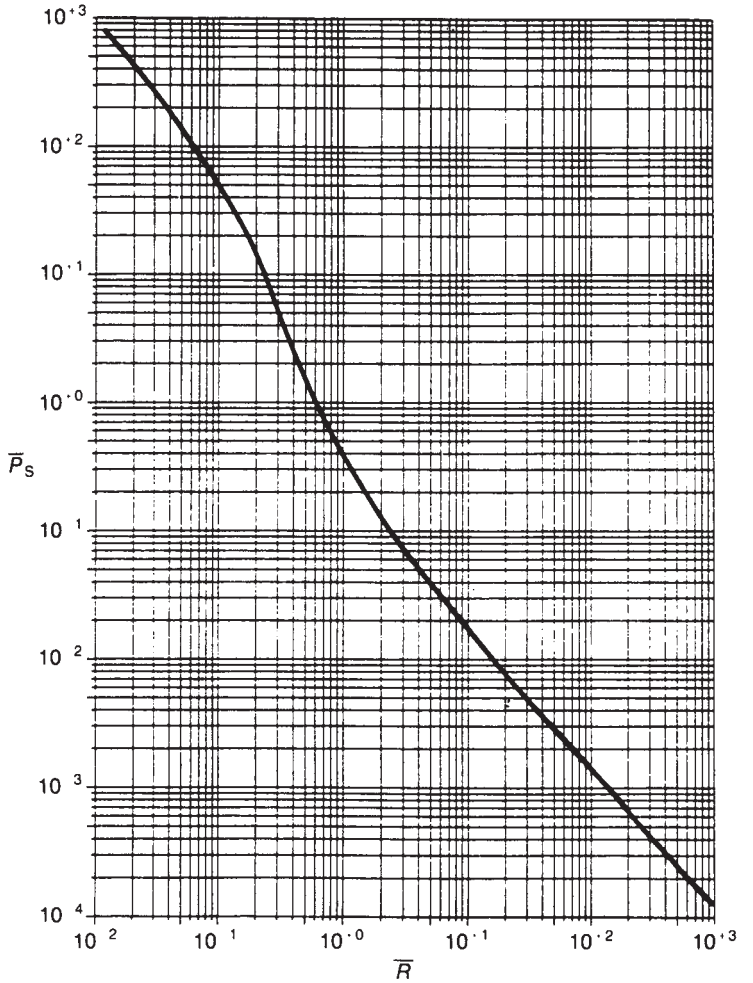

Figure 17.60 *Scaled peak side-on overpressure (W.E. Baker et al., 1975)*

glass spheres. Another set of small scale experiments using such apparatus is that of Esparza and Baker (1977). In this latter work the spheres ranged up to 102 mm in diameter and the burst pressures up to 5.25 MPa.

Experiments with metal containers were conducted by Pittman (1972a,b), using volumes up to 0.17 m^3. The burst pressures were about 4 MPa for cylindrical vessels and 55 MPa for spherical ones. Subsequently, Pittman (1976) carried out tests on 0.28 m^3 metal spheres with burst pressures up to 100–345 MPa.

17.27.2 Empirical features

This work brings out several relevant empirical features.

The work of Pittman (1972a,b), which involved high pressures, demonstrates the need to take into account in estimating the energy of explosion for such cases the non-ideal behaviour of the gas. The differences between the behaviour of the blast wave from a condensed phase explosion and that from a vessel burst are illustrated in the work of Esparza and Baker (1977), who found that for the latter the blast wave tended to have a lower overpressure, a longer positive phase duration, a larger negative impulse and a stronger second shock.

17.27.3 Vessel burst pressure

The explosion energy in a vessel burst is a function of the initial pressure, which in turn depends on the failure scenario. The higher the pressure, the larger the explosion.

Three cases may be distinguished: (1) overpressure, (2) mechanical failure and (3) fire engulfment.

If the vessel fails because it is exposed to a high operating pressure and because the pressure relief has failed, the vessel will burst at a pressure which is some factor of the design pressure, typically for mild steel a factor of 4. This is the worst case.

If a mechanical failure of the vessel occurs, which may be due to a metallurgical defect, corrosion or impact, the burst pressure will be the operating pressure.

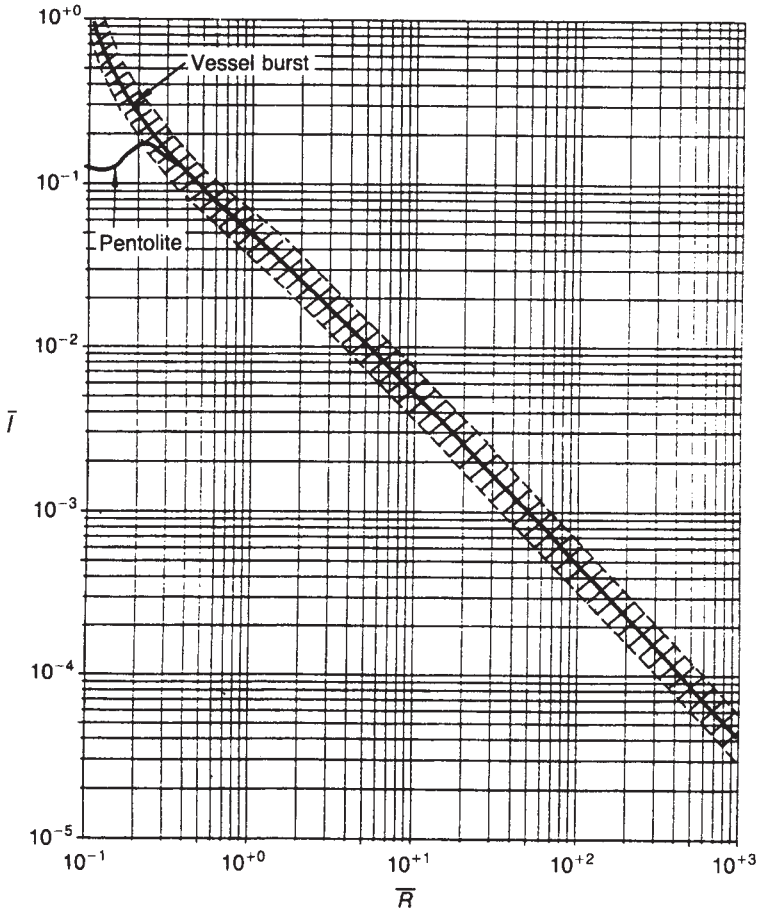

Figure 17.61 *Scaled side-on impulse for a pentolite explosion (W.E. Baker et al., 1975)*

If the vessel fails due to fire engulfment, but with the pressure relief operating, the pressure at burst will be the accumulation pressure. This is the typical scenario of a BLEVE.

17.27.4 Vessel burst energy distribution

The estimation of the energy of the explosion in a vessel burst is discussed below, but it is appropriate first to consider briefly the distribution of this energy.

In principle, the energy available will be partitioned as energy in (1) vessel expansion, (2) vessel rupture, (3) blast and (4) fragments.

If failure is due to high operating pressure, some expansion of the vessel occurs. However, this can be neglected both because the energy is provided to the system prior to the burst and because it is very small anyway.

Some energy is required to rupture the vessel, but this too is very small. The Centre for Chemical Process Safety (CCPS) gives a value of 1–10 kJ for the rupture of a pressure vessel; an explosion with 100 times this energy would still be regarded as small.

Essentially therefore, the energy available goes into the blast and the fragments. The proportion which goes as kinetic energy in the fragments has been briefly discussed in Section 17.4 and is considered again in Section 17.34.

17.27.5. Vessel burst modelling

There have also been studies involving the numerical and analytical modelling of vessel bursts. In some cases the main interest of the work has been with other types of explosion for which the bursting of a gas-filled sphere serves as a limiting case.

Investigations involving numerical and parametric modelling have been described by W.E. Baker *et al.* (1975), Erode (1955), Adamczyk (1976), Guiraio and Bach (1979), Chushkin and Shurshlov (1982) and Raju and Strehlow (1984).

The study most relevant here is that of W.E. Baker *et al.* (1975), who conducted a parametric exploration of vessel bursts and developed a method of estimating the blast parameters analogous to that for a condensed phase explosion.

Also of interest is the work of Adamczyk (1976) which indicates that vessel burst explosions approximate in the far field to condensed phase explosions only for high pressure and temperature ratios.

The investigation by Guiraio and Bach (1979) was concerned with fuel–air explosions. They studied cases of a combustion process in which the reactants are converted instantaneously to products and found that for such cases only some 27–37% of the combustion energy was converted to work.

Raju and Strehlow (1984) studied the effect of a non-spherical source in the form of a combustible gas mixture. The initial gas cloud had the form of an ellipse rotated on its major axis, or spheroid oriented with its major axis perpendicular to the ground. The lead shock wave was elliptical but tended towards sphericity as the wave moved out. This is explained by the facts that the strength of the initial shock wave varied with the direction and that strong shock waves tend to travel faster than weak ones.

17.27.6. Model of Baker *et al.*: basic method

A method for the estimation of the blast parameters for the bursting of a gas-filled pressure vessel is now described. The method is that of W.E. Baker *et al.* (1975), and relates to a free-air burst of a massless spherical vessel containing an ideal gas. The background to this method has just been described and the account here concentrates on its application.

The explosion energy is obtained from the Erode model given as Equation 17.4.29.

Applying the second method of Baker and co-workers, based on Equations 17.26.6–17.26.8, the scaled distance R is calculated, using Equation 17.26.6.

The scaled peak overpressure is then obtained from Figure 17.62(a), using the curve for high explosive, and the scaled impulse from Figure 17.63, or from Figure 17.61, which covers a wider range.

The actual peak side-on overpressure p_s and side-on impulse i_s are then obtained from Equations 17.26.7 and 17.26.8.

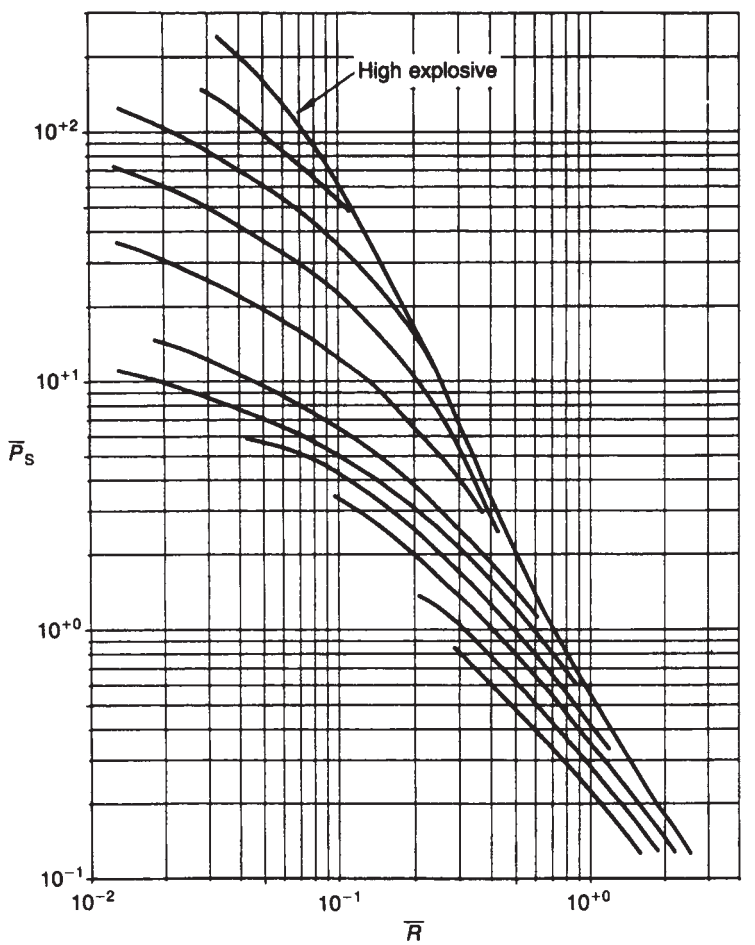

Figure 17.62 *Scaled peak side-on overpressure for a vessel burst explosion (W.E. Baker et al., 1975)*

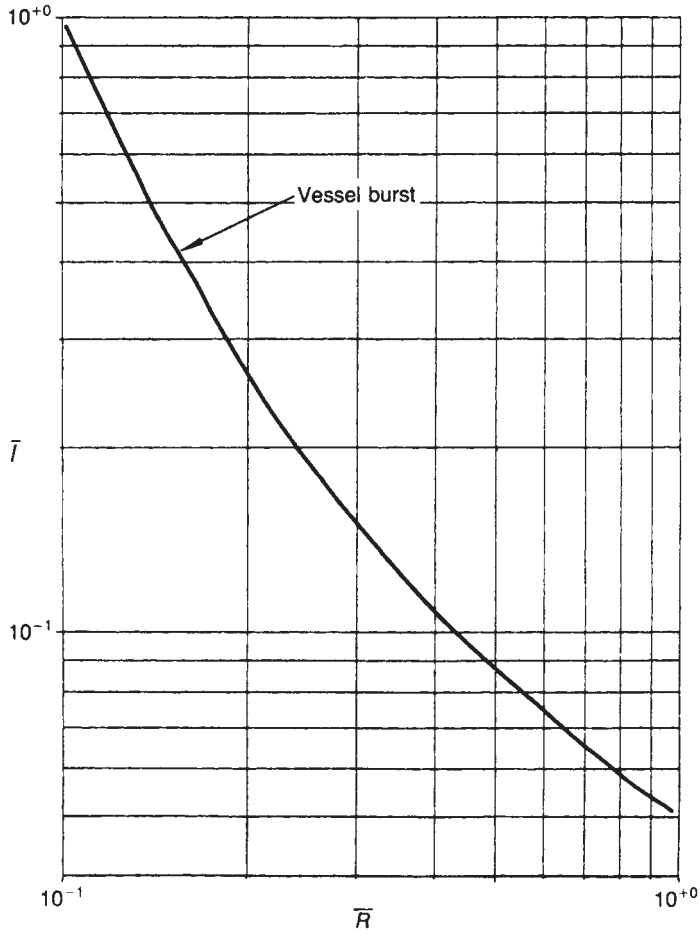

Figure 17.63 *Scaled side-on impulse for a vessel burst explosion (W.E. Baker et al., 1975)*

This method is oriented to the estimation of the blast parameters in the far field, and its accuracy in the near field is limited. There are two checks which should be made with regard to the latter.

The first check is on the value of the scaled distance $\bar{R}$. If this is less than 2, use should be made of a modification to the method appropriate for the near field, which is described below. The other check is on the value of the peak side-on overpressure p_s, discussion of which is deferred.

The near field modification is as follows. First an effective radius for the equivalent hemisphere formed by the initial gas volume is calculated:

$$r_o = \left(\frac{3V_1}{2\pi}\right)^{3/4} \qquad [17.27.1]$$

where r_o is the effective radius of the equivalent hemisphere (m) and V_1 is the volume of the gasified vessel (m^3). The corresponding scaled distance $\bar{R}_o$ is then calculated using Equation 17.26.6. The peak side-on overpressure is then determined using, in conjunction with Equation 17.26.7, the relation

$$\frac{p_1}{p_o} = (\bar{P}_{so} + 1)\left(1 - \frac{(\gamma_1 - 1)(a_o/a_1)\bar{P}_{so}}{\{2\gamma_o[2\gamma_o + (\gamma_o + 1)]\bar{P}_{so}\}^{1/2}}\right)^{-2\gamma_1/(\gamma_1 - 1)} \qquad [17.27.2]$$

where a is the velocity of sound (m/s), p_o is the absolute pressure of the ambient air (Pa), p_1 is the absolute initial pressure of the gas (Pa), $\bar{P}_{so}$ is the scaled peak side-on overpressure at $\bar{R}_o$, γ is the ratio of the specific heats and subscripts o and 1 denote ambient air and compressed gas in the vessel, respectively.

Equation 17.27.2 is an implicit equation. It may be solved by the usual methods for such equations. Alternatively, use may be made of graphs given for convenience by the authors. One of these is shown in Figure 17.64.

The method then proceeds as follows. The pair of values of $\bar{R}$ and $\bar{P}_{so}$ is used to locate the 'starting point' on

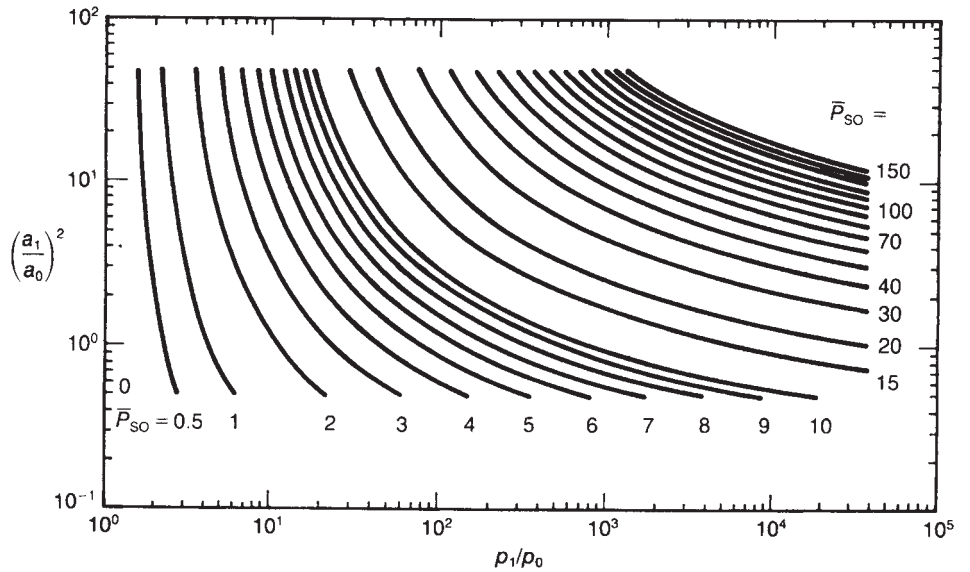

Figure 17.64 *Scaled peak side-on overpressure in the near field for a vessel burst explosion (W.E. Baker et al., 1975).* $\gamma_1 = 1.4$

Figure 17.62. This identifies a particular curve in the family of curves on Figure 17.62 and this curve is then used in making further estimates of the scaled peak overpressure.

As indicated earlier there is a further check to be made, on the value of the peak side-on overpressure p_s. It is possible that the value calculated for p_s exceeds the initial pressure in the vessel. If so, p_s should be set equal to this initial pressure.

17.27.7 Model of Baker *et al.*: extensions of method

As already stated, the method just described applies to the free-air burst of a massless spherical vessel containing an ideal gas. There are several extensions which may be needed in practical cases. These relate to (1) non-ideal fluids, (2) energy imparted to fragments, (3) bursts at ground level and (4) other vessel geometries.

For the ideal gas case, the energy of explosion is obtained from the Erode model as given in Equation 17.4.29. For the cases of non-ideal gas, vapour or flashing liquid use should be made of the alternative method described in Section 17.4.

This gives the total energy available. Any energy imparted to the fragments should then be subtracted from this value to obtain the energy participating in the blast.

For the case of a burst at ground level, this blast energy is then multiplied by the usual factor of 2 before it is used in Equations 17.26.6 and 17.26.8 to obtain the blast wave parameters. Baker *et al.* have given sets of adjustment factors for two types of departure from the basic model. One set is for use with cylindrical as opposed to spherical vessels. The other set is for a spherical vessel slightly elevated above the ground. These are shown in Table 17.28.

Table 17.28 *Method of Baker et al. for blast parameters from a vessel burst: adjustment factors (W.E. Baker et al., 1975)*

A Adjustment factors for cylindrical vessels

$\bar{R}$	*Multiplier for:*	
	$\bar{P}_s$	$\bar{I}$
<0.3	4	2
$0.3 \leq \bar{R} \leq 1.6$	1.6	1.1.1
$1.6 \leq \bar{R} \leq 3.5$	1.6	1
>3.5	1.4	1

B Adjustment factors for spherical vessels slightly elevated above the ground

$\bar{R}$	*Multiplier for:*	
	$\bar{P}_s$	$\bar{I}$
<1	2	1.6
>1	1.1	1

17.27.8 COPS method

The CCPS *Fire and Explosion Model Guidelines* (1994/15) include as part of the method for a BLEVE a method for vessel burst explosions. The energy of the explosion is obtained using the CCPS method for that described in Section 17.4. The blast parameters are then obtained using the method of Baker and co-workers described in Section 17.27.6 with the extension given in Section 17.27.7. The *Guidelines* give sample problems for BLEVEs in which use is made of the vessel burst model. These problems are described in Section 17.3.2.

17.28 Vapour Cloud Explosions

When a cloud of flammable vapour burns, the combustion may give rise to an overpressure or it may not. If there is no overpressure, the event is a vapour cloud fire, or flash fire, and if there is overpressure, it is a vapour cloud explosion (VCE).

A VCE is one of the most serious hazards in the process industries. VCEs do occasionally occur and they tend to be very destructive.

A feature of a vapour cloud is that it may drift some distance from the point where the leak has occurred and may thus threaten a considerable area.

The relative importance of the VCE hazard has grown in recent years. Whereas in the early days of the chemical industry the largest disasters tended to be those caused by explosives, including ammonium nitrate, many of the largest disasters are now due to VCEs.

Accounts of VCEs include those given in *Unconfined Vapour Cloud Explosions* (Gugan, 1979), *Explosion Hazard and Evaluation* (W.E. Baker *et al.* 1983), *Fuel–Air Explosions* (Q.H.S. Lee and Guirao, 1982a) and *Major Chemical Hazards* (V.C. Marshall, 1987) and those by Brasie and Simpson (1968), Strehlow (1973b), Strehlow and Baker (1976), V.C. Marshall (1976a,c,d), Davenport (1977b, 1983), Kletz (1977d), J.H.S. Lee *et al.* (1977), Slater (1978a), Wiekema (1980, 1983a,b, 1984), J.H.S. Lee (1983), Pikaar (1983) and Rasbash (1986b).

Until the early 1980s a VCE was generally referred to as an unconfined vapour cloud explosion (UVCE). However, since in combustion of a vapour cloud the occurrence of overpressure tends to occur due to the presence of structures and obstacles and of partial confinements, the term 'unconfined' is now generally omitted.

There are many gaps in the state of knowledge on VCEs and there is no completely satisfactory theoretical model, although much progress has been made in modelling. The practical approaches tend to combine theoretical and empirical inputs.

In this section consideration is confined to the characteristics of the explosion itself. The effects of the explosion are considered below.

The energy of the explosion of a vapour cloud is normally computed as the product of the heat of combustion and a yield factor, as described in Section 17.4 and discussed further below. In this section the energy of explosion, or explosion energy, is used in this sense.

Selected references on VCEs are given in Table 17.29.

17.28.1 Vapour cloud explosion incidents

There are a number of compilations of major VCEs. V.C. Marshall (1987) gives details of some 11 such compilations. The principal lists are those of Strehlow (1973b), Davenport (1977b, 1983), Gugan (1979), the ACMH (Harvey, 1979b), Wiekema (1983a,b, 1984) and Lenoir and Davenport (1992). The account by Davenport (1977b) also lists incidents in which a vapour cloud formed but did not explode.

It is emphasized by their compilers that the lists may be incomplete, since the extent to which incidents are reported varies between different countries. Where the lists include unignited vapour clouds, these are particularly likely to be incomplete, since such clouds are often not reported.

Table 17.29 *Selected references on vapour cloud explosions*

HSE/SRD (HSE/SRD/WP28); Ministry of Defence (n.d.); Stokes (1849); Sachs (1944); G.B. James (1947–49); Whitham (1950); Toland (1957); Thornhill (1960); Glasstone (1962); Laderman, Urtiew and Oppenheim (1963); Reider, Otway and Knight (1965); Urtiew, Laderman and Oppenheim (1965); F.A. Williams (1965, 1976a, 1983); Bulkley and Jacobs (1966); Struck and Reichenbach (1967); Brasie and Simpson (1968); Strehlow (1968a,b, 1971, 1973a,b, 1975, 1981); Bach, Knystautas and Lee (1969, 1971); Benedick, Morosin and Kennedy (1971); D.J. Lewis (1971, 1980c,d); R.P. Anderson and Armstrong (1972, 1974); Ford (1972); Oppenheim, Kuhl and Kamel (1972a,b); J.A. Brown (1973); Kuhl, Kamel and Oppenheim (1973); Strehlow, Savage and Vance (1973); Beaubois and Demand (1974); Coevert *et al.* (1974); Collins (1974); Decker (1974); Geiger (1974, 1982, 1983, 1986, 1987); Monday and Cave (1974); Tanimoto (1974); Anon. (1975d); Eisenberg Lynch and Breeding (1975); Kletz (1975c,e, 1977j, 1979b, 1986l); J.H.S. Lee, Knystautas and Guirao (1975); J.H.S. Lee *et al.* (1975); Leyer, Guerraud and Manson (1975); Lind (1975); Lind and Strehlow (1975); V.C. Marshall (1975d, 1976a–d, 1977a,b,d, 1982d, 1987); Monday (1975a,b, 1976a,b, 1979); R.J. Parker (1975); Sadee (1975); Samuels and O'Brien (1975); Strehlow and Baker (1975, 1976); D.C. Bull *et al.* (1976); Gugan (1976, 1979, 1980a,b); Guirao, Bach and Lee (1976); Harvey (1976, 1979b); W.G. High (1976); Nettleton (1976, 1977c, 1980a,b, 1987); Sadee, Samuels and O'Brien (1976–77); Strehlow and Ricker (1976); Anthony (1977a); Chiu, Lee and Knystautas (1977); V.J. Clancey (1977a,c); Davenport (1977a,b, 1983); Eichler and Napadensky (1977); Fay and Lewis (1977); Hertzberg *et al.* (1977); Kolodner (1977a); J.H.S. Lee (1977, 1980, 1983b); J.H.S. Lee *et al.* (1977); J.G. Marshall (1977, 1980); Maurer *et al.* (1977); Auton and Pickles (1978, 1980); HSE (1978b, 1980 TP 7, 1981a); Slater (1978a); M.W. Taylor, Lind and Cece (1978); Benedick (1979, 1982); D. Bradley (1979); D.C. Bull (1979, 1982a,b, 1992); Girard *et al.* (1979); Nicholls *et al.* (1979); Strehlow, Luckritz *et al.* (1979); TNO (1979); Ale and Burning (1980); van den Berg (1980, 1982, 1985); Cronenberg and Benz (1980); Diaconicolaou Mumford and Lihou (1980); Fumarola *et al.* (1980); Geiger and Synofzyk (1980a,b); Giesbrecht *et al.* (1980); Houweling (1980); J.H.S. Lee and Moen (1980); Wiekema (1980, 1983a,b, 1984); C.W. Wilson and Boni (1980); Zalosh (1980a, 1982); Zeeuwen and Schippers (1980); Considine (1981); R.A. Cox (1981); Eidelman *et al.* (1981); Fishburn, Slagg and Lu (1981); Oran, Boris *et al.* (1981). Phillips (1981b, 1982, 1986, 1987, 1989); Scilly (1981); Ebert and Becker (1982); Funk *et al.* (1982); Geiger (1982, 1987); J.H.S. Lee and Guirao (1982a); Leyer (1982); Moen (1982b, 1993); Moen, Murray *et al.* (1982); Oran, Boris *et al.* (1982); Oran, Young *et al.* (1982); A.F. Roberts and Pritchard (1982); Urtiew (1982a,b); H.G. Wagner (1982); D.G. Bowen (1983); CEC (1983 EUR 8482 EN, 1984 EUR 8955 EN, EUR 9593 EN, EUR 9541 EN/I and EN/II, EUR 9592 EN); Elsworth, Eyre and Wayne (1983, 1984); Fredholm (1983); Hasegawa and Sato (1983); Hertzberg and Lamrevik (1983); Mackenzie (1983 SRD R262); Nikodem (1983); Pickles and Bittleston (1983); Pikaar (1983, 1985); Schildknecht and Geiger (1983); Spalding (1983); Urtiew, Brandeis and Hogan (1983); C.J.M. van Wingerden and Zeeuwen (1983, 1986); Benedick, Knystautas and Lee (1984); J.R. Bowen *et al.* (1984a,b); Brossard *et al.* (1984); Fry and Book (1984); M.R.O. Jones (1984); J.H.S. Lee, Kynstautas and Freiman (1984); Moen *et al.*

(1984); Raju and Strehlow (1984); Schildknecht, Geiger and Stock (1984); Ungut, Schuff and Eyre (1984); Brandeis (1985); Catlin (1985); Prugh (1985–, 1987a–c); P.H.Taylor (1985a,b); Elsworth and Eyre (1986); A. Evans and Puttock (1986); Jaggers *et al.* (1986); Mudan (1986); Ogiso, Fujita and Uehara (1986); Ogiso *et al.* (1986); Pasman and Wagner (1986); Rasbash (1986b); AIChE (1987/66); van den Berg *et al.* (1987); Nettleton (1987); Skarka (1987); Giesbrecht (1988); Zeeuwen and van Wingerden (1988); Lannoy and Leroy (1989); J.B. Moss (1989); Pu, Mazurkiewicz *et al.* (1989); Puttock (1989); C.J.M. van Wingerden (1989a,b); C.J.M. van Wingerden, van den Berg and Opshoor (1989); C.J.M. van Wingerden, Opschoor and Pasman (1990); Q.A. Baker and Baker (1991); van den Berg, van Wingerden and The (1991a,b); Carnasciali *et al.* (1991); Clerehugh (1991); D.M. Johnson, Sutton and Wickens (1991); C.R. Kaplan and Oran (1991); K.G. Phillips and Henshelwood (1991); Pineau *et al.* (1991); Sawides and Tarn (1991); J.E. Shepherd, Melhem and Athens (1991); Tieszen *et al.* (1991); K. van Wingerden, Visser and Pasman (1991); Buckmaster and Lee (1992); Giesbrecht *et al.* (1992); Mancini (1992); van den Berg and Lannoy (1993); Kinsella (1993); Lenoir and Davenport (1993); Leyer *et al.* (1993); Mercx, van den Berg and The (1993); Mercx, van Wees and Opschoor (1993); Madsen and Wagner (1994); K. van Wingerden, Pedersen and Wilkins (1994)

Selected experimental work

Fuel–air explosions: Kiwan (1970a,b, 1971)

Early field trials of combustion in unconfined vapour clouds: Lutzke (1971); Humbert-Basset and Montet (1972); AGA (1974); MITI (1976); Raj, Moussa and Aravamuden (1979a,b)

Early work on detonation in unconfined vapour clouds: Lind (1975); D.C. Bull, Ellsworth and Hooper (1979a,b)

Combustion in unconfined vapour clouds – closely controlled tests: Lind and Whitson (1977); Deshaies and Leyer (1981); Okasaki, Leyer and Kageyama (1981); Schneider and Pfortner (1981); Brossard *et al.* (1985); R.J. Harris and Wickens (1989)

Combustion in unconfined vapour clouds – field trials: Blackmore, Eyre and Summers (1982); MIT-GRI Safety and Res. Workshop (1982); Goldwire *et al.* (1983); Hirst and Eyre (1983); Zeeuwen, van Wingerden and Dauwe (1983)

Combustion in vapour clouds with obstructions – closely controlled tests: Dorge, Pangritz and Wagner (1981); C.J.M. van Wingerden and Zeeuwen (1983); A.J. Harrison and Eyre (1986, 1987a); R.J. Harris and Wickens (1989)

Combustion in vapour clouds with obstructions – field trials: Zeeuwen, van Wingerden and Dauwe (1983)

Jet ignition of vapour clouds: Schildknecht and Geiger (1982); Schildknecht (1984); Schildknecht *et al.* (1984); Stock and Geiger (1984); Moen *et al.* (1985); A.J. Harrison and Eyre (1987a); McKay *et al.* (1988)

Combustion of turbulent jets: Seifert and Giesbrecht (1986); Stock (1987)

Combustion following vessel burst: Giesbrecht *et al.* (1981)

Combustion of a pipeline leak: Hoff (1983)

Hydrogen explosions

Bulkley and Jacobs (1966); Berman (1982); Tamm, Harrison and Kumar (1982); L. Thompson (1982); Hawksley (1986 LPB 68); V.C. Marshall (1987)

Suppression by water sprays

Acton, Sutton and Wickens (1990); D.C. Bull (1992); Brenton, Thomas and Al-Hassan (1994)

As mentioned above, VCEs have come to increasing prominence. Strehlow (1973b) lists the numbers of vapour cloud explosions as follows:

1930–39, 4
1940–49, 12
1950–54, 17
1955–59, 17
1960–64, 18
1965–69, 25
1970–72 (Jan.), 15

The *Second Report* of the ACMH (Harvey, 1979b) refers to Strehlow's work and to more recent data and comments that the frequency of VCEs has increased from about four per decade to a rate of over 60 per decade.

Some principal VCE incidents are given in Table 17.30. The estimates of the quantities released in the table are given as quoted in the literature; most appear to refer to the total quantity originally in the containment, but may in some cases refer to the flammable vapour in the cloud. Other incidents are given in Table A1.2. Further lists of VCE incidents illustrating particular points are given in Tables 17.33 and 17.34 below. Experimental work on VCEs is listed in Table 17.31.

Four VCEs in particular have been particularly influential. In 1967 a very destructive VCE occurred at the refinery at Lake Charles in Lousiana after an escape of liquid isobutylene due to a valve failure; there were seven deaths (Case History A40). The fires burned for 2 weeks. In 1968 a slops tank in the refinery at Pernis in the Netherlands boiled over and the explosion of the resultant vapour cloud killed two people and destroyed an appreciable fraction of the refinery (Case History A41). Another massive VCE took place in 1970 at Port Hudson, Missouri, where liquid propane leaked from a pipeline into a valley; on this occasion there were no fatalities (Case History A52).

In 1974 in Flixborough in the United Kingdom a large escape of cyclohexane from a temporary pipe on a train of reactors gave rise to a vapour cloud which exploded with a TNT equivalent of some 16 te. The explosion demolished much of the works and killed 28 people, and the fires burned for over a week. This incident, which is described in Appendix 2, was particularly influential in the development of major hazard controls in the United Kingdom and in the EC.

These were not, however, the first major VCEs. Two major explosions which occurred earlier at Ludwigshafen, Germany, in 1943 and 1948, were more destructive of human life, resulting, respectively, in 57 and 207 deaths. In the second incident the explosion was caused by an escape of dimethyl ether when a rail tank car overheated in the sun and burst (Case History A17). For this explosion the TNT equivalent has been estimated as 20 te.

VCEs have continued to occur. Also, in 1974, only a few months after Flixborough, there was an escape of propane following a rail tank car accident in a marshalling yard at Decatur, Illinois, which caused seven deaths and did extensive damage (Case History A71).

In 1975 at Beek in the Netherlands an escape of propylene, apparently from brittle fracture of a feed drum on a depropanizer, gave rise to a VCE which killed 14 and caused extensive damage to the works (Case History A75).

Table 17.30 *Some incidents involving vapour cloud fires and VCEs*

Date	*Location*[a]	*Chemical*	*Mass released*[b] (te)	*TNT equivalent*[c] (te)
1939	Newark, NJ	Butane		
1943	Ludwigshafen, Germany	Butadiene, butylene	16.5[d]	
1945	Los Angeles, CA	Butane		
1948	Ludwigshafen, FRG	Dimethyl ether	30	20
1949	Detroit, IL	Propane, butane	1.6	
1951	Baton Rouge	HCs		
1953	Campana, Argentina	Gasoline		
1954	Portland, OR	LPG	250 m^3	
1955	Freeport, TX	Ethylene	0.68–1.36	
	Wilmington, CA	Butane		
1956	Baton Rouge, LA	Butylene	10	
	North Tonawanda, NY	Ethylene	2.5	
1957	Sacramento, CA	LPG		
1958	Ardmore, OK	Propane		
	Augusta, GA	LPG		
1959	Meldrin, GA	LPG	18	
1961	Freeport, TX	Cyclohexane	18	0.025
	Lake Charles, LA	Butane		
1962	Berlin, NY	Propane	14.3	
	Fawley, UK			
	Houston, TX	Gasoline		
	Ras Tanura, Saudi Arabia	Propane	1.1	
1963	Plaquemine, LA	Ethylene		0.9
1964	Jackass Flats, NV	Hydrogen	0.09	0.027
	Liberal, KS	Propane		1.0
	Orange, TX	Ethylene	0.18	0.27
1965	Baltimore	Benzene		
	Baton Rouge, LA	Ethyl chloride	19.3	135–180
	Escambia, USA	Hydrogen, carbon monoxide	(0.070)	(0.012)
	Lake Charles, LA	Methane or ethylene		
1966	Raunheim, FRG	Methane	1–1.5	2.7
	Scotts Bluff, LA	Butadiene	0.45	
1967	Lake Charles, LA	Isobutylene	9	12
1968	Pernis, Netherlands	Light HCs	55–110	20
1969	Escombreras, Spain	Propane		(0.012)
	Fawley, UK	Hydrogen, naphtha	23	
	Glendora, MS	VCM		
	Houston, TX	Natural gas		
	Texas City, TX	Butadiene		
1970	Big Springs, TX			
	Linden, NJ	Hydrogen, HCs	114	45
	Port Hudson, MO	Propane	27–55	45
1971	Baton Rouge, LA	Ethylene	3.6	0.45
	Houston, TX	Butadiene	12	
	Longview, TX	Ethylene	0.45	0.5
1972	East St Louis, IL	Propylene	53.5	2.5
1973	Gladbeck, FRG			
	Noatsu, Japan	VCM	4.2	0.2
	St-Amand-les-Eaux, France			
	Tokuyama, Japan	Ethylene		
1974	Beaumont, TX	Isoprene	7.6	0.9
	Climax, TX	VCM	110	
	Cologne, FRG	VCM		
	Decatur, IL	Isobutane	69	20–125
	Fawley, UK	Ethylene	0.9–2.7	
	Flixborough, UK	Cyclohexane	36	18
	Holly Hill, FL	Propane		
	Houston, TX	Butadiene	<80	20–57
	Petal, MO	Butane		
	Roumania	Ethylene		
	Zaluzi, Czechoslovakia	Ethylene		

Table 17.30 *(continued)*

Date	*Location*[a]	*Chemical*	*Mass released*[b] (te)	*TNT equivalent*[c] (te)
1975	Antwerp, Belgium	Ethylene	2.5	
	Beek, Netherlands	Propylene	5.5	2.2
	Cologne, FRG	Hydrogen, naphtha		
	Eagle Pass, TX	LPG	18.2	
	Rosendaal, Netherlands	Gasoline	25–50	1.0
	Watson, CA	Hydrogen	0.3	0.018
1976	Longview, TX	Ethylene		
1977	Baytown, TX	Gasoline	300	
	Brindisi, Italy	Light HCs		
	Dallas, TX	Isobutane	68.2	1.6
	Port Arthur, TX	Propane		
1978	Abqaiq, Saudi Arabia	Methane, then LPG		24
	Denver, CO	Propane		
	Immingham, UK	Syngas	0.2–0.3	0.03
	Pitesti, Roumania	Propane, propylene		
	Poblado Tres, Mexico	Natural gas		
1979	Texas City, TX	Propane	3.1	0.9
	Torrance, CA	C_3–C_4s		
	Ypsilanti, MI	Propane		
1980	Borger, TX	Light HCs		
	Enschede, Netherlands	Propane	0.11	
	New Castle, DE	Hexane, propylene	12.7	
1981	Czechoslovakia	Syngas		
	Gothenburg, Sweden	Propane	30–40 m^3	
1982	Philadelphia, PA			
1983	Port Newark, NJ	Gasoline		
1984	Romeoville, IL	Propane		
	Sarnia, Ontario	Hydrogen	0.03	0.91
1985	Cologne, FRG	Ethylene		4.1
	Edmonton, Alberta	NGL	4900 m^3	
	Lake Charles, LA	Propane		
	Mont Belvieu, TX	Ethane, propane		
1987	Pampa, TX	Acetic acid, butane		
	Ras Tanura, Saudi Arabia	Propane	300 m^3	0.9
1988	Beek, Netherlands	Ethylene		
1988	Norco, LA	Light HCs	9	
	Raines, Norway	VCM	25	
		Ethylene dichloride	30	
1989	Baton Rouge, LA	Ethane, propane, butane		11–14
	Minnebeavo, USSR	Propane		
	Pasadena, TX	Isobutane	37.8	
	Ufa, USSR	NGL		10,000
1990	Cincinnati, OH	Xylene, solvent		
	Maharastra, Bombay	Ethane, propane		
	Porto de Leixhas, Portugal	Propane		
	Tomsk, USSR	Gas		
1991	Kensington, GA	Butadiene		
	Pajaritos, Mexico	Propane		
	Seadrift, TX	Ethylene oxide		

[a] Further details are given in Appendix 1, including Table A1.2.
[b] Source: Lenoir and Davenport (1992).
[c] Source: Lenoir and Davenport (1992), supplemented (values in parentheses) by values from Gugan (1979).
[d] V.C. Marshall (1987).

One of the most serious VCEs in recent years, however, has been that of a cloud of isobutane vapour at Pasadena, Texas, in 1989, which caused 23 fatalities and resulted in as serious a business loss as Piper Alpha. This incident, is described in Appendix 6.

Also, in 1989 there occurred at Ufa in the Soviet Union a vapour cloud explosion much more disastrous in human terms (Case History A127).

17.28.2 Empirical features

Some observations and generalizations can be made by analysing explosion incidents.

A compilation of VCE incidents and corresponding statistical data has been presented by Davenport (1977b). These data relate to 43 incidents where overpressures were created, of which 32 were in industrial plant, 8 in transport and 3 elsewhere. Of those in industrial plant,

Table 17.31 *Some experimental work on vapour cloud explosions*

Investigators	*System*	*Gas*
A Combustion of dispersed vapour clouds		
A1. Work on fuel–air explosions		
Kiwan (1971a,b, 1971)		
A2. Early field trails of combustion in unconfined vapour clouds		
Lützke (1971)	Field test site	
Humbert-Basset and Montet (1972)	Field test site	LNG
AGA (1974)	Field test site	LNG
Raj, Moussa and Aravamuden (1979)	Field test site	LNG
MITI (1976)	Field test site	Ethylene
A3. Early work on detonation in unconfined vapour clouds		
Lind (1975)	Balloons	Methane, propane
D.C. Bull, Elsworth and Hooper (1979a.b)	Field test site	Methane, ethane
A4. Combustion in unconfined vapour clouds: closely controlled tests		
Deshaies and Leyer (1981)	Soap bubbles	Methane, propane, ethylene
Okasaki, Leyer and Kageyama (1981)	Soap bubbles	Ethylene
Lind and Whitson (1977)	Hemispherical balloons	Various, including methane, acetylene
Brossard *et al.* (1985)	Spherical balloons	Ethylene, acetylene
Schneider and Pförtner (1981)	Hemispherical balloons	Hydrogen
R.J. Harris and Wickens (1989)	Tent-type rig, 45 m long	Natural gas, propane, cyclohexane, ethylene
A5. Combustion in unconfined vapour clouds: field trials		
Blackmore, Eyre and Summers (1982); Hirst and Eyre (1983)	Field test site	LNG, propane
MIT-GRI (1982); Goldwire *et al.* (1983)	Field test site	LNG
Zeeuwen, van Wingerden and Dauwe (1983)	Field test site	Propane
A6. Combustion in vapour clouds with obstructions: closely controlled tests		
Dörge, Pangritz and Wagner (1981)	Apparatus with wire mesh	Methane, propane, acetylene
A.J. Harrison and Eyre (1986, 1987a)	Cylindrical sector, see Figure 17.65	Natural gas, propane
R.J Harris and Wickens (1989)	Tent-type rig, 45 m long	Natural gas, cyclohexane
C.J.M. van Wingerden and Zeeuwen (1983)	Single plate supporting 1 cm vertical obstacles	Methane, propane, ethylene, acetylene
A7. Combustion in vapour clouds with obstructions: field trials		
Zeeuwen, van Wingerden and Dauwe (1983)	Vertical sewer pipes, diameter 1 m, height 2 m	Propane
A8. Combustion in partially confined vapour clouds without or with obstructions: work using tubes		
Chapman and Wheeler (1926, 1927)	Pipe, 50 mm diam., 2.4 m length, with orifice plates	Methane
Dörge, Pangritz and Wagner (1981)	Pipe, 40 mm diam., 2.5 m length, with orifices	Methane
C. Chan *et al.* (1980)	Pipes: (1) 63 mm diam., 0.45 length; (2) 152 mm diam., 1.22 m length; both with orifices	Methane
Moen, Lee *et al.* (1982)	Pipe, 2.5 m diam., 10 m length	Methane
Hjertager (1984)	As Moen, Lee *et al.* (1982)	Propane
J.H.S. Lee, Knystautas and Chan (1984)	Pipe, 50 mm diam., 11 m length	Hydrogen
Hjertager, Bjorkhaug and Fuhre (1988b)	As Hjertager (1984)	Propane
A9. Combustion in partially confined vapour clouds without or with obstructions: work using parallel plates		
Moen, Donato, Knystautas and Lee (1980); Moen, Donato, Knystautas, Lee and Wager (1980)	Two plates, 2.5 m diam., with tube obstacles	Methane, Hydrogen sulphide
C.J.M. van Wingerden and Zeeuwen (1983)	Two plates 0.6 × 0.6 m, with 'forest'-type obstacles	Methane, propane

Table 17.31 *(continued)*

Hjertager (1984)	Disc, 1 m diam., with flat and pipe-type obstacles	Methane, propane
C.J.M. van Wingerden (1984)	Two plates 2 × 4 m, with cylindrical obstacles	Ethylene
A10. Combustion in partially confined vapour clouds without or with obstructions: work using channels		
Urtiew (1981)	Open channel, with baffles	Propane
C. Chan, Moen and Lee (1983)	Channel, variable top opening, with obstracles	Methane
Elsworth, Eyre and Wayne (1983)	Open channel, some work with baffles	Propane
Sherman *et al.* (1985)	Channel, variable top opening, with obstacles	Propane
P.H. Taylor (1986)	Channel, variable top opening, with obstacles	Propane
A11. Jet ignition of vapour clouds		
Schildknecht and Geiger (1982); Schildknecht (1984); Schildknecht *et al.* (1984); Stock and Geiger (1984)	Enclosure, 1×1×4 m: (1) tent-type enclosure; (2) open top channel	Ethlyene, hydrogen
Moen *et al.* (1985)	Ballon	Acetylene
A.J. Harrison and Eyre (1987a)	Cylindrical sector, see Figure 17.65	Natural gas
McKay *et al.* (1988)		
B Combustion of turbulent jets		
Seifert and Giesbrecht (1986)	Jet	Natural gas, hydrogen
Stock (1987)	Jet	Propane
C Combustion following vessel burst		
Giesbrecht *et al.* (1981)	Vessels, 0.226–1.01	Propylene
D Combustion of a pipeline leak		
Hoff (1983)	Gas pipeline	Natural gas

8 were in refineries and 24 in the petrochemical industries.

The sources of spill material in the industrial plant incidents were:

Process equipment 24
Storage tank 4
Transportation vehicle within plant 3
Unknown 1

The modes of release for all incidents were:

Vessel failure 13
Piping, valves or fittings failure 26
Release from venting facilities 3
Unknown 1

In a further paper, Davenport (1983) has given additional incidents but without statistical data.

Some questions which are capable of resolution by an empirical approach are

(1) frequency of release;
(2) quantity of material released;
(3) fraction of material vaporized;
(4) probability of ignition of cloud;
(5) distance travelled by cloud before ignition;
(6) time delay before ignition of cloud;
(7) probability of explosion rather than fire;
(8) existence of a threshold quantity for explosion;
(9) efficiency of explosion.

Early discussions of these problems were given by Strehlow (1973b), V.C. Marshall (1976a) and Kletz (1977j).

An early but fairly comprehensive treatment of the empirical features of vapour cloud explosions was given by Kletz (1977j), and this is now described. He gives estimates of the frequency of such explosions as shown in Table 17.32. A special pipeline is one on which special care can be taken, such as a short pipe without pumps or other intervening equipment between two vessels. A severe duty pump is one on a very hot or very cold liquid. The figure for pressure vessel failure is based on the data of Phillips and Warwick (1968 UKAEA AHSB(S) R162) and Engel (1974).

On items where the frequency of leaks is high there is a strong case for emergency isolation valves. The fitting of emergency isolation valves on a normal pipeline is usually impractical, but may well be justified on a pump. Kletz suggests that if a remotely controlled emergency isolation valve is fitted, it may be assumed that it will be operated within 5 min, but that if only a local isolation is available, it should be assumed that it will not be operated and that the leak continues until it is isolated by other means or until all the inventory has leaked out.

The material escaping may be a gas, or a volatile liquid, superheated or subcooled. Flashing superheated liquids

tends to give rise to the largest vapour clouds. Most VCEs have been caused by such flashing liquids. It is suggested by Kletz that the fraction vaporized be obtained from the common rule of thumb that the amount of liquid spray formed equals the amount of vapour formed by adiabatic flash. Thus, if the fraction of liquid vaporized is as high as a half, this assumption implies that all the liquid turns into vapour and spray.

There are few data from which the probability of ignition can be estimated. Kletz suggests that for large leaks (>10 t) this probability is greater than 1 in 10 and perhaps as high as 1 in 2. For small leaks the probability of ignition is much less. Kletz quotes a value of 10^{-4} for small leaks on polyethylene plants, where the high pressure causes good jet mixing.

The distance drifted by a cloud of flammable vapour depends on the situation. The drift determines the explosion centre and the blast intensity near this. It has less effect on the blast intensity further away. Kletz states that there is no reported case of a cloud drifting a significant distance in a factory before exploding. He suggests that the assumption of no drift is probably good enough for most calculations but that a drift of 100 m may occur in 1 case in 5 or 10. The distance drifted by the cloud before ignition is unlikely to be great in any industrial or urban area.

In open situations with few sources of ignition the vapour cloud may drift much further. In the Port Hudson explosion (NTSB 1972 PAR-72-01) the cloud travelled 1500 ft in a long plume before igniting. In the flash fire at Austin (NTSB 1973 PAR-73-04), ignition did not occur until the cloud had travelled 2400 ft. Data on the distance travelled by the vapour cloud in 81 rail tank car spills have been given by G.B. James (1947–48), who states that 58 % found a source of ignition within 50 ft and 76 % within 100 ft and all which ignited did so within 300 ft.

A separate but related question is the time delay before ignition. Strehlow (1973b) states that a delay as long as 15 min has been reported. The quantity of material which can accumulate in this time may be very large. The explosion can be a large one, however, even if the time delay is short. The delay before ignition at Flixborough was probably in the range 30–90 s. An estimate of 45 s has been widely quoted.

In many instances the cloud is formed from a turbulent momentum jet. This was the case at Flixborough. In such situations the cloud may reach an equilibrium size within about 10–20 s. Once such a steady state has been reached, the mass of material available in the cloud for combustion does not increase, even if there is an appreciable delay before ignition.

The probability that ignition will cause an explosion rather than a flash fire depends on complex factors, some of which are discussed below. Kletz states that there is about one serious VCE every 2 years; Strehlow reports about five VCEs/flash fires per year and these two factors in combination perhaps support the view that about one vapour cloud ignition in 10 gives an explosion.

A number of vapour releases have been analysed by V.C. Marshall (1976a), as shown in Table 17.33. The table indicates that whereas the larger releases have resulted in explosions, the smaller ones have produced fires instead. The data given show no explosions in clouds of less than 15 t. Marshall has also pointed out, however, that the explosion at Beek in 1975 involved a release of only about 5.5 t and therefore tends to undermine this argument. In addition, the data of Davenport (1977b) include a number of

Table 17.32 *Estimated frequencies of VCE (after Kletz, 1977j)*

		Frequency (explosions/ plant-year)[a]
(1)	Caused by failure of pressure vessel	10^{-5}[b]
	Pipeline – special pipeline	10^{-5}–10^{-4}
	–normal pipeline	10^{-4}–10^{-3}
	Pump – normal pump	10^{-2}
	– severe duty pump	10^{-1}
	Reciprocating compressor	10^{-1}
(2)	Caused by leak from	10^{-2}–10^{-1}
	Batch reactor	
	Tanker-filling house	10^{-2}–10^{-1}

[a] Plant is defined as a major unit such as ethylene or aromatics plant or collection of smaller units – something smaller than a typical UK works or US plant.
[b] The estimated failure rate of a pressure vessel is 10^5/vessel-year.

Table 17.33 *Some data on quantity released and on occurrence of fire or explosion in vapour clouds (after V.C. Marshall, 1976a)*

Location	*Date*	*Chemical* (t)	*Quantity*	*Deaths*	*Nature of incident*	*Further details*
Pernis, Netherlands	1968	Mixture of hydrocarbons	140	2	Explosion	Slopover
		Butane	77		Explosion	
		LNG	53		Explosion	
Lake Charles, LA	1967	Isobutane	46	7	Explosion	Accidental opening of large valve
		Propylene and propane	40		Explosion	
Port Hudson, MI	1970	Propane	29	0	Explosion	Pipeline break
Flixborough, UK	1974	Cyclohexane	25	28	Explosion	Process pipe break
		Butane	15.5		Fire	
		Butane	7.7		Fire	
Los Angeles, CA		Butane	2.0		Fire	
		Methane	1.0		Fire	
		Propane	0.06		Fire	

explosions of vapour clouds containing less than 15 t of flammable material.

The question of whether there is a minimum size of cloud below which an explosion will not occur has been much discussed, and a threshold quantity of 10–151 has been suggested.

It is argued by Kletz that there is no theoretical basis and no detailed survey to support the assumption that there is a threshold quantity for an explosion to occur. In one well-attested case a fraction of a ton of methane exploded, causing serious damage. Moreover, there have been a number of experiments with balloons filled with flammable mixtures in which violent explosions have been obtained with quantities of less than 1 t. Kletz concludes that although it may not be correct to assume a threshold quantity, the probability of an explosion certainly appears to be much less if the quantity is small. He suggests that if there are 10 t of vapour, the probability of explosion is at least 1 in 10, whereas if there is 1 t or less the probability of explosion is of the order of 1 in 100, or, more likely, 1 in 1000.

The ratio of the energy in the blast wave to the energy theoretically available from the heat of combustion, or efficiency of explosion, is another quantity about which much uncertainty exists. The fraction of the heat of combustion that is used to produce the blast wave usually lies between 1 and 10% based on the total mass released.

The Bureau of Mines is sometimes quoted as recommending the use of an explosion efficiency of 10%. Kletz points out, however, that this should be taken in conjunction with another recommendation that the quantity of material considered should be that leaking within 30 s.

Kletz suggests that is the release is fairly rapid, it is reasonable to assume an explosion efficiency of 1%, whereas if it is not, an overall efficiency becomes meaningless and it is necessary to attempt to calculate the amount within the flammable range and within congested regions.

Burgess and Zabetakis (1973 BM RI 7752) have given such a calculation for the Port Hudson explosion (Case History A52).

In some cases a much higher explosion efficiency has been reported. Davenport gives an explosion efficiency of 25–50% for a vapour cloud explosion at Decatur, Illinois, in 1974 but this value may well be anomalous; it is discussed in the account of the incident (Case History A71).

Values of the explosion efficiency, or yield factor, are not always quoted on the same basis, and this is a cause of variation in the figures. Sometimes the value quoted is based on the total amount of vapour in the cloud and sometimes on that part of the vapour which is within the flammable range. The two may differ by a factor of 10 or more. Thus, Kletz points out that although the yield factor at Port Hudson is widely quoted as being 20%, this is based on the part of the cloud which was within the flammable range. Based on the whole cloud the value is 7.5%. Further variability is introduced by the fact that the total quantity of vapour released is generally subject to uncertainty. A typical factor of uncertainty is 2.

Kletz'account of the empirical features of VCEs is intended primarily as a guide to plant design. It may be regarded as an integrated treatment such that using the various empirical values given the result obtained is reasonable. The application of the values may be less valid if used as part of an eclectic approach.

Kletz (1979b) has applied this approach to obtain guidance on plant layout. This was described in Chapter 10.

More recently, Wiekema (1984) has carried out a statistical study on some 165 vapour cloud ignitions. Incidents were not included where no ignition occurred or where ignition was virtually simultaneous with the release, as in a BLEVE. On the other hand, no incident was excluded simply because some information on it was lacking. The study is based on reported incidents and, as the author points out, is therefore a biased sample.

The features selected for analysis are given under the following headings: (1) mass, (2) reactivity, (3) ignition source, (4) drift, (5) explosion, (6) location, (7) delay, (8) fatalities, (9) injured, and (10) domino effects. The gas is classed as being of high, medium or low reactivity; the ignition sources as continuous or non-continuous; the combustion as a flash fire or explosion; the location as containing obstacles and therefore being semi-confined or as being free from obstacles and not semi-confined; and the situation as one where vulnerable objects were absent and a domino effect was not possible, where such objects were

Table 17.34 *Some principal statistical features of ignited vapour clouds of material of medium reactivity (after Wiekema, 1984) (Courtesy of Elsevier Science Publishers)*

	Explosion		*Flash fire*	
	No.	*Percentage*	*No.*	*Percentage*
Mass (kg)				
$<10^2$	0	3	1	4
10^2–10^3	6	14	3	12
10^3–10^4	15	43	10	38
10^4–10^5	12	31	7	27
$>10^5$	3	9	5	19
Ignition				
Continuous	13	65	12	55
Not continuous	7	35	10	45
Drift (m):				
$<10^2$	16	55	19	61
10^2–10^3	12	41	11	35
$>10^3$	1	4	1	4
Location				
Semiconfined	37	100	15	65
Unconfined	0	0	8	35
Delay (min)				
<1	5	25	3	14
1–5	7	37	10	48
6–15	5	25	3	14
16–30	3	16	0	0
>30	0	0	5	24
Fatalities				
0	21	39	24	50
1–5	19	35	17	36
6–15	8	15	5	10
16–50	5	9	2	4
>50	1	2	0	0
Injured				
0	7	15	15	44
1–5	10	22	12	35
6–15	9	20	3	9
16–50	11	24	3	9
>50	9	20	1	3

present and a domino effect occurred and where such objects were present but no domino effect occurred.

The results of the survey are shown in Figure 17.69. Since for many incidents some information was lacking, the number of cases given for each of the subfigures varies. Most of the releases were of medium reactivity materials. For these the analysis gave the results shown in Table 17.34.

Wiekema draws from his analysis the following conclusions:

(1) In 87 out of 165 incidents the distance within which ignition occurred was known. More than 60% of these 87 vapour clouds were ignited within 100 m from the location of the spill. In only 2% of these cases did the vapour cloud drift more than 1 km before ignition took place.
(2) In 150 out of 165 incidents it was known whether an explosion or flash fire occurred. In nearly 60% of these cases the ignition resulted in an explosion; in the other cases a flash fire occurred.
(3) In 143 out of 165 incidents the number of fatalities was known. In about 40% of these cases there were no fatalities and in 25% no one was hurt.
(4) The amount spilled did not influence the probability of an explosion for the investigated incidents in the spill range 1–100 te.
(5) Explosions occurred only in semi-confined situations and never in unconfined situations.
(6) A short delay time to ignition enhanced the probability of an explosion.
(7) For delay times to ignition larger than half-an-hour only flash fires occurred.
(8) Outside the combustible cloud no one was killed due to primary blast effects.
(9) For flash fires the number of injured was of the same order as the number of fatalities. For explosions the number of injured was one order of magnitude larger than the number of fatalities.

VCE is one of the hazards considered in the two Convey Reports. The treatment given in these reports is described in Appendix 7.

17.28.3 Combustion in vapour clouds

The combustion of vapour clouds in the open air was already a subject of research before the four major explosions just mentioned, but their occurrence provided a further stimulus to work on what was then generally referred to as unconfined VCEs.

Fundamental aspects of VCEs have been discussed by various authors, including Brasie and Simpson (1968), Strehlow (1973b), Gugan (1976, 1979), Munday (1976a,b), Anthony (1977a), V.J. Clancey (1977a), J.H.S. Lee *et al.* (1977), W.E. Baker *et al.* (1983), J.H.S. Lee (1983b), Pikaar (1983) and D.C. Bull (1992).

'Open-air' explosions usually occur with at least part of the vapour cloud in a congested region of a processing plant. Except in rare instances these explosions are deflagrations. Deflagrations can be highly damaging.

In the early work much attention centred on the question of detonation of the vapour cloud. Detonations are more damaging than deflagrations, but the distinction can often be expressed as detonations produce smaller fragments.

It is known that flame speeds obtained in vapour clouds are greater than the normal burning velocity. Strehlow quotes a burning velocity of 9 m/s for stoichiometric hydrogen–oxygen mixtures as measured on a bunsen burner and velocities of 68–120 m/s obtained using balloons. These velocities are typical of a flash fire rather than an explosion. The acceleration of the flame in a vapour cloud and the influence of factors such as apertures and turbulence has been the subject of many experiments. A major focus is to determine what degree of turbulation induction will accelerate flame speed to a deflagration let alone a detonation. Some of the problems associated with detonation are:

(1) which fuels have a high reactivity leading to detonations;
(2) existence of detonability limits;
(3) occurrence of unconfined detonation;
(4) direct initiation of detonation;
(5) characteristics of flame propagation;
(6) transition from deflagration to detonation.

Only a few fuels are considered highly reactive and can detonate lacking confinement. These include ethylene, acetylene, ethylene oxide and methyl nitrate.

There are in the literature statements to the effect that the limits of detonability are essentially the flammability limits. Thus, Burgess *et al.* (1968 BM RI 7196) state: 'A consensus has gradually developed that almost any gas mixture that is flammable is also detonable if initiated with a sufficiently energetic source.'

It has been shown, however, that detonability limits are in fact distinct from flammability limits, but they are more complex and more difficult to measure. Information on detonability limits for spherical detonation is especially sparse and the limits are a function of the strength of the ignition source. Detonability limits were discussed in Section 17.2 and are considered further below.

The violence of some VCEs suggests that they might well be detonations, but the occurrence of detonation as opposed to deflagration in an unconfined vapour cloud was for a long time considered to be highly unlikely, even impossible. However, in an account of the Port Hudson explosion Strehlow (1973b) stated: 'The Port Hudson explosion is a proven example of an accidental vapour-cloud detonation'. And again: 'There is no question but that detonation has occurred in accidental explosions, or that detonation can be initiated without delay in an unconfined cloud using a sufficiently strong ignition source.' He also stated: 'More commonly, the vapour cloud simply deflagrates. However, deflagration velocities are commonly observed to be quite high and extensive blast damage can occur even for this type of vapour-cloud combustion, particularly if the cloud contains a sufficiently large volume of combustible mixture at the time of ignition'.

The problem which concerned workers in this area, however, was the initiation of detonation. As Munday (1976a) commented: 'It seems highly unlikely that detonative combustion occurs in unconfined conditions unless a priming confined or condensed explosive source is ignited'.

In the Port Hudson explosion it is believed that the cloud may have been ignited by a strong ignition source in a building enveloped by the cloud.

As the debate developed in the mid-1970s there was some reversion to the view that detonation in vapour clouds is highly unlikely. There are difficulties in envisaging the mechanism by which the flame speed in an unconfined

cloud can accelerate to such a degree as to reach the speeds characteristic of detonation. The consensus view developed that if detonation occurs, it is likely to be associated with special circumstances, such as the occurrence of an initiating detonation within the cloud or interaction of the blast wave with structures, resulting in flame acceleration and higher local pressures.

The *Second Report* of the ACMH (Harvey, 1979b) probably represented current opinion in stating in its discussion of the Port Hudson incident: 'Since no other single case is on record, and many deliberate attempts to detonate unconfined hydrocarbon/air clouds have failed, it would seem more justifiable to regard the occurrence of true detonation in an unconfined vapour cloud as so improbable as to be disregarded for design purposes'.

As far as direct initiation of detonation is concerned, Strehlow states that direct initiation of detonation in a vapour cloud can occur if the ignition source is sufficiently strong, and quotes experiments which demonstrate this. This has since been confirmed by further research, including both work directed to determination of detonability limits and other work directed to vapour cloud detonation as such.

It is possible that a deflagration may turn into a detonation. The dominant view has been that this is difficult to envisage in a truly unconfined situation, but the shock waves to promote the transition might arise from interaction with structures.

Although much work has been done, and continues to be done, on the detonation of vapour clouds, the focus of attention has gradually shifted to the effect of confinement on the flame and, in particular, on the conditions which promote its acceleration to very high flame speeds.

The view which emerges from this work is that significant overpressure in vapour cloud combustion tends to be associated with a degree of confinement and that the extent of this overpressure is highly dependent on the details of the confinement.

With this model the mass of flammable gas available to participate in the explosion is not the total flammable mass but that part which is within the confinement.

Another feature which is better appreciated is the importance of the initial combustion zone. This may be envisaged as a spherical zone in which the flame front expands until it breaks through the envelope of the cloud. Once this happens, relief occurs and the pressure falls. It follows from this that the overpressure developed depends on features such as cloud height and vertical confinement.

Traditionally, vapour clouds have been treated as hemispherical, but in practice many vapour clouds are pancake shaped. Increasingly, this feature is being taken into account in studies of vapour cloud combustion.

It will be apparent from the foregoing that VCEs are not yet well understood. Experimental studies have therefore been undertaken to improve understanding, while design approaches have been developed based on correlation of empirical features. These aspects are now described.

17.28.4 Experimental studies

There is now a considerable body of experimental work on VCEs. Reviews include those of J.H.S. Lee (1983b), Pikaar (1985), D.C. Bull (1992) and the CCPS (1994/15).

Some experimental studies of vapour cloud fires and VCEs are given in Table 17.31. A listing of experimental work suitable for the testing of VCE models is given by Madsen and Wagner (1994).

The review by Pikaar (1985) covers (1) release phenomena, (2) vapour cloud generation and dispersion, (3) vapour cloud combustion, and (4) interactions. Vapour cloud combustion is divided into (1) combustion of premixed clouds and (2) combustion of fuel-rich clouds. The combustion of premixed clouds covers (1) combustion in open terrain, (2) influence of partial confinement and obstacles, and (3) pressure waves. The interactions considered are (1) the effect of deliberate dispersion by water sprays and (2) the effective lower flammability limit following dispersion.

In his review, D.C. Bull (1992) covers large scale work on both vapour clouds in the open and vapour mixtures in large enclosures such as modules, and gives the following classification of the research done:

State		*Phase*	
		Single	*Aerosol +hybrid*
'Unconfined'	Intially quiescent	A	B
	Initially turbulent	C	D
With congestion	Intially quiescent	E	(F)
	Initially turbulent	G	(H)
With congestion	Intially quiescent	I	J
	Initially turbulent	K	(L)
With congestion	Intially quiescent	M	(N)
and confinement	Initially turbulent	O	(P)

No large scale work was found in the classes shown in parentheses.

The review by the CCPS (1994/15) is under the following headings: (1) unconfined deflagration under controlled conditions, (2) unconfined deflagration under uncontrolled conditions and (3) partially confined deflagration.

A. Combustion of dispersed vapour clouds

A1. Work on fuel–air explosions. Much research has been done on the use of fuel–air explosion (FAE) weapons. Although this work is mainly in the military domain and unpublished, some accounts are available (e.g. Kiwan 1970a,b, 1971). Fuels used include ethylene oxide, propylene oxide, *n*-propyl nitrate and methyl acetylene/ propadiene/ propylene (MAPP). Further information is given by W.E. Baker *et al.* (1983).

A2. Early field trials of combustion in unconfined vapour clouds. Early work on the combustion of unconfined vapour clouds includes the field trials on liquified natural gas (LNG) described by Liitzke (1971), Humbert-Basset and Montet (1972), the American Gas Association (AGA) (1974) and Raj, Moussa and Aravamudan (1979a,b) and those on ethylene by the Ministry of International Trade and Industry (MITI) (1976).

The large scale tests on LNG carried out by Gaz de France (Humbert-Basset and Montet, 1972), described earlier, included experiments in which ignition sources were disposed at the edge of the cloud. The main purpose in this case was to obtain a cross-check on the cloud concentrations.

Tests on the explosion of ethylene–air mixtures in the open were carried out as part of the experiments, described earlier, conducted by MITI (1976) in Japan. In one test an ethylene–air mixture containing 4.08 kg of ethylene and giving a 7% mixture in air was held in a polyvinyl chloride tent and exploded by a detonator. The blast pressure was 4.9 bar at 5 m and 0.49 bar at 20 m distance. It was correlated by a straight line on a log–log plot of peak overpressure vs scaled distance. The TNT equivalent of the explosion was estimated as 49.2 kg. The duration time was 10 ms at 10 m distance. It was concluded that for flammable gas explosions the TNT equivalent model fits reasonably well for the peak overpressure, but that the duration time is rather longer.

A3. Early work on detonation in unconfined vapour clouds. A major theme in early research on VCEs was the definition of the conditions under which detonation might occur.

It is known that the transition from deflagration to detonation is difficult to induce in an unconfined vapour cloud, and investigations have concentrated on features which promote defregration to detonation transition (DDT), such as obstacles and partial confinement.

The problem was approached from two directions. One was the study of flame speeds in unconfined clouds. Work by Lind (1975) indicated early on that flame speeds, and overpressures, in truly unconfined vapour clouds are very low.

Other work was directed to the study of the potential modes of detonation and the conditions for their occurrence. This includes research on (1) the direct initiation of detonation, (2) the deflagration to detonation transition (DDT), (3) the effect of obstructions and of partial confinement, and (4) the minimum size of cloud for detonation.

Work on direct initiation of explosions has frequently utilized an explosive charge. Typical is the work of Bull, Elsworth and Hooper (1979a) on the detonation limits of ethane–air mixtures. A review of work in which detonation has been induced using an explosive charge is given by Bull (1979).

A small amount of research has been done to establish the size of cloud in which overpressures can be induced. Thus, Maurer *et al.* (1977) have shown that overpressures can occur in even very small clouds of mass 0.5–500 kg. Fundamental approaches to the estimation of the minimum size of cloud in which detonation might occur have been described in Section 17.2. Some fundamental aspects of detonation in vapour clouds have also been discussed in Section 17.2, including DDT and minimum cloud size.

The consensus which emerged from this work on detonation in vapour clouds was that it is more fruitful to focus attention primarily on the conditions associated with high flame acceleration and high deflagration overpressure rather than on detonation as such.

A4. Combustion in unconfined vapour clouds: closely controlled tests. A number of workers have performed experiments on combustion of gas–air mixtures inside soap bubbles or balloons. They include Lind and Whitson (1977), Deshaies and Leyer (1981), Okasaki, Leyer and Kageyama (1981), Schneider and Pfortner (1981), Brossard *et al.* (1985), A.J. Harrison and Eyre (1986, 1987) and R.J. Harris and Wickens (1989). The flame speeds for gases of moderate or low reactivity obtained were low ($\leq$24 m/s) as were the overpressures ($\leq$0.06 bar), where measured.

The rig used by A.J. Harrison and Eyre (1986, 1987) is shown in Figure 17.65. It represents a sector of a pancake-shaped vapour cloud. For natural gas and propane the

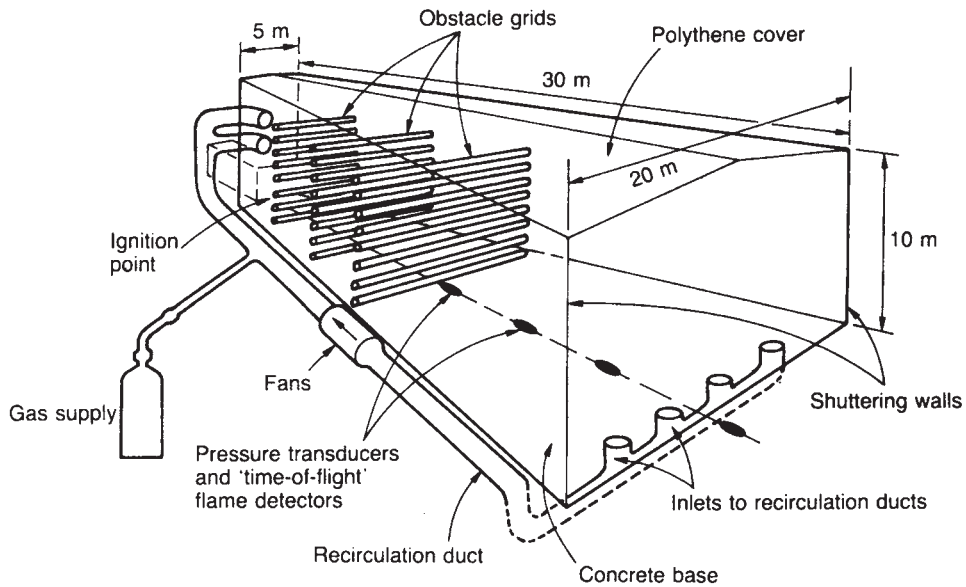

Figure 17.65 *Experimental work on vapour cloud explosions: rig representing a sector of a shallow, cylindrical cloud (A.J. Harrison and Eyre, 1986) (Courtesy of Institution of Chemical Engineers)*

flame speeds and overpressures obtained in the absence of a high-energy ignition source or obstructions were low.

R.J. Harris and Wickens (1989) conducted tests in a tent-type rig of rectangular cross-section and 45 m long with a plywood floor and with polyethylene sheeting on the sides and roof. The gases used were natural gas, propane, cyclohexane and ethylene. The basic experiment was to fill the rig with a stoichiometric mixture, ignite it at one end and measure the flame speeds and overpressures generated.

One set of experiments was conducted without any obstruction of the space in the rig and without confinement of the ignition region. For this base condition the flame speeds observed were about twice those measured in the laboratory. The authors give the following data:

Gas	*Laminar burning velocity* (m/s)	*Flame speed* (m/s)	
		Laboratory tests	*Rig tests*
Natural gas	0.45	3.1	8
LPG	0.52	3.6	10
Cyclohexane	0.52	3.6	10
Ethylene	0.83	5.8	19

Thus, without obstructions the flame speeds obtained were low.

The last two sets of investigators also performed experiments using obstructions, as described below.

This research has thus provided further confirmation that the flame speeds in unconfined vapour clouds of moderate or low reactivity substances are not such as to give high overpressures and deflagrations, let alone detonations.

In balloon tests, high reactivity gases gave rather higher flame speeds (acetylene 38 m/s and hydrogen 84 m/s), still less than the deflagration range.

A5. Combustion in unconfined vapour clouds: field trials. The early 1980s saw a number of large scale field trials on dense gas dispersion, some of which were supplemented by trials involving cloud ignition.

Accounts of this work are given by Blackmore, Eyre and Summers (1982) for trials with LNG and propane at the Maplin Sands site, Hogan (1982), MIT-GRI (1982) and Goldwire *et al.* (1983) for LNG trials at China Lake and Zeeuwen, van Wingerden and Dauwe (1983) for propane trials at Musselbanks.

For LNG the maximum flame speed observed was 13.3 m/s at China Lake, and for propane 28 m/s at Maplin Sands and 32 m/s at Musselbanks.

Field trials on combustion of vapour clouds are also considered in Chapter 16 in relation to flash fires.

A6. Combustion in vapour clouds with obstructions: closely controlled tests. The absence of evidence in work on unconfined vapour clouds of flame speeds sufficiently high to give high overpressures has led to investigation of the effect of obstacles in promoting flame acceleration.

Controlled tests using obstacles have been conducted by Db'rge, Pangritz and Wagner (1981), C.J.M. van Wingerden and Zeeuwen (1983), A.J. Harrison and Eyre (1986, 1987) and R.J. Harris and Wickens (1989).

The apparatus in the work of Db'rge, Pangritz and Wagner (1981) contained a wire mesh, whilst that of C.J.M. van Wingerden and Zeeuwen (1983) consisted of a 60×60 cm plate with 1 cm vertical obstacles placed on it.

Using in their rig a blockage ratio of 40% with six grids of pipe-type obstacles, A.J. Harrison and Eyre (1986, 1987) obtained in one test on natural gas a flame speed of 119 m/s and an overpressure of 0.21 bar. They observed that the flame accelerated on entering the obstructed region and decelerated on leaving it. The tests showed that with natural gas a high degree of congestion is required to obtain high flame speeds and overpressures.

R.J. Harris and Wickens (1989) utilized the 45 m long tent-type rig already described. Again the gases used were natural gas, propane, cyclohexane and ethylene. The obstructions were placed in the central portion of the rig. The effect of these was to cause the deflagration flame to accelerate. On entering the subsequent unobstructed portion the flame decelerated again. This is illustrated in Figure 17.66(a), which shows results for cyclohexane. The flame speeds obtained were up to 10 times higher than for the unobstructed case.

Both of the last two sets of investigators studied the effect of a strong ignition source. A.J. Harrison and Eyre (1987) utilized a jet flame emerging from a partially confined region. Using natural gas, they observed in one test a flame speed of 170 m/s and an overpressure of 0.71 bar.

R.J. Harris and Wickens (1989) conducted tests with a strong ignition source using cyclohexane and propane. The tests involved the use of a central obstructed region and a modified method of ignition, obtained by confining the end region in which ignition took place. In experiments on cyclohexane the flame emerged from this region with a flame speed of about 150 m/s. The results obtained are illustrated in Figure 17.66(b), which shows that the flame ran up to detonation in the obstructed portion and that the detonation was maintained when it entered the subsequent unobstructed portion. The detonation velocity was 1700 m/s. The corresponding velocities for propane were 300 m/s leaving the confined region and 1800 m/s for detonation.

Overall, the work of Harris and Wicken illustrated the effect of a combination of fuel reactivity, ignition conditions and an obstructed region. It showed that with an obstructed region and an ignition source giving a high initial flame speed more reactive fuels can run up to detonation. On the other hand it also confirmed the much lower flame speeds associated with natural gas.

A7. Combustion in vapour clouds with obstructions: field trials. Experiments on the effect of obstacles on the course of VCEs have also been carried out on the field scale. Zeeuwen, van Wingerden and Dauwe (1983) have described work at TNO on field trials using obstacles which complement the small scale work described earlier. Tests were conducted both without and with partial confinement. For the former, two types of obstacle were used: a set of large horizontal pipes and a set of sewer pipes, each 1 m in diameter and 2 m high, stood on end. The latter system, shown in Figure 17.67, consisted of seven rows of 10 pipes on a 3 m pitch. In some tests this array was open at the top and in

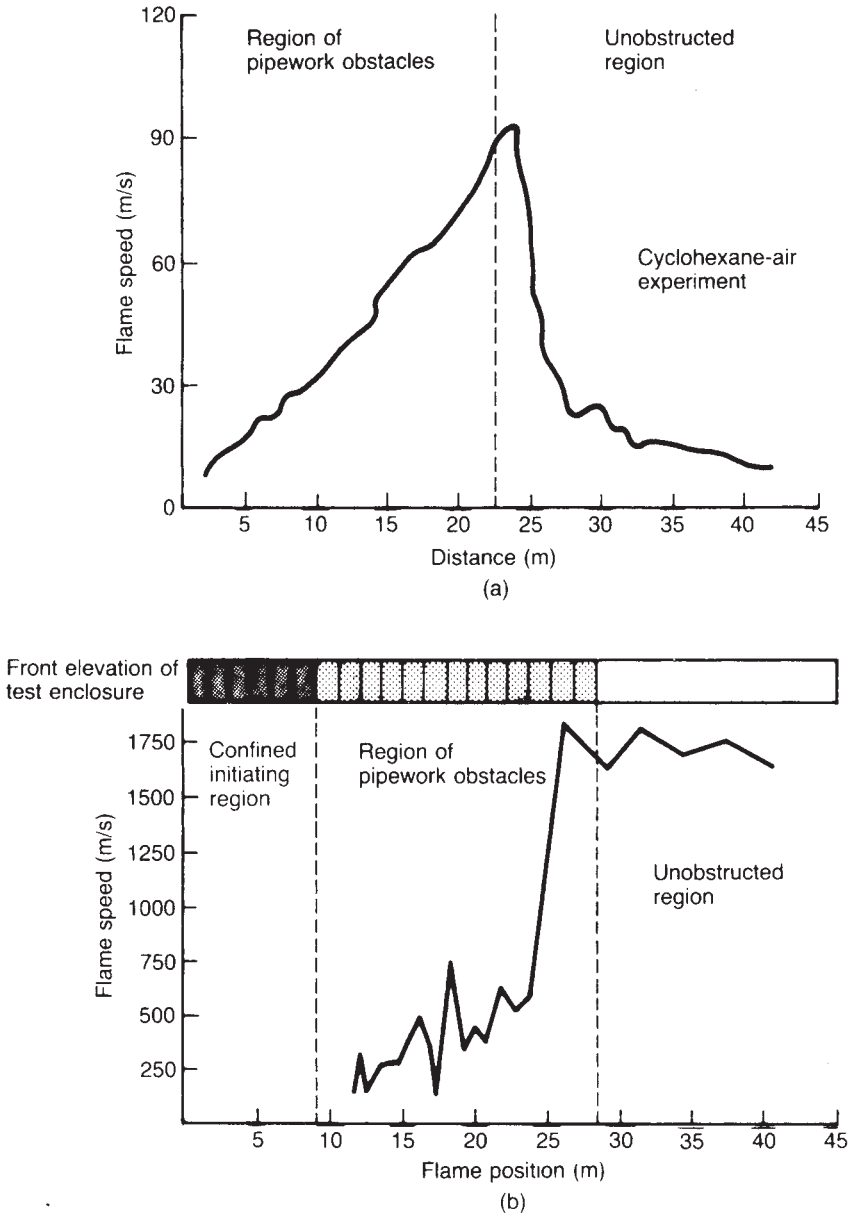

Figure 17.66 *Experimental work on vapour cloud explosions: effects of obstructions and of jet flame ignition (R.J. Harris and Wickens, 1989): (a) flame acceleration on entering obstructed region and flame deceleration on leaving it and (b) flame accelertion on entering obstructed region with transition to detonation, following jet flame ignition. Cyclohexane in both cases (Courtesy of the Institution of Gas Engineers)*

others it was partially or totally covered. The vapour clouds consisted of 1000 kg of propane, which was introduced over a period of some 1–2 min through a water pond 15 m in diameter and 1 m high. The dimensions of the cloud within the flammable limits were estimated as 130 m long, 75 m wide and 2 m high. In the tests without obstacles the flame speed was generally low at 3–10 m/s, although one case was recorded of 32 m/s, and no overpressure was measured. In the tests with horizontal pipes the flame accelerated to 16 m/s at the pipes and then fell again.

In the tests with the vertical pipes uncovered the flame speed was similar to the unconfined case. In the tests with cover, the area covered was 7×7 m^2, then 13×13 m^2 and finally the whole array. In all but the first of these tests the

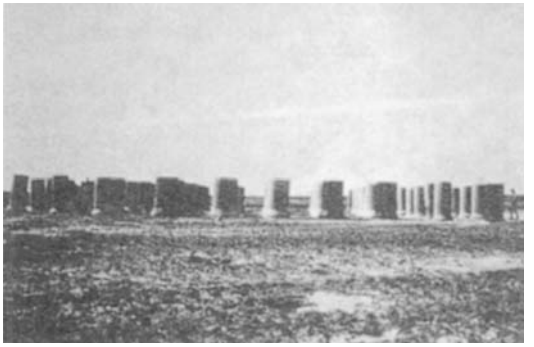

Figure 17.67 *Experimental work on vapour cloud explosions: obstacle array for field trials (Zeeuwen, van Wingerden and Dauwe, 1983) (Courtesy of the American Institute of Chemical Engineers)*

flame speed increased in the covered area and decreased beyond it. With the array completely covered the flame accelerated continuously, and flame speeds of 50–66 m/s were obtained, as were maximum overpressures of 20 mbar in the cloud and 6 mbar 75 m away.

A8. Combustion in partially confined vapour clouds without or with obstructions: work using tubes. The foregoing account indicates that the flame speed in a vapour-air mixture is affected by partial confinement as well as by obstacles. Investigators have studied a number of different geometries, notably (1) tubes, (2) parallel plates, and (3) channels, the first two being representative, respectively, of one- and two-dimensional flame propagation.

Work on the behaviour of flames in tubes antedates interest in VCEs. Early work on this topic was carried out by Chapman and Wheeler (1926, 1927) and their co-workers, using both empty tubes and tubes containing obstacles. An account of this work has been given in Chapter 16.

Combustion in tubes, especially shock tubes, is the staple of research on detonation and has been the subject of innumerable studies.

A series of investigations using tubes specifically related to vapour cloud explosions has been described by Lee, Moen, Hjertager and co-workers (C. Chan *et al.*, 1980; Moen, Lee *et al.*, 1982; Hjertager, 1984; J.H.S. Lee, Knystautas and Chan, 1985). Other work includes that of Wagner and co-workers (Db'rre, Pangritz and Wagner, 1981) and Andrews and co-workers (Andrews, Herath and Phylaktou, 1990; Phylaktou and Andrews, 1991a,b).

Moen, Lee *et al.* (1982) and Hjertager (1984) carried out experiments in a pipe 2.5 m in diameter and 10 m long containing obstructions. The former obtained for methane overpressures of 4 bar and the latter for propane pressures of 13.9 bar.

Subsequently, Hjertager and co-workers (Hjertager, Bjorghaug and Fuhre, 1988; Hjertager, Fuhre and Bjorghaug, 1988a) performed similar experiments with a non-homogeneous mixture more representative of that from a plant leak. For non-stoichiometric mixtures the pressures obtained tended to be less than those with a stoichiometric homogeneous mixture. For non-homogeneous mixtures the pressures were equal to or less than those for homogeneous mixtures.

A9. Combustion in partially confined vapour clouds without or with obstructions: work using parallel plates. The second widely used system is a pair of parallel plates. Among the investigators who have studied this configuration are Moen, Donate, Knystautas and Lee (1980), Moen, Donate, Knystautas, Lee and Wagner (1980), C.J.M. van Wingerden and Zeeuwen (1983), Hjertager (1984) and C.J.M. van Wingerden (1984, 1989).

Moen, Donate, Knystautas and Lee (1980) used plates 60 cm in diameter with obstacles, and obtained for methane flame speeds up to 130 m/s, whilst further work by Moen, Donate, Knystautas, Lee and Wagner (1980) using 2.5×2.5 m plates, again with methane, gave flame speeds up to 400 m/s and overpressures of 0.64 bar.

In the work of C.J.M. van Wingerden and Zeeuwen (1983), already mentioned, experiments were carried out in a closed vessel using a configuration consisting of vertical sticks held either on a single plate or between two plates. Enhancements of flame speed were observed in the confined volume, but these were much greater where the space was confined by the second, top plate. The increases in flame speed were attributed to two mechanisms. One is the stretching of the flame front as it passes through the opening between the obstacles and the other is the folding and wrinkling of the flame front due to turbulence. The authors discuss the relative importance of these two factors, which is somewhat complex.

Using a 0.5 m disc with obstructions Hjertager (1984) obtained a flame speed of 160 m/s and an overpressure of 0.8 bar for methane and a flame speed of 225 m/s and overpressure of 1.8 bar for ethylene.

In work by C.J.M. van Wingerden (1984 CEC EUR 9541 EN/II) on ethylene using 4×4 m plates with obstacles a flame speed of 420 m/s and an overpressure of 0.7 bar were obtained.

C.J.M. van Wingerden (1989) also used a plate apparatus to perform experiments with a range of gases of differing reactivity: methane, propane, ethylene and acetylene. He showed that reactivity can be related to the laminar flame speed and that this can be used as the basis for a method of scaling in VCE work.

A10. Combustion in partially confined vapour clouds without or with obstructions: work using channels. The third configuration to have attracted investigation is the channel on which work has been reported by Urtiew (1981), C. Chan, Moen and Lee (1983), Elsworth, Eyre and Wayne (1983), Sherman *et al.* (1985), P.H. Taylor (1986) and P.H. Taylor and Bimson (1989).

Working with ethylene in an open channel containing baffles Urtiew (1981) obtained a flame speed of 20 m/s.

C. Chan, Moen and Lee (1983) also used a channel with baffles and with a top containing perforations such that the degree of top confinement could be varied. For methane with high confinement a flame speed of 120 m/s was observed, but with only 10% confinement this figure fell to 30 m/s.

The experiments by P.H. Taylor (1986) also involved a perforated duct top in which the top confinement could be varied. Working with propane he obtained a flame speed of 80 m/s with a 50% blockage ratio and an 88% confinement.

Elsworth, Eyre and Wayne (1983), in tests relevant to a spill between a vessel and a jetty, investigated using an open channel the behaviour of propane systems both premixed and simulating a liquid propane spill, using baffles

in some tests. The maximum flame speed in the premixed tests was 12.3 m/s.

The work on channels brings out the effect of top venting in reducing the flame speeds in vapour-air mixtures.

A11. Jet ignition of vapour clouds. Other work on VCEs includes studies of the effect of a strong ignition source in the form of a flame jet issuing into the cloud.

Work on this form of strong ignition source by A.J. Harrison and Eyre (1987) and R.J. Harris and Wickens (1989) has been described above. It was shown to yield high flame speeds and even detonation.

B. Combustion of turbulent jets. Leaving now the combustion of dispersed vapour clouds to consider that in other vapour–air release scenarios, another important case is that of the turbulent free jet. It was ignition of such a jet which gave rise to the explosion at Flixborough.

Work on this problem has been described by Seifert and Giesbrecht (1986) and Stock (1987). The former workers studied ignition of jets of methane and of hydrogen. Measurements were taken of the flame velocities and of the overpressures and duration times at different distances from the cloud.

Stock (1987) investigated jets of propane and measured overpressures within the cloud. The work included investigations of the effect of obstacles and partial confinement. For the particular configurations studied, partial confinement with 0.5 m high obstructions within 2 m high parallel walls, the overpressure in the cloud increased by a factor of about 4.

C. Combustion following vessel burst. Another release scenario is that of the rupture of a vessel, reported in accounts by Maurer, Giesbrecht, Seifert and co-workers. The account by Maurer *et al.* (1977) was concerned primarily with experiments on the dispersion aspects but included some results for the overpressure from the physical burst. Giesbrecht *et al.* (1981) have described the explosion resulting from ignition of the flammable vapour cloud formed.

The experiments were done using vessels ranging in size from 0.226 to 1.0 l, containing propylene at 40–60 bar. Figure 17.68 shows a plot of the variation of the principal variables with the initial mass in the vessel. Also shown on the plot are the extrapolations for the VCEs at the BASF works at Ludwigshafen in 1943 and 1948 and at Flixborough in 1974.

D. Combustion of a pipeline leak. Another scenario investigated is that of the ignition of a leak of flammable vapour from a pipeline. Work on this has been done by Hoff (1983).

His tests involved full bore ruptures of a 10 cm diameter gas pipeline operating at 60 bar. Ignition was effected by firing a bullet at the gas jet. The flame speeds observed

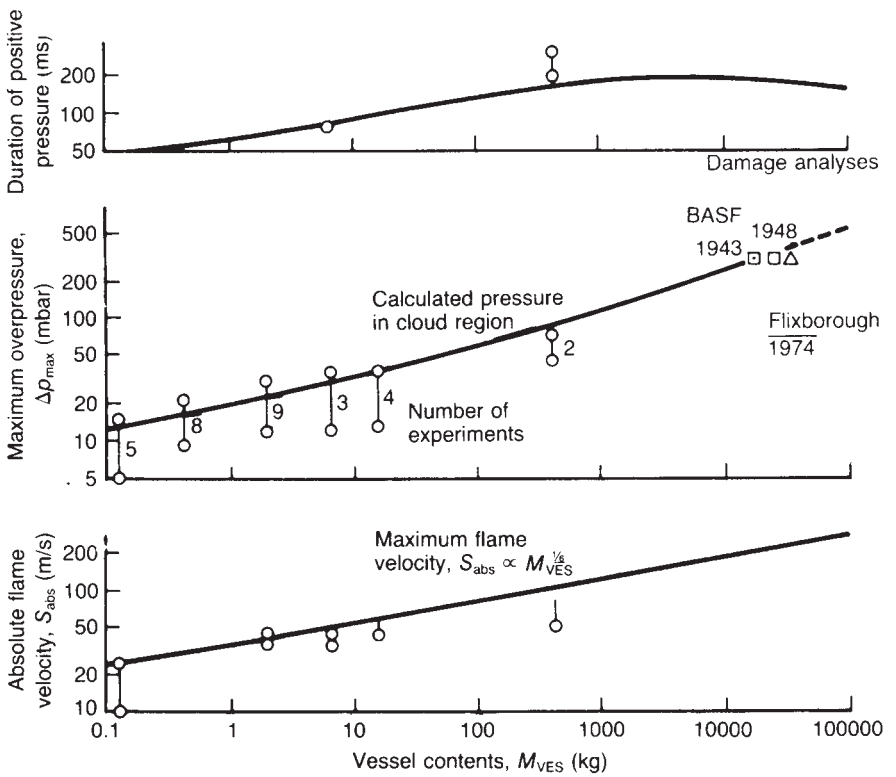

Figure 17.68 *Experimental work on vapour cloud explosions: flame velocity, peak overpressure and duration time in explosions of flammable vapour cloud formed following vessel burst (Giesbrecht et al., 1981) (Courtesy of German Chemical Engineering)*

were of the order of 15 m/s, and the overpressure at a distance of 50 m was measured as 1.5 mbar.

E. Some factors affecting combustion of dispersed vapour clouds. It is useful at this stage to summarize some of the salient points on the combustion of dispersed vapour clouds brought out by the experimental work just described. The summary is mainly confined to qualitative observations.

Fuel reactivity. One important factor which determines the flame speeds and overpressures attained is the reactivity of the fuel.

Fuels are generally classed as being of low, moderate or high reactivity. Methane may be considered of low reactivity, propane of moderate reactivity and acetylene of high reactivity.

A classification developed by the Factory Mutual Research Company (FMRC) (1990) from the work of D.J. Lewis (1980d) is given in Section 17.28.9. In this classification, although more reactive than methane, propane and butane are classed as low reactivity fuels.

Cloud inhomogeneity: flame speed and overpressure. The standard vapour–air mixture used in most work on VCEs has been stoichiometric and homogeneous. Only a small amount of work has been done involving more realistic vapour–air mixtures. The work appears to indicate that whilst flame speeds tend to be lower in mixtures which depart significantly from the stoichiometric, in spaces where the mass of vapour is such that good mixing would give a mixture close to stoichiometric it is unwise to assume that the flame speed will be much reduced by a degree of inhomogeneity.

Cloud inhomogeneity: effective lower flammability limit. It has long been appreciated that due to concentration fluctuations pockets of flammable vapour–air mixture of a concentration above the lower flammability limit (LFL) may occur beyond the nominal envelope bounded by the concentration corresponding to the LFL.

It is conventional to take this effect into account by using an effective LFL and to treat that part of the cloud calculated to be within this effective LFL as potentially flammable. A common practice has been to take the effective LFL as half the actual LFL, in other words taking a peak-to-average, or P/A, ratio of 2. This is illustrated in the work of Feldbauer *et al.* (1972) used in the hazard assessment done for the *First Canvey Report*, as described in Appendix 7.

The problem has been discussed by Pikaar (1985), who points out that it may be approached either from the standpoint of gas dispersion or that of combustion. As regards dispersion, there is no doubt that the P/A concentration ratio can be high. On the other hand, combustion of vapour clouds in large field trials such as those at Maplin Sands indicates that pockets of gas can be ignited without igniting the main cloud.

On the basis of such considerations, Pikaar proposes the use of a P/A ratio of 1.4.

A discussion of this problem from the viewpoint of gas dispersion is given in Chapter 15.

Cloud shape. The typical vapour cloud formed by dispersion of a dense gas is pancake shaped. This has a significant effect on combustion in the cloud.

One consequence of this cloud geometry is that the gas is able to expand, or vent, through the top of the cloud, so that there is less compression of the unburned gas ahead of the flame front and the flame speed is correspondingly lower. The same thing has been found for aspect ratio, with long, narrow vapour clouds, overpressures are lower because energy escapes out the sides of the congested area as the flame progresses.

Another effect relates to the possibility of detonation in the cloud. There is a minimum cloud thickness for detonation to occur, this thickness being a function of the cell size, which is characteristic of the gas. For the fully unconfined case the thickness needs to be of the order of 10–13 cell sizes, whilst for the practical case of a cloud bounded by the ground it is about 5–6.5 cell sizes.

Obstructions and partial confinement. The experimental work described demonstrates that the flame speed is enhanced by the presence of obstructions, but it also indicates that the extent of this enhancement varies. For a low reactivity gas without even partial confinement the increase may be relatively limited.

The addition of partial confinement in combination with obstructions can result in a much greater enhancement of flame velocity.

Obstruction configuration. One type of obstruction which has been used by several workers is a series of grids set one behind the other at regular intervals and consisting of horizontal cylinders simulating pipework. For the particular experimental set-up, correlations have been obtained of the effect on flame speed of variables such as the blockage ratio, the spacing and the construction of the grid.

Ignition source strength. Another enhancing factor is the strength of the ignition source. The strong ignition sources principally investigated are explosives and jet flames. The latter are regarded as a credible ignition source.

Experiments on jet flame ignition have involved obstacles and some partial confinement also. They have shown that in combination with these other factors this form of ignition can give high flame speeds and in some cases detonation.

Combination of enhancing effects. The principal enhancing effects mentioned are fuel reactivity, obstacles, partial confinement and jet flame ignition. The experimental evidence suggests that these factors are most effective in producing high flame speeds, even detonation, where they are present in combination.

Water sprays. There have been a number of studies on the use of water spray to mitigate the effects of a flammable gas release by dispersing it.

Pikaar (1985) sounds a note of caution on the use of water sprays, in so far as they increase the turbulence in the cloud and could thereby make things worse. He refers to the work of Eggleston, Herrera and Pish (1976), in which flame speeds were apparently increased, although opinions differ on the interpretation of this work.

17.28.5 Vapour Cloud Explosion modelling

Although there are many gaps in the understanding of VCEs, considerable progress has been made in modelling such explosions.

Work on fundamental models has been described by a number of authors, including G.I. Taylor (1946), F.A. Williams (1965), Kuhl, Kamel and Oppenheim (1973), Strehlow (1975, 1981), Munday (1975a,b, 1976a,b), Gugan (1979), Wiekema (1980), W.E. Baker *et al.* (1983) and van den Berg (1985).

Other work has been directed to the correlation of experimental results and to the development of semi-empirical models. This includes the work of C.J.M. van

Wingerden (1989), C.J.M. van Wingerden, van den Berg and Opschoor (1989), C.J.M. van Wingerden, Opschoor and Pasman (1990) and K. van Wingerden, Pedersen and Wilkins (1994).

Some of the approaches to modelling have been described by Munday (1976a). These are:

(1) point source models
  (a) TNT equivalent model,
  (b) self-similarity model;
(2) fuel-air cloud model;
(3) bursting vessel model;
(4) piston model
  (a) constant velocity piston model,
  (b) accelerating piston model.

In the TNT equivalent model the explosion is taken to be equivalent to that of a TNT explosion with the same energy of explosion. This model is therefore an empirical one, but it was for some time virtually the only practical model available. It was considered in Section 17.26 and is discussed further below.

The TNT equivalent model has a single parameter, the mass of TNT. It can be made more flexible by the introduction of a second parameter, the height above ground zero at which the explosion occurs. The effect of increased height is to reduce the overpressures near the centre. The use of an arbitrary assumed explosion height is useful in obtaining better fits to overpressures assessed from damage in actual explosions.

In the self-similarity model, the blast parameters such as peak overpressure are correlated in terms of the ratio of radial distance to time. In its simplest form the model gives a power law relation for the variation of peak overpressure with distance.

In the fuel–air cloud model it is assumed that a detonation propagates through the fuel–air mixture without any expansion of the cloud. However, there is some expansion of a burning cloud during a deflagration. A shock wave with a high peak overpressure is produced at the cloud boundary. With combustion thus complete, subsequent decay of the shock wave is similar to that for the point source models.

Another approach is to assume that the fuel–air mixture undergoes combustion in a hemispherical vessel, defined by the cloud boundary, and that when combustion is complete, the vessel bursts. The state of the gas, after combustion but before bursting, is determined by standard methods. Subsequent decay of the shock wave may be calculated by numerical solution of wave propagation equations.

A widely used method has been to treat the flame front as a constant velocity piston. Early work on the piston model was done by G.I. Taylor (1946). This approach has been taken forward by Kuhl, Kamel and Oppenheim (1973), Strehlow (1981), Tang and Baker (1999) and other workers.

Figure 17.70 illustrates the variation of the overpressure with time in the TNT equivalent model and constant velocity piston models of a VCE.

The constant velocity piston approach has also been used by Wiekema (1980) at TNO. His model is a practical one and is quite widely used. It is described below.

Van den Berg (1985) at TNO has developed this work to produce a multienergy (ME) model, also described below, which reflects the fact that the main energy release is from the confined parts of the cloud.

Finally, TNO have presented an empirical model for the damage circles caused by a VCE.

Before considering these models, however, mention should be made of several other concepts which are important in modelling.

One of these is that of flame acceleration. Some of the factors which influence this have been considered by C.J.M. van Wingerden and Zeeuwen (1983) in their work on the influence of obstacles. They describe two effects which enhance flame speed. One is the stretching of the flame front as it passes through an opening. The flame front velocity V_f is

$$V_f = \frac{\rho_u S}{\rho_b} \quad [17.28.1a]$$

$$= \frac{\rho_u}{\rho_b}\frac{A_f S_L}{A_o} \quad [17.28.1b]$$

where A_f is the disturbed flame surface area, A_o is the undisturbed flame surface area, S is the burning velocity, S_L is the laminar burning velocity, ρ is the gas density and the subscripts b and u denote burned and unburned, respectively. For the case where this effect, rather than that of turbulence, is the dominant factor a simple relation may be derived for the flame acceleration. If the flame front velocity is V_{fo} before an obstacle and V_{fl} after it, then

$$V_{fl} = V_{fo}(1 + \Delta A/A) \quad [17.28.2]$$

where $\Delta A/A$ is the relative increase in flame surface area. Hence, the flame front velocity V_{fn} after n obstacles is

$$V_{fn} = V_{fo}(1 + \Delta A/A)^n \quad [17.28.3]$$

with n in terms of flame front radius, r, and pitch, p:

$$n = r/p \quad [17.28.4]$$

or, if the flame front velocity V_{fo} entering the obstacles is some multiple α of the base value V_L.

$$\frac{V}{V_L}(r) = \alpha(1 + \Delta A/A)^{(r-r_o)/p} \quad [17.28.5]$$

where r_o is the radius at the entry to the obstacles.

Another basic concept is the relation between the flame velocity, u, and the overpressure generated, ΔP. This has been derived by several workers in the form $\Delta P \propto \frac{1}{2}\rho u^2$, where ρ is the density of the unburned vapour. Figure 17.71 shows a typical plot of this relation.

17.28.6 Mass of fuel

The estimation of the mass of fuel within the flammable range in the vapour cloud is not entirely straightforward. For a defined release scenario the mass of fuel within the flammable range may be estimated using gas dispersion models. This is discussed in Chapter 15 and has been reviewed by a CCPS book (Woodward, 1997).

Many of the expressions given are based on models for neutral density gas. Treatments used on such models have been given by Burgess *et al.* (1975), Eisenberg, Lynch and Breeding (1975), V.J. Clancey (1977a), van Buijtinen (1980),

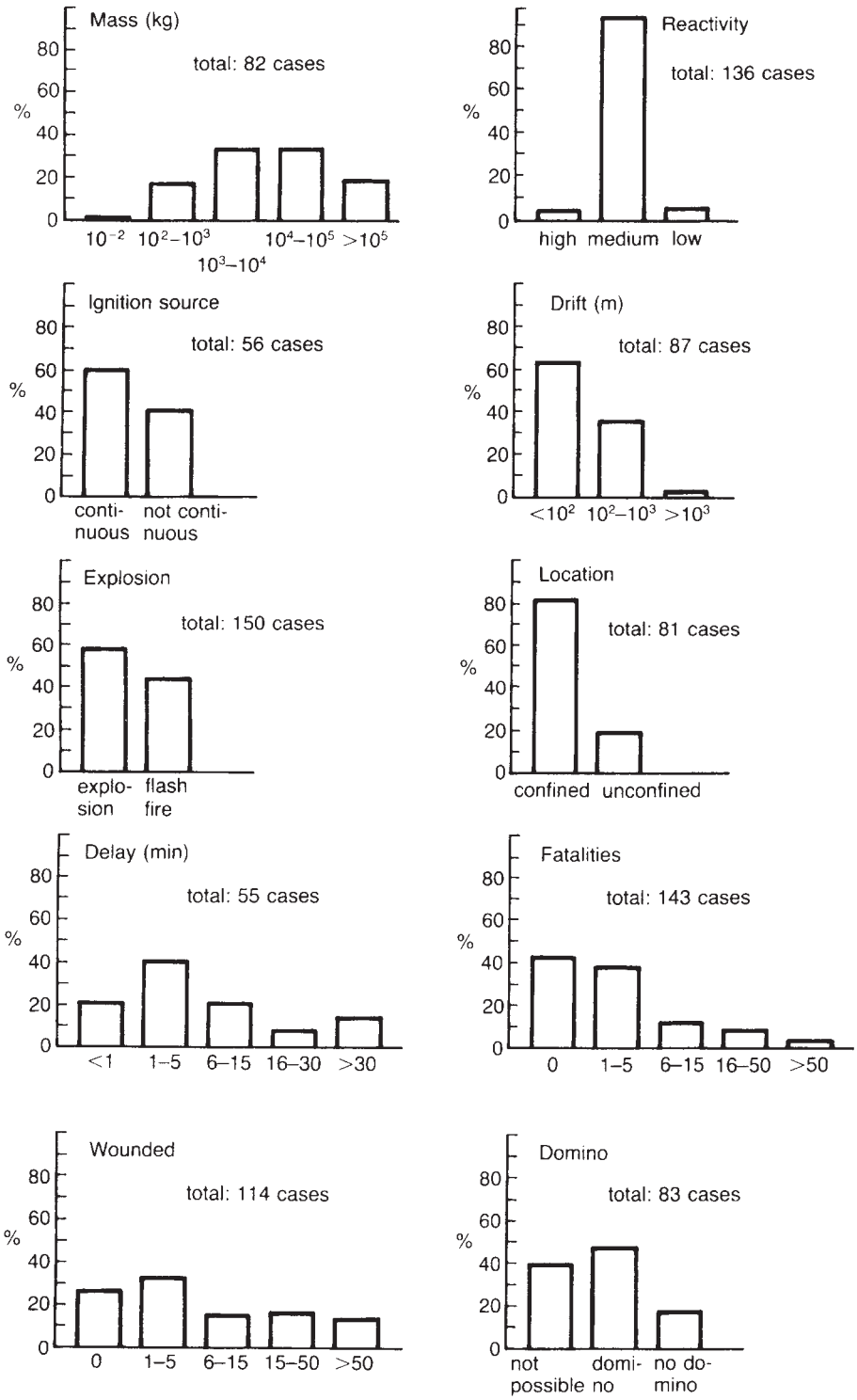

Figure 17.69 *Histograms showing selected features of a vapour cloud explosion (Wiekema, 1984) (Courtesy of Elsevier Science Publishers)*

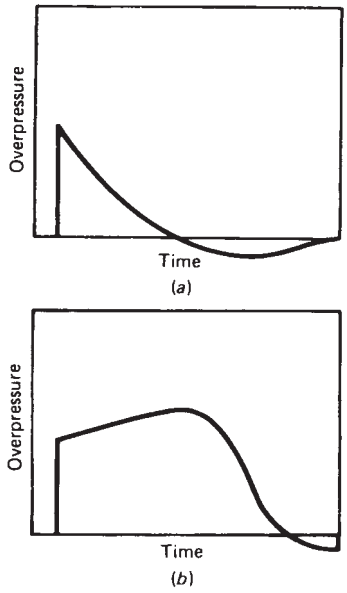

Figure 17.70 *Variation of overpressure with time in TNT equivalent and constant velocity piston models of an vapour cloud explosion (after Munday, 1976a): (a) TNT equivalent model and (b) constant velocity piston model (Courtesy of the Institution of Chemical Engineers)*

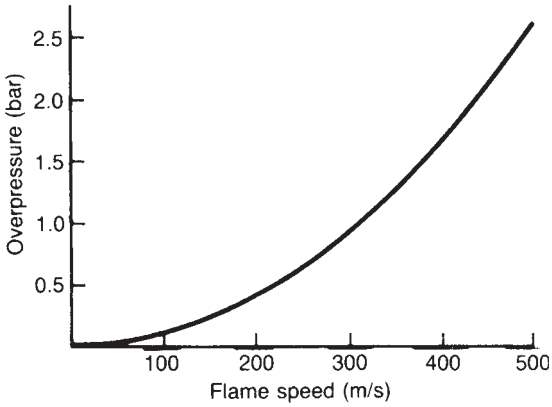

Figure 17.71 *Overpressure in a vapour cloud deflagration as a function of flame speed (R.J. Harris and Wickens, 1989; after Kuhl, 1981) (Courtesy of the Institution of Gas Engineers)*

J.G. Marshall (1977, 1980), Hesse (1991) and the TNO Yellow Book (1997).

Generally, dense gas dispersion models will be more appropriate. The typical dense model is a box or slab model in which the gas cloud is defined in terms of its radius and height. For an instantaneous release box model the gas concentration within the cloud is assumed to be uniform. In such a model the available mass of fuel remains constant, until at some time the concentration falls below the lower flammability limit. Or for a continuous release a slab model takes the variation of concentration with distance into account so that the available mass of fuel changes with distance.

Some problems concerning the definition of the mass of fuel have been identified and discussed by R.A. Cox (1981). He reviews the merits of basing estimates on the mass within the flammable range, or flammable mass, or the total mass released. The ratio of the flammable mass to the total mass released is likely to be highly variable. It will be small for a large inventory escaping through a small hole, but may be as high as half for an instantaneous burst. In view of this variability the blanket application of a single explosion efficiency is not likely to give accurate results.

Cox discusses but dismisses suggestions that there may be lower and upper limits to the size of cloud which can explode. He draws attention to the Badische Anilin und Soda Fabrik (BASF) work, mentioned above, which shows that overpressures can be induced in clouds of 0.5 kg mass. As for the suggestion of an upper limit of 50 te, he concludes that there is no real evidence for this either.

Cox draws attention to the fact that where the release is a turbulent jet there may be entrainment into the jet of fuel from outside the flammable envelope. In the absence of such entrainment the mass in the cloud is often quite modest, but it can be appreciably enhanced by entrainment.

Various authors have developed procedures for the determination of the size of the vapour cloud, generally for design purposes and frequently for use with a TNT equivalent model. Some of these are described in Chapter 15.

17.28.7 Energy of explosion

The energy of explosion in a VCE is usually only a small fraction of the energy available as calculated from the heat of combustion. This point has already been discussed in Section 17.4. As stated there, the explosion efficiency, or yield factor, may be quoted on the basis of the total mass released or of the flammable mass. Although the latter is the more fundamental basis, the former is the more convenient and the more common.

Values of the yield factor in VCEs discussed by Kletz were quoted in Section 17.27.5.

The *Second Report* of the ACMH (Harvey, 1979b) discusses the location and design of works buildings, and in this context suggests that a yield factor of 3% be provisionally assumed. In some cases a much higher yield factor has been reported. Davenport gives a yield factor of 25–50% for a VCE at Decatur, Illinois, in 1974. Similarly, Gugan (1979) quotes for this case a yield factor of 32–65%. This anomaly has been examined by V.C. Marshall (1980d), who concludes that the TNT equivalent quoted is not well founded, being based on a small number of damage points which lie well within the scatter of points obtained for the Flixborough explosion. He presents evidence of damage to support the view that the strength of the explosion at Decatur was not more, and was probably less, than that at Flixborough.

The yield factor is discussed further in Section 17.28.14.

17.28.8 TNT equivalent model

The TNT equivalent model has been widely used to model VCEs. The TNT equivalent model has been widely

applied to VCEs, as described by van den Berg (1985). It is one of the types of model used in the CCPS methodology. It also has its critics, who regard it as obsolete. An example of this viewpoint is the account by Pasman and Wagner (1986).

An early application was that of Brasie and Simpson (1968), who used it to study the damage from three accidental explosions.

The TNT equivalent model was also used by Sadee, Samuels and O'Brien in their investigation of the VCE at Flixborough. In this case a two-parameter model was used, utilizing the height of the explosion as well as the mass of TNT. This work is described in Appendix 2.

There are, however, important features of a VCE which differentiate it from one of TNT. These include (1) the large volume of the cloud, (2) the lower overpressure at the explosion centre, (3) the different initial shape of the blast wave, and (4) the longer duration time of the blast wave.

A discussion of these characteristics has been given by Baxen and Baker (1991) and in the *Second Report* of the ACMH (Harvey, 1979b). The report gives the following estimate for the size of the vapour cloud in the Flixborough explosion:

Flixborough $0.5 \times 10^6\ m^3$

St Paul's Cathedral (internal volume) $0.2 \times 10^6\ m^3$

The overpressure at the explosion centre of a vapour cloud is much less than at that of a TNT explosion. The report suggests that a theoretical upper limit might be calculated related to the pressure which would be achieved if the equivalent mass of TNT after detonation were confined within particular boundaries under adiabatic conditions. For a TNT explosion the boundaries would be those of the TNT charge and the pressure developed would be about 0.5 million bar. For a VCE the boundaries would be those of the cloud and the pressure developed would be about 8 bar. In both cases the practical upper limit of overpressure would be some fraction of the theoretical maximum value, particularly for a vapour cloud. The report suggests that on the basis of the rather meagre data available the practical upper limit is probably about 1 bar at the centre and about 0.7 bar at the boundary of the cloud.

The overpressure at the explosion centre at Flixborough may have been about these values, as discussed in Appendix 2.

In a VCE the shape of the initial blast wave is different from that in a TNT explosion. But it is frequently assumed that after the blast wave has travelled a certain distance it becomes indistinguishable in form from the wave of a TNT explosion. In other words, it assumes the shape shown in Figure 17.57.

The shape of the overpressure profile according to the TNT equivalent model and to some possible models of VCEs is shown in Figure 17.72.

The apparent TNT equivalence of a VCE changes with distance. In the far field the quantity of TNT required to obtain a fit for the overpressure tends to be appreciably higher than in the near field.

The blast wave from a VCE also differs from that of a TNT explosion in duration time. The duration time of a VCE is generally considered to be appreciably longer than that of the equivalent TNT explosion.

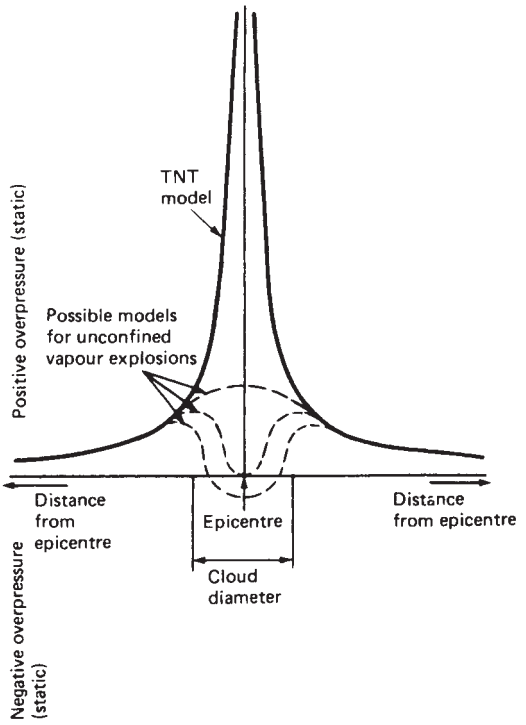

Figure 17.72 *Overpressures given by the TNT equivalent model and by some possible models of vapour cloud explosion (V.C. Marshall, 1976c) (Courtesy of the American Institute of Chemical Engineers)*

Thus, TNT gives a 'hard' explosion with high overpressure and short duration time, whilst a vapour cloud gives a 'soft' explosion with low overpressure and long duration time. The lower overpressure reduces the relative destructiveness but the longer duration time increases it.

There is, however, little information on the duration time for VCEs. This is a serious deficiency, because a knowledge of duration time is needed for the design of works buildings.

The *Second Report* of the ACMH suggests, in the context of the design of works buildings and in conjunction with the assumed overpressure of 1 bar at the cloud centre, that a duration time of 30 ms be provisionally assumed.

17.28.9 TNT equivalent models: influencing factors and special features

Some of the various TNT equivalent models developed tend to emphasize a particular influence on or feature of VCEs. These include (1) the reactivity of the fuel, (2) the effect of cloud size, (3) the effect of obstructions, (4) the variation of TNT equivalence with distance, and (5) the peak overpressure at the edge of the cloud. The treatments of these factors are of value quite apart from their use in the particular models.

For the reactivity of the fuel, the FMRC (1990) has developed the following classification, based on the work of D.J. Lewis (1980d):

Class		*TNT equivalence* (%)
I	Relatively unreactive materials (e.g. propane, butane and ordinary flammable materials)	5
II	Moderately reactive materials (e.g. ethylene, diethyl ether, acrolein)	10
III	Highly reactive materials (e.g. acetylene)	15

In the method given by Prugh (1987a) the effect of cloud size is taken into account by making the yield of the explosion a function of the mass of fuel in the cloud.

Two different approaches to the effect of obstructions are used in the methods of Exxon (n.d.) and R.J. Harris and Wickens (1989). In the Exxon method a distinction is made between a cloud in the open and one in partially obstructed terrain. In that of Harris and Wickens the mass participating in the explosion is limited to that in the part of the cloud in the obstructed area.

The variation of TNT equivalence with distance is taken into account by Prugh (1987a) by the use of a virtual distance method in which the virtual distance is a function of the mass of fuel involved in the explosion. The effective distance is then the sum of the virtual distance correction and the actual distance; by this expedient he obtains a single curve to fit the far field overpressures and approximate those in the near field.

The concept of virtual distance is also utilized by R.J. Harris and Wickens (1989), but in this case to obtain a match for the peak overpressure at the edge of the cloud.

All these approaches have something to offer, but there does not appear to be any single method which incorporates them all.

17.28.10 TNT equivalent models: Brasie and Simpson model

The basic TNT equivalent model was stated in a classic paper by Brasie and Simpson (1968). Their expression for the TNT equivalent is now generally written in the form

$$W_{\mathrm{TNT}} = \alpha \frac{W \Delta H_{\mathrm{c}}}{E_{\mathrm{TNT}}} \qquad [17.28.6]$$

where E_{TNT} is the energy of explosion of TNT (kJ/kg), ΔH_{c} is the heat of combustion of the hydrocarbon (kJ/kg), W is the mass of hydrocarbon (kg), W_{TNT} is the equivalent mass of TNT (kg) and α is the yield factor.

Brasie and Simpson noted that the values quoted for the energy of explosion of TNT varied between 1800 BTU/lb (4190 kJ/kg) and 2000 BTU/lb (4650 kJ/ kg), and adopted the latter.

From analysis of three VCE incidents they obtained values of the yield factor of 0.03–0.04, and on this basis proposed for use tentative values, intended to be conservative, of 0.02 in the near field and 0.05 in the far field, taken as that where the peak overpressure is 1 psi or less.

Brasie and Simpson also gave a graph and a table of damage vs peak overpressure, and made proposals for damage estimation.

17.28.11 TNT equivalent models: ACMH model

The *Second Report* of the ACMH (Harvey, 1979b) discusses the problem of VCEs. In particular, it gives an equation for the cloud size, a suggested value for the explosion efficiency and an overpressure curve based on the TNT equivalent model. This information taken as a whole may be regarded as a form of model.

The relation for cloud size was quoted as equation 15.46.47, and the suggested value of the yield was given as 0.03, as described in Section 17.27.7. The curve for peak overpressure is reproduced in Figure 17.73. The curve utilizes a damage classification based on bomb damage to dwelling houses in the Second World War. The classes given in the report as most relevant are:

Damage classification	*Damage*
A	Almost complete demolition
B	So severe as to necessitate demolition
Cb	House uninhabitable but not totally irreparable

'Glass damage' is expressed as the percentage of windows broken.

17.28.12 TNT equivalent models: Harris and Wickens model

The experimental work of R.J. Harris and Wickens (1989) has been described in Section 17.28.3. These authors also present a model of the TNT equivalent type. In the Harris and Wickens model, the mass of gas participating in the VCE is restricted to the confined and congested part of the plant, and that in the unconfined part of the cloud is neglected. The yield on this more limited mass is taken as 0.20. The energy of explosion of TNT is taken as 4.6 MJ/kg and the heat of combustion of the hydrocarbon as 46 MJ/kg, a difference of a factor of 10. Then, from the relation

$$M_{\mathrm{TNT}} = \alpha \frac{M_{\mathrm{gas}} E_{\mathrm{gas}}}{E_{\mathrm{TNT}}} \qquad [17.28.7]$$

the authors obtain

$$M_{\mathrm{TNT}} = 2M_{\mathrm{gas}} \qquad [17.28.8]$$

where E_{gas} is the heat of combustion of the hydrocarbon (MJ/kg), E_{TNT} is the energy of explosion of TNT (MJ/kg), M_{gas} is the mass of gas (in the confined/congested region) (te), M_{TNT} is the mass of TNT (te) and α is the yield factor. Equation (17.28.8) is obtained from Equation 17.28.7 with $E_{\mathrm{gas}}/E_{\mathrm{TNT}} = 10$ and $\alpha = 0.20$. Then, taking for the density for the hydrocarbon–air mixture a low value of 0.08 kg/m^3 (normal densities at 20 C are around 1.3 kg/m^3), yields from Equation 17.28.8

$$M_{\mathrm{TNT}} = 16 \times 10^{-5} V \qquad [17.28.9]$$

where V is the volume of gas (in the confined/congested region) (m^3).

The blast correlation used is that of the ACMH as given in Figure 17.73 (TNT curve).

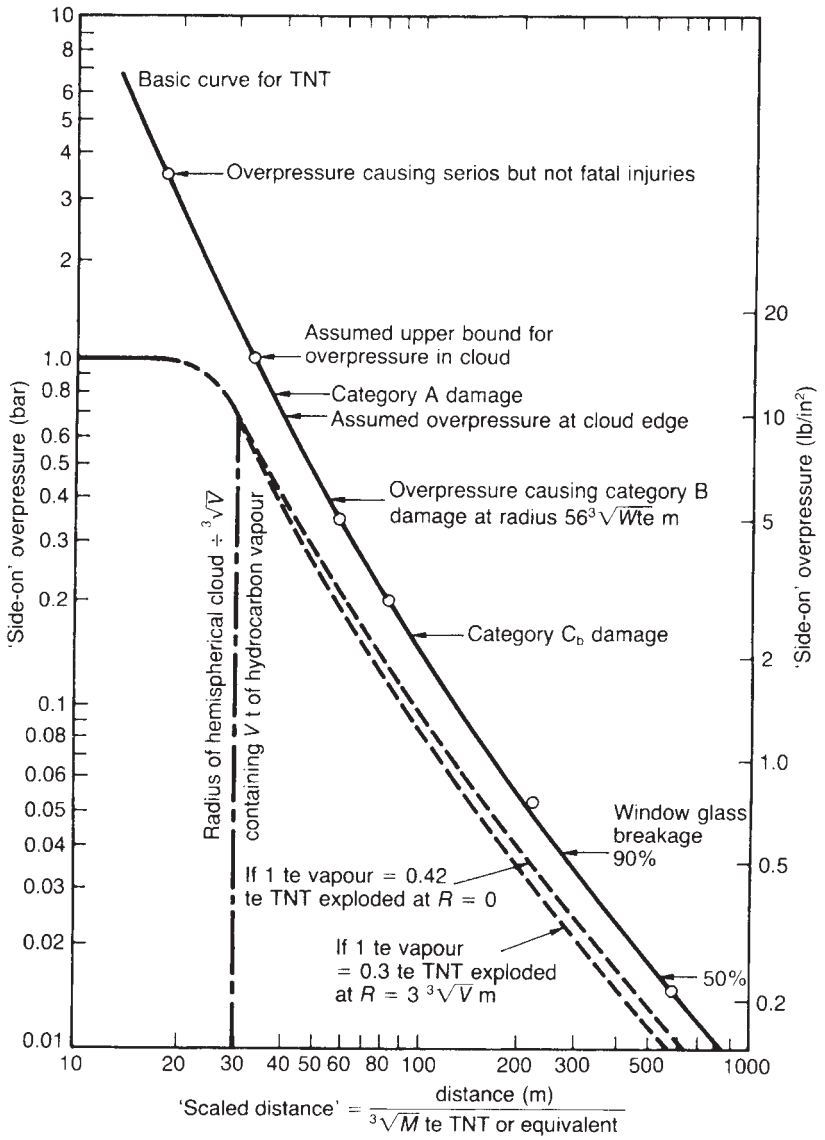

Figure 17.73 *Peak side-on overpressure for a vapour cloud explosion: ACMH correlation (Harvey, 1979b) (Reproduced by permission of HM Stationery Office. Copyright. All rights reserved)*

As already described, these authors obtained for the peak overpressure at the edge of the vapour cloud a value of 4 bar, rather than the value of 1 bar proposed by the ACMH. They take this finding into account by determining the scaled distance for an overpressure of 4 bar on the ACMH graph, which is 16 ($m/te^{1/3}$) and proposing the use of an effective scaled distance of

$$16 + \frac{R}{(M_{TNT})^{1/3}} \qquad [17.28.10]$$

where R is the actual distance (m). This is effectively a virtual source correction.

17.28.13 TNT equivalent models: other models

In addition to those just described, several other TNT equivalent models for VCEs have been developed, published or unpublished. They include those of Exxon (n.d.), Eichler and Napadensky (1977), Prugh (1987a), the FMRC (1990) and IRI (1990). These are reviewed by the CCPS (1994/15).

As already indicated, such models tend to differ in the methods used for (1) the mass of vapour participating in the explosion and (2) the yield factor of the explosion. Other differences relate to (3) the value used for the energy of explosion of TNT and (4) the correlation used for the peak overpressure of TNT.

Several of these models include a procedure for estimating the mass of flammable vapour which participates in the explosion. This aspect of the models is considered in Chapter 15.

The other main distinguishing feature of the models is in the estimation of the yield factor. This is considered in the next section.

The CCPS states that values used for the explosion energy of TNT lie in the range 4140–4650 kJ/kg, the same as that considered by Brasie and Simpson.

The blast correlations used in the models are given in Section 17.28.15.

The methods described are coherent procedures considered by their authors to give reasonable results. It is not appropriate to abstract particular features and use them indiscriminately. Each model is a 'package deal'.

It should also be borne in mind that models are developed for different purposes. The majority are essentially guides to the plant designer, particularly in relation to plant layout and control room design. Care should be exercised in applying such a model to hazard assessment or incident investigation.

17.28.14 TNT equivalent models: yield factor

The values used in the models mentioned for the yield factor are

Method	*Scenario/comment*	*Yield factor*
Brasie and Simpson	Near field	0.02
	Far field	0.05
ACMH		0.03
Exxon	Open terrain	0.03
	Partially confined and obstructed terrain	0.10
Eichler and Napadensky		0.02–0.40
Prugh	Mass of vapour cloud = 100 kg	0.02
	Mass of vapour cloud = 10^6 kg	0.70
Harris and Wickens	Mass in obstructed region only	0.20
FMRC	Relative non-reactive material	0.05
	Moderately reactive material	0.10
	Highly reactive material	0.15
IRI		0.02

The model of Eichler and Napadensky is for safe separation distances between nuclear power plants and transport routes and refers to the far field (peak overpressure 1 psi (0.07 bar)) and is evidently conservative. The higher of the two values given by Prugh refers to a very large cloud.

17.28.15 TNT equivalent models: blast correlation

The graphical correlations used for the peak overpressure from a TNT explosion are principally the following: Glasstone (1962) (Brasie and Simpson) and Glasstone and Dolan (1980) (IRI); V.C. Marshall (1976c) (ACMH); ACMH (Harris and Wickens); Kingery and Panill surface bursts (1964) (Exxon); and the US Army, Navy and Air Force (1990) (the Tri-Service Manual) (FMRC).

The ACMH correlation is based on that of V.C. Marshall (1976c). This has been reproduced in the literature with different scaled distances. In the ACMH graph the mass used in the scaled distance is in tonnes, in the graph given by the CCPS (1994/15) the mass is explicitly stated to be in kilograms.

17.28.16 TNT equivalent models: yield ratio

For completeness in the treatment of the TNT equivalent model, it is convenient to deal at this point with the question of the yield ratio, or symmetry factor.

As explained earlier, if a free-air burst correlation is used for the blast parameters, but the application is to a ground burst, an appropriate yield ratio is applied to the actual energy of explosion, or equivalent mass of TNT, to obtain an effective energy, or mass, for use in calculation of the scaled distance.

The simple, and conservative, approach is to take this yield ratio as 2.

The value of the yield ratio is discussed by the CCPS (1994/15). It suggests that the value of the yield ratio will generally lie in the range 1.7–2. The lower value may be preferred if the epicentre of the explosion is slightly above the ground.

17.28.17 Taylor model

An early model of a VCE was given in a classic paper by G.I. Taylor (1946). He considers small pressure disturbances, as in acoustics, so that the system equations can be linearized. The treatment which he describes is in terms of an expanding piston for which from the conservation equations in spherical geometry he obtains the wave equation

$$r^2 \frac{\partial^2 \phi}{\partial t^2} = a_o^2 \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial \phi}{\partial r} \right) \right] \qquad [17.28.11]$$

with the velocity potential ϕ such that

$$u = \frac{\partial \phi}{\partial r} \qquad [17.28.12]$$

$$p - p_o = -\rho_o \frac{\partial \phi}{\partial t} \qquad [17.28.13]$$

where a_o is the speed of sound, p is the absolute pressure, p_o is the ambient pressure, r is the radial distance, t is the time, u is the velocity, ρ_o is the density of the ambient gas and ϕ is the velocity potential. The term $(p - p_o)$ is thus the overpressure.

The boundary condition used is such that the velocity of the medium is equal to that of the piston. From this Taylor obtains the velocity potential as

$$\phi = a_o \frac{M_p^3}{1 - M_p^2} \frac{(r - a_o t)^2}{r} \qquad [17.28.14]$$

and hence

$$\bar{p} = 2\gamma \frac{M_p^3}{1 - M_p^2} \left(\frac{a_o}{r} - 1 \right) \qquad [17.28.15]$$

with

$$\bar{p} = \frac{p - p_o}{p_o} \qquad [17.28.16]$$

where M_p is the Mach number of the piston, $\bar{p}$ is the dimensionless overpressure and γ is the ratio of the specific heats.

Equating the mass within the piston flow field and that within the flame flow field yields the following relation between the piston and flame Mach numbers:

$$M_p^3 = M_f^3\left(\frac{\alpha - 1}{\alpha}\right) \qquad [17.28.17]$$

where M_f is the flame Mach number and α is the expansion ratio.

17.28.18 Strehlow model

The VCE model given by Strehlow (1981) also follows the acoustic approach, but utilizes a constant velocity piston.

It was shown by Stokes (1849) that a source of mass with mass flow $\dot{m}(t)$ generates a sound wave in three dimensions which has an overpressure that is proportional to the mass addition acceleration $\ddot{m}(t)$. Lighthill (1978) gave this concept the specific formulation

$$p - p_o = \frac{\ddot{m}(t - r/a_o)}{4\pi r} \qquad [17.28.18]$$

where a_o is the velocity of sound, p is the absolute overpressure, p_o is the ambient pressure and r is the characteristic radius of the source region. Here, $\ddot{m}(t)$ is replaced by $\ddot{m}(t - r/a_o)$ because the wave is propagating away from the source at the velocity of sound.

Then, for deflagrative combustion the effective rate of volume addition $\dot{v}(t)$ is related to that of mass addition $\ddot{m}(t)$:

$$\ddot{m}(t) = \rho_o \dot{V}(t) \qquad [17.28.19]$$

where ρ_o is the initial density of the gas.

The acceleration of volume addition can be expressed in terms of the rate of change of the flame surface. Hence

$$\ddot{m}(t) = \gamma\rho_o\left(\frac{V_b - V_u}{V_u}\frac{d}{dt}[S_u(t)A_f(t)]\right) \qquad [17.28.20]$$

where A_f is the effective frontal area of the flame, S_u is the burning velocity, V_b is the specific volume of the burned gas and V_u the specific volume of the unburned gas.

Then, from the expression for the velocity of sound in an ideal gas $a_o^2 = p_o/\rho_o$ and from Equations 17.28.18 and 17.28.20

$$\bar{p} = \frac{\hat{q}}{4\pi r a_o^2 \gamma}\frac{d[S_u(t)A_f(t)]}{dt} \qquad [17.28.21]$$

with

$$\hat{q} = \gamma\frac{V_b - V_u}{V_u} \qquad [17.28.22]$$

where $\bar{p}$ is the dimensionless overpressure, $\hat{q}$ is the dimensionless rate of energy addition and γ is the ratio of specific heats.

For a constant velocity flame, Equation 17.28.21 reduces to

$$\bar{p} = \frac{\hat{q}}{4\pi r a_o^2 \gamma}S_u\frac{dA_f(t)}{dt} \qquad [17.28.23]$$

Then, for spherical geometry, utilizing in Equation 17.28.23 the relations for the area, radius and velocity of the flame front

$$A_f = 4\pi r_f^2 \qquad [17.28.24]$$

$$\frac{dr_f}{dt} = S_b = u_f \qquad [17.28.25]$$

$$S_b = S_u\frac{V_b}{V_u} \qquad [17.28.26]$$

and the definition of $\hat{q}$, applying the constant velocity flame relation

$$r_f = S_b t \qquad [17.28.27]$$

and substituting for t the term $(t - r/a_o)$, yields

$$\bar{p} = 2\gamma\left(1 - \frac{V_u}{V_b}\right)\left(\frac{V_b}{V_u}\right)^2 M_{su}^3\left(\frac{a_o t}{r} - 1\right) \qquad [17.28.28]$$

where M_{su} is the Mach number in the unburned gas.

The relation between this model and that of Taylor at low flame speeds may be demonstrated as follows. Using Taylor's relation between the flame and piston Mach numbers, Equation 17.28.17, and the relations

$$\alpha = V_b/V_u \qquad [17.28.29]$$

$$M_f = M_{su}\frac{V_b}{V_u} \qquad [17.28.30]$$

where u_f is the velocity of the flame front. If $M_p \ll 1$ or for low values of the flame Mach number M_f, the denominator in Equation 17.28.15 is approximately unity and Equation 17.28.28 is equivalent to Equation 17.28.15.

Equation (17.28.23) is a general relation which may be applied to vapour clouds of different geometries. The different cases may be examined by substituting different expressions for A_f and hence dA_f/dt. For spherical geometry utilizing for A_f Equation 17.28.24 gives

$$\bar{p} = \frac{2\hat{p}S_u^2 r_f}{r a_o^2}\frac{V_b}{V_u}, \quad r \geq r_f \qquad [17.28.31]$$

Using alternative expressions for the flame area A_f and the rate of change of the flame radius dr_f/dt, Strehlow obtains expressions for the overpressure in explosions of vapour clouds of other geometries and other points of ignition. These include an ellipsoid, a cigar-shaped cloud with end point ignition and pancake clouds with centre and with edge ignition. Thus, for a pancake cloud

$$A_f = 2\pi r_f H \qquad [17.28.32]$$

where H is the height of the cloud. Then

$$\bar{p} = \frac{\hat{q}S_u^2 H V_b}{2a_o^2 r_{obs} V_u} \qquad [17.28.33]$$

where r_{obs} is the distance of the observer from the centre of the cloud.

Strehlow also obtains an order of magnitude estimate of the effect of cloud size. For an overpressure of 0.1 bar at a

Table 17.35 *Strehlow model for VCE: effect of burning velocity and flame area (after Strehlow, 1981) (Courtesy of American Institute of Chemical Engineers)*

A $dS_u/dt = 0$	
S_u (m/s)	dA_f/dt (m^2/s)
1	1.7×10^7
10	1.7×10^6
100	1.7×10^5
B $dA_f/dt = 0$	
A_f (m^2)	dS_u/dt (m/s^2)
10^2	1.7×10^5
10^4	1.7×10^3
10^6	1.7

distance 100 m from the cloud centre and with a velocity of sound of 350 m/s Equation 17.28.21 reduces to

$$A_f \frac{dS_u}{dt} + S_u \frac{dA_f}{dt} = 1.6 \times 10^7 m^3/s^2 \qquad [17.28.34]$$

Then, the use of the alternative limiting assumptions $dS_u/dt = 0$ and $dA_f/dt = 0$ allows values of dA_f/dt and dS_u/dt, respectively, to be calculated. Table 17.35 shows the values given by Strehlow. The table shows that even for a high flame velocity the rate of increase of flame area must also be very high to generate even a weak blast wave, while only a very large flame area, with a very large acceleration, is able to produce a weak blast wave. He concludes that for a significant overpressure to be generated by deflagrative combustion alone a very large cloud is required.

Further development of this approach for clouds of different aspect ratios has been described by Raju and Strehlow (1984).

17.28.19 Model of Kuhl, Kamel and Oppenheim

In another classic paper, Kuhl, Kamel and Oppenheim (1973) presented an 'exact' similarity solution for the conservation equations which they give in the form

$$\frac{F}{2Z}\frac{dF}{dZ} = \frac{Z - (1-F)^2 + (\gamma - 1)(1-F)F}{3Z - (1-F)^2} \qquad [17.28.35]$$

$$\frac{F}{X}\frac{dX}{dF} = \frac{-Z + (1-F)^2}{3Z - (1-F)^2} \qquad [17.28.36]$$

with

$$F = \frac{u}{U_s X} \qquad [17.28.37]$$

$$Z = \left(\frac{a}{U_s X}\right)^2 \qquad [17.28.38]$$

$$X = \frac{r}{r_s} \qquad [17.28.39]$$

where a is the speed of sound, r is the radial distance, r_s is the radial distance of the leading shock, u is the particle velocity and U_s is the velocity of the leading shock.

Their model is based on a constant velocity piston. The leading shock travels ahead of the piston with the flame front in between.

In the form given, the model has to be solved numerically.

The authors explored the implication of their model for flame speeds ranging from 0.5 to 120 m/s. The maximum overpressure ratio obtained was 6, with flame speeds of 5–10 m/s being associated with overpressure ratios of the order of 0.05–0.10. They give a set of curves showing the strong increase of overpressure with flame speed.

17.28.20 Williams model

A number of workers have obtained approximate analytical solutions of the constant velocity piston case based on self-similarity. The model of F.A. Williams (1976), also discussed by Anthony (1977a), is illustrative of this approach.

In the model it is assumed that ignition occurs at a point source, that the flame front which develops travels out from the 'core' at a flame speed S and that the pressure waves produced by the flame generate a weak shock which travels ahead of the flame at a velocity $V(t)$ which varies with time. It is also assumed that the pressure and density in the 'shell' between the flame and shock fronts are constant.

Then, for spherical symmetry the model equation for conservation of momentum across the shock wave is

$$p_1 - p_o = \rho_o \left(\frac{dR}{dt}\right)^2 \left(1 - \frac{\rho_o}{\rho_i}\right) \qquad [17.28.40]$$

or in dimensionless form

$$p = 1 + (1 - K)\left(\frac{dy^2}{d\tau}\right) \qquad [17.28.41]$$

The other basic equations, also in dimensionless form, are for conservation of mass for a sphere of radius R,

$$\theta p x^3 + \frac{(y^3 - x^3)}{K} = y^3 \qquad [17.28.42]$$

and for conservation of mass for the burned core,

$$\frac{x^2 s}{K} = \frac{d}{d\tau}(\theta p x^3/3) \qquad [17.28.43]$$

The similarity solution is

$$s = \frac{Kq\theta p(p-1)^{1/2}}{(1 - K\theta P)^{1/3}(1-K)^{1/6}} \qquad [17.28.44]$$

with

$$p = p_1/p_o \qquad [17.28.45a]$$

$$s = S/a_o \qquad [17.28.45b]$$

$$x = r/R_o \qquad [17.28.46a]$$

$$y = R/R_o \qquad [17.28.46b]$$

$$\theta = T_o/T_2 \qquad [17.28.47a]$$

$$K = r_o/r_1 \qquad [17.28.47b]$$

$$\tau = a_o t/R_o \qquad [17.28.47c]$$

where a_o is the speed of sound ($=(p_o/\rho_o)^{1/2}$), p_i is the absolute pressure in region i, r is the flame radius, R is the shock radius, R_o is the initial value of the shock radius, S is the flame speed, t is the time, T_i is the absolute temperature in region i, ρ_i is the gas density in region i and τ is the dimensionless time. The subscripts o, 1, 2 of p, T and ρ refer, respectively, to conditions in the undisturbed gas, the shocked gas (shell) and the burnt gas (core). The variables K, θ and p are time dependent.

The model yields a number of interesting results. One is that from Equation 17.28.40 the shock wave pressure has a well-defined upper limit. Another is that for transition to detonation the flame speed must be an appreciable fraction of the speed of sound:

$$s > (K/3)[(p-1)(1-K)]^{1/2} \qquad [17.28.48]$$

17.28.21 Other similarity models

The model just described is one a number of approximate analytical models.

A review of this work is given by the CCPS (1994/15), which presents for some of the models a set of graphs of the flow field parameters, in each of which the curves of particular workers are compared with those of the 'exact' solution.

17.28.22 Gugan model

In his review of VCEs, Gugan (1979) includes a model based on self-similarity which he uses to examine the characteristics of such explosions. This model is not in the mainstream of VCE models, but constitutes an interesting approach, particularly to behaviour in the near field.

The blast wave from a VCE is inherently unstable, and at a point quite close to the centre of the explosion it transforms into a shock wave. Beyond this transformation point, in the far field, no distinction can be made between a condensed phase explosion and a VCE on the basis of the shock wave. But between the explosion centre and the transformation point, in the near field, some interesting features emerge.

Gugan uses the following relation for the pressure profile:

$$p = \frac{p_c t}{2}\left[1+\cos\left(\frac{\pi r}{at}\right)\right], \quad 0 < r \le at \qquad [17.28.49]$$

where a is the velocity of sound in the normal atmosphere, p is the pressure, p_c is the pressure at the centre of the explosion, r is the distance from the centre of the blast symmetry and t is the time. The term $p_c t$ is therefore the pressure at the centre of the explosion. The form of curve given by this equation is the 'companion to the cycloid'.

Utilizing the relations for the energy E contained in the compressed gases $E = \int V\,\mathrm{d}p$ and for the relation between the pressure p and the volume V for an isentropic expansion $\int V\,\mathrm{d}p = \gamma \int V\,\mathrm{d}p$ (where γ is the ratio of the gas specific heats) together with Equation 17.28.49, Gugan obtains for the pressure at the centre of the explosion

$$\dot{p}_c t = \frac{E_o}{0.57(at_o)^3} \qquad [17.28.50]$$

where E_o is the total energy release and t_o is the time of termination of the rapid energy release. Equation 17.28.50, and alternative relations derived by the author, provide the value of the term $p_c t$ in Equation 17.28.49 and allow estimates to be made of the pressure profile.

The author compares the relation which he derives for the pressure profile from a VCE with that from a condensed phase explosion. These relations indicate that for the same energies and distances, the amplitude of the shock wave from a condensed phase explosion exceeds that from a VCE by one or two orders of magnitude. Yet the shock waves from VCEs are very destructive. He concludes that this is due to the longer duration time of the positive phase in VCEs and suggests that the factor of 2, which is sometimes given for the ratio of the duration time in a VCE to that in a condensed phase explosion, is probably an underestimate.

Gugan defines an explosion efficiency 77:

$$\eta = E_e/E_u \qquad [17.28.51]$$

where E_e is the explosive energy release and E_u is the vapour cloud energy release. For the latter

$$E_u = m\Delta H_c \qquad [17.28.52]$$

where ΔH_c is the heat of combustion and m is the mass of fuel in the cloud. He obtains for the explosion efficiency expressions of the general form

$$\eta = \frac{f(m;\Delta H_c;M;\epsilon;v)}{f(R)} \qquad [17.28.53]$$

where M is the molecular weight of the vapour, n is the stoichiometric ratio and v is the flame speed.

The expression for the explosion efficiency shows the efficiency as a function of various characteristics of the fuel. In the near field it falls off rapidly with distance R, being inversely proportional to R^3.

This model proved controversial and was criticized by Ale and Bruning (1980). One feature is the decay of efficiency, which did not appear to sit well with the effects of actual explosions. A review has been given by H. Phillips (1981b).

17.28.23 Baker–Strehlow model

Strehlow, Luckritz and co-workers conducted numerical studies, using the CLOUD code, exploring for spherical geometry the characteristics of flames travelling at constant velocity and with acceleration (Luckritz, 1977; Strehlow *et al.*, 1979) and obtained relationships for the blast wave parameters. This work was extended by W.E. Baker *et al.* (1983) to yield the Baker–Strehlow method for VCEs.

The scaled peak overpressure and the scaled impulse given by this method are shown in Figures 17.74 and Figure 17.75, respectively. The scaled variables are given by Equations 17.26.7–17.26.9. The graphs are for spherical symmetry.

Figures 17.74 utilizes two Mach numbers, M_w, which relates to fixed coordinates, and M_{su}, which is relative to the gases moving ahead of the flame front. The relationship between these two Mach numbers is discussed by Strehlow *et al.* (1979). At high Mach numbers $M_{su} \rightarrow M_w$. The solid lines in the figure represent numerical calculations, and the broken lines extensions of Taylor's model to the very low Mach number range. Also shown in the figure are curves

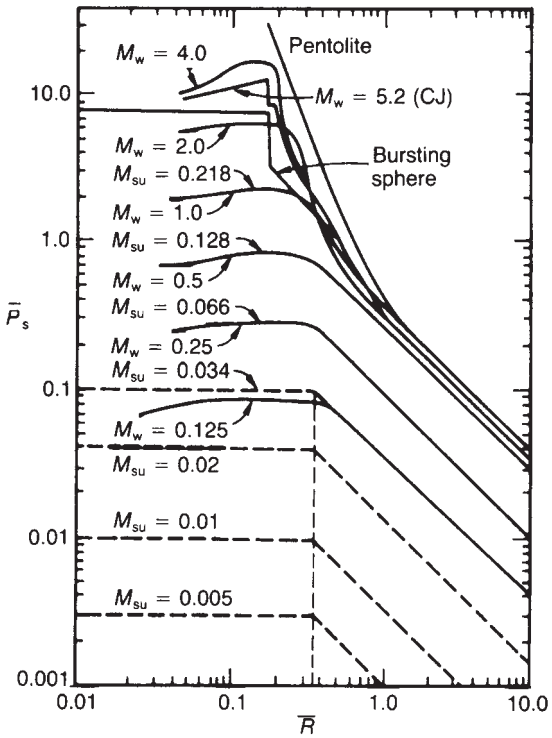

Figure 17.74 *Scaled peak side-on overpressure for a vapour cloud explosion (Strehlow et al., 1979). Curves and Mach numbers are explained in the text (Courtesy of the Combustion Institute)*

for pentolite, for a bursting sphere and for detonation (CJ curve).

The method requires values of the energy of explosion and the flame speed. The explosion energy may be determined using one of the methods described in Section 17.28.14 in relation to the TNT equivalent model. The flame speed is estimated by considering the effect of the combination of factors known to influence it: the reactivity of the fuel, the strength of the ignition source and the degree of confinement and congestion.

17.28.24 Wiekema model (TNO shock wave model)

Three models of VCE have been developed by TNO. The first of these is the shock wave model described in the Yellow Book and by Wiekema (1980). The model is also known as the expanding piston or piston blast model. It allows the peak overpressure and the duration time of the explosion to be estimated.

The model is a composite one derived from separate models for deflagration and detonation in the cloud. Considering first the model for deflagration, it has been shown by Strehlow, Savage and Vance (1973) that given the pressure–time profile it is possible to derive the energy of an explosion. Wiekema uses this result, inverting it to obtain the pressure–time profile from an arbitrary energy release.

The cloud is assumed to be a hemisphere of unburnt gas volume V_o which expands during the combustion process to a hemisphere volume V_1. In this process the energy added to the unburnt gas is assumed to be added by a hemispherical piston, this process effectively replacing the combustion process. This energy E_o is

$$E_o = \int_0^\infty p \frac{dV}{dt} dt \qquad [17.28.54a]$$

$$\approx p_o(V_1 - V_o) \qquad [17.28.54b]$$

$$= n_1 R_g T_1 - n_o R_g T_o \qquad [17.28.54c]$$

$$= p_o V_o \left[\frac{n_1 T_1}{n_o T_o} - 1\right] \qquad [17.28.54d]$$

where E_o is the total energy of the explosion (J), n is the number of moles, p is the absolute pressure (Pa), R_g is the universal gas constant (J/mol K), T is the absolute temperature (K), V is the volume (m^3) and the subscripts o and 1 denote initial and final conditions, respectively. But

$$E_o = \frac{2}{3}\pi R_o^3 E_c \qquad [17.28.55]$$

where E_c is the energy of combustion per unit volume (J/m^3) and R_o is the radius of the initial cloud (m).

A characteristic explosion length L is defined as

$$L = \left(\frac{E_o}{P_o}\right)^{1/2} \qquad [17.28.56a]$$

$$= \left(\frac{2}{3}\pi R_o^3 \frac{E_c}{p_o}\right)^{1/3} \qquad [17.28.56b]$$

where L is the characteristic length (m), and a parameter λ as

$$\lambda = \frac{L}{t_b} \qquad [17.28.57]$$

where t_b is the time (s) at which the expansion process is incomplete. A reduced distance $\bar{R}$, reduced overpressure $\bar{P}$, reduced time t and reduced duration time $\bar{T}$ are then defined as follows :

$$\bar{R} = \frac{R}{L} \qquad [17.28.58]$$

$$\bar{P} = \frac{p - p_o}{p_o} \qquad [17.28.59]$$

$$\bar{t} = \frac{t}{t_b} \qquad [17.28.60]$$

$$\frac{\bar{T} = t_+ c_o}{L} \qquad [17.28.61]$$

where c_o is the local velocity of sound (m/s), R is the distance (m) and t_+ is the duration time (s).

The reduced overpressure is taken as inversely proportional to the reduced distance:

$$\bar{P} = \frac{A}{\bar{R}} \qquad [17.28.62a]$$

$$= \frac{AL}{R} \qquad [17.28.62b]$$

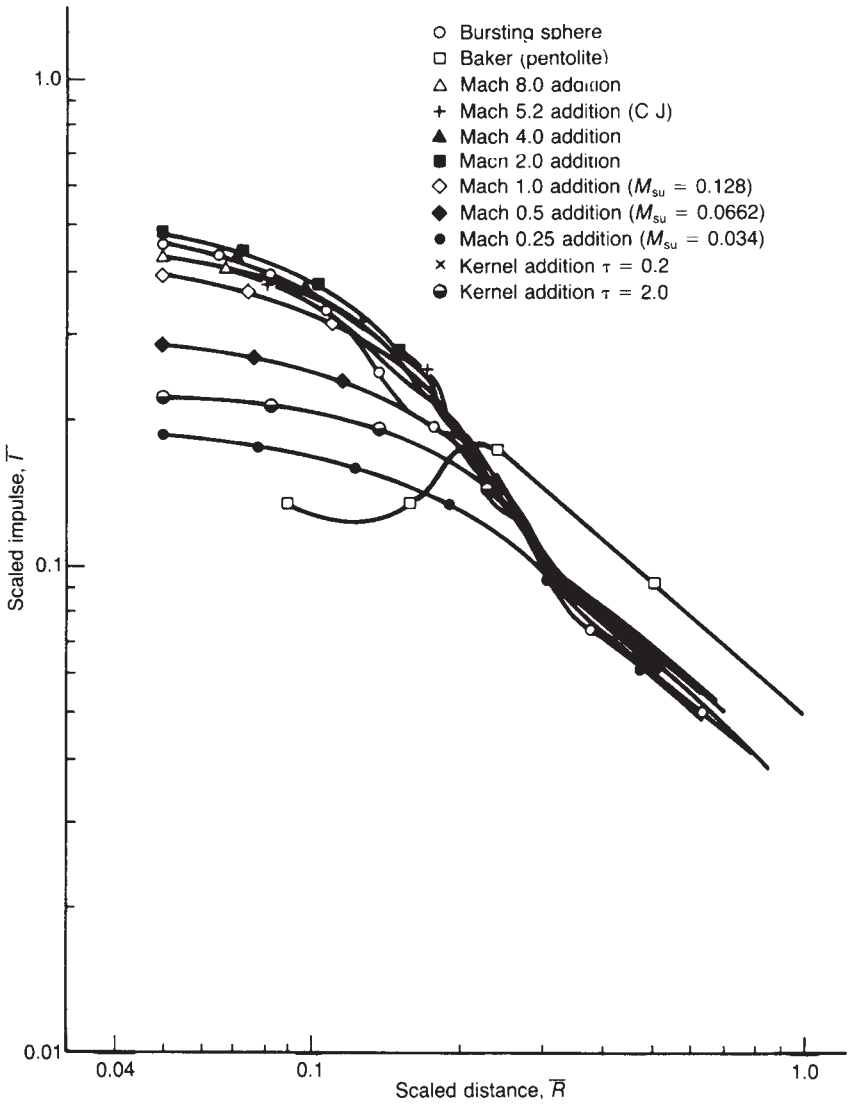

Figure 17.75 *Scaled side-on impulse for a vapour cloud explosion (Strehlow et al., 1979) (Courtesy of the Combustion Institute)*

where A is a constant. From shock wave theory

$$U_{sw} = \frac{dR}{dt} \qquad [17.28.63a]$$

$$= c_o\left(1 + \frac{\gamma+1}{4\gamma}\bar{P}\right) \qquad [17.28.63b]$$

where U_{sw} is the velocity of the shock wave (m/s) and γ the ratio of specific heats for air. Taking $\gamma = 1.4$,

$$\frac{dR}{dt} = c_o\left(1 + \frac{3}{7}\bar{P}\right) \qquad [17.28.64a]$$

$$= c_o\left(1 + \frac{3AL}{7R}\right) \qquad [17.28.64b]$$

The duration time is determined as the difference between the arrival times of the shock wave and the sound wave and at the radius R_1 of the burnt cloud it is

$$t_+ = R_1\left(\frac{1}{\bar{v}_{fl}} - \frac{1}{c_o}\right) \qquad [17.28.65]$$

where $\bar{v}_{fl}$ is the average flame speed (m/s).

The velocities of the shock wave and sound wave in the cloud and beyond are shown in Figure 17.76.

Integrating Equation 17.28.64b gives

$$t_+ = R_1\left(\frac{1}{\bar{v}_{fl}} - \frac{1}{c_o}\right) + \frac{3}{7}A\frac{L}{c_o}\ln\left(\frac{1 + 7R/3AL}{1 + 7R_1/3AL}\right), \quad R > R_1 \qquad [17.28.66]$$

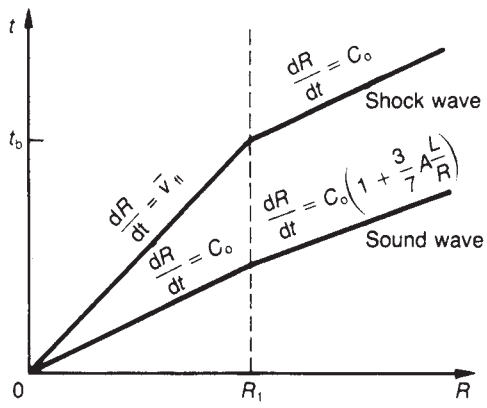

Figure 17.76 *TNO shock wave model for vapour cloud explosions: propagation of flame front and sound wave (Wiekema, 1980) (Courtesy of Elsevier Science Publishers)*

At the cloud boundary ($R = R_1$), Equation 17.28.66 reduces to Equation 17.28.65. The reduced duration time is then

$$\bar{T} = \frac{R_1}{L}\left(\frac{c_o}{\bar{v}_{fl}} - 1\right) + \frac{3}{7}A\ln\left(\frac{1 + 7R/3AL}{1 + 7R_1/3AL}\right), \quad R > R_1 \qquad [17.28.67a]$$

In evaluating Equation 17.28.67 use is made of the relation

$$R_1/L = 0.456 \qquad [17.28.67b]$$

derived from the definitions given in the work.

The following numerical values are assumed in the work:

$$\frac{n_1 T_1}{n_o T_o} = 7$$

$$E_c = 3.5 \times 10^6\ \text{J/m}^3$$

The energy added per unit volume, which is the energy available for shock wave formation, is 6×10^5 and is thus some 17% of the available combustion energy, assuming a stoichiometric mixture. The velocity of sound c_o in air may be taken as 330 m/s.

The method involves selecting an assumed flame speed. The set of flame speeds $\bar{v}_{fl}$ quoted are 40, 80 and 160 m/s, and the corresponding values of the parameter A are 2×10^{-2}, 6×10^{-2} and 15×10^{-2}, respectively.

The reduced overpressure $\bar{P}$ and reduced duration time $\bar{T}$ are both functions of the reduced distance $\bar{P}$, as shown in Figure 17.77.

As an illustration of the method, consider the estimation of the peak overpressure and duration time at a distance P of 500 m for a VCE in a hemispherical cloud of initial radius R_o of 100 m assuming an average flame speed of 80 m/s. Then, from Equation 17.28.56b

$$L = \left[\frac{2}{3}\pi(100)^3 + \frac{3.5 \times 10^6}{10^5}\right]^{1/3}$$
$$= 418\,\text{m}$$

Hence, from Equation 17.28.67a:

$$R_1 = 0.456L$$
$$= 0.456 \times 418$$
$$= 191\,\text{m}$$

From Equation 17.28.58

$$\bar{R} = 500/418$$
$$= 1.2$$

From Equation 17.28.62, taking the value of A corresponding to the average flame speed v_{fl} of 80 m/s,

$$\bar{P} = 6 \times 10^{-2}/1.2$$
$$= 0.05$$

Hence, from Equation 17.28.59 the peak overpressure $(p - p_o)$ for an initial pressure p_o of 10^5 Pa (1 bar) is

$$p - p_o = 0.05 \times 10^5\ \text{Pa} = 0.05\ \text{bar}$$

And from Equation 17.28.67a

$$\bar{T} = 0.456\left(\frac{330}{80} - 1\right) + \frac{3}{7} \times 6 \times 10^{-2}$$
$$\times \ln\left(\frac{1 + (7 \times 1.2)/(3 \times 6 \times 10^{-2})}{1 + (7 \times 0.456)/(3 \times 6 \times 10^{-2})}\right)$$
$$= 1.45$$

Hence, from Equation 17.28.61

$$t_+ = 1.45 \times 418/330$$
$$= 1.83\,\text{s}$$

The model just described is applicable to a deflagration. For the case of detonation in a vapour cloud Wiekema utilizes results obtained by Kogarko, Adushkin and Lyamin (1966), from which he obtains the following relations for the reduced overpressure and reduced duration time:

$$\bar{P} = 0.518\bar{R}^{-1.7}, \quad 0.29 < \bar{R} < 1.088 \qquad [17.28.68a]$$
$$= 0.2177\bar{R}^{-1}, \quad \bar{R} > 1.088 \qquad [17.28.68b]$$
$$\bar{T} = 0.1853\bar{R}^{1/2}, \quad 0.36 < \bar{R} < 12.6 \qquad [17.28.69a]$$
$$= 0.20 + 0.0933\ln(1 + 10.7\bar{R}), \quad \bar{R} > 12.6 \qquad [17.28.69b]$$

Since in the detonation work no results are given for $\bar{T}$ for $\bar{R} > 12.6$, Equation 17.28.69b is based on the deflagration work.

Wiekema then consolidates these two models, for deflagration and detonation in a vapour cloud, into a single VCE model. The reduced overpressure $\bar{P}$ and reduced duration time $\bar{T}$ are shown as functions of the reduced distance $\bar{R}$ in Figure 17.78.

The lines shown in Figure 17.78 are the boundaries of materials of low, medium and high reactivity. Reactivity is essentially sensitivity to flame acceleration. For each class the lower boundary is used unless there is reason to expect a relatively high flame acceleration.

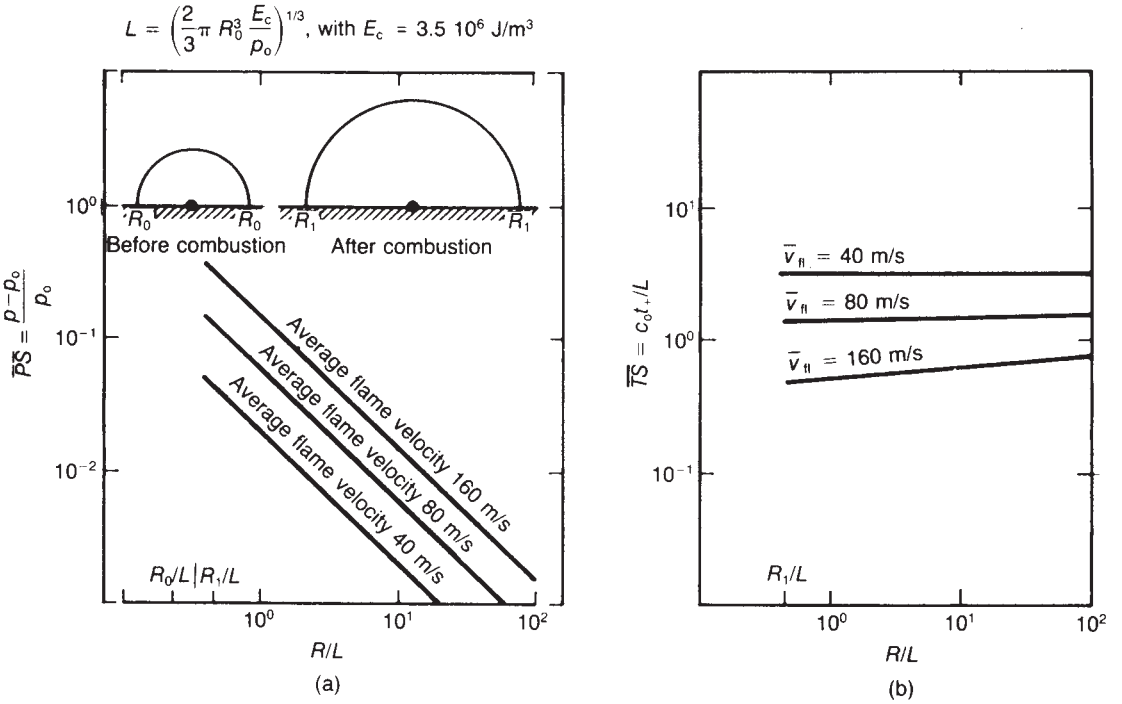

Figure 17.77 *TNO shock wave model for vapour cloud explosions – peak overpressure and duration of the blast wave, as a function of flame speed (Wiekema, 1980): (a) scaled peak overpressure and (b) scaled duration time (Courtesy of Elsevier Science Publishers)*

The reduced overpressure $\bar{P}$ is again inversely proportional to the reduced distance $\bar{R}$, except at the upper boundary for high reactivity materials. Wiekema states that methane is considered as a fuel of low reactivity, ethane and butane as fuels of medium reactivity and hydrogen, ethylene oxide and acetylene as fuels of high reactivity.

17.28.25 TNO correlation model

The second TNO VCE model is the correlation model; this too is described in the Yellow Book. The model allows an estimate to be made of the radius of defined damage circles. It does not give explosion parameters such peak overpressure or duration time.

The model is based on a correlation for VCE incidents of damage effects outside the gas cloud.

The correlation is based on the energy content E of the part of the cloud within the explosive range. This energy is

$$E = M_e \Delta H_c \qquad [17.28.70]$$

where E is the energy content of the part of the cloud within the flammable range (J), M_e is the mass of fuel in the cloud within the flammable range (kg) and ΔH_c is the heat of combustion (J/kg).

If the energy content $E < 5 \times 10^9$, corresponding to approximately 100 kg of hydrocarbon, the cloud is so small that no serious damage would be anticipated, while if $E > 5 \times 10^{12}$ the cloud is so large that no data are available on which to base a correlation. The model is applicable only to clouds with an energy content within those bounds.

The energy actually released is only a fraction η of the energy content E. This fraction, or efficiency, is the product of two separate efficiencies:

$$\eta = \eta_c \eta_m \qquad [17.28.71]$$

where η_c is a yield factor which takes account of the fact that the flammable part of the cloud is not a stoichiometric mixture and η_m is another yield factor which gives the mechanical energy yield of the combustion. The factor η_m is given different values, depending on whether combustion is at constant pressure or constant volume:

Constant pressure combustion $\eta_m = 0.18$
Constant volume combustion $\eta_m = 0.33$

Since combustion of a VCE tends to be associated with a degree of confinement, the constant volume value of η_m (= 0.33) is recommended. The relation for the radius of the damage circles is

$$R(S) = C(S)(\eta E)^{1/3} \qquad [17.28.72]$$

where $C(S)$ is a constant which is a function of the degree of damage S (m/J$^{1/3}$), E is the energy content (J), $R(S)$ is the radius of the damage circle (m) and η is the explosion efficiency.

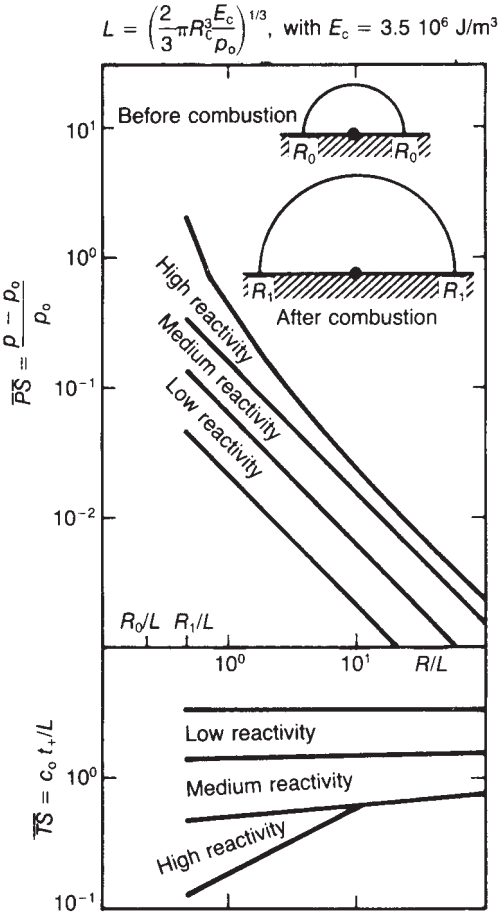

Figure 17.78 *TNO shock wave model for vapour cloud explosions – peak overpressure and duration of the blast wave, as a function of fuel reactivity (Wiekema, 1980): (a) scaled peak overpressure and (b) scaled duration time (Courtesy of Elsevier Science Publishers)*

The values of the constant C(S) are as follows:

Damage	*C(S)* (m/J$^{1/3}$)
Heavy damage to buildings and to processing equipment	0.03
Repairable damage to buildings and facade damage to dwellings	0.06
Glass damage causing injury	0.15
Glass damage (≈10% of panes)	0.4

17.28.26 van den Berg model (TNO multienergy model)

The third TNO VCE model is the ME model described by van den Berg (1985). This model allows the peak overpressure, peak dynamic pressure and duration time to be estimated.

The starting point for this model is recognition of the role of partial confinement in VCEs. It is assumed in the model that the explosion in those parts of the cloud which are confined is of much higher strength than in those where it is unconfined. The method involves estimating the combustion energy available in the various parts of the cloud and assigning to each part an initial strength.

This initial strength is denoted by a number in the range 1–10, where 1 applies to an explosion of insignificant strength and 10 to a detonation. Confined parts of the cloud are usually assigned a strength greater than 6 or 7.

The peak overpressure, peak dynamic pressure and duration time are estimated using Figure 17.79. For a given part of the cloud the energy of explosion in that part is determined, an initial strength is estimated and the blast parameters are then calculated.

The simplest case is that of a cloud with a single high strength source of reasonable size. The situation is more complex if this high strength source is small or if there are multiple high strength sources. Some judgement is required, therefore, in applying the method.

van den Berg gives as an illustration of the method the estimation of the peak overpressure and duration time of the VCE at Flixborough.

17.28.27 Numerical modelling

An alternative approach to the modelling of VCEs is the use of computational fluid dynamics (CFD) codes. An account of their application is given by the CCPS (1994/15).

The CFD modelling of VCEs is not entirely straightforward. There is a difficulty due to discontinuities, both contact discontinuity between the burned and unburned gases and shock discontinuity. For a blast flow field conventional numerical methods tend to yield inaccurate results.

In order to overcome these problems researchers have resorted to two devices. One is the use of artificial viscosity and the other the use of flux-corrected transport (FCT). The former was introduced by von Neumann and Richtmyer (1950) and the latter is described by Boris (1976) and Boris and Book (1976).

Both Eulerian and Langrangean formulations are used. The difference between these in their application to gas dispersion is touched on in Chapter 15 and discussed in standard texts (e.g. Meteorological Office, 1972).

Many workers have used the artificial viscosity method with the gas dynamics in Lagrangean form. They include Fishburn (1976), van den Berg (1984) and van Wingerden (1984 CEC EUR 9541 EN/II).

The use of artificial viscosity tends, however, to introduce some inaccuracy. Other workers have therefore used the FCT method with Eulerian gas dynamics. Amongst these are van den Berg (1980), with the BLAST code, and Guirao, Bach and Lee (1979) and H. Phillips (1980).

This work on numerical simulation of VCEs has produced a number of significant results. One concerns the fraction of the heat of combustion which is converted into blast energy, or mechanical work done on the surrounding gas/air, in other words, the yield factor of the explosion. In the work of Fishburn (1976) this fraction was found to be 38%. Guiraio, Bach and Lee (1979) performed a study in which they compared a volumetric fuel–air explosion and a fuel–air detonation, and confirmed the finding of Oppenheim *et al.* (1977) that the difference in the fraction of energy converted to blast is small.

Strehlow *et al.* (1979) made an extensive numerical study of the properties of a blast wave for constant velocity

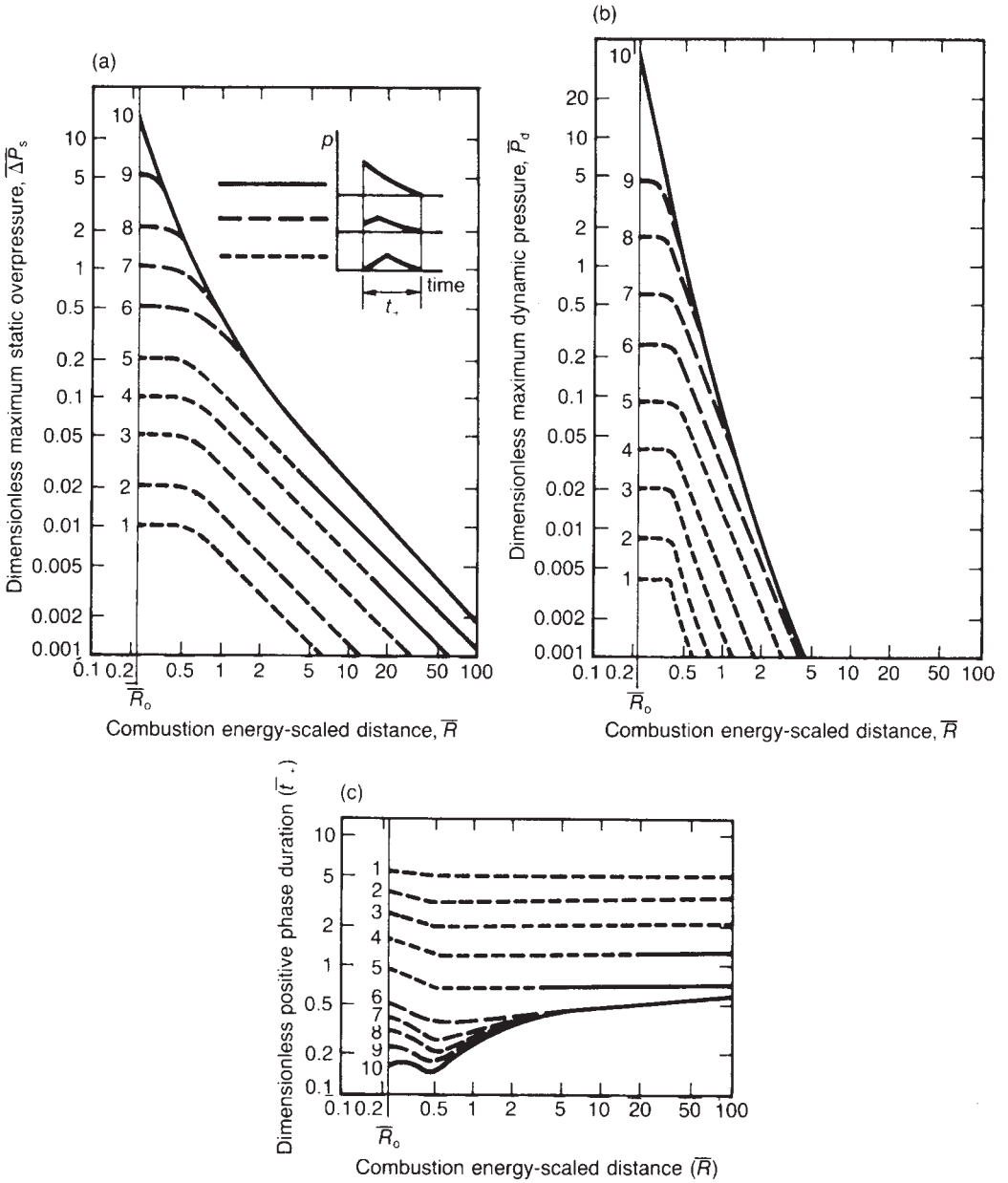

Figure 17.79 *TNO multienergy model for vapour cloud explosions (van den Berg, 1980): (a) peak overpressure; (b) dynamic pressure; and (c) duration. C_o, ambient velocity of sound; E, combustion energy; P_d, dynamic pressure; P_o, ambient pressure; R_o, fuel-air charge radius; t_+, duration time; $\bar{P}_d$, P_d/P_o; $\Delta\bar{P}_s$, $\Delta P_s/P_o$; $\bar{R}$, $R(P_o/E)^{1/3}$. t_+, $t_+C_o(P_o/E)^{1/3}$ (Courtesy of Elsevier Science Publishers)*

flames over a wide range of flame speeds in spherical symmetry. They found that the calculated blast effects from the simulation, using as the constant flame speed the highest value observed, did not exceed the observed blast effects. This work was the basis of the Baker–Strehlow model, as already described.

The basic approach in this work has been to treat combustion as a fixed addition of energy at the particular flame speed. This does less than justice to the interaction of flow, combustion and turbulence and the associated positive feedback which occurs. The work of Hjertager (1982) advanced the art with a more fundamental treatment of

transient compressible turbulent flow with reaction. It has given rise to two major CFD codes, FLACS and EXSIM.

An illustrative example of the use of the EXSIM code is given in Appendix F of the CCPS *Fire and Explosion Model Guidelines* (1994/15). The problem considered is combustion of a vapour cloud released amongst items of equipment on a plant in the open. The results include pressure vs time and flame speed vs distance profiles and contours of gas concentration, overpressure and wind velocity broadly similar to those shown in Plate 28.

Other codes include REAGAS, described by van den Berg (1989), Auto REAGAS, described by van den Berg (1995) and CLICHE, described by Catlin (1990).

17.28.28 Hydrogen explosions

Vapour clouds of hydrogen are somewhat unusual and need separate treatment. An account of hydrogen VCEs has been given by Bulkley and Jacobs (1966).

These authors describe a number of incidents in which hydrogen–air explosions have occurred. Of particular importance is an explosion which took place during the intentional release of hydrogen from Los Alamos Scientific Laboratory at Jackass Flats, Nevada, in 1964 and which has been described by Reider, Otway and Knight (1965). The incident was recorded by high speed photography. The discharge rate had been at a peak of 430,000 lb/h but had been cut back to 125,000 lb/h when spontaneous ignition occurred. The resulting explosion was estimated to have caused a pressure wave of 0.5 psi at buildings less than 200 ft way. From the photographs it was estimated that the cloud of hydrogen–air mixture which took part in the explosion was 30 ft in diameter and 150 ft high and contained 200 lb of hydrogen and that the flame speed reached 100 ft/s. The flame speed was thus considerably above the normal burning velocity but had not reached detonation velocity.

On the assumption that one-fifth of the heat released is converted to blast energy, Bulkley and Jacobs calculate that 1 lb of hydrogen can give a blast effect equivalent to 5 lb of TNT, provided detonation occurs.

They state, however, that if a detonation does not occur, then the results from the Jackass Flats incident indicate that the distances for a particular blast intensity calculated using this TNT equivalent are overestimated by a factor of about 4.

Hydrogen is frequently vented to the atmosphere. Bulkley and Jacobs present results of calculations on the flow rates which might give rise to 10 lb of hydrogen in the flammable range. They estimate that the detonation of 10 lb of hydrogen could cause severe structural damage at about 150 ft and moderate structural damage at about 300 ft. Assuming that the exit velocity is of the order of 1000 ft/s, calculations for free jets indicate that the inventory of hydrogen in the flammable range would be equivalent to 2–8 s of flow and that therefore the hydrogen flow should not exceed 4000–18,000 lb/h if excessive damage is to be avoided. The account of the Jackass Flats explosion by Reider, Otway and Knight mentions that the hydrogen is normally flared off if the release flow exceeds 3600 lb/h.

Emergency releases of hydrogen-rich streams of 50,000–150,000 lb/h are not uncommon.

Many releases are not pure hydrogen, but also contain hydrocarbons. The addition of hydrocarbons narrows the flammable range and reduces the burning velocity. It may also increase the volume of flammable mixture necessary for detonation. On the other hand, it also increases the molecular weight, which means that the jet maintains its integrity longer, so that the volume of flammable mixture is greater, and it increases the energy per unit volume. The overall result is uncertain, but Bulkley and Jacobs suggest that it is prudent to assume that a hydrogen-rich stream has the same hazard potential as one of pure hydrogen.

The authors discuss hydrogen venting, and suggest that emergency venting flows be reviewed and that if high vent flows may occur they should either be released directly to the atmosphere via multiple vents or should be flared.

Other incidents described include two disasters with hydrogen-filled dirigible airships. These are the disaster of the R-38 at Hull in 1921, in which there was an explosion, and that of the LZ-19, the Hindenbttrg, at Lakehurst, New Jersey, in 1937, in which the hydrogen burned with no overpressure. The fatalities in these two accidents were 44 and 36, respectively.

A method of estimating the peak overpressure from hydrogen explosions has been given by Hawksley (1986 LPB 68). The method is applicable to a typical, relatively small release. The two scenarios considered are a jet and a buoyant plume. The mass of fuel in the vapour cloud is determined using modifications of the equations given by J.G. Marshall (1980). The peak overpressure is then obtained from the TNT equivalent model using an explosion yield of 4%.

Hydrogen explosions are also discussed by V.C. Marshall (1987), who deals particularly with hydrogen-filled airships. He gives data showing the ultimate fate of some 129 airships. Of these, 41 (33.5%) caught fire or were set on fire by enemy action, 20 (15%) in flight and 21 (16%) in their sheds, whilst three (2.5%) exploded in flight.

17.28.29 Methane and LNG combustion

Large quantities of methane are handled as LNG, and the behaviour of methane and LNG vapour clouds is therefore of particular interest.

There is now considerable evidence that vapour clouds of methane at normal temperatures burn, but do not readily explode. Many experiments have been done in which attempts have been made to initiate explosions in methane clouds, but in which no explosion occurred.

The occurrence of VCEs involving methane has been reviewed by V.C. Marshall (1987). He cites expert opinion to the effect that there has been no case of an unconfined VCE with natural gas, but also the account given by Gugan (1979) of an explosion involving methane at Raunheim, West Germany, in 1966.

It may be noted that in the *First Canvey Report* (HSE, 1978b) it was conservatively assumed that a vapour cloud of LNG might explode.

17.28.30 Explosion yield limit

As already stated, in VCE work the fraction of the energy of combustion which is converted to blast energy is frequently expressed as a TNT equivalent.

The generally quoted limit for this fraction is about 40%. This is the value given, for example, by the CCPS (1994/15), which also refers to numerical simulation work in which the highest fraction obtained was 38%, as described above.

In his work on VCEs, Gugan (1979) gave equations and listed incidents for which the TNT equivalent was cited as above 50%. Ale and Bruning (1980) took issue with this on the basis that it violated the law of thermodynamics

governing the conversion of energy into mechanical work. The matter was further considered by H. Phillips (1981b).

The difficulty appears to lie in the use of the TNT equivalent. In an investigation of an explosion incident the equivalent mass of TNT is obtained by examining the damage effects. It does not follow, however, that for a given level of damage the explosion energies in a TNT explosion and a VCE are the same. A TNT explosion involves a very high drop in overpressure in the near field and a shorter impulse. In other words, the energy released in a TNT explosion may be less effective in causing damage than that in a VCE.

Further, there are uncertainties in the peak overpressure for a TNT explosion and in the correlation of damage effect with peak overpressure. Phillips states that differences in blast correlations can introduce a factor of as much as an order of magnitude.

A VCE may therefore have an apparent TNT equivalent greater than 40% even if the actual fraction of the energy of combustion converted to blast energy does not exceed that value.

17.28.31 CCPS method

The *CCPS Fire and Explosion Guidelines* (1994/15) include a set of methods for VCEs. Both TNT equivalent and fuel–air models are given. For the TNT equivalent method use is made of Equation 17.28.6. The sample problem utilizes an energy of explosion of TNT of 4650 kJ/kg and a yield of 0.03. The fuel–air models used are the Baker–Strehlow model, the Wiekema expanding piston model and the van den Berg ME model.

The *Guidelines* give two sample problems, one a hazard assessment of a VCE at a storage site and the other an assessment of the overpressure at Flixborough. To each of these they apply both the TNT equivalent model and the ME model.

17.28.32 Plant design

The VCE hazard may be mitigated by plant design. Two aspects which have been considered particularly are limitation of the size of potential releases and the layout of plant to deal with the effects of any explosion.

For some plants handling flammable liquids the avoidance of large-bore pipes which could, if ruptured, give a large release has been a specific design objective.

In plant layout, suitable separation distances may be used to decrease the likelihood of unacceptable damage, while buildings such as control rooms which may be affected can be suitably designed. The effect of a possible VCE in a works may be explored by assuming the explosion of vapour clouds of different sizes and degrees of drift and constructing diagrams showing the areas affected by blast, or 'petal diagrams'. A petal diagram given by Kletz (1977J) is shown in Figure 17.80. Guidelines on plant layout for VCE hazard are given in Chapter 10.

17.29 Boiling Liquid Expanding Vapour Explosions

Another of the most serious hazards in the process industries is the BLEVE. Generally, this occurs when a pressure vessel containing a flammable liquid is exposed to fire so that the metal loses strength and ruptures.

Accounts of BLEVEs have been given by Kletz (1977J), Reid (1979), A.F. Roberts (1981/82, 1982), Manas (1984), Pietersen (1985), Skandia International (1985), Blything and Reeves (1988 SRD R488), Selway (1988 SRD R492), D.M. Johnson and Pritchard (1991) and the CCPS (1994/15).

When a vessel containing liquid under pressure is exposed to fire, the liquid heats up and the vapour pressure rises, increasing the pressure in the vessel. When this pressure reaches the set pressure of the pressure relief valve, the valve operates. The liquid level in the vessel falls as the vapour is released to the atmosphere. The liquid is effective in cooling that part of the vessel wall which is in contact with it, but the vapour is not. The proportion of the vessel wall which has the benefit of liquid cooling falls as the liquid vaporizes. After a time, metal which is not cooled by liquid becomes exposed to the fire; the metal becomes hot and weakens and may then rupture. This can occur even though the pressure relief valve is operating correctly. A pressure vessel is designed to withstand the relief valve set pressure, but only at the design temperature conditions. If the metal has its temperature raised, it may lose strength sufficiently to rupture.

Most BLEVEs involve a pressure storage vessel, rail tank car or road tanker containing a flammable liquid, typically a liquefied flammable gas, which becomes exposed to a fire or flame, and in due course ruptures, often giving a fireball. Another common situation which gives rise to a BLEVE is a derailment. The development of the BLEVE is illustrated in Figure 17.81. A pressure relief valve on one tank car operates, the release ignites and the flame plays on another tank car. The liquid in this vessel heats up, the pressure rises and the relief valve operates, the release being ignited by the flame playing on the vessel. For a time the metal of this vessel is kept cool by liquid in contact with it, but the level falls as the liquid is vaporized, metal cooled only by vapour is exposed, becomes hot, weakens and ruptures. A large fraction of the flammable liquefied gas released, vaporizes and forms a burning vapour cloud, often a fireball.

A BLEVE of a vessel containing a flammable liquid gives rise to the following effects: (1) blast wave, (2) fragments, and (3) fireball.

Following Flixborough much attention was focused on VCEs. It was pointed out by Kletz (1977J) that BLEVEs can cause as many casualties as VCEs and that by comparison they were being relatively neglected. This view has been amply justified by the subsequent record.

Selected references on BLEVEs are given in Table 17.36.

17.29.1 BLEVE incidents

Compilations of BLEVE incidents are less numerous and comprehensive than those for VCEs. The principal lists are those of Pietersen (1985), Skandia International (1985) and Selway (1988 SRD R492). Incident data are also available from the MHIDAS databank of the SRD.

Some principal BLEVE incidents are given in Table 17.37. Other incidents are listed in Table A1.2.

The BLEVE at Feyzin on 1966 has received particular attention (Case History A38). In this incident an operator draining water from the bottom of a propane sphere lost control. A vapour cloud formed, ignited and flashed back to the vessel. The pressure in the vessel rose and the relief valve lifted, but the metal of the vessel lost strength and some 90 min after ignition the vessel burst. The death toll was 18. Plate 32 shows one of the fire engulfed spheres.

A remarkably similar event took place at the Duque de Caxais refinery at Rio de Janeiro in 1972 (Case History A61).

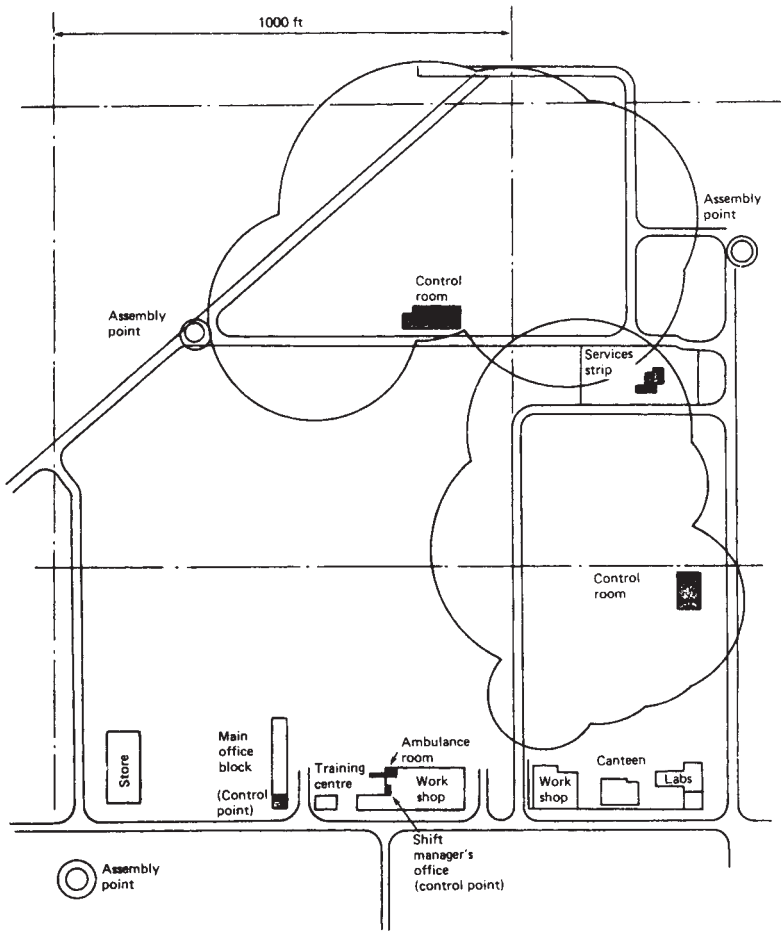

Figure 17.80 *Petal diagram showing areas affected by possible vapour cloud explosions (Kletz, 1977J) (Courtesy of the Institution of Chemical Engineers)*

Again an operator lost control of a draining operation on an LPG sphere, a vapour cloud formed, ignited and flashed back to the sphere, engulfing it in fire, so that after about 15–20 min it suffered a BLEVE.

In these incidents the release at, and BLEVE of, the vessel was the initial event. There have also been instances where a release from one storage vessel has led to a fire which has caused BLEVE of an adjacent one. Such was the case at Montreal, Quebec, in 1957, when overfilling of a butane sphere caused a release which led to a pool fire (Case History A25).

In 1978 at Texas City, Texas, overfilling of an LPG sphere led to a fire which caused the BLEVE of an adjacent sphere.

In other cases BLEVEs have occurred due to engulfment in a vapour cloud fire. Such a fire occurred at Port Newark, New Jersey, in 1951 and led to the destruction of over 70 bullet tanks, many by BLEVE (Case History A19).

Engulfment in a vapour cloud fire was also the cause of destruction, largely by BLEVE, of four storage spheres and 48 cylindrical vessels holding LPG at Mexico City, Mexico, in 1984. Some 500 people were killed. This incident, shown in Plate 35, is described in Appendix 4.

BLEVEs also occur in transport, typically when flammable material is released and ignited following an accident, so that a transport tank becomes engulfed in fire. They have occurred particularly on rail tank cars, often when a jet flame from the relief valve on one tank has played on another.

A derailment of nine rail tank cars at Crescent City, Illinois, in 1970 caused a release of propane which led to a fire and caused a succession of tank car BLEVEs (Case History A50).

The BLEVEs were accompanied by large fireballs and missiles, including rocketing tanks. One of the fireballs is shown in Plate 33.

Other rail tank car BLEVEs include those at Laurel, Mississippi, in 1969 (Case History A44), Houston, Texas, in 1971 (Case History A53), Kingman, Arizona, in 1973 (Case History A63), Oneonta, New York, and West St. Paul, Minnesota, in 1974, Des Moines, Iowa, in 1975, Belt,

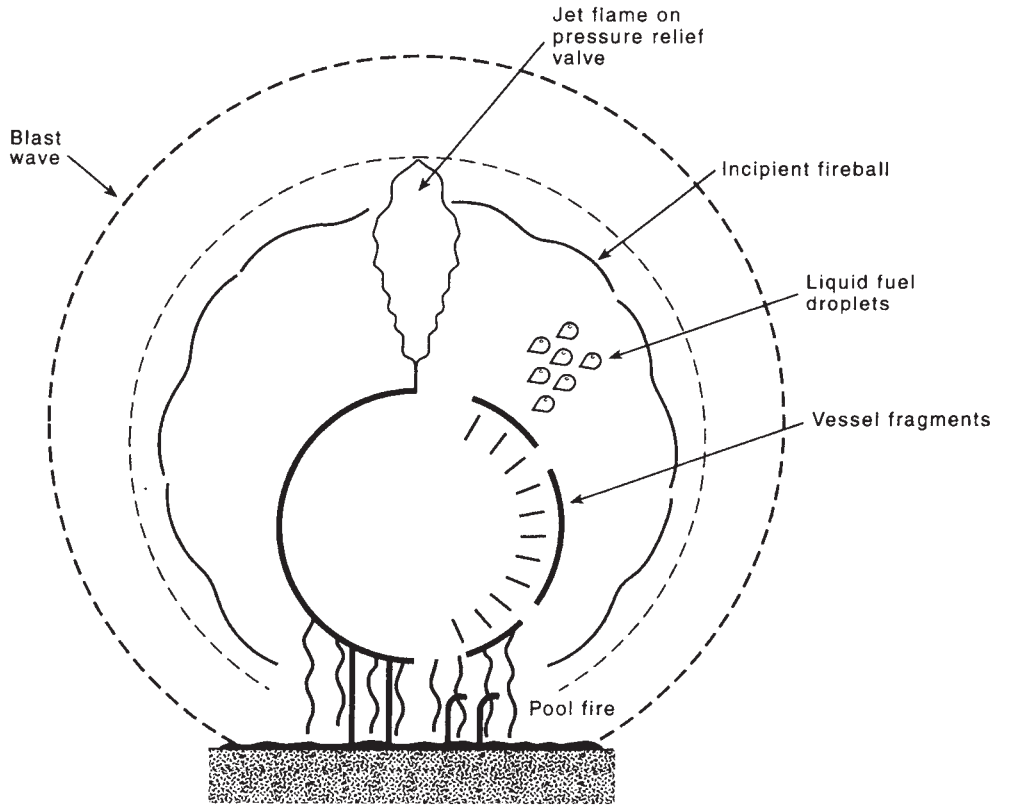

Figure 17.81 *A BLEVE event*

Table 17.36 *Selected references on boiling liquid expanding vapour explosions (BLEVEs)*

CEC (n.d./l); Exxon (n.d.); C. Andersen and Morris (1974); Hess, Hoffman and Stoeckel (1974); M.R. Johnson *et al.* (1974); Kletz (1977d, 1981n); Maurer *et al.* (1977); Buivid and Sussman (1978); Walls (1978,1979); R.C. Reid (1979, 1980); A.F. Roberts (1981/82, 1982); Considine, Grint and Holden (1982); Crawley (1982); Pantony and Smith (1982); Blything (1983 SRD R263, 1986); A.F. Roberts, Cutler and Billinge (1983); Solberg and Borgnes (1983); Manas (1984); Martinsen (1984); Tune and Venart (1984/85a,b); D.L.M. Hunt and Ramskill (1985); D.J. Lewis (1985); Pietersen (1985, 1986a,b); Skandia (1985); Johannson (1986); Martinsen *et al.* (1986); Pitblado (1986a); McDevitt, Steward and Venart (1987); Skarka (1987); Blything and Reeves (1988 SRD R488); Holden (1988 SRD R477); Nazario (1988); Selway (1988 SRD R492); J.B. Moss (1989); Lemoff (1989); Johnson *et al.* (1990); McDevitt *et al.* (1990); Venart (1990a); D.M. Johnson and Pritchard (1991); Pineau *et al.* (1991); Prugh (1991); Scilly and Crowther (1992); Melham, Croce and Abraham (1993); Venart *et al.* (1993); Birk and Cunningham (1994); Martinsen and Marx (1999)

Montana, in 1976 and Livingston, Louisiana, in 1982 (Case History A103). Road tank car BLEVEs include those at Lynchburg, Virginia, in 1972 (Case History A59) and Los Angeles, California, in 1979.

17.29.2 The BLEVE event

An account of the origin of the term 'BLEVE' is given by the CCPS (1994/15), which states that the term was introduced by workers at the FMRC. An early account of the phenomenon was that of Walls (1979) at the National Fire Protection Agency (NFPA). A review of events which can lead to a BLEVE has been given by Prugh (1991), who gives the term a fairly wide interpretation and lists the following: (1) fire exposure, (2) mechanical damage, (3) overfilling, (4) runaway reaction, (5) overheating, (6) vapour space explosion, and (8) mechanical failure.

The essential features of a BLEVE are that (1) the vessel fails, (2) the failure results in flash-off of vapour from the superheated liquid, and, if the liquid is flammable, (3) the vapour ignites and forms a fireball.

The accompanying effects are (1) blast, (2) fragments, and, for flammable liquids, (3) a fireball.

The BLEVE creates an overpressure. The phenomena associated with this are (1) the expansion of the vapour, (2) the flash vaporization of the liquid, and, for flammable

Table 17.37 *Some BLEVE incidents*

Date	*Location*	*Material*	*Plant/transport involved*	*Deaths/ injuries*	*Fireball*	
					Quantity released (te)	*Radius* (m)
A	**BLEVE incidents**					
1951	Port Newark, NJ	LPG	Storage cylinder (70 on site)	14i		
1955	Ludwigshafen, FRG		Rail tank car	2i		
	Cottage Grove, OR	LPG	Storage vessel	12d, 12i		
1958	Celle, FRG		Rail tank car			
1957	Montreal, Quebec	Butane	Storage sphere	1d		
1959	McKittrick, CA	LPG	Storage cylinder (six on site)	2i		
1966	Feyzin, France	LPG	Storage sphere (eight on site)	18d, 81i		
1968	Dunreith, IN	Ethylene oxide	Rail tank car	5i		
1969	Laurel, MS	LPG	Rail tank car (derailment, 15 cars)	2d, 976i(?)		
1970	Crescent City, IL	Propane	Rail tank car (derailment, nine cars)	66i	75	75–100
1971	Houston, TX	VCM	Rail tank car (derailment, 18 cars)	1d, 50i	165	150
1972	Lynchburg, VA	Propane	Road tanker	2d, 5i	9	60
	Rio de Janeiro, Brazil	LPG	Storage spheres (five on site) and cylinders	37d, 53i		
1973	Kingman, AZ	Propane	Rail tank car	13d, 95i	45	150
1974	Bielefeld, FRG		Rail tank car (derailment, 36 cars)			
	Oneonta, NY	LPG	Rail tank car	25i		
	West St. Paul, MN	LPG	Storage vessel	4d	10	50
1975	Des Moines, IA	LPG	Rail tank car	3i		
1976	Belt, MN	LPG	Rail tank car	22i	80	150
1977	Dallas, TX	Isobutane	Rail tank car	1i		
1978	Texas City, TX	LPG(?)	Storage vessel	7d, 10i		
	Waverly, TN	Propane	Rail tank car	16d, 43i		
1979	Paxton, TX	Chemicals	Rail tank car	8i		
	Los Angeles, CA	Gasoline	Road tanker	2d, 2i		
1982	Livingston, LA	Flammables	Rail tank car	0d, 0i		
1984	Romeoville, IL	Propane	Process vessel	15d, 22i		
1985	Mexico City, Mexico	LPG	Storage spheres and cylinders	≈650d, ≈6400i		
B	**Fireball incidents**					
1956	Amarillo, TX	Oil	Storage tank	20d, 32i		
1974	Aberdeen, UK	Butane	Road tanker		2	35
1975	Eagle Pass, TX	LPG	Road tanker	17d, 34i		
1976	Gadsden, AL	Petrol	Tank farm	4d, 28i		
1977	Goldona, VA	LPG	Rail tank car	2d, 9i	70	160
1978	Donnellson, IA	LPG	Pipeline	2d, 2i (?)	435	305
	Lewisville, AR	VCM	Rail tank car	2i	110	155

liquids, (3) the combustion of the vapour. These events are not completely simultaneous, but have been measured as separate effects.

A BLEVE usually generates missiles. These may be fragments created by the rupture event and also the body of the vessel itself. The pressure at the instant of burst is high and the reaction force is often large enough to cause the main part of the vessel to rocket.

A BLEVE resulting from the fire engulfment of a vessel containing a flammable liquid also gives rise to a fireball.

Although most BLEVEs of interest here involve a liquid which is flammable, this is not a necessary feature of a BLEVE. The rupture of a vessel containing superheated water can constitute a BLEVE. Likewise, although engulfment in fire is the common cause of BLEVE, it too is not a necessary feature. Any rupture of a vessel containing a superheated liquid may be termed a BLEVE.

It is possible, therefore, though not common, for a BLEVE event not caused by an engulfing fire to provide the source for a large vapour release, leading to a flash fire or VCE.

17.29.3 Experimental studies

As described in Chapter 16, there have been a number of experimental studies of fireballs. The BLEVE event as a whole has not been so well served.

C. Anderson *et al.* (1975) describe work at the Association of American Railroads (AAR) on fire engulfment of a 125 m^3 rail tank car which suffered a BLEVE.

Experimental work on BLEVEs has been described by Hardee and Lee (1975), who did tests involving 420 kg of

propane and modelled the processes of bursting and mixing with air.

Tests on vessel bursts directed to the same end are given by Maurer *et al.* (1977), but these authors also report measurements of the overpressure associated with the burst, as described in Chapter 15.

Work in the same series is that described by Giesbrecht *et al.* (1980), who used 450 kg of propylene and modelled the bursting, mixing and combustion processes.

Work at the Bundesansalt fur Materialpriifung (BAM) on fire engulfed vessels containing liquid propane, described by Schulz-Forberg (1984), Droste and Schoen (1988) and Schoen, Probst and Droste (1989), involved tests on 4.84 m^3 tanks with generation of fireball and fragments.

Further larger scale experiments have been performed at British Gas by D.M. Johnson and Pritchard (1991). Their base case was a 5.66 m^3 vessel containing 2 te of butane at a pressure of 15 barg. They performed five tests, with the base case and with the following four variations: (1) lower mass, (2) lower pressure, (3) different vapour/liquid ratio, and (4) using propane. Vessel failure was effected by explosive charges and ignition was by propane lances.

The purpose of this BG work was to investigate the overpressure and thermal radiation. With regard to overpressure, the authors state that the vapour expansion and flash vaporization tended to merge. The overpressure from vapour expansion agreed well with predictions for overpressure from a bursting vessel. The overpressure from flash vaporization was substantially less than that predicted, apparently because the liquid temperature was below that required to give homogeneous nucleation, or superheat limit.

The overpressure from the combustion came somewhat later and had a much longer duration, of the order of 100–300 ms. The overpressure trace which the authors give shows the maxima of the two overpressure pulses to be comparable. These traces show the overpressures measured at 150 m from the vessels to have been of the order of 4 mbar. The authors state, however, that the combustion overpressure was often greater.

With regard to the fireball, this showed in some tests an appreciable degree of asymmetry. For the mass of fuel in the fireball, the authors quote the limit of 35% theoretical flash vaporization above which flash-off of the whole contents is often assumed. The theoretical flash in their work was over 45% and complete flash-off was assumed. This was supported by the visual records, which showed only small amounts of liquid fuel burning on the ground.

The fireball diameter and duration were broadly as predicted by models such as that of A.F. Roberts (1981/82). Except in one test the height of the centre of the grounded fireball was between 0.8 and 1.35 times the equivalent maximum diameter, which compares with the suggestion by Moorhouse and Pritchard (1982) that it be taken as the maximum diameter.

For the thermal radiation from the fireball, the surface emissive power was somewhat higher than the values commonly quoted, with peak values up to 500 kW/m^2 and the remainder in the range 250–350 kW/m^2.

The CCPS (1994/15) describes one of the BAM and one of the British Gas tests and states that the liquid temperature exceeded the superheat limit in the former but not in the latter.

Melham, Croce and Abraham (1993) describe a series of BLEVE tests carried out by the NFPA in conjunction with the production of a successor to its earlier film 'BLEVE', entitled 'Bleve Update'. The purpose of the tests was to establish a database of experiments and to obtain film of BLEVE events. There were six tests, two each with a simulated pool fire, an impinging gas jet flame and an impinging liquid jet flame. The vessels tested were 1.89 m^3 propane tanks. In these tests peak overpressures up to 37 kPa were measured at a distance of 15 m from the tanks.

17.29.4 Empirical features

It is also helpful to consider some features of BLEVEs from an empirical viewpoint. Those discussed here are (1) the time to BLEVE, (2) the mode of rupture, (3) the blast effects, (4) the fireball, (5) the missiles, and (6) the release of flammable fluids. Time to BLEVE is treated in the following subsection and the other items here.

With regard to the mode of rupture, cylindrical tanks usually rupture longitudinally, though some rupture circumferentially. The latter particularly tend to take off like rockets and may travel long distances. This was true of some of the cylindrical tanks at Mexico City. Spheres often explode, but in some cases may simply split at the top as occurred both at Feyzin and Mexico City.

The pressure at the instant of rupture must approximate to that in the vessel. Generally, therefore, it will be appreciably greater than that at the centre of a VCE, which is commonly estimated to have a maximum overpressure of about 1 bar. Thus, in a BLEVE the overpressure at the vessel at the instant of rupture may be an order of magnitude higher than that at the centre of a VCE. The blast wave from a BLEVE can cause damage. At Feyzin the blast wave caused extensive though minor damage in a village 500 m away and broke some windows at a distance of 3 km.

The flammable vapour released forms a fireball. The fireball can be large and it can rise to an appreciable height. Fireball diameters at Mexico City are estimated from film records to have been of the order of 200 or 300 m with a duration time of some 20 s. The fireball at Crescent City rose to a considerable height, as shown in Figure A1.4 (see Appendix 1).

At Mexico City there was also a fire column which resembled a huge flare rather than a fireball and which film records show to have lasted 90 s.

The maximum distances at which injury due to heat radiation has been reported are 300 m at Feyzin and 400 m at Mexico City, while the maximum distance at which death has been reported is 300 m at Kingman.

Survivals have been reported at distances comparable with the estimated radius of the fireball. At Belt the reported fireball diameter was 1000 ft. The calculated diameter is 540 ft, based on the 80 te of flammable material believed to have been involved, though there is some doubt on this quantity. Firemen within 200 ft survived (Kletz 1981n). Further details of survival at this distance and of fireballs are given by Crawley (1982).

BLEVEs tend to generate massive missiles, including the main part of the vessel. Missiles from BLEVEs are considered in more detail in Section 17.34, but a brief mention is made here. At Feyzin the sphere BLEVE generated five large fragments, of which three each had a mass of over 100 te and were thrown distances of 150–350 m. One piece knocked over another sphere which itself in due course underwent a BLEVE.

The BLEVEs which occurred in the vapour cloud fires at Port Newark in 1951, Texas City in 1978 and Mexico City in 1984 all generated large missiles. At Port Newark one large

tank section about 17 m long was hurled over half a mile and demolished a petrol filling station. At Mexico City the spheres generated 25 major fragments which travelled 100–590 m, whilst one bullet tank was propelled 1200 m. This latter appears to be the maximum distance travelled by a BLEVE missile.

The liquid in the vessel does not necessarily vaporize completely. At Tewkesbury, Massachusetts, in 1972 some 35% of the propane flashed off, the remaining liquid being scattered in all directions.

BLEVEs do not generally give rise to VCEs. But they may scatter flammable liquid spray which gives a spray fire and/or falls on people and property, rendering them more flammable and liable to ignition. Hot missiles may also cause fires.

17.29.5 Time to BLEVE

The time between the occurrence of an engulfing or torch fire and BLEVE is of significance not just for the general characterization of BLEVEs but for the design of fire systems to protect against them and for fire fighting.

For the sphere at Feyzin in 1966 the time between ignition of the leak and vessel rupture was about an hour and a half. This time to BLEVE is much longer than in most other incidents.

More commonly, for storage vessels the time to BLEVE has been of the order of 5–30 min. A period of 3–10 min was observed for some vessels at Montreal, McKittrick and Mexico City. A time of some 30 min was observed for other vessels at these three incidents.

Hazard assessments of storage vessels in respect of BLEVE have been made by Blything and Reeves (1988 SRD R488) and Selway (1988 SRD R492). Blything and Reeves studied a horizontal cylindrical storage vessel holding butane, with a nominal capacity of 100 te and actually holding 85 te, being thus 75% full. They considered scenarios involving (1) partial fire engulfment and (2) jet flame impingement, and obtained time to BLEVE estimates of between 4 and 48 min.

Selway describes an equivalent study for a 2000 m^3 storage sphere containing some 1000 te of LPG when full. For scenarios of total fire engulfment, partial fire engulfment and jet flame impingement he obtained times to BLEVE of 7–11, 25–38 and 5.5–7 min, respectively. These times are a function of the degree of fill. A vessel which is empty has a much shorter time, whereas the difference in times between a vessel which is half full and one which is full is small. Thus, for example, for the partial engulfment case, the times to BLEVE given for the states virtually empty, half full and full are 25, 36 and 38 min, respectively.

Times to BLEVE for tanks in transport accidents, particularly rail tank cars, have also been mainly in the range 5–30 min.

17.29.6 Vessel burst pressure

The explosion energy released in BLEVE is a function of the initial pressure.

The various different scenarios for vessel burst pressure have been discussed in Section 17.27, where a distinction was made between the following causes: (1) operating overpressure, (2) mechanical failure, and (3) fire engulfment.

17.29.7 Liquid superheat limit

The energy of the explosion which is part of the BLEVE event depends on the conditions in the vessel. In particular, under certain conditions, explosive flashing of the superheated liquid can occur, giving a large release of energy.

The explanation of what happens which has received most acceptance is the liquid superheat limit theory of Reid (1976, 1979, 1980). If a liquid has a sufficient degree of superheat and the pressure on it is suddenly removed, microscopic vapour bubbles form and a large fraction flashes off within milliseconds.

The degree of superheat necessary for this effect to occur is determined by the homogeneous nucleation temperature, or superheat limit temperature. There are a number of correlations for this, which differ according to the equation of state used. Using van der Waals's equation of state, Opshoor (1974) obtained

$$T_{sl} = 0.84\,T_c \qquad [17.29.1]$$

whilst using the Redlich–Kwong equation of state Reid (1976) obtained

$$T_{sl} = 0.895\,T_c \qquad [17.29.2]$$

where T_c is the critical temperature (K) and T_{sl} the superheat limit temperature (K).

Reid also confirmed that for a wide range of industrial substances the coefficient in Equation 17.29.2 lies within the range 0.89–0.90.

Reid studied particularly the superheat limit temperature of propane, for which the value generally quoted is 53°C. The values given by Equations 17.29.1 and 17.29.2 are 38 and 58°C, respectively.

Data on the liquid superheat limit temperature are given by Lide (1994). Where it is necessary to predict it, use is generally made of Equation 17.29.2.

Other mechanisms to explain explosive flashing have been suggested. Board *et al.* (1975) apply the superheat limit concept in conjunction with that of atomization of the liquid by shock waves at the vapour–liquid interface, whilst Venart (1990a) combines the concept with the effect of the depressurization–repressurization cycles associated with the operation of a pressure relief valve.

If the degree of superheat is not sufficient to promote explosive flashing, the energy release in a BLEVE is that due to the pressure energy in the vapour space, which is generally an order of magnitude less.

The superheat limit model of a BLEVE is discussed further in Section 17.29.9.

17.29.8 Modelling of BLEVEs

There are several different approaches to the modelling of BLEVEs. They include (1) the superheated liquid explosion model, (2) the cloud formation model, and (3) the bursting vessel model.

The modelling of a BLEVE is closely related to the modelling of a fireball, as described in Chapter 16.

17.29.9 Superheated liquid explosion model

The superheated liquid explosion model is that of Reid, which has been outlined in Section 17.29.7. Reid suggests that this theory may explain the behaviour of the liquid at the moment of BLEVE.

The application of the theory to a BLEVE may be explained by considering the specific case of the depressurization of a vessel containing propane. The vapour pressure and superheat limit lines for propane are given in Figure 17.82. The superheat limit is the limit to which propane may be heated before spontaneous nucleation occurs,

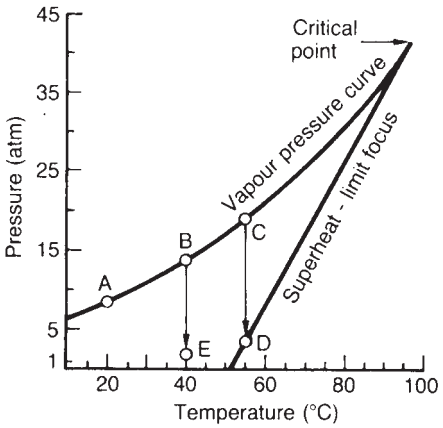

Figure 17.82 *Vapour pressure and superheat curves for propane (R.C. Reid, 1997) (Courtesy of Science)*

giving a vapour explosion. Prior to the accident the propane is at an absolute pressure of 8–9 atm and ambient temperature at point A on the graph. In the accident conditions the liquid is heated up by the fire on the vessel. The behaviour of the liquid then depends on the temperature which it has reached when rupture and sudden depressurization occur. If depressurization occurs when the temperature is that corresponding to point B, the pressure will fall to atmospheric pressure at point E. There will be violent boiling but no vapour explosion, since the superheat limit line has not been reached. If depressurization occurs at point C with fall in pressure to point D, the superheat limit line is reached at about 3.3 atm, and a vapour explosion could occur. The superheat limit temperature at atmospheric pressure is thus a limit below which a superheated liquid explosion will not occur. For propane this is 53°C.

In support of this hypothesis Reid quotes experiments by C. Anderson *et al.* (1974) and Hess, Hoffman and Stoeckel (1974) and a number of industrial accidents as being consistent with the hypothesis.

The theory has implications for prevention of superheated liquid explosions under these conditions. Such an explosion will not occur if depressurization occurs at a pressure corresponding to a temperature below the superheat limit temperature. The pressure relief valve may be set to operate below this pressure and thus to protect against the explosion. Another possible measure is to seed the liquid with solid particles to assist nucleation, but experimental work on these lines has not been encouraging. The measures described are addressed specifically to the mitigation of the problem of superheated liquid explosions and will not prevent explosion from other causes such as the pressure of the vapour in the vessel.

17.29.10 Cloud formation models

Models for vapour cloud formation following depressurization have been given by Hardee and Lee (1975), Maurer *et al.* (1977) and Giesbrecht *et al.* (1980) and have been compared by A.F. Roberts (1982). The first model is based on conservation of momentum with the momentum created by the liquid release appearing explicitly as a function of the initial conditions; the second model is based on turbulent diffusion and the initial conditions do not appear explicitly. Both models give similar predictions of cloud growth for releases of the order of 100 kg and have been verified experimentally at this level, but diverge for larger releases. Roberts bases his treatment on the model of Hardee and Lee.

A model by Martinsen and Marx (1999) makes use of experiments by Johnson *et al.* (1990) to predict time-varying cloud development and buoyant lift-off.

17.29.11 Bursting vessel model

The overpressure created by a BLEVE is complex, since, as discussed above, it is in principle caused by three distinct phenomena.

The aspect where the most progress appears to have been made is in estimating the overpressure associated with the expansion of the vapour. It is suggested by W.E. Baker *et al.* (1983) that as a first approximation the blast wave from a vessel which undergoes BLEVE may be estimated by applying to the vapour space in the vessel the method, described in Section 17.27, for the bursting of a vessel filled with gas.

This approach appears to give reasonable predictions, as now described.

In order to apply this latter method it is necessary first to determine the pressure at which the vessel will burst. The following formula is quoted by Selway (1988 SRD R492) as that used in the ENGULF code for the burst pressure of a sphere:

$$P_b = 2\sigma_y \ln R\left(1 - \frac{\sigma_y}{\sigma_u}\right) \qquad [17.29.3]$$

with

$$R = r_o/r_i \qquad [17.29.4]$$

where P_b is the burst pressure, r is the vessel radius, R is the radius ratio, σ_u is the ultimate tensile strength, σ_y is the yield strength and the subscripts i and o denote inner and outer, respectively.

Pietersen (1985) has applied the method of W.E. Baker *et al.* (1983, p. 149), based on the Erode equation, for the energy in, and overpressure generated by the bursting of, a gas filled vessel to obtain the overpressure caused by the vapour expansion phase of a BLEVE, utilizing the volume of the vapour space and taking as 40% the fraction of the pressure energy which enters the blast wave. He obtains the following peak overpressures (bar) for vessels with a bursting pressure of 13.4 bar and different vapour space volumes:

Distance (m)	*Vapour space volume* (m^3)			
	20	100	800	1200
10	0.44	1.0	2.3	2.6
50	0.04	0.08	0.23	0.29
100	0.018	0.033	0.09	0.10
200	0.0075	0.012	0.033	0.04

Some experimental confirmation is provided by the finding of D.M. Johnson and Pritchard (1991) that the overpressures predicted using a model based on that for the bursting of a gas filled vessel were in reasonable agreement with those measured in their tests for the vapour expansion phase.

17.29.12 BLEVE method

An integrated BLEVE model should comprise models for the main effects of (1) blast, (2) fragments, and (3) fireball. Treatments covering these aspects are given in Sections 17.27 and 17.34 and Chapter 16, respectively. The model may also include a model for fire engulfment, which is treated in Chapter 16.

17.29.13 CCPS method

The CCPS *Fire and Explosion Model Guidelines* (1994/15) give a method for the treatment of the various effects of a BLEVE. The treatment covers (1) blast, (2) fragments, and (3) fireball.

For the blast the *Guidelines* method utilizes the CCPS vessel burst model, essentially that of W.E. Baker *et al.* (1975), given in Section 17.27.

The energy of explosion for use in this model is obtained by first determining whether the liquid temperature is greater than the superheat limit. Then, if the superheat limit temperature is not exceeded, use is made of the Erode equation, whilst if it is, use is made of the method for flashing liquid given in Section 17.4.6. The fraction flashing off is taken as the equilibrium value yielded by the isentropic expansion.

For the fragments the *Guidelines* use the CCPS fragments model given in Section 17.33.

For the fireball the *Guidelines* use the CCPS fireball model given in Chapter 16.

The *Guidelines* devote a chapter to worked examples of BLEVE calculations. These include a problem on a fireball from a propane tank truck; problems on blast from a propane storage vessel, from a propane tank truck and at Mexico City and problems on fragments from overpressure of a gas filled pressure vessel and from fire engulfment of a propane storage vessel.

17.29.14 Energy release and overpressure

The foregoing models provide the background for the estimation of the energy release and blast overpressure in a BLEVE. The two principal sources of energy are the compressed vapour in the vapour space and the superheated liquid as it undergoes flashing. The estimation of the energy release from these two sources has been discussed in Section 17.4. The superheat limit temperature model provides guidance on the extent to which liquid flashing is a significant contributor. A further discussion of the energy release in a BLEVE is given by Prugh (1991).

Given an estimate of the energy release, the overpressure from a BLEVE may be estimated using the methods outlined in Section 17.27.

It has been suggested by Venart *et al.* (1993) that in certain circumstances there may occur an event in which the energy release and explosion overpressure are much higher than in a regular BLEVE. This is discussed in Section 17.29.15.

17.29.15 Boiling liquid collapsing bubble explosions

The interaction between homogeneous nucleation and the vessel itself has been further investigated by Venart and co-workers (Venart, 1990a; Venart *et al.*, 1993), who have developed the concept of the boiling liquid collapsing bubble explosion (BLCBE).

The BLCBE has three aspects, involving the behaviour of (1) the liquid, (2) a crack in the vessel wall, and (3) the liquid–vessel system. If the vessel wall in the vapour space is subject to heating by a flame, a crack may develop. The behaviour of this crack then depends on the degree of fill. If the fill is high, the crack may be arrested, still in the vapour space section of the wall, by plastic blunting. If the fill is lower, there may be sufficient energy in the vapour to cause the crack to propagate plastically to the cold metal, where it can then propagate elastically without restraint and with only minimal energy requirement.

This second case, with the lower fill, corresponds to the regular BLEVE. The first case has the potential for a much greater release of physical energy associated with homogeneous nucleation. If the fill is high, one of two effects may occur: (1) a massive two-phase jet or (2) a violent vessel failure with total loss of containment caused by a homogeneously nucleated liquid.

It is this second type of event in a vessel with high fill which constitutes a BLCBE. It occurs with a liquid homogeneous in temperature and depressurizing. The sequence of events is envisaged to be typically as follows. The liquid is depressurized, say by operation of the pressure relief valve, and due to this becomes nucleated. When the crack occurs, there is an almost instantaneous swell of low-void liquid which chokes in the crack. There is a rapid repressurization of the vessel contents. The resultant liquid shock pressures are very high (1–3 kbar). The crack propagates elastically through the now cooled wall of the vapour space and on to the wall of the liquid space. The vessel fails and the highly compressed two-phase contents are again depressurized. Expansion of the high pressure vapour bubbles shatters the liquid and results in ejection of the whole of the superheated liquid as a fine aerosol. If flammable, this aerosol may then be ignited.

Venart *et al.* (1993) describe tests in which prenucleated R112 and R123 were used and events of the type just described were observed, with destruction of the vessel in times as short as about 200 μs. They give details of the pressure effects in the vessel, including measurement of the rapid pressure transient below the liquid in excess of the static pressure in the vessel and an estimate of the instantaneous overpressure at the crack. The vessel static pressure was some 790 kPa (100 psig), the average excess pressure 490 kPa (70 psi) and the estimated overpressure at the crack itself some 62 bar (900 psig). These authors also give estimates of the diameter of the bubbles (1–3 mm), the diameter of the resultant aerosol droplets (100 μm) and the evaporation time of the droplets (40 ms). They state that there were significant blast overpressures.

These effects were obtained with a liquid temperature more than 50°C below the superheat limit temperature.

Venart *et al.* suggest that all three types of event described (regular BLEVE, two-phase jet and BLCBE) occurred at Mexico City.

They draw attention to the fact that a BLCBE may be caused by a leak, and discuss the implications of this for the leak-before-break philosophy.

17.30 Explosions in Process Plant

Some of the principal types of explosion which occur on process plant have already been described. These are (1) explosions in chemical reactors, (2) explosions of high pressure gases inside plant, (3) explosions of flammable gas–air mixtures inside plant and in buildings, (4) VCEs, and (5) BLEVEs.

In addition, there are certain types of explosion which may occur in particular processes, operations or equipment.

Some of these have already been mentioned, such as explosions in driers, centrifuges and vaporizers, and in oxygen and chlorine plants.

Other explosion hazards include (1) aerosol explosions, (2) crankcase explosions, (3) superheated liquid explosions, (4) air system explosions, and (5) molten metal–water explosions. These various types of explosion are now discussed.

17.30.1 Explosions of aerosols

Under the conditions of an accident, a cloud of finely divided drops of flammable liquid in air, in the form of a mist or spray, may be produced which has many of the characteristics of a flammable gas–air mixture and which can burn or explode.

The combustion of such aerosols has been discussed in Chapter 16, which includes treatment of flame propagation, minimum ignition energy and burning velocity. Here, consideration is given to the extent to which combustion of such clouds has the propensity to generate overpressure, and, more specifically, to undergo detonation.

As described in Chapter 16, if the droplet size of the cloud is sufficiently small, the lower flammability limit, minimum ignition energy and burning velocity are essentially the same as those of a vapour–air mixture of the same concentration, measured in mass per unit volume.

The problem of crankcase explosions, described below, indicates that confined hydrocarbon mists can undergo explosions.

The detonation of aerosols has been discussed by Nettleton (1977b, 1987). The information available is rather limited. It has been shown that some aerosols of hydrocarbons are detonable under confined conditions. The work has been done using hydrocarbon–oxygen mixtures and there is little on mixtures with air. Information is also lacking on detonability limits, as distinct from the flammability limits, which are treated in Chapter 16.

When detonation occurs in an aerosol the detonation waves cause disintegration of the droplets. It is known that it is not necessary for the fuel to be present in extremely finely divided form for detonation to occur.

It is known also that with an aerosol the reaction zone is wider than in a homogenous mixture with consequent effects on peak pressure and duration time.

A particular type of aerosol explosion is the 'smoke explosion'. An account is given by Croft (1980/81). In this case the flammable aerosol cloud is formed by smouldering combustion in a confined space such that low volatility, flammable aerosol is released. The aerosol cloud is liable to ignite suddenly. This type of explosion is therefore a particular hazard to fire fighters. One such incident occurred in a warehouse fire at Chatham dockyard involved smouldering mattresses, and two men were killed. The phenomenon is sometimes known as a 'Chatham mattress' fire.

17.30.2 Heavy aerosol explosions

The work of Burgoyne and co-investigators on the combustion of flammable mists and spray, described in Chapter 16, was undertaken in large part in relation to the problem of mist explosions in crankcases. This has been investigated by Burgoyne, Newitt and Thomas (1954) and Burgoyne and Newitt (1955).

Heavy aerosol explosions are relatively rare, but a marine crankcase explosion in 1947, which claimed 28 lives, showed that a serious hazard existed and led to the initiation of research. Leaks at hydraulic fluids have also caused explosions.

The suspension of oil in air in an engine crankcase during normal running is a mechanical spray with some condensed mist from the lubricated parts which are at temperatures above the average in the crankcase. If there is serious overheating, however, condensed mist formation is accelerated, a condition often referred to as 'smoke'.

Measures which may be taken to avoid a crankcase explosion are ventilation to keep the atmosphere below the lower flammability limit, or injection of inert gas to suppress flammability, and explosion relief. The design of the latter requires a knowledge of the burning velocity.

As described earlier, the work on condensed oil mists demonstrated that these have flammability characteristics similar to those of the mixture given by the same amount of substance wholly in vapour form at the somewhat higher temperature necessary for vaporization. The lower flammability limit was 0.049 g/l. Flammability was suppressed when the air contained 28.3% of carbon dioxide.

It is now usual to fit crankcases with explosion relief devices.

17.30.3 Superheated liquid explosions: explosions in plant

A liquid may become superheated in various ways. It may be heated while under hydrostatic pressure or it may be heated in a boiling regime which favours superheating. The superheat energy may then be released.

Normally, superheat is released without great violence by the generation of nucleated bubbles. This occurs, for example, in normal heat transfer to a boiling liquid.

In some cases the release of vapour is rather more violent. A layer of water at the bottom of the tank of hot oil, for example, may become superheated so that there is a sudden evolution of vapour.

It has been suggested by R. King (1975a–c, 1976a,b, 1977, 1990) that such an occurrence may have contributed to the Flixborough disaster. A temporary 20 in. pipe was installed between reactor Nos. 4 and 6. Reactor No. 4 was fitted with an agitator, but this had not been in use for some time. It is possible that in the absence of agitation a layer of water may have built up in the bottom of the reactor and, on being heated up during start-up, may have caused a sudden evolution of vapour sufficient to rupture the pipe assembly. During a tank fire, the hydrocarbon layer in the tank can conduct heat to a water layer below. When the water layer heats above its boiling point, it can suddenly boil and displace hot burning hydrocarbon.

Another type of superheat explosion can occur when a refrigerated liquid hydrocarbon mixture such as LNG is poured on to water. This type of explosion is considered in Section 17.29.7.

17.30.4 Air system explosions

Explosions in compressed air system have been reported over the years in coal mines and, more recently, in the process industries also. An explosion in a compressed air line in Germany in 1963 killed 19 people.

Accounts of the explosion hazard in compressed air systems have been given by Mallow (1964a,b), Fowle (1973) and Burgoyne and Craven (1973).

Characteristically, a compressed air system explosion occurs on the air line from a reciprocating compressor with oil lubricated cylinders. Often the compressor has a record of faulty operation and high outlet temperature prior to the

explosion. Carbonaceous residues are frequently found just downstream of the compressor outlet.

Explosions in compressed air systems are essentially oil mist explosions. The thickness of the oil film capable of giving a flammable mist is given by Burgoyne and Craven as follows:

$$t = \frac{CDP}{4\rho} \qquad [17.30.1]$$

where C is the concentration of oil mist in air necessary to produce an explosive mixture at atmospheric pressure (g/m^3), ρ is the density of the oil (g/m^3), D is the diameter of the pipe (m), P is the absolute pressure (atm) and t is the thickness of the oil film (m). The minimum value of C is the lower flammability limit, which for hydrocarbons in general is about 49 g/m^3, but work by Loison (1952) indicates that the practical value is about 138 g/m^3, which is about 2.8 times the theoretical value.

If this oil film is dispersed into an oil mist by some primary shock or explosion, the conditions are created for a more powerful secondary explosion. High outlet temperatures (>250°C) of the compressed air can vaporize and ignite the oil. Sudden release of high pressure can cause simultaneous mist formation and ignition. Carbonaceous residues can undergo self-heating and give ignition.

It should be emphasized that fires are more common than explosions in compressed air systems, but the fire creates an explosion hazard.

The oil film explosion which occurs in a compressed air line with a thin film of flammable oil is somewhat unique. Typically, during a detonation in the line the air line is ruptured at intervals over its length. The problem has been discussed by Burgoyne and Craven.

A number of oil film explosions have occurred in the compressed air starter systems of large diesel engines. In these cases, the explosion generally appears to have been initiated by the diesel engine rather than by the air compressor.

There are a number of measures which can be taken to prevent air system explosions. One is to use oils which are non-flammable or have reduced flammability. The oils available and the problems associated with their use are discussed by Burgoyne and Craven.

It is usually suggested that the risk of explosion can be reduced if high oil usage is avoided. This is not a complete answer, however, as explosions have occurred in systems where oil usage was not abnormally high.

The deposition of oil can be minimized by the design of the air compressor. The air velocity in the outlet pipe should be high, although a velocity which might cause vibration should be avoided. The air flow in the aftercooler should be downwards so that it is in the same direction as the oil film flow. There should be drain points so that oil can be removed from the system.

In operating the compressor, particular attention should be paid to the air outlet temperature. Various authors have suggested outlet temperature maximum limits in the region of 140–150°C.

In Germany the maximum air outlet temperature of air compressors is determined by law. The maximum temperature was set at 160°C in 1934, but explosions continued to occur. In 1963 it was reduced to 140°C.

It has been suggested by Burgoyne and Craven, however, that for pressures above 10 atm this may still not be the safe working temperature. They recommend a maximum normal working temperature of 145°C for a final stage outlet pressure of 10 atm gauge, but one of 124°C for a pressure of 100 atm gauge, with automatic cut-off temperatures 10°C higher in both cases. A more detailed table of values is given by these authors.

It is also important for there to be a high standard of maintenance both of the air compressor and also of the rest of the air system.

Other detailed precautions are described by the authors quoted.

17.30.5 Molten metal–water explosions

A violent explosion can occur if water comes into contact with molten metal. This hazard is of particular concern in the nuclear and metallurgical industries, but may sometimes occur in the process industries.

Molten metal–water explosions can occur either where water is added to molten metal or where molten metal is added to water.

There are a number of theories of molten metal–water explosions, including theories of superheat not unlike those described in Section 17.29.7, but the phenomenon is not well understood.

An investigation of molten metal–water explosions with special reference to continuous casting is given in *A Study of the Causes of Molten Metal and Water Explosions* by the HSE (1977/18). This report describes the various theories of such explosions.

A molten–metal water explosion was the cause of the Scunthorpe disaster in 1975 in which a large leak of water from the cooling water pipe ran down into a torpedo ladle of molten iron (Case History A78).

17.30.6 Superheated liquid explosions: explosions on water

As mentioned above, one form of superheated liquid explosion is that occurring inside plants. Another is that which can occur when a refrigerated liquefied hydrocarbon is spilled onto water.

Accounts of this type of explosion have been given by Katz and co-workers (Katz and Sliepcevich, 1971; Katz, 1972), R.P. Anderson and Armstrong (1972, 1974), Enger and Hartman (1972a,b) and Reid, Drake and co-workers (Drake, Jeje and Reid, 1975; Reid, 1976, 1978; Drake and Reid, 1977; Reid and Smith, 1978).

Attention was drawn to the potential for such an explosion during work on the hazards associated with the transport of LNG and involving its spillage onto water at the Bureau of Mines (BM) (Burgess, Murphy and Zabetakis, 1970 BM S 4105; Burgess, Biordi and Murphy, 1972 BM PMSRC 4177). In the 56th test of an otherwise uneventful series, a sharp explosion destroyed the experimental water tank. Later, a similar but larger explosion was experienced when 0.25 m^3 of LNG was spilled on a pond in the open.

Explosions of this kind are variously known as physical vapour explosions, flameless vapour explosions, or simply vapour explosions, and as rapid phase transition (RPT) explosions.

A theory to explain such explosions is given by Reid (1976). The explosion is a form of superheated liquid explosion and is governed by the superheat limit temperature. An explosion of this kind can occur in a BLEVE, and the phenomenon is considered as an aspect of BLEVE in

Section 17.29. As stated there, Reid's expression for the superheat limit temperature (SLT) is

$$T_{sl} = 0.895\ T_c \qquad [17.30.2]$$

where T_c is the critical temperature (K) and T_{sl} is the superheat limit temperature (K). If a liquid is heated above its SLT, rapid vapour bubble nucleation occurs followed by an explosive evolution of vapour.

According to this theory, spillage of a cold liquid onto a hotter one can result in a superheat limit explosion. As the BM work indicates, this occurs only in a few of cases.

The limiting conditions for occurrence of an SLT are discussed by Reid with reference to those for propane. The SLT of propane is 326 K (53°C). The range of water temperatures within which vapour explosions of propane of any violence occur is 326–344 K. Below 326 K the water temperature is less than the SLT of propane whilst above 344 K the phenomenon appears to be suppressed by the film boiling regime.

For small temperature differences the heat transfer regime is nucleate boiling, but as the temperature difference increases film boiling takes over. The heat transfer in this latter regime is reduced so that the cold liquid then has only a thin film above the SLT. Limited to this thin film, the violence of the SLT explosion is much less.

Thus, although liquefied gases such as ethane and methane have lower SLTs, they do not in their pure form give vapour explosions.

The same applies to LNG which is essentially pure methane. However, it is found that if an LNG contains a sufficient proportion of higher hydrocarbons a vapour explosion can occur. A vapour explosion is thus a credible event.

The proportion of higher hydrocarbons in an LNG which would not undergo a vapour explosion may be increased by ageing or by differential vaporization of the methane to the point where it would.

The initial vapour explosion may be followed by a more violent one; the primary explosion may result in further contacting of the cold and hot liquids due to the pressure wave and to droplet formation.

Several groups of workers have reported research on the industrial aspect of the hazard from such explosions. In addition to the BM work they include R.P. Anderson and Armstrong (1972, 1974) and Enger and Hartman (1972a,b).

Enger and Hartman consider particularly the situation where LNG is subject to depletion of the methane content to the point where a vapour explosion is possible. They point out that in these circumstances the weathering is likely to be uneven so that in any given instant an explosion would occur only at part of the interface.

These workers estimate the mechanical energy release as some 0.5 cal/m^2 of interface area.

The consensus view which appears to have emerged is that such vapour explosions are not a prime cause of concern.

17.31 Effects of Explosions

An explosion may give rise to the following effects: (1) blast damage, (2) thermal effects, (3) missile damage, (4) ground shock, (5) crater, and (6) injury.

Not all these effects are given by every explosion. An aerial blast, for example, tends not to form a crater.

Many of the data on the effects of explosions come, not surprisingly, from studies of military and industrial explosives, but an increasing amount of information is available from the investigation of process plant explosions.

Information on the effects of explosions has been given in *Explosions, Their Anatomy and Destructiveness* (C.S. Robinson, 1944), *Structural Defence* (Christopherson, 1946), the *Textbook of Air Armaments* (Ministry of Supply, 1952), *The Effects of Nuclear Weapons* (Glasstone, 1962; Glasstone and Dolan, 1980), *Hazards of Chemical Rockets and Propellants* (Qensen, 1972), *Workbook for Predicting Pressure Waves and Fragment Effects of Exploding Propellant Tanks and Gas Storage Vessels* (W.E. Baker *et al.*, 1975), *Handbook for Estimating the Effects of Accidental Explosions in Propellant Handling Systems* (W.E. Baker *et al.*, 1978), *Explosion Hazard and Evaluation* (W.E. Baker *et al.*, 1983), *Methods for the Determination of Possible Damage to People and Objects Resulting from Releases of Hazardous Materials* (the *Green Book*) (CPD, 1992b) and by Jarrett (1968), Brasie and Simpson (1968), V.J. Clancey (1972b), Eisenberg, Lynch and Breeding (1975) and Gilbert, Lees and Scilly (1994a–i).

Selected references on the effects of explosions are given in Table 17.38.

Table 17.38 *Selected references on effects of explosions*

Blast effects, blast theory, blast scaling laws
MOD, ESTC (n.d.); Hugoniot (1887–89); Christopherson (1944, 1946); C.S. Robinson (1944); Sachs (1944); E. Fisher (1950, 1953a,b); Los Alamos Scientific Laboratories (1950); von Neumann and Richtmyer (1950); Weibull (1950); Prentiss (1951); Goldstein and von Neumann (1953); Erode (1955, 1957, 1959); Hoffman and Mills (1956); Hoerner (1958); Shear and Day (1959); Ericsson and Edin (1960); Goodman (1960); Shear and McCane (1960); Glasstone (1962); Kinney (1962); Langefors and Kihlstrom (1963–); Kingery and Pannill (1964); Office of Civil Defense (1965); Wistoski and Snyer (1965); Keefer *et al.* (1966); Kingery (1966); Brasie and Simpson (1968); Callahan (1968); E. Cohen (1968); Dobbs, Cohen and Weissman (1968); Jarrett (1968); D.L. Jones (1968,1970); Masso and Rudd (1968); Petes (1968); Stagg and Zienkiewicsz (1968); Teller *et al.* (1968); Lehto and Larson (1969); Penney, Samuels and Scorgie (1970); Stephens (1970); Zimmer, McDevitt and Dale (1970); Woolfolk (1971); Anon. (1972e); V.J. Clancey (1972b, 1982); Jensen (1972); Pittman (1972a,b, 1976); Westine (1972, 1977); W.E. Baker (1973); J.W. Reed (1973); Rindner and Wachtel (1973); Woolfolk and Ablow (1973); Geiger (1974); W.G. High (1974, 1976); W.E. Baker *et al.* (1975); Eisenberg, Lynch and Breeding (1975); K. Kaplan, Gabrielsen and von Horn (1975); Strehlow and Baker (1975, 1976); Swisdak (1975); Reissler, Pettit and Kennedy (1976, 1977); Strehlow and Ricker (1976); W.E. Baker *et al.* (1978); M.R. Baum (1979); Department of Energy (USA) (1980); Glasstone and Dolan (1980); Zeeuwen and Schippers (1980); W.E. Baker *et al.* (1983); Held (1983a,b); Hannum (1984); Kingery and Bulmash (1984); Dowding (1985); Kinney and Graham (1985); MHAP (1986 LPB 68, 1989); Cruice (1986); Dangreaux (1986); Esparza (1986); E.G. Bell (1987); van Loo and Opschoor (1989); P.A. Davies (1993)
Explosions in confined spaces: W.I. Taylor (1968); Weibull (1968); Stretch (1969); Slack (1971); Lazari, Burley and Al-Hasani (1991) (see also Table 17.13)

Vapour cloud explosions: J.H.S. Lee (1977); A.F. Roberts and Pritchard (1982); S.F. Hall *et al.* (1982); Zeeuwen, van Wingerden and Dauwe (1983); Giesbrecht (1988); Pritchard (1989); C.J.M. van Wingerden, van den Berg and Opschoor (1989); Guibert *et al.* (1992); CCPS (1994/15)

Effect of blast on structures
Ministry of Home Security (Appendix 28, n.d.b); Philip (1945); Christopherson (1946, 1949); R.F. Meyer (1957); Healy (1959); Stretch (1969); Alexander and Hambly (1970); F. Morton (1970); Slack (1971); Wiehle and Bockholt (1971); Mainstone (1972); Alexander and Taylor (1973a,b); ASCE (1974/3, 1985/21, 1986/26); Westine and Baker (1974); FRS (1976 Fire Res. Note 1054); W.E. Baker *et al.* (1983); Jowett (1984 SRD R295); D.M. Brown and Nolan (1985, 1987); Cruice (1986); Jowett and Byrne (1986 SRD R376); Jowett, Byrne and Roberts (1986 SRD R377); Scilly and High (1986); Weerheijm (1988); US Army, Navy and Air Force (1990); Mercx, Weerheijm and Verhagen (1991); Baker, Spivey, Baker (1991); Opschoor, van Loo and Pasman (1992); van Wees and Mercx (1992); Whitney, Barker and Spivey (1992); Barker, Whitney and Waclawczyk (1993)
Brickwork: Astbury *et al.* (1970); Sinha and Hendry (1970); Paterson and Rowe (1970); Hendry and Sinha (1971); Hendry, Sinha and Maurenbrecher (1971); J. Morton, Davies and Hendry (1971); Astbury and Vaughan (1972); Astbury, West and Hodgkinson (1972, 1973); J. Morton and Hendry (1973); H.W.H. West, Hodgkinson and Webb (1973); Beak *et al.* (1994)

Blast resistant structures
Samuely and Hamann (1939); Christopherson (1946); J.F. Baker, Williams and Lax (1948); Earthquake Engineering Research Institute (1952); Newmark (1956a,b); Porter *et al.* (1956); Loving (1957); US Army, Corps of Engineers (1957); Norris *et al.* (1959); Browne *et al.* (1961); Rebenstorf (1961); Weber *et al.* (1961); Glasstone (1962); Kinney (1962); R.G. Rose and Howell (1962); ASCE (1963); J.B. Martin and Symonds (1966); AIA (1967); W.G. High (1967, 1974); C.V. Moore (1967); E. Cohen (1968); E. Cohen and Dobbs (1968a,b); Dobbs, Cohen and Weissman (1968); H.G. Johnston (1968); R.Y. Levine (1968a); Ruyters (1968); Sewell and Kinney (1968); Department of the Army, the Navy and the Air Force (1969); Alexander and Hambley (1970); Allgood and Swihart (1970); Recht (1971); C.E. Reynolds (1971); Granstrom (1972); Whitman (1973); W.E. Lawrence and Johnson (1974); Westine and Baker (1974); E.G. Cox and Saville (1975); Langeveld (1976); Balemans and van de Putte (1977); D.K. Pritchard (1981, 1983, 1989); Forbes (1982); Pritchard (1983); Tunkel (1983); D.M. Brown and Nolan (1985, 1987); Nolan and Brown (1986); Power and Krier (1986); Bailly *et al.* (1989); D.M. Brown (1986).
Vapour cloud explosions: Geiger (1987)

Effect of blast on plant and equipment
J.R. Wilson (1968); F.E. Walker (1969); M.M. Stephens (1970, 1973); Pickering and Bockholt (1971); Weldon (1972); Hymes (1984); D.M. Brown and Nolan (1985, 1987); Nolan and Brown (1986); Dangreaux (1986); Scilly and High (1986); Verheij (1988)

Missiles, including generation, characteristics and flight
Didion (1860); Helie (1884); Petry (1910); Cranz and Becker (1921); Cranz (1926); Gurney (1943, 1946); Christopherson (1946); Anon. (1951); I.G. Bowen, Strehler and Wetherbe (1956); J.N. Nielsen (1960); Synge and Griffiths (1960); I.G. Bowen, Albright *et al.* (1961); E. R. Fletcher, Albright *et al.* (1961); Shapiro (1961); I.G. Bowen *et al.* (1963a,b); Grodzovksy and Kukanov (1965); E.R. Fletcher and Bowen (1968); Gwaltney (1968); Rindner (1968); R.C. Smith and Smith (1968); B. Brown (1969); D.E. Taylor and Price (1971); Zaker (1971, 1975a,b); Pittman (1972a,b, 1976); W.E. Baker, Cox *et al.* (1973); Bessey (1974); W.E. Baker *et al.* (1975); Clancy (1975); Bessey and Kulesz (1976); Ardron, Baum and Lee (1977); W.E. Baker, Westine and Cox (1977); Westine (1977); W.E. Baker *et al.* (1978); W.E. Baker, Cox *et al.* (1978); HSE (1978b); SIPRI (1978); M.R. Baum (1979, 1984, 1988, 1989, 1991, 1993); J.H. Bowen (1980); Munday (1980); Porter (1980); Tulacz and Smith (1980); W.E. Baker *et al.* (1983); Holden and Reeves (1985); Hunt and Wood (1985 SRD R341); Pietersen (1985); Hart and Croft (1988); McCleskey (1988a,b, 1992); Naz (1989); de Mestre (1990); M.C. Miller (1990); Pineau *et al.* (1991); Scilly and Crowther (1992); Twisdale and Vickery (1992); Twisdale *et al.* (1992); CCPS (1994/15)
Missiles from craters: Henny and Carlson (1968)

Missile impact and impact effects
NDRC (1946); Duwez, Clark and Bohnenblast (1950); Parkes (1955); Loving (1957); Ezra (1958); Zabel (1958); Goldsmith (1960); Kolsky (1963); R.W. White and Botsford (1963); Cottrell and Savolainen (1965); C.V. Moore (1967); E.R. Fletcher, Bowen and Ferret (1965); Gwaltney (1968); Symonds (1968); Kinslow (1970); Calder and Goldsmith (1971); A.J. Morris and Calladine (1971); W. Johnson (1972); W.G. High (1974, 1980); Linderman (1974); B.C. Cox and Savffle (1975); N. Jones (1976, 1983); R.P. Kennedy (1976); Berriaud *et al.* (1978); HSE (1978b) SIPRI (1978); Barr *et al.* (1980); Bokor (1980); J.H. Bowen (1980); I.L. Davies (1980); Hopkirk, Lympany and Marti (1980); A.J. Neilson (1980); Porter (1980); Porter *et al.* (1980); Tulacz and Smith (1980); Woisin (1982); W.E. Baker *et al.* (1983); Hunt and Wood (1985 SRD R341); ASME (1986 PVP 106, 1989/173); Jowett (1986 SRD R378); Wierzbicki and Myung Sung Suh (1986); Barr (1987 SRD R439); Ciolek (1988); Vazques-Sierra, Marti and Molina (1988); Lu (1989); A.C. Palmer (1989); Scilly and Crowther (1992)

Windows, glass fragments
Beckett (1937, 1958); Preston (1942); C.S. Robinson (1944); T.C. Baker and Preston (1946); N.J. Thompson and Cousins (1949); Charles (1958); Iverson (1968); J.W. Reed *et al.* (1968); Mainstone (1971); E.R. Fletcher, Richmond and Jones (1973,1976); H.W.H. West (1973); E.R. Fletcher (1974); E.R. Fletcher and Richmond (1974); Eisenberg, Lynch and Breeding (1975); E.R. Fletcher, Richmond and Richmond (1974); Ministry of Social Affairs (1976); M.R. Marshall, Harris and Moppett (1977); Harvey (1979b); E.R. Fletcher, Richmond and Yelverton (1974); J.W. Reed (1980, 1992); Pritchard (1981); W.E. Baker *et al.* (1983); Dangreaux (1986); Harmanny and Opschoor (1986); Scilly and High (1986); CPD (1992a,b); Baker (1994); Baker and Doolittle (1996)

Effect of explosions on people, explosion injury
Ministry of Home Security (Appendix 28); Zuckerman (1940, 1941a,b); Blocker (1949); Blocker and Blocker (1949); Surgeon General (1950); Ministry of Supply (1952); C.S. White (1963, 1965, 1968a,b, 1971, 1974); C.S. White, Bowen and Richmond (1964); E. Cohen (1968); von Gierke (1968); A.E. Hirsch (1968); R.K. Jones and Richmond (1968);

Richmond, Damon *et al.* (1968); Department of the Army (1969); Richmond and Fletcher (1971); Fugelso, Weiner and Schiffman (1972); E.R. Fletcher, Bowen *et al.* (1972); E.R. Fletcher, Richmond and White (1974); Eisenberg, Lynch and Breeding (1975); Fricke (1975); W.E. Baker *et al.* (1978); HSE (1978b, 1981a); V.C. Marshall (1978); Crawley (1982); Hymes (1984); Cruice (1986); Dangreaux (1986); Hadjipavlou and Carr-Hffl (1986); MHAP (1986 LPB 68, 1989); Withers (1988); Mercx (1990); Pineau *et al.* (1991); Withers and Lees (1991); CPD (1992b); Opschoor, van Loo and Pasman (1992); Sorenson, Carnes and Rogers (1992); Gilbert, Lees and Scilly (1994a–i); Oswald and Baker (2000)

Direct blast effects – lung haemorrhage: Zuckerman (1940, 1941); O'Reilly and Gloyne (1941); Stewart, Russel and Cone (1941); Krohn, Whitteridge and Zuckerman (1942); Clemedson (1956); Richmond, Taborelli *et al.* (1957); Richmond, Wetherbe *et al.* (1957); C.S. White (1959, 1961); C.S. White and Richmond (1959, 1960); Richmond, Clare *et al.* (1961); Richmond and White (1962a,b); C.S. White, Bowen and Richmond (1965); Betz *et al.* (1965); Damon *et al.* (1966); I.G. Bowen, Fletcher and Richmond (1968); I.G. Bowen, Fletcher *et al.* (1968); Damon *et al.* (1968); Richmond, Damon *et al.* (1968); E.R. Fletcher and Richmond (1971); C.S. White, Jones *et al.* (1971); E.R. Fletcher, Bowen *et al.* (1972); C.S. White, Jones *et al.* (1972); Coppell (1976); Rawlins (1977–78); Stapczynski (1982); Y.Y. Phillips (1986); Zheng (1990)

Direct blast effects – eardrum rupture: Zalewski (1906); Vadala (1930); Blake *et al.* (1941); Zuckerman (1941); G.A. Henry (1945); F.G. Hirsch (1968); Reider (1968); C.S. White, Bowen and Richmond (1970); Kerr and Byrne (1975a,b)

Bodily translation, tumbling: Gurdjian, Webster and Lissner (1949); Taborelli and Bowen (1957); Taborelli, Bowen and Fletcher (1959); Swearingen *et al.* (1960); I.G. Bowen, Woodworth *et al.* (1962); I.G. Bowen, Fletcher and Ferret (1965); E.R. Fletcher and Bowen (1968); A.E. Hirsch (1968); E.R. Fletcher and Richmond (1970); E.R. Fletcher, Richmond and Jones (1971a,b); E.R. Fletcher, Richmond *et al.* (1971); Richmond (1974); E.R. Fletcher, Yelverton *et al.* (1975); R.K. Jones, Richmond and Fletcher (1975)

Injury by building debris: Bowles *et al.* (1991); Gilbert, Lees and Scilly (1994h)

Crushing: Burzstein (1989)

Injury by missiles, wound ballistics

Bircher (1899); Journee (1907); Gurney (1944); Grundfest *et al.* (1945); Anon. (1947); Andrus *et al.* (1948); Harvey (1948); Goldizen, Richmond and Chiffelle (1957); Goldizen *et al.* (1961); Beyer (1962); French and Callender (1962); A. Palmer (1962); Sperraza and Kokinakis (1967,1968); Clemedson, Hellstrom and Lindgren (1968); Mattoo, Wani and Askegar (1974); R.C. Gray and Coppell (1975); Zaker (1975a,b); di Maio (1981); di Maio *et al.* (1982); Neades and Rudolph (1983); Trunkey (1983); J.H. Lewis *et al.* (1987); McCleskey, Needes and Rudolph (1990); Timberwolf Consulting Services (1991); Gilbert, Lees and Scilly (1994f–i)

Injury by flying glass

R.C. Bell (1944); I.G. Bowen, Richmond *et al.* (1956); Sperrazza and Kokanis (1967, 1968); E.R. Fletcher (1974); E.R. Fletcher and Richmond (1974); E.R. Fletcher, Richmond and Yelverton (1980); W.E. Baker *et al.* (1983); Connell (1983, 1992); Gilbert, Scilly and Lees (1994h)

Injury inside buildings

C.S. White (1957); Department of the Army, the Navy and the Air Force (1969); Richmond (1971, 1972); Richmond and Kilgore (1971); Fricke (1975); Withers and Lees (1991); Hewkin (1992); Gilbert, Lees and Scilly (1994a–d,h,i); Oswald and Baker (2000)

Dust injury, asphyxiation: Ministry of Supply (1952); C.S. White (1957)

Crush injury: Michaelson, Taitelman and Burstein (1984); Michaelson *et al.* (1984); Ron *et al.* (1984); Burstein (1989)

Combined injuries

R.K. Jones (1971); Schildt (1972); CPD (1992b); Gilbert, Lees and Scilly (1994h)

Injury by weapons, including wartime air raids and terrorist bombs

Anon. (n.d.b); Blake and Douglas (n.d.); Lyons and Gardner (n.d.a–c); Zuckerman (1940, 1941); Payne (1941); Osborn (1943); R.C. Bell (1944); Commissioner of Police (1945); Public Record Office (1945a–e); Anon. (1946); Howgrave-Graham (1947); Dunn (1952); Ministry of Supply (1952); Home Office (1953); O'Brien (1955); Collier (1957); Healy (1959); Irving (1963); MacNalty and Mellor (1968); Blocker *et al.* (1969); Mellor (1972); Rutherford (1972–73); Caro and Irving (1973); Ramsey (1974, 1983, 1987); Fricke (1975); R.C. Gray and Coppell (1975); T.L. Kennedy and Johnson (1975); Tucker and Lettin (1975); Waterworth and Carr (1975); J. Reed (1977); Sainsbury (1977); Lord Baker (1978); Madden, Rutherford and Merett (1978); J.F. Hill (1979); Longmate (1981, 1985); Brismar and Bergenwald (1982); R.V. Jones (1982); Pyper and Graham (1982–83); G.J. Cooper *et al.* (1983); Rely (1987); Fryckberg and Tepas (1988); Patience (1989); Neville (1990); Moran (1992); Baker and Bennett (2001)

17.31.1 Blast damage

One of the principal effects of an explosion is the creation of a blast wave, and much of the energy of the explosion is expended on this.

A description of blast effects must take into account both the nature of the blast wave and the damage caused by the blast to structures. The energy entering the blast wave was considered in Section 17.4 and the characteristics of the blast wave in Section 17.25 and its damage effects are described in Sections 17.32 and 17.33.

17.31.2 Missile damage

Another principal effect of an explosion is the generation of missiles, and this takes up most of the energy not transmitted to the blast wave.

A description of missile damage involves both the generation and flight of missiles and the damage caused by missiles to structures. The energy imparted to missiles was considered in Section 17.4 and the generation and flight of missiles and the damage done by them is described in Sections 17.34 and 17.35.

17.31.3 Thermal effects

The combustion process involved in a chemical explosion can give rise to intense local heat radiation, which may cause damage or injury.

Information on the effects of thermal radiation in explosions, mostly derived from nuclear explosions, was given in Chapter 16.

17.31.4 Ground shock

In industrial explosions ground shock effects are usually small and less than those due to blast and assessment of such effects is generally not undertaken.

The effects of ground shock may, however, furnish useful information in accident investigation. An account of ground shock in this context has been given by V.J. Clancey (1972b).

The ground shock produced by an explosion may be regarded as a sinusoidal disturbance and may be characterized by its frequency and amplitude and thus also by its maximum velocity and maximum acceleration:

$$V_{\max} = 2\pi f A \qquad [17.31.1]$$

$$a_{\max} = 4\pi^2 f^2 A \qquad [17.31.2]$$

where a is the acceleration, A is the amplitude, f is the frequency, V is the velocity and the subscript 'max' denotes the maximum value.

For a charge exploded at the ground surface the ground shock depends mainly on the quantity of explosive and the nature of the ground.

An equation widely used to determine the amplitude of ground shock is

$$A = 0.001\frac{KE^{1/2}}{d} \qquad [17.31.3]$$

where A is the amplitude (in.), d is the distance (ft), E is the mass of explosive (lb) and K is a constant. The constant K depends on the nature of the ground. It may be taken as 100 for hard rocks and 300 for clay.

In order to avoid damage to a building owned by others, the amplitude should be limited to a value of 0.008 in. for an average structure or 0.003 in. for a delicate one. The persons responsible for the blast hazard may, however, opt to take the risk of some damage to their own building and allow an amplitude of 0.016 in.

For comparison, an amplitude of 0.001 in. is detectable by someone who is on the lookout for a tremor and one of 0.003 in. may be produced by heavy traffic nearby.

The frequency of the ground shock may be as low as 3–5 Hz in soft or loose soil and as high as 30–100 Hz in rock.

The damage done by ground shock to normal houses has been correlated by Langefors and Kihlstrom (1963) in terms of the quantity

$$\phi = \frac{Q}{R^{3/2}} \qquad [17.31.4]$$

where Q is the mass of explosive (kg) and R is the distance (m).

Some data on damage to normal houses caused by ground shock are given by Langefors and Kihlstrom for hard rock, and further derived data are given by Clancey for soft rock, as shown in Table 17.39. The relationship is not valid for distances less than 2–3 times the depth at which the explosion takes place. The values given are for damage to normal houses built on the rock in which the explosion occurs. For concrete structures the f value needed to give the same degree of damage is 2–4 times greater.

Table 17.39 *Some data on damage to normal houses by ground shock*

$Q/R^{3/2}$		*Damage to normal houses*
Hard rock ($kg/m^{3/2}$)	*Soft rock* ($kg/m^{3/2}$)	
0.008	0.02	Fall of plaster, no cracking
0.06	0.25	Insignificant cracking (threshold value)
0.12	0.50	Cracking
0.25	1.0	Major cracking

Sources: Hard rock: Langefors and Kihlstrom (1963). Soft rock: C lancey (1972b).
Data in this table from *Rock Blasting* by U. Langefors and B. Kihlstrom, 1963, are reproduced with permission of the authors and of the publishers, Almqvist & Wiksell Forlags.

For an explosion at or near the surface, damage by blast will extend to a much greater distance than damage by ground shock.

17.31.5 Crater

A condensed phase explosion tends to give rise to a crater. For industrial explosions this effect is not usually assessed beforehand, but may provide information useful in accident investigation.

Accounts of cratering are given by C.S. Robinson (1944) and V.J. Clancey (1972b, 1977d).

The factors which affect the crater produced by an explosion are the position of the charge relative to the ground surface, the nature of the ground and the type and quantity of explosive. A charge exploded at the ground surface gives a wider and shallower crater than one exploded just beneath the surface.

The crater is larger in rock than in soft sand. In the latter there is very little shock transmission; in the former, however, the initial shock propagates and produces cracks as the pressure wave passes. The expanding gases enter the cracks and accelerate the fragmented rock.

It may be noted that understanding of the effects of the nature of the soil on crater size has developed over the years and the effects just outlined differ from those described by Robinson.

A high brisance explosive generally gives a large crater, and a low brisance explosive a small one or none at all. VCEs tend not to give craters; there was no crater at Flixborough.

An equation for crater size which applies to the explosion of dynamite, a high brisance explosive, at the ground surface on average soil is the Olsen formula

$$V = 0.4Q^{8/7} \qquad [17.31.5]$$

where Q is the mass of explosive (lb) and V is the volume of the crater (ft^3).

Robinson gives the experimental data on crater size shown in Table 17.40. The third case is the explosion at Oppau in 1921 (Case History A5). The corresponding crater volumes calculated from Equation 17.31.5 are 3200 and 75,000,000 ft^3, respectively. Thus, the low brisance ammonium nitrate gave a crater size considerably smaller than

Table 17.40 *Crater dimensions (after C.S. Robinson, 1944)*

Explosive		*Crater dimension*		
Type	*Charge* (lb)	*Diameter* (ft)	*Height* (ft)	*Volume* (ft^3)
Dynamite	50	6	2	30
Dynamite	2,400	31	9	3,200
Ammonium nitrate	9,000,000	400	90	10,000,000

that calculated by the equation derived for the high brisance explosive.

An equation relating the diameter of a crater to its volume has been given by V.C. Marshall (1987). He obtains from Robinson's figures the relation

$$D = 3\frac{V^{0.5}}{h} \qquad [17.31.6]$$

where D is the diameter of the crater (m), h is its depth (m) and V is its volume (m^3). Then, utilizing the rule-of-thumb attributed by Robinson to Olsen that the height of the crater is on average half its diameter ($h = D/2$), he gives

$$D = 6V^{0.25} \qquad [17.31.7]$$

Assuming that crater volume is proportional to the cube of the radius, Equation 17.31.5 is broadly consistent with the other main relation used to describe crater dimensions

$$r \propto W^{1/3} \qquad [17.31.8]$$

where r is the radius of the crater and W the mass of explosive.

As mentioned in Section 17.3, there is a reasonably good correlation between the crater radius and the mean detonation distance for ground surface explosions, so that relation 17.31.8 is similar to Equations 17.3.5 and 17.3.6.

Cratering can occur even without an explosion. The V-2 rockets, which had very high kinetic energy, were capable of giving a large crater even when not armed.

17.31.6 Injury

The effects of an explosion on people include injury caused by (1) blast, (2) missiles, (3) thermal effects, and (4) toxic effects. These injury effects are described in Sections 17.38 and 17.39.

17.32 Explosion Damage to Structures

17.32.1 Air blast loading

The general nature of the air blast from an explosion has been discussed in Section 17.25, where the blast characteristics were described essentially in terms of an ideal condensed phase explosion such as that of TNT, while the differences in the blast between a condensed phase explosion and a VCE were considered in Sections 17.26 and 17.28.

The loading of structures by air blast is described by Glasstone (1962) and Glasstone and Dolan (1980). In general, the effective pressure p_e on a given face of a structure is the sum of the overpressure p and the drag pressure p_d:

$$p_e(t) = p(t) + p_d(t) \qquad [17.32.1]$$

The drag pressure p_d is a function of the dynamic pressure q:

$$p_d(t) = C_D q(t) \qquad [17.32.2]$$

where C_D is the drag coefficient. Glasstone and Dolan treat various structures, including (1) a closed, box-like structure, (2) a partially open, box-like structure, (3) an open frame structure, (4) a cylindrical structure, and (5) an arched structure.

For the case of a closed, box-like structure, it is possible to determine (1) the average front face loading, (2) the average side and top loading, (3) the average back face loading, and (4) the net horizontal loading.

If a blast wave reaches the structure and its incidence on the front face is normal, the overpressure p_f at that face rises very rapidly to the peak reflected overpressure p_r^o. As the wave moves around the structure, the front face pressure falls rapidly to the stagnation pressure p_s at the stagnation time t_s,

$$p_f = p_s = p(t_s) + p_d(t_s) \qquad [17.32.3a]$$

$$= p(t_s) + q(t_s) \qquad [17.32.3b]$$

since for this face C_D is unity. The stagnation time is

$$t_s = 3S/U \qquad [17.32.4]$$

where S is the distance through which pressure relief is obtained and U is the shock velocity. S is the height H or the half-breadth $B/2$, whichever is smaller. Thereafter, the front face pressure falls:

$$p_f = p(t) + q(t) \qquad [17.32.5]$$

The front face pressure is shown in Figure 17.83(a).

The average side face and top pressure is obtained from Equations 17.32.1 and 17.32.2 as follows. The side face is fully loaded when $t = L/U$, where L is the structure length, and at this time the pressure reaches a maximum value p_o corresponding to that at $t = L/2U$. Thereafter the average pressure is that corresponding to $t - L/2U$, until it falls to zero at $t = t_d + L/2U$. The drag coefficient is approximately -0.4. The average side face and top pressure is shown in Figure 17.83(b).

The average back face pressure is obtained from Equations 17.32.1 and 17.32.2 as follows. The shock front reaches the back face at time $t = L/U$, but it requires an additional time of $4S/U$ for the average pressure to build up to the maximum value p_b corresponding to that at $t = (L + 4S)/U$. Thereafter, the average pressure is that corresponding to $t - L/U$, until it falls to zero at $t = t_d + L/U$. The drag coefficient is approximately -0.3. The average back face pressure is shown in Figure 17.83(c).

The net horizontal loading is the front face loading less the back face loading. This is shown in Figure 17.84.

The response of the walls depends primarily on the loadings on the individual faces, while the response of the frame depends on the net loading. For the shock strengths

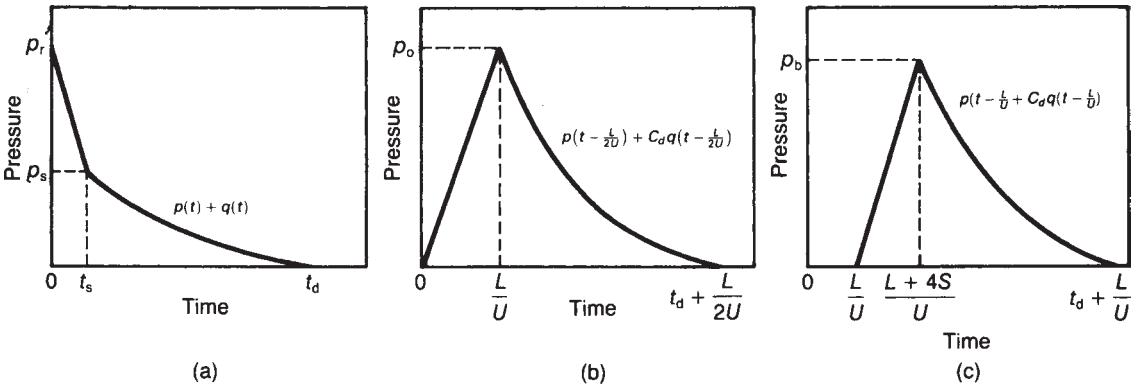

Figure 17.83 *Blast loading of structures – average pressure loading on a closed cuboid structure (Glasstone and Dolan, 1980): (a) average front face loading; (b) average side and top loading; and (c) average back face loading (Courtesy of Castle House Publications)*

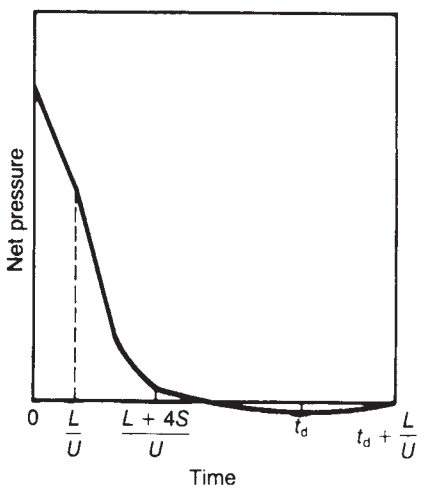

Figure 17.84 *Blast loading of structures – net pressure loading on a closed cuboid structure (Glasstone and Dolan, 1980): net horizontal loading (Courtesy of Castle House Publications)*

of interest here the values required for the drag coefficient C_D are those applicable to the subsonic range. Some values of the drag coefficient are given in Table 17.41.

Table 17.41 *Drag coefficients (W.E. Baker et al., 1983 after Hoener, 1958)*

Shape	*Sketch*	C_D
Right circular cylinder (long rod), side-on	Flow	1.20
Sphere		0.47
Rod, end-on	Flow	0.82
Disc, face-on	Flow or	1.17
Cube, face-on	Flow	1.05
Cube, edge-on	Flow	0.80
Long rectangular member, face-on	Flow	2.05
Long rectangular member, edge-on	Flow	1.55
Narrow strip, face-on	Flow	1.98

17.32.2 Diffraction and drag loading

In the air blast loading of structures a distinction is made between diffraction loading and drag loading. Diffraction loading is determined primarily by the peak overpressure, drag loading by the dynamic, and hence the drag, pressure.

There are two types of diffraction loading. One is that due to the pressure differential between the front and back faces. Except for long structures this load is short-lived. The other loading is that due to the pressure differential between the inside and outside of the building. This approximates a static load and is more prolonged. With diffraction loading the damage potential is a function of the peak overpressure and the duration.

Drag loading is due to the drag pressure on the structure.

The loading is a function both of the air blast and the structure. A given structure may display diffraction-or-drag-type behaviour, depending on the duration. A short duration tends to load by diffraction, a long one by drag.

For a closed structure the duration of diffraction loading is approximately the time for the wave to pass from front to back, which is a relatively short period. Drag loading exists for the whole duration of the positive phase and for a short time thereafter. This is a long period compared with that of diffraction loading.

Certain types of structure are more prone to damage by diffraction, others by drag. Diffraction-type targets tend to be closed or semi-closed structures such as buildings with small window areas and storage tanks. Drag-type targets tend to be tall, thin objects such as telegraph poles and lamp posts. Buildings with large window areas may also constitute drag-type targets.

Drag loading is relatively more important for explosions which give long duration times, such as nuclear explosions, than for those giving short duration times, such as TNT.

17.32.3 Structure response

A typical load-displacement diagram is illustrated in Figure 17.85(a) and other related diagrams are shown in Figures 17.85(b)–(d).

The response of a structure is usually modelled by treating it as a lumped system. The simplest model is the one-mass model. The one-mass system is illustrated in Figure 17.86(a). The general equation of motion is

$$m\frac{d^2x}{dt^2} + c\frac{dx}{dt} + R(x) = F(t) \qquad [17.32.6]$$

where c is the damping factor, F is the applied force, m is the mass, R is the restoring force, t is the time and x is the displacement. It is usual to assume zero damping. Hence, Equation 17.32.6 becomes

$$m\frac{d^2x}{dt^2} + R(x) = F(t) \qquad [17.32.7]$$

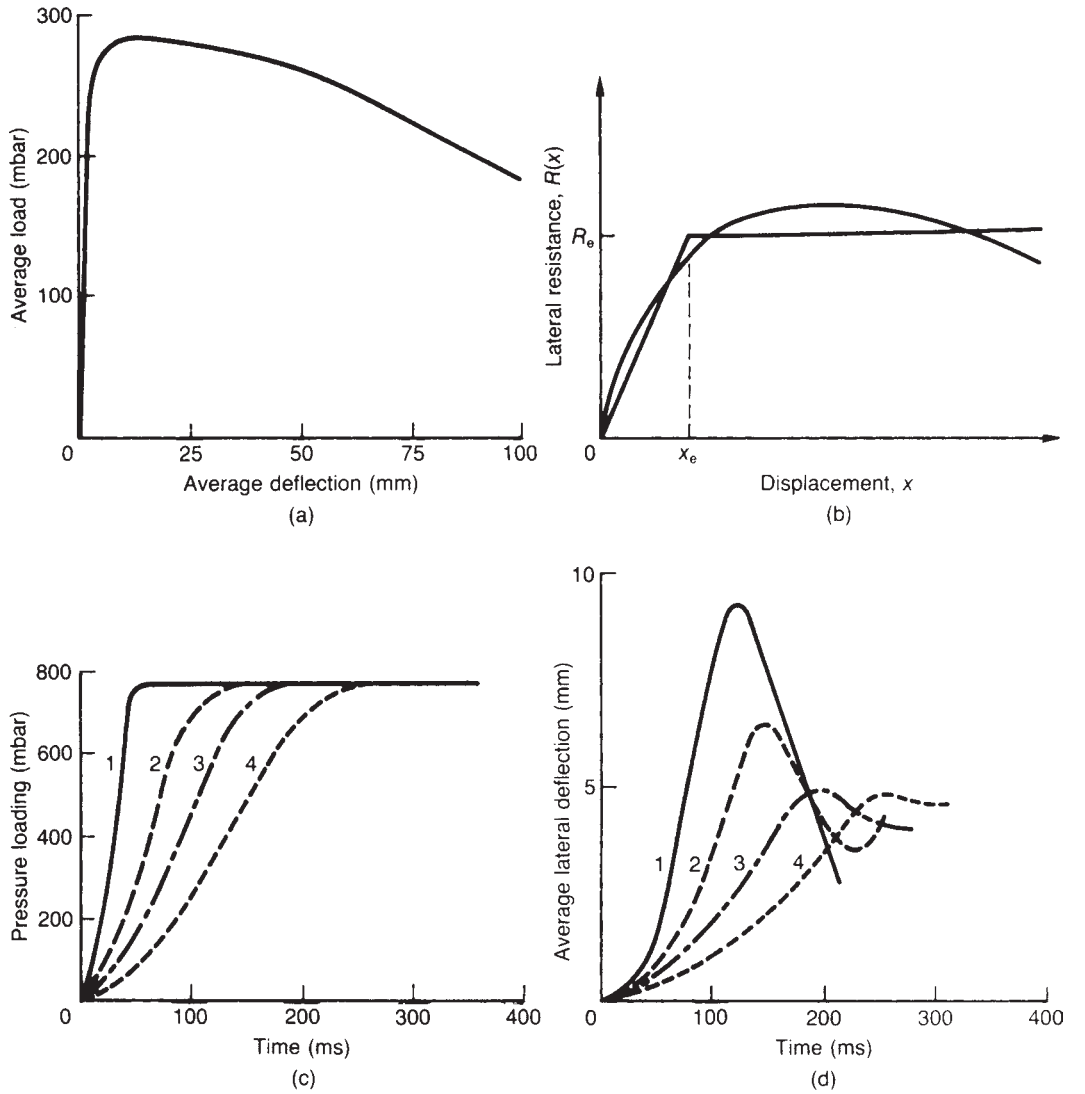

Figure 17.85 *Blast loading of structures: load–displacement and related diagrams: (a) load–displacement diagram; (b) resistance–displacement diagram; (c) load–time diagram; and (d) displacement–time diagram. 1–4, rise times*

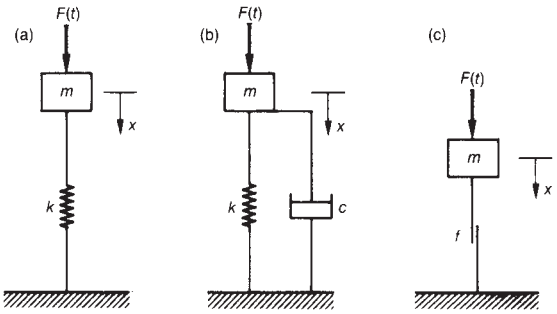

Figure 17.86 *Blast loading of structures – one-mass representation of a structure: (a) undamped elastic spring system (linear oscillator); (b) damped elastic spring system (viscous damping); and (c) rigid-plastic system (Coulomb friction)*

For a system in the elastic regime the retarding force R is proportional to the displacement x. Hence, Equation 17.32.6 becomes

$$m\frac{d^2x}{dt^2}+c\frac{dx}{dt}+kx=F(t) \qquad [17.32.8]$$

Or neglecting damping, as illustrated in Figure 17.86(b)

$$m\frac{d^2x}{dt^2}+kx=F(t) \qquad [17.32.9]$$

where k is the elastic constant.

For a system in the plastic regime the retarding force is the Coulomb friction, or retarding, force f. Hence, as illustrated in Figure 17.86(c), Equation 17.32.9 becomes

$$m\frac{d^2x}{dt^2}+f=F(t) \qquad [17.32.10]$$

In this case motion occurs only if $F>f$.

Considering first the one-mass vibrator, shown in Figure 17.86(a), the equation of motion may be written as

$$r^2\frac{d^2x}{dt^2}+2\zeta\tau\frac{dx}{dt}+x=F^* \qquad [17.32.11a]$$

$$\frac{1}{\omega_n^2}\frac{d^2x}{dt^2}+\frac{2\zeta}{\omega_n}\frac{dx}{dt}+x=F^* \qquad [17.32.11b]$$

with

$$F^*=F/k \qquad [17.32.12]$$

$$\tau=\left(\frac{m}{k}\right)^{1/2} \qquad [17.32.13]$$

$$\omega_n=\left(\frac{k}{m}\right)^{1/2} \qquad [17.32.14]$$

$$\zeta=\left(\frac{c^2}{4mk}\right)^{1/2} \qquad [17.32.15]$$

where ζ is the damping factor, τ the natural period and ω_n the natural frequency.

If there is no damping, the one-mass vibrator becomes an elastic oscillator, as shown in Figure 17.86(b). The behaviour of the elastic oscillator gives important insight into the response of structures. If the system is subject to an applied force which decays exponentially such that

$$F(t)=F\exp(-t/T) \qquad [17.32.16]$$

where T is the time constant of the decay of the force, Equation 17.32.9 becomes

$$m\frac{d^2x}{dt^2}+kx=F\exp(-t/T) \qquad [17.32.17]$$

The general solution of Equation 17.32.17 is

$$\frac{x}{F/k}=f(\omega_n t,\ \omega_n T) \qquad [17.32.18]$$

and the solution x_m for maximum values of x is

$$\frac{x_m}{F/k}=f(w_n T) \qquad [17.32.19]$$

where $x_m/(F/k)$ is the amplification factor and $\omega_n T$ the duration ratio. The relation between these two quantities is given in the oscillator diagram shown in Figure 17.87. The asymptotes of the curve given in Figure 17.87 are

$$\frac{x_m}{F/k}=\left(\frac{k}{m}\right)^{1/2}T=\omega_n T,\quad \omega_n T<0.4 \quad \text{impulsive loading} \qquad [17.32.20a]$$

$$=2\,\omega_n T>40 \quad \text{quasi-static loading} \qquad [17.32.20b]$$

$$=f(\omega_n T)\quad 0.4<\omega_n T<40 \quad \text{dynamic loading} \qquad [17.32.20c]$$

In sketching the curve it is also helpful to note that at the value of $\omega_n T$ where the asymptotes intersect the value of $x_m/(F/k)$ on the actual curve is approximately half that at the point of intersection. Then, in the impulsive loading domain

$$x_m\propto FT=I \qquad [17.32.21]$$

where I is the impulse, whilst in the quasi-static loading domain

$$x_m=2F/k \qquad [17.32.22]$$

Equation 17.32.22 means that the dynamic displacement, or deflection, is twice the static displacement. This dynamic load factor of 2 is widely used in structural engineering. It is also of interest to consider the corresponding energy relations. For impulsive loading the maximum strain energy may be equated with the initial kinetic energy. The initial velocity is

$$\left(\frac{dx}{dt}\right)_{t=0}=\frac{I}{m} \qquad [17.32.23]$$

and the initial kinetic energy E_{ko} is

$$E_{ko}=\frac{m}{2}\left(\frac{I}{m}\right)^2=\frac{I^2}{2m} \qquad [17.32.24]$$

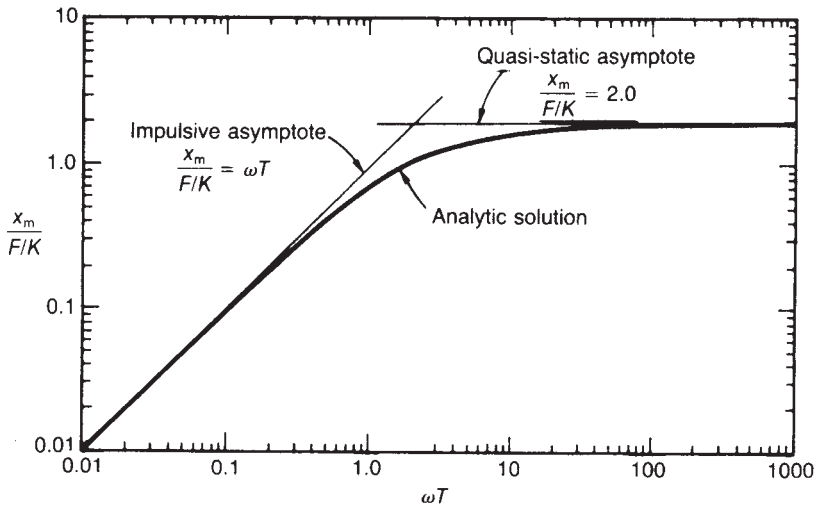

Figure 17.87 *Blast loading of structures response of an elastic structure: (after W.E. Baker et al., 1983) (Courtesy of Elsevier Science Publishers)*

The maximum strain energy E_{sm} is

$$E_{sm} = 1/2\,kx_m^2 \qquad [17.32.25]$$

Equating the two energies to obtain the asymptote

$$\frac{I}{(km)^{1/2}x_m} = 1 \qquad [17.32.26]$$

Similarly, for quasi-static loading the maximum strain energy may be equated with the maximum work W_m. The latter is

$$W_m = Fx_m \qquad [17.32.27]$$

Equating the two energies

$$\frac{2F}{kx_m} = 1 \qquad [17.32.28]$$

as in Equation 17.32.22.

These relationships may be represented graphically in the form of a force–impulse, or F–I, diagram, as illustrated in Figure 17.88, which shows again the three domains of impulsive loading and quasi-static loading separated by dynamic loading.

The force–impulse diagram is readily converted to a pressure–impulse, or P–I diagram, as described below.

A similar treatment may be applied to the plastic regime. In this case the maximum strain energy is

$$E_{sm} = fx_m \qquad [17.32.29]$$

Equating energies as before gives

$$\frac{F}{f} = 1 \qquad [17.32.30]$$

$$\frac{I}{(2mfx_m)^{1/2}} = 1 \qquad [17.32.31]$$

There are also more complex multiple-mass models of structural response.

An account of the practical application of these concepts to the buildings typical of chemical plants has been given by Whitney, Barker and Spivey (1992). The work included investigations of the structural damage in a number of plant accidents and covered peak reflected overpressures of 0.1–15 psi and duration of 5–100 ms. The authors distinguish three types of blast load: impulsive, quasi-static and dynamic. They classify the loads as low, moderate and high, defined in terms of the combination of peak overpressure and duration. They then tabulate for each load class the typical damage to frames, purlins, girts and joists, metal decking and windows, and they indicate the level of protection afforded by the structure and make recommendations for design.

The response of buildings to blast is generally analysed using a static load of long duration. The authors state that the metal frame buildings common in chemical plant tend to have greater impulsive and dynamic resistance than the static analysis indicates. It is quite common for plant buildings to experience a dynamic response in which the duration of the load is close to the natural period of the structure. The conventional plant buildings which perform best are those which allow plastic response without failure. The thrust of the design recommendations is to enhance this plastic behaviour.

17.32.4 Structure parameters

Some parameters which govern the structure response are (1) the natural period, (2) the elastic limit, (3) the ductility ratio, and (4) the resistance function.

The elastic behaviour of a structure may be described in terms of the following parameters:

$$T_n = 1/f_n \qquad [17.32.32]$$

$$= 2\pi/\omega_n \qquad [17.32.33]$$

$$= 2\pi(m/k)^{1/2} \qquad [17.32.34]$$

where f_n is the natural cyclic frequency, T_n the natural period and ω_n the natural frequency.

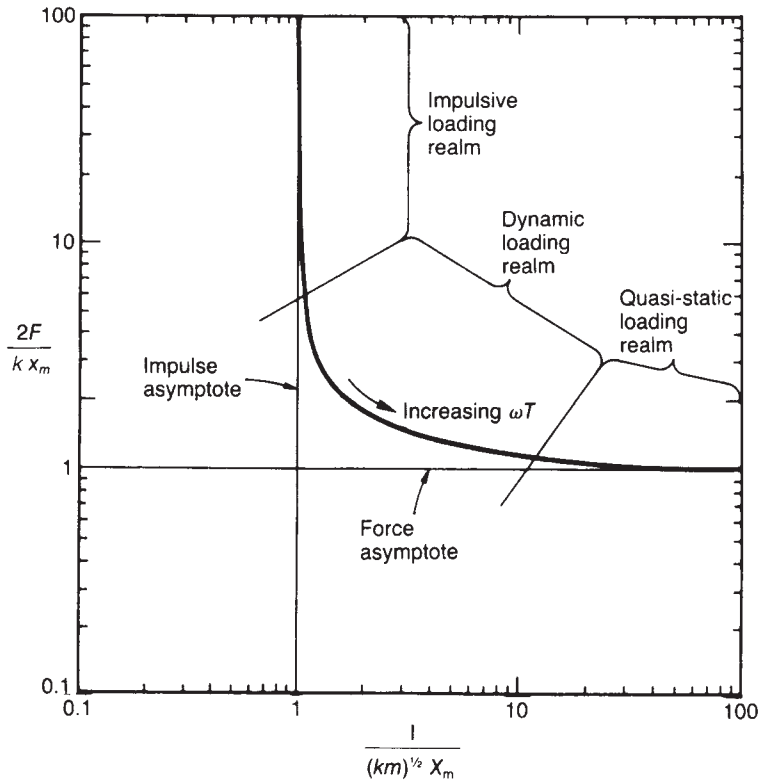

Figure 17.88 *Blast loading of structures: force–impulse (F–I) diagram of a structure (Strehlow and Baker, 1976) (Reprinted from R.A. Strehlow and W.E. Baker, Progress in Energy and combustion Science, 2, 27, © 1976, with permission from Pergamon Press)*

Equation 17.32.34 may be used to determine the elastic constant from the natural period, and vice versa. Some typical values of the natural period given by R.J. Harris (1983) are brick walls 20–40 s, concrete walls 10–15 s concrete floors 10–30 s.

A table of equations for the determination of the natural period is given by W.E. Baker *et al.* (1983). The following empirical equation is given by Kinney (1962) for the estimation of the natural period of a reasonably modern building:

$$T = 0.05\frac{H}{B^{1/2}} \qquad [17.32.35]$$

where B is the breadth of the building (ft), H is its height (ft) and T is its natural period (s). The natural frequencies of buildings is given for a number of common building types in the TNO *Green Book* (1989).

The extent of elastic behaviour is determined by the elastic limit, which is essentially the limit for a static load. Information on the elastic limit is available for most materials of interest. For structural response, where the time of application of the load may be very short, the relevant limit may be the dynamic elastic limit. Some approximate data on the elastic limit for structural materials have been given by Kinney (1962). According to these data the ratio of the dynamic to the static resistance for structural steel is about 1.58 up to a time to yield of 5.5 ms and that for reinforced concrete is about 1.38 up to a time to yield of 10 ms. For both materials the ratio falls to about 1.15 at a time to yield of 100 ms.

Kinney states that the time to reach the maximum elastic displacement, or time to yield t_e, has been investigated using the equation of motion, and may be approximately represented by the relation

$$t_e = \frac{T}{4}\left(\frac{p_m}{r_e}\right)^{-1/2} \qquad [17.32.36]$$

where p_m is the blast pressure (N/m^2), r_e is the maximum elastic resistance per unit area (N/m^2), t_e is the time to yield (s) and T is the natural period (s).

The ductility ratio p, is the ratio of the total sustainable deformation to the elastic deformation:

$$\mu = \frac{x_f}{x_e} \qquad [17.32.37]$$

where x_e is the displacement at the elastic limit and x_f is that at the failure limit. A material with a low ductility ratio is brittle, one with a high ratio ductile.

The behaviour of a structure under load is given by the load-displacement curve, which was illustrated in Figure 17.85(a). If this curve is treated as a resistance-displacement curve, the resistance function R may be obtained from it by approximating the curve by two

straight lines, as shown in Figure 17.85(b). At the maximum elastic displacement x_e there is a maximum elastic resistance R_e, or yield resistance.

17.32.5 Component failure

The behaviour of a structural component may be illustrated by considering that of a brick wall. Work on the response of load-bearing brick structures to gas explosions has been described by Astbury *et al.* (1970), and their report contains an appendix by Paterson and Rowe (1970) on experimental work on the dynamic loading of brick panels.

Figure 17.89 shows the load-displacement diagram for brick panels of varying thickness. There is a rise to a maximum load F_m with a given central deflection x_m. The load decays to zero at a failure deflection x_f. These three parameters are functions of the bricks, the mortar, the panel thickness, the aspect ratio and the edge-fixing conditions. The failure deflection x_f is usually somewhat more than the panel thickness. From other work the ratio of central to average deflection is taken as 1:0.44.

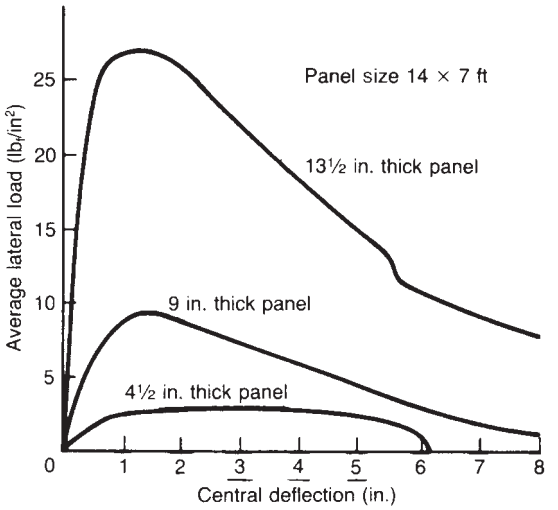

Figure 17.89 *Blast loading of structures: load–displacement diagram for brick panels (after Astbury et al.,1970) (Courtesy of the British Ceramics Research Association)*

From experimental work several simple rules have been derived for scaling load-deflection curves. It is found that if the linear dimensions of a panel are altered by a uniform scaling factor, the lateral strength remains constant. It is also found that the strength is proportional to the square of the thickness. Further, comparing a square with a rectangle comprising two such squares, it is found that the strength of the latter is half that of the former, that for intermediate values of the aspect ratio it is possible to interpolate and that for greater values the strength remains constant at the value for the rectangle.

Although the elasticity of brickwork is very limited, for rapidly applied loads the dynamic strength is somewhat greater than the static strength. In other words, there is some increase in maximum deflection with increase in rate of pressure rise. This is illustrated for a 9 in. brick wall in Figure 17.90.

There is a marked increase in dynamic deflection as the failure loading is approached. This is illustrated for a 4.5 in. brick wall in Figure 17.91, which shows that at explosions with maximum pressure P_m of 4 $lb_f/in.^2$ the deflection is slight, but that at a pressure of 4.2 $lb_f/in.^2$ there is a large deflection, failure finally occurring at 5.1 $lb_f/in.^2$.

Some information is available on the failure pressures of building components. Tables are given by Astbury *et al.* (1970) and R.J. Harris (1983).

17.32.6 Overpressure damage data

Structural damage caused by blast waves from explosions has traditionally been correlated in terms of the peak overpressure of the explosion. There are available a large

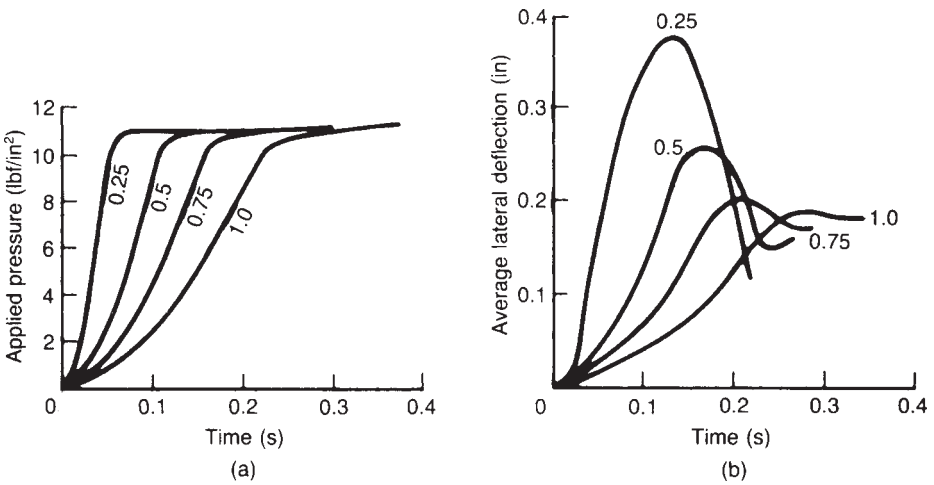

Figure 17.90 *Blast loading of structures–effect of rapidly applied loads on a 9 in. brick wall (after Astbury et al., 1970): (a) applied load and (b) average lateral deflection. Curve parameters on both figures are fractions of longest rise time 200* ms *(Courtesy of the British Ceramics Research Association)*

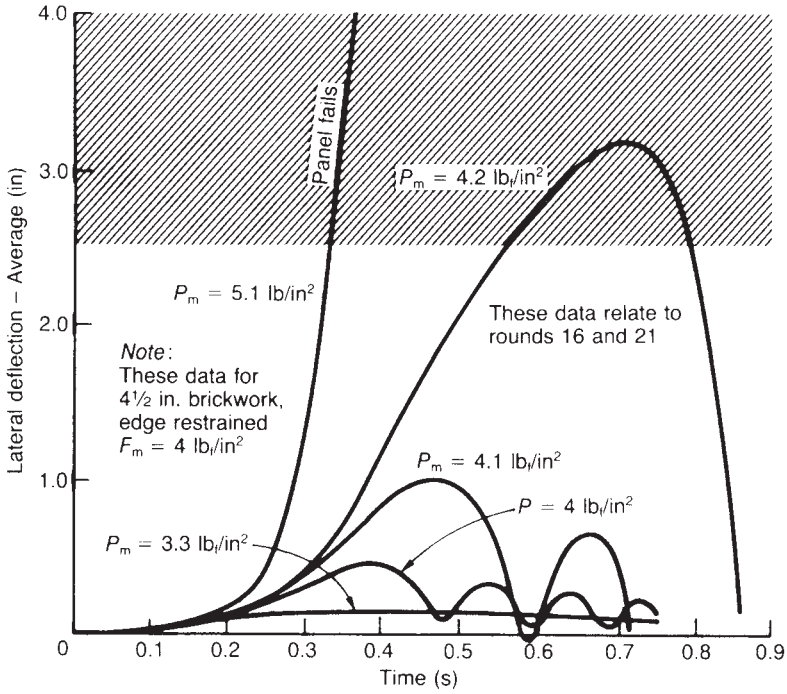

Figure 17.91 *Blast loading of structure: effect of rapidly applied loads on a 4.5 in. brick wall as failure loading is approached (after Astbury et al., 1970). F_m ultimate strength; P_m maximum explosion pressure (Courtesy of the British Ceramics Research Association)*

number of tables and graphs giving damage levels in terms of the peak overpressure.

The applicability of such data is greater for quasi-static loading than it is for impulsive loading. In the latter regime this approach is liable to result in considerable overestimate of the damage.

Thus, W.E. Baker *et al.* (1983) recommend against the use of simple overpressure damage data. Preferred methods are the use of pressure–impulse, or P–I, diagrams and distance–charge, or R–W correlations.

However, useable data in these alternative forms are often not available. In addition, some refinement of the overpressure approach has been effected. It still appears worthwhile, therefore, to consider first this approach.

A survey of damage effects caused by accidental explosions has been made by C.S. Robinson (1944), who also gives graphs of the limits of serious damage, minor damage, glass breakage and missile flight vs charge for both barricaded and unbarricaded installations. The data given by Robinson for unbarricaded installations are plotted in Figure 17.92.

A large amount of information on blast damage is given by Glasstone (1962) and Glasstone and Dolan (1980). These include buildings of various kinds, gas works, oil storage tanks, LPG installations, electrical transmission systems, gas, water and sewage systems and vehicles and ships. These data are based mainly on blasts caused at Hiroshima and Nagasaki by the explosion of a nuclear bomb of approximately 20,000 t TNT equivalent over each city in 1945 and by tests conducted at the Nevada Test Site, supplemented by data from accidental explosions.

Some of the damage effects described by Glasstone are as follows. In the Texas City explosion in 1947, oil storage tanks were severely damaged out to the overpressure region of 3–4 psi.

In the Nevada tests in 1955 a complete 18,000 US gal bulk storage plant containing propane with pump, compressor, piping, valves and fittings, and with a cylinder filling building, was located at the point where the overpressure was 5 psi. The building was demolished and the filling line was broken at the point where it entered the building, but otherwise the installation received only superficial damage.

In the Nagasaki explosion in 1945 the water supply system suffered extensive damage, so that it became virtually impossible to extinguish fires. Breakage of pipes occurred almost entirely in or at the entrance to buildings and structures rather than underground. The exception was a 12 in. cast iron water main 3 ft below ground which did break, but this was in a filled area where the ground was irregular. There appeared to have been little effect on underground gas mains.

Glasstone gives a large amount of data on levels of damage to both diffraction- and drag-type structures, including a number of tables and nomograms. In particular, the data shown in Table 17.42 have been widely quoted. The data given in Table 17.42(A) are from an original table of Glasstone. Those given in Table 17.42(B) are quoted together with the data from section A by Brasie and

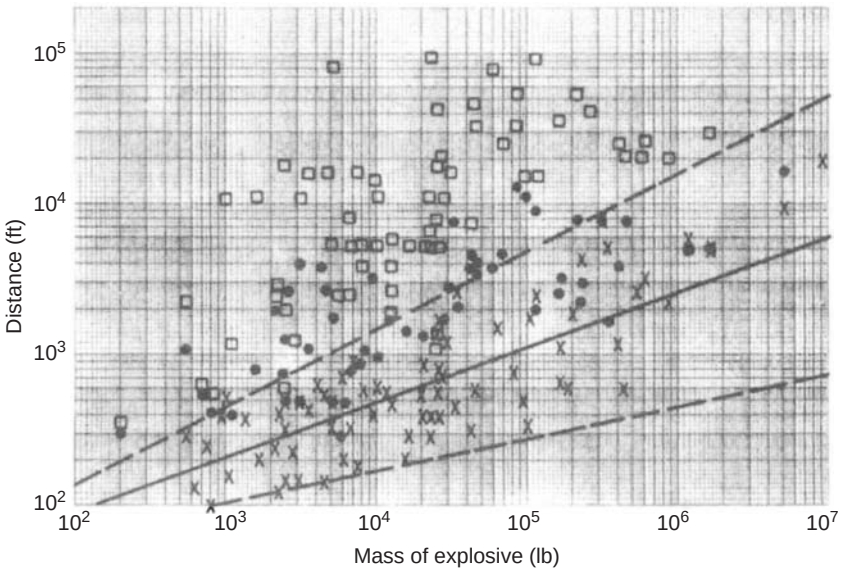

Figure 17.92 *Damage effects of explosions: limits of serious damage, missile flight and glass damage for accidental explosions for unbarricaded installations (after C.S. Robinson, 1944): x, severe damage; ●, missile flight; □, glass breakage. The full and broken lines give, respectively, the average and the outer limits for serious damage (Reproduced with permission from Explosions: their Anatomy and Destructiveness by C.S. Robinson, © 1944, McGraw-Hill Book Company)*

Table 17.42 *Some damage effects produced by a blast wave – 1 (after Glasstone, 1962; Brasie and Simpson, 1968)*

Structural element	*Failure*	*Peak side-on overpressure (approximate)* (psi)
A Original data of Glasstone[a]		
Glass windows, large and small	Shattering usually occasionally frame failure	0.5–1.0
Corrugated asbestos siding	Shattering	1.0–2.0
corrugated steel or asbestos panelling	Connection failure followed by buckling	1.0–2.0
Brick wall panel, 8 or 12 in. thick, not reinforced	Shearing and flexure failures	3.0–10.0 (7–8)
Wood siding panels, standard house construction	Usually failure occurs at the main connections, allowing a whole panel to be blown in	1.0–2.0
Concrete or cinder-block wall panels, 8 or 12 in. thick, not reinforced	Shattering of wall	1.5–5.5 (2–3)
B Additional data of Brasie and Simpson[b]		
Self-framing steel panel building	Collapse	3–4
Oil storage tanks	Rupture	3–4
Wooden utility poles	Snapping failure	5
Loaded rail cars	Overturning	7

[a] Glasstone and Dolan (1980), table 5.145. in parentheses are from Brasie and Simpson (1968).
[b] Brasie Simpson (1968), table 3.

Simpson (1968), and are possibly taken from the text of Glasstone. The table given by Brasie and Simpson has frequently been quoted.

Another damage table is that given by V.J. Clancey (1972b) in the context of accident investigation and reproduced in Table 17.43.

Commenting on these tables, Scilly and High (1986) state that both the tables of Brasie and Simpson and that of Clancey are largely derived from the nuclear weapons data and theoretical analyses in Glasstone together with some additional data for condensed phase explosives from Robinson.

Table 17.43 *Some damage effects produced by a blast wave – 2 (after V.J. Clancey, 1972b)*

	Peak side-on overpressure	
	(psi)	(kPa[a])
Annoying noise (137 dB), if of low frequency (1–15Hz)	0.02	
Occasional breaking of large glass windows already under strain	0.03	0.2
Loud noise (143 dB); sonic boom glass failure	0.04	
Breakage of windows, small, under strain	0.1	0.7
Typical pressure for glass failure	0.15	1.0
'Safe distance' (probability 0.95 no serious damage beyond this value)	0.3	2.0
Missile limit		
Some damage to house ceiling; 10% window glass broken		
Limited minor structural damage	0.4	2.8
Large and small windows usually shattered; occasional damage to window frames	0.5–1.0	3.5–6.9
Minor damage to house structures	0.7	4.8
Partial demolition of houses, made uninhabitable	1.0	6.9
Corrugated asbestos shattered	1–2	6.9–13.8
Corrugated steel or aluminium panels, fatenings fail, followed by buckling		
Wood panels (standard housing), fastening fail, panels blown in		
Steel frame of clad building slightly distorted	1.3	9.0
Partial collapse of walls and roofs of houses	2	13.8
Concrete or cinder block walls, not reinforced, shattered	2–3	13.8–20.7
Lower limit of serious structural damage	2.3	15.9
50% destruction of brickwork of house	2.5	17.3
Heavy machines (3000 lb) in industrial building suffer little damage	3	20.7
Steel frame building distorted and pulled away from foundations		
Frameless, self-framing steel panel building demolished	3–4	20.7–27.6
Rupture of oil storage tanks		
Cladding of light industrial buildings ruptured	4	27.6
Wooden utilities poles (telegraph, etc.) snapped	5	34.5
Tall hydraulic press (40,000 lb) in building slightly damaged		
Nearly complete destruction of houses	5–7	34.5–48.3
Loaded train wagons overturned	7	48.3
Brick panels, 8–12 in. thick, not reinforced, fail by shearing or flexure	7–8	48.3–55.2
Loaded train boxcars completely demolished	9	62.1
Probable total destruction of buildings	10	69.0
Heavy (7000 lb) machine tools moved and badly damaged		
Very heavy (12,000 lb) machine tools survived		
Limit of crater lip	300	2000

[a] These SI values are given by Gugan (1979).

A damage classification which is widely quoted is that by Stephens (1970), who defines the following categories:

Zone	*Damage level*	*Peak side-on overpressure* (kPa)
A	Total destruction	>83
B	Severe damage	>35
C	Moderate damage	>17
D	Light damage	<3.5

The damage levels typical of these zones are such that in A the building may be damaged beyond economical repair, in B it suffers partial collapse and/or failure of some structural members, in C it is still usable but structural repairs are required and in D damage includes broken windows, light cracks in walls and damage to wall panels and roofs.

Fugelso, Weiner and Schiffman have described damage to frame structures from an explosion equivalent of 5001 TNTequivalent. The following data have been quoted in the vulnerability model by Eisenberg, Lynch and Breeding (1975) from this work:

Structural damage (%)	*Peak overpressure*	
	(psi)	(N/m^2)
1 (threshold)	0.9	6,200
50	3.0	20,700
99	5.0	34,500

They derive from these data a probit equation relating structural damage to peak overpressure:

$$Y = -23.8 + 2.92 \ln p^{o} \qquad [17.32.38]$$

where p^{o} is the peak overpressure (N/m^2) and Y is the probit.

In further development of the vulnerability model, Rausch, Eisenberg and Lynch (1977) have dealt with the

disintegration of walls and the resultant flying debris. Rausch, Tsao and Rowley (1977) review explosion damage to various types of structure, including frame structures, low office blocks and warehouses. They also give data from Pickering and Bockholt (1971) on explosion damage to process storage such as floating roof tanks, vertical pressure vessels and spherical tanks. The damage levels are quoted at 20% (structural damage) and 99% (total destruction):

Damage level (%)	*Peak overpressure*	
	(psi)	(N/m^2)
Steel floating roof petroleum tank		
20	3.5	24,132
99	20.0	137,895
Vertical cylindrical steel pressure vessel		
20	12.0	82,737
99	14.0	96,527
Spherical steel petroleum tank		
20	8.0	55,158
99	16.0	110,316

A description of the effects of the overpressure in the Flixborough explosion has been given by Sadee, Samuels and O'Brien (1976–77). Among the installations at Flixborough were some storage tanks which were situated about 250 m from the epicentre of the explosion and were severely damaged. It is estimated in the *First Canvey Report* (HSE, 1978b) that, assuming an explosion equivalent to 20–30 t of TNT, the tanks would have been subjected to an overpressure of about 0.1 bar. This overpressure for tank failure is used in the report.

A further account of overpressure damage to various items of plant and transport equipment is given in the study by Gugan (1979).

There is a considerable amount of other data on the effect of air blast on buildings. An overpressure of 1 psi is sufficient to cause partial demolition, whilst one of l0 psi usually causes total destruction.

Table 17.44 is another damage table, given by Scilly and High (1986) for use in estimating damage for explosions with yields in the range 1–100 te TNT equivalent. The preferred approach of these authors is use of R–W or P–I methods, but the table is given for use where data in those forms are not available. The provision of separate data for explosions of different sizes makes some allowance for factors other than overpressure.

A further damage table is given by the CCPS (1994/15).

17.32.7 R-W correlations

An approach to the correlation of structural damage from blast waves now increasingly preferred is the use of a distance–charge, or R–W, correlation. Discussions of the use of the R–W method are given by W.E. Baker *et al.* (1983) and Scffly and High (1986).

The R–W method was effectively used by C.S. Robinson (1944) in his correlation of damage effects. He gives various limits of damage for the explosion of a 100,000 lb charge of high explosive. Some of these are shown in Table 17.45 together with the equivalent scaled distance $R/W^{1/3}$.

Extensive work on the correlation of structural damage to buildings has been done by the Explosives Storage and Transport Committee (ESTC) in the United Kingdom. The aim of the work was the setting of safety distances for the

Table 17.44 *Some damage effects produced by a blast wave – 3 (Scilly and High, 1986) (Courtesy of Societe de Chimie Industrielle; reproduced with permission)*

Structural element	*Failure mode*	*Peak side-on overpressure*[a] *(approximate)* (psi) *at different explosive charge*		
		1 te	10 te	100 te
Window frames	5% broken	0.15	0.1	0.1
	50% broken	0.36	0.24	0.21
	90% broken	0.9	0.6	0.54
Houses	Tiles displaced	0.64	0.42	0.38
	Doors and window frames	1.3	0.86	0.77
	Frames may be blown in			
	Category D damage	0.71	0.44	0.42
	Category Ca damage	1.8	1.15	1.10
	Category Cb damage	4.0	2.4	2.3
	Category B damage	11.5	5.2	5.0
	Category A damage	26.5	11.5	11.0
Telegraph poles	Snapped	52	26	24
Large trees	Destroyed	57	26	24
Primary missiles	Limit of travel	0.2	0.14	0.12
Rail wagons	Limit of derailment	26.5	11.5	11.0
	Bodywork crushed	20	8.7	8.4
	Damaged but easily repairable	11.5	5.7	5.5
	Superficial damage	4.6	2.6	2.5
Railway line	Limit of destruction	205	97	93

[a] All distances (and equivalent overpressures) are measured to the furthest point of the structure from the explosion source.

storage of explosives. The work has been described by Jarrett (1968).

The classification of housing damage used by Jarrett is shown in Table 17.46(B). Jarrett gives the following equation for the determination of the average circle radius for each damage category:

$$R = \frac{kW^{1/3}}{[1 + (7000/W)^2]^{1/6}} \qquad [17.32.39a]$$

Table 17.45 *Some limits of the effects of the explosion (charge weight 100,000 lb) of a high explosive charge (after C.S. Robinson, 1944)*

Effect	*Limit of effect* (ft)	*Scaled distance* $R/W^{1/3}$ (ft/lb$^{1/3}$)
Minor damage, inner zone	1,000	21.5
Average serious damage	1,180	25.4
Earthquake damage, normal ground	2,100	45.2
Average missile flight	5,000	108
Minor damage outer zone	10,000	215
Average glass breakage limit	100,000	2150

where R is the average circle radius for the specified damage category (ft) and W is the mass of explosive in TNT equivalents (lb). The constant k has the values shown in Table 17.47(A). An alternative formulation is to express the circle radius in terms of the RB value, or ratio of the radius to the radius PB for the B damage category, and these ratios also are given in Table 17.47(A). In SI units, Equation 17.32.39a becomes

$$R = \frac{kW^{1/3}}{[1 + (3175/W)^2]^{1/6}} \qquad [17.32.39b]$$

where R is the distance (m) and W is the mass of explosive (kg). The corresponding values of k are given in Table 17.47(B).

The average circle radii define idealized circles for which for a particular damage category the area of houses which suffer that damage outside the circle is balanced by the area of those which do not suffer such damage inside the circle. Definitions of housing damage circles are considered further in Section 17.33.

The use of the R–W method for the correlation of blast damage from VCEs in the TNO correlation model has been described in Section 17.28.

17.32.8 P–I diagrams

The other preferred approach to the correlation of blast damage is the use of the pressure–impulse, or P–I, diagram.

Table 17.46 *Housing damage categories*

A	**Wartime damage categories (Ministry of Home Security, 1945)**
A	Complete demolition
B	Partial demolition – houses not repairable and will need to be demolished
C	Houses so badly damaged as to be uninhabitable, but are repairable
D	Houses not so badly damaged as to be uninhabitable, but sufficiently so as to cause appreciable discomfort or inconvenience
	Beyond D damage area, there will be considerable amount of minor damage to roof coverings, odd windows, etc.
B	**Jarrett damage categories (Jarrett, 1968)**
A	Almost complete demolition
B	50–75% external brickwork destroyed or rendered unsafe and requiring demolition
Cb	Houawa uninhabitable – partial or total collapse of roof, partial demolition of one to two external walls, severe damage to load-bearing partitions requiring replacement
Ca	Not exceeding minor structural damage, and partitions and joining wrenched from fittings
D	Remaining inhabitable after repair – some damage to ceilings and tiling, more than 10% window panes broken
C	**Damage categories given by Scilly and High (1986)**
A	House completely demolished, i.e. with over 75% of the external brickwork demolished
B	Houses so badly damaged that they are beyond repair and must be demolished when opportunity arises. Property is included in this category if 50–75% of the external brickwork is destroyed, or in the case of less severe destruction the remaining walls have gaping cracks rendering them unsafe
Cb	Houses which are rendered uninhabitable by serious damage, and need repairs so extensive that they must be postponed until after the war. Examples of damage resulting in such conditions include partial or total collapse of roof structures, partial demolition of one or two external walls up to 25% of the whole, and severe damage to load-bearing partitions necessitating demolition and replacement
Ca	Houses that are rendered uninhabitable, but can be repaired reasonably quickly under wartime conditions, the damage sustained not exceeding minor structural damage, and partitions and joinery wrenched from fixings
D	Houses requiring repairs to remedy serious inconveniences, but remaining habitable. Houses in this category may have sustained damage to ceilings and tilings, battens and roof coverings, and minor fragmentation effects on walls and window glazing. Cases in which the only damage amounts to broken glass in less than 10% of the windows are not included

Table 17.47 *Constants and RB distances for the Jarrett equation*

Damage category	*Constant, k*	*RB ratio*
A Eauation constants (British units) and RB ratios (Jarrett, 1968)		
A	9.5	0.675
B	14	1
Cb	24	1.74
Ca	70	5
D	140	10
B Equation constants (SI units) and RB ratios (after Jarrett, 1968)		
A	3.8	0.675
B	5.6	1
Cb	9.6	1.74
Ca	28	5
D	56	10
C Equation constants (SI units) and RB ratios (Gilbert, Lees and Scilly, 1994c)		
A	4.8	0.675
B	7.1	1.00
Cb	12.4	1.74
Ca	21.3	3.0
D	42.6	6.0

A P–I diagram given by W.E. Baker *et al.* (1983) for some of the Jarrett damage categories is shown in Figure 17.93. This diagram is considered further in Section 17.33.

The use of the P–I diagram method is inhibited by the fact that there are few P–I diagrams available in the literature.

17.32.9 Window damage

The shattering of glass is an important blast damage effect, since flying glass can cause severe injury. It is considered in Section 17.40.

17.33 Explosion Damage to Housing

Explosion damage to housing is usually expressed in the form of distance-charge, or R–W, relations or of pressure–impulse, or P–I, relations. In the description just given of these two methods the application considered is housing damage.

The ESTC, or Jarrett, equation (Equation 17.32.39a) has for some decades held the field as the principal method of determining housing damage, but within the last decade several proposals have been made for the modification of this basic R–W correlation or its associated P–I diagram, including the work of Scilly and High (1986) and Gilbert, Lees and Scilly (1994b,c).

Before considering this more recent work it is appropriate to consider the background to the Jarrett equation.

17.33.1 Housing damage categories

During the Second World War it became the practice in the United Kingdom to assign air raid housing damage to the categories A, B, Cb, Ca and D.

There are several definitions of these categories, as shown in Table 17.46. Table 17.46(A) gives the definitions used in report S104, one of the wartime reports of the Ministry of Home Security (1945). A slightly different set of definitions is given in the paper by Jarrett (1968) describing explosives safety distances as shown in Table 17.46(B). Table 17.46(C) from Scilly and High (1986), contains further amplification of the definitions.

Some wartime reports use an undifferentiated C damage category to describe Cb damage.

17.33.2 Philip equation

In an analysis of wartime damage the following equation was derived in a Ministry of Works report REN 558 by Philip (1945) for the distance PB lor B category damage. In the original British units the equation is

$$R_B = \frac{14W^{1/3}}{[1 + (7000/W)^2]^{1/6}} \qquad [17.33.1a]$$

where R is the distance (ft) and W is the mass of explosive (lb). In SI units this equation is

$$R_B = \frac{5.6W^{1/3}}{[1 + (3175/W)^2]^{1/6}} \qquad [17.33.1b]$$

where R is the distance (m) and W is the mass of explosive (kg). The mass of explosive is quoted as the TNT equivalent. This equation was adopted as a standard.

Gilbert, Lees and Scilly (1994c) have reviewed the basis of Equation 17.33.1a as described by Philip (1945). They conclude that although she referred to the mass of explosive in several weapons and incidents in terms of the TNT equivalent, she appears to have used in the equation a mass of explosive W which is the actual mass of explosive and to have based the equation on data for SC bombs, all of which had the same charge/weight ratio, so that strictly speaking the equation is applicable only to this family of weapons. For other weapons she gives a set of calibration constants, or correction factors.

Equation 17.33.1a was effectively endorsed in a report to the ESTC by Healy (1959), who applied it to a large number of incidents.

17.33.3 Jarrett equation

The paper by Jarrett (1968), already mentioned, was the first open publication of, and gave wider currency to, Equation 17.33.1a. He also gave explicit constants for the A, Cb, Ca and D damage categories. In British units, Jarrett's equation is

$$R = \frac{kW^{1/3}}{[1 + (7000/W)^2]^{1/6}} \qquad [17.33.2a]$$

where R is the distance (ft) and W is the mass of explosive (lb). In SI units this equation is

$$R = \frac{kW^{1/3}}{[1 + (3175/W)^2]^{1/6}} \qquad [17.33.2b]$$

where R is the distance (m) and W is the mass of explosive (kg). Equation 17.33.2a is frequently referred to as the

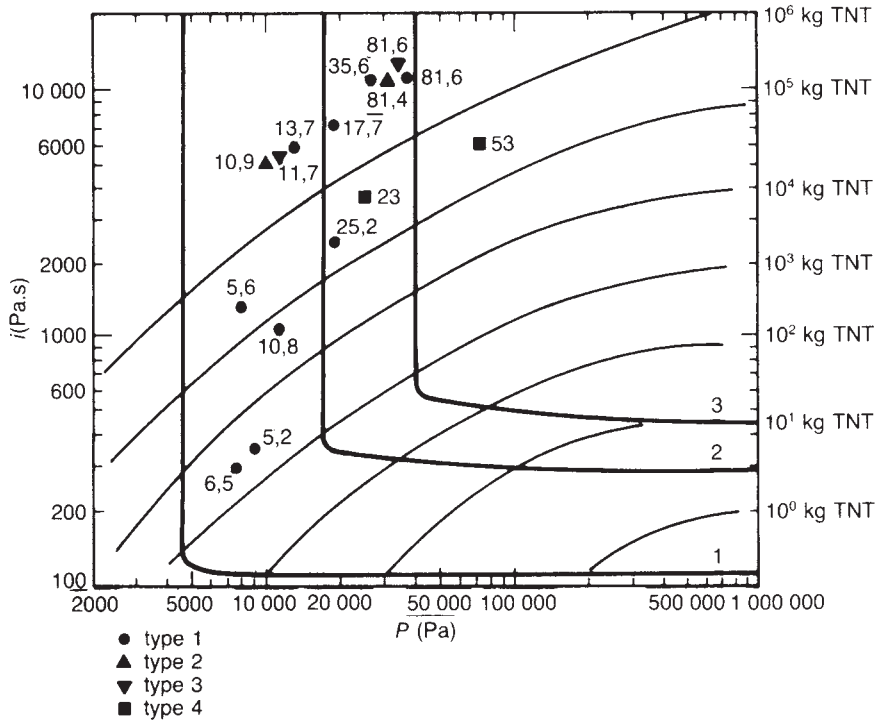

Figure 17.93 *Damage effects of explosions: P–I diagram for housing damage – 1 (after W.E. Baker et al., 1983; Merck, Weerheijm and Verhagen, 1993). Curves are those given by the first set of authors and are as follows: curve 1, threshold for minor structural damage; curve 2, threshold for major structural damage; and curve 3, threshold for partial demolition. Experimental points are those given by the second set of authors and refer to the percentage damage (expressed as building costs) for house types 1–4: type 1,two-floor wooden house; type 2, two-floor masonry house; type 3, single-floor wooden house; and type 4, two-floor masonry house*

Jarrett equation. The values of the constant k given in British units by Jarrett and the SI equivalents are given in Table 17.47 (A) and (B) respectively. The RB ratios are also given.

Equation 17.33.2a was given by Jarrett in a paper on explosives safety distances. He states that his equation is derived from an analysis by the ESTC of 24 well-documented explosions and from the study of records of explosions dating from 1871 and from the experience of enemy bombing in the United Kingdom. He also mentions another examination by the ESTC of 110 reports of accidental explosions. He further states that the quantity of explosive involved ranged from 300 lb to 5.3 million lb, and the types of explosive included dynamite, TNT, Torpex and guncotton. However, Jarrett seemingly overlooked the fact that Equation 17.33.1a was derived for the specific case of SC bombs. The effect of this is that Equation 17.33.2a purports to apply to weapons in general but does not in fact allow for the effect of the weapon casing on the blast potential.

With regard to the constants quoted by Jarrett, these appear to derive from the paper by Healy. Copies of this paper contain hand-written notes suggesting values of the constants for all the damage categories (A–D). For A, B and Cb damage these values are those of Philip. The latter does not, however, give values for Ca and D damage. The values for Ca and D damage of $R_B = 5$ and $R_B = 10$, respectively, quoted by Jarrett, are evidently taken from the hand-written notes in Healy's paper. In the text of this paper, however, these R_B values refer to window breakage rather than housing damage.

Summarizing, the Jarrett equation – Equation 17.33.2a – is in effect the Philip equation – Equation 17.33.1a – as endorsed by Healy, but with extensions to other damage categories as just described.

17.33.4 Housing damage circles

The radius used in Equation 17.33.2 is the average circle radius (ACR) for the damage category. It is defined as the radius of the circle such that the number of houses inside the circle which do not suffer the defined degree of damage is balanced by the number outside which do; this radius is denoted here as $R_{100/0}$. Use is sometimes made of another radius, R_{50}, the radius at which there is a 50% probability of a defined degree of damage. Conceptually, these two radii are quite distinct. In practice, they will often have similar numerical values. They converge where the intensity of the physical phenomenon decays rapidly and where its effect on the target passes through a narrow zone from 0 to 100% effect. A quantitative treatment has been given by Lees, Poblete and Simpson (1986).

It is convenient to mention at this point another method of expressing housing damage. This is the use of the

following relation to obtain from the observed values of R_A, R_B and R_C an average value $\bar{R}_B$:

$$\bar{R}_B = \frac{1}{3}\left(\frac{R_A}{0.675} + \frac{R_B}{1.0} + \frac{R_C}{1.74}\right) \quad [17.33.3]$$

17.33.5 Model of Gilbert, Lees and Scilly

A revision of the Jarrett equation has been undertaken by Gilbert, Lees and Scilly (1994b,c), based on analysis of the original wartime documents for damage from bombs, V-1 flying bombs and V-2 rockets.

These authors first analyse the effective charge of the various weapons used, allowing for the particular explosive filling and for the effect of the casing. They then analyse the damage done by each type of weapon.

From this analysis they conclude that for B category damage the value of the constant k to be used in Equation 17.33.2b in SI units should be 7.1 instead of 5.6. They also give revised values of the constant for the other damage categories, as shown in Table 17.47(C).

It may be noted that whereas the k values for A, B and Cb category damage are somewhat higher than those given by Jarrett, the values for Ca and D damage are less. The KB values for A, B and Cb damage are the same but those for Ca and D damage are less. These latter values agree with those proposed by Scilly and High (1986) in an earlier critique.

The model of Gilbert, Lees and Scilly is therefore Equation 17.33.2b with the constants given in Table 17.47(C). In terms of the R_B distance this equation is

$$R_B = \frac{7.1W^{1/3}}{[1 + (3175/W)^2]^{1/6}} \quad [17.33.4]$$

where R is the distance (m) and W is the mass of explosive (kg).

Some characteristics of the revised equation are illustrated in Table 17.48.

17.33.6 P–I diagrams

The housing damage correlations just given are R–W correlations. As described above, it is also possible to correlate housing damage in terms of a P–I diagram.

The P–I diagram for housing damage based on the Jarrett equation given by W.E. Baker *et al.* (1983) has been given above as Figure 17.93. This diagram is reproduced in the *Green Book*.

This same diagram has been quoted by Mercx, Weerheijm and Verhagen (1991), who have plotted on it data from experimental tests detailed by Glasstone and Dolan (1980). These data also are shown in Figure 17.93. The figure shows iso-damage curves for B, Cb and Ca category damage.

The corresponding P–I diagram given by Gilbert, Scilly and Lees, constructed from the data in Table 17.48, is shown in Figure 17.94. The figure shows iso-damage curves for A, B and Cb category damage.

In Figure 17.94, the influence of the two variables, peak overpressure and impulse, may be examined by moving orthogonally from a curve for a category of less severe damage to that for the next most severe category. The iso-damage curves have peak overpressure and impulse asymptotes. On the right-hand side of the diagram, in the region of lower charge weights, the curves exhibit impulse symptotes. In moving orthogonally from a lower damage to a higher damage curve, there is an increase in impulse but not in overpressure. In other words, in this region an increase in damage occurs due to an increase in impulse. By contrast, in the top left region of the diagram, that of higher charge weights, the curves exhibit overpressure asymptotes. In moving orthogonally from a lower damage to a

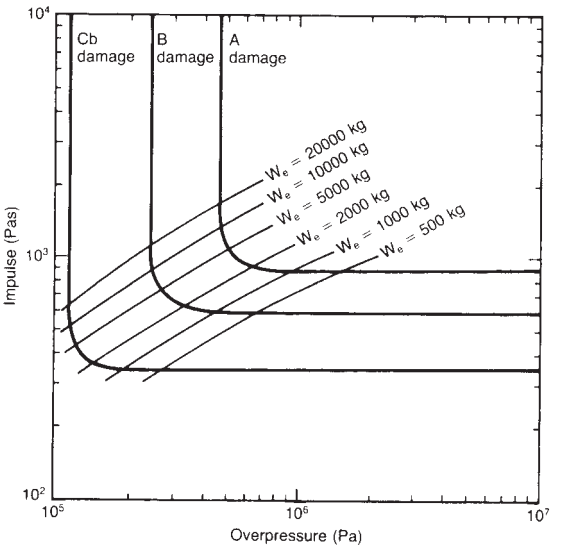

Figure 17.94 *Damage effects of explosions: pressure–impulse (P–I) diagram for damage – 2 (Gilbert, Lees and Scilly, 1994c)*

Table 17.48 *Housing damage model of Gilbert, Lees and Stilly: some characteristics of the model*[a] *(Gilbert, Lees and Scilly, 1994c)*

Effective charge (kg)	R_B *distance* (m)	*Scaled distance* ($m/kg^{1/3}$)	*Peak overpressure* (Pa)	*Impulse* (Pa s)
100	10.4	2.24	2.19×10^5	606
200	16.5	2.82	1.32×10^5	609
500	30.3	3.82	0.717×10^5	614
1,000	47.6	4.76	0.473×10^5	623
2,000	72.5	5.76	0.340×10^5	650
5,000	115	6.71	0.266×10^5	759
10,000	151	6.99	0.250×10^5	917
20,000	192	7.07	0.245×10^5	1140

[a] Revised equation for housing damage: some characteristics of damage circle equation for B damage.

higher damage curve, there is an increase in overpressure but not in impulse. In other words, in this region an increase in damage occurs due to an increase in overpressure. Transition occurs in the region where the charge weights are between 2000 and 5000 kg.

Thus, for many charge weights of interest both peak overpressure and impulse are relevant. For this reason housing damage is correlated by Gilbert, Lees and Scilly directly in terms of charge weight rather than in terms of overpressure.

For the same reason they take the scaled distance appropriate to housing damage as

$$z' = \frac{R}{W^{1/3}[1 + (3175/W)^2]^{1/6}} \qquad [17.33.5]$$

where z' is a modified scaled distance ($m/kg^{1/3}$).

17.34 Explosion Damage by Missiles

If the explosion occurs in a closed system, fragments of the containment may form missiles. In addition, objects may also be turned into missiles by the blast.

Accounts of missiles are given in *Explosions, Their Anatomy and Destructiveness* (C.S. Robinson, 1944), *Structural Defence* (Christopherson, 1946), the *Textbook of Air Armaments* (Ministry of Supply, 1952) and *Explosion Hazards and Evaluation* (W.E. Baker *et al*,. 1983) and by V.J. Clancey (1972b), Jensen (1972), W.E. Baker *et al.* (1975, 1978), Holden and Reeves (1985) and Pietersen (1985).

Brown (1985) reviewed studies on blast and fragmentation of pressurized vessels.

Much of the early work on missiles relates to artillery and other projectiles. Basic work in the field is described by Didion (I860), Helie (1884), Petry (1910) and Cranz and Becker (1921). Further work by the military on ballistics includes that of Gurney (1943, 1946). Other data derive from civil defence work such as that of Christopherson (1946).

Studies have also been made of missiles from the bursting of gas filled vessels in relation to aerospace systems and nuclear power plants. These include work by D.E. Taylor and Price (1971), Pittman (1972a,b, 1976), Bessey (1974), Bessey and Kulesz (1976), W.E. Baker *et al.* (1975, 1978) and Garrison (1975).

A significant source of large missiles in process plant incidents is BLEVEs. Studies of the missiles from such sources have been described by Holden and Reeves (1985) and Pietersen (1985).

17.34.1 Some incidents involving missiles

The generation, size and range of missiles, and the damage which they can cause, have already been discussed to some extent above, mainly in relation to BLEVEs.

Table 17.49 gives some major incidents which involved either escalation by missiles or near misses.

17.34.2 Sources, types and generation of missiles

Missiles are generally classified as primary and secondary. Primary missiles are those resulting from the bursting of a containment so that energy is imparted to the fragments which become missiles. Secondary missiles occur due to the passage of a blast wave which imparts energy to objects in its path, turning them into missiles. Missiles from the bursting of a wall due to an internal explosion are treated here as primary missiles.

Accounts of the source, types and generation of primary missiles include those of Ardron, Baum and Lee (1977), J.H. Bowen (1980), Munday (1980), Porter (1980), Tulacz and Smith (1980) and W.E. Baker *et al.* (1983).

As far as concerns primary missiles from plant, three cases are commonly distinguished: case 1, bursting of a vessel into a large number of relatively small fragments; case 2, separation and rocketing of a vessel or vessel end; case 3, ejection of a single item.

17.34.3 Vessel burst pressure

The explosion energy imparted to fragments in a vessel burst is a function of the initial pressure. The various different scenarios for vessel burst pressure have been discussed in Sections 17.27 and 17.29.

17.34.4 Number and size of missiles

The number of missiles formed in an explosion involving rupture of a containment varies widely. At one extreme is the bursting of a weapon such as high explosive shell or grenade which normally gives a large number of fragments. Large numbers of missiles are also produced by fragmentation of a gas filled pressure vessel. At the other extreme is the ejection of a single item such as a valve component due to failure in a high pressure system.

Of particular interest here is rupture of a pressure vessel. This may involve either brittle or ductile fracture. The differences between these two modes of failure are discussed by Tulacz and Smith (1980). In general, failure is more likely to be ductile. Ductile failure does not usually produce missiles, but if it does they are likely to be small in number but may have potential to do severe damage. It is brittle fracture which is most likely to produce failures in which quite a large number of fragments are generated.

Failure of a vessel may occur under normal pressure loading due to an existing defect or to weakening or it may occur under abnormal pressure such as excessive gas pressure or hydrostatic pressure due to liquid expansion or explosion pressure due to combustion or reaction runaway.

In a cylindrical vessel the initiating crack is typically in the axial direction, but there is a tendency for this crack to turn and propagate circumferentially.

As already stated, for rupture of a gas filled vessel, two main modes are distinguished: (1) bursting into a large number of fragments and (2) separation into two parts. In the former case it is a common assumption that the fragments all have the same mass.

If more refined information is available, it may be correlated as a fragment mass distribution. Methods of correlation are discussed in Section 17.36.

There is some limited information available on the number of fragments formed in the bursting of pressure vessels. W.E. Baker *et al.* (1978) have compiled data on the number and size distribution of fragments for 25 accidental bursts as shown in Table 17.50. The corresponding fragment mass distributions for some of the event groups are shown in Figure 17.95.

Another such compilation is that of Scilly and Crowther (1992). This work is described in Section 17.34.21.

For BLEVEs, Schulz-Forberg, Droste and Charlett (1984) have described tests on fire engulfed vessels, one output from which is plots of the fall of fragments.

Table 17.49 *Some incidents involving escalation, or near misses, by missiles*

Marrietta, OH, 1962
Benzene vapours from a 6 in. relief valve on a phenol plant ignited and an explosion occurred. Flying debris ruptured pipework, releasing flammable liquids.

Louisville, KY, 1965
A compressor circulating gaseous monovinylacetylene exploded. Fragments from the explosion, together with jet flames and transmission through piping, led to a series of further explosions.

Feyzin, France, 1966
A refinery storage sphere suffered a BLEVE, throwing pieces of steel up to l00 tons some three quarters of a mile. One fragment cut the legs from under an adjacent sphere, toppling it and breaking its 8 in. connecting pipe. Another landed on a pipeway and severed 40 lines.

Texas City, TX, 1969
A 100 ft high refinery column disintegrated, apparently due to detonation of vinyl acetylene. Pieces were distributed uniformly over a radius of 1500 ft. One section weighing some 800 lb travelled 3000 ft.

Romeoville, IL, 1977
Roof fragments from an exploding cone roof tank in a refinery struck a covered floating roof tank and a floating roof tank, both of which ignited.

Abqaiq, Saudi Arabia, 1978
Jetting effects of gas escaping from a pipeline threw a 22 ft pipe section 400 ft, where it struck the vapour space of a storage spheroid and released further flammable vapour.

Texas City, TX, 1978
Rupture of a refinery storage sphere due to overpressure led to a large vapour cloud fire. This set off a series of BLEVEs which generated numerous missiles, causing further vessel failures. In addition the original sphere, two further spheres, five horizontal bullets and four vertical bullets were destroyed.

Bantry Bay, Eire, 1979
Explosions on an oil tanker at the jetty generated numerous missiles. One fragment weighing 1000 Il was found at the foot of a large crude oil storage tank 1800 ft from the ship.

Linden, NJ, 1979
A vapour cloud entered an unused control room. When the cloud exploded, debris from this building severed pipes, releasing more hydrocarbons.

Ponce, Puerto Rico, 1979
A 13 ft diameter dimerizer vessel suffered massive failure. The 15 ton steel end travelled 1900 ft and struck an adjacent paraxylene plant, setting it on fire.

Mexico City, Mexico, 1984
See Appendix 4.

Romeoville, IL, 1984
A massive failure occurred of a 55 ft high $\times$8 ft diameter refinery absorption column. Most of the vessel was propelled 3500 ft where it struck and toppled a 138 kV power transmssion tower. Later in the incident, a piece of a vessel which had suffered a BLEVE travelled 500 ft. shearing off pipes.

Pascagoula, MS, 1986
Fragments, from an explosion in the area of a batch still, punctured two atmospheric storage tanks and a pressure storage vessel, releasing flammable material.

Grangemouth, UK, 1987
Overpressure of a low pressure separator due to gas 'breakthrough' caused the 30 ft high times 10 ft diameter vessel to disintegrate. One piece weighing 3 tons was thrown 3300 ft.

Torrance,CA, 1987
A propane treater vessel failed and rocketed into a central pipe rack, cutting several pipes, including the refinery flare lines.

Antwerp, Belgium, 1989
An explosion on an ethylene oxide distillation column caused a large fire and generated missiles which caused extensive damage throughout the plant

Table 17.50 *Behaviour of fragments in some vessel explosions – 1 (W.E. Baker et al., 1978)*

Event group	*No. of events*	*Material*	*Source energy* (J)	*Vessel details*		*No. of fragments*
				Shape	*Mass* (kg)	
1	4	Propane, anhydrous ammonia	$1.49–5.95 \times 10^5$	Rail tank car	25,542–83,900	14
2	9	LPG	3814–3921	Rail tank car	25,464	28
3	1	Air	5.2×10^{11}	Cylinder pipe and spheres	145,842	35
4	2	LPG, propylene	550	Semitrailer (cylinder)	6,343–7,840	31
5	3	Argon	$244–1133 \times 10^{10}$	Sphere	48.3–187	14
6	1	Propane	24.8	Cylinder	512	11

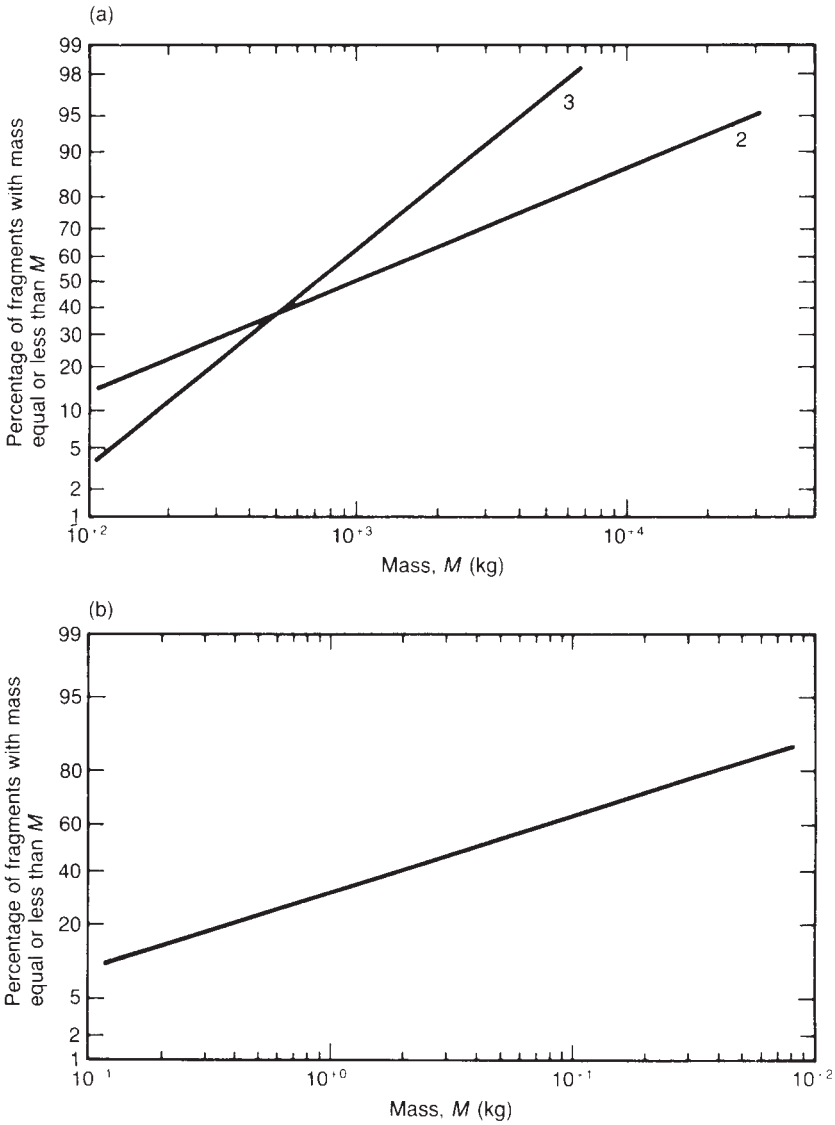

Figure 17.95 *Missile effects of explosions – fragment mass distribution from some accidental events (W.E. Baker et al., 1978): (a) event groups 2 and 3 and (b) event group 6*

A specific study of fragments from BLEVEs has been made by Holden and Reeves (1985). For non-fire events they found that there were three events which gave one fragment, one giving two fragments, one giving three fragments, two giving four fragments and one giving seven fragments. Further information is given in Section 17.34.19.

17.34.5 Initial velocity of missiles

There are a number of different approaches to the estimation of the initial velocity of a missile. They include consideration of (1) the force or pressure on the missile, (2) the transfer of momentum to the missile, and (3) the transfer of energy to the missile.

The force acting on a missile depends on the scenario. Considering first the rupture of a pressure vessel containing gas, the overpressure may occur due to a slow application of pressure or due to an explosion which gives a very high rate of pressure rise. The bursting of the vessel gives rise to a shock wave. In principle, there are two forces which act to accelerate the fragments from the vessel. One is the differential between the gas pressure and the ambient pressure. The other is the dynamic pressure, or wind. In practice, as described below, the pressure differential acts only for a very short time, and the acceleration of the fragments is due essentially to the dynamic pressure.

Another scenario is the rupture of a partition wall by an explosion. Again, the forces acting on the fragments from the wall are the pressure differential between the front face of the wall and the ambient pressure and the dynamic pressure. In principle, if the pressure incident on the wall is that of a rapidly rising blast wave and the wall configuration is such that the pressure differential across it persists until the wall ruptures, the relevant pressure is the reflected pressure. If, on the other hand, the pressure on the wall rises relatively slowly, the pressure differential is simply that between that pressure and the ambient pressure. In practice, in either case, the pressure differential again usually acts only for a very short time and the acceleration of the fragments is due mainly to the dynamic pressure.

Another approach for the bursting of a gas filled vessel is to estimate the fraction of the available energy which is converted into the kinetic energy of the fragments. This approach echoes that used in the treatment of fragments from weapons.

For the ejection of an item such as a valve spindle by a high pressure jet of fluid, an approach based on conservation of momentum is convenient.

Some of the methods for the estimation of missile acceleration and initial velocity are now considered.

17.34.6 Initial velocity of missiles: fragmentation of a gas filled vessel

For missile acceleration and initial velocity, the first case considered (case 1) is that of the bursting of a gas filled vessel into a large number of fragments. Accounts of this include those of C.V. Moore (1967), D.E. Taylor and Price (1971), Ardron, Baum and Lee (1977), Munday (1980) and Baum (1984, 1987). Experimental work is described by Glass (1960) and Pittman (1972a,b).

An account of the initial velocity of fragments from vessels has been given by Ardron, Baum and Lee (1977). They distinguish two main fundamental treatments, one based on the stored energy and the other on fluid mechanics. The models of C.V. Moore (1967) and Munday (1980), given in Sections 17.34.7 and 17.34.8, respectively, exemplify these two approaches. Another family of methods, also based on fluid mechanics, has developed from a model of D.E. Taylor and Price (1971), who studied the rocketing of the two hemispheres from the symmetrical rupture of a sphere. This work was developed by Bessey (1974), Bessey *et al.* (1976) and W.E. Baker *et al.* (1978), who extended it, respectively, to cases of spheres giving more than two equal fragments, cylinders giving multiple equal fragments and both spheres and cylinders giving multiple unequal fragments.

This work has indicated that the fraction of the energy of explosion which translates to kinetic energy of the fragments is relatively low. A more realistic model of this energy has been developed by Baum (1984), as described in Section 17.34.9.

A variant of the problem of the bursting of a gas filled vessel is the rupture of a pipe. Since the pipe is usually part of a pressure system to which it is connected, it is much less easy in this case to define the relevant available fluid energy.

17.34.7 Initial velocity of missiles: Moore model

In the stored energy, or energy partition, method the initial kinetic energy, and velocity, of the fragments is obtained from the energy stored in the vessel. This method has been used by C.V. Moore (1967). The stored energy is obtained by methods such as those given in Section 17.4. Then

$$\frac{M_v u_i^2}{2} = E_f M_f \qquad [17.34.1]$$

where E_f is the energy stored in the vessel per unit mass of fluid, M_f is the mass of fluid stored, M_v is the mass of the vessel itself and u_i is the initial velocity of the fragment. Then

$$u_i = (2E_f M_f / M_v)^{1/2} \qquad [17.34.2]$$

The assumption underlying Equation 17.34.1 is that all the fragments have the same velocity. Some support for this is given in the observations of Glass (1960) and Pittman (1972a) that when a vessel breaks into many pieces, fragments moving in different directions attain comparable terminal velocities.

Moore has also given for the initial velocity of fragments from vessels semi-empirical formulae which are extensions of the well-known formula of Gurney (1946) for the initial velocity of fragments from a cased explosive. His formula is

$$u_i = 1.1(E_f K)^{1/2} \qquad [17.34.3]$$

with

$$K = \frac{M_f}{M_v(1 + 3M_f/5M_v)} \quad \text{sphere} \qquad [17.34.4]$$

or

$$K = \frac{M_f}{M_v(1 + M_f/2M_v)} \quad \text{cylinder} \qquad [17.34.5]$$

where K is a geometric factor.

Ardron, Baum and Lee have compared the predictions of Equations 17.34.2 and 17.34.3 with experimental results for the bursting of a sphere containing superheated water. For this case, Equations 17.34.2 and 17.34.3 overestimate the measured fragment velocities by factors of 5 and 4, respectively. In other words, in this case only about 3% of the fluid energy is imparted to the fragments.

The relations for the available energy of fluid filled vessels given in Section 17.4 yield results which show that the available energy of a gas filled vessel exceeds by an order of magnitude that of a similar liquid filled vessel. Hence, the above result for the water filled vessel is not unexpected. However, Ardon, Baum and Lee also report that even for a gas filled vessel agreement between the measured velocities and the predictions of Equation 17.34.2 was only slightly better than for the water filled case. It would seem, as the authors suggest, that Equation 17.34.2 should be regarded as giving an upper bound on the initial velocity.

17.34.8 Initial velocity of missiles: Munday model

An alternative approach based on the fluid mechanics of the shock wave has been described by Munday (1980). In this model the process of acceleration is envisaged as occurring in the following way. When the vessel ruptures, there is a phase in which the fragment is accelerated by the pressure differential between the gas and the surrounding air, but the duration of this phase is very short, being related to the time for a sound wave to traverse the fragment. Thus, the fragment is surrounded by moving gas before an appreciable increase in velocity has occurred.

The acceleration is caused by the dynamic pressure, or wind. The equation of motion of the fragment may be written as

$$m\frac{\mathrm{d}u}{\mathrm{d}t} = C_{\mathrm{D}}A\rho_{\mathrm{g}}(u_{\mathrm{g}} - u)^2 \qquad [17.34.6]$$

where A is the mean presented area of the fragment, C_{D} is the drag coefficient, m is the mass of the fragment, u is the velocity of the fragment, u_{g} is the velocity of the surrounding gas and ρ_{g} is the density of that gas.

The velocity of the surrounding gas is related to that of the shock front. This latter velocity is determined using an empirical model. The velocity of the surrounding gas is then obtained assuming that it falls linearly from that at the shock front to 0 at a distance halfway between the shock front and the centre of the vessel.

Methods are available for the characterization of the shock front in the bursting of a vessel. Brinkley and Kirkwood (1961) have given a theoretical model. Ardron, Baum and Lee (1977) have plotted the experimental results on bursting of gas filled vessels of Larsen and Olson (1957) and Pittman (1972a) to show the extent to which they fit a TNT equivalent model; the fit is fair with considerable scatter.

17.34.9 Initial velocity of missiles: explosion energy

Expressions for the energy of explosion in a vessel burst are given in Section 17.4. The two principal relations are the Erode equation (Equation 17.4.29) and the Baker equation (Equation 17.4.31).

However, it is apparent from the foregoing that only a fraction of the energy of explosion appears as kinetic energy of the fragments. This has long been appreciated. Various estimates of this fraction are available in the literature. Those given in the *High Pressure Safety Code* have been quoted in Section 17.4. Another value given by Porter (1980) is some 5–10%.

The above problem has been addressed by Baum (1984), who takes as his starting point the Baker equation (Equation 17.4.31), written in the form

$$E_{\mathrm{k}} = k\frac{P_1 V_1}{\gamma_1 - 1} \qquad [17.34.7]$$

with

$$k = 1 - \left(\frac{P_{\mathrm{o}}}{P_1}\right)^{(\gamma-1)/\gamma} \qquad [17.34.8]$$

where E_{k} is the explosion energy imparted to the fragments and k is a parameter. Baum then treats k as a constant to be evaluated. From experimental data reported in the literature he found the value of k to vary between 0.2 and 0.5. On this basis the CCPS (1994/15) proposes that for rough initial calculations a value of $k = 0.2$ be used.

As stated, the foregoing applies to a vessel filled with an ideal gas. As described in Section 17.4, if this is not the case, the energy of explosion is affected. If the fluid is not an ideal gas but is instead a non-ideal gas, vapour or flashing liquid, the energy of explosion should be obtained from thermodynamic data using the method given in Section 17.4.

The CCPS refers to work by Wiederman (1986a,b) on cases involving non-ideal gases and vapour and vapour–liquid systems. In general, the effect of gas non-ideality is to reduce somewhat the initial velocity of the fragments. In some limited tests, the effect of a flashing liquid was found to cause some increase in fragment velocity compared with an ideal gas fill. For this case the CCPS quotes the fraction of the energy of explosion, estimated from thermodynamic data, which translated to kinetic energy of fragments as some 20%

17.34.10 Initial velocity of missiles: separation and rocketing of a gas filled vessel

The second case (case 2) is that of the separation of a gas filled vessel into two parts and the rocketing of one or both of these.

The two parts which separate may be two equal halves such as the two hemispheres of a spherical vessel or two unequal ones such as the end and body of a cylindrical vessel. In either case the rapid discharge of fluid results in a strong reaction force on the separating parts of the vessel.

Models for this situation have been given by D.E. Taylor and Price (1971) and Tulacz and Smith (1980).

The model of Tulacz and Smith (1980) is a single equation for conservation of momentum. The authors give the following illustration of the results obtained. For an autoclave of volume 0.238 m^3 and mass 3131 kg at a pressure of 41.38 bara, from which the head, with area 0.114 m^2 and mass 598 kg, blows off the initial discharge produces a rapid initial acceleration but the velocity attained is only 12 m/s.

17.34.11 Initial velocity of missiles: model of Baker *et al.*

As already mentioned, another method of estimating the initial velocity of fragments from a vessel burst has been developed by W.E. Baker *et al.* (1975, 1978), and is described

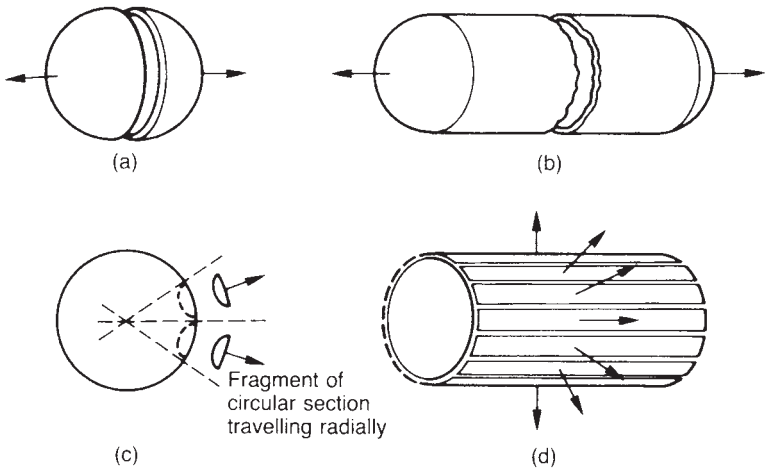

Figure 17.96 *Missile effects of explosions – generation of missiles from vessels (W.E. Baker et al., 1983): (a) sphere bursting into two equal fragments; (b) cylinder bursting into two equal fragments; (c) sphere bursting into n equal fragments; and (d) cylinder bursting into* n *equal strip fragments (Courtesy of Elsevier Science Publishers)*

by W.E. Baker *et al.* (1983). The method covers spherical and cylindrical vessels breaking into two equal fragments or into n equal fragments as shown in Figure 17.96. The velocities are obtained from a parametric study based on the equations of motion of the fragments, solved using a computer code. The results are correlated in terms of a dimensionless pressure P defined as

$$\bar{P} = \frac{(p - p_o)V_o}{M_c a_g} \qquad [17.34.9]$$

and a dimensionless initial velocity $\bar{u}_i$

$$\bar{u}_i = \frac{u_i}{K a_g} \qquad [17.34.10]$$

with

$$a_g = (\gamma R_m T)^{1/2} \qquad [17.34.11]$$

where a_g is the velocity of sound in the gas, M_c is the mass of the vessel, p is the pressure in the vessel, p_o is atmospheric pressure, R_m is the mass basis gas constant, T is the absolute temperature of the gas, u_i is the initial velocity of the fragment, V_o is the volume of the vessel, V is the ratio of the gas specific heats and K is a constant.

For equal-sized fragments, K is unity. The correlation obtained is shown in Figure 17.97(a).

These authors also give a method of estimating the initial velocity of a fragment from a cylindrical vessel with a length/diameter, or L/D, ratio of 10 breaking into two unequal parts. For this case the constant K is determined using Figure 17.97(b). The initial velocity is then obtained as before from Figure 17.97(a) with this value of K and taking n as 2.

The CCPS (1994/15) draws attention to some apparent discrepancies which cast doubt on the factor K.

17.34.12 Initial velocity of missiles: Baum model

Another method for the initial velocity of fragments from a vessel burst is that of Baum (1987), who gives a set of empirical correlations. He treat the following cases: (1) end cap breaking from a cylindrical vessel, (2) cylindrical vessel breaking into two parts in a plane perpendicular to its axis, (3) disintegration of a spherical or cylindrical vessel into multiple fragments, and (4) a single small fragment ejected from a vessel. The first three of these are considered here, and the last in the next section.

The relations given by Baum utilize a parameter F which is defined as

$$F = \frac{(P_1 - P_o)r}{m a_o^2} \quad \text{large no. of fragments} \qquad [17.34.12]$$

$$F = \frac{(P_1 - P_o)Ar}{m_f a_o^2} \quad \text{small no. of fragments} \qquad [17.34.13]$$

where a_o is the speed of sound, A is the area of the detached portion of the vessel wall, m is the mass per unit area of the vessel wall, m_f is the mass of the fragment, P_o is the atmospheric pressure, P_1 is the absolute initial pressure in the vessel and r is the radius of the vessel.

The correlations for the three cases referred to are then

$$u_i = 2a_o F^{0.5} \qquad [17.34.14]$$

$$u_i = 2.18\, a_o [F(L/r)^{1/2}]^{2/3} \qquad [17.34.15]$$

$$u_i = 0.88\, a_o F^{0.55} \qquad [17.34.16]$$

where L is the length of the cylinder. In Equation 17.34.15 F is obtained using $A = \pi r^2$.

17.34.13 Initial velocity of missiles: ejection of a plant fitting

The third case considered here (case 3) is the ejection of a fitting such as a valve stem by a high pressure jet of gas.

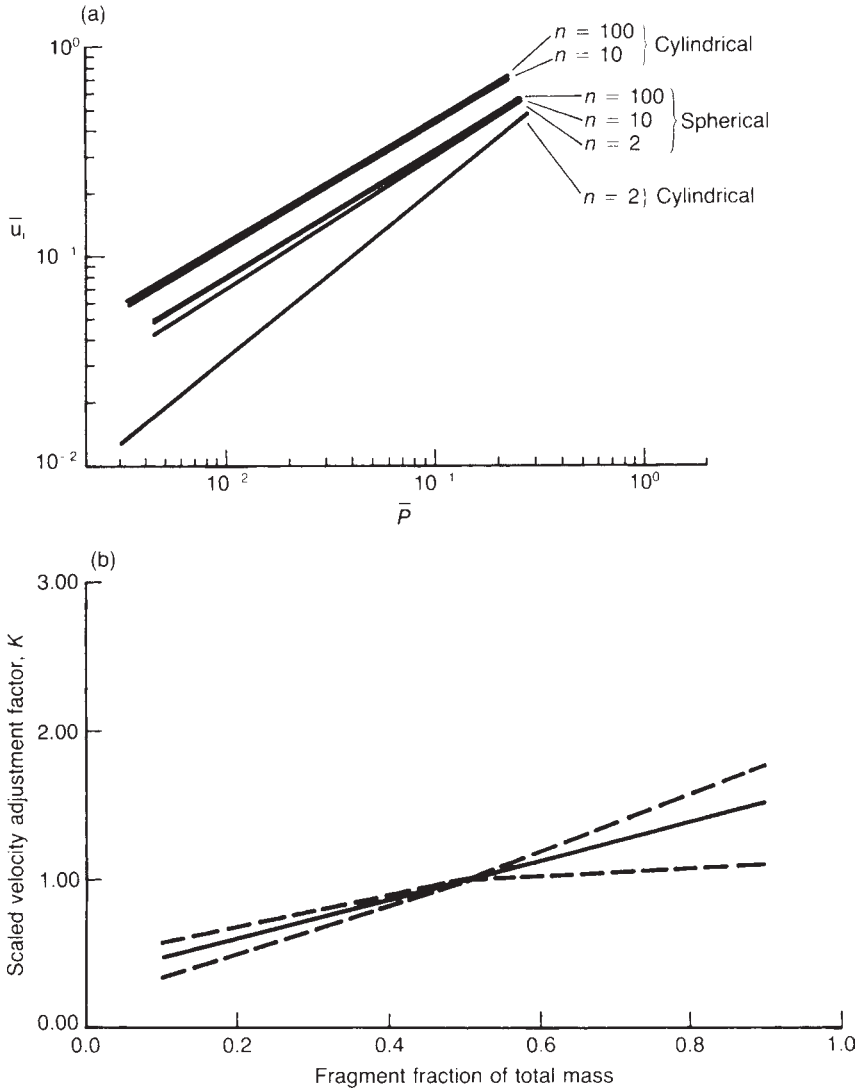

Figure 17.97 *Missile effects of explosions – initial velocity of fragments from a bursting vessel (W.E. Baker et al., 1983): (a) initial velocity correlation and (b) velocity adjustment factor for unequal masses (Courtesy of Elsevier Science Publishers)*

This is a relatively well-defined situation, and modelling based on fluid mechanics is appropriate. Models have been developed by a number of workers, including Cottrell and Savolainen (1965), Gwaltney (1968) and Ardron, Baum and Lee (1977).

The usual approach is based on momentum transfer. The momentum of the jet is assumed to be transferred to the missile and the residual momentum of the jet is neglected.

Gwaltney (1968) has given a number of simple analytical methods for particular cases of ejection of fittings by a jet of gas.

Ejection of a small fragment from a cylindrical vessel is one of the cases treated by Baum as described in the previous section. For this case he gives

$$u_i = 2a_o\left(\frac{F_S}{r}\right)^{0.38} \qquad s < 0.3r;\ \gamma = 1.4;\ 20 < P_1/P_o < 300 \qquad [17.34.17]$$

where s is the dimension of the fragment.

17.34.14 Initial velocity of missiles: comparison of methods

The comparison of methods made by Ardron, Baum and Lee (1977) has already been mentioned. Another more

recent comparative study is that of Baum (1984). This is discussed and extended by the CCPS (1994/15).

The following are some of the findings of the CCPS comparative study.

In comparing models, use is made of the scaled energy, which is defined as

$$E = \left(\frac{2E_{ex}}{Ma_o^2}\right)^{1/2} \quad [17.34.18]$$

where E is the scaled energy, E_{ex} is the energy released in the explosion and M is the mass of the vessel.

An upper limit to the initial velocity of the fragments is set by the case of a hypothetical massless fragment for which the velocity is the maximum velocity of the expanding gas, or peak contact surface velocity. This velocity is a function of the pressure ratio P_1/P_o.

Differences between models tend to become significant for small values of the scaled energy.

The Moore model, which is based on high explosion energies, whilst tending to give an upper limit value, nevertheless compares quite favourably with other models for both low and high energies.

In the lower energy range the CCPS discusses the relative merits of the models of Baum and Baker *et al.* For certain specific comparisons Baum's model yielded higher velocities for spheres but lower ones for cylinders.

17.34.15 Angle of departure of missiles

In order to determine the flight of a missile it is necessary also to have information on the angle of departure. The extent to which this is known depends on the particular case. For ejection of a fitting, the direction of the gas jet and, hence, the angle of departure of the fitting is usually defined. Likewise, this will generally be so for the two parts in the separation and rocketing of a gas filled vessel.

The angles of departure in the case of the bursting of a gas filled vessel into a large number of fragments are less well defined. The common assumption is that the fragments are projected uniformly in all directions. Alternatively, the more conservative approach may be adopted in which the spatial density of the fragment is assumed to be greater in the direction of the vulnerable targets.

For some methods the results for an individual fragment can be sensitive to the angle of departure. The CCPS (1994/15) report this to be the case for the model of rocketing fragments.

17.34.16 Shape and air resistance of missiles

The behaviour of the fragment in flight depends on its shape. Some fragments are chunky, with dimensions similar along the three main axes, while others are less symmetrical, with dissimilar lengths along these axes.

A fragment in flight is acted on by a lift force normal to the trajectory and a drag force along the trajectory. These forces are defined in Equations 17.34.47 and 17.34.48 below in terms of a lift coefficient C_L and a drag coefficient C_D.

In ballistic terms a fragment may be characterized as a drag-type fragment if it is chunky so that for any orientation $C_D \gg C_L$ and as a lifting type fragment if it is such that for some orientation $C_L \geq C_D$.

The force resisting the flight of the missile is a function of its velocity, but the relationship is not a simple one. The velocity range of interest for projectiles is termed the ballistic range. At very low velocities, below the ballistic range, the resistance is proportional to the velocity. At ballistic but subsonic velocities the resistance is proportional to the square of the velocity. At supersonic velocities the resistance is a complex function.

17.34.17 Flight of missiles

The flight of a projectile is a standard problem in mechanics and is treated in texts on this topic (e.g. Synge and Griffiths, 1960; R.C. Smith and Smith, 1968; B. Brown, 1969).

Three cases are considered here: case 1, no air resistance, case 2, air resistance proportional to the velocity and case 3, air resistance proportional to the square of the velocity. The first case is not realistic and results in gross overestimates of velocity and range, but provides a useful illustration of the general approach. The third case is realistic for ballistic velocities in the subsonic range.

Considering first the flight of a projectile in the absence of air resistance (case 1), the equations of motion are

$$\frac{d^2x}{dt^2} = 0 \quad [17.34.19]$$

$$\frac{d^2y}{dt^2} + g = 0 \quad [17.34.20]$$

where g is the acceleration due to gravity, t is the time and x and y are the distances in the horizontal and vertical directions, respectively.

Since there is no horizontal component of acceleration, in the x direction, both at $t = 0$ and subsequently

$$\frac{dx}{dt} = u_i \cos \alpha \quad [17.34.21]$$

where u is the velocity along the line of flight, α is the angle of departure and the subscript i denotes initial. Integrating with initial conditions $t = 0$, $x = 0$

$$x = u_i(\cos \alpha)t \quad [17.34.22]$$

In the y direction, at $t = 0$

$$\frac{dy}{dt} = u_i \sin \alpha \quad [17.34.23]$$

Integrating Equation 17.34.20 with initial conditions $t = 0$, $dy/dt = u_i \sin\alpha$

$$\frac{dy}{dt} = u_i(\sin \alpha) - gt \quad [17.34.24]$$

Integrating again with initial conditions $t = 0$, $y = 0$

$$y = u_i(\sin \alpha)t - \frac{1}{2}gt^2 \quad [17.34.25]$$

For t from Equation 17.34.22

$$t = \frac{x}{u_i \cos \alpha} \quad [17.34.26]$$

For the relation between x and y, eliminating t from Equations 17.34.22 and 17.34.25

$$y = x \tan \alpha - \frac{gx^2}{u_i^2 \cos^2 \alpha} \quad [17.34.27]$$

For the distance travelled, or range, setting $y = 0$ in Equation 17.34.27

$$x = \frac{2u_i^2 \cos \alpha \sin \alpha}{g} \quad [17.34.28]$$

For the velocity u

$$u = \left[\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2\right]^{1/2} \quad [17.34.29]$$

Then, from Equations 17.34.21, 17.34.24 and

$$u = \left[u_i^2 - 2u_i(\sin \alpha)gt + g^2t^2\right]^{1/2} \quad [17.34.30]$$

For the angle of approach to earth, or angle of return, β noting that

$$\tan \beta = \frac{dy}{dx} = \frac{dy}{dt}\frac{dt}{dx} \quad [17.34.31]$$

from Equations 17.34.21 and 17.34.24

$$\tan \beta = \tan \alpha - \frac{gt}{u_i \cos \alpha} \quad [17.34.32]$$

For the time of return to earth from Equation 17.34.25 with $y = 0$

$$t_r = \frac{2u_i \sin \alpha}{g} \quad [17.34.33]$$

Note that return to earth distance is the horizontal velocity times the time in flight.

The maximum range, which occurs at a projection angle of 45°, is

$$x_r = t_r u_i \cos \alpha \quad [17.34.34]$$

For the angle of approach β at the point of return to earth, or angle of return, from Equations 17.34.32 and 17.34.34 $\tan \beta = -\tan \alpha$. For the velocity at return to earth from Equations 17.34.30 and 17.34.34 $u = u_i$.

For a projectile subject to a resistance k proportional to the velocity (case 2), the equations of motion are

$$\frac{d^2x}{dt^2} + k\frac{dx}{dr} = 0 \quad [17.34.35]$$

$$\frac{d^2y}{dt^2} + k\frac{dy}{dt} + g = 0 \quad [17.34.36]$$

Following an approach similar to that for the first model, it can be shown that

$$\frac{dx}{dt} = u_i \cos \alpha \exp(-kt) \quad [17.34.37]$$

$$\frac{dy}{dt} = \frac{1}{k}(ku_i \sin \alpha + g)\exp(-kt) - \frac{g}{k} \quad [17.34.38]$$

$$x = \frac{u_i \cos \alpha}{k}[1 - \exp(-kt)] \quad [17.34.39]$$

$$y = \left(\frac{u_i}{k}\sin \alpha + \frac{g}{k}\right)[1 - \exp(-kt)] - \frac{gt}{k} \quad [17.34.40]$$

For a projectile subject to a resistance proportional to the square of the velocity (case 3), the equations of motion are

$$\frac{d^2x}{dt^2} + k\left(\frac{dx}{dt}\right)^2 = 0 \quad [17.34.41]$$

$$\frac{d^2y}{dt^2} + k\left(\frac{dy}{dt}\right)^2 + g = 0 \quad [17.34.42]$$

Beyond this point, the attempt to apply to cases 2 and 3 the treatment used for case 1 becomes increasingly intractable.

However, there is an alternative approach which for case 3 yields much simpler results. This involves working in terms not of the velocity u along the flight path but of the velocity v relative to the ground. The relation between the two initial velocities is

$$v_i = u_i \cos \alpha \quad [17.34.43]$$

The relevant equation of motion is

$$\frac{dv}{dx} + kv = 0 \quad [17.34.44]$$

which is obtained from Equation 17.34.41 utilizing $dx/dt = v$. Integrating with initial conditions

$$\begin{aligned} &x = 0, \quad v = v_i \\ &v = v_i \quad \exp(-kx) \end{aligned} \quad [17.34.45]$$

An empirical formula which allows for air drag quoted by V.J. Clancey (1972b) is

$$v = v_i \exp(-kc_d x/m^{1/3}) \quad [17.34.46]$$

with

$k = 0.002$ velocity supersonic
$= 0.0014$ velocity subsonic

where c_d is the drag coefficient, v is the velocity of the projectile (ft/s), v_i is the initial velocity of the projectile (ft/s),

m is the mass of the projectile (oz), x is the distance travelled by the projectile (ft) and k is a constant. The drag coefficient c_d is a function of fragment shape but is generally approximately 1.5–2.

Equation 17.34.46 is of the same form as Equation 17.34.45. It also appears to be related to the equations for the flight of fragments from exploding weapons given by Christopherson and quoted in Section 17.36.

17.34.18 Range of missiles

The range of a missile in the absence of air drag is given by Equation 17.34.28 and the maximum value of that range for an angle of departure of 45° by Equation 17.34.34.

However, these relations greatly overstate the actual ranges obtained. For example, using the initial velocities from TNT charges given by V.J. Clancey (1972b) as quoted in Section 17.36, ranges of 5×10^5 ft and upwards are obtained. Therefore, it is clearly necessary to take air drag into account.

Clancey also gives a relation for the maximum horizontal range of fragments from a cased charge of TNT on the ground surface as shown in Figure 17.98. The correlation is based on experimental determination with TNT in lightweight containers. Most of the fragments do not travel the maximum distance, but fall at distances between 0.3 and 0.8 of the maximum.

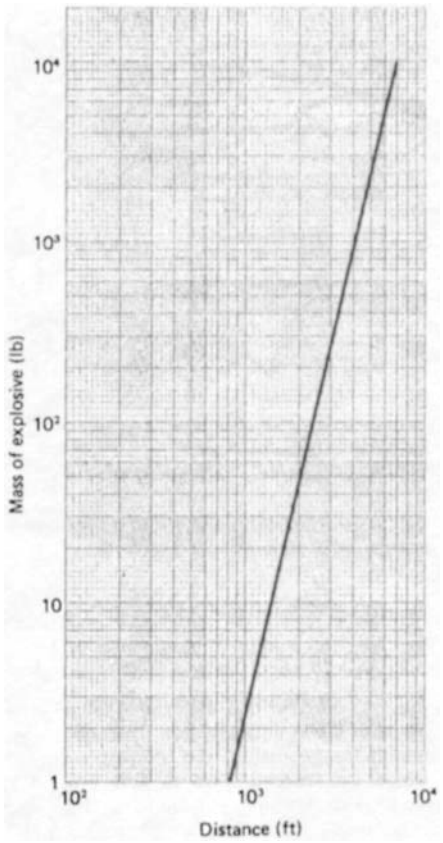

Figure 17.98 *Missile effects of explosions: maximum horizontal range of fragments from a cased charge of TNT on the ground surface (V.J. Clancey, 1972b)*

The probability that there would be at least one fragment which travels the maximum distance increases with the number of fragments and is therefore greater for a large explosion.

As stated above, a fragment in flight is acted on by a lift force, which is normal to the trajectory and opposes gravity, and a drag force, which is along the trajectory. These forces are

$$F_L = C_L A_L \frac{\rho u^2}{2} \qquad [17.34.47]$$

$$F_D = C_D A_D \frac{\rho u^2}{2} \qquad [17.34.48]$$

where A_D is the drag area, A_L is the lift area, C_D is the drag coefficient, C_L is the lift coefficient, F_D is the drag force, F_L is the lift force, u is the velocity of the fragment and ρ is the density of air.

A fundamental approach to the estimation of fragment range has been developed by W.E. Baker *et al.* (1975, 1978) and is described by W.E. Baker *et al.* (1983). The range is obtained by solving the equations of motion for acceleration of the fragment in the horizontal and vertical directions, utilizing for the drag and lift forces Equations 17.34.47 and 17.34.48. The results are correlated in terms of the dimensionless $\bar{u}_i$, velocity defined as

$$\bar{u}_i = \frac{C_D A_D \rho_o u_o^2}{Mg} \qquad [17.34.49]$$

and the dimensionless range $\bar{R}$

$$\bar{R} = \frac{C_D A_D \rho_o R}{M} \qquad [17.34.50]$$

and the lift/drag ratio

$$= \frac{C_L A_L}{C_D A_D} \qquad [17.34.51]$$

where g is the acceleration due to gravity, M is the mass of the fragment, R is its range, u_o is its initial velocity and ρ_o is the density of air. The treatment is based on the assumption that the fragment is spinning and applies to fragment velocities up to Mach 1 or about 340 m/s. The equations were solved using the computer code FRISB.

The correlation obtained is shown in Figure 17.99. For values of the lift/drag ratio not given, interpolation can be used, but it becomes inaccurate on the steep portions of the curve.

Many fragments from explosions are chunky and have a lift coefficient C_L, and hence a lift/drag ratio, of 0. Other fragments may be pieces of plate for which the lift/drag ratio is more complex. A method of estimating the lift/drag ratio for these latter is given in appendix E of W.E. Baker et al. (1983).

Data on missile flight are available in many descriptions of accidental explosions. Jacobs *et al.* (1973) state that in the explosion at the American Oil Company refinery at Whiting, Indiana (Case History A22):

> The vessel fragments were scattered for several hundred feet away from the unit site. One 60-t piece landed on a tank of gasoline, smashing it severely and igniting and scattering its contents.

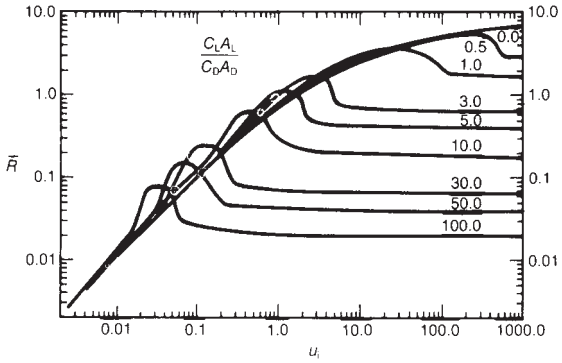

Figure 17.99 *Missile effects of explosions: distance travelled by missiles (W.E. Baker et al., 1983) (Courtesy of Elsevier Science Publishers)*

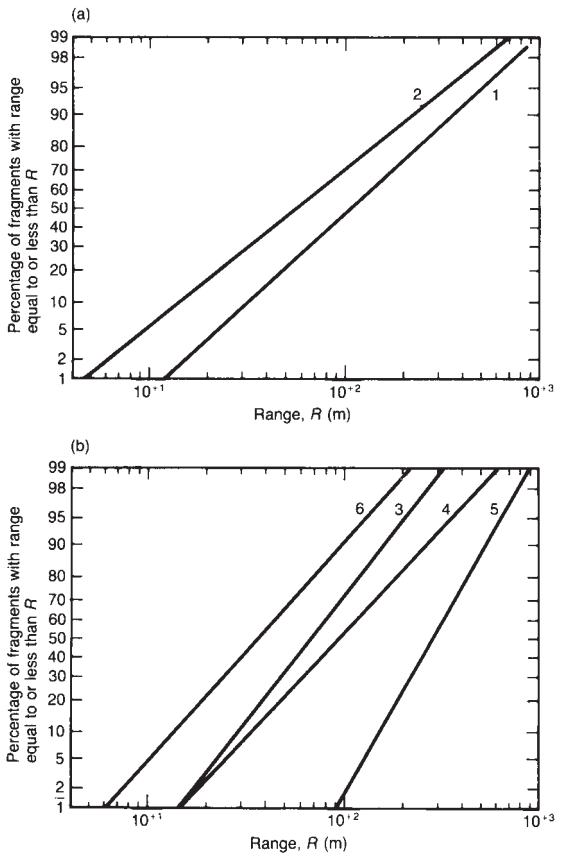

Figure 17.100 *Missile effects of explosions: fragment range distribution from some accidental event (W.E. Baker et al., 1978): (a) event groups 1 and 2 and (b) events groups 3–6*

The investigation of the explosion at the Dow Chemical Company's works at King's Lynn by the HSE (1977b) gives a map of the fragments from the explosion (Case History A81). In one ship explosion investigated by V.J. Clancey (1976b) a deck cover of 400 t was thrown 100 ft.

The study of accidental explosions by W.E. Baker *et al.* (1978) referred to in Section 17.34.4 and tabulated in Table 17.50 also yielded data on fragment range. The graphs of fragment range for the different event groups are shown in Figure 17.100.

An absorber column exploded from a hydrogen-rich fuel and air mixture that skattered 16 large fragments. The energy of the explosion was evaluated by three alternative methods by Woodward and Ketchum (2001). Fragment range analysis, using Figure 17.99, gave 30–83 kg TNT equivalence. Modelling the fuel combustion energy gave 78–96 kg TNT equivalence. Window breakage analyses gave 37 kg TNT equivalence.

17.34.19 Missiles from BLEVEs

A particular type of explosion which is prone to generate missiles is the BLEVE. A study of missiles from BLEVEs has been described by Holden and Reeves (1985).

Much of the information obtained in the work relates to vessels used in transport, but no reason was seen why it should not apply to fixed plant also. A distinction is made between cylindrical and spherical vessels, which are treated separately. For cylindrical vessels information was obtained on (1) probability of fragment generation, (2) number of fragments, (3) range of fragments, and (4) direction of fragments, and for spherical vessels on the last three features.

For cylindrical vessels there were 113 events involving fire on which sufficient information was available and of these 89 involved fragment generation. The probability of fragment generation was estimated from this as 0.8.

The number of fragments generated by a cylindrical vessel was obtained for 27 events involving LPG vessels and ranged from one to four. The number of events generating one, two, three and four fragments were 8, 7, 10 and 4, respectively. This excluded a fire engulfment test at White Sands reported by C. Anderson and Morris (1974), in which 10 fragments were generated and which appears to be anomalous in comparison with the accident data.

The range of fragments was taken as the ultimate end point after landing and travelling across the ground, through structures, etc. The range for fragments from LPG vessels is shown in Figure 17.101. Figure 17.101(a) gives the range for all events together with a comparison with data from an earlier study by W.E. Baker *et al.* (1978). Figure 17.101(b) shows the effect of vessel size and Figure 17.101(c) the difference between end tub fragments and other fragments. There is a clear tendency for fragments from vessels with a capacity $<90 m^3$ and for end tubs to travel further. Figure 17.101(d) gives the range for fragments from spherical vessels. A further graph is given for the range of fragments from vessels containing ammonia, ethylene oxide and vinyl chloride.

The authors comment that the ranges found tend to be much less than those obtained from theoretical estimates of maximum range using the corresponding launch angle, which can exceed 3 km to first ground impact, that launch angle is important, and that their empirical data include implicit allowance for factors such as launch angle, inventory, etc.

With regard to direction of fragments from cylindrical vessels, for some 11 incidents involving 15 vessels,

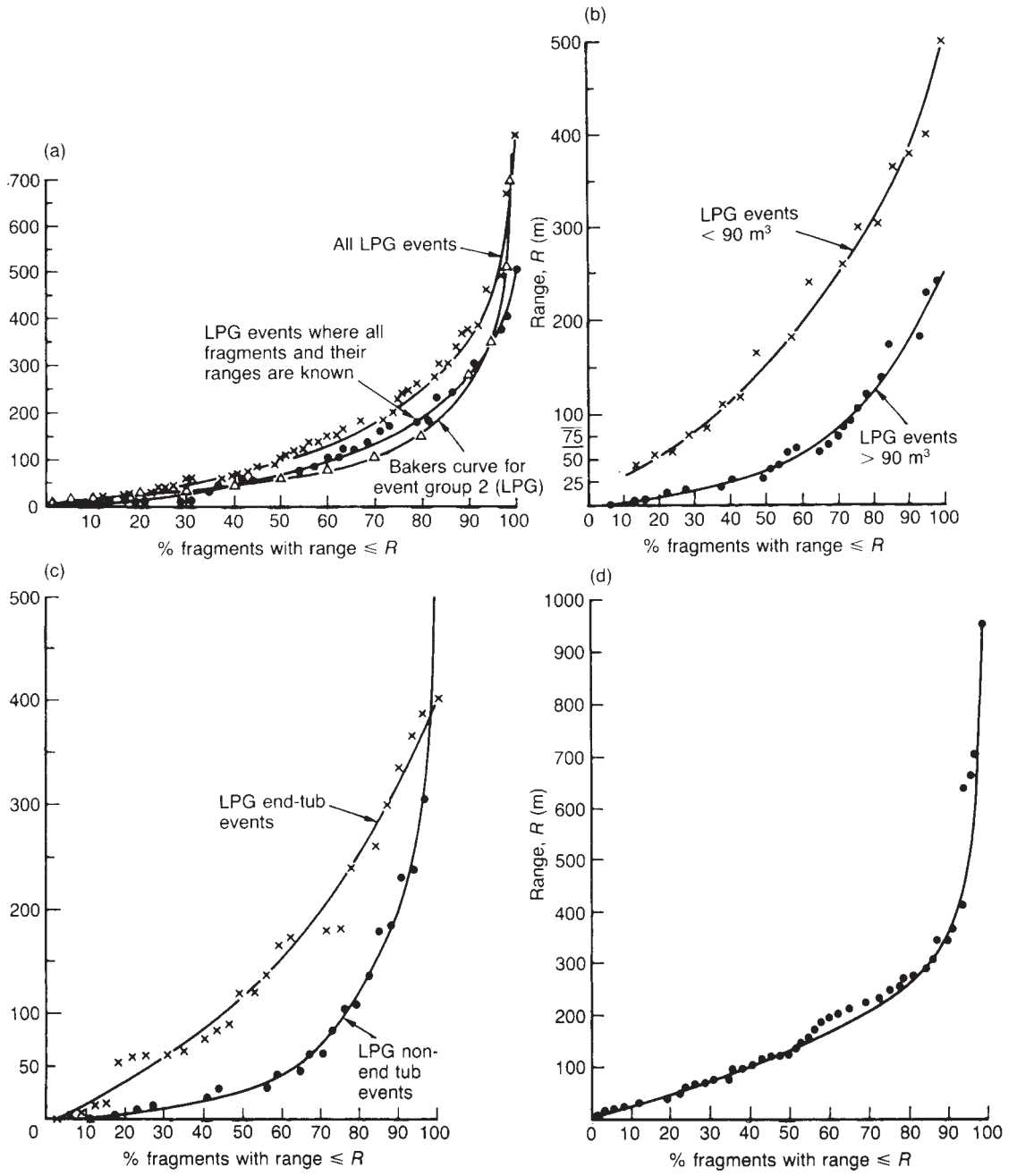

Figure 17.101 *Missile effects of explosions: distance travelled by missiles from bursting of LPG vessels (Holden and Reeves, 1985): (a) all events; (b) effect of vessel size; (c) end tub and other fragments and (d) spherical vessels (BLEVEs) (Courtesy of the Institution of Chemical Engineers)*

mainly LPG, about half the fragments were projected into about a third of the total area, in arcs of 30° to either side of the vessel front and rear axial directions. The correlation given for LPG vessel fragments is shown in Figure 17.102.

For spherical vessels the sample of events was only seven. The number of fragments generated in these vents was 3, 4, 5, 5, 6, 16 and 19, giving an average of 8.3 fragments per event. This number is appreciably higher than for cylindrical vessels.

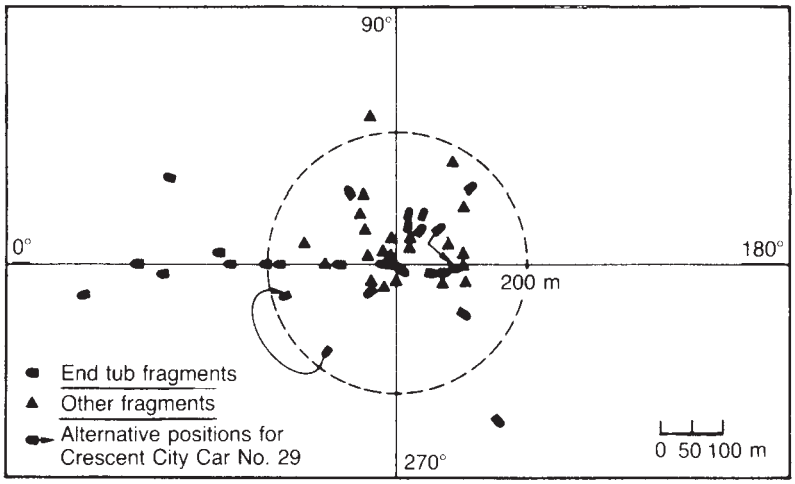

Figure 17.102 *Missile effects of explosions: direction of travel of missiles bursting of LPG vessels (Holden and Reeves, 1985) (Courtesy of the Institution of Chemical Engineers)*

Figure 17.101(d) shows that the range of the fragments from spherical vessels is marginally higher than for cylindrical vessels.

Fragments from spherical vessels tend to be projected in a non-uniform distribution of directions. Taking the favoured direction in each incident and treating this as an arbitrary 0° and then overlaying the plots for the individual incidents to give an overall plot divided into 30° sectors, it was found that a fragment is 17 times more likely to be projected in the favoured direction than in the least favoured.

The authors describe a number of incidents where fragments from BLEVEs have caused damage or injury. At Crescent City a propane rail tank car exploded, generating two main fragments, one of which punctured the head of another such tank and the other sheared the housing and valves off a third tank (Case History A50).

Similarly, at Laurel a fragment from the BLEVE of a tank car pierced another propane tank car (Case History A44). Escalation may also occur by disablement of other equipment. At Laurel a fragment from one of the rail tank cars hit a pumphouse and cut an 8 in. water main, reducing the fire water pressure. At Puebla, Mexico, in 1977 a fragment from the BLEVE of a vinyl chloride storage sphere hit the main site water tank and carried it across the perimeter fence (Case History A87). At Texas City in 1978 a fragment from the BLEVE of an LPG sphere travelled 210 m and hit the site fire water tank.

Fragments from BLEVEs are also a cause of injury. In the LPG road tanker BLEVE at Deer Lake, Pennsylvania, in 1959 it was a rocketing fragment which was responsible for most of the 11 dead and 10 injured. These bystanders were at a distance of more than 200 m and beyond the range of thermal hazard in that case. At West St. Paul, Minnesota, in 1974 fragments from the BLEVE of an LPG storage vessel were held responsible for the deaths of three fire fighters and a bystander.

A further study of missiles from BLEVEs is that of Pietersen (1985), who investigated the disaster at Mexico City, Mexico, in 1984, described in Appendix 4. For 44 cylindrical bullet tanks he found that 4 were still on their supports and a further 11 still in their original bund, and that of the remaining 29, the distribution of bullets and end tubs was as follows:

Distance (m)	*No. of fragments from bullets*	*No. of fragments from end tubs*
<100	17	3
100–200	4	4
200–300	3	3
300–400	2	2
400–700	1	1
700–1000	1	1
1000–1200	1	1
Total	29	15

For the spheres, 25 major fragments were collected lying as follows: six within 100 m, six between 100 and 200 m, seven between 200 and 300 m, one between 300 and 400 m, three between 400 and 500 m, one between 500 and 590 m and one at 590 m.

Pietersen discusses the mechanism of rocketing of part of a cylindrical bullet. He takes as the energy transferred to the missiles 60% of the total available energy of a gas filled vessel as given by the Erode equation and then utilizes a relation equivalent to Equation 17.34.1. On this basis he obtains for the larger vessels on the site

Vessel volume (m^3)	*Vessel mass* (kg)	*Initial velocity of missile* (m/s)
270	70	149
1600	215	206
2400	300	214

which gives maximum velocities of about 150 m/s for cylinders and 200 m/s for spheres. He also quotes a velocity of 60 m/s for the vapour of the LPG in the cylinder undergoing flash vaporization. He states that calculations based on these figures indicate that without lift the maximum range of the fragment is of the order of 360 m, though the figure is not very accurate. It is sufficient to show, however, that lift must play a significant role.

17.34.20 CCPS method

The CCPS *Fire and Explosion Model Guidelines* (1994/15) include as part of the treatment for BLEVEs a method for fragments.

The method used for the estimation of the energy of explosion used has been described in Section 17.27.

For the number of fragments the value of the scaled energy given by Equation 17.34.18 is used to discriminate between the case where the fragments are few and that where they are numerous. The region where the scaled energy lies between 0.1 and 0.4 is one where the number of fragments generated tends to be small.

Use is also made of Baker's event groups as described in Section 17.34.4. An event group is selected which approximates the case in hand, and the event group data are then used to obtain an estimate of the expected number of fragments and of their mass distribution.

For the initial velocity of the fragments three methods are given. Method 1 is to obtain the energy of explosion using the methods given in Section 17.34.9 and to apply to it a factor of 0.2 to obtain the kinetic energy available to the fragments and then to assume this is distributed equally among the fragments as in Equation 17.34.1. Method 2 is that of Baker *et al.* outlined in Section 17.34.11. Method 3 is that of Moore, which is given here as Equation 17.34.3. The choice of method to use is governed by the scaled energy relation 17.34.18.

For the range distribution of the fragments use is made of the method of Baker *et al.* which is described in Section 17.34.18.

Ranges may also be estimated using the event group data.

17.34.21 Missile damage method of Scilly and Crowther

A method for assessment of the risk of missile impact on a process plant site has been described by Scilly and Crowther (1992).

These authors give data on the fragments generated in eight incidents, as shown in Table 17.51.

The method which they describe involves for a given target estimation of the following features: (1) the number of fragments, (2) the range distribution, (3) the mass distribution, (4) the orientation factor, (5) the effective range interval, and (6) the probability of a strike.

They illustrate the method by reference to the case of a distillation column 50 m high, 2.4 m in diameter and 12.5 mm thick subject to a sudden pressure increase due to a rapid decomposition.

In general, the number N of fragments depends on a variety of factors, including the vessel size and shape, the material of construction, the operating temperature and the rate of pressure rise. The authors obtain the estimate of the number of fragments N by inspection of Table 17.51. For their illustrative example they take N as 35.

As already described, the distribution of fragments may exhibit directionality. The authors suggest there is some justification for allowing for this by the use of a correction factor of 2, applied to N.

For the distribution of the ranges of the fragments, they utilize not the fragment with maximum range R_{max} but that with the next farthest range, or penultimate range, R_{pen}, arguing that the latter is more meaningful. The range distribution is found to be log-normal, and is fitted by the authors using a probit equation. They give the following tentative relations:

$$R_{med} = 2.8P_v \qquad [17.34.52]$$

$$R_{pen} = 4.1R_{med} \qquad [17.34.53]$$

where P_v is the vessel pressure (barg), R_{med} is the median range (m) and R_{pen} is the range of the penultimate fragment (m). A probit equation for the probability P of a fragment falling at a range R may then be constructed from the pair of points ($P = 0.5$, R_{med}) and ($P = N_{pen}/N$, R_{pen}), where $N_{pen} = N - 1$.

Given that for vessels of size exceeding 20 m^3 the great majority of fragments will have energy sufficient to penetrate steel containments, which are unlikely to have a wall thickness greater than 15 mm, the distribution of mass is much less important. However, for the case where it is desired to estimate the mass distribution for vessels of such size, the authors propose that the median mass of the fragments be taken as that of the vessel divided by 73 and that the slope of the associated probit equation be taken as 1.5.

The orientation factor F_{or} is

$$F_{or} \approx \frac{W}{2\pi R} \qquad [17.34.54]$$

where R is the range of the fragment (m) and W is the combined width of the target and the fragment (m). The width of a fragment is taken in the illustrative example as 4 m.

The target is vulnerable to any fragment falling between a minimum range R and a maximum range $R + L$, where L may be termed the effective range interval. For a target consisting of a sphere supported on legs the authors derive by geometry for fragments directed, respectively, at the midpoint and at the edge of the sphere

$$L = (H - r + r\ \sec\theta)\ \tan\theta + r \quad \text{sphere midpoint} \qquad [17.34.55]$$

$$= (H - r)\tan\theta + r \quad \text{sphere edge} \qquad [17.34.56]$$

where H is the height of the top of the sphere (m), L is the effective range interval (m), r is the radius of the sphere (m) and θ is the angle of descent (°). For the angle of descent the authors suggest 45° as a conservative value. They use 60° in their illustrative example.

The probability P_{ri} that a fragment falls within the effective range interval L is then determined from the probit equation for the range distribution by taking the difference between the probabilities of a fragment reaching $R + L$ and of one reaching R.

The probability of a strike P_{st} is then

$$P_{st} = F_{or}NP_{ri} \qquad [17.34.57]$$

As already stated, the authors effectively take as unity the probability of puncture of the target given a strike.

For an explosion in the vessel used to illustrate the method, described above, and for a target consisting of a

Table 17.51 *Behaviour of fragments in some vessel explosions – 2 (after Scilly and Crowther, 1992) (courtesy American Institute of Chemical Engineers)*

Incident[a]	*Vessel details*			*Vessel pressure*		*No. of fragments*	*Missile range*			*Missile mass*		
	Diameter (m)	*Volume* (m^3)	*Thickness* (mm)	*Operating* (barg)	*Burst* (barg)		*Median*	*Penultimate/ median* (m)	*Probit slope*	*Median*	*Vessel/ median* (kg)	*Probit slope*
1a	3.1	90		16	75–85	29	94	4.4	1.60			
1b	7.2	1560	63	16	75–85	14	95	3.7	1.03	16,900	27	1.95
2	1.7	210	38	9	155	3						
3	2.7	57	13	0	63	10	156	3.4	1.87	170	52	1.92
4	2.3	200/53[b]	16	3	60	≥50						
5	3.0	73	19	8	50	21	117	4.8	1.20	173	100	1.10
6	2.5	162	12, 16, 19	3	32[c]	35	140	4.0	2.46	539	67	1.63
7	0.94	1.3	6.5	−1	34	24	14	11.4	3.60	4	77	1.21

[a] Incidents are as follows: 1a and 1b, separator and reactor respectively, at Whiting, Indiana, 1957 – fuel/air combustion probably leading to detonation; 2, Ponca City, 1959 – probable fuel/air combustion; 3, Doe Run, 1962 – probable liquid phase polymerization and gas phase decomposition of ethylene oxide; 4, Texas City, 1969 – liquid phase decomposition of vinyl acetylene; 5, Grangemouth, 1987 – breakthrough of high pressure (155 bar) gas; 6, Antwerp, 1987 – decomposition of ethylene oxide during distillation; 7, Wendstone Chemicals, 1988 – liquid phase decomposition of *o*-nitrobenzaldehyde containing nitrate esters.

[b] Distillation column had a volume of 200 m^3, but only the central section of volume 53 m^3 disintegrated.

[c] Authors suggest that this value is understand and that it should be at least 43 barg.

sphere 12 m in diameter supported on 3 m legs at 150 m distance from the exploding vessel, the authors obtain a calculated burst pressure $P_v = 45$ barg, a number of fragments $N = 35$, a range of fall between 150 and 199 m, the range probit $Y = -1.44 + 3.066 \log_{10} R$, a probability that a fragment falls within the effective range interval of 0.14, an orientation factor $F_{or} = 0.016$, and a probability of strike $P_{st} = 0.08$.

17.34.22 Flying glass

Glass fragments from the breaking of windows are significant for injury of personnel. This effect is considered in Section 17.40.

17.34.23 Falling masonry and glass

Another form of missile which is relevant particularly to an explosion in a built-up area is falling masonry and glass.

A model for this hazard is included in the set of submodels in the model for a condensed phase explosion in a built-up area given by Gilbert, Lees and Scilly (1994h). A person in the street near a building is vulnerable to falling masonry and glass. The extent of the hazard from these two sources will vary. The relative importance of falling glass may be expected to rise where the buildings in question are large city skyscrapers.

Casualties occurred from falling masonry in air raids, but the interpretation of such data needs to take account of the fact that in many cases the weapons exploded inside buildings.

The model tentatively proposed by Gilbert, Lees and Scilly (1994h) for the estimation of the risk from falling masonry and glass is as follows. The approach used is to designate a band of specified width on the pavement beside the building and to assume that persons in this band do not survive. The width of the band is intended to allow both for the density and size distribution of falling debris within a wider band and for the probability of a fatality given a hit. The default value used for the width of the band is 1 m. This value is for use where the height of the building does not exceed 15 m.

17.34.24 Crater ejecta

Some explosions create a crater and in this case fragments are ejected. Craters have been treated in Section 17.31. The account here is confined to the crater ejecta.

A treatment of the fragments from cratering has been given by Richmond and Fletcher (1971). These authors base their work on data given by Henny and Carlson (1968) for crater ejecta from explosions in rock and in soil. The charges were half buried in the ground. The missiles considered are those with a mass exceeding 0.5 lb.

For the maximum range of fragments Richmond and Fletcher give the following equations:

$$R_{max} = 70W^{0.4} \quad \text{rock} \qquad [17.34.58a]$$

$$= 30W^{0.4} \quad \text{soil} \qquad [17.34.58b]$$

where R is the range (ft) and W is the mass of explosive (lb) (of TNT equivalent) and the subscript max denotes maximum.

The probability P of being struck by one or more such missiles is

$$P = 1 - \exp(-a/A) \qquad [17.34.59]$$

where a is the projected area of the body (ft^2) and A is the specific area, or surface hemispherical area per missile (ft^2/missile). The projected area a is taken as 6.2 ft^2.

The authors deal primarily with fragments from cratering in rock and consider particularly the conditions for 50 and 1% probability of being struck. The fragment specific areas at these levels of probability are 9 and 600 ft^2/fragment, respectively.

For cratering of rock the authors give a graph showing curves for the 50 and 1% probability of being hit as a function of mass of explosive and distance, but give no guidance on obtaining other values. However, their data may be correlated approximately by the following relations:

$$A = \frac{A_h}{n_e} \qquad [17.34.60]$$

with

$$n_e = \phi_n n m \qquad [17.34.61]$$

$$\phi_n = 1, \quad R < 200 \qquad [17.34.62]$$

$$\phi_n = 3.46 - 0.466 \ln R, \quad 200 \le R \le 900 \qquad [17.34.63]$$

where A_h is the area of the hemisphere on the surface of which the human target is standing (ft^2), m is the mass of explosive (tons), n is the near field number of missiles per ton of explosive (missiles/t), n_e is the number of missiles at distance R (missiles/t), R is the distance (ft) and ϕ_n is a correction factor which allows for the reduction in the number of missiles with distance. The value of n is 230 missiles/t.

The authors state that the average mass of the missiles is well above 0.5 lb and argue that the probability of serious injury given a hit is likely to be high.

The application of this work to the cratering caused by an explosive load in a street has been discussed by Gilbert, Lees and Scilly (1994h). From an analysis of the crater in the Peterborough explosion (HSE, 1990c), which involved an explosive load equivalent to some 800 kg of TNT on a vehicle in a built-up area, they conclude that it is probably not necessary to make any correction for the height of the load above ground or for the nature of the ground, but suggest that some correction seems appropriate for the fact that in the experimental work described the charges were half buried and suggest a reduction in the near field number n of fragments from 230 to 150 missiles/t.

17.34.25 Impact effects

There are available a number of empirical equations for estimating the penetration of fragments in various types of target. However, it is pointed out by W.G. High (1980) that most of these relations are for fragments from high energy density sources, where the sources of interest in process plant, such as high pressure vessels, are of relatively low energy density.

It is convenient to quote first some of the empirical equations for determining fragment penetration given in the *High Pressure Safety Code* by E.G. Cox and Saville (1975),* which may be regarded as a coherent set selected by the authors for plant design purposes. Other individual

*Reproduced with permission of the High Pressure Technology Association.

formulae for penetration into reinforced concrete and into steel plate are given in Sections 17.34.26 and 17.34.27.

A treatment of the impact of missiles on pipework is given in Section 17.35.

The equations quoted in the *High Pressure Safety Code* assume penetration normal to the surface. They are valid for projectile velocities not exceeding 1000 m/s, above which there is often a quite different mechanism in which target and projectile are melted by the impact energy.

For penetration by small fragments, the depth of penetration is given by the relation

$$t = Km^{n_1} V^{n_2} \qquad [17.34.64]$$

where m is the mass of the fragment (kg), t is the thickness of the barricade needed just to stop the fragment (m), V is the velocity of the fragment (m/s), K is a constant and n_1 and n_2 are indices. The values of the constant K and the indices n_1 and n_2 for different target materials are:

	K	n_1	n_2
Concrete (crushing strength 35 MN/m^2	18×10^{-6}	0.4	1.5
Brickwork	23×10^{-6}	0.4	1.5
Mild steel	6×10^{-5}	0.33	1.0

Equation 17.34.64 is valid for compact blunt steel fragments such as solid cylinders with the length equal to the diameter with a mass of not more than 1 kg.

For penetration by larger fragments the depth of penetration may be calculated from

$$t = \frac{Cm}{A} \log_{10}(1 + 5 \times 10^{-5} V^2) \qquad [17.34.65]$$

where A is the presented area of the fragment (m^2) and C is a constant. The constant C has the following values:

	C
Concrete (unreinforced, crushing strength 15 MN/m^2)	10×10^{-4}
Concrete (1.4% reinforcement, crushing strength 40 MN/m^2)	3.5×10^{-4}
Brickwork	25×10^{-4}
Mild steel	0.5×10^{-4}
Alloy steel	0.3×10^{-4}

Equation 17.34.65 applies for large blunt fragments with a mass exceeding 1 kg.

For penetration by rod shaped missiles for concrete

$$t = 2 \times 10^{-7} \frac{mV^{1.5}}{d^{1.8}} \qquad [17.34.66]$$

and for mild steel plate

$$t = \left(0.33 \times 10^{-9} \frac{mV^2}{d^3}\right)^{1/1.41} \qquad [17.34.67]$$

where d is the diameter of the fragment (m).

Fragments of irregular shape, such as are usually produced by the bursting of a pressure vessel, have much lower penetrating power, often only half, than compact blunt fragments, while pointed projectiles have appreciably more.

Further relations for impact of fragments on various types of target have been given by W.E. Baker *et al.* (1983). They consider the following targets: (1) thin metal plates and sheets, (2) roofing materials, and (3) reinforced concrete. For the latter the treatment includes steel pipe, utility pole and rod missiles.

The impact relations given by these authors are correlated in terms of a non-dimensional projectile velocity, a non-dimensional target deflection and non-dimensional target thickness.

As the size of the projectile increases, the response of the target becomes more significant. Work by R.P. Kennedy (1976) has shown that the target response may be modelled by assuming it to be subject to a rectangular pulse forcing function. With this assumption it is then possible to apply conventional structural response techniques.

Another aspect of fragment impact on concrete targets is spalling and scabbing, and correlations are available for the threshold and for depth attained.

17.34.26 Impact effects: penetration of reinforced concrete

There has been a considerable amount of work on the penetration of reinforced concrete by missiles. Accounts are given by Chelapati, Kennedy and Wall (1972), R.P. Kennedy (1976), Barr *et al.* (1980), Porter (1980) and Tulacz and Smith (1980).

Some principal correlations are those of Petry (1910), the Army Corps of Engineers (ACE), the Ballistics Research Laboratory (BRL) and the National Defense Research Committee (NDRC) (1946). These correlations are given by Tulacz and Smith (1980).

Of these models, the modified NDRC correlation (NDRC, 1946) particularly appears to have found widespread acceptance. It is applicable to a flat-faced cylindrical missile. The equation is given in SI units by Barr *et al.* (1980) as follows:

$$G(x/d) = 2.74 \times 10^{-5} (\rho d^{0.2} / \sigma_c^{0.5}) \mu^{1.8} \qquad [17.34.68]$$

with

$$G(x/d) = (x/2d)^2, \qquad x/d \leq 2 \qquad [17.34.69]$$

$$G(x/d) = (x/d) - 1, \quad x/d > 2 \qquad [17.34.70]$$

$$\rho = m/d^3 \qquad [17.34.71]$$

where d is the diameter of the missile (m), ρ is its calibre density (kg/m^3), m is its mass (kg), μ is its velocity (m/s), x is the penetration depth (m) and σ_c is the compressive strength of concrete (Pa). The limits of applicability of Equation 17.34.68 are discussed by Gwaltney (1968) and Tulacz and Smith (1980).

Equation 17.34.68 is a penetration correlation. NDRC has also developed perforation formulae for use in conjunction with this equation. These are

$$\frac{e}{d} = 3.19\frac{x}{d} - 0.718\left(\frac{x}{d}\right)^2, \quad \frac{e}{d} < 3 \qquad [17.34.72]$$

$$\frac{e}{d} = 1.32 + 1.24\frac{x}{d}, \quad 3 \leq \frac{e}{d} \leq 18 \qquad [17.34.73]$$

where e is the perforation thickness (m). This is the thickness of target which the missile will just perforate. Another model for penetration by a flat-nosed cylinder, again based on extensive testing, is the Commissariat à 1'Energie Atomique/Electricite de France (CEA/EDF) formula, described by Berriaud *et al.* (1978) and discussed by Barr *et al.* (1980):

$$\mu_p^2 = 1.7\sigma_c\rho^{1/3}\left(\frac{de^2}{m}\right)^{1/3} \qquad [17.34.74]$$

where μ_p is the perforation velocity (m/s) and p is the density of the concrete (kg/m^3); the other symbols are as defined above.

The limits of applicability of Equation 17.34.74 are discussed by Berriaud and Barr *et al.*

A three-dimensional computer code, CRASH, for the investigation of impact effects on various types of target, including reinforced concrete and steel plate, has been described by Hopkirk, Lympany and Marti (1980).

17.34.27 Impact effects: penetration of steel plate

There has also been a good deal of work on the penetration by missiles of steel plate. Accounts are given by Neilson (1980) and Tulacz and Smith (1980).

Some principal correlations are those of Christopherson (1946), Stanford Research Institute (SRI), the Ballistics Research Laboratory (BRL) and the NDRC.

Of these models, that of SRI, described by R.W. White and Botsford (1963), appears to have found wide acceptance. It is given in SI units by Neilson as

$$\frac{E_c}{d} = \frac{S_u}{10.29}(42.7h^2 + wh) \qquad [17.34.75]$$

where d is the diameter of the missile (m), E_c is its critical impact energy (J), h is the thickness of the target panel (m), S_u is the ultimate tensile strength of the panel (Pa) and w is the width of the panel (m).

Equation 17.34.75 was derived originally for relatively long missiles striking thin panels (<7 mm thick). The limits of applicability and behaviour of the equation are discussed by Neilson and by Tulacz and Smith.

The latter also give the BRL and NDRC formulae and discuss the comparative behaviour of the three models.

Mention has already been made of the general impact computer code CRASH, which can be used for steel plates. Neilson also describes the use for this purpose of the codes EURDYN and CADROS.

17.34.28 Impact effects: impact on a storage sphere

A treatment of the impact of a fragment from a BLEVE on a storage sphere has been given by Pietersen (1985). The method involves calculating (1) the force at the point of impact to deform the sphere up to the yield point, and the corresponding energy E_y, and (2) the energy E_r to deform the sphere in the plastic region between yield and rupture. Utilizing relations given by Roark and Young (1975) and taking the impact area as five times the vessel wall thickness, these two energies are found to be $E_y = 7$ kJ and $E_r = 64$ kJ. Assuming that plastic deformation of the impacting fragment uses up an amount of energy equal to that used in the sphere itself the total energy required for rupture is 135 kJ. From simple kinetic energy considerations, for a fragment of mass 20 te (1/10th of a sphere) the velocity required to effect rupture is then 3.7 m/s and for one of 2 te (1/100th of a sphere) it is 11.6 m/s. This calculation indicates that the velocities to cause rupture are well below the initial velocities of fragments from a sphere undergoing BLEVE, which have been discussed above, and therefore that rupture of a sphere close by is to be expected.

17.34.29 Barricade design

In some cases use is made of barricades around a potential source of explosion. Barricades are utilized particularly in work with explosives, but may also be used around other potential explosion sources such as high pressure equipment. There is also considerable interest in barricades in the nuclear industry.

Accounts of the design of barricades include those given in the *High Pressure Safety Code* by E.G. Cox and Saville (1975) and by Loving (1957), W.G. High (1967) and C.V. Moore (1967).

The essential first step in design of a barricade is to determine the failures against which protection is required. In other words, it is necessary to start with hazard identification.

In barricade design, provision of protection against an explosion of flammable gas is generally treated as a special case. Excluding this, the design resolves into provision of a barricade which offers resistance to (1) blast and (2) fragments. Broadly, design against blast is often based on an equivalent static pressure approach and design against fragments on fragment penetration correlations.

Design methods for barricades to protect against vessel rupture are discussed in the *High Pressure Safety Code*. It is relatively easy to provide a barricade for vessels with energy contents in the range 10^3–10^5J, but it becomes progressively more difficult as the energy content rises, and for energy contents capable of giving a shock wave of 50×10^6 to 100×10^6 J it is usually impractical.

The preferred method is a closed cubicle. For protection against blast using the equivalent static pressure method the *Code* gives the relevant pressure as

$$P = 7.6[(E \times 10^{-6})/V]^{0.72}, \quad P < 70 \qquad [17.34.76]$$

where E is the shock wave energy (J), P is the equivalent static pressure (bar) and V is the volume of the enclosure (m^3). Equation 17.34.76 is applicable where the ratio of the maximum to the minimum dimension of the enclosure does not exceed 2.

Cylindrical cubicles can be designed as thin-walled pressure vessels. Small cubicles can be made of angle iron and steel plate. Large cubicles should be of reinforced concrete. Since the shock wave has positive and negative phases, reinforcement is required on both inner and outer faces.

Some transmission of the shock wave occurs through the walls of the cubicle. This creates the hazard that persons outside may be injured by eardrum rupture. The Code gives the following method of estimating this. The impulse incident on an isolated wall is given as

$$I = 0.008E^{1/3}(R/E^{1/3})^{-1/2}, \quad 0.004 < (R/E^{1/3}) < 0.2 \qquad [17.34.77]$$

where I is the impulse per unit area (N s/m^2) and R is the distance (m). Also for an isolated wall the initial velocity of the wall, assumed unconstrained, is

$$u = I/m \qquad [17.34.78]$$

where m is the mass of the wall per unit area and u is the velocity (m/s). For the wall of a cubicle the impulse is taken as three times the value given by Equation 17.34.77 and the initial velocity of the wall is then that given by Equation 17.34.78.

If the value of the initial velocity u so calculated is less than 10 m/s, the shock wave generated outside should be too small to cause eardrum rupture.

If the plant in the cubicle contains flammables or toxics an opening may be necessary to allow dispersion of small leaks by ventilation. The *Code* states that the design of a vented cubicle is essentially the same as that for a closed cubicle.

With a vented cubicle, however, the escaping shock wave will tend to cause overpressure similar to that which would exist if there was no cubicle and the explosion was in the open. The *Code* gives the following equation for the estimation of the peak incident overpressure:

$$P = 8.45 \times 10^{-5}(E^{1/3}R)^{2.3} - 0.16(R/E^{1/3}) + 0.06, \quad 0.004 < (R/E^{1/3}) < 0.2 \qquad [17.34.79]$$

where P is the peak incident overpressure (bar).

The cubicle should also withstand the fragments generated. Since the distances are usually short, such a fragment will tend to be at its initial velocity. Much of the work on fragment penetration, described above, has been done to assist with barricade design.

Safety walls may be used instead of a cubicle. For a safety wall the impulse from the blast wave is as given by Equation 17.34.77 without application of the factor of 3 and the initial velocity as given by Equation 17.34.78. There will, however, be diffraction of the shock wave around the wall which is difficult to estimate.

The thickness of the barricade should be such as to enable it to withstand both shock wave and fragment penetration.

The barricade may be required to survive the simultaneous assault of the shock wave and of fragments. This problem is discussed in the *Code* and also by Moore.

Information on viewing ports for cubicles is given by Moore (1967).

17.34.30 Plant design

The hazard from missiles has not generally been a major factor in plant design, but rather more attention is now paid to it.

Design of plant for the hazard of missiles may focus on the source or on the target. On the whole it makes more sense to concentrate on the source, since the probability that a given plant item will be the target of a missile, even if a missile-generating explosion occurs, is very low.

Attention should be paid in design to features such as doors, vents and other fixtures on plant which may become missiles and measures should be taken to minimize this.

Where a serious missile hazard exists, use may be made of barricades and safety walls as described above.

17.35 Explosion Damage to Plant by Missiles

The treatment just given of missile impact effects constitutes a rather general account, with emphasis on penetration of concrete walls and steel plates. This is now supplemented by consideration of a particular problem, taken as representative for missile impacts on plant, that of damage to pipework.

The account given draws particularly on evidence given to the Piper Alpha Inquiry by A.C. Palmer (1989), which considered the mechanisms of, and potential for, damage to a 4 in. high pressure gas condensate line in B Module from fragments from the firewall between B and C Modules set in motion by an explosion in C Module.

17.35.1 Fragment velocity and energy

The velocity and energy of fragments has been considered in the previous section. Essentially, a fragment is accelerated by a force which will vary with the circumstances. The point which is relevant here is that in a large proportion of cases, the principal force causing acceleration is that due to the dynamic pressure, or wind. The acceleration of the fragment up to its maximum velocity then requires a finite distance, which may be several metres. This fact can be significant if the target is close to the source of the fragments.

17.35.2 Distribution of energy

Only a part of the kinetic energy of the fragment is transferred to the target and is available to cause damage. Some of the energy goes into the deformation, and possible disintegration, of the fragment itself. The distribution of energy between the fragment and the target depends on their relative stiffness and is highly variable. If the fragment is more readily deformed than the target, it absorbs more energy than it transmits.

The relative stiffness is itself a function of the velocity of impact. If the impact velocity is low, the relative stiffness is governed by the overall deformation of the two objects, whilst if it is high deformation may be localized and the energy distribution may alter.

The energy transferred to the target is itself divided into that energy which causes local damage and that which causes the whole target to respond. This latter energy is taken into account in some treatments but not in others.

17.35.3 Impact effects

Before considering damage caused by the fragment, it is appropriate to mention several effects associated with the impact of a high velocity object on a steel target.

Accounts of impact and its effects include *Impact by Goldsmith* (1960) and *Impact Strength of Materials* by W. Johnson (1972).

The impact effects of principal interest here are those which bear on the effective force exerted, the effective strength of the material and the nature of the target response.

The force exerted by a rapidly applied load is twice that of a slowly applied load. Thus, consider, as an approximate treatment, a vertical rod with a disc at the bottom and with an annular weight around the rod of the same radius as the disc and of mass m. Let this weight be suddenly applied from effectively zero height, to the disc so that it produces in the rod an extension x. Then, by energy balance the force F exerted on the disc is

$$mgx = \frac{1}{2}Fx$$

Hence

$$F = 2mg$$

This is twice the force exerted by a static load for which $F = mg$.

If a load is applied very rapidly to a steel object so that the strain rate is high, there is an increase in the effective strength of the material. This may be expressed as the ratio of the yield stress to the static yield stress, the ratio increasing with the strain rate. From the work of N. Jones (1983) this dynamic strength factor is of the order of 2 at a strain rate of 10^2 and 3 at one of 10^3.

The nature of the impact also affects the response of the target and the mode of deformation. If the load is applied slowly, quasi-static failure modes apply, whilst if it is applied very rapidly, dynamic failure modes come into play. Further, if the velocity of impact is very high, the effect may be intense, but localized.

The rapidity of loading at which these different effects come into play varies with the effect.

17.35.4 Modes of damage

Some modes of damage to pipework are exemplified by those considered in relation to the 4 in. condensate line mentioned. This pipe passed through the firewall from C Module into B Module, took a 90° bend and ran parallel to the wall, then took another 90° bend and ran away from the wall, into the main oil line. The pipe was understood to have had an outside diameter of 114 mm and a wall thickness of 11.1 mm (revised from an initial value of 8.6 mm) and to have been operating at a pressure of about 62 bar. In the analysis the steel was treated as having a yield stress of 260 N/mm^2, an elastic modulus of 210 N/mm^2, a Poisson ratio of 0.3 and a density of 7850 kg/m^3.

The modes of damage considered by Palmer are listed in Table 17.52.

17.35.5 Models for damage

In general, the energy absorbed, or work done, during deformation caused by a slowly applied load is obtained from the relation

$$U = \frac{1}{2}FS \qquad [17.35.1]$$

with

$$\delta = le \qquad [17.35.2]$$

Table 17.52 *Estimated minimum energy or velocity requirements for failure of the 4 in, condensate line on Piper Alpha (after A.C. Palmer, 1989)*

Mode of deformation	*Estimated minimum values*	
	Energy (kJ)	*Velocity* (m/s)
Loads applied relatively slowly		
1. Tensile failure	112	
2. Bending failure[a]	82	
3. Shear failure[b]	9	
4. Cutting		
(a) Cutting to leak[c]	11	
(b) Cutting off	143	
5. Denting		
(a) Denting by a concentrated force	36	
(b) Denting by an edge:		
Dent ½ diameter deep	26	
Dent 1 diameter deep	70	
Loads applied very rapidly		
6. Dynamic tensile failure	19	60
7. Dynamic puncturing	7	40

[a] Bending through a 90° angle.
[b] Unlikely to occur without bending.
[c] Pipe severed over one eighth of circumference.

where e is the strain, F is the force applied (N), l is the length of pipe stretched (m), U is the energy absorbed (J) and δ is the resultant elongation (m). As shown above, for a load applied rapidly, as in impact, the force is twice the static force.

Considering first the failure modes for a load applied relatively slowly, the tensile failure mode involves failure of a section of the pipe under tension due to application of a load which causes the ultimate tensile stress to be exceeded. For this mode, the model for energy absorbed, or work done, is given by Equation 17.35.1 using the impact force value.

For bending, two regimes were considered: elastic bending and plastic bending. When a pipe is bent, it first responds elastically and then starts to yield. Once yielding has begun, an increasing proportion of the cross-section deforms plastically, in compression on one side of the pipe and in tension on the other. The pipe cross-section becomes oval and then a buckle forms on the compression side. For this mode, the model for energy absorbed, which is that applicable to the plastic regime, the energy absorption in the elastic regime being negligible, is essentially

$$U = \phi\theta \qquad [17.35.3]$$

where θ is the angle of the bend (rad) and ϕ is the plastic moment (Nm).

For shear, the limiting shear force depends on the details of the loading. One approach is to assume that the distribution of the shear stress is similar to that in a circular tube acting as a beam. An estimate may then be made of the energy for the shear displacement of one pipe wall thickness.

For cutting, two distinct modes are considered: cutting to leak and cutting off. The first involves cutting through to

the extent that a leak occurs and the second cutting to the extent of a complete guillotine break. For this mode, the model used for energy absorbed is that of Lu (1989). This model is based on measurement of the energy absorbed when a sharp rigid wedge is pushed through a flat steel plate. This energy is

$$\frac{U}{\sigma_y t^3} = 3\frac{L}{t}, \quad \frac{L}{t}\text{small} \qquad [17.35.4]$$

$$= 2.5\left(\frac{L}{t}\right)^{1.3}, \quad 5 < \frac{L}{t} < 100 \qquad [17.35.5]$$

where L is the length of the cut (m), t is the thickness (m) and σ_y is the yield stress (N/m^2). The length of the cut is taken for cutting to leak as part of the circumference and for cutting off as the whole circumference.

For denting, again two modes are considered: denting by a concentrated force and denting by an edge. These evidently correspond to denting by a blunt and by a sharp-edged object, respectively. For the first mode, in which the load is assumed to be a radial force applied over a circular area of the pipe, the model for energy absorption used is that of A.J. Morris and Calladine (1971). The force for plastic collapse is determined and the energy absorbed is obtained from this force and the depth of the dent, using Equation 17.35.1.

For the second mode of denting, in which the load is assumed to be applied by a sharp-edged object at right angles to the pipe, the model for energy absorption used is that of Wierzbicki and Myung Sung Su (1986).

Moving on to the failure modes for a load applied very rapidly, these modes occur only if at impact the fragment has a certain minimum velocity as well as the requisite minimum energy. For these modes, therefore, Table 17.52 gives minimum values for both velocity and energy.

Dynamic tensile failure is caused by the very sudden application of a tensile load. For the minimum velocity, the model used is based on the work of Kolsky (1963) on tensile plastic waves in a bar whose end is suddenly given a velocity v. It applies to the case where the velocity thus imparted exceeds that at which the steel just becomes plastic. The velocity v is related to the strain e_p behind the plastic wave front set up by the impact. If the velocity is high enough for this strain to reach the ultimate tensile strain, failure occurs. The relation between the velocity v and the strain e_p is

$$v = \int_0^{e_p} [\sigma_t(e)/\rho]^{1/2}\, de \qquad [17.35.6]$$

where e is the strain, e_p is the strain behind the plastic wave front, v is the imparted velocity (m/s), ρ is the density of steel (kg/m^3) and σ_t is the tensile stress (N/m^2).

For the minimum energy for dynamic tensile failure, the approach is similar to that for the quasi-static tensile failure described above, except that a factor, taken as 3, is applied to the yield stress to allow for the suddenness of the application of the load, or dynamic effect.

Dynamic puncturing is gouging caused by high velocity impact. For the minimum velocity the model used is based on the velocity required to raise the local compressive stress to the yield point and thus just to enter the plastic regime and is

$$\sigma_c = \rho c v \qquad [17.35.7]$$

where c is the velocity of elastic compression waves in steel (m/s), v is the velocity of impact of the missile (m/s) and σ_c is the compressive stress caused by the impact (N/m).

For the minimum energy for dynamic puncturing, the model used is that of W. Johnson (1972). This model gives the energy required to gouge out a cavity and is

$$U = 3\sigma_y V_c \qquad [17.35.8]$$

where V_c is the volume of the cavity (m^3). The yield stress used here is again enhanced by a factor of 3 to allow for the dynamic effect.

17.36 Explosion of a Cased Explosive

Another event which can give rise to missiles is the explosion of a cased explosive. This is considered in this section. Whilst the discussion has most relevance to an explosion involving munitions, there are features which have wider application.

There is obviously a large volume of work done by the military dealing with the various aspects of this problem. In particular, the accounts given in *Structural Defence* by Christopherson (1946) and in the *Textbook of Air Armaments* (referred to below as the *Textbook*) by the Ministry of Supply (1952) provide a basic starting point, though this needs to be supplemented by more recent work on the specific aspects.

A model for an exploding object which draws on this work has been given by Gilbert, Lees and Scilly (1994f,g), and the account here is based mainly on this.

In addition to the models specifically for fragments from cased explosives described below, further material on missiles is given in Section 17.34.

17.36.1 Exploding object

The exploding object primarily considered is a cased high explosive, typically a shell or bomb. The explosive could be some combination of TNT and RDX. The following treatment, therefore, is in terms of weapons.

17.36.2 Fragment mass distribution

The fragmentation behaviour of a cased explosive varies depending on the nature of the casing. A plain casing will undergo natural fragmentation. An armament such as a shell may be high explosive or shrapnel. In the latter case the casing is designed to give a particular pattern of fragments.

The fragment mass distribution of this latter type of casing is obtained experimentally by conducting an explosion and collecting the fragments formed. In some cases information is also obtained on the fall of the fragments.

Work on fragment mass distribution (FMD) includes that of Mott (1947), Held (1968, 1979, 1990), Grady (1982a,b), C.E. Anderson, Predebon and Karpp (1985), Burman (1989), Helwig, Klee and Hubner (1989) and Jagusch (1989).

An early method of representing the FMD was that of Mott (1947). That described here is the method developed by Held (1968, 1979, 1990). The correlation is

$$M(n) = M_o[1 - \exp(-Bn^{\lambda})] \qquad [17.36.1]$$

where $M(n)$ is the cumulative fragment mass, or overall mass of the fragments of number n, starting with the

largest fragment, M_o is the total mass of fragments, n is the number of the nth largest fragment, or cumulative fragment number, and B and λ are constants.

The mass m of the nth fragment is obtained from Equation 17.36.1 by differentiation:

$$m = \frac{dM(n)}{dn} = M_o B\lambda n^{\lambda-1} \exp(-Bn^{\lambda}) \quad [17.36.2]$$

Held (1990) gives as an example the fragment mass distribution of the Hispanic Suiza 30 × 170 mm incendiary high explosive projectile. The parameters which he obtains for this weapon are $M_o = 288.7$ g, $B = 0.511$ and $\lambda = 0.7318$.

In some cases an improved fit for higher values of n is obtained by replacing M_o with a modified mass M_{oB} defined as that value which best fits the set of equations

$$M_{oB} = \frac{M(n)}{1 - \exp(-Bn^{\lambda})} \quad [17.36.3]$$

Equation 17.36.1 then becomes

$$M(n) = M_{oB}[1 - \exp(-B_B n^{\lambda_B})] \quad [17.36.4]$$

where B_B and λ_B are constants.

The risk from explosion of a cased explosive depends on the number and size of the fragments. As the number of fragments increases, the risk initially increases but eventually decreases as the fragments become too small to cause injury.

Often it is a stack of weapons which is of interest. Stack effects on FMD are considered in Section 17.36.11.

17.36.3 Projection angle of fragments

Methods exist for the estimation of the angle at which the fragments from a single weapon are projected. Treatments include those of Christopherson (1946), G.I. Taylor (1963a,b) and Karpp and Predebon (1974).

A discussion of the direction in which fragments are projected is given by Christopherson (1946). He states, 'Fragments of the case are, in general, projected normally to the inner surface on which the pressure of the explosive gases acts at the moment of break-up.'

Weapons such as bombs have some curvature along their length, which tends to spread fragmentation over a wider zone. If detonated at one end the casing becomes conical rather than cylindrical, directing fragments away from the initiating end.

A study of the fragmentation of tubular bombs was conducted by G.I. Taylor (1963a,b). He gives the following equation for the angle ϕ formed by the deforming case relative to the direction of the detonation wave:

$$2 \sin \phi = u_o/D \quad [17.36.5]$$

where D is the velocity of detonation (VOD), u_o is the initial velocity of the fragment (VOF) and ϕ is the angle to the axis of the tube at which fragments are projected. ϕ is known as the Taylor angle.

In practice, these models of projection angle appear of limited use in accident modelling, where the appropriate approach depends on the particular case. Considering the plan view, it will be sufficient in many scenarios to assume that for a weapon on its side, fragments of the cylindrical part of the casing are ejected in two broad sectors, whilst for a weapon standing vertically the fragments are ejected in all directions; in both cases the end cap and base can be taken as travelling along the axis of the weapon.

It is also necessary to consider the angle of elevation. In principle, for the case of an exposed person standing vertically, three cases need to be considered, as illustrated in Figure 17.103. In the near field, shown in Figure 17.103(a), the fragments hitting the human target are those projected at low angle α; the fragments approach the target with near normal incidence. In the medium field, shown in Figure 17.103(b), the target is struck by some fragments of low trajectory issuing at angle $\beta \pm \delta_1$ and others of high trajectory issuing at angle $\gamma \pm \delta_2$; in both cases the fragments approach the target obliquely. Finally, at the limit of the fragment range, shown in Figure 17.103(c), these two trajectories combine; again the fragments approach the target obliquely. This is an idealized model. In practice, due to air drag, fragments slowing below a critical velocity will tend to stall.

Frequently weapons are in an ordered stack. Alternatively, in an accident, they may be in a disordered pile. In each case there is an effect on the angle of projection. Stack effects on projection angle are discussed in Section 17.36.11.

17.36.4 Initial velocity of fragments

Methods of determining the initial velocity of the fragments from a weapon include those given in the *Textbook, in Structural Defence* and by Gurney (1943), V.J. Clancey (1972b), Kamlet and Finger (1979) and E. Hirsch (1986).

One approach to the estimation of the initial velocity of fragments is the use of empirical rules. The *Textbook* suggests values for the initial velocities of 4000 ft/s for bomb fragments and 3000 ft/s for shell fragments.

For fragments from the bursting of a cased TNT charge the following empirical values of initial velocity have been given by V.J. Clancey (1972b) in the context of incident investigation:

Thin case	8000 ft/s
Medium case	6000 ft/s
Thick case	2000 ft/s

This approach provides a useful guideline, but as Clancey points out, it assumes that any size charge will propel fragments the same distance, which is not the case – larger explosions tend to project fragments further.

One equation for the initial velocity of the fragments is that given in *Structural Defence* by Christopherson (1946):

$$V_o = \{8.22 \times 10^7[1 - \exp(-0.69E/C)]\}^{1/2} \quad [17.36.6]$$

where C is the mass of the uniform cylindrical case per unit length (lb), E is the mass of charge per unit length (lb) and V_o is the initial velocity (ft/s). Equation 17.36.6 is a generalization of an empirical equation obtained by Payman for small tetryl filled bombs. Christopherson states, 'for a medium case bomb, the initial velocity of fragments will not exceed approximately 7500 ft/s.'

The correlation for initial velocity which appears to be most widely used is that of Gurney (1946). The Gurney model is based on a fundamental energy balance. The sum

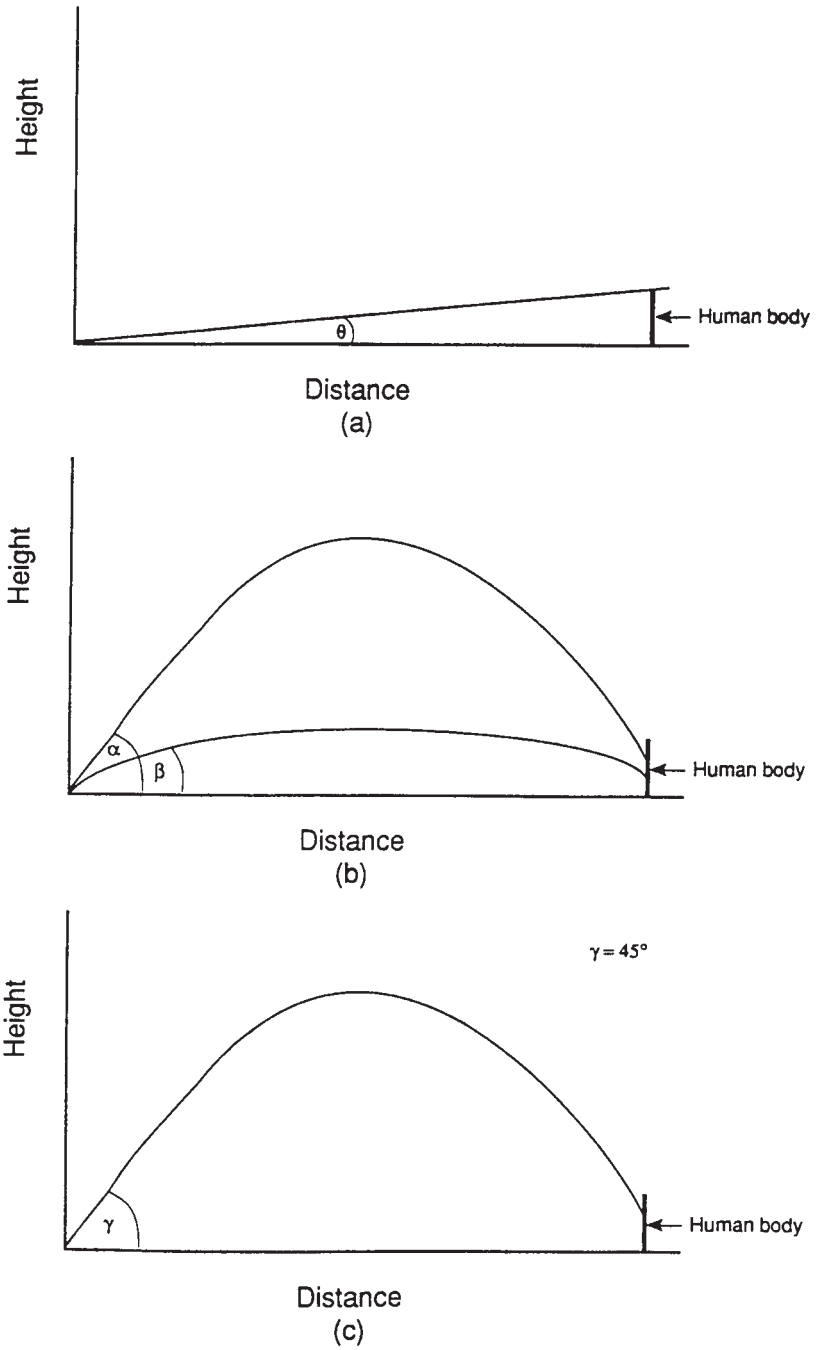

Figure 17.103 *Angle of projection in the vertical plane of missiles from a cased explosive: (a) near field (b) medium field and (c) limit of range (Gilbert, Lees and Scilly, 1994f)*

of the kinetic energy of the fragments and the energy of the expanding explosion products is equated to the internal energy of explosion. It is assumed that all the fragments are projected out at the same velocity and that the velocity of the gaseous explosion products increases from 0 at the centre of the mass of the explosive to a maximum which is also the velocity of the fragments at the moment of break-up of the casing.

The equation given by Gurney for the initial fragment velocity u_o is

$$u_o = C_G\left(\frac{C/M}{1+(C/M)/2}\right)^{1/2} \quad [17.36.7]$$

with

$$C_G = [2(-\Delta E)]^{1/2} \quad [17.36.8]$$

where C is the mass of explosive (kg), ΔE is the internal energy of explosion per unit mass of explosive (J/kg), M is the mass of the cylindrical section of the casing, and hence of the sidewall fragments (kg), u_o is the initial fragment velocity (m/s) and C_G is the Gurney constant (m/s). C_G is also commonly known as the Gurney velocity.

The Gurney constant is one of the standard parameters of an explosive. Values for a number of the more common explosives are given by Kinney and Graham (1985).

The use of the Gurney equation to determine the velocity of fragments from an explosion is known as a Gurney analysis. Accounts of such analysis have been given by G.E. Jones, Kennedy and Bertholf (1980) and Kinney and Graham (1985).

Further treatments of the Gurney method have been described by Kamlet and Finger (1979) and E. Hirsch (1986). Kamlet and Finger give for the Gurney constant the following relation:

$$C_G = 0.887\phi^{0.5}\rho_o^{0.4} \quad [17.36.9]$$

with

$$\phi = NM^{0.5}Q^{0.5} \quad [17.36.10]$$

where C_G is the Gurney constant (km/s), M is the average molecular weight of the products of explosion, N is the number of moles of gas produced by the explosion, Q is the heat of detonation (cal/g), ρ_o is the explosive loading density (g/cm^3) and ϕ is a parameter. Stack effects on initial velocity are considered in Section 17.36.11.

17.36.5 Flight of fragments

Treatments of the flight and retardation of fragments include those in the *Textbook* and in *Structural Defence* and by Zaker (1971) and Naz (1989). For the retardation of fragments the *Textbook* gives

$$u = u_o \exp(-s/284\,m^{1/3}) \quad [17.36.11]$$

where m is the mass of the fragment (oz), s is the distance travelled (ft), u is the velocity of the fragment (ft/s) and u_o is its initial velocity (ft/s).

In his account in *Structural Defence*, Christopherson states:

> Immediately after the case has broken up, the shock front expands more rapidly than the case, and thus at this stage the fragments are surrounded by air moving outwards, at a velocity comparable to their own. It is not long, however, before the rapid deceleration of the shock front due to the falling shock-wave pressure allows the fragments to overtake it and pass through it into the zone of undisturbed air beyond. As soon as this happens – and it happens within a few feet of the bomb – the fragments are retarded by a force which is proportional to the square of their velocity, and to the area presented. Under these conditions, it is easy to show that the velocity at a distance x ft from the origin is given by an equation of the form

$$u = u_o \exp(-kxA/m) \quad [17.36.12]$$

> where A is the area of the fragment, u is the velocity of the fragment, u_o is the velocity of the fragment at the commencement of retardation by air drag, m is the mass of the fragment, x is the distance and k is a constant.

It should be noted that Christopherson's statement that the drag force is proportional to the square of the velocity applies to the subsonic regime only.

Christopherson quotes the following relations for the velocity of a fragment in air, based on a generalization of an equation given by Payman for tetryl filled tubes

$$u = u_o \exp(-0.00204xa/m^{1/3}), \quad u \geq u_s \quad [17.36.13a]$$

$$u = u_o \exp(-0.00137xa/m^{1/3}) \quad u < u_s \quad [17.36.13b]$$

with

$$a = A_m/Q^{2/3} \quad [17.36.14]$$

where a is the dimensionless coefficient of area, A_m is the mean area presented by the fragment in flight (ft^2), Q is the fragment volume (ft^3), u is the velocity of the fragment (ft/s), u_o is the initial velocity of the fragment (ft/s), u_s is the velocity of sound (ft/s), m is the mass of the fragment (oz) and x is the distance (ft). The value quoted for the velocity of sound is 1100 ft/s.

For natural fragmentation Christopherson quotes work at the Safety in Mines Research Station to the effect that

$$a = 1.93 + 1.3m \quad [17.36.15]$$

Christopherson states that for a cube the value of a is 1.5, but that for natural fragments it is higher. He argues that there will be very few fragments for which the term $a/m^{1/3}$ is less than 2. Equation 17.36.15 gives for $a/m^{1/3}$ a minimum value of 3.2 at m = 0.75 oz.

A large fragment tends to retain its velocity. Such a fragment will travel some hundreds of feet before its velocity is halved.

The model for fragment flight given by V.J. Clancey (1972b) and quoted in Section 17.34 appears very similar to that of Christopherson.

Another relation for the flight of a fragment from a weapon is that given by Naz (1989):

$$u = u_o \exp\left(-\frac{C_x A_s}{2m}\rho_a x\right) \quad [17.36.16]$$

where A_s is the effective area of the fragment (m^2), C_x is the drag coefficient, m is the mass of the fragment (kg), u is the velocity of the fragment (m/s), u_o is its initial velocity (m/s), x is the distance (m) and ρ_a is the density of air (kg/m^3). For the effective area A_s Naz gives

$$A_s = (\pi/4)a^2 \quad \text{sphere} \quad [17.36.17a]$$

$$A_s = (3/2)a^2 \quad \text{cube} \quad [17.36.17b]$$

where a is the diameter of the sphere or the side of the cube (m).

For the coefficient C_x Naz gives relations from the work of Suterlin (1966), which show the coefficient for spheres, cubes and cylinders as a function of Mach number. He also quotes work by McCleskey (1988a) which shows that there is a considerable scatter in observed values of the coefficient.

17.36.6 Range of fragments

The account of fragment flight given by Christopherson in *Structural Defence* also includes a treatment of the maximum range of a fragment. From Equation 17.36.13a and taking $a/m^{1/3}$ as 2,

$$u = u_o \exp(-0.00409x) \qquad [17.36.18]$$

Then, from this equation the distance at which the velocity u falls to the velocity of sound u_s is

$$x = [\ln(u_o/u_s)]/0.00409 \qquad [17.36.19]$$

For an initial velocity of 7500 ft/s Christopherson obtains a distance of 475 ft.

Then, noting that $u = dx/dt$ and integrating Equation 17.36.18 with respect to time gives

$$x = [\ln(1 + 0.00409u_o t)]/0.00409 \qquad [17.36.20]$$

or

$$t = [\exp(0.00409x) - 1]/(0.00409u_o) \qquad [17.36.21]$$

From Equation 17.36.21 the time for transition to subsonic velocity is only 0.2 s. This is a negligible proportion of the total flight time.

Utilizing Equation 17.36.13b again with a value of the term $a/m^{1/3}$ of 2 and integrating as before, taking the initial velocity now as that of sound gives

$$x = [\ln(1 + 0.00273u_s t)]/0.00273 \qquad [17.36.22]$$

Christopherson obtains a maximum value of the flight time of 330 s, on the basis that the flight time is necessarily less than the flight time to maximum range in the absence of air resistance, which is $V_v/2g$, where V_v is the initial vertical velocity (ft/s), and that the value of this term for maximum range is necessarily less than $V_o/2^{1/2}$. Then, substituting this flight time of 330 s in Equation 17.36.22 gives a travel distance of 2530 ft, which together with the distance of 475 ft travelled in the supersonic range yields for the maximum range of the fragment a total distance of 3005 ft. He compares this with the distance of 1000 yards usually taken as the danger area for a 1000 lb medium capacity (MC) bomb and comments that the latter is certainly on the safe side, though not so grossly as might be expected in view of the crudeness of the method adopted.

There is also available some empirical guidance on the range of fragments from cased explosives. The empirical correlation for the maximum horizontal range of fragments from a cased charge given by V.J. Clancey (1972b) has been described in Section 17.4.

Guidance is also available from relationships for safety distances. A formula of this type is the US safety distance in bomb disposal work. This is given by Kinney and Graham (1985), quoting Lenz (1965), as follows:

$$r = 120W^{1/3} \qquad [17.36.23]$$

where r is the safety distance (m) and W is the mass of explosive (kg). There is a minimum distance of 90 m. However, since this is a safety formula it may be expected to incorporate a safety factor.

17.36.7 Mean presented area of fragments

The mean presented area (MPA) of the fragments is relevant both to their flight and to their injuring power. In the treatment just given, which is concerned with flight, the MPA is given by Equations 17.36.14 and 17.36.15.

17.36.8 Number of fragments hitting target

Following the *Textbook*, the number n of incapacitating fragments is

$$n(x) = \int_0^\infty q(v, x)r(x)\mathrm{d}v \qquad [17.36.24]$$

where n is the number of incapacitating fragments, q is the number of fragments of equivalent velocity v at a distance x, r is the proportion of fragments of equivalent velocity v at a distance x capable of causing incapacitation, v is the velocity of the fragment (ft/s) and x is the distance (ft).

The density of incapacitating fragments over the area of a sphere centred on the exploding object is

$$\frac{N(x)}{A_p} = \frac{n(x)}{4\pi x^2} \qquad [17.36.25]$$

where A_p is the projected area of the exposed person (ft^2) and N is the average number of incapacitating fragments at a distance x. Hence

$$N(x) = \frac{n(x)A_P}{4\pi x^2} \qquad [17.36.26]$$

The value of the projected area A_p does not appear to be given explicitly in the *Textbook*, but a value of 2.8 ft^2 may be inferred.

The probability p of being hit by one or more incapacitating fragments is taken as given by the Poisson distribution and is therefore

$$p = 1 - \exp[-N(x)] \qquad [17.36.27]$$

A vulnerable area A_v may be defined as the equivalent ground area in which probability of incapacitation is unity. This vulnerable area is

$$A_v = \int_0^\infty p(x)x\,\mathrm{d}x \qquad [17.36.28]$$

where A_v is the vulnerable area (ft^2).

The vulnerable area so defined takes no account of any hard cover which may provide protection from the fragments.

The *Textbook* gives as an illustrative example the determination of the fragments from a British 20 lb bomb. The example is described by Gilbert, Lees and Scilly (1994f).

17.36.9 Textbook model

The model of an exploding weapon given in the *Textbook* utilizes the framework relations Equations 17.36.24–17.36.27 together with the following supporting equations. The FMD is obtained from experimental values for the particular weapon. The fragments are evidently assumed to be projected equally in all directions with an initial velocity obtained from the empirical values quoted. The flight and retardation of the fragments are given by Equation 17.36.11. As described in Section 17.42, the *Textbook* also includes an injury model.

17.36.10 Model of Gilbert, Lees and Scilly

In the model of Gilbert, Lees and Scilly (1994f) use is again made of Equations 17.36.24–17.36.27 as the framework, but with a different set of supporting relations. The FMD is based on fitting the experimental values for the weapon to Equation 17.36.1 of Held. The angles of projection in plan and elevation depend on the problem considered and guidance is given on this aspect. For the initial velocity use is made of the Gurney equation (Equation 17.36.7) with the Gurney constant given by Equation 17.36.9 of Kamlet and Finger. The flight and retardation of the fragments is described by Equation 17.36.13 of Christopherson, which covers both sonic and subsonic regimes.

The model is used in conjunction with the model for injury from penetrating fragments given by the authors and described in Section 17.42.

Gilbert, Lees and Scilly (1994g) also describe a computer program EXFRAG which gives for an exploding weapon the probability of defined degrees of injury as a function of distance and give an illustration of the results obtained.

17.36.11 Stack effects

In the foregoing treatment the exploding object is taken as a single weapon. In many situations of practical interest it is likely to be a stack of weapons. There is a potential stack effect on each of the following features: (1) the number of fragments, (2) fragment mass distribution, (3) the projection angle of the fragments, and (4) the initial velocity of the fragments.

There is little published information which can be used to quantify these effects, but the following qualitative comments can be made. In a stack explosion, a significant proportion of the fragments hit other objects within the stack and do not leave the stack. This potentially affects not only the number but also the mass distribution of fragments leaving the stack. The angle of projection of the fragments depends on the nature of the stack, which may be an ordered stack or a disordered pile. The former has to be dealt with on a case by case basis, whilst for the latter the common assumption is that the fragment density is the same in all directions. There may also be stack effects on the initial velocity in so far as fragments may be further accelerated by the hot gases from the explosion.

17.37 Explosion of an Explosive Load

Another situation which it may be necessary to model is the explosion of a load of condensed phase explosives, either uncased or cased. The former might typically be blasting explosives, the latter munitions.

Models for the explosion of a condensed phase explosive, particularly in a built-up area, have been given by Withers and Lees (1991) and Gilbert, Lees and Scilly (1994a–i). The model of the latter is encoded in the program EXMOD, which incorporates the program EXFRAG.

The following account of the modelling of this situation is based on the work described by the latter authors. Using appropriate physical models, it is possible to estimate as a function of distance the intensity of the various physical effects and hence, using the corresponding injury relations, the probability of defined types of injury for defined types of exposure. Then, using a suitable model for the numbers with each type of exposure as a function of distance, an estimate can be made of the numbers suffering each type of injury. Where the explosion occurs not at the start but during the course of an incident, separate estimates can be made for different times into the incident.

17.37.1 Exploding object

The exploding object is envisaged as a load of explosives, typically uncased civil explosives or cased explosives in the form of munitions such as shells, bombs, etc.

17.37.2 Explosion scenario

The elements of the scenario are the events prior to the situation of imminent risk; the explosion itself; the persons at risk; the physical characteristics of the location and the human behaviour prior to the explosion.

The most common scenario for the realization of the hazard is that of engulfment of the explosive load in a fire which lasts long enough to initiate an explosion. This scenario is important not only by virtue of its relative frequency, but also because all the features just mentioned are relevant, which is not the case for every scenario.

The approach to scenario development takes as its starting point the persons at risk, in other words the targets of the explosion. Categories of persons exposed are defined which are intended to be exhaustive over the whole course of the scenario and estimates made of the numbers in each category at the start of the scenario and of the change in these numbers with time until the explosion occurs.

If the explosion is caused by a sudden event such as impact, the start is the explosion itself. If it is caused by a more gradual event such as fire, the start is the occurrence of an event observable either by the vehicle crew or the public.

17.37.3 Explosion effects

The principal effects of a condensed phase explosion such as the explosion of a load of cased explosives on a lorry are:

(1) blast;
(2) fireball;
(3) missiles
  (a) primary fragments,
  (b) secondary missiles;
(3) crater;
(4) building damage.

Primary fragments include those generated by the disintegration of the casing and are also taken to include those from the vehicle. Secondary fragments include fragments from the crater and objects set in motion by the blast wave, not only objects travelling in a more or less horizontal direction, but others such as glass, falling vertically. The blast wave may also cause translation of the human body,

causing it to fly through the air or to tumble along the ground, and possibly to impact with some hard object.

There may also be other effects. For example, in some large explosions of explosives in ships at docks, hot fragments have been ejected which then caused secondary fires. These effects are not, however, considered in the model.

17.37.4 Population exposure

These explosion effects act on an exposed population. For this particular type of incident it is necessary to model this population in some detail. The exposure model used covers the population density, the population's disposition indoors and outdoors, the categories of exposure, the incident scenarios and the vulnerabilities of persons in each exposure category in given scenarios.

For exposure a basic distinction is between persons indoors and those outdoors, since this affects vulnerability to the individual injury mechanisms. For example, persons outdoors are more vulnerable to fragments from the casing and those indoors to building collapse.

For each of these groups further distinctions are made based on situation or behaviour. For those indoors the classification used is:

I1 Persons unaware or aware of the incident who go about their normal business
I2 Persons aware of the incident who observe it through a window (or those unaware who happen to be close to a window).

The classification used for those outdoors is:

O1 Persons on foot unaware or aware of the incident who go about their normal business.
O2 Persons occupying vehicles near to the scene.
O3 Persons on foot aware of the incident who have come to the scene as spectators.
O4 Members of the emergency services who have come to the scene.

As stated above, the numbers of persons in each category will in principle change with time, but the scope for such change will depend on the interval between the start of the scenario and the explosion.

At the start of the scenario, there are persons in categories I1, I2, O1 and O2 but, by definition, in no other category. Persons in O1 are essentially pedestrians who are passing by or gathered for some purpose such as an open market.

If the scenario takes a finite time to develop, the numbers in each indoor category may be expected to change. Persons indoors may observe the scene through windows. Alternatively, they may take evasive action against the risk of an explosion, either by moving further away or by changing posture. Some pedestrians may continue about their business, but others will take evasive action, essentially by quitting the scene. Those who by contrast are attracted to the scene are classed as spectators. Likewise, the occupants of vehicles may continue on their journey or may stay near the scene, possibly as spectators, but more probably owing to obstruction of the traffic. In due course, members of the emergency services will arrive. The total number exposed is not assumed to be constant; it may decrease or increase.

The model therefore gives the number of persons exposed in each category at the start of the scenario and over its course. It may be used to obtain an instantaneous picture, or 'snapshot', of these numbers at any time up to the explosion.

17.37.5 Blast

The blast effects for a condensed phase explosive used in the blast submodel are the peak incident overpressure and impulse and the peak dynamic pressure and dynamic pressure impulse, obtained from the relations given in Section 17.26.

Eardrum rupture is a function of peak incident overpressure. Lung injury is a function of peak incident overpressure and, for some postures, of peak dynamic pressure and of impulse. Whole body displacement is a function of peak dynamic pressure and dynamic impulse. The relevant injury relations are given in Section 17.38.

17.37.6 Fireball

The fireball from a condensed phase explosive is described by a submodel different from that for a hydrocarbon fireball. The relevant model is given in Chapter 16. Injury from the fireball occurs due to engulfment in the fireball or thermal radiation from it. It is assumed in the model that a person engulfed in the fireball is killed. The injury relations for thermal radiation are those given in Chapter 16 and are the same as those for injury by radiation from hydrocarbon fireballs or pool fires.

17.37.7 Missiles

The missile submodel treats six types of missile: (1) primary fragments from the casing, if any; (2) fragments from the vehicle; (3) fragments ejected from the crater; (4) secondary missiles set in motion by the blast; (5) falling masonry and glass; and (6) flying glass.

The prime application of these models is to persons outdoors. However, they are also applicable to persons indoors who are near windows; the effect of falling masonry on persons indoors is taken into account in the separate housing damage model given in Section 17.39.

An outline of the model used for fragments from the casing and the vehicle has been given in Section 17.36. The models for crater ejecta and for falling masonry and glass are described in Section 17.34 and that for flying glass in Section 17.40.

No separate model is used for the effects of secondary missiles on persons outdoors; the effect of such missiles indoors is taken into account in the housing damage model.

17.37.8 Building damage

The building damage submodel used is actually a housing damage model.

The housing damage submodel used is the correlation between category of housing damage and mass of explosive as given by the revision by Gilbert, Lees and Scilly (1994c) of the Jarrett equation. This model is described in Section 17.33.

17.37.9 Injury to persons outdoors

The model for explosion injury outdoors is therefore based on four separate broad causes of injury: (1) blast causing eardrum rupture and lung injury, (2) blast causing injury by whole body displacement, or bodily translation, (3) injury from the fireball, and (4) injury from the following

types of missile: (4a) primary fragments from the casing, if any, (4b) fragments from the vehicle, (4c) crater ejecta, (4d) falling masonry and glass, and (4e) flying glass. The models for injury from these various causes have just been described. The probability of injury outdoors is estimated by applying each of these submodels in turn.

The model gives the probability of lethal injury for all the injury modes mentioned; in some cases it also gives the probability of sublethal types of injury, e.g. eardrum rupture.

Allowance is made in the model for multiple injury, as described in Chapter 9 and in Section 17.38.

17.37.10 Injury to persons indoors

The model for explosion injury to person indoors is based on the correlation between category of housing damage and probability of injury described in Section 17.39. The latest is the model of Oswald and Baker (2000).

This correlation gives the probability not only of lethal injury but also that of severe injury and light injury.

This model for injury to persons indoors includes injury from flying glass, but, where appropriate, this latter may be accorded separate treatment, using the model for injury from flying glass given in Section 17.40.

17.37.11 Large targets

The model also includes an estimate of the probability that an explosion occurring at random in a built-up area will find a target comprising a large number of people, such as a block of flats or a large store or market. The estimate is based on the size distribution of targets hit by V-2 rockets. From these data the authors give the following estimates of incident size versus probability of occurrence:

Deaths	*Probability*
≥ 10	0.089
≥ 33	0.014

It should be borne in mind that the data include a number of cases where there was a direct hit and that the population densities in wartime London were much higher than they are today, by a factor in the range 1.5–2.

17.38 Explosion Injury to Persons Outdoors

For persons in the open there is a large amount of information available on specific explosion injury causes and modes. Accounts are given in *The Effects of Nuclear Weapons* (Glasstone, 1962; Glasstone and Dolan, 1980) and in *Explosion Hazards and Evaluation* (W.E. Baker *et al*., 1983).

Much of the data on injury from explosions derives from the work of Zuckerman and co-workers in the 1940s, from work on the effects of nuclear weapons described by Glasstone (1962) and Glasstone and Dolan (1980) and from an extensive programme of research at the Lovelace Foundation in the 1960s, 1970s and 1980s, which has been reported by Bowen, Fletcher, Richmond, White and other workers. Some of this latter work is listed in Appendix 28.

A set of correlations of explosion injury is given in the *Green Book*.

The causes of explosion injury to a person in the open include the following: (1) blast, (2) whole body displacement, (3) missiles, (4) thermal effects, and (5) toxic effects.

The modes of explosion injury due to these causes include (1) eardrum rupture, (2) lung haemorrhage, (3) whole body displacement injury, (4) missile injury, (5) burns, and (6) toxic injury.

In the case of outdoor exposure, it is generally possible to apply the injury relations for the individual physical causes, provided that where applicable due allowance is made for the effects of more than one cause.

There are several ways in which injury may be correlated. One is in terms of single values of the injurious physical effect, of which the threshold value and the value for 50% probability of injury are particularly important. Another is a probit equation, which also generally correlates the probability of injury with a single physical effect, typically overpressure. A third is in the form of a P–I diagram.

Data in forms such as threshold and 50% probability values are illustrated by those given in Table 17.53 from the work of Glasstone and of White.

Probit equations have been widely used to express injury relations. The use of probit equations is illustrated by the many correlations of injury given by the Lovelaci Foundation workers which are cast in this form.

The probit equation form is also that used in the vulnerability model described by Eisenberg, Lynch and Breeding (1975). Much of the data on which these relations are based derives from the work of Fugelso, Weiner and Schiffman (1972). These relations have beer quite widely used, mainly for lack of other data, and some are described below, but comparison with the other relations given indicates that they generally predict considerably higher levels of injury than those by other researchers.

Table 17.53 *Some data on the injury effects of explosions: direct blast effects*

Effect	*Effective peak overpressure*[a] (psi)		
	Duration		
	Glasstone[b]	*White*[c]	
	'Long'[b]	3 ms[c]	400 ms
Eardrum rupture			
Threshold	5	5	5
50% ($\geq$20 years old)	15–20	15–20	15–20
50% ($\leq$20 years old)	30–35		
Lung damage			
Threshold	12 (8–15)	37–49	12–15
Severe	25 (20–30)	$\geq$98	$\geq$37
Lethality			
Threshold	40 (30–50)	112–156	37–52
50%	62 (50–75)	156–217	52–72
100%	92 (75–115)	217–302	72–100

[a] This overpressure is described as the maximum effective overpressure. It is stated that this may be one of the three defined overpressure, one of which is the maximum incident overpressure for free-stream exposure if the axis of the subject is parallel to the direction of travel of the blast wave.

[b] Tentative criteria for some injury effects applicable to a fast-rising, long-duration overpressure (after Glasstone, 1962).

[c] Tentative criteria for some injury effects in young adults applicable to fast-rising, short- or long-duration overpressure (after C.S. White, 1968b).

The third form of P–I diagram is illustrated by those given by W.E. Baker *et al.* (1983).

17.38.1 Eardrum rupture

The data for eardrum rupture given by Glasstone (1962) and by C.S. White (1968b) are shown in Table 17.53. Both sets of data apply to rapidly rising overpressure. In general, White distinguishes between short- and long; duration overpressures, but his data for eardrum rupture are identical.

Relations for eardrum rupture are given in the vulnerability model described by Eisenberg, Lynch and Breeding. They quote the following data from Fugelso, Weiner and Schiffman:

Probability of eardrum rupture (%)	*Peak overpressure*	
	(psi)	(N/m^s)
1 (threshold)	2.4	16,500
10	2.8	19,300
50	6.3	43,500
90	12.2	84,000

They derive from these data a probit equation relating eardrum rupture to peak overpressure:

$$Y = -15.6 + 1.93 \ln p^o \qquad [17.38.1]$$

where p^o is the peak overpressure (Pa) and Y is the probit.

Eardrum rupture has been discussed by F.G. Hirsch (1968), who reviews the physiology of the ear and injury to it and summarizes the available data on the blast conditions causing rupture.

The ear responds to sound waves, and a blast wave is physically the same phenomenon. For sound waves the ear responds over the frequency range 20–20,000 Hz and at very low energy levels. It is unable, however, to respond faithfully to a pulse with a period of less than 0.3 ms, and the attempt to do so results in a single, large excursion, and it is this which causes rupture. The response is governed by the peak overpressure and the rise time of the overpressure.

Hirsch states that it has been established that there is a direct relation between peak overpressure and eardrum rupture.

He states further that there is evidence that other parameters such as rate of rise and positive and negative duration also have an influence. Rapid rise of overpressure tends to increase the probability of rupture. Hence, data from loading by explosion overpressures is more applicable than data from loading by static pressures.

Zalewski (1906) performed tests in which cadavers were subjected to static pressures. He obtained a mean pressure for rupture of 22.9 psi. Zuckerman and co-workers (Blake *et al.*, 1941) did work on cadavers, but used slow rising overpressures from explosions. They found for 50% probability an overpressure of about 1 atm (14.7 psi). In other studies on air raid casualties they obtained for 50% probability of rupture a lower limit of 15 psi and an upper limit of 50 psi.

G.A. Henry (1945) studied 292 men who had been subjected to a landmine explosion, 52% of whom had suffered eardrum rupture. He estimated the overpressure as 17 psi. Other data reported on eardrum rupture are those of Vadala (1930) for anti-aircraft gun blast and those of Reider (1968) for two industrial explosions. These data have been plotted by Hirsch as shown in Figure 17.104.

Hirsch reviews the data for threshold and 50% probability of eardrum rupture and obtains for a fast rising overpressure, pulse estimates of 5 and 15 psi, respectively.

The probit equation for eardrum rupture obtained from Figure 17.104 is

$$Y = -12.6 + 1.524 \ln p^o \qquad [17.38.2]$$

Equation 17.38.2 is that given for eardrum rupture in the *Green Book*.

On the basis of the data given by Hirsch, W.E. Baker *et al.* (1983) have derived a P–I diagram for eardrum rupture. The lines for the threshold and 50% probability values are horizontal lines and correspond to peak overpressures of 5 and 15 psi, respectively.

17.38.2 Lung injury

Direct blast effects, particularly lung haemorrhage, have been studied by a number of workers, including Zuckerman (1940, 1941), Krohn, Whitteridge and Zuckerman (1942), Glasstone (1962), I.G. Bowen, Fletcher and Richmond (1968), Richmond, Damon *et al.* (1968), C.S. White (1968b) and C.S. White *et al.* (1971).

Early work on direct blast effects was carried out by Zuckerman (1940), who combined experimentation on the exposure of tethered goats to explosions with analysis of air raid casualties. In the experiments he used 70 lb charges, giving an overpressure of about 15 psi at 30 ft with a duration time of about 5 ms. Zuckerman estimated that for a 500 lb bomb the lethal overpressure for man is between 400 and 500 psi (between 27.6 and 34.5 bar).

The data of Glasstone and of White are shown in Table 17.53. These data indicate for long overpressure pulses a 50% lethality at an overpressure of about 60 psi

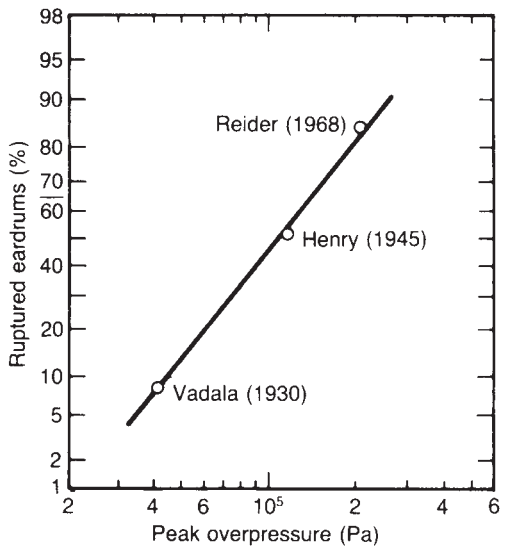

Figure 17.104 *Injury effects of explosions: eardrum rupture (after F.G. Hirsch, 1968) (Courtesy of the New York Academy of Science)*

(4.1 bar), but for short pulses much higher values of overpressure.

Work by Withers and Lees (1991) suggests that the overpressure for 50% lethality increases from about 10 bar for charges of 10 kg TNT to 4 bar for charges of 1000 te TNT.

Relations for death due primarily to lung haemorrhage are given in the vulnerability model by Eisenberg, Lynch and Breeding. They quote the following data from Fugelso, Weiner and Schiffman:

Probability of facility	*Peak overpressure*	
	(psi)	(N/m^2)
1 (threshold)	14.5	100,000
10	17.5	120,000
50	20.5	140,000
90	25.5	175,000
99	29.0	200,000

They derive from these data a probit equation relating death primarily from lung haemorrhage to peak overpressure:

$$Y = -77.1 + 6.91 \ln p^{o} \qquad [17.38.3]$$

Extensive work on direct blast effects was conducted in the 1950s and 1960s at the Lovelace Foundation and has been reported by Bowen, Fletcher, Richmond, White and co-workers (e.g. I.G. Bowen, Fletcher and Richmond, 1968; Richmond, Damon *et al.*, 1968; C.S. White *et al.* 1971).

This work has yielded a large amount of data on blast effects. The effects were studied for a variety of positions of the subject (standing, lying, etc.) and of situations of the subject (free stream, near wall, etc.). It was therefore necessary to correlate the results not only in terms of the peak incident overpressure, but also of various peak reflected overpressures.

J.G. Bowen, Fletcher and Richmond (1968) distinguish between the cases shown in Figure 17.105. Figure 17.105(a) shows the case where the longitudinal axis of the body lies

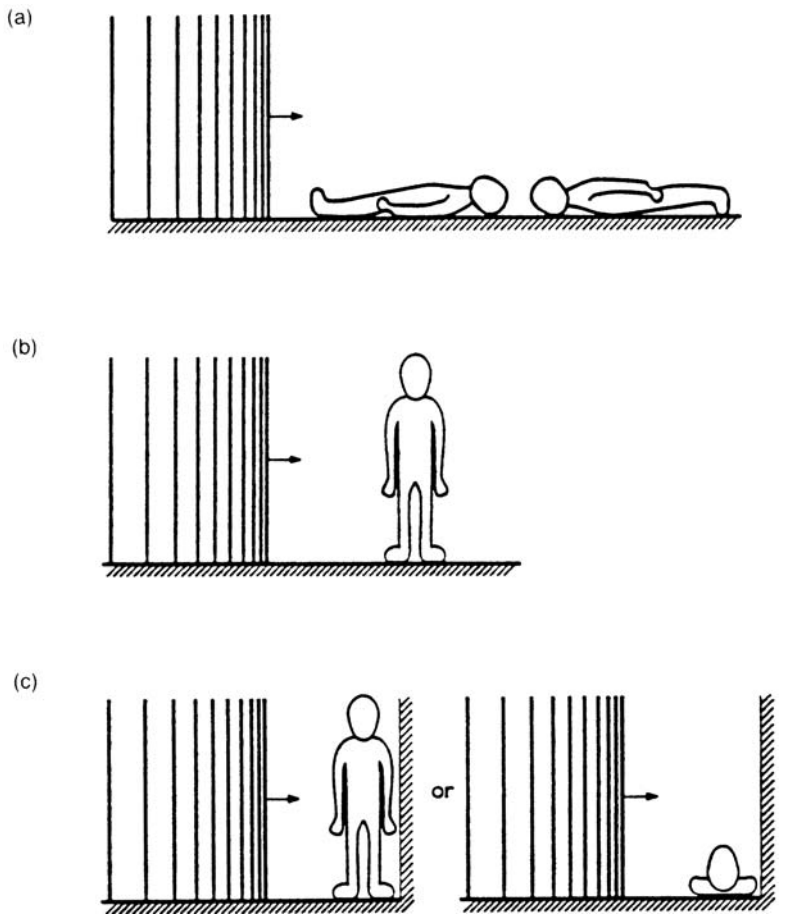

Figure 17.105 *Injury effects of explosions – postures determining lung injury (I.G. Bowen, Fletcher and Richmond, 1968): (a) long axis of body parallel to the direction of the blast wave; (b) long axis of body perpendicular to the direction of the blast wave; (c) thorax near a surface against which the blast wave reflects at normal incidence*

in the direction of the shock wave. For this case the peak applicable overpressure is

$$p_a^o = p^o \quad [17.38.4]$$

where p^o is the peak incident overpressure (Pa) and $p_a{}^o$ is the peak applicable overpressure for lung injury (Pa). In Figure 17.105(b) the longitudinal axis of the body is perpendicular to the shock wave. The peak applicable overpressure is in this case

$$p_a^o = p^o + q^o \quad [17.38.5]$$

where q^o is the peak dynamic pressure (Pa). The dynamic pressure is given by the *Green Book* as $q^o = 5P_s^2/(2p_s + 14 \times 10^5)$ for p_s in p_a. The case where the body is in any arbitrary position in front of a surface on which the shock wave reflects is shown in Figure 17.105 (c). In this case the peak applicable overpressure is

$$p_a^o = p_r^o \quad [17.38.6]$$

where p_r^o is the peak reflected overpressure. Expressions for the peak dynamic pressure and peak reflected overpressure are given in Equations 17.25.5 and 17.25.7, respectively.

One of the correlations for lung injury caused by the peak applicable overpressure is shown in Figure 17.106.

These injury relations have been converted by W.E. Baker *et al.* (1983) to the alternative form of a P–I diagram as shown in Figure 17.107. The definition of the scaled peak applicable overpressure and scaled impulse for use in this figure are

$$\bar{p}_a^o = \frac{p_a^o}{p_a} \quad [17.38.7]$$

$$\bar{i} = \frac{i}{p_a^{1/2} m^{1/3}} \quad [17.38.8]$$

where i is the impulse (Pa s), $\bar{i}$ is the scaled impulse ($Pa^{1/2}$ s/$kg^{1/3}$), m is the mass of the body (kg), p_a is the atmospheric pressure (Pa) and is the scaled peak applicable overpressure. These authors recommend the following values for body mass: babies 5 kg, small children 25 kg, adult women 55 kg and adult men 70 kg. These correlations of Bowen, Fletcher and Richmond and of Baker *et al.* are referred to in the *Green Book*, which gives a P–I diagram broadly similar to Figure 17.107 together with the following associated probit equation:

$$Y = 5 - 5.74 \ln S \quad [17.38.9]$$

with

$$S = \frac{4.2}{\bar{p}_a^o} + \frac{1.3}{\bar{i}} \quad [17.38.10]$$

where S is a 'damage number' and Y the probit for fatal injury.

17.38.3 Whole body displacement

Another blast effect is bodily translation, or whole body displacement. Accounts of whole body displacement are given by Glasstone (1962), Clemedson, Hellstrom and Lindgren (1968), C.S. White (1968b, 1971), Richmond and Fletcher (1971), W.E. Baker *et al.* (1983), Hadjipavlou and Carr-Hill (1986) and in the *Green Book*.

The data of Glasstone (1962), Clemedson, Hellstrom and Lindgren (1968), C.S. White (1968b, 1971) and Richmond and Fletcher (1971) are shown in Table 17.54.

The treatment for body translation in the vulnerability model by Eisenberg, Lynch and Breeding is somewhat complex. They derive a probit equation relating lethality for body translation to impulse:

$$Y = -46.1 + 4.82 \ln J \quad [17.38.11]$$

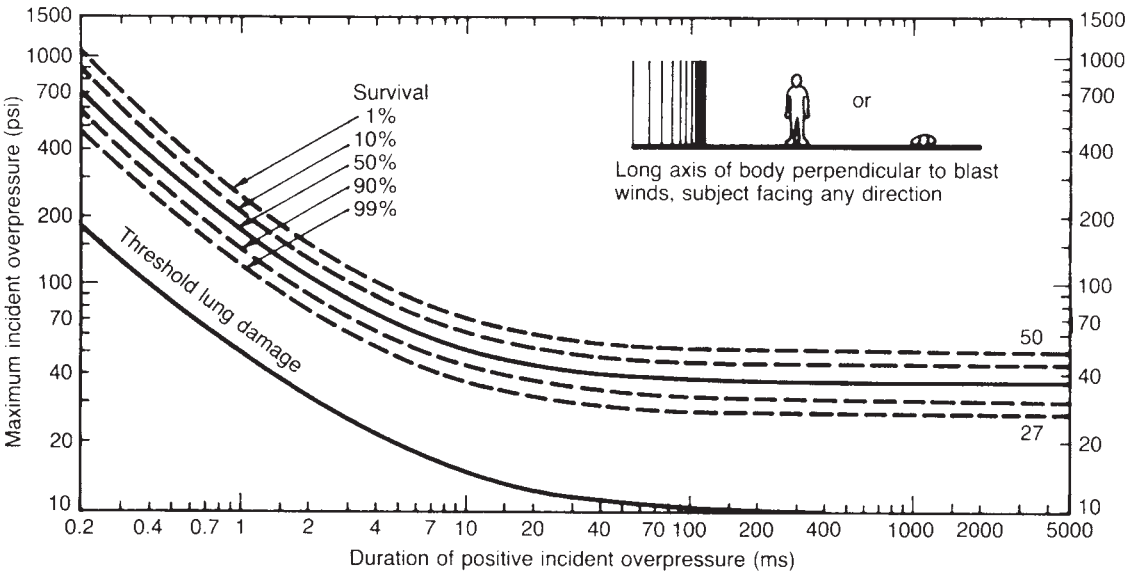

Figure 17.106 *Injury of explosions: lung injury – 1 (I.G. Bowen, Fletcher and Richmond, 1968). Survival curves for a 70 kg man in a free-stream situation with the long axis of the body perpendicular to the direction of the blast wave*

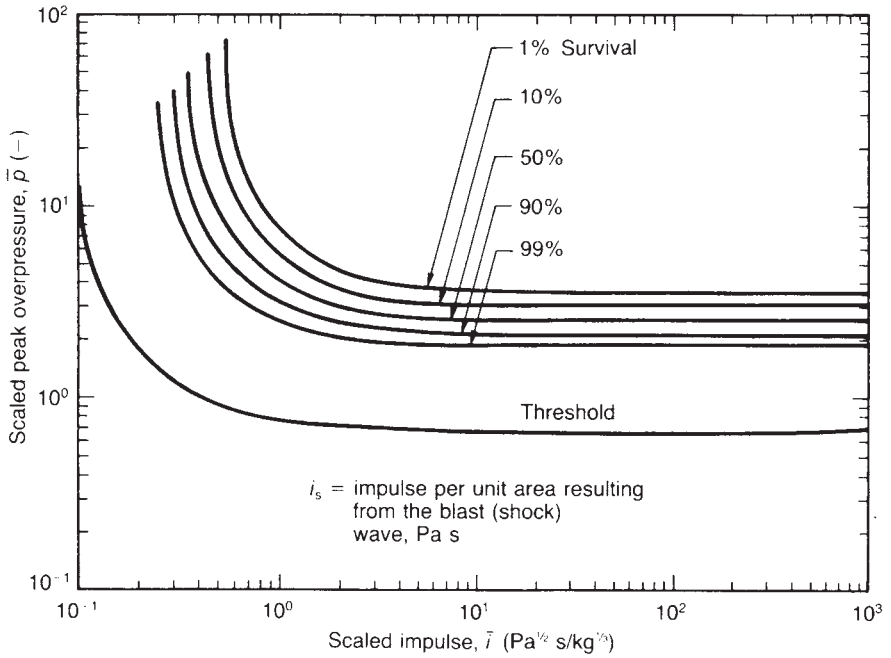

Figure 17.107 *Injury effects of explosions: lung injury – 2 (W.E. Baker et al., 1983). P–I diagram for survival applicable to all three standard postures and to different body weights (see text) (Reproduced by permission of Elsevier Science Publishers)*

with

$$J = \int_0^{t_d} p(t)\,\mathrm{d}t \qquad [17.38.12]$$

where J is the impulse (Pa s), p is the incident overpressure (Pa) and t_d is the duration time (s). They also derive a probit equation relating serious injury for body translation to impulse:

$$Y = -39.1 + 4.45 \ln J \qquad [17.38.13]$$

A fundamental treatment of whole body displacement of a person standing involves consideration of the following effects: (1) displacement from the upright to the prone posture, (2) bodily translation followed by impact of the skull, (3) bodily translation followed by impact of the whole, body and (4) tumbling across open terrain, or decelerative tumbling. In the first three cases, injury is due mainly to impact, whilst in the fourth flailing of the limbs is a significant contributor.

Considering these effects in turn, the treatment of displacement from upright is broadly as follows. It is first necessary to consider the force acting on the body. An account of the force acting on structures and objects of different configurations is given in Section 17.32. If the human body is treated like an element in an open structure, the relevant force is that due to the dynamic pressure. Then the force acting on the body initially is

$$F = C_D q^o A \qquad [17.38.14]$$

where A is the projected area of the body (m^2), C_D is the drag coefficient and F is the force acting on the body (N). The dynamic pressure decays from the peak dynamic pressure to 0 over the period of the dynamic pressure duration t_q. Assuming that the shape of the dynamic pressure impulse i_q can be approximated by a triangle,

$$i_q = \tfrac{1}{2} q^o t_q \qquad [17.38.15]$$

where i_q is the dynamic pressure impulse (Pa s) and t_q is the dynamic pressure duration (s). Neglecting deceleration, the velocity u attained by a body of mass m due to this impulse is given by

$$mu = \frac{F t_q}{2} \qquad [17.38.16]$$

where m is the mass of the body (kg) and u is the velocity imparted to the body (m/s).

Relations for the peak dynamic pressure and dynamic pressure impulse are given in Section 17.25. These in combination with the equations just given allow the velocity imparted to the body to be estimated.

A more refined model for bodily translation is given by Hadjipavlou and Carr-Hill (1986), which they term the 'centre-of-mass' model. This model is

$$\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} = \alpha L(t) - F(t) \qquad [17.38.17]$$

Table 17.54 *Some data on the injury effects of explosions: whole body displacement*

A Data in terms of body velocity (Glasstone, 1962)

	Impact velocity	
	(ft/s)	(m/s)
Standing stiff legged impact		
Mostly 'safe'		
No significant effect	<8	<2.44
Severe discomfort	8–10	2.44–3.05
Injury:		
Threshold	10–12	305–3.7
Fracture threshold (heels, feet, legs)	13–16	4.0–4.9
Seated impact		
Mostly 'safe'		
No significant effect	<8	<2.44
Serve discomfort	8–14	2.44–4.3
Injury:		
Threshold	15–26	4.6–7.9
Skull fractures[a]		
Mostly 'safe'	10	3.0
Threshold	13	4.0
50%	18	5.5
Near 100%	23	7.0
Total body impact[b]		
Mostly 'safe'	0	3.0
Lethality threshold	21	6.4
Lethality 50%	54	16.5
Lethality near 100%	138	42

B Data in terms of dynamic impulse (Richmond and Fletcher, 1971)

	Dynamic pressure impulse (psi ms)	*Peak horizontal body velocity*	
		(ft/s)	(m/s)
No personnel blowdown	1.25	0.3	0.092
50% personnel blowdown	8.3	2.0	0.61
1% serious injury from being blown down[c]	54	13	4.0

[a] Data quoted by Clemedson, Hellstrom and Lindgren (1968); C.S. White (1968b, 1971).
[b] Earlier data were given by C.S. White (1968b). The values given here are later, revised values given by C.S. White (1971).
[c] Serious injury such as bone fracture or rupture of internal organs could occur from impact with the ground; high probability of minor injuries such as bruises and lacerations.

with

$$\frac{dx}{dt} = u \qquad [17.38.18]$$

$$\alpha = \frac{AC_D}{m} \qquad [17.38.19]$$

$$L(t) = P_e(t) \qquad [17.38.20]$$

where A is the projected area of the body (ft^2), C_D is the drag coefficient, F is the deceleration due to friction (ft/s^2), L is the loading on the body (lb_f), m is the mass of the body (lb), P_e is the effective pressure on the body (lb_f/ft^2), t is the time (s), u is the velocity of the body (ft/s), x is the distance travelled by the body (ft) and α is the acceleration coefficient (ft^2/lb).

The authors use for the loading an effective pressure which includes an overpressure as well as a dynamic pressure term. They give values of the acceleration coefficient α for a number of postures. That for a person standing with the body square on to the blast wave is 0.052 ft^2/lb. Then from Equation 17.38.19 for a body area A of 8.9 ft^2 and mass m of 165 lb, the corresponding value of the drag coefficient C_D is about 1.0. They quote for the deceleration of the body the following equation of E.R. Fletcher and Bowen (1968):

$$F(t) = 8.9u(t)^{0.383} \qquad [17.38.21]$$

This centre-of-mass model may be rewritten as

$$m\frac{du}{dt} + m\phi_{fr}(t) = L(t) \qquad [17.38.22]$$

where L is the loading (N), m is the mass of the body (kg), t is the time (s), u is the velocity of displacement (m/s) and ϕ_{fr} is

the deceleration due to friction (m/s^2). If the load is taken as due only to the dynamic pressure

$$L(t) = C_D q(t) \quad [17.38.23]$$

The deceleration term is obtained, with suitable change of units, from Equation 17.38.21.

Hadjipavlou and Carr-Hill give an extensive treatment of the velocity attained by a body subject to a blast wave.

The injury effects arising from whole body displacement may then be determined from the data given in Table 17.54.

Several authors have given probit equations for such injury effects. For lethal injury due to body translation with impact of the skull on a hard surface the following equation is given by Hadjipavlou and Carr-Hill (1986) based on the data of Gurdjian, Webster and Lissner (1949):

$$Y = -6.04 + 7.11 \ln u \quad [17.38.24]$$

where u is the velocity of the body (m/s). For lethal injury due to body translation with impact of the whole body on a hard surface, R.K. Jones, Richmond and Fletcher (1969) give

$$Y = -2.14 + 2.54 \ln u \quad [17.38.25]$$

E.R. Fletcher, Yelverton *et al.* (1975) also give an equation for serious injury due to impact on a hard surface:

$$Y = 0.82 + 2.697 \ln u \quad [17.38.26]$$

The basis of this equation is unclear, but it is suggested by Hadjipavlou and Carr-Hill that it appears to be based on Equation 17.38.25 of Jones, Richmond and Fletcher with a reduction in the severity of the effect considered and a corresponding reduction in velocity.

A treatment of injury by whole body displacement is given by W.E. Baker *et al.* (1983) utilizing P–I diagrams.

The *Green Book* gives the following equations for lethal injury due to body displacement followed by impact with a hard surface. For skull impact

$$Y = 5 - 8.49 \ln S \quad [17.38.27]$$

with

$$S = \frac{2.43 \times 10^3}{p^o} + \frac{4 \times 10^8}{p^o i}, \quad p^o < 4 \times 10^5 \quad [17.38.28]$$

where i is the overpressure impulse (Pa s), p° is the peak incident overpressure (Pa) and S is an injury factor. For whole body impact

$$Y = 5 - 2.44 \ln S \quad [17.38.29]$$

with

$$S = \frac{7.38 \times 10^3}{p^o} + \frac{1.3 \times 10^9}{p^o i} \quad p^o < 4 \times 10^5 \quad [17.38.30]$$

The *Green Book* also gives the corresponding P–I diagrams.

Turning to decelerative tumbling, Glasstone (1962) describes experimental work in which cadavers of several animal species, including sheep and goats, were dropped from the back of a vehicle travelling at speeds of between 10 and 60 mph (4.5 to 27 m/s). All the animals assumed a rolling posture along their long axis regardless of initial orientation. One conclusion of this work was that a person tumbling over a smooth surface might survive even if the initial velocity were high provided head injury and flailing of the limbs were avoided. Another was that injury is likely to result not so much from the initial impact of the blast wave as from impact of the body with a hard object in its path.

Glasstone gives a graph for 50% casualties in decelerative tumbling over (a) open terrain and (b) terrain with structures for a 1 kt explosion. Casualties of 50% occur at 550 ft (168 m) and 680 ft (207 m), respectively. He also proposes the scaling law

$$d = d_r W^{0.4} \quad [17.38.31]$$

where d is the distance for 50% casualties (ft), d_r is the distance for 50% casualties for a 1 kt TNT explosion (ft) and W is the mass of TNT (te). Equation 17.38.31 gives for this size of explosion a 50% probability of casualty at 222 and 274 m for open terrain and terrain with structures, respectively.

E.R. Fletcher and Bowen (1968) have given for the decay of velocity in decelerative tumbling Equation 17.38.21 above.

An alternative treatment is that described by W.E. Baker *et al.* (1983). The work of W.E. Baker *et al.* (1975) is used to predict the translation velocity of the human body, the correlation being in the form of a P–I diagram with translational velocity as the parameter. Use is then made of data on the relation between level of injury and impact velocity given by Clemedson, Hellstrom and Lindgren (1968) and by C.S. White (1968b, 1971) as shown in Table 17.54. The authors state that there is some debate as to whether skull fracture or whole body injury is more important. They therefore present data for both injury modes.

17.38.4 Flying glass

Blast generates missiles, the main type of missiles considered in treatments of blast injury being fragments of flying glass. The injury caused by flying glass is considered in Section 17.40.

17.38.5 Thermal and toxic effects

An explosion, like a fire, gives rise to thermal and toxic effects. These effects have been dealt with in Chapter 16 on fire and are not considered further here.

17.38.6 Distribution of injury modes

The correlations just given may be used to obtain an estimate of the relative probabilities of injury in the different modes, or injury mode distribution. The distribution of injury modes for both outdoor and indoor exposure is considered in Section 17.39.

17.38.7 Combination of injury effects

In some cases there are finite probabilities of injury in more than one injury mode and/or injury by more than one item within a given mode. For example, a person may be exposed to injury by blast and by missiles. He or she may also be

exposed to injury by several items within one mode such as multiple fragments or different toxic gases.
The problem of multiple injuries and of double counting of injuries, including injuries from explosions, is discussed in Chapter 9.

17.39 Explosion Injury to Persons Indoors

For persons indoors, information on the specific explosion injury causes and modes applicable to persons in the open has some limited use, but for the most part it is necessary to rely on the correlation of injury with damage to structures, principally housing. Accounts of the latter are given in the *Green Book* and by Withers and Lees (1991), Gilbert, Scilly and Lees (1994h) and Oswald and Baker (2000).

The causes of explosion injury to a person indoors include those causing injury to a person in the open, namely, (1) blast, (2) whole body displacement, (3) missiles, (4) thermal effects, and (5) toxic effects but, in addition, (6) falling masonry and (7) asphyxiating dust.

There are also certain differences between the outdoor and indoor situations which modify the effect of some of these causes. Indoors the distances which the body can travel before impact are short and there are many more objects which can become missiles, including walls and windows.

The modes of explosion injury due to these causes include, for the causes common to outdoors and indoors, (1) eardrum rupture, (2) lung haemorrhage, (3) whole body displacement injury, (4) missiles injury, (5) burns, and (6) toxic injury and, for those specific to indoors, (7) crushing and (8) asphyxiation.

A large proportion of indoor casualties are due to the two causes specific to the indoor situation, falling masonry and asphyxiating dust, and a large proportion of the casualties are therefore in the two injury modes of crushing and asphyxiation. Injury due to these two causes, and in these two modes, is difficult to model by any means other than by correlation with structural damage.

17.39.1 Models based on housing damage

Hence, for the indoor situation the prime approach to estimation of injury is by correlation with structural damage. This may be complemented to some degree by appropriate application of the outdoor injury correlations.

It is convenient here to base the treatment on damage to, and injury to persons in, housing, followed by some limited discussion of the treatment for other structures.

Withers and Lees (1991) have analysed various events which have caused housing damage and associated fatalities, including tornadoes, earthquakes, air raids and chemical and gas explosions. They utilize two categories of injury. Primary injuries are those due to blast effects other than housing damage such as lung haemorrhage, whole body displacement, etc., and secondary injuries those due to housing damage such as falling masonry and asphyxiating dust. They define an additional category of housing damage U, uninhabitable, which is intermediate between the Cb and Ca damage categories. By reference to the original Jarrett equation, Equation 17.33.2, for which in British units the values of the constant k are 24 for Cb damage and 70 for Ca damage, they give a value of 33 for U damage. They estimate the number of fatalities by determining the area within the U damage circle and then taking a fatality rate of 0.1 persons per house, based on an occupancy of 2.5 persons/house. Some results given by their model for an explosion of TNT occurring at random and without warning in a built-up area are:

Mass of explosive (te)	*Primary fatalities*	*Secondary fatalities*	*Total fatalities*
10^{-2}	0.07	0.009	0.079
10^{-1}	0.45	0.19	0.62
1	2.46	3.9	6.2
10	11.3	33	44
100	80.4	186	263

Gilbert, Lees and Scilly (1994h) give a model for several different degrees of injury which they define as follows: K, killed; SI, serious hospital casualty; LI, slight hospital casualty and U, no injury requiring hospital treatment. They also define the following probabilities of injury: P(K) probability of fatal injury, P(K + SI) probability of fatal or serious injury and P(K + SI + LI) probability of fatal, serious or light injury. Further, they subdivide the A housing damage category into two further categories, Ab and Aa, where Ab corresponds to complete demolition and Aa almost complete demolition. Then, to obtain the numbers with each degree of injury they utilize their revised Jarrett equation, Equation 17.33.2 again, but with the revised values of the constant k, to determine the housing damage and the correlation given in Table 17.55 for injury as a function of housing damage. The latter is based on data giving the probabilities of injury in 12 V-2 rocket incidents.

Figure 17.108 shows the number of casualties predicted by the model of Gilbert, Lees and Scilly for the explosion of a charge of TNT located at random on a built-up area with a population density of 4000 persons/km^2.

By comparison with a load on a road vehicle, for which in most instances the road and its verges provide a degree of separation, the figures overestimate the casualties.

Oswald and Baker (2000) have developed a more general simplified vulnerability model primarily for industrial buildings that predicts the percentage of building occupants with serious, life-threatening injuries. Acta (2001) has developed a similar simplified model that predicts building damage and percentages of occupants with serious and fatal injuries in blast-loaded industrial buildings. W.S. Atkins has developed a more detailed model that

Table 17.55 *Injury as a function of housing damage for a condensed phase explosion occurring at random and without warning in a built-up area (Gilbert, Lees and Scilly, 1994h)*

Housing damage category	*Probability of injury*		
	P(K)	P(K + SI)	P(K + SI + LI)
Aa	0.96	1.0	1.0
Ab	0.57	0.66	0.82
A	0.62	0.71	0.84
B	0.086	0.15	0.38
Cb	0.009	0.043	0.13
Ca	0	0.002	0.006
D	0	0	0

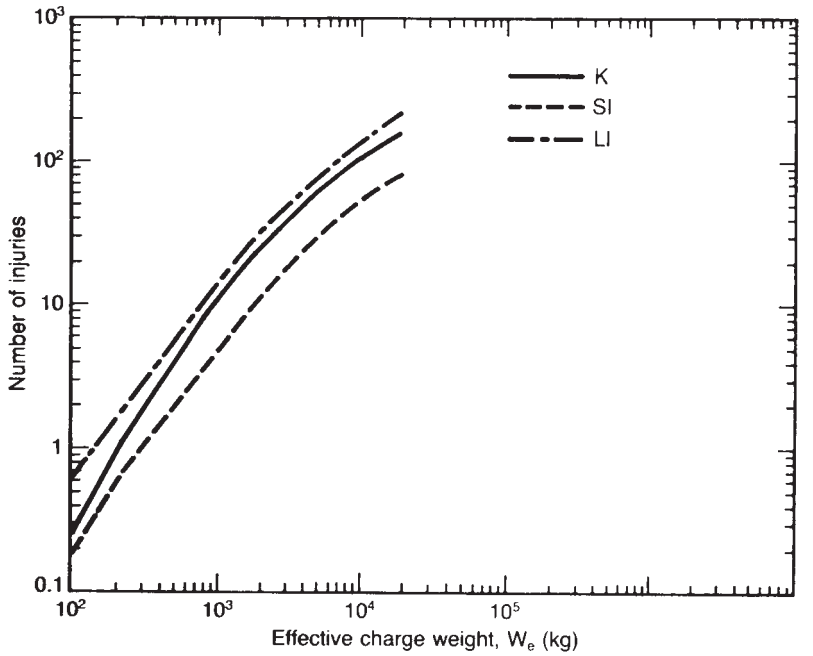

Figure 17.108 *Injury effects of explosions: number of injuries from explosion of a condensed phase explosive in a built-up area (Gilbert, Lees and Scilly, 1994h). Total injuries indoors and outdoors. Charge located in area at random. Population density 4000 persons/km^2. K, killed; SI, seriously injured; LI, lightly injured*

predicts the percentage of fatalities among occupants of blast-loaded buildings (HSE, 1997), including typical industrial buildings in the United Kingdom. This report was critiqued using available injury data in a subsequent HSE publication (HSE, 1998). Oswald (2003) also presents an overview of available injury data on occupants of blast-loaded buildings including some recent terrorist bombing events.

The treatment of injury due to building damage in the *Green Book* refers to building collapse and is based primarily on information relating injury to building collapse in earthquakes. It refers to the work of Blume (1971), who estimates that building collapse in an earthquake results in the death of 50% of the occupants, and to that of the US Department of Commerce (1973), which gives for these circumstances an estimate of 20% dead and 80% injured. The authors of the *Green Book* conclude from these and other data that building collapse in an earthquake causes between 20 and 50% dead and adopt the same figures for explosions. Building collapse is not defined, at least not at this point in the text.

It may be noted that the estimates of the *Green Book* and of the model of Gilbert, Scilly and Lees become consistent if building collapse is taken as a degree of housing damage somewhat more severe than A category but much less severe than B category damage.

17.39.2 Injury inside other structures

Information on the casualty rate in Britain in the Second World War was expressed in terms of standardized casualty rates. One such was the Standardized killed and hospitalized casualty rate (SKHCR). The following data are given in the *Textbook* for all weapons used in air raids:

	In open	*In dwellings*	*In other buildings*	*In shelters*	*All exposures*
SKHCR	18.85	5.31	5.45	1.94	5.07
Ratio	3.55	1.00	1.03	0.37	0.95

where the ratio is that of the SKHCR in question to the SKHCR for dwellings.

17.39.3 Distribution of injury modes

There is available some information on the distribution of injury modes from explosions for persons outdoors and indoors.

There are available a number of accounts of the casualties from explosions, both military and industrial. Descriptions of the casualties admitted to individual hospitals in the Emergency Medical Services (EMS) system for handling air raid casualties have been given by Payne (1941) for bomber raids and by R.C. Bell (1944) for V-1 flying bomb raids.

Bell gives an analysis of 259 flying bomb casualties. The breakdown of injuries is shown in Table 17.56. Some of the casualties had more than one type of injury so that the total number of entries is greater than 259. Theatre treatment was required in 83 cases.

Although these air raid data provide an indication of the injury modes, there are inevitable biases. They usually

exclude casualties who died on the spot, including those who died from asphyxiation by fumes and dusts.

More detailed information is given in the *Textbook*. Table 17.57 gives a breakdown of injuries to persons outdoors and persons indoors and overall, by cause in section A and by mode in section B. The data in Table 17.57 show that a large proportion of injuries indoors were caused by falling debris and asphyxiating dust.

Table 17.56 *Distribution of injuries in casualties requiring surgery*[a] *admitted to a London hospital during the V-1 flying bomb raids (after R.C. Bell, 1944) (Courtesy of the British Medical Journal)*

	Cases		*Deaths*	
	No.	%	*No.*	%
Glass	100	47.4	1	6.3
Bomb splinters	24	11.4	3	18.7
Masonry	52	24.6	9	56.2
Blast	26	12.3	2	12.5
Burns	9	4.3	1	6.3
Total surgical	211			

[a] There were 259 casualities admitted, but some are classified in more than one category, so that there were 211 surgical cases.

A study of 81 chemical and gas accidents has been described by Settles (1968). Of these, 44 involved fire and explosion, 23 fire only and 14 a detonation reaction. Settles states:

> The 14 accidents in which detonating forces were present resulted in injuries to 35 persons and 34 fatalities. It appears from information available that only one of these 34 deaths resulted from blast overpressures that are associated with a detonating reaction. However, this one fatality was not the result of blast damage to human tissue. Rather, the blast pressure caused this individual to be propelled as a projectile. The other 33 persons who died in these 14 accidents were located at points where the density of flying fragments and in some cases, the lethal searing of radiant heat, were so great that their deaths were certain, even though there were no blast effects.

17.39.4 Models based on injury modes

An alternative approach to models based on housing damage is to try to estimate the overall probability of injury from the individual modes. Correlations for injury to persons outdoors which may be relevant here are those for lung haemorrhage, whole body displacement injury, missile injury, including that from flying glass, and thermal and toxic injury. However, models are lacking for two of the principal modes, crushing and asphyxiation. This makes it difficult to construct a satisfactory model of indoor injury in this way.

Table 17.57 *Causes and modes of injury (proportion, %) by bombs in Second World War air raids (Ministry of Supply, 1952)*

A Injury causes[a]

	In dwellings			*Outdoors*			*All exposures*		
	Fatal	*Hospitalizing*	*Total*	*Fatal*	*Hospitalizing*	*Total*	*Fatal*	*Hospitalizing*	*Total*
Bomb fragments	14.1	4.7	9.1	38.5	32.8	34.9	19.7	13.7	16.3
Burns	2.7	1.2	1.9	4.4	1.1	2.4	3.8	1.5	2.5
Blast	2.4	0.2	1.3	1.3	0.2	0.6	1.8	0.2	0.9
Flying glass	0.2	10.6	5.8	0	2.7	1.7	0.4	6.2	3.7
Flying debris	16.3	19.5	18.0	17.6	32.6	26.9	16.0	24.2	20.6
Falling debris	46.1	45.4	45.7	10.9	7.3	8.7	36.0	34.5	35.2
Falls, etc.	5.8	11.7	8.9	13.5	19.0	16.9	9.5	13.8	11.9
Other/unknown	12.3	6.6	9.2	13.8	4.2	7.9	12.9	5.8	8.9
Total injuries	439	498	937	160	261	421	850	1,117	1,967
Total casualties	353	303	656	122	159	281	680	684	1,364

B Injury modes

	In dwellings		*Outdoors*		*All exposures*	
	Fatal	*Non-fatal*	*Fatal*	*Non-fatal*	*Fatal*	*Non-fatal*
Asphyxia	21	–	4	–	17	–
Gross injuries[a]	20	1.5	17.5	1.6	18	1
Penetrating injuries	9	24	22	47	11	30
Fractures	19	50	28.5	38	23	47.2
Crush injuries	14	1.6	9	0.8	12	1
Bruises/abrasions	–	8	–	4	–	4.4
Eye injuries	–	5	–	2	–	5
Other/unknown	17	9	19	8.2	19	11
Total injuries	439	196	158	126	850	483
Total casualties	353	122	122	77	680	306

[a] Gross injuries include cases where the victim was blown to bits.

17.39.5 Models based on total injury

The foregoing account has given information on individual modes of injury. Studies have also been done to assist in the determination of total injury by all modes.

Rausch, Eisenberg and Lynch (1977) have described studies in support of the vulnerability model in which an attempt has been made to assess total injury. They deal in particular with the disintegration of walls and the resultant flying debris, other flying objects and bodily translation. They also refer in particular to work by Longinow *et al.* (1973) and Fricke (1975) on injury from nuclear explosions and from low yield nuclear explosions, respectively. These authors have studied total injury by all the principal modes for people in the open and indoors in various types of building. The work on low yield explosions is of particular relevance and although the work was classified some information was released.

The estimates of the overpressures associated with 50% probability of fatality for people outdoors and indoors for such low yield explosions are shown in Figure 17.109. The yields are for nuclear weapons and should be divided by 2 obtain the TNT equivalent. Figure 17.109(a) shows the basic injury mode curves from which the other graphs are derived. Figure 17.109(b) shows the curves for injury to persons outdoors in the open and outdoors in a built-up area and Figure 17.109(c) to persons indoors in housing. Figure 17.109(d) shows the curves for all situations. There is one curve for injury by all modes to persons outdoors in the open and one for injury by all modes to persons outdoors in a built-up area or indoors in housing. The figures also gives curves for 50% probability of burdening injury. For persons subject to injury by glass fragments, however, the peak overpressures for 50% probability of fatality and burdening injury are taken as 11 and 1 psi, respectively.

17.40 Explosion Injury from Flying Glass

The shattering of window glass is an important blast damage effect, since flying glass can cause severe injury.

17.40.1 Experimental studies

There have been a number of experimental studies of the behaviour of, and injury by, flying glass and also studies of glass breakage following accidental explosions and of injury by flying glass in accidents and air raids.

Experiments on the breaking of glass windows by internal gas explosions have been described by Mainstone (1971 BRE CP 26/71) and M.R. Marshall, Harris and Moppett (1977).

The Eskimo series of trials, which involved the breaking of windows using large external charges of TNT, have been described by E.R. Fletcher, Richmond and Jones (1973) and E.R. Fletcher, Richmond and Richmond (1974). In Eskimo II the charge was 12.6 te and in Eskimo III 159 te.

Window breakage is among the damage effects of the explosion of 5001 TNT equivalent referred to by Fugelso, Weiner and Schiffman (1972).

There are also a number of accounts of the extent of window breakage following accidental explosions. Window breakage is one of the explosion effects analysed by C.S. Robinson (1944). Healy (1959) deals with window breakage in air raids.

The window breakage resulting from a large accidental explosion at Medina, San Antonio, Texas in 1963 has been described by Reed and co-workers (Q.W. Reed *et al.* 1968; J.W. Reed, 1980, 1992). The explosion involved 111, 500 lb of high explosive, equivalent to 145, 000 lb of TNT.

A review of window breakage is given by D.K. Pritchard (1981).

17.40.2 Flying glass models

A model for the behaviour of flying glass should cover the following features: (1) breaking pressure, (2) fragment characteristics, (3) velocity of fragments, (4) spatial density, and (5) distance travelled by fragments. These features are now considered in turn.

17.40.3 Breaking pressure

The pressure at which windows break is generally quoted in terms of the peak side-on overpressure.

The force acting on the window is that of the peak reflected pressure. For a window directly facing the source of the explosion, the peak reflected pressure is some two times the peak side-on overpressure. For random orientation of windows J.W. Reed (1992) estimates an average reflection factor not of 2 but of 1.32.

The strength of window glass is very variable. It is not uncommon for an explosion to cause isolated window breakages at very considerable distances, and correspondingly low overpressures, while bangs from supersonic aircraft sometimes break windows at overpressures much less than those usually regarded as necessary to cause damage. Such instances, however, rarely cause injury.

Estimates of the peak side-on overpressure which causes window breakage have been given by a number of authors. Brasie and Simpson (1968) quote for the breaking pressure of glass windows a typical pressure of 1 kPa (0.145 psi). They also refer to breakage at low pressures of 0.2 kPa (0.029 psi) by sonic boom. Iverson (1968) gives the range of breaking pressures as 1–10 kPa (0.145–1.45 psi).

Some information on window breakage has already been given in Figure 17.92 and in Tables 17.43–17.44. Robinson's data show that for large explosions glass breakage can occur at great distances, of the order of 20 miles. The average glass breakage limit given in Table 17.44 is estimated by Brasie and Simpson (1968) to correspond to an overpressure of 0.006 psi, and they suggest that this is unrealistically low for estimation purposes.

Healy (1959) correlates window breakage in terms of the RB distance, and gives the following estimates:

RB distance	*Window breakage* (%)
5	90
10	50
20	5

These same estimates are given by Scilly and High (1986).

Glasstone (1962) gives the peak overpressure for window breakage as 0.5–1.0 psi (0.34–0.068 bar), as shown in Table 17.43, but without defining the proportion of windows broken.

Fugelso, Weiner and Schiffman (1972) give for the 5001 TNT equivalent explosion described above data on glass breakage also. These data have been analysed by Eisenberg, Lynch and Breeding (1975). The threshold or 1% level of glass breakage was 0.25 psi. They assume that the threshold level of structural damage corresponds

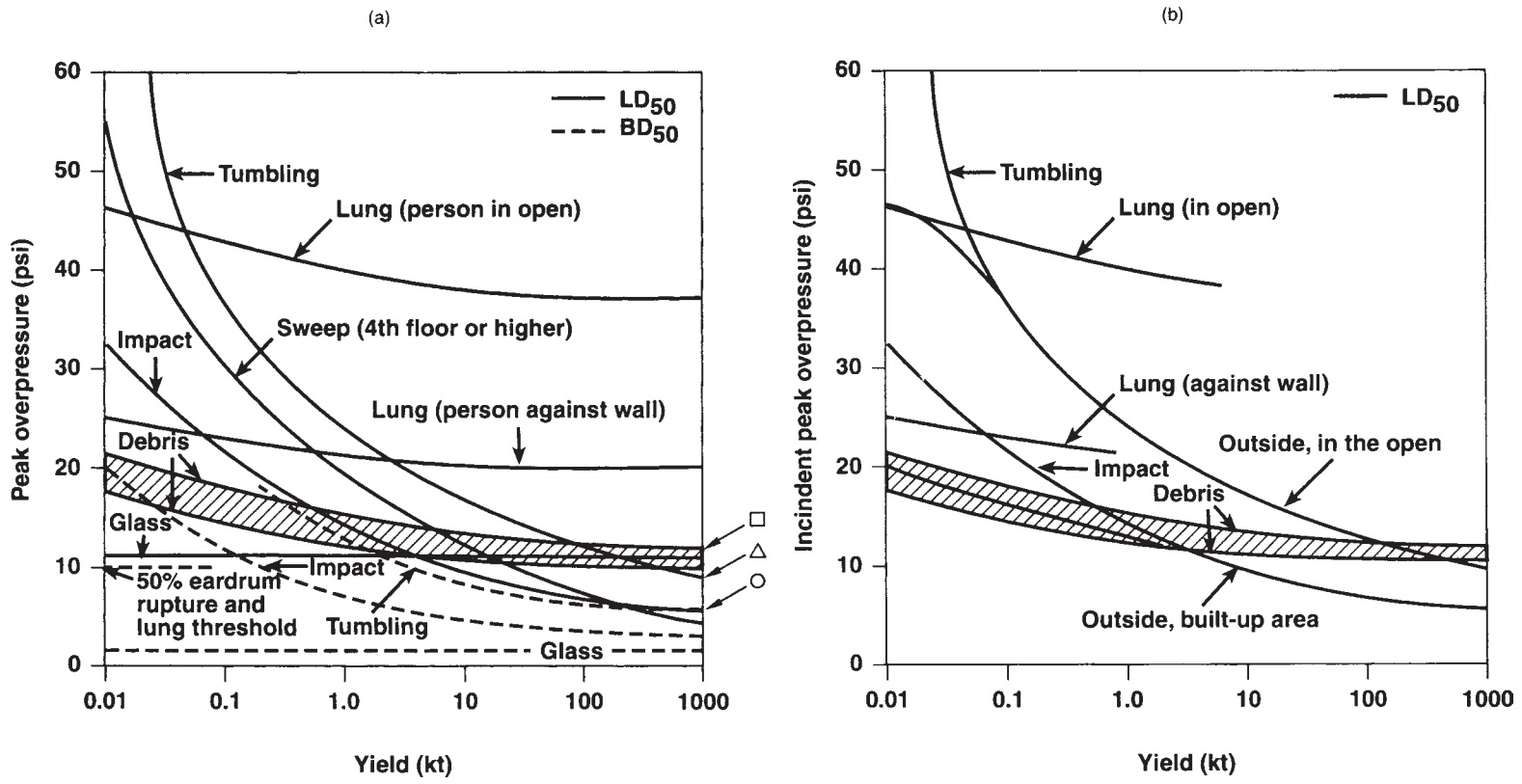

Figure 17.109 *Continued*

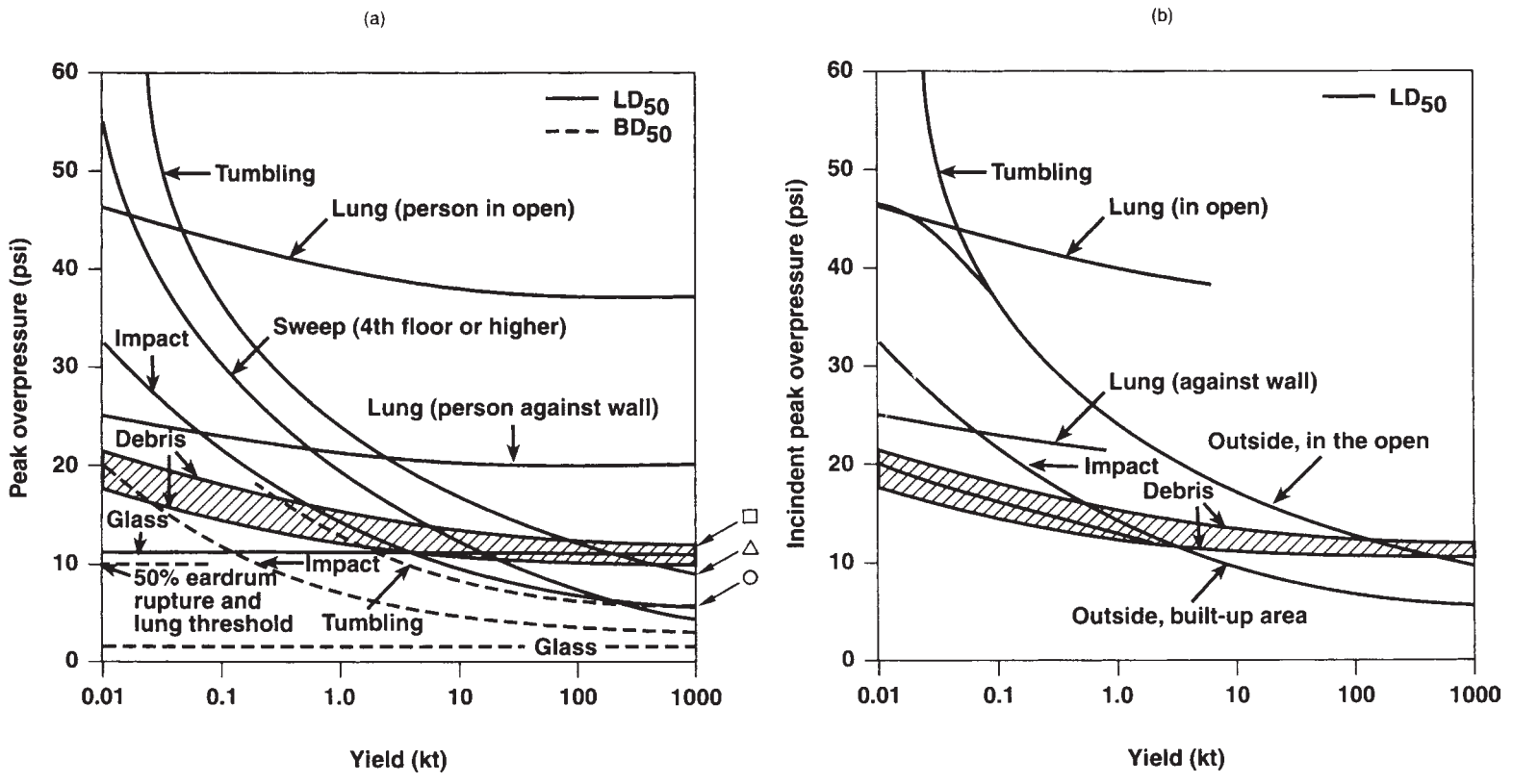

Figure 17.109 *Injury effects of explosions: lethal effects of low yield nuclear explosions (see text) (Fricke, 1975) BD_{50}, LD_{50}, load for 50% probability of burdening, lethal injury, respectively. (a): ○, LD_{50} for first three floors of buildings with weak walls, brick buildings and residences. △, LD_{50} for basements of wood-frame and brick-veneer residences; basements of steel and reinforced concrete framed buildings with flat plate ground floor. □, LD_{50} for first three floors of building with 'strong walls'; basements and sub-basements of steel and reinforced concrete framed building having flat slab or slab and beam ground floor construction. (d): 1, home basements; basements and sub-basements of multi-storey buildings; first three floors of strong-walled multi-storey buildings. 2, outside, in the open. 3, outside, built-up area; residence, above ground; first three floors of weak-walled multi-storey buildings. 4, fourth or higher floors of multi-storey buildings. 5, outside, in the open. 6, outside, built-up area; residences, above ground; multi-storey buildings, above ground. 7, basements*

to the 90% level for glass breakage and thus obtain the following data:

Glass breakage	*Peak overpressure* (%)	
	(psi)	(N/m^2)
1 (threshold)	0.25	1700
90	0.9	6200

They derive from these data a probit equation relating glass breakage to peak overpressure:

$$Y = -18.1 + 2.79 \ln p^{o} \qquad [17.40.1]$$

where p° is the peak incident overpressure (Pa) and Y is the probit.

In the Eskimo trials described by E.R. Fletcher, Richmond and Jones (1973) and E.R. Fletcher, Richmond and Richmond (1974), the thickness of the panes tested ranged from 0.08 to 0.128 in. (from 2 to 3.25 mm) and from 0.203 to 0.264 in. (from 5.16 to 6.7 mm). All the windows were positioned directly facing the blast wave and the peak effective overpressure was taken as the peak reflected pressure, or twice the peak incident overpressure. Although the duration times in Eskimo II were significantly shorter than in Eskimo III, this did not significantly alter the breaking pressure, indicating that for such large explosions at least the breaking pressure is essentially independent of duration. Some results from these trials are as follows:

Window size	*Breaking pressure*			
(m)	*Eskimo II*		*Eskimo III*	
	(Pa)	(psi)	(Pa)	(psi)
1.14×1.14	4830	0.70	4830	0.70
0.86×1.22	5930	0.86	5860	0.85

Window breakage in the Medina explosion has been analysed by Reed and co-workers (Q.W. Reed *et al.*, 1968; J.W. Reed, 1980, 1992). The typical window is given by J.W. Reed (1992) as single-strength glass 2 ft × 2 ft × 2 mm thick. He gives a graph showing the probability of breaking vs the peak incident overpressure. Gilbert, Lees and Scilly (1994h) found that the relationship is a log-normal one, and give the following probit equation for breaking of a 'Reed' window:

$$Y = -4.77 + 1.09 \ln p^{o} \qquad [17.40.2]$$

where p° is the peak effective overpressure (Pa) and Y is the probit. These authors also give the following relation for the determination of the peak effective overpressure for other windows for use in the above equation:

$$p_{e}^{o} = \left(\frac{A/0.372}{t/0.002}\right) p^{o} \qquad [17.40.3]$$

where A is the area of the pane (m^2), p° is the peak incident overpressure (Pa), p_{e}° is the peak effective overpressure for use in Equation 17.40.2 (Pa) and t is the thickness of the glass (m).

As already mentioned, experimental work on window breakage from internal gas explosions has been described by Mainstone (1971 BRE CP 26/71). Figure 17.110 shows the pressure for breakage for sheet glass panes of various thicknesses.

W.E. Baker *et al.* (1983) suggest that these data of Mainstone be treated as the quasi-static regime asymptote values.

Further experimental work on window breakage in internal gas explosions has been done by M.R. Marshall, Harris and Moppett (1977). Results from this work are given in Figure 17.111(a)–(d), showing breaking pressure as a function of glass thickness and window area.

These workers also investigated the behaviour of Georgian wired glass and glass treated with shatter resistant film, with the results shown in Figure 17.111.

Gilbert (1994) has analysed the results of Marshall, Harris and Moppett for plain glass windows as follows:

Window thickness (mm)	*Window size* (m × m)	*Pane area* (m^2)	*Breaking pressure*		*Ratio of thickness to area* (1/m)
			Range (kPa)	*Average* (kPa)	
5	1.0×1.0	1.03	6.2–7.6	6.9	0.00471
	1.0×0.5	0.515	8.3–11.7	10.0	0.0189
	0.48×0.48	0.233	15.2–20.7	18.0	0.0921
3	1.0×1.0	1.03	3.5–5.2	4.35	0.00283
	1.0×0.5	0.515	6.9–8.3	7.6	0.0113
	0.48×0.48	0.233	10.3–12.4	11.35	0.0553
4 (32 oz)	1.0×1.0	1.03	4.8	4.8	0.00377

and derives from them the relation

$$p_{br}^{*} = 132\frac{t}{A} + 5.43 \qquad [17.40.4]$$

where p_{br}^{*} is the breaking pressure (kPa) and t is the thickness of the pane (m).

The overpressures necessary to cause window breakage have been reviewed in the *Second Report* of the ACMH (Harvey, 1979b). The report quotes for a typical dwelling house window of 24 oz glass of area 1 m^2 the work of Marshall, Harris and Moppett, indicating that a peak overpressure between about 0.03 and 0.05 bar is needed to break it. It concludes that for typical dwelling house windows the peak overpressures at which 50 and 90% window breakage is likely to occur are 0.016 and 0.038 bar, respectively, but emphasizes that the breaking pressure is a function of a large number of variables.

17.40.4 Fragment characteristics

I.G. Bowen *et al.* (1963b), cited by Hadjipavlou and Carr-Hill (1986), have given correlations for the mass and initial velocity of fragments from window breakage, though it is unclear under what conditions. They found that the mass distribution was log-normal and gave the following probit equation:

$$Y = 5.97 + 0.86 \ln m \qquad [17.40.5]$$

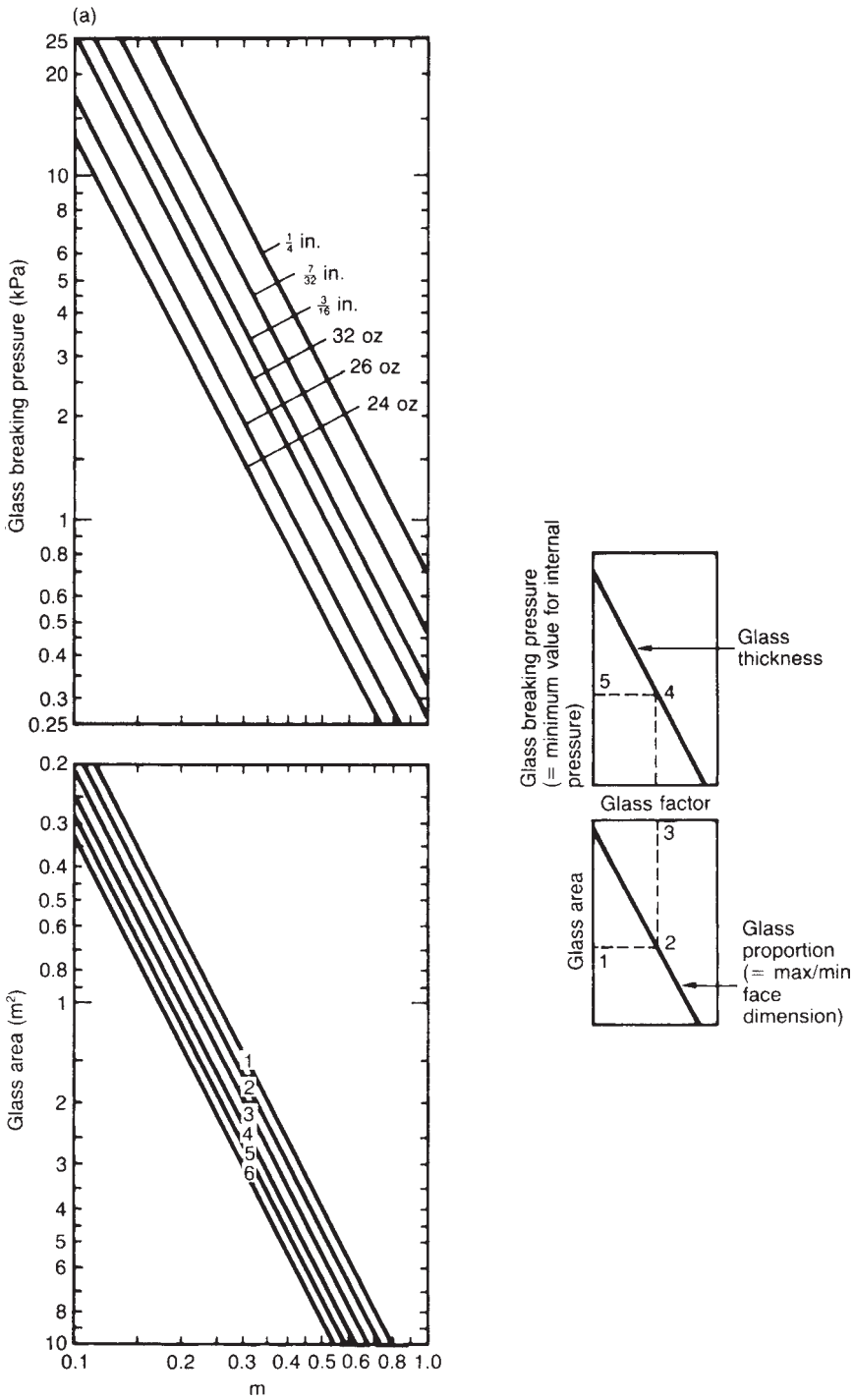

Figure 17.110 *Window breakage and flying glass from an internal gas explosion – breaking pressure of sheet glass panes (Mainstone, 1971): (a) sheet glass panes; and (b) plate glass panes (Courtesy of the Building Research Establishment)*

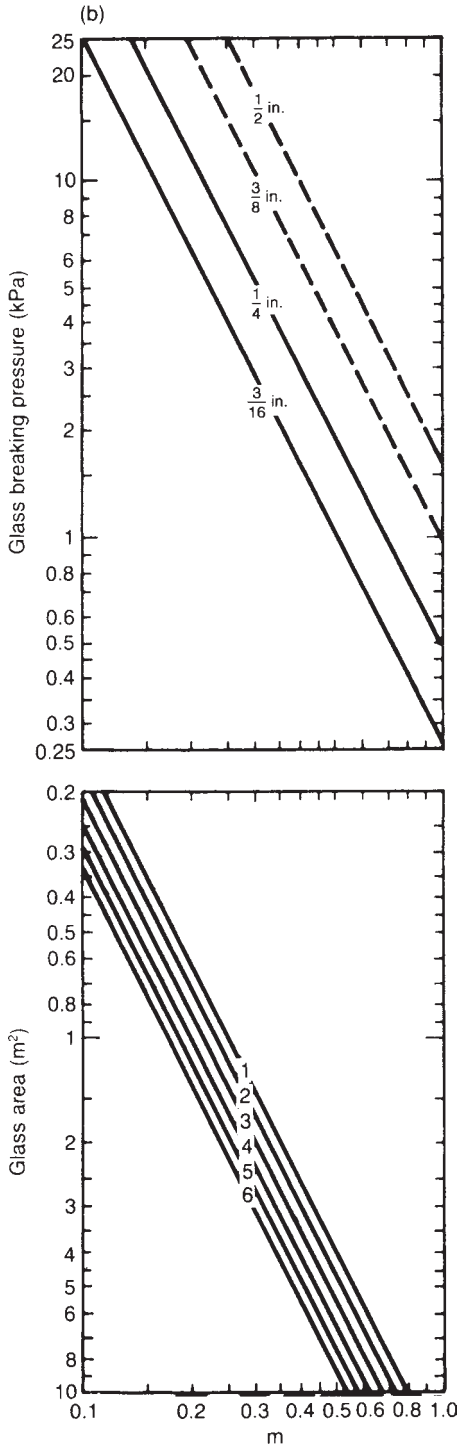

Figure 17.110 *Continued*

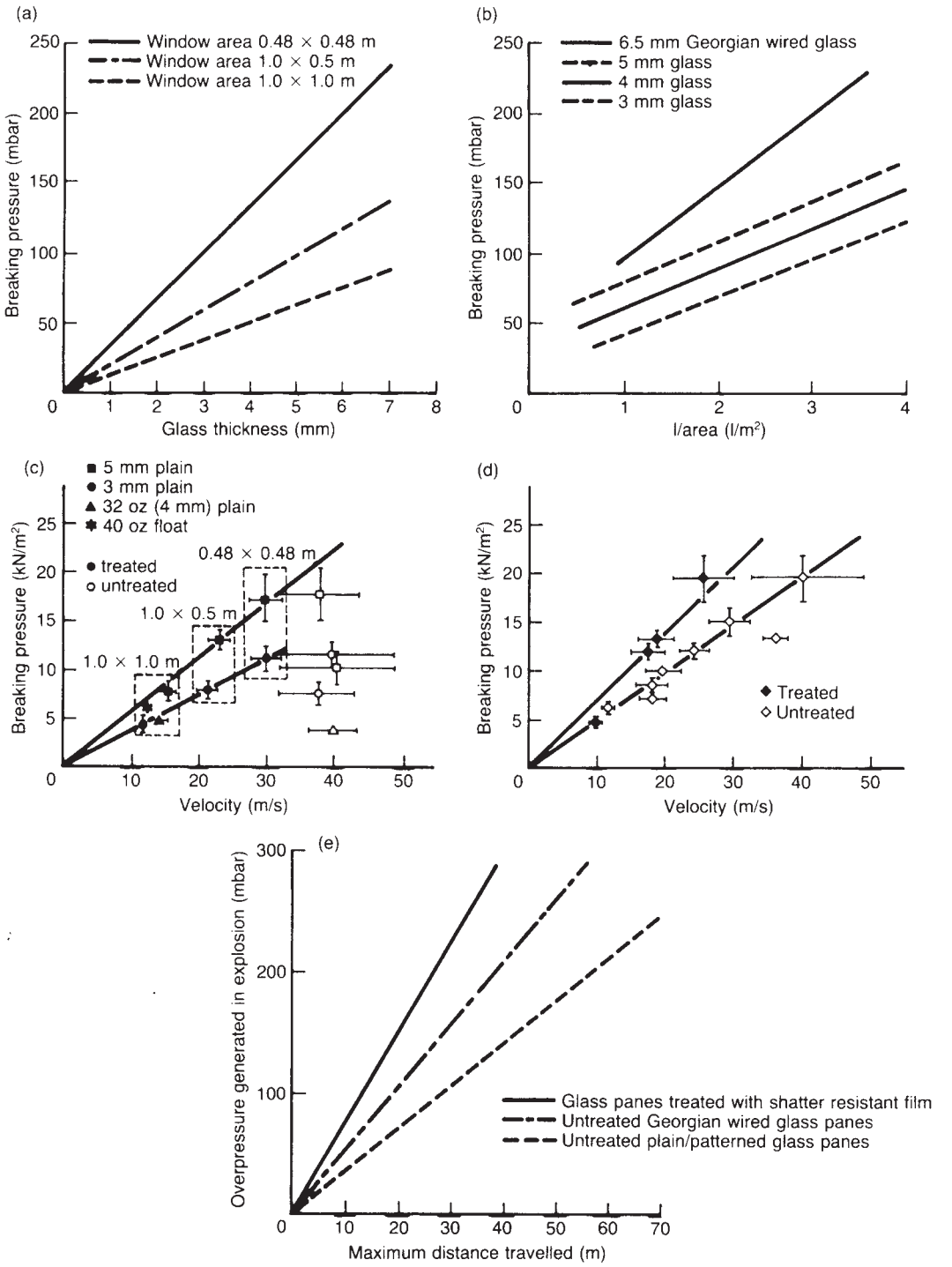

Figure 17.111 *Window breakage and flying glass – breaking pressure of windows and characteristics of flying (M.R. Marshall, Harris and Moppett, 1977): (a) breaking pressure as function of glass thickness; (b) breaking pressure as function of window area; (c) velocity of glass fragments, plain glass; (d) velocity of glass fragments, Georgian wired glass; and (e) distance traveled by glass fragments (Courtesy of the Institution of Chemical Engineers)*

where m is the mass of the fragment (g) and Y is the probit. The median value of the mass ($Y = 5$) is thus 0.324 g.

E.R. Fletcher, Richmond and Richmond (1974) characterize glass fragments in terms of the mean mass m_{50} and mean frontal area A_{50}. Their expression for the latter, in the form given by E.R. Fletcher, Richmond and Yelverton (1980), is

$$\ln A_{50}^{*} = 4.2643 - (12.5 + 0.003\,43 p_{e^*}^{\circ\,2})^{1/2} \qquad [17.40.6]$$

where A_{50}^{*} is the mean frontal area (cm^2) and $p_e^{\circ}*$ the peak effective overpressure (kPa).

The mean mass m_{50} may be then obtained as

$$m_{50} = A_{50}\rho_{gl}t \qquad [17.40.7]$$

where A_{50} is the mean frontal area of the fragment (m^2), m_{50} is the mean mass of the fragment (kg), t is the thickness of the fragment (m) and ρ_{gl} is the density of glass (kg/m^3).

This mean frontal area is not necessarily the mean presented area (MPA) on impact. This latter depends on the behaviour of the fragment during flight. Consider a fragment of rectangular cross-section and uniform thickness with a length : width ratio of 2 : 1. If the length of the long side is l and the thickness is t, the width is 1/2 and the area A_{50} is $l^2/2$. For a fragment approaching a target square on there are three possible MPAs: $l^2/2$, lt and $lt/2$. Taking the second of these, or the intermediate case, the MPA is then

$$A_{mp} = (2A_{50})^{1/2}t \qquad [17.40.8]$$

where A_{mp} is the MPA of the fragment on impact (m^2) l is the length of the fragment (m) and t is the thickness of the fragment (m).

A further treatment of fragment characteristics is given in Section 17.40.6.

17.40.5 Velocity of fragments

A treatment of the velocity of glass fragments is given by Glasstone (1962). He gives a correlation in terms of the geometric mean velocity V'_{50}, or antilogarithm of the mean of the logarithms of the velocities. He uses a scaled geometric mean velocity $\bar{V}'_{50}$, which allows for the thickness of the glass and which is defined as

$$\bar{V}'_{50} = \frac{V'_{50}}{0.83 + 0.019(t' - 0.03)^{-0.93}} \qquad [17.40.9]$$

where t' is the pane thickness (in.), V_{50} is the geometric mean velocity (ft/s) and $\bar{V}_{50}$ is the scaled geometric mean velocity (ft/s). The correlation relates the scaled geometric mean velocity to the peak effective overpressure applicable to conventional explosions of 15–500 t. Glasstone states that the correlation is based on experiments with various types of glass ranging from 0.25 in. thick plate glass, through various standard thicknesses of single- and double-strength glass, to non-standard glass panes 0.064 in. thick. This correlation may be represented as

$$\ln \bar{V}'_{50} = 3.746 + 0.546 \ln p_e'^{\circ} \qquad [17.40.10]$$

where p'° is the peak effective overpressure (kPa).

In the work described earlier, I.G. Bowen *et al.* (1963b) found that the velocities of fragments from window breakage had a log-normal distribution, and gave the probit relation

$$Y = -11.7 + 4.41 \ln u \qquad [17.40.11]$$

where u is the velocity of the fragment (m/s). The median value of the fragment mass was 0.324 g and the median value of the velocity from Equation 17.40.11 is 44 m/s.

A correlation of the initial velocity in the Eskimo trials is given by E.R. Fletcher, Richmond and Richmond (1974). Their expressions for the latter, in the form given by E.R. Fletcher, Richmond and Yelverton (1980), are as follows. A scaled velocity $\bar{V}_{50}$ is defined as

$$\bar{V}_{50} = \left(\frac{V_{50}}{0.833 + 0.04465(t^* - 0.0762)^{-0.928}}\right) \qquad [17.40.12]$$

where t^* is the thickness of the pane (cm), V_{50} is the geometric mean velocity (m/s) and $\bar{V}_{50}$ is the scaled geometric mean velocity (m/s). The correlation is

$$\ln \bar{V}_{50} = 1.5241 + 0.547 \ln p_e^{\circ}* \qquad [17.40.13]$$

where $p_e^{\circ}*$ is the peak effective pressure (kPa).

E.R. Fletcher, Richmond and Yelverton (1980) also give data on average impact velocity of fragments from which the following relation may be inferred:

$$\ln u = 1.5241 + 0.55 \ln p_e^{\circ}* \qquad [17.40.14]$$

where $p_e^{\circ}*$ is the peak effective overpressure (kPa) and V is the average velocity (m/s).

For an internal gas explosion the velocity of fragments from a breaking window is given by M.R. Marshall, Harris and Moppett (1977) in the work described earlier, as shown in Figure 17.111 (c). The velocity concerned is the average velocity over the first 6 m of travel. The mean values of the velocities in Figure 17.111(c) are in the range 35–40 m/s.

These data have been analysed by Gilbert, Lees and Scilly (1994h). The data for untreated unwired windows show wide scatter, but from those for wired glass there appears to be a factor of about 1.38 between the velocities from untreated and treated windows. Applying this same factor to the velocities from treated, unwired windows gives for untreated, unwired windows

$$u = 11.57\frac{p_{br}^{*}}{0.001t} \qquad [17.40.15]$$

where p_{br}^{*} is the breaking pressure (kPa), t is the thickness of the glass (m) and u is the average velocity of the fragments (m/s).

17.40.6 Velocity of fragments: method of Baker *et al.*

W.E. Baker *et al.* (1983) give the following treatment for the velocity of fragments from breaking windows based on the work of E.R. Fletcher, Richmond and Jones (1973, 1976). An effective peak overpressure P_e is defined, which for windows side-on or back-on to the blast wave is equivalent to the peak incident overpressure P_s and for those face-on, to the peak reflected overpressure P_r.

The latter may be obtained as follows:

$$\bar{P}_r = 2\bar{P}_s + \frac{(\gamma+1)\bar{P}_s^2}{(\gamma-1)\bar{P}_s + 2\gamma'} \quad \bar{P}_s \leq 3.5 \qquad [17.40.16]$$

with

$$\bar{P}_s = P_s/P_o \qquad [17.40.17]$$

$$\bar{P}_r = P_r/P_o \qquad [17.40.18]$$

where P_o is atmospheric pressure (Pa), P_e is the peak effective overpressure (Pa), $\bar{P}_r$ is the peak reflected overpressure (Pa), $\bar{P}_r$ is the dimensionless peak reflected overpressure, $\bar{P}_s$ is the peak side-on overpressure (Pa), and $\bar{P}_s$ is the dimensionless peak side-on overpressure. For $\bar{P}_s > 3.5$ the authors give an alternative equation (their Equation 3.5).

On the assumption that all the fragments are square, the mass of a fragment is

$$M = y^2 t \rho_{gl} = A t \rho_{gl} \qquad [17.40.19]$$

where M is the mass of the fragment (kg), t is the thickness of the glass (m), y is the length of the square edge (m) and ρ_{gl} is the density of glass (kg/m^3). The density of glass may be taken as 2471 kg/m^3.

The geometric mean frontal area A'_{50} of the fragments is given by the equation

$$A'_{50} = 6.45 \times 10^{-4} \exp\{2.4 - [12.5 + (5.86 \times 10^{-5} P_e)^2]^{1/2}\} \times 0 < P_e < 96,500 \qquad [17.40.20]$$

where A'_{50} is the geometric mean frontal area (m^2).

If all the fragments travel with the flat face forward, the presented area A of the fragments is

$$A = A'_{50} \qquad [17.40.21]$$

while if all fragments travel edge forward

$$A = t A'^{1/2}_{50} \qquad [17.40.22]$$

where A is the presented area of the fragment (m^2).

The ratio A/M for these two cases is, respectively

$$\frac{A}{M} = \frac{1}{t\rho_{gl}} \qquad [17.40.23]$$

and

$$\frac{A}{M} = \frac{1}{\rho_{gl} A'^{1/2}_{50}} \qquad [17.40.24]$$

The lower value of A/M given by these two alternative equations is selected.

The geometric mean velocity V_{50} of the fragments is given in SI units by the equation

$$V_{50} = [0.2539 + (1.86 \times 10^{-4})(t - 7.62 \times 10^{-4})^{-0.928}] \times (0.344 P_e^{0.547}) 690 < P_e < 689,000; t \geq 7.62 \times 10^{-4} \qquad [17.40.25]$$

where V_{50} is the geometric mean velocity (m/s).

17.40.7 Spatial density of fragments

A correlation for the spatial density of glass fragments from window breakage based on the Eskimo trials is given by E.R. Fletcher, Richmond and Richmond (1974). Their expression for the latter, in the form given by E.R. Fletcher, Richmond and Yelverton (1980), is as follows. A scaled spatial density $\bar{\rho}'_{sd}$ is defined as

$$\bar{\rho}'_{sd} = \frac{\rho_{sa}}{4.91 \exp(-5.0121) + 22.28} \qquad [17.40.26]$$

and gives the correlation

$$\ln \bar{\rho}'_{sd} = 3.1037 + 0.058\,57 p^{\circ}_e * \qquad [17.40.27]$$

where $p^{\circ}_e *$ is the peak effective overpressure (kPa), ρ_{sd} is the spatial density (fragments/m^2) and t is the glass thickness (cm).

17.40.8 Range of fragments

For an internal gas explosion the distance travelled by fragments from a breaking window is given by M.R. Marshall, Harris and Moppett (1977) in the work already described, as shown in Figure 17.111(e).

17.40.9 Injury relations

Glasstone (1962) gives the data on injury effects caused by glass fragments of different impact velocities shown in Table 17.58.

Methods for the estimation of serious injury from flying glass have been given in the vulnerability model by Eisenberg, Lynch and Breeding (1975) and by W.E. Baker *et al.* (1983). These are described in Sections 17.40.10 and 17.40.11, respectively.

Hadjipavlou and Carr-Hill (1986) have analysed data from animal experiments and have proposed the following probit equations for laceration and for penetration:

$$Y = -12.23 + 0.83 \ln mu' \quad \text{laceration} \qquad [17.40.28]$$

$$Y = -8.35 + 0.61 \ln mu' \quad \text{penetration} \qquad [17.40.29]$$

Table 17.58 *Some data on injury effects caused by glass fragments (after Glasstone, 1962)*

A Penetration of abdomen wall: impact velocity

Mass of glass fragment (g)	*Probability of penetration* (%)		
	1	50	99
0.1	235	410	730
0.5	160	275	485
1.0	140	245	430
10.0	115	180	355

B Injury from penetrating 10 g fragments

Effect	*Impact velocity* (ft/s)
Skin laceration	
Threshold	50
Serious wounds	
Threshold	100
50%	180
Nearly 100%	300

where m is the mass of the fragment (g) and u' is its velocity (ft/s).

A method of determining the probability of fatality for a person standing behind a window is given in the *Green Book* and is described in Section 17.40.12.

Gilbert, Lees and Scilly (1994f) have given a model for fatal and non-fatal injury by any potentially penetrating fragment. This is applicable to flying glass, as described in Section 17.42.

17.40.10 Injury relations: vulnerability model method

The treatment of injury by flying glass in the vulnerability model described by Eisenberg, Lynch and Breeding is as follows. The impact velocity of a missile V_i is related to the impulse J by the equation

$$MV_i = C_D AJ \qquad [17.40.30]$$

where A is the presented area of the missile (m^2), C_D is the drag coefficient, J is the impulse (Pa s), M is the mass of the missile (kg) and V_i is the impact velocity (m/s). The value of the drag coefficient C_D is taken as unity.

For injury from flying glass they consider a 10 g fragment and quote the data given in the second and third columns of the following table, which are derived from information given by the Department of the Army (1969):

Injury	*Peak overpressure* (psi)	*Impact velocity* (m/s)	*Impulse* (psi ms)	*Impulse* (Pa s)
Skin laceration				
Threshold	1–2	15	74.2	512
Serious wound				
Threshold	2–3	30	148.4	1024
50%	4–5	55	272.1	1877
Near 100%	7–8	90	445.3	3071

They derive from this the impulse values given in columns four and five of the above table and hence a probit equation relating serious injury from missiles, particularly glass, to impulse:

$$Y = -27.1 + 4.26 \ln J \qquad [17.40.31]$$

It is assumed in the application of Equation 17.40.31 that all personnel not inside buildings who are in the region traversed by a blast wave of sufficient strength suffer injury from missiles. The density of flying fragments and the target area presented by people are not factors affecting the probability of injury in this analysis. Thus, the equation overestimates by a considerable factor the extent of injury by flying fragments. This particular probit equation, therefore, should be regarded as representing an upper bound.

17.40.11 Injury relations: method of Baker *et al.*

The treatment for injury by glass fragments given by W.E. Baker *et al.* (1983) is based on the work of Sperrazza and Kokinakis (1967, 1968), but is essentially similar. For the fragment velocity they use the correlations obtained by Fletcher and co-workers and described in Section 17.40.6.

Sperrazzo and Kokinakis carried out experiments on the perforation of the skin of animals. Baker *et al.* give a straight-line graph of the results of this and other work, including that quoted by Glasstone, to which they fit with the relation

$$V_{50} = 22.30 + 1247.1 \frac{A}{M}, \quad \frac{A}{M} < 0.09;\ M \leq 0.015 \qquad [17.40.32]$$

where A is the presented area of the fragment (m^2), M is its mass (kg) and V_{50} is the velocity for 50% probability of perforation (m/s).

It is assumed by Sperrazzo and Kokinakis that if a fragment perforates the skin, its residual velocity will be sufficient to do severe injury. Baker *et al.* suggest that this assumption incorporates a margin of safety.

17.40.12 Injury relations: *Green Book* method

The *Green Book* gives a probit equation for fatality due to impact of glass fragments on the head of a person standing 1.75 m behind the window pane. The equation is

$$Y = 2.67 + \ln\left(\frac{f_{dl} P^o}{P_{st}}\right) \qquad [17.40.33]$$

where f_{dl} is the dynamic load factor, P° is the peak incident overpressure (Pa) and P_{st} is the static strength of the pane (Pa).

The basis of this equation is tests in which the peak reflected pressure was twice the dynamic failure load P_{df} of the panes and in which the probability of fracture of the skull was estimated as 94%. Then, for these conditions $P_{df} = P_{st}/f_{dl}$ and $P^\circ = 2P_{st}/f_{dl}$. Hence, $P^\circ/(P_{st}/f_{dl}) = 2$. It was assumed that for 1% lethality $P^\circ/(P_{st}/f_{dl}) = 1$. The probit equation is derived from these two values.

The static strength of the pane is obtained from the relations

$$f_t = \frac{2 \times 10^6}{A^{0.18} d^{0.7}} \qquad [17.40.34]$$

and

$$f_t = 0.225 P_{st} \frac{a^2}{d^2} \qquad [17.40.35]$$

where a is the smaller of the two dimensions of the pane (m), A is the area of the pane (m^2), d is the thickness of the pane (m) and f_t is the tensile strength of the pane (Pa).

Thus, a window $1.5 \times 1.0 \times 0.005$ m has a tensile strength $f_t = 75.9 \times 10^6$ Pa and a static strength $P_{st} = 8.43 \times 10^3$ Pa.

The dynamic load factor f_{dl} is a function of the ratio t_d/T of the duration time t_d to the natural period of vibration T. It has a value less than 1 for a short duration ($t_d \ll T$) and of 2 for a long duration ($t_d \gg T$).

17.40.13 Flying glass: model of Gilbert, Lees and Scilly

Gilbert, Lees and Scilly (1994f) have given a model for the probability of incurring various degrees of injury due to impact of a potentially penetrating fragment. This model is

described in Section 17.42. It is applicable to injury by fragments from window breakage.

In another paper, Gilbert, Lees and Scilly (1994h) have used this model in combination with some of the relations given above to provide an integrated treatment for the estimation of injury from flying glass. The model is applicable to the explosion of a condensed phase explosive external to the building.

The approach used in this integrated model is as follows. The characteristics of the window typical of the scenario considered are determined. Following Reed, the average peak reflected overpressure is taken as 1.32 times the peak incident overpressure. From Equation 17.40.3 the peak incident overpressure to produce an equivalent load on a 'Reed' window is estimated. Using Equation 17.40.2, the probability of window breakage is estimated. Given that the window is broken, Equations 17.40.6, 17.40.7, 17.40.14 and 17.40.27 are used to obtain the mean frontal area, mass, velocity and spatial density of the fragments. Then, using the fragment injury model of the authors, the probability of fatal and non-fatal injury is determined.

17.40.14 Flying glass hazard

The question of injury from flying glass is considered in the *Second Report* of the ACMH (Harvey, 1979b). The report is particularly concerned with the risks from a VCE.

In general, much of the concern about possible injury from flying glass relates to injury to people indoors. The shattering of glass as a result of an explosion has occurred at distances up to 20 miles. In such cases, however, the energy of the fragments is very low. The evidence appears to indicate that there are surprisingly few injuries to people from glass fragments even in buildings where most of the windows have been shattered by blast.

The report describes first the historical record. A large number of windows were broken in the VCEs both at Flixborough and at Beek. At Beek there were 2508 cases of damage outside the factory and these were almost entirely glass breakage (Case History A75). One person was injured by glass.

The report refers to the experimental work M.R. Marshall, Harris and Moppett (1977) on the breakage of glass windows by explosions inside buildings. In this work the peak overpressure was in the range 0.03–0.25 bar (0.44–3.6 psi). The fragment velocities measured were high, being of the order of 40 m/s, and varied relatively little. The report argues, however, that these results are not applicable to the very different conditions of explosions outside buildings.

This latter situation is then considered. It is estimated in the report that the overpressures required to effect 50 and 90% breakage of windows are about 0.016 bar (0.23 psi) and 0.038 bar (0.46 psi), respectively. A breakage of 50% implies a non-breakage of 50% of the windows, which suggests that the fragment velocity is likely to be low.

The report quotes experimental work in the United States in which windows 1/8 in. (3.17 mm) and 1/4 in. (6.35 mm) thick were mounted at various distances from large masses of TNT so that overpressures of 0.3 psi (0.02 bar), 0.5 psi (0.035 bar) and 0.6 psi (0.04 bar) with a duration time of 250 ms were applied to them, and fragment masses and velocities were determined. Separate experiments were conducted to find the probability that such fragments would penetrate bare skin, or clothed skin, or 1 cm of soft tissue. Only one fragment, out of 90, from the thicker windows broken at the highest pressure was found to have a 10% probability of penetrating 1 cm. No other fragment had even 1% probability of this degree of penetration.

It is concluded in the report that there is ample justification for regarding as negligible the risk of injury from flying fragments of window glass for an explosion which gives a peak overpressure outside the building of 0.6 psi (0.04 bar) or less.

17.41 Explosion Injury from Penetrating Fragments

One of the principal modes of injury from an explosion is wounding by penetrating fragments. In this section the information available on the wounding and incapacitating power of fragments is reviewed and several criteria and models for injury by a penetrating fragment are given. A further model for such injury by Gilbert, Lees and Scilly (1994f) is described in the next section.

This problem is of particular interest to the military, and much of the data are from military sources. These include the *Textbook* and the work of Gurney (1944), Dunn and Sterne (1952) and Beyer (1962). The work of the Stockholm International Peace Research Institute (SIPRI) (1978) is also relevant.

17.41.1 Definition of injury

The degree of injury of prime interest to the military is incapacitation, and much of the information available on injury by penetrating fragments relates to this. An account of the incapacitating power of weapons has been given in a review by SIPRI (1978).

This review emphasizes that the interpretation of incapacitating power is not straightforward. The military interest is in the ability of a projectile to cause rapid incapacitation, in other words its stopping power. Stopping power, however, is not synonymous with wounding power.

Work in the United States during and after the Second World War showed that immediate incapacitation is obtained only by severe injury to parts of the spinal column or brain. It is harder to achieve than fatal or severe injury, which results from injury to major organs or blood vessels.

Dunn and Sterne (1952) carried out experiments in which projectiles were fired at goats. They found that the probability of incapacitation was much less than for ultimate fatal or severe injury. SIPRI summarize their work to the effect that even for the most effective projectile the probability of fatal or severe injury is three to four times greater than the probability of immediate incapacitation.

The main sources of data on the injuring power of fragments refer to incapacitation, but in order to be able to utilize them it is necessary to be able to interpret incapacitation and to relate it to fatal and severe injury.

The meaning of incapacitation is discussed in the *Textbook*. It states:

> Despite the shortcomings of the available information, it is safe to conclude, from the data that have been summarized here, that any penetrating splinter wounds of the head, neck and trunk are highly dangerous, and that almost any wound may be regarded as incapacitating (which for convenience may be defined as a wound necessitating medical attention), provided that the missile concerned gets through the skin into the underlying tissues. In the case of limbs, single splinter wounds are not as dangerous, and the relative number of hits by small

splinters which would prove incapacitating is clearly smaller.

The Textbook then discusses wounds by small splinters, treating separately the head and neck, the thorax and abdomen, and the limbs. The criteria used for incapacitating wounds are:

Head: perforation of the skull;
Thorax and abdomen: perforation of trunk;
Limbs: penetration to half-depth and hitting central supporting bone.

The *Textbook* states that a rough estimate of the proportion of the total projected area of the body which represents the vital organs, where a battle injury due to a small missile would result in almost certain death, is roughly 10–15%.

The most vulnerable parts of the body are the head and neck and the thorax and abdomen. These account for some 39% of the projected area of the body.

17.41.2 Causative factor

There are two basic types of relation which are used for the damaging, or injuring, power of a fragment, or projectile. One is the relation for kinetic energy

$$E = mu^2/2 \qquad [17.41.1]$$

where E is the kinetic energy (J), m is the mass of the fragment (kg) and u is the velocity (m/s). This equation also may be written in the alternative form

$$um^{0.5} = \text{constant} \qquad [17.41.2]$$

or more generally

$$um^c = \text{constant} \qquad [17.41.3]$$

where c is an index.

It is now recognized that the mean presented area (MPA) of the fragment is also relevant. This is discussed in Section 17.42.

17.41.3 Incapacitation criteria

At the turn of the last century the German army adopted a projectile kinetic energy of 78 J (58 ft lb) as incapacitating to military personnel. This is also the value which has traditionally been used in Britain and the United States.

Other criterion values quoted by SIPRI are the French, Swiss and Russian values of 39, 62 and 235 J, respectively.

According to Beyer (1962) this type of criterion has proved a better indicator of incapacitating power than measures such as penetration into solid objects such as pine boards.

The 78 J criterion has been discussed by Gurney (1944), who states that it is valid for fragments in the range 50 mg to 30 g.

More sophisticated criteria have since been developed for weapons design, based on actual casualty data and taking into account the different areas of the body hit.

A computer code for the estimation of incapacitation by bullets, COMPUTER MAN, has been developed by the US Army. In this code the human body is divided into small sections ($5 \times 5 \times 25$ mm) with the tissue type within the each section specified. The model is then utilized in conjunction with information on the impact points of bullets, their ballistic properties, etc., to obtain a ranking on a relative incapacitation index (RII).

A commercial computer code, WBD2, is also available, developed by Timberwolf Consulting Services (1991), which embodies a wound ballistics simulation model.

An interpretation of the 78 J incapacitation criterion has been given by Gilbert, Lees and Scilly (1994f), who conclude that in terms of the *Textbook* incapacitation model, described below, the criterion corresponds approximately to a 90% probability of incapacitation.

17.41.4 *Textbook* model

A model for the incapacitating power of a penetrating fragment is given in the *Textbook*. The basic relation used is the penetration equation

$$P = ku^b m^c \qquad [17.41.4]$$

where m is the mass of the fragment (mg), P is the penetration (ft) and u is the velocity (ft/s), k is a constant and b and c are indices. It follows from Equation 17.41.4 that for a given incapacitating power

$$u^b m^c = \text{constant} \qquad [17.41.5]$$

or

$$v = u(m/m_r)^{c/b} \qquad [17.41.6]$$

where m_r is the mass of a reference fragment (mg) and v is the equivalent velocity (ft/s). The values given for b and c are 1 and 0.4, respectively.

A standard fragment is defined for which the value of m_r is 52 mg. The *Textbook* gives probit relations for incapacitation by 52 mg fragments of different shapes. The relations are formulated in terms of velocity as the causative factor. The probability of incapacitation by a fragment of given mass and velocity is then obtained by determining the equivalent velocity from Equation 17.41.6 and using this value in the probit relations.

It may be noted that this standard fragment size of 52 mg is small but that a large proportion of the fragments are of this size or below. However, some doubt must attach to extrapolation of the correlation to much larger fragment sizes.

This model applies to a soldier wearing the full complement of land service clothing and equipment, including a helmet.

The *Textbook* model has been cast in convenient form by Gilbert, Lees and Scilly (1994f). For a 52 mg cuboid fragment the probit relation in terms of the velocity u is

$$Y = -8.25 + 1.96 \ln u \qquad [17.41.7]$$

where u is the velocity of the fragment (m/s).

As just indicated, Equation 17.41.7 is specific to a 52 mg fragment. Generalizing for other fragments, by using the causative factor $um^{0.4}$ used in the *Textbook*, these authors obtain

$$Y = -0.51 + 1.96 \ln(um^{0.4}) \qquad [17.41.8]$$

where m is the mass of the fragment (kg).

Gilbert, Lees and Scilly have also adapted the *Textbook* model to the estimation of fatal and serious injuries (K + SI). This is based on equating a 10% probability of incapacitation to a 30% probability of fatal or serious injury, whilst retaining the slope of the probit equation. The equation obtained is

$$Y = 0.24 + 1.96 \ln(um^{0.4}) \qquad [17.41.9]$$

17.42 Explosion Injury from Penetrating Fragments: Model of Gilbert, Lees and Scilly

A model for injury from fragments and missiles generated by an explosion has been given by Gilbert, Lees and Scilly (1994f,g). The model is applicable to the assessment of injury caused by impact of any missile which has the potential to penetrate the skin; it is not intended for the assessment of impact by blunt objects. It was developed primarily with reference to the hazard of fragments from the casing of munitions.

17.42.1 Classification of injury

The injury classification used is:

K Injury which is fatal, either immediately or in hospital.
S Injury which is serious, involving perforation of the skin, and which necessitates medical attention, implying hospitalization.
M Injury which is generally not serious, involving perforation of skin, but which deserves medical attention.
T Injury which is trivial, possibly penetrating the skin but not perforating it, or no injury at all.

A serious injury is defined more specifically as one involving the following:

Head and neck: perforation of the skull;
Thorax: penetration of the 'vulnerable area';
Abdomen: penetration of the 'vulnerable area';
Limbs: penetration of the 'vulnerable area'.

The abdomen is taken to mean the abdomen proper and that part of the thorax which is not protected by bone, whilst the thorax is taken as that part of the chest which is so protected.

17.42.2 Probability of injury

The following probabilities are defined:

P(H) probability of hit by fragment;
$P(H_i)$ probability of hit by fragment in body region i;
P(K) probability of fatal injury;
$P(K_i)$ probability of fatal injury in body region i;
P(S) probability of serious injury;
$P(S_i)$ probability of serious injury in body region i;
$P(P_{vul,i})$ probability of penetration of vulnerable area of body region i, equal to probability of fatal or serious injury in that region;
$P(P_{skin})$ probability of perforation of skin;
$P(P_{skull})$ probability of perforation of skull;
$P(P_{thor})$ probability of penetration of vulnerable area of thorax;
$P(P_{abd})$ probability of penetration of vulnerable area of abdomen;
$P(P_{limb})$ probability of penetration of vulnerable area of limb.

Use is also made of the subscripts lwlimb and uplimb to denote lower and upper limbs, respectively. The last four probabilities are conditional probabilities, as defined below.

It is assumed that if the body is hit at all by a fragment, the effect is classified using one of the four categories. The trivial injury category covers the cases where the injury is trivial or where no injury is sustained, so that the sum of the probabilities of injury in these four categories is always unity.

The probability of a hit on body region i is

$$P(H_i) = A_i/A \qquad [17.42.1]$$

where A is the total MPA of the body and A_i is the MPA attributable to region i.

The probability of perforation of the skin is a function of fragment mass, projected area and velocity. It is assumed that perforation of the skin by a fragment will result in fatality, serious injury or medium injury (K, S or M).

The probability of penetration to a vulnerable area in a particular region i of the body is

$$P(P_{vul,i}) = P(P_{vul,i}|P_{skin})P(P_{skin}) \qquad [17.42.2]$$

Specifically, for each region considered,

$$P(P_{vul,i}|P_{skin}) = P(P_{skull}) \quad \text{head and neck} \qquad [17.42.3]$$
$$= P(P_{thor}) \quad \text{thorax} \qquad [17.42.4]$$
$$= P(P_{abd}) \quad \text{abdomen} \qquad [17.42.5]$$
$$= P(P_{limb}) \quad \text{limb} \qquad [17.42.6]$$

Then, for the head and neck

$$p(P_{vul,i}) = P(P_{skull})\ P(P_{skin}) \qquad [17.42.7]$$

for the thorax

$$P(P_{vul,i}) = P(1P_{thor})P(P_{skin}) \qquad [17.42.8]$$

for the abdomen

$$P(P_{vul,i}) = P(P_{abd})P(P_{skin}) \qquad [17.42.9]$$

and for the limbs

$$P(P_{vul,i}) = P(P_{limb})P(P_{skin}) \qquad [17.42.10]$$

In this model, the probability of fatal or serious injury (K or S) in body region i is defined by $P(P_{vul,\,i})$. The probability of fatal injury is

$$P(K_i) = P(K_i|P_{vul,i})P(_{vul,i}) \qquad [17.42.11]$$

The probability of serious injury in body region i is then

$$P(S_i) = P(P_{vul,i}) - P(K_i) \qquad [17.42.12]$$

The overall probability of fatal injury is

$$P(K) = \sum P(K_i) \qquad [17.42.13]$$

and that of serious injury is

$$P(\mathrm{S}) = \sum P(\mathrm{S_i}) \qquad [17.42.14]$$

The overall probability of trivial or no injury is

$$P(\mathrm{T}) = 1 - P(\mathrm{P_{skin}}) \qquad [17.42.15]$$

and that of medium injury is simply the residue

$$P(\mathrm{M}) = 1 - [P(\mathrm{K}) + P(\mathrm{S}) + P(\mathrm{T})] \qquad [17.42.16]$$

The probabilities which need to be estimated for this model are therefore for the perforation of the skin $P(\mathrm{P_{skin}})$ and the following probabilities for each body region i: $P(P_{\mathrm{vul,i}}|P_{\mathrm{skin}})$ and $P(K|P_{\mathrm{vul,i}})$.

17.42.3 Causative factor

Traditionally the criterion for military incapacitation has been expressed in terms of a kinetic energy. Later it became recognized that the presented area of the fragment was also relevant.

It has become usual to work, therefore, in terms of the following causative factor X:

$$X = mu^2/A \qquad [17.42.17]$$

where A is the projected area of the fragment (m^2), m is its mass (kg), u is its velocity (m/s) and X is the causative factor (J/m^2).

17.42.4 Perforation of skin

A distinction is made between skin penetration, or epidermis perforation, and skin perforation, or full-depth perforation.

The problem of skin perforation is relatively complex. In a review of work on this topic Di Maio (1981) makes a distinction between experiments carried out on samples of skin with, and without, subcutaneous tissue attached. Skin seems to be more resistant to fragment penetration when it is *in situ*, with underlying muscle and fat still attached.

Some information on the properties of the skin is provided by Mehta and Wong (1967). Experimental work on skin perforation using unattached skin has been described by Grundfest *et al.* (1945) and Sperrazza and Kokinakis (1968). Accounts of experiments on attached skin have been given by Journee (1907), Mattoo, Wani and Askegar (1974) and Di Maio *et al.* (1982). A review of work on penetrating trauma has been given by Neades and Rudolph (1983) as part of an attempt to improve on the widely used criterion for incapacitation of 78 J.

The model adopted by Gilbert, Lees and Scilly is that of J.H. Lewis *et al.* (1987). These latter authors give an empirical formula for the probability of complete skin perforation (full-thickness skin laceration) which is said to apply to both primary and secondary fragments (debris).

Experiments were performed using goat skin to simulate human tissue. This approach follows the work of Sperraza and Kokinakis (1968), who found no significant difference between goat and human skin in this respect.

The results were correlated using the logistic equation

$$P(\mathrm{P_{skin}}) = \frac{1}{1 + \exp[-a + bmu^2/A)]} \qquad [17.42.18]$$

where A is the projected area of the fragment (cm^2), m is its mass (g), u is its velocity (m/s) and a and b are constants.

Values of the constants given for bare skin and for two-layer and six-layer uniforms are:

Target	*Constant*	
	a	*b*
Bare skin	−28.42	2.94
Two-layer uniform	−49.47	4.62
Six-layer uniform	−50.63	4.51

The corresponding probit equation for bare skin is

$$Y = -20.5 + 1.54\ln(mu^2/A) \quad \text{bare skin} \qquad [17.42.19]$$

where A is the projected area of the fragment (m^2), m is its mass (kg) and u is its velocity (m/s).

Analysis by the authors of the data for skin *in situ* indicated that there is strong evidence to support the adoption of the following thresholds for skin penetration and skin perforation:

$$mu^2/A = 3 \times 10^5 \text{ J/m}^2 \quad \text{skin penetration}$$
$$= 3.6 \times 10^5 \text{ J/m}^2 \quad \text{skin perforation}$$

On the basis of these findings a revision was made to the correlation of J.H. Lewis *et al.* (1987). The threshold was taken to be equivalent to a probability of 1%. The probit equation of Lewis *et al.* given in Equation 17.42.19 was revised by adjusting the intercept but retaining the slope. The result for bare skin is

$$Y(\mathrm{P_{skin}}) = -17.0 + 1.54\ln(mu^2/A) \qquad [17.42.20]$$

The model assumes that on perforation of the skin there is a reduction in the causative factor (mu^2/A) of 360,000 J/m^2, the threshold value for skin perforation. The residual energy is then available for further penetration of the body region in question.

17.42.5 Penetration to vulnerable areas

Head and neck

Information on penetration of the skull by fragments is given in the *Textbook*. A series of 54 shots were made using eight fresh skull caps obtained at autopsy at velocities in the range 280–960 m/s. The data given are for penetration by a 53 mg fragment, and are shown in Table 17.59(A). It is recommended in the *Textbook* that the crude data for the normal velocity be increased by 10% to allow for experimental error and this adjustment is shown in the second column of the table. The probit equation obtained from Table 17.59(A) is

$$Y(\mathrm{P_{skull}}) = -40.5 + 3.03\ln(mu^2/\mathrm{A}) \qquad [17.42.21]$$

Thorax

An essentially similar treatment is available for penetration of the sternum, the information again deriving from the *Textbook*. A series of 56 shots were made using 13 fresh sterna obtained at autopsy at velocities in the range

Table 17.59 *Penetration of vulnerable areas by fragments*

A Skull[a]

Normal impact velocity (ft/s)	*Adjusted impact velocity,*[b] (ft/s)	*Causative factor,* mu^2/A (J/m^2)	*Probability of perforation,* $P(P_{skull})$ (%)
312	343	1.40×10^6	0
408	449	2.40×10^6	12.7
507	558	3.70×10^6	75.2
591	650	5.03×10^6	82.1
769	846	8.52×10^6	100

B Sternum[a]

Normal impact velocity (ft/s)	*Adjusted impact velocity,*[b] (ft/s)	*Causative factor,* mu^2/A (J/m^2)	*Probability of perforation,* $P(P_{stern})$ (%)
173	190	0.431×10^6	42.1
220	242	0.697×10^6	77.0
295	325	1.25×10^6	77.0
373	410	2.03×10^6	91.6
519	571	3.88×10^6	100

C Limb

Limb	*Bone* (ft^2)	*MPA Vessels and nerves* (ft^2)	*Vulnerable parts* (ft^2)	*Total* (ft^2)	*Conditional probability of penetration,* $P(P_{vul}|P_{skin})$
Upper limb	0.31	0.12	0.43	0.92	0.467
Lower limb	0.55	0.22	0.77	1.65	0.467

[a] *Source*: *Textbook of Air Armament* (Ministry of Supply, 1952): table C1. Data for a 3/32 in. sphere, of mass 53 mg.
[b] Adjusted as explained in text.

153–530 m/s. The data given are for penetration by a 53 mg fragment and are shown in Table 17.59(B). It is recommended in the *Textbook* that the crude data for the normal velocity be increased by 10% to allow for experimental error, and this adjustment is shown in the second column of the table.

The vulnerability of the thorax, given penetration of the skin, is obtained in the model from the vulnerability to perforation of the sternum. A fraction, say two thirds, of the thorax may be considered to be protected by the sternum or other bones. The remaining one third is treated as unprotected and is lumped with the abdomen. This redistribution is effected by adjusting the values of the MPA A used for these two parts of the body.

Then, applying to the thorax the probit equation obtained for the sternum from Table 17.59(B)

$$Y(P_{thor}) = -7.37 + 0.948 \ln(mu^2/A) \qquad [17.42.22]$$

Abdomen

Data given below indicate that 84% of the injuries to the abdomen result in death or serious injury. This value is taken as the probability $P(P_{abd})$ of penetration to a vulnerable area given perforation of the skin.

Limbs

The vulnerable parts of the limbs are bones and vessels and nerves outside the bone area. The *Textbook* gives the MPA of these vulnerable areas and the probability $P(P_{limb})$ is then simply the ratio of the vulnerable area of the limb to its total MPA. The data are shown in Table 17.59(C).

17.42.6 Fatal injury

All parts of the body

An approximate estimate of the probability of fatality given fatal or serious injury may be obtained from the data on civilian air raid casualties given in the *Textbook* and shown in Table 17.60(A). This table gives the overall probability of fatality as 0.26, which may be compared with the value of 0.27 given in the *Textbook* for 'all regions'.

It should be noted that the probability given in this table is the probability of fatality given a hit, not the probability of fatality given penetration to a vulnerable area.

The *Textbook* also gives information on British military casualties in the First World War as given in Table 17.60(B). These data have been used in relation to fatal injuries of the trunk, as described below.

Head and neck

Further information on fatal injuries arising from penetration of the skull is given by A. Palmer (1962). He gives data on the mass distribution of flak fragments in 30 cases recovered from fatal and non-fatal fracture wounds to the skull. The proportion of the cases which were fatal is 77%. On this basis the probability of fatality given perforation of the skull $P(K|P_{vul,skull})$ is taken as 0.8.

Thorax and abdomen

For fatal injuries involving the thorax and abdomen use has been made of data given in the *Textbook* on military casualties in the First World War shown in Table 17.60(B). The effect of an injury to the trunk tends to be serious. From the data in the table the probability $P(K|P_{vul,thor})$ of fatal injury given penetration to the vulnerable area for the

Table 17.60 *Fatal injury by a fragment penetrating to a vulnerable area*

A British air raid casualties in the Second World War[a]

Region, i	*Proportion of MPA, P (H_i/H)*	*Conditional probability of fatal injury P (K_i/H_i)*
Head and neck	0.12	0.60
Thorax	0.16	0.40
Abdomen	0.11	0.56
Upper limb	0.22	0.07
Lower limb	0.39	0.14

B British military casualties in the First World War[a]

	Proportion of effective wounds in each part of body (%)			*Proportion of fatal or serious injury* (%)	*Conditional probability of fatal injury,* $P(K_i|P_{vul,i})$
	Dead	*Seriously wounded*	*Slightly wounded*		
Head and neck	25.8	27.8	46.4	53.6	0.481
Thorax	59.6	20.7	19.7	80.3	0.782
Abdomen	61.1	23.1	15.7	84.2	0.726
Upper limb	3.0	36.3	60.7	39.3	0.076
Lower limb	3.9	44.4	51.7	48.3	0.081

[a] *Source: Textbook of Air Armament* (Ministry of Supply, 1952). Section A: table 3; section B: table 2.

thorax is taken as 0.75 and similarly for the probability $P(K|P_{vul,abd})$.

Limbs

Palmer also gives information on fatal injuries arising from penetration of vulnerable parts of limbs. He gives data on the mass distribution of flak fragments recovered from fatal and non-fatal extremity fracture wounds. The proportion of the cases which were fatal for the upper limb is 5.9% and for the lower limb 15.4%.

An alternative approach is to utilize the Second World War data given in Table 17.59(C) and Table 17.60(A). From these tables it may be inferred that for the upper limb

$$P(K|P_{vul,uplimb}) = 0.07/0.467 = 0.15$$

and for the lower limb

$$P(K|P_{vul,lwlimb}) = 0.14/0.406 = 0.345$$

17.42.7 Effect of advances in medicine

Surveys of battle casualties generally conclude that rapid first aid, medical treatment and modern surgery can greatly reduce mortality from wounds to the extremities, or limbs, although this is of little help in the case of wounds to the head. This is supported by statistics which show that US battle deaths from extremity wounds were reduced from about 13% of all deaths in the Second World War to 7.4% in Vietnam.

The probability of fatality given penetration to a vulnerable part of a limb $P(K|P_{vul,\ limb})$ during the Second World War is therefore reduced in the model to half its crude estimated value by taking credit for medical advances.

No other credit for medical advances is taken in the model.

17.42.8 Effect of clothing

Clothing may in principle affect the probability of skin perforation. The work of French and Callender (1962) indicates that although exhibiting a finite threshold velocity for perforation, light clothing is much less resistant than skin. It is assumed in the model that the type of clothing worn by civilians offers very little protection against missiles and hence bare skin criteria are used.

17.42.9 Injury model

The model of injury by fragments may be summarized as follows. The adjusted values of proportion A_i/A of MPA assigned to body region i are:

Body region	A_i/A
Head and neck	0.12
Thorax	0.11
Abdomen	0.16
Upper limb	0.22
Lower limb	0.39

$P(P_{skin})$ Equation 17.42.20 for bare skin.

Following skin perforation, X is reduced by 360,000 J/m^2 to account for the energy expended:

$P(P_{skull})$	Equation 17.42.21;
$P(P_{thor})$	Equation 17.42.22;
$P(P_{abd})$	= 0.84;
$P(P_{lwlimb})$	= 0.467 from Table 17.59 (C);
$P(P_{uplimb})$	= 0.467 from Table 17.59 (C);
$P(K|P_{skull})$	= 0.8;
$P(K|P_{thor})$	= 0.75;
$P(K|P_{abd})$	= 0.75;
$P(K_{uplimb}|P_{vul,uplimb})$	= 0.15;
$P(K_{lwlimb}|P_{vul,lwlimb})$	= 0.345.

If allowance is made for medical advances since the Second World War, the last two values become 0.07 and 0.15, respectively.

17.43 Dust Explosions

Another explosion hazard in the process industries is the explosion of flammable dusts. Explosions of dust suspensions have characteristics in common with gas explosions, but there are also some important differences. Fire and explosions can also occur in dust layers. Legal requirements for plant handling flammable dusts are given in the Factories Act 1961, section 31. This section includes the following:

(1) Where, in connection with any grinding, sieving or other process giving rise to dust, there may escape dust of such a character and to such an extent as to be liable to explode on ignition, all practicable steps shall be taken to prevent such an explosion by enclosure of the plant used in the process, and by removal or prevention of accumulation of any dust that may escape in spite of the enclosure, and by exclusion or effective enclosure of possible sources of ignition.
(2) Where there is present in any plant used in any such process as aforesaid dust of such a character and to such an extent as to be liable to explode on ignition, then, unless the plant is so constructed as to withstand the pressure likely to be produced by any such explosion, all practicable steps shall be taken to restrict the spread and effects of such an explosion by the provision, in connection with the plant, of chokes, baffles and vents, or other equally effective appliances.

There are other statutory requirements relating to particular flammable dusts.

Accounts of dust explosions are given in *Dust Explosions in Factories* (HSE, 1970 HSW Bklt 22), *Dust Explosions and Fires* (K.N. Palmer, 1973a), *Explosions* (Bartknecht, 1981a), *Dust Explosions* (Cross and Farrer, 1982), *Dust Explosions* (Field, 1982), *Development and Control of Dust Explosions* (Nagy and Verakis, 1983), *Venting Gas and Dust Explosions* (Lunn, 1984b, 1992), *Dust Explosions* (Bartknecht, 1989), *Dust Explosions in the Process Industries* (Eckhoff, 1991) and by Wilkes (1948), Maisey (1965), H.E. Rose (1970, 1975), K.N. Palmer (1971, 1974a–c, 1975a,b, 1975–76, 1977, 1981a, 1982, 1983, 1990), O'Reilly (1972), Schwab (1986) and Lunn (1989a,b, 1990).

Relevant codes are NFPA 68: 1994 *Explosion Venting* and NFPA 69: 1992 *Explosion Prevention* Systems. In addition, there are a number of codes relevant to particular industries which deal with dusts such as NFPA 61 series (foodstuffs), NFPA 654 (chemicals, dyes, pharmaceuticals and plastics), NFPA 655 (sulphur) and NFPA 651 (aluminium and magnesium).

Selected references on dust explosions are given in Table 17.61 and on dust explosibility in Table 17.62.

17.43.1 Industrial dusts

Many industrial materials are at some stage handled as dusts or powders and many final products are in dust/powder form. Some typical industrial dusts/powders are

(1) wood;
(2) coal;
(3) food (e.g. starch, flour, sugar, cocoa, feedstuffs);
(4) chemicals (e.g. drugs, dyestuffs);
(5) plastics (e.g. urea formaldehyde resin, polyethylene, polystyrene);
(6) metals (e.g. aluminium, magnesium).

Some of the operations in which such dusts are produced are considered in Section 17.49.

Table 17.61 *Selected references on dust explosions*

W.M. Jones (1940a,b); Burgoyne (1945); Wilkes (1948); Hartman (1948a, 1950, 1957); Drinker and Hatch (1954); Fishkin and Smith (1964); Schwab and Othmer (1964); Nagy and Surincek (1966 BM RI 6811); Eggleston (1967); Essenhigh (1967); Vegter (1969); HSE (1970 HSW Bklt 22, 1975 SHE 830); H.E. Rose (1970, 1975); FPA (1974 CFSD 6015, 1989 CFSD FS 6021, 6023, 6023, 6024); Kuhnen (1971); Bartknecht (1971, 1972a,b, 1973, 1974a, 1975, 1980, 1981a, 1989); Clague (1972); O'Reilly (1972); Ritter (1972); Hess (1973); Nettleton and Stirling (1973); K.N. Palmer (1973a, 1981a, 1990); FRS (1973 Fire Res. Note 992); Suchan (1973); Anon. (1976 LPB 8, p. 7); Griffith (1978); BRE (1979 TIL 63); Cardfflo and Anthony (1979); Deasy (1979); Clavel and Estrabaud (1980); CMI (1980 CMI 790750–1); P.E. Moore (1980); Cross (1981); IBC (1981/13, 1982/23, 1984/49 Pt 2); Jacobsen (1981); Napier (1981); Tait (1981); Cross and Farrer (1982); Field (1982); Moen (1982b); Siwek (1982); Tamanini (1982); Thorne (1982); Wolanski (1982a,b); Zeeuwen (1982,1988); Nagy and Verakis (1983); Boiko *et al.* (1984); Kauffman *et al.* (1984); Wolanski *et al.* (1984); N. Gibson, Harper and Rogers (1986); Schwab (1986); Cartwright (1987, 1990); NFPA (1989 NFPA 61A, 61B); W.E. Baker, White and Hokanson (1991); Eckhoff (1991, 1993); Godbey (1991); Cashdollar *et al.* (1992); Ural (1992); Anon. (1993 LPB 113, p. 0)

Ignition
Blactin and Robinson (n.d.); Morse (n.d., 1958); Boyle and Llewellyn (1950a,b); Underwriters Laboratories (1953); K.N. Palmer (1957, 1973a, 1976b, 1981b); K.N. Palmer and Tonkin (1957); Chauvin (1973); Eckhoff (1976a,b, 1991); Eckhoff and Enstad (1976); J.F. Hughes and Bright (1979); Anon. (1980 LPB 35, p. 1); Cross (1980); Department of Agriculture (1980); N. Gibson and Rogers (1980); Glor and Boschung (1980); Krishna and Berland (1980); Leuschke (1980,1981); Dahn (1981); Petino (1981); Cross and Farrer (1982); Zeeuwen (1982); Borisov *et al.* (1984); Hertzberg, Conti and Cashdollar (1985); Pedersen and Eckhoff (1987); Tyler and Henderson (1987); Anon. (1988l); Henderson and Tyler (1988); Bruderer (1989b); FPA (1989 CFSD FS 6023); Schuber (1989); Amyotte, Baxter and Pegg (1990)

Combustion
Cassel, Das Gupta and Guruswamy (1949); Cassel, Liebman and Mock (1957); Essenhigh and Woodhead (1958); Cassel and Liebman (1959); Butlin (1971); Rae (1971); Ishihama and Enomoto (1973, 1975); Eckhoff (1977); Liebman, Conti and Cashdollar (1977); Eckhoff and Mathisen (1978); N. Gibson and Rogers (1980); Kansa and Perlee (1980); Pineau (1982); Tulis and Selman (1982, 1984); Ballal and Lefebvre (1983a,b); Veyssiere (1984); Kauffman *et al.* (1985); Pineau, Chaineaux and Ronchail (1986); Bao-Chun, Fan and Sichel (1988); Proust and Veyssiere (1988); Amyotte and Pegg (1989); D. Bradley, Chen and

Swithenbank (1989); Britton and Chippett (1989); Fan and Sichel (1989); Pu, Jarosinksi *et al.* (1989); Pu, Marunkiewicz *et al.* (1989); Aldis and Gidaspow (1990); Zhang and Gronig (1991); Hertzberg *et al.* (1992); Kumar, Bowles and Mintz (1992); Eidelman and Xiaolong Yang (1993); Seung Wook Back, Kook Young Aim and Jong Uck Kim (1994)
Particular materials: Underwriters Laboratories (1953); K.N. Palmer (1982); Ogle *et al.* (1988)

Hazardous area classification
Moodie (1971); ICI/RoSPA (1972 IS/91)

Dust fires
K.N. Palmer (1957, 1973a, 1981b, 1983); K.N. Palmer and Tonkin (1957); Verkade and Chiotte (1978a); Leisch, Kauffman and Sichel (1985)

Process plant handling
EEUA (1968 Hndbk 19); R.W. Nelson (1972); K.N. Palmer (1973a, 1975a,b, 1984 LPB 54); Schafer (1973b); Theimer (1973); Pollock (1975); Dressier (1977); Aldis and Lai (1979); J.F. Hughes and Bright (1979); Gillis and Dale (1980); N. Gibson (1981); Hoenig (1981, 1989); Anon. (1988l); Bartknecht (1989); FPA (1989 CFSD FS 6024); Gelfand *et al.* (1989); Siwek (1989b); Eckhoff (1991); Siwek and Cesana (1993); Maddison (1994)
Bags: Bruderer (1993)
Bucket elevators: K.C. Brown (1951); Gillis and Dale (1980); Gillis (1981); Kossebau (1982)
Driers: Reay (1977, 1979 LPB 25); Bartknecht (1981a); Schmalz (1982); Bruderer (1989a); Crowhurst (1989); Abbott (1990)
Dust collectors, filters: K.N. Palmer (1974a); J. Palmer (1980); Bartknecht (1981a); Frank (1981); Reinauer (1981); Cairns (1984); N. Bennett, Cairns and Cooper (1986); van Laar (1993)
Grinding mills: Schmalz (1982)
Silos: Themier (1973); Bartknecht (1981a, 1985); CMI (1982 CMI 813307-1); Eckhoff (1982, 1984, 1991); Eckhoff *et al.* (1982, 1988); Radant (1982); Britton and Kirby (1989)
Metal dusts: H. Brown (1941 BM 1C 7148)

Explosion prevention and protection
SMRE (Explosion 4); W.M. Jones (1940b); Valentine and Merrill (1942); Burgoyne and Fauls (1963); Burgoyne (1967a); Craven and Foster (1967); K.N. Palmer (1967b, 1973a, 1973 FRS Fire Res. Note 961, 1974a); Coffee (1968); Bartknecht (1971, 1972a,b, 1973, 1974a, 1975, 1977, 1981a,b, 1989); R.W. Nelson (1972); N. Gibson (1973a); Hess (1973); FPA (1974 CFSD FS 6015, 1989 CFSD FS 6022); Cocks (1979); S. Clark (1981); P. Moore (1981); Brennecke (1982); IB (1982/23, 1984/49 Pt 2, 1988/74, 1992/90); Rickenbach (1982); Ritter (1982); Stalder (1982); Wetterich (1982); Wiemann (1982); Ebert (1982/83); Nagy and Verakis (1983); European Information Centre on Explosion Protection (1984); Janssens (1984); Lunn (1984b, 1988a, 1992); Schofield (1984); Butters (1985 LPB 66); BSI (1986); NFPA (1988 NFPA 654, 1992 NFPA 69); Schofield and Abbott (1988); Hoenig (1989); Anon. (1990 LPB 95, p. 7); Amrogowicz and Kordylewski (1991); Amyotte, Mintz and Pegg (1992); Amyottte and Pegg (1992); Ebadat (1993) VDI 2263: 1990–

Explosion relief
FRS (Fire Res. Note 830, 1973 Fire Res. Note 961); Hartmann (1946); Hartmann and Nagy (1946 BM RI 3924, 1957); Nagy, Zeilinger and Hartmann (1950 BM RI 4636); K.C. Brown (1951); K.C. Brown and Curzon (1962, 1963); K.C. Brown *et al.* (1962); Maisey (1965); Heinrich (1966, 1972, 1974, 1975); K.N. Palmer (1967b, 1971, 1973a, 1974a–c, 1975/76, 1977); Donat (1971a, 1977a); Heinrich and Kowall (1971, 1972); Pineau (1973); Bartknecht (1974a,b, 1977a, 1981a, 1985, 1986, 1989); Pineau, Giltaire and Dangeaux (1974, 1976, 1978); Matsuda and Naito (1975); N. Gibson and Harris (1976); Burgoyne (1977); Hattwig (1977); Nettleton (1977a); Rust (1979); W.E. Baker, Hokanson and Kulesz (1980); M.R. Marshall (1980); BRE (1981 N81/81, N101/81); Eckhoff (1982, 1989, 1990, 1991); Field (1982, 1984); Scholl (1982); Eckhoff and Fuhre (1983); Lunn (1984b, 1989a,b, 1990, 1992); Schofield (1984); IBC (1985/63, 1987/72); Lunn and Cairns (1985); Eckhoff, Fuhre and Pedersen (1986, 1987); Pineau, Chaineaux and Ronchail (1986); Simpson and Woinsky (1986); Eckhoff *et al.* (1988); Lunn, Brookes and Nicol (1988); Lunn, Crowhurst and Hey (1988); Zeeuwen (1988); P. Moore (1990); Siwek (1989a, 1994); M. Epstein *et al.* (1990); Tamanini (1990); Hey (1991); IChemE (1992/33); Siwek, Glor and Torregiani (1992); K. van Wingerden (1993); Scheuermann (1994); NFPA (1994 NFPA 68) VDI 3673: 1979
Disposal of vented material: K.N. Palmer (1973a); Bartknecht (1981a, 1989)

Explosion suppression
Bartknecht (1971, 1973, 1977b, 1981a,b); Rae and Thompson (1979); P. Moore (1982b, 1984, 1986, 1990); P. Moore and Bartknecht (1986); Senecal (1989a,b); Kordylewski and Amrogowicz (1992)

Hybrid explosions
Cardfflo and Anthony (1978); Pellmont (1979, 1982); Kauffman *et al.* (1984); Senecal (1989b); Torrent, Fuchs and Fernandez (1990); Torrent, Fuchs and Borrajo (1991); W.E. Baker, White and Hokanson (1991)

Grain elevators, inc. explosions
Morse (1958); Anon. (1978f); Verkade and Chiotte (1978a,b); Anon. (1979 LPB 27, p. 76); Aldis and Lai (1979); Atallah (1979); Anon. (1980q); Tait, Repucci and Tou (1980); Brasie (1981); Kauffman (1981, 1982, 1986); W.E. Phillips (1981); Winsett (1981); Pedersen and Eckhoff (1987); NFPA (1989 NFPA 61B)

Hazard assessment
Brasie (1981)

Table 17.62 *Selected references on dust flammability and explosibility*

Wheeler (1935a); Hartmann, Nagy and Brown (1943 BM RI 3722); Hartmann and Nagy (1944 BM RI 3731, RI 3751, 1949, 1957); Underwriters Laboratories (1944); Hartmann and Greenwald (1945); Bowes, Burgoyne and Rasbash (1948); Hartmann (1948a, 1957, 1958); Hartmann, Cooper and Jacobsen (1950 BM RI 4725); Hartman, Nagy and Jacobsen (1951 BM RI 4835); Hartman, Jacobsen and Williams (1954 BM RI 5052); Carpenter (1957); Carpenter and Davies (1958); Dorsett *et al.* (1960 BM RI 5624); Jacobsen *et al.* (1961 BM RI 5753); Nagy and Portman (1961 BM RI 5815); Jacobsen, Nagy and Cooper (1962 BM RI 5971); Maguire, Slack and Williams (1962); Cassell (1964 BM RI 6651); Jacobsen, Cooper and Nagy (1964 BM RI 6516, 1965 BM RI 6851); W.F. Marshall, Palmer and Seery (1964); Nagy, Cooper and Stupar (1964 BM RI 6561); Nagy, Dorsett and Jacobsen (1964 BM RI 6543); Singer (1964 BM RI 6369);

Nagy, Dorsett and Cooper (1965 BM RI 6597); Leuschke (1966); Craven and Foster (1967); W.E. Mason and Wilson (1967); K.N. Palmer (1967a, 1973a,b); Singer, Cook and Grumer (1967 BM RI 6931); Dorsett and Nagy (1968 BM RI 7132); Gillis (1968); HM Factory Inspectorate (1968); Nagy, Cooper and Dorsett (1968 BM RI 7208); Schwab (1968, 1986); Singer, Bruzsak and Grumer (1968 BM RI 7103); Grumer (1971 BM RI 7552); Fris (1972); N. Gibson (1972); Heinrich (1972); Kohlschmidt (1972); Lutolf (1972); Mintschew *et al.* (1972); Novotny, Pantoflicek and Lebr (1972); Raftery (1972, 1975 FRS Fire Res. Tech. Pap. 21); Ishihama and Enomoto (1973); Mitsui and Tanaka (1973); CMI (1975 CMI 72001-12, 1987 CMI 77005-2); Eckhoff (1975, 1976a,b, 1985, 1991); Tonkin (1975 FRS Fire Res. Note 1028); Eckhoff and Enstad (1976); Kelley and Forkner (1976 BM RI 8201); Lovachev (1976, 1978b); Napier (1977b); Burgoyne (1978); Eckhoff and Mathisen (1978); Nettleton (1978a); Hertzberg, Cashdollar and Opferman (1979 BM RI 8360); P.E. Moore (1979a); Scholl *et al.* (1979); Kalkert and Schecker (1980); Nomura and Tanaka (1980); Sinclair and Sweis (1980); Bartknecht (1981a, 1989); Cocks and Meyer (1981); Deguingand and Galant (1981); Hertzberg, Cashdollar and Lazzara (1981); Jacobson (1981); I. Swift (1981, 1982); BRE (1982 CP5/82, 1983 SO 37); Field (1982, 1983, 1985 LPB 66); Hertzberg (1982); Hertzberg *et al.* (1982); Siwek (1982); Zeeuwen (1982, 1988); Felstead, Rogers and Young (1983); Nagy and Verakis (1983); Nomura, Torimoto and Tanaka (1984); Tulis and Selman (1982, 1984); Sweis and Sinclair (1985); Dahn, Ashum and Williams (1986); N. Gibson *et al.* (1986); Sweis (1987); Lunn (1988b); Cashdollar, Hertzberg and Zlochower (1989); M. Ward (1989); Amyotte *et al.* (1991); Continfflo *et al.* (1991); Hertzberg, Zlochower and Cashdollar (1991, 1992); Pu *et al.* (1991); Torrent, Fuchs and Borrajo (1991); Cashdollar and Chatrathi (1992); Liu and Katsabanis (1993); Mintz (1993); Zhang and Wall (1993); Cashdollar (1994); Chatrathi (1994); Hensel *et al.* (1994)

Dusts may be formed by condensation from vapours of materials which condense to form solids directly or by mechanical size reduction of solid materials. In the former case the particle size tends to be much smaller.

The terms 'dust and powder' tend to be used interchangeably and have no agreed definition. It is desirable, however, to set some limits to the particle size of materials under consideration. BS 2955: 1958 defines as 'powder' material with a particle diameter of less than 1000 μm (16 BS mesh size) and as 'dust' material with a particle diameter of less than 76 μm (200 BS mesh size). K.N. Palmer (1973a) takes a somewhat wider definition and does not exclude from his treatment information on materials with a particle diameter coarser than 1000 μm.

17.43.2 Dust explosions

The hazard of a dust explosion or fire exists wherever flammable dusts are handled. Generally, a dust explosion occurs only if the dust is dispersed in air, but transition from a fire to an explosion can occur, and vice versa. If a burning dust is disturbed, a dust suspension may be formed and ignited. This initial explosion may generate further dust clouds, which in turn explode. On the other hand, burning particles from an explosion may act as the source of ignition for a fire of other flammable materials.

The explosive effect of a dust explosion is caused by the rapid release of heat and the accompanying rapid pressure rise or expansion of the hot gases.

In dust explosions the combustion process is very rapid. The flame speed is high, comparable with that in gas deflagrations. Maximum explosion pressures are often close to the theoretical values calculated assuming no heat loss during the explosion.

It is uncertain whether detonation can occur in dust explosions in industrial plant. The flame speed in dust explosions is high and in some cases has been reported as approaching that found in detonations. Most of the evidence for detonations in dust suspensions relates to coal mine galleries where the explosion was initiated by a strong ignition source. It is not clear whether detonations can develop from weak ignition sources in industrial plant.

As far as explosion protection is concerned, K.N. Palmer (1973a) states:

> It is general practice in considering protection against dust explosions, in industrial plant, to assume that deflagrations rather than detonations occur. This procedure has proved to be satisfactory in practice, which is fortunate, because deflagrations are simpler to deal with than detonations.

The sequence of events in a serious industrial dust explosion is often as follows. A primary explosion occurs in an item of plant. The explosion protection is not adequate to prevent the flame issuing from the plant, due either to rupture of the plant or to poor explosion venting. The air disturbance disperses the dust in the work room and causes a secondary explosion. The quantity of dust in the secondary explosion often exceeds that in the primary one. Moreover, the building in which the secondary explosion occurs may be weaker than the plant itself. The secondary explosion is thus often more destructive than the primary one.

In some cases the primary explosion also occurs in the open and disturbs dust deposits, and this causes a secondary explosion. In other cases the primary explosion occurs in one unit of the plant and the explosion propagates within the plant to other units.

The possibility of a highly destructive secondary explosion makes dust explosions rather unpredictable.

It is characteristic of plant handling dusts that it is generally very weak relative to the stresses exerted by a dust explosion. Frequently, it can withstand pressures of only 7–15 kPa (1–2 psi). This compares with the pressures of up to 1000 kPa (140 psi) which have been reported for dust explosions under the most unfavourable conditions.

Similar considerations apply to buildings containing plants handling dusts. Generally, buildings cannot withstand more than about 7 KN/m^2 (1 $lb_f/in.^2$) pressure.

Some very destructive dust explosions have occurred in multi-storeyed buildings. The failure of walls on a lower floor has led to collapse of floors and walls on higher storeys. A particular hazard in multi-storeyed buildings is vertical bucket elevators handling dust. A bucket elevator may allow an explosion to propagate through many storeys of the building.

The dust explosion problem is aggravated by the increasing size of plants. The damage caused by an explosion in a large volume may be more than proportionately

greater than that resulting from a small volume explosion, because the larger unit is frequently relatively weaker.

A particular problem arises where it is desired to use plant designed for a low explosibility dust to handle a high explosibility one. In this case it is essential to check very carefully whether the plant is suitable or needs modification.

17.43.3 Dust explosion incidents

Accounts of dust explosion accidents have been given in *Dust Explosions* (D.J. Price and Brown, 1922), *Report of Important Dust Explosions* (NFPA, 1957/1) and *Dust Explosions in Factories* (HSE, 1970 HSW Blkt 22) and by K.C. Brown and James (1962), Beach (1964), K.N. Palmer (1973a) and Kaufman (1986).

The HSE booklet lists a wide range of industries and operations in which serious dust fires/explosions have occurred. Beach gives a detailed analysis of dust explosions, excluding those in coal mines, in the period 1900–59. He lists 1110 explosions and 648 fatalities.

Some principal dust explosions are given in Table 17.63.

Historically, industries particularly affected by dust explosions have been flour milling, grain storage and coal mining. A classic flour mill explosion was that in a flour mill in Turin in 1785 (Morozzo, 1795). Serious flour mill explosions have occurred in the United Kingdom, including one at Bow, London, in 1965 which killed five people.

An explosion in a starch/corn plant at Cedar Rapids, Iowa, in 1919 killed 43 people and one at a similar plant in Peking, Illinois, in 1924 resulted in 42 deaths.

Grain storage facilities are liable to serious dust explosions. In 1977 a series of dust explosions occurred in a set of grain silos at Westwego, near New Orleans, Louisiana, which killed 35 people (Case History A89). This disaster was thus on the same scale as that of Flixborough.

Many severe dust explosions have also occurred in coal mines, but these are not considered here.

Some statistical data on dust explosions are given by Lunn (1992). In the United Kingdom in the period 1958–67, there were 247 reported explosions with 9 fatalities and 324 non-fatal injuries, and in the period 1962–79 there were 474 explosions reported with 25 fatalities and 633 non-fatal injuries; 10 of the 25 fatalities in this latter period occurred in two incidents.

Lunn also quotes two other surveys. One is by the HSE covering the periods 1979–84 and 1985–88, and gives breakdowns by type of event, dust involved, equipment involved and ignition source. In the total period 1979–88 there were 36 dust fires with injury, 123 fires with no injury, 41 explosions with injury and 95 explosions with no injury. Principal items of equipment involved were mills, grinders, filters, driers, silos/hoppers and ducts with 51 (17%), 47 (16%), 43 (14%), 19 (6%) and 15 (5%) events, respectively; 95 (31%) events were classified in the category 'other'. The second survey is by the Berufsgenossenschaftliches Institut fur Arbeitssicherheit (BIA) and gives breakdowns by plant group, equipment involved and ignition sources.

17.44 Dust Explosibility Characteristics

17.44.1 Dust explosibility parameters

Important explosibility characteristics of dust suspensions are:

(1) explosibility classification;
(2) minimum explosive concentration;
(3) minimum ignition temperature;
(4) minimum ignition energy;
(5) maximum permissible oxygen concentration to prevent ignition;
(6) explosion pressure characteristics
  (a) maximum explosion pressure,
  (b) maximum rate of pressure rise,
  (c) average rate of pressure rise.

An account is given first of the factors which influence dust explosibility, then of the tests used to determine the explosibility parameters and then of the explosibility parameters themselves.

Table 17.63 *Some dust explosion incidents*

Date	*Location*	*Material*	*Plant/building*	*Deaths/injuries*
1911	Glasgow, UK			5d, 8i
	Liverpool, UK			37d, 100i
	Manchester, UK			3d, 5i
1913	Manchester, UK			3d, 5i
1919	Cedar Rapids, IA	Corn starch	Starch plant	43d
1924	Peking, IL	Corn starch	Starch plant	42d
1930	Liverpool, UK			11d, 32i
1941	Liverpool, UK			6d, 40i
1944	Kansas City, KS	Grain dust	Corn mill	4d, 20i
1955	Waynesboro, GA	Grain dust	Feed plant	3d, 13i
1962	St Louis, MO	Grain dust	Feed plant	2d, 34i
1964	Paisley, UK			5d, 2i
1965	Bow, London, UK	Flour	Flour mill	5d
1970	Kiel, FRG	Grain dust	Grain silo	6d, 18i
1977	Galveston, TX	Grain dust	Grain silo	15d
1977	Westwego, LA	Grain dust	Grain silo	36d, 10i
1979	Hamburg, FRG	Grain dust	Grain silo	2i
1979	Lerida, Spain	Grain dust	Grain silo	7d
1980	Naples, Italy	Grain dust	Grain silo	8i

17.44.2 Factors influencing dust explosibility

The explosibility of dust suspensions in air is characterized by parameters similar to those which define the flammability of gas–air mixtures as described in Chapter 16, but there are some significant differences.

The explosibility of a dust may be regarded as increasing as the minimum explosible concentration, the minimum ignition temperature and the minimum ignition energy decrease and the burning velocity and maximum rate of pressure rise increase.

The characterization of particles is a complex matter, but general characteristics which affect the behaviour of particles include those of the individual particle itself such as particle composition, density, size, shape, surface properties and moisture content and those of the bulk powder such as bulk density and flow properties.

Some factors which influence dust explosibility are:

(1) chemical composition;
(2) particle size;
(3) moisture content;
(4) oxygen concentration;
(5) inert gas;
(6) admixed inert dust concentration.

Nagy and Verakis (1983) give a large number of plots showing the effect of these factors on the dust explosibility parameters, mainly for particular dusts.

There are certain chemical groups such as COOH, OH, NH_2, NO_2, C≡N, C=N and N=N which tend to be associated with higher dust explosibility and certain others such as Cl, Br and F with lower explosibility.

Dusts of pure metals generally react with air to form metallic oxides. In this case the explosive increase in pressure is due to expansion of the nitrogen of the air caused by the heat release. In some cases metals actually react violently with the nitrogen itself to form a metallic nitride.

Volatile matter in the dust tends to enhance the explosibility, although there is generally little increase for volatile contents below 10%. Coal dust in particular can contain a high proportion of volatile matter.

Interestingly, according to Nagy and Verakis, pure carbon dust does not explode. They speculate that the reaction rate of pure carbon with oxygen is too low. But carbon dust containing 8% volatile matter is explosive.

If the dust contains inert material this reduces its explosibility. This includes coal dust with clay and some polymeric materials that contain inert fillers.

Dust explosibility is strongly affected by particle size. Particle size is usually defined in terms of an equivalent particle diameter. Generally, a dust with a particle diameter greater than 500 μm is unlikely to be responsible for initiation of an explosion, though it may undergo combustion in one already occurring. At the other end of the range, reduction in particle size below about 50–74 μm does not normally result in any significant increase in explosibility. The particle diameter of dusts used in dust explosibility testing normally does not exceed 75 μm.

A dust usually contains a range of particle sizes. A relatively small proportion of fine particles enhances the explosibility of a dust. Moreover, attrition caused by handling the dust tends to generate fine particles.

Figure 17.112 illustrates the effect of particle size on some of the more important dust explosibility parameters. These results are for atomized aluminium, which is a rather extreme case, but nevertheless they illustrate general trends.

Moisture content has a strong effect on dust explosibility, although the effect is generally weak for moisture contents below 10%. At the other end of the range, dust with a moisture content greater than 30% is unlikely to be responsible for initiation of an explosion.

The oxygen concentration in the surrounding atmosphere has a strong effect on dust explosibility, which increases as the oxygen concentration increases. Conversely, the explosibility decreases as the oxygen concentration decreases and the inerts concentration increases.

Dust explosibility is affected by the concentration of any admixed inert dust, although the effect is generally weak for inert dust concentrations below 10–20%.

17.44.3 Dust explosibility tests

The tests which are carried out on dust explosibility vary between countries and a large variety of tests are in use. It is convenient to start with those developed at the Bureau of Mines (BM) in the United States, since these have also been widely used in other countries, including the United Kingdom.

Accounts of the various tests in the Bureau of Mines scheme have been given in a series of reports, in particular that by Dorsett *et al.* (1960 BM RI 5624). A summary has been given by Nagy and Verakis. Some of the apparatus used in these tests is illustrated in Figure 17.113.

Dust explosibility is determined in the Hartmann apparatus, shown in Figure 17.113(a). The Hartmann apparatus is a vertical tube of volume 1.2 l. The dust is dispersed by an air blast. The ignition source is a hot wire or spark igniter. If any flame propagation is observed, the dust is explosible.

Two other types of apparatus which are also used to determine whether a dust is explosible are the horizontal tube apparatus and the inflammator apparatus, shown in Figures 17.113(b) and (c), respectively. In the horizontal tube apparatus, the dust is dispersed by an air blast. The ignition source is a hot coil. In the inflammator apparatus, the dust suspension is injected into the apparatus against a deflector plate and falls onto the ignition source a hot wire or spark igniter. The apparatus is useful for dusts which are not readily dispersed.

The minimum ignition temperature for explosion of a dust suspension is measured in the Godbert–Greenwald furnace, shown in Figure 17.113(d). A dust suspension is injected into a vertical tube held in a constant temperature furnace and the appearance of flame at the open bottom mouth of the furnace is observed.

A separate determination is made of the minimum ignition temperature of a dust layer, which in general differs from that of the dust in suspension. Again, the Godbert–Greenwald furnace is used, but in this case the dust is held in a wire mesh basket 1 in. in diameter and ½ in. deep. Another method which is also used is ignition of the layer on a hot plate.

The minimum ignition energy for explosion of a dust suspension is measured in the Hartmann vertical tube apparatus. The dust is dispersed by an air blast. The ignition source is a capacitor discharge spark igniter. Any propagation of flame is observed.

The maximum oxygen concentration to prevent ignition is measured in the open Hartmann vertical tube using spark ignition and in the Godbert–Greenwald furnace.

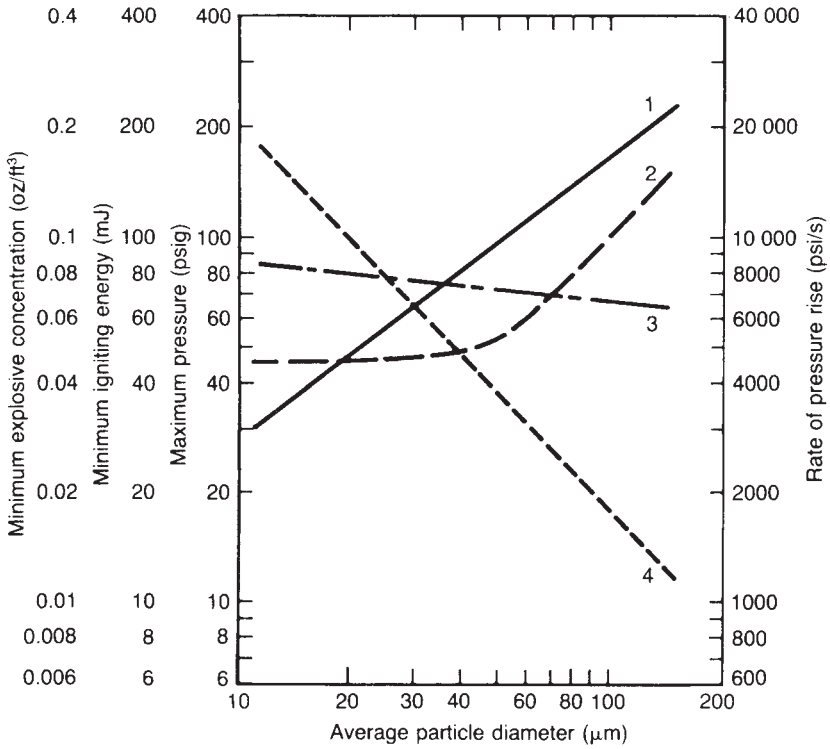

Figure 17.112 *Dust explosibility characteristics: effect of particle size on some principal parameters for atomized aluminium (Nagy and Verakis, 1983). 1, minimum ignition energy; 2, minimum explosive concentration; 3, maximum explosion pressure; 4, maximum rate of pressure rise*

The pressure–time profile is measured in a closed Hartmann vertical tube apparatus, or Hartmann bomb. The explosion pressure characteristics are obtained from this.

The Hartmann test for the pressure–time profile is the subject of ASTM E789-81 1981 Test for Pressure and Rate of Pressure Rise for Dust Explosions in a Closed Vessel (Hartmann test).

In the United Kingdom dust explosibility testing is done at the Fire Research Station (FRS), Borehamwood, and the test scheme covers the explosibility characteristics listed above. These tests have been described by K.N. Palmer (1973a), Raftery (1975 FRS Fire Res. Tech. Pap. 21) and Field (1982).

Dust explosibility classification is performed using the vertical tube, the horizontal tube and the inflammator apparatus. The dust is classed as explosible if a positive result is obtained in any one of the three types of test. The minimum explosive concentration is measured in the vertical tube apparatus, the minimum ignition temperature in a modified form of the Godbert–Greenwald furnace and the minimum ignition energy in a modified form of the vertical tube apparatus.

The maximum permissible oxygen concentration to avoid ignition used to be measured in the Godbert–Greenwald furnace but is now measured in the vertical tube apparatus at ambient temperature. The dust is dispersed by a blast of the reduced oxygen mixture. The ignition source is a hot coil or spark igniter. Any propagation of flame is observed.

The explosion pressure parameters are obtained by measuring the pressure–time profile in a stronger form of the vertical tube apparatus. A typical pressure–time curve, given by K.N. Palmer (1973a), is shown in Figure 17.114. The pressure p_1 is caused by the entry of dispersing air into the vessel. The maximum explosion pressure p_{max} is normally calculated as

$$p_{max} = p_2 - p_1 \qquad [17.44.1]$$

An alternative definition is

$$p_{max} = \frac{\rho_o}{\rho_1 + \rho_o}(p_2 - p_1) \qquad [17.44.2]$$

where p_{max} is the maximum explosion pressure, p_o is the atmospheric pressure, p_1 is the small initial pressure rise and p_2 is the pressure defined in Figure 17.114.

Since p_1 is usually about 40 kPa, the values of p_{max} calculated from Equation 17.44.2 differ by about 40% from those calculated from Equation 17.44.1. In using values of maximum explosion pressure given in the literature, care should be taken to check the definition used.

The maximum rate of pressure rise $(dP/dt)_{max}$ is determined from the maximum slope of the pressure rise curve

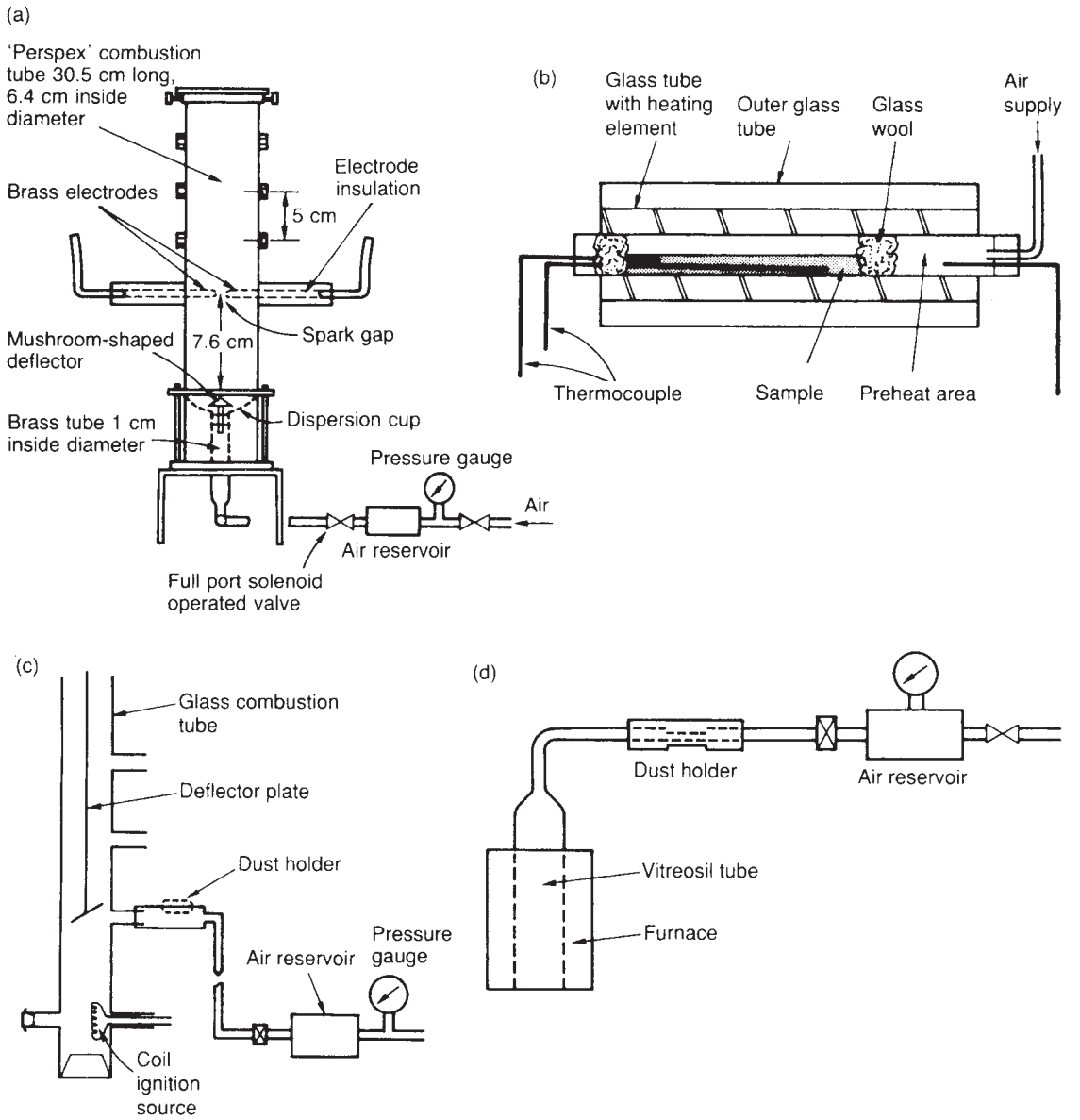

Figure 17.113 *Dust explosibility characteristics – Bureau of Mines test apparatus (Cross and Farrer, 1982): (a) Hartmann vertical tube apparatus; (b) horizontal tube apparatus; (c) inflammator apparatus; (d) Godbert–Greenwald furnace (Courtesy of Plenum Publishing Corporation)*

a/b and the average rate of pressure rise $(\mathrm{d}P/\mathrm{d}t)_{\mathrm{av}}$ is calculated as $(p_2 - p_1)/(t_2 - t_1)$.

Another important dust explosibility test scheme is that developed in Switzerland by Bartknecht. Accounts are given by Bartknecht (1981a) and Field (1982). Various workers have shown that the Hartmann vertical tube test involves wall effects and gives less than ideal dust dispersion. In this scheme, therefore, basic test for dust explosibility is performed in a 20 l spherical vessel, shown in Figure 17.115. This test is an alternative to the Hartmann vertical tube test in the BM scheme.

In the 20 l sphere test the dust is injected into the sphere from a separate container. The ignition source is located in the centre of the sphere and is usually a chemical igniter with an ignition energy of 10 kJ. A standard time delay is used between injection and ignition.

The 20 l sphere test is used, like the Hartmann vertical tube, for both qualitative and quantitative determinations.

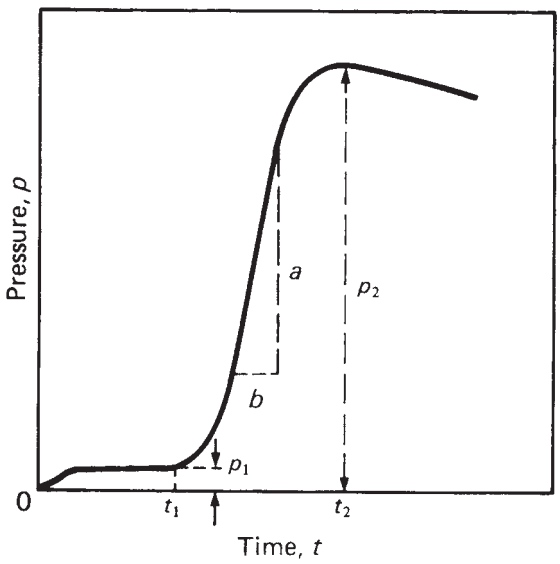

Figure 17.114 *Dust explosibility characteristics: explosion pressure curve in a vertical tube apparatus (K.N. Palmer, 1973a) (Reproduced with permission from Dust Explosions and Fires by K.N. Palmer, 1973, Chapman and Hall)*

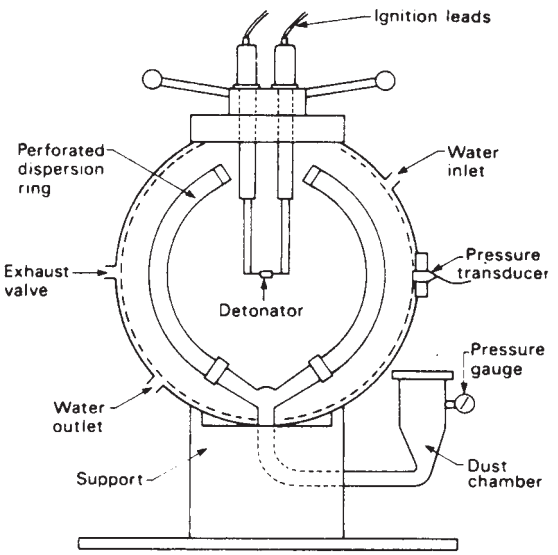

Figure 17.115 *Dust explosibility characteristics: 20 l sphere test apparatus (Field, 1982; reproduced by permission of Elsevier Science Publishers)*

It is used both to determine whether a dust is explosible and to measure the maximum explosion pressure and the maximum rate of pressure rise.

Use is also made of a 1 m^3 sphere as an alternative to the 20 l sphere.

The general approach taken in this scheme is to use these spheres to determine also the other explosibility characteristics. Thus, the spheres are used to determine the minimum explosible concentration and the minimum ignition energy.

The analysis of the results is similar to that used for gas explosions. The cube root law is written in the form

$$\left(\frac{dP}{dt}\right)_{max} V^{1/3} = K_{st} \qquad [17.44.3]$$

where K_{st} is the dust explosibility constant (or K_{st} value), P is the absolute pressure, t is the time and V is the volume of the vessel. The K_{st} value is the basis of the dust explosibility classification and is a measure of the maximum rate of pressure rise. It corresponds to the K_G value for gases.

Another dust explosibility test scheme is that developed by Eckhoff at the Christian Michelsen Institute (CMI) in Norway. An account is given by Field (1982). Eckhoff has shown that the minimum ignition energy obtained in a test apparatus depends critically on the ignition source used. He has developed for this test an ignition source with a long duration spark which is a particularly efficient igniter for dusts.

Dust explosibility testing in Germany is performed by the Bundesanstalt fur Materialprufing (BAM). Accounts of the test scheme have been given by Leuschke (1966) and Field (1982). For dust explosibility use has been made of the vertical tube and inflammator types of apparatus, but increasing use is made of the 20 l and 1 m^3 spheres. Other parameters such as minimum explosive concentration and minimum ignition energy are determined in relatively large (~1 m^3) vessels.

Turning to the background, and interpretation, of these various tests, the two main apparatus for dust explosibility testing are the Hartmann vertical tube and the 20 l sphere. The Hartmann tube is liable not to give uniform conditions for dust dispersion and turbulence. Further, it is subject to wall effects. After initial spherical expansion the flame travels as two fronts up and down the tube. These conditions give a lower rate of combustion and of pressure rise. Consequently, the strength of the pressure rise in the Hartmann bomb is less than that in the 20 l sphere.

These problems are largely overcome by the use of a sufficiently large spherical test vessel. The two principal vessels adopted are 20 l and 1 m^3 spheres. It has been shown that the former is close to the critical size below which effects of vessel size occur and above which they do not. This is illustrated in Figure 17.116.

A large amount of the earlier work on dust explosibility was done at the Bureau of Mines using the Hartmann apparatus. Much recent work has been done using the 20 l vessel. Moreover, methods have been developed for dust explosion venting which depend on experimental data for one or other apparatus. It is therefore of some interest to be able to relate the results obtained in one apparatus to those obtained in the other. Unfortunately, the results often do not agree and may even give different rankings.

The problem of relating results for the two methods has been examined by Field and Abrahamsen (1981 BRE N81/81). They conclude that there is no simple relation, although Field (1982) does quote the table given in NFPA 68: 1978 relating the dust class to the maximum rate of pressure rise in the Hartmann apparatus; this relation is given below.

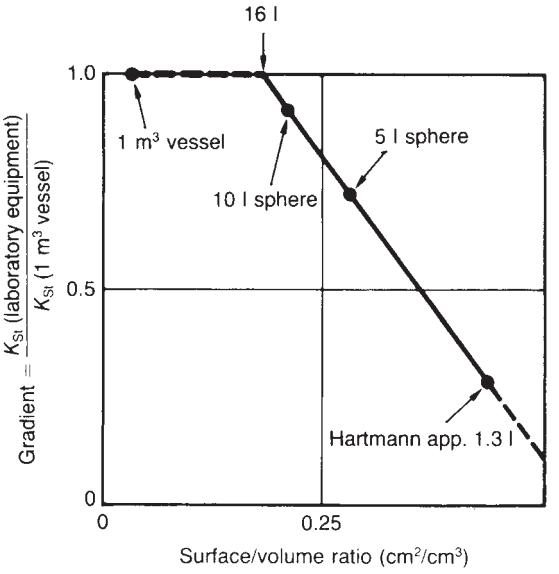

Figure 17.116 *Dust explosibility characteristics: effect of test vessel size on K_{st} value (Bartknecht, 1981a) (Courtesy of Springer-Verlag)*

The furnace apparatus for the determination of the minimum ignition temperature gives a relatively short residence time. Cross and Farrer comment that a lower minimum ignition temperature may be possible if the dust suspension is held at an elevated temperature for a prolonged period.

With regard to the minimum ignition energy, it has gradually become clear that the Hartmann vertical tube has a number of deficiencies. The test appears to overestimate the minimum ignition energy by a factor of between 2 and 5, and is therefore not conservative.

The ignition source in the Hartmann vertical tube test is a capacitive spark igniter. This has two disadvantages. One is that the spark energy tends to be less than the theoretical energy ($\frac{1}{2}CV^2$) due mainly to loss in the transformer. The other is that it is not possible to control the duration of the spark, which is a significant variable.

An alternative igniter is the direct capacitive spark, which uses a circuit without a transformer, and the inductive spark, developed by Eckhoff. Both these igniters give much lower values of the minimum ignition energy than the Hartmann apparatus. Thus, the Hartmann apparatus, the direct capacitance and Eckhoff igniters give the value of the minimum ignition energy of wheat dust as 40, 25 and 7 mJ and that of fine aluminium powder as 1–15, 7.5 and 1 mJ, respectively.

All early data on minimum ignition energy are likely to have been determined using the Hartmann vertical tube test.

The maximum oxygen concentration to prevent ignition was originally measured, as stated above, using the furnace test, but since the operating temperature of the furnace is high and since this concentration is a function of temperature, the values obtained were excessively low. In the United Kingdom the measurement is now made using the vertical tube apparatus at ambient temperature. Typical values of the maximum oxygen concentration obtained using the furnace test are 4–7% compared with 10–15% using the vertical tube test.

17.44.4 Dust explosibility classification

In the United Kingdom the dust explosibility classification used over a number of years is:

Group A: Dusts which ignited and propagated flame in the test apparatus.
Group B: Dusts which did not propagate flame in the test apparatus.

Tests are made using all three types of apparatus described, and the dust is classified as Group A if flame propagation occurs in any one apparatus.

Group A dusts should be regarded as capable of causing a dust explosion. Group B dusts are non-explosible, but can burn.

The classification into Groups A and B applies only to dust dispersions at near atmospheric temperature. At higher temperatures some dusts in Group B may be capable of causing a dust explosion.

This classification system replaced an earlier scheme in which dusts were classified as Class I, II or III. Broadly, class I corresponds to Group A and Classes II and III to Group B.

In the United States the NFPA classification of hazardous materials is Class I for gases and vapours and Class II for dusts. The latter are subdivided into E, metal dusts, F, carbonaceous dusts, and G, flour dusts.

The Bureau of Mines has developed an index of explosibility which ranks dusts relative to Pittsburgh coal. The index of explosibility IE is the product of the explosion severity ES and the ignition sensitivity IS

$$\mathrm{IE} = \mathrm{IS} \times \mathrm{ES} \qquad [17.44.4]$$

with

$$\mathrm{IS} = \frac{(\mathrm{MIT} \times \mathrm{MIE} \times \mathrm{MEC})_{\mathrm{Pc}}}{(\mathrm{MIT} \times \mathrm{MIE} \times \mathrm{MEC})_{\mathrm{sample}}} \qquad [17.44.5]$$

$$\mathrm{ES} = \frac{(\mathrm{MEP} \times \mathrm{MRPR})_{\mathrm{Pc}}}{(\mathrm{MEP} \times \mathrm{MRPR})_{\mathrm{sample}}} \qquad [17.44.6]$$

where MEC is the minimum explosive concentration, MEP is the maximum explosion pressure, MIE is the minimum ignition energy, MIT is the minimum ignition temperature and MRPR is the maximum rate of pressure rise, and the subscripts Pc and sample denote Pittsburgh coal and sample.

The index of explosibility is a relative one, and is to this extent less dependent on the apparatus used, but its determination requires the conduct of the full range of tests.

The K_{st} method has already been described. The actual K_{st} classification, its relationship to Hartmann bomb data and to some typical industrial dusts are given in Table 17.64.

17.44.5 Minimum explosive concentration

A dust suspension in air is usually explosible only within certain concentration limits. The upper concentration limit, however, is ill-defined. The lower limit is known as

Table 17.64 *Dust explosibility characteristics: the K_{st} classification*

A Dust explosion classes

Dust explosion class	K_{st}^{a} (bar m/s)	*Explosion features*
St 0	0	No explosion
St 1	>0–200	Weak
St 2	201–300	Strong
St 3	>300	Very strong

B Relation of K_{st} and Hartman bomb data[b]

K_{st}[a] (bar m/s)	*Hartman bomb*, $(dP/dt)_{max}$ (psi/s)
≤200	≤7300
201–300	7300–22000
>300	>22000

C Typical dusts

Dust explosion class	*Typical dust*
St 0	Non-explosive dust
St 1	Grain dust
St 2	Organic pigment
St 3	Fine metal dust

[a] These figures are for a strong ignition source (10,000 J). For a weak ignition source (10 J) the corresponding figures are given by NFPA 68: 1978 as: 0, >0–100, 101–200 and >200.
[b] NFPA 68: 1978.

the minimum explosive concentration or the lower explosive limit (LEL), the two terms being interchangeable, and the upper as the upper explosive limit (UEL).

It is found empirically that for a large number of dusts the lower explosive limit lies in the range 20–60 g/m^3 and the upper explosive limit in the range 2–6 kg/m^3.

Some progress has been made in the theoretical estimation of the explosive limits for dusts.

The minimum explosive concentration decreases as the particle size decreases and the volatile matter content and oxygen concentration increase and increases as the moisture content and concentration of admixed inert dust increase.

Dust suspensions in industrial plant are often above the upper limit, but it is not generally practical to use this as a design parameter. For design it is the minimum explosible concentration which is of prime interest.

17.44.6 Minimum ignition temperature

The minimum ignition temperature decreases as the particle size decreases and the volatile matter content and oxygen concentration increase and increases as the moisture content and concentration of admixed inert dust increase.

17.44.7 Minimum ignition energy

The minimum ignition energy decreases as the particle size decreases and the volatile matter content and oxygen concentration increase and increases as the moisture content and concentration of admixed inert dust increase.

17.44.8 Maximum permissible oxygen concentration

There appears to be relatively little data on the variation of the maximum oxygen concentration to prevent ignition with the various influencing factors. As already described, the maximum oxygen concentration decreases as temperature increases.

17.44.9 Maximum explosion pressure

The maximum explosion pressure increases as the particle size decreases, but the effect is relatively weak. There does not appear to be much data on the effect of the other influencing factors.

17.44.10 Maximum rate of pressure rise

The maximum rate of pressure rise increases as the particle size decreases and the volatile matter content and oxygen concentration increase and decreases as the moisture content and concentration of admixed inert dust increase.

An investigation of the relationship between the initial and maximum rates of pressure rise in dust explosibility testing using a 1 m^3 vessel has been described by Chathrathi (1994). No such relationship was found.

17.44.11 Burning velocity

Another parameter of interest in relation to dust explosions is the burning velocity. Knowledge of this parameter would allow the use of the large number of methods and models developed for gas explosions and gas explosion venting. The burning velocity is not the subject of standard tests, but some work has been done to estimate burning velocities of dusts.

Maisey (1965) has used an 'equivalent burning velocity' for dust mixtures. His basic approach is to compare the maximum rate of pressure rise for dust mixtures with that obtained for gases with known burning velocity and thus to calibrate the dusts.

Burgoyne (1967a, 1978) has tabulated for gases maximum rates of pressure rise determined in the Hartmann bomb and burning velocities for gases. His data are shown in Table 17.65. These data have then been used by Field (1982) to give the relation between maximum rate of pressure rise in the Hartmann bomb and burning velocity shown in Figure 17.117.

Nagy and Verakis (1983) have given values of the burning velocity of dust mixtures obtained by applying Equation 17.7.77, which gives a relation between the rate of pressure rise and the burning velocity, to the experimental data on the rate of pressure rise of such mixtures determined in work at the Bureau of Mines.

Table 17.65 *Dust explosibility characteristics: relation between maximum rate of pressure rise in Hartmann bomb and burning velocity (after Burgoyne, 1978) (Courtesy of the Society of Chemical Industry)*

Gas	*Maximum rate of pressure rise* (bar/s)	*Maximum burning velocity* (m/s)
Methane	181	0.37
Propane	248	0.46
Ethylene	536	0.70
Hydrogen	1,276	3.35

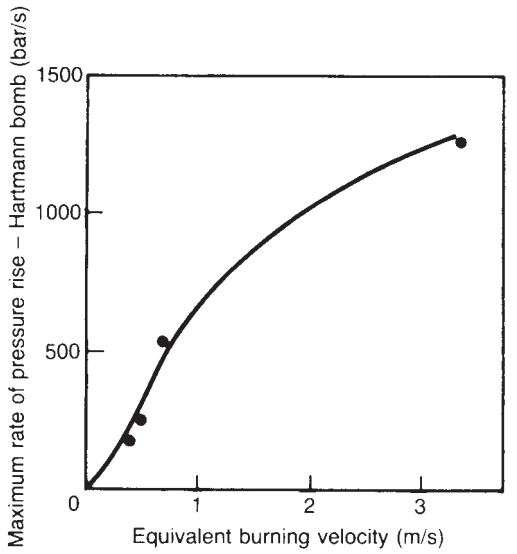

Figure 17.117 *Dust explosibility characteristics: relationship between maximum rate of pressure rise in the Hartmann bomb and burning velocity (Field, 1982; reproduced by permission of Elsevier Science Publishers)*

17.44.12 Minimum ignition temperature of dust layer

The minimum ignition temperature of a dust layer is a function both of the dust and of the thickness of the layer, the ignition temperature decreasing as the thickness of the layer increases.

The two methods of measurement, by furnace and by hot plate, give results which differ by up to about 30°C.

The layer ignition temperature decreases as the particle size decreases and the volatile matter content and oxygen concentration increase.

In Germany, use is made of a maximum permissible surface temperature (MPST) for equipment on which dust may settle. An account of work related to this is given by Hensel *et al.* (1994). The MPST is established by determining the glow temperature of the dust and substracting a safety margin, set at 75°C. The glow temperature is the temperature at which a 5 mm dust layer is ignited in a hot plate test. As indicated, a dust layer thicker than 5 mm may give a lower glow temperature. The authors describe work on models based on constant surface temperature and the alternative of constant surface heat flux, utilizing thermal explosion theory.

17.44.13 Hybrid dust–gas mixtures

If flammable gas is present in addition to the dust, the explosibility of the dust is enhanced. Increase in the concentration of flammable gas results in decrease in the minimum explosive concentration, minimum ignition temperature, minimum ignition energy and increase in the maximum rate of pressure rise.

The presence of flammable gas can therefore render explosive a dust–gas mixture at a dust concentration which is below the normal lower explosive limit for the dust and at a gas concentration below the normal lower explosive limit for the gas. Another important effect is to make explosive a dust with a particle size large enough to keep it normally non-explosive.

For such hybrid dust–gas mixtures Cardillo and Anthony (1978) have applied Le Chatelier's equation in the form

$$\frac{c_d}{l_d} + \frac{c_g}{l_g} = 1 \qquad [17.44.7]$$

where c is the concentration (g/m^3) and l is the lower explosive limit (g/m^3) and subscripts d and g denote dust and gas, respectively. They modify this relation empirically to give

$$\frac{c_d}{l_d} + \frac{c_g}{l_g} = 0.8 \qquad [17.44.8]$$

An alternative relation has been given by Pellmont (1979) as follows:

$$l_{dh} = l_d \left(\frac{c_g}{l_g} - 1 \right)^2 \qquad [17.44.9]$$

where l_{dh} is the lower explosive limit of the dust given the presence of flammable gas.

Where the hybrid mixture rises due to contamination of a dust by solvent, it is convenient to be able to express Equation 17.44.8 in terms of the mass of solvent contaminated dust and of the mass fraction of solvent in that dust. Thus, following Field (1982), Equation 17.44.8 can be rearranged to yield

$$m_{sd} = \frac{0.8 l_d}{1 + \phi_s[(l_d/l_g) - 1]} \qquad [17.44.10]$$

where m_{sd} is the mass concentration of solvent contaminated dust (g/m^3) and ϕ_s is the mass fraction of solvent in that dust.

As already mentioned, the presence of flammable gas also affects the other explosibility characteristics. In particular, it affects the maximum rate of pressure rise and hence the K_{st} value. Bartknecht gives data showing the effect of different concentrations of methane and propane on the dust explosion class of polyvinyl chloride dust. Dust of class St 0 changes to classes St 1, 1/2, 2 and 3 at methane concentrations of 1, 3, 5 and 7%, respectively, and to classes 1, 2/3 and 3 at propane concentrations of 0.9, 2.7 and 4.5%, respectively.

For hybrid mixtures the minimum ignition energy is also lower than that of the dust alone.

17.44.14 Dust explosibility data

There are available a number of compilations of dust explosibility data. Most of these data derive either from the work of the Bureau of Mines or from that of Donat and Bartknecht.

The explosibility classification of a number of dusts is given in SHW 830 *Dust Explosions in Factories. Classification List of Dusts That Have Been Tested in the form of a Dust Cloud* by HM Factory Inspectorate (1968).

Compilations of data have been given by Maisey (1965), K.N. Palmer (1973a), Cross and Farrer (1982), Field (1982) and Nagy and Verakis (1983). Field gives two tables, one for data obtained in tests in small scale apparatus and one for data from large apparatus.

Some explosibility properties of selected dusts in air are given in Table 17.66.

The more modern apparatus such as the 20 l vessel tends to yield much higher values for the maximum explosion pressure and the maximum rate of pressure rise. A comparison of values is given by Nagy and Verakis (1983).

An account of current results from dust explosibility testing at the BM, using the 201 vessel and covering a wide and representative range of dusts, has been given by Cashdollar (1994).

17.44.15 Variability of dust explosibility data

Like the data on flammability characteristics, data on dust explosibility exhibit considerable variability. Nagy and Verakis (1983) begin their account with a table of data to emphasize the point. Another set of data illustrating the data variability are those given by Cross and Farrer (1982) on polyethylene.

It may be expected that the considerable progress made in dust explosibility testing has reduced this variability, but it should always be borne in mind, particularly in assessing data for early work.

17.45 Dust Ignition Sources

An account of ignition sources was given in Chapter 16 with particular reference to ignition of gases. The ignition sources for dusts are broadly similar, although there are certain points specific to dusts and dust-handling plant. The account given here is therefore relatively brief.

Discussions of ignition for dusts are given by K.N. Palmer (1973a), Field (1982), Cross and Farrer (1982) and Eckhoff (1991).

Some principal ignition sources for dusts include:

(1) flames and direct heat;
(2) hot work;
(3) incandescent material;
(4) hot surfaces;
(5) electrostatic sparks;
(6) electrical sparks;
(7) friction sparks;
(8) impact sparks;
(9) self-heating;
(10) static electricity;
(11) lightning.

As with gases, it is not easy to compare ignition effects. Different ignition sources are naturally characterized by different quantities such as temperature, energy and power, as reflected in the laboratory tests performed, so that comparison of different ignition sources is difficult. However, in general terms, dusts can be ignited by low energy as well as high energy ignition sources.

Ignition sources which can occur inside the plant are of particular importance. They include incandescent material, hot surfaces, sparks, self-heating and static electricity.

Some account of the control of ignition sources for dusts is given in this section. A further discussion is given in Section 17.46.

17.45.1 Flames and direct heat

Incident statistics show that a large proportion of dust ignitions are caused by flames. A flame is a very effective source of ignition for dust suspensions.

One source of flames is direct fired equipment. This source may be eliminated by the use of indirect heating using hot water or steam. If this course is adopted, the basis of safety should not be negated by any additional means of heating provided as a standby.

17.45.2 Hot work

Another principal ignition source for dusts is hot work such as welding and cutting. Again a welding flame is a very effective source of ignition.

In this case it is frequently a dust layer inside equipment which is ignited. Such a dust layer may have an ignition temperature in the range 100–200°C and is readily ignited by hot work. Incidents occur because this hazard is not appreciated and the dust is not cleaned out of the equipment before work is started.

17.45.3 Incandescent material

Burning dust, or other incandescent material, is another important ignition source. Considerable efforts are made to prevent ignition by burning dust.

Burning dust is an ignition source which can occur inside dust-handling equipment. One consequence of this is that it may travel through the plant. Another is that it may remain undetected.

A direct firing system is one potential source of incandescent particles. In direct-fired driers the air inlet is protected by a fine screen to prevent ingress of such incandescent material.

17.45.4 Hot surfaces

Hot surfaces are another important ignition source. One type of hot surface is equipment with a hot surface such as a steam pipe or electric lamp. Another is overheated moving equipment such as a distressed bearing.

Ignition due to a hot surface is particularly likely to occur with dust layers. As already mentioned, the surface temperature which can cause ignition of a dust layer is frequently no more than 100–200°C. The ignition temperature of a dust layer decreases as the thickness of the layer increases. It is frequently found in investigations of ignition that a dust layer has ignited at an unexpectedly low temperature.

Bowes and Townshend (1962) have applied self-heating theory to the prediction of the temperature at which a dust layer is liable to ignite.

Practical considerations should also be borne in mind. For example, contamination with oil may effect an appreciable reduction in the ignition temperature of a dust layer. Another factor which may lead to a lower ignition temperature is thermal degradation of the material.

The dust itself may contribute to its own ignition. Dust is a poor conductor of heat and a layer of dust on equipment may reduce heat loss to atmosphere and thus cause the surface to be hotter than it would be otherwise. Or again, dust may enter a bearing and cause it to run hot.

Hot surface ignition is a particular problem with driers of various types. A discussion of the problem with different types of drier is given by Field (1982) and detailed guidance is given in the *IChemE Drier Guide* (Reay, 1977; Abbott, 1990). Field summarizes the general recommendations of

Table 17.66 *Some explosibility properties of selected dusts (K.N. Palmer,1973a) (data in this table from Dust Explosions and Fires by K.N. Palmer, are reproduced with permission of the author and of the publishers, Chapman & Hall)*[a]

Dust	*Minimum explosible concentration* (g/l)	*Minimum ignition temperature*		*Minimum ignition energy* (mJ)	*Maximum permissible oxygen concentration to prevent ignition* (%v/v)	*Maximum explosion pressure* ($lb_f/in.^2$)	*Maximum rate of pressure rise* ($lb_f/in.^2$ s)	*Average rate of pressure rise* ($lb_f/in.^2$ s)
		Cloud (°C)	*Layer* (°C)					
Aluminium, atomized	0.045	650	760	50	–	84	>20,000	3,500
Carbon, activated	0.100	660	270	–	–	92	1,700	–
Cellulose acetate	0.035	340	–	20	5	114	6,500	2,800
Coal, 37% volatile	0.055	610	170	60	–	90	2,300	–
Magnesium	0.030	560	430	40	–	116	15,000	–
Nylon	0.030	500	430	20	6	95	4,000	–
Phthalic anhydride	0.015	605	Melts	15	11	72	4,200	1,300
Polyethylene	0.020	390	–	10	–	80	7,500	–
Polystyrene	0.020	500	500	15	–	100	7,000	2,400
Sawdust	–	430	–	–	–	97	2,000	–
Sugar	0.045	370	400	30	–	109	5,000	1,600
Sulphur	0.035	190	220	15	–	78	4,700	1,700
Trinitrotoluene	0.070	–	–	75	–	63	2,100	–
Urea formaldehyde resin	0.020	430	–	34	–	110	1,600	–
Wheat flour	0.050	380	360	50	–	109	3,700	–
Wood flour	0.050	430	–	20	7	94	8,500	–

Sources: All properties except average rate of pressure rise: K.N. Palmer (1973a). Average rate of pressure rise: HSE (1970 Bklt 22).

[a] See text for discussion of higher values of parameters such as maximum explosion pressure and maximum rate of pressure rise obtained in modern test apparatus.

the latter to the effect that inlet temperatures should be at least 50°C below the minimum ignition temperature of the dust suspension and 20°C below that of any dust layer likely to form.

Electric lamps give hot surfaces which may ignite dust suspensions. There are available lamps with special protection for use in dusty atmospheres. Alternatively, areas which may contain dust suspensions, may be illuminated by lamps which are separated on the other side of an armoured glass panel.

A number of incidents have occurred, particularly in silos, involving the use of wander lamps supplied by the mains. These should be avoided and portable battery lamps used instead.

Hot surfaces may also occur as a result of distress in machinery such as pumps and motors. It may be necessary in some cases to monitor features such as bearing temperatures.

17.45.5 Electrostatic sparks

As stated in Chapter 16, there are three main types of spark which may serve as an ignition source: (1) electrostatic sparks, (2) electrical sparks, and (3) friction/impact sparks. The first two involve an electrical discharge, but the difference is that the first is a capacitive or inductive discharge spark and the second a spark from a voltage source.

The standard minimum ignition energy tests use an electrostatic ignition source and are therefore most directly applicable to electrostatic spark ignition, but less so to electrical sparks.

An electrostatic spark may occur due to a discharge from electrical equipment. Protection against such discharges is based on hazardous area classification and the associated safeguarding of electrical equipment. Intrinsically safe equipment is designed so that incendive capacitative or inductive discharges cannot occur.

17.45.6 Electrical sparks

Electrical sparks occur in the normal operation of certain equipment such as switches and relays and may occur in electrical equipment generally as a result of malfunction.

Again, protection against electrical sparks is based on hazardous area classification and safeguarding. In particular, flameproof equipment is used. Where dust is present this equipment should exclude dusts. A distinction may be drawn between equipment which is dust tight and excludes dust entirely and equipment which is dustproof and lets in only an insignificant amount of dust. An account of the two types of equipment is given by Field (1982).

A more detailed discussion of hazardous area classification and of safeguarding of electrical equipment, including equipment for use in dusty conditions, is given in Chapter 16.

17.45.7 Friction sparks

Another important contributor to incidents is frictional sparks associated with rubbing or grinding. These can occur in plant handling dust in several ways. The dust itself may block the equipment and cause overloading, leading to spark generation. Preventive measures include control of dust flow and machine overload trips. Foreign materials such as tramp iron can cause sparks. Removal of such objects can be done by magnetic or pneumatic separation, and is especially desirable if the material is to pass through a mill. Failure of equipment can also give rise to sparks.

17.45.8 Impact sparks

Much concern has centred around the potential of hand tools to create an incendive impact spark, although there is little evidence from incidents of single impact ignition.

There has, however, been a good deal of work done on the potential of hand tools as an ignition source. Most of the work on this has been done on gases and an account is given in Chapter 16.

As described there, the incendive potential of an impact such as that of a metal tool on a metal surface arises from the heating of that surface. In other words, the ignition source is not the spark itself but the heated surface. The problem is the transfer of the heat from the metal surface to the dust.

Experimental work on impact ignition of dusts has been performed by Morse (n.d.), Brown (1941 BM 1C 7148) and N. Gibson, Lloyd and Perry (1967). The work is summarized by Cross and Farrer (1982) to the effect that dust ignitions have been obtained either if the dust was a sensitive one, such as aluminium, magnesium, zinc or sulphur, or if the thermite reaction occurred, but no ignition of a non-sensitive dust in the absence of the thermite reaction has been obtained.

17.45.9 Self-heating

An account of self-heating was given in Chapter 16, where the general features and quantitative aspects where discussed. Consideration here is limited to a few basic points.

Self-heating, or spontaneous combustion, is another significant ignition source.

There are a wide variety of reactions which can give rise to self-heating. They include not only oxidation reactions but reactions with water or wood. For many reactions the reaction rate accelerates with temperature, according to the Arrhenius equation. But there are also autocatalytic reactions which may accelerate due to production of a catalyst or removal of an inhibitor. Induction times may be long and the self-heating may be slow to start but may then proceed undetected for a long period. Account should also be taken of the effect of contaminants such as oil and of thermal degradation. It follows that the first step is screening of the dust to determine whether it is liable to self-heating.

Control of the temperature of dust in process and in storage is another means of preventing self-heating. One aspect of this is control of hot surfaces, which may arise in normal operation or due to fault conditions.

In general, situations in which there is a large mass of dust stored at a high initial temperature tend to present the greatest hazard. Dust in a pile has a high surface area and sufficient air circulation, both of which favour self-heating.

Measures should be taken to avoid unintended accumulation of deposits of dust which could undergo self-heating.

A situation which has frequently led to trouble is the discharge of hot dust from a drier into a hopper. It may be necessary to cool the dust prior to storage. Another measure which is sometimes used is to recirculate dust from storage through a cooling system.

Another precaution which is taken is the monitoring of the temperature of dust in storage.

17.45.10 Static electricity

Static electricity is a further significant ignition source for dusts. This too has been treated in Chapter 16 so that again

consideration here is limited to a few basics. A more detailed discussion is given by Cross and Farrer (1982).

In general terms, the static charge on dusts is a function of the work done on them. Hence, the charge tends to be a stronger function of the process than of the material. This is illustrated by the data on charges for different dust-handling processes given in Chapter 16. For sieving and pouring the charges are low, but for size reduction they are much higher.

It is not easy to screen for situations where static electricity might present a hazard in dust handling. Laboratory tests for this are not well developed.

There are certain types of dust-handling plant in which static electricity is readily generated. These include mills, conveyor belts and pneumatic conveying systems. The hazard in such equipment should therefore be carefully considered.

As with liquids, static charge can accumulate at the centre of a large storage hopper; it may then be discharged by an earthed probe. But there is also a hazard unique to dusts, that of sliding of highly charged material towards an earthed container wall.

Plastic surfaces such as those used in chutes may give rise to sparks. Bags used for transporting dusts can also create sparks. A detailed discussion of these is given by Cross and Farrer.

An operation which has resulted in a number of incidents is the pouring of powder from a polyethylene bag into a flammable solvent.

The human body can carry a charge sufficient to make it a potential ignition source. In the manual handling of dusts, the hazard of static electricity from the human body becomes significant if the dust has a minimum ignition energy less than 25 mJ.

As far as the human body is concerned, the main precaution is the use of conducting footwear or antistatic footwear and conductive flooring.

If the minimum ignition energy is less than 10 mJ, it is advisable to provide antistatic flooring and to use antistatic clothing and footwear.

Factors which tend to reduce the hazard of dust explosions from static electricity are the relatively high minimum ignition energy of dusts and the tendency of dusts to give corona discharge.

Measures to counter static electricity include modification of the processing conditions and of the plant. The reduction of static electricity by controlling the atmosphere at a higher relative humidity is particularly relevant to handling dusts.

In storage bins use may be made of earthed wire meshes on the wall and of earthed rods in the bulk powder. These do, however, have the disadvantage that if they lose their connection to earth, they may aggravate the situation. Another measure which is particularly relevant to storage bins is the use of passive dischargers on the material entering.

17.45.11 Ignition incidents

Some information on ignition sources in dust explosion incidents is given in Table 17.67. Apart from the usual problem of consistency of classification, the data show that different studies tend to highlight different ignition sources. For example, the proportion of incidents attributed to welding and cutting in the three sections of the table is 10, 3 and 24.3%, respectively.

Another important point which is illustrated particularly by Table 17.67(C) is the multiplicity of situations which can give rise to ignition. This reinforces the point often made that it is prudent to assume that the necessary attempt to eliminate all ignition sources may not be completely successful.

Further statistical data on ignition sources for dust explosions are given by Lunn (1992), as mentioned in Section 17.43. The HSE survey for 1979–88 gives the principal ignition sources as friction/mechanical failure, overheating/spontaneous heating, flames/flaming material, tramp material and welding/cutting, with 56 (18%), 51 (17%), 44 (15%), 21 (7%) and 20 (7%) events, respectively; 83 (27%) events were classified in the category 'unknown'. In the BIA survey, the main ignition sources were mechanical sparks, smouldering clumps, mechanical heating and electrostatic discharge, with 26.1, 11.3, 8.9 and 8.7% events, respectively; 16% of events were classified in the category 'unknown'.

17.46 Dust Explosion Prevention

As for flammable gases, control of dust explosions may be approached by way of prevention or protection.

Accounts of dust explosion prevention include those given in *Dust Explosions in Factories* (HSE, 1970 HSW Bklt 22) (the HSE *Dust Explosion Guide*), *Guide to Dust Explosion Prevention and Protection. Part 2: Ignition Prevention, Containment, Inerting, Suppression and Isolation* by Schofield and Abbott for the IChemE (1988/30) (the IChemE *Dust Explosion Protection Guide*), EPA FS 6022: 1989 *Explosible Dusts: Control of Explosions*, FS 6023: 1989 *Explosible Dusts: Elimination of Ignition Sources* and NFPA 69: 1992 *Explosion Prevention Systems* and by K.N. Palmer (1973a), Bartknecht (1981a, 1989) and Eckhoff (1991).

There are several approaches to the prevention of dust explosions. They include (1) use of a dust-free process, (2) avoidance of flammable dust suspensions, (3) elimination of sources of ignition, and (4) inerting.

17.46.1 Dust-free processes

A fundamental solution to the dust explosion problem is to use a dust-free process. In particular, it may be possible to process the materials wet rather than dry, so that dust suspensions do not occur at all. This approach is in effect an application of the principle of inherently safer design. Where it is applicable, it is one of the most satisfactory methods.

17.46.2 Dust control

If flammable dust has to be handled dry, it is generally not possible to prevent the occurrence of dust concentrations above the lower explosive concentration in some parts of the plant. Nevertheless, much can be done to minimize the volume of any dust clouds formed and to reduce the probability of formation.

Where dust suspensions may occur, large volumes should be avoided as far as practicable. Often it may be appropriate to have several smaller volumes rather than one large one. Overdesign of a unit, such as a hopper, should be avoided so that it does not operate empty all the time.

Situations should be avoided which encourage dust cloud formation such as the free fall of dust from a height into a hopper.

Table 17.67 *Ignition sources for dust explosions*

A Ignition sources for primary dust explosion[a]

Ignition source	*Proportion* (%)
Welding and cutting	10
Friction in bucket elevator	8.5
Fire (other than welding)	7.8
Electrical	4.3
Lightning	2.8
Motors	2.1
Static electricity, foreign material, spontaneous heating, other	4.5
Unknown	60

B Ignition sources for dust explosions[b]

Ignition source	*All dusts* 1860–1957		*Grain elevators,* 1958–75		*Feed mills,* 1958–75		*Total*	
	No.	(%)	*No.*	(%)	*No.*	(%)	*No.*	(%)
Foreign material	209	18.66	–	–	16	32.00	225	17.22
Fire or flame	179	15.98	11	8.03	6	12.00	196	15.00
Friction	157	14.02	12	8.76	2	4.00	171	13.08
Hot sparks, overheating	78	6.96	–	–	–	–	78	5.97
Electrical equipment	54	4.82	9	6.57	2	4.00	65	4.97
Welding and cutting	20	1.79	14	10.22	6	12.00	40	3.03
Static electricity	25	2.23	–	–	–	–	25	1.91
Spontaneous combustion	16	1.43	2	1.46	1	2.00	19	1.45
Lightning	4	0.36	4	2.92	–	–	8	0.61
Unknown	378	33.75	85	62.04	17	34.00	480	36.73
Total	1,120	100	137	100	50	100	1,307	100

C Probable ignition sources in elevator incidents[c]

Ignition source	*Number*	*Proportion* (%)
Welding and cutting	16	24.3
Hot bearings	7	10.6
Tramp metal	6	9.1
Electrical	4	6.0
Explosive vapour	2	3.1
Heating system	2	3.1
Dust system	2	3.1
Lightning	1	1.5
Static electricity	1	1.5
Blockage in leg	1	1.5
Extraction of oil from corncake	1	1.5
Switch engine on rail dump	1	1.5
Choked leg	1	1.5
Electrical cord in leg	1	1.5
Volatile solvent escaped from processing of soybeans	1	1.5
Grain hung up in drier	1	1.5
Fan blade caused spark	1	1.5
Unknown	17	25.7
Total	66	100

[a] After Spiegelman (1981).
[b] K.N. Palmer (1891a) after Jacobsen (1981). Original sources: NFPA (1957) for all dusts; Verkade and Chiotti (1987b) for grain elevator and mills.
[c] After Cross and Farrer (1982). Original source: Department of Agriculture (1980).

Dust should be removed from suspension at as early a stage as process considerations permit. Thus, if dust has to be removed from a gas stream, it is better to do this as soon as practicable as the gas leaves the plant rather than to transfer it down long ducts to a central cleaning point.

Buildings which contain plant handling flammable dusts should be designed to minimize the accumulation of dust deposits and to facilitate cleaning.

Avoidance of dust suspensions depends as much on operation as on design. Dusts should not be allowed to accumulate at the gas cleaning plant, but should be removed regularly in accordance with the design. Buildings which have plant handling dust should be cleaned to prevent accumulation of dust deposits.

It should be borne in mind that even if a dust suspension within the explosive range is not present in normal operation, it may be so during start-up, shut-down or fault conditions.

17.46.3 Control of ignition sources

Measures should be taken to eliminate ignition sources which could give rise to a dust explosion.

Control of ignition sources needs to be addressed both in the design and operation of the plant. Measures which can be taken in design include the location or elimination of direct firing and the avoidance of situations where static electricity can give rise to incendive sparks.

Measures to ensure close control of operations is particularly necessary for activities such as welding and cutting. Training to ensure that personnel understand the reasons for the precautions is an integral part of this.

Good housekeeping, and particularly avoidance of accumulation of dust deposits, has a role to play which is especially important in plants handling dusts.

Hazardous area classification provides a formal framework for the control of ignition sources. An account of hazardous area classification, including that for areas where combustible dusts may occur, was given in Chapter 16. Two points made there merit repetition. First, although hazardous area classification was originally concerned primarily with ignition by electrical sources, it has developed into a comprehensive system for the control of all ignition sources which might ignite a release outside the plant. Second, the effectiveness of hazardous area classification depends as much on operation as on design.

However, hazardous area classification is concerned essentially with releases from plant rather than with ignition within plant. Dusts particularly are prone to ignition from ignition sources within the plant. It is necessary, therefore, to complement the measures taken by hazardous area classification with other measures to eliminate in-plant ignition sources.

Maintenance of equipment to minimize the fault conditions which could constitute ignition sources is another significant aspect of control of ignition sources not only outside but inside equipment.

The IChemE *Guide* gives detailed measures for the control of ignition sources covering the following operations/equipment: (1) size reduction, (2) pneumatic conveying, (3) screw conveyors, (4) drag link and mass conveyors, (5) belt conveyors, (6) bucket elevators, (7) storage bins and silos, and (8) dust filters.

It is generally imprudent, however, to assume that an ignition source will not occur.

17.46.4 Inerting

The suspension of a flammable dust in air may be rendered non-explosive by the addition of inert gas.

Guidance on inerting of dust-handling plant is given in the NFPA 69 and the IChemE *Guide*.

The main gases used for inerting of dust-handling plant are nitrogen, carbon dioxide, flue gas and inert gas from a generator. The IChemE *Guide* gives guidance on the factors governing selection of a suitable gas.

One factor is any hazards associated with the use of the gas. One such hazard is reaction with the dust: carbon dioxide can react violently with aluminium dust, and nitrogen can react at high temperature with magnesium dust. Carbon dioxide can also generate static electricity, as described in Chapter 16.

Other relevant factors are the availability and cost of supply.

In using inerting, complete replacement of oxygen by inert gas may be uneconomic. An alternative approach in such cases is to keep the oxygen content well below the maximum permissible oxygen concentration to prevent ignition. This concentration is obtained using the test referred to earlier.

The IChemE *Guide* also cites certain rules-of-thumb relating the maximum permissible oxygen concentration for carbon dioxide C_o and that for nitrogen N_o:

$$N_o = C_o - 2$$

or

$$N_o = 1.3C_o - 6.3$$

These rules are attributed to Germany and NFPA 69: 1978, respectively.

The maximum permissible oxygen concentrations to prevent ignition which are reported in the literature are normally measured at ambient temperature. If it is proposed to use inerting for dust at high temperatures (say $>100°C$), the maximum permissible oxygen concentration to prevent ignition should be determined by tests. Likewise tests are called for if there is a hybrid vapour–dust mixture.

With regard to the safety margin to be employed, the IChemE *Guide* suggests a minimum margin of 2%. Thus, if the maximum permissible oxygen concentration to prevent ignition is 11%, the oxygen concentration should be kept below 9%. It also recommends a larger margin where there are large plant volumes, extended hot surfaces or high explosibility dusts (St 3).

There will be a certain out-leak of inert gas from the plant and a certain in-leak of air, and this needs to be taken into account, by design measures to minimize these leaks and by monitoring the oxygen concentration.

Often the plant is totally enclosed and dust is added and removed through valves which give only a small loss of inert gas. Inert gas is supplied to make up these losses. Where the inert gas is recycled through the plant, it is important to avoid the accumulation in the gas of fine particles which are not removed by gas cleaning equipment and which constitute a much increased hazard if ignition occurs.

Careful design and testing of the plant is necessary to ensure that the concentration of oxygen is below the maximum permissible oxygen concentration throughout. Dead

spots where there is no gas circulation should be eliminated, and low pressure points where air could leak in should be checked. Usually it is necessary to distribute the inert gas to a number of different points on the plant.

The inert gas demand is liable to vary due to causes such as material flows in the plant, materials withdrawal, temperature changes and leaks. The supply of inert gas should be sufficient to meet peak demands. It should also be reliable.

The gas should be free of moisture, rust and noxious gases. There should be controls to ensure a balanced supply to the different parts of the plant. There should be non-return valves to prevent the entry of dust into the inert gas system. It is usual to provide means of cleaning inert gas leaving the plant.

There should be continuous monitoring of the oxygen content of the gas in the plant and a trip system to shut the plant down if the concentration rises towards a hazardous level. Since the gas contains dust, there may be problems in the measurement of the oxygen level.

The inerting solution is particularly useful in handling dusts of very high explosibility ($K_{st} > 600$ bar/s).

Inerting is not necessarily effective in eliminating dust fires.

The IChemE *Guide* gives examples of the application of inerting to grinding and spray drying operations.

It is also possible with dust suspensions to use inert dust to effect inerting. This method is utilized in certain specialized applications, of which the principal example is coal mining. Thus, in the United Kingdom, limestone dust is used on the floor of mine roadways to prevent a coal dust explosion propagating. The use of inert diluent dusts is discussed in the IChemE *Guide*. The proportions of inert dust quoted as necessary to provide effective inerting are high, generally more than 60%.

Inerting may be used in combination with dust explosion suppression or venting. This is an approach which may be considered where complete elimination of combustion by inerting is judged uneconomic. In such circumstances the effect of partial inerting is to reduce the strength of the explosion to be handled by the suppression or venting system.

17.47 Dust Explosion Protection

Accounts of dust explosion protection include those given in FS 6015: 1974 *Explosible Dusts, Flammable Liquids and Gases: Explosion Suppression*, the HSE *Dust Explosion Guide* (1970 HSW Bklt 22), *Explosions* (Bartknecht, 1981a), the *IChemE Dust Explosion Protection Guide* (1988/30), *Dust Explosions* (Bartknecht, 1989), EPA FS 6022: 1989 *Explosible Dusts: Control of Explosions, Dust Explosions in the Process Industries* (Eckhoff, 1991) and NFPA 69: 1992 *Explosion Prevention Systems* and by KN. Palmer (1973a), P.E. Moore (1979b, 1981, 1982b, 1984, 1986, 1990), J. Singh (1979a), Maisey (1980), Kirby (1985a), Kirby and Siwek (1986), P.E. Moore and Bartknecht (1986), Chatrathi (1992b,c) and P.E. Moore and Cooper (1993).

A relevant standard is BS 6713: 1986 *Explosion Protection Systems*.

Methods of protection against dust explosions include (1) explosion containment, (2) explosion isolation, (3) explosion suppression, and (4) explosion venting. The first three methods are considered in this section and the fourth in the following section.

17.47.1 Explosion containment

The first option for dealing with a dust explosion is total containment.

A general discussion of pressure containment as opposed to pressure relief has been given by Wilday (1991), as described in Chapter 12. Accounts of the containment method for dust explosions include those given in the IChemE *Guide* and by Bartknecht (1981a), Kirby (1985) and Kirby and Siwek (1986).

In some ways containment is an attractive option, since it is an essentially passive method and avoids the problem of relief disposal. It is not usually practicable, however, to design the whole of a dust-handling plant so that it can withstand the pressures generated by dust explosions. This is particularly the case with large plants. Normally, it is preferable to use some other method of protection. Containment may be practicable, however, on small scale units and on particular equipments. Thus, a grinding mill, for example, may be made strong enough to withstand a dust explosion.

The maximum explosion pressure for most flammable gases and dusts is given by Bartknecht (1981a) as about 7 barg. The IChemE *Guide* quotes for dusts the range 7–10 barg.

The static pressure is not, however, the sole criterion. The rate of pressure rise in a dust explosion is high, and the vessel must be able to withstand this dynamic loading.

The IChemE *Guide* distinguishes two basic options for containment: 'pressure resistance' and 'pressure shock resistance'. In the first the vessel is designed to withstand the explosion without deformation, whilst in the second some deformation is allowed provided the explosion is contained. If using this latter method an explosion occurs which is sufficiently severe, it may not be possible to reuse the vessel, but experience shows that generally the vessels are reusable, presumably because the explosions are not especially severe.

The use of containment raises the issue of its coverage within pressure vessel codes. Companies using the technique have tended to develop their own codes. In the United Kingdom the matter has been considered by the BSI Pressure Vessel Technical Committee (PVTC) (BSI, 1986). The IChemE *Guide* summarizes its findings to the effect that a vessel designed to BS 5500 should have sufficient reserve of strength to withstand quite rapid rates of pressure rise up to the design pressure on a one-off basis.

There are a number of engineering issues involved in the use of pressure vessels for containment of dust explosions. They include pressure piling and modes of failure, including brittle fracture. Such design is therefore a specialist matter.

One basic principle is to use rotational symmetry and to avoid large flat surfaces and angular parts.

In designing to contain a dust explosion, particular attention should be paid to the points at which dust is fed or withdrawn from the plant and to connections between units.

An alternative to full containment is partial containment. This involves the use of a stronger vessel combined with explosion relief.

17.47.2 Explosion isolation

Another option for dealing with a dust explosion is isolation.

The three basic methods of isolation are (1) automatic isolation, (2) automatic explosion suppression, and (3) material chokes.

Taking these in turn, automatic isolation is applied to a pipe and involves the use of a quick acting shut-off valve. The general arrangement is similar to that used for flammable gases, as described in Section 17.11.

Details of this type of explosion isolation are given in the IChemE *Guide*. Detection of the explosion is by means of pressure and/or optical sensors. The former are usually preferred, since an optical detector can be blinded. On the other hand, a pressure sensor may not detect a weak pressure wave. A common threshold pressure setting is 0.1 bar.

Typically, the quick acting isolation valve is located about 5–10 m along the pipe from the detectors and has a closure time of some 25 ms.

Bartknecht (1981a) states that rapid action barrier devices can be used to protect against explosions of dust and hybrid dust–gas mixtures, but that for dusts, rapid action slide valves are preferable to rapid action valves with moving parts in the cross-section of the pipe.

The second type of isolation is automatic explosion suppression applied to a pipe. Again the general arrangement is similar to that used for flammable gases, as described in Section 17.11.

The explosion is detected by instrumentation similar to that just described for automatic isolation. The suppressant barrier is located some 5–10 m from the detectors.

Quick acting valves operate most effectively on pipes up to about 0.5 m in diameter. Suppressant barriers have been found effective in pipes up to 2.5 m in diameter.

With both techniques the pipe should be designed to withstand the local pressure, given in the *Guide* as up to 10 barg.

The third type of isolation is the use of a material choke. This is applicable where it is necessary to have a flow of dust between units. A treatment of this method is given in the HSE *Dust Explosion Guide*.

Two commonly used types are rotary valves and worm conveyors, as shown in Figure 17.118. A variety of other types are illustrated in FS 6022.

A rotary valve, which is installed vertically and is driven by a motor, is generally designed to act as a dust explosion choke even in the absence of a head of dust above it.

There have not been many tests of the effectiveness of rotary valves as dust explosion chokes. It has been found, however, in one test, with an explosion above the valve, that the explosion was transmitted by the valve unless arrangements were made to trip the motor within 0.5 s of the detection of the explosion.

If a rotary valve is installed on the inlet of a hopper, there should be arrangements to prevent it from continuing to turn if the hopper becomes overfilled, since this could cause ignition by overheating the dust or overloading the motor.

A worm conveyor, which may be installed horizontally, vertically or inclined and is driven by a motor, is an alternative type of dust explosion choke. One turn of the helix is removed to prevent the choke emptying if the feed is interrupted. If the conveyor is mounted horizontally, a baffle plate is also necessary.

The motor on a worm conveyor is rather liable to be overloaded and should be provided with an overload trip. A worm conveyor is not suitable for dusts which flow less freely when heated.

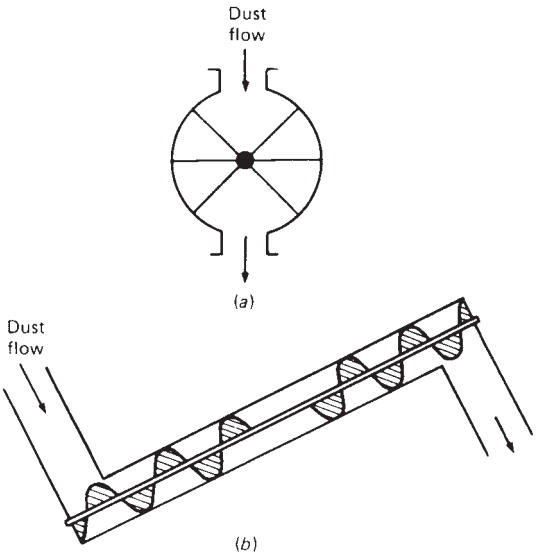

Figure 17.118 *Chokes for the isolation of sections of dust-handling plant: (a) rotary valve and (b) worm conveyor*

Again there have been few tests on the effectiveness of worm conveyors. Since the residence time in a worm conveyor is much longer than that in a rotary valve, the former may be expected to be more effective as a dust explosion choke, but smouldering dust could still pass through unless the motor is tripped.

The choke should prevent the passage of the dust explosion and of any burning material. There should be arrangements to trip the motor. Depending on the application it may be appropriate to provide inerting or suppression.

17.47.3 Explosion suppression

Explosion suppression is the third option. Its application to explosion isolation in a pipe has been described above. Here, consideration is given to its use against explosion in vessels.

Accounts of explosion suppression include those given in FS 6015 and the IChemE *Guide* and by P.E. Moore (1979b, 1981, 1982b, 1984, 1986, 1990), Bartknecht (1981a), P.E. Moore and Bartknecht (1986), Chatrathi (1992) and P.E. Moore and Cooper (1993).

Also relevant is BS 6713: 1986 *Explosion Protection Systems. Part 4: Method for Determination of Efficacy of Explosion Protection Systems*.

The general principle is similar to that for suppression of explosions of flammable gases, described in Section 17.11. Most published work on explosion suppression refers, however, to dusts, and a fuller account is given at this point.

Design of an explosion suppression system is based on the maximum rate of pressure rise in the explosion. This parameter has been discussed in detail in Section 17.44. It may be characterized in terms of the dust St class. In applying the basic data, account should be taken of the features of the particular application, in the light of

knowledge of the factors which influence the violence of such an explosion. These include the initial pressure and turbulence and the vessel aspect ratio.

Explosion suppression requires the use of a control system, which has several functions. These are (1) to detect the explosion and inject suppressant, (2) to shut-down the plant, and (3) to prevent restart of the plant unless it is safe to do so.

Detection of the explosion is generally by means of a pressure sensor. Detectors are available which are robust to most materials, to condensation and corrosion, and to shock. In some cases use is made of two detectors oriented in different planes. Activation occurs when the pressure reaches its threshold value, typically of the order of 0.05 bar. In some systems use is also made of the rate of pressure rise.

The mechanisms of suppression of the explosion are (1) quenching, (2) free radical scavenging, (3) wetting, and (4) inerting. Of these the principal mechanism is quenching, or abstraction of heat. The contribution of free radical scavenging is specific to the particular explosion reaction. Wetting of unburned particles is applicable to liquid suppressants. There is also some inerting effect.

The principal suppressants used are halons, dry powders and water. The general characteristics of these have been outlined in Chapter 16. The halons used are principally Halon 1011 (chlorobromomethane), which is effective but toxic, and the less toxic Halons 1211 and 1301. The dry powder most widely used is ammonium phosphate based.

With regard to dry powder, the point has been made earlier that its effectiveness depends on complete extinction of the flame in the initial discharge. Reignition, whether due to incomplete extinction or to hot surfaces, is therefore a potential problem characteristic of this type of suppressant.

Another issue in the selection of suppressants is contamination. With halons the problem is minimal, but with dry powders it can be significant. Water may constitute a contaminant in some cases.

The IChemE *Guide* gives guidance on selection of suppressants. The use of halons is mainly confined to dust class St 1, whilst dry powders are used for both St 1 and St 2. Water is used for hydrophilic St 1 and St 2 dusts.

The effectiveness of suppression depends in large measure on the injection system. The requirement on this is that it be capable of injecting a large quantity of suppressant in a very short time and with adequate reach to all parts of the space protected. An injection system should be capable of a high mass discharge rate, a high discharge velocity and hence good 'throw' and good angular coverage.

The response time of the sensor to the explosion depends on the size of the vessel. The explosion will propagate at the speed of sound, giving a delay, or equalization time, of the order of 4 ms/m distance between the ignition source and the detector. The response of the suppression system is very rapid. The time taken for the suppressant to reach the flame depends on the discharge velocity, which initially is of the order of 40 m/s.

Two injection devices are in common use. One is a hemispherical suppressor with chemical detonator installed inside the vessel. This type is used with a liquid suppressant, usually halon. It has a limited throw, about 2.5 m, and contains only a small quantity of suppressant. The time to complete discharge is about 10–30 ms. It is suitable for protection of smaller vessels.

The other injection device is the high discharge rate (HDR) bottle, installed on the outside of the vessel and pressurized with nitrogen at 20–100 bar. This type is much more versatile, being able to handle most common suppressants and available in capacities from 0.003 to 0.1 m^3. The time to complete discharge is about 100 ms.

The size of vessel which can be protected by suppression is limited by the factors described. Over the years various figures have been quoted for the limiting size. The figure given in FS 6016: 1974 was 115 m^3. That quoted in the IChemE *Guide* is 1000 m^3. Relevant work is described by P.E. Moore (1986).

An effective suppression system requires rapid detection, rapid injection and an adequate quantity of suppressant. The IChemE *Guide* gives a number of graphs of the course of failed suppressions which illustrate these points.

Extinction of the flame is not, however, the only requirement of the suppression system. Its other function in respect of the explosion itself is to limit the pressure developed. Factors affecting this pressure are the dust St class and the detection and injection times.

One measure which may be taken to limit the pressure is the use of multiple injection points.

BS 6713: Part 4 gives the criteria to be applied in determining the safe operating regime of an explosion suppression system.

Various applications of explosion suppression are described in the IChemE *Guide*, which treats (1) mills, (2) bunkers, (3) mixers, (4) elevators, and (5) spray driers.

17.48 Dust Explosion Venting

The use of explosion venting is generally an effective and economic method of providing protection against dust explosions, and is the method normally considered.

Dust explosion venting is dealt with in most of the publications referred to at the start of Section 17.43, and particularly in *Dust Explosions in Factories* (HSE, 1970 HSW Bklt 22), *Dust Explosions and Fires* (K.N. Palmer, 1973a), *Dust Explosions* (Field, 1982), *Development and Control of Dust Explosions* (Nagy and Verakis, 1983) and *Dust Explosions in the Process Industries* (Eckhoff, 1991).

The set of monographs on gas and dust explosions published by the IChemE includes the following on dust explosion venting: *A User Guide to Dust and Fume Control* by C.R. Smith (1981) with a second edition by D.M. Muir (1985) and a revised second edition by Lunn (1992a) and *Guide to Dust Explosion Prevention and Protection* (the IChemE *Dust Explosion Protection Guide*), in three parts: Part 1, *Venting* by Schofield (1984) with a second edition by Lunn (1992b) (the IChemE *Dust Explosion Venting Guide*); Part 2, *Ignition Prevention, Containment, Inerting, Suppression and Isolation* by Schofield and Abbott (1988) and Part 3, *Venting of Weak Explosions and the Effect of Vent Ducts* by Lunn (1988).

Further guidance is given in NFPA 68: 1994. Much of the literature refers to the earlier 1974 edition (reaffirmed 1978).

Venting is suitable only if there is a safe discharge for the material vented. Preferably the plant should be in the open. If it is in a building, it should be possible to effect a discharge through a short duct. Any such duct will have an effect on the maximum vented pressure and the whole problem should therefore be considered at an early stage of the design.

The venting solution is not appropriate if the plant contains toxic dusts, or other associated toxic substances, which cannot be vented to atmosphere, or is awkwardly sited so that safe discharge is not possible.

17.48.1 Dust explosion venting of vessels

The venting of gas explosions was dealt with in Section 17.12. For dust explosion venting, the general approach and some of the methods are similar, but there are also some important differences.

A dust explosion can occur only if the dust is dispersed. It follows, therefore, that one of the conditions for a dust explosion is a degree of turbulence. A gas explosion on the other hand may occur with a gas mixture which is initially quiescent.

Another difference is that the dust cloud tends not to be uniform, although a high degree of turbulence tends to promote uniformity.

The comments made in Section 17.12 concerning the definitions and units used in explosion venting of gases apply equally to dust explosion venting. The definitions and units used here are summarized in the Notation.

17.48.2 Factors influencing dust explosions

An account of the factors which affect dust explosibility was given in Section 17.44. There are in addition other factors which influence the strength of an explosion of a dust of given explosibility.

The maximum explosion pressure and maximum rate of pressure rise are affected by a number of factors. These are discussed by Cross and Farrer (1982), Field (1982) and Nagy and Verakis (1983). They include

(1) vessel size and shape;
(2) dust concentration;
(3) initial pressure;
(4) initial temperature;
(5) initial turbulence;
(6) ignition source;

and the presence of

(7) flammable gas;
(8) inert gas or dust.

The maximum explosion pressure is essentially independent of vessel size provided heat effects are disregarded.

Experimental measurements of maximum explosion pressure tend to show considerable scatter. Data given by Nagy and Verakis show scatter with most points lying within the $\pm 15\%$ band.

For elongated vessels the heat loss tends to be more significant and the maximum explosion pressure less.

The maximum rate of pressure rise is affected by vessel size and shape. Equation 17.7.48 shows that the maximum rate of pressure rise follows the cube root law and is inversely proportional to $V^{1/3}$. Equation 17.7.75 shows that it is proportional to the surface area/volume ratio S/V.

The dust concentration with the highest explosibility, as measured by the characteristics described earlier such as minimum ignition temperature, minimum ignition energy and maximum rate of pressure rise, tends to be several times greater than the stoichiometric concentration. This contrasts with gas mixtures where the most explosive concentration is usually close to, though not at, the stoichiometric value. The effect of dust concentration is illustrated in Figure 17.119.

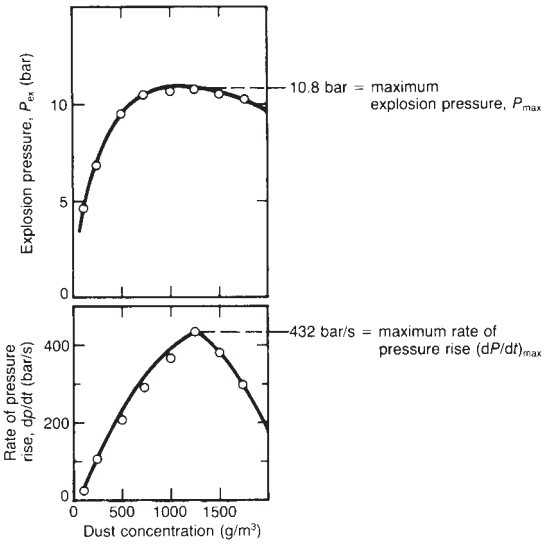

Figure 17.119 *Dust explosion pressure: effect of dust concentration (Bartknecht, 1981a) (Courtesy of Springer-Verlag)*

There is surprisingly little information on the effect of initial pressure. One reason may be that most plant handling dusts operates close to atmospheric pressure. The account of the effect of this parameter given by Nagy and Verakis is in fact relative to gas explosions. According to Field, whereas in a gas explosion the maximum explosion pressure is proportional to the initial pressure, the effect is less for dust explosions. However, data given by Bartknecht for starch dust show maximum explosion pressure proportional to initial pressure for initial pressures up to 2 bara. The same data set shows that the maximum rate of pressure rise is also proportional to initial pressure for the same range of initial pressures.

The initial temperature may have several effects. These include reduction of the mass of air available for combustion and reduction of the moisture content of the dust. The net effect of an increase in initial temperature may therefore be to reduce rather than increase the maximum explosion pressure. An increase in initial temperature does, however, increase the maximum rate of pressure rise through its effect on the combustion rate, and also through any reduction in moisture content.

As already indicated, it is difficult to envisage a dust explosion without a degree of initial turbulence. Turbulence tends, however, to be non-uniform and difficult to measure or quantify. In general terms, an increase in initial turbulence will have only a weak effect on the maximum explosion pressure, but a strong effect on the maximum rate of pressure rise. Situations associated with high turbulence include grinding operations.

The effect of the ignition source on the strength of the explosion is complex and depends essentially on the nature as well as the strength of the ignition source. This aspect

was discussed in Section 17.44. In brief, some experiments have shown that similar K_{st} values are obtained for ignition by condenser discharge with an ignition energy in the range 0.005–8 J and by chemical detonator with an ignition energy of 10,000 J.

The effects of the presence of flammable gas and/or inert gas or inert dust have already been described in discussing dust explosibility.

17.48.3 Experimental studies

There have been a number of experimental studies of dust explosion venting of vessels. Some of the principal studies are listed in Table 17.68.

Early work on dust explosion relief was done at the Bureau of Mines by Hartmann, Cooper and Jacobsen (1950 BM RI 4725) using corn starch and by Hartmann and Nagy (1957) using cellulose acetate. According to Nagy and Verakis (1983), the Bureau of Mines has performed some 10,000 experiments on vented explosions. The principal enclosures used were 0.32, 1, 64 and 216 ft^3 in size, the first being cylindrical, the second cubical and the others rectangular galleries.

Schwab and Othmer (1964) carried out experiments using plastics and metallic stearate dusts.

Donat (1971b) has carried out experiments in 1 and 30 m^3 vessels on coal, organic pigment, dextrin and aluminium dusts.

Bartknecht (1981a) has described experiments, including those of Donat, in a 20 l sphere and a/m^3 sphere on a number of parameters for a wide variety of dusts.

The HSE has carried out experiments on a 20 l sphere and an 18.5 m^3 cylindrical vessel to investigate a number of features of venting, including extension of the K_{st} method (Lunn, Brookes and Nicol, 1988) and the effect of vent ducts (Lunn, Crowhurst and Hey, 1988).

Experimental studies of dust explosion relief of silos have been performed by Eckhoff and co-workers (e.g. Eckhoff *et al.*, 1982, 1984; Eckhoff and Fuhre, 1983; Eckhoff, Fuhre and Pedersen, 1986, 1987) and Radant (1982), as described below.

17.48.4 Empirical methods

In contrast to the situation with gas explosion venting there is a lack of empirical methods which do not rely on experimental data. This is not surprising in view of the difficulty of characterizing dust explosibility other than by test data and the complexity of dust explosions.

17.48.5 Scaling methods

The empirical approach used for dust explosions is the use of scaling laws validated over a wide range of experimental conditions.

The three scaling methods used are similar to those used for gas explosion venting: the vent ratio method, the vent coefficient method and the K_{st} method.

In dust explosion venting, the traditional approach has been to express the venting requirement as a vent area per unit volume of space protection, the vent ratio approach. This contrasts with the approach which has developed in gas explosion venting where the venting requirement is generally expressed as a vent area per unit cross-sectional area of space protected, the vent coefficient approach.

17.48.6 Vent ratio method

The vent ratio f is defined as for gas explosions as

$$f = A_v/V \qquad [17.48.1]$$

where A_v is the vent area, f is the vent ratio and V is the volume of the enclosure.

As already mentioned, a common method of characterizing the vent area required is to plot the reduced explosion pressure as a function of vent ratio. Such a plot for dusts given by Hartmann, Cooper and Jacobsen for data covering a range of volumes from 1 to 216 ft^3 is shown in Figure 17.120. Numerous other plots for dusts are given by Lunn.

Recommended values of the vent ratio have been given by various sources. Table 17.69 gives some values which have been available for some time, but which are also quoted by Lunn. Table 17.69(A) gives values recommended for volumes up to 1000 ft^3 by K.N. Palmer (1973a) on the

Table 17.68 *Dust explosion venting: some experimental studies*

Investigators	*Vessel or enclosure type*	*Volume*	*Dust*
Hartmann, Cooper and Jacobsen (BM 1950 RI 4275)	Galleries	1, 64, 216 ft^3	Corn starch
Hartmann and Nagy (1957)	Gallery	1 ft^3	Cellulose acetate
Schwab and Othmer (1964)	Cylindrical chamber	0.0461 ft^3	Plastics dusts, metallic stearate dusts
Donat (1971b)	Sphere	1 m^3	Coal dust, dextrin, organic pigment, aluminium dust
Eckhoff and Fuhre (1983)	Silo	500 m^3	
Eckhoff, Fuhre and Pedersen (1986, 1987); Eckhoff *et al.* (1988)	Silo	236 m^3	Maize starch
Radant (1982)	Silo	20 m^3	
Nagy and Verakis (1983)[a]	Galleries	0.32, 1, 64, 216 ft^3	Various[b]

[a] Account based essentially on earlier work at the Bureau of Mines.
[b] Dusts tested comprised some 19 dusts including atomized aluminium, cellulose acetate, chromium dust, coal dust, cornstarch, magnesium dust, wheat starch, several plastics dusts and several flours. Not all of these were tested in each chamber.

basis of the Hartmann bomb maximum rate of pressure rise values. Table 17.69(B) gives values recommended by NFPA 68: 1978 without reference to dust explosibility measurements.

Palmer states that dusts with a very high maximum rate of pressure rise (say >12,000 $lb_f in.^2$ s) should be treated with particular caution. For these, venting may not be sufficient or even appropriate.

17.48.7 Vent coefficient method

The vent coefficient K is likewise defined as for gas explosions:

$$K = A_c/A_v \qquad [17.48.2]$$

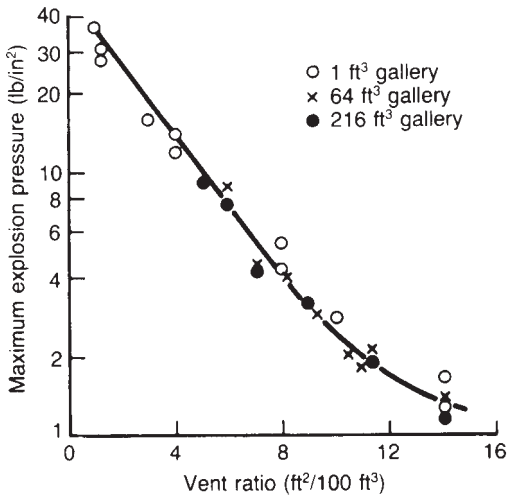

Figure 17.120 *Dust explosion venting: effect of vent ratio on reduced explosion pressure (Hartmann, Cooper and Jacobsen, 1950 BM PI 4725)*

with

$$A_c = L_1 L_2 \qquad [17.48.3]$$

where A_c is the area of the smallest cross-section of the enclosure, K is the vent coefficient and L_1 and L_2 are the two smallest dimensions of the enclosure.

N. Gibson and Harris (1976) have shown that a vent coefficient $K = 3$ gives good agreement with Donat's data for organic pigment and for St 2 dust. Their results have been given in Figure 17.24.

17.48.8 K_{st} method

The K_{st} method developed by Bartknecht is based on the cube root law given in Equation 17.44.3. The cube root law in terms of the maximum rate of pressure rise is

$$\left(\frac{dP}{dt}\right)_{max} V^{1/3} = K_{st} \qquad [17.48.4]$$

and in terms of the rate of pressure rise with venting

$$\left(\frac{dP}{dt}\right)_{Pred} V^{1/3} = K_{st} \qquad [17.48.5]$$

Thus, for the same reduced pressure the vent ratio f also follows the cube root law:

$$fV^{1/3} = \text{constant} \qquad [17.48.6]$$

Bartknecht gives a set of nomographs for the vent area A_v where

$$A_v = f(V, K_{st}, P_{stat}, P_{red}) \qquad [17.48.7]$$

where P_{red} is the reduced pressure and P_{stat} the vent opening pressure.

Table 17.69 *Dust explosion venting: vent ratio recommendations*

A Smaller volumes (≤1000 ft^3) (K.N. Palmer, 1973a)

Maximum rate of pressure rise in Hartman bomb, $(dP/dt)_{max}$ ($lb_f/in.^2$ s)	*Vent ratio* (ft^2/ft^3)
<5000	1/20
5000–10,000	1/15
>10,000	1/10

B Large volumes (NFPA 68: 1978; Lumm 1984b)

Volume (ft^3)	*Other details*	*Vent ratio* (ft^2/ft^3)
1000–25,000	–[a]	1/30–1/50
>25,000	Small fraction obstructed, and	
	Heavy reinforced concrete construction	1/80
	Light reinforced concrete construction	1/60–1/80
	Lightweight construction	1/50–1/60
	Large fraction obstructed	1/10–1/50

[a] An attempt should be made to predict the location of the ignition source and the volume of the dust suspension.

The derivation of these nomographs has been described by Lunn, Brookes and Nicol (1988). The equation from which the nomographs are derived is that of Heinrich, derived in Section 17.48.13.

$$A_v = \frac{V^{2/3} V_L^{1/3} (dP_{ex}/dt)_{P_{red}, V_L}}{C_d (2RT/M)^{1/2} P_{red}^{1/2} (P_{red} - P_a)^{1/2}} \quad [17.48.8]$$

where C_d is the coefficient of discharge, M is the molecular weight of the vented gas, P_a is the atmospheric pressure, P_{red} is the reduced pressure, $(dP_{ex}/dt)_{P_{red}}$, V_L is the maximum rate of pressure rise in the test vessel, R is the universal gas constant, T is the absolute temperature of the vented gas, V is the volume of the vessel and V_L is the volume of the test vessel. The derivation of this equation is given below.

Bartknecht has given the correlations for dust explosion venting in nomograph form. His nomograph method is that adopted in VDI 3673: 1979 *The Pressure Relief of Dust Explosions*, NFPA 68 and the IChemE *Dust Explosion Venting Guide*.

The nomographs were adopted in NFPA 68: 1988, are given in the 1998 edition of NFPA 68 and are shown in Figure 17.121. The nomographs are for a high energy (10,000 J) ignition source, and there is a separate nomograph for each value of the vent opening pressure P_{stat}. The three values of P_{stat} are 0.1, 0.2 and 0.5 barg and that of P_{red} is 0.2–2.0 barg.

NFPA 68: 1978 gave two separate sets of nomographs, for strong (high energy) and weak (low energy) ignition sources. Only the first set is given in the later editions.

The nomographs apply to dusts with $K_{st} < 300$ bar m/s and with maximum explosion pressure P_{max} up to 10 barg and to dusts with $K_{st} > 300$ bar m/s and with P_{max} up to 12 barg.

The nomographs are valid within a limited range of conditions. Their use is not recommended for $V > 1000$ m^3, $K_{st} < 50$ bar m/s and the values of P_{stat} and P_{red} just stated.

The vent area given by the nomographs for both gases and dusts in a vessel of volume 1 m^3 was given in Figure 17.22.

Bartknecht distinguishes between small and large vessels, defining the latter as $V > 30$ m^3. He states that the nomographs tend to oversize the vent area for large volumes.

An equation equivalent to the Bartknecht nomographs shown in Figures 17.121(a)–(c) has been given by Simpson (1986) and is quoted in NFPA 68: 1994. It is

$$A_v = a V^{2/3} K_{st}^b P_{red}^c \quad [17.48.9]$$

with

$$a = 0.000571 \exp(2P_{stat}) \quad [17.48.10a]$$

$$b = 0.978 \exp(-0.105 P_{stat}) \quad [17.48.10b]$$

$$c = -0.687 \exp(0.226 P_{stat}) \quad [17.48.10c]$$

where the units are as follows: A_v (m^2), K_{st} (bar m/s), P_{red} (bar), P_{stat} (barg) and V (m^3). The range of validity of the equation is

$$1 \le V \le 1000; \quad 50 \le K_{st} \le 600;$$
$$0.1 \le P_{stat} \le 0.5; P_{stat} + 0.1 \le P_{red} \le 2$$

Figures 17.121(a)–(c) are given in terms of the K_{st} value. NFPA 68: 1994 also provides nomographs in terms of the K_{st} value. For the latter it gives the following equation, attributed to Schwab:

$$\log A_v + C = a \log V + \frac{b}{P_{red}^d} \quad [17.48.11]$$

with the following values of the constants:

P_{stat} (barg)	C			a	b	d
	St 1	*St 2*	*St 3*			
0.1	1.88854	1.69846	1.50821	0.67005	0.96027	0.2119
0.2	1.93133	1.71583	1.50115	0.67191	1.03112	0.3
0.5	1.94357	1.69627	1.50473	0.65925	1.20083	0.3916

where the units are A_v (m^2), P_{red} (barg), P_{stat} (barg) and V (m^3).

Extension and extrapolation of the nomographs is discussed in NFPA 68: 1994.

The Bartknecht nomographs have been extended by Lunn, Brookes and Nicol (1988). The extrapolation is based on Equation 17.48.8. This equation does not include P_{stat} explicitly. But the experiments of Donat give values of $(dP_{ex}/dt)_{P_{red}} V_L$ for the three values of P_{stat}. The authors plot $(dP_{ex}/dt)_{P_{red}}, V_L$ vs $(dP/dt)_{P_{red}}, V_L$ for the three P_{stat} values. Then, applying the cube root law (Equation 17.44.3) and taking $V_L = 1$ m^3 yields

$$\left(\frac{dP_{ex}}{dt}\right)_{P_{red}, V_L} = BK_{st} \quad [17.48.12]$$

The values of B are 0.283, 0.333 and 0.5 for values of P_{stat} 1.1, 1.2 and 1.5 bara, respectively. They take B as a function of P_{stat} so that the effect of P_{stat} enters Equation 17.48.8 via the term $(dP_{ex}/dt)_{P_{red}}, V_L$:

The extended nomographs given by these authors are shown in Figure 17.122. The nomographs show extension down to $K_{st} = 10$ bar m/s, $P_{stat} \le 1.1$ bara and $P_{red} = 1.02$ bara. The authors recommend that for $1.05 < P_{red} < 1.2$ the lower limit of P_{stat} be taken as $P_{stat} \le [1 + (P_{red} - 1)/2]$.

The nomographs have been validated by tests with low K_{st} dusts in a 18.5 m^3 vessel. Like the original nomographs they incorporate a safety factor. However, where the K_{st} value is low, it is important that it be determined accurately and that in using the nomograph the next highest value of K_{st} be used. The detailed limitations of the extended nomographs are discussed by the authors.

The IChemE *Dust Explosion Protection Guide* Part 3 gives detailed guidance on the application of venting to weak explosions and on the effect of vent ducts. It contains a large number of graphs for the estimation of the reduced explosion pressure in vent ducts which are straight (Appendix 1) or have a single, sharp 45° bend (Appendix 2) or a single sharp 90° bend (Appendix 3).

The 2002 edition of NFPA 68 does not offer nomographs, but rather plots of the following equation for vent area and dust explosions:

$$A_v = (8.535 \times 10^{-5})(1 + 1.75 P_{stat}) K_{st} V^{0.75} \left(\frac{1 - R}{R}\right)^{1/2} \quad [17.48.13]$$

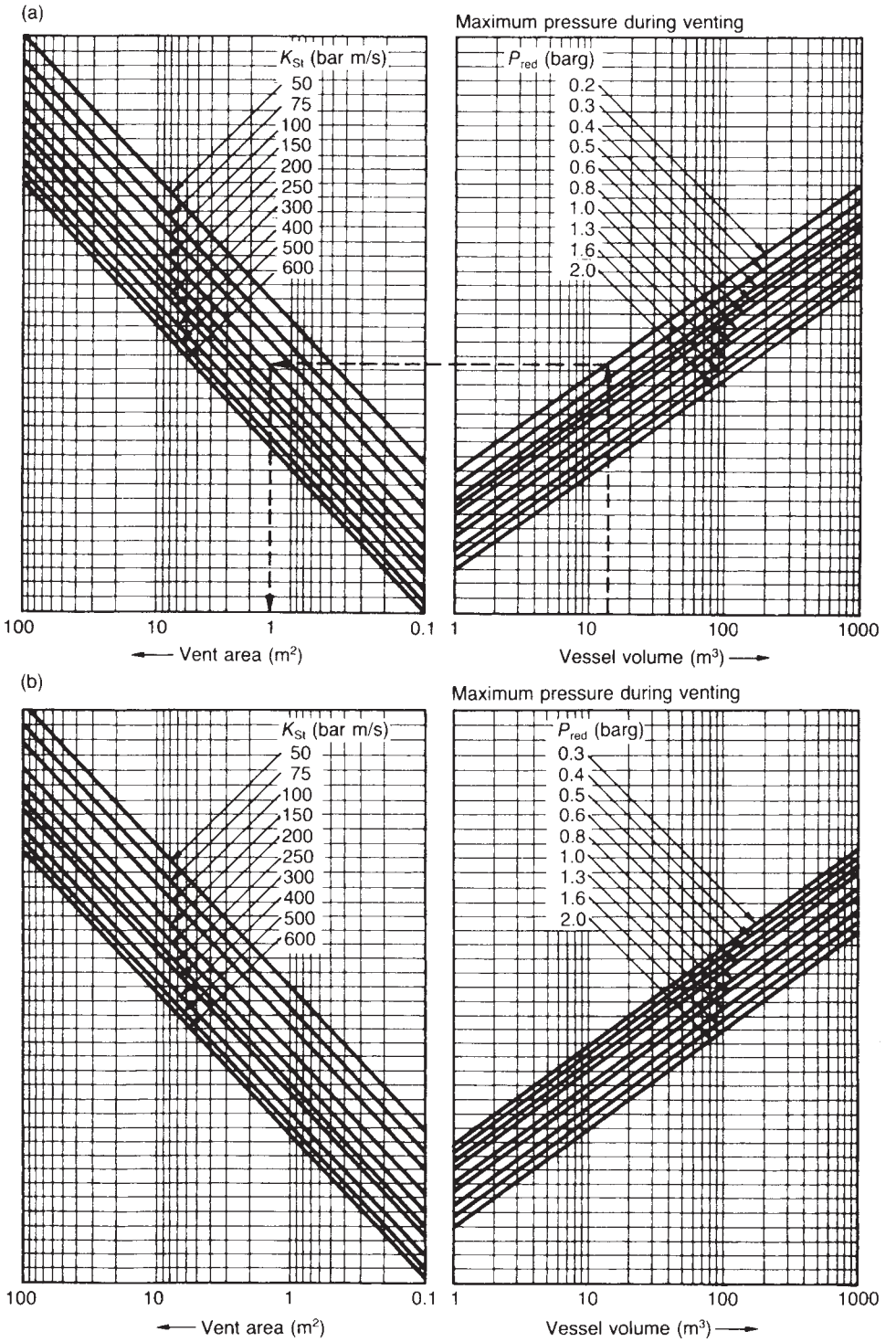

Figure 17.121 *Continued*

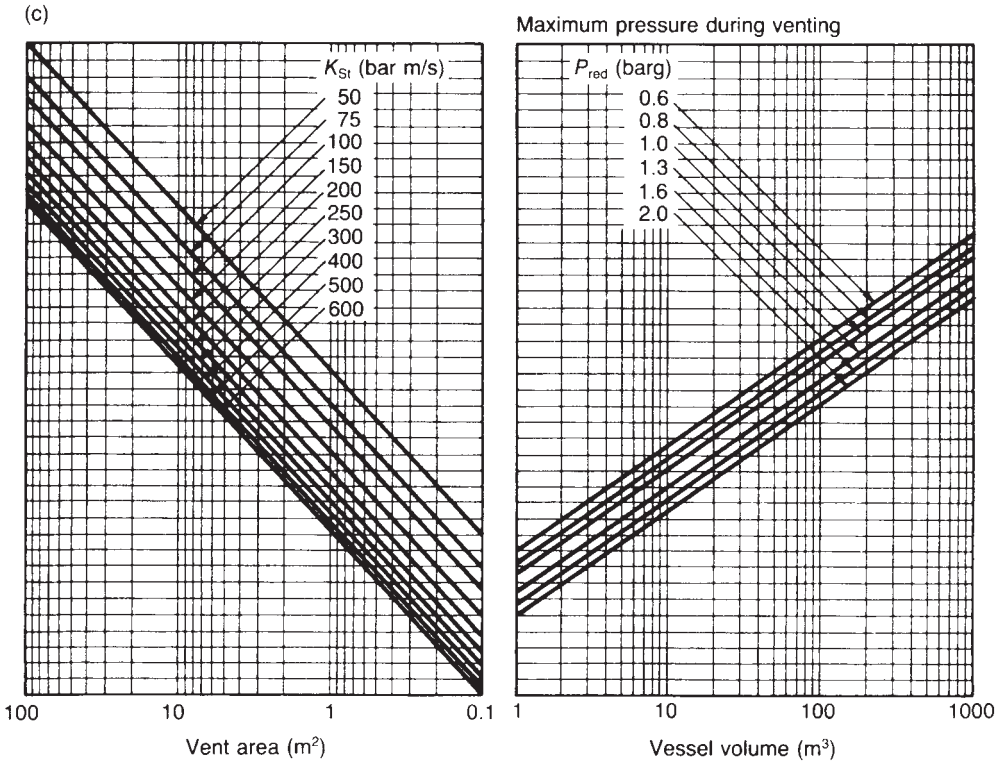

Figure 17.121 *Dust explosion venting: nomographs for vent area for high energy ignition source (NFPA 68: 1994). (a) $P_{stat} = 0.1$ barg; (b) $P_{stat} = 0.2$ barg; and (c) $P_{stat} = 0.5$ barg; see text for details and note to figure 17.25 (Reprinted with permission from NFPA 68 Deflagration Venting, © 1994, National Protection Association, Quincy, MA 02269)*

where A_v = vent area (m^2), P_{stat} = static burst pressure of the vent (bar), K_{st} = deflagration index (bar m/s), V = volume of room (m^3), $R = P_{red}/P_{max}$, P_{red} = reduced pressure after venting (bar) and P_{max} = maximum pressure of a deflagration (bar).

For L/D values greater than 2 and less than 6, the vent area, A_v, calculated by Equation 17.48.13 is increased by adding the area ΔA as calculated from:

$$\Delta A = 1.56 A_v \left[\frac{1}{P_{red}} - \frac{1}{P_{max}}\right]^{0.65} \log\left[\frac{L}{D} - 1\right] \qquad [17.48.14]$$

where L = longest dimensions of enclosure (m), $D = 2(A^*/\pi)^{1/2}$ and A^* = cross-sectional area normal to the longitudinal axis of the space (m^2).

The 2002 edition of NFPA 68 also treats partial volume explosions that apply when dust concentrations in some process equipment and buildings are inherently limited to only a fraction of the enclosure volume. When the volume fill fractions, X_r, can be determined, the minimum required vent area is calculated from the following equation:

$$A_v = A_{vo} X_r^{-1/3} \left[\frac{X_r - R}{1 - R}\right]^{1/2} \qquad [17.48.15]$$

where A_{vo} = vent area for full volume deflagrations determined from Equations 17.48.13 and 17.48.14, and the other terms are as used in these equations.

17.48.9 Schwab and Othmer method

Schwab and Othmer (1964) presented an empirical correlation of experimental tests performed using a Hartmann bomb type of apparatus of volume 1.3 l. The dusts tested included powders of polymers and metal stearates. They expressed their results in the form

$$P_{red} = \frac{P_{max}}{10^{Sf}} \qquad [17.48.16]$$

where f is the vent ratio, P_{red} is the reduced pressure and S is a constant.

For the rates of pressure rise, Schwab and Othmer gave the equations

$$\left(\frac{dP}{dt}\right)_{max} = \frac{5500}{10^{2.443K}} \qquad [17.48.17a]$$

$$\left(\frac{dP}{dt}\right)_{av} = \frac{2700}{10^{2.443K}} \qquad [17.48.17b]$$

where $(dP/dt)_{max}$ and $(dP/dt)_{av}$ are the maximum and average rates of pressure rise (psi/s), respectively. These equations are equivalent to

$$\left(\frac{dP}{dt}\right)_{max} = \frac{k_{max}}{10^{Kf}} \qquad [17.48.18a]$$

$$\left(\frac{dP}{dt}\right)_{av} = \frac{k_{av}}{10^{Kf}} \qquad [17.48.18b]$$

where k_{av} and k_{max} are constants.

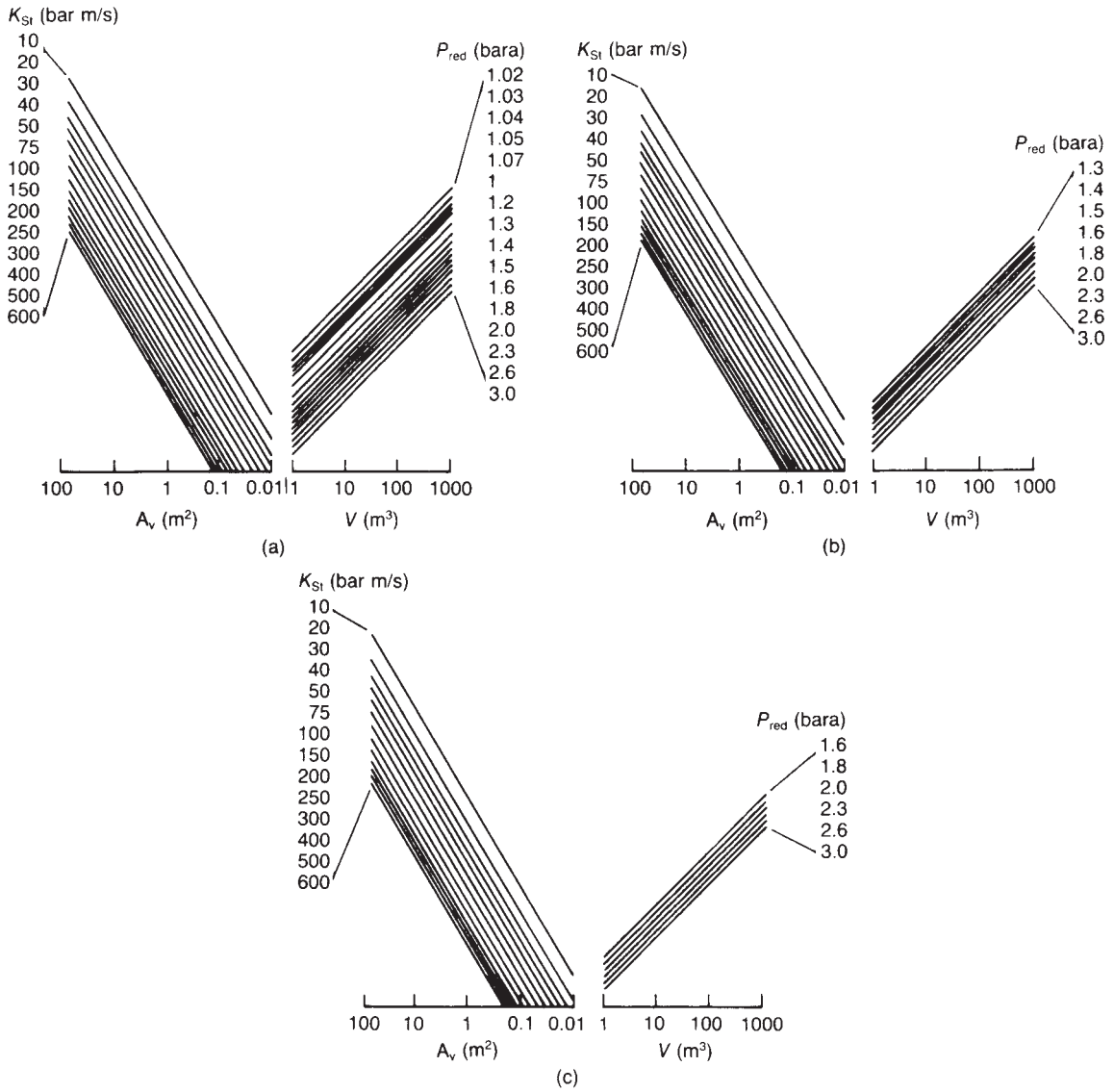

Figure 17.122 *Dust explosion venting: nomographs for vent area extended to lower reduced pressure (Lunn, Brookes and Nicol, 1988): (a) $P_{stat} \leq 1.1$ bara; (b) $P_{stat} = 1.2$ bara; and (c) $P_{stat} = 1.5$ bara (Courtesy of Butterworth-Heinemann)*

The authors give a nomograph for the determination of the vent ratio f. This is shown in Figure 17.123.

17.48.10 Runes method

The method of Runes was described in Section 17.12.

The Runes equation is

$$A_v = C\frac{A_c}{(\Delta P)^{1/2}} \qquad [17.48.19]$$

where ΔP is the explosion overpressure and C is the Runes constant.

NFPA 68: 1978 gives values of the Runes constant C in metric units as 6.8 for organic dusts and 10.5 for high flame speed metal dusts. These compare with values of 6.8 for propane and 10.5 for ethylene.

NFPA 68: 1994 gives a relationship similar to Equation 17.48.16 and containing a constant C. It is described in

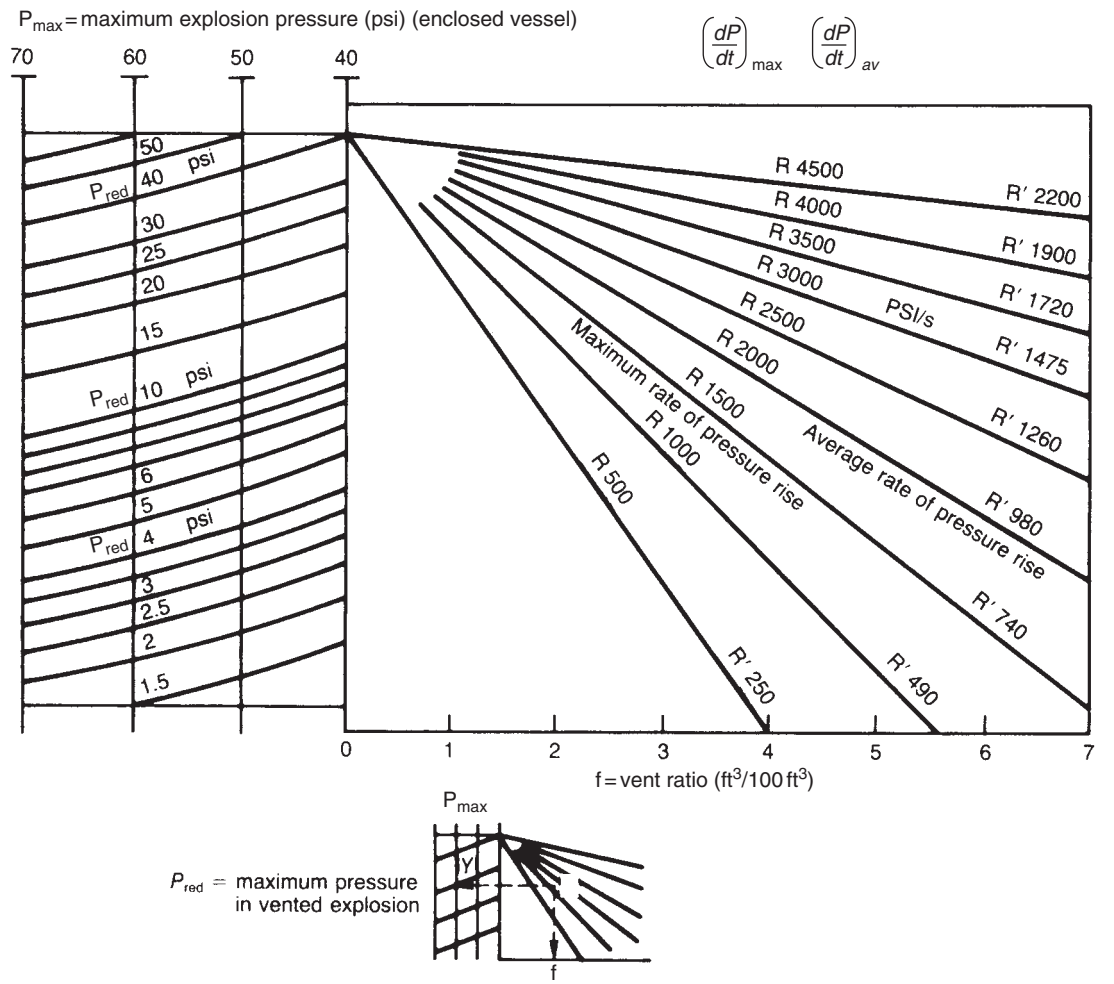

Figure 17.123 *Dust explosion venting: Schwab and Othmer nomograph for vent area (Lunn, 1984b; after Schwab and Othmer, 1964) (Courtesy of the Institution of Chemical Engineers)*

Section 17.14. The code gives the following value of C for dusts:

Dust class	C (bar$^{1/2}$)
St 1	0.026
St 2	0.030
St 3	0.051

17.48.11 Critique of empirical methods

A review of experimental studies comparing the predictions of empirical methods with experimental results is given by Lunn.

Comparison of the empirical correlations for gas explosion venting of Cubbage and Simmonds, Rasbash, Decker, Dragosavic, Cubbage and Marshall and of Runes with the experimental work of Hartmann, Cooper and Jacobsen and of Donat gave generally poor agreement. The Schwab and Othmer method gave excellent agreement with the results of Hartmann, Cooper and Jacob.

The methods considered by Lunn are primarily the vent ratio, vent coefficient and K_{st} methods and the methods of Heinrich and Rust. He gives a set of graphs comparing the predictions given by these methods with the results of Donat for 1 and 30 m^3 spheres. One of these graphs is shown in Figure 17.124. The vent coefficient and vent ratio methods were assessed by scaling up the results on the smaller vessel to the larger vessel, so that predictions were available only for the 30 m^3 vessel. The vent ratio method consistently overestimated the explosion pressure. The vent coefficient method gave closer agreement, but tended to underestimate the explosion pressure. Predictions for the K_{st} method were made for both sizes of vessel. For the 1 m vessel the low ignition energy source nomographs gave good predictions for dusts in classes St 1–3. For the 30 m^3

vessel the low ignition energy source nomographs again gave reasonable agreement, but always tended to underestimate the explosion pressure, sometimes substantially.

Overall, Lunn recommends the use of the K_{st} method. It generally tends to overestimate the vent area and will normally give adequately sized vent areas. He points out, however, that the method can give underestimates, as shown by the work of Eckhoff on silos.

Lunn also states that if reliable Hartman bomb data are available, the Schwab and Othmer method yields good results.

17.48.12 Modelling of dust explosion venting

In principle methods developed in the modelling of gas explosion venting given in Section 17.12 may be used for dust explosion venting also, but in practice there are difficulties. These arise mainly because the models involve the use of the burning velocity and a turbulence factor which are difficult to specify for dust explosions. Therefore, models for dust explosion venting tend to be constructed so that they can incorporate experimentally measured parameters.

17.48.13 Heinrich method

One of the first methods to use this approach was that of Heinrich (1966, 1974). The method is discussed by Matsuda and Naito (1975), Lunn (1984b) and Nicol (1988).

Heinrich made the assumption that the condition for effective relief is

$$\left(\frac{\mathrm{d}P}{\mathrm{d}t}\right)_{P_{\mathrm{red}},V} = \left(\frac{\mathrm{d}P_{\mathrm{ex}}}{\mathrm{d}t}\right)_{P_{\mathrm{red}},V} \qquad [17.48.20]$$

where P is the absolute pressure, P_{ex} is the pressure due to the explosion, t is the time and the subscripts P_{red} and V refer to venting at reduced pressure and in volume V, respectively. The right-hand side of Equation 17.48.20 represents the rate of pressure increase due to the explosion, and the left-hand side represents the rate of pressure decrease due to venting. The terms are equal at $\mathrm{d}P/\mathrm{d}t = 0$ and $P = P_{red}$, where P_{red} is the absolute reduced pressure.

The rate of pressure rise in the actual vessel is related to that in a test vessel by use of the cube root law

$$\left(\frac{\mathrm{d}P_{\mathrm{ex}}}{\mathrm{d}t}\right)_{P_{\mathrm{red}},V} V^{1/3} = \left(\frac{\mathrm{d}P_{\mathrm{ex}}}{\mathrm{d}t}\right)_{P_{\mathrm{red}},V_{\mathrm{L}}} V_{\mathrm{L}}^{1/3} \qquad [17.48.21]$$

where V is the volume of the actual vessel, V_L is the volume of the test vessel and the subscript V_L refers to the test vessel volume.

The volume rate of generation of burned gas is

$$\frac{V}{P}\frac{\mathrm{d}P}{\mathrm{d}t} \qquad [17.48.22]$$

and the mass rate is

$$\frac{V\rho}{P}\frac{\mathrm{d}P}{\mathrm{d}t} \qquad [17.48.23]$$

where ρ is the density of the burned mixture.

The mass velocity of vent outflow for the isothermal case is given by Equation 17.12.62. Then, equating the mass rate of generation of burned gas given by Equation 17.48.23 to the mass vent outflow obtained from Equation 17.12.62 and utilizing Equation 17.48.21 gives for the vent area

$$A_{\mathrm{v}} = \frac{V^{2/3}V_{\mathrm{L}}^{1/3}(\mathrm{d}P_{\mathrm{ex}}/\mathrm{d}t)_{P_{\mathrm{red}},V_{\mathrm{L}}}}{C_{\mathrm{d}}(2RT/M)^{1/2}P_{\mathrm{red}}^{1/2}(P_{\mathrm{red}} - P_{\mathrm{a}})^{1/2}} \qquad [17.48.24]$$

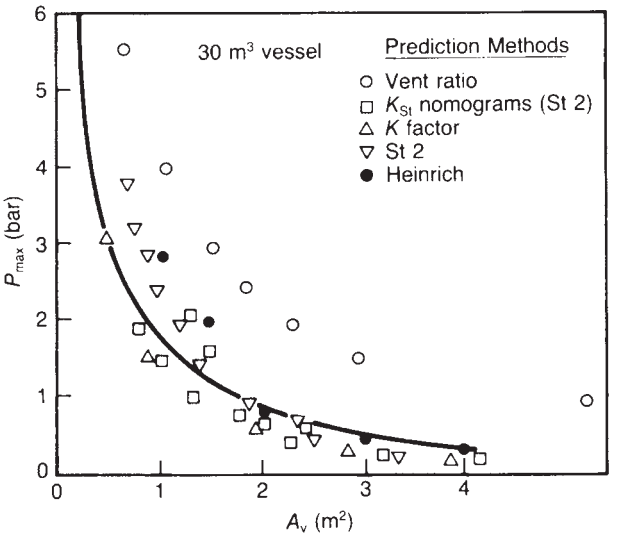

Figure 17.124 *Dust explosion venting: comparison of selected methods of vent area prediction with experimental results of Donat (Lunn, 1984b). The curve is Donat's experimental results for organic pigment in a 30 m³ vessel (Courtesy of the Institution of Chemical Engineers)*

where P_a is the atmospheric pressure. From this equation the pressures are evidently absolute pressures.

A corresponding equation may be derived for the adiabatic case using Equation 17.12.55.

The method requires the specification of a suitable value of $(dP_{ex}/dt)_{P_{red}}, V_L$ for use in Equation 17.48.24. In general, this term is a function of the maximum rate of pressure rise:

$$\left(\frac{dP_{ex}}{dt}\right)_{P_{red},V_L} = K_f \left(\frac{dP_{ex}}{dt}\right)_{max,V_L} \quad [17.48.25]$$

where K_f is a constant. The values of K_f recommended for use in Equation 17.48.25 are given in Table 17.70.

The nomograph due to Heinrich for the estimation of vent areas is shown in Figure 17.125.

As stated earlier, the Bartknecht nomograph method draws on this work.

17.48.14 Palmer method

The method given by K.N. Palmer (1974c) takes as its starting point experimental measurements on the maximum closed explosion pressure and rate of pressure rise for the dust mixture. He considers two cases: a low pressure case where the venting pressure is close to atmospheric and a high pressure case.

For the low pressure case the venting pressure is close to atmospheric:

$$P/P_o \approx 1 \quad [17.48.26]$$

where P_o is atmospheric pressure. For this case Palmer uses Equation 17.12.63 for the mass velocity G_v of vent outflow. Then, utilizing relation 17.48.26

$$G_v \approx C_d[2P_o\rho_o \ln(P/P_o)]^{1/2} \quad [17.48.27]$$

where C_d is the coefficient of discharge and ρ_o is the density of the gas at atmospheric pressure. From these equations the pressures are evidently absolute pressures. In the closed vessel at the point where the rate of production of burned gas is at a maximum, the rate of pressure rise is $(dP/dt)_{max}$, the corresponding pressure is P_c and the rate of volume production is

$$\frac{V}{P_c}\left(\frac{dP}{dt}\right)_{max} = \frac{dV}{dt} \quad [17.48.28]$$

He takes account of the fact that with venting, combustion conditions approximate to constant pressure rather than constant volume. By introducing the ratio of specific heats γ, then writing

$$\rho = \rho_o P/P_o \quad [17.48.29]$$

the maximum mass rate of production is

$$\frac{PV\rho_o}{P_o\gamma P_c}\left(\frac{dP}{dt}\right)_{max} = \frac{dm}{dt} = \frac{s\,dV}{dt} \quad [17.48.30]$$

Then, equating this rate of mass rate of production with the mass vent outflow given in Equation 17.48.27 and utilizing the relation

$$\rho = \rho_c P_a/P_c \quad [17.48.31]$$

and the empirical relation

$$P_c = 0.6P_{max} \quad [17.48.32]$$

gives

$$P - P_o = \frac{2.3P_o\rho_c}{C_d^2\gamma^2 P_{max}^3}\left(\frac{V}{A_v}\right)^2\left(\frac{dP}{dt}\right)^2_{max} \quad [17.48.33]$$

where A_v is the vent area and the subscript c refers to the point at which the maximum rate of pressure rise occurs. Palmer defines the density ρ_o as the density of the unburned gas at P_o and as that of the combustion products ρ_c at P_c. Equation 17.48.33 is the equation for the low pressure case.

For the high pressure case the mass velocity of venting is given by Equation 17.12.55. Then, utilizing relation 17.48.26 and rearranging,

$$G_v = C_d\left[\frac{\rho_o\gamma}{P_o}\left(\frac{2}{\gamma+1}\right)^{(\gamma+1)/(\gamma-1)}\right]^{1/2} P \quad [17.48.34]$$

$$= KP \quad [17.48.35]$$

with

$$K = C_d\left[\frac{\rho_o\gamma}{P_o}\left(\frac{2}{\gamma+1}\right)^{(\gamma+1)/(\gamma-1)}\right]^{1/2} \quad [17.48.36]$$

Also for this case the author takes the mean mass flux of venting as

$$G_{v,av} = \frac{K}{2}(P - P_o) \quad [17.48.37]$$

The duration of the explosion in the closed vessel, from ignition to maximum pressure, is

$$\frac{P_{max} - P_o}{(dP/dt)_{av}} \quad [17.48.38]$$

where P_{max} is the maximum unvented explosion pressure and the subscript av denotes average. Then, from Equations 17.48.37 and 17.48.38 the total mass vented is

$$\frac{KA_v}{2}\frac{(P - P_o)(P_{max} - P_o)}{(dP/dt)_{av}} \quad [17.48.39]$$

Table 17.70 *Dust explosion venting: the Heinrich K parameter*

Vent opening pressure (bar)	*Maximum rate of pressure rise in closed vessel,* $(dP_{ex}/dt)_{max}, V_L$ (bar/s)	K_f
1.15	1000	0.5
	2000	1.0
1.6–1.8	1000	0.5
	1000–2000	0.67
	2000	1.0

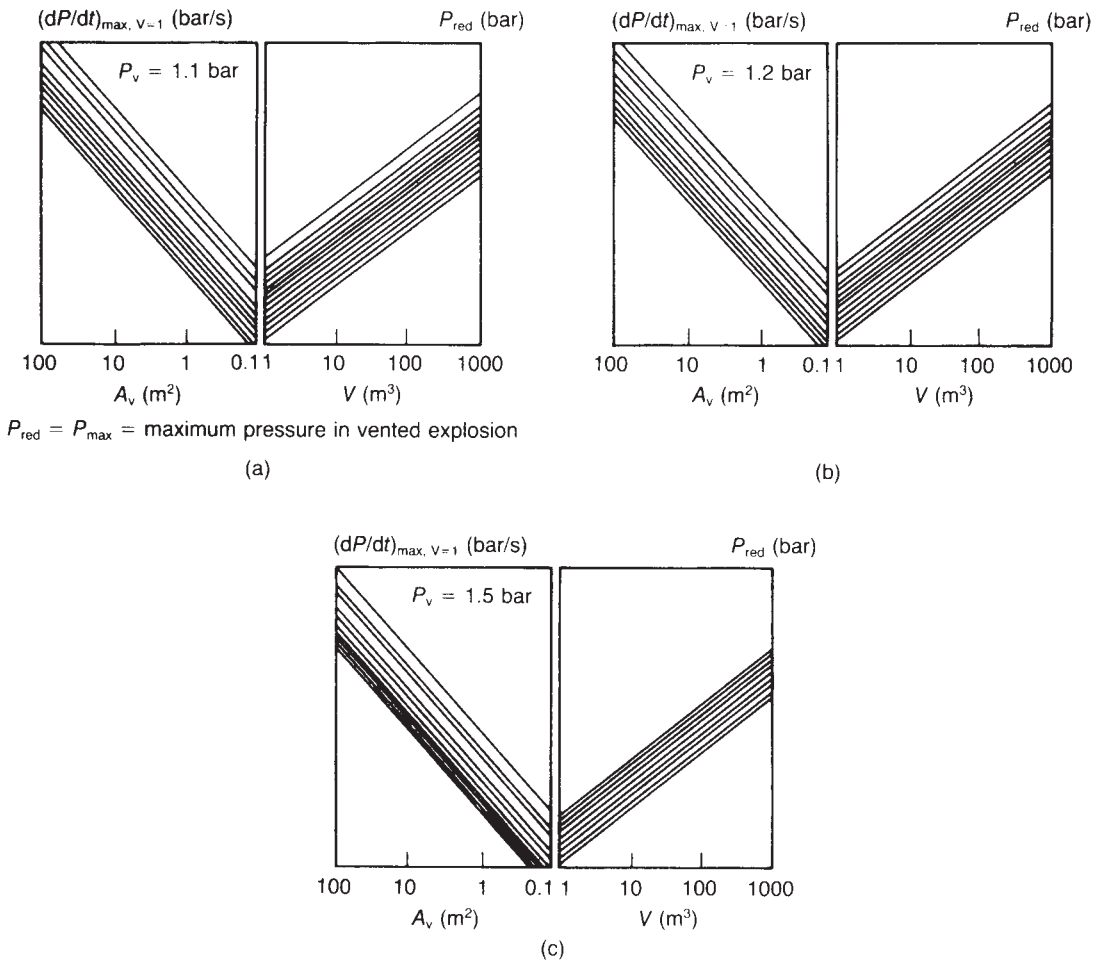

Figure 17.125 *Dust explosion venting: Heinrich nomographs for vent area (Lunn, 1984b; after Heinrich, 1974) (Courtesy of the Institution of Chemical Engineers)*

The total mass originally present was $V\rho_c$. Hence, the fraction of the mass remaining is

$$1 - \frac{KA_v}{2}\frac{(P - P_o)(P_{max} - P_o)}{V\rho_c(dP/dt)_{av}} \qquad [17.48.40]$$

Utilizing the empirical relation

$$\left(\frac{dP}{dt}\right)_{av} = 0.4\left(\frac{dP}{dt}\right)_{max} \qquad [17.48.41]$$

Equation 17.48.40 gives for the fraction of mass remaining

$$1 - KA_v\frac{(P - P_o)(P_{max} - P_o)}{0.8V\rho_c(dP/dt)_{max}} \qquad [17.48.42a]$$

$$= \frac{P}{P_{max}} \qquad [17.48.42b]$$

At P_{max}

$$P \gg P_o \qquad [17.48.43]$$

So Equations 17.48.42 become

$$\frac{1}{P - P_o} = \frac{1}{P_{max} - P_o} + \frac{KA_vP_{max}}{0.8V\rho_c(dP/dt)_{max}} \qquad [17.48.44]$$

Equation 17.48.44 is the equation for the high pressure case.

17.48.15 Rust method

Another method described in Section 17.12 is that of Rust (1979). This method was in fact derived originally for the venting of dust explosions in low-strength plants. For a dust mixture initially at atmospheric pressure

$$P = \frac{K_Dt^3}{V} \qquad [17.48.45]$$

with

$$K_D = \frac{4}{3}\pi u^3 P_{max} \quad [17.48.46]$$

where K_D is an explosion parameter, P is the absolute pressure, t is the time, u is the velocity of the flame front, V is the volume of the vessel and the subscript max denotes maximum. Then, as before, the vent area is

$$A_v = \frac{kF(P_{max}V)^{2/3}K_D^{1/3}}{P_{red}^{1/2}} \quad [17.48.47]$$

where P_{red} is the reduced pressure (gauge) and k is a constant. The value of k is given in Section 17.12.

The parameter K_D may be determined from the pressure rise in tests. Thus, differentiating Equation 17.48.48 gives

$$\frac{dP}{dt} = \frac{3K_D t^2}{V} \quad [17.48.48]$$

17.48.16 Nagy and Verakis method

The model given by Nagy and Verakis (1983), described in Section 17.12, is applicable to dust explosions. Using the notation given in Section 17.12, for explosion venting of a cylinder with an open vent, with ignition at the closed end, with subsonic flow and with venting of burned gas

$$\frac{P_{red}}{(P_{red}-P_o)^{1/2}} = \frac{RT_u k_{v1} P_o L(A_v/V)}{T_b^{1/2}\alpha S_u(P_m - P_o)} \quad [17.48.49]$$

The left-hand side term in Equation 17.48.49 is termed the pressure coefficient. For dust explosions it may be measured directly.

For venting with an initially closed vent, Equation 17.48.49 becomes

$$\frac{P_{red}+P_v}{(P_{red}-P_o)^{1/2}} = \frac{RT_u k_{v1} P_o L(A_v/V)}{T_b^{1/2}\alpha S_u(P_m - P_o)} \quad [17.48.50]$$

where ΔP_v is the vent overpressure at which the vent opens ($lb_f/in.^2$).

17.48.17 Elongated vessels

There is relatively little information available on the dust explosion venting of elongated vessels. Most treatments are either for compact vessels or for pipes.

17.48.18 Critique of available methods

The methods available for the estimation of the vent area for a given reduced explosion pressure have been reviewed by Lunn (1984b). Of the empirical methods, his preferred methods are the K_{st} nomograph method and, where suitable data are available, the Schwab and Othmer method.

The theoretical methods all rely more or less heavily on experimental data. Lunn finds that the Heinrich method gives upper limits of the reduced pressure for St 1 and 2 dusts, but should not be used for St 3 dusts. The Palmer method gives good predictions for St 1 and 2 dusts, but tends to underestimate the reduced pressure for St 3 dusts in larger vessels. The Rust method is better for St 1 dusts than for St 2 and 3 dusts, and can be highly inaccurate in some cases. The Pittsburgh method requires information on the burning velocity and turbulence factor which are generally not available and is of limited application.

For silos Lunn states that the only available method is that given in VDI 3673, which tends to overestimate the vent area. He suggests that the Rust method may also be used for quiescent conditions.

In his later treatment, Lunn (1992) concentrates on the Bartknecht nomograph, the vent ratio and venting coefficient, or K factor, methods.

17.48.19 Venting of low-strength plants

The maximum safe pressure for many plants handling dusts is 15 kPa (2 $lb_f/in.^2$), and this maximum pressure is used in some of the design methods. Dust-handling plants are often constructed, however, in thin metal sheet which is unable to withstand pressures of more than 7 kPa (1 $lb_f/in.^2$), even if the large flat sections of plant are provided with additional stiffening.

There is some difference of practice between the United Kingdom and the United states on the one hand and continental Europe on the other. Plant in the latter tends to be designed to a somewhat higher pressure rating.

Several authors have addressed the problem of dust explosion venting for low-strength plant. The method given by Rust (1979) is explicitly intended for this application. The worked example given by Rust is for a filter with a maximum allowable pressure of 23.9 kPa (3.47 psi).

The lowest reduced pressure for which the Bartknecht nomographs apply is 0.2 barg, but, as already described, Lunn, Brookes and Nicol (1988) have extended the nomograph method down to reduced pressures of 0.05 barg, or even less.

17.48.20 Venting phenomena

If the vent is an open one, venting will result in the emergence of a flame. With a dust the flame tends to be considerably larger than with a gas. This is illustrated by the series of photographs given by Bartknecht (1981a) for gas and dust explosion venting.

If the vent has a duct, there is the potential of unburned dust to undergo combustion, possibly resulting in overpressure in the duct.

17.48.21 Vent design and details

In general terms, the design of vents for dust explosion venting and the details of the vents are similar to those used for gas explosion venting. Details are given in NFPA 68: 2002.

17.48.22 Vent ducting effects and design

As described in Section 17.12, the vent duct can have a marked effect on the maximum pressure in a vented explosion.

Figure 17.126 given by Bartknecht (1981a) shows the effect of dust class, dust concentration and duct length on the reduced pressure in a 2 m^3 vessel with a vent area of 0.13 m^3.

The general recommendations given by Bartknecht for vent ducts apply to gases and dusts. The vent duct should be straight, as short as practicable and preferably cylindrical. It should have the same pressure rating as the vessel. Since detonations may develop in pipes of 10–30 m in length, the vent duct should be limited to 10 m. Reaction forces should be allowed for.

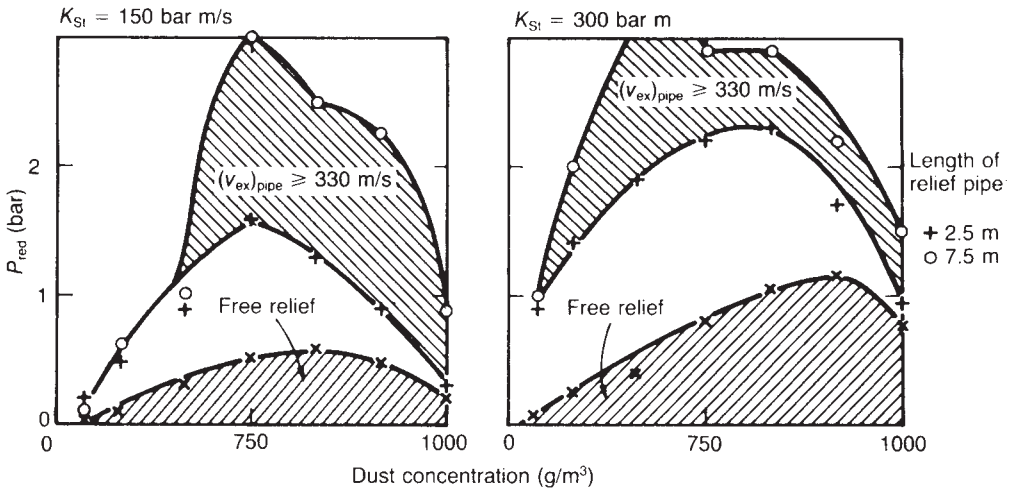

Figure 17.126 *Dust explosion venting: effect of dust explosibility and concentration and of length of duct on reduced pressure (Bartknecht, 1981a). Vessel volume 2 m³, vent area 0.13 m² (Courtesy of Springer-Verlag)*

A graph to determine the maximum allowable length of smooth, straight pipe or vessel which is closed at one end and vented at the other which is applicable to propane and to dusts is given in NFPA 69: 1994 and has been given as Figure 17.36. If the L/D ratio is greater than that shown, there is a risk of detonation. There are separate curves for dusts with $K_{st} \leq 200$ and $K_{st} > 200$ bar m/s.

There are available several correlations to assist in allowing for the effect of the vent duct. Figure 17.127 given by Bartknecht (1981a) gives the relationship between the reduced pressure with the duct and that without the duct. There are two lines, the parameter being the duct length. Figure 17.128 gives a further correlation for the same relationship, but in this case the parameter is the gas velocity. Both correlations were given in NFPA 68: 1988, but only the first is retained in NFPA 68: 1994.

The correction given in the NFPA 69: 2002 edition for ducts of lengths 2–6 m (10–20 ft) is:

$$P'_{red} = 0.172(P_{red})^{1.936}$$

where P'_{red} is the reduced pressure resulting with a vent duct (bar or psi).

Figure 17.129, also given in NFPA 68: 1994, shows the maximum explosion pressure developed in deflagration of dust in a smooth, straight pipe open at one end with an initial flow velocity of less than 2 m/s.

17.48.23 Safe discharge

Explosion venting gives rise to three effects: a pressure wave and discharges of flame and unburned material. It is essential that all three effects be handled safely.

The discharge of unburned dust can be particularly strong and can result in a large flame. With dusts the problem of the toxicity of the vented material can be particularly severe.

17.48.24 Dust explosion venting of ducts and pipes

The gas explosion venting of ducts and pipes was considered in Section 17.13. There is relatively little guidance available on dust explosion venting of ducts and pipes.

Early work by K.C. Brown (1951) on elevator casings showed a general similarity between gas explosions and dust explosions and the value of vents near the point of ignition.

In his discussion of explosion venting of pipes, Bartknecht (1981a) states explicitly that the course of gas and dust explosions in pipes is similar and that his recommendations for explosion venting apply to all combustible materials.

Lunn (1984b) recommends that in the absence of specific information for dusts the guidelines for gas explosion venting be used.

Dust-carrying pipelines will generally require multiple vents. NFPA 68: 1988, 1994 and 2002 gives guidance on the spacing of vents. This is shown in Figures 17.38 and 17.39, which apply to propane and dusts.

The treatment given in the IChemE *Dust Explosion Venting Guide* is based on these graphs.

17.48.25 Dust explosion venting of buildings

The strength of buildings is discussed in Section 17.8. A pressure of 7 kPa (1 psi) is often quoted as sufficient to destroy a typical brick building.

Methods for the explosion venting of buildings are discussed in Section 17.14. The two principal methods for the gas explosion venting of buildings are those of Rasbash and of Runes. The Runes method is that most often mentioned for the dust explosion venting of buildings and is that given for that purpose in NFPA 68: 1978. The use of the Runes equation for the explosion venting of buildings was described in Section 17.14 and the values of the Runes constant C for dusts were given in Section 17.48.10.

17.49 Dust-handling Plants

Operations in which dusts are generated or handled include

(1) size reduction;
(2) conveying
    (a) manual,
    (b) mechanical,

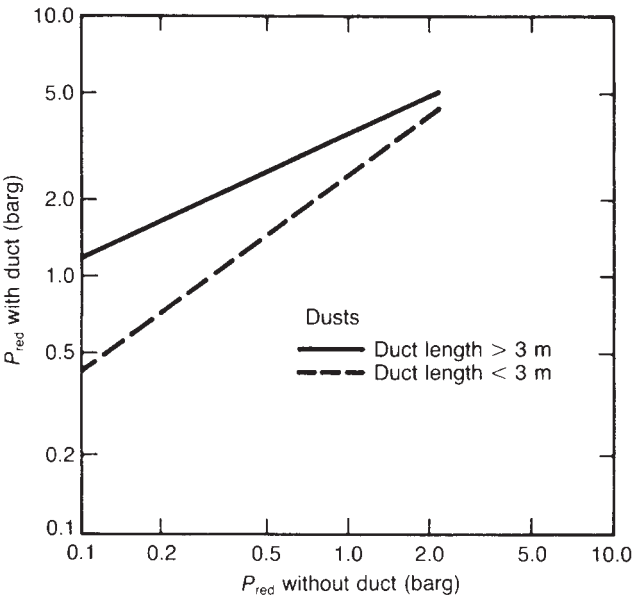

Figure 17.127 *Dust explosion venting: effect of length of vent duct on reduced pressure (NFPA 68: 1994). See text for details and note to Figure 17.25 (reprinted with permission from NFPA 68 Deflagration Venting, © 1994, National Fire Protection Association, Quincy, MA 02269)*

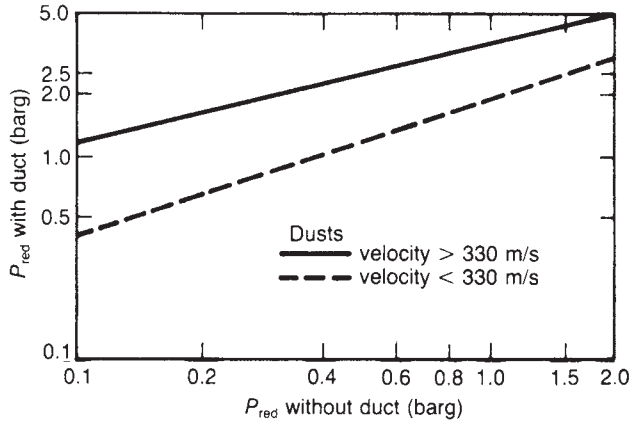

Figure 17.128 *Dust explosion venting: effect of velocity in vent duct on reduced pressure (NFPA 68: 1988). See text for details and note to Figure 17.25 (reprinted with permission from NFPA 68 Deflagration Venting, © 1988, National Fire Protection Association, Quincy, MA 02269)*

(c) pneumatic;
(3) separation
  (a) settling chambers,
  (b) cyclones,
  (c) filters,
  (d) scrubbers,
  (e) electrostatic precipitators;
(4) driers
  (a) tray driers,
  (b) rotary driers,
  (c) fluidized bed driers,
  (d) pneumatic driers,
  (e) spray driers;
(5) screening and classifying;
(6) mixing and blending;
(7) storage;
(8) packing;
(9) fired heaters.

In many cases, there is a choice of different methods of carrying out a particular operation. The hazard of a dust explosion should be a factor in selecting a suitable method.

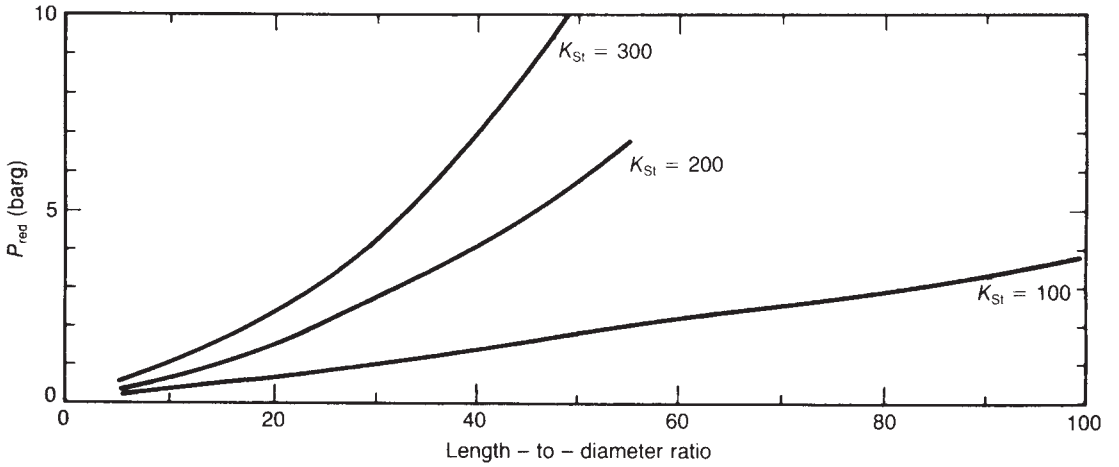

Figure 17.129 *Dust explosion venting: reduced explosion pressure in deflagration of dust/air mixture in a smooth, straight pipe or duct closed at one end (NPFA 68: 1994). See text for details and note to Figure 17.25 (reprinted with permission from NFPA 68 Deflagration Venting, © 1994, National Fire Protection Association, Quincy, MA 02269)*

All plants handling flammable dusts should have a combination of sufficient strength and explosion protection to withstand a dust explosion safely.

Some other basic principles in the design and operation of dust-handling plants are (1) minimization of space filled by dust suspensions, (2) maintenance of design operating conditions, (3) minimization of mechanical failure and overheating, (4) precautions against static electricity and (5) precautions against passage of burning dust.

Some particular types of dust-handling plants, namely, grinding mills, conveyors, dust separators, driers and storages, are considered below.

Operations involving screening and classifying or mixing and blending tend to create dust suspensions. Plants for such operations should be enclosed and preferably run under a slight vacuum. Precautions should be taken against static electricity and explosion protection should be provided.

Where dusts such as pulverized coal are used as fuels for fired heaters or furnaces, an explosive dust suspension is burned under controlled conditions. As with other fuels the principal hazard is loss of ignition followed by reignition and explosion.

Accounts of the safe design of dust-handling plants are given by K.N. Palmer (1973a), Bartknecht (1981a) and Field (1982).

17.49.1 Grinding mills

There is a large variety of size reduction equipment from jaw crushers to micronizers. In equipment which produces powders or dusts by size reduction, there is inevitably a real possibility of a dust explosion. The dust concentrations in a mill may be in the explosive range and the grinding elements in the mill, or possibly foreign bodies, may act as sources of ignition.

There are various steps which can be taken to minimize the dust explosion hazard in a mill. The free volume should be kept low so as to avoid a large volume of dust of explosible concentration. Large free volumes can occur if the mill is oversized or the feed to the mill is too low.

Overloading of or blockage in the mill can cause it to run hot and give ignition. The motor should be protected with an overload trip.

In general, mills are relatively robust. Even the larger mills with a volume of some tens of cubic metres can be designed to withstand pressures up to 350 kPa (50 $lb_f/in.^2$). However, explosion relief should be provided if necessary.

Bartknecht (1981a) gives three designs for complete grinding mill systems, with inerting, explosion suppression and explosion venting.

17.49.2 Conveyors

Dust may be conveyed by manual methods or by mechanical or pneumatic conveyors.

Applications of manual dust handling are restricted largely to operations such as bagging up of dust products or removal of unwanted dusts in limited quantities. There should be good local ventilation at places where dust may be generated such as bagging points and there should be a high standard of housekeeping on the plant.

Methods of mechanical conveying include screw and drag-link conveyors, belt conveyors and bucket elevators. A screw conveyor has minimal free volume and is an effective conveyor for dusts. So also is a drag-link conveyor, although the return leg contains free space which usually requires explosion protection. A belt conveyor is suitable for dusts only if enclosed. The free volume within the enclosure is likely to be larger than for a drag-link conveyor and the hazard correspondingly greater. If a belt conveyor is used, the enclosure should have explosion protection.

All mechanical conveying methods involve the risk of overheating due to mechanical failure, and appropriate steps should be taken in design and operation to minimize this hazard. In addition, belt conveyors are particularly liable to generate static electricity, and suitable safeguards should be provided.

17.49.3 Bucket elevators

The use of a bucket elevator to convey dust involves severe hazards unless there are suitable safeguards. There have

been a number of explosions in bucket elevators and, as already mentioned, one of the few pieces of work on dust explosions in ducting is the work of K.C. Brown (1951) on elevator casings. Precautions for bucket elevators are discussed by K.N. Palmer (1973a) and Field (1982).

A bucket elevator tends to have a dust suspension virtually continuously, particularly at the boot and the head. The ignition source for an explosion is commonly a slipping belt or impact of the buckets on the casing.

Features of design to minimize the hazard include the provision of separate delivery and return legs, making the casing dust tight and able to contain fire, provision of isolation chokes at both ends and location of the elevator outside the building.

Explosion suppression may often be a suitable option, particularly if the elevator is inside a building. For explosion venting, Field recommends a vent ratio of $^1/_6$ m^2/m^3 with vents at the boot and head and, if the elevator is longer than 6 m, vents at intervals along it.

17.49.4 Pneumatic conveying

There are two basic systems for pneumatic conveying described by K.N. Palmer (1973a). These are (1) low volume/high pressure air and (2) high volume/low pressure air. The high pressure system uses relatively strong piping. It may be possible, therefore, to design it to withstand a dust explosion. There may be a risk, however, of erosion and consequent thinning of the pipe wall. The low pressure system utilizes weaker pipework and usually requires additional explosion protection such as vents.

Field (1982) states that in most pneumatic conveying systems the dust concentration is normally operated well above the upper explosive limit, though this may not apply at start-up and shut-down, and that the pipework is of a sufficient rating to withstand the full explosion pressure. The application of explosion protection is therefore mainly to the plant connected to the conveying system.

Precautions against ignition by static electricity or burning dust are particularly important in pneumatic conveying systems.

Further aspects of dust explosion hazards in pneumatic conveying systems are described by Palmer and Field.

17.49.5 Dust separators

In selecting a method of separation of a dust from a gas an important factor as far as dust explosions are concerned is the free volume. A settling chamber tends to involve a rather large free volume and usually is not a very desirable method.

Two of the main types of dust separator are dust filters and cyclones, which are considered below.

For both types of separator, precautions against ignition by static electricity or burning dust are especially important.

An alternative type of separator, in which the dust explosion hazard is much reduced, is the wet scrubber. Thus,in the United kingdom the use of wet scrubbers has been a statutory requirement in the grinding of magnesium. Wet scrubbers are used mainly to remove unwanted materials.

High efficiency cleaning of gases is often effected by an electrostatic precipitator. Although the inlet concentration of dust is normally below the explosive limit, mechanical rapping of the electrodes can create an explosive dust concentration. Electrostatic precipitators are not generally very suitable for removal of flammable dusts.

17.49.6 Dust filters

A widely used separation device is the bag filter. Such filters may be fitted after a cyclone or on their own. An explosive concentration of dust is liable to arise in bag filters which are cleaned by mechanical shaking and occurs during the cleaning operation. Again the ignition source may be dust ignited elsewhere.

Precautions for dust filters are discussed by K.N. Palmer (1973a), Bartknecht (1981a) and Field (1982).

Explosion suppression is an option which may have merit for a dust filter. For explosion venting, Field indicates that the volume on which the venting is based should be the free volume, or total volume less the volume of the filter bag assembly. Where the filter is lightly constructed, he states that the vent ratio method is suitable for smaller volumes ($<30\ m^3$), but that the vent coefficient method is preferable for larger volumes, whilst where the filter is able to withstand a reduced explosion pressure of 0.2 barg, the regular K_{st} nomograph method is suitable. He also says that there is evidence that the nomograph method may overestimate the vent area, absorption of heat by the filter bags being a possible factor in this. The location of the vent is important in the case of dust filters. For the filter configuration which he considers, vents on the top tend to be less effective probably due to the obstacle-induced turbulence as flame propagates through the filter assembly. His recommendation is for vents located near the bottom of the rear side.

Bartknecht gives an account with detailed design of several filters.

17.49.7 Cyclones

Another common means of separation is the cyclone. Explosions in plant handling dusts occur not infrequently at a cyclone. Often the source of ignition is not at the cyclone itself but dust ignited elsewhere in the plant.

Precautions for dust cyclones are discussed by K.N. Palmer (1973a), Bartknecht (1981a) and Field (1982).

In a cyclone there is a concentration gradient of dust with a very low concentration at the wall. At some intermediate point the dust concentration is in the explosive range. This unique pattern of dust concentration could mean that the usual correlations for dust explosion venting may be less applicable. On the other hand, the explosion pressure in a cyclone may well rise due to ignition elsewhere in the plant and in this case the normal dust pattern in the cyclone may be disturbed.

For cyclones with the product offtake connected to other plant as in a spray drier system, Bartknecht recommends an isolation choke on product offtake.

Explosion suppression is an option which can be considered for cyclones. For explosion venting, Field refers to work by K.N. Palmer (1974b) and Tonkin and Berlemont (1972 FRS Fire Res. Note 942) showing that the vent ratio method tends to overestimate the vent area. Cyclones are often of too light a construction for the regular K_{st} nomograph method to be applicable. The vent is most effective if located on the top of the cyclone.

17.49.8 Driers

There are a large number of different types of drier, but there are certain common hazards. These types include

(1) tray driers, (2) rotary driers, (3) fluidized bed driers,(4) pneumatic driers, and (5) spray driers.

Precautions for driers are discussed by K.N. Palmer (1973a), Bartknecht (1981a) and Field (1982). The IChemE *Drier Guide* also gives detailed guidance.

In many driers, the liquid driven off is itself a flammable vapour and constitutes an explosion hazard. The main method of prevention is to use ventilation to keep the vapour concentration well below its lower flammability limit.

Direct firing of driers creates a strong ignition source and for this reason indirect heating is often used instead.

Other hazards in driers arise if the plant is not operated according to design conditions. Thus, if the feed rate is low, the material may become overheated and may ignite. Overheating may also occur if material from a previous batch is exposed to hot air on start-up. Similar hazardous conditions can arise in shut-down or emergency situations. The control of drier operating conditions is therefore particularly important.

The hot product from a drier is another hazard. It may be necessary to cool it before storage if self-heating is to be avoided.

17.49.9 Fluidized bed driers

Fluidized bed driers may be batch or continuous. According to Bartknecht, incidents in such driers have mainly been with hybrid dust–gas mixtures.

The explosion suppression option is more difficult to apply to fluidized bed driers, because it is hampered by the high air velocities. Nevertheless, Bartknecht gives an account of its application.

For explosion venting, Field states that any of the three main methods, vent ratio, vent coefficient or regular K_{st} nomograph, may be used. He gives details of the optimum vent location.

Bartknecht gives an account with detailed design of several fluidized bed driers, including explosion suppression and explosion venting. Figure 17.130 shows one of his graphs for explosion venting, illustrating the effect of locating the explosion relief on the clean side of the dust filters.

17.49.10 Spray driers

In spray driers the dust concentration is usually calculated to be below the lower explosive limit, but air currents may create higher concentrations. Deposits of dried product may build up and may undergo thermal degradation or become contaminated with oil so that the ignition temperature is lowered. Ignition may occur if the air inlet temperature is too high or if part of the high speed atomizer breaks off and causes an incendive spark.

Precautions for spray driers are discussed by Bartknecht (1981a) and Field (1982).

These precautions include ensuring that the air inlet temperature is below the decomposition temperature of the product and that the product does not form layers which may undergo thermal degradation.

The atomizer should be regularly serviced. Other precautions against its acting as an ignition source are to monitor its vibration and the bearing temperature as well as the power consumption of its motor.

Inerting, explosion suppression and explosion venting are all options which may be used with spray driers.

Field states that if flammable solvents are present, the only suitable option is inerting. Explosion suppression is a suitable option for smaller volumes but he does not recommend it for larger ones. For explosion venting, he states that any of the three main methods, vent ratio, vent coefficient

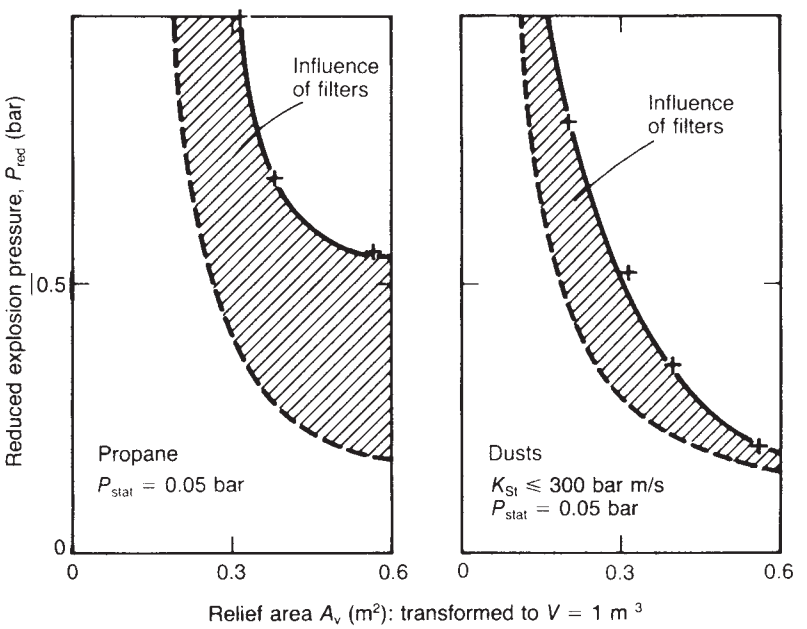

Figure 17.130 *Dust explosion venting: vent area requirement for a fluid bed driver (Bartknecht, 1981a) (Courtesy of Springer-Verlag)*

or regular K_{st} nomograph, may be used, although the vent ratio method overestimates the vent area for large volumes.

Bartknecht gives detailed designs for three complete spray drier systems, based on inerting, explosion suppression and explosion venting.

In the particular design which he considers for the second of these options, explosion suppression is used in the drier and the cyclones and an extinguishing barrier in the pipe between the drier and the cyclones. All three are activated independently, and activation of any one causes shut-down. He states that design of an explosion suppression system for a volume $>100\,m^3$ is a specialist matter.

In the design based on explosion venting, he considers first driers with $H/D < 5$. He states that for dusts a vent area may be used which is less than that given by the K_{st} nomograph method, since this tends to oversize the vent area for larger volumes. Moreover, the drier will never be full of an explosive dust suspension. For driers processing material with flammable solvents and thus containing hybrid dust–gas mixtures the nomograph for propane should be used, but the design is a specialist matter. For driers with $H/D > 5$ the vent area should be the whole roof.

For explosion venting, Bartknecht uses rapid action valves for isolation between the drier and the air heater and between the drier and the cyclones, and a rotary choke valve at the product offtake. Likewise, he gives isolation arrangements for the explosion suppression case.

He also emphasizes that in the event of an explosion there should be automatic shut-down and water sprinklers should be available to deal with the resultant dust fire.

17.49.11 Silos

As already described, a number of the principal dust explosions have occurred in silos. In a silo it is virtually inevitable that a dust suspension will exist in at least part of the space.

Precautions for silos are discussed by Bartknecht (1981a), Field (1982) and Eckhoff (1991).

A silo should be provided with feed arrangements which minimize the formation of dust suspensions. A silo may be filled by letting the dust fall from the roof or by introducing it down a vertical feeder duct so that it flows sideways onto the existing dust pile, the latter minimizing dust cloud formation.

The explosion suppression option is applicable to silos. Field states that it can be used effectively for volumes up to $60\,m^3$, but that beyond this careful consideration needs to be given to the dust explosibility and to the ability of the suppressant to fill the volume rapidly.

For explosion venting, Field states that the vent coefficient and regular K_{st} nomograph methods are applicable, but that the vent ratio method overestimates the vent area, and that none of the methods works well for H/D ratios greater than 3–5.

The explosion venting of silos has been considered in detail by Bartknecht. He treats it as an example of an elongated vessel and applies to it the principles which govern the venting of a pipe at one end. As with that case, the vent needs to be along the axis and to utilize the whole cross-sectional area of the end, which in this instance is the roof.

Bartknecht considers in particular the allowable height of the silo. This is essentially governed by two principles. One is that the cross-sectional area defines the maximum volume which can be vented and the other is that the maximum volume should be limited to $1000\,m^3$. Figures 17.131 and 17.132 illustrate the limits on the allowable height of a silo based on these principles.

17.49.12 Grain elevators

Other storages which have been the site of some of the main dust explosions are grain elevators. In consequence, there have been a number of studies of grain elevator explosions and of the precautions which should be taken.

In many incidents, poor standards of training, housekeeping and maintenance appear to have been major contributors.

The ignition sources identified in grain elevator explosions were given in Section 17.45.

Two of the principal components of grain elevators are the silos and the bucket elevator, both of which have just been discussed. Another main component is the horizontal conveyor, which conveys grain from the receiving point to the boot of the bucket elevator and from the offtakes of the silos to the loading point.

17.50 Dust Fires

It is convenient to deal at this point with dust fires. An account of dust fires is given by K.N. Palmer (1973a).

Dust fires occur in dust deposits and are of two types – laming and smouldering fires.

The type of fire that is produced by a particular dust is not predictable and can only be determined by experiment, but some general guidelines can be given. A flame can be sustained only if sufficient volatile matter is evolved from the dust. If the dust is able to smoulder, the volatiles may be produced by this smouldering, otherwise they must be generated by the flame itself.

Characteristics of the dust which particularly affect this combustion process are volatile content, melting point and particle size.

The flame may spread across the surface of the dust or may burn down from the surface into the dust layer. If the flame is able to release sufficient volatiles, it may travel quite rapidly across the surface. Otherwise, its propagation over the surface is determined by the smouldering rate. Smouldering combustion may continue into the dust layer with the flame burning on the surface.

If the particle size of the dust is sufficiently large, the flame may propagate through the dust layer. In this case combustion is likely to be rather rapid.

On the other hand, a large particle size tends to give a low smouldering rate. In the limit the particle size may be too great for smouldering to persist.

Another feature which favours rapid combustion is an air flow caused by ventilation or by convection currents, including those arising from the combustion process itself.

If a smouldering fire starts below the surface of the dust and works its way up, it may burst into flame and spread more rapidly when it reaches the surface.

Smouldering rates are commonly determined by measuring the rate of travel of smouldering combustion along a 'dust' train of stated dimensions. Typical smouldering rates for dusts are about 5 cm/h for wood and about 20 cm/h for coal with a bed depth of 1 cm. An extreme value is given by magnesium dust with a smouldering rate of 14 m/h.

There is a minimum depth of dust layer for sustained smouldering. Minimum depths typically range from approximately 2 mm upwards.

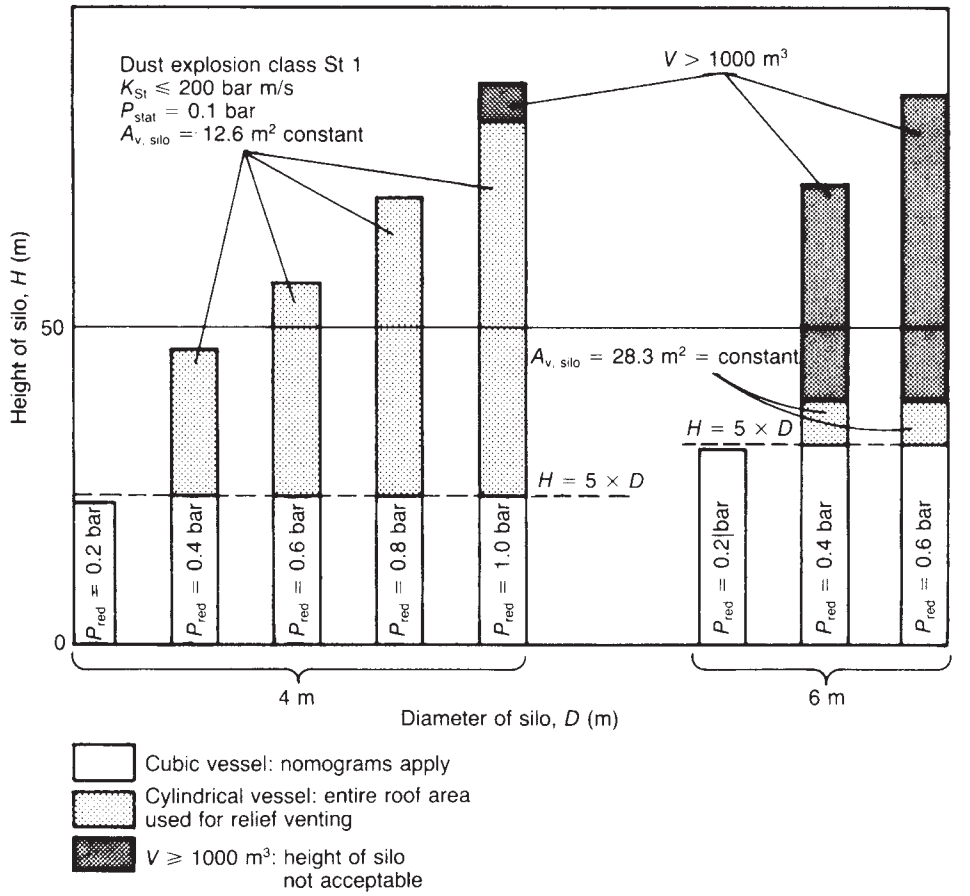

Figure 17.131 *Dust explosion venting: allowable height of a silo – 1 (Bartknecht, 1981a). The figure is based on the use of Bartknecht nomographs (Courtesy of Springer-Verlag)*

Detection of dust fires is difficult. There are no special types of detector for dust fires. The effects given by smouldering are usually weak and difficult to detect with the sensors normally used in automatic fire protection systems. It may be appropriate, however, to monitor the temperature in the interior of large dust piles with thermocouples.

A dust deposit can undergo smouldering for a long period. It is not unknown for large dust piles to smoulder for a matter of years. Both air access and heat loss are restricted so that combustion is very slow, but is sustained. Such smouldering may not give rise to readily detectable effects. In particular, there may be no smoke or smell from the burning.

This delay between ignition and outbreak of flaming can create hazards. Fire may break out unexpectedly in a factory shut-down overnight or at the weekend, or the cargo of a ship may be discovered to be on fire when it is being unloaded.

Hazards of dust fires include those of a dust explosion resulting from the formation and ignition of a dust suspension, of the ignition of other flammables and of the evolution of toxic combustion products.

In general, dust deposits around the factory should be minimized by good housekeeping. As already indicated, the dust layer does not need to be very thick to sustain smouldering.

Extinction of the dust fire may be effected by letting the fire burn itself out, by applying extinguishing agents or by starving the fire of oxygen.

Whichever approach is used, however, it is essential to avoid disturbing the dust in such a way as to allow a suspension to form and ignite.

Water is the usual extinguishing agent and is suitable unless it reacts with the dust or electrical equipment is involved. The water should not be applied, however, as a high pressure jet, which could raise a dust cloud, but as a low pressure spray which simply dampens the dust deposit. The penetration of this water into the dust layer can be assisted by the addition of about 2% of a wetting agent such as a detergent.

The use of fire fighting foam generally offers little advantage over water. Foam has the additional capability of cutting off air to the fire, but this is unlikely to have much effect in a slow smouldering combustion which requires very

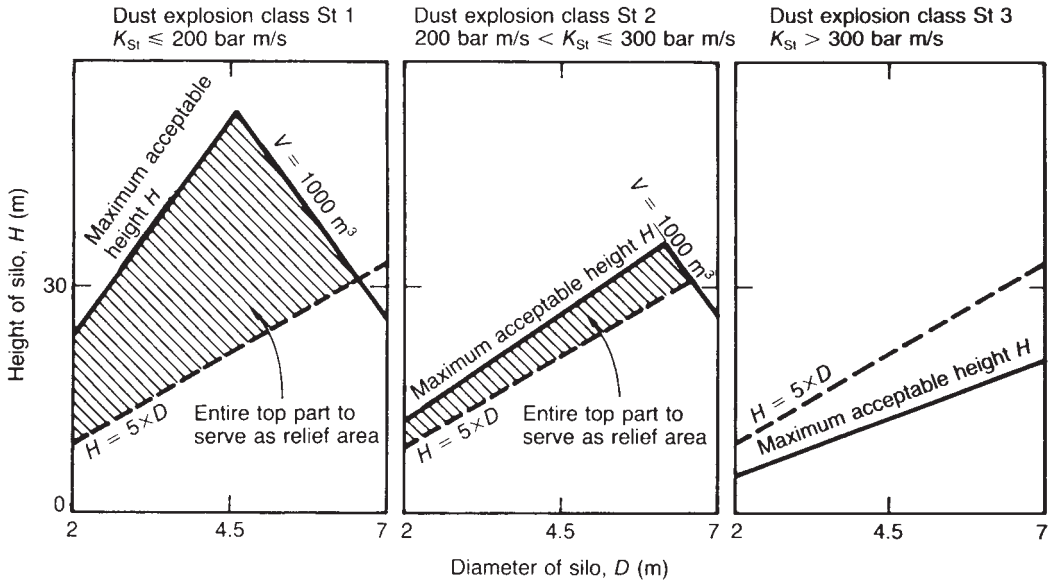

Figure 17.132 *Dust explosion venting: allowable height of silo – 2 (Bartknecht, 1981a). The figure is based on the use of Bartknecht nomographs, $P_{stat} = 0.1$ bar; $P_{red} = 0.4$ bar (Courtesy of Springer-Verlag)*

little air anyway. Since the foam is largely water, it should not be used in applications where water is unsuitable.

The other non-gaseous fire fighting agents are of limited application. Dry powder is appropriate if the dust is one which reacts with water, as do some metal dusts. Vaporizing liquids are appropriate if electrical equipment is involved, but should not be used on reactive metal dusts.

Inert gases may be used as extinguishing agents and can be effective if the dust is held in a relatively gas tight container such as a hopper or a ship's hold. It is necessary, however, not only to cut off the supply of oxygen, but also to effect sufficient cooling to prevent reignition when the air supply is restored. Thus, the inerting may need to be maintained for a long period.

In some situations, however, the fire cannot be extinguished sufficiently rapidly by fire extinguishing agents alone. A smouldering fire in a ship's hold, for example, could immobilize the whole ship. In such cases it may be necessary to dig the material out. This involves a number of hazards and suitable precautions should be taken against them. The operations should be conducted in such a way as not to raise a dust cloud. The atmosphere should be monitored and any necessary breathing equipment worn. The danger of subsidence of the dust due to the creation of burnt-out hollows beneath the surface should be allowed for.

In other instances a more gradual extinction of the fire is acceptable. This might be the case, for example, with a fire smouldering inside a tip. The methods used in such situations are generally based on excluding air and include covering the heap with a layer of non-combustible such as earth or pumping a limestone slurry into fissures in the heap. A hazard in the first method is subsidence due to hollows, and in the second, movement in the tip due to the slurry. Alternatively, but generally as a last resort, the heap may be dug out.

17.51 Explosion Hazard

The types of explosion typical of the process industries are those described above. The hazard of a large industrial explosion may be assessed by consideration of assumed scenarios using appropriate hazard and effects models or of the historical record of explosions and their effects.

17.51.1 Historical experience

A large proportion of the major accidents which have occurred in the process industries have involved explosions. In particular, explosions account for the preponderance of cases where there has been substantial loss of life.

A classification of process industries explosions has been given in Section 17.1. The main headings are (1) physical explosions, (2) condensed phase explosions, (3) VCEs, (4) BLEVEs, (5) confined explosions with reaction, (6) vapour escape into, and explosions in, buildings and (7) dust explosions. Some principal condensed phase explosions have been listed in Table 17.24, VCEs in Table 17.30, BLEVEs in Table 17.37 and dust explosion in Table 17.63. A fuller listing of all types of explosion with references is given in Table A1.2. The statistical features have been given in Chapter 2 and Section 17.1.

The process industries have suffered major explosions in virtually all the categories of the classification in Section 17.1. Considering these in turn, and starting with physical explosions, these may occur as (1) a mechanical failure, (2) overpressure, (3) underpressure, (4) overtemperature or (5) undertemperature of the system. The essential distinction is that in the first case the failure occurs whilst the process conditions are within the design envelope, so that the failure is due to a mechanical defect, and in the other cases it occurs because the process conditions have been taken outside the design envelope.

A failure of a pressure system due to mechanical defects occurred in 1984 at a refinery at Romeoville, Illinois, where a 55 ft high × 8 ft diameter absorption column suffered massive failure such that most of the 201 vessels rocketed about 3500 ft and struck and toppled a 138 kV power transmission tower (Case History A111).

Overpressure of a pressure system is exemplified by the explosion at Grangemouth in Britain in 1987 when gas 'breakthrough' caused the disintegration of a 30 ft high × 10 ft diameter low pressure separator (Case History A116). One 3 t missile from this explosion travelled 3300 ft.

Condensed phase explosions in the process industries include explosions of (1) high explosives, (2) ammonium nitrate, (3) organic peroxides, and (4) sodium chlorate. An account of condensed phase explosions has been given in Section 17.26.

With regard to high explosives, the explosion of the munitions ship Mont Blanc at Halifax, Nova Scotia, in 1917 destroyed a large part of the town and killed 1963 people (Case History A3). An explosion of TNT at a munitions factory in Silvertown, London, in 1917 caused 69 deaths (Case History A4).

Many of the large explosions in the early years of the chemical industry involved ammonium nitrate (AN). The AN explosion at Oppau, Germany, in 1921 destroyed hundreds of houses and killed 561 people (Case History A5).

The explosions at Texas City in 1947 occurred in two ships, the Grandcamp and the High Flyer, both of which were carrying AN (Case History A16). They damaged thousands of buildings, hurled missiles several miles and killed 552 people.

Major explosions involving organic peroxides occurred at Tonawanda, New York, in 1953 and at Los Angeles in 1974 (Case History A72).

Two warehouse fires in Britain, at Renfrew in 1977 and Salford in 1982, resulted in large sodium chlorate explosions (Case History A85).

In recent years, the most destructive explosions in the process industries have tended to be VCEs or BLEVEs.

Some of the principal VCEs have been described in Section 17.28. They include those at the Ludwigshafen works in 1953 and 1958, the refinery at Lake Charles in 1967, the refinery at Pernis in 1968, a pipeline at Port Hudson in 1970, a rail tank car at East St Louis in 1972, the works at Flixborough in 1974, the rail tank car at Decatur in 1974, a petrochemical plant at Beek in 1975 and a petrochemical plant at Pasadena in 1989. Flixborough and Pasadena are described in Appendices 2 and 6, respectively, and the other incidents in Appendix 1, as referenced in Section 17.28.

Some of the principal BLEVEs have been described in Section 17.29. Major incidents in which the BLEVE occurred due to release from the vessel involved or a similar, adjacent vessel include those at a storage in Montreal in 1957, the refinery at Feyzin in 1966, a rail tank car at Crescent City in 1970, a refinery in Rio de Janeiro in 1972 and a storage at Texas City in 1978. Those at Feyzin, Crescent City and Rio are described in Appendix 1, as referenced in Section 17.29.

In other instances, BLEVEs have occurred as a result of engulfment in a major vapour cloud fire. Incidents where this was the case include those at the storage in Port Newark in 1951 (Case History A19) and at Mexico City in 1984 (Appendix 4).

Turning to confined explosions with reaction, these include (1) explosions involving vapour combustion, (2) reactor explosions and (3) other explosions involving liquid phase reactions. In the first category is the detonation in a 127 ft high × 22.5 ft diameter reactor at Whiting 1955 (Case History A22). The vessel disintegrated, hurling one 60 te fragment onto a tank farm 1200 ft away and causing two deaths.

There have been a large number of reactor explosions, usually incurring a medium level of casualties and loss. One of the more serious occurred at Geismar in 1976, when a large polygylcol ether reactor exploded, throwing the reactor head 1400 ft (Case History A80).

Liquid phase reactions occurring in other equipment have also led to major incidents. One such occurred at Doe Run in 1962, when backflow of ammonia from a reactor into an ethylene oxide feed tank resulted in a severe explosion (Case History A31).

Incidents of vapour escapes into, and explosions in, buildings (VEEBs) are exemplified by those at St Paul in 1951 and Attleboro in 1964 (Case History A33). In the first an escape of LPG at a loading terminal caused an explosion which killed 14 people. In the second a massive leak of vinyl chloride from a reactor into the building resulted in an explosion which led to seven deaths.

The explosion on Piper Alpha, which occurred in a partially confined module, might also be regarded as falling in this category (Appendix 19).

Finally, there have also been a number of serious dust explosions inside (1) plant and (2) buildings. An explosion inside a grain silo at Westwego in 1977 resulted in 36 deaths (Case History A89).

Most, though not all, of the incidents just described are in the M&M Large Loss List. Details of casualties and loss are given in Table A1.2.

17.51.2 Mortality index for explosions

The relation between the size of an explosion and the number of people killed has been investigated by V.C. Marshall (1977b), who has developed a mortality index (deaths/t) for explosions.

Data on the relation between the size of the explosion and the number of fatalities, and on the mortality index, are plotted in Figure 17.133. The solid squares which do not have a specific reference are accidental explosions. The full line is the best fit for these accidental explosions.

Mortality data on the number of casualties by shell explosions are available from the First World War. According to one account, the belligerents used 2.23×10^6 t of high explosive in 1.39×10^9 shells and caused 10^7 casualties. The latter figure includes wounded as well as dead, and the deaths are estimated at 2.4×10^6. Thus, on average a shell contained 1.6 kg of explosive. Allowing for 10% dud shells, the fatalities per shell are approximately 0.0019, which gives a mortality index of 1.2.

The Second World War data for conventional bombing give mortality indices between 0.96 for Germany and 3.40 for Japan. This is no doubt influenced by factors such as population density, construction of houses and degree of shelter.

The mortality indices for the nuclear bombs at Hiroshima and Nagasaki are 2.05 and 1.0, respectively. The bombs were assumed to have a nominal yield each of 20, 000 t of TNT.

The mortality indices of the Halifax explosion in 1917 and the Oppau explosion in 1921 are 0.64 and 0.25, respectively.

For accidental explosions the data used are the data given by C.S. Robinson (1944) and some unpublished data

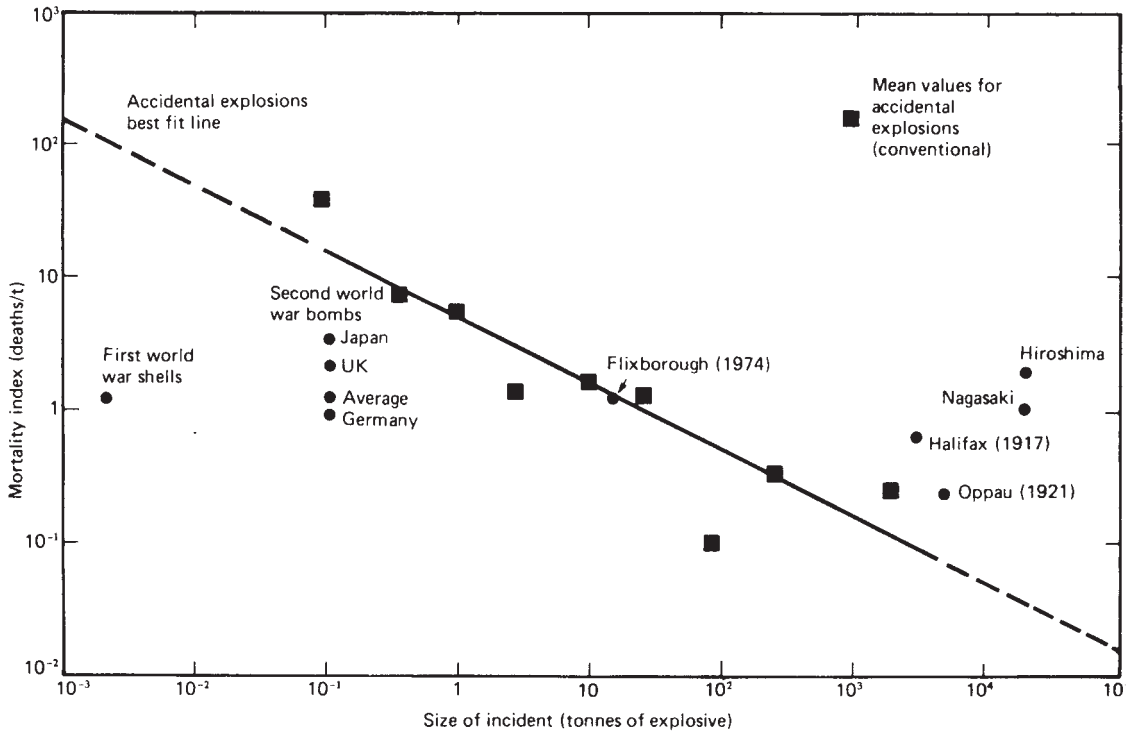

Figure 17.133 *Mortality index for explosions (after V.C. Marshall, 1977b) (Courtesy of the Institution of Chemical Engineers)*

by Healy (1965), and they have been grouped by Marshall in size intervals.

As Figure 17.133 shows, the mortality index decreases as the size of the explosion increases. The line has a slope of about −0.5. This differs somewhat from the slope suggested by theoretical considerations. From the blast scaling laws the radius r at which a given blast intensity occurs is related to the mass of explosive W by the relation

$$r \propto W^{1/3} \qquad [17.51.1]$$

The number of fatalities f is proportional to the area:

$$f \propto r^2 \propto W^{2/3} \qquad [17.51.2]$$

The mortality index MI is the ratio of the number of fatalities to the mass of explosive:

$$\mathrm{MI} \propto \frac{f}{W} \propto W^{-1/3} \qquad [17.51.3]$$

Marshall suggests that a possible explanation is that small explosions which do not kill people tend not to be well reported, which has the effect of exaggerating the mortality index for small explosions. VCEs are also considered by Marshall, as shown in Table 17.71. Since for such explosions the TNT equivalent is generally unknown, the mortality index in this case is based on the mass of vapour involved.

Other aspects of historical experience with explosions are discussed in Sections 17.28–17.30 and 17.31–17.34.

17.51.3 Hazard assessment

Hazard assessment of explosion on process plants tends to be rather more varied than that of fire. As stated in Section 17.1, explosions in the process industries include (1) physical explosions, (2) condensed phase explosions, (3) VCEs, (4) BLEVEs, (5) confined explosions with reaction, (6) vapour escape into, and explosions in, buildings, and (7) dust explosions. The extent to which these different types of explosion are represented in the hazard assessment literature varies.

In principle, a hazard assessment involves formulation of a scenario and a full assessment of the frequency and consequences of the event. An assessment which is confined either to the estimation of the frequency of the event or to the modelling of the consequences is a partial one. Hazard assessments may be generic or may relate to a specific situation.

The scenario which has received most attention is the release and ignition of a vapour cloud, which may result either in a vapour cloud fire or a VCE. Thus, the hazard assessment of VCEs involves the development of a set of scenarios for explosion, by release and ignition, and of the associated event trees; the estimation of the frequency/probability of the initial events and of the events in the branches of the event trees from a mixture of historical data and synthesis of values, often using fault trees, and the modelling of the outcome events in the event tree, including both physical events and damage/injury.

Up to the point of damage and injury, the assessment of a VCE involves essentially the same set of models as those

Table 17.71 *Some data on the relation between size of flammable release and number of fatalities (after V.C. Marshall, 1977b) (Courtesy of the Institution of Chemical Engineers)*

Date	*Location*	*Chemical*	*Material released*		*Nature of incidents*	*Fatalities*	*Mortality index* (deaths/t)
			Liquid spilled (t)	*Vapour involved* (t)			
1943 Jan. 18	Los Angeles, CA	Butane		14	Fire	5	0.35
1944 Nov. 15	Cleveland, OH	LNG		180	Fire	213	1.18
1959 June 28	Meldrin. GA	LPG		18	Explosion and fire	23	1.27
1962 July 26	New Berlin, NY	LPG		17	Explosion and fire	10	0.58
1967[a] Aug. 6	Lake Charles, LA	Isobutane		13	Explosion	7	0.53
1968 Jan. 20	Pernis, Netherlands	Hydrocarbon vapour		50	Explosion	2	0.04
1970 Dec. 9	Port Hudson, MO	Propane		27	Explosion	0	0
Oct. 23	HuU, UK	Propane	4	0.20	Fire	2	10.0
1971 July 11	Pensacola, FA	Cyclohexane		30	No ignition	0	0
1972 Jan. 22	East St. Louis, IL	Propylene		70	Explosion	0	0
Mar. 19	Lynchburgh, VA	Propane	9	1.5	Fire	2	1.33
Sep. 21[a]	New Jersey	Propylene		18	Pressure rupture followed by fire	2	0.11
1973 Feb. 23	Austin, TX	Natural gas liquids	720	70	Fire	8	0.11
1974 June 1	Flixborough, UK	Cyclohexane	125?	40	Explosion	28	0.70
June 29	Climax, TX	Vinyl chloride		75	Explosion	0	0
1975 Nov. 7	Beek, Netherlands	Propylene		5.5	Explosion and fire	14	2.54
Total of 16 incidents				630		316	
Mean of 16 incidents				39.4		19.7	0.49

[a] Date quoted in the original paper have been corrected (F.P.L.).

used for the modelling of vapour cloud fires, as described in Chapter 16. If the event gives an overpressure, it is a VCE, otherwise it is a vapour cloud fire.

A hazard assessment of the kind just described constitutes a full hazard assessment. The types of explosion which are most fully represented are high explosives and ammonium nitrate explosions, VCEs and BLEVEs.

Overviews of generic process plant explosion scenarios have been given for LPG by Rasbash (1979/80) and Crocker and Napier (1988a) and for LNG by Napier and Roopchand (1986).

Some principal types of model used for hazard assessment of explosions on process plants are those for (1) condensed phase explosions, (2) explosions of vessels, (3) VCEs, (4) BLEVEs and (5) dust explosions.

An early, essentially generic, hazard assessment of explosion is that given in the vulnerability model by Eisenberg, Lynch and Breeding (1975), who studied the area affected by a flammable vapour cloud and the lethality of a VCE in such a cloud. The events of principal interest which they consider are marine spillage of 20,750, 83 and 0.8 te of LNG on water with drifting of the vapour cloud towards populated areas. Their treatment of these scenarios is described in Chapter 16. For explosion injury they utilize their own probit equations described in Section 17.38. The populations at risk are defined in terms of the cell model already described. Some results obtained have been given in Chapter 16.

The *First Canvey Report* (HSE, 1978b) included assessments of the hazard at the specific installations at Canvey from an explosion of ammonium nitrate; a VCE from the British Gas LNG storage and VCEs from several LPG storages.

These assessments were refined in the second report. An account of this work is given in Appendix 7.

The *Rijnmond Report* (Rijnmond Public Authority, 1982) gives specific hazard assessments for storages of acrylonitrile, propylene and LNG. It considers VCEs and BLEVEs. An account of this work is given in Appendix 8.

The *Transport Hazard Report* of the Advisory Committee on Dangerous Substances (ACDS) (1991) gives hazard

assessments for the transport of hazardous substances in ports, by road and by rail which are applicable to transport nationwide, although based in some cases on generalization from a sample of specific situations. The hazards covered include explosion of high explosives and of ammonium nitrate and VCEs and BLEVEs from LPG and flammable liquids.

For physical explosions, hazard assessments have been mainly treatments of the frequency of explosion without modelling of the consequences. Studies of this type on specific plant have been described for overpressure of a storage tank by gas breakthrough by Kletz and Lawley (1982), overheating of a distillation column by Lawley and Kletz (1975) and undertemperature of a pipeline by Lawley (1980).

For condensed phase explosions, the hazard assessments of explosions of high explosives are represented by those in the ACDS study and of ammonium nitrate explosions by those in the Canvey Reports and the ACDS study. These are for specific situations, although in the ACDS study the results are then generalized.

For VCEs and BLEVEs, there are a number of hazard assessments which cover these events. They include a generic study of storage installations by Considine, Grint and Holden (1982) and studies of specific installations by Panthony and Smith (1982) and Ramsay, Sylvester-Evans and English (1982).

There are also generic assessments of the frequency of BLEVEs by Drysdale and David (1979/80), Blything and Reeves (1988 SRD R488) and Selway (1988 SRD R492).

For confined explosions with reaction, hazard assessment of explosions involving vapour combustion include the estimations of explosion frequency for an ethylene oxide reactor system by R.M. Stewart (1971) and for a hydrocarbon sweetening plant by Kletz (1972a) and of explosion involving liquid phase reactors by Roy, Rose and Parvin (1984).

Vapour escapes into, and explosions in, buildings and dust explosions are not well represented in the hazard assessment literature.

17.52 Hazard Range of Explosions

The estimation of the hazard range of an explosion depends on the type of explosion considered.

The two main types of explosion of interest here are condensed phase explosions such as those of TNT, together with explosions which can be characterized in terms of TNT equivalent, and VCEs.

17.52.1 Condensed phase explosions

The blast wave from a condensed phase explosion is characterized by the peak side-on overpressure and the impulse.

The variation of peak overpressure of a condensed phase explosion with distance is given by the scaling law and values of the overpressure may be obtained from graphs such as those given in Section 17.26. Thus

$$p^{\circ} = f(z) \qquad [17.52.1]$$

with

$$z = \frac{r}{W^{1/3}} \qquad [17.52.2]$$

where p° is the peak overpressure, r is the distance, W is the mass of explosive and z is the scaled distance. Over a limited range the curve of p° vs z may be approximated by a straight line so that

$$\frac{(\rho^{\circ})r}{p^{\circ}} = \left(\frac{r_{\mathrm{r}}}{r}\right)^{n} \qquad [17.52.3]$$

where n is an index and subscript r is reference value. From the Baker curve for the overpressure range 1.0–0.1 bar the index n is approximately 1.7. A similar approach may be used for the determination of the impulse.

The effects of the explosion may then be determined from the overpressure and impulse utilizing the methods given in Sections 17.31–17.35.

For housing damage, the variation of the degree of damage, or damage category, with distance may be obtained from the revision by Gilbert, Lees and Scilly of the Jarrett equation; this revision is given by Equation 17.33.2b with revised values of the constant k.

The graph given by C.S. Robinson (1944) and reproduced as Figure 17.92 summarizes in convenient form the range of many of the principal damage effects.

17.52.2 Vapour cloud explosions

For a VCE, it is necessary to take into account the movement of the cloud, which is likely then to be the dominant factor.

The variation of cloud size with distance may be estimated from gas dispersion relations given in Chapter 15. An account is given there of the method of Considine and Grint (1985) which allows an estimate to be made of the size of the cloud for an LPG release.

Considine and Grint have also given for LPG methods for estimating the hazard range for fires and explosions. For a VCE they use the ACMH method based on the TNT equivalent. They give for the overpressure the relations

$$p^{\circ} = 138\left(\frac{I^{1/3}}{r_{\mathrm{c}}}\right)^{1.558} \qquad r < r_{\mathrm{c}};\ \ 0.05 < p^{\circ} < 1 \qquad [17.52.4a]$$

$$p^{\circ} = 138\left(\frac{I^{1/3}}{r}\right)^{1.558} \qquad r > r_{\mathrm{c}};\ \ 0.05 < p^{\circ} < 1 \qquad [17.52.4b]$$

where I is the mass of vapour in the cloud (te), p° is the peak overpressure (bar) and r_{c} is the radius of the cloud (m).

These authors quote from the *First Canvey Report* the estimates of 50 and 1% fatalities at overpressures of 0.36 and 0.18 bar, respectively. Within the cloud, 100% fatalities are assumed.

For a quasi-instantaneous release, the cloud range R and the cloud radius r_{c} vary with time. The mass m of vapour in the cloud may be taken as the total mass released. The cloud is flammable, however, only whilst its concentration is within the flammable range.

For a quasi-continuous release, the approach taken is to treat the plume as if it were fully established. In this case the cloud is non-circular and the following relation is given for the equivalent value of cloud radius r_{c}:

$$r_{\mathrm{c}} = \left(\frac{1.2k^{*}R_{\mathrm{LFL}}^{5/3}}{\pi}\right)^{1/2} \qquad [17.52.5]$$

where R_{LFL} is the distance to the LFL (m) and k^* is a constant defining crosswind range. This constant is described in Chapter 15.

The TNT equivalent method for a VCE is obsolescent. More modern methods, particularly the TNO and Baker Strenlow methods, are available, as described in Section 17.28, and may be preferred. However, the method of determining the cloud size may still be found useful.

In reality, for a VCE the peak overpressure is inversely proportional to the distance, and this is reflected in the more modern models. An illustration is the decay of the peak overpressure with distance shown in Figure 17.79(a).

17.53 Notation

Ma	Mach number
Re	Reynolds number
g	acceleration due to gravity
t	time
T	absolute temperature
γ	ratio of gas specific heats

Superscripts

.	time derivative
..	second time derivative

Subscript

max	maximum

Note:
(a) Some of these variables have different local definitions, for example: t (thickness of glass), T (time constant, natural period),
(b) The symbol R generally denotes the universal gas constant but is also used for distance, range. It is therefore not defined globally for the chapter.

Section 17.2

Subsections 17.2.3–17.2.9

a	velocity of sound
$\bar{c}_v$	mean specific heat at constant volume
D	velocity of shock wave
d_c	critical tube diameter (mm for detonatation)
D_H	ratio of E_c^* for a fuel to that of acetylene
e	specific internal energy
E_c	critical (minimum) energy for initiating spherical detonation
E_c^*	minimum value of E_c
Δe	specific internal energy change
h	specific enthalpy
i	impulse
L_i	induction zone length
L_c	length of cell
Ma	Mach number
p	absolute pressure
p_{pl}	plateau pressure
p_v	pressure of constant volume combustion
q	energy addition per unit mass
S	width of cell
T	temperature
T_i	induction time
u	velocity
v	specific volume
V_1	velocity of gas entering shock wave
w	particle velocity
α	angle defined in Figure 17.1(d)
ξ	fractional completion of reaction
Δ	induction length for detonation
ρ	density

Subscripts

CJ	Chapman–Jouguet condition
s	shock wave
1	entering shock wave
2	leaving shock wave
Q_L, Q_U	fuel mole frequency to stoichiometric mole frequency at lower and upper limits for detonation

Subsection 17.2.10

a_o	velocity of sound in burned gas
d	diameter of tube
k_n	Bessel function derivative
p	pitch of spin
γ_o	ratio of specific heats of detonation products
λ	wavelength of spin

Subsections 17.2.11 and 17.2.12

a_o	velocity of sound in mixture
d_c	critical diameter for transmission of detonation
E_c	critical energy for initiation of spherical detonation
L_c	length of detonation cell
L_i	length of induction zone
n	constant
S	width of detonation cell
Δ	induction length
τ_i	induction time
ϕ	fuel–air ratio

Subscripts

1	lower limit
st	stoichiometric
u	upper limit

Subsection 17.2.13

c	velocity of sound
d_c	critical diameter for transmission of detonation
D_h	detonation hazard parameter
E_c	critical energy
E_c^*	minimum critical energy
p	absolute pressure
u	particle velocity
λ	stoichiometric ratio

Subscript

D	detonation state

Subsections 17.2.15–17.2.17

c	velocity of sound in uncompressed gas
d	diameter of tube

d_c	critical diameter for transmission of detonation
d_{min}	minimum diameter of vapour cloud to support detonation
g_f	acceleration of flame
L_c	length of detonation cell
S_u	maximum fundamental burning velocity
X_d	run-up distance
X_f	distance from origin of flame to its position at time when shock first forms
X_s	distance from origin to position at which shock is produced
β	ratio of velocity of flow just ahead of flame to that of flame
γ	ratio of specific heats of reactant
ϵ	expansion ratio
θ_{cr}	critical angle for transition to regular reflection
θ_w	angle between shock wave traveling horizontally and a surface

Equations 17.2.56–17.2.57

A_t	area of truncation
d	diameter of nozzle
D_{CJ}	C–J velocity
E_c	critical energy
L_c	length of detonation cell
p	pressure of planar detonation
S	width of detonation cell
t_c	time at which heads of expansio fan cross axis of symmetry
u_{CJ}	gas velocity behind C–J front
W	work done

Subscripts

c	critical
CJ	C–J
o	actual

Section 17.3

Subsection 17.3.2

p°	peak overpressure
r	distance
r_c	radius of crater
r_{50}	distance at which there is 50% chance of sympathetic detonation, mean detonation distance
R	radius of damage circle
W	mass of explosive
z	scaled distance

Subsection 17.3.3

k	constant
R	distance (ft)
W	mass of explosive (lb)

Subsection 17.3.4

Equation 17.3.8

k	constant
n	index
R	distance
W	mass of explosive

Equations 17.3.9–17.3.11

R	distance (ft)
W	mass of explosive (lb)

Subsection 17.3.5

B	blast effect
B^*	blast effect required for certainty of detonation
j	site counter
k	constant
n_1, n_2	indices
p	probability of further detonation
p'	parameter defined by Equation 17.3.15
$P(j)$	probability that j sites are involved in detonation
r	distance
T	threshold of p' below which no propagation occurs
W	mass of explosive

Section 17.4

A	Helmholtz free energy
E	internal energy
F	Gibbs free energy
H	enthalpy
ΔH_c	heat of combustion
ΔH_{cl}	heat of combustion with initial reactant as liquid
ΔH_{clw}	heat of combustion with final water product as liquid
ΔH_{cv}	heat of combustion with initial reactant as vapour
ΔH_{cvw}	heat of combustion with final water product as vapour
ΔH_v	latent heat of vaporization
ΔH_{vw}	latent heat of vaporization of water
n	number of moles
P	absolute pressure
R	universal gas constant
S	entropy
T	absolute temperature
V	volume
W	work
γ	ratio of gas specific heats

Superscript

o	standard state

Subscripts

f	formation
p	products
r	reactants
1	initial state
2	final state

Subsection 17.4.3

U_l	liquid strain energy
V	volume of vessel
β	bulk modulus of liquid

Subsection 17.4.4

E	Young's modulus
K	diameter ratio
U_m	metal strain energy
V	volume of vessel
v	Poisson's ratio

Equation 17.4.34

R_o	scaling radius (m)

Equation 17.4.35

E	explosion energy (te of TNT)
P_o	pressure of surroundings (kPa)
P_1	initial pressure in vessel (kPa)
V	volume of vessel (m^2)

Subsection 17.4.5

E	internal energy
V	volume of vessel
γ	ratio of gas specific heats

Subscripts

AG	Aslanov–Golinsky
Ba	Baker
Br	Erode
ex	explosion
Ki	Kinney
o	atmospheric

Subsection 17.4.6

e	specific internal energy
E_{ex}	energy of explosion
H	specific enthalpy
P	absolute pressure
S	specific entropy
v	specific volume
x	mass fraction of vapour
ϕ	dummy variable

Subscripts

f	saturated liquid
g	saturated vapour
o	atmospheric

Subsection 17.4.8

E_s	total energy in system
E_1	chemical energy
E_2	fluid expansion energy
E_3	vessel strain energy

Subsection 17.4.11

B	batch availability (kcal/mol)
ΔB	batch availability correction term (kcal/mol)
C_p	specific heat at constant pressure (kcal/mol)
m	number of species
P	absolute pressure (Pa)
R	universal gas constant (kcal/mol/K)
T	absolute temperature (K)
x	mole fraction
ϕ_o	standard batch availability (kcal/mol)

Subscripts

a	ambient
i	species i
pr	products
r	reactants

Section 17.5

E	expansion ratio
M	molecular weight
n	number of moles
P	absolute pressure

Subscripts

b	bursting
1	initial
2	final

Subsection 17.5.4

P_{ex}	absolute explosion pressure
v_d	displacement velocity
v_{ex}	explosion velocity
v_n	normal burning velocity
ϕ	ratio of area of flame front to cross-sectional area of pipe

Section 17.6

P	absolute pressure

Subscripts

1	initial
2	final

Section 17.7

a	radius of spherical vessel
A_f	area of flame front
C_n	calorific value of gas mixture
E	expansion ratio
F	constant
G_1–G_4	constants
h	enthalpy
k_1–k_4	constants
K	constant
K_G	constant
K_1	constant
L	length of cylinder
m	mass of gas
m_o	mass of gas in vessel
M	molecular weight
$\bar{M}$	mean molecular weight
n	fractional degree of combustion
n	(with subscript) moles of gas
P	absolute pressure
ΔP	pressure rise
Q	heat lost from burned products
r	radius
r_b	radius of burnt core of gas (after combustion)
r_c	radius of cylinder
r_i	radius of burnt core of gas (before ignition)
R	universal gas constant
R_g	mass basis gas constant
S	surface area of vessel
S_f	flame speed
S_u	burning velocity

T_{bP}	absolute temperature corresponding to pressure P
u	velocity
u_u	velocity of unburnt gas into flame front
U	internal energy
v	mass specific volume
V	volume
V_o	volume of vessel
α	coefficient of turbulence
v	molar specific volume
ρ	mass density

Superscript

–	normalized

Subscripts

b	burned
e	end value (after combustion)
i	initial state of burned gas (before ignition)
j	gas state j
m	maximum
o	initial value (before ignition)
u	unburned
1	unburned
2	burned

Equations 17.7.72–17.7.78

α	flame area factor

Equations 17.7.131–17.7.171

a	$=1/\gamma_u$
r_s	radius of spherical vessel; radius of burned gas at end of spherical stage
α	parameter defined by Equations 17.7.143–17.7.145

Section 17.8

C	volumetric concentration
C_i	effective inlet volumetric concentration
C_o	concentration on cessation of release
Q	total volumetric flow
Q_a	volumetric flow of air
Q_g	volumetric flow of contaminant gas
V	volume of space
τ	volume/throughput ratio, or time constant

Subsection 17.8.7

a	index
K	constant
p	peak pressure (bar)
Q	mass of explosive (kg)
V	volume of chamber (m^3)

Section 17.10

c	volumetric concentration of component
E	number of changes of atmosphere
Q	volumetric flow of gas through vessel

Subscript

o	initial value

Equation 17.10.4

D	diameter of jet orifice (ft)
K	constant
V_o	nozzle velocity (ft/min)
V_x	required velocity (ft/min)
X	distance from jet to most remote corner (ft)

Section 17.11

Subsection 17.11.5

D	internal diameter of pipe (m)
g_L	laminar velocity gradient (s^{-1})
u_T	turbulent flashback velocity

Subsection 17.11.7

a	fractional free area of arrester
d	diameter of arrester apertures (cm)
n	number of apertures per unit area of arrester surface (cm^{-2})
p	explosion pressure at arrester
p_o	atmospheric pressure
V	flame speed at arrester (m/s)
y	thickness of arrester elements (cm)

Subsection 17.11.9

a	fractional free area of arrester
d	diameter of arrester apertures (in.)
V	flame speed at arrester (ft/s)
y	thickness of arrester (in.)

Equation 17.11.6

Q	heat of detonation of gas mixture (cal/g)
V	detonation velocity (ft/s)
γ	ratio of specific heats of gas mixture at combustion temperature

Section 17.12

(See text for units in particular equations)

$a–d$	constants
A, B	constants (Equation 17.12.11)
A, B, C	constants (Equation 17.12.31)
A_c	cross-sectional area of volume vented
A_m	maximum area of flame front
A_v	vent area
ΔA_v	correction term for A_v
C	Runes constant
C_d	coefficient of discharge
E	expansion ratio, expansion factor
f	vent ratio
g	acceleration due to gravity
k	constant
K	vent coefficient
K_G	K_G value
L	length of enclosure
L_1, L_2	two smallest dimensions of enclosure
m	mass of gas
$\bar{M}$	mean molecular weight
n	(with subscript) moles of gas
P	pressure
ΔP	vented explosion pressure
P_a	atmospheric pressure
P_I	back pressure due to the inertia of the vent

P_m	final pressure
P_{max}	maximum pressure in an unvented explosion
P_{red}	actual, or reduced, pressure in a vented explosion
P_{stat}	vent opening pressure
P_v	vent opening pressure
P_1	pressure of first peak
P_2	pressure of second peak
Q_m	rate of volume production
Q_v	volumetric vent outflow
r_b	radius of burned gas
R	universal gas constant
S_u	burning velocity
V	volume of vessel; volume of gas
V_f	flame speed
w	inertia of vent
W_v	mass of vent cover
Y	constant
α	coefficient of turbulence
ρ	density of gas
ψ	vent ratio

Subscripts

b	burned
e	vented
f	flame
o	initial
P_{red}	pressure in vented enclosure
u	unburned
v	vent conditions

Subsection 17.12.4

c	speed of sound
D	duet diameter
f_a	frequency of oscillation
f_H	frequency of Helmholtz oscillation
L	length of duct
r_s	radius of spherical vessel
α	correction factor
λ_1	constant

Subsection 17.12.7

f	turbulence factor

Subsection 17.12.10

T	absolute temperature of burnt gas

Subsection 17.12.20

f_v	vent outflow parameter
f_{v1}–f_{v4}	vent outflow parameters
f_{vs1}	vent outflow parameter for sonic flow
f_{vsb2}	vent outflow parameter for subsonic flow
G_v	vent mass velocity
P	absolute pressure
P_a	absolute atmospheric pressure
w	pressure ratio
w_c	critical pressure ratio
ρ_o	density of gas at atmospheric pressure

Subsection 17.12.21

a	radius of spherical vessel
W	mass rate of combustion

Subsection 17.12.22

a	characteristic length (for a sphere, the radius)
G	venting area parameter
ΔP_m	maximum explosion pressure
α	venting parameter
ρ_{bo}	density of burned gas at initial pressure
ρ_{uo}	density of unburned gas at initial pressure
X	turbulence correction factor

Subsection 17.12.23

a	velocity of sound
$\bar{A}$	vent area ratio
A_s	surface area of spherical vessel
A_v	vent area
C_d	coefficient of discharge
f_{v2}	vent outflow parameter
m_v	mass vented
P	absolute pressure
S	burning velocity
$\bar{S}$	dimensionless burning velocity at vent conditions
$\bar{S}_o$	dimensionless burning velocity at initial conditions
V_v	volume vented
ζ	vent flow coefficient
ρ	density of gas

Superscript

–	dimensionless

Subscripts

b	burned
o	initial
u	unburned
v	vent conditions

Subsection 17.12.24

A_F	largest spherical surface in enclosure
A_s	surface area of sphere having same volume as enclosure
A_v	vent area
E	expansion ratio
F	shape factor
K	parameter defined by Equation 17.12.100
P	absolute pressure
ΔP	pressure difference
P_{max}	absolute maximum pressure of unvented explosion
P_o	absolute initial pressure
P_{red}	reduced pressure (gauge)
Q_v	volumetric vent outflow
r	radius of burned gas before expansion
u	velocity of flame front
V	volume of sphere
V_f	final volume of burned gas after combustion
V_{fl}	time-dependent volume of fuel consumed, of burned gas before combustion
V_t	time-dependent volume of burned gas after combustion

Subsection 17.12.25

A	area of flame front (ft^2)
A_v	vent area (ft^2)
k_{v1}	vent outflow constant (mol in. °R/$lb^{1/2}$ ft^2 s)
k_{v2}	vent outflow constant (mol $in.^2$ $°R^{1/2}$/lb ft^2 s)
L	length of cylinder (ft)
n	number of moles (lb mol)
P	absolute pressure ($lb_f/in.^2$)
P_m	absolute maximum pressure of unvented explosion ($lb_f/in.^2$)
P_o	atmosphere pressure ($lb_f/in.^2$)
P_{red}	absolute reduced pressure ($lb_f/in.^2$)
ΔP_v	overpressure at which vent opens ($lb_f/in.^2$)
R	gas constant (lb $ft^2/in.^2$ mol°R)
S	burning velocity (ft/s)
t	time (s)
T	absolute temperature (°R)
V	volume (ft^3)
α	coefficient of turbulence

Subscripts

b	burned
e	end of combustion
m	final
o	initial
u	unburned
1	closed end side
2	vent end side

Subsection 17.12.26

$\bar{A}$	dimensionless vent area
A_f	area of flame front (m^2)
A_s	surface area of sphere (m^2)
A_v	vent area (m^2)
A_x	cross-sectional area of cylinder (m^2)
k	constant
n	index
ΔP_m	maximum pressure rise (atm)
r_c	radius of cylinder (m)
r_s	radius of sphere (m)
$\bar{S}_o$	dimensionless burning velocity at initial conditions
T_f	adiabatic flame temperature (K)
ρ	density of gas (kg/m^3)

Subscripts

b	burned
o	initial
u	unburned

Subsection 17.12.27

A_v	vent area
B	dimensionless burning number
C_d	coefficient of discharge
G_v	vent mass velocity
m	mass
P	absolute pressure
P_a	atmospheric pressure
P_f	absolute final pressure of vented explosion, reduced pressure
P_{max}	absolute maximum pressure of unvented explosion
P_o	absolute initial pressure
P_{set}	absolute vent opening pressure
r_b	radius of burned gas
S_u	burning velocity
V	volume of vessel
Z	dimensionless burned volume
λ	dimensionless vent opening pressure
ρ	density of gas
ϕ	turbulence correction factor

Subscripts

b	banned
e	outflow
o	initial
u	unburned

Section 17.12.28

As Section 17.7.5

Subsection 17.12.32

A_v	vent area
F_r	force due to back reaction
P_{red}	reduced pressure (gauge)
u	velocity of fluid
ρ	density of fluid

Subsection 17.12.36

a	acceleration of vent panel
A	area of vent panel
C	parameter defined by Equation 17.12.163
D	'density' of vent panel
E	parameter defined by Equation 17.12.165
F	force on vent panel
g	acceleration due to gravity
K	parameter defined by Equation 17.12.100
L	length of vent panel
M	mass of vent panel
P	pressure (gauge)
P_v	vent opening pressure (gauge)
s	distance travelled by vent panel
S	distance defined by Equation 17.12.158
t_v	time of start of venting
v	velocity of vent panel
w	vent inertia
W	width of vent panel
θ	angle of rotation of vent panel

Section 17.13

A_v/V	vent ratio
D	diameter of duct (ft)
k_1–k_4	constants
K	vent coefficient
K_{st}	dust K_{st} value
L	length of duct (ft)
L_1	distance between relief openings (ft)
L_{1max}	maximum distance between relief openings (ft)

L_2	distance between relief openings for gas other than propane (ft)
P	maximum pressure (lbf/in.^{2})
P_1	maximum pressure resulting from explosion of propane (lbf/in.^{2})
P_2	maximum pressure for gas other than propane (lb$_f$/in.^{2})
S_u	maximum fundamental burning velocity for gas other than propane (ft/s)

Equations 17.3.5–17.13.6

L	maximum distance between vents
P_{red}	reduced pressure
S	maximum fundamental burning velocity

Subscripts

p	propane
x	gas other than propane

Section 17.14

Subsection 17.14.4

A_c	smallest cross-sectional area of building space (m^2)
A_v	total area of combustion vents (m^2)
f	turbulence factor
K	venting ratio
P_I	back pressure due to inertia of vent (gauge) (kPa)
P_{red}	maximum pressure reached during venting, reduced pressure (gauge) (kPa)
P_v	pressure with building space at which vent opens (gauge) (kPa)
S_u	maximum fundamental burning velocity (m/s)
V	volume of enclosure (m^3)
w	vent inertia (kg/m^2)

Subsection 17.14.5

Equations 17.14.1–17.14.6

A_v	vent area (ft^2)
C	Runes constant ((lb$_f$/in.^{2})$^{1/2}$)
E	expansion ratio
L_1, L_2	two smallest dimensions of building (ft)
ΔP	vented explosion overpressure (lb$_f$/in.^{2})
u_f	flame speed (ft/s)
ρ	density of gas (Ib/ft^3)

Equation 17.4.7

A_v	building vent area (m^2)
C	constant
L_1, L_2	two smallest dimensions of building (m)
P	maximum internal building pressure (kPa)

Subsection 17.14.6

a	constant
A_s	area of side of enclosure (m^2)
A_v	vent area (m^2)
K	venting ratio
P_m	maximum pressure reached during venting (mbar)
P_v	pressure at which vent opens (mbar)
P_1	first peak pressure (mbar)
P_2	second peak pressure (mbar)
S_u	burning velocity (m/s)
V	volume of enclosure (m^3)
w	vent inertia (kg/m^2)

Subsection 17.14.7

A_s	internal surface area of enclosure (m^2)
A_v	vent area (m^2)
C	venting constant (bar$^{1/2}$)
P_{red}	maximum pressure which can be withstood by weakest structural element not intended to fail (bar)

Subsection 17.14.8

f	turbulence factor
k_1, k_2	constants
K_1	vent coefficient for compartment 1
K_2	vent coefficient for compartment 2
K_{12}	vent coefficient between compartments 1 and 2
$(Kw)_{2av}$	average value of Kw for compartment 2
P_1	vented explosion pressure of compartment 1 (mbar)
P_2	vented explosion pressure of compartment 2 (mbar)
S_u	maximum fundamental burning velocity (m/s)
V_1	volume of compartment 1 (m^3)
V_2	volume of compartment 2 (m^3)

Subsections 17.16–17.19

A	vent area (m^2)
A_o	vent area for zero overpressure (m^2)
C	specific heat of reaction mass (kJ/kg)
D	diameter of vent line (m)
D_o	diameter of vent line in bench-scale apparatus (m)
F	flow correction factor for vent line
G	mass velocity (kg/m^2/s)
G_o	mass velocity in bench-scale apparatus (kg/m^2/s)
h	specific enthalpy (kJ/kg)
h_{fg}	latent heat of vaporization (kJ/kg)
ΔH_r	heat of reaction (kJ/kg)
ΔH_v	latent heat of vaporization (kJ/kg)
k	constant
K	discharge coefficient
L	length of vent line (m)
m	mass in vessel (kg)
m_o	initial mass in vessel (kg)
N	non-equilibrium parameter defined by Equation 17.18.2
P	absolute pressure (Pa)
ΔP	overpressure (Pa)
P_a	atmospheric pressure (Pa)
P_g	absolute partial pressure of gas (Pa)
P_o	absolute stagnation pressure (Pa)
P_s	absolute set pressure (Pa)
P_v	absolute partial pressure of vapour (Pa)
q	heat release rate per unit mass (kW/kg)
Q	heat release or input rate (kW)

Q_g	volumetric gas evolution rate (m^3/s)
Q_v	volumetric vapour evolution rate (m^3/s)
r	rate of reaction ($kg/m^3/s$)
t	time (s)
Δt	time interval (s)
Δt_p	emptying time (s)
Δt_v	venting time (s)
T	absolute temperature (K)
T_o	absolute stagnation temperature (K)
ΔT	temperature rise (°C)
$(dT/dt)_s$	self-heat rate at set pressure (°C/s)
u	specific internal energy (kJ/kg)
v	specific volume (m^3/kg)
V	volume of vessel (m^3)
W	mass flow (kg/s)
x	mass fraction of vapour, or quality
α	void fraction
β	parameter defined by Equation 17.16.10
μ	viscosity
ρ	density (kg/m^3)
τ_t	turnaround time for temperature (s)
ω	critical flow scaling parameter

Subscripts

a	atmospheric
d	at disengagement
ERM	equilibrium rate model
f	liquid
fg	liquid–vapour transition
g	gas or vapour
l	liquid
L	laminar
m	peak pressure
o	initial
s	set point
T	turbulent
v	vapour

Equation 17.16.6

Δt	time interval to maximum allowable pressure (s)
ΔT	temperature difference at equilibrium between initial pressure and maximum allowable pressure (°C)

Equation 17.16.8

ΔT	temperature rise corresponding to overpressure ΔP (°C)

Equations 17.18.2–17.18.3

ΔP	total available pressure drop (Pa)

Equation 17.18.7

ΔT	temperature rise corresponding to overpressure ΔP (°C)

Equation 17.19.1

ρ	density of reaction mass (kg/m^3)

Equations 17.19.5 and 17.19.7

α_d	void fraction at disengagement
α_o	initial void fraction

Equations 17.19.7 and 17.19.8

Δt_v	time to temperature turnaround (s)

Equation 17.19.12

Q_g	peak volumetric gas evaluation rate
Q_v	peak volumetric vapour evaluation rate

Subsection 17.19.10

Δt_A	measured adiabatic rise time (s)
Δt_E	measured vessel emptying time (s)

Subscripts

LS	large scale
T	test

Section 17.20

A	vent area
A_0	vent area for zero overpressure
C	specific heat of liquid at constant volume
C_{pf}	specific heat of liquid at constant pressure
C_{pg}	specific heat of gas at constant pressure
C_{vf}	specific heat of liquid at constant volume
e	base of natural logarithms
G	mass velocity of vent flow
h	specific enthalpy
h_{fg}	latent heat of vaporization
m	mass of material in vessel
m_o	initial mass of material in vessel
P	absolute pressure
q	heat release rate per unit mass
Q	heat generation or input rate
Q_T	total heat input
R	universal gas constant
V	volume of vessel
u	specific internal energy
v	specific volume
W	mass flow from vessel
x	mass fraction of vapour, or quality
ρ	density

Subscripts

f	liquid
fg	liquid–vapour transition
g	vapour
i	phase i
m	peak pressure or temperature
o	initial
s	relief set pressure
1	vent inlet

Section 17.21

As Section 17.20, plus

Q_g	volumetric gas generation rate at temperature and pressure in reactor during relief
ΔT	difference in saturation temperature between set pressure (as redefined) and maximum allowable pressure
α	void fraction
α_d	void fraction at disengagement
α_o	initial void fraction

Subscript

m	mean value between set pressure (as redefined) and maximum allowable pressure

Section 17.22

C	drag coefficient
d	particle diameter (m)
g	acceleration due to gravity (m/s^2)
k	constant
u	vapour velocity (m/s)
u_d	dropout velocity (m/s)
μ	viscosity of gas (cP)
ρ_l	density of liquid (kg/m^3)
ρ_v	density of vapour (kg/m^3)

Section 17.24

a	radius of vent
A	vent area
F	flow reduction factor
g	acceleration due to gravity
h	height
h_{fg}	latent heat of vaporization
ΔP	pressure drop through vent system
P_s	set pressure
Q_T	total heat input to tank
Q_v	energy release rate
s	radius of hemisphere
u	velocity of vapour through vent
u_E	entrainment velocity
u_o	velocity up vent
u_s	velocity across hemispherical surface
u_{scr}	critical velocity across hemispherical surface
ρ_g	density of vapour
ρ_l	density of liquid
σ	surface tension

Equation 17.24.8

R_m	mass basis gas constant

Section 17.25

c_o	velocity of sound in air
i_p	positive phase overpressure impulse, impulse
i_q	dynamic pressure impulse
i_s	scaled impulse
p	overpressure
p_a	absolute ambient pressure (ahead of shock front)
p°	peak overpressure
p_r°	peak reflected overpressure
p_s	scaled pressure
q	dynamic pressure
q°	peak dynamic pressure
r	distance
t_a	arrival time
t_d	duration of positive phase, duration tin
t_q	dynamic pressure duration time
u	particle velocity
U	shock velocity
W	mass of explosive
z	scaled distance
α	decay parameter
γ	ratio of specific heats of air
λ	yield factor
ρ	density of air (behind shock front)
τ	scaled time
τ_a	scaled arrival time
τ_d	scaled duration time

Subscripts

o	reference value

Equation 17.25.5

i_q	dynamic pressure impulse (psi/ms)
R	distance (ft)
W	mass of explosive (lb)

Section 17.26

i_p	impulse (Pas)
i_s	scaled impulse (Pas/kg$^{1/3}$)
p°	peak overpressure (Pa)
p_a	atmospheric pressure (Pa)
p_s	scaled peak overpressure
t_a	arrival time (s)
t_d	duration time (s)
W	mass of explosive (kg)
z	scaled distance (m/kg$^{1/3}$)
τ_a	scaled arrival time (s/kg$^{1/3}$)
τ_d	scaled duration time (s/kg$^{1/3}$)

Equations 17.26.1 and 17.26.2

a, b	constants
c_i	constants
i_p	impulse (kPa ms)
p°	peak side-on overpressure (kPa)
t_a	arrival time (ms)
t_d	duration time (ms)
U	variable defined by Equation 17.26.1
z	scaled distance (m/kg$^{1/3}$)
ϕ	parameter defined by Equation 17.26.2

Equations 17.26.3–17.26.5

i_p	impulse (bar/ms)
p_s	scaled peak overpressure
t_d	duration time (ms)
W	mass of explosive (kg)
z	scaled distance (m/kg$^{1/3}$)

Equations 17.26.6–17.26.8

a_o	speed of sound in gas (m/s)
E_{ex}	explosion energy (J)
i_s	side-on impulse (Pas)
$\bar{I}$	scaled side-on impulse
p°	absolute pressure of ambient air (Pa)
p_s	absolute peak side-on overpressure (Pa)
$\bar{P}_s$	scaled peak side-on overpressure
r	distance (m)
$\bar{R}$	scaled distance

Section 17.27

a	speed of sound (m/s)
a_o	speed of sound in air (m/s)
a_1	speed of sound in compressed gas (m/s)
p_o	absolute pressure of ambient air (Pa)
p_1	absolute initial pressure of gas (Pa)
p_s	absolute peak side-on pressure (Pa)
$\bar{P}_{so}$	scaled peak side-on overpressure at R_0
r_o	effective radius of equivalent hemisphere (m)

$\bar{R}_o$	scaled distance
V_1	volume of gas-filled vessel (m^3)
γ_0	ratio of specific heats of air
γ_1	ratio of specific heats of compressed gas

Subscripts

0	ambient air
1	compressed gas in vessel

Section 17.28

R	gas constant

Subsection 17.28.5

$\Delta A/A$	relative increase in flame surface area
A_f	disturbed flame surface area
A_o	undisturbed flame surface area
n	number of obstacles
p	pitch
r	radius of flame front
r_o	radius for flame front at entry to obstacles
S	burning velocity
S_L	laminar burning velocity
V_f	flame front velocity
V_{f1}	flame front velocity after one obstacle
V_{fn}	flame front velocity after n obstacles
V_{fo}	flame front velocity at entry to obstacles
V_L	base value of flame front velocity
α	multiplier
ρ	gas density

Subscripts

b	burned
u	unburned

Subsection 17.28.10

E_{TNT}	energy of explosion of TNT (kJ/kg)
ΔH_c	heat of combustion of hydrocarbon (kJ/kg)
W	mass of hydrocarbon (kg)
W_{TNT}	equivalent mass of TNT (kg)
α	yield factor

Subsection 17.28.12

E_{gas}	heat of combustion of hydrocarbon (MJ/kg)
E_{TNT}	energy of explosion of TNT (MJ/kg)
M_{gas}	mass of gas (in confined/congested region) (te)
M_{TNT}	mass of TNT (te)
R	distance (m)
V	volume of gas (in confined/congested region) (m)
α	yield factor

Subsection 17.28.16

a_o	speed of sound
M_f	flame Mach number
M_p	piston Mach number
p	absolute pressure
$\bar{p}$	dimensionless overpressure
p_o	ambient pressure
r	radial distance
u	velocity
α	expansion ratio
ρ_o	density of ambient gas
ϕ	velocity potential

Subsection 17.28.17

a_a	velocity of sound
A_f	effective frontal area of flame
H	height of cloud
$\dot{m}$	rate of mass addition
$\ddot{m}$	rate of change of mass addition rate
M_f	flame Mach number
M_{su}	Mach number in unburned gas
p	absolute pressure
$\bar{p}$	dimensionless overpressure
p_o	ambient pressure
$\hat{q}$	dimensionless rate of energy addition
r	characteristic radius of source region
r_f	radius of flame
r_{obs}	distance of observer from centre of cloud
S_b	flame speed
S_u	effective burning velocity
u_f	velocity of flame front
$\dot{V}$	rate of volume addition
V_b	specific volume of burned gas
V_u	specific volume of unburned gas
α	expansion ratio
p_0	initial density of gas

Subscript

su	unburned gas

Subsection 17.28.18

a	speed of sound
F	parameter defined by Equation 17.28.3
r	radial distance
r_s	radial distance of leading shock
u	particle velocity
U_s	velocity of leading shock
X	parameter defined by Equation 17.28.3
Z	parameter defined by Equation 17.28.3

Subsection 17.28.19

a_o	speed of sound
K	parameter defined by Equation 17.28.47b
p	parameter defined by Equation 17.28.45
p_i	absolute pressure in region i
r	flame radius
R	shock radius
R_o	initial value of shock radius
s	parameter defined by Equation 17.28.45b
S	flame speed
T_i	absolute temperature in region i
V	velocity
x	parameter defined by Equation 17.28.46
y	parameter defined by Equation 17.28.46b
θ	parameter defined by Equation 17.28.47
ρ_i	density in region i

τ	dimensionless time defined by Equation 17.28.47c

Subscripts

0	undisturbed gas
1	shocked gas (shell)
2	burnt gas (core)

Subsection 17.28.21

a	velocity of sound in normal atmosphere
E	energy
E_e	explosive energy release
E_o	total energy release
E_u	vapour cloud energy release
ΔH_c	heat of combustion
m	mass of fuel in cloud
M	molecular weight of vapour
p	pressure
p_c	pressure at centre of explosion
r	distance from centre of blast symmetry
R	distance from centre of explosion
t_o	time of termination of rapid energy release
V	volume
ϵ	stoichiometric ratio
η	explosion efficiency
v	flame speed

Subsection 17.28.22

M_{su}	Mach number with coordinates relative to gases moving ahead of flame front
M_w	Mach number with fixed coordinates

Subsection 17.28.23

A	constant
c_o	local velocity of sound (m/s)
E_c	energy of combustion per unit volume (J/m^3)
E_o	energy added to unburned gas during combustion process (J)
L	characteristic length (m)
n	number of mols
p	absolute pressure (Pa)
$\overline{PS}$	reduced overpressure
R	distance (m)
$\bar{R}$	reduced distance
R_g	universal gas constant (J/mol K)
R_0	radius of initial cloud (m)
R_1	radius of burned cloud
t_+	duration time (s)
$\bar{t}$	reduced time
t_b	time at which explosion process is complete (s)
T	absolute temperature (K)
$\overline{TS}$	reduced duration time
U_{SW}	velocity of shock wave (m/s)
$\bar{u}_{fl}$	average flame speed (m/s)
V	volume (m^3)
γ	ratio of specific heats of air
λ	parameter defined by Equation 17.28.57

Subscripts

0	initial
1	final

Subsection 17.28.24

$C(S)$	parameter ($m/J^{1/3}$)
E	energy content of part of cloud within flammable range (J)
ΔH_c	heat of combustion (J/kg)
M_e	mass of fuel in cloud within flammable range (kg)
$R(S)$	radius of damage circle (m)
S	degree of damage
η	fraction of energy released, explosion efficiency
η_c	yield factor relating to stoichiometry
η_m	yield factor relating to mechanical energy

Section 17.29

Subsection 17.29.7

T_c	absolute critical temperature (K)
T_{sl}	absolute superheat limit temperature (K)

Subsection 17.29.11

P_b	burst pressure
r	vessel radius
R	radius ratio
σ_u	ultimate tensile strength
σ_y	yield strength

Subscripts

i	inner
o	outer

Section 17.30

Subsection 17.30.4

C	mass of oil mist in air necessary to produce explosive mixture at atmospheric pressure (g/m^3)
d	density of oil (g/m^3)
D	diameter of pipe (m)
P	absolute pressure (atm)
t	thickness of oil film (m)

Subsection 17.30.6

As Section 17.29.7

Section 17.31

Subsection 17.31.4

Equations 17.31.1 and 17.31.2

a	acceleration
A	amplitude
f	frequency
V	velocity

Equation 17.31.3

A	amplitude (in.)
d	distance (ft)

E mass of explosive (lb)
K constant

Equation 17.31.4
Q mass of explosive (kg)
R distance (m)
ϕ ϕ value

Subsection 17.31.5
D diameter of crater (m)
h depth of crater (m)
Q mass of explosive (kg)
V volume of crater (m^3)

Equation 17.31.8
r radius of crater
W mass of explosive

Section 17.32

Subsection 17.32.1
B breadth of structure
C_D drag coefficient
H height of structure
L length of structure
p overpressure
p_a maximum value of average side and top pressure
p_b maximum value of average back face pressure
p_d drag pressure
p_e effective pressure
p_f overpressure at front face
p_r° peak reflected overpressure
p_s stagnation pressure
q dynamic pressure
S distance through which pressure relief is obtained
t time
t_s stagnation time
U shock velocity

Subsections 17.32.2 and 17.32.3
c damping factor
E_{ko} initial kinetic energy
E_{sm} maximum strain energy
f Coulomb friction force
f_n natural cyclic frequency
F applied force
F^* parameter defined by Equation 17.32.12
I impulse
k elastic constant
m mass of system
R restoring force
T time constant for force decay
T_n natural period
W_m maximum work
x displacement
x_m maximum displacement
ζ damping factor
τ natural period
ω_n natural frequency

Subsection 17.32.4
R resistance function
R_e maximum elastic resistance

Equations 17.32.32–17.32.34
f_n natural cyclic frequency
k elastic constant
m mass of system
T_n natural period
ω_n natural frequency

Equation 17.32.35
B breadth of building (ft)
H height of building (ft)
T natural period of building (s)

Equation 17.32.36
p_m blast pressure (N/m^2)
r_e maximum elastic resistance per unit area (N/m^2)
t_e time to yield (s)
T natural period (s)

Equation 17.32.37
x_e displacement at elastic limit
x_f displacement at failure
μ ductility ratio

Subsection 17.32.5
F_m maximum load
P_m maximum pressure
x_e displacement at elastic limit
x_f displacement at failure
x_m central deflection

Subsection 17.32.6
p° peak overpressure (N/m^2)
Y probit

Equation 17.32.39a
k constant
R average circle radius for specified damage category (ft)
W mass of explosive (lb)

Equation 17.32.39b
k constant
R average circle radius for specified damage category (m)
W mass of explosive (kg)

Section 17.33

Subsection 17.33.2
Equation 17.33.1a

R_B distance for B category damage (ft)
W mass of explosive (lb)

Equation 17.33.1b
R_B distance for B category damage (m)
W mass of explosive (kg)

Subsection 17.33.3
Equation 17.33.2a – as Equation 17.33.1a,
Equation 17.33.2b – as Equation 17.33.1b

Subsection 17.33.4

R_A	average circle radius for A category damage
R_B	average circle radius for B category damage
$\bar{R}_B$	average circle radius defined by Equation 17.33.3
R_C	average circle radius for C category damage

Subsection 17.33.5

Equation 17.33.4 – as Equation 17.33.1b

Subsection 17.33.6

I	impulse
P	pressure

Equation 17.33.5 – as Equation 17.33.1b plus

z'	modified scaled distance ($m/kg^{1/3}$)

Section 17.34

Subsection 17.34.7

E_f	energy stored in vessel per unit mass of fluid
K	geometric factor
M_f	mass of fluid stored
M_v	mass of vessel
u	velocity of fragment

Subscript

i	initial

Subsection 17.34.8

A	mean presented area of fragment
C_D	drag coefficient
m	mass of fragment
t	time
u	velocity of fragment
u_g	velocity of surrounding gas
ρ_g	density of surrounding gas

Subsection 17.34.9

As Section 17.4.5 plus

E_k	explosion energy imparted to fragments
k	parameter defined by Equation 17.34.8

Subsection 17.34.11

a_g	velocity of sound in gas
K	constant
M_c	mass of vessel
p	pressure in vessel
p_o	atmospheric pressure
R_m	mass basis gas constant
T	absolute temperature of gas
u	velocity of fragment
V_0	volume of vessel
γ	ratio of gas specific heats

Subsections 17.34.12 and 17.34.13

a_o	speed of sound
A	area of detached portion of vessel wall
F	parameter defined by Equations 17.34.12 and 17.34.13
L	length of cylinder
m	mass per unit area of vessel wall
m_f	mass of fragment
P_o	atmospheric pressure
P_1	absolute initial pressure in vessel
r	radius of vessel
s	dimension of fragment
u	velocity of fragment
$\bar{u}$	dimensionless velocity of fragment

Subscript

i	initial

Subsection 17.34.14

a_o	speed of sound in gas at failure
$\bar{E}$	scaled energy
E_{ex}	energy released in explosion
M	mass of vessel
P	atmospheric pressure
P_1	absolute initial pressure in vessel

Subsection 17.34.16

C_D	drag coefficient
C_L	lift coefficient

Subsection 17.34.17

g	acceleration due to gravity
k	constant
u	velocity along line of flight
v	velocity relative to ground
x	distance in horizontal direction
y	distance in vertical direction
α	angle of departure
β	angle of return

Subscript

i	initial

Equation 17.34.46

c_d	drag coefficient
k	constant
v	velocity of projectile (ft/s)
m	mass of projectile (oz)
x	distance travelled by projectile (ft)

Subscript

i	initial

Subsection 17.34.18

A_D	drag area
A_L	lift area
C_D	drag coefficient
C_L	lift coefficient
F_D	drag force
F_L	lift force
g	acceleration due to gravity
M	mass of fragment
R	range of fragment
$\bar{R}$	dimensionless range
u	velocity of fragment
$\bar{u}$	dimensionless velocity of fragment
u_o	initial velocity of fragment

ρ density of air
ρ_o initial density of air

Subsection 17.34.21
F_{or} orientation factor
H height of top of sphere (m)
L effective range interval (m)
N number of fragments
N_{pen} $= N - 1$
P probability
P_{ri} probability that fragment falls within effective range interval L
P_{st} probability of a strike
P_v vessel pressure (barg)
r radius of sphere (m)
R range (m)
R_{med} median range (m)
R_{pen} range of penultimate fragment (m)
W combined width of target and fragment (m)
Y probit
θ angle of descent (°)

Subsection 17.34.24
a projected area of body (ft^2)
A area per missile (ft^2/missile)
A_h area of hemisphere on surface of which human target is standing (ft^2)
m mass of explosive (ton)
n near field number of missiles per ton of explosive (missiles/ton)
n_e number of missiles at distance R
P probability of being struck by missile
R distance (ft)
W mass of explosive (lb)
ϕ_o correction factor

Subsection 17.34.25
A presented area of fragment (m^2)
C constant
d diameter of fragment (m)
K constant
m mass of fragment (kg)
n_1, n_2 indices
t thickness of barricade to just stop fragment (m)
u velocity of fragment (m/s)

Subsection 17.34.26
d diameter of missile (m)
D calibre density of missile (kg/m^3)
e perforation thickness (m)
G parameter defined by Equations 17.34.68–17.34.70
m mass of missile (kg)
V velocity of missile (m/s)
V_p perforation velocity (m/s)
x penetration depth (m)
ρ density of concrete (kg/m^3)
σ_c compressive strength of concrete (Pa)

Subsection 17.34.27
d diameter of missile (m)
E_c critical impact energy of missile G)
h thickness of target panel (m)
S_u ultimate tensile strength of panel (Pa)
w width of panel (m)

Subsection 17.34.28
E_r energy to deform sphere in plastic region between yield and rupture (kJ)
E_v energy to deform sphere up to yield point (kJ)

Subsection 17.34.29
E shock wave energy (J)
P equivalent static pressure (bar)
R distance (m)

Equation 17.34.76
V volume of enclosure (m^3)

Equations 17.34.77 and 17.34.78
I impulse per unit area ($N/s/m^2$)
m mass of wall per unit area (kg/m^2)
V velocity (m/s)

Equation 17.34.79
P peak incident overpressure (bar)

Section 17.35

Subsection 17.35.3
F force on disc
g acceleration due to gravity
m mass of disc
x extension

Subsection 17.35.5
e strain
U energy adsorbed (G)
ρ density of steel (kg/m^3)
σ_y yield stress (N/m^2)

Equations 17.35.1–17.35.3
F applied force (N)
l length of pipe stretched (m)
U energy absorbed G)
δ elongation (m)
θ angle of bend (rad)
ϕ plastic moment (N/m)

Equations 17.35.4 and 17.35.5
L length of cut (m)
t thickness (m)

Equation 17.35.6
e_p strain behind plastic wave front
v imparted velocity (m/s)
σ_g tensile stress (N/m^2)

Equation 17.35.7
c velocity of elastic compression wave in steel (m/s)
v velocity of impact of missile (m/s)
σ_c compressive stress caused by impact (N/m^2)

Equation 17.35.8

V_c	volume of cavity (m^3)

Section 17.36

Subsection 17.36.2

B, B_B	constants
m	mass of nth fragment
$M(n)$	cumulative mass of fragments
M_o	total mass of fragments
M_{oB}	modified total mass of fragments
n	number of nth largest fragment
λ, λ_B	constants

Subsection 17.36.3

D	velocity of detonation
u_o	initial velocity of fragments
ϕ	angle beween initial trajectory of fragment and axis of tube, Taylor angle

Subsection 17.36.4

Equation 17.36.6

C	mass of cylindrical case per unit length (lb)
E	mass of charge per unit length (lb)
V_o	initial velocity of fragments (ft/s)

Equations 17.36.7 and 17.36.8

C	mass of explosive (kg)
C_G	Gurney velocity, Gurney constant (m/s)
ΔE	internal energy per unit mass of explosive (J/kg)
M	mass of cylindrical section of casing (kg)
u_o	initial velocity of fragments (m/s)

Equations 17.36.9 and 17.36.10

C_G	Gurney velocity (km/s)
M	average molecular weight of products of explosion
N	number of moles of gas produced by explosion
Q	heat of detonation (cal/g)
ρ_o	explosive loading density (g/cm^3)
ϕ	parameter defined by Equation 17.36.10

Subsection 17.36.5

Equation 17.36.11

m	mass of fragment (oz)
s	distance travelled (ft)
u	velocity of fragment (ft/s)
u_o	velocity of fragment at commencement of air drag (ft/s)
u_s	velocity of sound (ft/s)

Equation 17.36.12

A	area of fragment
k	constant
u	velocity of fragment
u_o	velocity of fragment at commencement of air drag
m	mass of fragment
x	distance

Equations 17.36.13–17.36.15

A	coefficient of area
A_m	mean area presented by fragment in flight (ft^2)
Q	fragment volume (ft^3)
u	velocity of fragment (ft/s)
u_o	velocity of fragment at commencement of air drag (ft/s)
u_s	velocity of sound (ft/s)
w	mass of fragment (oz)
x	distance (ft)

Equations 17.36.16 and 17.36.17

a	diameter of sphere or side of cube (m)
A_s	effective area of fragment (m^2)
C_α	drag coefficient
m	mass of fragment (kg)
u	velocity of fragment (m/s)
u_o	initial velocity of fragment (m/s)
x	distance (m)
ρ_a	density of air (kg/m^3)

Equation 17.36.23

r	safety distance (m)
W	mass of explosive (kg)

Subsection 17.36.8

A_p	projected area of exposed person (ft^2)
A_v	vulnerable area (ft^2)
n	number of incapacitating fragments
N	average number of incapacitating fragments at distance x
p	probability of being hit by one or more incapacitating fragments
q	number of fragments of equivalent velocity v at distance x
r	proportion of fragments of equivalent velocity v at distance x capable of causing incapacitation
u	velocity of fragment (ft/s)
x	distance (ft)

Section 17.38

C_D	drag coefficient
i	impuse (Pas)
$\bar{i}$	scaled impulse ($Pa^{1/2}s/kg^{1/3}$)
m	mass of body (kg)
p°	peak incident overpressure (Pa)
p_a	atmospheric pressure (Pa)
p_a^o	peak applicable overpressure for lung injury (Pa)
$\bar{p}_a^\circ$	scaled peak applicable overpressure for lung injury
p_r°	peak reflected overpressure (Pa)
q	dynamic pressure (Pa)
q^o	peak dynamic pressure (Pa)
Y	probit

Equations 17.38.9 and 17.38.10

S	damage number

Equations 17.38.11 and 17.38.13

J	impulse (Pa s)

p	incident overpressure (Pa)
t_d	duration time (s)

Equations 17.38.13–17.38.16

A	projected area of body (m^2)
F	force acting on body (N)
i_q	dynamic pressure impulse (Pas)
t_q	dynamic pressure duration (s)
V	velocity imparted to body (m/s)

Equations 17.38.17–17.38.21

A	projected area of body (ft^2)
F	deceleration due to friction (ft/s^2)
L	loading on body (lbf)
M	mass of body (ln)
P_e	effective pressure on body ($lb_f/in.^2$)
t	time (s)
u	velocity of body (ft/s)
x	distance travelled by body (ft)
α	acceleration coefficient (ft^2/lb)

Equations 17.38.22 and 17.38.23

L	loading (N)
m	mass of body (kg)
t	time (s)
u	velocity of displacement (m/s)
ϕ_r	deceleration due to friction (m/s^2)

Equations 17.38.24–17.38.30

S	injury factor

Equation 17.38.31a

d	distance for 50% casualties (ft)
d_r	distance for 50% casualties for 1 kt explosion (ft)
W	yield of a nuclear explosion (kiloton)

Equation 17.38.31b

d	distance for 50% casualties (m)
d_r	distance for 50% casualties for a 1 kte explosion (m)
W	mass of explosive (te)

Section 17.40

Subsections 17.40.3–17.40.5

A	area of pane (m^2)
A_p	presented area of fragment (m^2)
A_{mp}	mean presented area of fragment (m^2)
A_{50}	mean frontal area of fragment (m^2)
l	length of long side of fragment (m)
m_{so}	mean mass of fragment (kg)
p^*_{br}	breaking pressure (kPa)
p°	peak incident overpressure (Pa)
p^o_e	peak effective overpressure (Pa)
t	thickness of glass, fragment (m)
u	velocity of fragment (m/s)
u'	velocity of fragment (ft/s)
Y	probit
ρ_{gl}	density of glass (kg/m^3)

Superscripts

50	geometric mean
$^-$ (overbar)	scaled

Equations 17.40.5 and 17.40.6

A^*_{50}	mean frontal area fragment (cm^2)
m	mass of fragment (g)
$p^{\circ *}_e$	peak effective overpressure (kPa)

Equation 17.40.8

A_{mp}	mean presented area of fragment on impact (m^2)
t	thickness of glass, fragment (cm)

Equations 17.40.9 and 17.40.10

$p^{\circ\prime}_e$	peak effective overpressure (psi)
t′	thickness of pane (in.)
V'_{50}	geometric mean velocity of fragment (ft/s)
$\bar{V}'_{50}$	scaled geometric mean velocity of fragment (ft/s)

Equations 17.40.12 and 17.40.13

t^*	thickness of pane (cm)
$\bar{V}_{50}$	scaled geometric mean velocity of fragment (m/s)

Equation 17.40.14

$p^{\circ *}_e$	peak effective overpressure (kPa)
u	average velocity of fragments (m/s)

Equation 17.40.15

t	thickness of glass, fragment (m)
u	average velocity of fragments (m/s)
P^*_{br}	breaking pressure (kPa)

Subsection 17.40.6

A	presented area of fragment (m^2)
A'_{50}	geometric mean frontal area of fragment (m^2)
M	mass of fragment (kg)
P_e	peak effective overpressure (Pa)
P_o	atmospheric pressure (Pa)
P_r	peak reflected overpressure (Pa)
$\bar{P}_s$	dimensionless peak reflected overpressure
P_s	peak side-on overpressure (Pa)
$\bar{P}_s$	dimensionless peak side-on overpressure
t	thickness of pane, fragment (m)
u_{50}	geometric mean velocity of fragment (m/s)
y	length of square edge of fragment (m)
ρ_{gl}	density of glass (kg/m^3)

Subsection 17.40.7

$p^{\circ *}_e$	peak effective overpressure (kPa)
ρ_{sd}	spatial density of fragments (fragments/m^2)
$\bar{\rho}'_{sd}$	scaled spatial density of fragments
t	glass thickness (cm)

Subsection 17.40.9

m	mass of fragment (g)
u'	velocity of fragment (ft/s)
Y	probit

Subsection 17.40.10

A	presented area of missile (m^2)
C_D	drag coefficient
J	impulse (Pa s)
M	mass of missile (kg)
u_i	impact velocity (m/s)
Y	probit

Subsection 17.40.11

A	presented area of fragment (m^2)
M	mass of fragment (kg)
u_{50}	velocity for 50% probability of perforation (m/s)

Subsection 17.40.12

a	smaller of two dimensions of pane (m)
A	area of pane (m^2)
d	thickness of pane (m)
f_{dl}	dynamic load factor
f_t	tensile strength of pane (Pa)
P°	peak incident overpressure (Pa)
P_{df}	dynamic failure load (Pa)
P_{st}	static strength of pane (Pa)
t_d	duration time (s)
T	natural period of vibration (s)

Section 17.41

Subsection 17.41.24

c	index
E	kinetic energy (J)
m	mass of fragment (kg)
u	velocity of fragment (m/s)

Subsection 17.41.4

b, c	indices
k	constant
m	mass of fragment (mg)
m_r	mass of reference fragment (mg)
P	penetration (ft)
u	velocity of fragment (ft/s)

Equations 17.41.7 and 17.41.8

m	mass of fragment (kg)
u	velocity of fragment (m/s)
Y	probit

Section 17.42

See notation lists given in text, plus:

i	body region counter

Subsection 17.42.2

A	total mean presented area of body
A_i	mean presented area of body attributable to region i

Subsection 17.42.3

A	projected area of fragment (m^2)
m	mass of fragment (kg)
u	velocity of fragment (m/s)
X	causative factor (G/m^2)

Subsections 17.42.4 and 17.42.5

Equation 17.42.18:

a, b	constants
A	projected area of fragment (cm^2)
m	mass of fragment (g)
u	velocity of fragment (m/s)

Equations 17.42.19 – 17.42.22

A	projected area of fragment (m^2)
m	mass of fragment (kg)
u	velocity of fragment (m/s)

Section 17.44

c	concentration (g/m^3)
ES	explosion severity
IE	index of explosibility
IS	ignition sensitivity
K_G	gas explosibility constant, $K_G$value
K_{st}	dust explosibility constant, K_{st}value
l	lower explosive limit (g/m^3)
m_{sd}	mass concentration of solvent-contaminated dust (g/m^3)
MEC	minimum explosive concentration
MEP	maximum explosion pressure
MIE	minimum ignition energy
MIT	minimum ignition temperature
MRPR	maximum rate of pressure rise
P	absolute pressure
p_{max}	maximum explosion pressure
p_o	atmospheric pressure
p_1	small initial pressure rise
p_2	pressure defined in Figure 17.114
V	volume of vessel (m^3)
ϕ_s	mass fraction of solvent in solvent-contaminated dust

Subscripts

d	dust
dh	dust in presence of flammable gas, hybrid
g	gas
Pc	Pittsburgh coal
sample	sample

Section 17.46

C_o	maximum permissible oxygen concentration for carbon dioxide inerting
N_o	maximum permissible oxygen concentration for nitrogen inerting

Section 17.48

(See text for units in particular equations)

Subsection 17.48.6

A_v	vent area
f	vent ratio, A_v/V
V	volume of enclosure

Subsection 17.48.7

A_c	area of smallest cross-Section of enclosure
K	vent coefficient, A_c/A_v
L_1, L_2	two smallest dimensions of enclosure

Subsection 17.48.8

A_v	vent area
C_d	coefficient of discharge
K_{st}	dust explosibility constant, K_{st} value
M	molecular weight of vented gas
P	pressure
P_a	atmospheric pressure
$(dP_{ex}/dt)_{maxVL}$	maximum rate of pressure rise in unvented test vessel
$(dP_{ex}/dt)_{P_{red}VL}$	maximum rate of pressure rise in vented test vessel
P_{red}	reduced pressure
P_{stat}	vent opening pressure
R	universal gas constant
T	absolute temperature of vented gas
V	volume of vessel
V_L	volume of test vessel

Subscripts

red	reduced
VL	test vessel

Equations 17.48.9 and 17.48.10

a	constant
A_v	vent area (m^2)
b, c	indices
K_{st}	dust explosibility constant, K_{st} value (bar m/s)
P_{red}	reduced pressure (barg)
P_{stat}	vent opening pressure (barg)
V	volume of vessel (m^3)

Equation 17.48.11

a, b	constants
C	constant
d	index
P_{red}	reduced pressure (barg)
P_{stat}	vent opening pressure (barg)
V	volume of vessel (m^3)

Equation 17.48.12

B	parameter
K_{st}	deflagration index (bar m/s)
P_{red}	reduced pressure after venting (bar)
V_L	volume of test vessel

Subsection 17.48.9

t	time

Equations 17.48.13a, 17.48.14a and 17.48.14b

A	maximum pressure in unvented explosion (psi)
K	slope of line of A vs X
$(dP/dt)_{max}$	maximum rate of pressure rise
$(dP/dt)_{av}$	average rate of pressure rise
X	vent ratio ($ft/100\ ft^3$)
Y	reduced pressure in vented explosion (psi)

Equations 17.48.13b, 17.48.15a and 17.48.15b

f	vent ratio
k_{av}	constant
k_{max}	constant
P_{red}	maximum pressure in vented explosion, reduced pressure
P_{max}	maximum pressure in unvented explosion
$(dP/dt)_{av}$	average rate of pressure rise
$(dP/dt)_{max}$	maximum rate of pressure rise
S	constant

Subsection 17.48.10

A_c	area of smallest cross-Section of enclosure
A_v	vent area
C	Runes constant
ΔP	explosion overpressure

Subsection 17.48.13

K_f	constant
P	absolute pressure
P_a	atmospheric pressure
$(dP_{ex}/dt)_{P_{red},V}$	maximum rate of pressure rise in vented vessel
$(dP_{ex}/dt)_{P_{red},VL}$	maximum rate of pressure rise in vented test vessel
t	time
V	volume of vessel
V_L	volume of test vessel
ρ	density of gas mixture

Subscripts

ex	closed vessel explosion
P_{red}	reduced pressure
V	vessel
VL	test vessel

Subsection 17.48.14

A_v	vent area
C_d	coefficient of discharge
G_v	mass velocity through vent
K	constant
P	absolute pressure
P_o	atmospheric pressure
P_c	absolute pressure when rate of pressure rise is at its maximum
V	volume of vessel
ρ	density of gas
ρ_c	density of unburned gas at P_0 or density of combustion products at P_c
ρ_o	density of gas at atmospheric pressure

Subscripts

av	average
c	at maximum rate of pressure rise

Subsection 17.48.15

A_v	vent area
F	shape factor
k	constant
K_D	explosion parameter
P	absolute pressure
P_{max}	absolute maximum explosion pressure
P_{red}	reduced pressure (gauge)

u	velocity of flame front
V	volume of vessel

Subsection 17.48.16
As Section 17.12.25

Section 17.51

f	number of fatalities
MI	mortality index
r	radius
W	mass of explosive

Section 17.52

Subsection 17.52.1

n	index
p°	peak overpressure
r	distance
W	mass of explosive
z	scaled distance

Subscript

r	reference value

Subsection 17.52.2

I	mass of vapour in cloud (te)
k^*	constant
p°	peak overpressure (bar)
r	distance (m)
r_c	radius of cloud (m)
R_{LFL}	distance to LFL (m)

18 Toxic Release

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The third of the major hazards, after fire and explosion, is a release of a toxic chemical. The hazard presented by a toxic substance depends on the conditions of exposure and on the chemical itself. It ranges from a sudden brief exposure at high concentration to prolonged exposure at low concentrations over a working lifetime.

Both these situations present serious hazards. A very large release of a toxic chemical such as chlorine under the most unfavourable conditions is usually regarded as having a disaster potential greater than that of fire or explosion. However, a large toxic release is a much less frequent occurrence than a large fire or explosion.

The First Report of the ACMH (Harvey, 1976) states:

> With toxic materials, the sudden release of very large quantities could conceivably cause even larger numbers of casualties than a flammable escape. In theory such a release could, in certain weather conditions, produce lethal concentrations in places 20 miles from the point of release but the actual number of casualties (if any) would depend on the population density in the path of the cloud and the effectiveness of the emergency arrangements that might include evacuation.

In a quite different way the long-term toxic effects of exposure at even low concentrations of certain chemicals over a working lifetime can also affect large numbers of people.

The aspects of the problem considered here are the general effects of toxic substances, the limit values set for these, the effects of particular toxic chemicals and the assessment and control of the hazard of toxic releases. The treatment here is complemented by the account of occupational health given in Chapter 25.

Reference was made in Chapter 3 to the establishment by the Government of the Advisory Committees on Dangerous Substances (ACDS) and on Toxic Substances (ACTS) to advise the Health and Safety Commission (HSC). The terms of reference of both committees include toxic substances.

It cannot be too strongly emphasized that the assessment of the effect of toxic chemicals is a medical matter and that it is essential that the engineer seek expert advice on medical aspects such as interpretation of limit values and assessment of long-term effects.

Selected references on toxicology and toxic chemicals and on toxic release are given in Tables 18.1 and 18.2, respectively.

18.1 Toxic Effects

The treatment of toxic effects given here deals both with acute and chronic effects, but it is necessarily a brief one. Sources of information on the toxicity of chemicals are given in Section 18.3, and for carcinogens, in Section 18.7.

The effects of toxic substances are described in treatments of occupational diseases such as *Occupational Diseases and Industrial Medicine* (R.T. Johnson and Miller, 1960), *Diseases of Occupations* (Hunter, 1975), *National Occupational Exposure Survey* (NIOSH, 1974–/3), *Occupational Diseases – A Guide to Their Recognition* (NIOSH, 1977/4), *A Guide to Work-relatedness of Disease* (NIOSH/5, 1979), *Recognition of Health Hazards in Industry* (Burgess, 1981 ACGIH/5), *Chemical Exposure and Disease* by Sherman (1988 ACGIH/16) and Work Related Lung Disease Surveillance Report (NIOSH, 1991/20).

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Statistical interpretation
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Animal models, extrapolation between species
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Anon. (1981k); Pittom (1978); Relio (1978); C.R. Pearson (1982); Barnard (1984); Corn and Corn (1984); Deisler (1984a,b); Gough (1984); Karrh (1984); Lowrance (1984); Neal and Gibson (1984); Rijkels (1984); Rodricks and Tardiff (1984); Doull (1987); Rodricks and Taylor (1989); Cote and Wells (1991); Fairhurst and Turner (1993)

Process design and handling
Halley (1965); Prugh (1967); J.R. Hughes (1970); Constance (1971a); Gage (1972); Schaper (1973); Kusnetz (1974); Wirth (1975); J.T. Carter (1976, 1980); Garner (1976); Weissbach (1976); Toca (1977); Payne (1978); S.D. Green (1980); IBC (1982/27); Cralley and Cralley (1983); First (1983); Kusnetz and Phillips (1983); Kusnetz and Lynch (1984); Carson and Mumford (1986 LPB 67); Anon. (1989 LPB 86, p. 19); Jackson (1989 LPB 87); Desai and Buonicore (1990); Grossel (1990a); Doerr and Hessian (1991); Chadha and Parmele (1993)

Workplace exposure, environmental control, exposure monitoring; analytical methods (*see* Table 25.1)

Toxics detection and alarm
D. Doyle (1971); ACGIH (1972); Eckstrom (1973); Blears and Coventry (1974); Johanson (1974, 1976); Visanuvinol and Slater (1974); Dailey (1976); Thain (1976); Lichtenberg and McKerlie (1979); Warncke (1977); Ricci (1979a); Ellgehausen (1980); Cullis and Firth (1981); Rooney (1986); J.M. Rogers (1988); Thompson, Sekula and Whitson (1992)

Hygiene standards, threshold limit values, occupational exposure limits
ACGIH (n.d./1-3, 1992/78, 80); Elkins (1939); Bowditch *et al.* (1940); Anon. (1962a); Associated Octel Co. (1972 Bull. 24); ASTM (1973 DS 48); Levinson (1975); Ferguson (1976); HSE (1976 TDN2/73, 1993, EH 64, EH 65/4, EH 65/6, 1994 EH 40); Henschler (1979); Lauwerys (1983); IBC (1984/56); CIA (1985 PA23); P. Lewis (1985a, 1986a,b); Skinner (1985); AIHA (1987/12); Anon (1990h); ILO (1991/2); Weisburger (1994)
MAKWerte: Henschler (1979); Deutsche Forschungsgemeinschaft (1982); German Commission for Investigation of Health Hazards in the Workplace (1994)
Emergency exposure limits': Zielhuis (1970); Siccama (1973); CPD (1974); Balemans (1975); Eisenberg, Lynch and Breeding (1975); AIHA (1988–/13); ECIETOC (1991); Rusch (1993)
HSE limit system: Fairhurst and Turner (1993)
Dow Chemical Exposure Index: RA Smith and Miller (1988); Dow Chemical Co. (1994a)

Odour
(ASTM 164, 1973 DS 48); Leonardos, Kendall and Barnard (1969); Turk (1969); ASTM (1973 DS 48); Turk, Johnston and Moulton (1974); Cheremisinoff and Young (1975); Fazzalari (1978); Eugen (1982); Polak (1983); Lynskey (1984 LPB 60); J.C. Stevens, Cain and Weinstein (1987); AIHA (1989/17); CCPS (1989/4); R.M. Turner and Fairhurst (1989a); MacFarlane and Ewing (1990); ACDS (1991); de Weger, Pietersen and Reuzel (1991); CPD (1992b)

Toxicity of chemicals
Browning (n.d.a.b, 1965); HSE (Appendix 28 inc. Toxicology of Substances, MS, TON and TR series, SIR 21); MCA (1952–, SD series, 1972/21); Merck (1889); Flury and Zernick (1931); Brookes (1948); Patty (1948–); Sax (1957–); Matheson Co. (1961); C.H. Gray (1966); BCISC (1968/8); Skinner (1962); Braker and Mossman (1970); G.D. Muir (1971); Kinnersly (1973); National Library of Medicine (1974); Sumi and Tsuchiya (1976); Binns (1978); Skole (1978); Sittig (1979, 1981, 1994); Deutsch (1981); CONCAWE (1984 84/54, 1986 86/69); A. Allen (1988); Walsh (1988); van Loo and Opschoor (1989); Merck Co. (1989); Meyer (1989); NIOSH (1990/18); Franklin (1991); OSHA (1991/7); Kellard (1993); Tyler *et al.* (1994)

Carcinogens
HSE (TON series, 1973 TON 3, 1983 MS(B) 5); OSHA (n.d./2, OSHA 2220, 1977); Public Health Service (1941–); Bryan and Shimkin (1945); MCA (1952–, SD series); Hunter (1959, 1975); Mantel and Bryan (1961); Munn (1963); Surgeon Generals Advisory Committee on Smoking and Health (1964); J.A. Miller (1970); Ames (1971); J.G. Wilson (1971); Ad Hoc Committee on the Evaluation of Low Levels of Environmental Carcinogens (1972); Gadian (1972); IARC (1972–, 1979a, 1980); Abelson (1973); Ames *et al.* (1973); Hollaender (1973); Goldberg (1974); Ricci (1974, 1976a,b, 1977a); Tso and di Paulo (1974); Cairns (1975, 1981); R.L. Carter and Roe (1975); Environmental Mutagen Society (1975); Fraumeni (1975); Hoover and Fraumeni (1975); McCann *et al.* (1975–); Cinkotai *et al.* (1976); A.J. Fox and Collier (1976); Mehlman, Shapiro and Blumenthal (1976); Searle (1976–); Baxter *et al.* (1977); Boyland (1977); Doll (1977, 1979); Kraybill and Mehlman (1977); Schirripa (1977); Wynder and Gori (1977); Ashby and Styles (1978); S.S. Epstein (1978); Rawson (1978); Tarr and Damme (1978); Bowman (1979, 1982); B.E. Butterworth (1979); Doll and McLean (1979); Fairchild (1979); Fishbein (1979); Garner (1979); Grasso (1979); Higginson and Muir (1979); OSTP (1979); Peto (1979, 1980); P.P. Scott (1979); Sullivan and Barlow (1979, 1982); Vogel (1979); M.W. Anderson, Hoel and Kaplan (1980); ASTM (1980); Purchase (1980); Cairns (1981); CIA (1981, 1992 RC45); Doll and Peto (1981); S.E. Epstein and Swartz (1981); IBC (1981/14); A.E. M. McLean (1981); Sax (1981); C.R. Shaw (1981); Sontag (1981); Squire (1981); US Congress, OTA (1981); Anon. (1982n); Magnus (1982);

de Serres and Shelby (1982); Soderman (1982); Stich (1982–); Totter (1982); Bootman (1983); CBI (1983); Doyal and Epstein (1983); Hoel, Kapland and Anderson (1983); Barnard (1984); Corn and Corn (1984); Deisler (1984a,b); Gough (1984); Higginson (1984); Karrh (1984); Kirsch-Volders (1984); Kusnetz and Lynch (1984); Lowrance (1984); Neal and Gibson (1984); Rijkels (1984); Sagan and Whipple (1984); Crump and Crockett (1985); Wolf (1985); Blackburn and Kellard (1986); Anon. (1986l); CIA (1987 RC5); Tancrede *et al.* (1987); HSE (1990 EH 58, 1992 EH 62)
Benzene: Thorpe (1974, 1978a,b); NIOSH (1976 Publ. 74–137); Infante *et al.* (1977a,b); Laskin and Goldstein (1977); Kohn (1977b); Tabershaw and Lamm (1977); Pagnotto, Elkins and Brugsch (1979); Cahan (1980); Rushton and Alderson (1981); HSE (1982 TR 4); M.C. White, Infante and Chu (1982); ACGIH (1989/28); Foo (1990); HSE (1992 MS (A) 13); IP (1993 TP 25, 26)
Formaldehyde: HSE (1981 TR 2); Clary, Gibson and Waritz (1983); Starr (1983)
Vinyl chloride: OSHA (OSHA 2225); Viola (1970); Schaper (1973); Anon. (1974j); HM Chief Inspector of Factories (1974); BCISC (1974/14); Creech and Johnson (1974); Anon. (1975o); CIA (1975/8); Creech and Makk (1975); EPA (1975b,c); HSE (1975b, 1992 EH 63); Heath, Falk and Creech (1975); Lilis *et al.* (1975); Maltoni and Lefemine (1975); Nicholson *et al.* (1975); Selikoff and Hammond (1975); Veltman *et al.* (1975); Baxter *et al.* (1977); H.M. Clayton (1977); Meade and Press (1977); Stafford (1977); Tarpa (1977); Atherley (1978); Doniger (1978); Gehring, Watanabe and Park (1979); McPherson, Starks and Fryar (1979); Anon. (1980x); Conaway, Davenport and Norstrom (1980); Anon. (1984z); Rijkels (1984); Barr (1986); Wolf, Holland Rajaratnam (1987)

Dusts
HSE (TON 14, 1976 TON 1, 1979 EH 21, 1990 EH 46, 1991 EH 44, 1992 EH 59, 1993 EH 66, 1994 CRR 62); Stairmand (1951); C.N. Davies (1954); Bamford (1961); Owen (1974); T. Allen (1975); Batel (1976); Munns (1977); Kaye (1981); Vincent and Marks (1981); Bridgwater (1983); Orleman *et al.* (1983); Sexton, Spengler and Treitman (1984); BOHS (1985 TG5, 1987 TG7); D.M. Muir (1985); ACGIH (1987/13, 1988/18); Lloyd (1987); Mody and Jakhete (1988); Rood (1992a,b); Stanley-Wood and Lines (1992)
Silica dusts: HSE (1992 MS (A) 15)
Organic dusts: HSE (1977 MS 4); VDI 2263 Pt 1: 1990
Asbestos: HSE (Appendix 28 Asbestos, MA 4, TON 42, 1970 HSW Bklt 44, 1974 TON 13, 1975 TON 24, 35, 1982 RP 18, 1984 IND(G) 17(L), 1985 EH 41, 1986 Research Review 3, 1988 EH 50, MS 13, 1989 EH 35, 37, 51, 1990 EH 10, 36, 47, 1993 EH 57); Oliver (1902); Doll (1955); J.C. Wagner (1960); Gadian (1967); Elmes and Simpson (1971, 1977); Langlands, Wallace and Simpson (1971); Wallace and Langlands (1971); DoEm (1974/4); Parliamentary Commissioner (1975–76); Edge (1976); Fulmer Research Institute (1976); Harries (1976); W.P. Howard (1976); Kinnersly (1976); Lumley (1976); D.C.F. Muir (1976); Selikoff, Churg and Hammond (1976); Tait (1976); European Commission (1977); NIOSH (1977 Crit. Doc. 77–169); Woolf (1977); Cavaseno (1978c); HSC (1978a,b); Peto (1978); Savage (1978); British Society for Social Responsibility in Science (1979); Pye (1979); Carton and Kauffer (1980); Gee (1980); J.W. Hill (1980); Basta (1981a); Gentry *et al.* (1982); T. Nash (1982); ASTM (1984 STP 834); J.Bell (1984); Ouellette *et al.* (1986); WHO (1986 EHC 53); Holt (1987); ACGIH (1989/33, 1990/39)
Dust-fume mixtures: HSE (1994a)
Welding fumes: AWS (Appendix 28); Welding Institute (1981/35, 36, 1986/38, 1991/43); HSE (1990 EH 54, EH 55)

Aerosols
C.N. Davies (1961, 1967); Vincent (1980); Hinds (1982)

Metals
HSE (Appendix 28 EH series, Technical Data Notes); A. Tucker (1972); Goyer and Mehlman (1977); A. Williams (1977); Cohn and Linnecar (1979)
Arsenic: HSE (TON 9, 1990 EH 8); Lederer and Fensterheim (1983); OSHA (1983)
Cadmium: HSE (1975 TON 11, 1986 EH 1, MS(A) 7); Mennear (1979)
Chromium: HSE (1991 EH 2, MS(A) 16)
Lead, lead additives: API (69–7, EA 7102); HSE (TON 16, EH 3, MA 3, 1986 BPM 16, EH 28, MS(A) 1); OSHA (OSHA 2230); WHO (EHC 3); Cremer (1959, 1961); Cremer and Callaway (1961); R.K. Davis *et al.* (1963); Bryce-Smith (1971, 1982); Hepple (1971); Associated Octel Co. (1972 Bull. 24); NAS/NRC (1972b); DoEm (1973/3); Gething (1975); HSE (1978b); NIOSH (1978 Crit. Doc. 78–158); Anon. (1982d); Chamberlain (1983); Killington (1983); E. King (1983); ACGIH (1991/75); Sweetland (1993)
Mercury, including methyl mercury: WHO (EHC 1); OSHA (OSHA 2234); Katsuna (1968); Hartung and Dinman (1972); Bakir *et al.* (1973); OECD (1974); HSE (1978 MS 12); D. Taylor (1978); P.R. Edwards and Pumphrey (1982)

Inhalation toxicity
Barcroft (1918, 1920); Waldron (1980a); Hardy and Collins (1981); Witschi and Nettesheim (1981–); Fiserova-Bergerova (1983); ASTM (1985 STP 872)
Respiratory physiology: Krogh (1914–15); Forbes, Sargent and Roughton (1945); Forster (1957, 1964a,b); Ogilvie *et al.* (1957); Weibel (1963, 1973); Fenn and Rahn (1964); J.B. West (1965, 1977); Lippold (1968); Altaian and Dittmar (1971, 1974); Comroe (1974); Lambertsen (1974); Mountcastle (1974); Cotes (1979); Pickrell (1981); Keele, Neil and Joels (1982); Bramble (1983); Whipp and Wiberg (1983); Phalen (1984); Nixon (1985, SRDR 327); Vouketal (1985)

Lung diseases
Parkes (1974); C.K.W.M. Morgan and Seaton (1975); HSE (1977 MS 5); Khogali (1977)

Toxic gases
McEwen, Theodore and Vernot (1970); McEwen and Vernot (1972, 1974, 1976); Perry and Articola (1980); Buckley *et al.* (1984); CCPS (1989/4); R.M. Turner and Fairhurst (1989a); MacFarlane and Ewing (1990); ACDS (1991); de Weger, Pietersen and Reuzel (1991); CPD (1992b)
Gas warfare, war gases: Hendry and Horsburgh (1915); R. Parker (1915a,b); Sieur (1915); Wainwright (1915); Haldane (1917, 1919, 1925); Chemical Warfare Medical Committee (1918–); Edkins and Tweedy (1918); Hunt and Price Jones (1918); Parsons (1918); Baskervffle (1919); Carr (1919); Lidbetter and Monk-Jones (1919); Kerschbaum (1920); Tatham and Miles (1920); Lefebure (1921, 1928); Winternitz, Smith and McNamara (1920); Winternitz *et al.* (1920); Oudry (1924); Serrant (1924); Vedder (1925); Walton (1925); Le Wita (1925); Bloch (1926); Bressou (1926); Sesselberg (1926); von Deimling (1931); Hanslian (1931, 1934); T.J. Mitchell and Smith (1931); Abbott (1933); Dautrebaude (1933); Fessler, Gebele and Prandtl (1933);

Leroux (1933); Mordaq (1933); Zernik (1933); Heeressanitatsinspektion (1934); von Tschischwitz *et al.* (1934); Ferry (1935); Noskoff (1935); Prentiss (1937); Gerchik (1939); National ARP Animal Cttee (1939); G.W. Young (1953); O.K. Clark (1959); McNalty and Mellor (1968); Haber (1975, 1986); McWffliams and Steel (1985); Finch (1986); Withers and Lees (1987b); R.F. Griffiths and Fryer (1988); Butcher (1989a); V.C. Marshall (1989b); Lees and Withers (1992)

Aerosols: C.N. Davies (1961, 1966, 1967); Walton (1971, 1977)

Acrylonitrile: Dudley and Neal (1942); Dudley, Sweeney and Miller (1942); Ministry of Social Affairs (1972); Solomon, Rubin and Okrent (1976); Bochinski, Schoultz and Gideon (1979); HSE (1981 EH 27); EPA (1983); WHO (1983 ECH 28); R.M. Turner and Fairhurst (1989b)

Ammonia: Underwriters Laboratories (n.d.a); WHO (EHC 54); NIOSH (1974 Crit. Doc. 74–136); Lehmann (1886, 1899a); Hess (1911); Flury (1921a, 1928); Haggard (1924); Slot (1938); McCallan and Setterstrom (1940); Thornton and Setterstrom (1940); Weedon, Hartzell and Setterstrom (1940); Caplin (1941); Boyd, MacLachan and Perry (1944); Silver and McGrath (1948); Carpenter, Smyth and Pozzani (1949); Silverman, Whittenberger and Muller (1949); Ting (1950); Weatherby (1952); von Meythaller and Gross (1957); Derobert (1964); Gaultier (1964); Levy *et al.* (1964); Saifutdinouv (1966); Mulder and van der Zalm (1967); Niden (1968); Osmond and Tallents (1968); Zygadowski (1968); McGuiness (1969); Coon *et al.* (1970); Voison *et al.* (1970); Helmers, Top and Knapp (1971); E.S. White (1971); Kass *et al.* (1972); NAS-NRC (1972a); Pernot *et al.* (1972); Prokopeva, Yushkov and Ubasheev (1973); Slack and James (1973); Walton (1973); Eisenberg, Lynch and Breeding (1975); Prokopeva and Yushkov (1975); Taplin *et al.* (1976); Sobonya (1977); Verberk (1977); Vernot *et al.* (1977); Dalton and Bricker (1978); HSE (1978b); Hilado and Cumming (1978); Kondrasuov (1978); Richard, Bouley and Boudene (1978); Richard, Jounay and Boudene (1978); Hatton *et al.* (1979); Kane, Barrow and Alarie (1979); Alarie (1980); Montague and MacNeil (1980); Hofer, Reindle and Hruby (1981); Appelman, ten Berge and Reuzel (1982); Kapeghian *et al.* (1982); Flury *et al.* (1983); O'Kane (1983); S.K. Price *et al.* (1983); K. Ward, Murray and Costello (1983); R.F. Griffiths and Megson (1984); Arwood, Hammond and Ward (1985); Engelhardt and Holliday (1985); Lessenger (1985); WHO (1986 ECH 54); Withers (1986a); Markham (1987a,b); MHAP (1988); Pedersen and Selig (1989); Sakurai (1989); Payne, Delic and Turner (1990); Ryer-Powder (1991); Brockhoff, Petersen and Haastrup (1992)

Aniline: Anon. (LPB 30 1979, p. 165)

Bromine: Lehmann (1887, 1893); L.Hill (1915); Symes (1915a,b); Haggard (1924); Chlopin (1927–); Jolles (1966); Schlagbauer and Henschler (1967); Bitron and Aharonson (1978); Withers and Lees (1986b, 1987a); P.C. Davies and Purdy (1987)

Carbon monoxide: Lewin (1920); NIOSH (1972 Crit. Doc. 73-11000); OSHA (OSHA 2224); HSE (HSW Bklt 29, 1984 EH 43); WHO (EHC 13); Drescher (1920); API (1972 Publ. 4131); Connor (1984); Esposito and Alarie (1989); Sakurai (1989)

Carbon disulfide: WHO (EHC 10); Teissinger and Soucek (1949)

Chlorine: HSE (HSW Bklt 37); WHO (EHC 21); Lehmann (1887, 1899a,b); Anon. (1915a–g); Broadbent (1915); H. Campbell (1915); Golla and Symes (1915); Hake (1915); Klotz (1917); Anon. (1918); Anon (1919); Anon (1920); Underhill (1920); Anon. (1923); Vedder (1925); Anon. (1926); McCord (1926); Chlopin (1927–); Walton and Eldridge (1928); Anon. (1930); Anon. (1933c); David (1933a,b); Skljanskaia, Klaus and Ssidorowa (1935); Skljanskaia and Rappoport (1935); Arloing, Berthet and Viallier (1940); McCallan and Setterstrom (1940); Thornton and Setterstrom (1940); Weedon, Hartzell and Setterstrom (1940); Silver and McGrath (1942); Silver, McGrath and Ferguson (1942); Malone and Warm (1945); Tatarelli (1946); Chasis *et al.* (1947); Baader (1952); Joyner and Durel (1962); Gervais *et al.* (1965); Kowitz *et al.* (1967); C.G. Kramer (1967); Schlagbauer and Henschler (1967); Dixon and Drew (1968); Krause, Chester and Gillespie (1968); Capodaglio *et al.* (1969); Stahl (1969a); Weill *et al.* (1969); Patil *et al.* (1970); Sessa *et al.* (1970); Urogoda (1970); Zielhuis (1970); Adelson and Kaufman (1971); Leube and Kreiter (1971); NAS-NRC (1973a, 1976); BCISC (1975/1); Eisenberg, Lynch and Breeding (1975); T.B. McMullen (1975); Ministry of Social Affairs (1975); NIOSH (1976 Crit. Doc. 76-170); Schwartz (1976); Solomon, Rubin and Okrent (1976); Barrow *et al.* (1977); Bitron and Aharonson (1978); HSE (1978b); Dewhirst (1981a–c); Anon. (1984f); Chlorine Institute (1985 Publ. 63); P. Davies and Hymes (1985); Dokter *et al.* (1985); McWilliams and Steel (1985); MHAP (1985 LPB 64, 1987); Withers (1985, 1988); Withers and Lees (1985a,b, 1987b, 1992); Nussey, Mercer and Fitzpatrick (1986); R.F. Griffiths and Fryer (1988); Holton and Montague (1988); Zwart and Woutersen (1988); CIA, Chlorine Sector Group (1989); V.C. Marshall (1989b, 1990a); Sakurai (1989); R.M. Turner and Fairhurst (1990a); Brockhoff, Petersen and Haastrup (1992); Anon. (1993 LPB 113, p. 26)

Dimethylformamide: Bauer (1980)

Ethylene dichloride: Heppel *et al.* (1946)

Ethylene oxide: CISHC (1975/2); NIOSH (1978 Crit. Doc., 77-200); CIA (1979 RC 14); Flores (1983); Desai and Buonicore (1990)

Halogenated hydrocarbons: Lehmann and Schmidt-Kelh (1936); von Oettingen (1937)

Hydrogen chloride: WHO (ECH 21); Lehmann (1886); Leites (1929); Machle *et al.* (1942); Efflmova (1959, 1964); Jacobziner and Raybin (1962); Stahl (1969b,c); Nagoa *et al.* (1972); Hilado and Furst (1976); NAS/NRC (1976); Barrow *et al.* (1977); Hilado and Gumming (1978); Barrow, Lucia and Alarie (1979); Alarie (1980)

Hydrogen cyanide: Geppert (1889); Hess (1911); Flury and Heubner (1919); Fiihner (1919); Drescher (1920); Koelsch (1920); Reed (1920); Hasselmann (1925a,b); Chlopin (1927–); Schutze (1927); Dschang (1928); Flury (1928); Walton and Witherspoon (1928); Schwab (1929); Barcroft (1931); Hug (1932); Wirth and Lammerhirt (1934); Wirth (1935, 1937); Prentiss (1937); Kendall (1938); McCallan and Setterstrom (1940); Thornton and Setterstrom (1940); Weedon, Hartzell and Setterstrom (1940); Wachtel (1941); Waitt (1942); Wood (1944); British Intelligence Objective Subcommittee (1946); Brophy, Miles and Cochrane (1959); Hilado and Furst (1976); McNamara (1976); NIOSH (1977 Crit. Doc. 77-108); Vernot *et al.* (1977); Hilado and Gumming (1978); Ride (1984a); Holton and Montague (1988); Esposito and Alarie (1989); Sakurai (1989)

Hydrogen fluoride: Ronzani (1909); Muehlberger (1928); Simons (1931); Machle *et al.* (1934); Machle and Kitzmiller (1935); Machle and Scott (1935); Stokinger (1949); Rushmere (1954); Rosenholtz *et al.* (1963); McEwen and Vernot (1970); Darmer, Haun and MacEwan (1972); Hilado and Furst (1976); NIOSH (1976 Crit. Doc. 76-143); Vernot *et al.*

(1977); CIA (1978); Hilado and Cumming (1978); Valentine (1988); Mudan (1989a); HSE (1990 MS(A) 12); R.M. Turner and Fairhurst (1990b)
Hydrogen sulfide: Biefel and Poleck (1880); Lehmann (1892, 1893, 1899a); Haldane (1896); Hess (1911); Haggard and Henderson (1922); Sayers, Mitchell and Yant (1923 BM RI 2491); Haggard (1925); Sayers *et al.* (1925 BM Bull. 231); Gerbis (1927); Schutze (1927); Flury (1928); Walton and Witherspoon (1928); Aves (1929); Yant (1930); Scheidemantel (1933); McCallan and Setterstrom (1940); Thornton and Setterstrom (1940); Weedon, Hartzell and Setterstrom (1940); Slater (1950); Ahlbrog (1951); Kaipainen (1954); Hurwitz and Taylor (1954); Breysse (1961); Milby (1962); Kleinfeld, Geil and Rosso (1964); Kemper (1966); C.L. Evans (1967); Prouza (1970); Simpson and Simpson (1971); Anon. (1975 LPB 3, p. 17); Thorn and Douglas (1976); Archibald (1977); NIOSH (1977 Crit. Doc. 77–158); Vernot *et al.* (1977); NRC (1979); R.P. Smith and Gosselin (1979); WHO (1983 ECH 19); HSE (1985 LPB 63); Lynskey (1985 LPB 63); Amman (1986); Holton and Montague (1988); Kohout *et al.* (1988); R.M. Turner and Fairhurst (1990c)
Methyl isocyanate: Kimmerle and Eben (1964); ten Berge (1985)
Phosgene: Lehmann (1893); Muller (1910); Hess (1911); Dunn (1918); Meek and Eyster (1920); Underbill (1920); Winternitz *et al.* (1920); Flury (1921a, 1928); Laqueur and Magnus (1921); Zeehuisen (1922); Haggard (1924); Chlopin (1927–); Anon. (1928); Hegler (1928); Zangger (1932); Loschke (1933); Prentiss (1937); Kendall (1938); Sartori (1939); Cameron, Courtice and Foss (1941); Wachtel (1941); Waitt (1942); Boyland, McDonald and Rumens (1946); Courtice and Foss (1946); Weston and Karel (1946, 1947); Bickenbach (1947); Box and Cullumbine (1947); Karel and Weston (1947); Gilman *et al.* (1948); A.T. Jones (1952); Suess and Lerner (1956); Henschler and Laux (1960); Ardran (1964); Zielhuis (1970); Kawai (1973); NIOSH (1976 Crit. Doc. 76-137); de Rooij, van Eick and van de Meent (1981); Diller and Zante (1982); Diller (1985); Mulder *et al.* (1986); Mehlman (1987); Zwart (1987); MHAP (1993)
Sulfur dioxide, sulfuric acid: API (75-25); WHO (ECH 8); Ogata (1884); G.W. Jones, Capps and Katz (1918); Zeehuisen (1922); Haggard (1924); Kennon (1927); Flury (1928); Kehoe *et al.* (1932); Weedon, Hartzell and Setterstrom (1939, 1940); McCallan and Setterstrom (1940); Thornton and Setterstrom (1940); Amdur, Silverman and Drinker (1952); Amdur, Schulz and Drinker (1952); Logan (1953); C.A. Mills (1957); Amdur (1958); Leong, MacFarland and Sellers (1961); Anon. (1953); Zielhuis (1970); NIOSH (1977 Crit. Doc. 74-111); Amdur, Dubriel and Creasia (1978); Bitron and Aharonson (1978); Hilado and Cumming (1978); Alarie (1980); Silbaugh *et al.* (1981); Grint and Purdy (1990); R.M. Turner and Fairhurst (1992)
Ozone: Slater (1974); BOHS (1979 Monogr. 3); HSE (1983 EH 38)
Toxic fumes from burning materials, fire extinguishants: BRE (1974 CP 5/74, CP 11/74, CP 12/74); Underwood (1971); H.L. Kaplan and Hartzell (1984); Hartzell, Packham *et al.* (1985); Hartzell, Stacy *et al.* (1985); Hartzell, Priest and Switzer (1985); Alexeeff *et al.* (1986); Doe *et al.* (1986); Hartzell, Grand and Switzer (1987); Tsushiya and Nakaya (1986); Hartzell (1989); G.T. Atkinson, Jagger and Kirk (1992); Babrauskas *et al.* (1992); D.A. Carter (1992); Babrauskas (1993)

Ultratoxics (***see also*** **Table A3.1**) Lamanna (1959)

Table 18.2 *Selected references on toxic release*

Plant design and operation (***see also*** **Table 18.1**)
Crocker (1970); AIChE (1972/65); H.M. Chief Alkali Inspector (1974); Chementator (1975, Apr. 14, 33; Jul. 7, 34; 1977, Jan. 3, 37); Kiang (1976); Archibald (1977); Mukerji (1977); Payne (1978); Buxton (1980); Hewitt (1980); D. Hughes (1980); G.A. Hunt (1980); IChemE (1980/120); Lamb (1980); A. Price (1980); Mecklenburgh (1982); Prugh (1985–); Zanetti (1986a,b); ILO (1989); Grigoriev, Polyakov and Artemev (1990); Sutherland (1990); N.C. Harris (1991); Kuryla (1993)

Toxic gas detectors (***see also*** **Table 18.1**)
R. Zanetti (1986b); Atallah and Guzman (1987)

Toxic release mitigation
N.C. Harris (1987); Hiltz and Brugger (1989); Fthenakis and Zakkay (1990); Schatz and Koopman (1990); van Zele and Diener (1990); Diener (1991); Porter (1991)
Foam: Dimaio and Norman (1988, 1990); B.C. Norman and Swihart (1990)

Emergency planning
Duff and Husband (1974); Zajic and Himmelman (1978); Purdy and Davies (1985 LPB 62)

Shelter
D.J. Wilson (1987, 1990, 1991b); Glickman and Ujihara (1990); D.J. Wilson and Zelt (1990); Zelt and Wilson (1990); McQuaid (1991); Kakko (1992)

Protective clothing
Daugherty, Watson and Vo-Dinh (1992)

Decontamination
W.L. Owen, Sartor and van Horn (1960); Ayers (1964); P.E. James and Wilkin (1969); P.E. James and Menzel (1973); AEC (1975)

Hazard assessment
G.D. Bell (n.d.); Howerton (n.d., 1969); Simmons, Erdmann and Naft (1973, 1974); Dicken (1974, 1975); J.D. Reed (1974); van Ulden (1974); Westbrook (1974); Eisenberg, Lynch and Breeding (1975); Simmons and Erdmann (1975); Hewitt (1976); Setters (1976); Solomon (1976); Solomon, Rubin and Okrent (1976); Lautkaski and Mankamo (1977); V.C. Marshall (1977d, 1982b); HSE (1978b); Zajic and Himmelman (1978); Napier (1979a); N.C. Harris (1982, 1985); Mecklenburgh (1982); Pantony and Smith (1982); Fiksel (1985); Pape and Nussey (1985); IChemE (1986/128); Pietersen (1986c); Withers and Lees (1986a); Baldini and Komosinsky (1988); Thomson and Nightingale (1988); Boykin and Levary (1989); J.K.W. Davies (1989a); Egol (1989a); Gephart and Moses (1989); Vergison, van Diest and Easier (1989); G.T. Atkinson, Jagger and Kirk (1991); Biitzer and Naef (1991, 1992); Grint and Purdy (1990); Nussey, Mercer and Clay (1990); R.F. Griffiths (1991a,b); Touma and Stroupe (1991); Touma *et al.* (1991); Geeta, Tripathhi and Narasimhan (1993); Goldsmith and Schubach (1993); Dunbar *et al.* (1994); Tyler *et al.* (1994)

Particular chemicals
Acrylonitrile: Siccama (1973); Solomon, Rubin and Okrent (1976)
Ammonia: Resplandy (1967); W.L. Ball (1968b); Inkofer (1969); Medard (1970); Comeau (1972); MacArthur (1972); J.D. Reed (1974); Eisenberg, Lynch and Breeding (1975);

Lonsdale (1975); Luddeke (1975); V.C. Marshall (1977b); HSE (1978b); Harvey (1979b); Baldock (1980); R.F. Griffiths (1981a); Raj (1982); R.H. Roberts and Handman (1986); Markham (1987b); Gephart and Moses (1989); Fallen (1990); Sutherland (1990); Langeluedecke (1991)
Chlorine: G.D. Bell (n.d.); Howerton (n.d., 1969); Hanslian (1937); Prentiss (1937); Romcke and Evensen (1940); Simmons, Erdmann and Naft (1973, 1974); Dicken (1974, 1975); Westbrook (1974); Eisenberg, Lynch and Breeding (1975); Chlorine Institute (1975 MIR-71, 1982 Pmphlt 74); Haber (1975, 1986); Setters (1976); Solomon, Rubin and Okrent (1976); V.C. Marshall (1977b); HSE (1978b); Harvey (1979b); Meslin (1981); Emerson, Pitblado and Sharifi (1988); J.L. Woodward and Silvestro (1988); Anon. (1989 LPB 86, p. 1); Deaves (1989); Gephart and Moses (1989); Lin and Shroff (1991); Anon. (1993 LPB 113, p. 26)
Hydrogen cyanide: Solomon, Rubin and Okrent (1976)
Hydrogen fluoride: Crocker (1970); HSE (1978b); Hague and Pepe (1990); Schatz and Koopman (1990); Tilton and Farley (1990); van Zele and Diener (1990); Diener (1991)
Hydrogen sulfide: Echols (1976); Linskey (1985 LPB 63); Anon. (1989 LPB 87, p. 1); D.J. Wilson (1991a)
Phosgene: V.C. Marshall (1977b)
Sulfur dioxide: Sumner and Pfann (1976); Nyren and Winter (1987)
Vinyl chloride: McKinnon (1974); Kiang (1976); Mukerji (1977)

Indicators of cloud contour, including vegetation damage
Fryer and Kaiser (1979 SRD R152); Arner, Johnson and Skovronski (1986); R.F. Griffiths and Smith (1990)

Simulation of accidents
M.P. Singh, Kumar and Ghosh (1990)

18.1.1 Modes of exposure

Toxic chemicals enter the body in three ways: (1) inhalation, (2) ingestion and (3) external contact. Generally, gases, vapours, fumes and dusts are inhaled and liquids and solids are ingested. Entry may also occur through the intact skin or the mucous linings of the eyes, mouth, throat and urinary tract.

18.1.2 Effects of exposure

Exposure to some chemicals results in temporary or permanent damage to organs of the body, that is, poisoning. There is a wide variety of types of damage caused by toxic substances.

The effects of exposure to toxic chemicals may be acute or chronic. Acute effects result from a single exposure to a high concentration of the chemical; chronic effects result from exposure to low concentrations, perhaps over a large part of a working lifetime. With the latter type of exposure the effects may be latent and may show themselves only after many years. It is also possible for the effects of a single exposure to a high concentration to be latent.

A toxic chemical may induce a graded or a quantum response. A graded response refers to the symptoms shown by an individual, which become progressively more severe as the dose in increased. Exposure to carbon monoxide, for example, results in a set of symptoms of increasing severity. The graded responses for this and other gases are shown in Table 18.3.

A quantum response, on the other hand, refers to the effect of a toxic chemical on a population, in which some individuals suffer the defined injury and others do not. A person either has or does not have mesothelioma from crocidolite ('blue') asbestos. In this case it is the proportion of cases in the population that rises with an increasing dose level.

The effects of acute exposure to toxic chemicals include:

(1) irritation –
  (a) respiratory,
  (b) skin,
  (c) eyes;
(3) narcosis;
(4) asphyxiation –
  (a) simple,
  (b) chemical;
(2) systemic damage.

Inhalation of some substances (e.g. chlorine) causes respiratory irritation. This irritation can serve as a warning. There are some chemicals, however, which reach a toxic level before they cause appreciable irritation and thus give no warning.

Some substances (e.g. hydrocarbon vapours) have narcotic effects so that the person's responses are affected and he may become exposed to an accident. With certain chemicals (e.g. toluene diisocyanate) the effect is that the person becomes euphoric and oblivious of danger so that he is liable to perform hazardous acts.

Gases which act as simple asphyxiants (e.g. nitrogen and helium) merely displace oxygen in the atmosphere so that the concentration falls below that needed to maintain consciousness. But there are also chemical asphyxiants (e.g. carbon monoxide and hydrogen cyanide) that have a specific blocking action and prevent a sufficient supply of oxygen from reaching the tissues.

The effects of chronic exposure to toxic chemicals tend to be induction of injury or disease. One of the most important of these diseases is cancer. Some chemicals induce cancer. In addition to these carcinogens there also mutagens, which induce gene changes, and teratogens, which induce birth defects.

Some chemicals are much more liable than others to accumulate in the body over the long term. Such bioaccumulative chemicals are particularly harmful.

Different toxic chemicals affect different sites in the body. The effect of such chemicals depends on the target organ.

It will be apparent, therefore, that it is difficult to express the toxicity of different chemicals in terms of a common equivalent. Use is sometimes made of the term 'chlorine equivalent'. This is discussed in the First Report of the ACMH, which makes the following observations:

> Toxicity depends on a number of factors and no simple hard and fast rules can be laid down. The mode of action depends not only on the nature of the chemical but upon the dose received and the time scale of exposure. Strictly speaking the term 'chlorine equivalent' can be given relevance only in connection with slow, corrosive irritant chemicals having similar solubility in inhalation. Chemicals such as sulphur dioxide, ammonia, acrolein

Table 18.3 *Effects of different concentrations of some toxic gases*

Gas	*Concentration* (ppm)	*Reference*[a]
Ammonia		
TLV[c]	25	ACGIH
Concentration detectable by odour	20	Matheson
Concentration causing severe irritation of throat, nasal passages and upper nasal tract	400	Matheson
Concentration causing severe eye irritation	700	Matheson
Concentration causing coughing, bronchial spasms, possibly fatal for exposure of less than 30 min	1700	Matheson
Concentration causing oedema, strangulation, asphyxia, fatal almost immediately	5000	Matheson
Carbon monoxide	(%v/v)	
TLV	0.005 (50 ppm)	ACGIH
Concentration inhale for 1 h without appreciable effect	0.04–0.05	Matheson
Concentration causing a just appreciable effect for exposure of 1 h	0.06–0.07	Matheson
Concentration causing unpleasant symptoms but not dangerous for exposure of 1 h	0.1–0.12	Matheson
Concentration dangerous for exposure of 1 h	0.15–0.2	Matheson
Concentration fatal for exposure of less than 1 h	0.4	Matheson
Chlorine		
TLV	1	ACGIH
Minimum concentration detectable by odour	1	*Chlorine Code*
	3.5	Matheson
Maximum concentration inhalable for 1 h without damage	4	Matheson
Minimum concentration causing throat irritation	15	Matheson
Minimum concentration causing coughing	30	Matheson
Concentration dangerous for exposure of 30 min	40–60	Matheson
Concentration probably fatal after a few deep breaths	1000	Matheson
Hydrogen sulfide		
TLV	10	ACGIH
Concentration causing slight symptoms after exposure of several hours	70–150	Matheson
Maximum concentration inhalable for 1 h without serious effects	170–300	Matheson
Concentration dangerous for exposure of 0.5–1 h	400–700	Matheson
Phosgene		
TLV	0.1	ACGIH
Minimum concentration detectable by odour	0.5–2	*Phosgene Code*
	5.6	Matheson
Maximum concentration for exposure of 15 min	1	*Phosgene Code*
Minimum concentration affecting throat	3.1	Matheson
Concentration probably fatal for exposure of 30 min	5	Matheson
Concentration dangerous for exposure of 0.5–1 h	25	Matheson
Concentration rapidly fatal for short[b] exposure	50	*Phosgene Code*
Concentration capable of causing lung injury in 2 mm	167	Matheson

[a] ACGIH—Threshold Limit Values for 1976 (HSE, 1977 EH 15).
Matheson—*Matheson Gas Data Book* (Matheson Company, 1961).
Chlorine Code—Code of Practice for Chemicals with Major Hazards: Chlorine (BCISC, 1975/1).
Phosgene Code—Code of Practice for Chemicals with Major Hazards: Phosgene (CISHC, 1975/3).
[b] Presumably several minutes; this code defines 15 min as a prolonged exposure.
[c] TLV, threshold limit value.

and nitrogen dioxide are all irritant yet have such different sites of action and variable effects as to make even an approximate calculation of a 'chlorine equivalent' difficult. The problem becomes even more difficult when one considers the potential toxicity of chemicals such as carbon monoxide that are not predominantly irritant. Mechanisms of toxicity are almost as varied as the classes of chemical that could be released.

18.2 Toxic Substances

Some factors relevant to toxic substances include:

(1) generation of the substance;
(2) toxic concentrations;
(3) effects of exposure;
(4) detectability by odour;

(5) precautions in handling;
(6) leak detection;
(7) first aid.

Most toxic substances that present a hazard in the chemical industry are chemicals that are deliberately produced, but some are generated as by-products by accident. Carbon monoxide and carbon dioxide are generated by combustion processes either in the process itself or in fires. Nitrogen oxides may be given off in welding. Ultratoxics may arise from side reactions.

The number of chemicals used in industry is very large and grows each year. Various figures have been quoted for the number of chemicals involved. According to Langley (1978) in the decade prior to 1978 approximately 4 million new chemicals had been identified, although at least 75% of these had been cited only once in the literature. Of more practical relevance is the estimate of the UK Chemical Information Centre (UKCIS), also quoted by Langley, that there are some 20,000–30,000 chemicals manufactured in quantities greater than 1 te per annum.

For the number of new chemicals coming into use each year in the United Kingdom at this level of output, Langley gives an estimate of some 300–400. For the United States the annual number of new chemicals has been estimated as about twice this value.

The problems posed by toxic chemicals have generally been perceived primarily in terms of noxious effects resulting from chronic exposure to chemicals that possess a degree of toxicity which has not been appreciated. More recently, there has been increased concern over the threat of large scale acute poisoning from the accidental release of toxic chemicals.

Early instances of the discovery of the noxious properties of substances include those of radium, phosphorus, lead, asbestos and naphthylamines. More recent examples include: polychlorinated biphenyls (PCBs), vinyl chloride and benzene. Even if the toxicity of a particular substance has been established, instances of exposure may still occur.

Some examples of the discovery of toxic effects or of instances of exposure to a substance with known toxic effects that have made impact in the United Kingdom have been given by Pittom (1978) and include:

1965 Bladder cancer from antioxidants (rubber industry)
1972 Lead poisoning (Avonmouth, Isle of Dogs)
1974 Angiosarcoma from vinyl chloride (poly vinyl chloride (PVC) plants)
1975 Asbestos related diseases (Hebden Bridge)
1976 TCDD (2,3,7,8-tetrachlorodibenzo-*p*-dioxin) (Seveso)

The dates refer to the years when publicity was at its height.

It is necessary, therefore, to take measures to ensure that the long-term, or chronic, toxic hazard is kept under good control. Of particular importance is the control of exposure to carcinogens. One of the principal means of control is the establishment of exposure limits, or hygiene standards. Over the years these limit values have tended to be reduced, and in some cases the reductions have been dramatic. For example, in the United States the limits for asbestos were reduced over the period 1938–83 as follows (Corn and Corn, 1984): 1938, 30 fibres/cm^3; 1970, 12 fibres/cm^3; 1971, 2 fibres/cm^3; and 1983, 0.5 fibres/cm^3.

There have also been occasional large releases of toxic chemicals of which the escape of methyl isocyanate at Bhopal in 1984 was much the worst. Good control of the acute toxic hazard posed by a large release is equally important.

18.3 Toxicity Assessment

18.3.1 Toxicity data

Comprehensive accounts of occupational health risks involving toxic hazards are given in a number of texts, including the following: Toxicity of Industrial Metals (Browning, n.d.a), Toxicity of Industrial Organic Chemicals (Browning, n.d.b), Industrial Hygiene and Toxicology (Patty, 1948–), with its later edition *Patty's Industrial Hygiene and Toxicology* (Clayton and Clayton, 1991 ACGIH/73); Dangerous Properties of Industrial Materials (Sax 1957–), with its later edition-*Salt's Dangerous Properties of Industrial Materials* (Lewis, 1992 ACGIH/89); *Toxicity and Metabolism of Solvents* (Browning, 1965); *Toxicology of Drugs and Chemicals* (Deichmann and Gerarde, 1969); *Hazards in the Chemical Laboratory* (G.D. Muir, 1971–); *Registry of Toxic Effects of Chemical Substances* 1981–82 (Tatken and Lewis, 1984); *Rapid Guide to Hazardous Chemicals in the Workplace* (Sax and Lewis, 1986), with its later edition (Lewis, 1990 ACGIH/49); *Toxicology: the Basic Science of Poisons* (Casarett and Doull, 1975), with its later edition (Amdur, Doull and Klaassen, 1991, ACGIH/54); *Chemical Hazards in the Workplace* (Scott, 1989 ACGIH/29); *Neurotoxicity Handbook* (Singer, 1990 ACGIH/46); *Chemical Hazards of the Workplace* (Hathaway *et al*., 1991 ACGIH/55); *Hazardous Chemicals Desk Reference* (Lewis, 1991, ACGIH/60); and *Handbook of Toxic and Hazardous Chemicals and Carcinogens* (Sittig, 1991/ACGIH/59).

The American Conference of Government Industrial Hygienists (ACGIH) and the American Industrial Hygiene Association (AIHA) issue a number of publications on exposure limits for toxic chemicals. These are considered in Section 18.5.

The National Institute for Occupational Safety and Health (NIOSH) issues Criteria Documents for a large number of chemicals and also several other series: *Occupational Hazard Assessments, Joint Occupational Health Recommendations and Special Hazard Reviews*. Other publications include *Occupational Health Guidelines for Chemical Hazards* (NIOSH, 1981/6) and *Pocket Guide to Chemical Hazards* (NIOSH 1990/18). The Occupational Safety and Health Administration (OSHA) also issues the Chemical Information Manual (OSHA, 1991/1).

Chemical Safety Data Sheets on toxic chemicals were formerly issued by the Manufacturing Chemists Association (MCA), but many of these have been withdrawn.

Information on toxicity is given in a number of publications by the Health and Safety Executive (HSE). EH 40/94 *Occupational Exposure Limits 1994* (HSE, 1994) is supported by EH/64 *Occupational Exposure Limits: Criteria Document Summaries* (HSE, 1992). Series relevant to toxicity are the Environmental Hygiene (EH) series, the Medical (MS) series and the Toxicity Review (TR) series.

There are a number of databases for the toxicity of chemicals, many of which are available on computer. They include the following:

CHRIS	Chemical Hazard Response Information System (US Coast Guard)
OHMTADS	Oil and Hazardous Materials Technical Assistance Data System (Environmental Protection Agency (EPA))

RTECS	Registry of Toxic Effects of Chemical Substances (NIOSH)
TOXLINE	National Library of Medicine toxic substances database
HSELINE	HSE toxic substances database

An account of these and other systems is given in Chapter 29.

There is a good deal of guidance available on the handling of individual toxic substances. An early compilation was the Gas Data Book (Matheson Company, 1961). This deals with toxic concentrations, symptoms of exposure, precautions in handling and first aid.

Much relevant information is given in materials safety data sheets (MSDSs), which are described in Chapter 8. There are a number of MSDS compilations. They include Compilation of Safety Data Sheets for Research and Industrial Chemicals (Keith and Walters, 1985–), Chemical Safety Data Sheets (Walsh, 1988, vol. 1; A. Allen, 1988, vols 2–5; Kluwer Publishers, 1992) and Croner's Substances Hazardous to Health (Kellard, 1993).

Other guidance is given in codes such as Codes of Practice for Chemicals with Major Hazards by the Chemical Industries Association (CIA) and in the EH series of the HSE.

The toxicity of chemicals is a field in which, at present, the situation changes particularly rapidly and the importance of seeking the most up-to-date information cannot be too strongly emphasized.

18.3.2 Toxicity testing

Information on toxicity is often incomplete or non-existent. This is not surprising, since the number of chemicals used in industry is so large. Therefore, in some cases it is necessary to conduct tests in order to obtain information on toxicity. Toxicity testing is now a well-established activity which is conducted to ensure safety not only in the manufacture of chemicals but also in the use of food, drugs and cosmetics. General accounts are given by Hemsworth (1974), J.T. Carter (1976) and Neal and Gibson (1984).

Methods that are used to assess toxicity include (1) micro-organism tests and (2) animal experiments. The object of toxicity testing is to obtain quantitative information on toxic effects. The simple classification of substances as 'toxic' or 'non-toxic' is of little value.

Toxicity testing is expensive. According to C.R. Pearson (1982) the cost of the Base Set of tests required under the EEC Sixth Amendment to the Dangerous Substances Directive is £25,000–50,000. Detailed information on cost of specific tests for the United States is given by A.S. West (1986). He also estimates the costs of the EEC Premanufacturing Data Set of tests and of the Level 1 and Level 2 sets as $100,000, $500,000 and several million dollars, respectively.

The assessment of toxicity is a matter for experts. There are a number of organizations which specialize in toxicity testing and assessment, as described below.

18.3.3 Micro-organism tests

Accounts of micro-organism tests are given in In Vitro Toxicity Testing of Environmental Agents (Kolber *et al.* 1983) and by Neal and Gibson (1984). Studies of the effects of chemicals on micro-organisms are used for screening chemicals, particularly for possible carcinogenic, mutagenic or teratogenic effects. Developments in this area include, in particular, the tests used by Ames and co-workers (Ames, 1971).

18.3.4 Animal experiments

The other main type of test is experimentation on animals. This allows the use of the normal techniques of controlled experimentation. Although some earlier work made use of other animals such as monkeys, dogs, cats and rabbits, the animals now almost universally used are mice and rats.

The testing is done according to a strict protocol. The animal is given a fixed dose of chemical or is exposed to a gas of a given concentration for a fixed time and its health is then monitored for a defined observation period. Pathological investigation may also be performed. For certain types of test, such as those on inhalation toxicity, the observation period may be 10–14 days. For other types, such as those on carcinogens, it may extend to 2 or 3 years.

For many tests the objective is to determine the dose or concentration which is lethal to 50% of the animals. This is the lethal dose LD_{50} for an orally administered substance and the lethal concentration LD_{50} for an inhaled gas (see Section 18.11). In the latter case the period of exposure must also be defined. Frequently there is a legislative requirement for the determination of the LD_{50} as an index of toxicity. The corresponding index of aquatic toxicity is the median tolerance limit $TL_m x$, which is the concentration lethal to 50% of the test species for an exposure period of x hours.

There are various problems in the use of animal experiments. The first of these is the ethical problem. For this reason there are increasing pressures to limit such experiments to those for which high priority can be established.

Animal experiments are also both expensive and time-consuming. As already mentioned, experiments on the long-term effects of exposure to low concentrations of chemicals may involve extensive observation periods.

In order to obtain statistically valid results it is necessary to use quite large numbers of animals. This is a problem in almost all instances, but particularly so where the level of risk which is of interest is low. There is then the further problem of interpreting the results obtained and extrapolating them from other species to man.

18.3.5 Epidemiology

Another approach to the assessment of toxicity is epidemiology. Epidemiological studies are based on comparisons of disease or abnormality between the group under study and a control group. This approach is applicable to situations where a number of people have been exposed, often, though not always, over a period of years.

Accounts of epidemiology are given in Medical Record Linkage (Acheson, 1967), *Epidemiology and Disease* (Q.P. Fox, Hall and Elvaback, 1970), *An Introduction to Epidemiology* (Alderson, 1976), *Guide for the Management, Analysis and Interpretation of Occupational Mortality Data* (NIOSH, 1990/19), *Exposure Assessment for Epidemiology and Hazard Control* (Rappaport and Smith, 1991 ACGIH/56), and by Harrington (1980a) and Neal and Gibson (1984).

There have been a number of important epidemiological investigations of toxic substances, including those of radium, β-naphthylamine, lead, asbestos and vinyl chloride.

Epidemiological studies have the great drawback that, by their nature, they yield information on the existence of a toxic effect only after people have fallen victim to it. This drawback is most serious where the effects are latent rather than acute, because in this case even the initiation of control measures cannot prevent disease, due to the backlog of previous exposure. This problem of lag has become much more important as the rate at which new substances are

introduced has increased. Despite this, epidemiology is an important tool for toxicity assessment, as evidenced by the number of chemicals that have been identified as noxious by this means.

There are certain methodological problems in the epidemiological approach. One is the difficulty of determining the degree of exposure. In some cases, for example, the best estimate which investigators have been able to make of the level of exposure has been the threshold limit value current in the period concerned. Another difficulty is in defining the control group.

In practice, where a positive correlation is obtained between exposure and disease, this tends to be in cases in which a relatively small number of people have been exposed to quite high concentrations. Conversely, cases where a large number of people have been exposed to low concentrations tend to yield negative results.

The epidemiological approach has certain limitations. It is relatively easy to show a correlation between an agent and a disease, but it may only be possible to establish a causal relation by experiments that cannot normally be justified. Another is that, whereas a rare disease can be detected as a relative excess of the disease among small numbers of people, the demonstration of a common disease as a relative excess requires the investigation of a large population.

The epidemiological method may be modified by investigating not only overt manifestations of the disease but also pre-disease phenomena such as those revealed by urine tests or radiography.

18.3.6 Toxic load

The correlation of toxicity data requires the definition of the toxic load. This is the independent variable in terms of which toxic injury is expressed. Toxic load is thus a form of injury factor.

In the case of an orally administered dose, the toxic load L is simply the dose d:

$$L = d \qquad [18.3.1]$$

In the case of an inhaled gas the toxic load is, in general, some function of concentration c and the time t:

$$L = f(c, t) \qquad [18.3.2]$$

This function may simply be the product

$$L = ct \qquad [18.3.3]$$

but it may alternatively be of the form

$$L = ct^{m} \qquad [18.3.4]$$

For acute inhalation toxicity of irritant gases the value of m for animals tends to be less than unity and is often of the order of 0.5 (Doe and Milburn, 1983).

18.3.7 Toxic load-response relation

Given the form of the toxic load, a correlation may be sought between the toxic load and the proportion of the population suffering a defined degree of injury. This correlation is the toxic load-response relation. This term is preferred here to the more usual dose-response relation, since toxic load is a more general term than dose.

A distribution that is widely used to correlate data for toxic injury, as for injury of other kinds, is the log-normal distribution. Associated with the log-normal distribution is the probit equation.

A particular problem arises at low levels of toxic load, because the precise relationship between toxic load and the proportion affected is a critical issue in setting exposure limits. Figure 18.1 illustrates two possible relations. With the linear relation A there is no lower limit below which there is no noxious effect, whereas with the sigmoidal relation B, there may be said to be a 'threshold' below which the effect of the toxic load is negligible.

It is frequently difficult to distinguish between these two types of curve and to establish whether there is or is not a threshold. This is the case particularly where the numbers of workers involved are small and the conditions of exposure are variable.

There are relatively few toxic load-response relations established for toxic substances. Apart from those for tobacco, alcohol and certain drugs, Acheson and Gardner (1981) recognize for cancer only two such relations: one for chrysotile asbestos and one for ionizing radiation. The former is that given in the work of Liddell, McDonald and Thomas (1977) in a study of the effect of chrysotile asbestos dust on some 11,000 workers in Quebec, which gives a linear relation passing close to the origin and is interpreted by these authors as indicating no safe threshold.

Further discussions of the toxic-load response are given by C.C. Brown (1984) and Snyder (1984). The latter describes different ways of plotting the load-response curve and gives a number of such curves obtained in animal experiments.

Various equations have been developed for the toxic load-response relations at low levels of toxic load, and statistical methods have been applied to obtain fits to the data. There are deficiencies, however, in a purely statistical approach and it may be more fruitful to support such work with exploration of the toxicokinetics. An example of work on these lines is that of Gehring, Watanabe and Park (1979), who studied the load-response relation for vinyl chloride by modelling the metabolism of the chemical in the body and examining different empirical equations for this relation in the light of the model. A further treatment of the relation

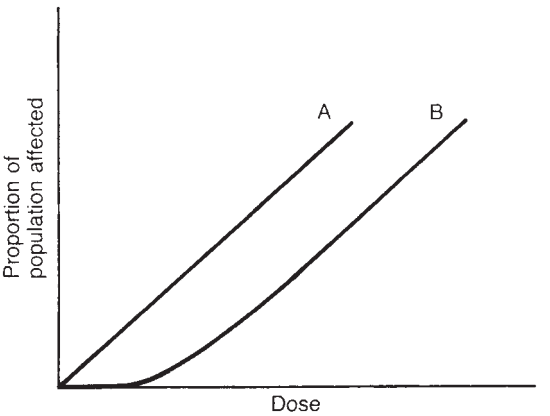

Figure 18.1 *Some idealized load-response relations for quantum response*

between load-response curve and toxicokinetic modelling is given by C.C. Brown (1984).

18.3.8 Toxicokinetic modelling

The unsteady-state modelling of the effects of chemicals in the body is widely practised by pharmacologists, who have developed a number of pharmacokinetic models. The typical model is for a drug which is taken in a single dose. Accounts of such models include those given for E. Nelson (1961), Casarett and Doull (1975), Tuey (1980), Rogers, Specter and Trounce (1981) and Albert (1985).

One of the simplest models is the one-compartment model with finite rate elimination, which is illustrated in Figure 18.2. For this model the two cases commonly treated are the impulse and the step response, the first corresponding to the instantaneous introduction of the chemical and the second to the constant input of the chemical into the body, the prior concentration being zero in both cases. For the first case

$$\frac{dX}{dt} = -k_e X \qquad [18.3.5]$$

with

$$X(0) = D_0 \qquad [18.3.6]$$

where D_0 is the dose of the chemical, k_e is the elimination constant and X is the mass of chemical in the body. For the second case

$$\frac{dX}{dt} = D - k_e X \qquad [18.3.7]$$

where D is the dose rate. The concentration C is given by

$$C = X/V_d \qquad [18.3.8]$$

where V_d is the apparent volume of distribution of the chemical in the body. The chemical is distributed between the bloodstream and other body matter, both aqueous and non-aqueous, and the total effective capacity constitutes the apparent volume of distribution. For elimination after an instantaneous input of the chemical

$$C = C(0)\exp(-k_e t) \qquad [18.3.9]$$

From Equation 18.3.5 the half-life $t_{1/2}$ of the chemical in the body is $0.693/k_e$. Some typical half-lives of drugs in the body, as given by Albert (1985), are aspirin 0.3 h, morphine 3 h, quinidine 6 h, diazepam 50 h and phenobarbital 86 h.

The model describes the variation of concentration with time of the chemical in the body and is based on the assumption that the body has a mechanism for elimination of the chemical. Elimination occurs by metabolism or secretion.

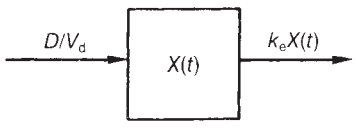

Figure 18.2 *One compartment model of a toxic chemical in the human body*

Similar models may be used to explore toxic effects, and are then termed toxicokinetic models. Toxicokinetic models provide valuable guidance on the interpretation of empirical results, both in applying the results of animal experiments to man and in assessing the shape of the toxic load-response curve at low toxic loads.

18.3.9 Statistical interpretation

Statistical methods have an important part to play in the design and interpretation of animal experiments, in the interpretation of toxic load-response data and in estimating the parameters of correlations.

Accounts of the application of statistics to these problems are given in *The Statistics of Bioassay* (Bliss, 1952) and *Probit Analysis* (Finney, 1971).

For obvious reasons the number of animals, which can be used in gas toxicity experiments has to be kept as low as possible and the statistical interpretation of the results is therefore crucial. It has been shown by Trevan (1927) that for a particular dose–mortality determination the confidence level depends on the number of animals and on the mortality. He applied the binomial expansion

$$(p+q)^N = 1 \qquad [18.3.10]$$

where p and q are the probabilities of death and survival, respectively, and N is the number of animals in the experiment. Then for the distribution

$$\text{Mean} = Np$$

$$\text{Standard deviation } \sigma = (pqN)^{1/2}$$

$$\text{Confidence limits} = Np + z\sigma$$

where z is the number of standard deviations corresponding to the confidence level.

Applying Trevan's method with a 95% confidence level, the results given in Table 18.4 and Figure 18.3 are obtained. It can be seen that for experiments with small numbers of animals the confidence limits for 50% mortality are wide and those for other mortalities such as 25% (or 75%) and 10% (or 90%) they are even wider.

Thus for a given confidence level it is necessary to use more animals to determine an LC_{10} or LC_{90} than an LC_{50}

Table 18.4 *Expected numbers of deaths in experimental animals (Withers and Lees, 1985a; after Trevan, 1972) (Courtesy of Elsevier Science Publishers)*

Mortality (%)	*N*	σ	$z\sigma$	*Np*	*Range*
50	10	1.581	3.099	5	2–8
	20	2.236	4.383	10	6–14
	30	2.739	5.368	15	10–20
	40	3.162	6.198	20	14–26
	50	3.536	6.931	25	18–32
	60	3.873	7.591	30	22–38
	70	4.183	8.199	35	27–43
	80	4.472	8.765	40	31–49
	100	5.000	9.800	50	40–60
25	30	2.372	4.649	7.5	3–12
	100	4.330	8.487	25	17–33
10	30	1.643	3.220	3	0–6
	100	3.000	5.880	10	4–16

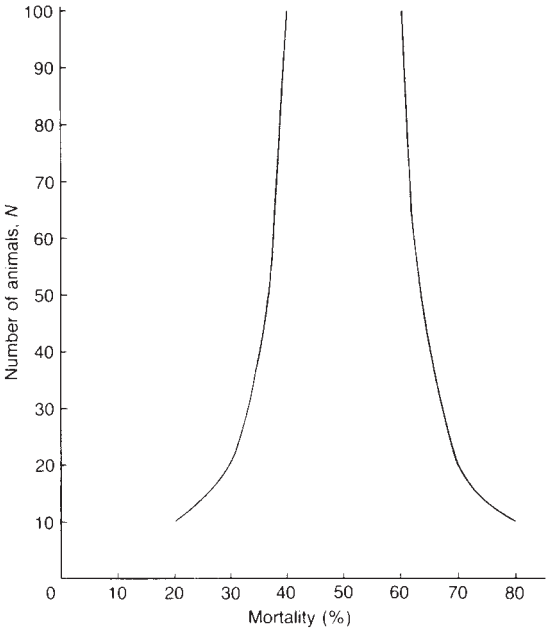

Figure 18.3 *Expected numbers of deaths in experimental animals (Withers and Lees, 1985a; after Treven, 1927) (Courtesy of Elsevier Science Publishers)*

(see Section 18.11). Alternatively, and this is the more usual case experimentally, for a given number of animals the confidence in the LC_{10} and LC_{90} values is less than that in the LC_{50}.

A method widely used for determining the lethal toxicity parameters and confidence limits in a study where groups of animals are exposed to different concentrations for a fixed period is that of Litchfield and Wilcoxson (1949). The method requires information on the numbers of animals and the numbers of concentrations and yields the LC_{50}, the LC_{16} and the LC_{84} and the confidence limits.

18.3.10 Extrapolation between species

The application to man of results from experiments on animals is an area of considerable difficulty and uncertainty. With many substances different species exhibit similar reactions and extrapolation to man may be made. But there are also many examples of different reactions to the same chemical in different species. For example, penicillin causes lethal haemorrhage enteritis in guinea pigs, but is used medically in man, while β-napthylamine, which is carcinogenic to man, does not cause bladder cancer in rats.

Accounts of the principles underlying the extrapolation of empirical results between species are given in *Detoxification Mechanisms* (R.T. Williams, 1959), *Hawk's Physiological Chemistry* (Oser, 1965), *Mammalian Protein Metabolism* (Munro, 1969) and *Drug Metabolism: From Microbe to Man* (Parke and Smith, 1977) and by Freireich *et al.* (1966), S.B. Baker, Tripod and Jacob (1970), Rail (1970), F.J. Miller, Menzel and Coffin (1978), Paddle (1980), Purchase (1980), Oser (1981), Menzel and Smolko (1984) and ten Berge and Zwart (1989).

One general principle is that the toxic effect is likely to be similar only if the target organ is the same in the two species. Another general principle is that what matters is the quantity of the toxin which reaches the target organ, rather than simply the quantity which enters the body. These two principles are applicable in the interpretation of the chronic effects of chemicals such as carcinogens.

The extent to which extrapolation can be made between two species is illustrated by the data given by Purchase (1980). He examined data on 250 chemicals tested for carcinogenicity on rats and mice and found the following results:

126 chemicals positive for cancer in rats; 87% positive for mice also
119 chemicals negative for cancer in rats; 82% negative for mice also
130 chemicals positive for cancer in mice; 84% positive for rats also
115 chemicals negative for cancer in mice: 85% negative for rats also

A widely used rule-of-thumb in toxicology is that if consistent results are obtained for three animal species, they may be treated, with caution, as applicable to humans.

For the inhalation toxicity of irritant gases, the target organ is the respiratory system and the quantity of toxic gas reaching the organ is relatively well defined. In this case the specific loads of toxic gas on the respiratory system of each species may be compared.

18.3.11 Toxic risk assessment

The information obtained from toxicity assessments of the kind just described may be used to make a toxic risk assessment for a particular chemical or plant. There are two rather different kinds of toxic risk assessment. One is the risk assessment undertaken by the regulatory agency in order to determine the precautions to be taken and to set the hygiene limits. The other is that carried out by a manufacturer in order to define the requirements for plant design and operation.

Accounts of toxic risk assessment are given in *Risk Assessment in the Federal Government: Managing the Process* (NAS/NRC, 1983), *Assessment and Management of Chemical Risks* (Rodricks and Tardiff, 1984a), *Toxicological Risk Assessment* (Clayson, Krewski and Munro, 1985), *The Risk Assessment of Environmental Hazards* (Paustenbach, 1989 ACGIH/37) and by Bridges (1985).

The National Academy of Sciences (NAS) report considers toxic risk assessment as involving four stages: (1) hazard identification, (2) dose-response assessment, (3) exposure assessment and (4) risk characterization.

Some of the problems of dose-response, or toxic load-response, assessment have already been considered. Clearly the existence or otherwise of a threshold value below which any noxious effect is negligible is a key issue. The definition of the level of exposure to be expected is also difficult but important. Once the risks have been assessed, they may be evaluated using suitable risk criteria.

In the United States, toxic risk assessment has been used in the setting of hygiene standards. Thus for inorganic arsenic, the OSHA estimated, using a linear dose-response model, that for 1000 workers over a working lifetime there would be 8 excess deaths at a level of 10 mg/m^3, 40 at 50 mg/m^3 and 400 at 500 mg/m^3, and on the basis of this assessment reduced the hygiene standard from 500 to 10 mg/m^3.

In justifying this decision, the OSHA stated

> The level of risk from working a lifetime of exposure at 10 mg/m^3 is estimated at approximately 8 excess lung cancer deaths per 1000 employees. OSHA believes that this level of risk does not appear to be insignificant. It is below risk levels in high-risk occupations but it is above risk levels in occupations with average levels of risk.

18.3.12 Relevant organizations

There are a rather large number of organizations involved in the assessment of toxic hazards, as regulatory bodies, research institutes, industrial groupings and so on. Some of these are listed in Table 18.5. Brief accounts of the function and activities of many of these organizations are given by Deisler (1984b), as shown in the table.

18.4 Control of Toxic Hazard: Regulatory Controls

There is a worldwide trend towards much stricter regulatory control of toxic chemicals. Elements of such control include determination of the properties of the substances, limitation of emissions to the atmosphere, setting of limits for airborne concentrations, monitoring and control of airborne concentrations, monitoring of health of workers and assessment of risk to workers. The legislation in the European Commission, the United Kingdom and the United States on toxic chemicals has been outlined in Chapter 3. This section gives further details.

18.4.1 Control strategies

The control of the chronic toxic hazard needs to be based on a coherent strategy. The outline of such a strategy is given by Lowrance (1984), in a review which is concerned specifically with carcinogens, but which is of wider applicability. He argues that there is need for a framework that allows different risks to be compared and that the approach taken should be more explicit.

18.4.2 Regulatory controls in Europe

In the European Commission, the Sixth Amendment to the Dangerous Substances Directive (79/831/EEC) creates requirements for the notification and testing of new chemicals. Existing chemicals are listed in the European Core Inventory of Existing Substances (ECOIN) and the European Inventory Existing of Commercial Chemical Substances (EINECS).

For new chemicals a manufacturer is required to submit a premarketing notification (PMN). The information required covers the chemical and its chemical and physical properties, the health effects, the ecological effects, the production volume and major uses, and the storage, transport and ultimate disposal. The level of manufacture that attracts notification is 1 te per annum. Intermediates for use only on site and polymers are excluded from the notification requirements. The inventory of chemicals is a static one. A manufacturer of a chemical must notify a new chemical that is not on the list, even if this has already been done by another manufacturer.

The information required on the properties of the chemical was originally defined in the Base Set given in the Sixth Amendment and subsequently specified in the minimum premarketing data (MPD) set shown in Table 18.6.

For chemicals to be manufactured in quantities larger than 1 te per annum further tests are required. The trigger levels are:

Table 18.5 *Some organizations involved in assessment of toxic hazards*

	Reference[a]
A EEC	
Advisory Committee on Safety, Hygiene and Health at Work (to Council of Ministers)	201
Association of Plastics Manufacturers in Europe	208
European Federation of Chemical Engineering (CEFIC) Committees	205
CONCAWE	208
European Industry Ecology and Toxicology Centre (ECETOC)	206
B UK	
Health and Safety Executive (HSE)	208
Advisory Committee on Toxic Substances	
British Industrial Biological Research Association (BIBRA)	
Chemical Industries Association	
Huntingdon Research Centre	
Medical Research Council (MRC), Toxicology Unit	
C USA	
Consumer Products Safety Commission (CPSC)	226
Department of Agriculture	238
Department of Health and Human Services	88
Environmental Protection Agency (EPA)	26
Food and Drug Administration (FDA)	218
National Institute for Occupational Safety and Health (NIOSH)	87
Occupational Safety and Health Administration (OSHA)	25
American Conference of Government Industrial Hygienists (ACGIH)	107
American Industrial Health Council	131
American Industrial Hygiene Association (AIHA)	102
Chemical Industry Institute of Toxicology (CIIT)	130
Chemical Manufacturers Association (CMA)	
Interagency Regulatory Liaison Group (IRLG)	238
Interagency Testing Committee (ITC)	A.S. West (1986)
National Academy of Sciences (NAS)	92
National Cancer Institute	86
National Center for Health Statistics	88
National Center of Toxicogical Research (NCTR)	82
National Institute for Environmental Health Sciences	239
Office of Science and Technology Policy (OSTP)	93
Office of Technology Assessment (OTA)	93
Society of Toxicology (SOT)	219

Table 18.5 *(continued)*

Programs	
Health Interview Survey (HIS)	8
Health and Nutrition Examination Survey (HANES)	88
National Cancer Program	70
National Toxicology Program (NTP)	78
Surveillance, Epidemiology and End Results Program (SEER)	87

[a] References are to page numbers in Deisler (1984b), unless otherwise stated.

Marketing level (te/year)	*Tests required*
1–10	MPD set
10–100	Some Level 1 testing may be required
100 (or 500 te total)	Level 1
1000 (or 5000 te total)	Level 2

The Level 1 and Level 2 sets comprise further toxicology and ecotoxicology tests.

Accounts of the Sixth Amendment have been given by Langley (1978), C.R. Pearson (1982) and A.S. West (1986). An account by Rijkels (1984) on the control of carcinogens in Europe gives additional background. Further directives cover exposure to toxic chemicals (89/677/EEC) and carcinogens (90/394/EEC).

18.4.3 Regulatory controls in the United Kingdom

In the United Kingdom, the control of toxic substances has been primarily through the Health and Safety at Work etc. Act 1974 (HSWA) with the HSE as the enforcing authority. In particular, these arrangements have applied to control of toxic substances in the workplace and to hygiene standards.

The EC Sixth Amendment is implemented by the Notification of New Substances Regulations 1982. The requirements are essentially as described in the previous section.

Table 18.6 *EC minimum premarketing data set*

Physical/chemical data	
Melting point	Octanol/water partition coefficient
Boiling point	Flashpoint
Density	Flammability limits
Vapour pressure	Explosive properties
Surface tension	Auto-flammability
Water solubility	Oxidizing properties
Fat solubility	UV and visible spectra
Toxicity data	
Acute oral toxicity	Eye irritation
Acute dermal toxicity	Repeated dose (28 day)
Acute inhalation toxicity	Mutagenicity (bacterial)
Skin irritation	Mutagenicity (non-bacterial)
Skin sensitization	
Exotoxicity data	
Fish acute toxicity	Degradation (biotic and abiotic)
Daphnia toxicity	

An account of the background to these regulations has been given by C.R. Pearson (1982).

The Control of Substances Hazardous to Health Regulations 1988 (COSHH) creates a comprehensive system of controls. HSE guidance is given in an associated ACOP L5 Control of Substances Hazardous to Health and Control of Carcinogenic Substances (HSE, 1988). The occupational exposure limits (OELs) are given in EH 40/94 *Occupational Exposure Limits 1994* (HSE, 1994). The COSHH Regulations cover carcinogens and dusts. HSE guidance on carcinogens is given in the ACOP L5, as just described.

There are also regulations dealing with certain specific substances. They include the Lead at Work Regulations 1980 and the Control of Asbestos Regulations (CAWR) 1987. These are described below. More detailed accounts of the COSHH Regulations and the CAWR are given in Chapter 25.

The control of plants with major inventories of toxic chemical is exercised under the Control of Major Accident Hazards (CIMAH), Regulations 1984 as described in Chapters 3 and 4.

Requirements for the reporting of toxic releases are given in the Reporting of Injuries, Diseases and Dangerous Occurrences Regulations 1985 (RIDDOR), as described in Chapter 3.

18.4.4 Regulatory controls in the United States

In the United States, the OSHA has responsibility for the control of toxic substances in the workplace. It promulgates and enforces hygiene standards under the Occupational Safety and Health Act 1970. The OSHA may adopt by administrative action any health and safety standards in federal legislation or in codes or guidelines produced by consensus groups. It has in fact adopted various American National Standards Institute (ANSI) standards and many ACGIH threshold limit values (TLVs).

The OHSA issues Permanent Health Standards. The list of standards, as of 1983, is shown in Table 18.7.

The Toxic Substances Control Act (TSCA) 1976 provides a framework for the control of toxic chemicals in manufacture and transport. The enforcing authority is the EPA, which has extensive duties and powers under the act. The TSCA has been described in a series of papers by A.S. West (1979, 1982, 1986).

The TSCA lays down requirements for the notification of new chemicals, and is in this respect the equivalent of the EC Sixth Amendment, but it also contains requirements for existing chemicals. Some principal sections of the TSCA are listed in Table 18.8. Existing chemicals are listed in the TSCA Chemical Substance Inventory (EPA, Office of Toxic Substances, 1979, 1982).

For new chemicals a manufacturer is required under Section 5 to submit a premanufacture notice (PMN). The information required covers the chemical, the health effects, the exposure of workers, the major uses and production

Table 18.7 *OSHA Permanent Health Standards 1983*[a]

Acrylonitrile	Coke-oven emissions
Arsenic	Cotton dust
Asbestos	1,2-Dibromo-3-chloropropane
Benzene	Lead
14 Carcinogens	Vinyl chloride

[a] Standards promulgated in accordance with the Occupational Safety and Health Act, Section 6(b).

Table 18.8 *Some principal sections of the Toxic Substances Control Act 1976*

Section	
4	Issue of testing rules for selected substances
	4(e) Establishment of priority list of chemicals
5	Premanufacture notices
6	Regulation of selected substances
7	Regulation of imminent hazards
8	Reporting and retention of information
	8(a) Reporting on existing chemical substances
	8(e) Notice of substantial risks

volumes, the by-products and the ultimate disposal of the main product and by-products. There is no requirement for a base set of toxicity data, but an assessment is required of the health risk.

Notification is attracted at any level of manufacture. Intermediates used only on site are included, as are polymers, with some exceptions, but chemicals in research and development are excluded. Once a chemical has been notified by a single manufacturer, it is added to the TSCA Inventory, which is therefore a dynamic inventory.

While the TSCA is broadly similar to the Sixth Amendment, there are some important differences. The TSCA covers existing as well as new chemicals and it has no threshold level for notification, but there is no requirement for a base set of toxicity data and the inventory of chemicals is dynamic. Detailed comparisons are given by Doyal and Epstein (1983) and A.S. West (1986).

Under Section 4 of the TSCA the EPA is both empowered and required to initiate toxicity testing of existing chemicals. Recommendations for such testing are made by the Interagency Testing Committee (ITC), which issues periodic lists. The EPA is required to initiate testing or show cause why it has not done so, and it also issues periodic lists of chemicals for priority testing.

The factors which the EPA is required to take into account in regulating a chemical and in establishing a rule for testing a chemical are specified in Section 6 of the TSCA and are listed in Table 18.9, Sections A and B, respectively.

There have been a number of important legal cases that have influenced the control of toxic chemicals in the United States. The Delaney Amendment to the Federal Food, Drug and Cosmetic Act in 1958 banned the deliberate addition to food of any additive that is carcinogenic as determined from animal experiments or human response. This absolute requirement was subsequently modified on appeal to the effect that the Food and Drug Administration (FDA) was not required to bar containers in which very small amounts of a carcinogen, actually acrylonitrile monomer, were liable to migrate into the food.

In 1977, the OSHA promulgated an Emergency Temporary Standard for benzene, followed by a permanent rule, after an epidemiological study that seemed to show that benzene was more toxic than previously supposed. In the Benzene Case (Industrial Union Department vs American Petroleum Institute) in 1980, the Supreme Court set aside the benzene standard and ruled that the OSHA could not adopt a standard unless it finds both that there is a significant risk and that the standard will significantly reduce that risk.

The Formaldehyde Case (Gulf South Insulation vs United States Consumer Product Safety Commission) in 1983 involved a ban by the Consumer Product Safety Commission (CPSC) on urea formaldehyde foam insulation in homes and schools. The case centred on the interpretation of epidemiological data. The court took the view that the methodology and data used in extrapolating to low exposure levels were unsatisfactory and did not meet the substantial evidence criterion.

The control of major chemical hazards is exercised through Title III of the Superfund Amendments and Reauthorization Act (SARA) 1988, enforced by the EPA, as described in Chapters 3 and 4. SARA Title III, Section 6, requires the EPA to create a toxic chemicals inventory, the toxic release inventory (TRI).

These and other developments in the control of toxic chemicals in the United States may be followed through the references given in Table A1.4.

18.5 Hygiene Standards

There are two main types of toxic limit. For exposure over a working lifetime there are hygiene standards in the form of OELs, whilst for emergency exposure there are emergency exposure limits. Occupational hygiene standards are considered in this section and in Section 18.7, and emergency exposure limits are considered in Section 18.10.

Three principal sets of occupational hygiene standards are the TLVs used in the United States, the OELs used in the United Kingdom and the MAK-Werte used in Germany.

18.5.1 US threshold limit value system

A set of threshold limit values (TLVs) is published in the United States by the ACGIH. The TLV system is widely used, not only in the United States but also in many other countries.

The US TLVs are given in the *Threshold Limit Values and Biological Exposure Indices 1992–1993* (ACGIH, 1992/80). Other related documents are the *Guide to Occupational Exposure Values* – 1992 (ACGIH, 1992/78), which also gives the German MAK-Werte; *Documentation of Threshold Limit Values and Biological Exposure Indices* (ACGIH/3); and *Documentation for the Biological Exposure Indices* (ACGIH/1).

There are a number of critiques of the TLV system, including that by Doyal and Epstein (1983).

18.5.2 Former UK TLV system

As far as concerns the limits for workplace exposure to toxic chemicals in the United Kingdom, for many years use was made of a modified version of the US TLV system. This replaced an earlier system based on maximum allowable concentrations (MACs). In 1980, the United Kingdom moved to a system of OELs. The latter system is described in the following section.

Since the TLV system has now been superseded, it is not appropriate to give a detailed description here. On the other hand, the TLV system is referred to frequently in the literature and is still in widespread use in many countries. The general nature of the system is indicated by the following information taken from EH 15 TLVs for 1976 (HSE, 1977).

In order to avoid misuse, the nature and limitations of TLVs need be appreciated. Some principal features are:

(1) a TLV is not a sharp dividing line between 'safe' and hazardous concentrations;

Table 18.9 *Factors to be considered by EPA under the Toxic Substances Control Act 1976 in regulating and in establishing a rule for testing a chemical*

A Regulation of a chemical
1 Effects on health and magnitude of exposure of human beings
2 Effects on the environment and magnitude of exposure of the environment
3 Benefits of various uses and the availability of substitutes for each use
4 Reasonably ascertainable economic consequences of regulation after consideration of the effect on the national economy, small business, technological innovation, the environment and public health
B Rule for testing a chemical
1 The relative costs of the various test protocols and methodologies
2 The reasonably foreseeable availability of facilities and personnel to perform such tests
Health and environmental effects for which standards for development for test data may be prescribed include:
1 Carcinogenesis
2 Mutagenesis
3 Teratogenesis
4 Behaviour disorders
5 Cumulative or synergistic effects
6 Any other effect related to unreasonable risk of injury to health or the environment
Characteristics for which standards may be prescribed include:
1 Persistence
2 Acute toxicity
3 Subacute toxicity
4 Chronic toxicity
5 Any other characteristic which may present such a risk

(2) the absence of a substance from the list does not mean that it is necessarily safe;
(3) the best practice is to keep the concentration of a substance in the atmosphere to a minimum, regardless of whether it is known to present a hazard and whatever the value of the TLV;
(4) the application of a TLV to a particular case is a specialist matter.

There are three categories of TLV: (1) threshold limit value, time-weighted average (TLV-TWA); (2) threshold limit value short-term exposure limit (TLV-STEL) and (3) threshold limit value-ceiling (TLV-C).

The TLV-TWA is the time-weighted average (TWA) concentration for a normal 8-h workday or 40-h workweek to which nearly all workers may be repeatedly exposed, day after day, without adverse effect. Excursions above the limit are allowed, provided they are compensated by other excursions below the limit. There is also a limit on the maximum concentration. In some cases it may be permissible to use the average concentration over a workweek rather than over a workday.

The TLV-STEL is the maximum concentration to which workers can be exposed for a period of 15 min continuously without suffering from (1) intolerable irritation, (2) chronic or irreversible tissue change, or (3) narcosis of sufficient degree to increase accident proneness, impair self-rescue or materially reduce work efficiency, provided that no more than four excursions per day are permitted, with at least 60 min between exposure periods, and provided that the daily TLV-TWA is not exceeded.

The TLV-C is the concentration that should not be exceeded even instantaneously. Substances that are given a TLV-C are those that are predominantly fast-acting and require a limit related to this aspect.

The TLVs on the list are expressed in two units: ppm (parts of gas or vapour per million parts of contaminated air at 25°C and 760 mmHg) and mg/m^3 (milligrams of substance per cubic metre of air). For particulate materials the unit is mppcf (millions of particles per cubic foot of air).

TLVs are based on the best available information from industrial experience and from experimental studies of humans and animals and, where possible, from all three. The basis of the values thus varies. In some cases it is freedom from irritation, narcosis or other stress, in others it is the absence of effects impairing health.

The limits based on physical irritation should be regarded as equally binding as those based on health impairment, since there is increasing evidence that irritation can initiate or promote impairment.

There is a wide variation in the susceptibility of individuals to low levels of airborne contaminants. A small proportion may be seriously affected.

The nature and amount of information on which a TLV is based varies widely and the degree of confidence that can be placed in a particular TLV is therefore variable.

TLVs are intended for use in industrial hygiene and their interpretation is a specialist matter. They should not be used or adapted for other purposes, in particular not (1) as a relative index of toxicity, (2) for air pollution work or (3) for the assessment of toxic hazard from a continuous, uninterrupted exposure. They should also not be used as proof or disproof of an existing disease or physical condition or in countries where working conditions differ substantially from those in the United States.

The use of a TLV implies that there must be a system for monitoring the concentration of the substance in the air

and that the measurements must be, if not continuous, at least frequent enough for the purpose.

In addition to giving TLVs, EH15 also deals with the following:

(1) skin effects;
(2) mineral dusts;
(3) nuisance particulates;
(4) simple asphyxiants;
(5) carcinogens.

18.5.3 Other OSHA limits

There are a number of other limit values. Some that are used by the OSHA include:

STEL Short-term exposure limit: maximum exposure concentration for a period of exposure less than a workshift.
MAC Maximum acceptable ceiling: maximum exposure concentration regardless of period of exposure.
PEL Permissible exposure limit: applied variously to the TLV, STEL or MAC.
AL Action level: one-half the PEL; the concentration below which additional measurements of the same exposure will probably not exceed the PEL.

18.5.4 MAK-Werte limit system

The German system of hygiene standards is the MAK-Werte system. As stated above, values of the MAK-Werte are included in *Guide to Occupational Exposure Values – 1992* (ACGIH, 1992/78). The MAK-Werte and also the Technische Richtskonzentrazionen (TRK) systems are described by Rijkels (1984).

18.5.5 International exposure limits

An international set of OELs are the *Occupational Exposure Limits for Airborne Toxic Substances*, published by the International Labour office (ILO, 1991/2).

As already mentioned, many countries use the US TLV system, with or without modifications. An account of the limits adopted is given in *Occupational Exposure Limits – Worldwide* (Cook, 1987, AIHA/12).

18.6 Hygiene Standards: Occupational Exposure Limits

The system of OELs now used in the United Kingdom is described, as stated above, in EH 40/94 *Occupational Exposure Limits* 1994 (HSE, 1994). Two sets of limits are used. These are (1) the maximum exposure limits (MELs) and (2) the occupational exposure standards (OESs). The difference between these two types of limit is that, whereas an OES is set at a level at which there is no indication of risk to health, for an MEL a residual risk may exist.

These OELs are to be viewed in the context of the regulations governing occupational health, specifically the COSHH Regulations 1988 and the accompanying Approved Code of Practice ACOP L5 Control of Substances Hazardous to Health and Control of Carcinogenic Substances (HSE, 1988). These regulations are discussed in detail in Chapter 25, the discussion here being confined to the OELs themselves.

18.6.1 Maximum exposure limits

A MEL is the maximum concentration, averaged over a reference period, to which an employee may be exposed by inhalation in any circumstances. MELs are listed in Schedule 1 of the COSHH Regulations 1988 and also in EH 40/94, which also give the reference periods.

There are two reference periods, a long-term period and a short-term period. The long-term period is an 8-h TWA period. The short-term period given in EH 40/94 is 15 min. This is a recent change from a previous value of 10 min. Selected values of the MEL from EH 40/94 are given in Table 18.10, Section A.

18.6.2 Occupational exposure standards

As already stated, an OES is a concentration at which there is no indication of risk to health. OESs are listed in EH 40/94, which is referred to in the COSHH Regulations as the list of Approved OESs. The reference periods are the same as for the MELs, the long-term one being an 8-h TWA and the short-term one being 15 min. Selected values of the OES from EH 40/94 are given in Table 18.10, Section B.

18.6.3 Occupational exposure limit system

Maximum exposure limits and OESs are set by the HSC on the recommendations of the ACTS, following assessment by the Working Group on the Assessment of Toxic Chemicals (WATCH).

A substance is assigned an OES if it meets all three of the following criteria:

Criterion 1: the available scientific evidence allows for the identification, with reasonable certainty, of a concentration averaged over a reference period, at which there is no indication that the substance is likely to be injurious to employees if they are exposed by inhalation day after day to that concentration; and
Criterion 2: exposure to concentrations higher than that derived under criterion 1 and which could reasonably occur in practice, are unlikely to produce serious shorter long-term effects on health over the period of time it might reasonably take to identify and remedy the cause of excessive exposure; and
Criterion 3: the available evidence indicates that compliance with the OES, as derived under criterion 1, is reasonably practicable.

A substance is assigned an MEL if it meets either of the following criteria:

Criterion 4: the available evidence on the substance does not satisfy criterion 1 and/or 2 for an OES and exposure to the substance has, or is liable to have, serious health implications for workers; or
Criterion 5: socio-economic factors indicate that although the substance meets criteria 1 and 2 for an OES, a numerically higher value is necessary if the controls associated with certain uses are to be regarded as reasonably practicable.

The setting of an OES proceeds, in principle, by identifying the critical health effect, determining a no observable adverse effect level (NOAEL) and determining a limit. Generally the data available are from animal experiments, and judgement has to be exercised with respect to confidence levels and extrapolations.

A substance is assigned an MEL only if there are serious health implications for workers, which may be serious effects for a small number of workers or less serious effects for a large number. Most substances to which MELs have

Table 18.10 *Occupational exposure limits (OELs) of some chemicals (HSE, 1994 EH 40) (Courtesy of HM Stationery Office)*

	Long-term exposure Limit (8-h TWA reference period)		*Short-term exposure limit (15-min reference period)*		*Note*
	(ppm)	(mg/m^3)	(ppm)	(mg/m^3)	
A Maximum exposure limits (MELs)					
Acrylonitrile	2	4			Sk[a]
Asbestos	See EH 40				
Benzene	5	16			
Buta-1,3-diene	10	22			
Carbon disulfide	10	30			Sk
Ethylene oxide	5	10			
Formaldehyde	2	2.5	2	2.5	
Hydrogen cyanide			10	10	Sk
Isocyanates, all (as NCO)		0.02		0.07	Sen[b]
Lead compounds	See EH 40				
Silica		0.4			
Styrene	100	420	250	1050	
Trichloroethylene	100	535	150	802	Sk
Vinyl chloride[c]	7				
B Occupational exposure standards (OESs)					
Acetone	750	1780	1500	3560	
Ammonia	25	17	35	24	
Carbon dioxide	5000	9000	15000	27000	
Carbon monoxide	50	55	300	330	
Carbon tetrachloride	See EH 40				
Chlorine	0.5	1.5	1	3	
Ethylene glycol, vapour[d]		60		125	
Hydrogen chloride			5	7	
Hydrogen fluoride (as F)			3	2.5	
Hydrogen sulfide	10	14	15	21	
Isopropanol[e]	400	980	500	1225	Sk
LPG[f]	1000	1800	1250	2250	
Methanol	200	260	250	310	Sk
Naphthalene	10	50	15	75	
Nitric acid	2	5	4	10	
Nitrobenzene	1	5	2	10	Sk
Nitrogen dioxide	3	5	5	9	
Nitrogen monoxide	25	30	35	45	
Ozone	0.1	0.2	0.3	0.6	
Phenol	5	19	10	38	
Phosgene[g]	0.1	0.4			
Sulfur dioxide	2	5	5	13	
Toluene	50	188	150	560	Sk

[a] Sk, can be absorbed through the skin.
[b] Sen, capable of causing respiratory sensitization. The identified substances are those which: (1) are assigned the risk phrase R42: 'may cause sensitization by inhalation' in Part IA1 of the Approved List; (2) are listed under the Social Security Act 1975 or Schedule 2 of the Reporting of Injuries, Diseases and Dangerous Occurrences Regulations 1985 in connection with prescribed or reportable diseases, respectively.
[c] Vinyl chloride is also subject to an overriding MEL of 3 ppm, as described in EH 40.
[d] Ethane-1,2-diol.
[e] Propan-2-ol.
[f] Liquefied petroleum gas.
[g] Proposed change for 1995 is a long-term OES of 0.02 ppm (0.08 mg/m3) and a short-term OES of 0.06 ppm (0.25 mg/m^3).

been assigned are carcinogens or chemicals for which no threshold of effect can be identified and for which there is doubt about the seriousness of exposure.

In setting OESs account is taken of the indicative limit values given in EC Directive 91/332/EEC.

Synopses of the data used in setting limits are given in EH 64 *Occupational Exposure Limits: Criteria Document Summaries* (HSE, 1992), which is updated annually.

The units of measurement for OELs are as follows: for gases and vapours in air, either ppm or mg/m^3; for airborne

particles (fume, dust, etc.), mg/m^3; and for fibres, either mg/m^3 or fibres/ml. For dusts, limits are given as 'total inhalable' fraction unless specified as 'respirable' fraction.

The treatment of substances assigned an MEL under the COSHH Regulations, specifically Regulation 7(4), differs from that of those assigned an OES.

The lists of OESs and MELs are updated annually in EH 40. This publication also includes a table of new or revised entries in the list and a table showing substances which are under review.

18.6.4 Long- and short-term exposure limits

The basic OEL is the long-term, 8-h TWA limit, which is intended to control effects caused by prolonged or accumulated exposure. Where a substance has effects which occur after only a brief exposure, a short-term, usually 15-min, limit is applied. Some substances have only a long-term limit, others have both a long-term and a short-term limit, and others again have only a short-term limit. Where a substance is governed by both types of limit, the short-term limit restricts the extent of any excursion above the average concentration during longer exposures. Where there is no short-term limit, EH 40 recommends that short-term excursions should not exceed three times the long-term limit. For some substances the effects of a brief exposure may be critical, and for these a short-term limit is used; a separate long-term limit is considered unnecessary and the short-term limit is applied throughout the shift. The period to which the limits apply are termed the reference periods, the periods being, as stated, 8 h and 15 min for long- and short-term limits, respectively.

18.6.5 Application of occupational exposure limits

An MEL is a maximum limit. The long-term, 8-h limit attracts requirements for monitoring under the COSHH Regulations, unless an assessment shows such monitoring to be unnecessary. The Regulations also require that the exposure of personnel be kept as far below this level as reasonably practicable. The short-term, 15-min, MEL should never be exceeded.

Control to or below an OES can always be regarded as adequate under the COSHH Regulations. However, it is still incumbent on the occupier to follow good occupational hygiene practice and it is prudent to reduce exposure below the OES to allow for concentration fluctuations in the workplace. There are certain circumstances in which control may still be deemed adequate even if an OES is exceeded; these are described in Chapter 25.

18.6.6 Limitations of occupational exposure limits

Occupational exposure limits are intended to be used for normal working conditions in factories and other workplaces. Their application is not to be extended to other situations, and specifically they should not be used as limits either for emergencies or for pollution.

18.6.7 Mixed exposures

The majority of OELs are for individual substances, although a few relate to complex mixtures such as white spirit. In some situations workers are exposed to a mixture of substances. In some instances, an OEL for a mixture may be already established. In this case it can be used, but should it not be extrapolated to situations where the concentrations are different.

For mixtures, three different situations are recognized: (1) synergistic substances, where the presence of one substance causes another to produce a much greater toxic effect; (2) additive substances, where the effects of the substances are additive and (3) individual substances, where there are no known or likely synergistic or additive effects.

Synergistic effects may arise because one substance enhances the toxicity of another, or because it potentiates the other, causing it to act in a qualitatively different way. Where effects are additive, EH 40 gives the following formula for the overall OEL:

$$L = \sum_{i=1}^{n} \frac{C_i}{L_i} \quad L<1 \qquad [18.6.1]$$

where C_i is the TWA of the ith component, L_i its OEL and L the overall OEL. Where effects are individual, it is sufficient to comply with each OEL separately.

It will be apparent that in many situations involving mixtures expert advice is required.

18.6.8 Skin effects

For certain substances there exists the hazard of absorption through the skin as well as by inhalation. EH 40 uses the skin notation 'Sk' against the substance in the lists. For these substances special precautions should be taken to prevent skin contact.

18.6.9 Sensitizer effects

Certain substances act as sensitizers in that they may cause sensitization of the respiratory tract if inhaled or of the skin if contact occurs. Respiratory sensitizers can cause asthma and other conditions, skin sensitizers cause allergic contact dermatitis. Individuals exposed may react even to minute amounts of the sensitizing substances. EH 40 uses the sensitizer notation 'Sen' against substances in the lists that are in certain defined categories and which have been identified as respiratory sensitizers. For these substances particular care should be taken to minimize airborne concentrations and to prevent their spread to other areas.

18.6.10 Asphyxiants

Some gases and vapours act as simple asphyxiants. They are hazardous insofar as they may reduce the oxygen content in the workplace. They include acetylene, argon, ethane, ethylene, helium, hydrogen, nitrogen, propane and propylene. Many of these substances are colourless and odourless and are thus not readily detected.

As the list just given shows, many asphyxiants are also flammable, and the concentration at which they present a fire or explosion hazard (the lower flammability limit) is generally lower than that at which they cause asphyxiation. It may be noted that many hydrocarbons are not classed as simple asphyxiants, but have an OEL value. Butane is one example.

Asphyxiants do not rank as substances hazardous to health for the purposes of the COSHH Regulations.

18.6.11 Carcinogens

As described earlier, some carcinogenic substances are prohibited. Other substances that have or may have carcinogenic potential are listed in Appendix 9 of EH 40/ 94 and are assigned the 'Risk phrase' 'R45; may cause cancer' in the current edition of the *Authorised and Approved*

List: Information Approved for the Classification, Packaging and Labelling of Dangerous Substances for Supply and Conveyance by Road (the Approved List).

Some substances listed in EH 40/94, Appendix 9, and assigned the 'Risk phrase' are given an MEL. They include acrylonitrile, benzene, ethylene oxide and vinyl chloride. Other substances are simply listed in the appendix.

Guidance on carcinogens under the COSHH Regulations is given in the second of the two ACOPs in L5 Control of Substances Hazardous to Health and Control of Carcinogenic Substances (HSE, 1988).

18.6.12 Dusts

For dusts a distinction is made between 'total inhalable dust' and 'respirable dust'. The former approximates to the fraction of the airborne material that enters the mouth and nose during breathing and is therefore available for deposition in the respiratory tract. The latter refers to the fraction that penetrates to the gas exchange region of the lung. Details are given in MDHS 14 *General Method for the Gravimetric Determination of Respirable and Total Inhalable* Dust (HSE, 1989). Some dusts are assigned an OEL. EH 40/94 gives OELs for a number of dusts, including grain dust and silica (crystalline), which have an MEL, and emery, graphite, limestone, silica (amorphous) and starch, which have an OES. Dust of crystalline silica, or quartz, is of particular importance as the cause of silicosis and attracts a low OEL. It has a long-term MEL for the respirable dust of 0.4 mg/m^3.

The former TLV system used in the United Kingdom identified some dusts as toxic and assigned a TLV, but treated other dusts as nuisance dusts, which were not considered toxic, although they could be unpleasant to breathe and could cause irritation by abrasive action.

In the current system there are dusts that do not attract an OEL. EH 40/94 states that in the absence of a specific limit and of any indication for the need for a lower limit, exposure should be controlled below 10 mg/m^3 for an 8-h TWA. A concentration at this level or above is to be taken as a 'substantial concentration' for the purposes of Regulation 2 of the COSHH Regulations and as rendering the dust a substance hazardous to health under those regulations.

18.6.13 Asbestos

Asbestos is controlled by the CAWR 1987. It is considered in Section 18.8.

18.6.14 Lead

Lead is controlled by the Control of Lead at Work Regulations 1980, which is complemented by COP2 Control of Lead at Work (HSE, 1985). The lead-in-air standards given in this ACOP, and in EH 40/94, are as follows. The 8-h TWA (as Pb) is 0.15 mg/m^3 for lead and lead compounds other than tetraethyl lead, and 0.10 mg/m^3 for tetraethyl lead.

18.6.15 Working conditions

In applying OELs regard should be had to working conditions that may impose additional stress and may enhance toxic effects. These include exposure to high temperature, high humidity or UV radiation.

18.7 Carcinogens

18.7.1 Cancer risk

There are a number of accounts of the contribution of cancer to mortality. They include *The Causes of Cancer* (Doll and Peto, 1981) and other treatments by Doll (1979), Peto (1979), A.E.M. (McLean 1979) and (Higginson 1984).

As infectious diseases have declined as a cause of death, the proportion of deaths attributable to cancer has tended to rise. Cancer is now a major cause of death. In developing countries it accounts for some 20% or more of deaths. This is also the case for the United Kingdom and the United States. The numbers of people who die of cancer are therefore large. In 1980, in England and Wales, the number of deaths from cancer was 130,000 and the proportion 22%. In 1977, cancer caused 382,000 deaths in the United States.

The factors that cause cancer are physical, biological and cultural as well as chemical. Two of the principal factors are cultural. One of these is smoking, which is perhaps the most generally accepted major cause of cancer. There is also strong evidence that diet is another major cause. Estimates of the proportions of avoidable cancers given by Higginson and Muir (1979) in a case study done in England are given in Table 18.11, together with figures quoted by Doll and Peto (1981) in a study done in the United States.

The trend in cancer mortality has been reviewed by Doll (1979), who found that over the 40-year period 1931–35 to 1971–75, for 26 sites in the male body and 28 sites in the female body, the age standardized mortality at 45–64 years of age showed less than 1% variation at 25 sites, a progressive decrease of more than 1% at 16 sites and a progressive increase of more than 1% at 13 sites. He concludes that where increases in cancer rates have occurred this is due mainly to personal and dietary habits rather than to exposure to chemicals.

The proportion of cancer deaths that are attributable to occupational exposure, that includes exposure to chemicals at work, is estimated by many authorities as about 5%. In this respect the estimates given in Table 18.12 are typical. A review of these estimates has been given by Corn and Corn (1984).

This view is strongly disputed by certain workers, who believe that the contribution of chemicals, in the workplace, in food and in the environment, is underestimated by 'establishment' workers, and they represent a 'radical' view. Statements of this viewpoint are given in *The Politics of Cancer* (S.S. Epstein, 1978) and *Cancer In Britain. The Politics of Prevention* (Doyal and Epstein, 1983). It is argued by these workers that exposure to chemicals may account for some 40% of cancer deaths.

Table 18.11 *Estimates of the proportion of avoidable cancers*[a] *(after Higginson and Muir, 1979)*

Feature	*Proportion of avoidable deaths* (%)	
	Male	*Female*
Tobacco	30	7
Alcohol	5	3
Life-style	30	63
Occupation	6	2
Iatrogenic	1	1
Geophysical	11	11
Congential	2	2
Unknown	15	11

[a] Figures given by Doll and Peto (1981) for the United States include the following proportions for both sexes: tobacco 30%; alcohol 3%; life-style 42%; infection 10%; and occupation 4%.

Table 18.12 *Estimates of cancer deaths attributable to occupational exposure (after US Congress, Office of Technology Assessment, 1981)*

	Preferred estimate (%)	*Period to which estimate applies*	*Reference*
Male incidence, USA	4	1976	Wynder and Gori (1977)
Female incidence, USA	2	1976	
Male cancer, England	6	1968–72	Higginson and Muir (1979)
Female cancer, England	2	1968–72	
Male mortality, USA	6.8	1977	Doll and Peto (1981)
Female mortality, USA	1.2	1977	

These critics (e.g. S.S. Epstein, 1978) argue that there is a tendency to estimate the proportion of cancers attributable to chemicals as the residue remaining after estimates have been made of those attributable to other causes and that this approach is unsound. On the other hand, it is argued (e.g. Peto, 1980) against these critics that they tend to make their estimates of potential cancer mortality from a particular chemical by combining the numbers exposed to any level of the chemical with the risk attributable to persons exposed to very high levels.

The authors of the *Health and Safety Statistics* 1990–91 (HSE, 1992b) discuss the number of premature deaths from cancer. On the basis of the work of Doll and Peto it might be estimated that about 4% of cancers are work-related, which would give some 5000 premature deaths. A death from cancer might be avoided by the removal of any one of a number of contributing factors, of which workplace exposure is only one. The only hard statistics given are that there were some 78 cases of awards for occupational cancer other than mesothelioma (from asbestos).

18.7.2 Regulatory controls in Europe

The Sixth Amendment to the EC Directive on Dangerous Substances (79/831/EEC) creates controls on the introduction of new chemicals and thus of potential carcinogens. There is, in addition, a specific Directive that deals with carcinogens (90/394/EEC).

There is also an ILO Convention on Carcinogenic Substances and Agents. An account of the European arrangements for the regulation of carcinogens is given by Rijkels (1984).

18.7.3 Regulatory controls in the United Kingdom

The Carcinogenic Substances Regulations 1967 prohibit the use of certain human carcinogens and the Carcinogenic Substances (Prohibition of Importation) Order 1967 prohibit their importation.

As stated earlier, the COSHH Regulations 1988 cover carcinogens. HSE guidance is given in the associated ACOP L5 Control of Substances Hazardous to Health and Control of Carcinogenic Substances (HSE, 1988). The OELS are given in EH 40/94 *Occupational Exposure Limits 1994* (HSE, 1994). Carcinogens are one of the categories of substance given in the MEL list.

The control of one particular important carcinogen, asbestos, is effected through the CAWR 1987.

18.7.4 Regulatory controls in the United States

In the United States the framework legislation for the control of carcinogens, as for other toxic chemicals, is the Occupational Safety and Health Act 1970 administered by OSHA, but other legislation of particular relevance is the TSCA 1976 administered by the EPA. The control of carcinogens in the workplace is effected through the system of standards set by the OSHA.

The standards that may now be adopted are constrained by the results of the Benzene Case and the Formaldehyde Case, described above. Between 1977 and 1980, the OSHA attempted in the document *Identification, Classification and Regulation of Occupational Carcinogens* (OSHA, 1977) to set a generic standard for carcinogens. The Benzene Case increased the difficulty of creating such a standard and a generic standard was not adopted.

18.7.5 Carcinogenic chemicals

Some information on the toxicity of carcinogens is given in works on the toxicity of chemicals in general, of which carcinogenic chemicals are a subset, but there are also a number of specific treatments. Accounts of carcinogenic substances are given in *Cancer Causing Chemicals* (Sax, 1981), *Carcinogenically Active Chemicals: A Reference Guide* (Lewis, 1991 ACGIH/53) and *Handbook of Toxic and Hazardous Chemicals and Carcinogens* (Sittig, 1991 ACGIH/59).

The identification of chemicals that are carcinogenic is one of the main tasks of the International Agency for Research on Cancer (IARC). By 1979 the IARC (1979a) had identified 16 chemicals and industrial processes, as well as soot and vinyl chloride, for which there is sufficient epidemiological evidence to indicate a link between exposure and excess cancer in man. It has also identified a further 18 chemicals which the epidemiological evidence indicates as being probable human carcinogens.

According to Corn and Corn (1984), there are some 350 chemicals that are suspected of being human carcinogens. A list of carcinogens regulated by the OSHA for airborne concentrations in 1980 is given in Table 18.13.

18.7.6 Benzene

Benzene is an important chemical in the petroleum and petrochemical industries and the numbers of people who have been exposed to it in some degree is large. For many years it was regarded as not particularly toxic. The attitude to exposure both in industry and in laboratories was relatively relaxed. More recently the long-term effects of benzene on the blood and bone marrow and its carcinogenic properties have been better appreciated and the hygiene limits have been greatly reduced.

Reviews of toxicity are given in Criteria Document Publ. 74–137 *Benzene* (NIOSH, 1974), *TR 4 Toxicity Review: Benzene* (HSE, 1982), *Benzene: Occupational and Environmental Hazards* (Mehlman, 1989 ACGIH/28) and EH 64

Table 18.13 *OSHA list of carcinogens for airborne concentrations 1980*

2-Acetylaminofluorene[a]	3,3-Dichlorbenzidine[a]
Acrylonitrile[a]	4-Dimethylaminoazobenzene[a]
4-Aminodiphenyl[a]	Ethyleneimine[a]
Arsenic[a]	4,4-Methylene-bis (2-chloronile)
Asbestos[a]	β-Naphthylamine[a]
Benzene[a]	Nickel (and salts)
Benzidine[a]	4-Nitrobiphenyl[a]
Bis(chloromethyl)ether[a]	*N*-Nitrobiphenyl[a]
Chromic acid and chromates[b]	Propiolactone[a]
Coke-oven emissions[a]	Soots, tars, and mineral oils
1,2-Dibromo-3-chloropropane	Vinyl chloride[a]

[a] Permanent standards promulgated after Administrative Procedures Act rule-making.
[b] From the ANSI list.

Occupational Exposure Limits: Criteria Document Summaries (HSE, 1992).

The development of controls on benzene is described by Thorpe (1978a,b) and by Barnard (1984). The following extracts from a table by Thorpe (1978a) illustrate the tightening of exposure standards in the United States:

Year	*Limit* (ppm)	*Standard*
1946	100	ACGIH TLV
1947	50	ACGIH TLV
1957	25	ACGIH TILV-TWA
1963	25	ACGIH TLV-C
1969	10	ANSI TLV-TWA, with ceiling of 25 ppm
1976	1	OSHA (proposed) with 5 ppm excursion

The HSE paper reviews the toxicity of benzene and microorganism tests, animal experiments and epidemiological data. Benzene affects the formation of blood cells in bone marrow. It may reduce the number of red cells, white cells or platelets, or all three. It may cause anaemia or leukaemia.

Although in all three types of toxicity investigation there are many studies that have given negative results, some have demonstrated injurious effects. Carcinogenic, mutagenic and teratogenic effects have all been demonstrated for benzene in animal experiments. The review describes a number of epidemiological studies of workers exposed to benzene. A study by Infante *et al.* (1977a,b) of 748 workers on rubber film in Ohio found a significant increase in leukaemia. The authors quote low levels of exposure, below 15 ppm in most cases, but have apparently subsequently accepted that the levels may have been 100 ppm or more. Another study in which a significant increase in leukaemia was found is that by Pagnotto, Elkins and Brugsch (1979) on 549 workers at a Dow Chemical plant in the United States with very low exposures, about 2 ppm, but the workers concerned had a varied history of exposure to chemicals and there was no significant increase in leukaemia among other workers exposed to higher concentrations. Other studies that either are inconclusive or have shown no significant increase in leukaemia include those by Thorpe (1974) on 38,000 workers exposed to petroleum products, and Rushton and Alderson (1981) on 35,000 oil refinery workers.

The HSE review concludes that there is considerable evidence that exposure to high concentrations of benzene may eventually cause leukaemia, but that there is no conclusive evidence of leukaemia in workers exposed to lower concentrations. The only work reviewed in which there was an increase in leukaemia among workers exposed to less than 100 ppm was the Dow Chemical study just described. Increasing awareness of the toxicity of benzene has led to a progressive reduction in the hygiene limits. This is illustrated by the data given earlier. There has also been a corresponding tightening of the regulatory controls. As described above, in the United States this led to the attempt by the OSHA to introduce a very low benzene standard and the rejection of this by the courts in the Benzene Case. In the United Kingdom benzene has a long-term MEL of 5 ppm.

18.7.7 Vinyl chloride

Vinyl chloride monomer (VCM) is manufactured on a large scale and polymerized to give PVC, which is one of the most common plastics. It has a boiling point of $-13^{\circ}C$ and therefore is a gas at ambient temperatures.

Accounts of the toxicity of vinyl chloride are given in Criteria Document Publ. 78–205 (NIOSH, 1978), EH 64 *Occupational Exposure Limits: Criteria Document Summaries* (HSE, 1992), and in the other references quoted below.

Until the mid-1970s, vinyl chloride was regarded as a mild narcotic less harmful than chloroform. The ACGIH TLV was 500 ppm and the UK TLV was 200 ppm (HSE, 1972 TON 2/72).

It was also well known that vinyl chloride could give rise to acro-osteolysis, which involves deterioration of the bones, particularly the fingers, and certain other conditions. These diseases have been found mainly in PVC workers in circumstances where the exposure may well have been at concentrations appreciably above 1000 ppm. However, in 1974 it was found, that vinyl chloride is a carcinogen.

Accounts of the development of the vinyl chloride problem are given in the *Annual Report of HM Chief Inspector of Factories 1974* (HMFI, 1974) and by Atherley (1978), Doyal and Epstein (1983) and Corn and Corn (1984).

Indications of the carcinogenicity of vinyl chloride were given by animal experiments conducted by Viola (1970), but the first widespread impact was made by a report from a BE Goodrich plant in the United States that three cases of a rare liver cancer, angiosarcoma, had been discovered and were probably associated with exposure to high levels of vinyl chloride. The men concerned had been autoclave cleaners in plant polymerizing vinyl chloride to PVC. The average time for the condition to develop after first exposure was 19 years.

It is noteworthy that the cancer associated with vinyl chloride is a rare one. The discovery of a carcinogenic effect could have been much more difficult if the cancer had been of a type that also has other causes, such as the lung cancer that can be caused by cigarette smoking. It is probably fair to say that this discovery has had as great an impact in the area of chronic toxic exposure as the Flixborough disaster has had in the area of fire and explosion.

By the end of 1974, some 25 cases of angiosarcoma in workers exposed to vinyl chloride had been established

worldwide. These were mostly in the United States and mostly in one company.

In the United States, the OSHA reduced the standard from 500 ppm to an interim standard of 50 ppm and then to a TLV of 1 ppm and a maximum of 5 ppm. It was envisaged, however, that it might be necessary to rely on the extensive use of respirators to meet these levels of exposure.

In the United Kingdom, the HSE issued Vinyl Chloride Code of Practice for Health Precautions (HSE, 1975b), which gave as an interim standard a TLV of 25 ppm and a maximum of 50 ppm.

Guidance to industrial users of the monomer was given in *Vinyl Chloride Monomer. Advisory Notes for PVC Processors* (BCISC, 1974/14). Notes on best practicable means for PVC polymer plants were given in the *Annual Report on Alkali, etc. Works 1974*. The publication *Vinyl Chloride and You* was issued to workers.

The monitoring of very low concentrations of vinyl chloride requires sensitive analytical methods. In the 1970s, there was intense activity in this area. Methods of analysis were described in The *Determination of Vinyl Chloride – A Plant Manual* (CIA, 1975/7).

Various other countries adopted very low standards for vinyl chloride. The United Kingdom approach was based on the argument that it is preferable to devote effort to reducing the concentration of vinyl chloride in the atmosphere by improved engineering than to rely on respirators, which may well not be used.

The reduction of concentrations of vinyl chloride to very low levels is a difficult engineering problem. Early experience was that it was more difficult to eliminate occasional peaks over 50 ppm than to achieve the TWA of 25 ppm.

A survey of the atmospheric concentrations of vinyl chloride at plants in the United Kingdom was made in 1974 by the CIA (quoted by McKinnon, 1974). The survey established that the approximate exposure levels in the plant atmosphere were:

	Explosure level (ppm)
Plants polymerizing VCM to PVC	50
Plants producing VCM	5
Plants fabricating PVC	0–5

The survey obtained the following figures for the weekly average gas concentration in the seven polymerization plants in the United Kingdom:

Plant	*Weekly average concentration* (ppm)
A	25
B	10
C	10
D	25
E	20
F	40
G	30

The CIA stated that the ultimate for most existing plants is 10 ppm and that entirely new plants with the most modern techniques might achieve 5 ppm.

Accounts are also available of measures taken at that time to reduce exposure at plants in the United States and elsewhere (e.g. Chementator, 1975 Apr. 14, 33; Jul. 7, 34; 1977, Jan. 3, 37). Indications were that the achievement of low levels of exposure did not prove as difficult as was sometimes anticipated (e.g. Meade and Press, 1977).

Information on plant emissions of vinyl chloride has been given by Sittig (1978), who quotes vent and fugitive emission rates. The development of controls on vinyl chloride in the United States may be followed through the references given in Table A1.4.

In the United Kingdom vinyl chloride has a long-term MEL of 7 ppm with an overriding annual MEL of 3 ppm.

18.7.8 Acrylonitrile

In 1977, several animal and epidemiological studies were published which showed carcinogenic effects from acrylonitrile. One of these was an epidemiological study by Dupont on 470 workers in an acrylic fibre plant in South Carolina, which showed the incidence of excess cancers.

As described by Karrh (1984), the company made its data, interpretation and recommendations available to the OSHA that accepted these and based a standard on them. The standard set by the OSHA was 2 ppm. This case is therefore an interesting example of co-operation between industry and the regulatory authorities. The author adds that, to his knowledge, this is the only OSHA health standard which has not been the subject of litigation.

In the United Kingdom, the practicality of the 2 ppm standard was a matter of some debate, but by 1981 this level was accepted, as described by Doyal and Epstein (1983). Acrylonitrile now has a long-term MEL of 2 ppm.

18.7.9 Other substances

Other substances with carcinogenic potential include *bis*(-chloromethyl) ether (BCME), formaldehyde, inorganic arsenic and asbestos.

For BCME the toxicity and development of controls are described Doyal and Epstein (1983) and by Kusnetz and Lynch (1984).

Chloromethyl ether (CME) is manufactured by reacting formaldehyde and hydrogen chloride. BCME is an intermediate and a contaminant in the CME. BCME has long been known to be a highly toxic irritant gas, but awareness of its carcinogenic properties dates from various epidemiological and animal studies done in the 1960s and 1970s. In 1982, the ACGIH classified BCME as a carcinogen. In the UK BCME has a long-term MEL of 0.001 ppm.

For formaldehyde a review of toxicity is given in TR2 *Toxicity Review: Formaldehyde* (HSE, 1981). The toxicity and the development of controls on formaldehyde are described by Neal and Gibson (1974), Doyal and Epstein (1983), Barnard (1984), and Gough (1984).

Formaldehyde has been shown to be carcinogenic to rodents, but there is disagreement among experts on the extent of its human carcinogenicity. In the Formaldehyde Case the CPSC used some of the animal experiments and interpretations in support of its ban on urea formaldehyde insulation, but its assessment was not accepted by the court. Following a further expert review under the aegis of the National Center of Toxicological Research (NCTR), the OSHA decided not to alter its standard for formaldehyde. In the United Kingdom, formaldehyde has long- and short-term MELs that are both 2 ppm.

For inorganic arsenic the toxicity and development of controls are described by Lowrance (1984), Neal and Gibson (1984) and Sagan and Whipple (1984). There is epidemiological evidence of the human carcinogenicity of inorganic arsenic (OSHA, 1983). In 1983, on the basis of this evidence, the OSHA adopted a standard of 10 $\mu g/m^3$. As described above, the reasoning given by the OSHA in support of this standard, though not necessarily the numerical values, is commended by Lowrance (1984) as a model. In the United Kingdom, inorganic arsenic has a long-term MEL of 0.1 mg/m^3.

Asbestos is a carcinogenic dust and is considered in Section 18.8.

18.8 Dusts

There are many industrial chemicals that are used in powder form and can give rise to dust in the atmosphere. Dust may also be generated by the attrition of materials.

Dusts are covered by the OEL system, and OELs for dusts have been described in Section 18.6.

Some dusts are not classified as having any specific toxic effect, but can cause irritation. Excessive quantities of such dust are unpleasant to inhale, can deposit in the eyes and ears, and can injure the skin or mucous membranes by chemical or mechanical action or through the cleaning procedures necessary to remove them.

Other dusts can cause injurious effects. One such dust is silica in the crystalline, or quartz, form. A well-known example is the silica dust produced in coal mining, which causes pneumoconiosis, a progressive fibrosis of the lung tissue.

Fibrosis can also be caused by asbestos dust. In addition, this dust is a carcinogen. Asbestos is considered in more detail below.

Metal dusts that are sufficiently fine can enter the lungs and give rise to the toxic symptoms associated with the parent metal.

Other dusts which are themselves non-fibrogenic may produce an allergic response in the lungs that leads eventually to fibrosis. Such conditions are 'farmer's lung' and byssinosis, an asthmatic condition prevalent in the cotton industry. Process workers involved with enzyme washing powders have experienced similar asthmatic conditions.

The control of dust in the workplace is considered in Chapter 25.

18.8.1 Asbestos

'Asbestos' is a generic term that is applied to a number of naturally occurring, hydrated mineral silicates. More than 90% of the world production of asbestos is as is chrysotile ('white') asbestos. Virtually all the rest is amosite ('brown') and crocidolite ('blue') asbestos.

Accounts of the toxicity of asbestos include Criteria Document Publ. 77–169 *Asbestos* (NIOSH, 1977), *Asbestos: Medical and Legal Aspects* (Castleman, 1990 ACGIH/39), EH 64 *Occupational Exposure Limits: Criteria Document Summaries* (HSE, 1992) and the other references quoted below. Other HSE publications on asbestos are given in Chapter 25.

Asbestos has been in widespread use as a material for building products, fireproofing, lagging, brakes, glands and many other purposes. Asbestos dust is generated to some degree in many of these applications, particularly in cutting and demolition operations.

There are two injurious effects caused by asbestos dust, the fibres of which enter the lung. One is asbestosis, a fibrosis of the lung. The other is mesothelioma, a rare cancer of the lung and bowels, of which asbestos is the only known cause.

Evidence of the hazard of asbestos appeared as early as the 1890s. Of the first 17 people employed in an asbestos cloth mill in France, all but one were dead within 5 years. Oliver (1902) describes the preparation and weaving of asbestos as 'one of the most injurious processes known to man'.

In 1910, the Chief Medical Inspector of Factories, Thomas Legge, described asbestosis. A high incidence of lung cancer among asbestos workers was first recognized in the 1930s and has been the subject of continuing research. The synergistic effect of cigarette smoking, which greatly increases the risk of lung cancer to asbestos workers, was also discovered (Doll, 1955). The specific type of cancer, mesothelioma, was identified in the 1950s (Q.C. Wagner, 1960).

In the United Kingdom, an Act passed in 1931 introduced the first restrictions on the manufacture and use of asbestos. It has become clear, however, that the concentrations of asbestos dust allowed by industry and the Factory Inspectorate were too high. In consequence, numbers of people have been exposed to hazardous concentrations of the dust over long periods.

The problem was dramatically highlighted by the tragedy of the asbestos workers at Acre Mill, Hebden Bridge. The case was investigated by the Parliamentary Commissioner (Ombudsman, 1975–76). It was found that asbestos dust had caused disease not only to workers in the factory but also to members of the public living nearby.

Although all types of asbestos can cause cancer, it is held that crocidolite, or blue asbestos, is the worst offender.

By the late 1960s, growing concern over the asbestos hazard in the United Kingdom led to action. The building industry virtually stopped using blue asbestos in 1968 and the Asbestos Regulations 1969 prohibited the import, though not the use, of this type of asbestos.

The problem of asbestos continued to be a subject of controversy (e.g. Kinnersley, 1976; W.P. Howard, 1976). Criticisms included the failure of industry and government to act earlier, the adequacy of current concentration standards, the particular hazard of blue asbestos, and the effect of 'casual' exposures. Obviously the problem is more difficult if it is not confined to blue asbestos and if even occasional exposure can cause cancer.

Most cases of disease from asbestos are associated with exposure over a period of years and often in high dust concentrations, but several cases have been quoted of contraction of the cancer after apparently very short exposure. However, in some of these at least, it has been shown that the exposure, though short, was in fact quite intense.

As a result of continuing concern, in 1976 the Government set up an Advisory Committee on Asbestos (ACA). The asbestos industry also set up its own Asbestos Advisory Committee. In contrast to most of the other chemicals discussed earlier, and in particular to VCM, asbestos is a material widely used by the public. The industry was therefore faced with the problem of allaying the fears of numerous and relatively unsophisticated users.

The Asbestos Regulations 1969 were followed by further legislative requirements. These include The Asbestos

(Licensing) Regulations 1983 and the Asbestos (Prohibition) Regulations 1985.

The CAWR 1987, which revoke the Asbestos Regulations 1969, now provide a comprehensive set of controls on asbestos. The corresponding ACOP is L27 The Control of Asbestos at Work (HSE, 1988).

The CAWR 1987 set control limits for asbestos. These limits are reproduced in EH 10 *Asbestos – Exposure Limits and Measurement of Airborne Dust Concentrations* (HSE, 1990) and in EH 40/94. They are given in Chapter 25 where the CAWR 1987 are discussed in more detail. A more stringent limit is applied for crocidolite or amosite asbestos.

Although there is now much more stringent control of asbestos dust, the backlog of exposure in previous years is likely to claim victims for some time to come. The Health and Safety Statistics 1990–91 (HSE, 1992b) give, for 1990, 882 deaths recorded as due to mesothelioma and another 163 deaths recorded as due to asbestosis (excluding those where mention is made of mesothelioma).

18.8.2 Dust and fume atmospheres

Not infrequently, dusts occur as part of a mixture of dusts, fumes, gases and vapours. This is the situation, for example, in ferrous foundries. A recent review of airborne ferrous foundry particulates (HSE, 1994a) has highlighted the enhanced risk of lung cancer from such atmospheres.

18.9 Metals

The toxic effects of metals and their compounds vary according to whether they are in inorganic or organic form, whether they are in the solid, liquid or vapour phase, whether the valency of the radical is low or high and whether they enter the body via the skin, lungs or alimentary tract.

Some metals that are harmless in the pure state form highly toxic compounds. Nickel carbonyl is highly toxic, although nickel itself is fairly innocuous. The degree of toxicity can vary greatly between inorganic and organic forms. Mercury is particularly toxic in the methyl mercury form.

The wide variety of toxic effects is illustrated by the arsenic compounds. Inorganic arsenic compounds are intensely irritant to the skin and bowel lining and can cause cancer if exposure is prolonged. Organic compounds are likewise intensely irritant, produce blisters and damage the lungs, and have been used as war gases. Hydrogen arsenic, or arsine, is non-irritant, but attacks the red corpuscles of the blood, often with fatal effects.

Hazard arises from the use of metal compounds as industrial chemicals. Another frequent cause of hazard is the presence of such compounds in effluents, both gaseous and liquid, and in solid wastes. Fumes evolved from the cutting, brazing and welding of metals are a further hazard. Such fumes can arise in the electrode arc welding of steel. Fumes that are more toxic may be generated in work on other metals such as lead and cadmium.

The HSE has issued a number of Guidance Notes on metals and their hazards, including notes on cadmium (EH 1), chromium (EH 2), arsenic (EH 8), beryllium (EH 13), mercury (EH 14), antimony (EH 17) and lead (EH 29). There are also notes on the compounds arsine (EH 11), stibine (EH 12) and phosphine (EH 20).

18.9.1 Lead

One of the metals most troublesome in respect of its toxicity is lead. Accounts of the toxicity of lead are given in Criteria Document Publ. 78–158 *Lead, Inorganic* (NIOSH, 1978) and EH 64 *Occupational Exposure Limits: Criteria Document Summaries* (HSE, 1992).

The toxicity of lead and its compounds has been known for a long time, since it was described in detail by Hippocrates. Despite this, lead poisoning continues to be a problem, particularly where cutting and burning operations, which can give rise to fumes from lead or lead paint, are carried out. Fumes are emitted above about 450–500°C. These hazards occur in industries working with lead and in demolition work.

Legislation to control the hazard from lead includes the Lead Smelting and Manufacturing Regulations 1911, the Lead Compounds Manufacture Regulations 1921, and the Lead Paint (Protection against Poisoning) Act 1926 and the Control of Lead at Work Regulations 1980. The associated ACOP is COP 2 Control of Lead at Work (HSE, 1988).

The limits for lead, which is referred to as the 'lead-in-air standard', are given in COP 2 and in Appendix 5 of EH 40. They have been given in Section 18.6.

Monitoring of lead in the working environment is dealt with in EH 28 *Control of Lead: Air Sampling Techniques and Strategies* (HSE, 1986).

The *Annual Report of HM Chief Inspector of Factories* 1974 records 36 cases of lead poisoning in that year. Also, 154 employees were removed from lead work because of increased lead absorption. The number of cases of lead poisoning was 82 in 1972 and 59 in 1973. The *Health and Safety Statistics* 1990–91 (HSE, 1992b) do not quote cases of lead poisoning but the statistics given show that in 1990–91 some 258 male workers and 26 female workers were suspended from work due to the levels of lead in their blood.

18.9.2 Mercury

Another highly toxic substance is mercury. This is used on a large scale in the chemical industry in the manufacture of chlorine by the mercury cell process.

Mercury is particularly toxic in the organic form, and especially as methyl mercury. Organic mercury was responsible for the tragedy at Minimata, Japan, where many members of the public were poisoned and deformed by liquid effluent containing mercury.

Mercury vapour from spillage of the metal should also be treated as hazardous.

Industrial use of mercury is dealt with in EH 17 *Mercury – Health and Safety Precautions* (HSE, 1977).

18.10 Emergency Exposure Limits

Limits for occupational exposure are complemented by limits for emergency exposure. A number of types of limit for exposure in an emergency have been defined by various bodies, but it is fair to say that there is no system with a status comparable to that of the TLV or OEL systems.

Some emergency exposure limits, emanating from various bodies, include the following:

EEGL	Emergency exposure guidance level
EEI	Emergency exposure index
EEL	Emergency exposure limit
ERPG	Emergency response planning guideline

IDLH Immediately dangerous to life and health (limit)
PEEL Public emergency exposure limit
SPEGL Short-term Public Emergency Guidance Level

The National Research Council (NRC) Committee on Toxicology has, since the 1940s, submitted to the Department of Defense EEGLs for toxic chemicals. An EEGL is a concentration that is judged acceptable and which will permit exposed individuals to perform specified tasks during emergency conditions lasting from 1 to 24 h. The NRC has also developed SPEGLs. These are acceptable concentrations for exposures of members of the general public. Some early limits were those given in the Guides for Short Term Exposure of the Public to Air Pollutants (NAS/NRC, 1972a, 1973). More recent publications are the Guidance Levels for Emergency and Continuous Exposure to Selected Airborne Contaminants (NAS, 1984–).

A number of EELs were developed in the early 1970s in the Netherlands, as described by the Committee for the Prevention of Disasters (CPD) in the Netherlands (1974) and by Zielhuis (1970), Siccama (1973) and Balemans (1975).

The NIOSH has published a set of IDLH limits. NIOSH data are given in the *Pocket Guide to Chemical Hazards* (NIOSH, 1990/18).

The AIHA publishes a series *Emergency Response Planning Guidelines* (AIHA, 1988–/13). An ERPG is the maximum airborne concentration below which, it is believed, nearly all individuals could be exposed for up to 1 h without experiencing or developing certain defined effects. Three ERPGs are used, the defined effects being as follows:

ERPG-1 Effects other than mild transient adverse health effects or perception of a clearly defined objectionable odour.
ERPG-2 Irreversible or other serious health effects or symptoms that could impair an individual's ability to take protective action.
ERPG-3 Life threatening health effects.

So far some 40 ERPGs have been published. The ERPG-2 is broadly similar to the EEGL.

Another emergency limit is the EEI given in Emergency Exposure Indices for Industrial Chemicals (ECETOC, 1991). Three EEIs are defined, namely EEI-1, EEI-2 and EEI-3, which separate four zones of effect: detection, discomfort, disability, and permanent incapacity/death.

Another limit used is the PEEL. This is a maximum airborne concentration to which a member of the public may be exposed without significant adverse effects.

Critical reviews of emergency exposure limits are given in the QRA Guidelines (CCPS, 1989/4) and by Franklin (1991).

18.10.1 Dow Chemical Exposure Index

There are also indices for acute toxic exposures that are not a simple concentration value, but take account of other parameters also. One such is the Chemical Exposure Index (CEI) developed by the Dow Chemical Company (1994a) and described by R.A. Smith and Miller (1988).

The CEI takes account of (1) toxicity, (2) quantity, (3) distance, (4) molecular weight and (5) process variables, and the index is computed as the product of a set of 'scale factors' which allow for these features. The authors give full details, including proformas and credit factors.

18.11 Gas Toxicity

18.11.1 Industrial gases

Some of the principal toxic gases which are handled in the chemical industry and the toxic effect which each exerts are:

Gas	*Toxic effect*
Ammonia	Irritant
Bromine	Irritant
Chlorine	Irritant
Hydrogen chloride	Irritant
Hydrogen cyanide	Systemic
Hydrogen fluoride	Systemic (fluoride poisoning), irritant
Hydrogen sulfide	Systemic irritant
Phosgene	Irritant
Sulphur dioxide	Irritant

All except one of these gases are irritants. In this context 'irritation' is a technical term: the effect ranges from mild discomfort to death. An irritant gas attacks the respiratory tract and the lungs. The locus of action depends mainly on the solubility of the gas, the more soluble gases attacking the respiratory tract and the less soluble the lungs. The action of irritant gases has been described by Haggard (1924) as follows:

> Ammonia produces intense congestion of the upper respiratory passages and immediate death from laryngeal spasm or oedema; on the other hand phosgene and nitrogen peroxide cause little irritation of the upper respiratory tract but induce pneumonia or lung oedema through their action upon the lung alveoli; chlorine in its action is intermediary between ammonia on the one hand and phosgene and nitrogen peroxide on the other.

Of the irritant gases, ammonia and hydrogen fluoride are miscible with water. Bromine is more soluble than chlorine, which in turn is more soluble than phosgene. As indicated, ammonia and hydrogen fluoride attack the upper respiratory tract. The main action of chlorine is on the lungs, but there is some effect on the respiratory tract. Bromine, being more soluble than chlorine but less soluble than ammonia, attacks both the respiratory tract and the lungs. Phosgene, being less soluble than chlorine, enters deep into the lungs where its action occurs.

Hydrogen sulfide is an irritant gas, but also attacks the nervous system and causes respiratory paralysis. It is oxidized in the blood stream to pharmacologically inert compounds. Hydrogen fluoride is again an irritant gas but also gives rise to fluoride poisoning in the body.

Hydrogen cyanide is the only one of the gases listed which is not an irritant; it causes cyanide poisoning. The most important effect of this is probably the inhibition of cytochrome oxidase, which in turn prevents the utilization of molecular oxygen by the cells. The cyanide is excreted in the urine.

18.11.2 Lethal concentration and load

In general, the injurious effect of the inhalation of a toxic gas is a function of concentration and of time that may be expressed by the relation

$$c^n t^m = \text{Constant} \qquad [18.11.1]$$

where c is the concentration, t is the time, and m and n are indices.

If the exposure time is constant, a lethal concentration LC_i may be defined such that for this exposure time C_i is the concentration that is lethal at the i% level. Widespread use is made of the LC_{50} value and also of other values such as LC_{10}, LC_{05} and LC_{01}.

If the exposure time is not constant, but the injurious effect is proportional to the product ct of the concentration and time ($m = n = 1$), and hence to the dosage D, a lethal dosage LD_i may be defined with

$$D = ct \qquad [18.11.2]$$

If the injurious effect is proportional to some other function ($m \neq n$), it is necessary to use the concept of toxic load L and to define a lethal load LL_i with

$$L = ct^m \qquad [18.11.3]$$

An alternative toxic load, L^* may also be defined

$$L^* = c^n t \qquad [18.11.4]$$

with $m = 1/n$. This second form of the lethal load is that most often used in hazard assessment studies.

In such studies it is usually necessary to estimate mortality for exposures at a number of different combinations of concentration and time and in this case the lethal load function is usually expressed in the form

$$L^* = \sum C^n T \qquad [18.11.5]$$

where C is the concentration (ppm) and T is the time (min). The lethal load function in the form of Equation 18.11.5 has been widely used in hazard assessment.

For the case where $n = 1$ so that the load becomes $L = ct$, it is possible to define the LCt value. In particular, use is made of the LCt_{50}.

The relation between toxic load and mortality is usually a log-normal distribution and may therefore be plotted on log-probability paper. It may also be expressed as a probit equation

$$Y = k_1 + k_2 \ln L^* \qquad [18.11.6]$$

where Y is the probit and k_1, k_2 are constants.

It is a matter of indifference which expression, Equation 18.11.3 or Equation 18.11.4, is used to define the toxic load that causes a specified degree of injury; both give the same numerical results. In principle, it would be possible to distinguish between the two forms if one fitted better than the other the load–mortality distribution generally used, but in fact the distribution almost universally used for intensity–injury relationships in hazard assessment, not just for toxic gases but also for fire and explosion, is the log-normal distribution. With this distribution, if L is log-normally distributed, so is L^*.

Similarly, in the corresponding probit equation use of L^* instead of L is equivalent to multiplying the constant k_2 by m. Thus it is not possible to distinguish between the two forms.

There are, however, other arguments. From the point of view of hazard assessment, in which it is usually necessary to integrate the lethal load function, the definition of load given in Equation 18.11.4, or its discrete form Equation 18.11.5, is the more convenient.

There are also arguments, however, for the alternative form. Here toxicokinetic models appear relevant. For example, a one-compartment model for the body fluid concentration of the toxin with first-order excretion and constant gas concentration is equivalent to a first-order exponential stage with a step input, which gives a concentration rise of the form $[1-\exp(-kt)]$, where k is a constant. It may be significant that this exponential rise may be approximated by a suitably scaled expression in $t^{1/2}$.

18.12 Gas Toxicity: Experimental Determination

The main source of information on the lethal toxicity of gases is experimentation on animals, particularly mice. In a typical study, groups of mice are exposed to different concentrations of gas for a single exposure period and the mortality is determined over a given period of observation after the exposure is over.

For a particular gas, assuming there are any data, there will typically be between one and half a dozen studies quoted in the literature that appear applicable. There may be one or two in which the exposure period has been varied. There may also be one or two studies with other species such as rats, guinea pigs, rabbits, and, in older work mainly, cats and dogs.

The determination of the lethality of a toxic gas by inhalation experiments with animals is a difficult undertaking and is subject to various sources of error. In addition to the concentration of the gas and the exposure time, other important variables are the caging conditions, the breed, sex, age and health of the animals, and their behaviour, including their breathing rate. The animals may not die immediately and it is necessary to observe delayed deaths over a period of time, usually 10 days, and to record both immediate and delayed deaths. A sufficient number of animals needs to be used to obtain results with a high level of confidence, and pathological examinations should be conducted. The toxicity data sought are usually for a given exposure time and comprise the LC_{50} together with suitable values nearer the extremes of mortality such as the LC_{10} and LC_{90}.

18.12.1 Statistical interpretation of experiments

The statistical interpretation of experiments in toxicology was discussed in Section 18.3.

The method of Litchfield and Wilcoxon (1949) is convenient for the statistical treatment of results on inhalation toxicology. The application of this method to concentration mortality data for dogs exposed to chlorine is given in Section 18.18.

The lethal toxicity estimates required for hazard assessment are essentially the LC_{50}, the slope of the concentration mortality line, which may be expressed in terms of the ratio LC_{90}/LC_{10}, and the toxic load function, which defines the equivalence between concentration and time.

18.12.2 Estimation of lethal toxicity to animals

Usually, if there are any data at all, there will be enough to permit some estimate to be made not only of the LC_{50} but also of the ratio LC_{90}/LC_{10}, but the latter estimate will generally be such as to yield much less confidence in the LC_{10} than in the LC_{50}.

For some gases there may be a single set of experiments on one species, for others several sets on one species and for others again several sets on different species.

In the first case the estimate is straightforward, but where there are several sets of experiments on one species, there may be appreciable differences, say a factor of 2, in the LC_{50} reported by different authors, even though each group of workers reports relatively narrow confidence limits for its results.

In the second case where there are differences in the LC_{50} reported, it is necessary to decide whether to average the results or to select those that appear of highest quality. Each case must be treated on its merits.

The third case, where different species are involved, is discussed below.

In general, the lethal toxicity is a function of concentration and time. Although concentration may sometimes be completely dominant, there tends to be a trade-off between the two, so that at a particular value of the toxic load there is a given degree of lethality.

The experimental data from which to determine the index m in Equation 18.6.3 or n in Equation 18.6.4 are often sparse and in weak agreement. Work by Doe and Milburn gives a value for n of about $\frac{1}{2}$ for many of the irritant gases but about 1 for some other gases.

18.12.3 Extrapolation between species

Extrapolation of results obtained on one particular species to another species is beset with many difficulties, but it is an unavoidable step in the estimation of toxicity. Some accounts of the principles were mentioned in Section 18.3. In relation to inhalation toxicity specifically, reference may also be made to the accounts given by Flury and Zernik (1931) and Wachtel (1941), who worked on the toxicity of war gases, and to the Major Hazards Assessment Panel (MHAP) monographs (MHAP, 1987, 1988, 1993) described below.

The crucial question is whether or not the toxic effects are the same, or at least sufficiently similar, in the two species, thus providing a basis for extrapolation. Other important features are the relative modes and rates of inhalation and the mechanisms and rate of elimination, or metabolism.

In the case of irritant gases the toxic effects in the main laboratory animals and in man appear to be broadly similar, in that gas attacks the respiratory system. The fact that for these gases it is, the respiratory system that is the target means that metabolism is not significant. It is necessary to consider, however, the locus of action for each gas in each species, bearing in mind the solubility of the gas and the anatomy and respiratory behaviour.

18.12.4 Animal physiology

In many cases extrapolation from animals to humans is supported by an argument based on the ratio of physiological quantities such as the minute volume or body weight.

Information on animal physiology is given in *The Rat – Data and Reference Tables for the Albino Rat* (Donaldson, 1924), *The Rat in Laboratory Investigation* (Farris and Griffiths, 1949), *Handbook of Biological Data* (Spector, 1956a), Blood and Other Body Fluids (Altaian and Dittmer, 1961), *Metabolism* (Altaian and Dittmer, 1968), *Respiration and Circulation* (Altaian and Dittmer, 1971), *Biology Data Book* (Altman and Dittmar, 1974), *Clinical, Biochemical and Hematological Reference Values in Normal Experimental Animals* (Mitruka and Rawnsley, 1977) and *Inbred and Genetically Defined Strains of Laboratory Animals. Part 1, Mouse and Rat* (Altman and Katz, 1979).

Data on some of the principal parameters of animal physiology relevant here are given in Table 18.14.

18.12.5 Vulnerable populations

Extrapolation from animals to man is usually done in the first instance for healthy young adults. It may be necessary, however, to allow for vulnerable members of the population.

It is commonly assumed in hazard assessment that a section of the population, including young children and old people, is particularly vulnerable. In the case of toxic gas hazard, those with respiratory disease are also included. However, this is an aspect on which very little work has been done.

It may be preferable to derive separate estimates of the lethal toxicity for the regular and vulnerable populations. This makes it possible to allow for differences in the numbers and composition of the exposed population at different times of day.

18.13 Gas Toxicity: Physiological Factors

18.13.1 Respiration

Any attempt to model the toxic effects of inhaled gases requires some understanding of the respiratory process.

Accounts of the respiratory system, the effects of gases on this system and the absorption of gases into the blood include those given in: standard texts on general physiology, such as *Handbook of Physiology* (Fenn and Rahn, 1964), *Medical Physiology* (Mountcastle, 1974) and *Samson Wrights Applied Physiology* (Keele, Neil and Joels, 1982); texts on the respiratory system, such as The *Morphometry of the Human Lung* (Weibel, 1963), *Ventilation Blood Flow and Gas Exchange* (Q.B. West, 1965), *Human Respiration* (Lippold, 1968), *Physiology of Respiration* (Comroe, 1974), *Lung Function* (Cotes, 1979), *Lung Connective Tissue* (Pickrell, 1981), *Modelling and Control of Breathing* (Whipp and Wiburg, 1983), *Inhalation Studies* (Phalen, 1984) and MS 5 *Lung Function* (HSE, 1977); and in texts on the inhalation of gases, such as *Modeling of Inhalation Exposure to Vapor* (Fiserova-Bergerova, 1983).

The account given here describes in outline the respiratory process and some of the quantitative data and relations in respiratory physiology. This information is the starting point for modelling the effect of toxic gases, both irritant gases that attack the lungs and other gases which enter the blood. The data given are taken mainly from Mountcastle (1974) and apply to a young adult male, unless otherwise stated.

The respiratory system is illustrated in Figure 18.4. Air entering the lung passes through the trachea, then down the bronchioles and through the alveolar duct into the alveolar sac. Interchange between the air and the blood occurs at the surface of the alveoli.

The walls of the capillaries lining the alveoli are extremely thin. The equilibrium partial pressure of a solute gas in the alveoli is effectively the same as that above the blood, neglecting the membrane. Mass transfer between the air and the blood is very rapid.

The volume of air moved in one respiratory cycle is less than the total capacity of the lungs. Moreover, not all the air moved enters the alveolar space, since there is dead space. It is necessary, therefore, to define a number of

Table 18.14 *Some principal physiological parameters of animals, including humans, relevant to respiration (Withers a nd Lees, 1986a) (Courtesy of the Institution of Chemical Engineers)*

A Animals, including man (after Altman and Dittmer, 1974)

	Species				
	Mouse	*Rat*	*Rabbit*	*Dog*	*Man*
Body weight (kg)	0.023	0.14	3.6	22.8	75.0
Lung volume (ml)	0.74	6.3	79	1501	7000
Alveolar surface area (m^2)	0.068	0.39	5.9	90	82
Minute volume (at rest) (ml/min)	24	84	1042	2923	6000
Minute volume/body weight (ml/min kg)	1043.5	600	289.4	128.2	80
Minute volume/lung volume (ml/min ml)	32.4	13.3	13.2	1.95	0.86
Minute volume/alveolar surface area (ml/min m^2)	352.9	215.4	176.6	32.5	73.2
Lung volume/alveolar surface area (ml/m^2)	10.9	16.2	13.4	16.7	85.4

B Man (after Mountcastle, 1974)

		Reference[a]
Body weight (kg)	75	1009
Lung volume (ml)	6000	1367
Tidal volume (ml)	500	1382
Alveolar volume (ml)	350	J.B. West (1965)
Anatomical dead space (ml)	150	J.B. West (1965)
Breathing rate (at rest) (breaths/min)	12	1382
Minute volume (at rest) (ml/min)	6000	1382
Alveolar surface area (m^2)	70	1387
Pulmonary diffusion capacity for carbon monoxide, D_{LCO} (ml/min mm Hg)	61	1391
Mean thickness of alveolar capillary tissue barrier (μm)	1.7	Altman and Dittmar (1974)
Volume of lung capillaries (ml)	140	1387
Residence time of blood in lung capillaries (s)	0.75	1387
Volume of blood (ml)	5000	844
Volume of plasma (ml/kg body weight)	45	1020
Volume of cell fluid (ml/kg body weight)	30	1020

[a] Page number in Mountcastle (1974), unless otherwise noted.

components of lung volume as shown in Figure 18.5. These include:

Tidal volume (TV)	Volume of air entering and leaving the lungs in one natural respiratory cycle.
Inspiratory reserve volume (IRV)	Volume of air additional to the tidal volume that can be inhaled by maximum effort.
Expiratory reserve volume (ERV)	Volume of air additional to tidal volume which can be exhaled by maximum effort.
Residual volume (RV)	Volume of air remaining in lungs after exhalation with maximum effort.
Vital capacity (VC)	Sum of tidal, inspiratory reserve and expiratory reserve volumes.
Inspiratory capacity (IC)	Volume of air which can be inhaled with maximum effort; sum of tidal volume and inspiratory reserve volume.
Functional residual volume (FRV)	Volume of air left in lungs at end of natural exhalation.
Total lung capacity (TLC)	Sum of vital capacity and residual volume. Also sum of inspiratory capacity and functional residual capacity.

Thus

$$TLC = VC + RV = IRV + TV + ERV + RV$$
$$= IC + FRC$$
$$VC = IRV + TV + ERV$$
$$IC = IRC + TV$$
$$FRC = ERV + RV$$

The tidal volume consists of the alveolar space and the anatomical dead space. Some typical values are:

Tidal volume, $V_T = 500$ ml

Alveolar space, $V_A = 350$ ml

Anatomical dead space, $V_D = 150$ ml

The typical respiration rate at rest is

Respiration rate, $f = 12$ breaths/min

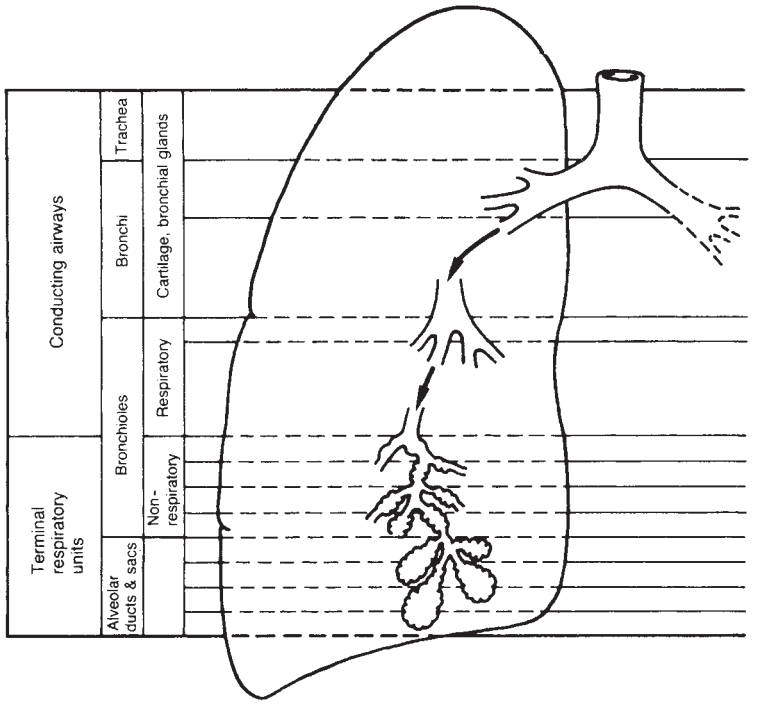

Figure 18.4 *The structure of the respiratory tree in the lung (after Weibel, 1973)*

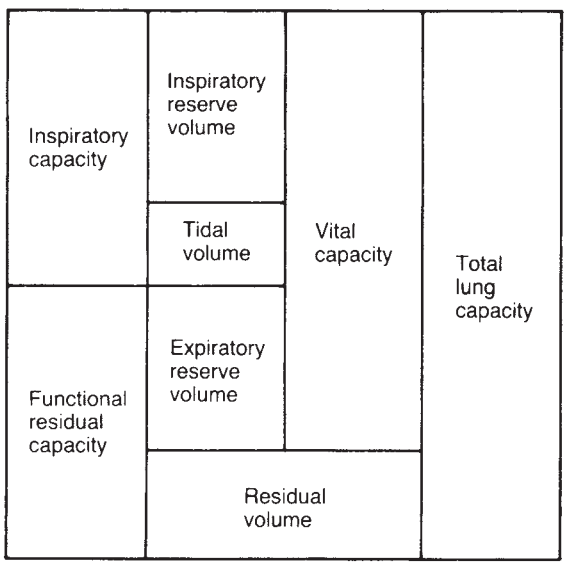

Figure 18.5 *Components of lung volume (after Lambertsen, 1974; Cotes, 1979)*

The product of the tidal volume and the respiration rate is termed the minute volume, V_T and that of the alveolar space and the respiration rate the alveolar ventilation, V_A. Typical values of these two quantities are

$$\text{Minute volume, } V_T = 12 \times 500 = 600\,\text{ml/min}$$
$$\text{Alveolar ventilation, } V_A = 12 \times 350 = 4200\,\text{ml/min}$$

The lungs contain some 3×10^8 alveoli with an alveolar area of about 70 m^2. The thickness of the capillary membrane is about 0.3–2.5 μm. The capillary volume is some 140 ml and the transit time of the blood is some 0.75 s at rest and 0.34 s during exercise.

The flow of blood through the capillaries of the lung depends on the cardiac output, which is a function of the heart rate and the stroke volume. The heart rate is typically 75 strokes/min and the stroke volume some 77 ml, and the cardiac output about 5000 ml/min.

It is the function of the lung to absorb oxygen from the air into the blood and to desorb carbon dioxide from the blood into the air. The measure of the ability of the lung to do this is pulmonary diffusion capacity D_L. The pulmonary diffusion capacity for oxygen is defined by the relation

$$D_{LO2} = \frac{\dot{V}_{O2}}{P_{AO2} - P_{AO2'}} \qquad [18.13.1]$$

where D_{LO2} is the pulmonary diffusion capacity for oxygen (ml/min mmHg), P_{AO2} is the partial pressure of oxygen in the alveolar space (mmHg), $P_{AO2'}$ is the equilibrium partial pressure of oxygen in the alveolar space and above the pulmonary capillaries (mmHg) and V_{O2} the rate of absorption of oxygen (ml/min). The diffusion capacity for carbon dioxide D_{LCO2} is defined in a similar way.

In practice, the principal measured values relate to the diffusion capacity of carbon monoxide D_{LCO}. Carbon monoxide has a very high affinity for haemoglobin, some 210 times that of oxygen, so that the equilibrium partial pressure of carbon monoxide in the alveolar space is very small and may be neglected in estimating the diffusion coefficient.

The diffusion capacity of a gas is proportional to its solubility and inversely proportional to the square root of its molecular weight. The solubilities of oxygen and carbon dioxide at 37°C are for water 2.386 and 56.7 ml gas/100 ml fluid atm and for plasma 2.14 and 51.5 ml gas/100 ml fluid atm, respectively. The diffusion capacity for oxygen D_{LO2} is $1.23\times D_{LCO}$ and that for carbon dioxide is $24.6\times D_{LCO}$. The ratio D_{LCO2}/D_{LO2} is 20.

The value of D_{LO2} at rest is about 75 ml/min mmHg.

	Partial pressure of oxygen (mmHg)
Ambient air	158
Tracheal air	149
Alveolar air	100
Exhaled air	116

The partial pressure of the exhaled air is the weighted average of the tracheal and alveolar air. The equilibrium partial pressure of oxygen above arterial blood $P_{O2a'}$ is about 95 mmHg and that above venous blood $P_{O2v'}$ about 40mmHg.

Blood comprises plasma and cells. The volume of plasma is some 45 ml/kg body weight and that of cells some 30 ml/kg body weight. For a man of 70 kg the volume of plasma is therefore about 3150 ml and that of blood about 5250 ml.

Extracellular fluid comprises some 20% and plasma some 5% of body weight. Thus extracellular fluid other than plasma has a volume some 3 times that of the plasma. All but a very small fraction of this extracellular fluid is in diffusion equilibrium. The specific gravity of plasma is 1.026.

Some principal relations for lung volumes, ventilation rates and partial pressures are

$$V_T = V_E = V_A + V_D \qquad [18.13.2]$$

$$\dot{V}_A = V_A f \qquad [18.13.3]$$

$$\dot{V}_E = V_E f \qquad [18.13.4]$$

$$\dot{V}_I = \frac{F_{EN2}}{F_{IN2}} \dot{V}_E \qquad [18.13.5]$$

$$\dot{V}_{O2} = \dot{V}_I F_{IO2} - \dot{V}_E F_{EO2} \qquad [18.13.6]$$

$$F_{EO2} = (F_{IO2} V_D + F_{A02} V_A)/V_E \qquad [18.13.7]$$

$$\dot{V}_{O2} = D_{LO2}(P_{AO2} - P_{AO2'}) \qquad [18.13.8]$$

$$P_{AO2'} \approx P_{O2A'} \qquad [18.13.9]$$

$$P_{O2'} = C_{O2}/H_{O2} \qquad [18.13.10]$$

where C_{O2} is the concentration of oxygen in the liquid phase (ml O_2/ml fluid), D_{LO2} is the pulmonary diffusion capacity for oxygen (ml/min mmHg), F_{AO2} is the concentration of oxygen in alveolar space (ml O_2/ml space), F_{EN2} is the concentration of nitrogen in the exhaled air (ml N_2/ml air), F_{EO2} is the concentration of oxygen in the exhaled air (ml O_2/ml air), F_{IN2} is the concentration of nitrogen in the exhaled air (ml N_2/ml air), F_{IO2} is the concentration of oxygen in the inhaled air (ml O_2/ml air), H_{O2} is Henry's law constant for oxygen (ml O_2/ml fluid (mmHg O_2)), P_{AO2} is the partial pressure of oxygen in the alveolar space (mmHg), $P_{AO2'}$ is the equilibrium partial pressure of oxygen at the capillary membrane (mmHg), $P_{O2'}$ is the equilibrium partial pressure of oxygen (mmHg), $P_{O2a'}$ is the partial pressure of oxygen above arterial blood (mmHg), V_A is the alveolar volume (ml), is the alveolar minute volume (ml/min), V_D is the anatomical dead space (ml), V_E is the volume exhaled (ml), $\dot{V}_E$ is the exhaled minute volume (ml/min), $\dot{V}_I$ is the inhaled minute volume (ml/min), $\dot{V}_{O2}$ is the oxygen consumption minute volume (ml/min), V_T is the tidal volume (ml), and f is the respiration rate (breaths/min).

Some principal physiological parameters in man relevant to respiration have been given in Table 18.14. Further data on the lung in man are summarized in Table 18.15.

18.13.2 Toxicokinetic models

The treatment just given of the respiratory system provides the front-end part for a toxicokinetic model describing the absorption and distribution of the toxin in the body.

Such toxicokinetic models for an inhaled gas may be developed by modelling the absorption of gas in the lung into the bloodstream. The difference between the mass

inhaled and that exhaled equals the mass transferred across the membrane of the lung and this in turn equals the mass deposed in the body. Then if the chemical enters the main bloodstream, its concentration in the blood will be a function of the rates of absorption and of elimination. In simple terms, this situation may be modelled as a single exponential stage with a time constant that is a function of the apparent volume of distribution. The equilibrium back pressure of the chemical at the lung surface will depend on the concentration in the blood.

A toxicokinetic model of this general type is applicable where the toxic gas does not attack the respiratory system, but enters into the bloodstream and attacks some other organ in the body. There is, however, a lack of models relevant to hazard assessment.

18.13.3 Irritant gases

Such models are, in any case, less applicable to the important class of irritant gases, which act directly on the surface of the respiratory tract and/or lung rather than by accumulation in the body fluids. In this case the respiratory system acts as a sink for the chemical. This clearly requires a different model but, again, models suitable for hazard assessment are lacking.

18.13.4 Inhalation rates

In most cases the inhalation rate is a dominant factor in the entry of toxic gas into the system. It is therefore of great importance both in modelling the effects of and in extrapolating from experiments on toxic gases.

In applying to man the results of animal experiments on gas toxicity it is necessary to make allowance for the effect of inhalation rate. If the base case for comparison between animals and man is that each has the inhalation rate which is normal at rest, there are two separate allowances, or factors, which need to be applied. The first is between the inhalation rate of the animal at rest and in the experiment, the second between that of man at rest and in the accident conditions envisaged in the hazard assessment. It can be seen from Table 18.14 that there are appreciable differences in the inhalation rates, as related to features such as body weight and lung surface area.

Information on the breathing of animals during exposure is recorded in some experiments, although quantitative data appear to be relatively rare. By contrast, the variation of the inhalation rate of man with different degrees of exercise is well documented. Some data given by Henderson and Haggard (1943) are shown in Table 18.16.

Table 18.15 *Some principal parameters of the lung in man (after Mountcastle, 1974) (Courtesy of CV Mosby Company)*

A Lung volumes	
	Volume (ml)
Total lung capacity	5970
Tidal volume	500
Expiratory reserve volume	980
Residual volume	1190
Vital capacity	4780
Inspiratory capacity	3790
Functional residual volume	2180
Anatomical dead space	150[a]
Alveolar volume	350[a]
B Respiration rate	
	Rate (breaths/min)
At rest	12

[a] J.B. West (1965).

18.13.5 Other factors

The respiratory system is not the only organ that is a target for toxic gases. The eyes and the skin may also be affected. Accounts of the eye relevant here are given in Toxicology of the Eye (Grant, 1962) and *Synopsis of Ophthalmology* (Havener, 1971).

18.14 Gas Toxicity: Toxicity Data

Before considering the toxicity of some of the principal industrial gases, attention is drawn to some of the general sources of data on toxicity, particularly toxicity to humans.

Sources of toxicity data have been described in Section 18.3. Some texts which deal particularly with gas toxicity include: *Kompendittm der praktischen Toxikologie* (Kobert, 1912); *Industrial Poisoning* (Rambousek, 1913); *Kurzes Lehrbuch der Arbeits- und Gewerbehygiene* (Lehmann, 1919); *Industrial Poisons in the United States* (Hamilton, 1925); *Lehrbuch der Toxikologie* (Flury and Zanger, 1928), *Noxious Gases* (Henderson and Haggard, 1943); *Industrial Hygiene and Toxicology* (Patty, 1948–), with its later editions (Cralley and Cralley, 1978; Wands, 1981; Clayton and Clayton, 1991 ACGIH/73); *Dangerous Properties of Industrial Materials* (Sax, 1957–), with its later edition (Lewis, 1992 ACGIH/89); *Toxicology of Drugs and Chemicals* (Deichman and Gerarde, 1969); and *Toxicology: the Basic Science of Poisons* (Casarett and Doull, 1975), with its later edition (Amdur, Doull and Klaassen, 1991 ACGIH/54).

At the turn of the century an appreciable amount of research was done in Germany by Lehmann and others on the effects on humans of many gases of industrial interest. This includes work by Lehmann himself (Lehmann, 1886, 1887, 1893, 1899a) and by Matt (1889); there is also later work by Hess (1911), Drescher (1920), Dschang (1928) and Beck (1959).

Table 18.16 *Inhalation rate for various levels of activity for man (after Henderson and Haggard, 1943)*

Activity	*Inhalation rate*[a] (l/min)	*Oxygen consumption rate*[b] (l/min)
Rest in bed, fasting	6	0.240
Sitting	7	0.300
Standing	8[c]	0.360
Walking, 2 mile/h	14	0.650
Walking, 4 mile/h	26	1.200
Slow run	43	2.000
Maximum exertion	65–100	3.000–4.000

[a] Measured at 0°C and 760 mmHg.
[b] Measured at 20°C.
[c] This value is quoted by A. Meyer (1938) and also by Prentiss (1937).

Many of the main industrial gases have also been used in warfare, particularly in the First World War. Accounts of the military use of these gases do not generally provide usable quantitative data, but some give pointers to the effects of the gases on humans that constitute a collateral check on data from animal experiments, which is the main source.

Accounts of the gas warfare are given in *The Poison War* (A.A. Roberts, 1915), *Reports of the Chemical Warfare Medical Committee* (1918–), *Atlas of Gas Poisoning* (MRC, 1918), *The Lethal War Gases* (Underbill, 1920), *Chemical Warfare* (Fries and West, 1921), *History of the Great War, Medical Services, Diseases of the War*, vol. II (Macpherson *et al.*, 1923), *Gas Warfare* (Fischmann, 1924), *Poisoning Warfare Gases* (Gilchrist, 1924), *Fünf Vortrage aus den Jahren 1920–1923* (F. Haber, 1924), *La Guerre Chimique* (Le Wita, 1925), *The Medical Aspects of Chemical Warfare* (Vedder, 1925), *The Medical Department of the United States Army in the World War, vol. 14: Medical Aspects of Gas Warfare* (Ireland, 1926), *Der Gaskampf und die chemischen Kampfstoffen* (J. Meyer, 1926), *History of the War: Military Operations in France and Belgium* (Edmonds and Wynne, 1927), *A Comparative Study of World War Casualties from Gas and Other Weapons* (Gilchrist, 1928), *Manual of Treatment of Gas Casualties* (Anon., 1930), *Schadliche Case* (Flury and Zernik, 1931), *Grun und Gelbkreuz* (Buscher, 1932), *Die wichtigsten Vergiftungen* (Loschke, 1933), *Die Gasschutzfrage* (Zangger, 1932), Gas. The Story of the Special Brigade (Foulkes, 1934), *Leitfaden der Pathologie und Therapie der Kampjgaserkrankungen* (Muntsch, 1935), *Die Tiere im chemischen Krieg* (Richters, 1936b), *Der chemische Kreig* (Hanslian, 1937), *Chemicals in War* (Prentiss, 1937), *Breathe Freely* (Kendall, 1938), *Gaz de Combat* (A. Meyer, 1938), *The War Gases* (Sartori, 1939), *Chemical Warfare* (Wachtel, 1941), *United States Army in World War II: The Technical Services: Chemical Warfare Service* (Brophy, Miles and Cochrane, 1959), *The Problem of Chemical and Biological Warfare, vol. 1: The Rise of CB Weapons* (Q.P. Robinson, 1971) and *The Poisonous Cloud. Chemical Warfare in the First World War* (L.F. Haber, 1986). Other work on war gases is described by L. Hill (1915, 1920), Haldane, Meakins and Priestley (1918a,b, 1918/19), Herringham (1919, 1920), Flury (1921a,b), Haggard (1924), Chlopin (1927–) and Richters (1936b).

Accounts of the physiological and medical aspects of gas poisoning are given in *Respiratory Function of the Blood* (Barcroft, 1925), *Respiration* (Haldane and Priestley, 1935), and *Pulmonary Oedema and Inflammation* (Drinker, 1945).

Some authors have dealt in a single publication with a number of different gases. They include Lehmann (1893, 1899a), Ronzani (1908, 1909), Hess (1911), Zeehuisen (1922), Haggard (1924), Schutze (1927), Walton and Witherspoon (1928), Carpenter, Smyth and Pozzani (1949), Smyth and Carpenter (1949), Zielhuis (1970), Higgins *et al.* (1972), MacEwen and Vernot (1972), Vernot *et al.* (1977) and ten Berge, Zwart and Appelman (1986).

Setterstrom and co-workers (McCallan and Setterstrom, 1940; Thornton and Setterstrom, 1940; Weedon, Hartzell and Setterstrom, 1940) have studied ammonia, chlorine, hydrogen cyanide, hydrogen sulfide and sulfur dioxide.

A somewhat separate area of work that also yields toxicity data is that on the toxicity of combustion products. Accounts of research in this area, notably by Hilado and co-workers and by Hartzell and co-workers, are given in Section 18.22.

An early collection of gas toxicity data for hazard assessment is that given in the Vulnerability model of Eisenberg, Lynch and Breeding (1975), and extended by Perry and Articola (1980). Their work is discussed below. Another collection of data on gas toxicity is that made by Back, Thomas and MacEwen (1972).

8.15 Gas Toxicity: Vulnerability Model

18.15.1 Initial model

As just stated, some of the first correlations for the toxicity of industrial gases relevant to major releases were those given in the vulnerability model by Eisenberg, Lynch and Breeding (1975). These workers analysed data for the toxicity of chlorine and ammonia and obtained probit equations for the lethality of these two gases. For chlorine they found that the line for composite lethality in animals passes through the following points:

Arbitrary units	*Percent affected*
0.54	3
0.59	5
1	50
1.5	90
1.8	97 (extrapolated)

They also refer to the *Guide for Short-Term Exposure for Chlorine* (NAS/NRC, 1973), which describes an exposure of 14–21 ppm for 0.5–1 h as 'dangerous' and one of 34–51 ppm for 1–1.5 h as 'lethal'. They suggest that the terms 'dangerous' and 'lethal' might be interpreted as 5% and 90% lethal.

Eisenberg, Lynch and Breeding quote limit values given in the *Guides for Chlorine* (NAS/NRC, 1973) and ammonia (NAS/NRC, 1972b). At the short-term exposure limit (STEL), there is mild odour, minimal irritation and no health hazard. The STEL values for chlorine and ammonia are:

Time (min)	*Concentration* (ppm)	
	Chlorine	*Ammonia*
10	1	20
30	0.5	10
60	0.5	10

At the public emergency limit (PEL), there is strong odour and some irritation. The PEL values, which are ceilings, not averages, for chlorine and ammonia are:

Time (min)	*Concentration* (ppm)	
	Chlorine	*Ammonia*
10	3	100
30	2	75
60	2	50

In addition, they quote for chlorine the EEL suggested by Zielhuis (1970):

Time (min)	*Concentration* (ppm)
5	7
15	5
30	4
60	3

On the basis of such arguments the authors give for chlorine the following response relations:

Chlorine concentration (ppm)	*Time of exposure*	*Effect*
3	Any	No risk, but some harassment
7	1 h or more	Strong to intolerable irritation, with some risk to highly susceptible individuals
20	Severals hours	50% lethal (their estimate)
33	c.1 h	50% lethal (estimate based on NAS/NRC report)
60	c.10 min	50% lethal (their estimate)

Eisenberg, Lynch and Breeding took the causative factor V in the probit equation for chlorine as

$$V = \sum C_i^n T_i \qquad [18.15.1]$$

where C is the concentration (ppm), T is the time interval (min), and n is an index. From analysis of the data, they obtained a value of $n = 2.75$. The probit equation for chlorine lethality derived by these authors is then

$$Y = -17.1 + 1.69 \ln\left(\sum C_i^{2.75} T_i\right) \qquad [18.15.2]$$

where Y is the probit.

A similar treatment was applied to ammonia. For this gas the authors give the following response relations:

Ammonia concentration (ppm)	*Time of exposure*	*Effect*
20	Any	Odour detected by majority of population
100	Any	Irritation and complaint
500	Any	Strong to intolerable irritation, with some risk to highly susceptible individuals
2500–5000		Fatalities mostly from a few in the first 5 min to 90–100% after 1 h, depending on concentration
>5000		100% fatal. Heavy casualties in 5–10 min, and shorter exposures are unlikely in practice

and derive the following probit equation for ammonia lethality:

$$Y = -30.57 + 1.385 \ln\left(\sum C_i^{2.75} T_i\right) \qquad [18.15.3]$$

The relationships described apply to healthy adults. The population also includes more susceptible individuals such as infants, old people and people with advanced pulmonary/cardiovascular disease. The authors propose for such high risk populations the scaling shown in Table 18.17, which is applied to specific concentrations and exposure times for chlorine and ammonia.

Eisenberg, Lynch and Breeding also consider non-lethal injury from chlorine. They give the following estimated response:

Chlorine concentration (ppm)	*Percent affected*
6	1
10	25
13	50
20	90

In this case the causative factor is taken simply as $V = C$. The probit equation for non-lethal injury from chlorine is then

$$Y = -2.40 + 2.90 \ln C \qquad [18.15.4]$$

Non-lethal injury is here taken to mean hospitalization without or with lasting impairment of health.

The authors discuss the possible long-terms effects of exposure to chlorine. They state:

The most recent paper seen was Weill *et al.* (1969). They say that their data for subjects seven years after an accidental exposure to chlorine 'are consistent with the prevailing clinical view that significant permanent lung damage does not result from acute exposure to chlorine gas'. Reports referenced in their paper support this finding: for example, 'no evidence that chlorine intoxication produced residual pulmonary disease' in the 33 most severely affected victims of a major accident; a large survey of industrial exposures did not find 'any evidence of permanent damage to the respiratory tract' another study including war casualties found that 'permanent pulmonary injury was rare'.

18.15.2 Development of model

A further set of probit equations for lethality for use in the Vulnerability model was derived by Perry and Articola (1980). For chlorine the authors quote without reference a set of 'best estimates' which seem close to the data set given by Eisenberg, Lynch and Breeding (Table 6–4) but use a slightly different value of n (2.64 instead of 2.75). For ammonia, they refer again to the data set given in Eisenberg, Lynch and Breeding (Table 6–4). They use in this case an appreciably different value of n (1.36 instead of 2.75).

Table 18.17 *Relation between the lethal concentration of chlorine for the general population and a vulnerable population (Eisenberg, Lynch and Breeding, 1975)*

Level of effect	*Deaths* (%)	
	General population	*High risk population*
Severe harassment with some risk	0	25
Lethal	3	50
Lethal	50	100

For hydrogen cyanide the authors use estimates made by McNamara (1976) based on animal data. They also adapt these data for two other gases, acrylonitrile and hydrogen sulfide, having found no suitable data for these substances. In the latter case they quote C.L. Evans (1967) on the similarities between the effects of the two gases. For acrylonitrile they use the same lethal dose values and probit equation as for hydrogen cyanide, whilst for hydrogen sulfide they double the lethal dose values compared with hydrogen cyanide and thus obtain a different probit equation.

For hydrogen fluoride they utilize data from an earlier study for the Vulnerability model by Rausch, Tsao and Rowley (1977) based on data from Braker and Mossman (1970), Darmer, Haun and MacEwen (1972), Higgins *et al.* (1972), MacEwen and Vernot (1974) and Wohlslagel, DiPasquale and Vernot (1976). They adopt the same value of n namely $n = 1$; in other words, Haber's law.

For hydrogen chloride, Perry and Articola utilize data from another previous study for the Vulnerability model by Rausch, Eisenberg and Lynch (1977). The value of n is 1.0. They use same lethal dose values and value of n for sulfur dioxide (in mg/m^3), the difference in the probit equations being due to the conversion to parts per million.

For phosgene, the authors again utilize data from Rausch, Eisenberg and Lynch. The value of n is 1.0.

Two probit equations for non-lethal injury are also given: by Eisenberg, Lynch and Breeding for chlorine and one derived by the authors themselves for hydrogen fluoride.

The values of the parameters in the probit equations obtained by Perry and Articola are given in Section 18.20.

The support for the probit equations in the Vulnerability model is in some cases rather slight and the level of physical activity to which they are applicable is not well defined.

18.16 Gas Toxicity: Major Industrial Gases

The toxicity of a number of major industrial gases is now considered in more detail. In general, toxic hazard from these gases arises from their manufacture, storage and use in the manufacture of other chemicals. In some cases, hazard arises from another cause. For example, a common cause of gassing by hydrogen sulfide is its presence as an impurity in crude oil and in confined spaces. The overview of the physiological effects of the main industrials gases given in *Noxious Gases* (Henderson and Haggard, 1943) provides a useful introduction to this aspect.

For irritant gases, an important parameter is the solubility in water, which largely determines the part of the respiratory system attacked. Haggard (1924) gives the following relative figures for the solubility of such gases in water at 40°C: ammonia, 444 (extrapolated); hydrogen chloride, 385; sulfur dioxide, 18.7; bromine, 9.4; and chlorine, 1.4. No value is given for phosgene, which decomposes in water.

Incidents involving toxic gases are described in Section 18.27.

18.16.1 Chlorine

There are two industrial toxic gases which in liquefied form are handled on a large scale and are readily dispersed and which therefore present a major toxic hazard. Chlorine is one, and ammonia the other.

Chlorine is a highly toxic gas. The long- and short-term OESs are 0.5 and 1 ppm, respectively. The values represent a small reduction from the TLV (TWA) of 1 ppm that held for many years. Physiologically, chlorine is an irritant gas. The effects of a single exposure include irritation of the mucous membranes, attack of the respiratory tract and pulmonary oedema. A fuller account is given in Section 18.18.

Early work on chlorine includes that Eulenberg (1865), Lehmann (1887, 1899a,b) and Hess (1911). Chlorine was the first gas used in major gas attacks and is treated in virtually all the war gas texts referred to in Section 18.14, and in particular in Underbill (1920), Winternitz, Lambert *et al.* (1920), Gilchrist (1924), F. Haber (1924), Vedder (1925), Flury and Zernik (1931), Prentiss (1937), and by Black, Glenny and McNee (1915), Bradford and Elliott (1915–16), L. Hill (1915, 1920), Schafer (1915), Kramer (1917), Haldane, Meakins and Priestley (1918a,b, 1918–19), Schultz (1918a,b), Schultz and Hunt (1918), Achard (1919), Barbour (1919), Barbour and Williams (1919), Baskervffle (1919), Burrell (1919), Herringham (1919, 1920), Hjort and Taylor (1919), Meakins and Priestley (1919), Vinet (1919), Gunn (1920), Flury (1921a, 1928), Chlopin (1927–), Flury and Zernik (1932), Abbott (1933), Gilchrist and Matz (1933) and Freitag (1940). More recent work includes that by Ceiling and McLean (1941), Cralley (1942), Silver and McGrath (1942), Silver, McGrath and Ferguson (1942), Fowell (1949), A.T. Jones (1952), Elmes and Bell (1963), Gay (1963), Flake (1964), D.P. Bell and Elmes (1965), Kowitz *et al.* (1967), C.G. Kramer (1967), Rupp and Henschler (1967), Schlagbauer and Henschler (1967), Krause, Chester and Gillespe (1968), Beach, Jones and Scarrow (1969), Chester, Gillespie and Krause (1969), Sartorelli (1969), Faure *et al.* (1970), Sessa *et al.* (1970), Kaufman and Burkons (1971), Leube and Kreiter (1971), Barrow and Smith (1975), Colardyn *et al.* (1976), Barrow *et al.* (1977), Chester *et al.* (1977), Bitron and Aharonson (1978), Barrow and Dodd (1979), Barrow *et al.* (1979), Withers and Lees (1985a,b), Withers (1986a) and Zwart and Woutersen (1988). Work on chlorine is also included in treatments dealing with a number of gases, including those by Zeehuisen (1922), Haggard (1924), Setterstrom and coworkers (McCallan and Setterstrom, 1940; Thornton and Setterstrom, 1940; Weedon, Hartzell and Setterstrom, 1940), Carpenter, Smyth and Pozzani (1949), Beck (1959), and Buckley *et al.* (1984).

The toxicity of chlorine has been reviewed in *Chlorine and Hydrogen Chloride* by the (WHO, 1982 EHC21) and in the *Chlorine Toxicity Monograph* (MHAP, 1987); an account from the latter work has been given by Withers (1985). The Monograph estimates that in the absence of any subsequent medical treatment the LC_{50} for 30 min for healthy adults is of the order 400 ppm.

Probit equations for chlorine have been given by Eisenberg, Lynch and Breeding (1975), Perry and Articola (1980), ten Berge and van Heemst (1983), Withers and Lees (1985b), and ten Berge, Zwart and Appelman (1986), in the Rijnmond Report (Rijnmond Public Authority, 1982), and by the Center for Chemical Process Safety (CCPS) and the CPD. Dangerous dose values are given by the HSE, as described below.

Chlorine is one of the gases considered in the hazard assessment study of Back, Thomas and MacEwen (1972). The evidence is that serious long-term effects of non-lethal single exposure to chlorine are rare. This aspect is discussed in Section 18.15.

A fuller treatment of chlorine toxicity is given in Section 18.18.

18.16.2 Ammonia

The other principal industrial toxic gas is ammonia. Like chlorine, it is a severe toxic hazard because it is handled on a large scale, it is a liquefied gas and is therefore readily dispersed, and it is highly toxic. Ammonia has long- and short-term OESs of 25 and 35 ppm, respectively.

Physiologically, ammonia is an irritant gas. The effects of a single exposure include irritation of the mucous membranes, attack of the respiratory tract and pulmonary oedema. Ammonia is very much more soluble in water than chlorine, and therefore tends to attack particularly the upper respiratory tract, stripping the lining, and inducing laryngeal oedema.

Early work on ammonia includes that by Lehmann (1886, 1893), Matt (1889), Hess (1911) and Ronzani (1908, 1909). Ammonia does not appear to have been a candidate war gas, but it is discussed by Flury (1921a, 1928), Flury and Zernik (1931) and Henderson and Haggard (1943). More recent work includes that by Boyd, MacLachlan and Perry (1944), Silver and McGrath (1948), Silver-man, Whittenberger and Muller (1949), Alpotov and Michailov (1963), H.A. Mitchell (1963), Alpotov (1964), Helmers, Top and Knapp (1971), Mayan and Merilan (1972), Hilado, Casey and Furst (1977), Verberk (1977), Richard, Jounay and Boudene (1978), Dodd and Gross (1980), Appelman, ten Berge and Reuzel (1982), Kapeghian *et al.* (1982), ten Berge and van Heemst (1983), Withers (1986b) and Pedersen and Selig (1989). Work on ammonia is also included in treatments dealing with a number of gases, including those by Haggard (1924), Setterstrom and co-workers (McCallan and Setterstrom, 1940; Thornton and Setterstrom, 1940; Weedon, Hartzell and Setterstrom, 1940), Carpenter, Smyth and Pozzani (1949), Coon *et al.* (1970), Stupfel *et al.* (1971), Vernot *et al.* (1977) and Buckley *et al.* (1984).

The toxicity of ammonia in the specific context of process plants has been considered by D.P. Wallace (1979).

The toxicity of ammonia has been reviewed in *Ammonia* (WHO, 1986 EHC54) and in *Ammonia Toxicity Monograph* (MHAP, 1988).

Probit equations for ammonia have been given by Eisenberg, Lynch and Breeding (1975), Perry and Articola (1980), ten Berge, Zwart and Appelmann (1986), the CCPS and the CPD. Dangerous dose values are given by the HSE, as described below.

Ammonia is one of the gases considered in the hazard assessment study done by Back, Thomas and MacEwen (1972).

There is little evidence of serious long-term effects of non-lethal single exposure, except where the exposure has been so serious that death has been prevented only by medical attention, when respiratory deficiencies may occur.

18.16.3 Acrylonitrile

Acrylonitrile is an irritant gas and is also assigned the 'risk phrase' R45. It has a long-term MEL of 2 ppm, but no quoted short-term limit.

Physiologically, acrylonitrile vapour causes various irritant effects including pulmonary oedema. Various other effects such as vomiting, convulsions and incoordination have been reported in animals.

Most work on the toxicity of acrylonitrile has been carried out since 1940. Studies include those of Dudley and Neal (1942), Dudley, Sweeney and Miller (1942), R.H. Wilson (1944), R.H. Wilson, Hough and McCormick (1948), Carpenter, Smyth and Pozzani (1949), McOmie (1949), Smyth and Carpenter (1949), Brieger, Rieders and Hoders (1952), Knobloch *et al.* (1971), Rogaczewska (1975), McNamara (1976), Appel, Peter and Bolt (1981) and ten Berge, Zwart and Appelman (1986).

Probit equations for acrylonitrile have been given by Perry and Articola (1980), ten Berge, Zwart and Appelman (1986), the CCPS and the CPD. Dangerous dose values are given by the HSE, as described below.

18.16.4 Bromine

Bromine is a highly toxic gas. It has long- and short-term OESs of 0.1 and 0.3 ppm, respectively. The toxic properties of bromine are somewhat similar to those of chlorine, but there are also significant differences.

Physiologically, bromine is an irritant gas. The effects of a single exposure include irritation of the mucous membranes, attack of the respiratory tract and pulmonary oedema. Bromine is less soluble than ammonia, but more soluble than chlorine. It tends to attack the upper respiratory tract as well as the lungs, stripping the lining and, inducing suffocation. It also tends to cause more severe sublethal injury than chlorine.

Most work on bromine has been conducted in conjunction with work on chlorine, which has led experimenters to compare the toxicity of the two gases. Early work on bromine was carried out by Lehmann (1887, 1893) and Hess (1911). Experiments conducted during the First World War are described by L. Hill (1915, 1920), Symes (1915a,b) and Chlopin (1927–). More recent work includes that by Rupp and Henschler (1967), Schlagbauer and Henschler (1967) and Bitron and Aharonson (1978). Work on bromine is also included in treatments dealing with a number of gases, including that of Haggard (1924).

From this work Withers and Lees (1986b) concluded that bromine is some 1.5 times as toxic as chlorine. Adopting essentially the same methodology as in their work on chlorine, described below, they give for the standard level of activity for the regular population the following probit equation for the lethality of bromine:

$$Y = -9.04 + 0.92 \ln L^* \qquad [18.16.1]$$

with

$$L^* = \sum C^2 T \qquad [18.16.2]$$

where C is the concentration (ppm), L^* is the toxic load ($ppm^2 min$) and T is the exposure time (min). This probit equation is discussed by P.C. Davies and Purdy (1987) and Withers and Lees (1987a).

Further probit equations for bromine have been given by ten Berge, Zwart and Appelman (1986), the CCPS and the CPD, as described below.

18.16.5 Carbon dioxide

Carbon dioxide is an asphyxiant, but also a toxic gas. It has long- and short-term OESs of 5,000 and 15,000 ppm, respectively. At a concentration of 10% it can cause unconsciousness within 1 min. It is odourless.

Hazard from the use of carbon dioxide in manufacturing arises where it is used in processes or where it is generated by combustion.

18.16.6 Carbon monoxide

Carbon monoxide is a chemical asphyxiant. It combines with haemoglobin in the blood, thus displacing the oxygen. It has long- and short-term OESs of 50 and 300 ppm, respectively. It is odourless.

Hazard from carbon monoxide arises where it occurs as a process gas or where it is generated, as in combustion processes. Carbon monoxide is responsible for a significant proportion of deaths from gas poisoning.

18.16.7 Hydrocarbons

Hydrocarbons vary in toxicity. Some are asphyxiants, for example, propane; others are assigned an OES, for example, butane, which has long- and short-term OESs of 600 and 750 ppm, respectively.

18.16.8 Hydrogen chloride

Hydrogen chloride has a short-term OES of 5 ppm with no quoted long-term value. Physiologically, hydrogen chloride is an irritant gas. The effects of a single exposure include irritation of the mucous membranes, attack of the respiratory tract and pulmonary oedema.

Early work on hydrogen chloride includes that by Lehmann (1886) and Hess (1911). Hydrogen chloride does not appear to have been a serious candidate war gas. More recent work includes that by Machle *et al.* (1942), Greenfield *et al.* (1969), Darmer, Kinkead and Dipasquale (1972, 1974), Nagao *et al.* (1972), Hilado and Furst (1976), Barrow *et al.* (1977), Hilado and Gumming (1978), Barrow, Lucia and Alarie (1979), Hartzell *et al.* (1985) and Hartzell (1989). Work on hydrogen chloride is also included in treatments dealing with a number of gases, including those of Haggard (1924), Higgins *et al.* (1972), MacEwen and Vernot (1972), Vernot *et al.* (1977) and Buckley *et al.* (1984).

The toxicity of hydrogen chloride has been reviewed in *Chlorine and Hydrogen Chloride* (WHO, 1982 EHC21).

Probit equations for hydrogen chloride have been given by Perry and Articola (1980), ten Berge, Zwart and Appelman (1986), the CCPS and the CPD, as described below.

Hydrogen chloride is one of the gases considered in the hazard assessment study of Back, Thomas and MacEwen (1972).

18.16.9 Hydrogen cyanide

Hydrogen cyanide has a short-term MEL of 10 ppm with no quoted long-term value. Physiologically, hydrogen cyanide is chemical asphyxiant. It causes cyanide poisoning, which is a form of asphyxia caused by the arrest of internal respiration. Its action can be very rapid.

Early work on hydrogen cyanide includes that by Geppert (1889), Matt (1889), Ahlmann (1905), Hess (1911), Fiihner (1919), Drescher (1920), Koelsch (1920), Reed (1920), Hasselmann (1925a,b), Dschang (1928), R. Schwab (1929), Hug (1932), Wirth and Lammerhirt (1934) and Wirth (1935, 1937). Hydrogen cyanide was considered for use, but found little application, as a war gas, and its toxicity is dealt with in some of the texts on war gases, including those of F. Haber (1924), Vedder (1925), Ireland (1926), Flury and Zernik (1931), Foulkes (1934), Muntsch (1935), Hanslian (1937), Prentiss (1937), Wachtel (1941), Henderson and Haggard (1943) and by Flury (1921, 1928) and Chlopin (1927–). More recent work includes that of MacNamara (1976), Hilado and Furst (1976), Hilado and dimming (1978), Hartzell, Priest and Switzer (1985) and Hartzell (1989). Work on hydrogen cyanide is also included in treatments dealing with a number of gases, including those of Schutze (1927), Walton and Witherspoon (1928) and Setterstrom and coworkers (McCallan and Setterstrom, 1940; Thornton and Setterstrom, 1940; Weedon, Hartzell and Setterstrom, 1940), Higgins *et al.* (1972) and Vernot *et al.* (1977).

Probit equations for hydrogen cyanide have been given by Perry and Articola (1980), ten Berge, Zwart and Appelman (1986), the CCPS and the CPD, as described below.

Hydrogen cyanide is one of the gases considered in the hazard assessment study done by Back, Thomas and MacEwen (1972).

18.16.10 Hydrogen fluoride

Hydrogen fluoride has a short-term OES (as F) of 3 ppm, with no quoted long-term value. Physiologically, hydrogen fluoride is an irritant and also has systemic effects. The irritant effects of a single exposure include irritation of the mucous membranes, attack of the respiratory tract and pulmonary oedema. There is also evidence of systemic effects on organs including the liver, kidney, heart, spleen and thymus.

Hydrogen fluoride is subject to oligomerization, the extent depending on the pressure and temperature. At typical atmospheric conditions the apparent molecular weight is in the range 68–78.

Accounts of the properties of hydrogen fluoride are given by Muehlberger (1928), Simons (1931), Rushmere (1954), Maclean *et al.* (1962), Schotte (1987) and Clough, Grist and Wheatley (1987).

Early work on hydrogen fluoride includes that by Matt (1889), Ronzani (1908, 1909), Kehoe *et al.* (1932), Machle *et al.* (1934), Machle and Kitzmiller (1935) and Machle and Scott (1935) and Stokinger (1949). Hydrogen fluoride does not appear to have been a serious candidate as a war gas, but it is discussed by Flury and Zernik (1931) and Henderson and Haggard (1943). More recent work on the gas includes that by Rosenholtz *et al.* (1963), MacEwen and Vernot (1970), Darmer, Haun and MacEwen (1972), Hilado and Furst (1976), Hilado and Cumming (1978), Valentine (1988) and Mudan (1989a). Work on hydrogen fluoride is also included in treatments dealing with a number of gases, including those of Higgins *et al.* (1972), Wohlslagel, DiPasquale and Vernot (1976) and Vernot *et al.* (1977).

Probit equations for fatal injury by hydrogen fluoride have been given by Perry and Articola (1980), ten Berge, Zwart and Appelman (1986), Mudan (1989a), the CCPS and the CPD. Dangerous dose values are given by the HSE, as described below.

Mudan (1989a) derives his probit equation as follows. He utilizes primarily the more recent work of Rosenholtz *et al.*, MacEwen and Vernot, Darmer, Haun and McEwen, Higgins *et al.*, Wohlslagel, DiPasquale and Vernot, and the preliminary results of Valentine; MacEwen and Vernot give raw data, some of which is used by Darmer, Haun and MacEwen. From the results of these various workers he first establishes, using four data sets, that Haber's law applies, namely, $ct =$ Constant. He then obtains LCt_{50} values of 26,880 ppm min for mice, 46,900 ppm min for small rats, 84,000 ppm min for large rats, 64,900 ppm min for guinea pigs and 106,440 ppm min for monkeys. Applying the toxicologist's rule-of-thumb that consistent results from three animal species may be applied to humans, he obtains for the latter the estimated LCt_{50} of 59,200 ppm min. Next he obtains separate probit equations for each of the species and from these a median best estimate

of the slope of 4.853, thus yielding the desired probit equation:

$$Y = -48.33 + 4.853 \ln L^* \quad [18.16.3]$$

Where

$$L^* = Ct \quad [18.16.4]$$

where C is the concentration (ppm) and t is the time (min). Mudan also determines the 90% confidence limits on the slope as 2.854 and 8.348. Using the lower value of the slope he obtains the further '90% slope probit' equation:

$$Y = -26.36 + 2.854 \ln L^* \quad [18.16.5]$$

The mortality given by these two probit equations is shown together with the experimental values in Figure 18.6.

Hydrogen fluoride is one of the gases considered in the hazard assessment study done by Back, Thomas and MacEwen (1972).

18.16.11 Hydrogen sulfide

Hydrogen sulfide has long- and short-term OESs of 10 and 15 ppm, respectively. Physiologically, hydrogen sulfide is an irritant and a chemical asphyxiant. The irritant effects of a single exposure include irritation of the mucous membranes, attack of the respiratory tract and pulmonary oedema. It also has an asphyxiant effect, caused by inhibition of cytochrome oxidase and resulting in arrest of respiration at the brain.

The gas can be detected at low concentration, but the sense of smell is lost after 2–15 min exposure, thus making it impossible to detect dangerous concentrations. Moreover, the odour of hydrogen sulfide can be masked by the presence of other chemicals: tests have shown that concentrations below 1 ppm could be detected by odour in air, but in the presence of light hydrocarbons such as propane or butane even 5–10 ppm could not be smelt.

Early work on hydrogen sulfide includes that by Biefel and Pollock (1880), Lehmann (1892, 1893, 1899a), Hess (1911), Haggard and Henderson (1922), Haggard (1925),

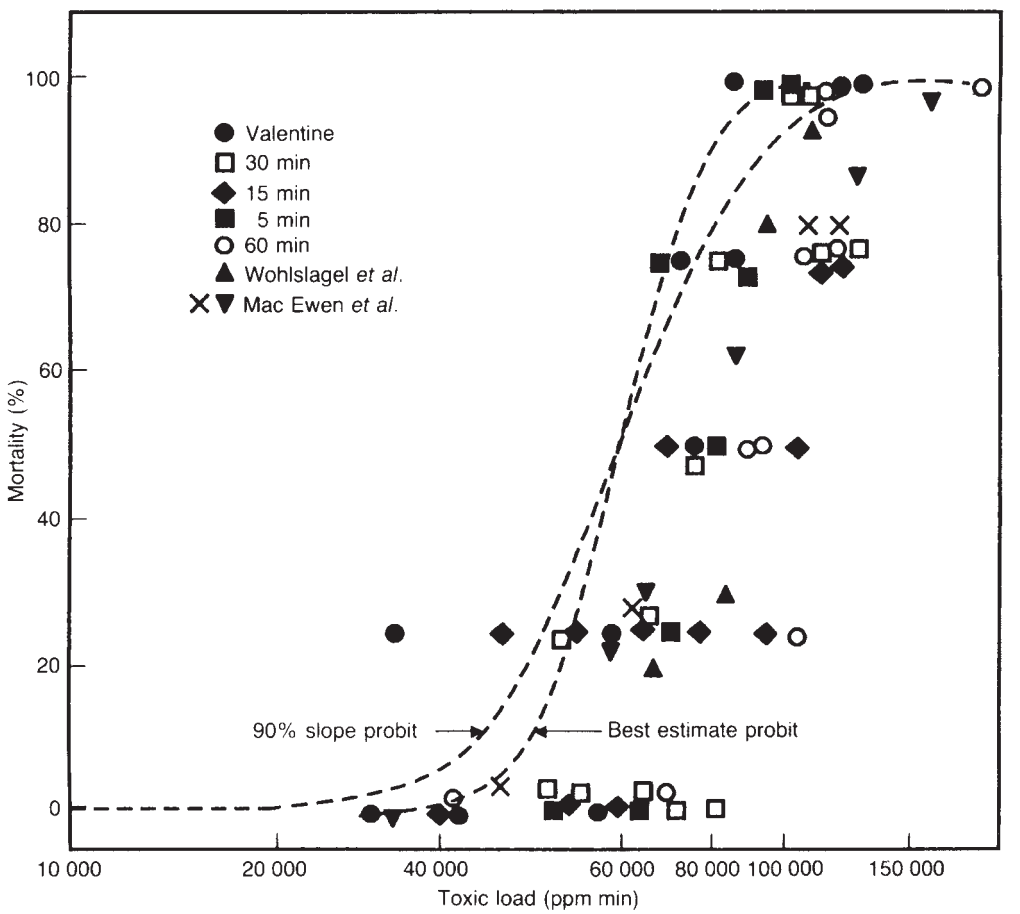

Figure 18.6 *Mortality–toxic load response from best estimate probit for hydrogen fluoride (Mudan, 1989a) (Courtesy of the American Institute of Chemical Engineers)*

C.W. Mitchell and Yant (1925), Gerbis (1927), Flury (1928), Aves (1929) and Yant (1930). Hydrogen sulfide was considered for use, but found little application as a war gas, and its toxicity is dealt with in some of the texts on war gases, including those of Vedder (1925), Flury and Zernik (1931), Foulkes (1934), Muntsch (1935), Hanslian (1937), Henderson and Haggard (1943) and by Flury (1928). More recent work on the gas includes that by Rubin and Arieff (1945), Adelson and Sunshine (1966), Lund and Wieland (1966), Kosmider, Rogala and Pacholek (1967), Hays (1972), Archibald (1977), Beck, Cormier and Donini (1979), NRC (1979), Tansy *et al.* (1981), Ammann (1986), Lopez *et al.* (1987), Prior *et al.* (1988) and Lopez *et al.* (1989). Work on hydrogen sulfide is also included in treatments dealing a number of gases, including those of Schutze (1927), Walton and Witherspoon (1928) and Setterstrom and co-workers (McCallan and Setterstrom, 1940; Thornton and Setterstrom, 1940; Weedon, Hartzell and Setterstrom, 1940) and Vernot *et al.* (1977).

The toxicity of hydrogen sulfide has been reviewed in *Hydrogen sulphide* (WHO, 1983 EHC19).

Probit equations for hydrogen sulfide have been given by Perry and Articola (1980), ten Berge, Zwart and Appelman (1986), the CCPS and the CPD. Dangerous dose values are given by the HSE, as described below.

Hydrogen fluoride is one of the gases considered in the hazard assessment study done by Back, Thomas and MacEwen (1972).

18.16.12 Methyl isocyanate

Methyl isocyanate (MIC) has, like all isocyanates, long- and short-term MELs (as NCO) of 0.02 and 0.07 mg/m^5, respectively. Physiologically, MIC is an irritant and its effects include pulmonary oedema.

MIC came to prominence as the gas responsible for the toxic gas disaster at Bhopal, described in Appendix 5.

Prior to Bhopal, there seems to have been relatively little work published on the toxicity of MIC, with the exception of a study by Kimmerle and Eben (1964). Subsequent work has been done by ten Berge (1985). Probit equations for MIC have been given by ten Berge (1985), the CCPS and the CPD, as described below.

18.16.13 Oxides of nitrogen

Oxides of nitrogen are toxic gases. They have little irritant effect, but inhalation can cause death some hours later. Nitrogen monoxide has long- and short-term OESs of 25 and 35 ppm, respectively. Nitrogen dioxide has long- and short-term OESs of 3 and 5 ppm, respectively.

Hazard from oxides of nitrogen arises from their use in the manufacture of sulfuric and nitric acids and from their generation in welding.

18.16.14 Phosgene

Phosgene has long- and short-term OESs of 0.02 and 0.06 ppm, respectively. Until recently the gas had a long-term OES of 0.1 ppm, with no quoted short-term value (see EH 40/92). The current values therefore represent a significant reduction.

Physiologically, phosgene is an irritant. The effects of a single exposure include pulmonary oedema. Phosgene is less soluble than chlorine, attacks the respiratory tract less, but passes deep into the lung. Its effects may not be felt immediately, but may develop some hours later.

Early work on phosgene includes that of Lehmann (1893), Matt (1889) and Hess (1911). Phosgene followed chlorine as a prime war gas, generally as a phosgene–chlorine mixture. Its toxicity is dealt with in most of the main texts on war gases including Underbill (1920), Fries and West (1921), Gilchrist (1924), F. Haber (1924), Vedder (1925), Ireland (1926), Flury and Zernik (1931), Foulkes (1934), Muntsch (1935), Hanslian (1937), Prentiss (1937), Wachtel (1941), Henderson and Haggard (1943), Courtice and Foss (1916), Dunn (1918), Eyster and Meek (1920), Herringham (1920), L. Hill (1920), Winternitz *et al.* (1920), Flury (1921a, 1928), Laqueur and Magnus (1921), Chlopin (1927–), Flury and Zernik (1932) and Richters (1936a,b). More recent work includes that by Cameron, Courtice and Foss (1941), Boyland, McDonald and Rumens (1946), Weston and Karel (1946, 1947), Box and CuUumbine (1947), Karel and Weston (1947), Gerard (1948), Suess and Lerner (1956), Henschler and Laux (1960), Ardran (1964), de Rooij, van Eick and van de Meent (1981), Diller and Zante (1982), Diller (1985), Mulder *et al.* (1986) and Zwart (1987). Work on phosgene is also included in treatments dealing with a number of gases, including those by Zeehuisen (1922) and Zielhuis (1970).

The toxicity of phosgene as a war gas has been the subject of extensive study. It was evidently his work on phosgene which led Haber to formulate his law that ct = Constant. He expressed the toxicity of gases in terms of a mortality product, or lethal index. Haber (1924) himself gave for cats a value of 450 mg/m^3 of this index, whilst Wachtel gives a value of 900 mg/m^3. From analysis of comments by Flury and Zernik (1932), Withers and Lees (1985a) conclude that the value of 900 mg/m^3 is equivalent to the LCt_{50}. This corresponds to $LCt_{50} = 220$ ppm min. They also quote Wachtel to the effect that cats are particularly sensitive to toxic gases and that as a rough approximation the corresponding value for man is twice as great, in other words $LCt_{50} = 440$ ppm min.

Experience of phosgene in war shows that personnel who have been gassed by it have often not felt immediate effects and have continued working, only to fall dead some hours later. The toxicity of phosgene has been reviewed in *Phosgene Toxicity Monograph* (MHAP, 1993).

Probit equations for phosgene have been given by Perry and Articola (1980), the CCPS and CPD, as described below.

Phosgene is one of the gases considered in the hazard assessment study done by Back, Thomas and MacEwen (1972).

18.16.15 Sulfur dioxide

Sulfur dioxide has long- and short-term OESs of 2 and 5 ppm, respectively. Physiologically, sulfur dioxide has various irritant effects.

Early work on sulfur dioxide includes that of Ogata (1884), Lehmann (1893) and Ronzani (1908, 1909). Sulfur dioxide does not appear to have been a serious candidate as a war gas. More recent work on sulfur dioxide includes that of Leong, McFarland and Sellers (1961) and Bitron and Aharonson (1978). Work on sulfur dioxide is also included in treatments dealing with a number of gases, including those of Zeehuisen (1922), Setterstrom and co-workers (McCallan and Setterstrom, 1940; Thornton and Setterstrom, 1940; Weedon, Hartzell and Setterstrom, 1940), Zielhuis (1970) and Buckley *et al.* (1984).

Sulfur dioxide is a principal lethal component of smog such as that which was once prevalent in London. A thick fog which covered the Meuse Valley in Belgium in 1930

resulted in several hundred cases of severe respiratory disturbance, followed shortly after by 63 deaths which were attributed to it (Weedon, Hartzell and Setterstrom, 1939; Logan, 1953). The lethality of the four day London smog of December, 1952, has been studied by Anon. (1953) and Logan (1953). The latter attributes to the fog some 4000 deaths. The Los Angeles smog is described by A. Mills (1957).

Probit equations for sulfur dioxide have been given by Perry and Articola (1980), the CCPS and the CPD, as described below. An account is also given below of the HSE dangerous dose values for sulfuric acid mist.

Sulfur dioxide is one of the gases considered in the hazard assessment study of Back, Thomas and MacEwen (1972).

18.16.16 Toluene diisocyanate

Toluene diisocyanate (TDI), like all isocyanates, has long- and short-term MELs (as NCO) of 0.02 and 0.07 mg/m^3, respectively.

Physiologically, TDI has a systemic effect, attacking the nervous system. It is a sensitizer, carrying the notation 'Sen'. The effects of exposure may be immediate and/or delayed. Exposure to TDI can cause firefighters to become euphoric and disregard danger. Delayed effects include nervous disorders.

Hazard arises from its manufacture and use, and from its generation from polyurethane foam or in hot cutting operations.

18.17 Gas Toxicity: MHAP Studies

The toxicity of three gases – chlorine, ammonia and phosgene – is the subject of a set of monographs by the MHAP, convened under the auspices of the Institution of Chemical Engineers (IChemE).

18.17.1 Chlorine

The Chlorine Toxicity Monograph (MHAP, 1987) is in two parts: the First Report of the Working Party and an account by Davies and Hymes of the HSE of the approach by that body to the development of criteria for hazard assessment.

The working party reviews the data on chlorine toxicity. Many of the data quoted for humans are derivative and appear poorly founded. It is therefore necessary to resort to the use of animal data. The authors present data for the LC_{50} for different exposures and for a number of species. These animal data indicate a mean lethal concentration for a 30 min exposure of $LC_{50} = 400$ ppm and a concentration–time relation of the form $ct^{1/2} = \text{Constant}$, or, alternatively $c^2t = \text{Constant}$.

In respect of the concentration lethal to man, the authors find that: the effects of acute inhalation of chlorine are similar in animals and humans, the prime lethal effect being pulmonary oedema; the factors bearing on differences between species may be divided into those which govern delivery of the chemical to the target organ and those which govern the effect on this and other organs; and that the effect of chlorine is to cause damage to the respiratory system itself, so that metabolic factors do not come into play.

The dose per unit body weight is some ten times greater for animals such as mice and rats than for humans at comparable levels of physical activity, but whereas humans are likely to respond to exposure to chlorine with a high level of activity, experimental animals are very passive. There is also the fact that rodents are obligatory nose breathers, which results in a degree of filtering and reduces somewhat the concentration reaching the respiratory tract, though the authors do not attach great importance to this feature. They conclude that there is little basis for supposing that the sensitivity of humans to chlorine is significantly different from that of small animals.

The working party suggest, therefore, that the relations for the lethal toxicity of chlorine quoted above for animals can be applied to humans also, namely for a 30 min exposure:

$$LC_{50} = 400 \text{ ppm}$$

$$C^2t = \text{Constant}$$

where C is the concentration (ppm) and t is the time (min). They consider, however, that the data do not justify the derivation of a probit equation for the lethality of chlorine to humans.

The monograph also gives an account of medical measures for handling cases of gassing by chlorine and summaries of some 11 papers on its toxicity.

The contribution by Davies and Hymes states the, then developing, HSE view that for the purpose of land use planning a toxic load criterion corresponding to a much less severe level of injury than 50% lethality is appropriate and quotes the Major Hazards Assessment Unit (MHAU) as using for this purpose the criterion

$$C^{2.75}t = 3.2 \times 10^6 \qquad [18.17.1]$$

where C is the concentration (ppm) and t is the time (min). This echoes the views expressed earlier by the same authors (P. Davies and Hymes, 1985) and foreshadows the development of the HSE specified level of toxicity (SLOT) values described in Section 18.21.

18.17.2 Ammonia

The *Ammonia Toxicity Monograph* (MHAP, 1988) follows a broadly similar format. The data on ammonia toxicity are reviewed and animal data are presented for the LC_{50} for different exposures and for a number of species. These animal data indicate a lethal concentration for a 30 min exposure of $LC_{50} = 11{,}500$ ppm and a concentration–time relation of the form $ct^{1/2} = \text{Constant}$. The authors consider that for ammonia the animal data available are of higher quality than those for chlorine.

With regard to the applicability of these data to man, the authors advance the following argument. Like chlorine, ammonia has an irritant action, but due to its solubility the relative effect on the tracheal as opposed to that on the bronchial region is much more marked. They identify two opposing factors. On the one hand, there is the much higher dose per unit body weight in animals than in humans, but on the other, due to the less effective filtering in humans, a greater proportion of the gas will reach the trachea. The authors conclude that taking these factors into account, it is reasonable apply the animal data to humans.

They therefore propose that the relations for the lethal toxicity of ammonia quoted above for animals can be applied to humans also, namely:

$$LC_{50} = 11{,}500 \text{ ppm for a 30 min exposure}$$

$$C^2t = 6.3 \times 10^4 \qquad [18.17.2]$$

They derive from this the probit equation for the lethality of ammonia

$$Y = -35.9 + 1.85 \ln C^2 t \qquad [18.17.3]$$

where C is the concentration (ppm) and t is the time (min). They advise caution, however, in the application of this relation outside the limits of 20–80% lethality.

The monograph also gives an account of medical measures for handling of cases of gassing by ammonia, brief descriptions of case histories involving the gas and summaries of some 24 papers on its toxicity.

18.17.3 Phosgene

The *Phosgene Toxicity Monograph* (MHAP, 1993) again rejects many of the data quoted for humans as being second-hand and unreliable. The same applies to many of the animal data, but a small number of data sets are considered to be of high quality. These animal data indicate a lethal concentration–time relation of the form ct = Constant, or Haber's law, and a lethal load of

$$LCt_{50} = 570 \text{ ppm min}$$

The authors also refer to work on the gassing of human subjects by phosgene given in evidence by Bickenbach (1947). The experiments were barbarous, but the data exist and cannot be neglected. The median lethal concentration for a 25 min exposure was 22.8 ppm, yielding

$$LCt_{50} = 570 \text{ ppm min}$$

In respect of the application of the animal data to humans, the authors argue that the main acute effect of phosgene for both animals and humans is on the lung, that large differences in response between species would not be expected and that this is borne out by the similarity of the results obtained for the various species, including man. They conclude that the animal data may be applied to humans.

Utilizing the most appropriate sets of animal data and applying these to man, they obtain for the lethal toxicity of phosgene for humans

$$LCt_{50} = 552 \text{ ppm min}$$

and the probit equation

$$Y = -27.2 + 5.1 \ln Ct \qquad [18.17.4]$$

where C is the concentration (ppm) and t is the time (min).

The monograph also gives an account of medical measures for handling of cases of gassing by phosgene and brief descriptions of case histories involving the gas.

18.18 Gas Toxicity: Chlorine

A further account is now given of the toxicity of chlorine, based on the work of Withers and Lees (1985a,b). This work is described in some detail, both because the hazard of chlorine is important in its own right and because the work illustrates the problems of and possible approaches to the toxicity of irritant gases.

There are in the literature a number of estimates of chlorine toxicity that vary widely. Generally, individual estimates are not well supported by critical review and the choice of a particular value has often tended to be arbitrary.

An estimate of chlorine toxicity that has had considerable currency in hazard assessment is that of Eisenberg, Lynch and Breeding (1975), who gave in the Vulnerability model a probit equation for chlorine. The LC_{50} for a 30 min exposure given by this probit equation is about 35 ppm for healthy adults. More recent estimates tend towards a considerably higher figure.

Withers and Lees review information on the lethal toxicity of chlorine and present a model for its toxicity to humans. The model gives values of 500 and 250 ppm for the LC_{50} for 30 min for base and standard cases for healthy adults.

18.18.1 Experimental work on and estimates of toxicity

Data on chlorine toxicity are given by Flury and Zernik (1931). Many of the values quoted are attributed to Lehmann, who published a series of papers over the period 1887–99 (e.g. Lehmann, 1887, 1883, 1899a,b) and to Hess (1911).

Chlorine was the first main toxic gas used in the First World War and work on chlorine toxicity was carried out by the principal combatants, particularly the Germans. The German work is described by F. Haber (1924), Flury and Zernik (1931), Muntsch (1935) and Wachtel (1941).

Haber's work, apparently that on phosgene in particular, seemed to indicate for lethality the relation

$$ct = \text{Constant} \qquad [18.18.1]$$

which became known as Haber's law and gave rise to the concept of a lethal dosage, also known as the mortality product or lethal index.

Values of the lethal index are quoted by military authors such as Hanslian (1937), Vedder (1925) and Prentiss (1937). There are considerable variations in the values given. Withers and Lees suggest that values refer variously to the LC_{10}, the LC_{50} and the LC_{50}, and quote comments by Flury and Zernick (1932) in support of this.

An important series of experiments on dogs was carried out towards the end of the war by Underhill (1920). For chlorine he used some 112 animals in seven groups ranging in size from 9 to 23. The exposure period was 30 min. The results of this work are shown in Table 18.18 and are plotted in Figure 18.7. The figure shows the best line through the points and the 95% confidence limits obtained from the method of Litchfield and Wilcoxson (1949). The LC_{50} for a 30 min is 650 ppm.

Since 1918 there have been a number of studies on chlorine toxicity, using mainly rodents. Some of the principal sets of experiments are briefly described here.

More detailed accounts are given by Withers (1986) and Withers and Lees (1985a).

Weedon, Hartzell and Setterstrom (1940) carried out experiments in which mice and rats, in groups of 4 and 8, respectively, were exposed to concentrations of chlorine of 16, 63, 250 and 1000 ppm for periods of 1, 4, 15, 60, 240 and 960 min until they died, or for a maximum period of 960 min. The three latter concentrations corresponded to the LC_{50} for mice at exposure periods of >960, 440 and 28 min, respectively, and to that for rats at exposure periods of >960, 440 and 53 min, respectively.

Lipton and Rotariu (1941), in a report by Ceiling and McLean, describe experiments in which mice in groups of 20 were exposed to concentrations of chlorine ranging from 310 to 2357 ppm for a period of 10 min with an observation period of 10 days. The LC_{50} obtained was 628 ppm.

Silver and McGrath (1942) carried out experiments on 49 groups of mice, 45 groups of 20 and 4 groups of 40, in two series. In the first series certain sources of error were revealed which were corrected in the second series. In the two series of experiments mice were exposed to concentrations of chlorine in the range 252–1139 ppm for 10 min with a 10-day observation period. In the first series the LC_{50} was 524 ppm and in the second series 597 ppm. Most of the deaths occurred within the first 24 h.

Silver, McGrath and Ferguson (1942) carried out further experiments on 15 groups of 20 mice. Again they used a 10 min exposure time and a 10-day observation period. In this third series the concentrations of chlorine used were in the range 379–890 ppm and the LC_{50} was 676 ppm. Out of 154 deaths, one was due to mild oedema and congestion, and two to pneumonia; the rest were due to severe oedema. Most of the deaths occurred within the first 24 h.

Table 18.18 *Concentration of chlorine lethal to dogs in Underhill's work (Withers and Lees, 1985a; after Underhill, 1920). Exposure time 30 min (Courtesy of Elsevier Publishing Company)*

	Concentration[a]						
(mg/l) (ppm)	*0.16–0.80* *50–250*	*1.27–1.58* *400–500*	*1.58–1.90* *500–600*	*1.90–2.22* *600–700*	*2.22–2.53* *700–800*	*2.53–2.85* *800–900*	*2.85–6.34* *900–2000*
Deaths within 3 days	0	1	2	9	9	20	13
Delayed deaths	1	4	2	5	2	1	0
Total deaths	1	5	4	14	11	21	13
Total No. of animals	9	17	10	21	18	23	14
Overall mortality (%)	11	29	40	67	61	91	93

[a] The conversion of concentrations from mg/l to ppm by Underhill in this table corresponds to a temperature of 0°C. Henceforth, these concentration values in ppm have been recalculated to a temperature base of 25°C.

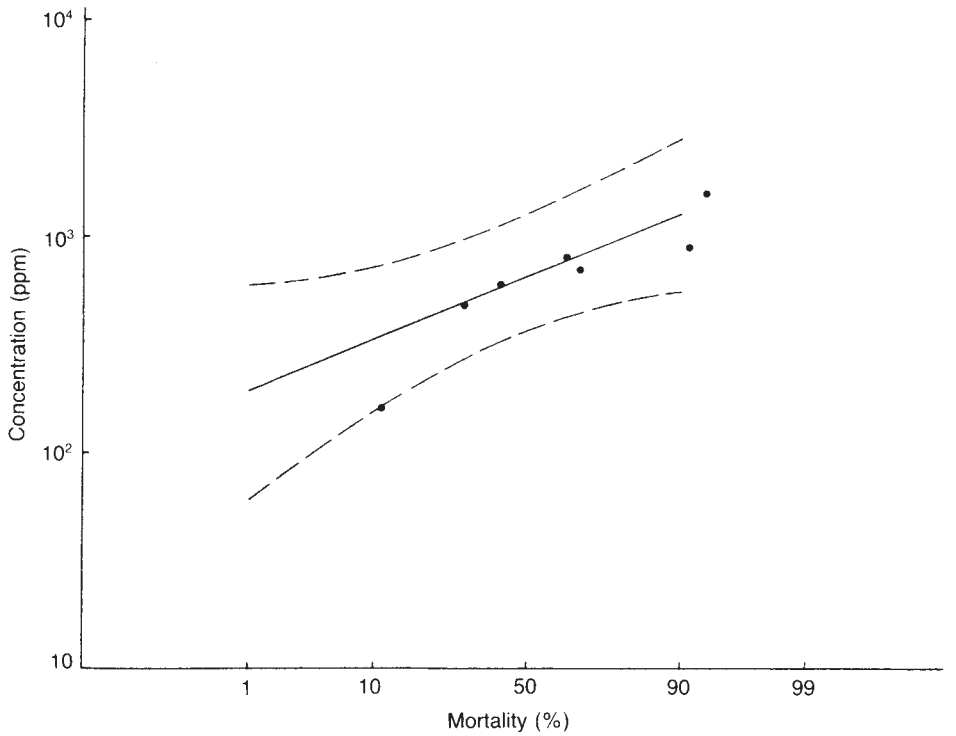

Figure 18.7 *Concentration of chlorine lethal to dogs in Underhill's work (withers and Lees, 1985a; after Underhill, 1920). Exposure time 30 min. Dotted lines are 95% confidence limits (Courtesy of Elsevier Science Publishers)*

Schlagbauer and Henschler (1967) carried out experiments in which mice in groups of 10 were exposed for 30 min to concentrations of chlorine of 55, 62, 69, 110, 125, 132, 145, 160 and 179 ppm. The deaths occurring in the intervals 0–2 and 2–4 days after exposure were recorded. There were no deaths later than 4 days after exposure. The LC_{5O} obtained was 127 ppm.

These authors also report work at lower chlorine concentrations and longer exposure periods. They carried out experiments in which 10 mice were exposed for 3 h to concentrations of chlorine of 10 and 22 ppm with an observation period of 4 days. The mortality of the mice at these two concentrations was 8/10 and 10/10, respectively.

Experiments were carried out by Bitron and Aharonson (1978) in which mice in groups of 16 were exposed to concentrations of chlorine of 170 and 290 ppm for periods of 15–160 and 5–30 min, respectively. The times of death after exposure were recorded over an interval of 30 days. The LC_{50} values obtained were 170 and 290 ppm for exposures of 55 and 11 min, respectively.

The LC_{50} values obtained by these and certain other authors are shown in Table 18.19. The concentration lethal to various animal species, based on the research just described and on other work, is shown in Figure 18.8.

In addition to the LC_{50}, it is desirable also to be able to estimate the LC_{10} and LC_{90} or the ratio LC_{90}/LC_{10}, which is the slope of the concentration–mortality line. There are three data sets, those of Underhill, of Silver, McGrath and Ferguson and of Schlagbauer and Henschler, from which estimates of this ratio may be obtained.

Underhill's work yields values of the LC_{10} and LC_{90} of 334 and 1,266 ppm, respectively, and hence a value of the ratio LC_{90}/LC_{10} of 3.8.

There are two sets of experiments, those of Weedon, Hartzell and Setterstrom and of Bitron and Aharonson, in which the exposure time was varied and which may therefore be used to estimate the trade-off between concentration and time. These two data sets are shown in Table 18.20.

Then using Equation 18.11.3 for the lethal toxic load, the data in Table 18.20 suggest that the best estimate of the index n is 0.5 so that

$$L = CT^{0.5} \qquad [18.18.2]$$

The range of concentrations and time covered by the data on which this equation is based are 170–1,000 ppm and 11–440 min.

Equation 18.18.2 may be used to convert different sets of experiments to a common exposure time. Such sets may also be normalized with respect to the LC_{50} found in each case to give a set of data that may be used to determine the slope of the concentration–mortality line. Three such sets of data are shown in Table 18.21.

Information on acute and delayed deaths is also relevant. In the work of Lipton and Rotariu and of Silver, McGrath and Ferguson most of the deaths occurred within the first 24 h. Likewise, in Schlagbauer and Henschler's work almost all the deaths occurred in the interval 0–2 days after exposure. The only deaths in the interval 2–4 days were at a concentration of 132 ppm, for which two of the six deaths were in this interval. In Bitron and Aharonson's work, by contrast, most of the deaths were delayed deaths, the mortality being only 10% or less during the day after exposure and most of the deaths occurring in the interval 5–7 days after exposure.

Further information on acute deaths is given by the work of Underhill on dogs. He defines acute death as a death occurring within the first 3 days after exposure. Figure 18.9(a) and (b) shows the proportion of acute deaths in his work as

Table 18.19 *Concentrations of chlorine that are lethal to rodents, as given by various authors (Withers and Lees, 1985a) (Courtesy of Elsevier Publishing Company)*

Author(s)	*Species*	*Concentration lethal to 50%* (ppm)	*Exposure time* (min)
Zeehuisen (1922)	Guinea pigs, white rats	>3330	30
Weedon, Hartzell and Setterstrom (1940)	Mice	1000	28
		250	440
		63	>960
	Rats	1000	53
		250	440
		63	>960
Lipton and Rotaríu (1941)	Mice	628	10
Silver and McGrath (1942); Silver, McGrath and Ferguson (1942)	Mice	618[a]	10
Elmes and Bell (1963); Bell and Elmes (1965)	Mice	117[b]	1800
Schlagbauer and Henschler (1967)	Mice	127	30
Back, Thomas and Macewen (1972)	Mice	137[c]	60
	Rats	293[c]	60
Bitron and Aharonson (1978)	Mice	290[d]	11
		170	55
Alarie (1980)	Mice	302	10

[a] Value obtained by averaging values of 524 and 597 ppm and then averaging again with value of 676 ppm.
[b] Exposure of 30 h limited to 3h/day.
[c] These values are also given by Vernot *et al.* (1977).
[d] These values are for a 30 day observation period.

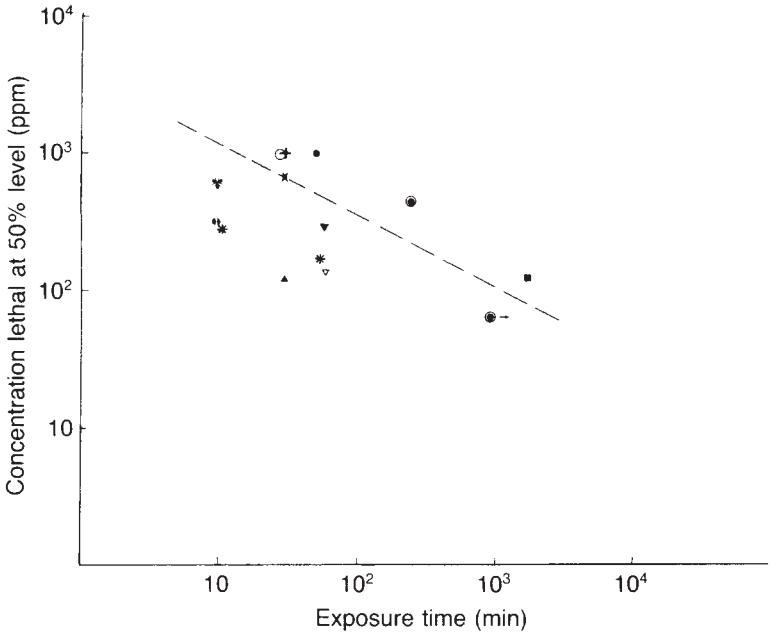

Figure 18.8 *Concentration of chlorine that is lethal to various animal species at the 50% level (Withers and Lees, 1985a). Dotted line has slope of −0.5. (○) Weedon et al. (1940), mice; (★) Lipton and Rotariu (1941), mice; (▲) Schlagbauer and Henschler (1967), mice; (▽) Back, Thomas and MacEwen (1972), mice; (✹) Bitron and Aharonson (1978); mice (◐) Alarie (1980), mice; (●) Weedon et al. (1940), rats; (■) Bell and Elmes (1965), rats; (▼) Back, Thomas and MacEwen (1972), rats; (×) Underhill (1920), dogs; (+) Chlopin (1927–), horses (fatal concentration, not necessarily LC_{50}) (Courtesy of Elsevier Science Publishers)*

Table 18.20 *Concentrations of chlorine lethal to rodents at the 50% level as a function of time (Withers and Lees, 1985a) (Courtesy of Elsevier Publishing Company)*

Author (s)	*Species*	C (ppm)	T (min)	CT	$CT^{0.4}$	$CT^{0.5}$	$CT^{0.6}$
Weedon, Hartzell and Setterstrom (1940)	Mice	1000	28	28,000	3792	5292	7384
		250	440	110,000	2853	5244	9639
	Rats	1000	53	53,000	4895	7280	10,828
		250	440	110,000	2853	5244	9639
Bitron and Aharonson (1978)	Mice	290	11	3190	757	962	1222
		170	55	9350	844	1261	1882

a function of the concentration and as a function of the mortality, respectively.

18.18.2 Physiology and pathology of poisoning

The physiology and pathology of chlorine gas poisoning have been studied by a number of workers, including many of those already mentioned.

Many of those who have done experimental work on animals have discussed this aspect. Lehmann gives a wide-ranging discussion of the topic. Accounts by German workers active around the time of the First World War include those by Flury and Zernik (1931) and Wachtel (1941) and among American workers those of Underbill (1920) and Winternitz *et al.* (1920). The overall picture that emerges is that while chlorine attacks the whole of the respiratory system, the cause of death is lung oedema.

There is also a large amount of information that is directly applicable to man. There are a number of accounts of the treatment of chlorine gas casualties by British doctors. The Chemical Warfare Committee of the Medical Research Council did extensive work, including that of Gunn (1920) on the action of chlorine on the respiratory system. The official military account is given in *Diseases of the War* (Macpherson *et al.*, 1923).

The extensive American work from that time is described by Underbill and Winternitz *et al.*, while the official military account is given by Ireland (1926). Additional information is given by Haggard (1924) and by Henderson and Haggard (1943). Further accounts are given by other military authors such as Vedder (1925) and Prentiss (1937).

Investigations of the long-term effect of gas warfare exposure are described by Meakins and Priestley (1919),

Table 18.21 *Mortality of animals exposed to chlorine, adjusted to an exposure period of 30 minutes and normalized with respect the LC_{50} (Withers and Lees, 1985a) (Courtesy of Elsevier Publishing Company)*

Author(s)	*Species*	LC_{50} (ppm)	*Concentration* (ppm)	*Normalized concentration*	*Mortality* (%)
Underhill (1920)	Dogs	650	164[a]	0.25	11
			491	0.76	29
			600	0.92	40
			710	1.09	67
			819	1.26	61
			928	1.43	91
			1583	2.44	93
Silver and McGrath (1942); Silver, McGrath and Ferguson (1942)	Mice	388	219[b]	0.56	10
			317	0.82	45
			317	0.82	25
			337	0.87	5
			364	0.94	40
			368	0.95	45
			398	1.03	15
			408	1.05	60
			410	1.06	55
			430	1.11	70
			458	1.18	75
			486	1.25	40
Schlagbauer and Henschler (1967)	Mice	131	62	0.47	10
			69	0.53	10
			110	0.84	30
			125	0.95	30
			132	1.01	60
			143	1.09	60
			160	1.22	80

[a] Converted from 0°C to 25°C.
[b] Converted from original data for 10 min exposure period.

Vedder (1925), Gilchrist and Matz (1933) and Penington (1954).

Chlorine is a strong oxidizing agent. A number of different explanations have been given of the way in which it causes damage. An early suggestion was that its effect is through the formation of hydrochloric acid. Another early suggestion was that it gives rise to nascent oxygen. More recent suggestions are the action of hypochlorous acid and of chlorine itself.

Chlorine is an irritant gas and the most serious effect of acute chlorine poisoning is damage to the respiratory system. Another important irritant gas that was also used as a war gas is phosgene and many discussions of gas poisoning treat the two gases together, although there are differences. The symptoms of chlorine poisoning are: at a concentration of about 15 ppm, irritation of the nose, throat and eyes with cough and tears; at about 30 ppm, restriction of breathing and chest pain; and from about 50 ppm, development of pulmonary oedema. Other symptoms are described in some of the accounts given below.

The description by Haggard (1924) of the action of irritant gases on the respiratory tract has already been quoted.

In the present context it is severe acute poisoning that is of primary interest. Herringham (1920) states:

> The whole course of events, and the various degrees of severity, are all due to but one cause, the want of oxygen in the blood due to the wall of oedema interposed between the air and the blood vessels.

An extensive discussion of chlorine poisoning is given in *Diseases of the War* and the following extracts give an overview of the principal aspects. The threat to life is due almost entirely to pulmonary oedema and other effects are relatively unimportant, but later infection can also be dangerous:

> The respiratory organs, eyes and skin, bore the brunt of the attack. Yet even if one recognizes this, one must be prepared for serious effects that are secondary to these primary lesions. Severe though temporary shortage of oxygen, resulting from acute pulmonary oedema or interference with the oxygen-carrying power of the blood, may exercise lasting effects on the heart, the central nervous system, or other organs of the body, while secondary bacterial infection may delay recovery or even be the prelude to a fatal termination.
>
> The points where the gases classed as acute lung irritants exercise their most pronounced effect are the alveoli of the lungs and the smaller bronchial tubes, and the great danger to be feared, which is common to them all, is the onset of acute pulmonary oedema. It is in the main this oedema which, in the acute stage of poisoning, threatens the life of the subject, for if abundant it causes death by

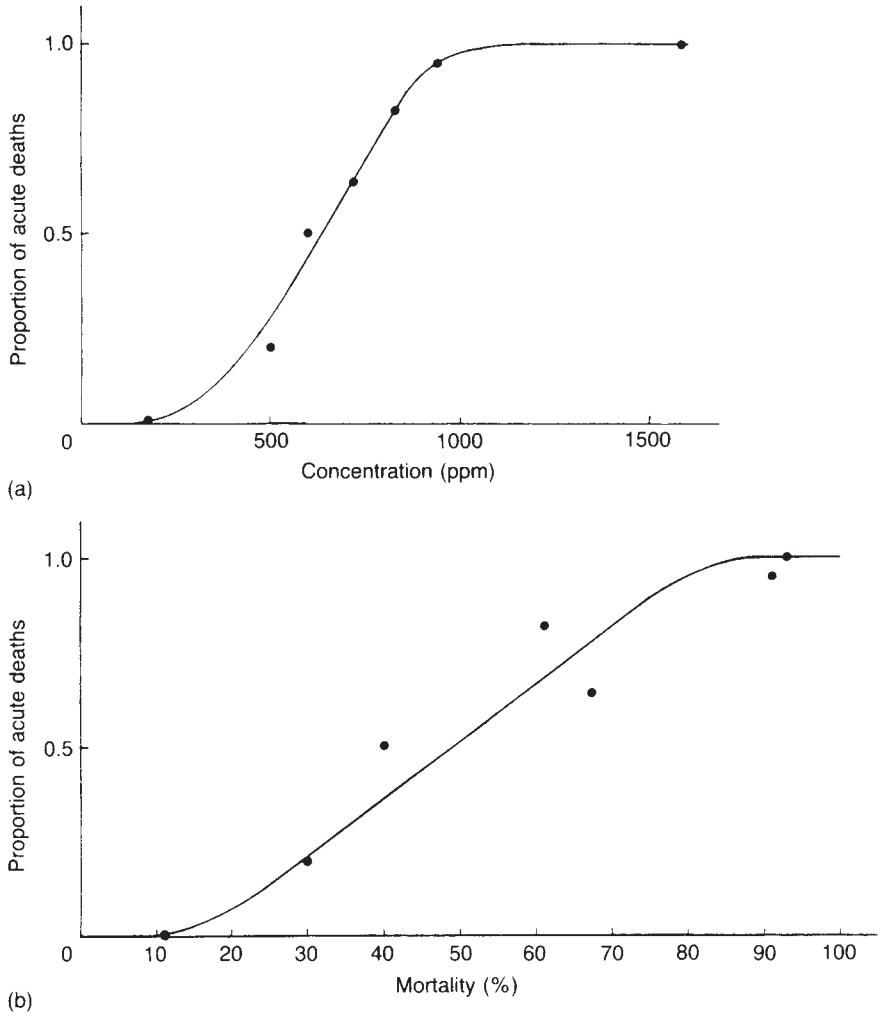

Figure 18.9 *Proportion of acute deaths by chlorine poisoning in Underhill's work (Withers and Lees, 1985a). Exposure time 30 min, (a) Proportion of acute deaths as a function of concentration; (b) proportion of acute deaths as a function of mortality (Courtesy of Elsevier Science Publishers)*

asphyxiation, the patient being in fact drowned by his own eduction.

The rate of onset and the degree of oedema are dependent on the particular gas and on its concentration, and, though in some cases to a less degree, on the duration of exposure.

Any pathological changes found in organs of the body other than the lungs are really attributable to changes resulting secondarily from the gross damage in the respiratory apparatus, and from the consequent asphyxia, and that the direct effects of the gas are limited to the lungs and bronchial tubes.

The effect of oedema is to cause a reduction in the supply of oxygen to the blood:

> These gross changes in the lungs are responsible for serious interference with the gaseous exchange between blood and air, and the indications for asphyxia were obvious in all severe cases of poisoning by the acute lung irritant gases. The cases fell into two categories: the one was characterized by intense florid and deep cyanosis, with vascular congestion and engorgement of the veins, the other exhibited no venous engorgement but pallor akin to that seen in collapse, with grey or lilac-coloured lips and tongue. Both classes had the common feature that the colour of the blood indicated a grave deficiency of oxygen.

The symptoms tended to follow a common pattern:

> All the men gave a similar description of what they felt as the greenish-yellow fumes enveloped them. Immediate choking, coughing, gasping for breath and inability to speak proved the irritation and spasm of the respiratory tract. In many the eyes smarted and ran with water. Retching was at once experienced by some, but many did not vomit until an hour or two later. There was severe pain behind the sternum, which soon radiated outward on each side into the chest and added greater suffering to the distressed breathing. The throat burned and the dry mouth produced an intense sensation of thirst.
>
> Very soon the developing pulmonary oedema led to the phenomenon of oxygen shortage, with headache, a sense of weakness in the legs, and such1 lassitude that the men dropped prone upon the ground, the spasmodic violence of their respiratory efforts being then largely quietened.
>
> Milder cases in areas where the concentration of chlorine in the air was relatively low, suffered chiefly from lassitude and a great sense of fatigue.

The complete arrest of breathing due to spasm was not observed and is not regarded as an important factor:

> The question has often been discussed as to whether a man might be killed by immediate asphyxiation on the field through such a spasmodic closure of his larynx and bronchi that respiration was completely arrested. Sudden shock and collapse from extreme sensory irritation has been noted in animals immediately upon exposure to chloropicrin; and it might be that this factor would also play its part in determining early death upon the field. But no proof was ever obtained that a man has thus been choked to death on the field. If it ever did happen, it was of little practical importance. No medical officer in the trenches ever had the chance of attempting to treat such a case.

Pulmonary oedema and its effects are therefore the important factors:

> A rapid development of pulmonary oedema, interfering with gaseous respiration and also with the circulation itself, was probably always the actual cause of death.
> It is thought that the entire action of pulmonary irritants is exercised solely upon the surface layers of the body with which the gases come into contact, the early circulatory failure being caused only the influence of pulmonary oedema upon gaseous respiration and blood-flow and by 'shock'.

A similar picture emerges from the accounts of their work given by Underbill and by Winternitz *et al.* Acute death is associated with oedema and blood changes. Underhill attributes the effects of oedema not so much to the blockage of oxygen transfer in the lung as to a decrease in the fluid content of the blood and a consequent increase in the solids content and viscosity and a reduction in the oxygen-carrying capacity.

Physical exertion following gassing can be dangerous, even for men apparently unaffected:

> When the tension of a gas attack had passed way, it sometimes happened that, among those who had been exposed to the irritant vapour but who had not reported sick, a man would stop working, complain that he felt done in, and die in a few minutes. Others might survive for an hour or two after a similarly sudden collapse. Their deaths were at first thought to have been caused by heart failure due to a direct intoxication by the gas. Autopsies, though not made in the dramatic cases of abrupt death, always proved the existence of advanced pulmonary oedema, the condition being really identical with that of 'grey' collapse as seen after the ordinary acute onset.

The effect of exertion after exposure appears, however, to have been observed mainly with phosgene rather than with chlorine.

There has been some expression of doubt about the prevalence of pulmonary oedema among those who have treated people gassed by chlorine in industrial accidents. Thus A.T. Jones (1952) states that in the period 1932–48 he and his colleagues dealt with 820 such cases, of which 9 were severe, but even in these cases neither pulmonary oedema nor pneumonia ensued, although he indicates awareness of pneumonia in other cases. Industrial gassing is also discussed by Haggard, who states

> Even an exposure insufficient to induce the acute symptoms of lung irritation may lead to the development of pneumonia and under industrial conditions the infections thus produced constitute a greater cause of death than primary oedema.

Although the descriptions quoted on the effect of irritant gases are undoubtedly strongly influenced by experience with phosgene, the account of Black, Glenny and NcNee (1915), who treated 685 cases of poisoning from chlorine between 2 and 7 May, 1915, before phosgene had been used, shows clearly that the acute deaths involved pulmonary oedema. This was confirmed by 210 post-mortems carried out by these doctors.

If acute death does not occur, there is still the danger of delayed death. The cause of delayed death is described variously as bronchitis, bronchial pneumonia or pneumonia. Black, Glenny and McNee state that the acute stage passes off in about 36 h, that there is then a quiet stage of some 12 h and that the bronchial infection is then liable to develop. Underbill found that the dogs which survived gassing were liable to die of pneumonia, and set 3 days after gassing as the dividing line between acute and delayed deaths.

The mortality from chlorine gassing may be reduced by appropriate medical treatment. It is not clear how much can be done to increase the chances of survival of acute cases, but for the delayed cases the prospects appear much better. There are descriptions of the treatment given and of its effects in many of the accounts already quoted.

The long-term effects of chlorine gassing are also important. Broadly speaking, both the statistical and clinical evidence suggest that these effects are not great. Weill *et al.* (1969) studied 12 people who were severely gassed in an accidental chlorine accident near La Barre in 1961. All had pulmonary oedema when examined just after the accident, but when examined 3 and 7 years after the event showed little long-term damage.

A summary of the findings of these authors given by Eisenberg, Lynch and Breeding (1975) has been quoted in Section 18.15. The evidence from this work is that persons who survive acute exposure to chlorine gas tend not to suffer significant permanent lung damage.

18.18.3 Concentrations intolerable to humans

Some values given in the literature for chlorine concentrations tolerable and intolerable to humans are shown in Table 18.22.

At concentrations of about 4 ppm irritation is said to be experienced and normal work to be impossible. Dangerous concentrations are variously given as 14–21 and 40–60 ppm for 0.5–1 h, but the degree of danger is ill defined. A concentration of about 50 ppm is said to cause loss of fighting efficiency and one of 100 ppm to incapacitate and to be intolerable. The data were apparently obtained by observation of the effects of chlorine on man. The basis of the data is different, therefore, from those for the lethality to man derived from animal experiments. They include, presumably, the effects of any enhancement of activity which may have occurred.

18.18.4 Concentrations lethal to humans

Some values given in the literature of chlorine concentrations lethal to humans are shown in Table 18.23.

18.18.5 Limit values for humans

The TLV for chlorine recommended by the ACGIH has for many years been 1 ppm. In the United Kingdom the OES is now an 8-h TWA of 0.5 ppm.

Zielhuis (1970) has made proposals for EELs for chlorine. His values are 7, 5, 4 and 3 ppm for exposures of 5, 15, 30 and 60 min, respectively. The proposals of the NAS-NRC (1973a) for public emergency limits (PELs) are 3, 2, and 2 ppm for exposures of 10, 30 and 60 min, respectively.

18.18.6 Probit equations given in literature

Probit equations both for lethality and non-lethal injury due to chlorine were given by Eisenberg, Lynch and Breeding (1975) in the Vulnerability model. The probit equation for the lethality of chlorine is

$$Y = -17.1 + 1.69 \ln \left(\sum C^{2.75} T \right) \qquad [18.18.3]$$

And that for non-lethal injury due to chlorine is

$$Y = -2.40 + 2.90 \ln C \qquad [18.18.4]$$

where C is the concentration (ppm) and T is the time (min).

Equation 18.18.3 gives an LC_{50} for 30 min of some 35 ppm. It is apparently derived from a graph consisting of an arbitrary concentration scale vs a percentage mortality scale on which various sets of experimental results for animals are plotted as straight lines. The LL_{50} points on these lines are: for dogs, 70; for rats, 3.5 and 1.4; for mice, 20,

Table 18.22 *Concentrations of chlorine tolerable and intolerable to man (Withers and Lees, 1985b) (Courtesy of Elsevier Publishing Company)*

Author(s)	*Effect*	*Concentration* (ppm)	*Exposure time*	*Source*
Rupp and Henschler (1967)	Odour threshold	0.02–0.05		
ACGIH	Threshold limit value	1		
Kobert (1912)	Minimum concentration to detect odour	3.5		
	Concentration which causes immediate irritation	14		
	Concentration which causes coughing	28		
	Dangerous concentration	40	1 h	
Flury and Zernick (1931)	Concentration tolerable without immediate or later consequences	3.5	0.5–1 h	Lehmann–Hessa[a]
	Concentration at which work can be continued without interference	1–2		Matt(1889)
	Concentration at which work becomes impossible	4		Matt (1889)
	Dangerous concentration	14–21	0.5–1 h	Lehmann–Hessa[a]
Henderson and Haggard (1943)	Maximum concentration allowable for physical exertion	0.35–1		
	Minimum concentration to detect odour	3.5		
	Maximum concentration allowable for short exposure	4	0.5–1 h	
	Dangerous concentration for short exposure	40–60		
Vedder (1941)	Concentration which incapacitates man (crying, coughing) in a few seconds	100		
Wachtel (1941)	Concentration which causes severe irritation	3		
	Concentration which causes loss of fighting capacity	47		
Patty (1962)	Concentration which causes irritation	3–6		
	Intolerable concentration	100	1 min	

[a] Quoted without reference by Flury and Zernik (1931).

15, 3.5 and 0.7; composite for all animals, 1; and for man, 0.25. It is not clear what the justification is for this low value for man, but the choice appears to be a conservative one.

In a further development of the Vulnerability model, Perry and Articola (1980) give revisions of the Eisenberg equations. Their equation for the lethality of chlorine is

$$Y = -36.45 + 3.13 \ln (\Sigma C^{2.64} T) \qquad [18.18.5]$$

and that for chlorine injury is again Equation 18.18.4.

The industrial comment on the *Rijnmond Report* (Rijnmond Public Authority, 1982) proposes the equation

$$Y = -11.4 + 0.82 \ln (\Sigma C^{2.75} T) \qquad [18.18.6]$$

This equation is also recommended by N.C. Harris and Moses (1983). ten Berge and van Heemst (1983) propose the equation (in the units used here)

$$Y = -5.04 + 0.5 \ln (\Sigma C^{2.75} T) \qquad [18.17.7]$$

Harris and Moses effectively argue that there is no justification for taking a low value of the ratio of the lethal load for man to that of animals, or for assuming a very narrow spread of response, and set the parameters in Equation 18.18.6 accordingly. ten Berge and van Heemst apparently derive their parameters from the work of Bitron and Aharonson (1978), together with information on the concentrations causing irritation in man.

The probit equations given in the literature for the lethal toxicity of chlorine are summarized in Table 18.24. Further probit equations produced subsequent to this study are described below.

18.18.7 Toxicity values used in hazard assessments

Some values of the lethal concentration or dosage of chlorine used in a number of hazard assessments are given in Table 18.25. Most correspond to an LC_{50} for 30 min of about 35 ppm. The much higher value of 430 ppm used by Meslin (1981) is an exception.

18.18.8 Model for humans

On the basis of the information just described, Withers and Lees (1985b) have derived for chlorine a model for the lethal

Table 18.23 *Lethal concentrations of chlorine quoted in standard toxicology texts (Withers and Lees, 1985b) (Courtesy of Elsevier Publishing Company)*

Author(s)	*Effect*	*Concentration* (ppm)	*Exposure time*	*Source*
Flury and Zernik (1931)	Lethal concentration for man	900 (2.5mg/l)	Immediate	
	Lethal concentration for man	35–50 (0.1–0.15 mg/l)	0.5–1 h	Hess[a]
	Dangerous concentration for man	14–21 (0.04–0.06mg/l)	0.5–1 h	Hess[a]
	Lethal concentration for man	1000	Short exposure	Kobert (1912)
	Dangerous concentration for man	40–60	Short exposure	Kobert (1912)
Patty (1962)	Lethal concentration for large animals	1000	After brief exposure	Flury and Zernik (1931)
	Concentration which may be lethal to cats	300	60 min	
	Concentration which is rarely lethal to dogs	650	30 min	
	Concentration which is never lethal to cats	280	30 min	
	Dangerous concentration for man	14–21	0.5–1 h	
Tatken and Lewis (1984)	LCL_0 mam[b]	500	5 min	Flury (1928)
	LC_{50} mus (mouse)	137	1 h	Back, Thomas and MacEwen (1972)
	LC_{50} rat	293	1 h	Back, Thomas and MacEwen (1972)
	LCL_0 gpg (guinea pig)	330	7 h	Lehmann (1887)
	LCL_0 cat	660	4 h	Lehmann (1887)
	LCL_0 dog	800[c]	30 min	Barbour (1919)
	LCL_0 hmn (man)	873	30 min	Prentiss (1937)
Sax (1984)	As Tatken and Lewis (1984)			
Henderson and Haggard (1943)	Lethal concentration	1000	Short exposure	
Matheson Co. (1961)	Lethal concentration	1000	After a few breaths	
Stahl (1969)	Dangerous concentration	20	30 min	

[a] Quoted without reference by Flury and Zernik (1931).
[b] Lowest lethal concentration recorded.
[c] A death was recorded in the concentration range 50–250 ppm (his values) at a 30 min exposure in Underhill's work (1920).

toxicity to humans. The model is based on estimates for humans of the LC_{50}, the slope of the concentration–mortality line, or ratio LC_{90}/LC_{10}, and the lethal load function together with factors for inhalation rate and for medical treatment, and involves a separate treatment of the vulnerable population. Before considering the model proper, it is convenient to consider these latter aspects.

18.18.9 Physical activity

It is to be expected that man will not simply remain passive in the face of a toxic threat but will react by some form of physical activity such as seeking to escape or to obtain shelter.

There are two main effects of such activity. The first is that larger volumes of contaminated air are inhaled. Data on inhalation rates were given in Table 18.16. It is clear from these data that the inhalation rate is greatly increased by activity and that the factor can be as high as 15. The injury suffered as a result of more rapid inhalation is likely to be increased, and allowance needs to be made for this.

The other effect of enhanced activity is that larger amounts of oxygen are required by the body. Data on this aspect also were given in Table 18.16. This increased oxygen demand may occur during exposure and/or after exposure.

The level of physical activity is taken into account by defining a base level of activity, which corresponds to rest, and a standard level of activity that corresponds to a normal mixture of sitting, standing and moving about and for which the inhalation rate is twice that of the base level.

18.18.10 Inhalation rate

The effect of inhalation rate on the injury caused by a given concentration of chlorine in air is not obvious, but it is important because it is quite conceivable that high inhalation rates will increase the injury several-fold. The assumption made in the model is that over a given inhalation period injury is a function of the mass of chlorine absorbed.

The rate of absorption of chlorine in the lung is a mass transfer process and this process may be modelled. An account of the respiratory system, including quantitative data, was given in Section 18.13. The amount of chlorine absorbed is the product of the alveolar ventilation rate and the difference in the inhaled and exhaled chlorine concentrations. It is also equal to the product of the pulmonary diffusion capacity and the difference between the actual and equilibrium partial pressures of chlorine at the alveolar membrane wall. Finally, it is also equal to the sum of the amount of chlorine transported out of the lung capillaries by the blood and of that reacted in the alveolar tissue.

The situation with respect to the solubility of chlorine is complicated by the hydrolysis of chlorine to hypochlorous acid. The solubility of chlorine and its hydrolysis have been extensively studied and data are available on the solubility of unhydrolysed chlorine and on the equilibrium and rate constants for the hydrolysis. There do not appear to be any data on the solubility of chlorine in blood plasma, but the solubility of other gases such as oxygen, carbon dioxide and nitrogen is some 10% less in plasma than in water.

If it is assumed that the chlorine is simply absorbed into the blood, there will be a gradual accumulation of chlorine in the blood that will exert a corresponding equilibrium partial pressure at the alveolar membrane so that the concentration of chlorine in the blood will rise exponentially to an equilibrium value and absorption will tail off. However, this model does not appear to be consistent with

Table 18.24 *Some probit equations for chlorine given in the literature (Withers and Lees, 1985b) (Courtesy of Elsevier Publishing Company)*

		Lethal concentration for 30 min exposure period (ppm)		
		LC_{10}	LC_{50}	LC_{90}
A Equations for fatality				
Eisenberg, Lynch and Breeding (1975)	$Y = -17.1 + 1.69\ln(\Sigma C^{2.75}T)$	26	34	44
Perry and Articola (1980)	$Y = -36.45 + 3.13\ln(\Sigma C^{2.64}T)$	36	42	49
Rijnmond Report Industrial Comment (Rijnmond Public Authority, 1982); N.C. Harris and Moses (1983)	$Y = -11.4 + 0.84\ln(\Sigma C^{2.75}T)$	237	418	738
ten Berge and van Heemst[a] (1983)	$Y = -5.04 + 0.5\ln(\Sigma C^{2.75}T)$	170	430	1093
B Equations for injury				
Eisenberg, Lynch and Breeding (1975); Perry and Articola (1980)	$Y = -2.40 + 2.90\ln C$			

[a] Original equation:
$Y = -6.5 + 0.5\ln(\sum C^{2.75}T)$
where C is concentration (mg/m^3) and T is time (min).

Table 18.25 *Values of the lethal concentration of chlorine used in various hazard assessments (Withers and Less, 1985b) (Courtesy of Elsevier Publishing Company)*

Author(s)	*Effect*	*Concentration* (ppm)	*Exposure time* (min)	*Source*
Howerton (n.d., 1969)	Dangerous concentration[a]	35	Not defined	
Dicken (1974, 1975)	Fatal concentration[a]	90[b]	10	
		70	30	
		40	100	
	Dangerous concentration[a]	30	10	
		15	100	
Simmons, Erdmann and Naft (1973, 1974)	LD_{50}	1000 ppm min (say, 35 ppm for 30 min)		Chlorine Institute
Eisenberg, Lynch and Breeding (1975)	Lethal concentration LC_{50}	35	30	Self
Solomon, Rubin and Okrent (1976)	LD_{50}	40–60	30–60	
Meslin (1981)	Lethal dose	430	30	NIOSH
Rijnmond Public Authority (1982)	Lethal concentration LC_{50}	35	30	Eisenberg, Lynch and Breeding (1975)

[a] Concentration not further defined.
[b] Approximate values read from graph.

the information available on the damage done to the body by chlorine. The evidence indicates that the damage is essentially confined to the lung.

A more appropriate assumption appears to be that the lung is a sink for the chlorine, which reacts with the alveolar tissue. This means that the venous blood entering the lung capillaries will contain very little chlorine. The maximum concentration of chlorine in the blood leaving the lung may then be obtained by solving the mass balance. Simple calculations based on the physiological parameters and the solubility of unhydrolysed chlorine indicate that for a man at rest the concentration of exhaled chlorine will be less than half the inhaled concentration. The actual value will be less than this maximum, since the concentration in the blood will be reduced both by hydrolysis and by reaction with the tissues. Thus even at rest almost all the chlorine inhaled will be absorbed. This will also be true for moderate increases in physical activity, since the increase in inhalation rate is accompanied by an increase in the circulation of blood through the lungs.

Further support for this interpretation is afforded by experiments by Lehmann (1893), who measured the inlet and outlet concentrations of chlorine in chlorine-contaminated air breathed by men. The inlet concentration was 2 ppm, the outlet concentration was undetectable, the absorption thus being total. This evidence is not conclusive, since the chlorine concentration was low, but it points in the right direction.

As a first approximation, therefore, the inhalation rate is taken into account by defining a factor ψ_1 that is applied directly to the concentration in order to correct for inhalation rate.

18.18.11 Medical treatment

Appropriate medical treatment may effect a reduction in the mortality from exposure to chlorine. It is likely to be much more effective in preventing delayed deaths than acute deaths.

As described above, the proportion of acute deaths is a function of mortality. From analysis of war gas casualties the proportion P_a of acute to total deaths, or the acute death factor, is

$$P_a = 0.8 + 0.2P \qquad [18.18.8]$$

where P is the total mortality.

The effect of medical treatment is taken into account by defining a factor ψ_2 that is applied to the proportion of delayed deaths, or rather, in this context, potential delayed deaths, to yield the proportion of recoveries.

18.18.12 Vulnerable populations

So far consideration has been limited to the effect of toxic gas on healthy adults. A significant proportion of the population, however, is more vulnerable. It is necessary to distinguish, therefore, between the less vulnerable, or regular, population and the more vulnerable, or simply vulnerable, populations, which together make up the general, or average, population.

The principal categories of people vulnerable to chlorine gas are children, old people and people with respiratory or heart disorders. The less vulnerable members of the population are healthy youngsters and adults. The estimate given by Hewitt for the proportion of vulnerable people was given in Table 9.26. A rough value is some 25% of the population.

One approach that has been used in hazard assessment is that of Eisenberg, Lynch and Breeding, who used for chlorine and ammonia the relations between the general population and the vulnerable population given in Table 18.17. There are several points that should be noted in connection with this table. The general population is not well defined, particularly as to whether or not it includes the vulnerable population. Also it has been shown by Withers and Lees that the relations given imply a lower spread of lethal concentrations for the vulnerable than for the regular population.

The vulnerability of part of the population may be handled either by treating the whole population as a single homogeneous population with vulnerable members or by treating the regular and vulnerable sections as two populations. In the first approach there is a single distribution, whereas in the second there are two separate distributions with distinct modal values. It is not self-evident which approach is most likely to fit such data as may exist, but it is clear that for hazard assessment it is more convenient to handle the vulnerable population separately and to have a separate distribution applicable to that population. This is therefore the approach adopted. It may be noted, however, that if two distinct distributions are used, they do not in general yield a distribution of the same type for the average population. Specifically, if the distributions for the regular and vulnerable populations are both log-normal, that for the average population cannot be expected to be log-normal.

18.18.13 Lethal load

The different forms of the lethal load function have been described in Section 18.11. The lethal load functions used in the model are

$$L = CT^m \qquad [18.18.9]$$

and

$$L^* = \Sigma C^n T \qquad [18.18.10]$$

Equation 18.18.9 is the natural form for the correlation of the basic data, but Equation 18.18.10 is the more convenient for hazard assessment.

The animal experiments indicate for m a value of 0.5 and this is used in the model for humans. The corresponding value of n is 2.

18.18.14 Lethal concentration: regular population

In the model the estimate of the LC_{50} is based primarily on the judgement that the most weight should be given to the work on dogs by Underbill, and this is then interpreted in the light of the other animal experiments.

The animal experiments described above give average LC_{50} values for 30 min exposures of 256, 414 and 650 ppm for mice, rats and dogs, respectively. The LC_{50} used in the model for man is 500 ppm for 30 min for the regular population at the base level of activity.

The high weight given to Underbill's work on dogs is based on a number of factors. One is the similarity of the respiratory systems of dog and man. Another is the quality of the experimental work.

In Underbill's work, the dogs tended to lie passively with their paws folded so that movement was minimal. This behaviour has been taken as corresponding to the base level of activity.

This estimate of the LC_{50} for man is intended to be a best estimate rather than a conservative one.

The slope of the concentration–mortality line, or ratio LC_{90}/LC_{10}, which is used in the model is 4. This also is based primarily on the value of 3.8 obtained from Underbill's work on dogs. The two other values obtained from the animal work are 4.4 (Silver and McGrath, 1942; Silver, McGrath and Ferguson, (1942) and 1.9 (Schlagbauer and Henschler, 1967) on mice.

The lethal load at the base level of activity then follows directly. For 50% mortality at a 30 min exposure

$$LL_{50} = CT^{0.5} = 5000 \times (30)^{0.5} = 2,739 \text{ ppm min}^{1/2} \qquad [18.18.11]$$

Similarly, the lethal loads for 10% and 90% mortality are 1,369 and 5,477 ppm $\text{min}^{0.5}$, respectively.

18.18.15 Lethal concentration: vulnerable population

The lethal concentrations for the vulnerable population are based on an estimate that the LC_{10} for a 30 min exposure for the vulnerable population at the base level of activity is 100 ppm. This estimate is derived partly from information derived from the animal experiments and partly from the concentrations reported as intolerable to man. In the experimental work on animals there was no fatality at a concentration below 50 ppm for a 30 min exposure. The nearest approach was a single fatality at 62 ppm in Schlagbauer and Henschler's work. A concentration of 100 ppm is shown in Table 18.22 as being some four times that which causes coughing and equal to that which is intolerable or incapacitating.

It is also assumed in the model that the slope of the concentration mortality line, or ratio LC_{90}/LC_{10}, is same as for the regular population. This gives for the vulnerable population values of 200 and 400 ppm for the LC_{50} and LC_{90} for 30 min.

18.18.16 Inhalation rate factor

The inhalation rate factor ψ_1 used in the model is the ratio of the inhalation rate at the actual level of activity to that at the base level, which corresponds to rest in bed and for which the inhalation rate is 6 l/min. This factor is applied directly to the inhaled concentration.

The normal, or standard, level of activity involves some movement and for this the inhalation rate is about 12 l/min. Thus for the standard level of activity $\psi_1 = 2$.

It is intended in the model that for the regular population the default level of activity be taken as the standard level, unless there is a reason to take some other level. For the vulnerable population the level of activity for old people and young children may approximate to the base level and the standard level, respectively.

18.18.17 Medical treatment factor

In the model the proportion of delayed deaths is estimated from Equation 18.18.8 and the effectiveness of medical treatment in converting delayed deaths into recoveries is accounted for using the medical treatment factor ψ_2. This is taken as 0.9 and 0.7 for the regular and vulnerable populations, respectively, which means that for these populations some 90% and 70% of the potential delayed deaths convert to recoveries. These are necessarily approximate estimates, but their overall effect on the mortality is not great, since most deaths are sudden rather than delayed.

It is not appropriate to claim credit for the mitigating effect of medical treatment unless there exist the organization, the expertise and the facilities commensurate with the accident envisaged.

18.18.18 Probit equations

From the foregoing the following probit equations may be derived:

Regular population
Base level of activity:

$$Y = -9.57 + \ln(\Sigma C^2 T) \qquad [18.18.12]$$

Standard level of activity:

$$Y = -8.29 + 0.92 \ln(\Sigma C^2 T) \qquad [18.18.13]$$

Vulnerable population
Base level of activity:

$$Y = -7.88 + 0.92 \ln(\Sigma C^2 T) \qquad [18.18.14]$$

Standard level of activity:

$$Y = -6.61 + 0.92 \ln(\Sigma C^2 T) \qquad [18.18.15]$$

The lethal concentrations for exposure times of 10 and 30 min for the regular and vulnerable populations given in the model, as expressed in these probit equations, are shown in Tables 18.26 and 18.27, respectively.

18.18.19 Overall methodology

The overall methodology used in the model for the estimation of the mortality from an accidental chlorine release given the concentration–exposure time profile may be summarized as follows.

A straightforward estimate of the mortality for the regular and vulnerable populations with the standard level of activity may be obtained using Equations 18.18.13 and 18.18.15, respectively.

If it is desired to derive an estimate that takes account of other conditions and makes at least some allowance for the other factors discussed, the approach is as follows:

(1) Estimate the inhalation rate factor and apply it to the concentration;
(2) estimate the toxic load using the corrected concentration;
(3) calculate the uncorrected mortality, estimate the acute deaths factor and apply it to this mortality;
(4) estimate the medical treatment factor and apply it to the proportion of potential delayed deaths;
(5) calculate the corrected mortality.

Table 18.26 *Concentrations of chlorine proposed as lethal to humans for an exposure time of 10 min (Withers and Lees, 1985b) (Courtesy of Elsevier Publishing Company)*

Cocentration (ppm)	*Mortality* (%)	*Toxic load,* $CT^{0.5}$ (ppm $\text{min}^{0.5}$)
A Regular population: standard level of physical activity		
217	10	685
433	50	1369
866	90	2739
B Vulnerable population: standard level of physical activity		
87	10	274
173	50	548
346	90	1095
C Average population: standard level of physical activity		
139	10	438
364	50	1150
805	90	2547

18.18.20 Gas warfare cross-checks

Since chlorine was the first major war gas, attempts have been made to cross-check estimates for the lethal toxicity of chlorine against the effects of gas attacks. One such attempt is that by Nussey, Mercer and Fitzpatrick (1986). Another is that by Withers and Lees (1987b, 1992) to check the model just described. Critiques of this work by R.F. Griffiths and Fryer (1988) and V.C. Marshall (1989b)

Table 18.27 *Concentrations of chlorine proposed as lethal to humans for an exposure time of 30 min (Withers and Lees, 1985b) (Courtesy of Elsevier Publishing Company)*

Concentration (ppm)	*Mortality* (%)	*Toxic load,* $CT^{0.5}$ (ppm $\text{min}^{0.5}$)
A Regular population: base level of physical activity		
250	10	1369
500	50	2739
1000	90	5477
B Vulnerable population: base level of physical activity		
100	10	548
200	50	1095
400	90	2191
C Regular population: standard level of physical activity		
125	10	685
250	50	1369
500	90	2739
D Vulnerable population: base level of physical activity		
50	10	274
100	50	548
200	90	1095
E Average population: standard level of physical activity		
80	10	438
210	50	1150
465	90	2547

have held that the uncertainties surrounding these attacks are simply too great to make a cross-check.

18.19 Gas Toxicity: Green Book Relations

Another, more recent, treatment of the toxicity of industrial gases is that given in *Methods for the Determination of Possible Damage* by the CPD in the Netherlands (1992b) (the Green Book) based on research by TNO. An account is given by de Weger, Pietersen and Reuzel (1991).

This work was preceded by the study of probit equations for individual species by ten Berge of Dutch State Mines (DSM) and Zwart and van Heemst of TNO (ten Berge, Zwart and Appelman 1986), to which reference has already been made.

In this methodology a distinction is made between locally acting substances and systemically acting substances.

18.19.1 Locally acting substances

For a locally acting substance the specific dose D'' is defined as

$$D'' = D/A \qquad [18.19.1]$$

where A is the surface area of the lungs (m^2), D is the inhaled dose (mg) and D'' is the inhaled dose per unit area of lung (mg/m^2). The dose D is taken as

$$D = (V_a/1000)Ct \qquad [18.19.2]$$

where C is the concentration of gas in the atmosphere (mg/m^3), t is the exposure time (min) and V_a is the minute volume (l/min). From empirical physiological relations

$$V_a \propto W^{0.70} \qquad [18.19.3]$$

$$A \propto W^{0.92} \qquad [18.19.4]$$

where W is the body mass (kg).

Then from Equations 18.19.2–18.19.4

$$D'' \propto W^{-0.22} \qquad [18.19.5]$$

The body masses of man, the rat and the mouse are 70, 0.3 and 0.03 kg, respectively. It follows then from relation 18.19.5 that the load on a rat and on a mouse are, respectively, some 3.3 times and 5.5 times that on a man.

This treatment has not allowed for absorption of gas in the air passages. Such absorption hardly occurs in humans, but most test animals are nose breathers and absorption occurs to a much greater degree.

There is considerable uncertainty as to whether the same dose per unit area of lung has the same effect on humans and animals. A safety factor, f, of 5 is applied to allow this.

18.19.2 Systemically acting substances

For a systemically acting substance the specific dose D' is defined as

$$D' = D/W \qquad [18.19.6]$$

where D' is the inhaled dose per unit body mass (mg/kg). In this case the mass absorbed is proportional to the oxygen consumption rather than the minute volume. Oxygen consumption is in turn, a function of body weight, being proportional to $W^{0.7}$ as in relation 18.19.3. Hence from relations 18.19.2, 18.19.3 and 18.19.6

$$D' \propto W^{-0.3} \qquad [18.19.7]$$

Then using the same body masses as before, relation 18.19.7 implies that the load on a rat and on a mouse are, respectively, some 5.1 times and 10.2 times that on a man.

There is uncertainty as to whether the same dose per unit body mass has the same effect on humans and animals. In this case a safety factor, f, of 10 is applied.

18.19.3 Extrapolation factor

The foregoing treatment incorporates certain safety factors, of 5 for locally acting substances and 10 for systemically acting ones. The dose values apply to inhalation rates for persons at rest. A further safety factor of 2 is then applied which allows for increased inhalation rates in the population during a toxic gas emergency.

An extrapolation factor f_d is now determined for extrapolation of results from each species to humans. Thus, for example, for a rat:

Load animal f_d = *Load man*	*Safety factor*	*Extrapolation factor*
Local effect	3.3	5×2 0.33 0.25 } 0.25
Systemic effect	5.1	10×2 0.26 0.26 }

The LC_{50} value for humans is obtained by multiplying the LC_{50} value for the test animal by the extrapolation factor. Values of the extrapolation factor f_d are as follows: rat, 0.25; mouse, 0.5; guinea pig, 0.2; and hamster, 0.3.

18.19.4 Probit equations

Probit equations for use in hazard assessment are then derived as follows. The basic approach is to assume a value for k_2 in Equation 18.11.6 and, if necessary, a default value of n, and to determine the constant k_1 from animal LC_{50} data.

The constant k_2 is assigned a value of 1.0 in all cases. This corresponds to a high value of the ratio LC_{95}/LC_{05}, and for concentrations below the LC_{50} is the conservative assumption. For the index n the default value used is 2.

Then starting from an animal LC_{50} value for some time t, the first step is to obtain the LC_{50} for 30 min. This is then converted to a 30-min LC_{50} for humans by application of the extrapolation factor f_d.

Where there are data for more than one animal species, a further step is taken. This is to obtain the average animal 30-min LC_{50} and to multiply it by a factor of 2 before applying the extrapolation factor f_d to obtain the 30-min LC_{50} for humans. This has the effect of reducing the overall safety factor that is applied.

The probit equations obtained are considered further in Section 18.20.

18.20 Gas Toxicity: Probit Equations

As described above, probit equations are available for a number of the toxic gases of industrial interest. They include in particular the collections given for the Vulnerability model by Perry and Articola (1980), in the *QRA Guidelines* by the CCPS (1989/4) and in the *Green Book* by the CPD (1992b). The limitations of probit equations have been discussed in Chapter 9 and need not be rehearsed here.

In addition to the inherent limitations of probit equations, it is also necessary to consider in each particular case

both the situation to which it is intended to apply and the degree of conservatism incorporated. The basic data are generally obtained from experiments on animals that tend to remain passive, but the use of the correlation is presumably for humans in an emergency situation. In some cases the probit equation is explicitly conservative, whilst in others it is not, reflecting a difference of philosophy as to the point at which any safety factor should be applied.

Table 18.28 gives the parameters for probit equations for industrial toxic gases.

18.21 Gas Toxicity: HSE Dangerous Dose

As described in Chapter 9, the HSE use for the purpose of land use planning the concept of a 'dangerous dose'.

For toxic substances the interpretation of the dangerous dose concept and the methodology by which a value is derived is described in *Assessment of the Toxicity of Major Hazard Substances* (R.M. Turner and Fairhurst, 1989a).

The authors discuss the paucity of data on the effect of toxic gases on man and the problems of probit equations. They propose for land use planning the use not of probit equations but of a toxic load value that they call the SLOT. This is expressed in the form of an equation for the dangerous toxic load (DTL) and of a set of values for the SLOT computed from this relation.

The SLOT is defined as a value associated with a situation in which: (1) almost all persons suffer severe distress; (2) a substantial fraction require medical attention; (3) some persons are seriously injured, requiring prolonged treatment; or (4) any highly susceptible person might be killed. Typically the SLOT used corresponds to a mortality of 1–5%. The SLOT selected depends, however, on the substance, and in some cases it may be appropriate to use several SLOTs.

Essentially the SLOT is a criterion for individual risk. For societal risk the authors refer to the use of the method described by Poblete, Lees and Simpson (1984) and extended by Lees, Poblete and Simpson (1986), which is described in Chapter 9.

The methodology described by Turner and Fairhurst for the derivation of a SLOT is broadly as follows. Since there is a lack of toxicity data for humans, it is necessary to resort to the use of data from experiments on animals. The most

Table 18.28 *Parameters in probit equations for lethality for some principal industrial toxic gases*

Substance	*Probit equation parameters*[a]					
	CCPS[b]			*CPD*[c]		
	k_1	k_2	n	k_1	n	*30-min* LC_{50}
Acrolein	−9.931	2.049	1	−4.1	1.0	304
Acrylonitrile	−29.42	3.008	1.43	−8.6	1.3	2533
Ammonia[d]	−35.9	1.85	2	−15.8	2.0	6164
Benzene[e]	−109.78	5.3	2	–	–	–
Bromine[e]	−9.04	0.92	2	−12.4	2.0	1075
Carbon monoxide[e]	−37.98	3.7	1	−7.4	1.0	7949
Carbon tetrachloride	−6.29	0.408	2.5	–	–	–
Chlorine[d]	−8.29	0.92	2	−14.3	2.3	1017
Ethylene oxide[e]	–	–	–	−6.8	1.0	4443
Formaldehyde[e]	−12.24	1.3	2	–	–	–
Hydrogen chloride	−16.85	2.0	1.00	−6.7	1.0	3940
Hydrogen cyanide	−29.42	3.008	1.43	−9.8	2.4	114
Hydrogen fluoride	−35.87	3.354	1.00	−8.4	1.5	802
Hydrogen sulfide	−31.42	3.008	1.43	−11.5	1.9	987
Methyl bromide	−56.81	5.27	1.00	−7.3	1.1	3135
Methyl isocynate[e]	−5.642	1.637	0.653	−1.2	0.7	57
Nitrogen dioxide[e]	−13.79	1.4	2	−18.6	3.7	235
Phosgene	−19.27	3.686	1	−0.8	0.9	14
Propylene oxide	−7.415	0.509	2.00	–	–	–
Sulfur dioxide	−15.67	2.10	1.00	−19.2	2.4	5784
Toluene	−6.794	0.408	2.5	–	–	–

[a] Both sets of parameters are for toxic gas fatality probit equations of the form

$$Y = k_1 + k_2(c^n t)$$

where t is the time (min). In the CCPS equation (and in those of Perry and Articola (1980)) the units of concentration c are ppm, whilst in the CPD equation the units are mg/m^3.

[b] CCPS *QRA Guidelines* (1989/5). Except as described in (d) and (e) below, these are the values given by Perry and Articola (1980), who discuss the derivations.

[c] CPD *Green book* (1992b); de Weger, Pietersen and Reuzel (1991). In all cases $k_2 = 1$.

[d] Perry and Articola give:
Ammonia: $k_1 = -28.33$; $k_2 = 2.27$; $n = 1.36$;
Chlorine: $k_1 = -36.45$; $k_2 = 3.13$; $n = 2.64$;
Hydrogen fluoride: $k_1 = -25.87$; $k_2 = 3.354$; $n = 1.00$.

[e] Perry and Articola do not give values for these substances.

reliable data generally relate to the LC_{50} values and the associated exposure times, and it is this that is taken as the starting point. Data are gathered for a number of species and usually the data adopted are those for the most sensitive species. Next, estimates are made of the LC_{50} or LC_{01} values. In some cases the data available permit an extrapolation based on probits. If this is not possible, an alternative approach is to use an empirical value of the ratio LC_{50}/LC_{05}, or LC_{50}/LC_{01}, as the case may be.

At this stage, therefore, the method yields a single value of the SLOT LC_{50} or LC_{01} with an associated exposure time. It is then necessary to determine the trade-off between the concentration c and the time t, or, in other words, the value of the index in the toxic load $c^n t$. Essentially this requires data on concentration vs time for a given level of effect, such as the LC_{50}. The authors warn against the use for this purpose of values from different sets of experiments on different species, since the results may then owe more to differences between species than to differences in exposure time.

The SLOTs obtained are then correlated as a DTL equation. These SLOTs and the DTL are applicable to an animal species. Collateral evidence may then be sought to confirm that it is reasonable to apply the relation to humans.

One feature of this approach is that the use of an LC_{50} or LC_{01} rather than an LC_{50} value means that there is more likely to be some data on humans that can be used as collateral evidence. Another feature is that, insofar as the animal data used are generally for the most sensitive species, the approach may be regarded as conservative.

The application of this methodology is now illustrated for a number of industrial toxic gases. Table 18.29 shows for these gases some physico-chemical properties and the SLOTand DTL values. Each of the studies described gives a table detailing results of single exposure inhalation studies in animals and a table of LC_{50} values for different species.

The accounts given below are necessarily brief summaries; the arguments adduced in support of the values chosen are much fuller in the original references and these should be consulted.

18.21.1 Acrylonitrile

The SLOT values for acrylonitrile are derived in *Toxicology of Substances in Relation to Major Hazards: Acrylonitrile* (R.M. Turner and Fairhurst, 1989b). The gas has an irritant effect.

The experimental data for animals are sparse and most are for long exposures; none were found for exposure periods of less than 30 min. The more sensitive species were dogs, in work by Brieger, Rieders and Hoders (1952), and mice, in work by Knobloch *et al.* (1971). From the data for these species the authors derive the single SLOT value of 40 ppm for 4 h. They do not give a precise interpretation of this SLOT, but it would appear to correspond to a value of the order of LC_{05} to LC_{01}. They make use of several studies which bear on the relation between concentration and time and settle on a value of $n = 1$. The resultant SLOTs and DTL equation are then as given in Table 18.29.

18.21.2 Ammonia

The SLOT values for ammonia are derived in *Toxicology of Substances in Relation to Major Hazards: Ammonia* (Payne, Delic and Turner, 1990). Ammonia is an irritant gas which, being highly soluble, tends to attack the upper respiratory tract, causing laryngeal oedema, as well as pulmonary oedema. The authors suggest that reported cases of laryngeal spasm probably involved laryngeal oedema. The essential toxic effect is therefore irritation.

For ammonia there is a considerable amount of experimental data on animals. The most sensitive species is the mouse, but the authors also make some use of data for rats. For mice, the work of Silver and McGrath (1948) yields an LC_{50} of 10,150 ppm for a 10 min exposure and that of Kapeghian *et al.* (1982) an LC_{50} of 4230 ppm for a 60 min exposure. From work on rats by Appelman, ten Berge and Reuzel (1982) a value of the index $n = 2$ may be obtained. It happens that this value of $n = 2$ is also consistent with the two LC_{50} values just mentioned. Data from these same studies were used to estimate values of the LC_{05} and LC_{01}. The resultant values for the LC_{01} are 6,129 and 3,296 ppm, respectively. Adopting the former and utilizing the value of

Table 18.29 *HSE DTL and SLOT values for some principal industrial gases*

	Acrylonitrile	*Ammonia*	*Chlorine*	*Hydrogen fluoride*	*Hydrogen sulfide*	*Sulfuric acid mist*
MW	53.06	17.03	70.9	20.0	34.1	98.1
Boiling point (K)	350.3	−33.42°C	328.4	292.5	211.2	563–603
Freezing point (K)	189.5	−77.74°C	172	190	187.5	283[c]
Conversion factor (ppm–mg/m^3)[a]	2.2	0.7	2.9	0.83	4.4	
DTL	9600 ppm min	3.76×10^8 ppm^2 min	108,000 ppm^2 min	2,400,000 ppm^2 min	2×10^{12} ppm^4 min	2.16×10^5 (mg/m^3) min
SLOT values (ppm)[b]						
5 min	1920	8670	147	693	800[d]	208 mg/m^3
10 min	960	6130	100	490	669	147 mg/m^3
30 min	320	3540	60	283	508	85 mg/m^3
60 min	160	2500	42	200	427	60 mg/m^3
120 min	80	1770	30	141	359	42 mg/m^3
240 min	40				302	
480 min						21 mg/m^3

[a] Conversion factor for vapour at 25°C and pressure 1.0133×10^5 Pa, except for hydrogen fluoride for which the conversion is based on 0°C.
[b] Units for all gases except for sulfuric acid mist, for which the units are mg/m^3.
[c] Value for 100% acid.
[d] Ceiling value for exposure period 0–5 min.

n quoted yields the SLOTs and DTL equation given in Table 18.29.

18.21.3 Chlorine

The SLOT values for chlorine are derived in *Toxicology of Substances in Relation to Major Hazards: Chlorine* (R.M. Turner and Fairhurst, 1990a). The gas has an irritant effect.

For chlorine there is a considerable amount of experimental data on animals. The mouse appears the most sensitive species. For mice, the work of Schlagbauer and Henschler (1967) gives an LC_{50} of 127 ppm for a 30 min exposure. Data from this study were used to estimate values of the LC_{05} and LC_{01} for this exposure time, the values obtained being 70 and 56 ppm, respectively. The index n is obtained from a critical review of the large variety of values quoted in the literature, the authors settling on $n = 2$. The resultant SLOTs and DTL equation are then as given in Table 18.29.

The generally conservative nature of the approach taken is illustrated in this case. The LC_{50} value derived from the work of Schlagbauer and Henschler on which the SLOTs are based towards the lower end of the range of LC_{50} values for animals given in the literature.

18.21.4 Hydrogen fluoride

The SLOT values for hydrogen fluoride are derived in *Toxicology of Substances in Relation to Major Hazards: Hydrogen Fluoride* (R.M. Turner and Fairhurst, 1990b).

Hydrogen fluoride is an irritant gas, but it also has some systemic effects. Whilst there is little information on the long-term effects of a single non-lethal exposure, the general toxicological properties of the gas point to the possibility of permanent injury.

For hydrogen fluoride there is a limited amount of experimental data on animals, the most sensitive species being the mouse. The work of Wohlslagel, DiPasquale and Vernot (1976) gives for mice an LC_{50} of 342 ppm for a 60 min exposure. Using data from this same study, Turner and Fairhurst obtain for the LC_{05} and LC_{01} at this same exposure time values of 230 and 205 ppm, respectively. From work on rats by Rosenholtz *et al.* (1963) they derive a value of the index $n = 2$. This then yields the SLOTs and DTL equation given in Table 18.29.

18.21.5 Hydrogen sulfide

The SLOT values for hydrogen sulfide are derived in *Toxicology of Substances in Relation to Major Hazards: Hydrogen Sulphide* (R.M. Turner and Fairhurst, 1990c).

In addition to being an irritant gas hydrogen sulfide also causes inhibition of intracellular respiration. The second of these effects grows in relative importance as the concentration increases.

For hydrogen sulfide the limited amount of experimental data on animals available show reasonable consistency. Turner and Fairhurst distinguish several concentration regions: 750–100 ppm; 450–750 ppm and 200–350 ppm. High concentrations, in the range 750–1000 ppm, cause rapid unconsciousness and death within a few minutes. The authors therefore take 800 ppm as a ceiling value, independent of exposure time. From examination of data on a number of species, including work by Prior *et al.* (1988) and Tansy *et al.* (1981), the authors obtain the following LC_{50} estimates: 300 ppm for 4 h; 400 ppm for 60 min; and 500 ppm for 30 min. This set of values corresponds to a value of the index of $n = 4$. In the study by Prior *et al.* for an exposure time of 4 hours the LC_{50} was 501 ppm and the LC_{10} was 422 ppm, giving an LC_{50}/LC_{10} ratio of 1.19, which was then used to obtain the SLOTs. The resultant SLOTs and DTL equation are then as given in Table 18.29.

18.21.6 Sulfuric acid mist

The SLOT values for sulfuric acid mist are derived in *Toxicology of Substances in Relation to Major Hazards: Sulphuric Acid Mist* (R.M. Turner and Fairhurst, 1992).

Sulfuric acid mist is an irritant that has two main effects. One is constriction of the airways (bronchioconstriction and possibly laryngeal spasm). The other is damage to the respiratory tract accompanied by oedema and haemorrhage. These toxic effects depend on the size of the droplets.

Sulfuric acid mist is formed from releases of sulfur trioxide or oleum, a mixture of sulfuric acid and sulfur trioxide. On release these react with water in the atmosphere and form a dense cloud of mist. The mist is likely to contain submicron droplets that remain airborne until they absorb additional water and rain out or are deposited onto surfaces. In an accident, the size of the droplets inhaled can be expected to exceed that on release and the authors assume a droplet size of 1 μm. As it happens, this is the size for which most of the data are available.

For sulfuric acid mist the bulk of data on animal experiments relates to guinea pigs. This is also the most sensitive species. From the work of Amdur, Schulz and Drinker (1952) the authors obtain an estimate of the LC_{50} of 60 mg/m^3 for a 60 min exposure. For the index n Turner and Fairhurst use the values of the LC_{50} at an 8 h exposure of 18, 30 and 50 mg/m^3 reported by Amdur, Schulz and Drinker and by Wolff *et al.* (1979), and obtain the value $n = 2$. These data form the basis of the SLOTs. There is no explicit recourse to LC_{05} or LC_{01} values, but the LC_{50} is that for the experiments in which the animals were most sensitive; in other work by Treon *et al.* (1950) and Amdur (1958) no deaths were recorded at concentrations up to 42 and 121 mg/m^3 for an exposure time of 60 min. The resultant SLOTs and DTL equation are then as given in Table 18.29.

18.22 Gas Toxicity: Combustion Gases

A somewhat separate problem concerns the toxicity of combustion products. Much of the research interest in such gases centres on the combustion of furnishings, but work in this area is also relevant to toxic clouds from combustion of materials on plant and in storage, particularly warehouses.

Work on the toxicity of combustion products has been described in a number of publications. This includes work described in *Smoke and Products of Combustion* (Hilado, 1973) and by Hilado and co-workers (Hilado and Furst, 1976; Hilado, Casey and Furst, 1977; Hilado, Cumming and Casey, 1978; Hilado and Cumming, 1978; Hilado and Huttlinger, 1980, 1981b,c), Hartzell and co-workers (Kaplan and Hartzell, 1984; Hartzell, Packham *et al.,* 1985; Hartzell, Priest and Switzer, 1985; Hartzell, Stacy *et al.,* 1985; Hartzell, 1987, 1989; Hartzell, Grand and Switzer, 1987), Underwood (1978), Alexeeff *et al.* (1986), Tsuchiya and Nayaka (1986) and the CPD (1992b).

The toxicity of combustion products in the context of hazard assessment has been considered by D.A. Carter (1989), G.T. Atkinson, Jagger and Kirk (1992) and

G.T. Atkinson and Jagger (1994). The toxicity of the breakdown products of the fire extinguishant bromochlorodifluoromethane (BCF) has been studied by Doe *et al.* (1986).

18.23 Ultratoxic Substances

The Seveso disaster in 1976 showed that there is a serious hazard from small quantities of ultratoxic substances. At Seveso some 2.5 kg of 2,3,7,8-tetrachlorodibenzoparadioxin (TCDD) were released to the atmosphere. Abnormal reaction conditions occurred in a chemical reactor, the pressure rose and the relief valve operated. The TCDD was not a normal reaction product but the product of a side reaction that occurred at an appreciable rate only under abnormal conditions. The toxicity of TCDD is such that it is more akin to a chemical warfare agent than an industrial chemical and it has been called the most poisonous substance in existence. The surrounding area was contaminated and had to be evacuated. People in the area at the time of the incident suffered rashes. But, more seriously, there were expected to be long-term carcinogenic, teratogenic and/or mutagenic effects. Further details of the Seveso incident are given in Appendix 3.

A further disaster involving a very highly toxic, if not ultratoxic, chemical occurred at Bhopal in 1984, where a reaction occurred in a storage tank containing methyl isocyanate (MIC), the relief valve lifted and released a cloud of the gas onto housing, killing a large number of people, the official death toll being now 4,000, but other estimates being rather higher. This was much the worst accident experienced at a chemical plant. Further details of the Bhopal incident are given in Appendix 5.

18.24 Plant Design for Toxic Substances

Plants handling toxic substances need to be designed to minimize both large accidental releases and fugitive emissions. An overview of the design of plant for the handling of toxic substances is given by S.D. Green (1980). He deals with: the collection and assessment of toxicological information; process reviews covering random leaks and intermittent releases; design strategies of substitution, prevention and containment; ventilation; separation distances; and protection measures.

18.24.1 Design against large releases

As far as concerns large toxic releases, this is not solely a matter of the mechanical design of the plant, important though that is. Inherently safer design also has an important part to play, in minimizing the effects of any failure through the choice of the substances used in the in process and the operating conditions.

The mechanical design of plants, and particularly pressure systems, to high standards of integrity is treated in Chapter 12, and is not considered further here.

18.24.2 Design against fugitive emissions

There are a number of accounts, both by plant designers and occupational hygienists, of the design and operation of plant handling toxic substances to counter fugitive emissions and the resultant chronic toxic hazard. These include *Fugitive Emissions of Vapours from Process Equipment* (Jones *et al.,* 1984, BOHS TG3), (the BOHS *Fugitive Emissions Guide*), *Health Hazard Control in the Chemical Process Industry* (Lipton and Lynch, 1987) and *Handbook of Health Hazard Control in the Chemical Process Industry* (Lipton and Lynch, 1994) and by Payne (1978), S.D. Green (1980), Kusnetz and Phillips (1983), Kusnetz and Lynch (1984), Whitehead (1987) and Crowl and Louvar (1990).

Other potential sources of guidance are design practices for chemical plant under vacuum and for nuclear plant.

Emissions of toxic substances to the atmosphere are not confined to continuous leaks from the plant. They also occur as a result of operations carried out on the plant, particularly those involving purging or breaking into equipment for operations or maintenance purposes. The design of plants to minimize exposure to toxic substances is essentially a two-pronged one, based on the reduction of fugitive emissions and the provision of ventilation.

The problem of fugitive emissions on process plants is discussed in Chapter 15. There has been a growing concern over the emission of hydrocarbons and of volatile organic compounds (VOCs). Two points made there bear reiteration. One is that there is considerable variability between plants in the levels of emission, and the other that it is possible for plants to achieve very low levels of emissions, though as always this is easier in the design of a new plant.

Most of the data on fugitive emissions relate to hydrocarbons and VOCs. They provide a useful initial indication, but in view of the wide differences in the results obtained and the rather different nature of the problem in the case of toxic materials, care should be exercised in applying them to toxic emissions.

The BOHS *Fugitive Emissions Guide* provides guidance on the main leak sources: flanges and seals, with applications of the latter on valves, agitators, pumps and compressors.

The topics treated by Lipton and Lynch (1987) are (1) occupational health hazards, (2) sources of exposure, (3) exposure evaluation, (4) fugitive emissions, (5) hazard control, (6) rotating equipment, (7) valves and flanges, (8) sampling, and (9) drains, sewers and wastewater emissions.

18.24.3 Ventilation

Design to minimize fugitive emissions is complemented by provision of good ventilation. Ventilation is discussed in Chapter 10 in relation to plant layout, and again in Chapter 25 in relation to occupational hygiene, and is therefore not treated at this point.

18.24.4 Material transfer

On plants handling toxic materials, transfer systems such as pumps are one of the main sources of emissions, which can occur either as random leaks or in the course of activities such as maintenance. An account of this problem and measures to deal with it has been given by Grossel (1990a).

This author considers centrifugal pumps, positive displacement pumps, sealless pumps, jet pumps, pressurized gas and vacuum systems. He describes centrifugal pumps for toxic-liquids which are fitted with double mechanical seals, in double inside or tandem arrangement, and with a seal failure alarm. A buffer liquid may be used, which may have to be cooled to remove heat or heated to reduce its viscosity. A minimum flow bypass is often desirable and may need to be provided with a cooler. For a heat sensitive toxic liquid it may be necessary to provide the pump with a high temperature trip.

For low flows, positive displacement pumps are frequently used. Diaphragm metering pumps or air-operated

diaphragm pumps have no seals and are able to operate at low flow without excessive temperature rise. For highly toxic liquids, Grossel advises double diaphragm pumps. The space between diaphragms can be monitored. For rather higher flows use may be made of rotating positive displacement pumps such as the gear, vane, lobe or screw types, fitted with double mechanical seals or using magnetic drives. Positive displacement pumps require pressure relief to an external source. Grossel emphasizes the need for such external relief even where the pump is equipped with an internal relief valve.

Sealless pumps such as canned pumps and magnetic drive pumps are another option, but these also are not without problems. One weak point may be the shell, which may be relatively thin so as not to impede the magnetic field. Another may be the bearings which are lubricated by the pumped fluid. Failure of a bearing can cause the rotor to rub against the can and rupture it. Manufacturers offer various arrangements to overcome these problems, such as secondary containment with monitoring of the intervening space or monitoring of the bearings. Operating problems include flashing of low-boiling liquids, dry running and blockage by solids.

Grossel also gives details of systems for transfer by pressurized gas or by vacuum, and discuss other aspects such as plant layout, equipment installation, remotely operated isolation valves and ventilation hoods.

18.25 Toxic Gas Detection

A release of toxic gas may be detected by the visual appearance of the cloud, by its odour or by instrumentation. Detection by these means is discussed in the *Vapor Release Mitigation Guidelines* (CCPS, 1988/3).

18.25.1 Colour

Some gases have a characteristic colour. Chlorine gives a gas cloud of greenish-yellow colour, bromine one of reddish-orange colour, and so on. Even if there is no such colour, the gas may well form a visible fog. Some gases tend to form a fog by taking up moisture from the air to form an aerosol. Such gases include ammonia, hydrogen chloride, hydrogen fluoride and sulfur trioxide. Liquefied gases such as Liquefied natural gas (LNG), liquefied petroleum gas (LPG), liquid ethylene and liquid ammonia cause water in the atmosphere to condense and create a fog.

18.25.2 Odour

Many gases give a characteristic odour. The concentrations at which such an odour is detectable vary by orders of magnitude.

Accounts of odour are given in *Human Responses to Environmental Odors* (Turk, Johnston and Moulton, 1974), *Industrial Odor Technology and Assessment* (Cheremisinoff and Young, 1975), *The Identification and Measurement of Refinery Odours* (CONCAWE, 1975 8/75), *Compilation of Odor and Taste Threshold Values Data* (Fazzalari, 1978), *The Perception of Odors* (Eugen, 1982) and *Odor Thresholds for Chemicals with Established Occupational Standards* (AIHA, 1989/17), and by Leonardos, Kendall and Barnard (1969), Amoore and Hautala (1983), Polak (1983), Lynskey (1984 LPB 60) and J.C. Stevens, Cain and Weinstein (1987). Odours are also discussed in Appendix 11.

Some odour thresholds (OTs) are very low indeed. The threshold for hydrogen sulfide is given in the CONCAWE document as 0.001–0.014 ppm and in the CCPS Guidelines as 0.0002 ppm. The latter give data on the relation between the OT and the immediately dangerous to life and health (IDLH) limit. These include the following:

Gas	*OT* (ppm)	*IDLH* (ppm)	*IDLH*/*OT*
Carbon monoxide	(none)	1500	N/A
Phosgene	0.47	2	4.3
Ammonia	21	500	25
Chlorine	0.31	25	80
Hydrogen sulfide	0.0002	300	1,500,000

In some cases a person can become desensitized to an odour. The classic case is hydrogen sulfide. This is discussed in Section 18.16.

18.25.3 Instrumentation

In some cases it is appropriate to install toxic gas detectors. Accounts of toxic gas detectors and detection are given in *Detection and Measurement of Hazardous Gases* (Cullis and Firth, 1981) and by Dailey (1976), Johanson (1976), Warncke (1977), Lichtenberg and McKerlie (1979), Harbert (1983, 1984), Krigman (1984), Zanetti (1986b) and Atallah and Guzman (1987).

Whereas much flammable gas detection is based on combustible gas detectors, toxic gas detection tends to utilize a wider variety of detectors, corresponding to the variety of toxic gases. Some principles of operation in the sensors used include (1) hot wire combustion, (2) catalytic combustion or reaction, (3) some other chemical reaction, (4) electrical effects, and (5) absorption and scattering effects. Use is also be made of closed circuit TV monitors. Details of sensors and their response times are given in the CCPS Guidelines.

The purpose of a toxic gas detection system should be clearly defined. One purpose may be to give a rapid warning of a major release. Another may be to detect fugitive emissions of a toxic gas for occupational hygiene purposes. It is the former that is considered at this point.

In locating the detectors there is a choice between monitoring specific potential leak sources and giving good area coverage. For the monitoring of a leak source Johanson (1976) suggests an angular separation between detectors of 10° and a separation between detectors of no more than 30 ft (10 m). He recommends detector heights of 1.5 ft (0.5 m) and of 6–8 ft (2–2.5 m) for buoyant gases.

The CCPS Guidelines emphasize that a toxic gas detection system with an insufficient number of detectors or inadequate maintenance may be worse than no system at all, particularly if it leads to less human surveillance or to confusion arising because a field report of a leak is not confirmed by the detection system.

Guidance is available on gas detection systems for specific toxic gases. For chlorine information is given in the *Chlorine Manual* (Chlorine Institute, 1986 Pmphlt 1). The monitoring of ammonia is discussed by Lichtenberg and McKerlie (1979).

18.26 Toxic Release Response

Essentially the control of the toxic release hazard means, on the one hand, the prevention of serious loss of containment and, on the other, the elimination of hazardous

concentrations in the environment. There are also the intermediate problems of dealing with small quantities of toxic materials arising mainly from leaks and spillages and from maintenance operations.

Aspects of the process and plant design and of the storage and transport of toxic chemicals are described in Chapters 11, 12, 22 and 23, respectively. Another aspect is planning for toxic emergencies, which is described in Chapter 24. The assessment of the hazard of large toxic releases is dealt with in Sections 18.28–31.

Elimination of hazardous concentrations in the working environment requires assessment of leaks and other sources of toxic substances. Engineering measures can then be taken to improve the leak-tightness of plant.

It is also necessary to have ventilation and monitoring of the atmosphere and medical checks on personnel. These latter aspects comprise industrial hygiene and are discussed in Chapter 25.

In addition, there should be procedures for the handling of abnormal leaks and spillages.

18.26.1 Leaks and spillages

If the plant is in the open, small leakages from the plant may be dispersed by the wind. If the plant is in a building, mechanical ventilation is necessary. The toxic hazard should be a principal consideration in deciding whether to put a plant in a building or in the open.

Provision should be made for handling larger emissions. It may be necessary to have emergency isolation valves and relief, blowdown and gas absorption facilities in order to reduce the amount likely to escape.

Methods of dealing with liquid spillages vary with the chemical concerned. Thus, for example, the treatments recommended in the respective codes are different for chlorine and for phosgene. In both cases the principle applies of restricting by containment the area available for evaporation. But, whereas the evaporation of chlorine can be reduced by applying mechanically produced water-based protein foam, this should not be utilized for phosgene, for which the use of kerosene impregnated with dry sawdust is suggested.

In dealing with spillages, actions should be avoided which actually increase the rate of evaporation. For example, water should not be sprayed on a chlorine spillage. In contrast, a spillage of ethylene oxide, which is miscible with water, may be diluted and rendered more safe by the addition of large quantities of water. Restricted amounts of water, however, may only serve to increase the vaporization.

The handling of toxic liquids spilled into bunds, and the use of foams, is considered in more detail in Chapter 15.

18.26.2 Emergency action

The effect of a large toxic release can be greatly mitigated if the people exposed take the right action. In plant handling toxic materials workers have protective buildings and equipment and are trained in emergency procedures. It is commonly considered that, provided these precautions are taken, workers in the factory itself are at no more risk than members of the public.

In order to prepare instructions to be issued to the public in the event of a large release, it is necessary to decide whether it is safer for a person to flee from the gas cloud or to stay indoors taking measures to prevent ingress of the chemical. Methods are available for the calculation of the rate at which a toxic gas diffuses into buildings. An account of these methods was given in Chapter 15.

The usual practice in assessing a toxic release hazard is to consider a range of scenarios. For some scenarios the best course of action may be to evacuate, while for others it may be to stay indoors. It should be borne in mind, however, that any instruction to be issued to the public should be simple and clear. In most cases the preferred advice to the public is to stay indoors and shut doors and windows.

Emergency procedures for toxic releases are treated in more detail in Chapters 20 and 24.

18.27 Toxic Release Case Histories

By far the worst accident in the history of the process industries occurred on 3 December 1984 at Bhopal, where water entered a storage tank of methyl isocyanate, causing overheating and release of methyl isocyanate vapour which spread over a shanty town close to the works and killed some 4000 people. This incident is described in Appendix 5.

There have been a number of major accidents involving chlorine. A list of major chlorine accidents worldwide has been given by Simmons, Erdmann and Naft (1974) and is reproduced in Table 18.30. Another list of chlorine accidents has been given by V.C. Marshall (1977b) and is shown in Table 18.31.

In 1939, failure of a chlorine storage tank at Zarnesti, Romania, resulted in the death of about 60 people. This is the largest death toll from any industrial chlorine accident.

As the tables show, tank failures were also the cause of two other major chlorine accidents: at St. Auban, France, in 1926, for which the death toll is given variously as 19 and 40; and at Rauma, Finland, in 1947, where 19 died.

An explosion in a rail tank car at Mjodalen on 26 January 1940 resulted in a chlorine release of 7–8 te and caused the gassing of 85 people, of whom three died (Römcke and Evensen, 1940; Hoveid, 1966).

A large release of chlorine occurred at Baton Rouge, Louisiana, on 10 December 1976 (Case History A79), which the *Second Report* of the ACMH (Harvey, 1979b) described at the time as believed to be the largest civil chlorine release recorded. An explosion occurred which is thought to have dislodged a chlorine tank and caused it to fall on a protruding object and to puncture. Approximately 90 te of chlorine escaped, but there were no deaths.

Another smaller but more lethal chlorine release occurred from a derailed rail tank car at Youngstown, Florida, on 26 February 1978 (Case History A94). Seven people were killed.

Another large release of chlorine occurred on 1 August 1981 when a train derailment near Montana, Mexico (Case History A100), resulted in the rupture of two 55 te chlorine tankers. The gas spread through a narrow valley and caused the deaths of 17 people.

A derailment of a chlorine train at La Barre, Louisiana, on 31 January 1961 (Case History A29) gave rise to a release of chlorine. There was a house occupied by a family only 50 yd from the crashed chlorine rail tank car. A child taken out of doors died, but an infant who remained in the house survived. The incident is of interest, therefore, in relation to the protection provided by buildings.

There have also been a number of non-fatal chlorine releases. The chlorine accidents at Cornwall, Ontario, in 1962, at Philadelphia, Pennsylvania, in 1963, and at Los Angeles, California, in 1966, resulted in the gassing, but not the deaths, of quite large numbers of people.

Table 18.30 *Significant chlorine accidents (after Simmons, Erdmann and Naft, 1974) (Courtesy of the American Institute of Chemical Engineers)*

Date	*Location*	*Chlorine release* (ton)	*Fatalities*	*Comments*
Storage tanks				
1926 Dec. 13	St. Auban, France	25	19	Tank burst
1929 May 10	Syracuse, NY	25	1	Tank burst, H_2–Cl_2 explosion
1939 Dec. 24	Zarnesti, Roumania	25	*c.* 60	Tank burst
1947 Nov. 5	Rauma, Finland	30	19	Tank burst from overfilling
1952 Apr. 4	Wilsum, Germany	15	7	Tank failed (a converted old boiler)
Barges				
1960 Apr. 13	–		1	Loading hose ruptured
1961 Feb. 23	–	0		Wychem 112 sinking, no leak
1965 Sep. 12	Nr. Baton Rouge, LA	0		Sunk during Hurricane Betsy, no leak
1970 Jul. 28	–		1	Unloading pump break
1972 Mar. 19	Nr. Louisville, KY	0		Broke from tow and rested on dam, no leak
Rail tank cars				
1934 Feb. 28	Niagara Falls, NY	16		Anchor failure
1935 Mar. 13	Griffith, IN	30		Anchor failure
1947 Feb. 4	Chicago, IL	18		Release caused by heat from fire
1961 Jan. 31	La Barre, LA	30	1(114 'gassed')	Train wreck, tank punctured
1962 Nov. 30	Cornwall, Ont.	30	(89 gassed)	Anchor failure
1963 Apr. 28	Brandtsville, PA	9		Valves sheared off in wreck
1963 Aug. 9	Philadelphia, PA		(430+ gassed)	Loading line broken when tank was rammed
1967 Nov. 8	Newton, AL	55		Tank punctured in wreck
Truck tanks				
No significant accidents				
1-ton containers				
1928 Jul. 7	Asbokan, NY			Exploded, contamination with NCl_3
1928 Jul. 13	Asbokan, NY			Exploded, contamination with NCl_3
1969 May 8	Cleveland, OH		2	–
Pipelines				
1936 Nov. 12	Johnsonburg, PA	3	1	Transfer line broken by housing
1949 Sep. 1	Freeport, TX	5		8 in. line burned in attempted welding
1964 Jul. 12	Mobile, AL		1	–
Cylinders				
1920	Niagara Falls, NY		3	150 lb cylinder burst
1925	De Noya, OK		1	Suckback of gasoline
1947 Jan. 13	Natrium, VA		2	150 lb cylinder exploded
1954 Jun. 25	Montreal, Quebec		1	Cylinder fell into hold of steamship

Three chlorine releases from pipelines at Dominguez, California, in 1966 and 1967, are recorded by Solomon, Rubin and Okrent (1976). In each instance the amount of chlorine released was 500 lb. In one case the pipe was accidentally cut by a welder, in the other two it was accidentally dug up.

The release of 100 lb of chlorine from a cylinder into the subway system of Brooklyn, New York, in 1944, which is described by Chasis *et al.* (1947), resulted in the gassing, but not the deaths, of 208 people. It illustrates the effect of an escape in a confined space.

Another chemical that presents a serious toxic release hazard is ammonia. A list of ammonia accidents has been given by V.C. Marshall (1977b), as shown in Table 18.31.

A road tanker crash that released ammonia at Lieven, France, in 1968 resulted in five deaths (Medard, 1970), and an ammonia release from a crashed rail tank car at Crete, Nebraska, in 1969 killed eight people.

There was a release of 160 ton of ammonia from a storage tank at Blair, Nebraska, in 1970 (Case History A47), but there were no casualties.

The ammonia accident at Potchefstroom, South Africa, on 13 July 1973 (Case History A65), in which 18 people were killed when an ammonia storage tank failed and released an estimated 39 ton, appears to be the worst accident involving ammonia for which details are available.

In 1976, a road tanker crashed on the Southwest Freeway, Houston, Texas (Case History A84), and released 19 te of ammonia which killed six people.

Table 18.31 *Some data on the relation between size of toxic release and number of fatalities (after V.C. Marshall, 1977b) (Courtesy of the Institution of Chemical Engineers)*

Date	*Location*	*Equipment*	*Material released* (t)	*Fatalities*	*Mortality index* (deaths/t)
Chlorine					
1947 Nov. 5	Rauma, Finland		30	19	0.63
1939 Dec. 24	Zarnesti, Roumania		25	*c.*60	*c.*2.40
1926 Dec. 13	St. Auban, France		25	40[a]	1.60
1929 May 10	Syracuse, NY		22.5	1	0.004
1952 Apr. 4	Wilsum, Germany	Storage tank	15	7	0.46
1917	Wyandotte, MI		13.6	1	0.073
1956 Mar. 10	Lake Charles, LA		2.7	0	0
1967 Nov. 8[b]	Newton, AL		50[c]	0	0
1935 Mar. 13	Griffith, IN		27.5[c]	0	0
1961 Jan. 31	La Barre, LA		27.5[c]	1	0.036
1962 Nov. 30	Cornwall, Ont.		27.5[c]	0	0
1947 Feb. 4	Chicago, IL		16.3[c]	0	0
1973 Mar. 5	Loos, BC		15.5	0	0
1934 Feb. 28	Niagara Falls, NY		14.5[c]	0	0
1963 Apr. 28	Brandtsville, PA	Rail tank car	8[c]	0	0
1940 Jan. 26	Mjodalen, Norway		8	3	0.375
1914?	Chrome, NJ		7	0	0
1966 Jun. 14	La Spezia, Italy		7	0	0
1957 Oct. 19	Runcorn, UK		2–3	0	0
1928 Jul. 7, 13	Asbokan, NY		2	0	0
1950 Jul. 20	Billingham, UK		0.5	0	0
1969 May 8[b]	Cleveland, OH	Two 1-ton containers	1	1	1
1961 Feb. 23	Billingham, UK		12	0	0
1949 Sep. 1[b]	Freeport, TX		5	0	0
1936 Nov. 12[b]	Johnsonburg, PA	Pipeline	3	1	0.33
1970 Oct. 19	Javle, Sweden		2	0	0
1920	Niagara Falls, NY		0.066	3	45
1947 Jan. 13	Natrium, WV		0.066	2	30
1925	De Noya, OK	Cylinder	0.066	2	30
1954 Jun. 25	Montreal, Canada		0.066	1	15
Total of 30 incidents			271	142	
Mean of 30 incidents			9.03	4.73	0.52
Ammonia					
1970 Nov. 16	Blair, NE		145	0?	0?
1973 Jul. 13	Potchefstroom, SA	Storage tank	38	18	0.71
1969 Feb. 18	Crete, NE		64	6	0.094
1968 Aug. 21	Lievin, France	Rail tank car	15?	5	0.33?
1971 Jun. 5	Floral, AR		570	0	0
1973 Dec. 6	Kansas City,[d] KS	Pipeline	210	0	0
Total of 6 incidents			1042	29	
Mean of 6 incidents			173	4.83	0.027
Phosgene					
1928 May 20	Hamburg, Germany	Storage tank	10?	10	1.0?

[a] This value differs from that given by Simmons, Erdmann and Naft (1974).
[b] The date quoted in the original reference has been corrected (F.P.L.).
[c] This value is about 10% less than that given by Simmons, Erdmann and Naft (1974).
[d] This incident is referred to elsewhere in this book as McPherson, Kansas.

An ammonia release at Cartegena, Columbia, in 1977, is reported to have caused a death toll which is now set at 21 (MHAP, 1988). This is the largest number of deaths from an industrial ammonia accident.

On 20 March 1989 a refrigerated atmospheric ammonia storage tank containing some 7,000 te of liquid ammonia failed at Jonova, Lithuania (Case History 128). The ammonia ignited and an ammonium nitrate storage caught fire. It is estimated that some 1400 te of ammonia evaporated and that a further 700 te of ammonia and nitrous fumes participated in the toxic fire plume. The plume is described as spreading some 35 km and affecting an area of some 400 km^2. Seven people were killed.

There have also been a number of non-fatal releases of ammonia. A release of about 600 ton of ammonia occurred from a pipeline in Floral, Arkansas, in 1971 (Chementator, 1971 Jul. 26, 55). There was a fish kill, but no injuries. There was an escape of some 230 ton of ammonia on a pipeline at McPherson, Kansas (Case History A64), in 1973.

Further incidents involving ammonia release are related by Slot (1938), Caplin (1941) and Trotter (1983). Other accounts are referenced by Payne, Delic and Turner (1990).

In general, the recorded releases of ammonia usually involve larger quantities than those of chlorine, but are not more lethal. As Table 18.31 shows, there are a number of recorded ammonia releases in excess of 100 te.

The toxicity of ammonia is appreciably less than that of chlorine and, although it behaves on release as a heavy gas, it has a molecular weight (MW 17), less than that of air, which eventually aids dispersion.

Some other major toxic release accidents include those tabulated below:

Date	*Location*	*Chemical*	*Deaths/injuries*
1928	Hamburg, Germany	Phosgene	10 d
1930	Lüttich, Belgium	Hydrogen fluoride, sulfur dioxide	63 d
1950	Poza Rica, Mexico	Hydrogen sulfide	22 d, 320 i
1978	Chicago, IL	Hydrogen sulfide	8 d, 29 i

The phosgene release in Hamburg in 1928 (Case History A6) was due to a pressure vessel failure. It caused the gassing of some 300 people and resulted in 10 deaths.

A gassing incident involving hydrogen sulfide at Poza Rica, Mexico, in 1950, is described by McCabe and Clayton (1952). There are numerous accounts of lesser hydrogen sulfide gassing incidents, including those by Haldane (1896), Poda (1966) and Burnett *et al.* (1977). Other accounts are referenced by R.M. Turner and Fairhurst (1990).

There have also been several fire incidents, described by the MHAP (1993), in which significant quantities of phosgene are said to have been generated. More generally, large fires are a source of toxic products. A fire in a fertilizer warehouse at Nantes in 1987 led to the evacuation of some 40,000 people (Pietersen, 1988b). The decision to evacuate was made on the basis of one measurement, taken inside a car, and may well have been unnecessary.

A even larger evacuation was that at Mississauga, Toronto, in 1979 (Case History 97), when a holed chlorine rail tank car led to an extended emergency in which some 215,000 people were evacuated. This incident is also described in Chapter 24.

Another major evacuation occurred at Glendora, Mississippi, in 1969 (Case History A43), where a ruptured rail tank car of VCM caused some 30,000 people to be evacuated.

In some cases the material release is flammable as well as toxic. The ignition of the ammonia release at Jonova has already been described. Another case where a toxic release was ignited occurred at Nuremburg in 1980, when vinyl chloride issuing from a large hole in a derailed rail tank car found a source of ignition within seconds (Ernst, 1983).

Another type of toxic incident is the release of an ultra-toxic substance, such as TCDD. Case histories involving TCDD are given in Appendix 3 on Seveso in 1976.

18.28 Toxic Release Risk

18.28.1 Historical experience

Only a small proportion of the major accidents listed in the loss prevention literature are toxic releases. Many toxic releases disperse rapidly, causing relatively few casualties.

In general, for all three major hazards – fire, explosion and toxic release – the large number of fatalities given by some theoretical estimates, assuming the most unfavourable and improbable circumstances and using models which may prove to be based on pessimistic assumptions, has been in contrast with the small number of fatalities shown by the historical record. Until 1984, this discrepancy was particularly striking for toxic releases. However, in that year the disaster at Bhopal demonstrated that, very rarely, an event occurs which gives some credence to the more pessimistic estimates.

Of the incidents described in Section 18.27, the worst accidents for particular major industrial toxic gases have been:

		No. of deaths
Bhopal	Methyl isocyanate	*c.*4000
Lüttich	Hydrogen fluoride, sulfur dioxide	63
Zarnesti	Chlorine	60
Poza Rica	Hydrogen sulfide	22
Cartegena	Ammonia	21
Hamburg	Phosgene	10

Prior to Bhopal, the most serious toxic incidents involved mainly chlorine and or/ammonia.

Analysis of chlorine incidents has indicated that, with one exception, fatalities occur within about 400 m of the release, and generally within 250 m (MHAP, 1987).

In the United Kingdom there have been very few fatal accidents in chlorine factories and, as far as is known, none to the public, if such accidents as those arising from misuse of chemicals such as sodium hypochlorite are excluded.

The relation between the size of toxic release and the number of people killed has been investigated by V.C. Marshall (1977b), who has developed a mortality index (deaths/te) for toxic releases similar to that for explosions described in Chapter 17.

The list of toxic accidents given by V.C. Marshall (1977b), which is similar to but not identical with that given by Simmons, Erdmann and Naft (1974) and which also includes ammonia and phosgene accidents, has been given in Table 18.31. The table shows the number of fatalities and the mortality index.

In addition to the overall mortality index for chlorine, which is given in Table 18.31 as 0.52, the mortality index for chlorine storage tanks is also of interest. The value obtained for this from the incidents listed in Table 18.31 is 0.96.

Some values of the mortality index from the table are plotted in Figure 18.10. This figure may be compared with Figure 17.133, which gives a mortality index for explosions;

the broken line in Figure 18.10 is that given for explosions in Figure 17.133.

Of these industrial releases those from cylinders tend to have a high mortality index. The amount of gas released is generally small, but the release probably often occurs in a building. A few deaths from such a release are sufficient to give a high value of the index.

It should be emphasized, however, that whereas in the case of explosions there is a well-established relationship between the quantity of material and the explosion overpressure from which lethal effects can be estimated, there is at present no such relation for toxic releases.

18.28.2 Hazard assessment

The alternative approach to the determination of the risk from a large toxic release is the use of hazard assessment involving assumed scenarios of release and with appropriate estimates of emission, dispersion and toxic effects. The hazard assessment may be generic or may address a particular situation, whether at a fixed site or in transport.

The largest number of hazard assessment studies has been done for chlorine. A large chlorine release has generally been regarded as one of the most serious hazards. The following account deals principally with chlorine, but some mention is made of other toxic substances, notably the other main toxic gas, ammonia.

Some early generic studies were those by Howerton (n.d., 1969) and Simmons, Erdmann and Naft (1974) on chlorine; Eisenberg, Lynch and Breeding (1975) on the vulnerability model on chlorine and ammonia; and Solomon, Rubin and Okrent (1976) on a variety of chemicals.

These studies had a number of features that would now be regarded as inappropriate. They generally made very pessimistic assumptions, as the authors emphasize. Two points may be noted in particular. Some of the release rates assumed are extraordinarily high, and in most cases no credit is given for mitigation. In addition, the studies used passive gas dispersion models.

Studies were also made for specific situations. These include a study of chlorine releases from a factory by Dicken (1974, 1975) and Sellers (1976) and a study of the modes of transport for chlorine by Westbrook (1974).

The next stage in hazard assessment of toxic releases is exemplified by the two Canvey Reports (HSE, 1978b, 1981a) and the Rijnmond Report (Rijnmond Public Authority, 1982). The Canvey Reports gave hazard assessments for ammonia and hydrogen fluoride, and the Rijnmond Report for acrylonitrile, ammonia, chlorine, and hydrogen sulfide, from a hydrodesulfurizer. These reports are described in Appendices 7 and 8, respectively. These studies are characterized by a more detailed treatment of the emission scenarios and flows, the use of heavy gas dispersion models and, to some extent, an allowance for

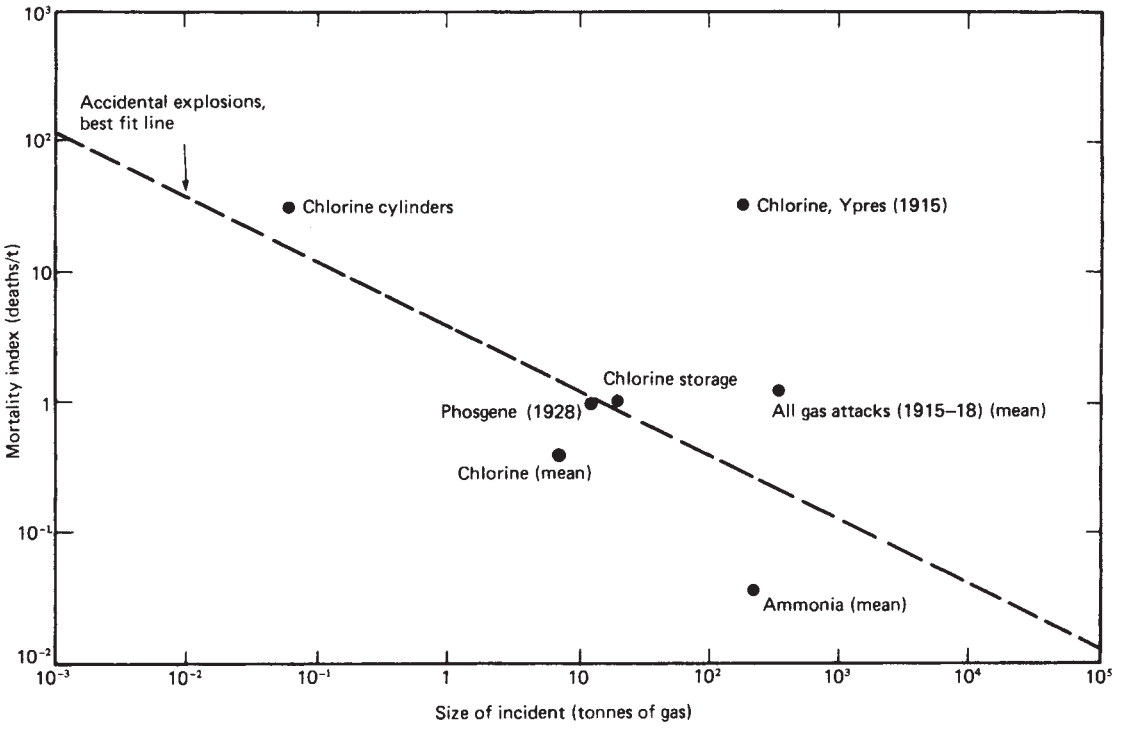

Figure 18.10 *Mortality index for Releases (after V.C. Marshall, 1977b) (Courtesy of the Institution of Chemical Engineers)*

mitigating factors. Subsequent work on the hazard assessment of toxic releases has generally retained the basic approach, but has significantly refined the methodology.

A further stage is the hazard assessment of toxic gases is the work described in the ACDS Transport Hazards Report (1991), which covers chlorine and ammonia and which is described in Chapter 23 and Appendix 17.

Accounts are given in Sections 18.29 and 18.30 of some of the hazard assessments just mentioned and in Section 18.31 of developments in the methodology. These should be taken in conjunction with the accounts in the Canvey Reports, the Rijnmond Report and the ACDS Transport Hazards Report.

18.29 Chlorine Hazard Assessment

18.29.1 Fixed installations

A major study of the assessment and control of the hazard of chlorine release from a large chlorine factory in the United Kingdom has been described by Dicken (1974, 1975), Sellers (1976) and Hewitt (1976). The chlorine factory concerned is shown in outline in Figure 18.11. It includes cell-rooms, compression plant, liquefaction plant, gas absorption plant and distribution to user plants. The study falls into three parts: the development of risk criteria, the assessment of the hazards and the recommendations for improvements.

Four categories of hazard were defined. Category 0 involves no nuisance to the public, whereas Categories I-III do involve such a risk. Category I is the least serious and constitutes a nuisance to the public, but no more. Category II is a more severe release that could cause distress to people and damage to vegetation, and could give rise to claims for compensation. Category III is a major emission which, in addition, could result in injury or loss of life. The maximum frequencies suggested for events in Categories I and II were once in 1 and 10 years, respectively. A Category III release was considered acceptable once in 100 years, which was estimated to be roughly equivalent to a risk to the public of 10^{-7}/year per person.

Information on the toxicity of chlorine was studied and the relations between toxicity and exposure shown in Figure 18.12 were produced. The hazard categories were then defined more closely in terms of the toxic effects and the relations shown in Figure 18.13 were derived.

In assessing the effects of toxic substances, consideration needs to be given to members of the public who may be more susceptible than the average adult worker. Some relevant data quoted by Hewitt (1976) in this study were given in Table 9.22.

The historical data on chlorine releases throughout the works were also collected. These are shown in Table 18.32. Using these data as a guide, the works was divided into some 23 units and each unit was allocated a proportion of the target level of risk for the whole works. This allocation is shown in Table 18.33. Three two-man teams were then set up to study the 23 units, using in particular the hazard and operability study method.

With the situations leading to release thus identified, quantitative assessments were made of the frequency, size and effect of such releases. Estimates of frequency were based on reliability calculations and data, those on size on emission calculations, and those on effects on dispersion calculations, and toxicity data. These methods have been described in Chapters 7–9 and 15.

Extensive gas dispersion calculations were carried out using a specially developed computer program. The

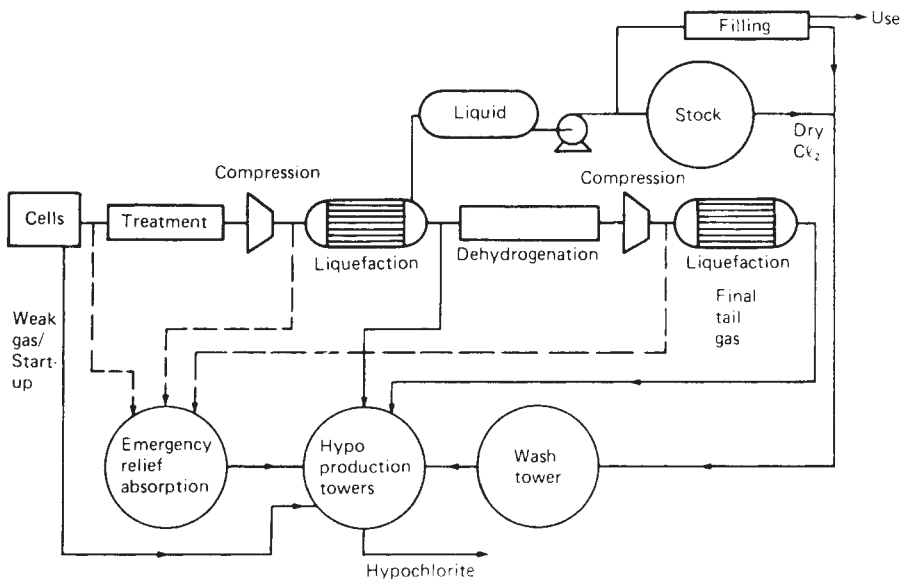

Figure 18.11 *Chlorine production, liquefaction and distribution system (Dicken, 1974) (Courtesy of the Electrochemical Society)*

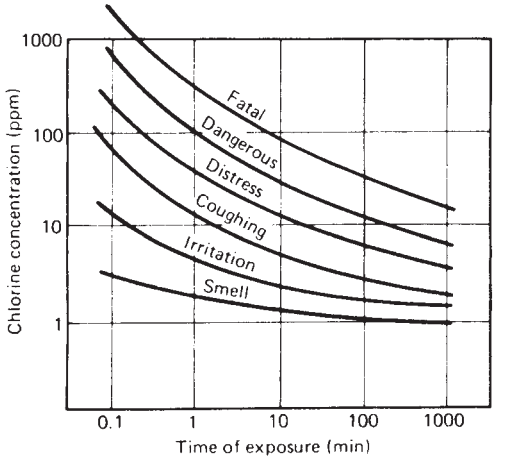

Figure 18.12 *Effects of exposure to different concentrations of chlorine vapour (Dicken, 1974) (Courtesy of the Electrochemical Society)*

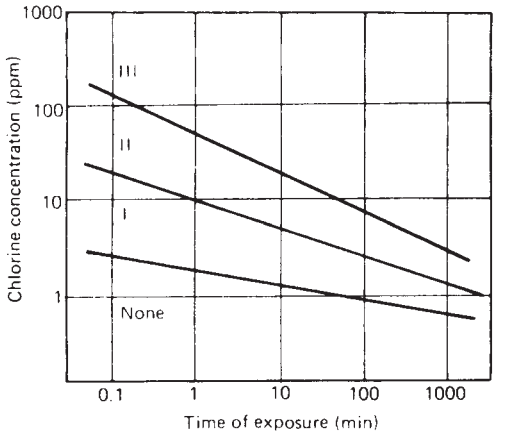

Figure 18.13 *Categories of chlorine release (Dicken, 1974) (Courtesy of the Electrochemical Society)*

dispersion equation quoted is that formulated by Pasquill (1961) and used by Bryant (1964 UKAEA AHSB(RP) R42):

$$C = \frac{168QF}{\theta hdu} \qquad [18.29.1]$$

with

$$F = \exp(-2.303H^2/h^2) \qquad [18.29.2]$$

where C is the ground level concentration on the axis of the plume (m^3/m^3), d is the downwind distance (m), F is the stack correction factor, h is the vertical spread of the plume at distance d (m), H is the effective height of the stack (m), Q is the gas release rate (m^3/s), u is the wind speed (m/s); and θ is the lateral spread of the plume (°). The lateral spread θ and the vertical spread h are both functions of the atmospheric stability. Equation 18.29.1 is discussed in more detail in Chapter 15.

It is also stated that both instantaneous and continuous releases were studied. For a given emission point the investigation covered 18 wind directions, 6 wind speeds and 6 stability categories, making 648 permutations. Other factors taken into account were plume rise from the stack (where applicable), downwash from neighbouring buildings and multipoint sources such as ventilation ducts on the cellroom roof.

For a given emission situation and one permutation of weather conditions the maximum concentration at or outside the works boundary was computed and converted to a hazard of Category 0, I, II or III. From all the permutations the probabilities of hazards in the different categories were determined. Some examples of the results obtained are given in Table 18.34.

The validity of the assessment procedure was checked by comparison with historical data. Normally the ratio of the predicted to the observed frequency of release was in the range 1–2.

The study made recommendations for improvements both of hardware and of software, although not all proved practical. Some £1 m capital was spent, of which about a third was on the emergency absorption plant.

Hardware changes included the installation of additional equipment, such as stand-by power supplies or duplicate pumps, and of extra instrumentation. The availability of the equipment has sometimes been poor. Changes in software covered areas such as operating instructions and inspection and test methods. It is claimed that the work has resulted in a 40% reduction in the number of chlorine

Table 18.32 *Chlorine releases at a major works in the UK – period 1966–70 (Dicken, 1974)*

Source	(%)	*Prime cause*	(%)
Chlorine cellroom	15	Instrument/control failure	17
Dechlorination of brine	13	Human error	12
Hypochlorite tower	12	Machine failure	9
Tail gas treatment plant	11	Leaks	8
Drains	10	Maintenance/start-up	6
Chlorinated organic plants	7	Service failure	5
Chlorine filling/loading	6	Miscellaneous	18
Cell gas treatment plant	6	Unknown/not recorded	25
Others	20		

Source: Originally presented at the 145th Spring Meeting of the Electrochemical Society in San Francisco, CA, and are reproduced by permission of the author and of the Society.

releases recorded in the areas covered and in an increase in plant availability.

Similar investigations have been carried out for other gases such as bromine, hydrogen chloride, hydrogen fluoride and phosgene. Another study in this area is the assessment of the hazard from acrylonitrile storage tanks described by Siccama (1973).

18.29.2 Transport

Howerton (n.d., 1969), in a generic study of the hazards of chlorine handling and transport, gives estimates of the areas affected by different chlorine releases based on calculations of (1) liquid and vapour discharges from containers, (2) flash-off and evaporation from liquid chlorine, and (3) dispersion from instantaneous and continuous point sources at ground level.

He considers both instantaneous and continuous releases and uses the Pasquill–Gifford equations. The equation used for a continuous point source is Equation 15.16.41 that gives the concentration profiles. The values of the dispersion coefficients used are those given by Singer and Smith (1966).

The scenarios considered are an instantaneous release of 25,000 lb and continuous releases of 1, 5 and 10 lb/s of chlorine in a 5 mile/h wind in both moderately stable and moderately unstable conditions. The dangerous chlorine concentration is taken as 35 ppm. Graphs are given showing the lines of constant chlorine concentration, or chlorine isopleths, for these eight cases. For the instantaneous release the cloud is hemispherical in shape and travels with the speed of the wind. The cloud first expands in size and then contracts. But, whereas under stable conditions the cloud is continuing to expand even at a distance of 10 miles, under unstable conditions it starts to contract again after some 1.5 miles, as shown in Figures 18.14(a) and 18.14(b), respectively. In both cases the envelope of the area swept by the cloud is cigar shaped, but for stable conditions Figure 18.14(a) shows only the expanding part of the envelope, while for unstable conditions Figure 18.14(b) shows the envelope terminating within about 2.5 miles. The time of passage of the cloud in stable conditions is quite short, about 5–15 min. For the continuous release of 10 lb/s the isopleth under stable conditions is approximately cigar shaped and reaches about 3 miles as shown in Figure 18.14(c), while under unstable conditions it is ovoidal and reaches only about 1/8 mile as shown in Figure 18.14(d).

The conditions under which the highest gas concentration can occur at large distances are those of an instantaneous release under stable weather conditions at low (but not zero) wind speeds. In this sense, this is the worst scenario. In such a case, however, the cloud travels slowly and the warning time is long.

Simmons, Erdmann and Naft (1974) in another generic study of the hazards of chlorine transport have estimated the area affected by a chlorine release. They consider an instantaneous release and use the Pasquill–Gifford equations. The equation used is Equation 15.16.66a, which gives the dosage profiles. The values of the dispersion coefficient σ_y used are those given by D.B. Turner (1970). They are fitted to the following equation:

$$\sigma_y = kx^n \qquad [18.29.3]$$

with

	Pasquill category
$k = 0.20$	C
$k = 0.13$	D
$k = 0.078$	E, F
$n = 0.91$	

Table 18.33 *Allocation of proportion of works chlorine releases between works units (Sellers, 1976) (Courtesy of the Institution of Chemical Engineers)*

	Percentage of works acceptable level
Major cellrooms	20
Emergency absorption plant	10
Compression and liquefaction plant	10
Small cellrooms	10
Liquid storage and pipelines	7
Container filling	4
Drum, cylinder and hypochlorite users	1
User plants (6 at 5% each)	30

Table 18.34 *Predicted chlorine releases and their consequences (Sellers, 1976) (Courtesy of the American Institute of Chemical Engineers)*

Incident	*Frequency* (events/year)	*Release rate* (m^3/h)	*Release duration* (min)	*Severity of event*					
				Percentage in class (%)			*Frequency of class* (events/year)		
				I	*II*	*III*	*I*	*II*	*III*
Cell offtake shut	0.7	70	5	30	2	0	0.21	0.014	0
Cell explosion	1.5	2	5	11	0	0	0.17	0	0
Control fails but relief operates	0.95	60	3	29	0	0	0.28	0	0
Control fails and relief fails	0.011	840	2	16	39	13	0.002	0.004	0.001
Total							0.7	0.02	0.001

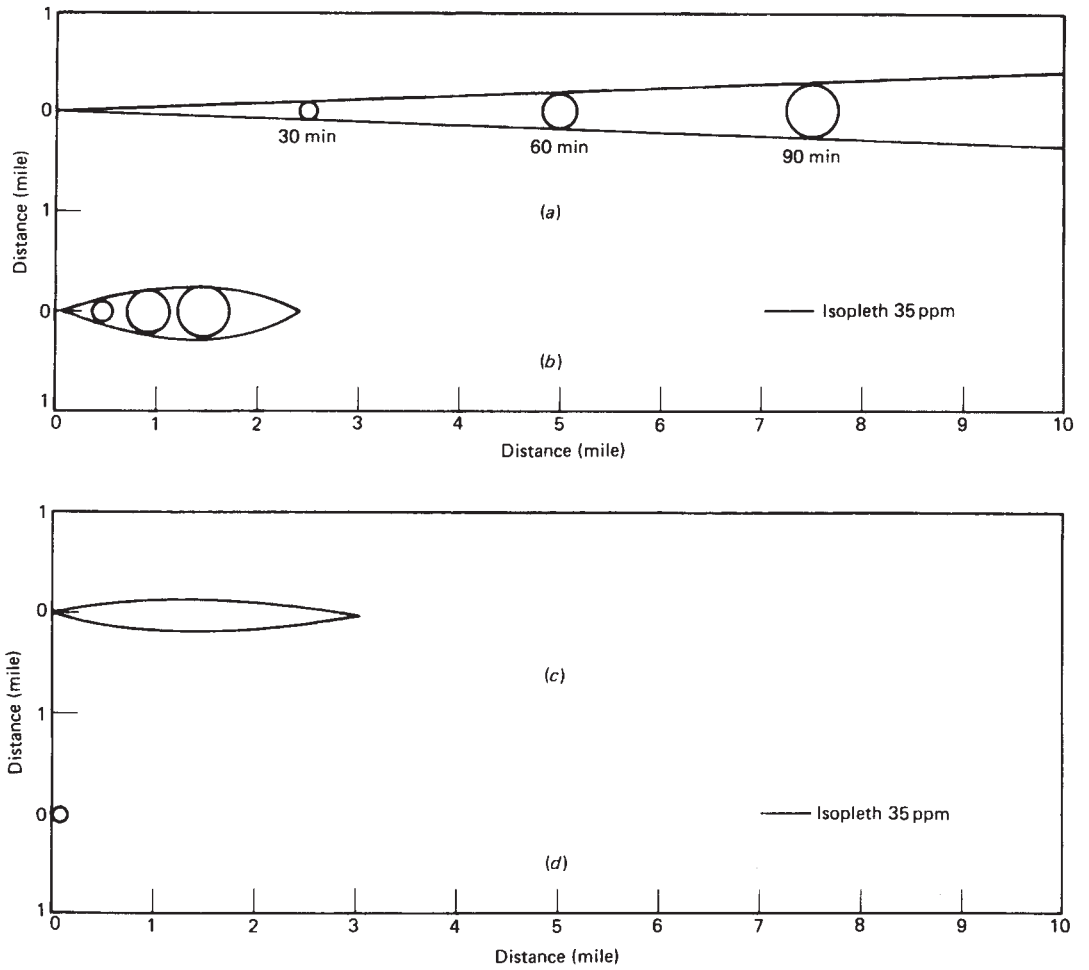

Figure 18.14 *Concentration profiles for chlorine release from a point source at ground level (after Howerton, 1969): (a) instantaneous release of 25,000 lb in stable conditions; (b) instantaneous release of 25,000 lb in unstable conditions; (c) continuous release of 10 lb/s in stable conditions; (d) continuous release of 10 lb/s in unstable conditions (Courtesy of American Institute of Chemical Engineers)*

where x is the distance in the downwind direction (m), σ_y is the dispersion coefficient in the crosswind direction (m), k is a constant, and n an index. It is assumed that the dispersion coefficient σ_z is

$$\sigma_z = 0.2\sigma_y \qquad [18.29.4]$$

where σ_z is the dispersion coefficient in the vertical direction (m).

The relation between dosage and fatalities is taken to be as follows. For chlorine vapour in air

$$1 \text{ ppm} = 2.9 \text{ mg/m}^3 = 2.9 \times 10^{-6} \text{ kg/m}^3$$

The lethal dosage LCt_{50} is taken as

$$LCt_{50} = 1000 \text{ ppm min} = 0.17 \text{ kg s/m}^3$$

The scenario considered is the initial flash vaporization of 15.7 ton of chlorine from a spillage of 90 ton of chlorine, this being the capacity of a standard chlorine rail tank car. The area of lethal dosage LCt_{50} is a function of wind speed and stability conditions and may be represented by the equation

$$A = k'u^{-n'} \qquad [18.29.5]$$

where A is the area of lethal dosage (km^2), u is the wind speed (m/s), k' is a constant, and n' is an index. For the case considered:

	Pasquill category
$k' = 1.72$	A–C
$k' = 2.83$	D
$k' = 4.92$	E, F
$n = 1.06$	

The areas of lethal dosage for this case are shown in Figure 18.15.

The conditions under which the area of lethal dosage from an instantaneous spillage is greatest are again those of release under stable weather conditions at low wind speeds. In this sense, this is again the worst case.

The authors compare their method of calculating the area of lethal dose with that of Howerton. For the 25,000 lb instantaneous release considered by Howerton the area of 4 km^2 calculated by him is greater by a factor of almost 4 than that obtained by their method. This is attributed to the use of different values of the dispersion coefficient.

The estimate of the area of lethal dosage is then used by Simmons, Erdmann and Naft in conjunction with data on the frequency of particular meteorological conditions and on population densities to calculate the potential fatalities for transport accidents, as described below. These are presented as histogram data for a range of accidents of increasing severity. The most severe accident calculated involved 5000–20,000 deaths with a frequency of 2.6×10^{-4}/year.

Eisenberg, Lynch and Breeding (1975) in the vulnerability model work already described have studied among other things the area affected by, and the lethality of, chlorine and ammonia releases.

They consider any instantaneous release from a marine spillage and use the Pasquill–Gifford equations. The equation used for an instantaneous release is Equation 15.16.40.

For chlorine the scenarios considered are instantaneous releases of 0.9, 15 and 1090 te of chlorine. The latter corresponds to the load of a large barge. The relation between dosage and fatalities is that given in the probit Equation 18.15.2. The populations at risk are defined in terms of the cell model already described.

Some results obtained are given in Table 18.35. These results indicate that the conditions under which the calculated lethality of the release is highest depend on the size of the release. For the small release of 0.9 te the lethality is higher under neutral conditions. With unstable conditions the gas is more rapidly diluted below its lethal concentration. For the large release of 1090 te the lethality is higher under unstable conditions. With unstable conditions the gas is more rapidly dispersed, but remains above its lethal concentration. The authors draw attention to the need to use short time steps in the calculation of $\sum C_i^n T_i$ in Equation 18.15.2 if accurate results are to be obtained.

For ammonia the scenarios considered are instantaneous releases of 8.2, 251 and 16,340 te. The relation between dosage and fatalities is that given by the probit Equation 18.15.3.

Some results obtained are as follows:

Ammonia spillage (t)	*Time of travel* (min)	*Distance travelled* (km)	*Fatalities*
8.2	Any	Any	0
251	10	2.4	921
	30	7.2	8,033
16340	10	2.4	2,177
	30	7.2	18,151

The wind speed was 4 m/s. Toxic injuries were not assessed.

Major assessments of the hazard of chlorine transport have been described by Simmons, Erdmann and Naft (1974) and Westbrook (1974). Simmons, Erdmann and Naft have reviewed the methods used for the transport of chlorine in the United States, the historical experience of accidents involving chlorine and the hazards arising from its transport. They found that chlorine ranked sixth among chemicals in terms of the quantity produced. Some 4.4×10^6 ton of liquid chlorine were transported in 1972 and this amount was expected to rise to about 10×10^6 ton by 1990. Transport of chlorine is important, because accidents to carriers are relatively frequent, population densities along the main transport routes are relatively high, and the substance is very toxic.

The sizes of chlorine containers are basically as follows. Storage is typically in large pressure vessels or refrigerated atmospheric tanks containing 1000 or 2000 ton each.

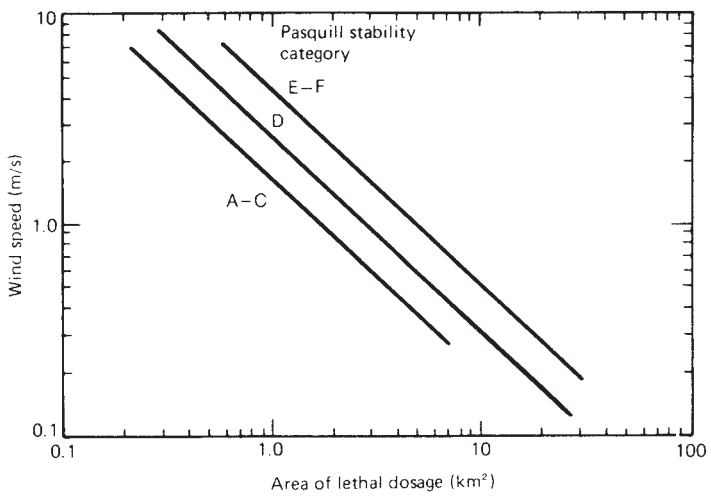

Figure 18.15 *Areas of lethal dose for initial flash vaporization from a 90 ton chlorine spill (Simmons, Erdmann and Naft, 1974) Courtesy of the American Institute of Chemical Engineers)*

Table 18.35 *Effects of marine spillages of chlorine (after Eisenberg, Lynch and Breeding, 1975)*

Chlorine spillage (t)	*Stability condition*	*Wind speed* (m/s)	*Time of travel* (min)	*Distance travelled* (min)	*Distance travelled* (km)	*Fatalities*	*Injuries*
0.9	Neutral		4	10	2.4	277	645
	Unstable	5	8	2.4	0	0	
	Neutral		4	30	7.2	277	5748
	Unstable	5	24	7.2	0	2	
15	Neutral	4	4	10	2.4	921	0
	Unstable	4	10	2.4	921	0	
	Unstable	5	8	2.4	0	921	
	Neutral		4	30	7.2	9,995	865
	Unstable	4	30	7.2	1,020	6,334	
	Unstable	5	24	7.2	340	7,425	
1090	Neutral	4	4	10	2.4	921	0
	Unstable	5	8	2.4	1,823	5,734	
	Neutral		4	30	7.2	13,628	937
	Unstable	5	24	7.2	18,152	4,946	

Barges usually carry four pressure vessels each containing 275 ton, making 1,100 ton total capacity. Rail tank cars are pressure vessels ranging in size from 16 to 90 ton, but only the latter size is now made. Road tankers are also pressure vessels and normally have a capacity of 16 ton. Cylinder sizes are usually 1 ton, 150 lb or smaller.

All containers for chlorine transport are pressure vessels made in steel and equipped with safety devices such as pressure relief valves and excess flow valves, and are regularly inspected and pressure tested. Details of chlorine containers are given in the publications of the Chlorine Institute.

Chlorine is also transported by pipelines. Such pipelines range from 1 to 6 in. in diameter. The longest run quoted is 10,000 ft of a 4 in line.

The authors' tabulation of chlorine accidents has already been given in Table 18.30. Storage of chlorine had not resulted in a single accident in the United States in the 40 years up to 1974. There have been several accidents in small storages in Europe, but it is possible that these have been due to the presence of water and the resultant corrosion; this is avoided in good modern practice.

Barge accidents are few, possibly because the barge structure forms a means of protection for the chlorine tanks, in contrast to the situation on petroleum barges, where the barge shell is also the containing wall.

Rail tank car accidents have been more frequent. One major cause of these, the cracking of the tank at the anchor, which is the attachment of the tank body to the frame, has been largely eliminated by replacing forged anchors with welded ones, but accidents still occur, mainly by derailments and collisions. Department of Transportation (DOT) statistics indicate that there are approximately five rail tank car accidents per year that result in the release of chlorine, but only a small proportion of these involves a multiton release.

Road tanker transport is less significant and gives rise to fewer accidents.

Accidents with containers of 1 ton or less are important. As Figure 18.10 shows, some of the worst accidents have resulted from releases from cylinders and other small containers. This is probably because the releases took place in buildings and other confined spaces. It is considered by the authors that the dominant hazard is transport of chlorine by rail tank car. Some chlorine transport accidents are described in Case Histories A94, B66 and B67.

It was estimated by the Chlorine Institute that the proportions of chlorine distributed by the different modes of transport in the years 1965 and 1966 were: rail, 70% pipeline, 20%; and barge, 7%. Thus, assuming the same division, some 3.1×10^6 ton of chlorine were transported by rail in 1972 and this figure was expected to grow to about 7.2×10^6 ton by 1990. It is clear from these data that rail transport is the dominant mode of distribution.

The problem principally considered by Simmons, Erdmann and Naft, therefore, is incidents involving rail tank cars carrying 90 ton of chlorine. Their treatment consists of the determination of (1) the frequency of accidents involving chlorine spillage and (2) the number of fatalities resulting from spillage.

Statistics kept by the Railroad Administration of the DOT and by the Chlorine Institute showed that there are some 7,000 chlorine rail tank cars in service, that each tank car makes an average six trips a year and that the average length of journey is 250 miles. Since 1930 there have been seven accidents in which most or all of the contents of a tank car have been lost, although three of these were due to the failure of a forged tank anchor, a cause presumably now eliminated. On the other hand, the amount of traffic is increasing. On balance, therefore, the best estimate of accident frequency from these data is once in 10 years.

Other data are available on accidents to the same type of rail tank car as is used for chlorine in the transport of liquid ammonia and LPG. In a study covering 1966–70 the Association of American Railroads (AAR) found that for this type of rail tank car and for all cargoes, including chlorine, the accident rate was 2.3×10^{-5} per trip. Applied to the approximately 40,000 trips (7,000 tank cars×6 trips/year) made by chlorine tank cars these data would give an accident rate of once per year. The order of magnitude difference between this and the previous figure remains an unresolved discrepancy, but the authors suggest that it may be due to the way in which chlorine shipments are handled. They tentatively adopt the lower figure of 0.1 accidents per year.

The determination of the area of lethal dosage for spillage from a 90 ton tank car with flash vaporization of 17.5% of the tank contents, or 15.7 ton, was described above. This calculation is then combined by Simmons, Erdmann and

Naft with the above estimate of frequency and with data on the frequency of meteorological conditions to obtain estimates of potential casualties.

The population density assumption made is that a large spill is equally likely anywhere along the rail shipping route. This assumption is not conservative, since data for all rail accidents indicate a somewhat higher frequency in urban areas, the higher speeds in rural areas presumably being more than balanced by the higher density of traffic and switching activities in towns.

Estimates of potential fatalities were made for some 13 different weather conditions and 9 population densities, making 117 permutations in all. Accidents were then divided into 7 size ranges and a histogram was constructed. There were some 75 accidents involving 50 or more potential fatalities and the average number of fatalities was 13 per year. The histogram data are approximately as shown in Table 18.36.

From these histogram data the authors derive for the number N of fatalities the density function $f(N)$

$$f(N) = 0.15N^{-1.61} \qquad [18.29.6]$$

Simmons, Erdmann and Naft quote unpublished work by G.D. Bell (n.d.) on toxic releases that likewise gives an exponent of −1.6 for Equation 18.29.4, although in this latter case there were insufficient data to determine a realistic value of the constant factor.

The fatalities calculated in this work are described as 'potential', because no allowance is made for the effectiveness of any post-accident action to limit the effects. In fact, public warning and evacuation would probably greatly reduce the number of deaths.

It should be noted in particular that the conditions that give the highest number of fatalities are those in which the wind speed is low and the time available for evasive action is relatively long. In such cases, therefore, it is more probable that evacuation will be effective and that the ratio of actual to potential deaths will be relatively low.

For the 40-year period covered by the data given in Table 18.30, 204 people were gassed and one killed (excluding the small release in the Philadelphia incident) in railroad chlorine accidents. This compares with a value from the histogram data and equation 18.29.4 of 570 persons expected to be killed. The comparison indicates, on the one hand, support for Equation 18.29.6, in that the figures for people affected agree quite well, and on the other the effectiveness of evacuation, in that people fled and were gassed, but were not killed.

Table 18.36 *Accident scale–frequency relationship for chlorine rail transport accidents (after Simmons, Erdmann and Naft, 1974)*

Accident size (Potential deaths)	*Frequency* (events/year)
50–100	1.4×10^{-2}
100–250	1.0×10^{-2}
250–500	4.0×10^{-3}
500–1000	1.5×10^{-3}
1,000–2,500	1.2×10^{-3}
2,500–5,000	7.2×10^{-4}
5,000–20,000	2.6×10^{-4}

It is emphasized by the authors, however, that estimates of this kind involve many unknown factors, particularly in respect of accident frequency, and that the associated uncertainty is estimated to be a factor of 10.

The method described uses a mixture of historical data for accident frequency and estimation of the scale and frequency of the results of the accident.

As the authors point out, in some cases the historical data may be too sparse or non-existent, and then the accident frequency must also be estimated.

Simmons, Erdmann and Naft compare the risk to the whole US population from chlorine railroad accidents of 13 potential fatalities per year with other risks to which the public are exposed. These include estimated risks in the range of 10–100 fatalities per year from the failure of dams and in the same range for aircraft crashes (persons on the ground only).

Westbrook (1974) has made a comparative study of the relative hazards of the transport of chlorine by rail, road and pipeline by the principal UK producer, ICI.

Much of the work was concerned with the determination of accident data. Here difficulties were experienced because data tend to be reported in forms that are not readily convertible, for example ton-miles, vehicle-miles, train-miles. The approach adopted, therefore was to consider the transport of the entire amount shipped (200,000 ton/ year) by each mode in turn.

The investigations involved the determination of (1) the frequency of significant accidents, (2) the probability that a significant accident results in a spillage and (3) the number of fatalities resulting from a spillage.

The frequency of accidents was determined from accident records. The accidents referred to are 'significant' accidents. For rail, such an accident is the one that is judged to be potentially most dangerous, and includes all derailments and most collisions. Such accidents represent 32% of all reported train accidents. For road, a significant accident is one that results in injury or death and is what the police call a 'reportable' accident.

The relevant accident data for rail for 1971 were:

Capacity of rail tank car = 28 ton
Number of rail tank cars in chlorine train = 4
Number of rail journeys = 200,000/(4 × 28) = 1786
Distance travelled per train journey = 160 mile
Total distance travelled as train journeys = 1786 × 160 = 286,000 train-mile/year
Accident frequency for goods trains = 3.79×10^{-6} accidents/train-mile
Accident frequency for chlorine trains = 286,000 × 3.79×10^{-6} = 1.08 accidents/year

The data for road were:

Capacity of road tanker = 19 ton
Number of vehicle journeys = 200,000/19 = 10,526
Distance travelled per journey = 160 mile
Total distance travelled = 10,526 × 160 = 1.684×10^{6} vehicle-mile/year
Accident frequency for goods vehicles = 2.03×10^{-6} accidents/vehicle-mile
Accident frequency for chlorine vehicles = 1.684×10^{6} × 2.03×10^{-6} = 3.42 accidents/year

The above data refer to all journeys, but on average half the journeys made are with empty tanks. Thus the numbers of

significant accidents by the two modes of transport become:

Accident frequency for rail transport (loaded) = 0.54 accidents/year
Accident frequency for road transport (loaded) = 1.71 accidents/year

The probability that a significant accident results in a spillage was estimated from consideration of mechanical strength of the tank and of the force of impact. It was thought initially that at normal road tanker speeds of about 30 mile/h there might not be sufficient energy to puncture the pressure vessel. It was shown, however, by tests and calculations, that puncture can occur under expected accident conditions and that all road tanker accidents should be assumed to be potential spillage accidents.

The probability of puncture is a function of kinetic energy. It was found, however, that the average speeds of chlorine rail tank cars and road tankers are almost equal. Thus it was possible to consider damage levels in terms of mass only.

A rail tank car in a train is subject to wagon-to-wagon collisions. A relation was derived for the damage to a wagon in a train involved in a front-end collision with an immovable object. It is assumed that the damage is proportional to the mass of the wagon involved and that it is shared equally between the wagons. Then for the first wagon behind the engine the damage D is proportional to its own mass W for the first collision, which is with the engine, to $\frac{1}{2}W$ for the second collision, which is between the first and second wagons, to $\frac{1}{3}W$ for the third collision, which is between the first three wagons, and so on. Thus:

$$D_1 = W\left(1+\frac{1}{2}+\frac{1}{3}+\frac{1}{4}+\cdots\right) \qquad [18.29.7a]$$

where D_i is the damage to wagon i (mass units) and W is the mass of a single wagon (mass units). For the second wagon

$$D_2 = W\left(\frac{1}{2}+\frac{1}{3}+\frac{1}{4}+\cdots\right) \qquad [18.29.7b]$$

And for the nth wagon in a train of N wagons

$$D_n = \left(\frac{1}{n}+\frac{1}{n+1}+\frac{1}{n+2}+\frac{1}{n+3}=\cdots+\frac{1}{N}\right) \qquad [18.29.7c]$$

A group of m adjacent chlorine rail tank cars can occupy $N-m+1$ positions in the train. Then, assuming $W=1$, the average damage per train D_{tn} is

$$D_{\text{tn}} = \frac{1}{N-m+1}\sum_{n=1}^{N-m+1}(D_n + D_{n+1} + D_{n+2} + D_{n+3}) \qquad [18.29.8]$$

and the average damage per rail tank car D_{rc} is

$$D_{\text{rc}} = \frac{D_{\text{tn}}}{m} \qquad [18.29.9]$$

The probability that the rail tank car will be punctured is proportional to the average damage.

If the train has 25 wagons ($N=25$) and if there are four chlorine rail tank cars ($m=4$)

$D_1 = 3.82$ mass units
$D_2 = 2.82$ mass units
$D_3 = 2.32$ mass units
$D_{25} = 0.04$ mass units

and

$D_{\text{tn}} = 3.645$ mass units
$D_{\text{rc}} = 0.911$ mass units

A chlorine road tanker and a rail tank car have a mass of 30 and 40 ton, respectively. Thus on the assumption that the probability of puncture is proportional to the mass, the ratio r of the probability of puncture for a rail tank car to that for a road tanker is as follows:

$$\text{First position behind engine } r = \frac{3.82}{30}\times 40 = 5.1$$

$$\text{Average position in train } r = \frac{0.911}{30}\times 40$$
$$= 1.22 \text{ for one tank car}$$
$$= 4 \times 1.22$$
$$= 4.86 \text{ for train}$$

The analysis is relevant to the positioning of chlorine rail tank cars in the train in that it indicates that for a front-end collision the least desirable position is immediately behind the engine.

Collisions other than front-end collisions are also considered by Westbrook. A head-on collision of two trains is considered no worse since, although more energy is involved, it is distributed among more wagons. On the same argument, a back-end collision of two trains is less serious, since the energy involved is no greater than a front-end collision, but it is distributed among more wagons.

An absolute estimate of the probability of a spillage given a significant accident was made from the North American data for rail furnished by the Chlorine Institute and shown in Table 18.37. Over the period 1960–72 there were 67 accidents to chlorine trains, of which six resulted in spillage of chlorine. The probability of chlorine spillage in a significant rail accident in North America was therefore taken as $6/67 = 0.09$.

This use of North American data was necessary, because equivalent data for the United Kingdom were lacking. American conditions differ, however, in a number of respects:

	UK	*North America*
Rail tank car mass	40 ton	87 ton
Average No. of goods Wagons	25	100
Average No. of chlorine Rail tank cars	4	2
Average speed	15 mile/h	23 mile/h

The American pressure vessel is 0.753 in thick compared with the British 0.526 and requires 26% more energy to pierce it.

Table 18.37 *Accidents in bulk carriage of chlorine in the USA and Canada (Westbrook, 1974) (Courtesy of Elsevier Publishing Company)*

	Significant leakage – no accident	*Accident*	*Accident, leakage*	*Accident, fire*	*Accident, leakage, fire*	*Accident, leakage, death*
1961		3				1
1962	1	1			1	
1963		1			1	
1964		4	1			
1965		8				
1966		1	1	1		
1967		7		1		
1968		7				
1969		6				
1970		8		1		
1971	1	8		1		
1972		4	1			
Total	2	58	3	4	2	1

Since under American conditions there are two rail tank cars in a 100-wagon train

$D_{\text{tn}} = 1.967$ mass units

But the mass units in this case are greater than those for the British case by the following factor, which takes into account the different kinetic energy:

$$\frac{87}{40} \times \left(\frac{23}{15}\right)^2 \times \frac{1}{1.26} = 4.05$$

Then the probability of chlorine spillage in a significant rail accident in the United Kingdom is estimated as

Probability of chlorine spillage for rail transport
$= 0.09 \times \dfrac{3.645}{1.967} \times \dfrac{1}{4.05} = 0.041$ occasions/accident
Frequency of chlorine spillage for rail transport
$= 0.041 \times 0.54 = 0.022$ spillages/year

and the probability of chlorine spillage in a significant road accident in the United Kingdom is

Probability of chlorine spillage for road transport
$= 0.041/4.86 = 0.0084$ occasions/accident
Frequency of chlorine spillage for road transport
$= 0.0084 \times 1.71 = 0.0144$ spillages/year

The number of fatalities resulting from a spillage depends on the following factors listed by Westbrook: (1) warning time; (2) emission from the tank; (3) dispersion over the downwind area; (4) population density in the area affected; (5) chance of escape.

The time elapsing before warning is given was estimated as 24 min for rail and for road. A random sample of 17 accident reports from the files of British Rail headquarters at Marylebone indicated that it took, on average, 12 min for the first public aid vehicle (police, fire or ambulance) to arrive at the scene of a rail crash. It was considered that this delay was no longer than might be expected for a road accident. The figure of 12 min was then doubled to allow for the communication of an effective warning to the public.

For emission it was assumed that the initial temperature in the tank was 38°C, that the puncture holes in the vapour space were 19 in. and those in the liquid space were 7 in., and that the latter hole was at a level that allowed only one-third of the tank contents to remain in the tank. Under these conditions it was estimated that some two-thirds of the chlorine liquid would flash off or form spray and vaporize within the first 4 min and that the remaining liquid would boil off over a period of about 2 h.

The situation for dispersion is intermediate between an instantaneous and a continuous release. At a given point downwind there is a distance/velocity lag before the cloud arrives, then the concentration rises rapidly to a maximum as the instantaneous release cloud passes and then falls to a steady value as the continuous release plume becomes established. Dispersion calculations were done using the Pasquill method assuming a 5 mile/h wind speed and a dangerous chlorine concentration of 20 ppm. On the assumption that 24 min would elapse before effective warning would be given, the chlorine cloud would have drifted 2 miles. Then the areas in which a dangerous chlorine concentration would exist were estimated to be:

Area of dangerous chlorine concentration for rail spillage
$= 0.076\,\text{mile}^2$
Area of dangerous chlorine concentration for road spillage
$= 0.052\,\text{mile}^2$

Estimates of population density were made on the rail and road routes to one of the principal customers for chlorine. Estimates of the number of people within, on average 100 ft, of an accident were made by travelling the road route by car and the rail route by brake van. The numbers obtained were three and five persons on the rail and road routes, respectively. But, since road accidents tend to give rise to congestion, the figure for the road case was increased to 20. Other coarser scale surveys of the routes were made using maps, but in this case there was little difference in population density, and the average value of 700 persons/mile^2 applicable to Great Britain was taken.

Then, applying this population density to the areas at risk from spillage and including those people within 100 ft:

Number of people at risk from rail spillage
$= 0.076 \times 700 + 3 = 56$
Number of people at risk from road spillage
$= 0.052 \times 700 + 20 = 56$

The chances of escape were estimated as follows. The Chlorine Institute data given in Table 18.37 indicate that there were eight substantial chlorine spillages in North America in the period 1960–72. If on each occasion two-third of the tank contents had been released, then calculations show that the area affected within a 24-minute period would have been 0.133 mile^2. With an average population density of 60 persons/mile^2 the number of people at risk from the eight incidents would have been

$8 \times 0.133 \times 60 = 64$

But in fact in these incidents 156 people received medical treatment and one person died. These figures suggest that the population density at the scene of the accidents may have been higher than average and that the assumed warning period of 24 min may be too low. Press reports of the incidents suggest that a high proportion of those at risk received medical attention.

Applying a ratio of 1 death in 156 to the number of people at risk from either a rail or a road spillage gives:

Frequency of fatalities from rail or road spillage
$= 1 \times \dfrac{56}{156} = 0.359$ deaths/spillage

Then:

Frequency of fatality from rail transport
$= 0.022 \times 0.359 = 0.0079$ deaths/year
Frequency of fatality from road transport
$= 0.0144 \times 0.359 = 0.0052$ deaths/year

Westbrook also discusses the sensitivity of the calculations to changes in the assumptions. He considers three such changes:

A Rail and road tankers both suffer one significant accident per year more than the national average.
B Damage estimate in rail crashes is pessimistic and is reduced by factor of 2.
C Estimate of number of people at risk in road accidents is optimistic and is increased by 50.

The frequency of fatalities then becomes

Case	*Frequency of fatalities*	
	(rail deaths/year)	(road deaths/year)
A	0.023	0.0082
B	0.0039	0.0052
C	0.0079	0.0098

These calculations suggest that neither rail nor road has a marked advantage over the other from the point of view of safety in the transport of chlorine.

The study also considered the distribution of chlorine by pipeline and by vehicles with refrigerated atmospheric tanks. For the pipeline the case considered was a line of 4 in. diameter and 20 mile long carrying 25 ton/h of chlorine at 15°C for 2,000 h/year. From a study of pipeline records in the United Kingdom and the United States, it was concluded that a pipeline of this length might sustain damage once in 10 years and that on one occasion in 10 there would be a massive release of chlorine. The fracture was assumed to occur between excess flow valves 2 miles apart, 1.5 miles from one valve and 0.5 mile from the other, allowing emission of chlorine from both ends. It was further assumed that the excess flow valves would take 30 s to close. The calculations involved the difficult problem of emission under two-phase flow conditions. The results obtained were

Initial flow rate of chlorine = 60.3 ton/h per 4 in. orifice
= 120.6 ton/h total
Total quantity of chlorine emitted in 24 min = 28.4 ton
Size of cloud of dangerous concentration = 0.101 mile^2
Number of people at risk = 74
Frequency of fatalities from pipeline break
= 0.48 deaths/break

$$= \frac{0.48}{10 \times 10}$$
$= 0.0048$ deaths/year

The pipeline conveys 50,000 ton/y of chlorine over 20 miles. Comparison with rail or road transport requires that they be put on the same basis. If this is done, the frequency of fatalities is 0.0005 and 0.00032 deaths/year for rail and road transport, respectively. Therefore rail and road transport appear to be an order of magnitude safer than a pipeline.

It may be noted, however, that the assumption made by Westbrook on the frequency of damage to a chlorine pipeline is perhaps pessimistic. Information on pipeline failure rates is given in Chapter 23.

The transport of chlorine using refrigerated vehicles has not been studied so thoroughly at the time of writing. Preliminary work suggests that low temperature transport would be safer, perhaps by a factor of about 4, but it would not affect the choice between rail and road.

This work of Westbrook illustrates an approach to the assessment of the hazards of transport of toxic substances. Many assumptions and uncertainties are involved and the results are both approximate and tentative. It should be emphasized that the study is concerned with a comparative assessment of the different modes of transport, particularly rail and road. Such comparative assessment is difficult and demands accurate estimates if the results are to be meaningful in discriminating between transport modes.

18.30 Other Chemicals Hazard Assessment

Solomon, Rubin and Okrent (1976), from a study on the hazards of the storage of chemicals, give estimates of the areas affected by and the lethality of releases of chlorine, acrylonitrile, hydrogen cyanide and parathion. Parathion has the formula $(C_2H_5O)_2PSOC_6H_4NO_2$ and is much heavier than air.

They consider both instantaneous and continuous releases and use the Pasquill–Gifford equations. The equations used are, for instantaneous and continuous releases, Equations 15.16.40and 15.16.41, respectively, and for dosage, Equation 15.16.66a. The values of the dispersion coefficents used are those given by Equations 18.29.3 and 18.29.4.

The relations assumed between dosage and fatalities or injuries for the chemicals studied are given in Table 18.38. The lethal dosages used are as follows:

Chlorine	40-60 ppm for 30--60 min
Acrylonitrile	200-400 ppm for 30 min
Hydrogen cyanide	100 ppm for 1 min
Parathion	30 mg (dermal)

The authors refer to these as LD_{50} lethal doses, but in terms of the terminology used here the first three are strictly LCt_{50} lethal dosages.

The base scenario considered for all the chemicals is a release rate of 100 kg/s with 20% flash-off for 30 min exposure in an area of a population density of 1000 persons/km^2 under stability conditions Pasquill category A and at a wind speed of less than 2.5 m/s. For parathion it is assumed that there is no deposition from the air to the ground.

Cases without and with evacuation are considered. With evacuation the evacuation half-time was 30 min. Some results obtained are shown in Table 18.39. Of the 12,000 deaths calculated for chlorine, about 3000 occur as a result of the initial flash-off and the remainder as the result of the subsequent steady flow.

Assuming a tank rupture rate of 1×10^{-6}/tank-year and the probability of the assumed meteorological conditions as 5×10^{-2}, the frequency of the maximal chlorine accident considered is estimated by the authors as 5×10^{8}/year for such a storage tank in such an area.

Table 18.38 *Assumed relationship between dosage and fatality for toxic releases (after Solomon, Rubin and Okrent, 1976)*

Lethal dosage (%)	*Assumed mortality* (%)	*Assumed decrease in life expectancy* (years)
<1	0	0
1–10	5	0.08
10–25	10	0.25
25–50	20	1
50–100	40	1
100–200	65	10
>200	95	20

Table 18.39 *Effects of releases of some toxic chemicals without and with evacuation (after Solomon, Rubin and Okrent,1976)*

Chemical release	*Evacuation*	*Fatalities*
Chlorine	No	12,000
	Yes	9,800
Acrylonitrile	No	5,500
Acrylonitrile	No	5,500
	Yes	4,600
Hydrogen cyanide	No	49,000
	Yes	39,000
Parathion	No	9,600
	Yes	6,600

18.31 Hazard Assessment Methodology

Developments in the methodology for the hazard assessment of toxic releases have occurred in a number of areas, including the following: (1) source term, (2) heavy gas dispersion, (3) concentration fluctuations, (4) mitigation by barriers and sprays, (5) mitigation by shelter and evacuation, (6) toxicity relations, (7) degree of injury, (8) specific gases, (9) population exposure, (10) plant layout, (11) warehouse fires and (12) computer aids.

18.31.1 Source term

One area in which the hazard assessment of toxic releases has become much more realistic is in the handling of the source term. Much early work was based on the outright failure of a pressure vessel and, often, the ejection of its entire contents.

It is recognized that the total failure of a pressure vessel is very rare. Better estimates are available of lesser failures such of those of pipework. Allowance is made for emergency action such as the closure of emergency isolation valves.

As described in Chapter 15, methods have been developed to guide the choice between continuous and quasi-instantaneous release models, and thus reduce the proportion of cases where the more pessimistic quasi-instantaneous case is assumed.

Progress has been made in the modelling of the release of pressurized or refrigerated fluids. Models are available for the behaviour of the inventory on rupture of a pressure vessel and for two-phase flow from leaks on pipework. The models for evaporation from the pool formed following emission of a liquid are also much improved.

18.31.2 Gas dispersion

In most cases, the vapours of the principal toxic liquids exhibit heavy gas behaviour and great strides have been made in heavy gas dispersion modelling. The methods now available, which include models for manual use such as the Workbook models, computer codes such as HEGADAS and the three-dimensional models as well as physical modelling using wind tunnels, provide a set of tools capable of handling not only dispersion over flat, unobstructed terrain, but also the effects of slopes, buildings, barriers and water sprays. The concentration estimates yielded by these heavy gas models tend to be quite different from those of passive gas dispersion models.

18.31.3 Concentration fluctuations

It has long been appreciated that there are considerable fluctuations in the concentrations at a fixed point in a gas cloud. Methods are now available which allow estimates to be made of these concentration fluctuations. It is also appreciated that these fluctuations must have some influence on the effective toxic load, as pointed out by R.F. Griffiths and Harper (1985). Methods of treating this

aspect are given by D.J. Wilson and Sims (1985), D.J. Wilson (1991a) and J.K.W. Davies (1987, 1989a).

18.31.4 Mitigation: terrain, barriers and sprays

As just stated, the heavy gas dispersion models available can now treat situations where mitigatory features exist. Since the typical release occurs in a works, the gas dispersion will be strongly affected by the presence of buildings, which tend to enhance the dispersion. An illustration of a hazard assessment of a toxic release in the presence of buildings is given by Deaves (1987b).

Further mitigation can be obtained by the use of barriers and sprays, and models are available to allow these to be taken into account in the assessment (e.g. Meroney, 1991).

18.31.5 Mitigation: shelter and evacuation

Another major form of mitigation occurs where the exposed population remains indoors and thus benefits from shelter. Methods have been developed to estimate the indoor concentration–time profile, and hence toxic load, given the profile of the outdoor concentration. The development of models for the effect of shelter is illustrated by the work of P.C. Davies and Purdy (1986) and D.J. Wilson (1987, 1990, 1991b).

18.31.6 Toxicity relations

The form of injury relation generally used in the hazard assessment of toxic releases has been the probit equation. An account has been given above of the development of probit equations for this purpose.

The use of probit equations involves a number of problems. In large part these reflect the basic difficulty of determining the human response to a toxic load. One problem is that a probit equation is available only for a relatively small proportion of toxic gases. Even where a probit equation exists, it may be subject to considerable uncertainty. The accuracy of the relation can be expected to be highest close to the LC_{50}, but relatively low when extended to an LC_{05} or LC_{01} level. Yet in many cases the number of persons exposed to these lower loads is much higher than that for those exposed to the higher load; where there is a cordon sanitaire around the site, as there usually is to some degree, the difference is increased.

There has been some exploration of alternatives to probit equations. The use of the IDLH value as an alternative to the probit equation in hazard assessment has been explored by MacFarlane and Ewing (1990).

Particularly where the purpose of the hazard assessment is to identify the contour for a particular level of toxic effect, as in land use planning, use may be made not of a probit equation but of some fixed toxic load, such as the HSE SLOT value.

18.31.7 Degree of injury

Whereas the effect commonly estimated in hazard assessments of toxic releases has tended in the past to be the number of fatalities, there is some trend to estimate lesser degrees of injury. Thus the HSE SLOT value is a toxic load that is estimated not to be fatal to the vast majority of persons exposed. However, this type of criterion tends to be used not to determine the total number of persons exposed to the toxic load but the location of the contour around the site where the load will occur.

18.31.8 Specific gases

There have also been significant advances in the characterization of the toxicity of a number of common industrial gases, as described in Sections 18.15–18.21. In particular, reference may be made to the CPD Green Book probit equations, the HSE SLOT values and the toxicity estimates and probit equations of the MHAP.

18.31.9 Population exposure

Another area that has become more sophisticated is the characterization of the exposed population. As described in Chapter 9, there now exist what are, in effect, population exposure models, such as those given by Petts, Withers and Lees (1987) and in the *Green Book* (CPD, 1992b).

18.31.10 Plant layout

Increasingly, the effect of flammable and toxic releases is taken into account in plant layout, although the extent to which this is practical is greater for flammable and explosive materials than for toxic ones. An account of the work of Mecklenburgh (1985) on the use of hazard assessment in plant layout is given in Chapter 10.

18.31.11 Warehouse fires

Another type of toxic hazard is that arising from warehouse fires. Most work on the quantitative treatment of this hazard is relatively recent. It includes the work of D.A. Carter (1989), G.T. Atkinson, Jagger and Kirk (1992) and G.T. Atkinson and Jagger (1994).

18.31.12 Computer aids

The computation either of the consequences of a toxic release or of the risk to the population around an industrial site or along a transport route is a natural application for computer codes, and a considerable number of codes are available. Accounts of certain codes such as WHAZAN, SAFETI and RISKAT are given in Chapters 9 and 29.

18.32 Notation

C	concentration
k_1, k_2	constants
LC_i	concentration lethal at i% level
LCt_i	concentration–time product lethal at i% level
LD_i	dose lethal at i% level
LL_i	toxic load lethal at i% level
T	exposure time interval
Y	probit

Section 18.3

c	concentration
d	dose
D	dose rate
D_o	dose
k_e	elimination constant
L	toxic load
m	index
t	time
$t_{1/2}$	half-life
V	apparent volume of distribution of chemical in body
X	mass of chemical in body

Section 18.6

C_i	time-weighted average concentration of ith component
L	overall occupational exposure limit
L_i	occupational exposure limit of ith component

Section 18.11

c	concentration
C	concentration (ppm)
D	dosage
k	constant
L	toxic load
L^*	toxic load (alternative formulation)
m, n	indices
t	time
T	time interval (min)

Section 18.13

C_{O2}	concentration of oxygen in liquid phase (mol O_2/ml fluid)
D_L	pulmonary diffusion capacity (ml/min (mmHg))
D_{LCO}	pulmonary diffusion capacity for carbon monoxide (ml/min (mmHg))
D_{LCO2}	pulmonary diffusion capacity for carbon dioxide (ml/min (mmHg))
D_{LO2}	pulmonary diffusion capacity for oxygen (ml/min (mmHg))
ERV	expiratory reserve volume (ml)
f	respiration rate (breaths/min)
F_{AO2}	concentration of oxygen in alveolar space (ml O_2/ml air)
F_{EN2}	concentration of nitrogen in exhaled air (ml N_2/ml air)
F_{EO2}	concentration of oxygen in exhaled air (ml O_2/ml air)
F_{IN2}	concentration of nitrogen in inhaled air (ml N_2/ml air)
F_{IO2}	concentration of oxygen in inhaled air (ml O_2/ml air)
FRV	functional reserve volume (ml)
H_{O2}	Henry's law constant for oxygen (ml O_2/ml fluid (mmHg O_2))
IC	inspiratory capacity (ml)
IRV	inspiratory reserve volume (ml)
P_{AO2}	partial pressure of oxygen in alveolar space (mmHg)
$P_{AO2'}$	equilibrium partial pressure of oxygen in alveolar space and above pulmonary capillaries (mmHg)
$P_{O2'}$	equilibrium partial pressure of oxygen (mmHg)
$P_{O2a'}$	equilibrium partial pressure of oxygen above arterial blood (mmHg)
$P_{O2v'}$	equilibrium partial pressure of oxygen above venous blood (mmHg)
RV	residual volume (ml)
TLC	total lung capacity (ml)
TV	tidal volume (ml)
V_A	alveolar space (ml)
$\dot{V}_A$	alveolar minute volume, alveolar ventilation (ml/min)
V_D	anatomical dead space (ml)
V_E	volume exhaled (ml)
$\dot{V}_E$	exhaled minute volume (ml/min)
$\dot{V}_I$	inhaled minute volume (ml/min)
$\dot{V}_{o2}$	rate of absorption of oxygen, oxygen consumption minute volume (ml/min)
V_T	tidal volume (ml)
$\dot{V}_T$	minute volume (ml/min)
V_C	vital capacity (ml)

Section 18.15

C	concentration (ppm)
n	index
T	time interval (min)
V	causative factor

Section 18.16

C	concentration (ppm)
L^*	load (ppm min)
T	time interval (min)

Section 18.16.10

t	time (min)

Section 18.17

C	concentration (ppm)
t	time (min)

Section 18.18

P	probability of death
P_a	probability that death is acute
ψ_1	inhalation rate factor
ψ_2	medical treatment factor

Section 18.19

A	surface area of lungs (m^2)
C	concentration of gas in atmosphere (mg/m^3)
D	inhaled dose (mg)
D'	inhaled dose per unit body mass (mg/kg)
D''	inhaled dose per unit area of lung (mg/m^2)
f	safety factor
f_d	extrapolation factor
t	exposure time (min)
V_a	minute volume (1/min)
W	body mass (kg)

Section 18.29

Equations 18.29.1 and 18.29.2

C	ground level concentration on axis of plume (m^3/m^3)
d	downwind distance (m)
F	stack correction factor
h	vertical spread of plume at distance d (m)
H	effective height of stack (m)
Q	gas release rate (m^3/s)
u	wind speed (m/s)
θ	lateral spread of plume (deg)

Equations 18.29.3–18.29.6

A	area of lethal dosage (km^2)
$f(N)$	density function for fatalities
k, k'	constants
n, n'	indices
N	number of fatalities
u	wind speed (m/s)
x	distance in downwind direction (m)

σ_y, σ_z dispersion coefficients in cross-wind, vertical directions (m)

Equations 18.29.7–18.29.9

D_n damage to wagon n (mass units)

D_{rc} average damage per rail tank car (mass units)

D_{tnc} average damage per train (mass units)

m number of adjacent chlorine rail tank cars

n wagon counter

N number of wagons in train

r ratio of probability of puncture of rail tank car to probability of puncture of road tanker

W mass of wagon (mass units)

19 Plant Commissioning and Inspection

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19.1 Plant Commissioning

The commissioning, or initial start-up, is a period when the plant is particularly at risk. It is also a time when equipment may be maltreated or damaged so that its subsequent operation is affected. Moreover, delays in bringing the plant up to full output can have a marked effect on the economics of the plant. For all these reasons it is essential to organize the commissioning of the plant efficiently and to allocate sufficient resources to it.

An account of plant commissioning is given in *Process Plant Commissioning* (Horsley and Parkinson, 1990), *Process Plant Design and Operation* (D. Scott and Crawley, 1992) and by Troyan (1960), Finlayson and Cans (1967), Kingsley, Kneale and Schwartz (1968–69), Gans and Benge (1974), Unwin, Robins and Page (1974), Fulks (1982), Gans, Kiorpes and Fitzgerald (1983), Fraylink (1984), Ruziska *et al.* (1985) and Smet (1986).

In the following sections an account is given of plant commissioning and of some of its problems and hazards. It should be said at the outset, however, that in many cases these have been very successfully overcome by good organization and engineering so that, for example, large ethylene plants have been brought up to full output within about 3 days (Chementator, 1977 6 June, 67; 24 October, 73). Selected references on plant commissioning are given in Table 19.1.

Extensive use is made during plant commissioning of checklists. It is common for a writer on the topic to include one or two such checklists. A rather comprehensive set is given by Horsley and Parkinson, both in the text and the appendices, as indicated in Table 19.2.

19.1.1 Contract

The responsibility for the construction and commissioning of the plant is normally shared between the user company and its contractors, but the division of responsibility may vary considerably. The different types of contract are discussed by Horsley and Parkinson. The project may be predominantly in-house, utilizing a small number of subcontractors, or it may be undertaken as a 'turnkey' by a contractor. The contract may be fully reimbursable or fixed cost.

It is essential that the conditions of contract use unambiguous terminology and give clear guidance on the responsibilities of the parties for the various stages of the commissioning and for the associated documentation. Model conditions of contract for different types of contract are available and those of the Institution of Chemical Engineers (IChemE) are widely used for process plants, as described in Chapter 11.

The procedure developed by one UK process plant contractor to define responsibilities is illustrated in Table 19.3 (from Horsley and Parkinson). These authors give further demarcation schedules governing phases A–G of the project.

Table 19.1 *Selected references on plant commissioning*

Ames, Sturgis and Weeks (1959); Troyan (1960, 1961b,c); Lieber and Herndon (1965, 1973); Loen (1966, 1973); Bacchetti (1967); J.E. Baker and Burt (1967); Bopp (1967); Finlayson and Gans (1967); Garcia (1967); Holroyd (1967); Murray and Wright (1967); de Regules (1967); J.R. Bradley and Nimmo (1968); Finneran, Sweeney and Hutchinson (1968); Kingsley, Kneale and Schwartz (1968–69); MacNeish (1968); Feldman (1969); Lofthouse (1969); Matley (1969); Tucker and Cline (1970, 1971); Whyte (1970); Andrew (1971); Bacchelli and Bianco (1971); Clifton, Vinci and Gans (1971); McCallister (1971); Murphey (1971); Parsons (1971b); Swain and Hopper (1971); R.G. Wright (1971); Buyers (1972); Goldman (1972); G.M. Miller (1972); Ryan (1972); BCISC (1973/12); Galluzzo (1973); Godard (1973); A.J. Morton (1973); Asquith (1974); J.D. Baker (1974); Barnes (1974); Gans and Benge (1974); IChemE (1974/32); Mackey (1974); T. Robbins (1974); P.C. Russell and Herbert (1974); Spearing (1974); Turnbull, Buyers and Smith (1974); Unwin, Robbins and Page (1974); Voss and Ludbrook (1974); Gans (1976a); Anon. (1977 LPB 18, p.2); L. Pearson (1977a,b); Whiston (1977); British Gas (1978 Comm. 1104); Puckorius (1978); Vincent and Gent (1978); API (1981 Publ. 700); Westerman (1981); Fulks (1982); Cans, Kiorpes and Fitzgerald (1983); Fraylink (1984); Kletz (1984k); Ruziska *et al.* (1985); Smet (1986); Horsley and Parkinson (1990); Kingsley (1990)

Table 19.2 *Some checklists for plant commissioning (after Horsley and Parkinson, 1990)*

A Appendices

	Appendix no.
Demarcation of construction and commissioning tasks	2.1–2.5
Reservation checklist: pipelines and pipework	3.1
Reservation checklist: chemicals and hydrocarbons in	3.2
Modifications assessment	3.3
Mechanical commissioning	5.2.1
Packed columns	5.2.2
Control panels	5.3.1
Orifice plates	5.3.2
Relief valves	5.3.3
Piping systems	5.3.4
Electrical systems	5.4.1
General electrical installation	5.4.2
Control loop	6.1
Sequence operation (batch process)	6.2
Instrument loop	6.3.1
Storage tank	7

B Text

	Page no.
Pre-process commissioning	44
Instrument checking	36; table 6.1
Instrument documentation	42
Computer commissioning	Figure 6.1
Continuous reactor process commissioning	49

Table 19.3 *Demarcation between contractor and client of work and responsibility in construction and commissioning (Horsley and Parkinson, 1990) (Courtesy of the Institution of Chemical Engineers)*

Construction and pre-commissioning:

PHASE A	Prepare plant/equipment for pre-commissioning/mechanical testing
PHASE B	Prepare services: clean and pressure test systems
PHASE C	Check and prepare major mechanical equipment, instrumentation and protection systems
PHASE D	Final preparations for start-up

Commissioning:

PHASE E	Charge with feedstock, etc. Start-up plant and operate
PHASE F	Performance test and plant acceptance
PHASE G	Remainder of maintenance period

PHASE	A	B	C	D	E	F	G
1 Control of works by:		Contractor construction				Client	
2 Basic responsibilities and phases for various categories of staff at site							
Construction		Site manager and team of construction specialists			Defects correction under contractor's direction		Return for corrective work
Contractor Comm		Witnessing inspection & testing			Advising start-up & operation of plant	Witnessing performance test	
			Training client's operators				
Client		Witnessing inspection & testing			Plant maintenance and normal adjustments by client		
			Operators receiving training		Preparing for start-up: staring up and operating plant		
Equipment vendors		Testing and commissioning presence on site				On-call to site to end of maintenance period	
3 On completion of construction			CERTIFICATE OF MECHANICAL COMPLETION/TAKING OVER CERTIFICATE				
					CERTIFICATE OF ACCEPTANCE OF PLANT PERFORMANCE		
							FINAL CERTIFICATE

In the account that follows, it is convenient to assume that, unless otherwise stated, the project is a turnkey one undertaken by a major contractor.

19.1.2 Commissioning phases

The overall process of plant commissioning passes through a number of phases. It starts with the completion of erection. This term covers the end of installation of the equipment and is used sometimes, but not here, to cover also pre-commissioning. There then follows the phase of pre-commissioning. During this period there occurs mechanical completion and pre-commissioning; installation and checking of the control system and process commissioning.

By the end of process commissioning the various sections of the plant have been operated with process fluids. There then follows the performance testing in which the plant is operated and, if it meets its specification, accepted.

The activities during these phases may be illustrated by considering those in phases A–E of the contract scheme just mentioned. In broad terms, these are:

A Safety precautions; preparation of utilities; gland packing; preparation for line flushing.
B Commissioning utilities; machine rotation; pressure and leak testing; vessel cleaning; line flushing; relief value testing and re-installation.
C Chemical cleaning; machine alignment; lubrication systems; machine short running tests; instrumentation checks.
D Final preparations for performance testing.
E Charging of feedstock.
F Performance testing.

In the scheme described, the three areas of responsibility are supervision, trades and labour and inspection. Essentially, the responsibility for the first lies with the contractor, and in phase C the vendor also; responsibility for the second is with the contractor up to phase D, when the client has a roughly equal input and responsibility for the third passes increasingly from the contractor to the client over phases A to E. It is the client who carries out the performance testing of phase F.

19.1.3 Organization

It is important to organize the commissioning thoroughly and to provide the appropriate personnel. There is no simple model for the organization and personnel for commissioning. These depend on the nature of the process, the size of the plant, the involvement of other parties, such as licensors and contractors and so on. What is essential is that the management allocate sufficient resources to do the job efficiently. The commissioning of a large plant is a major enterprise and failure to recognize this is likely to increase costs and hazards.

The main conditions for success in commissioning, as listed by Kingsley (1990), are: an ably led, well balanced, well trained and committed commissioning team; a well structured relationship at senior level with site construction management and future operational management; thorough planning and implementation of preparations; adequate involvement in design stages and safety studies; meticulous attention to hazards and safety; ready availability of assistance from supporting disciplines and an expeditious approval system for plant modifications.

Some aspects of the organization of plant commissioning are

(1) regulatory and code requirements;
(2) contractual arrangements;
(3) quality assurance;
(4) safety;
(5) personnel and other resources;
(6) budgetary control;
(7) planning and scheduling;
(8) modification arrangements;
(9) communications;
(10) documentation.

The design, construction and operation of the plant are subject both to regulatory requirements and to the requirements of the codes and standards adopted. The latter should be clearly specified and there should be full information available about both sets of requirements.

The regulatory constraints on the discharge of gaseous effluents to the atmosphere and of liquid effluents to drains are generally of particular importance in commissioning.

The design, construction and operation of process plant are governed by quality assurance (QA). The extent of the QA system and its requirements varies between companies, but the trend is towards a formal system. The QA requirements need to be clearly laid down and arrangements put in place to ensure compliance. The QA system will generally cover the quality of the equipment and services supplied by the contractors and subcontractors and the installation and testing of the equipment. Where a full QA system is in operation, it will generally cover many of the aspects of plant commissioning discussed below.

Similarly, the plant design, construction and operation have to conform to the safety system and requirements. These too need to be clearly laid down and arrangements made to ensure compliance.

The definition of the relative responsibilities of contractors and the user needs to be particularly clear in both areas of QA and safety.

Plant commissioning requires the deployment of a considerable resources of various kinds and its organization is in large part concerned with ensuring that they are available in sufficient quantity and at the right time. Foremost among these resources is a wide range of personnel, who are considered below.

The various activities which have to be performed as part of the commissioning should be reviewed and arrangements made to furnish the necessary resources, of personnel, equipment or services. Mechanical precommissioning, process commissioning and performance testing are phases that may well require special resources.

A budget needs to be prepared for the cost of these resources. Full allowance should be made both for extra costs incurred by the main categories of personnel involved, such as overtime, travel and accommodation, and for costs of back-up services. It may be necessary to separate the costs of pre-commissioning from those of commissioning. In some cases, the two sets of costs are on a different basis, with the former being fixed price and the latter reimbursable.

Plant commissioning involves the planning and scheduling of a large number of activities. This aspect is treated in Section 19.1.5.

Arrangements need to be made to handle the plant modifications that are almost invariably required during commissioning. These should ensure that proposals to modify the plant are subject to review and that, where appropriate, the proposal is referred back to the design authority. Steps should be taken to ensure that this process is rapid and does not cause undue delay in the commissioning. This aspect is treated in Section 19.1.10.

Communications between the parties involved are always important in process plants and never more so than during plant commissioning. The information needs and the communication arrangements should be reviewed. Relevant aspects include documentation, written communications and meetings.

It should be arranged that the necessary documentation is available throughout the various stages of the project and that at termination of the commissioning the project is adequately documented.

It has been not uncommon that the commissioning period involves a series of crises, but this is not the most efficient way of doing it. As it has been put by Horsley (1974):

> It is also evident that the fun and personal satisfaction of being in the thick of things, having a tremendous degree of responsibility, working long hours and so on, are not efficient ways to start-up a plant. In fact, an efficient start-up without the emergence of numerous challenging technical problems would probably be slightly dull and disappointing to technologists and experts.

19.1.4 Personnel

Responsibility for the commissioning should rest with a single individual. It is normal to appoint a commissioning manager who has this responsibility. For the case

considered, that of a turnkey project, the commissioning manager is appointed by the contractor.

The typical composition of a contractor's commissioning team for a large ammonia plant is given by Horsley and Parkinson as a commissioning manager and deputy, four shift leaders, four assistants, a chemist and mechanical, electrical and instrument specialists.

Where the project is done in-house, a common practice is to appoint a plant manager for the new plant some time in advance to let him familiarize himself with it, and to make him the commissioning manager. The job of the project manager is normally a separate one. Experience indicates that it is usually not good practice to attempt to combine the roles of project manager and commissioning manager. The commissioning team for an in-house project should be a strong one, with good technical capability and relevant experience. The team may consist of the personnel assigned to the plant supplemented by others who are brought in for the limited period of the commissioning only. It is necessary that the commissioning manager should be able to command the resources necessary to carry through the commissioning. Unforeseen problems can often result in considerable demands on resources. It may be desirable, particularly on large projects, to create an additional troubleshooting team. The organization of an extra field-work team for this purpose has been described by Horsley (1974). Some of the many variations in commissioning team composition are described by Troyan (1960), Finlayson and Cans (1967) and Garcia (1967).

There are many variations in the ways of organizing the management team for commissioning. One is to design and impose the organization. An alternative, described by Horsley (1974), is to let this evolve by negotiation of roles among the managers with division of 'ownership' of particular features among them.

During commissioning there is likely to be conflict between individuals. This may be due, to some extent, to clashes of personality, but it is generally due mainly to differences of role and hence viewpoint which are inherent in the situation.

There is also a need for specialists, particularly with regard to proprietary items such as rotating machinery. Many problems which would otherwise prove difficult and time-consuming can be resolved if an expert is present at the right time.

The workload of individuals should be checked to ensure that it is not extreme. If someone is excessively overloaded and tired, he tends to become both less effective and more prone to error.

19.1.5 Planning and scheduling

Plant commissioning requires the coordination of a large number of activities carried out by many different people. Some aspects for which planning is particularly important include:

(1) commissioning activities –
  (a) pre-start-up activities,
  (b) initial start-up;
(2) budgets;
(3) documentation;
(4) recruitment;
(5) training.

The design and construction of a large process plant is normally scheduled using such methods as the project evaluation and review technique (PERT) and critical path scheduling (CPS). Usually these methods are implemented on a computer.

The scheduling of commissioning may be done as a separate exercise. An account of such scheduling has been given by Cans and Benge (1974), who quote typical figures of effort required of 1000 man-hours for a major project, or alternatively, 3 man-hours per major piece of equipment.

The method of scheduling is broadly as follows. All activities are broken down into their constituent parts. The man-hours and machine-hours needed to perform each activity are determined. The length of time required to perform the activity is calculated on the basis of the availability of men and machines. The duration of the activity is then assessed, taking account of such factors as running-in time. The conditions at which work can begin on the activity are then determined.

Again methods such as PERT and CPS may be used, but it is more common with commissioning than it is with design to do the scheduling by hand, using aids such as bar charts and arrow diagrams.

Modifications are then made such as speeding up an activity or paralleling activities. When this has been done, it is possible to calculate the slack, which is the difference between the earliest and latest time at which an activity can start, to work out programmes for a day or a week, to determine the resources of men and machines required and to assess the expenditures involved.

In many large plants, critical path features are the reactors or the instrumentation.

It is easy to incur extra expenditure during commissioning and it is necessary to exercise close control on costs by controlling budgets for the various cost centres.

The communication of information is crucial in commissioning and it is essential to ensure that adequate documentation is available at the time when it is needed. Planning should include, therefore, a review of the documentation required.

The recruitment of personnel needs to be carefully planned. There is usually some uncertainty about the precise start time of various activities and this makes recruitment something of a problem. The problem is aggravated if there are difficulties at the recruitment end. In view of the uncertainties, recruitment in advance of requirement may be necessary, but it should be borne in mind that an excessive period waiting to start work can be demoralizing.

The training of both the management and the workforce needs to be planned. Important aspects are the scheduling and documentation of training.

19.1.6 Management preparation and training

The effectiveness of the commissioning depends to a considerable extent on the thoroughness of preparation by management. The commissioning manager normally prepares himself by studying the process and the plant, by visiting or working on similar plants, by involvement in the project through work on design committees, by preparing plant documentation and operator training schemes, and so on.

There are some particular aspects on which he is well advised to brief himself thoroughly. One is process information and know-how which has been purchased from outside. If problems arise in a bought-in process, it tends to be more difficult to put them right. Somewhat similar considerations apply to proprietary equipment, such as

package units and complex machinery. It is also desirable for him to have a good grasp of the general economics and contractual features of the project. These range from raw material supply contracts to acceptance conditions for equipment.

It should not be assumed that it is only the process operators who need preparation and training for commissioning. These are required by management also. Some of the training requirements of the plant manager, and in particular the safety aspects, are discussed in Chapter 6.

19.1.7 Operations preparation and training

The operation of process plant requires the creation of a large number of systems and procedures. Many of these have to be formulated by the plant manager prior to and during commissioning.

The operating instructions are particularly important. These should be drafted early on, so that they can be used for operator training, but they are likely to need some modification in the light of operating experience.

It is also necessary to create a system of process records. The process log kept by the operator is one element in this, but there are numerous other records required for management purposes.

A process plant often receives its raw materials from or sends its products and/or by-products to other plants. The commissioning of such a plant tends to involve some degree of disruption of these plants. There is need, therefore, to coordinate the initial start-up so as to minimize such disruption. It may also be necessary to make arrangements to deal with unusable materials produced during the start-up, such as off-specification product.

Another feature that requires consideration is laboratory analysis and quality control. Safe operation requires a capability to analyse the material in the plant and ensure that it is within acceptable limits. This means working out methods of sampling and analysis, devising suitable tests and setting acceptance levels for raw materials, intermediates and products. It is also necessary to specify the associated paperwork.

The main training of the process operators is usually carried out jointly, during commissioning, by the training department and the plant management. The principal objectives of the training are to familiarize the operators with the chemicals handled, with the nature of the equipment and its location on the plant and with the procedures for operating the plant. A more detailed account of some of the principles and content of the training is given in Chapters 14 and 28 and a list of some of the documentation required for training is given in Chapter 6. Specific training in safety and loss prevention should be worked in with the other training material.

It may be appropriate to use lectures for the communication of certain basic information, but in general participative methods are likely to be more effective, and the commissioning situation lends itself well to the use of such methods. Workshops may be used to familiarize personnel with the hazards and with precautions and procedures. In some cases, use is made of a simulator to provide training in normal operating and emergency procedures.

Further training is obtained on the plant itself, where the trainees become familiar with the layout and learn to operate equipment and instrumentation. Testing with safe fluids provides particularly valuable experience. Often a strong team spirit develops during this period of training.

The operators should become familiar at an early stage with the hazards of the materials, the plant and the process and the alarm, fire and emergency systems. There should be drills for evacuation and fire fighting.

The commissioning environment is one where participation by the whole workforce is natural. It offers the opportunity, if management is so minded, to build the participative culture required for total quality management.

Generally, the training activities reveal certain inadequacies in the procedures and these should be rectified. The appropriate changes should be made in the documentation.

Usually much of the instruction is done by managers and supervisors who can benefit greatly from this, since instructing others is an effective way of learning. It is necessary to allow a sufficient number of management personnel to ensure that training is effective. It is a not uncommon experience that the level of training achieved at the end of the commissioning period is not bettered during the subsequent life of the plant.

Further accounts of process operator training during commissioning are given by Finlayson and Gans (1967), de Regules (1967), Kingsley, Kneale and Schwartz (1968–69) and R. Parsons (1971a).

19.1.8 Maintenance preparation and training

Prior to and during commissioning the maintenance engineer should set up the appropriate maintenance systems and documentation. Each major item of equipment should be given an identification code, which should be marked on the equipment itself.

The maintenance manuals for the equipment should be obtained from the manufacturer and reviewed. Sometimes the manuals will be considered inadequate in some respect. If so, the manufacturer should be contacted concerning modification. More often, however, problems arise because the manuals have not been consulted.

The maintenance of the equipment, both preventive and breakdown maintenance, should be planned. Schedules for regular preventive maintenance should be drawn up. A system of maintenance records should be instituted, containing details of the equipment in the plant and of the maintenance and modification work done. Details of the records required for pressure vessels, for example, are given in Section 19.3, but the records should not be limited to such equipment. The quality of the data available for analysis for reliability, availability and maintenance of the plant depends critically on these records. It is far easier to create an effective system initially than to try to improve a defective one. It is particularly important to obtain good information on the symptoms and causes of faults, and on the action taken.

A system of spares holdings should be created. Important features of such a system are that it show clearly what spares are available, what spares are being consumed and what the delivery situations are. Only if this information is available, is it possible to make rational decisions on the spares holdings.

A system for the control of slip plates should be devised so as to ensure that at each stage, such as normal operation or shut-down, all the slip plates required, but no others, are in position. The system should include provisions to prevent confusion with contractors' slip plates.

Maintenance personnel should check the plant during construction for accessibility and ease of maintenance. It may be necessary to make some alterations to the layout, to

the equipment or to the lifting arrangements. The maintenance function is also involved in many of the pre-start-up activities such as checking and testing, and suitable preparations need to be made for this.

Maintenance personnel typically serve a number of plants and generally receive only limited instruction in respect of a particular plant, but they do need to be trained in the hazards of the materials, in the alarms and emergency procedures and in the maintenance of equipment specific to the plant. This may include some training at the vendor's works.

19.1.9 Pre-commissioning documentation

It is difficult to overemphasize the importance of having a comprehensive and up-to-date set of documentation. The documentation as a critical feature of the management system was described in detail in Chapter 6.

It is appropriate here, therefore, only to re-emphasize certain aspects that are of particular importance in commissioning. The documentation available at the pre-commissioning stage should include:

(1) operating manual;
(2) operating instructions;
(3) safety instructions;
(4) permit system documents;
(5) pressure vessel register;
(6) pressure piping systems register;
(7) protective device register;
(8) maintenance systems and documents;
(9) checklists.

The plant should be covered by a comprehensive system of permits-to-work as described in Chapter 21. These are needed during the commissioning as much as during operation and should be developed in good time.

The registers for pressure vessels, pressure piping systems and protective devices should be established before commissioning. Details of individual items can then be entered as they are installed and examined. The registers are described more fully in Sections 19.3 and 19.4.

There are several systems of documentation required for maintenance, as already described.

A major part of commissioning is the checking of systems, both of hardware and of software. This is greatly assisted if suitable checklists have been prepared.

19.1.10 Modification control

There should be a system for the control of modifications during commissioning, as described in Chapter 21, so as to ensure that a safe design is not rendered unsafe by a modification. The system should ensure that proposed changes are identified and routed to the design authority and that there is a prompt response.

There should be a single channel through which modifications are communicated to the contractor, so that there is less risk of confusion. On a large project, this may require the appointment of a commissioning modifications engineer.

Any modification arising from the commissioning should be referred for examination by a hazard and operability (hazop) study in a manner akin to that pertaining during design and using similar criteria to decide whether such a study is necessary.

A modification proposed may be to an existing plant rather than to the plant or plant section being commissioned, in which case there will be additional matters to allow for. A major consideration is whether the modification is to be done during a plant shut-down or with the plant in operation. In either case, it is necessary to take account of the hazards, to see that the plant is in a stable operating condition and to ensure that contractors are aware of the hazards.

19.1.11 Mechanical completion and pre-commissioning

A particular aspect of pre-commissioning is mechanical completion. The term is applied to individual items of equipment and is used to cover the activities between installation and process commissioning.

Mechanical completion ensures that the installed equipment is ready for commissioning and involves checking that it is installed correctly, that the component parts operate as specified and that any ancillary equipment is installed and working. Some typical checks and tests carried out on process equipment and machinery are listed in Table 19.4.

The plant should be given a thorough visual inspection. A check should be made on all plant equipment and pipework to ensure that it is installed in accordance with the engineering drawings. Any discrepancies should be marked on drawings to show the 'as built' condition. These discrepancies should be reviewed and corrected if necessary. In one instance, for example, a safety shower was found to contain not water but caustic soda. The inspection should check for items such as loose bolts or missing valve wheels and for construction aids or debris left in the plant.

The plant layout should be checked with respect to features such as: means of access and escape routes; floors, stairs and handrails; lighting; fire equipment and safety equipment.

Mechanical equipment should conform to the specified codes and standards, should be installed in accordance

Table 19.4 *Some checks and tests carried out on process equipment and machinery during plant commissioning*

Pre-installation inspection, checking and testing of:
pressure vessels
process machinery
Plant checking against piping and instrument diagram
Checks on materials of construction
Pressure vessel and system tests:
inspection
pressure tests
leak tests
protective devices tests
Process machinery tests:
inspection
dry runs
load runs
performance runs
Subsystem and system tests:
dynamic safe fluid test (water test)
dynamic process fluid test
Also tests on:
utilities
instrumentation
unit operations
simulated faults

with the relevant drawings and should meet the performance tests specified.

Each item of equipment received should be checked for compliance with specification. In some cases, this may mean witnessing aspects such as examination or testing at the manufacturer's works.

Errors in the materials of construction actually installed are quite common. A check should be made, therefore, on the materials. In critical applications it may be appropriate to carry out a 100% check using a device such as a Metascope.

The installation of internal fittings, such as trays, weirs, downcomers and thermocouple pockets in distillation columns, should be checked. It is important that these internal fittings have the right dimensions, are correctly located and are firmly secured.

For rotating equipment, checks are required on foundations, lubrication systems, other ancillary systems, alignment and vibration-related features.

Piping systems should be checked for: conformity with pipework isometric and other drawings; the presence of fittings such as isolation valves, drain and sample points, etc; the orientation of fittings such as non-return valves, where applicable; satisfactory making of joints; adequate pipework supports and for satisfactory installation of expansion joints and bellows. A test sheet for piping systems given by Horsley and Parkison is shown in Table 19.5. Much use is made of checklists in assuring mechanical completion. Many of the checklists given in Table 19.2 apply to this phase.

For virtually all the features mentioned there are associated documents and/or drawings. The process of checking involves the marking up of drawings and the completion of test certificates and various forms of contractual certificate.

There are also a number of pre-commissioning activities to be carried out on the mechanical systems. These activities need to be coordinated both with the site construction manager and with the plant operations and maintenance management.

Typically the pre-commissioning activities include: first, commissioning of the utilities so that services are available; checks on the individual equipments and systems for mechanical completeness and listing of missing items; pressure tests on pressure vessels and defined pressure piping systems; cleaning of vessels and flushing out of pipework; loading in of catalysts and packings and leak testing.

The inspection and testing of pressure vessels is described in Section 19.3.

At the same time, rotating machinery is run off-load and instrumentation is set up, calibrated and given functional tests.

A list of some of the checks and tests carried out on process machinery such as pumps, compressors and centrifuges, is given in Table 19.6.

It is common practice to fit start-up filters on rotating equipment to protect it from debris which could cause damage. Sensitive instrumentation that could be damaged is also temporarily removed.

Subsystems are frequently tested using a safe medium, usually air or water, prior to testing with the process fluid. Compressors may be run on air on open circuit, and pumps may be run on water.

19.1.12 Control systems

The installation of the instrument and control system cannot be completed until most of the mechanical equipment is installed. Its installation tends to overlap with the commissioning of the rest of the plant.

Guidance on the installation and testing of instrument and control systems is given in BS 6739: 1986 *Code of Practice for Instrumentation in Process Control Systems: Installation Design and Practice*.

Most control systems are now based on some form of computer control, and this is assumed in the account given here. The computer is first tested at the supplier's works. These tests cover the computer hardware, the input/output equipment and any non-standard software. The functions to be performed through the configurable software are entered, such as signal conditioning, trend records, overview displays, alarms, control algorithms, etc., and are then tested. Likewise, applications software for functions such as sequential control or fault diagnosis is entered and tested.

Table 19.6 shows some of the checks carried out on instruments. A check should be made that the instrument is installed in accordance with the drawings and with the manufacturer's instructions. It should also be checked that shipping restrictions have been removed. Usually parts and springs are wired down, critical parts are covered with protective coating and leads may be plugged; all these restrictions need to be taken out.

Installation of the instrumentation is followed by checking. The responsibility for this normally lies with the contractor, but involvement of the user's instrument personnel assists familiarization.

Circuits should be checked for continuity from the panel to the instrument, and back. The movement of a control valve should be checked by 'stroking' it and that of a controller by observing its response to the output of the measuring element. The response of the alarms and interlocks to the measuring elements should be checked, as should the alarm settings and the actions of devices actuated by the interlocks. Similar checks should be made on trip systems.

Instrumentation received will have been calibrated by the manufacturer but some degree of recalibration on site may be required, whether as a result of damage ELD, engineering line diagram; GA, general arrangement; NDT, non-destructive testing; NR, non-return; RV, relief valve sustained or as a matter of policy, and this necessitates appropriate test equipment.

These checks are then followed by functional testing. Some functions are commonly executed by the main, computer-based system and some by separate systems.

Early installation of the computer system allows progress to be made with the testing of the instrumentation connected to it and of the functions allocated to it, in particular of non-standard systems software, configurable software and applications software.

Some common functions that are often separate from the computer system are (1) management information, (2) specialized instruments, (3) packaged units, (4) control loops, (5) trips, (6) sequence control, (7) emergency shut-down and (8) stand-by supplies.

Checklists for the functional testing of a control loop and of a sequence are given by Horsley and Parkinson (1990). The headings of the checklist for a control loop are (1) input channel, (2) faceplate/bar display, (3) trend display, (4) archiving, (5) alarm handling, (6) control functions, (7) output channel and (8) documentation. Those for a sequence are (1) declarations, (2) structure, (3) timing, (4) contention handling, (5) operator access, (6) recovery options, (7) recipe

Table 19.5 *Typical pressure piping test sheet (Horsley and Parkinson, 1990) (Courtesy of the Institution of Chemical Engineers)*

Design and Test Data		
Availability of the following data relevant to the piping systems	Engineering line diagram	
	Piping test schedule	
	Piping arrangement drawing	
	Pipe, line schedule	
	Piping and valve specifications	
	Piping isometrics	
	Piping test procedure	
	Piping fabrication and erection codes	
	Pipe support details and schedule	
Test certificates for	Off-site fabricated piping	
	Heat treatment or other	
	Process/Utility valves, control valves, etc.	
	NDT (X-or γ-ray, etc.)	
	In-line process equipment	
Piping and valve material analysis certificates		
Welders qualification certificates		
Pre-test Visual Inspection		
Routing and size correct to ELD arrangement drawing/ piping isometric		
Installation of piping and piping components complete	Joints bolts nuts and gaskets expansion loops and bellows	
	Fixed anchors, sliding supports, guides spring or fixed hangers	
	Jacket/jumpers,tracing conductive bolts/ earthing straps	
Installation/orientation with respect to flow	Process and utility valves, NR valves process control valves orifice plates and flowmeters	
Location of in line components for access, operation maintanence and safety of operatives		
Location and installation of	Vents, drains, drip legs, drip rings, utility station connections, steam traps, filters, strainers line blinds, spectable plates, bypasses, instrument tapping points for pressure, temperature and flow, plugs, rodding out points	
Installation of field mounted instruments that is Thermowells, pressure guages, etc.		
Check and ensure system devoid of insulation and paint		
Pre-test Preparation		
Prepare a written test plan and mark ELD/GA with location of all spools, spades, blanks, vent valves, strainers, etc., agree with site manager and initiate		
Obtain spades, blanks, strainers, vent valves, bolts, nuts, gaskets and fabricate pipe spools		
Remove RVs for bench, testing and orifice plates for checking, make good joints or blank off		
Remove or spade off any control valve or instrument liable to damage under test pressure, replace with spool or make good joint and open any bypass valves		
Spade off or isolate process equipment with lower allowable pressure than test pressure		
Spade off all overflows, close drains, fit vent valves, ensure test medium available		
Calibrate test gauge and check range adequate for test pressure and detect pressure loss		
Define testing fluid		
Pressure Test Procedure		
Site manager's clearance obtained, other contractors informed and safety notices positioned		
Ensure all test personnel are competent and briefed regarding extent, duration and limits of test		
Open up system, flush or blow through to remove mill scale/rubbish, fit temporary strainers and close		
Hook up test pump to line and test medium, open vents and commence filling system		
Conduct test per test procedure, attend to remedial works and bring to test pressure and hold		
Invite client's representative to witness test		
Prepare test certificate and record	System title, line numbers, plant reference	
	Numbers, date, time and duration of test	
	Pressure, test certificate number and obtain client's signature	
Post-test Procedure		
Open up, drain down, remove and account for all spades, blanks, spools, plugs, vent valves, strainers and test equipment, flush or blow through and dry out		
With new gaskets, re-install at bench tested RVs, orifice plates, control valves, thermowells, flowmeters pressure gauges and remove safety notices, etc.		
Check installation complete and purge or chemically clean if part of take-over procedure		
Complete construction works, for example paint, insulate, colour code. etc.		

Table 19.6 *Some elements of the checking and testing of process machinery and instruments (after Gans and Benge, 1974) (Courtesy of the Institution of Chemical Engineers)*

Process machinery:
Field disassembly and reassembly
Lubrication system: cleaning and check on circulation (flow, temperature)
Cooling water system: cleaning and check on circulation (flow, temperature)
Pre-commissioning of instruments
Check on free and unhindered rotation
Check on anchor bolts
Disconnection of piping to check that it does not stress equipment
Installation of temporary filter
Setting of system for 'no load' running
Running of motor uncoupled
Coupling of motor
Check on alignment
Check on vent system
Check on seal system
Dry run: check on vibrations and overheating of bearings
Load run
Performance run
Instruments:
Instrument checking against drawings and manufacturer's requirements
Removal of shipping restrictions
Calibration
Continuity check
Movement check
Alarms check
Interlocks check
Analysers check

handling, (8) firmware interface, (9) sequence display and (10) batch logging.

The pre-commissioning of the control system should be governed by formal procedures. Test forms should be specified for each system to be tested. Guidance and model forms are given in BS 6739: 1986.

Proposals for modification to functional specifications or to the computer software should be referred for review by a hazop study in a manner similar to that pertaining in design. There should be a formal system to ensure that changes made to the computer software are recorded and that development of the software proceeds by way of discrete, identifiable and documented versions.

It is necessary to ensure by formal means that the segregation of signals is not compromised by modification. Segregation of signals may be according to signal type, plant area and process function, and has implications for features such as intrinsic safety, electrical isolation and emergency shut-down.

Formal control should be exercised over access to the computer system. Parties requiring access are control engineers commissioning the control system and process engineers commissioning the plant. Levels of access should be defined and controlled by means such as passwords or key switches.

The checks on the instrumentation should be extended where practical to cover operation with process fluids and conditions that are realistic but nevertheless safe.

Documentation for the instrument and control system should include: the system manuals; piping and instrument diagram; loop diagrams; wiring/circuit diagrams; termination rack layouts; tag number lists; database tables; sequence flow diagrams; etc.

19.1.13 Process commissioning

Process commissioning is begun only when the pre-commissioning is complete and the defects identified have been corrected to the extent judged necessary. This commissioning may be undertaken on equipments or sections of plant as they become available, but only under close control so as to prevent hazardous interaction between the two activities of plant construction and process operation. One method of control is to require for the equipment a formal handover certificate verifying mechanical completion, with minor deficiencies listed. Before the process commissioning starts, it is usual to carry out a final check. Checklists applicable at this stage are one of those most commonly given.

The order in which the process commissioning is done may vary. The typical sequence cited by Horsley and Parkinson (1990) is (1) utilities, (2) laboratory, (3) raw material storage, (4) ancillary equipment, (5) reaction system, (6) work-up system and (7) product storage. Where there is no reaction system, the overall process system may be substituted for stages (5) and (6).

The quality control laboratory needs to be in a position to take samples from the plant and conduct analyses as specified. If there is any deficiency in its ability to do this, which is sufficiently serious, commissioning should not be started. The laboratory needs also to be prepared to handle the augmented number of analyses likely to be required during the commissioning period.

Ancillary equipment can often be commissioned separately from the equipment that it serves. Where this is possible, it is prudent to do this, so that when commissioning of the main equipment is begun, the ancillary equipment is ready for use.

A supply of raw materials is necessary for the process commissioning. These may come from a bulk storage or from other containments such as drums or transportable containers. Bulk raw materials storage will normally be commissioned some time in advance. It is also necessary to commission the intermediates and products storage, which is generally bulk storage. A checklist for the commissioning of a storage tank is referenced in Table 19.2.

The reaction section may be continuous or batch. Since this section is generally a critical one, its commissioning should be prepared with particular care. The commissioning team should be at full strength and fresh.

For a continuous reactor, the commissioning will aim to start-up and achieve a steady state as smoothly as possible. Critical features in achieving this are the utilities, the feeds, the machinery and the control system. A checklist for the commissioning of a continuous reactor is referenced in Table 19.2.

It may well happen that the conditions obtained are not those desired or that some fault occurs and the product produced is off specification. Horsley and Parkinson advise that, provided it is safe to do so, it may be better to continue running until it is established that the desired

product quality can be made before shutting down, thus avoiding repetition of start-up and shut-down.

For a batch reactor the problems are rather different. Here the requirement is to ensure that correct charges are made, that the desired sequence is followed, and that at each stage the process is controlled as specified. Critical features in this case are the charging, the control system for the sequences and the process conditions.

For both types of reactor a full record of the trials should be kept to allow the design to be checked and any deficiencies experienced corrected.

19.1.14 Handover: contractor project

The conditions for acceptance of the plant from the constructor by the operator are normally specified in the contract. A handover certificate is usually issued which contains a list of reservations of items on which further work is required. The handover needs to be carried out formally and with particular regard to safety. The plant should be in a safe condition when it is handed over.

With a large plant it may be desirable to have selective handover of plant systems as they are completed. This applies particularly to such systems as steam-raising plant, steam pipework and cooling water systems.

If parts of the plant are to be operated while other plants are still under construction, it is essential to take steps to ensure that these two activities do not interact in such a way as to create a hazard. The problem is similar to that arising in a major plant extension, and this is discussed in Chapter 21.

A typical reservations checklist is given by L. Pearson (1977b) and is shown in Table 19.7. The checklist referenced in Table 19.2 is similar.

19.1.15 Start-up and performance testing

With the end of the process commissioning, the next stage is to charge the feedstocks and start-up and operate the whole plant and subject it to performance testing in order to determine whether it meets its specification. This initial start-up of the plant should be thoroughly prepared. It should be recognized that the start-up may be prolonged and arrangements made to relieve personnel so that they do not have to work excessively long hours. It is valuable to keep fairly comprehensive records of the start-up, and personnel should be briefed on the recording requirements.

All the formal systems for control of hazards and errors should be operational. These include in particular the permit-to-work systems as well as the systems for the control of slip plates and of vents and drains.

Before start-up, a careful check should be made by 'walking the plant'. The inspection should include a check on the state of all valves, which may be assisted by use of marked drawings and a register. Likewise, a check is required to ensure that all slip plates that need to be removed have been removed; again this can be done, using drawings and a register.

It may be necessary during start-up to use filling and bypass lines that need to be closed again when the plant is operating. A register of such lines is needed to ensure that this action is taken.

The disarming of certain trips may also be necessary during start-up, particularly those for low flow, pressure and temperature. There should be a formal system to cover this which ensures that such disarming occurs only as authorized and that the instruments are restored again when the need for disarming has passed.

Checklists given by L. Pearson (1977b) of measures to be taken before process fluids are admitted are given in Table 19.7. The checklists referenced in Table 19.2 are similar. Start-up procedures are described further in Chapter 20.

The purpose of performance testing is to confirm that the plant can be operated at design conditions and that with a specified raw materials quality and at these conditions it will perform to specification in respect of throughput, yield and product quality. There may also be specifications for features such as utility usage, effluent quantities and compositions and reliability. A schedule of performance tests will have been drawn up and the levels of performance that the plant must meet specified.

The feedstocks are charged to the plant and it is started up and operated to determine whether it meets these performance criteria. The outcome of the performance testing may be: (1) that the plant performs satisfactorily; (2) that the plant does not perform satisfactorily and there is minimal prospect that it ever will or (3) that the performance of the plant, whilst falling short of specification, can be remedied. In case (3) the contractor may either put the matter right at his own expense or agree compensation with the client, whilst in case (2) the contractor has a financial liability.

19.1.16 Handover: in-house project

For a turnkey contract, the system of formal handover sets a term to the commissioning period. For an in-house project, the possibility exists that the commissioning period will become unduly extended.

The commissioning period should not be terminated until the plant is giving reasonably satisfactory operation. The rate of improvement inevitably slows down when the additional support of the special commissioning team is withdrawn. On the other hand, the development of a plant is a continuing process and the commissioning cannot be allowed to drag on indefinitely.

Some criteria for termination are given by Kingsley, Kneale and Schwartz (1968–69) as follows: (1) competence of operating staff; (2) reasonable level of plant reliability; (3) attainment of acceptable quality standards; (4) satisfactory use of resources (staff, materials, utilities, throughput) and (5) acceptable level of maintenance.

19.1.17 Safety audit

The plant should be given a comprehensive safety audit during the commissioning period. The audit should cover both hardware and software aspects. Details of such a safety audit have been given in Chapter 8.

19.1.18 Commissioning problems

Many of the problems associated with commissioning have been mentioned explicitly or are implicit in the comments made, but it is appropriate at this point to give a further review of some of the problem areas in commissioning. These include:

(1) lack of process information;
(2) design changes;
(3) unsuitable equipment;
(4) lack of expert advice;
(5) lack of spares and supplies;
(6) construction and maintenance errors;
(7) safe fluid testing;
(8) water traces;
(9) operating errors.

Table 19.7 *Checklists of measures to be taken before process fluids are admitted on a chemical plant (L. Pearson, 1977b) (Courtesy of Hydrocarbon Processing)*

(a) Pipelines and pipework checklist

(1) Screwed plugs in pipes, only permissible on air, water, nitrogen under 100 psi, $1\frac{1}{2}$ in. NB and below
(2) Faulty welding
(3) Correct joints
(4) Odd sized bolts
(5) Black bolts in cold joints
(6) Faulty pipeline supports
(7) Pipe not resting on supports
(8) Are expansion slippers safe (e.g. will they push off structure when line is hot?)
(9) Check spring hanger settings
(10) Faulty spring hangers
(11) Low point drains fitted where necessary, and high points vents
(12) Lagging – missing, damaged, loose, etc.
(13) Vent and drain blanks fitted where necessary
(14) 'Weep holes' in relief valve exhaust lines, only on non-H/C or atmospheric, RVs
(15) Have all slip plates been removed and spectacle plates turned?
(16) Spring hangers – have restraining pins been removed?
(17) Make sure pipework is up to the piping and instrument diagram specification
(18) Necking-off hazard – is there any equipment or small bore pipe projection that can be accidentally broken off?
(19) Are small branches, that is drains, sufficiently clear of pipe supports?
(20) Do drain lines run to underground drains? They should not flow over paved areas
(21) Flanges lagged up

(b) 'Chemicals and hydrocarbons in' checklist (jobs to be done before chemicals or hydrocarbons can be safely brought into the plant)

(1) Complete all necessary reservations
(2) Nitrogen purge systems prepared and leak tested
(3) Blowdown system 'live'
(4) Oil/water separator in commission
(5) New perimeter fence erected, with 'dematched area' notices
(6) Dematching hut in position and gateman available
(7) Brief all construction people on consequence of plant becoming a 'dematched area'
(8) Fire alarm I/C and all position tested
(9) Compressed air sets in position
(10) Fire extinguishers in position
(11) Eye wash bottles in position
(12) Personnel showers in position and checked
(13) Fire hoses in position
(14) Fire main I/C and check that hoses fit hydrants
(15) Drench water sprays tested
(16) Fire steam hoses in position and check they connect securely
(17) Fire permits in use
(18) Flush drains to prove them free from obstructions
(19) Plant areas clean (fire hazards removed – rags, paper, wood, etc.)
(20) Check plant lighting
(21) Remove contractors' buildings, tarpaulins, etc.
(22) Remove non-flameproof equipment
(23) Nominate shift fire teams and arrange practice alarm
(24) List all possible welding jobs – get most done beforehand
(25) Check that welding sets pass works electrical inspection
(26) Check gas detectors
(27) Hazard and safety notices to be in position
(28) Obtain 'means of escape' certiciate
(29) Check that segregation plates can be easily removed
(30) Inform fire station
(31) Invite safety department to inspect and pass comment
(32) Carry out through search for matches
(33) Make sure that neighbouring plants know how this affects them
(34) Inform services (affect their drains)
(35) Inform Factory Inspector and Alkali Inspector
(36) Inform local authorities
(37) Inform records sections

H/C, hydrocarbon; I/C, in commission; NB, nominal bore; RV, relief valve.

The difficulties inherent in a situation where basic information about the process is inadequate have already been mentioned. This is due sometimes, but by no means always, to the purchase of know-how from outside.

Although some modifications of the original design are almost inevitable, they tend to be disruptive and expensive, and should be kept to a minimum.

Unsuitable equipment can be a source of much trouble. It is sometimes suggested that equipment that comes as a package unit or is purchased from the main contractor can be troublesome. It may well be, however, that in many cases the problem lies with the user. Certainly, it is essential that he gives a full specification for such equipment as for other items.

The need for expert advice has already been mentioned. The behaviour of equipment during the running-in period may be different from that in normal operation. In one case, for example, commissioning was delayed because the lubricating oil from the bearing of a ball mill was found to contain a high concentration of metal particles: the vendor then confirmed that this was normal during running-in.

Shortages of spares and other materials can result in delays. The need for an adequate spares system has already been emphasized, but provision of other items is equally important.

Mistakes in construction are commonplace. In addition to the use of incorrect materials of construction for the

main equipments and pipework, errors often occur in minor items such as bolts or gaskets. For example, mild steel bolts may be fitted where stainless steel bolts have been specified, which in a low temperature application is a serious hazard. Likewise, a hazard can be introduced by the use of a wrong gasket.

Safe fluid testing can sometimes introduce its own problems. The use of water instead of a hydrocarbon means that the weight of the fluid is greater. There may be a risk of overpressuring the base of tall columns or of overstressing vessel supports.

Likewise, it is not unknown for damage to be done to compressor systems by an air inlet line choked by polyethylene bags.

Certain plants, notably cryogenic plants, are sensitive to even small quantities of water. Ice and hydrates can cause numerous problems, particularly on instrumentation. It may be necessary to remove water by blowing through the drains and by a warm air purge of the plant.

Inexperience on the part of the process operators can result in maloperation that does considerable damage to the plant. For example, a pump may be allowed to run dry or to pump against a closed valve.

Operation of equipment at higher temperatures than intended so that the creep rate is greatly increased can be particularly serious. It is quite possible to use up a large proportion of the creep life, say 30%, during the commissioning. It is important, therefore, that this be avoided as far as possible and that the records be kept such as to allow an estimate of creep effects during commissioning to be made.

Some specific problems arising during commissioning have been reviewed by Kingsley, Kneale and Schwartz (1968–69) and are summarized in Table 19.8. Design errors do occur, but are most frequent in detailed rather than fundamental aspects. Emulsions and foams may occur on the full-scale plant, even though these have not shown up in the pilot plant. Gas phase balancing errors can lead to difficulties with levels and flows. Lack of a net positive suction head causes pumps to cavitate. Heat transfer phenomena that can be troublesome include polymerization and scaling up. The former occurs more frequently than is admitted. Separation operations, especially those involving particulate systems, give rise to many difficulties.

Automatic control problems include measurement of unusual variables, the oversizing of control valves and the control of non-linear variables and of loops with large time lags and/or dead time.

Table 19.8 *Some typical problems arising during plant commissioning (after Kingsley, Kneale and Schwartz, 1968–69) (Courtesy of the Institution of Mechanical Engineers)*

Design errors:
emulsions and foams
venting arrangements
liquid head arrangements
Heat transfer phenomena:
polymerization
scaling up
Separation operations:
liquid–liquid separation, for example centrifuges
liquid–solid separation, for example filtration
gas–liquid separation, for example demisting
gas–solid separation, for example gas filtration
Automatic control:
long time lags, dead time
valve sizing
control of non-linear variables, for example pH
unusual measurements
unsuitable equipment
Leaks:
sudden leaks
leaks in vacuum equipment
Vibration phenomena
Mounting errors
Mechanical handling equipment
Materials of construction

19.1.19 Commissioning hazards

The process and plant designs should already have been subjected to the various checks described in Chapter 8. In particular, the hazop study conducted should have covered operations that are carried out only in commissioning. There are certain specific hazards associated with commissioning.

The pressure testing of equipment, which is described in Section 19.7, is a hazardous operation. The hazard is minimized by the use of hydraulic rather than pneumatic testing, but the energy released if the vessel fails is appreciable even with a hydraulic test, and it is important to ensure that the correct test procedure is followed and that personnel not involved in the test are cleared from the area.

Many of the test and other operations carried out during commissioning require the use of temporary connections. These are often hoses. Hose connections have been responsible for many accidents and particular care should be exercised with them.

Plant are tested for leaks, but, even so, leaks tend to develop due to features such as loose joints, open valves, gasket and seal failures, vibration, thermal expansion and contraction and corrosion. It is important, therefore, to keep a lookout for such leaks. Leaks from high pressure plant can cause direct injury to personnel, leaks of flammable materials can cause a fire or explosion and leaks of flammable liquids can contaminate lagging, creating a further fire hazard.

Nitrogen purging is a frequent operation in commissioning. The use of nitrogen for large-scale purging operations involves the hazard of asphyxiation of personnel.

Commissioning requires the use of utilities in large quantities. It is important to ensure that other plants are not run short of essential utilities and so put at risk. There is the further hazard of contamination of the utilities by fluids from the plant being commissioned.

19.1.20 Post-commissioning documentation

During the commissioning a large amount of information is generated which needs to be properly documented. Modifications are made to the plant; a wide variety of tests and examinations are performed on individual items of equipment and on the plant as a whole; the computer software is modified and parameters entered; modifications are made to the systems and procedures and the associated documentation; reviews are made of safety and environmental features and there are matters to be carried forward.

Some principal features of the post-commissioning documentation are:

(1) modifications records;
(2) equipment examination records –
  (a) pressure vessels,
  (b) pressure piping,
  (c) protective devices;
(d) equipment test records –
  (a) pressure and leak tests,
  (b) pressure relief valve tests,
  (c) rotating machinery tests,
  (d) instrument tests,
  (e) computer system tests;
(f) computer records;
(g) spare inventories;
(h) safety reviews records –
  (a) hazop follow-up,
  (b) safety audit,
(c) environmental review records;
(d) reservation list.

There should be records of any modifications made to the plant and also to the process. This aspect has already been discussed.

The registers for the pressure vessels, pressure piping systems and protective devices should have been prepared prior to commissioning, but much information on the equipment and on its initial examination and testing will be entered at the commissioning stage.

Records should be kept of the tests done on the whole range of equipment, including pressure vessels and the pressure piping system, pressure relief valves, rotating machinery, instruments and the computer system. Any modifications made to the computer software or to the parameters entered should be recorded.

It is common practice to hold an inventory of commissioning spares. With the end of commissioning this should be replaced by the regular spares inventory, which should be documented.

There should be records of any safety and environmental reviews conducted. The safety reviews should include any matters requiring follow-up consequent on the main hazop study or any further hazop studies performed as a result of commissioning modification and the post-commissioning safety audit.

There will also have been modifications made to the various types of documentation such as operating instructions, test procedures, etc., and these changes should now be incorporated and tidy documents produced.

19.2 Plant Inspection

Plant inspection is an essential aspect of the fabrication, construction, commissioning and operation of pressure systems. Accounts of plant inspection are given in *Pressure Vessel Systems* (Kohan, 1987) and *Inspection of Industrial Plant* (Pilborough, 1989) and by Erskine (1980).

Relevant codes are the *Pressure Vessel Examination* Code (IP, 1993 MCSP Pt 12) and the *Pressure Piping Systems Examination* Code (IP, 1993 MCSP Pt 13). These are codes with international application but are aligned with the Pressure Systems and Transportable Gas Containers Regulations 1989.

Another code is the *Registration and Periodic Inspection of Pressure Vessels Code* (ICI/RoSPSA 1975 IS/107) (the ICI *Pressure Vessel Inspection Code*). This is now out of print but remains a good illustration of the fundamental principles of such codes.

In the United States, the *Guide for Inspection of Refinery Equipment* by the API (1962–) has long been a principal inspection code but is now out of print. The *Guide* has some 20 chapters that are listed in Appendix 27. It is being replaced by other publications. One of these is API RP 510: 1989 *Pressure Vessel Inspection Code: Inspection, Rating, Repair and Alteration*.

The following description is concerned mainly with the inspection of pressure vessels, pipework and protective devices, but it illustrates general principles for inspection which are relevant also to many other types of equipment.

Selected references on plant inspection, testing and monitoring are given in Table 19.9.

19.2.1 Regulatory requirements

The statutory requirements for inspection of pressure vessels and the legislative background to these were described in Chapter 3. The basic position in the United Kingdom is that until 1989 there were statutory requirements covering the construction and maintenance, including inspection of steam boilers and receivers, air receivers, gasholders and gas cylinders and containers for transport, but not for other pressure vessels. Thus, many pressure vessels containing hazardous substances were not subject to specific statutory controls. Moreover, the pressure system components which were the subject of statutory requirements were strictly limited. Principally they were the protective devices associated with steam boilers and receivers and air receivers. Thus many pressure system components containing hazardous substances, including pipework and other components listed in Section 19.3, were not subject to specific statutory requirements. However, although many pressure systems were not covered by specific statutory controls, the general duty to provide safe equipment, which is strengthened by the Health and Safety at Work etc. Act 1974, might be considered to require that the integrity of pressure systems handling hazardous substances should not be less than that of systems handling steam and air.

The Pressure Systems and Transportable Gas Containers Regulations 1989 (the Pressure Systems Regulations), described in outline in Chapter 3, have introduced comprehensive controls on pressure systems as well as pressure vessels. Guidance on these regulations is given in HS(R) 30 *A Guide to the Pressure Systems and Transportable Gas Containers Regulations* 1989 (HSE, 1990). The regulations are supplemented by COP 37 *Safety of Pressure Systems* (HSE, 1990). The scope and general requirements of the Pressure Systems Regulations are described in Chapter 12 and the those for inspection are described here.

It is normal industrial practice to exercise close control of all parts of a pressure system, including both pressure vessels and other components, and to do this throughout the life of the system, starting with design and continuing through fabrication, installation, commissioning, operation, inspection, maintenance and modification, by means of external and in-house standards and codes. The inspection system is the main means of exercising this control after the design stage.

Nevertheless, in the United Kingdom there have in the past been some differences between pressure vessels that

Table 19.9 *Selected references on plant inspection, testing and monitoring*

API (Appendix 27, 1967– *Refinery Inspection Guide*, 1984 Publ. 2002, 2004, 1990 RP 574, 1991 RP 573, 1992 RP 510, 572); NRC (Appendix 28 *Inspection*); Welding Institute (Appendix 27, 28); BCISC (1959/3); Honeyman (1960); Barnhart (1963); Kirchner (1967); ASME (1979– *Pressure Piping Code*, 1992 *Boiler and Pressure Vessel Inspection Code*); Ministry of Technology (1969a); Kobrin (1970); Pilborough (1971, 1989); Welding Institute (1972 Item 22); M.J. Neale (1974, 1980); Collacott (1975, 1976a, b, 1977a, b, 1985); ICI/RoSPA (1975 IS/107); IMechE (1975/18); Dickenson (1976); Edeleanu (1976, 1981); Fromme (1976); IChemE (1976/63); IP (1976, 1993 MCSP Pt 12, 14); R. James and Bloch (1976); Harvey (1976, 1979b); R. Morris (1976); Filetti and Trumpler (1977); National Vulcan (1977); R.L. Clark (1978); Himmelblau (1978); HSE (1978b); R. King and Magid (1979); Czaga and Drury (1981); Kister (1981b); Marre and Reichert (1979); Sims (1980); London (1982); Anon. (1983f); Wamsley (1983); Coley (1985); Chowdhury (1986); Erskine (1986); Conroy (1987); Krisher (1987); R.L. White (1987); Plant Safety Ltd (1990); Depue (1991); Witherill (1991) BS (Appendix 27 *Test Methods*), BS 5500: 1991

Fault diagnosis
Pau (1975, 1981a, b); R. Morris (1976); Anon. (1977 LPB 14, p. 17); Chamberlain (1980); Schweitzer (1982); Edgar *et al.* (1984); M.W.J. Lewis (1984); Marney and Foord (1984); M.J. Lewis (1993)

Pressure vessels, piping, fittings
Gibbs and White (1961); Buhrow (1971); O'Neill and Jordan (1972); Toogood (1972); Whenray (1972); Lautzenheiser (1974); ICI/RoSPA (1975 IS/107); Dunt (1976); Erskine (1976b, 1980); Kussmaul, Blind and Ewald (1977); Ludwig (1978); IP (1979); Nichols (1979b); Jessop (1980); Kussmaul *et al.* (1980); McDermod (1982); Baker-Counsell (1985f); Guth and Clark (1985); Tayler (1985c); Burke and Moore (1990); K.P. Singh (1990); IMechE (1991/132, 1993/154) BS 3889: 1966–, BS 470: 1984

Columns: Bowman (1991)

Tanks
Truscott and Livingstone (1978); Hallan (1994)

Glass equipment
Lofberg (1965)

Paints
Berger (1983)

Rotating machinery
Sela (1978); E.R. Bowen, Rotondi and Reid (1980); Finley (1980); B.R. Singh and Thomas (1980); Godse (1990, 1991); R.F. Wong (1992)

Pipelines
AGA (Appendix 28); British Gas (Appendix 27 *Commissioning and On-Line Inspection*, 1989 Comm. 1409); Holm (1984); Clerehugh, Shannon and Jackson (1983); Braithwaite (1985); Gordon, Murphy and Dean (1985); L. Jackson, Shannon and Adley (1985); Jamieson (1985); Watanabe and Himmelblau (1986); IGasE (1987 IGE/SR/10); Weisweiler and Sergeev (1987); Ellul (1989); Clerehugh (1991); Stouffs and Giot (1993)

Pipeline location detection: British Gas (1987 Comm. 1345, 1989 Comm. 1410)

Ammonia plants
Truscott and Livingstone (1978); Madhavan and Sathe (1987); Prasek (1988); Burke and Moore (1990)

Test procedures
Shaw, Sykes and Ormsby (1980); British Gas (1986 Comm. 1305); G.J. Gibson (1987); ASME (1991 PTC1 – 1991)

Structures: Collacott (1985)
Steam plant: ASME (1980 PTC 39.1–1980); van Kapel (1990)
Centrifuges: AlChE (1980 E-21)
Driers, including spray driers: AlChE (1985 E-23, 1988 E-26)
Mixers: AlChE (1965 E-7, 1986 E-25)
Pressure vessels: API (1967– Refinery Inspection Guide, 1992 RP 510, 572); T.E. Taylor (1968–69); ASME (1992 *Boiler and Pressure Vessel Code*)
Distillation columns: AlChE (1962 E-10, 1986 E-24)
Heat exchangers: AlChE (E-15)
Tanks: Truscott and Livingstone (1978); Briggs, Richards and Fiesinger (1986)
Pipelines: British Gas (Appendix 27 **Testing**); ASME (1979– Pressure Piping Code); API (1991 RP 1110)
Welds: Bartholome and Vasoukis (1975); Eisenberg (1975)
Steam traps: ASME (1980 PTC 39.1)
Valves: API (1992 RP 574); BS 6755: 1986–
Fired heaters: AlChE (1977 E-16, 1989 E-27); API (1991 RP 573)
Steam turbines: ASME (1976 PTC 6–1976)
Compressors: ASME (1974 PTC 10–1974); BS 1571: 1975, BS 3122: 1990–
Pumps: AlChE (E-5, 1968 E-14, 1984 E-22), Shull and Church (1991), BS 599: 1966, BS 5316: 1976–
Fans: BS 848: 1980
Pressure relief devices: API (1960 RP 525, 1974 *Refinery Inspection Guide* Pt 16, 1992 RP 575); ASME (1988 PTC 25.3–1988)
Incinerators: ASME (1978 PTC 33)
Other process equipment: AlChE (1977 E-18, 1978 E-19, 1980 E-20)
Fire protection equipment: MCA (SG-13); P. Nash (1975b,c); R. Phillips (1981); NFPA (1994/41)

Visual inspection
Pilborough (1971, 1989); Elliott (1976); Keymed Industrial (1983); Dooner (1986)

Pressure testing
Ferge (1972); Anon. (1979 LPB 26, p. 39); Hearfield (1980b); AGA (1981/36, 1984/40); Kiefner and Forte (1985); Anon. (1986 LPB 72, p. 7); Kletz (1987d); Gwynn (1988); Dooner and Marshall (1989 LPB 86); HSE (1992 GS4)

Leak testing
Rubin (1961); Graham (1964); Roehrs (1967); Pilborough (1971, 1989); Blackmar (1973); Bloomer and Smalley (1975); Leslie and Ferguson (1985); Anon. (1987t); Palluzzi (1987) BS 3636: 1963

Leak monitoring
British Gas (Appendix 27 *Leakage Control*); NRC (Appendix 28 *Leak Detection*); CONCAWE (1973 5/73); D. Harrison and Watkins (1983); Watanabe and Himmelblau (1986); Saiga *et al.* (1991); Stouffs and Giot (1993)

Non-destructive testing
ASTM (STP 112, 145, 213, 1965 STP 371, 1977 STP 624); NRC (Appendix 28 *Nondestructive Examination*); Welding Institute (Appendix 27, 28, 1972/19, 1974/27); McMaster (1959); Hogarth and Blitz (1960); D.M. Lewis (1961); Gleekman (1966); Nittinger (1966); Parrish (1966); Birchon, Bromley and Wingfleld (1967); Ostrofsky (1968); Egerton (1969); D.J. Evans (1970); Welding Institute (1972/19, 1973/23, 1974/27); Birchon (1975, 1988); Detlor (1975); Holloway and Kellum (1975); Callister (1976); Erskine (1976b); Gumm and Turner (1976); L M. Rogers (1976); British Gas (1979 BGC/PS/CP/SND1, 1987 Comm. 1346); Stinchcomb (1980); Buhrow (1983); Laskowski (1984); Nichols (1984); AGA (1986/45); R.K. Miller and Mclntyre (1987); Weisweiler and Sergeev (1987); Institute of Materials (1989 B447); Kletz (1989d); Sattler (1989a–d, 1990); Dressel, Heinke and Steinhoff (1991); Sadler and Matusz (1994) BS (Appendix 27 *Non-Destructive Testing*)

Radiography
ASTM (STP 28A); Wiltshire (1957); L.A. White (1963); Rockley (1964); Halmshaw (1971); Welding Institute (1973/23); Dishart and Bruce (1975); Chynoweth (1986) BS 2600: 1973–, BS 5288: 1976, BS 5650: 1978, BS 2910: 1986

Dye penetrant methods
BS 6443: 1984

Magnetic particle methods
ASTM (STP 62, 85, 1965 STP 371); British Gas (1992 DAT43) BS 6072: 1981, BS 4069: 1982

Eddy current methods
NRC (Appendix 28 *Eddy Current Inspection*); G. Johnson and McFarlan (1978); ASTM (1981 STP 722); Holloway, Bauer and Pittman (1981); AGA (1989/64, 1990/70, 1992/87)

Non-destructive identification
Feigel (1958); Imgram and McCandless (1972); ASTM (1973 STP 550); Duff (1976); Ostrofsky (1980–); M.J. Bowen and Campbell (1986); Anon. (1989 LPB 86, p. 23); R.J. Sherwood (1989)

Condition monitoring, performance monitoring
Collacott (1976b, 1977b); de Guerin (1977); Henry (1979); M. Neale and Associates (1979); M.J. Neale (1980); Sims (1980); B. Stephenson (1981); Stewart Hughes (1981); D.W. Butcher (1983); Ghia *et al.* (1983); D. Harrison and Heath (1983); R.M. Stewart (1983); Thomson and Deans (1983); Dodd (1984); Grantom (1985); Meeker (1985); D. Thomas (1985); P. Cooper (1986–); Pocock and Allen (1986); R. Smith (1986); Chesterton Int. (1987); English (1987); J.B. Smith (1987); G. Baker (1989); IMechE (1990/120); AGA (1991/16); Darling (1991); Rao (1991) BS (Appendix 27 *Condition Monitoring*)

Vibration monitoring
Rathbone (1939); Collacott (1947, 1975, 1976a, 1977a,b); Yates (1949); Blake (1964, 1966); Nittinger (1964); Buscarello (1968); Maten (1967, 1970); C. Jackson (1969, 1972b, 1974, 1975–); Bently (1970); Fieldhouse (1970); R.L. Martin (1970); R.H. Wallace (1970); Beranek (1971); Tustin (1971); D. Wright (1971); Borhaug and Mitchell (1972); P.J. Brown (1972); Erskine (1973, 1976a); Maddox (1973, 1977); Bentley (1974); Black *et al.* (1974); Diehl (1974, 1975); Lorio (1974); Nicholls (1974); Prentice, Smith and Virtue (1974); ASME (1975/34); Harry and Shipp (1975); IMechE (1975/24, 1977/43); R.S. Morrow (1975); O'Dea (1975); Pekrol (1975); Schanzenbach (1975); Beebee (1976); Biggs (1976); Harker (1977); M.H. Price (1977); Irwin and Graf (1979); Broch (1980); Kitchen (1980); J.H. Maxwell (1980, 1981); API (1981 Std 678, 1986 Std 670); Crawley and Erskine (1981); L.L. Fisher (1981); Tan and Dawson (1983); Goldman (1984, 1986); Spencer and Hansen (1985); Barratt (1986); Gorter and Klijn (1986); Leblanc (1986); Goggin (1987); G.R. Kent (1989); Serridge (1990); Scheithe (1992); B. Sheppard (1992); Haq (1993); Heckman (1993); Hussain (1993); ANSI S series, ANSI S2.2–1959, ANSI S2.5–1962, ANSI S2.10–1971, ANSI S2.4–1976; BS 4675: 1976–; VDI 2056: 1964, VDI 2062: 1976
Vibration: Morse (1936–); Collacott (1947); Jacobsen and Ayre (1958); C.T. Morrow (1963); Crede (1965); R.H. Wallace (1970); Cremer and Heckle (1973); Timoshenko, Young and Weaver (1974); Meirovitch (1975); C.M. Harris and Crede (1976); Bishop and Johnson (1979); Lalanne, Berthier and der Hagopian (1983) ISO 3945: 1985

Loose parts monitoring
NRC (Appendix 28 *Loose Parts Monitoring*)

Balancing and alignment
C. Jackson (1971a,b, 1976a,b); Sandner (1978); Broch (1980); M.G. Murray (1980a); Bloch (1991) ANSI S2.7–1982; ISO 2371: 1974, ISO 2953: 1985; VDI 2060: 1966

Ultrasonics
ASTM (STP 101, 1986 E100); Filipczynski (1960); Tribolet (1964); Krautkramer and Krautkramer (1969); Newman, Ryden and Lamb (1970); Ostrofsky and Heckler (1970); Welding Institute (1971/15); Marlow (1975); Weatherburn and Clinck (1976); Browne and Constantinis (1983); Fousek (1983); Crocker (1985); Schmer and Goodman (1990); AGA (1991/71) BS 3923: 1972–, BS 4331: 1972–, BS 4124: 1991

Thermal image monitoring, thermography
Prescott (1972); H.C. Wright (1973); Bichard and Rogers (1976a,b); Norda (1976, 1977); Weismantel and Ramirez (1978); Lister (1980); Imgram and McCandless (1982); B.G. Jones and Duckett (1985); Tuss (1985); Anon. (1986m); Baker-Counsell (1986c); Anon. (1990a); Miljure (1992); B. Smith (1992)

Risk-based inspection
Ichikawa (1985,1987); Research Task Force on *Risk-Based Inspection Guidelines* (1992)

Underwater inspection
Bayliss, Short and Bax (1988)

Acoustics, acoustic emission monitoring
NRC (Appendix 28 *Acoustic Emission Monitoring*); Witt (1971a); ASTM (1972 STP 505, 1975 STP 571, 1979 STP 697, 1987 E1211, 1989 E610–89A, E1062, 1991 E569–91E1); ASME (1975/56, 128, 1982, 1983, 1989); Diehl (1975); Koerner, Lord and Deisher (1976); Nichols (1976a); Parry (1976, 1980); Bloch (1977b); Anon. (1979 LPB 27, p. 59); Fowler (1980, 1986, 1987, 1988, 1992); Fowler and Scarpellini (1980); Adam (1982); Cole (1983, 1988, 1990, 1992); L.M. Rogers and Alexander (1983); Treleaven (1983); Wylde and Shaw (1983); International Study Group on Hydrocarbon Oxidation (1985); M.P. Kelly (1985); Pollock (1986); L.M. Rogers (1986); Clough (1987); Heiple and Carpenter (1987); SPI (1987); Frieshel and Jones (1988); Prasek (1988); Zhang (1988); AGA (1989/62, 63);

Monsanto Corp. (1990); AAR (1991); Cole and Hunter (1991); Hewerdine (1991, 1993); Vahaviolos, Pollock and Lew (1991); Gandy and Bailey (1992); Bouchard, Payne and Szysko (1994)

Strain measurement
Shannon (1973); L.M. Rogers (1976)

Electrical resistance measurement
Moreland (1976)

Holography
Butters (1971); H.M. Smith (1975)

Wear monitoring, oil analysis, debris examination
Bond (1965); A.E. Davies (1972); Drust (1972); M.G. Murray (1975); D. Scott (1975); Collacott (1976a,b, 1977b); Ricca and Bradshaw (1984); Wilkie (1987a); Rudston (1989)

Radioactive tracers
Brennan (1962); Charlton (1976)

Corrosion monitoring
Ailor (1971); R. Lee (1972); Luddeke (1975); Hancock and Clifton (1976); Rowlands and Moreland (1976); Arnold (1978); Harrell (1978); Hines (1978); Moreland and Hines (1978); Rak (1978); Whitney (1978); Rothwell (1979); Anon. (1981d); Strutt, Robinson and Turner (1981); Biarnes (1982); Sague and Davis (1982); Asher *et al.* (1983); Dawson, Eden and Hladky (1983); Diacci, Rizzi and Ronchetti (1983); M.J. Robinson and Strutt (1983); Baker-Counsell (1985b,g); Gregory (1985); M. Turner and King (1986).

External corrosion: Batterham (1985)

Interpretation
Welding Institute (1969, 1972/19); D. Scott and Smith (1975); Bellingham and Lees (1976a,b); Boogaard (1976); IMechE (1976/31); Collacott (1977b)

were covered by specific regulations and those that are not. In general, with the former the letter of the law applied, whilst with the latter the degree of flexibility based on engineering judgement was rather greater.

One aspect that is of particular importance is the inspection interval. Basic statutory inspection intervals were 14 months for steam boilers and 26 months for large steam boilers, steam receivers and air receivers. In principle, dispensations for longer intervals might be granted by the Health and Safety Executive (HSE), but these were difficult to obtain and it remained the case that the statutory inspection intervals for these items are an inhibiting factor in industry.

As described in Chapter 12, the Pressure Systems Regulations extend the scope of pressure systems to cover essentially all systems that depart significantly from atmospheric pressure. They create a requirement for a formal system of records and examinations. Regulation 5 requires that certain information be provided about the pressure system, Regulation 8 that there be a written scheme of examination, Regulation 9 that examinations be conducted in accordance with this written scheme and Regulation 13 that records be kept.

Regulation 5 requires that sufficient information be provided about the pressure system in respect of design, construction, examination, operation and maintenance, and about any repairs or modifications made to it.

Regulation 8 requires that there be a written scheme for the periodic examination by a competent person of

(a) all protective devices;
(b) every pressure vessel and every pipeline in which (in either case) a defect may give rise to danger; and
(c) those parts of the pipework in which a defect may give rise to danger.

It states that such a scheme shall not be drawn up unless it is suitable and

(a) specifies the nature and frequency of examination;
(b) specifies any measures necessary to prepare the pressure system for safe examination other than those it would be reasonable to expect the user (in the case of an installed system) or owner (in the case of a mobile system) to take without specialist advice; and
(c) where appropriate, provides for an examination to be carried out before the pressure system is used for the first time.

Before the regulations were made, there was much discussion as to how 'pipework' should be covered. The term has been widely defined but the *Guidance* states that the effect of Regulation 8 and of COP 37 is to exclude most 'pipework' from the written scheme.

In contrast to the legislation which they replace, the regulations do not give specifed intervals for any equipment; the intervals formerly specified for steam boilers and for steam and air receivers are not carried forward. In practice, however, these intervals are often retained in examination schemes.

Regulation 9 requires that the examination be performed by a competent person and that a written report be produced of the examination. The report should: state which parts have been examined, the condition of the parts and the results of the examination; specify any repairs or modification required and the date by which they should be done; give the date beyond which the equipment should not be operated without further examination and state whether the scheme of examination is suitable or whether it needs modification, and if so why.

Regulation 13 requires that records be kept which include: the basic information specified in Regulation 5; the report of the last examination; the previous reports where they contain information on whether the system is safe to operate or whether any repairs or modifications to the system can be carried out safely and information on any postponement of an inspection beyond the previously specified date.

The statutory controls are not the only external influence which industry has to consider. Adherence to a system similar to the statutory one is generally a condition of obtaining insurance. Much inspection of process plant is in fact carried out by insurers.

19.2.2 Inspection bodies

There are a number of parties who may conduct inspection of a pressure vessel during its manufacture. They include (1) government, (2) the manufacturer, (3) the user, (4) an insurer and (5) a consultant. The same set of parties, except for the manufacturer, may undertake inspection during operation.

Government inspection may be undertaken for two rather different purposes. One is to assure the quality of the government's own purchases, and the other is for regulatory purposes.

In the United Kingdom, the requirements of government, particularly in defence, have greatly influenced the evolution of inspection systems. Mention should be made in particular of the Aeronautical Inspection Directorate (AID), renamed in 1969 the Aeronautical Quality Assurance Directorate (AQD), which has developed an inspection system which is the basis of many contracts by government and by other organizations. Some basic principles of the system are that: there must be verification that every requirement of every specification and drawing has been met; there is a complete chain of responsibility for inspection at every stage and there are full inspection records. The manufacturer's inspection system has to be approved. His subcontractors also have to be approved or else special arrangements made. The full requirements of the system are expensive, however, so that a user who does not require this degree of control may adopt a modified system.

It will be apparent that this system was a forerunner of the QA systems, based on BS 5750 and ISO 9000, which are now becoming widespread throughout industry.

A different type of government involvement is inspection by government inspectors in relation to statutory requirements under such legislation as the Factories Act 1961 or the Nuclear Installations Act 1959.

The manufacturer usually has his own inspection system to assure quality. In some cases, the user may be involved in specifying the type of inspection system which the manufacturer should operate. Often the user sends his inspectors to carry out inspections of the equipment during its manufacture. This is routine procedure with large oil and chemical companies.

Pressure vessels are often built to the survey of insurers, particularly in the oil and chemical industries. The oldest and best known insurance organization is Lloyds of London and the certification 100 Al at Lloyds is an accepted cachet of high quality.

Inspection is also carried out by consultant engineers, some of whom specialize in this work.

19.2.3 Approval organizations

In the United Kingdom, the *Report of the Committee of Enquiry on Pressure Vessels* (Ministry of Technology, 1969a) led to the setting up of the Pressure Vessel Quality Assurance Board (PVQAB) in 1981. The PVQAB operates a system of approval for inspection organizations.

In the United States, an approval system is operated by the National Board of Boiler and Pressure Vessel Inspectors (the National Board).

19.2.4 Inspection organization

Within the company, it is essential to have a management system which ensures effective control of all aspects of the plant, and in particular of the pressure system, throughout all the stages of its life. Such a management system was described in Chapter 6.

The inspection organization plays a key role in this system. It is responsible for the initial inspection of new equipment during its fabrication and construction, and for the periodic inspection of operating equipment throughout its working life.

The framework within which the inspection organization operates is determined by the design and operating authorities. The design authority should determine the parameters within which the plant is to operate, should specify the design codes and should carry out the actual design. It should also specify the standards for fabrication, construction and testing and should prescribe the documentation required on these aspects. The operating authority should provide a code for the regular inspection of the plant. In addition, it should create a system to control both plant and process modifications.

The inspection organization may be a part of the design authority or it may be an external body such as an engineering inspection agency or an insurance company, but whatever arrangement is adopted the inspection organization should be independent of the operating authority.

In many cases, the inspection work is divided between the company's own inspection organization and an external inspection agency. In particular, outside inspectors are commonly used to carry out the statutory inspections of steam boilers and receivers and air receivers.

The inspection organization is concerned normally with pressure vessels, pipework and protective devices. The inspection of many other types of equipment such as rotating machinery or instrumentation is carried out by the appropriate specialists, who are usually not part of the inspection organization.

19.2.5 Competent persons

Inspection is a specialist matter and should be done only by a qualified inspector. For statutory equipment such as steam boilers, the competence of the inspector has been a specific requirement of the Factories Act 1961, section 33(9).

The question of the competent person for the inspection of boilers and pressure vessels was considered in the *Report of the Advisory Committee on the Examination of Steam Boilers in Industry* (Honeyman, 1960) (the *Honeyman Report*). The report states in connection with the requirement for a competent person:

> What appears to be contemplated is that the person should have such practical and theoretical knowledge and actual experience of the type of machinery or plant which he has to examine as will enable him to detect defects or weaknesses which it is the purpose of the examination to discover and to assess their importance in relation to the strength and functions of the particular machinery or plant.

The Pressure Systems Regulations 1989 require that certain functions such as approval of the scheme of examination for pressure vessels be done by a competent person. This is discussed further in Section 19.3.

19.2.6 Inspection in manufacture and operation

Inspection activities cover the stages of (1) manufacture, (2) commissioning and (3) operation. It is hardly necessary to emphasize that the existence of an inspection system and the presence of an inspector has an important influence on the quality of the work done. Frequently the function of inspection is combined with that of progressing the work, since this has been found to be an effective way of reducing lead times.

An important aspect of inspection is planning. Specifications and drawings should be made available to the inspector as early as possible so that he can plan the stages

of inspection. The inspector should try to make sure that the manufacturer's personnel are fully informed of the inspections required at the different stages of fabrication. The inspection of features such as the base metal properties and the dimensions of components should be timed to fit in with the overall fabrication schedule.

The results of inspections should be recorded as detailed inspection/test reports, but in addition it is normal to issue release notes or inspection statements, which are less detailed, or, in the case of non-acceptance, a rejection note.

The inspection of welds and other features is discussed below.

Inspection of pressure vessels during commissioning covers essentially similar features together with pressure and leak tests and other commissioning tests as described in Sections 19.7 and 19.8.

Inspection of pressure vessels during operations is carried out regularly according to a system such as that defined in Section 19.3. This relies basically on visual examination supplemented by other methods of non-destructive examination and non-destructive testing (NDT) and by condition monitoring methods. In some cases, pressure testing is necessary.

The basic principles of inspection apply also to the inspection of other equipment such as rotating machinery. In this case, however, the inspection is particularly concerned with checking the condition of the main components of the machine, the performance of the machine under the various test conditions specified and the alignment and balancing of the installed machine, as well as the condition and performance of ancillary equipment such as lubrication systems.

A certain amount of information is available in the human factors literature on errors in inspection. The main finding is that the probability of detecting a defect decreases as the probability of the defect decreases.

19.2.7 Inspection of welds

One of the most important aspects of the inspection of pressure vessels is checking the quality of welds. The methods of welding were described in Chapter 12. Minimum inspection requirements for the fabrication of welds are laid down in BS 5500: 1991 and other standards. Welds are also one of the main aspects inspected in regular inspections during operation.

An inspection system exercises control of weld quality by (1) approval of welders, (2) specification of welding materials, (3) specification of welding methods, and (4) examination/testing of welds.

There are standard qualifications and tests for various classes of welder, including BS 1295: 1987, BS 4872: 1976– and the American Society of Mechanical Engineers (ASME) *Boiler and Pressure Vessel Code, Section IX*. In general, a welding method is specified, giving details of electrodes, welding rods, flux, shielding, metal preparation, actual welding, heat treatment and testing.

Visual examination of a weld should ensure (Pilborough, 1971):

(1) freedom from undercut, cracks, craters, blowholes and marked irregularities;
(2) correct profile;
(3) good appearance – a smooth even finish and freedom from pockets will avoid the possibility of stress concentrations leading to cracking;
(4) smooth joints where new electrodes have been started;
(5) good penetration at the root of the weld, as judged from the bead on the underside (in the case of a butt weld) prior to the application of the sealing run.

Illustrations of typical weld defects are given in BS 499: 1980 – *Welding Terms and Symbols*.

In some cases pressure vessels are fabricated on site, because they are too large to be transported. The conditions of site fabrication often make it advisable to carry out more comprehensive checks on materials and welds than the minimum code requirements.

19.2.8 Inspection of other features

Other features that are examined in pressure vessel inspection include:

(1) equipment dimensions;
(2) base metal;
(3) surface condition;
(4) wear situations;
(5) high stress situations;
(6) dissimilar metals;
(7) stray electric currents;
(8) gaskets, seals and joints;
(9) lagging;
(10) protective finishes;
(11) venting and draining;
(12) access.

The inspection should check that the dimensions of the equipment are within the permitted tolerances, that the base metal used is that specified, and that it has met the requirements. The condition of the metal surface should be inspected for defects that may give rise to crack growth. A check should be made on assemblies which may be subject to wear and on stress raisers such as sharp angles, changes of section and attachments such as nozzles or lugs. The presence of dissimilar metals and stray electric currents that may give rise to corrosion should be considered. The suitability of joints, gaskets and seals should be checked, as should that of the lagging and protective finishes. The adequacies of the vents and drains on the vessel should be confirmed and the means of access reviewed.

Other aspects of inspection, such as tests during commissioning and pressure and leak testing, are considered in Sections 19.1, 19.7 and 19.8, respectively.

19.2.9 Inspection register and records

It is essential to keep a register of the equipment to be inspected and records of the results of the inspections. The precise contents of the register depend on the item concerned, but in general should include:

(1) identification number, order number and drawing number;
(2) specification, design parameters, process fluids;
(3) inspection/test reports during manufacture;
(4) inspection category, interval, method;
(5) special features relevant to deterioration, failures;
(6) materials/parts list;
(7) design life/remnant life prediction;
(8) date of entry into service.

Such a register is equally appropriate to pressure vessels, protective devices, rotating machinery or instrumentation.

The specific information requirements given in the Institute of Petroleum (IP) *Pressure Vessel Examination Code* for the registration of pressure vessels are described in Section 19.3.

For a pressure vessel there should be full information on the inspections/tests done during its manufacture, including reports on tests on the material of construction, radiographs or other records of tests on welds, and reports on pressure and leak tests.

Reports of the regular inspections/tests on the equipment should be prepared and filed in the register. These reports should generally cover the results of the main inspection/test and of any additional monitoring and tests, any deterioration or failure detected and repairs carried out, and any modifications or changes of duty.

19.3 Pressure Vessel Inspection

The inspection of pressure vessels and their protective devices is crucial to the maintenance of the integrity of the pressure system and is a principal activity of the inspection authority.

Pressure vessels come within the Pressure Systems Regulations 1989 and are covered in the guidance HS(R) 30 and in COP 37. A relevant code is the *Pressure Vessel Examination Code* by the IP (1993 MCSP Pt 12). The account of pressure vessel inspection given here is based primarily on this code.

19.3.1 Competent person

The IP *Pressure Vessel Examination Code* defines the competent person as the person or body authorized by the user to draw up or approve the scheme of examination and to perform the examination. In the United Kingdom, the competent person may be company personnel or an external body specializing in the inspection of pressure vessels. The attributes of the competent person are given in COP 37.

19.3.2 Design authority

The design of the pressure vessel is the responsibility of the design authority. The IP *Pressure Vessel Examination Code* states that the design authority may be a vessel design group responsible to the user, an authorized design contractor, an independent design consultant, the engineering authority or the competent person. In some countries, the design authority is a state agency.

19.3.3 Engineering authority

The engineering authority is responsible for the maintenance of the pressure vessel and is authorized to do this by the user.

19.3.4 Definition

In considering an inspection scheme, it is necessary first to define the equipment which is to be brought within the scope of the pressure vessel inspection system. The IP *Pressure Vessel Examination Code* defines a pressure vessel as follows:

> A closed vessel consisting of one or more independent chambers, any or each of which may be subject to an internal pressure greater than 0.5 barg, or as defined by National Legislation.

The code explicitly excludes vessels subject to pressure solely by static head and storage tanks designed and constructed to codes and standards such as BS 2654 and BS 2594.

This definition of a pressure vessel supersedes that given in the previous *Pressure Vessel Inspection Safety Code* by the IP (1976 MCSPPt 12) which was:

> (i) A closed vessel of not less than 0.1 m^3 capacity consisting of one or more independent chambers any or each of which may be subject to an internal pressure greater than 70 mbar gauge or less than 930 mbar absolute or
>
> (ii) A closed vessel wherein $P \times V > 1$ where P is the internal pressure in bars and V is the enclosed volume in cubic metres.

Also of interest is the definition given in the ICI *Pressure Vessel Inspection Code* for vessels falling within the scope of that code:

> A pressure vessel is a closed vessel of any capacity consisting of one or more independent chambers, any or each of which is or may be subjected to internal pressure greater or less than atmospheric.

This definition includes:

> (a) Vessels not normally subject to internal pressure but in which internal pressure would occur in the event of a failure of any part, maloperation, isolation or other circumstances, for example, the failure of an internal steam coil in a vessel not adequately vented to prevent a pressure rise.
>
> (b) Vessels in which vacuum can develop, for example, steam receivers, steam condensers and other vessels containing condensable gases and vapours.

For other equipment the code states:

> Consideration should also be given to the registration and routine inspection of other items which although not normally classified as pressure vessels may give rise to hazardous situations, e.g. fired equipment, large diameter piping, expansion bellows, and pressurized equipment subjected to erosive or corrosive conditions. Where cross-country pipelines are employed special arrangements will be necessary for their routine examination.

The *IP Pressure Vessel Examination Code* defines a protective device as:

> A device designed to protect the pressure system against system failure and certain devices designed to give warning that system failure might occur, safety valves, bursting discs or combination of both.

The definition of a protective device given in the ICI *Pressure Vessel Inspection Code* is:

> Any automatic device which protects equipment from over-pressure, over-temperature, over-filling, corrosion, explosion or other hazardous conditions; including atmospheric vents, lutes, flame traps, deadweight flaps, some non-return valves, relief valves, fusible plugs, bursting discs and instrumental trip systems, many of which incorporate an advance alarm indication.

The ICI *Code* also lists equipment which, subject to approval, may be excluded from the requirements of the code itself, although it may still require some degree of inspection. Some important items in this list are vessels subject to static head only or to applied pressure not exceeding +0.07 bar (+1 $lb_f/in.^2$) and not subject to corrosive risks; parts of prime movers and machines driven by them; protective devices whose failure does not result in a hazard.

19.3.5 Registration

A pressure vessel identified as such should be registered before it is brought into service. The system given by the IP *Pressure Vessel Examination Code* is broadly as follows.

The vessel should be given an identification number and there should be created for it a records file and, where applicable, a scheme of examination.

The required contents of a records file as described in the IP *Code* are essentially similar to those given in the ICI *Pressure Vessel Inspection Code*, which are as follows:

> For equipment the file shall include its identification number, the order number, the drawing reference, specifications, materials lists, inspection reports during manufacture, test certificates relating to the material and tests on the completed equipment. It shall also contain details of the design conditions, the process fluids, of the expected operating conditions, and the date of entry into service. In addition, the file shall include a note of any special kinds of deterioration – for example, stress corrosion – to which the equipment may be subject.

The IP *Code* requires that the information include the safe operating limits of the vessel and, where available, the limit criteria for its retirement with notes on their derivation.

The record file should give the equipment classification and inspection categories. It should specify the initial and subsequent inspection intervals, the type of inspection to be done and, where appropriate, the inspection acceptance standards.

To this initial information should be added other relevant information generated during the life of the equipment. This includes: reports of periodic inspections and tests; reports of failures, failure examinations and repairs; records of corrosion and other condition monitoring and details of modifications or changes of duty. Where a document cannot be kept in the record file itself, there should be a cross-reference to it.

The registration of protective devices is along broadly similar lines. The IP *Code* requires that its record file contain information on its function and operation, including drawings, a specification of the duty, supplier's details on the style and type of device, materials of construction and any special features, together with reports of examinations and tests.

19.3.6 Classification

A pressure vessel is generally classified according to whether or not it is subject to legal requirements for inspection. The IP *Pressure Vessel Examination Code* assigns a vessel to Classification A or B. Class A includes all vessels and their protective devices that are subject to periodic examination in accordance with national or regional legal requirements. The extent of the classification is therefore a function of the country or state where the vessel is to be used. Class B includes all vessels and their protective devices not assigned to Class A. It covers all vessels which are not subject to legal requirements.

Where the legal requirements permit, Class A pressure vessels and protective devices should be further allocated to a grade, namely to Grade 0, 1, 2 or 3, as described in Section 19.3.7.

The code states that the regulatory requirements in the United Kingdom are primarily aimed at ensuring the periodic examination of equipment which contains significant quantities of stored energy from compressible fluids and that many items of equipment which contain flammable or toxic liquids are effectively exempt, but that such examination is nevertheless beneficial, and it suggests that the inspection philosophy described for Class A equipment be applied to Class B equipment also.

19.3.7 Grading

As stated above, the IP *Pressure Vessel Examination Code* requires that, where legal requirements permit, the pressure vessel and its protective device be allocated to a grade. The grade indicates the maximum interval that may elapse between major examinations.

The principles of grading are that: the vessel receives a pre-commissioning examination before entering service; it is initially allocated to Grade 0 and is given a first thorough examination after a relatively short period of service; it is then either retained in Grade 0 or allocated to Grade 1 or 2; subsequently, after a second thorough examination, it is allocated to Grade 1, 2 or 3 and, as it approaches the end of its design life or predicted remaining life, it is reallocated to a lower grade if necessary.

Equipment is allocated to Grade 0 when it first enters service and also where the foreseeable deterioration is at a fairly rapid rate, but still consistent with this grade, or where there is insufficient knowledge of operational effects to predict its behaviour in service.

Equipment is allocated to Grades 1 or 2 where deterioration is at a rate that is predictable and consistent with the grade, the knowledge of its actual behaviour justifies allocation to the grade or where there are reliable means of assessing the operational effects and/or the associated deterioration.

Equipment is allocated to Grade 3 where deterioration is at a rate that is low and consistent with the grade, or the knowledge of actual service conditions justifies allocation to the grade.

Transfer between grades, either upwards or downwards, is made on the basis of the examinations.

A variation to this procedure may be used where a group of vessels are substantially the same with regard to design and construction and to conditions of service so that they may reasonably be expected to deteriorate in a similar way and, where the appropriate grade is Grade 1 or above, grading may be based on sample examinations of vessels in the group. The IP *Code* gives the rules governing this procedure.

Another permitted variation applies where a substantially new vessel is the same with regard to design and construction as an existing vessel and is to be used under the same, known conditions of service. In this case, the vessel may be allocated the same grade as the existing vessel.

A grading review of a vessel is required in any one of the following circumstances: (1) there is a significant change in its conditions of service; (2) an abnormal incident has

occurred which could affect its deterioration; (3) on-line inspection indicates a significant change in its condition or (4) it is approaching its design life, or it is proposed to extend its service life beyond the design value.

The grading of protective devices is subject to two general principles. The interval between examinations for the device should not exceed that for the vessel protected and it should not exceed that given in Section 19.3.8. Factors which govern the inspection interval are discussed in Chapter 13.

19.3.8 Examination intervals

The maximum examination intervals given in the IP *Pressure Vessel Examination Code* are shown in Table 19.10, Section A. The longest of these maximum intervals is therefore 144 months, or 12 years. On the basis of the classification of equipment it is possible to specify inspection categories that define the interval between inspections.

19.3.9 Examination principles

The IP *Pressure Vessel Examination Code* states that the purpose of examination is:

> To ensure that equipment remains in a satisfactory condition for continued operation consistent with the prime requirements of safety, compliance with statutory regulations and economic operation until the next examination.

The code distinguishes between the pre-commissioning examination, the first examination (after the vessel has been put into service) and subsequent examinations. The purpose of the pre-commissioning examination is to ensure that the examination and tests specified for the manufacture of the equipment have been done, that the documentation is in place with a record of any significant defects, that there is a basis for the assessment of deterioration in future examinations and that a check is made to ensure that no damage has occurred since the examination during manufacture. The first in-service examination is done to ensure that any defect in design or materials is detected and that suitable components are selected, examined and measured, so as to form the basis for the assessment of corrosion or wastage in future examinations.

The ICI *Pressure Vessel Inspection Code* defines the objectives of inspection as follows:

> The objective of vessel inspection is to detect any deterioration such as corrosion, cracking or distortion indicating possible weaknesses that may affect the continued safe operation of the vessel. Primarily inspection should be visual, but it shall be supplemented by other techniques and measurement when necessary to determine the extent of any losses of thickness, pitting, cracking, etc. Resorting to a pressure test as the sole method of periodic inspection is an inferior alternative to examination and should be used only when examination is not practicable or the findings of the visual examination are inconclusive.

The inspection should also include an examination of protective devices.

19.3.10 Examination practices: pressure vessels

The maximum interval between examinations is set by the grade to which the vessel is allocated. The IP *Pressure Vessel Examination Code* gives a number of additional factors that are to be taken into account in deciding on the actual interval. These include: any regulatory requirements; the works policy; the severity of the duty; the performance of other vessels on similar duty; the ability to carry out meaningful on-stream inspection and the remaining design life and the predicted remaining life. Other factors in particular applications are catalyst life and regeneration intervals, and performance of internal linings. It is also necessary to consider the consequences of failure.

The IP *Code* also refers by way of caution to three aspects that may require special attention: (1) lined vessels; (2) internal fittings and (3) external lagging, cladding and fireproofing. Lining failure may cause a vessel to deteriorate rapidly and this should be taken into account in setting the examination interval. Internal fittings hinder inspection and are often difficult to remove, but may also promote deterioration; they should be removed as necessary to permit adequate examination. Parts of the outer shell and

Table 19.10 *Maximum examination intervals for pressure vessels, protective devices and piping systems (Institute of Petroleum, 1993 MCSP Pts 12 and 13) (Reproduced by permission)*

A Pressure vessels and protective devices

Equipment	*Recommended maximum examination period* (months)			
	Grade 0	*Grade 1*	*Grade 2*	*Grade 3*
Process pressure vessels and heat exchangers	36	48	84	144
Process storage vessels	60	72	108	144
Protective devices	24	36	72	–

B Piping systems

Equipment	*Recommended maximum examination period* (months)			
	Grade 0	*Grade 1*	*Grade 2*	*Grade 3*
Piping systems	36	48	84	144

features such as anchor bolts, skirt attachments and saddle support surfaces may need to be checked at each examination. Sections of lagging or fireproofing may need to be removed for examination where conditions favourable to external corrosion exist.

There are various preparatory measures that need to be taken before an inspection is carried out. The inspector should brief himself on the history of the vessel and, where applicable, on that of other similar vessels.

The vessel is normally taken out of service, isolated, emptied and cleaned. The surfaces of the vessel are then exposed and prepared for examination. This may involve such measures as cleaning of internal surfaces, the removal of some internal fittings and the removal of lagging from the outside of the vessel. These activities should be covered by appropriate procedures and permit-to-work systems, as described in Chapter 21. The examination is then carried out.

The matters to be recorded following the examination are given in the IP *Code*. They should cover: the scope of the examination; the items examined and the examination techniques used; a qualitative description of the findings backed up by a quantitative measure; a specification of any repairs or modifications required; relevant repair and non-destructive examination procedures; a note of any changes to the safe operating limits or any remaining life predictions; a review of the scheme of examination and the grading previously selected and a date for the next examination. The *Code* gives an appendix containing examples of examination reports.

The IP *Code* recognizes the value of on-stream methods of examination, but states that in general they complement rather than replace visual examination.

19.3.11 Examination practices: protective devices

The IP *Pressure Vessel Examination Code* divides protective systems into pressure-actuated devices and other devices. In the former category it discusses regular safety valves, pilot-operated safety valves and bursting discs.

For a safety valve, the code requires that the valve be removed, immediately tested on a suitable test rig to determine the pressure at which the valve would have lifted in service and the results recorded. The valve should then be dismantled, cleaned, repaired, restored, lapped and reset to the correct cold differential test pressure. For pilot-operated safety valves, where it is not normally practical to remove the main valve, the testing is confined to the pilot valve.

In the second category the IP *Code* deals with: fusible plugs; thermal sensors, alarms and trips; sensors and alarms on other variables and non-return valves.

The *Code* also discusses the need to maintain adequate overpressure protection of the vessel at all times and the isolation practices necessary to achieve this.

19.3.12 Modification and repair

The *IP Pressure Vessel Examination Code* requires that any modification necessary on a pressure vessel should be approved by the design authority and the competent person, and that the design and execution of any modification or repair be under the control of the latter. The effect on any protective devices on the piping system of any modifications or repairs on that system should be considered.

Records should be kept of any modifications or repairs carried out, and should include the original approval procedure documents together with details of materials and techniques, drawings and test certificates.

Where a vessel has been subject in its construction to stress relief or heat treatment, welding should not be undertaken without the approval of the competent person.

19.3.13 Vessel testing

The *IP Pressure Vessel Examination* Code discusses five forms of testing: (1) strength testing, (2) leak testing, (3) NDT, (4) destructive testing and (5) materials analysis. Any of these may be used at the various stages of the vessel's life, but the last two are used mainly at the construction stage or in connection with modification or repair.

Pressure and leak testing are considered in Sections 19.7 and 19.8, respectively.

19.3.14 Defects and failures

An account of defects and failures in pressure vessels is given by Pilborough (1989). Some of the features that may be revealed by an inspection are:

(1) internal corrosion;
(2) surface defects;
(3) weld defects;
(4) wear defects;
(5) deposits and debris;
(6) high stress situations;
(7) inadequate drainage;
(8) external corrosion.

Some of the types of internal corrosion that occur in process plant were described in Chapter 12. Corrosion may reduce not only the thickness of the metal but also its strength. Methods of detection include visual examination, thickness measurement, including measurements by ultrasound and corrosion monitoring. Changes to a base metal such as graphitization or hydrogen embrittlement may be detected by metallurgical examination.

Surface defects such as cracks or pitting arising from such causes as corrosion, erosion or crack growth may be detected by visual examination or by methods such as magnetic particle or dye penetrant techniques. The avoidance of surface defects is particularly important where there is a risk of fatigue failure, since a rough surface can greatly reduce the fatigue strength of steel.

These methods of crack detection may also be used to find weld defects. The latter include weld deterioration, which may arise due to the roughness of the weld, or weld decay, which is intergranular corrosion and occurs in austenitic stainless steels.

Cracks may be particularly serious as they can grow and lead to failure. It is often possible to remove a crack from a weld by chipping it out and depositing fresh weld metal. Small cracks may sometimes be stopped by drilling small holes at the extremity, which reduces the stress concentrations.

Wear on moving parts is normally found by visual examination and may result in failure if not rectified.

The build-up of deposits of materials and/or debris can create a hazard if equipment such as pipes and valves, or devices such as vents, pressure relief valves or instruments become blocked. Such deposits are revealed by visual examination.

There are certain undesirable features which, insofar as is practicable, are eliminated in the original design of equipment, but which may be reintroduced by plant modifications. High stress situations may have been created at vessel connections or at lugs. There may be elements that

are under stress due to the limitation of thermal expansion or contraction. Similarly, modifications may have been made which impede complete drainage. Visual examination may detect these facts.

External corrosion of the plant is detected by visual examination. It can be severe and can lead to serious loss of metal thickness.

19.4 Pressure Piping Systems Inspection

Most releases occur not from pressure vessels but from the associated piping systems. Inspection of piping systems is therefore important. Pressure piping systems come within the Pressure Systems Regulations 1989 and are covered in the guidance HS(R) 30 and in COP 37. A relevant code is *Pressure Piping Systems Examination Code* (IP, 1993 MCSP Pt 13). The account of pressure piping systems inspection given here is based primarily on this code. The provisions of this code largely mirror those of the *Pressure Vessel Examination Code* (IP, 1993 MCSP Pt 12), and to the extent that this is so they are not repeated here.

The definitions of the competent person, the design authority and the engineering authority for piping systems are essentially the same as those for pressure vessels, with the former term being substituted for the latter one.

19.4.1 Selection

The process of selecting pipework for registration in the inspection system is the equivalent to the definition of pressure vessels. The IP *Pressure Piping Systems Examination Code* states that pipework need not be physically identified on site by an identification number provided the major plant items are so marked that pressure piping attached to them can be identified.

The criteria for selecting piping for registration are that there is a legal requirement or that the piping is known or suspected to deteriorate and its failure would give rise to an unacceptable situation.

19.4.2 Registration

For new piping the IP *Pressure Piping Systems Examination Code* recommends that the records file contain the identification number, the drawing references, the isometric drawing, specifications, materials lists, the material specification, the constructional acceptance and test certificates, the design data/safe operating limits, the scheme of examination and the retirement limit criteria.

For existing piping the *Code* states that where some of the above information is not available, the recommended records are the identification number, the drawing references, an up-to-date drawing/sketch defining the extent of the system, the piping specification to which repairs or modifications should conform, the design data/safe operating limits, the scheme of examination and a recent assessment report.

For piping systems there is no process corresponding to that of the classification of pressure vessels, but it is necessary to make arrangements to ensure that unregistered piping systems are nevertheless examined so that they remain fit for continued service.

19.4.3 Grading

The IP *Pressure Piping Systems Examination Code* states that, where legal requirements permit, a registered piping system should be allocated to a grade.

The principles of grading are that: the piping system receives a pre-commissioning examination before entering service; it is allocated to Grade 0 unless knowledge of service conditions is such that it can be allocated to Grade 1 or 2; subsequently, following the first and second thorough inspections and on the basis of knowledge of service conditions and of the condition of the piping system, it is allocated to Grade 1, 2 or 3 and as it approaches the end of its design life or predicted remaining life it is reallocated, where necessary, to a lower grade.

The detailed rules for grade allocation and grading review of piping systems given in the *Code* are essentially similar to those for pressure vessels. For protective devices, the code refers to the IP *Pressure Vessel Examination Code*.

19.4.4 Examination intervals

The maximum examination intervals prescribed by the IP *Pressure Piping Systems Examination Code* are given in Table 19.10, Section B. The longest of these intervals is thus 144 months, or 12 years.

19.4.5 Examination principles

The purpose of the examination of piping systems given by the IP *Pressure Piping Systems Examination Code* is essentially the same as for pressure vessels.

The *Code* distinguishes between the pre-commissioning examination, the first examination (after the piping system has been put into service) and subsequent examinations. For the former it also draws a distinction between new and existing installations. For new installations the purpose of the pre-commissioning examination is to ensure that the examination and tests specified have been done and that the documentation is in place, whilst for an existing installation it is to establish any history of deterioration and to ensure that the condition of the pipework is surveyed. The first in-service examination is done to ensure that any defect in design, fabrication or materials is detected and that suitable components are selected, examined and measured, and the results recorded, so as to form the basis for the assessment of corrosion or wastage in future examinations.

19.4.6 Examination practices

The maximum interval between examinations is set by the grade to which the piping system is allocated. The IP *Pressure Piping Systems Examination Code* gives in Appendix A a number of additional factors which are to be taken into account in deciding on the actual interval. They include: any regulatory requirements; the age and general condition; the severity of the duty, in terms of corrosion, erosion and vibration; the proximity to systems containing corrosive fluids; any abnormal flows; any vulnerable components such as bellows and expansion joints and small bore connections; the pipework supports; any special features and the ability to carry out meaningful on-stream inspection. It is also necessary to consider the consequences of failure.

Any necessary preparatory measures should be taken before an examination is carried out. These may include the provision of a means of access and lighting and preparation of surfaces.

The matters to be recorded following the examination are given in the IP *Code*. They should cover: the scope of the examination; the items examined and the examination techniques used; a qualitative description of the findings,

backed up by a quantitative measure; a specification of any repairs, renewals or modifications required; the relevant repair and NDE procedures; any changes to the safe operating limits or any remaining life predictions; a review of the scheme of examination and of the grading previously selected and a date for the next examination.

The IP *Code* also refers by way of caution to several aspects that may require special attention: (1) lined pipes; (2) external lagging and fireproofing; (3) valves and fittings; (4) buried piping and (5) bellows. The considerations relevant to lined pipe and external lagging and fireproofing are broadly similar to those pertaining to pressure vessels. Valves and fittings need special consideration on account of possible casting defects, regions of high turbulence, local stress concentrations due to thermal expansion and other stresses and vibration. Buried pipelines are usually protected from external corrosion by cathodic protection (CP), but there are vulnerable areas near ground level where protection can break down and corrosion occurs. The CP systems themselves should be subject to periodic examination and a record kept of the CP potentials. Consideration should be given to the inspection of the inside of the pipeline by an 'intelligent pig'. Bellows should be examined immediately after commissioning to check: that the relative movement is being absorbed as intended and examined periodically to look for cracks or leaks; for any distortion or yielding of anchors or seizing or binding of guides; for any unanticipated movement of the parent piping and for any permanent distortion of the bellows.

If the pipework has been subjected to any abnormal operating conditions or other abnormal conditions such as fire, appropriate checks should be made. Possible causes of deterioration may be: damage to bellows; cracking of ferritic alloy or austenitic stainless steels; hardening of air-hardening ferritic alloy steel or zinc embrittlement of stainless steel.

The examination practices for protective devices are essentially as given in the IP *Pressure Vessel Examination Code*.

19.4.7 On-stream examination methods

The IP *Pressure Piping Systems Examination Code* states that some piping systems may be satisfactorily examined by means of on-stream methods and gives in Appendix B guidance on methods that may be applied.

The methods described are: (A) walking the main; (B) selective and (C) extensive non-destructive testing (NDT) for thickness gauging; (D) selective and (E) extensive removal of insulation and external examination; (F) monitoring by indirect measurement; (G) use of thermal indicators and thermal imaging; (H) profile radiography and (I) flash radiography. The methods of indirect measurement cited include corrosion probes and coupons and pH recording. The thermal indicators mentioned are temperature sensitive paints or crayons. Profile radiography involves firing a beam tangential to the wall of the pipe and produces a profile image of the internal and external profile of the pipe. Flash radiography is similar but gives information on the external surface.

Features to be checked in walking the main include: damage to the pipe; damage to insulation; the condition of joints, valves and fittings; lack of adequate support; lack of ground clearance; vibration or excessive movement; leaks from or onto the pipe and abuse of the pipe.

The *Code* also gives in the same appendix the following off-stream methods: (J) hammer testing; (K) pressure testing; (L) internal examination; (M) interval viewing and (N) special techniques.

19.4.8 Modification and repair

The IP *Pressure Piping Systems Examination Code* requires that any modification made to a registered pressure system should be approved by the design authority and any repair be subject to the approval of the competent person.

The effect on any protective devices on the piping system of any modifications or repairs on that system should be considered. Following modification or repairs a grading review should be carried out.

Records should be kept of any modifications or repairs carried out, and should include the original approval procedure documents together with details of materials and techniques, drawings and test certificates.

Where there may have been in the original construction of piping system a requirement for heat treatment, a check should be made and, if it was required, reference should be made to the engineering authority or competent person who should then define any requirements.

19.4.9 Piping system testing

The account of testing given in the IP *Pressure Piping Systems Examination Code* follows essentially that given in the IP *Pressure Vessels Examination Code*, and deals mainly with strength testing by hydraulic or pneumatic pressure tests and with leak testing.

19.5 Non-destructive Testing

Non-destructive testing techniques are used to detect defects in equipment such as pressure vessels and pipework during both its construction and its operational life.

Equipment is tested by NDT testing methods during fabrication. Pressure vessel codes such as BS 5500: 1991 lay down detailed NDT requirements. These are minimum requirements. For some pressure equipment, it may be necessary to carry out more extensive testing. This is particularly the case where equipment has been fabricated on site.

It may be necessary to carry out further NDT of some equipment during construction and commissioning.

The condition of the equipment during the operation of the plant is checked by NDT, particularly, but not exclusively, during plant shut-down.

Once the plant is operational, it becomes difficult to obtain access for visual examination of some parts of the equipment, for example the internal surface of a refrigerated storage tank, so that NDT techniques that can be used externally become very attractive.

Accounts of NDT are given in *Non-Destructive Testing* (Hinsley, 1959), *Techniques of Non-Destructive Testing* (Hogarth and Blitz, 1960), *Principles and Practice of Non-Destructive Testing* (Lamble, 1962), *Non-Destructive Testing* (Birchon, 1975), *Pressure Vessel Systems* (Kohan, 1987), *Non-Destructive Testing of Large Diameter Pipe for Oil and Gas Transmission Lines* (Weisweiler and Sergeev, 1987) and *Inspection of Industrial Plant* (Pilborough, 1989).

Some NDT and monitoring methods are:

(1) visual inspection –
    (a) boroscopes;
(2) radiography –
    (a) X-rays,
    (b) γ-rays;

(3) ultrasound;
(4) magnetic methods –
  (a) magnetic particles,
  (b) magnetic prints,
  (c) eddy currents;
(5) dye penetrant methods;
(6) stress wave emission monitoring;
(7) holography;
(8) electrical measurements –
  (a) resistivity,
  (b) capacitance.

These methods are now described in more detail.

19.5.1 Visual examination

Visual examination is the original and most widely used method of inspection and is non-destructive. Accounts are given in *Visual Examination* (Keymed Industrial, 1983) and by Elonka (1975), Kohan (1987) and Pilborough (1989).

Visual inspection is effective in detecting surface defects ranging from cracks to corroded areas, and defective assemblies.

The range of visual examination can be extended by the use of aids such as periscopes or boroscopes. Boroscopes are available with lens or fibre optics. They are used to examine the condition of internal components such as the blades of turbines and compressors.

BS 5500 requires only visual examination for Category 3 pressure vessels.

19.5.2 Radiography

An important NDT method is X-ray radiography. Radiographic examination is covered by BS 2600: 1973– *General Recommendations for the Radiographic Examination of Fusion Welded Butt Joints in Steel* and in various other British Standards, some of which are given in Appendix 27. Accounts are given by Kohan (1987) and Pilborough (1989).

X-ray radiography is used during fabrication to detect internal defects, principally in welds but also in the parent material.

BS 5500 requires NDT by radiography and/or ultrasound for welded joints on Category 1 and 2 pressure vessels. Details are given below.

The X-rays used are produced by an X-ray machine which is relatively immobile and expensive. X-rays are recorded on a photographic plate. In X-ray radiography it is important that there be a high quality image. Standards generally call for a technique which is capable of recording deviations from the normal of not more than 2% of the maximum thickness of the item under test and specify the use of image quality indicators, or penetrameters. Image indicators are dealt with in BS 3971: 1980.

The interpretation of X-ray radiographs is a skilled matter and contains a considerable subjective element. The first step is to identify the type of defect and the second is to quantify it, if quantification is appropriate. The terminology and symbols for weld defects are given in BS 499: 1980 and BS 4727: Part 5, Group 01: 1985. Some of the principal defects that occur in welds are:

(1) planar defects –
  (a) cracks,
  (b) lack of fusion (side, root, interrun),
  (c) lack of root penetration;
(2) cavities –
  (a) porosity (isolated, localized, linear),
  (b) wormholes (isolated, aligned),
  (c) crater pipes,
  (d) surface cavities;
(3) slag inclusions;
(4) other solid inclusions –
  (a) tungsten,
  (b) copper.

Once a defect has been identified, it is necessary to decide whether it is sufficiently serious to require that the weld be rejected. This has again tended to be a subjective matter and has therefore caused considerable difficulty. In consequence, much work has been done to develop acceptance standards. BS 5500 contains a list of defects similar to that given above, together with corresponding acceptance levels.

X-ray radiography is used to detect internal defects in the parent metal, such as in pressure vessel walls, pipework or castings, as well as in welds.

γ-rays are also used for radiography. They are produced by a radioactive isotope source such as cobalt-60. Equipment using γ-rays is portable and relatively cheap. It is used particularly for the radiography of castings. The method is to arrange the castings in a circle with the γ-ray source in the centre and with photographic plates behind the castings. Isotope sources have a relatively large area emitting radiation (usually about 2–6 mm diameter) and therefore tend not to give such good definition as X-rays.

If a permanent record is not required, X-rays may be used with a fluorescent screen instead of a radiographic plate. X-ray fluoroscopy is widely used for the rapid inspection of components on conveyor belts in order to detect coarse defects and unwanted objects. Another technique for rapid inspection is nucleonic gauging of the thickness of materials by passing β-rays through the material.

19.5.3 Ultrasonics

Ultrasonics is another important NDT technique. This is dealt with in BS 3923: 1972– *Methods for Ultrasonic Examination of Welds*, and the terminology is given in BS 3683: Part 4: 1985. Accounts are given by Birchon (1975), Kohan (1987), Weisweiler and Sergeev (1987) and Pilborough (1989).

Ultrasonics is used during fabrication as an alternative to radiography, to detect internal defects in parent metal and in welds. It is also used to measure thickness. BS 5500 generally gives ultrasonics as an acceptable alternative to radiography for examining welded joints on Categories 1 and 2 pressure vessels.

Ultrasonic waves are generated by a transmitter and detected by a receiver and are usually displayed on an oscilloscope or recorder. Two basic techniques in ultrasonics are (1) transmission and (2) reflection.

In a transmission method the ultrasonic waves are generated by a transmitter on one side of the item under test and are detected by a receiver on the other. The method is shown in Figure 19.1 (a).

The reflection method generally uses pulsed waves that are generated by a transmitter and detected by a receiver on the same side of the item. One way in which the method may be applied is shown in Figure 19.1(b), which is known as the A scan. Another application is the B scan, which is shown in Figure 19.1(c). Both these methods give the depth of the

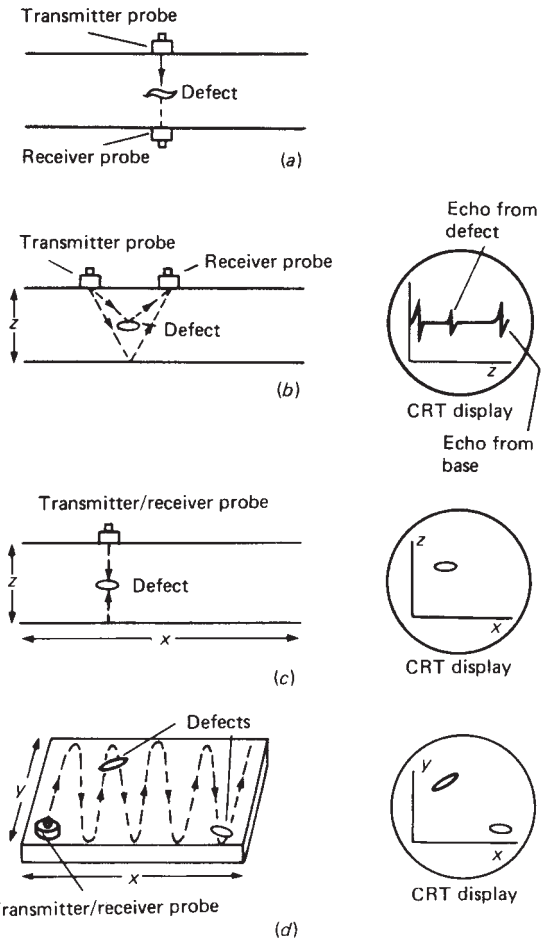

Figure 19.1 *Some ultrasonic testing methods: (a) transmission method; (b) reflection method – A scan; (c) reflection method – B scan; (d) reflection method – C scan*

defect. A third method is the C scan, shown in Figure 19.1 (d), which does not show the depth.

A number of other arrangements for the application of ultrasonics are described by Weisweiler and Sergeev (1987).

The beam of waves produced in ultrasonics is not a simple parallel bundle of uniform intensity over the cross-section, and some expertise is required in the interpretation of ultrasonic measurements.

With regard to the choice between radiographs and ultrasonic techniques for welded joints, BS 5500 states:

> Radiographic and ultrasonic methods both have advantages and disadvantages in so far as flaw detection, identification and sizing are concerned. Radiography is particularly suitable for the detection and identification of Volume' defects such as cavities and solid inclusions and incomplete penetration where a gap exists. Ultrasonic flaw detection is very suitable for the detection and sizing of planar defects such as cracks, lack of fusion and 'tight' incomplete penetration in ferritic steels. The two techniques are therefore to be regarded as complementary and the method chosen which is most suited to the particular application and material. An important consideration is joint geometry that may have an overriding influence on the choice of method. In exceptional cases it may be necessary to employ both methods on the same seam.

Ultrasonics is also used during operational inspections to detect weld defects and to measure thickness.

19.5.4 Magnetic particle methods

A method applicable mainly to surface defects is magnetic particle inspection. This is treated in BS 6072: 1981 *Method for Magnetic Particle Flaw Detection* and in several other British Standards, some of which are listed in Appendix 27. The terminology is given in BS 3683: Part 2: 1985. Accounts are given by Birchon (1975), Kohan (1987) and Pilborough (1989).

Magnetic particle methods are applicable to ferromagnetic materials and are used to detect surface and some

subsurface defects. BS 5500 gives magnetic particle techniques as an acceptable method for the testing of welds for surface defects.

There are various methods of magnetic particle testing, but the basic principle is to magnetize the item and coat it with a dry powder of iron or iron oxide particles, or, more usually, a wet powder or 'ink' of particles suspended in kerosene. The particles concentrate at places where there is no continuous magnetic path such as cracks. Defects may then be detected visually. As a further aid to visual detection, a fluorescent substance may be added to the particles and an ultraviolet lamp used. Defects show up best when they are at right angles to the lines of magnetic flux, and it is usual to test the component in two different planes. It is often necessary to demagnetize the item, which is usually done by subjecting it to a magnetic field in the reverse direction to that of the initial one and then gradually reducing the field strength.

19.5.5 Eddy current methods

Magnetic particle methods are applicable only to ferromagnetic materials. An alternative that can be used for the detection of defects in conducting materials, ferrous and non-ferrous, is eddy current testing.

Eddy current testing is dealt with in BS 3889: 1966 *Methods for Non-destructive Testing of Pipes and Tubes* and terminology is given in BS 3683: Part 5: 1965. Accounts are given by Birchon (1975), G. Johnson and McFarlan (1978), Holloway, Bauer and Pittman (1981), Kohan (1987 and Pilborough (1989).

In eddy current testing the item is subjected to an alternating magnetic field that induces eddy currents in it. These induced currents are measured and defects are detected from variations in the current.

Eddy current testing is used principally for the detection of flaws in tubes, both in production lines and on plant. Figure 19.2 shows a defect in a brass tube which passed a 1000 lb/in.^{2} hydraulic test but was detected by eddy current testing.

In the process industries, eddy current testing is used particularly on heat exchanger tubes. An account of this application is given by G. Johnson and McFarlan (1978), who describe the testing of tubes by the insertion of a probe. Defects that can be detected include pitting corrosion and wall thinning.

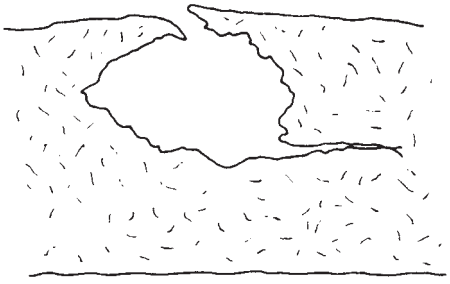

Figure 19.2 *Defect in the wall of a brass tube which had passed a hydraulic test but which was found by an eddy current test (Pilborough, 1989) (Courtesy of Gower Press)*

An account of eddy current testing of furnace and reformer tubes with emphasis on the metallurgical aspects, is given by Holloway, Bauer and Pittman (1981).

19.5.6 Dye penetrant methods

Another method for the detection of surface flaws is dye penetrant testing. This is covered in BS 6443: 1984 *Method for Penetrant Flaw Detection* and the terminology is given in BS 3683: Part 1: 1985. Accounts are given by Birchon (1975), Kohan (1987) and Pilborough (1989).

BS 5500 gives dye penetrant methods as an acceptable method of testing welds for surface defects, and requires this method, rather than magnetic particle testing, to be used for austenitic steels.

The original dye penetrant method was to immerse the item in a heated mixture of paraffin and oil, dry it and clean it, and then dust it with chalk. On cooling, the oil seeps out of any cracks in the article and stains the chalk. More modern methods use variations on this, such as special white developer and red dye.

19.5.7 Other methods

There are a growing number of other NDT methods, such as stress wave emission analysis, holography and electrical resistance methods. In some cases these techniques are used for inspection mainly during fabrication, but in others their application is to operational inspection. Some of the latter are considered in Section 19.11.

19.5.8 Non-destructive testing of welds

The distinction between different categories of pressure vessel is largely based on the extent of the NDT of welds. For vessels in Category 1, BS 5500 gives the following requirements for the examination of internal flaws:

> The full length of all Type A welds shall be examined by radiographic or ultrasonic methods. Unless otherwise agreed between the purchaser and the manufacturer (see table 1.5), the full length of all welded joints of Type B in or on pressure parts shall be examined by ultrasonic and/or radiographic methods where the thinnest part to be welded exceeds the limits given in table 5.6.4.1.1.

For the examination of surface flaws, the Standard states:

> The full length of all Type B and all other attachment welds shall be examined by magnetic particle or penetrant methods. Type A welds shall be examined by these methods when agreed between the manufacturer, the purchaser and the Inspection Authority (see table 1.5).

For vessels in Category 2 the requirements of the Standard for internal flaws are radiographic and/or ultrasonic examination of 10% of the welds at certain defined locations, the minimum length of weld to be examined at each location being 200 mm or the length of the weld, whichever is the lesser. There are also certain requirements for particular features. For surface flaws the Standard requires examination by magnetic particle and/or dye penetrant methods and states that examination is to be conducted on both of the following:

> (a) the full length of welds attaching nozzles, branches and compensating plates, to shell and end plates; (b) at least 10% of the length of all other attachment welds to pressure components.

For vessels in Category 3 the Standard does not require NDT for internal flaws unless details producing significant thickness tensile stress are used. Magnetic particle or dye penetrant methods may be used as an aid to visual examination, which is required.

19.5.9 Acceptance standards

It is difficult to overemphasize the importance of acceptance standards. Unless the increasing number of techniques that are capable of detecting defects is matched by the development of standards that define levels of defects below which no action is necessary, there is an obvious danger of unnecessarily frequent rejection.

Much work has been done on the problem by bodies such as the Welding Institute and the American Welding Society, and there is an increasing amount of guidance available.

As mentioned above, BS 5500 lists acceptance levels for certain defects. BS PD 6493: 1980 *Guidance on Some Methods for the Derivation of Acceptance Levels for Defects in Fusion Welded Joints* gives an approach based on fracture mechanics.

19.6 Materials Verification

The fact that, not infrequently, an incorrect material is used in the construction of the plant creates a requirement for inspection to identify such situations. Accounts of material verification are given by Ostrofsky (1980–) and R.J. Sherwood (1989).

The range of tests and instruments available to identify materials is described by Ostrofsky. They include (1) chemical and acid spot tests, (2) tests with tools such as a hammer and chisel or a file, (3) fracture tests, (4) eddy current tests, (5) thermoelectric characterization, (6) spark tests, (7) optical emission spectroscopy and (8) X-ray emission spectroscopy.

The author describes a number of spot tests. A more detailed account is given in *Spot Tests* (Feigel, 1958). Spot tests are also the subject of ASTM STP 550. Ostrofsky also gives details of spark tests, with an illustration of the characteristic sparks obtained with materials such as low carbon steel, high carbon steel and nickel, and of instruments for field testing which are based on some of these techniques. There are several which utilize optical emission spectroscopy. These include the Metascope referred to earlier.

A programme for verifying the materials installed in the piping of some ten plants is outlined by R.J. Sherwood (1989). Plant sections where the design required materials other than carbon steel were identified; marked-up drawings, pipework tables and inspection procedures were done; access was gained and surfaces prepared and tests were made using ultrasonics, magnetic particle detection and field analysis instruments.

19.7 Pressure Testing

It is normal to carry out a pressure test on a pressure vessel in order to check that it can be safely operated at the design pressure, but such testing is a potentially hazardous operation. Pressure testing is covered in BS 5500, in the *Pressure Vessel Examination Code* and the *Pressure Piping Systems Examination Code* by the IP (1993 MCSP Pts 12, 13), and also in the ICI *Pressure Vessel Inspection Code* (ICI/RoSPA, 1975 IS/107) and is discussed by Pilborough (1989). Safety precautions are given in these sources and in GS/4 Safety in *Pressure Testing* (HSE, 1992). Also relevant is *A Guide to the Pressure Testing of In-service Equipment* (EEMUA, 1990 Publ. 168).

BS 5500 requires that a pressure test be carried out on any vessel constructed in accordance with the Standard and that the first test should be carried out in controlled conditions with appropriate safety precautions. Adherence to BS 5500 is given in the guidance to the Pressure Systems Regulations 1989 by the HSE (1990 HS(R) 30) as a means of compliance.

The Standard requires that the pressure test procedure should be agreed at the design stage. The test should be performed in the presence of the Inspecting Authority.

19.7.1 Types of pressure test

The types of pressure test given in BS 5500 are:

(1) standard hydraulic acceptance test;
(2) pneumatic acceptance test;
(3) hydraulic proof test;
(4) combined hydraulic/pneumatic test.

A 'standard' test for acceptance is carried out on a pressure vessel where the required thickness of all pressure parts can be calculated. The object of the test is to confirm that the calculated design pressure is a safe work-ing pressure.

If it is not possible to calculate the strength of a vessel satisfactorily, a 'proof' test for acceptance may be conducted to establish a design pressure. In this case, the purpose of the test is to determine whether the expected design pressure is a safe working pressure.

In addition to these tests, which are carried out just before or after installation, there are periodic routine tests that are carried out during the operational life of the vessel.

BS 5500 gives certain basic requirements for any type of test. Factors to be considered in the choice of test method include the test fluid and the size and location of the vessel. The procedure should define any areas at risk and the controls to be applied to these.

19.7.2 Standard test pressure

The standard test pressure for a hydraulic, pneumatic or hydraulic/pneumatic test given in BS 5500 is for Category 1 and 2 vessels

$$p_t = 1.25\frac{pf_a t}{f_t(t-c)} \qquad [19.7.1]$$

where c is the corrosion allowance, f_a is the nominal design strength at the test temperature, f_t is the nominal time-independent design strength, or its nearest equivalent, at the design temperature (or the highest temperature at which time-independent strengths are given in the standard, if this is lower than the design temperature), p is the design pressure, p_t is the test pressure, and t is the nominal thickness of the section under consideration. For Category 3 vessels the standard test pressure is that given by Equation 19.7.1 or by

$$p_t = 1.5p \qquad [19.7.2]$$

whichever is the higher. Various qualifications to these test pressures are given in the standard. Other test pressures are given for proof tests.

19.7.3 Basic test method

Before any test is carried out, the vessel should be given as thorough a visual inspection as is practicable. It may also be desirable to carry out a leak test and, provided that the pressure is not raised to more than 10% of the design pressure, this may be done without the full set of precautions otherwise required for a pneumatic test.

The basic test method described in BS 5500 is to raise the pressure in the vessel gradually to 50% of the specified test pressure and thereafter to increase it in stages of approximately 10% until the test pressure is reached. The test pressure is to be maintained for 30 min, except for certain smaller vessels.

The vessel should be inspected during the test for defects, but this needs to be done with care. BS 5500 states:

> At no stage shall the vessel be approached for close inspection until the pressure has been positively reduced to a level lower than that previously attained. The pressure (s) at which the vessel will be approached for close inspection shall be specified in the test procedure. Such pressure (s) need not exceed design pressure but, if in excess of this figure, shall not exceed 95% of the pressure already obtained and held for at least 15 min.

During the test, the vessel should exhibit no sign of plastic yielding.

The test is normally carried out at about ambient temperature. The risk of brittle fracture should be assessed at the design stage. This may affect the choice of material and/or of the temperature at which the test is performed.

There are special test requirements for vessels with multiple compartments.

19.7.4 Hydraulic test

The method of pressure testing preferred in the Standard is the hydraulic rather than the pneumatic method. In the latter, the energy available is large and any failure during the test is likely to be highly explosive. This aspect is discussed in Chapter 17.

For a hydraulic test, the test fluid should normally be water, but other liquids may be utilized instead if necessary. If another liquid is used, any appropriate precautions should be observed.

Where hydraulic testing with water is not used, the reasons are generally that the vessel and the structure cannot withstand the weight of water, that the water may be difficult to remove completely or that it may freeze.

19.7.5 Pneumatic test

BS 5500 states that pneumatic testing should only be carried out

> Either on vessels of such design and construction that it is not practicable for them to be filled with liquid, or on vessels for use on processes that cannot tolerate trace liquids and where the removal of such liquids is impracticable.

Testing should only be carried out in consultation with the Inspecting Authority.

Before a pressure test is performed, BS 5500 requires that all welds that have not already been non-destructively tested should be tested by magnetic particle and/or dye penetrant methods.

All suitable precautions should be taken against the hazard of vessel failure. BS 5500 refers in particular to:

> (1) The adequacy of blast protection; (2) the extent of area cleared for test safety purposes; (3) the degree of confidence in stress analysis of vessel details; (4) the adequacy of any non-destructive testing carried out before the test; (5) the resistance of the vessel material to fast fracture; (6) the procedure to prevent local chilling during filling and emptying of the vessel and (7) the extent of remote monitoring provided during the test.

BS 5500 states that it is permissible to carry out pressure testing with air or gas up to 1.1 times the design pressure on any vessel that has satisfactorily withstood the standard hydraulic, pneumatic or combined hydraulic/pneumatic test.

19.7.6 Proof hydraulic test

In a proof hydraulic test the vessel normally is equipped with strain gauges or is covered with a strain-indicating coating. The pressure is increased gradually until either the standard test pressure for the expected design pressure is reached or significant yielding of some part occurs. From this test the design pressure and a corresponding standard test pressure can be determined. Further details are given in BS 5500.

19.7.7 Pressure testing: safety precautions

The safety precautions to be taken in the pressure testing of pressure vessels are described in GS 4.

The test should be conducted by a competent person. There should be safe systems of work covering *inter alia* the conduct of the test itself and the regular examination of the equipment used in testing, using, respectively, suitable permit-to-work systems and inspection systems. GS 4 details a number of features that should be included in these systems.

All personnel should be kept out of the test area by a system for the control of access. Personnel conducting the test should do so at a suitable distance and with facilities for remote viewing of the vessel.

Hazards which should be considered are the explosion of the vessel and ejection of blanks and plugs, of high velocity fluid jets and of dirt.

Increasingly, pressure vessels under test are monitored for acoustic emissions (AEs), this being a prime application of the technique. Further details of the method are given in Section 19.14.

19.7.8 Hydraulic testing: safety precautions

There are various precautions that should be taken before doing a hydraulic test using water. Checks should be made on the effects of static head, on the ability of the vessel and the structure to withstand the weight of water, and on the strength of any temporary pipes, connections or blanks.

The hazard of brittle fracture should be considered. In order to avoid the risk of freezing, the temperature of the water should be not less than 7°C.

If water is used with austenitic stainless steel, it is essential to control the chloride and alkali content. The ICI *Code* specifies the use of demineralized or clean condensate with a chloride content less than 1 ppm.

Measures should be taken to prevent overpressure of the vessel during the test. Accurate and reliable means of measuring the pressure should be provided in the form of a

pressure gauge that is freshly calibrated and preferably duplicated. The possibility of overpressure due to water temperature rise and expansion should be considered and, if necessary, a liquid relief valve should be provided. The vessel should have suitable vents so that air can be completely removed. Pockets of air left in the vessel constitute a pneumatic explosion hazard. All filling lines and other equipment that are not intended to be subject to the test pressure should be disconnected before that pressure is applied. Any blanking off devices should be secured so that they will not be ejected during testing.

If a test liquid other than water is used, the hazards should be reviewed. With regard to the choice of liquid, the ICI *Code* states that the liquid should be well below its boiling point and, if flammable, should have a flashpoint above 45°C. The precautions described for water testing are applicable to testing with other liquids.

The test pressure to be applied should be such as not to overstress the vessel. It is normally specified in standards and codes. GS 4 states that in the absence of such guidance the test pressure should be limited to 90% of the proof, or yield, strength. It should be applied gradually in 10% increments.

The vessel under test should not be subject to any form of shock loading such as hammer testing.

19.7.9 Pneumatic testing: safety precautions

As stated, pneumatic testing should be employed only where hydraulic testing is impractical. In particular, pneumatic testing should be avoided if the vessel is constructed of a material that is liable to brittle fracture. Where the system consists of a number of items that can be tested separately, this is good practice insofar as it minimizes the volume under test, and thus the energy release potential.

If a pneumatic test is to be conducted, a review of the hazards should be undertaken. The vessel should be inspected in accordance with the *Code* requirements, as described above. Inspection requirements are also detailed in GS 4.

Consideration should be given to the possibility of condensation in the vessel, which can defeat the purpose of using pneumatic testing which has been chosen in order to exclude water.

Local chilling effects should be minimized in order to reduce the risk of brittle fracture. A gas let down from high pressure may undergo a significant temperature drop due to the Joule–Thomson effect. A pneumatic test should be carried out in such a way that the temperature of the gas entering the vessel does not fall below the test temperature. Similar considerations apply to gas flows out of the vessel.

If the source of pressure is higher than the test pressure, the vessel should be provided with protection against overpressure by the use of suitable reducing valves, pressure gauges and pressure relief valves.

Where pneumatic testing is conducted using a range of air pressures, positive measures may be taken to ensure that the correct test pressure is applied by arranging that there is for each pressure a different type or size of connection on the air supply, with a corresponding connection on the vessel.

Flexible connections used in pneumatic testing should be firmly secured. Safety restraints may be used to reduce the risk to persons nearby. Equipment used in pneumatic testing, such as pressure relief devices and flexible connections, should be subject to regular examination. Details are given in GS 4. The vessel under test should not be subject to any form of shock loading.

The personnel carrying out the test should be provided with a safe place from which the progress of the test can be observed and controlled. On completion of the test the vessel should be emptied in such a way as not to cause underpressure and collapse.

Underwater pneumatic testing may be employed as a form of a combined pressure test/leak test. The precautions required in such a test are detailed in GS 4.

19.7.10 Multi-compartment vessels

The testing of multi-compartment vessels involves additional hazards and gives rise to fatalities. These tend to occur when a person enters the vessel to inspect leaks from the compartment walls before the strength of the latter is fully tested. Walls may collapse at quite low pressure differentials. Entry should not be made into a multi-compartment vessel for the purpose of leak inspection until the integrity of the compartments has been established by appropriate pressure testing.

19.8 Leak Testing and Detection

19.8.1 Leak testing

Leak testing is carried out to check that a pressure vessel does not have significant leaks at the design operating conditions.

Leak testing is described in BS 3636: 1963 *Methods for Proving the Gas Tightness of Vacuum or Pressurized Plant*, the *Pressure Vessel Examination Code* and the *Pressure Piping Systems Examination Code* of the IP (1993 MCSP Pts 12, 13), the ICI Pressure Vessel Inspection Code and by Troyan (1960) and Pilborough (1989). Safety precautions in leak testing are given in these sources and in GS 4 (HSE, 1992).

19.8.2 Pressurization for leak testing

Most leak testing methods involve pressurizing the equipment, although the pressure used may be well below the design pressure. In general, pneumatic leak testing should not be performed until the integrity of the vessel has been established by pressure testing.

It is sometimes desirable, however, to leak test a vessel before a pressure test. As stated above, BS 5500 allows this to be done without observing the requirements for a pneumatic test, providing the pressure during the leak test does not exceed 10% of the design pressure. The guidance given in GS 4 is similar.

Once a pressure test has been carried out, leak testing may be done at pressures in excess of 10% of the design pressure. Nevertheless, the pressure used in leak testing should be kept as low as possible. There is usually little to be gained by the use of high pressures.

The vessel to be leak tested should first be inspected. GS 4 advises that visual examination may need to be supplemented by inspection using NDT methods.

If a pressure leak test is used and if the source of pressure is higher than the test pressure, the vessel should be provided with protection against overpressure by the use of suitable reducing valves, pressure gauges and pressure relief valves.

As described below, there are methods of leak testing available which do not involve pressurizing the vessel.

19.8.3 Leak location methods

Leak testing is performed for two distinct, but related, purposes: to locate the leak and to determine the leak rate. The main methods used for leak location are:

(1) pressure testing;
(2) search gas methods.

There are a number of leak location methods which involve pressurizing the vessel and then detecting leaks visually. The equipment may be pressurized hydraulically and liquid leaks observed. Detection of leaks may be assisted by the use of some kind of coating which shows them up more clearly. Alternatively, pressurization may be pneumatic and detection effected using a soap bubble or similar technique. If the vessel is sufficiently small to be immersed in a liquid, the evolution of air bubbles may be used to detect leaks in a manner similar to that used in repairing a bicycle inner tube puncture.

Another group of methods is based on the use of a search gas. The gas is introduced into the air pressurizing the vessel and is detected by a suitable device. Some commonly used combinations are:

Search gas	*Detector*
Halogen gas	Halide torch Halogen diode detector
Hydrogen	Thermal conductivity detector
Helium Nitrous oxide	Infrared absorption detector

A variation of this method is to use not a search gas but a radioactive tracer.

Some practical aspects of leak detection are discussed by Troyan (1960).

19.8.4 Leak rate

The leak rate may be defined in terms of the fall in pressure in the vessel

$$L = -V\frac{\mathrm{d}P}{\mathrm{d}t} \qquad [19.8.1]$$

where L is the leak rate (Pa m^3/s), P is the pressure (Pa), V is the volume of vessel (m^3) and t is the time (s).

Until quite recently, the internationally agreed unit of leak rate has been the torr l/s ($=0.133$ Pa m^3/s). Thus in Equation 19.8.1 if, instead of the units given, $V = 1$ l and $\mathrm{d}P/\mathrm{d}t = 1$ torr/s, then $L = 1$ torr l/s. Since this unit is rather large, use has also been made in the United Kingdom of the lusec (1 lusec $= 0.001$ torr l/s). An account of leak rate units is given by Pilborough (1989).

Since the leak rate depends on the difference between the vessel pressure and atmospheric pressure, this should be specified when quoting leak rates. Where the leak rate is for a vacuum plant and the difference is not specified, the assumption is that the pressure difference is 1 atm.

Typical leak rates are given by Pilborough (1971) as follows:

	Leak rate (lusec)
Water can	10
Chemical plant	1
Vacuum plant	0.01

19.8.5 Leak rate methods

The main methods for leak rate determination are:

(1) pressure decay method;
(2) flow method;
(3) search gas flow method.

The pressure decay method is to pressurize the system, isolate it and measure the rate of pressure decrease.

The flow method involves measuring the inlet flow required to maintain the pressure constant.

In the search gas flow method, air is passed over the surface of the equipment and through some form of hood or containment and the flow of air and concentration of search gas in the air are measured.

19.8.6 Leaks in vacuum plant

Leaks are particularly important in vacuum plant. Their detection and measurement is a specialist activity. Accounts are given in texts on vacuum technology and by Pilborough (1989).

19.8.7 On-line leak detection

Methods are also required for the detection of leaks in operating plant. In some cases it is possible to utilize the techniques just described such as the soap bubble, pressure decay and search gas methods.

For high pressure leaks, use may be made of AE monitoring, as described in Section 19.14. For leaks in pipelines another form of acoustic monitoring may be used, as described in Section 19.16.

19.9 Plant Monitoring

The plant equipment, including the pressure vessels and pipework and the process machinery, may be monitored during commissioning and over its operational life.

The monitoring of the state of the equipment may be based on (1) performance or (2) condition. The difference is self-explanatory. Performance monitoring is able to detect faults which have an effect on performance, but there are many others which have little effect until failure actually occurs. The latter may often be detected, however, by monitoring the condition.

The monitoring of instrument performance and condition has been discussed in Chapters 13 and 14 and such monitoring of other equipment is discussed below.

19.9.1 Monitoring strategy

Plant monitoring can yield great benefits, but it can consume appreciable resources. It is essential, therefore, to define clearly the purposes for which such monitoring is to be carried out and to adopt a coherent monitoring strategy.

This is particularly relevant with some types of monitoring, of which AE monitoring is one, and the point is discussed further below in relation to this type of surveillance.

19.9.2 Monitoring interval

The interval between condition monitoring checks depends on the nature of the signal. If the development of a failure is shown by a slow and reproducible increase in signal level over a long time interval, periodic monitoring may be sufficient, but if the failure gives little advance warning and the signal level is liable to rise from a low to a high level suddenly, then continuous monitoring is necessary.

The problem is one of information sampling and is in many ways similar to that considered in Chapter 14, in relation to the sampling of information by the process operator. Continuous monitoring is generally more expensive and the choice of monitoring interval is usually a compromise between these factors.

Where the quantity monitored is not the state of the plant but changes in that state, as in AE monitoring, different considerations apply. In this case, periodic monitoring, undertaken during changes in the plant state, is the norm.

19.9.3 Action level

The problem of acceptance standards in inspection and NDT is paralleled by that of the action level for condition monitoring. The decision has two dimensions, since it is necessary to decide not only whether to take action but also whether action must be immediate or whether it can be deferred.

A condition monitoring device produces a signal which varies with time. The signal characteristic of normal operation tends to be specific to the individual equipment monitored. It is a deviation from the equipment's own normal signal rather than from some ideal signal which indicates its abnormal condition.

In many cases, there is a fairly reproducible and unambiguous increase in signal level when a failure is imminent. In others, however, the signal is liable to fluctuate, rising to quite high levels and then subsiding, and/or to increase suddenly to failure. There is a considerable problem in these latter situations in deciding whether to take action.

The methods of reliability engineering have been applied to the treatment of the results from condition monitoring. Bellingham and Lees (1976b) describe a method of using the monitor signal to make a running estimate of the probability of survival, that is the reliability of the equipment. The method assumes that *a priori* information is available on (1) the failure density function of the equipment and (2) the probability density function of the signal, and uses the signal to condition this information to give the reliability estimate.

An illustrative example of the type of information obtained is shown in Figure 19.3. In the case considered, the failure distribution of the equipment is assumed to be exponential. Curve 1 gives the reliability calculated from the failure distribution without using the signal information. Curves 2 and 3 show the reliability estimated from the *a priori* information and the signal for the cases where the signal level is low and high, respectively. The former case indicates a healthy condition and the reliability in the immediate future is high, while the latter case indicates an unhealthy condition and the reliability falls off rapidly.

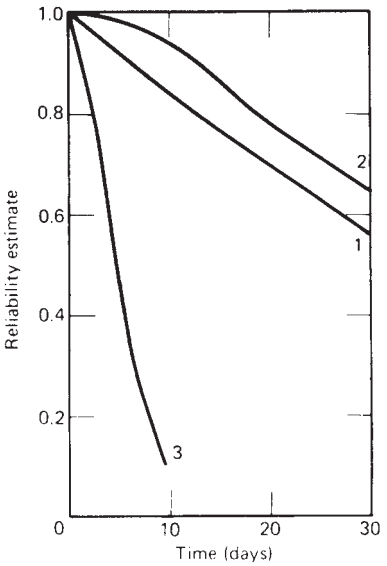

Figure 19.3 *Use of monitor signal to condition the estimate of equipment reliability (Bellingham and Lees, 1976b): curve 1, no monitor signal; curve 2, monitor signal healthy; curve 3, monitor signal unhealthy (Horsley and Parkinson, 1990; reproduced by permission of the Institution of Chemical Engineers)*

Applications of the extreme value distribution to the interpretation of results from ultrasonic survey have been described by Wylde and Shaw (1983). One application given is the estimation of the remaining life of a tank wall from measurements of the wall thickness at various points on a corroded band of the wall. Another example quoted is the estimation of the number of deep pits per unit length of pipe from measured values of pit depth.

19.9.4 On-condition maintenance

The various techniques of non-destructive examination and condition monitoring may be used to determine when maintenance should be done on an equipment, as an alternative to either breakdown or scheduled maintenance. This policy is known as on-condition maintenance. An account of on-condition maintenance as a maintenance policy is given in Chapter 7.

19.9.5 On-condition maintenance: illustrative example

Some of the condition monitoring techniques described below involve specialist equipment and sophisticated inter-pretation. But, as the following example shows, on-condition maintenance may also be based on some very simple measurement.

A maintenance policy for a paper machine has been described by A. Kelly (1981). One component which was prominent in the maintenance was a rotary joint, the main failure being that of one of the seals, which had a life varying between 6 and 30 months. It was realized that the wear on this seal could be determined by measuring the movement of the housing relative to the rotating part of

the joint. Thus, the condition of the seal could be monitored using a simple measurement of position.

19.10 Performance Monitoring

One basic approach to the surveillance of the health of equipment is to monitor its performance. Typically, performance monitoring is based on the use of a model of the equipment performance with ranges of values of the parameter in the healthy state. These parameters are monitored to detect excursions into unhealthy states. The technique tends to involve the measurement of a number of parameters and to require fairly high measurement accuracy.

Some performances which may be monitored include: (1) the equipment pressure drop; (2) heat exchanger efficiency; (3) the pump characteristic and efficiency and (4) the compressor, turbine characteristic and efficiency.

Performance monitoring is carried out on large machines such as turbines and compressors in the aerospace, marine, power and process industries. It is usually done not only to detect failures but also to obtain improved performance. Since performance monitoring generally requires multiple measurement, computation and display facilities, it is a natural task for a process computer.

The performance monitoring of reciprocating compressors by computer has been described by Gallier (1968). The monitoring covered changes in compressor leakage and volumetric efficiency, in compressor and driver power efficiency and in loading capability.

Thus leakage was determined by measuring temperatures and using the equations

$$L = \frac{T_s - T_o}{(T_o + \Delta T_H) - T_i} \qquad [19.10.1]$$

$$\frac{T_o}{T_s} = \left(\frac{p_o}{p_i}\right)^{(1-\mu)/\mu} \qquad [19.10.2]$$

where L is the fraction of gas leaking, p_i is the suction pressure, p_o is the discharge pressure, ΔT_H is the correction for Joule–Thomson effect, T_i the inlet temperature (before the addition of bypass gas), T_o is the discharge temperature, T_s is the suction temperature, and μ is a constant, approximately equal to the ratio of the gas specific heats.

Collacott (1976b) has described the monitoring of a more complex set of 'gas path' relations in a single spool compressor. A simplified form of the model described is

$$\begin{bmatrix} \Delta P_d \\ \Delta T_d \\ \Delta W_f \\ \Delta A \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{bmatrix} \begin{bmatrix} \Delta T_i \\ \Delta G_a \\ \Delta \eta \\ \Delta N \end{bmatrix} \qquad [19.10.3]$$

where A is the jet nozzle exhaust area, G_a the compressor air pumping capacity, N the compressor speed, P_d is the compressor discharge pressure, T_d is the compressor discharge temperature, T_i is the turbine inlet temperature, W_f is the fuel flow, η is the compressor efficiency, and Δ is the normalized increment of the variable (change in value/absolute value).

The performance of the machine is monitored by observing changes in the Δ values of the variables. The method may be summarized as follows. First the coefficients a_{11}–a_{44} in Equation 19.10.3 are evaluated in healthy operation. Then to make a check of machine performance the dependent variables P_d, T_d and W_f are measured at constant speed and the normalized increments ΔP_d, ΔT_d and ΔW_f are calculated. Since the speed is constant, $\Delta N = 0$ and equation 19.10.3 can be evaluated by considering first the top left-hand, third-order matrix. Thus the normalized increments of the independent variables ΔT_i, ΔG_a and $\Delta \eta$ are determined. The normalized increment ΔA is then calculated.

If all the normalized increments are close to zero, there is no performance change. If there is a deterioration, however, ΔG_a, $\Delta \eta$ and ΔT_i; normally rise. An increase in ΔA indicates erosion of the nozzle.

Collacott describes the performance monitoring of a power station steam turbine in which there was a sudden reduction in the load, first stage pressure, intercept valve pressure and feedwater flow of about 4% in each case. It was decided that there was a restriction at the front end of the turbine. In fact, the stem of one of the four control valves had broken so that the sequence of valve opening was interrupted.

19.11 Condition Monitoring

The alternative to performance monitoring is condition monitoring, for which a variety of techniques are available.

Accounts of condition monitoring have been given in *Mechanical Fault Diagnosis* (Collacott, 1977b) and *On-line Monitoring of Process Plant* (D.W. Butcher, 1983) and by Kobrin (1970), Trotter (1973) and D. Neale (1974).

An account of the application of a number of NDT and condition monitoring techniques to ammonia plants has been given by Madhavan and Sathe (1987).

There are a large and growing number of condition monitoring methods. Some of these are as follows:

(1) vibration monitoring;
(2) corrosion monitoring;
(3) acoustic emission monitoring;
(4) ultrasonics;
(5) infrared thermography;
(6) strain measurement;
(7) debris analysis;
(8) magnetic signature monitoring;
(9) temperature measurement;
(10) position measurement;
(11) speed measurement;
(12) torque measurement.

There is, therefore, no shortage of methods for condition monitoring. The problem is rather to select the appropriate technique, inspection interval and action level.

The inspection interval depends on the rate at which the fault monitored can develop. There are some faults that can occur within a matter of minutes, while others take weeks or months to develop. Continuous monitoring is necessary to detect faults that develop rapidly.

Whereas NDT methods are well established and are formally recognized in pressure vessel construction codes such as BS 5500, the role of condition monitoring techniques in inspection codes is generally less well defined.

The use of the process computer for monitoring performance and condition is discussed in Chapter 30.

19.11.1 Vibration monitoring

A widely used method of condition monitoring is the monitoring of vibrations. This is applied mainly to rotating process machinery, but also to static plant equipment. For rotating machinery in particular, it is often possible to relate the vibrations obtained to specific faults in the machine. Since large rotating machines are often critical to the operation of process plants, vibration monitoring has proved an especially valuable aid. It is described in more detail in Section 19.12.

19.11.2 Corrosion monitoring

Another widely practised form of monitoring is corrosion monitoring, which is applied principally to static plant. Corrosion monitoring may be used to track corrosion progressing at a relatively uniform rate and also to identify bursts of intense corrosion activity and to relate these to particular process conditions. The monitoring of corrosion is described further in Section 19.13.

19.11.3 Acoustic emission monitoring

Another monitoring technique which is finding growing application is AE monitoring, which is applied to static plant and also to leaks. This method is based on the detection of the AEs that occur as defects undergo changes, notably those accompanying crack growth. It thus differs from most other techniques for monitoring static plant in that it is not the steady state of the defects that are measured but the dynamic changes. A fuller account of AE monitoring is given in Section 19.14.

19.11.4 Ultrasonics

Ultrasonics is widely used not only for the initial examination of plant equipment, as described in Section 19.5, but also for on-going monitoring. In particular, it is extensively used to determine metal thickness and to identify and characterize cracks in metal structures.

19.11.5 Infrared thermography

An infrared camera can be used to detect differences in the surface temperature of, and hence heat radiation from, plant. The different temperatures may be displayed as different colours or shades of black and white on a cathode ray tube or on a photograph. The technique is known as infrared thermography or thermal image monitoring. Accounts are given by Norda (1976, 1977), L.M. Rogers (1976), Weismantel and Ramirez (1978), Imgram and McCandless (1982), E.G. Jones and Duckett (1985), Tuss (1985) and Baker-Counsell (1986c). Plate 18 shows the thermal image of a distillation column. Some applications of thermography are:

(1) refractory and lagging deterioration –
  (a) refractory wear,
  (b) lagging loss,
(2) furnace tube deterioration –
  (a) hot spots,
  (b) coking,
(3) process flow abnormalities –
  (a) heat exchangers,
  (b) steam traps,
  (c) relief valves,
(4) electrical equipment faults –
  (a) cable terminations,
  (b) cable splicing faults,
(5) machinery faults –
  (a) gearboxes,
  (b) couplings,
(c) corrosion.

Thermography has long been used by electrical engineers to detect faults in electrical power systems, but there are now numerous applications in the process industries. Wear of refractories, loss of lagging or moisture penetration of lagging shown up as hot or cold spots. In furnaces, corrosion or other thinning of tubes and coking up of tubes are revealed by temperature changes. The deterioration of flow patterns in a heat exchanger gives a changed temperature pattern. Leaks in steam traps and relief valves which discharge into closed pipelines are shown by a change in the temperature of these lines. Defects in electrical equipment such as bad terminations or cable splicing faults often show up as hot spots. Deterioration of machinery such as couplings or gearboxes tends to generate heat. It is even possible to detect some forms of corrosion.

Figure 19.4 shows a pair of normal and thermographic photographs of refractory lined vessels. The arrows in Figure 19.4(b) indicate areas of one of the vessels where the refractory is wearing thin.

A number of routine applications of thermography in one company are described by Weismantel and Ramirez (1978). These include the detection of leaking steam traps, faults in gearboxes and couplings, and electrical cable splicing defects. Another use described by these authors is to detect leaks beneath the insulation on liquefied natural gas (LNG) tanks.

Imgram and McCandless (1982) describe the use of thermography to detect leaking pressure relief valves. They also describe applications to the deterioration of a catalytic cracker refractory lining wear, a crude heater insulation loss and furnace tube coking. Plates 17 (a) and 17(b) show an application similar to the one described by these authors; of the pair of pressure relief valves shown, the one on the right-hand side is leaking.

The application of thermography to the identification of blockages in the relief header of a synthetic rubber plant is described by E.G. Jones and Duckett (1985). The technique used was to pass steam along the line and to observe the thermal transient, blockage points appearing initially as cold spots.

The applications mentioned by Baker-Counsell (1986c) include the use of thermography to detect hydrogen corrosion. The blisters formed cause a decrease in heat transfer and hence, when steam is used, a cold spot.

The main application of thermography is as a method for the normal inspection of the plant, but it may also be used for other purposes such as the acceptance testing of new equipment.

The distances between the thermal camera and the object may be as much as 100 m or more. Coverage of the temperature range −30°C to 2000°C and accuracies within 1°C are claimed. Thermographic equipment is relatively expensive.

19.11.6 Strain measurement

There are a number of methods of measuring strain in plant equipment. They include

(1) displacement measurement;
(2) strain gauges;

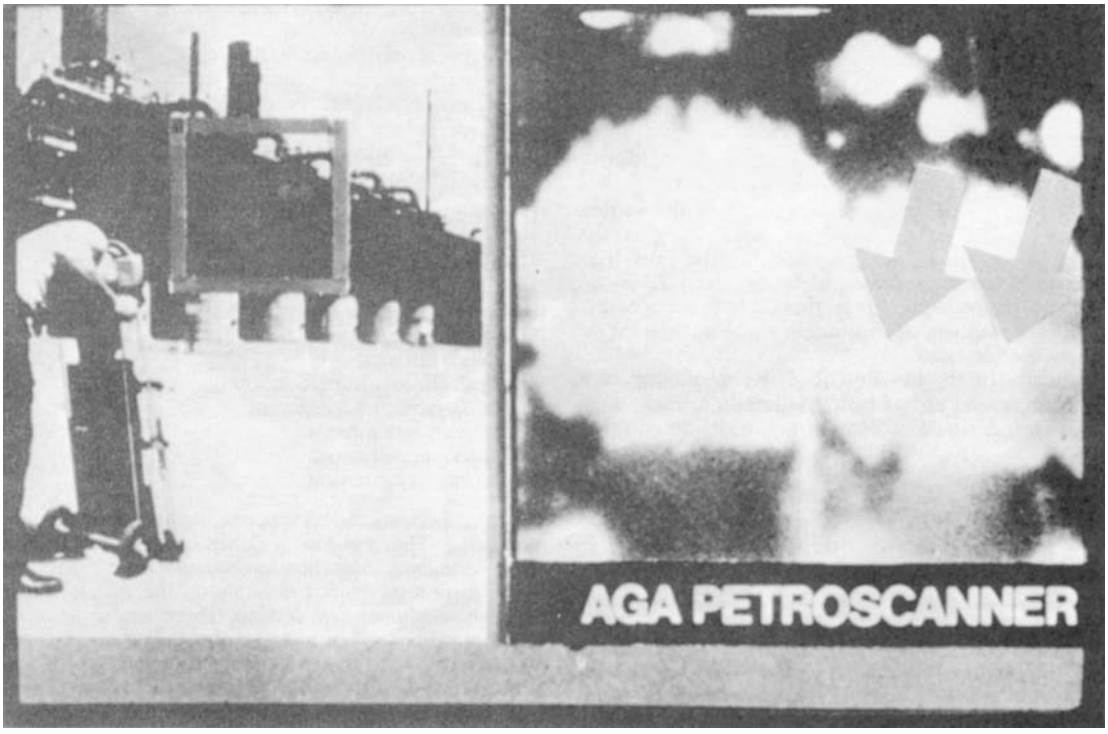

Figure 19.4 *Normal and thermographic photographs of a refractory lined vessel (A GA Ltd): (a) normal photograph; (b) thermographic photograph, with arrows indicating thin spots*

(3) lacquers and coatings;
(4) X-ray diffraction;
(5) interferometry –
  (a) Moire grid,
  (b) speckle,
  (c) holographic.

Strain may be measured by mechanical displacement or by electrical strain gauges. The latter are widely used as a means of measuring strain in a laboratory, but are rather less suitable for site work. A strain gauge measures strain in one direction only and has relatively low sensitivity. The application of the strain gauge method to the monitoring of steam pipework has been described by Ghia *et al.* (1983).

Photoelastic coatings and brittle lacquers may be used to give an indication of the existence of strain.

Interferometric techniques are available which show a two-dimensional strain pattern and are more sensitive. In the Moiré grid method a linear grid is applied to the object and distortions of the grid are measured.

If the diffusely reflecting surface of an object is illuminated by a laser beam, a speckle pattern is produced. This pattern undergoes regular changes if the surface is displaced by strain. Oxidation of the surface may affect the pattern, but special coatings are available to deal with this problem.

The procedure in the holographic method involves taking a silicone replica of the strained surface and analysing it in a laboratory using a fairly powerful laser (>1 W). Figure 19.5 shows a crack around a fatigue specimen obtained by the Optecord holographic method.

19.11.7 Debris analysis

The debris produced by process machinery in distress may be used to obtain information about the wear which is occurring by using the techniques of debris analysis. Accounts are given by A.E. Davies (1972), Collacott (1975), Wilkie (1987a) and Rudston (1989). The fundamentals of wear are treated by M.C. Shaw (1971).

Debris analysis techniques have been developed primarily in the aerospace and defence fields. Their application is widespread in the transport industry, where debris analysis is utilized for aircraft, marine, rail and road equipment, but its exploitation in the process industries has been somewhat slower.

Debris analysis is closely related to lubrication technology and is also referred to as lubricant monitoring. A monitoring package generally includes analysis of the lubricant itself as well as of the debris which it contains.

The lubricant tests in such a package are fairly standard. They include measurements of: the density of the oil; the viscosity of the oil; the breakdown products of the oil; the contaminants in the oil, such as water and insolubles; the total base number and the characterization of the metal particles.

The fate of metal particles in the system depends on their size. In essence, large particles (0.1 to <0.5 mm) settle out in the lubricant return tank; medium sized particles ($10-50\,\mu$m) circulate but may be trapped by a filter; and small

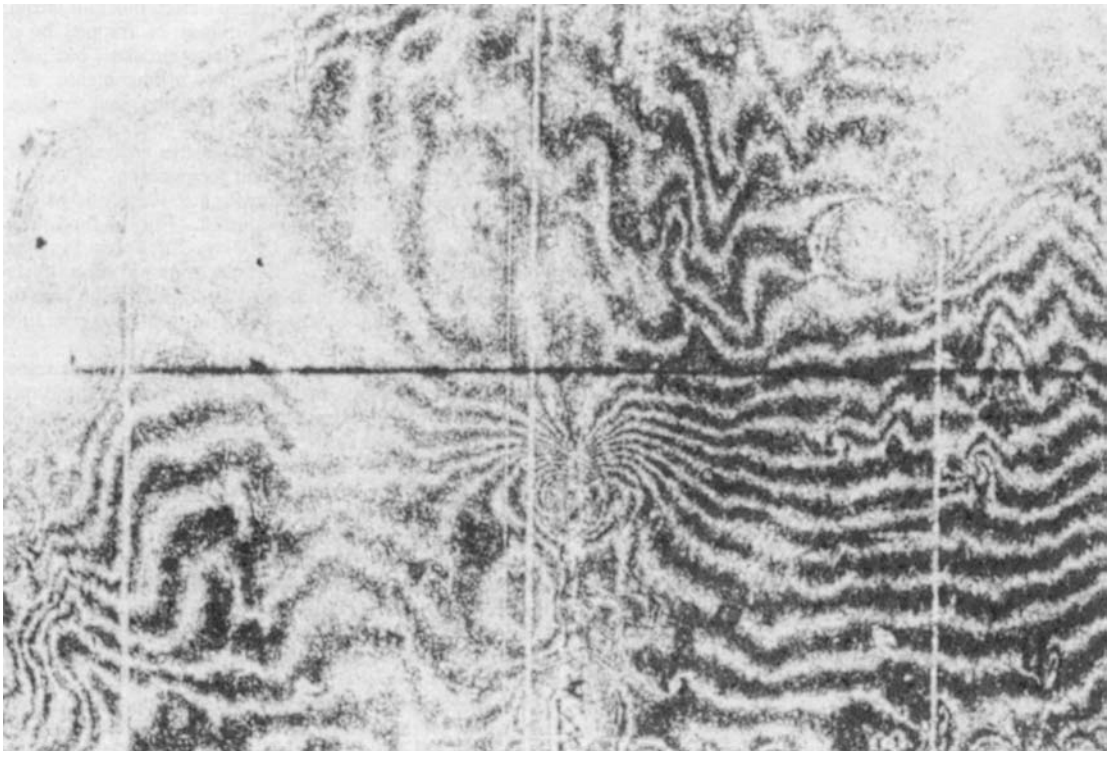

Figure 19.5 *Holographic investigation of a fatigue crack: (a) specimen; (b) holographic photograph (Reproduced with permission of Scottish Technical Development Ltd and the University of Strathclyde)*

particles (1–5 μm) also circulate, but pass through any filter. The filtering arrangements are generally designed to minimize abrasion and erosion from metal particles.

There are two main methods for the analysis of the metal particles: spectrometry and ferrography.

Spectrometric oil analysis involves the analysis of the chemical elements in the oil itself. The method was originally developed by the US Navy Air Force and has been known in the United Kingdom as the spectrometric oil analysis programme (SOAP). The method is claimed to be able to detect wear debris at the level of one part in 10^{12} (Collacott, 1975).

Figure 19.6 (A.E. Davies, 1972), shows the wear rates of an Olympus engine in the *Concorde* prototype aircraft as measured by spectrometric oil analysis. Stripping of the engine revealed heavy fret wear on the port gearbox-driven bevel splined location on the lay shaft.

For ferrography, metal particles may be obtained by magnetic chip detection or filter collection. Magnetic chip detection is used in lubricating or hydraulic oil systems to collect debris from ferromagnetic materials. The detector is periodically examined and the debris analysed. The use of magnetic chip detectors is quite widespread in the process industries. Filters in oil systems are also used to collect debris particles for analysis.

In the aircraft industry the analysis of debris is a well developed technique. Filter elements are removed under conditions of almost clinical cleanliness and the debris is examined by microscope and analysed chemically. Samples of filter washings are preserved under transparent covers on record cards.

Some typical normal and alert wear/corrosion ranges given by Rudston (1989) are as follows:

	Spectroscopic metals		*Ferrographic readings*	
	Ferrous	*Non-ferrous*	*Large debris*	*Small debris*
Rotating Machinery	≥8 (0–5)	≥8 (0–5)	≥15 (0–5)	≥2 (0–5)
Reciprocating Machinery	≥150 (0–100)	≥20 (0–15)	≥120 (0–100)	≥40 (0–30)

The values shown without brackets are alert values and those shown in brackets are normal values. These provide a general guide, but monitoring of a given machine is usually based on deviations from the previous pattern shown by that machine.

Particular wear processes tend to give characteristic particle shapes and much can be learned by examining the particles under a microscope. Some typical debris characteristics are shown in Table 19.11.

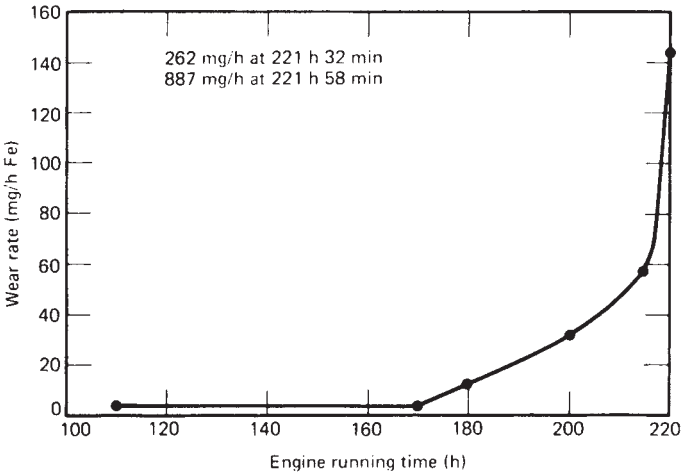

Figure 19.6 *Trend record of a spectrometric oil analysis on an Olympus 59332 engine in the Concorde prototype aircraft (A.E. Davies, 1972) (Courtesy of the Institution of Marine Engineers)*

Table 19.11 *Some typical characteristics of metal particle debris in lubricating oil*

A

Conditions	*Particle appearance*
Running in	Feathery or flaky
Roller bearing distress	Heavy rectangular shape with regular crossing marks (team lines)
Ball bearing distress	Shiny, roughly circular, petalled chips

B

Damage process	*Particle type*	*Surface appearance*
Mild wear (delamination)	Small flat reflective flakes	As machined but with more plateau area
Adhesion/scuffing	Larger ragged flakes often with temper colours	Rough and torn
Abrasion/cutting	Bright slivers and curls	Scratched and scored
Fatigue	Sharp metallic chunks and small spheres	Cracked and spalled
Erosion	Bright chunks or spheres	Pits or grooves with rough surface
Fretting	Fine red-brown iron oxide	Localized staining or indentation
Corrosive wear	Powdery non-reflective deposit	Fitted and discoloured

Sources: Collacott (1975); Rudston (1989).

19.11.8 Other general methods

Other methods that are used to monitor condition include the measurement of conventional variables such as temperature, position, speed and torque, and magnetic field measurements.

Temperature is used in particular to monitor plain bearings. It is not so good an indication for ball bearings, however.

Blades of rotating machinery such as turbines or fans may be magnetized or, if made of non-magnetic material, may be seeded with a magnetic implant. The 'magnetic signature' caused by the rotation of the magnetized part may then be monitored by a magnetic sensor.

There are numerous other physical phenomena that may be made the basis of a method of condition monitoring. Barnhart (1963) has listed some 387 physical laws and effects.

19.11.9 Specific ad hoc methods

In addition to the general methods described, there are a number of *ad hoc* methods for monitoring specific items of equipment. A good illustration of such methods is the rotary joint application described in Section 19.9.

Two further examples will suffice, one on pumps and one on valves. The first is the work of D. Harrison and Watkins (1983) on instability in pump mechanical seals, prompted by severe difficulties on main oil line pumps offshore. The problem involves vaporization between the seal faces of the pumped fluid that normally lubricates the seals. The

authors describe the measurement of the seal leak chamber pressure as an indicator of the onset of instability.

D. Harrison and Heath (1983) have described work on the use of changes in valve torque as a measure of incipient failure to achieve the fully open or closed position.

19.11.10 Adaptive noise cancellation

In many monitoring applications there is an appreciable degree of background noise. One technique which has been developed specifically to deal with this problem is that of adaptive noise cancellation (ANC), described by Widrow *et al.* (1975).

An account of the application of ANC to the monitoring of rolling element bearings has been given by Tan and Dawson (1983).

19.12 Vibration Monitoring

Vibration monitoring is described in *Mechanical Fault Diagnosis* (Collacott, 1977b) and *Mechanical Vibration and Shock Measurements* (Broch, 1980) and by Fieldhouse (1970), Tustin (1971), F.G. Jones (1971), C. Jackson (1975–), Erskine (1976a,b), Goldman (1984) and Goggin (1987).

19.12.1 Machine vibration

Much information on the condition of machinery can be obtained by monitoring vibrations. Monitoring needs to be combined with a theoretical analysis of the vibration modes so that particular faults can be distinguished.

Accounts of vibration include *Vibration and Sound* (Morse, 1936), *Mechanical Vibrations* (den Hartog, 1956), *Engineering Vibrations* (Jacobsen and Ayre, 1958), *Shock and Vibration Engineering* (C.T. Morrow, 1963), *Structure-Borne Sound* (Cremer and Heckl, 1973), *Vibration Problems in Engineering* (Timoshenko, Young and Weaver, 1974), *Elements of Vibration Analysis* (Meirovitch, 1975), *Shock and Vibration Handbook* (C.M. Harris and Crede, 1976) and *Mechanics of Vibration* (Bishop and Johnson, 1979).

Broch gives an account of vibration and shock that covers its characterization, the response of mechanical systems to it, its effect on mechanical systems, its measurement, its analysis, and its use for machinery health monitoring.

As an illustration, consider the pinion gear assembly described by Fieldhouse (1970) and shown in Figure 19.7. The analysis given by this author of some of the frequencies of vibration generated by this mechanism is summarized in Table 19.12.

Numerous other analyses of the modes of machine vibration are available.

19.12.2 Vibration quantities

Vibration quantities that are measured are (1) displacement, (2) velocity and (3) acceleration. Each quantity is measured using a different type of transducer.

Displacement measurement is utilized for detecting the change in clearances. It is particularly useful on reciprocating machines. It discounts and is not suitable for high frequencies (>1000 Hz).

Velocity measurement is a commonly used method for both machines and structures. It gives equal weighting to both low and high frequencies, since it is the product of the displacement and frequency of each harmonic component.

Acceleration measurement is useful for detecting impact effects. It discounts and is not suitable for low frequencies.

The choice of vibration quantity and measurement device is discussed by Broch (1980). There has been a trend towards higher frequencies, and measurements may be made at 10 Hz or higher. Broch's account emphasizes the use of accelerometers, with velocity or displacement obtained by integration.

The units of measurement commonly used are

Displacement	μm	mil
Velocity	mm/s	in./s
Acceleration	m/s^2	ft/s^2

There are also several different signal quantities that may be measured. These are (1) peak, (2) peak-to-peak, (3) average and (4) root mean square (rms). All these quantities are used in the various instruments currently available for the measurement of the vibration quantities (displacement, velocity and acceleration).

The peak and peak-to-peak values give, respectively, the peak vibration loading and the swing in loading; the average and rms values give, respectively, the average vibration loading and the power in the loading. The peak and peak-to-peak values are dependent on the waveform, but the average and rms values are not.

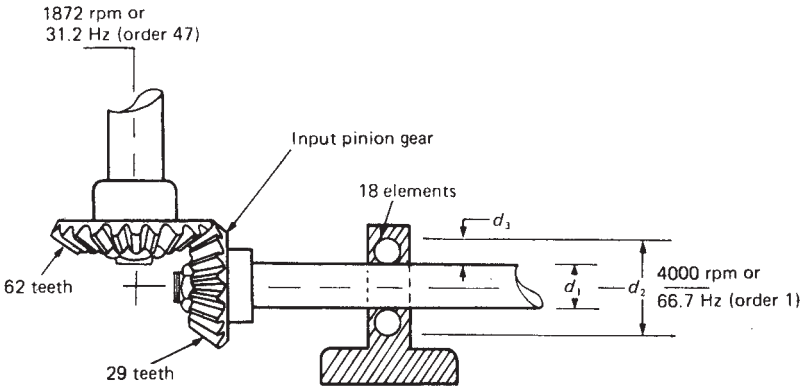

Figure 19.7 *Pinion gear assembly (Fieldhouse, 1970) (Courtesy of Sound and Vibration)*

Table 19.12 *Some frequencies arising from a pinion gear assembly (after Fieldhouse, 1970) (Courtesy of Sound and Vibration)*

Assembly parameters:	
No. of teeth on input gear, N_1	29
No. of teeth on output pinion, N_2	62
Diameter of inner race, d_1	3 in.
Diameter of outer race, d_2	4 in.
Diameter of balls, d_3	0.5 in.
Number of balls, N	18
Speed of rotation of input shaft, n_1	4000 rev/min
Constant D_1 ($= d_1/(d_1+d_2)$)	0.428
Constant D_2 ($= d_2/(d_1+d_2)$)	0.572

Assembly frequencies:	Hz	Order
Frequency of rotation of input shaft, f_{n1}	66.7	1
Fundamental gear mesh frequency, f_{gm}($=f_{n1}N_1$)	1934.3	29
Frequency of rotation of output shaft, f_{n2} ($=f_{gm}$ / N_2)	31.2	0.47
First upper sideband of gear mesh frequency, f_u ($=f_{gm}+f_{n1}$)	2001	30
First lower sideband of gear mesh frequency, f_1($=f_{gm}-f_{n1}$)	1867.6	28
Differential frequency of rotation of inner and outer races, f_r ($=f_{n1}$)	66.7	1
Frequency of ball spin, f_s ($=f_rD_1(d_2/d_3)$)	228	3.4
Frequency of ball train passage, f_t ($=f_rD_1$)	28.5	0.43
Frequency of flaw on inner race, f_{f1}($=f_rND_2$)	687	10.2
Frequency of flaw on outer race, f_{f2}($=f_rND_1$)	514	7.7
Frequency of flaw on ball, f_{f3}($=2f_s$)	456	6.8

The peak vibration velocity is the quantity generally considered to be the most useful signal by some authors (e.g. Erskine, 1976a). If a peak value is required, it is important to ensure that a true peak reading meter is used, as described below.

Alternatively, the full power spectrum of the signal may be produced. Spectral analysis instruments are available to generate the power spectrum.

An illustrative example showing the value of signal filtering is given by Goldman (1984). He considers the monitoring of a gearbox which has a mesh frequency of 1 Hz and an outer race ball pass frequency of 236 Hz. Typical signals might be:

	Velocity (in./s)		
Week	*Overall*	*Mesh* (1 Hz)	*Bearing* (236 Hz)
1	0.1	0.1	0.01
2	0.1	0.1	0.02
3	0.1	0.1	0.03
4	0.1	0.1	0.04
5	0.11	0.0	0.05

Measurement of the strength of the overall signal would show relatively little change, but separate measurement of the mesh and bearing signals would show the bearing beginning to fail at about week 3 and being close to failure by week 5.

19.12.3 Vibration measurement

The instrumentation used for vibration monitoring consists of a transducer, a signal conditioning amplifier and a readout meter. The transducer may measure displacement, velocity or acceleration directly. Alternatively, acceleration may be integrated to give velocity, and velocity to give displacement. An account of vibration measurement is given be Broch (1980).

The function of the amplifier is to give a larger power signal and to transform it into the signal quantity required. Many instruments scaled for peak, peak-to-peak or rms values in fact read the average value. The different types of circuitry are described by Erskine (1976a).

There are a number of practical aspects that need to be observed if satisfactory results are to be obtained in vibration monitoring work. On each occasion, the measurement should be taken at the same point and in the same direction. Therefore, if a portable monitor is used it is useful to indicate the point with a small circle of white paint with a small hole drilled in the centre. The tendency for a portable transducer to bounce can be overcome by the use of a 'mole' wrench as a clip. The same instrument should always be used to take a given reading, since instruments which ostensibly read the same parameter may in fact have different internal circuitry. The transducer should be calibrated at intervals of 18 months or less and the instruments at intervals of 3 months.

As far as possible vibration measurements should be made under the same machine conditions. Some variable speed machines have a rotor critical speed within the operating range, although the machine should not be operated at this speed. If it is being so operated, the additional vibration detected is an indication of maloperation rather than malfunction.

19.12.4 Vibration criteria

For rotating process machinery such as turbines, compressors, pumps and fans there are some general guidelines

available to determine the level of vibration at which action is required, that is the vibration criteria. Early vibration criteria were those proposed by Yates (1949) and Rathbone (1963). A widely used set of vibration criteria is that of the IRD, the details of which are quoted by Collacott (1977b).

One of the most widely used guidelines for general process machinery is that given in VDI 2056: 1964 *Standards for Evaluation of Mechanical Vibration of Machines*.

Criteria for the balancing of machines are given in ISO 1940: 1986–*Mechanical Vibration–Balance Quality Requirements for Rigid Rotors,* ISO 2371: 1974 *Field Balancing Equipment: Description and Evaluation,* ISO 2953: 1985 *Balancing Machines: Description and Evaluation* and ISO 3945: 1985 *Mechanical Vibration of Large Rotating Machines with Speed Range from 10 to 20 r/s: Measurement and Evaluation of Vibration Severity in situ*.

Vibration criteria, both for independent bearings and for bearing housings in barrel casings, which have been developed from the VDI method and used in ICI, have been described by Erskine (1976a) and are given in Figure 19.8 The quantity used is the peak vibration velocity, which has the advantage that it is independent of the machine speed and vibration frequency. Experience also indicates that Figure 19.8 can be used for gearboxes if they are treated as Group T.

These vibration criteria provide general guidance. In practice, it is usual to take an initial baseline set of measurements on the particular machine and thereafter to monitor the trend on that machine.

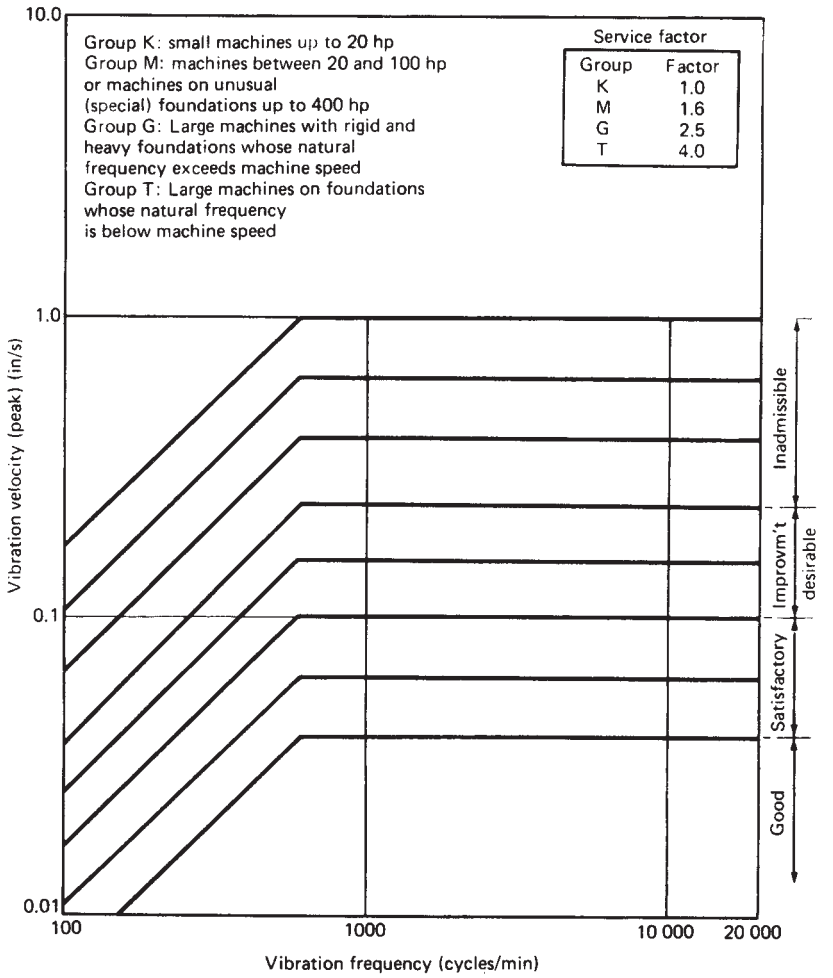

Figure 19.8 *Vibration criteria for process machinery (Erskine, 1976a) (Courtesy of the Institution of Chemical Engineers)*

Another useful source of information for comparison may be the vibration levels on similar machines in a group.

Use may be made of certain rules of thumb. Goldman refers to the rule that a doubling of the signal strength is an indication of trouble, whilst a trebling is cause for concern.

19.12.5 Shock pulse monitoring

A particular type of vibration monitoring which is based on selective filtering is shock pulse monitoring. The shock pulse meter (SPM) exploits two facts. One is that at the natural frequency of a mounted accelerometer a large electrical output can be obtained from a small excitation. The other is that an instantaneous impact gives a signal that contains all frequencies at equal amplitude, in other words white noise. Thus, the signal given by an impact will contain the frequency required to excite the accelerometer. In a SPM, the signal at this frequency is amplified by the accelerometer, filtered and then measured.

The main application of the SPM is the monitoring of faults in ball bearings. If, for example, a single spall develops in the outer race, an impulse occurs each time a ball passes over the spall. As deterioration occurs, the level of white noise, and the signal from the meter, should increase.

In practice, there are certain problems which can arise. There may be sources of white noise which are unrelated to the defect and, as the defect grows, the signal generated may no longer be white noise. The situation can occur where the meter signal actually reduces as the deterioration progresses.

An enhancement of the SPM technique is the use of a stress wave analyser (SWAN), which exploits the fact that the amplitude of the impulse is proportional to the relative velocity between the two bearing surfaces and to the depth of the imperfection, and gives a signal proportional to the area of the bearing fault.

19.12.6 Plant applications

Vibration monitoring can be applied both to rotating machines and to static plant. The quality of information that can be obtained goes far beyond the detection of the fact that something is wrong, and it is often possible to pinpoint the fault quite precisely.

Some typical information given by vibration frequencies, particularly those that are multiples of the speed of rotation, is shown in Table 19.13.

Figure 19.9 illustrates time histories and power spectra of vibration signals for some typical rotating machine conditions.

Vibration methods can also be applied to static plant such as distillation and gas absorption columns and heat exchangers. Figure 19.10 shows the power spectrum of a heat exchanger under normal and abnormal conditions.

In many cases, the level of vibration at a particular frequency or frequency range is low, unless there is an abnormal condition. In such cases, arrangements can be made to filter out all other frequencies so that the level of signal retained is an unambiguous indication of the abnormality. Thus for the heat exchanger shown in Figure 19.10 a suitable filter is one which retains only frequencies in the range 250–750 Hz. The resultant signal can then be used to indicate heat exchanger rattling.

19.12.7 Monitoring policy

There is now considerable vibration monitoring activity in process plants. Some machine conditions are monitored by permanent instruments, others are checked by portable meters. On critical items such as turbines, compressors and large pumps there is a high proportion of continuous monitoring with alarms and trips. These machines are also the subject of further spot checks and of sophisticated spectral analysis by specialist staff. For other less critical machines, spot checks by less skilled personnel using portable meters are often sufficient.

An account of monitoring policy is given by Goldman (1984). Continuous monitoring is likely to be appropriate if (1) the machine is critical to production, (2) it is costly to replace and/or (3) its failure would be hazardous. Periodic monitoring may be carried out on machines where (1) the machine is moderately important for production, (2) its replacement is costly, (3) it is a major machine but is spared or (4) it has a poor operating history.

The vibration criteria at which action is required depend on the application. For meter checks by unskilled people it is essential to have very simple criteria, while specialist personnel may base their decisions on much more complex analysis.

Table 19.13 *Frequencies detected for some common process machinery faults*

Fault	*Frequency*[a]
Oil whirl	$\frac{1}{2} \times N$
Unbalanced, eccentric journals	$1 \times N$
Misaligned shaft	$1 \times N$
Aerodynamic forces (fan)	$1 \times N$
Reciprocating forces	$1, 2 \ldots \times N$[b]
Bent, cracked shaft	$1, 2 \times N$[c]
Misalignment of couplings or bearings	$1, 2, 3 \times N$[d]
Mechanical looseness	$1, 2, 3, 4 \times N$[e]
Defective gear	$n_g \times N$
Blade defect	$n_t \times N$
Failing coupling	$n_c \times N$
Defective belt drive	$1, 2, 3, 4 \times n_b$
Defective bearings	Very high, several times N
Defective mountings (soft foot)	$1, 2 \times N$[f]
Structural resonance	$1 \times N$[g]

Sources: Lees (1980b); Goldman (1984); Goggin (1987).

[a] N, the rotational speed of the machine (rpm); n_b, the rotational speed of the complete belt; n_g, the number of gear teeth; n_t, the number of blades.

[b] $1, 2 \times N$ and higher orders.

[c] Goldman gives $2 \times N$; Goggin usually gives $1 \times N$, or $2 \times N$ if bent at coupling.

[d] Goldman gives $2 \times N$; Goggin usually gives $1 \times N$, sometimes $2,3 \times N$.

[e] Goldman gives $1, 2, 3, 4 \times N$; Goggin gives $1, 2, 3 \times N$.

[f] Usually $1 \times N$, sometimes $2 \times N$.

[g] $1 \times N$, but often odd non-synchronous frequency.

19.13 Corrosion Monitoring

There are available a number of methods for the monitoring of corrosion, both on-line and otherwise. Accounts of corrosion monitoring are given in *Industrial Corrosion Monitoring* (Hines, J.G. (chrmn) (1978) and by Harrell (1978), Rothwell (1979), Strutt, Robinson and Turner (1981), Asher *et al.* (1983), Dawson, Eden and Hladky (1983), Robinson and Strutt (1983) and M. Turner and King (1986).

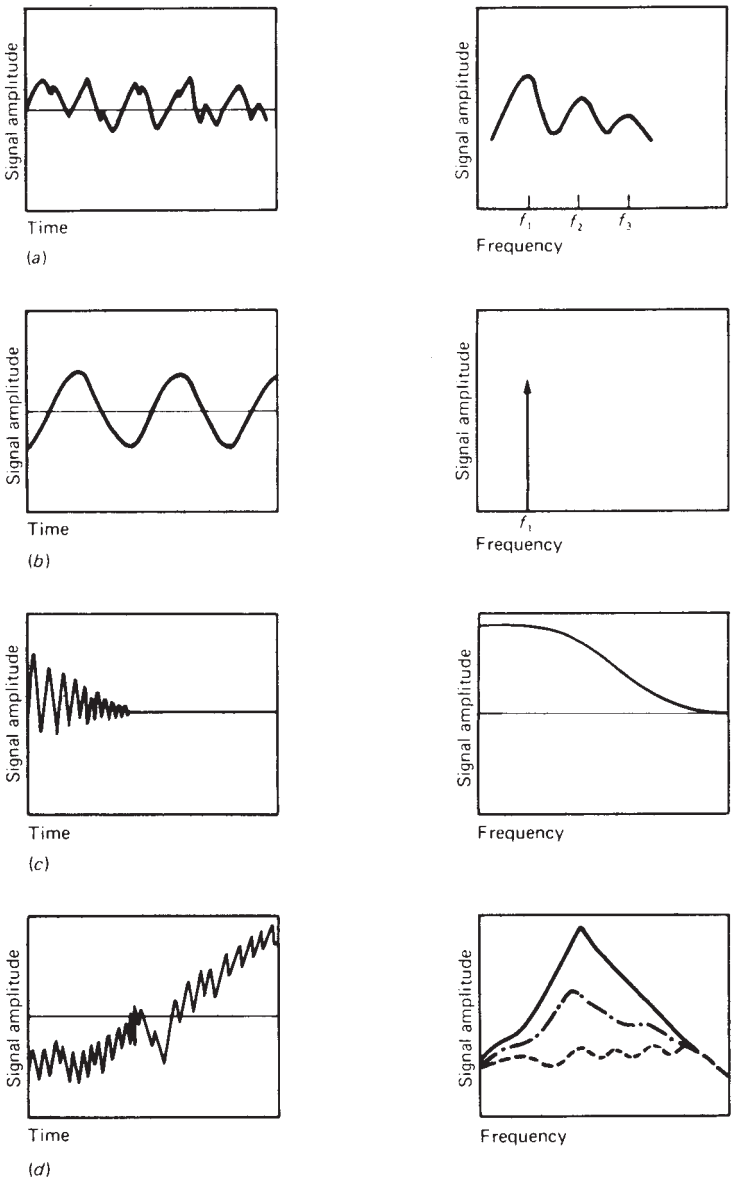

Figure 19.9 *Trend records and power spectra of some typical machine conditions (Collacott, 1975): (a) normal operation; (b) imbalance; (c) shock; (d) impending major failure*

Corrosion monitoring may be undertaken for a variety of reasons. It may be used to (1) inspect for corrosion and, in particular, give early warning of severe corrosion, and to (2) diagnose a problem, (3) monitor a solution to a problem, (4) correlate the corrosion regime with the plant operating conditions, (5) monitor the operation of the plant and (6) control the operation of the plant.

Corrosion is a complex phenomenon. This is so even under the controlled conditions of the laboratory and even more so on an operating plant. Corrosion has a number of causes and it is not advisable to place total reliance on a single method.

Some corrosion monitoring techniques identify the corrosion regime in the plant, whilst others indicate or measure the corrosion actually occurring. Taking the latter first, some principal methods are visual inspection, coupon testing and sentinel holes.

Visual examination requires access and is used particularly at shut-downs. There are a variety of aids to visual examination, including closed circuit TV and optical

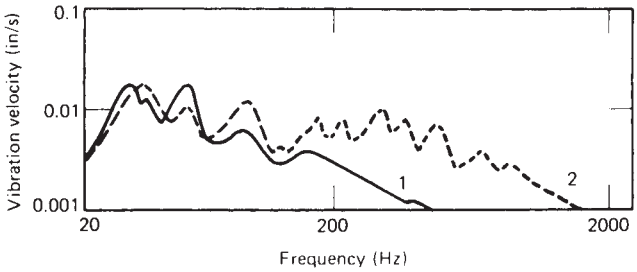

Figure 19.10 *Power spectrum of a heat exchanger (Erskine, 1976a): curve 1, exchanger quiescent; curve 2, exchanger rating (Courtesy of the Institution of Chemical Engineers)*

techniques. Coupon testing involves locating a sample element in the equipment and measuring the degree of corrosion of the element. A sentinel hole is a hole drilled through from the outside to a point close to the internal surface, so that it will leak if significant internal corrosion occurs.

Some authors include among the techniques of corrosion monitoring NDT methods such as radiography, ultrasonics, eddy current testing, AE testing and thermography.

Electrochemical methods of corrosion monitoring are described by Strutt, Robinson and Turner (1981). These methods are used for investigating the corrosion regime and include (1) chemical analysis, (2) the corrosion potential method, (3) linear polarization resistance (LPR), (4) electrochemical impedance, (5) potentiodynamic scans (PDSs) and (6) electrochemical noise.

The LPR, electrochemical impedance and PDS techniques all involve the investigation of current and voltage using a set of probes. The main difference between them is the form of input signal to the probe and the analysis performed on the output.

Electrochemical methods are best suited to providing early warning of corrosion behaviour and to correlating the corrosion regime with the operating conditions.

The control of electrochemical corrosion measurements and the display of data in various forms is a natural application for a microprocessor. The authors illustrate a number of plots that may be displayed, including trend charts, scatter diagrams, control charts, polarization diagrams and Nyquist diagrams. A polarization diagram is a plot of potential vs current and a Nyquist diagram a plot of resistance vs reactance over a range of frequencies.

An overview of corrosion monitoring methods is given by Rothwell (1979), who tabulates for each technique the type of information which it yields, the type of corrosion for which it is suitable, the environment in which it may be used, the time taken for the measurement to be made, the response to changes in corrosion, the application of the technique to an operating plant, and the ease of interpretation.

A method widely used to measure the actual rate of corrosion is coupon testing. The corrosion of the coupon may be measured gravimetrically by periodically removing and weighing it. It is important to locate the coupon so that it is representative of the corrosion to be monitored. It should generally be flush and in continuity with the vessel or pipe unless it is specifically desired to measure local corrosion/erosion effects. The choice of element size is a compromise between measurement sensitivity and replacement frequency.

The coupon testing method may be adapted to form the basis of an instrument for the measurement of the corrosion rate. The electrical resistance of the sample element increases as its cross-sectional area decreases and thus provides a measure of the cross-section remaining. Since the electrical resistance is sensitive to temperature, corrosion meters need to be temperature-compensated by using a reference element that is not exposed to corrosion. The corrosion rate is obtained by differentiating the reading of a corrosion meter.

The current in an electrical resistance corrosion meter is appreciable. For use in a hazardous area the intrinsic safety of the system may need to be checked.

Another technique for the measurement of the corrosion rate is radioactivation, as described by Baker-Counsell (1985g). This involves making mildly radioactive the surface which is subject to corrosion and measuring the change in radioactivity. In the thin layer activation version of this method, only a thin layer at the surface is activated. This has the advantages that the sensitivity of the measurement is high and the radioactivity so low as to obviate the need for taking any special precautions against it.

Typical corrosion rates are of the order of 10 mil/year (1 mil = 0.001 in.), but rates can vary widely and, in particular, under certain process conditions may accelerate dramatically.

Examples of the use of corrosion monitoring are given by Rothwell (1979). Case histories are described by Harrell (1978). A detailed account of the monitoring of a standard corrosion experiment, the corrosion behaviour of 316 stainless steel in 0.1 M NaCl, is given by Strutt, Robinson and Turner (1981).

Another method of monitoring corrosion and erosion is to measure the wall thickness by using ultrasonics. The use of ultrasonics in this application, and in particular as a method of obtaining results reproducible enough to track the progress of any thinning, is described by Browne and Constantinis (1983).

19.14 Acoustic Emission Monitoring

Many physical phenomena are associated with the emission of noise. Examples are the creaking of the branch of a tree and the 'cry' of tin. AEs may be picked up by a microphone and used to monitor both pressure vessels and process machinery.

AE monitoring is dealt with in *Mechanical Vibration and Shock Measurements* (Broch, 1980), the two IChemE

guides described below, and by McFarland (1970), Witt (1971a), Fowler and Scarpellini (1980), Cole (1983, 1988, 1990, 1992), LM. Rogers and Alexander (1983), Treleaven (1983), Fowler (1986, 1987, 1988, 1992), Pollock (1986), Clough (1987), Heiple and Carpenter (1987), Frieshel and Jones (1988), Prasek (1988), Zhang (1988) and Hewerdine (1991).

The earlier guide published by the IChemE, *Guidance Notes on the Use of Acoustic Emission Testing in Process Plants*, was prepared by a working party of the International Study Group on Hydrocarbon Oxidation (ISGHO) (1985), and the current guide, *Plant Integrity Assessment by Acoustic Emission Monitoring* (Hewerdine, 1993) (the IChemE AE Monitoring Guide), was prepared by the International Process Safety Group (IPSG), the successor to the ISGHO.

19.14.1 AE sources

When a defect undergoes change, such as a crack experiencing growth, there is a release of energy, part of which is converted to elastic waves. This acoustic energy may be detected, and this forms the basis of AE monitoring. Some principal AE sources are crack growth, corrosion product fracture and local yielding.

19.14.2 AE signals

An AE occurs when a defect in a metal plate is put under stress. An elastic stress wave travels through the plate. The measurement of this wave is the basis of the AE technique. The emissions of interest occur in 'bursts', each burst being known as an event. Figure 19.11 illustrates a typical AE event. The start of the event occurs with the initial signal at arrival time t_o. There then occur a number of excursions, or counts, outside the set threshold. The event is characterized by the arrival time, the duration, the number of counts and the amplitude of the largest count, or maximum amplitude.

An AE is not emitted on all occasions when a defect is put under stress. It was held in early work that an emission occurs only when the stress is taken to a value higher than that previously applied. This is the Kaiser effect and it assumes that the energy release is irreversible. Later work showed that this was not the whole story, and that if a sufficient recovery period is allowed the emissions can again be obtained at lower stresses. This disappearance of the Kaiser effect is known as the Felicity effect. The significance of this is that if the fading of the Kaiser effect did not occur, it would be possible to use AE monitoring only for applications where a vessel was subject to successively higher pressures, which would be a severe limitation.

Different materials exhibit different AE characteristics and in order to apply the technique it is necessary to establish these. AE monitoring has been applied *inter alia* to carbon steel, stainless steel and fibre reinforced plastic (FRP) equipment.

19.14.3 AE measurement

A typical set-up for the AE monitoring of a vessel is a set of three or more probes. By using a set of three probes to give 'triangulation' and utilizing the travel times of the emission waves measured by the probes, it is possible, in principle to locate the source of the emission.

There are in fact a number of practical problems in doing this: the level of background noise; interference between one event and another; the assumption that the stress wave travels at a constant, known velocity and the calibration of the AE equipment.

The assumption of a constant stress wave velocity applies to flat steel plate. There are differences in velocity for waves in flat steel plate and in the curved walls of vessels. Also, the different frequency components travel at different velocities.

An approach based on zone location rather than source location, described by Fowler (1987), attempts to overcome some of these difficulties.

19.14.4 AE signal analysis

Early approaches to AE monitoring concentrated primarily on the location of defects. More recent work has extended this to the characterization of the parameters of the signal and of the defects. To this end extensive use is made of computer processing of the signals obtained.

19.14.5 AE monitoring characteristics

AE monitoring is therefore a technique for detecting the occurrence, and measuring of the magnitude of, dynamic changes occurring in defects rather than of the static defects. This is a fundamental difference between AE monitoring and conventional NDT methods. It has a number of implications.

One is that AE signals occur only whilst changes are taking place. Thus AE monitoring is typically conducted on a periodic basis, when plant loading is being altered, rather than continuously.

Another consequence is that a site which gives a signal detectable by AE monitoring may not give one detectable by NDT methods, and vice versa. AE monitoring can detect cracks that are growing, even though they may still be small, whereas NDT detects only larger cracks. On the other hand, the AE technique may not detect even such larger cracks unless they are experiencing growth at the time when the measurements are made.

Since AE methods give information on defect changes they complement well the techniques of fracture mechanics described in Chapter 12.

AE has the advantage that it is a global monitoring technique that allows the whole of a structure or vessel to be monitored. This distinguishes it from many NDT methods, such as ultrasonics or eddy current testing, which inspect a limited area. Furthermore, AE monitoring requires only limited access to the equipment and allows remote detection and location of flaws.

Limitations of AE monitoring are that: the structure has to be loaded; the source activity is highly dependent on the material; there may be interference from noise; the interpretation of the results can be difficult; the location of the flaw may not be very accurate; and identification of the type of defect may not be readily made.

19.14.6 AE monitoring standards and codes

There are a number of standards and codes applicable to AE monitoring. ASTM standards include: ASTM E 569–91E1, giving general guidance; ASTM E 1067–89, on FRP tanks and vessels and ASTM E 1211–87, on leak detection.

Treatments proposed by the ASME include those on the use of AE in lieu of radiography (1982), FRP vessels (1983) and on metallic pressure vessels (1989).

The Society of the Plastics Industry (SPI) (1987) has also issued a recommended practice for FRP tanks and vessels.

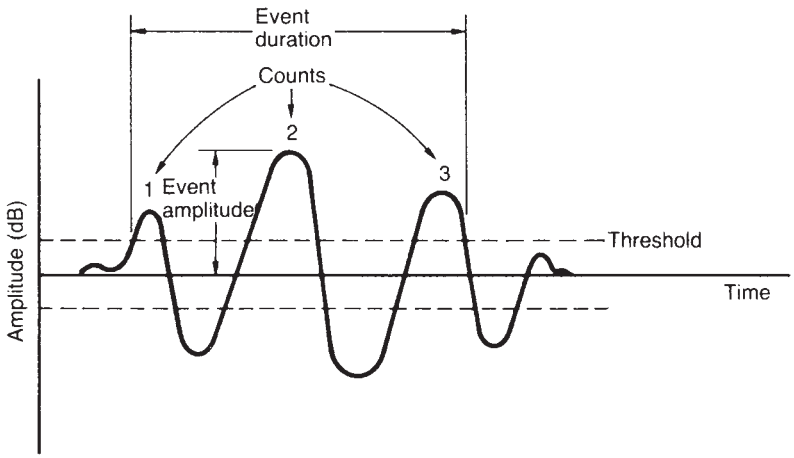

Figure 19.11 *A typical signal from an acoustic emission test*

Rail tank car monitoring is covered by a procedure of the Association of American Railroads (AAR) (1991).

With regard to the status of AE monitoring as a recognized method in pressure vessel codes, the technique has not achieved this status. The testing of new vessels is adequately covered by existing NDT techniques. Where AE has found a niche is: in the testing of new FRP vessels, where conventional NDT methods are less effective; as a complement to hydrostatic testing and in the operational monitoring of critical vessels. Since AE is a global inspection method, it appears a strong contender to satisfy any code requirements that may be developed for the inspection of pipework.

19.14.7 AE monitoring procedures

The effective application of AE monitoring requires adherence to a properly formulated procedure. A widely used procedure is MONPAC, developed in and licensed by Monsanto (1990). The procedure specifies the material and equipment covered, the maximum background noise, and the maximum sensor spacing.

The results obtained in the procedure are allocated to one of five grades, from A indicating minor source/no action, to E indicating intense source/immediate action. An account of the use of MONPAC is given by Cole (1990).

19.14.8 AE monitoring applications: FRP vessels

AE monitoring was applied early to the testing of new metal pressure vessels, but at first with limited success. It was found, however, that AE monitoring was of particular value in the testing and monitoring of FRP pressure vessels.

The use of AE for the testing and monitoring of FRP vessels has been described by Fowler and Scarpellini (1980) and Fowler (1987, 1988), who give an account of its development in one company. Initially the failure rate of FRP vessels, both new and in service, was unacceptable, some of the failures being total ruptures. Many of the conventional NDT techniques are not, however, applicable to FRP. It was therefore attractive to use AE, provided it could be made to work. In fact some problems which occur with the use of the technique on metal vessels, such as background noise, are less severe with FRP. The method proved successful to the extent that there is no record of any significant FRP defect escaping AE testing, and that it became possible to prevent catastrophic failures of FRP vessels. The technique has been adopted within the FRP industry in the United States.

Some relevant standards and codes are given Section 19.14.6.

19.14.9 AE monitoring applications: metal equipment

Despite initial difficulties, AE monitoring of metal equipment has been developed and now constitutes the main area of use. The applications of AE to metal equipment are principally for the monitoring of pressure vessels during hydrostatic pressure testing and of operating pressure vessels, particularly during the transients that occur during start-up and shut-down.

AE monitoring is also used in the testing of certain equipment such as large field-erected storage tanks and vessels in certain special materials such as titanium.

Since it is defect changes that AE monitoring detects, continuous monitoring is less common, but is practised in some instances. In some cases, vessels are fitted with permanent equipment for AE monitoring.

The use of AE monitoring during the hydrostatic testing of pressure vessels has been described by McFarland (1970). Adam (1982) has given an account of its use on ammonia storage spheres. Its application to large, refrigerated storage tanks for liquid ammonia, which are difficult to inspect internally, is described by Prasek (1988). Parry (1980) has given an account of its use to investigate potential problems on ammonia converters, including stress corrosion cracking and fretting of shrunk-on bands.

Some applications of AE monitoring to process equipment have been described by Cole (1983). These include a jacketed reactor, a reactor train, a multi-wall high pressure vessel and storage tanks, as well as FRP vessels. For the jacketed reactor, the technique was able to detect defects in the inaccessible space between the shell and the jacket (the 20 min period following admission of steam to the jacket

giving strong AEs) and associate with thermal stress and corrosion. The reactor train exemplifies early detection of stress corrosion cracking. The multi-layer reactor is an illustration of an equipment that is difficult to inspect by conventional means. The application to storage tanks exploits the technique's ability to give good volumetric coverage.

The application of AE monitoring to propagating fatigue cracks in node joints and crane pedestals on offshore structures is described by L.M. Rogers (1983). Of particular value is the ability of the technique to give global coverage of all welded joints, including those that are otherwise inaccessible.

An application of continuous AE monitoring is that on the blast furnace stove domes at Redcar, described by Cole (1983). Other applications are described in the IChemE *AE Monitoring Guide*.

19.14.10. AE *monitoring applications: leaks*

High pressure and high velocity leaks give characteristic noise, as does pump cavitation, and the detection of these is another application of AE monitoring. The use of this method to detect tube failures in heat exchangers and boilers has been described by Ghia et al. (1983).

19.14.11 IChemE AE Monitoring Guide

The IChemE *AE Monitoring Guide* deals with the technique under the following headings: (1) scope, (2) role in structural integrity assessment, (3) applicability to process vessels and pipework, (4) practical requirements, (5) specific examples and (6) practical experience, as given by a user survey. It includes appendices on (1) AE basics, (2) AE test and report specifications, (3) standards and codes, (4) survey returns, (5, 6) questionnaires and (7) bibliography.

The *Guide* emphasizes the importance of defining the purpose for which AE monitoring is to be conducted and gives a flow diagram for the development of the monitoring strategy. The work should be undertaken only if both the plant and the technique are suitable, the level of background noise is not excessive and the exercise is economic.

Under practical requirements the *Guide* deals with the definition of the responsibilities of the operator and the AE contractor, the establishment of the feasibility of AE testing, the experience and qualifications of the contractor, the essential information on the containment, and the test specification, covered in Appendix 1.

The practical applications described cover a liquefied petroleum gas (LPG) storage sphere, an ammonia storage sphere, an ethylene storage bullet, a refrigerated ammonia storage tank and storage tank floor; a nitric acid column, a stainless steel column and an insulated carbon steel and stainless steel columns; a Hastelloy B reactor; a boiler drum; a deaerator; glass reinforced plastic storage tanks for sulfuric acid and hypochlorite; pipework; a crane and bearings.

Detailed results are given from the user survey, the sections of which cover the number of tests done by the participant companies, the types of test done, the types of structure tested, the materials of construction of these structures, the perceptions of success and the future intentions. It contains in Appendix 4 single-sheet summaries of individual applications.

The survey indicates that the majority of applications are to metal structures and use commercial packages, principally MONPAC. The main use is for in-service testing of pressure storage vessels and other vessels and storage tanks. More experienced users also conduct pre-service tests.

The *Guide* gives recommendations on the use of AE monitoring.

19.15 Plant Monitoring: Specific Equipment

As the foregoing account indicates, monitoring techniques can be applied to a wide range of plant equipment.

For defects in rotating equipment, prime techniques are performance monitoring and vibration monitoring. Another important method is debris analysis.

For static equipment such as tanks, vessels, columns and pipework, widespread use is made of ultrasonics. Such NDT methods are increasingly being complemented by AE monitoring. Corrosion monitoring is another technique that is widely applied, to static plant particularly.

19.16 Pipeline Inspection and Monitoring

19.16.1 Pipeline inspection

Pipelines present a rather different inspection problem from that posed by regular process plant in that they are outside the factory fence, are very long, are usually buried, and are normally required to operate without shutdown.

Traditional methods of inspection include liaison with local farms through whose land the pipeline passes, walking the pipeline and aerial survey of the pipeline. In some cases, bar holes may be sunk near the pipeline to take gas detectors. Use may be made of a search gas or radioactive tracer.

Inspections may also be made of the CP of the pipeline such as checking on coupons of the material and on the pH of the electrolyte in contact with the protected surface.

19.16.2 Inspection vehicles

The alternative to these conventional, and rather limited, methods is the use of an inspection vehicle, or 'intelligent pig'. This device is now routinely used by British Gas for the inspection of its pipeline grid. An account has been given by Braithwaite (1985). The company operates some 17,000 km of high pressure natural gas transmission pipeline in Britain. A typical line interval for inspection is about 80 km.

The inspection specification for the pig required that it should detect, locate and size defects and distinguish defects from other features with a low incidence of spurious indications. Three types of defect were of interest. One is geometric damage, which includes ovality, dents and wrinkles. Another is metal loss due to corrosion or impact. The third is crack-like defects such as plate rolling laminations, stress corrosion cracks and fatigue cracks. The avoidance of spurious indications is of some importance, because frequent spurious indications leading to the excavation of the pipeline would rapidly cause a loss of credibility.

The engineering specification required that it be capable of passing through the line without sudden changes of speed and without jamming in the line.

The pig is designed to operate in pipelines containing gaseous or liquid hydrocarbons. The pig contains three principal systems: the NDT equipment, the electronics and the power pack. There are three NDT systems: one surveys the geometry of the pipe, another detects metal loss, and the third inspects for cracks.

The quantity of data generated by the inspection equipment is very large. An area of 1 cm^2 is significant in defect terms and a typical line section of 80 km has an area of some $3 \times 10^9 cm^2$. It is not practical to store all the data generated and a computer is included to perform on-board data handling.

Braithwaite also describes the selection of the maximum inspection intervals, the field operations and the reporting and rectification procedures.

19.16.3 Pipeline leak monitoring

There are a number of methods available for monitoring the detection of leaks in pipelines. An account is given by Ellul (1989).

One approach is the use of acoustic monitoring. When a leak occurs, the sudden pressure drop creates a rarefaction wave that propagates away from the leak point at the speed of sound. This wave can be detected by acoustic monitoring.

Acoustic monitoring gives information on the existence and location of a leak, but little on its size. In ideal conditions it can detect very small leaks, but it is less effective against a background of noise from compressors and valves.

An alternative approach is to monitor the behaviour of the pipeline using some form of model. One technique is to determine a line volume balance model over some fixed period. This involves calculating the difference between the inflow and outflow, or net inflow. Different balance intervals are appropriate for different purposes. For a typical pipeline, a short-term balance over 1–2 h is suitable for relatively rapid detection of the leak, whilst a long-term balance over 3–6 h gives greater accuracy. Detection of a leak as small as 0.5% of throughput may be achieved.

Use may also be made of a more sophisticated model incorporating values of the pressure, temperature, flow and density at various points in the pipeline. The operation of the line is monitored by comparing the measured and the model values. The occurrence of a leak should cause excursions of some of these parameters outside their control limits. Criteria can be devised to flag the existence of a leak.

19.17 Notation

Section 19.7

c	corrosion allowance
f_a	nominal design strength at test temperature
f_t	nominal time-independent design strength (see text)
p	design pressure
p_t	test pressure
t	nominal thickness of section under consideration

Section 19.8

L	leak rate (Pa m^3/s)
P	pressure (Pa)
t	time (s)
V	volume of vessel (m^3)

For alternative units see text

Section 19.10

Equations 19.10.1 and 19.10.2

L	fraction of gas leaking
p_i	suction pressure
p_o	discharge pressure
T_i	inlet temperature (before addition of bypass gas)
T_o	discharge temperature
T_s	suction temperature
ΔT_H	correction for Joule-Thomson effect
μ	constant, approximately equal to ratio of gas specific heats

Equation 19.10.3

A	jet nozzle exhaust area
G_a	compressor air pumping capacity
N	compressor speed
P_d	compressor discharge pressure
T_d	compressor discharge temperature
T_i	turbine inlet temperature
W_f	fuel flow
Δ	normalized increment of variable
η	compressor efficiency

20 Plant Operation

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Accidents on process plants arise as often from deficiencies of operations as from those of design. It is difficult, therefore, to overstress the importance of plant operations in safety and loss prevention.

Accounts of plant operation include *Process Plant Design and Operation* (D. Scott and Crawley, 1992) and those by E. Edwards and Lees (1973) and London (1982). Some reference to plant operation is also made in many of the Chemical Industries Association (CIA) codes and guidelines and the Health and Safety Executive (HSE) guidelines mentioned in Chapter 11. Selected references on plant operation are given in Table 20.1.

Many aspects of operation are dealt with in other chapters. In particular, these include: plant management (Chapter 6); hazard identification (Chapter 8); pressure systems (Chapter 12); process control (Chapter 13); human factors (Chapter 14); fire protection (Chapter 16); plant inspection (Chapter 19); plant maintenance and modification (Chapter 21); emergency planning (Chapter 24); personal safety (Chapter 25); and information feedback (Chapter 27).

The present chapter deals with some important aspects of operation which are not treated elsewhere. These are:

(1) operating discipline;
(2) operating procedures;
(3) emergency procedures;
(4) handover and permit systems;
(5) operator training;
(6) plant patrols;
(7) modifications to the process;
(8) operation and maintenance;
(9) start-up and shut-down;
(10) start-up of refinery units;
(11) shut-down of refinery units;
(12) operation of fired heaters;
(13) operation of driers;
(14) operation of storage;
(15) operational activities and hazards;
(16) sampling;
(17) trip systems;
(18) identification measures:
(19) exposure of personnel;
(20) security.

Before considering these detailed aspects, however, it is emphasized again that the safe operation of hazardous plants requires in particular competent and experienced managers and formal, well considered and fully understood systems of work. The aspects of operation mentioned are now discussed.

20.1 Operating Discipline

The safe operation of a process plant requires adherence to a strict operating discipline. This discipline needs to be formulated, along with the safety precautions, during design and then enforced in operation. An account of operating discipline is given by Trask (1990).

The impetus for the development of operating disciplines in the author's company came in the 1960s from the perceived need to ensure that the technology was uniformly applied in all the company's plants, both in the United Kingdom and overseas, and in the 1970s from the need to ensure that human technical skills were maintained in the face of increasing automation.

The steps involved in developing the operating discipline are: (1) to identify the important operating parameters, specify operating limits on these parameters, and arrange for them to be measured, controlled and monitored, using both trend records and alarms; (2) to ensure mass and energy balances and (3) to develop and document operating procedures, safety precautions and remedial actions.

20.1.1 Operating envelope

The design of the plant specifies the conditions at which it is to operate. In some cases, such as operation at different throughputs, it may specify several sets of conditions. There is, however, a degree of latitude in operation, and some divergence from the nominal design conditions is acceptable. In fact, since the design embodies inaccuracies of various kinds, it is inevitable.

It is necessary, therefore, to define the envelope of conditions within which variations are allowed but across which excursions are not permitted. In the first instance, this envelope is defined by the designer in terms of constraints related to the pressure envelope, such as vessel design pressure and temperature limits, and also to the process conditions such as flow limits related to static electricity or temperature limits related to freezing or hydrate formation. The envelope may subsequently be modified to some degree on the initiative of the plant management, but in consultation with the design function. At any given time, however, the operational envelope should be clearly defined and strictly enforced.

20.2 Operating Procedures and Instructions

Fundamental to the safe operation of plant is the development of suitable operating procedures. The procedures are normally formulated during the plant design and are modified as necessary during the plant commissioning and operation.

20.2.1 Regulatory requirements

In the UK the provision of operating procedures is a regulatory requirement. The Health and Safety at Work etc. Act (HSWA) 1974 requires that there be safe systems of work. A requirement for written operating procedures, or operating instructions, is given in numerous codes issued by the HSE and the industry.

In the USA the Occupational Safety and Health Administration (OSHA) draft standard 29 CFR: Part 1910 on process safety management (OSHA, 1990b) states:

(1) The employer shall develop and implement written operating procedures that provide clear instructions for safely conducting activities involved in each process consistent with the process safety information and shall address at least the following:
    (i) Steps for each operating phase:
        (A) initial start-up;
        (B) normal operation;
        (C) temporary operations as the need arises;
        (D) emergency operations, including emergency shut-downs, and who may initiate these procedures;
        (E) normal shut-down and
        (F) start-up following a turnaround, or after an emergency shut-down.

Table 20.1 *Selected references on plant operation*

NRC (Appendix 28 *Nuclear Power Plant Operation, Operational Safety Reliability Program, Operation*); American Oil Company (n.d./1–10); MCA (SG-2); J.R. Howard (1959); Steinhoff (1959, 1973); Anon. (1961a); Gimbel (1965a); W.H. Richardson (1966); Holroyd (1967); Badger (1968); Lofthouse (1969); O.M. Allen and Hanna (1971); E. Edwards and Lees (1973, 1974); IP (1973 Eur. MCSP Pt 1); Kauber (1973); API (1975 RP 50); Neal (1976); Anon. (1977 LPB 14, p. 2); Blair (1977); *Chemical Engineering* Staff (1980); IBC (1981/21); Kister (1981a,b, 1990); London (1982); Roodman (1982); H.W. Martin (1983); Kolff and Mertens (1984); Burgoyne (1985c); Tayler (1985d); Rausch (1986); G.K. Chen (1987); AGA (1988/55); Cloke (1988); EPA (1988/1); Trask (1990); McConnell (1992); D. Scott and Crawley (1992); R.E. Sanders (1993b)
Site register: RoSPA (IS/77)
Communications: Bach (1968); Anon. (1976 LPB 10, p. 4)
In-plant chemicals labelling: Kmetz (1990)
Production control, material balance, quality control: Tingey (1962); Hearfield (1975); Oakland (1981)

Start-up and shut-down, turnarounds
American Oil Company (n.d./4); Anon. (1960f); Ballmer (1964); Bonnel and Burns (1964); Hayes and Melaven (1964); Lieber and Herndon (1965, 1973); Loen (1966, 1973); Nobles (1967); Luus (1971); EPA (1972/16); Barnett (1973); H.S. Moody (1974); Kister (1979, 1981a); API (1982 *Refinery Inspection Guide* Ch. 18); Bauman (1982); H.V. Bell (1982); Rattan and Pathak (1985); Feuless and Madhaven (1988); Butler, Nayar and Wheeler (1993); Nimmo (1993)

Boilers, burners, furnaces, flares (*see also* Table 12.3)
S.R. Green (1952); Bluhm (1961, 1964b); P.W. Taylor (1964); FMEC (1967); OIA (1971 Bull. 501); Charlton (1973); HSE (1975 TON 25); NEPA (1990 NEPA 86)

Storage, terminals
H.T. Fuller and Bristline (1964); J.R. Hughes (1970); PITB (1973/5); Hearfield (1975); MCA (1975 TC-8, TC-27, TC-28, TC-29); Anon. (1976 LPB 9, p. 1); Chlorine Institute (1979 Pmphlt 9, 66, 1982 Pmphlt 5, 1984 Pmphlt 78, 1986 Pmphlt 1); API (1982/5); NEPA (1990 NEPA 307)

Operating activities
Purging: AGA (1954, 1975); Constance (1980); Anon. (1989 LPB 90, p. 1); Levinson (1989); Schneider (1993)
Sampling: MCA (SG-16); Ducommun (1964a,b); ICI/RoSPA (1970 IS/74); Gitzlaff and Batton (1979); Lovelace (1979); Chlorine Institute (1984 Pmphlt 77); Anon. (1989 LPB 88, p. 1); Anon. (1990 LPB 92, p. 27); Anon. (1992 LPB 106, p. 19)
Draining: Klaassen (1980b); Anon. (1991k)
Additives, catalysts: W.S. Wood (1963); Brand and Burgess (1973)

Operating procedures, instructions, manuals (see Table 14.2)

Leaks and spillages
ICI/RoSPA (1970 IS/74); Bess (1972); Home Office (1972/9); MCA (1973/22); AIChE (1974/99, 1988/100); Kletz (1975b, 1981g, 1982i); Anon. (1987 LPB 74, p. 1)

Winter conditions
IRI (n.d./1); Buehler (1967); House (1967); API (1983/8)

Security
EPA (CFSD SEC series, 1972/19); NRC (Appendix 28 Security); IRI (n.d./4); Hamilton (1967); NEPA (1971/7); Payne (1971); IMechE (1972/5); Oliver and Wilson (1972); K.G. Wright (1972); C. Ward (1973); G. Green and Faber (1974); Flood (1976); Atallah (1977); W. Price (1978); D.L. Berger (1979); Spranza (1981, 1982, 1991, 1992); Bailey (1983); Lobel (1985); Anon. (1987 LPB 77, p. 17); Pitt (1987)

(ii) Operating limits:
  (A) consequences of deviation;
  (B) steps required to correct and/or avoid deviation; and
  (C) safety systems and their functions.
(iii) Safety and health considerations:
  (A) properties of, and hazards presented by, the chemicals used in the process;
  (B) precautions necessary to prevent exposure, including administrative controls, engineering controls, and personal protective equipment;
  (C) control measures to be taken if physical contact or airborne exposure occurs;
  (D) safety procedures for opening process equipment (such as pipe line breaking);
  (E) quality control of raw materials and control of hazardous chemical inventory levels; and
  (F) any special or unique hazards.

(2) A copy of the operating procedures shall be readily accessible to employees who work in or maintain a process.

(3) The operating procedures shall be reviewed as often as necessary to assure that they reflect current operating practice, including changes that result from changes in process chemicals, technology and equipment; and changes to facilities.

20.2.2 Operating procedures

Accounts of the generation of operating procedures and instructions have been given by R. King (1990) and I.S. Sutton (1992).

In designing a plant, the designer necessarily has in mind the way in which it is to be operated. It is desirable that this design intent be explicitly documented, otherwise it has to be inferred from the equipment provided. In the case of batch and other sequential processes the designer normally defines the operations required to execute the sequence.

Practice in the formulation of operating procedures varies. The lead is normally taken by the plant manager. In the case of a new plant the commissioning manager is often the prospective plant manager, and will therefore undertake the task.

Operating procedures may be developed using a team of experienced people who examine successively the procedures necessary for testing and pre-start-up activities, normal start-up, normal shut-down, emergency shut-down, etc.

The information required in order to formulate procedures includes: the order in which operations should be carried out; the valve states and valve changes associated

with each operation; the time required to perform the operation; and the operations which have to be completed before another operation can be initiated.

For a new plant an initial set of operating procedures is devised, but these are likely to be modified as the result of experience during the commissioning. Likewise, procedures for an existing plant will undergo changes based on operating experience, as well as changes due to process or plant modifications.

The extent to which process operators are involved in the formulation of operating procedures varies. Some operating procedures are modelled on the practice of the 'best' operator. Operators also devise short cuts. These should be examined, and accepted or rejected, as appropriate, with reasons given.

A formal method of analysing the operator's task is available in task analysis, which is described in Chapter 14.

It is the task of management in formulating operating procedures to clear up muddled thinking, to identify incorrect assumptions, to resolve differences and to eliminate inconsistencies. The ultimate responsibility for the operating procedures rests with the plant manager.

20.2.3 SRDA Operating Procedures Guide

A systematic approach to the development of operating procedures is given in *Developing Best Operating Procedures* (Bardsley and Jenkins, 1991 SRD SRDA-R1) (the SRDA *Operating Procedures Guide*).

The SRDA *Guide* distinguishes between two basic types of documentation to support operator performance: (1) manuals and (2) job aids. Essentially a manual is a resource, which is a store of information to which managers, engineers and trainers may refer. The information contained in it, however, is usually not in a form best adapted for direct use by the operator. What he requires for immediate use is a job aid.

Operator support documentation may take the form of (1) procedures, (2) checklists or (3) decision aids. The simplest form of procedure is a set of actions which are performed in sequence with a minimal feedback requirement. More complex procedures involve actions which are dependent on a lapse of time and/or the state of the process, or which involve sets of actions other than a straightforward sequence. The typical checklist is an *aide memoire* used to check the state of items on the plant, notably valves, prior to undertaking some operation such as start-up. Decision aids, in the form of decision trees, or flowcharts or algorithms, guide the operator through the decision pathways. There are also other types of decision aids, used particularly for fault diagnosis, such as functional diagrams. In addition to these specific forms, documents often contain explanations.

The *Guide* poses six basic questions to be asked concerning the operator's use of a support document. The writer needs to ask how the operator decides when to use the document, how he locates the document itself and how he locates the required help within it. Furthermore, the writer must ask whether the document provides the information sought in a form such that appropriate action is selected, whether it indicates the circumstances in which an alternative course of action is required and whether it states how the action is to be controlled. Finally, the writer should check that the document has been successful by means such as monitoring of feedback.

In addressing the question of operator support documentation, the first step is to establish that there really is need for it. One general justification is compliance with regulatory requirements or company policy. Another justification is the nature of the task.

On this the *Guide* both gives some general pointers and also outlines some specific techniques. With regard to the former, some task characteristics that may indicate the need for job aids are that: it is critical; it is difficult, for example fault diagnosis; it is performed infrequently, for example an emergency procedure; and/or it is long and involves memory load. If a job aid is to be provided, there must be time for it to be located and used.

It needs to be borne in mind that a job aid may not prove as effective as expected. Some reasons for this are that it remains unused, that it is seen as taking the skill from the task and that it may restrict the choices available to a skilled person.

The specific techniques referred to are those of task analysis and human reliability analysis.

The *Guide* describes the process of designing and implementing an operating support document in terms of the following stages: (1) the definition of the purpose and scope and the selection of a format (manual or job aid), (2) the establishment of collaboration with sources of information, (3) the establishment of information content, (4) the prototyping, (5) the preparation of a draft, (6) a review of the draft both for technical content and usability, (7) implementation and (8) maintenance.

An account is given of hierarchical task analysis and of human reliability analysis, both of which have been described in Chapter 14. In respect of the latter, the two techniques considered are SHERPA and CADA.

The writing of an operating support document which can be understood requires careful attention both to the written text and to the alternatives to such text. Aspects of the written text treated in the *Guide* are: the use of a comprehensive vocabulary, supported if necessary by a glossary, and of conventional terms as opposed to jargon; the use of the active rather than the passive tense; care with the use of negatives; retention of the definite and indefinite articles; the use of short sentences; the presentation of instructions as a sequence; and an indication of any applicable preconditions. The *Guide* gives detailed guidance on character style, punctuation and layout.

The *Guide* also describes the use of tables and figures. Tables provide a good format for stating the courses of action to be taken in different situations. The types of tables given are the condition-action table and the decision table, both akin to a truth table, and the look-up table. The types of figures described are decision aids in the form of flowcharts, and various kinds of equipment diagrams, including photographs. Equipment diagrams include: drawings, or sketc-hes, of single equipments or ensembles, which are useful for identifying and locating components; line diagrams showing the main items of equipment and the connections between them; and functional flow diagrams giving the functional as opposed to the physical structure of the system.

Guidance is also given on document organization and layout. A hierarchical organization is recommended and aids to moving around the document are described. The need for consistency is emphasized.

Finally, the *Guide* discusses the tools available for the production of the document such as word processors, desk

top publishing packages, object oriented drawing packages and so on.

20.2.4 Operating instructions

Accounts of the writing of operating instructions from the practitioner's viewpoint are given by Kletz (1991e) and I.S. Sutton (1992).

Operating instructions are commonly collected in an operating manual. The writing of the operating manual tends not to receive the attention and resources which it merits. It is often something of a Cinderella task.

As a result, the manual is frequently an unattractive document. Typically it contains a mixture of different types of information. Often the individual sections contain indigestible text; the pages are badly typed and poorly photocopied; and the organization of the manual does little to assist the operator in finding his way around it.

Operating instructions should be written so that they are clear to the user rather than so as to absolve the writer of responsibility. The attempt to do the latter is a prime cause of unclear instructions.

A set of instructions which illustrates the above principles has been given by Kletz, as shown in Figure 20.1. Further examples are given by Sutton.

This latter author describes a method of writing the operating instructions, and of creating the operating manual. Basic requirements for the operating instructions are that they should be complete, up-to-date, properly indexed and easy to use.

The operating manual is organized in the format of a tree that is developed from the top down. It starts with broad categories of procedure such as start-up, normal operation, normal shut-down, etc., and is developed until it reaches, at the bottom level, the sets of specific operating procedures, or modules. It may be noted that this layout conforms closely to the tree structure used in task analysis.

A distinction is made between information, rules, procedures and checklists. Information is provided for reference, but selectively. Rules are stated, although these are likely to be of more interest to managers and supervisors than to operators. Checklists are given as appropriate.

Instructions are given for each procedure. The procedure may be based on a generic procedure, such as that for pump start-up, but with specific modifications for the operation in question. The level of the instructions should be such as to allow an experienced operator to run the plant with minimal reference to the supervisor. Each instruction should have an imperative verb in the active tense. Warnings, cautions and notes are inserted in the text of the procedure, as appropriate; a warning should precede the procedure.

As described by Sutton, a module may be referenced in any part of the manual and by any writer, but only by its title; reference should not be made to the content of the

ACTION TO TAKE WHEN A-SIDE ID FAN TRIPS

1 CHECK A SIDE FURNACES HAVE TRIPPED
2 ADJUST KICK-BACK ON COMPRESSORS TO PREVENT SURGING
3 REDUCE CONVERTER TEMPERATURES
4 CHECK LEVEL IN STEAM DRUMS TO PREVENT CARRYOVER

Panel Operator

1 Shut TRCs on manual
2 Reduce feed rate to affected furnaces
3 Increase feed to Z furnace
4 Check temperature of E54 column

Furnace Operator

1 Fire up B side and Z furnaces
2 Isolate liquid fuel to A side furnaces
3 Change over superheater to B side
4 Check that output from Z furnace goes to B side

Centre Section Operator

1 Change pumps onto electric drive
2 Shut down J43 pumps

Distillation Operator

1 Isolate extraction steam on compressor
2 Change pumps onto electric drive

Figure 20.1 *Format of operating instructions: extract from a plant instruction showing the action to be taken by an operating team of one supervisor and four operator when the induced draught (ID) fan providing air to a row of furnaces (known as A side) stops (Kletz, 1991e) (Courtesy of the Instituition of Chemical Engineers)*

module. This discipline, which has much in common with that followed for computer program subroutines, facilitates the updating of the manual by allowing a single module to be replaced at any time.

The manual is more readable by basing it on graphics rather than text so that the text supports the graphics rather than vice versa. Modules are written in a two-page format, which is what the user actually sees at a given time.

The manual should define clearly the authorization for particular actions.

Commonly the manual contains a section on troubleshooting. This activity is quite different from that of following a procedure for normal operation. Such a procedure is a closed activity and the instructions for it are intended to be followed without deviation. Troubleshooting, by contrast, is open-ended and creative. The procedures for it are not definitive and do no more than offer guidance.

The creation of the operating manual involves, first, the definition of the manual structure, then the collection of the information and, finally, the writing of the modules. Sutton estimates that his method may involve an effort which is an order of magnitude greater than the conventional approach. A further account of the creation and contents of the operating manual is given by R. King (1990), with a detailed discussion of suitable contents.

Commonly the operating manual is a hard copy document. It should be available on the plant. Some personnel may be given a personal copy. Authority to make modifications to the manual should be clearly defined. The manual should be kept up to date, including personal copies where issued.

The advent of computer aids such as word processing and graphics packages opens up an alternative approach in which the master version of the operating manual is kept in the computer with various options for hard copy.

In addition to the treatment given by these three authors the following comments may be made. Regard should be had to the intended users of the operating instructions. These include (1) novice operators, (2) operators whose experience has been on other plants but who are being trained for the plant in question and (3) operators experienced on that plant. The organization of the operating manual into successively more detailed levels goes some way towards meeting their different needs. An experienced operator may require operating instructions mainly for safety critical operations or operations performed only rarely.

The simplest operating instruction is a linear sequence of actions. There is a limit to the degree to which an operating instruction may be extended to include decision trees, branches and loops. Generally these are avoided if possible, except for diagnosis. On the other hand, it is common to include general advice about and/or specific instructions for recovery from potential problem situations.

Practice with regard to use of graphics appears to vary. As stated, Sutton's approach is that the text is there to support the graphics. At the other end of the spectrum operating instructions are written which make minimal use of graphics.

Operators are typically provided with operating instruction sheets/checklists which may well be reproductions of sheets in the operating manual and which they can take out onto the plant. It may also be appropriate to provide other aids such as a list of alarms and trips.

The writing of the operating instructions is a significant task. Some principal sources of information are the quantities flowsheet, the engineering line diagram, the design manual and vendors' manuals. The contractors may provide very little and vendor information may become available only late in the day. The situation is eased if an operating manual is available from a previous plant.

The first task faced by the person charged with producing operating instructions tends actually to be the provision of instructions for commissioning. This can be as large a task as the creation of the instructions for normal operation. Commissioning activities for which instructions may need to be provided include plant water testing, control loop testing, load cell testing and checks on vessel fill times, completeness of vessel emptying, and heating and cooling rates. The instructions should also cover checks to ensure that before an equipment is brought into use each of its instruments is operational.

Many operations involve the reading of instruments. The instructions need to specify the readings at which action must be taken. A considerable part of the effort required to write the instructions may have to be devoted to specifying these readings and the writer may have to search through a number of documents. In addition, water testing requires some readings to be specified also for water as the fluid.

In devising operating instructions regard should be had to the practicality of the individual actions and sequence of actions required. It is not desirable, for example, to create a sequence of actions in which one has to be performed at the top of a tower, the next back down at ground level and the next up at the tower top again. Another area where thought is necessary is the response to alarms and the settings on alarms. For example, the implications of and the response times available for a particular fractional fill may be different from one vessel to another.

If the plant is a computer-controlled batch plant the number of operator interventions may be quite small and may involve relatively little decision-making. In this case the proper operating instructions are likely to be a mix of computer sequences with occasional manual operations such as additions and instructions on recovery from problems.

The operators will require training in the operation of the plant based on the operating instructions. It is necessary, therefore, to provide a training manual. This may draw on the operations manual. Typically it contains an operating instruction section together with other material such as a training plan, workbook exercises, an assessment plan and performance criteria. The need for a training manual may be regarded as a principal justification for the creation of the operating manual. Training in operating procedures is discussed in Chapter 14 and is mentioned in many other chapters.

20.3 Emergency Procedures

A set of operating procedures of particular importance are the emergency procedures. It is generally recognized that it is not possible to provide detailed procedures for all possible emergency scenarios. In the *Guide to Safe Practice in the Use and Handling of Hydrogen Fluoride* (CIA, 1978) the following two-pronged approach is recommended:

> Firstly, careful consideration should be given to what major emergencies can be reasonably foreseen, and the detailed procedure for tackling these (few) serious situations should be dealt with specifically both by training sessions and special instructions.

Secondly, since it is impossible to cover all eventualities by instructions which will be effectively remembered or found for reference during an emergency, it is advisable to give a series of general instructions, amply backed by training, which will provide guidance for the correct action in those emergency or potential emergency situations which have not been dealt with by specific cases. Such aspects as equipment isolation, the recognition of hazardous conditions, and communications are fundamental matters which can be treated in this way.

Emergency procedures are commonly treated in codes under the following headings: (1) leak detection and characterization; (2) raising the alarm and associated actions; (3) isolation of leaks; (4) handling of leaks and spillages; (5) action against fire; (6) emergency equipment and (7) special features of particular chemicals.

These topics are considered at this point, except that raising the alarm and associated actions are treated in Chapter 24 and the treatment of action against fire is limited – the main account being given in Chapter 16.

20.3.1 Emergency equipment

Emergency equipment commonly listed in codes includes (1) protective clothing, (2) breathing apparatus, (3) emergency tool kits and (4) fire fighting equipment.

20.3.2 Leaks and spillages

Leaks and spillages are a relatively common occurrence on process plants and it is necessary to have procedures for dealing with them. Discussions of leaks and spillages have already been given in Chapters 10, 15, 16 and 18 in relation to plant layout, dispersion, fire and toxic release. It is appropriate here, however, to review some of the more general aspects of the problem from the operational point of view.

Plant management should formulate procedures for dealing with leaks and spillages. The range of actions required varies with the nature and size of the leak. In all cases personnel handling the leaks should wear any necessary protective clothing and breathing apparatus.

A small leak may often be stopped relatively easily. If the leak is more serious, other measures are required. The ICI LFG Code (ICI/RoSPA 1970 IS/74) lists these for liquefied flammable gases. If it is practical to do so, the leak should be isolated. This is not always possible with manually operated valves that may be enveloped in the gas cloud. Remotely operated isolation valves may be used if installed. Instructions should take account of possible difficulties in effecting isolation. Other measures to reduce leakage include depressurizing and blowdown.

Personnel involved in controlling the situation should avoid entering the vapour cloud. The leak should be approached only from upwind. Other personnel should not be allowed in the area. There should be some method of warning and evacuating them, and also of sealing off the area.

Measures should be taken as appropriate to disperse or contain the leakage. This aspect is discussed in Chapters 15 and 16.

The area to which a flammable vapour cloud is likely to spread should be cleared of sources of ignition, which include not only activities such as hot work but also traffic. It may be necessary to close roads and railways that the vapour could reach.

The emergency services should be alerted as appropriate.

After the incident is over, any record required by the reporting system should be made.

20.3.3 Leaks and spillages: detection and characterization

For large releases, detection of a leak and characterization of the resultant cloud are important. These are discussed in the CCPS *Guidelines for Vapor Release Mitigation* (1988/3).

For detection the first line of defence is gas detectors. The *Guidelines* discuss the detectors available and their positioning. Accounts of detectors for flammable and toxic gases are given in Chapters 16 and 18, respectively.

In most plants there are personnel who may detect the presence of the gas. Detection by humans is discussed in *The Perception of Odors* (Eugen, 1982) and data on odour thresholds are available in texts such as *Compilation of Odor and Taste Threshold Value Data* (Fazzalari, 1978). Selected data are given in the *Guidelines*. Appendix 11 contains a further discussion of odours.

If a leak occurs, which gives rise to a large vapour cloud, it assists in handling the emergency if personnel are able to estimate the size and movement of the cloud. Their ability to do so depends on its visibility. A small number of substances yield, at a sufficiently high concentration, a vapour cloud which is visible by virtue of its colour. Principal examples are chlorine and bromine, which give a greenish-yellow and a reddish-orange cloud, respectively.

A more common form of visible cloud is that caused by fog formation. Liquefied flammable gases and other liquefied gases such as ammonia, hydrogen chloride and hydrogen fluoride may give rise to fog, depending on the conditions of release and the atmospheric humidity. The *Guidelines* devote an appendix to fog correlations and give the following relation for the concentration at the interface between the regions where fog is and is not generated

$$C = k\ln(1/\psi) \qquad [20.3.1]$$

with

$$k = \frac{1.75 \times 10^6}{H_s^{2/3}} \qquad [20.3.2]$$

where C is the interface concentration (ppm), H_s is the heat of solution (cal/gmol), ψ is the fractional humidity (% relative humidity/100) and k is a constant.

20.3.4 Leaks and spillages: water and foam

One method of dealing with a liquid spillage is the application of foam. Regular foam is mainly water and its use will often actually increase the rate of vaporization of the spilled liquid, thus making the situation worse. On the other hand, there are legitimate uses of foam. The use of foam on liquid spillages is discussed in Chapter 15. Some limited comments are given below.

If the chemical is completely miscible with water, water may be applied to dilute it. However, the number of industrial chemicals which pose a significant hazard and which are water miscible are limited.

20.3.5 Leaks and spillages: particular chemicals

The response to a leak or spillage emergency depends also upon the specific characteristics of the chemical released.

For hydrocarbons the main hazard is that of fire or explosion, and also that of injury by freezing due to contact with cold liquefied gas. The best way of dealing with an unignited leak of hydrocarbon is to shut it off by isolation. A spillage of liquid hydrocarbon should be contained to the extent possible. This is principally a matter of plant layout and the operational measures which can be taken are fairly limited.

The CIA codes and guidelines give some guidance on handling leaks and spillages of other substances. Mention is made here of just one or two of these to illustrate the principles involved.

An acrylonitrile spillage should be contained with sand or earth and covered with a 150 mm layer of mechanical foam and an emulsifying agent or absorbent material. Aqueous solutions may be treated with calcium or sodium hypochlorite in appropriate proportions. Where these treatments are not readily available, surface spillages may be diluted with large quantities of water.

A spillage of ethylene oxide may be handled by diluting it with a quantity of water sufficient to render it non-flammable. This may be done using water sprays or, where available, water monitors. It may be noted, however, that in discussing the disposal of the contents of a storage tank the guidelines state that it is not usually practical to dilute liquid ethylene oxide to the point of non-flammability and that liquid which has not been rendered non-flammable needs to be treated as a flammable liquid.

For a vinyl chloride spillage the preferred method of control is the use of high expansion mechanical foam. For this not to aggravate the situation, the pool needs to be not still spreading but contained and at least 2 in. deep.

20.3.6 Action against fire

A large proportion of plant fires are due to hydrocarbons. If the fire consists of an ignited leak burning as a jet flame on the plant, the usual practice is to let it burn. It is generally not desirable to seek to extinguish the flame on such a leak, since this risks creating a vapour cloud, which might then explode. The other main form of hydrocarbon fire is a pool fire. The fighting of hydrocarbon fires is discussed in Chapter 16.

There is a limited amount of guidance in the CIA codes and guidelines on action against fire of other substances. The guidance given for pool fires of vinyl chloride (CIA, 1978 PA15) illustrates some of the principles. For a large pool fire, foam can be effective in limiting vaporization and thus in controlling the fire. There is an option to seek to extinguish the fire by using a larger quantity of foam but, unless there are pressing reasons for doing otherwise, it is preferable to let the fire burn out under controlled conditions.

Vinyl chloride also illustrates the problem of toxic combustion products, the products in this case being hydrogen chloride and carbon monoxide. Use may be made of water sprays to disperse and absorb some of the hydrogen chloride. But in any event, persons downwind should be evacuated.

20.3.7 Case history

A case history has been described which illustrates the value of good emergency procedures (Anon., 1991 LPB 98 p. 25). In the course of a stress relieving operation on a 50 mm pipe on a chlorine storage module, a 0.5 m section was burned away by an iron-chlorine fire. The leak was picked up by the gas detectors, the gas alarms operated and the operator went to investigate. He called on the lead operator to sound the chlorine alarm, donned a breathing apparatus set and went and closed the appropriate valves. The site emergency teams arrived and within 3 minutes set up water curtains, but these were not needed as the leak had already been isolated and the cloud was dispersing.

20.4 Handover and Permit Systems

20.4.1 Handover systems

Most large process plants operate round the clock on a shift system. It is essential that information on the state of the plant be communicated by the outgoing shift to the incoming shift. A formal handover system is necessary to ensure this.

The lack of such a system was held to have been a cause of the Piper Alpha disaster. As described in Appendix 19, the operating crew attempted to start-up a pump which was actually under maintenance and thus initiated the leak. The lead maintenance hand told the Inquiry that there were no written procedures for handover and no specification of the information to be communicated at handover. Thus maintenance work was not always covered in the operator's log. He stated: 'There were always times when it was a surprise when you found out some things that were going on'. As it happens, the Piper Inquiry also heard evidence that shortly before the disaster a fatal incident had occurred in which there had been inadequate communication of information from the day shift to the night shift.

There should be a formal and detailed procedure for shift handover. It should cover both operating and maintenance personnel. On the operating side these will normally include the lead operator, the control room operator and other operators who are normally out on the plant, and the lead maintenance hand. There should be a formal logbook that is signed by the incoming person responsible for the particular function. Such a system requires that sufficient time be allowed for the handover to take place and for the outgoing shift to brief fully their counterparts on the incoming one.

An aspect of handover which is of particular importance is the status of permits-to-work. Much of the information which needs to be communicated at handover is likely to relate to such permits.

20.4.2 Permit systems

Another important form of communication is the permit-to-work system just mentioned. Permits are raised mainly in connection with maintenance work and discussion is deferred to Chapter 21. Here it is sufficient to note that the actions of handing over a section of plant to maintenance, and receiving it back, are important not only for maintenance but also for the operating function.

20.5 Operator Training

The process operator runs the plant and deals with the faults which arise in it. He has many training needs which must be met if he is to do the job properly. An account of the principles underlying the training of process operators has been given in Chapter 14. This chapter also discusses some of the specific topics in the area of process operation on which the operator requires training. Safety training of

operators is considered in Chapter 28. Other references to operator training are given throughout the text.

As regards the content of operator training, consideration needs to be given not just to the operating procedures and safety training, but also to other topics where the operator has some responsibility. These include, for example, plant maintenance and modification and plant security.

The training of process operators should not be a once-and-for-all exercise, but should involve updating as appropriate. There may also be special additional training such as that associated with the commissioning of a new plant.

20.6 Plant Patrols

One of the principal functions of operators on process plants is the detection of faults. The detection of faults by the process operator in the control room has already been discussed. Other faults, particularly leaks, are detected by operators during routine patrols.

In one study of the detection of nearly 400 abnormal occurrences, analysis showed that some 40% were detected by routine patrols and another 5% by people who were in the plant area.

An investigation of pipework failures by Bellamy, Geyer and Astley (1989) found the following pattern of detection:

	No. of incidents	*Proportion of incidents* (%)
Alarm	12	26
Automatic detection	4	8.5
Human	27	57
Delayed	4	8.5
Total	47	100.0

Routine patrolling is therefore important and specific arrangements need to be taken to ensure that it is carried out. In particular, steps may be taken to ensure that certain vulnerable features are regularly passed by an operator. Thus in design certain instruments may be located at points which cause the operator to pass by such features, whilst in operation, instructions may be issued for the taking of regular readings from such instruments.

20.7 Modifications to the Process

A process rarely operates for long without undergoing some modification. There are almost always changes in raw materials, in the operating conditions, such as flows, pressures and temperatures, concentrations, or in other aspects. The Flixborough disaster has drawn attention to the potential hazards of modifications to the plant. But modifications made to the process are also potentially hazardous.

As it happens, Flixborough provides an illustration of a process modification also. The reactors were provided with agitators, but at the time when the explosion occurred the agitator in No. 4 Reactor was not in use. The absence of agitation is a crucial point in the hypothesis advanced by R. King (1975c, 1977, 1990) that there was a sudden evolution of water vapour in that reactor.

There is clearly little point in paying meticulous attention to ensuring close control of plant modifications so that the pressure system retains its capability to handle the design conditions for the operating variables, if there is no check on changes made to these parameters. A system is required, therefore, for the management of change in the process as well as in the plant. A system for the control of both process and plant modifications is described in Chapter 21.

20.8 Operation and Maintenance

Maintenance and modification work may present hazards both to the plant and to the workers involved. It is important, therefore, for the plant manager to give full consideration to the implications of such work being carried out on his plant and for him to take appropriate precautions. As a minimum these precautions should be the operation of a suitable permit-to-work, as described in Chapter 21, but in addition some operations require extra measures.

The types of precaution which may be required are illustrated by those described by Hahn (1975) for hot tapping. This is a potentially hazardous operation involving drilling a hole into and fitting a branch on a pipe while it is still on line; the technique is described more fully in Chapter 21. The aspects requiring consideration include (1) pipeline fluid conditions, (2) elimination of leaks, (3) local hazards, (4) emergency isolation, (5) warning system, (6) access and escape routes, (7) fire and rescue services, (8) welders' protective clothing, (9) welding supervision and (10) operations supervision.

The plant manager should check the pipeline fluid conditions, such as flow, pressure and temperature, under normal operation, should agree with the welding manager the conditions to be held during the hot tapping operation and should take steps to ensure that these are maintained. The drains in the area of the welding operation should be sealed off and a review made of sources of flammable or obnoxious materials such as leaking joints or lutes. Any local hazards, including those not connected with the welding operation, should be considered and the personnel involved should be fully briefed about these hazards. Arrangements should be made to isolate the pipeline and affected areas in the event of an emergency. A warning system should be set up to inform plant personnel and emergency services if an emergency occurs. Access should be checked so that emergency services can reach the tapping point and the plant, and the areas sealed off to other traffic if necessary. A check should also be made on escape routes, which at night may need additional illumination. A rescue man from the works fire service should stand by during the operation with a radio link to the fire station to summon the fire rescue services in an emergency. He should be prepared for fire fighting and should have the necessary equipment. A plant fireman should also stand by. A check should be made that the welders have the appropriate protective clothing. The work should be supervised by personnel from both the welding and the plant functions. If possible, the plant manager should be present.

The arrangements described indicate that some maintenance or modification work requires the rather close involvement of the operations side.

20.9 Start-up and Shut-down

As take off and landing are more hazardous operations for an aircraft, so on a process plant the hazard is greater during start-up and shut-down. General principles of plant start-up and shut-down are discussed by D. Scott and Crawley (1992). The procedures for the start-up, operation

and shut-down of particular types of plant are considered in the following sections.

Most accounts of the operation of process plants distinguish the following modes:

(1) normal start-up;
(2) normal operation;
(3) normal shut-down;
(4) emergency shut-down.

Shut-down is not always total. Sometimes there is a partial shut-down to a condition of 'hot standby'. This avoids the need to go through the full sequence of shut-down and start-up operations, and allows operation to be resumed more quickly.

There are, however, further relevant distinctions. Leaving aside the initial start-up when the plant is commissioned, there are variations in start-up depending on the condition of the plant prior to start-up. Some distinctions are:

(1) normal shut-down condition;
(2) hot standby condition;
(3) emergency shut-down condition;
(4) major scheduled shut-down, or turnaround, condition;
(5) prolonged shut-down, or mothballing condition.

The condition of the plant following emergency shut-down depends on the cause of the shut-down, and hence this category actually includes a whole set of different pre-start-up conditions.

The start-up considered here is not the initial commissioning, which is dealt with in Chapter 19, but the resumption of operation after a shut-down.

The actual procedures for start-up and shut-down depend on the process, and vary somewhat. Start-up of a plant with a low temperature section, for example, has special features.

20.9.1 Normal start-up

Start-up requires that the plant be taken through a predetermined sequence of stages. It is important that this sequence be planned so that it is safe and avoids damage to the plant and so that it is flexible enough to handle difficulties which may arise. The conceptual and detailed design of the start-up sequence is discussed in Chapter 11. The personnel involved in the start-up should understand the reasons for the sequence chosen and should adhere to it.

The extent to which detailed procedures can be formulated for start-up depends on the condition prior to start-up. For start-up following a major scheduled shut-down it may not be practical to provide fully comprehensive instructions and it may be necessary to rely instead on the use of checklists for equipment and activities. On the other hand, for start-up from hot standby or a short shut-down it may be possible to provide relatively complete procedures.

Start-up is an operation which needs to be properly planned so that all the resources are available when required. This applies particularly to personnel, for example instrument fitters, and to utilities, for example inert gas.

Start-up should be preceded by a series of pre-start-up checks. These should be governed by a formal system. The plant is first checked to ensure that it is mechanically complete, that there are no missing items such as valves, pipes or instruments, that the status of vent, drain and sample points is correct and that slip plates have not been erroneously left in pipework. A check is then made to ensure that the instruments are working. The availability of the utilities is confirmed. The hand valves are then checked to ensure that the status of each is correct.

In many cases the plant is linked through flows of products and by-products to other plants and the start-up needs to be co-ordinated with the operation of these interlinked plants. Similar considerations apply to the utilities.

Many plants generate services such as fuel gas, steam or electricity which they reuse and recover heat through complex heat exchange arrangements. Features of this sort add considerably to the complications of start-up.

The start-up period is one when serious damage can be inflicted on plant equipment. Thus mention has already been made of the danger of using up a large proportion of the creep life during commissioning. Similar damage can be inflicted in regular start-ups.

Start-up is a time when there is a much higher than average risk of getting unwanted materials such as air or water into the plant. It is necessary to pay particular attention to these hazards.

Instruments are of particular importance during start-up, but unfortunately are likely to be less accurate or reliable than during normal operation. This should be borne in mind if an instrument failure could give rise to a hazardous condition.

It is an essential requirement, therefore, that there be a formal but practical system to control start-ups, that there be proper documentation and that the personnel be fully trained in the procedures.

20.9.2 Normal operation

The normal operation of the plant is discussed in Chapter 13 and is not considered in detail in this section, but there are several points that may be restated.

The plant management should ensure that the objectives of, and constraints on, the operation of the plant are clearly defined and well understood by the process operators.

There should be a full understanding of the relative roles of the operator and the trip system in the face of a developing abnormal condition. In essence, it is the function of the operator to try to prevent this condition developing to the point where a parameter goes outside its permitted envelope and that of the trip system to shut-down if such an excursion is imminent.

It is desirable that there be holding states, or fall-back positions, short of full shut-down, to which the operator can move the plant while a problem is sorted out.

In any event, management must make it clear beyond doubt that any conflict between production and safety is to be resolved in favour of the latter.

20.9.3 Normal shut-down

Normal shut-down starts from the condition of normal operation and its preceding condition is therefore relatively well defined. This makes it practical to formulate shut-down procedures more fully than for some of the start-up situations mentioned.

Many of the features of start-up mentioned earlier, such as the effect on other plants and on utilities, apply *mutatis mutandis* to shut-down.

20.9.4 Emergency shut-down

Emergency shut-down may be effected by an automatic protective system or by the operator. In the first case the

operator's function is to forestall the activation of the automatic system by averting the threatened parameter excursion, whilst in the second he has the additional function of performing the shut-down if it becomes necessary.

In some systems an intermediate case occurs, where the automatic system shuts down part of the plant but it is left to the operator to shut-down other parts. This is the case, for example, on some oil production platforms, where the main oil line may be shut-down automatically but the gas lines to and from the platform, which are linked to other platforms, are shut-down manually, thus allowing a degree of co-ordination with other platforms which would be affected.

The emergency shut-down procedure is generally designed so that the conditions which should trigger it are unambiguously identified and the actions to be taken are clearly defined. A typical shut-down condition is the imminent excursion of a parameter. Typical shut-down actions are shutoff of heat input and depressurization of vessels.

For emergency shut-down by the operator, emergency shut-down procedures should be provided, in the form of a general emergency shut-down procedure. There may be some variability in this procedure depending on the event forcing the shut-down, but an excessive number of variations should be avoided.

These emergency shut-down procedures are to be distinguished from the procedures required to deal with escapes from the plant, which are generally referred to as emergency procedures.

Emergency shut-down is discussed further in Chapters 13 and 14.

20.9.5 Prolonged shut-down

If shut-down is prolonged, precautions should be taken to prevent deterioration of the plant. Typical examples are inspection of equipment to check for external corrosion and 'turning over' of pumps to avoid 'brinelling'. Prolonged shut-down, and start-up from this condition, is discussed further in Chapter 10.

20.9.6 Restart after discovery of a defect

If it is necessary to shut the plant down on account of a fault, the cause and implications of the fault should be established and any necessary measures taken before the plant is started-up again. This situation should be covered by a procedure which details the steps to be taken after such a fault is discovered and before the plant is restarted.

At Flixborough it was found that No. 5 Reactor had developed a crack 6 ft long, but the plant was put back on stream without a thorough examination of the other reactors, an omission which is criticized in the Flixborough Report.

20.10 Start-up of Refinery Units

Accounts of the start-up and shut-down of refinery units are given in *Safe Ups and Downs* (American Oil Company, Amoco/4) and by Hayes and Melaven (1964). Some principal hazards are:

(1) mixing of air and hydrocarbons;
(2) contacting of hot oil and water;
(3) water shots and water freezing;
(4) over- and underpressuring of equipment;
(5) thermal and mechanical shock to equipment;
(6) corrosive and poisonous fluids;
(7) pyrophoric iron sulfide.

The last item is a hazard mainly during shut-down, but the other hazards occur during both start-up and shut-down. Fired heaters present particular hazards and are dealt with in Section 20.12. Start-up should include the following phases:

(1) preparatory activity;
(2) removal of air;
(3) leak testing;
(4) disposal of purge material;
(5) removal of water;
(6) bringing on stream.

The plant should be inspected to check that it is ready for start-up. The auxiliary systems such as the utilities, instruments and gland oil systems should be activated. Shut-down blinds should be removed and running blinds installed.

There are various hazards associated with the activation of the steam system, including water hammer, over-pressuring, and thermal and mechanical shock. Steam should be introduced into the unit gently, with vents and drains open. When the unit is up to temperature, the vents and drains should be closed and the steam traps commissioned. Measures should be taken to avoid collections of condensate which may give rise to water hammer or may freeze.

The activation of the water system presents the hazards of introducing water where it is not wanted and of its freezing. Water connections used only for washing down during shut-down should be blinded off.

There should be a formal procedure with proper documentation for the installation and removal of blinds, so as to ensure that all blinds installed for shut-down purposes are removed and all blinds required for running are installed.

Air should be removed by purging with a suitable material. This is commonly done using water or steam. Use is also made of inert gases such as nitrogen, carbon dioxide or gas from an inert gas generator.

Steam is an effective material for purging. Besides removing air, it vaporizes water, melts ice and reveals blockages in vents and drains. The purging should be done with high-point vents and low-point drains open, but with instrument connections closed except on pressure gauges. The steam should generally be introduced at the bottom of the unit, not only because it is lighter than air and tends to rise but also because this gives a refluxing and cleaning action which is not otherwise obtained.

Purging may also be carried out by filling with water. High-point vents should be opened and the unit filled until the water flows out of the top. Water purging may be done by filling several equipments simultaneously. This method is suitable, however, only if the water will do no damage to process features, for example catalysts, and if the equipment is capable of supporting the weight of water.

Another method of purging is the use of inert gas. The purging should be done with vents and drains open. The pressure should be kept positive, but low so as not to waste gas.

If an inert gas generator is used, the quality of the gas should be monitored. It is necessary for the oxygen content of the gas to be kept well below the target value for the atmosphere in the unit in order to avoid using excessive quantities of the gas.

Closed systems, such as flare and blowdown systems into which relief valves discharge, should also be purged with inert gas. This may require special purge connections.

With steam or inert gas, purging should be continued until analysis shows that the oxygen content is below the desired level. This is typically 0.5% v/v or less.

The vent and drain points at which analytical tests are to be made should be specified and records kept of the tests.

Vacuum equipment may be freed of air by evacuating and refilling with inert gas, this cycle being repeated two or three times.

The equipment should then be raised to a suitable pressure to allow testing for leaks. The testing is carried out by closing the vents and drains after purging and admitting more steam, water or inert gas until the required pressure is reached. All joints and connections should then be inspected for leakage. Leak testing is considered in more detail in Chapter 19.

The positive pressure should be maintained in the equipment after the test. With steam or water a few high-point vents may be opened and a small flow maintained. Condensate should be drawn off periodically from low-point drains. With inert gas, vents and drains should be kept closed.

Vacuum equipment should be given a leak test under pressure, as just described, followed by a vacuum test.

It is then necessary, except for vacuum equipment, to remove the purge materials. This is normally done using fuel gas, which is an essentially hydrocarbon material, is readily available and can be returned to the fuel gas system.

If steam is the purge material, there should be a gradual and simultaneous opening of the fuel gas valve and closing of the steam valve. Drains should be cleared of condensate and both vents and drains closed when the fuel gas flows out.

It is important to allow sufficient fuel gas in the unit to maintain a positive pressure and avoid either allowing air in if the vents are open or underpressuring the unit if the vents are closed.

If the purge material is water, the vents should be closed, the fuel gas admitted at the high point, the drains opened, and the water gradually displaced. Drains should be closed when the fuel gas comes out.

If inert gas purging is used, the fuel gas should be allowed to flow in and mix with the inert gas.

In all cases the fuel gas flow should be maintained until the required pressure is reached. If this is the normal fuel gas line pressure, the unit may be left connected to the line, while if it is some lower pressure, the unit should be shut off or left connected but under pressure control.

With vacuum equipment the purge gas is removed by evacuation.

Residual water should now be removed before hot oil is introduced. This is done by circulating oil which is initially cold (10–40°C) and is then heated to warm (40–80°C) or hot (80–175°C or above). Generally, the oil used is that normally charged to the unit, but suitable low pour point gas oil can be utilized.

While the cold oil is circulating, water should be drained from the system. Since a water–oil emulsion may form, the circulation should be interrupted every 30–40 minutes to let the emulsion break and the water settle so that it can be drained off.

When water is no longer draining, the oil temperature should be raised to warm. This may release some more water by melting ice and breaking emulsions. This water also should be drained away.

If the unit normally operates below the boiling point of water, it is not usually necessary to raise the oil temperature further, but if it operates at higher temperatures, then the oil temperature should be raised to hot.

Usually at this stage the oil flow is changed from circulatory to once-through, the oil being pumped to specified receivers.

Units which operate at higher temperatures often have their own fired heaters and these can be started up and used to heat the oil.

The instrumentation should be brought into service as far as is possible during these operations.

Additional flushing of sections of the unit such as reflux lines and drums and blowdown lines should also be carried out using warm oil. There should be frequent draining of water to prevent violent contact with hot oil. The exact procedures depend on the type of unit.

Finally, the unit should be brought on stream by making the specified staged adjustments to the main parameters, such as flow, pressure and temperature, until the normal operating conditions are reached. This is generally straightforward, but certain hazards may occur. The equipment may be subjected to overpressure or thermal or mechanical shock. Common causes are too rapid changes in operating parameters or a lack of appreciation of the temperature relations between different parts of the system. Water and air may again find their way into the plant from various sources.

20.11 Shut-down of Refinery Units

The same sources also describe the shut-down of refinery units. Shut-down should include the following phases:

(1) cooling and depressurizing;
(2) pumping out;
(3) removal of residual hydrocarbons;
(4) removal of corrosive or toxic materials;
(5) removal of water;
(6) blinding activities;
(7) removal of pyrophoric iron sulfide.

The heat input to the unit should be stopped and fired heaters shut-down. The feed flow should be reduced and then cut off. Excess pressure should be relieved by releasing the hydrocarbon gases to the gas collecting system.

If cooling might cause underpressure, inert gas should be introduced to maintain the pressure close to atmospheric.

Vacuum units should be cooled, the vacuum-producing equipment shut off and the vacuum broken by introducing inert gas.

When the unit is cooled and depressurized, the materials should be pumped out to specified receivers.

Care should be taken that during pumping out centrifugal pumps are not allowed to lose suction completely, since even a short period of running dry can do serious damage. Reciprocating pumps are less susceptible.

The oil pumped out should be cooled so that it is below its flashpoint and is sufficiently cold not to cause trouble if it contacts water in the lines.

The pressure in the unit should be maintained during pumping out by admitting inert gas so that under-pressure and air inleak are avoided.

Residual hydrocarbons should then be removed by purging with steam, water, or water followed by steam. Details of shut-down purging methods are given by Hayes and Melaven (1964).

After purging, air should be allowed into the unit. The inflow of air should be sufficient to prevent under-pressure.

Residual corrosive or toxic materials that may be present should likewise be removed. Essentially similar purge materials and methods may be used. A further discussion of equipment purging and cleaning for maintenance is given in Chapter 21.

Water left in the unit from normal operations or from purging should be removed to prevent damage during the downtime and start-up. Freezing of water in the equipment can do serious damage and should be avoided. The water should be completely drained from the unit and blocked drains identified and cleared.

The installation of shut-down blinds and the removal of running blinds should then be carried out under the control of a proper procedure with appropriate documentation, as already described. The methods of isolation and line breaking are described in Chapter 21.

If there is a possibility that pyrophoric iron sulfide might be present, men should stand by ready to spray the sulfide when the equipment is opened up. The fluid used may be water or a suitable light oil. The latter wets more thoroughly and evaporates less rapidly, and may be preferable unless it constitutes a further fire hazard. Complete mechanical removal of the sulfide should then be carried out.

20.12 Operation of Fired Heaters

The operation of a rather different item of plant is illustrated by that of fired heaters. Some of the hazards of fired heaters and some features of their design relevant to safety are discussed in Chapter 12. Here consideration is given to the safe start-up and operation of such units.

Safe operation of fired heaters is dealt with in *Safe Furnace Firing* (American Oil Company, Amoco/3), *Handbook of Industrial Loss Prevention* (FMEC, 1967) and the CCPS *Engineering Design Guidelines* (1993/13) and in the codes and other publications cited in Chapter 12.

20.12.1 Burner start-up

The essential features of the safe start-up of burners have been described above, but some of these may be re-emphasized in relation to operation.

Every effort should be made to prevent the leakage of fuel into the firing space. Shut-off valves should be checked for leak tightness. Double block and bleed valves should be operated as intended, with the bleed valve open when the block valves are closed.

It should be appreciated that it may not take long for fuel sufficient to create a flammable atmosphere to pass into the firing space. With oil firing the quantity flowing in the few seconds between the flame extinction and shut-off valve may be enough, while with gas firing a flammable mixture may form by leakage through a shut-off valve during the few minutes which it takes to remove a slip plate. Partly for this reason slip plates are not considered a good means of isolation for gaseous fuel. Leakage flows of gas through shut-off valves are often in the range 1–10 l/min.

The air flow should be established and the firing space purged by opening the dampers and starting the fans.

The atmosphere in the firing space should be tested before ignition is attempted. Delay between this test and the ignition should be avoided. If time does elapse, a repeat test should be made.

If a separate device such as a pilot burner is used to effect ignition, this should be lit before the fuel to the burner is turned on. A check should be made that the pilot light is established. The check should be on the flame itself rather than on some quantity from which the presence of the flame might be inferred.

If the main flame goes out, the proper start-up procedure, including purging and testing of the firing space, should be carried out. Short cuts such as simply attempting to relight the burner should not be taken.

The presence of a flame should be monitored by a flame failure device. The device should 'see' the flame to be monitored and not other flames such as the pilot light.

If there are multiple burners, it should be borne in mind that fuel may leak through from burners which are shut off so that a flammable mixture is formed and is then ignited by an operating burner. In some circumstances, it may be appropriate to avoid this by firing with all the burners.

The flame is normally extinguished by shutting off the fuel and injecting snuffing steam.

The possibility of interactions between furnaces linked by common headers should be borne in mind.

20.12.2 Tube failures

Overheating of furnace tubes can result in rapid or delayed failure. Rapid failure can occur if the flow of feed through the tubes is too low or is lost altogether, or if there is direct flame impingement on the tubes. Failure can also result from less intense overheating over long periods. It is very easy to cause a drastic reduction in the creep life of tubes by maloperation.

Typically a furnace tube has a creep life of 10 years at 500°C. Then its creep life will be reduced approximately as follows by operation at higher temperatures:

Temperature (°C)	*Creep life*
506	6 years
550	3 months
635	20 hours

The reduction in creep life is *pro rata*. Thus, for example, the creep life for a tube with the characteristics just given will be used up by operation for 5 years at 500°C and $1\frac{1}{2}$ h months at 550°C.

The measurement of the furnace tube temperature is difficult, but temperature measuring devices are available for this duty. It is now normal practice to measure the tube temperature. The measurements may be used to generate alarms to warn the process operator and/or to initiate trips which shut the furnace down. A trip system may be effective against gross overheating, but is less appropriate to prevent overheating which is not so severe, but which can nevertheless cause a serious reduction in creep life.

It is essential, therefore, for the process operator to understand the penalties of overheating and, in particular, those arising from the relatively small increases of tube temperature that he may otherwise regard as insignificant.

20.13 Operation of Driers

An item of equipment which has much in common with a fired heater but is rather more complex is a drier. An account of the start-up, operation and shut-down of a drier is given in *Prevention of Fires and Explosions in Driers* (the IChemE *Drier Guide*) (Abbott, 1990).

There are a number of different types of drier. Abbott gives first a general account of the operation of a drier, which, broadly, is applicable to any type, and then considers the variations applicable to particular types of drier. The account given here is based on this general account and assumes that inerting is used.

20.13.1 Pre-start-up checks

Before the drier is started up, checks should be made on the mechanical condition of the plant, its internal state, its instrumentation and the control settings. There should be no leaks of fuel or lubricating oil and the air filter should be clean. Explosion vents should be intact and clear to operate. The plant should be free of spillages and deposits and of maintenance equipment. The instrument should be operational, as should explosion suppression devices. The damper settings should be correct. It should also be checked whether there has been any modification to the plant or the material to be dried.

20.13.2 Normal start-up

Essentially, the operation of a drier involves steering a course between overheating or underdrying the product. The product temperature must not be allowed to rise to a point where a runaway reaction can occur and deposits in the drier must not reach their self-ignition temperature. On the other hand, the product must not be underdried which, besides giving off-specification material, can cause blockage in the discharge system and caking in conveying and storage.

It is also necessary to ensure that the exhaust gas temperature remains above its dewpoint in the dust recovery equipment. The exhaust gas temperature is controlled by manipulating (1) the heat input, (2) the feed flow and/or (3) the evaporative load. The heat input is the variable principally used, but the response may be slow due to large time lags.

The plant should be started up by starting the product discharge valves and conveyors and the fans. On an indirectly heated drier the heating medium should then be admitted. Assuming, as stated, that the system is operated under inert gas, it should be purged until the outlet oxygen concentration has fallen to the operating value. Assuming also that the heater is fired by gas or oil, it should be started up using a safe fired heater start-up procedure. Once the exhaust gas temperature has reached its operating value, the feed of wet material should be started.

The drier is then gradually brought up to full load, within the constraints mentioned. This is generally the stage of the process that is most difficult to control.

20.13.3 Normal operation

In normal operation the same control objectives apply, that is to avoid overheating or underdrying the product, and the same means of control are available. The operation of the heater should be closely monitored. The product should be checked for specks of burned, charred or discoloured material, signs of a smouldering or burning deposit in the drier.

20.13.4 Normal shut-down

The same control objectives apply for normal shut-down. Again the process passes through a critical stage as conditions pass through a transient.

The shut-down is initiated by shutting off the feed. Then the heater is shut off. Purging with inert gas is continued until all the product material has left the drier. The inert gas is then purged from the drier with air. The fan, discharge valves and conveyors can then be switched off.

The inside of the drier should be inspected under a permit-to-work system. Potential hazards include a low oxygen content and smouldering material.

20.13.5 Emergency shut-down

The appropriate procedure for emergency shut-down depends on the condition causing the emergency. This may be a material blockage, an equipment failure, or a fire or explosion.

For either of the first two events, the objective should be to prevent overheating of the product. Methods available are to shut off the heat input, to get the material out of the drier and to maintain the evaporative load. One way of effecting the latter is the use of a water spray.

The emergency procedures for dealing with a fire or explosion are given in the *Drier Guide*.

20.14 Operation of Storage

A large number of incidents occur associated with the bursting or collapse of atmospheric storage tanks due to maloperation.

An atmospheric storage tank is typically designed to withstand an internal pressure of 8 in. WG (20 mbar) or a vacuum of $2\frac{1}{2}$ h in. WG (6 mbar). These are very low pressures, which it is easy to exceed unless there is careful operation.

If the pressure inside the tank is not kept within these limits, the failure of the roof or of the side walls may occur. Two principal modes of failure are overstressing of the roof due to excessive internal pressure and instability of the side walls due to excessive vacuum.

Generally a roof fails under internal pressure either at the seams between the roof and the side walls or along the diametral seams in the roof itself. The failure typically has a cod's mouth appearance. Large tanks are particularly vulnerable.

For internal pressure the shear stress σ_s in the seam between the roof and the wall is proportional to the pressure p and the diameter d and inversely proportional to the thickness of the tank wall t:

$$\sigma_s \propto pd/t \qquad [20.14.1]$$

The bending stress σ_b in the roof itself is proportional to the internal pressure and the square of the diameter and inversely proportional to the square of the thickness:

$$\sigma_b \propto p(d/t)^2 \qquad [20.14.2]$$

The side walls are designed to withstand the maximum head of liquid which can occur in the tank. The internal pressure is thus relatively less important in this case. But, again, the hoop stress in the side wall σ_h due to the internal

pressure is proportional to the pressure and the diameter and inversely proportional to the thickness:

$$\sigma_h \propto pd/t \qquad [20.14.3]$$

The vulnerability of large storage tanks to overpressure may be illustrated by considering the relative stresses in the roof and side walls of (1) a baked bean tin and (2) a 1000 m^3 fixed roof storage tank. It is assumed that the baked bean tin has a diameter of 7.5 cm and a thickness of 0.25 mm, and that the storage tank has a diameter of 12 m and a thickness of 5 mm. Then the ratios of the stresses in the tin and in the storage tank are as follows:

	Stress in storage tank / *Stress in baked bean tin*
Side wall, σ_h	8
Roof, σ_b	64

Similarly, for vacuum the stresses are much greater in large tanks.

The effect of vacuum on the side walls of a storage tank is to induce instability. The analysis of tank instability is complex, but some understanding may be obtained by considering the effects of slight distortions in the shape of the tank. These effects may be summarized by saying that for internal pressure small changes in shape do not tend to cause the side walls to fail, but for vacuum such changes do tend to cause failure.

This situation may be explained by the following simplified argument (Aird, 1977b). Consider a small element of the wall of the storage tank, as illustrated in Figure 20.2(a), where r is the radius of the tank, t is the thickness of the wall, δ is the width of the element and the angles α and ϕ and the vectors of forces F_1 and F_2 are as shown. Then with an internal pressure p and an external pressure of zero

$$F_1 = \int_{-\alpha}^{\alpha} p\delta r \cos\theta \, d\theta \qquad [20.14.4a]$$

$$= 2p\delta r \sin\alpha \qquad [20.14.4b]$$

$$= 2p\delta r\alpha \qquad \alpha \ll 1 \qquad [20.14.4c]$$

$$F_2 = \sigma_h t\delta \qquad [20.14.5]$$

where σ_h is the hoop stress.

The vector of forces ΣF in the vertical direction in Figure 20.2 (a) is thus

$$\Sigma F = F_1 - 2F_2 \sin\phi \qquad [20.14.6a]$$

At equilibrium this vector of forces must be zero

$$\Sigma F = 0 \qquad [20.14.6b]$$

For the case where there is no distortion of the element

$$\phi = \alpha \qquad [20.14.7]$$

Hence from Equations 20.14.4–20.14.7

$$\sigma_h = \frac{pr}{t} \qquad [20.14.8]$$

and

$$F_2 = pr\delta \qquad [20.14.9]$$

Now consider the cases where distortion occurs. For a small inwards distortion

$$\phi < \alpha \qquad [20.14.10]$$

and hence

$$\Sigma F = 2p\delta r(\sin\alpha - \sin\phi) > 0 \qquad [20.14.11]$$

Thus the net resultant force due to distortion tends to move the element outwards and so to return it to its original shape. For outwards distortion

$$\phi > \alpha \qquad [20.14.12]$$

and hence

$$\Sigma F < 0 \qquad [20.14.13]$$

Thus the resultant force due to distortion tends to move the element inwards and so again to return it to its original shape. These effects are shown in Figure 20.2(b).

Conversely, with an internal vacuum the vector of forces in the vertical direction is

$$\Sigma F = -F_1 + 2F_2 \sin\phi \qquad [20.14.14]$$

For inwards distortion relation 20.14.10 applies and hence

$$\Sigma F < 0 \qquad [20.14.15]$$

Thus the resultant force due to distortion tends to move the element inwards and so reinforce the distortion. For outwards distortion relation [20.14.12] applies, and hence

$$\Sigma F > 0 \qquad [20.14.16]$$

Thus the resultant force due to distortion again tends to move the element outwards and so reinforce the distortion. These effects are shown in Figure 20.2(c).

A fuller treatment is given by den Hartog (1952, p. 274).

Atmospheric pressure is maintained in a storage tank by a vent to the atmosphere. The tank may be subjected to pressure or vacuum which it cannot withstand, not only if this vent is blocked, but also if it does not have the capacity to handle the flows required to equalize the pressure.

Some ways in which overpressure can occur include (1) pumping in liquid too fast, (2) an increase in the temperature of the liquid contents, (3) pumping hot liquid into water and (4) blowing in air, steam or gas.

An increase in the temperature of the liquid in the tank can occur due to pumping in hot liquid or to a high ambient temperature. For many substances a temperature rise of 6°C is enough to give an increase in vapour pressure of 8 in. WG. Pumping hot oil into water raises the water temperature and causes it to exert a higher vapour pressure, or even to boil off as steam.

Similarly, ways in which vacuum can occur include (1) pumping out liquid or emptying liquid under gravity too fast, (2) a decrease in the temperature of the liquid contents and (3) condensation of the steam or vapour contents or a depletion of the gas content.

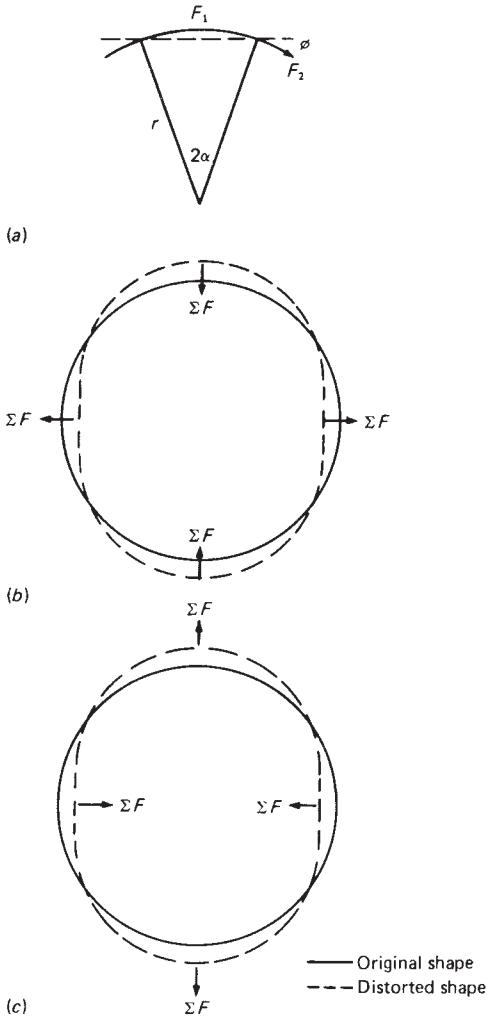

Figure 20.2 *Forces acting on the side wall of an atmospheric storage tank: (a) element of side wall; (b) positive internal pressure – resultant forces tend to correct distortion; (c) negative internal pressure – resultant forces tend to reinforce distortion*

Condensation of steam or vapour in the tank can occur as a result of a sudden shower of rain.

Vents on tanks are liable to blockage by debris or by polymerization or crystallization of the liquid. The vent normally has a flame arrester, which is particularly liable to blockage. Vents are sometimes blanked off to allow maintenance work to be done.

It is emphasized, however, that it is not necessary for a vent to be blocked for a tank to burst or collapse. All that is required is for the vent capacity to be insufficient to handle the flow required to equalize the pressure.

The systems to which an atmospheric storage tank is likely to be connected mostly are at, or can generate, pressures sufficient to overpressure the tank. This applies to equipment such as transfer pumps and to services such as steam, air or nitrogen.

Some situations which can lead to the bursting or collapse of a storage tank are shown in Figures 20.3 and 20.4. Bursting or collapse may result from a combination of the vent conditions shown in Figure 20.3 and the operations or situations shown in Figure 20.4.

As an illustration of storage tank collapse, consider the following case. Welding had to be done near the roof of a storage tank containing a volatile flammable liquid soluble in water. The tank had an open vent with a flame arrester on it. The maintenance supervisor connected a flexible tube to the flame arrester and immersed the other end of the tube in a drum filled with water. When liquid was run out of the tank a vacuum developed and the tank, designed to withstand $2\frac{1}{2}$ in. WG, collapsed inwards. Moreover, if instead liquid had been run into the tank, overpressure would have developed corresponding to the depth of immersion of the tube and the tank, designed for 8 in. WG internal pressure, would have burst.

Other examples of storage tank collapse are described in Case Histories B44–B48.

20.15 Operational Activities and Hazards

20.15.1 Water hammer

The term 'water hammer' is applied to two somewhat different phenomena, both of which generate forces sufficient to rupture the pipeline.

One kind of water hammer, or hammer blow, results from the sudden closure of a valve in a long pipeline filled with water. The force on the valve is then proportional to the rate of dissipation of the momentum of the fluid. Such water hammer is familiar in domestic water systems, where its effects are usually not serious. On an industrial scale, however, hammer blow can be very destructive. The phenomenon is considered in more detail in Chapter 12.

The other kind of water hammer occurs when a slug of condensate is flung against the pipework by steam. Typical features of a situation giving rise to this effect are as follows. The steam main is not used for some time, but the steam pressure is maintained. Condensate collects at low points. The steam traps and drains that should drain the condensate out are not working. The steam flow is suddenly increased and water hammer occurs. Again the effect can be highly destructive.

Steam mains should be designed to allow condensate to be drained from low points by steam traps and drains. These traps and drains need to be maintained so that they work effectively. It is a help if they are so installed that they can be drilled through under pressure if they get blocked.

It is also essential to exercise care when it is necessary to make large alterations to steam flows, particularly in situations such as start-up. Suitable precautions are checks on condensate accumulation and on the operation of steam traps, and slow operation of the steam valves. It should be appreciated that alteration of the opening of a valve in a steam ring main can have a great effect on the flows in that main.

Both kinds of water hammer, but particularly the first, can occur with fluids other than water.

20.15.2 Slopover

If hot oil is brought into contact with water, there is liable to be a rapid evolution of water vapour and the formation of a

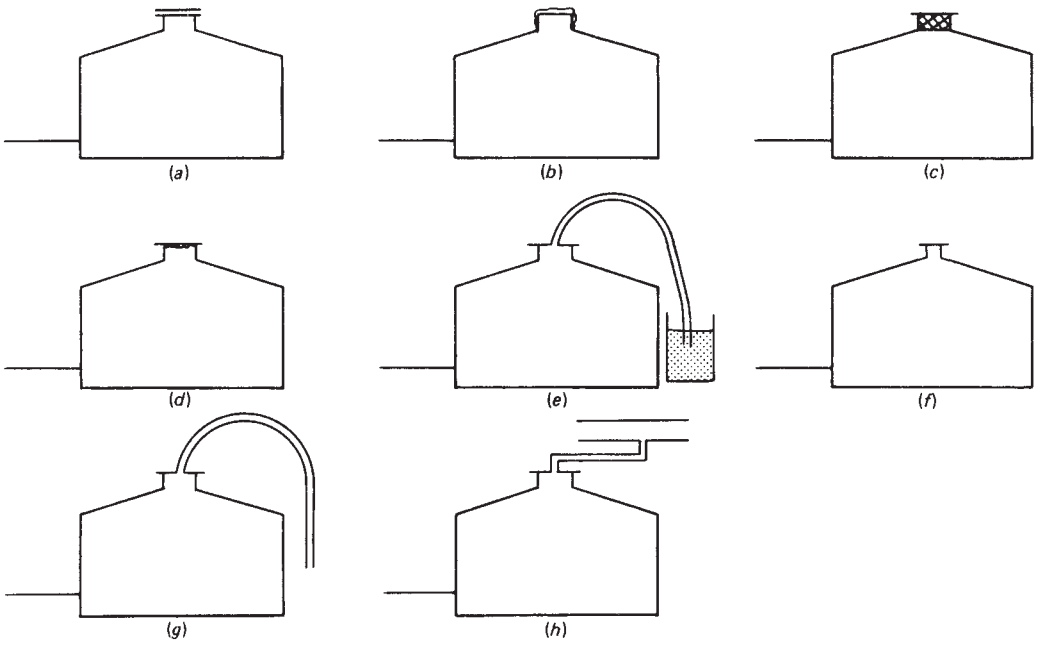

Figure 20.3 *Some vent conditions which can lead to the bursting or collapse of an atmospheric storage tank: (a) vent blanked off; (b) plastic bag over vent; (c) vent choked; (d) flame trap choked; (e) vent connected to water seal; (f) vent too small; (g) flexible tubing connected to vent; (h) vent modified*

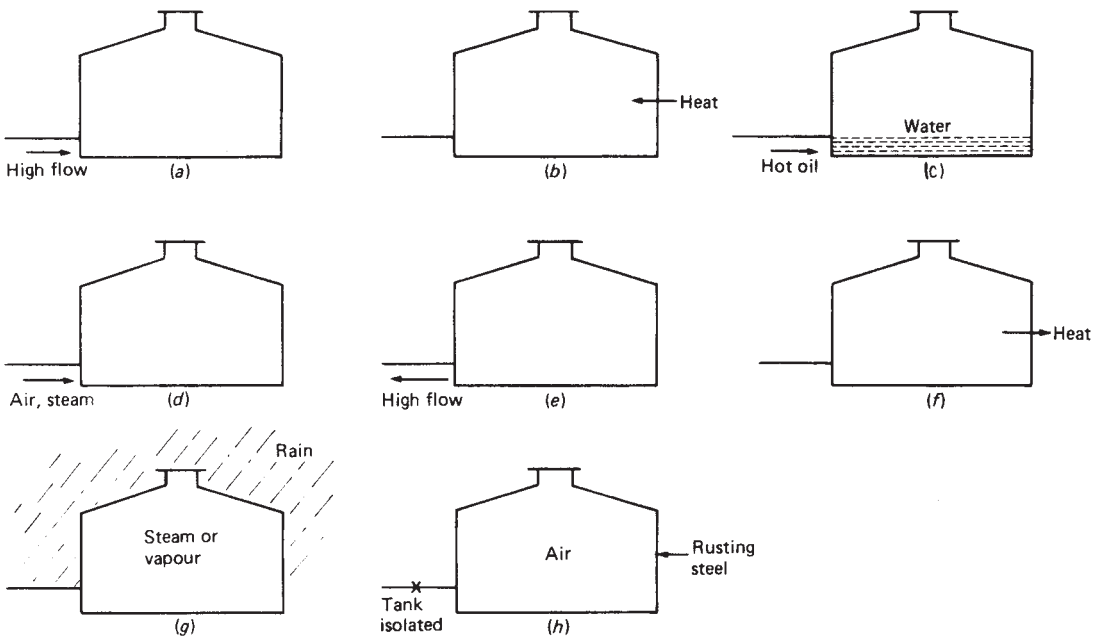

Figure 20.4 *Operations and situations which can lead to the bursting or collapse of an atmospheric storage tank: (a) overpressure – pumping in liquid too fast; (b) overpressure – increase in the temperature of liquid contents; (c) overpressure – pumping hot oil into water; (d) overpressure – blowing in air, steam or gas; (e) vacuum – pumping out liquid too fast; (f) vacuum – decrease in the temperature of liquid contents; (g) vacuum – condensation of steam or vapour; (h) vacuum – depletion of oxygen*

large volume of foam. This condition typically occurs when oil with a water layer is heated up or when hot oil is run into a vessel containing water, or oil and water. The effect is similar to that occurring when wet chips are put into boiling fat in a chip pan. It is variously known as 'slopover', 'boilover', 'foamover' and 'puking'.

The effect created when water is vaporized is illustrated by the eruption of the volcano Krakatoa in 1883. A cubic mile of water was vaporized and a cubic mile of rock was thrown into the air. Rock fragments travelled to a height of 14 miles and the sound was heard 3000 miles away.

Incidents involving slopover are quite frequent and can be serious. Slopover is one of the hazards described in *Hazard of Water* (American Oil Company, Amoco/1).

Although it is water which is most commonly involved, a similar phenomenon can occur with a volatile oil. A serious accident which was probably caused by this effect occurred at the Shell refinery at Pernis in 1968 (Fontein, 1968). Hydrocarbons in a slops tank boiled over. A vapour cloud formed, found a source of ignition and exploded violently, causing extensive blast damage and a large fire. Owing to cold weather, it had been necessary during the two previous weeks to heat the oil in the tank. It is believed that the steam coils had become covered in a water-in-oil emulsion which reduced the heat transfer to the supernatant oil, so that the two oil layers were at substantially different temperatures, and that vapour formation at the interface between the oil layers initiated mixing, causing further vapour evolution so that the tank overflowed, the hydrostatic pressure at the bottom of the tank was reduced and violent boil-up occurred. The incident is described in Case History A41.

20.15.3 Water draining

In the storage of liquefied petroleum gas (LPG) small amounts of water usually accumulate in the vessel. This water is commonly removed by the periodic action of an operator who drains it off manually. If for any reason the operator loses control, a hazardous situation is liable to arise in which the fluid issuing from the drain point is no longer water but LPG.

This hazard was realized in the Feyzin disaster in 1966, described in Case History A38, where an operator found himself unable to shut off the valves at the bottom of a propane storage sphere and a large vapour cloud formed, ignited and caused a series of BLEVEs.

As described in Chapter 22, the preferred arrangement is the use of a drain line with two valves. The method of operation of these valves is described in *The Storage of LPG at Fixed Installations* (HSE, 1987 HS(G) 34) as follows:

> Particular care should be taken when draining storage vessels in service in order to minimize the escape of LPG. Of the two drain valves, that nearer the vessel, should be fully opened first and draining then controlled by gradually opening the second valve. If, on opening the second valve, no flow occurs, both valves should be closed immediately to allow subsequent investigation. On completion of the draining operation, the valve furthest from the storage vessel should be closed first, then the other valve.

20.15.4 Gas cylinders

There are a number of hazards that can arise from the use of gas cylinders. One of the most frequent types of incident is misidentification of the gas in the cylinder. Thus, for example, oxygen may be used in an application where an inert atmosphere is required. Gas cylinders are marked with an identifying colour code. Common causes of incidents are that the coloured paint has been rubbed off or that people handling the cylinders are not familiar with the code. Cylinders on which the code is not clear should be taken out of service and personnel should be trained to recognize the identification scheme.

Overfilling of cylinders sometimes occurs. This may be due to a defective filling machine or to the use of a machine too small for the cylinder, so that only part of the cylinder rests on the machine.

Cylinders are sometimes heated to give a steady gas supply. There is then the hazard that the isolation valve is turned off and the cylinder explodes. It may be possible, however, to design a cylinder heating system that will not allow the cylinder to overheat sufficiently to cause an explosion, even if the isolation valve is closed accidentally. A suitable system is heating with warm air, the air itself being heated by steam or electricity. Heating of a cylinder by steam or a heat transfer medium is best avoided, because these methods are more liable to cause not only overheating but also corrosion of the cylinder.

The correct method of drawing gas from a cylinder is to set the pressure regulator screw to zero and then to open the isolation valve. Failure to observe this procedure on an oxygen cylinder, for example, can lead to rupture of the regulator diaphragm and an explosion/fire.

With oxygen there is the hazard of igniting materials, such as the plastic caps used to cover the nozzle. Such caps should be entirely removed before the valves are opened.

Another hazard with gas cylinders is that the isolation valve may be damaged in such a way as to allow a rapid flow of gas from the cylinder. In such circumstances the cylinder can become a projectile propelled by the escaping gas.

20.16 Sampling

Sampling is a common cause of accidents to personnel in the chemical industry. It needs to be addressed by the provision of suitable equipment and of formal systems of operation. Accounts of sampling have been given by Ducommun (1964a,b) and Lovelace (1979) and in the ICI LFG Code.

Sampling is carried out to monitor product quality, the material balance or equipment operation, or for the purposes of troubleshooting.

A sampling technique should aim to minimize the risk of leakage from the sample point, to safeguard the person taking the sample, to provide a safe means of carriage of the sample to the laboratory and to protect the laboratory personnel handling the sample.

Two principal problems are corrosive liquids and flammable gas and liquids. Before considering these, consideration is given to some general points on liquid sampling.

20.16.1 Liquid sampling

An approach to the safe sampling of liquid streams has been described by Lovelace (1979). He utilizes a proforma for the specification of liquid sampling which covers: the hazards; the sampling conditions, including the frequency of sampling and the size of sample required; any special considerations; the equipment, both installed and portable; and the details of the installed equipment.

The sample point should be treated as a piece of equipment in its own right and designed accordingly. There is no single system that is suitable for all applications.

Sampling systems may be classified as direct or indirect line systems. An ordinary sample valve is a direct line system. Another device is the piston-type sampling valve, in which the sample offtake is set at a 45° angle and is normally kept closed by a piston that moves along the axis of the main sample line. This gives a positive rodding out action and is used in applications where blockage may occur.

In an indirect line system the sample is trapped in a fixed volume and then withdrawn. A simple device which effects this is a sampling plug valve which is installed in line in a pipe. This is a type of ball valve with a sample offtake line and a vent line located in the body of the valve perpendicular to the main pipe, so that when the valve is rotated, the sample trapped in the plug can flow down the sample line. In another type of device the sample is withdrawn using a piston.

A sample chamber is attached directly to the line to be sampled and the liquid is admitted to it by a valve system. One system which minimizes leaks is a double block and bleed valve arrangement.

For syringe sampling use may be made of a septum.

Where sampling can give rise to hazardous fumes, good ventilation is essential. Another method of protection against fumes and leaks is the use of a sampling enclosure, essentially a simple box with the sample pipe entering through the top and the sample bottle connection through the bottom. Details of the design of such an enclosure are given by Lovelace.

20.16.2 Corrosive liquids

The following procedure may be used for the sampling of corrosive liquids. The person taking the sample should wear the appropriate protective clothing such as goggles and gloves. The sample bottle should not be held in the hand but on a stand. It is desirable that the sample point be provided with remote operation or with a protective covering around the sample point. The sampler should stand as far as possible from the sample point. If there is no remote operation, he should turn the sample valve using an outstretched arm. The sample bottle should be carried in a bottle carrier.

20.16.3 Flammable fluids

Flammable gases and liquids are usually sampled using a metal bomb. Typical sampling methods are described in the ICI *LFG Code*. For a liquefied flammable gas (LFG) the bomb is a stainless steel cylinder as shown in Figure 20.5(a). A liquid sample is taken as follows. The ullage end of the bomb is connected to the sample point, the bomb is held vertically with the ullage end at the bottom, and both the top and the bottom valves are fully opened. The needle valve is then opened slowly and the bomb is filled. When it is full, liquid emerges from the top valve and all the valves are closed. The bomb is then disconnected from the sample point and inverted so that the ullage end is at the top. The top valve is opened so that liquid issues out until the level in the bomb falls below the bottom of the ullage pipe. When vapour starts to come out instead of liquid, the valve is closed. The ullage for LFG is 20%.

Methods of sampling LFG as gas include (1) evacuation of the bomb before sampling, and (2) purging of the bomb with the gas sampled, the purge being passed to the vent system. Suitable bombs for these two methods are shown in Figures 20.5(b) and 20.5(c), respectively. The ICI *LFG Code* should be consulted for full details of these sampling procedures. Failure to vent a bomb after sampling LFG may result in an explosion if the liquid warms up by heat transfer from the atmosphere. A sample bomb explosion from this cause has been described by Ducommun (1964a).

Ducommun (1964b) also describes a system for avoiding such incidents. The bomb itself is effectively treated as a small pressure vessel, is of special design and is regularly inspected. There is a requirement that the bomb be vented immediately after sampling to give the specified ullage and that this be checked by weighing or other means. The sampling procedure is simple and standardized, personnel are well trained in it and notice of sampling operations is given to the process personnel. The sampling operations are monitored and documented by the laboratory.

20.16.4 Particular chemicals

Certain chemicals require special sampling methods. Techniques for particular chemicals are given, for example, in some of the *Codes of Practice for Chemicals with Major*

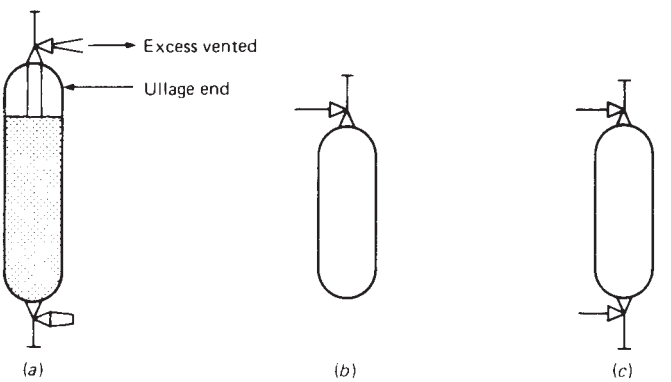

Figure 20.5 *Some sample 'bombs' for liquefied flammable gases (LFGs) (Imperial Chemical Industries Ltd, ICV RoSPA 1970 IS/74; reproduced by permission): (a) sample bomb for liquids; (b) sample bomb for gases (inlet only); (c) sample bomb for gases (inlet and outlet)*

Hazards by the CIA, such as those for ethylene dichloride and phosgene.

20.17 Trip Systems

Trip systems are provided to protect the plant against certain hazardous situations by shutting it down if particular parameters go outside the specified limits.

There are differences, however, in the extent to which it is essential to provide trip protection with no disarming allowed and in the level to which trip systems can be economically engineered to ensure this. Some trip systems are very sophisticated and provide protection not only during normal operation but also during other conditions such as start-up. In other cases, however, it is necessary to disarm the trip system temporarily to allow the plant to be started up.

Disarming of trips is a permissible practice provided that it is done in accordance with the design intent and with proper procedures. Otherwise, it is an extremely dangerous practice. Probably the most common error is to disarm a trip temporarily, usually during start-up, and to forget to restore it.

The *Flixborough Report* (R.J. Parker, 1975, para. 40) revealed that an automatic system, which initiated safety actions such as shut-off of the air supply and initiation of a nitrogen purge if the level of liquid nitrogen supply fell too low, could be readily overridden by setting to zero the timer for fixing the duration of the purge. Although such action does not appear to have contributed to the explosion, such disarming is a hazardous practice.

If the disarming of trips is to be practised, there should be a procedure that ensures that the trip is correctly restored. Methods used to ensure that disarming is done safely include both key interlocks and permit systems.

If spurious trips occur due to trip initiator unreliability, the operator has an incentive to disarm the trip in order to continue operating, and incidents occur in which operators disarm trips for this reason. Again hardware or software methods may be used to prevent disarming. But it is highly desirable in such cases to improve trip system reliability.

Disarming is not the only way in which a trip can be rendered ineffective. A similar result is often achieved by an alteration of the trip setting. It is equally essential, therefore, to ensure that there is no interference with trip settings.

A trip system should be designed so that it does not reset itself when the trip condition disappears, for example valves closed by the trip action should not reopen. It is important, however, that the operations side appreciate the hazards that can arise if the trip system does reset itself. A typical hazard in this case might be the entry of atmospheric air into a vessel filled with hydrocarbon vapours so that an explosive mixture is formed.

20.18 Identification Measures

It is essential, if errors are to be avoided, that plant vessels and equipment be given appropriate marking so that they are readily identified and any hazards associated with them are understood. Equipment identification is of particular importance for maintenance work and is considered in Chapter 21. Here consideration is confined two aspects that particularly concern process operators. These are the identification of hand valves and the labelling of in-plant containers.

20.18.1 Valve identification

One of the principal ways in which the plant is affected by operator actions is through the opening and closing of isolation valves, or hand valves. It is not uncommon for the operator to have difficulty in identifying the right valve, as described in Chapter 14. Yet an error in the identification of a valve can have serious results.

The identification of hand valves is discussed by R. King (1990). A hand valve should be identified on the piping and instrument diagram (P&ID), in the operating manual and on the plant. The P&ID should allow space for the hand valve identification numbers to be inserted; it is often difficult to insert such numbers due to lack of space. The operating instructions should identify hand valves by number.

On the plant a problem arises in maintaining permanent identification of a hand valve. A tag may be put on the valve, but a valve tends to lose its tag or, if it does retain it, it may be removed and put back at some other point. A method that overcomes these difficulties is the marking of the valve number on the pipework, or insulation, with an arrow pointing to the valve in question.

20.18.2 In-plant container labelling

The operation of a process plant can involve the transfer within the plant of a number of chemicals and it is necessary to ensure that these are correctly identified at all times. A programme for the in-plant labelling of containers for such substances has been described by Kmetz (1990).

These containers are those entering the plant, those generated within and retained with the plant, and those leaving the plant. Each container is required to have three pieces of information: the name of the substance, the hazard warning and the party responsible for it.

Employees are responsible for checking that an incoming chemical is labelled. The party initiating shipment is responsible for seeing that an outgoing chemical is labelled and has a material safety data sheet. For in-plant labelling some latitude is allowed. A container used by one person within one shift does not have to be labelled.

20.19 Exposure of Personnel

Of the two main ways of reducing the size of a potential disaster, mention has already been made of one, that is the limitation of inventory in the process design. The other is the limitation of exposure of personnel in plant operation.

The *First Report* of the Advisory Committee on Major Hazards (ACMH) (Harvey, 1976) suggests that limitation of exposure should be an explicit objective. The Second Report (Harvey, 1979b) gives guidelines for the limitation of exposure.

The hazard to which personnel are exposed may be a large fire, an explosion or a toxic release. Various scenarios for such hazards should be reviewed so that zones in which exposure is controlled can be delimited on a rational basis.

Exposure is most simply limited by not having people there in the first place. For those whose presence is essential much may be done to provide protection, particularly through the siting and design of buildings. This latter aspect is discussed in Chapters 10 and 24. Only the

reduction in the numbers present by management control is considered here.

Typically, a large process plant has a number of shift process operators who man the control room and work about the plant opening and closing valves, changing pumps, replacing filters, taking samples and performing various other tasks. Some operators spend most of their time in the control room, others are mainly out on the plant. There are also several shift mechanical and instrument maintenance fitters. All these personnel patrol the plant and observe any abnormalities such as leaks or spillages and they are available to deal with plant upsets. Laboratory personnel also go out on to the plant to take samples for analysis.

In general, the numbers of shift operating and maintenance personnel on modern process plants are already at the minimum level consistent with safe and efficient operation. In most cases further reduction would make it difficult to deal with emergency situations.

During the day there is a rather larger number of maintenance personnel on the plant. The plant manager and the plant engineer are also on the plant during the daytime. In addition, there are often other technologists concerned with carrying out investigations of all kinds.

If a plant extension is being carried out, there will also be a fairly large number of construction personnel on the plant or very near it.

The numbers of men on a large process plant might be expected to be approximately as follows:

Shift operating personnel	5–25
Shift maintenance personnel	0–5
Day maintenance personnel	10–100
Managers, technologists	2–10
Construction workers	10–50

In the event of an emergency, the shift personnel have specific instructions on the action which they should take and on the alarm or other instruction at which they should evacuate. The order to leave the plant is given to the day maintenance personnel and to construction workers on the appropriate alarm signal or on instruction from their respective supervisors.

For the purposes of limitation of exposure, personnel may be divided into the following categories of exposure in the hazard area:

Category 1 Continuous exposure (e.g. process operator).
Category 2 Intermittent exposure:
(a) short periods (e.g. technologist);
(b) infrequent long periods (e.g. fitter).
Category 3 Infrequent exposure (e.g. accounts clerk).

The works site may be divided up into areas of (1) major hazard, (2) intermediate hazard and (3) low hazard.

The limitation of exposure of personnel is effected by controlling (1) permanent location and (2) movement.

The number of people permanently located in a major hazard area should be kept to a minimum consistent with safe and efficient operation. In particular, personnel in Category 2 should be there only if their presence is essential, as opposed to merely convenient. Examples of such personnel include technologists, training officers, maintenance planners, laboratory analysts and clerical assistants.

Personnel usually located in the intermediate hazard area include maintenance and other services. Again the number should be kept as low as is reasonably practicable.

Personnel should be given protection by suitably designed buildings, as described in Chapter 10. In the major hazard area the main protective building is the control room. The type of protection afforded by this will depend on the nature of the hazard (fire, explosion or toxic release). Buildings in the intermediate hazard area should also offer some protection. The ACMH suggests that personnel exposed to this intermediate level of hazard should have a work base such that they would not expect to be seriously hurt. Buildings such as the site office should be in the low hazard area, but should still be designed to minimize injury.

The other main control is on movement. There should be formal procedures, including a permit system for entry into the major hazard area. This permit system should be enforced and audited. The procedure should ensure that the number of people in the major hazard area is considered and that their identity is known at any given time.

It is particularly important for the system to afford good control of situations such as major plant construction and modification, in which there may be quite large numbers of people in the major hazard area. It should be borne in mind that the presence of a large construction team, who are relatively unfamiliar with the plant, is in itself a further cause of hazard.

20.20 Security

Another important aspect of plant operation is security. This is treated in *Vandalism* (C. Ward, 1973), *Introduction to Security* (G. Green and Farber, 1974) and *Industrial Security* (D.L. Berger, 1979). The *Compendium of Fire Safety Data* (FPA, 1992) contains a section on security precautions (the SEC series). Accounts are also given by Hamilton (1967), Oliver and Wilson (1972), K.G. Wright (1972), Spranza (1981, 1982, 1991, 1992) and Pitt (1987).

Security systems management is described by Spranza as being essentially a blend of traditional security concepts and modern management methods.

The management system should include an explicit requirement for a review of the security system. This review should cover both hardware and software aspects and should involve a critical examination in which problems are identified, alternative solutions are generated, and a suitable approach is selected and implemented.

In assessing the security problem the categories of person who need to be considered include employees, visitors and intruders; the types of behaviour to be considered include innocent actions, theft and malicious acts.

Central to security is control of access. The security system should ensure that unauthorized persons do not have access to the site, whether or not they have hostile intent. The minimum requirement is a formal pass system that covers employees and visitors. There then needs to be physical arrangements to ensure that access to the site is controlled at all points. This aspect of security is clearly related to plant layout and is considered in Chapter 10. The Flixborough Report found that, although in general proper attention was paid to security, there were two unguarded gates through which it was possible for anyone at anytime to gain access to the site.

In addition, it may be necessary to exercise control of access to particular areas within the site.

It is also desirable for the operational system to be capable of detecting the presence of any unauthorized persons who do get onto the plant. The patrolling of the plant by the process operators is relevant here. So also are formal arrangements for the limitation of exposure of personnel by the control of access to major hazard plant.

With regard to intruders, there are available various devices which may be used to give warning. Good lighting is one obvious feature. Other measures include detectors buried in the earth between two fences, heat sensitive detectors and closed circuit TV cameras. The use of some devices may, however, encounter difficulties on process plant, such as those due to heat radiation from the plant itself.

Another basic principle of security is to create conditions that assist in the rapid detection of any unauthorized deviation. A simple illustration is the maintenance of tidy storage of laboratory chemicals, so that a missing item is readily detected. But the principle is of much wider application.

Some facilities have their own characteristic problems with regard to security. Those of storage are described by Pitt (1987). One common defect is access by unauthorized vehicles. Other defects occur in drum and cylinder storage, where drums are often placed too close to the boundary fence and cylinders are left all over the place. The particular problems of security in laboratories, also discussed by Pitt, are considered in Appendix 9.

The most difficult security problem is a deliberate attack by well trained and organized saboteurs. Defence against such an attack is a matter for the military which is outside the scope of this book. There are several things, however, which can be done to make such an operation more difficult. The potentially more vulnerable units can be sited away from the periphery and can, to some extent, be designed to limit the damage caused by explosives, and an effective security system can reduce the amount of material which a saboteur can bring in and the time which he can spend on his task.

The security problem is not confined to outsiders, however; the threat not infrequently comes from the company's own employees. Theft by employees can in some cases pose a threat to the plant, particularly where there are high priced materials which it may be attractive to steal. The sort of incident which occurs and which may have safety implications is the theft of sections of copper cabling carrying the power supply to electric motors while the plant is shut down.

More serious interference by employees may involve sabotage or arson. Arson is one of the causes of fire on process plants considered in Chapter 2. The *Compendium of Fire Safety Data* (FPA, 1992) contains an 'arson dossier' (the AR series). Arson is one of the topics dealt with in the *NFPA Handbook* (Cote and Linville, 1986).

The effective operation of a security system requires that all involved are fully trained so that they understand what the functions of the system are, how it works, what their own role is and how they should discharge it.

20.21 Notation

Section 20.3

C	interface concentration (ppm)
H_s	heat of solution (cal/gmol)
k	constant
ϕ	fractional humidity (% relative humidity/100)

Section 20.14

d	diameter of tank
F_1, F_2	forces defined in Figure 20.2(a)
ΣF	vector of forces defined in Figures 20.2(b) and 20.2(c) for positive and negative internal pressures, respectively
p	pressure
r	radius of tank
t	thickness of tank wall
α	angle defined in Figure 20.2(a)
δ	width of element in Figure 20.2(a)
σ_b	bending stress in tank roof
σ_h	hoop stress in tank wall
σ_s	shear stress between tank roof and wall
ϕ	angle defined in Figure 20.2(a)

21 Equipment Maintenance and Modification

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21.1 Management of Maintenance

The need for maintenance of equipment implies some abnormality and often some change or increase in hazard. The conduct of the maintenance work may also introduce its own hazards to the equipment. In addition, the maintenance activities may be a hazard for the personnel involved in them. Careful control of maintenance work must be exercised in order to eliminate hazards to the equipment and to the personnel.

The consequences of failure to exercise this control can be serious. The Piper Alpha disaster was caused by failures in isolation procedures, the permit system and the handover system associated with maintenance work.

Some work constitutes change rather than maintenance. In previous chapters emphasis has been placed on the need to maintain the integrity of the equipment. This integrity may be degraded by equipment modifications unless they are closely controlled. The Flixborough disaster was judged to have been caused by a change which reduced equipment integrity.

Thus, both equipment maintenance and equipment modification require systems of control with a fairly high degree of formality. Equipment maintenance needs to be administered through some kind of permit system, while equipment modification requires a system to manage changes.

Maintenance activities are regulated by numerous codes, standards and guidelines. Some of which are: Occupational Safety & Health Administration (OSHA), Environmental Protection Agency (EPA), Department of Transportation (DOT), Department of Energy (DOE), Nuclear Regulatory Commission (NRC), National Institute for Occupational Safety & Health (NIOSH), National Fire Protection Association (NFPA), American Society of Mechanical Engineers (ASME), American Institute of Chemical Engineers (AIChE), National Association of Corrosion Engineers (NACE), Institute of Electrical & Electronics Engineers (IEEE), International Electrotechnical Commission (IEC), American Society of Testing & Materials (ASTM), American National Standards Institute (ANSI), National Board Inspection Code (NBIC) and American Petroleum Institute (API).

The safe maintenance of process equipment is dealt with in *Safety in Inspection and Maintenance of Chemical Plant* (BCISC, 1959/3), *Safety and Management* (ABCM, 1964/3), *Permit Systems* (CAPITB, 1977 Inf. Pap. 16A), *Refining Safety Code* (IP, 1981 MCSP Pt 3), *Deadly Maintenance* (HSE, 1985b), *Liquefied Petroleum Gas*: vol. 1, *Large Bulk Pressure Storage and Refrigerated LPG* (IP, 1987 MCSP Pt 9) (the IP *LPG Code*), *Guidance on Permit Systems in the Petroleum Industry* (OIAC, 1991) (the OIAC *Permit Systems Guide*) and *Maintenance of Process Plant* (the IChemE *Maintenance Guide*) (Townsend, 1992). Selected references on equipment maintenance are given in Table 21.1.

21.1.1 Safe systems of work

The US Occupational Safety and Health Act of 1970 requires employers to provide a workplace free from recognized hazards that are causing or likely to cause death or serious physical harm to employees. Employees are also required to comply with Occupational Safety and Health Standards (29CFR1910) promulgated under the Act of 1970.

The requirement of the UK Health and Safety at Work Act (HSWA) 1974, for safe systems of work is particularly

Table 21.1 *Selected references on equipment maintenance*

Plant maintenance, general (*see also* Table 7.1)
NRC (Appendix 28 *Maintenance*); NSC (Safe Practice Pmphlt 70); L.C. Morrow (1957); F.L Evans (1962); MCA (1962–/1–4); J.E. Miller and Blood (1963); H.V. Stewart (1963); Goldman and Slattery (1964); Newborough (1967); Blanchard and Lowery (1969); IMechE (1969/2, 1975/19); Iron and Steel Institute (1969); J.R. Hughes (1970); HSE (HSW Bklt 28); Jardine (1970a,b, 1973); Cunningham and Cox (1972); G.H. Mitchell (1972); Gradon (1973); B.J. Lewis and Low (1973); D.J. Smith and Babb (1973); E.N. White (1973); Clifton (1974); Priel (1974); Elonka (1975); Lees (1975); Corder (1976); Husband (1976); Higgins and Morrow (1977); A. Kelly and Harris (1978, 1983); Nertney (1978); Buffa (1980); Worrall and Mert (1980); D.J. Smith (1981, 1991); API (1982/3); Blackney (1982); Rosaler and Rice (1983); Hickman and Moore (1986); A. Kelly (1986); Langley (1986); McAlister (1986); G.T. Edwards (1987c); A. Hunt (1989); Dunlop (1990); T.A. Henry (1990); Hirata (1990 LPB 96); File (1991); Parkinson (1991)

Human factors in, and training for, maintenance
NRC (Appendix 28 *Maintenance Personnel Reliability Model*); Landeweerd and Rookmaaker (1980); Nawrocki (1981); Spiker, Harper and Hayes (1985); Salvendy

Terotechnology
Dol (n.d./1, 1975/2–6, 1976/7, 1977/8, 9); IMechE (1973/6, 1975/21); Tracht (1964); R.P. Reynolds (1974, 1976); J.A. Richardson (1976); Berg (1977); Rappini *et al.* (1977); Parkes (1978); K. Lewis (1979); Partington (1980)

Design-out of maintenance, design for maintenance
Alford (1965); Constable and Parkes (1979); Lieberman (1997)

Plant maintenance, process industries
BCISC (1959/3); Staniar (1959); Signorini (1961); F.L. Evans (1962, 1967, 1969); Dodds (1963); Roughley (1963); ABCM (1964/3); Stratmeyer (1964); Alford (1965); Elgee (1965); D.T. Smith (1965b); Verseput (1965); H.R. Carter (1966); E. Johnson (1966); Matley (1970); Trotter (1970, 1973); Cason (1971); Hodnick (1971); Jumper (1971); Virgils (1971); Anon. (1972d); Finley (1972, 1973, 1978, 1987); C.F. King and Rudd (1972); Nowlan (1972); *Chemical Engineering* (1973b); McCullough (1973); Husband (1974, 1976); A. Kelly (1974, 1980, 1981, 1986); H.S. Moody (1974); Snyder (1974); Warburton (1974); Anon. (1975 LPB 39, p. 8); Anon. (1975 LPB 4, p. 9); Goyal (1975); Harris and Kelly (1975); Roseman (1975); Bosselaar (1976); Husband and Basker (1976); Piper (1976); Anon. (1977 LPB 14, p. 2); Balaam (1977); Bellinger and Wright (1977); Innes (1977); Mann (1977); Wanner (1977); Buttery (1978); A. Davies (1978); R. King and Magid (1979); Marre and Reichert (1979); Vargas (1979, 1980a,b); Chamberlain (1980); *Chemical Engineering* Staff (1980); J.D. Edwards (1980); Iverstine and Sturrock (1980); Schmid (1980); Chandler and Brooks (1981); Creaney (1981); Hellhake (1981); Seddon and Kelly (1981); Hay (1982); Kirby (1982); de Matteis (1982); D.T. Smith (1982); API (Publ. 2007); Charlton and Huitson (1983); A. Kelly and Harris (1983); Wilkie (1985b); Baguley (1986); Langley (1986); Wireman, Saletan (1994); ASTM (1986, 1996); Tropp (1986); Deacon (1988); Riance (1988); T.A. Henry (1990, 1993a,b);

Hirata (1990); Ng Tong Leng (1990); Cans, Kohan and Palmer (1991); FM Int. (1991a); Godse (1991); Moubray (1991); Snow (1991); M. Taylor (1991); Anon. (1992 LPB 104, p. 12); Crawley (1992 LPB 102); Mundy (1992); Townsend (1992); Vouets (1992); S.C. Leonard (1993); Worledge (1993); Hulme (1994)

Contract maintenance
J.H. Jordan (1968); Sarappo (1969); C.J. Carter (1980); Whitaker (1993); API RP 2220 (1991); RP 2221 (1996)

Life cycle costing, replacement decisions
Anon. (1961c); Fisher (1963); Munro (1963); J.P. Epstein (1967); J.R. Hughes (1970); Maristany (1968); Jelen and Cole (1971); Fair (1973, 1974); Finley (1973); Anon. (1974f); Perkins (1975); Jelen and Yaws (1977); Parkes (1978); J.L James (1979); Lees (1983b); Grundfos Pumps (1984); Hudson (1997); ASME (1998); Frenning (2001)

Revalidation, remaining life assessment
ASME (1980/81, 1983/89, 1986 PVP 112, 1987 PVP 129, 1988 PVP 138, 1989 PVP 171, 1991 B31G); Zeis and Eschenbrenner (1980); Baker-Counsell (1987b); Grosshandler (1987a); British Gas (1990 Comm. 1438, 1439); Baas and Warner (1992)

Computer-based systems
Eason and White (1977); Beatson (1978); Trotter (1979); Redding (1980); McChrystal (1982); Anon. (1987c); Grosshandler (1987a); Collington (1989); Anon. (1990b); Project Software and Development Inc. (1991); Wireman (1994); Mather

Particular equipment
Foundations: Renfro (1975, 1978, 1979); Vick, Witthaus and Mayo (1980)
Gas plant: IGasE (1987 IGE/TD/11)
High pressure equipment: McClelland (1968); Andrews and Weber (1993)
Electrical equipment: Autenriet (1962); Erb (1975); HSE (1980 HS(G) 13); NEPA (1990 NFPA 70B); API RP 500 (1997), RP 505 (1997), RP 540 (1999), Std 546 (1997)
Piping: McNaughton (1979); Lee (1999); API RP 570 (1998), RP 574 (1998), RP 578 (1999), RP 581 (2000), Rp 591 (1998), RP 751 (1999)
Heat exchangers: Yokell (1983); Stegelman and Renfftlen (1983); Fijas (1989); Pugh *et al.* (1993); API RP 510 (1997), RP 572 (2001), RP 581 (2000), RP 751 (1999), Std 661 (2002), Std 662 (2002)
Fin Fans: API RP 572 (2001), RP 751 (1999)
Steam traps: Isles (1977)
Valves: Kletz (1984l); Charbonneau (1985); Irhayem (1985); Anon. (1989 LPB 85, p. 1 and 3); Anon. (1989 LPB 87, p. 9); Anon. (1992 LPB 103, p. 25 and 29); Anon. (1992 LPB 107, p. 27); API RP 591 (1998)
Heaters: Goyal (1967); Sharp (1977); API 531 (1980), RP 536 (1998), RP 573 (2003), Std 530 (2003), Std 560 (2001)
Boilers: API 573 (2003), NB23
Combustion systems: R. Fletcher (1979)
Flare stacks: Anon. (1992 LPB 107, p. 23), API 521 (1997)
Machinery: W.E. Nelson (1974, 1980); L.D. Martin, Young and Banks (1977); Houghton (1979); Vargas (1982); Murray (1983); Parry (1990); Gresh (1992); Rutan (1993): API RP 686 (1996), Std 614 (1999)
Pumps: Love (1972); Yedidiah (1974, 1977); R. James (1976); Grundfos Pumps (1984); French (1992); Bitterman (1993); Pradhan (1993); API Std 610 (2003), Std 671 (1998), Std 674 (1995), Std 675 (1994), Std 676 (1994)
Power transmission: G.W. Howard (1971, 1977)
Pressure relief valves and systems: Lortz (1966); Woolfolk and Sanders (1984, 1987); J.K. Rogers (1988); Duckworth and McGregor (1989); Coulston (1993); API RP 510 (1999), RP 520 (2000), RP 521 (1997), RP 576 (2000), RP 751 (1999), Std 526 (2002), Std 527 (1991)
Instrumentation: Sherman (1960); Upfold (1971); Barbin (1973); IP (1980 MCSP R 14); Hasselbaum (1992); API 553 (1998), 554 (1995), 555 (2001); ISA 20 (1981)
Vessels: Megow and Dawson (1977); Snow (1979); R.S. Brown (1982); Quraidis (1982); Pritchard (1983); Guth and Clark (1985); API RP 510 (1997), RP 572 (2001), RP 579 (2000), RP 580 (2002), RP 581 (2000), RP 751 (1999), Pub 939-B (2002)
Tanks: H.V. Bell (1982); Shtayieh (1983a,b): Huston (1983); API RP 575 c(1995), RP 2350 (1996), Spec 12D & F (1994), Std 620 (2002), Std 650 (1998), Std 653 (2001), Std 2601, Pub 850 (997), Pub 2026 (1998)
Compressors: API Sts 617 (2002), Std 618 (1995), Std 619 (1997), Std 671 (1998), Std 672 (1991), Std 681 (1996)
Gears: API Std 613 (1995), Std 677 (1997)
Turbines: API Std 611 (1997), Std 612 (1995), Std 616 (1998)
Chlorine systems: BCISC (1975/1); Chlorine Institute (1975 Publ. 41, 1981 Publ. 42, 1982 Publ. 39)
LPG systems: LPGLTA (1984 LPG Code 14, 1986 LPG Code 1, R 3)
Fire protection equipment: MCA (SG-13); FMEC (1986 LPB 71); NFPA (1987 NFPA ISA, 1993/33); API 2001 (1998)
Pipelines: McNaughton (1979); P.M. Scott and Kiefner (1984); AGA (1990/69); IGasE (1990 IGE/SR/18, IGE/ER/1); API RP 2200 (1993), API 1130 (2002)

Used equipment
J.P. Epstein (1967, 1978); C. Butcher (1992d, 1993a)

Unused equipment, dead ends
Anon. (1983 LPB 49, p. 28); Kletz (1989 LPB 87)

Mothballing
Twigg (1985); R.G. Miller and King (1987); Savage, Portnoy and Parkinson (1988)

Permit systems
ROSPA (n.d./l); BCISC (1959/3); ABCM (1964/3); O'Driscoll (1965); J.R. Hughes (1970); CAPLTB (1977 Inf. Pap. Suppl. 16A); IP (1981 MCSP R 3, 1987 MCSP R 9, 1993 TP 11); Kletz (1982f); Anon. (1984 LPB 55, p. 11); HSE (1986 IND(G) 39(L), 1992 IND(G) 98(L)); V.C. Marshall (1986b); Trowbridge (1987); OIAC (1986, 1991); Anon. (1989 LPB 85, p. 3); FPA (1989 CFSD GP 3); Anon. (1990 LPB 92, p. 7, 10, 18 and 21); Anon. (1990 LPB 93, p. 32 and 35); British Gas (1990 BG/PS/G11); Cullen (1990); Anon. (1992 LPB 104, p. 5); Anon. (1992 LPB 107, p. 27); S. Scott (1992); Townsend (1992); Anon. (1993 LPB 112, p. 20); Butler and Bonsai (1993)

Interlocks
Anon. (1983 LPB 49, p. 7); ISA 84.01 (1996), 91.00 (2001)

Maintenance activities
Bolting: NRC (Appendix 28 *Bolts*); British Gas (1979 TIN10); K. Gibson (1986); Bett (1989); Davie (1989); Ritchie (1989); Standen (1989); Whalley (1989); Garner (1993)
Equipment isolation: Anon. (1990 LPB 91, p. 17); Anon. (1990 LPB 92, p. 19)

Line breaking: BCISC (1959/3)
Blockage clearing: Anon. (1990 LPB 92, p. 9); Anon. (1991k)
Lifting, rigging: N.L. Owen (1965); van Amerongen (1968, 1970); Mallinson (1968); EEMUA (1984 Publ. 101)
Manholes: Bond (1987 LPB 78)
Vessel entry, entry into confined spaces: MCA (SG-10, 1962–/1–4); SMRE (Gas detection 1, 2, 4, 10); BCISC (1959/3); ABCM (1964/3); Wareing (1969); DoEm (1971/1); Huggett (1973); HSE (1974 TON 46, 1975 TON 47, 1977 GS 5, 1991 Construction Sheet 15); Anon. (1975 LPB 3, p. 8); FRS (1975 Fire Res. Note 1044); NIOSH (1979 Crit. Doc. 80–106, 1987 Publ. 87–113); Anon. (1980 LPB 31, p. 11); Burnett (1980); Anon. (1983 LPB 53, p. 15); Anon. (1984 LPB 56, p. 26); API (1984 Publ. 2217, 1987 Publ. 2217A); Bond (1984 LPB 59); Anon. (1985 LPB 63, p. 31); Kletz (1985b); Keller (1987); IGasE (1987 IGE/SR/5); Anon. (1988 LPB 81, p. 29); Anon. (1991 LPB 98, p. 19); Anon. (1992 LPB 102, p. 27); Crawley (1992 LPB 104); NFPA (1993 NFPA 326); Suruda *et al.* (1994); OSHA (1999)
Tank cleaning, repair and demolition: Anon. (n.d.a); API Publ. 2013 (1991), Publ. 2015 (2001), Publ. 2026 (1988), Publ. 2027 (2002), Publ. 2202 (1991) Std 653; HSE (1970 HSW Bklt 32, 1975 TON 18, 1985 CS 15); Barrell (1971); Associated Octel Co. (1972 Bull. 20, 1975); Luckritz and Schwing (1973); (1075 Bull. 28), FRS (1975 Fire Res. Note 1044, 1977 Fire Res. Note 1074); Savage (1975); Fardell and Houghton (1976); Amey (1977a,b); A.A. Briggs (1979); Vick, Witthaus and Mayo (1980); IP (1989 MCSP Pt 16); Jacob (1990); Moros, Howells and Ryall (1993); NFPA (1993 NFPA 327)
Welding, hot work: AWS (Appendix 28, 1976/1, 1978/2, 1992/13); ASTM (STP 11, 494); IRI (n.d./2); NSC (Safe Practice Pmphlt 105); Welding Institute (Appendix 28, 1981/35, 36, 1986/38, 1991/43); API (1988 Publ. 2009, 1991 RP 1107); BCISC (1959/3); Voelker (1965, 1973); Sanderson (1969); HSE (1970 HSW Bklt 38, 1978M 15, 1979c, 1979 HS(G) 5, IND(G) 35 (L), 1986 PM 64, 1989f); Voelker and Zeis (1972); Bales (1977a); A.J. Williams and Mallone (1977); Eutectic and Castolin (1979); R. King and Magid (1979); Schell and Matlock (1979); Anon. (1980 LPB 32, p. 15); CGA (1981 SB-8); AIHA (1984/6, 8); Nock (1985); NIOSH (1988 Crit. Doc. 88–110); FPA (1990 CFSD GP 2); Gregory (1990); Balchin (1991 Welding Institute/12); Stippick (1992); ANSI Z49.1–1988; BS (Appendix 27 *Welding*)
Onstream repairs: API (1978 Publ. 2209); Bloom and Pebworth (1979); G.W. Harrison (1980); Anon. (1981); Pennington (1992); API RP 2009 (2002)
Leak repair: Hutton (1973); Stroud (1981); Bareness (1982); Maushagen (1984 LPB 55); Anon. (1986n); Bond (1986 LPB 69); J.K Rogers (1988)
Hot tapping: Hahn, Brownlee and Thompson (1969); de Hertogh and Illeghems (1974); Britt (1975); Elder and Batten (1975); Hahn (1975); W.B. Howard (1975a); Howden (1975); Letchford (1975); Warren (1975a); API (1985 Publ. 2201, 1991/19); AGA (1988/57, 1989/61)
Cleaning with water, chemicals: C.T. Fox (1967); Engle (1971); Loucks (1973); Vanmatre (1977); Roebuck (1978); Anon. (1980 LPB 35, p. 7); Anon. (1981 LPB 38, p. 23); Shorthouse (1983); Hyde (1985); Donaldson (1986); HSE (1988 PM 29); Junique (1988); J.O. Robinson (1993)
Cleaning in place: Kirkland (1986); Someah (1992)
Water jetting: High Pressure Water Jetting Contractors (1982)
Decontamination: Dransfield and Greig (1982); EEMUA (1989 Publ. 154)

Maintenance equipment
HSE (Appendix 28 GS, PM series)
Tools: EEUA (1958 Doc. 4); Anon. (1962e); IGasE (1970/9); FPA (1975 Sll); Kletz (1977i); HSE (1978 PM 14, 1990 PM 32); R. King and Magid (1979); Anon. (1984J); API (1989 Publ. 2214)
Lifting equipment: ICI/RoSPA (IS/102); SMRE (Engineering Metallurgy 2, 3, 5); Bates (1992); BS (Appendix 27 *Lifting Equipment*)
Scaffolding: DoEm (1974/5); Anon. (1989 LPB 89, p. 9 and 18); BS 5973: 1990
Cranes: RoSPA (IS/29); HSE (1973 TON 26, 1974 TON 27, 1976 PM 3, 1979 PM 9, 1980/11, 1985/17); Aitken (1987); BS (Appendix 27 *Cranes*), BS COP 3010: 1972
Forklift trucks, power trucks: MCA (SG-6); RoSPA (IS/38; Rochester (1969); Partridge (1977); HSE (1979 HS(G) 6); NFPA (1992 NFPA 505)
Engine-driven equipment: API (1987 Publ. 2203)
Robots: Collins (1982); IMechE (1982/62); T.J. Williams (1983); Siddle (1986b); R.M. Taylor and Lewis (1987); HSE (1988 HS(G) 43); NIOSH (1988 Publ. 88–108); Mitler (1989)

Maintenance hazards
HSE (1985 PML 7, 1985/16,1987/20, 1992 HA 1, 1992/30); API 750 (1990), 751 (1999), 752 (1995)

Construction, demolition
Construction: HSE (HSW Bklts 6A–6F, 1983 GS 24, 1984 GS 28, 1985 GS 33, IND(G) 30(L), 1991 Construction Sheet 15, GS 6); Hayward (1969); Oil and Chemical Plant Constructors Association (1974); National Federation of Building Trades Employers (1975); RoSPA (1975 IS/13); ES 6187: 1982
Construction equipment: HSE (1981 PM 27, 28, 1982 GS 15, 1983 PM 30, 1984 GS 31, 1987 G5 42)
Demolition: Stuart (1974); Oberhansberg (1977); HSE (1989 GS 29); Anon. (1992 LPB 104, p. 10); BS 6187: 1982

Construction, demolition hazards
HSE (1981/2)

relevant to the maintenance of process equipment, where there are many jobs which involve degree of potential hazard, but which can be done safely provided proper control is exercised. It is also characteristic of maintenance that it often involves quite a large number of people and that systems to ensure good communications are important.

Basic elements of the overall safe system of work are: equipment documentation – written procedures for non-trivial tasks; permit and handover systems; systems for control of a large workforce and for dealing with contractors and supervision and training.

21.1.2 Equipment documentation

Critical information on all equipment must be documented so the design basis, operating parameters and materials of construction are known. The primary document is a piping and instrument diagram for mechanical equipment and electrical one-line diagrams for electrical equipment. Various other sources like equipment specification sheets, equipment drawings, instrument loop diagrams, pump curves, relief system design, safety system documentation and material certifications will provide detailed

information. The documentation must be kept accurate and up to date.

21.1.3 Maintenance procedures

Any regular maintenance task which is non-trivial should be governed by a formal written procedure. This procedure should address the specific task and should complement the general permit and handover systems described below. In particular, there should be formal procedures for the installation and removal of slip blinds and blind flanges. The principles underlying the writing of operating procedures are applicable in large part to maintenance procedures also.

21.1.4 Permit system

Maintenance work should be governed by a formal permit system. The purposes of such a system are: to see that proper consideration is given to the job, its hazards and the precautions required; to ensure that these are understood by all persons involved; and to facilitate effective communication between the parties concerned.

The permit system is intimately bound up with the hazards of maintenance and with the various preparations and precautions required to make a plant safe for maintenance work. These are therefore described first and the permit thereafter in Section 21.8.

21.1.5 Handover system

The permit system should be complemented by formal shift handover procedures. These procedures are described in Chapter 20 with particular reference to handover between operators, but essentially similar considerations apply to the maintenance function.

21.1.6 Control of workforce

The workforce involved in maintenance and related work may be quite large and varied. The core maintenance workforce of company employees may be supplemented by contractors working on routine maintenance and on equipment testing and recertification. In addition to the workforce thus engaged, there may well be extended periods when other plant modification or expansion work is going on involving a considerable number of people. All this work needs to be controlled through the permit system. The need to exercise control may in some cases set a limit on the volume of work which can be undertaken.

21.1.7 Contractors

A portion of the workforce engaged in maintenance work may be contractors. The trend in recent years has been towards increasing use of contractors, not only on construction work but also on more routine jobs such as equipment testing and recertification. The reasons for the use of contract maintenance are discussed by C.J. Carter (1980) and the identification and control of contractor hazards are described by Whitaker (1993).

There should be a system of quality assurance for work to be bid out. It is normal to require the contractor to provide evidence of the quality and safety of his work, supervision and training, and of his own quality assurance and safety procedures. The OSHA process safety management standard requires employers to obtain and evaluate information regarding contractor's safety performance and programmes. The standard defines employer and contractor responsibilities. A sample contractor pre-qualification form was jointly created by the Chemical Manufacturers Association (CMA) and the API.

In some cases a contractor's personnel may work on a site for years on end and become as familiar with the systems as company personnel, but in others they may be there for quite a short time. In any event, it is necessary that before new personnel from a contractor start work they are properly trained in these systems. Contractor safety orientations should be held for all contract employees highlighting the plant safety requirements and hazards.

The need for this was highlighted by the Piper Alpha disaster, where a two-man team of contractors was carrying out testing and recertification work on pressure relief valves on the platform, but the senior of the two was on his first tour as supervisor and had not received adequate instruction in the permit system.

21.1.8 Supervision and training

It will be evident that supervision and training are essential in ensuring that maintenance work is done safely. The permit and handover systems provide a structure for the supervision of maintenance work, but by no means exhaust the contribution of supervision.

With regard to training, maintenance personnel should be trained not only in their own craft, but also in the hazards of the chemicals and the equipment, the jobs which they do such as isolation and vessel entry, in the permit and handover systems, and in making the distinction between a routine maintenance task and a modification. The training of maintenance personnel is considered further in Chapter 27.

21.2 Hazards of Maintenance

As already stated, maintenance work on process equipment involves a number of hazards. An account of maintenance hazards and accidents is given in *Deadly Maintenance* the (HSE, 1985b), *Dangerous Maintenance* (HSE, 1987a) and HS(G) *49 Human Factors in Industrial Safety* (HSE, 1989) and by Deacon (1988).

The first of these is a study by the Accident Prevention Advisory Unit (APAU) of the Health and Safety Executive (HSE) of maintenance accidents in British industry during the period 1980–82. In this period, there were over 100 deaths per year caused by maintenance work, and over the 3-year period there were a total of 106 deaths (33%) associated with the maintenance of equipment and machinery. The fatalities were assigned to the following categories: breakdown and scheduled maintenance work, 66%; cleaning, 25%; and examination, lubrication, painting, 9%. A feature of these statistics is the prominence of accidents in cleaning.

Although maintenance craftsmen comprised the largest single category of deaths (37%), fatalities to operators were almost as numerous (33%). Other groups included labourers (7%), service engineers (6%), and managers, supervisors and proprietors (13%). The relatively large number of deaths among operators is accounted for only in part by cleaning operations.

The accidents were classified by equipment type, accident type and major cause. There were 66 accidents assigned to identified categories of machinery and 32 to identified categories of equipment, the balance of 8 being assigned to machinery and equipment in general. Of the machinery accidents, 23 were caused by conveyors and

elevators, but few of the others identify process machinery. The breakdown of plant accidents is: storage tanks, 7; furnaces and associated equipment, 6; boilers, heating and ventilation equipment, 5; chemical, gas, oil, process equipment, 5; dust or fume extraction equipment, 5; and degreasing equipment 4.

The classification by accident type is: machinery, 50, of which 17 involved entanglement and the rest some form of crushing; falls, 21; burns, 10; gassing, 9; electrocution, 6; asphyxiation, 5; and struck by falling materials or equipment, 5.

By major cause, the classification is: absence or failure of system of work, 35; absent or defective equipment, guards or working platforms, 23; failure of management organization or supervision, 11; inadequate or lack of training, instruction or information, 8; human error, 10; unauthorized activity, 5; defective design of equipment or machinery, 5; and unknown or unforeseeable incident, 9.

The authors present three case studies of generic types of accident, associated with (1) conveyors and elevators, (2) overhead travelling cranes and (3) confined spaces.

The APAU publication also contains some 99 case histories of accidents in maintenance work. Other specialized collections include *Safety in Maintenance* (API, 1981 Safety Digest 4) and that given by Kletz (1982f), whose other work is also replete with maintenance case histories. Complete maintenance work also features strongly in many general collections of case histories.

Confined spaces present a number of hazards, and these are described in Section 21.7. Other hazards are mentioned throughout this chapter.

21.3 Preparation for Maintenance

There are a number of preparatory measures which may need to be taken before maintenance work is started. The principal means of control of such work is the permit system. The preparatory measures to be taken should be specified on the permit.

Many of these measures are aimed at allowing work inside equipment to be done safely. If work is to be done internally on an item of equipment, it should be prepared by the following operations: (1) depressurization, (2) cooling down, (3) isolation, (4) removal of contents (gas, liquid, solids) and (5) cleaning.

21.3.1 Identification of equipment

Many incidents occur on process equipment due to errors in the identification of the equipment on which work is required. Plants can often seem a confusing maze of vessels and piping, much of it lagged, and it is often difficult to identify equipment unaided simply by tracing the course of piping or by the use of other clues. This point has already been made in Chapter 14 in relation to the work of the process operator. It is necessary, therefore, to adopt a more positive policy for the identification of equipment.

One method which may be used is to attach a permanent identification to a particular equipment. This is an effective system provided precautions are taken against certain types of error which can occur.

There are certain standards and codes of practice for the identification of equipment. In particular, mention may be made of BS 1710: 1984 *Specification for Identification of Pipelines and Services*.

Identification should be consistent and should agree with reasonable expectations. It is asking for trouble to number equipment unsequentially, when it forms a natural sequence, such as pumps in parallel or reactors in series. Another situation to be avoided is ambiguity as to which of two adjacent pieces of equipment an identifier refers to.

Much maintenance work involves breaking into pipe joints. Permanent identifiers are not as suitable in this case. An identification tag can be used.

The identification of pipe joints is particularly important, because incidents are frequent in which the wrong joint is broken. Many such occurrences could be avoided by a positive system in which the identification tag is put on the joint to be broken.

For the type of work described, a permit is required. The identification of the equipment, whether permanent or temporary, should be given on the permit form. A walk down by the operator issuing the permit and the maintenance technicians to physically locate the equipment is beneficial.

The system described is not foolproof, of course. The person putting the identification tag on the equipment can make a mistake. But, in general, it does appear to be an effective system in practice.

The use of the identification tag system is preferable to merely pointing out to the maintenance fitter the equipment to be repaired. Incidents have occurred which suggest that this is not always adequate.

21.3.2 Depressurization

If the equipment contains liquid heated above its boiling point under pressure, it may be necessary to let it cool down prior to depressurization in order to avoid excessive flash-off. Depressurization should be performed in accordance with the design intent. For flammable or toxic gases this should preferably be to another part of the process. Alternatively, it may be to flare, to a scrubber system, or in some cases to the atmosphere. For inert gases venting is often to a vent stack or vent pipe.

21.3.3 Cooling

If the equipment has not already been cooled down sufficiently prior to depressurization, it should now be cooled down. Cooling involves the hazard of vacuum collapse. This may be guarded against by inert gas injection to maintain the internal pressure at atmospheric pressure.

21.3.4 Isolation

When the equipment has cooled down, the equipment to be worked on should be isolated. This includes isolation of vessels and piping from process and utilities, isolation of machinery from its power sources (electric, hydraulic, pneumatic) and isolation of electrical equipment. Isolation is crucial both to the safety of the equipment and to that of the personnel. It is considered in detail in Section 21.4.

21.3.5 Emptying of liquids

Once the equipment has been isolated, the next step is to remove its contents. If it contains liquid, this is usually pumped away to another part of the equipment or to storage, or, if non-hazardous, to drain. The liquid may leave behind hazardous residues, which are considered in Section 21.3.7.

21.3.6 Gas freeing

If the contents of the equipment are gas or vapour, there are a number of methods of gas freeing which may be used to

replace them with air. These methods include (1) forced ventilation, (2) flushing with water and forced ventilation, (3) purging, (4) steaming and (5) chemical cleaning.

Equipment often contain flammable or toxic residues. If these are sufficiently volatile, they may constitute a continuous source of contamination.

The choice of method of gas freeing depends on the type of equipment, on its initial contents, including residues, and on the work to be done. Where steaming is used for cleaning, gas freeing occurs at the same time.

Purging is discussed in Section 21.5. Other methods of gas freeing are described in relation to tank cleaning in Section 21.12. An account of the gas freeing of crude oil storage tanks is given by Moros, Howells and Ryall (1993).

21.3.7 Removal of solids

Solid process materials include raw materials and final products, and catalysts and adsorbents. Raw materials are often removed by continuing to run the process until they are exhausted. Products, catalysts and adsorbents are generally transferred to suitable containers.

There are a number of hazards associated with solid process materials which need to be guarded against. Solid materials may be flammable, toxic or pyrophoric. Flammable dusts may give rise to a dust explosion. Adsorbents may give off flammable or toxic material, and in some cases ignite spontaneously in the presence of air.

The other type of solid is residues in the form of deposits and sludge. These also may be flammable or toxic. It is generally necessary to remove these by cleaning, although for certain activities there may be alternative sale methods of working, as described below.

A particular pyrophoric material often encountered in refinery processes is iron sulfide. If dry, this will burst into flames on contact with air, but if wet it is harmless. It may be dealt with by injecting inert gas and soaking the iron sulfide with water.

Oil soaked insulation, removed while it is still hot, can behave like a pyrophoric material and burst into flames on contact with air.

21.3.8 Cleaning

There are a number of methods available for cleaning. The choice of method of cleaning depends on the type of equipment, on its initial contents, including residues, and on the work to be done. The methods are described in Section 21.6.

21.4 Isolation

As already described, much maintenance work is subject to potential hazards from noxious materials, energy sources, rotating equipment and electrical power. Where work is to be done, the necessary isolations should be made to ensure that it can be done safely. Accounts of isolation are given in the IP *Refining Safety Code*, the IP *LPG Code*, the OIAC *Permit Systems Code*, the IChemE *Maintenance Guide* and by Kletz (1982f).

Isolation is governed by OSHA standards 1910.147 *The Control of Hazardous Energy* (Lockout/tagout) and 1910.146 *Permit Required Confined Spaces*. Isolation may be required prior to installation, inspection, repair, cleaning or dismantling. Where a job involves isolation of equipment, there should always be a permit for the job. Permit systems are described in Section 21.8.

21.4.1 Isolation of vessels and pipes

The methods available for isolating a vessel or pipe are, in ascending order of effectiveness, the use of (1) a closed and locked valve, or valves, (2) a double block and bleed valve system, (3) a blind and (4) physical disconnection.

The least effective of these methods of isolation is the use of a closed and locked isolation valve. There have been numerous incidents in which either the valve has corroded or jammed and has passed fluid or it has been opened in error. Even two isolation valves in series do not always prevent the passage of fluid.

More positive isolation is obtained by the use of a double block and bleed valve system as shown in Figure 21.1(c) The two block valves are closed, the bleed valve is open and all three are locked. If the fluid passes through the first block valve, it is vented by the bleed valve so that no pressure should build up which would allow the material to pass through the second block valve. A build-up of pressure can occur if the bleed line is too small or too long, or if it discharges into a vent system in which there may be a back pressure.

As shown in Figure 21.1(a), isolation may be accomplished by the insertion into the line of a slip blind. In the system shown, the valve is first closed and locked and the slip blind is then inserted. If a spacer blind or figure 8 blind is installed, it may be used instead of a slip blind.

The most positive method of all, shown in Figure 21.1(b), is complete physical disconnection of the line, with a blind flange, or blank, put on the 'live' line.

Where isolation is by means of a closed valve, this should be an isolation valve rather than a control valve, unless the latter can be tightly shut, disconnected from any power source, locked in the closed position and the isolation tested as being effective.

Isolation valves should be locked and tagged. The preferred arrangement is a valve which can be locked with a captive key system or which has lugs for padlocking. The alternative is the use of a chain and padlock. A tag should be securely attached to the valve, stating whether it is locked in the open or closed position and prohibiting unauthorized movement of it, and showing the equipment identification number, the isolation lock number and the isolation permit number.

On systems containing hazardous fluids such as hydrocarbons under pressure, the arrangements for closing off the end of a line with a blind flange should ensure that the joint is leak tight. The fixed flange and the blind flange should be inspected for deterioration, a ring-joint blank should be fitted with a new ring and the bolts should be properly tightened.

The blind used should be strong enough to withstand the highest pressure which may occur in the main if the shut-off valves are opened accidentally. The blind must be thick enough to withstand hydrotest pressure if the system isolated has to be hydrotested. Each blind should have an identification tag.

Where there is to be work on a pressurized hydrocarbon system or entry into a vessel, physical disconnection is the recommended method of isolation. If this method is not reasonably practicable, the next best method is the insertion of a blind.

The closed and locked isolation valve method should be used only for the isolation of low hazard fluids. Another principal use is to effect preliminary isolation while a blind is inserted.

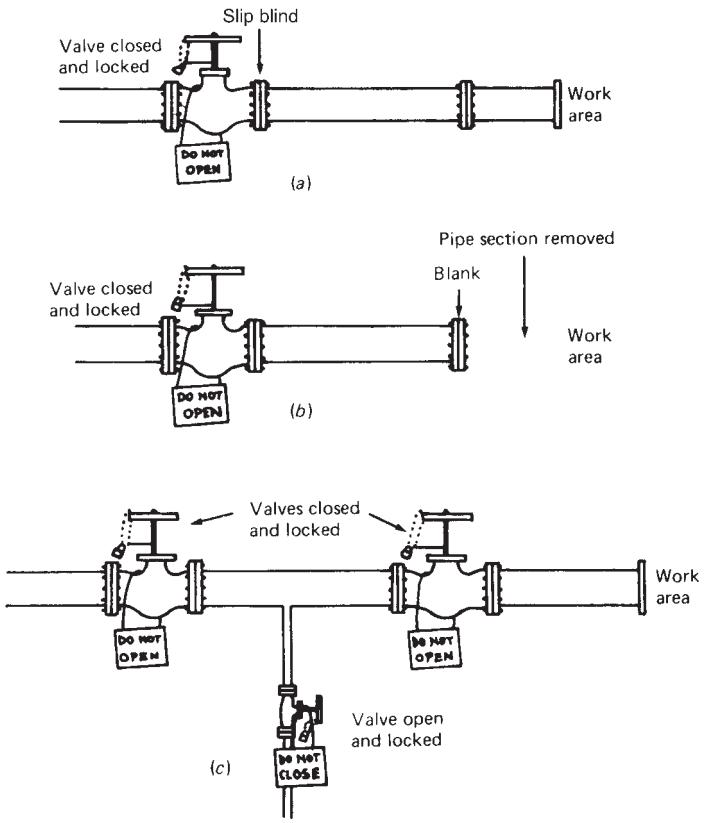

Figure 21.1 *Some methods of isolation of piping – 1: (a) locked valve with slip blind; (b) locked valve with blind flange and with section removed; (c) locked double block and bleed valves*

The double block and bleed system is more effective than a closed isolation valve and is used for more hazardous fluids. It does not, however, provide adequate isolation for long periods. This method also finds a principal use in effecting preliminary isolation while a slip plate is inserted.

Figure 21.2 shows the methods of isolation given in the IChemE *Maintenance Guide*. In addition, there are certain preferred arrangements for isolation in specific cases. For entry into a vessel or confined space, isolation should be by physical disconnection.

For the isolation of relief valves and vent lines, physical disconnection is again the preferred method. Where this is not possible, the relief valve or vent line should be blinded off first and deblinded last.

The need should be considered for isolation of drains and sewers through which hazardous materials may spread to other sections of the plant.

The equipment should be designed to facilitate isolation, particularly at points where isolations are likely to be frequent. A pressure gauge and drain point can be provided downstream of an isolation valve which is used to provide preliminary isolation for the insertion of a blind. A double block and bleed valve system can be installed to provide more positive isolation for the same purpose. Spectacle blinds can be provided. All critical valves should be identified with a permanent marking.

There should be a system for the identification and control of blinds and blind flanges for different duties. The system should ensure that blinds are correctly identified and that they do not become mixed up. It should also ensure that blinds are neither left in when they should be taken out nor left out when they should be inserted. For equipments where a number of blinds need to be inserted for isolation, it is helpful to have a blind list and a diagram showing the insertion points. Permanent blinds should also be labelled and shown on P&IDs.

21.4.2 Isolation of machinery

Where work is to be done on powered machinery, the source of power should first be isolated. Sources of power include electrical, hydraulic and pneumatic power, and engines.

A hydraulic or pneumatic supply should be isolated as follows. First, preliminary isolation should be completed by closing a valve. Then the supply and return pipes should be disconnected, or otherwise made safe. The isolation of electrical supplies is described below.

Isolation of an engine-driven system should be done by shutting off the engine fuel supply and then isolating and disconnecting all starting systems.

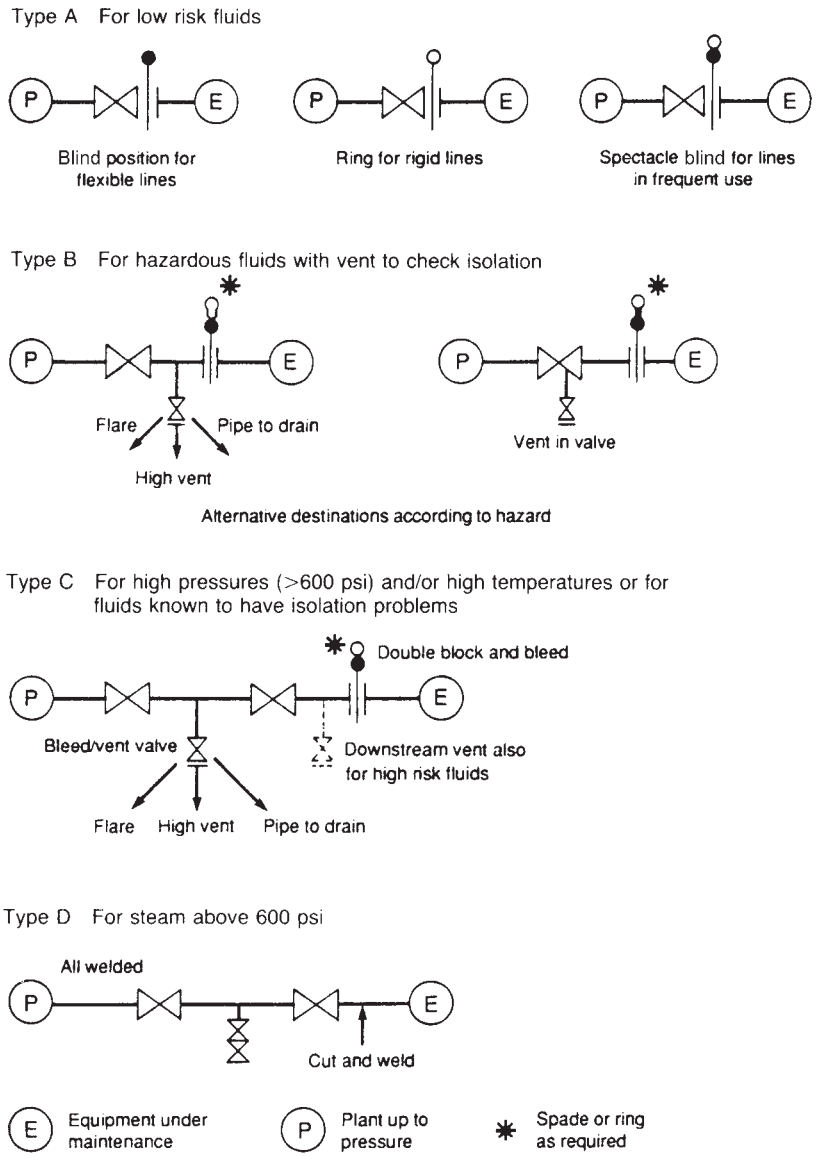

Figure 21.2 *Some methods of isolation of piping – 2 (Townsend, 1992) (Courtesy of the Institution of Chemical Engineers)*

It may sometimes be possible for the machinery to move even though it is disconnected from its power source, and in such cases it should be secured to prevent such movement.

A lockout/tagout system should be used based on principles similar to that for the isolation of equipment.

21.4.3 Isolation of electrical equipment

Electrical isolation may be required either to immobilize machinery or to protect personnel working on electrical equipment.

Situations involving electrical isolation include work on powered equipment, including rotating machinery and machinery with moving parts, and entry into vessels which contain stirrers or agitators.

Where isolation of fluids is required, electrical isolation should be a complement to, but not a substitute for, mechanical isolation.

OSHA standards 1910.147 and Subpart S, govern maintenance work on electrical systems. The isolation of electrical equipment is governed by the UK *Electricity at Work Regulations* 1989 and advice is given in the associated *Memorandum of Guidance* (HSE, 1989 HS(R) 25). Electrical isolation should be performed only by an electrically competent person.

Two methods of isolating electrical equipment are to withdraw the fuses and to lock-out the breaker. There is evidently some difference of view on the merits of the two methods. Some references describe systems based primarily on breaker lock-out. The IChemE *Maintenance Guide* describes fuse withdrawal as suitable where breaker lock-out is not available, as with instruments, heaters, lighting circuits. Anon. (1983 LPB 49, p. 7) argues that a fuse is always liable to be replaced. On the other hand, Kletz (1982f) states that experience has shown that breaker lock-out is not always effective. He recommends fuse withdrawal where the work to be done is on electrical circuitry. A system of electrical isolation based on breaker lock-out is described by Anon. (1983 LPB 49, p. 7).

A lock-out device is a mechanism or arrangement which allows the use of key operated padlocks to hold a switch lever or handle in the 'off' position. The lock-out procedure is to switch off or de-energize electric power, lock-out, tagout and confirm lock-out by checking that the equipment will not restart. The lock-out should be applied to the breaker or disconnect switch itself and not to some remote stop/start button, selector switch or interlock. Where there is more than one power source, all should be locked out and tagged.

The lock-out system is as follows. For operations, each padlock should be issued through the operations foreman and should be capable of being opened only by the one key issued with it. There should be a lock-out log for recording the identification of the locked-out equipment, the date and time of application of the padlock and the operator applying it, and the date and time of its removal and the operator removing it. The maintenance craftsman applies his own lock to the breaker before starting work and removes it when they are finished. Where the equipment is to be worked on by several crafts, each craftsman applies this procedure. If a shift change occurs, the outgoing craftsman removes his lock and the relieving one applies his own lock. When the job is complete, the last lock to be removed is that of the operator.

With regard to the isolation of electrical systems, to protect personnel working on or near them, guidance is given in the relevant OSHA standards, API recommended practices and British Standards.

All items of electrical equipment should have permanent labels, and their separate parts should be identifiable. For a prime mover, the IChemE *Guide* gives these as the drive unit, the breaker/disconnect and the stop/start button. A system of warning tags should also be used.

21.5 Purging

Purging involves replacing one gas or vapour with another. It is performed for a variety of purposes and using a number of different purging media. Guidance on purging is given in *Purging Principles and Practice* (AGA, 1975) (the AGA *Purging Guide*). Further accounts of purging are given in the IP *Refining Safety Code*, CS 15 (HSE, 1985), the IP *LPG Code*, the IChemE *Maintenance Guide*, and by Kletz (1982f).

Purging may be used to take a unit out of service by replacing flammable or toxic process gas with an inert medium and then with air. It may be used to bring a unit back into service by replacing air with an inert medium and then with the process gas.

The AGA *Purging Guide* gives purging end-points for a number of different cases. The end-point data cover two purge gases: nitrogen and carbon dioxide. Values are quoted for the concentration which will just render a mixture non-flammable and for that which allows a 20% 'safety factor'. Selected purge end-points taken from the guide, are shown in Table 21.2. Section A gives inert gas end-points for purging into service (i.e. purging air out of a system subsequently to be filled with flammable gas), together with an alternative set of oxygen end-points which may be more convenient to use. Section B of the table gives inert gas end-points for purging out of service (i.e. purging flammable gas out of a system subsequently to be filled with air), together with an alternative, and often more convenient, set of combustible gas end-points. The values given without brackets are the concentrations required to just render the mixture non-flammable, while those in brackets give the 20% safety factor.

Further details of the purging of equipment prior to entry or hot work, including sources of purge gas, purge end-points and precautions, are given in Section 21.12. The purging of refinery units is described in Chapter 20.

21.6 Cleaning

There is a wide variety of methods of cleaning equipment. They include (1) water washing, (2) chemical cleaning, (3) steaming, (4) water jetting, (5) solvent jetting, (6) shot blasting and (7) manual cleaning.

The choice of cleaning method depends on the type of equipment and on the nature of the material to be cleaned out. Most of these methods are described in CS 15 and/or the IChemE *Maintenance Guide*.

Some methods of cleaning are now described. Further details of cleaning of tanks prior to entry or hot work are given in Section 21.12.

21.6.1 Water washing

In some instances, adequate cleaning may be obtained by flushing with water. In most cases, however, something more is required.

Washing with cold water, or even purging with air, have sometimes been used in an attempt to remove oil, but these are generally not effective methods for this purpose and reliance on them has been the cause of many accidents.

Another process, also referred to as water washing, comprises immersion of the article in a boiling aqueous caustic or detergent solution. This may be used for small equipment which can be completely immersed. It is necessary to select the cleaning agent so as to avoid chemical attack, to exclude air and to boil for at least 30 min.

Another form of water washing is the use of a high pressure jet of hot detergent solution directed onto the interior surfaces. This latter method is used in combination with steaming to clean drums.

21.6.2 Chemical cleaning

Equipment may be cleaned by chemical cleaning using special chemicals. Surfactants can be used as a general cleaning agent. Some forms entrain hydrocarbon. Chemicals such as acids can be circulated through equipment to clean the system. All chemical cleaning solutions and by-products must be disposed of properly.

21.6.3 Steaming

Steam cleaning is used particularly for fixed and mobile equipment. The basic procedures is as follows. Steam is

Table 21.2 *Selected end-points for purging (after American Gas Association, 1975)*

A Inert gas and oxygen end-points for purging into service

Gas	*Concentration of gas to render mixture non-flammable* (% v/v)[a]	
	Nitrogen	*Oxygen*
Hydrogen	71 (77)	5.0 (4.0)
Methane	36 (49)	12.1 (9.7)
Propane	42 (54)	11.4 (9.1)
Butane	40 (52)	12.1 (9.7)
Ethylene	49 (59)	10.0 (8.0)
Propylene	42 (54)	11.5 (9.2)

B Inert gas and combustible gas end-points for purging out of service

Gas	*Concentration of gas to render mixture non-flammable* (% v/v)[a]	
	Nitrogen	*Combustible gas*
Hydrogen	95 (96)	5 (4)
Methane	86 (89)	14 (11)
Propane	94 (95)	6 (5)
Butane	95 (96)	5 (4)
Ethylene	94 (95)	6 (5)
Propylene	96 (97)	4 (3)

[a] Values without brackets are the concentrations to just render the mixture non-flammable, those in brackets are the concentrations which give a 20% safety factor.

added to the equipment, taking care that no excess pressure develops which could damage it. Condensate should be drained from the lowest possible point, taking with it the residues. The temperature reached by the equipment walls should be sufficient to ensure removal of the residues. A steam pressure of 30 psig (2 barg) is generally sufficient, and this temperature is held for a minimum of 30 min. The progress of the cleaning may be monitored by the oil content of the condensate.

There are a number of precautions to minimize the risk from static electricity. There should be no insulated conductors inside the equipment. The steam hose and equipment should be bonded together and well grounded; it is desirable that the steam nozzle have its own separate ground. The nozzle should be blown clear of water droplets prior to use. The steam used should be dry as it leaves the nozzle; wet steam should not be used, as it can generate static electricity even in small equipment, but high superheat should also be avoided, as it may damage equipment and even cause ignition. The velocity of the steam should initially be low, though it may be increased as the air in the equipment is displaced. Personnel should wear conducting footwear.

Consideration should be given to other effects of steaming. One is the thermal expansion of the equipment which may put stress on associated piping. Another is the vacuum that occurs when the equipment cools again. Equipment openings should be sufficient to prevent the development of a damaging vacuum.

Truck tankers and rail tank cars may be cleaned by steaming in a similar manner. Steaming may also be used for large tanks, but in this case the supplies of steam required can be very large. There is also the hazard of static electricity, and in some companies it is policy for this reason not to permit steam cleaning of large storage tanks which have contained volatile flammable liquids.

21.6.4 Water jetting

Another method of cleaning is high pressure water jetting. A high pressure water jet can cut through most metals and polymers and can clean a surface of paint or deposits. Accounts of water jetting are given by Donaldson (1986) and Jacob (1990). The relevant code is *Code of Practice for the Use of High Pressure Water Jetting Equipment* (High Pressure Water Jetting Contractors, 1982).

The technique is widely used for a variety of purposes, varying from the cleaning of buildings, roads and drains to the removal of spalled concrete. It is now being increasingly used in the process industries. One application is the removal of deposits from equipment such as heat exchangers and tanks. Another is the cutting of metal, which is used for the cutting up structural steel, equipment and piping during demolition.

In water jetting, the jet is held quite close to the surface, about 3–4 in. (75–100 mm). A water jet can remove material from a surface if the energy transferred per unit area exceeds a threshold value which is characteristic of the material. Since the energy is a function of the jet velocity and this in turn is a function of the pressure, this threshold energy can be specified in terms of the nozzle pressure for typical practical flows. The pressures used in water jetting have risen from about 3000 psi (200 bar) through 15,000 psi (1000 bar) and are now up to 30,000 psi (2000 bar).

A 30,000 psi (2000 bar) jet may operate with a flow as low as 2.5 gpm (10 l/min). At this flow, the reaction force is of the order of 33 lbf (15 kgf), which is manageable for an operator. A maximum recommended value is 1055 lbf (25 kgf). The cutting rate is controlled by adjusting the flow rather than the nozzle pressure and any increase in flow results in an increase in reaction force. One hazard of water jetting is the loss of control of the jet. Numerous incidents have occurred where water jet operators have injured themselves with the high pressure water.

Another potential hazard is the aerosol produced, which can be harmful, depending on the material involved. The use of protective clothing is necessary.

In addition to manual cleaning operations, water jetting is used in fixed systems for cleaning tanks and vessels. A typical arrangement is a set of four jets set at right angles to each other on the same plane and mounted on a head which itself rotates to give coverage in all directions. In such equipment cleaning applications, the travel distance for the jets is much greater, and their removing power correspondingly less.

Static electricity hazard can be a hazard in water jetting.

21.6.5 Solvent jetting

Another method used for cleaning is high pressure solvent jetting, with recirculation of the solvent. The method is promoted for difficult residues. The solvents used are flammable and create a flammable atmosphere inside the equipment. It is necessary to take precautions

against static electricity and to undertake gas freeing afterwards.

21.6.6 Shot blasting

A quite different method of cleaning is the use of shot blasting, or grit blasting. In this method a stream of fine abrasive particles is directed at the surface to be cleaned in a jet of air. The method is widely used for cleaning surfaces, particularly for painting. Walnut shell blasting has been used to clean rotating machinery internals.

21.6.7 Manual cleaning

In some cases it is necessary to resort to manual cleaning. This method may have to be used, for example, where a equipment contains residues which are difficult to shift in any other way but physically removing them. A typical case is the removal of flammable residues or solids in a large equipment in preparation for hot work. Manual cleaning is generally a last resort; it is laborious and unpleasant, and requires full precautions against flammable, toxic and asphyxiation hazards. Proper protective equipment must be worn.

21.6.8 Cleaning in place

A method of cleaning which is now a standard one in the pharmaceutical, as well as the food industry, is cleaning in place (CIP), using detergents. Accounts are given by Hyde (1985) and Kirkland (1986).

CIP systems offer a number of advantages. They minimize downtime by more rapid cleaning and generate less effluent, and can be less costly. They minimize manual operations and hence, both safety and health problems. In particular, hazards of vessel entry and slippery surfaces are reduced.

CIP systems come both as systems dedicated to particular units and as mobile systems which can be used on a number of units. They may operate under manual control or under automatic control, with a program sequence.

The equipment to be cleaned may be closed or open. For open equipment, Kirkland describes the use of a spray ball, custom-designed by computer, for the particular vessel.

A typical CIP sequence is: (1) a water pre-rinse, to remove gross material; (2) detergent circulation, to remove debris and scale; (3) an intermediate water rinse, to remove detergent; (4) sterile circulation, to destroy residual organisms; and (5) a final water rinse, to remove CIP solutions.

There are various techniques for water recovery and for minimizing the quantity of solutions used.

21.6.9 Line clearing

It is often necessary to remove debris, as distinct from shifting a complete blockage, from a line by flushing with water or blowing it with air.

A treatment of the effectiveness of this operation has been given by Junique (1988). This is based on the following simple model of flushing or blowing:

$$F \propto \rho u^2 \qquad [21.6.1]$$

where F is the drag force on the particle, u is the fluid velocity relative to the particle and ρ is the density of the fluid. He defines a cleaning disturbance factor such that

$$C = \frac{\rho_1 u_1^2}{\rho_2 u_2^2} \qquad [21.6.2]$$

where C is the cleaning disturbance factor and subscripts 1 and 2 denote cleaning and operating conditions, respectively. The condition for effective flushing or blowing is $C > 1$.

The author gives an example of the application of the method.

21.6.10 Waste minimization

Cleaning operations generate an appreciable fraction of the liquid effluents from process equipments and measures to reduce effluents from this source can contribute significantly to waste minimization. This aspect is considered in Appendix 11.

21.7 Confined Spaces

Accidents associated with entry into and work in confined spaces and vessels have occurred with depressing regularity. This activity is recognized as presenting particular potential hazards and is governed by a statutory requirement for a permit. Permits as such are considered in Section 21.8. The account given here is confined to the hazards of confined spaces and to precautions which should be taken. Accounts of these hazards and precautions are given in the IChemE *Maintenance Guide*, in a series of articles in the *Loss Prevention Bulletin* (Anon., 1975 LPB 3, p. 8; Anon., 1980 LPB 31, p. 11; Anon., 1983 LPB 53, p. 15; Anon., 1984 LPB 56, p. 24; Anon., 1985 LPB 63, p. 31), in the work of Kletz (notably Kletz, 1982f, 1985b), and by Arney (1977a,b), Bond (1984 LPB 59), Keller (1987) and Trowbridge (1987).

Requirements for confined spaces are governed by OSHA 1910.146 *Permit Required Confined Space*, NIOSH *Recommended Standard for Working in Confined Spaces*, API 2217A *Guidelines for Confined Space Work in the Petroleum Industry* and ANSI Z117.1 *Safety Requirements for Confined Spaces*. Current guidance for the United Kingdom is given in Construction Sheet 15 *Confined Spaces* (HSE, 1991).

21.7.1 Confined spaces

In some cases it is fairly obvious what constitutes a 'confined space', in others it is less so. OSHA 1910.146 defines confined space as:

(1) large enough and so configured that an employee can bodily enter and perform assigned work;
(2) limited or restricted means for entry and exit;
(3) is not designed for continuous employee occupancy.

1910.146 further defines a 'permit-required confined space (permit space)' as a confined space that has one or more of the following characteristics:

(1) contains or has a potential to contain a hazardous atmosphere;
(2) contains a material that has the potential for engulfing an entrant;
(3) has an internal configuration such that an entrant could be trapped or asphyxiated by inwardly converging

walls or by a floor which slopes downwards and tapers to a smaller cross-section;
(4) contains any other recognized serious safety or health hazard.

Permit spaces must be labelled with appropriate signage. The HSE (1991 Construction Sheet 15) defines a confined space in the following terms:

> A closed equipment with restricted access may be the obvious example of a confined space, but it also includes open manholes, trenches, pipes, flues, ducts, ceiling voids, enclosed rooms such as basements, and other places where there is inadequate natural ventilation.

Open top tanks, furnaces and ovens, even those with a large aperture open to the atmosphere, are confined spaces.

21.7.2 Flammable substances

It is frequently necessary for personnel to enter a equipment or vessel which has contained flammable materials. Before this is done, it is obviously necessary to empty the equipment and to purge and clean it so that flammable materials are no longer present. Despite this, incidents occur in which a flammable atmosphere builds up and is ignited. Other incidents occur in which the flammable residues are ignited when hot work is done.

If a flammable mixture is ignited inside an equipment or vessel, the resultant explosion is likely to destroy it, since even pressure vessels are not generally designed to withstand an explosion. Unburned and burned gases and burning liquid may be expelled and missiles generated from the disintegration of the equipment.

There are several situations which can lead to the existence of a flammable atmosphere in the equipment. One is simply that flammable vapour which was originally present has not been completely removed. Another is that flammable residues remain in the equipment and evaporate. In some cases, the residues are trapped in structural members. In other cases, there may be solid residues which vaporize when heat is applied such as from welding. Another way in which flammable gases may build up again is through isolations which are not leak-tight. In particular, the use of a single closed isolation valve is an unreliable means of isolation and there have been many instances where flammable fluid has entered a equipment through a passing isolation valve. A fourth way is the generation of a flammable gas by chemical reactions, for example the action of water on steel can generate hydrogen.

Liquid residues should be drained, while solid residues should be removed by cleaning. Fluid leakage into equipment should be prevented by positive isolation, as described in Section 21.4.

Prior to entry into equipment, a gas test should be done to confirm that the space is free of flammable gas. In some incidents there has been a failure to free the equipment completely of flammable gas and to test for this. More commonly, however, incidents occur because flammable gas builds up in the equipment atmosphere after it has been checked and found to be free of flammables.

Even if gas tests show the equipment atmosphere to be essentially free of flammables, however, there may still be flammable residues or deposits which can be ignited by hot work. It is necessary, therefore, to check separately for these and to clean them away before hot work is undertaken.

21.7.3 Toxic substances

There is a parallel hazard with toxic substances. The precautions taken to ensure that the equipment atmosphere is free of toxic gas are essentially similar to those taken from flammable substances. The equipment should be emptied, purged, cleaned and tested for the relevant toxic gases. But a toxic atmosphere may still arise from residues remaining in the equipment or from leaks through inadequate isolation.

21.7.4 Hazardous atmospheres

Hazardous atmospheres may expose employees to the risk of death, incapacitation, impairment, injury, or acute illness from one or more of the following causes:

(1) flammable gas, vapour or mist in excess of 10% of its lower flammable limit (LFL);
(2) airborne combustible dust at a concentration that meets or exceeds its LFL;
(3) atmospheric concentration below 19.5% or above 23.5%;
(4) atmospheric concentration of any substance for which a dose or a permissible exposure limit is published and which could result in employee exposure in excess of its dose or permissible exposure limit;
(5) any other atmospheric condition that is immediately dangerous to life or health.

21.7.5 Oxygen-deficient atmospheres

The removal of flammable gas from a equipment is often accomplished by purging with nitrogen. This inert gas is then replaced with air by purging or ventilation so as to give a breathable atmosphere. Incidents occur in which workers are asphyxiated because the atmosphere is deficient in oxygen.

An oxygen-deficient atmosphere may arise in several ways. The original purging or ventilation may be inadequate. Alternatively, the purge may have been conducted inadvertently using nitrogen instead of air. One way in which such inadvertent use of nitrogen in place of air may occur is where the air line has been connected to a nitrogen supply line. Another is the use of a cylinder which is supposed to contain air, but contains some other mixture.

An atmosphere can also be rendered oxygen deficient if there is some process occurring which consumes the oxygen present, such as the rotting of vegetation or the rusting of metal. Oxygen may be adsorbed on steel surfaces, especially where these are damp.

Where the hazard of an oxygen-deficient atmosphere exists, a test of the oxygen content should be done.

Requirements for the oxygen content of breathable air vary. The oxygen content of air at sea level is 21%, but at high altitudes it can fall to 19.5%. The concentration usually quoted to sustain life is 16%. OSHA 1910.146 quotes a minimum of 19.5% oxygen by volume. CS 15 quotes a minimum oxygen concentration of 19%.

21.7.6 Oxygen-enriched atmospheres

In some cases, an oxygen-enriched atmosphere may occur in a confined space. Such an atmosphere is hazardous because it can enhance strongly the flammability of clothing. Oxygen-enriched atmospheres contain more than 23.5% oxygen by volume.

One way in which the atmosphere may become oxygen rich is by leakage of oxygen from an oxygen cylinder used in cutting or welding operations.

Another way is where the atmosphere is originally a mixture of nitrogen and oxygen which is nitrogen rich compared with air and where oxygen has been added in an attempt to raise the concentration to that present in air. This is poor practice because it involves this hazard.

21.7.7 Noxious fumes

There are a number of other ways in which noxious fumes may enter a confined space. One is from processes being carried out in that space. A common source is the fumes arising from welding. Another source is an adjoining space which has not been isolated. Other sources of noxious fumes are sludge and residues and combustion products.

Trenches, tunnels and manholes can fill with carbon dioxide. Other fumes may occur where the ground is contaminated. Where these spaces are connected even temporarily to sewers, the atmosphere may become contaminated with flammable and/or toxic gases or rendered oxygen deficient.

21.7.8 Atmosphere gas tests

Prior to entry into equipment, internal atmospheres shall be tested for oxygen content, flammable gases and vapours and for potential toxic air contaminants. The gas tests which are commonly done are for hydrocarbons, carbon monoxide and hydrogen sulfide and oxygen, together with tests for any toxic substance which has been contained in the equipment.

21.7.9 Air supplies

Measures to ensure that nitrogen is not supplied when it is intended to supply air to render an atmosphere breathable are described by Anon. (1975 LPB 3, p. 8). Incidents have occurred where an air line has been connected to a nitrogen supply, a nitrogen cylinder has been used instead of an air cylinder, and where an air cylinder has contained an oxygen deficient mixture.

There are certain precautions which may be taken to ensure that an air line is not connected in error to a nitrogen supply line. One is to put an identification sign at each nitrogen take-off point. A more positive measure is to ensure that the connections for nitrogen and air lines are different and that their designs are such as to prevent an air line from being connected to a nitrogen line.

Measures should also be taken to ensure that where air is to be supplied from a cylinder, the gas obtained actually is air. A positive means of preventing inadvertent use of a nitrogen cylinder instead of an air cylinder is the provision of different connections on the two types of cylinder, though this is outside the authority of the user company. Otherwise, procedures should be established to avoid identification errors.

Cylinders of breathable air should be analysed at a frequency that is sufficient to ensure the contents meet the specifications.

It is preferable not to use reconstituted air, made by blending nitrogen, oxygen and other gases, for breathing purposes, but if this is done each cylinder should be analysed.

21.7.10 Entry into confined spaces

It will be apparent that entry into a confined space or vessel needs to be governed by procedures which ensure that the hazards are identified and precautions taken. This is accomplished by the permit system, which is now considered. Entry procedures are a prime example of the application of a permit system.

21.8 Permit Systems

Maintenance work on process equipments should be controlled by a formal permit system. Accounts of such systems are given in *Permit Systems* (CAPFTB, 1977 Inf. Pap. 16A), *Guidance on Permit Systems in the Petroleum Industry* (OIAC, 1991) (the OIAC *Permit Systems Guide*) and the IChemE *Maintenance Guide*, and by Kletz (1982f), V.C. Marshall (1986b), S. Scott (1992) and Butler and Bonsall (1993).

21.8.1 Regulatory requirements

US companies use a work permit system to control maintenance activities in process units and entry into equipment. The United Kingdom uses a similar system of permits-to-work (PTWs).

In the United States of America, OSHA 1910.146 Permit Required Confined Spaces defines the requirements for entering in confined spaces. OSHA Process Safety Management Standard 1910.119k addresses hot work permit requirements. The OSHA Occupational Safety and Health Act of 1970 requires safe work places.

In the United Kingdom, there has long been a statutory requirement for a permit system for entry into vessels or confined spaces under the Chemical Works Regulations 1922, Regulation 7. There is no exactly comparable statutory requirement for other activities such as line breaking or welding. The Factories Act 1961, Section 30, which applies more widely, also contains a requirement for certification of entry into vessels and confined spaces. Other sections of the Act which may be relevant in this context are Sections 18, 31 and 34, which deal, respectively, with dangerous substances, hot work and entry to boilers. The requirements of the Health and Safety at Work etc. Act 1974 to provide safe systems of work are also highly relevant.

21.8.2 Objectives of permit system

In essence, the objectives of the permit system are to exercise control over the maintenance activities by assigning responsibilities, ensuring communication between interested functions, and requiring that proper consideration be given to the job, its hazards and the precautions required. More explicitly, the objectives are to ensure that:

(1) there is a system of continuous control of the work to be done;
(2) the persons responsible for overall control of the work and for its execution are identified;
(3) the person responsible for the operation of the equipment is aware of the work;
(4) the other functions with an interest in the work are identified and communications with them are established and maintained;
(5) the work is properly defined;
(6) the work is properly authorized by the person responsible;
(7) the person responsible for the operation of the equipment is aware of what is going on;
(8) the personnel involved in doing the work understand its exact nature and extent, the hazards involved,

any limitations on the extent, and the time allotted for the work;
(9) the isolations and de-isolations required are properly performed;
(10) the precautions to be taken are specified and understood;
(11) the equipment is available and the arrangements are in place to support these precautions;
(12) there is cross-referencing of permits where there is interaction between jobs;
(13) the permits are suitably displayed;
(14) there is a formal handover procedure from operations to maintenance;
(15) there is a formal handback procedure from maintenance to operations;
(16) there is a procedure covering situations where the work extends beyond a single shift;
(17) there is a procedure covering situations where the work has to be suspended;
(18) there is a record showing that the nature of the work and the precautions necessary were checked by the appropriate person(s).

21.8.3 Issuing and performing authorities

It is a principal objective of the permit system to define the responsibilities of all concerned. In the normal system there is an issuing authority and a performing authority. The issuing authority is the operations supervisor. The performing authority is usually the maintenance craftsman who is to do the work, but may sometimes be the maintenance supervisor.

It is the responsibility of the issuing authority to ensure that the equipment is safe for the work to proceed. The performing authority is responsible for ensuring that the further working precautions are taken. In certain cases, such as maintenance work on switchgear, the operations supervisor is not competent to give clearance, and so the maintenance supervisor has a greater degree of responsibility than usual.

It is the responsibility of these same two authorities to terminate the permit. The normal system is that on completion of the work, the performing authority signs that the work is complete and the issuing authority, after inspecting the work site, signs that the permit is complete.

There may be a requirement that in certain defined cases, where work at a particular unit may affect an adjacent unit, the operations supervisor on the latter should countersign the permit.

21.8.4 Types of permit

There is a variety of types of permit, some of which have special names, for example clearance certificates, fire permits, etc. Permits may be classified by reference to the operation to be performed, the equipment to be worked on, the classification of the areas where the work is to be done, the special hazards which may be encountered, the equipment to be used or the time of day specified for the work. A list of typical permits, which illustrates all these categories, is as follows:

Operations
Equipment removal
Excavation
Hot work
Leak sealing
Line breaking
Vessel entry
Waste disposal

Equipment worked on
Electrical equipment
Interplant pipelines
Sprinkler system

Area classification
Flammable area

Special hazards
Corrosive substances
Fire
Toxic substances
Ionizing radiations

Equipment used
Mobile crane

Time of day
After-hours work

A common basic set of permits covers entry, cold work, hot work and electrical work. Some companies use a single permit system to cover all work activities. The IP *Refining Safety Code* gives model permit forms for the following: general work, electrical work, hot work and work involving ionizing radiations; line disconnecting and vessel opening; entry; and excavation.

21.8.5 Permits for isolation

Isolation before a job and de-isolation after it should be treated as separate activities in their own right. Thus, for a job which requires isolation there may be permits for (1) isolation, (2) the main job and (3) de-isolation.

Some equipment is isolated and de-isolated solely by operations. Operations work is typically not permitted, so the only permit required would be for the maintenance work. Some systems cover the entire job from isolation to de-isolation using a single permit.

21.8.6 Contents of permit

The contents of a permit need to be carefully defined. Accounts of permit contents are given in the OIAC *Permit Systems Guide*, the IChemE *Maintenance Guide* and by S. Scott (1992). Such accounts usually distinguish between features which are essential and those which are desirable. The essential features of a permit are:

(1) company name and address;
(2) permit title;
(3) permit number;
(4) period of validity;
(5) location of work (unit, equipment);
(6) description of work;
(7) isolation;
(8) hazard identification;
(9) precautions required;
(10) protective equipment required;
(11) authorization;
(12) expansion;
(13) handback;
(14) cancellation.

The period of validity, in terms of the date, start time and end time, should be entered, as an elementary requirement

for control. The location of the work should be specified in terms of the unit, area or building and vessel or equipment. Proper titles should be used, not informal names. The equipment may be identified by an identification tag/name and this should be cross-referenced on the permit. The description of the work should state the work to be done, the reason for it and the method to be used and any limitations on the extent of the work. There should be confirmation that the isolation required has been accomplished. The potential hazards should be identified. In some cases these may be partially covered by a checklist of actions to be taken such as depressurization, cleaning, etc., in which case it is the residual hazards which are entered. The precautions already taken and those still to be taken should be stated. The protective clothing and equipment to be used should be specified. The issuing authority should sign that the work is authorized to start and the performing authority should sign that the permit is accepted. On completion, the performing authority should sign to indicate that the work is complete and the issuing authority should sign to show that the permit is completed.

Particular types of permit require additional features. For example, a hot work permit should contain an entry for the hazardous area classification of the location of the work and gas test results.

The IChemE *Maintenance Guide* gives a number of additional desirable features. It is desirable to include a caution to the effect that the permit is a legal document; a caution to the issuing authority that, although work may be delegated, responsibility remains with them; an indication of the levels of hazard, so that high hazard situations are highlighted and those involved are prompted to consider whether there are other parties who should be consulted; an indication of work progress, so that cases are identified where the work is tending to expand beyond that originally envisaged and those involved are prompted to reappraise it.

21.8.7 Design of permit forms

Sample permit forms are given in a number of publications, including the IP *Refining Safety Code*, the IP *LPG Code* and the IChemE *Maintenance Guide*.

A typical permit, referred to by the company concerned as a clearance certificate, is shown in Figure 21.3. This permit dates from 1977, but still provides a clear illustration of many of the basic principles.

Figure 21.4 shows the typical entry permit given in the IChemE *Maintenance Guide*.

21.8.8 Entry permits

Entry into vessels and other confined spaces has resulted in numerous accidents. As a result this operation has had a unique status.

OSHA 1910.146 defines entry permit requirements. The entry permit identifies:

(1) permit space to be entered;
(2) purpose of entry;
(3) date and authorized duration of the entry permit;
(4) authorized entrants by name;
(5) personnel, by name, serving as attendants;
(6) individual, by name, currently serving as entry supervisor;
(7) hazards of permit space to be entered;
(8) measures used to isolate the permit space and to eliminate or control permit space hazards before entry;
(9) acceptable entry conditions;
(10) results of initial and periodic gas tests;
(11) rescue and emergency services that can be summoned and the means for summoning those services;
(12) communication procedures used by authorized entrants and attendants to maintain contact during the entry;
(13) equipment such as personal protective equipment, testing equipment, communications equipment, alarm systems and rescue equipment to be provided;
(14) any other information necessary to ensure employee safety;
(15) any additional permits such as hot work that have been issued to authorize work in permit spaces.

Vessel and confined space entry have a specific legal requirement for a permit system. This requirement is given in the Chemical Works Regulations 1922, Regulation 7, now superseded, and in the Factories Act, Section 30. It is appropriate, therefore, to describe this permit in some detail as an illustration. In order to avoid repetition it is also convenient to describe here the associated hazards and procedures.

Entry permits are dealt with in *Safety and Management* (ABCM, 1964/3), *Permit Systems* (CAPFTB, 1977 Inf. Pap. 16A) and by Kletz (1982f). Early HSE guidance was given in TON 47 *Entry into Confined Spaces: Hazards and Precautions* (HSE, 1975) and GS 5 *Entry into Confined Spaces* (HSE, 1977) and current guidance in Construction Sheet 15 *Confined Spaces* (HSE, 1991). The hazards of work in a vessel or confined space are described in Section 21.7.

A significant proportion of accidents in vessels or confined spaces are fatal and some involve multiple deaths. OSHA 1910.146 and The Factories Act 1961, Section 30, describes precautions which have to be taken where work has to be done inside equipment in which the atmosphere is liable to be such as to involve the risk of people being overcome by dangerous fumes or lack of oxygen.

The requirements of the Act are summarized in TON 47 for atmospheres in which dangerous fumes are liable to be present:

> No-one may enter or remain for any purpose in a confined space which has at any time contained or is likely to contain fumes liable to cause a person to be overcome unless

(1) He is wearing a suitable breathing apparatus.
(2) He has been authorized to enter by a responsible person.
(3) Where practicable, he is wearing a belt with a rope securely attached.
(4) A person keeping watch outside and capable of pulling him out is holding the free end of the rope.

Alternatively, a person may enter or work in a confined space without breathing apparatus provided that

(1) Effective steps have been taken to avoid ingress of dangerous fumes.
(2) Sludge or other deposits liable to give off dangerous fumes have been removed.
(3) The space contains no other material liable to give off such fumes.

WILTON WORKS – CLEARANCE CERTIFICATE

PROCEDURES USED SHALL BE IN ACCORDANCE WITH THE LOCAL WORKS GENERAL INSTRUCTIONS
AT THE REQUEST OF ANY MAN WORKING ON THE JOB A COPY OF THIS CLEARANCE CERTIFICATE MUST BE SHOWN TO HIM

PLANT: **SECTION OR EQUIPMENT:** **VALID UNTIL: DATE** **TIME** Serial **Nº**

PART A PREPARATION

A 1 WHILE DOING THE JOBS DETAILED IN B.1 THE FOLLOWING HAZARDS MAY BE MET

Strike out those for which there will be no hazard specific to the job when preparation is complete

Gas, Fume	Electricity
Corrosive hot and other liquids	Moving Machinery
Gas or liquid under pressure	Overhead Cranes
Fire and explosion	Traffic (Road and Rail)
Hot metal	Radioactive substances
Steam	Asbestos
Noise	Other jobs nearby

Add other hazards .....

A 2 PHYSICAL ISOLATION (other than electrical)

Strike out TWO Statements

Physical isolation is NOT APPLICABLE
The place, equipment, etc is NOT ISOLATED
The place, equipment, etc is ISOLATED

METHOD OF ISOLATION delete as appropriate
SINGLE/DOUBLE ISOLATION VALVE CLOSED AND LOCKED OFF
LINES SLIP PLATED
PHYSICAL DISCONNECTION - OPEN END BLANKED OFF
VENT, DRAIN OR BLOW OFF OPEN
Other Methods .....

A 3 PRECAUTIONS ALREADY TAKEN .....

A 4 FIRE PERMIT

Strike out ONE Statement

A fire permit is NOT NECESSARY
A fire permit is NECESSARY Permit Issued No .....
Further Permits can be noted on the back of the Clearance

A 5 FACTORIES ACT 1961, Section 30, and CHEMICAL WORKS REGULATION 7

Strike out ONE Statement

DO NOT APPLY
DO APPLY – I have seen the Signature of the responsible person on Certificate No .....
Further Entry Certificates can be noted on the back of the Clearance.

A 6 INSTALLED RADIOACTIVE SOURCES

Strike out as Necessary

There is NO INSTALLED RADIOACTIVE SOURCE
There is AN INSTALLED RADIOACTIVE SOURCE and the Safety Instruction for the installation
DOES NOT REQUIRE
DOES REQUIRE
the authority of the qualified person before work is done

I have made the installation safe for the duration of the Clearance Certificate by .....

Signature of qualified person .....

A 7 ELECTRICAL ISOLATION

Strike out TWO Statements

Electrical isolation is NOT APPLICABLE
Electrical equipment is NOT ISOLATED
Electrical equipment is ISOLATED and I have tested the isolation.
Method of isolation .....

High Voltage Permit to Work Card No .....

Signature .....

A 8 PREPARATION COMPLETE

Signature .....

PART B OPERATION

B 1 JOBS TO BE DONE — Tag Nos.

Equipment Rotation Check: NECESSARY / NOT NECESSARY
(To be carried out in accordance with Plant Instructions)

B 2 PRECAUTIONS TO BE TAKEN AND WHY

(Strike out those printed precautions not required, enter others in the space provided)

PROTECTIVE CLOTHING – EQUIPMENT

Wear P.V.C. Suit	Wear full face shield
Wear P.V.C. Gloves	Wear goggles
Wear ear protection (State type)	Beware Trapped Pressure – Wear Gloves and Goggles for first break in

OTHER PRECAUTIONS THAT RELATE TO THE HAZARDS IN A.1

Beware trapped pressure — Beware hot metal

PART C TRANSFER AND ACCEPTANCE OF RESPONSIBILITY

THIS CERTIFICATE IS ONLY VALID WHEN ALL SECTIONS (A1 TO C1 INCLUSIVE) HAVE BEEN COMPLETED

C.1 HANDED OVER — Name (Printed) — Signed or Initialled — Date – Time

By .....
To .....

C.2 ENDORSEMENT BY ENGINEERING SERVICES (WILTON) LIMITED OR OTHER TRADES OR CONTRACTORS

	(1)	(2)	(3)	(4)
Signing On				
Trade				
Name (Printed)				
Signed or Initialled				
Tel. No.				
Date				

(Where daily endorsements required use the back of this Clearance Certificate)

Signing Off				
Name (Printed)				
Signed or Initialled				
Date				

C.3 COMPLETION OF JOB

Strike out ONE Statement

THE JOB IS COMPLETE
THE JOB IS INCOMPLETE and a further Clearance Certificate is required for the following work:

.....

HANDED BACK Signatures By ..... Date .....
To ..... Time .....

C.4 INSTALLED RADIOACTIVE SOURCES *(Delete if not applicable)*

I have recommissioned the installation in accordance with the Safety Instruction.

Signature of qualified person .....

C.5 ELECTRICITY MADE AVAILABLE *(Delete if not applicable)*

Method ..... Date .....
Signature ..... Time .....

C.6 EQUIPMENT ROTATION CHECK *(Delete if not applicable)*

Strike out ONE Statement

DIRECTION IS INCORRECT
DIRECTION IS CORRECT
Signed .....

C.7 FACTORIES ACT 1961, Section 30, and CHEMICAL WORKS REGULATION 7

If these apply, the following declaration is to be completed by the person taking back the plant. I have notified Mr. ..... the person responsible for Entry Certificate No ..... that this clearance certificate has been withdrawn.

Signature ..... Date .....

Figure 21.3 *Clearance certificate (Imperial Chemical Industries Ltd, 1977; reproduced by permission)*

XY CHEMICALS ENTRY PERMIT Serial . . . . . .

DATE AND TIME OF INITIAL 8 HOUR PERIOD — From . . . . . To . . . . . Work site . . . . .

EQUIPMENT NAME/NUMBER . . . . . .

DESCRIPTION OF WORK . . . . . .

MARK: Required ✗ Checked ✓	Yes	No	Ch'kd
A. Has equipment to be:			
1 Depressured			
2 Drained			
3 Isolated by			
blanking? blank list No.			
disconnecting?			
valving?			
4 Steamed?			
5 Waterflushed?			
6 Purged with inert gas?			
7 Ventilated by natural/			
mechanical means?			
8 Neutralised?			
B. 1 Are sewers, drains etc			
within 50 ft of worksite			
sealed			
2 Is site clear of combustible			
materials?			

MARK: Required ✗ Checked ✓	Yes	No	Ch'kd
3 Is fire protection sited?			
4 Is suitable access and exit			
provided?			
5 Are stand-by personnel			
required?			
6 Are lifelines, harness and			
breathing apparatus required?			
7 Is air compressor sited			
correctly?			
8 Neutralizing solution on			
9 HF F/Aid kit available			
C. Excavations:			
1 Are sides safely stored?			
2 Is a barrier erected?			
D. 1 Have repeat gas/toxic/			
oxygen tests to be made?			

AUTHORITY GRANTED TO ISOLATE . . . . . Issuing authority . . . . . Time . . . . . Date . . . . .

EQUIPMENT ISOLATED . . . . . Electrical section . . . . . Time . . . . . Date . . . . .

PROTECTIVE CLOTHING TO BE WORN: indicate by 'X' (OPERATING AUTHORITY)

☐ Full protective clothing ☐ Face shield ☐ Goggles ☐ TEL clothing ☐ PVC

☐ Dust mask ☐ Air-line BA ☐ Self-contained BA ☐ Ear protection

ALKYLATION UNIT

☐ Acid area clothing ☐ Air fed hood ☐ Air fed suit

SPECIAL INSTRUCTIONS . . . . . .

GAS TEST RESULTS	*Combustible/toxic/oxygen Date/time	Result	Signature	*Combustible/toxic/oxygen Date/time	Result	Signature
Initial check						
Re-check						
Re-check						
Re-check						
Re-check						
Re-check						
Re-check						

*Delete when not applicable

SITE PREPARATION IS COMPLETE — Permission is granted for work to commence.

To be signed by issuing authority	Initial check	Date/time	Re-check	Date/time	Re-check	Date/time

I am aware that this work is in progress and that conditions are as above.

To be signed by operator in charge	Initial check	Date/time	Re-check	Date/time	Re-check	Date/time

PERFORMING AUTHORITY INSTRUCTIONS: . . . . . .

I understand the precautions to be taken and have instructed the person/persons carrying out the work accordingly.

To be signed by operator in charge	Initial check	Date/time	Re-check	Date/time	Re-check	Date/time

	Time	Date	Signed
Work completed			
Electrical supply returned to equipment			Performing authority / Electrical section

Figure 21.4 *Entry permit (Townsend, 1992) (Courtesy of the Institution of Chemical Engineers)*

(4) The space has been adequately ventilated and tested for fumes.
(5) There is a supply of air adequate for respiration.
(6) The space has been certified by a responsible person as being safe for entry for a specified period without breathing apparatus.

The person who enters the confined space must be warned when the safe period specified in (6) above will expire. In all cases a sufficient supply of approved breathing apparatus, belts and ropes, and suitable reviving apparatus and oxygen must be kept readily available, properly maintained and regularly examined.

The requirements for oxygen-deficient atmospheres are summarized in TON 47 as follows:

> No-one may enter or remain in a confined space in which the atmosphere is liable to be deficient in oxygen unless either he is wearing a suitable breathing apparatus, or the space has been and remains adequately ventilated and a responsible person has tested and certified it as safe for entry without breathing apparatus.

The same section of the Act also requires confined spaces to be provided with manholes and specifies minimum dimensions. Circular manholes, for example, should not be less than 18 in. in diameter or, on tank wagons and mobile plant, 16 in. in diameter. Manholes larger than these minimum sizes should be provided wherever possible. In particular, practical tests have shown the minimum size on mobile equipment to be barely negotiable by men of average build.

The control of work in vessels and confined spaces is described in TON 47, which lists the following features:

(1) assessment;
(2) withdrawal from service;
(3) isolation;
(4) cleaning and purging;
(5) testing;
(6) certification;
(7) precautions during work
  (a) entry without breathing apparatus,
  (b) entry where breathing apparatus is necessary,
  (c) rescue;
(8) cancellation of permit;
(9) return to service.

The issuance of the permit should be done by the responsible person in accordance with the procedures described in Section 21.8.3. The issuing authority should have a sufficient familiarity with both the chemistry and the engineering aspects of the situation and should check personally the actions required.

The need for entry should be considered carefully and entry should not be made unless it is essential. The hazards of vessel entry should be reviewed, paying particular attention to any hazard arising from nearby plant and to any special circumstances or precautions.

Withdrawal from service should be a formal procedure. Operating personnel should be informed and warning notices displayed.

The isolation of the vessel should be completed in accordance with the procedures described in Section 21.4. The recommended method of isolation for vessel entry is physical disconnection. A closed and locked valve is not an adequate method.

If there is machinery inside the vessel, such as an agitator or mixer, it should be isolated by electrical isolation or by physical disconnection. In addition, if necessary, it should be secured to prevent its moving. There may also be pumps which should be isolated electrically. The vessel should then be emptied.

Cleaning of the vessel may be accomplished in several ways. Steaming out is a common method. This may be preceded by washing with water, solvent or neutralizing agent. The steaming itself should be continued long enough to clean the vessel thoroughly. The steaming time is often determined by experience, but it is essential to continue steaming until the vessel is clean rather than simply for a predetermined time. It is important to ensure that equipment attached to the main vessel is also cleaned thoroughly. The period of steaming and the completion of steaming should be checked by the responsible person. If several hours elapse after steaming, it is advisable to steam the vessel again immediately before entry. It should be ensured that the steaming is done safely and without either overpressuring the vessel with steam or causing it to collapse under the vacuum created by steam condensation.

Other cleaning methods include thorough washing with cold or hot water or with solvents or neutralizing agents and boiling with water. Some cleaning agents such as solvents can create a secondary hazard and may need to be removed by steaming. Boiling water cleaning requires precautions against overpressure and vacuum collapse of the vessel.

It is sometimes necessary to resort to hand cleaning to remove sludge and residues. In such cases, it is essential to work with the full precautions of breathing apparatus, a safety line, and rescue equipment and personnel.

On the completion of cleaning all liquid should be run out and the manholes opened for ventilation. If steam cleaning has been used, opening of the manholes while the vessel is hot assists air circulation by natural convection. It may be necessary, however, to use forced ventilation from a blower or compressed air line.

If the vessel is hot, it should be allowed to cool before any entry is made.

If the vessel has contained a flammable gas or vapour, it may be purged with an inert gas such as nitrogen or carbon dioxide. This then creates, however, an asphyxiation hazard. It is thus necessary to purge the inert gas with air.

Testing of the atmosphere in the vessel must be carried out before it is certified as safe to enter or before the safety precautions for entry are specified. The tests should check the presence of toxic and/or flammable fumes and, if necessary, the adequacy of the oxygen content. The tests should be conducted by a competent person. If the work is at all prolonged, the tests should be repeated. Continuous gas testing may be required throughout the work and must be noted on the permit.

The general testing of working atmospheres is dealt with in Chapter 25 and is therefore not considered here. As far as testing in vessels is concerned, entry into the vessel should be avoided if possible. Instead, samples should be drawn from inside the vessel through sample tubes. It is essential, however, to test throughout the vapour space; factors which may cause this not to be homogeneous include release of fumes from sludge or residues and layering of inert gases.

If entry into a vessel for testing is unavoidable, this should be done with breathing apparatus, a safety line, and rescue equipment and personnel.

With regard to the permissible concentration of toxic materials, it has been common practice for many years to use the threshold limit value (TLV).

When the above stages have been completed, the responsible person can decide on the precautions to be taken on entry and, in particular, whether (1) entry is safe for a specified period without breathing apparatus or (2) entry requires breathing apparatus, a safety line and other precautions.

The permit can then be issued detailing the safety measures already taken (e.g. isolation, cleaning and purging, testing), those to be taken (e.g. ventilation, repeat testing, breathing apparatus, a safety line, and rescue equipment and personnel) and the period of validity.

Precautions during the work depend on whether the method of entry involves the use of breathing apparatus or not. If breathing apparatus is not used, good ventilation is essential. This means at least several changes of air per minute. If there are sufficient top and bottom openings, natural ventilation may suffice, but more usually forced ventilation is necessary using compressed air or blowers. The air line or blower piping should extend to the bottom of the vessel to assure the removal of heavy fumes and give good air circulation. If there is a static electricity hazard, it may be necessary to bond the air line or piping to the metal of the vessel. Gaseous oxygen should not be introduced into the vessel to increase the oxygen content of the atmosphere, since it creates the hazard of an oxygen-enriched atmosphere.

If breathing apparatus has to be used, it should be either the self-contained breathing apparatus type or the air line type. Canister respirators should not be used, because they do not provide adequate protection against high concentrations of toxic flumes and are useless in atmospheres deficient in oxygen.

The person entering the vessel should also wear a safety harness and lifeline wherever practical. The free end of the line should be held by a person outside. The harness should be worn so that the worker can be pulled head first up through the opening.

It is the duty of the person outside, or safety watch, to keep hold of the safety line and observe the person working inside the vessel. They should have a means of summoning assistance rapidly. If possible, there should also be other workers nearby.

If the person in the vessel is overcome, the safety watch should raise him head first through the opening. An unconscious man is a heavy weight and the safety watch should have both adequate strength and training for his task.

There should be rescue equipment, such as additional breathing apparatus and safety lines and reviving equipment and medical oxygen.

The restrictions on entry apply also to entry for rescue. In addition, if entry has been permitted without breathing apparatus and the person inside has been overcome, entry for rescue should be made only wearing breathing apparatus and a safety line and with other personnel available to give assistance. Multiple fatalities have occurred where men have gone in to rescue their fellows without proper protection.

When the work is finished, the equipment used should be removed, the work site should be inspected and the permit completed in accordance with the procedures given in Section 21.8.3.

Personnel should be warned that the vessel is no longer safe for entry. Accidents occur due to persons entering vessels which are no longer safe in order to recover tools, etc.

The de-isolation of the vessel should be done in accordance with the procedures described earlier and the vessel returned to service.

21.8.9 Types of permit system

The normal permit system is a single permit issued by the issuing authority to the performing authority. As stated earlier, the norm is that the issuing authority is the operations supervisor and the performing authority the person who is to do the work, but in some cases the performing authority is the maintenance supervisor.

There are, however, variations on this system. In some companies, certain permits are issued by the safety officer.

In a particular permit system, a given job may require more than one document. There may well be other certificates which are necessary before the main permit can be issued. One example is an isolation permit, in a system where separate permits are used for isolation, and de-isolation. Another is a test certificate for analysis of the working atmosphere.

Some types of permit relate to higher levels of hazard than others, so that there can be a hierarchy of permits.

21.8.10 Design of permit systems

The effectiveness of a permit system depends in large part on the way in which the system is designed and operated.

Aspects of the design of a permit system include (1) standardization, (2) the personnel involved, (3) scope, (4) cross-referencing, (5) display, (6) multiple jobs, (7) change of intent, (8) suspension, (9) handback, (10) training and (11) monitoring, auditing and review.

It is desirable that the permit system used within a company be as uniform as is practicable. This applies not just to the design of permit forms but to the whole system. A standard system eases the problem of training and reduces the probability of confusion and hence error.

There are constraints, however, on complete standardization. A permit system is a means of communication between the interested parties and must, therefore, reflect the organizational structure. It is also a formalization of the operating and maintenance procedures. While uniformity is desirable, a mismatch between the permit system and either this structure or the procedures is too high a price to pay, in that it is likely to undermine acceptance of the permit system and hence compliance with it.

The personnel involved in the issue of a permit should be identified. In some systems, the number may be quite large, perhaps as high as 15–20.

There may be a requirement that in certain defined cases, where work at a particular unit may affect an adjacent unit, the operations supervisor on that unit should countersign the permit.

The permit should ensure that the scope of the work to be done is fully defined.

The design of the permit form should allow for the necessary cross-referencing. There should be cross-references to: other jobs, by description of job as well as permit number; isolations and the associated permit numbers; and equipment identification tags. In particular,

the cross-referencing should cover the case where isolation is common to more than one job.

A copy of the permit should be clearly displayed in the control room.

Another copy should be displayed at the work site, except when the job is done at a number of locations, in which case it should be kept by the person in immediate charge of the work. If this person is not also the performing authority, the latter should also have a copy.

For given equipment, there should be only one permit, but it may cover work by more than one trade.

Sometimes there is a change of intent while the job is being done. An example is a change from work on pump seal flush lines which does not involve breaking into the process line, to a pump overhaul which does. If such a change of intention occurs, a separate permit may be issued.

It may well happen that it is necessary to suspend the work. This can occur because: work is carried out only for one shift each day; spares are on order; the activity is incompatible with another which has higher priority, as with suspension of hot work while a flammable gas sample is taken; or there is an emergency.

One option is that the permit is cancelled so that resumption of the work requires a new permit. This may well be the best policy if the work is being suspended for an undefined and possibly extended period and the equipment can be rendered safe. Alternatively, the permit itself may be suspended. If this option is taken, the permit should be clearly displayed in a suitable place and clearly marked as suspended; the condition in which the equipment has been left and the consequences for other activities should be stated; and prior to reactivation the issuing authority should verify that it is safe for the work to proceed. The OIAC *Permit System Guide* gives further guidance on the procedures for the suspension of a permit.

A suspended permit was at the centre of the events which led to the Piper Alpha disaster and the view was then urged that the suspension of a permit should not be an option. The Inquiry recognized the dangers but did not recommend prohibition.

The procedures for handback of the permit, described earlier, should be clear.

The permit system should ensure that both operations and maintenance personnel, company employees as well as contractors are trained in the system which applies at the actual plant where they work. It is not enough to have instruction in the general principles of a permit system; personnel must be clear about the details of the operation, and the reasons for, the particular permit system governing their own work.

There should be built into the permit system arrangements to ensure that the operation of the system is monitored regularly and is subject to a more searching audit at specified intervals, and that a review of the appropriateness of the system is undertaken at specified, longer intervals.

21.8.11 Operation of permit systems

If the permit has been well designed, the operation of the system is largely a matter of compliance. If this is not the case, the operations function is obliged to develop solutions to problems as they arise.

As just stated, personnel should be fully trained so that they have an understanding of the reasons for, as well as the application of the system.

It is the responsibility of management to ensure that the conditions exist for the permit system to be operated properly. An excessive workload on the plant, with numerous modifications or extensions being made simultaneously, can overload the system. The issuing authority must have the time necessary to discharge his responsibilities for each permit.

In particular, he has a responsibility to ensure that it is safe for maintenance to begin and to visit the work site on completion to ensure that it is safe to restart operation.

Where the workload is heavy, the policy is sometimes adopted of assigning an additional supervisor to deal with some of the permits. However, a permit system is in large part a communication system, and this practice introduces into the system an additional interface.

The communications in the permit system should be verbal as well as written. The issuing authority should discuss, and should be given the opporutnity to discuss, the work. It is bad practice to leave a permit to be picked up by the performing authority without discussion.

The issuing authority has the responsibility of enforcing compliance with the permit system. He needs to be watchful for violations such as extensions of work beyong the original scope.

21.8.12 Deficiencies of permit systems

An account of deficiencies in permit systems found in industry is given by S. Scott (1992). As already stated, some 30% of accidents in the chemical industry involve maintenance and of these some 20% relate to permit systems.

The author gives statistics of the deficiencies found. Broadly, some 30–40% of the systems investigated were considered to be deficient in respect to system design, form design, appropriate application, appropriate authorization, staff training, work identification, hazard identification, isolation procedures, protective equipment, time limitations, shift change procedure and handback procedure, while as many as 60% were deficient in system monitoring.

21.8.13 Audit of permit systems

It is not enough to create a permit system to control maintenance work. There should also be a routine audit of the system to ensure that it is operating properly. These may consist of a specific instruction to the plant manager to check each week a portion of the permits issued.

21.8.14 Checklist for permit systems

The OIAC *Permit Systems Guide* gives a checklist for permit systems. This is shown in Table 21.3.

21.9 Maintenance Equipment

21.9.1 Tools

Tools such as hammers and wrenches have been considered a possible source of ignition, and so-called non-sparking tools have been developed. Materials used in such tools are, typically: aluminium, bronze or monel, for tools that have to withstand impact or torque such as hammers, wrenches and crowbars; copper–beryllium alloy, for tools requiring a cutting edge or gripping teeth such as knives, chisels, saws, drills, pliers and shears; and plastics, leather, fibre and wood, for shovel and scraper tools.

These tools have a number of disadvantages. Generally, they are more expensive and they are softer and tend to burr. Moreover, particles can more easily become

Table 21.3 *A checklist for permit-to-work systems (Oil Industry Advisory Committee, 1991) (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

The purpose of this checklist is to help everyone concerned with the preparation of permit-to-work systems to decide whether a particular example covers all the points which are considered essential. If the answer to any of the questions below is 'no', the system may need to be reconsidered and changed.

The system

1. Does the permit system in force satisfy all the legal requirements applying to that site or installation?
2. Is the permit system recognized throughout the site or installation as being essential for certain types of work?
3. Are the types of work, types of job or areas where permits must be used clearly defined and known to all concerned?
4. Does the permit system extend to contractors and their employees?
5. Is it clearly laid down who may issue permits?
6. Is it clearly laid down how permits should be obtained for specific jobs?
7. Is the permit system flexible enough to allow it to be applied to other potentially hazardous work, apart from that which may have been specifically identified when the system was established?
8. Is the issue of a permit by a person to themselves prevented?
9. Does the system provide both for the recipient to retain the permit and for a record of live permits and suspended permits to be maintained at the point of issue?
10. Does the system require a copy of the permit to be displayed at the workplace?
11. Does the system require the display of live and suspended permits so that process operating staff can readily see and check plant status?
12. Is there a set of properly documented isolation procedures for working on potentially dangerous items of plant and does it provide for long term isolation?

Training and competence

13. Is the permit system clearly covered during site or installation safety induction training?
14. Are personnel who have special responsibilities under the permit system, e.g. issuing and isolating authorities, properly authorized and trained to undertake the duties required of them?
15. Do these people have sufficient time to carry out these duties properly?
16. Does the system require formal assessment of competence of personnel before they are given responsibilities under the permit procedure?
17. Is a record of training and assessment maintained?
18. Do training and competence requirements include contractors?
19. Are individuals provided with written confirmation of successful completion of relevant training and are these documents checked before appointments are made within the permit-to-work system?

The permit

20. Is there a clear requirement for work being done under a permit to be stopped if any new hazards have arisen or old hazards recurred?
21. Does the permit contain clear rules about how the job should be controlled or abandoned in the event of an emergency?
22. Do permits specify clearly the job to be done?
23. Do permits specify clearly to whom they are issued?
24. Does the system require the potential hazards at the work site to be clearly identified and recorded on the permit?
25. Does the permit clearly specify the precautions to be taken by the issuing and performing authorities?
26. Do permits specify clearly the plant or geographical area to which work must he limited?
27. Does the recipient have to sign the permit to show that they both read the permit and understood the conditions laid down in it?
28. Do permits specify clearly a time limit for expiry or renewal?
29. Does the permit include a handover mechanism for work which extends beyond a shift or other work period including work which has been suspended?
30. Is a handback signature required when the job is complete?
31. Is there a procedure to bring to the attention of the site manager tasks which require inhibiting safety devices, e.g. fire detectors, to ensure that contingency plans and precautions are in place?

Co-ordination

32. Are copies of permits issued for the same equipment/area kept and displayed together?
33. Is there a means of co-ordinating all work activities to ensure potential interactions are identified?
34. Is there provision on the permit form to cross-reference other relevant certificates and permits?
35. Is there a procedure to ensure that the agreement of others who could be affected by the proposed work is obtained before starting the work or preparations for it?
36. Where there are isolations common to more than one permit, is there a procedure to prevent the isolation being removed before all the permits have been signed off?

Monitoring

37. Is there a system of spot checks to ensure that permits are being followed?
38. Is there a procedure for reporting any incidents that have arisen during work carried out under a permit and for reviewing procedures as necessary?
39. Are audits carried out on the permit-to-work system at least once a year, preferably by people not normally employed at that site or offshore installation?

embedded in them, thus reducing their non-sparking qualities.

The American Petroleum Institute (API) has issued a number of reports over a period of years on the appropriateness of using non-sparking tools in petroleum operations. The general conclusion is that an incendive spark of steel would be unlikely to be produced manually and that power operation would be needed. Its current position is stated in API Publ. 2214: 1989:

> The Institute's position is that the use of special non-ferrous hand tools, sometimes referred to as nonsparking tools, is not warranted as a fire-prevention measure applicable to petroleum operations.

Certain gases handled in the chemical industry are particularly susceptible to spark ignition, notably hydrogen, acetylene, ethylene and carbon disulfide. One policy described on non-sparking tools in this industry is that instead of utilizing all types of non-sparking tool in flammable areas a more limited use is made, restricting their application to the use of non-sparking hammers (though not wrenches) for the hardening up of joints on lines containing the above four gases.

The extent to which tools may act as ignition sources is discussed in more detail in Chapter 16.

21.9.2 Lifting equipment

Lifting equipment has been the cause of numerous accidents. There have long been statutory requirements, therefore, for the registration and regular inspection of equipment such as chains, slings and ropes. Extreme care should be taken with handling and storage of lifting equipment to prevent damage. It should never be modified and repair work should be performed by manufacturer or qualified personnel.

The rated capacity of lifting equipment must never be exceeded. Charts are available from the manufacturer, published standards and numerous professional organizations. Before each use, lifting equipment should be examined and verified that it is capable of handling its intended function.

Lifting equipment is governed by OSHA 1910.184 Slings and 1926.251 Construction Rigging Equipment. UK requirements are given in the Factories Act 1961, Sections 22–27, and in the associated legislation, including the Chains, Ropes and Lifting Tackle (Register) Order 1938, the Construction (Lifting Operations) Regulations 1961 and the Lifting Machines (Particulars of Examination) Order 1963. Some of these regulations are superseded by the consolidating Provision and Use of Work Equipment Regulations 1992.

In process plant work incidents sometimes occur in which a lifting lug gives way. This may be due to causes such as incorrect design or previous overstressing. Ultrasonic testing or X-ray of lifting lugs may be necessary if there is concern over its integrity.

21.9.3 Lift plans/permits

Critical or major lifts should have a detailed lift plan prepared. This includes detailed drawings of the lift and swing, calculations on lifting equipment and crane(s), certification of lifting equipment, review of matting and ground conditions (surface and underground) as well as potential hazards.

The use of lift permits is required by some companies. This requirement documents the lift to be made and enables a review by the appropriate personnel.

21.9.4 Mobile cranes

Mobile cranes present several different types of hazard. One is that of collision with process equipment, particularly pipe racks, when the crane is on the move. A minimum measure to prevent this is clear identification of pipe racks including labelling with clearance height. A spotter should be used to walk mobile equipment when it is being moved. A positive protection is the installation of a crossbeam in front of the pipe rack.

Another type of hazard is the overloading or overturning of the crane onto process equipment. Each crane must have a capacity chart for lifting over the rear and over the side either posted on the crane or available in the cab. For a given crane, there is a maximum safe load and maximum safe radius. There is normally a safe load indicator, but nothing to indicate the safe radius. If either is exceeded, the potential for an incident exists. If the radius is exceeded, the crane may topple. Numerous crane failures are in the literature. It is equally important that personnel performing the rigging and lifting are trained in determining capacity of lifting equipment and cranes. They also must know proper set-up and limitations of lifting. It is important for crane drivers to be well trained in the operation and limitations of their cranes and in the special hazards of process equipment.

Another hazard with crane operation is overhead electrical lines. A minimum 10 ft separation distance is required. Additional guidance is provided in OSHA 1910.333. A rather less obvious hazard in cranes hired from outside contractors is the use of cab heaters which are not suitable for hazardous areas. A heater is needed, but it should be of an appropriate type.

Regulatory reference is OSHA 1910.180 Crawler Locomotive and Truck Cranes, 1926 (Construction) Subpart N, O and 1926.952.

21.9.5 Lift trucks

Lift trucks, including forklifts, present another set of hazards. One is the hazard due to any moving vehicle, especially in a relatively congested plant area. A specific aspect of this is impact on equipment. Incidents are numerous in which lift trucks are driven into and damage buildings and equipment; pipe racks are particularly at risk. Impact is more likely if the truck is travelling with arms extended. A lift truck may also run over and crush pipe or cabling.

Overturning is another hazard, the causes of which include misleading, sudden braking or sharp turning and traversing of rough or sloping terrain.

Personnel operating lift trucks should be well trained in the operation and limitations of their cranes and in the special hazards of process equipment.

A lift truck is a vehicle with projecting and moving parts. It, therefore, has some of the characteristics of a machine. The power source, batteries or engine, on a lift truck may act as a source of ignition.

Guidance on lift trucks is given in OSHA 1910.178 Powered Industrial Trucks, HS(G) 6 Safety in Working with Lift Trucks (HSE, 1992). HS(G) 6 states that lift trucks are responsible for about one-third of the 20,000 reportable injuries each year which involve transport. In the period 1986–1991, 112 people were killed in accidents involving lift trucks.

Prevention of lift truck accidents requires attention to (1) equipment layout, (2) working practices and (3) training.

Specific preventive measures fall mainly under the following headings: (1) traffic, (2) imbalance, (3) impact and crushing and (4) moving parts.

Measures which address the traffic aspects include the layout of the lift truck workplace, use of driving practices which specifically address lift truck dangers, limitation of driving to trained personnel, avoidance of obscuration of the driver's view by the load and removal of people from the vicinity of the truck, using both segregation and warning devices. Prevention of imbalance requires the application of loading rules and avoidance of unsuitable terrain. Measures to prevent impact include use of layout and barriers and travelling with lift arms lowered. The danger from working parts may also be minimized by suitable layout and working practices.

21.9.6 Manlifts

Manlifts are used to hoist personnel. They provide quick access for work at elevated heights. Personnel operating the manlift must exercise care so as not become entangled in the work area. They should never exit the manlift platform.

It is important for manlift operators to be well trained in the operation and limitations of their manlifts and in the special hazards of their use.

OSHA 1910.68 governs manlifts.

21.9.7 Scaffolding

Scaffolding is used as a temporary platform for work. It should be constructed by qualified personnel. Before initial use, scaffolding should be inspected by a competent person and certified as safe for use. A tagging system is commonly used to indicate that the scaffold is safe for use or that it is being built and should not be used.

Scaffolding is governed by OSHA 1910.28 Safety Requirements for Scaffolding.

21.9.8 Robots

A less conventional form of equipment is a robot. The use of robots in relation to process equipment is most developed in the nuclear industry and in offshore activities, but a gradual growth of their use in special applications on conventional process plants can be envisaged.

Accounts of robots are given by Collins (1982), T.J. Williams (1983), Siddle (1986b) and R.M. Taylor and Lewis (1987). HSE guidance on robots is given in HS(G)43 Industrial Robot Safety (1988) (the HSE Robot Safety Guide).

The term 'robot' has been used to describe a variety of devices. The definition given by the Robot Institute of America (RIA) is a 'reprogrammable', multifunctional manipulator designed to move materials, parts, tools or specialized devices through variable preprogrammed motion for the performance of a variety of tasks'. The Japanese Industrial Robot Association defines four levels of complexity in robots. The first level is a manual manipulator which performs preset sequences; a typical application is as a means of remote manipulation in hazardous environments. The other three levels are playback robots, numerically controlled robots and intelligent robots. A robot is distinguished from a manual manipulator by its program, and from the single-task devices used in much factory line production by its flexibility.

Features of a robot are the program, the control system, the power, the sensors, the axes of movement and the lifting capacity. A common form of control system is one in which the robot is taken through a sequence under manual guidance, the sequence is repeated automatically to check it out and it is then committed to memory.

Industrial applications include robots which perform the operations of pick-and-place, spraying and painting, resistance welding, continuous path welding, and assembly.

The more advanced applications of robots depend heavily on the availability of suitable sensors, both contact and non-contact types.

The use of robots to reduce exposure of personnel at a nuclear plant is described by R.M. Taylor and Lewis (1987). They use the term 'robot' to include non-programmable remotely operated manipulators and a large proportion of the robots used are evidently of this type. Three applications are described. One is a bagout facility robot and another is a sampling aisle robotic system. In both cases the point-to-point movement is programmed while the operator selects and monitors the sequence of moves. The third application is a large robotic system used to dismantle obsolete equipment. This consists of a five-axis manipulator integrated with a three-axis gantry serving a $70 \times 20 \times 20$ ft work area. The operator can operate the manipulator by remote control as well as carry out sequences under automatic control.

Robots may be used to relieve humans of tasks which involve a degree of hazard, and this is likely to be a principal use in the process industries. They do, however, bring their own hazards in that a robot is both powered and capable of movement.

HS(G) 43 deals primarily with the fixed 'teach and play back' type of robot. For the purposes of the treatment given, the guide takes the term to mean ' a manipulating device which is automatically controlled, is reprogrammable and is capable of serving a number of different purposes'. It deals with robot safety under the following headings: (1) safeguarding robot systems, (2) safety in design and manufacture, (3) safety during installation and commissioning, (4) safety during use, (5) safety during programming and (6) safety during maintenance. It also deals with training for robot safety and gives a number of appendices which cover *inter alia* hazard identification and risk assessment, safeguarding methods and case studies.

The hazards posed by a fixed robot are those of a machine, essentially striking and trapping and entanglement. The characteristic problem with a robot is the realization of these hazards due to aberrant behaviour. Two potential causes of such behaviour are power transients and program errors.

The approach to the safeguarding of robot systems described in HS(G) 43 is based on: hazard identification, including failure modes and effects analysis; formulation of strategies of hazard elimination and mitigation; definition of levels of integrity for the safety controls and interlocks; and risk assessment for the system as a whole.

The conventional methods of machine guarding, described in BS 5304 and also BS 2771 and BS 6491 and PM 41, are in large part applicable to robots also. Their application is considered in Appedix 2 of the *Guide*.

These may be complemented by critical examination of the need for close approach to the robot and the development of a suitable strategy for situations where close approach is unavoidable, the principal elements of which are that the robot should be operated at low speed and that its control should rest in the hands of the person who is to approach it.

There are a number of features which can be incorporated in the design of a robot to minimize hazards. Trapping points should be avoided. Variable speed controls and a facility for single stepping should be provided and the control pendant ergonomically designed. The robot should have brakes and/or hydraulic stop valves to arrest movement. The arcs of movement of the robot's arms should be restricted, and suitable stops, fixed or adjustable, provided. Another precaution is limitation on the forces which can be exerted by the arms. A gripper should be designed so that it can cope with the static and dynamic forces created by the load, including emergency stop, and so that it does not release the load on power failure. The design should provide a parking position and should cater for the return of the robot to normal operation after different types of interruption, with movement always being by a specified trajectory. The *Guide* also details numerous aspects of the design of the control pendant. The robot should be supplied with high quality documentation. Design aspects of the overall robot system include a layout to facilitate viewing and the use of interlocks.

The robot system should be subject to suitable methods of hazard identification and risk assessment, as described in Appendix 1 of the *Guide*. The hazard identification should include a review of the states of the robot, its functions and its interaction with the plant.

With respect to installation and commissioning aspects of robot safety, HS(G) 43 deals mainly with the development of safe working procedures. The safe use of a robot largely centres around control of access. A fixed robot generally operates in a 'cell', the access to which is controlled using appropriate methods of safe-guarding Appendix 2 of the Guide describes the various options. The approach taken follows that of BS 5304, which details the methods and gives an approach to selection based on the level of risk. Basic protection is provided by perimeter fencing and interlocks. Electrosensitive safety systems are available uitlizing various forms of proximity sensor such as photoelectric (PE) devices, capacitance devices and pressure sensitive mats. Other safety devices include: trips and emergency stops; brakes; positive stops; and enabling controls, or devices working on the dead man's handle principle. A form of the latter suited to robots is the two-hand control, requiring the use of both hands, which it thus protects.

Safety is also consideration in the programming of the robot. For this HS(G) 43 refers to the guidance given in the HSE *PES Guide*.

Safe maintenance of a robot requires well thought-out maintenance procedures and precautions to prevent sudden, unpredictable movements.

Robot case studies given in HS(G) 43 include a robot serving in a machine installation, robot arc welding and robot water jetting.

21.10 Flanged Joints

21.10.1 Making joints

The normal pipe joint on a process plant is the flanged joint, as described in Chapter 12. The two main varieties are the gasketed joint and the ring-type joint. For high pressures, the ring-type joint is used.

Accounts of the making up of flanged joints, and in particular of bolt tightening, are given by Graves (1966), Briscoe (1976), K. Gibson (1986) and Garner (1993).

The joint to be made up may be between two sections of pipe, between a section of pipe and equipment such as a vessel, valve or pump or between a section of pipe and a blind flange, closing off the end of the pipe.

If the joint is a gasketed one, the surfaces of the flanges should be free of deterioration, clean, and the gasket used should be of the correct type. Metallic spiral wound gaskets are the most common type used. When a flanged joint is opened, the gasket should be not be reused. A new gasket should always be installed.

In the case of a ring-type joint, the surfaces of the flanges should again be free of deterioration, clean, and the ring used should be of the correct type. New rings should always be used whenever the joint is opened.

The bolts or studs used should be those specified in all relevant respects. They should be of the correct diameter, length and material of construction. The nuts likewise should be of the right material. Short bolting is not acceptable.

The pipe or other equipment to which the flanges to be joined are attached should be properly supported and aligned so as to facilitate the making of the joint.

In making up a flange, it is bad practice to tighten all the bolts on one side, then the bolts on the other side. The proper procedure is sequence tightening, which involves gradual tightening of the bolts following a criss-cross pattern.

There are a number of methods of tightening the bolts. Taking the case of a ring-type joint, one is to screw the nuts on until they are finger tight. This method is suitable for attaching a blind flange for the purpose of keeping out dirt, but not as a method of making up a leak-tight flange. A flange may be made up hand tight by tightening with a wrench, a hammer wrench and hammer or with an impact.

The bolt tightness obtained by such methods are variable and there is a trend to the use of more sophisticated methods, as described by K. Gibson (1986). Three basic methods are available, two involving cold tightening and one hot tightening. The first cold tightening method is the regular one of rotating the nut against the thread helix angle. The other is to stretch the bolt longitudinally, index the nut and release the stretching load. The hot tightening method is to heat the bolt, causing it to undergo thermal expansion, index the nut and let the bolt cool down.

There are a variety of tightening tools available. They include: traditional wrenches and torque wrenches, where the applied torque varies with the length of the lever arm; impact wrenches, either hydraulic or pneumatic; pneumatic torque multipliers; and hydraulic torque wrenches. There are various bolt stretching devices, notably direct-acting bolt tensioners. Likewise, there are a variety of techniques for measuring bolt stress. One of the simplest is the micrometer, which measures strain, from which stress may then be calculated.

In order to stretch a bolt accurately by a torque method, it is necessary to exercise accurate control of the torque and to know the coefficient of friction of the thread and nut-set interfaces. Alternatively, the tension may be determined by measurement as just described.

As indicated, a bolt or stud has a design pre-tension or pre-stress. This pre-stress should be such that the bolt is not stretched beyond the elastic limit. In this condition, the bolt acts like a spring. It then exerts on the flange the rated damping force. If the pre-stress is too low, the bolt may work loose. If it is too high, the bolt may yield or fracture.

The pre-stress is obtained by the application of torque. However, as indicated, a large proportion of the torque is

lost in friction of the thread, under the bolt head and/or the seating surface of the nut. Garner (1993) estimates this proportion as 60–90%. The bolt manufacturer provides data on the relation between torque and pre-stress, but these are necessarily based on average values for the friction.

Lubrication may be used to reduce the friction and to give more uniform tensioning. The lubricant should be matched to the application, selection being a specialist matter.

A particular problem in bolt tightening is that of leaks on heat exchangers, which is discussed by Briscoe (1976). He quotes the results of experiments using both hand wrenches and hammer wrenches, showing the unreliability of standard torque-tension relations. On one of his graphs the lowest stress is 43,000 psi and the highest 120,000 psi. He indicates that in heat exchanger work for studs larger than 1 in. diameter the only method found to be reliable is hydraulic stud tensioning.

There are a number of problems with studs on heat exchanger flanges. One is differential expansion of the flange itself and of the stud, equivalent in the example quoted to a differential force of 21,000 psi. Another is the difference in the temperatures of studs at different positions on the flange, with the air beneath the flange cold but that above it hot; in one case quoted, the temperatures of the studs at the 6 and 12 o'clock positions were 220°F and 440°F, respectively, which is equivalent to a differential force of more than 45,000 psi. Another feature is the effect of insulation on stud temperature.

Live loading of flanged joints has become a common practice to maintain the required bolt tension to keep the gasket seal pressure substantially above the required minimum. Live loading prevents flange leakage due to high temperatures and varying pressure and temperature. On 26 May 1983 at Bloomfleld, New Mexico, a compressor head gasket ruptured, resulting in a gas leak and an explosion in the compressor house (Case History A105). The investigation report (NTSB, 1983 PAR-83–04) found that the bolts on the compressor head flange had been improperly tightened and that there were wide variations in the bolt tightness. One of the potential leak scenarios considered at this inquiry was a leak due to failure of bolts on the reciprocating compressors (Bett, 1989). Inspections in the first half of 1988 revealed that on one cylinder on the A machine, 7 stud bolts out of 16 had failed. The condition was described by the expert witness as potentially serious. An inspection of a cylinder on the B machine 4 months later found 5 failed bolts.

The leak-tightness of a blind flange on the end of a pipe was a key issue at the Piper Alpha Inquiry (Cullen, 1990). Evidence given included: an account of the making up of a joint, and in particular the different methods of bolt tightening (Ritchie, 1989; Whalley, 1989); experimental measurements of bolt stretch vs torque, which illustrated the variability of the bolt extensions (Davie, 1989); and measurement of the torques obtained by hand tightening and by hammering up (Standen, 1989).

Defects in flanged joints include: the use of incorrect or defective bolts, studs or nuts; the use of incorrect or defective gaskets or rings; undertightening of the bolts so that the joint is not leak-tight; overtightening of the bolts so that they are overstretched; and subjecting the bolts to additional stresses.

It is not unusual for a flanged joint to leak. A common response is to tighten the bolts. This may be effective if the bolts were loose in the first place. However, further tightening of bolts which were correctly tensioned originally is bad practice. The National Transportation Safety Board (NTSB) report states:

> Bolted assemblies should not be tightened under pressure. *Never* 'tighten down' a leaking gasket in an assembly that is properly torqued. The assembly should be taken apart and inspected for causes of the leak and a new gasket installed on reassembly.

Another incorrect response to a leaking flange is the use of larger, strong bolts. As explained by Graves (1966), this is liable to make the flange bow and to exacerbate the leak.

21.10.2 Breaking joints

Breaking into a line can involve a number of hazards and it is necessary to exercise considerable care. OSHA Process Safety Management 1910.119(o) requires safe work practices for opening process equipment or piping. Safe methods for the breaking of pipelines are described in *Safety in Inspection and Maintenance of Chemical Plant* (BCISC, 1959/3).

For the breaking of a line there should be clear instructions on the work and on the area in which it is to be done. Information should be given on the material in the line and its hazards, and on the precautions to be taken. The joint to be broken should be indicated by an identification tag. The work is normally covered by a permit.

Some preliminary measures and precautions include:

(1) isolation of the working area and posting of warning notices;
(2) provision of safe access;
(3) support of the pipe on either side of the joint;
(4) isolation of the pipe section;
(5) release of pressure from the pipe section;
(6) draining of the pipe section and disposal of the fluid drained;
(7) precautions against fire;
(8) protection of personnel.

The joint to be broken should be isolated. Pumps and other devices which could put the joint under pressure should be switched off and locked out. Measures should be taken to release the pressure in the line.

It should be assumed, however, that the pipe may be full and under pressure, and precautions should be taken accordingly. In particular, it may be necessary to use protective hoods or equivalent equipment.

There is a correct way to break a joint. The principle is to loosen adjacent nuts and bolts first so that they can be retightened quickly if necessary. The loosening should be done slowly and continuously. The preferred sequence is shown in Figure 21.5. Bolt 1, which is the furthest away, is slackened first, then bolts 2 and 3. Bolt 4, which is the nearest, should not be slackened until the wedge has been used to open the joint and drain the line completely.

Some joints are difficult to break and thus constitute a potential hazard. A persistently troublesome joint should be reported by the maintenance personnel. An alert supervisor will recognize such a joint as a problem.

The piping designer also has a contribution to make by building into the design enough 'spring' to facilitate the breaking of joints which must be broken frequently. Alternatively, a swing blind may be installed.

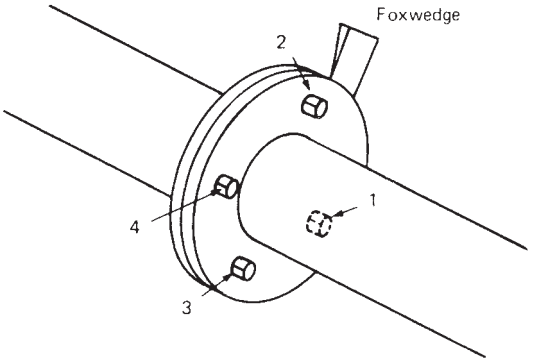

Figure 21.5 *Sequence of operations in breaking a flanged joint*

It can occur that a bolt, or stud, breaks while it is being undone. The correct procedure for dealing with a broken bolt, in a single isolation situation, is to replace it with a new one before proceeding.

The danger of not following this procedure is illustrated by the following incident (Anon., 1977 LPB 14, p. 2), which occurred during the breaking of a flange on a liquefied petroleum gas (LPG) main at 200 psig. As the joint was being broken, a first stud snapped, the opposite one was tried and also snapped. A third one was attempted but broke also, whereupon the fourth stud sheared. The single isolation, which had been tested and was thought to be good, did not prevent a release of liquid.

After breaking, a line is sometimes found to be plugged. The blockage may be removed by means such as digging it out. It is not good practice to clear blockages by using air or gas pressure. The danger here is that the plug of material will be ejected as a projectile.

After breaking, the ends of lines should be blinded off.

21.10.3 Breaking joints on valves

A particular hazard occurs on certain types of valve, where a joint containing the process fluid is liable to be broken in error. An account of this hazard is given by Kletz (1982f, 1984l).

Some situations where this hazard has been realized are shown in Figure 21.6. In the incident on the valve shown in Figure 21.6(a), the fitter was required to remove the valve actuator, secured on a stud which also held in place the valve bonnet; the latter was removed by mistake. Figure 21.6(b) illustrates the valve involved in another incident. In this case, it was intended that the air motor should be removed, but the joint on the valve itself was undone. In the third incident, on the valve shown in Figure 21.6(c), the fitter removed a piece which he thought was an adaptor but which was in fact a integral part of the valve itself.

21.11 Hot Work

Hot work such as welding and cutting is a common activity on process equipment, but involves potential hazards both to equipment and personnel, and needs to be closely controlled. OSHA 1910.119(k) requires a hot work permit and 1910 Subpart Q provides general requirements for welding, cutting and brazing operations. Additional guidance is provided by API RP 2009: *Safe Welding, Cutting and other Hot Work Practices in the Petroleum and Petrochemical Industries*, API Publ. 2201: *Procedures for Welding or Hot Tapping on Equipment in Service*, API RP 1107: 1991 *Pipeline Maintenance Welding Practices* and NFPA 51B: 1999 *Cutting and Welding Processes*. Also relevant is HS(G) 5 *Hot Work* (HSE, 1979) (the HSE *Hot Work Guide*).

The HSE *Hot Work Guide* deals with hot work operations under the following headings: (1) general principles, (2) environment, (3) equipment, (4) methods, (5) operations in buildings, (6) limitation of operations, (7) prohibited operations, (8) welding technology, (9) control of operations and (10) procedure. It includes appendices on the regulatory requirements, various types of seal plug, welding on water-sealed and waterless gas holders and flammable gas detectors.

The *Guide* deals particularly with welding operations on equipments containing flammable fluids, which is also the aspect of hot work of principal concern here. The welding should be confined to manual electric arc methods.

The welding methods described in the *Guide* require for their safe performance strict adherence to the procedures laid down. The account given here draws on the *Guide*, but is no more than an outline. The *Guide* itself should be consulted for the conduct of such welding operations.

Welding as such is treated in Chapter 12 and the personal safety aspects of welding are discussed in Chapter 25.

21.11.1 Regulatory requirements

Welding operations are covered by Section 31(4) of the Factories Act 1961, which states:

> No plant, tank or vessel which contains or has contained any explosive or inflammable substance shall be subjected
>
> (a) to any welding, brazing or soldering operation;
> (b) to any cutting operation which involves the application of heat;
> (c) to any operation involving the application of heat for the purpose of taking apart or removing the plant, tank or vessel or any part of it; until all practicable steps have been taken to remove the substance and any fumes arising from it, or to render them non-explosive or non-inflammable; and if any plant, tank or vessel has been subjected to any such operation, no explosive or inflammable substance shall be allowed to enter the plant, tank or vessel until the metal has cooled sufficiently to prevent any risk of igniting the substance.

Section 31(5) provides that, where he is satisfied that compliance is unnecessary or impracticable, the Chief Inspector may grant exemption from any of the above requirements by the issue of a certificate, which may contain conditions.

21.11.2 Control of welding operations

The welding operations should be controlled by a permit system. The general arrangements of a permit system are described in Section 21.8, but certain points of particular relevance to welding merit mention.

The issuing authority should have both the knowledge required to appreciate the hazards of the work and the precautions to be taken and the authority necessary to draw on and coordinate specialist expertise. The permit should

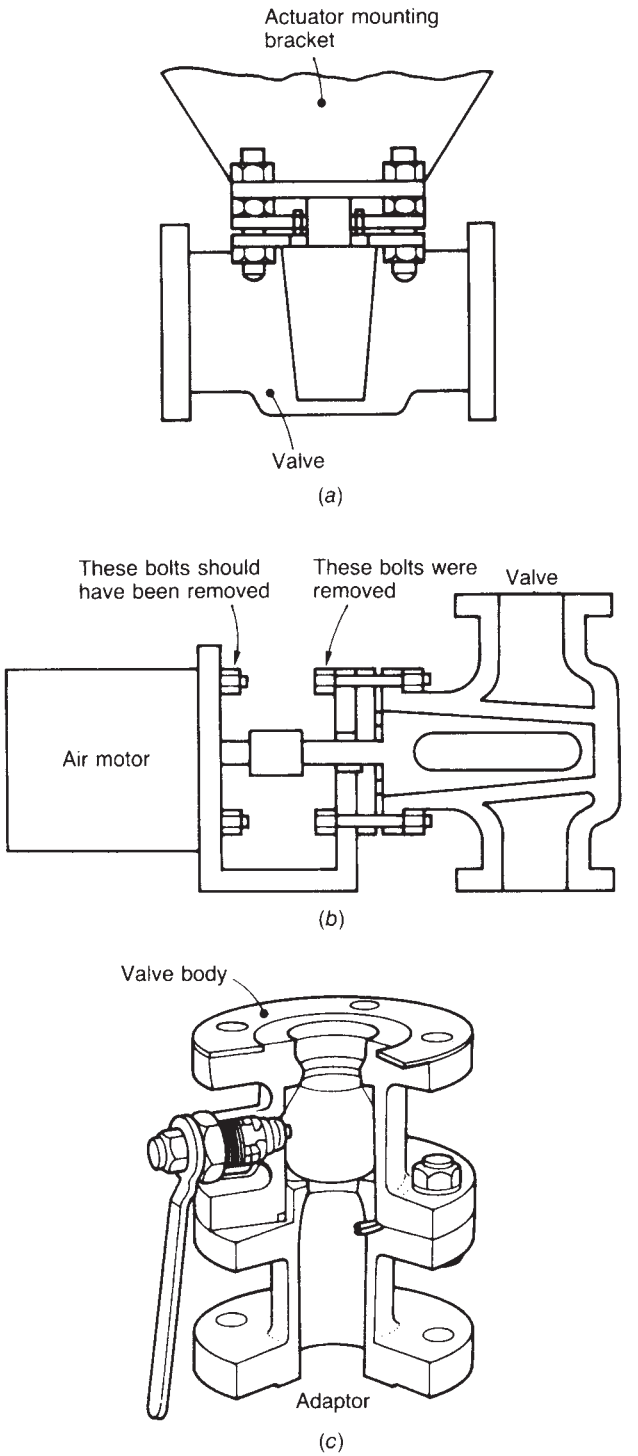

Figure 21.6 *Some valve types involved in joint breaking incidents (Kletz, 1984l): (a) valve and actuator, held by same bolts; (b) valve and actuator, held by separate bolts; (c) valve with adaptor – an integral part of valve (Courtesy of the Institution of Chemical Engineers)*

specify clearly, and in detail, the date and time authorized for hot work, the equipment on which the work is to be done, the precise nature of the operation, the weld point, and fire prevention and protection requirements. The issuing authority should inspect the work site to ensure that all necessary precautions are in place. A full explanation of the work, the hazards and the precautions to be taken is particularly necessary where the work is to be done by contractors.

21.11.3 Precautions for welding operations

A principal hazard of welding is that it introduces a source of ignition. If the work is to be done at a location where this fact is significant, and particularly within a classified hazardous area where sources of ignition are normally excluded, this should be entered on the permit and special precautions taken.

The welding site should be free of flammables, whether gases, liquids or solids. The atmosphere to a radius of 45 ft (15 m) and to a height of 6 ft (2 m) above ground level or above the point at which welding is to be done, whichever is the greater, should be free of flammable gas. The surfaces of the surrounding equipment should be free of flammable deposits. There should be no flammable liquids on the ground within a radius of 45 ft (15 m). Drains over the same area should be covered. It may also be necessary to provide shielding to contain weld spatter.

The equipment to be worked on should normally be isolated, emptied and cleaned, tested for flammables and inspected before welding is undertaken. There are certain procedures which are exceptions, as described below, but they in no way weaken this general rule.

There should be good access to the welding site for the welders and equipment and also for emergency services. For elevated locations, suitable staging and scaffolding should be provided, again with good access. There should be adequate lighting. For welding on underground pipelines, an excavation should be made of sufficient size, with adequate shoring, ladder access and secondary means of escape.

For welding in any confined space, including an excavation, there should be ventilation sufficient to ensure dispersion of fumes.

Suitable protective clothing should be provided for all persons involved in the welding operation. There should be present as a 'fire watch' at least one person, who should be provided with fire extinguishers, the dry powder type being generally used. First aid equipment such as breathing apparatus and resuscitation equipment should be to hand.

Personal safety in welding operations is considered in Chapter 25.

21.11.4 Welding on equipment containing flammable fluids

The conditions under which welding may be carried out on equipment containing flammable fluids are defined in API 2201 and HSE *Hot Work Guide*.

For welding on the external surface of equipment containing a flammable liquid, the metal at the location of the weld should be wetted by liquid. For welding on the external surface of a tank, the weld should be below the liquid level and for welding on a pipeline, the pipeline should be full of liquid. In the latter case it is also necessary to ensure that abnormal pressures cannot arise due to the generation of vapour or expansion of the liquid. The usual method of avoiding this is to maintain a liquid flow that is high enough to prevent overheating but not so high as to cause overcooling; a liquid velocity of at least 3 ft/s (1 m/s) is usually required. Measures should be taken to ensure that penetration of the metal does not occur. These include ensuring that the thickness of the metal in the area of the weld is sufficient and that the welding is performed properly.

Where welding is to be done on the internal surface of equipment, which has contained a flammable liquid, precautions should be taken to ensure that the surfaces are free of deposits and that no liquid is trapped in hollow members or behind metal linings or wear plates. Trapped liquid should be released by drilling suitable holes and the space purged with steam, air or inert gas, as appropriate.

Welding on the equipment containing a flammable gas involves a higher potential hazard in that the gas has a much lower capacity for the removal of heat than does liquid. There is, thus, a greater risk of overheating which may result in penetration by the welding operation or rupture due to the internal pressure. The operating pressure and temperature should be adjusted to allow for this.

21.11.5 Methods of temporary isolation

Some of the welding operations described below require the temporary isolation of a section of pipe. Where possible, isolation should be accomplished by conventional means, but in some cases it is necessary to use seal plugs or bag seals.

Four types of seal are used. These are (1) atmospheric seal plugs, (2) high pressure stopple or seal plugs, (3) frozen product seal plugs and (4) bag seals.

An atmospheric seal plug is inserted into the open end of a pipe which has been isolated by other means, drained and cold cut, but which has not been cleaned along its entire length and into which flammable liquid or gas may leak. It consists of a rubber sealing ring compressed between two discs so as to provide a peripheral seal against the inside of the pipe. It provides isolation between the welding point and the empty line.

A high pressure stopple is inserted into an operating pipeline, using a stopple insertion unit. There are a number of designs of such seal plugs. The insertion of two high pressure stopples allows a section of pipe to be isolated.

A frozen product seal plug is created by freezing the liquid in a section of the line, using a freezing mixture, commonly of solid carbon dioxide and isopropanol. Where the liquid cannot be frozen in this way, it may be possible to use the alternative method of replacing it with water which can then be frozen.

A bag seal is inserted into an operating gas pipeline through a bag tube. The bag consists of an inflatable rubber bladder with an outer fabric cover. Bag seals are used only for pipelines containing gases at low pressure.

Full details of each of these seal methods, of their applicability and limitations, and of the precautions to be taken in their use are given by numerous companies supplying these services and in the HSE *Hot Work Guide*.

21.11.6 Welding on operating pipes/pipelines

API 2201, 1107 and the HSE *Hot Work Guide* describes the method to be followed in welding operations on pipelines carrying flammable fluids. They deal primarily with welding on a pipeline for the purpose of replacing a length of pipe. It treats both the case where the pipeline has to remain in operation and that where it can be taken out of service.

For the former case, the method described is to isolate the section of pipeline on either side of the pipe section to be replaced. If the isolations cannot be achieved by conventional means, use may be made of a suitable seal plug. This will often be a high pressure seal plug. The method of inserting such a seal plug is broadly as follows. A stub connection is welded to the pipeline, a special valve is mounted on the connection and the drill is mounted on the valve. A check is made to ensure that the fittings and welds can withstand the pipeline pressure. The valve is then opened, the drilling is done, the drill is withdrawn again, the valve is closed and the drill is removed. The stopple insertion unit is mounted and the stopple inserted. If the flow is to be maintained, this may be done by putting in first a temporary bypass, again by welding on stub connections and tapping in a similar manner, and joining the bypass pipe on by a flanged or welded joint. Further stubs are welded on to the pipe section to take vent and drain connections and these are tapped. The arrangement is illustrated in Figure 21.7. The pipe section is drained and vented and a check is made that the stopples are making satisfactory seals. The pipe section is then removed, which should be done by cold cutting; this does not include the use of an abrasive wheel. The pipe ends are cleaned and the new section of pipe is then fitted, either with flanged or welded joints. If there is to be a delay before the pipe section is fitted, the open ends should be sealed with atmospheric seal plugs or bag seals and the space behind these seals vented by flexible hose to a safe area.

A permanent branch connection may be installed to an operating pipeline in a manner essentially similar to that just described for installing a temporary bypass, and a valve or flowmeter may be installed in a manner similar to that described for installing a new section of pipe.

Another case is where the pipeline can be taken out of service and the section of pipeline isolated and drained, but it is not practical to clean and purge it over its whole length. In this case, the isolations should be checked and the line drilled to ensure it is depressurized to atmospheric pressure. The pipe section is then removed by cold cutting. As before, the pipe ends are cleaned and the new section of pipe is then installed, with fitting of seals and venting of the space behind them if installation of the new pipe section is to be delayed.

Yet another case is where it is necessary to make a repair on an operating pipeline to counter internal or external corrosion. It is sometimes possible to use a mechanical clamp, but often the only recourse is to weld over the affected area a patch or leak box.

21.11.7 Limitations and prohibitions on welding operations

There are a number of limitations on the welding operations on equipment containing flammable fluids. Welding should not generally be carried out on equipment where the metal thickness is less than 0.2 in. (5 mm); on the external surface of a tank at a point less than 3 ft (1 m) below the liquid surface, or on equipment at a temperature below 45°F (7°C), unless it can be shown to be safe to do so.

Welding on a pipeline should not be undertaken where the operating pressure and temperature exceed those which ensure that the thickness and strength of the metal are such as to preclude failure and that the strength remains unaffected on cooling.

Welding should not be done on the vent and blowdown systems of operating equipment, unless it can be shown to be safe to do so. Such systems should not be isolated while the equipment is operating unless alternative arrangements have been made.

There are also a number of prohibitions on welding operations on equipment containing flammable fluids. Welding should not be carried out where: either the equipment contains a flammable mixture or the welding itself may create one; the equipment contains a substance liable to undergo reaction or decomposition; or the equipment contains either compressed air or an oxygen-enriched mixture together with hydrocarbons deposited on internal surfaces or otherwise present.

Furthermore, welding should not be carried out on: equipment in ferritic steel containing gas in which the partial pressure of hydrogen exceeds 100 psi (7 bar), unless it can be shown by tests to be safe to do so; equipment in a material susceptible to stress corrosion cracking, unless appropriate stress relief treatment can be given; equipment

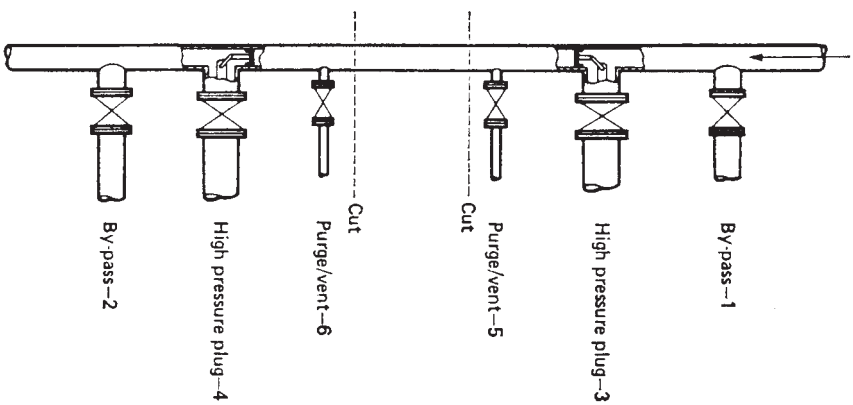

Figure 21.7 *Arrangement for welding on an operating pipeline (HSE, 1979 HS(G) 5) (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

for which post-weld heat treatment is necessary; equipment designed to advanced, or high stress, codes; or any part of a flare system over which effective control cannot be exercised.

There is an extreme hazard of welding on equipment containing pure liquid or gaseous oxygen. For equipment containing high purity ethylene gas it had been demonstrated that welding may be safely done at pressures up to 400 psi (28 bar) and temperatures up to 300°F (150°C) and that work was continuing on this topic.

21.11.8 Procedures for welding operations

The HSE *Hot Work Guide* gives the procedures to be followed in welding operations on a pipeline in the form of a checklist, under the headings of: (1) initial planning of operations, (2) site preparations, (3) stand by services, (4) pipeline preparation, (5) fitting alignment, (6) welding procedure, (7) action immediately prior to welding, (8) action during welding, (9) integrity of the completed weld and (10) final completion.

The initial planning covers: inspections on regulatory requirements and company codes; notifications to external interested parties; reviews of the process conditions, of the condition the pipeline, of the fittings and consumables and of the site conditions; lists of the fittings, equipment, and services required, plans of the site; sketches of the work; a list and plan of emergency procedures; and preparation for the issue of the permit. The site preparations are essentially the precautions given in Section 21.11.3, but include also the provision of adequate supports for the pipeline, fittings and any other equipment, and removal of groundwater where necessary, likewise, the stand by services to be provided as appropriate are those mentioned in that section.

The pipeline preparations include checking the material of construction of the pipeline, removing insulation, cleaning the surface, checking the roundness, measuring the wall thickness, examining the external condition, investigating where necessary the internal condition, and grinding flush any external weld which might interfere with a flush fitting.

The fittings alignment requires that the fittings be correctly positioned and aligned, the pipeline and fittings adequately supported, and the weld preparation and the clearances checked. The welding procedures cover the competence and approval testing of welders, the routing of the welding cables though areas free of flammable gases and liquids, the condition of these cables, and the clamping of the return current cable close to the weld point.

The actions immediately prior to welding are to confirm the identity of the pipeline to be welded, the pipeline operating conditions, the welder and welding supervisor's understanding of the work to be done, the temperature of the pipe wall and fitting, the welding current and compliance with the permit. The actions during welding are to monitor the pipeline operating conditions and the absence of flammables in the environment.

The integrity of the completed weld should be such that it is able to withstand any operating conditions to which the pipeline may be subject, after heat treatment where necessary. The integrity of the weld should be checked by some suitable means. Reference is made to hydraulic pressure testing, pneumatic leak testing and non-destructive testing. Where the latter is used, the acceptance standards utilized should be stated. Where pressure testing is used, care should be taken to avoid over pressurizing the pipeline itself.

The final completion consists of the usual termination procedures: a check that the site is left free of hazards, notification to interested parties that the work is complete and signoff of the permit.

21.11.9 Hot tapping

The procedure of fitting a branch onto a pipeline which is still operational is known as hot tapping. This procedure has already been described in outline but is of sufficient importance to merit further discussion. As already stated, guidance is available in API RP 2201, RP 1107 and the HSE *Hot Work Guide*.

Several of the accounts on hot tapping published in the mid-1970s provide useful background information. They include those of Elder and Batten (1975), Hahn (1975), W.B. Howard (1975a), Howden (1975), Letchford (1975) and Warren (1975a). Howden (1975) describes a long-term programme of work on hot tapping in the American Gas Association (AGA) line Pipe Research programme at the Battelle Columbus Laboratories. Guidelines produced by the American Society of Mechanical Engineers (ASME) Gas Piping Standards Committee are outlined by Elder and Batten (1975). The development of a code of practice for hot tapping has been described by Letchford (1975) of British Gas.

It is expensive to shut-down units or equipment and there is a strong economic incentive to make the modification when the equipment is in service. Nevertheless, hot tapping should be avoided as far as possible and should only be done in essential cases.

The Factories Act 1961, Section 31(4), quoted above, forbids work on plant, tanks or vessels containing any explosive or flammable substance which entails the application of heat until all practicable steps have been taken to remove the substance and any fumes arising from it and to render it non-explosive or non-flammable.

If air or other oxidizing substance is excluded from equipment which contains a fluid that can burn or explode when mixed with air, then the fluid may be regarded as non-explosive and non-flammable. Such exclusion is the basis for the justification of hot tapping as an industrial practice (Hahn, 1975).

There are several hazards in hot tapping. One is that there will be a leak during the hot tapping operation itself. This is most likely to result from welding, but could also occur if the hot tap valve or tapping machine were to fail or if the tapping machine were to pierce the pipe on the far side. Another hazard is the explosive decomposition of the fluid in the pipe due to the heat applied during the welding. A third hazard is the failure of the modified equipment at some later date. There are also the usual hazards of welding on the equipment.

The normal hot tapping arrangement is shown in Figure 21.8. A branch is welded onto the pipe, a valve is put on the branch and a tapping machine is used to drill via the valve and branch into the pipe.

Hot tapping requires careful preparation, including consideration of the following factors:

(1) the process fluid and the process design operating conditions in the pipeline;
(2) the process operating conditions at the start of work;
(3) the material of construction, the dimensions and the condition of the pipeline;
(4) welding constraints, preparations and procedures;

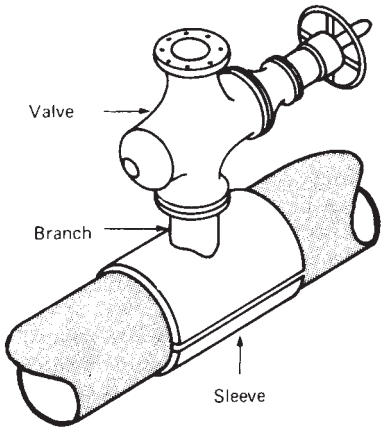

Figure 21.8 *Valves arrangement for hot tapping*

(5) the fittings and equipment required for the work;
(6) the services required for the work;
(7) the equipment operational procedures and precautions;
(8) the permit systems, notification to third parties and emergency arrangements.

If possible, the pipeline should be taken out of service to make the hot tap. Where this cannot be done, the operating pressure above atmospheric should be reduced as far as possible while the work is being done so that the hazard is also reduced.

The material of construction, the thickness and the condition of the pipe to be welded should be thoroughly checked. The material of construction is important for strength calculations and for the selection of welding electrodes. There is a minimum thickness below which the pipe should not be welded. Welding should not be carried out if the condition of the pipe has deteriorated so as to make operation unsafe, and the pipeline should be thoroughly checked by non-destructive testing (NDT).

Some guidelines on what is and what is not permitted in one company, ICI, have been given by Hahn (1975). Basically, these restrict hot tapping to the following conditions:

(1) pipelines to be made of specified grades of steel;
(2) pipe wall thickness to be not less than 0.22 in.;
(3) process fluid pressure to be not greater than 550 psig and not less than atmospheric; if hydrogen is present, the partial pressure to be not greater than 100 psig;
(4) process fluid temperature to be between 7°C and 370°C throughout the operation; preheating by steam or electrical methods, but not flame heating, to be used as necessary to achieve this;
(5) welding not to be done on lines containing
    (a) oxygen (except under 1%),
    (b) compressed air,
    (c) decomposables,
    (d) caustic soda,
    (e) process materials which could cause hardening by reaction with hot metals to a dangerous degree.

Hahn also discusses the extent to which these basic restrictions can be modified and states the conditions under which his company would do hot tapping on low alloy steels, on thinner pipes, at higher pressures and outside the given temperature range. On the other hand, he also gives certain limits which would not be overridden: welding would not be done on oxygen or chlorine pipes, because steel can burn in these materials, nor on compressed air lines, which often contain oil or carbon deposits that might ignite if heat were applied to the pipe. Areas of doubt which he discusses are pipelines containing ethylene and those containing hydrogen above 100 psig partial pressure.

The problem of ethylene decomposition during welding on ethylene pipelines is considered by W.B. Howard (1975a), who describes experiments to determine the process conditions under which hot tapping may be regarded as safe. Hahn states that his company has gone from a policy of permitting such work to a complete ban and thence to a partial relaxation of the ban. It is of interest that during the period of the complete ban, a method was developed for bonding fittings in place using epoxy resins.

With regard to hydrogen, Hahn suggests that the hazard which is a greater limitation than that associated with hydrogen partial pressure is that the red hot part of the heat-affected zone may reach the pipe internal surface with the result that the hydrogen diffuses rapidly through the weld pool, so that weld cracking occurs.

The welding work has several important aspects. The welding is done by the electric arc method. The welding procedure should be defined in respect of the electrode selection, the welding technique, the preheat and the post-weld treatment, if any.

Preheat may be provided by steam or electrical methods. Different views have been expressed on the advisability of flame heating. The ICI instructions described by Hahn state that it should on no account be used. On the other hand, Letchford describes its use in British Gas.

The surfaces to be welded should be uniform and free of pipe coating, rust, scale, oil and moisture. The pipe should be supported on both sides of the section to be welded.

The welding current should be checked. The ammeter on the welding set is not always reliable. It is usually required that the meter be checked using scrap material. The pipe should be completely grounded and the risk of arcing at the ground clamp eliminated.

The welders should be fully qualified, experienced and reliable, and should wear appropriate protective clothing.

If the weather conditions are bad, the welding should be stopped.

There can be a significant cooling effect from the gas flow. This may require the use of higher welding current to overcome this cooling effect. It can also result in cracking due to the quench effect when the source of heat is removed.

The hot tap valve requires special attention. Such a valve may be subjected to pressure and temperature shocks and its integrity should be assured. The valve should be new. It should be given NDT, pressure and leak tests.

The hot tapping equipment should also be carefully checked. This check should again include NDT and pressure testing and tests on the cutter teeth and pilot drive.

The equipment operational procedures and precautions which should be taken during hot tapping were described in Chapter 20 as an illustration of the role of plant management during plant work.

Hot tapping is a complex operation which is potentially hazardous, but which can be done safely if the correct

practices are followed. It is emphasized, however, that hot tapping is a matter for specialists.

21.12 Tank Cleaning, Repair and Demolition

A set of operations of some importance in the maintenance of equipment is the cleaning, repair and demolition of tanks for storage of flammable liquids. Guidance is given in OSHA 1910.146: *Permit Required Confined Space*, API Std 2015: *Requirements for Safe Entry and Cleaning of Petroleum Storage Tanks*, API Std 653: *Tank Inspection, Repair, Alteration, and Reconstruction*, NFPA 326: *Safeguarding of Tanks and Containers for Entry, Cleaning and Repair*, CS 15 *The Cleaning and Gas Freeing of Tanks Containing Flammable Residues* (HSE, 1985).

21.12.1 Preparation for entry or hot work

Two principal purposes for which entry into a tank is required are inspection and repair or modification, which usually involves hot work.

It cannot be assumed that a tank which has been emptied and gas freed, or even one which has been cleaned with a water wash, is completely free of flammable or toxic gas. Before entry, ventilation of the tank should be established, the atmosphere should be gas tested to be free of flammable or toxic gas, and repeat gas tests should be made at intervals to confirm that the atmosphere is still gas free. On entry, a check should be made for potentially hazardous residues.

Ventilation and monitoring of the atmosphere in the tank should continue and personnel should not remain inside if the concentration of flammables rises to over 25% of the lower flammability limit. The source of the vapours must be located and controlled.

If it is not possible to establish a safe atmosphere in the tank, entry may be made using breathing apparatus.

Before hot work is undertaken, a thorough inspection should be made for hazardous residues and any such residues first removed by cleaning. Gas testing should also be performed.

It may be possible, particularly for smaller tanks, to avoid the need for hot work by cold repair techniques such as the use, where suitable, of materials based on epoxy resins, fibre glass or elastomers. Care should be taken not to incorporate into the tank structure elements which increase the hazard from static electricity.

21.12.2 Gas freeing of tanks

Methods of gas freeing are described in Section 21.6. They are forced ventilation, water washing and steam cleaning. Particularly with large tanks, the gas freeing or cleaning operation may involve the venting of quantities of flammable or toxic vapour, which is often denser than air, and therefore liable to collect at low points and poorly ventilated areas. Such operations should not be performed unless suitable precautions have been taken to disperse the gas and exclude ignition sources.

In some cases the operations will evolve quantities of flammable vapour sufficient to require measures to control its dispersion. Flammable purge gas mixture is sometimes burned off at an elevated vent stack, fitted with a pilot flame and a flame arrester to prevent flashback. Where large equipment, and therefore large volumes of flammable vapour, are involved, the dispersion of the vapour should be monitored, by measurement if necessary, and venting suspended if the vapour fails to disperse. Other precautions required include the covering off of drains and sewers to prevent ingress of vapours and restriction of access to the area. It may also be necessary to take measures to prevent ingress of vapour into buildings.

21.12.3 Emptying of liquid from equipment

Liquid should be emptied into a suitable receiver. Large equipment is typically pumped out, while small vessels may be drained.

A particular technique used to flush out light hydrocarbons from a tank bottom is to introduce water and raise the hydrocarbons to the level of the suction line so that they can be pumped out. Care is needed to avoid generating static electricity either by high fluid velocities or by splashing, bearing in mind the enhancing effect of the water content on the generation of static electricity in liquid hydrocarbons.

Where a vessel has an external jacket for the circulation of a flammable heat transfer liquid, it is suggested that this may be drained out and replaced with water, maintaining a vent open to the atmosphere to prevent any pressure build-up during hot work.

Suitable measures should be taken to ensure that ancillary equipment does not constitute a hazard. Ionizing radiation sources should be locked out and removed by a competent person. Stirrers and heaters should be isolated. Cathodic protection should have its power supply isolated 12 hours in advance so that depolarization occurs. Where it is necessary to maintain heating from steam coils or an electric immersion heater in order to assist pumping out of the liquid, the heat input should be isolated before the liquid falls to within 1.5 ft (0.5 m) of the heating surfaces or temperature sensors.

21.12.4 Ignition at equipment

Precautions should be taken to ensure that ignition of flammables does not occur. The main precautions are the elimination of a flammable mixture and the avoidance of hot work where there may be flammable residues; but where there are flammables which might be ignited, control of ignition sources should be exercised. Ignition sources and situations which are particularly relevant to equipment are: direct flames from hot work; hot surfaces occurring due to hot work; self-heating of oil-soaked insulation; and pyrophoric iron sulfide. Hot surfaces may cause ignition either by hot surface ignition or by raising the temperature of the bulk gas to its autoignition temperature. There is a volume effect for autoignition, the autoignition temperature decreasing with an increase in volume, and since the volume differences are large between the volumes in which determinations have been made and those of large equipment, it is prudent to assume that any significant rise in the wall temperature may ignite a flammable mixture in a large tank.

21.12.5 Gas freeing and cleaning of small equipment

For small equipment, drums and other small containers, use should be made of positive gas freeing methods and reliance should not be placed on natural ventilation. One positive method of gas freeing is forced ventilation. Gas freeing also occurs as a result of cleaning by water washing or steam cleaning.

Methods of cleaning small equipment are water washing, steam cleaning and solvent jetting. An account of the use of these methods for the cleaning of small equipment is given in Section 21.6.

21.12.6 Gas freeing and cleaning of mobile tanks

Mobile tanks are those on truck tankers and rail tank cars. Positive methods should be used for gas freeing. One such method is thorough water washing and forced ventilation by the use of an air eductor or air mover. Another is to do gas freeing as part of steam cleaning. The usual method of cleaning, and thus of gas freeing, is the use of steam cleaning. The procedure is similar to that for small equipment.

Before hot work is undertaken on a multi-compartment tank vehicle, the design of the tank should be reviewed and a check made that there is no flammable material trapped in the bulkheads or other cavity.

21.12.7 Gas freeing and cleaning of large equipment

The usual method of gas freeing large equipment is by forced ventilation using air eductors or air movers. The eductor or blower is lowered to the equipment bottom and the equipment is freed of gas through the roof manholes. The opening of manholes in the side of the equipment may release dense vapour creating a potential hazard, as described above. Precautions should be taken against ignition.

Ventilation should be continued until the concentration of vapour falls to less than 5% of the lower flammability limit. At this point, the risk of an outflow of flammable mixture is minimal and all the manholes may be opened. The flammable concentration should be allowed to fall to zero and to stay there for at least 30 min.

Methods of cleaning large equipment are steam cleaning, water jetting, solvent jetting and manual cleaning. An account of the use of these methods for the cleaning of large equipment is given in Section 21.6.

In many cases, the bottoms of large tanks are covered with sludge, residues and corrosion products, and are perforated to some degree. There may be hazardous residues in defective seams or in voids. It is necessary to check on, and deal with, such residues before hot work is undertaken.

Relevant advice is given in API Publ. 2207: 1999 *Preparing Tank Bottoms for Hot Work*. If there is flammable liquid under the tank bottom, one technique of dealing with it is to drill and flood the bottom with water to displace the liquid.

21.12.8 Hot work on outside of equipment

If it is required to carry out hot work on the outside of a equipment, which for some reason cannot be gas freed and cleaned, an alternative procedure is to inert the equipment. This method is not suitable if the product concerned is one which decomposes, such as ethylene oxide. Another procedure is to fill the equipment with the flammable liquid and then perform the hot work, as described in Section 21.11.

21.12.9 Inerting of equipment

Inerting may be accomplished by filling with water or with an inert gas such as nitrogen, carbon dioxide or combustion gas. A simple method of inerting for small equipment is filling with water. Any necessary check should be made on the load created by the water on the equipment and its supports.

The inert gas method requires that the gas be mixed effectively. Mixing is promoted by the introduction of the inert gas at a number of points and with high velocity. Failure to achieve good mixing creates various problems. It is difficult to monitor the uniformity of mixing and it may be necessary to maintain the gas flow throughout the period of the hot work.

Nitrogen is less reactive than carbon dioxide and may be used where products might be adversely affected by the latter. It is available as compressed gas in cylinders or as the bulk liquid. Where the latter is used, the vaporizers should be large enough to ensure an adequate supply and should be able to warm the gas to at least 14°F (−10°C) to guard against low temperature embrittlement. Using nitrogen inerting, which gives a mixture of hydrocarbons, nitrogen and oxygen, the limiting concentration of oxygen for combustion is about 12% and it is usual to purge down to below 5% to allow an adequate safety margin.

Carbon dioxide is more reactive than nitrogen. It too is available as compressed gas in cylinders or as the bulk liquid. Carbon dioxide has a tendency to form solid particles. In the case of cylinders, this creates a risk from static electricity. The use of the cylinder gas is not advised for this reason. Discharge from the bulk liquid should be designed to prevent the formation of 'snow'. It should be checked that the equipment can withstand the low temperature caused by liquid or solid carbon dioxide. Precautions should be taken to protect personnel from 'cold burns'. Using carbon dioxide inerting, the limiting concentration of oxygen for combustion is about 14%, and for safety it is usual to purge to below 5%.

A third type of inert gas is combustion gas obtained from the controlled combustion of hydrocarbons in gas generators, followed by purification. The resultant mixture typically contains 12–15% carbon dioxide, 12% oxygen and the remainder nitrogen.

Another inerting technique involves the use of foam. The foam may be an air foam or a nitrogen foam. High expansion foam blown with air has been used to inert equipment which have held high flashpoint liquids, but there is some doubt whether air foam will prevent flame propagation if vapour is evolved in any quantity and it should not be used for liquids with a low flashpoint <90°F (<32°C). Instead use may be made of nitrogen foam. The principal advantage of using nitrogen in foam form is economy in the use of the gas. Since the gas in the equipment is displaced by the foam rather than removed by completing a number of purge gas changes.

21.12.10 Demolition of equipment

Methods for the demolition of equipment are given in API Std 653: *Tank Inspection, Repair, Alteration and Reconstruction* and GS 29/3 *Health and Safety in Demolition Work. Part 3: Techniques* (HSE, 1984).

A demolition survey should be made and the demolition procedures defined. The equipment should be emptied and gas freed. Ignition sources should be controlled. The roof should be removed by cold cutting. If a power tool is used, precautions should be taken to avoid its acting as an ignition source. Before any hot work is done, the equipment should be cleaned from the outside, by use of steam hoses, washing with water or water sprays. Washing with a high flashpoint oil is another method, but the oil should not be sprayed. The wash fluid should be collected and pumped away.

If steam is used, the usual precautions should be taken, the steam pipe being grounded and bonded to the equipment. The equipment should be allowed to cool and the atmosphere tested before entry is made.

In some cases, the technique is used of covering the bottom sludge with about 6 in. (0.15 m) of water.

Further details of equipment demolition are given GS 29/3, which also describes specific methods for the demolition of various types of equipment, including small and large fixed roof tanks, floating roof tanks and leaded petroleum tanks. It also deals with tank walls and tank floors.

21.13 On-Line Repairs

There has been a steady growth in the development of techniques for on-line, or on-steam repair and in their application. An account of on-line repair methods in general is given by G.W. Harrison (1980).

The growth of such techniques has been driven by a number of factors, including general economic pressures and the need to accommodate the lengthening of times between scheduled shut-downs, or turnarounds; to keep major pipelines operating; to economize on energy and reduce steam leaks; and to reduce hydrocarbon emissions.

One family of on-line repair methods is that concerned with carrying out hot work on operating pipelines, including hot tapping. This has already been described in Section 21.11.

Among the applications of on-line repair described by Harrison are the use of: drill-and-tap methods to repair packing on leaking valves and also on pumps and agitators; leak sealing methods to eliminate flanged joint leaks, piping and fitting leaks, vessel leaks and compressor and turbine case joint leaks; hot tapping and line stopping on pipelines; various leak sealing methods for heat exchangers; and the crimping of deteriorated reformer tubes.

An account of on-line repair of insulation is given by Bloom and Pebworth (1979).

21.13.1 General leak sealing

One of the most common types of on-line repair is the sealing of a leak. A variety of simple methods are used to seal leaks such as steam leaks, including clamps and various forms of enclosure or box. These may often be applied without the need to weld on an operating line.

21.13.2 Compound leak sealing

A specialized leak repair technique is that of on-line compound leak sealing. One of the main points where a leak is liable to occur is at a flanged joint. If the leak is severe, there may be no choice but to shut-down and repair it, unless it can be repaired on line with the equipment still operating. Accounts of compound leak sealing are given by Stroud (1981), Maushagen (1984 LPB 55), Bond (1986 LPB 69) and J.K. Rogers (1988).

Compound leak sealing of a flanged joint involves putting a containment around the joint and injecting a sealant under pressure. J.K. Rogers (1988) describes the Furmanite system of leak sealing. This is applicable over the pressure range vacuum to 5000 psi (350 bar) and the temperature range cryogenic to 1000°F (600°C). A family of sealing compounds is used, depending on the application. The applications quoted are not only to flanged joints on pipes but to various other types of equipment, including riveted joints, welded joints, screwed couplings, valves and heat exchangers.

An investigation of the hazards associated with this technique is described by Maushagen (1984 LPB 55). In essence, the process of leak sealing tends to lead to an increase in the stress on the flange and on the bolts. There is thus, a potential hazard of rupture at the flange, which is particularly likely to be realized if the flange assembly has a burst pressure below the nominal value due to incorrect design, incorrect materials or deterioration. The author defines a factor relating the stress on the bolts after sealing to that on the bolts as installed, and quotes values of up to 2 for this factor. Each application needs, therefore, to be assessed before sealing is undertaken.

He also describes a number of case histories of flange rupture during leak sealing. In one case in Czechoslovakia in 1981, a 12 in. (300 mm) diameter pipe at 4350 psi (300 bar) pressure containing synthesis gas for an ammonia plant developed a leak at a ring joint. A leak sealing operation was undertaken by non-specialists. During the injection of the sealant there was a massive failure of the flange, resulting in a fire and explosion which killed four people.

Further leak sealing incidents are described by Bond (1986 LPB 69). Nevertheless, he argues that leak sealing is not a particularly risky operation. In the United Kingdom, some 25,000 leaks are sealed each year by some 100 technicians.

Bond outlines the precautions required to minimize the risks of leak sealing. Where possible, it is preferable to use conventional means of repair, such as repair or renewal of components, rejointing of flanges and repacking of glands.

If leak sealing is to be undertaken, it should be assessed by a competent engineer and a formal work plan agreed, covered by a permit. The assessment should cover: the hazard of a major release; the residual thickness of the pipe, including the method of, and apparatus for, its measurement, the bolts, including materials, deterioration, initial and final stresses; the external loads on the pipe and flange; the record of past injections; the maximum injection pressure to be used; the design codes and procedures for the boxes and clamps; the possibility of internal blockage of the pipe by the sealing compound; the access to the site; the personal protection required; and the expected life of the temporary repair. The temporary repair should be dismantled and a conventional repair performed at the earliest opportunity.

The work should be done by a competent contractor. The author highlights in particular, competence in the design of boxes and clamps. Once the method to be used has been decided, no deviation should be permitted.

21.13.3 Pipeline repair

On-line repair methods have been used for many years for pipeline repair. The methods of hot tapping were developed in this application.

An account of the technique of half-soling is described by P.M. Scott and Kiefner (1984). This consists of welding to the pipeline a curved plate which is concentric with, and extends around, one-half the circumference of the pipe. The half-sole may be cold formed from steel plate or obtained by splitting a segment of pipe longitudinally, the former being the more usual. It is attached to the pipeline by a fillet weld. The technique is used both for leaking and non-leaking defects.

Numerous pipe wrap materials are also available. These are pliable woven material that can be wrapped around the

pipe sealing a leak or preventing one from happening on thin lines until the pipe can be replaced.

21.14 Maintenance of Particular Equipment

The deterioration and failure of equipment, which is dealt with by maintenance, has causes in design and installation as well as operation, and has first to be detected by inspection. The intimate links between maintenance and these other activities may be illustrated by considering the maintenance of some particular types of equipment. OSHA PSM standard 1910.119 (j) Mechanical Integrity requires programs to maintain the integrity of various types of process equipment. These include: pressure vessels, and storage tanks, piping systems including components, relief and vent systems and devices, emergency shut-down systems, controls and pumps. Accounts of maintenance of particular equipment are given in the Standard Plant Operators Manual (Elonka, 1975), Pressure Vessel Systems (Kohan, 1987) Plant Engineers Reference Book (Snow, 1991) and Marks Handbook.

21.14.1 Pressure vessels

The assurance of the integrity of pressure vessels depends largely on inspection and pressure relief. Pressure vessel maintenance and inspection guidance is provide API RP 510: Pressure Vessel Inspection Code, RP 572: Inspection of Pressure Vessels, RP 579: Fitness-for-Service, RP 580: Risk Based Inspection, RP 573: Inspection of Fired Boilers and Heaters, RP 570: Inspection, Repair, Alteration, and Rerating of In-Service Piping Systems.

The maintenance function should maintain a general oversight of pressure vessels, focusing on external corrosion, support defects, stress inducing features, disabled relief protection and disabled instrumentation.

The ancillary features of a pressure vessel should be maintained in good condition. The condition and tension of the bolts on flanged joints should be correctly maintained. The relief system of the vessel should be maintained, as described below.

Where it is necessary to carry our repairs on a pressure vessel, this should be done in accordance with the appropriate codes and systems. In the United States of America, the code is the ASME *Boiler and Pressure Vessel Code*. The National Board of Boiler and Pressure Vessel Inspectors (NB) certifies organizations for the repair of pressure vessels and issues the National Board Inspection Code, which gives guidance on pressure vessel repair. In the United Kingdom, the relevant code is BS 5500.

Some of the problems which may occur in field repairs of pressure vessels by welding are discussed by Kohan (1987). They include: incomplete removal of the defect being repaired; increased stress and distortion; slag inclusions; undercut, overlap and incomplete joint penetration; weld porosity; weld cracks; and unfavourable access and environmental conditions.

Repairs described by Kohan include: pitting repair; repair of wasted or general corroded areas; flush-welded inserts; repair to cracks, including weld cracks and lap cracks; repairs to heat exchangers; repairs to stainless steel; and repairs to dissimilar metals.

21.14.2 Pressure relief devices

Pressure relief systems provide essential protection for pressure systems and much effort goes into their design. This is negated if the relief system is not properly maintained. Guidance on inspection of pressure relief systems is provided in API RP 576: Inspection of Pressure Relief Devices. Accounts of the maintenance of relief systems are given by Anon. (1977 LPB 14, p. 2; 1977 LPB 17, p. 15), Woolfolk and Sanders (1984, 1987), J.K. Rogers (1988) and Duckworth and McGregor (1989). The account by Duckworth and McGregor covers the maintenance of relief devices along with their installation and inspection.

The maintenance of relief devices such as pressure relief valves and bursting discs requires suitable training. Maintenance personnel need to understand the reasons for the use of such devices, the types of device, the methods of installation and the methods of testing. They should appreciate that these are delicate items of equipment and should be treated on a par with, say, instrumentation.

When installing a relief device, attention should be paid to the orientation, the alignment, the gaskets and the bolt torquing. A bursting disc assembly may be rendered useless if it is incorrectly assembled, installed upside down or interfered with by an unsuitable gasket.

Before removing a relief device for testing, a check should be made on its general condition to see whether it has suffered damage or interference, whether it has suffered excessive corrosion or whether there is any process fluid or deposit which could affect its operation. In the shop, inspections should be made as to whether the set pressure is correct and whether there is any wear, damage, corrosion or restriction which could affect its operation. Where relapping of a relief valve seat is required, this should be done on a proprietary lapping machine or a good quality lapping plate.

A large site will generally have a large number and wide variety of types, duties and settings of pressure relief valves. There is considerable potential for incorrect installation. One measure to prevent this is to mark the valve location with a permanent code number and to put the same number on the valve itself.

An account of a program for the maintenance of safety relief valves (SRVs) on a 688-acre site with 20 separate units has been given by Woolfolk and Sanders (1987). The program described covers relief at 2200 locations with valves ranging in size from 1/4 in. to 12 in. and made by 25 different companies. The SRVs are tested, disassembled, cleaned, examined, repaired, lubricated, reassembled, retested and sealed.

The original test equipment utilized a low air volume. The testing of SRVs on this was not satisfactory and it was replaced by a system of larger volume, which proved more suitable. The authors comment that it is sometimes claimed that where an SRV has a bursting disc installed below it, it can be tested *in situ*, but that since the volume between the disc and the valve is small, this is equivalent to the use of a low air volume test system.

In SRV testing, the valve seat usually receives attention to ensure that the valve is leak-tight. Woolfolk and Sanders also place emphasis on the guide area. This should be cleaned, polished and lubricated.

Woolfolk and Sanders give details of the test intervals which they generally use, which are as follows. A 12-month interval is used for boilers (local legal requirement), process vessels with heat sources, vessels containing corrosive chemicals, and positive displacement pumps or compressors; a 24-month interval is used for process steam headers and storage; vessels with no heat sources; and a 36-month interval is used for instrument air manifolds

within dehumidified control rooms and lubricating relief valves on enclosed systems.

Methods have been developed for the *in situ* testing of pressure relief valves, as described by J.K. Rogers (1988). The principle is to overcome the closing force of the valve spring by the application of an external hydraulic force. Then from knowledge of the valve seat area and line pressure at the valve, the set pressure of the valve may be determined. The test can also determine whether the valve has been fully stroked.

A critique of *in situ* testing is given by Woolfolk and Sanders, who express the view that it has limitations where there are aggressive fluids and that it could fail to detect corrosion, partly bent or galled stems, partially plugged nozzles and certain misadjustments.

Some case histories of relief valve maintenance are described by Anon. (1977 LPB 14, p. 2).

21.14.3 Storage tanks

The maintenance of atmospheric storage tanks presents a quite different set of problems. Guidance on inspection of storage tanks is provided in API RP 575: *Inspection of Atmospheric and Low-Pressure Storage Tanks*, RP 653: *Tank Inspection, Repair, Alteration, and Reconstruction*. Accounts are given by Huston (1983) and Shtayieh (1983a,b).

Maintenance of storage tanks often involves entry into the tank. In this case, a large part of the maintenance activity is the purging and cleaning required before entry can be gained. This aspect is described in Section 21.12 and is not, therefore, repeated here.

The ancillary features should be maintained in good condition. In particular, the tank vent system should be maintained by a system similar to that applied to relief valves on pressure vessels.

Most descriptions of storage tank maintenance are concerned with leaks. The case described by Huston involved a storage tank with a leaking floor, a not uncommon occurrence. The identification of leaks, which may be no more than 3/16 in. (5 mm) diameter, is usually difficult due to the poor lighting in the tank and to the state of the tank floor. The author describes a method of improving the detection of the leaks by forcing water under the tank and filling the underside of the floor with water, so that water comes up through the leaks.

An account of leak detection and repair in a refrigerated propane tank is given by Shtayieh (1983b). The tank was of double wall construction with insulation between the inner and outer walls. Monitoring of the gas space between the two walls showed the presence of hydrocarbons at a concentration of 15–20%, indicating the existence of leaks. A thermographic survey was carried out on the outside wall which showed two cold spots at a temperature 35°F (1.5°C) lower than the rest of the wall. The tank was entered and eventually leaks were found. The main leak was on a manhole, where there was a faulty gasket and a badly machined blind flange gasket face and cover. There were two lesser leaks at the two 2 in. diameter nozzles of the level indicator, due again to damaged flanges. No leaks were found at the points suggested by the thermography. This example demonstrates the trouble caused by deficiencies in common installation activities, in this case the making up of flanges.

21.14.4 Ammonia storage spheres

The occurrence of stress corrosion cracking in ammonia storage spheres has created a considerable problem in the maintenance of such storages. Accounts are given by R.S. Brown (1982) and Guth and Clark (1985). They illustrate both the procedures for isolation, emptying, purging and entry, and for bringing back on stream for such storages and the procedures for inspection and repair. This work is discussed further in Chapter 22.

21.14.5 Heat exchangers

Heat exchangers are pressure vessels, but in addition their maintenance is affected by certain characteristic features of their own. Accounts are given by Yokell (1983) and Fijas (1989).

Where a heat exchanger is delivered to a construction site and is left in the open for sometime before it is installed, it may well suffer deterioration even before it begins operation. In order to avoid this, it should be stored carefully before installation and its surfaces cleaned periodically. The necessary measures are described by Fijas.

Heat exchanger tubes are liable to leak or even rupture and these faults may be induced by maintenance activities. One such activity is tube bundle withdrawal. There should be procedures for bundle withdrawal. The bundle should be supported on the tube sheets, baffles or blocks contoured to the bundle, but not on the tubes themselves.

It is usually necessary to clean the tubes to remove scale. If cleaning is deferred too long, maldistribution may occur in some tubes and the resultant differential thermal expansion of these tubes can cause damage and leaks.

Methods of cleaning heat exchangers are described by Fijas. Soft deposits may often be removed from the shell or tube sides of a heat exchanger by washing with hot oil and soft salt deposits by washing with hot fresh water. More stubborn deposits may be removed by chemical cleaning. He recommends against cleaning tubes by blowing steam through them, since it is liable to cause overheating and thermal expansion and thus induce tube leaks. Nor should tubes be hammered with a metallic tool. If they must be scraped, the tool should not be sharp enough to cut them.

Heat exchanger tubes are subject to vibration, which is liable to cause leaks. One cause of tube vibration is operation at too high a fluid velocity. Another is vibrations transmitted from a pump or compressor. A pulsation damper may be used to reduce vibrations from such a source.

When starting up and shutting down a steam heated exchanger, condensate should be drained out as a precaution against water hammer. If shut-down is at all prolonged, it may be necessary to drain the fluids from the exchanger to prevent freezing or corrosion.

21.14.6 Equipment supports

Equipment supports provide another illustration of the interaction between design, inspection and repair. An account of the maintenance of such supports is given by B.N. Pritchard (1983). The types of support which he considers are concrete supports and steel supports fireproofed by encasing them in concrete. Causes of deterioration include corrosion, overstressing, frost damage and also fire or explosion.

Concrete protects buried steel against corrosion partly by constituting a physical barrier to oxygen and moisture and partly by passivation of the steel by water made alkaline by the concrete. This latter effect decreases as the alkalinity falls off.

If the steel under the concrete does corrode, corrosion products are formed which have eight times the volume of the steel which they replace. This creates stresses which result in cracking and spalling of the concrete.

The author reviews the effects on the corrosion of steel encased in concrete of chlorides, sulfates and acids. In rare cases it may be promoted by a cement aggregate reaction.

Corrosion of steel encased in concrete may be reduced by: the use of dense concrete; good steel – concrete bonding; shaping the concrete so as to exclude rainwater, or the use of rainwater flashings; and the application of a suitable coating to the outside of the concrete. The author states that for fireproofing cast *in situ* concrete appears superior to gunnite, though the reason is unclear.

Paint applied to the steel provides a degree of protection not only for bare steel but also for steel encased in concrete or provided with lightweight fire-proofing.

Corrosion occurring inside the concrete casing may be detected by visual examination, and also by tapping. In general, hairline cracks are tolerable but stained cracks may indicate a more serious situation. For certain cases, the use of more sophisticated inspection may be justified. Early detection is highly desirable. Suitable timings for inspection are at 1 year after commissioning or after a material change of duty or environment, and at 4 year intervals thereafter. Formal records should be kept of the supports and their inspection.

Factors which govern the repair of supports are the features which have caused the deterioration, the further deterioration expected, the effects of the damage on the structure, the importance of the structure, the operating history of the equipment and the cost of repairs. The repairs should incorporate measures to remove the causes of the deterioration. Repair techniques include the sealing of cracks, cutting back to sound concrete and cutting back to the steel. Temporary supports may be necessary while repairs are being completed.

21.14.7 Foundations and dikes

Foundations and dikes also may require repair. Accounts of the repair of foundations are given by Renfro (1978, 1979). Containments are discussed by Hazen (1991).

21.15 Equipment Removal

The removal of equipment from the unit to the shop can create a hazard if flammable or toxic material are trapped inside it. It is necessary to have some procedure to deal with this problem.

21.15.1 Unused equipment

Equipment which is installed but is no longer required should normally be removed. This applies to all kinds of equipment whether it be vessels, pumps, pipes, instruments, etc. Unused and often disconnected equipment is a fertile source of accidents.

21.15.2 Equipment sent off site

Where equipment is sent away from the plant, whether for repair or because it is no longer required, the state of the equipment should be reviewed, any hazard identified and appropriate measures taken. In particular, there is the potential hazard that equipment may still contain residues of flammable or toxic material. Equipment should be tagged indicting its prior usage and potential hazards.

21.16 Deteriorated Equipment

The equipment on the plant starts to deteriorate from the first day of operation, and sometimes earlier if it has been neglected prior to installation. As the plant ages, it becomes necessary to take a view on the continued operation of some equipment.

21.16.1 Remaining life assessment

Some equipment is designed to have a limited life. The prime example here is equipment with a limited creep life. Creep is described in Chapter 12 and the shortening of creep life by abuse during operation is discussed in Chapter 20. Where there is reason to think that the latter has occurred, it may be necessary to attempt an assessment of the remaining life.

Another major form of deterioration is corrosion and, insofar as a particular corrosion allowance is made, in this case also the design implies a limit to the life of the equipment. The possibility of periods of corrosion at rates much higher than average means that here too there is a need for life assessment.

The assessment of the remaining useful life of equipment, or the remaining life assessment (RLA), is an established activity. API RP 579 provides guidance on evaluating the present integrity of the equipment and the projected remaining life. RLA is described by Baker-Counsell (1987b) and Grosshandler (1987a). If the equipment is nearing the end of its life, RLA provides the necessary wanting, while if it still has an appreciable fraction of its life left, the RLA provides assurance that it can continue in operation.

Much work in RLA is concerned with creep effects. Some techniques used are metallography, strain measurement, accelerated creep testing and stress analysis. The results of RLA may be expressed as a cumulative probability of failure, which allows the company to make its own judgement on how much longer to continue to operate the equipment.

A specific example of the application of RLA to corrosion of a pressure vessel and its nozzle is described by Grosshandler (1987a). Further accounts of obsolescence include those of Munro (1963) and Baas and Warner (1992), who describe the assessment of the remaining useful life of an ethylene plant.

21.16.2 Used equipment

The situation can arise where it is necessary to consider either the purchase or the sale of used equipment. Some of the considerations which arise have been described by J.P. Epstein (1967, 1978) and C. Butcher (1992d).

For purchase, three approaches may be taken: purchase 'as is', on approval, and rebuilt and guaranteed. Most equipment is bought 'as is'.

When purchasing equipment, inspections should be made on: the dimensions of equipment; the pressure integrity of pressure vessels; the wear sustained by moving parts of machinery; any ancillary equipment; and conformance to any regulatory requirements. Useful information can often be obtained by inspecting the equipment while it is still on site and in use. Equipment allowed to stand idle even for a short time can deteriorate or take on a bad appearance.

Specialist companies exist which deal with used equipment and it may be beneficial to use their expertise.

21.16.3 Fire damaged equipment

In the aftermath of a large fire, there may be equipment which has been in the fire. The question then arises as to the

continued safe use of the equipment. In all such cases an inspection should be made. Pressure system integrity is of particular importance and should be investigated by experts.

A case history of the assessment of fire damage of a vessel is described by Dooner (1986). The vessel was to be used in a low temperature application down to −196°C. It had been in a fire which lasted some 2 hours and subject to an estimated temperature in the range 400−600°C. A metallurgical investigation showed that no significant deterioration had occurred and the vessel was put into service.

21.17 Some Maintenance Problems

21.17.1 Materials identification

Misidentification of materials is a significant problem. Mention has already been made in Chapter 19 of errors during the construction and commissioning stages, particularly in the materials used in piping. Materials errors also occur in maintenance work. Situations in which they are particularly likely are those where materials look alike, for example low alloy steel and mild steel, or stainless steel and aluminium painted steel. It is necessary, therefore, to exercise careful control of materials. Methods of reducing errors include marking, segregation and spot inspections.

Positive Material Identification efforts have been used on piping systems. It is not uncommon to find that 20% of the components are not the proper material.

21.17.2 Component identification

Another problem is mistakes in identifying components or equipments. Confusion can arise, for example, over pressure relief valve components, with the result that a relief valve may be put back with too high a setting. This type of error can readily occur with similar components made by the same manufacturer. Similarly, it is easy for blinds to become mixed up so that a slip blind suitable only for a low pressure duty is used on a high pressure application.

A particular type of component identification error is installing a component that alters equipment performance. Thus, the capacity of a control valve may be increased by putting in the wrong trim, or the delivery pressure of a pump may be increased by installing the wrong impeller.

21.17.3 External corrosion

External corrosion beneath insulation is a considerable problem on process equipment. It has already been described in Chapter 12. It is important that the maintenance system should check on external corrosion.

Such corrosion occurs particularly on steel equipment in the temperature range 32−257°F (0−125°C). Below 0°C, the surface is protected by ice, while over 125°C water evaporates. Use of types of mineral wool insulation that are acidic can exacerbate the problem.

There are various forms of corrosion which can occur due to agents other than water. Chloride attack occurs from chlorides which are leached out of some insulation materials. It can also arise from thermal decomposition of polyvinyl chloride (PVC) labels on very hot pipe surfaces. Nitrate attack arises from the use of nitrite treated water on equipment surfaces.

Supports for storage tanks and vessels are a common site of external corrosion.

21.17.4 Pumps and other equipments

Pumps are the source of a large proportion of leaks and fires. A common fault is seal failure with resultant leakage. The leakage often ignites and causes a pump fire. Another frequent fault is a bearing failure, which can induce a seal failure. After a pump fire it is not always easy to tell whether the seal or bearing has failed first.

Reduction of pump failures is partly a matter of design and selection, but maintenance aspects are also important. Many faults can be prevented by a careful overall check when a pump is taken out for other maintenance work.

In addition, it is not uncommon for faults to be introduced in the course of maintenance work. A simple example is misalignment of the impeller shaft when the pump is reassembled. Faults of this kind point to the need for proper systems of work for maintenance and for adequate training. Similar problems arise with other types of equipment.

21.17.5 Small bore connections

Small bore connections are another source of leaks and fires. Such connections are often abused. Heavy pressure gauges or valves may be fitted to them without adequate support. They are frequently over tightened, sometimes with a pipe wrench. People may stand on them to reach isolation valves.

21.17.6 Dead legs

Dead legs in piping systems are where no flow occurs. This can lead to internal corrosion from stagnation or freezing during inclement weather causing leakage. Dead legs should be removed.

21.18 Major Shut-Downs

Two particular kinds of shut-down merit specific mention. These are major scheduled shut-downs and mothballed shut-downs.

21.18.1 Scheduled shut-downs

Most units require a periodic major scheduled shut-down, or turnaround, in order to carry out maintenance and other jobs which cannot be done while the unit is operating. Accounts of turnarounds are given by Vargas (1979), Tropp (1986) and Feuless and Madhaven (1988).

The turnaround arrangements described are broadly as follows. The responsibility for the turnaround is assigned to a turnaround manager. The turnaround passes through four stages: (1) formulation, (2) planning, (3) implementation or execution and (4) start-up.

In the formulation stage, the turnaround manager solicits job requests from the interested parties. Each job is defined, given a priority rating and assigned to a person who is responsible for it. Three levels of priority may be used: (1) the job can be done only during turnaround and has high priority; (2) the job can only be done during turnaround, but is not critical; and (3) the job can, if necessary, be done outside turnaround. The responsibilities for the total set of jobs are spread widely, but for each job there is only one person responsible. A deadline is set a few weeks before the turnaround start date, and thereafter only priority jobs are accepted. A master job list is drawn up and a critical path network developed for each job. The parts and special tools required for each job are identified and the

process is begun of obtaining them and transferring them to the tool room or warehouse storage.

Tropp (1986) states that the two faults to which turnarounds are most subject are unsuitable assignment of responsibilities and inadequate exchange of information. The normal roles which people play are often not appropriate to a turnaround. Failure to recognize this is a main cause of communication failures.

He describes a system of categorization of jobs by logical, chronological and priority groups. With regard to the first two, the logical group covers categories such as time, information, safety, manpower, materials, tools, etc., and the chronological group covers those of preparation, implementation and review. He gives detailed responsibility charts for the preparation and implementation stages. Entries in the chart are R, I, C and N for responsible, implement, consult and notify, respectively.

In the planning stage, the overall critical path network is developed together with a bar chart showing the start and end time of each job and the personnel required. A manpower requirements list is drawn up. Computer aids are available to assist in such planning. The plan needs to be flexible and able to accommodate unexpected jobs. Work continues to ensure that the parts and tools required are moved to storage and a parts review is carried out to ensure that nothing is missing.

Throughout the formulation and planning stages, there should be meetings to ensure that all interested personnel understand their role and make an appropriate contribution to the plan.

The job times should be the subject of detailed review by planners/estimators. Planning norms or a library of time estimates may be used. In estimating job, times allowance should be made for the fact that the time spent on turnaround jobs tends to be rather longer than that spent on equivalent routine jobs, and the fact that time is required to obtain materials, to purge and clean, and to await supporting functions such as safety or inspection.

Some of the worksheets developed are illustrated by Vargas (1979) and Feuless and Madhaven (1988). The former also gives a detailed account of the critical path scheduling.

The management of the implementation stage needs to be sufficiently flexible to accommodate the facts that some jobs may reveal problems, that some may take longer than planned, or require parts other than those expected, or that some completely new jobs may need to be done. It is not uncommon for 25% of the jobs done in a turnaround to be identified during execution. A meeting of those concerned is normally held daily to report progress and to modify plans as necessary.

There needs to be a procedure for dealing with those cases where the parts or materials specified are not available and the use of some alternative is proposed. Management of change procedures must be followed. For example, piping in some special steel may be on too long a delivery and there may be an intention to use a substitute material, or the type of pressure transducer specified may be unavailable but another type may be used which is equivalent.

The purpose of the turnaround is to get the work completed and the unit started up again. The emphasis, therefore, should be on the start-up, rather than simply completion of the turnaround.

When the start-up is over, the personnel involved should be debriefed and a report written while matters are still fresh in the mind. In particular, note should be made of times actually taken and the resources used for various jobs and activities, of problems encountered, equipment required, techniques developed or lessons learned, and of jobs which will need to be done in the next turnaround.

As soon as the turnaround is over, preparation for the next one should begin. Many of the jobs for the next turnaround will be based on the work just completed.

21.18.2 Mothballed shut-downs

During an economic recession, the decision may be made to take a unit out of commission and to 'mothball' it, with the intent to recommission it when times are better. Accounts of mothballing, and de-mothballing, are given by Twigg (1985), R.G. Miller and King (1987) and Savage, Portnoy and Parkinson (1988).

Mothballing is applied to a variety of installations and equipment, including oil field production systems, refineries, chemical plants, drilling rigs, oil tankers and special equipment. It is much used for military equipment, including vehicles, ships and aircraft.

The mothballing of entire plants or units is not an exercise to be undertaken lightly and the alternatives of selling or scrapping it should be carefully considered. The circumstances which make decommissioning necessary are attended by a number of problems. Personnel may well be somewhat demoralized. There is uncertainty as to how long the plant will be out of action. There is likely to be pressure to do a cheap job. The staff concerned will generally lack experience of laying up a full installation. The compilation of a complete set of documentation for the equipment is an unattractive chore.

There are a number of factors that affect the way in which the mothballing is done. The length of the shut-down is relevant, since the measures required to preserve the equipment for a few months differ from those required preserving it for 10 years, but is often unknown. The location affects factors such as the climatic conditions and vandalism. A hot, humid site promotes corrosion. A run-down urban area is more prone to theft and damage by outsiders. Some fluids such as seawater and sour gas are more corrosive and some materials of construction such as stainless steel have particular vulnerabilities.

It may not be appropriate to mothball every item. Some items of equipment and much instrumentation are particularly prone to obsolescence. For other items, such as small bore piping and valves, it may be more economic to let them go and replace them when the unit is recommissioned.

There are a number of methods used to guard the equipment against corrosion and other deterioration while it is mothballed. Items of equipment may be removed from the unit and stored after suitable treatment in a warehouse. Measures may be taken to ensure that the fluids in the equipment are benign. Examples are replacing seawater by fresh water, purging with nitrogen and adding an inhibitor to condition vapours. The equipment can be isolated from its environment by the use of various forms of barrier such as: paint, greases and waxes, boxes or bags, or cocoons. Other anticorrosion measures may be taken, such as the use of cathodic protection. Some parts of the unit may be kept in continued operation and some items may be periodically stroked or rotated, as the case may be. Methods particularly favoured by the military are the use of greases and waxes, and of cocooning.

Corrosion is liable to be much higher during a prolonged shut-down than in normal operation. R.G. Miller and King (1987) contrast a storage tank corrosion loss of 3 mpy (thousandths of an inch per year) in normal operation with one of 100 mpy in the shut-down condition, with an associated change from general to pitting corrosion. Corrosion may be worst in summer as warm air is driven out of equipment during the day and cold air with high humidity is drawn back in at night.

Cooling water systems can be troublesome unless suitable precautions are taken. Failure to protect adequately can result in rust and scale blocking of the tubes of heat exchangers all over the plant for months, or even years, after restart.

One form of internal corrosion which often occurs is microbiological corrosion. Precautions against this involve the use of good quality water and of organic biocides. Chlorination of the water tends to be ineffective.

If equipment becomes severely corroded, the penalty can be high. A case is quoted by Miller and King where breaking the line at a spool piece with corroded bolts took a team of 5 men using heavy equipment 5 days.

Two widely used methods of reducing corrosion are the use of dry inert atmospheres in vessels and the coating of surfaces with oil. Corrosion is reduced by the exclusion of oxygen, and filling vessels with nitrogen is an effective anticorrosion measure. The gas should be dry, with a dew point at least 40°F (5°C) below that of the lowest expected ambient temperature.

Oils or oil-based products can be used to reduce corrosion. Refinery equipment is frequently protected by filling it with oil and then running the oil out again. The thin film of oil gives protection until it eventually drains down. Alternatively, surfaces may be coated in oil or grease. Small items may be dipped in oil. Vapour phase inhibitors may be used for areas which are not readily wetted by oils.

The type of protection provided against corrosion may be matched to the intended period of shut-down, if this is known. Twigg suggests that for short period shut-downs, it may often be sufficient to flush and drain, while for longer ones greasing or painting may be necessary. Similarly, Miller and King suggest that for some equipment washing down and coating with diesel oil may suffice for a shut-down of 18 months, while shot blasting and painting may be preferable for one lasting 5 years.

External corrosion is liable to occur under insulation and on equipment supports. Features which promote such corrosion are damage to the insulation and chlorides from the insulation. One policy sometimes adopted to combat external corrosion during mothballing is to remove the insulation completely. Alternatively, if the insulation is not removed, any damage to it should be made good and it should be sealed.

Cocooning involves the use of strippable plastic coatings and gives an enclosure not dissimilar to vacuum packing. It can be very effective provided that moisture is excluded but moisture can pass through due to the breathing of the membranes and corrosion can occur unless the dew point of the air inside is kept low. The coatings have a tendency to come off in high winds.

Valves left unused for long periods are liable to seize up due to the hardening of lubricants. One solution is to remove them to store. Another is to leave them in but maintain and operate them occasionally.

Some parts of the unit may best be preserved by operating them periodically. Savage, Portnoy and Parkinson (1988) describe the preservation of a cooling system by running a high chromate solution through the system once every 2 weeks throughout the mothball period.

Rotating equipment should be turned at intervals to avoid 'brinelling'. Frequencies recommended are typically in the range 1–6 months, depending on the type of bearings.

Cannibalization of the plant or units should not be permitted. Where there is a protective envelope, breaking in can negate it and lead to severe corrosion. The loss of parts is liable to be disproportionately disruptive when the time comes to recommission the equipment. Moreover, when equipment is removed in this way, damage is frequently done to other items.

The mothballing of equipment does not remove the need to inspect and maintain, or even to operate parts of it. Inspection is still required, but the techniques involved are somewhat different. There is also a need for some degree of maintenance.

A full set of documentation on the plant, and on its operating and maintenance procedures, needs to be compiled. Such documentation is necessary for any equipment, but it is crucial for one which is to be recommissioned at some date in the future by personnel who are likely to be unfamiliar with it. The documentation should include full details of the mothballing itself, of any items removed from the unit and the state of the remaining equipment.

The methods of protection used in mothballing may also be applicable where equipment arrives on site but cannot be installed immediately. Heat exchangers, in particular, are prone to deteriorate rapidly if left unprotected prior to installation.

The problems which arise when demand turns up and de-mothballing can be considered are discussed by Savage, Portnoy and Parkinson. Again, there are often alternatives such as debottlenecking and revamping existing units or building new units, and in view of the problems likely to be encountered in recommissioning, these should be given full consideration. If recommissioning is decided on it may well be combined with modifications to the equipment to achieve better product quality, higher output or improved efficiency. A prerequisite for recommissioning is the retrieval of a full set of documentation on the equipment.

Some items or systems are likely to have suffered considerable deterioration. Some equipment, such as valves, may well need to be reconditioned and some, such as small bore piping, may need to be replaced. Other equipment may need replacement due to obsolescence, which is particularly rapid in some instances, such as the instrument systems, including computers.

It will be apparent from the account just given that in addition to all the usual measures necessary for a commissioning, a recommissioning after mothballing needs to be preceded by an extremely thorough inspection of the equipment and review of the documentation if hazards are to be minimized.

21.19 Maintenance Information Systems

21.19.1 Maintenance information system

Information on equipment failures, repairs, and incidents is needed both for maintenance and safety and loss

prevention (SLP) purposes. It should be a specific objective of the maintenance system to generate such information.

The principal data required are those for failure, repair and availability. The data are more valuable if they are of good quality. Failure data should preferably give for each equipment the time to failure in each failure mode rather than overall failure rates. Availability data should give throughput density rather than a single downtime figure. There are also other data which are needed. These include data on leaks and fires and on human errors.

Data on failure and related aspects are essential to the loss prevention approach. The maintenance engineer, therefore, has a crucial role to play here. They should make it their business to have an information system which generates the data. Such data are equally useful, of course, to the maintenance engineer. They normally monitor failures and failure modes at least in a semi-quantitative way, but if higher quality data is available they can analyse it to obtain additional information. Thus an early failure (Weibull parameter, $\beta < 1$) may point to the need for better supervision or training of maintenance workers or for the work to be done under less dirty conditions, while wear out failure ($\beta > 1$) may indicate the possibility of preventive replacement.

21.19.2 Maintenance information feedback

The requirement for failure data is one aspect of the more general need for feedback of information from the maintenance to the design function. This is the theme of terotechnology, which is discussed in relation to maintenance by Husband (1976). Again the maintenance engineer can play a key role in ensuring effective feedback of information and so reducing unreliable and hazardous features, and he should make this a definite objective.

21.19.3 Maintenance policies and effectiveness

The maintenance policies which are followed in a process plant can have a marked influence on its reliability, and availability, and hence its safety and economics. There is, however, no universally applicable policy. The policy appropriate in a given case depends on the failure pattern and the overall situation. Traditional policies have been based on breakdown maintenance and/or scheduled maintenance, and also opportunity maintenance, which are supplemented increasingly by on-condition maintenance and reliability-centred maintenance.

The effectiveness of the maintenance should be monitored using measures suitable for the policy adopted. Maintenance policies and effectiveness have been discussed in more detail in Chapter 7.

21.19.4 Maintenance of protective devices

Maintenance of the protective devices on the equipment is particularly important and should be covered by a formal system with full documentation.

Some of the principal protective devices are:

(1) pressure relief valves;
(2) bursting discs;
(3) tank vents and filters;
(4) other pressure relief devices;
(5) non-return valves;
(6) mechanical trips and governors;
(7) instrument trips;
(8) other instrumentation;
(9) alarm systems;
(10) fire and gas detection systems;
(11) sprinkler systems;
(12) fire water systems.

This list includes not only the more obvious protective devices, such as pressure relief valves, but also some other critical items which are not always thought of as protective devices, such as tank vents.

The maintenance of instrument trip systems is very important. The design of such systems is based on the assumption of proof testing at fixed intervals and is invalidated if this is not done correctly.

It is also important that the other instrumentation be maintained to a high standard. If the general instrument system is allowed to degrade with numerous incorrect measurements, false alarms and control loops on manual, the probability of control errors is greatly increased.

Fire protection equipment should be well maintained so that it is available when required. There have been many instances where equipment has failed to operate, often with serious consequences. Maintenance of such equipment is dealt with in NFPA 25: *Inspection, Testing and Maintenance of Water-Based Fire Protection Systems*.

21.20 Spares Inventory

The control of the spares inventory, or stock control, is of particular importance on process equipments, where the cost of downtime is generally very high. Accounts are given by Alford (1965), Corder (1976), Husband (1976), A. Kelly and Harris (1978), Vargas (1980b) and D.J. Smith (1985a). Generally, the proportion of management effort devoted to spares inventory control is small relative to that given to control of the workforce.

21.20.1 Spares holdings

Policy on the spare parts to be held in stock has to be a compromise between holding a large number of parts in an attempt to provide for virtually every contingency and holding only a small number in order to keep holding costs down. Some studies of maintenance systems have highlighted spares, or lack of them, as the main problem faced by the maintenance function.

Standard methods of stock control are the maximum–minimum level and the economical order quantity methods. The former sets minimum and maximum stock levels together with a reorder level. The economical order quantity for an item is given by the relation

$$Q = (2RP/H)^{1/2} \qquad [21.20.1]$$

where H is the annual cost of holding the item, P is the cost of procuring it, Q is the optimal order quantity and R is the annual requirement. This formula takes no account of the criticality of the item, the lead time for its delivery or of the relationship between the item and other items.

The methods of reliability engineering may in certain cases be used to determine the spares holdings. Some reliability models which may be used for this purpose are described by D.J. Smith (1985a). For an equipment which has n identical parts and a spares holding of r parts and for which the failure rate of these parts is known, the Poisson distribution may be used to determine the probability that over a specified period a situation will arise where the

spares have run out. This model assumes that the equipment is a series system with respect to the n parts; it does not take account of any redundancy in the equipment involving some of the n parts or of the time to replace a part. These and other features may, however, be taken into account by the use of Markov models.

It is concluded by Husband that the soundest approach to the use of models may often be to base the holding on Pareto analysis of the main relevant features such as usage, criticality, lead time and cost.

Guidance on spares holdings may be available from the equipment manufacturer in the form of a recommended list of parts to maintain the equipment for a specified period. Such a list will generally be based on the manufacturer's experience and judgement. It may also utilize information on the number of parts which have been supplied to users on request. This information is hard data, but is liable to be incomplete, because many parts are either ordered from other suppliers or fabricated by the user company itself. It may well be, therefore, that better information even on the frequency of demand for particular parts is generated by the maintenance function itself. Certainly, maintenance is in a better position to assess the criticality of items and the lead times.

The level of spares will be affected by the degree of standardization. Indeed, it is a principal aim of standardization to reduce spares holdings.

Another feature affecting spares holdings is the least replaceable assembly. This is the module or part at which during maintenance the process of fault diagnosis terminates and a replacement is made.

Some of the factors relevant to the setting of spares holdings which are unique to a single equipment are the tolerable unavailability of the equipment, the failure frequency of the parts, the lead time and the costs of the parts.

Where spares are common to a number of equipments, the situation may become either more complex or simpler. If the number of other equipments is small and the failure frequency of the parts is low, it may be necessary to consider the set of equipments as a whole and the interaction between them. But if the frequency of demand for the parts becomes high, the simpler treatments such as the Poisson model may well become applicable.

Many accounts of spare holdings treat the demand for spares as a random process. In fact, where preventive maintenance (PM) is practiced, the demand for spares for PM work is more predictable. PM will also identify cases where parts will be needed in the near future.

Management should assess the need to hold slow-moving but critical items, and unjustified pressure to reduce the holding of such an item should be resisted. It may be possible to quantify the probability of requiring such an item and of not having it in stock and the consequences and costs of such a situation. But in any event it may be regarded as an insurance spare.

The spares holdings will be strongly affected by the extent to which a 'just-in-time' policy is practiced. While, in principle, many of the factors just described still apply, the actual values of the optimum spares holdings may be appreciably different.

21.20.2 Stores organization

Features of the spares organization are the stores layout, the stores documentation, the coding system, policies on aspects such as used parts and cannibalization of parts and access to the store. An explicit policy should be formulated for the stores and their organization.

Equipment spares may be grouped either by equipment or by common items, the latter being common to a number of plant equipment, for example bearings and seals. The system may well be a hybrid. There are three main types of item held in a store: equipment spares, consumables and tools.

The stores documentation should be designed to implement the stores policy. An account of typical stores records is given by Corder (1976). Since the use of computer systems is virtually universal in maintenance, the documentation must be compatible.

The system for coding of items is liable to become extremely cumbersome unless it is well designed. Corder gives the example of a bearing made by three bearing manufacturers and installed in the machines of six machine manufacturers, which then may well have 18 different code numbers. He discusses the method of classification and coding designed to overcome this.

It is necessary to establish a policy with respect to used parts. Parts may be reconditioned and returned to the store, but the mixing of used and deteriorated parts with new or as-new parts is not good practice.

A policy is also required on cannibalization. This can be extremely disruptive, which is an argument for prohibiting it. On the other hand, situations are likely to arise where a rigid ban could not only be very costly but could bring the policy into disrepute. It may be judged preferable to have a policy to control it.

Access to the store should be controlled, but in some cases it is policy to provide an open store with free access for minor items, where the cost of wastage is less than that of the control paperwork.

Materials for a major project should be treated separately from those for normal maintenance. Failure to do this can cause considerable disruption to the maintenance spares inventory. In this context a turnaround may count as a major project requiring its own dedicated store, as already described.

21.21 Computer Systems

The use of some form of computer system is virtually universal for maintenance systems on process equipment. Accounts are given by Trotter (1979), Redding (1980), McChrystal (1982), Collington (1989) and Project Software and Development Inc. (PSDI, 1991) and M. Taylor (1991).

Some functions which a computer-based maintenance information system may perform include (1) work orders, (2) planning and scheduling, (3) failure analysis, (4) cost and (5) budget.

Many computer-based systems have started as accounting systems dealing with the costs of maintenance work. Such systems may or may not adapt readily to a wider variety of functions. The constraints which may be posed by an existing system are not considered further here. The maintenance system will link closely with the accounting system.

Another system with which the maintenance system should link, and with which it may well be integrated, is the system for equipment inspection and inspection records.

The design of a computer-based system should start by trying to ensure that the source of data fed to it is of high quality. This is both important and difficult. The people who have most of the information required are

the maintenance craftsmen. The problem has traditionally been that these craftsmen are reluctant to spend time on paperwork.

With a manual system, it is difficult to give maintenance personnel much incentive to furnish high quality information. A computer-based system, however, does provide the means of offering such an incentive by creating a system where they have access to information which is useful to them.

The basic building element of a computer-based system, as of a manual one, is the work order. Work orders for regular jobs can be held and orders for new jobs entered. The work order for a particular job will generally contain a wide range of information such as resources (labour and equipment, spares, timing and costs). This provides the basic data for the other features of the system.

Closely linked with the work order is the detailed plan for performing the work. The system facilitates the generation of job plans which give a complete description of the work to be done. This makes it easier to ensure that nothing is missed and that even small issues are corrected before they escalate.

A computer-based system is a natural tool for the planning and scheduling of the work orders. This includes orders both for breakdown maintenance and for PM. Resources such as labour and equipment can be scheduled. Work can be held until material is on-site. Schedules can be developed to accommodate backlogs and priorities.

Failure analysis is another widely utilized function, but the meanings attached to this term vary. It may involve an analysis of the causes, frequency and cost of repairs. Or it may extend to more sophisticated analyses such as Weibull analysis to determine the failure regime.

As already mentioned, cost was one of the first functions. There are a variety of features which come under this heading. Basic features include the cost of labour and parts. For routine jobs, standard cost estimates may be used. More advanced cost features include the handling of depreciation and assisting decisions on repair vs replacement.

Budgetary control is a standard feature, which facilitates not only determination of the budget for some forthcoming period, but control of day-to-day expenditure.

It may be advantageous to order items in a hierarchy within the system so that an overview can be obtained not only of basic elements but also of aggregations which constitute complete equipments or plant functions.

There are a number of pitfalls in the implementation of a computer-based system. One is the input of the initial data. One strategy to ease this task is to identify critical features and enter them, and then to build up the rest as particular jobs arise.

Experience of computer-based systems indicates a number of beneficial effects. One is that effort is freed so that more attention can be devoted to planning and to preventive work. A simple example cited is a reduction in the ratio of breakdown to PM jobs from 0 : 1 to 2.5 : 1. The reduction in the proportion of breakdown jobs means that the maintenance function gets more on top of its work and enters a virtuous circle. As preventive work becomes relatively more prevalent, the timing of such work becomes less critical, since the equipment is a better state of maintenance.

Another important benefit is in increase in the credibility of the maintenance function, because the data is available to support reliable operation. Improved relations with the operations function is another gain, signalled when production take the initiative in asking for equipment to be included in the PM schedule. More generally, an effective computer-based maintenance system becomes an important resource for many other functions, notably those of design and SLP.

The use of a computer-based system to handle the problem of a half-yearly PM whose schedule has slipped is outlined by Collington (1989). He describes in effect the creation of a form of expert system to assist with the current and future decisions.

A description of a particular computer-based system for an LPG terminal has been given by the PSDI (1991).

21.22 Modifications to Equipment

Some work goes beyond mere maintenance and constitutes modification or change. Such modification involves a change in the equipment and/or process and can introduce a hazard. The outstanding example of this is the Flixborough disaster. The Flixborout Report (R.J. Parker, 1975, para. 209) states: 'The disaster was caused by the introduction into a well designed and constructed plant of a modification, which destroyed its integrity'.

It is essential, for there to be a system of identifying and controlling changes. Changes may be made to the equipment or the process, or both. It is primarily equipment changes which are discussed here, but some consideration is given to the latter.

OSHA PSM 1910.119 (l) requires a written program to manage changes to process chemicals, technology, equipment, procedures and facilities. OSHA PSM 1910.119 (i) also requires a pre-start-up safety review. The control of plant expansions is dealt with in *Major Hazards. Memorandum of Guidance on Extensions to Existing Chemical Plant Introducing a Major Hazard* (BCISC, 1972/11). The hazards of equipment modification and systems for their control are discussed by, Henderson and Kletz (1976) and by Heron (1976). Selected references on equipment modification are given in Table 21.4.

21.22.1 Types of changes

Changes may be classified according to the stage at which they are made:

(1) design;
(2) commissioning;

Table 21.4 *Selected references on equipment modification*

IChemE (1966/43, 1985/125); FPA (1970/10, 11); K. Wood (1971); BCISC (1972/11); Booth (1976); Cannon (1976); Henderson and Kletz (1976); Heron (1976); Kletz (1976l, 1982l, 1984d, 1985g, 1991d); W.W. Russell (1976); Anon. (1980 LPB 34, p. 1); van den Berg *et al.* (1980); R.E. Sanders (1983, 1992, 1993b); Wang and Patel (1984); Baker-Counsell (1985e); Sha and Bohlinsky (1985); Speedie (1985); MacFarlane (1986); R. Atkinson (1987); Eishout and Kilstrom (1988); Kesler (1988); Ramsay (1990); Tian and Wang (1990); Anon. (1994 LPB 119, p. 17); Anon. (1994 LPB 120, p. 13); Turney (1994 LPB 120)
Modification chains: Kletz (1986f)
Plant retrofitting, updating: NRC (Appendix 28 Retrofitting); Kletz (1981e,h)

(3) operating.

They may be distinguished by the degree of permanence:

(1) temporary;
(2) permanent.

These different situations tend to have their own characteristic hazards. Some of these are illustrated by *Case Histories* B52–B56.

Changes made during the design process really fall outside the present discussion, which is mainly concerned with the stages of commissioning and operation. It is sufficient here to re-emphasize the points already made concerning the need to ensure that at the design stage there is an adequate system of identifying and documenting any changes made. The commissioning stage, and the immediately preceding pre-commissioning stage, is often a period when large numbers of changes are made, frequently under intense pressure. Commissioning changes tend to be aimed at making the equipment work. In the operations stage, the object is rather to keep the equipment going. But again changes may be done under considerable stress.

The scale of changes and the level at which expenditure is approved vary greatly. At one extreme there are minor changes with minimal approval but documentation required by the individual making the change. At the other end are changes requiring approval by senior management. For major changes, project approval is required to control costs and change approval is required to ensure safety. All changes must be managed properly.

21.22.2 Pressure relief and blowdown hazards

A major hazard which is liable to arise as a result of change and one which is particularly dangerous is the pressure relief and blowdown invalidation. Some illustrations of the way in which this can occur have been given by Henderson and Kletz (1994) and are shown in Figures 21.9–21.11. The situations are self-explanatory.

Another type of change is the de-rating of a equipment to a lower operating pressure. In this case, while the need to

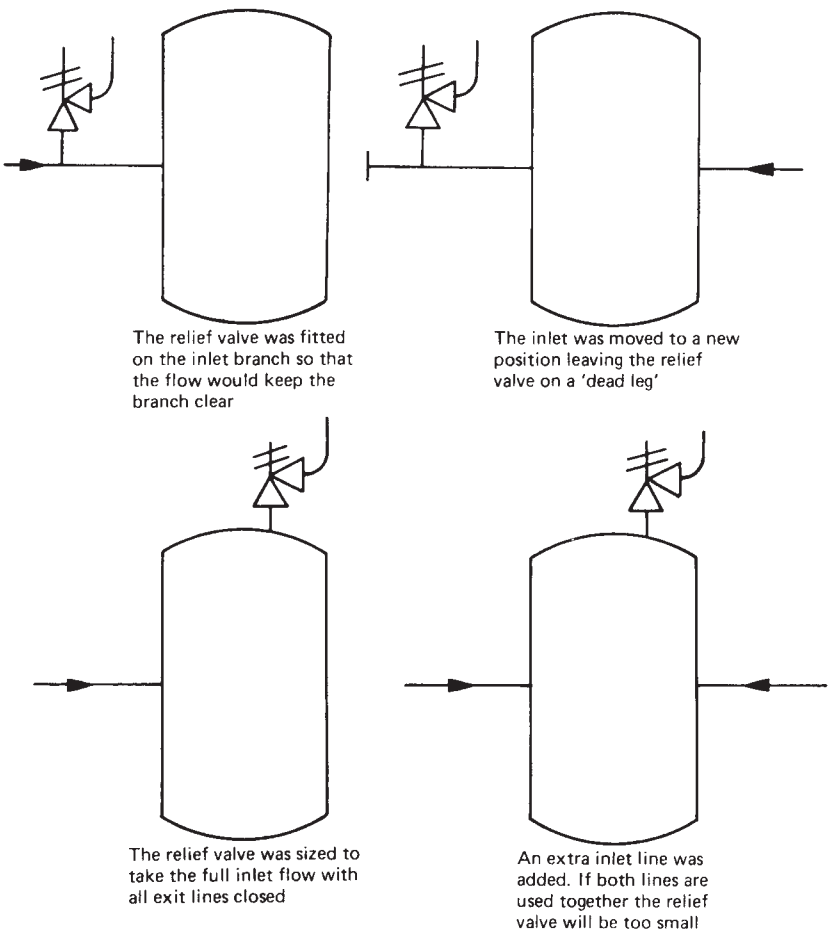

Figure 21.9 *Modifications invalidating pressure relief arrangements – 1 (Henderson and Kletz, 1976) (Courtesy of the Institution of Chemical Engineers)*

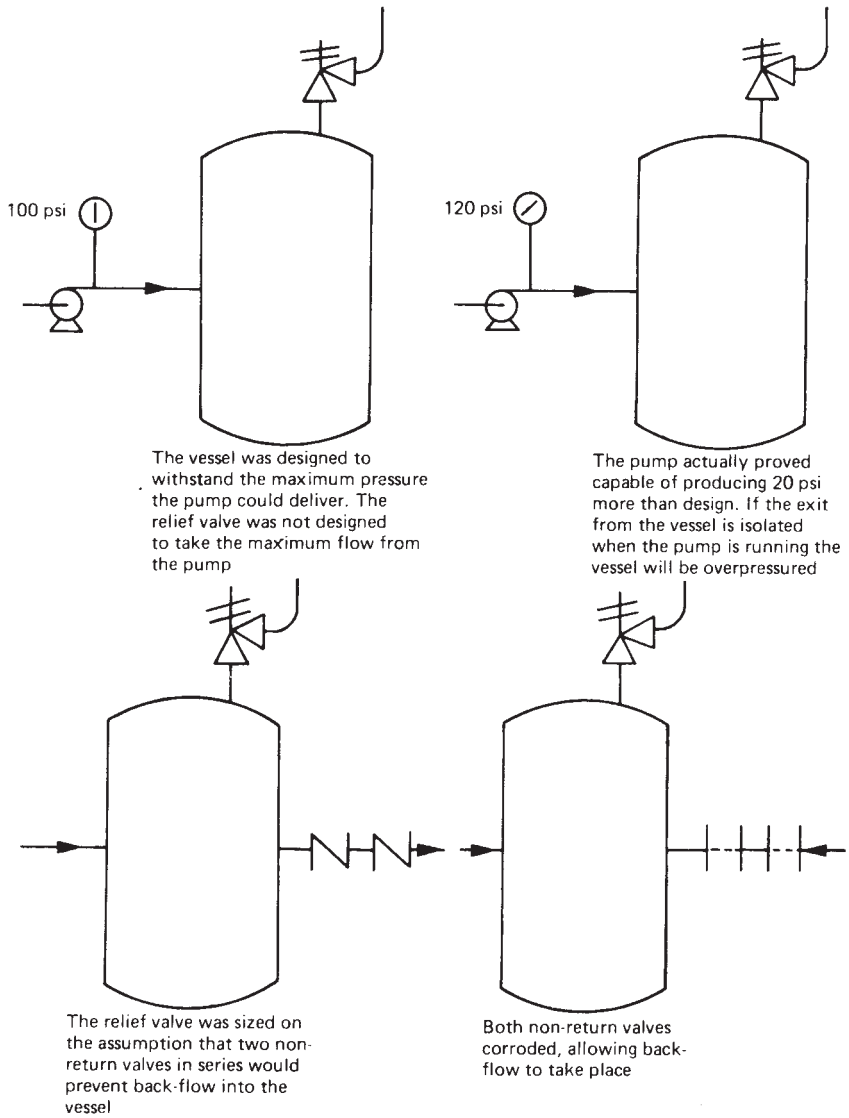

Figure 21.10 *Modifications invalidating pressure relief arrangements – 2 (Henderson and Kletz, 1976) (Courtesy of the Institution of Chemical Engineers)*

alter the pressure relief valve setting is usually appreciated, it is sometimes forgotten that it is necessary also to check the relief valve capacity, which is reduced by the de-rating. Similarly, an increase in equipment throughput may require a change in pressure relief valve capacity.

The ease with which hazards associated with pressure relief arise mean that the review of pressure relief is particularly important.

21.22.3 Other hazards of changes

Other hazards which can arise due to changes are exemplified by the case histories given in Appendix 1. Some of the general features from these are considered here.

Changes can invalidate not only pressure relief but also instrument systems. In particular, a situation may be created where an important measurement signal is degraded by the interposition of a restriction, filter, etc. This is illustrated by *Case History* B52.

A common change is the temporary replacement or bypassing of equipment such as a reactor or heat exchanger with a length of pipe. This appears to be a simple matter, but it is still necessary to design the pipe properly and to provide supports. The hazard is shown by the Flixborough disaster.

An alteration of a device which in some way limits flow or pressure can create a hazard. Examples include the removal of a regulator, orifice, etc. installed specifically to

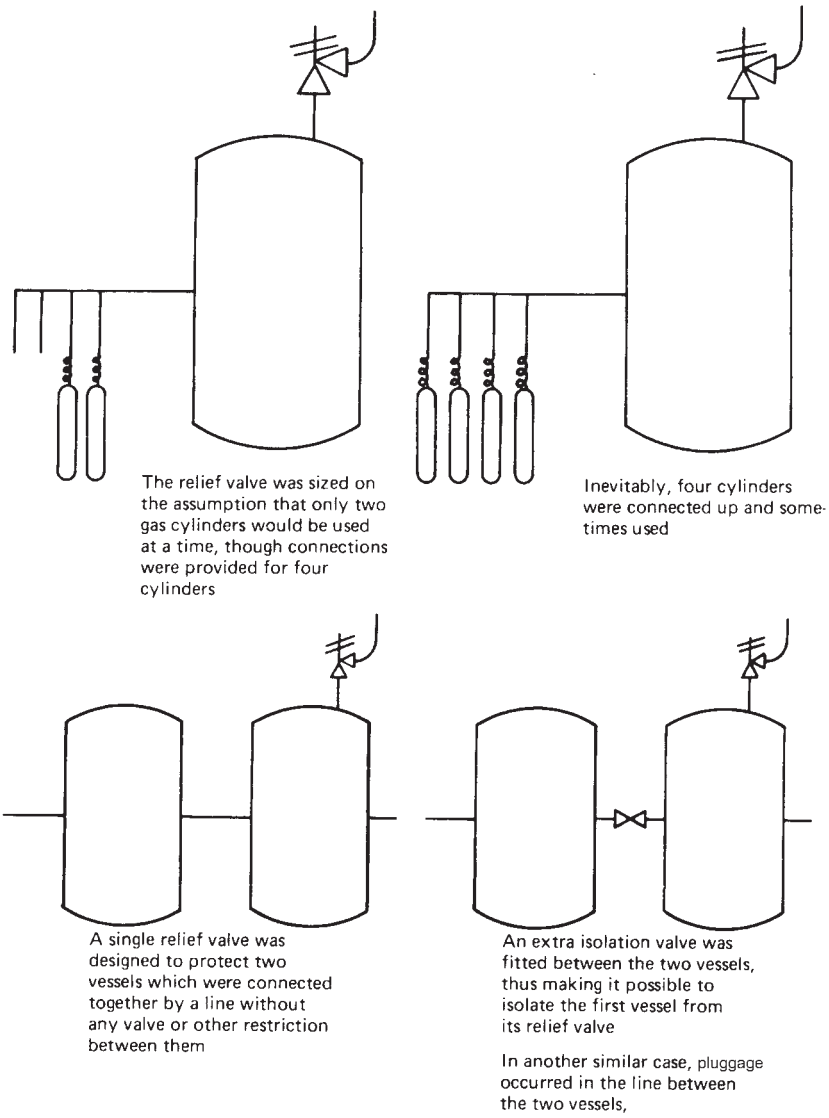

Figure 21.11 *Modifications in validating pressure relief arrangements – 3 (Henderson and Kletz, 1976) (Courtesy of the Institution of Chemical Engineers)*

restrict flow, and the increase in the size of a valve trim or installation of a pump impeller capable of a greater head.

Changes which appear quite minor can nevertheless introduce hazards. Other hazards are listed in the form for the control of modifications shown in Figure 21.12.

21.22.4 Changes to the process

The lesson commonly drawn from the Flixborough disaster is the importance of maintaining the integrity of the equipment and of avoiding degradation due to an equipment change. The equipment can also be put at risk, however, by the operation of the process outside the envelope of operating conditions for which the pressure system is designed. It is essential, therefore, to control such process changes as well.

Moreover, even if the envelope of operating conditions remains the same, a change in operating practice may affect features such as inspection and test intervals, which tend to be based on historical equipment experience.

21.23 Managing Change

The elements of a system for managing change are (1) procedures, (2) assessment, (3) inspection, (4) documentation and (5) training.

There should be a formal procedure which requires all modifications to be authorized by competent persons and a

Safety Assessment

Plant **Title** **Reg no**

Underline those factors which have been changed by the proposal.

Process conditions
temperature
pressure
flow
level
composition
toxicity
flash point
reaction conditions

Operating methods
start up
routine operation
shutdown
preparation for maintenance
abnormal operation
emergency operation
layout and positioning of
controls & instruments

Engineering methods
trip and alarm testing
maintenance procedures
inspection
portable equipment

Safety equipment
fire fighting and
detection systems
means of escape
safety equipment for
personnel

Environmental conditions
liquid effluent
solid effluent
gaseous effluent
noise

Engineering hardware and design
line diagram
wiring diagram
plant layout
design pressure
design temperature
materials of construction
loads on, or strength of
foundations
structures
vessels
pipework/supports/bellows
temporary or permanent:
pipework/supports/bellows
valves
slip-plates
restriction plates
filters
instrumentation and control
systems
trips and alarms
static electricity
lightning protection
radioactivity
rate of corrosion
rate of erosion
isolation for maintenance
mechanical electrical
fire protection of cables
handrails
ladders
platforms
walkways
tripping hazard
access for
operation
maintenance
vehicles
plant
fire fighting
underground/overhead
services
equipment

Within the categories listed below, does the proposal	Yes or no	What problem has been created which affects plant or personnel safety and what action is recommended to minimise it	Signed & date
Relief and blowdown			
1 Introduce or alter any potential cause of over/under pressuring (or raising or lowering the temperature in) the system or part of it?			
2 Introduce a risk of creating a vacuum in the system or part of it?			
3 In any way affect equipment already installed for the purpose of preventing or minimising over or under pressure?			
Area classification			
4 Introduce or alter the location of potential leaks of flammable material?			
5 Alter the chemical composition or the physical properties of the process material?			
6 Introduce new or alter existing electrical equipment?			
Safety equipment			
7 Require the provision of additional safety equipment?			
8 Affect existing safety equipment?			
Operation and design			
9 Introduce new or alter existing hardware?			
10 Require consideration of the relevant Codes of Practice and Specifications?			
11 Affect the process or equipment up-stream or downstream of the change?			
12 Affect safe access for personnel and equipment, safe places of work and safe layout?			
13 Require revision of equipment inspection frequencies?			
14 Affect any existing trip or alarm system or require additional trip or alarm protection?			
15 Affect the reaction stability or controllability of the process?			
16 Affect existing operating or maintenance procedures or require new procedures?			
17 Alter the composition of, or means of disposal of effluent?			
18 Alter noise level?			

Safety Assessor date

Checked by Plant Supervisor Checked by Engineer

Figure 21.12 *Safety assessment form for plant modification work (Henderson and Kletz, 1976) (Courtesy of the Institution of Chemical Engineers)*

standard method of making the safety assessment; there should be a system of inspection of changes by a competent person to make sure the work has been done as intended and is complete; there should be a system of documentation to record the change; and there should be adequate training so that all personnel concerned understand the system of control.

OSHA PSM Standard requires a written procedure to manage changes. Several considerations must be addressed:

(1) technical basis;
(2) impact of change on safety and health;
(3) modifications to operating procedures;
(4) necessary time period for the change;
(5) authorization requirements.

Additional management of change (MOC) requirements are:

(1) employees involved in operating and maintaining the equipment shall be informed of, and trained in, the change prior to implementation of the change;
(2) process safety information shall be updated;
(3) operating procedures or practices shall be updated.

21.23.1 Identification of changes;

The identification of changes is a crucial problem. It is necessary, but not always easy, to identify items which in fact constitute changes. This requires that a change be defined. A simple definition of change is any addition, modification or replacement that is not a replacement-in-kind.

The following two-part definition is given by Henderson and Kletz:

(1) Any change in the equipment, temporary or permanent, which may affect the safety of the process or safety and integrity of the equipment. It does not include changes in engineering equipment which are not in contact with the process and cannot affect the safety of the process or the safety and integrity of the equipment.
(2) Any change in process materials, services, operating conditions or operating procedures, and including experimental programmes, which fall outside established practice.

The first part of this definition covers those equipment changes which are normally understood as equipment modifications. The second part brings in the process modifications also.

In the system described by these authors, it is the responsibility of the plant manager and plant engineer to identify modifications.

21.23.2 Authority for changes

Systems for managing change and the levels at which particular types of change can be authorized vary somewhat, but the basic principles are quite clear. There should be a well defined and understood system of authorization.

The system described by Henderson and Kletz (1976) is that any change to equipment or process must be authorized in writing by a competent manager and engineer. This applies to any change, however inexpensive and temporary, as well as permanent changes. The level of authorization is usually the lowest level of technical management. It is important that a proper review is held on every change. A varying group of individuals will be required based on the change being proposed. At a minimum, the operation, process and mechanical personnel should review and approve changes. If the change involves instruments or electrical modifications, an instrument and electrical engineer should also review and approve. The review team should be comprised of the personnel necessary to adequately review the change being proposed. It is essential that these personnel be capable of recognizing problems which lie outside their area of competence and be willing to consult other resources. Modifications proposed are not always necessary. Sometimes the proposal is a symptom of a problem which is better dealt with in some other way. The technique of critical examination, described in Chapter 11 in relation to design, is applicable to modifications also. Questions which may be asked concerning a modification are: Is it necessary? Is it economic? Is there a better alternative?

21.23.3 Design authority

Some changes require complete design by a specialty engineering group. There is a problem area here. Many plants are designed and built by outside contractors, who initially have the greatest expertise about the process and equipment, but also eventually lose touch with it. There is, therefore, typically a transfer of expertise to a design authority within the organization and often outside the company. Plant personnel must assure that design groups adhere to the safety requirements and change policy.

21.23.4 Procedure for changes

The procedure given by Henderson and Kletz requires that before authorizing a modification particular attention should be paid to ensuring that:

(1) The number and size of relief valves required are not changed (or any necessary changes are specified).
(2) The electrical area classification is not changed (or any necessary changes to the electrical equipment are specified).
(3) There are no effects on trips or alarms (or any necessary changes are specified).
(4) There are no other effects which might reduce the standard of safety.
(5) The appropriate engineering standards are followed.
(6) The right materials of construction and fabrication standards are used.
(7) Existing equipment is not subjected to conditions beyond the design basis without checking that it can withstand the new conditions.
(8) Any necessary changes in operating conditions are made.
(9) Adequate instruction and training are provided to operating and maintenance teams.

21.23.5 Safety assessment of modifications

The above procedures need to be supplemented by a system for the identification of hazards in the modification. The method described by Henderson and Kletz makes use of the safety assessment form shown in Figure 21.12. The form is best completed not by a single individual but by two or three people working together. The top half of the form provides check words which form the basis for a hazard and operability study and the bottom half gives a more conventional checklist. A similar assessment checklist and

guidance is provided in CCPS, AIChE: *Guidelines for Hazard Evaluation Procedures*.

It is found helpful in making the safety assessment to assume that, until it is shown otherwise, any isolation valve or other restriction will isolate an equipment from its protective device, for example a vessel from its relief valve, and that any new line will introduce some unwanted contamination, overpressure of some equipment or more flow into some equipment than its outlet pipes can handle.

This procedure, therefore, makes use of a standard form to initiate a safety assessment which goes beyond the use of a checklist.

21.23.6 Inspection of modifications

It is the responsibility of the person authorizing a modification to carry out a pre-commissioning inspection of that modification and to satisfy himself that it is in accordance with the design intent, that the standards for design, construction and testing have been followed, that the provisions of the safety assessment have been met and that the work is complete.

21.23.7 Documentation of modifications

It is essential that equipment documentation be kept up to date and therefore that any modification be recorded. This requirement may be met by the use of a formal change procedure. If the modification requires alterations to operating or inspection practices, it is necessary that the appropriate changes be made in the documentation covering these aspects.

21.23.8 Training on modification systems

A system for the control of modifications can only work if all the personnel involved are aware of and have an understanding of the system through training. The process operator who may turn off an agitator, the maintenance fitter who may blind off a vent, and the instrument technician who may alter a trip setting, all need to be aware of the hazards which these types of modification may involve and of the system of control of modifications.

The plant supervisors and engineers who authorize modifications need to have the theoretical knowledge, general practical experience and experience of the particular process and equipment to recognize potential hazards, and also to appreciate situations where they should call in expert assistance.

21.23.9 Commissioning modifications

The commissioning stage tends to involve numerous modifications at a time when the plant staff are heavily loaded. It may be appropriate, therefore, to appoint special personnel to check these modifications. People who have been involved in hazard identification during the design stage may well be suitable for this task. It is also advisable to conduct a post-commissioning check of the pressure relief and blowdown arrangements about a year after start-up.

21.23.10 Variations in modification control

The system for control of modifications just outlined is essentially that described by Henderson and Kletz, and is intended primarily for larger continuous petrochemical plants. Other systems may be more appropriate for other types of equipment, although the basic principles remain applicable.

21.24 Some Modification Problems

21.24.1 Design codes and standards

Like equipment design, change should be done in accordance with applicable standards or codes. Design standards or codes are not applied retrospectively to existing equipment and its changes.

There is a problem, however, which arises from the nature of the advanced codes such as the ASME *Boiler and Pressure Vessel Code*, Section VIII, Division 2, BS 5500, and earlier BS 1515. The design criteria in such codes are quite complex, may require analysis of stress concentration sites, of fatigue and creep and assume finite equipment life. Design according to these codes is a specialist matter. Expert advice is necessary for any change to equipment designed to codes. Moreover, such advice may well be required in some cases for repairs on such equipment.

21.24.2 Repair and modification codes

The main guide for equipment repairs and modifications is API RP 510: *Inspection, Rating and Repair of Pressure Vessels in Petroleum Refinery Service*. API RP 510 gives an account of its origin as a complement to the ASME *Boiler and Pressure Vessel Code* before Section VIII of the latter was split into two divisions. The ASME *Code* is written for new construction. With respect to repair or modification, RP 510 states that where due to its new construction orientation the ASME *Code* cannot be followed, RP 510 has precedence.

21.24.3 Materials aspects

The materials for changes or repair should be 'suitable' and should have properties at least equal to that of the parent material originally used. If the codes apply, the materials should have guaranteed minimum properties and should be so certified. It is also necessary that both parent and replacement materials should be capable either of withstanding the fabrication processes without losing their required properties or of having these properties restored.

The availability of suitable materials may be a problem, either because a material is no longer made or because delivery times are long.

The parent material is sometimes degraded and may require treatment before welding can be done on it. Thus, for example, if there is surface sulfur contamination, it may be necessary to remove the contamination by grinding and then to preheat to allow welding. In some cases, the parent metal may have been rendered unweldable by high temperature exposure or hydrogen attack.

The application of quality control procedures can give rise to difficulties. There has been continuous progress in the measurement of defects in materials and in acceptance standards. The situation can easily arise, therefore, where the quality demanded for the replacement materials far exceeds that of the original equipment material.

The properties of both parent and replacement materials may be affected by activities such as cold working, preheating or welding. Material properties may be restored to some extent by suitable heat treatment, but the heat treatment operations which can be carried out are strictly limited.

21.25 Major Plant Expansions

Major plant expansions are in large part covered by the procedures for design, on one hand, and for change on the

other. Nevertheless, such major expansion merits at least brief consideration in its own right. Reference has already been made to the British Chemical Industry Safety Council publication on plant extensions (BCISC, 1972/11). The control of major extensions is discussed by K. Wood (1971).

21.25.1 Design of changes

A major expansion involves changes on a greater scale than a normal equipment modification. This means that it is particularly necessary to check on the various facilities which may become inadequate or overloaded as a result of the expansion. Some features of the design which should be checked with this in mind are: (1) pressure relief valves; (2) vent, flare, blowdown and absorption systems; (3) drains and sewers and (4) safety trip systems.

The design, location and capacity of the pressure relief valves should be checked and sufficient spares provided. A review should also be made of the need for liquid thermal relief on long sections of off-site piping which could be blocked in.

The facilities for gas and vapour relief, for flaring, for liquid blowdown and for emergency absorption should be checked.

The check on sewers and drains should cover not only the capacity of the underground sewers, but also that of the surface drainage so as to ensure disposal of fire water.

A major expansion also involves more extensive changes of equipment configuration. It is particularly important, therefore, to check not only that there are suitable safety trip systems on the expansion itself, but that those on the existing equipment are also still appropriate.

21.25.2 Layout for expansions

The problems of piping work during the expansion should be given special attention. The number of live pipelines passing through the non-operating areas should be kept to a minimum. Despite the best safe-working procedures, incidents are frequent in which live lines are broken or cut open by construction personnel.

Utilities lines should be isolated from the non-operating area by block valves. Sewers should also be isolated from the non-operating area, since they present the hazard that flammable gas may flow through them from the operating into the non-operating area. Sewers should be isolated completely.

There should be adequate provision of blind points to permit pre-commissioning testing of equipment such as compressors on air or gas recycle, while maintaining isolation of the non-operating areas from flammable gas and utilities.

21.25.3 Safe-working procedures

A major expansion usually means that there are on site a large number of contractors' personnel. This situation is a particularly severe test of the safe working procedures and the normal procedures should be reviewed to check that they are adequate.

The original equipment usually continues in operation while construction work is in progress on the expansion. It then shuts down so that it can be tied in to the expansion facilities. It is necessary to control work in the non-operating area closely, so as not to interfere with the operating unit, and it is desirable that if it is necessary to carry out gas-freeing operations on shut-down, then hot work in the non-operating area should cease until this has been done.

The permit system is usually that in normal use. But the number of permits issued is likely to increase greatly and operations personnel may need to be assigned full time to analytical testing of atmospheres and issuing of permits.

In these circumstances, the identification of equipment becomes even more important. Permits should specify clearly the equipment to be worked on and there should be positive identification of equipment. A colour code agreed with the contractors may be used as an additional means of identification. Pipelines and equipment in the non-operating area which are live should be clearly marked with an agreed code, colour and tags.

It is necessary to ensure that the contractors' blinds are kept separate. The contractors blinds should be uniquely identified (physical features, colour, etc.) to distinguish them from normal facility blinds. Furthermore, there should be an instruction that neither party must remove the other's blinds. Incidents occur in which contractors' personnel remove blinds from live lines. As mentioned earlier, in some permit systems a separate permit is needed for the insertion or removal of blinds. This is particularly appropriate for work on major expansions.

There is need for an alarm system to cover the hazard of flammable gas release from an operating unit while hot work is being done in the non-operating area. Personnel in the non-operating area should be instructed to stop hot work when the alarm is raised. The normal alarm system should also be explained to them.

The hazard of illicit smoking should be reduced by the only effective means available, which is the provision of smoking areas.

The personnel involved in the expansion should be given training on the hazards and procedures.

21.26 Notation

Section 21.6

C	cleaning disturbance factor
F	drag force on particle
u	fluid velocity relative to particle
ρ	density of fluid

Subscripts:

1	cleaning
2	operating

Section 21.20

H	annual cost of holding item
P	cost of procuring item
Q	optimal order quantity of item
R	annual requirement for item

22 Storage

Contents

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By far the largest quantities of chemicals are found in storage facilities, which may be at chemical plants or in other storage terminals. The prevention of loss in storage is therefore extremely important.

It has long been appreciated that loss of containment from storage of toxic chemicals could have particularly serious consequences. The hazard of toxic release has been considered, therefore, in some detail in Chapter 18. The hazard was realized at Bhopal, which was the worst disaster which has ever occurred in the chemical industry. A toxic release with consequences on this scale, or anything approaching it, is extremely rare and stringent measures are taken to avoid it.

Losses through fires in storage, on the other hand, constitute a major part of the losses sustained by the industry. Mostly these result in financial loss rather than loss of life and tend to make relatively little public impact. But there are exceptions such as the disasters at Feyzin, Caracas and Mexico City.

Some idea of the potential for fire loss may be obtained by considering the value represented by a single storage tank. A 'jumbo' tank might contain 500,000 barrels of oil worth US$10 per barrel and might itself be worth US$4 per barrel capacity, making a total value of US$7 million (OIA, 1975 Loss Control Bull. 400–1). Jumbo tanks of from 300,000 to 1,000,000 barrels capacity are currently being used to store not only crude oil but also flammable intermediate and finished products.

Storage is one of the areas in which there is a good deal of legislation. This was described in Chapter 3.

Much storage is sited in or near urban areas. It is generally reckoned to be relatively safe and unlikely to cause large loss of life, but it is nevertheless a source of some public concern. There is, therefore, the problem of siting and of the relation between siting and preventive measures. This aspect is considered in Chapter 4. Storage is frequently one of the topics dealt with under the headings of plant siting and layout, and some aspects of storage have been considered in Chapter 10.

The location of storage in relation to the process is also important. Storage is most likely to be put at risk by a process. It is necessary, therefore, for the two to be segregated. This reduces the risk of a process incident hazarding the very large inventory in storage. It also makes it less likely that a minor incident in storage will put the process at risk.

There are numerous standards and codes of practice which are applicable to storage. The treatment of storage given here attempts to outline some of the principles described in the codes. There are differences, however, between codes and there are critics of the codes, and some of these points are mentioned also. The practices described should be regarded only as typical. In particular, the codes themselves should be used for design work.

Safety in storage is as much a matter of operation and maintenance as of design. Some aspects of operation and maintenance of storage were discussed in Chapters 20 and 21, respectively.

Good operation and maintenance depend on an effective management system. While it should be possible to assume that such a system exists in a large chemical works, there is potentially a problem in situations where products such as liquefied petroleum gas (LPG) or chlorine are stored and used in non-chemical and low technology industries. In this case, a particular responsibility rests on the supplier of the chemical to advise the user.

There is no UK code specifically for the storage of chemicals in general except insofar as these are covered by codes for petroleum products, flammable liquids, LPG and liquefied flammable gas (LFG), but there are codes for a number of individual chemicals.

The treatment given here deals in turn with the storage of flammable materials, the storage of toxic materials, loading and unloading facilities, drum and cylinder storage and warehouses. It also describes case histories and hazard assessments of storage.

Selected references on storage of hazardous materials are given in Table 22.1.

Table 22.1 *Selected references on the storage of hazardous materials*

Aldrich (1960a,b); Grover and Wilson (1960); Hower (1961); Leach (1962); Duggan (1964b); Fuller and Bristline (1964); Risinger (1964h); Zick and Clapp (1964); Hughson (1965); IP (1980 Fur. MCSP Pt 2, 1981 MCSP Pt 3, 1987 MCSP Pt 9); Redington (1965); Voegelen (1965); IChemE (1966/44); FMEC (1967); Salot (1967); Wardale and Todd (1967); Cotton and Denham (1968); Denham, Russell and Wills (1968); Home Office (1968/1, 1971/2); Zick and McGrath (1968); D.M. Johnson (1969); Boberg (1970); FPA (1970/12,1972/17, 1989 FS 6011, 6012); Hearfield (1970); J.R. Hughes (1970); ICI/RoSPA (1970 IS/74); J.S. Clarke (1971); Simpson (1971); McGrath (1973, 1975, 1976); Mecklenburgh (1973, 1976, 1985); R.C. Ross (1973); Shinnar (1973); Vervalin (1973a,f); Chicago Bridge and Iron Co. (1974, 1975a,b, 1976a,b); Unwin, Robins and Page (1974); Walsham (1974); OIA (1975 Loss Control Bull. 400–2); HSE (1977 CS/2); Wafelman and Burhmann (1977); Ghali (1979); Santi (1979); Malina (1980); API (1981 *Refinery Guide* ch. 13, 1982/5, 1984 Publ. 2008, 2001 Std 620, 1998 Std 650); Burk (1981); Anon. (1982 LPB 47, p. 26); Doi and Osawa (1983); Gallagher (1983); Giger, Gygax and Hoch (1983); Petherbridge and Kinder (1983); Prieto (1985); Ackermann (1986); AlChE (1986/85); Anon. (1987w); Frey and Handman (1987); Sims (1987); Nazario (1988); ILO (1989); Sanders, Haines and Wood (1990); ACGIH (1991/4, 1987/15); Seton, Fitterer and Harris (1992); Bartlett, Hall and Gudde (1993); Rorty and McLearn (1993); Shah, Shah and Mody (1993); ANSI MH5.1.3M-1982 BS (Appendix 27 *Pressure and Other Vessels*), BS 4994: 1987; NFPA (2002/NFPA13, 2003/NFPA 230)

Low temperature storage
H.V. Bell (1982); Pieper, Zick and Fave (1982); Aarts and Morrison (1981); EEMUA (1986 Publ. 147); CGA (2002 CGA-341); Anon. (1988 LPB 79, p. 25) BS 4741: 1971, BS 5387: 1976

High temperature storage
Karcher (1978, 1981)

Atmospheric tanks (see also *Particular chemicals*, below)
Ulm (1963); Zick and McGrath (1968); Anon. (1975 LPB 0, p. 3); McGrath (1976); CIA (1978/11); H.I. Epstein and Buzek (1978); Morgenegg (1978); Anon. (1980 LPB 32, p. 1); Winegar (1980); G. Allen (1984); API (1985/15, 2001 Std 620, 1998 Std 650); C. Clark (1987); Kletz (1988m); ASME (1999 B96.1); IGasE (IGE/SR/7); HSE (1991 HS(G) 52); Hassan (1992); W.B. Howard (1992a); BS 799 Pt 5: 1987, BS 2654: 1997

Overfill protection: API (1996 RP 2350)
Tank stability, collapse: McGrath (1963); Anon. (1975 LPB 0, p. 3); Cuperus (1979, 1980); Skowronski (1980); Winegar (1980); Anon. (1981 LPB 37, p. 1); J.C. Thompson (1985); Anon. (1988m); Trbojevic and Gjerstad (1989); Trbojevic and Slater (1989); Neville and White (1991); Peters and Hansel (1992)
Layering, rollover: Chatterjee and Geist (1972); Sarsten (1972); Drake, Geist and Smith (1973); Germeles (1975a,b); Drake (1976); Bellus *et al.* (1977); Anon. (1979 LPB 29, p. 124); Heestand, Shipman and Meader (1983); Nakano *et al.* (1983); Takao and Suzuki (1983); Anon. (1992 LPB 107, p. 1)

Tank foundations, settling
W.W. Moore (1963); Rinne (1963); Morrison and Marshall (1970); C.C. Hale (1974); Esrig, Ahmad and Mayo (1975); Comeau and Weber (1977); Lichtenberg (1977); BRE (1978 CP14/78); Vick, Witthaus and Mayo (1980); Russo and Haydel (1983); Martinez, Madhavan and Kellett (1987)

Tank linings
Sumbry and Bogner (1993)

Concrete storage tanks
E.L. Smith (1966); Edmondson (1984 LPB 54)

Secondary containments, bunds
Comeau (1972); MacArthur (1972); C.C. Hale (1974); J.D. Reed (1974); CIA (1975/8); Anon. (1978 LPB 24, p. 164); Anon. (1979 LPB 26, p. 52); Koerner and Lord (1987); Barnes (1990 SRD R500); FPA (1990 CFSD FS 6027); Wilkinson (1991 SRD R530); Rakoczynski and Long (1993)
Bund overflow: Greenspan and Young (1978); Greenspan and Johansson (1981); Michels, Richardson and Sharifi (1988); Barnes (1990 SRD R500); Wilkinson (1991 SRD R530)
Impounding basins: Roopchand and Moderegger (1993)

Vents, reliefs, flame arresters
Cinnamon and Myers (1965); HSE (1965 HSW Bklt 34); API (1966 Bull. 2521, 1982 PSD 2210, 2000– RP 520, 1997 RP 521, 1991 Publ. 2028, 1998 Std 2000); Anon. (1972k); G.F. Bright (1972); Cude (1974a,b); Gustin and Novacek (1979); Anon. (1980 LPB 36, p. 1); Gerardu (1981); Anon. (1986 LPB 72, p. 1); Förster, Schampel and Steen (1986); Kletz (1986 LPB 67); Leung *et al.* (1988); W.B. Howard (1992a,b); NFPA (1994 NFPA 68)

Evaporation, vapour recovery
Zabaga (1980); Beychok (1983); Laverman (1984); Rapp (1984); Durr and van Laerhoven (1985)

Tank inerting
Kletz (1971); Craven (1975); Förster, Schampel and Steen (1986); W.B. Howard (1992a)

Tank insulation
Leach (1962); Adorjian, Crawford and Handman (1982); Huther, Zehri and Anslot (1985); Kaups (1985); Krause (1985)
Heat gain, loss: Falicoff and Popovich (1981); Kumana and Kothari (1982); Scheirman and Rogers (1985)

Tank farms
D.M. Johnson (1969); OIA (1975 Loss Control Bull. 400–2); Burk (1981); Ahmed (1984)

Gas storage, gasholders
IGasE (n.d./1, 1986 IGE/SR/14)

Above ground storage
AGA (1981/37, 1986/47); UL (1987 UL 142); API (1997 RP 651, 652, 1991 Publ. 301)
Leak detection: API (1991 Publ. 306, 307)

Underground storage
Scisson (1969); J.R. Hughes (1970); ICI/RoSPA (1970 IS/74); Sherman (1970); Temple (1973); Beam and Giovannetti (1975); Weismantel (1978); Dwyer (1985); UL (1985 UL 58, 1986 UL 1316); Russell and Hart (1987); Schwendeman and Wilcox (1987); K.W. Brown and Thomas (1988); Haxo (1988); Anon. (1989c); Darilek and Parra (1989); Higgins and Byers (1989); E. Johnson (1989a); Lindblom (1989); Semonelli (1990); Chidambariah *et al.* (1991); Bellani, Cannalire and Beltrame (1992); Geyer (1992); NFPA (1992 NFPA 328, 329); IBC (1993/107); Maresca *et al.* (1993); J.E. Robinson (1993)

In-ground barriers
API (1993 Publ. 315); Khinnavar *et al.* (1991)

Frozen earth storage
Massey (1964); Ferguson (1975); HSE (1978b, 1981a); Boulanger and Luyten (1983a,b)

Loading and unloading facilities
OIA (Publ. 711); Herzog, Ballard and Hartung (1964); ICI/RoSPA (1970 IS/74); API (1986 Bull. 1003); Houghton, Simmons and Gonso (1976); Anon. (1977 LPB 15, p. 2); Rees (1981); Ackermann (1986); Lichtenberg (1987); Anon. (1992 LPB 103, p. 24)
Hoses: CGA (1983 TB-3, 1985 P-7); UL (1984 UL 536, 1985 UL 1, 1986 UL 21); BS (appendix 27 *Hoses and Hose Couplings*)

Filling ratios
ICI/RoSPA (1970 IS/74) BS 5355: 1976

Marine terminals
J.R. Hughes (1970); NFPA (2000 NFPA 307)

Container storage
HSE (1991 HS(G) 51); NFPA (2003 NFPA 55)
Drum storage: Anon. (1979 LPB 27, p. 68); Anon. (1979 LPB 28, p. 115); Anon. (1985cc)
Intermediate bulk container storage: Spivey (1992)
Cylinder storage: Home Office (1973/4); Anon. (1978 LPB 20, p. 45); BCGA (1988 GN2)

Warehouses (*see also* Tables 16.1 and 16.2)
FPA (1970/9, 13); HSE (1971 HSW Bklt 47); Mecklenburgh (1973, 1985); CIA (1983 RC28); Sims (1987); Heels (1988 LPB 84); C.R. Pearson (1988); Anon. (1989 LPB 88, p. 9); HSE (1991 HS(G) 64, 1992 HS(G) 71); NFPA (2003 NFPA 230); R. Gibson (1992); ANSI MH21.1–1974

Fire, explosion (*see also* Table 16.2)
Vervalin (1964a, 1973a); Hearfield (1970); Simpson (1971); Kovacs and Honti (1974); OIA (1974 Loss Inf. Bull. 400–1); R.B. Robertson (1976b); Kobori, Handa and Yumoto (1981); Fauske (1989b)

Fire protection (*see also* Table 16.2)
FPA (S9, 1986 CFSD GP 7, 1988 CFSD GP 6); Bray (1964, 1966); Allinson (1966); Chaillot (1966); J.R. Hughes (1970); ICI/RoSPA (1970 IS/74); Kletz (1971, 1974e, 1975b,d, 1976g, 1977d); Craven (1975); Zuber (1976); Anon. (1978 LPB 20, p. 20); Anon. (1978 LPB 22, p. 114); Blything (1983 SRD R263);

British Gas (1984 BGC/PS/SFP1); Williams (1984); Raine (1986); Fullam (1987); IBC (1988/75); Nazario (1988); Schoen and Droste (1988); Schoen, Probst and Droste (1989); NFPA (1993/34); BS 5908: 1990
Insulation: Feind (1978); Katzler (1980); Uppal (1980); Anon. (1985q)

Particular chemicals
Ammonia (anhydrous): American Oil Co. (n.d./9); HSE (HS(G) 30); W.L. Nelson (1948); T.J. Dawson (1956); Jenkins (1962); Applegate (1965); Crowley (1965); Husa and Bulkley (1965); Laing and Henderson (1965); G.O. Morgan and Reed (1965); Eddy, Schroedter and Strauch (1966); J.A. Lawrence (1966); Hoffman (1967); Resplandy (1967); W.L. Ball (1968b); Scisson (1969); Morrison and Marshall (1970); A. Nielsen (1971); Comeau (1972); Lichtenberg (1972); MacArthur (1972); C.C. Hale (1974, 1980, 1982, 1984, 1987); J.D. Reed (1974); Vidalin and Bertram (1974); CIA (1975/8); Esrig, Ahmad and Mayo (1975); Lonsdale (1975); van Grieken (1976); Arup (1977); Comeau and Weber (1977); Feind (1978); Truscott and Livingstone (1978); Gustin and Novacek (1979); C.C. Hale and Lichtenberg (1980, 1990); Hendriks (1980); Vick, Witthaus and Mayo (1980); Winegar (1980); Aarts and Morrison (1981); Blanken (1982, 1984, 1987); R.S. Brown (1982); Shah (1982); Anon. (1984 LPB 58, p. 13); Guth and Clark (1985); Badame (1986); P.P. Briggs, Richards and Fiesinger (1986); Josefson (1987); Shah (1987); J.L. Woodward and Silvestro (1988); Stephens and Vidalin (1988); Byrne, Moir and Williams (1989); CGA (1989 TB-2); ILO (1989); W.G. Jones *et al.* (1989); J.R. Thompson and Carnegie (1989); Appl *et al.* (1990); Burke and Moore (1990); Selva and Heuser (1990); J.H. Thompson (1990); Conley, Angelsen and Williams (1991); Squire (1991); Herbertsson (1992); Tilton *et al.* (1992); ANSI K61.1—1999
Ammonia (aqueous): Henderson (1975)
Asphalt, bitumen: API (1988 Publ. 2023); IP (1990 MCSP R 11); Davie, Nolan and Hoban (1993, 1994); Davie *et al.* (1993); Davie, Nolan and Tucker (1993)
Chlorine: BCISC (n.d./l); HSE (HSW Bklt 37, 1985 CS 16, 1986 HS(G) 28, 1987 HS(G) 40); CIA (1980/13); Chlorine Institute (1982 Pmphlt 5, 1986 Pmphlt 1); ILO (1989)
Hydrogen: A.D. Little (1960); Vander Arend (1961); Cassut, Madocks and Sawyer (1964); Scharle (1965); Stoll (1965); Angus (1984); NFPA (1989 NFC 50A, 50B)
LNG (*see* Table 11.23)
LPG (*see also* Table 11.22): IGasE (n.d./5); FPA (1964/ 1); Sommer (1965); J.R. Hughes (1970); ICI/RoSPA (1970 IS/74); Home Office (1971/2, 1981 HS(G) 15, 1987 HS(G) 34); LPGITA (1972– Codes 1, 3, 7, 9, 12, 14, 19, 22); Considine, Grint and Holden (1982); HSE (1973 Bklt 30, 1981 CS 5, CS 6, 1986 CS 4); Blything (1983 SRD R263, 1986); Lindblom and Quast (1983); Nozaki *et al.* (1983); I. Williams (1984); Howell and Schuller (1985); Morand, Claude and Herbreteau (1985); Sugawara and Minegishi (1985); Ackermann (1986); Davenport (1986, 1988); van der Schaaf (1986); IP (1987 MCSP Pt 9); Blomquist (1988); API (1989 Std 2510); Droste and Mallon (1989); ILO (1989); Lindblom (1989); NFPA (1992 NFPA 58, 59); Paff (1993); British Gas (1994 GBE/DAT27)
Monomers (see also *Styrene monomer and Vinyl chloride monomer*, below): Shelley and Sills (1969); Bond (1985 LPB 65); Anon. (1992 LPB 106, p. 14); Chakravarty, Fisher and Voyt (1993)
Petroleum: H. Watts (1951); Home Office (1968/1); J.R. Hughes (1970); IP (1990 Eur. MCSP R 2, 1981 MCSP R 3)

Particular chemicals: other chemicals

Acrylic acid: Wampler (1988)
Ammonium nitrate: American Oil Co. (n.d./9); HSE (1986 CS 18); NFPA (1993 NFC 490)
Carbon dioxide: HSE (1985 CS 9); Coleman (1989)
Corrosive chemicals: Anon. (1977 LPB 16, p. 21); Anon. (1979 LPB 26, p. 31)
Ethylene: Litchfield *et al.* (1959); Frank and Wardale (1970); Wardale and Frank (1970); Anon. (1985q)
Ethylene oxide: CISHC (1975/2); Curtis (1990)
Explosives: Home Office (1972/3)
Hydrogen chloride: BCISC (1975/2)
Liquefied gas: Dharmadhikari and Heck (1991)
Organic peroxides: HSE (1991 CS 21); NFPA (1993 NFPA 43B)
Oxidizing materials: NFPA (1986 NFPA 43C, 1990 NFPA 43A)
Oxygen: HSE (1977a); NFPA (1990 NFC 50)
Plastics, plastic foams: MCA (SG-5); HSE (1975 TON 29)
Shock sensitive materials: MCA (SG-7)
Sodium chlorate: HSE (1985 CS 3)
Styrene monomer: Shelley and Sills (1969)
Toxic chemicals: Ecology and Environment Inc. (1985); Croce *et al.* (1988); Drake and Croce (1988)
Vinyl chloride monomer: Shelley and Sills (1969); Unwin, Robins and Page (1974); Mukerji (1977); CIA (1978/12)

Hazard assessment (*see also* Table 9.1)
Husa and Bulkley (1965); Resplandy (1967); Siccama (1973); Solomon, Rubin and Okrent (1976); HSE (1978b, 1981a); Drysdale and David (1979/80); Considine, Grint and Holden (1982); R. Davies (1982); Suokas (1982); Drivas, Sabnis and Teuscher (1983); Lees (1983d); T.A. Smith (1985, 1986 SRD R314); Trbojevic and Maini (1985); Blything (1986); Blything and Reeves (1988 SRD R488); Clay *et al.* (1988); Selway (1988 SRD R492); Smith-Hansen (1988); Boykin and Levary (1989); Ziomas, Zerefos and Bais (1989); Haastrup and Brockhoff (1990); Khan (1990); P. Roberts (1990); Chidambariah *et al.* (1991); Nejedly, Topinka and Skarka (1992)

22.1 General Considerations

22.1.1 Purpose of storage

The purpose of storage is to smooth fluctuations in the flows in and out. If the quantity in stock does not vary, there is no point in having storage. The exception is where the storage is held purely as an insurance.

Thus, there may be various ways of satisfying the design objective. The types of storage, which are economic in these alternative designs, may be different and may have different safety implications also. There may be considerable differences, for example, in the pressure and in the inventory. An account which illustrates the interaction between storage requirements and storage method is given by Hower (1961).

22.1.2 Storage conditions

The main sets of conditions for gas or liquid storage are

(1) liquid at atmospheric pressure and temperature (atmospheric storage);
(2) liquefied gas under pressure and at atmospheric temperature (pressure storage);

(3) liquefied gas under pressure and at low temperature (refrigerated pressure storage, semi-refrigerated storage);
(4) liquefied gas at atmospheric pressure and at low temperature (fully refrigerated storage);
(5) gas under pressure.

The fluids so stored are referred to for convenience as (1) volatile liquids, (2) flashing liquefied gases, (3) semi-refrigerated liquefied gases, (4) refrigerated liquefied gases and (5) gases under pressure, respectively.

The characteristics of these different types of storage have been discussed in Chapter 15. A leak of volatile liquid held at atmospheric temperature and pressure results only in a relatively slow evaporation of the liquid. Escape of a refrigerated liquefied gas at atmospheric pressure gives some initial flash-off and then an evaporation which is relatively slow but faster than the first case. Loss of containment of a liquefied gas under pressure and at atmospheric temperature, however, causes immediate flashing of a large proportion of the gas, followed by a slower evaporation of any residue, and is usually much the most serious case. The hazard from a gas under pressure is normally much less in terms of the amount of material held, but the physical energy released if a confined explosion occurs is large.

The economics of storage of liquefied gases are that it is usually attractive to use pressure storage for small quantities, pressure or semi-refrigerated storage for medium to large quantities and fully refrigerated storage for very large quantities.

It is generally considered, however, that there is a greater hazard in storing large quantities of liquefied gas under pressure than at low temperature, so that the trend is towards replacing pressure storage by refrigerated storage for large inventories.

22.1.3 Storage capacity

Methods of the estimation of the capacity of particular types of tank or vessel are given by Santi (1979) and Gallagher (1983).

22.1.4 Storage hazards

The hazards presented by storage depend on the material and on the type of storage. In broad terms, the principal hazardous events are as shown in Table 22.2, Section A. Some principal initiating events are given in Section B of the table.

On very rare occasions, a vessel or tank fails catastrophically. This may occur due to mechanical or metallurgical defects. The vessel or tank may be overpressured by overfilling. A tank may be overpressured by too rapid filling and underpressured by too rapid emptying. Other causes of tank failure are given in Chapter 20.

More commonly, release occurs from other equipment or from pipework or fittings. Equipment which may leak includes, in particular, pumps. Release from pipework may occur due to a crack or pinhole or by full bore rupture, or by a leak or failure at a flange, gasket or valve.

Release may occur due to an explosion in the tank or vessel. There are various ways in which this can happen. One is physical overpressure which causes the vessel or tank to burst. Another is the ignition of a flammable mixture. Another is evolution of gas due to the reaction of an impurity, material of construction, etc. A fourth is a runaway reaction within the vessel or tank.

Fire at a vessel or tank can cause it to fail. The fire may be a fire beneath it or a jet flame playing on it.

An operational activity which may cause either direct release or vessel or tank rupture is overfilling. Other operational events which may give rise to a release include draining and sampling operations. Maintenance activities may result in a release, generally by admission of fluid to a section which is not fully isolated.

Impact events which may cause loss of containment from a storage include impact from a carried item, a dropped load, a vehicle or an aircraft. A missile from an explosion is another form of impact, but is primarily an escalating rather than a true initiating event.

Natural events which may cause loss of containment include high winds, rainstorms, flooding, tsunamis and earthquakes, whilst lightning may start a fire.

Arson or sabotage are other causes of hazardous events. Sabotage may take the form of interference with the plant or direct initiation by impact, fire or explosion.

22.2 Petroleum Products Storage

It is convenient to start with a consideration of the storage used in the oil industry for crude oil and petroleum products.

There exist a number of standards and codes for the storage of petroleum products and flammable liquids generally. Standards and codes include API Std 620: 1990 *Design and Construction of Large, Welded, Low-pressure Storage Tanks* and Std 650: 1988 *Welded Steel Tanks for Oil Storage*, NFPA 30: 1990 *Flammable and Combustible Liquids Code* and the *Refining Safety Code* of the IP (1981 MSCP Pt 3). HSE guidance is given in HS(G) 50 *The Storage of Flammable Liquids in Fixed Tanks (up to 10,000* m^3 *Total Capacity)* (1990) and HS(G) 52 *The Storage of Flammable Liquids in Fixed Tanks* (Exceeding 10,000 m^3 Capacity) (1991).

Storage of petroleum is discussed here under the following headings:

(1) storage tanks and vessels;
(2) storage layout;
(3) venting and relief;
(4) fire prevention and protection.

These are now considered in turn.

22.3 Storage Tanks and Vessels

The main types of storage tanks and vessels for liquids and liquefied gases are (1) atmospheric storage tanks, (2) low pressure storage tanks, (3) pressure or refrigerated pressure storage vessels and (4) refrigerated storage tanks.

The API standards for storage tanks are API Std 620: 1990 *Design and Construction of Large, Welded, Low-pressure Storage Tanks* and Std 650: 1988 *Welded Steel Tanks for Oil Storage*. Relevant British Standards are BS 2594: 1975 *Specification for Carbon Steel Welded Horizontal Cylindrical Storage Tanks* and BS 2654: 1989 *Specification for Manufacture of Vertical Steel Welded Non-refrigerated Storage Tanks with Butt-welded Shells for the Petroleum Industry.*

Some of the main types of storage tanks and vessels are shown schematically in Figure 22.1 and are illustrated in Figures 22.2–22.5. Fuller descriptions and illustrations of storage tanks and vessels are available in various sources (e.g. J.R. Hughes, 1970; API, 1981 *Refinery Inspection Guide*, ch. 13; HSE, 1973 HSW Bklt 30). Tanks and vessels for the

Table 22.2 *Some principal hazardous events and initiating events for storage*

A Hazardous events

Materials	*State*	*Storage*	*Hazardous events*
Flammable	Liquid	Atmospheric	Liquid release, then Tank or bund fire Tank explosion, then Tank or bund fire
	Liquefied gas	Pressure	Flashing liquid release – flammable vapour cloud, liquid pool, then Pool fire Running liquid fire Jet fire Vapour cloud fire Vapour cloud explosion Fire engulfed vessel, then Jet fire BLEVE
	Liquefied gas	Refrigerated	Flashing liquid release – flammable vapour cloud, liquid pool, then Tank or bund pool fire Running liquid fire Vapour cloud fire Vapour cloud explosion Fire engulfed tank, then Tank or bund pool fire Running fire
Toxic	Liquid	Atmospheric	Liquid release, then Toxic gas cloud Tank explosion, then Toxic gas cloud
	Liquefied gas	Pressure	Flashing liquid release – flammable vapour cloud, liquid pool, then Toxic gas cloud Fire engulfed vessel, then BLEVE Toxic gas cloud
	Liquefied gas	Refrigerated	Flashing liquid release – flammable vapour cloud, liquid pool, then Toxic gas cloud Fire engulfed tank, then Toxic gas cloud

B Initiating events

Catastrophic failure of vessel or tank
Failure of or leak from other equipment, pipework or fittings
Explosion in vessel or tank
Fire engulfing vessel or tank
Jet flame playing on vessel or tank
Overfilling of vessel or tank
Release occasioned by operations
Release occasioned by maintenance
Impact event
Natural event
Arson, sabotage

storage of LPG, liquefied natural gas (LNG), ammonia and chlorine are considered further below.

22.3.1 Atmospheric storage

Some typical atmospheric storage tanks are shown in Figures 22.1(a–f). Figure 22.1(a) is a horizontal cylindrical tank. These tanks usually have riveted flat or welded dished ends. Figures 22.1 (b) and 22.1 (c) are vertical cylindrical fixed tanks with coned and domed roofs, respectively. Figures 22.1(d) and 22.1(e) are, respectively, another larger fixed roof tank and a large floating roof tank. Figure 22.1 (f) is a vapour dome tank with a flexible diaphragm in the dome.

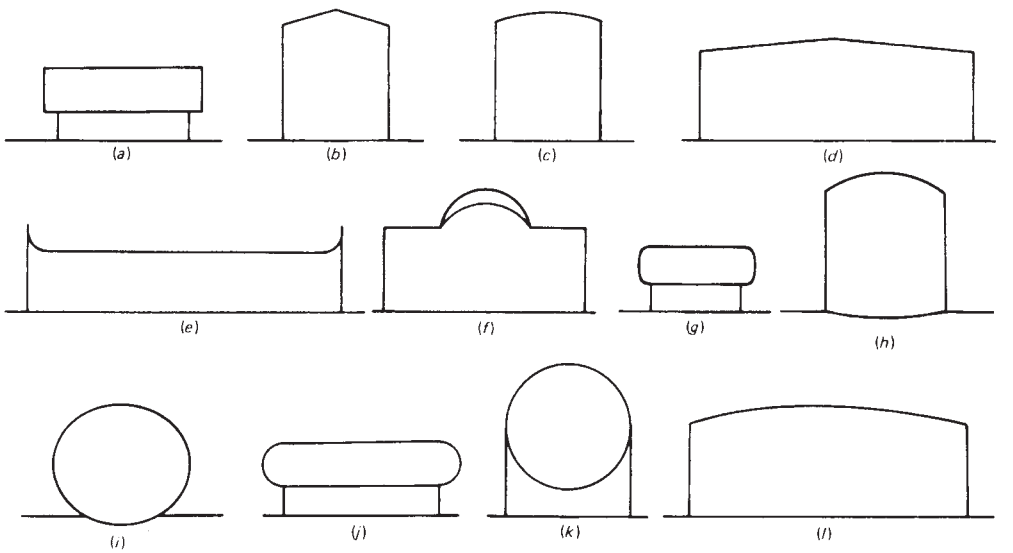


Figure 22.1 *Storage tanks and vessels: (a) horizontal cylindrical atmospheice tank; (b) vertical fixed roof atmospheric tank (coned roof); (c) vertical fixed roof atmospheric tank (domed roof); (d) vertical fixed roof atmospheric tank (large coned roof); (e) vertical floating roof atmospheric tank; (f) vapour dome atmospheric tank; (g) horizontal cylindrical low pressure tank; (h) vertical cylindrical hemispheroidal low pressure tank; (i) spheroidal low pressure tank; (j) horizontal cylindrical pressure vessel; (k) spherical pressure vessel (Horton sphere); (l) vertical fixed roof refrigerated atmospheric tank (domed roof)*

Atmospheric tanks are designed to withstand an internal pressure/vacuum of not more than 1 psig (70 mbar). Further details are given below.

Horizontal cylindrical tanks have a relatively small capacity. Domed roof tanks go up to about 60 ft (20 m) diameter. Coned roof tanks are built up to 250 ft (76 m) diameter and 60 ft (20 m) height. Floating roof tanks may be 250 ft (76 m) in diameter and 72 ft (22 m) high.

In a floating roof tank, the roof floats on the surface of the liquid. There are different kinds of floating roof such as the pan, annular pontoon and double-deck types. The two latter have a double layer at the annulus and over the whole area, respectively, and therefore have greater buoyancy than a pan roof. Sealing between the floating roof and the tank wall is effected by a number of means such as spring-loaded fabric or rubber tube seals. In addition, a floating deck may also be used inside a fixed roof tank. Its main purpose is the reduction of vapour loss.

A traditional divide between the different sizes of storage tank is a nominal capacity of 12,000 UKgal (55m^3), which has corresponded to the approximate limit of shop fabrication. The design of petroleum storage tanks up to this capacity is governed by BS 799: 1972—Oil Burning Equipment. Another applicable standard is BS 2594: 1975, which covers tank sizes both below and above 12,000 UKgal.

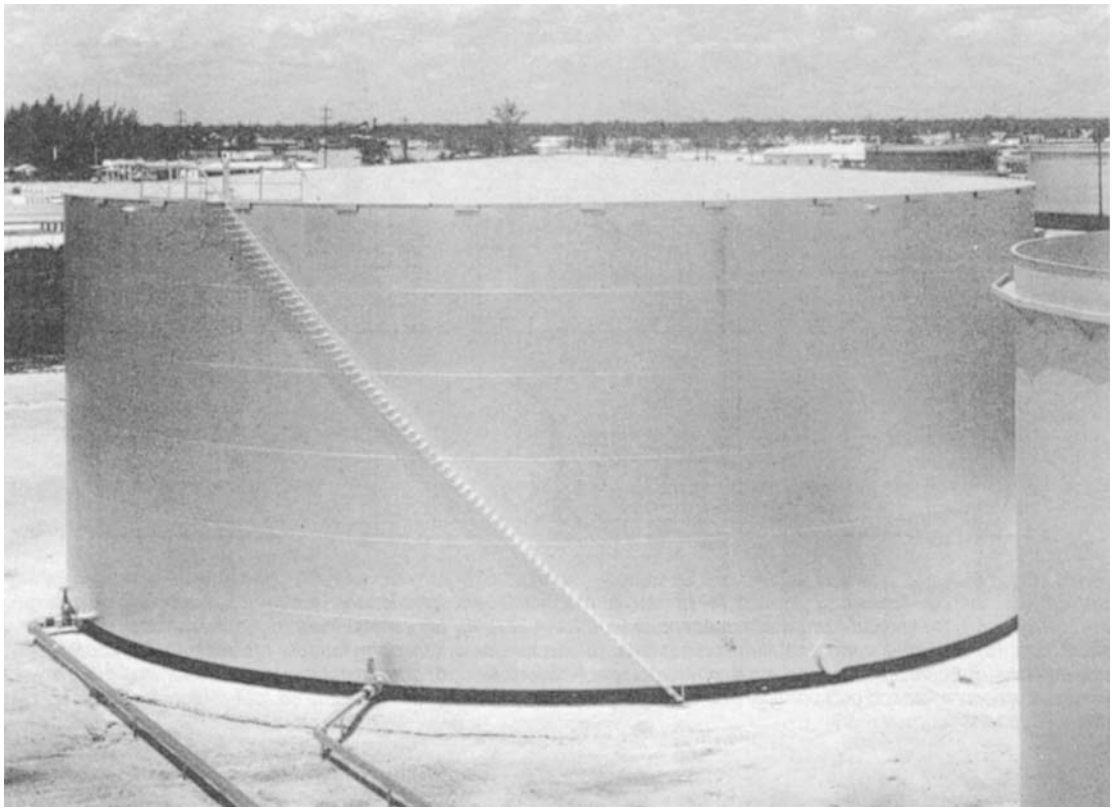
Large petroleum storage tanks are normally site erected and of mild steel welded construction. The design, fabrication, erection, inspection and testing of these tanks is specified in API Std 650: 1988 and BS 2654: 1989.

For fixed roof tanks, a traditional distinction (see BS 2654: 1961; J.R. Hughes, 1970) has been between 'non-pressure' and 'pressure' tanks. For tanks up to 128 ft diameter, non-pressure tanks were designed for an internal pressure of 3 in. WG (7.5 mbar) and a vacuum of 2½ in. WG (6 mbar) and pressure tanks for an internal pressure of 8 in. WG (20 mbar) and 2½ in. WG (6 mbar) plus superimposed load. The user was allowed to specify, however, an internal pressure greater than 8 in. WG. Pressure tanks up to 64 ft could be designed up to 21½ in. WG (54 mbar) provided the allowable stress did not exceed that given in the standard.

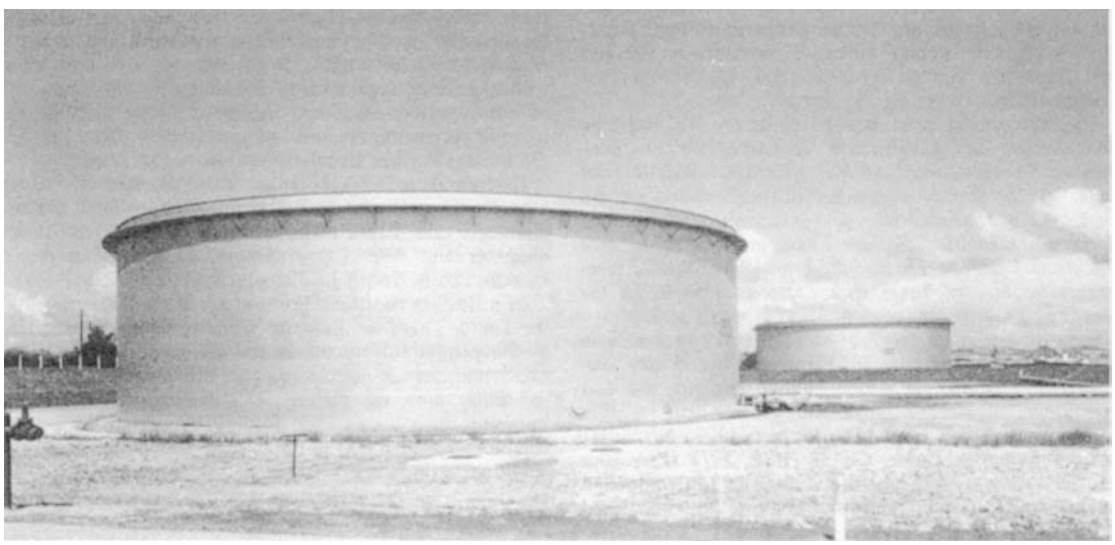
The designation of atmospheric storage tanks with a design pressure well below 1 psig as 'pressure' tanks is a possible source of confusion. As described below, there are other tanks designed for the low pressure range 0.5—15 psig which are termed 'low pressure'.

Non-pressure tanks are normally vented by an atmospheric vent and pressure tanks by a breather vent, as described below. Non-pressure tanks tend to have relatively high vapour losses from the 'breathing' of the vent. Pressure tanks with breather vents reduce these losses but are limited in diameter. Floating roof tanks provide an alternative which has low vapour losses and is available in large sizes.

The definitions of storage tanks now recognized in BS 2654: 1989 are somewhat different. The standards defines three categories of tank: (1) 'non-pressure' tanks designed for an internal pressure of 7.5 mbar (4 mbar for column-supported roofs) and a vacuum of 2.5 mbar; (2) 'low-pressure' tanks designed for an internal pressure of 20 mbar and a vacuum of 6 mbar and (3) 'high-pressure' tanks designed for an internal pressure of 56 mbar and a vacuum of 6 mbar. The maximum design pressure covered by the standard is thus 56 mbar (0.81 psi). BS 2654 also covers floating roof tanks.

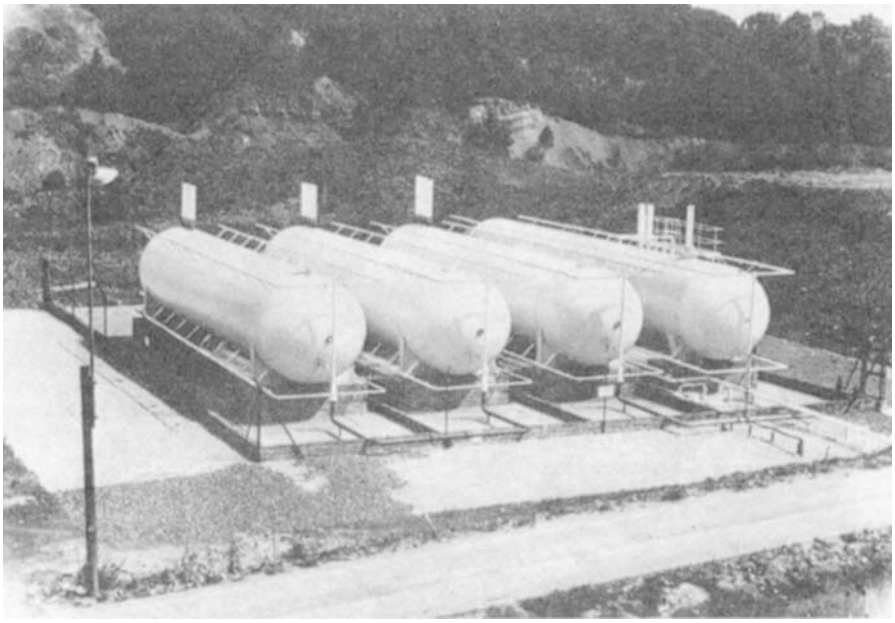


(a)

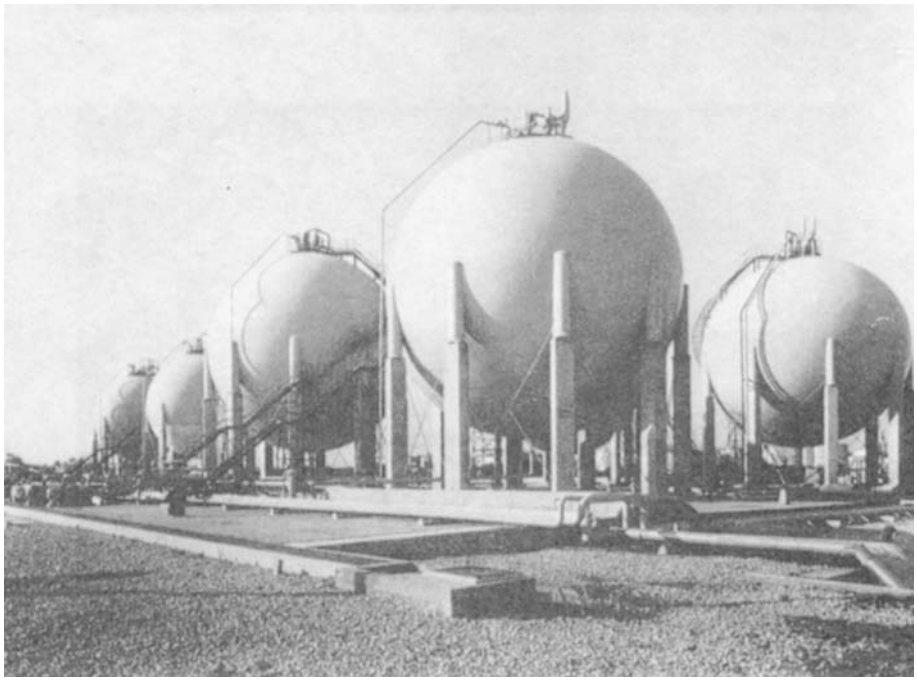


(b)

Figure 22.2 *Atmospheric storage tanks (Chicago Bridge and Iron Co.): (a) cone roof tank; (b) floating roof tank*



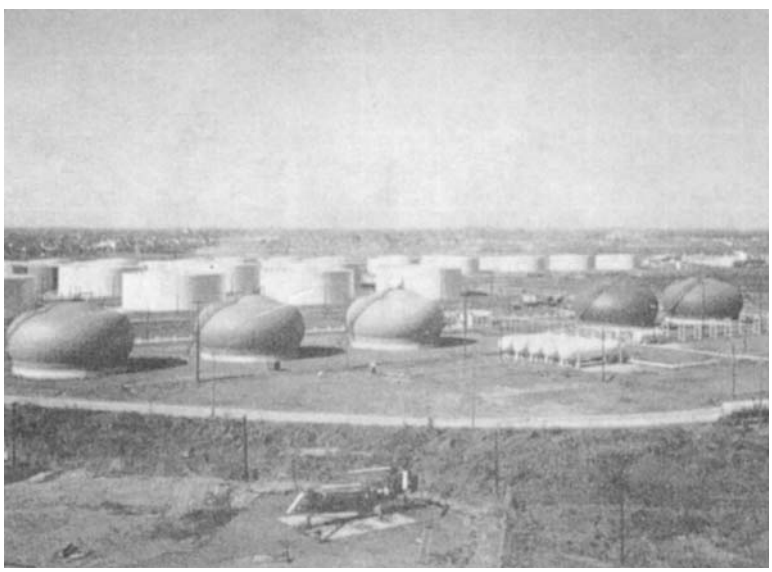
(a)



(b)

Figure 22.3 *Pressure storage vessels (a) horizontal cylindrical vessels for LPG (Health and Safety Executive); (b) spherical vessels for liquid propane/butane (Horton spheres) (Whessoe Ltd)*

(a)



(b)

Figure 22.4 *Large storage complexes, including: (a) cone roof and floating roof tanks and spherical pressure vessels (Chicago Bridge and Iron Co.); (b) cone roof tanks, spheroidal vessels and cylinderical pressure vessels (Chicago Bridge and Iron Co.)*

Atmospheric tanks are used for the storage of liquids at ambient temperature and also for the storage of refrigerated storage liquids, as described below.

22.3.2 Low pressure storage

Some typical low pressure storage tanks are shown in Figures 22.1(g–i). Figure 22.1(g) shows a horizontal cylindrical tank with dished ends. Figure 22.1(h) shows a vertical cylindrical hemispheroidal tank. Figure 22.1(i) shows a spheroidal tank which has the shape of a squashed sphere. The two latter types are also made in noded as well as plain versions.

Low pressure tanks are designed to withstand internal pressure in the range 0.5–15 psig. The design of low pressure tanks is governed by API Std 620.

Low pressure tanks are suitable for the storage of liquids which are too volatile for atmospheric storage. Gasoline is a typical petroleum product to which this applies. Use is also made of low pressure tanks in refrigerated storage, as described below.

22.3.3 Pressure and refrigerated pressure storage

Some typical pressure storage vessels are shown in Figures 22.1(j) and 22.1(k). Figure 22.1(j) shows a horizontal cylindrical pressure vessel and Figure 22.1(k) a spherical pressure vessel, or Horton sphere.

Pressure storage vessels are regular pressure vessels and can be designed to high pressures as required. The lower end of the scale for pressure storage is 15 psig.

In the United States, the design of pressure vessels is governed by the American Society of Mechanical Engineers (ASME) *Boiler and Pressure Vessel Code*, Section VIII (1991) and by API Std 2510: 1989 *Design and Construction of Liquefied Petroleum Gas Installations (LPG)*. The British Standards for pressure vessel design were BS 1500: 1958 and BS 1515: 1965–, which have been superseded by BS 5500: 1991, introduced in 1976. Pressure vessels have been discussed in Chapter 12. Horizontal cylindrical vessels have a relatively limited capacity and for large quantities spheres are used.

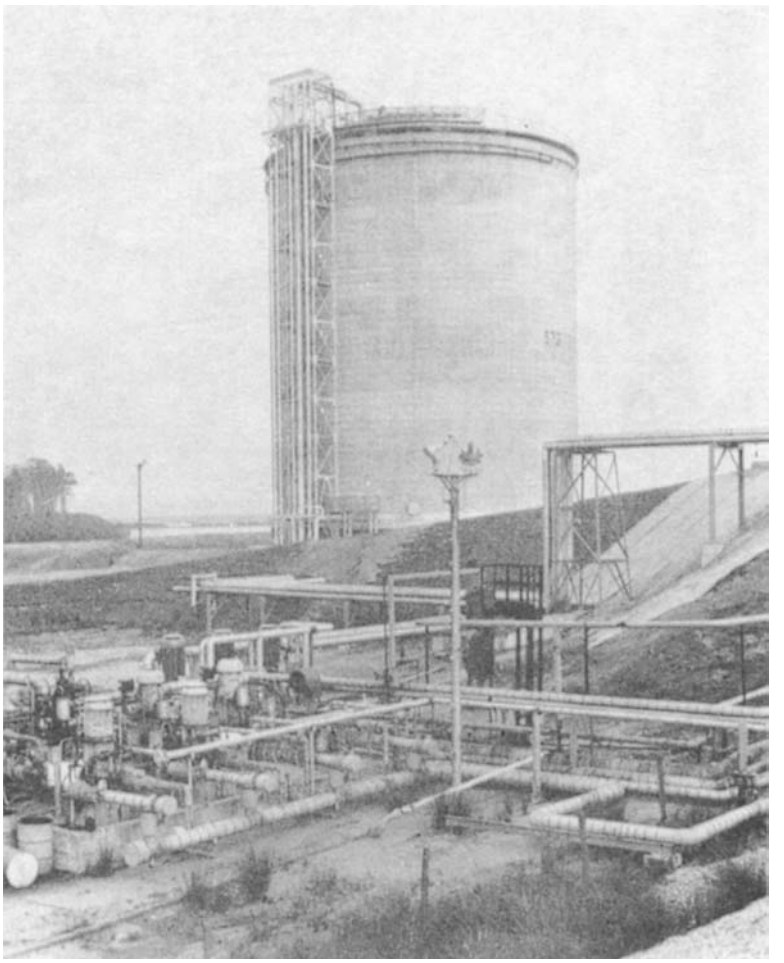


Figure 22.5(a) *Refrigerated atmosphere storage tank for liquid propane (Whessoe Ltd)*

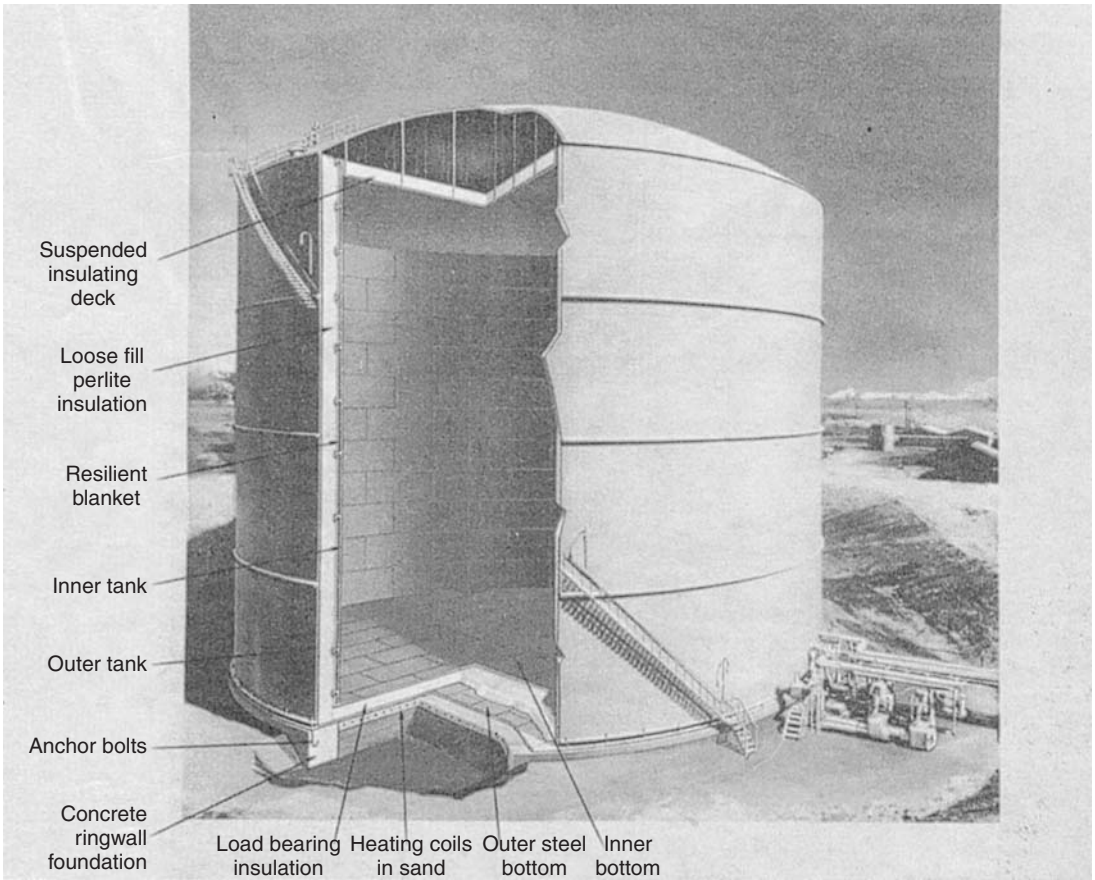


Figure 22.5(b) *Refrigerated atmospheric dome roof double wall tank for LNG (Chicago Bridge and Iron Co.)*

Spherical pressure vessels have a number of advantages. The surface to volume ratio is minimal and only 88% of that of a vertical cylindrical tank, which reduces heat leak. The foundation structure is simpler and there is no danger of soil freezing. The stresses under low temperature conditions are easily determined.

Pressure storage vessels are suitable for the storage of liquefied gases such as LPG and ammonia. Pressure storage vessels are also used for refrigerated pressure, or semi-refrigerated, storage.

22.3.4 Refrigerated storage

A typical refrigerated storage tank is shown in Figure 22.1(l). This is a domed roof, flat bottomed tank. It is essentially an atmospheric tank, with a design pressure below 1 psig. Low pressure tanks may also be used for refrigerated storage.

22.3.5 Concrete storage tanks

The need for very large storage capacities for LNG has led to the development of pre-stressed concrete storage tanks which are protected by an earthen embankment, or berm, and are internally insulated.

22.3.6 Underground cavity storage

Underground cavities may also be used for storage. Natural gas has been stored for many years in underground reservoirs, which are frequently depleted oil or gas fields. Use may also be made of such man-made cavities as worked-out salt formations or mined cavities to store gases. The well is usually operated with a brine system, but dry wells are possible also.

22.3.7 Earth pit storage

A method of storing LNG in pits, where a hole was excavated and the surrounding earth then frozen, was developed and used but the operating problems were such that it has fallen into disuse.

22.3.8 Gas storage

Gasholders are used to store gases such as hydrogen and acetylene close to atmospheric pressure. Storage of gas under pressure is usually done in gas cylinders or horizontal cylindrical pressure vessels. As already mentioned, gas may also be stored in underground cavities.

22.3.9 Glass reinforced plastic tanks

Widespread use is now made of vessels and tanks made of glass fibre reinforced plastic (GFRP), also known as glass

reinforced plastic (GRP), fibre reinforced plastic (FRP) or fibreglass. GRP tanks are widely used to store corrosive materials. They are considered further in Section 22.23.

22.4 Storage Layout

The siting and layout of storage in relation to the process are discussed in Chapter 10. Here the layout within the storage area is considered.

As mentioned in Chapter 10, the storage, process and terminals should be suitably arranged relative to one another, an appropriate layout being one in which the storage is located between the process and the terminals. The storage should be built on ground able to support the heavy load involved and with ground contours and wind characteristics which minimize the hazard of flammable liquid or vapours from storage collected in hollows or flowing across to the process and finding an ignition source.

22.4.1 Segregation

The segregation and separation of materials within the storage area is largely based on classification of the materials stored, on secondary containment, on hazardous area classification (HAC) and on fire protection measures.

The classification of liquids is described in Chapter 10. Principal classifications are those given in the IP *Refining Safety Code* and in National Fireprotection Association (NFPA) 30.

Traditionally, the flashpoint classification has been used as a guide to segregation of liquids in storage. Using the earlier classification into classes A, B and C, the main distinction was between Classes A/B and C. This was the basis of the system used in the 1965 version of the IP *Refining Safety Code*. The current code places less emphasis on this type of distinction as far as concerns segregation.

It is convenient to segregate materials which require secondary containment such as bunding, from those which do not. Where the requirements for HAC are different, it may be convenient to segregate on this basis.

The fire protection which needs to be provided is a fourth means of classification. Fire protection is considered below.

22.4.2 Separation distances

Minimum recommended separation distances for storage are given in various codes and other publications. These were listed in Chapter 10. The separation distances for petroleum products given in the IP *Refining Safety Code* are shown in Table 22.3. The code gives a number of layouts illustrating these separation distances.

Table 22.3 *Minimum recommended separation distances for the storage of petroleum products: IP Refining Safety Code (Institute of Petroleum,1981 Refining Safety Code)*

Factor		*Type of tank roof*	*Recommended minimum distance*
(1)	Within a group of small tanks	Fixed or floating	Determined solely by construction/maintenance/ operational convenience
(2)	Between a group of small tanks and another group of small tanks or other larger tanks	Fixed or floating	10 m minimum, otherwise determined by size of the larger tanks (see (3) below).
(3)	Between adjacent individual tanks (other than small tanks)	(a) Fixed	Half the diameter of the larger tank, but not less than 10 m and need not be more than 15 m
		(b) Floating	0.3 times the diameter of the larger tank, but not less than 10 m and need not be more than 15 m[a]
(4)	Between a tank and the top of the inside of the wall of its compound	Fixed or floating	Distance equal to not less than half the height of the tank (Access around the tank at *compound* grade level must be maintained)
(5)	Between any tank in a group of tanks and the inside top of the adjacent *compound* wall	Fixed or floating	Not less than 15 m
(6)	Between a tank and a public boundary fence	Fixed or floating	Not less than 30 m
(7)	Between the top of the inside of the wall of a *tank compound* and a public boundary fence or to any fixed *ignition source*	–	Not less than 15 m
(8)	Between a tank and the *battery limit* of a process plant	Fixed or floating	Not less than 30 m
(9)	Between the top of the inside of the wall of a *tank compound* and the *battery limit* of a process plant	–	Not less than 15 m

[a] In the case of crude oil tankage this 15 m option does not apply.

Notes: (1) Small tanks are those of up to 10 m diameter; (2) a group of small tanks with a total capacity of 8000 m^3 may be treated as one tank; (3) where future changes of service are anticipated, the layout should be designed for the most stringent case; (4) in order to allow access for fire fighting, the number of rows of tanks between adjacent access roads should be limited to two; (5) fixed roof tanks with internal floating covers should be treated for spacing purposes as fixed roof tanks; (6) where fixed roof tanks and floating roof tanks are adjacent, the spacing should be designed for the most stringent case; (7) where tanks are erected on compressible soils, the spacing should be such as to avoid excessive distortion; (8) for Class III(1) and Unclassified petroleum liquids, spacing of tanks is governed only by constructional and operational convenience.

Separation distances for flammable liquids are given in HS(G) 50 and HS(G) 52. Figure 22.6 shows a general layout given in HS(G) 52 and Table 22.4 lists the separation distances given in this guide. These separation distances are for flammable liquids with flashpoints up to 55°C. There are, however, certain relaxations for liquids with a flashpoint in the range 32–55°C, which are described in the guide.

22.4.3 Separation distances: fire models

An alternative approach is to base separation distances on engineering principles. Two main factors which should determine separation are (1) the heat from burning liquid and (2) the ignition of a vapour escape. These principles and their application were discussed in Chapter 10.

The application of such engineering calculations to the separation distances for storage tanks has been treated by Hearfield (1970) and R.B. Robertson (1976b). Calculations on separation distances related to heat effects are usually based on direct flame impingement and on heat radiation.

It is commonly assumed that in a storage tank fire, the tank is effectively a pool of liquid with a flame burning on this liquid and that on a tank of diameter D the height of the flame in still air is $2D$.

If there is a wind, however, the flame is distorted. At a wind speed of 2 m/s it has been observed that the flame is deformed to an angle of 45° to the horizontal and that on the downward side of the fire the flame hugs the ground for a distance of about $0.5D$.

For the heat radiated from the flame, it is usually assumed, for simplicity, that still-air conditions prevail. The heat radiated is calculated and compared with limit values.

An equation given by Hearfield and by Robertson for the heat radiated from the envelope of a flame burning on a liquid pool in a storage tank is:

$$Q = k_1 A r \rho C \qquad [22.4.1]$$

where A is the surface area of the pool (m^2), C is the calorific value of the liquid (kj/kg), Q is the heat radiated from the flame envelope (kW), r the liquid burning rate (m/s), ρ is the density of the liquid (kg/m^3) and k_1 is a constant.

The value of the constant k_1 generally used by these authors is 0.3. Robertson gives liquid burning rates of 0.083–0.17 mm/s (5–10 mm/min). Hearfield gives liquid burning rates of 0.1, 0.3 and 0.4 in./min for 1, 7 and 35 ft diameter pools, respectively.

The application of Equation 22.4.1 is described by Robertson as follows. It is assumed that the heat is radiated from the envelope of a cylinder diameter D and height D, and that in turn this is equivalent to radiation from a radiating area which is a vertical rectangular plane of width D and height $2D$. The heat flux received by another storage tank is obtained from the view factor method. He states that for most hydrocarbon flames, the heat radiation from the surface of the cylinder is approximately 170–240 kW/m^2 and suggests that a suitable limit for the heat received by an adjacent storage tank is 37.8 kW/m^2. Other limit values for heat radiation which are relevant to separation were given in Chapter 10.

It is pointed out by Robertson that the separation distances in some storage installations are less than ideal. For example, on many small chemical plants storage tanks approximately 6 m diameter and 6 m high are spaced 2 m apart. If a fire occurs when the wind direction is along the line of the tanks and the wind speed is 2 m/s, the fire would spread rapidly by direct flame impingement. It may not

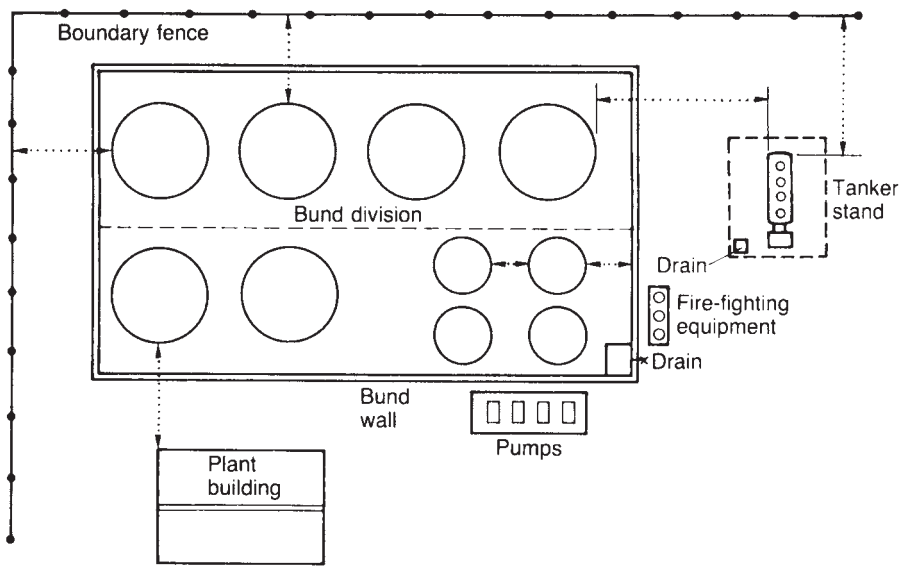


Figure 22.6 *Layout for storage of flammable liquids (Health and Safety Executive, 1991 HS(G) 52). The distances shown by dotted lines should be as in the text and Tables 1 or 2 of HS(G) 52. (Courtesy of HM Stationery Office* © *All rights reserved)*

Table 22.4 *Minimum recommended separation distances for the storage of flammable liquids: HS(G) 52 (Health and Safety Executive, 1991 HS(G) 52) (Courtesy of HM Stationery Office © All rights reserved)*

A Fixed roof tanks

Factor	*Minimum separation distance from any part of the tank* (m)
(a) Between groups of small tanks[a] (see note below)	15
(b) Between a group of small tanks and any tank outside the group	15
(c) Between tanks not being part of a group of small tanks	Half the diameter of the larger tank, the diameter of the smaller tank, or 15 m, whichever is least, but never less than 10 m
(d) Between a tank and any filling point, filling shed or building, not containing a possible source of ignition	15
(e) Between a tank and outer boundary of the installation, any designated non-hazardous area, or any fixed source of ignition	15

B Floating roof tanks

Factor	*Minimum separation distance from any part of the tank* (m)
(a) Between two floating roof tanks	10 m for tanks up to and including 45 m diameter; 15 m for tanks over 45 m diameter. The size of the larger tank should govern the spacing
(b) Between a floating roof tank and a fixed roof tank	Half the diameter of the larger tank, the diameter of the smaller tank or 15 m, whichever is least, but never less than 10 m
(c) Between a floating roof tank and any filling point, filling shed or a building not containing a possible source of ignition	10
(d) Between a floating roof tank and outer boundary of the installation, any designated non-hazardous area or any fixed source of ignition	15

C LPG storage[b]

	Distance from flammable liquid tank (m)	*Distance outside bund wall around a flammable liquid tank* (m)
LPG cylinders (> 50 kg total capacity)	3 (3)	3 (0)
LPG vessel	6 (6)	6 (3)

[a] A group of small tanks, 10 m in diameter or less, may be regarded as one tank. Such small tanks may be placed together in groups, no group having an aggregate capacity of more than 8000 m^3. The distance between individual tanks in the group need be governed only by constructional and operating convenience but should not be less than 2 m.
[b] The figures in brackets relate to liquids with a flashpoint greater than 32°C.

always be possible to have the ideal separation, but the decision on the separation distance should be made with full awareness of the implications. A similar approach may be taken using the more recent models given in Chapter 16.

22.4.4 Secondary containment

Some types of liquid storage tank are normally surrounded by a bund, or dike, and/or provided with a pit to retain any spillage of the liquid, or impounding basin. Bunds are made of earth or concrete.

In general, bunds are provided for atmospheric storage tanks and for fully refrigerated storage tanks of liquefied gas, but not for pressure or semi-refrigerated storage of liquefied gas or for acid or alkali storage, although this generalization needs some qualification.

The object of bunding is to retain the liquid so that it can be dealt with in a controlled manner, by evaporation from a specially designed catchment/evaporation area, by foam blanketing or other measures.

Thus, the relatively weak atmospheric storage tanks are generally provided with full bunds, while pressure storage vessels may not be. Bunds tend not to be used for pressure vessels because these rarely fail, the emission when it does occur is mainly in vapour/spray form and the dispersion of small leaks and spillages is hindered. Even where a full bund is not used, however, a low wall may be provided which gives the vessel some protection from damage by vehicles. Low walls may also be used to keep flammable liquids from some external source from reaching a storage vessel.

It may be noted that experience shows that in most cases of tank rupture only a proportion of the liquid in the

tank is lost and in many other cases most of the liquid is retained in the tank.

Some practical aspects of the design of bunds for flammable liquids have been discussed by Hearfield (1970). He draws attention to the fact that a leak in the side of a tank may form a horizontal jet and may jump the bund if the latter is too close to the tank, an effect known as spigot flow. The bund wall should be far enough from the side of the tank to prevent a jet jumping over or, alternatively, the bund should be surrounded by an impervious surface sloped inward to the bund drain area. The corners of the bund should be rounded and not at a right angle. It is difficult to extinguish a fire in a 90° angle corner because of the air compression effect.

The IP *Refining Safety Code* gives requirements for tank compounds. It states that Class I, II(1), II(2) and III(2) petroleum liquids should be completely surrounded by a wall or walls. Alternatively, the ground should be so sloped that spillages are directed to an impounding basin.

The *Code* gives the following restrictions on the total capacity of tanks in one bunded area: (1) single tanks: no restriction; (2) groups of floating roof tanks, 120,000 m^3 maximum; (3) groups of fixed roof tanks, 60,000 m^3 maximum and (4) crude tanks, not more than two tanks of greater individual capacity than 60,000 m^3. The figures for (2) and (3) may be exceeded for groups of not more than three tanks where conditions are suitable, that is there is no hazard to the public or risk of pollution.

The *Code* states that the net capacity of a tank compound should generally be equivalent to the capacity of the largest tank, but that a capacity of 75% will provide reasonable protection and may be used where conditions are suitable. The net capacity of the compound should be calculated by deducting from the total capacity the volume of all tanks, other than the largest, below the top of the compound wall and the volume of all intermediate walls within the compound.

For Class III(1) and Unclassified petroleum liquids, the code states that a low wall, which need not be more than 0.5 m high, should be constructed around the tankage, where conditions are such that the liquid could escape and cause damage or pollution.

Guidance on bunding for flammable liquids is given in HS(G) 50 and HS(G) 52. In respect of the restrictions on tankage within one bund and of bund capacity, the requirements are consistent with, but less detailed than, those of the IP *Code*.

HS(G) 52 states that the height of the bund wall should be restricted in order to ensure good ventilation, access for fire fighting and means of escape. It should not normally exceed 1.5 m, though it may go up to 2 m provided these factors have been taken into account.

For removal of rainwater, HS(G) 52 requires that where a bund drain is used it should have a valve on the outside of the bund with a system of work to ensure that the valve remains closed, and preferably locked, except when water is being removed. If the liquid stored is immiscible with water, there should be an interceptor to prevent flammable liquid entering the main drainage system. If the liquid is miscible with water, special arrangements are needed.

Guidance on bunds is also given in NFPA 30 and BS 5908. A further discussion of bunding is given in Section 22.21.

22.4.5 Hazardous area classification

Control of ignition sources in storage areas is exercised through the system of hazardous area classification (HAC). The principles of HAC have been described in Chapters 10 and 16.

Guidance on HAC for refineries, including storage, is given in API RP 500: 1991 *Recommended Practice for Classification of Locations for Electrical Installations* at *Petroleum Facilities*. This supersedes the separates RPs 500A, 500B and 500C, which covered refineries, offshore rigs and platforms, and pipelines, respectively. Guidance on HAC for storage is given in the *Area Classification Code for Petroleum Installations* of the IP (1990 MCSP Pt 15) (the IP *Area Classification Code*). The guidance of the Health and Safety Executive (HSE) is given in HS(G) 50 and HS(G) 52.

Figure 22.7 shows some HAC classification diagrams for petroleum storage tanks given in the IP *Area Classification Code*. Table 22.5 from HS(G) 52 gives some principles for the delineation of the zones around storage tanks in the HAC.

22.5 Venting and Relief

22.5.1 Atmospheric vents

A fixed roof atmospheric storage tank is connected to the atmosphere by some form of a vent, generally either a simple free flow atmospheric vent or a pressure/vacuum (PV) valve.

Vents for atmospheric storage tanks are dealt with in BS 2654: 1989 in appendix F and in API Std 2000: 1992 *Venting Atmospheric and Low Pressure Storage Tanks (Non-refrigerated and Refrigerated)*.

Since atmospheric tanks can withstand pressure/vacuum of only a few inches WG, it is essential that atmospheric vents should remain free. Blockage can occur accidentally due to debris, icing up, solids formation, polymerization, etc.

A flame arrester on the end of a vent also serves to keep out debris. If there is no arrester, a coarse wire mesh guard is usually provided. But there is a danger of blockage of flame arresters and guards. The use of flame arresters is considered further below.

The tank may also suffer overpressure or underpressure if the capacity of the vent is not sufficient. Pressure changes occur mainly during filling and emptying, but also in other circumstances.

Situations in which tank failures tend to occur due to accidental blockage or deliberate sealing off of a vent, or to lack of capacity in the vent, were described in Chapter 20.

22.5.2 Pressure/vacuum valves

A PV valve, also called a breather valve or conservation vent, actually has two vent valves – a pressure valve which opens to let vapour out and a vacuum valve which opens to let air in.

A fixed roof tank tends to breathe fairly heavily and appreciable vapour loss can occur through an atmospheric vent, particularly for a volatile liquid. A PV valve is effective in reducing this loss.

Avoidance of blockage and provision of adequate capacity are important for PV valves also. PV valves are subject to failure from icing up and deposition of material on the valve diaphragms or in the branch on the tank. The danger of ice formation is usually most severe just after the tank has been water tested, and the valve diaphragms are often removed for about 2 weeks until the water content of the liquid has reduced to normal, although the problem is less with newer diaphragm materials such as PTFE.

22.5.3 Flame arresters

If the vapour space above the liquid in a fixed roof atmospheric storage tank contains a flammable mixture, there is

a possibility that it will be ignited via the vent. A flame arrester may be used to prevent this.

Flame arresters have already been discussed in Chapter 17. General accounts are given in *Guide to the Use of Flame Arresters and Explosion Relief* by the HSE (1965 HSW Bklt 34) and API Publ. 2028: 1991 *Flame Arresters in Piping Systems*. The discussion here is limited to the question of their use on storage tank vents.

The object of a flame arrester is to prevent a flame passing back through a vent to ignite a flammable mixture in the vapour space of the tank. Consideration needs to be given, therefore, to the conditions under which a flammable mixture can exist. The range of materials stored is such that for some the vapour mixture is below the lower flammability limit, while for others it is above the upper flammability limit, but for others again it is in the flammable range.

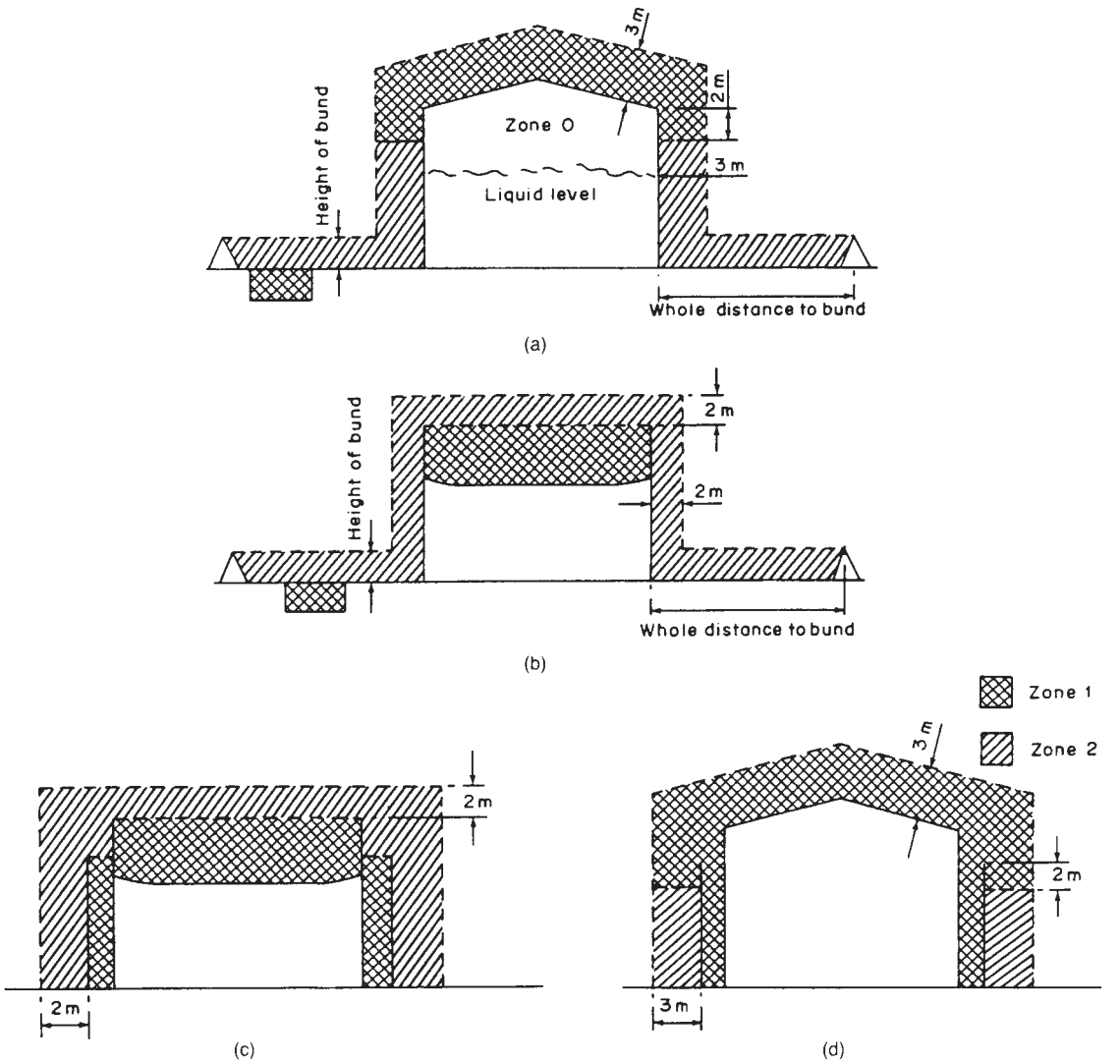


Figure 22.7 *Hazardous area classification of petroleum storage tanks: (a) cone or dome roof tank – Classes I, II(2) and III(2); (b) floating roof tank, where roof will not be grounded on its leg during operational cycle; (c) floating roof tank with outer protective wall; (d) cone roof tank with outer protective wall, for (a), because of the possibility of mist, spray or foam formation the ullage space of Class II(1) and III(1) tanks should also be regarded as Zone 0. It is recommended that the area surrounding any vents or openings on the roof of such a tank be regarded as Zone 1 to a diameter of 1 m (Institute of Petroleum, 1987 LPG storage Code; reproduced by permission)*

Table 22.5 *Guidelines for the hazardous area classification of the storage of flammable liquids (Health and Safety Executive, 1991 HS(G) 52) (Courtesy of HM Stationery Office. © All rights reserved)*

Item	*Extent of area*	*Classification*
Above-ground tanks	(a) Vertically from ground level to the height of the bund wall, and horizontally from the tank shell to 1 m outside the bund wall	Zone 2
	(b) Within 2 m of the tank shell	Zone 2
Underground tanks	Within any manhole chamber containing filling connections	Zone 0
Tank connections (all tanks)	Within a horizontal radius of 4 m from tank filling connections, and vertically from ground level up to 1 m above the connections	Zone 2
All tanks	Within the vapour space	Zone 0
Vent pipes	(a) Within a radius of 3 m in all directions of the open end of any vent pipe	Zone 1
	(b) The area below the Zone 1 area of any vent pipe, for a radius of 3 m around the discharge point and down to ground level	Zone 2
Pumps and sample points	Within a horizontal radius of 4 m and vertically from ground level to 2 m above the unit	Zone 2
Road and rail tankers (at loading/unloading points)	(a) Withn 300 mm in any direction of any opening on the tanker, and down to ground level	Zone 1
	(b) Within 2 m of the shell of the tanker	Zone 2
	(c) Within a horizontal radius of 4 m from tanker discharge connections and vertically from ground level up to 1 m above the connections	Zone 2
	(d) Within a radius of 1.5 m of any opening on the tank top, and down to ground level	Zone 1
	(e) On the top of the tank within the valence	Zone 1

Notes:
(1) Where an area is classified under more than one heading the more stringent classification should be adopted.
(2) Any pit, trench or depression in a Zone 1 or Zone 2 area should be considered a Zone 1 area throughout.
(3) Where tanks are mounded or buried in a hillside, etc., and access is by means of a tunnel or adit, typically 2 m or more in height, the space in the tunnel should normally be considered a Zone 1 area.

The situation is also affected by the use of a floating deck. This reduces the concentration of vapour, but does not necessarily eliminate flammable mixtures. The vapour space above the floating deck may in fact go from a mixture above the upper flammability limit near the deck to one below the lower flammability limit near the fixed roof.

It is also necessary to consider the conditions under which a flame can occur at the vent outlet. For this to happen the vent must be exhaling vapour. It may be assumed that it does this, on average, half the time. The situations which give rise to exhalation of vapour are, in particular, filling operations and temperature rises. Thus the conditions under which a flame may flash back and cause an explosion are when the vapour space in the tank contains an explosive mixture and the vent is exhaling vapour.

The desirability of using flame arresters has been a matter of some debate. Insurance companies have often recommended their use. Thus the Factory Mutual Engineering Corporation (FMEC, 1967) recommends their use on atmospheric vents for liquids with flash points below 110°F (43°C) and for liquids which may be heated above their flashpoints.

A discussion of the problem is given in API Publ. 2210: 1982 *Flame Arresters for Vents of Tanks Storing Petroleum Products*, though this is no longer listed. Flame arresters are a potential cause of vent blockage and tank collapse and their use needs to be justified.

The case for the use of a flame arrester in addition to a PV valve is less than clear. API Publ. 2210 suggests that where a PV valve is used, there is no good reason to put a flame arrester on.

The argument supporting this view is broadly on the following lines. Tank fires caused by lightning were a problem on the older wooden-roofed tanks, but with the advent in about 1920 of truly gas-tight steel roofs combined with PV valve, such fires are rare. The probability of tank fires via vents is low, because most oil industry stocks do not give a vapour mixture in the flammable range above the liquid, and ignition sources are excluded from the vicinity of vents. Moreover, it is notoriously difficult to keep flame arresters well maintained and this introduces the hazard of vent blockage and tank collapse.

API Publ. 2210 concludes: 'There is no supportable basis for requiring that an outdoor above-ground tank provided with a pressure—vacuum valve must also be equipped with a flame arrester. The use of flame arresters is discouraged unless the user is able to institute the maintenance necessary to ensure that the required venting capacity is maintained.'

API Std 2000: 1992 takes a similar stance, stating: 'A flame arrester is not considered necessary for use in conjunction with a PV valve because flame speeds are less than vent velocities through PV valves'. It does, however, go on to say: 'Open vents with a flame-arresting device may be

used in place of PV valves on tanks in which oil with a flash point below 100°F (37.78°C) is stored and on tanks containing petroleum and petroleum products where the fluid temperature may exceed the flash point'.

The IP *Refining Safety Code* states that fixed roof tanks for Class I and II liquids are usually fitted with PV valves and tanks for Class III and Unclassified liquids with open vents. It further states that PV valves or open vents should not be fitted with fine mesh gauze, which is liable to clog.

HS(G) 50 and HS(G) 52 state that a flame arrester should normally be installed on an open vent on a fixed roof tank storing liquid with a flash point below 21°C. But a flame arrester is not necessary on a PV valve and should not be used where the liquid is liable to block the arrester by polymerization or otherwise.

22.5.4 Fire relief

It is also necessary for fixed roof storage tanks to provide for the effect of fire which heats the liquid, increases its vaporization and causes a rise in pressure. Tanks can normally withstand a pressure of only a few inches WG. It is normal not to size atmospheric vents or PV valves for fire relief but to provide for this by separate emergency venting.

Methods of providing emergency venting for fire are described in API 2210. They include larger or additional open vents, larger or additional PV valves, lifting manhole covers or hatches and a weak roof-to-shell connection.

This latter arrangement involves the use of a weak roof-to-shell attachment, otherwise known as a frangible joint or rupture seam. This involves making the seam between the shell and the roof deliberately weak so that it is the first to rupture, thus ensuring that the shell stays intact and contains the liquid. The incorporation of such a frangible joint as an emergency vent in accordance with API 2210 is allowed for in API Std 650. Not all companies consider it good practice to rely on a rupture seam for fire relief, although one may still be used to relieve explosions.

The methods given in API Std 2000 for the determination of the heat input into storage tanks in a fire, and hence of the venting capacity required, are described in Chapter 16.

22.6 Fire Prevention and Protection

Accounts of fire prevention and protection of petroleum storage are given in *Storage and Handling of Petroleum Liquids* by J.R. Hughes (1970) and *Fire Protection Manual for Hydrocarbon Processing Plants* by Vervalin (1964a, 1973a). Relevant standards and codes are API RP 2001: 1984 *Fire Protection in Refineries*, the IP *Refining Safety Code*, NFPA 30: 1990 *Flammable and Combustible Liquids Code*, BS 5306: 1976– *Fire Extinguishing Installations and Equipment on Premises* and BS 5908: 1990 *Code of Practice for Fire Precautions in the Chemical and Allied Industries*. HSE guidance is given in HS(G) 50 and HS(G) 52.

Fire prevention in and protection of storage has several objectives. These are (1) to minimize the risk to personnel, (2) to minimize loss due to the initial fire, and (3) to prevent the spread of fire to other vessels and equipment. Personnel are at risk principally from an explosion or sudden spread of fire.

Implementation of fire protection for storage takes the two forms (1) fighting the fire and (2) protecting the storage vessels. Methods of fire prevention and protection in general have been described in Chapter 16. The discussion there includes some treatment of storage, including the application rates of fire-fighting media.

A major contribution to fire prevention in storage is made by layout, as described in Section 22.4. Important aspects of storage layout are the practice of segregation, the provision of separation distances and HAC.

22.6.1 Inerting of storage tanks

An effective method of fire prevention in storage is inerting. This is widely used to reduce the hazard of fire in atmospheric storage tanks. The value of inerting in reducing fire/explosion in storage tanks was discussed in Chapter 16 and methods of inerting were described in Chapter 17.

22.6.2 Fire protection of storage tanks

There are two main effects of fire on an atmospheric storage tank. One is that those parts of the tank which are not cooled by the liquid inside may become hot and weaken. The other is that the liquid inside the tank is heated up and its vaporization is increased. In a fixed roof storage tank, this results in a pressure rise and, as explained earlier, relief of such pressure is now normally effected by the use of some form of emergency vent.

Fire protection for atmospheric storage tanks is provided by fixed water or foam sprays, which may be supplemented by fireproof thermal insulation, and by mobile water and foam sprays.

Fixed water sprays are effective in giving immediate cooling of exposed surfaces and are particularly useful where manpower is limited or access for mobile equipment is difficult. But the main water sprays are normally provided by mobile equipment and are used both to fight the fire and to cool exposed surfaces. There are also mobile water curtains which can be interposed to protect vessels if sufficient manpower is available.

For cooling of an unwetted tank surface a rate of application of water of 0.2 UKgal/ft^2 min (10 l/m^2 min) has been found satisfactory. It is desirable to cool the wetted surface also to minimize the rise in pressure, but the effectiveness of water cooling then depends on the boiling point of the stored liquid. If this is below the boiling point of water, the water does not vaporize and the cooling due to the latent heat effect is not obtained. If, however, the boiling point of the liquid is above that of water, then the water does vaporize and is much more effective.

Foam is used to extinguish fires rather than to cool surfaces. The type of foam used is normally mechanical foam. Fixed foam pourers are used to direct foam to the inside of the tank shell so that the foam flows over the liquid surface. Another fixed device which puts foam on the liquid surface is the Swedish semi-subsurface foam system. This consists of a hose which is connected through the tank shell to a foam supply and is normally at the bottom of the tank. Injection of foam inflates the hose, the top end of which rises to the liquid surface and sprays the foam.

Mobile foam-spraying equipment consists of mobile monitors and portable foam towers. A monitor projects jets of foam in a manner similar to that of conventional fire water jets. A portable tower is a light tube which is put upon the side of the tank and pours foam on the top of the liquid. There are various types, some assembled manually and others of telescopic design extended mechanically or hydraulically.

Mobile foam monitors are available with a foam output of 5000 UKgal/min and a range of 60 m (200 ft) in still air. For extinguishing fire, a rate of application of foam of 0.1 UKgal/ft^2 min (4.5 l/m^2 min) has been found necessary.

Fixed equipment such as foam pourers is very vulnerable to damage by explosion.

The application of foam from foam monitors requires some skill. An experienced operator can project foam so that it hits the inside of the tank on fire and runs down and blankets the burning liquid.

The amount of foam used is large and it is necessary to make arrangements for adequate supplies.

22.6.3 Pipework and fittings

Fire can also have a very damaging effect on pipework, which sometimes may withstand the fire for only about 10 min. Pipework is very vulnerable to fire and should be protected as far as possible. Fireproof insulation on pipework near storage vessels may be appropriate.

A small fire at a leaking flange can have a torch effect and this possibility should be borne in mind in designing pipework. A fire of this type was one of the causes considered at the Flixborough Inquiry.

22.7 LPG Storage

Some aspects of the storage of other fuels and chemicals are now considered, starting with LPG. The handling and processing of many of these substances were treated in Chapter 11 and the design of pressure systems in Chapter 12, and these topics are therefore not discussed here. However, attention is drawn to the fact that aspects such as the materials of construction, the pipework, the valves and the pumps are particularly important for these chemicals.

Propane and butane are referred to as LPG. They are described in *An Introduction to Liquefied Petroleum Gas* (LPGITA, 1974/1). A general account of LPG is given in Chapter 11.

Codes and standards for LPG were given in Chapters 10 and 11. HSE guidance on LPG storage is given in HS(G) 34 *The Storage of LPG at Fixed Installations* (1987). Other relevant codes are *Design, Installation and Maintenance of Bulk LPG Storage at Fixed Installations* (LPGITA, 1991 COP 1 Part 1) (the LPGA LPG Storage Code), NFPA 58: 1989 *Storage and Handling of Liquefied Petroleum Gases* (also published as the *Liquefied Petroleum Gases Handbook*) and NFPA 59: 1989 *Storage and Handling of Liquefied Petroleum Gases at Utility Plants*. The code *Liquefied Flammable Gases Storage and Handling* (ICI/RoSPA 1970 IS/74) (the ICI *LFG Code*), though out of print, contains much valuable guidance.

LPG is stored at petroleum storage terminals, at chemical works and at many non-chemical factories.

22.7.1 Regulatory requirements

The storage of LPG is governed by the Notification of Installations Handling Hazardous Substances (NIHHS) Regulations 1982 and the Control of Industrial Major Accident Hazards (CIMAH) Regulations 1984. The NIHHS notifiable inventory is 25 te for pressure storage and 50 te for refrigerated storage. The CIMAH inventory for either type of storage for which demonstration of safe operation may be required (Regulation 4) is 50 te and that which attracts a safety case (Regulation 7) is 200 te. An account of the regulatory requirements for LPG in Germany has been given by Ackermann (1986).

22.7.2 Storage conditions

Fully refrigerated storage is essentially at atmospheric pressure and at the boiling points of the substances concerned. For pressure storage, the temperature follows the ambient temperature and the pressure is the corresponding vapour pressure of the substance. The boiling point of pure propane is −42°C and that of pure *n*-butane is 0°C. The boiling point of commercial propane is −45°C and that of commercial butane is −2°C. At a pressure reference temperature of 38°C the vapour pressure exerted by commercial propane is 4.83 barg and that exerted by commercial butane is 14.5 barg.

22.8 LPG Storage: Pressure Storage

22.8.1 Storage vessels

Pressure storage of LPG is in horizontal cylindrical or spherical pressure vessels. The former are used for smaller quantities and the latter for larger ones.

The design of pressure vessels for LPG pressure storage is discussed in the Liquefied Petroleum Gas Association (LPGA) LPG *Storage Code*. The design pressures and temperatures should take into account the extreme ambient and service conditions to which the storage may be subject. The *Code* states that the design conditions should not be less onerous than the following:

	Commercial butane	*Commercial propane*	
		Liquid offtake	*Vapour offtake*
Maximum temperature (°C)	38	38	38
Maximum pressure (barg)	4.83	14.5	14.5
Minimum temperature (°C)	−18	−18	−40
Minimum pressure (mbarg)	−524	Zero gauge	Zero gauge

The values given for the maximum temperature, or pressure reference temperature, are for a vessel finished in white; a higher maximum design temperature and pressure should be used for a vessel in a finish which reduces normal reflection of solar radiation. A higher minimum temperature should be used only for dedicated service where controls are provided to limit the lowest fluid temperature to a value higher than that shown. A higher minimum pressure for butane should be used only if means are provided to ensure that an unacceptable vacuum does not occur or if the ambient temperature is such as to ensure that the fluid temperature will be higher than −18°C.

As the LPGA *Code* indicates, more stringent design pressures and temperatures may be appropriate. Some of the factors which bear on this are discussed in the ICI LPG *Code*. For the maximum reference temperature in the United Kingdom the *Code* suggests that the following temperatures be assumed for a hot summer day:

Temperature	*Tank capacity* (m^3)
47.5	<5
42.5	5–30
41	30–100
40	>100

The *Code* states that the design pressure at the top of the vessel should be set equal to the greater of (1) 110% of the maximum operating pressure or (2) the maximum operating pressure plus 1 bar (14.5 psi), and that the design pressure at the bottom of the vessel should be set equal to that at the top plus the static head of the product or water, whichever is the greater.

The choice of design pressure should also be considered in conjunction with relief and blowdown arrangements, since these can be expensive, and it may be economic to increase further the design pressure.

The maximum design temperature for pressure storage vessels is determined by the loss of strength in the metal at high temperatures. Increased temperature always leads to loss of strength, but the fall-off is much greater for a vessel designed to an advanced code rather than a conventional one. The ICI code states, for example, that the design stress for a vessel designed to BS 1500 does not reduce significantly until 400°C, whereas that for a vessel designed to BS 1515 falls off rapidly above 50°C, so that the maximum design temperature needs to be considered particularly carefully when using BS 1515. The maximum temperature reached by the metal is likely to be during a fire. The temperature of unprotected metal rises rapidly in a fire, but there are several features which may mitigate this. The metal is normally protected by fire insulation and water sprays, and metal in contact with the liquid inside is cooled by the liquid boil-off.

The minimum design temperature for pressure storage vessels is normally set by the loss of ductility and hence brittle fracture in the metal at low temperatures. There are several ways in which a low metal temperature may occur. The ambient temperature may be low, although in this case there is normally a time lag due to insulation. The metal may come in contact with low temperature liquid due to abnormal operating conditions in the process or loss of pressure and liquid boil-off in the vessel. This latter effect, however, is likely to signal its presence and the *Code* suggests that it may be assumed that for a vessel of reasonable size action would be taken before the temperature has fallen to that corresponding to atmospheric pressure.

The combinations of pressure and temperature which may occur should also be considered.

The material of construction of most storage vessels is carbon steel, but other materials may be used.

A classic set of general arrangements for pressure storage vessels is given in the ICI *LPG Code*. Figure 22.8(a) shows those for a horizontal cylindrical vessel and Figure 22.8 (b) shows those for a spherical vessel. Another set of general arrangements for such vessels given by Nazario (1988). Figure 22.9 shows the arrangements for horizontal cylindrical storage vessels given in HS(G) 34.

22.8.2 Separation distances

Separation distances for pressurized LPG storage are given in HS(G) 34, the IP *LPG Code* and NFPA 58.

Minimum separation distances for LPG pressure storage vessels given in HS(G) 34 are shown in Table 22.6. Guidance is also given on separation distances between LPG and storages of flammable liquids, toxic substances, LPG cylinders and cylinder filling buildings. For flammable liquids, the separation distance is 6 m to the bund wall for liquids with a flashpoint <32°C or 6 m to the tank and 3 m to the bund wall for liquids with a flashpoint of 32–65°C. For toxic or hazardous substances the separation distance is as given in Table 22.6 for buildings, etc., subject to a minimum value of 15 m. HS(G) 34 also gives the separation distances between LPG and liquid oxygen storages.

The approach to minimum separation distances in NFPA 58 is broadly similar. This code also gives separation distances between LPG and both oxygen and hydrogen storages.

The approach to minimum separation distances in Germany is described by Ackerman (1986).

22.8.3 Separation distances: fire models

As described earlier, an alternative approach to the setting of minimum separation distances is the use of models for vapour dispersion and fire radiation. An account of the application of this approach to petroleum storage is given in Section 22.4.

The separation distances for LFG given in the ICI *LPG Code*, and shown in Table 22.7, owe something to this approach, and are an early, if implicit, example of its use. Two methods of determining the heat received by pressure vessels are also presented in this *Code*, but these are not used there to determine separation distances, which are obtained from Table 22.7. The two methods are used to calculate the requirements for pressure relief and for drench water as described below. The modelling approach to separation distances is now entering mainstream codes. The minimum separation distances given in the IP *LPG Code* for LPG pressure storage are specified in terms of the thermal radiation flux from certain defined fires. These fires are jet fires from the vessel relief valve and spillages from the vessel, its associated equipment and other identified leak sources, with spillage possibly forming a pool in the bund or impounding basin. The *Code* gives guidance on potential leak sources and emission rates and on the thermal radiation from jet and pool fires. The minimum separation distances given in the code are shown in Table 22.8.

22.8.4 Secondary containment

For pressure storage vessels containing LFG a full bund is not used. It is true that an appreciable proportion of a spillage remains as liquid after the initial flashing off of vapour. For example, if liquid propane at 16°C escapes to atmosphere the theoretical proportion of liquid remaining after flashing off is 67%.

However, complete loss of containment from a properly designed, maintained and operated pressure vessel is rare, material is in any case ejected mainly as vapour/spray, and smaller spillages from valvework can be dealt with by other means. Moreover, it is essential to allow free circulation of air so that small leaks and spillages are safely dispersed.

The arrangement recommended in the ICI *LFG Code* is that there should be a diversion wall with only the vessel on one side and all the joints and valvework on the other. The only requirement on the vessel side of the wall, where the risk of spillage is remote, is that the ground should slope away from the vessel, but on the other side there should be not only sloped ground and a catchment area but also such diversion walls as are necessary to ensure that a spillage flows into the latter. In an existing installation or other installation in which it is not possible to eliminate joints and valvework under the vessel, these diversion walls should be put around the vessel.

The vessel and its pipework should also be protected against damage by vehicles, by the use of some form of crash barrier if necessary.

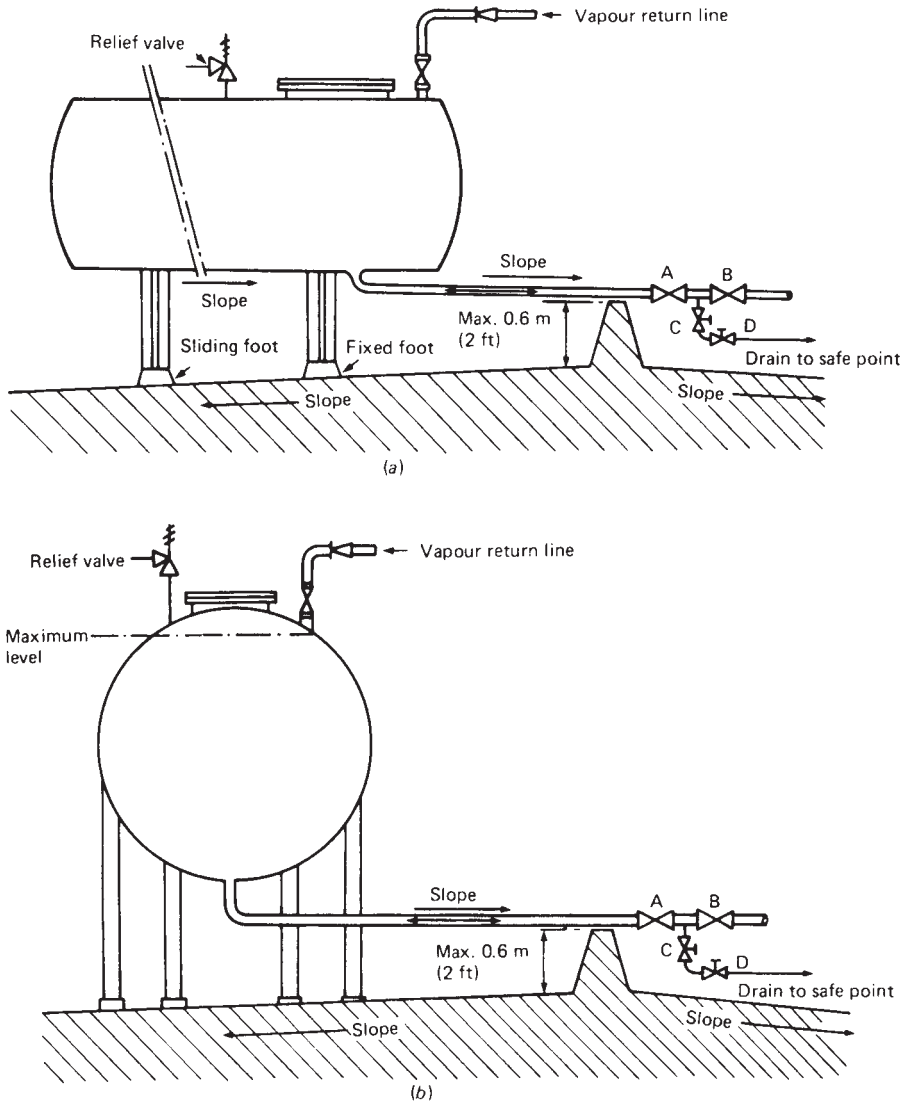


Figure 22.8 *General arrangement of LPG pressure storage vessels with special reference to piping: (ICI/RoSPA 1970 IS/74; reproduced by permission): (a) horizontal cylindrical vessel; (b) spherical vessel*

HS(G) 32 adopts a broadly similar approach, based on the principles of sloping the area under pipework connections, the use of diversion walls and an evaporating area, and the provision of a crash barrier against vehicle impact. It requires that the ground be impervious beneath the pipework connections, that the height of diversion walls should not exceed 0.5 m and that the evaporation area should be not less than 3 m from the vessel.

The IP *LPG Code* explicitly states that a bund is not normally required and its provisions are in line with the approaches just described.

The ICI *LFG Code* also considers pressure storage of non-hydrocarbon LFGs which are miscible with water and which it may be desirable to dilute. Thus, if the liquid can be rapidly diluted with water and rendered harmless, this is appropriate, and it is then not necessary to provide a catchment area for spillage. But some materials may need to be diluted for other reasons, for example toxicity. In this case, a full bund should be provided sufficient to take both the spillage and the dilution water. Walls should not exceed 2m (6 ft 6 in.) in height and they should have at least two access points.

22.8.5 Diversion walls and fire walls

Diversion walls can be used to divert large vapour flows to areas where they can be dealt with more safely.

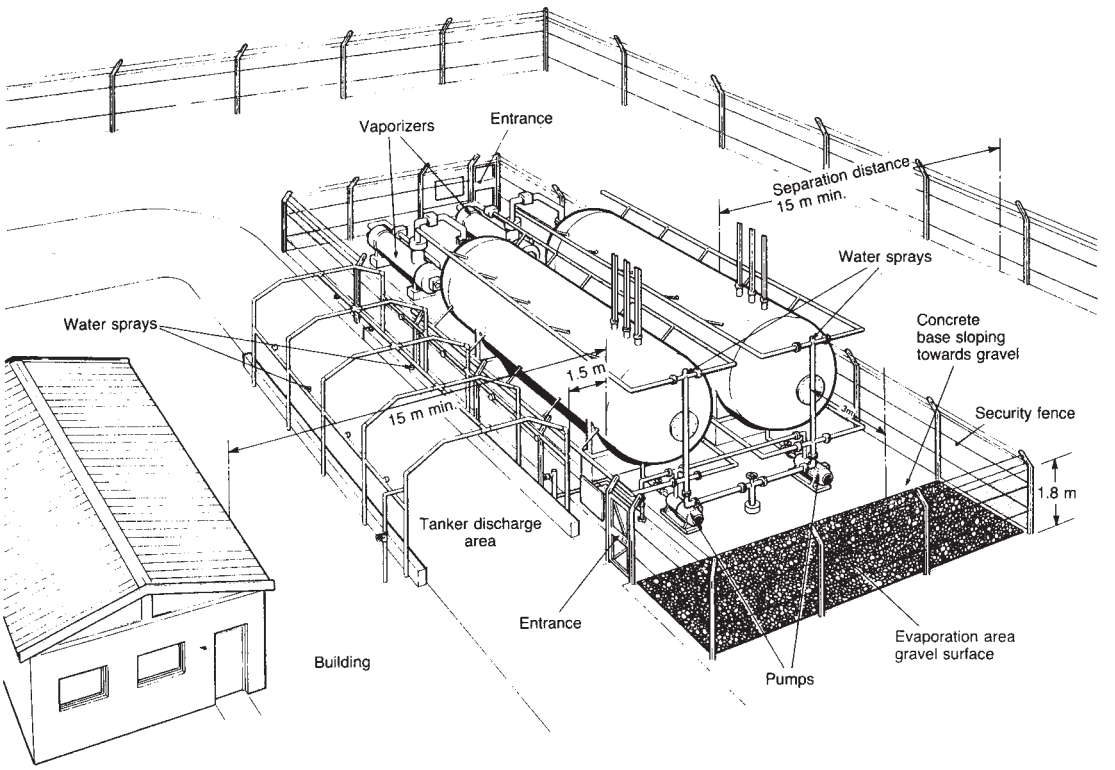


Figure 22.9 *General arrangement of LPG horizontal pressure storage vessels (Health and Safety Executive, 1987 HS(G) 34) (Courtesy of HM Stationery Office © All rights reserved)*

Table 22.6 *Minimum recommended separation distances for LPG pressure storage: HS(G) 34 (Health and Safety Executive, 1987 HS(G) 34) (Courtesy of HM Stationery Office © All rights reserved)*

Vessel capacity (te)		*Distance* (m)[a]		
Single vessel	*All vessels in a group*	*From buildings, boundary, property line or fixed fire source of ignition*	*With fire wall*	*Between vessels*
4–60	200	15	7.5	1.5
60–150	450	22.5	11	–[b]
>150	1000	30	15	–[b]

[a] These distances apply to above ground vessels. For mounded vessels the distances are as follows. The distances between buildings, etc., and the valve assembly are the same as those for above ground vessels with a fire wall; the distances between buildings, etc., and the vessel itself are 3 m in each case. The distances between vessels are 1.5 m for the lowest set of capacities quoted, but for the two higher sets the spacing should be determined by the site conditions and the requirements of installation, testing, maintenance and removal.
[b] One-quarter of the sum of the diameters of two adjacent vessels.

Steam curtains may also be considered as a means of maintaining separation from an ignition source, although they are actually used mainly around process plants.

Fire walls are utilized to give protection against flame or heat radiated from a fire.

Trenches leading from the storage area should be fire stopped at or near the boundary by barrier walls or bunds across the pipes. Drains with openings in the storage area should have means to prevent the transmission of insoluble flammable and noxious products to the general drainage system.

22.8.6 Hazardous area classification

Guidance on the HAC for LPG pressure storage is given in API RP 500, the IP *Area Classification Code*, and also in NFPA 58 and 59, the LPGA *LPG Storage Code* and HS(G) 34.

A table of guidelines for delineation of the zones round LPG pressure storage vessels for HAC is given in the LPGA *LPG Storage Code*. The virtually identical table given in HS(G) 34 is shown in Table 22.9.

Table 22.7 *Minimum recommended separation distances for LFG storage: IC1 LFG Code (ICI/RoSPA, 1970; reproduced by permission*

Minimum distance	*Material stored*					
	Hydrocarbons		*Non-hydrocarbons insoluble in water*		*Non-hydrocarbons soluble in water*	
Pressure storage[1]						
To boundary, process units, buildings containing a source of ignition, or any other fixed sources of ignition	Ethylene C_3s C_4s	60 m (200 ft) 45 m (150 ft) 30 m (100 ft)	Methyl chloride Vinyl chloride Methyl vinyl ether Ethyl chloride	23 m (75 ft) 23 m (75 ft) 15 m (75 ft) 15 m (50 ft)	Methylamines	15 m (50 ft)
To building containing flammable materials, for example filling shed		15 m (50 ft)		15 m (50 ft)		15 m (50 ft)
To road or rail tank wagon filling points		15 m (50 ft)		15 m (50 ft)		15 m (50 ft)
To overhead power lines and pipebridges		15 m (50 ft)		15 m (50 ft)		15 m (50 ft)
To other above ground power cables and important pipelines or pipelines likely to increase the hazard	(2)	7.5 m (25 ft)	(2)	7.5 m (25 ft)	See Note (3)	
Between pressure storage vessels	One-quarter of sum of diameters of adjacent tanks					
To low pressure refrigerated tanks	15 m (50 ft) from the bund wall of the low pressure tank, but not less than 30 m (100 ft) from the low pressure tank shell					
To flammable liquid[4] storage tanks	15 m (50 ft) from the bund wall of the flammable liquid tank					
Low pressure refrigerated storage[5]						
To boundary, process units, buildings containing a source of ignition, or any other fixed sources of ignition [6]	Ethylene 90 m C_3s C_4s	(300 ft) 45 m (150 ft) 15 m (50 ft)			Ethylene oxide	15 m (50 ft)
To building containing flammable materials, for example filling shed		15 m (50 ft)				15 m (50 ft)
To road or rail tanker filling point		15 m (50 ft)				15 m (50 ft)
To overhead power lines and pipebridges		15 m (50 ft)				15 m (50 ft)
Between low pressure refrigerated tank shells	One-half of sum of diameters of adjacent tanks					
To flammable liquid[4] storage tanks	Not less than 30 m (100 ft) between low pressure refrigerated LFG and flammable liquid tank shells, but LFG and flammable liquids must be in separate bunds					
To pressure storage vessels	As defined above under Pressure Storage					

Notes (to original table)

(1) Measured in plan from the nearest point of the vessel, or from associated fittings from which an escape can occur when these are located away from the vessel.

(2) If this distance cannot be achieved, the need for suitable fire protection of the cable or pipeline should be considered.

(3) The tanks containing water soluble non-hydrocarbons being bunded (see Clause 8.6.2), power cables and pipelines at ground level should be outside the bund and so protected by the bund from fire in the tanks.

(4) Flammable liquids are those with flashpoints up to 65.5°C (150°F).

(5) Measured in plan from the nearest part of the bund wall (see Clause 8.6.3), except where otherwise indicated.

(6) The Home Office *Code for Storage of LPG at Fixed Installations* recommends 45 m (150 ft) for C_4 as well as C_3, storage, which is considered to be unnecessarily conservative. The designer may be able to persuade the Licensing Authority of the adequacy of the ICI *Code* in this respect, in view of the significant difference in rate of vaporization of the respective materials.

Additional notes (communicated by ICI c. 1977):

(1) The separation distances quoted in this table are those within which leaks from pumps, valves, flanges, etc., will normally disperse to a safe level. They are not 'safety distances' for vapour cloud explosions.

(2) Refrigerated storage tanks are now often constructed with an outer wall of concrete which will retain any spillage. This design may permit the use of lower separation distances but no definite figure has been agreed.

Table 22.8 *Minimum recommended separation distances for LPG pressure and refrigerated storages: IP LPG Storage Code (Institute of Petroleum, 1987 LPG Storage Code)*

A Pressure storage

Site	*Maximum radiation flux levels*	
	(kW/m^2)	($BTU/h\ ft^2$)
Equipment		
The outer surfaces of adjacent *pressure storage vessels* (1):		
Thermally protected (2)	44	13,750
Unprotected (3)	8	2,500
The outer surfaces of adjacent storage *tanks* containing *flammable* products (4) and process facilities:		
Thermally protected (2)	32	10,000
Unprotected (3)	8	2,500
Filling/discharge points	8	2,500
Personnel inside boundary		
Process area (5)	8	2,500
Protected work area (6)	8	2,500
Work area (7)	5	1,500
Critical area (8)	1.5	500
Plant boundary		
Remote area (9)	13	4,000
Urban area (10)	5	1,500
Critical area (8)	1.5	500

B Refrigerated storage

Site	*Maximum thermal radiation flux levels*	
	(kW/m^2)	($BTU/hr\ ft^2$)
Equipment		
The outer surfaces of adjacent *refrigerated storage tanks:*		
Thermally protected (2)	32	10,000
Unprotected (3)	8	2,500
The outer surfaces of adjacent storage *tanks* containing *flammable* products (4):		
Thermally protected (2)	32	10,000
Unprotected (3)	8	2,500
The outer surfaces of adjacent LPG *pressure storage vessels* and process facilities (11)	8	2,500
Personnel inside boundary		
Process area (5)	8	2,500
Protected work area (6)	8	2,500
Work area (7)	5	1,500
Critical area (8)	1.5	500
Plant boundary		
Remote area (9)	13	4,000
Urban area (10)	5	1,500
Critical area (8)	1.5	500

Notes:

(1) The distance from an LPG *pressure storage vessel* to a *refrigerated storage tank* is determined by the requirement of Chapter 3 (see 3.3.1) and Table 2 of this appendix.
(2) Such facilities/areas are protected by means of water sprays, insulation, radiation screens or similar systems.
(3) Protection is provided by spacing alone.
(4) Special consideration should be given to the location of floating roof tanks containing high vapour pressure products since effective water cooling of their roof structures is impracticable.
(5) A normally unoccupied area occasionally manned by trained and suitably clothed persons familiar both with escape routes and opportunities for temporary shelter afforded by the process plant.
(6) A permanent building where personnel inside are shielded and/or have a shielded means of escape.
(7) An open area or small (e.g. temporary) building without a shielded means of escape.
(8) This is either an unshielded area of critical importance where people without protective clothing may be required at all times including during emergencies or a place difficult or dangerous to evacuate at short notice (e.g. a sports stadium).
(9) An area only infrequently occupied by small numbers of persons, for example moorland, farmland, desert.
(10) An area which is neither a remote area nor a critical area.
(11) The allowable thermal radiation flux level is restricted for these facilities in view of the potentially longer duration of exposure resulting from a *refrigerated tank/bund* fire.

Table 22.9 *Guidelines for hazardous area classification of LPG pressure storage (Health and Safety Executive, 1987 HS(G) 34) (Courtesy of HM Stationery Office © All rights reserved)*

Factor		*Area classification*
Storage vessels	(a) Within 1.5 m in all directions from the discharge orifice of fixed liquid level gauges, rotary or dip gauges, filler openings	Zone 1
	(b) Up to 1.5 m above ground level and within the distances set out for a fixed source of ignition in Table 2 column (a)[b]	Zone 2
Relief valve discharge	(a) Within direct path of discharge	Fixed electrical equipment should not be installed
	(b) Within 1.5 m in all other directions from point of discharge	Zone 1
	(c) Beyond 1.5 m but within 4.5 m, or the separation distance in Table 2 column (a)[b] in the case of vessels with a capacity not exceeding 2500 l, in all directions from point of discharge	Zone 2
Tanker loading and unloading	(a) Within 1.5 m in all directions from a point where connections are regularly made or disconnected for a product transfer	Zone 1
	(b) Beyond 1.5 m but within 4.5 m or the separation distance in Table 2 column (a)[b] in the case of vessels with a capacity not exceeding 2500 l, from point of connection or disconnection	Zone 2
Pumps, compressors and vaporizers other than direct fired		
(a) Outdoors in open air, at or above ground level[a]	(a) Within 1.5 m in all directions	Zone 1
	(b) Beyond 1.5 m but within 4.5 m in all directions or the separation distance in Table 2 column (a)[b] in the case of vessels not exceeding 2500 l capacity	Zone 2
(b) Indoor location with adequate ventilation	The entire room and any adjacent room not separated by a vapour-tight partition	Zone 1

[a] Where there is a high standard of maintenance of pumps and pump seals the area within 1.5 m in all directions from the pump may be classified as Zone 2.
[b] Of HS(G) 34.
Notes:
(1) Where any area is classified under more than one factor the higher classification should prevail.
(2) Any pit, trench or depression falling within a Zone 1 or Zone 2 area should be treated as a Zone 1 area throughout.
(3) The term 'outdoors in open air' includes pumps, compressors and vaporizers which are covered by a canopy.

For LPG storage during distribution, the IP *Area Classification Code* refers to the LPGA *Code*, whilst for storage under the more varied conditions which pertain in refineries and process plants it advises the use of the point source method.

22.8.7 Pipework and fittings

The pipework, valves and other fittings for storage systems should be designed in accordance with approved practice for such equipment. Pipework for pressure systems was described in Chapter 12 and the discussion here is limited to aspects particularly relevant to storage.

Pipework and fittings for LPG pressure storage are dealt with in the main LPG codes mentioned and also specifically in *LPG Piping System Design and Installation* (LPGA, 1990 COP 22) (the LPGA *Piping Systems Code*).

The types of consideration which should be taken into account in pipework for storage are illustrated by the following recommendations for pipework for LFG taken from the ICI *LFG Code*.

The minimum temperatures which may be attained by the piping should be carefully considered and materials of construction selected accordingly. Storage systems are subject to such operational conditions as rapid blowdown, which can result in low temperatures.

Allowance should be made in the pipework for stresses due to movement, expansion/contraction and vibration. In storage systems, typical causes of stress are shifting and settling of vessels and expansion/contraction due to temperature changes.

Joints should be welded or flanged. Welded joints are preferable and flanged joints should be kept to a minimum.

Valves should be of the wedge gate or ball type. Ball valves give a more positive shut-off than wedge gate valves and should be used on the critical filling/discharge and drain lines.

The ball valves should be dual directional, should be of the fire-safety type and should have antistatic protection. Ball valves welded into lines should be such that they can be maintained *in situ* by 'top entry'.

With a ball valve, liquid can be trapped in the body cavity. In low temperature, LFG duties conditions can occur which cause the liquid to expand. Provision should be made for relieving this expansion which does not render the valve unidirectional.

The main filling/discharge line should have a minimum diameter of 4 in. The drain line should be 2 in., reducing to ¾ in.

The preferred pipework arrangement for a horizontal storage vessel is shown in Figure 22.8(a). There are no flanges, valves or other fittings on the filling/discharge line on the vessel side of the separation wall, only a single butt weld. Valves A–C are butt-welded ball valves and valve D is a flanged, spring-loaded valve. Valve A is the main shut-off valve, which is remotely operated and has fail-safe action, closing on air failure.

There is also an alternative arrangement in which flanged joints are allowed on the vessel side of the separation wall.

The preferred pipework arrangement for a spherical storage vessel is shown in Figure 22.8(b).

If possible, the main filling/discharge pipe should be the only one below the liquid level. Another inlet may be provided at the top of the vessel if mixing of the liquid by pumping is necessary. There may also be a vapour return line to the vessel. With a horizontal cylindrical vessel, it is desirable to put the filling/discharge line and the vent at opposite ends to assist purging of the vessel.

The vessel branch sizes should be 4 in. minimum for the filling/discharge line and 1 in. minimum for all other branches.

Sections of pipe, such as those between shut-off valves, in which liquid may become trapped and may then undergo further expansion, should be provided with liquid expansion relief valves.

There should be good access to valves. Permanent access should be provided for valves which are operated or maintained regularly, or which may need to be used in an emergency.

The pipework should be protected against mechanical damage from external sources.

Pipework is very vulnerable to fire and should be protected as far as possible. Fireproof insulation on pipework near storage vessels may be appropriate.

A small fire at a leaking flange can have a torch effect and this possibility should be borne in mind in designing pipework. A fire of this type was one of the causes considered at the Flixborough Inquiry.

Remotely operated shut-off valves should be provided on all discharge or drain lines from storage vessels and these valves should be stable in fire conditions. Other valves in the storage area should be of fire-safe design.

Turning to the guidance on pipework and fittings in the main LPG codes, detailed treatments are given in the LPGA *LPG Storage Code*, the LPGA *LPG Piping Systems Code* and the IP *LPG Storage Code*. These codes cover materials of construction, pipe thickness, pipe joints, welding, flanges, gaskets, bolts, valves, pipe supports, etc.

The LPGA *LPG Storage Code* gives detailed requirements for the minimum set of fittings on an LPG pressure storage vessel. These are (1) a pressure relief valve on the vapour space, (2) a drain or other means of emptying the vessel, (3) a maximum level indicator, (4) a filling connection, (5) a service connection and (6) a pressure gauge on the vapour space on vessels of over 5000 l.

The *Code* requires the provision of a manual shut-off valve on all liquid and vapour connections, except on the pressure relief valve or very small diameter (<1.4 mm) connections.

Another requirement of the *Code* is that any connection on the vessel greater than 3 mm diameter for liquid or 8 mm diameter for vapour, except that for a relief valve, should be protected with an emergency shut-off valve (ESV). The types of ESV mentioned are excess flow valves, remotely operated isolation valves and back-check valves. The detailed applications of the three types are given in the *Code*.

A back-check valve is a spring-loaded non-return valve held in the closed position. The valve remains closed against reverse flow until the upstream pressure exceeds that of downstream, when the valve opens.

HS(G) 34 requires a remotely operated ESV on all liquid lines greater than 19 mm in diameter if they supply an activity which requires frequent making and breaking of connections or one where the general public have access or if the vessel is large (>225 m^3).

22.8.8 Water drainage facilities

As described in Chapter 20, small amounts of water tend to accumulate at the bottom on an LPG storage vessel and this water is commonly removed by the periodic action of an operator who drains it off manually. Loss of control by the operator can result in a breakthrough and escape of LPG.

Methods of dealing with this problem have been discussed by Klaassen (1980b), who describes valve arrangements for the bottom of LPG spheres designed to minimize the chances of such an escape. He describes a system with a 2 in. line coming out of the bottom of the sphere, reducing to ¾ in. on the downstream part of the drain line. Basic principles underlying the system are: (1) a reduction in the line size, as just mentioned; (2) the installation of a first ball valve in the 2 in. line dedicated to isolation rather than manipulation, and preferably remotely controlled; (3) the provision of two further ball valves on the drain line, the downstream one being a spring-loaded valve; (4) a separation between the drain valve and the drain funnel and (5) the provision of an indication of water level which is visible at the point where the draining operation is performed.

Guidance on water draining arrangements is given in HS(G) 34 *The Storage of LPG at Fixed Installations* (HSE, 1987) as follows:

> 66. Drain connections should be less than 50 mm in diameter and fitted with two shutoff valves in series. The length of piping between the valves should be at least 0.5 m to minimize the risk of simultaneous obstruction of both valves by the freezing of any water present in the LPG. The piping downstream of the second valve should not discharge beneath the vessel. The second valve and piping should be adequately supported and secured to prevent mechanical damage or breakage by vibration or jet forces. Both valves on the drain systems should have means of actuation which cannot be readily removed or

moved from the closed position except by intentional operation.

67. Alternatively, a satisfactory arrangement for drain lines could be a single valve and a plug or blanking plate fitted on the discharge side of the valve. Additional pipework should be fitted, when required, in accordance with paragraph 66.

68. No drain lines should discharge within 6 m of any drainage system where this would be liable to create a hazard.

22.8.9 Ancillary facilities

The ancillary facilities required for LPG pressure storage include, in particular, pumps and vaporizers. It is important that these items, which effectively introduce a process element, should not hazard the storage. A pump should not be located directly under a vessel.

Pumps are a potential source of leakage of flammable vapours. This is particularly the case for pumps with packed glands. Pumps with mechanical seals are to be preferred. The type of pump used also has implications for the HAC.

A positive displacement pump needs to have a bypass or other appropriate protection against overpressure. The thermal expansion of LPG in a pump which is isolated and is then started up can be particularly damaging.

LPG storage is often provided with vaporizers. Descriptions of, and requirements for, vaporizer systems are given in NFPA 58 and 59, the LPGA *LPG Storage Code* and HS(G) 34. Vaporizers may be heated by direct firing or by an indirect heating medium such as steam or hot water. Some principal features of a vaporizer system include the vaporizer itself, drain connections, pressure relief and instrumentation. Direct fired and certain other types of vaporizer constitute ignition sources.

22.8.10 Instrumentation

An LPG pressure storage vessel should be provided with suitable measurements and alarms on liquid level, pressure and temperature. A discussion of instrumentation for LFG pressure storage is given in the ICI *LFG Code*. Instrumentation is essential to the safe operation of LPG pressure storage. It is important both that the instruments function correctly and that they do not themselves hazard the process.

Vessels should be protected against maloperation by alarm and trip systems. Overpressure is obviously one condition against which protection is necessary. It is often caused by overfilling, and so high level alarms and trips are important. But this is not the only condition requiring protection – overtemperature and undertemperature are important too.

The measurement of level in pressure storage may present some difficulties. In order to avoid leakage, it may be policy not to put additional branches on the vessel simply for level measurement, which rules out conventional differential pressure measurements. The *Code* recommends duplicate internally mounted level measuring instruments as the primary measurements with a magnetic float gauge or radioactive gauge as the secondary measurement. Separate high and low level switches are also required for the alarm and trip systems. Here the *Code's* recommendation is that the switch should be put in an externally mounted float chamber, the top connected to the top of the storage vessel and the bottom to the filling/discharge line between the ball valves and the manifold.

Debris from instruments should not create a hazard. It may be necessary to take precautions to prevent a loose float from a level measuring device blocking the branches to the relief valves.

For the measurement of temperature, a long thermocouple pocket is recommended. It should be inserted from the top and reach the bottom so that the temperature at any level can be measured. The bottom of the pocket should be guarded or supported in some way to reduce the risk of fracture by vibration.

Specific instrumentation requirements are contained in the main LPG codes, particularly in respect of level gauging. The LPGA *LPG Storage Code* requires the installation of a fixed maximum liquid level device, which should be of the type that allows vapour or liquid to be bled from a valve attached to a dip-tube to indicate when the maximum permitted level is reached during filling. The connection through the vessel should be no larger than 1.4 mm in diameter unless an excess flow valve is fitted. For a vessel of more than 5 m^3 capacity the *Code* also requires the provision of a pressure gauge connected to the vapour space. It requires that the connection be protected either by a tapping reduced internally to a bleed hole not larger than 1.4 mm or by a suitable excess flow valve or shut-off valve.

The provision of a contents gauge is also advised. The IP *LPG Storage Code* suggests that consideration be given to the installation of two independent level gauges in addition to the maximum level device.

Sampling is another aspect which merits careful attention, because it tends to be a source of leakage. The ICI *LPG Code* makes the following recommendations on this. Sampling should be done from pipelines rather than from vessels. If a representative sample is required from a vessel, the product should be circulated and a sample taken from the circulation line. Sample points should be carefully sited with respect to HAC, safe disposal of vented samples and access.

Sample connections should be limited, preferably to 1 in. reducing to 1/4 in. There should be double manual isolation with a 1 in. ball valve followed by a 1/4 in. valve. The valves should be close together but with a minimum separation of 1 m to avoid simultaneous blockage of both valves by ice or hydrate.

Operations involved in sampling were considered in Chapter 20.

Gas, flame and smoke detectors are another important aspect of instrumentation for storage. These have been discussed in Chapter 16.

22.8.11 Pressure relief

A pressure storage vessel should be protected against overpressure by a pressure relief valve. Pressure relief valves have been discussed in detail in Chapter 12. Only those aspects relevant to storage are considered here.

Pressure relief valves for LPG pressure storage vessel should be designed according to a recognized code such as BS 5500: 1991 or the ASME *Boiler and Pressure Vessel Code, Section VIII*. In this particular case, other appropriate codes are the LPGA *LPG Storage Code*, API RP 520 and NFPA 58 and 59.

Protection is required against overpressure due to (1) abnormal operating conditions and (2) fire exposure. It

may be provided by a single pressure relief valve or by separate relief valves for each category.

Operational relief

A pressure relief valve for abnormal operating conditions should be designed to handle the most severe conditions which are likely to arise. Typical abnormal operating conditions include overfilling, high rundown liquid temperature and high tank temperature due to solar radiation.

Overpressure due to abnormal operating conditions may develop slowly or suddenly. The most common cause of a rapid increase in pressure is overfilling. The worst case here is obtained by considering the maximum liquid flow obtainable through the fully open control valve, and bypass if fitted, on the supply line.

Fire relief

A pressure relief valve for fire exposure should be designed to deal with the vapour generated by this. The vapour generated may be calculated from the latent heat of the liquid and from the heat input.

There are a number of measures which can, in principle, reduce the heat absorbed during a fire and hence the quantity of vapour to be handled. The most basic is to slope the ground under the vessel so as to ensure that any flammable liquid spill is drained away. Other measures to reduce heat absorbed include fireproofing, depressurization and water sprays.

A method of estimating the heat absorbed in a fire is given in API RP 520, Appendix D. For a bare surface two equations are given:

$$Q = 21{,}000\ FA^{0.82} \qquad [22.8.1]$$

and

$$Q = 34{,}500\ FA^{0.82} \qquad [22.8.2]$$

where A is the total wetted surface (ft^2), F is an environmental factor and Q is the total heat absorption (BTU/h). Equation 22.8.1 is applicable where there is adequate drainage and prompt fire fighting, and Equation 22.8.2 where these conditions are not met.

In this method, any credits allowed for other measures are incorporated in the environmental factor F. The value of F is unity for a bare vessel. No credit is given for depressurization or water application facilities, and even with these the value of F is still unity. Credit is given, however, for fireproof thermal insulation, provided it will resist dislodgement by fire hose streams. For a vessel furnished with fireproof insulation with a thermal conductance of 4 BTU/ft^2h °F the value of F is 0.3. Lower values of F are given for insulation with lower thermal conductances.

The LPGA *LPG Storage Code* and NFPA 58 and 59 give pressure relief valve capacities in tabular form and also give an equation for large vessels. The LPGA *Code* states that these capacities cover fire relief.

The pressure relief valve setting, both for operational and for fire relief, is considered in Chapter 12, and valve sizing is discussed in Chapter 15. For pressure storage, valves should be able to handle flashing, two-phase flow.

Combined relief

A single pressure relief valve may be used to provide both operational and fire relief. Alternatively separate valves may be used for operational and fire relief.

The arrangements are discussed in the ICI *LPG Code*. The *Code* states that where there is a single pressure relief valve, the relieving capacity should be at least equal to the greater of the individual capacities required for operational and fire relief, and that where separate operational and fire relief valves are provided the combined capacity of the two valves may be set against the fire relief requirement.

Fluid phase

A discussion of the fluid phase during pressure relief is given in API RP 520, although the account is not specifically concerned with storage. The IP *LPG Storage Code* states that for overfilling the relief discharge would be a flashing liquid, whilst for fire relief it treats the discharge as a vapour.

Relief disposal

A discussion of relief disposal for LFG storage vessels is given in the ICI *LFG Code*. The *Code* states that it is preferable that relief valves, whether for operational or fire relief, should discharge into a closed system.

An operational relief valve should discharge into a closed system which is led to an atmospheric vent or to a flare. The closed system should be designed to handle liquid discharge and to take the full flow from the valve. A fire relief valve should also discharge to a closed system. If this is not practical, it can be discharged vertically upwards to the atmosphere via a vent pipe.

Direct discharge to atmosphere should be done in such a way as to ensure that flammable material is diluted below its lower flammability limit before it reaches an ignition source, and toxic material should be below the appropriate exposure or odour limit before it reaches ground level outside the plant area.

These requirements for direct discharge are fairly readily met for vapours lighter than air which can be vented at a point above plant structures at low velocities, but for those heavier than air it is more difficult. The *Code* states that for vapours heavier than air it is necessary to use a velocity of at least 150 m/s (500 ft/s) to ensure jet mixing with air sufficient to give rapid dilution. The problem is discussed by Cude, who indicates that current experience is that this criterion can be reliably met only by the use of pilot-operated relief valves rather than ordinary relief valves. A fuller account of dispersion from relief valves is given in Chapter 15.

Most LPG pressure storage vessels are fitted with vertical vent pipes so that the relief discharge is directed upwards. The LPGA *LPG Storage Code* states that a vent pipe should have its outlet at least 1.8 m above the top of the vessel and should be not less than 3 m above ground level. HS(G) 34 gives similar requirements, but states that for large vessels the pressure relief system may discharge to the vent collecting system of a flare.

22.8.12 Vacuum protection

In severe cold weather the temperature of the contents of an LPG pressure storage vessel may fall below 0°C. For the storage of commercial butane in particular, this can cause the vapour pressure of the liquid to fall below atmospheric and thus create vacuum conditions.

This problem and the measures that can be taken to protect against it are discussed in the LPGA *LPG Storage Code*. The *Code* states that, in the absence of more specific information, a butane vessel should be designed for a minimum temperature of −18°C, which is the lowest

ambient temperature recorded in the United Kingdom as sustained over a period of 12 h.

One approach is to design for full vacuum. Alternative approaches are (1) the prevention of unacceptable vacuum conditions, (2) the provision of high and low pressure alarms and (3) the use of methods based on product composition or vacuum breaking.

A low pressure alarm serves to give warning of the development of vacuum conditions.

Two methods of preventing an unacceptable vacuum are hot gas return and propane vapour pressurization. Hot gas return involves feeding hot butane vapour from a local vaporization source, and propane vapour pressurization involves connecting the vapour space of the butane vessel to that of a local propane storage vessel or to propane cylinders. Details of the procedures to be used are given in the LPGA *Code*.

In certain special cases, and by agreement with the supplier, the composition of butane to BS 4250: 1987 may be controlled so that the vapour pressure at the lowest service temperature will be above the minimum design pressure of the vessel. It should be confirmed that at this composition the vessel can withstand the vapour pressure at the reference temperature.

Other methods of limiting vacuum are the use of vacuum breakers or the introduction of inert gas. Both methods tend to lead to operating problems due to the introduction of air or inert gas and the first particularly is a specialist matter.

22.8.13 Vaporizers

LPG in vapour form may be obtained from a pressure storage installation using a vaporization facility. Vaporizers for LPG are treated in HS(G) 34.

LPG vaporizers may be heated with low pressure steam or hot water or heated electrically or by direct firing. The equipment should be located with suitable separation distances, in a well ventilated location and with the ground sloped to drain away any leak to a safe place.

HS(G) 34 gives the following minimum separation distances between vaporizers and the nearest important buildings or line of adjoining property. For vaporizers of capacity up to 36 kg/h, 3 m; of capacity >36 to 227 kg/h, 7.5 m; and of capacity >227 kg/h, 15 m. Separation distances between LPG vessels and direct fired or non-explosion protected electrically heated vaporizers are as given in column 3 of Table 22.6, which gives the distances for sources of ignition. The separation distance from LPG vessels for other types of vaporizer is 1.5 m.

Other features detailed in HS(G) 34 include the arrangements for draining, pressure relief and control of liquid level and temperature.

22.8.14 Fire protection

Fire prevention and protection of LPG pressure storage is dealt with in the main codes mentioned and also specifically in *Recommendations for Prevention or Control of Fire Involving LPG* (LPGA, 1972 COP 3) (the LPGA *Fire Code*). A further relevant standard is BS 5908: 1990. Other accounts include those by Kletz (1977d), Fullam (1987), Nazario (1988), Schoen and Droste (1988) and Schoen, Probst and Droste (1989).

The effect of fire on a pressure vessel is broadly similar to that on an atmospheric tank. The unwetted parts of the vessel become hot and lose strength. As a result the vessel may burst, even though it is below its design pressure. Overtemperature is just as serious as overpressure. The loss of strength is greater with vessels designed to advanced pressure vessel codes.

The other effect of fire is to heat the liquid in the vessel so that the pressure rises and causes the pressure relief valve to lift. Further heat input causes the liquid to vaporize without further rise in pressure, provided the valve has enough capacity to vent the vapour. If the valve fails to operate or has insufficient capacity, the rise in pressure may burst the vessel.

Failure of a pressure vessel in a fire may therefore be due to either overtemperature or overpressure. The failure of the vessel at Feyzin, for example, occurred due to overtemperature, even though the relief valve had lifted.

A discussion of fire prevention and protection is given in the ICI *LPG Code*. Some of the measures given in the *Code* have already been discussed, such as diversion and fire walls (see Section 22.8.5), fire protection of pipework and fittings (see Section 22.8.7) and fire and gas detection systems (see Section 22.8.10).

The ICI *Code* specifies measures to minimize spillages. The vessels and pipework should be made to give high standards of safety in both normal and emergency operations, by appropriate design calculation methods. The number of connections below the top liquid level should be kept to a minimum, preferably just one filling/discharge line if possible. The minimum size connections should be used for draining and sampling. The installations should be protected against external damage from such sources as vehicles and other plants. There should be good level measurement and other control instrumentation, and attention should be paid to the filling arrangements.

Measures for controlling spillages are also specified. The basic principle is that any vapour cloud resulting from a spillage should be safely diluted by air below its lower explosive limit before it can find a source of ignition. This dispersion should preferably be effected by air movement but, if necessary, some form of barrier may be required to contain and disperse the cloud.

Thus the installation should be sited with regard to factors such as ground contours and the prevailing wind. The provision of gas detectors should be considered. If necessary, consideration should be given to the provision of barriers or steam curtains to contain, direct or disperse the vapour cloud. Attention should be given to possible sources of ignition.

Finally, the *Code* specifies measures for controlling fire. The layout should ensure that liquid spillages are drained away from under vessels to a catchment area where they can be pumped out or burned. Vessels should be provided with water cooling or fireproof insulation and supports should be fireproofed. Consideration should be given to the provision of fire-fighting equipment to control and extinguish burning hydrocarbon liquids.

Figure 22.10 shows a classic diagram by Kletz (1977d) of the methods of fire protection for an LPG pressure storage vessel. They are (1) sloping of the ground beneath the vessel, (2) fire insulation, (3) a remotely operated depressurization valve, (4) water sprays and (5) a pressure relief valve.

Fixed water sprays are effective in giving immediate cooling of exposed surfaces and are widely used. On both horizontal cylinders and spheres there is a tendency for water to come off the vessel at the 'equator' and therefore sprays are usually provided both above and below this line.

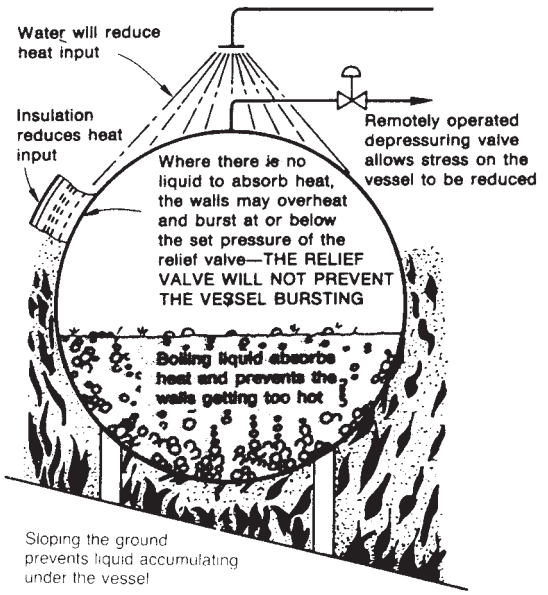


Figure 22.10 *Fire protection arrangements for an LPG pressure storage sphere (Kletz, 1977d) (Reproduced with permission from Hydrocarbon Processing, August, 1977)*

The ICI *LPG Code* gives the following method of calculating the amount of water required. For a vessel enveloped in fire the rate of application of water needed to remove the total heat input is 0.2 UKgal/ft^{2}min. But for a vessel designed to the *Code*, a lower rate of application in the range 0.06–0.2 UKgal/ft^{2}min is acceptable, provided the ground beneath the vessel is impervious and sloped away to a catchment area and the pipework is carried beyond the vertical projection of the vessel with no flanges or other fittings beneath the vessel.

The rate of application of water may be determined by heat flux calculations and from the rise in the temperature of the water from the mains temperature to a temperature close to boiling point at 100°C.

The *Code* gives the following method for the calculation of the heat flux. It is assumed that the separation distances given earlier in Table 22.7 are observed and that the fire is in the catchment area as shown in Figure 22.11. Then the heat radiated and the intensity of heat radiation from the flame burning on the liquid pool are calculated from the equations

$$Q = 5.1 \times 10^{-5} LW\rho C \qquad [22.8.3]$$

$$I = \frac{2.5 \times 10^{-5} LW\rho C}{(L+W)h + LW} \qquad [22.8.4]$$

where C is the net calorific value of the liquid in the pool (kj/kg), h is the height of the flame ($=2W$) (m), I is the intensity of heat radiation from the flame envelope (kW/m^2), L is the length of the pool (m), Q is the heat emitted by fire (kW), W is the width of pool (m) and ρ is the density of the liquid (kg/m^3).

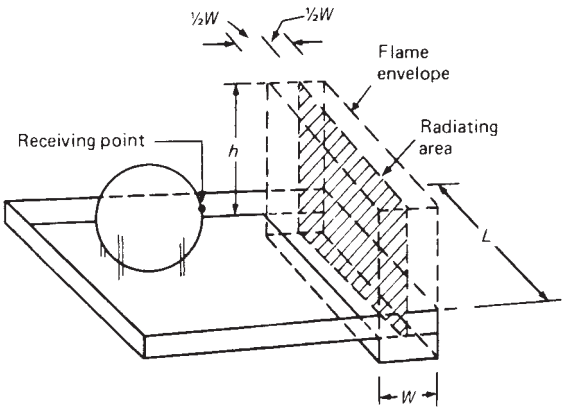


Figure 22.11 *Heat radiation from a fire burning in a catchment area to a pressure storage vessel (ICI/RoSPA 1970 IS/74; reproduced by permission)*

It is assumed that the heat is radiated from a radiating area which is a vertical rectangular plane through the centre line of the flame envelope cube prism parallel to the nearest point on the equator of the vessel, as shown in Figure 22.11. The heat flux received by this vessel is obtained by using the view factor method.

A fixed water spray system is normally maintained dry so that it cannot become frozen. When this system is required to operate, water is supplied by a deluge valve. This valve may be operated manually or automatically. If operation is manual, the valve should be in a place accessible during the fire. The preferred system, however, is automatic operation triggered by fire detectors.

Automatic detectors should be fast acting in order to protect the pipework in particular. Manual override control should be provided on an automatic system to allow sprays to be turned on to protect adjacent surfaces, even though the automatic controls have not brought them on.

It is desirable that, if possible, only those fixed sprays are activated which contribute to dealing with the fire concerned. Large installations should be subdivided to conserve water, which is likely to be needed to fight the fire. Again, the main water sprays are normally provided by mobile equipment and are used both to fight the fire and to cool exposed surfaces.

Fireproof thermal insulation may be used on pressure vessels as an alternative to, or in addition to, fixed water sprays. Such insulation reduces the rate of heat input from a fire to the vessel and this lag gives time in which fire-fighting measures such as mobile water sprays may be brought into play and the fire extinguished, or in the worst case an evacuation organized.

Fireproofing should be such as to provide protection for 2 h before the vessel becomes dangerously overheated. This insulation should be designed in conjunction with the arrangements for fire pressure relief. A fireproof insulation suitable for this purpose may be obtained by the use of vermiculite cement with a minimum thickness of 2 in.

Some of the measures described have their difficulties. The use of fire insulation is not straightforward. Some of the problems are considered by Fullam (1987). The use of such insulation inhibits inspection of the vessel. Corrosion

and water ingress are liable to occur. There are potential problems with the durability of the insulation and its resistance to water jets. He states that these problems are serious enough to prevent the general adoption of this measure.

Likewise, the use of depressurization is controversial, as discussed by Nazario (1988). One problem is the time required to depressurize. Another is that the depressurization lowers the liquid level and increases the area of unwetted metal exposed to the fire. The approach described by Nazario is to use fire insulation as the preferred method for horizontal storage vessels, but not for spheres. On the other hand, water sprays and not insulation are used for spheres.

Turning to the guidance on fire prevention and protection in the main LPG codes, and also specifically in the LPGA *Fire Code*, detailed treatments are given in API Std 2510, AP RP 520, NFPA 58 and 59, the LPGA *LPG Storage Code*, the IP *LPG Storage Code* and HS(G) 34.

The LPGA *LPG Storage Code* gives a summary table of fire protection arrangements for storages of different sizes. For storages below 25 te it is generally sufficient to provide a water supply; for storages greater than 25 te but less than 50 te, fixed or portable water monitors should be available; and for storages greater than 50 te there should be a fixed water spray installation. This system should be automatic unless the plant is continuously attended.

With regard to the wetting rate required to effect protection for an uninsulated vessel, the *Code* states that a full film of water needs to be established over the whole vessel surface and supports at a rate of 7 l/m^2min, and that the typical design spray rate required to achieve this is 9.8 l/m^2min; the *Code* refers to the work of Billinge, Moodie and Beckett (1986). In some cases, one of these figures is quoted without the other; the IP *LPG Code* refers to the lower figure and HS(G) 34 to the higher one.

There should be adequate drainage to remove the fire water, and where necessary water sealed interceptors should be provided to prevent LPG entering the storm drains.

The LPGA *LPG Storage Code* recognizes fire insulation as an alternative to water sprays, provided it is capable of limiting the vessel temperature below 450°C for a period of at least 60 min in full fire engulfment. The *Code* requires, however, that the insulation should: (1) be non-corrosive to the vessel surface; (2) be impervious to water vapour, either by cellular construction or by provision of an effective vapour barrier; (3) be resistant to a hose directed jet; (4) be durable and easily repairable, and strong enough that minor mechanical damage will not destroy the vapour barrier; (5) be unaffected by environmental conditions and (6) not itself be a hazard, by spalling, spreading flames or emitting toxic fumes.

The LPGA *Fire Code* deals particularly with fire fighting of LPG fires.

HS(G) 34 gives guidance similar to that in the LPGA *LPG Storage Code*, again with a summary table of fire protection measures.

22.8.15 Inspection

Pressure storage vessels for LPG should be inspected in the manner and at the frequency given in the relevant codes, as described in Chapter 19.

22.8.16 Mounded storage

LPG is also stored in pressure vessels set in earthen mounds. Accounts of this method of storage are given in HS(G) 34 and by Bonnafous and Divine (1986) and Bellani, Cannalire and Beltrame (1992).

The arrangements for a mounded LPG horizontal cylindrical pressure storage vessel given by the HSE in HS(G) 34 are shown in Figure 22.12. The external surface of the vessel should be given an external coating to prevent corrosion. It should be placed on a firm foundation and installed so as to prevent movement or flotation. The backfill material should be inert and free of material likely to damage the external coating. The HSE advise that the depth of cover be at least 0.5 m.

Some of the installations of mounded LPG vessels are very large. Bonnafous and Divine describe mounded storages with horizontal pressure vessels of capacity 3500 m^3. In these systems the vessel is supported on a compacted sand bed in a 120° circular cradle. The depth of cover is one metre minimum.

Mounded storage offers enhanced protection against external fire, thus avoiding: a boiling liquid expanding vapour explosion (BLEVE); external explosion; impact from external threats such as vehicles or aircraft; and sabotage.

22.8.17 Hydrogen related cracking

In certain circumstances LPG pressure storage vessels are susceptible to cracking. The problem has been described by Cantwell (1989 LPB 89). He gives details of a company survey in which 141 vessels were inspected and 43 (30%) found to have cracks; for refineries alone the corresponding figures were 90 vessels inspected and 33 (37%) found to have cracks.

The cracking has two main causes. In most cases it occurs during fabrication and is due to hydrogen picked up in the heat affected zone of the weld. The other cause is in-service exposure to wet hydrogen sulfide, which results in another form of attack by hydrogen, variously described as sulpfide stress corrosion cracking (SCC) and hydrogen assisted cracking.

LPG pressure storage has been in use for a long time and it is pertinent to ask why the problem should be surfacing now. The reasons given by Cantwell are three aspects of modern practice. One is the use of higher strength steels, which are associated with the use of thinner vessels and increased problems of fabrication and hydrogen related cracking; the use of advanced pressure vessel codes, which involve higher design stresses and the greater sensitivity of the crack detection techniques available.

He refers to the accident at Union Oil on 23 July 1984 in which 15 people died following the rupture of an absorption column due to hydrogen related cracking (Case History Alll). Cantwell states: 'The seriousness of the cracking problems being experienced in LPG vessels cannot be overemphasized'.

The steels most susceptible to such cracking are those with tensile strengths of 88 ksi or more. Steels with tensile strengths above 70 ksi but below 88 ksi are also susceptible.

Cantwell also describes measures for the avoidance of the problem. For new vessels he recommends the use of lower strength steels which have controlled chemistry and welding and post-weld heat treatment and which have good toughness both at ambient and low temperatures. For existing vessels the recommendations centre on inspection techniques and intervals and on repair methods. A measure applicable to both cases is the elimination of breakthrough of wet hydrogen sulpfide into LPG rundown.

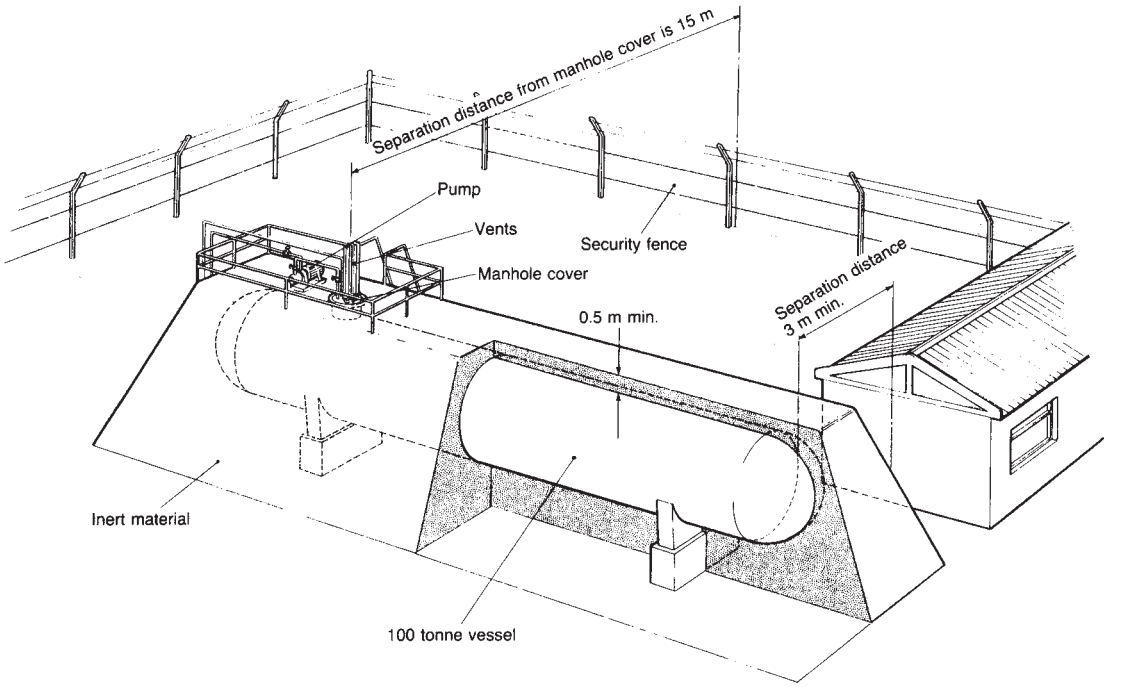


Figure 22.12 *General arrangement of LPG mounded pressure storage vessel (Health and Safety Executive, 1987 HS(G) 34) (Courtesy of HM Stationery Office © All rights reserved)*

22.8.18 LPG-air plants

LPG storage may be associated with an LPG–air plant, which is an installation for the production of LPG–air mixtures. Such plants are covered by the Recommendations for LPG–Air Plants (LPGA, 1972, COP 9). The main elements of such plant are pumps and vaporizers.

22.9 LPG Storage: Refrigerated Storage

Codes and standards for LPG deal mainly with pressure storage rather than with refrigerated storage, but the guidance in NFPA 59 does cover refrigerated storage. Other guidance is available which deals primarily with storage tanks for low temperature duty. Further information may be sought in codes for refrigerated storage of LNG.

22.9.1 Storage tanks

Tanks for the refrigerated storage of LPG and LNG have developed from those for atmospheric storage of petroleum products. A relevant British Standard is BS 4741: 1971 *Specification for Vertical Cylindrical Welded Steel Storage Tanks for Low-temperature Service: Single-wall Tanks for Temperatures down to −50°C.*

There is available a variety of tank systems which may be used for the storage of LPG or LNG. A more detailed account is deferred to Section 22.11 on LNG, and only a brief account is given here.

Tank systems for LPG have been described by Morand, Claude and Herbretau (1985). They distinguish the following tank systems: (1) single wall tank, (2) double wall tank, (3) double integrity tank and (4) membrane tank.

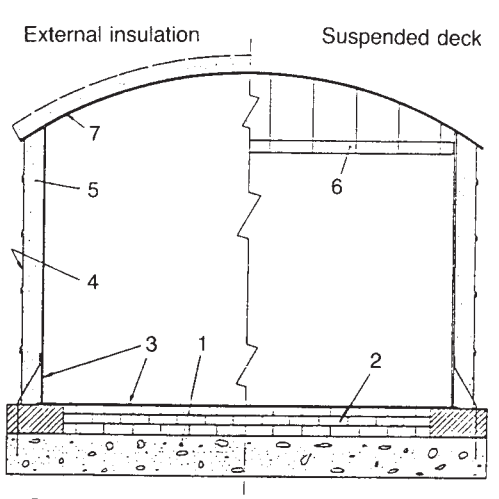
A single wall tank has a wall made of low temperature steel with external insulation covered by a vapour barrier. A double wall tank has an inner wall of low temperature steel and an outer wall of carbon steel with insulation in between. The outer wall is not designed to withstand the cold liquid, so that this system still gives only a single effective containment. A double integrity tank system has an inner tank of low temperature steel with a suspended deck and an outer wall either of low temperature steel or pre-stressed concrete, but in either design the outer wall also is capable of containing the cold liquid. The membrane tank consists of a pre-stressed concrete containment with an aluminium foil membrane. These four tank systems are shown in Figure 22.13.

Morand, Claude and Herbretau have given a detailed account of the GMS 2000 membrane tank system, adapted from the GMS membrane tank system developed for marine use. In such a membrane system, the functions of mechanical strength and leak-tightness are separated and are provided by separate features.

The minimum design temperature for refrigerated storage tanks should take account of the lowest temperature to which they may be subjected. The tank may be cooled down to the minimum temperature of the refrigeration system if there is little movement of the contents, or even lower if there is malfunction of the system.

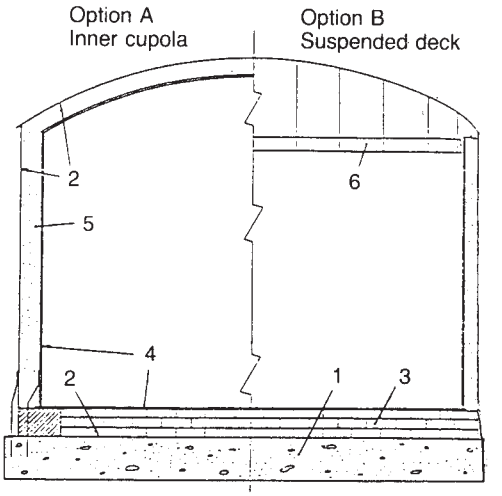
22.9.2 Separation distances

Separation distances for refrigerated LPG storage are given in the IP *LPG Code* and NFPA 59, and also in the ICI *LPG Code*.



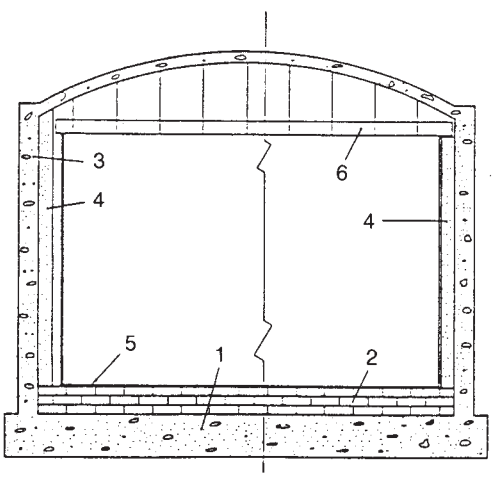
1 Concrete slab
2 Load bearing insulation
3 Metallic tank killed steel
4 Mechanical protection vapour barrier
5 Insulation polyurethane foam glass
6 Suspended deck
7 Cupola carbon steel

(a)



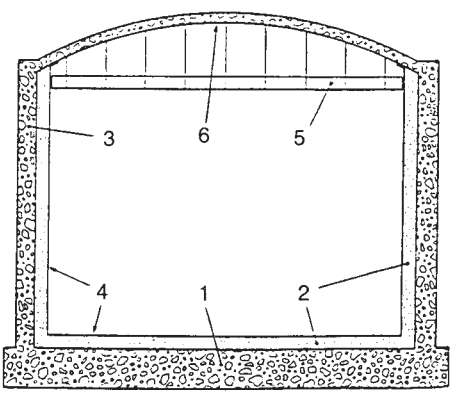
1 Concrete slab
2 Outer tank carbon steel
3 Load bearing insulation foam glass
4 Inner tank killed steel
5 Insulation perlite
6 Suspended deck

(b)



1 Concrete slab
2 Load bearing insulation
3 Outer tank concrete
4 Polyurethane foam insulation
4 Perlite
5 Inner tank killed steel
6 Suspended deck

(c)



1 Concrete slab
2 Load bearing insulation
3 Outer structure pre-stressed concrete
4 Tight membrane
5 Suspended deck
6 Internal liner

(d)

Figure 22.13 *LPG refrigerated storage tanks (Morand, Claude and Herbretau, 1985): (a) single wall tank; (b) double wall tank; (c) double integrity tank with concrete outer wall; (d) membrane tank (QMS 2000) (Courtesy of Gastech)*

22.9.3 Secondary containment

Secondary containment for refrigerated LPG storage tanks is treated in the same codes. An LPG storage tank should be provided with a full bund. The typical LPG refrigerated storage tank is sufficiently large to have its own bund, but in any event tanks containing other materials should not be located in the same bund as one holding refrigerated LPG.

If the topography is such, either naturally or by addition of diversion walls, that any spill can be contained and drained to an impounding basin, this provides an acceptable alternative to a bund.

Walls for full bunding should not be so high as to hinder fire fighting. The ICI *LPG Code* suggests a maximum height of 2 m (6 ft 6 in.) with an allowance of 0.15 m (6 in.) freeboard above the predicted liquid level. This leaves room for a foam blanket. There should be a minimum of two access points on opposite sides of the bund to allow safe access/escape in all wind directions. Access may be provided by steps over the bund.

22.9.4 Foundations

Refrigerated LPG storage tanks require good foundations and insulation for the bottom of the tank. The foundations need to be protected against 'frost heave'. The usual method of construction is to insulate the bottom of the tank and support it on a structure which has only limited contact with the ground and gives good air circulation. An account of foundation systems used for refrigerated storage tanks is given in Section 22.12.

22.9.5 Insulation

Refrigerated LPG storage tanks are insulated to reduce heat inleak.

On a single wall tank the insulation over the walls and roof is typically polyurethane foam (PUF). The insulation between the two walls of a double wall tank is usually perlite. The insulation between the walls of a double integrity tank may be PUF or perlite. A load-bearing foam glass insulation is used between the bottom of the tanks and the foundation.

Important features of the insulation on a single wall tank are the vapour sealing and the fire resistance. Vapour sealing of the insulation is necessary to prevent ingress of humid air and the consequent ice formation. The thermal insulation may also be given a degree of fire resistance, as described below.

22.9.6 Ancillary facilities

Ancillary facilities for refrigerated LPG tanks include the refrigeration system, the pumping facilities and vaporization equipment.

Reciprocating compressors are used for the direct re-liquefaction of vapour boiled off due to heat inleak. Use is also made of reciprocating compressors on refrigeration sets. Malfunction of a refrigeration set can cause the liquid refrigerated to be cooled below its normal temperature.

Reciprocating compressors can be a source of leakage of flammable vapour. They are subject to crankcase explosions and should normally be protected against this by an explosion relief valve.

Pumps should not normally be located inside a bund, where they introduce an additional hazard and are themselves at risk. It is desirable to locate them outside the bund. This also allows them to be used to pump down the storage tank during a fire.

22.9.7 Instrumentation

A refrigerated LPG storage tank should be provided with suitable measurements and alarms on liquid level, pressure and temperature and on boil-off gas flow.

Principal features of the instrumentation are the arrangements to prevent overpressure and overfilling. Pressure control is an integral part of the refrigeration system.

22.9.8 Pressure relief

The tank also requires pressure relief and vent disposal arrangements. There should be arrangements for both pressure relief and vacuum relief. Details of pressure relief systems are given in NFPA 59.

22.9.9 Vaporizers

Refrigerated LPG storage is commonly equipped with a vaporization facility to supply LPG in vapour form. An account of vaporizers for LPG has been given in Section 22.8.

22.9.10 Fire protection

Fire protection for refrigerated LPG storage tanks has much in common with that for other types of storage tanks for flammable products. The effect of fire on a refrigerated storage tank is basically similar to that on an ordinary atmospheric tank, but the heating and vaporization of the liquid are much more rapid.

Guidance on fire protection is given in NFPA 59. This refers to the need for HAC, for flammable gas detection and to a range of fire control and extinguishing systems such as water sprinkler, foam and dry chemical systems.

Passive fire protection for refrigerated LPG storage tanks is discussed in the ICI *LPG Code*. Tanks are provided with conventional thermal insulation, such as cork, polyurethane or perlite. Cork is combustible, but only burns slowly. In a fire risk area, it is usually vapour sealed with fire resistant mastic. Polyurethane is used in a similar way, and the 'high char' variety gives significant fire protection. Perlite is non-combustible, but needs to be contained in a steel jacket not easily damaged by fire. The conventional insulation, therefore, furnishes appreciable fire protection. A further fireproof finish may be added to bring the fire resistance up to a minimum of 2 h.

Such fire resistant thermal insulation provides a basic protection, which may be supplemented by fixed and mobile water sprays. Insofar as the insulation buys time for active fire fighting, automatic initiation of a fixed spray system may be less necessary.

22.9.11 Inspection

There is relatively little published on the inspection of, and inspection intervals for, refrigerated LPG storage tanks.

22.9.12 Underground storage

A number of installations have been built in which LNG is stored underground in an earth pit, as described in Section 22.10. The performance of these storages has been unsatisfactory and the method has essentially been abandoned. LPG may, in principle, be stored in a similar manner, but the same difficulties apply.

22.10 LNG Storage

22.10.1 Regulatory requirements

The storage of LNG is governed by the NIHHS Regulations 982 and the CIMAH Regulations 1984. The NIHHS

notifiable inventory is 50 te. The CIMAH inventory for which demonstration of safe operation may be required (Regulation 4) is 50 te and that which attracts a safety case (Regulation 7) is 200 te.

22.10.2 LNG composition

LNG is not a homogeneous material. There are appreciable differences in composition between LNGs from different sources. Chatterjee and Geist (1972) give the properties of typical LNGs as follows:

Source	*Composition*								
	N_2	C_1	C_2	C_3	C_4	C_{5+}	SG	α	β ($^\circ F^{-1}$)
US	0.40	95.90	2.70	0.40	0.30	0.30	0.440	0.62	0.00164
Algeria	1.70	87.00	7.90	2.30	0.80	0.30	0.474	0.59	0.00151
Libya	0.40	68.60	24.20	9.40	2.00	0.40	0.538	0.50	0.00125

In the above table, c_4 denotes nC_4 and iC_4. The coefficients of expansion of the liquid with respect to concentration and temperature, α and β, respectively, are given by $\alpha = (1/\rho)(\delta\rho/\delta x)$ and $\beta = (1/\mathrm{p})(\delta\rho/\delta T)$, where T is the absolute temperature, x is the mole fraction of methane and ρ is the density of the liquid.

For LNGs having a molecular weight in the range 16–24, the specific gravity lies approximately in the range 0.42–0.54, respectively.

22.10.3 Storage conditions

LNG is generally stored fully refrigerated at −161°C and at atmospheric pressure.

22.11 LNG Storage: Refrigerated Storage

22.11.1 Storage tanks

As stated earlier, tanks for the refrigerated atmospheric storage of LNG have been developed from the conventional atmospheric storage tanks. The design of atmospheric storage tanks is governed by API Std 620: 1990 *Design and Construction of Large, Welded, Low-pressure Storage Tanks* and API Std 650: 1988 *Welded Steel Tanks for Oil Storage*. For refrigerated storage frequent reference is made to API Std 620, Appendix Q: *Low-pressure Storage Tanks for Liquefied Hydrocarbon Gases* and Appendix R: *Low-pressure Storage Tanks for Refrigerated Products*. A relevant British Standard is BS 5387: 1976 *Specification for Vertical Cylindrical Welded Steel Storage Tanks for Low-temperature Service: Double-wall Tanks for Temperatures down to* −196°C.

Tank systems for LNG have been described by Aarts and Morrison (1981), Nassopoules (1982), Closner and Wesson (1983), Collins *et al.* (1983), Steimer (1983), Gilbert *et al.* (1985), D.A. Jones (1985), Crawford, Durr and Handman (1986) and Morrison (1987). The following tank systems may be distinguished: (1) single wall tank, (2) double wall tank, (3) double integrity tank and (4) membrane tank.

A single wall tank has a wall made of low temperature steel with external insulation covered by a vapour barrier. A double wall tank has an inner wall of low temperature steel and an outer wall of carbon steel with insulation in between. The outer wall is not designed to withstand the cold liquid, so that this is still only a single containment system. A double integrity tank system has an inner tank with a suspended deck and an outer wall. Three permutations of materials of construction are used. In the first, both the inner and outer walls are of low temperature steel. In the second, the inner wall is of low temperature steel and the outer one is of pre-stressed concrete. In the third, both walls are of pre-stressed concrete. In all three of these designs the outer wall also is capable of containing the cold liquid. The membrane tank consists of a pre-stressed concrete containment lined with a stainless steel membrane.

Details of the internals of an LNG storage tank are shown in Figure 22.14. The construction of LNG storage tanks is discussed by Steimer (1983).

22.11.2 Separation distances

Separation distances for LNG storage are given in NFPA 59A.

22.11.3 Secondary containment

Where the tank itself provides only single containment, secondary containment may be provided in the form of a bund. The bund height may be low, intermediate or high. Since the bund has to contain the full contents of the tank; a low bund has to be located at some distance from the tank; a high bund can be located close to the tank; and the intermediate height bund can be located at an intermediate distance from the tank. Such bunds may be used with a single wall tank or a double wall tank. A high concrete bund should not be confused with the outer pre-stressed concrete wall of a double integrity tank. The latter is not structurally independent of the tank, whereas the former is. A high bund may, however, appear to be part of the tank, since it may be very close to it and may have its own roof.

22.11.4 Foundations

Foundations for LNG tanks are of two main types. One is an elevated pilecap foundation, with free air circulation. The second is a ringwall foundation with a heating system. An account is given by Steimer (1983).

The monitoring of the settlement of the foundations has been described by Morrison (1987).

22.11.5 Insulation

A typical insulation for a single wall tank is polyurethane with a metal jacket. For double wall tanks, use is made of perlite between the two walls. Insulation materials used for the suspended deck include perlite, mineral wool and fibreglass.

22.11.6 Ancillary facilities

Ancillary facilities for refrigerated LNG tanks include the refrigeration system and the pumping facilities. Accounts are given by Collins *et al.* (1983), Gilbert *et al.* (1985), Crawford, Durr and Handman (1986) and Morrison (1987).

An LNG storage is likely to be part of a terminal and vapour is generated from a number of sources, as described by Collins *et al.* Apart from those associated with the tank itself, these sources include superheated liquid rundown from process units, heat inleak into pipework and flash vapour formed during the loading of ships. The maximum vapour load may well occur during ship loading. Refrigeration facilities are provided to deal with these loads, but peak vapour flows are sent to the flare.

Pumping is required both for loading and for circulation, in order to prevent stratification. The tank system

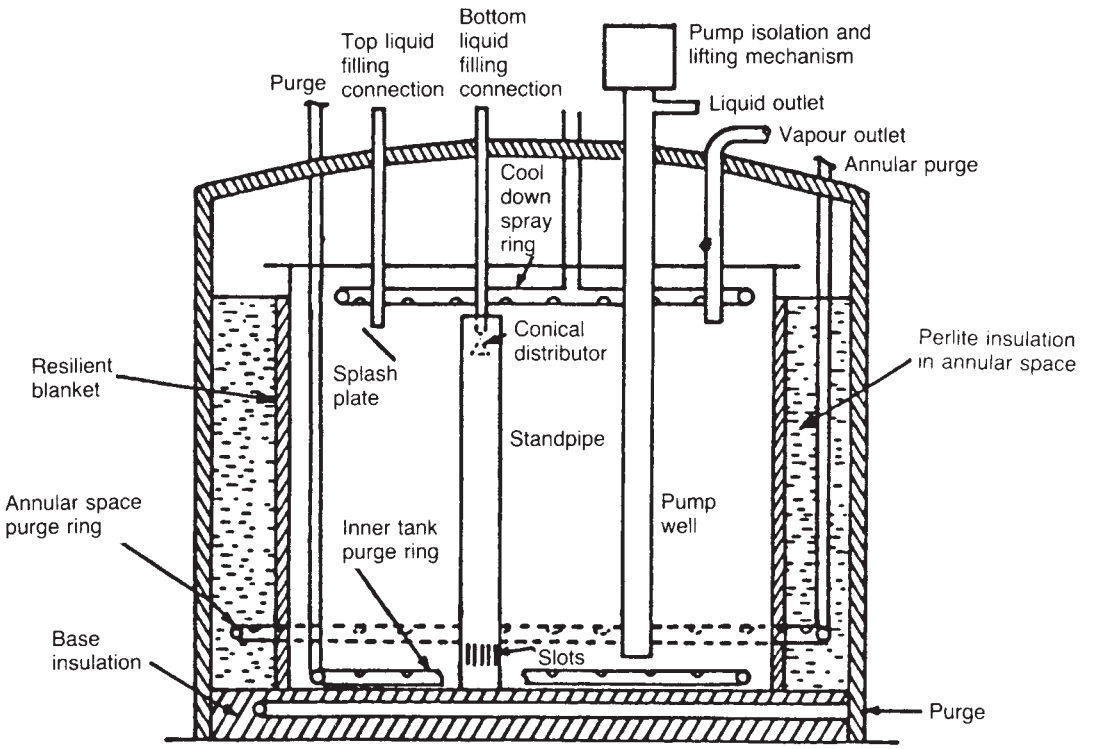


Figure 22.14 *LNG refrigerated storage tank internals (Crawford, Durr and Handmann, 1986) (Courtesy of Gastech)*

described by Morrison has six in-tank loading pumps and one circulation pump.

22.11.7 Instrumentation

A refrigerated LNG storage tank should be provided with suitable measurements of and alarms for the liquid level, the pressure and temperature in the tank and the boil-off gas flow.

Principal features of the instrumentation are the arrangements to prevent overpressure and overfilling. Pressure control is an integral part of the refrigeration system.

The monitoring of the movement of the inner tank has been described by Steimer (1983).

NFPA 59A requires that an LNG facility have an emergency shut-down system and gives details of the system to be provided.

22.11.8 Pressure relief

The tank also requires pressure relief and vent disposal arrangements. Accounts are given by Crawford, Durr and Handman (1986) and Morrison (1987).

Pressure rises may occur due to heat inleak into the tank, high liquid in-flows, the in-flow of superheated liquid, vaporization due to pumped recirculation, a fall in barometric pressure, failure of the pressure control system, heat input during a fire, or rollover. Causes of vacuum include high liquid withdrawal flows, the in-flow of subcooled liquid, and a rise in barometric pressure.

Pressure relief is provided by pressure relief valves and vacuum protection by vacuum breaker valves. In the system described by Crawford, Durr and Handman (1986), the pressure relief valves vent to atmosphere and the vacuum breakers admit air.

The pressure control system may be arranged so that if the vapour flow is too great for the refrigeration system to handle, vapour is vented to the flare before opening of the pressure relief valves occurs. Operation of the vacuum breakers may be forestalled by vacuum control, which admits fuel gas.

22.11.9 Fire protection

Fire protection of refrigerated LNG storage tanks has much in common with that for other types of storage tanks for flammable products. Guidance is given in NFPA 59A Further accounts are those by Closner and Wesson (1983) and Morrison (1987).

NFPA 59A refers to the need for HAC, for flammable gas detection and to a range of fire control and extinguishing systems such as water sprinkler, foam and dry chemical systems.

Closner and Wesson describe a number of fire protection measures. These are: (1) containment systems which limit the size of the pool, and hence of any fire; (2) protective coating systems; (3) foam systems and (4) water deluge systems.

The tank system described by Morrison is designed to withstand a collapse of the roof and the resultant tank fire. In these circumstances, the outer wall would be subject to hydrostatic pressure and severe thermal gradients from the flame, which is assumed to be tilted.

22.11.10 Annular space

In a double wall tank, some attention needs to be given to the annular space between the two tanks, and in particular to the entry of LNG into the space. One way in which this can occur is by condensation, caused by an increase in pressure in the tank. In some cases, the annular space is purged with nitrogen.

Another situation is that which results from a leak of LNG from the inner tank. If this is sufficiently large, the formation of vapour may generate a pressure sufficient to rupture the inner tank. An account of this problem in a double wall ammonia tank and its solutions has been given by Squire (1991), as described in Section 22.18.

22.11.11 Inspection

There is relatively little published on the inspection of, and inspection intervals for, refrigerated LNG storage tanks. An account of the design of storage tank internals to facilitate the decommissioning and recommissioning of the tank has been given by Crawford, Durr and Handman (1986), who describe these operations in detail.

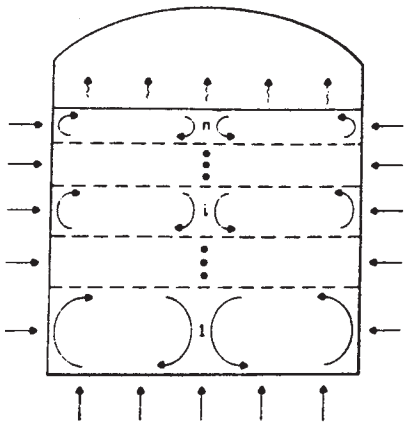


Figure 22.15 *An LNG storage tank with the liquid stratified into n cells (Germeles, 1975b)(Courtesy of the Plenum Publishing Corporation)*

22.11.12 Rollover

Under certain conditions, 'rollover' of the liquid in an LNG tank can occur, resulting in the rapid evolution of a large quantity of vapour with the potential to overpressure the tank.

Stratification can occur in an LNG tank if the density of the liquid 'cargo' charged to the tank is significantly different from that of the 'heel' already in the tank. As described above, there are in fact appreciable differences in density between LNGs from different sources.

A model of rollover in LNG tanks has been given by Germeles (1975b), who develops an earlier model by Chatterjee and Geist (1972). The liquid in the tank is assumed to be stratified into a number of 'cells' with heat inleak from the sides and from the bottom of the tank as shown in Figure 22.15. The model consists essentially of the unsteady-state heat and mass balance equations for these cells and of supporting correlations.

The model draws on previous work by J.S. Turner (1965) on the mass and heat transfer between the interfaces of cells in stratified layers of saline solutions of different strength. He defines an interface stability parameter R

$$R = \left|\frac{\beta\delta S}{\alpha\delta T}\right| \qquad [22.11.1]$$

where S is the concentration of the solute (mass fraction), T is the absolute temperature (K), α is the coefficient of expansion with respect to the temperature, T and β is the coefficient of expansion with respect to the concentration. The heat and mass transfer coefficients are given as functions f_1 and f_2 of R.

Another relation used in the Germeles model is the boil-off model by Hashemi and Wesson (1971). The boil-off rate b is given by

$$b = 0.328\,\frac{\rho_o C_p}{H_v}\,\frac{(g\alpha k^2)^{1/3}}{\rho\mu C_p^2}(T_n - T_s)^{4/3} \qquad [22.11.2]$$

where b is the boil-off mass flux, C_p is the specific heat of the liquid, g is the acceleration due to gravity, H_v is the latent heat of vaporization of methane, k is the thermal conductivity of the liquid, T_n is the absolute temperature of the top or nth cell, T_s is the absolute saturation temperature of methane in LNG, μ, is the viscosity of the liquid, ρ is the density of the liquid and ρ_o is the average reference density of the liquid.

In the Germeles model, equilibration of the liquid densities is taken as the necessary and sufficient criterion for mixing. In this aspect his model differs from that of Chatterjee and Geist, which requires equilibration of both temperature and composition.

Some results from a simulation of the La Spezia rollover obtained by Germeles using his model are given in Figure 22.16. As Figure 22.16(a) shows, there is at rollover equilibration of density, but not necessarily of temperature or composition. Figure 22.16(b) shows the rapid increase in boil-off. The computed time to rollover is 34 h, which compares with a time of 31 h in the actual incident.

Further theoretical and experimental investigations of rollover in LNG tanks have been reported (e.g. Nakano *et al.*, 1983; Takao and Suzuki, 1983).

There are a number of measures which can be taken to reduce the risk of rollover. Accounts of such measures are given by Chatterjee and Geist (1972) and by Drake, Geist and Smith (1973). They include:

(1) limitation of the variation in LNG composition;
(2) mixing of the tank contents by the use of top and bottom filling points;
(3) mixing of the tank contents by pump recirculation;
(4) pressure control of the tank;
(5) monitoring of parameters related to stratification;
(6) provision of a high capacity vent.

In some cases it may be possible to limit the variation of LNG composition, but in others this is not attractive. Mixing of the tank contents may be effected during filling by using top or bottom filling to charge a cargo which is more or less dense than the heel. Mixing during filling may be enhanced by jet mixing devices. Mixing during and after filling by recirculation pumps may also be used, although this is a

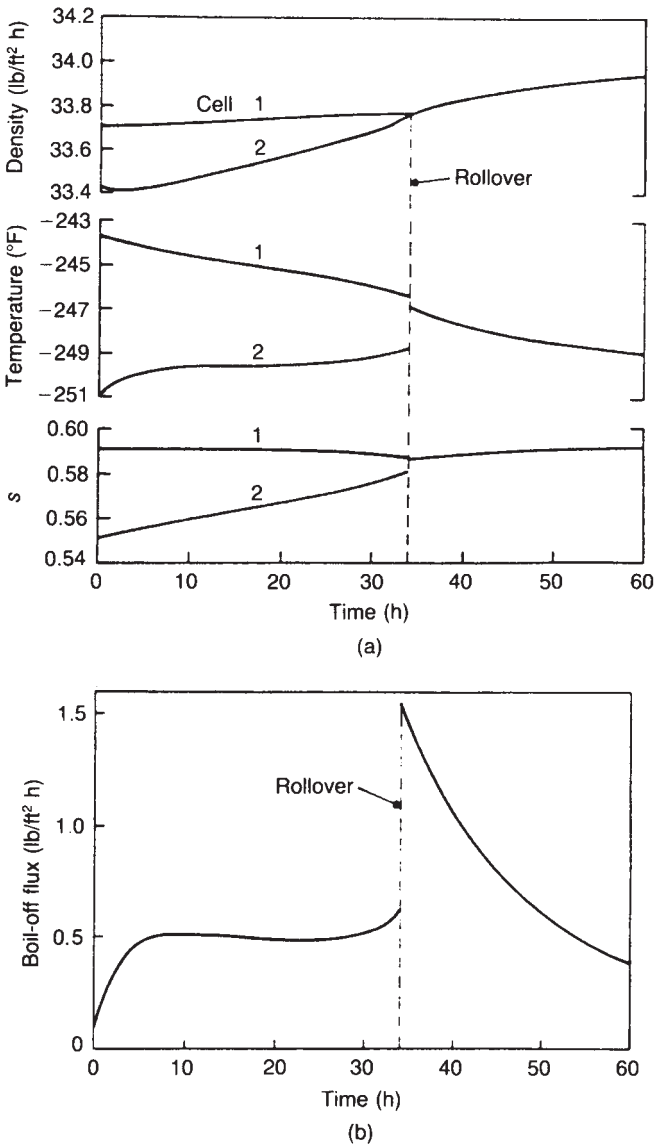


Figure 22.16 *Simulation of the rollover of LNG in the tank in the La Spezia incident (Germeles, 1975b): (a) density, temperature and impurity concentration S; (b) boil-off flux (Courtesy of the Plenum Publishing Corporation)*

slow method and it may take too long; it also increases the heat inleak. Control of pressure in the tank may be used to give controlled evolution of vapour from the liquid. There are several parameters which may be used to monitor stratification. One is the liquid temperature profile in the tank. Another is the difference in density between the feed and the tank liquids, a third is the vaporization rate in the tank. Protection of the tank if rollover occurs despite these other measures requires the provision of a high capacity vent. The peak vapour evolution rate resulting from a rollover is difficult to estimate and the vent needs to be generously sized.

The rollover hazard receives mention in a number of accounts of LNG tank systems, including those by Collins *et al.* (1983), Crawford, Durr and Handman (1986) and LeChat and Caudron (1987).

22.11.13 Particular installations

There are a number of accounts of particular refrigerated atmospheric storage installations for LNG.

The Montoir de Bretagne LNG terminal is described by Lechat and Caudron (1987). They discuss the potential for

rollover due to differences in the composition of the LNG cargoes received, and the precautions taken.

An account of the LPG and LNG terminal at Das Island is given by Morrison (1987). He describes in detail the tanks, foundations, ancillary equipment, pressure relief and fire protection.

22.11.14 Storage vessels

Although an atmospheric storage tank is the norm for refrigerated land-based LNG storage, a pressure vessel may also be used, as described by Itoyama *et al.* (1989). The vessel is essentially an adaptation of the MRV storage sphere used on LNG carriers. It has an inner shell of aluminium, to ensure strength at a cryogenic condition, and an outer shell of mild steel.

22.11.15 Underground storage

A number of early LNG storages took the form of an earth pit. The ground around the pit was frozen by the cold liquid, thus providing a seal. One such installation was the 21,000 te LNG storage at the British Gas terminal at Canvey.

Experience with such earth pit storages, described by Ferguson (1975), was not good. Problems were experienced in making the containment leak-tight and waterproof and with fissuring of the ground. The heat inleak resulted in a boil-off rate which was uneconomic. Thus, whereas the boil-off for a good above-ground tank is of the order of 0.04% per day by volume, that for an earth pit storage is some 0.1–0.3%.

The abandonment of earth pit storage at Canvey meant that of some dozen such storages, by 1975 only one remained in use. However, the concept of underground storage remains alive. Conceptual designs for cavity storage of LPG and LNG have been described by Lagron, Boulanger and Luyten (1986).

22.11.16 Mounded storage

More success has been achieved with mounded storage in which the LNG pressure vessel is set in an earth mound. This method has already been described in relation to LPG storage.

The method has been used in Japan, as described by Collins *et al.* (1983). In some cases use has been made of a concrete tank with its roof at grade, whilst in others the tank has been constructed at ground level and surrounded by a full earth berm.

22.12 Hydrogen Storage

Hydrogen is stored both as a gas and as a liquid. Relevant codes are NFPA 50A: 1989 Gaseous Hydrogen Systems at Consumer Sites and NFPA 50B: 1989 Liquefied Hydrogen Systems at Consumer Sites. Also relevant are *The Safe Storage of Gaseous Hydrogen in Seamless Cylinders and Containers* (BCGA, 1986 CP 8) and *Hydrogen* (CGA, 1974 G-5). Accounts are also given by Scharle (1965) and Angus (1984).

The principal type of storage for gaseous hydrogen is some form of pressure container, which includes cylinders. Hydrogen is also stored in small gasholders, but large ones are not favoured for safety reasons. Another form of storage is in salt caverns, where storage is effected by brine displacement. One such storage holds 500 te of hydrogen.

A typical industrial cylinder has a volume of 49 l and contains some 0.65 kg of hydrogen at 164 bar pressure. The energy of compression which would be released by a catastrophic rupture is of the order of 4 MJ. There is a tendency to prohibit the use of such cylinders indoors.

Liquid hydrogen is stored in pressure containers. Dewar vessel storage is well developed with vessels exceeding 12 m diameter.

NFPA 50A requires that gaseous hydrogen be stored in pressure containers. The storage should be above ground. The storage options, in order of preference, are in the open, in a separate building, in a building with a special room and in a building without such a room. The code gives the maximum quantities which should be stored in each type of location and the minimum separation distances for storage in the open.

For liquid hydrogen NFPA 50B requires that storage be in pressure containers. The order of the storage options is the same as for gaseous hydrogen. The code gives the maximum quantities which should be stored in each type of location and the minimum separation distances for storage in the open.

Where there are flammable liquids in the vicinity of the hydrogen storage, whether gas or liquid, there should be arrangements to prevent a flammable liquid spillage from running into the area under the hydrogen storage. Gaseous hydrogen storage should be located on ground higher than the flammable storage or protected by diversion walls.

In designing a diversion wall, the danger should be borne in mind that too high a barrier may create a confined space in which a hydrogen leak could accumulate. Scharle (1965) draws attention to the risk of detonation of hydrogen when confined and describes an installation in which existing protective walls were actually removed for this reason.

Pressure relief should be designed so that the discharge does not impinge on equipment. Relief for gaseous hydrogen should be arranged to discharge upwards and unobstructed to the open air.

Hydrogen flames are practically invisible and may be detected only by the heat radiated. This constitutes an additional and unusual hazard to personnel which needs to be borne in mind in designing an installation.

22.13 Toxics Storage

The topic of storage has tended to be dominated by flammables. It would be an exaggeration to say that the storage of toxics has been neglected, since there has for a long time been a good deal of information available on storage of ammonia, chlorine and other toxic materials. Nevertheless, the disaster at Bhopal has raised the profile of the storage of toxics, especially in respect of highly toxic substances.

In the United States, in particular, there is a growing volume of legislation, as described in Chapter 3, for the control of toxic substances. Attention centres particularly on high toxic hazard materials (HTHMs).

Some of the factors which need to be taken into account in relation to storage of HTHMs are now considered.

22.13.1 Inherent toxic hazard

The starting point is the characterization of the toxic hazard. The toxicity of the substance is one aspect of this. Another is the inventory. But the potential for harm also depends very much on features of the substance and its storage which determine its emission and dispersion.

There are a variety of toxic exposure limits which have been devised for different purposes such as the threshold limit value (TLV) and the emergency exposure limit (EEL), but these tend to be of limited use in assessing the toxic hazard. Various attempts have been made to devise more appropriate indices such as the Dow Chemical Exposure Index (CEP). These exposure limits and indices are described in Chapter 18.

The most realistic approach to the characterization of the inherent toxic hazard, however, would appear to be some form of hazard assessment, which need not necessarily amount to a full risk assessment, but may be limited to consequence assessment.

22.13.2 Inherently safer design

As for other process activities, so for HTHM storage the principle of inherently safer design should be applied. In the case of HTHM storage this means in particular examining the products made and the whole series of processes used to make them, whether at the assessor's site or elsewhere, with a view to the use of more benign chemicals and to the reduction of toxics inventories throughout the production and transport chains. In particular, it should be an aim to eliminate intermediate storage. Illustrations of the application of inherently safer design with regard to toxics, including toxics storage, are given in Chapter 11.

Another aspect of inherently safer design in storage is the storage conditions. The choice between pressure and refrigerated storage is the obvious example. But storage can be made inherently safer in other ways also, such as choosing the storage temperature such that it reduces the load on the disposal system should it become necessary to depressurize.

22.13.3 Storage siting and layout

Storage for HTHMs should be sited so as to minimize the frequency and the consequences of any release. The consequences of a release may be reduced by the provision of separation distances between the storage and potential targets, exploitation of the terrain and provision of escape routes. Measures to reduce frequency include segregation from flammables, minimization of interactions with transport terminals and minimization of domino effects.

22.13.4 High integrity design

Plant used for the storage of HTHMs should be high integrity plant. The high integrity design features should cover, among other things, (1) plant layout, (2) vessels and tanks, (3) pipework, (4) loading and unloading facilities, (5) secondary containment, (6) instrumentation, (7) pressure relief and disposal systems and (8) contaminant control.

For the most part, the codes and standards which govern plant design are oriented to flammables rather than toxics. There is relatively little guidance on toxics specifically.

The American Society of Mechanical Engineers (ASME) *Boiler and Pressure Vessel Code* does, however, recognize a category of 'lethal service', where the gases or liquids contained are of lethal toxicity. The ASME main piping code B31.3 has a Category M which is of similar purport.

The plant layout for HTHMs should include arrangements for the containment of liquid spillages by the use of bunds or other measures.

Pressure vessels and atmospheric tanks for HTHM storage should be built to high integrity standards. It is not usual to use double integrity tanks for HTHMs, though they are used for ammonia. But other measures to enhance integrity such as full radiography of welds, stress relieving and so on, should be used. Foundations and supports should also be of high integrity.

Likewise, pipework and fittings and equipment such as pumps should be to high integrity standards. Special attention should be paid to potential weak points such as nozzles, welds, flanges, gaskets and pipe supports. Events which might cause failure of pipework or equipment, such as hammerblow or vibration in the pipe or deadheading or cavitation in pumps, should be given extra consideration.

There are two quite separate aspects to pipework integrity. The measures just described are aimed at the prevention of serious failures. It is also necessary to aim for a high degree of leak-tightness in order to prevent fugitive emissions.

The disposition of the pipework into and out of the storage is another relevant feature. Lines connected below the liquid surface are a major source of large leaks and are to be avoided.

Provision needs to be made to shut-off or reduce leaks which may occur in the form of excess flow valves, remotely operated isolation valves, and so on.

Extra consideration should be given to external threats to the containment, whether due to impacts such as dropped loads or vehicles or to natural events.

Associated with storage are loading and unloading facilities which are another potential source of release. Features of such facilities which are not present in storage itself and which tend to increase the risk include: (1) a higher level of activity; (2) the involvement of personnel from different companies; (3) connections which are constantly made and unmade and which may be relatively fragile; (4) the movement of vehicles, including moving off whilst still connected and (5) the absence of secondary containment. The design should aim to minimize these problems.

The provision of secondary containment should be considered. Types of secondary containment include double integrity containments, double-walled pipes, dump tanks, bunds, drainage and sump systems and enclosures.

Some part of the instrument and control systems for HTHM storage may need to be high integrity. At the very least good practice should be followed in matters such as the use in critical applications of a sensor separate from that of the control loop for an alarm or a trip. It may be necessary in some cases to consider high reliability instrument systems based on the use of redundancy.

Systems for pressure relief on HTHM storage should receive extra attention. The relief and disposal system appropriate depends on the nature and quantity of fluid to be handled. Whatever system is selected, it too should be of high integrity.

A storage can be put at risk by the entry of a contaminant which either itself reacts with the material stored or catalyzes a reaction. For some chemicals it is necessary to include in the design features that prevent such contamination.

22.13.5 High integrity operation

High integrity in the design needs to be complemented by high integrity in the operation of the plant. It is not appropriate to rehearse here the various features of good practice in operation and maintenance, but a few salient points can be made.

Storage is not simply a passive adjunct to the main process plant. It too is actively operated by filling and

emptying. These operations have the potential to cause destructive overpressure or underpressure and to cause overfilling, and they need to be carefully controlled.

The storage should be operated so as to exclude contaminants which might cause reaction of the material held. Likewise, operations should not result in serious depletion of any necessary stabilizer.

Where the HTHM is flammable as well as toxic, measures should be taken to control ignition sources, including procedures to prevent ignition by static electricity.

Activities in the vicinity of storage, such as lifting of loads or movement of vehicles, should be controlled so that they do not pose an impact threat.

Storage systems tend to have a quite large proportion of items for use only in an emergency and which tend to be neglected and are often found to be either in poor condition or in the wrong state. Examples are blocked pipes or closed valves on water spray systems or open valves on water drainage lines through bunds.

With regard to maintenance, some aspects of particular importance in HTHM storage include (1) the identification and ranking of critical features, (2) inspection to detect unrevealed failures, (3) preventive maintenance, (4) isolation procedures and (5) documentation.

The operating discipline should ensure that all protective features are maintained in operational condition, whether these be heating or cooling systems, instrumented protective systems, relief systems or fire protection systems.

22.14 High Toxic Hazard Materials: CCPS *Guidelines*

The Center for Chemical Process Safety (CCPS) has published guidance on the storage of HTHMs, and this is now described.

22.14.1 CCPS *Guidelines for Safe Storage and Handling of High Toxic Hazard Materials*

The CCPS *Guidelines for Safe Storage and Handling of High Toxic Hazard Materials* (1988/3) (the CCPS *HTHM Storage Guidelines*) cover a wide range of topics on HTHM storage. Many of these topics are dealt with in other parts of the present text. Table 22.10 gives an indication of the chapters or sections in which these topics are treated.

Table 22.10 *Some principal topics in the CCPS High Toxic Hazard Material Storage Guidelines and their treatment in this text*

	Chapter No.
1. Overview	
2. Risk assessment	9
3. Plant design	
3.1 Inherently safer design	11
3.2 Plant siting	10
3.3 Plant layout	10
4. Design of storage and piping	12, 22
5. Loading and unloading facilities	22, 25
6. Instrumentation and control	13
7. Isolation and containment	12, 22
8. Inspection and maintenance	19, 21
9. Operating procedures and training	14, 20, 28
10. Emergency planning	24

22.15 Chlorine Storage

Storage of chlorine as a liquid is mainly either at chemical works or at installations where it is required for water treatment such as waterworks, power stations and swimming baths. Its boiling point is −34°C.

Guidance on the handling and storage of chlorine is given in HS(G) 28 *Safety Advice for Bulk Chlorine Installations* (HSE, 1986). This guidance is based on the earlier *Guidelines for Bulk Handling of Chlorine at Consumer Installations* (CIA, 1980/14) (the CIA *Chlorine Storage Guide*), which itself followed *Code of Practice for Chemicals with Major Hazards: Chlorine* (BCISC, 1975/1) (the CIA Chlorine Code). HS(G) 28 is the guidance now listed by the Chemical Industries Association (CIA).

Further guidance is given in the various publications of the Chlorine Institute, including *Chlorine Manual* (1986, Pmphlt 1), *Non-refrigerated Liquid Chlorine Storage* (1982, Pmphlt 5), *Refrigerated Liquid Chlorine Storage* (1984, Pmphlt 78), *Piping Systems for Dry Chlorine* (1985, Pmphlt 6), *Operation of Chlorine Vaporizing Equipment* (1979, Pmphlt 9) and *Chlorine Tank Car Loading, Unloading, Air Padding, Hydrostatic Testing* (1979 Pmphlt 66).

The account given here is confined to chlorine storage. Chlorine itself is discussed in Chapter 11, pipework for chlorine systems is discussed in Chapter 12 and chlorine unloading facilities are described in Section 22.26.

22.15.1 Regulatory requirements

The storage of chlorine is governed by the NIHHS Regulations 1982 and the CIMAH Regulations 1984. The NIHHS notifiable inventory is 10 te. The CIMAH inventory for which demonstration of safe operation may be required (Regulation 4) is 10 te and that which attracts a safety case (Regulation 7) is 75 te.

22.15.2 Storage conditions

Chlorine is generally stored under pressure at atmospheric temperature, but may also be stored fully refrigerated at −34°C and atmospheric pressure.

22.15.3 Storage systems

Chlorine should be stored in bulk only if it is used in quantities which make the use of drums impractical. A chlorine storage vessel should have a capacity appreciably greater than a full load from a road tanker or rail tank car. It is preferable to keep the number of vessels to a minimum in order to avoid complexity and proliferation of potential leak sources, but flexibility and continuity of supply require at least two vessels.

The *Chlorine Code* gives a well defined philosophy for the storage of chlorine. In view of the importance of the hazard of toxic release from storage, the *Code's* statement of the problem is of interest:

> Liquid stored in bulk is the potential source of the most serious incidents.
>
> Stored liquid could be released:
>
> (1) By failure of the vessel holding it.
> (2) By failure of pipework or equipment connected to that vessel.
>
> Stocks necessarily carried to conduct normal operation in the businesses are such that the techniques of design and operation of any storage must eliminate the risk of complete vessel failure leading to release of its contents.

(1) Liquefied gas storage can be designed, fabricated, inspected and maintained so that there is no possibility of a tank releasing its contents while it is kept within design conditions.
(2) Protective systems of quantified high reliability and availability can be designed to ensure that these physical conditions are maintained.
(3) Impurities can be controlled to obviate abnormal corrosion.
(4) These measures may be backed up by relief systems such that the combination of vessel design, protection, quality control and relief eliminates the possibility of complete vessel failure.
(5) Liquefied gas storages can be sited, or given protective barriers, such that they are fully protected from external damage other than civil commotion, sabotage, act of war or falling aircraft.

From these first premises it follows that, although the risk of some damage to a storage vessel cannot be totally eliminated, the main dangers derive from failure of pipework or equipment whether on producing or using plants or connected to storage.

The critical factors in preventing escapes are:

(1) Arrangements for isolation of stocks from all other equipment.
(2) Arrangements for isolation of process vessels from all other equipment.
(3) Protection from external damage.
(4) Means of maintaining design conditions and relieving abnormal conditions.
(5) Means for disposal of purged or vented material.
(6) The effect of chemicals and conditions in using processes on the design and operating requirements.
(7) Means for the retention of spillages near the point of origin and for their treatment. The capacity of the retention area shall be sufficient for, but need not be more than, the largest spillage which can reasonably be envisaged. The walls of the retention area shall, however, be sufficiently high to contain also any material used in treating the spillage.

22.15.4 Materials of construction

Materials of construction for chlorine handling are discussed in Chapters 11 and 12, and are therefore not dealt with in detail here, but there are a few matters which merit mention at this point. The normal material of construction for chlorine storage vessels is mild steel. Mild steel is satisfactory for the handling of dry gaseous or liquid chlorine, but not of wet chlorine. There are, however, upper and lower temperature limits for mild steel in chlorine which should not be exceeded.

22.15.5 Storage vessels

Chlorine pressure storage vessels are usually horizontal cylindrical vessels for the smaller capacities and spherical vessels for the larger ones. Pressure storage spheres up to 400 te capacity have been used for chlorine, but some large vessels have been taken out of use, thus reducing the hazardous inventory.

A chlorine pressure storage vessel should be designed to BS 5500: 1991 Category 1 or equivalent, but with the additional requirements of HS(G) 28.

HS(G) 28 states that a chlorine storage vessel should have a minimum design pressure of 12 barg (174 psig). The minimum design temperature should be −35°C, the temperature to which liquid chlorine will drop if completely depressurized. The normal design range for temperature is −35°C to 45°C.

With regard to the filling ratio, there is no standard equivalent to BS 5355: 1976 for transportable liquid containers. HS(G) 28 states that for chlorine the figure normally used is 1.25 kg of liquid chlorine/litre of capacity, which ensures that even at 50°C the volumetric fill does not exceed 95%.

The connections on a chlorine storage vessel should be held to a minimum and kept simple. Connections required are (1) a liquid chlorine inlet, (2) a liquid chlorine outlet, (3) vent and padding air lines, (4) a relief system and (5) instrument connections. Lines entering below the liquid level are to be avoided so that any release is of gas rather than of liquid. The preferred arrangement is that all the connections should be through a manhole located on the top of the vessel. Detailed design of these lines is described HS(G) 28.

The vent and padding air lines may have separate connections or may be through a single combined connection. The vent should go to the gas absorption system.

The arrangements given in HS(G) 28 for a chlorine storage vessel and the associated unloading facilities are shown in Figure 22.17.

Chlorine storage vessels should be located above ground and provided with a bund. The bund should be able to take the contents of the largest storage vessel with adequate freeboard. The ground under a storage vessel should be sloped to allow drainage into a sump. Provision should be made to remove rainwater over the bund wall rather than through it.

22.15.6 Ancillary facilities

Ancillary facilities required for chlorine storage include: an expansion vessel to take any chlorine vented in the event of overfilling; a gas absorption unit for the disposal of the vented material; equipment for the transfer of liquid chlorine from storage to consumer plants; and vaporization equipment to provide chlorine gas to consumer plants. These facilities are described below.

22.15.7 Instrumentation

A chlorine storage vessel should be provided with suitable measurements and alarms on liquid contents, pressure and temperature. The measurement of the liquid contents should preferably be by means of load cells or a weighbridge.

Protection against overfilling should receive particular attention. As already stated, the vessel itself should be larger than the road tankers and rail tank car containers which deliver to it. There should be a high contents alarm, and possibly an extra-high contents alarm. A low contents alarm may also be appropriate. An ullage pipe may be provided on the vent line with a low temperature or other alarm to warn of entry of liquid chlorine into the line.

The storage should be provided with a chlorine gas detector system.

22.15.8 Pressure relief

For a chlorine storage vessel, pressure relief should be provided as an ultimate safeguard. HS(G) 28 requires that the pressure relief arrangements be a double stream system

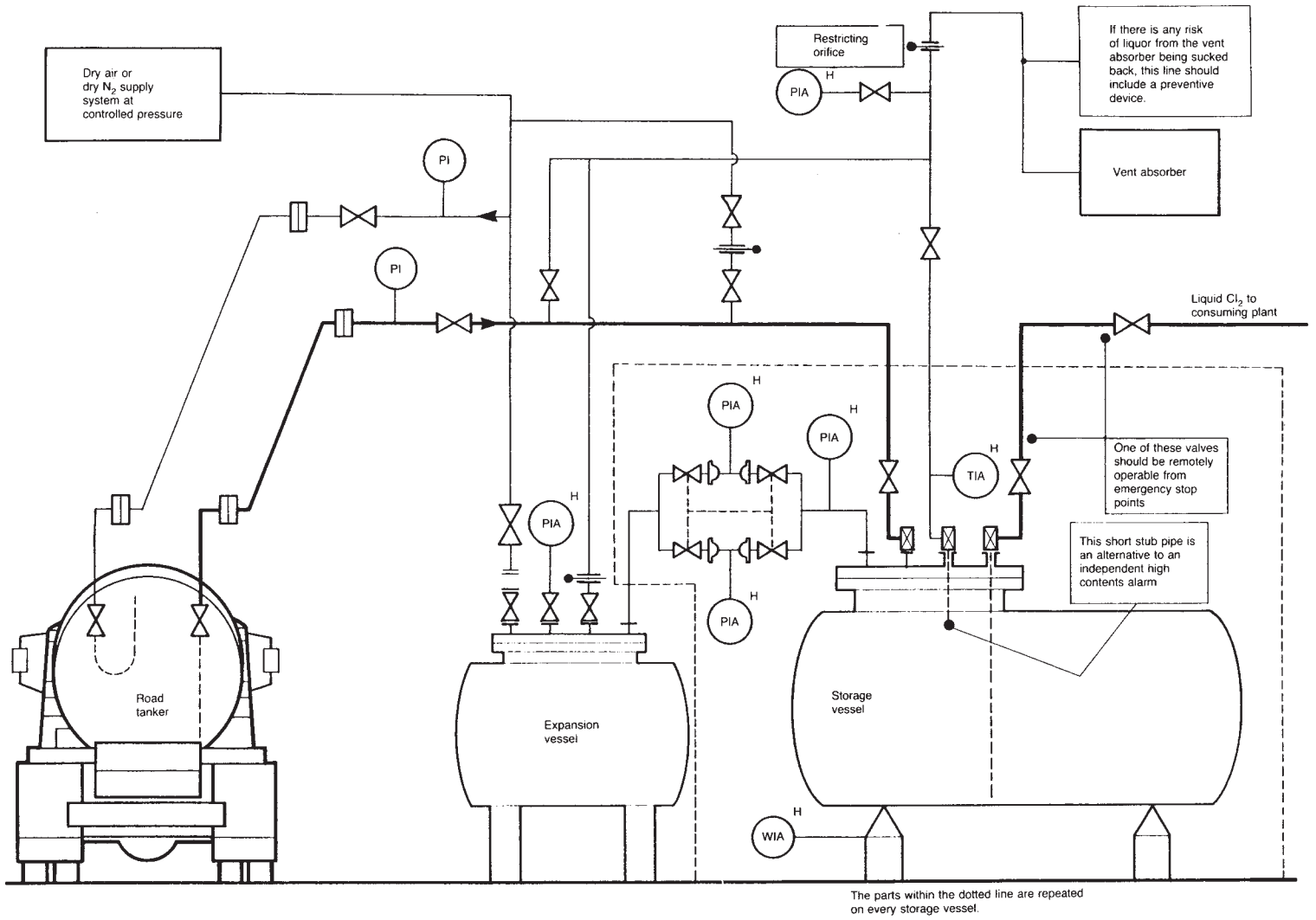


Figure 22.17 *General arrangement for a chlorine pressure storage installation and road loading facility (Health and Safety Executive, 1986 HS(G) 28). The original diagram contains cross-references to certain paragraphs in HS(G) 28. (Courtesy of HM Stationery Office © All rights reserved)*

with isolation valves on the upstream and downstream sides of each stream, so that one stream can be operational whilst the other is under maintenance. There should be a safeguard against the risk of the simultaneous isolation of both streams, either by means of a mechanical interlock on the isolation valves or of a procedure for locking the valve.

For each relief stream, the relief devices should be either two bursting discs arranged back to back or a bursting disc followed by a pressure relief valve. Either way, there should be a pressure gauge on the space between the two devices. A pressure relief valve alone should not be used, owing to the risk of corrosion.

A single stream system with locked open isolation valves is in common use, but the arrangements described are the preferred ones.

An expansion vessel should be provided to receive the relief. It should be designed to the same standard as the storage vessels and should have a capacity about 10% of that of the largest vessel. It should be capable of being vented manually to the disposal system and should have its own high pressure alarm.

22.15.9 Absorption system

There should be suitable arrangements for the absorption of any chlorine vented. In some systems it is possible to arrange for the chlorine to be absorbed on a user plant, but normally a dedicated gas absorption system is required. As shown in Figure 22.17, the gas absorption system receives chlorine gas from normal venting and, via the expansion vessel, gas from the relief system.

The gas absorption system should be instrumented to ensure that the circulation of liquid and the concentration of absorbent are correct and to measure the concentration of chlorine in the outlet gas stream.

22.15.10 Transfer arrangements

The transfer of liquid chlorine from a storage vessel to consumer plants may be effected by vapour pressure alone, by padding gas pressure or by pumping. The first two methods are the most common.

The padding gas may be nitrogen or compressed dry air. Nitrogen for padding may be obtained from a liquid nitrogen vaporization unit. Compressed air should be dry to a dewpoint below −40°C and should be oil free. The padding gas should be held in a receiver with an operating pressure and with protective devices and instrumentation such that the storage cannot be over-pressured by the padding gas. Detailed arrangements are described in HS(G) 28.

For pumping, which may be utilized where a higher pressure is required or where the padding gas cannot be tolerated, use is made both of submerged pumps installed inside the tank and of external pumps. For the latter a special pumping system has been developed in which the liquid chlorine is first transferred from the storage vessel to a separate pumping vessel and then fed to the pumps.

22.15.11 Vaporizers

Where chlorine is required in vapour form, a limited supply may be obtained from cylinders or drums, but the supply of any appreciable quantity requires vaporization facilities. It is not good practice to draw the gas from the vapour space of a chlorine storage vessel, as this creates the risks that process liquid may be drawn into the vessel and that less volatile impurities such as nitrogen trichloride may become concentrated.

HSE guidance on chlorine vaporizers is given in CS 16 *Chlorine Vaporizers* (1985) and HS(G) 28.

Three heating media are in use in chlorine vaporizers: hot water, steam and heat transfer fluids. The most common method is the use of hot water at about 60–70°C. Where steam is used it should be saturated and pressure limited to prevent overheating.

Four main types of vaporizer are used, as shown in Figure 22.18. Type 1 has some form of vertical tube bundle, Type 2 is a coiled tube immersed in a heating bath, Type 3 is a concentric tube, or jacketed pipe, unit and Type 4 is a kettle, reboiler unit. HS(G) 28 discusses the characteristics of the different designs.

There are a number of potential problems and hazards associated with vaporizers. One is overpressurization. A vaporizer commonly operates at 70°C, at which temperature the vapour pressure of chlorine is some 21 bar. This pressure can be realized in the vaporizer if it is isolated whilst containing the hot liquid. It is not usual in the United Kingdom to fit a pressure relief valve to a vaporizer.

Overheating can result in more rapid corrosion and, in the extreme, the combustion reaction between steel and chlorine. A temperature limit of 120°C is normally observed. The pressure of steam used for heating is limited to 1 barg (15 psig), corresponding to a temperature of 120°C, with the steam saturated rather than superheated.

If the flow to the vaporizer is excessive, the heating is insufficient or the heat transfer surfaces are fouled, the chlorine vapour may lose superheat, liquid droplets may be entrained or the vaporizer may flood. It is even possible that ice may form on the heating surfaces. An indication of these problems may be obtained from the gas flow and temperature from the vaporizer. HS(G) 28 gives details of the controls required. A knockout pot may also be installed to remove liquid droplets.

If the chlorine becomes contaminated by water, whether by a pinhole leak of water or steam heating medium, or otherwise, rapid corrosion of mild steel can result. If vaporization of chlorine is partial rather than total, a concentration of impurities, notably nitrogen trichloride, can occur with the attendant risk of explosion.

Concentration of less volatile impurities such as nitrogen trichloride must be avoided. In some cases, the vaporizer itself is designed to ensure that the nitrogen trichloride is vaporized together with the chlorine. Otherwise a separate purge and vaporizer circuit may be required to deal with the impurity residues.

Reverse flow of a process fluid into the vaporizer may occur if the pressure at the vaporizer falls or the process pressure rises or if the chlorine vapour condenses, creating a vacuum and causing suck-back.

Precautions need to be taken against these various hazards. Detailed measures are described in HS(G) 28.

22.15.12 Inspection

HS(G) 28 requires that an initial inspection be made when the vessel is brought into service and that there should be a first thorough in-service inspection within 5 years of commissioning. Thereafter the inspection interval should be determined by the inspecting authority, but should normally not exceed 5 years.

The guide gives details of the procedures to be followed in decommissioning and recommissioning the vessel and of the features to be inspected and the methods of inspection.

22.15.13 Storage operation

The principles governing the operation of chlorine storage are outlined in HS(G) 28.

22.15.14 Emergency arrangements

Emergency planning for chlorine storage is dealt with in HS(G) 28.

22.16 Ammonia Storage

Anhydrous ammonia is stored as a liquid, mainly either in chemical works or, particularly in the United States, in storage terminals supplying agricultural users. Its boiling point is −33°C.

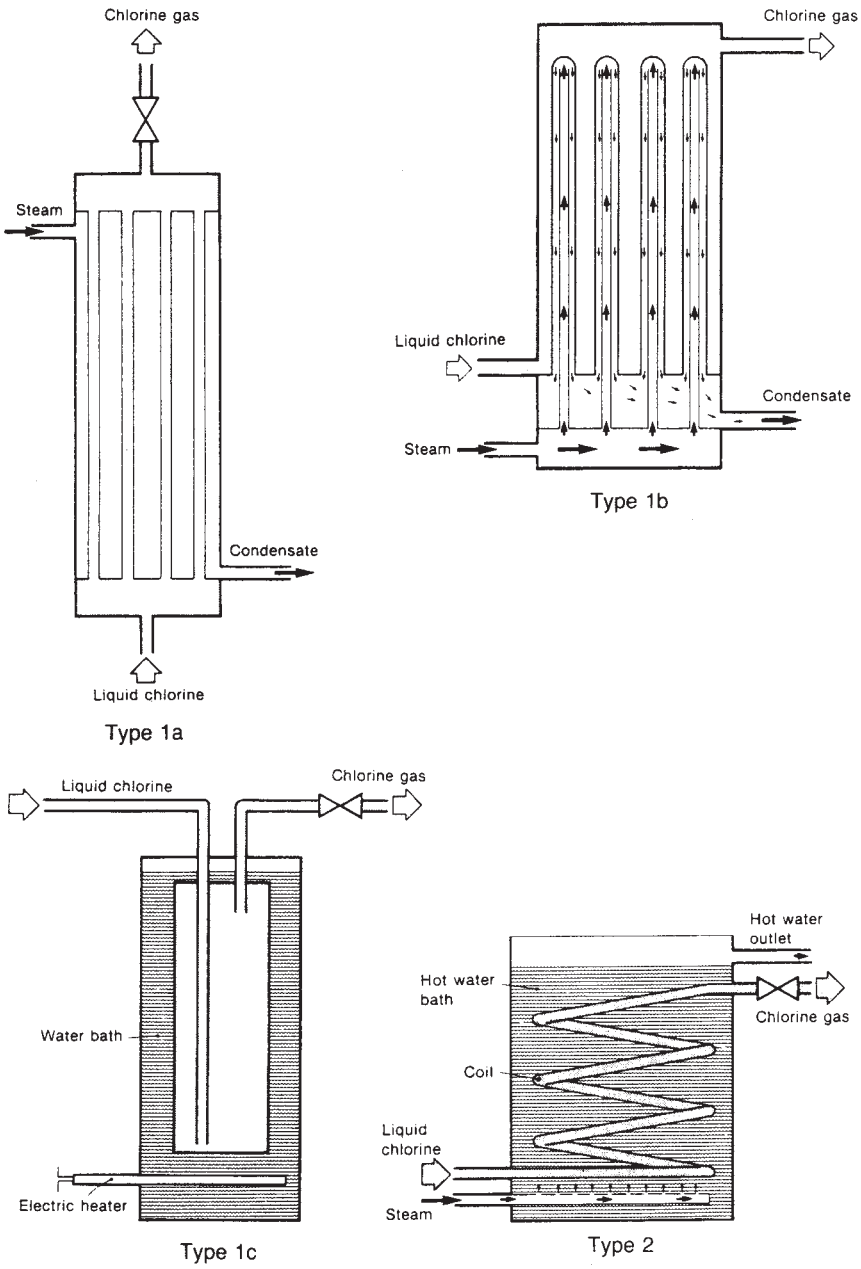


Figure 22.18 *continued*

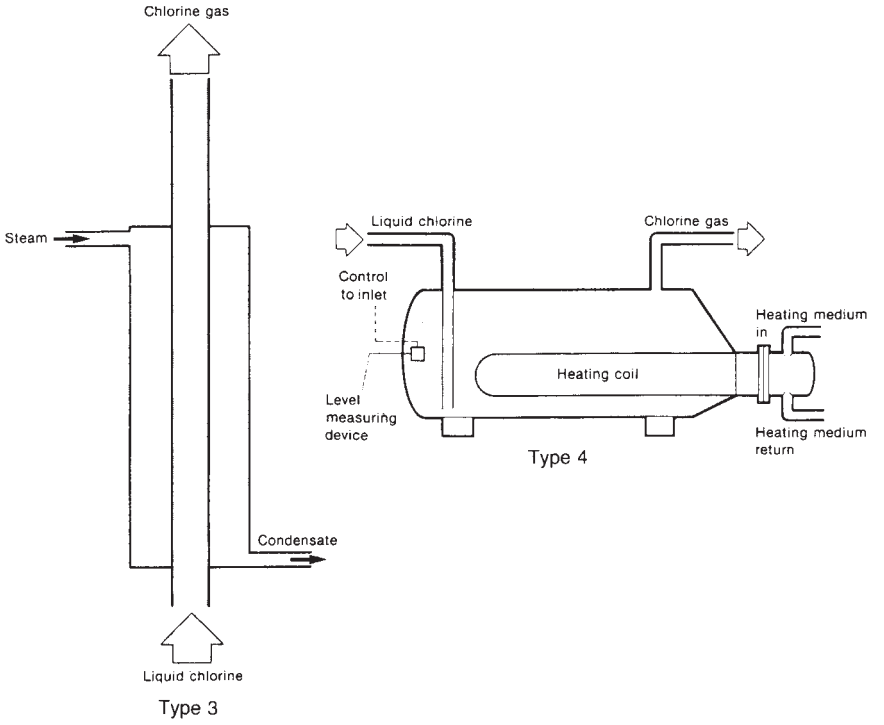


Figure 22.18 *Some types of chlorine vaporizer (Health and Safety Executive, 1986 HS(G) 28): (1a) shell and tube; (1b) steam bayonet; (1c) hot water bath; (2) coil tube immersed in heating bath; (3) concentric tube unit and (4) kettle type evaporator (Courtesy of HM Stationery Office © All rights reserved)*

The handling of ammonia, including its storage, has been a major preoccupation of the industry and this is reflected in the *Chemical Engineering Progress Series Safety in Air and Ammonia Plants* (American Institute of Chemical Engineers (AIChE) 1960–69/17–26) and *Ammonia Plant Safety (and Related Facilities)* (AIChE 1970–1994/31–52). The work of the industry storage committee has been described by Ball (1968b).

Guidance on ammonia storage is given in HS(G) 30 *Storage of Anhydrous Ammonia under Pressure in the United Kingdom* (HSE, 1986). Two CIA codes, *Code of Practice for the Storage of Anhydrous Ammonia under Pressure in the United Kingdom* (1975/13) (the CIA *Pressure Storage Code*) and *Code of Practice for the Large Scale Storage of Fully Refrigerated Anhydrous Ammonia in the United Kingdom* (1975/8) (the CIA *Refrigerated Ammonia Storage Code*), are no longer listed. A relevant US code is ANSI K61.1: 1989 *Safety Requirements for the Storage and Handling of Anhydrous Ammonia*.

The account given here is confined to ammonia storage. Ammonia itself is discussed in Chapter 11, pipework for ammonia systems in Chapter 12 and ammonia loading and unloading facilities in Section 22.26.

22.16.1 Regulatory requirements

The storage of anhydrous ammonia is governed by the NIHHS Regulations 1982 and the CIMAH Regulations 1984. The NIHHS notifiable inventory is 100 te. The CIMAH inventory for which demonstration of safe operation may be required (Regulation 4) is 50 te and that which attracts a safety case (Regulation 7) is 500 te.

22.16.2 Storage conditions

Ammonia is generally stored either under pressure at atmospheric temperature or fully refrigerated at −33°C and atmospheric pressure. A review of storage conditions has been given by C.C. Hale (1974).

22.16.3 Materials of construction

Materials of construction for ammonia handling are discussed in Chapters 11 and 12, and are, therefore, not dealt with in detail here, but there are a few matters which merit mention at this point. The normal material of construction for ammonia storage vessels and tanks is carbon steel. Ammonia reacts with copper and copper alloys, particularly if even traces of water are present, and they should not be used.

Materials of construction for ammonia handling need to be resistant to low temperatures and to SCC. High yield strength steels are more susceptible to SCC than lower yield strength steels, and an upper limit on strength may be specified. Austenitic steels are resistant to low temperature brittle fracture.

22.16.4 Storage statistics

Surveys of refrigerated ammonia storage with copious statistics have been given by C.C. Hale (1974, 1980, 1984) and

C.C. Hale and Lichtenberg (1990). The following subjects are among those covered, though not every subject is dealt with in every survey: (1) number of tanks, (2) size of tanks, (3) types of tank, (4) total storage capacity, (5) location of storage (by state), (6) siting of storage, (7) fill sources, (8) operating temperatures and pressures, (9) foundations, (10) insulation, (11) secondary containment, (12) vapour recovery systems, compressors and condensers, (13) flare systems, (14) inert gas purge systems, (15) utilities, (16) manning, (17) inspection, (18) downtime, (19) accident prevention programmes, and (20) emergency planning.

22.16.5 Storage policies

As for LPG and LNG, so for ammonia, the last decade has seen a considerable evolution of storage policy. Some accounts of these changes are given by W.G. Jones *et al.* (1989), J.R. Thompson and Carnegie (1989) and Squire (1991).

J.R. Thompson and Carnegie (1989) describe the policy of Dupont to replace pressurized storage of ammonia with high integrity refrigerated atmospheric storage.

The policy of ICI is described by W.G. Jones *et al.* (1989). There the policy is to retain in use existing pressure storage spheres, but for new storage to use small stress relieved cylindrical vessels and refrigerated atmospheric tanks.

22.16.6 Storage operation

The principles governing the operation of ammonia storage are outlined in HS(G) 30 and in the CIA *Refrigerated Ammonia Storage Code*.

The point was made earlier that in many of its aspects storage is not a low technology activity. This is illustrated by the comment of Squire (1991) in an account of the measures taken to ensure the integrity of a particular large refrigerated ammonia storage tank: 'Most, if not all, of the personnel associated with the ammonia tank did not understand the "technology of the tank" '.

22.16.7 Emergency arrangements

Emergency planning for ammonia storage is dealt with in HS(G) 30 for pressure storage and in the CIA *Refrigerated Ammonia Storage Code* and by C.C. Hale (1980). Hale describes an ammonia terminal emergency programme with emphasis on the properties and hazards of ammonia itself and on protective equipment for personnel.

22.17 Ammonia Storage: Pressure Storage

22.17.1 Storage vessels

Ammonia pressure storage vessels are usually horizontal cylindrical vessels for the small capacities and spherical vessels for the larger ones. It has been common practice to use pressure storage spheres with a capacity in the range 500 to 3000 te, but many spheres have suffered problems of SCC and some have been taken out of use.

An ammonia pressure storage vessel should be designed to BS 5500 Category 1, or equivalent, with due regard to Appendix D, which deals with low temperature steels, and taking into account the guidance given in HS(G) 30. HS(G) 30 gives separate treatments for cylindrical and spherical vessels, and this distinction is followed here.

22.17.2 Spherical vessels

HS(G) 30 states that an ammonia pressure storage sphere should be designed to withstand the stresses imposed when the vessel is full and the pressure in the vapour space is equal to the vapour pressure of ammonia at the maximum design temperature plus the partial pressure of any inert gases which may be present. The minimum design temperature should preferably be $-33°C$, which is the temperature to which liquid ammonia will drop if completely depressurized, but in any event should not be greater than $-10°C$.

The design should be such as to minimize the risk from SCC. The steel used should be not a high yield strength steel but one with a yield strength not exceeding 350 N/mm^2. The vessel should be fully stress relieved. These requirements apply to the design of a new vessel and are not necessarily met in existing vessels.

The inspection requirements given in HS(G) 30 include 100% magnetic particle inspection of all internal welds.

22.17.3 Secondary containment

It has been traditional to put bunds around all types of ammonia storage. But this practice has been questioned, for example by J.D. Reed (1974), in relation to pressure storage on the grounds that in this case sudden loss of containment tends to result in ejection of all the contents in the form of vapour, or spray, leaving no residual liquid.

HS(G) 30 recognizes this argument, but requires that an ammonia storage sphere should be provided with a bund. The bund should be able to take 20% of the capacity of the sphere, should be positioned outside the sphere radius and should be not less than 1 m high. The ground under the vessel should be sloped to allow drainage into a sump.

22.17.4 Ancillary facilities

The ancillary facilities required for ammonia storage include, in particular, pumps for the transfer of liquid ammonia from storage.

22.17.5 Instrumentation

An ammonia storage sphere should be provided with suitable measurements and alarms on liquid level, pressure and temperature. For level there should be at least two independent indicators. There should be a high level alarm independent of any indicators.

22.17.6 Pressure relief

HS(G) 30 requires that pressure relief on an ammonia storage sphere should be provided by means of at least two pressure relief valves. In addition, unless the sphere is designed for full vacuum, it should be protected by a vacuum break valve. Use may be made of separate pressure and vacuum valves or of the combined pressure/vacuum type.

There should be an isolation valve between each relief valve and the sphere, and a system should be incorporated to ensure that at any one time only one relief valve can be isolated.

22.17.7 Inspection

HS(G) 30 requires that an initial inspection be made when the sphere is brought into service and that there should be a first in-service inspection within 2 years of commissioning. A principal purpose of the inspection should be to detect any SCC which may have occurred, as described below. Provided the results of inspection are satisfactory, the inspection interval may be increased in steps of 2 years up to a maximum interval of not more than 6 years.

The guide gives details of the procedures to be followed in decommissioning and recommissioning the vessel and of the features to be inspected and the methods of inspection.

22.17.8 Stress corrosion cracking

Much of the treatment of operation and inspection in HS(G) 30 is concerned with SCC. This problem is considered at more length in Section 22.19, but the recommendations of the guide may be noted at this point. These are to the effect that the oxygen content of the liquid ammonia should not exceed 2.5 ppm when the water content is as low as 100 ppm, and that serious consideration should be given to maintaining the water content at 0.2% w/w.

22.17.9 Cylindrical vessels

As mentioned above, HS(G) 30 gives a separate treatment for cylindrical pressure vessels for ammonia storage. The guide states that an ammonia pressure storage cylinder should be designed for a pressure of at least 15.5 bars. The design temperatures given are essentially as for a storage sphere. The arrangements given in HS(G) 30 for a ammonia storage cylinder and the associated unloading facilities are shown in Figure 22.19. For a storage cylinder, the guide does not require a bund, but there should be protection against vehicle impact.

The inspection requirements given in HS(G) 30 include 100% radiography of all butt welds, and ultrasonic and/or magnetic particle inspection of all other welds.

22.17.10 Semi-refrigerated vessels

It is convenient to deal here with pressure vessels for the semi-refrigerated, or semi-pressure, storage of ammonia. These are normally pressure spheres and are treated in HS(G) 30 together with pressure spheres for storage at atmospheric temperature. Principal differences are that with semi-refrigerated storage it is necessary to allow for the heat gain and resultant boil-off by provision of suitable thermal insulation and refrigeration.

Insulation materials that may be used include foam glass and PUF. HS(G) 30 draws attention to the importance of a vapour barrier and to measures to prevent the integrity of the containment being impaired by the materials used in, or the attachment of, the insulation.

22.18 Ammonia Storage: Refrigerated Storage

22.18.1 Storage tanks

Refrigerated liquid ammonia is stored in atmospheric storage tanks. Accounts of such storage are given in the CIA *Refrigerated Ammonia Storage Code* and by Shah (1982), Blanken (1987), J.R. Thompson and Carnegie (1989) and Herbertsson (1992).

Tanks used for refrigerated ammonia have developed from conventional atmospheric storage tanks. The design of atmospheric storage tanks in general is governed by API Std 620: 1990 *Design and Construction of Large, Welded, Low-pressure Storage Tanks* and API Std 650: 1988 *Welded Steel Tanks for Oil Storage*. For refrigerated ammonia storage frequent reference is made to API Std 650, Appendix R.

There are now in use a number of tank systems similar to those used for LNG. The single wall tank has a wall made of low temperature steel with external insulation covered by a vapour barrier. A double wall tank has an inner wall of low temperature steel and an outer wall of carbon steel with insulation in between. The outer wall is not designed to withstand the cold liquid, so this is still only a single containment system. A double integrity tank system has an inner tank with a suspended deck and an outer wall. Both the inner and outer walls are of low temperature steel. Accounts of tank systems make little reference to the use of pre-stressed concrete for either the inner or outer wall or of membrane systems.

22.18.2 Foundations

The foundations of refrigerated ammonia storage tanks require be protected against 'frost heave'. The problem and its prevention have been discussed by Morrison and Marshall (1970). Two principal types of foundation are used. One involves a tank bottom slab on piling so that there is free air circulation. In the other, the bottom slab is provided with insulation and electrical heating.

Further descriptions of foundation systems are given in the CIA *Refrigerated Ammonia Storage Code* and by C.C. Hale (1980) and C.C. Hale and Lichtenberg (1990).

22.18.3 Insulation

A refrigerated ammonia storage tank requires thermal insulation. The type of insulation which is suitable depends on the tank system. Principal types of insulation for single wall tanks are foam glass, PUF, reflective multi-layered aluminium and Styrofoam. For doubled wall tanks use is made of perlite insulation. The suspended deck used in double wall tanks counts as another form of insulation.

Insulation failures on single wall tanks are not unusual. A common cause is the penetration of moisture. Insulation problems have been described by a number of authors, including Hoffman (1967) and C.C. Hale (1974, 1980). Loss of a section of lagging is undesirable, because it allows rapid heat leak into the tank with a consequent increase in vaporization; it may also cause 'bump boiling'.

Reviews of the failure rates of insulation systems have been made by C.C. Hale (1974, 1980). He found that double wall tank systems filled with expanded perlite and reflective multi-layer aluminium systems had a good record compared with foam glass, PUF and Styrofoam systems.

Further descriptions of insulation systems are given by C.C. Hale (1984) and C.C. Hale and Lichtenberg (1990).

Squire (1991) has discussed the effect of insulation in a double integrity tank system in the event of a leak from the inner tank into the annular space. Tests showed that as the ammonia vaporized, the perlite insulation behaved like a spouted bed, resulting in a pressure of 55–69 kPA (8–10 psi). Solutions were to vent to annular space or install block Styrofoam insulation. No satisfactory way was found of doing the former, and for the tank in question the latter solution was adopted.

22.18.4 Secondary containment

Refrigerated ammonia storage tanks may be provided with some form of secondary containment. Accounts are given by Comeau (1972), MacArthur (1972), C.C. Hale (1974, 1980), J.D. Reed (1974), Hendriks (1980), Shah (1982), Blanken (1987) and C.C. Hale and Lichtenberg (1990).

Escape from refrigerated ammonia storage results in immediate flashing of only about 2% of the liquid. Even a primitive secondary containment should hold some 90% of the liquid.

Bunds and other measures to prevent dispersion of ammonia from refrigerated storage have been discussed by Comeau (1972). It is not necessarily enough simply to catch the liquid released. If a low bund with a large surface area is used, the large quantities of ammonia vapour vaporized from the liquid will still present a serious hazard. It is

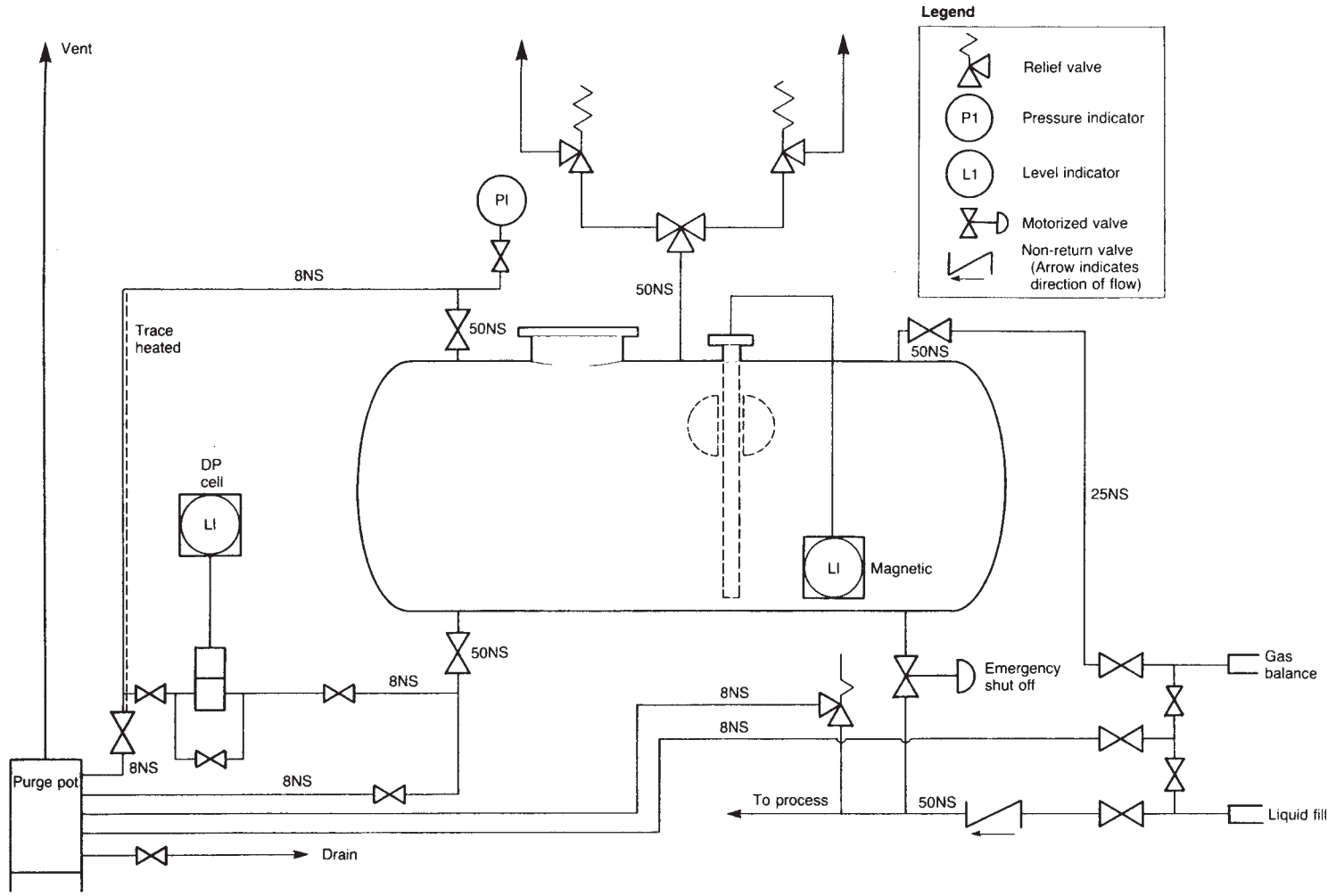


Figure 22.19 *General arrangement for an ammonia pressure storage installation (Health and Safety Executive, 1986 HS(G) 30) (Courtesy of HM Stationery Office © All rights reserved)*

therefore desirable to reduce the surface area. There are various methods of doing this. Use may be made of controlled drainage which runs the liquid off to a pit where its evaporation is reduced. Foam blanketing is another possibility, provided the area to be covered is not excessive. However, the most effective method of reducing the surface area available for evaporation is the use of a high bund.

The CIA *Refrigerated Ammonia Storage Code* requires that for a refrigerated atmospheric ammonia storage tank in the United Kingdom, means must be provided to contain the liquid safely in the event of failure of the main tank. The two methods which are acceptable are the use of a double integrity tank or the use of a concrete wall of approximately the same height as the tank wall. For the latter it is recommended that the width of the annulus is 1.5 m. The *Code* recognizes that in remote locations a low bund may sometimes be acceptable.

22.18.5 Ancillary facilities

Ancillary facilities for refrigerated ammonia tanks include refrigeration systems. Accounts are given by C.C. Hale (1980, 1984), C.C. Hale and Lichtenberg (1990) and Herbertsson (1992).

Refrigerated ammonia storage requires the provision of refrigeration facilities to liquefy vapour boil-off caused by heat inleak. Where the storage is part of an ammonia manufacturing plant, the main ammonia refrigeration facility may be used with just a backup set for storage, but generally the facility is a dedicated one. The principal elements are the refrigeration compressors and the ammonia condensers. There may also be a purge system to remove inerts from the ammonia condenser or receiver.

22.18.6 Instrumentation

A refrigerated ammonia storage tank should be provided with suitable measurements and alarms on the liquid level, pressure and temperature in the tank, and on boil-off gas flow.

Principal features of the instrumentation are the arrangements to prevent overpressure and overfilling. Pressure control is an integral part of the refrigeration system and there may also be a pressure control valve for emergency venting to flare.

In addition to the usual level instrumentation, use may be made of an interlock system to prevent overfilling by the operator.

In a double wall or double integrity tank system, instrumentation may be provided to detect any leak into the annular space between the two tanks.

22.18.7 Pressure relief

The tank also requires pressure relief and vent disposal arrangements. Accounts are given by C.C. Hale (1974, 1980), J.R. Thompson and Carnegie (1989) and C.C. Hale and Lichtenberg (1990).

Pressure relief is provided by a pressure relief valve. Most tanks also have vacuum relief. PV valves are a common method of providing both forms of relief.

Venting to atmosphere has been common practice, provided that the location is suitable and the venting is done at a safe height, but the trend is away from such venting. In the normal operation of refrigerated ammonia storage, however, there is very little venting. Vapour is reliquefied by the refrigeration set and returned as liquid to the tank.

The main requirement for venting is in an emergency. In many systems, flares are provided to handle emergency venting. The flares may be on the tank, or inside or outside the bund. Venting to the flare may be by a separate pressure control valve rather than the main pressure relieve valve. Complete combustion of the ammonia flared, and avoidance of odour, is assisted by the addition of fuel gas.

22.18.8 Inspection

The inspection of refrigerated ammonia storage tanks presents a number of problems and needs to be governed by a well thought out policy. Accounts are given by Truscott and Livingstone (1978), Shah (1982, 1987), P.P. Briggs, Richards and Fiesinger (1986), W.G. Jones *et al.* (1989), Conley, Angelson and Williams (1991) and Squire (1991). Inspection practice is one of the topics covered in the surveys by Hale.

One type of problem is the determination of an inspection interval. A difficulty here is that the opening up of the tank system is liable to introduce oxygen into it and may thus itself become a cause of deterioration. Another is that the outage period can be several months. A third difficulty concerns the degree of confidence which can be placed in the predictive techniques.

The problem may also come in the form of a need to decide whether to open up a tank on a particular occasion. An account of a review of a particular refrigerated ammonia storage tank, its features and its hazards, has been given by Squire (1991), who describes the reasoning behind a decision not to open up the tank for inspection.

There are also problems in the reliability of inspection techniques, as described below.

The stages of decommissioning a tank for inspection and recommissioning it after inspection have been described by Shah (1982) and P.P. Briggs, Richards and Fiesinger (1986). The latter give an account of the arrangements for continuity, emptying and purging, tank entry and cleaning, inspection and repair, and purging and refilling.

22.18.9 Rollover

There has been some concern that in refrigerated atmospheric storage tanks temperature stratification might occur, leading to 'rollover', which is defined as 'a spontaneous and sudden migration of a substantial mass of liquid ammonia from the bottom of the tank to the surface'. The effect of rollover is to release large quantities of vapour which could overpressure the tank.

Rollover has been the subject of an investigation by the Ammonia Storage Committee, as described by Ball (1968b). Calculations showed that only a very small temperature gradient is required to initiate natural circulation and prevent temperature stratification. The calculations have been confirmed experimentally. It has also been shown, however, that there is a possibility of stratification in ammonia containing over 5000 ppm of water.

An account of conditions which might lead to what he terms 'thermal overload' has been given by Squire (1991). They include the introduction of contaminated or wrong material such as wet ammonia or even water; the introduction of warm ammonia; or a strong heat input such as might occur through loss of thermal insulation.

22.19 Ammonia Storage: Stress Corrosion Cracking

As already indicated, SCC has been a widespread problem in ammonia pressure storage vessels. Accounts have been

given by W.D. Clark and Cracknell (1977), Truscott and Livingstone (1978), Lemoine *et al.* (1986), Loginow (1986), Stephens and Vidalin (1988), Byrne, Moir and Williams (1989), Appl *et al.* (1990), Burke and Moore (1990), Selva and Heuser (1990) and Conley, Angelsen and Williams (1991).

Although ammonia has been used without apparent problems in the chemical and refrigeration industries for many decades, the use of liquid ammonia for agricultural purposes, which began after the Second World War, saw a number of cases of failure in the vicinity of welds on the pressure vessels used. A survey by T.J. Dawson (1956) found that about 3% of these pressure vessels failed within 3 years of entering service. In the chemical industry, concern intensified in the 1970s. A 1982 survey by the AIChE, described by Blanken (1982) and referred to by Burke and Moore (1990), reported inspection results for 72 pressure storage spheres in 37 of which SCC had been found.

Extensive investigation, and in particular the work of Lunde (Lunde, 1984; Lunde and Nyborg, 1987, 1989, 1990) in the Kjeller Ammonia Stress Corrosion Project (KASP) has given a clearer picture of the conditions under which SCC occurs. This work has shown that (1) uncontaminated ammonia does not cause cracking, (2) contamination with oxygen at a concentration as low as 1 ppm promotes cracking and (3) 0.2% w/w water inhibits cracking in oxygen-contaminated ammonia in the liquid phase.

It is also necessary to consider the vapour phase. Even where the liquid ammonia contains water, SCC can occur in the vapour phase, where due to the vapour–liquid equilibrium relations the concentration of oxygen is some 650 times higher than that in the liquid phase, whilst the concentration of water is some 500 times lower.

The metallurgy of the steel is also a factor. SCC occurs more readily where stress relief has not been carried out and in high yield strength steels. Measures to prevent SCC are therefore the use of stress relief by post-weld heat treatment and of low yield strength steels.

With respect to crack growth, it has been found that under conditions typical of those known to cause SCC (3 ppm oxygen, 500 ppm water), crack growth rates are similar to those which occur in-service, of the order of 2–6 mm/year, depending on the stress intensity. Crack growth rates tend to be rapid initially, but to decrease markedly over time.

Whereas SCC has been widespread in ammonia pressure storage vessels, this has not been the case with refrigerated atmospheric ammonia storage tanks – as recently as 1987 it was largely discounted (Blanken, 1987). However, SCC has now been found in refrigerated ammonia storage tanks, as described below.

22.19.1 Inspection and repair

There are a number of accounts of the inspection of pressure vessels and of refrigerated tanks for ammonia storage in order to detect SCC. Inspections of pressure vessels have been described by R.S. Brown (1982) and by Guth and Clark (1985). They illustrate both the procedures for isolation, emptying, purging and entry, and bringing back on-stream such storages, and the procedures for inspection and repair.

Brown describes the inspection and repair in 1978 of two ammonia spheres installed in 1961 and 1962. Although the recommendation in 1962 to maintain the ammonia water content at 0.2% was followed, the spheres may have contained some ammonia which did not contain water. The inspection was performed using both magnetic particle and dye penetrant methods and significant cracks were found, which were diagnosed as being due to SCC. A maximum crack depth of 7.8 mm, or 25% of the shell weld cross-section, was found. Repairs were carried out in accordance with the ASME *Boiler and Pressure Vessel Code and the Compressed Gas Association* (CGA) *Guidelines for Inspection and Repair of Cargo Tanks*. Cracks were removed by mechanical grinding or arc gouging to sound metal. The area was then pre-heated and weld repaired. Further inspection and repair were conducted in 1980.

Another instance of cracking in two ammonia spheres in 1982 is described by Guth and Clark. Acoustic emission was used to detect the faults. In one sphere the repair method used was to grind down to the parent metal, repair the weld and hammer to relieve stresses. In the other sphere the crack was ground out and the welder then pre-heated the metal, repaired it, and peened it.

The discovery of SCC in a refrigerated ammonia storage tank has been described by Byrne, Moir and Williams (1989). The tank in question was a 12,000 te tank at Seal Sands, acquired by BASF from another company. The previous owners had relied on acoustic emission testing to extend the inspection interval for the tank and had detected no SCC. An inspection performed by the new owners using magnetic particle inspection discovered SCC. The SCC was found to occur mainly at the site of internal cleats and was attributed to defective welding procedures, the effect of which was aggravated by the use of high strength steel. A detailed account of the treatment of defects in this tank has been given by Selva and Heuser (1990).

Appl *et al.* (1990) have given an account of the inspection of two further refrigerated ammonia storage tanks owned by BASF. They describe in detail the taking out of service, preparation, magnetic particle inspection, repair and bringing back into service.

Principal techniques for the detection of cracks are magnetic particle inspection, dye penetrant testing and acoustic emission testing. The use of dye penetrant testing is described by Brown, but not by the other authors mentioned.

As already indicated, there is a view that acoustic emission testing is not a reliable method. Vessels with SCC may not produce significant acoustic emission. Furthermore, Conley, Angelson and Williams (1991) describe a case where it was found that acoustic emission activity was greater in a vessel which had been repaired than in one with SCC which had not been repaired.

The inspection technique mainly quoted is magnetic particle inspection. However, the same authors state that even this does not necessarily reveal all the defects and that different operators tend to produce different results.

22.19.2 Fracture mechanics

Fracture mechanics, described in Chapter 12, has been applied to SCC both in ammonia pressure vessels and refrigerated ammonia storage tanks.

Accounts of the application of fracture mechanics to ammonia pressure vessels have been given by W.G. Jones *et al.* (1989) and Burke and Moore (1990).

Byrne, Moir and Williams (1989) describe the application of fracture mechanics to the Seal Sands refrigerated ammonia storage tank. The task of removing all the defects found was enormous. The interest lay, therefore, in reducing this activity to an acceptable level. In many cases, it was possible to determine that the crack would exhibit leak-before-break behaviour. Those cracks for which this

could not be demonstrated were removed. Further details of this fracture mechanics work are given by Selva and Heuser (1990).

The use of fracture mechanics to set the inspection interval for refrigerated ammonia storage tanks is described below.

22.19.3 Control policy

The maintenance of the integrity of ammonia storage requires a policy for the control of SCC. Accounts of such policies have been given by W.G. Jones *et al.* (1989), Appl *et al.* (1990), Squire (1991) and Conley, Angelson and Williams (1991).

W.G. Jones *et al.* (1989) describe the policy of ICI for the control of SCC in ammonia pressure vessels. As stated earlier, the overall ammonia storage policy is to move away from pressure storage spheres to smaller fully stress relieved pressure vessels and refrigerated storage tanks. They postulate two extreme scenarios for pressure spheres. An unpurged, unlagged sphere handling imported ammonia from a variety of sources at relatively high temperature and without vapour export may well experience a comparatively high level of SCC, whereas a purged, lagged sphere handling site-produced ammonia at a low temperature with continuous vapour offtake may experience little, if any. Operational measures to control SCC include purging to remove oxygen, maintenance of the water content, and cooling of the liquid.

An account of policy at Dupont for the control of SCC in ammonia pressure vessels has been given by Conley, Angelson and Williams (1991). The approach includes the use of fracture mechanics to predict the probability of failure and to determine inspection intervals.

Appl *et al.* (1990) of BASF rehearse some of the problems of controlling SCC in pressure storage vessels. There are difficulties in excluding oxygen and in keeping the oxygen content of the liquid ammonia below 1 ppm. There are some applications for which the ammonia is required to be dry and for which a requirement to maintain a water content of 0.2% w/w is highly undesirable. They state that stress relief by post-weld heat treatment appears to be the only reliable way to avoid SCC and that, whereas it has been necessary to scrap an older ammonia sphere due to SCC, a new stress relieved sphere inspected after 2 years of operation has shown no SCC.

22.20 Other Chemicals Storage

The storage of particular chemicals involves in some cases features which do not occur in the storage of the materials so far described. The general characteristics and handling of some of these chemicals are described in Chapter 11. The account given here seeks to highlight some features characteristic of the storage of individual chemicals; no attempt is made to give a comprehensive treatment of the storage of any given chemical, which is covered in the code cited.

Table 22.11 lists some topics on storage dealt with in codes and guidance for particular chemicals.

22.20.1 Acrylonitrile

Guidance on the storage of acrylonitrile (AN) is given in *Codes of Practice for Major Hazards: Acrylonitrile* by the CIA (1978 PAH) (the CIA Acrylonitrile Code).

AN has a boiling point of 77.3°C. It is typically stored in atmospheric fixed roof storage tanks. An AN storage tank should be provided with a suitable bund.

AN has a tendency to polymerize rapidly under certain conditions and in bulk storage it needs to be stabilized. The *Acrylonitrile Code* mentions three stabilizers. One is the methyl ether of hydroquinone (MEHQ), which is used when the AN contains dissolved oxygen. Another is ammonia, which combines with AN to form stabilizing compounds and thus in due course becomes depleted. The third stabilizer is water, which at a concentration of 0.2% w/w confers a degree of stabilization. Strong alkali or peroxides should be excluded.

Under certain conditions a flammable mixture can form in the vapour space of the tank. Precautions mentioned in the *Code* are the safe location of the vent, the installation of a flame arrester on the vent and the inciting of the vapour space.

Table 22.11 *Some topics on storage covered in certain codes of practice and guidance documents for particular chemicals*[a]

	Acrylonitrile	*Ammonia*	*Chlorine*	*Ethylene dichloride*	*Ethylene oxide*	*Hydrogen fluoride*	*Phosgene*	*Vinyl chloride*
Storage	7	3	10	4	26	4	8, 11	4, 6
Siting		6, 22						
Design conditions		7, 22	10				3, 12	
Filling ratio			11			18	31	App. IV
Foundations		10, 25						
Bunds	8	10, 25						
Insulation		13, 25						
Pressure relief	8		15					
Instrumentation	8						12, 15	
Ancillary equipment		10, 25						
Drums and cylinders	8, 10				27		29	
Stabilization	7							
Terminals	9		2,20		19			15

[a] The entries give the page numbers. The documents referred to are as follows: acrylonitrile (CIA, 1978 PA11); ammonia (HSE, 1986 HS(G) 30); chlorine (HSE, 1986 HS(G) 28); ethylene dichloride (CIA, 1975 PA13); ethylene oxide (CIA, 1992 RC14); hydrogen fluoride (CIA, 1978 PA14); phosgene (CISHC, 1975/3); vinyl chloride (CIA, 1978 PA15). Aspects other than storage are considered separately in Chapter 11.

22.20.2 Ethylene dichloride

Guidance on the storage of ethylene dichloride (EDC) is given in *Codes of Practice for Major Hazards: Ethylene Dichloride* by the CIA (1975 PA13) (the CIA *Ethylene Dichloride Code*).

EDC has a boiling point of 84.4°C. It is generally stored, dry or water saturated, in atmospheric storage vessels, which may contain several thousand tonnes. An EDC storage vessel should be provided with a suitable bund.

Under certain conditions a flammable mixture can form in the vapour space of the tank. The *Ethylene Dichloride Code* advises that consideration be given to protecting the vapour space from ignition and requires that means be provided for preventing over- and underpressure, including explosion relief.

Fire protection of larger EDC storage vessels tends to be by water spray systems, and that of small vessels is by fire insulation.

22.20.3 Ethylene oxide

Guidance on the storage of ethylene oxide (EO) is given in *Guidelines for Bulk Handling of Ethylene Oxide* by the CIA (1992 RC14) (the CIA *Ethylene Oxide Code*).

EO has a boiling point of −17.8°C. It is stored as a liquefied gas, mainly in pressure vessels, although refrigerated storage is an option. The separation distances appropriate for EO are of the same order as those quoted in codes for LPG, but should not be less than 15 m.

An EO storage vessel should be provided with a suitable bund. Since an EO spillage is commonly dealt with by dilution, the bund and drain arrangements should be able to handle water used for this purpose as well as the usual fire-fighting purposes of equipment cooling and fire control.

Many EO bulk storages are associated with plants which use a catalyst to polymerize the EO. Stringent precautions are necessary to ensure that the catalyst is excluded from the bulk storage. Three ways in which contamination may occur are (1) backflow from user plants, (2) introduction by a diluent gas pressurizing system and (3) inadvertent contamination during supply offloading. Both design and operations measures are required to prevent contamination. The design measures are described in Chapter 11.

22.20.4 Hydrogen fluoride

Guidance on the storage of hydrogen fluoride (HF) is given in *Guide to Safe Practice in the Use and Handling of Hydrogen Fluoride* by the CIA (1978 PA14) (the CIA *Hydrogen Fluoride Code*).

HF has a boiling point of 19.5°C. Liquid HE is stored in pressure vessels of a few tonnes upwards.

The storage temperatures range from −5°C to 30°C, at which temperatures the vapour pressures of HE are 0.4 and 1.5 bars, respectively. Assistance is therefore required to effect transfer from storage, and this may be by the use of inert padding gas or, more commonly, by pumping.

The *Hydrogen Fluoride Code* lays particular emphasis on lines connected to the vessel below the liquid surface.Where these are unavoidable, it requires that there be a means of isolation integral to the vessel and independent of any external valve used for routine isolation and control, and that this external valve be capable of remote operation.

22.20.5 Oxygen

The storage of oxygen is the subject of two codes by the British Compressed Gases Association (BCGA) – *Bulk Liquid Oxygen at Production Plants* (BCGA, 1990 Code 20) and *Bulk Liquid Oxygen at Users' Premises* (BCGA, 1992 Code 19) – and of one by the NFPA – NFPA 50: 1990 *Bulk Oxygen Systems at Consumer Sites*.

The hazard posed by liquid oxygen is the reaction with combustible or flammable materials. The layout for the storage of liquid oxygen should include the use of non-combustible surfaces, the provision of separation distances between storages of liquid oxygen and flammable liquids, and the prevention of contact between the two through flows of liquids, by ground contour or diversion.

22.20.6 Phosgene

Guidance on the storage of phosgene is given in *Codes of Practice for Major Hazards: Phosgene* by the CIA (CISHC, 1975/3) (the CIA *Phosgene Code*).

Phosgene has a boiling point of 8.2°C. It is stored as a liquid in pressure vessels.

The *Phosgene Code* advises that the storage temperature be kept below 8°C so as to reduce the load on the disposal system if the vessel has to be depressurized.

Particular emphasis is placed in the *Code* on the integrity of the pressure vessel, with requirements such as 100% radiography of butt welds and exclusion of installed lifting devices in the immediate vicinity of the vessel.

The *Code* requires that all branches in the top of the vessel be fitted with dip pipes which protrude at least to the maximum liquid level under normal operating conditions to ensure that the tank cannot be accidentally overfilled. There should be no lines connected to the vessel below the liquid surface, but if this is unavoidable they should be provided with a remotely operated isolation valve.

22.20.7 Monomers

An important class of liquid chemicals which require to be stored are monomers. Accounts of the storage of monomers is given by Shelley and Sills (1969) and Bond (1985 LPB 65).

A problem in the storage of monomers is polymerization. One hazardous consequence of such polymerization may be heat release, which causes both a rise in pressure and an acceleration in the reaction, resulting in the extreme case in the explosion of the tank. Another hazardous effect may be the blockage of vents and pressure relief devices.

It is common practice to dose monomers with additives. A discussion of their use has been given by Bond (1985 LPB 65). Types of additive include (1) inhibitors, (2) stabilizers, (3) anti-oxidants, (4) preservatives and (5) stenching agents. The function of inhibitors and stabilizers is to prevent polymerization, while anti-oxidants prevent decomposition, preservatives prevent bacterial or fungicidal attack and stenching agents impart an odour.

Typically, an inhibitor is effective only in the presence of oxygen. The use of nitrogen to blanket the liquid can reduce the oxygen content both in the liquid and in the vapour space and render the inhibitor ineffective in both phases. The liquid monomer may polymerize in a runaway reaction and the monomer vapour may polymerize and block vents.

A fuller account of the storage of monomers is given in the IChemE training package *Safer Use of Chemical Additives*, described in Chapter 27. This package includes a list of chemicals which are commonly dosed with an additive, and gives the purpose of the additive, an example of the additive used, the quantity added and an indication of requirement for dissolved oxygen.

The interactions between the various factors are illustrated by the account given by Shelley and Sills (1969) of options in the storage of styrene in the late 1960s. They describe the use of *p-t*-butyl catechol (TBC) as the inhibitor. The TBC also acts as an anti-oxidant but it is effective as an inhibitor only in the presence of oxygen. Storage under air suffices to maintain an adequate concentration of oxygen in the liquid phase. However, there remains the problem of polymerization in the vapour phase on the internal surfaces of the tank. This is liable to occur in older tanks with rusty surfaces, but is largely eliminated by coating the surface. One policy for older, uncoated tanks is the use of a nitrogen blanket, since in the absence of oxygen polymerization in the vapour phase is much reduced. Where such a nitrogen blanket is used, separate measures are taken to maintain the oxygen content of the liquid.

22.20.8 Vinyl chloride

Guidance on the storage of vinyl chloride is given in *Codes of Practice for Chemical with Major Hazards: Vinyl Chloride* by the CIA (1978 PA15) (the CIA *Vinyl Chloride Code*), and also in *Precautions against Fire and Explosion: Vinyl Chloride* also by the CIA (1978/12). An account is also given by Shelley and Sills (1969).

22.21 Bunds

An important form of secondary containment is a bund, or dike. Accounts of bunding are given in *The Design of Bunds* (Barnes, 1990 SRD R500) and *Bund Overtopping – The Consequences Following Catastrophic Failure of Large Volume Liquid Storage Vessels* (Wilkinson, 1991 SRD R530).

Barnes discusses: the bunding recommendations given in codes and standards; the philosophy of, and practice in, bunding; the design of bunds; the effectiveness and failure of bunds; and the use of high bunds and double integrity systems. He gives case histories of storage, and particularly bund, incidents and some statistics on storage failures. He draws particularly on the report Liquefied Energy Gases Safety (GAO, 1978) and on a study by Buckley and Weiner (1978).

Common practice is to provide a bund for refrigerated atmospheric storage of LPG and other LPGs and for ammonia, but not for pressure storage of LPG or ammonia.

For atmospheric storage tanks, containing such hazardous chemicals as acids and alkalis, it is again not usual to have a bund. If there is a danger of spillage onto roads, pathways or working areas, or of hazardous interaction between spillages of two liquids, separation by distance is appropriate.

22.21.1 Code requirements

Barnes reviews the requirements for bunding given in a large number of codes, including not only those for oil, LPG and LNG, but also for ammonia, chlorine and the various chemicals covered by the CIA codes. The overall picture is of considerable arbitrariness and some inconsistency.

Codes differ, for example, in their requirements for features such as capacity and permitted wall height. They even differ as to whether or not a bund is required at all. Liquid ammonia and liquid chlorine have similar adiabatic flash fractions, at 16% and 18.3%, respectively, but Barnes identifies one code for ammonia which recommends a high bund, and another for chlorine which practically dismisses the use of a bund altogether. One code may set a maximum wall height to permit fire fighting in the bund, which would rule out the use of a high bund recommended in another code.

22.21.2 Philosophy of bunding

Barnes attempts, therefore, to develop a more coherent philosophy of bunding. He distinguishes between: liquids which are (1) flammable, (2) toxic, (3) corrosive and (4) reactive; liquids which are stored at a temperature (1) above the boiling point and (2) below it; and liquids which have (1) a high vaporization rate and (2) a low vaporization rate. Figure 22.20 shows his three decision trees for flammables, toxics and corrosives.

He takes a reactive material as being one which does not in its own right present a flammable, toxic or corrosive hazard, but which on contact with some other material, such as water or acidic or alkaline effluent, could produce a substance which does constitute a hazard. For this case he gives a simple two-branch tree, in which bunding is not required if the reactive material could not come into contact with another reactant but may be required if it could, depending on the assessed hazard.

22.21.3 Bund design

The elements of bund design, which Barnes addresses, are (1) bund capacity, (2) materials of construction, (3) wall design, (4) surface water drainage, and (5) common bunding.

Codes differ in their recommendations on bund capacity which vary between 75% and 110% of the nominal capacity of the container protected. Barnes also quotes data from the General Accounting Office (GAO) report which illustrate the capacity allowed in practice. For the nine storages for which information is given, the capacities range from 50% to 139%.

In the selection of materials of construction, factors which have to be considered are the mechanical strength, the vaporization rate and, for low temperature liquids, the resistance to thermal shock. The materials used both for bunded areas and for bund walls are mainly earth and concrete. Use is also made of insulating concrete.

A low bund wall facilitates firefighting, and up to about 1980 many codes set a maximum height for the bund wall, often of the order of 2 m. This restriction is now less common, reflecting a trend towards high wall bunds. Codes may also set a minimum height for a bund wall, such as the 1.5 m height set in the NFPA codes.

Most codes do not give clear guidance on the arrangements for the drainage of surface water. A major problem here is that if the arrangement for the removal of rainwater is through a drain hole with a valve on it which should normally be kept closed, the valve is liable to be left open, thus allowing any liquid released into the bund to escape from it.

The use of common bunding is widespread, but it is not regarded as good practice to co-bund incompatible materials.

22.21.4 Bund sizing

Relations for bund sizing have been given by Barnes, and reformulated by Wilkinson. Following the latter, for a cylindrical tank in a circular shaped bund

$$\pi R^2(H-h) = \pi(R+L)^2 h - \pi R^2 h \qquad [22.21.1]$$

whence

$$h \geq R^2H/(R+L)^2 \qquad [22.21.2]$$

where h is the height of the bund, H is the original height of the liquid, L the distance between the tank wall and the bund and R is the radius of the tank. For a rectangular bund

$$\pi R^2(H-h) = xyh - \pi R^2 h \qquad [22.21.3]$$

whence

$$h > \pi R^2 H/xy \qquad [22.21.4]$$

where x and y are the dimensions of the bund walls.

22.21.5 Vaporization from bunds

For many hazardous materials the magnitude of the consequences of a release depends largely on the rate of vaporization from the pool formed. In the main, this depends partly on the area of the bund and partly on the material of construction used.

A high bund gives a much smaller total area for vaporization. Another approach applicable with a low bund system is the use of a ditch within the bund, which for all but the largest releases, reduces the effective area for vaporization. There are a number of bund floor materials, such as insulating concrete, which give an appreciable reduction in the rate of vaporization. Another approach to the reduction of vaporization is to blanket the liquid surface, either with foam or with plastic spheres.

Vaporization from surfaces such as bund areas is discussed further in Chapter 15.

22.21.6 Spillage from bunds

With a low bund system in particular, if the release of liquid is sufficiently large it may flow as a wave which overtops the bund wall. Such overtopping has occurred in a number of cases. One of the most dramatic was at Qatar, where an LPG storage tank contained in a 50% capacity bund suffered a catastrophic failure. A 'tidal wave' of LPG overtopped the bund and caused massive destruction. Barnes quotes an estimate that, even if the capacity of the bund had been 100%, it would still have been overtopped by a wave some 5 m high.

Another major overtopping, from a bund that was 20% undersized, occurred at Moose Jaw, Saskatchewan, in 1980, following the catastrophic failure of an oil storage tank.

The GAO study gives results of modelling of bund overtopping by a tidal wave at a number of particular facilities. The six results for low bunds quoted by Barnes indicate overtopping in each case, with an average overspill of 58% of the tank contents.

Further work on overtopping of low bunds has been done by Greenspan and Young (1978), who derived an analytical model based on the shallow water equations, and by Greenspan and Johansson (1981), who performed model experiments. They correlated the fraction Q of the original liquid volume which spills over as function of the ratio h/H, where h is the height of the bund and H is the original height of the liquid in the tank, with the bund r radius and wall angle θ as parameters.

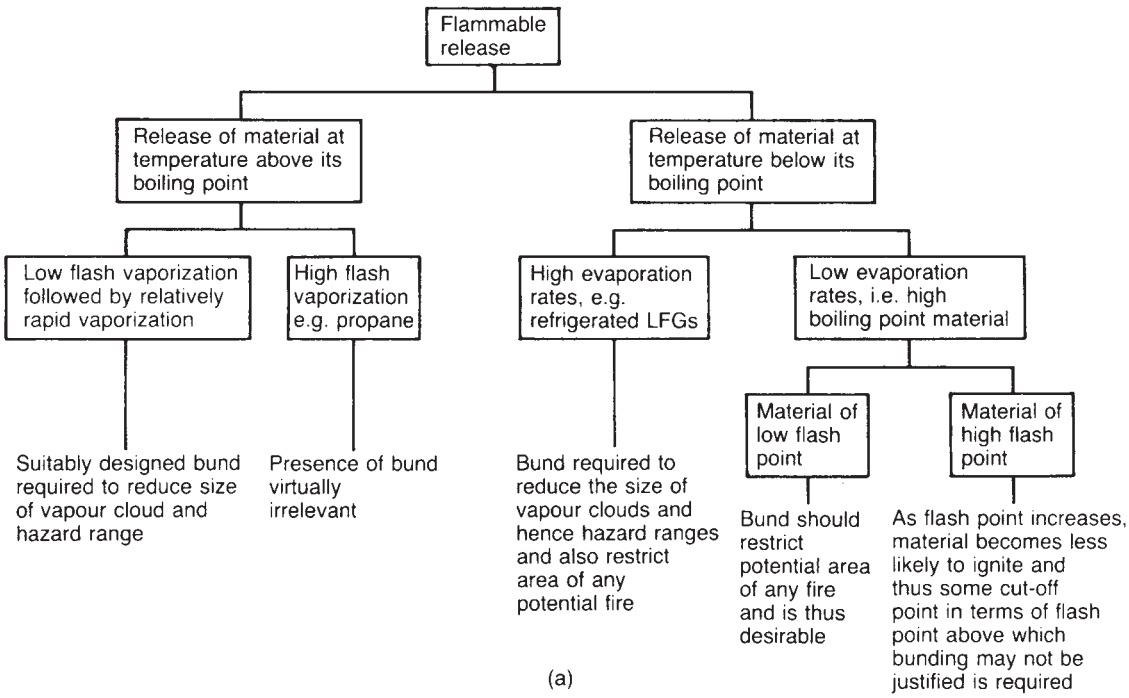
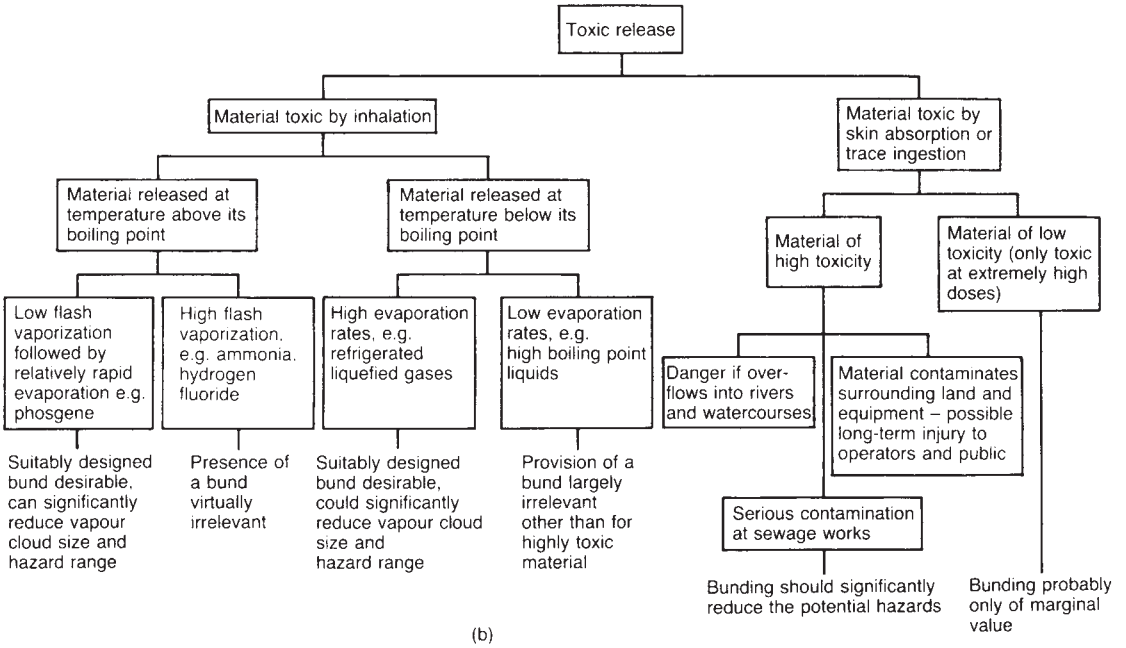


Figure 22.20 *continued*



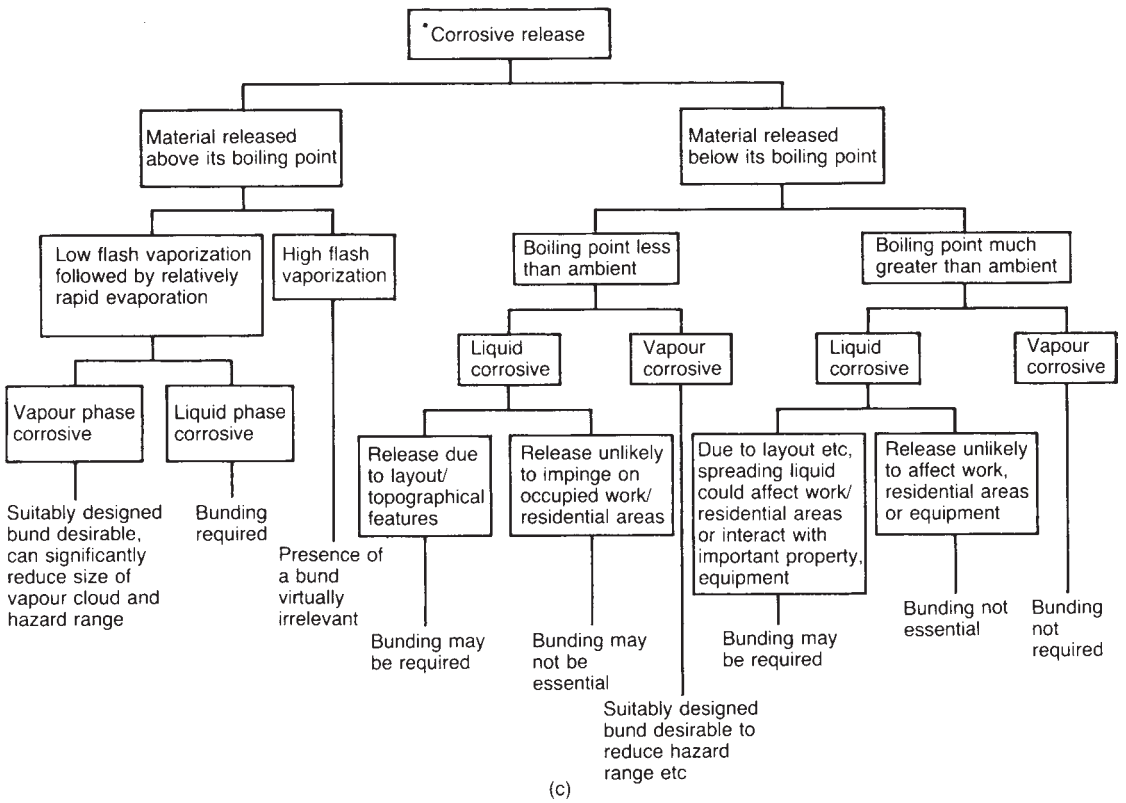


Figure 22.20 *Decision trees for the design of bunds (Barnes, 1990 SRD R500): (a) flammable material (b) toxic material; and (c) corrosive material (Courtesy of the UKAEA Safety and Reliability Directorate)*

Another form of escape from a bund is spigot flow in which the liquid issues from the containment as a jet which has a 'throw' sufficient to carry it over the bund wall. Spigot escapes also are dealt with in the GAO report.

22.21.7 High bunds

There is an increasing tendency to install high bunds, for which there are two main designs. In the first, the bund is some one-half to two-thirds the height of the tank wall and located about 7–8 m from it. In the second, the bund is the full height of the tank and separated from it by a distance of 3 m or less. There may be a weathershield between the tank and the bund so that the existence of a separate bund is not obvious. In both designs the bund is structurally independent of the tank.

Storage systems with bunds are to be distinguished from double integrity tanks which have two walls, both capable of containing the liquid, and in which the outer wall is concrete.

22.21.8 Dynamic loading of bunds

If a sudden, catastrophic failure of the tank wall occurs, and a large release of liquid occurs, the bund is subject to a dynamic load. It has been common to design bunds for the hydrostatic load of the liquid in the tank, but not for this dynamic load. Attention was drawn to the problem by Cuperus (1979, 1980), and it has subsequently been the subject of a number of studies.

Most of the work has been done in respect of double integrity tank systems rather than bunds. For such a system Cuperus concluded on the basis of modelling work that the impact loading was highly asymmetric and that the pressure at the base of the outer wall could be six times the hydrostatic pressure of the stored liquid.

Adorjan, Crawford and Handman (1982) have modelled the behaviour of the release allowing for the resistance of the insulation between the two walls. This modelling has been extended by Vater (1985) using the basic relation

$$h\rho - \frac{\rho u^2}{2g} = (M_f + M_s)\frac{du}{dt} - R(x) \qquad [22.21.5]$$

where g is the acceleration due to gravity, h is the initial height of the liquid in the tank, M_f is the effective fluid mass, M_s is the effective mass of the tank shell, R is the resistance to flow, t is the time, x is the distance, u is the velocity and ρ is the density of the fluid. Solution of the equation requires the determination of the initial acceleration du/dt, for which the techniques of finite difference hydrodynamic analysis were used.

Finite difference studies on this problem have also been described by Trbojevic and co-workers (Trbojevic and Maini, 1985; Trbojevic and Gjerstad, 1989; Trbojevic and Slater, 1989). These authors have investigated both double integrity systems and bunds. Figures 22.21 and 22.22 show typical results for a high bund and a low bund, respectively.

Vater found that for the specific example which he considered the pressure at the base of the bund due to dynamic loading was some 2.65 times that due to hydrostatic load. The value obtained by Trbojevic and Gjerstad was 2.5. Higher load amplifications were found higher up the bund wall.

22.21.9 Consequences of spillage

A study of the consequences of spillage over a bund wall has been made by Wilkinson (1991 SRD R530). Predictions are given for the hazard ranges for various materials and scenarios using the GASP code for vaporization and the DENZ and CRUNCH codes for dense gas dispersion.

22.22 Underground Storage Tanks

Over the last 15 years there has come to prominence, particularly in the United States, the problem of leakage from underground storage tanks (USTs).

Underground storage tanks are treated in *Underground Storage Systems* (Schwendeman and Wilcox, 1987). Further accounts are given by Dwyer (1985), D.L. Russell and Hart (1987) and Semonelli (1990).

In the United States, the Resource Conservation and Recovery Act (RCRA) was amended in 1984 to extend the responsibilities of the Environmental Protection Agency (EPA) to underground storage tanks containing hazardous substances. Regulations on USTs came into force in 1988.

Various estimates have been given of the scale of the problem. The EPA has estimated that there are in the United States some 700,000 USTs of which about 25% are 'non-tight'. Evidence obtained by the EPA was to the effect that leaks came predominantly (84%) from loose tank fittings or faulty piping rather than from the tank itself.

The hazardous substances, to which the controls apply, are those given in the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) list. A tank is defined as a UST if more than 10% of the volume of the tank and its pipework are below ground.

The regulations require that: new UST systems for hazardous substances have a secondary containment such as a double-walled tank, an external liner or other acceptable system; the piping have secondary containment such as double-walled piping or trench lining; and pressurized piping have an automatic leak detection system. The requirement for secondary containment of tank and pipework does not apply to new UST systems for petroleum. For these the requirements are for: periodic monitoring to detect leaks on the tank; periodic leak-tightness testing or monitoring on the piping; and, on pressurized piping, an automatic leak detection system. There are less stringent requirements for existing tanks.

Secondary containment systems are required to contain any leak until it is detected and removed, to prevent any release to the environment, and to be monitored at monthly intervals. Where external liners are used, they should be such that they surround the tank completely and prevent lateral as well as vertical migration of a leak; can contain the whole contents of the tank; and prevent interference of rain or groundwater with the ability to contain and detect a leak.

Design of UST systems and methods of leak monitoring are discussed by D.L. Russell and Hart (1987). The designs include: a reinforced concrete tank with an external liner; a fibreglass tank with an external liner; and a regular horizontal tank placed in a reinforced concrete secondary containment.

The authors discuss the methods available for leak detection. Volumetric leak detection techniques rely on the change in level in the tank. Other techniques are based on detection of the leak itself. A further account of leak detection is given by Higgins and Byers (1989).

Methods used for decontamination of land where a UST has leaked are described by E. Johnson (1989a).

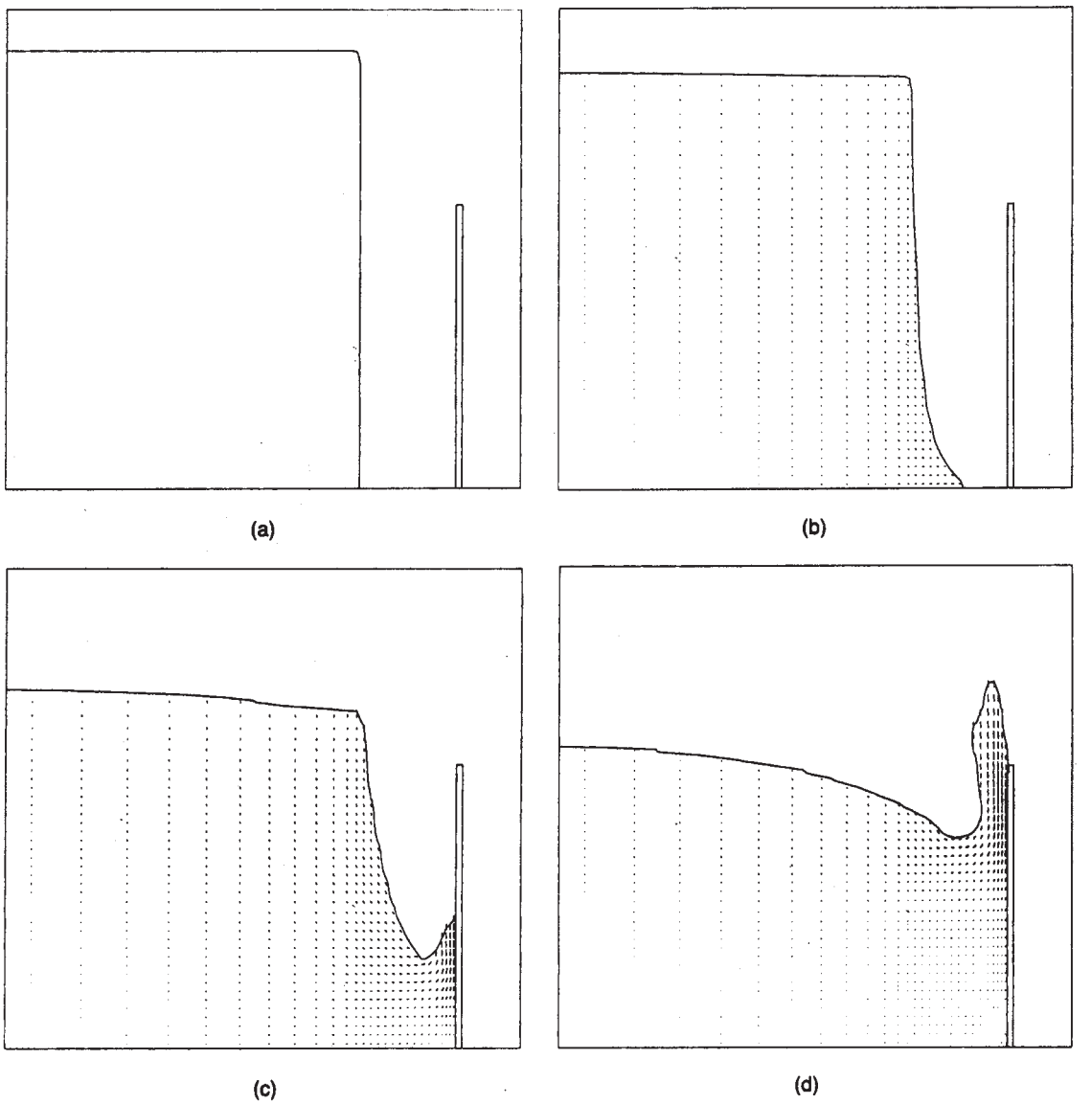


Figure 22.21 *Simulation of liquid behaviour following the failure of a single wall storage tank inside a high bund (Trbojevic and Slater, 1989): (a) time t = 0 s; (b) t = 0.6 s; (c) t = 1.2 s; (d) t = 1.8 s (Courtesy of the American Institute of Chemical Engineers)*

HSE guidance on underground storage tanks is given in HS(G) 52.

The environmental aspects of underground storage tanks are considered further in Appendix 11.

22.23 Glass Reinforced Plastic Storage

Most storage is constructed in steel but widespread use is also made of GRP, or FRP, containments.

An account of the use of GRP containers in the process industries is given in *Composite Materials Handbook* (Schwartz, 1991). HSE guidance on GRP containments is given in PM 75 *Glass Reinforced Plastic Vessels and Tanks: Advice to Users* (1991).

The design of GRP containment is governed by BS 4994: 1987 *Specification for Design and Construction of Vessels and Tanks in Reinforced Plastics*.

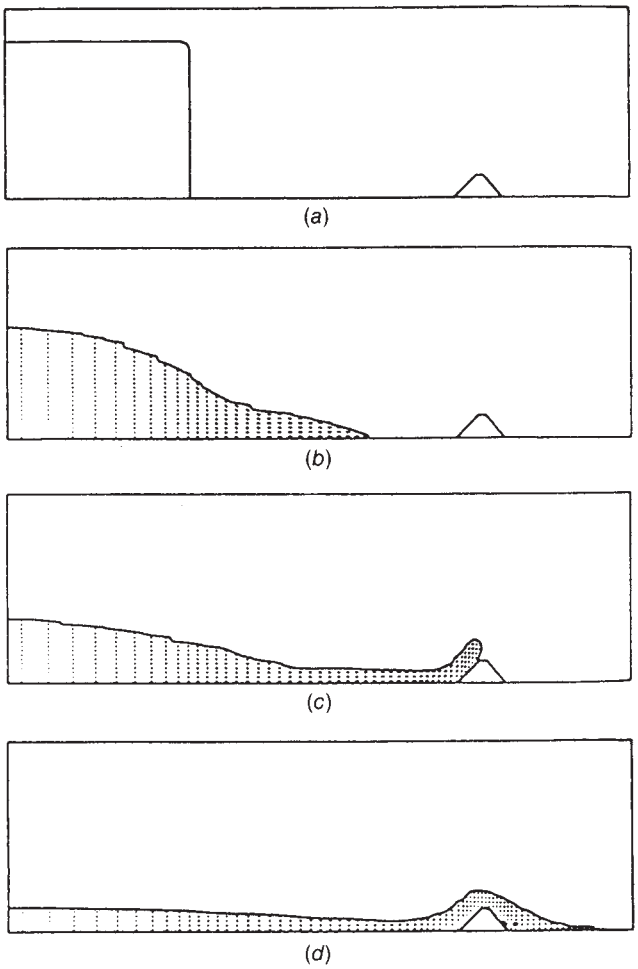


Figure 22.22 *Simulation of liquid behaviour following the failure of a single wall storage tank inside a low bund (Trbojevic and Slater, 1989): (a) time t = 0 s; (b) t = 1.5 s; (c) t = 2.5 s; and (d) t = 4.0 s (Courtesy of the American Institute of Chemical Engineers)*

GRP tanks and vessels are widely used to store corrosive materials. In addition to good corrosion resistance, they have the further advantage that they are readily fabricated into complex shapes. GRP does not suffer from external corrosion and it can have a suitable self-colouring. These factors minimize the maintenance costs of GRP storage.

However, GRP tanks are not without their hazards. In a small but significant number of instances tanks have failed. Some of these have been outright, or catastrophic, failures which have released the entire contents. The resultant tidal wave of liquid is capable of demo-lishing a bund wall, or, if the tank is indoors, a building wall.

GRP is subject to creep under sustained load, it is susceptible to chemical attack and some types may fail at temperatures below 100°C.

Typically, a GRP tank failure is due to environmental stress cracking in which the tank is subjected to excessive stress and crack propagation occurs, at first slowly and then with increasing rapidity. Prior to failure the tank often exhibits leaking or 'weeping'.

Resin rich layers are used to protect the glass reinforcement. Matrix cracking can expose the glass fibres to chemical attack.

Another cause of failure is excessive temperature. There have been cases where a GRP tank containing water has failed at 70°C.

As a material of construction, GRP has a number of features which distinguish it from steel. One is that it is anisotropic and thus has different strengths in different directions. The degree of difference depends on the fabrication, but it can be significant. Compared with steel, GRP is softer, it can only withstand much lower temperatures and it has a lower impact resistance but a coefficient of expansion three times higher.

Different GRP formulations are required for the containment of different chemicals. With an incorrect material

deterioration can be caused by even small traces (ppm level) of impurity. This has obvious implications for the change of use of tanks and for the use of second-hand tanks.

GRP tanks are often provided with liners.

PM 75 describes the salient features of safety in the use of GRP storage, covering design, fabrication, installation and operation.

Design and fabrication should be to BS 4994: 1987, which grades GRP containments into three categories, Categories I–III. The strictest requirements are those for Category I, the application of which is governed by factors which include size, operating conditions and hazards.

Important features of the design are the use of the correct material and the limitation of the liquid temperature. PM 75 advises that the operating temperature should not exceed the design limits and should be no higher than 110°C.

The purchaser of a GRP tank should supply the manufacturer with a full specification of the tank duty. PM 75 reproduces from BS 4994 an appendix giving the suggested information.

Design and installation should ensure that the tank is not overstressed by providing good support for both the tank itself and the attached pipework. Care should be taken to avoid damaging the tank during erection.

In-service the tank should be subject to periodic inspection. Inspection techniques used include: ultrasonics to assess wall thickness, etc.; acoustic emission monitoring to detect defects; spark testing of welds and liner adhesion; and surface hardness testing and strain measurement.

22.24 Filling Ratio

The maximum permissible working capacity of a storage vessel, or permissible fill, is generally expressed either in terms of the filling ratio or of the maximum permissible volume. Other measures used are the filling density and the filling volume.

Filling ratios for transport of liquefied gases by road in the United Kingdom are given in BS 5355: 1976 *Specification for Filling Ratios and Developed Pressures of Liquefiable and Permanent Gases*. This standard gives formulae for the determination of the filling ratio, guidance on reference temperature for the United Kingdom and on maximum shade temperatures in other countries, and values of the filling ratio for the United Kingdom. It is considered further in Chapter 23. The formula used to calculate the filling ratio is generally of the form

$$\eta = \frac{\rho_p}{\rho_w}(1 - \phi) \qquad [22.24.1]$$

where η is the filling ratio, ρ_p is the density of the liquid at the reference temperature, ρ_w is the density of water at 15°C and ϕ is the fractional free space. The formula may also include a term for the confidence limits on the density of the liquid. The reference temperature is the maximum temperature which the product should reach in-service.

For the United Kingdom, BS 5355: 1976 gives for low pressure liquefiable gases in vessels of volume greater than 5 m^3 a reference temperature of 38°C. The corresponding shade temperature is given as < 35°C.

Filling ratios for LFG storage vessels are given in the ICI *LFG Code*. The *Code* takes for LFG a free space of 3% and a reference temperature of 38°C for vessels over 5 m^3. This yields the following filling ratios:

Propane	0.46
Propylene	0.47
n-Butane	0.54
Vinyl chloride	0.85

A formula for the maximum filling capacity of LPG storage vessels is given by the LPGA (1991 COP 1). This is

$$U_{max} = 0.97 \frac{g_i}{g_t} V \qquad [22.24.2]$$

where g_i is the specific gravity of the liquid at the reference temperature, g_t is the specific gravity of the liquid at its lowest likely temperature at filling, U_{max} is the maximum permissible volume and V is the internal volume of the vessel. The lowest likely temperature at filling is usually taken as 5°C.

It should be noted that while in Equation 22.24.1 the denominator is the density of water at 15°C, in Equation 22.24.2 it is the density, or rather specific gravity, of the liquid in question at the filling temperature.

Guidance on filling density is given for LPG in NFPA 59 and for LNG in NFPA 59A Guidance on the filling ratio for chlorine is given in the CIA *Chlorine Code*.

22.25 Loading and Unloading Facilities

Closely associated with bulk liquid storage are the arrangements for the loading and unloading of road tankers and rail tank cars. An appreciable proportion of accidents occur in the unloading and loading facilities.

Guidance on loading and unloading facilities is given for petroleum products in NFPA 30, the IP *Refining Safety Code* and HS(G) 50 and HS(G) 52; for LPG it is given in NFPA 58 and 59, the LPGA *LPG Storage Code*, the IP *LPG Storage Code* and HS(G) 34; and for toxic materials in general in the CCPS *HTHM Storage Guidelines*, for ammonia in HS(G) 30 and for chlorine in HS(G) 28. HAC is covered in the IP *Area Classification Code*. Further guidance is given by the Oil Industry Association (OIA, Pub. 711) and in the ICI *LPG Code*.

The account given here is concerned with the loading and unloading facilities associated with bulk storage in the main process industries, essentially at sites where the facilities and systems of work are those that are normal in these industries. It does not deal with facilities at small sites such as petrol filling stations.

It is convenient to consider first facilities in general terms, but with reference essentially to road tanker facilities for petroleum products, and then to deal with aspects specific to rail tankers and to particular chemicals.

22.25.1 Hazards

Before considering the facilities as such, it is worth reviewing some of the hazards which are characteristic of unloading and loading facilities. There are four broad categories of hazard at a tanker terminal. These are fire/explosion from leaks and spillages, fire/explosion of product in the tanker, toxic release and accidents arising from the transfer of the wrong products.

These hazards arise from: (1) overfilling of the container; (2) failure of the connection; (3) damage caused by

movement of the vehicle itself; (4) vehicle movement whilst connected; (5) damage caused by impact by other vehicles; (6) ignition by static electricity; (7) equipment failures; (8) misidentification and (9) maloperation.

Overfilling of the tank during loading of the storage vessel is one of the most common accidents at such facilities, as witnessed by the extent of the measures taken to counter it. The temporary connections between the tank and the storage are a weak link, and again attract much effort to maintain their integrity. A particular cause of failure with some connections is a lack of flexibility to accommodate the normal movement of the tank on its suspension during the transfer operation.

Damage may be done to the fixed plant or to the vehicle itself as it moves to and from the loading bay. Releases also occur due to the movement of the vehicle whilst still connected to fixed system. This occurs most commonly when the vehicle is driven off, but other causes can be an unsecured vehicle on unlevel ground or impact by another vehicle. Impact by another vehicle may also lead to a release due to the rupture of the connections.

Any of the releases described may result in a fire, or occasionally an explosion. Another cause of fire/explosion is ignition of a flammable mixture in the tank of the vehicle.

22.25.2 Fire and explosion

A fire/explosion of the product during top loading constitutes a serious problem. The type of product which is the most hazardous is one which gives a flammable mixture in the vapour space. Liquids which give a lean mixture below the lower limit or a rich mixture above the upper limit of flammability are less troublesome.

Ignition of the product is usually due to static electricity. This may be generated if the liquid is allowed to fall free and splash from the filling pipe into the tank, so it is normal practice to position the tip of the filling pipe near the bottom of the tank. But charge may be generated at the start of the filling before the pipe is fully submerged. It is also possible for the liquid to acquire a charge before it reaches the tank. Build-up of charge due to flow in the pipe itself is usually not critical, but product filters with cotton, paper or felt elements are prolific generators of static electricity. It has usually been considered that a relaxation time of 30 s between the filter and the outlet of the filling pipe is necessary to dissipate this charge. Moreover, there has been a trend to purer, drier products for which the relaxation time tends to be in the range 100–500 s. A fuller account of the hazard of ignition by static electricity, including the specific case of tanker loading, is given in Chapter 16.

Fire/explosion also occurs due to spillage. Hose spillages are particularly frequent. Often they occur because a tanker is driven away from the gantry with the hose still connected. Also, hoses may burst because they are not strong enough.

22.25.3 Switch loading

A particularly hazardous situation occurs when a less volatile product is put in a tank which previously contained a more volatile one. This hazard is described by the OIA. There is often a tendency for the residue of the latter to form a flammable mixture, while the former does not readily dissipate static charge. According to the OIA, such 'switch loading' has accounted for some 70–80% of severe losses at loading bays. These appear to occur most often when compartments are one-quarter to one-third full and when temperatures are close to SOT (−1°C).

The IP *Refining Safety Code* states that, wherever possible, switch loading should be avoided.

22.25.4 Siting

Since loading and unloading facilities are areas of relatively high risk, their siting is important. A suitable approach is to locate the facility on the far side of the storage from the process, where this is practical. The location should also be chosen to allow good access for the vehicles to be loaded or unloaded, but to be as free as possible from any form of interference, particularly from other vehicles. Siting is considered in more detail in Chapter 10.

22.25.5 Layout

The layout of the loading and unloading facilities can make a major contribution to the elimination and minimization of incidents. Some aims of layout are to avoid releases, to minimize the size of any release, to prevent the ignition of a release, and to control any fire from an ignited release.

Some features of layout which contribute to these aims include: (1) minimum separation distances, (2) the general form of the loading/unloading bay, (3) ground slope and drainage, (4) ventilation, (5) access and escape, (6) lighting, (7) routing of pipelines, (8) protection against vehicle impact, (9) control of movements of vehicles, (10) control of the movement of personnel, (11) vessel, connection and equipment identification, (12) direct lines of sight, (13) control of ignition sources, including HAC, (14) fire protection and (15) emergency equipment.

Minimum separation distances for the loading and unloading facilities for particular materials are given in the codes for those materials, as described in Section 22.26.

There should be sufficient space so that congestion is avoided. It is desirable that vehicles are able to drive in and out without reversing. The ground at a loading/unloading bay should be firm and impervious. At the filling point it should slope away so that spillage does not collect under the tanker and there should be suitable drainage. Where top loading is practised, there should be a platform with good access, including access to the top of the tanker, and a means of escape. The facility should be well ventilated and well lit.

The layout should assure protection both of the fixed equipment and of the tanker from impact by another vehicle. Attention should be paid to the routing of pipelines connected to the facility. Damage from vehicles can largely be avoided by the provision of high kerbs around the loading island and also of barriers to protect equipment and by controlling the movement of vehicles. It may also be necessary, particularly where other persons may be passing, to provide barriers or other means to control vehicle movements.

Storage vessels, filling connections and other equipment such as pumps should be provided with a means of identification. The layout should provide direct lines of sight so that personnel conducting transfer operations can observe the effects of their actions.

Where a fire hazard exists, the control of ignition sources should be exercised through HAC and fire protection facilities should be provided. The HAC of loading and unloading facilities is considered in Section 22.25.6 and fire protection is discussed in Section 22.25.11.

Emergency equipment appropriate to the material handled should be available at the facility.

There should be arrangements at a filling point to run part or all of tanker's contents back to the storage vessel if necessary.

22.25.6 Hazardous area classification

Loading and unloading facilities are among the cases dealt with by the method of direct example in the IP *Area Classification Code*, which covers petroleum products. The code gives detailed recommendations for the HAC of road and rail transportation, dealing separately with loading and unloading, including the unloading of road tankers at petrol filling stations. The *Code* gives some ten figures showing the HAC zoning in plan and elevation for different facilities and situations.

Further guidance on the HAC for petroleum products is given in NFPA 30 and guidance on the HAC for LPG is given in HS(G) 34 and NFPA 58 and 59.

22.25.7 Filling arrangements and connections

There are three main types of connection used for the transfer of liquids between the fixed facility and the tank of the vehicle. These are (1) flexible hoses, (2) articulated arms and (3) flexible couplings. A description of the three types of system as used for chlorine is given in HS(G) 28.

Connection is frequently by means of a hose. Articulated arms with swivelled joints are used on installations with a high throughput. Flexible couplings are used for certain products such as chlorine.

Good practice in respect of hoses is illustrated by the guidance given in HS(G) 34 on flexible hoses for LPG. A hose should be designed and made to an appropriate standard such as BS 4089; it should be suitable for the product to be handled; it should be provided with means of identification; it should be protected both in respect of its end fittings against damage and ingress of foreign matter and, where necessary, in respect of external damage, using a procoil or similar device; it should be subject to a full system of maintenance and test, including inspection records, annual hydraulic testing, periodic examination for kinks, weakness and end fitting deterioration and electrical discontinuity; and it should be kept in a safe place when not in use and replaced or repaired when worn or damaged.

The filling of tankers is carried out through a pipe in the top or in the bottom of the tank, that is by top or bottom loading. Top loading is often done by a rigid arm system and bottom loading by a hose. Pipes should be arranged so that the line between the tanker and the plant can be emptied before the tanker is uncoupled. Incidents sometimes occur due to a failure of the hydraulic system on a filling arm which causes it to drop and foul a tanker, and a locking device should be provided to prevent this.

Vapour recovery systems are becoming more widely used, mainly to meet pollution requirements. These systems have a filling arm which makes a gas-tight fit over the tank hatch, a short pipe which gives splash filling and a float switch which cuts off the flow when the tank is full. There is a separate vapour line which goes to a compressor and gasholder. Loss experience with these devices is good.

22.25.8 Shut-off arrangements

There are measures which can be taken to avoid overfilling and a number of devices which can be used to effect rapid shut-off if a leak occurs due to overfilling, failure of a filling connection or otherwise.

These include (1) vessel identification, (2) vessel sizing, (3) ullage control, (4) pre-set filling meters, (5) pump trips, (6) high level alarms, (7) dead man's handle arrangements, (8) non-return valves, (9) excess flow valves, (10) remotely operated isolation valves, (11) remote control of pumps and (12) self-sealing couplings.

The marking of vessels to ensure correct identification is one elementary measure to prevent releases. The use of a storage vessel with a capacity at least that of the largest tanker from which transfer may be attempted is another: this is particularly important for chlorine facilities. Attention to the ullage in the container to which transfer is to be made is a third.

A pre-set filling meter may be used to ensure that the quantity transferred does not exceed the capacity of the container. The filling pump may be provided with a trip to stop the pump and preferably close a shut-off valve when the pre-set quantity has been delivered. There may also be a manual control for the pump and the shut-off valve at the loading point. On storage a high level alarm may be provided to warn if overfilling is occurring.

An arrangement which guards against an operator starting the filling and then having his attention diverted elsewhere is the use of a spring-loaded self-closing filling valve which remains open only as long as the operator's hand is on it, that is a dead man's handle valve.

Means are available for cutting off flow from a damaged or disconnected connection, for example non-return valves, excess flow valves and remotely operated isolation valves.

Whatever the other arrangements, means should be provided for stopping all pumps immediately if an incident occurs. This should be a manual control in an attended terminal and an automatic one in an unattended one.

As described below, another means of shutting off a leak, applicable to the case where the vehicle moves away whilst still connected, is the use of a self-sealing coupling.

22.25.9 Vehicle control

Likewise, there are a number of methods which can be used to prevent a vehicle from moving away whilst it is still connected to the fixed plant by a filling connection, and thus causing a release. These mostly involve some form of interlock. There are also devices to shut-off flow.

The measures used differ somewhat between road and rail, and those described here are those applicable to road tankers. The ground at the filling point should be level and chocks should be used to hold the tanker in position.

Movement of the vehicle may be prevented by the use of an interlock system. One method is the use of an interlocked barrier. Another is an arrangement which locks the vehicle's braking system when the delivery hose is taken from its stowage position and releases the system only when the hose is restowed. A third is a brake flap arrangement which must be moved aside to gain access to the filling branch, the action of which actuates the vehicle's braking system.

Flow may be cut off if the tanker moves by use of a self-sealing breakaway coupling. Other emergency shut-off devices have already been described.

22.25.10 Static electricity control

There are various precautions which may be taken against the hazard of ignition of product by static electricity.

An account of these measures is given by the OIA. Two measures which it considers very desirable, although they are not generally adopted, are the complete elimination of switch loading and the use of inerting of the tank during filling. The latter tends to be rather expensive and time-consuming.

Measures which are normally taken are earthing and bonding to dissipate static charges on the metal containment. The filling pipe, the product line and the gantry should be electrically continuous and earthed. The electrical resistance of the gantry should not exceed $10^4\ \Omega$ and should be checked periodically.

Bonding involves connecting the product line to the tank. This prevents static discharge between the filling pipe and the tank. It is usually done using a wire with alligator clips. It is considered adequate if the electrical resistance of the bond does not exceed $10^6\Omega$. The bond should be inspected and its electrical resistance checked periodically. The bond should be such as to avoid damage if the vehicle is driven off before the bond is disconnected. Devices which drop down from the gantry to touch the tank are not considered effective for bonding.

As mentioned in Chapter 16, however, it may be desirable to aim for lower electrical resistances than those just quoted in order to ensure that the latter are reliably achieved. The bonding should be attached before the filling pipe is inserted into the tank and it should remain in place until the operation is completed.

However, earthing and bonding do not immediately dissipate the charge on the surface of a non-conducting liquid in the tank. A relaxation time should be allowed after filling has been completed and before the filling pipe is withdrawn, to permit static charge on the liquid surface to dissipate to the pipe or tank shell. The minimum time is 1 min, but longer periods are advisable with some products, as indicated above.

Where switch loading is practised, there are various additional precautions which may be taken. These include the use of inerting, low filling rates, special filling tips and static neutralizing devices, and longer relaxation times. The initial filling rate should be 3 ft/s maximum, rising to 15 ft/s when the filling pipe outlet is fully submerged. Special filling pipe regulator tips are available to give this initial flow limitation. Static neutralizers may be installed in the product line. Longer relaxation times may be allowed before withdrawing the filling pipe.

Bottom loading does not eliminate the static electricity hazard, particularly in switch loading, and still requires earthing.

With vapour recovery systems, splash filling would theoretically appear to increase the hazard on switch loading. The OIA therefore recommends against their use in switch loading situations.

22.25.11 Fire protection

A loading/unloading facility should be provided with appropriate fire protection. The arrangements depend on the particular installation and especially on the product transferred, the amount of material and the number of tankers handled, the location of the terminal, and the potential for damage and business interruption.

Fixed water sprays may be provided to cool tankers at filling points. The failure of tankers in a fire can be relatively rapid. The OIA makes recommendations for fixed sprays of water, foam or dry chemicals for terminals for flammable liquids. It is particularly concerned with automatic systems for unattended terminals. It suggests that fixed sprays should be located both in the roof and along the loading island so that extinguishing media can be directed under tankers. For fixed water sprays, a rate of application of 0.25 USgal/ft^{2}min over the whole loading area is recommended.

The ICI *LPG Code* recommends fixed water sprays for terminals handling more than one tanker simultaneously or more than four tankers per day. The rate of application of water should be 0.2 UKgal/ft^{2}min of tank surface. In multi-bay installations, there should be arrangements to control the sprays selectively. Automatic operation is not essential, as it is assumed that the terminal is manned during transfer operations.

The *Code* also states that if fixed water sprays are not provided there should be fire hydrants capable of the same rate of application of water, but that if fixed sprays are installed the hydrant capacity can be reduced by 50%.

For LFG fires the method of extinction is to cut off the supply of fuel. Water from spray nozzles may be used to cool tankers and equipment, particularly to prevent direct flame impingement, to bend flames away from equipment and to cool the flames themselves. But putting water directly on an LFG spillage has the effect of increasing the evaporation rate and this generally makes the fire worse. In addition, it is undesirable to extinguish an LFG fire with water because of the danger of a subsequent explosion. Water should not be used, therefore, on LFG fires, except for very small spillages. Foam may be used to limit the evaporation rate, but it will not normally extinguish a fire and, as just stated, it is not desirable that it should.

Portable fire extinguishers and sand should be provided for dealing with small spillages or vehicle fires.

Drains should be provided which will handle flammable liquids and fire water, along the lines previously described.

Electrical cabling should be routed outside the high risk areas of the terminal or should be protected so that emergency services are maintained and any subsequent interruption minimized.

It is desirable that the tanker at a terminal have some degree of fire resistance. There are large aluminium tankers which may fail within only 1 min when exposed to intense ground fires and these represent a serious hazard.

The OIA draws attention to the increase in the number of unattended or 'keystop' terminals for flammable liquids. In such terminals there are problems of damage to loading equipment, of a lack of supervision of loading practices and of the absence of personnel to control fires.

22.25.12 Rail facilities

Most of the features of loading and unloading facilities for road apply also to rail, but there are some which are characteristic of the latter.

Rail tracks should be laid straight and level, though a small gradient can be tolerated. HS(G) 52 gives a limit of 1 in 400. The track and line-side equipment should be maintained to the appropriate British Rail standard.

There should be arrangements for the control of locomotives whilst filling is in progress.

There should be earthing and bonding to dissipate the static charges. Rails should be bonded together and to the product lines. A separate bond to the tank is necessary only if the earthing between the tank and the rails via the wheels is inadequate.

Stray currents constitute an additional hazard. These may arise from electrified main line tracks, rail circuit signal systems or cathodic protection systems. If the siding is part of an electrified system, it should be electrically isolated from the rest of the system and bonded to the site main earth. Precautions which may be necessary against stray currents are insulating inserts in the rails where they enter and leave the loading siding and an insulating flange between the product line and the filling pipe together with a flexible bond between the rail tank and the filling pipe.

22.25.13 Operation

As with other aspects of process installations, the safety of loading and unloading facilities depends as much on operation as on design.

A significant issue is the manning of the facility, which tends to vary and which has more than one aspect. One is control of the transfer. In some cases transfer is conducted by plant personnel and in others by the driver of the tanker. Another aspect is the back-up available if something goes wrong, such as the outbreak of a fire or a toxic release sufficient to overcome the person effecting the transfer.

Safe systems of work should be provided and enforced which cover all aspects of the operation, from the identification of materials, vessels, connections and equipment, through the transfer operations themselves, to the emergency procedures.

There should be a good standard of housekeeping at the facility.

During filling all ignition sources should be excluded from the area of the filling point, including road or rail traffic. The engines of road tankers should be turned off.

22.26 Loading and Unloading Facilities: Particular Chemicals

22.26.1 Petroleum products

As stated above, guidance on the loading and unloading facilities for petroleum products is given in NFPA 30, the IP *Refining Safety Code* and HS(G) 50 and HS(G) 52, and also by the OIA.

The account already given has been based largely on facilities for petroleum products and these may therefore be treated briefly. Features specific to such products given in the guidance just mentioned include: minimum separation distances; HAC; top and bottom filling arrangements; spillage disposal arrangements and fire protection.

22.26.2 LPG

For the loading and unloading facilities for LPG, guidance is given NFPA 58 and 59, the LPGA *LPG Storage Code*, the IP *LPG Storage Code* and HS(G) 34, and also in the ICI *LFG Code*.

For LPG, the requirements for minimum separation distances are different. Particular importance attaches to the arrangements for the control of ignition sources, including the control of static electricity; HAC and fire protection. The discussion of fire protection in Section 22.25 covers LPG facilities.

22.26.3 High toxic hazard materials

Guidance on the loading and unloading facilities for HTHMs is given in the CCPS *HTHM Storage Guidelines*. In essence, the *Guidelines* cover ground similar to that just considered, both in respect of the hazards and the measures taken to control them, at least as regards loss of containment, though the hazard from the flammability of the material may not apply. It is worth emphasizing, however, that the points which do apply do so with particular force to HTHMs and that for such materials the standards of integrity required are high.

The *Guidelines* point out that in the case of loading and unloading facilities it is not possible to apply the philosophy of secondary containment.

With toxic materials even the small release which occurs as the tank is filled with a high vapour pressure liquid may be unacceptable. In such cases use should be made of a dual transfer line system, with one line used for transfer of liquid to and from the container and the other line used for venting vapour during filling.

22.26.4 Chlorine

Guidance is given on the unloading facilities for chlorine in HS(G) 28. Some specific aspects include potential incidents, minimum separation distances, filling connections, padding gas arrangements and systems of work.

For chlorine, flexible couplings are the normal method of connection and HS(G) 28 gives details of their use. Methods of transfer of liquid chlorine described in HS(G) 28 are the use of dry compressed air or nitrogen or of chlorine vapour, obtained by recompression or vaporization.

The system of work should ensure that one person, the driver, is present throughout the unloading, and that a second is present during connection and disconnection and is available throughout the unloading operation.

22.26.5 Ammonia

General guidance on the handling of ammonia is given in HS(G) 30, but this does not give guidance on loading and unloading facilities comparable with that for chlorine just described.

Some of the issues arising in relation to loading facilities for ammonia are discussed by Lichtenberg (1987) the use of meters vs scales; the use of hoses vs articulated arms; blowing off vs the use of integral blowdown systems; and loading by the driver or by plant personnel.

Articulated systems include vertical articulated arm systems and also compact horizontal articulated arm systems with integral blowdown.

22.27 Drum and Cylinder Storage

Another type of storage is storage in drums and similar containers and in cylinders. Although such storage is, in principle, very simple, the hazards are not trivial.

HSE guidance on drum and cylinder storage is given in CS 4 *The Keeping of LPG in Cylinders and Similar Containers* (1986), HS(G) 40 *Chlorine from Drums and Cylinders* (1987) and HS(G) 51 *The Storage of Flammable Liquids in Containers* (1990). Another relevant code is *Storage of Full and Empty LPG Cylinders and Cartridges* (LPGA, 1967 Code 7).

22.27.1 Drum storage

Chemicals are stored in containers at supplier and user sites in the chemical industry and at depot and warehouse sites.

For flammable substances guidance is given in HS(G) 51. This supersedes earlier guidance given both in CS 2 and a Home Office code. HS(G) 51 does not cover reactive

chemicals such as organic peroxides, LPG or large containers.

The containers considered in this guidance include drums, portable tanks and tank containers. Reference is made to containers of 200 l. A typical container in the United Kingdom is the standard 40 UKgal drum.

Relevant British Standards on container construction are BS 814: 1974– for steel drums and BS 3951: Part 2: 1978 – for freight containers.

The general approach to drum storage is broadly as follows. The preferred option is storage in the open. The storage should be in a defined area which should have an impervious surface and should be provided with a low bund or a drain and sump system. Where use is made of a bund, it is typically 150 mm high and should be large enough to hold 110% of the contents of the largest container. Within the storage area, the drums should be stored in stacks which should be marked off. The stacks should have good access and ventilation. There should be separation distances between occupied buildings, the boundary, process units, flammable liquid tanks and fixed ignition sources. There should also be a maximum stack size. Guidance is given on maximum stack sizes and minimum separation distances to the objects mentioned and to LPG storage. The area around the storage should be free of combustibles and tidy. The area should be fenced off, with one or two access gates, depending on the size of the site. The storage should have a HAC as a Zone 2 area. Firefighting facilities should be provided. If there is difficulty in providing the separation distances recommended, some relaxation may be obtained by the provision of fire walls or fixed water sprays systems.

Alternatively, storage may be in a separate building dedicated to that purpose or in a building used also for other purposes. The latter case requires additional fire resistant construction, particularly fire walls. A building used for such storage is essentially a warehouse, to which consideration is given in the next section.

Further guidance on drum storage is given by two anonymous authors (Anon., 1979 LPB 27, p. 68); Anon. (1979 LPB 28, p. 115).

22.27.2 Cylinder storage

As for other containers, chemicals are stored in containers at supplier and user sites in the chemical industry and at depot and warehouse sites.

For LPG guidance is given in CS 4. The basic principles are essentially the same as for drum storage, but there are differences of detail such as in the specific values of maximum stack size and minimum separation distances.

22.28 Warehouses

Warehouses constitute a quite different kind of storage. A wide variety of materials are stored in warehouses in many different forms. Material may be simply stored in a stockpile on the warehouse floor, but more often there are bays which hold discrete items such as paper, drums and spare parts. Chemicals in packages and drums are also stored in warehouses.

The Dangerous Substances (Notification and Marking of Sites) Regulations 1990 (the NMS Regulations) create a requirement for the notification and marking of sites which has particular relevance to warehouses. Guidance is given in HS(R) 29 *Notification and Marking of Sites*. *The Dangerous Substances* (*Notification and Marking of Sites*) *Regulations* 1990 (HSE, 1990).

HSE guidance on warehouses is given in HS(G) 51 *The Storage of Flammable Liquids in Containers* (1990), HS(G) 64 *Assessment of Fire Hazards from Solid Materials and the Precautions Required for their Safe Storage and Use* (1991) and HS(G) 71 *Storage of Packed Dangerous Substances* (1992). Further guidance is provided in *Guidelines for Safe Warehousing* by the CIA (1990 RC28) (the CIA *Warehouse Guide*).

Also relevant are NFPA 231: 1990 *General Storage* and NFPA 231C: 1991 *Racked Storage of Materials*.

22.28.1 Regulatory requirements

Sites which store large inventories of hazardous substances are covered by the NIHHS Regulations 1982 and CIMAH Regulations 1984. These regulations do not, however, apply to most warehouses. In a typical warehouse the quantity of any given chemical is below the threshold quantities which trigger these regulations. The necessity for the control of warehouses, however, has been highlighted by a number of incidents. The NMS Regulations 1990 were brought in to close this loophole.

In particular, the regulations are intended to provide the fire services with information to assist them in setting priorities for the inspection of sites and to warn firefighters arriving at an incident of the presence of dangerous substances.

Regulation 4 defines dangerous substances as those listed in Part 1A2 of the Approved List of the CPL Regulations 1984 and other substances with the characteristic properties set out in Schedule 2, Part 1, of those regulations. Notification is required if the warehouse stores a total of 25 te or more of dangerous substances. Regulation 5 gives requirements for access marking and Regulation 6 requirements for location marking.

There are a number of other pieces of legislation which are relevant to warehouses. In addition to those already mentioned, they include the Petroleum (Consolidation) Act 1928 (P(C)A), the Fire Precautions Act 1971, the Highly Flammable Liquids and Liquefied Petroleum Gases Regulations 1972 (HFLR), the Safety Signs Regulations 1980, the Control of Pesticides Regulations 1986, the Control of Substances Hazardous to Health Regulations 1988 (COSHH) and the current Building Regulations.

22.28.2 Management system

For the most part the companies which operate warehouses handling chemicals are not in the mainstream of the chemical industry and its culture. The operation of a chemical warehouse nevertheless demands a management system essentially similar to that in the industry.

Specifically, the management system should ensure that among other things there are formal systems which cover the identification, assessment and control of hazards; the use of suitable buildings; the storage and segregation of chemicals; the provision and maintenance of fire protection and the use of and training in suitable operating procedures.

The responsibilities of those involved in warehouse operation are outlined in the CIA *Warehouse Code*, which covers the supplier or owner of the goods, the warehouse keeper, the warehouse supervisor and the warehouse employee.

An essential aspect of the management system is good communications.

22.28.3 Warehouse siting and layout

The siting of warehouses is often far from ideal. Many existing warehouses are located in a built-up area and close to housing. Siting of new warehouses should be such as to minimize the risks to the surrounding area. Likewise, these risks should be taken into account when considering an extension to an existing warehouse. Fire and explosion are the events which are most likely to present a threat to the surrounding population.

Many warehouses are located on waterways where they serve as transit points. This increases the risk of pollution of these waterways by chemicals released during an incident.

The layout of the warehouse site should be such as to facilitate the movement of vehicles that are unloading or loading, with adequate access and parking. The layout should aim to minimize collisions and to allow incidents such as spillages or small fires to be readily dealt with.

The layout should also assist security. Access should be gained only through access gates. Each separate warehouse building should be capable of being securely locked.

22.28.4 Warehouse buildings

The construction of a warehouse building is subject to the Building Regulations. For industrial storage buildings there is an approved document which sets out standards for compartment size and fire resistance.

Some high fire hazard substances require separation distances between the building and the boundaries in excess of those specified in the Building Regulations. These include flammable liquids, oxidizing substances and organic peroxides.

A warehouse for dangerous substances should preferably be constructed in non-combustible materials. Where flammable substances are involved there may be specific regulatory requirements for fire resistance.

Guidance on warehouse building construction is given in the CIA *Warehouse Guide*. This guidance is intended to illustrate the approach which might be taken by a chemical company in constructing a new facility. The code deals with (1) frame, (2) infill, (3) floors, (4) roof, (5) ventilation, (6) drainage, (7) emergency exit doors, (8) internal doors, (9) internal partitions, (10) wall and roof linings, (11) fire protection, (12) special facilities, (13) lighting and (14) electrical installations.

Where the dangerous substances stored are liquids, floors should be impervious and resistant to the liquid. There should be bunds to contain the liquid and sills to prevent its spread through doorways. In areas where the risk of spillage is high, there should be a separate drainage system with sloped floor, a bund and a collection sump.

Rainwater should be taken away from the roof and outside areas in drains with roof downpipes sealed at ground level. The drainage arrangements should aim to prevent contamination of surface water by water used in fighting a fire in the warehouse.

22.28.5 Material identification

There should be a formal system for the identification and tracking of the dangerous substances handled. The system should be based on the classification systems for dangerous substances. Most such substances arriving on site will be marked with the conveyance labels specified in the Chemical Hazard (Information and Packaging) Regulations (CHIP) and goods in international transit should be labelled with the United Nations labels. The supplier should normally provide in addition the information required under the CHIP supply labelling system.

Some substances may require special storage conditions. These should be identified in advance by the supplier and accepted only if these conditions can be provided. Some substances may degrade or become unstable during prolonged storage. These too should be identified by the supplier.

All dangerous substances should be identified on receipt and their storage in and transfer from the warehouse documented. The documentation system should ensure both that records are made and that they are held securely.

22.28.6 Material segregation

The most serious incidents occur when a small event escalates and involves large quantities of material. The main cause of this is fire. An effective means of preventing such escalation is the segregation of materials.

One purpose of segregation is to separate dangerous substances from materials which may ignite or burn readily in the early stages of a fire. Another is to keep dangerous substances out of general storage where their presence is liable to aggravate the difficulties of firefighters.

Table 22.12 is the segregation table given in HS(G) 71. It is based on the conveyance labelling requirements of the CPL Regulations and is compatible with the *UN Recommendations for the Transport of Dangerous Goods*. The table does not include Class 1, Explosives, Class 6.2, Infectious Substances, or Class 7, Radioactive Substances, which are covered by separate guidance. The numbers in the table refer to the segregation of different classes of substance on the same floor of a building. Vertical segregation between different classes of material is not accepted except where there is an imperforate floor/ceiling with 1 h fire resistance. The general guidance given in the table is overridden where there is advice specific to a particular class of material.

The International Maritime Dangerous Goods Code may also be used as guidance, provided allowance is made for the different factors which apply to land storage.

22.28.7 Mechanical handling

Modern warehouses make full use of mechanical handling aids. There is also a trend towards automated warehouses under computer control. The mechanical handling facilities should accommodate the full range of packages to be stored, so that improvisation is avoided. Widespread use is made in warehouses of pallets and forklift trucks. Guidance on the use of forklift trucks is available (HSE, 1992 HS(G) 6). Forklift trucks are also considered in Chapter 21.

22.28.8 Storage operation

There are a number of basic operating principles which should be covered by formal operating procedures.

When a consignment is received, the substance should be identified and the integrity of the package should be checked. Damaged packages should not be accepted into store but dealt with by repacking or disposal.

Each location should have a specified storage capacity which should be adhered to. There should be maximum stack sizes and heights. The heights should take into account the potential for damage to the packages at the bottom and for fire spread. The racking used should be well constructed and should not be overloaded. Goods should not be stored so close to a wall as to interfere with ventilation or in gangways so that they inhibit access.

Table 22.12 *Segregation table for storage of dangerous substances in warehouses[a] (Health and Safety Executive, 1992 HS(G) 71) (Courtesy of HM Stationery Office. © All rights reserved)*

To be read in conjunction with Appendix 1[b]	*Class* 2			*Class* 3	*Class* 4			*Class* 5		*Class* 6	*Class* 8
	2.1	2.2	2.3		4.1	4.2	4.3	5.1	5.2		
2 Compressed gases											
2.1 Flammable	–	1	2	2	2	2	2	2	3	1	1
2.2 Non-flammable toxic	1	–	1	1	0	2	0	0	2	0	1
2.3 Toxic	2	1	–	2	1	2	1	0	2	0	1
3 Flammable liquids	2	1	2	–	1	2	2	2	3	1	1
4 Flammable solids											
4.1 Readily combustible	2	0	1	1	–	1	2	2	2	1	0
4.2 Spontaneously combustible	2	2	2	2	1	–	1	2	3	1	1
4.3 Dangerous when wet	2	0	1	2	2	1	–	1	2	0	0
5 Oxidizing substances											
5.1 Oxidizing substances	2	0	0	2	2	2	1	–	2	1	1
5.2 Organic peroxides	3	2	2	3	2	3	2	2	–	1	1
6 Toxic substances	1	0	0	1	1	1	0	1	1	–	0
8 Corrosive substances	1	1	1	1	0	1	0	1	1	0	–

[a] The table shows general recommendations for the separation or segregation of different classes of dangerous substance.
The miscellaneous dangerous substances in UN Class 9 and other dangerous substances in CPL have quite varied properties and no general advice can be given regarding segregation. Advice should be obtained from the supplier.
[b] Of HS(G) 71.

Key:

0 *Separation may not be necessary,* but suppliers should be consulted about requirements for individual substances. In particular, it should be noted that some types of chemicals within the same class may react violently, generate much heat if mixed or evolve toxic fumes.

1 *'Keep apart'.* Separate packages by at least 3 m or one gangway width, whichever is the greater distance in the store room or storage compound outdoors. Materials in non-combustible packaging which are not dangerous substances and which present a low fire hazard may be stored in the 3 m space. At least this standard of separation should be provided between substances known to react together readily, if that reaction would increase the danger.

2 *'Segregate from'.* These combinations should not be kept in the same building compartment or outdoor storage compound. Compartment walls should be imperforate, of at least 30 min fire-resisting construction and sufficiently durable to withstand normal wear and tear. Brick or concrete construction is recommended. An alternative is to provide separate outdoor compounds with an adequate space between them.

3 *'Isolate'.* This is used for organic peroxides, for which dedicated buildings are recommended. Alternatively, some peroxides may be stored outside in fire-resisting secure cabinets. In either case, adequate separation from other buildings and boundaries is required.

Where a particular material has the properties of more than one class, the classification giving the more onerous segregation requirements should be used.

Note: The table is to be read in conjunction with the following paragraphs from the text of HS(G) 71. Paragraphs 20 and 21 explain the logic behind the table and paragraphs 13, 15, 22 and 23 give certain caveats.

20 Often the first material ignited in a fire is not itself a dangerous substance. For this reason, stocks of combustible materials such as easily ignitable packaging should not be kept in store rooms with dangerous substances. Separate storage areas should be provided. Similarly, even small quantities of dangerous substances stored in a warehouse for general goods may seriously increase the consequences of any fire, and in particular add to the dangers for the fire brigade. Dangerous substances should preferably be stored in dedicated warehouses or compartments of warehouses which are effectively fire separated from the remainder of the building.

21 The intensity of a fire, or its rate of growth, may be increased if incompatible materials are stored together. In addition, a fire may grow and involve dangerous substances which of themselves are not combustible. In this way, toxic materials may be widely dispersed. To prevent this type of escalation a system of segregation is necessary in warehouses storing dangerous substances.

13 The conveyance labels alone do not give adequate information for all purposes associated with storage, and the supplier should normally provide at least the additional information required under the CPL supply labelling system. This includes standard risk and safety phrases. In most cases, drivers making deliveries of a dangerous substance are required to carry on the vehicle information about the hazards of the substance(s) being carried. This may be useful if safety data sheets are not already held for substances being delivered.

15 On arrival, the contents of each consignment or individual packages should be checked, identified and assessed against the shipment documents to verify acceptability. Dangerous substances should usally be identifiable by the conveyance labelling attached to the outer layer(s) of the packaging, and for most purposes can be assesed accordingly. The additional information obtained from the suppliers may identify specific examples of non-compatibility, and storage location should take account of this.

22 The table overleaf gives recommedations for the segregation of dangerous substances of different types. The classification scheme is based on the conveyance labelling requirements of the CPL Regulations, and is consistent with the United Nation *Recommendations on the Transport of Dangerous Goods*. The table excludes Classes 1, Explosives; 6.2, Infectious substances; and 7, radioactive substances for which guidnce is given elsewhere (see Appendix 3)[b]

23 Numbers in the Table relate to segregation of different classes of substance on the same floor of a building. Vertical segregation between different classes of material is not acceptable unless provided by an imperforate floor/ceiling of at least 60 minutes' fire-resisting construction.

Stock held for a prolonged period should be inspected for degradation. Where a substance has a maximum storage time this should not be exceeded. If this is close to occurring, the advice of the manufacturer should be sought.

There should be arrangements for dealing with spillages. This is partly a matter of building design, as already described, but it is also necessary to provide an absorbent and to have procedures for dealing with and disposing of the spillage.

Where appropriate, an operation should be governed by a permit-to-work.

22.28.9 Fire protection

The fire potential in a warehouse is high. The fire load is very high and the conditions for fire spread are nearly ideal, there being large amounts of combustibles close together and with good air circulation. In fact a large proportion of fire loss in storage is due to warehouse fires. The prevention of fires in warehouses is therefore extremely important.

Fire protection in warehouses includes the following measures: (1) building construction, (2) control of ignition sources, (3) fire detection systems (4) fire protection systems and (5) operational measures.

As already stated, the building should preferably be constructed in non-combustible materials and have a degree of fire resistance. The starting point is a concrete or steel frame. Other aspects of fire resistant construction are concrete protection of the steel supporting columns, separation of the arrival and dispatch areas from the storage area by fire resistant walls, and further separation by fire resistant walls within the storage area.

Whereas in process plant handling flammables the first line of defence is to remove the fuel by keeping the flammable material contained, in a warehouse storing flammable substances the fuel is to hand. Hence close control needs to be exercised over ignition sources.

The warehouse should be covered by HAC. Normally the appropriate classification is Zone 2 and the arrangements should then be such that no operation requires a more stringent classification.

Forklift trucks are a particular potential ignition source which require control. Where a HAC applies, only trucks suitable for use in that area should be used.

Fire detection systems are valuable in giving rapid warning of a fire. Whether detection is followed first by warning to personnel and manual fire-fighting methods or by immediate activation of automatic fire protection systems such as sprinklers depends on the circumstances. Problems with the latter include false alarms and water damage.

Sprinklers are the principal form of fire protection device used and are generally effective. For high warehouses, sprinklers on the roof may be insufficient and they may need to be provided at lower levels as well. Sprinkler protection is discussed further in Chapter 16.

There should be a working discipline, essentially similar to that required in a process plant, which ensures that procedures are observed. These include general good housekeeping, the avoidance of obstructions to corridors and fire doors and the elimination of ignition sources.

The HSE has developed a test, described in HS(G) 64 (HSE, 1991) and referred to as the HSE Test, which may be used to assess the need for particular forms of fire protection. Details of the test are given by Wharton (1990). The test characterizes a material in terms of (1) the maximum rate of vent temperature rise and (2) the total smoke evolution. For each of these two features the material is placed in one of two hazard categories according to the following scheme:

Category	*Temperature rise* (°C/min)	*Smoke* (m3 ODml)
HIGH	≥700	≥400
NORMAL	<700	<400

[a] OD, optical density – see Wharton (1990).

In some cases it may be a condition of a fire certificate under the FPA (1971) that certain precautions be taken for the storage of a HIGH fire hazard material. In any event it is desirable that a HIGH fire hazard material should be stored in a separate area, either in a separate building, a single storey extension of the main building or in the open air. Where it is not reasonably practicable to store such a material elsewhere than in the main building, it should be stored in an area separated from the rest of the building by a 30 min fire partition. A HIGH fire hazard material should not be stored in a basement or below an occupied floor. Exceptions to this are given in HS(G) 64 such as cases where the quantities are small or the risk is reduced by the type of packaging used or by some combination of spacing and active fire protection.

The problem of fire protection in warehouses is complex. The discussion of the problem, in relation to automated high bay warehouses, by the FPA (1970/9) outlines some of the difficulties.

Arson is a potential problem in warehouses. Guidance from the FPA also includes a treatment of the prevention and control of arson (1992 AR2).

22.28.10 Hazard assessment

Substances stored in warehouses may be hazardous by virtue of their being combustible, flammable, explosive, toxic, corrosive, unstable, reactive with air and/or water, pyrophoric or liable to spontaneous combustion or oxidizing.

There should be a system for the identification of the hazards. A checklist approach may in large part fulfil this function.

A hazard assessment should be performed, broadly on the lines of those made for process plant, but allowing for the characteristic features of warehouses. Initiating events may be associated with: liquid spillage due to leaks or the opening of valves; spillages of solid materials due to damage to packages or to repackaging operations; dust clouds; or small fires. Scenarios of escalation may include a major fire, a series of explosions, a release of toxic gases and vapour within the warehouse or beyond, a large smoke cloud (possible highly toxic) or the overflow of large quantities of contaminated fire water.

22.28.11 Emergency planning

There should be an emergency plan for the warehouse, adapting the basic principles described in Chapter 24 to warehouse conditions. The plan should be suited to the level of the assessed risk and should be developed in consultation with the local emergency services. Personnel should be trained in the plan and in their own role in it, and exercises should be conducted.

22.29 Warehouses: Particular Chemicals Storage

There are certain chemicals which are stored in warehouses that merit particular consideration.

22.29.1 Sodium chlorate

Sodium chlorate is a crystalline solid which is relatively stable and is a strong oxidant. It has a melting point of 248°C and starts to decompose at 265°C with the evolution of oxygen.

Guidance on the storage of sodium chlorate is given in CS 3 *Storage and Handling of Sodium Chlorate and Other Similar Strong Oxidants* (HSE, 1985). This guidance also applies to the several other strong oxidants listed.

There have been several warehouse fires, two of which are described below, in which the involvement of sodium chlorate has resulted in violent explosions.

One hazard of sodium chlorate is that it may become involved in a fire and explode, as just described. Another is that it may become mixed with a readily oxidizable material, such as a fuel. Such a mixture can be ignited by relatively mild stimuli and can burn with explosive violence.

Sodium chlorate should be stored in a secure and separate area. It should be segregated from combustible materials and contaminants should be excluded. Control should be exercised over ignition sources and measures should be taken to prevent the material becoming involved in a fire.

Storage for sodium chlorate may be in the open on a concrete pad, with or without a roof, but should preferably be fully enclosed. Any structure should be built of non-combustible materials and the floor should be smooth, impervious and non-carbonaceous. CS 3 gives maximum stack sizes and minimum separation distances for the storage of sodium chlorate.

Packaging of sodium chlorate is preferably in metal drums with a plastic liner. International agreements on transport also authorize the use of certain soft packaging materials such as flexible intermediate bulk containers.

Wooden pallets should not be used for the routine handling of sodium chlorate as they are liable to become impregnated with it, thus creating a fuel–oxidant mixture. CS 3 advises, however, that where wooden pallets do form an integral part of an International Maritime Organization (IMO) Code approved package and the wood is new, they may be allowed for one-off storage.

In view of the fact that the fires in the two warehouse incidents described in Section 22.30.7 were caused by outsiders, security assumes particular importance in the storage of sodium chlorate.

22.29.2 Organic peroxides

Organic peroxides are highly reactive and thermally unstable substances which undergo self-accelerating decomposition. They have oxidizing properties and some are also toxic.

Guidance on the storage of organic peroxides is given in CS 21 Storage and Handling of Organic Peroxides (HSE, 1991).

In the pure state some organic peroxides detonate. For commercial use organic peroxides are desensitized, but even so they are capable of runaway decomposition. Such decomposition may be caused by heating or contamination.

The self-accelerating decomposition temperature (SADT) of an organic peroxide is determined by test. The SADT tends to decrease with package size. A control temperature is specified which is the maximum storage temperature, and an emergency temperature at which emergency procedures should be implemented. The relationships between these two temperatures and the SADT are given in CS 3. Another aspect of temperature control is that in some cases an organic peroxide can separate out of solution if cooled, resulting in a concentrated peroxide which may be shock sensitive.

Organic peroxides should be stored in the original containers in a dedicated storage and segregated from other materials. They should be maintained within the specified temperature limits. Contaminants should be excluded.

Further detailed guidance on the storage of organic peroxides is given in CS 3. They are classified into four flammability types, Types 1–4. A distinction is made between storages up to 150 kg and above 150 kg. Minimum separation distances are given. A list is given of packaged organic peroxides by flammability type.

22.29.3 Ammonium nitrate

Ammonium nitrate (AN) is a crystalline solid with a melting point of 170°C which decomposes above 210°C. Most of the commercial material stored is some form of mixture.

Guidance on the storage of AN is given in CS 18 *Storage and Handling of Ammonium Nitrate* (HSE, 1986).

AN is an oxidizing agent. It is not itself combustible, but it can assist the combustion of other materials, even if air is excluded. It is insensitive to the friction and impact of normal handling, but it can be detonated under conditions of heat and confinement or by severe shock. The probability of explosion is much increased if the AN is mixed with organic matter. In a fire, molten AN may form and flow into areas, such as drains, where it becomes confined and/or contaminated, and it may then explode. Furthermore, when heated in a fire, AN gives off toxic fumes, mainly oxides of nitrogen.

The main requirements in the storage of AN are to avoid heating or involvement in a fire, serious confinement and contamination.

CS 18 makes a distinction between AN and AN fertilizers with $<28\%$ nitrogen and those with $>28\%$ nitrogen. It deals mainly with the latter.

Storage of AN with $>28\%$ nitrogen should be in a dedicated building constructed in materials which are not readily combustible and with good ventilation or in the open on a concrete pad. Measures should be taken to avoid the hazard of molten AN becoming confined or contaminated, particularly in drains.

AN in storage should be segregated from other materials. The storage should be located away from potential sources of heat, fire or explosion, including combustible and flammable materials. CS 18 gives maximum stack sizes and minimum separation distances.

Packaging of ammonium nitrate is typically in 50 kg bags of material impermeable to oil or water. Paper packaging should not be used. The bags should preferably be palletized. If wooden pallets are used, they should be uncontaminated.

With regard to AN fertilizers with $<28\%$N, whilst most are not combustible, a few are capable of self-sustaining decomposition with strong evolution of toxic fumes. These are known as 'cigar burners'.

AN storage should be provided with good security. CS 18 states that access should be prevented not only of unauthorized persons but also of animals. Whilst it does not elaborate, the point is presumably that an animal may not only damage packaging but may leave behind organic material.

22.30 Storage Case Histories

22.30.1 Oil storage

In the storage of petroleum products, there have been numerous cases of tank overpressure or vacuum collapse and of fire, and some cases of release from tanks.

A review of the failure of storage tanks containing oil and similar products has been given by Wilkinson (1991 SRD R530). He divides the incidents into mechanical and brittle fracture failures and failures following an explosion or bund fire.

On 30 August 1983, a fire started on the floating roof of an oil storage tank at a refinery at Milford Haven, Wales (Case History A106). The tank contained some 47,000 ton of light crude oils. There were fine cracks in the floating roof through which oil had seeped out. It is believed to have been ignited by hot carbon particles from the flare. The fire was massive, with three boilovers of burning oil. It was not extinguished until 2 days later.

On 2 January 1988, at Floreffe, Pennsylvania, a storage tank containing diesel oil suffered a sudden collapse (Case History A120). The tank split vertically and the force of the oil spurting out moved the tank 100 ft off its foundations. The tank cracked, collapsed and crumpled. A proportion of the oil flowed over the bund and entered the waterways. The tank had been reassembled after removal from another site and the failure occurred on its first filling after reassembly.

22.30.2 LPG storage

A review of LPG storage incidents has been given by Davenport (1986), who describes incidents at: Port Newark, New Jersey, on 7 July 1951; Feyzin, France, on 4 January 1966; Texas City, Texas, on 30 May 1978; and Mexico City, Mexico, on 19 November 1984. Accounts of these incidents are given in Case Histories A19, A38, A92 and in Appendix 4, respectively.

The Port Newark site had 100×115 m^3 horizontal pressure vessels for propane, in two groups, one of 70 vessels and the other of 30 vessels, separated by a distance of 106 m. A leak of unknown origin occurred in pipework near the vessels in the larger group. Within a few minutes the first vessel burst. Eventually all 70 tanks in the group ruptured with varying degrees of violence. None of the vessels in the smaller group failed.

At Feyzin, there were four 1200 m^3 propane and four 2000 m^3 butane pressure storage spheres. An escape of liquid propane occurred whilst water was being drained from the bottom of one of the propane spheres. The vapour cloud formed was ignited by a vehicle on a nearby road and the vapour cloud fire caused a series of BLEVEs which resulted in 18 deaths and the destruction of five of the spheres.

At both Texas City and Mexico City, the initiating event is believed to have been overpressure of a vessel which was being filled from a pipeline. At Texas City, there were three pressure storage spheres and a number of other pressure vessels. The hypothesis is that the sphere which was overpressured developed a crack and released material which found a source of ignition. It was reported that the vapour cloud fire then changed to a jet flame at the sphere. Within a short time the sphere failed, giving a huge fireball. This was followed by a series of explosions and fires, and the failure of the other two spheres.

The site at Mexico City contained four 1600 m^3 and two 2400 m^3 pressure storage spheres and 48 horizontal cylindrical pressure vessels for storing propane and butane. The leak gave rise to a vapour cloud which ignited at a neighbouring plant and, within a short time, one or possibly two of the spheres ruptured. There followed a series of explosions and fires, which killed some 500 people and destroyed many of the storage vessels.

Another significant incident is that of a 260,000 bbl refrigerated LPG tank at Umm Said, Qatar, on 3 April 1977 (Case History A88). A massive failure occurred and a wave of liquid propane swept over the bunds and inundated the process area of the associated NGL plant before igniting. The NGL plant was completely destroyed.

22.30.3 LNG storage

One of the earliest process industry disasters was the failure on 20 October 1944 of an LNG storage tank at Cleveland, Ohio (Case History A12). The cause of the rupture is believed to have been the use of a low carbon steel which was unsuitable for the low temperatures involved. A vapour cloud of LNG formed and ignited in the plant itself, whilst LNG liquid flowed into storm sewers, where it mixed with air and gave rise to a series of explosions. Some 128 people were killed.

A quite different case is the disaster at Staten Island, New York, in 1973 (Case History A67). Work was being done inside an empty LNG storage tank when flammable residues were ignited. Some 40 people died in the resultant fire.

A rollover incident occurred on 21 August 1971 at the SNAM LNG terminal at La Spezia in Italy (Case History A54). A sudden increase in pressure occurred in the tank, causing a discharge from the tank safety valves and tank vent. The release from the safety valves lasted for 75 min and that from the vent lasted 3 h and 15 min.

22.30.4 Ammonia storage

A review of the failure of ammonia storage failures has been given by Markham (1987b). He presents information on the ammonia concentrations as a function of distance in these incidents and on the physiological effects of ammonia on humans, animals and plants.

On 13 July 1973, a sudden failure occurred on a horizontal ammonia pressure storage vessel at Potchefstroom, South Africa (Case History A65). The cause of the failure was brittle fracture of the dished end. The ammonia spread as a dense gas cloud over the works and to an adjacent township. Eighteen people were killed.

On 16 November 1970, a 40,000 ton refrigerated atmospheric ammonia tank at Blair, Nebraska, was overfilled (Case History A47). The ammonia overflowed and formed a massive dense gas cloud which extended some 9000 ft. The area was sparsely populated and no one was killed.

In 1982, defects were observed on a 20,000 te refrigerated atmospheric ammonia tank at Arzew, Algeria (Martinez *et al.*, 1987). They included tilting, extensive degradation of the tank wall insulation and failures of the anchor bolts. The cause is not known, but two hypotheses were advanced. One is an earthquake – there were earthquakes nearby in 1980 and 1981. The other is frost heave, due to poor drainage, with the resultant accumulation of water in the aeration tubes and hence a reduction in the efficiency of the foundation heating.

On 2 October 1984, a 15,000 ton refrigerated ammonia storage tank at Geismar, Louisiana, suffered a catastrophic failure of the roof-wall weld two-thirds of the way around its circumference (Badame, 1986). There was some release of ammonia which gave a small cloud, but evidently had no

serious consequences. The tank had suffered a mild overpressure of some 0.5 psi. The refrigeration compressors were down at the time. The relief valve opened but did not have the capacity to prevent the pressure from increasing. The weld had been subjected over the 17 years of the tank life to some 80,000 cycles and was held to have failed due to low cycle fatigue. It also showed extreme lack of penetration.

Another refrigerated atmospheric ammonia tank failure occurred on 20 March 1989 at Jonova, Lithuania (Case History A124). Some warm ammonia had been charged to the tank and in due course it erupted, causing a sudden increase in pressure. A massive failure occurred between the wall and the bottom of the tank and liquid ammonia rushed out. At the same time the tank was dislodged from its foundations and smashed violently through the containing wall on the far side from the escape, ending up 40 m away. A pool of liquid ammonia formed which in places was 70 cm deep. The ammonia suddenly ignited and the whole plant area was engulfed in flames. A burning conveyor belt transmitted the fire to a store of NPK fertilizer. Seven people were killed.

22.30.5 Pressure storage vessels

In 1986 a pressure storage vessel holding 25 te of carbon dioxide ruptured (Coleman, 1989). The report on the failure concluded that the steel was brittle at its service temperature and that inadequate leg attachments had created high local stress. The metallurgical evidence indicated that the heat treatment had not been properly carried out. There was also doubt whether the steel used in fabrication was the same as that on which the impact tests required had been performed.

22.30.6 Pressure storage vessels: decommissioning

Accounts of the decommissioning of pressure storage vessels also merit mention, even though in these cases no release occurred.

Squire (1991) records the case of an ammonia pressure storage vessel as follows:

> A bullet tank in refrigeration service had been cleverly made by turning a high-pressure distillation column on its side. While possessing considerable strength at ambient temperature, subsequent analysis showed no strength (<2 ft-lb) at 0°C. The bullet was immediately removed from service after identification. Great care was taken during the deinventory so as not to fracture the vessel.

Coleman (1989) describes an investigation into the state of a set of pressure vessels for the storage of carbon dioxide. The investigation was prompted by the carbon dioxide storage vessel failure just described. The company commissioned an investigation of its other carbon dioxide storage vessels, of which there were 24 vessels ranging in age from brand new to 26 years old. The work addressed in particular the risk of brittle fracture, and the methods used included visual examination, replica metallurgy and ultrasonic testing. The result of the investigation was that three vessels were taken out of service because it was found that their dished ends had been overheated during hot forming. Suspect metallurgy led to the withdrawal of a further six vessels, five of which had not only low toughness but also problems such as laminations and inclusions, weld defects and directly attached support brackets. All but one of these vessels were built before 1970, and most dated from before 1965.

22.30.7 Warehouses

On 4 January 1977, a serious fire and explosion destroyed a chemicals warehouse and adjacent whisky warehouse at Braehead and resulted in widespread window and roof damage within a 1 mile radius (Case History A85). Subsequent experimental investigation showed that explosions of this severity can be caused by the involvement of sodium chlorate under intense heat conditions. The warehouse had contained some 67 te of sodium chlorate in steel drums. The fire was started by boys who had built a 'den' beside the warehouse and had lit a fire there to warm themselves.

On 25 September 1982, a fire, followed almost immediately by an explosion, occurred in the warehouse of B&R Hauliers at Salford (HSE, 1983b) (see also Case History A85). The warehouse contained some 2000 te of chemicals, including 25 te of sodium chlorate. There was evidence that the original fire had been started outside the building by vandals and also that, earlier, persons had entered the warehouse where various containers were opened and chemicals mixed. The management had been unaware of the guidance issued by the HSE on sodium chlorate.

Another warehouse incident which involved a much smaller amount of sodium chlorate, some 2.45 te, but which nevertheless proved serious enough, occurred on 21 January 1980 at Barking, Essex (HSE, 1980a) (see also Case History A85). A fire started, probably caused by a domestic bar fire, possibly drying wet clothing and spread through packaging materials to involve various chemicals. There were three explosions, probably one was of an LPG cylinder and the other two of sodium chlorate. Nine firemen were injured.

22.31 Storage Risk

22.31.1 Historical record

The risks from the process industries arise from processes, storage and transport. The historical record shows that storage is a major contributor. Storage figures prominently in the case histories given in Appendix 1 and elsewhere in this book. An attempt to quantify the contribution made by storage to the overall risks from the process industries is given below.

22.31.2 Hazard assessment

Another approach to the estimation of the risks from storage is hazard assessment. Two major hazard assessment exercises in which storage figures prominently are the *Canvey Report* and the *Rijnmond Report*, which are described in Appendices 7 and 8, respectively.

An account is given below of hazard assessments of the storage of the principal hazardous substances: LPG, LNG and ammonia.

22.31.3 Storage vs process

Although the quantities of hazardous materials held in storage are much larger than in process, it is usually considered that process is the principal hazard. This view is reflected in the distinction made in the EEC Directive on Major Accident hazards between process and process associated storage on the one hand, and isolated storage on the other.

A study of the relative risks from process and storage has been made by Lees (1983d). He considered the following three principal sets of data:

(1) accidents involving 10 or more deaths;
(2) accidents involving 2 to 9 deaths;
(3) fire losses.

The data used in this study are given in Tables 22.13–22.15. The accidents listed in Table 22.13 were taken from the list given in Appendix 3 of the first edition of the present book. The table shows process and storage as the source of 14 and 9 accidents, respectively, making the latter 39% of the total. Table 22.14 shows the contribution of storage, rising from 13% for accidents involving 2 deaths to 36% for accidents involving 6–9 deaths. Of the fires given in Table 22.15, 195 were in process and 23 in storage. Storage was thus the source of 11% of the fires. However, 72% of the financial loss was attributable to storage.

Lees states:

> What the foregoing data appear to indicate is that the contribution of storage to deaths in multiple fatality accidents in the oil and chemical industries tends to increase with the number of fatalities and for accidents involving 5 or more fatalities to approach a figure of the order of 20–35%. Thus the idea that material in storage presents a much lower risk than that in process is a half-truth and cannot be accepted without qualification. As far as concerns multiple fatality accidents, and in particular large multiple fatality accidents, the contribution of storage is appreciable.

Since this study the accidents at Mexico City and Bhopal have occurred, both of which involved storage.

22.32 LPG Storage Hazard Assessment

Turning now to hazard assessment of storage, treatments fall into three groups: (1) overview, (2) generic study and (3) specific study. A particular form of the second group is the guidance issued by the HSE or industry associations on safety cases.

Table 22.13 *Some major accidents involving 10 or more deaths in the oil and chemical industries (Lees, 1983d) (Courtesy of Elsevier Science Publishers)*

Date	*Location*	*Deaths*	*Process/storage*
1926	St Auban	19	Storage
1928	Hamburg	10	Storage
1939	Zarnesti	c.60	Storage
1944	Cleveland	128	Storage
1944	Denison	10	Storage
1947	Rauma	19	Storage
1950	Poza Rica	22	Process
1959	Ube	11	Process
1960	Kingsport	15	Process
1962	Toledo	10	Process
1965	Louisville	12	Process
1966	Feyzin	18	Storage
	LaSalle	11	Process
1968	GDR	24	Process
1972	Brazil	37	Storage
	Weirton	10	Process
1973	Potchefstroom	18	Storage
1974	Czechoslovakia	14	Process
	Flixborough	28	Process
1975	Beek	14	Process
	Scunthorpe	11	Process
1976	Chalmette	13	Process
1977	Columbia	30	Process

Overviews of the hazard assessment of LPG pressure and refrigerated storage have been given in the *Canvey Reports* (HSE, 1978b, 1981a), and by Rasbash (1979/80) and Lyon, Pyman and Slater (1982). Generic hazard assessments of LPG pressure and refrigerated storage have been described by Considine, Grint and Holden (1982) and of pressure storage by Drysdale and David (1979/80), T.A. Smith (1985), Crossthwaite (1984, 1986) and Clay *et al.* (1988). Guidance on safety cases for LPG has been issued by the LPGA (1989 GN1). Specific hazard assessments of LPG pressure and refrigerated storage are given in the *Canvey Reports*, and of pressure storage by Khan (1990).

The hazard assessments of LPG given in the *Canvey Reports* are described in Appendix 7 and are therefore not considered further at this point.

The hazard assessments by Crossthwaite and Clay *et al.* are part of a generic methodology for the assessment of LPG, and by extension similar flammable materials, developed by the HSE; they are described in Chapter 9.

The studies by Drysdale and David and by Considine Grint and Holden are essentially generic risk assessments, the former dealing mainly with risk to plant personnel and the latter with risk to the public.

22.32.1 Pressurized storage

The classification of initiating events and hazard scenarios for the pressure storage of liquefied gas shown in Table 22.2 is broadly applicable to LPG. For a pressure storage vessel containing LPG principal hazardous events are catastrophic failure of the vessel, a major crack on the vessel,

Table 22.14 *Some lesser accidents involving two to nine deaths in the oil and chemical industries (Lees, 1983d) (Courtesy of Elsevier Science Publishers)*

	No. of deaths per accident				
	2	3	4	5	6–9
Process					
No. of accidents	26	13	9	4	11
Total no. of deaths	52	39	36	20	81
Storage					
No. of accidents	4	3	3	1	5
Total no. of deaths	8	9	12	5	46
Deaths from storage (%)	13	19	25	20	36

Table 22.15 *Some fire loss data for the petroleum industry*[a] *(Lees, 1983d) (Courtesy of Elsevier Science Publishers)*

	No. of fires	*Frequency of fires* (fires/100 properties)	*Cost per fire* (US$)
Refineries	176	141.9	2,04,000
Natural gas plants	19	3.72	49,000
Tank farms	3	1.05	127,000
Bulk terminals (shore)	11	2.06	313,000
Bulk plants (inland)	9	0.97	195,000

[a] Data are for fires in 1977, as given by the API survey.

a major leak from the associated pipework, release due to overfilling of the vessel, a jet fire and an engulfing fire.

In the hazard assessment made by Drysdale and David (1979/80), the object considered is a 600 te propane pressure storage sphere with, at the four points of the compass, open sea at a distance of 50 m, a chemical plant at 150 m, a main road at 200 m and a loading bay at 50 m. They treat the following events: (1) a crack in the vessel, (2) a small leakage from the pipework and (3) a large leakage from the pipework. They consider the scenarios of a fire at the vessel, leading to a BLEVE, a vapour cloud flash fire and a vapour cloud explosion (VCE).

The authors give fault trees for the estimation of the frequency of: a fire at the sphere due to a small leak and for one due to a large leak; a BLEVE under fire conditions; and for a VCE. Some of the event frequency and probability estimates which they use are shown in Table 22.16, Section A. Many of these estimates are judgement figures and some differ from other literature values.

For ignition they assume the following probabilities for the presence of an ignition source: at the chemical plant, 1.0; at the main road, 0.5; and at the loading bay, 0.05. They further assume that the probability of ignition by the ignition source is 0.5 in each case.

With regard to consequences, these authors make the assumption that all the propane released evaporates. They use the Gaussian passive gas model to estimate the travel distances of the resultant cloud. The principal hazardous outcomes which they consider are a BLEVE and a VCE, the other outcomes being a vapour cloud flash fire and dispersion without ignition.

They assess the risks to the public as very low, but draw attention to the appreciable risk to firefighters from a BLEVE, a risk which was realized at Feyzin.

The object assessed by Considine, Grint and Holden (1982) is one of two 1500 te butane spheres. Two sites are considered, both a 500 m square site with the storage object located at one corner. The urban site is surrounded on all sides by population at 100 m from the site and the remote site by population at a radial distance of 1000 m in all directions. They treat the following scenarios: (1) a catastrophic failure of the vessel (explosive failure), (2) a catastrophic failure (equivalent to a 6 in. nozzle), (3) a fracture of a liquid line, (4) a fracture of a vapour line, (5) overfilling, (6) a serious leak from the pipework and (7) a leak due to a draining or sampling operation.

The authors consider the scenarios shown in Table 22.16, Section B, and give the event frequencies shown in that table.

Their model for ignition at source is as follows:

Release	*Probability of ignition*		
	Immediate	*Delayed*	
		Wind over site	*Wind not over site*
Large instantaneous	0.25	0.25	0.25
1000 te	0.25	0.25	0.1
250 kg/s, 50 kg/s	0.25	0.25	0.1
30 kg/s, 16 kg/s	0.15	0.15	0.05

The probability of ignition of a cloud reaching the edge of the populated area is taken as 0.7 and that of ignition over the populated area as 0.2.

For both for the pressure storage and refrigerated storage cases, Considine, Grint and Holden consider the following scenarios (1) immediate ignition at source, (2) delayed ignition at source, (3) ignition at the edge of the population zone and (4) ignition over the centre of the population zone.

For pressure storage, the immediate ignition at source of an instantaneous release is assumed to give rise to a fireball, and the immediate ignition of a continuous release is assumed to give rise to a jet flame, or torch fire. If ignition is not immediate, the cloud drifts. For an instantaneous release the assumption of complete vaporization is made and the gas dispersion is modelled using the DENZ dense gas dispersion code. The method used for the dispersion of the continuous releases is unclear, but appears to be the Gaussian model. For the three cases of delayed ignition the outcomes are flash fires and VCEs.

The authors assumed that catastrophic explosive failure of one of the spheres would cause failure of the other also. Furthermore, a proportion of torch fires are capable of causing a BLEVE of a sphere. The total frequency of torch fires was assessed as 3×10^{-3}/year and that of BLEVEs as 7.1×10^{-5}/year.

Thus the principal outcomes considered are: an explosive failure, generating missiles and causing failure of the other sphere; a fireball; jet flames; a BLEVE; a vapour cloud fire and a VCE. The authors outline the models used and the associated injury relations.

The risks estimated in this hazard assessment are given in Section 22.32.3.

It will be apparent from this description that different analysts tend to formulate scenarios in somewhat different ways, even where the events considered are similar.

22.32.2 Refrigerated storage

The classification of initiating events and hazard scenarios for the refrigerated storage of liquefied gas shown in Table 22.2 is broadly applicable to LPG.

For a refrigerated storage tank containing LPG the principal hazardous events are catastrophic failure of the tank, explosion in the vapour space of the tank, rollover, a major leak from the associated pipework and release due to overfilling of the tank.

The object assessed by Considine, Grint and Holden (1982) is a single refrigerated atmospheric fixed roof, single-wall storage tank containing butane positioned at the same location as the two pressure storage spheres already described. They treat the following events: (1) catastrophic failure of the tank, (2) rollover, (3) overfilling, (4) a fracture of a liquid line and (5) a leak from the pipework.

The authors consider the scenarios shown in Table 22.16, Section C, and give the event frequencies shown in that table. They use the same ignition model as for the releases from pressure storage.

As for the pressure storage case they consider the four cases of immediate ignition at the source and of delayed ignitions at the source, at the edge of and over the population zone.

For instantaneous release by catastrophic failure of the refrigerated storage tank, Considine, Grint and Holden take into account overtopping of the bund. Immediate ignition of an instantaneous release is assumed to give a pool fire. If ignition is not immediate, vaporization occurs, which the authors estimate using the SPILL code. Immediate ignition of a continuous release is evidently also assumed to result in

Table 22.16 *Event frequency/probability estimates given in two LPG hazard assessments (after Drysdale and David 1979/80; Considine, Grint and Holden, 1982)*

A Pressure storage sphere: Drysdale and David

	Frequency/probability (per year)
Crack in pipe	10^{-4}/year
Gasket failure	5×10^{-5}/year
Flange failure	4×10^{-5}/year
Valve seating failure	3×10^{-2}/year
Drainage/sampling valve not properly shut	10^{-4}/year
Pipe rupture due to:	
Vehicle impact	10^{-5}/year
Vibration	10^{-2}/year
Corrosion	10^{-4}/year
Repair whilst operating	10^{-4}/year
Excess pressure (blockage)	$10\sim^{7}$/year
Fatigue	10^{-4}/year
Creep	10^{-5}/year
Sabotage	2×10^{-3}/year
During filling operation:	
Operator fails to stop filling when correct level is reached	0.1
Operator fails to stop pump quickly enough when release occurs	10^{-2}
Fixed water spray inoperative because:	
Water shut-off	10^{-2}
Activation fails	2×10^{-2}
Water frozen	5×10^{-4}
Pipes completely blocked	10^{-4}
Low main pressure	3×10^{-3}
Sprinkler system damaged	10^{-5}
Fixed water spray system ineffective because:	
Pipes partially blocked	3×10^{-4}
Low mains pressure	2×10^{-3}
Some heads blocked	8×10^{-4}

B Pressure storage: Considine, Grint and Holden

Event	*Frequence*[a]*/probability*	*Flow*[b]
Catastrophic failure of vessel:		
Complete failure	3×10^{-6}/vessel-year	Instantaneous release of 1500, 2250 or 3000 te
Failure equivalent to 6 in. nozzle	7×10^{-6}/vessel-year	15 te/min
Fracture of 6 in. liquid line[b]		1 te, or 1 te + 50 kg/s
Pipework	3×10^{-7}/m-year	
Equivalent failure of fittings	5×10^{-6}/item-year	
Release due to overfilling[c]	10^{-4}/vessel-year	30 kg/s
Fracture of 2 in. vapour line	3×10^{-6}/m-year	1 kg/s
Serious leak from equipment or pipework (1 kg/s):		
6 in. pipework	6×10^{-6}/m-year	
2 in. pipework	6×10^{-5}/m-year	
Flange	3×10^{-4}/flange-year	
Pump seal	5×10^{-3}/seal-year	
Release in course of draining or sampling (1.5 kg/s):		
Release per operation	10^{-4}	
Draining operations	50/year	
Sampling operations	100/year	
Failure to recover during draining	10^{-1}	
Failure to recover during sampling	10^{-2}	

Table 22.16 *continued*

C Refrigerated atmospheric storage: Considine, Grint and Holden[b]

Event	*Frequency*[a]	*Flow*[b]
Catastropic failure of tank	5×10^{-6}/tank-year	Instantaneous release of 1500, 2250 or 3000 te
Rollover[e]	10^{-5}/tank-year	Instantaneous release of 1500, 2250 or 3000 te
Overfilling[d, f], of which:	10^{-5}/tank-year	
With tank failure[e]	10^{-5}tank-/year	Instantaneous release of 1500, 2250 or 3000 te
Without tank failure[e]	9×10^{-5}/year	50 kg/s
Fracture of 6 in. liquid line	As Section B	50 kg/s
Leak from pipework, etc.	As Section B	1 kg/s

[a] Basic frequencies for a single vessel or tank.
[b] The flows given are complex; quantities quoted here are specimen values and in some cases are not sustained for more than 1 minute.
[c] Probability of emergency shut-off failure 0.2
[d] Based on protective system design.
[e] Probability of wall-base failure 0.25; probability of wall-roof failure 0.75.
[f] Probability that operator switches off pump and limits the event to a release into the bund rather than tank failure, 0.9.

a pool fire. The dispersion of releases which are not immediately ignited at source is modelled using the same method as for the pressure storage study. Outcomes of delayed ignition of these releases are pool fires, torch fires, vapour cloud flash fires and VCEs.

Further principal sources of information on the frequency or probability of events, on consequences and on assessed risk for LPG storage are the *Canvey Reports* and the *Rijnmond Report*.

22.32.3 Pressurized vs refrigerated storage

The study conducted by Considine, Grint and Holden was primarily directed at the comparison of the risks arising from the two types of butane storage in the two types of location. The comparative risks assessed by these authors for the specific configurations considered are:

Site	*Storage*	*Individual* ($\times10^{-6}$ year^{-1})	*Societal risk (casualties >N)* ($\times10^{-6}$ year^{-1})			
			>10	>100	>1000	>5000
Urban	Pressurize	102	159	84	76	40
	Refrigerate	35	66	7.1	7.0	1.6
Rural	Pressurize	12	76	76	76	36
	Refrigerate	0.26	2.0	2.0	0.08	–

Pantony (1985), D.F. Cooper and Chapman (1987) and P. Roberts (1990).

The classification of initiating events and hazard scenarios for the refrigerated storage of liquefied gas shown in Table 22.2 is broadly applicable to LNG.

Considering some of the accounts mentioned, the treatment given by Kopecek (1977) is fairly general but includes a somewhat more detailed treatment than is generally found of the following natural events: (1) severe winds and tornadoes, (2) storm waves, tsunamis, (3) earthquakes and (4) meteorites.

R.A. Cox *et al.* (1980) deal with the hazard assessment of terminals rather than storage *per se*. The storage which they considered is a double integrity tank with inner steel and outer concrete walls and an earthen berm. They give for catastrophic failure of the inner tank leading to outer roof collapse and for partial fracture of the outer roof due to

22.33 LNG Storage Hazard Assessment

Overviews of the hazard assessment of refrigerated LNG storage have been given in the two *Canvey Reports* (HSE, 1978b, 1981a) and the *Rijnmond Report* (Rijnmond Public Authority, 1982) and by Kopecek (1977), R.A. Cox *et al.* (1980), Philipson (1980), Kunreuther and Lathrop (1981), Lyon, Pyman and Slater (1982), Nassopoules (1982), Philipson and Napadensky (1982), Valckenaers (1983), Wicks (1983), D.A. Jones (1985), Valk and Sylvester-Evans (1985), Napier and Roopchand (1986), D.F. Cooper and Chapman (1987) and Navaz (1987). Specific hazard assessments of LNG refrigerated storage are given in the *Canvey Reports* and the *Rijnmond Report* and by Philipson (1980), Dale and Croce (1985), D.A. Jones (1985), Setters, Luck and

overpressure typical frequencies of 2×10^{-6} and 2×10^{-5}/year, respectively. They also give a typical failure frequency of 2×10^{-6}/year for catastrophic failure of a refrigerated ethane storage tank.

The accounts by Nassopoules (1982) and Closner and Wesson (1983) are concerned primarily with tank system designs, the former with a membrane system and the latter with double wall systems. Both give detailed consideration to the scenario of a tank fire in an adjacent tank. Closner and Wesson also consider a release from the inner tank, and earthquakes, missiles and blast.

D.A. Jones (1985) reviews refrigerated LNG storage systems, identifies five basic design concepts and summarizes the hazard assessments performed for installations

embodying each of these concepts. Details of the assessments are sparse except for the Canvey studies. He does, however, give the following summary of the overall risks for exemplars of three of the five types of system:

Design	*Individual*	*Societal risk*
1. Single wall tank+low bund	2×10^{-6} 1.8×10^{-6}	9.3×10^{-6} 5.5×10^{-6}
2. Single wall tank+high bund	4×10^{-12} 8.5×10^{-9}	Negligible[a] 9×10^{3}[b]
3. Double integrity tank system	Nil	Nil

[a] No more than two offsite casualties.
[b] Risk for 100–1000 casualties.

The overview of hazard assessment methodology by Napier and Roopchand (1986) quotes the frequency estimates for LNG terminals given by R.A. Cox *et al.* and those of release duration on LNG plants given by H.H. West, Pfenning and Brown (1980). Napier and Roopchand also give information on models for vaporization, heavy gas dispersion, pool fires, flash fires and VCEs.

The account by P. Roberts (1992) refers to a hazard assessment of a double integrity LNG tank with a prestressed concrete outer wall. Failure of the tank roof was considered and the consequences found to be limited, provided the integrity of the tank walls was maintained. An analysis was undertaken to demonstrate the integrity of the outer wall. Consideration was given to the various initiating events such as earthquakes, severe impacts, frost heave, settlement and blast. The risk was assessed as negligibly low.

Further principal sources of information on the frequency or probability of events, on the consequences and on the assessed risk for LNG storage are the Canvey Reports and the Rijnmond Report.

22.34 Ammonia Storage Hazard Assessment

Overviews of the hazard assessment of ammonia pressure and refrigerated storage are given in the *Canvey Reports* (HSE, 1978b, 1981a) and overviews of pressure storage are given in the *Rijnmond Report* and by Resplandy (1967). Guidance on safety cases for ammonia has been issued by the CIA (1989 GN1). Specific hazard assessments of ammonia pressure and refrigerated storage are given in the *Canvey Reports*, of pressure storage in the *Rijnmond Report* and of refrigerated storage by Squire (1991).

The classification of initiating events and hazard scenarios for the pressure and refrigerated storage of toxics shown in Table 22.2 is broadly applicable to ammonia.

The hazard assessments of ammonia storage in the first *Canvey Report* and the *Rijnmond Report* are described in Appendices 7 and 8, but mention may be made here of the scenarios considered in those studies.

For the Fisons ammonia pressure storage sphere the First *Canvey Report* considers for the vessel occurrences of spontaneous failure, engulfment in fire, blast effects and missile impact. Ignition of the thermal insulation on the vessel was identified as a possible scenario, but was quickly discounted. The Shell refrigerated ammonia storage tank system was of the high bund type. For this tank the report considers the scenario of a fire engulfing the bund wall. Apart from this, the report states: 'The concrete collar ensures that the failure of the main tank cannot create a major hazard. The actual consequence of inner tank failure with the bund intact is virtually zero'. Various events initiating release from pipework associated with the storage were also taken into account. By the time of the Second *Canvey Reports*, both the pressure storage sphere and the refrigerated storage tank were no longer in use.

One of the six objects studied in the *Rijnmond Report* was the UKF ammonia pressure storage sphere. Initiating events considered were catastrophic failure of the vessel, a major crack in the vessel and full bore fracture of the liquid and vapour lines on the vessel.

An account is given by Squire (1991) of measures for enhancing the integrity of a refrigerated ammonia storage tank, which includes reference to a hazard assessment. The site handles a number of toxic substances, but the ammonia tank was assessed as constituting 50% of the total risk. Scenarios considered included catastrophic failure and rollover, or at least thermal overload, of the tank, and release from large pipework.

As indicated, the main sources of information on the frequency or probability of events, on the consequences and on the assessed risk for ammonia storage are the First *Canvey Report* and the *Rijnmond Report*.

22.35 Notation

Section 22.4

A surface area of pool (m^2)
C calorific value of liquid (kj/kg)
D diameter of tank (m)
k_1 constant
Q heat radiated from the flame envelope (kW)
r liquid burning rate (m/s)
ρ density of liquid (kg/m^3)

Section 22.8

Equations 22.8.1 and 22.8.2

A total wetted surface (ft^2)
F environmental factor
Q total heat absorption (BTU/h)

Equations 22.8.3 and 22.8.4

C net calorific value of liquid in pool (kj/kg)
h height of flame (m)
I intensity of heat radiation from the flame envelope (kW/m^2)
L length of pool (m)
Q heat emitted by fire (kW)
W width of pool (m)
ρ density of liquid (kg/m^3)

Section 22.10

T absolute temperature of liquid
x mole fraction of methane
α coefficient of expansion of liquid with respect to concentration
β coefficient of expansion of liquid with respect to temperature
ρ density of liquid

Section 22.11

Equation 22.11.1

R interface stability parameter
S concentration of impurity (mass fraction)
T absolute temperature of liquid
α coefficient of expansion with respect to temperature
β coefficient of expansion with respect to concentration

Equation 22.11.2

b boil-off rate
C_p specific heat of liquid
g acceleration due to gravity
H_v latent heat of vaporization of methane
k thermal conductivity of liquid
T_n absolute temperature of liquid in top or nth cell
T_s absolute saturation temperature of methane in LNG
μ viscosity of liquid
ρ density of liquid
ρ_o average reference density of liquid

Section 22.21

Subsection 22.21.4

h height of bund
H original height of liquid
L distance between tank wall and bund
R radius of tank
x, y dimensions of bund walls

Subsection 22.21.8

g acceleration due to gravity
h initial height of liquid in tank
M_f effective fluid mass
M_s effective mass of tank shell
R resistance to flow
t time
u velocity of fluid
x distance
ρ density of fluid

Section 22.24

Equation 22.24.1 only

η filling ratio
ρ_p density of liquid at reference temperature
ρ_w density of water at 15°C
ϕ fractional free space

Equation 22.24.2 only

g_i specific gravity of liquid at reference temperature
g_t specific gravity of liquid at its lowest temperature of filling
U_{max} maximum permissible volume
V internal volume of vessel

23 Transport

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So far the loss prevention problems discussed have been principally those of fixed installations. It is necessary, however, to consider also the transport of hazardous materials.

Some aspects of this transport which need to be considered include:

(1) regulatory control;
(2) classification;
(3) packaging and labelling;
(4) transport containers;
(5) hazards;
(6) hazard assessment;
(7) emergency planning.

For each mode of transport, consideration has to be given to:

(1) controls and codes;
(2) hazard scenarios;
(3) design;
(4) operation.

In addition, the features particular to a mode must be considered.

A general account of regulatory controls and of codes applicable to transport internationally and in the United Kingdom has been given in Chapter 3. More detailed information on controls and codes is given in the following sections for road, rail, waterway, pipeline and sea transport.

A major source of information on transport and the associated hazards and risks is *Major Hazard Aspects of the Transport of Dangerous Substances* by the Advisory Committee on Dangerous Substances (ACDS, 1991) (the ACDS *Transport Hazard Report*). This report deals with marine, road and rail transport, and describes the regulatory regimes and transport environments as well as the hazards and risks. It considers in particular four substances which are both representative as well as themselves constituting a large proportion of the movements of dangerous substances: motor spirit, liquefied petroleum gas (LPG), ammonia and chlorine. The report also deals with explosives and ammonium nitrate. The ACDS *Transport Hazard Report* is described in more detail in Appendix 17.

Selected references on the transport of hazardous materials are given in Table 23.1.

Sources of Information on Transportation of Hazardous Materials

Because transportation regulations, requirements and best practices are changing constantly, the following is a list of reference websites which contain up-to-date information on regulatory and non-regulatory information concerning transport of hazardous materials.

International

www.iata.org

The International Air Transport Association (IATA) fosters safe and efficient air transport, including transportation of hazardous materials.

www.imo.org

The International Maritime Organization (IMO) is the United Nations specialized agency responsible for improving maritime safety and reducing pollution from ships.

Table 23.1 *Selected references on the transport of hazardous materials*

NRC (Appendix 28 *Transport*); D.R. Davis (1958); R. Lee (1961); Anon. (1962a); J.E. Browning (1969b); Pence (1969); Byrd (1970); J.R. Hughes (1970); McConnaughey *et al.* (1970); A.W. Clarke (1971a,b); A.B. Kelly (1971); National Transportation Safety Board (NTSB) (1971); Bigelow (1972); Institution of Fire Engineers (1972); *Chemical Engineering* (1973a); NFPA (1973/10); Pignataro (1973); Walmsley (1973, 1974); W.S. Wood (1973, 1982b); MCA (1974TC-20); Unwin, Robins and Page (1974); Westbrook (1974); Gay (1975); Malcolm (1975); Meadowcroft (1975); Peeler (1975); Whitbread (1975); Cantilli *et al.* (1976); D.R. Davies and Mackay (1976); Horodniceanu *et al.* (1976, 1977); Philipson (1976); Appleyard (1977); CONCAWE (1977 7/77); Druijff (1977); Flynn and Morrissette (1977); John (1977); Mullins (1977); Zedde (1977); ICE (1978); Horodniceanu and Cantilli (1979); IBC (1979/4, 1981/20, 1982/37, 1985/65, 1992/94, 1993/106); Napier (1979a); Nimptsch (1979); Luckritz and Schneider (1980); Cannon (1983b); Vumbaco (1983); Bierlein (1984); Ichniowski (1984, 1987); Belardo, Pipkin and Seagle (1985); Ackermann (1986); Carnes (1986); Kazarians, Boykin and Kaplan (1986); Kletz (1986J); Dryden and Gaweckie (1987); Frey and Handman (1987); Walker (1987); Chemical Industries Association (CIA) (1989 RC27); Belanger (1990); Burns (1990); N. Lees (1990); Beroggi and Wallace (1991); Canadine (1991); UN (1991); Croner Publishing (1993); B. Davies (1993)

Containers, packaging
Dowling (1960); Norden (1960d); Ayers and Rhodes (1963); Uncles (1966); Home Office (1968); McKinley (1968); J.E. Browning (1969b); A.W. Clarke (1971b); Lunn (1971, 1975); Raymus (1973); Swinbank (1973, 1975); Bohlman (1975); G.J. Lewis (1975); R.K. Roberts (1975); Steel (1975a,b); Department of Trade (1977); IMCO (1977); H. Morris (1977); Bond (1978); Boocock (1978); Cronin (1978); Gregory (1978); Anon. (1980 LPB 32, p. 15); Chlorine Institute (1980 Publ. 17, 1985 Publ. 8); Petherbridge and Kinder (1983); HSE (1986 CS 17, HS(G) 26,1992 CRR 37, HS(G) 78); Schilperoord (1986); Ashmore (1988 LPB 80); Blumel and Schulz-Forberg (1989); Shattes (1986); Anon. (1990c); NFPA (1990 NFPA 386); CIA (1991 RC35, RC37,1992 RC59); UN (1991); Simpson and Jones (1992)

Gas cylinders
BCGA (Appendix 27, 1988 GN2); CGA (Appendix 28, 1966/1); HSE (1990 IND(G) 78(L))

Labelling
MCA (SG-18, 1976/24); D.L. Davies (1975); Rees (1975); Anon. (1978j); Williamson (1978); Anon. (1979h); Selikoff (1979); Anon. (1980 LPB 32, p. 15); O'Connor and Lirtzmann (1984)

Radio-telephones
ACDS (1991); British Gas (1992 GBE/DAT31); IP (1993 TP20)

COSHH in transport
CIA (1991 RC50)

Road
Department of Energy (n.d., 1974, 1976a); DoT (n.d., 1978, 1987a,b, 1992b, 1993a,b); NSC (n.d./5, 8); NTSB (Appendix 28 *Highway*

Accident Reports); OIA (Publ. 711); Brantley (1964); Steymann (1966); BCISC (1967/6); Danskin (1969); Olsen (1969); H. Lewis (1971); Rohleder (1971); Brobst (1972); Harvison (1972, 1973, 1981); Ramsey (1972); CIA (1973/4, 5, 1988 CE4, PA16, 1990 RC26); DoE (1974/5); IMechE (1975/20, 23, 1976/26, 30, 1977/32, 1978/48, 1983/72); Rutherford (1975); P.N. Anderson (1977); Ashton (1977); Davison (1977); Hudson (1977); Rickett (1977); Watters (1977); Anon. (1978 LPB 19, p. 1); HSE (1978b, 1981a, 1983 GS 26 91990 IND(G) 96(L)); Napier (1979a); Anon. (1981 LPB 39, p. 17); Botkin (1981); Chlorine Institute (1981 Publ. 76, 1984 Publ. 49); Eiber (1981); Heller (1981); A.D. McLean (1981); Rudram and Lambourn (1981); ASME (1982/191); Anon (1984jj,ll); M. Griffiths and Linklater (1984); Jäger (1984); Sewell (1984a); Bressin (1985); Hawkins (1985); Lambourn (1985); Allsop *et al.* (1986); API (1986 Publ. 2219, 1988 RP 1004); L.A. James (1986); Kessler (1986); Anon. (1987 LPB 76, p. 30); Grime (1987); Walker (1987); Glickman (1988); Canadine and Purdy (1989); Harwood, Russell and Viner (1989); Saccomanno *et al.* (1989); Anon. (1990c); Anon. (1990 LPB 94, p. 10); Gorys (1990); Harwood, Viner and Russell (1990); NFPA (1990 NFPA 385, 512, 513, 1992 NFPA 498); Ouellette, Hoa and Li (1990); Rhyne (1990); Saccomanno, Shortreed and Mehta (1990); Steward and van Aerde (1990a,b); ACDS (1991); UN (1991); Croner Publishing (1993); Department of Transport (DTp) (1993a); Purdy (1993); IP (1994/4, 5)

Pressure relief: Hawksley (1990 LPB 91): UN (1991)

Rail

BR (n.d.a,b); NTSB (Appendix 28 *Railroad Accident Reports*); Danielson (1964); Walton (1964); Heller (1965); Steymann (1966); Engel (1969); ASME (1971/188); Barren (1971); Maughan (1971); E.A. Phillips (1971); AAR (1972); Banks (1972); O'Driscoll (1972, 1975b, 1976, 1978); Stanek (1973); MCA (1974 TC-7); CIA (1975 PA1); Fizer (1976); P.J. Lynch (1977); HSE (1978b); Chlorine Institute (1979 Publ. 66); Napier (1979a); National Supply Co. (UK) Ltd (1979); R.K. Cooper (1980); Taig (1980); Sanderson (1981); IMechE (1983/72); Schlitchtarle and Huberich (1983); Ichniowski (1984); Jopson and Bale (1984); Hawkins (1985); Glickman (1988); J.L. Woodward and Silvestro (1988); Canadine and Purdy (1989); G.O. Rogers and Sorenson (1989); Saccomanno and El-Hage (1989); Saccomanno *et al.* (1989); J.L. Woodward (1989b); Gorys (1990); Rhyne (1990); Saccomanno, Shortreed and Mehta (1990); ACDS (1991); DTp (1993b); Janes Information Group (1993c); Tenniswood, Sharp and Clark (1993)

Tunnels

W.E. Baker *et al.* (1979); Larson, Reese and Wilmot (1983); Anon. (1985ee); HSE (1985e); A. Jones (1985); Considine (1986); M.M. Grant (1989); NFPA (1992 NFPA 502); Charters, Gray and McIntosh (1994)

Waterways

Martinson (1964); H.P. Nelson (1964); Steymann (1966); Briley (1967); Sohnke (1971); French and Richards (1973); Backhaus and Janessen (1974); Chlorine Institute (1984 Publ. 79); Ligthart (1980); Backhaus (1982); Boniface (1989); J.R. Thompson *et al.* (1990); API (1991 RP 1125)

Pipelines

AGA (Appendix 28); ASCE (Appendix 28, 1965/19, 1975/5, 1978/7, 1979/8, 1983/14, 1984/17, 20, 1988/37, 1991/44); ASME (Appendix 28 *Pipeline Engineering*); British Gas (Appendix 27, 28); NTSB (Appendix 28 *Pipeline Accidents Reports,* 1978); Henderson (1941); Anon. (1964c); Lennart (1964); H.P. Nelson (1964); IGasE (1965/7, 1967/89, 1976/10); F.C. Price (1965, 1974a,b); BRE (1966/3); Chilton (1966); FPC (1966); Hubbard (1967); IP (1967 Model Code Pt 6); N.W.B. Clarke (1968); Inkofer (1969); Rohleder (1969); Prescott (1970); Wasp, Thompson and Snoek (1971); Cleveland and Young (1972); Davenport and Brameller (1972); Walker, Coulter and Norrie (1972); Weiner, Mercer and Gibson (1972); Gibson, Knowles and Mercer (1973); N.W. Roberts and Stewart (1973); Smelt and James (1973); Devine *et al.* (1974); DOT (1974); C.C. Hale (1974); Anon. (1975f); L.J. Allen (1975); DOT, OPS (1975); Luddeke (1975); Newmark and Hall (1975); Szilas (1975); CONCAWE (1977 9/77); Demars *et al.* (1977); DOT, OPSO (1977b); Gulf Publishing Co. (1977); IGasE (1977 Comm. 1044, IGE/TD 1); Knowles, Tweedle and van der Post (1977); McKay *et al.* (1977); Sterling (1977); Dickson (1978); HSE (1978b,d, 1980a,c); ASME (1979 *Pressure Piping Code* B31.4, 1989 *Pressure Piping Code* B31.8); Bryce and Turner (1979); Muleski, Ariman and Auman (1979); Riley (1979); Shinozuka, Takadu and Ishakawa (1979); Tasucher and Streiff (1979); Wang and Cheng (1979); Thorley (1980); M.J. Turner (1980); de la Mare and Andersen (1981); Sheffy (1981); Stephenson (1981a); Chlorine Institute (1982 Publ. 60); N.C. Harris (1982); Sabnis, Simmons and Teuscher (1982); Whalley and Long (1982); Whittaker *et al.* (1982); Considine (1983); Diab (1983); API (1984/14, 1985 Publ. 1108, 1988 Std 1104, 1991 RP 1107, 1110, 1118, 1119, 1120, 1993 RP 1102, 1109, 1113); Blything (1984 SRD R326); Forsyth (1984); G.G. King (1984); Pipeline Industries Guild (1984); Berryman and Daniels (1985); Bruce (1985); Fearnehough (1985); Jinsi (1985); Kipin (1985); Lund *et al.* (1985); Stripling, Khan and Dillon (1985); True (1985); Darton (1986); Redman (1986a,b); BP Petroleum Development Ltd (1988); C.C. Hale and Lichtenberg (1988); NRC, Transportation Research Board (1988); Bolt and Logtenberg (1989); D.A. Carter (1991); Colombari *et al.* (1992); Ahammed and Melchers (1993); DTI (1993); de la Mare and Bakouros (1994)

Corrosion protection, cathodic protection: AGA (1979/29, 1990/67); British Gas (1992 GBE/ECP)

Plastic pipelines: British Gas (1985 Comm. 1281, 1986 BGC/PS/PL2); AGA (1989/12)

Trenchless technology: International Society for Trenchless Technology (1991); ACGIH (1992/86)

Sea

ICS (Appendix 27, 1974); IP (n.d.); NTSB (Appendix 28 *Marine Accident Reports);* OCIMF (Appendix 27); SIGTTO (Appendix 28); Wardle (n.d.); Minorsky (1959); Burgoyne (1965a); Rawson and Tupper (1968–); Comstock and Robertson (1969); Dickinson (1969); Dyer (1969); Advisory Committee on Carriage of Dangerous Goods by Sea (1971); DTI (1971); Lakey (1971, 1973, 1976); Neal (1971); Page and Gardner (1971); Stirling (1972); H.D. Williams (1972, 1973); F.A. Smith (1973); European Petroleum Organisations (1974); Kahn, Talbot and Woodward (1974); Mostert (1974); Boe and Foleide (1975); Chapman (1975); Eisenberg, Lynch and Breeding (1975); Swinbank (1975); Henderson, Srinivansan and Gower (1976); NPC (1976); JJ. Smith (1976); Davison (1977); IMCO (1977); Mullins (1977); Tanker Safety Group (1977); HSE (1978b, 1981a); ICS/OCIMF (1978); van Poelgeest (1978); Snow (1978); Planning Research Corp.

(1979); Bockenhauer (1980); Rutherford (1980); B.White (1980); Gardenier (1981); Gregory (1981); Aldwinkle and Slater (1983); van den Brink (1983); Georgas (1983); Hendrickx and Lannoy (1983); van der Horst and van der Schaaf (1983); Hough (1983); Preston (1983); Colonna (1984, 1986); Fleming (1984); Champness and Jenkins (1985); ACDS (1991); API (1991 RP 1140, 1993 RP 1139); DoT (1992); Janes Information Group (1993b); Paris Memorandum (1993); Donaldson (1994); Gilbert (1994); Hodges (1994); K James (1994); Jenkins (1994); Rawson (1994)

Codes, classification rules, regulation: AW. Clarke (1971a); DTI (1971); Lakey (1971, 1973, 1976); Kvamsdal (1973); R.K. Roberts (1973); International Chamber of Shipping (1974); IMCO (1977); Anon (1984r); R. Pearson (1984); J. Smith (1994)

Cargo compatibility: Flynn and Rossow (1970a,b); Flynn and Morrisette (1977); Morrisstte (1979)

Hazard information systems: DOT, CG (1974a–d); Butt (1975); Myatt (1975); Rappaport (1975); Willis and Cece (1975)

Human factors: Page (1971); Leeper (1973); Hooft, Keith and Porricelli (1975); D. Anderson, Istance and Spencer (1977)

Vessel design: Comstock (1967); Rawson and Tupper (1968); Barnaby (1969); J. Cox (1971); R.K. Roberts (1973, 1983); Hansen and Vedeler (1974); Chapman (1975); N. Jones (1976, 1983); Eyres (1978); HSE (1978b, 1981a); Kitamura, Okumoto and Shibue (1978); Bockenhauer (1982,1985); Clayton and Bishop (1982); Farrell (1982); Huther and Benoit (1983); Jean and Lootvoet (1983); Kinkead (1983, 1985 SRD R324); Betille and Lebreton (1986); Egge and Bockenhauer (1991)

Cargo tanks: Schampel and Steen (1975, 1976); Bockenhauer (1982)

Ship movement: A.G. Robinson (1971); Bovet (1973); Computer Sciences Corp. (1973); P.W.W. Graham (1973); US Coast Guard (1973); McDuff (1974); Eda (1976); J.W. Miller, Schneider and Varchok (1976); NPC (1976); Port of London Authority (1977); HSE (1978b, 1981a); Transportation Systems Centre (1978); ASCE (1980/11, 1983/14, 1986/28, 1989/37); Ligthart (1980); Brok and van der Vet (1984); Mankabady (1982); Technica (1985); ACDS (1991)

Collision, grounding: E. Chen (1975); Kinkead (1978 SRD R91, 1985 SRD R342); Vaughan (1978); Ligthart (1980); Poudret *et al.* (1981); Asadi and Vaughan (1990): ACDS (1991)

Ship–shore transfer: B.White (1980); Armitage (1983); T.B. Morrow *et al.* (1983); Bond (1986 LPB 71); Holtkamp and Keech (1989)

Emergency response, planning: Preston (1983); NFPA (1990 NFPA 1405); ACDS (1991)

Pollution: Stubberud (1973); European Petroleum Organisation (1974); Hann and Jensen (1975); Lakey (1976); Fleming (1984)

Tank purging, cleaning, inerting and flame protection: Page and Gardner (1971); Bang and Birkeland (1973); Boddaert (1975); Harth (1975); Savage (1975); Schampel and Steen (1975, 1976, 1977); Steensland, Askheim and Vossgard (1975); R.P.Wilson and Atallah (1975); Berkel (1982); Astleford, Morrow and Buckingham (1983); Anon. (1984s); Astleford, Bass and Colonna (1985)

Vapour emission, vapour emission control: T.B. Morrow (1980, 1982b, 1985); T.B. Morrow *et al.* (1980); API (1989/17, 1991 RP 1124, 1992/20); Lawrence and Cross (1994)

Fire, explosion: Burgoyne (1965a); Schb'n (1968); Page and Gardner (1971); Victory and Roberts (1971); Wilse (1974); Barreto (1975); Goland and Critelli (1975); Kitagawa (1975); J.H. Lee, Knystautas *et al.* (1975); Rushbrook (1979); Takeda (1988)

Static electricity: H.R. Edwards (1983); J.S. Mills and Oldham (1983); M.R.O. Jones and Bond (1984, 1985)

Fire protection: Page and Gardner (1971); Tanner (1976); Rushbrook (1979); Anon. (1980o, 1982k); Dicker and Ramsey (1983); Dimmer (1986); Wynne (1986); Gebhardt (1989); McKenna (1989); ACDS (1991); NFPA (1993 NFPA 306)

Containers, packing: Savi (1971); Stubberud (1971); Buschmann (1973); Kemler (1975); Swinbank (1975); Department of Trade (1977); UN (1991)

Ports, port storage

McKinley (1968); Meijer (1968); Dickinson (1969); Murdoch (1971); Siccama (1971); Bohlin (1973); J.R. Bradley (1973); Vossenaar (1975); Davison (1977); Hartlich (1977); HSE (1978b, 1980 HS(G) 7, 1981a, 1986 GS 40); ASCE (1980/11, 1983/15, 1986/29, 1989/38); Bryce (1980); Gebhardt (1980, 1989); P. Lewis (1981); NFPA (1990 NFPA 307); ACDS (1991)

Air

Pike (1975a,b); Civil Aviation Authority (CAA) (1977); K Warner (1981); Wilkinson (1989); Janes Information Group (1993a)

Particular chemicals

Ammonia: Heller (1965, 1981); Briley (1967); Inkofer (1969); Olsen (1969); Rohleder (1969, 1971); Medard (1970); Cato and Dobbs (1971); Caserta (1972a); C.C. Hale (1974); CIA (1975/9, PAI); Eisenberg, Lynch and Breeding (1975); Luddeke (1975); O'Driscoll (1975a); Sterling (1977); Fiber (1981); DCMR (1985); Josefson (1987); C.C. Hale and Lichtenberg (1988)

Chlorine: Chlorine Institute (Appendix 28, 1979 Pmphlt 66, 1981 Pmphlt 76, 1982 Pmphlt 60, 1984 Pmphlt 49, 79, 1986 Pmphlt. 1); Danielson (1964); H.P. Nelson (1964); R.L. Mitchell (1971, 1972, 1982); Mathiesen, Bakke and Boe (1973); Westbrook (1974); Eisenberg, Lynch and Breeding (1975); Macdonald (1977); DCMR (1985); Hunter (1988); J.L. Woodward and Silvestro (1988); Canadine and Purdy (1989); Rhyne (1990)

Explosives: P.A. Davies (1990, 1993); ACDS (1991); Sorenson, Carnes and Rogers (1992); Gilbert, Lees and Scilly (1994a–i)

LNG (*see* Table 11.23)

LPG: Faridany and Ffooks (1983); Jäger (1984); Puklavec and Lindenau (1985); Davenport (1988); Anon. (1990c)

Monomers: Butcher and Sharpe (1983); Kurland and Bryant (1987)

Petroleum: J.R. Hughes (1970); Page and Gardner (1971); F.A. Smith (1973); IP (1982 MCSP Pt 6)

Particular chemicals: other chemicals

Carbon dioxide: Brumshagen (1983)

Ethylene: Anon. (1962f); Waddams and Cann (1974); McKay *et al.* (1977); Backhaus and Olschlager (1985)

Lead additive: Associated Octel (1972 Bklt 23/72, 1975 Bklt 22/75)

Liquefied gases: Purdy *et al.* (1988)

Peroxides: Anon. (1984ee)

Polybrominated biphenyls (PBBs): Jacobs, Chou and Tiedje (1976); Kay (1977)

Radioactive materials: Pike (1975a,b); DoE (1975/5); Wilson (1981 LPB 42); Tuler, Kasperson and Ratick (1989)
Self-heating materials: Stone, Williams and Hazlett (1976)
Sulfur: Landry and Hiller (1975)
Vinyl chloride: Dowell (1971); Kogler (1971); O'Mara, Crider and Daniel (1971); Wheeler and Sutherland (1975); Mukerji (1977)

Fire (*see* Tables 16.1 and 16.2)
Spill control (*see also* Table A11.1)
R.L. Mitchell (1971, 1972, 1982); Baier *et al.* (1975); Brugger and Wilder (1975a,b); G.W. Dawson (1975); Pilie *et al.* (1975); Bulloff and Sinclair (1976); Froebe (1976, 1985); Temple *et al.* (1978); Thorne (1978a); Zadic and Himmelman (1978); R.E. Warren (1978); Tenzer *et al.* (1979); R.H. Hall *et al.* (1980); Norman and Dowell (1980); Temple *et al.* (1980); Anon. (1982h); Cumberland (1982); R.M. Hiltz (1982); R.L. Mitchell (1982); Scholz (1982); H.M. Freeman (1984); Neely and Lutz (1985); P.J. Warren (1985); Deckert (1986)
Leak control, sealing: Anon. (1977J); R.L. Mitchell (1982)

Hazard assessment
Buschmann (1968); Crouch (1968); D.L Katz (1968); Lindeijer (1968); McConnaughey (1971); Siccama (1971); McQueen *et al.* (1972); Coates (1973); Fortson *et al.* (1973); French and Richards (1973); Kneebone and Boyle (1973); McKinley (1973); Swalm (1973); Woodward-Lundgren and Associates (1973); Dunn (1974); Dunn and Tullier (1974); A.D. Little (1974); Philipson (1974b); Allan, Brown and Athens (1975); BDM Corp. (1975); Bohlman (1975); Domalski and Tsang (1975); Droppo and Watson (1975); Fedor, Parsons and de Coutinho (1975); Gardenier *et al.* (1975); Humphrey (1975); Philipson and Schaeffer (1975); Simmons (1975); Simmons and Erdmann (1975); Tihansky (1975); Frenkel and Hathaway (1976); USCG (1976a); Stoehr *et al.* (1977); Tanker Safety Group (1977); HSE (1978b,d, 1980c, 1981a); Napier (1979a); Jennsen and Larsen (1980): N.C. Harris (1982); Philipson and Napadensky (1982); Bello, Romano and Dosi (1983); Bergmann and Riegel (1983); van der Horst and van der Schraaf (1983); Lucas, Roe and Waterlow (1983); Windebank (1983); DCMR (1985); N.C. Harris and Roodbol (1985); Moffow (1985); Ackermann (1986); Allsop *et al.* (1986); D.A. Jones and Fearnehough (1986); Medland (1986); Purdy *et al.* (1987, 1988); van Aerde, Stewart and Saccomanno (1988); Cummings and Bradley (1988); Ormsby and Le (1988); J.L Woodward and Silvestro (1988); Abkowitz and Cheng (1989); Andreassen and Gjerstadt (1989); Canadine and Purdy (1989); Guy (1989); Hoftijzer, van der Schaaf and Lupker (1989); Hubert and Pages (1989); V.C. Marshall (1989a, 1991b); Sellers and Bendig (1989, 1990); Birk, Anderson and Coppens (1990); Ramachandran (1990b); Saccomano, Shortreed and Mehta (1990); J.R. Thompson *et al.* (1990); ACDS (1991); Brockhoff (1992); R.T. Hill (1992); Goh, Tan and Ching (1993); Medhekar, Gekler and Bley (1993); Purdy (1993); Romer *et al.* (1993); Song, Black and Dunn (1993); Tenniswood, Sharp and Clark (1993)
Comparative studies — modes of transport: Westbrook (1974); Beattie (1989); Saccamano *et al.* (1989); ACDS (1991)
Comparative studies — alternative routes: Rhyne (1990); ACDS (1991),
Comparative studies — transport vs fixed installations: Haastrup and Brockhoff (1990); Haastrup and Styhr Petersen (1992)
Explosives: Chapman and Holden (1987 SRD R412); P.A. Davies (1990); ACDS (1991)

Transport statistics, transport accident statistics
Hicks *et al.* (1973); Gay (1975); Department of Energy (1977b); Ichniowski (1987); ACDS (1991)
Road: North (1974); DoT (1982, 1985); CSO (1986); A. James (1986); Grime (1987); ACDS (1991); P.A. Davies and Lees (1991b, 1992)
Rail: ACDS (1991); P.A. Davies and Lees (1991a)
Rotorcraft: NTSB (1981)

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www.unece.org

The United Nations Economic Commission for Europe (UNECE) provides links to all European nations's transportation regulatory websites.

www.cefic.be/Templates/shwStory.asp?NID = 27 &HID = 365

CEFIC is the European Chemical Industry Council (similar to ACC in the United States). The above link is to their Transport and Logistics section.

UK

www.hse.gov.uk

The Health and Safety Executive (HSE) website provides multiple references to transport safety, as well as links to other, related sites at the following link:

www.hse.gov.uk/spf/cdg/links.htm

US

Governmental Links:

www.dot.gov

The United States Department of Transportation (DOT) website provides information similar to the HSEs, specific to the United States. In particular, the following links provide useful information:

www.hazmat.dot.gov

This link provides information on general Hazmat safety, including links to the Research and Special Programs Administration (RSPA), which is responsible for coordinating a national safety programme for the transportation of hazardous materials by air, rail, highway and water.

www.geosbush.com/ctpat.htm

This is a link to the Customs-Trade Partnership against Terrorism (C-TPAT) website. C-TPAT is a joint government-business initiative to build cooperative relationships to strengthen border security.

www.hazmat.dot.gov/gydebook

This is a link to the on-line version of the *DOT Emergency Response Guidebook*, 2000 edition. A revised edition is due out in 2004.

www.fra.dot.gov

The Federal Railroad Administration (FRA) provides information specific to transport by rail in the US.

www.faa.gov/regulations

The Federal Aviation Agency (FAA) governs air traffic in the United States. The regulations section of their website lists both mandatory and non-mandatory guidance.
Non-Governmental Links:

www.transcaer.org/public/home.cfm

TRANSCAER is a voluntary national outreach effort that focuses on assisting communities to prepare for a possible hazardous materials transportation incident.

www.americanchemistry.com

The American Chemistry Council (ACC) represents the leading companies engaged in the business of chemistry. Council members apply the science of chemistry to make innovative products and services that make people's lives better, healthier and safer. The Council is committed to improved environmental, health and safety performance through Responsible Care, common sense advocacy designed to address major public policy issues, and health and environmental research and product testing.

www.chemtrec.org

Chemtrec, sponsored by the ACC provides a 24-h hazardous communications centre for member companies and associates.

www.chemtelinc.com

CHEM-TEL is a 24-h emergency response telecommunications service for industry.

www.umtri.umich.edu

The University of Michigan's Transportation Research Institute conducts research into transportation safety.

www.usroads.com

USRoads provides a compilation of links to commercial sites dealing with transportation issues.

www.aar.com

The American Association of Railroads (AAR) provides information, research and training on the control and response to hazardous materials incidents in transport by rail.

www.trucking.org

The American Trucking Association (ATA) provides information on truck transport in the United States.

Canada

www.tc.gc.ca

Transport Canada provides information in both French and English. It also provides the 2000 edition of the *North American Emergency Response Guidebook* on-line in French, English and Spanish.

www.tc.gc.ca/canutec/en/menu

Canutec provides hazard communications services in Canada similar to Chemtrec in the United States.

Australia

www.aph.gov.au/library/intguide/law/transportlaw.htm
The Australian Parliament provides links to transport law, as well as non-governmental informational links.

Mexico

www.aniq.org.mx/setiq/setiq.htm
SETIQ in Mexico provide similar services as CANUTEC and CHEMTREC provide in Canada and the United States.

23.1 General Considerations

The ability to transport the raw materials to and the products from the plant is very important in determining the viability of a project. This aspect was briefly considered in Chapter 1 in relation to ethylene plant economics.

The type of transport used may greatly affect the storage requirements. A mode of transport which involves larger but infrequent deliveries is, in general, likely to require more storage than one which gives continuous flow. Ship, rail, road and pipeline thus constitute a spectrum of modes of transport ranging from large discrete to continuous deliveries. The associated storage requirements have corresponding economic and safety implications.

In transport as in other aspects of loss prevention, training is of the greatest importance. It is essential that all personnel involved in the transport of chemicals are thoroughly trained in the properties of the chemicals and the associated hazards and in the normal operating and emergency procedures.

23.1.1 Modes of transport

The following modes of transport are used for the movement of hazardous materials:

(1) road;
(2) rail;
(3) waterway;
(4) pipeline;
(5) sea;
(6) air.

23.1.2 Transport movements

For the United Kingdom, information on the movements of hazardous materials is given in *Transport Statistics Great Britain 1991* by the DTp (1992b), which is part of an annual series.

Further data on the movements of hazardous materials by road and rail in the United Kingdom are quoted in the ACDS *Transport Report* and are given below in Sections 23.6 and 23.8, respectively.

For the United States, corresponding information is provided in the annual reports of the NTSB. The NTSB *Annual Report* for 1979 states that there were in that year some 250,000 hazardous materials shipments per day. Reports of accidental releases numbered about 16,000 and there were 19 fatalities and 942 injuries. The breakdown

of fatalities by commodity was as follows: gasoline 32.5%, LPG 21.7%, chlorine 9.6%, corrosive liquids 9.6%, anhydrous ammonia 6%, aviation fuel 2.4%, compressed gas, 2.4% and others 15.6%. The *Annual Report* for 1991 quotes the same number of daily shipments of hazardous materials.

23.1.3 Transport conditions

The main sets of conditions for gas or liquid transport are:

(1) liquid at atmospheric pressure and temperature (atmospheric transport);
(2) liquefied gas under pressure and at atmospheric temperature (pressure transport);
(3) liquefied gas at atmospheric pressure and at low temperature (fully refrigerated transport);
(4) gas under pressure.

The behaviour of fluids released from such conditions has been described in Chapters 15 and 22. An account related specifically to transport is given by V.C. Marshall (1991b).

23.1.4 Transport hazards

The transport of hazardous materials may present a hazard to (1) the transporter, (2) the crew or (3) the public. The relative importance of these varies between the different modes of transport.

The hazards presented by the transport of chemicals are:

(1) fire;
(2) explosion;
(3) toxic release
    (a) conventional toxic substances,
    (b) ultratoxic substances.

As with fixed installations, so with transport, the most serious hazards arise from loss of containment.

Modes of transport such as road, rail, waterway and pipeline can give rise to release of flammable gas or vapour, which may result in a flash fire or a vapour cloud explosion, or of flammable liquid which may lead to a pool fire. Flammable liquid can also spread and then ignite, giving rise to a flowing fire. Jet flames may occur on the containers. The contained material may undergo a boiling liquid expanding vapour explosion (BLEVE) or other form of explosion. In general, a flammable fluid is more likely to give rise to fire than to explosion.

An explosion hazard also exists with substances that are to some degree unstable.

If the material is toxic, release may result in a toxic gas cloud. Toxic or corrosive materials may also spread as liquids.

With waterway and sea transport, the release of vaporizable materials onto the water is liable to give rise to very rapid vaporization, resulting in a large vapour cloud.

Transport accidents are particularly liable to cause pollution, since material spilled is often not recovered, but is dispersed into the environment.

The initiating factor in a transport accident may be (1) the cargo, (2) the transporter or (3) the operations.

The cargo may catch fire, explode or corrode the tank; the transporter may be involved in a crash or derailment or fire; the operations such as charging and discharging may be wrongly executed.

Thus, the events which can give rise to hazards include particularly (1) container failure, (2) accident impact and (3) loading and unloading operations.

Although the attention in transport of hazardous materials by moving vehicles focuses on the injury caused by release from containment, fatalities also occur due to the movement of the vehicles themselves. This should be taken into account also, particularly in comparative studies of different modes of transport, since although the deaths from this cause in any one accident tend to be small in number, they may in total equal or exceed those from the releases.

23.1.5 Size of units

As with fixed installations, so with transport, the question arises as to whether it is safer to handle a given quantity of hazardous material in a few large units or in many smaller ones. In particular, there is a wide range of possibilities with sea transport. The choice made affects not only the size of the ship but also that of the associated storage on land. In general, a small number of large units appears safer in the sense that the product of scale and frequency tends to be less. This is because, with fewer units, it is easier to achieve a more uniformly high standard of design and operation, and the frequency of incidents is less. The scale of the most serious accident, however, is greater. The problem has been considered by the Tanker Safety Group (1977), which has reviewed the historical experience with large crude oil tankers and supertankers.

23.1.6 Multi-use containers

The use of the same container to carry different chemicals is quite normal; it is fairly common practice in road tankers, barges, ships and pipelines. This not only creates potential problems of compatibility between materials carried, but also means that the carrier is less familiar with the substances he is transporting.

23.1.7 Loading and unloading

Many of the hazards associated with transport arise during loading or unloading. This aspect was treated in relation to storage in Chapter 22 and is considered only occasionally in this chapter.

23.2 International Codes

The transport of chemicals is an international activity and international codes assumes a dominant role. These codes govern not only the classification, packaging and labelling of substances, but also the transport containers. There are four main codes which are relevant here and these are now described.

23.2.1 UN Transport Code

A basic code for international transport is provided by the *Recommendations on the Transport of Dangerous Goods* (United Nations, 2001) (the UN *Transport Code*).

Topics dealt with in the code include: (1) classification, including testing; (2) packing; (3) labelling; (4) transport containers, including intermediate bulk containers and tank containers (IBCs) and (5) consignment procedures.

The classification of dangerous goods for transport given in the UN *Transport Code* provides a framework

which is followed by other codes. The classification scheme, which is based on classification by class of substance, is shown in Table 23.2.

In addition to this classification, there is for Class 1, explosives, a further categorization by compatibility group. The compatibility groups are A–H, J–L, N and S. The general nature of these compatibility groups is illustrated by the following entries:

Group A Primary explosive substance.
Group B Article containing a primary explosive substance and not containing two or more effective protective features.

Dangerous goods of all classes other than Class 1, 2, 5.2, 6.2 and 7 are assigned for packing purposes to one of three groups according to the degree of danger which they represent:

Packing group
I Great danger.
II Medium danger.
III Minor danger.

The *Code* contains a set of specimen hazard warning signs for the labelling of dangerous goods. Further details of the classification, packaging and labelling provisions of the code are given in Section 23.3.

The *Code* gives recommendations for the mechanical design, service equipment and pressure relief arrangements for transport containers, as described in Section 23.4. It also contains recommendations on consignment procedures, including packages and the provision of transport documentation. In addition to the general recommendations of the *Code*, there are special recommendations applicable to each class of substance.

Table 23.2 *UN Transport Code: classification of substances (United Nations, 2001)*

Class 10	**Explosives**
Division 1.1	Substances and articles which have a mass explosion hazard
Division 1.2	Substances and articles which have a projection hazard but not a mass explosion hazard
Division 1.3	Substances and articles which have a fire hazard and either a minor blast hazard or a minor projection hazard or both but not a mass explosion hazard
Division 1.4	Substances and articles which present no significant hazard
Division 1.5	Very insensitive substances which have a mass explosion hazard
Division 1.6	Extremely insensitive articles which do not have a mass explosion hazard
Class 2	**Gases**
Division 2.1	Flammable gases
Division 2.2	Non-flammable, non-toxic gases
Division 2.3	Toxic gases
Class 3	**Flammable liquids**
Class 4	**Flammable solids; substances liable to spontaneous combustion; substances which in contact with water emit flammable gases**
Division 4.1	Flammable solids
Division 4.2	Substances liable to spontaneous combustion
Division 4.3	Substances which in contact with water emit flammable gases
Class 5	**Oxidizing substances; organic peroxides**
Division 5.1	Oxidizing substances
Division 5.2	Organic peroxides
Class 6	**Poisonous (toxic) and infectious substances**
Division 6.1	Poisonous (toxic) substances
Division 6.2	Infectious substances
Class 7	**Radioactive materials**
Class 8	**Corrosive substances**
Class 9	**Miscellaneous dangerous substances**

23.2.2 European Road Carriage Agreement (ADR)

The European code for international transport is the *European Agreement Concerning the International Carriage of Dangerous Goods by Road* (ADR) issued by the DTp (2003a).

The document contains the Articles of the Agreement and two Annexes, Annex A and Annex B. Annex A, Provisions Concerning Dangerous Substances and Articles, has three parts: Part I on general provisions, Part II on special provisions for substances in the various Classes, and Part III a set of appendices. These appendices cover the following topics: A1, stability and safety conditions relating to explosive substances and articles, flammable solids and organic peroxides; A2, containers for Class 2 substances, including aluminium alloy containers and containers for fully refrigerated gases; A3, tests for substances; A5, general packing conditions; A6, intermediate bulk containers; A7, Class 7, radioactive materials; A9, symbols and labels. A4 and A8 are not used.

Annex B, Provisions Concerning Transport Equipment and Transport Operations, has two parts and a set of appendices; Part I dealing with general provisions and Part II with special provisions for the various Classes whilst the appendices cover the following topics: Bl, containers including fixed and demountable tanks, tank containers and reinforced plastic tanks; B2, electrical equipment; B3 certificates of approval for vehicles; B5 list of substances; and B6, certificate of driver's training. B4 is not used.

The provisions for classification, packaging and labelling provisions are considered further in Section 23.3 and those for transport containers are discussed in Section 23.4.

23.2.3 International Rail Carriage Regulations (RID)

There have for some time been a set of Uniform Rules concerning the Contract for International Carriage of Goods by Rail (CIM) and there is a Convention concerning International Carriage by Rail (COTIF) of 1980. The international code for rail transport is the *Regulations Concerning the International Carriage of Dangerous Goods by Rail* (RID) issued by the DTp (2003b); it constitutes Annex 1 of the Uniform Rules.

The document, which is itself an annex, contains extracts from the Articles of the Convention and from the Uniform Rules, which are Appendix B of the Convention. It

has three parts: Part I on general regulations, Part II on special regulations for substances in the various Classes, and Part III a set of appendices. These appendices cover the following topics: I, stability and safety conditions relating to explosive substances and articles, flammable solids and organic peroxides; II, containers for Class 2 substances, including aluminium alloy containers and containers for fully refrigerated gases; III, tests for substances; V, general packing requirements; VI, intermediate bulk containers; VII, Class 7, radioactive materials; DC, symbols and labels; X,construction, testing and use of tank containers; and XI, construction, testing and use of tank wagons. IV is not used.

The provisions for classification, packaging and labelling provisions are considered further in Section 23.3 and those for transport containers are discussed in Section 23.5.

23.2.4 International Maritime Dangerous Goods (IMDG) Code

For sea transport, the relevant code is the *International Maritime Dangerous Goods Code (IMDG Code*) issued by the IMO (2002 IMO-200). The classification for dangerous goods for maritime transport given in the *IMDG Code* is again virtually the same as that of ADR, as shown in Table 23.2.

23.3 Classification, Packaging and Labelling

There is a large international trade in dangerous goods and it is particularly important that the arrangements for the classification, packaging and labelling of these substances be accepted internationally.

23.3.1 Regulatory controls and codes

As already described, the international codes governing the transport of dangerous goods, namely the UN *Transport Code*, ADR, RID and the *IMDG Code*, give detailed recommendations on classification, packaging and labelling.

Classification, packaging and labelling is the subject of EC Directive 67/548 (the Dangerous Substances Directive). In the United Kingdom, this directive was implemented for the road transport of hazardous materials by the Classification, Packaging and Labelling Regulations (CPL) 1984. The associated Approved Codes of Practice (ACOPs) are COP 19 *Classification and Labelling of Substances Dangerous for Supply and/or for Conveyance by Road 1984*, Revision 1 (HSE, 1990) and COP 40 *Packaging of Dangerous Substances for Conveyance by Road 1984*, Revision 2 (HSE, 1990). Guidance is given in HS(R) 22 *A Guide to the Classification, Packaging and Labelling Regulations 1984* (HSE, 1985). Also relevant is COP 33 *Transport of Compressed Gases in Tube Trailers and Tube Containers* (HSE, 1989).

The Chemicals (Hazard Information and Packaging) Regulations 1993 (CHIP) now supersede the CPL Regulations.

These regulations are complemented by the Road Traffic (Carriage of Dangerous Substances in Packages etc.) Regulations 1992 and the Road Traffic (Carriage of Dangerous Substances in Road Tankers and Tank Containers) Regulations 1992, which are described in Section 23.5.

Guidance on cargo transport units (CTUs) for marine transport is given in HS(G) 78 *Container Packing* (HSE, 1992).

For explosives there are the Classification and Labelling of Explosives Regulations 1983 (CLER) and the Packaging of Explosives for Carriage Regulations 1991.

23.3.2 UN Transport Code

The classification scheme of the UN *Transport Code* has been given in outline in Table 23.2. The *Code* gives guidance on assignment to a class, or a division within a class. For some classes of substances, notably explosives and organic peroxides, there are specified tests. These tests, and the flow charts for assignment, are described in Chapter 8.

For Class 3, Flammable liquids, there is a hazard grouping based on boiling point and flashpoint. This is

Packing group	*Flashpoint (closed cup)* (°C)	*Initial boiling point* (°C)
I	–	<35
II	<23	>35
III	>23, <60.5	>35

For Class 6, Poisonous (toxic) substances, there are grouping criteria for solids and liquids based on oral toxicity and dermal toxicity, both characterized by an LD_{50} value (the lethal dose at the 50% level) and for dusts and mists by an LC_{50} value (the lethal concentration at the 50% level) for a 1 h exposure. For toxic vapours, the grouping criteria are shown in Figure 23.1. The *Code* gives a list of the dangerous goods most commonly carried. It also gives guidance on the assignment of a substance which is not in the list and which presents more than one hazard. The guidance is in the form of (1) a list of classes and divisions in the order of precedence and (2) a precedence table.

The UN *Transport Code* gives detailed definitions of forms of packaging and specifies requirements for testing and marking.

23.3.3 European Road Carriage Agreement (ADR)

The classification for dangerous goods for transport by road given in the ADR is shown in Table 23.3. The classification is similar, but not identical, to that of the UN *Transport Code.*

A special feature of ADR is that the classes are either restrictive or non-restrictive. The restrictive classes are Classes 1, 2, 6.2 and 7. For a restrictive class, only the goods specifically listed may be carried and goods not listed are prohibited. For a non-restrictive class, some goods, although not specifically listed by name, may fall under one of the generic descriptions in the class, and are then carried according to the provisions which apply to that group, whilst other goods which display the dangerous properties of the class, but are not listed either specifically or generically, may be carried free of ADR. However, there are for non-restrictive classes some goods which are prohibited.

ADR gives a further classification for Class 2, Gases, which is particularly relevant here. This is shown in Table 23.4.

23.3.4 International Rail Carriage Regulations (RID)

The classification for dangerous goods for transport by rail given in RID is the same as that shown Table 23.3, with the slight modification given in the footnote to that table.

23.3.5 CHIP Regulations 2002

Like the CPL Regulations which they replace, the (CHIP) Regulations 2002 deal with classification, packaging and labelling of chemicals.

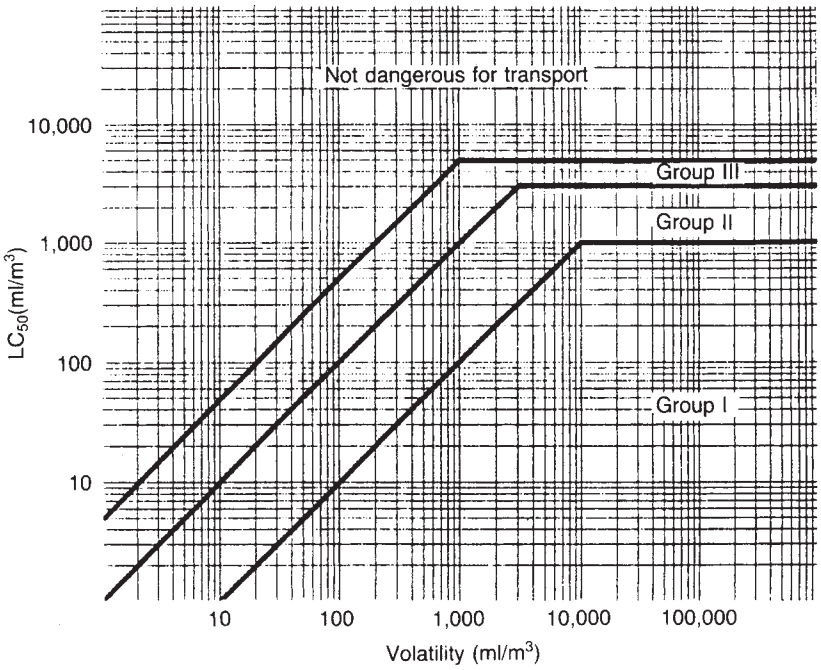


Figure 23.1 *UN Transport Code: grouping criteria for toxic vapours (United Nations, 1993; reproduced by permission)*

Table 23.3 *European Agreement for Road Transport (ADR): classification of substances*[a] *(Department of Transport, 2003a)*

Class 1	Explosive substances and articles
Class 2	Gas: compressed, liquefied or dissolved under pressure
Class 3	Flammable liquids
Class 4.1	Flammable solids
Class 4.2	Substances liable to spontaneous combustion
Class 4.3	Substances which give off flammable gases on contact with water
Class 5.1	Oxidizing substances
Class 5.2	Organic peroxides
Class 6.1	Toxic substances
Class 6.2	Repugnant substances and substances liable to cause infection
Class 7	Radioactive material
Class 8	Corrosive substances
Class 9	Miscellaneous dangerous substances and articles

[a] The classification given in the RID is identical with the above, except that very slightly different wording is used for Classes 4.3 (Substances which, in contact with water, emit flammable gases) and 6.2 (Infectious and repugnant substances).

There are three HSE documents issued in support of these regulations. Guidance is given in L38 *Approved Guide to the Classification and Labelling of Substances and Preparations Dangerous for Supply* (the *Approved Classification and Labelling Guide*) (2002). L37 (2002) gives guidance on materials safety data sheets. The third document is the *Approved Supply List*, described below.

The CHIP Regulations cover both supply and conveyance. The supply provisions are designed to provide protection to those who handle dangerous substances, the conveyance provisions protection to those concerned with their conveyance.

The regulations distinguish between substances and preparations, the latter being mixtures of substances. They also distinguish in classification between supply and conveyance. Regulation 4 defines two approved lists. The *Approved Supply List* is given in *Information Approved for the Classification and Labelling of Substances and Preparations for Supply* and the *Approved Carriage List* is given in *Information Approved for the Classification and Labelling of Substances and Preparations for Carriage*.

Regulation 5 requires that a substance or preparation dangerous for supply should not be supplied unless it meets the requirements of this regulation, which include that it is in the *Approved Supply List*, that it is a new substance classified in accordance with the Notification of New Substances Regulations 1982, or that it is classified in accordance with Schedule 1 of the CHIP regulations. Regulation 6 requires that the supplier should provide a safety data sheet. Regulation 7 requires that a substance or preparation dangerous for carriage should not be carried unless it has been classified by reference to the *Approved Carriage List* in the manner specified in the regulation.

Regulation 8 gives requirements for the packaging of substances or preparations dangerous for carriage or supply.

Table 23.4 *European Agreement for Road Transport (ADR): classification of Class 2, Gases (Department of Transport, 1993a)*

A Subclasses of Class 2[a]

A	Compressed gases having a critical temperature below −10°C
B	Liquefied gases having a critical temperature of −10°C or above
	(a) Liquefied gases having a critical temperature of 70°C or above
	(b) Liquefied gases having a critical temperature of −10°C or above, but below 70°C
C	Deeply refrigerated liquefied gases
D	Gases dissolved under pressure
E	Aerosol dispensers and non-refillable containers of gas under pressure
F	Gases subject to special requirements
G	Empty receptacles and empty tanks

B First subdivision, mainly relating to pure/gas or mixture

	Pure and technically pure gases	*Mixtures of gases*
A	1°	2°
B(a)	3°	4°
B(b)	5°	6°
C	7°	8°
D	9°	
Also		
E	10° aerosol dispensers; 11° non-refillable containers	
F	12° various mixtures of gases; 13° test gases	
G	14° empty receptacles and empty tanks, uncleaned	

C Second subdivision, relating to chemical properties

(a)	Non-flammable
(at)	Non-flammable, toxic
(b)	Flammable
(bt)	Flammable, toxic
(c)	Chemically unstable
(ct)	Chemically unstable, toxic

[a] These subdivisions are used in a hierarchy which may be illustrated by that of subclass A which is ordered: A; 1°; (a); (a t); (b); (b t); (c t); 2°; etc.

These requirements cover three main points. The package should be designed, constructed, maintained and closed so as to prevent the leakage of the contents when the overall package is subjected to normal handling. Any packaging material likely to come into contact with the substance should be compatible with it. The closure on a container which is repeatedly reused should be designed so that even after repeated use it will not leak. These requirements are essentially similar to those of the CPL Regulations.

Regulation 9 gives requirements for the labelling of substances and preparations dangerous for supply. These include the name and address of the supplier, information about the substance, symbols and risk and safety phrases. Regulation 10 gives requirements for the labelling of substances and preparations dangerous for carriage. These include the name and address of the supplier and the hazard warning sign.

Schedule 1 of the regulations gives three bases of classification: (1) physico-chemical properties, (2) health effects, and (3) environmental effects. Classification on the basis of physico-chemical properties is made using the headings: (1) explosive, (2) oxidizing, (3) extremely flammable, (4) highly flammable and (5) flammable. Classification on the basis of health effects is made under the headings: (1) very toxic, (2) toxic, (3) harmful, (4) corrosive, (5) irritant, (6) carcinogenic, (7) mutagenic and (8) teratogenic.

Schedule 2 gives the indications and symbols for substances and preparations dangerous for supply, and Schedule 3 the hazard warning signs for substances and preparation dangerous for carriage. Schedule 4 gives classification provisions for preparations dangerous for supply and Schedule 5 gives those for pesticides. Schedule 6 lists the headings under which particulars are to be provided in safety data sheets.

L38 gives guidance particularly on: (1) the classification by physico-chemical properties, health effects and environmental effects; and (2) labelling and risk and safety phrases. For the classification of substances, the data necessary are essentially those of the base set given in the Notification of New Substances Regulations 1982. The guide refers particularly to the test methods of EC Directive 84/449/EEC.

With regard to labelling, L38 gives two separate sets of formal phrases: the risk phrases and the safety phrases. A risk phrase which figures prominently in occupational hygiene is R45: May cause cancer.

Another risk phrase which occurs frequently in L38 is R48: Danger of serious damage to health by prolonged exposure. L38 gives detailed guidance on when R48 should be used. Other typical risk phrases are R23: Toxic by inhalation, and R35: Causes severe burns. Some typical safety phrases are S15: Keep away from heat, S22: Do not breathe dust, and S29: Do not empty into drains.

Detailed guidance on packaging is given in COP 40, an ACOP to the CPL Regulations. Aspects covered include: normal handling, dropping, stacking, abrasion and vibration of packaging and weather effects on packaging; packaging of liquids and venting of packages; and repeated use of packages.

A major feature of this code is the packaging of organic peroxides. It gives in Appendix A1, a list of such peroxides, in Appendix A2, a list of special provisions for these peroxides and in Appendix A3, a list of recommended packagings. It also gives in Appendix B, criteria for the packaging of organic peroxides not listed in Appendix A, utilizing the concept of the self-accelerating decomposition temperature.

As with classification, so with labelling, a distinction is made between supply and conveyance. In general, for supply there should be labelling on each discrete layer of packaging, while for conveyance, labelling is required only on the other layer.

For supply, the particulars to be shown are:

(1) designation of the substance;
(2) indication(s) of the general nature of risk and the
(3) corresponding symbols;
(4) risk phrases;
(5) safety phrases;
(6) name and address of the manufacturer, importer, wholesaler or other supplier.

For conveyance, the particulars are:

(1) designation of the substance;
(2) substance identification number;
(3) hazard warning sign;
(4) additional information, covering such matters as
    (a) nature of the dangers,
    (b) advice on first aid,
    (c) action in case of fire,
    (d) measures to deal with any spillage,
    (e) instructions about any safety equipment;
(5) name and address or telephone number of consignor or expert from whom advice on the hazard is available.

The CHIP Regulations are designed to be consistent with the international codes such as the UN *Transport Code*, ADR, RID and the *IMDG Code*.

23.3.6 Hazard warning symbols and signs

The hazard warning labels, that is, signs and symbols, are international. The UN *Transport Code* gives specimen labels. Hazard warning signs for supply (brown) and symbols for carriage (multi-coloured) are given in the CHIP Regulation 2002. Hazard warning panels for road tankers are given in the Road Traffic (Carriage of Dangerous Substances in Road Tankers and Tank Containers) Regulations 1992.

23.3.7 HAZCHEM system

The CIA operates the HAZCHEM scheme described in *Hazard Identification – A Voluntary Scheme for the Marking of Tank Vehicles and Dangerous Substances* (1975/X).

Top panel of the HAZCHEM shows the HAZCHEM code number (2PE), the UN classification number (1230), the emergency telephone number and the hazard warning sign.

The HAZCHEM guide gives information under the following letter code: A, emergency action code; B, substance identification number; C, hazard warning sign; D, specialist advice; and E, evacuation. The first character in the code number refers to A, the emergency action code. The numbers 1, 2, 3 and 4 refer to the firefighting methods to be used. The first letter P, R, S, T or W, X, Y, Z, refers to the spillage action to be taken. The second letter E is added where there is need to consider evacuation of the area.

There is also a European Transport Emergency Card, or TREMCARD, system operated by the European Council of the Chemical Manufacturers Federation (CEFIC) (CIA/1).

23.3.8 US arrangements

For the United States, accounts of controls on classification, packaging and labelling of dangerous substances are given in the *NFPA Handbook* (2003) and by Bierlein (1984). The regulating authority is the DOT.

NFPA 704 provides a labelling system based on the classification system given in that code. The National Fire Protection Association (NFPA) diamond is shown in Figure 23.2.

The DOT has a placard and labelling system. The system uses the United Nations (UN) hazard diamonds. Details of the system are given in the *NFPA Handbook*.

23.4 Transport Containers

23.4.1 Regulatory controls and codes

The containers used for transport, whether fixed on a vehicle or multi-modal, are the subject of detailed requirements in the UN *Transport Code*, ADR, RID and the *IMDG Code*. The general nature of the requirements for transport containers may be illustrated by considering those given in the UN *Transport Code* and in the ADR for road transport.

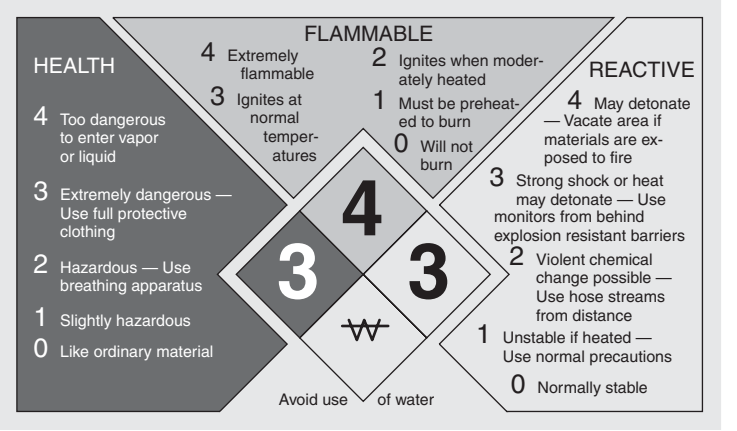


Figure 23.2 *NFPA 704 diamond (National Fire Protection Association, 2001), (Copyright © 2001 National Fire Protection Association Quincy, MA 02269. This warning system is intended to be interpreted and applied only by properly trained individuals to identify fire, health and reactivity hazards of chemicals. The user is referred to a certain limited number of chemicals with recommended classifications in NFPA 49 and NFPA 325M which would be used as a guideline only. Whether the chemicals are classified by the NFPA or not, anyone using the 704 system to classify chemicals does so at their own risk.)*

23.4.2 Types of container

The types of container used in the transport of dangerous goods include: (1) tanks fixed to road vehicles and rail cars; (2) multi-modal tank containers, which can be transported by several different modes of transport and (3) IBCs. There are also demountable tanks, which differ from tank containers in that they are not intended to be loaded and unloaded whilst fully charged.

The UN *Transport Code* defines a tank container as a tank having a capacity of not less than 0.45 m^3 whose shell is fitted with the items of service equipment and structural equipment necessary for the transport of dangerous liquids.

It defines an IBC as a rigid, semi-rigid or flexible packaging having a capacity of not more than 3 m^3 which is designed for mechanical handling and is resistant to the stresses produced in handling and transport, as determined by tests. Excluded from this definition are the forms of packaging dealt with in Chapter 9 of the code, which covers items having a mass of less than 400 kg or a capacity of less than 0.45 m^3.

Tank containers are treated in the UN *Code* in terms of requirements for pressure vessels. IBCs are treated rather in terms of the requirements for packaging, with emphasis on tests for such packaging. There are pressure test requirements, however, for certain metal IBCs such as drums.

The ADR contains provisions for fixed tanks, or tank vehicles, and for tank containers.

23.4.3 Tank containers

In the UN *Transport Code*, transport containers are mainly dealt with in Chapter 12 on multi-modal tank transport, which covers tank containers for Classes 3–9 and for non-refrigerated liquefied gases, and Chapter 17 on multi-modal tank containers for refrigerated liquefied gases. The treatment is under the following broad headings: (1) general requirements, (2) cross-sectional design, (3) minimum shell thickness, (4) service equipment, (5) bottom opening, (6) safety relief, (7) pressure relief devices, (8) setting and (9) capacity.

The treatment of transport containers in the ADR is mainly in Appendix A6 on IBCs and in Appendices Bla–c, dealing with tanks other than tank containers, tank containers, and tanks made of reinforced plastics, respectively. The treatment is under the headings: (1) general scope and definitions; (2) construction; (3) items of equipment; (4) type approval; (5) tests, (6) marking and (7) operation.

23.4.4 Road tankers

The other main type of tank of interest here is fixed tanks on road tankers and rail tank cars. The general principles are similar for the two modes of transport and it is road tankers which are now considered.

The requirements for road tankers, or tank vehicles, are treated in detail in the ADR. In the account that follows, the provisions quoted relate to the general requirements for tank vehicles. For some classes, there are also specific requirements.

23.4.5 Tank shell construction

The mechanical design of the tank shell on a tank vehicle is treated in detail in the ADR. The shell should be designed and constructed in accordance with a suitable code. The ADR gives certain minimum requirements covering, among other things, (1) the material of construction, (2) the minimum wall thickness, (3) the design pressure and test pressure and (4) the transport shocks.

23.4.6 Material of construction

The general requirement of the ADR is that the shell of a tank vehicle should be made of a suitable metallic material which is resistant to brittle fracture and stress corrosion cracking between −20°C and 50°C, except where another temperature range is prescribed for a particular class.

The usual material of construction for the shell is mild steel. Lined mild steel is also used. The usual linings are plastics and rubber. In this case, it is necessary to maintain the lining carefully, especially at the joints.

Other materials are used for tanks for particular chemicals. For example, aluminium alloy is utilized for hydrogen peroxide.

23.4.7 Minimum wall thickness

ADR gives the following formula for the calculation of the thickness of the cylindrical wall of the shell of a tank vehicle and of the ends and cover plates:

$$e = \frac{PD}{20\sigma\lambda} \qquad [23.4.1]$$

where D is the internal diameter of the shell (mm), e is the thickness of the metal (mm), P is the calculation pressure (bar), σ is the permissible stress (N/mm^2) and λ is a coefficient, not exceeding unity, which allows for any weakening due to welds.

There is also a minimum wall thickness. For a shell not exceeding 1.8 m diameter, this minimum thickness is 5 mm for mild steel, and for one of larger diameter it is 6 mm. For other metals, an equivalent thickness is applicable, determined from a formula based on the general relation:

$$e_1 = e_0\left(\frac{R_{m0}A_0}{R_{m1}A_1}\right)^{1/3} \qquad [23.4.2]$$

where A is the fractional minimum elongation of the metal on fracture under tensile stress, R_m is the minimum tensile strength, and subscripts 0 and 1 denote mild steel and the metal under consideration, respectively.

23.4.8 Design pressure

For the design pressure of the shell of a tank vehicle, the general provisions of the ADR define four categories of duty. The fourth covers shells for use with substances having a vapour pressure of more than 1.75 bara at 50°C. For this case, the calculation pressure should be 1.3 times the filling or discharge pressure, but in any case not less than 4 barg.

23.4.9 Transport shocks

The shell, and its fastenings, on a tank vehicle are required by the general provisions of the ADR to withstand the following forces:

(1) In the direction of travel: twice the total mass.
(2) At right angles to the direction of travel: the total mass.
(3) Vertically upwards: the total mass.
(4) Vertically downwards: twice the total mass.

23.4.10 Tank equipment

The ADR general provisions detail the equipment which should be provided on the shell of a tank vehicle. This includes shut-off devices on bottom-discharge shells and pressure relief devices.

A bottom discharge should be equipped with two mutually independent shut-off devices. The first should be an internal stop valve fixed directly to the shell and the second a sluice valve, or equivalent device, mounted in series, one at each end of the discharge pipe socket. In addition, the openings of shells should be capable of being closed by screw-threaded plugs, blank flanges or equivalent devices.

The internal shut-off valve should be operable from above or below, and its setting (whether open or closed), should if possible be verifiable from the ground. The valve should continue to be effective in the event of damage to the external control.

23.4.11 Pressure relief

The general provisions of the ADR require that a shell for carriage of a liquid with a vapour pressure exceeding 1.1 bara at 50°C should either be fitted with a safety valve or be hermetically sealed. A hermetically sealed shell is one with hermetically closed openings and without a safety valve, bursting disc or similar device, or one fitted with a safety valve preceded by a bursting disc.

The special provisions for Class 2, gases, state that a shell for gases in 1° to 6° and 9° may be fitted with safety valves. But they also state that for carriage of toxic gases in 1° to 9°, a shell should not have a safety valve unless it is preceded by a bursting disc. In this latter case, the arrangement should be satisfactory to the competent authority. These provisions also state that for shells intended for carriage by sea, the provisions of ADR do not prohibit the fitting of safety valves conforming to the regulations of the *IMDG Code*.

The fitting of a pressure relief valve to a road tanker is not a straightforward matter. It cannot be assumed that the fluid to be relieved will necessarily be vapour; in some cases, with the tanker lying on its side, the fluid may be liquid. He considers the problems which this poses.

23.4.12 Filling ratio

The general provisions of the ADR contain a number of formulae for the degree of filling (DF). These are of the general form:

$$\mathrm{DF} = \frac{\chi}{1 + \alpha(50 - t_\mathrm{F})} \qquad [23.4.3]$$

with

$$\alpha = \frac{d_{15} - d_{50}}{35 \times d_{50}} \qquad [23.4.4]$$

where d_{15} and d_{50} are the densities of the liquid at 15°C and 50°C, respectively, t_F is the mean temperature of the liquid at the time of filling (°C), α is the mean coefficient of cubical expansion of the liquid between 15°C and 50°C and χ is a proportion (%) which has values dependent on (1) the nature of the fluid and (2) the pressure relief arrangements, these values ranging between 95% and 100%.

23.5 Road Transport

23.5.1 Regulatory controls and codes

At the international level, codes for the road transport of dangerous goods are the UN *Transport Code* and the ADR.

In the United Kingdom, road transport is governed by three principal sets of regulations. The first set is the (CHIP) Regulations 2002, which cover these aspects as they apply to road transport. These regulations, and the associated ACOPs and guidance, have been described in Section 23.3.

The second set is the Road Traffic (Carriage of Dangerous Substances in Packages) Regulations 1992 (PGR). The regulations deal with: the design, construction and maintenance of vehicles; the marking of vehicles; loading, stowage and unloading; precautions against fire and explosion; information to be provided to the operator; information for, instructions to and training of drivers; supervision of parked vehicles; and information for the police. Regulation 11 places limitations on the carriage of certain substances. It contains requirements that an organic peroxide or flammable solid subject to self-accelerating decomposition be kept below its control temperature.

The third set of regulations is the Road Traffic (Carriage of Dangerous Substances in Road Tankers and Tank Containers) Regulations 1992 (RTR). The regulations deal with: the construction, maintenance and testing of tankers and tank containers; the marking of vehicles with hazard warning panels; loading, filling and securing of closures; information to be provided to the operator; information to be carried with the vehicle; precautions against fire and explosion; information for, instructions to and training of drivers; parking of vehicles and their supervision when parked; and information for the police.

Both the PGR and RTR give definitions of dangerous substances, referring in particular to the *Approved List*. The PGR also contains a schedule which gives criteria by which to determine whether a substance not in the list is to be classed as a dangerous substance.

The regulations which preceded these two sets of road traffic regulations, PGR 1993 and RTR 1993, namely PGR 1986 and RTR 1981, were supported by a number of ACOPs and guidance documents. The ACOPs are COP 11 *Operational Provisions of the Dangerous Substances (Conveyance by Road in Road Tankers and Tank Containers) Regulations 1981* (HSE, 1983); COP 14 *Road Tanker Testing: Examination, Testing and Certification of the Carrying Tanks of Road Tankers and Tank Containers used for the Conveyance of Dangerous Substances by Road (in support of SI 1981 1059*) (HSE, 1985); and COP 17 *Notice of Approval of the Operational Provisions of the Road Traffic (Carriage of Dangerous Substances in Packages etc.) Regulations 1986 by the Health and Safety Commission* (HSE, 1987). The guidance is HS(R) 13 *Guide to the Dangerous Substances (Conveyance by Road in Road Tankers and Tank Containers) Regulations 1981* (HSE, 1981) and HS(R) 24 *Guide to the Road Traffic (Carriage of Dangerous Substances in Packages etc.) Regulations 1986* (HSE, 1987).

These documents are currently in the process of being updated, with a single L series document replacing both ACOPs and the guidance. A single document will replace COP 11 and HS(R) 13, another will replace COP 14 and a third will replace COP 17 and HS(R) 24.

The design and construction of road tankers is covered in the following documents: L16 *Design and Construction of*

Vented Non-pressure Road Tankers used for the Carriage of Flammable Liquids (HSE, 1993); L17 *Design and Construction of Road Tankers used for the Carriage of Carbon Bisulphide* (HSE, 1993); L18 *Design and Construction of Vacuum Insulated Road Tankers used for the Carriage of Deeply Refrigerated Gases* (HSE, 1993); and L19 *Design and Construction of Vacuum Operated Road Tankers used for the Carriage of Hazardous Wastes* (HSE, 1993).

The road transport of explosives is covered by the Road Traffic (Carriage of Explosives by Road) Regulations 1989. The associated ACOP is COP 36 *Carriage of Explosives by Road* (HSE, 1989).

23.5.2 Hazard scenarios

The bulk of hazardous materials transported by road are carried as liquids or liquefied gases in road tankers. The main types of road accident associated with these are leaks due to tank puncture resulting from a collision or overturning or due to failure or maloperation of the tank equipment. Other causes of loss of containment are tank rupture due to overfilling, overheating or a defect and due to fire.

If the tank is ruptured by overfilling or overheating, a physical explosion may occur, giving rise to a blast wave and to missiles.

Material released from the tank by whatever cause may be flammable or toxic and in vapour or liquid form. A release of flammable vapour will form a vapour cloud which may ignite to give a flash fire or vapour cloud explosion. A flammable liquid spill may ignite to give a pool fire or flowing liquid fire. A toxic material will give a toxic gas cloud or toxic liquid spill.

A fire at the tank itself may cause rupture of the tank and, if the tank contains flammable liquid, may lead to a BLEVE, with its associated fireball. Road tankers do not, however, suffer BLEVEs as commonly as rail tankers, because there is not the torch effect from relief valves on other tanks which occurs in rail crashes.

Other hazardous materials are solids which are carried in goods vehicles. These include explosives and related substances. With these there is, therefore, the hazard of explosion.

There are several characteristics of road transport which bear on the nature of the hazard. The vehicle is moving through an environment over which the driver has relatively little control. If there is an accident, it may occur at a variety of points along the route with very different vulnerabilities. On the other hand, the quantity carried is limited, and it may be possible to move the vehicle to a less vulnerable location.

One important aspect of vulnerability is the number of people exposed at a particular location. The extent and composition of the population exposed varies widely with the location. Another aspect is the susceptibility to environmental pollution at that point. A road accident may pose a threat not only to life but also to the environment.

A feature of road accidents is that access for the emergency services is generally relatively easy compared with rail. On the other hand, the accessibility of a road accident increases the likelihood that spectators will gather.

23.5.3 Road tanker design

Requirements for the design of road tankers are given in the Road Traffic (Carriage of Dangerous Substances in Road Tankers and Tank Containers) Regulations 1992 (RTR). An outline of these requirements has been given in Section 23.5.1. Associated guidance is given in L16 for flammable liquids and L18 for deeply refrigerated liquids.

The RTR are essentially a set of goal-setting regulations and do not specify matters such as wall thickness or overpressure protection. In particular, the requirements of the RTR for design and for testing and examination, given in Regulations 6 and 7(1), respectively, are very general, and much less detailed than those given in the ADR. The RTR states in Regulation 8(5) that the aforementioned regulations do not apply to the carrying tank of a road tanker or to a tank container where that tank and its fittings comply with the ADR, RID or the IMDG *Code*. In other words, compliance with the ADR is in effect one way of meeting the requirements of the RTR.

There are also several industry codes which deal with the design and/or operation of road tankers. These include *Safe Handling and Transport of LPG in Bulk by Road* by the (LPGITA, 1974 COP2), *Code of Practice for Road Tank Vehicles Equipped with Bottom Loading and Vapour Recovery* (IP, 1987), *Road Transport of Dangerous Substances in Bulk* (CIA, 1990 RC26) and *Steel Containers for the Carriage of Hazardous Materials* (CIA, 1991 RC37).

For the more hazardous substances, it is common practice to use top rather than bottom connections and to provide the vehicle with additional features such as side protection.

23.5.4 Carriage tank fittings

The provision of suitable carriage tank fittings can make a major contribution to minimizing any loss of containment, both in road accidents and in loading and unloading. Good practice with respect to such provision is illustrated by the features specified in the ADR, some of which have been described in Section 23.4.

One particular feature is the arrangements for protection against overpressure. For flammables, the practice is to fit pressure relief. HSE guidance is given in L16, and L18. L16 for flammable liquids, requires each tank to be fitted with pressure relief devices, which it specifies. L18, for non-toxic, deeply refrigerated gases, likewise requires pressure relief devices on each tank, and specifies them.

For toxics, such provision is more controversial. In COP 38 on transportable gas containers, the HSE states that containers for toxic fluids should not normally be fitted with pressure relief devices.

23.5.5 Road tanker operation

The RTR also contains requirements for the operation of road tankers, which reflect some of the elements of good practice.

The documentation supplied should contain the information necessary for all the parties concerned, which include the consignee, the driver, the police and the fire service.

The driver should be well trained in and provided with the information that he requires. The training should cover: loading and unloading operations, including precautions against overfilling and measures to secure closures; arrangements at lorry stopover points; and handling emergencies, including both spillage and fire.

The vehicle, the carriage tank and its fittings need to be maintained to a high standard.

23.5.6 Filling ratio

It is essential that a tank should not be overfilled, with the consequent hazard of rupture due to expansion of the liquid. The permissible extent of filling is specified in terms of the filling ratio.

Guidance is given in the BS 5355: 1976 *Filling Ratios and Developed Pressures for Liquefiable Gases and Permanent Gases*. This standard, as amended in 1981, defines the filling ratio as:

> The ratio of the mass of gas introduced into a container to the mass of water (water capacity) at 15°C that fills the container fitted as for use, i.e. complete with valve, dip tube, float, etc. as necessary.

BS 5355 gives in Appendix A formulae for the filling ratio (FR). It distinguishes between a low pressure liquefiable gas, which has a critical temperature between −10°C and 70°C, inclusive, and a high pressure liquefiable gas, which has a critical temperature above 70°C. For single components, the FR formula is of the general form:

$$\mathrm{FR} = \frac{\chi\rho_l(1 - C/100)}{\rho_w} \qquad [23.5.1]$$

where C is the confidence limits on the value of the liquid density (%), ρ_l is the density of the liquid, ρ_w is the density of water and χ is a parameter which has the value 0.97 for low pressure liquefiable gases and 0.98 for high pressure liquefiable gases. The liquid density is to be evaluated at the appropriate reference temperature.

The standard also give values of the filling ratio in tabular form for a large number of gases.

23.5.7 Reference temperature

The reference temperature is the assumed maximum temperature which the tank contents could reach during carriage. It is used to determine the filling ratio and also the developed pressure.

BS 5355: 1976 gives reference temperatures for the United Kingdom and also information which allows reference temperatures to be determined for other parts of the world. It classifies areas according to the maximum shade temperature. The United Kingdom is classified as a climatic area with a shade temperature <35°C. In addition to Class UK, there are Classes A–E, with maximum shade temperatures of 37.5, 42.5, 47.5, 52.5 and > 52.5°C, respectively.

Then for the United Kingdom, the reference temperature for container volumes *(V)* over 1 m^3 are as follows:

Type of contents	*Reference temperature for filling ratio CO*		*Reference temperature for developed pressure CO*	
	$V = 1$–5 m^3	$F > 5$ m^3	$F = 1$–5 m^3	$F > 5$ m^3
Low pressure liquefiable gases	42.5	38	47.5	42.5
High pressure liquefiable gases			50	45

For low pressure liquefiable gases in winter, the standard gives a relaxation in reference temperature for filling ratio for volumes exceeding 5 m^3.

The choice of reference temperature is a very debatable subject. If a single reference temperature is used, simplicity is achieved, but the temperature selected has to be much higher than is necessary and economic for a large proportion of cases. Discussions of this point are given in the Home Office *Containers Report* and by A.W. Clarke (1971b). The latter states that reference temperatures as high as 65°C have been used in international codes.

The reference temperatures provide overall guidelines, but it is necessary also to observe any requirements of international transport and of the country of delivery.

23.5.8 Hazardous materials

For a given mode of transport, there are some hazardous materials which may not be conveyed. Road transport is a case in point. Writing in 1971, A.W. Clark (1971b) gave the following list of substances prohibited for road transport in West Germany:

Class 2 Gases: chlorine, hydrogen bromide, hydrogen chloride, hydrogen fluoride, hydrogen sulfide, phosgene, sulfur dioxide.

Class 3 Flammable liquids: carbon disulfide. Class 6 Poisons: acetone, cyanohydrin, acetonitrile, acrylonitrile, allyl alcohol, allyl chloride, aniline, epichlorohydrin, lead alkyls, organophosphorus compounds.

Class 8 Corrosives: bromine, fluoboric acid, hydrazine, liquid acid halides and liquid chlorides which give off acid fumes in contact with moist air (e.g. antimony pentachloride).

For certain chemicals which are transported by road special measures are required. These include:

(1) substances liable to polymerization;
(2) substances carried fused;
(3) hydrogen peroxide;
(4) organic peroxides;
(5) sulfur trioxide;
(6) bromine;
(7) lead alkyls.

Some chemicals, such as butadiene or ethylene oxide, have a tendency to polymerize. It is essential to prevent polymerization from starting, because if polymerization occurs heat is evolved and the reaction speeds up. One method of prevention is the use of an insulated tank, but this is increasingly being replaced by the alternative method, which is the use of polymerization inhibitors.

Some substances which are solids at ambient temperature, such as sulfur, phosphorus, alkali metals and naphthalene, are often carried in fused form in overdesigned and insulated tanks.

High strength hydrogen peroxide is transported in aluminium or special steel tanks. Materials which could react with the peroxide such as wood or valve lubricants are excluded from the vehicle. A water tank is carried to deal with any accident.

Organic peroxides are a somewhat similar case. They are sometimes carried in refrigerated insulated tanks to minimize the hazard due to their instability.

Sulfur trioxide is a solid at ambient temperatures and is carried heated in overdesigned and insulated tanks. It is stabilized to present polymerization. Bromine is usually transported in lead-lined steel tanks. Lead alkyls are carried in overdesigned and externally protected tanks.

23.6 Road Transport Environment

23.6.1 Road network and vehicles

The assessment of major hazards arising in the road transport of hazardous materials requires the use of a wide range of data on the road transport environment.

The road transport environment varies somewhat from one country to another. Accounts relevant to the United Kingdom have been given by Appleton (1988 SRD R474) and P.A. Davies and Lees (1992), and accounts relevant to North America have been given by Glickman (1988), Harwood and Russell (1989), Harwood, Russell and Viner (1989), Harwood, Viner and Russell (1990), Steward and van Aerde (1990a) and Gorys (1990).

As in hazard assessment generally, two situations can arise with respect to the estimation of the frequency of particular accident scenarios. Either it is possible to estimate the frequencies of these scenarios from historical data, or it is necessary to synthesize the frequencies, by methods such as modelling or fault tree analysis.

Thus, for scenarios such as release of materials which are transported in large quantities (e.g. gasoline and LPG), it may well be possible to obtain historical data. For other scenarios, such as a release of chlorine or an explosion of explosives during transport, it is much more difficult. Moreover, even where historical data exist, it may still be necessary to resort to modelling for reasons such as the need to adapt the data to the particular assessment or to explore the effect of possible mitigatory measures.

As will become apparent from the data given below, a large proportion of incidents involving hazardous materials are not due to traffic accidents, but to other causes. The prime concern here is with incidents which occur during transport rather than during loading and unloading or in temporary storage, but some of the data sets also cover the latter.

Hazardous goods are taken here to be goods defined as such under the United Nations classification and regulated by the Classification, Packaging and Labelling Regulations 1984 (CPL). These hazardous materials are mainly flammable and/or toxic liquids and liquefied gases, reactive chemicals and explosives.

The principal source of information on road transport and on road accident statistics is the DTp. Other important sources are the Home Office and the Transport and Road Research Laboratory (TRRL), which is part of the DoE.

Unfortunately, as so often happens, there are difficulties in relating information from one source to that from another. For example, DTp statistics are for heavy goods vehicles (HGVs) with unladen weights of not less than 1.5 te, whereas the principal TRRL study of HGV fatal accidents deals with HGVs with unladen weights not less then 3 te.

Road network

There are two classifications of roads used in Britain. Roads are generally classified as trunk, principal, secondary, etc., whilst in accident statistics, roads are described as A class, B class, and 'other'. Broadly speaking, trunk and principal roads are equivalent to A class roads, whilst secondary roads are equivalent to B class and 'other' roads (P.P. Scott, 1983). The length of the road network (km) in Great Britain in 1973 was given by H.D. Johnson (1981) as follows:

Length of road (km)						
BUA[a]			*Non-BUA*			
Trunk/principal	*Class II and below*[b]	*Total*	*Trunk/principal*	*Class II and below*[b]	*Total*	*Motorways*
13,874	117,052	130,926	32,383	163,587	195,970	1752

[a] BUA: built-up area.
[b] Of these totals, Class II roads are 8746 km in BUAs and 19,643 km in non-BUAs.

Heavy goods vehicles

Vehicles may be classed as HGVs, light goods vehicles (LGVs), cars, and motor cycles (MCs). HGVs may be subdivided according to the number of axles. The vast majority of hazardous materials are carried in HGVs. The most common HGV is the rigid two-axle vehicle.

The mass unladen of a typical two-axle HGV is some 7.5 te and that of a typical three-axle HGV is some 11.5 te, while that of an LGV is some 1.5 te. The maximum load of a two-axle HGV is some 12 te. Approximately, 50% of HGVs carry full load and 25% is empty, with the remainder carrying part loads. The load of an LGV is some 1.5 te.

A total of 435,000 HGVs were registered in 1986 (DTp, 1987b). The distribution of HGV weights for 1985 (JMP Consultants, 1986) was

Gross vehicle weight (te)	*Proportion of vehicles* (%)
<20	70
20–22	3
22–24	3
24–26	2
26–28	2
28–30	4
30–32	6
32–34	4
34–36	2
36–38	3
>38	1

Figure 23.3 shows some principal HGVs together with their classifications.

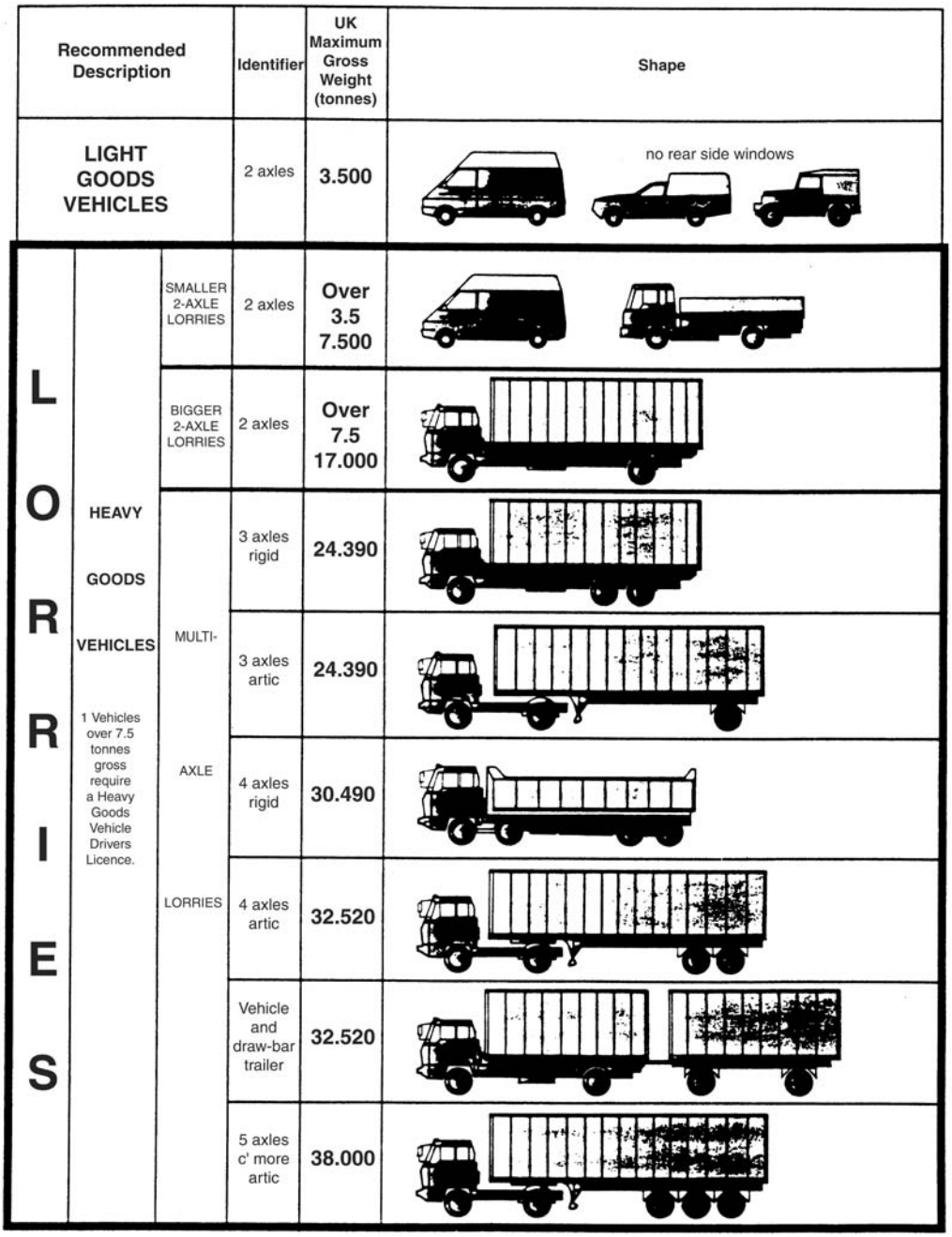


Figure 23.3 *Some principal goods vehicles*

Distances travelled

The journeys travelled by HGVs in 1986 are shown in Table 23.5, Section A, by body type and road type. HGVs travelled a total of 221×10^8 km (DTp, 1987b). The average annual distance travelled per vehicle is thus 50,800 km (221×10^8/435,000). Section B of the table gives a breakdown of the HGV distances travelled by road class.

Table 23.5 *Road transport environment in Great Britain: journeys by heavy goods vehicles in 1986 (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Distances travelled by body type and road type

HGV type	*Distance* ($\times 10^8$ km)		
	All speed limits	*Non-BUR*[a]	*BUR*
Rigid	152	103	49
Articulated	65	58	7
Total[b]	221	165	56

B Proportion of distance travelled on each road class

Road class	*Proportion of vehicles* (%)	
	Non-BUR[c]	*BUR*
A	87.0	61.0
B	6.0	11.5
Other	7.0	27.5
Total	100	100

[a] BUR, built-up road. Non-BUR includes motorways.
[b] Figures for rigid and articulated vehicles are for defined axle configurations. Total includes cases where the axle configuration was not reported.
[c] Non-BUR excludes motorways.

Speed in built-up areas

The severity of an accident depends on the speed of the vehicle(s). Of particular interest is the speed of vehicles in built-up areas (BUAs). Work on this has been done by the TRRL (N. Duncan, 1987). Their data for the speeds of good vehicles generally, LGVs as well as HGVs, are:

Time of day	*Average speed* (mph)	
	Small towns	*Large towns*
Peak period	13.1	20.5
Off-peak period	14.9	23.6

The figures refer only to the time when the vehicle is actually moving, the time spent stationary is discounted. With regard to the distribution of speeds, the assumptions made by TRRL are that the normal distribution applies and that the standard deviation is $^1/_5$ of the mean. Using these assumptions estimates may be made of the probability that a vehicle may be travelling at a particular speed.

More specific data on vehicle speeds at the moment of impact may be obtained from tachograph records, as described below.

HGVs conveying hazardous materials (HGV/HMs)

Some estimates are now made for HGVs conveying hazardous materials (HGV/HMs) in Great Britain.

It has been estimated by Kletz (1986J) that in 1986 there were some 14,000 road tankers in operation. The authors have confirmed that this approximate figure is still valid. Kletz also gives the annual distance travelled per tanker as 60,000 miles (96,500 km).

There are, in addition, HGVs other than tankers carrying hazardous materials. The number of such vehicles which at some time transport hazardous materials may be quite large, but what matters in the present context is the number of equivalent 'full-time' vehicles. There appears to be no reliable source of information for this figure. An estimate has therefore been made. The data for hazardous cargoes in the United States given in Section B of Table 23.20 (see below) indicate that the ratio of non-tank truck to tank truck HGV/HMs is about 0.6. Those given in Section B of Table 23.18 (see below) for significant spillages indicate that the ratio of non-tank truck to tank truck HGV/HM spillages is about 0.9. The former figure is regarded as a better guide. A roadside survey conducted by the authors is consistent with this estimate. The ratio of 0.6 is used for Great Britain also, which yields:

No. of tanker HGV/HMs = 14,000
No. of non-tanker HGV/HMs = $0.6 \times 14{,}000 = 8400$
No. of HGV/HMs = $14{,}000 + 8400 = 22{,}400$

Distance travelled by HGV/HMs

For the distance travelled by HGV/HMs, loaded and unloaded:

Distance travelled by individual vehicle = 60,000 miles = 96,500 km
Distance travelled by fleet = $22{,}400 \times 60{,}000 = 13.4 \times 10^8$ miles = 21.6×10^8 km

This figure is probably an upper bound, since non-tankers may well not travel as high an annual distance as tankers.

The ACDS figures given in Table 26.6 for that part of the tanker fleet carrying motor spirit, on relatively short journeys, imply an annual distance travelled, loaded and unloaded, of 1.64×10^8 km.

Proportion of route in built-up area

The severity of a road transport accident depends in part on whether it occurs in a BUA. The proportion of a route which passes through areas which are urban or suburban is typically of the order of 10–15%, but it varies. Detailed values for some particular routes are given in the ACDS report.

Movements of certain hazardous materials

The ACDS report of a detailed breakdown of the movements of the four materials considered is shown in Table 23.6.

23.6.2 Road accidents

Statistics on road accidents in Britain are given in the *Annual Abstract of Statistics* by the Central Statistical Office (CSO). Further information is given in the series *Road Accidents Great Britain* by the DTp.

An accident may be classified as a collision with other vehicle (COV) or a single vehicle accident (SVA). The latter may be subdivided into a collision with a stationary object (SVO) or overturning (OT).

Accident definitions

Accidents are commonly classified in the United Kingdom as personal injury (PI) accidents and damage-only (DO) accidents.

Road accident statistics derived from police records relate to personal injury accidents. The number of DO accidents generally has to be estimated from the number of PI accidents. For example, R.F.F. Dawson (1971) in a study of the cost of accidents gives the number of PI accidents in

Table 23.6 *Road transport environment in Great Britain: tanker capacities and movements for four hazardous materials (Advisory Committee on Dangerous Substances, 1991) (Courtesy of HM Stationery Office © All rights reserved)*

A Tanker capacities

Substance	*Tank capacity* (te)
Motor spirit	20–25
LPG	15
Ammonia	15
Chlorine	17

B Tanker movements

	Motor spirit	*LPG*	*Ammonia*	*Chlorine*
Total loaded movements (loaded tanker km/yr)	82×10^6	19.54×10^6	632,233	1,121,358
Total loaded journeys (loaded tanker journeys/yr)	1.3×10^6	63,667	2,974	9,871
Average loaded journey (km)	64	307	213	114

1968 as 264,200 and estimates the number of DO accidents as 1,583,000, giving a DO/PI accident ratio of 6. Appleton states that values of the ratio given in DoT and TRRL studies are in the range 6–12. He also states that a survey by the Safety and Reliability Directorate (SRD) of a small number of local authorities found a value of the DO/PI ratio of 2–3 but the reporting was not consistent. In any event, the problem of defining what constitutes an accident is more severe for DO than for PI accidents. Moreover, an accident severe enough to endanger the integrity of a load is likely to result in some personal injury. It is convenient, therefore, to work in terms of the PI accident criterion.

The main exception to the above is fires. Fire brigade records allow the derivation of fire statistics. Major studies of fires have been made by North (1974) and McLean (1981).

The significance of the definition of an accident depends on the use to which it is to be put in the hazard assessment. Broadly speaking, the definition is important if historical data on releases are lacking, but this is less so if such statistical information is available. The reason why is that, in the latter case, it is possible to work with a definition of an accident which is to a degree arbitrary and to work in terms of the probability of release given an accident so defined. If, on the other hand, data are not available and it is necessary to model the accident in order to determine the probability of release, the definition of what constitutes an accident becomes more significant, since it determines the accident frequency.

In the following, the UK accidents considered are injury accidents, except for fires.

Injury accidents

For vehicles generally, H.D. Johnson and Garwood (1971) found that the proportion of fatal accidents in the total of serious injury and fatal accidents for the period 1959–65 was in the range 5.1–9.2% for roads with speed restrictions of 30 or 40 mph and in the range 8.3–14.5% for other roads.

A study by the DTp (1987a) obtained for the ratio of fatal accidents to all injury accidents values in the range 0.018:1 to 0.025:1.

Some data on casualties in HGV accidents are given in Table 23.7. A study of fatal accidents involving HGVs in 1976 has been given by Riley and Bates (1980).

Grattan and Hobbs (1978) studied injuries to occupants of HGVs. In 1975, there were 3200 occupant casualties in HGVs, of which 800 were serious or fatal, the latter numbering 71. These casualties were usually the result of collision between two HGVs or between an HGV and a roadside obstacle. A 5% sample of the serious or fatal injuries was studied. All fatal injuries were associated with either massive intrusion of the cab structure or ejection of the occupant.

Hobbs, Grattan and Hobbs (1979) have examined various classifications of injury, in a study which relates the injury classifications to the length of stay in hospital.

Kletz (1986J) quotes figures given by Hills (1981) for the number of deaths from the road transport of hazardous chemicals in the United Kingdom in the period 1970–80 as 16 deaths overall, making an average of 1.23 deaths/year. From the context these are the deaths attributable to the load. Kletz also states that the average number of deaths per fatal accident is 1.5.

HGV accident frequency

In 1986, HGVs travelled 221×10^8 km and there were 13,429 accidents involving HGVs. A number of accidents involve more than one HGV. The number of HGVs involved in accidents is thus somewhat more than the number of accidents involving an HGV. The number of HGVs involved in accidents in 1986 was nearly 15,000.

Statistics on accidents involving HGVs are given Tables 23.8–23.11 gives, in Section A, the number of HGVs involved in accidents; in Section B, Table 23.8 the number of accidents involving HGVs by body type and road type; and in Section C, a breakdown of the road class on which the accidents occurred. Table 23.9 gives the number of HGV accidents in 1986, by the combination of vehicles involved. Table 23.10 gives the frequency of HGV accidents by body type, road type and road class. Table 23.11 gives the proportion of HGV accidents by junction type and by impact position.

The basic annual accident statistics for HGVs in 1986 are:

No. of accidents = 13,429/year
No. of vehicles involved in accidents = 15,000
Proportion of vehicles involved in accidents
$= 15{,}000/435{,}000 = 3.4\%/\text{year}$
Frequency of accidents $= 134{,}297(221 \times 10^8)$
$= 0.62 \times 10^{-6}/\text{km}$

Impact accidents

A study of the impact speed of HGVs in accidents has been made by P.A. Davies and Lees (1991a,b) based on tachograph records. Table 23.12 gives the impact speeds obtained in this study. The accidents may be regarded as a biased sample in that the accidents were sufficiently serious for the police to have an interest and may tend therefore to give an overestimate of the impact speed in injury accidents generally.

Table 23.7 *Road transport environment in Great Britain: casualties in HGVs in 1986 (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Number of casualties

Other vehicle type	*Fatalities*	*Casualties*
HGV	24	672
LGV	–	137
Bus/coach	–	47
Car	4	622
Motorcycle	–	17
Pedal cycle	1	8
SVA (no pedestrian)	32	1045
SVA (pedestrian)	171	1184
Other	28	747
Total	260	4479

B Number of HGVs involved in injury accidents: rigid HGVs

Road type	*No. of vehicles involved*							
	Fatal accidents				*All accidents*			
	2-axle	*3-axle*	*4-axle*	*All*	*2-axle*	*3-axle*	*4-axle*	*All*
Non-BUR	239	41	50	330	3672	714	657	5082
BUR	164	32	25	221	3988	631	463	5043
All speed limits	403	73	75	551	7660	1345	1120	10125

C Number of HGVs involved in injury accidents: articulated HGVs

Road type	*No. of vehicles involved*							
	Fatal accidents				*All accidents*			
	2-axle	*3-axle*	*4-axle*	*All*	*2-axle*	*3-axle*	*4-axle*	*All*
Non-BUR	35	127	83	245	447	1444	872	2763
BUR	15	39	15	69	283	674	316	1273
All speed limits	50	166	98	314	730	2118	1188	4036

D Number of casualties by road type

Road type	*Fatalities*	*All casualties*
Non-BUR		
A roads	451	6,452
B roads	34	838
Other roads	37	1,095
All roads	522	8,385
BUR		
A roads	205	4,926
B roads	34	933
Other roads	74	2,316
All roads	313	8,175
All speed limits		
Motorways	73	1,888
A roads	656	11,378
B roads	68	1,771
Other roads	111	3,411
All roads	908	18,448

Table 23.7 *(continued)*

E Proportion of casualties by road type

Road type	*Fatalities* (%)	*All casualties* (%)
Non-BURs	57.5	45.5
BURs	34.5	44.3
Motorways	8.0	10.2

F No. of occupant casualties

Occupants	*Fatalities*			*Casualties*		
	Non-BUR	*BUR*	*All*	*Non-BUR*	*BUR*	*All*
Drivers	53	8	61	1987	773	2760
Passengers	14	8	22	354	205	559
All occupants	67	16	83	2341	978	3319

Table 23.8 *Road transport environment in Great Britain: number of HGV accidents in 1986 (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Number of HGVs involved in accidents

HGV type	*Road type*		
	All speed limits	*Non-BUR*[a]	*BUR*
Rigid	10,125	5,043	5,082
Articulated	4,036	2,763	1,273
Total[b]	14,773	7,958	6,815

B Number of accidents involving HGVs

HGV type	*Road type*		
	All speed limits	*Non-BUR*[b]	*BUR*
Rigid	9,601	4,782	4,819
Articulated	3,828	2,621	1,207
Total	13,429	7,403	6,026

C Proportion of HGV accidents by road class

Road class	*Proportion of accidents*[c] (%)	
	Non-BUR	*BUR*
A	76	60
B	10	11
Other	14	29
Total	100	100

[a] BUR, built up road. Non-BUR includes motorways.
[b] Figures for rigid and articulated vehicles are for defined axle configurations. The total includes cases where the axle configuration was not reported.
[c] Data exclude motorways.

Table 23.9 *Road transport environment in Great Britain: number of HGV accidents in 1986 by combination of the vehicles involved (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A All accidents

Accident type	*Number*	*Proportion* (%)
Single vehicle	1,994	14.8
Two vehicles	8,452	63.0
Three or more vehicles	2,983	22.2

B Two-vehicle and single-vehicle accidents

Accident type	*Number*	*Proportion* (%)
Single vehicle	890	8.5
Car	5,271	50.4
Bus coach	186	1.8
LGV	594	5.7
HGV	529	5.1
Motorcycle[a]	1,012	9.7
Pedal cycle	723	6.9
Pedestrian	1,104	10.6
Other	137	1.3
Total	10,446	100.0

C Two-vehicle accidents only

Vehicle	*Proportion* (%)
Car	62.4
Bus/coach	2.2
LGV	7.0
HGV	6.3
Motorcycle[a]	12.0
Pedal cycle	8.6
Other	1.5
Total	100.0

[a] Motorcycles include combinations.

Fire accidents

An investigation of fire in road vehicles was carried out by North (1974). Although reported in 1974, most of the data relate to 1971 and are therefore rather old. The study does, however, contain some information on certain special aspects of vehicle fires, which are given below after a consideration of the main fire statistics.

Information on the causes of fires in vehicles in 1985 has been given by the DTp (1985). In that year, out of some 248,000

Table 23.10 *Road transport environment in Great Britain: frequency of HGV accidents in 1986 (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Accidents by road type

HGV type	*Frequency* (accidents/10^6 km)		
	All speed limits	*Non-BUR*[a]	*BUR*
All HGVs	0.62	0.46	1.08

B Accidents by road class (DoT, 1987b)

Road class	*Frequency* (involvements/10^6 km)	
	Non-BUR	*BUR*
A class	0.57	1.19
B class	1.15	1.21
Other	1.30	1.28
All	0.48	1.22

C Accidents by road class

HGV type	*Frequency* (accidents/10^6 km)					
	Non-BUR			*BUR*		
	A	*B*	*Other*	*A*	*B*	*Other*
All HGVs	0.66	1.32	1.51	1.05	1.08	1.13

D Accidents by body type, road class and combination of vehicles involved: car, bus/coach and motorcycle

HGV type	*Frequency* (accidents/10^6 km)								
	Car			*Motorcycle*			*Coach/bus*		
	A	*B*	*Other*	*A*	*B*	*Other*	*A*	*B*	*Other*
All HGVs	0.56	0.57	0.60	0.11	0.11	0.12	0.02	0.02	0.02

E Accidents by body type, road class and combination of vehicles involved: LGV, HGV and pedal cycle

HGV type	*Frequency* (accidents/10^6 km)								
	LGV			*HGV*			*Pedal cycle*		
	A	*B*	*Other*	*A*	*B*	*Other*	*A*	*B*	*Other*
All HGVs	0.06	0.06	0.07	0.06	0.06	0.06	0.08	0.08	0.08

F Accidents involving only a single vehicle by body type and road class: BURs

HGV type	*Frequency* (accidents/10^6 km)								
	SVA (no pedestrian)			*SVA (pedestrian)*			*Total SVA*		
	A	*B*	*Other*	*A*	*B*	*Other*	*A*	*B*	*Other*
All HGVs	0.07	0.07	0.07	0.08	0.08	0.09	0.15	0.15	0.16

G Accidents involving only a single vehicle by body type and road class: non-BURs

HGVtype	*Frequency* (accidents/10^6 km)								
	SVA (no pedestrian)			*SVA (pedestrian)*			*Total SVA*		
	A	*B*	*Other*	*A*	*B*	*Other*	*A*	*B*	*Other*
All HGVs	0.04	0.08	0.09	0.05	0.10	0.12	0.09	0.18	0.21

[a] Non-BUR includes motorways.

Table 23.11 *Road transport environment in Great Britain: road position and impact position for HGV accidents (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Road position (after DpT, 1987b)

Junction type	*Proportion of accidents* (%)			
	Rigid		*Articulated*	
	Non-BUR	*BUR*	*Non-BUR*	*BUR*
Roundabout	3.4	5.5	5.0	8.9
T or staggered junction	13.7	36.0	10.0	32.9
Y junction	1.3	1.7	1.1	1.4
Crossroads	4.2	13.6	3.1	12.5
Multiple junction	0.5	1.7	0.5	2.7
Slip road	2.7	0.5	4.1	1.3
Private entrance	5.0	5.0	3.0	5.2
Other	1.0	1.6	1.0	2.1
Not at or within 20 m of junction	68.2	34.4	72.2	33.0
Total	100.0	100.0	100.0	100.0

B Impact position (after Riley and Bates, 1980)

Impact position	*Proportion of impacts* (%)				
	Car	*MC*	*LGV*	*HGV*	*All vehicles*
Front	66	41	63	53	59.4
Side	16	31	9	15	18.6
Rear	14	26	28	24	18.1
Other	4	2	0	8	3.9
Total	100	100	100	100	100.0

Table 23.12 *Road transport environment in Great Britain: impact speeds of HGVs in accidents (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Collisions involving other vehicles

Impact speed (mph)	*Non-BUR*	*BUR*	*Motorways*
0–9	1	3	0
10–19	2	4	0
20–29	1	10	2
30–39	5	12	1
40–49	9	5	2
50–60	2	2	2
>60	1	0	0
Total	21	36	7

B Single-vehicle accidents

Impact speed (mph)	*Non-BUR*	*BUR*	*Motorways*
0–9	1	0	0
10–19	3	4	0
20–29	2	11	0
30–39	2	5	1
40–49	1	6	1
50–60	0	0	2
>60	0	0	1
Total	9	26	5

Table 23.13 *Road transport environment in Great Britain: causes of fires in road vehicles 1984 (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

Cause	*Number*	*Proportion* (%)
Deliberate ignition	7,434	22.0
Smokers' materials	1,165	3.4
Wiring of vehicle	8,980	26.6
Oil and petroleum in contact with hot components	8,475	25.1
Crash, collision	881	2.6
Other	4,042	12.0
Unknown	2,793	8.3
Total	33,770	100.0

accidents, there were some 33,000 fires. The causes of these fires are given in Table 23.13. It can be seen from the table that the vast majority of vehicle fires are non-crash fires.

Information from the Home Office quoted by Davies and Lees for goods vehicle fires specifically indicates that in 1986, fire brigades attended 7212 van and lorry fires. Not all of these were on a public highway.

Of the 2578 HGV fires, 2559 (99.3%) were non-crash fires and 19 (0.7%) were crash fires. No breakdown is available for non-crash fires by vehicle type, but for crash fires, the breakdown is as shown in Table 23.14, Section A. The causes of the HGV non-crash fires are given in Table 23.14, Section B.

The study by North gives some information on the location of vehicle fires. His data for lorries and tankers are

given in Table 23.14, Section C. They show that for HGVs, some 82% of fires occur on roads. About another 10% occur in car parks, yards and garage forecourts, probably for the most part in BUAs.

North also gives information on the number of fatalities and on the damage caused in vehicle fires, which may help to determine the severity of such fires. In 1971, there were 241 vehicle fires, of which 16 were in lorries and 10 in tankers, and in two lorry fires there was one death in each fire and in two tanker fires one death in each. In 1972, there were 289 vehicle fires, of which 19 were in lorries and 12 in tankers and in one tanker fire there were two deaths, there being no deaths in the lorry fires. Thus, for lorries, out of 35 fires, 2 were fatal (6%) and, for tankers, out of 22 fires, 3 were fatal (14%).

North gives information on the resultant damage in a sample of car fires in 1971. Out of 200 fires, 73 caused minor damage, 44 damaged the original compartment, 24 damaged or severely destroyed the original compartment, 15 damaged more than one compartment, 2 damaged the exterior, 40 (20%) damaged or destroyed the whole car and 2 had no recorded result.

From the above, the following annual estimates can be made for HGV fires:

No. of crash fires = 19
Crash fires as a proportion of accidents = 19/13,429 = 0.14%
No. of non-crash fires = 2559
Non-crash fires as a proportion of accidents = 2559/13,429 = 19%

Table 23.14 *Road transport environment in Great Britain: fires in HGVs 1986 (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Number of crash fires

	Non-BUR	*BUR*	*All speed limits*
All HGVs	11	8	19

B Frequency of crash fires

	Frequency (fires/10^8 km)		
	Non-BUR	*BUR*	*All speed limits*
All HGVs	0.06	1.15	0.09

C Location of lorry and tanker fires (North, 1974)

Location	*Proportion of fires* (%)	
	Lorries	*Tankers*
Road or verge	71.7	67.4
Motorway	10.5	15.2
Field, open land	6.4	4.9
Car park, yard	10.1	9.7
Garage forecourt	0.7	0.5
Garden	0.1	0.5
Other (specified)	0.5	1.6
Total	100	100

Load-threatening accidents

Investigations of accidents which might threaten the load of a large HGV transporting radioactive waste have been made by I.A. James (1986) and by Allsop *et al.* (1986). The study by James is concerned with articulated, five-axled HGVs. For the determination of accident frequency, he assumes that only serious accidents, that is, those involving death or serious injury have the potential to threaten the load. Thus, James considers only accidents where the subject vehicle was an articulated HGV having a gross vehicle weight (GVW) of more than 1.5 tonne, where death or serious injury was involved, and where the accident either was a SVA or involved another HGV of GVW greater than 1.5 tonne. Table 23.15 shows his data for the number and frequency of such accidents.

Also shown in the table are the results obtained by Allsop *et al.* They considered all injury accidents involving either four-axle or five-axle HGVs in overturning or side damage. The accident frequencies obtained by these workers are appreciably higher. For motorways and A roads, their results are higher than those of James by a factor of 2–3. The factor is greater for B roads and other roads, but James' data show that the distance travelled by these large HGVs on the lower class roads is relatively small.

Chemical accidents

An account of the chemical accidents attended by the UK public fire service in 1980 has been given by McLean (1981). There were 983 special service calls in which dangerous chemicals were involved and 968 actual incidents. The incidents occurred at both fixed installations and in transport.

Table 23.16 gives the nature and number of these incidents. The principal chemicals involved, together with the number of incidents, were: hydrochloric acid (66), ammonia (65), LPG (42), sulfuric acid (34) and sodium hydroxide (30). There were 14 incidents involving petroleum and 10 involving ammonium nitrate. Of these incidents, 132 were fires in

Table 23.15 *Road transport environment in Great Britain: number and frequency of a certain type of load-threatening accident (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

Road type	*No. of accidents*	*Distance travelled* ($\times 10^6$ miles)	*Accident frequency*[a]	
			($\times 10^{-8}$ accidents/mile)	($\times 10^{-8}$ accidents/km)
Motorway	310	3202	9.68	6.0
A class	740	3855	19.2	11.9
B class	47	172	27.0	10.4
Total	1097	7229	15.2	9.4

[a] Allsop *et al.* (1986) give an accident frequency (accidents/10 km) as follows: motorways, 11.5; A roads, 36.5; B roads, 114; other roads, 83.1.

Table 23.16 *Road transport environment in Great Britain: nature of chemical incidents attended by the UK public fire services in 1980 (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

Nature of incident	*Number of incidents*	*Proportion of incidents* (%)
Chemical overheated	9	1
Spillage	419	43
Leakage	211	22
Vapour, gas escape	80	8
Potential spillage	11	1
Fire	173	18
Explosion	10	1
Chemical found	19	2
Other	20	2
Unknown	16	2
Total	968	100

which the presence of the chemical affected the firefighting to a significant degree, 18 were fires in which dangerous chemicals behaved in an abnormal manner and 25 were fires in which dangerous chemicals were present and gave rise to casualties.

For all transport incidents, both road and rail, there were 419 incidents, excluding cases in which chemicals were washed ashore. Of these, 105 (25%) occurred in rural areas, 187 (45%) in urban industrial areas, 113 (27%) in urban residential areas, and the remaining 14 (3%) in unrecorded locations.

As far as concerns the road transport incidents, there were 335 incidents, of which 21 (6%) were on motorways, 120 (36%) on A class roads, 56 (17%) on B class roads, 29 (9%) on unclassified roads, 96 (29%) occurred in a parking area off the public roads, and the remaining 14 (3%) were in unrecorded locations.

In 243 (73%) of the incidents, the vehicle was attended. Therefore, the number of incidents in which it was unattended was as high as 92 (27%).

In only 36 (11%) of the cases was an accident reported as the primary cause of the incident.

Background on accidents

A discussion of the UK accident statistics is given by H.D. Johnson and Garwood (1971). McBean (1982) attempts to assess the influence of road features on accident frequency and P.P. Scott (1983) that of traffic density, whilst Storie (1984) considers the effect of driver characteristics.

A study of HGV accidents was made in 1979 by Neilson, Kemp and Wilkins (1979), but the data given above are more up to date.

23.6.3 Road accidents: HGV/HMs

Accident frequency for HGV/HMs

HGVs carrying hazardous materials have a higher standard of design and operation, although the extent of this is variable. It may therefore be expected that the accident rate would be less. Information obtained by P.A. Davies and Lees (1992) for munitions vehicles indicates a reduction factor of about 0.1–0.33. For HGV/HMs, it seems doubtful whether such a large reduction is appropriate. The estimate used by Davies and Lees is 0.8.

M. Griffiths and Linklater (1984) found that the proportion of HGV/HMs suffering an accident was the same as for HGVs generally. Although a lower accident rate per unit distance travelled is assumed here for HGV/HMs, these vehicles travel a greater distance per year, and the net effect is to give them an annual accident rate comparable with or rather greater than that of other vehicles.

Taking the estimate:

Ratio of HGV/HM to HGV accident rates $= 0.8$

then for HGV/HM accidents

Frequency of accidents $= 0.8 \times 0.62 \times 10^{-6}$/km
$= 0.50 \times 10^{-6}$/km

No. of accidents $= 0.50 \times 10^{-6} \times 21.6 \times 10^{8}$
$= 1080$ accidents/year

No. of vehicles involved in accidents
$= (15{,}000/13{,}429) \times 1080 = 1206$

Proportion of vehicles involved in accidents
$= 1206/22{,}400 = 5.4\%$/year

For Ministry of Defence munitions vehicles (MVs), taking the estimate

Ratio of MV to HGV accident rates $= 0.2$

then

Frequency of accidents $= 0.12 \times 10^{-6}$/km

Release frequency and probability for HGV/HMs

An estimate of the frequency and probability of release given an accident can be made from the data given by Maclean. From his data:

No. of releases due to traffic accidents $= 36$

then

Frequency of release $= 36/(21.6 \times 10^{8})$
$= 0.017 \times 10^{6}$ releases/km $= 0.027 \times 10^{6}$ releases/mile
Probability of release given traffic accident
$= 36/1080 = 0.033 = 3.3\%$

These estimates are based on attendance by a fire brigade and should be regarded as lower limits.

These results may be compared with the US figures. Tables 23.18–23.20 (see below) give for the USA data on the probability of release and on the frequency of release per unit distance travelled. Again, in both cases, a distinction has to be made between releases occurring as a direct result of a traffic accident and releases due to other causes. The data given in Table 23.19 are particularly relevant in this regard.

Fatal accidents for HGV/HMs

Ratio of fatal accidents to injury accidents $= 0.022$
No. of fatal accidents $= 0.022 \times 1206 = 26.5$/year
No. of fatalities per fatal accident $= 1.5$
No. of fatalities from accidents $= 1.5 \times 26.5 = 39.8$, say 40

About one death per year is attributable to the load and the rest are due to traffic accidents.

23.6.4 Collision modelling: impact speed

The attempt to estimate the frequency of a particular type of event arising from an HGV collision will depend both on the probability of the event given a collision with a particular effective impact velocity, and on the frequency of a collision of sufficient severity with this impact velocity.

The effective impact velocity will depend on the closing, or impact, speed. For an SVA all that is required is the impact speed of a single HGV. Data which may be used to construct a probability density function for HGV closing speeds in accidents are given in Table 23.12. For an accident involving two vehicles, it is necessary to combine the probability density functions of the two vehicles. In such cases, the probability density function for the HGV impact speed may be used for both vehicles.

An approach to the determination of the probability of a given combined impact speed in a head-on collision of two HGVs is as follows. Given that there is available a distribution of HGV impact speeds such as that shown in Table 23.12, the distribution of the impact speeds of an HGV–HGV head-on collision and the probability that the speed lies within a certain range may be obtained as follows. Consider a normal distribution of HGV impact speeds $f(x)$ on built-up roads, where x is the impact speed, with a mean $\bar{x}$ and standard deviation σ. Then for the distribution $f(x_c)$ of the combined (i.e. summed) impact speeds

$$\bar{x}_c = 2\bar{x} \quad [23.6.1]$$

$$\sigma_c^2 = 2\sigma^2 \quad [23.6.2]$$

$$\sigma_c = 2^{1/2}\sigma \quad [23.6.3]$$

The probability P that the combined impact speed x_c lies between x_{c1} and x_{c2} is then

$$P(x_{c1} < x_c < x_{c2})$$

$$= P\{[(x_{c1} - \bar{x}_c)/\sigma_c] < x_c < [(x_{c2} - \bar{x}_c)/\sigma_c]\} \quad [23.6.4]$$

$$= P(a < x_c < b) \quad [23.6.5]$$

$$= I(b) - I(a) \quad [23.6.6]$$

$$= P \quad [23.6.7]$$

where subscripts 1 and 2 denote bounding values of speed. Values of $I(a)$ and $I(b)$ can be obtained from standard tables of the normal distribution. As an illustration, consider the following example:

$$\bar{x} = 30.6 \text{ mph}$$

$$\sigma = 12.2 \text{ mph}$$

$$\bar{x}_c = 2 \times 30.6 = 61.2$$

$$\sigma_c = 2^{1/2} \times 12.2 = 17.3 \text{ mph}$$

The probability that the collision speed is between 110 and 130 mph is then

$$P[(110 - 61.2)/17.3 < x_c < (130 - 61.2)/17.3]$$

$$= P(2.28 < x_c < 3.98) = 7(3.98) - 7(2.82)$$

$$= 0.9999 - 0.9976 = 2.3 \times 10^{-3}$$

This method provides a simple and rapid estimate of the probability of the combined collision speed, given a collision. The results are, however, only as good as the quality of fit of the distribution used. Specifically, the method utilizes the tail of the distribution. The fitting and use of tails is a common problem in the use of distributions. In some cases, it may be preferable to use alternative methods such as Monte Carlo simulation using the actual histogram data for collision speeds.

23.6.5 Collision modelling: impact consequences

There are several collision scenarios which may be relevant to the conveyance by road of hazardous materials. Loss of containment of hazardous liquids in bulk transport is the prime problem, but explosion of loads sensitive to shock may also be of concern.

The modelling of vehicle collision is discussed in *Handbook of Road Safety Research* (Grime, 1987).

For loss of containment of a hazardous liquid, there will be critical combinations of the impact velocities at which penetration of the tank occurs. For a frontal collision of two vehicles, by conservation of energy

$$\tfrac{1}{2}(m_1 v_1^2 + m_2 v_2^2) = \tfrac{1}{2}(m_1 + m_2)v^2 + E \quad [23.6.8]$$

and by conservation of momentum

$$v = \frac{m_1 v_1 + m_2 v_2}{m_1 + m_2} \quad [23.6.9]$$

where E is the energy absorbed in the collision, m_1 is the mass of the first vehicle, m_2 is the mass of the second vehicle, v is the residual velocity of the two vehicles after the collision, and v_1 is the initial velocity of the first vehicle and v_2 is that of the second vehicle. The mass of each vehicle is defined here as that of the vehicle plus its load which is assumed to be restrained. From Equations 23.6.8

$$E = \tfrac{1}{2}[m_1 v_1^2 + m_2 v_2^2 - (m_1 + m_2)v^2] \quad [23.6.10]$$

Equation 23.6.10 may be used to determine the critical combination of velocities v_1 and v_2 which give the critical energy absorption E_{cr} for rupture of the containment. The latter factor is obtained from mechanical considerations for the particular tanker.

An early example of such an approach was the investigation by Westbrook (1974) of the comparative risks of chlorine transport by road, rail and pipeline. The study included a road tanker collision analysis to determine the probability of puncture given a crash.

A series of collision analysis studies for HGVs for US conditions is available in Gardner and Moffatt (1982).

For the explosion of a shock sensitive load, there will be some critical impact velocity of the load at which explosion occurs. For a frontal collision of a vehicle carrying such a load unrestrained with another vehicle as shown inFigure 23.4, by conservation of momentum, the residual velocity v of the two vehicles is given by Equation 23.6.9. This velocity may be positive or negative. Then the impact velocity v_ℓ of the load is

$$v_l = v_1 - v \quad [23.6.11]$$

Equation 23.6.11 may be used to determine the critical combination of velocities v_1 and v_2 which give the critical impact velocity v_{cr} for the load.

The treatment of ship collision, described below, presents close parallels to road collision analysis of the type just described.

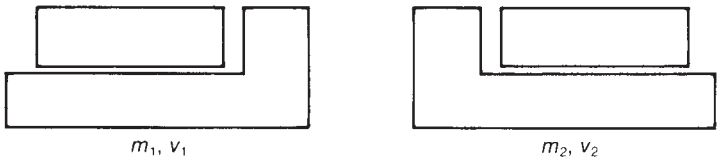


Figure 23.4 *Vehicle collision model*

Table 23.17 *Road transport environment in Great Britain: number of spills of motor spirit August 1980–August 1985*[a] *(Advisory Committee on Dangerous Substances, 1991) (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

Initiating event	*Spill mechanism*	*Spill size* (kg)			
		<15	15–150	150–1500	>1500
Rollover	Puncture			1	4
	Equipment		1	1	3
	Not specified		2		
Collision	Puncture		1		2
	Equipment		1	1	
	Not specified		1		
Body material and equipment failure	Top hatch		1		
	Pipework	1	2		
	Material crack	1	2		
Total		2	11	3	9

[a] The period considered is given in tables 4 and 5 of the report as starting in August 1981, but in table 6 as starting in 1980. The latter fits the estimate given for motor spirit tankers on p. 235, para 32, of the report for the puncture frequency $= 1.9 \times 10^{-8}$ per loaded tanker km and is adopted here.

23.6.6 Releases

Moving on to accidents resulting in releases, the ACDS report considers two categories of accident: (1) the puncture of a tank wagon in an accident and (2) failure or maloperation of the tanker equipment.

It considers the four study materials in turn. For motor spirit

$$\text{Distance travelled} = 82 \times 10^6 \text{ tanker-km/year}$$

This figure, and the others quoted in this section, refer to loaded journeys only.

The number of spills of motor spirit in the 5-year period ending in August 1985 is shown in Table 23.17. The spills are classed as nuisance (<15 kg), small (15–150 kg), medium (150–1500 kg) and large (>1500 kg).

For spills of motor spirit due to punctures:

$$\text{Frequency of spills due to punctures of motor spirit tankers} = \frac{8}{5} \times \frac{1}{82 \times 10^6} = 1.9 \times 10^{-8}/\text{tanker-km}$$

The frequency of medium spills due to punctures is 1.4×10^{-8}/tanker-km and that of large spills 0.24×10^{-8}/tanker-km.

There were no punctures of LPG, ammonia or chlorine tankers in the observation period, if two incidents involving the transport of ammonia and LPG in improperly designed tankers are disregarded. However, from an ICI analysis of US data showing 12 LPG puncture incidents, the frequency of spills due to puncture of US LPG tankers was estimated as 8.1×10^{-9}/tanker-mile. Then, allowing for the higher frequency of level crossing incidents in the United States and for differences in tanker design, the frequency of spills due to puncture of UK LPG tankers was obtained as 4.8×10^{-10}/tanker-km. A similar value was assumed for ammonia, whilst for chlorine the frequency was estimated as 0.8×10^{-10}/tanker-km.

For motor spirit spills due to equipment failures, the frequency of small spills, including those with causes not specified, is 1.9×10^{-6}/journey, that of medium spills 3.0×10^{-6}/journey and that of large spills 4.5×10^{-6}/journey.

With regard to spill size, the average size of spill in six puncture incidents was 4015 kg and that in three equipment failure incidents was 3640 kg.

For the other three substances, the frequency of leaks due to equipment failure was obtained from fault trees which are given in the report. The results for all spills other than nuisance spills were as follows:

	Frequency of spill (spills/journey)
LPG	5.2×10^{-9}
Ammonia	7×10^{-9}
Chlorine	3.6×10^{-9}

23.6.7 Release ignition

For the probability of ignition of a spill of flammable material, the ACDS report states that none of the 25 spills considered ignited. It disregards the two nuisance spills (<15 kg) and obtains from the remaining unignited

spills, an expected value of 0.7 ignitions in 23 spills, or an ignition probability of 0.033.

This value is lower than that adopted for rail spills, as described below. This appears surprising, since other vehicles are potential sources of ignition. The report gives as possible reasons the good drainage of roadways and the emergency action taken by tanker drivers. It also quotes expert judgement that a probability of ignition of 1 in 30 is about right.

23.6.8 Fires

The other main event which may give rise to an incident is fire. The frequency of fires on HGVs was considered in Section 23.6.2. With regard to fire, for HGVs, generally non-crash fires are much more frequent than crash fires. The Australian work indicates, not surprisingly, that this is less so for road tankers carrying flammable materials. Nevertheless, the figures suggest that even for such tankers, non-crash fires may be more significant.

23.6.9 Lorry stopover point incidents

The ACDS report also considers the hazard at lorry stopover points. These may vary from overnight lorry parks to points where the stopover is less than 1 h.

COP 11 states that when a vehicle is not being driven, it should be parked in a safe place or supervised at all times by the driver or other competent person. It recommends that for periods of parking in excess of 1 h, or for overnight parking, use should be made of a lorry park or some other place where the public do not have access.

The report states that UK records contain no puncture incident in a lorry stopover point. The authors therefore attempt to derive an estimate by adapting the *en route* puncture frequency data described above. These data, which are expressed as a frequency of puncture per tanker-km, are converted to a frequency of puncture per tanker-hour using a notional average speed of 60 mph. The data are corrected to allow for the low speed of vehicles in lorry stopovers by applying for motor spirit tankers and LPG tankers correction factors of 0.1 and 0.01, respectively. The frequency of punctures per journey is then obtained using appropriate values for the length of a stopover, taken as typically half an hour, and for the number of stopovers, taken as averaging 1.5 per journey.

For LPG, the *en route* frequency of puncture of a tanker is 4.8×10^{-10}/tanker-km and there are 63,667 journeys/year. Then, following the approach just described

Frequency of puncture of tanker
$= 0.01 \times 60 \times 4.8 \times 10^{-10}$/tanker-km
$= 2.88 \times 10^{-10}$/tanker-h

With 1.5 stopovers/journey and a stay of 0.5 h/stopover

Frequency of puncture of tanker
$= 1.5 \times 0.5 \times 2.88 \times 10^{-10}$
$= 2.2 \times 10^{-10}$/journey
$= 63{,}667 \times 2.2 \times 10^{-10}$
$= 1.4 \times 10^{-5}$/year

The frequency of leaks due to equipment failure was obtained from fault trees, one of which, that for LPG, is given in the report.

Using this methodology the results obtained for all four study substances in lorry stopover points are as follows:

	Frequency of puncture (punctures/journey)	*Frequency of spills due to equipment failure* (failures/h)
Motor spirit	2.9×10^{-9}	–
LPG	2.2×10^{-10}	2.6×10^{-9}
Ammonia	1.4×10^{-10}	3.9×10^{-9}
Chlorine	1.4×10^{-11}	1.3×10^{-9}

No evaluation of equipment failure frequency was made for motor spirit, since the consequences were judged to be minor.

23.6.10 Exposed population

The population exposed in a road transport accident is the *en route* population and the other road users together with the emergency services. Meaningful assessment of the societal risk from road transport requires the use of a reasonably refined population exposure model. The models used in the ACDS report are described in Appendix 17.

Population density and other characteristics

A study of the density and other characteristics of the population which might be exposed to hazardous materials has been made by Petts, Withers and Lees (1987). The information given includes data for the United Kingdom on population densities, both by day and by night, on the proportions of persons indoors and outdoors, and on the proportion of the population which may be considered particularly vulnerable.

There have also been specialist studies of the population density along routes taken in the transport of hazardous materials. These include the TRIP programme referred to in the Second *Canvey Report* (HSE, 1981a) and the study by Canadine and Purdy (1989) already mentioned.

High density targets

Of particular interest is the probability that any incident will occur at a location where large numbers of people are exposed. An estimate of this probability for BUAs may be made from V-2 rocket incidents. The distribution of the rockets which fell on London was effectively random. Analysis of the 517 V-2 incidents in London gives 8.9% which caused >10 deaths and 1.4% which caused >33 deaths.

Emergency services

In addition to the population that is normally in the area, emergency services personnel who attend the accident are also at risk. It is not uncommon in an incident involving the road transport of hazardous materials that a significant proportion of the casualties include such personnel.

A typical road accident involving injury and fire would probably be attended by one police patrol car (2 persons), one fire tender (4–5 persons) and one ambulance (2–3 persons). If the incident is considered serious and if time permits, additional fire tenders may attend.

23.6.11 Emergency services

Attendance times

In assessing the consequences of an incident, the time for the fire services to attend may be important. In accordance with Home Office guidance, fire brigades classify areas

into different categories of risk. For each category there is a specified minimum number of pumps (i.e. fire engines) which are required to attend the scene and a maximum time for their arrival. A vehicle fire is normally attended by one fire engine. Information from the London Fire Brigade obtained by P.A. Davies and Lees (1992) indicates that a vehicle fire is normally attended by one fire engine and that for the type of area through which, for example, road transport of explosives takes place, the maximum attendance time is 20 min. The mean attendance time is between 10 and 15 min.

23.6.12 North American environment

There have been a number of studies in North America on the transport of hazardous materials. Several of the more recent studies are considered here.

A review of accidents involving, and releases from, vehicles carrying hazardous materials has been given by Glickman (1988). The data are based on the reporting system of the DoT, Office of Hazardous Materials Transportation. The basic data consist of the distance travelled by trucks carrying hazardous materials and the number of accidents involving a spillage.

The reporting system requires the recording of any unintentional release occurring during loading/unloading, transportation, or temporary storage. The author equates such releases to spillages. Spillages are treated as significant if they involve more than 5 US gallons or 40 lb of material. From these reporting requirements, from the data given by Maclean above and from other data given below, it would seem that most of these spillages do not in fact occur due to road traffic accidents on the public highway.

Some data from the study are shown in Table 23.18. The frequency of spillages is obtained by simply dividing the number of spillages by the distance travelled by the vehicles.

There are several points of interest in these data. One is the rather high ratio of the distance travelled by vehicles other than tank trucks to that travelled by tank trucks. Another is the rather lower ratio of the number of significant spillages for vehicles other than tank trucks to the number for tank trucks. Also of interest is the striking difference in the frequencies of spillage between private trucks and trucks for hire.

The overall frequency of significant spillages is

$$\text{Frequency of significant spillages} = 16{,}677(16{,}220 \times 10^6)$$
$$= 0.10 \times 10^{-6} \text{ spillages/vehicle-mile}$$
$$= 0.062 \times 10^{-6} \text{ spillages/vehicle-km}$$

Harwood, Russell and Viner (1989) have collated information on hazardous material (HAZMAT) accidents. This information was obtained from the DoT's RSPA Hazardous Materials Incident Reporting (HMIR) System database. The system is based solely on self-reporting by carriers. No minimum release quantity or damage level is specified and, technically, any release, however small, is reportable. The requirements apply, however, only to interstate transport, and carriers engaged solely in intrastate transport are not required to report HAZMAT incidents under this scheme.

Data were analysed for the period 1981–85. During this time, there were 28,433 HAZMAT incidents reported. Some data on these incidents are given in Table 23.19. As the table shows, the proportion of HAZMAT incidents due to traffic was 11%. However, the proportion of severe incidents due to traffic lay between 35% and 68%, depending on the definition of severity. The authors give one definition of a severe incident as one involving injury or death, a fire or explosion or more than US$50,000 dollars worth of damage.

The authors also give information from another database, the Motor Carrier Accident Report maintained by the FHWA Bureau of Motor Carrier Safety (BMCS), now renamed the Office of Motor Carriers. This database gives information on trucks involved in accidents, including

Table 23.18 *Road transport environment in North America: the distance travelled and the number and frequency of spillages for US trucks carrying hazardous materials in 1982 (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Distance travelled

Type of vehicle	*Distance travelled* (10^6 vehicle miles)
Trucks	
Private	6,416
For hire	9,804
Total	16,220
of which	
Tank trucks	
Private	4,121
For hire	307
Total	4,228

B Number of spillages

Type of vehicle	*No. of spillages*	
	Total	*Significant*
Trucks		
Private	357	233
For hire	5,314	1,434
Total	5,671	1,667
of which		
Tank trucks		
Private	248	178
For hire	936	692
Total	1,184	870

C Frequency of spillages

Type of vehicle	*Frequency of spillages* (spillages/10^6 vehicle miles)	
	Total	*Significant*
Trucks		
Private	0.0556	0.0363
For hire	0.542	0.146
of which		
Tank trucks		
Private	0.0602	0.0432
For hire	3.049	2.254

Table 23.19 *Road transport environment in North America: hazardous material incident data from the US Department of Transportation RPSA database for 1981–85 (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Location of incidents

Location	*Proportion* (%)	*Number*
On public highway	48	13,547
Off public highway	39	*c.*11,089
Unknown	13	*c.*3,797
Total	100	28,433

B Failure involved in incidents on public highway

Failure type	*Number*	*Proportion* (%)
Traffic accident	1,427	10.8
Body or tank failure	2,741	20.2
Valve or fitting failure	3,289	24.3
Cargo shifting	4,945	36.5
Fumes or venting	15	0.1
Other	1,100	8.1
Total	13,547	100.0

C Hazardous materials involved in incidents on public highway

Material	*All incidents* (%)	*Traffic incidents* (%)
Flammable liquids	46	71
Toxic liquids	5	
Corrosive liquids	40	13

D Consequences of incidents on public highway

Count	*Number of incidents*		
	Traffic incidents	*Other incidents*	*All incidents*
No. of incidents	1,457	12,090	13,547
No. of deaths	50	4	54
No. of injuries	115	358	473

Table 23.20 *Road transport environment in North America: data on HAZMAT trucks involved in accidents from the US Department of Transportation BMCS database for 1984–85 (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Truck accidents

Truck type	*Number*
Non-HAZMAT trucks	71,164
HAZMAT trucks	3,703
of which	
No release	3,183
Release	530

B Cargoes of HAZMAT trucks in accidents

Cargo	*Number of accidents*		
	No release	*Release*	*Total*
General freight	680	61	741
Gases in bulk	238	21	259
Solids in bulk	28	12	40
Liquids in bulk	1486	345	1831
Explosives	63	7	70
Empty	210	10	220
Other	467	62	529

C Consequences of HAZMAT truck accidents

Count	*Number of accidents*		
	No release	*Release*	*Total*
No. of incidents	3183	520	3703
No. of deaths	273	53	326
No. of injuries	2514	441	2955

whether the truck was carrying hazardous materials and whether a release occurred. The reporting system applies, however, only to interstate carriers. Data from this source are given in Table 23.20.

An analysis of accident rates in three states (California, Illinois and Michigan) and of release probabilities overall in the United States has been given in a study by Harwood, Viner and Russell (1990), which follows on from the authors' earlier work (Harwood and Russell, 1989; Harwood, Russell and Viner, 1989). The data were obtained from the accident reporting systems of these states. Table 23.21 gives data on release frequencies and probabilities.

The accident frequencies differ appreciably between the different classes of highway. They also apparently differ appreciably between states. The probabilities of release given an accident, however, are relatively similar for rural highways as a group and for urban highways as a group.

An analysis of incidents in Canada in which there were releases of gasoline or LPG has been made by Steward and van Aerde (1990a). The incidents were those reported under the regulatory system as dangerous occurrences in the period 1986 to August 1987 (1.7 years). Thus, not all accidents were reported and the data are therefore not comparable with those reported under the US HAZMAT scheme.

There were 41 incidents involving gasoline. A proportion of these may not have been transport incidents. The proportion known to be transport incidents was 81%, leaving between 0% and 19% which may not have been. Table 23.22 gives the number of incidents by type of release.

The three major types of incident were collision, collision/overturn and overturn. The proportion of lading released in these cases was 30–40%. For fires, the release was large (98%) except in one case where it was very small (3%). Of these three types of incident, overturns caused most container damage. The authors suggest that in collision accidents, a large proportion of the energy is dissipated in other parts of the vehicle.

There were four evacuations of the public in the 41 incidents.

A similar analysis is given for the LPG incidents, but there were only nine of these.

Further more general data are given in the review of transportation of hazardous materials in Ontario by Gorys (1990).

Griffiths and Linklater (1984) have reported a study performed in 1980 of some 42 accidents involving road

Table 23.21 *Road transport environment in North America: probability and frequency of release of material in truck accidents in the USA (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Probability of release by accident type: single vehicle accidents

Accident type	*Probability of release*
Non-collision accidents	
Run off road	0.331
Overturn	0.375
Other	0.169
Collisions with:	
Fixed object	0.012
Parked vehicle	0.031
Train	0.455
Non-motorist	0.015
Other object	0.059

B Probability of release by accident type: multiple vehicle accidents

Accident type	*Probability of release*
Collision with:	
Passenger car	0.035
Truck	0.094
Other vehicle	0.037

C Probability and frequency of release by road type

Road type	*Probability of release*	*Frequency of release* (release/10^6 vehicle-miles)
Rural		
Two-lane	0.086	0.19
Multi-lane (undivided)	0.081	0.36
Multi-lane (divided)	0.082	0.18
Freeway	0.090	0.06
Urban		
Two-lane	0.069	0.60
Multi-lane (undivided)	0.055	0.77
Multi-lane (divided)	0.062	0.77
One-way street	0.056	0.54
Freeway	0.062	0.14

tankers transporting flammable materials in New South Wales (NSW). In 1979, in NSW, there were some 3000 road tankers carrying flammable loads and some 100 pressurized tankers. The annual crash rate was 2.5%, which was the same as for all vehicles.

There were 42 accidents investigated, 11 involving non-articulated vehicles and 31 involving articulated vehicles. There were 18 rollovers, 5 for the non-articulated vehicles and 13 for the articulated vehicles.

In 24 cases there was no leakage of the bulk load but in three of these there was leakage of the prime mover fuel tanks. In 10 of the rollover cases, there was substantial leakage. In two of the non-rollover cases, the tank was punctured and burned out. Of the other non-rollover cases, one involved the loss of 'a lot' of product from a fractured pipe fitting, one a loss from a discharge pipe and two from vents.

The authors state that fire occurred in 5% of cases. This would seem to cover the two cases of burnout just mentioned and to imply that none of the other cases involved a fire.

The authors obtained data on the various factors which influenced the accident under the headings: mechanical, environmental, behavioural and general.

Factors causing rollover included high centre of gravity, 'soft' roll stiffness and sloshing of the liquid. None of the tankers appeared to have side baffles.

From these data, the following estimates may be made for crash fires:

No. of crash fires = 2

Crash fires as proportion of accidents = 2/42 = 4.8%

23.6.13 Individuality of accidents

It is easy in a preoccupation with incident statistics to lose sight of the individual nature of some of the accidents which have occurred involving the road transport of hazardous materials. Mention has already been made of the chlorine tanker crash with a lorry travelling down hill at 60 mph. Other incidents with rather unusual features include the San Carlos campsite disaster (Appendix 16), which may not have been initiated by either crash or fire and which involved a vulnerable target, and the explosion of an explosives lorry at Peterborough (Case History A125), which involved a fire rather than a crash and occurred off the road in a company yard.

Moreover, enough has been said to indicate that, even where historical data do exist, the data may or may not be directly applicable. A case in point is the provision of side protection on tankers. This is provided on the ICI chlorine vehicles but not on the Australian road tankers described. In such cases, it may be appropriate to modify any historical data to take account of the difference between the conditions to which those data apply and the conditions of the problem in hand. Again this may involve modelling and the use of data appropriate to that.

23.7 Rail Transport

23.7.1 Regulatory controls and codes

The international transport of dangerous goods by rail is the subject of the Convention Concerning International Carriage by Rail (COTIF) and is governed by the *Regulations Concerning the International Carriage of Dangerous Goods by Rail* (RID) (DTp, 1993b), as described in Section 23.2.

In addition, the International Union of Railways (IUR) issues information of an obligatory or recommended nature.

In the United Kingdom, British Rail (BR) has a number of internal regulations. There is no requirement on BR to accept dangerous goods for carriage. It has published the document *List of Dangerous Goods and Conditions of Acceptance* (LOG) (BR 22426) which lists the dangerous substances that it is prepared to accept and the conditions of such acceptance. The list is based on the United Nations (UN) classification. It incorporates relevant statutory requirements such as those for radioactive materials. The conditions cover maximum quantities, forms of packaging, labelling, documentation, etc., and conform as far as

Table 23.22 *Road transport environment in North America: tanker accidents involving release of gasoline in Canada (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

Accident type	*No. of releases* (%)						*Proportion* (%)
	Spill	*Leak*	*Spill/fire*	*Fire*	*Other*	*Total*	
Collision	2			1		3	7
Collision/overturn	5		1			6	15
Overturn	19	1			1[a]	21	51
Brake failure	2					2	5
Puncture	2	1				3	7
Fitting/hose failure		1		1		2	5
Fire				2[b]		2	5
Military exercise	1					1	2
Bridge collapse	1					1	2
Total	32	3	1	4	1	41	

[a] Environmental contamination.
[b] One of these is classified as a spill/fire.

possible with UN recommendations. The Railways Act 1845 requires the consignor to give written indication of goods which are dangerous, and the Railways Act 1921 requires it to comply with the rules laid down by BR.

In addition to BR's general regulations, rules and procedures, for dangerous goods there are specific instructions to staff given in *The Working Manual for Rail Staff*, Part 3, *Handling and Carriage of Dangerous Goods* (BR 30054/3), commonly known as the 'Pink Pages'. This deals with the definition of dangerous goods and gives procedures for acceptance, marking, loading, unloading, marshalling and movement, and for incidents and fires.

In the United States, rail transport of hazardous materials is regulated by the DOT. The DOT Hazardous Materials Regulations (49 CFR Pt 179) apply to carriage by rail. The AAR complements the work of the DOT by setting standards.

23.7.2 Hazard scenarios

The hazard scenarios for rail transport of hazardous materials do not differ greatly from those for road described in Section 23.5. Thus, pool fires, torch fires, vapour cloud fires and explosions, and toxic releases may all occur in a broadly similar manner, as well as physical explosions and condensed phase explosions.

There are, however, a number of differences. One is that the energy in a train collision is much greater than that associated with a vehicle collision on a road. Another is that a train typically contains a number of tank wagons and these may be vulnerable to the initiating incident. A particular instance of this is that torch fires in which the flame from one tank wagon plays on another are much more significant. The rail environment also differs in respect of the population exposed to the event and of the access for the emergency services.

23.7.3 Rail tank wagon design

The RID gives requirements for the design of rail tank wagons which parallel those in the ADR for road tankers. For more hazardous materials, it is good practice to provide a strongly protected filling connection cover and buffer override protection.

Information on rail tank cars in the United States is given by Fitch (2003) in the *NFPA Handbook*. American rail tank cars are built to standards for freight cars generally and in addition must comply with the DOT Hazardous Materials Regulations and the *Specifications for Tank Cars* of the AAR. There are four main types of tank car:

(1) non-pressure tank cars;
(2) pressure tank cars;
(3) cryogenic liquid tank cars;
(4) other
    (a) high pressure service tank cars,
    (b) multi-unit tank cars.

Non-pressure tank cars have tank test pressures of 100 psi (6.89 bar) and pressure tank cars have test pressures of 100–600 psi (6.89–41.4 bar). Both types have capacities ranging from 4000 to 45,000 USgal (145–170 m^3). Cryogenic liquid tank cars carry liquids at −130 to −423°F (−90 to −253°C). The insulation is designed to protect the cargo for a 30-day period. Multiunit tank cars, or ton containers, carry demountable tanks which can be taken off the car for filling and emptying.

About 90% of the tank cars are constructed in carbon steel and most of the rest in aluminium. The regulations specify the following thicknesses of plate for the construction of tank cars: for non-pressure tanks, $^7/_{16}$ in. (11.1 mm) steel or $^1/_2$ in. (12.7 mm) aluminium, and for pressure tanks, $^9/_{16}$ in. (14.3 mm) steel and $^5/_8$ in. (15.9 mm) aluminium.

Tank cars may be provided with thermal insulation. The principal materials used are fibreglass and polyurethane foam. For cryogenic tanks, perlite is used. Some tanks are lined and some have heating coils.

The DOT has promoted a programme of protective measures to lessen the risk of tank rupture by overheating or puncture. These are:

(1) Thermal protection;
(2) Shelf couplers;
(3) Head shields.

The thermal protection is designed to protect the tank against a pool fire for 100 min or against a torch fire for 30 min. The shelf couplers are of a design which is less likely to disengage in a derailment. The head shields protect the lower part of the tank heads against puncture.

23.7.4 Rail system operation

The development of British practice in the movement of bulk chemicals by rail has been described by Sanderson (1981). The older method was to move small numbers of wagons through a series of marshalling yards; the newer method is to make up complete trainloads, or block trains, running between two points, so that rail transport becomes an integral part of the production line linking two works.

BR controls the movement of freight through the Total Operations Processing System (TOPS) computer system. This system makes it possible to keep track both of the movement of each individual wagon and of its position on the train. The system is particularly valuable in an emergency.

23.8 Rail Transport Environment

The basic sources of information on the rail transport environment in the United Kingdom are the Department of Transport and British Rail.

The *Transport Statistics Great Britain* 1976–86 (DTp, 1987b) and *Rail Safety – Report on the Safety Record of the Railways in Great Britain 1986* (DTp, 1987a) provide certain basic information. There are also available an appreciable number of accident reports.

Studies of the UK rail transport environment are given in the ACDS *Transport Hazards Report* (ACDS, 1991) and by P.A. Davies (1990). As already stated, the former considered four hazardous materials (motor spirit, LPG, chlorine and ammonia, and also explosives) whilst the latter was concerned with explosives, particularly munitions. Essentially these studies utilize two basic categories of information: (1) rail movements and (2) incident records.

23.8.1 Rail network and rolling stock

BR operates a rail network with 22,423 km of running line and 3601 km of sidings. There are some 70 marshalling yards.

In 1986, the distance travelled by freight trains was 54×10^6 km. In the year 1985–86, the distance travelled by loaded tank wagons containing both hazardous and non-hazardous chemical and petroleum products was 47.4×10^6 tank-wagon-km.

The ACDS report gives a detailed breakdown of the movements of the four materials considered, as shown in Table 23.23.

Table 23.23 *Rail transport environment in Great Britain: tank wagon capacities and movements for four hazardous materials (after ACDS, 1991) (Courtesy of Elsevier Science Publishers)*

A Tank wagon capacities

Substance	*Tank capacity* (te) 2-*axle*	*Bogies*
Motor spirit	32	75
LPG	20	40
Ammonia	–	53
Chlorine	29	–

B Tank wagon movements

	Motor spirit	*LPG*	*Ammonia*	*Chlorine*
Total movements (wagon-km/year)	10,199,095	13,90,590	1,348,080	313,668
Total wagon journeys (wagon-journey/year)	55,814	4,334	4,500	2,342

23.8.2 Rail accidents

Information on accidents involving freight trains generally is given in the study by Davies. The three main types of accident considered are collisions, derailments and fires.

The ACDS study deals mainly with accidents resulting in releases and with the ignition of releases of flammable materials.

From a study of general rail accident statistics, Davies gives the following breakdown of freight train accidents (FTAs) in 1986:

Type of accident	*No.*	*Proportion* (%)
Collision	113	35
Derailment	158	49
Fire	53	16
Total	324	100

He also made a study of some 187 accident reports, of which 38 were for FTAs. This is referred to as the FTA study. In this study, he obtained the following breakdown of:

Type of accident	*No.*	*Proportion* (%)
Collision	26	68
Derailment	8	21
Fire	1	3
Other	3	8
Total	38	100

23.8.3 Collisions

In general, freight train collision accidents are more severe than derailments. For collisions in 1986, Davies gives:

Type of collision	*No.*	*Proportion* (%)
FTvsFT	8	7
FTvsPT	1	1
FT vs ECS	10	9
Buffer stop	55	49
Level crossing	6	5
Miscellaneous obstacles	22	19
Animals	9	8
Other	2	2
Total	113	100

where ECS denotes empty coaching stock, FT denotes freight train and PT denotes passenger train. The most severe collisions are with rolling stock. From the data just given, there were 19 such incidents (17%) which break down to give:

Type of collision with rolling stock	*No.*	*Proportion* (%)
FTvs FT	8	42
FTvsPT	1	5
FT vs ECS	10	53

From the FTA study, he found that some 70% of collisions with rolling stock were head-on or front/rear collisions and obtained for these the following breakdown:

Type of collision with rolling stock	*Proportion* (%)
Head on	40
Front on rear	40
Rear by front	20

The other 30% of collisions with rolling stock were side impacts or glancing blows.

The most frequent type of collision was with buffer stops but the speed at which these collisions occurred was generally 10 mph or below. This type of collision was considered sufficiently minor that in 1987 the practice of recording it was discontinued. It is worth noting, however, that a major disaster due to a collision of this type on a passenger train on the London Underground occurred at Moorgate station in 1975.

The number of collisions at level crossings involving freight trains was small, but for all trains the following breakdown was obtained:

Type of collision	*No.*	*Proportion* (%)
Train on car or van	18	78
Car or van on train	5	22
Total	23	100

The closing speeds at which collision accidents occurred are not known, but from an analysis of the FTAs in the FTAs survey, P.A. Davies and Lees (1991a) obtained the estimates shown in Table 23.24, Section A.

23.8.4 Derailments

Turning to derailments, these are generally less serious than collisions. The most severe derailments tend to be those which result in subsequent collisions. A study of derailments has been made by Taig (1980). He found that some 10% of derailments involve subsequent collision, 4% being with other rolling stock and 6% with other objects. Taig also presents a graph showing data on the speed at which derailments occur. These data are given in tabular form by Davies and Lees, as shown in Table 23.24, Section B.

23.8.5 Fires

As stated above, in 1986 there were 53 fires recorded on freight trains. Small fires are a not uncommon occurrence, but very few become severe.

Table 23.24 *Rail transport environment in Great Britain: accident speeds of freight trains (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Freight train closing speeds in collisions with rolling stock[a]

Closing speed (mph)	*No. of collisions*	*Proportion of collisions* (%)
1–10	1	5
11–20	8	40
21–30	4	20
31–40	3	15
41–50	3	15
51–60	1	5

B Derailment speeds of freight trains[b]

Derailment speed (mph)	*Proportion of derailments*	
	On plain track (%)	*Not on plain track* (%)
1–10	15	54
11–20	20	20
21–30	6	6
31–40	18	4
41–50	26	4
51–60	9	4
61–70	3	4
71–80	2	4
81–90	1	0

[a] Estimated from accident reports. Sample size = 20.
[b] After Taig (1980). Sample size = 300.

Fires may be classified as crash fires and non-crash fires. In the 187 accident reports for all trains initially reviewed for the FTA study, only one involved a non-crash fire, which was not on a freight train. By contrast, in the 38 reports of FTAs, there were 6 crash fires. Four of these resulted from collisions and two from derailments. All 6 fires were quite severe. On this basis, the ratio of crash to non-crash fires is of the order of at least 6 : 1. Since there were 34 crashes (collisions and derailments) in the survey, the probability of a fire given a severe crash is 0.18 (= 6/34).

23.8.6 Releases

Turning to accidents resulting in leaks, the ACDS report considers two categories of accident: (1) puncture of a tank wagon by collision or derailment and (2) failure or maloperation of the tank wagon equipment.

It considers each of the four study materials in turn. For motor spirit

$$\text{Distance travelled} = 10.2 \times 10^6 \text{ tank-wagon-km/year}$$

There were four puncture incidents in a 6.25-year period, giving:

$$\text{Frequency of puncture of motor spirit tank wagon} = 6.3 \times 10^{-8}/\text{tank-wagon-km}$$

The report also mentions a BR estimate of puncture frequency of 10^{-8}/tank-wagon-km.

For the liquefied gases, it refers to a study by ICI on incidents with the possible potential to cause puncture of a chlorine or ammonia tank wagon. In the 7-year period 1980–86, there were on tank wagons generally seven puncture incidents. These all occurred on tank wagons with 'thin' (6 mm) walls. It was estimated that for such incidents the average probability of puncture of a chlorine tank wagon was 0.0385 and that for an ammonia wagon 0.103. Then utilizing the figure of 47.4×10^6 tank-wagon-km travelled by all laden tank wagons each year, the following estimates are obtained:

Frequency of puncture of chlorine tank wagon
$= 0.9 \times 10^{-9}$/tank-wagon-km

Frequency of puncture of ammonia tank wagon
$= 2.5 \times 10^{-9}$/tank-wagon-km

The frequency of puncture of an LPG tank wagon was taken as the same as that for an ammonia wagon.

The other leak mode is failure or maloperation of the tank wagon equipment. These leaks were assumed to be relatively small. Estimates of the frequency of such leaks per 10-h journey were made using fault trees, which are given in the report. The following results were obtained:

	Frequency of leak (leaks/journey)
LPG	0.83×10^{-8}
Chlorine	3.1×10^{-8}
Ammonia	1.3×10^{-8}

No evaluation was made for motor spirit, since the consequences were judged to be minor.

23.8.7 Release ignition

For the probability of the ignition of a leak of flammable material, BR incident reports showed that of five leaks over a period of 6.25 years, one ignited. The ACDS report bases its estimates partly on these data and data from fixed sites, and partly on judgement. It gives for small spills, whether of motor spirit or LPG, probabilities of 0.1 for immediate ignition, 0 for delayed ignition and 0.9 for no ignition. For large spills of motor spirit, the corresponding probabilities are 0.2, 0.1 and 0.7 and those for large spills of LPG are 0.2, 0.5 and 0.3, respectively.

23.8.8 Marshalling yard incidents

The ACDS report also considers activities in marshalling yards. BR operates some 70 such yards, but the majority of movements of dangerous goods are by block trains which do not enter marshalling yards.

In the 8-year period to the end of 1987, there were two puncture incidents. These involved methanol tank wagons punctured in collisions, one by a coupling hook and the other by a shunting engine. On this basis, the report obtains a generic value for the puncture frequency of 'thin' walled tank wagons:

Frequency of puncture $= 3.6 \times 10^{-3}$/yard-year

This implies similar levels of traffic at all yards.

For the four study substances, the proportions travelling by Speedlink service are: motor spirit, <1%; LPG, 28%; chlorine, 53%; and ammonia, >1% (occasional wagon load returned to its origin).

Based on arguments relating to the differences between thin- and thick-walled tank wagons, the probabilities of puncture given an incident of the type just described were estimated as 0.01 for LPG and ammonia tank wagons and 0.005 for a chlorine tank wagon.

One of the busiest marshalling yards was selected for detailed study. The substance principally considered there was chlorine. The yard handles some 78% of the Speedlink chlorine traffic, or some 1500 chlorine tank wagons per year. It was estimated that the yard handles a total of 7990 laden tank wagons of hazardous substances per year.

The frequency of a chlorine leak due to a puncture of a tank wagon at this particular yard was then obtained as:

Frequency of puncture of chlorine tank wagon

$$= 3.6 \times 10^{-3} \times 0.005 \times \frac{1500}{7990}$$

$$= 3.4 \times 10^{-6}/\text{year}$$

It may be noted that in deriving this figure for a busy yard, it is the generic figure for puncture frequency for all yards which is used.

For leaks due to failure or maloperation of equipment, use was made of the data obtained in the *en route* study, as given in Section 23.8.6. On the assumption that one-tenth of the total journey time is spent in the marshalling yard, the probability of a chlorine leak due to this cause was obtained as 3.1×10^{-9} journey. Then

Frequency of leak due to equipment failure of chlorine tank wagon $= 1500 \times 3.1 \times 10^{-9}$
$= 4.6 \times 10^{-6}$/year

The other main study substance passing through marshalling yards is LPG. The yard studied handles some 200 laden wagons per year. However, LPG tank wagons are not actually marshalled. In view of this, the generic puncture frequency was reduced by a factor of 5. Then, taking the probability of puncture of an LPG tank wagon in an incident which would puncture a thin-walled wagon as 0.01, as given above, the frequency of an LPG leak due to puncture of a tank wagon at this particular yard was then obtained as:

Frequency of puncture of LPG tank wagon

$$= 3.6 \times 10^{-3} \times \frac{1}{5} \times \frac{200}{7990}$$

$$= 4.6 \times 10^{-6}/\text{year}$$

23.8.9 Exposed population

The population exposed in a rail transport accident comprises the *en route* population and the other rail users, particularly passengers in other trains, together with the emergency services.

Meaningful assessment of the societal risk from rail transport requires the use of a reasonably refined population exposure model. The models used in the ACDS report are described in Appendix 17.

23.8.10 US environment

In the United States, the total railroad track mileage in 1981 was 327,000. From a survey of US and Canadian Class 1

railroads for 1983, the length of line surveyed was 145,881 which was 69.5% of the total track. This therefore gives for those two countries a total mileage of 209,900 for this class of track.

In 1986, there were in use in the United States some 183,000 tank cars, which comprised some 10% of the total fleet of freight wagons.

The NTSB *Annual Report* 1980 gives the railroad accident rate in 1979 for passenger and freight trains in the Unites States as 12.8 accidents per 10^6 train-miles. The 1981 *Report* gives for 1980 the following breakdown of causes of train accidents: track defects, 41%; mechanical/electrical failures, 17%; human factors, 28%; and other, 14%.

The main causes of accidents leading to loss of containment of hazardous materials from rail tank cars are derailments and collisions. One principal casue of such accidents is the state of the track and of the rolling stock.

23.9 Road and Rail Tunnels

Both road and rail systems include tunnels. In principle, differences may be expected from open routes with respect to both the frequency and the consequences of incidents, but there are certain common features between road and rail tunnels as well.

Accounts of tunnels tend to be either descriptions of incidents or hazard assessments. Case histories involving tunnels are described in Section 23.21 and hazard assessment is described in Section 23.26.

23.10 Waterway Transport

The extent of waterway movement of hazardous materials is small in the United Kingdom, but it is considerable in Europe and the United States. The Rhine and the Mississippi are major arteries. Accounts of waterway transport have been given by H.P. Nelson (1964), Backhaus and Janssen (1974) and Ligthart (1980).

In the United Kingdom, British Waterways bylaws apply to the transport of dangerous goods on canals. It issues a document on the terms and conditions of acceptance.

In the United States, the responsibilities of the US Coast Guard extend to inland waterways. The US Army Corps of Engineers is also involved through its responsibility for waterfront structures and embankments, canals, bridges and dams.

Backhaus and Janssen quote the maximum size of LNG barge which might be used on the Rhine as 108 m long × 11.4 m broad. Alternatively, use might be made of four barges with a push tug with total dimensions 185 m long × 22.8 m broad.

The construction of the barge tends to vary with the type of material which it carries. In the United States, for example, for petroleum, the barge shell is also the container wall, whereas for chlorine there are separate chlorine tanks within the barge structure.

A principal hazard of barge transport is collision. It is important to minimize the risk of this, not only when the barge is on the move but also while it is loading or unloading.

Another hazard of barge transport arises where barges are used to carry a variety of chemicals. While skilled people are generally available to assist at the loading point, the barge operator may well be on his own at the unloading point.

In the United States, the Coast Guard has attempted to improve the competence of barge crews by encouraging them to take specific training as chemical tankermen.

The NTSB annual reports describe measures to reduce collisions. In particular, efforts have been made to improve bridge-to-bridge communications.

A study of the hazards of transport of LPG on inland waterways has been described by Ligthart (1980). He states that serious risk arises only from collisions, although he qualifies this by excluding risks from cargo treatment, cleaning and repair.

23.11 Pipeline Transport

23.11.1 Regulatory controls and codes

The movement of hazardous materials by pipeline in the United Kingdom is regulated by the Pipelines Act 1962 and enforced by the Pipelines Inspectorate. The Act distinguishes between local pipelines (less than 10 miles long) and cross-country pipelines (greater than 10 miles long).

In the United States, pipeline transport is regulated by the DOT through the Natural Gas Pipeline Safety Act 1968 and related legislation for other hazardous materials. Relevant regulations include Pipeline Safety Program Procedures (Part 190) and Transportation of Natural and Other Gas by Pipeline: Minimum Federal Safety Standards (Part 192).

Some standards and codes for pipelines include BS CP 2010: 1970 – *Design and Construction of Steel Pipelines in Land*, the ASME *Code for Pressure Piping* B31.4: 1974 *Liquid Petroleum Transportation Systems* and B31.8: 1975 *Gas Transmission and Distribution Piping Systems*, the IP *Pipeline Safety Code* (1982 MCSP Pt 6) and IGE/TD/1 *Steel Pipelines for High Pressure Gas Transmission* (IGE, 1984).

23.11.2 Hazard scenarios

For a pipeline carrying flammable gas, some principal hazard scenarios are a jet fire and a flammable vapour cloud, leading to a flash fire or vapour cloud explosion, whilst for one transporting liquid, the scenario is a liquid spillage leading to a pool fire or flowing liquid fire. The main hazard scenario for a pipeline carrying toxic gas or liquid is a toxic vapour cloud.

23.11.3 Pipeline economics

The economics of pipeline transport have been discussed by Lennart (1964). The cost breakdown for pipelines is quite different from that for other modes of inland transport. At that time, for pipelines, the total costs were approximately 70% fixed costs and 30% variable costs, whilst for waterways, road and rail, the fixed costs were 30%, 15% and 5% and the variable costs 70%, 85% and 95%, respectively. Moreover, the cost index n relating the capital cost C to the throughput P

$$C = kP^n \qquad [23.11.1]$$

where k is a constant, is very low. Lennart gives the capital cost of a 6 in. line as only about 45% more than that of a 4 in. line. Thus, for the supply of an assured market at a fixed point, a pipeline is a very attractive mode of transport.

23.11.4 Pipeline systems

In Western Europe and North America, there are large pipeline systems carrying predominantly hydrocarbons.

For the former, statistics on the pipeline network are given in *Performance of Oil Industry Cross-Country Pipelines in Western Europe: Statistical Summary of Reported Spillages – 1991* (CONCAWE, 1991 4/92), which is part of an annual series.

In 1991, Western Europe had 210 service pipelines with a total length of 21,000 km. These pipelines carry some 593 million cubic metres of crude oil and refined products, giving a total movement of 101×10^9 m^3-km. Maps showing the pipelines in Western Europe as a whole and in particular areas are given in the CONCAWE report.

Statistics on pipelines in the United States are collected by the Federal Energy Regulatory Commission (FERC). Periodic reviews are given in the *Oil and Gas Journal*. In the review of the 1984 figures by True (1985), the mileage of interstate pipelines is given as, for gas, 258,204 miles and, for liquid, 173,922 miles.

Sources of information on pipeline failures also often contain information on the size of pipeline systems.

23.11.5 Pipeline design and operation

Pipelines are usually buried about 1 m below ground. Their environmental impact is therefore usually minimal and they can be difficult to detect even by aerial survey unless there are sufficient marker posts.

The extent to which the temperature of the gas in a pipeline varies depends on the depth at which it is buried, but for most pipelines in the United Kingdom the variation is small, although this is not always so in other countries.

The standards of construction and protection of pipelines have improved markedly over the years. The older pipelines were of mild steel or cast iron. The former have often corroded, while the latter have often withstood conditions better. There are cast iron brine mains, for example, which have remained in good condition. But cast iron has a relatively low resistance to impact and is not an ideal material for pipelines for hazardous substances.

Mild steel is now generally used for pipelines, but it is of much higher quality, being more uniform and better extruded or seam welded. Welds on the pipeline are more carefully done.

Pipelines are also much better protected. The older pipelines had no specific external protection. Then the wrapping of lines was developed, culminating in the present practice of using a coal tar/glass fibre wrap. But this was not the whole answer, because corrosion still occurred at points where the wrapping was badly done or was damaged or where there were line joints.

This problem has been largely overcome by the use of cathodic protection. Corrosion of steel involves iron passing into solution as an ion. This process may be reduced by impressing on the pipe a suitable voltage. It is still necessary to wrap the pipe, because the currents required with unwrapped pipe are excessive. But cathodic protection gives effective protection at defects and gaps on a wrapped pipe.

The modern method of external protection, therefore, utilizes a combination of wrapping and cathodic protection. With this system, minimum external corrosion rates are obtained.

Internal corrosion depends on the material transported, but in many cases, it is very low.

Pipelines are regularly inspected for corrosion, both external and internal. The internal surface of the pipe may be checked by instrumentation transported through the pipe by an 'intelligent pig'.

A code of practice for pipelines is provided by the *Pipeline Safety Code* by the IP (1982 MCSP Pt 6). This deals with the design, materials, land and rights of way, construction, testing, cathodic protection, operation, maintenance and emergency procedures.

The internal pressure of the pipeline should not be less than the normal maximum working pressure plus any anticipated surge pressure. The minimum wall thickness for a straight pipe under internal pressure is determined by the formula

$$t = \frac{pD}{20 f_y a} \qquad [23.11.2]$$

where a is a design factor, D is the external diameter of the pipe (mm), f_y is the specified minimum yield strength (N/mm^2), p is the internal design pressure above atmospheric pressure (bar), and t is the design thickness of pipe wall (mm). The design factor a is taken as 0.72 for gas and liquid pipelines in remote areas.

Protective devices such as pressure relief devices and shut-down systems should be fitted to prevent the line pressure rising more than 10% above the internal design pressure and to deal with fluid expansion effects.

The Institute of Petroleum (IP) code describes a number of additional protective measures which may be provided to avert damage to a pipeline. They are: (1) increased earth cover; (2) increased coating strength; (3) an additional protective coating of concrete, provided this does not screen cathodic protection currents; (4) additional position markers on the surface; (5) increased pipe wall thickness; (6) provision of a casing sleeve and (7), for above ground pipelines, provision of impact protection.

In some areas, design of the pipeline against earthquakes assumes greater importance. Accounts of the seismic design of pipelines include those of Newmark and Hall (1975), Shinozuka, Takada and Ishikawa (1979) and Jinsi (1985).

Increasingly use is made of trenchless technology, in which a pipeline is installed, replaced or repaired without removing the earth above it. It is used particularly for water and gas distribution systems. An account of the set of technologies which come under this heading is given in *Introduction to Trenchless Technology* (International Society for Trenchless Technology, 1991). Whilst the techniques are applicable to distribution rather than transmission systems, they have been used for pressure piping and for quite large diameter pipes. Upsizing of pipes of 225 and 355 mm diameter is well established and pipes of up to 600 mm diameter have been done.

23.11.6 Hydrocarbon pipelines

The majority of pipelines carry flammable gases such as natural gas, ethylene or LPG or flammable liquids such as crude oil, oil products or NGL. It is to hydrocarbon pipelines that the account given so far mainly relates.

23.11.7 Ammonia pipelines

There are some very extensive liquid anhydrous ammonia pipeline systems, especially in the United States. The ammonia is mainly used by farmers in the corn belt as fertilizer.

Descriptions of the Mid-America Pipeline System are given by Rohleder (1969) and by Luddeke (1975) and of the Gulf Central System by Inkofer (1969).

The Gulf Central pipeline described by Inkofer has a 10 in. diameter trunk line 548 miles in length running south to north with two spur lines off it. One of these has 417 miles of 8 in. line and 235 miles of 6 in. line, the other has 234 miles of 8 in. line and 153 miles of 6 in. line. The design study was for a line operating at a pressure of 1440 psig (100 bar) and in the temperature range 35–75°F (2–24°C). Details of the design codes, materials and inspection methods are given by Inkofer.

The hazard of brittle fracture was given special consideration. Cases have occurred where brittle fracture has propagated along a pipeline at a velocity close to that of sound in the metal. Thus, a large length of line could be affected. The maximum transition temperature for the pipeline was set at 0°F (−17.8°C), which is well below the normal operating temperature range. Above the transition temperature, ductile shear failures may occur, but these were considered less serious.

The composition of the anhydrous ammonia is closely controlled to prevent attack on the pipeline. Impurities in ammonia, such as air or carbon dioxide, can cause stress corrosion cracking. This is largely inhibited, however, if the ammonia contains 0.2% water and this water content is specified as a minimum.

The pipeline has at approximately 10-mile intervals shut-off valves which can be closed manually. At the same points there are also check valves which prevent back flow from the line section ahead of the rupture point. At rather greater intervals there are pump stations with instrumentation that detects any sudden changes of pressure caused by a line break and stops pumps and closes automatic shut-off valves.

The situation arising in the event of a leak is considered by Inkofer. For a small leak, he suggests that, in theory, the ammonia should freeze the surrounding ground, but this was queried in the discussion, where it was pointed out that practical experience indicates that small leaks of ammonia actually tend to dissolve in water and generate heat.

With a large leak due a major pipeline rupture, the line break detectors would stop the pumps and shut the isolation valves at the upstream pump station and the suction pressure controls would stop the pumps at the downstream pump stations, so that the pipeline break would be isolated to a single section.

There would be an initial high pressure spurt of ammonia as the pipeline pressure vented. The line pressure would then fall to that corresponding to the vapour pressure of ammonia at the line temperature, that is, 107 psia at 60°F. Several other effects would further reduce the rate of discharge. Vapour locks would form at humps along the pipeline, and these would cause a back pressure due to the accumulated liquid heads created by each rise in the line ending in a vapour pocket. Flashing of vapour would cool the remaining liquid. The overall results of these effects would probably be that after the initial spurt of flashing liquid there would be a period of prolonged and spasmodic ejection of liquid and vapour.

The proportion of ammonia flashing off from saturated liquid at 60°F and 107 psia is approximately 10%. The remaining liquid would be cooled to −28°F and would form a pool. The evaporation from this pool would be in the range 1–7 lb/ft^2 h and thus fairly slow.

A 10-mile section of 10 in. line at 60°F contains 591 ton of ammonia and, assuming 90% of this forms a pool at −28°F, the resulting 24,990 ft^3 could form a pool of 12,495 ft^2 with a depth of 24 in., or one of 149,940 ft^2 with a depth of 2 in.

The pipeline is continuously monitored by a pipeline dispatcher. In the event of a line break, he will know the location between the particular pump stations. He then sends out a team to locate the break more precisely, to shut all isolation valves in the section affected and to open blowdown valves in order to encourage the formation of vapour locks. The basic procedure for containing the spillage is to dike around it. The line is then excavated and the rupture repaired. If necessary, stopple plugs are inserted into the line to shut off the flow.

The vapour from an ammonia line break is initially cold and heavier than air. It can travel in lethal concentration several miles. The dispersion of vapours from ammonia spillages was considered in more detail in Chapter 15.

The description given by Rohleder and by Luddeke of the Mid-America Pipeline system is broadly similar.

23.11.8 Chlorine pipelines

Pipeline transport of chlorine is much less extensive than that of ammonia. Chlorine lines are dealt with in *Chlorine Pipelines* (Chlorine Institute, 1982 Pmphlt 60). Further discussions are given by Danielson (1964) and H.P. Nelson (1964).

The chlorine may be transported either as vapour or as liquid. A vapour line should be operated with vapour phase only and a liquid line with liquid phase only. The situations which might give rise to mixed phase conditions should be identified and measures taken to avoid them.

The Chlorine Institute recommends that for any chlorine pipeline the maximum pressure should not exceed 300 psig (21 bar). However, this should not be construed as the design criterion. It recommends also that the maximum temperature at any section of the pipeline should not exceed 250°F (121°C).

The pipeline may be above or below ground. A line above ground is easier to monitor for external corrosion but an underground line may be safer in some circumstances. If the line is buried, consideration should be given to the frost line.

Internal corrosion is very low if the chlorine is dry, but is markedly increased by small quantities of water. It is essential, therefore, to design the line to facilitate drying out, to ensure that thorough drying is carried out and to keep the chlorine product dry.

Liquid chlorine has a very high coefficient of thermal expansion and it is necessary, therefore, to protect lines against hydrostatic rupture. The Chlorine Institute recommends the use of a pressure relief valve or bursting disc discharging to a receiver or safe area or, alternatively, the use of an expansion chamber. Nelson states that an expansion chamber should have a capacity of 20% of the line volume. If an expansion chamber is used, it should be properly operated and maintained, so that air in the chamber is not gradually replaced by chlorine.

The provision of a means for the control of line breaks is particularly important with a chlorine pipeline. Automatic shut-off valves may be installed for gas or liquid lines, while excess flow valves may be used as an alternative on liquid lines. A combination of both devices may be preferable for the liquid case.

23.11.9 Pipeline failures

For Western Europe, the publication *Performance of Oil Industry Cross-country Pipelines in Western Europe 1991* (CONCAWE, 1992 4/92), one of a continuing series, gives details of pipeline failures.

In the United States there appears to be no single body which regularly publishes information on pipeline failure. Pipeline operators are required to report leaks to the DOT. The DOT issues an annual report on natural gas pipelines. Major pipeline accidents are investigated by the NTSB. Both organizations periodically publish information on pipeline failures.

A survey on the *Safety of Interstate Natural Gas Pipelines* by the Federal Power Commission (FPC) (1966) gives information on failures in these pipelines in the $15^1/_2$-year period from January 1950 to June 1965. The length of transmission pipelines covered was 204,730 miles in 1964. The number of failures recorded in the period was 1058 line failures, 121 compressor or metering station or other facilities failures, and 1115 field testing failures. Employees suffered 35 deaths and 135 injuries, and non-employees 29 deaths and 87 injuries. Of the 64 deaths, 42 arose from failures in lines and 17 from failures in compressor or metering stations or other facilities. The causes of the line failures are analysed in Table 23.25. The relations between the number of failures and of casualties over the $15^1/_2$-year period and the pipe sizes are given in Table 23.26.

The *Annual Report on the Administration of the Natural Gas Pipelines Safety Act of 1968* by the DOT for 1974 states that in 1974 there were 335,000 miles of natural gas gathering and transmission pipelines, and that in the period 1970–74 there were 2093 failures. From these data, the failure rate for such pipelines was 1.25×10^{-3} per mile per year. In this period, there were eight fatalities to employees and the same number for non-employees. Causes of the 460 failures in 1974 are broken down as follows:

Cause	*Proportion* (%)
Damage by outside forces	59.5
Corrosion	17.0
Construction defect or material failure	17.6
Other	5.9

The annual report on pipeline failures up to 1976 by CONCAWE (1977 9/77) states that between 1972 and 1976, the combined length of oil industry pipelines increased from 15,800 to 18,100 km and that in the period 1972–76, there were 93 spillages. From these data, assuming an average of 17,700 km of pipeline over the period, the failure rate obtained for such pipelines is 1.05×10^{-3}/km-year. The causes of the 93 failures are categorized in Table 23.27, first column. The corresponding report up to 1991 by CONCAWE (1992 4/92) states that in 1991 there were some 21,000 km of pipeline and that in the period 1987–91 there were 50 spillages. Assuming an average of 20,000 km of pipeline over the period, the failure rate obtained is 0.5×10^{-3}/km year. The causes of the 50 failures are categorized in Table 23.27, second column.

Further information on gas pipelines operated by the British Gas Corporation (BGC) has been given by Knowles, Tweedle and van der Post (1977). They state that since 1970, all faults on the transmission system have been recorded and that up to August 1977 there had been 309 repairable incidents, of which 73 were defined as 'lost gas' incidents. The following classification is given:

Table 23.25 *Failure of interstate natural gas transmission pipelines in the USA 1950–65: causes of failure (after Federal Power Commission, 1966)*

Pipeline punctured by plough, bulldozer, excavating shovel, road grader or other earth-moving equipment	279
Corrosion	193
External	148
Internal	45
Weld failures	190
Action of the elements	84
Coupling failures	65
Damage during installation	58
Fatigue failures	35
Defective pipe	26
Thermal stress	21
External explosion	14
Miscellaneous	38
Unknown or unreported	55
Total	1058

Table 23.26 *Failure of interstate natural gas transmission pipelines in the USA 1950–65: failures by pipe diameter (after Federal Power Commission, 1966)*

Pipe diameter (in.)	*No. of failures reported*	*Failures per* 1000 miles	*No. of casualties reported*
0–5.0	141	10.6	4
5.1–10.0	324	11.6	25
10.1–15.0	132	9.0	9
15.1–20.0	278	12.0	43
20.1–25.0	97	5.9	35
25.1–30.0	62	2.6	31
>30.0	5	2.8	11
Unreported	19	–	9

Mechanical interference (including coating damage)	204
Corrosion (internal and external)	32
Other faults (including faulty seal on pig trap door, leaking flanges, cathodic protection pad weld crack, etc.)	56
Girth weld	9
Pipe defect	5
Ground movement	3
Total	309

The interference incidents are further broken down as shown in Table 23.28. The total number of leaks includes broken connections and piercing of the carrier pipe, while

the number of leaks due to excavating machinery covers piercing of the carrier pipe only.

A failure rate of 5×10^{-3}/mile-year for chlorine pipelines was used by Westbrook (1974) in his assessment of the hazard of this mode of chlorine transport, as described in Chapter 18.

A study of pipeline failure rates in which the prime concern was with failure of offshore pipelines in the North Sea has been described by de la Mare and Andersen (1981). The work draws on the data sources already mentioned, that is, the DOT for the United States, CONCAWE for Western Europe and British Gas for the United Kingdom, and also the USCG for the Gulf of Mexico, Gaz de France (GdF) and the E&P Forum for the Arabian Gulf. The authors quote the following failure rates: CONCAWE, for onshore crude oil and product pipelines in Western Europe 1966–76, 0.39×10^{-3}/km-year for crude oil, 1.11×10^{-3}/km-year for products, and overall 0.69×10^{-3}/km-year; British Gas, for its gas transmission network 1970–77, 0.65×10^{-3}/km-year; Gaz de France, for its gas transmission network 1967–77, 3.3×10^{-3}/km-year; USCG, for offshore pipelines (6–18 in.) in the Gulf of Mexico, for oil 17.4×10^{-3}/km-year and for gas 12×10^{-3}/km-year. The North Sea had recorded two failures, giving a failure rate of 0.7×10^{-3}/km-year, but with 95% confidence limits 0.067–2.5.

The authors conclude that: the failure rates of pipelines appear similar even where the fluid handled and the environment are different; that the failure rates of oil pipelines depend on the diameter; that about half the failures can be attributed to external factors; and that pipelines tend to exhibit wearout failure. On this latter point, they quote CONCAWE data for the times to the first, second and later failures, and analyse these data to demonstrate that wearout failure occurs.

Another study of pipeline failure, confined to oil lines, is that given by Blything (1984 SRD R326), who considers pipeline failures in the United States, Canada and Western Europe, using data from the DOT and NTSB, the Canadian Petroleum Association (CPA) and CONCAWE, but mainly from the latter. Some of their analyses of the CONCAWE data for Western Europe are given in Table 23.29. Section A of the table gives the number of failures by pipe diameter and cause, Section B, the overall frequency of failure by pipe diameter and Section C, the size of the defects and spills.

Section A shows that the most important causes of failure are third party activity (TPA) and external corrosion. Both are dependent on the diameter of the pipe. The other two causes are less significant and less diameter dependent. External corrosion is also a function of the fluid carried and is most frequent on lines conveying heavy fuel oil (HFO). This mode of failure is often by pinhole leaks and tends to have a low potential for major hazard.

Section B of the table shows that the overall failure rate of the pipeline decreases with increasing pipe diameter.

The data on size of defects were somewhat sparse. Some 21 incidents were found in the data for Western Europe and Canada where defect size was recorded. Of these, 15 were caused by TPA. The defects were either holes or partial penetrations which failed at a later date. For some of

Table 23.27 *Failure of oil pipelines in Europe 1972–76: causes of failure (after CONCAWE, 1977 9/77)*

Cause of failure	*1972–76*[a]	*1987–91*[b]
Mechanical failure		
Construction	7	8
Material	14	7
Operational error		
System	2	–
Human	2	2
Corrosion		
External	34	8
Internal	2	5
Natural hazard		
Subsidence	3	2
Flooding	–	–
Other	–	–
Third party activity		
Accidental	24	13
Malicious	–	2
Incidental	5	3
Total	93	50

[a] CONCAWE (1977 9/77).
[b] CONCAWE (1992 4/92).

Table 23.28 *Failure of British Gas Corporation gas transmission pipelines 1970–77: failures by pipe wall thickness (after Knowles, Tweedle and van der Post, 1977)*

	Wall thickness (in.)					
	<0.374		*0.375–0.499*		*0.500–0.625*	
	No.	*No./1000 mile-year*	*No.*	*No./1000 mile-year*	*No.*	*No./1000 mile-year*
Total no. of interference incidents	98	3.36	60	2.96	34	1.70
No. of incidents due to excavating machinery	69	2.36	33	1.63	18	0.90
Total no. of leaks	15	0.51	4	0.19	2	0.10
No. of leaks due to excavating machinery	5	0.17	0	0	1	0.05
Mileage at risk		3579		2480		2439

Table 23.29 *Failure of oil pipelines in Western Europe 1975–80 (after Blything 1984 SRD R326, from CONCAWE)*

A No. of failures by pipe diameter and cause

Cause	*Pipeline diameter* (mm)						
	150–275	300–360	400–460	500–560	600–700	>800	*All diameters*
External corrosion	14	5	3	0	0	0	22
Third party	17	5	5	1[a]	0	0	28
Mechanical	3	0	1	4	1	4	13
Natural hazard	1	2	1	1	2	0	7
All causes	35	12	10	6	3	4	70

B Overall failure rates by diameter

Pipeline diameter		*Length* (km)	*Frequency of failure* (failures/km-year)
(mm)	(in.)		
150–275	6–10	4967	1.2×10^{-3}
300–360	12–14	2598	7.7×10^{-4}
400–460	16–18	3118	5.3×10^{-4}
500–560	20–22	2402	4.2×10^{-4}
600–700	24–30	2358	2.1×10^{-4}
>800	>32	2757	2.4×10^{-4}
All diameters			6.3×10^{-4}

C Size of defects[b]

Pipeline system	*Cause of failure*	*Defect diameter range* (mm)	*No. of incidents*	*Spillage volume* (m^3)
WE oil pipelines, 1978	Third party activity	<50	1	2.5
		50–100 (80)	2	58
	Mechanical	<50	1	19
		>100	1	2000
Canadian oil pipelines	Third party activity	<50 (40)	3	50, 28, 24
		50–100 (76)	4	12, 48, 953, ?
		>100 (151)	3	64, 935

[a] Failure caused by loss of support due to indirect third party activity.
[b] Also some Canadian data.

these incidents, it was possible to estimate the size of the spill. Data for these incidents are given in Section C of Table 23.29. Details on each of the 21 incidents are given by Blything.

These two reports give a wealth of further information on pipeline failures. As described, the main cause of failure in pipelines is interference, or TPA. In particular, damage occurs to pipelines from earth-moving and excavating equipment. Most pipelines can be punctured by the tooth of a mechanical excavator with the possible exception of very large mains, which have a thickness of about $\frac{1}{2}$ in. In rural areas, this may arise particularly from ditching and land drain work; in urban areas from work on services such as water, gas, electricity and sewage. It is essential, therefore, for the pipeline operator to keep a close watch on activities which may give rise to the hazard and for him to liaise with the authorities involved with planning and utilities. Moreover, it should be borne in mind that the person who needs to know is the excavator operator, and the organizations concerned should understand their responsibilities to ensure this.

23.12 Marine Transport: Shipping

Marine transport is distinguished from the other modes of transport in a number of ways. These include its international nature, which has many aspects; the size of the cargoes carried; and the marine environment.

General accounts of marine transport are given in the ACDS *Transport Hazards Report* (1991), *Safer Ships, Cleaner Seas* (Donaldson, 1994) (the *Donaldson Report*) and *The Carriage of Bulk Oil and Chemicals at Sea* (Rawson, 1994), which may be supplemented by the references cited below.

23.12.1 Shipping industry

Marine safety needs to be viewed against the background of the shipping industry and its particular characteristics. An account of this background is given by Gilbert (1994). Since 1945, international trade has experienced an explosive growth. One consequence has been a massive increase in vessel size. Contrary to what might be expected, the industry is a 'low entry' one. As Gilbert states, 'In boom

times, banks and financial institutions have been only too willing to lend money to almost anyone who could submit a reasonable prospectus'.

Most ships are custom built. The owner identifies a particular market. Shipyards are then prepared to tailor the design to the owner's requirements. Ships are built with single or double hulls, single or twin screws, and slow or medium speed engines, in combination with a wide variety of cargo, ballast and fuel systems. This is in marked contrast, for example, with the situation pertaining to the design of aircraft.

Another characteristic feature is manning. Crews often contain many nationalities, some of whom may have difficulty in communicating with each other.

Shipping is vulnerable to the international economic cycle, so that in bad times large numbers of ships are laid up and sections of the industry are barely viable. This increases reluctance to incur expenditure on safety.

The international nature of the industry and the resistance of a large part of it to effective controls has meant that international agreements have tended to represent the lowest common denominator.

23.12.2 Hazard scenarios

A marine accident may pose a major threat not only to life but also to the environment.

A loss of containment of a material may occur due to damage to the cargo tanks or during loading and unloading operations. A serious hazard to life may arise from the release of a large quantity of flammable or toxic liquefied gas onto water, where it will vaporize rapidly, in or near a port. The USCG has commissioned studies of the hazard arising in this situation, such as the one by Eisenberg, Lynch and Breeding (1975). However, although much feared, this hazard has not so far been realized on a large scale.

Shipboard fire and explosion is another serious hazard and one which does occur periodically. The initiating event may be a fire in the engine room, the pump room, a cargo tank or elsewhere. Or it may be an explosion in the engine room or cargo tank. A particular hazard exists if the ship carries explosive substances. Some of the most devastating explosions have occurred from the explosion of ammonium nitrate cargo.

Loss of cargo also presents a threat to the environment. Here oil cargoes present a particular threat, since oil is carried in large quantities and is liable to do damage to the marine environment which it is difficult to prevent.

23.12.3 Ship design

Fundamentals of ship design are described in *Principles of Naval Architecture* (Comstock, 1967), *Basic Ship Theory* (Rawson and Tupper, 1968–), *Basic Naval Architecture* (Barnaby, 1969) and *Mechanics of Marine Vehicles* (Clayton and Bishop, 1982). Liquefied gas carrier (LGC) design is described in *Liquefied Gas Handling Principles on Ships and in Terminals* (SIGTTO, 1986/3). Accounts of ship design and construction with special reference to hazards are given in *Incidents Involving Aircraft, Shipping and Railways* (Home Office, 1985 *Manual of Firemanship* Bk 4) and in the *NFPA Handbook*.

A ship is essentially constructed as a box girder formed by the hull and the main deck and strengthened by members such as the keel, frames, bulkheads and other decks.

Cargo ships are of two broad types: (1) dry cargo ships and (2) bulk cargo ships. The first group is general purpose dry cargo ships carrying smaller quantities in packages, drums and tank containers, and includes general purpose ships, container ships, and roll-on/roll-off (RoRo) passenger (and cargo) ships. The second group is ships for the bulk transport of (1) crude oil, (2) petroleum products, (3) LNG, (4) LPG and other liquefied gases and (5) chemicals.

Figure 23.5 illustrates some typical vessel designs. Figure 23.5(a) shows a cargo vessel; Figure 23.5(b) an ore/bulk/oil (OBO) carrier; and Figure 23.5(c) a chemical tanker, or tank vessel. An oil tanker is broadly similar to the latter in respect of the layout of the holds, but tends to be very large. Figures 23.5(d) and (e) show two types of LPG carrier, and Figure 23.5(f) shows an LNG carrier.

Older tank vessels have pump rooms, one forward and one aft between the engine room and the last cargo tank. In newer vessels the pump rooms are eliminated by the use of deep well pumps.

A gas carrier, for liquefied gases, has cargo tanks which may operate at atmospheric pressure or higher pressure. Such tanks may be integral with the vessel or independent of it.

Further treatment of ship design is deferred to Section 23.16, where a description is given of liquefied flammable gas (LFG) carriers and chemical tankers.

An account of the influence of the chemicals carried on ship design and operation, as reflected in the provisions of the IMO codes, has been given by Farrell (1982).

23.12.4 Ship operation

The transport of hazardous materials by ship calls for an approach to loss prevention very similar to that required for land installations. The management and the systems and procedures are crucial. There should be identification and assessment of hazards. An effective instrument system, with trips where necessary, is required. There needs to be a variety of fire protection measures. Operations such as loading and unloading should be carried out in accordance with specified procedures. There should be an inspection system with appropriate record keeping akin to that used for pressure systems. The equipment should be well maintained and control exercised over modifications. There should be a permit-to-work system. Personnel should be thoroughly trained in all these aspects.

Operations of particular relevance here are the loading and discharge of cargo and the operations on cargo tanks. These are discussed in Sections 23.14–23.17.

Inspection of tanks is covered in *Guidance Manual for the Inspection and Condition Assessment of Tanker Structures* (ICS, 1986/5), *Guidelines on Surveys Required by the 1978 SOLAS Protocol, the IBC Code and the IGC Code Fire Test Procedures* (IMO, 1987 IMO-858), *Inspection Guidelines for Bulk Carriers* (OCIMF, 1989/8), *Inspection Guidelines for Ships Carrying Liquefied Gases in Bulk* (OCIMF, 1990/10) and *Condition Evaluation and Maintenance of Tanker Structures* (ICS, 1992/12)

23.12.5 Particular chemicals

An important category of substances moved by sea is liquefied gases. These are not confined to LNG and LPG or even other hydrocarbons, but include a number of other major chemicals.

A gas tanker is often designed to carry not only LPG but also ethylene, ammonia and vinyl chloride monomer as the principal cargoes, but the list of products may well be

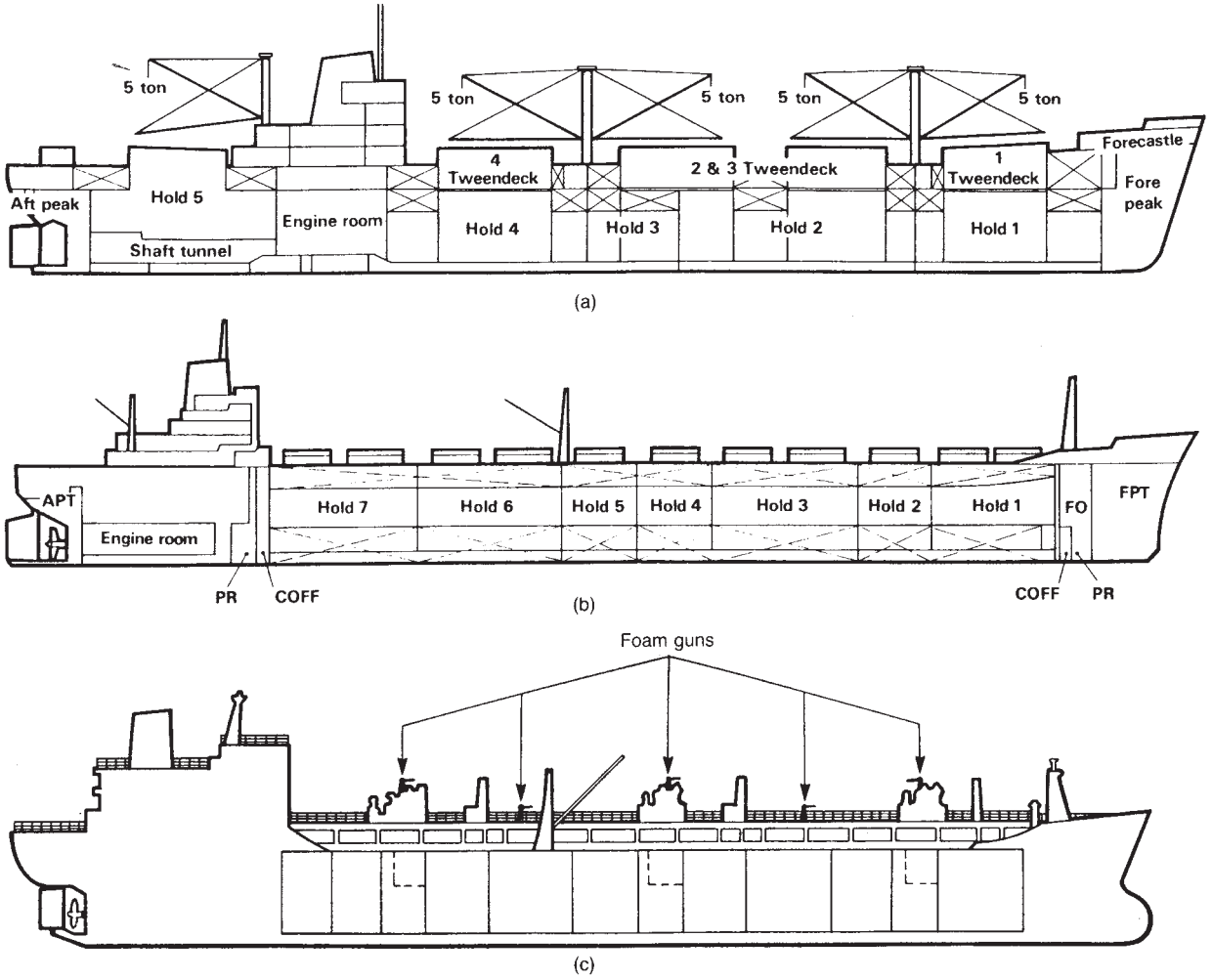


Figure 23.5 *continued*

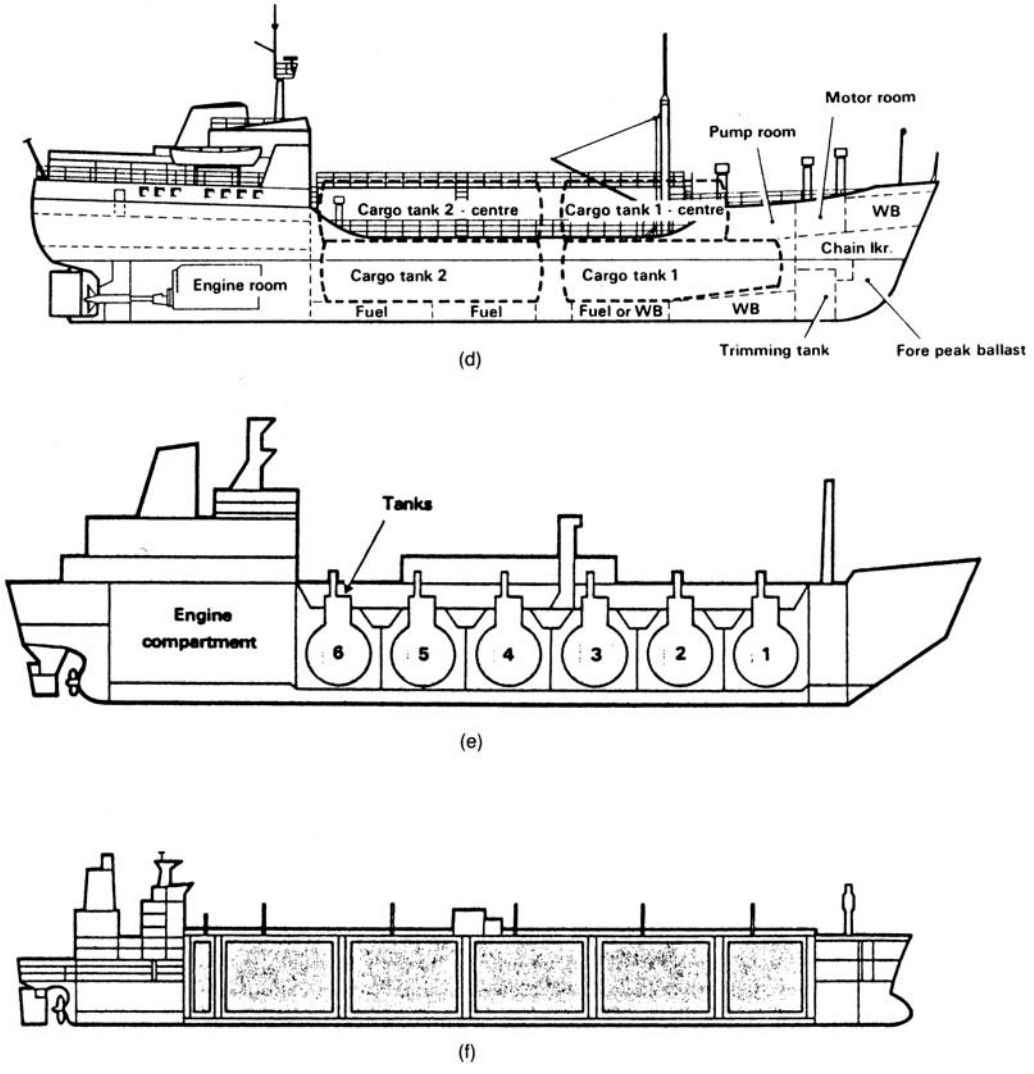


Figure 23.5 *Some typical vessels (Home Office, 1985 Manual of Firemanship Bk 4): (a) cargo ship; (b) oil tanker; (c) chemical tanker; (d) and (e) LPG carriers; and (f) LNG carrier (Courtesy of HM Stationery Office, © All rights reserved)*

more extensive. A cargo list for such a tanker is given by Puklavec and Lindenau (1985):

Ethylene	*n*-Butane, *i*-butane	Mixtures of ethylene oxide/propene oxide
Ethane	Butadiene	Acetaldehyde
Propene	Butylenes	Monoethylamine
Propane	Vinyl chloride monomer	Methyl chloride
Ethane/ propane mixtures	Isoprene monomer	Dimethylamine
Anhydrous ammonia	Propene oxide	Diethyl ether

Other products are carried in general chemical tankers, or chemships.

The *Bulk Carrier Code* (IMO, 1996 IMO-100) has both ship type and additional requirements which are a function of the chemical carried.

An important class of chemical in sea transport is monomers. Monomers such as vinyl acetate need to be inhibited during transport. The effectiveness of inhibition depends on the oxygen concentration and problems can occur from polymerization due to low oxygen concentration. An account of inhibitors for vinyl monomers has been given by Douglas, von Bramer and Jenkins (1982) and of the specific problem of vinyl acetate inhibition by D.W. Butcher and Sharpe (1983).

Other accounts of the transport of particular chemicals include that of R.W. Macdonald (1977) on chlorine and that of Brumshagen (1983) on carbon dioxide.

23.12.6 Ship movement

The control of ship movement in restricted waters is necessary because the risk of collision or grounding is greater and the consequences may often be more serious. The arrangements for ship control vary in different countries, but many of the principal waterways have some form of movement control. This may vary from speed restrictions and a requirement for pilotage to a full system akin to that used in air traffic control.

There have been a number of studies of ship movement and of ship traffic control systems. The USCG has undertaken a programme of work on this topic. Table 23.30 shows typical ship movements in a major waterway as given by Sanders and Aldwinckle (1987). An account of ship movement at the approaches to Rotterdam has been given in a study of ship incident probabilities by Ligthart (1980). The speed restrictions required by the Port of London Authority as described in the *Canvey Reports* are discussed in Appendix 7.

The proportion of 'errant vessels' in traffic lanes on the UK continental shelf has been studied by Technica (1985). This report was a follow-up to previous work on ship–platform collisions, which showed that the main risk is from errant vessels. One of the main points made is that errancy is not restricted to particular vessels, crews or captains, but may occur at some time in any vessel, although the frequency of such periods will vary between vessels. The findings were that the proportion of vessels which are errant at a given time is about 1.6%, both with good visibility and with bad, but that the proportion likely to recover from being on an imminent collision course fell for vessels of <40,000 DWT from 78% in good visibility to 8% in poor visibility and for vessels of >40,000 DWT from 39% to 4%, respectively.

23.12.7 Factors enhancing risk

In recent years, there have been a number of developments which have combined to increase the risk of vessel failure. An account is given by Gilbert (1994). Among these developments are the massive increase in the size of vessels. This is not just a matter of increase in the hazard. Gilbert states 'Many of these cape-size vessels (100,000 to 170,000 DWT) have been lost over the last two years due to suspected structural failure'.

Structurally, important factors have been the reduction in scantlings, the use of high tensile steels or inferior coatings, increased stress caused by high capacity loading systems and poor lay-up provisions.

Gilbert describes the three main modes of vessel failure: fire, collision and grounding. He also draws attention to the risk from piracy, which in some regions is not negligible. He states 'In some instances, fully-loaded tankers have been left to steam at full speed in enclosed waters with no-one on the bridge, because pirates have locked up or otherwise restrained the crew'.

23.13 Marine Transport: Regulatory Controls

23.13.1 International regulatory controls and codes

The international marine transport of dangerous goods is the concern of the IMO (formerly the International Maritime Consultative Organization (IMCO)). This organization has a fairly complex structure of committees, which

Table 23.30 *Typical ship movements in a major waterway (Sanders and Aldwinckle, 1987) (Courtesy of Gastech)*

Ship size ($\times 10^3$ GRT)	*Ship type*				
	Oil tanker	*Chemical tanker*	*Gas carrier*	*Other*	*All*
0–1	42	0	9	1,064	1,115
1–2	22	153	21	1,374	1,570
2–4	74	62	28	1,591	1,755
4–6	130	48	64	2,044	2,286
6–15	316	65	227	8,043	8,651
15–30	702	33	165	4,361	5,261
30–80	2,317	78	0	3,621	6,016
80>	537	0	0	556	1,093
Total	4,140	439	514	22,654	27,747

include the Maritime Safety Committee (MSC) and the Marine Environment Protection Committee (MEPC).

Other interested bodies include the International Chamber of Shipping (ICS), the Oil Companies International Marine Forum (OCIMF) and the Society of International Gas Tanker and Terminal Operators (SIGTTO), together with International Association of Ports and Harbours (IAPH), the International Petroleum Industry Environmental Conservation Association (IPIECA) and the International Tanker Owners Pollution Federation (ITOPF).

Accounts of the international controls and codes for the marine transport of dangerous goods are given in the *NFPA Handbook* (2003) and by the ACDS (1991).

Some principal international conventions and conferences include the International Convention for the Prevention of Pollution of the Sea by Oil 1954 (OILPOL), the International Conference on Revision of the International Regulations for Preventing Collisions at Sea 1972, the International Convention of Prevention of Pollution from Ships 1973 (MARPOL), the International Convention on the Safety of Life at Sea 1974 (SOLAS), the International Convention on Training, Certification and Watchkeeping for Seafarers 1978 (STCW), and the Convention on the International Maritime Organization 1984.

The resolutions of the periodic SOLAS conferences are a continuing source of provisions in the international system of control. The SOLAS Convention 1974 contains mandatory requirements concerning carrier safety. Chapter VII of the Convention deals with dangerous goods.

Some principal IMO codes include the *Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk* (the *BCH Code*) (IMO, 1993 IMO-772), the *International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk* (the *Bulk Carrier Code*, or *IBC Code*) (IMO, 1996 IMO-100) and the *International Maritime Dangerous Goods Code* (the *IMDG Code*) (IMO, 1992 IMO-200).

There are three IMO codes for LGCs: the *Code for Existing Ships Carrying Liquefied Gases in Bulk* (IMO, 1976 IMO-788), the *Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk* (IMO, 1983 IMO-782) and the *International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk* (the *Gas Carrier Code*, or *IGC Code*) (IMO, 1993 IMO-104). The first code applies to ships built up to 1976 and the second generally applies to ships built after 31 December 1976 and before 1 July 1986.

Guidance issued by the ICS and other bodies includes *Safety in Chemical Tankers* (ICS, 1977/1), *Safety in Oil Tankers* (ICS, 1978/2), *Safety in Liquefied Gas Tankers* (ICS, 1980/3), *Liquefied Gas Handling Principles on Ships and in Terminals* (SIGTTO, 1986/3), *International Safety Guide for Oil Tankers and Terminals* (*ISGOTT*) (ICS, 1991/11), the *Tanker Safety Guide* (*Chemicals*) (ICS, 1971/13) and the *Tanker Safety Guide (Liquefied Gases*) (ICS, 1993/14).

23.13.2 Paris Memorandum

The responsibility for enforcement of international agreements on marine safety lies with the state in which the vessel is registered (the flag state). Standards are variable and, as a secondary measure, the states at whose ports the vessel calls (the port states) are empowered to carry out inspections and to detain the vessel whilst repairs are done. This latter arrangement is governed by the Paris Memorandum of Understanding on Port State Control of 1982 (the Paris Memorandum, or Paris MOU). An account of this system is given in the *Donaldson Report* (Donaldson, 1994), described below, and its operation is reported in the annual reports of the Paris Memorandum.

23.13.3 Classification societies

In international shipping, an important role is played by the classification societies, of which the best known is Lloyds of London. An account of the work of Lloyds is given by McLean and Cripps (1986). The relationship of Lloyds to many of the international organizations mentioned is shown in Figure 23.6.

The classification societies operate a system of classification rules, as described below. In addition, the major societies are authorized by over 125 administrations to apply the requirements of specified IMO conventions and to issue certificates of fitness. The Lloyds Register requirements for gas ship construction and class maintenance are outlined in Figure 23.7.

23.13.4 Classification rules

Major sets of rules at Lloyds are the *Rules and Regulations for the Classification of Ships* and the *Rules for Ships for Liquefied Gases*.

An account of Lloyds' Classification Rules is given by J. Smith (1994). The hull of a ship must be able to withstand the forces due to still water and specified wave-induced loads. It must possess the local strength to resist buckling, fatigue, yielding and brittle fracture. In the Classification system, this is achieved by compliance with the Rule materials requirements, hull arrangements and scantling formulations. The Rules are intended to provide basic proven design methods whilst leaving freedom to innovate. They prescribe design methods for the ship's hull and certain other features and equipment. The system recognizes the principle of 'equivalence' and permits an alternative combination of arrangements and scantling, provided that it can be demonstrated to be of equal strength.

23.13.5 UK regulatory controls

In the United Kingdom, the transport of hazardous materials by sea is regulated by the Department of Trade (DoT) through the Merchant Shipping Act 1965 and succeeding Merchant Shipping Acts and through a series of regulations which include the Merchant Shipping (Cargo Ship Construction and Survey) Regulations 1984, the Merchant Shipping (Fire Protection) Regulations 1984, the Merchant Shipping (Gas Carrier) Regulations 1986, the Merchant Shipping (BCH Code) Regulations 1987, the Merchant Shipping (IBC Code) Regulations 1987 and the Merchant Shipping (Dangerous Goods and Marine Pollutants) Regulations 1990.

The DTp maintains a Standing Advisory Committee, which has for some years issued the *Recommendations for the Carriage of Dangerous Goods in Ships*, commonly known as the '*Blue Book*', covering variations from and additions to the *IMDG Code* judged appropriate for the United Kingdom. The 1990 edition of the *IMDG Code* with the 25th set of amendments provides comprehensive coverage of matters dealt with in the *Blue Book*, which is now superseded.

British law has held that the act of sending to sea an unseaworthy vessel is a misdemeanour. The Merchant Shipping Act 1979 replaced the wording 'unseaworthy' by 'dangerously unsafe'. The Merchant Shipping Act 1988, Section 30, gives powers to prosecute the owner and master

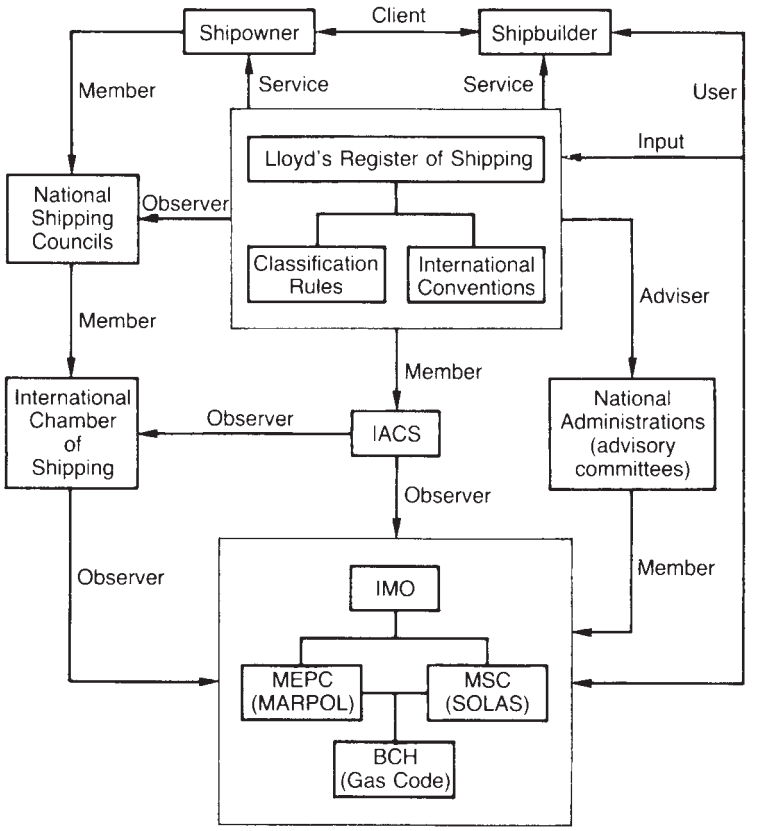


Figure 23.6 *Relationship of the Lloyds Register classification society with regulatory bodies and the liquefied gas shipping community (McLean and Cripps, 1986) (Courtesy of Gastech)*

of unsafe British ships in any port worldwide and of unsafe foreign ships in British ports.

In the United Kingdom, enforcement of the Paris Memorandum is the responsibility of the Marine Safety Agency (MSA). Accounts of the regulatory framework in the United Kingdom are given by Hodges (1994) and K. James (1994).

23.13.6 Seaworthiness

In British maritime law, an important concept in marine safety, as described by Hodges (1994), is that of the 'seaworthy' vessel, legally defined as one which is in 'a fit state as to repairs, equipments, crew and in all other respects, to encounter the ordinary perils of the sea'. The definition is thus limited to the perils 'of the sea' rather than 'on the sea'.

Aspects of seaworthiness which have been the subject of court judgements include: the ship's suitability to carry its cargo, or its cargoworthiness; its design and construction; its machinery, equipment and navigational aids; the sufficiency and competence of the crew; the sufficiency and quality of the fuel; and the stability and stowage of the cargo.

The seaworthiness of a ship is a particular aspect of its safety. For example, a deficiency in the medical supplies would detract from safety, but would not render the ship unseaworthy.

23.13.7 Donaldson Report

The *Braer* disaster in 1993 was the subject of an inquiry reported in *Safer Ships, Cleaner Seas* by Lord Donaldson (1994) (the *Donaldson Report*). The report reaffirms the duty of the flag state to enforce controls on the safety of vessels registered with it, but states that: There is clear evidence that some Flag States are failing in their responsibilities . . . '. It recommends various measures to strengthen the controls exercised by the port states.

23.13.8 Safety case

Following the Piper Alpha incident and the *Cullen Report*, the new UK offshore regulatory regime is based on formal safety assessment and the safety case. This has led some to advocate a similar regime for ships at an international level. The question of a regime for ships based on a safety case is discussed by J. Smith (1994).

The critique of a safety case for an individual ship has two main aspects, the potential benefits and the practical difficulties. With regard to benefits, the question concerns the extent to which the design and operation of the ship itself involves the type and degree of hazard for which the safety case methodology is suitable. The other question is the practicality of applying a safety case regime to international shipping, particularly given the difficulties

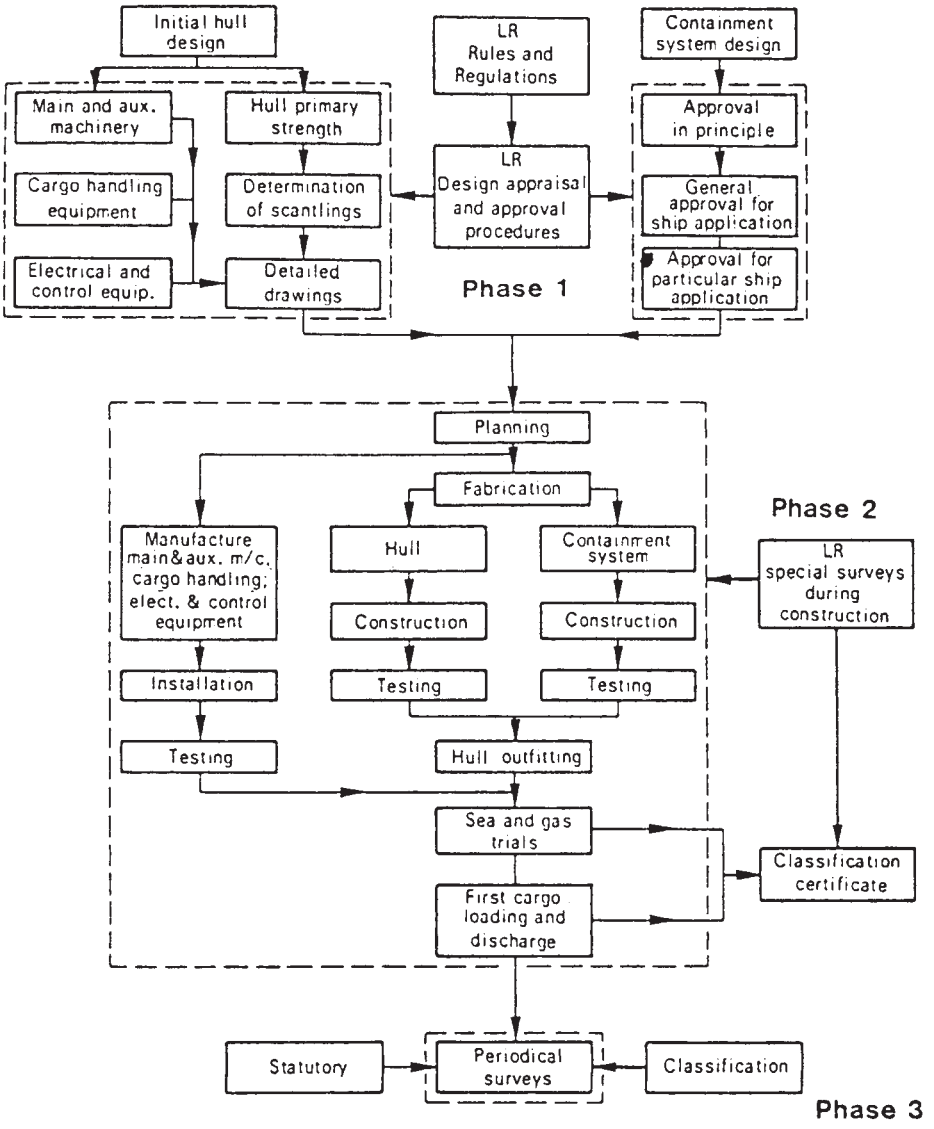


Figure 23.7 *Lloyds Register requirements for liquefied gas ship construction and class maintenance (McLean and Cripps, 1986) (Courtesy of Gastech)*

experienced in enforcing even a relatively straightforward prescription-based regime.

There may well be benefits to be had from generic formal safety assessment studies. The question of formal safety assessment of ports, sea lanes, etc., is another matter and is well established.

23.13.9 US controls

In the United States, ships trading in US waters have to meet the requirements of the USCG. The USCG have responsibility for ensuring the safety both of US vessels and US ports.

The USCG requirements for gas carriers are given in the Code of Federal Regulations, Title 46. The requirements for new ships are given in Part 154 and those for existing ships in Part 38. New ships are essentially those which meet the IMO *Gas Carrier Code* and existing ships are those which do not. An account of the USCG controls has been given by Rowek and Cook (1986).

The United States has now taken action to raise the standard of ships calling at its own ports. The Oil Pollution Act 1990 (OPA) provides that, from the year 2010, all such vessels must have double hulls.

23.13.10 Pressure for change

Shipowners are currently subject to a number of pressures to enhance the safety of vessels. Some of these are described by Rawson (1994). They include: IMO initiatives, unilateral legislation such as the OPA 1990 and the Paris Memorandum; the requirements of the classification societies and of the insurers, which are gradually tending to become more stringent; and the growth of litigation. Regulatory controls are thus increasingly being reinforced by economic pressures. There is, however, a long way to go.

23.14 Marine Transport: Ports and Harbours

23.14.1 Regulatory controls and codes

Ports and harbours are controlled through the Docks Regulations 1988 and dangerous substances are controlled through the Dangerous Substances in Harbour Areas Regulations 1987 (OSHA). Guidance is given in HS(R) 27 *A Guide to the Dangerous Substances in Harbour Areas Regulations 1987* (HSE, 1988) and GS 40 *The Loading and Unloading of Flammable Liquids and Gases at Harbours and Inland Waterways* (HSE, 1986). Also applicable are the regulations for fixed sites, including the Notification of Installations Handling Hazardous Substances Regulations 1982 (NIHHS), the Control of Industrial Major Accident Hazards Regulations 1984 (CIMAH), the Dangerous Substances (Notification and Marking of Sites) Regulations 1990 and the Planning (Hazardous Substances) Regulations 1992.

Interested organizations include the International Association of Ports and Harbours (IAPH) and the Independent Tank Storage Association (ITSA).

The OSHA Regulations are divided into 10 parts: (1) interpretation and application, (2) entry of dangerous substances into harbour areas, (3) marking and navigation of vessels, (4) handling dangerous substances, (5) liquid dangerous substances in bulk, (6) packaging and labelling, (7) emergency plans and untoward incidents, (8) storage of dangerous substances, (9) explosives, and (10) miscellaneous and general.

Some principal regulations of the OSHA Regulations are: Regulation 6 on the notice of entry of dangerous substances; Regulation 7 on harbour masters' powers of prohibition of dangerous substances, etc.; Regulation 18 on precautions against fire and explosion; Regulation 19 on the fitness of vessels; Regulation 20 on permission for transfer between vessels; Regulation 21 on safety precautions for loading, unloading and transfer; Regulation 26 on the preparation of emergency plans by harbour authorities; Regulation 27 on emergency arrangements at berths; Regulation 28 on untoward incidents; Regulation 29 on the storage of dangerous substances; Regulation 30 on storage tanks; Regulation 31 on the storage of freight containers, etc.; Regulation 32 on the parking of road vehicles; Regulation 34 on the need for an explosives licence; Regulation 37 on the security of explosives; Regulation 41 on deteriorated explosives; Regulation 43 on the power of harbour authorities to make bylaws; and Regulation 44 on enforcement. Regulation 28 deals both with the action in the event of untoward incidents and on reporting of such incidents. Regulation 34 defines the cases where there is need for an explosives licence; Regulations 37–42 on explosives apply irrespective of whether a licence is required.

HS(R) 27 contains in Appendix 3 guidance on emergency plans and in Appendix 4 a checklist of duties under the Regulations, covering some 18 categories of person, including: the harbour authority, berth owner and berth operator; the harbour master; the harbour and the berth explosives security officers; the masters of vessels; the operators of barges and harbour craft, road tankers, rail tank wagons, and storage; consignors; drivers; and employers and the self-employed.

COP 18 expands on some of these requirements, giving more details on aspects such as the information to be provided by incoming tankers, which includes the substances carried, the equipment available such as an inert gas system, defects on the ship and the expected time of arrival (ETA); the control of rail traffic in harbour areas; the ship–shore transfer of dangerous liquids; precautions against fire and explosion, which include the elimination of ignition sources and the provision of firefighting facilities; storage tanks for dangerous substances; the handling, storage and security of explosives; the discharge of harmful dusts and vapours to the atmosphere; and emergency planning, at both harbour and berth level. It contains an appendix giving a checklist for ship–shore transfer.

23.14.2 Port design and operation

Accounts of the handling of hazardous materials at ports have been given by Gebhardt (1980, 1989) and by P. Lewis (1981). Cargo is handled at a port in four basic modes:

(1) bulk materials;
(2) packaged goods;
(3) containers;
(4) roll-on/roll-off.

The characteristics of these modes are discussed by Lewis.

Some aspects of the design and operation of ports relevant to the handling of hazardous materials include:

(1) ship traffic control;
(2) ship–shore transfer;
(3) emission control;
(4) hazardous area classification;
(5) jetty fire protection.

Control of ship traffic is considered in Section 23.12, ship–shore transfer is considered in Section 23.14.3, and jetty fire protection is discussed in Section 23.14.4.

Some emission of flammable gas is unavoidable during loading operations. As with land-based plant, it is necessary to consider the dispersion of such gas. Similarly, it is necessary to have a hazardous area classification of the ship and the jetty.

23.14.3 Ship-shore transfer

The loading and discharge of cargo is a hazardous operation over which strict control needs to be exercised. Accounts are given in *Liquefied Gas Handling Principles on Ships and in Terminals* (SIGTTO, 1986/3), *Guidelines for the Alleviation of Excessive Surge Pressure in ESD* (SIGTTO, 1987/4) (the SIGTTO *ESD Surge Pressure Guidelines*) and *Recommendations and Guidelines for Linked Ship/Shore Emergency Shutdown of Liquefied Gas Cargo Transfer* (SIGTTO, 1987/5) (the SIGTTO *ESD Guidelines*) and by Gebhardt (1980), Armitage (1983), B. White and Cooke (1983), Holdsworth (1985) and Whitmore and Gray (1987).

Loading arms are covered in *Design and Construction Specification of Marine Loading Arms* (OCIMF, 1987/5).

There is also guidance on manifolds (OCIMF, 1987/7 and 1991/12) and on hoses (OCIMF, 1991/11).

Accounts of the development of the SIGTTO guidelines on ship–shore transfer and emergency shut-down (ESD) are given by Holdsworth (1985) and Whitmore and Gray (1987).

The transfer of hazardous materials between ship and shore during loading and unloading depends on the effective operation of a number of systems which include:

(1) mooring system;
(2) loading arms;
(3) pumping system;
(4) pressure relief.

Some hazards of ship–shore transfer are:

(1) ship movement;
(2) leakage;
(3) overfilling;
(4) overpressure;
(5) pressure surge.

Mooring systems have already been discussed. A good mooring is required to ensure that the ship does not break away during transfer. It is also desirable that the motion of the ship be minimal.

There are various arrangements for connecting the ship's cargo tanks to the land terminal. Types of loading arm in common use include Chiksan loading arms and Kvaerner arms.

In order to prevent leakage, pressure surge, overfilling or overpressure of tanks, it is necessary to design for these hazards and to establish a suitable link between ship and shore which allows orderly shut-down to be carried out.

There should be a trip system so that shut-off can be effected in the event of a serious leak. The operating pump should be interlocked to stop if the shut-off valve closes.

If shut-off is too rapid, pressure surge is liable to occur and can be very damaging. The prevention of pressure surge in this situation is an important feature of the SIGTTO arrangements (SIGTTO, 1987/4 and 5). It has been discussed by Armitage (1983).

Measures need also to be taken to avoid overfilling and overpressure. Particular consideration should be given to the relief arrangements at the receiving end in relation to the delivery flow and pressure in order to ensure that overpressure does not occur.

The operating arrangements, discussed by Gebhardt (1980), are equally important. The transfer operation should be planned. There need to be sufficient personnel available on ship and on shore. At each end there should be an engineer in charge of the transfer. There should be good communication between ship and shore and the principal tasks of the transfer operation should be coordinated.

The SIGTTO *ESD Guidelines* (SIGTTO, 1987/5) describe a standardized link connecting ship and terminal ESD systems to communicate and initiate ESD safely and rapidly. They give in an appendix a practical example of an intrinsically safe ship–shore ESD link system.

The SIGTTO *ESD Surge Pressure Guidelines* (SIGTTO, 1987/4) describe the hazards of surge pressures and give sets of guidelines common to ships and terminals and others specific to the ship or the terminal. The former cover (1) safe transfer rates, (2) valve characteristics and closure times, (3) pipeline design pressure and pipeline anchors, (4) linked ship and terminal ESD systems, and (5) operational factors. The guidelines also include an engineering treatment of surge as applied to loading systems and unloading systems and design approaches to alleviate surge pressures, including (1) pump shut-down/diversion of flow and (2) surge pressure relief.

A checklist for ship–shore transfer has been given by B. White and Cooke (1983).

Guidance on ship–ship transfer is given in *Ship to Ship Transfer Guide (Liquefied Gases)* (ICS, 1980/4) and *Ship to Ship Transfer Guide (Petroleum)* (ICS, 1988/7).

23.14.4 Jetty fire and fire protection

An account of fire and fire protection at jetties has been given by Dicker and Ramsey (1983). The minimization of the fire hazard at a jetty depends not only on the specific fire protection measures but also on the general standard of design, operation and maintenance. The ship–shore transfer systems are one important feature here. The arrangements for dealing with leaks and spillages are another.

The objectives of fire protection may be summarized as:

(1) prevention of fires and explosions;
(2) extinguishment of small fires;
(3) control of fires that cannot be extinguished;
(4) cooling of vulnerable equipment;
(5) protection to permit escape;
(6) protection to permit ship/shore access.

It may not always be possible to extinguish a fire, and in such a case, the fire should be controlled, and vulnerable equipment such as tanks, loading arms, pipelines and manifolds on shore or on ship should be kept cool.

The resources available on site should be such that an effective initial response to the fire can be mounted whilst the arrival of the outside fire services is awaited.

The approach to fire protection at a jetty is broadly similar to that on a plant. Basic elements include:

(1) control of leaks;
(2) control of ignition sources;
(3) fire control system;
(4) means of escape;
(5) means of access.

The fire control system includes:

(1) fire warning system;
(2) fire detection system;
(3) fixed firefighting system;
(4) mobile firefighting system;
(5) fire water supply system.

First consideration should be given to avoidance of leaks of flammable materials. Potential leak sources should be reviewed and appropriate action taken.

A source of flammables which is peculiar to jetties is flammable vapour vented from ship cargo tanks.

Most of the common sources of ignition may be present at a jetty. These include hot work, repair work, vehicles and smoking. There are also activities specifically associated with shipping which may cause ignition such as use of ship's galley equipment, repair work involving hammering or paint chipping, blowing of funnel uptakes or boiler tubes, or disconnection of ship–shore cargo pipelines.

Control of ignition sources should be based on a hazardous area classification. The *Area Classification Code for Petroleum Installations* by the IP (1990 MCSP Pt 15) gives guidance on hazardous area classification for jetties.

In this connection, Dicker and Ramsey deprecate the use of a blanket approach in which flameproof equipment is applied without detailed study. They suggest that there is benefit to be gained from the source of hazard method which gives a better understanding of the potential leak sources. These authors also state that it has to be accepted that complete elimination of all sources of ignition from hazardous areas is not practicable in all circumstances at jetties.

It is usual to provide a variety of means for fighting and controlling fire. For cargoes of crude oil or flammable liquids, the principal firefighting agent used is foam, which is applied by foam monitors. Low expansion foam is the most suitable for a jetty since it has a reasonable range. Fixed foam monitors may be used and may be remotely controlled. They may be supplemented with mobile monitors. Foam is usually not recommended for burning liquefied gas fires, since the gas tends to penetrate the foam blanket.

If the fire is on a gas or vapour leak, the preferred course of action is to stop the leak. Extinguishing the flame without stopping the leak risks allowing the creation of a flammable vapour cloud which may give a more violent flash fire or vapour cloud explosion.

Water monitors are used to cool exposed items, as already described. In the jetty situation, cooling of the gangways between the ship and shore is important for escape.

The capacity of the foam and water systems should match the firefighting requirements. For large vessels, these can be appreciable.

Effective fire control depends on coordination between shore and ship. One aspect of this is the compatibility between the ship and shore fire mains. It is necessary to ensure that connection of the ship's fire water system to that on shore does not result in overpressurization.

Another aspect is the responsibility for fire control in the early stages. Since in the event of fire the ship's crew need to attend to other actions, particularly the closure of pipelines and actions to prevent fire spread, it may be advantageous to control initial firefighting from the shore.

There should be good ship–shore communications. These are particularly important in the jetty situation, not only for firefighting but also for assisting escape. Regular exercises of the fire control system should be held.

Accounts available of the fire protection arrangements at major terminals include those of the arrangements at Rotterdam by Vossenaar (1975), at Wilhelmshaven by Hartlich (1977) and at Hamburg by Gebhardt (1980, 1989).

Vossenaar quotes for the port of Rotterdam traffic of 34,000 ships and 170,000 barges per annum. The area fire brigade has some 500 full time firemen who deal, each year, with about 5,000 fire and other emergencies. The fire brigade is equipped with high capacity pumps capable of delivering 4,000 l/min. There are also 14 fire boats, most of which have an output of 15,000 l/min and carry substantial quantities of foam, as well as a fire fort, a converted ferry, with a 30 m tower.

Hartlich gives a detailed account of the construction of the Mobil terminal at Wilhelmshaven and of the firefighting arrangements. There are separate fire water systems which draw on sea water and on the refinery fire water supply. The sea water pumps are protected against pack ice and freezing.

The foam supply is estimated to last 60 min, supplying $2 \times 5{,}000$ l/min and 3×800 l/min foam monitors. The monitors can be operated from the control building and also from other auxiliary control points. Use of the refinery mobile foam monitors extends the period of foam application to some 2 h.

The foam monitors have a range of 85 m. This is not enough to give coverage of the whole deck of a supertanker, but such ships have their own systems.

The foam induction rate is 5%. Devices are used to keep the induction rate constant at variable water flows. The foam compound is highly viscous and its flow velocity is low so that large diameter mains are necessary. These have a holdup of some 10,000 l of the compound.

There are water monitors with an output of 3,000 l/min for cooling ships' gangways and hulls. Dry powder systems also are provided for fighting fires on platforms and around manifolds.

Two of the jetties at this terminal are on an island. For this situation, it is necessary to provide facilities somewhat similar to those on an oil platform, such as lifeboats and fireproof shelter.

Somewhat similar arrangements at the Shell terminal at Kattwyk at Hamburg-Harburg are described by Gebhardt.

Evacuation of the ship in the event of a spillage of liquefied gas may be assisted by the use of a water curtain to reduce the level of thermal radiation to which the crew is exposed. A study of such a system has been described by S. Stephenson and Coward (1987).

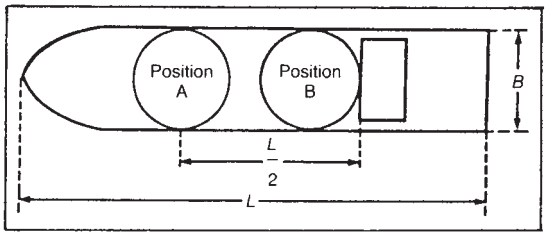
Two principal scenarios are considered, the first, shown in Figure 23.8(a) being for a fire on deck, and the second, shown in Figure 23.8(b), for a fire on the sea. The fire considered in the first case was a pool fire with diameter equal to the width of the ship, and sufficient fuel for burning to be maintained and evacuation to be necessary, and the second case considered was a fire on a continuous spill onto the sea. A model for heat transmission through water curtains was developed and embodied in the computer program PRINCE, as described in Chapter 16.

The target heat fluxes for the two design basis fires are shown in Table 23.31. It is concluded that the water curtain considered would reduce the heat flux received by the human targets from 16 to 5 kW/m^2 and that this provides a significant contribution to safe evacuation.

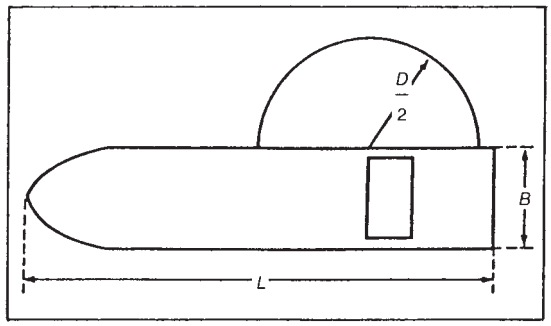
23.15 Marine Transport: Shipboard Fire and Fire Protection

An account of fire and explosion on board ships of all kinds is given in *Fire Aboard* (Rushbrook, 1979). This work lists all recorded ship fires between 1800 and 1977 and describes in detail many of the principal incidents. It describes the general maritime legislation and that pertaining to fire-related aspects of ship design and construction. It covers fire protection aboard ship, including fire-proofing of ships, fire equipment on ships and firefighting on ships, and fire protection of ports and offshore structures.

The fire-proofing of ships is governed by the Merchant Shipping (Construction) Rules 1965 and, for cargo ships, the Merchant Shipping (Cargo Ship and Survey) Rules 1965. Rushbrook's account follows closely the requirements of these rules and covers watertight doors, fire resisting and fire retarding divisions, fire resisting materials, electrical equipment and installation, oil fuel installations, ship structure, and construction aspects such as means of



(a)



(b)

Figure 23.8 *Design basis fires for an LNG/LPG carrier (S. Stephenson and Coward, 1987); (a) position of fires on the deck; (b) position of a fire on the sea (Courtesy of Gastech)*

Table 23.31 *Design basis fires for an LNG/LPG carrier (S. Stephenson and Coward, 1987) (Courtesy of Gastech)*

A Fire on deck[a]

Fire position	*View factor*	*Wind velocity* (m/s)	*Flame tilt* (°)	*Target heat flux* (kW/m^2)
A	0.06	0	0	5
A	0.06	5	34	11
A	0.06	10	46	12
B	0.35	0	0	33
B	0.35	5	34	37
B	0.35	10	46	44

B Fire on sea

Size of carrier (m^3)	*B* (m)	*L* (m)	*Spill rate* (kg/s)	*D* (m)	*View factor*	*Atmospheric transmissivity*	*Target heat flux* (kW/m^2)
2,500	13	80	10	9.5	0.08	0.95	8
2,500	13	80	100	30	0.19	0.95	18
2,500	13	80	1,000	95	0.24	0.95	23
25,000	25	200	10	9.5	0.04	0.95	4
25,000	25	200	100	30	0.13	0.92	12
25,000	25	200	1,000	95	0.22	0.90	20
25,000	25	200	1,0000	300	0.25	0.90	22
125,000	42	280	10	9.5	0.02	0.90	2
125,000	42	280	100	30	0.08	0.90	7
125,000	42	280	1,000	95	0.18	0.88	16
125,000	42	280	1,0000	300	0.24	0.85	20

[a] Flame height/diameter ratio H/D = 3 in zero wind. Atmospheric conditions: good visibility, 10% humidity. Emissive power of fire = $100\ kW/m^2$.

escape and facilities to shut-off forced ventilation. He also treats under this heading, fire detection systems and sprinkler systems.

Requirements for firefighting equipment on ships are contained in the Merchant Shipping (Fire Appliances) Rules 1965. Features covered by Rushbrook include: fire pumps and pump siting, fire water hydrants, fire hoses and hose reels, and portable fire extinguishers; fire fighter's breathing apparatus, including hose reel and trolley compressed air apparatus, and high pressure air charging equipment; fire smothering arrangements, including inert gas generators, funnel gas inerting systems, steam smothering systems and high pressure water sprays; fire detection and alarm systems; and certain special topics such as foam installations in mechanical spaces and crankcase monitoring.

Rushbrook emphasizes the need for training for the whole range of tasks required in ship operation. He quotes legal cases establishing the employer's obligation to provide training. Aspects of fire training mentioned include fire patrolling and firefighting, but the issue is much wider than this.

A detailed account of firefighting under different conditions is given by Rushbrook. Situations considered include fires in holds, in accommodation space, in refrigerated space, in fore and after peaks, and in engine rooms and machinery spaces.

He gives a detailed discussion of the problem of fires in holds. In general it is a golden rule of firefighting to hit the fire fast and hard, but this is not necessarily the right approach to a hold fire. There is a tendency to open up the hold too soon. It may often be better to develop a coherent plan of attack and make suitable preparations and, if there is an inerting system, to activate it and let it do its work. There are exceptions, however; immediate action is necessary when the cargo is nitrates, sulfates or explosives.

If quantities of water are pumped into the ship to fight a fire, they may lead to instability. Stability is determined by the relation between the ship's centre of gravity and its centre of buoyancy. The centre of gravity is the point at which its weight may be taken to act, in the vertical direction. The centre of buoyancy is the centre of gravity of the water displaced. If a vertical line is drawn through the centre of gravity of a body floating in a liquid and a second vertical line is drawn through the centre of buoyancy when the body is slightly displaced from its equilibrium position, the two lines meet at a point known as the metacentre. If the centre of gravity is below the metacentre, the ship is stable and will right itself, as shown in Figure 23.9(a), but if the centre of gravity is higher, the ship is unstable and tends to capsize, as shown in Figure 23.9(b). One solution to the problem of instability due to fire water is the use of an ejector, but this also has its limitations.

23.15.1 Cargo tanks

The problem of flammable cargoes and of the associated fire and explosion hazards is discussed in detail in *Petroleum Tankship Safety* (Page and Gardner, 1971).

Although oil tankers at any rate are now required to have inert gas systems to prevent tank fires, an understanding of such fires remains important.

A typical tank system for a petroleum cargo ship is shown in Figure 23.10. The tank is designed to operate at a pressure of about 1.17 bar (2.5 psig) and can withstand about 1.24 bar (3.5 psig). If this latter pressure is exceeded, the decks and bulkheads may give way.

The tank is fitted with an atmospheric vent which has a pressure/vacuum (PV) valve for normal operation and a bypass for loading. The PV valve is set to maintain the pressure within narrow limits, 0.14 bar (2 psi) above atmospheric and 0.035 bar (0.5 psi) below atmospheric.

During loading, the bypass is used, since the flow of gas necessary to equalize pressure is too great for the PV valve to handle. At other times, the bypass is kept shut.

It is important that vapour issuing from the vent during loading should not form a hazardous flammable or toxic cloud and it is desirable, therefore, for it to leave the vent at a velocity sufficient to promote mixing with the air. If loading is slow, the vapour may issue slowly and may accumulate. This problem may be overcome by fitting a minimum efflux velocity valve.

There may or may not be an inert gas system which is used to prevent the occurrence of a flammable mixture in the tank. If no such system is provided, there may be a flammable atmosphere during certain stages of the transport cycle. The air mixture found in the space depends on the volatility of the liquid.

Assuming that this is a volatile oil, which in this context means an oil above its flash point, then if the tank is clean and gas free, and contains only air before loading, the mixture in the vapour space will go from a too lean to a too rich mixture during loading. The diffusion of the vapour is slow, however, and a period of hours or even days may elapse before the space is saturated. Initially there may be a

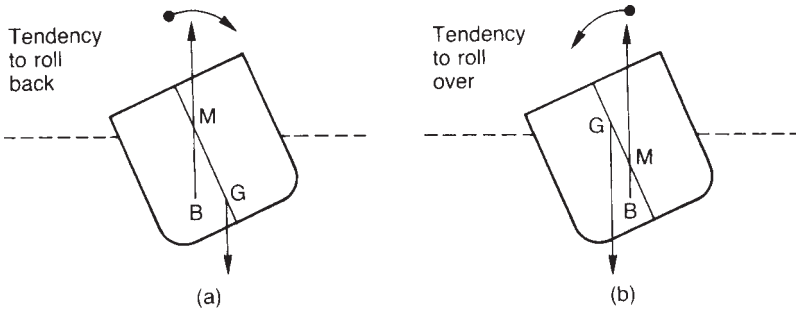


Figure 23.9 *Effect of the centre of gravity on ship stability: (a) tendency to roll back; (b) tendency to roll over. B, centre of buoyancy; G, centre of gravity; M, metacentre*

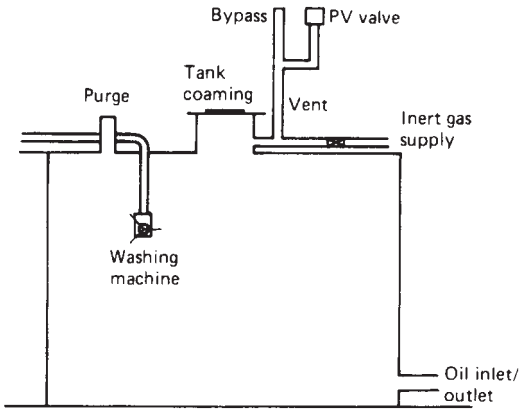


Figure 23.10 *Typical cargo tank system on a petroleum tanker*

range of conditions in the tank from a too lean mixture near the roof to a too rich mixture in the vapour layer just above the liquid. During loaded passage the atmosphere remains too rich. The vapour concentration falls again, however, during unloading. If the rate of unloading is high, the turbulence of the air entering tends to give a homogeneous atmosphere in the vapour space, while if it is too low, there may be layering. At the end of unloading, the atmosphere may be too lean, flammable, or too rich, depending on the volatility of the oil. The same applies if the tank is left empty but dirty during passage.

If the oil is involatile, then in principle a flammable mixture does not form, but this may occur if the oil is heated to assist pumping so that it rises above its flashpoint or if the tank contains traces of a volatile oil.

The pressure in the tank is maintained close to atmospheric by ejecting air through the vent bypass during loading, by the operation of the PV valve during loaded passage and by letting air in through the vent bypass during unloading.

In addition to loading and unloading operations, there are also those of tank cleaning and gas freeing. Tank cleaning is carried out by washing machines. If at all possible, it should be done with a too lean atmosphere. Gas freeing is effected by steaming out or by diluting the atmosphere with air drawn through it by extractor fans or steam eductors or blown in by windsails.

It is essential to eliminate all source of ignition. Some sources which are particularly relevant are as follows:

(1) direct heat
  (a) cigarettes,
  (b) welding,
  (c) hot soot;
(2) mechanical sparks
  (a) metal tools,
  (b) cigarette lighters,
  (c) heavy objects;
(3) chemical energy
  (a) metal smears,
  (b) spontaneous combustion,
  (c) autoignition,
  (d) pyrophoric iron sulfide;
(4) electrical equipment;
(5) static electricity.

Heavy objects which may produce a spark if they fall inside the tank include washing machines and anodes of cathodic protection systems.

Static electricity may arise from several causes. Charge separation occurs as the oil flows through the loading pipe. It also occurs if the oil is splashed or sprayed or if the turbulence of the oil raises up water droplets which then settle through the oil. Charge recombination may then occur due to an earthed probe such as a washing machine, the use of an ullage tape or the presence of a floating metal object such as a tin can or piece of wood with metal bolts. Precautions include the elimination of earthed probes and floating objects and the adoption of suitable ullage measuring arrangements.

The use of steam for tank cleaning may also involve a static electricity hazard, but this is minimized by using only fixed apparatus bonded to the ship's structure, keeping the steam velocity low and eliminating earthed probes.

Further details of the precautions necessary in loading and unloading and in tank cleaning and gas freeing are given by Page and Gardner.

If there is an inert gas system, this may be used to maintain an inert atmosphere in the tank. The inert gas produced with good combustion practice and after cooling and purification has a composition of approximately 3% oxygen, 13% carbon dioxide and 84% nitrogen. Under less ideal combustion conditions, the gas may contain carbon monoxide or more oxygen.

Prior to loading, the tank is purged with inert gas down to an oxygen concentration of about 5%, the purge gases being discharged through the purge pipe. During loading, the gas displaced by the liquid is discharged through the vent bypass. The pressure in the tank during passage is maintained by the PV valve. When the liquid is unloaded, more inert gas is allowed into the tank to prevent a vacuum developing. After unloading, the tank may be cleaned with its atmosphere still inerted.

An inert gas–vapour mixture is rather similar to a too rich mixture – it may become flammable if it is diluted with air. Situations in which this may happen include venting to atmosphere and rupture of the tank.

The types of explosion which can occur in a tank vary. One factor is the volume of flammable mixture. This is a maximum when there is no liquid in the tank and a flammable mixture fills the whole space, a situation which may occur after loading or during cleaning. Another factor is the power of the explosion. If the mixture is close to its flammability limits and the flame speed is correspondingly low, the explosion tends to be low powered and the pressure rise gradual, so that the tank ruptures and the burning gases escape without further pressure rise in the tank.

There are several situations in which a low powered explosion may give rise to a more powerful one. The initial explosion may overheat adjacent tanks. If the original mixture was close to the upper flammability limit, the explosion may cause dilution by air to give a more flammable concentration, while if the mixture was close to the lower limit, the explosion may vaporize more liquid to yield again a more flammable concentration.

Usually tanker explosions occur without prior warning, but sometimes the possibility of an explosion can be assessed from the nature of the flame issuing from the deck openings. A yellow-orange flame accompanied by black smoke indicates that the tank atmosphere is too rich and the flame will not pass back into it. A snapping, blue-red, nearly smokeless flame signifies that the tank contains a flammable mixture and that the flame may pass back. In this latter case, an explosion is imminent and the deck should be evacuated immediately.

A fire on deck does not usually cause a cargo tank to explode, provided that the tank is completely closed.

There is a trend towards the provision on tankers of an accommodation 'citadel' in which the crew are protected against fire in the cargo tanks, the cargo deck area, the engine room or the pump room. Measures are taken to reduce the risk of fire in the citadel itself. The ventilation system of the citadel and of the engine room should be such as to minimize the hazard from the entry of noxious gases.

23.15.2 Static electricity

Static electricity as a cause of ignition of flammable mixtures in cargo tanks has already been considered in general terms. Detailed studies of the hazard have been carried out in support of the chemical industry's case against compulsory inerting. Accounts of this work have been given by H.R. Edwards (1983) and by Jones and Bond (1984).

Edwards describes a series of experiments to determine whether the operations of loading, water washing and steam cleaning are capable of giving potentials sufficient to cause an incendive spark. Five trials were done on four vessels.

The minimum potentials required to produce incendive sparks were estimated as follows: for loading, the required potential was taken as 20 kV based on work by Rees (1981) and by Strawson and Lyle (1975b). For water washing, work by van de Weerd (1975) indicates a required potential of 15 kV, but a value of 10 kV was adopted. The same value of 10 kV was also taken as the required potential for steam cleaning.

In the loading experiments, the liquid used had a relatively low resistivity and high potentials were not obtained, the maximum surface potential being 3.4 kV. Estimates were made for other conditions using the method of Carruthers and Wigley (1962). It was estimated that the maximum surface value for a very high resistivity liquid (1 pS/m) would be 16.5 kV. The surface potential is a function, however, of tank size and this maximum value is obtained only with tanks smaller than those normally used. With such a liquid there is also the option of limiting the charge rate. It is concluded that loading is not likely to give rise to the potential required for an incendive spark.

Experiments on water washing in tanks up to 2500 m^3 gave a maximum potential of 7.9 kV except for certain esters. There are, however, certain features which would tend to increase the safety factor. One is that the potential was measured in the middle of the earth free volume, but an earthed probe is unlikely to exist at this point. Moreover, chemical tankers use washing machines which do not produce large slugs of water and probably in these conditions the potential required for an incendive spark exceeds 15 kV. It is concluded that in water washing also the potential required for an incendive spark is unlikely to occur.

The potential obtained in water washing for ethyl acetate, however, was 11.7 kV and that for methyl acrylate was also higher. These esters are therefore special cases.

The steam cleaning experiments gave a maximum potential of 18 kV in a 1200 m^3 tank. It is concluded that in this case an incendive spark could, in principle, occur. However, steam cleaning is used only after water washing so that a flammable atmosphere should not be present.

Further work on this topic is described by Jones and Bond, who define a tank centre space potential (TCSP) as the criterion to be considered. They develop a model to estimate the hazard threshold value of this potential. The model does not, however, predict the actual value of the potential which will occur in a given situation; this must be obtained by other means. They also give information on incidents and incident rates for cargo tank fires and explosions on chemical tankers, as described below.

23.15.3 Inert gas systems

One of the principal means of preventing fire on ships carrying flammable materials is the use of inerting. Inerting is treated in *Inert Gas Systems* (IMO, 1990 IMO-860) and by Rushbrook (1979), Gebhardt (1980), Berkel (1982), R.K. Roberts (1983), Anon. (1984r), Anon. (1984s) and Oellrich (1987).

An account of the methods available for generating an inert gas, usually nitrogen, and of its applications has been given by Oellrich (1987), who lists the following methods of generation:

(1) combustion processes;
(2) catalytic combustion of ammonia;
(3) pressure swing adsorption;
(4) permeation processes;
(5) cryogenerators;
(6) boiler flue gas.

These processes differ in various respects, including the required oxygen purity, energy consumption, convenient plant size and economics.

Some basic requirements of a nitrogen generation process are high purity oxygen, preferably $<0.3\%$, high capacity and low space requirements.

There are several functions for which inert gas may be required. They include:

(1) gas freeing;
(2) inciting prior to loading;
(3) purging and padding.

Gas freeing is the purging of a tank with inert gas prior to purging with air for tank inspection. Purging and padding is carried out to render the gas space above the cargo in the tank inert and to keep it so.

Inciting is typically used to reduce the oxygen content of the space incited to below 5%.

There are certain problems and hazards associated with the use of inciting. These include:

(1) contamination of cargo;
(2) overpressure of tank;
(3) neutralization of inhibitors;
(4) asphyxiation of crew.

The use of inert gas such as boiler flue gas may contaminate the chemicals carried. The inciting operations

may cause overpressure of the tank. Certain inhibitors used to prevent polymerization of monomers may be rendered ineffective unless there is sufficient oxygen in the atmosphere. An example is hydroquinone which is used as an inhibitor in vinyl acetate. The large quantities of inert gas required present a hazard of asphyxiation to the crew.

The IMO requirements for inciting are given in *Inert Gas Systems* (IMO, 1990 IMO-860), which covers oil tankers, product carriers and combination carriers and also deals with chemical tankers. As already described, there are also inciting requirements in the *IGC Code* and the *IBC Code*.

The use of inciting is an accepted practice for oil tankers, but has been controversial for chemical tankers. For oil tankers, the provision of an inert gas system has become mandatory. Under SOLAS 1974, it is required for tankers >100,000 DWT and under SOLAS 1978 for existing tankers >40,000 DWT, and new tankers >20,000 DWT.

The IMO has also considered a proposal for a requirement for chemical tankers, but there are certain problems and the proposal has been resisted. The problem has been discussed by H.R. Edwards (1983). Difficulties in the use of inert gas on chemical tankers are the facts that the most common method of inciting, that is, the use of inert gas from oil firing, is liable to contaminate the cargo and that inhibition of polymerization of monomers is less effective due to lack of oxygen. Given these difficulties, the relatively low number of incidents and the appreciable costs, it is argued that inciting is not justified.

The work by M.R.O. Jones and Bond (1984, 1985) on static electricity and on fires and explosions in chemical tankers may be regarded as a contribution to assessing the risks from these latter hazards. A study by Lloyd's Register showed that for chemical tankers, the use of inciting would lead to only a marginal reduction in the frequency of fire but an appreciable increase in the frequency of tank entry incidents (Anon., 1984s).

The IMO requirements for environmental control, or control of the atmosphere in the vapour space of the cargo tanks, are given in Chapter 9 of the *IBC Code*. This states that vapour spaces 'may require to have specially controlled atmospheres' and describes four methods, of which inerting is one.

23.16 Marine Transport: Liquefied Flammable Gas

23.16.1 Regulatory controls and codes

The controls and codes for ships carrying hazardous materials have already been described. For gas carriers transporting LFG, the *IGC Code* is of particular relevance.

23.16.2 Hazard scenarios

Principal hazards from gas carriers are spillage of a large quantity of LFG onto water, as a result of grounding, collision or leak during transfer, and a large fire or explosion on the ship, particularly in or near a port.

23.16.3 Ship design and operation

The design of LGCs is described in the *IGC Code* and in *Liquefied Gas Handling Principles on Ships and in Terminals* (SIGTTO, 1986/3). As stated earlier, gas carriers are designed with cargo tanks integral with the vessel or with separate tanks. Plate 29 shows a typical gas carrier, in this case one with separate spherical tanks.

Gas carriers fall into six groups: (1) fully pressurized carriers, (2) semi-refrigerated/semi-pressurized carriers, (3) semi-pressurized/fully refrigerated carriers, (4) fully refrigerated LPG carriers, (5) ethylene carriers and (6) LNG carriers. The first three groups are most suitable for smaller cargoes and the fourth for larger cargoes of LPG or ammonia.

The principal contents of the *IGC Code* are shown in Table 23.32, Section A, and illustrate many of the most important features of gas carriers.

The code specifies degrees of damage and flooding which the ship itself should be designed to survive.

The *Code* recognizes five types of cargo containment system: (1) independent tanks, (2) membrane tanks, (3) semi-membrane tanks, (4) integral tanks and (5) internal insulation tanks. Independent tanks are classified as Type A, B or C. Type A tanks are basically constructed of plane surface. Type B tanks may be constructed of plane surface

Table 23.32 *Principal contents of the IGC Code and the IBC Code (International Maritime Organization, 1996 IMO-782 and 1990 IMO-100)*

A IGC Code 1996

Chapter No.	
1	General
2	Ship survival capability and location of cargo tanks
3	Ship arrangements
4	Cargo containment
5	Process pressure vessels and liquid, vapour and pressure piping systems
6	Materials of construction
7	Cargo pressure/temperature control
8	Cargo tank vent systems
9	Environmental control
10	Electrical installations
11	Fire protection and fire extinction
12	Mechanical ventilation in the cargo area
13	Instrumentation (gauging, gas detection)
14	Personnel protection
15	Filling limits for cargo tanks
16	Use of cargo as fuel
17	Special requirements
18	Operating requirements
19	Summary of minimum requirements

B IBC Code 1990

Chapter No.	
1–4	Titles essentially as *IGC Code*
5	Cargo transfer
6–14	Titles essentially as *IGC Code*
15	Special requirements
16	Operational requirements
16A	Additional measures for the protection of the marine environment
17	Summary of minimum requirements
18	List of chemicals to which the code does not apply
19	Requirements for ships engaged in the incineration at sea of liquid chemical waste

or as pressure vessels. For a Type B, tank, the stress analysis is more comprehensive than that for a Type A tank. Type C tanks are normally cylindrical or spherical pressure vessels. Figure 23.11(a)–(c) illustrates these three types. Figure 23.11(d) and (e) show two principal membrane systems, those of Gaz Transport and Technigaz.

The *Code* gives requirements for the pressure system, including cargo and process piping, type tests on piping components, piping fabrication and jointing details, testing of piping, cargo system valves, cargo hoses, cargo transfer methods and vapour return connections. It requires remotely operated emergency shut-down valves on each cargo hose connection, operable from at least two points on the ship.

The *IGC Code* contains a number of requirements for materials of construction, specifying a range of steels for successively lower minimum design temperatures down to −165°C, and for welding and non-destructive testing.

The *Code* gives detailed requirements for cargo tank venting, both pressure relief and vacuum relief, including settings and capacities. The pressure relief valve capacity should be able to handle the maximum capacity of the cargo tank inciting system or the fire exposure, whichever is the greater. There is also a requirement for an additional pressure relieving system for liquid level control. The *Code* gives the formulae for valve sizing.

Under the heading of environmental control, the code contains requirements for the gas freeing of cargo tanks, including for flammable gases the use of inert gas. There are also requirements for environmental control in the hold spaces for cargo containment systems other than Type C independent tanks and for the spaces surrounding tanks of this latter type.

In respect of fire protection, ships carrying products which are flammable or toxic are required by the *IGC Code* to have a water spray system for cooling, fire prevention and crew protection, and those carrying flammables are required to have dry powder systems. The *Code* specifies the areas and features to be protected by each system and gives equipment capacities and application rates.

Matters covered under the special requirements of the *Code* are: (1) materials of construction; (2) independent tanks; (3) refrigeration systems; (4) deck cargo piping; (5) exclusion of air from vapour spaces; (6) moisture control; (7) inhibition; (8) permanently installed toxic gas detectors; (9) flame screens on vent outlets; (10) the maximum allowable quantity of cargo per tank; (11) submerged electric cargo pumps; and (12) various chemicals, including chlorine, ammonia, ethylene oxide, propylene oxide/ethylene oxide mixtures and vinyl chloride.

The code gives a tabular summary of minimum requirements, covering (1) product name, (2) United Nations (UN) number, (3) ship type, (4) independent Type C tank, (5) control of vapour space in cargo tanks, (6) vapour detection, (7) gauging, and (8) special requirements.

One of the principal liquefied gases carried is LNG. Some features of LNG carrier design include (1) cargo tank design, (2) cargo protection, (3) cargo tank cooling, (4) cargo tank insulation, (5) boil-off, (6) reliquefaction and (7) propulsion.

For LNG carriers, there are three principal cargo tank designs in use. These are the Gaz Transport (GT) membrane, the Technigaz (TGZ) membrane and the Moss Rosenberg spherical tank. The three types have been described by Bouckaert and Cappoen (1984). An account of the GT design has been given by Jean and Bourgeois (1985) and of the Technigaz design by Ogawa *et al.* (1986).

Protection of the cargo tanks against grounding and collision is an important aspect of the tank design. Designs based on independent tanks have obvious advantages here, but membrane design has also given good protection in practice.

Since the LNG carried is very cold, it is necessary to ensure that its loading does not create a hazard due to thermal shock. The empty tanks may be sprayed with LNG before loading to cool them down or the tanks may be kept permanently cool. In the GT system, the solution adopted is the use of invar as the membrane material.

There must also be good thermal insulation. There are a number of different insulation systems in use. Accounts are given by Bouckaert and Cappoen (1984) and Bö ckenhauer (1987). The effectiveness of the insulation is such that the boil-off rate achieved is very low. The boil-off may be used as fuel for the ship's boilers. Alternatively, a reliquefaction system may be provided.

There is a trend towards the use of diesel engines as the propulsion system. Accounts have been given by Engesser *et al.* (1987), Grone and Pedersen (1987) and Terashima *et al.* (1987).

LPG carriers are often designed as flexible carriers able to handle not only LPG but also other liquefied gases. A typical cargo list for such carriers was given in Section 23.12. The design of flexible semi-refrigerated carriers has been described by Faridany and Ffooks (1983) and by Backhaus and Olschlager (1985), the first being for an LPG carrier with multi-lobe tanks and the second an ethylene carrier with tri-lobe tanks.

With respect to operation, Chapter 18 of the *IGC Code* treats the following topics: (1) cargo information, (2) compatibility, (3) personnel training, (4) entry into spaces, (5) low temperature cargoes, (6) protective equipment, (7) systems and controls, and (8) cargo transfer.

23.16.4 Terminal design and operation

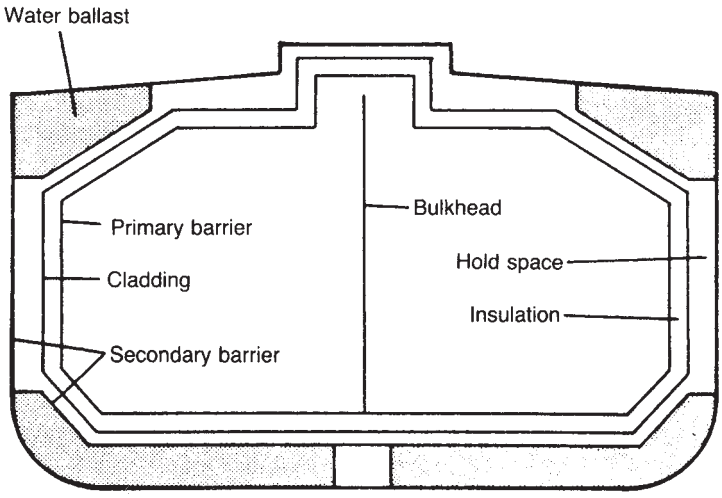
A terminal for LFG is either an export or an import terminal and normally handles mainly either LPG or LNG. Some principal LFG terminals are listed in Table 23.33.

An account of LPG terminals in Europe has been given by de Sola (1985). Some principal export terminals are those at Sullom Voe (Shetlands), Flotta (Orkneys), St Fergus-Mossmorran, Grangemouth, Teesside (UK) and at Kaarstoe (Norway). Some principal import terminals are those at Canvey and Killingholme (UK), Rotterdam, Terneuzen and Flushing (Netherlands), Antwerp (Belgium) and Lavera (France).

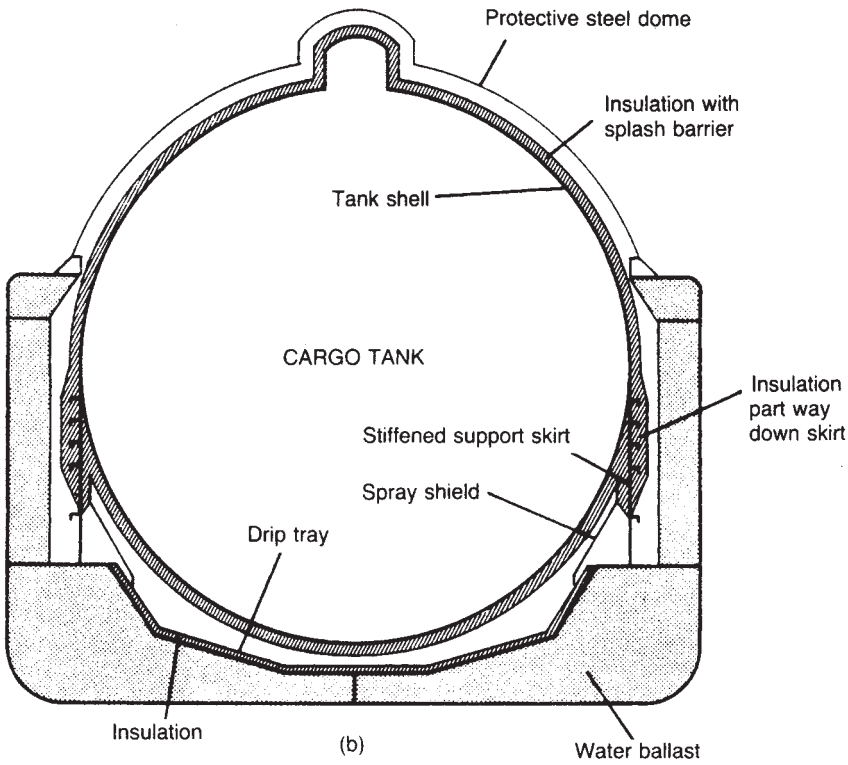
The LPG terminal at Mossmorran has been described by Sellers, Luck and Pantony (1985). An account of the LNG terminal at Arzew, Algeria, has been given by Benazzouz and Abbou (1987). The authors give a description of the first 20 years of operation of the site. This includes a detailed listing of the principal failures and associated down-time.

Terminals differ depending on whether they are import or export terminals. An account of the differences for LNG has been given by R.A. Cox, Comer *et al.* (1980). The main elements of an import terminal are

(1) berth for LNG ships and handling facilities;
(2) LNG storage tanks;
(3) pressure control system for tanks;
(4) gas separation and dispatch system.



(a)



(b)

Figure 23.11 *continued*

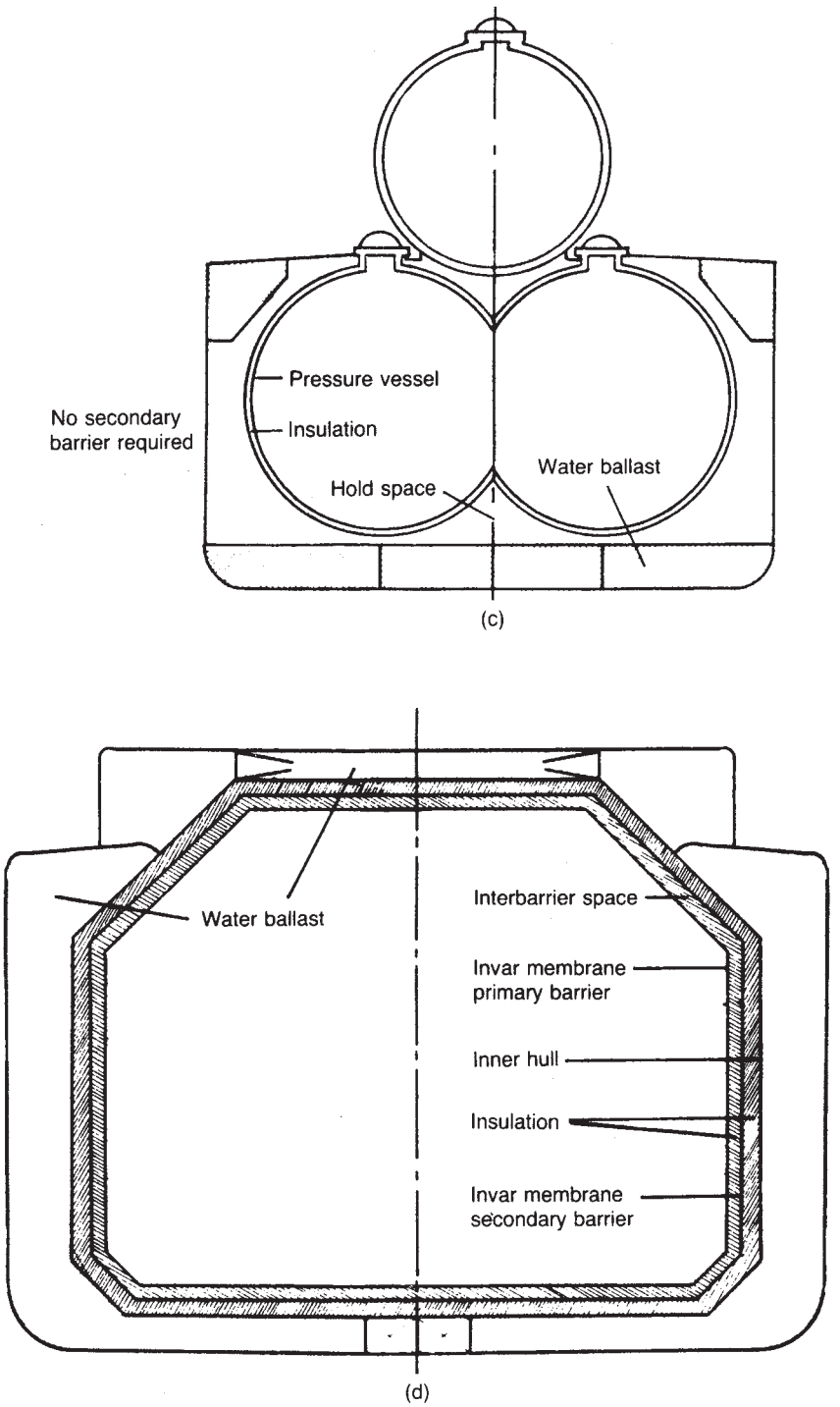


Figure 23.11 *Liquefied gas carrier cargo containment systems (Society of International Gas Tanker and Terminal Operators, 1986/6; reproduced by permission): (a) Type A prismatic self-supporting tank for fully refrigerated gas; (b) Type B spherical self-supporting tank; (c) Type C tank for semi-pressurized/fully refrigerated gas; (d) Gaz Transport membrane containment system for LNG; (e) Technigaz membrane barrier and insulation system for LNG*

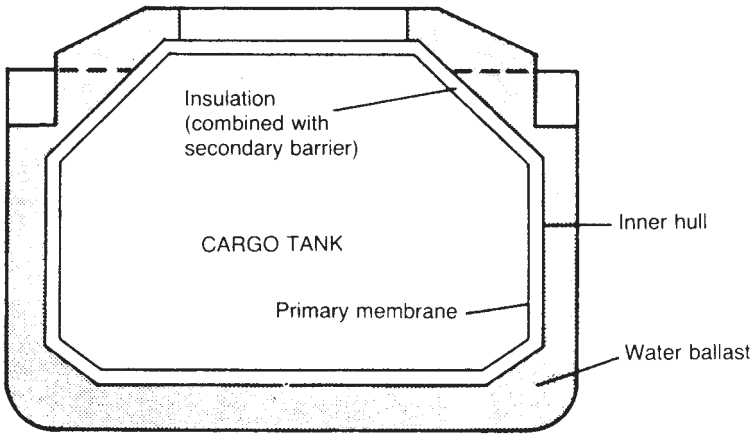


Figure 23.11 *continued*

Table 23.33 *Some LFG terminals*

A LNG	
Location	*Reference(s)*
Antwerp, Belgium	McKinney and Oerlemans (1985)
Arzew, Algeria	Filstead (1965); Pierot (1968); Rerolle (1968); Laur (1970); Bourguet (1972); Seurat, Hostache and Gros (1978); Benazzouz and Abbou (1987)
Brunei	C. Gibson (1973) ; Jenkins, Frieseman and Prew (1974); Ploum (1977)
Convey, UK	Ward and Hildrew (1968a–b); Eke, Graham and Malyn (1974)
Cove Point	Erne, Kime *et al.* (1980)
Fos-sur-Mer, France	Asselineau *et al.* (1972); Leray, Petit and Paradowski (1986a,b)
Kenai, Alaska	Horn *et al.* (1974)
Memphis	Stanfill (1968)
Montoir-de-Bretagne, France	Colonna, Lecomte and Caudron (1986)
Skikda, Algeria:	Dolle and Gilbourne (1976); Khenat and Hasni (1977)
Floating terminal	Anspach, Baseler and Glasfeld (1979)
Offshore terminal	Rust and Gratton (1980)
B LPG	
Location	*Reference(s)*
Port Bonython, Australia	Craker, Scott and Dutton (1986); Chauvin and Bonjour (1985)
Offshore terminal	Branchereau and Bonjour (1986)
C NGL	
Location	*Reference*
Mossmorran	Sellers, Luck and Pantony (1985)

The main elements of an export terminal are

(1) gas liquefaction and fractionation units;
(2) LPG storage facilities;
(3) LNG storage tanks;
(4) berth for LNG ships and handling facilities; and sometimes
(5) slugcatcher.

These differences affect the hazards of the terminal.

23.17 Marine Transport: Chemicals

23.17.1 Regulatory controls and codes

The controls and codes for ships carrying hazardous materials have already been described. For chemical tankers, the *IBC Code* is of particular relevance.

23.17.2 Hazard scenarios

Chemical tankers tend to present different hazards from those of gas carriers. These hazards include those of a

runaway reaction, an explosion, a toxic release and severe pollution.

23.17.3 Ship design and operation

It is convenient at this point to consider chemical tankers, or tank ships, which increasingly have come to share common features with gas carriers. Thus, as shown in Table 23.32, Section B, the headings of the *IBC Code* are very similar to those of the *ICG Code*.

Cargo containment systems are of four types: (1) independent tank, (2) integral tank, (3) gravity tank, and (4) pressure tank.

The cargo tank vent system is either an open vent or a controlled venting system using pressure/vacuum valves. The code gives requirements on the type of system for each product.

The *IBC Code* recognizes four types of environmental control system: inerting, padding, drying and ventilation. It gives requirements on the type of system for each product.

Matters covered under the special requirements of the *Code* include requirements concerning (1) acids, (2) toxic products, (3) inhibited cargoes, (4) high vapour pressure cargoes, (5) cargoes with a wide flammable range and low ignition temperature and (6) cargo contamination, together with requirements for a number of specific chemicals.

The *Code* gives a tabular summary of minimum requirements covering (1) product name, (2) UN number, (3) pollution category, (4) hazards, (5) ship type, (6) tank type, (7) tank vents, (8) tank environmental control, (9) electrical equipment, (10) gauging, (11) vapour detection, (12) fire protection, (13) materials of construction, (14) respiratory and eye protection and (15) special requirements.

With respect to operation, chapter 16 of the *IBC Code* treats the following topics: (1) tank filling, (2) cargo information, (3) personnel training, (4) opening of and entry into tanks, (5) stowage of cargo samples and (6) cargoes not to be exposed to excessive heat.

There are an appreciable number of chemicals to which the code does not apply, and these are listed in it.

23.18 Marine Transport Environment

23.18.1 Shipping

Information on the number of ships is available through Lloyds Register. The world fleet of oil tankers, chemical tankers and LGCs as given by Lloyds for 1986, quoted by Sanders and Aldwinckle (1987), is Further information on LGCs is given in Section 23.16.

Ship type	*No. of ships*	*Deadweight tonnage* ($\times 10^6$ te)
Oil tanker	5,985	240.2
Oil/chemical tanker	502	7.3
Chemical tanker	861	6.1
Gas carrier	770	10.1
Total	8,133	263.7
World fleet	75,266	647.6

23.18.2 Marine incidents

Lloyds Register also provides information on shipping incident statistics. Other sources of information are the *Interim Report of the Tanker Safety Group* (Tanker Safety Group, 1977) and *Analysis of Serious Casualties to Sea-Going Tankers* 1968–80 by the IMO.

Table 23.34 gives data from the Tanker Safety Group report. The accident rates are similar for all classes of ship. There is no evidence that very large ships, particularly very large crude carriers (VLCCs) are more liable to accidents. The yearly figures show no discernible trend with time.

For chemical tankers, information on fires and explosions has been given by M.R.O. Jones and Bond (1984), as shown in Table 23.35, which gives the number of fires and explosions, the size of vessel involved, the operation involved in each case and the source of ignition.

23.18.3 Substandard vessels

A study of the relation between the standards of ship design and operation and the probability of a ship accident has been reported in *Substandard Tankers* (van Poelgeest, 1978). In a comparison between 37 tankers owned by a Greek tanker operator and 37 oil company-owned tankers for the year 1973, this author found that whereas the latter ships were involved in some 10 incidents, mostly relatively minor, with a loss of 10 vessel-days, 28 of the former were involved in accidents, in many cases sustaining serious damage, and some in more than one incident, with a loss of 1072 vessel-days. The total of substandard tankers in the world tanker fleet of vessels of 6000 GRT and larger is estimated by van Poelgeest as approximately 450 vessels or 13–15% of the fleet.

Further information on substandard vessels is available in the 1993 *Annual Report* of the Paris Memorandum (1993). This gives statistics on the number of vessels, the number delayed/detained following inspection and the major categories of deficiency. In 1993, there were 17,294 inspections covering 112,523 ships, with 43,071 deficiencies and 926 detentions. The average proportion of vessels detained is about 8%, with some 10 states having at least double this proportion. The proportions for France, Germany, the UK and the USA are 4%, 3%, 2% and 0%, respectively. The proportion of the total delays/detentions attributable to different types of vessel includes 1.3% for gas carriers, 5.3% for chemical carriers and 10.7% for tanker/combination carriers, the proportions of each of these types detained being 6%, 8% and 7%, respectively. The breakdown of the major categories of deficiency is: life-saving appliances, 24.3%; firefighting appliances, 16.8%; general safety, 12.9%; navigational equipment, 11.6%; ship's certificates, 5.2%; MARPOL requirements, 4.7%; and other, 24.6%. The report refers to the 'increasingly ageing world fleet operating in a marginal market'.

23.18.4 Shipping: LPG

There is a large trade worldwide in LFGs. Accounts of this trade are given in *LNG Log* by SIGTTO (1986) and by Aprea (1983), Bouckaert and Cappoen (1984) and Glass (1987).

LNG Log contains statistical information on individual LNG carriers and terminals; on cargo containment systems; and on carrier movements, or voyages. In 1986, there were 963 movements of LNG carriers.

Further data on the number of LNG and LPG carriers are provided by Aprea (1983), Blything and Edmondson (1983), Bouckaert and Cappoen (1984) and Aldwinckle and

Table 23.34 *Serious casualties to and cargo fires/explosions on tankers carrying oil and chemicals during the period 1968–75 (Tanker Safety Group, 1977) (Courtesy of Trade and Industry)*

A Serious casualties[a]

Year	*Tanker size* (dwt)					
	10,000 to <150,000			>150,000		
	No. of ships	*No. of serious casualties*	*Serious casualty rate per tanker per year*	*No. of ships*	*No. of serious casualties*	*Serious casualty rate per tanker per year*
1968	2,927	79	0.0270	16	0	–
1969	2,934	72	0.0245	57	4	0.0702
1970	2,928	57	0.0194	121	3	0.0248
1971	2,956	56	0.0189	198	8	0.0404
1972	2,950	67	0.0227	267	7	0.0262
1973	2,930	63	0.0215	351	2	0.0570
1974	2,988	64	0.0214	455	5	0.0110
1975	2,971	78	0.0263	582	10	0.0172
Total	23,584	536	0.0227	2047	39	0.019

B Fires

Year	*Tanker size* (dwt)			
	10,000 to <150,000		>150,000	
	No. of cargo fires/explosions	*Cargo fire/explosion rate per tanker per year*	*No. of cargo fires/explosions*	*Cargo fire/explosion rate per tanker per year*
1968	13	0.0044	0	–
1969	9	0.0031	3	0.00526
1970	9	0.0031	0	–
1971	7	0.0024	1	0.0051
1972	19	0.0064	2	0.0075
1973	9	0.0031	2	0.0057
1974	10	0.0033	0	–
1975	5	0.0017	0	–
Total	81	0.0034	8	0.0039

[a] Serious casualties are those involving loss of life, structural damage or pollution.

McLean (1985). Tables 23.36 and 23.37 give data on the world LNG and LPG fleets, respectively.

The number of LNG carriers (*c.* 1984) is given in Table 23.36, Section B, as 81. A vessel capacity of 125,000 m^3 has become the standard size for a modern LNG carrier. For LPG carriers, the number (*c.* 1984) given in Table 23.37, Section B is 708. Of these, 213 were >5000 m^3 capacity.

Only a proportion of the LPG fleet consists of refrigerated carriers, the rest being pressure carriers. Holdsworth (1985) states that a figure of 107 ships represents 44% of world capacity in refrigerated LPG ships, which suggests a world fleet of some 243 vessels.

The approximate worldwide deep sea movements per year of LFGs other than LNG and LPG are given by Glass (1987) as 370 for ethylene, 290 for propylene and 520 for butadiene.

23.18.5 Marine incidents: LPG

Incident statistics for LNG carriers are given by R.A. Cox, Comer *et al.* (1980) and Aldwinckle and McLean (1985), while Blything and Edmonson (1983) give data on fires and explosions. For LPG carriers, data on incident statistics are given by Aldwinckle and McLean (1985) and data on fire and explosion are given by Blything and Edmondson (1983).

Table 23.38 gives incident data for the world LNG and LPG fleets and, for comparison, for the world cargo fleet. These include incidents involving fire and explosion as well as grounding and collision. Further data on LNG carrier incidents is given in Table 23.39, which again provides information both on grounding and collision and on fire and explosion. Data on LPG carrier fire and explosion are shown in Table 23.40 and data an stranding and collision are given in Table 23.41. For the world LGC fleet, which includes both LNG and LPG carriers, data are given in Table 23.42.

These overall data on incidents and incident rates may be supplemented by data for specific waterways and ports. Incident data for the port of Rotterdam have been given by Ligthart. Figure 23.12 gives information on collision and stranding determined for this port.

For the Thames estuary, accident data are given in the two *Canvey Reports* as described in Appendix 7.

Table 23.35 *Fire and explosions on chemical tankers in the period 1973–83 (after M.P.O. Jones and Bond, 1984)*

A Number of incidents

Location	*No. incidents*
Cargo tank	14
Pump room	9
Engine room	34
Other	11
Total	68

B Cargo tank incidents: vessel size

Vessel size (DWT)	*No. incidents*
<1,000	7
1,000–9,999	2
10,000–19,999	2
>20,000	3
Total	14

C Cargo tank incidents: operations involved

Operation	*No. incidents*
Loading	2
Steaming out tank	2
Water washing with rubber hose and wooden nozzle	1
Inspection/cleaning by persons inside tank	3
Handling of slops	3
Polymerization of product	1
Overpressurization of tank with nitrogen	1
'While being pushed by a tug'	1
Total	14

D Cargo tank incidents: source of ignition

Ignition source	*No. incidents*
Static electricity (attributed or probable)	5
Frictional spark	1
Light bulb	2
Flare stack	2
Unknown	2
No ignition[a]	2
Total	14

[a] Of these two incidents classed as fire/explosion, one was a case where the tank was overpressurized by nitrogen, and the other was a case where polymerization of acrylic acid occurred, causing a high temperature but no fire or explosion.

23.18.6 Ship collision

Two principal ship accident modes which may give rise to large loss of containment are collision and grounding. Both have been the subject of study. Studies of collision include those of Minorsky (1959), Kinkead (1978 SRD R91, 1980), Böckenhauer (1980) and F.S. Harris (1986).

The requirements for collision resistance are given by Harris as stability after collision, avoidance of spillage and energy absorption by the structure.

Table 23.36 *World LNG fleet*

A Blything and Edmondson (1983) – Date: 1981

Ship capacity (m^3)	*No. of ships*
<5000	7
>5000	64
Total	71

B Aldwinckle and McLean (1985): No. of ships

Ship capacity (m^3)	*Ship age* (year)					
	0–4	5–9	10–14	15–19	20–24	*Total*
<5,000	1	1	8	1		11
5,000–9,999	1					1
10,000–29,999		1	1	1	2	5
30,000–49,999		2	5	1		8
50,000–69,999			1			1
70,000–99,999		3	6	2		11
100,000–129,999	10	26				36
>130,000	7	1				8
Total	19	34	21	5	2	81

Minorsky presented a model of collision damage based on the equations for conservation of energy and momentum. These are respectively

$$\tfrac{1}{2}m_1v_1^2 = \tfrac{1}{2}(m_1 + m_2)V^2 + E \qquad [23.18.1]$$

and

$$V = \frac{v_1 m_1}{m_1 + m_2} \qquad [23.18.2]$$

where E is the energy absorbed in the collision, m_1 is the effective mass of the striking ship, m_2 is the effective mass of the struck ship, v_1 is the speed of the striking ship before collision and V is the residual speed of the two ships after the collision.

Minorsky took the effective mass of the struck ship as the actual mass plus the added hydrodynamic mass δm, which he estimated as 0.4 m_2.

He defined a resistance factor R_T as

$$R_T = \sum P_N L_N t_N + \sum P_n L_n t_n \qquad [23.18.3]$$

where L is the length of damage, P is the depth of damage and t is the thickness, and the subscripts N and n refer to the Nth member in the striking ship and the nth member in the struck ship.

From ship collision data, he obtained an empirical correlation between E and R_T, as illustrated in Figure 23.13. The relation may be expressed in the form:

$$E = mR_T + c \qquad [23.18.4]$$

where c and m are constants.

Table 23.37 *World LPG fleet*

A Blything and Edmondson (1983) – Date: 1981

Ship capacity (m^3)	*No. of ships*
<5,000	409
>5,000	159
Total	568

B Aldwinckle and McLean (1985): No. of ships

Ship capacity (m^3)	*Ship age* (year)							
	0–4	5–9	10–14	15–19	20–24	25–29	>30	*Total*
Unknown	6	3	1				2	12
<5,000	93	97	92	121	49	18	13	483
5,000–9,999	30	17	4	7	1			59
10,000–29,999	14	17	7	20	5		2	65
30,000–49,999	3	2	3	3	1	1		13
50,000–69,999	5	8	9	1				23
70,000–99,999	14	27	8	1				50
100,000–129,999		1	2					3
Total	165	172	126	153	56	19	17	708

Minorsky also defined an absorbed energy coefficient K and a ratio R of mass of the striking and struck ships:

$$K = \frac{m_2 + \delta m}{m_1 + m_2 + \delta m} \qquad [23.18.5]$$

$$R = m_1/m_2 \qquad [23.18.6]$$

Figure 23.14 shows the relation given by Minorksy between the two parameters. As $R \to 0$, $K \to 1$, and as $R \to 0$, $K \to 0$. The relationship is not very sensitive to the value of δm. Using this model, Minorsky was able to determine the critical impact speed of the striking ship required to cause a given degree of damage.

The following treatment by Böckenhauer (1980) for collision damage to a gas carrier is typical of analyses based on the Minorsky method. From Equations 23.18.1 and 23.18.2

$$E = \frac{m_1 m_2}{2(m_1 + m_2)} v_1^2 \qquad [23.18.7]$$

Then at the critical impact speed v_{cr} of the striking ship and at the corresponding critical energy absorption E_{cr}

$$E_{cr} = \frac{m_1 m_2}{2(m_1 + m_2)} v_{cr}^2 \qquad [23.18.8]$$

or

$$v_{cr} = \left(\frac{2E_{cr}(m_1 + m_2)}{m_1 m_2} \right)^{1/2} \qquad [23.18.9]$$

The critical energy absorption E_{cr} is given either as the sum of the energy absorptions of the striking ship E_2, and of the struck ship E_2:

$$E_{cr} = E_1 + E_2 \qquad [23.18.10a]$$

or as

$$E_{cr} \approx 2E_2 \qquad [23.18.10^*]$$

whichever is the lesser. The energy absorption E_2 is obtained from the resistance factor using an expression similar to Equation 23.18.3 but with a different definition of the resistance factor.

If the struck ship is moored at a jetty so that the residual speed V is zero

$$\tfrac{1}{2} m_1 v_1^2 = E \qquad [23.18.11]$$

$$v_{cr} = \left(\frac{2(E_{cr} + E_f)}{m_1} \right)^{1/2} \qquad [23.18.12]$$

where E_f is the energy absorption of the fender. This is taken as

$$E_f \leq 0.3 \qquad [23.18.13]$$

Some critical impact speeds where the struck ship is an LNG or LPG carrier as obtained by Böckenhauer are given in Table 23.43.

Kinkead (1978 SRD R91) has studied the collision of LNG carriers using a method based on that of Minorsky but extended by a more detailed analysis of the energy absorbed in the processes causing damage, which he calls the substantiation analysis.

Figure 23.15 shows Minorsky-type curves obtained in this work. The dotted line is based on the more detailed substantiation analysis. Its principal feature is that it

Table 23.38 *World LNG, LPG and cargo fleet incident frequency (incidents/1000 ship-years) (after Aldwinckle and McLean, 1985) (Courtesy of Gastech)*

Casualty type[a]		*Ship type*			
		LNG carriers	*LPG carriers*	*Total gas carriers*	*Dry cargo ships*
Collision	A	0	0.36	0.32	0.82
	B	0	1.08	0.95	5.82
	C	0	1.43	1.27	6.64
	D	0	0	0	2.97
Contact	A	0	0	0	0.21
	B	0	0.36	0.32	1.88
	C	0	0.36	0.32	2.08
	D	0	0	0	0.23
Fire/explosion	A	0	0.72	0.63	1.82
	B	0	3.58	3.16	3.37
	C	0	4.30	3.79	5.20
	D	0	2.87	2.53	4.98
Foundering	A	0	1.43	1.26	2.61
	B	0	0.36	0.32	0.33
	C	0	1.79	1.58	2.94
	D	0	0	0	8.35
Hull/machinery damage	A	0	0	0	0.29
	B	2.65	9.32	8.52	8.08
	C	2.65	9.32	8.52	8.36
	D	0	0	0	0.27
Miscellaneous	A	0	0	0	0.02
	B	0	0	0	0.22
	C	0	0	0	0.25
	D	0	0	0	0
Missing	A	0	0	0	0.15
	B	0	0	0	0.01
	C	0	0	0	0.16
	D	0	0	0	3.73
War loss/hostility	A	0	0	0	0.25
	B	0	0	0	0.62
	C	0	0	0	0.88
	D	0	0	0	1.03
Wrecked/stranded	A	0	1.79	1.58	2.81
	B	10.59	2.51	3.47	7.38
	C	10.59	4.30	5.05	10.19
	D	0	0	0	1.20
Total	A	0	4.30	3.79	8.98
	B	13.24	17.20	16.73	27.71
	C	13.24	21.50	20.52	36.69
	D	0	2.87	2.53	22.76

[a] A, No. of reported losses; B, No. of reported serious casualties; C = A + B; D, No. of people killed or missing. All per 1000 ship-years.

indicates that for striking ships in the displacement range 15,000–30,000 ton, the critical impact speed is considerably less than the simpler analysis suggests.

Kinkead also gives a set of curves for the critical impact speed of the striking ship hitting an LNG carrier under different conditions, as shown in Figure 23.16.

23.18.7 Ship grounding

Of at least equal importance are ship groundings. Here there are two somewhat different scenarios which need to be considered. One is where the ship is moving at speed and its bottom is torn by a rock. Treatments of this situation have been given by Kitamura, Okumoto and Shibue (1978) and by Vaughan (1978). It has been shown by Poudret *et al.* (1981) that Vaughan's approach fits well such a grounding incident which occurred with the *El Paso Paul Kayser*, as described below.

The other scenario is grounding of the ship at low speed as a result of weather, currents, loss of control, etc. This is probably the situation which is most likely to occur in confined waterways. It has been studied by Johnsen and Jensen (1983) for the case of smooth rocks and by Kinkead (1983 SRD R 342, 1983) for that of sharp rocks.

The ships considered by Kinkead are LPG carriers in the capacity range 11,754–58,950 m^3. Grounding may occur with the ship moving forwards or sideways. For the ridged

Table 23.39 *World LNG carrier fleet incidents*

A General incidents (R.A. Cox, Comer *et al.*, 1980) – Period: 1964–77

Incident type	*No. of incidents*	*Incident frequency* (incidents/1000 movements)		
		LNG traffic	*UK port survey*	
			Open sea port	*Estuarial port*
Grounding, stranding, drifting	3	0.45	0.17	0.16
Collision, impact, ramming	4	0.6	1.22	0.17
Leaks from tanks or during transfer	6	0.9	–	–
Other	6	0.9	–	–

B Fire and explosions (Blything and Edmondson, 1983) – Period: 1971–81

Ship capacity (m^3)	*No. of ship-years*	*No. of incidents*
<100,000	305	2
>100,000	145	2
Total	450	4

Table 23.40 *World LPG carrier fire and explosions (after Blything and Edmondson, 1983) (Courtesy of the Institution of Chemical Engineers)*

A Incidents per year

Ship capacity (m^3)	*No. of incidents*	*No. of ship-years*	*Incident frequency* (incidents/ship-year)
<5000[a]	14	1850	7.6×10^{-3}
>5000[b]	8	662	1.2×10^{-2}

B Incidents per voyage

Ship capacity (m^3)	*No. of incidents*	*No. of voyages*	*Incident frequency* (incidents/voyage)
<5000[a]	14	14,854	8.4×10^{-4}
>5000[b]	18	6,259	2.9×10^{-3}

C Ship area and marine location

Ship area	*Ship capacity* (m^3)	*No. of incidents*		
		At sea	*In port or restricted waters*	*Total*
Engine room	<5000	4	2	18
	>5000	9	3	
Cargo pumps/ compressors	<5000	–	2	4
	>5000	–	2	
Cabins/galley	<5000	2	–	3
	>5000	–	1	
Other	<5000	–	–	1
	>5000	–	1	
Unknown	<5000	2	2	6
	>5000	1	1	

[a] Over period 1977–81.
[b] Over period 1971–81.

Table 23.41 *World LPG carrier groundings and collisions 1977–81 (after Blything and Edmondson, 1983) (Courtesy of the Institution of Chemical Engineers)*

Incident type	*Ship capacity* (m^3)	*No. of incidents*	*No. of ship-years*	*Incident frequency* (incidents/ship-year)
Stranding	<5000	13	1850	7.0×10^{-3}
	>5000	18	662	27×10^{-3}
Collision	<5000	48	1850	2.6×10^{-2}
	>5000	25	662	3.8×10^{-2}

Table 23.42 *World LGC carrier incidents (after Aldwinckle and McLean, 1985) (Courtesy of Gastech)*

Cause of damage	*Ship area*[a]																*No. of ships*
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	*All*	
Collision	8					17	6				1	2	3			37	15
Grounding			1		27	1						4	1	7		41	9
Pounding					4											4	3
Ice														1		1	1
Cargo shift																	
Excess pressure	2	2	10	8		6	1						3		3	35	8
Vibration												4	7			11	4
Cargo handling							1									1	1
Wear and tear	7	1	5	5	61	24	8					4	6	10	4	135	23
Mooring													6	6		3	
Other													1		2	3	2
Contact	2	5	2		13	32						6	5	1	1	67	21
Sloshing																	
Heavy weather	6	12	12	10	23	12	6					8	3	2	3	97	20
Fire												3	1			4	1
Flooding																	
Unknown	14	6	29	16	76	70	9					16	32	34	18	320	42
All	39	26	39	59	204	162	31				1	47	62	55	37	762	48
No. of ships	17	16	21	13	33	35	13				1	20	21	22	20		48
Proportion of all areas (%)	5.1	3.4	7.7	5.1	26.8	21.3	4.1				0.1	6.2	8.1	7.2	4.9	100	
Incidence (per 100 months)	0.64	0.42	0.96	0.64	3.33	2.65	0.51				0.02	0.77	1.01	0.90	0.60	12.45	

[a] 1, Fore end structure; 2, forecastle and deck; 3, transverse bulkheads (in way of cargo space); 4, longitudinal bulkheads (in way of cargo space); 5, bottom structure (in way of cargo space); 6, side structure (in way of cargo space); 7, deck structure (upper); 8, deck structure (tween); 9, weather deck hatchways and covers; 10, tween deck hatchways and covers; 11, bridge/deck houses and decks (excluding poop and forecastle); 12, engine room (including bottom structure); 13, aft end structure (excluding engine room, sternframe and rudder); 14, rudder (excluding bow); 15, miscellaneous.

rock formation considered, he obtains using a Minorsky-type analysis for a 15,495 m^3 carrier for forward grounding, a critical grounding velocity of 5.57 knot and for a 31,296 m^3 carrier one of 5.11 knot. The sideways critical grounding velocities for these two vessels obtained from Minorksy analysis are 3.82 and 3.23 knot, respectively. However, using a more detailed analysis the latter two values reduce to 2.69 and 2.86 knot, respectively. The analysis contains some conservative assumptions. One is that the rock is not friable, another that no energy is absorbed by other rock projections.

Kinkead states that imperfectly controlled manoeuvres during berthing of supply vessels at offshore platforms have occurred with sideways collision impact velocities of between 2.9 and 4.0 knot (between 1.5 and 2.0 m/s). Thus, the impact velocities which occur under imperfect control are of the same order as the estimated critical grounding velocities.

23.18.8 Piracy

A quite different kind of risk is that posed by piracy. The activities of pirates are monitored by the regional piracy centre of the International Maritime Bureau in Kuala Lumpur. Most attacks have occurred in the South China Sea, off Hong Kong and around Indonesia, and also off Somalia. In 1994, 60 vessels were boarded by pirates, almost twice as many as in the previous year. In several cases, ships were taken over and sailed to a port, where the cargo was unloaded and stolen. Most of the ships attacked were dry cargo vessels, but eleven oil tankers, four gas carriers and two chemical tankers were also involved.

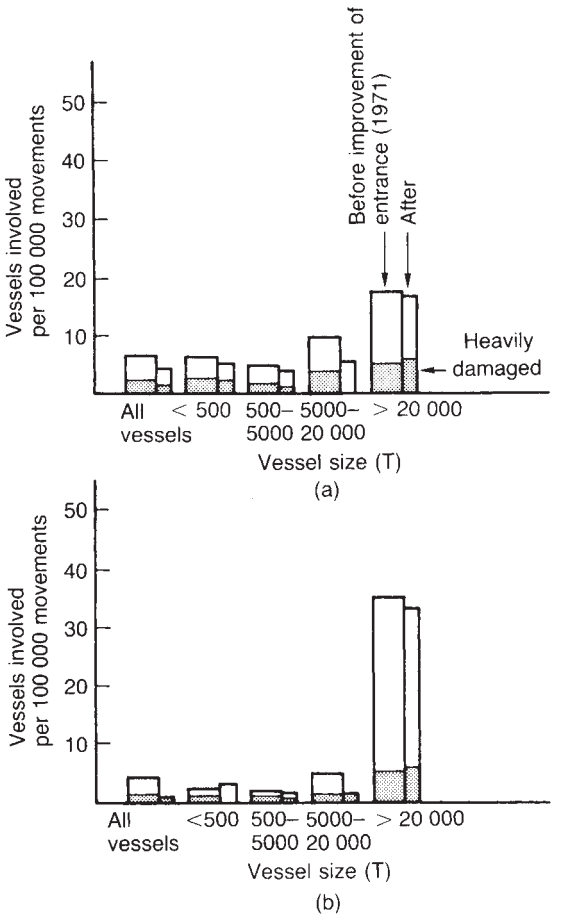


Figure 23.12 *(a) Collision ratio and (b) stranding ratio per tonnage class for vessels entering and leaving Rotterdam. T, gross registered ton (= 100 ft^3) (Ligthart, 1980) (Courtesy of Elsevier Science Publishers)*

23.19 Air Transport

Regulatory control of the carriage of hazardous materials by air has traditionally been the concern of the Restricted Articles Board of the International Air IATA. The IATA Restricted Articles Regulations have placed restrictions on the type and quantity of chemicals which are carried and specify requirements for packaging and labelling. These regulations are binding on IATA member airlines and are applied by many which are not members. They are also generally accepted by governments, who apply them to all aircraft registered with them.

In 1983, the International Civil Aviation Organization (ICAO) issued its *Technical Instructions for the Safe Transport of Dangerous Goods by Air* (the *Technical Instructions*). These introduced into air transport the UN system for the classification and packaging of dangerous goods. These *Technical Instructions* have largely superseded the IATA regulations.

In Britain, the Air Navigation (Dangerous Goods) Regulations 1985, and subsequent amending regulations, require dangerous goods to be carried in accordance with the *Technical Instructions*. The enforcing authority is the CAA.

The IATA continues to publish its Dangerous Goods Regulations. These are broadly compatible with the *Technical Instructions* and continue to be used by many operators.

The *Technical Instructions* give specific instructions for the packaging and set maximum quantities for carriage.

There are some substances the carriage of which is forbidden. These forbidden substances fall into three categories: (1) forbidden unless authorized by the state of origin; (2) forbidden unless authorized by all the states concerned; (3) forbidden in all circumstances. In the United Kingdom, requests for exemptions must come from the air operator and any exemption is issued to him.

The quantities of hazardous materials moved by air are quite large. In general, the quantities permitted for carriage are larger for cargo than for passenger aircraft. There has been, however, a steady decline in the proportion of cargo aircraft, so that increasingly carriage is in passenger aircraft.

The carriage of radioactive substances is governed by the IATA Regulations on Radioactive Materials, which embody the International Atomic Energy Agency (IAEA) Regulations on the Safe Transport of Radioactive Materials.

In general, the carriage of hazardous materials does not appear to be a significant cause of, or aggravating feature in, aircraft accidents. However, improperly packed and loaded nitric acid was declared the probable cause of a cargo jet crash at Boston, MA, in 1973, in which three crewmen died (Chementator, 1975 Mar. 17, 20).

Information on aircraft accidents in the United States is given in the NTSB *Annual report* 1984. In 1984, for scheduled airline flights, the total and fatal accident rates were 0.164 and 0.014 accidents per 10^5 h flown, respectively. For general aviation, that is, all other civil flying, the corresponding figures were very much higher at 9.82 and 1.73.

23.19.1 Rotorcraft

There is increasing use made of rotorcraft – helicopters and gyroplanes. Although these are used to transport people rather than hazardous materials, it is convenient to consider them here.

An account of accidents is given in *Review of Rotorcraft Accidents 1977–1979* by the NTSB (1981). In 64% of cases (573 out of 889), pilot error was cited as a cause or related factor. Weather was a factor in 17% of accidents. The main cause of the difference in accident rates between fixed wing aircraft and rotorcraft was the higher rate of mechanical failure in rotorcraft accidents.

The NTSB *Annual report* 1981 gives for rotorcraft an accident rate of 11.3 and a fatal accident rate of 1.5 per 100,000 h flown.

23.20 Transport Emergency Planning and Spill Control

23.20.1 Emergency planning

The transport of hazardous materials requires emergency planning, but the nature of the emergency plans depends on the mode of transport. Road transport is covered by the CHEMSAFE scheme. Accounts of emergency planning for transport include those in HS(R) 27 and in the ACDS Transport Report (Cooney, 1991) and those by Bosman (1980), Cumberland (1982) and Cooney (1985). The topic is discussed in Chapter 24 and treatment here is limited to two aspects not dealt with there: marine emergencies and spill control.

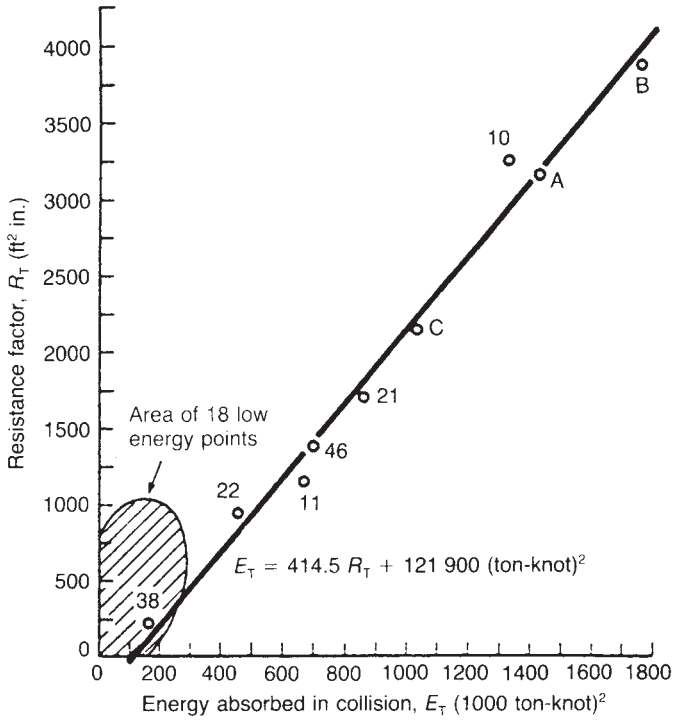


Figure 23.13 *Minorsky model of ship collision: empirical correlation between resistance to penetration and energy absorbed in collision (Minorsky, 1959) (Courtesy of the Journal of Ship Research)*

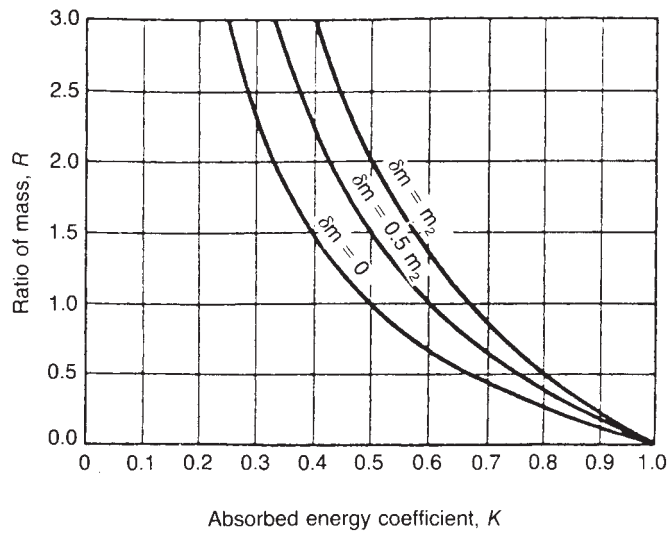


Figure 23.14 *Minorsky model of ship collision: effect of added virtual mass of water on energy absorbed in collision (Minorsky, 1959) (Courtesy of the Journal of Ship Research)*

Table 23.43 *Estimated critical impact speeds for ship collision[a] for gas carriers (after Böckenhauer, 1980) (Courtesy of Gastech)*

	Critical impact speed (knot)			
Struck ship	*Sister ship*	*LPG carrier* (6000 m^3)	*Dry cargo ship*	*Oil tanker*
LPG carrier:				
6000 m^3	–	2.6 (2.0)	2.3 (1.5)	4.5 (1.1) 3.5 (1.8)[b]
54,000 m^3	1.9 (1.5)	3.4 (3.2)	2.8 (2.5)	1.3 (0.9)[c]
LNG carrier:				
125,000 m^3, membrane	3.7 (2.8)	5.0 (4.8)	4.0 (3.8)	4.0 (2.5)
125,000 m^3, spheres	5.9 (4.5)	9.0 (8.6)	6.5 (6.1)	4.8 (3.0)

[a] Values in brackets are for struck ship moored at jetty.
[b] Oil tanker fully loaded.
[c] Oil tanker in ballast.

23.20.2 Marine emergencies

The CIMAH Regulations 1984 contain a requirement for emergency planning for the fixed site to which they are applicable, which may include a port area. The DSHA Regulations 1987, Regulations 26 and 27, require ports handling hazardous substances to undertake emergency planning. HS(R) 27 gives in Appendix 3 detailed guidance for emergency planning in ports.

IMO guidance is contained in *Emergency Procedures for Ships Carrying Dangerous Goods* (IMO, 1991 IMO-254) (EmS). Other guidance is given in *Liquefied Gas Handling Principles on Ships and in Terminals* (SIGTTO, 1986/3), *Guide to Contingency Planning for the Gas Carrier Alongside and within Port Limits* (ICS, 1987/6), *Contingency Planning and Crew Response Guide for Gas Carrier Damage at Sea and in Port Approaches* (ICS, 1989/8), *Guide to Contingency Planning for Marine Terminals Handling Liquefied Gases in Bulk* (ICS, 1989/9) and *Guidelines for the Preparation of Shipboard Oil Spill Contingency Plans* (OCIMF, 1990/9).

Emergency shut-down of ship–shore transfer is covered in *Guidelines for the Alleviation of Excessive Surge Pressure in BSD* (SIGTTO, 1987/4) and *Recommendations and Guidelines for Linked Ship/Shore Emergency Shutdown of Liquefied Gas Cargo Transfer* (SIGTTO, 1987/5).

Firefighting is covered in *Cargo Firefighting on Liquefied Gas Carriers* (SIGTTO, 1986/2) and *Guide on Marine Terminal Fire Protection and Emergency Evacuation* (OCIMF, 1987/6).

Marine spill control is covered in *Guidelines for the Preparation of Shipboard Oil Spill Contingency Plans* (OCIMF, 1990/9).

23.20.3 Spill control

There are a number of basic techniques for spill control, but there are also some measures which are specific to the mode of transport.

Accounts of spill control are given in *Highly Hazardous Materials Spills and Emergency Planning* (Zadic and Himmelman, 1978) and *Hazards Materials Spills Handbook* (G.F. Bennett, Feates and Wilder, 1982) and by R.L. Mitchell (1971, 1982), R.H. Hiltz (1982), Scholz (1982), H.M. Freeman (1984) and Deckert (1986)

The ease of detection of a spill varies with the mode of transport. The driver of a road tanker will generally know at once. A spill on a rail tank wagon may not be appreciated immediately. A leak from a pipeline may remain undetected for a considerable time.

The general principles of spill control in the field are described by Scholz (1982). The spill may be a continuing escape or a complete spillage of the whole contents. In the former case, the first step is the termination, or at least reduction, of the discharge.

The measures which can be taken to effect this depend on the circumstances. If the leak is below the liquid level, it may be reduced by changing the orientation of the tank so that it is vapour rather than liquid which comes out; often, however, this is not practical.

If the source of the leak is a valve, measures may be taken to shut it off. If the leak is from a puncture of the tank itself, it may be possible to plug it. The liquid in the leaking tank may be transferred to another vehicle, either as the prime method of terminating the discharge or after that has been done by some other method. Resort has also been had to dumping the liquid in a pit and then 'neutralizing' it.

It may be possible to plug the leak by bolting on a patch plate. There are also special plugging devices such as the foam plugger developed by the EPA.

Following any measures to effect (1) termination of discharge, the other measures for spill control are (2) containment, (3) suppression of evaporation, (4) removal and (5) disposal.

Whether the spill is a virtually instantaneous release of the whole tank contents or a more gradual leak, the liquid will form a pool on the ground. Priorities are to prevent the liquid entering drains and sewers, and water courses, and to limit the size of the pool formed.

Depending both on the nature of the material spilled and the population exposed, there may be a need to reduce the rate of evaporation of the liquid pool. General methods of doing this are described below, but they may or may not be practical in a given case.

Methods of removal include pumping and use of sorbents. The pumps used must be able to handle the liquid with which they are presented, which will include not that originally spilled but any added to control evaporation with, possibly, earth and other solid matter. Sorbents include straw and synthetic sorbents. The material recovered is transferred to temporary storage and then passes to disposal.

Spill control measures which are available in principle may be impractical in many transport situations, because they require additional equipment or materials, or for some other reason. Accounts are available of measures actually used in the field, including those of R.L. Mitchell (1982) and Scholz (1982).

23.20.4 Spill control: evaporation

As just described, it may be necessary for highly hazardous materials to take measures to reduce the rate of evaporation. An account of methods available to do this is given by R.H. Hiltz (1982). They include the use of (1) liquid phase modification, (2) surface cooling, (3) mechanical covers, (4) films and foams and (5) sorbents.

For some liquids, the rate of evaporation may be reduced by modifying the liquid phase in some way. Some basic principles are dilution with water, reaction with another chemical and turning the liquid into a gel by use of a gelling agent.

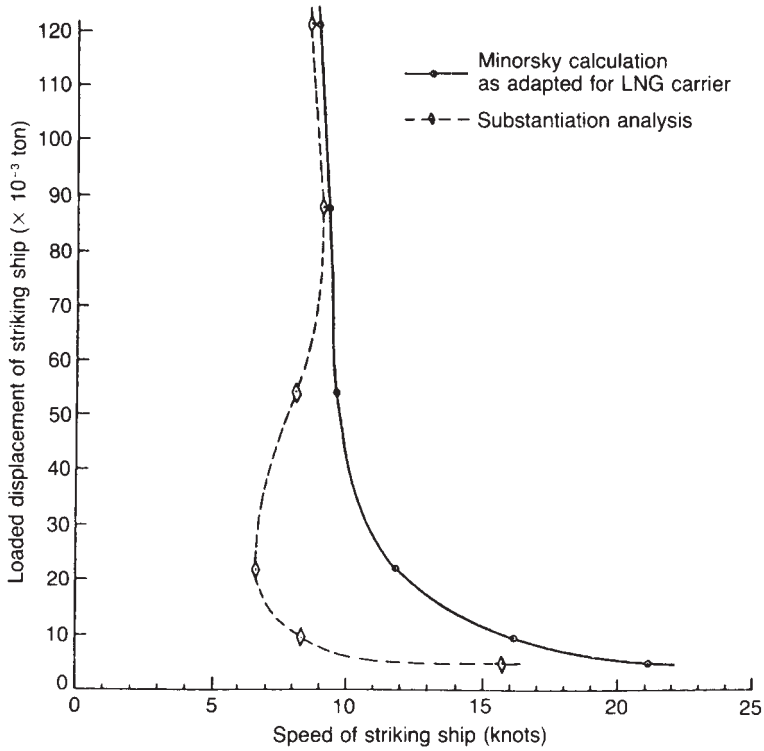


Figure 23.15 *Kinkead model of ship collision: comparison with Minorsky model for the case of a methane carrier stationary in mid-channel (Kinkead, 1978 SRD R391) (Courtesy of the UKAEA Safety and Reliability Directorate)*

Dilution with water can be effective in some cases, provided the spilled liquid is miscible with water and the pool is sufficiently well confined that addition of water does not cause it to spread.

There is available a Universal Gelling Agent which for a number of substances has been shown to be effective in forming a gel. These substances include water, gasoline and sulfuric acid. An account of this work is given by Pilie *et al.* (1975) and Baier *et al.* (1975/76) and the list of substances is quoted by R.H. Hiltz (1982). Hiltz states that although the formation of a gel may reduce the rate of evaporation, its value lies primarily in effecting immobilization of the spill. Further, the usefulness of the technique may be limited by the time taken for the gel to form. Few gels form within minutes and some take hours.

The vapour pressure of the liquid, and hence the evaporation, may be reduced by cooling the liquid surface, using ice, dry ice or liquid carbon dioxide. To be effective, this method requires good mixing of the coolant and the liquid.

One form of mechanical covers is cloth covers. Another is particulate covers such as small plastic spheres or the like. Sprays based on materials such as urethane are also sometimes classed as mechanical covers.

Films provide essentially a two-dimensional cover and foams a three-dimensional one. Surfactant films act partly by film resistance and partly by quiescence. They may be applied as a spray or in the form of a foam which rapidly collapses. There is a wide variety of foams and a good deal of work has been done to assess their suitability for the control of the evaporation of particular chemicals. Accounts include those of Baier *et al.* (1975), R.H. Hiltz and Friel (1976), Gross (1978), Norman and Dowell (1978), R.H. Hiltz (1982, 1987) and R.H. Hiltz and Brugger (1989). A matrix of foam suitability is given by R.H. Hiltz (1982). This shows high expansion surfactant foam as the best formulation for many of the substances listed, including gasoline, LNG, chlorine and ammonia.

Sorbents are used both to reduce evaporation and to remove spilled liquid. With regard to the former function, the sorbent needs to be continuously replenished. If it is simply allowed to become saturated, it may be ineffective in reducing, and, by increasing the surface area, may even promote vaporization.

23.20.5 Spill control: road transport

The control of a spill from a road tanker illustrates many of the basic principles of spill control. An account of the control of chlorine spills has been given by R.L. Mitchell (1982), with particular reference to the work in the United States of the Chlorine Institute.

The methods which he describes include: shutting off leaking valves; plugging or patching of punctures; transferring the load; and dumping the load into a pit and then neutralizing it.

A large proportion of cases involve leaking valves. The handling of a spill situation is greatly facilitated if the valves and manways are standardized. As Mitchell

describes, for the carriage of chlorine in the United States, standardization of these items has been achieved for both rail tank cars and tank trucks. The Chlorine Institute has developed a number of emergency kits which include the equipment to assist in valve shut-off.

Some measures may be taken immediately by the tanker driver such as notifying the incident, clearing the area and, if possible, creating temporary diking to divert or contain the liquid spill. Others such as load transfer or dumping and neutralization require additional equipment and/or materials and need to be undertaken by a trained team.

23.20.6 Spill control: pipelines

For pipelines spill control is treated in *Methods of Prevention, Detection and Control of Spillages in West European Oil Pipelines* (CONCAWE, 1987 1/87) and spill clean-up in *Revised Inland Oil Spill Clean-up Manual* (CONCAWE, 1981 7/81).

CONCAWE 1/87 deals with causes of spillage, which are essentially: mechanical failure, operational failure, corrosion, natural hazards and TPA; prevention by design, construction and operation; detection by visual observation monitoring of pipeline parameters; control by operational measures; and emergency procedures.

Pipeline parameters which may provide an indication of a leak, and which may be monitored for this purpose, include pressure and flow. A leak may be detected by a fall in pressure or flow, or an excursion of the volume balance. Other methods of detection are based on negative pressure waves and on ultrasonic noise. Pipeline leak detection is discussed further in Chapter 19.

Emergency procedures for dealing with a pipeline spill include: notification of the leak; actions to reduce or stop the flow; location of the leak point; and measures to stop the hole.

Spill clean-up is treated in CONCAWE 7/81 under the headings of (1) behaviour of oil spills, (2) identification of contaminated zones, (3) clean-up strategy, (4) clean-up methods for oil on ground surfaces, (5) clean-up methods for subsoil, (6) clean-up methods for ground waters, (7) clean-up methods for surface waters, (8) clean-up methods in ice and snow, (9) integrated clean-up methods and (10) emergency kits for inland oil spills.

23.21 Transport Case Histories

23.21.1 Packaging and labelling

Misidentification of chemicals can have very serious consequences. This was highlighted by the *Firemaster* tragedy in Michigan in 1973, which has been described in *Bitter Harvest, The Poisoning of Michigan* (Egginton, 1980) and by Getty, Rickert and Trapp (1977), Kay (1977) and Selikoff (1979). A consignment of *Firemaster*, a fire-retardant chemical (polybrominated biphenyl, PBB), was dispatched from the Michigan Chemical Company instead of an animal feed additive which had a rather similar name. The consequences were a serious contamination of food eaten by animals and humans throughout much of the state. Cattle showed severe symptoms of poisoning. Somewhat similar symptoms were also found among residents of the state.

23.21.2 Road transport

Some principal incidents in the road transport of hazardous materials are shown in Table 23.44. Many of these incidents are described in Chapters 16–18 on fire, explosion and toxic release or are given in the case histories in Appendix 1.

In particular, attention is drawn to: the incidents at Deer Lake in 1959 (Case History A27) and Eagle Pass, Texas, in 1975 (Case History A76) involving BLEVEs and/or fireballs; those at Berlin, New York, in 1962 (Case History A30), at Lynchburg, Virginia, in 1972 (Case History A59) and at St Amand-les-Eaux, France, in 1973 (Case History A66), involving vapour cloud explosions; and those at Lievin, France, in 1968 and Houston, Texas, in 1976 (Case History A84), involving toxic releases.

On 14 July 1978, a road tanker carrying propylene ruptured near a camp site at San Carlos de la Rapita, Spain, and there was a flash fire which resulted in an eventual death toll of some 210 people (Appendix 16).

23.21.3 Rail transport

Some principal incidents in the rail transport of hazardous materials are shown in Table 23.45. Many of these incidents are described in Chapters 16–18 on fire, explosion and toxic release or are given in the case histories in Appendix 1.

In particular, attention is drawn to: the incidents at Crescent City, Illinois, in 1970 (Case History A50), Kingman, Arizona, in 1973 (Case History A63), Belt, Montana in 1976 and Waverly, Tennessee in 1978 (Case History A93), involving BLEVEs and/or fireballs; those at East St Louis, Illinois in 1972 (Case History A57) and at Decatur, Illinois, in 1974 (Case History A71), involving vapour cloud explosions; those at La Barre, Louisiana in 1961 (Case History A29) and at Cornwall, Ontario, in 1962, at Crete, Nebraska in 1969 and at Youngstown, Florida in 1978 (Case History A94), involving toxic releases; and that at Glendora, Mississippi in 1969 (Case History A43), involving a major evacuation.

On 10 November 1979, a freight train fire occurred in a BUA of Mississauga, Toronto (Case History A97). The fire was on a tank car containing flammable liquid, but the hazard was much increased by the fact that an adjacent tank car contained chlorine. A major evacuation took place. In fact, the emergency response was effective and the incident was contained, but the incident showed the importance of segregating flammable and toxic substances, so that a fire involving the former does not put the latter at risk.

A derailment of a freight train occurred on 28 September 1982 at Livingston, Louisiana (Case History A103). Some 43 cars were derailed and there was a massive fire. A cause of the accident was the misapplication of the brakes by an unauthorized rider in the locomotive cab, a clerk who was 'substituting' for the driver. The driver was found to have consumed a large amount of alcohol shortly beforehand.

There have also been incidents in tunnels. On 20 December 1984, a train conveying 835 te of petrol derailed in the Summit Tunnel, near Todmorden, Yorkshire (A. Jones, 1985). A spill occurred and was ignited, giving rise to a fire. One tank wagon suffered a BLEVE. The fire, which reached a mean temperature of 1300°C and 1530°C in places, destroyed the train and severely damaged the 2638 m long tunnel. Columns of flame and smoke rose high above the ventilation shafts.

23.21.4 Waterway transport

Some principal incidents in the inland waterway transport of hazardous materials are shown in Table 23.46.

A collision on the Seine, below Rouen, between the two product tankers *Foyoh Maru* and *Vitoria*, in ballast after discharging a cargo of gasoline, resulted in a violent explosion on the latter killing six of the crew. The vessel itself broke in two and was completely destroyed, whilst fragments from it fell over a wide area.

Table 23.44 *Some principal incidents in the road transport of hazardous materials*

A LNG

Date	*Location*	*Incident*	*Deaths/injuries*	*Reference*[a]
1971, Jun. 25	Waterbury, VT	Blowout, leak		Davis
1971, Aug. 28	Warner, NH	Crash (SV), leak		Davis
1971, Oct. 8	N. Whitehall, WI	Crash (TV), petrol and tyre fire		Davis
1973	Junction 80/95, NJ	Crash (SV)		Davis
1973, Oct.	Raynham, MA	Crash (TV), trailer overturn		Davis
1974, Feb. 18	Hamilton Tnpk, NJ	Wheel fire, leak		Davis
1975, Nov.	Dalton, GA	Crash (SV)		Davis
1976, Jan.	Chattanooga, TN	Trailer overturn		Davis
1976, Sep. 16	Pawtucket, RI	Crash (TV), tanker o/turn		Davis
1977, Mar./Apr.	Connecticut Tnpk	Crash (TV)		Davis
1977, Jul.	Waterbury, CT	Crash (TV), trailer o/turn		Davis

B LPG

Date	*Location*	*Incident*	*Deaths/injuries*	*Reference*[a]
1943, Jan. 18	Los Angeles, CA	VCF	5d	Table A1.2
1948, Oct. 13	Sacramento, CA	Fire	2d	Table A1.2
1950, Aug.	Wray, CO	VCF	2d	Table A1.2
1958, Oct. 18	Littlebury	Fire		Davis
1962, Jul. 25	Berlin, NY	VCE	l0d, 17i	Table A1.2
1970, Nov. 12	Hudson, OH	Fire	6d	Table A1.2
1972, Mar. 9	Lynchburg, VA	Fireball	2d, 5i	Table A1.2
1972, Sep. 21	NJ Turnpike, NJ	Fire	2d, 28i	Table A1.2
1973, Feb. 1	St Amand, France	VCE	9d, 37i	Table A1.2
1974, Feb. 2	High Prairie, Alberta	Fire, explosion	1d, several i	Davis
1975, Apr. 30	Eagle Pass, TX	Fireball	17d, 34i	Table A1.2
1978, Jul. 16	Tula, Mexico	Explosion		Table A1.2
1978, Jul. 15	Xilatopic, Mexico	VCF	l00i, 220i	Table A1.2
1982, Dec. 29	Florence, Italy	Explosion	5d, 30i	Table A1.2
1990, Sep. 24	Bangkok, Thailand	VCF	68d, >100i	Table A1.2

C Other

Date	*Location*	*Incident*	*Deaths/injuries*	*Reference*[a]
1956, Aug. 7	Call, Columbia	Explosives explosion	≤1200d	Table A1.2
1968, Aug. 21	Lievin, France	Ammonia leak	5d, 20i	Table A1.2
1970, May 30	Brooklyn, NY	Oxygen leak, fire	2d, 30i	Table A1.2
1975, Dec. 14	Niagara Falls, NY	Chlorine leak	4d, 80i	Table A1.2
1976, May 11	Houston, TX	Ammonia leak	6d, 178i	Table A1.2
1976, Sep. 11	Westoning, UK	Petrol explosion	3i	Table A1.2
1978	Mexico City	Propylene fire	12d	Table A1.2
1978, Jul. 11	San Carlos, Spain	Propylene fire	216d, 200i	Table A1.2
1980, Nov. 25	Kenner, LA	Gasoline fire	7d, 6i	Table A1.2
1980, Mar. 3	Los Angeles, CA	Gasoline BLEVE	2d, 2i	Table A1.2
1982, May 3	Galdecott Tunnel, CA	Gasoline fire	7d	Table A1.2
1989, Mar. 22	Peterborough, UK	Explosives explosion	1d, 107i	Table A1.2

BLEVE, boiling liquid expanding vapour explosion; SV, single vehicle; TV, two vehicle; VCE, vapour cloud explosion; VCF, vapour cloud fire.
[a] L.N. Davis (1979).

On 30 August 1979, near Good Hope, Mississippi, the MV *Inca Tupac Yupanqui* lost steering and collided with the butane tank barge *Panama City* moored at a dock (Case History A96). The freighter's bow struck the barge amidships, cutting it in two and causing a fire and explosion which killed 12 people and did extensive damage to the dock. Half the butane barge drifted downstream and continued burning for about 24 h.

At St Louis on 2 April 1983, a four-barge tow pushed by the towboat *City of Greenville* hit a bridge, causing the breakway of three barges and an oil spill fire. The burning barges caused further fires along a 2-mile stretch of the river front. A year later on 24 April 1984, the same bridge was hit by a 12-barge tow of grain barges and a breakway of these barges resulted in a chain reaction of other barge breakaways along the waterfront until some 150 barges were adrift.

Table 23.45 *Some principal incidents in the rail transport of hazardous materials*

A LPG

Date	*Location*	*Incident*	*Deaths/injuries*	*Reference*[a]
1949, Oct.	Winthrop, MO	Fire	1d	Table A1.2
1959, Jun, 2	Deer Lake, PA	BLEVE	11d, 10i	Table A1.2
1959, Jun. 28	Meldrin, GA	VCE	23d	Table A1.2
1969, Jan. 25	Laurel, MS	BLEVE	2d, 33 + i	Table A1.2
1970, Jun. 21	Crescent City, IL	BLEVE	66i	Table A1.2
1973, Jul. 5	Kingman, AZ	BLEVE	13d,95i	Table A1.2
1973, Nov. 6	Ventura County, CA	Leak	2d, 4i	Table A1.2
1974, Feb. 12	Oneonta, NY	BLEVE	25i	Table A1.2
1975, Oct. 22	Fertile, MN	BLEVE		Davis
1976, Nov. 26	Belt, MX	BLEVE	22i	Table A1.2
1977, Jun. 2	Kent, OH	Explosion		Davis
1978, Feb. 24	Waverly,TN	BLEVE	16d, 43i	Table A1.2

B Chlorine

Date	*Location*	*Incident*	*Deaths/injuries*	*Reference*[a]
1914	Chrome, NJ	Leak	0d	Table A1.2
1934, Feb. 28	Niagara Falls, NY	Leak	0d	Table A1.2
1935, Mar. 13	Griffith, IN	Leak	0d	Table A1.2
1940, Jan. 26	Mjodalen, Norway	Leak	3d	Table A1.2
1947, Feb. 4	Chicago, IL	Leak	0d	Table A1.2
1961, Jan. 31	La Barre, LA	Leak	1d, 114i	Table A1.2
1962, Nov. 30	Cornwall, Ont.	Leak	89i	Table A1.2
1963, Apr. 28	Brandtsville, PA	Leak	0d	Table A1.2
1963, Aug. 9	Philadelphia, PA	Leak	430 + i	Table A1.2
1967, Nov. 8	Newton, AL	Leak	0d	Table A1.2
1973, Mar. 5	Loos, BC	Leak	0d	Table A1.2
1978, Feb. 26	Youngstown, FL	Leak	8d, 114i	Table A1.2
1979, Nov. 19	Mississauga, Ont.	Leak	Mass evacuation	Table A1.2
1981, Aug. 1	Montana, Mexico	Leak	17d, 280i	Table A1.2

C Other materials

Date	*Location*	*Incident*	*Deaths/injuries*	*Reference*[a]
1915, Sep. 27	Ardmore, OK	Petrol fire	40d	Table A1.2
1943, Jul. 29	Ludwigshafen, Germany	Butadiene VCE	57d, 439i	Table A1.2
1948, Jul. 23	Ludwigshafen, Germany	DME VCE	207d, 3818i	Table A1.2
1958, Jan. 22	Niagara Falls, NY	Nitromethane explosion	200i	Table A1.2
1969, Feb. 18	Crete, NE	Ammonia leak	9d, 53i	Table A1.2
1969, Sep. 11	Glendora, MS	VCM leak, VCE	1i	Table A1.2
1974, Jun. 26	Climax,TX	VCM VCE	7d	Table A1.2
1974, Jul. 19	Decatur, IL	Isobutane VCE	7d, 152i	Table A1.2
1974, Sep. 21	Houston,TX	Butadiene VCE	Id, 235i	Table A1.2
1974, Aug. 6	Wennatchee,WA	MMN explosion	2d, 113i	Table A1.2
1978, Sep. 27	Oviedo Province, Spain	Gasoline fire	7d	Table A1.2
1979, Apr. 8	Crestview, FL	HMs leak	14i	Table A1.2
1983, Nov. 2	Dhurabar, India	Kerosene explosion	47d	Table A1.2
1987, Aug. 23	Lhanzou, China	Gasoline fire	5d	Table A1.2

BLEVE, boiling liquid expanding vapour explosion; DME, dimethyl ether; HM, hazardous materials; MMN, monomethylamine nitrate; VCE, vapour cloud explosion; VCM, vinyl chloride monomer.
[a] L.N. Davis (1979).

23.21.5 Pipeline transport

There have been a number of major accidents arising from the pipeline transport of hazardous materials.

One of the worst disasters in the process industries was a pipeline accident. On 24 February 1984, petrol leaked from a pipeline passing through a shanty town at Cubatao, Brazil, forming a large liquid pool which then ignited (Case History A108). The death toll is uncertain, but is believed to have run to some hundreds.

An explosion on a natural gas pipeline at Natchitoches, Louisiana, on 4 March 1965 caused a massive split in the pipe and killed 17 people (Case History A37).

Table 23.46 *Some principal incidents in the inland waterway transport of hazardous materials*[a]

Date	*Location*	*Incident*	*Deaths/injuries*
1978, Oct. 3	Pilottown, LA	*Burmah Spar* – collision with vessel	
1979, Aug. 30	Good Hope, MS	*Panama City* – collision with vessel	12d, 25i
1980, Mar. 29	New Orleans, MS	*Exxon Baltimore* – collision with vessel	
1980, Dec. 12	New Orleans, MS	*Pisces* – collision with vessel	
1983, Apr. 2	St Louis	*City of Greenville* – collision with bridge	

[a] *Source*: NTSB *Annual Reports* 1979–84.

A leak of propane from a ruptured 8 in pipeline at Port Hudson, Missouri, on 9 December 1970, resulted in a massive vapour cloud explosion (Case History A52).

At Hearne, Texas, on 14 May 1972, a rupture on an 8 in. oil pipeline led to a flowing liquid fire (Case History A58).

A rupture of a 10 in. NGL pipeline at Austin, Texas, on 22 February 1973 resulted in the formation of a vapour cloud which ignited some 20 min later, killing six people (Case History A62).

On 13 March 1990, a gas cloud formed from a rupture of a liquid propane pipeline flowed downhill into the village of North Blenheim, New York (NTSB, 1991 PAR-91-01). The cloud ignited, flashing back to the pipeline rupture. Two people were killed.

Another major pipeline disaster occurred on 3 June 1989 at Ufa in Western Siberia (Case History A127). A leak occurred from a pipeline carrying mixed LPG near a railway line. A massive vapour cloud formed and ignited as two trains were passing. The strength of the explosion has been estimated as equivalent in the far field to 10,000 te of TNT. Initial reports put the death toll at 462, with many others severely burned.

An incident involving a vapour leak on an ammonia pipeline occurred on 6 December 1973 near McPherson, Kansas (Case History A64).

23.21.6 Marine transport

The case histories considered here may be classed as: collisions, groundings and driftings; lightning strikes, fires and explosions; and oil spillages.

On 9 November 1974, the oil/LPG carrier *Yoyo Marti* was in collision in Tokyo Bay with the cargo ship *Pacific Ares*. A 24 m gash was cut in the *Yoyo Maru's* hull and naphtha spilled out and ignited, giving a fire with flames 70 m high. The vessel also had LPG in other cargo tanks, but the LPG tanks and fittings withstood the fire, although LPG from the tank vents burned. Firefighting vessels were for some time unable to approach close due to the heat. The vessel was towed out to sea, where it continued to burn and was eventually sunk by air strikes. The death toll was 33.

In some cases, collisions occur while the vessels are proceeding at full speed. On 9 February 1982, off North Carolina, the barge carrier *Lash Atlantico* and the freighter *Hellenic Carrier* were in collision in thick fog as both vessels were at full speed. There were no injuries, but both vessels were badly damaged, the latter beyond repair. Ten days later, the barge carrier *Del Norte* and the freighter *African Pioneer* collided in the Gulf of Mexico, again both moving at full speed in thick fog. This time there were two serious injuries and again both ships were severely damaged.

On 21 August 1980, the tanker *Texaco North Dakota* travelling at full speed struck a partially constructed oil platform in the Gulf of Mexico (NTSB, 1981 MAR-81-04). The tanker was partly loaded with petroleum products, several cargo tanks were ruptured and fire broke out which gutted the vessel.

On 6 March 1982, the tankship *Golden Dolphin* exploded, burned and sank in the Atlantic 1000 miles to the southeast of Bermuda (NTSB, 1983 MAR-83–07). The vessel was in ballast and an empty cargo tank was being cleaned when a series of massive explosions occurred. An inert gas system had just been fitted but was not in use. The crew abandoned ship but nine died.

On 27 February 1984, in the Gulf of Mexico, the tanker *American Eagle* was wracked by an explosion and broke up (NTSB, 1985 MAR-85-06). Three crew died in the explosion, and two more died later and two were missing in the sinking.

Some shipboard fires and explosions are caused by lightning strikes. On 19 April 1979, the tankship *Seatiger* was hit by lightning while unloading oil at Port Neches, Texas (NTSB, 1980 MAR-80–12). Most of the cargo tanks exploded and the ship was destroyed. A similar explosion occurred on 1 September 1979 at Deer Park, Texas, when the tankship *Chevron Hawaii* exploded while unloading oil at a refinery (NTSB, 1980 MAR-80–18). Lightning ignited flammable cargo vapours on deck which propagated into an empty cargo tank, where the explosion occurred. Amongst the many fragments was a 15 m × 2.1 m section of hull which penetrated an onshore ethanol tank 250 m away. Burning cargo spread across the water and ignited the contents of three petroleum barges, which exploded and sank. Casualties are variously given as 3 or 4 killed and 9–13 injured.

Incidents of fires and explosions on chemical tankers with special reference to ignition in cargo tanks due to static electricity have been given by Jones and Bond (1984).

Some of the worst disasters due to chemicals have been shipboard explosions of ammonium nitrate. On 16 April 1947, a fire broke out on an ammonium nitrate vessel, the *Grandcamp*, in Texas City Harbor (Case History A16). After about an hour, the ship disintegrated with a tremendous explosion, killing all those in the dock. Fire spread to another vessel, the *High Flyer*, which also carried ammonium nitrate, and during the night this vessel too exploded. There were 552 deaths and over 3000 injuries.

On 8 January 1979, a large explosion and fireball occurred on board the *Betelgeuse* which was unloading at an oil terminal at Whiddy Island, Bantry Bay, Eire (Case History A95). All 42 members of the crew were killed as well as a crewman's wife and seven terminal operators.

Further case histories of fire and explosion on vessels in port are given by Rushbrook (1979) and by Dicker and Ramsey (1983).

Large-scale oil spills are a major threat to the environment. Major oil spills are those from the *Torrey Canyon* in 1967, the *Amoco Cadiz* in 1978, the *Exxon Valdez* in 1989 and the *Braer* in 1993. Further details are given in Appendix 11.

23.21.7 Marine transport: LPG

Some principal incidents to LFG carriers are given in Table 23.47. An account of incidents involving LNG carriers has been given by Lakey and Thomas (1983). L.N. Davis (1979) describes incidents with both LNG and LPG vessels.

On 29 June 1979, the LNG carrier *El Paso Paul Kayser* ran aground at Gibraltar. The bottom plating on the starboard side was ripped open but, although deformed, the Gaz Transport containment system, including both the primary and secondary containment barriers, remained liquid tight.

Another grounding of an LNG tanker occurred on 12 December 1980 when the *LNG Taurus* ran aground at Mutsure Anchorage, near Tobata, Japan. The initial damage in this case was less, but was aggravated during 4 days aground.

Worse damage than in either of these cases was sustained by the *El Paso Columbia* when it grounded on 16 December 1981 near Cape Sable in Nova Scotia. The engine room and, apparently, one cargo tank were flooded, but the vessel was in ballast.

In the autumn of 1968, the LPG carrier *Claude* collided with another vessel in Southampton Water. The crew abandoned ship and the vessel drifted until it ran aground. Another ship was chartered to remove the cargo of butane, but backed off when one of the unloading hoses sprang a leak, giving a vapour cloud. The leak was stopped by other boarders.

There have been a number of spills of LNG on the decks of LNG carriers. In 1965, fracture of the mild steel deck of the *Methane Princess* occurred due to a small LNG spill. In the same year, at Arzew another LNG carrier, the *Descartes*, also suffered deck fracture from an LNG overfilling.

LNG carriers have also experienced cargo tank rupture. On 17 November 1969, rupture of a cargo tank occurred on the *Polar Alaska* due to violent sloshing of the LNG liquid. In 1970, the LNG carrier *Arctic Tokyo* suffered cracking of a cargo tank due to sloshing.

On 30 June 1974, there was a pump room explosion and fire aboard the semi-refrigerated LPG carrier *MiUi* as she began unloading butylene at Grangemouth. A butylene vapour cloud estimated at 50 te spread around the area near the ship. The captain, who was in the pump room, died.

There have been several lightning strikes followed by fires on LNG carriers. On 25 December 1964, this occurred to the *Methane Progress* just after loading at Arzew. The next year the same ship again suffered a lightning strike and fire. In 1977, the *LNG Aquarius* unloading at Tobata, Japan, was struck by lightning followed by fire. Lightning strike and fire have also been experienced by the LNG carrier *Jules Verne*.

On 12 October 1984, the LPG tanker *Gas Fountain*, originally the *Gay Lussac*, was attacked by an Iranian aircraft in the Gulf. Three rockets hit the vessel. The crew abandoned ship and were rescued. One rocket caused a rupture of the pipework of No. 2 tank; propane escaped and caught fire. A second rocket penetrated the deck into the containment space of No. 3 tank and exploded near the cargo tank, creating a hole some 3 m × 2 m. Butane escaped and ignited giving a large fire on deck. It is estimated that some 130 te of butane may have escaped during this initial depressurization. The next day, a salvage vessel arrived, extinguished the fires using water jets, and took the vessel in tow. Extensive repairs were carried out. About a month later, most of the LPG cargo, some 17,200 of the original 18,400 te, was transferred to another vessel. An account of this salvage is given by J.A. Carter (1986).

23.22 Transport Risk

23.22.1 Historical record

The risks from the process industries arise from processes, storage and transport. The historical record shows that transport is a major contributor. Transport figures prominently in the case histories given in Appendix 1 and elsewhere in this book. An attempt to quantify the contribution made by transport to the overall risks from the process industries is given below.

23.22.2 Hazard assessment

Another approach to the estimation of the risk from transport is hazard assessment. A major hazard assessment exercise for transport is the ACDS *Transport Hazards Report*, which is described in Appendix 17. An account is given below of hazard assessments of transport by the principal modes of road, rail, ship and pipeline for the principal hazardous substances of LNG, LPG, chlorine and ammonia.

23.22.3 Fixed installations vs transport

A study of the relative risks from fixed installations and transport by road, rail, pipeline and waterway and sea has been made by Haastrup and Brockhoff (1990). They identified in the literature 1793 accidents in both fixed installations and transport. The breakdown of the accidents was as follows:

	No. of accidents	*No. of accidents with fatalities*
Fixed installations	998 (56%)	454 (67%)
Loading/unloading	104 (6%)	47 (7%)
Transport	691 (39%)	181 (27%)
Total	1793	682

and for the transport modes

	No. of accidents	*No. of accidents with fatalities*
Road	205 (30%)	54 (30%)
Rail	257 (37%)	41 (23%)
Pipeline	133 (19%)	56 (31%)
Inland waterway	38 (5%)	4 (2%)
Marine	58 (8%)	26 (14%)
Total	691	181

The authors quote the analysis of transport accidents in the Major Hazards Incidents Data Service (MHIDAS) database made by Appleton (1988 SRD R474), who found that 17% involved road, 36% rail and 21% pipelines.

The authors selected for study accidents occurring after 1959, which gave a total of 510 accidents with fatalities. They present a set of frequency-number curves, including one showing an overall worldwide curve for fixed installations and a corresponding curve for all transport modes. The transport curve lies somewhat above that for fixed installations, but for accidents with the number of fatalities exceeding four there was found to be no statistically significant difference between the two curves. Another of the graphs gives a set of separate curves for worldwide transport by road, rail and pipeline. The three curves lie very close to each other.

Table 23.47 *Some principal incidents to LPG carriers*

A Groundings, standings, driftings

Date	*Location*	*Vessel*	*Cargo*	*References*[a]
1966, May 1	Thames	*Methane Progress*	LNG	Cox
1968, Sep.	Mexico	*Aristotle*	LNG	
1974, Apr. 19	Arzew, Algeria	*Methane Progress*	LNG	Cox
1974, Oct. 28	Rhone Delta, France	*Hassi R'Mel*	LNG	Cox
1974, Nov.	Le Havre, France	*Euclides*	LNG	Davis
1978, Jan. 11	Canvey, UK	*LNG Aries*	LNG	Davis
1979, Sep. 30	Takari Bay, Lagos, Nigeria	*Babounis Costas*	LPG	Lakey
1980, Dec. 12	Mutsure Anchorage, Tobata, Japan	*LNG Taurus*	LNG	Lakey
1981, Dec. 16	Cape Sable Island Nova Scotia	*El Paso Columbia*	LNG	Lakey

B Collisions, rammings, impacts

Date	*Location*	*Vessel*	*Cargo*	*References*[a]
		Methane Princess	LNG	Cox
1968, Autumn	Southampton, UK	*Claude*	LPG	Davis
1968, Sep. 12	Flushing, Belgium	*Havfrost*	LPG	Harris[b]
1968, Dec. or 1969, Jan.)	Canvey, UK	*Methane Princess*	LNG	Davis
1969, Feb. 10		*Methane Princess*	LNG	Cox
1969, Feb. 25	Straits of Malacca	*Gohshu Maru*	LPG	Harris
1970, Oct. 19		*Methane Progress*	LNG	Cox
1970, Oct. 21	Konigsforde, W. Germany	*Mariotte*	LPG	Harris
1971, Jun. 17	Tokyo Bay, Japan	*Gohshu Maru*	LPG	Harris
1972, Jul. 21	Heroya, Norway	*Monomer Venture*	LPG	Harris
1973, Jan. 14	Bilbao, Spain	*Alexander Hamilton*	LPG	Harris
1973, Mar. 28	Straits of Malacca	*World Bridgestone*	LPG	Harris
1973, Dec. 16	Ras Tanura, Saudi Arabia	*Beava*	LPG	Harris, Lakey
1974, Aug.	Terneuzen, Belgium	*Euclides*	LNG	Davis
1974, Nov. 9	Tokyo, Japan	*Yoyo Maru*	LPG	Davis, Harris, Lakey
1974, Dec. 6	London, UK	*Methane Progress*	LNG	Cox
1975, Jun. 9	Buenos Aires, Brazil	*Gazana*	LPG	Harris
1975, Jul. 14	Pentland Firth, UK	*M.P. Grace*	LPG	Harris
1977, Jun. 7	Bahrain	*LNG Challenger* and *Lincolnshire*	LNG	Davis
1978, Aug. 14	Singapore	*Khannur*	LNG	Davis
1978, Aug. 26	Bahrain	*LNG Challenger*	LNG	Davis
1978, Oct. 29	Suez Canal	*Lord Kelvin*	LPG	Harris
1980, Jan. 30	Singapore	*Pine Queen*	LPG	Harris
1980, Feb. 19	Porto Marghera, Italy	*Gazana*	LPG	Harris
1982, Jan. 24	Curacao	*Faraday*	LPG	Harris
1982, Apr. 28	Cristobal, Panama	*Luigi Casala*	LPG	Harris
1983, Apr. 3	Tampico, Mexico	*Reynosa*	LPG	Harris
1983, Aug. 3	Yugecho, Japan	*Kazutama Maru*	LPG	Harris
1985, Apr. 11	Choshi, Japan	*Berge Arrow*	LPG	Harris
1985, May 31	Coatzacoalcos	*Mariano Escobedo*	LPG	Harris

C Leaks

Date	*Location*	*Vessel*	*Cargo*	*References*[a]
1965		*Methane Princess*	LNG	Lakey
1965, May		*Jules Verne*	LNG	Lakey
1969, Nov. 19		*Polar Alaska*	LNG	Cox
1974, Dec.		*Jules Verne*	LNG	Cox
1975, May 1		*Methane Progress*	LNG	Cox

Table 23.7 *(continued)*

1976, Dec. 20	Kenai	*Polar Alaska*	LNG	Cox
1977, May 14	Chiba, Japan	*HUH*	LNG	Cox
1977, Sep. 16	Bontang	*LNG Aquarius*	LNG	Lakey
1979, Apr. 8	Cove Pt, MD	*Mostafa Ben Boulaid*	LNG	Lakey
1979, Apr. 25	Everett, MA.	*Pollenger*	LNG	Lakey
1981, Jul. 31	Sines, Portugal	*Olav Trygvason*	LNG	Lakey
Voyage 2		*Descartes*	LNG	Cox

D Lightning strike and fire

Date	*Location*	*Vessel*	*Cargo*	*References*[a]
1964, Dec. 25		*Methane Progress*	LNG	Lakey
1965	Nr Arzew, Algeria	*Methane Progress*	LNG	Lakey
1977, Sep. 3	Tobata, Japan	*LNG Aquarius*	LNG	Lakey
Unknown		*Jules Verne*	LNG	Lakey

E Other incidents

Date	*Location*	*Vessel*	*Cargo*	*References*[a]
1964 Small fire		*Methane Princess*	LNG	Cox
1966, Aug. 30 Small fire		*Methane Princess*	LNG	Cox
1971, Sep. 14 Weather damage to tank		*Arctic Tokyo*	LNG	Cox
1974, Jun. Pump room explosion	Grangemouth, UK	*Milli*	LPG	Davis Lakey
1974, Jul. 7 Valve overpressurized, canopy cracked		*Massachusetts*	LNG	Cox
1976, Dec. 1 Broke moorings	Marseilles, France	*Benjamin Franklin*	LNG	Cox
1978, Oct. 10 Pump fire	Donges, France	*Danian Gas*	LPG	Lakey
Voyage 2 Overfilling, deck brittle fracture		*Jules Verne*	LNG	Cox

[a] R.A Cox, Comer *et al.* (1980); LN. Davis (1979); F.S. Harris (1986); Lakey and Thomas (1983).
[b] LPG vessels in incidents quoted by Harris were all refrigerated carriers.

Some major transport accidents include the ammonium nitrate explosions at Halifax, Nova Scotia, in 1917 and at Texas City in 1947, the road tanker fire at San Carlos in 1978, the pipeline rupture and fire at Cubatao in 1984 and the pipeline rupture and explosion at Ufa in 1989.

23.23 Transport Hazard Assessment

The hazards of transport tend to differ from those of fixed installations, whether process or storage, in a number of ways.

Disregarding pipelines for the moment, transport is characterized by the large amount of energy in the vehicles and vessels, both those carrying the hazardous materials and others. The order of increasing energy is road, rail and marine.

Another difference is the transport environment, which is much less subject to control by management. A transport vehicle or vessel is exposed to a variety of external threats to an extent that the situation is qualitatively different from that on fixed plant.

A third difference is in the variety of locations where an accident may occur and in the population exposed to any incident.

These last two points also apply to some degree to pipelines, but these are fixed installations and tend to have more in common with other fixed installations in the process industries.

The differences between transport and fixed installations are reflected in the hazard assessments. In the hazard assessment of transport, the characteristic features tend to be the incident scenarios, the associated frequency estimates and the population models. By contrast, the hazard models used to determine consequences are generally those developed for fixed installations, although there are some special cases such models for explosions in ship cargo holds or for events in tunnels.

As already mentioned, the most comprehensive hazard assessment for transport is the ACDS *Transport Hazards Report*, which is described in detail in Appendix 17. This deals with the risks from transport by road, rail and sea, though not by pipeline, for the set of four study substances motor spirit, LPG, chlorine and ammonia and also for explosives.

Some other hazard assessments of transport are now described.

23.24 Road Transport Hazard Assessment

The road transport environment has been described in Section 23.6. The account given there includes estimates made in the ACDS report of the frequency of release for the four study substances. The substance which has been most intensively studied is chlorine. Accounts of studies on the risks of chlorine transport include those of Westbrook (1974), Lautkaski and Fieandt (1980) and Canadine and Purdy (1989).

The work of Westbrook (1974) has been described in detail in Chapter 18. In this early study of chlorine transport in the United Kingdom, the author used data for road tankers generally and obtained the following estimate, which he then applied to chlorine tankers also:

$$\text{Frequency of accidents} = 0.63 \times 10^{-6}/\text{tanker-km}$$

The reference distance is for loaded journeys only. Westbrook then assumed that all tanker accidents are potentially

spillage accidents. This approach is, therefore, very conservative.

Lautkaski and Fieandt (1980) in a study of the road and rail transport of hazardous materials in Finland made the following estimate for road tankers generally:

Frequency of releases $= 2 \times 10^{-8}$/tanker-km

It is unclear whether the reference distance is for loaded and unloaded journeys or for loaded journeys only. They state that some 15% of releases are due to valve failures and 85% to road accidents.

Canadine and Purdy (1989) describe a hazard assessment of the rail and road transport of chlorine. This study, which is evidently part of the background work preceding the ACDS report, does not explicitly quote release frequencies, although it does give some figures for societal risk. It does, however, provide insight into the factors bearing on a hazard assessment for chlorine road transport.

The principal producer of chlorine in the Unites Kingdom is ICI. The company has some 19 road tankers with payloads of 15–21 te. Over a 60-year period, there have been three leaks. Two were due to incompletely closed valves and were quickly rectified and the third was minor.

The frequency with which these tankers are involved in accidents is significantly lower than for commercial transport generally. The vehicles are fitted with various arrangements to reduce the accident rate, such as high quality suspension, anti-skid devices, anti-jack-knife systems, fuel cut-off devices, additional fire protection, and regular lights and fog lights. The tankers have their liquid and vapour valves protected in a recessed valve chest at the front of the vehicle. They have excess flow valves, and the two latest vehicles also have remotely operated shut-off valves.

Since 1976, the company has taken additional measures to reduce the consequences of any collision. Additional rear and side protection has been fitted to resist penetration, absorb energy and spread the load in the case of collision. The value of these measures was illustrated in 1985 when the most serious accident recorded to date occurred. A chlorine tanker was hit by a 38 te articulated lorry travelling at an estimated 60 mph down a hill near Baslow in Derbyshire. The vehicle veered diagonally across the road and hit the chlorine tanker on its front offside, stopping it dead and driving it sideways across the road. The side protection on the tanker absorbed most of the collision energy and spread the load as it was designed to do; there was no leak.

As described in Section 23.6, the ACDS report gives estimates for the road transport of chlorine which distinguish between releases due to punctures and those due to equipment failure. The frequency of the latter is expressed as releases per journey, but using the average journey length quoted, the following estimates for releases from chlorine tankers are obtained

Frequency of release due to puncture

$= 0.008 \times 10^{-8}$/tanker-km

Frequency of release due to equipment failure

$= 0.003 \times 10^{8}$/tanker-km

Frequency of release $= 0.011 \times 10^{-8}$/tanker-km

The reference distance is for loaded journeys.

23.25 Rail Transport Hazard Assessment

The rail transport environment has been described in Section 23.8. The account given there includes estimates made in the ACDS report of the frequency of release for the four study substances.

As for road transport, the substance which has been most intensively studied is chlorine. Accounts of studies on the risks of chlorine transport include those of Westbrook (1974), Lautkaski and Fieandt (1980), N.C. Harris and Roodbol (1985), Purdy *et al.* (1988) and Canadine and Purdy (1989).

The early study of Westbrook (1974), described in Chapter 18, on chlorine transport in the United Kingdom, used data for freight trains generally combined with a train model for the probability of a release given an accident and obtained for chlorine tank wagons the following estimates:

Frequency of accidents $= 1.18 \times 10^{-6}$/train-km

Probability of release $= 0.041$

Hence

Frequency of release $= 4.8 \times 10^{-8}$/train-kmn or

for an average of 4 tank-wagons per train

Frequency of release $= 1.2 \times 10^{-8}$/tank-wagon-km

The reference distance is for loaded journeys only.

In their study for Finland, Lautkaski and Fieandt (1980) made the following estimates for rail tankers generally:

Frequency of releases $= 0.41 \times 10^{-8}$/tank-wagon-km

The reference distance is unclear. This figure excludes releases due to valve failure, which the authors state amounts in the case of rail transport to 99.5% of all releases. They also say that the additional protective features of chlorine tank wagons were considered, but do not state what allowance, if any, was made for them.

N.C. Harris and Roodbol (1985) describe a hazard assessment of the rail transport of chlorine for the Netherlands. The accident and release estimates which they quote include the following values:

Country	*Event frequency*		
	Accident (train-km)	*Minor release* (tank-wagon-km)	*Major release* (tank-wagon-km)
UK	0.35×10^{-6}	1×10^{-8}	
Netherlands	0.88×10^{-6}	1×10^{-8}	0.1×10^{-8}
USA	6×10^{-6}	6×10^{-8}	1.5×10^{-8}

The reference distance is unclear.

Purdy *et al.* (1988) describe the hazard assessment of chlorine rail transport. This study, which is evidently part of the background work preceding the ACDS report, resembles the treatment given in the latter and is not therefore considered further here.

Another precursor to the ACDS report, the work of Canadine and Purdy (1989), deals with rail as well as road transport of chlorine. As for the road study, figures are given for societal risk though not for release frequency, but the account provides insight into the relevant factors.

The principal chlorine producer, ICI, operates some 40 braked tank wagons which take a 28 te load. This contrasts with the fleet of about 300 unbraked tank wagons of 14 te capacity in the 1950s. The company has never experienced puncture of a chlorine rail tank wagon or a major release.

The older type of tank wagon was involved in some major collisions, including one in which a loaded wagon travelling at 60 mph demolished a signal box, though it did not leak. Since the introduction of the larger wagons, accidents have been limited to minor derailments and collisions in marshalling yards.

The modern wagons have a number of safety features. They are fitted with top mounted needle valves, each with an internal excess flow valve, and protected with a heavily reinforced low profile dome. They are provided with buffer override protection consisting of a reinforced hollow steel section mounted below the buffers across the width of the tank.

As described in Section 23.8, the ACDS report gives estimates for rail transport of chlorine which distinguish between releases due to punctures and those due to equipment failure. The frequency of the latter is expressed as release per journey, but using the average journey length quoted, the following estimates for releases from chlorine tank wagons are obtained:

Frequency of release due to puncture
$= 0.09 \times 10^{-8}$/tank-wagon-km

Frequency of release due to equipment failure
$= 0.02 \times 10^{-8}$/tank-wagon-km

Frequency of release $= 0.11 \times 10^{-8}$/tank-wagon-km

The reference distance is for loaded journeys.

23.26 Tunnel Transport Hazard Assessment

Studies of road tunnel hazards include those of the Larson, Reese and Wilmot (1983) and Considine (1986), and several others referenced by the latter.

In the study by Considine (1986), the two principal events considered are spills and fires. For the estimation of the frequency of these events, the approach adopted was to extrapolate from open route data, the information on incidents in tunnels being inadequate. The author's estimates for road tankers are as follows:

Frequency of spills from tankers $= 5 \times 10^{-8}$/tanker-km

Frequency of fires on tankers $= 1 \times 10^{-8}$/tanker-km

He states that for vehicles carrying packages, the frequency of spills is about twice, and that of fires about half, the above figures. Many package spills occur when the package falls off the vehicle.

Events in tunnels may be initiated by a leak from a container, an explosion in a container, a fire of the load or an explosion of the load. The scenarios considered are fire, explosions (physical, condensed phase and vapour cloud) and toxic release.

The hazard models used to predict the consequences are for the most part adaptations of those developed for events in the open. For pool spread, a two-dimensional adaptation of the SPILL code was utilized. Gas dispersion is dominated by the tunnel ventilation. For heavy gas dispersion, use was made of a two-dimensional adaptation of the DENZ and CRUNCH codes for instantaneous and continuous releases, respectively, with the cloud advected at the ventilation velocity. For physical explosion the code GASEX was used. For condensed phase explosions, empirical correlations given in Christopherson (1946) were used to predict overpressure and impulse as a function of charge size, tunnel cross-section and distance. For vapour cloud deflagration, a simple combustion model was used based on a constant flame velocity and shock velocity, followed on completion of combustion by transition to a one-dimensional fluid flow code.

Four tunnels were studied. The data given include the following:

	Tunnel 1	*Tunnel 2*	*Tunnel 3*	*Tunnel 4*
Length (m)	1030	1483	1436	650
No. of tubes/lanes per tube	2/2	1/2	1/2	2/3
Lane width (m)	3.65	2.41	3.65	3.65
Headroom (m)	5.1	4.72	5.03	5.1
Ventilation system	Longitudinal	Semi-transverse	Semi-transverse plus section of longitudinal	Longitudinal
Construction	Submerged section	Driven tube	Driven tube	Cut and cover

An explosion may cause damage to the tunnel. In general, experiments indicate that damage in a large tunnel correlates better with mean overpressure than with transient peak overpressures. For the condensed phase explosions, peak overpressures were high, but the serious structural failures predicted were limited to two tunnels. These failures were of the roof and median wall in Tunnel 4 and of the road support in Tunnel 3 and were confined to a few tens of metres. The effects did not worsen dramatically for increasing charge sizes. The most damaging event was found to be deflagration of a vapour cloud filling the whole cross-section along an appreciable length. The effects obtained were comparable with those of a TNT explosion, but with a longer section sustaining damage. For injury from explosions, use was made of the injury relations given by Eisenberg, Lynch and Breeding (1975) and by W.E. Baker *et al.* (1979).

A fire in a tunnel differs in its effects from one in the open in that the flames, hot gas and smoke are confined and are thus much more lethal. Persons exposed are principally other road users and the general public.

The results of the hazard assessment included the following findings. The risks are mainly to other road users, those to the general public being typically an order of magnitude less. The dominant contributor (>70%) to these risks is flammable liquids.

At the lower end of the spectrum ($N > 1$ and $N > 10$), the factor mainly determining the societal risks to road users is traffic density rather than tunnel design. In this region, the risks are remarkably similar to those on the open road. The effect of tunnel design is seen, however, at the upper end of the spectrum ($N > 100$). This is illustrated by the following values of the ratio of the frequency for $N > 100$ to that for $N > 1$:

Tunnel 1	0.27
Tunnel 2	0.39
Tunnel 3	0.28
Tunnel 4	0.03

The low ratio for Tunnel 4 reflects the fact that it has a short length and a large cross-section, and the high value for Tunnel 2 reflects the fact that it carries two-way traffic and a small cross-section.

23.27 Pipeline Transport Hazard Assessment

A hazard assessment of a hydrocarbon pipeline is described in *A Safety Evaluation of the Proposed St. Fergus to Moss Morran Natural Gas Liquids and St. Fergus to Boddam Gas Pipelines* (HSE, 1978d).

The proposed natural gas liquids (NGLs) pipeline would run for approximately 200 km from St Fergus to Moss Morran. The pipe would be 16 in. (406 mm) diameter and would operate at a maximum pressure of 1000 psig (70 bar) and a minimum pressure of 246 psig (18 bar) with a typical fluid temperature of 10°C. The pipeline would transport up to 110,000 bbl/d (approximately 100 kg/s). The composition of the NGL would vary between summer and winter conditions. For the former, the NGL would contain approximately 50% ethane and 30% propane.

The failure rates of comparable pipelines and the factors influencing such failures are discussed in detail. The data considered include those of the US petroleum pipeline system, the European petroleum pipeline system and the UK gas transmission system, which have been described above. The report presents additional data on the UK petroleum pipeline system and on the UK gas transmission system.

The oil company pipeline system in the United Kingdom is only approximately 1500 miles long. In the period 1963–76, some 17 accidents were recorded. It was concluded that this is too small a number on which to base an estimate.

The data for the European petroleum pipeline system (CONCAWE, 1977 9/77) were analysed. Many of the types of incident recorded were considered inapplicable to the proposed pipeline. On the basis of applicable incidents, the incident rate of the pipelines was 2.32×10^{-4}/km year.

The data for the UK gas pipeline system were provided by the BGC. The applicable incident rate of the pipelines was again 2.32×10^{-4}/km year. This value was based on 31 faults. The distribution of rupture sizes of these faults was:

Equivalent diameter (mm)	*No. of faults*
>80	1 (3%)
20–80	3 (10%)
<20	27 (87%)

The hole sizes considered in the assessment were 80 and 20 mm equivalent diameters in the proportions 10% and 90%, respectively.

The emission rates from a rupture of the NGL pipeline were estimated as follows. Small orifices through which the maximum rate of emission as liquid would be less than 100 kg/s, the approximate maximum pump delivery rate, would release NGL as liquid. Orifices which could deliver more than 100 kg/s would give an initial liquid flow, followed by choked two-phase flow as the pressure fell locally to the saturated vapour pressure. At this lower flow the pressure would rise again and reversion to liquid flow would occur. There would follow an oscillation between liquid flow and two-phase flow. It was assumed for simplicity that the flow through this intermediate size of orifice would be 100 kg/s. The largest orifices would be able to deliver 100 kg/s or more with two-phase flow. For this latter case, the flow under two-phase discharge was calculated as the geometric mean of the flows of pure liquid and pure gas. The flows calculated for the 20 and 80 mm holes were 15.2 and 100 kg/s, respectively.

These estimates were made for the first 5 min after the rupture. It was assumed that after this time, the pumps would be shut off. The conditions after 5 min were not investigated, since it was considered that the leak would probably reach a critical phase in respect of ignition in less than 5 min.

The dispersion of the gas cloud from the pipeline was calculated assuming a neutral buoyancy gas and using the Pasquill equations. The effect of possible heavy gas behaviour was considered, but it was concluded that at the existing state of knowledge, it is not unreasonable to assume that the increased entrainment of air approximately compensates for the slumping effect.

The heat radiated from a flame ignited at the pipeline was calculated by the methods given in API RP 521: 1969. The three heat radiation levels considered were 1, 8 and 16 kW/m^2. These were chosen because they are, respectively, the level which is just tolerable to a clothed person, that which would result in death within minutes unless adequate shelter were found and that which causes spontaneous ignition of wood. Some of the data given in the report for these hazards are shown in Table 23.48.

The frequency of 'interactions' between the pipeline and the exposed populations was assessed. The most exposed population group considered was that at Glenfarg, which is 250 m from the pipeline. For this population the frequency of interaction for all releases up to 100 kg/s was

Table 23.48 *Hazards from the rupture of an NGL pipeline (Health and Safety Executive, 1978d) (Courtesy of the Health and Safety Executive)*

A Thermal radiation from burning vapours – distance from flame centre (m)

Release rate (kg/s)	*Radiation level* (kW/m^2)		
	1	8	16
20	128	45	32
100	282	100	70
250	450	160	112
1000	892	315	223

estimated as 4.4×10^{-5}/year. A further account of the approach taken in this work has been given by Bryce and Turner (1979).

Following a proposal to increase the diameter of this pipeline from 16 in. (406 mm) to 24 in. (610 mm), a reappraisal of the risks was undertaken (HSE, 1980c). Essentially the same methodology and data were used. The assessment found that the frequency of interactions remained highest for the population, at Glenfarg. For this population, the frequency of interactions for releases of 242 kg/s was estimated as 4×10^{-6}/year.

An treatment of the hazard assessment of pipelines from a broader perspective has been given by M.J. Turner (1980).

The hazard assessment of the British Gas pipeline in Morecambe Bay has been described by Considine (1983). The pipeline connects the offshore platform to the onshore terminal. It consists of a line about 40 km long and 36 in. diameter containing some 1774 te of gas and 612 te of liquid.

Scenarios for failure of the pipeline both on land and under water were considered. For the latter, there was uncertainty as to how the fluids released, particularly the liquid components, would behave. For the case of immediate ignition of the release, two scenarios were considered, one in which the release burns as a torch and the other in which it burns as a liquid pool on the surface with the gas confined to the area of the pool. For the case where the release does not ignite immediately, a gas cloud forms and drifts with the wind.

Consideration was also given to interaction with a passing ship. For this, three cases were envisaged: (1) the gas cloud drifts towards the vessel; (2) the vessel sails through the cloud; and (3) the vessel itself causes the release in some way such as by grounding or dragging its anchor.

23.28 Marine Transport Hazard Assessment

The mid-1970s saw a growing public awareness of the hazards from process installations and one manifestation of this was concern over ports and terminals, and the associated traffic, and in particular LNG terminals.

The USCG initiated an extensive programme of work on the hazards of ships carrying hazardous materials. One outcome was the vulnerability model developed by Eisenberg, Lynch and Breeding (1975) and their co-workers, which is described in Chapter 9. Other work performed or sponsored by the USCG and other bodies includes that of Fortson *et al.* (1973), Woodward-Lundgren and Associates (1973), Dunn and Tullier (1974), A.D. Little INC. (1974b), the National Materials Advisory Board (1974), Frenkel and Hathaway (1976), Stoehr *et al.* (1977) and the Planning Research Corp. (1979).

A scenario of particular concern was the spillage onto the sea of a large quantity of flammable liquid such as LNG or LPG. In the worst case, such a spill could be massive and could be expected to spread and to vaporize rapidly, giving rise to a very large vapour cloud. There were similar concerns over liquefied toxic gases, particularly ammonia.

Treatments of, and models for, the spill hazard were described by Burgess, Murphy and Zabetakis (1970 BM RI 7448), McQueen W. *et al.* (1972), Fay (1973), Kneebone and Boyle (1973), Kneebone and Prew (1974), Drake and Reid (1977) and Hogan (1982). This hazard also figures strongly in the Vulnerability model.

The frequency of realization of such hazards, particularly that of collision, was dealt with in other studies such as those by Horner (1974), Horner and Ecosystems Inc. (1974), Kahn, Talbot and Woodward (1974) and Ligthart (1980).

At the same time, studies were undertaken on particular projects, or project proposals, such as those for Staten Island, Los Angeles, Oxnard, Point Conception, Everett and Matagordo Bay. Studies include those by the Federal Power Commission (1974, 1976, 1977), Philipson (1974, 1980), Gratt and McGrath (1975a,b, 1976), Philipson and Schaefer (1975), Socio-Economic Systems (1977) and Nikodem (1978, 1980).

Accounts of the methodologies used in such work have been given by Philipson and Schaefer (1975), Kopecek (1977), Philipson (1978a,b, 1980), R.A. Cox, Comer *et al.* (1980), Lyon, Pyman and Slater (1982) and Philipson and Napadensky (1982).

More recent accounts of hazard assessments of particular terminals include those for Canvey (British Gas) by Lucas, Roe and Waterlow (1983), Horn *et al.* (1974) and Dale and Croce (1985), Mossmorran (Shell) by Sellers, Luck and Pantony (1985), St Fergus (British Gas) by Valk and Sylvester-Evans (1985), and an assessment by Bello, Romano and Dosi (1983).

Treatments of oil as opposed to LNG terminals are much less numerous. An example is that given by Bergmann and Riegel (1983) for the oil terminal at Galveston.

Aldwinkle and Slater (1983) have described the hazard assessment of a novel project, a process and storage ship (PASS).

More recent accounts of methodology include those of Valckenaers (1983), Valk and Sylvester-Evans (1985), Sellers and Luck (1986) and Navaz (1987).

The perspective of the HSE has been presented by Hough (1983), Wicks (1983), D.A. Jones (1985) and Crossthwaite (1986), while Considine and Grint (1985) have given a set of rapid assessment models, as described in Chapters 15–17.

23.28.1 Hazardous events

In marine transport, ships are at risk as the port approaches, in the port and during berthing, and whilst loading and unloading cargo. Accounts of scenarios of hazardous events during these different stages include the generic treatments by Solberg and Skramstad (1982), Hough (1983) and Cummings and Bradley (1988) as well as specific studies such as that of Lucas, Roe and Waterlow (1983). The studies by Aldwinckle and Slater (1983) on the PASS system and by Considine (1983) on the Morecambe Bay pipeline also contain relevant material.

The initial events fall into three broad categories: (1) release from cargo tanks, (2) release from a ship–shore transfer lines and (3) events associated with ship operations. The cargo which has been most studied is LNG and the following account refers primarily to this.

There are a number of events which have the potential to cause loss of containment of an LNG cargo. Two principal, and much studied, events are collision and grounding. Other events which have been examined as possible causes include: ship structural defects; liquid sloshing in a cargo tank; overpressurization of a cargo tank; a spillage on deck leading to brittle fracture; a fire on deck; a fire in a cargo tank; a fire on the sea; explosion in a cargo tank; an explosion in the engine room; and an explosion external to the vessel. Some of these rank as escalation events rather than initiating events.

A 125,000 m^3 gas carrier would typically have six 22,000 m^3 cargo tanks. The worst case scenario is a virtually instantaneous release of the ship's whole cargo of LNG, but this, whilst not physically impossible, is unrealistic. A more common, but still pessimistic assumption is a release from one cargo tank. More detailed assessments consider the extent of damage from the initiating event under consideration, such as collision or grounding, and estimate the flow through the aperture thus created.

A detailed treatment of release flows and spill sizes is given Solberg and Skramstad (1982). The flow from a damaged cargo tank depends on the location of the hole. The authors present a graph for LNG showing the flow from different cargo tanks as a function of hole location, hole size and time.

The location of the hole also affects the total size of the spill. The largest spill size is given by a tank penetration at sea level. Solberg and Skramstad give another graph showing the fraction of the cargo which is released as a function of the hole elevation.

A spill of LNG from a cargo tank may or may not be ignited immediately. Solberg and Skramstad mention as possible ignition sources in a collision: sparks; heating of steel above the methane ignition temperature due to absorption of collision energy; and ignition sources present in the bow of the striking ship.

For a spill onto the sea, if there is immediate ignition, a large release will give rise to a pool fire. If the release does not ignite immediately, a large flammable cloud will form. If this cloud is then ignited, the combustion will take the form of either a flash fire or a vapour cloud explosion. Alternatively, LNG may be spilled within the double hull structure of the ship and ignited, resulting again in either fire or explosion.

Solberg and Skramstad suggest that a fire occurring in the double hull structure of the ship is likely to be starved of oxygen, unless the opening is very large and the spillage massive. For a pool fire on the sea beside the ship, they give a detailed model, as described below.

This model indicates that, although a large pool fire will raise the temperature of both the outer hull and, after some delay, the inner hull, to a value at which some loss of strength will occur, this will not necessarily compromise the structural integrity of the whole ship. In this respect, a spill which is relatively small but prolonged may present the greater threat. A much larger fire may be of too short duration to induce tank failure.

The creation of a flammable mixture in the double hull structure may result in an explosion. The hull contains void spaces interconnected by openings of different size. An explosion propagating through these voids could be very destructive. For a case where the whole space is filled by a mixture within the flammable range, Solberg and Skramstad estimate the explosion overpressure as of the order of 5–10 bar.

For a vapour cloud explosion over the sea outside the ship's hull, they consider the effect of the overpressure at a distance of twice the radius from the centre of the cloud, which they take as about 0.1 bar. Treating the structural response as a quasi-static one, this overpressure is low compared with the strength of the hull and would not be expected to cause damage to the hull structure of the containment.

Another principal scenario for a massive spill is rupture of the ship–shore transfer system during loading or unloading. This event is considered by Lucas, Rowe and Waterlow (1983) and Cummings and Bradley (1988); the former authors also examine its escalation. Two possible causes of failure of the transfer system are failure of the expansion bellows and rupture of the transfer arm. A possible cause of transfer arm rupture is excessive movement between the ship and the jetty.

Estimates of the size of spill which could result from transfer system rupture is usually based on the full bore flow and the time to shut off the flow. Lucas, Rowe and Waterlow quote a transfer flow of 17 te/min and a response time to shut-down of 30 s or less.

These authors identify four ways in which, in principle, such a spill might escalate. If LNG is spilled on the deck of the ship, this may result in embrittlement and cracking of the steel. They conclude, however, that, given the low stresses, the cracks would arrest without extending beyond the embrittled zone.

More serious is the third path to escalation, that is, an explosion resulting from the entry of the liquefied gas into the ballast tanks. Lucas, Roe and Waterlow describe the estimation of the resultant overpressure. In a totally confined enclosure, the overpressure generated could be some 7 bar, which is well in excess of the pressure which most structures will withstand unless specifically designed to do so. However, commonly some weaker section fails and vents, thus reducing the pressure attained. Moreover, a high water level in the tanks tends to reduce the overpressure. The authors describe studies in which the overpressures calculated ranged from 0.07 bar for high water levels to 2 bar for nearly empty tanks, and other studies which indicated that in the absence of embrittlement by LNG such explosions would be unlikely to cause damage to the cargo tank.

The fourth path to escalation which these authors consider is an explosion in the engine room. In general, no scenario for engine room explosion was identified which could cause cargo tank failure other than entry of a large quantity of flammable gas. For the latter case, use was made of wind tunnel modelling and explosion simulation. It was concluded that in the worst case, the peak overpressure in the engine room could be some 6 bar, which compares with a cargo tank failure pressure of 3–4 bar.

Events which may occur associated with operations on the ship are described by Cummings and Bradley (1988). They include (1) ignition of a vapour plume from a cargo tank, (2) improper control of ballasting/deballasting operations and (3) rollover of LNG in the cargo tank.

The foregoing account has dealt with LNG. LPG presents a broadly similar set of hazards. Some relevant differences are that it is not so deeply refrigerated and that it is more likely than methane to give a vapour cloud explosion.

Other materials may have their own characteristic hazards. Thus, a monomer may undergo a runaway polymerization reaction. Monomers are stabilized using an inhibitor but Cummings and Bradley refer to work on the risk that delays at sea may cause the inhibitor to become exhausted.

23.28.2 Hazard models

As already mentioned, one of the first sets of hazard models for marine transport was the Vulnerability model (VM)

of Eisenberg, Lynch and Breeding (1975) and of other workers. This included constituent models for evaporation of pools on water, gas dispersion, pool fires, flash fires and vapour cloud explosions.

Another set of hazard models which has been applied to marine transport is that of Considine and Grint (1985). These authors present convenient parameterizations of a number of models widely used in hazard assessment, including models for heavy gas dispersion, pool fires, flash fires and vapour cloud explosions.

Whilst such sets of hazard models constitute a basic toolkit, other models also are required for hazard assessment. Treatments of collision and grounding have been described in Section 23.18.

Models are also required for the effect of fire outside the ship's hull on the integrity of the cargo tanks. Such models have been described by Solberg and Skramstad. The set of models given by these authors covers: the size and duration of a pool fire beside the hull as a function of the size of hole in the damaged cargo tank; the heat flux from such a fire as function of the fire base diameter; the heat flux received by the ship's deck; and the unsteady-state temperature profiles of the outer and inner hulls.

Another group of models is that for explosions in confined spaces such as between the inner and outer hulls and in ballast tanks. These include both models for the overpressures generated in a confined explosion and for the damage caused by such an explosion. The former may be analytical models or explosion simulation codes.

23.28.3 Some hazard assessments

As already described, there have been a considerable number of hazard assessments for marine transport, covering shipping, ports and terminals.

An early generic study was that given in the vulnerability model by Eisenberg, Lynch and Breeding (1975), as described in Chapters 16–18.

A hazard assessment of marine transport at an oil terminal at the Deep Water Port, Galveston, Texas, has been described by Bergmann and Riegel (1983). The scenarios considered were collisions and groundings, giving rise to a fire or explosion.

The authors' estimates of the frequencies and probabilities of these events are as follows. The frequencies of collision and grounding are estimated, respectively, as 1.5×10^{-4}/movement and 3.5×10^{-4}/movement, and the probabilities, given collision, of spill, fire and explosion as 0.25, 0.33 and 0.1. They give the following figures:

Casualty type	*Frequency of casualty* (casualties/movement)	*Probability of spill* (spills/movement)	*Probability of fire* (fires/movement)	*Probability of explosion* (explosions/movement)
Collision	1.5×10^{-4}	4.3×10^{-5}	4.4×10^{-5}	1.6×10^{-5}
Dockside fire/explosion	1.4×10^{-4}	9.8×10^{-7}	1.0×10^{-5}	3.7×10^{-6}

They take as negligible the probability that, given a soft bottom with no hard underwater object, a grounding would result in a spill or fire.

The authors found that for collisions only one in 23 spills resulting in fire propagated into an explosion, but that all explosions had resulted in spill and fire. Records indicate that where an explosion occurs, between 29% and 94% of the cargo tanks become involved, but that where a fire occurs some 10–13% of the cargo is spilled and burned. They take the proportion of cargo involved as 36% for an explosion and 12% for a fire.

Bergmann and Riegel have developed event trees for the three scenarios of collision, grounding and dockside fire/explosion. They assess the effects of explosion using the methods of W.E. Baker *et al.* (1978), including correlations of overpressure vs scaled distance for a fuel-air explosive and of damage in terms of the pressure–impulse diagram. For fire, the treatment is largely concerned with firefighting and mitigatory measures, and appears essentially qualitative.

The two *Canvey Reports*, described in Appendix 7, cover marine risks, including collision, grounding and loading/unloading, and give a full assessment of individual and societal risks.

A further hazard assessment of marine transport at the British Gas LNG terminal at Canvey is described by Lucas, Rowe and Waterlow (1983). This study details the various hazard scenarios, as described in Section 23.28.1, and gives an engineering assessment of each one. As a result of this assessment, some postulated scenarios are rejected, whilst others are accepted and countermeasures are described. For example, it is concluded that failure of the bellows expansion units in the ship–shore transfer line would be manifested by a small crack rather than sudden rupture, and that the latter is not a credible failure mechanism. Likewise, major failure due to low temperature brittle fracture following LNG spillage on the ship's deck is discounted. Further, a fire on deck or on the sea is not expected to cause failure or overpressure of the inner hull. On the other hand, the authors do consider to be credible explosions in the ballast space or, with ingress of flammable vapour, in the engine room. They describe various measures taken to counter these hazards such as improved emergency shut-down, deck protection and engine room explosion relief.

One countermeasure described is to arrange that in operation the man-way hatches to each ballast tank are closed, though not secured. This, it was calculated, would allow sufficient pressure to build up as the first LNG entering the tank vaporizes that further entry of LNG through cracks would be inhibited. This is an example of the exploitation of the characteristics of the initial event to prevent escalation.

The authors comment that whilst a full quantitative risk assessment (QRA) has its place, in many instances, most of the benefits may be obtained from the detailed engineering analysis which should in any case be part of a good QRA. It is often more fruitful to put effort into discovering unidentified problems rather than into quantifying those already identified. This should be done in cooperation with the engineers involved in the design and operation of the system.

The ACDS *Transport Hazard Report* gives a set of hazard assessments for specific ports and utilizes this to obtain an assessment of national societal risks.

23.29 Transport Hazard Assessment: Comparative Risks

There have been a number of hazard assessments which have sought to determine the relative risks of different modes of transport, of the transport of different chemicals, or of transport in different countries.

An early study of this nature was that of Westbrook (1974), described in Chapter 18, on the risks of chlorine transport by road, rail and pipeline.

Ormsby and Le (1988) give frequency-number (FN) curves for the transport of natural gas, gasoline, LPG chlorine and ammonia in the United States, and also make comparisons with other parts of the world. For LPG, the dominant large event is the one that occurred at San Carlos. The study by Haastrup and Brockhoff (1990), described earlier, gives FN curves for transport in North America, Western Europe and other countries.

Sellers and Bendig (1989) have described a comparative study for transport by road and pipeline associated with two terminals.

The most comprehensive comparison of the risks of road vs rail is that given in the ACDS *Transport Hazard Report*. As described in Appendix 17, this study concludes that at least for the United Kingdom and for the four study substances, there is no basis for preferring one of these modes of transport to the other.

23.30 Security Issues

The US DoT issued HM 232 Final Rule, 'Transportation Security' on March 25, 2003.

23.30.1 Enhanced security requirements

September 11, 2001, brought home the reality of terrorism to all Americans. The terrible events of that day and the later anthrax scare, along with earlier bombings at the World Trade Center in 1993 and in Oklahoma City in 1995, mean that we all need to play our part in combating terrorism in order to maintain the type of lifestyle we enjoy. The DoT's RSPA is responsible for the safe and secure transportation of hazardous materials. Hazardous materials are essential to the economy of the United States and the well-being of its people.

Since 11 September 2001, RSPA has worked closely with hazardous materials shippers and carriers, as well as Federal, state, and local government agencies, to improve the security of hazardous materials in our Nation's transportation system. There are two strategies that are critical to managing transportation security risks. The first is to develop and implement security plans. The second is to assure that employees who handle and transport hazardous materials are trained to recognize and react to potential security problems. RSPA has established new security requirements that make use of these two strategies for hazardous materials transported in commerce.

20.30.2 Hazardous materials transportation enhanced security requirements

Companies must develop and implement a security plan if they offer for transportation or transport the following types or quantities of hazardous materials:

(1) A hazardous material in an amount that must be placarded in accordance with the Hazardous Materials Regulations;
(2) A hazardous material in a bulk packaging having a capacity equal to or greater than 13,248 'l (3500 gallons) for liquids or gases or more than 13.24 m^{-3} (468 cubic feet) for solids; or
(3) A select agent or toxin regulated by the Centers for Disease Control and Prevention under 42 CFR part 73.

At a minimum, the security plan must include the following elements:

(1) Personnel security;
(2) Unauthorized access;
(3) En route security.

The security plan must be in writing and must be retained for as long as it remains in effect and must be revised as necessary to reflect changing circumstances.

23.30.3 Training

Companies must provide training to their employees who are responsible for implementing the security plan. This training should cover the following topics.

20.30.4 Security plans

(1) Company security objectives;
(2) Specific security procedures;
(3) Employee responsibilities;
(4) Actions to take in the event of a security breach; and
(5) Organizational security structure.

In addition, all hazmat employees – that is, employees who directly affect hazardous materials transportation safety – must receive training that provides an awareness of the security risks associated with hazardous materials transportation and methods to enhance transportation security. This training should also include a component that covers how to recognize and respond to possible security threats.

The following guidance should assist you in developing a security plan appropriate to your industry and operations. Even if you are not covered by the security plan requirements in the Hazardous Materials Regulations, you may want to review your current security programme and make any necessary adjustments to improve it.

Begin with a security assessment

To develop a security plan, a company should begin with a security assessment. List the materials they handle and identify those with the potential for use as a weapon or target of opportunity. Then, review their current activities and operations from a transportation security perspective. A security risk assessment model can be used to identify security risks and develop appropriate measures to reduce or eliminate those risks.

A Security Template found on RSPA's hazmat safety homepage (http://hazmat.dot.gov) utilizes the following steps:

(1) Scoping – determine the scope of operations that should be subject to security risk management. Iden-

tify the types of hazardous materials handled and the modes of shipment used.
(2) Knowledge of operations – collect detailed information about the company's transportation operations: (1) quantities of material transported; (2) baseline security programmes; (3) current security procedures; and (4) related safety programmes and procedures.
(3) Assessment – analyse potential security threats and identify security risk control points. Risk control points are points in the transportation process where the company can make an impact by improving procedures or operations.
(4) Strategy – rank or group security risks, prioritize opportunities for security risk reduction, and decide on preventative actions. Create a written document summarizing these decisions which becomes the company's security plan.
(5) Action – implement the security plan.
(6) Verification – monitor implementation of the security plan.
(7) Evaluation – determine if goals are being met and benchmark strategy and results with other companies.

Suggested security measures

The following are specific security measures that could be considered for inclusion in a security plan. At a minimum, a security plan must include the following elements: personnel security, unauthorized access, and en route security.

Personnel security

Be aware of the possibility that an employee may pose a potential security risk. Establish a process to confirm the information provided by applicants on application forms or resumes, including checking with former and current employers, and personal references provided by job applicants. Such confirmation must be consistent with applicable Federal and State laws and requirements concerning employment practices and individual privacy. Employees can be one of the most critical assets for insuring the security of shipping or transportation operations. Under the new RSPA security requirements, employees must be familiar with the security plan and are properly trained in its implementation. Training should include company security objectives, specific security procedures, employee responsibilities, and organizational security structure. In addition, consideration should be given to taking one or more of the following actions:

(1) Encourage employees to report suspicious incidents or events.
(2) Implement routine security inspections.
(3) Convene regular employee/management meetings on security measures and awareness.
(4) Communicate with employees using an internal communication system to provide information on facts, trends and other security issues. Because Internet communications may be accessed by others, consider alternative methods for communicating sensitive information.

Unauthorized access

Access to hazardous materials in transportation and to a facility should be another security concern. Consider utilizing one or more of the following security measures to prevent unauthorized access:

(1) Establish partnerships with local law enforcement officials, emergency responders, and other public safety agencies with jurisdiction over the facility. Through such relationships, exchange information about threats, trends, and unsuccessful security programmes.
(2) Request a review of the facility and security programme by local law enforcement and fire safety officials.
(3) Restrict the availability of information related to the facility and the materials handled. Encourage authorities in possession of information about the facility to limit disclosure of that information to a need-to-know basis.
(4) Add perimeter security and increase off-hour security patrols. Request that law enforcement personnel increase off-hour patrols.
(5) Check the adequacy of locks and other protective equipment. Consider equipping access gates with timed closure devices. Conduct frequent inspections.
(6) Install additional lights, alarm systems, or surveillance cameras.
(7) Restrict access to a single entry or gate.
(8) Place limits on visitor access, especially when the Homeland Security Alert System raises its threat level; require visitors to register and show photo identification, and have someone accompany visitors at all times.
(9) Require employees to display identification cards or badges.
(10) Conduct security spot checks of personnel and vehicles.
(11) Upgradesecurity procedures for handling pick-ups and deliveries at the facility. Verify all paperwork and require pick-ups and deliveries be handled only by appointment with known vendors. Require that vendors call before a delivery and provide the driver's name and vehicle number. Accept packages and deliveries only at designated locations at the facility.
(12) Secure hazardous materials in locked buildings or fenced areas. Have a sign-out system for keys.
(13) Secure valves, manways, and other fixtures on transportation equipment when not in use. Lock all vehicle and delivery trailer doors when not in use. Secure all rail, truck, and intermodal containers when stored on site. Use tamper-resistant or tamper-evident seals and locks on cargo compartment openings.
(14) Periodically inventory the quantity of hazardous materials in order to recognize if a theft has occurred.
(15) Keep records of security incidents. Review records to identify trends and potential vulnerabilities.
(16) Report any suspicious incidents or individuals to your local Federal Bureau of Investigation (FBI) office and to local law enforcement officials.

En route security

Shippers and carriers should work together to assure the security of hazardous materials shipments en route from

origin to destination. Shippers should assess the security of transportation modes or combinations of modes available for transporting specific materials and select the most appropriate method of transportation to ensure their efficient and secure movement. Know the carrier and have a system for qualifying the carriers used to transport hazardous materials. Consider implementing one or more of the following measures:

(1) Use carrier safety ratings, assessments, safety surveys, or audits, and ask the carrier to provide information on security measures it has implemented.
(2) Verify that the carrier has an appropriate employee hiring and review process, including background checks, and an ongoing security training programme.
(3) Verify the identity of the carrier and/or driver prior to loading a hazardous material.
(4) Ask the driver for photo identification and a commercial driver's license for comparison with information provided by the carrier.
(5) Ask the driver to tell you the name of the consignee and the destination for the material and confirm with your records before releasing shipments.
(6) Identify preferred and alternative routing, including acceptable deviations.
(7) Strive to minimize product exposures to communities or populated areas, including downtown areas; avoid tunnels and bridges where possible; and expedite transportation of the shipment to its final destination.
(8) Minimize stops *en route;* if you must stop, select locations with adequate lighting on well-travelled roads, and check your vehicle after each stop to make sure nothing has been tampered with.
(9) Consider using two drivers or driver relays to minimize stops during the trip. Avoid layovers, particularly for high hazard materials.
(10) Shippers and rail carriers should cooperate to assure the security of rail cars stored temporarily on leased tracks.
(11) If materials must be stored during transportation, make sure they are stored in secure facilities.
(12) Train drivers in how to avoid high jacking or stolen cargo – keep vehicles locked when parked and avoid casual conversations with strangers about cargoes and routes.
(13) Consider whether a guard or escort for a specific shipment of hazardous material is appropriate.
(14) Consider using advanced technology to track or protect shipments *en route* to their destinations. For example, you may wish to install tractor and trailer anti-theft devices or use satellite tracking or surveillance systems. As an alternative, consider frequent checks with drivers by cell phone to ensure everything is in order.
(15) Install tamper-proof seals on all valves and package or container openings.
(16) Establish a communication system with transport vehicles and operators, including a crisis communication system with primary and back-up means of communication among the shipper, carrier, and law enforcement and emergency response officials.
(17) Implement a system for a customer to alert the shipper if a hazardous materials shipment is not received when expected.
(18) When products are delivered, check the carrier's identity with shipping documents provided by the shipper.
(19) Get to know your customers and their hazardous materials programmes. If you suspect you have shipped or delivered a hazardous material to someone who may intend to use it for a criminal purpose, notify your local FBI office or local law enforcement officials.
(20) Report any suspicious incidents or individuals to your local FBI office and to local law enforcement officials.

Additional information

Up-to-date information is a key element of any security plan. Companys should consider methods to:

(1) Gather as much data as they can about their own operations and those of other businesses with similar product lines and transportation patterns.
(2) Develop a communications network to share best practices and lessons learned.
(3) Share information on security incidents to determine if there is a pattern of activities that, when considered in isolation are not significant, but when taken as a whole generate concern.
(4) Revise security plans as necessary to take into account changing circumstances and new information.

23.30.5 C-TPAT – Customs-Trade Partnership Against Terrorism

C-TPAT is a joint government-business initiative to build cooperative relationships that strengthen overall supply chain and border security. C-TPAT recognizes that Customs can provide the highest level of security only through close cooperation with the ultimate owners of the supply chain, the importers, carriers, brokers, warehouse operators and manufacturers. Through this initiative, Customs is asking businesses to ensure the integrity of their security practices and communicate their security guidelines to their business partners within the supply chain.

Businesses must apply to participate in C-TPAT. Participants will sign an agreement that commits them to the following actions:

(1) Conduct a comprehensive self-assessment of supply chain security using the C-TPAT security guidelines jointly developed by Customs and the trade community. These guidelines, which are available for review on the Customs website, encompass the following areas: Procedural Security, Physical Security, Personnel Security, Education and Training, Access Controls, Manifest Procedures, and Conveyance Security.
(2) Submit a supply chain security profile questionnaire to Customs.
(3) Develop and implement a programme to enhance security throughout the supply chain in accordance with C-TPAT guidelines.

(4) Communicate C-TPAT guidelines to other companies in the supply chain and work towards building the guidelines into relationships with these companies.

C-TPAT offers businesses an opportunity to play an active role in the war against terrorism. By participating in this first worldwide supply chain security initiative, companies will ensure a more secure supply chain for their employees, suppliers and customers. Beyond these essential security benefits, Customs will offer potential benefits to C-TPAT members, including:

(1) A reduced number of inspections (reduced border times).
(2) An assigned account manager (if one is not already assigned).
(3) Access to the C-TPAT membership list
(4) Eligibility for account-based processes (e.g. bimonthly/monthly payments).
(5) An emphasis on self-policing, not Customs verifications.

C-TPAT is currently open to all importers and carriers (air, rail, sea). C-TPAT membership will be made available to all sectors of the supply chain. Customs will be consulting with the trade community to develop the most effective approach for each sector to participate in C-TPAT.
http://www.geosbush.com/ctpat.htm.

23.31 Notation

Section 23.4

Subsection 23.4.7

A_o	fractional minimum elongation of metal on fracture under tensile stress
D	internal diameter of shell (mm)
e	thickness of metal (mm)
P	calculation pressure (bar)
R_m	minimum tensile strength
λ	constant
a	permissible stress (N/mm^2)

Subscripts

0	mild steel
1	metal under consideration

Subsection 23.4.12

d_{15}	density of liquid at 15°C
d_{50}	density of liquid at 50°C
DF	degree of filling (%)
t_F	mean temperature of liquid at time of filling (°C)
∞	amean coefficient of cubical expansion of liquid between 15°C and 50°C
χ	parameter (%) (see text)

Section 23.5

C	confidence limits on value of liquid density (%)
FR	filling ratio
P_l	density of liquid
P_w	density of water
χ	parameter (see text)

Section 23.6

Equations 23.6.1–23.6.7

I	normal distribution parameter
P	probability
x	impact speed
x	mean impact speed
σ	standard deviation

Superscript

–	mean

Subscript

c	combined

Equations 23.6.8–23.6.11

E	energy absorbed in collision
m_1	mass of first vehicle
m_2	mass of second vehicle
v	residual velocity of two vehicles after collision
v_l	impact velocity of load
v_1	initial velocity of first vehicle
v_2	initial velocity of second vehicle

Subscript

cr	critical

Section 23. 11

Equation 23.11.1

C	cost
k	constant
n	index
P	throughput

Equation 23.11.2

a	design factor
D	external diameter of pipe (mm)
f_y	specified minimum yield strength (N/mm^2)
p	internal design pressure above atmospheric (bar)
t	design thickness of pipe wall (mm)

Section 23.18

c	constant
E	energy absorbed in collision
E_f	energy absorbed by fender
K	absorbed energy coefficient
L	length of damage
m	constant
m_1	effective mass of striking ship
m_2	effective mass of struck ship
δm	hydrodynamic mass
P	depth of damage
R	ratio defined by Equation 23.18.6
R_T	resistance factor
t	thickness
v_{cr}	critical value of speed of striking ship before collision

V_1	speed of striking ship before collision
	residual speed of two ships after collision

Subscripts

cr	critical value
n	*n*th member in struck ship
N	*N*th member in striking ship
1	striking ship
2	struck ship

24 Emergency Planning

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There is a considerable body of work on disasters of various kinds, both natural and man-made, and, whilst much of this may be only marginally relevant to process plant emergencies, it is helpful to have some awareness of this background (Table 24.1).

Table 24.1 *Selected references on emergency planning*

Disaster planning
BSC (n.d./2); Prentiss (1951); Featherstone (1962); Ministry of Health (1962); Grosser et al. (1964); H.B. Williams (1964); Inbbar (1965); Healy (1969); Chatham-Savannah Defense Council (1971); Home Office (1972); Office of Emergency Preparedness (1972); Puget Sound Council of Governments (1975); J.W. Richardson (1975); W.H. Gibson (1976); J. Howard (1976); League of Red Cross Societies (1976); Manning (1976); Abe (1978); Quarantelli (1978); de Boer and Baillie (1980a,b); H.D. Foster (1980); Frey and Safar (1980); Smulders (1980); Whittow (1980); Geipel (1982, 1991); R. Jackson (1986); May and Williams (1986); Society of Industrial Emergency Services Officers (1986); Theodore, Reynolds and Taylor (1989); Dupont, Theodore and Reynolds (1991); M.A. Hughes (1991); D.J. Parker and Handmer (1992)

Works emergency planning
MCA (SG-4); NRC (Appendix 28 *Emergency Response, Emergency Planning*); Anon. (1961b); Labine (1961); Tenneco Oil Co. (1964b); Kling (1965); D.T. Smith (1967); Fowler and Spiegelman (1968); Gilmore (1968); Bennett (1972); van Cleve (1973); Hunter (1973); *Hydrocarbon Processing Editors* (1973); IRI (1973/9); PITB (1973/4); K. Wright (1973); Associated Octel (1974 Bklt 20/74); Brannon (1974, 1976); Bruce and Diggle (1974); Duff and Husband (1974); Maas (1974); CIA (1976 RC20, 1991 RC31, RC47); CISHC (1976/6); Diggle (1976); Underwood, Sourwine and Johnson (1976); Chlorine Institute (1977 FIRE, 1982 Pmphlt 64, 1985 OPFLOW); H.R. Hill, Bruce and Diggle (1977); Searson (1977); Webb (1977); API (1978 Publ. 2025); Harvey (1979b); Blanchard (1980); Melancon (1980); Willems (1980); Davenport (1981a); DnV (1981 RP C106); Isman (1981); Lihou (1981 LPB 42); E. Wilson (1981); Ranby and Hewitt (1982); G. Martin (1984); Burgoyne (1985c); HSE (1985 HS(G) 25); Husbands (1985); Lynskey (1985, 1985 LPB 61); Vervalin (1985a); IBC (1986/67, 1989/76); Marlier and Roure (1986); Walford (1986); Wfflcock (1986); CONCAWE (1987 11/87, 1988 6/88, 1989 2/89); Kalinins (1987); Mullins (1987 LPB 87); O'Reilly (1987); AIHA (1988–/13); Cassidy and Pantony (1988); ILO (1989); Kharbanda and Stallworthy (1989); Lakey (1998); ACGIH (1989/35); Marlier (1989); Tavel, Maraven and Taylor (1989); Phong (1990); AGA (1991/74, 75); Essery (1991); Ham and Gansevoort (1992); Keyworth, Smith and Archer (1992); Marsden, Ferrario and Green (1992); J.N. Scott (1992); Zika and Matyas (1992); Schulein, Kloet and Stolk (1993)
Off-site aspects: Quarantelli *et al.* (1979); Gabor and Griffiths (1980); J. Gray (1981); J. Gray and Quarantelli (1981); Tierney (1981, 1982); CIA (1984 RC20a); Quantarelli (1984); HSE (1986b); Bellamy and Harrison (1988); Cassidy and Pantony (1988); de Larderei (1988); NSW Government (1988); Pietersen (1988b, 1993); Egol (1989a); ILO (1989); Belanger (1990); J. Singh and McBride (1990); C.R. Young (1990); Essery (1991); Rogers and Sorenson (1991); Ruggiero, Macchi and Morici (1992); S. Wilson (1992, 1993); Callen, Dipema and Miller (1993); Thwaites (1993); Stephan (1994)
Evacuation: Hans and Sell (1974); Ikeda (1982) Lynskey (1985); Purdy and Davies (1985, 1985 LPB 65); Fitzgerald (1991 LPB 97); Essery (1993)
Gas dispersion hazards: Ryckman and Peters (1982); M.E. Smith *et al.* (1983); Purdy and Davies (1985, 1985 LPB 62, 63); McNaughton, Worley and Bodner (1987); Chikhliwader and Gelinas (1988); Ginnity (1988); Bais, Zerefos and Ziomas (1989); Rusch (1993); J.R. Taylor (1993)

Police
Drabek (1969); B.E. Fisher (1978a,b, 1980b); C.S. Lees (1985)

Fire services (see also Table 16.2)
Central Fire Brigades Advisory Council (1978); Gebhardt (1984); Beech (1985); Stephan (1994)

Medical services
Savage (1971, 1977, 1979); J.W. Richardson (1975); W.H. Rutherford (1975); Fozard (1976); Baskett and Zorab (1977); Easton (1977a,b); Lea (1977); Plewes and Kindle (1977); Snook (1977); Blanshan (1978); D.J. Williams (1979); de Boer and Baillie (1980a,b); Smulders (1980); Lessenger (1985); Thornley (1985)

Computer aids (see Table 29.1)

Transport emergencies
MCA (CC-l-CC-87); M.M. Anderson (1971); M.T. Miller (1971); Scannell (1971); Boardman (1972); Franklin (1972); Hess (1972); Benner (1975b); Cumberland and Hebden (1975); Ashton and Butcher (1976); McNeil (1976); Mesler (1976); BCGA (1977 GN1); Camm (1977); W.E. Clayton (1977); Mansfield (1977); Zajic and Himmelman (1978); Nimptsch (1979); Bosnian (1980); Hart (1980); Somerville (1981); ASTM (1983 STP 825, 1990/1); Anon. (1984); Cooney (1985, 1991); Mascone (1986); O'Reilly (1987); Cashman (1988); CONCAWE (1988 5/88, 1989 7/89); Lakey (1988); Saccomanno and Allen (1988); Lycett *et al.* (1989); Rogers and Sorensen (1989); Quarantelli (1991); Sorensen, Carnes and Rogers (1992); Browne (1993); Stephan (1994)

Hazard information systems
Anon. (1986p); Cahffl (1989 LPB 85)
Data sheets, Chem Cards: MCA (CC and CIC series); Bigelow (1970, 1971)
HAZCHEM: Home Office (n.d./6); London Fire Brigade (1973); Walmsley (1973); CIA (1975); FPA (1989 CFSD FS 6041)
TREMCARDS: CIA (n.d./2); Walmsley (1973, 1974)
National Chemical Emergency Centre: Cumberland (1978); Goodwin (1984); W.C.J. White (1985)

Emergency response
Road: IP (1989/1); API (1992 RP 1112)
Rail: Barren (1971); Cato and Dobbs (1971); O'Driscoll (1975a); A.D. Williams and Catalan (1976)
Pipeline: API (1991 RP 1122)
Sea: Sohnke (1971); Balemans (1975); H.D. Williams (1975); Preston (1983)
Fire services: Hayes (1971); F. Taylor (1975)

Emergency, mutual aid schemes
Gabor (1991)
HI scheme: Bigelow (1970, 1971); Sylvia (1972a, 1974); Anon. (1973a)

G Centres: ICI (n.d.a); Walmsley (1973)
CHEMSAFE: CIA (1973/6.1991 RC32); Moddrel (1977)
CHEMTREC: Bigelow (1970, 1971); Rosenhah and Cole (1973); Zercher (1975, 1976); Anon. (1994e); Resen (1986); E. Meyer (1989); Donahue (1994)
CHRIS: G.H. Brown (1976)
Chloraid: CIA (1983, 1992 RC48); Carr (1986)
CAER: Vervalin (1985b); Mascone (1986)

Particular chemicals
Ammonia: Cato and Dobbs (1971); Luddeke (1975); Greiner (1984); Lessenger (1985)
Chlorine: R.L. Mitchell (1971); Carr (1986); CIA (1992 RC48)
Missisauga incident: Whitaker (1980); Wignal and Leek (1980); Fordham (1982 LPB 44)
Hydrogen cyanide: Gemmill (1961b)
LPG: Anon. (1984v).
Vinyl chloride: Dowell (1971)
Glendora incident: Dowell (1971); Kogler (1971)
Radioactive materials: Lindell and Perry (1980)

Spectators
Hymes (1985 LPB 65)

Public relations, community impact, community response
Essex County Council (n.d.); MCA (SG-12); Segaloff (1961); D.T. Smith (1967); Koran (1970); Nesmith (1970); Vervalin (1970); CISHC (1976/6); Attwood (1977); Windscale Local Liaison Committee (1979); CIA (1980); J. Gray (1981); J. Gray and Quarantelli (1981); Preece (1982); Walker (1982); J. Harris (1985)

Aftermath
Geipel (1982, 1991)
Stress, including post-traumatic stress disorder: Weisaeth (1988, 1992); Gill and Picou (1991)
Land reclamation: SCI (1980); Pratt (1993)

Accounts of this work include *Emergency and Disaster Planning* (Healy, 1969), *Disaster Preparedness* (Office of Emergency Preparedness, 1972), *Disaster Technology* (Manning, 1976), *Disaster Planning* (H.D. Foster, 1980), *Types and Events of Disasters Organization in Various Disaster Situations* (Frey and Safar, 1980), *Disasters* (Whittow, 1980), *Disaster Policy Implementation* (May and Williams, 1986), *Accident and Emergency Management* (Theodore, Reynolds and Taylor, 1989) and *Hazard Management and Emergency Planning Perspectives in Britain* (D.J. Parker and Handmer, 1992).

In the United Kingdom, the Disaster Prevention and Limitation Unit (DPLU) at the University of Bradford is a specialist resource on disasters. Another is the Disaster Research Center, Ohio State University, and latterly the University of Delaware in the United States.

For the process industries specifically, relevant materials are *Highly Hazardous Spills and Emergency Planning* (Zadic and Himmelman, 1978), *Guide to Emergency Planning* (Society of Industrial Emergency Services Officers, 1986) and *Emergency Response to Chemical Accidents* (O'Reilly, 1987).

24.1 Introduction

Process safety of a chemical plant encompasses several layers of protection. Control measures, shut-down systems, release absorption, accumulation of releases by dikes, and protection by barriers. These layers of protection are intended to prevent an event from propagating into severe consequences because of deviations from normal operation conditions. Emergency response is the last layer of protection that is intended to control an event if possible, or to reduce consequences in cases of loss of control. However, a reliable response to an emergency event requires planning. The three components of emergency planning are presented in Figure 24.1.

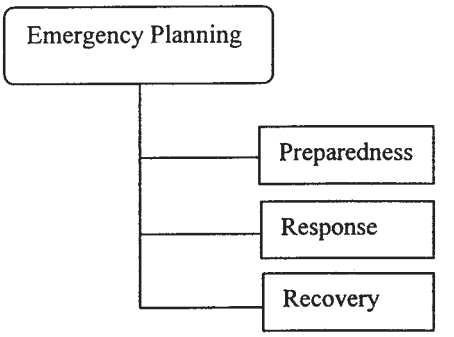

Figure 24.1 *Components of emergency planning*

Much of the material in the preceding chapters has been concerned with reducing the scale and frequency of hazards. Nevertheless, there remains for any hazard a finite possibility that it will be realized. It is necessary, therefore, to plan for such emergencies. Emergency planning is an integral and essential part of the safety and loss prevention strategy. Its objective is to mitigate the consequences of any incident that may occur.

The probability of the realization of a hazard is evaluated by a relatively sophisticated procedure, as already described. It is not then logical to assume that if this occurs, the worst consequences will necessarily follow. It is more appropriate to take a probabilistic approach to the evaluation of the consequences also.

There are two main types of emergencies with which the chemical industry is concerned. These are the works emergency and the transport emergency. They are somewhat different and require separate treatment. Whatever the type of emergency plan, the overall message is that it should be kept simple and flexible, but capable of being scaled up or down as circumstances demand.

24.2 On-site Emergency Planning

24.2.1 An overview

Unanticipated circumstances may yield emergency events. Emergency planning adds an additional layer of protection to circumstances where all of the other layers of protection failed to prevent the incident. Figure 24.1 demonstrates the three major components of emergency planning

Emergency preparedness process begins with identification of credible scenarios for which appropriate response strategies are developed. The analysis of resources and capabilities of facilities to respond to the emergency scenarios is part of the preparedness stage. This analysis examines the resources and the capabilities at

the facilities, at neighbour sites, and the resources that are available at the local community. The development of resources is conducted according to the resources assessment and the potential of cooperation among site emergency responders, neighbouring facilities, and neighbouring communities.

As mentioned above, at least three separate parties are involved in emergency situations, in addition to the network within the facility. Therefore, communication systems are crucial to successful execution of emergency plans in real-time situations as well as in drills.

The complex nature of emergency events requires a very clear hierarchy of command, and a procedure without any ambiguities. It is extremely important that every position in the hierarchy is assigned to personnel with the appropriate skills and personality. Training and assessment of the potential collaboration among these three groups is also extremely important. It is not uncommon for preparedness programmes to be revised based on assessments of drill results.

The development of physical facilities infrastructure consists of the following:

(1) Development of shelters and safe havens.
(2) Establishment emergency operations centre (EOC).
(3) Development of emergency communication capabilities.
(4) Development of appropriate medical support infrastructure.

As shown in Figure 24.2, emergency systems are developed in parallel with the development of physical facilities. The list below consists of typical items in emergency systems; however, it can vary according to special circumstances:

(1) Emergency power supply
(2) Emergency water supply
(3) Communication systems
(4) Emergency management computer support system
(5) Site and community alert systems
(6) Adequate incident command transportaion
(7) Appropriate control room protection measures.

24.2.2 Identification of credible scenarios

The problem

A process hazard evaluation yields a large list of potential incidents. This list should be assessed to determine likelihood and consequences of each of the events, and then prioritized according to the risk associated with these events.

Preparedness for emergencies involving worst case scenarios requires enormous resources and may overwelm the business operability of the facility. Therefore, the outcome for each scenario should be evaluated based on the consequences and probabilities of the scenario. It is important to consider management controls in these evaluations. Incidents such as instantaneous loss of conainment are a major concern in the process inductries. However, measures, such as control systems, overpressure reliefs, alarms, mechanical as well as non-destructive tests reduce the likelihood of development of such as scenario. Emergency planning may be effected by local regulations. The law may dictate the type of scenarios that emergency planning should be address.

The large number of chemicals along with the large number of equipment and the variety of potential incidents that can occur from the combinations of chemicals equipment lead to an enormous number of possible scenarios. As mentioned earlier, it is impractical to plan for all emergencies, and therefore it is neccesary to analyse and prioritize the scenarios. The process of scenario selection and prioritization is shown graphically in Figure 24.3.

Identification of process areas with high hazards

A large number of techniques are available for the identification of areas of major hazards. Dow Fire and Explosion Index (F&EI), and Dow Chemical Exposure Index (CEI) are examples of techniques that can be used to identify and evaluate hazards according to the nature of the substances, and other process physical conditions. The US National Fire Protection Agency (NFPA) Fire Hazard Indices is a classification methodology that classifies materials according to the reactivity, flammability and their possession of health hazards. The results of examination of the plant with these techniques will lead to a list of ranked areas that should then be analysed to identify credible scenarios.

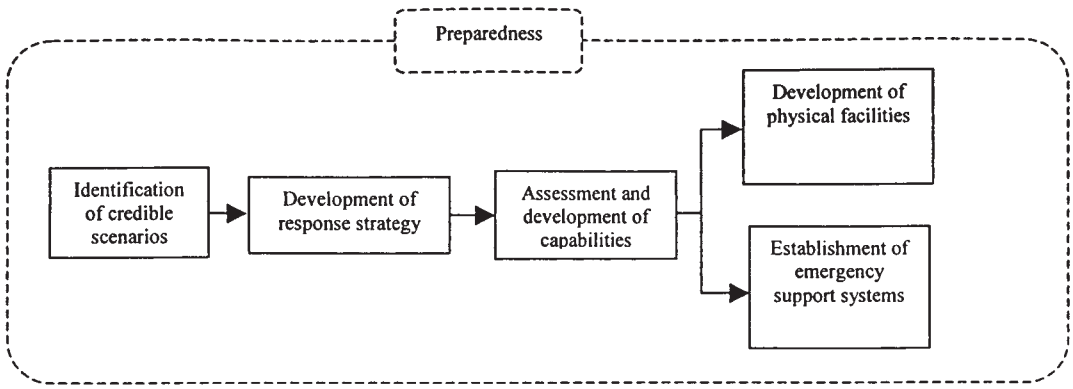

Figure 24.2 *Emergency preparedness flow chart*

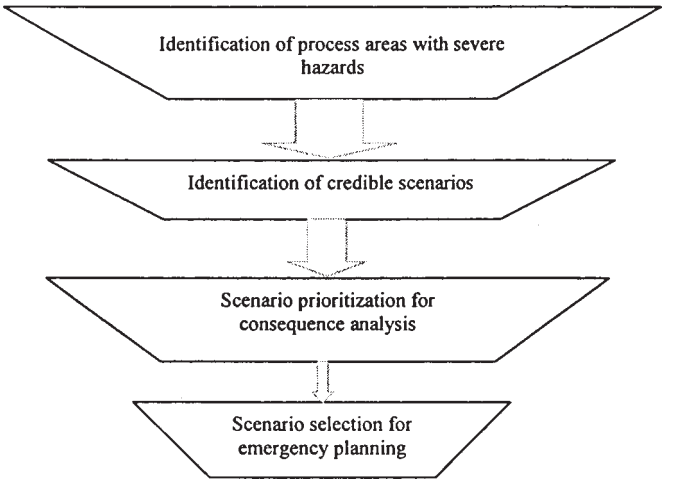

Figure 24.3 *Process of scenario selection for emergency planning*

Credible scenarios
A variety of techniques are available for identification of credible scenarios. The depth of analysis can vary from an informal review to a full Process Hazard Analysis session. The level of investigation is mainly dependent on the experience of the reviewers. Highly experienced reviewers are able to identify credible scenarios by an informal review only.

Consequence assessments
A preliminary screening of incidents is a helpful phase in reducing the number of consequence assessments, and in categorization of the incidents prior to the assessment stage. The following criteria could be helpful for the screening purpose:

(1) Incidents with only minor effects and low probability for escalation into a serious incident should be eliminated.
(2) Incidents with high similarity of discharge rates, locations, inventories and emergency response operations should be grouped.
(3) Two representative incidents should be grouped from each of the groups: (1) incident with high probability of occurrence, which may result in severe illness/injury or major property damage and (2) a credible worst-case scenario with critical/catastrophic consequences.

The screening procedure described above will establish a list of incidents for consequence assessment.

The common forms of incidents are fires, explosions and release of toxic material to the environment. Consequence assessment tools help in the estimation of the impact of these incidents on the employees, local communities, property and the environment. Source term modelling is used to estimate the release rate and quantity released. Explosion modelling, fire and thermal modelling, and dispersion modelling are applied for the assessment of the impact of the incidents. These are discussed in detail in previous chapters. The results of the consequence assessments lead to determination of areas that will be affected and the level of toxicity/thermal load/overpressure in these areas.

24.3 Resources and Capabilities

24.3.1 General

The development of strategy for emergency response requires consequence assessments of a list of credible incidents and data on resources and capabilities. Data should be gathered on the following:

(1) Emergency response equipment on-site.
(2) Emergency response equipment in neighbouring facilities.
(3) Emergency management service in local communities.
(4) On-site medical capabilities and medical facilities in local communities.

Appropriate resources and adequate capabilities are major factors in determining the severity of consequences of an incident. The following is a common list of physical facilities, equipment and systems that are useful in preparing for emergencies:

(1) shelters;
(2) safe havens;
(3) emergency power supply;
(4) adequate and alternate water supply;
(5) EOC;
(6) command post vehicle (CPV);
(7) emergency management computer system;
(8) media information centre;
(9) medical facilities;
(10) large-scale decontamination equipment;
(11) emergency evacuation transportation;
(12) communication centre;
(13) on-site and off-site alerting system;
(14) weather station.

The paragraphs below present the major components of the equipment and systems above that are relevant to emergency preparedness.

24.3.2 Facilities and equipment in emergency planning

On-site shelters and safe havens

Shelters and safe havens provide protection from toxic substances release incidents when an evacuation is not viable. While shelters provide passive protection by closing all air passages and shutting ventilation systems, safe havens consist of independent source of breathing air, such as compressed air bottles, or a specially designed active carbon filtration system. Because of the need to safely shut off (or control) critical systems, it is common to design control rooms as shelters, and sometimes as safe havens.

The process of emergency planning for shelters and safe havens should consider variables such as concentration of employees, distance from incident location, typical weather conditions, and alternate evacuation routes. Administration buildings are commonly used as shelters. When a building is selected as a shelter, the planner should verify that the spaces that are designated as shelter areas do not have holes and cracks, that doors and windows seal properly when closed, and that a ventilation system control (at least a shut-off control) is available.

Both shelters and safe havens should consist of support systems that are proportional to the estimated occupancy.

Emergency power supply

Emergency power supply is a critical system. Planners should verify that vital systems and locations have a power supply for all situations. Generators that are attached to internal combustion engines are most common as emergency supply systems. However, stored electrical energy as battery racks are used as well. *NFPA 110 – Emergency and Standby Power Systems, and NFPA 111 – Stored Electrical Energy Emergency and Standby Power Systems*, provide guidelines and codes for these systems.

Adequate and alternate water supply

Adequate water supply is extremely important for proper emergency response. Type of chemicals used in the plant, thermal load, demand of sprinkler systems, foam systems and hose streams are factors that should be considered in calculation of water reserves.

Alternate water supply is necessary to assure water delivery in an emergency. Ponds, lakes, reservoirs, and on-site tanks can be used as an alternate water source. However, for an adequate preventive maintenance programme, it is crucial to have the source as well as the equipment available. Moreover, heavy equipment is often required to access the alternate source of water, which will require hard surface pavement for the anticipated load. In case of extreme cold weather, measures should be taken to avoid freezing.

Emergency operations centre

It is not uncommon to designate a special room as an EOC. Location of the EOC should be carefully selected to minimize risk. The distance of EOC from processing areas and storage is an important variable in its functionality. The distance of the EOC from the normal residency of the management should be considered as well. The planner should designate an alternated EOC, which will be located opposite to the EOC in reference to the processing area. This will allow access to the alternate EOC in situations where access to the main EOC is not possible. An optimal EOC is one designed as a safe haven. *NFPA 101 – Life safety code*, consists of specifications for designing an EOC. An EOC should contain plans which facilitate the control of the emergency. Table 24.2 provides an example of a list of plans that should be available in the EOC. Documentation, material and equipment that may be necessary to monitor, administer and control the emergency should be provided. This includes the Emergency Plan and the list of personnel with their department, assembly point, home address, nearest relative, and telephone number, if applicable. Information from PHA studies scenarios should be available in an appropriate format so that the EOC personnel can carry out continuous speculative reviews of the possible development of the emergency. The EOC should be provided, as appropriate, with any equipment needed for dealing with the emergency, such as breathing apparatus, rescue gear, etc.

The EOC should be manned in an emergency by the senior emergency coordinator, nominated senior works personnel, senior officers of the outside services and any nominated assistants such as messengers. Other personnel should not be in the centre. If the hazard justifies it, the EOC may be manned continuously.

Command post vehicle

CPV allows the Incident Commander (IC) to control the efforts and activities in emergencies and be located at vantage points. The IC should be able to communicate with the management in the EOC, have access to essential documents, be able to document the scenario, and be able to monitor the environment. Therefore, the CPV should be selected to allow installation of all the equipment necessary and installation of power source that will be able to supply the consumption that this equipment demands.

Emergency management computation system

Emergency management computation systems (EMCS) are used for organization of information, estimation of severity of the incident by using source and dispersion models, data collection from the field if a network is installed, receiving monitoring data, etc. This information is essential to determine the magnitude of the event, and to make decisions as to announce an escalation and to determine the need of evacuation both on- and off-site. Modern wireless networks, computation capabilities, and mobilization of computation systems make these systems extremely useful. Advanced process safety management packages with well-developed emergency management, can be connected

Table 24.2 *Some plans required in the Emergency Control Centre*

Fire water system and alternative water supply
Other fire fighting equipment
Safety equipment
Works entrances and road system
Assembly points
Shelters and safe haven locations
Relation of works to immediate surroundings and plans which can be used as an emergency develops to show: (1) areas affected by hazard; (2) areas evacuated; (3) deployment of emergency teams and equipment. (4) inventories of hazardous materials

to weather station, alarm systems, local, state and federal authorities.

Media information centre

A significant incident may have an impact on the organization's reputation. Sharing information and collaborating with the media could reduce the snowball effect that an emergency event may have. Moreover, media can assist by announcing the emergency, and increase the awareness of the general public in areas that might be affected.

A large room such as a conference room can be designated a media information centre (MIC). The MIC should be located at a distance that will assure the safety of the reporters and should be designed as a shelter or safe haven.

Medical facilities

On-site medical facility can have the capability of a first-aid room or a medical department. In general, the adequate capability is a function of parameters such as number of employees in the plant, capabilities of the local community medical centres, distance to these centres, and the anticipated consequences in an emergency. Coordination between emergency team, on-site medical facility, and local community medical centres may have major impact on the severity of consequences in cases of multiple casualty events, especially if decontamination is required. Local emergency centres should be made aware of the chemicals in the plant, and the estimated number of injuries that are expected in emergency. A procedure that enables evacuation of injuries by airlift is very common and can help in cases where the medical centre is too far, or in cases where the situation requires specialties that are not available in the local medical centre.

Communication system

The design of communication system should address the following:

(1) Maintain on-site communication.
(2) Establish communication with off-site agencies and neighbouring facilities.
(3) Allow communication among management, emergency team and responders.

Communication equipment includes announcement system, alert system, phones, secure phone system, cellular phones, radio system, wireless computing systems and cable TV.

Alerting and announcement systems serve both on- and off-site. Use of alerting system requires coordination between the plant and the local agencies. An audio alerting system requires that a code be well communicated with the general public. In general, alerting systems are used to alert on weather hazards such as a tornado. Since man-made hazards are rare, emergency plan should verify public knowledge with regard to audio alerting systems. Cable TV is a very effective tool to notify the general public in local community with regard to hazards, and to deliver behav-ioural guidelines and directions. It is recommended that the planner not leave the notification of the general public to the local agencies. A computer dial-up system can be used as a tool to contact the general public in emergency.

On-site response equipment and supplies consist of a variety of items. An inadequate equipment and supply can worsen the consequences of an event. Therefore, the planner must verify that equipment and supplies will meet the needs in an emergency.

Response equipment and supplies

The success of the response team in mitigating an incident is dependent on the availability of adequate equipment, and implementation of an adequate procedure of inspection, maintenance and replenishment of this equipment. Response equipment and supplies can be divided to three main categories:

(1) personal protection,
(2) fire fighting, and
(3) decontamination.

Personal protection equipment allows the response team to function in the affected zone in order to continue with the efforts to control the incident and minimize the consequence. Personal protection equipment consists of two major types:

(1) respiratory protection and
(2) thermal and chemical protection.

The circumstance determines the level of respiration protection that is needed. In many cases, a mask equipped with a canned active carbon filter may answer the needs. In other cases, a self-contained breathing apparatus (SCBA) is required. This apparatus usually consists of a full face protection mask and a regulator connected to a compressed air cylinder that is carried by the responder. NFPA standard 1981 *Open-Circuit Self-Contained Breathing Apparatus* determines the requirement of SCBA.

A supplied air respirator (SAR) is a system that supplies air from a source that is located in a distance from the affected area. This system is known as an airline respiration system as well. The air is supplied through an air-line hose to the responder. The major advantages of this system are that it allows the responder to stay longer in the affected area, and that the responders are not required to carry heavy systems as with SCBA. The major disadvantages are that the responder is not as mobile as with SCBA, and that the air-line hoses are vulnerable to mechanical, thermal and chemical damage and therefore this arrangement is not approved for Immediate Danger to Life and Health environment, unless an emergency escape SCBA is carried by the responder as well.

As for fire fighting gear, these systems supply reasonable thermal protection for most fires. In incidents in which excessive thermal load is expected, the responder should wear adequate clothing. An ice vest is used when high ambient temperature is imposed on the responders. The vest consists of pockets in which ice can be installed. The ice absorbs the thermal load, and enables the responder to stay longer in high-temperature environment, or to get closer to the source of the heat.

NFPA 1991 – *Standard on Vapor-Protective Ensembles for Hazardous Materials Emergencies*, and NFPA – 1992 *Standard on Liquid Splash-Protective Ensembles and Clothing for Hazardous Materials Emergencies* assist in determining the proper clothes according to the characteristics of the hazards.

Fire fighting and decontamination equipment consist of (but not limited to) the items in Table 24.3:

A planner should determine the necessity of integrating heavy equipment as dump trucks, earth movers, and cranes, and integrating these in the planning.

Table 24.3 *Major fire fighting and decontamination equipment*

Fire extinguishers
Sprinkler system
Water and foam engines
Hydrant system
Portable pumps
Fire fighting truck
Inhibitors
Neutralizers
Sorbents
Hazardous material vehicle

24.4 Developing an Emergency Plan

24.4.1 Overview

Regulatory agencies require preparation for emergencies and documentation of emergency plans. The emergency team will respond to incidents according to this plan and therefore the importance of the accuracy and comprehensiveness of the written plan. Emergency plan consists of the following major components:

(1) Establishment of a set of credible scenarios.
(2) Study emergency plans of neighbouring facilities and local community.
(3) Study availability of resources and capabilities, and determining needs.
(4) Study emergency-related regulations and emergency authorities' requirement and responsibilities.
(5) Development of tactics to respond to fires and explosions, release of hazardous materials, natural hazards, terrorist threats, rescue, evacuation, and plan for medical response and emergency mitigation.
(6) Development of procedures to assess level of emergency.
(7) Training of emergency teams, other employees and contractors.
(8) Development and execution of drills (include neighbouring facilities and local communities).
(9) Development of drill-based improvement procedure.
(10) Communication of the emergency plan on- and off-site.

Component (1), (2) and (3) in the list above were discussed in detail earlier in this chapter.

24.4.2 Emergency organizations and regulations

Emergency-related regulations, requirements and responsibilities are different in different countries. The planner should study the requirements and regulations and develop the plan to meet these requirements. An active Local Emergency Planning Committee (LEPC) in the United States can assist a great deal in coordinating between the plant and the local community authorities and responding agencies. A central entity such as the LEPC in the United States may have in hand emergency plans from other sites and the emergency plan of the local community. Moreover, a mutual agreement that establishes a net of emergency equipment and supplies may be available and thus reduce the costs involved in preparing the plant for emergencies.

Local community planning should include diverse government, volunteer and private organizations. Table 24.4 consists of examples of such organizations.

Table 24.4 *Organizations that may be involved in local community emergency planning*

Local community emergency preparedness organization
Emergency management services
Fire department
Police department
Traffic control agencies
Hospitals
Red cross
Salvation army
Department of Health
EPA and OSHA (US)/HSE (UK)
Coast guard
Media
Mayor

When establishing a mutual framework for efforts in emergency, the planner should identify each one of the personnel that the plant should interact with, and establish a dialogue that will create mutual trust and commitment.

24.4.3 Development of response tactic

Initial assessments and criteria for decision on escalation of emergency are major issues in responding to an emergency. The planner should establish procedures for assessment of severity of the incidents, and a set of criteria that will help in the decision to declare on escalation of the situation. The emergency team management must understand that the safety of the employees and responders is their first priority. Next is preventing the incident from escalating. Environmental concerns are next and finally the prevention of property damage is the last priority among these. The actions to be taken should be developed according to these priorities for both: fires and explosions, and release of hazardous material. In both cases, the initial efforts should determine work zones, in which the responders will be able to respond from.

Following the initial assessment, the IC should determine what the objectives of the response are, for example, should the responders try to extinguish the fire (aggressive response), prevent it form spreading or, respond just to allow safe evacuation of employees (defensive)? This decision should be made based on the risk associated with level of intervention.

Next, location for mitigation efforts to take place should be determined as well as entrance and exit routes, the time frame for the variety of actions, and who will carry out the variety of responsibilities.

The planner should develop procedures for the following indirect response components:

(1) Warning and alerting
(2) Communication
(3) Distribution of managerial responsibilities
(4) Emergency shut-down
(5) Identification of missing employees
(6) Mutual assistance with the variety of external entities
(7) Reporting
(8) Declaration of escalation
(9) Security
(10) Dealing with the media and
(11) Special notification.

Procedures for direct response efforts should include the following:

(1) Evacuation
(2) Medical mitigation
(3) Rescue
(4) Fires and explosions
(5) Release of hazardous materials
(6) Terrorism threats
(7) High winds
(8) Flood
(9) Freeze.

Procedures for training, drills, effectiveness measurements and post-drill change management should be considered part of the response stage as well as part of the preparedness.

24.5 Training

24.5.1 Background

Training is the foundation of the success of emergency planning. The training verifies that all employees are familiar with the alerting and warning codes, and the location of shelters and safe havens. Members of the response team are introduced to their responsibilities and its role in the 'big picture'. The frame for training for emergencies was mandated by the government in the United States. Occupational Safety and Health Administration (OSHA), Environmental Protection Agency (EPA), and the Department of Transportation require training for emergencies. Other organizations established standards and good practices that are very useful. OSHA requires that an employer will train his employees at least once in three years.

24.5.2 Fundamental training

The most fundamental emergency training is the use of fire extinguishing systems and equipment. It is common for all employees to be trained to use these systems. Additional training that all employees should receive is familiarity with alert codes, evacuation routes, and the locations of shelters and safe havens. These training include identification of hazards, the type of response that is appropriate, and to whom these hazards should be reported, and which communication system is to be used.

24.5.3 Operators training

Operations personnel are required to be familiar with the site emergency plan, and to be familiar in details with the relevant part of the plan that is related to their processes. This part requires knowledge of safe work practices and emergency shut-down procedures. The operators should be trained on the procedure, and to the criteria for proper shut-down. This type of training is extremely important, and more important is exercising it, in order to increase the correct decision-making, and to prevent wrong decision-making as was made in the Piper Alpha incident in the North Sea.

24.5.4 Response teams

Response teams are required to have high level of familiarity with the emergency plan. They have to understand the inherent hazards that are characterizing the plant, and the list of credible incident that the emergency plan was developed for, hierarchy of command, reporting system, responsibilities, communication systems and all other relevant information and procedures that the emergency plan consists of. The response teams are required to have knowledge and skills in several types of response categories:

(1) Fire fighting
(2) Release of hazardous material (in all phases: leak of liquids, rain of vapour and drops, gas)
(3) Terrorism threats
(4) Rescue (natural hazards, man-made hazards, confined places)
(5) Medical and
(6) Evacuation.

In most cases the teams are designated to one or more of the categories; however, they are expected to be able to perform in other teams as well.

Several of the emergency response personnel should be trained to deal with the media and public relations. This is a very sensitive duty because of the impact that the incident and the media covering the events may have on the image of the organization.

24.6 Essential Functions and Nominated Personnel

24.6.1 Incident Commander

It is the IC responsibility to proceed to the scene of the incident and to coordinate the efforts. The following list describes the IC's major responsibilities:

(1) As soon as the IC becomes aware of an incident, he should assess its scale against predetermined criteria or emergency reference levels, and decide whether a major emergency exists or is likely. If so he should immediately activate the on-site plan and if necessary the off-site emergency plan.
(2) Ensure that emergency services have been called.
(3) Direct the shutting down and evacuation of the other plant areas, etc., likely to be affected.
(4) Ensure that key personnel have been notified.
(5) Direct all operation at the scene.
(6) Control the rescue and fire fighting operations activities until the arrival of the fire brigade, when he should hand over control to a senior fire officer.
(7) Search for casualties.
(8) Evacuate non-essential workers to assembly areas.
(9) Set up a communications point with radio, telephone or messenger contact with the EOC.
(10) Give advice and information as requested to the emergency services.
(11) Brief the site emergency management and keep them informed of developments.

Where a fire is involved, the IC will direct fire fighting until the outside Fire Brigade officer or the Fire Services arrives, he will then hand over control of this aspect to the senior officer of the fire brigade. The IC should be thoroughly familiar with the works situation; a suitable person is the shift section manager. It is important that the IC be readily recognizable when he is at the scene of the incident. This is facilitated if he wears a distinctive garment such as a brightly coloured or luminous jacket or helmet. This garment should be known to all concerned and should be

distinct from any which might be worn by others at the scene, including the outside services.

24.6.2 Emergency Operation Manager

The function of the Emergency Operation Manager (EOM) is to take overall control of the emergency operation activities from the EOC. The EOM controls the 'big picture' from the EOC, and takes an overall control of the scene. Among his responsibilities are the following:

(1) If he decides that a major scale emergency exists or is likely to be developed, then he should ensure that the emergency services have been called and the off-site plan activated.
(2) Ensure that key personnel are called in.
(3) Exercise direct operational control of those parts of the works outside the affected area.
(4) Continually review and assess possible developments to determine the most probable course of events.
(5) Direct the shutting down of plants and their evacuation in consultation with the IC and key personnel.
(6) Ensure that casualties are receiving adequate attention. Arrange for additional help if required. Ensure that relatives are informed.
(7) In case of emergencies that involve risk to outside areas from wind blown materials, contact the local meteorological office to receive early notification of impending changes in weather conditions.
(8) Liaise with chief officers of the fire and police services and provide advice on possible effects on areas outside the works, and ensure that personnel are accounted for.
(9) Control traffic movement within the works.
(10) Arrange for a log of the emergency to be maintained.
(11) Where the emergency is prolonged, arrange for the relief of site personnel and the provision of catering facilities.
(12) Issue authorized statements to the news media.
(13) Ensure that proper consideration is given to the preservation of evidence.
(14) Control rehabilitation of affected areas after the emergency.

The EOC should be familiar with the activities and should have the authority needed to take any necessary major decisions affecting these activities, the activities in the neighbouring facilities and the outside services. A suitable person is the shift manager. For both managers deputies should be appointed who can take over their duties if they are unavailable for any reason.

24.6.3 Other functions and personnel

There are numerous other functions that may have to be carried out in an emergency. Some of these functions are normal, though they can easily become overtaxed in an emergency, but most are specific to the emergency situation. Similar to the list of responsibilities of the IC and EOM, each of the key personnel should be familiar with all his responsibilities, all the relevant procedures, to whom he reports and who are those under his responsibilities, and to whom he reports if the primary person is not in duty for any reason.

24.7 Declaration and Communication of the Emergency

24.7.1 Raising the alarm

When a serious incident occurs, it is very desirable for the alarm to be raised as quickly as possible. Prompt action will in many cases forestall the development of a full emergency. Crucial aspects of raising the alarm are the authority to raise the alarm, the training of personnel and the alarm system. An efficient and widely practiced policy is to allow any employee to raise the alarm. Such a policy is more effective if personnel have been specifically trained in this aspect.

24.7.2 Declaration of the emergency

When the alarm has been raised, the emergency procedure is activated. The first stage is the decision as to whether the incident constitutes, or could develop into, an emergency. The IC should visit the scene of the incident. He then makes the decision whether to declare an emergency. The authority to declare an emergency need not be restricted to the IC; however, it is undesirable to allow the authority to be too widespread, but too close a restriction may introduce an undesirable delay into the declaration. Other competent personnel may therefore be vested with this authority.

24.7.3 Communication of the emergency

Once an emergency has been declared, it must be communicated to the following entities:

(1) EOM
(2) Personnel working within the areas affected
(3) Personnel that are needed to be called in from outside
(4) Off-site emergency services
(5) Key personnel on call-in
(6) Personnel in other threatened areas and facilities
(7) Police
(8) Medical services
(9) Media, and
(10) Headquarters.

As far as possible, the IC should be relieved of the task of communicating the emergency so that he can devote his efforts to dealing with it on site. However, the duties include communication of the emergency to interested parties until the EOM arrives. It may be appropriate to consider arrangements that assist the IC in this task.

It is desirable to work out in advance fairly formal procedures for the notification of an emergency. The order in which the different parties are to be notified is one obvious aspect. It is also necessary to avoid entering into lengthy explanations to personnel on call-in and, in such instances, use may be made of short pre-arranged messages. Personnel liable to call-in should be issued with identification which will allow them to pass through police barriers erected to control traffic and sightseers.

It is essential that the existence of an emergency be notified without delay to affected plants within the works, the emergency teams and the off-site services.

The emergency should be notified to any neighbouring firm that might be affected by it. This may be necessary if there is a threat to the firm's plant or personnel, if the firm's activities could compound the emergency, for example, create a traffic jam at a shift change, or if there are mutual assistance arrangements.

24.8 Cooperation and Drills

24.8.1 Planning cooperation with off-site services

The planning of cooperation and the development of understanding with the off-site services is vital to the success of response to emergency. The first step is obviously establishment of agreements to cooperate in emergencies. These agreements are established mainly by the senior managers of the organizations involved. But this needs to be followed up by active planning and drills by plant personnel.

The activities should be seen not as two disjoint activities, but as a single operation in which a growing weight of resources is brought to bear on the incident. The planning should aim to clarify not only what is to be done but also who is to do it.

Cooperation benefits greatly if there is a full-time liaison officer, and this can be justified in an area where there is large potential for emergencies. What is known in advance is the general location and nature of possible emergencies. Other factors will not be so well defined: time, weather, and number of people. Excessive detail in the planning should be avoided. The aim should be to plan broad areas of responsibility, chains of command and systems of communication.

Off-site services will require their own communications. On-site, the practice has been for the police, fire and medical services to be linked by radio to their own communications systems. The EOC should be available to them. Alternatively, they may wish to set up their own mobile control centres.

The off-site services will also normally need to tap into the on-site emergency internal communication. This should be allowed through the EOC. An alternative is to provide for their use portable radios as used by the emergency teams.

Each service should have its own emergency plans. The police have a Major Incident Plan that covers road, rail, aircraft and airports as well as industrial situations. The fire service probably has a number of emergency plans.

24.8.2 Emergency drills

Emergency drills are effective in familiarizing personnel with their functions. While drills with on-site personnel can be dictated by a routine, real-time simulation that involves all forces, on- and off-site are much more complicated to perform. However, the effectiveness of the plan, as well as the performance of each of the entities in the response stage can be assessed only in full-scale drills. It is common that full-scale emergency drill resulted in major changes in the plan, and sometimes it required conducting process hazard analysis in order to better understand the hazards, and the risks associated. In any case, the emergency plan should consist of a procedure for implementation of change management.

24.9 Public Relations

If a major incident occurs, it is important to provide the media with accurate information. To give no report in the press is not an option. All personnel should direct turns from the media to the spokesman. A good emergency plan will consist of a procedure that provides guidelines to answering questions. Several questions might be anticipated. The choice is between an attitude to the press that may foster informed and sympathetic reporting and one that almost guarantees ignorant and hostile comment. A company is unwise to expect sympathetic reporting unless over the long term it has built up with the press, as far as it is able, a relationship of trust based on openness about the hazards present and the preventive and protective measures adopted. It will normally be appropriate that the long-term handling of major hazard policies be done by the company's head office with reference to national policies and standards.

The following is a list of common questions that a media would query about:

(1) What happened and where?
(2) How it occurred?
(3) Was a hazardous material released and how much?
(4) What is the extent of the emergency?
(5) How long will the event last?
(6) Is the incident under control?
(7) What are the measures that are being taken to protect the public?
(8) Are there injuries and fatalities, and how many?
(9) On-going update on the emergency activities.
(10) Information on the criteria of declaring on escalation.

A periodic training of a spokesman can significantly improve the credibility and reliability of the firm's public relations.

24.10 Off-site Emergency Planning

Off-site emergency planning are developed within a jurisdiction, or a city, county or a region. An off-site emergency plan consists of procedures that address the following disciplines:

(1) Warning
(2) Communication
(3) Shelters and mass care
(4) Evacuation
(5) Fire fighting
(6) Spills of hazardous materials and petroleum products
(7) Law enforcement
(8) Health and medical services
(9) Hazard mitigation
(10) Public works
(11) Utilities
(12) Human services
(13) Search and rescue
(14) Transportation
(15) Donation management
(16) Terrorism threads.

The purpose of an off-site emergency plan is to outline strategic framework to respond to natural and man-made disasters. Since the terrorist attacks on the World Trade Center in New York on 11 September 2001, there is a significant emphasis on mutually supporting terrorism preparedness programmes, with the goal to enhance the capabilities by establishing a comprehensive programme for the full spectrum of terrorist threat and any other kinds of disasters.

The off-site emergency plan is similar in structure to the on-site emergency plan. However, coordination of off-site emergency plan requires much more energy and effort. While for on-site plans, the EOM has an authority to direct all the activities and disciplines in the plant, for off-site plans, the EOM may have partial authority only.

Warning procedures should use common channels of communication to advise the public on an emergency. However, some people who are directly threatened by the hazard may not hear and not understand the warning. It is necessary to address special needs groups such as sight and hearing impaired, and nursing home.

Communication system planning should assume that the hazards may neutralize the designated communication systems, and that additional communication equipment may be required.

Provision of shelters and mass care is a major responsibility, and a large number of parameters are involved in the process of designation of shelters. The efforts in the United States should be coordinated with the American Red Cross, which has been chartered under federal law to provide mass care in cases of natural disaster.

The characteristics of hazards, magnitude, intensity and anticipated duration are major factors in evacuation planning. Small- and large-scale evacuation should be addressed by the planner. The criteria for the decision of evacuation should be clear, and the planner should remove ambiguities from this procedure. A common assumption is that about 80% of the population at risk will respond to the first recommendation of evacuation. However, as the hazard becomes more obvious, more will respond. Some of the people will refuse to be evacuated under any circumstance. Some of them will demand that their pets be cared for too. All of these factors should be addressed, as well as the response rate at different parts of the day.

Large number of procedures, modular plans and templates are available for the disciplines listed above on the US Federal Emergency Management Agency and on states' Division of Emergency Management websites.

24.11 Transport Emergency Planning

24.11.1 Background

As described in Chapter 23, it is essential for hazardous chemicals to be transported in tanks and containers designed and maintained to high standards, for transport personnel to have any necessary training, for comparative studies of the different means of transport to be done and routes carefully selected, and for hazard studies to be carried out. Even so, it is still necessary to plan for possible transport emergencies.

As with safety in the transport of hazardous chemicals in general, so with transport emergency planning, the chemical industry has always tended to take the view that although strictly the responsibility lies with the shipper, it is very much in the interests and responsibility of the industry also to take measures to deal with transport emergencies. This attitude finds practical expression in companies' willingness to send emergency teams to situations in which their own products are not involved.

Transport emergency planning has something in common with works emergency planning, but there are some important differences. The main one is that even with careful routing, there is a vast range of locations at which the emergency can occur.

Transportation emergency planning includes the following elements:

(1) chemical data;
(2) information and labelling;
(3) incident control network;
(4) emergency procedures;
(5) emergency teams;
(6) outside services, and
(7) public relations.

The following paragraph discusses these elements.

Chemical data

Although the properties of chemicals that are shipped are usually understood well enough for most purposes, it is necessary that particular attention be paid to any property that is specially important in a transport emergency. In the Glendora incident described below, 30,000 people were evacuated because it was feared that lethal quantities of phosgene might be generated by burning vinyl chloride monomer (VCM). Although the manufacturer's expert on the spot discounted this hazard, the authorities proceeded with the evacuation. The incident led the industry to carry out research to determine more exactly the extent of the hazard from this source, which turned out to be small. Material Safety Data Sheet (MSDS) should be part of the delivery, to simplify the search for data.

Information and labelling

People involved in transportation incident need information about the chemical, but their needs differ. The amount of information required is different for the public, the personnel involved in the first few minutes and for those involved in longer term incident control and clearing up operations.

There are also different sources of information. The most accessible is the labelling of the container. Then there is usually more detailed information carried somewhere on the vehicle, if an MSDS is not reachable. The shipper and outside services, such as police and fire services, should have manuals that contain similar data. Finally, there is the manufacturer who may be contacted through the Federal Emergency Management Agency, EPA, and others. The UN classification code is commonly being used for labelling in transportation of hazardous materials.

Emergency procedures

There are certain priority actions that should be taken by the person at the scene of the incident. The priorities are as follows:

(1) keep people away;
(2) inform incident control;
(3) contain the chemical;
(4) avoid igniting the chemical, and
(5) obtain chemical data.

The communication with the EOC is important. The centre should be informed as follows:

(1) place and time of the incident;
(2) chemical involved;
(3) container condition;
(4) injuries or/and fatalities;
(5) the surrounding area (urban, rural);
(6) weather conditions;
(7) the assistance available (police, fire services), and
(8) the means of maintaining contact.

It is particularly important for the man on the spot to ensure that the control centre can keep in contact with him,

by using a cellular phone or any other communication measure. If possible, the chemical should not be allowed to get into sewers. A pool of liquid may often be rendered safer by covering it with a blanket of suitable foam.

Ignition of the material should be avoided if at all possible. Sources of ignition should be kept well away.

Some chemicals that are transported have properties that may increase the hazard of the incident. These include low boiling points, capacity for spontaneous ignition, and reaction with water.

Emergency teams

The manufacturer of a hazardous chemical normally arranges for an emergency team to be available to be sent to the scene as soon as a transport emergency is notified. In some cases this involves mutual assistance schemes.

The personnel comprising the emergency team are usually thoroughly familiar with the chemical and are trained in handling incidents. In addition to the general incident control measures already described, the emergency team usually has expertise in dealing with leaks and fires and in emptying damaged containers and clearing up.

A leak or spillage should not be ignited. If a leak has ignited, however, it may be the best policy to let it continue burning. The danger of putting out a fire without eliminating the leak is that the amount of flammables may build up and, if re-ignited, cause a more serious fire or explosion.

If other containers are present, as it typically the case in rail incidents, it may be necessary to cool these with water to prevent their overheating.

The emergency team is sent as soon as possible on receipt of notification, but several hours are likely to elapse before it reaches the scene of the incident.

24.11.3 External services

The general role of the external services such as the police and fire services has already been described. Some additional points relevant to transport emergencies may be mentioned briefly.

A transport emergency differs from emergency activities on-site. There is therefore much less scope for advance cooperation between a manufacturer and the services in his local authority area. The variety of hazardous chemicals that the services may have to handle is much greater.

Another feature of a transport emergency is that it may well occur in an urban area. This means that measures to keep people away from the scene, to divert traffic, to maintain access for emergency vehicles and possibly to evacuate the population assume particular importance.

Decisions on the advice to be given to the public, whether this be to take shelter or to evacuate, are particularly difficult. In some situations where it is not strictly necessary to involve large numbers of people, the authorities may nevertheless have little choice but to order action, unless precise information is available to them on the hazards of the chemical, particularly the toxic hazards. Likewise, information on fighting fires of the chemical is important for the fire services. In particular, the latter need to know whether the chemical reacts violently with water.

24.11.4 Rail transport

The foregoing account has been concerned primarily with road transport, but most of it is applicable to rail road transportation as well. In this case, the railway authority establishes its own procedures and trains its own personnel. Again the prime requirement from the manufacturer is full information about the chemicals.

Emergencies involving hazardous chemicals on railways tend to have some special features. One is the problem of access, particularly for fire engines. The track is often blocked by derailed rail vehicles. Another aspect is that there are usually a number of tank cars involved, with the danger of a spread of the fire/explosion. Frequently there is a hazard to other transport, such as to trains on other tracks, or to nearby roads.

24.12 Spectators

An incident that lasts for any appreciable length of time is liable to attract spectators. This is true not only of transport incidents occurring outside the site, but also of incidents on-site that are visible outside.

The effect of spectators is two-fold. The number of people at risk may be considerably increased, and the passages for the emergency services can become congested, with consequent delays.

The problem of spectators has been investigated by Hymes (1985 LPB 65), who describes quite a large number of incidents in which spectators suffered injury. Some of the cases cited involve people who became exposed to the threat and stood watching it develop instead of making their escape, whilst in others they were attracted to the incident as sightseers. Some of the incidents that he describes are summarized in Section 24.13.

The control of spectators is therefore an essential part of an off-site emergency plan and of a transport emergency plan. The responsibility for such control rests with the police.

24.13 Emergency Incidents

24.13.1 Historical data

Some information on emergencies in the process industries has been obtained in the course of a study on human factors as a cause of pipe work failures by Bellamy, Geyer and Astley (1989).

For failures of mitigation, the number of incidents due to each cause were as follows: delay, 23 (45%); design deficiency, 14 (27.5%) and lack of resources, 14 (27.5%). Examples in the first category were lack of procedures for handling the incident and defective fire fighting equipment; in the second category, examples were a layout leaving insufficient space for fire water jets to be directed at the source of the fire and the inaccessibility of shut-down equipment due to the leak itself and in the third category, examples were lack of manpower and lack of equipment.

The information on the implementation of emergency plans and on evacuation in this study is ambiguous. On the one hand, there were 42 cases recorded in which an emergency plan was put into effect. In 27 of these cases, the plan implemented was the on-site plan and in 11 it was the off-site plan; in the 4 remaining cases, the plan was not specified. On the other hand, there were 30 cases in which there was evacuation, either on-site or off-site or both, with 13 on-site and 24 off-site evacuations.

24.13.2 Incidents involving evacuation and/or shelter

There have been a number of instructive incidents involving evacuation and/or shelter. They include those at

La Barre in 1961, Glendora in 1969, Potchefstroom in 1973, Houston in 1976, and Mississauga in 1979.

In 1961, a rail crash occurred at La Barre, Louisiana, involving a chlorine rail tank car, only 50 yd from a house. A father was looking after a baby in the house, the infant began to choke and gasp, and the frantic father carried it outside, where the gas concentration was higher still. The child died in hospital.

In 1969, a group of eight rail tank cars containing VCM were involved in a crash at Glendora, Mississippi, and one started to leak. That evening one of the tank cars ruptured, with subsequent ignition of the leak. A heavy fog was observed over the area and it was considered that it might be VCM. The responders stated that in a VCM fire, phosgene could be formed. Further advice was sought from the manufacturer's representative, who stated that the principal problem was likely to be HCl and smoke, and university chemists, who stated that burning VCM could create phosgene that was potentially dangerous up to a radius of 35 miles. An evacuation was initiated involving some 30,000 people.

In 1973, a sudden failure occurred in an anhydrous ammonia storage tank at Potchefstroom in South Africa. Workers in a building 80 m from the release survived, but people who left their houses 180–200 m from it died.

In 1976 at Houston, Texas, a tank truck carrying 19 tons of anhydrous ammonia ruptured at a highway intersection. The resultant gas cloud enveloped the Houston Post building but the workers inside were not affected. Outside, 94 people caught in the cloud were injured, of whom 5 died.

24.13.3 Mississauga

A very large evacuation occurred on Saturday, 10 November 1979 at Mississauga, near Toronto. At 23.52 p.m., a train crashed and several propane rail tank cars exploded. The train manifest was found, but it was in code. A strong smell of chlorine was detected. At 01.30 the next morning, a readable version of the manifest was obtained. A rail tank car containing some 90 te of chlorine was identified as being in the train and it was concluded that this car was amongst the burning wreckage. At 03.00, the decision was taken to evacuate the surrounding population. An evacuation was begun which involved a total of about 215,000 people. The chlorine tank car was identified by helicopter and found to have a visible hole in it. At 09.00 on Tuesday morning, an initial attempt was made to plug the hole, but this failed; a second attempt later was successful. The tank was subsequently emptied. During Tuesday afternoon 143,000 evacuees were allowed to return to their homes in the areas more distant from the crash. The rest returned only after a total absence of 6 days.

24.13.4 Incidents involving spectators

The following incidents have been described in the study of spectators. At Deer Lake, Pennsylvania, in 1959, a road tanker carrying LPG was struck by a following truck in a wet street. LPG was released and ignited, engulfing the rear of the tanker. Fire services arrived, but expended water on a nearby building, and in due course the tanker suffered a boiling liquid expanding vapour explosion (BLEVE). Fragments, which included most of the tank, killed 11 spectators and injured 10 more. Emergency services were hampered both before the rupture and after it.

At Meldrin, Georgia, in 1959, a rail tank car suffered a partial rupture near a picnic site. A large gas cloud spread and for some time did not ignite. When it did ignite, a flash fire occurred. There were 23 dead, many of whom were found in their cars. Emergency services were greatly hampered because the site was remote and served only by a dirt road congested by spectators and relatives of the casualties.

At Kingman, Arizona, in 1973, a rail tank car carrying propane developed a leak that ignited. Despite police discouragement, a large crowd of spectators jostled to get a view. In due course the tank car underwent a BLEVE and a huge fireball erupted. Some 90 spectators 300 m away suffered injury.

At San Carlos de la Rapita, Spain, in 1978, a road tanker carrying propylene past the Los Alfaques campsite ruptured with a small explosion. A flammable gas cloud began to spread through the site. Campers who did not appreciate that the full hazard from the burning tanker had yet to develop stood around bemused whilst escape was still possible. Many wore bathing suits or light beachwear. There followed a major explosion and flash fire. The eventual death toll was about 210, a large proportion from severe burns.

Other incidents in which many of the deaths occurred among spectators are those at Texas City in 1947, and Caracas, Venezuela, in 1982. In the Texas City disaster, a fire developed aboard a ship in the harbour. The ship was carrying ammonium nitrate. In due course the ship disintegrated in an enormous explosion, killing all those in the dock, including firemen and spectators. This explosion and a further one in another ammonium nitrate carrier killed 552 people and injured another 3000.

The Caracas disaster involved a fire in an oil tank sited on a hill. A boilover occurred and the burning oil flowed down the hill. Forty firefighters were killed, together with many civil defence workers and spectators, giving a fatality toll of 153 with 7 missing.

24.14 Recovery

A recovery from a major emergency event is a process that requires major efforts and takes a significant period of time. The extant of the efforts is a function of parameters such as the resources that are required to rebuild and renovate, requirements of the enforcing agencies, personnel commitment, length of process purchasing and delivery, and more. The most important factor in the recovery process is leadership, and therefore the recovery management should be selected carefully. Recovery process consists of a very large number of details. The recovery manager needs to establish a recovery team that will represents all the disciplines in the plant. The team should include representatives from engineering, maintenance, production, purchasing, ES&H, legal department and other, as the circumstances require.

Following the emergency phase, the site should be secured and preservation of evidence and data collection need to take place. Parallel to these activities, human resources should provide assistance to employees and victim families. Incident that resulted in fatalities will require professional psychological support as well. Portion of the efforts of assessment of the damage to the environment and property and incident investigation could be integrated to avoid repetition of some of the phases. Clean up activities should be coordinated extremely carefully to avoid removal of evidence. It is recommended to consider involvement of the media in the process in order to improve public relation, and recovery of the damaged image.

24.15 Regulations and Standards

24.15.1 Regulations

In the United States, the OSHA established the Process Safety Management (PSM) requirements, following the issuance of the Clean Air Act section 112(r). The US EPA followed by issuance of the Risk Management Program (RMP), for Chemical Accidents Release Prevention.

The Health and Safety Executive in United Kingdom established guidance for writing on- and off-site emergency plans 'HS (G) 191 Emergency planning for major accidents: Control of Major Accident Hazards (COMAH) regulations 1999'. OSHA PSM standard consists of 12 elements. CFR 1910.38 in the standard states the requirements for emergency planning. However, other OSHA requirements such as CFR 1910.156 that establish requirements for training Fire Brigades, and CFR 1910.146 that states the requirement for training emergencies in confined spaces are related as well.

EPA RMP rule is based on industrial codes and standards, and it requires companies to develop an RMP if they handle hazardous substances that exceed a certain threshold. The programme is required to include the following sections:

(1) Hazard assessment based on the potential effects, an accident history of the last 5 years, and an evaluation of worst-case and alternative accidental releases.
(2) Prevention programme.
(3) Emergency response programme.

On the other hand, EPA requires that the communities will put the efforts from their side. The EPA Emergency Planning and Community Right-to-Know Act (EPCRA) establishes requirements for the industry, Federal, State and local governments, on reporting on hazardous and toxic chemicals.

EPCRA consists of four parts:

(1) Emergency planning (Section 301–303),
(2) Emergency release notification (Section 304),
(3) Hazardous chemical storage reporting requirements (Sections 311–312) and
(4) Toxic chemical release inventory (Section 313).

The purpose of the EPCRA is to help increasing awareness in the public on chemicals at individual facilities, their uses and releases into the environment. The act states that every community in the United States must be part of a comprehensive emergency plan.

Both, the Department of Transportation and the Department of Energy, address emergency planning. Information is available on their websites.

24.15.2 Standards

A large number of standards that addresses process safety and are relevant to process safety are available. However, the NFPA published a variety of standards that are useful in emergency planning and training for emergencies. List of NFPA publications is given in Appendix A. Similarly, the National Institute of Safety and Health and the American National Standards Institute (ANSI) provide guidelines and standards that can be helpful in planning for emergencies.

24.16 Literature

The references in the list below were considered during the review of this chapter:

1. DENNISON, M.S., (1994) *OSHA and EPA Process Safety Management Requirements: A Practical Guide for Compliance*, pp. 174–184 (New York: VNR Pub.).
2. AMERICAN INSTITUTE OF CHEMICAL ENGINEERS, (1995) *Guidelines for Technical Planning for On-Site Emergencies*, pp. 1–294 (New York).
3. AMERICAN INSTITUTE OF CHEMICAL ENGINEERS, (1995) *Guidelines for Process Safety Fundamentals in General Plant Operations,* pp. 285–303 (New York).
4. AMERICAN INSTITUTE OF CHEMICAL ENGINEERS, (1992) *Guidelines for Investigating Chemical Process Incidents* (New York).
5. AMERICAN SOCIETY OF SAFETY ENGINEERS, (2001) 'Criteria for Accepted Practices in Safety, Health, and Environmental Training', (Des Plaines, IL: ANSI Z490.1).
6. RE VELLE, J.B. and STEPHENSON, J. (1995) *Safety Training Methods: Practical Solutions for the Next Millennium*, 2nd ed., pp. 236–268 (New York: John Wiley & Sons, Inc.).

Appendix A: NFPA Publications

NFPA 1	Uniform Fire Code
NFPA 10	Standard for Portable Fire Extinguishers
NFPA 11	Standard for Low-, Medium-, and High-Expansion Foam Systems
NFPA 11A	Standard for Medium- and High-Expansion Foam Systems
NFPA 12	Standard on Carbon dioxide Extinguishing Systems
NFPA 12A	Standard on Halon 1301 Fire Extinguishing Systems
NFPA 13	Standard for the Installation of Sprinkler Systems
NFPA 13D	Standard for the Installation of Sprinkler Systems in One- and Two-Family Dwellings and Manufactured Homes
NFPA 13E	Recommended Practice for Fire Department Operations in Properties Protected by Sprinkler and Standpipe Systems
NFPA 13R	Standard for the Installation of Sprinkler Systems in Residential Occupancies up to and Including Four Stories in Height
NFPA 14	Standard for the Installation of Standpipe, Private Hydrants, and Hose Systems
NFPA 15	Standard for Water Spray Fixed Systems for Fire Protection
NFPA 16	Standard for the Installation of Foam-Water Sprinkler and Foam-Water Spray Systems
NFPA 17	Standard for Dry Chemical Extinguishing Systems
NFPA 17A	Standard for Wet Chemical Extinguishing Systems
NFPA 18	Standard on Wetting Agents
NFPA 20	Standard for the Installation of Stationary Pumps for Fire Protection
NFPA 22	Standard for Water Tanks for Private Fire Protection
NFPA 24	Standard for the Installation of Private Fire Service Mains and Their Appurtenances

NFPA 25	Standard for the Inspection, Testing, and Maintenance of Water-Based Fire Protection Systems
NFPA 30	Flammable and Combustible Liquids Code
NFPA 30A	Code for Motor Fuel Dispensing Facilities and Repair Garages
NFPA 30B	Code for the Manufacture and Storage of Aerosol Products
NFPA 31	Standard for the Installation of Oil-Burning Equipment
NFPA 32	Standard for Drycleaning Plants
NFPA 33	Standard for Spray Application Using Flammable or Combustible Materials
NFPA 34	Standard for Dipping and Coating Processes Using Flammable or Combustible Liquids
NFPA 35	Standard for the Manufacture of Organic Coatings
NFPA 36	Standard for Solvent Extraction Plants
NFPA 37	Standard for the Installation and Use of Stationary Combustion Engines and Gas Turbines
NFPA 40	Standard for the Storage and Handling of Cellulose Nitrate Film
NFPA 42	Code for the Storage of Pyroxylin Plastic
NFPA 45	Standard on Fire Protection for Laboratories Using Chemicals
NFPA 50	Standard for Bulk Oxygen Systems at Consumer Sites
NFPA 50A	Standard for Gaseous Hydrogen Systems at Consumer Sites
NFPA 50B	Standard for Liquefied Hydrogen Systems at Consumer Sites
NFPA 51	Standard for the Design and Installation of Oxygen-Fuel Gas Systems for Welding, Cutting, and Allied Processes
NFPA 51A	Standard for Acetylene Cylinder Charging Plants
NFPA 51B	Standard for Fire Prevention During Welding, Cutting, and Other Hot Work
NFPA 52	Compressed Natural Gas (CNG) Vehicular Fuel Systems Code
NFPA 53	Recommended Practice on Materials, Equipment and Systems Used in Oxygen-Enriched Atmospheres
NFPA 54	National Fuel Gas Code
NFPA 55	Standard for the Storage, Use, and Handling of Compressed Gases and Cryogenic Fluids in Portable and Stationary Containers, Cylinders, and Tanks
NFPA 57	Liquefied Natural Gas (LNG) Vehicular Fuel Systems Code
NFPA 58	Liquefied Petroleum Gas Code
NFPA 59	Utility LP-Gas Plant Code
NFPA 59A	Standard for the Production, Storage, and Handling of Liquefied Natural Gas (LNG)
NFPA 61	Standard for the Prevention of Fires and Dust Explosions in Agricultural and Food Processing Facilities
NFPA 68	Guide for Venting of Deflagrations
NFPA 69	Standard on Explosion Prevention Systems
NFPA 70	National Electrical Code® National Electrical Codë
NFPA 70A	Electrical Code for One- and Two-Family Dwellings and Mobile Homes
NFPA 70B	Recommended Practice for Electrical Equipment Maintenance
NFPA 70E	Standard for Electrical Safety Requirements for Employee Workplaces
NFPA 72	National Fire Alarm Codë
NFPA 73	Electrical Inspection Code for Existing Dwellings
NFPA 75	Standard for the Protection of Information Technology Equipment
NFPA 76	Recommended Practice for the Fire Protection of Telecommunications Facilities
NFPA 77	Recommended Practice on Static Electricity
NFPA 79	Electrical Standard for Industrial Machinery
NFPA 80	Standard for Fire Doors and Fire Windows
NFPA 80A	Recommended Practice for Protection of Buildings from Exterior Fire Exposures
NFPA 82	Standard on Incinerators and Waste and Linen Handling Systems and Equipment
NFPA 85	Boiler and Combustion Systems Hazards Code
NFPA 86	Standard for Ovens and Furnaces
NFPA 88A	Standard for Parking Structures
NFPA 90A	Standard for the Installation of Air-Conditioning and Ventilating Systems
NFPA 90B	Standard for the Installation of Warm Air Heating and Air-Conditioning Systems
NFPA 91	Standard for Exhaust Systems for Air Conveying of Vapors, Gases, Mists, and Noncombustible Particulate Solids
NFPA 92A	Recommended Practice for Smoke-Control Systems
NFPA 92B	Guide for Smoke Management Systems in Malls, Atria, and Large Areas
NFPA 96	Standard for Ventilation Control and Fire Protection of Commercial Cooking Operations
NFPA 97	Standard Glossary of Terms Relating to Chimneys, Vents, and Heat-Producing Appliances
NFPA 99	Standard for Health Care Facilities
NFPA 99B	Standard for Hypobaric Facilities
NFPA 99C	Standard on Gas and Vacuum Systems
NFPA 101	Life Safety Codë
NFPA 101A	Guide on Alternative Approaches to Life Safety
NFPA 101B	Code for Means of Egress for Buildings and Structures
NFPA 102	Standard for Grandstands, Folding and Telescopic Seating, Tents, and Membrane Structures
NFPA 105	Standard for the Installation of Smoke Door Assemblies
NFPA 110	Standard for Emergency and Standby Power Systems
NFPA 111	Standard on Stored Electrical Energy Emergency and Standby Power Systems
NFPA 115	Standard on Laser Fire Protection
NFPA 120	Standard for Coal Preparation Plants
NFPA 121	Standard on Fire Protection for Self-Propelled and Mobile Surface Mining Equipment
NFPA 122	Standard for Fire Prevention and Control in Underground Metal and Nonmetal Mines
NFPA 123	Standard for Fire Prevention and Control in Underground Bituminous Coal Mines

NFPA 130 Standard for Fixed Guideway Transit and Passenger Rail Systems
NFPA 140 Standard on Motion Picture and Television Production Studio Soundstages and Approved Production Facilities
NFPA 150 Standard on Fire Safety in Racetrack Stables
NFPA 160 Standard for Flame Effects Before an Audience
NFPA 170 Standard for Fire Safety Symbols
NFPA 203 Guide on Roof Coverings and Roof Deck Constructions
NFPA 204 Standard for Smoke and Heat Venting
NFPA 211 Standard for Chimneys, Fireplaces, Vents, and Solid Fuel-Burning Appliances
NFPA 214 Standard on Water-Cooling Towers
NFPA 220 Standard on Types of Building Construction
NFPA 221 Standard for Fire Walls and Fire Barrier Walls
NFPA 225 Model Manufactured Home Installation Standard
NFPA 230 Standard for the Fire Protection of Storage
NFPA 232 Standard for the Protection of Records
NFPA 241 Standard for Safeguarding Construction, Alteration, and Demolition Operations
NFPA 251 Standard Methods of Tests of Fire Endurance of Building Construction and Materials
NFPA 252 Standard Methods of Fire Tests of Door Assemblies
NFPA 253 Standard Method of Test for Critical Radiant Flux of Floor Covering Systems Using a Radiant Heat Energy Source
NFPA 255 Standard Method of Test of Surface Burning Characteristics of Building Materials
NFPA 256 Standard Methods of Fire Tests of Roof Coverings
NFPA 257 Standard on Fire Test for Window and Glass Block Assemblies
NFPA 258 Recommended Practice for Determining Smoke Generation of Solid Materials
NFPA 259 Standard Test Method for Potential Heat of Building Materials
NFPA 260 Standard Methods of Tests and Classification System for Cigarette Ignition Resistance of Components of Upholstered Furniture
NFPA 261 Standard Method of Test for Determining Resistance of Mock-Up Upholstered Furniture Material Assemblies to Ignition by Smoldering Cigarettes
NFPA 262 Standard Method of Test for Flame Travel and Smoke of Wires and Cables for Use in Air-Handling Spaces
NFPA 265 Standard Methods of Fire Tests for Evaluating Room Fire Growth Contribution of Textile Coverings on Full Height Panels and Walls
NFPA 268 Standard Test Method for Determining Ignitibility of Exterior Wall Assemblies Using a Radiant Heat Energy Source
NFPA 269 Standard Test Method for Developing Toxic Potency Data for Use in Fire Hazard Modeling
NFPA 270 Standard Test Method for Measurement of Smoke Obscuration Using a Conical Radiant Source in a Single Closed Chamber
NFPA 271 Standard Method of Test for Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter
NFPA 272 Standard Method of Test for Heat and Visible Smoke Release Rates for Upholstered Furniture Components or Composites and Mattresses Using an Oxygen Consumption Calorimeter
NFPA 273 Standard Method of Test for Determining the Degrees of Combustibility of Building Materials
NFPA 274 Standard Test Method to Evaluate Fire Performance Characteristics of Pipe Insulation
NFPA 284 Standard Test Method for Mattresses for Correctional Occupancies
NFPA 285 Standard Method of Test for the Evaluation of Flammability Characteristics of Exterior Non-Load-Bearing Wall Assemblies Containing Combustible Components Using the Intermediate-Scale, Multistory Test Apparatus
NFPA 286 Standard Methods of Fire Tests for Evaluating Contribution of Wall and Ceiling Interior Finish to Room Fire Growth
NFPA 287 Standard Test Methods for Measurement of Flammability of Materials in Cleanrooms Using a Fire Propagation Apparatus (FPA)
NFPA 288 Standard Method of Fire Tests of Floor Fire Door Assemblies Installed Horizontally in Fire Resistance Rated Floor Systems
NFPA 289 Standard Method of Fire Test for Room Fire Growth Contribution of Individual Fuel Packages
NFPA 290 Standard for Fire Testing of Passive Protection Materials for Use on LP-Gas Containers
NFPA 291 Recommended Practice for Fire Flow Testing and Marking of Hydrants
NFPA 301 Code for Safety to Life from Fire on Merchant Vessels
NFPA 302 Fire Protection Standard for Pleasure and Commercial Motor Craft
NFPA 303 Fire Protection Standard for Marinas and Boatyards
NFPA 306 Standard for the Control of Gas Hazards on Vessels
NFPA 307 Standard for the Construction and Fire Protection of Marine Terminals, Piers, and Wharves
NFPA 312 Standard for Fire Protection of Vessels During Construction, Repair, and Lay-Up
NFPA 318 Standard for the Protection of Semiconductor Fabrication Facilities
NFPA 326 Standard for the Safeguarding of Tanks and Containers for Entry, Cleaning, or Repair
NFPA 329 Recommended Practice for Handling Releases of Flammable and Combustible Liquids and Gases
NFPA 385 Standard for Tank Vehicles for Flammable and Combustible Liquids
NFPA 402 Guide for Aircraft Rescue and Fire Fighting Operations
NFPA 403 Standard for Aircraft Rescue and Fire Fighting Services at Airports
NFPA 405 Recommended Practice for the Recurring Proficiency Training of Aircraft Rescue and Fire-Fighting Services

NFPA 407	Standard for Aircraft Fuel Servicing
NFPA 408	Standard for Aircraft Hand Portable Fire Extinguishers
NFPA 409	Standard on Aircraft Hangars
NFPA 410	Standard on Aircraft Maintenance
NFPA 412	Standard for Evaluating Aircraft Rescue and Fire Fighting Foam Equipment
NFPA 414	Standard for Aircraft Rescue and Fire Fighting Vehicles
NFPA 415	Standard on Airport Terminal Buildings, Fueling Ramp Drainage, and Loading Walkways
NFPA 418	Standard for Heliports
NFPA 422	Guide for Aircraft Accident Response
NFPA 423	Standard for Construction and Protection of Aircraft Engine Test Facilities
NFPA 424	Guide for Airport/Community Emergency Planning
NFPA 430	Code for the Storage of Liquid and Solid Oxidizers
NFPA 432	Code for the Storage of Organic Peroxide Formulations
NFPA 434	Code for the Storage of Pesticides
NFPA 450	Guide for Emergency Medical Services and Systems
NFPA 471	Recommended Practice for Responding to Hazardous Materials Incidents
NFPA 472	Standard for Professional Competence of Responders to Hazardous Materials Incidents
NFPA 473	Standard for Competencies for EMS Personnel Responding to Hazardous Materials Incidents
NFPA 484	Standard for Combustible Metals, Metal Powders, and Metal Dusts
NFPA 490	Code for the Storage of Ammonium Nitrate
NFPA 495	Explosive Materials Code
NFPA 496	Standard for Purged and Pressurized Enclosures for Electrical Equipment
NFPA 497	Recommended Practice for the Classification of Flammable Liquids, Gases, or Vapors and of Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas
NFPA 498	Standard for Safe Havens and Interchange Lots for Vehicles Transporting Explosives
NFPA 499	Recommended Practice for the Classification of Combustible Dusts and of Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas
NFPA 501	Standard on Manufactured Housing
NFPA 501A	Standard for Fire Safety Criteria for Manufactured Home Installations, Sites, and Communities
NFPA 502	Standard for Road Tunnels, Bridges, and Other Limited Access Highways
NFPA 505	Fire Safety Standard for Powered Industrial Trucks Including Type Designations, Areas of Use, Conversions, Maintenance, and Operation
NFPA 520	Standard on Subterranean Spaces
NFPA 550	Guide to the Fire Safety Concepts Tree
NFPA 551	Guide for the Evaluation of Fire Risk Assessments
NFPA 555	Guide on Methods for Evaluating Potential for Room Flashover
NFPA 556	Guide on Methods for Evaluating Fire Hazard and Fire Risk of Vehicular Furnishing
NFPA 560	Standard for the Storage, Handling, and Use of Ethylene Oxide for Sterilization and Fumigation
NFPA 600	Standard on Industrial Fire Brigades
NFPA 601	Standard for Security Services in Fire Loss Prevention
NFPA 610	Guide for Emergency and Safety Operations at Motorsports Venues
NFPA 654	Standard for the Prevention of Fire and Dust Explosions from the Manufacturing, Processing, and Handling of Combustible Particulate Solids
NFPA 655	Standard for Prevention of Sulfur Fires and Explosions
NFPA 664	Standard for the Prevention of Fires and Explosions in Wood Processing and Woodworking Facilities
NFPA 701	Standard Methods of Fire Tests for Flame Propagation of Textiles and Films
NFPA 703	Standard for Fire Retardant Impregnated Wood and Fire Retardant Coatings for Building Materials
NFPA 704	Standard System for the Identification of the Hazards of Materials for Emergency Response
NFPA 705	Recommended Practice for a Field Flame Test for Textiles and Films
NFPA 720	Recommended Practice for the Installation of Household Carbon Monoxide (CO) Warning Equipment
NFPA 730	Guide for Electronic Premises Security
NFPA 731	Standard for the Installation of Electronic Premises Security Systems
NFPA 750	Standard on Water Mist Fire Protection Systems
NFPA 780	Standard for the Installation of Lightning Protection Systems
NFPA 801	Standard for Fire Protection for Facilities Handling Radioactive Materials
NFPA 804	Standard for Fire Protection for Advanced Light Water Reactor Electric Generating Plants
NFPA 805	Performance-Based Standard for Fire Protection for Light Water Reactor Electric Generating Plants
NFPA 820	Standard for Fire Protection in Wastewater Treatment and Collection Facilities
NFPA 850	Recommended Practice for Fire Protection for Electric Generating Plants and High Voltage Direct Current Converter Stations
NFPA 851	Recommended Practice for Fire Protection for Hydroelectric Generating Plants
NFPA 853	Standard for the Installation of Stationary Fuel Cell Power Plants
NFPA 900	Building Energy Code
NFPA 901	Standard Classifications for Incident Reporting and Fire Protection Data
NFPA 906	Guide for Fire Incident Field Notes
NFPA 909	Code for the Protection of Cultural Resources
NFPA 914	Code for Fire Protection of Historic Structures

NFPA 921 Guide for Fire and Explosion Investigations
NFPA 1000 Standard for Fire Service Professional Qualifications Accreditation and Certification Systems
NFPA 1001 Standard for Fire Fighter Professional Qualifications
NFPA 1002 Standard for Fire Apparatus Driver/Operator Professional Qualifications
NFPA 1003 Standard for Airport Fire Fighter Professional Qualifications
NFPA 1006 Standard for Rescue Technician Professional Qualifications
NFPA 1021 Standard for Fire Officer Professional Qualifications
NFPA 1031 Standard for Professional Qualifications for Fire Inspector and Plan Examiner
NFPA 1033 Standard for Professional Qualifications for Fire Investigator
NFPA 1035 Standard for Professional Qualifications for Public Fire and Life Safety Educator
NFPA 1041 Standard for Fire Service Instructor Professional Qualifications
NFPA 1051 Standard for Wildland Fire Fighter Professional Qualifications
NFPA 1061 Standard for Professional Qualifications for Public Safety Telecommunicator
NFPA 1071 Standard for Emergency Vehicle Technician Professional Qualifications
NFPA 1081 Standard for Industrial Fire Brigade Member Professional Qualifications
NFPA 1122 Code for Model Rocketry
NFPA 1123 Code for Fireworks Display
NFPA 1124 Code for the Manufacture, Transportation, Storage and Retail Sales of Fireworks and Pyrotechnic Articles
NFPA 1125 Code for the Manufacture of Model Rocket and High Power Rocket Motors
NFPA 1126 Standard for the Use of Pyrotechnics before a Proximate Audience
NFPA 1127 Code for High Power Rocketry
NFPA 1141 Standard for Fire Protection in Planned Building Groups
NFPA 1142 Standard on Water Supplies for Suburban and Rural Fire Fighting
NFPA 1143 Standard for Wildland Fire Management
NFPA 1144 Standard for Protection of Life and Property from Wildfire
NFPA 1145 Guide for the Use of Class A Foams in Manual Structural Fire Fighting
NFPA 1150 Standard on Fire-Fighting Foam Chemicals for Class A Fuels in Rural, Suburban, and Vegetated Areas
NFPA 1192 Standard on Recreational Vehicles
NFPA 1194 Standard for Recreational Vehicle Parks and Campgrounds
NFPA 1201 Standard for Developing Fire Protection Services for the Public
NFPA 1221 Standard for the Installation, Maintenance, and Use of Emergency Services Communications Systems
NFPA 1250 Recommended Practice in Emergency Service Organization Risk Management
NFPA 1401 Recommended Practice for Fire Service Training Reports and Records
NFPA 1402 Guide to Building Fire Service Training Centers
NFPA 1403 Standard on Live Fire Training Evolutions
NFPA 1404 Standard for Fire Service Respiratory Protection Training
NFPA 1405 Guide for Land-Based Fire Fighters Who Respond to Marine Vessel Fires
NFPA 1410 Standard on Training for Initial Emergency Scene Operations
NFPA 1451 Standard for a Fire Service Vehicle Operations Training Program
NFPA 1452 Guide for Training Fire Service Personnel to Conduct Dwelling Fire Safety Surveys
NFPA 1500 Standard on Fire Department Occupational Safety and Health Program
NFPA 1521 Standard for Fire Department Safety Officer
NFPA 1561 Standard on Emergency Services Incident Management System
NFPA 1581 Standard on Fire Department Infection Control Program
NFPA 1582 Standard on Comprehensive Occupational Medical Program for Fire Departments
NFPA 1583 Standard on Health Related Fitness Programs for Fire Fighters
NFPA 1584 Recommended Practice on the Rehabilitation for Members Operating at Incident Scene Operations and Training Exercises
NFPA 1600 Standard for Disaster/Emergency Management and Business Continuity Programs
NFPA 1620 Recommended Practice for Pre-Incident Planning
NFPA 1670 Standard on Operations and Training for Technical Rescue Incidents
NFPA 1710 Standard for the Organization and Deployment of Fire Suppression Operations, Emergency Medical Operations, and Special Operations to the Public by Career Fire Departments
NFPA 1720 Standard for the Organization and Deployment of Fire Suppression Operations, Emergency Medical Operations and Special Operations to the Public by Volunteer Fire Departments
NFPA 1851 Standard on Selection, Care, and Maintenance of Structural Fire Fighting Protective Ensembles
NFPA 1852 Standard on Selection, Care, and Maintenance of Open-Circuit SCBA
NFPA 1901 Standard for Automotive Fire Apparatus
NFPA 1906 Standard for Wildland Fire Apparatus
NFPA 1911 Standard for Service Tests of Fire Pump Systems on Fire Apparatus
NFPA 1912 Standard for Fire Apparatus Refurbishing
NFPA 1914 Standard for Testing Fire Department Aerial Devices
NFPA 1915 Standard for Fire Apparatus Preventative Maintenance Program
NFPA 1925 Standard on Marine Fire Fighting Vessels
NFPA 1931 Standard on Design of and Design Verification Tests for Fire Department Ground Ladders
NFPA 1932 Standard on Use, Maintenance and Service Testing of Fire Department Ground Ladders
NFPA 1936 Standard on Powered Rescue Tool Systems

NFPA 1951	Standard on Protective Ensemble for USAR Operations
NFPA 1961	Standard for Fire Hose
NFPA 1962	Standard for the Inspection, Care and Use of Fire Hose, Couplings and Nozzles; and the Service Testing of Fire Hose
NFPA 1963	Standard for Fire Hose Connections
NFPA 1964	Standard for Spray Nozzles
NFPA 1965	Standard for Fire Hose Appliances
NFPA 1971	Standard on Protective Ensemble for Structural Fire Fighting
NFPA 1975	Standard on Station/Work Uniforms for Fire and Emergency Services
NFPA 1976	Standard on Protective Ensemble for Proximity Fire Fighting
NFPA 1977	Standard on Protective Clothing and Equipment for Wildland Fire Fighting
NFPA 1981	Standard on Open-Circuit Self-Contained Breathing Apparatus for Fire and Emergency Services
NFPA 1982	Standard on Personal Alert Safety Systems (PASS)
NFPA 1983	Standard on Fire Service Life Safety Rope and System Components
NFPA 1989	Standard on Breathing Air Quality for Fire and Emergency Services Respiratory Protection
NFPA 1991	Standard on Vapor-Protective Ensembles for Hazardous Materials Emergencies
NFPA 1992	Standard on Liquid Splash-Protective Ensembles and Clothing for Hazardous Materials Emergencies
NFPA 1994	Standard on Protective Ensembles for Chemical/Biological Terrorism Incidents
NFPA 1999	Standard on Protective Clothing for Emergency Medical Operations
NFPA 2001	Standard on Clean Agent Fire Extinguishing Systems
NFPA 2010	Standard on Aerosol Fire Extinguishing Systems
NFPA 2112	Standard on Flame-Resistant Garments for Protection of Industrial Personnel Against Flash Fire
NFPA 2113	Standard on Selection, Care, Use, and Maintenance of Flame-Resistant Garments for Protection of Industrial Personnel Against Flash Fire
NFPA 5000	NFPA Building Construction and Safety Code

25 Personal Safety

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The majority of injuries or deaths on process plants are the result not of high technology but of quite simple situations. The number of people involved in a single accident is usually only one or two. Thus, although loss prevention is particularly concerned with technical aspects, it is appropriate nevertheless to devote some consideration to hazards to the person and to their control.

Moreover, the loss prevention approach has a contribution to make in this area also. The same management discipline is required to deliver good performance in the personal safety area as in that of high technology. Three aspects appear particularly relevant: formal systems and procedures, hazard identification and hazard assessment.

In addition to injuries from accidents, workers may also suffer impairment of health which sometimes becomes apparent only over a long period. It is necessary, therefore, to make some mention of this type of hazard and its control by occupational health measures.

Personal safety is dealt with in a large number of texts, which include *Safety and Management* by the Association of British Chemical Manufacturers (ABCM) (1964/3), *Industrial Safety Handbook* (Handley, 1969, 1977), *Industrial Hazard and Safety Handbook* (R. King and Magid, 1979), *Safety and Accident Prevention in Chemical Operations* (H.H. Fawcett and Wood, 1982), and *Safety at Work* (Ridley, 1993–) and *Safety in the Process Industries* (R. King, 1990). Selected references on personal health and safety are given in Table 25.1.

The general nature of the problem may be seen from the injury figures given in the *Health and Safety Statistics 1990/91* (HSE, 1992b) and shown in Table 25.2. These data refer to general industrial accidents and need to be supplemented for the chemical industry by data for that industry. These are reported on an occasional rather than an annual basis. Some accident data given in the *Annual Report* of HM Chief Inspector of Factories for 1985 are shown in Table 25.3.

The overall approach in questions of personal safety should always be, in order of descending preference, (1) hazard elimination, (2) hazard control and (3) personal protection. The principle of hazard elimination and control before resort to personal protection is a recurring theme.

Another recurring theme in personal safety is the need for thorough training and for effective supervision. The objectives of training should include not only the ability to use equipment and perform tasks, but also the understanding and motivation to do the work properly and safely. In other words, the worker should be convinced as well as instructed. Most of the hazards and activities described in this chapter have some training implications. The importance of training cannot be overemphasized. Similarly, it is essential to have good supervision so that malpractices are stopped and procedures are enforced.

25.1 Human Factors

Much can be done to reduce accidents by proper design of the work situation. This is the province of human factors. An account of human factors in general and of its application to the job of the process operator in particular is given in Chapter 14. Discussion here is confined to those aspects which are particularly relevant to personal accidents.

Guidance on human factors aspects is given in HS(G) 48 *Human Factors in Industrial Safety* (HSE, 1989). Further accounts are given in *Human Factors Engineering* (McCormick, 1957b), *Human Engineering Guide to*

Table 25.1 *Selected references on personal health and safety*

American Petroleum Institute (API) (EA-7402); Fire Protection Association (FPA) (S9, S10); HM Chief Inspector of Factories (annual); National Institute of Industrial Psychology (n.d.); OSHA (n.d./3, OSHA 2237, 1990/6); RoSPA (IS/106); MCA (1962–/1–4); M.E. Webb (1962); D.B. Campbell (1965); Berry (1969, 1977); Kershaw (1969); International Labour Office (ILO) (1972, 1980b); Robens (1972); McCormick (1974); Bond and Bryans (1975); PLTB (1975 Safety Training Guide 1); Kershaw and Symons (1977); Atherley (1978); R. King and Magid (1979); Bulloff (1987); H.E. Nelson (1987); National Fire Protection Association (NFPA) (1991 NFPA 101, 1992 NFPA 101M, 1994/40)

Human factors (see also Tables 14.1, 14.2 and 14.11) Hands (1969); American Industrial Hygiene Association (AIHA) (1971/1); Singleton (1976b); Stoecker (1976); Atherley (1977b); Dumitriu (1977); Hale and Glendon (1987); Health and Safety Executive (HSE) (1989 HS(G) 48); ACGIH (1992/76)

Occupational hygiene, industrial hygiene ACGIH (Appendix 28); ASTM (STP 164); Gauvain (n.d.); HSE (Appendix 28 Medical, SHW Leaflets, SIR 8, 1977e, 1982 HS(G) 20, 1984 SHW 395, 1987 Oil Industry 2, 1993 CRR 57); MCA (SG-1); National Institute of Occupational Safety and Health (NIOSH) (n.d./3, 1974 Crit. Doc. 75-126, 1977/4, 1979/5, 1980/22, 1981/6, 1985/8, 1988/9, 24, 1987/11, 1989/25, 1990/19, 1991/20, 1992/21); National Safety Council (NSC) (n.d./3, 1988/9, 1989/10); Harvey and Murray (1958); Hunter (1959, 1975); R.T. Johnson and Miller (1960); W.H. Meyer and Church (1961); Ministry of Labour (1962); Mort (1965); Coates (1966); SCI (1968); M.H. Hall (1969); Mayers (1969); Wilcox (1970); McElroy and Olishifski (1971); Schilling (1973); Kusnetz (1974); J.F. Morgan (1974); Socha (1974); AIHA (1975/2, 1984/7, 1988/14, 15, 1990/19); Scherberger (1977); Vlad (1977); Anon. (1978e); Atherley (1978); Munn (1978); D. Turner (1978); R. King and Magid (1979); Kohn (1979a); Thiess and Zapp (1979); Waldron (1979, 1989); Harvey (1980–); P. Lewis (1980); Waldron and Harrington (1980); Widmer (1980); Burgess (1981); Chissick and Derricott (1981); Cullis and Firth (1981); Woolhead (1981); D. Farmer (1982); Gill and Ashton (1982); Selman (1982); Harrington and Gill (1983–); Murphy (1982); T.J. Rose and Nourish (1982); British Occupational Hygiene Society (BOHS) (1983 Monogr. 10); Constance (1983); First (1983); IBC (1982/27, 30); ILO (1983/1); Kusnetz and Phillips (1983); Parmeggiani (1983); ASME (1984/196); CIA (1984 RC13); CONCAWE (1984 84/54, 1986 86/69, 1987 87/57); Wang (1984); J.R.P. Clarke (1985); Health and Safety Commission (HSC) (1986/6); Cralley and Cralley (1987); Foa *et al.* (1987); Lipton and Lynch (1987, 1994); Ricci and Cox (1987); Noma *et al.* (1988); R.M. Scott (1989); Abdullah and Yacob (1990); API (1990 Publ. 4519); Burge (1990); Carson and Mumford (1990 LPB 91); Dees and Taylor (1990); J.C. Edwards and Bujac (1990); Phoon and Tan (1990); Wolff (1990); Ryder (1991); IP (1993 MCSP Pt 18, 1993/3); Lin *et al.* (1993); Phoon (1993)

Skin diseases, dermatitis: BSC (n.d./3, 9); Department of Health Education and Welfare (n.d.); HSE (HSW Bklt 18, 1974 MS(B) 1, 1975 SHW 367, 1982 SHW 397, 1981 EH 26, 1983 MS(B) 6, 1990 EH 58, 1991 MS 24); R.P. White (1934);

L. Schwartz, Tulipan and Birmingham (1957); McCreanney (1969, 1977); Fregert (1974); Levene and Calnan (1974); Rycroft (1979, 1980, 1980 LPB 33); McNaughton (1982); Gadian (1983); W.A.D. Griffiths and Wilkinson (1985)
Allergies, asthma: Eppe, Fontanges and Grollier-Baron (1980); BOHS (1984 Monogr. 12); HSE (1991 MS 25)

Workplace exposure, environmental control, exposure monitoring
ACGIH (Appendix 28); AIHA (Appendix 28); ASTM (STP 164); HSE (MS 18, 1989 EH 42, 1990 HS(G) 61, 1992 EH 56); MCA (1968/15); Linch (1974, 1981); Newcombe (1974); API (1975 Publ. 4262); Chemical Society (1975); Zatek (1975); Marion (1979); Jardas (1980); Kung (1980); IBC (1981/14); British Gas (1987 TIN 25); Thorsen and Mølhave (1987); Grumbles (1990)

Analysis of working atmosphere, analytical methods
DoEm (Det. Bklts series); HSE (MSDS series); Sunshine (1969); ACGIH (1972, 1988/24, 1989/27); Associated Octel Co. (1974 Bull. 18); Lisk (1974); CIA (1975/8); Ratcliff (1975); Thain (1976); NIOSH (1977–78/2, 1978/1); Groves (1978); G.L. Lee (1980); Walton (1980); ASTM (1981 STP 721, 1982 STP 786); Lauwerys (1983); Lloyd (1987); OSHA (1990/5); AIHA (1993/9, 27) BS (Appendix 27 *Analytical Methods*)

Control of Substances Hazardous to Health Regulations (COSHH), including assessments
CIA (1989 RC9, RC11, 1990 RC10, RC12, 1991 RC38, RC39); HSE (1989/24, IND(G) 64(L), 65(L), 67(L), 1990/28); Hewitt (1991); Hopkin (1991); Luxon (1991); Samuels (1991)

Severe physical conditions
C.N. Davies, Davis and Tyrer (1967); Harrington (1980b); NIOSH (1987/15)
Hot environments: NIOSH (1972 Crit. Doc. 72-10269; 1986 Crit. Doc. 86-113); Bedford (1974); Gill (1980a); American Society of Heating, Refrigerating and Air Conditioning Engineers (ASHRAE) (1985 ASHRAE 55); Jefri and Daous (1989); McGrath (1993)
Environmental control: Bedford (1974); Waldron (1980b)

Corrosive chemicals
MCA (SG-1); OSHA (OSHA 2237); Harford (1969); W.I. Morton (1976); E.L. M. Roberts (1977); HSE (1984 SHW 395)

Dust, including asbestos (see Table 18.1)

Aerosols (see Table 18.1)

Ventilation
HSE (SIR 16, 1975a, 1975 TON 19, 1987 HS(G) 37, 1988 EH 22, 1990 HS(G) 54); Walls and Metzner (1962); Hemeon (1963); ACGIH (1968, 1982/6, 1988/21, 1989/38, 1991/58, 66–69); Grandidge (1969); IHVE (1970); ASHRAE (1972, 1973, 1988 ASHRAE 11, 1989 ASHRAE 62, 1991/4, 5, 1992/6, 1993/7); Baturin (1972); Leach and Bloomfield (1973, 1974 BRE CP 36/74); Mecklenburgh (1973, 1976, 1985); Bedford (1974); Croome-Gale and Roberts (1975); MacDermott (1976); Anon. (1977 LPB 15, p. 10); CIBS (1977a,b); Chartered Institute of Building Service Engineers (CIBSE) (1977, 1978–); Gill (1980b); ASTM (1982 STP 719); Caplan (1982); Goodfellow and Smith (1982); Anon. (1983 LPB 49, p. 15); Walsh, Dudney and Copenhauer (1983); Mitler (1984); Constance (1985); Goodfellow (1985, 1986); Hayashi *et al.* (1985); Huebener and Hughes (1985); M.R. Marshall (1983); Cassells (1986–); Fangerand Christensen (1986); M.R. Marshall and Stewart Darling (1986); BOHS (1987); Anon. (1988 LPB 80, p. 20); AIHA (1991/21, 22, 1993/25); Eycott (1989); J.C. Edwards and Bujac (1990); Andreopoulos, Karayanis and Markatos (1992); NFPA (1992 NFPA 91, 1993 NFPA 90A); McGrath (1993); ANSI Z9 series, ANSI Z9.2-1979, ANSI Z9.1-1991; BS 5720: 1979, BS 5925: 1991
Local exhaust ventilation (LEV): Dallavalle (1952); B. Fletcher (1977); Bender (1979); Goldfield (1980); Goodfellow and Bender (1980); D. Hughes (1980); Piney and Carrol (1983); J.D. Cook and Hughes (1986); B. Fletcher and Johnson (1986); Saunders (1987)

Compressed air
American Oil Co. (n.d./2); BSC (n.d./l); Paterson (1969, 1977); HSE (1989f, 1990 HS(G) 39)

Inert gas
Kletz (1980f); Anon. (1991 LPB 97, p. 5); Anon. (1991 LPB 102, p. 25); Anon. (1993 LPB 110, p. 8); Anon. (1993 LPB 112, p. 20)

Electricity
American Oil Co. (n.d./5); HSE (HSW Bklt 31, 1984 GS 27, 1985 GS 37, 1986 GS 38); RoSPA (IS/73); Haigh (1969); Consumers Association (1972); Bland (1977); Crom (1977); Bales (1977a,b); W.R. Lee (1977); BOHS (1985 Monogr. 2); Fordham Cooper (1986); Anon. (1990 LPB 92, p. 22); Anon. (1991 LPB 102, p. 25); Marks (1991); NFPA (1993 NFC 70); Anon. (1994 LPB 118, p. 16) BS (Appendix 27 *Electrical*)

Non-ionizing radiations
ACGIH (n.d./12, 1990/48); WHO (EHC 14); Battocletti (1976); AIHA (1977–/3); BOHS (1978 Monogr. 1); Harrington (1980b); Kanagasabay (1980); Chowdhury (1982); Kielman and Fawcett (1982); McKinlay (1982)

Ionizing radiations (see also Table A20.1)
ACGIH (n.d./12, 1990/48); MRC (1956, 1975a); Wiltshire (1957); Imperial College (1958); Blatz (1959); Cherubin (1960); US Congress, Joint Committee on Atomic Energy (1960); Kuhn (1964); H.H. Fawcett (1965c); CVCP (1966); P.S. Baker (1968); Black and Horn (1968); Coombe (1968); Department of Employment and Productivity (1968); Bennellick (1969); HSE (1970 HSW Bklt 13); L.S. Taylor (1971); NAS/NRC (1972c); Shapiro (1972); International Commission on Radiological Protection (ICRP) (1977c, 1979); Brodsky (1978–); R. King and Magid (1979); Doran (1980); Harrington (1980b); Holiday (1980 LPB 35); Dennis (1982); Kielman and Fawcett (1982); UN Scientific Committee on Effects of Atomic Radiation (1977, 1982); BOHS (1982 Monogr. 5); Chilton, Shultis and Faw (1984); NFPA (1991 NFPA 801) BS (Appendix 27 *Radioactivity*)

Lasers
ACGIH (n.d., 1990/41); Sliney and Wolbarsht (1980); Weber (1982); Winburn (1987, 1990); Pilborough (1989); CVCP (1992) BS 7192: 1989, BS EN 60825: 1992

Physical chemistry
Leach (1967); Jennings (1974a,b); Keey (1977)

Lifting and carrying
HSE (HSW Bklt 1, 1971 HSW Bklt 47, 1978 PM 16, 1981 PM 21, 27, 1985 PM 54, Research Review 2, 1986 GS 39,

1993 PM 15); Halliday (1969); R. King and Magid (1979); Ayoub, Mital, Asfur *et al.* (1980); Ayoub, Mital, Bakeen *et al.* (1980); Garg and Ayoub (1980); NIOSH (1981/7); Westerling and Kilblom (1981); Ayoub (1982); AIHA (1983/5, 1989/16); Ayoub, Selan and Liles (1983); A.R. Hale (1984); Mital (1984a,b); Parnianpour, Bejjani and Pavlidis (1987); Nicholson (1989); Genaidy (1991); Snook and Ciriello (1991); Kroemer (1992); Pizatella *et al.* (1992); Waters *et al.* (1993); Kuorinka, Lortie and Gautreau (1994)

Machinery, machine guarding
BSC (n.d./5); HSE (HSW Bklt 4, 14, 20, 33, 42, TON 32, 33, 38, 1970 HSW Bklt 41, 1971 HSW Bklt 3, 1980 MS 1, 1981 PM 21, 23, 1982 HS(G) 19, 1984 PM 1, 38, 1986 PM 65); Blackshield (1969); Bramley-Harker (1969); Fairclough (1969); S.F. Smith (1969); Harding (1977); Southwell (1977); R. King and Magid (1979); Kinsley (1980); Rouhianen (1982); Vartiala (1982) ANSI B7.1-1988; BS (Appendix 27 *Machinery*)

Construction, demolition (see Table 21.1)

Welding (see Tables 12.1 and 21.1)

Abrasive wheels
Blackshield (1969); Southwell (1977); HSE (1984 HS(G) 17)

Pneumatic tools
PNEUPROP (n.d., a,b, 1986)

Miscellaneous hazards
American Oil Co. (n.d./1, 2, 6); MCA (SG-11); HSE (1971 HSW Bklt 27, 1974 HSW Bklt 46); EPA (1974 S8); BDH (1977c); Russell (1982)

Plant layout (see Table 10.2)

Lighting (see Table 10.2)

Identification and labelling (see also Table 23.1)
R.F. Wilson (1960); Gloag (1961); Hurst (1969); ASME (1975 A13.1-1975); MCA (1976/24); BDH (1977a); Stancliffe (1977); HSE (1985 HS(G) 27); API (1993 RP 1109) BS (Appendix 27 *Identification of Equipment*)

Personal protection
NIOSH (1984/23, 1990/17); NRC (Appendix 28 Personal Protective Equipment, PPE); N.T. Freeman (1962); H.H. Fawcett (1965b, 1982c); C.S. Nicholson (1969); W.I. Morton (1976); K.R. Nicholson (1976); Zippier (1976); Riddell (1977); Chlorine Institute (1978 Pmphlt 65); R. King and Magid (1979); BS (Appendix 27 *Personal Protection*)
Protective clothing, including gloves: ACGIH (n.d./10, 1989/30); Associated Octel Co. (1974 Bull. 21); Gauerke (1972); J.S. Shaw (1978); E.J. West *et al.* (1978); Crockford (1980); Stull (1987a,b); Hoyle (1988 LPB 80); Jones (1988 LPB 80); Parson (1988); Preece (1988); AIHA (1990/18); Mellin (1991 LPB 100); Tooth (1991 LPB 100); Bensel (1993); Pal *et al.* (1993); Mitel, Kuo and Faard (1994)
Ear protection: Zohar, Cohen and Azar (1980)
Eye protection: Joyner (1959); Guelich (1965); Barker (1969, 1977); Wigglesworth (1974); Hill (1975); Nichols (1982); CIA (1990 RC22); ANSI Z87.1-1989; BS 2092: 1987
Footwear: FPA (1973 S4); ANSI Z41-1991; BS 1870: 1976–
Head protection: Anon. (1988 LPB 88, p. 14); ANSI Z89.1-1986; BS 5240: 1987–

Respiratory protective equipment (RPE), breathing apparatus (BA)
Fieldner, Katz and Kinney (1921); S.J. Pearce (1957); ACGIH and AIHA (1963); H.H. Fawcett (1965d, 1982d); Cheffers (1969); Home Office (1975 Manual of Firemanship Bk 6); Anon. (1977–); Vanchuk (1978); HSE (1979 RA1); M.S. Levine (1979); Ballantyne and Schwab (1981); Chlorine Institute (1982 Pmphlt 75); Evans and Leinster (1984 LPB 60); IGasE (1986 IGE/SR/13); Louhevara *et al.* (1986); NIOSH (1987/12, 14); Anon. (1988 LPB 80); CGA (1989 G-7, G-7.1); HSE (1990 EH 53, HS(G) 53); Anon. (1991c); AIHA (1991/23); CIA (1991 RC6); Anon. (1992 LPB 106, p. 17); ACGIH (1992/88); ANSI Z88.2-1992; BS (Appendix 27 *Personal Protection*), BS 4275: 1974, BS 4667: 1974–, BS DD 97: 1987– BS 7170: 1990, BS EN 132: 1991

Rescue
EEUA (1962 Doc. 12); Home Office (1964/8); Walters (1977); MoD (1989a); HSE (1992 RP23) BS (Appendix 27 *Personal Protection, Rescue*)

First aid
HSE (HSW Bklt 36); St John Ambulance Association (1961, 1992); Gardner and Roylance (1967); Taylor (1967); Cameron (1969, 1977); API (1979 Publ. 2017); BDH (1977b); R. King and Magid (1979); McKenna and Hale (1981, 1982); Chlorine Institute (1985 Publ. 63); ACGIH (1988/19, 32, 1991/64)

Isolated workstations
Bresson and Perez (1977)

Equipment Design (C.T. Morgan *et al.*, 1963), *Human Engineering Guide for Equipment Designers* (Woodson and Conover, 1964), *Human Factors Evaluation in System Development* (Meister and Rabideau, 1965), *Ergonomics* (Murrell, 1965a), *Human Performance in Industry* (Murrell, 1965b), *Human Factors* (Meister, 1971), *Handbook of Human Factors* (Salvendy, 1987), *Applied Ergonomics Handbook* (Burke, 1992 ACGIH/76) and *Human Factors in Design and Engineering* (Sanders, 1993). Accounts of human factors with specific reference to safety are given in *Ergonomics Guides* (AIHA, 1970–/1), *Human Aspects of Safety* (Singleton, 1976b) and *Human Factors in Process Operations* (Mill, 1992) and by Hands (1969, 1977).

Human factors should be considered from the beginning of the project. Much of the contribution which it can make to accident prevention is in areas such as the allocation of function between man and machine. If it is brought in later for detailed equipment design or in a rescue role, many of the options for design are already foreclosed.

Much work in human factors is concerned with human error. In fact, error rates are one of the main criteria used in scoring human factors experiments. Where an error leads to injury or other serious effect, it becomes an accident.

Error is to a large extent a function of the work situation. As such it is amenable to reduction by better design of the work situation, including not only equipment design but also all other relevant factors. Some error is certainly attributable to the individual, and variations in error rates between individuals can be investigated. But management should concentrate primarily on the work situation, since this is not only the factor which is most important but also that which it can most readily alter.

Table 25.2 *Injuries to employees by nature of accident and of injury and by severity of injury in the year 1990/91 (after HSE, 1992b)*[a]

A Nature of accident and severity of injury[b]

Nature of accident	*Severity of injury*		
	Fatal	*Non-fatal major*	*Total*
Contact with moving machinery or material being machined	29	1,738	9,491
Struck by moving, including flying or falling, object	51	2,371	25,788
Struck by moving vehicle	53	733	4,631
Struck against something fixed or stationary	3	781	11,074
Injured whilst handling, lifting or carrying	–	1,257	55,477
Slip, trip or fall on same level	1	6,396	39,849
Fall from a height:			
Up to and including 2 m	8	1,964	9,261
Over 2 m	66	1,337	3,162
Height not stated	7	973	4,517
All heights	81	4,274	16,940
Trapped by something collapsing or overturning	24	204	776
Drowning or asphyxiation	10	22	58
Exposure to or contact with a harmful substance	14	806	5,336
Exposure to fire	5	109	690
Exposure to an explosion	8	90	318
Contact with electricity or electrical discharge	24	298	929
Injured by an animal	3	72	928
Other kind of accident	28	651	7,960
Injuries not classified by kind	12	94	808
Total	346	19,896	181,053

B Nature and severity of injury[c]

Nature of injury	*Severity of injury*		
	Fatal	*Non-fatal major*	*Total*
Amputation	–	1,392	1,463
Loss of sight	–	20	29
Fracture	46	14,108	27,035
Dislocation	–	30	1,146
Concussion and internal injuries	16	147	1,290
Lacerations and open wounds	3	617	12,453
Contusions	37	371	29,221
Burns	9	859	5,827
Poisonings and gassings	25	224	822
Sprains and strains	–	153	59,752
Superficial injuries	–	263	17,478
Natural causes	–	5	20
Other injuries caused by contact with electricity	19	80	318
Injuries of more than one of the other natures	37	261	2,738
Injuries not elsewhere specified	21	68	1,228
Injury not known	85	327	11,128
Total	298	18,925	171,948

[a] *Source: Health and Safety Statistics 1990/91* (HSE, 1992b). Section A is an extract from table 9 and Section B is an extract from table 15.
[b] Injuries reported to all enforcing authorities, including offshore injuries.
[c] Injuries reported to the Factory and Agricultural Inspectorates and to local authorities.

Table 25.3 *Incidents in the chemical industry in 1983 (after HM Chief Inspector of Factories, 1986b)*

A Incidents

Incident type	*No of incidents*	*Proportion of incidents* (%)
Releases of chemicals[a]	222	34.5
Machinery incidents	77	12.0
Process-related fires and explosions	66	10.3
Falls from a height	56	8.7
Falls at same level and striking against objects	39	6.1
Pressure system and other equipment failures[b]	24	3.7
Hit by falling objects	23	3.6
Failure or overturning of lifting equipment	22	3.4
Struck or trapped by vehicle	15	2.3
Affected by chemicals during work[c]	13	2.0
Runaway exothermic reactions[d]	9	1.4
Manual handling and strains	8	1.2
Non-process related fires and explosions	7	1.1
Confined space incidents – people overcome	5	0.8
Electric short circuits	5	0.8
Not elsewhere classified	52	8.1
Total	643	100

B Other information

1. 17 incidents involved clear failures of the permit-to-work system
2. There were 30 pipework failures in addition to 37 incidents involving flexible hoses or insecure temporary joints
3. Of the 222 releases of chemicals, 127 (57%) affected people directly or indirectly to some degree, 92 (41%) occurred during normal operation with no immediate direct involvement of workpeople, 64 (29%) occurred during normal operations with direct involvement of workpeople, 68 (30%) occurred during cleaning, maintenance or repair activities
4. 49 cases of ill health were recorded, mostly associated with the release of chemicals or with confined spaces
5. 17 incidents involved tanker vehicles or tank containers
6. 62 incidents (9.6%) involved personnel other than those employed by the occupier, ie. contractors, visitors, etc.

[a] Including 97 toxic; 51 corrosive; 45 flammable; 23 hot, and 6 other materials.
[b] Where main risk was not from chemicals released.
[c] Examples are decanting, charging, etc., without significant escape or spill.
[d] With no major release of chemicals.

Principal influences on the frequency of errors, and hence of accidents, include (1) equipment design, (2) working methods, (3) motivation and (4) stress.

There is now a wealth of data on the design of equipment. The equipment should be physically easy to use. Valuable guidelines here are given by anthropometry, which is the study of human measurements.

It is often possible to build into equipment a barrier to error. A simple example is to prevent a plug being put into the wrong socket by making the relative shapes such that this is impossible. More complex methods for achieving similar results include interlocks.

Correct identification is important if error is to be avoided. There should be clear and consistent coding and labelling. A valuable form of coding is by colour.

Much information is available on the ways in which humans receive information through the senses. Some account of this has already been given in Chapter 14 in relation to the design of displays and controls.

It is necessary to train the operator in the use of equipment. The training should deal not only with how the operation is performed but also with why it is done that way.

Although training is important, it is not always the correct solution. Sometimes error is inherent in the design of the equipment. In this case, it is better to redesign the equipment than to use training to overcome the defects.

It is important to pay attention to motivation in the use of correct and safe methods of operation, and this should be a major objective of training.

Human performance is much affected by stress. Some factors which cause this stress include poor environmental conditions, bad equipment design, lack of time, fatigue and anxiety. Although there tends to be some improvement in performance at moderate levels of stress, beyond a certain threshold (which is different for each individual), it causes severe deterioration.

Important aspects of the environment are air quality, thermal conditions, illumination and noise. The first two are considered in Section 25.3. The last two are treated by Ragsdale (1969) and Atherley and Purnell (1969). Noise is also dealt with in Appendix 12.

25.2 Occupational Health

Occupational health is an established branch of medicine. It involves not only the investigation of industrial disease but also the provision of health services at the place of work.

Accounts of occupational health are given in *Occupational Diseases and Industrial Medicine* (R.T. Johnson and Miller, 1960), *Diseases of Occupations* (Hunter, 1975), *Occupational Health and Safety Concepts* (Atherley, 1978), *Recognition of Health Hazards in Industry* (Burgess, 1981 ACGIH/5), *Occupational Health* (Harrington and Gill, 1983–), *Chemical Exposure and Disease* (Sherman, 1988 ACGIH/16), *Occupational Health Practice* (Waldron, 1989), *Occupational and Environmental Health Management* (Kavianan and Wentz, 1990 ACGIH/47), *Health Fundamentals* (Hansen, 1991 ACGIH/71) and *Industrial Health* (Peterson, 1991 ACGIH/65). Epidemiological aspects are treated in *Exposure Assessment for Epidemiology and Hazard Control* (Rappaport and Smith, 1991 ACGIH/56) and *Introduction to Occupational Epidemiology* (Hernberg, 1992 ACGIH/79).

Guidance on occupational health arrangements is given in HS(G) 20 *Guidelines for Occupational Health Services* by the HSE (1980).

25.2.1 Industrial medical services

A chemical works usually has a medical centre with facilities for medical tests and which is able to handle a small number of casualties. The centre is typically staffed by a doctor working part time and a nurse working shifts. Descriptions of such medical services and of their liaison with hospital emergency departments are given by Cameron (1969, 1977) and M.H. Hall (1969, 1977), respectively, and the work of an industrial nurse is described by Mort (1965).

The medical personnel should be familiar with the chemicals and processes used in the particular factory. Information such as that given on materials safety data sheets provides a useful starting point.

Information on the medical history of individual workers is equally important. Careful interviewing and record keeping can assist in diagnosing early symptoms or high susceptibility in individuals. It can also make a significant contribution to the epidemiological investigation of industrial disease.

25.2.2 Employment Medical Advisory Service

The Employment Medical Advisory Service Act 1972 and the Health and Safety at Work etc. Act (HSWA) 1974, Part II define the role of the Employment Medical Advisory Service (EMAS). Information on EMAS is given in *Employment Medical Advisory Service Act 1972 – Guide to the Service*.

The service acts as the medical arm of the HSC, does work on medical matters for which there are statutory requirements, provides medical advice to the Factory Inspectorate and to employers, and furthers research on the epidemiology of industrial disease.

It is able to advise on the effects of particular jobs on health, on the medical precautions to be taken in working with substances which are toxic or otherwise hazardous to health, and on medical examinations, investigations and surveys.

There is a series of guidance notes on medical topics (the Medical Series (MS)) and also series of leaflets (the MS(A) and MS(B) series).

25.2.3 National Institute for Occupational Safety and Health

An important source of information on occupational health is the NIOSH. Some publications of the Institute are listed in Appendix 28.

25.3 Occupational Hygiene

Industrial chemicals tend to be noxious substances. It is essential, therefore, to take appropriate measures of occupational hygiene to ensure that those who work with them are not exposed to unacceptable risks.

Occupational health and hygiene are the subject of the Control of Substances Hazardous to Health Regulations 1988 (the COSHH Regulations). These are described together with the HSE guidance in Section 25.4.

Other regulations frequently referred to in this chapter are the Control of Lead at Work Regulations 1980 (the CLAW Regulations) and the Control of Asbestos at Work Regulations 1987 (the CAWR).

In addition to that specifically related to the COSHH Regulations 1988, HSE guidance includes EH 22 *Ventilation of the Workplace* (HSE, 1988), EH 42 *Monitoring Strategies for Toxic Substances* (HSE, 1989), HS(G) 61 Surveillance of People Exposed to Health Risks at Work (HSE, 1990), HS(G) 27 *Substances for Use at Work: the Provision of Information* (HSE, 1991) and EH 40/94 *Occupational Exposure Limits* (HSE, 1994).

Guidance by the BOHS is given in *Controlling Airborne Contaminants in the Workplace* (the BOHS *Airborne Contaminants Guide*) by Piney *et al.* (1987 BOHS/TG7) and by the AIHA in *Basic Industrial Hygiene: A Training Manual* (AIHA, 1975/2), *Engineering Field Reference Manual* (AIHA, 1984/7), and *A Strategy for Occupational Exposure Assessment* (Hawkins, Norwood and Rock, 1991 AIHA/24). A computer-based system is described in *LOGAN Workplace Evaluation System* (Dupont, 1990 AIHA/20).

Guidance on occupational hygiene in the petroleum industry is given in *Guidelines for Recording Industrial Hygiene Data* (CONCAWE, 1983 7/83), *Health Aspects of Worker Exposure to Oil Mists* (CONCAWE, 1986 86/69), *Review of Strategies for the Evaluation of Employee Exposures to Substances Hazardous to Health* (CONCAWE, 1987, 87/57) and *API Exposure Classification Scheme for Collection of Industrial Hygiene Monitoring Data* by the API (1990).

Further guidance is given in *Employment and Reproductive Health* by the Chemical Industries Association (CIA) (1984 RC13).

Occupational, or industrial, hygiene is also treated in *Occupational Health and Safety Concepts* (Atherley, 1978), *Occupational Health* (Harrington and Gill, 1983–), *Case Studies in Industrial Hygiene* (Perkins and Rose, 1987 ACGIH/9), *Industrial Hygiene Management* (Garrett, Cralley and Cralley, 1988 ACGIH/23), *Fundamentals of Industrial Hygiene* by the NSC (1988/13), *The Risk Assessment of Environmental Hazards* (Paustenbach, 1989 ACGIH/37), *Quantitative Industrial Hygiene: A Formula Workbook* (Caravanos, 1991 ACGIH/74) and *Industrial Hygiene Workbook* (Burton, 1992 ACGIH/85). Engineering aspects are treated in *Health Hazards Control in the Chemical Process Industry* (Lipton and Lynch, 1987), *Industrial Hygiene Engineering* (Talty, 1988 ACGIH/22) and *In-Plant Practices for Job-related Health Hazards* (Cralley and Cralley, 1989 ACGIH/36).

Guidance for dusts specifically includes EH 44 *Dust: General Principles of Protection* (HSE, 1991), the *User Guide to Dust and Fume Control* (Muir, 1985) (the IChemE *Dust Control Guide*) and the BOHS *Airborne Contaminants Guide*.

The elements of occupational hygiene include:

(1) identification of noxious substances or effects;
(2) establishment of criteria;

(3) assessment of exposure;
(4) prevention of exposure;
(5) control of exposure –
  (a) enclosure,
  (b) ventilation;
(6) provision of PPE;
(7) monitoring of workplace atmosphere;
(8) monitoring of personnel;
(9) keeping of records.

This general approach is applicable to toxic and corrosive chemicals, noxious dusts, and ionizing and non-ionizing radiations.

In addition to vapours and dusts, it is necessary to deal also with skin disease and noise. Skin care is treated in Section 25.8 and noise is discussed in Appendix 12.

25.3.1 Noxious substances

Information on the health effects of industrial chemicals is available from a large number of sources. These include: *Dangerous Properties of Industrial Materials* (Sax, 1957–), *Hazardous Chemicals Handbook* (Carson and Mumford, 1994) and other compendia; *Chemical Safety Data Sheets* (Walsh, 1988, vol. 1) and (A. Allen (1988, other volumes); the series *Information Sheets on Hazardous Materials* by the FPA and other collections of such data sheets; and the Environmental Hygiene (EH) series and criteria documents (EH 64 and 65) by the HSE.

Information on hazardous chemicals, including materials safety data sheets, is discussed in Chapters 8 and 18, and materials toxicity in the latter chapter.

Some aspects of health effects in the petroleum industry are treated in *The Health Experience of Workers in the Petroleum Manufacturing and Distribution Industry* (CONCAWE, 1987 2/87) and *Survey of Exposure to Gasoline Vapour* (CONCAWE, 1987 4/87).

25.3.2 Airborne contaminants

A classification of airborne contaminants is given by the HSE (1993, HS(G) 37). The particle size ranges given are:

	Size range (μm)
Dusts	0.1–75
Fume	0.001–1.0
Smoke	0.001–1.0
Mist	0.01–1.00

These figures refer to: dust generated by natural fragmentation or mechanical cutting or crushing; fume formed as solid particles of condensed vapour, especially metals; smoke as aerosol formed by the incomplete combustion of organic matter; and mist as an aerosol of droplets formed by condensation from the gaseous state, or as a dispersion of the liquid state. For vapour, a single value of 0.005 μm is quoted. This refers to the gaseous state of materials which are liquid or solid at room temperature and pressure.

The *BOHS Airborne Contaminants Guide* gives for contaminants of occupational importance a size range of 0.01–150 μm for both dust and mist, and of 0.001–1.0 μm for fume.

The particle size of a contaminant is determined by the process by which it is generated. Oil mist generated by metal cutting has a larger particle size than that of oil fumes formed by the condensation of oil vapour.

The behaviour of an airborne particle may be characterized in terms of the settling velocity and the stopping distance. The latter is the distance which a particle with a defined initial velocity will travel before coming to rest. The BOHS *Guide*, quoting Hinds (1982), gives the following values for settling velocity and stopping distance:

Particle diameter (μm)	*Settling velocity* (m/s)	*Stopping distance* (m)
0.01	7.0×10^{-8}	6.8×10^{-8}
1.0	3.5×10^{-5}	3.6×10^{-5}
100	0.25	0.127

The particle density used is 10 kg/m^3 and the initial velocity for the stopping distance is 10 m/s.

Fine particles sediment out only very slowly and thus remain airborne for long periods. They move with the air.

Where particles are emitted from a source, the larger particles travel some distance, but the distance travelled by the finer particles is very short. Even if their initial velocity is high, their movement follows that of the air.

As far as the health effects caused by particles are concerned, there is an upper limit of size above which a particle tends to be deposited before it reaches the lungs. The particle size range of interest for harmful effects by inhalation into the lungs is discussed in the *BOHS Guide*, which gives the range as being from the submicron level to about 25 μm in diameter.

25.3.3 Generation of contaminants

There is a variety of ways by which a contaminant may enter the workplace atmosphere. Four principal routes are (1) a contaminant-generating process or operation, (2) a leak, (3) opening up of plant and (4) handling fabrics saturated with the material.

For a vapour contaminant, a principal determinant is the vapour pressure. If a liquid is being handled under conditions where there is a route to the atmosphere and it is at a temperature at which it exerts an appreciable vapour pressure, a significant amount may escape.

In relation to industrial hygiene, a significant measure is the ratio of the vapour pressure to the occupational exposure limit. A vapour hazard index (VHI) is defined as

$$\text{VHI} = \frac{\text{Vapour pressure}}{\text{Occupational exposure limit}} \qquad [25.3.1]$$

where both the vapour pressure and the occupational exposure limit are measured in parts per million (ppm).

The conditions that must be met for a dust contaminant to enter the workplace atmosphere are that a route exists for it to do so and that it has imparted to it sufficient energy to follow that route.

Some conditions in which a contaminant, vapour or dust, may enter the atmosphere include (1) passage of air through the material, (2) free fall of the material, (3) pouring of the material, (4) agitation of the material, (5) transfer of the material, (6) opening of bags or drums of the material, (7) leak of the material, (8) opening up of plant containing

the material and (9) handling of fabrics saturated with the material.

In addition, vapour generation may occur due to (1) the evaporation of a liquid or (2) the heating of a liquid; and dust generation may occur due to (1) vibration of a powder or (2) a size reduction of the material.

Typical equipment and activities where contaminants are generated include reactor charging, mixing operations, powder handling and packing processes, grinding mills, conveyors and elevators, storage silos, hoppers and bins, bag emptying operations, drum and bag filling operations, and plant maintenance.

The situations in which fumes and mists are generated tend to be highly specific.

25.3.4 Leaks of contaminants

A common source of contamination is leaks from the plant. A gross leak may be readily identified, but this may not be so where the leak is small, but still large enough to cause significant contamination.

With regard to leaks of gas, vapour and liquid, an account has been given in Chapter 15 of fugitive emissions, particularly of volatile organic compounds (VOCs). Although originally work on such emissions was driven largely by concern over environmental pollution, the information is generally applicable equally to emissions into the workplace atmosphere.

Leaks of dust can also occur. If the dust is fine, the leak may not be visible. Figure 25.1 shows a leak of asbestos dust from a gaiter, made visible only by the use of a dust lamp, as described below.

25.3.5 Air movement

As already described, most contaminants move with the air in the workplace. This air movement is therefore of great importance in developing controls.

There are available a number of methods for the investigation of air movements. One is the use of a smoke tracer. Smoke is introduced from a smoke generator and its movement is observed or filmed.

Methods exist for the visualization of the presence and movement of dust particles in air. The dust lamp, or Tyndall lamp, technique is widely used. This makes visible the dust cloud in a manner similar to that which occurs when a shaft of sunlight falls across a room where there is dust in the atmosphere. This method permits observation of dust clouds of particles too fine to be seen otherwise. The use of a dust lamp is illustrated in Figure 25.1. Accounts of the dust lamp technique are given by the HSE (1975 TON 35) and in the *BOHS Guide*.

There is also an infrared (IR) technique which permits the movement of a vapour to be followed.

25.3.6 Monitoring variables and criteria

There is a hierarchy of methods which may be used as the basis for the monitoring and control of noxious substances. These are the measurement and monitoring of (1) the concentration of airborne contaminants in the workplace,

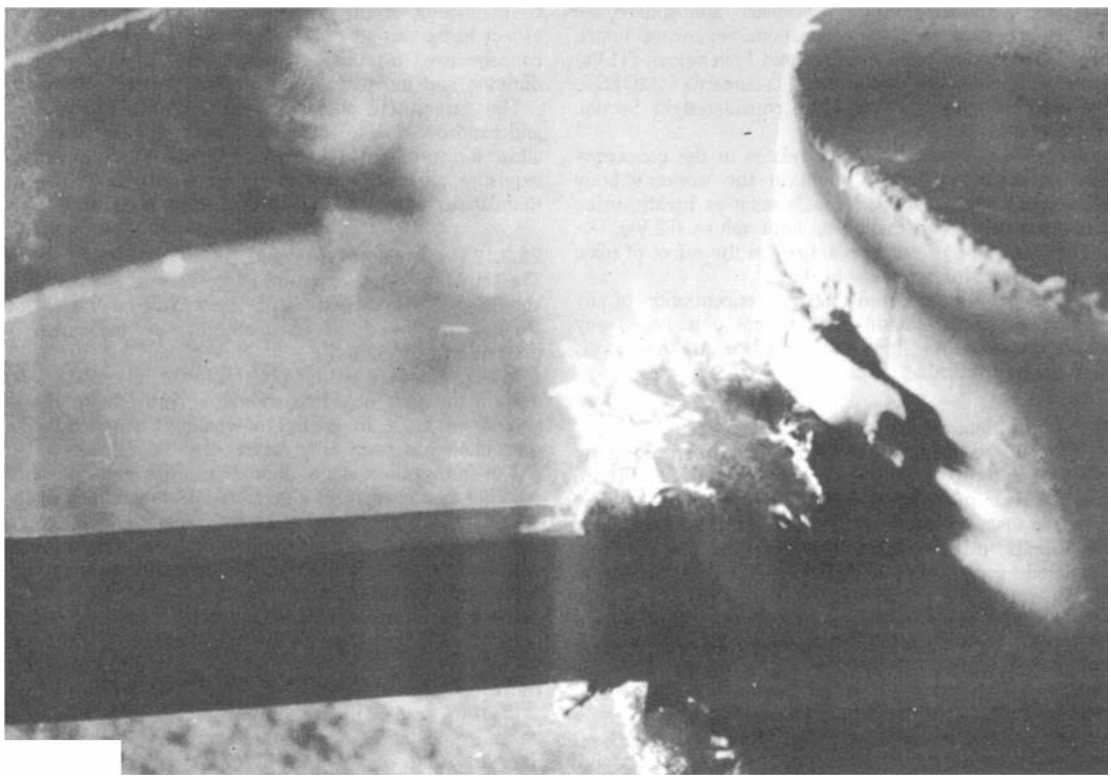

Figure 25.1 *Leakage of asbestos dust due to failure of a gaiter (HSE, 1975 TON 35) (Courtesy of HM Stationery Office)*

(2) their concentration in workers' body tissues and body fluids and (3) their effect on workers' health.

There are three corresponding types of criteria used in monitoring for occupational hygiene. For the concentration of contaminants in the workplace atmosphere, the criteria are expressed as occupational exposure limits. This type is exemplified by threshold limit values (TLVs) and occupational exposure standards (OESs). Occupational exposure limits are considered in Section 25.3.7.

The second type of criterion relates to the concentrations of toxic substances found in the worker's body tissues and fluids, especially fluids such as breath, urine and blood. These are biological limit values (BLVs).

The third type of criterion relates to the effect of toxic substances on the worker's health.

It should be emphasized that the concentration of any harmful substance should be kept not only below any maximum exposure limit (MEL) but as close to zero as is reasonably practicable.

25.3.7 Occupational exposure limits

In the United Kingdom, occupational exposure limits were formerly specified in terms of TLVs. There are now two main types of limit which apply: OESs and MELs. The latter apply to a relatively restricted group of chemicals which are listed in Schedule 1 of the COSHH Regulations 1988.

The larger group are covered by an OES. The current OES values are given in EH 40 *Occupational Exposure Limits 1994* (HSE, 1994). The basis of the limits is explained in EH 64 *Occupational Exposure Limits: Criteria Document Summaries* (HSE, 1993).

An account of the OES system is given in *Occupational Exposure Limits* (CIA, 1985 PA23).

Further guidance is given by the AIHA in *Workplace Environmental Exposure Level Guides* (AIHA, 1980–/4), *Occupational Exposure Limits – Worldwide* (Cook, 1987 AIHA/12), *Hygienic Guides* (AIHA, 1988/14) and *Odor Thresholds for Chemicals with Established Occupational Standards* (AIHA, 1989/17). The American Conference of Government Industrial Hygienists (ACGIH) guidance includes *Documentation of the Biological Exposure Indices* (ACGIH/1), *Documentation of Threshold Limit Values and Biological Exposure Indices* (ACGIH/3), *Guide to Occupational Exposure Values – 1992* (ACGIH/78) and *Threshold Limit Values and Biological Exposure Indices, 1992–1993* (ACGIH 1992/80). The ILO publishes *Occupational Exposure Limits for Airborne Toxic Substances* (ILO 1991/2).

25.3.8 Non-inhalation exposure

The account given so far has concentrated on exposure by inhalation. It is also necessary to consider exposure by ingestion and by skin absorption. The consumption of food and drink in contaminated conditions is one situation in which ingestion of a contaminant is prone to occur. Skin absorption is discussed in Section 25.8.

25.3.9 Assessment of exposure

If workers may be exposed to a noxious substance, an assessment needs to be made of the extent of the exposure. This assessment merits as much effort as is generally devoted to determining how noxious the substance is.

The foregoing account has indicated some of the processes, operations and activities which may cause contamination of the workplace atmosphere. The other aspect is the extent to which workers are exposed as a consequence of this contamination. The frequency, duration and intensity of exposure are all relevant.

The assessment should cover all modes of exposure and exposure due to activities as well as leaks. It should allow for foreseeable human behaviour. Assessment of exposure is an important aspect of the COSHH Regulations and is described further in Section 25.4.

25.3.10 Prevention of exposure

The minimization of exposure of workers to contaminants should be approached in a systematic manner and should be based on a hierarchy of measures of prevention and control.

In accordance with the philosophy of inherently safer design, the first objective should be prevention. Resort should be made to control only after the potential for prevention has been fully explored.

The prevention stage should address the following possible approaches: (1) elimination or substitution of the substance, (2) modification of the process, (3) segregation of processes, (4) elimination of leaks, (5) modification of operations and (6) arrangements for dealing with contaminated clothing.

Measures of prevention have two main objectives. One is to use substances which are less harmful. The other is to use processes and operations which are less prone to cause contamination.

In some cases it has proved possible to replace a harmful substance by substituting it by a less harmful one. In other cases, the harmful substance may be eliminated. This may occur by elimination of a harmful impurity or of a process, or process stage, in which the harmful substance is used. Modification of the process by alteration or substitution is another approach which has been used with success. A third method is to segregate the processes, or process stages, which are 'dirty' in respect of contamination from those which are 'clean'. Examples of these approaches are given in Chapter 11 and in the *BOHS Guide*.

Where leaks are a cause of contamination, measures should be taken to eliminate them.

Contamination of the working atmosphere may also arise from various activities on the plant, such as opening reactors, taking samples or opening up equipment for maintenance. This aspect may need to be controlled by specific procedures.

Workers may be exposed to contamination from work clothes or from protective clothing, and arrangements may need to be made to prevent this.

25.3.11 Control of exposure

When measures based on prevention have been exhausted, controls should be used to reduce exposure further. These controls are applied in a hierarchy which is broadly as follows:

(1) total or partial enclosure;
(2) LEV;
(3) general ventilation;
(4) limitation of exposure –
    (a) number exposed,
    (b) frequency and duration of exposure;
(5) PPE.

A further discussion of prevention and control is given in Section 25.4 in relation to the COSHH Regulations 1988.

25.3.12 Ventilation of workplace atmosphere

It is frequently necessary to use ventilation as one of the control measures taken to reduce exposure.

The siting of plant in the open air rather than in a building is often the most effective means of ventilation, since small leaks are then dispersed by the wind. But such open construction is not always appropriate, for various reasons, some of which were considered in Chapter 10. Moreover, as discussed below, it cannot be assumed that an outdoor location guarantees that exposure is negligible.

In most applications, the preferred method of indoor ventilation is LEV. The use of general ventilation tends to be less effective and more expensive. Where general ventilation is used indoors, it may be natural ventilation or mechanical ventilation.

An account of ventilation is given in Section 25.7.

25.3.13 Monitoring of workplace atmosphere

The monitoring of the workplace atmosphere involves identifying valid methods of sampling, measurement and evaluation, and the adoption of a suitable monitoring strategy.

HSE guidance on the measurement and monitoring of contaminants in the workplace atmosphere is given in EH 42 *Monitoring Strategies for Toxic Substances* (HSE, 1989) and in the series *Methods for the Determination of Hazardous Substances (MDHS).* The series includes MDHS 70 *General Methods for Sampling Airborne Gases and Vapours* (HSE, 1990) and MDHS 71 *Analytical Quality in Workplace Air Monitoring* (HSE, 1991).

Further guidance by the AIHA is given in *Quality Assurance Manual for Industrial Hygiene Chemistry* (AIHA, 1988/15), *Direct-Reading Calorimetric Indicator Tubes Manual* (Perper and Dawson, 1993 AIHA/9), *The Industrial Hygienists' Guide to Indoor Air Quality Investigations* (AIHA, 1993/26), and *Manual of Recommended Practice for Combustible Gas Indicators and Portable Direct-Reading Health Survey Meters* (AIHA, 1993/27). ACGIH guidance includes *Methods of Air Sampling and Analysis* (Lodge, 1988 ACGIH/24), *Air Sampling Instruments* (ACGIH, 1989/27) and *Air Monitoring for Toxic Exposures* (Ness, 1991 ACGIH/51).

For petroleum products, the guidance available includes *The Identification and Measurement of Refinery Odors* (CONCAWE, 1975 8/75) and *Method for Monitoring Exposure to Gasoline Vapour in Air* (CONCAWE, 1986 8/86).

Strategies for measuring and assessing personal exposure are described in *Review of Strategies for the Evaluation of Employee Exposure to Substances Hazardous to Health* (CONCAWE, 1987 87/57).

25.3.14 Health surveillance

It may not be sufficient to monitor the working atmosphere. It is often necessary also to monitor the people who work in it by a system of health surveillance. HSE guidance on health surveillance is given in HS(G) 61 *Surveillance of People Exposed to Health Risk at Work* (HSE, 1990).

HS(G) 61 lists the sets of regulations which contain requirements for medical surveillance. They include the CLAW Regulations, the CAWR and the COSHH Regulations.

Health surveillance may be carried out at different stages of an employee's involvement with the company. HS(G) 61 distinguishes between the types of surveillance which occur during recruitment, on employment, during work and on detection of an adverse effect.

HS(G) 61 gives the following purposes of health surveillance at work: (1) to identify adverse effects early, (2) to identify inadequacies in control, (3) to inform those at risk as soon as possible of any damage to their health and (4) to provide an opportunity to reinforce health education on the risk present.

It also describes some of the practicalities. (1) There are some substances which are impractical to control to a level which protects all those who may be exposed, due to differences in the susceptibility of individuals. A person sensitized to a lung allergen may develop asthma at a concentration level three orders of magnitude lower than would affect a previously unexposed person. (2) Control may not be equally effective in protecting all groups of workers. Controls designed to protect plant operators may not cover well maintenance personnel. (3) The controls may not do all they were intended to do. Early controls on cotton dust did not prevent byssinosis because they did not remove fine particles. (4) The type of injury may not be foreseen. This was the case with lung cancers from asbestos up to about 1940 and with mesothelioma from vinyl chloride monomer (VCM) until about 1974.

Employees should be informed of possible consequences of health surveillance. One potential consequence might be that an employee is moved to another job.

As with monitoring of exposure to airborne contaminants, so with monitoring of concentrations of toxic substances in the body, the aim should be to keep the concentrations as low as is reasonably practicable.

Guidance on monitoring against BLVs is given by the ACGIH in *Biological Monitoring of Exposure to Chemicals: Organic Compounds* (Dillon and Ho, 1987 ACGIH/8), *Methods for Biological Monitoring* (Knelp and Crable, 1988 ACGIH/25) and *Biological Monitoring of Exposure to Chemicals: Metals* (Dillon and Ho, 1991 ACGIH/52). AIHA guidance includes *Biohazards Reference Manual* (AIHA, 1985/10).

25.3.15 Hot environments

The environment may also be injurious to health because it is too hot. This aspect is treated in *Hot Environments* (NIOSH, 1986 Publ.86-113) and by Bedford (1974) and Gill (1980a).

Depending on the situation, countermeasures for hot environments may include the provision of ventilation, the use of protective clothing and the limitation of the working period.

25.4 COSHH Regulations 1988

A requirement for a comprehensive system for the protection of workers based on industrial hygiene principles is given in the COSHH Regulations 1988 (the COSHH Regulations). The corresponding Approved Code of Practice (ACOP), which also deals with carcinogenic substances is L5 (formerly COP 29) COSHH and Control of Carcinogenic Substances (HSE, 1991). It is convenient to refer to these two parts of the ACOP as the COSHH Code and the *Carcinogens Code*, respectively. Further guidance is given in COSHH Assessments (HSE, 1988b), HS(G) 27 Substances for Use at Work: the Provision of Information (HSE, 1988), EH 42 Monitoring Strategies for Toxic Substances (HSE, 1989) and HS(G) 61 Surveillance of People Exposed to Health Risks at Work (HSE, 1990).

Guidance from the CIA is given in the series *COSHH – Guidance on Assessments* (Reg. 6) (CIA, 1989 RC9), *COSHH*

– *Guidance on Health Surveillance* (Reg. 11) (CIA, 1989 RC11), *COSHH – Guidance on Information, Instruction and Training* (Reg. 12) (CIA, 1990 RC 12), *COSHH – Guidance on Setting In-house Exposure Limits* (Reg. 7) (CIA, 1990 RC10), *COSHH – Guidance on Collection and Evaluation of Hazard Information* (Reg. 2) (CIA, 1991 RC39) and *COSHH – Guidance on Recordkeeping* (CIA, 1991 RC 38).

Further treatments are given in *The COSHH Regulations: A Practical Guide* (Simpson and Simpson, 1991) and by P. Lewis (1980), Blain (1987), Waterman (1987) and Boniface (1990b). The principal contents of the COSHH Regulations are given in Table 25.4.

Regulation 2 defines a 'substance hazardous to health' (SHH) as covering the following: (1) a substance which is listed in Part 1A of the Classification, Packaging and Labelling of Dangerous Substances Regulations 1984 and for which the general indication of nature of risk is specified as very toxic, toxic, harmful, corrosive or irritant; (2) a substance for which the MEL is specified in Schedule 1 of the regulations or for which the HSC has approved an OES; (3) a micro-organism which creates a hazard to health; (4) dust of any kind, when present at a substantial concentration in air and (5) any other substance which creates a comparable hazard to health.

The regulations cover substances which have chronic or delayed effects such as substances which are carcinogenic, mutagenic or teratogenic.

Under Regulation 3, an employer has towards an employee the duties of: (1) assessment; (2) prevention or control of exposure; (3) use of control measures and their maintenance, examination and test; (4) provision of information and training; and, where appropriate; (5) monitoring of workplace exposure and (6) health surveillance. So far as is reasonably practicable, the employer should regard himself as having similar duties towards other persons at the premises, except that there is no duty of health surveillance, and as having the first three duties listed towards others likely to be affected by the work. These duties are not confined to the occupier but apply also to contractors. Thus, the duties of an employer are owed by a contractor to his employees.

Table 25.4 *Principal contents of the Control of Substances Hazardous to Health Regulations 1988 and the associated Guidance*

Regulation 2	Interpretation
Regulation 3	Duties under these Regulations
Regulation 4	Prohibitions relating to certain substances
Regulation 6	Assessment of health risk created by work involving substances hazardous to health
Regulation 7	Prevention or control of exposure to substances hazardous to health
Regulation 8	Use of control measures, etc.
Regulation 9	Maintenance, examination and test of control measures
Regulation 10	Monitoring exposure at the workplace
Regulation 11	Health surveillance
Regulation 12	Information, instruction and training for persons who may be exposed to substances hazardous to health
Schedule 1	List of substances assigned maximum exposure limits
Schedule 2	Prohibition of substances hazardous to health for certain purposes
Schedule 3	Frequency of thorough examination and test of local exhaust ventilation plant used for certain processes
Schedule 4	Specific substances and processes for which monitoring is required
Schedule 5	Medical surveillance
Appendix	Health records

Regulation 4 places prohibitions on certain substances listed in Schedule 2 to the extent specified in that schedule. This includes a prohibition on: the manufacture and use of 2-naphthylamine, benzidine, 4-aminodiphenyl and 4-nitrodiphenyl; the use of benzene for any purpose other than in an industrial process; and on the use of sand for sand blasting.

Regulation 6 requires that the employer make 'a suitable and sufficient assessment' of the risks created by the work and of the steps which need to be taken to ensure compliance. The assessment should be reviewed if there is reason to suspect that it is no longer valid or if there has been a significant change in the work.

Regulation 7 requires that exposure to substances hazardous to health should be prevented or, where this is not reasonably practicable, adequately controlled. Further, it requires that so far as is reasonably practicable, this be done without recourse to personnel protective equipment, but, that, where necessary, such equipment should be provided. Where a substance has a MEL specified in Schedule 1, the exposure should not exceed this limit and should be reduced below it to the extent which is reasonably practicable. Where a substance has an OES, the exposure should not exceed this standard, but if it does, the employer should identify the reason and take action to remedy the situation as soon as is reasonably practicable. The exposure referred to may be any route, including inhalation, ingestion, absorption through the skin or contact with it.

Regulation 8 requires that an employer providing any control measure, PPE or other item, should take all reasonable steps to see that these are properly applied and that an employee should apply them and report any defects.

Regulation 9 requires adequate maintenance, examination and test of control measures. It refers specifically to LEV and to RPE. For the former it lays down a maximum interval for examination and test of 14 months or, for plant specified in Schedule 3, the interval given in that schedule. It requires that a record be kept of the examination and test, and of any repairs effected.

Regulation 10 requires that, where necessary to ensure control of exposure or prevent harm, monitoring of the workplace should be carried out using a suitable procedure. For certain substances given in Schedule 4, monitoring is required at the minimum frequency specified in the schedule. The regulation requires that records, or suitable summaries, be made and that where they are representative of the personal exposure of identifiable employees, they should be kept for 30 years.

Regulation 11 requires that, where it is appropriate for the protection of the health of employees who are liable to be exposed to a SHH, the employer should set up a system of health surveillance. The regulation is a long one, with some 12 sections. Regulation 11(2) states that health surveillance is appropriate where the employee is exposed to one of the substances and is engaged in one of the processes listed in Schedule 5, unless the exposure is insignificant, or where

he is exposed to a substance so that an identifiable disease or adverse health effect may be related to the exposure, there is a reasonable likelihood that the disease or effect may occur given the conditions of his work, and there is a valid technique for detecting indications of the disease or effect.

Regulation 12 requires the employer to provide to an employee who does work which may expose him to a SHH such information, instruction and training as is suitable and sufficient for him to know the risks to health and the precautions to be taken. The information should include the results of any monitoring carried out in compliance with Regulation 10. If, in the case of a substance listed in Schedule 1, the MEL is exceeded, the employee should be informed immediately. The information should also include the collective results of any health surveillance carried out in compliance with Regulation 11, presented in a form where the data cannot be related to a particular individual.

Regulation 12(3) requires that any person, whether or not an employee, who carries out work in connection with the employer's duties under the COSHH should have the necessary information, instruction and training.

Regulation 6 requires that the person making the assessment be competent and refers to Regulation 12(3).

25.4.1 Substances hazardous to health

There are a number of factors mentioned in the ACOP which need to be borne in mind when considering whether a substance is hazardous to health. The same substance may be hazardous in one form but not in another. Thus, a substance in dust form may be hazardous but be safe in solid form. The fibrous form may also be hazardous. A substance may contain an impurity which is more hazardous than the substance which it contaminates. A substance may have been found by experience to be hazardous, even if the causative agent has not been identified. Some combinations of substances may have harmful additive, or synergistic, effects.

25.4.2 Suitable and sufficient assessment

The ACOP states that the purpose of the assessment is to obtain the information necessary to select suitable control measures. It also provides a demonstration that the relevant factors have been taken into account and the necessary measures taken.

A suitable and sufficient assessment should include an assessment of the risks to health, a determination of the measures which need to be taken to achieve control under Regulation 7, and an identification of any other action necessary to comply with Regulations 8–12.

The assessment of risks should identify the substances to which personnel are liable to be exposed, the effects of the substances on the body, the places where and the forms in which these substances are likely to be present, and the ways in which and the extent to which personnel could be exposed, allowing for foreseeable deterioration, or failure, of a control measure. It should include an estimate of the exposure given the engineering measures and systems of work adopted. This estimate should be compared with any available standards for adequate control.

If comparison indicates that control is likely to be inadequate, the assessment should go on to determine the measures which need to be taken to achieve adequate control. A record should be kept of the assessment, except in very simple and obvious cases which could be readily repeated and explained at any time.

The assessment should be reviewed if it is shown to be no longer valid by some new information, which may include: results from the periodic examination and test of the engineering controls; results from the monitoring of workplace exposure; results of health surveillance, or a confirmed case of occupationally induced disease; or new information on health risks. A review is also called for if there is a significant change in the work, including any change in the substances used, the process, the throughput, the work practices or the engineering controls.

Further guidance on the assessment is given in *COSHH Assessment*. The stages of the assessment are the gathering of information, the evaluation of the risks, the specification of the measures and precautions required and the recording of the assessment. Information needs to be gathered on the substances and their hazards and on the work and the working practices.

Evaluation of the risks from a substance involves assessing, on the one hand, the potential for harm from exposure to it and, on the other, the nature of any exposure. For the latter, it is necessary to determine the situations in which exposure may occur, the persons liable to be exposed, and the frequency and duration of exposures.

Where there is uncertainty about the magnitude or significance of the exposure in relation to the requirement for prevention or adequate control, exposure should be measured, provided there is a suitable method of measurement.

COSHH Assessment identifies five possible outcomes of the assessment, which may be summarized as:

(1) risks are insignificant now and for the foreseeable future;
(2) risks are high now, and not adequately controlled;
(3) risks are controlled now, but foreseeably could become higher;
(4) risks are uncertain – uncertainty concerns extent and degree of exposure;
(5) risks are uncertain – uncertainty due to lack of information.

Guidance is given on the action to be taken for each of these outcomes.

25.4.3 Competent person

COSHH Assessment also gives guidance on the competence required of the person who is to undertake the assessment. The guide distinguishes between basic skills and additional skills. The basic skills are an understanding of the regulations and the abilities to make a systematic assessment of the risks and the exposures, to specify the measures which need to be taken in light of the assessment, and to communicate the findings in a report.

The additional skills are qualifications, experience and training. The guide emphasizes particularly practical experience and an understanding of the behaviour of people as well as processes.

25.4.4 Occupational exposure limits

As already stated, the two types of occupational exposure limit mentioned in the regulations are the MEL and the OES. The MELs are listed in Schedule 1 and the OESs are contained in the List of Approved OESs. This is given in

EH 40 *Occupational Exposure Limits*, which is up-dated annually.

The status of these two exposure limits is described in the ACOP. A MEL is the maximum concentration to which an employee may be exposed by inhalation under any circumstances. The concentration is averaged over a reference period which is specified in Schedule 1. Further details of the application of MELs are given in the ACOP.

Where an OES is assigned, exposure should be reduced to that standard. However, if exposure by inhalation exceeds the OES, the control may still be deemed adequate provided the reason for the excursion has been identified and appropriate steps are being taken to comply with the OES as soon as is reasonably practicable.

Where a substance is not assigned an MEL or OES, the ACOP states that the concentration should be controlled to a level to which nearly all the population could be exposed, day after day, without adverse effects on health.

25.4.5 Measurement and monitoring

The ACOP states that compliance with an OES may be demonstrated by measuring and recording the exposure of employees in accordance with EH 42 *Monitoring Strategies for Toxic Substances* (HSE, 1989).

Guidance is given in the ACOP on those situations where monitoring is required. Paragraph 68 states that it is always required for substances in Schedule 4 and, in addition, unless it is immediately obvious that control is adequate or suitable procedures for monitoring do not exist and cannot be devised, the requirement exists (1) where failure or deterioration of the control measures could result in a serious health effect, either because of the toxicity of the substance or the extent of the potential exposure, or both, (2) where measurement is necessary to ensure that an MEL or OES or any self-imposed working standard is not exceeded or (3) an additional check is required on the effectiveness of any control measure required under Regulation 7.

EH 42 gives detailed advice on such monitoring, including sampling strategies and interpretation of results.

25.4.6 Prevention and control

The ACOP states that adequate control is achieved if certain standards set out in paragraphs 27–30 of the code are met. Paragraph 27 deals with substances assigned an MEL, paragraph 28 with substances assigned an OES, paragraph 29 with other inhaled substances and paragraph 30 with exposure by routes other than inhalation. Compliance with an OES may be demonstrated by monitoring, as just described.

As far as is reasonably practicable, prevention or adequate control of exposure should be achieved by means other than PPE. Circumstances in which it may be necessary to resort to the latter include those: (1) where it is not technically feasible to achieve adequate control by process, operational and engineering measures alone; (2) where a new or revised assessment necessitates the temporary use of personal protection until adequate control is achieved by other means; (3) where urgent action is required, such as that following a plant failure and (4) where routine maintenance operations have to be done. In deciding whether to use PPE, due allowance should be made for its limitations and the practicalities of its use.

The ACOP enumerates the measures which may be used for the prevention or control of exposure to a SHH. Prevention may be effected by elimination of the substance or by substitution of a less hazardous substance. Twelve measures are listed for control: (1) a totally enclosed process and handling system; (2) a plant, process or system of work which minimizes the generation of, or suppresses or contains, fumes, dusts, etc.; (3) a partially enclosed system, with LEV; (4) LEV; (5) sufficient general ventilation; (6) a reduction of the number of workers exposed and a restriction of access; (7) a reduction in the period of exposure; (8) regular cleaning of surfaces and walls; (9) the provision of a means of the safe storage and disposal of the substance; (10) suitable PPE; (11) prohibition of eating, drinking and smoking in contaminated areas and (12) provision of adequate facilities of washing, changing and storage of clothing, including laundry arrangements for contaminated clothing.

25.4.7 Personal protective equipment

PPE includes respiratory equipment, protective clothing, footwear and eye protection. The selection of such equipment for protection against a substance should take into account the ability of the material to resist penetration by the substance, the adequacy of the design of the clothing and its suitability for the intended use, the environment in which it is to be worn, and, in the case of dust, the dust release characteristics of the material.

25.4.8 Health surveillance

Guidance on health surveillance is given in the ACOP and also in HS(G) 61 *Surveillance of People Exposed to Health Risks at Work* (HSE, 1990). The ACOP describes the purposes of health surveillance, the type of surveillance suitable and the situations in which it should be undertaken.

The purposes of health surveillance are essentially the protection of the health of employees and the evaluation of health hazards and control measures. The surveillance should lead to action and, before it is undertaken, the options and criteria should be established.

The health surveillance procedures enumerated in the ACOP are: (1) biological monitoring; (2) biological effect monitoring; (3) medical surveillance; (4) enquiries about symptoms, inspection or examination by a suitably qualified person; (5) inspection by a responsible person and (6) a review of the records and occupational history during and after exposure. Biological monitoring is based on the measurement of agents or their metabolites in body tissues or fluids, whilst biological effect monitoring is based on the biological effects on the worker. In this context, a suitably qualified person is instanced as an occupational health nurse and a responsible person as a manager or supervisor. The latter might check, for example, for chrome ulceration.

Health surveillance is appropriate for any exposure which fulfils the criteria of Regulation 11(2). The judgement on the likelihood of disease or adverse effects should be related to the nature and degree of exposure and should take into account information on epidemiology, human exposure, human and animal toxicological data, as well as extrapolation from information about analogous substances or situations.

25.4.9 Schedule 5

Frequent reference has been made in the foregoing to Schedule 5. This contains in Column 1 the names of various

substances and in Column 2 processes in which they are involved.

One substance listed in this schedule is VCM. The processes given in column 2 opposite this substance are manufacture, production, reclamation, storage, discharge, transport, use or polymerization.

25.4.10 Carcinogenic substances

The ACOP contains a second, separate section, or code, covering the control of carcinogenic substances (the *Carcinogens Code*). The *Carcinogens Code* covers scope, prohibitions, assessment, prevention and control, monitoring, health surveillance and information, instruction and training. Its structure thus reflects that of the COSHH Regulations and code. It is an amplification of the *COSHH Code* and not a replacement for it.

With regard to scope, the code applies to substances assigned the 'risk phrase' 'R45: May cause cancer' of the Classification, Labelling and Packaging Regulations 1984 and listed in Part IA1 of the approved list and to substances listed in Appendix 1 and substances arising from processes listed in that appendix. Certain substances are prohibited and these are listed in Schedule 2.

The guidance on assessment and on prevention and control largely follows that of the *COSHH Code*, but there are particular emphases and specific measures.

Exposure to a carcinogen involves risk of cancer. The risk increases with the exposure but there may be no short-term manifestation of adverse effects. The dose–response relation is quantal rather than graded.

In the case of carcinogens, particular importance is attached to prevention. The use of carcinogenic substances should be kept to a minimum, these should be clearly labelled, and the areas where they are used should be delineated and non-essential personnel excluded.

The first choice for control should be a totally enclosed system. Where this is not practical, alternative effective engineering measures should be taken including, where appropriate, the use of LEV. Care needs to be taken, however, that control measures do not aggravate the risk in the workplace or the outside environment.

Since exposure to carcinogens can result in a serious health effect, monitoring is normally required under paragraph 68 of the *COSHH Code*.

The *Carcinogens Code* states that, unless exposure is insignificant, health surveillance is appropriate for all carcinogenic substances. For substances in Schedule 5 of the regulations, medical surveillance is required. The code explains the objectives and limitations of surveillance. Surveillance has limitations in the identification of susceptible persons and in early recognition of cancer. It is largely restricted to the keeping of records to protect workers through the detection and evaluation of health risks.

In view of the nature of the risk, workers who may be exposed should be given full information about it and on the importance of prevention, control and hygiene measures. This should include information on the long-term risk and on the need for continued surveillance.

25.5 Dust Hazards

In general industry, dust is one of the most serious hazards to health. Even in the chemical industry, where there are many toxic vapours, dust remains a relatively important airborne contaminant.

The HSE guidance on dust hazards and their control is given in *Principles of Local Exhaust Ventilation* (HSE, 1975a), MS 4 Organic Dust Surveys (HSE, 1977), EH 44 *Dust: General Principles of Protection* (HSE, 1991) and EH 40/94 *Occupational Exposure Limits 1994* (HSE, 1994). Further guidance is given in *User Guide to Dust and Fume Control* (Muir, 1985) (the *IChem Dust Control Guide*), the *BOHS Airborne Contaminants Guide* and *Dust Control Handbook* (Mody and Jakhete, 1988 ACGIH/18) and by Bridgwater (1983).

25.5.1 Health effects of dusts

Some dusts have harmful effects, and some of the most harmful airborne contaminants are dusts. There are many dusts, however, which are inert, although they are unpleasant to breathe. Some account of the effects of dust on health and of exposure limits is given in Chapter 18.

EH 40 requires that, in the absence of a specific exposure limit for a particular dust, exposure should be kept below both 10 mg/m^3 8-h time-weighted average (TWA) total inhalable dust and 5 mg/m^3 8-h TWA total respirable dust. Respirable dust is the fraction of inhalable dust which penetrates the lung.

Much of the most important harmful effect from dusts is the various forms of fibrosis such as silicosis from silica or asbestosis from asbestos dust. Metals which are essentially harmless in bulk form may have dusts which are to some degree toxic and cause severe lung inflammation. Some dusts are associated with lung cancer.

25.5.2 Measurement of dusts

As described earlier, techniques exist for the visualization of dust clouds so that the presence and movement of dust in the workplace atmosphere may be followed. Such visualization is often sufficient to check the general state of the atmosphere, to detect leaks and to investigate the effectiveness of measures for dust suppression.

However, if the concentration of the dust is to be controlled in accordance with exposure limits, then a quantitative measurement of the total particle concentration is needed. It may also be necessary to measure the particle size distribution. The measurement of particle concentration and size distribution is a specialist matter.

Methods for the sampling and measurement of dust in air are described in the *IChemE Dust Control Guide*, the *BOHS Airborne Contaminants Guide, Particle Size Analysis* (Lloyd, 1987) and *Particle Size Analysis* (Stanley-Wood and Lines, 1992), and by Stairmand (1951), T. Allen (1975), Munns (1977), Kaye (1981), Vincent and Mark (1981) and Rood (1992a,b).

25.5.3 Minimization of exposure to dusts

The general approach to the minimization of exposure is similar to that taken for airborne contaminants generally and is described in Section 25.3, which makes frequent reference to dusts.

Section 25.3 describes the generation of dusts and methods for the prevention and control of exposure. Amplifying these as regards prevention, there are a number of industrial examples of the elimination of dust by such means as the substitution of different materials or a change of process. The substitution of metal shot for silica sand in shot blasting eliminates silica dust. The change from dry to wet processes for asbestos products largely eliminates asbestos dust.

Another important aspect of prevention is the suppression of dust fines. Here one approach is to prevent the generation of fines by a modification of material or process. This is exemplified by the use of spray drying or fluidized bed processes to produce granular products. Another approach is the use of a de-dusting agent. This finds application in the treatment of many pigments with very small amounts of liquid de-dusting agent.

Where exposure cannot be reduced sufficiently by prevention, it is necessary to resort to control. The methods of control available are described in Section 25.3. These include in particular enclosure and LEV. Indeed, accounts of LEV are couched mainly in terms of the control of dusts.

Good housekeeping and hygiene measures assume particular importance for dusts, especially highly toxic dusts. The objective of good housekeeping is to prevent dust from being carried back into the atmosphere. It includes the construction of buildings to eliminate dust-collecting surfaces and permit easy cleaning, the avoidance of dust spillages, the removal of dust piles and of pastes which form dust when dried, and the cleaning of dust-collecting surfaces. Arrangements to prevent contamination by dusty clothing may also be necessary.

25.6 Asbestos Dust

Asbestos dust is a particularly important hazard and occurs in the process industries. It is appropriate, therefore, to give it separate consideration. The effect of asbestos dust on health was described in Chapter 18 and it is principally the control of the dust which is considered here.

The relevant regulations are the CAWR 1987. There are two ACOPs, L27 (formerly COP 21) *Control of Asbestos at Work* (HSE, 1993) and COP 3 *Work with Asbestos Insulation, Asbestos Coating and Asbestos Insulation Board* (HSE, 1988).

Further guidance on asbestos dust is given in EH 10 *Asbestos: Exposure Limits and Measurement of Airborne Dust Concentrations* (HSE, 1990). There are a number of other guidance documents from the HSE, including MS 13 *Asbestos* (HSE, 1988), EH 41 *Respiratory Equipment for Use Against Asbestos* (HSE, 1985), EH 50 *Training Operatives and Supervisors for Work with Asbestos Insulation and Coatings* (HSE, 1988), EH 51 *Enclosures Provided for Work with Asbestos Insulation, Coatings and Insulating Boards* (HSE, 1989), EH 35 *Probable Asbestos Dust Concentrations at Construction Processes* (HSE, 1989), EH 52 *Removal Techniques and Associated Waste Handling for Asbestos Insulation, Coatings and Insulation Boards* (HSE 1989), EH 37 *Work with Asbestos Insulating Board* (HSE, 1989), EH 47 *Provision, Use and Maintenance of Hygiene Facilities for Work with Asbestos Insulation and Coatings* (HSE, 1990) and EH 36 *Work with Asbestos Cement* (HSE 1990).

A US viewpoint is given in *Asbestos: Medical and Legal Aspects* (Castleman, ACGIH 1990/39).

The principal contents of the CAWR are given in Table 25.5. It can be seen from this table that the general structure of the CAWR mirrors that of the COSHH Regulations, with requirements for the assessment, prevention or reduction of exposure, control measures, maintenance of control measures, air monitoring, health records and medical surveillance, and information, instruction and training. The CAWR also contains, however, a number of other provisions which are described below and which serve as an additional model for exposures of this general type.

Table 25.5 *Principal contents of the Control of Asbestos at Work Regulations 1987 and the associated Guidance*

Regulation 2	Interpretation
Regulation 3	Duties under these Regulations
Regulation 4	Identification of the type of asbestos
Regulation 5 and 5A	Assessment of work which exposes employees to asbestos
Regulation 6	Notification of work with asbestos
Regulation 7	Information, instruction and training
Regulation 8	Prevention or reduction of exposure to asbestos
Regulation 9	Use of control measures, etc.
Regulation 10	Maintenance of control measures, etc.
Regulation 11	Provision and cleaning of protective clothing
Regulation 12	Duty to prevent or reduce spread of asbestos
Regulation 13	Cleanliness of premises and plant
Regulation 14	Designated areas
Regulation 15	Air monitoring
Regulation 16	Health records and medical surveillance
Regulation 17	Washing and changing facilities
Regulation 18	Storage, distribution and labelling of raw asbestos and asbestos waste
Regulation 19	Supply of products containing asbestos for use at work
Schedule 1	Particulars to be included in a notification

Regulation 4 requires that the type of asbestos to which exposure may occur be identified.

Regulation 2 defines action levels and control limits. The action levels are 96 fibre-hours/ml of air where exposure is solely to chrysotile, and 48 fibre-hours/ml of air where exposure is to any other form of asbestos alone or in mixtures including mixtures of chrysotile with any other forms of asbestos. Where both types of exposure occur separately over a 12-week period, a proportionate number of fibre-hours per ml of air applies.

The control limits given in this regulation are for chrysotile (1) 0.5 fibres/ml of air averaged over any continuous period of 4 h and (2) 1.5 fibres/ml of air averaged over any continuous period of 10 min. For any other form of asbestos, either alone or in mixtures, including mixtures of chrysotile with any other forms of asbestos, the control limits are (1) 0.2 fibres/ml of air averaged over any continuous period 4 h and (2) 0.6 fibres/ml of air averaged over any continuous period of 10 min.

In general, the regulations apply to any exposure to asbestos at work, but some particular regulations are triggered only if exposure is liable to exceed the action level. These are Regulations 6, 14 and 16, relating, respectively, to notification, designated areas and medical surveillance.

Regulation 6 requires notification of work with asbestos unless the exposure is not liable to exceed the action level or the employer is licensed under the Asbestos (Licensing) Regulations 1983.

Regulation 14 requires that any area in which work on asbestos is carried out be designated as: (1) an asbestos area, where the exposure of a person working for the whole of his working time is liable to exceed the action level; or (2) a respirator area, where the concentration of asbestos is liable to exceed any control limit.

General guidance on air monitoring is given in EH 42 *Monitoring Strategies for Toxic Substances* (HSE, 1989) and guidance for asbestos specifically is given in EH 10 *Asbestos: Exposure Limits and Measurement of Airborne Dust Concentrations* (HSE, 1990). EH 10 gives detailed information on the determination of action and control levels and on the monitoring and measurement of airborne asbestos, including accredited quality control laboratories, measurement methods, sampling and interpretation. It also contains a schedule dealing with sampling methods. Also relevant is *A Guide to Monitoring Airborne Asbestos in Buildings* (Keyes and Chesson, ACGIH 1989/33).

Further guidance on measurement is given in MDHS 39/3 *Asbestos Fibres in Air* (HSE, 1990).

Quality control laboratories are accredited for airborne asbestos measurement under the National Measurement Accreditation Scheme (NAMAS). This supersedes the earlier NATLAS scheme.

Where a process has the potential to generate asbestos dust, the methods of eliminating or reducing the generation of dust described in Section 25.5 should be exploited as far as is reasonably practicable.

Leaks from plant handling asbestos dust can cause serious contamination of the workplace atmosphere but are often invisible. They may be detected, however, using a dust lamp. This is illustrated in Figure 25.1 above, which shows the visualization of asbestos dust using a dust lamp.

An important part of the asbestos dust problem in the process industries relates to lagging. In many applications, there are satisfactory substitutes and the industry has moved towards the use of these. Any use of asbestos should be confined to white asbestos. In practice, the use of asbestos is limited and it may not be easy to obtain.

Dust is particularly likely to be raised in removing lagging. The work should be segregated and workers should wear protective clothing and RPE. The area should be thoroughly cleaned after the work is complete.

Maintenance is particularly important in plant where asbestos dust may arise or in plant with asbestos lagging.

Where asbestos dust may be present, housekeeping measures assume particular importance. A high standard of cleanliness is necessary in the workplace. There need to be good facilities for washing and changing, and for cleaning protective clothing.

25.7 Ventilation

If an assessment of the air quality in the workplace shows it to be necessary, ventilation should be provided. Accounts of ventilation are given in *Exhaust Hoods* (Dallavalle, 1952), *Plant and Process Ventilation* (Hemeon, 1963), *Fundamentals of Industrial Ventilation* (Baturin, 1972), *Basic Principles of Heating and Ventilation* (Bedford, 1974), *Air Conditioning and Ventilation of Buildings* (Croome-Gale and Roberts, 1975), *Handbook of Ventilation for Contaminant Control* (McDermott, 1976), *Advanced Design of Industrial Ventilation Systems for Contaminant Control* (Goodfellow, 1985) and by Grandidge (1969, 1977), Gill (1980b), Goldfield (1980), Caplan (1982), Cassells (1986–) and Fanger and Christensen (1986). The HSE guidance is given in *Principles of Local Exhaust Ventilation* (HSE, 1975a), HS (G) 37 *An Introduction to Local Exhaust Ventilation* (HSE, 1987), EH 22 *Ventilation of the Workplace* (HSE, 1988) and HS (G) 54 *The Maintenance, Examination and Test of Local Exhaust Ventilation* (HSE, 1990). Further guidance is given in the *BOHS Air Contaminants Guide*, the *CIBSE Guide* by the CIBSE* (1977), *Ventilation Requirements* by the Building Research Establishment (BRE, 1981 Dig. 208), *Design of Industrial Ventilation Systems* (Alden and Kane, ACGIH 1982/6), *Heating, Ventilation and Air-Conditioning Analysis and Design* (McQuiston and Parker, ACGIH 1988/21), *Ventilation for Control of the Work Environment* (Burgess, Ellenbecker and Treitman, 1989 ACGIH/38), *Guide for Testing Ventilation Systems* (ACGIH 1991/58), *Industrial Ventilation: A Manual of Recommended Practice* (ACGIH 1991/67), *Industrial Ventilation Workbook* (Burton, 1991 AIHA/21), *Laboratory Ventilation Workbook* (Burton, 1991 AIHA/22), *Industrial Ventilation: Engineering Principles* (Heinsohn, 1991 ACGIH/66) and *IAQ and HVAC Workbook* (Burton, 1993 AIHA/25) and in the handbooks of the ASHRAE (1990/4, 1991/5, 1992/6, 1993/7).

A relevant code of practice is BS 5925, which is particularly relevant to natural ventilation. The 1980 version was BS 5925: 1980 *Design of Buildings: Ventilation Principles and Designing for Natural Ventilation* which is the current one for much of the ventilation literature quoted here. The current version is BS 5925: 1991 *Code of Practice: Ventilation Principles and Designing for Natural Ventilation*. The code for mechanical ventilation is BS 5720: 1979 *Code of Practice for Mechanical Ventilation and Air Conditioning in Buildings*.

The reasons for ventilation and ventilation rates for normal purposes are discussed in Chapter 10. Briefly, a degree of ventilation which maintains a suitable thermal environment commonly suffices for the other requirements also. BS 5925: 1980 recommends for factories a rate of 0.8 l/s per m^2 of floor area.

If there is airborne contamination, however, the situation is different. In this case, the air requirement may depend primarily on the reduction of the contaminant concentration below the control limit.

As described in Section 25.3, the design should exploit, to the extent practical, methods of keeping the workplace atmosphere free of contamination which do not rely on ventilation.

If ventilation has to be used, there are two main methods available. These are general ventilation, which relies on dilution, and sometimes also on displacement, and LEV, in which contamination is removed close to its source so that the main workspace is not affected.

25.7.1 Local exhaust ventilation

HSE guidance on LEV is given in *Principles of Local Exhaust Ventilation* (HSE, 1975a), HS (G) 37 *An Introduction to Local Exhaust Ventilation* (HSE, 1987) and EH 22 *Ventilation of the Workplace* (HSE 1988). Further guidance is given in the *BOHS Air Contaminants Guide*.

LEV removes contaminants from the source directly into a ventilation system. It does not rely on the dilution or displacement effects of general ventilation. It should be designed to remove the contaminant from around the source rather than from around the operator.

An LEV system may be considered in terms of the following elements: (1) contaminant source, (2) hood, (3) ducting, (4) air filtration plant and (5) fan.

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* The Chartered Institute of Building Services Engineers has twice changed its name in recent years, the previous acronyms being Institution of Heating and Ventilation Engineers (IHVE) and Chartered Institute of Building Services (CIBS). The guide referred to is also known as the *IHVE Guide* and the *CIBS Guide*.

25.7.2 Contaminant source

The main problem in effecting LEV is the dispersion of the contaminant from the source. Once it has escaped from the immediate area of the source, it is very difficult to bring it under control. It is necessary, therefore, to obtain information on the behaviour of the contaminant leaving the source, such as its direction and velocity.

The air currents which influence the behaviour of the contaminant should also be studied. Air currents which are not essential to the process but are incidental or unconnected should be eliminated.

25.7.3 Enclosure and receptor hoods

It is usual to distinguish between two basic types of enclosure or hood systems used in LEV: (1) enclosures and receptor hoods and (2) captor hoods. Enclosures may be (1) total enclosures or (2) partial enclosures.

With a receptor hood, the emission source is either inside or at the mouth of the hood. The hood receives contaminated air brought into it by air currents. These are either hot air currents rising from the process or cold air currents induced by the process. The air currents from a furnace and from a grinding wheel illustrate the two processes, respectively. The function of the fan in this type of system is simply to suck away the air entering the hood.

Total enclosure is the most effective arrangement, but it is not always practical. It is used in the chemical industry and for the handling of radioactive materials. It may involve remote operation using manipulators.

Where a total enclosure is used, it needs to be air-tight so that it contains the vapour or dust handled, and strong enough to remain so. When such an enclosure is used, the space inside and the plant and equipment inside may be heavily contaminated. There is thus a need for measures to limit exposure when the enclosure has to be opened. These may include measures to remove the contaminant and measures such as procedures and/or interlocks to control access.

There are a number of types of partial enclosure, including (1) booths, (2) fume cupboards, (3) hoods over hot processes and (4) jet assisted hoods.

A partial enclosure should be no larger than is necessary for the purpose. The velocity of the air entering it should be high enough to overcome any tendency for the air inside to escape. Turbulence may be created within the enclosure by the working of equipment inside it and outside the enclosure by air currents. For a partial enclosure, the basic air flow required is given by

$$Q = AV \qquad [25.7.1]$$

where A is the area of the opening (m^2), Q is the volumetric air flow (m^3/s) and V is the inward superficial air velocity (m/s). The *BOHS Guide* states that whilst in quiet conditions an inward air velocity of 0.5 m/s may suffice, in more difficult circumstances, 2 m/s or more may be needed, and that for normal situations in factories, an air velocity of 1 m/s is often used. Depending on the nature of the enclosure, it may also be necessary to make an allowance for leakage at the joints of the enclosure. Guidance is given in the *BOHS Guide*.

A booth is a type of partial enclosure from which one side, or part of one side, is missing. It should be deep, since leakage due to eddies tends to occur round the edges of a shallow booth.

If the booth is large enough for an operator to work inside it, he should work at the front open face and not between the contaminant source and the air exhaust outlets.

A laboratory fume cupboard may be regarded as a special type of booth giving partial enclosure, but with a closure which can be closed to give almost total enclosure. There are many variations depending on the type of work to be done, but a fume cupboard usually takes the form of an open-fronted booth with a vertically sliding front window, or sash. The sash may be left open, partially closed or closed, and there are various arrangements designed to maintain a stable air flow and to ensure that air is drawn from both the top and bottom of the cupboard.

Relevant standards for fume cupboards are BS 7258: 1990 *Laboratory Fume Cupboards* and also BS DD 191: 1990 *Method for Determination of the Containment Value of a Laboratory Fume Cupboard*. Further guidance is given by D. Hughes (1980), Piney and Carroll (1983) and J.D. Cook and Hughes (1986).

Another receptor arrangement is a hood over a hot process. The design intent is that the hot gas rises from the process and flows into the hood. If the gas plume is not hot enough or if too much air is entrained into it, so that the total plume volume is too great and too cool, the hood may not operate as intended. The plume may miss the hood or may enter but may flow back out.

Methods are available for the design of such hoods. They include the plume models by Hemeon (1963) and Bender (1979) and methods of measuring plume volume and velocity, assisted by the use of cine or video film, developed by Bamford (1961) and Goodfellow and Bender (1980).

A further type of receptor arrangement is the jet-assisted, or push-pull, hood. This is used with an open surface such as a tank, where a jet of air is blown across the surface. The design intent may be frustrated if the jet is too powerful so that it carries the contaminant beyond the exhaust hood or if it strikes parts of the tank so that turbulence is created.

Models applicable to jet-assisted hoods of this type include those by Hemeon (1963) and Baturin (1972), whilst a practical application has been described by Huebener and Hughes (1985).

25.7.4 Captor hoods

The other main type of hood used in LEV is the captor hood. Whereas a receptor hood receives a flow of contaminated air carried into it, a captor hood draws the air flow in. The two types of hood may sometimes be similar in shape, but the principle of operation is different. A receptor hood operates on the push and a captor hood on the pull principle.

For a captor hood, the air velocity required depends critically on the distance between the hood face and the contaminant source. For a normal shape such as a circle, square or rectangle (although not for a slot), the air velocity at a point only one-hood face diameter from the centre of the hood face itself is typically only one-tenth of the face velocity. Thus, a broad rule-of-thumb for a practical system is that the contaminant source should not be more than one hood face diameter from the hood face.

A more scientific approach is based on the concept of a capture velocity, which is the velocity induced at the source sufficient to capture the contaminant. Whilst there is no real design alternative to the use of capture velocity, the concept has limitations. It is most applicable where the

contaminant at the source has a low velocity, but tends to break down where the contaminant is directed away from the hood at an appreciable velocity. The *BOHS Guide* states that, although capture velocities as low as 0.25 m/s are sometimes quoted, a value of 0.5 m/s should be taken as a practical minimum, and it uses in a subsequent illustrative example a velocity of 0.75 m/s.

A relation for the superficial velocity of air entering the hood has been given by B. Fletcher (1977). This is

$$\frac{V}{V_0} = \frac{1}{0.93 + 8.58\alpha^2} \qquad [25.7.2]$$

with

$$\alpha = \frac{X}{A^{1/2}}\left(\frac{W}{L}\right)^{-\beta} \qquad [25.7.3]$$

$$\beta = 0.2\left(\frac{X}{A}\right)^{-1/3} \qquad [25.7.4]$$

where A is the face area of the hood (m^2), L is the length of the hood (m), V is the capture velocity at distance X (m/s), V_0 is the superficial velocity at the face of the hood (m/s), W is the width of the hood (m), X is the distance from the hood (m), and α and β are indices.

The performance of a captor hood may be enhanced by the use of flanges around the face inlet. The design of such flanges is treated in the *BOHS Guide*.

The volumetric flow of air required for a captor hood can be very much greater than for a receptor hood. The *BOHS Guide* gives a comparison of four systems. Of these four systems, the one most economical in air is a receptor hood with a small aperture in the face side, the second is a receptor hood with the whole face side missing, and the third is a captor hood with a large flange and the last a captor hood with no flange. The ratio of the volumetric air flow required by the last of these arrangements to that required by the first is 100 : 1.

25.7.5 Low volume, high velocity system

A particular type of captor hood arrangement for LEV is the low volume, high velocity (LVHV) system. This system utilizes a small hood (typically $<6\ cm^2$) placed very close to the contaminant source and a high capture velocity ($\approx$50–100 m/s). It may be used for vapour sources such as welding and for dust sources such as grinding. However, it is not easy to use and tends to be limited in application. Successful use requires that it be unobtrusive, correctly adjusted and properly maintained.

25.7.6 General ventilation

LEV is the preferred method of ventilation, but there are circumstances in which it is not applicable, and in such cases it is resorted to general ventilation of the work space. However, such general ventilation is usually regarded as a comparatively ineffective method of contaminant control.

Some processes are operated outdoors, and it is often assumed that an outdoor location ensures negligible exposure. This is not necessarily so, and each case should be treated individually.

In indoors there tend to be wide variations between the concentrations at different locations in the work space; the concentrations can differ by orders of magnitude. The enhancement of general ventilation may have little or no effect on the concentration at a particular point.

In general, the variability of the concentration of a contaminant at a fixed point outdoors tends to be very high. Indoors, the variability at a fixed point is much less.

General ventilation may have two effects. One is simply to reduce the concentration of contaminant by the introduction of more air. The other is to move the contaminant in a particular direction by displacement of air.

As described in Chapter 10, methods are available for the determination of the volumetric flow of air due to natural ventilation. Guidance is available in BS 5925: 1980. The *BOHS Guide* gives a worked example based on the BS 5925 method.

The concentration of contaminant resulting from general ventilation may be obtained on the assumption of perfect mixing in the work space, as described in Chapter 10. In practice, the concentration may be considerably higher. One approach to this problem is the method used by the ACGIH for the determination of concentration of a contaminant relative to the TLV. This method utilizes an empirical factor K which takes into account variations in the concentration with space and time, and allows for the toxicity of the contaminant. Values of K range from 3 to 10.

25.7.7 Air jets

Air jets are sometimes used as part of a system of general ventilation. They are of two types: those that draw air from within the work space and those that draw air from outside. In the first type, the jet is used to promote mixing in the space. In the second type, it may be used as a fresh air jet to provide a volume where the concentration of contaminant is low, but in this case it must be sufficiently near the point in question to effect this; otherwise, the jet is liable to become contaminated with air from the work space.

The following equation is given by the CIBSE (1977) for the centre line velocity of a jet:

$$X = \frac{KQ}{V_x(A_f C_d)^{1/2}} \qquad [25.7.5]$$

where A_f is the free area of discharge (m^2), C_d is the coefficient of discharge, Q is the volumetric flow (m^3/s), V_x is the centre line velocity at distance x (m/s), X is the distance along the centre line (m) and K is a constant. The value of C_d is taken as 1.0 for a well-rounded nozzle and 0.6 for a sharp-edged orifice and that of K as 7.0 for a round nozzle and 5.7 for a standard grill, where the outlet velocity is 4–8 m/s.

The use of air jets can cause problems if the jet is not well integrated with the overall system design. Typical effects are undesired dispersion of the contaminant, interference with existing LEV systems, the creation of vortices where the contaminant becomes concentrated, and discomfort due to cold draught.

Use is also made of air curtains to provide a barrier to the flow of contaminant. The use of such a curtain can result in dispersion rather than containment of the contaminant and careful design is needed. Another device sometimes used is an air douche in which air is discharged at low velocity above the heads of workers.

25.7.8 Air replacement

The air removed by the ventilation system has to be replaced. It is usually recommended that this replacement air should enter through properly designed inlets. Air which simply leaks in through open doors, windows and cracks, may cause unpleasant draughts and may also set up air movements which affect the operation of an LEV system.

25.7.9 Design of ventilation systems

In designing a ventilation system for the control of a contaminant, this ultimate purpose needs to be borne constantly in mind. It is not uncommon for this objective to be lost sight of and for the design to degenerate into the mere provision of the mechanical elements of the system such as the hood, ductwork and fan. The *BOHS Guide* gives a series of quotations, starting with J.B.S. Haldane in 1907 and continuing into the 1980s. The following, from Hemeon (1963), though not the most recent, perhaps puts the problem most clearly:

> It sometimes seems that engineers experience such sheer satisfaction in their ability to handle the design of duct work on a neatly quantitative basis, that they are led to slight the initial problem of selecting suitable exhaust or ventilation rates as though they were a minor detail to be covered as quickly as possible . . . whereas the part they slight is the essential of industrial ventilation.

For this reason, the *Guide* advocates design leadership by an occupational hygienist.

Accounts of the mechanical design of ventilation systems are given in the texts quoted. In particular, *Local Exhaust Ventilation*, the *BOHS Guide* and the *IChemE Dust Control Guide* give detailed treatments, dealing with overall system design, ductwork, fittings, multi-branched systems, fans, and air cleaning and disposal.

Guidance on the commissioning of ventilation systems is given in *Principles of Local Exhaust Ventilation*, BS 5720, the *Commissioning Code of CIBSE* (CIBS, 1977; CIBSE, 1978–), and the *BOHS Guide*.

Where the system is a multi-branched one, the balancing of the flows is of particular importance.

25.7.10 Maintenance of ventilation systems

It is important that any ventilation system for the control of contaminants be properly examined and maintained. HSE guidance is given in HS(G) 54 *The Maintenance, Examination and Test of Local Exhaust Ventilation* (HSE, 1990).

Inspections have found that the effectiveness of many industrial ventilation systems is low. Sometimes this is due to inefficient functioning of the mechanical items due to poor maintenance. But it is also possible for these items to be working as intended but for the ventilation achieved to be ineffective. This may arise, for example, if the contaminant source has been moved somewhat further from the hood.

The prominence given in regulations to maintaining the whole system so that it operates as intended reflects the problem. As described earlier, Regulation 9 of the COSHH Regulations requires that for an LEV plant, the maximum interval for thorough examination and test is 14 months, or as given in Schedule 3 to that regulation. The CLAW Regulations and the CAWR also contain requirements for LEV system maintenance.

Checklists for the maintenance of LEV systems are given HS(G) 54 and the *BOHS Guide*.

25.8 Skin Disease

Thus far, the discussion has dealt with toxic substances which are airborne. It is also necessary to prevent corrosive and toxic chemicals from causing irritation of the skin leading to skin disease, or dermatitis, and from entering the body through the skin.

Guidance on skin disease is given in MS 3 *Skin Tests in Dermatitis and Occupational Chest Disease* (HSE, 1977), EH 26 *Occupational Skin Diseases* (HSE, 1981) and MS 24 *Health Surveillance of Occupational Skin Disease* (HSE, 1991). Further accounts of skin disease are given in *Occupational Diseases of the Skin* (L. Schwartz, Tulipan and Birmingham, 1957) and *Manual of Contact Dermatoses* (Fregert, 1974) and by McCreaney (1969, 1977), Rycroft (1979, 1980, 1980 LPB 58) and Gadian (1983). Aspects of skin disease in the petroleum industry are dealt with in *Petroleum Hydrocarbons: their Absorption Through and Effect on the Skin* (CONCAWE, 1984 84/54) and *Factors Affecting the Skin Penetration and Carcinogenic Potency of Petroleum Products Containing Polycyclic Aromatic Compounds* (CONCAWE, 1990 90/55).

Occupational skin disease is the most common cause of disablement in industry. Statistics are given in the Health and Safety Statistics 1990–91 (HSE, 1992b). There are a number of different ways of arriving at a figure for such disease, but the number of new cases is of the order of 40,000 per year.

The types of chemical which cause skin disease are classified as (1) contact irritants, (2) contact sensitizers and (3) photosensitizers. Contact irritants cause direct damage to the skin. Contact sensitizers cause a specific allergic response to develop over a period.

Photosensitizers may be either irritants or sensitizers, but require the additional stimulus of sunlight or ultraviolet (UV) light.

Substances which are liable to cause skin disease are chemicals, cutting oils, degreasing agents, tar and pitch. It may also be caused by physical agents such as heat, cold, humidity, light and ionizing radiations.

Prevention of skin disease should be based on engineering measures to eliminate the causal agent, supplemented where necessary by personal protection. Where chemicals have to be handled, it is essential to use the proper methods and to wear the appropriate protective clothing, to observe the highest standards of personal hygiene, to change working clothes, including underwear, frequently and to take a thorough shower each day. Any break in the skin should be covered. Skin rashes should be reported, and wounds treated, promptly.

25.9 Physico-chemical Hazards

There are a number of physico-chemical effects which are very simple and familiar to the engineer, but which have implications often not fully appreciated, particularly by process and maintenance personnel.

An account of some of these effects has been given by Jennings (1974a,b). They include:

(1) density differences –
  (a) gases and vapours,
  (b) liquids;
(2) phase changes;
(3) vapour pressure;

(4) flashing liquids;
(5) nearly immiscible liquids;
(6) heat of mixing;
(7) exothermic reactions;
(8) impurities.

At constant pressure, the density of a gas or vapour ρ_g is proportional to the molecular weight M and inversely proportional to the absolute temperature T:

$$\rho_g \propto \frac{M}{T} \qquad [25.9.1]$$

Density differences can cause the gas or vapour to flow in unexpected ways.

In one case, a manhole in a reboiler containing benzene was left open. Some benzene vapour escaped and poured down so quickly into the base of the room that the operator was killed before he could put on a respirator.

Another incident involved a hydrogenation vessel which was shut-down for repair, but into which hydrogen continued to leak through a valve that was only partially closed. When the top manhole cover was taken off to admit a charge of carbon dioxide as an inert blanket, there was a flash of fire. Since the hydrogen was much less dense, enough air had presumably entered to form a flammable mixture.

Differences in liquid density can give rise to very high pressure in equipment and to layering. In one incident, the discharge and suction valves were shut on a pump full of ethylene glycol and the pump was left running. The liquid heated up and the volumetric expansion of the liquid generated a pressure sufficient to crack the pump casing.

The effect of layering due to the difference of densities of two liquids is illustrated by the following case. A mixture of liquid caustic soda and phenol was being prepared in a reaction vessel by an operator. The addition was made without agitation and the phenol formed a separate layer on top of the caustic soda. When the agitator was switched on, there was a violent reaction and about half the charge was ejected through the top opening, which had a hinged lid, onto the operator.

The volume changes associated with a change of phase, particularly changes between liquid and vapour, can produce violent effects. At atmospheric pressure, for example, one volume of liquid water vaporizes to give about 1600 volumes of steam.

A road tanker was being filled with hot tar at a temperature just below 100°C when the pump failed. In accordance with normal practice, the tar line was blown out with steam. Since the tank was only half full, the driver went on to another site to top up and so obtain a full load. Here the tar was at a temperature in excess of 100°C and a few seconds after the filling began, hot tar was ejected from the manhole. The cause was vaporization of the steam condensate left in the tank from the steam blowing operation at the first site.

Conversely, sudden contraction of vapour can create a vacuum and cause a vessel to implode or to draw in air. A particular important case is a situation which occurs when heat input is lost on the reboiler of a distillation column. Rapid condensation of the vapour in the column may create a vacuum which draws air in through the vent and may thus cause an explosive mixture to form. This may be prevented by the use of nitrogen injection.

Powerful effects are also produced by the variation of the vapour pressure with temperature. For a pure liquid, the relation between the vapour pressure and temperature may be represented by the Antoine equation:

$$p^\circ = \exp\left(A - \frac{B}{T + C}\right) \qquad [25.9.2]$$

where p° is the vapour pressure, T is the absolute temperature, and A, B and C are constants. For most liquids, the vapour pressure doubles over a temperature range of about 8°C. For ideal liquid mixtures, Raoulf's law applies:

$$p_i = p_i^\circ x_i \qquad [25.9.3]$$

where p_i° is the vapour pressure of the pure component i, p_i is the partial pressure of component i and x_i is the concentration of component i (mole fraction).

But, if instead the liquids are immiscible, then for each liquid

$$p_i = p_i^\circ \qquad [25.9.4]$$

In both cases, the total pressure P is given by Dalton's law:

$$P = \sum pi$$

In the general case, some of the components may be inert gases.

The effect of vapour pressure is illustrated by a case in a works producing chlorine by the mercury cell process where a worker was found to have persistently high mercury in his urine, even though he hardly ever went into the cellroom. His main work was the removal of ebonite lining from mild steel sections used in the cellroom equipment. The work involved the application of heat. This heat was sufficient to cause traces of mercury lodged in cracks in the ebonite to exert an appreciable vapour pressure.

A common phenomenon associated with vapour pressure is cavitation in pumps. This occurs if the suction pressure is low and the liquid temperature is high. Pockets of vapour form and collapse as the local pressure falls below or rises above the vapour pressure. The resultant erosion and pitting is extremely damaging to the pump.

A Dowtherm furnace started up and the pressure rose suddenly from 15 to 110 psi. Water had entered the system and both liquids were exerting their full vapour pressure. In this instance, the pressure relief valve operated and prevented an accident.

If a liquid at a given pressure is let down to a lower pressure such that the boiling point at the lower pressure is less than the original temperature of the liquid, liquid immediately flashes off until the lower pressure boiling point is reached, the amount of vapour formed being determined by the heat balance.

A tank had been cleaned by boiling water in it under pressure. The operator opened a vent to release the pressure, but loosened a manhole before the venting was complete. Large amounts of boiling water and steam issued out around the cover.

Liquid systems in which there are two separate liquid phases are loosely referred to as 'immiscible', although there is always some mutual solubility, so that 'nearly immiscible' would be a more accurate description. Consider

a system with two nearly immiscible components A and B. At equilibrium, the phase which is nearly all A is saturated with a small quantity of B. If this phase has separated out, both A and B exert their full vapour pressure. If B has a high vapour pressure, a considerable proportion may be evolved.

An operator drained water from a tank in which there was a water layer covered with a benzene layer. The benzene in the water exerted an appreciable vapour pressure and the operator suffered benzene poisoning.

When two liquid chemicals are mixed together, there is a heat of mixing. Whilst this is zero for an ideal mixture and low for many mixtures, for others it is appreciable.

Owing to a failure of communication, a tanker of hydrochloric acid was unloaded into a storage tank used for sulfuric acid. When about half of the 3000 gal load had been transferred, there was a violent explosion, which raised the tank several inches off the ground and buckled it, and broke the inlet and outlet lines.

In another case, a violent explosion occurred when mixing took place between very strong caustic soda, which was lying on the bottom of a vessel and was covered by a solid crust, and weak caustic soda above it.

Reaction kinetic effects, especially in exothermic reactions, are discussed in Chapter 11.

A particular case of importance is situations in which there is inadequate agitation in a chemical reactor. The reactants are allowed to build up without agitation and then react explosively, either spontaneously or when agitation is started.

One incident involved a sulfonation process in which benzene and concentrated sulfuric acid were premixed before transfer to a reaction vessel. On one occasion, the agitator was not used and the reactants were transferred unmixed. The operator noticed this and quickly switched on the reactor agitator. There was a rapid reaction, benzene vapour was evolved, a flammable mixture was formed in the room and it ignited.

Impurities can cause violent reactions or severe corrosion.

An operator was transferring thionyl chloride by vacuum from a 55 gal drum through a stainless steel hose when the hose developed a leak. He obtained another hose, checked that nothing drained from it and substituted it for the first. When he opened the feed valve, the hose ruptured. The accident was caused by a small amount of water which was left in the hose and which reacted violently with the thionyl chloride, releasing large volumes of hydrogen chloride and sulfur dioxide. Calculation showed that one teaspoonful of water would be enough to generate a pressure of 2800 psig in the hose.

Corrosion not only reduces the strength of the equipment, but also generates gases.

An apprentice under training was erecting some pipework. He required a blank flange of a particular size and noticed one on some redundant pipework nearby. When he attempted to remove the blank, acid sprayed in his face. The pipework had been used previously for concentrated sulfuric acid and corrosion had generated hydrogen, which pressurized the pipe.

25.10 Ionizing Radiation Hazards

Materials and machines which give off ionizing radiation are widely used in industry. They are potentially very hazardous, but they may be handled safely by taking proper precautions.

The legislation covering the use of ionizing radiations is discussed in Chapter 3. That of principal relevance here is the Ionizing Radiations Regulations 1985. The associated ACOP is COP 16 *The Protection of Persons against Ionising Radiation arising from any Work Activity* (HSE, 1985).

Engineering aspects of ionizing radiations are described in *Radioactivity for Engineers* (Coombe, 1968) and health and safety aspects are described in *Radiation Hygiene Handbook* (Blatz, 1959), *Radiation Protection Standards* (L.S. Taylor, 1971), *Principles of Radiation Shielding* (Chilton, Shultis and Faw, 1984), *Industrial Radiation Hazards Deskbook* (Cheremisinoff, Cheremisinoff and Teresinski, 1987 ACGIH/12) and *Radiation Protection* (Shapiro, ACGIH 1990/48) and by H.H. Fawcett (1965c), Bennellick (1969, 1977), Brodsky (1978–), Doran (1980), Harrington (1980b), Dennis (1982) and Kielman and Fawcett (1982).

A code relevant to potential exposure to radioactive materials during a fire is NFPA 801: 1991 *Facilities Handling Radioactive Materials*.

The hazard from sealed sources, from machines designed to generate ionizing radiations such as X-rays and from machines which give off radiations adventitiously is one of external exposure, but unsealed sources present the further hazard of internal exposure arising from ingestion.

Ionizing radiations are a complex and specialist matter and only a very limited treatment is given here. A more detailed treatment of types and units of radiation is given in Appendix 20. COP 16 gives detailed coverage of a large number of industrial aspects.

25.10.1 Types and units of radiation

There are three main types of radioactive particle or ray: (1) α-particles, (2) β-rays and (3) γ- and X-rays. α-particles have a relatively large mass and short range, being stopped by an air gap of about 8 cm or a sheet of paper, and generally they present little external radiation hazard, but are dangerous if they get inside the body. β-rays (or particles) have a much smaller mass and greater penetrating power. Their range in air is about 10 m, but they are usually stopped by a few millimetres of solid material. γ-rays and X-rays are electromagnetic radiations which have a range of a few hundred metres, but can be stopped by a few millimetres of lead or by 0.5–1 m of concrete.

In the SI system, the units of radiation are: for activity, the becquerel (By); for absorbed dose, the gray (Gy); and for the dose equivalent, the sievert (Sv). The dose equivalent is the product of the absorbed dose and a quality factor (QF). The corresponding units in the older system are the curie (Ci), rad (rad) and rem (rem), respectively.

25.10.2 Effects of exposure

α-Particles destroy bone marrow so that the red corpuscles are not replaced. β-rays give rise to skin burns, skin cancer, dermatitis and eye disease. γ-rays and X-rays cause skin burns and cancer and ageing effects. Fairly severe exposure is required to cause sterility, but genetic effects are believed to be proportional to exposure.

25.10.3 Industrial applications

Industrial applications of ionizing radiations include the following:

(1) radioactive process materials;
(2) Radioactive auxiliary materials –
    (a) tracers,

(b) sorting aids,
(c) quality control aids,
(d) static eliminators,
(e) instruments;
(3) γ- and X-rays –
(a) non-destructive testing,
(b) quality control;
(4) irradiation –
(a) food preservation,
(b) cold sterilization,
(c) polymerization.

Some process materials, such as radioactive metals, are themselves radioactive.

Radioactive materials are commonly used as tracers. Examples are the use of ^{24}Na, ^{59}Fe and ^{60}Co in work on mixing, piston ring wear and refractory wear, respectively, and of various tracers in following the progress of pigs or of interfaces between products in pipelines and in detecting leaks in water and other pipe systems.

Items on which sorting or quality control is to be carried out may be tagged with a radioactive material. Radioactive sources are used to ionize the air and so dissipate static electricity. Instruments which use radioactivity include level measuring instruments that measure the height of the liquid surface and ionization chambers which detect the presence of smoke.

γ-Ray sources are used to detect flaws in castings. The castings are grouped around the source with photographic plates behind them. Similarly, the non-destructive testing of pressure vessels and components, and particularly welds, is carried out using X-rays. The latter are also used in X-ray fluoroscopy for the inspection of items on conveyor belts for quality control purposes.

Applications of irradiation in polymerization include the vulcanization of rubber and polymerization of high melting point polyethylene.

25.10.4 Measurement of radiation

Measurements of radiation are made both on the plant and on the personnel. In the first case, the objective is to check radiation flux levels and releases, in the second, to monitor exposure.

Portable devices for measuring the exposure of personnel include film badges and pocket ionization chambers. Both types measure β-, γ- and X-rays.

Radiation on the plant or from contamination is measured by instruments such as Geiger–Muller counters and scintillation counters. Except for scintillation counters, these instruments do not measure α-particles, but special α-measuring instruments are available.

25.10.5 Limits for exposure

Occupational exposure to radiation should always be kept as low as practicable. The established limits should be observed, but since any level of radiation may involve some risk, every effort should be used to minimize exposure.

Recommendations on limits for exposure are made by the ICRP. These recommendations are widely applied internationally.

In the United Kingdom, the National Radiological Protection Board (NRPB) makes recommendations to government on working limits, taking into account the ICRP recommendations.

The statutory limits for ionizing radiations are given in the Ionizing Radiations Regulations 1985 and are:

Adult workers: dose limit	50 mSv in any calendar year
Adult employees: investigation level	15 mSv in any calendar year
Members of public: dose limit	5 mSv in any calendar year
Members of public exposed over long periods: dose limit	1 mSv annual average

The following are the limits now recommended by the NRPB (1993):

Adult workers: dose limit	20 mSv in any calendar year
Adult employees: investigation level	15 mSv in any calendar year
Students and apprentices	6 mSv in any calendar year
Members of public: dose limit	1 mSv in any calendar year

0.3 mSv from any single source

25.10.6 Control of exposure

As in industrial hygiene generally, control of radiation exposure depends on deciding acceptable limits of exposure, designing the plant to minimize release, operating systems which minimize exposure and monitoring the personnel exposed.

Radiation may be contained within the equipment by shielding. This may take the form of lead a few millimetres thick. Protection of equipment giving off radiations may be provided by interlocks.

If some exposure is unavoidable, measures should be taken to minimize it. Since the dose is inversely proportional to the square of the distance and proportional to time, the distance from the radiation source should be as great and the time of exposure as short as possible.

Contamination from unsealed sources requires special measures for control and decontamination. These are discussed by Bennellick (1969, 1977).

All personnel who may be exposed to radiation should be monitored. Principal methods of monitoring include the carrying of personal radiation metres and the testing of blood. If tests indicate that a person is nearing the limit of exposure, he should be withdrawn temporarily or permanently from the work.

25.11 Non-ionizing Radiation Hazards

Ionizing radiation is not the only kind of radiation which may be hazardous. There are a number of types of non-ionizing radiation which can have harmful effects.

Accounts of non-ionizing radiation are given by Harrington (1980b), Kanagasbay (1980), Kielman and Fawcett (1982), McKinlay (1982) and Pilborough (1989). Guidance is available in the series *Nonionizing Radiation Guides* (AIHA, 1977–/3).

25.11.1 Electromagnetic spectrum

The electromagnetic spectrum is divided by wavelength into the following regions:

Cosmic rays	$<10^{-4}$ nm
γ-rays and X-rays	10^{-4}–10 nm
UV	10–400 nm
Visible region	400–700 nm
IR	700 nm–1 mm
Microwaves	1 mm–1 m
Radio waves	>1 m

The boundaries have developed by usage and are adopted by convention. Non-ionizing radiation is conventionally taken as that radiation which has a wavelength exceeding 100 nm, and thus starts within the UV region.

25.11.2 Artificial sources

Artificial sources of non-ionizing radiation include: in the UV region, welding; in the IR region, welding, furnaces and lasers; in the microwave and radio frequency (RF) regions, microwave ovens, communications equipment and radar.

25.11.3 Health effects

The health effects of exposure to non-ionizing radiation are felt mainly on the eyes and skin. UV, IR, and microwave and RF radiations can each cause damage to both these parts of the body.

Thermal injury occurs when the rise in the temperature of the tissue is more than a few degrees. Thermomechanical damage ensues when thermal expansion of tissue is at such a rate that it results in explosive disruption. Photochemical injury is caused by absorption of a greater dose of energy than the body's repair mechanism can handle.

25.11.4 Ultraviolet radiation

UV radiation is most harmful in the waveband 200–315 nm. Acute injury depends essentially on the total dose, whether this be received for a few seconds or over some hours.

The effect of overexposure on the eye is exemplified by such conditions as 'welder's flash' and 'snow blindness' a condition known as photokeratitis which is painful but generally reversible. The acute effect on the skin is erythma, or sunburn. Long-term overexposure of the skin leads to the chronic condition of skin cancer.

Guidance on UV radiation is given in *Ultraviolet Radiation* (AIHA, 1991/14a).

25.11.5 Infrared radiation

Visible and IR radiation entering the eye are focused on the retina and can cause damage, but this is usually averted. The reaction to a bright light is to avert the eye and this aversion response, occurring typically with 0.25 s, usually ensures that damage is avoided.

The main cause of injury to the skin from IR is thermal damage. A particularly hazardous form of IR radiation is that from a laser.

25.11.6 Laser radiation

A laser produces an intense monochromatic beam of non-ionizing radiation, either as continuous wave (CW), a single pulse or a series of pulses. The beam from some lasers can cause damage, particularly to the eye.

Guidance on lasers is given in PM 19 *Use of Lasers for Display Purposes* (HSE, 1980) and *Safety in Universities – Notes of Guidance*, Part 2:1 *Lasers by the Committee of Vice-Chancellors and Principals* (CVCP) (1992). A relevant code is BS EN 60825: 1992 *Radiation Safety of Laser Products, Equipment Classification and Users Guide*. Further guidance is given in *A Guide for the Control of Laser Hazards* by the ACGIH (1990/41).

Laser products are classified according to the maximum permissible exposure (MPE) of the eyes and skin, and to the associated accessible emission level (AEL).

Class 1 laser products are those which are inherently safe. Class 2 laser products are not inherently safe but have a power so limited that eye damage should not result over a duration of 0.25 s for a blink reflex. Classes 3A, 3B and 4 cover higher power products.

A laser may or may not produce a beam in the visible part of the electromagnetic spectrum, so that a person working with one which does not may be unaware that he has been exposed.

Personnel working with laser equipment should wear safety glasses appropriate to the class of laser concerned. A high level of ambient lighting is beneficial in that it restricts pupil size.

Since different classes of laser have very different power outputs, arrangements satisfactory for one class may not be so for a higher power class.

The use of lasers requires a safe system of work, the principal elements of which are control of access, warning notices and lights, and, possibly, interlocks.

Work with lasers should be subject to health surveillance.

25.11.7 Protection and control

The principles of protection from non-ionizing radiations have many similarities with those for protection against the hazards already considered. The first line of defence is engineering measures to eliminate or reduce exposure, the second is systems of work for the control of exposure and the third is PPE.

25.12 Machinery Hazards

Accidents caused by moving machinery have always been a serious problem in industry. The reduction of this type of accident has been one of the main concerns of industrial safety legislation. The development of this legislation has been described in Chapter 3.

Guidance on the hazards and safe use of machinery is given in two series of publications by the HSE, the HSW series (*Health and Safety at Work Booklets*) and the PM (*Plant and Machinery*) series. The former includes HSW 3 *Safety Devices for Hand and Foot Operated Presses* (HSE, 1971) and HSW 41 *Safety in the Use of Woodworking Machines* (HSE, 1970). The PM series includes PM 1 *Guarding of Portable Pipe-threading Machines* (HSE, 1984), PM 21 *Safety in the Use of Woodworking Machines* (HSE, 1981), PM 22 *Training Advice on the Mounting of Abrasive Wheels* (HSE, 1983), PM 23 *Photoelectric Safety Systems* (HSE, 1981), PM 41 *Application of Photo-electric Safety Systems to Machinery* (HSE, 1984) and PM 65 *Worker Protection at Crocodile (Alligator) Shears* (HSE, 1986). A relevant standard is BS 5304: 1988 *Code of Practice of Safety of Machinery*. Accounts of safe working with machinery are given by Haigh (1969, 1977) and Bramley-Harker (1969, 1977).

25.12.1 Machine guarding

The law on the safeguarding of machinery has become progressively stricter. Requirements are given in the Factories Act 1961, Sections 12–15. These sections state that prime movers and their flywheels should be securely fenced, as should electric motors and generators, transmission machinery and other dangerous machinery unless safe by construction or position, that devices for promptly cutting off the power from transmission machinery should be provided in every place where work is carried out, that efficient mechanical appliances should be provided to move driving belts to and from fast and loose pulleys and that driving belts should not rest or ride on revolving shafts when the belts are not in use.

Secure fixed fencing is the preferred method of guarding machinery. The fencing should be strong so that it fulfils its protective function and does not deteriorate as a result of frequent removal and replacement for maintenance. It should be secure and removable only by the use of tools.

The fencing should enclose the parts guarded completely. Many accidents occur on equipment where the fencing is incomplete and where a worker is liable to catch his hand between the moving part and the guard.

In some applications, however, complete enclosure by fencing is not possible, because it is necessary to feed material or components into the machine. In such cases, partial fencing may be used. The space left unprotected should be big enough to allow the required access for materials but should exclude the hand. Thus, complete fencing is normal for machinery such as revolving shafts, belt drives and gear wheels, but partial fencing is used on power presses and calenders.

Partial fencing may be complemented by distance fencing, which prevents the operator approaching too close to the machine.

If a fixed guard is not practical by reason of the nature of the operation, a permissible alternative for machinery other than prime movers or transmission machinery is a device which automatically prevents the operator from coming in contact with the dangerous plant.

Some other methods of providing protection on these lines are (1) feeders, (2) interlocks and (3) trips.

A feeder device such as a side, chute or roller is used to allow material or components to be fed into a machine without the necessity for a worker to put his hand in.

It is often necessary to have access to machinery for purposes such as maintenance. In this case, use may be made of an interlock which prevents access until the machine is stopped and prevents start-up while it is unguarded.

The stopping of the machine requires a braking system. The interlock should ensure that the machine has been completely stopped before access is possible.

With some machinery, fencing is not a practical solution. An alternative approach is the use of a trip. Trip devices include safety bars, photoelectric cells and proximity switches. Again a braking system is necessary to ensure that the machine stops quickly.

It is essential for there to be good maintenance both of the machine itself and of the fencing and other protective systems such as interlocks, trips and brakes.

Operators should be trained in the use of the machinery itself and in the protective systems. Likewise, maintenance personnel should have training in the maintenance of both machine and protective system. In some cases, this training is the subject of a specific statutory requirement. The Power Presses Regulations 1965, for example, specify the training required for the maintenance of such presses.

25.12.2 Running nips

A large proportion of the hazards on moving machinery arises from running nips. A running nip occurs when material runs onto or over a rotating cylinder. Running nips exist, for example, where a belt runs over a pulley wheel, a chain over a sprocket wheel, a conveyor over a roller or material over a drum, or where two rolls create an in-running nip. Running nips cause many accidents and the accidents are frequently serious.

An account of running nips is given by S.F. Smith (1969, 1977). One relevant code is BS 5667: 1979–*Specification for Continuous Mechanical Handling Equipment: Safety Requirements*, particularly Part 18 *Belt Conveyors – Examples of Guarding Nip Points* and Part 19: 1979 *Conveyors and Elevators with Chain Elements – Examples of Guarding Nip Points*. Another code is BS 7300: 1990 *Code of Practice for Safeguarding of the Hazard Points on Troughed Belt Conveyors*.

Typically accidents arise because an operator gets his clothing caught in a nip or slips and falls into one, because he tries to make some adjustment to the material running onto a cylinder or to remove foreign bodies or to clean rollers, or because the machinery is started up by mistake. Where material runs onto a roller, it is safer if it runs over the top so that the hazard is confined to the sides of the nip.

Most of the methods of protection described for machinery in general are applicable to running nips. The preferred method is complete fixed fencing, but partial fencing, distance fencing, feeders, interlocks and trips are also used. Again if interlocks or trips are used, it is essential that braking be such that it can stop the machinery sufficiently quickly. Often several measures are used in combination. Protection on a conveyor belt, for example, may use a combination of fixed fencing, distance fencing, interlocks and trip wires.

25.12.3 Inadvertent starts

Some accidents occur due to the inadvertent starting of machinery. A study of this type of accident has been made by Rouhiainen (1982), who investigated some 105 incidents involving inadvertent starting of machinery in a range of industries. Of the six incidents in the chemical industry, four involved presses and two involved guillotine shears, machinery not particularly characteristic of the industry. On the other hand, there were 14 accidents with conveyors, 8 with other transferring and lifting machines, and 3 with packaging machines.

The primary causes assigned included 24 intentional starts, 26 starts caused by human error, 21 starts caused by accidentally touching the start button, and 16 starts caused by the machine itself.

The author proposes measures to prevent inadvertent starts in both maintenance and normal operations. The former includes the disconnection of sources of electrical and mechanical energy, such as would be applied in a good permit-to-work system. The latter includes the use of barriers, interlocks and touch stopping devices.

The protective measures described in the guidance in Section 25.12.1 include protection against inadvertent starts.

25.12.4 Abrasive wheels

Accidents with abrasive wheels used for grinding are usually due to wheel failure. The number of accidents is small, but this is so only because great care is usually taken with grinding operations.

Relevant statutory requirements include the Grinding of Metals (Miscellaneous Provisions) Regulations 1925. Guidance is given in PM 22 *Training Advice on the Mounting of Abrasive Wheels* (HSE, 1983) and HS(G) 17 *Safety in the Use of Abrasive Wheels* (HSE, 1984). Accounts of abrasive wheels is given by Blackshield (1969) and Southwell (1977).

The main cause of wheel breakage is accidents, including damage to the wheel by mechanical shock and unchecked traverse of the work onto the side of the wheel.

Excessive rotational velocity is also dangerous. For a given wheel, a velocity is specified and should be adhered to. The velocity depends on the type of grinding. In high velocity grinding, the velocity is about twice that for normal grinding. It is essential to avoid using wheels made for normal velocity in high velocity work.

Other causes of breakage include excessive heating and excessive work pressure.

Safety measures in grinding work include selection and care of the wheels, proper mounting of the wheels, running at the specified speed and eye protection for the operator.

25.13 Electricity Hazards

Accidents in factories due to electricity are frequently associated with a failure to isolate or earth electrical equipment or to temporary or defective equipment.

The use of electrical equipment in factories is governed by the Electricity at Work Regulations 1989, which supersede the Electricity (Factories Act) Special Regulations 1908 and 1944. Guidance is given in HS(R) 25 *Memorandum of Guidance on the Electricity at Work Regulations 1989* (HSE, 1989). A further treatment is given in *Handbook on the Electricity at Work Regulations* (Marks, 1991).

HSE guidance on electrical safety is given in HS(G) 13 *Electrical Testing: Safety in Electrical Testing* (HSE, 1980), GS 27 *Protection Against Electrical Shock* (HSE, 1984), GS 37 *Flexible Leads, Plugs and Sockets* (HSE, 1985), PM 64 *Electrical Safety in Arc Welding* (HSE, 1986), PM 32 *Safe Use of Portable Electrical Apparatus (Electrical Safety)* (HSE, 1990) and GS 47 *Safety of Electrical Distribution Systems in Factories* (HSE, 1991). Further accounts are given in Electrical Safety Engineering (Fordham Cooper, 1986) and by Haigh (1969, 1977), Crom (1977) and Bales (1977a–c).

Some British Standards on electricity and electrical work are given in Appendix 27. One of particular relevance here is BS 2769: 1984 *Hand-held Electric Motor-operated Tools*. Part 1 of this standard gives general requirements for all types of tool and part 2, sections 0–14, describe requirements for some 14 types of tool.

Electrical equipment should be installed, inspected, tested and maintained only by competent electricians.

Equipment should be regularly inspected and serviced. Equipment on which repair is to be done should be disconnected from the supply until the work is complete. The importance of this instruction should be made clear to both electrical and other maintenance personnel. Defective equipment should be taken out of use and completely disconnected from the supply until it is repaired.

Temporary wiring should be avoided as far as possible, but if used should be to a safe standard and properly earthed. It should be regularly inspected and repaired as necessary and it should be replaced by a permanent installation as soon as possible.

Circuits should not be overloaded, as this increases the risk of fire. Loading should be carefully supervised and circuits protected by fuses or circuit-breakers.

Leads should have wires of the standard colours, which in the United Kingdom are brown for live, blue for neutral and green and yellow for earth. Leads of other colours on old or imported equipment should preferably be replaced.

A large proportion of electrical accidents involves portable tools. As described in BS 2769: 1984, the types of portable tool are (1) earthed tools and (2) all-insulated or double-insulated tools. It is essential to ensure that an earthed tool is not used unless it is properly earthed. All portable tools should be maintained and tested regularly.

Cables and plugs are vulnerable and require attention. Wear occurs particularly at the points where the cable enters the tool or plug. Cable grips reduce this problem. Flexible cables should be positioned so that they are not damaged by heavy equipment.

Tools with low voltage (110 Vor, in damp conditions, 50 V) should be used wherever practicable. The plug/socket system for such tools should be such as to prevent their being plugged into the normal mains.

25.14 Other Activities and Hazards

The hazards associated with certain common activities are considered in this section. Other activities and hazards are treated in other chapters. Those associated particularly with maintenance, for example, are covered in Chapter 21.

25.14.1 Lifting and carrying

Handling, lifting and carrying activities are discussed in HSW 1 *Lifting and Carrying* (HSE, n.d.), *Work Practices Guide for Manual Lifting* (NIOSH, 1981 Publ. 81–122) and *Manual Material Handling* (Kroemer, McGlothlin and Bobick, 1989 AIHA/16) and by Halliday (1969, 1977), A.R. Hale (1984) and Kroemer (1992).

The Factories Act 1961 states that 'a person shall not be employed to lift, carry or move any load so heavy as to cause injury'.

According to the Health and Safety Statistics 1990/91 (HSE, 1992b), accidents involving the handling, lifting and carrying of goods were responsible for some 55,477 injuries, including 2 fatalities and 1257 non-fatal major injuries reported to the HSE. In many cases, such accidents result in permanent injury, such as back trouble or hernia, and in long periods of absence from work.

These activities are often treated in terms of sudden injury arising from a single incident. But, in fact, much injury occurs due to cumulative strain caused by incorrect practices over a long period.

The first essential is that the ergonomics of the handling task should be right. This means not only that the weight to be handled should not be excessive, but also that the adoption of awkward positions should not be necessary and that suitable aids such as handles, platforms, rollers, etc., should be provided and sufficient time should be allowed.

Then, it is necessary that workers doing handling work observe some basic principles relating to grip, the position of the arms, chin and feet, back posture and the use of body weight. The grip should be a full palm rather than a fingertip grip. The arms should be held close to the body and fully extended so that the weight is taken by the body itself rather than the arms. The chin should be kept in, which reduces the risk of spinal injury. The back should be kept flat. This prevents compression of the abdominal contents, which leads to hernia, and in conjunction with correct foot positioning gives better mechanical advantage. The feet should be positioned slightly apart to give good balance. The weight of the body should be used ballistically, avoiding jerky actions. The use of body weight is one of the principles underlying judo and allows large weights to be moved with minimum effort.

There are wrong and right ways of lifting a heavy object. If the object is lifted with the back curved, the effort required is great and is placed on the back and abdominal muscles, whereas if it is lifted with the legs bent and the back straight, the effort is less and is taken by the leg and thigh muscles. These basic principles have been summarized in the 'six-point drill' of the NSC.

The heights to which heavy objects have to be lifted can often be reduced by the use of a platform.

A heavy object should be carried with the arms straight, with the head close to the body and with a straight back. Changes of grip and twisting movements should be avoided. So should blind carrying, in which the load prevents the carrier from seeing in front of him. The floors or other surfaces over which the carrying is done should not be slippery.

Any protective clothing necessary for handling should be worn. In particular, the task often requires the use of safety shoes or gloves.

A single worker should not attempt to handle an object which is too heavy for him alone. He should obtain the assistance of others.

The maintenance of a fixed position is one of the most tiring tasks for the muscles. Thus, even a seated task may cause muscle strain if it requires the operator to adopt awkward static positions.

In addition to recognized handling tasks, the occurrence of handling operations in such tasks as maintenance should be considered.

Handling objects requires good muscle tone. A worker should therefore be given time to tone his muscles up before being required to lift the heaviest loads if he is not used to such work.

It is important to give training in matters of handling. This is so not least because people often feel they know how to do it correctly, when in fact they do not. People often attempt from misjudgement, zeal or bravado, to handle loads which are too heavy. They should be discouraged from doing this.

A study of the effectiveness of safety training has been made by A.R. Hale (1984), which includes a case study of the effectiveness of training in handling loads. The basic principles commonly taught are those of the NSC's six-point drill mentioned earlier. The study found that conventional training tended to concentrate on injuries to the back, to the exclusion of other handling injuries, that it did not actually result in correct handling actions, and that recognition of good and bad postures was more important than action drills.

25.14.2 Hand and power tools

The proper use of hand tools is clearly essential for safety. But injuries also arise from the use of defective tools. A split hand file handle may come off and allow the file to penetrate the hand. A 'mushroomed' head on a cold chisel may loose fragments which could injure the eye. Another cause of injury is the use of the wrong tools. It is necessary, therefore, to provide suitable tools for the range of tasks to be performed, to store them securely, to maintain them properly and to have them regularly inspected by a competent person.

Guidance on the use of portable hand-held power tools includes PM 14 *Safety in the Use of Cartridge Operated Tools* (HSE, 1978) and *Pneumatic Tools – Safety in Operation, Safety Recommendations for the Use and Operation of Portable Pneumatic Tools* and *Recommendations for the Proper Use of Hand Held and Hand Operated Pneumatic Tools* by the European Committee of Manufacturers of Compressors, Vacuum Pumps and Pneumatic Tools (PNEUROP) (n.d.a, n.d.b, 1986, respectively). A further account is given by Bland (1977).

25.14.3 Welding

Welding operations may involve hazards to the plant and the welder. The former have been dealt with in other chapters, particularly Chapter 21, and only the latter are considered here.

Guidance on welding is given in MS 15 *Welding* (HSE, 1978) and PM 64 *Electrical Safety in Arc Welding* (HSE, 1986). Further sources of guidance are the publications of the Welding Institute (WI), the American Welding Association (AWS), the AIHA and the API. These include *Health and Safety in Welding and Allied Processes* by Balchin (1991 WI/43); the *Welding Handbook* (AWS, 7th ed. 1976–/1, 8th ed. 1987–/2), the EWH series *Effects of Welding on Health* (AWS, 1979–/3, 4), *Fumes and Gases in the Welding Environment* (AWS, 1979/5) and *Fire Safety in Welding and Cutting* (AWS, 1992/13); *Arc Welding and Your Health* (AIHA, 1984/6) and *Welding Health and Safety Resource Manual* (AIHA, 1984/8); and *Safe Welding and Cutting Practices in Refineries, Gasoline Plants and Petrochemical Plants* (API, 1988 Publ. 2009). Further accounts are given by Sanderson (1969, 1977). A relevant standard is BS 1542: 1982 *Specification for Equipment for Eye, Face and Neck Protection Against Non-ionizing Radiations arising during Welding and Similar Operations*.

The principal method of welding considered here is electric arc welding, which may be done by manual, semi-automatic or fully automatic methods and may take place in a welding shop or on site.

Electric arc welding uses power supplied by transformers or motor–generator sets which are supplied by the factory electrical system or by a self-contained engine-driven generator set. The circuit has three electrical connections: the welding lead, the welding return and the welding earth.

During welding, the electrode and parts of the holder are electrically live and hot, the arc gives off high intensity visible light and both IR and UV radiation and fumes are evolved. It is necessary, therefore, to take suitable precautions so that the operation can be done safely.

All the welding connections should be capable of carrying the full welding current. The welding lead should be robust and flexible enough for this purpose. The welding return, which is often the most neglected part, should

receive equal attention. It need not be as flexible and in a workshop may be a permanent installation. The welding earth should be as near the work as possible rather than at the source of supply, although this is not always practicable. All joints in these connections should be in good condition. Where it is unavoidable that the cables are laid over rough surfaces, there should be frequent inspection for defects.

The electrode holder should be of sufficient size and should be insulated. Gloves should not be relied on to achieve insulation. If work is temporarily interrupted, the safest procedure is to render the holder electrically dead.

In the United Kingdom, open circuit voltages up to 100 V are used for welding, but in certain situations, such as welding at height, in damp conditions or in vessels, this may be too high a voltage for safety. Low voltage devices can be fitted which reduce the open circuit voltage by about half. These restore the full voltage when the electrode is touched to the work so that the arc can be struck. The voltage across the arc then drops as usual to a much lower value.

Some portable welding sets, particularly semi-automatic gas shielded equipment, have hoses for gas and water supply. The equipment should not be pulled around by the cables and the hoses. Both the latter should be regularly inspected.

Proper protective clothing and equipment should be used for welding. This typically includes an apron or more extensive covering, leather gloves and a helmet which has suitable filter glass and which protects the back of the neck from other nearby arcs. Different filter glasses are required for different welding currents. A hand shield with filter glass may be used as an alternative for short periods.

Screens may be used to protect other people from the rays of the arc. Booths used for welding should have a matt finish to reduce reflected light. This is an important precaution, especially with heavy current welding and high density arcs.

There should be adequate ventilation, particularly when working in a confined space. One purpose of ventilation is to remove welding fumes. These are not particularly detrimental to health, although some fumes such as those from galvanized materials are more noxious, but exposures should be minimized. Ventilation is also needed to remove inert gases such as nitrogen, argon and carbon dioxide. The two latter are heavier than air and thus tend to accumulate in confined spaces. This is made more hazardous by the fact that the gases cannot be smelled and that the welder may be out of sight. The use of air-supplied BA is necessary in some cases.

In welding, care should be taken that hot metal does not damage equipment or set alight material, which may lead to a fire.

Since electric arc welding involves electricity, the statutory notice for electrical equipment should be posted.

25.14.4 Corrosive chemicals

Corrosive chemicals present two kinds of hazard. One is corrosion of the plant leading to failure and hence injury. The other is injury from direct contact with the chemical, usually during some operations or maintenance activity.

Accounts of the problem are given in *Safety and Management* by the ABCM (1964/3) and by Harford (1969) and E.L.M. Roberts (1977).

Chemical corrosion is hazardous if it causes leaks in the plant or a failure in features such as staircases and handrails. It is necessary, therefore, to design both the plant and the buildings or structures to resist corrosion.

The vessels and pipework of the plant itself should be designed so that they do not corrode excessively and so that the effects of corrosion such as leaks and blockages can be dealt with as easily as possible.

The plant should also have a suitable layout. Open vessels containing corrosive materials and similar hazardous features should be fenced off. Parts which may leak, such as pipe flanges, should not be located over walkways and should, if necessary, have handrails around them. Floors and other surfaces should be sloped to let spillages drain or be washed away and to avoid allowing corrosion of features such as stairways by spilled materials. The layout of the plant for corrosive materials is discussed more fully in Chapter 10.

There should be clear marking of equipment and pipework to minimize errors of identification.

The plant should be maintained to a standard commensurate with the corrosive hazard. Leakage of fluids at high pressure is particularly dangerous.

There should be regular inspection of buildings or structures which may become corroded. Items which are vulnerable or which may fail with serious consequences include stairways, ladders and handrails, high level walkways, anchor points and lifting tackle.

Adherence to systems such as the permit-to-work system and to procedures such as the procedures for line breaking or for sampling and the prompt repair of leakages and cleaning up of spillages are effective in reducing the hazard from direct contact.

The plant should be provided with showers, eye fountains, eye washes and other neutralizers as applicable.

25.14.5 Compressed air

Compressed air is widely used in plants and in workshops, and presents hazards which are often not appreciated. Guidance is given in HS(G) 39 *Compressed Air Safety* (HSE, 1990) and by Paterson (1969, 1977).

Compressed air is provided by air compressor systems and it is used in blow guns and pneumatic tools. Compressor systems are treated in Chapter 12 and pneumatic tools in Section 25.14.2.

Use is often made of compressed air from a blow gun to blow swarf, filings and chippings from equipment or machinery. The air blast needed to effect such cleaning is usually quite sufficient to blow debris into, and cause injury to, the eye.

Another practice is the use of compressed air to clean clothes or parts of the body such as the hair. This is a very hazardous procedure. Air may enter the bloodstream through cuts in the skin, possibly with fatal results, or it may cause injury to the eye, ears, nostrils or rectum. The pressure needed to burst the bowels is quite low, about 4 psig. Moreover, it is emphasized that clothing offers no protection.

Horseplay with compressed air is likewise extremely dangerous. Air lines put down the trousers or even up the rectum have caused fatal or near-fatal injury.

The nature of the hazard from compressed air is such that it may affect not only the operator but also other people nearby.

Guidance on safer types of blow gun is given in HS(G) 39. This states that only two types are suitable, those with reduced jet velocity safety nozzles and those with air curtain safety nozzles. Whilst not foolproof, these types greatly reduce the risk. Types of blow gun nozzle which consist simply of a reduced orifice in direct line with the supply hose can be extremely dangerous and should not be used unless preceded by a tamper-proof pressure regulator.

Compressed air may also cause dust deposits to rise and form a dust cloud, thus creating the risk of a dust explosion.

25.14.6 Oxygen

As already mentioned, an oxygen-enriched atmosphere greatly increases the flammability of many materials, including clothing. Oxygen leakage from the process or from oxygen cylinders can create a hazardous situation. A relevant code on this topic is NFPA 53M: 1990 *Fire Hazards in Oxygen-Enriched Atmospheres*.

Moreover, for this reason, oxygen should not be added to an oxygen-deficient atmosphere, such as that in a vessel, in order to make it breathable.

Oxygen is used in one type of self-contained breathing apparatus (SCBA). It should not be used in the alternative type which uses air.

Ozone is a hazard at very low concentrations, due to its powerful oxidizing effect, the OES being 0.1 ppm. Guidance is given in EH 38 *Ozone: Health Hazards and Precautionary Measures* (HSE, 1983).

25.14.7 Inert gas

Atmospheres of inert gases which do not support respiration are common in the process industries, especially in vessels and confined spaces.

Guidance on oxygen-deficient or inert atmospheres is given in *Oxygen-Deficient Atmospheres by the Compressed Gas Association* (CGA) (1983 SB-2) and *Guidelines for Work in Inert Confined Spaces in the Petroleum Industry* (API, 1987 Publ. 2217A).

Breathing equipment for use in oxygen-deficient atmospheres must have its own air supply. The air-purifying type is not suitable.

It should be appreciated that an oxygen-deficient atmosphere can occur outside the plant as well as inside it. Accidents have occurred in which a worker standing alongside a plant has been asphyxiated. The hazard is greatest if the plant has been opened up for some purpose such as repair.

25.15 Personal Protective Equipment

There are many tasks for which some form of PPE such as clothing or other equipment is necessary.

Accounts of PPE are given in *Chemical Protective Clothing* (CIA, 1986 RC7), *Guidelines for Selection of Chemical Protective Clothing* (Schweppe *et al.*, ACGIH 1987/10), *Chemical Protective Clothing Performance Index Book* (Forsberg and Keith, ACGIH 1989/30) and *Chemical Protective Clothing* (Johnson and Anderson, 1990 AIHA/18) and by H.H. Fawcett (1965b, 1982c), C.S. Nicholson (1969), K.R. Nicholson (1976), Riddell (1977), Crockford (1980), Parson (1988) and Preece (1988). Some British Standards and NFPA codes for protective clothing are given in Appendix 27.

A significant problem associated with PPE is the setting of the standards which the equipment is required to meet. This is discussed by Berry (1969, 1977).

Some tasks which may require PPE are (1) working with corrosive chemicals, (2) working with toxic chemicals, (3) working with dusts, (4) working in hot environments, (5) working in noisy environments, (6) welding, (7) fire fighting and (8) rescue.

Protective clothing should be regarded as a last line of defence. It is much preferable to remove or control the hazard, if this is practicable.

For some tasks there are specific statutory requirements that protective clothing should be worn. In the United Kingdom, such requirements were rare until the 1940s but they are now quite numerous. Even where specific statutory requirements do not exist, the use of protective clothing is often necessary to comply with the HSWA 1974, Section 2.

It is the responsibility of the management to specify when protective clothing and equipment are required and to provide them. The worker then has the duty to use them. If he is reluctant to do so, management is responsible for enforcing their use. The Factory Inspectorate has used the prohibition notice procedure on an individual worker to make him wear protective clothing.

According to the Act, Section 9, no charge may be levied on an employee for anything done or provided to meet a specific statutory requirement.

Some types of protective clothing and equipment are (1) body clothing, (2) gloves, (3) helmets, (4) shoes, (5) eye protection and (6) ear protection.

There is no point in providing protective clothing which is not used. In general, therefore, it is better to select practical clothing which offers a good level of protection rather than theoretically safer but more cumbersome clothing. But each case should be considered on its merits.

Protective clothing may be a general issue or may be issued to an individual. The latter policy is preferable wherever it is practicable.

For some substances, specific guidance is available, as exemplified by EH 27 *Acrylonitrile: Personal Protective Equipment* (HSE, 1981).

25.15.1 Eye protection

The eye is a vulnerable organ and the avoidance of eye injury is particularly important.

The Factories Act 1961, Section 65, states that eye protection may be specified in certain processes, and eye protection has been covered by the Protection of the Eyes Regulations 1974 which give a schedule of processes for which appropriate eye protection is required. These processes include various cleaning and blasting operations using shot, water jets and compressed air, various operations involving particular tools, especially power tools, and various processes with hot metal or molten salt. Of particular relevance here is item 11, which reads:

> The operation, maintenance, dismantling or demolition of plant or any part of plant which contains or has contained acids, alkalis, dangerous corrosive substances, whether liquid or solid, or other substances which are similarly injurious to the eyes, and which has not been so prepared (by isolation, reduction of pressure, emptying or otherwise), treated or designed and constructed as to prevent any reasonably foreseeable risk of injury to the

eyes of any person engaged in any such work from any of the said contents.

These regulations are now superseded by the Personal Protective Systems at Work Regulations 1992, which deal with all types of such protection, including eye protection. Requirements for eye protection are also contained in certain other regulations.

Guidance on eye protection is given in L25 *Personal Protective Equipment at Work* (HSE, 1992) and *Protection of the Eyes* (CIA, 1990 RC22) and by Guelich (1965), Barker (1969, 1977) and Wigglesworth (1974).

Flying objects, chemicals and radiations are the main hazards to the eye in the process industries. Flying objects come most often from the use of hand or power tools. Chemical splashes are typically caused by operations such as line breaking or sampling. Welding is the main source of injurious radiations.

The hazard to the eye from power tools such as grinding wheels is understood and the use of eye protection is normal. There is evidence that, as a result, injuries to the eye from hand tools are as frequent as those from power tools (Wigglesworth, 1974).

The general principle that personal protection should be used only if hazard elimination and control are not sufficient applies with particular force to eye protection. The main types of eye protection are spectacles, goggles and face shields.

Spectacles have either prescription or plain lenses, depending on whether the wearer does or does not wear glasses. The lenses are glass or plastic such as cellulose acetate, acrylic or polycarbonate material. For welding, filter lenses are used.

The most appropriate eye protection depends, in principle, on the task. A view which is not only widely held but is also supported by successful company systems is that the most effective approach is to issue safety spectacles to all personnel who need eye protection and to require their use. Although safety spectacles do not give total protection against all eye hazards, they do give perhaps 90% protection and are more likely to be worn than some other devices. In other words, a protection which is worn is better than a superior protection which is not worn. The objective of the system based on safety spectacles is to achieve a situation where these are worn as naturally as prescription spectacles. This means that the spectacles should be fitted individually.

The alternative approaches are systems based on eye protection areas, supervisor's orders or personal judgement.

Whatever system is adopted, there are tasks for which eye protection other than safety spectacles is required. In particular, some tasks require protection not only for the eyes but also for the whole face. This applies especially to persons handling corrosive chemicals or doing welding.

First aid for eye injuries is discussed in Section 25.17.

25.16 Respiratory Protective Equipment

There are a number of tasks in the process industries for which RPE, or breathing equipment, is necessary.

Guidance on RPE is given in HS(G) 53 *Respiratory Protective Equipment* (HSE, 1990) and also in *Respiratory Protection: A Manual and Guideline* (Colton, Birkner and Brosseau, 1991 AIHA/23) and by H.H. Fawcett (1965d, 1982d), Cheffers (1969, 1977), Vanchuk (1978), Crockford (1980), Louhevaara *et al.* (1986), Stull (1987a,b), Parson (1988) and Preece (1988). Some special applications are dealt with in EH 41 *Respiratory Equipment for Use against Asbestos* (HSE, 1985) and EH 53 *Respiratory Protective Equipment for Use against Airborne Radioactivity* (HSE, 1990).

Relevant standards are BS 4275: 1974 *Recommendations for the Selection, Use and Maintenance of Respiratory Protective Equipment* and BS 4667: Part 3: 1974 *Fresh Air Hose and Compressed Air Line Breathing Apparatus*.

25.16.1 Regulatory requirements

The Factories Act 1961, Section 20, and formerly the Chemical Works Regulations 1922, Sections 6–8, require the use of approved BA for work in vessels and confined spaces where the atmosphere may contain dangerous fumes or may lack oxygen. There are requirements for the use of RPE in the CLAW Regulations 1980, the CAWR 1987 and the COSHH Regulations 1988.

The use of RPE should not be a substitute for measures to maintain a breathable atmosphere. The regulations require that it be used only as a last line of defence in situations where it is not reasonably practicable to control exposure by other means.

The regulations deal not only with the situations in which RPE should be worn, but also with its suitability and specification. In essence, they require that it be suitable for use, in that it has a sufficient air supply, that it fits well and that it is worn properly. The regulations also require that the RPE should meet a laboratory test specification. For an application requiring a high level of protection, this means that the HSE must approve the equipment itself and issue an Approval Certificate. For a lower level of protection, it is sufficient that the equipment meet a laboratory test approved by the HSE.

25.16.2 Applications of RPE

As just stated, RPE should be used only where it is the only reasonably practicable approach. There are four main types of situation in which it is used. These are (1) temporary situations, (2) short duration situations, (3) maintenance work and (4) escape. Temporary situations are those which arise in non-routine circumstances such, as commissioning. An important particular case is for activities in emergencies. Short duration situations may arise routinely. It is not normal for a worker to wear RPE all the time, but he may wear it routinely for certain tasks, for example, sampling or vessel entry.

25.16.3 Types of RPE

There are two broad classes of RPE. One is the respirator, which takes in air from the workspace and filters or cleans it, removing noxious gases and vapours or dusts, before it is inhaled. It is not itself a source of air and is quite unsuitable for use where the bulk gas in the atmosphere is not breathable air but is an asphyxiating mixture.

The second class is air-supplied equipment which does have a source of clean air. This class may itself be subdivided into equipment to which air is supplied by a hose and BA. Air for equipment supplied by hose may be compressed air or from a fresh air source. BA may be of the compressed air line or self-contained type.

HS(G) 53 gives the classification of RPE shown in Table 25.6. It contains an appendix giving illustrated descriptions of the main types.

25.16.4 Air-purifying respirators

The disposable facepiece or the half-mask respirator fits over the nose but does not cover the whole face. A full face mask respirator does cover the whole face; the wartime 'gas mask' is of this type. A powered respirator has a fan to assist the flow of air through the filter.

Each type of respirator is available in three performance classifications. Thus, half-mask and full face mask respirators may be of the PI, P2 or P3 specification.

The filters available for respirators are of three types: (1) filters for particular gases and vapours only, (2) filters for dusts and other particulate materials and (3) combination filters for particular gases and vapours and for dusts and other particulates.

As already stated, the air-purifying respirator differs fundamentally from the air-supplied RPE in that it is not itself a source of air and is therefore of little use unless breathable air can be drawn through it from the surrounding atmosphere. It will not sustain breathing in an asphyxiating atmosphere.

The concentration of oxygen in normal air is approximately 21%. A person breathing air with an oxygen concentration of less than about 16% may manage to do light work for a few minutes, but is likely to exhibit symptoms ranging from laboured breathing to unconsciousness or death.

Respirators are produced for military, fire fighting and industrial uses. In the former case, they are commonly referred to as 'gas masks'. A respirator intended for one type of application should not be used for another.

The purifying element may work in several ways. Usually it adsorbs the gas. Alternatively, it may act as a catalyst: carbon monoxide is oxidized catalytically to carbon dioxide.

The element is designed to protect against a particular chemical or group of chemicals and should not be used for other substances. There are a number of toxic gases for which a respirator is quite unsuitable. Respirators should not generally be used against gases which have a high odour threshold or no odour at all, since odour is the only warning of failure of the respirator.

Some toxic gases are irritant to the face and for these full face protection should be used.

It is essential that respirators be kept in good condition and not held too long in stock; otherwise, the air-purifying element and/or the facepiece may deteriorate. The purifying element should be replaced after use or after the elapse of a certain time according to a specified policy.

It will be apparent that, although respirators are the most convenient form of RPE and have many legitimate applications, they also have some serious drawbacks and the circumstances in which they are used should be carefully considered.

Table 25.6 *Types of respiratory protective equipment (after HSE, 1990 HS(G) 53)*

A Respirators
A1 Filtering respirators
A1.1 Disposable filtering facepieces
A1.2 Half-masks + filters
A1.3 Full face masks + filters
A2 Powered respirators
A2.1 Half-masks
A2.2 Full face masks
A2.3 Visors
A2.4 Hoods and helmets
A2.5 Blouses (half-suits)
B Air-supplied equipment[a]
B1 Compressed air-supplied equipment
B2 Fresh air hose equipment
B2.1 Unassisted
B2.2 Manually assisted
B2.3 Power assisted
B3 Breathing apparatus
B3.1 Compressed air line apparatus: demand type
B3.2 Compressed air line apparatus: demand type with positive pressure
B3.3 Self-contained breathing apparatus: open-circuit compressed air type
B3.4 Self-contained breathing apparatus: closed-circuit compressed oxygen type

[a] HS(G) 53 classifies simple compressed air-supplied equipment in its figure 3 in terms of (a) blouses, (b) hoods, helmets and visors, (c) half-masks, and (d) constant flow equipment, but classifies fresh air hose equipment in terms of the assistance to the air flow.

25.16.5 Simple compressed air-supplied equipment

Simple compressed air-supplied equipment is so called to distinguish it from compressed air line BA, described below. In simple compressed air-supplied equipment, the air is supplied through a hose from an independent source of compressed air. There are various types, utilizing a full face mask, half-mask, hood or blouse.

The air supplied should meet the air quality standard described below. It should come from a high quality source which is capable of meeting the foreseeable needs of those requiring to use it. It should not be drawn for the compressed air supply intended for general works use. There should be suitable pressure reducing and pressure relief arrangements to protect the wearer from overpressure.

The hose used should comply with BS 4667: Part 3: 1974. The air line should be secured by a sturdy harness. Its route should be carefully chosen to keep it short, to allow escape and to avoid fouling and damage and it should be kept free of kinks.

The simple compressed air-supplied equipment is not a BA and it should not be used in situations where there is immediate danger to life or health; in other words, it should not be used in circumstances where an unprotected person would be rapidly overcome.

25.16.6 Fresh air hose equipment

In fresh air hose equipment, the air is supplied through a hose from a fresh air source. There are various types, utilizing a full face mask, half-mask, hood or blouse.

The requirements for air quality and for hose quality and routing for compressed air-supplied equipment apply also to fresh air hose equipment like simple compressed air-supplied equipment, fresh air hose equipment should not

be used in situations immediately dangerous to life or health.

25.16.7 Breathing apparatus

BA is of two types. One is compressed air line apparatus and the other is SCBA. BA, whether of the compressed air line or self-contained type, provides the highest degree of protection and is the only type suitable for use in an atmosphere immediately dangerous to life or health.

25.16.8 Compressed air line breathing apparatus

Compressed air line apparatus is used with a full face mask or a full enclosing suit. There are two different methods of supplying the air. One is negative pressure demand in which the suction in the face mask generated by inhalation opens a demand valve allowing air into the mask. The other is positive pressure demand. With the former, the pressure inside the mask is slightly below atmospheric, whilst with the latter it is mainly above atmospheric, although it can fall below at high inhalation rates.

25.16.9 Self-contained breathing apparatus

SCBA comes in two types. One utilizes compressed air on an open-circuit system and the other compressed oxygen on a closed- circuit system.

Open-circuit compressed air BA utilizes a full face mask to which air is supplied from compressed air cylinders carried on the wearer's back.

Closed-circuit compressed oxygen BA utilizes a full face mask to which oxygen is supplied from compressed oxygen cylinders carried on the wearer's back. Exhaled air is passed through a purifier which removes carbon dioxide and is recirculated.

SCBA offers the wearer mobility but requires him to carry on his back a bulky load.

Use of oxygen instead of air introduces certain problems. There may be physiological effects on the person breathing it. The flammability of the material is much increased in oxygen-enriched air.

The length of time for which breathable air is supplied by SCBA is typically $\frac{1}{2}$ and 1 h for both types, but the time for which an apparatus provides air depends on the breathing of the wearer. Heavy exertion may cause an apparatus to run out before the nominal period.

Exhaustion of the air supply is hazardous and may cause asphyxia. An adequate safety margin of time should be allowed. There is normally a timer which can be set to give warning when the time has run out.

SCBA is indispensable, but it is more complex to use than other types. Maintenance and training aspects are therefore especially important.

25.16.10 Escape breathing apparatus

A particular type of SCBA is that provided for escape. Such escape BA is intended for use over a short duration, typically less than 10 min, and should be used for this purpose only.

25.16.11 Air quality standard

There are air quality standards which apply to air supplied to any form of air-supplied RPE. Standards are given in BS 4275: 1974 and in HS(G) 53, Appendix 4. The latter states that: the air supplied should contain not more than 5 ppm of carbon monoxide and 500 ppm of carbon dioxide, with other impurities kept to a minimum; the air should be comfortable, being in the temperature range 15–22°C and with relative humidity no higher than 85%; and the air flow capacity should be a minimum of 120 l/min per person.

25.16.12 Selection of RPE

The procedure for the selection of a suitable RPE described in HS(G) 53 is a two-stage one. The first stage involves selection on the basis of the contaminant concentration and the second involves selection on the basis of work-related and personal factors.

The guide gives a set of charts formulated in terms of the maximum multiple of the occupational exposure limit for which a particular RPE is suitable. For example, the suitabilities of full face mask respirators for dusts and other particulates are shown as multiple values of about 5, 13 and 800 for filter classifications P1, P2 and P3, respectively. There are separate charts for respirators for gases and vapours, respirators for dusts and other particulates, and for simple compressed air-supplied and fresh air hose equipment.

In selecting a respirator, account should be taken of the suitability of the filter for the particular gas or vapour and of the time until 'breakthrough', when the filter becomes ineffective.

Work-related factors which need to be taken into account in the second stage of selection include the length of time for which the RPE is to be worn, the physical work rate, and the needs for mobility, visibility and communication.

Personal factors include medical fitness, face shape and size, facial hair and the use of spectacles. A worker should not be subjected to additional health risks by virtue of wearing an RPE. Persons with a respiratory disorder may find difficulty with respirators which rely on lung power to draw air through the filter.

A face mask should achieve a good fit to the face. Procedures for checking face fit are given in HS(G) 53, Appendix 5. A beard or even stubble is liable to prevent a good fit to a face mask. Where there is immediate danger to life or health, a wearer with facial hair should be provided with an alternative type such as a hood, blouse or air-fed suit.

For a wearer of spectacles, the side arms tend to interfere with the seal of a full face mask and an alternative should be used such as a hood or blouse. However, spectacles worn inside these may mist over or become dislodged. Spectacles should not be worn, therefore, where the wearer would be in immediate danger to health if he removed the equipment to adjust his glasses or would be unable to leave the contaminated area at once in case of a problem.

25.16.13 Procedures for using RPE

There should be written procedures covering the situations in which RPE should be used and the actual use of the equipment, and the use should be integrated in the permit-to-work system.

The use of RPE is liable to involve a degree of discomfort and the periods for which it is required to be worn should be set with this in mind.

For a respirator, an estimate should be made of the duration of the protection provided by the filter cartridge used.

The equipment should be used in accordance with the manufacturer's instructions. It should be checked before use and should not be used if it has not been cleaned or is defective. Equipment which relies on a face seal should be given a fit test on each occasion it is used.

Where the atmosphere in an area is immediately dangerous to life or health, only BA should be used. There should be continuous supervision of the wearer from outside the area of hazard. Either the wearer should be kept under continuous observation or should be in communication with the person supervising. Rescue equipment should be available.

Where contamination of the RPE is likely to occur due to dust or other substances hazardous to health, facilities for decontamination should be provided at the exit from the contaminated area, so that the spread of such substances is minimized.

25.16.14 Maintenance of RPE

There should be a system of records for RPE covering its storage and maintenance.

RPE for immediate use should be clean and free of defects before being put into storage and should be segregated from equipment awaiting maintenance. There should be an adequate stock of spares for items such as filters, head straps and batteries.

The maintenance required includes cleaning, disinfection, examination, repair and testing. HS(G) 53 gives details of good practice in maintenance and, in Appendix 6, of examination and testing.

25.16.15 Training for RPE

Persons involved in the use of RPE should be given suitable training. Management should have an appreciation of RPE, its applications, selection, use, maintenance and limitations. Wearers should be trained in the wearing and use of the equipment and its limitations. Maintenance personnel should receive training in the maintenance, repair and testing of the equipment.

Training should be both theoretical and practical. The former should include: the hazards of contaminants and asphyxiation and the use of RPE to control exposure; the operation, performance and limitations of the equipment; the operating procedures and permit systems which govern its use; the storage and maintenance of the equipment; and the factors which may reduce the protection which it provides.

Practical training should cover: practice in inspecting the equipment before use; obtaining a good fit to the face, where applicable; putting the equipment on, wearing it and removing it; cleaning it after use; storing it; and replacing parts such as filters and cartridges.

Training is particularly important for the types of RPE which are more complex and are used in atmospheres immediately dangerous to life or health such as SCBA.

25.17 Rescue and First Aid

Effective rescue and first aid arrangements are essential in the process industries.

The Factories Act 1961, Section 61, and formerly the The Chemical Works Regulations 1922, Sections 6–14, contain various provisions for rescue and first aid.

The responsibility for the provision of these services should be clearly defined. There are some features, such as rescue equipment, which might, in principle, come under either the safety, the fire or the medical department.

All rescue and first aid equipment should be located with care and properly maintained. Personnel should be fully trained in its use.

25.17.1 Rescue

An account of general rescue methods is given in *The Light Rescue Handbook* by the Ministry of Defence (MoD, 1989a) (the *MoD Rescue Handbook*). Rescue from confined spaces is treated in *Recommendations to Facilitate Rescue from Confined Spaces* (EEUA, 1962 Doc. 12). A further account is given by Walters (1977).

There should be a rescue system which is capable of handling all reasonably foreseeable situations which may arise on a process plant. Frequently this function is performed by the works fire services, supplemented if necessary by the local authority fire services.

Rescue apparatus such as stretchers should be provided at strategic points.

Arrangements for rescue are also part of certain routine tasks such as entry into vessels or confined spaces and of some special operations such as hot tapping.

The *MoD Rescue Handbook* is oriented to rescue tasks arising from both natural and man-made disasters such as earthquakes and hurricanes and road and rail crashes. It deals with: the aims of rescue; the organization of the rescue team; the responsibilities of the team leader; personal and rescue equipment; searching for casualties; the five stages of rescue (surface casualties, lightly damaged buildings, likely survival points, selected debris removal and general debris clearance); recovery of the dead; recovery of valuables; building construction; levering and jacking; strutting and shoring; repairs to utilities; rope and wire bonds; knots and lashings; and thermal image cameras.

25.17.2 First aid

Regulatory requirements for first aid are given in the Health and Safety (First Aid) Regulations 1981. COP 42 First Aid at Work. Health and Safety (First Aid) Regulations 1981 (HSE, 1990) is the relevant ACOP. The relevant manual is the *First Aid Manual* of the St John Ambulance Association (1992), the official manual of the three leading organizations in the United Kingdom in this field, the St John Ambulance Association, the St Andrews Ambulance Association and the British Red Cross. First aid is also treated in *First Aid Manual for Chemical Accidents* (Lefevre, 1989 ACGIH/32) and *Industrial First Aid: Reference and Training Manual* (ACGIH, 1991/64) and by Lord Taylor (1967), Cameron (1969, 1977) and McKenna and Hale (1981). Also relevant is *Emergency Care for Hazardous Materials Exposure* (Bronstein and Currance, 1988 ACGIH/19).

The requirements of the First Aid Regulations are largely contained in Regulation 3. This requires an employer to make provisions for first aid by providing suitable equipment and facilities and by appointing suitable persons. These appointed persons have to possess a first aid certificate from an organization recognized for this purpose by the HSE and receive refresher training at specified intervals.

The ACOP deals under Regulation 3 with: different work activities needing different provisions; the applicability of, and provision of first aider cover for, situations when access to treatment is difficult, employees work away from employer's premises or employees of more than one employer work together; provision for persons other than an employer's own employees and for trainees; first aid equipment and facilities, first aid boxes and kits, travelling first aid kits, supplementary equipment, first aid room and equipment; suitable persons; criteria for deciding adequate

and appropriate provisions for first aiders; number of employees and appointed persons; the recruitment and selection of first aiders; appropriate training for first aiders; access to skilled advice; recording first aid treatment; approval of first aid courses and qualifications; refresher courses; first aid training where specific hazards exist; emergency first aid training; first aid trainers and examiners; first aid examinations; and training of first aid lay trainers.

The number of first aiders required is specified in the ACOP as a minimum of 1 per 50 employees, a figure which applies to low risk situations. In hazardous situations, the employer should assess whether a higher proportion of first aiders is required.

Subjects to be included in the syllabus for first aid training given in the ACOP include (1) resuscitation, (2) treatment and control of bleeding, (3) treatment of shock, (4) management of the unconscious casualty, (5) contents of first aid boxes and their use, (6) purchasing first aid supplies, (7) transport of casualties, (8) recognition of illness, (9) treatment of injuries to bones, muscles and joints, (10) treatment of minor injuries, (11) treatment of burns and scalds, (12) eye irritations, (13) poisons, (14) simple record keeping, (15) personal hygiene in treating wounds with reference to hepatitis B and human immunodeficiency virus (HIV) and (16) communication and delegation in an emergency.

It is necessary to have a first aid system which can deal with the types of injury likely to be encountered on the plant, and where there are special hazards, first aiders should also receive additional training in respect of these. Normally first aiders in process plants are drawn from the process and maintenance personnel.

First aid equipment which should be provided includes first aid boxes and resuscitation apparatus. There should also be showers and eye wash equipment to deal with injuries from corrosive chemicals.

Showers are effective provided they are used, but there are certain practical problems. Measures need to be taken to ensure that the water supply is not frozen or turned off at a hand valve. And the reluctance of workers to make use of showers when fully clothed may have to be overcome by drills.

Guidance on first aid for eye injuries is given in *Protection of the Eyes* (CIA, 1990 RC22). Eye wash equipment includes eye wash fountains, pre-packed sterile washes, and eye wash bottles. The last two are a last resort, and are not supported by the ACOP.

Eye injuries from corrosive chemicals should preferably be dealt with by irrigation with water, using plenty of water and continuing for a long time. If sterile washes or eye wash bottles are used, they should contain an adequate volume. The CIA recommends, for example, for these two types of wash volumes of at least 500 ml and 1l, respectively.

Information is available also on first aid for particular chemicals. Materials safety data sheets may include such information. The *CIA Codes of Practice for Chemicals with Major Hazards* and related publications give guidance on first aid.

In some situations there is a danger that the first aider may himself be injured, and precautions should be taken to ensure that this does not happen. Cases mentioned in the ACOP include casualties from electric shock, chemical burns and gassing. It states that in a case of electric shock, the current should be switched off before the casualty is touched or, if this cannot be done, the first aider should stand on dry insulating material and free the casualty from the electrical source with a wooden or plastic implement. Where the casualty has a chemical burn, the first aider should avoid contaminating himself with the chemical. With a casualty who has been gassed, the use of suitable protective equipment is advised.

25.18 Notation

Section 25.7

Subsection 25.7.3

A	area of opening (m^2)
Q	volumetric air flow (m^3/s)
V	inward superficial air velocity (m/s)

Subsection 25.7.4

A	face area of hood (m^2)
L	length of hood (m)
V	capture velocity at distance X (m/s)
V_o	superficial velocity at face of hood (m/s)
W	width of hood (m)
X	distance from hood (m)
α, β	indices

Subsection 25.7.7

A_f	free area of discharge (m^2)
C_d	coefficient of discharge
K	constant
Q	volumetric flow (m^3/s)
V_x	centre line velocity at distance X (m/s)
X	distance along centre line (m)

Section 25.9

A, B, C	constants in the Antoine equation
M	molecular weight
p_i	partial pressure of component i
p°	vapour pressure
p_i°	vapour pressure of component i
P	total pressure
T	absolute temperature
x_i	concentration of component i (mole fraction)
ρ_g	density of gas

26 Accident Research

Contents

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Accidents in chemical plants may harm the process, the personnel or both. Research on accidents is relevant, therefore, both to accidents which result in property damage and those which cause personal injury.

Accident research as a discipline tends to concern itself primarily with those accidents in which people are involved. It is primarily concerned, therefore, with injury to personnel. But it does involve the study of the total accident situation. Often it is a matter of chance whether this situation hazards the process or the people. Clearly accident research is closely related to work in other fields such as human factors and, in particular, human error.

Accounts of accident research include *Occupational Accident Research* (Kjellen, 1984), *Information Processing and Human-Machine Interaction* (Rasmussen, 1986), *Individual Behavior in the Control of Danger* (A.R. Hale and Glendon, 1987) and *Human Error* (Reason, 1990). Many of the classic papers in the field are given with commentary in the collection *Accident Research, Methods and Approaches* (Haddon, Suchman and Klein, 1964).

Much work on the subject is concerned with areas which are not of prime interest here, such as accidents to children, accidents in the home and traffic accidents.

In addition to work on personal accidents, it is convenient to deal here briefly with some principal research programmes on, and test sites for, major hazards.

Selected references on accident research are given in Table 26.1.

26.1 General Considerations

The development of accident research has shown that there are a number of serious pitfalls in the investigation of accidents. There is a tendency for a particular feature to be studied as a possible cause of accidents and there is frequently a bias in favour of this feature. Often no information is given on any work with a control group. This situation was contrasted with that in medical work in a classic paper by Gordon (1949), who suggested that the approach taken in epidemiology is applicable to accident

Table 26.1 *Selected references on accident research*

E. Farmer (1932); Gordon (1949); Paterson (1950); Kerr (1957); Sheldon (1960); Rapoport (1961); Suchman (1961); Haddon, Suchman and Klein (1964); Surry (1969a,b); A.R. Hale and Hale (1970,1972); Ramsey (1973); Carr (1975); Hendry (1975); Pickbourne (1975); HSE (1976d, 1993a); Smillie and Ayoub (1976); Verhaegen *et al.* (1976); Saari (1977); Kjellen (1984); Leplat (1985, 1987); Pastorino *et al.* (1986); Rasmussen (1986); A.R. Hale and Glendon (1987); Beckers (1993)

Classification of accidents
HM Chief Inspector of Factories (annual); California State Department of Health (1953–57); ILO (1961); HSE (1983c, 1986c, 1992b)

Indices of harm
Solomon and Alesch (1989)

Accident models (see Table 2.1)
Accident proneness
Greenwood and Woods (1919); E. Farmer and Chambers (1926, 1939); Newbold (1926); E. Farmer (1932); Tillman and Hobbs (1949); Arbous and Kerrich (1953); Suchman and Scherzer (1960); Cresswell and Froggatt (1963); L. Shaw and Sichel (1971); Schafer (1973a); Cazamian (1983)

Judgement, risk-taking
J. Cohen and Hansel (1956); J. Cohen, Dearnaley and Hansel (1956, 1958); Fortenberry and Smith (1981)

Risk homeostasis
McKenna (1975, 1985); Wilde (1978, 1982a,b, 1985, 1988); Shannon (1986); J.G.U. Adams (1988); Janssen and Tenkink (1988)

Human error (see Table 14.10)
Reason (1977, 1979, 1986, 1987a,b, 1990, 1991)

Slips, trips and falls
Sheldon (1960b); P.R. Davis (1983); Manning (1983); Buck and Coleman (1985); Tisserand (1985)

Road accident research
I.D. Brown (1990b); Reason *et al.* (1990); Rumar (1990); Wagenaar and Reason (1990)

Major hazards research
Brugger and Wilder (1975b); Buckley and Weiner (1978); Schneider, Lind and Parnarouskis (1980); Blackmore *et al.* (1981); Benson and Sinclair (1982); Bless (1982); Bello and Romano (1983a); Desteese and Rhoads (1983); Puttock, Colenbrander and Blackmore (1983); Johnston (1984, 1985); McQuaid (1984b, 1991); Roebuck (1984 LPB 58); Anon. (1985bb); Koopman and Thompson (1986); Quarantelli, Dynes and Wenger (1986); Schnatz (1986); Anon. (1987h); Closner (1987b); Rubin (1987); Mellor *et al.* (1988); Thomson and von Zahn-Ullman (1988); CEC (1989); Teja (1989); Carmody (1990a); Shortreed (1990); Institute for Systems Engineering and Informatics (1991a,b); Michot, Bigourd and Pineau (1992); Storey (1992); Cole and Wicks (1994)

Research facilities: FPA (CFSD OR 5, 1991 CFSD OR 6); HSE (1983/14); Le Diraison and Bailleul (1986); Redman (1986a); British Gas (1988 Comm. 1381); Flood and Stephenson (1988); Groothuizen (1988); Clerehugh (1991); D.C. Bull and Strachan (1992); CMI (1992)

research. The epidemiology model, which is described below, has been widely used in work on accidents.

26.2 Definition of Accidents

The question of what actually constitutes an accident is worth at least brief consideration. It has been considered by Suchman (1961), who distinguishes three defining characteristics: (1) degree of expectedness, (2) degree of avoidability and (3) degree of intention. An event is more likely to be classed as an accident if it is unexpected, unavoidable and unintended.

Other secondary characteristics are (1) degree of warning, (2) duration of occurrence, (3) degree of negligence and (4) degree of misjudgement. Classification of an event as an accident is more probable if it gives little warning and happens quickly and if there is a large element of negligence and misjudgement.

It is suggested, however, by Suchman that as knowledge increases an event is more likely to be described in terms of its causal factors and less likely to be classified as an accident.

26.3 Classification of Accidents

Much work on accidents is concerned with accident statistics. These statistics are based on an accident classification of some kind. Accident classifications are therefore quite important. Unless a classification contains a particular category which is of interest, there is no means of retrieving information on it.

There are a number of standard accident classifications. These include the classification used by the HSE in its annual *Health and Safety Statistics,* published in the *Employment Gazette* and that used in the annual *Yearbook of Labour Statistics* published by the International Labour Office. Relevant standards are the American National Standards Institute (ANSI) Z16 series.

26.4 Causes of Accidents

The main aim of accident research is to understand accidents so that they can be prevented. The attempt to understand an accident is often equated with the search for its cause.

The concept of the cause of an accident, however, has become somewhat discredited. In accident investigation an administrative requirement to report a single cause usually does not do justice to the complexity of the situation. In accident research, there has been much criticism of work which isolates and overemphasizes a particular factor.

It is more acceptable, therefore, to regard an accident as arising from a particular combination of factors rather than from a single cause. There is thus a tendency to consider relationships between variables rather than causes.

While this approach is undoubtedly correct in general, the danger is that the accident situation then appears incredibly complex and the attempt to understand it, hopeless. The work of Rapoport (1961) provides something of an antidote to this. As he points out, the scientific technique of isolating the influence of one variable by controlled experimentation has been enormously fruitful and it should not be lightly abandoned.

Rapoport distinguishes between specific and non-specific causes both in the field of disease and in that of accidents. Progress in control of disease has come both from specific factors (e.g. vitamins), and non-specific ones (e.g. public hygiene).

Although much work on accidents is of a statistical nature, the value of the descriptive approach should not be underestimated. The work of Sheldon (1960) on accidents to old people involving falls has been cited as a classic in this regard.

The investigation of accidents is dealt with in Chapter 27, which describes an illustration of an accident investigation given by Houston (1971). The investigation does not aim to find a single cause, but rather to discover the many factors which contribute to the accident.

26.5 Accident Models

Recognition of the complexity of accidents has led to the development of a number of accident models. A particular model of the accident situation is that derived from epidemiology, following the work of Gordon (1949). The factors involved in an accident are defined as follows: (1) host, (2) agent and (3) environment. Although this model derives from medical work, it has been applied in many other fields.

The main agent in an accident is usually some form of energy which inflicts physical damage. Accidents not accounted for by energy have as an agent a toxin, which is the other principal agent.

A distinction is made between an agent and the vehicle for that agent. In an accident from a falling spanner, the agent is energy and the vehicle is the spanner.

Another model of the accident situation, which draws both on Gordon's model this one and on fault trees, is that developed by Houston (1971, 1977). In this model a driving force is activated by a trigger so that through some form of contact process it causes injury or damage to a target.

A second group of models is based on the concept that it is possible to define for a system a 'normal operating state', and hence deviations from that state, and that such deviations are associated with danger. The models of G.L. MacDonald (1972) and Kjellen (1983) exemplify this group. Figure 26.1 by Hale and Glendon illustrates MacDonald's model.

A third group of models is based on human information processing. They include those of Surry (1969b), A.R. Hale and Hale (1970) and A.R. Hale and Glendon (1987). The models of Surry and of Hale and Hale are both formulated in terms of perception, cognition and physiological response, or action. That of Surry is in two parts, the first dealing with the danger build-up and the second with the danger release or emergency. Each part has a similar structure, that for danger build-up being:

Perception	Warning of danger build-up?
	Perception of warning?
Cognitive process	Recognition of warning?
	Recognition of avoidance mode?
	Decision to attempt to avoid?
Physiological response	Ability to avoid?

Another important model in this group is that of Rasmussen (1986) based on the distinction between knowledge-based, rule-based and skilled activity. As characterized by A.R. Hale and Glendon (1987), following Leplat (1985), these three levels of function correspond at the cognitive level to interpretation, identification and

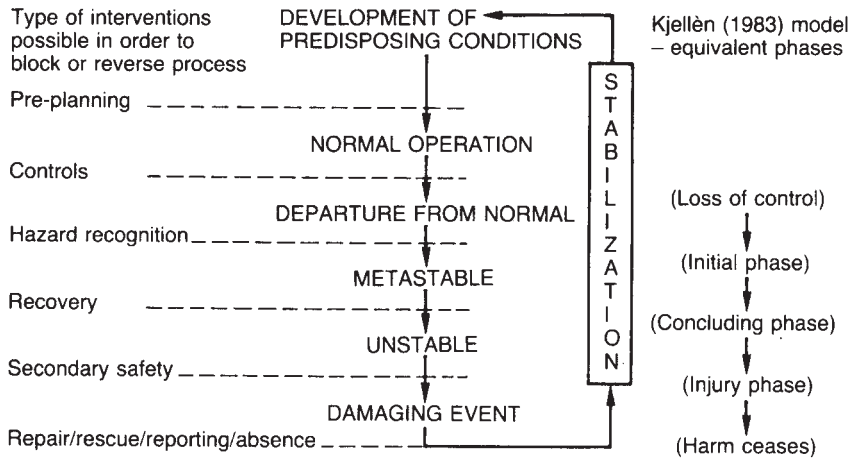

Figure 26.1 *Scheme illustrating accident models of MacDonald and Kjellen (A.R. Hale and Glendon, 1987 (reproduced by permission of Elsevier Science Publishers); after G.L. MacDonald (1972) and Kjellen (1983))*

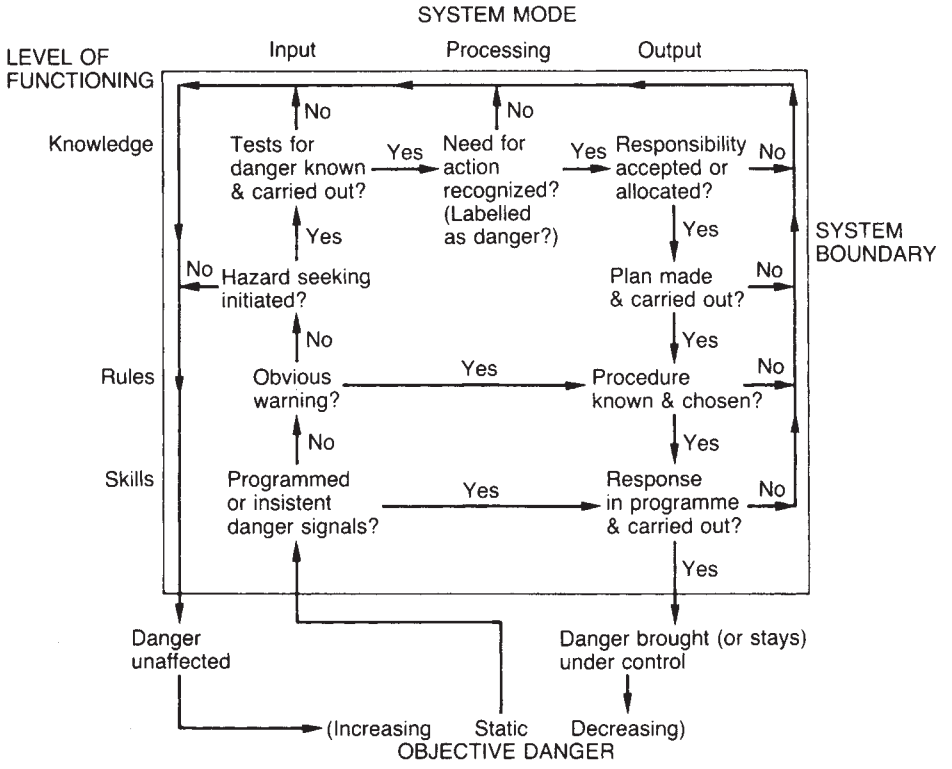

Figure 26.2 *'Behaviour in the face of danger' accident model (A.R. Hale and Glendon, 1987 (reproduced by permission of Elsevier Science Publishers))*

observation/activation and in terms of behaviour to evaluation/task definition, procedure and execution, respectively. The Rasmussen model is described in more detail in Chapter 14.

A model which draws on the foregoing models is the 'behaviour in the face of danger' model of A.R. Hale and Glendon (1987) shown in Figure 26.2. This has the general structure of Rasmussen's model but amplifies it using

stages drawn from Surry's model. The model shows what has to occur if the danger is to be averted. In other words it is a prescriptive model. The text by Hale and Glendon is an exploration of the factors affecting this behaviour and of the extent to which the behaviour is likely to lead to a successful outcome.

Other models, reviewed by Mill (1992), include those of the Institut National de Recherche sur la Securite (INRS) in France, the Occupational Accident Research Unit (OARU) in Sweden and the International Loss Control Institute (ILCI) in Georgia. The INRS model represents an accident as a deviation in the normal work situation and has a fault tree structure. The OARU model is intended for investigation of single person injuries and represents the accident as a chain of deviations. The ILCI model is a five layer model which progresses from basic causes in management deficiencies and progresses through to the immediate causes.

A number of other accident models, drawn mainly from the literature on process safety rather from than the psychological literature, are described in Chapter 2.

The contribution of human factors, and in particular the work situation, to accidents is considered in Chapter 14.

26.6 Accident Proneness Plan

The idea that certain people are accident prone is quite an ancient one. In fact the accident prone individual is a classic comic character. Accident proneness as a concept in accident research, however, dates from the classic paper of Greenwood and Woods (1919) of the Industrial Fatigue (later Health) Research Board on accidents to industrial workers. The interwar period saw a number of publications on various aspects of accident proneness by investigators at the boards, in particular those by Newbold (1926) and E. Farmer and Chambers (1939).

The fact that an individual has an above-average number of accidents does not in itself necessarily mean anything. It can be shown from the Poisson distribution that on the basis of chance alone there will be individuals who have quite large numbers of accidents. It is accidents that cannot be explained in this way which have given rise to the concept of accident proneness.

The terminology associated with the problem of the variation in accident rate between individuals tends to be a source of confusion. Accident repetition describes the observed fact that an individual has suffered an above-average number of accidents and that this is statistically significant. Accident proneness refers to a higher than average susceptibility to accidents which arises from psychological factors and tends to be permanent. Accident liability is a broader term describing an above-average accident rate which may be due to many factors, including work situations and personal stresses and which tends to be temporary. It is emphasized, however, that authors in this field have been criticized (e.g. Arbous and Kerrich, 1953) for lack of definition and consistency in their use of terms.

Greenwood and Woods (1919) showed that some industrial workers have more accidents than would be expected from chance alone, using the Poisson distribution. In other words, they established the fact of accident repetition. They offered as an explanation a theory of unequal liability to accidents, but did not themselves go so far as to suggest one of accident proneness.

These findings were confirmed in further work by Newbold (1926), who suggested that there might be a psychological explanation for them.

The phenomenon of accident repetition has subsequently been confirmed by numerous workers, many of whom have gone beyond the original investigators' more conservative conclusions to develop a theory of accident proneness.

An activity which has been studied particularly is driving (e.g. E. Farmer and Chambers, 1939; Tillman and Hobbs, 1949; Cresswell and Froggatt, 1963; L. Shaw and Sichel, 1971). Farmer and Chambers investigated driver accidents and concluded that accident proneness was an established fact. Yet the only significant correlation obtained between accident rate and individual characteristics was in tests on aesthetokinetics rather than on personality.

The concept of accident proneness has been severely criticized by Arbous and Kerrich (1953), while Suchman and Scherzer (1960) have given an evaluation of its status. The conclusion drawn is that accident proneness is difficult to establish, but that accident liability is a more acceptable concept. Accident liability may be connected with such factors as the work situation or stress, is usually temporary and does not depend primarily on personality traits.

The investigation of accident liability may in fact be a fruitful way of reducing accidents. An example is the work of Viteles at the Cleveland Railway Company (Arbous and Kerrich, 1953). He identified 50 individuals with accident liability and, taking a clinical approach, analysed the cases individually. The prime causes of accident liability which he identified are shown in Table 26.2. Various measures, including medical treatment, systematic instruction and increased supervision, were taken. As a result, the accident rate was almost halved. This approach requires, of course, a great deal of effort. In a further review, Cazamian (1983) takes it as established that certain individuals do have repeated accidents, but treats this as an acquired susceptibility rather than an inherent predisposition. Individuals may enter and leave the group of accident repeaters. Some factors can be identified which increase the susceptibility to repetition. Accidents are more common among young

Table 26.2 *Prime causes of accident liability in an industrial investigation after Viteles*

Prime cause	*Percentage of cases*
Faulty attitude	14
Failure to recognize potential hazard	12
Faulty judgement of speed and distance	12
Impulsiveness	10
Irresponsibility	8
Failure to keep attention constant	8
Nervousness and fear	6
Defective vision	4
Organic disease	4
Slow reaction	4
High blood pressure	2
Senility	2
Worry and depression	2
Fatigability	2
Improper distribution of attention	2
Inexperience	2
Miscellaneous	6

workers than mature adults, among those who lack training and experience and among those who are ill.

26.7 Human Error

Work on the psychology of human error is exemplified by the work of Reason, described in *Human Error* (Reason, 1990) and in other work (Reason, 1977, 1979, 1986, 1987a,b, 1991). One aspect of this work is the recognition that many accidents occur due to absent-mindedness and that, whilst in the vast majority of cases the consequences of such absent-mindedness are not serious, in a proportion of cases they are.

26.8 Risk-taking

Some accidents occur because people consciously take risks. In a given case the risk is generally judged to be small, but it is a finite risk nevertheless, and occasionally such behaviour results in an accident.

26.8.1 Risk homoeostasis definition? Maintaining an acceptable equilibrium

It is sometimes argued, particularly in relation to activities such as car driving, that there is a certain level of risk which people accept and that if physical measures are taken to reduce this risk, such as improved traffic engineering or vehicle crash resistance, the effect of these measures is cancelled by changes in individual behaviour so that the end result is that the risk remains the same.

A formal theory of risk homoeostasis has been given by Wilde (1978, 1982a,b, 1985, 1988). According to this theory, the loss due to road accidents per unit time is the output of a closed loop process in which the set-point is the target level of risk.

The concept of risk homoeostasis does not imply that all measures to improve road safety are doomed to failure. A distinction is drawn between physical and motivational measures. The latter act to influence the target level of risk and can indeed be effective. The theory is pessimistic, however, on the effectiveness of non-motivational measures.

A critique of the theory of risk homoeostasis has been given by McKenna (1975, 1985).

The measure of effectiveness in this debate is important. It is common ground that physical measures can reduce the accident rate per unit distance covered. It is argued, however, by Wilde that they have little effect in reducing the accident rate per unit driving time.

26.8.2 Risk judgement

Another type of situation which can also lead to accidents occurs when there is misjudgement of the risk. In relation to such accidents, a distinction has been drawn by J. Cohen, Dearnaley and Hansel (1956) between judgement and capability. They investigated the ability of bus drivers to drive a bus through a narrow opening. The work distinguished between lack of success due to misjudgement of the width of the opening and inability to drive the bus through it. In some cases, a generally capable driver would try to drive through an opening which was narrower than the bus itself. Obviously these two causes of failure have different implications for training.

An undesired outcome may occur either because the actions do not go as planned or because the plan is inadequate. It is with the first of these causes, 'actions-not-as-planned', that the work is concerned.

Reason conducted an experiment in which 35 subjects kept a diary of their actions-not-as-planned over a 2-week period. The classification of these errors and the proportion of errors in each main class are shown in Section A of Table 26.3, while Section B gives specific examples.

The classification is based on a computer program model of human activity. The discrimination errors are failures in classification of the inputs. The program assembly errors involve use of inappropriate subroutines. The test failures refer to failure to check on the progress of a sequence or to selection of an incorrect branch. The subroutine failures involve insertion into, omission from or mis-ordering within a sequence. The storage failures are forgetting or mis-recalling plans and actions.

Reason outlines a number of concepts which may help to explain the results obtained. Skilled performance involves switching between open and closed loop modes of control. Typically a large part of a task or series of tasks may be carried out under open loop control, but it is necessary to revert to closed loop control at certain critical decision points. A failure to make the necessary switch at the appropriate moment is likely to result in an error.

In some cases, a motor programme sequence shares a common subsequence with another sequence, but there is a critical decision point where it diverges from this second sequence. This is a situation particularly likely to lead to error.

Some motor programmes appear to acquire a strength which causes them to be activated contrary to the current plan. This is likely to apply particularly to a programme which has been used frequently or recently.

Reason goes on to propose certain hypotheses concerning such errors. He suggests that test failures occur when a critical decision point is reached while still under open loop control and where the strengths of the two motor programmes are markedly different, and that if an error occurs it is likely to involve the unintended activation of the strongest motor programme beyond the node.

Another hypothesis is that storage failures in the execution of a sequence are associated with some counting mechanism in the motor programme which checks off the actions as they are performed. It appears that on occasion this counter is unable to distinguish between planned actions and others which are similar in duration and degree of activity, so that if an interruption occurs the programme resumes at the wrong point.

In tasks such as maintenance, a large proportion of the errors involve omission. The practical application of the work described points to the provision of memory aids which assist the worker to remember which stage of the sequence he has reached.

This work leads to the distinction made by Reason (1990) between slips, lapses and mistakes. In essence, a slip is either an error in implementing a plan or an unintended action, a lapse is an error in which the intended course of action is not executed due to a failure of memory, and a mistake is an error in establishing the correct course of action.

26.9 Social Factors

The effect of physical features of the environment on accidents is readily appreciated. Less obvious, but often as important, is that of its social aspects. Social factors are effective in reducing accidents (1) if the socially approved

Table 26.3 *Classification and examples of actions-not-as-planned (after Reason, 1979)*

A	**Proportion of errors in each class**
1.	Discrimination failures (11%)
1.1	Perceptual confusions (objects confused are physically similar)
1.2	Functional confusions (objects confused are functionally similar)
1.3	Spatial confusions (objects confused are close together)
1.4	Temporal confusions (time is misperceived and inappropriate actions initiated)
2.	Program assembly failures (5%)
2.1	Behavioural spoonerisms (program elements are reversed)
2.2	Confusions between currently active programs
2.3	Confusions between ongoing and stored program
3.	Test failures (20%)
3.1	Stop-rule overshoots (actions proceed beyond intended end-point)
3.2	Stop-rule undershoots (actions cease before their intended end-point)
3.3	Branching errors (initial sequence of actions is common to two different routines and wrong branch is taken)
3.4	Multiple side-tracking (subject is apparently diverted from original intention by series of minor side-steps)
4.	Subroutine failures (18%)
4.1	Insertions (unwanted actions are added to a sequence)
4.2	Omissions (necessary actions are left out of a sequence)
4.3	Mis-ordering (actions carried out are correct but in wrong order)
5.	Storage failures (40%)
5.1	Forgetting previous actions
5.2	Forgetting discrete items in plan
5.3	Reverting to earlier plans
5.4	Forgetting the substance of plan
B	**Examples of actions-not-as-planned**
1.1	'I put my shaving cream on my toothbrush'
1.2	There were two objects before me on the draining board: a cloth and a container of cleaning fluid which I normally keep in the bathroom but had brought into the kitchen to use. I decided to return the cleaning fluid to its place in the bathroom, but set off with the cloth in my hand instead'
1.3	'I turned on my electric fire instead of my transistor radio which was on the floor near it'
1.4	'When I got up on Monday morning, I found myself putting on Sunday's sweater and jeans instead of my working clothes'
2.1	'I unwrapped a sweet, put the paper in my mouth and threw the sweet in the waste paper basket'
2.2	'My office phone rang. I picked up the receiver and bellowed "Come in" at it'
2.3	'I fetched a box of matches to light the electric fire'
3.1	'I brought the milk in from the front step to make myself a cup of tea. I had put the cup out previously. But instead of putting the milk into the cup, I put the bottle in the fridge'
3.2	'I was just about to step into the bath when I discovered that I still had on my underclothes'
3.3	'I intended to drive to Place X, but then I "woke up" to find that I was on the road to Place Y'
3.4	'I went upstairs to sort out and fetch down the dirty washing. I came down without the washing having tidied the bathroom instead. I went upstairs again to collect the washing, but somehow got side-tracked into cleaning the bathroom. I forgot all about the washing until I returned to the kitchen where the washing machine was pulled out in readiness'
4.1	'I came out of the sitting room in the daytime and flicked on the light as I left the room'
4.2	'I filled my electric kettle with water, plugged the lead into the back of the kettle and switched on the wall socket. When the kettle failed to boil I discovered I had not inserted the plug into the wall socket'
4.3	'Sitting in the car about to leave work, I realized I had put the car into gear and released the handbrake without first starting the engine'
5.1	'I started to walk home and had covered most of the distance when I remembered I had set out by car'
5.2	'I had intended to post a letter while I was out shopping but when I got home I found I still had the letter in my pocket'
5.3	'I decided to make some pancakes for tea. Then I remembered we didn't have any lemons so I decided not to bother. Five minutes later I started getting together the ingredients for pancakes, having completely forgotten my change of mind'
5.4	'I went upstairs to the bedroom, but when I got there I couldn't remember what I came for'

behaviour minimizes accidents and (2) if individuals adhere to that behaviour.

The effect of individual deviation from the approved standard has been considered by Paterson (1950). The basic argument may be illustrated by reference to Figure 26.3, which shows on the horizontal axis the strength of group conditioning, decreasing away from the origin, and on the vertical axis the number of people who exhibit that degree of conditioning. It is assumed that the optimal type of behaviour which minimizes accidents corresponds to that given by the highest degree of group conditioning. Curve A represents a highly disciplined society with a low mean. The

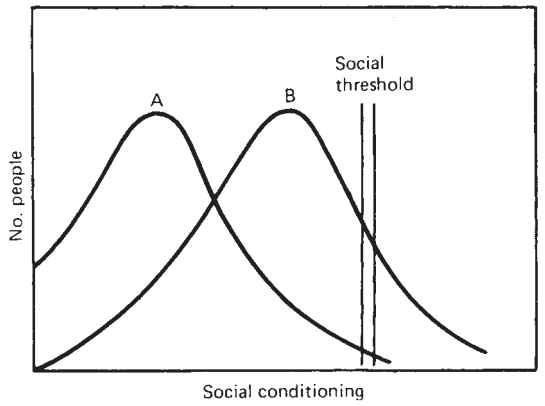

Figure 26.3 *Effect of social factors in behaviour affecting accident rates*

discipline may be due to the harshness of nature or to the social and political system. Curve B corresponds to a less disciplined society with a high mean. Also shown in the figure is the social threshold, which is the point at which the deviation from optimal behaviour results in marked increase in accidents. If the socially approved behaviour is optimal in reducing accidents, then clearly there will be more accidents in a society where there is greater individual deviation.

It cannot be assumed, however, that social pressures always tend to reduce accidents. On the contrary, the expectations of a small peer group may well run in the opposite direction and it is often this influence which is strongest. Thus the behaviour laid down in company safety procedures may be assumed to reduce accidents. But certain types of peer group pressure may increase them. Examples are neglect of permit-to-work procedures, failure to wear protective clothing and horseplay among apprentices.

26.10 Accident Prevention

Measures to prevent energy causing injury or damage may be based on the following four principles: (1) reduction of the energy available, (2) modification of the release of the energy, (3) separation by distance and (4) separation by a barrier.

Accident models such as that of Houston (1971, 1977) are useful in analysing potential accident situations and identifying appropriate preventive measures.

Accident prevention measures are not infrequently brought in without adequate understanding of the problem and without sufficient evaluation. Such measures are likely to be relatively ineffective. There is a tendency to believe that they must be better than nothing. But often they are an obstacle to progress, because they give the impression that something is being done about the problem.

This contrasts with the very thorough trials which are made on the effectiveness of drugs in countering disease. Proper evaluation is necessary for proposed accident prevention measures also. This again is in line with the more quantitative approach which characterizes loss prevention. The practical application of this principle is seen in the work of the Road Research Laboratory on the evaluation of road safety.

26.11 Safety Training

Most prescriptions for the prevention of accidents lay much emphasis on training, and rightly so. It is necessary, however, that the training be effective.

A study of the effectiveness of safety training by A.R. Hale (1984) found relatively little previous work on the topic. The essential finding of the study is that, unless effort is invested in analysing the problem and defining the training requirements, the training is liable to be ineffective and to get the activity a bad name. The author quotes the *Robens Report* (Robens, 1972) which states: 'Most people are agreed that safety training is of vital importance. There is no unanimity about what in practice should follow from that proposition'.

The requirements for training found in the legislation by the author are patchy, with power presses governed by a detailed training schedule whilst injection moulding machines have no specific provision. There are requirements of competence for drivers of coal mine face conveyors, but not for those of fork lift trucks.

26.12 Major Hazards Research

Research on major hazards is described throughout this book, particularly in Chapters 15--17 on emission and dispersion, fire and explosion. The treatment here is confined to an indication of some of the major experimental programmes and the sites where they have been conducted.

Large-scale experimental trials on dense gas dispersion have been conducted in the United Kingdom at Porton Down (Picknett, 1981a--c), Maplin Sands (Puttock, Colenbrander and Blackmore, 1983) and Thorney Island (A.G. Johnston, 1984, 1985; McQuaid, 1984b) and in the United States at China Lake, California (Ermak *et al.,* 1983), and at the Nevada Test Site (Koopman and Thompson, 1986).

Large-scale trials on fire phenomena have been performed at the Health and Safety Executive's (HSE) Explosion and Flame Laboratory at Buxton. This includes work on pool fires, fireballs and engulfing fires (A.F. Roberts, 1987; McQuaid, 1991).

Other work on fires has been done at Shell sites and at the British Gas sites at Fauld and at Spadeadam in cooperative projects involving a number of companies, including in particular trials on jet flames and on fire insulation. The Maplin Sands work on dense gas dispersion included trials on vapour cloud fires.

Explosion experiments on a large scale include those on condensed phase explosives such TNT and other military explosives at the Aberdeen Proving Ground (W.E. Baker, 1973) and other military sites. Buildings and equipment have been subjected to condensed phase explosions in Nevada (Glasstone and Dolan, 1980). Large-scale work on vapour cloud explosions has been done in the Netherlands at TNO (van Wingerden, 1989a).

In addition to the HSE laboratories just described other European centres include the Shell Thornton Research Centre (TRC) (D.C. Bull and Strachan (1992), the British Gas laboratories at Solihull, Loughborough and Killingworth and sites at Fauld and Spadeadam (Clerehugh, 1991), the Prinz Maurits Laboratory of TNO in the Netherlands (Groothuizen, 1988) and the Christian Michelsen Institute at Norway (CMI, 1992). UK centres specializing in fire include the Fire Research Station at Borehamwood and the Department of Fire Safety Engineering at Edinburgh University.

The European Community has had a wide-ranging programme of work on major hazards, particularly dense gas dispersion and vapour cloud explosions. This work is described by the Commission of the European Communities (CEC, 1989) and by Storey (1992). The commission maintains the Joint Research Centre QRC) at Ispra, Italy, which includes the European Laboratory for Structural Assessment (ELSA).

In the United States, research in many areas of process safety is conducted at the Mary Kay O'Connor Process Safety Center at Texas A&M University. In 2004, the Center had active research projects on Abnormal Situation Management, Aerosol Experiments and Modeling, Flammability Measurements and Modeling, Incident Database (Development, Analysis and Causation), Inherently Safer Design, Chemical Safety Assessment, Quantitative Risk Assessment, Reactive Chemicals (Thermal Analysis, Calorimetric Measurements, and Modeling) and Safety Performance Measurement Systems and Safety Metrics.

The work of many of these research centres is described in other chapters, mainly in Chapters 15--17.

27 Information Feedback

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27.9 Public Accident Inquiries 27/15
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The feedback of information about incidents, accidents and failures, and about the performance of preventive measures, is a crucial aspect of the management system.

Some aspects of information feedback are considered here. Others are dealt with in other chapters, in particular Chapters 6, 8, 21 and 28.

Selected references on information feedback are given in Table 27.1.

Table 27.1 *Selected references on information feedback (see also Tables 1.1, 6.1 and 28.1)*

Guelich (1956); Heinrich (1959); Simonds and Grimaldi (1963); ABCM (1964/3); H.H. Fawcett and Wood (1965, 1982); McElroy (1965); Gilmore (1967, 1970); BCISC (1969/9); Handley (1969, 1977); Arscott (1975); Byrne (1975); Hearfield (1975); Kletz (1975a, 1976a, 1979c,h); Wellman (1975); Dawes and Davies (1977); Pitts and Gowan (1977); R.W. Henry (1979); NFPA (1990 NFPA 901, 902M); Hancock (1992 LPB 105)

Incident reporting, total loss control
BSC (n.d./6, 7); NRC (Appendix 28 *Incident Reporting*); Heinrich (1959); Bird and Germain (1966); J.A. Fletcher and Douglas (1971); Webster (1974, 1976); Dukes (1975); Hearfield (1975); Laitinen (1982); Lewis (1989 LPB 87); I.D. Brown (1990a); HSE (1992b); Brazier (1994)

Incident investigation and analysis
NRC (Appendix 28 *Incident Investigation*); SMRE (*Incident Investigation* 1); Guelich (1956); ABCM (1964/3); Bulkley (1967); Lynch (1967, 1973); Spiegelman (1969); Webb (1969); Siebert (1970); Houston (1971); W.G. Johnson (1973a,b, 1975, 1977, 1980); Benner (1975a); D.G. King (1975); R.J. Parker (1975); A.R. Baker (1976); Gugan (1976); Nertney (1976, 1978); Strehlow and Baker (1976); W.E. Baker, Westine and Cox (1977); R. King and Taylor (1977); Leplat (1978a); Bruun, Taylor and Rasmussen (1979); Kletz (1979g,h, 1982a,b, 1983a, 1984a, 1986a, 1988h); Beyers (1980); HSE (1980 EMI, EMS); Robinson (1980 LPB 33); Ursenbach (1980, 1983); Burgoyne (1981/82, 1982); Sheehy (1981); W.E. Baker (1982); Feggetter (1982); Pimble and O'Toole (1982); Searson (1982); Wiestling (1982); Zilka (1982); Boissieras (1983); Kjellen (1983); Mollerhoj and Robert (1983); van der Schaaf and Steunenberg (1983); Suokas and Rouhiainen (1984); Benner (1985); Vaija, Jarvelainen and Dohnal (1985, 1986a); Anon. (1986 LPB 72, p. 21); S.J. Brown (1987); Duguid (1987); Hendrick and Benner (1987 ACGIH/14); Leplat (1987); Suokas (1987); Ferry (1988); Mosleh *et al.* (1988); van der Schaaf (1988); I.D. Brown (1990a); Dowell (1990); ILCI (1990); S.E. Anderson and Skloss (1991); Svenson (1991a,b); Livingston and Green (1992); Philley (1992b); Nishikawa (1993)
Fire, explosion investigation: FPA (CFSD AR series, AR 1, AR 5); J. Kennedy (1962); Huron (1963); Bulkley (1967); Kirk (1969); V. J. Clancey (1972b, 1981); W.B. Howard (1972); Sadee (1973a); Anon. (1975 LPB 2, p. 15); R.J. Parker (1975); AR. Baker (1976); FRS (1976 Fire Res. Note 1054); Guenther *et al.* (1976); Gugan (1976); Levinson (1977); Ettling (1978); Guenther, Goodwin and Brininger (1978); Dennett (1980); Yallop (1980); Beland (1981, 1982); Craven (1981, 1982); McIntyre (1981); Willis (1981); W.E. Baker (1982); Delplace and Vos (1983); D.A. Gray, Drysdale and Lewis (1983); R.J. Harris (1983); G.D. Davis (1987); Zeeuwen (1988); Cullen (1990); Taillet (1991); I.F. Thomas (1993, 1995); I.F. Thomas and Gugan (1993)
Transport investigations: NTSB (Annual reports); Lasseigne (1984)

Warnings, near misses
NRC (Appendix 28); Pitts and Gowan (1977); Laitinen (1982, 1984); Lees (1982b, 1983b, 1985); N. Carter and Menckel (1985); Anon. (1989 LPB 85, p. 7); van Kernel, Connelly and Haas (1990); A.R. Hale *et al.* (1991); Ives (1991); D.A. Lucas (1991); Reason (1991); van der Schaaf, Lucas and Hale (1991); van der Schaaf (1991a–c)

Safety effectiveness, safety measurement
HSE (OP 9, 1986 PML 10, 1992 Oil Industry 3); Wynn (1950); Grimaldi (1960, 1965, 1970); Pollina (1962); Tarrants (1965, 1970, 1973); Rockwell and Bhise (1970); Anon. (1975 LPB 2, p. 12); Hooper (1975); S. Dawson, Poynter and Stevens (1982); Pastorini *et al.* (1986); Kaufman (1988); Gruhn (1993); Marcombe, Krause and Finley (1993)

Governmental investigation, disaster inquiries
Mecklenburgh (1977a); Davidson (1984); Crossland (1991); Fennell (1991); Wells (1991); I.F. Thomas (1993); I.F. Thomas and Gugan (1993); Lees (1994b)

Particular inquiries (*see also* Appendices 1–3, 5, 6, 16, 19, 21, 22)
R.J. Adams (1967); H. Griffiths, Pugsley and Saunders (1968); F. Morton (1970); Merrison (1971); R.J. Parker (1975); Ministry of Social Affairs (1976); Orsini (1977, 1980); Gjerde (1977–78); Costello (1979); Shooter (1980); Naesheim (1981); Hickman (1984); Layfield (1987); Sheen (1987); Steel (1987); Fennell (1988); O'Riordan, Kemp and Purdue (1988); Hidden (1989); Barnes (1990); Cullen (1990); Donaldson (1994)

Information retrieval, organizational memory
Kletz (1980g, 1982 J, 1993c); A.F. Roberts (1980); R.W. Fawcett and Kletz (1982); Hancock (1989, 1992); K. Rasmussen and Gow (1992)

Information exchange, publication
Kletz (1985g,q); Resen (1985b); Glass and Rivard (1987)

HSE information services, HSELINE
Pantry (1986, 1987 LPB 78); HSE (1990 HSEL 1); Lewis (1993 LPB 114)

Education
Imperial College (1975); Butler, Ball and Pearson (1978); Beveridge (1979 LPB 27); Lees (1980b); Lihou (1981 LPB 40); D.B. Nelson (1982); HSC (1983); Mewis (1984); Anon. (1985f); Anon. (1985 LPB 62, p. 13); Talty (1986); Kaufman (1987); Kletz (1988l, 1990a); Levitzky (1988); Crowl and Louvar (1989); Nolan (1989); Craweley (1991 LPB 102); V.C. Marshall (1991c); Pitt *et al.* (1991); Crawley and Scott (1992); Hazards Forum (1992); Lemkowitz (1992a,b); R.B. Ward (1993b,c); Louvar and Kubias (1994)
CCPS: Anon. (1986c)
IChemE: Anon. (1988i,j,q)

27.1 The Learning Process

It is clearly essential that the industry should learn from its mistakes so that as far as possible it avoids repeating them.

This need to learn has long been recognized and is dealt with by a system of accident reporting and investigation.

On the basis of this information, accident statistics are compiled and an attempt is made to determine the trend in safety performance. Case histories are obtained and general lessons are derived. These lessons give rise to changes of practice, which are often embodied in standards and codes of practice or training programmes. These results are then publicized.

This system is essentially similar at company and at national level. There are statutory requirements for the reporting and investigation of accidents. Company requirements may be confined to these or may include other incidents. Accident statistics, safety performance trends and case histories are produced, changes in practice are made and publicity is given to these at both company and national level.

The effectiveness of this approach depends very much on the way in which it is implemented. There are wide differences, for example, in the quality of incident investigation and consequently in the benefit derived from it. There is also considerable variation in the extent to which the real lessons of case histories are appreciated and applied.

There are also other weaknesses in most systems for learning from incidents. One of the most fundamental has to do with the nature of the accident process itself. An accident normally occurs only when a number of conditions are fulfilled. If some of these conditions are not met, there may be instead an incident or 'near miss'. In general, the ratio of near misses to accidents is several orders of magnitude. This is seen most clearly in civil aviation, which is one of the few fields where there is a requirement to report near misses. Thus, in effect, a system based on reporting only of accidents reduces drastically the amount of information from which learning can take place.

The recognition of this fact is the basis of the total loss control approach, as described in Chapter 1. With total loss control there is a requirement for the reporting not only of personal injury but also of property damage accidents.

Not all near misses, however, result in property damage. Another important category of near misses is the operational incident. The aircraft near misses just mentioned are, in fact, mainly incidents associated with excursions outside operational limits rather than with damage to equipment. The chemical industry, however, does not appear to have a mechanism for learning from operational near misses.

Another weakness of the usual approach to learning stems from the nature of the hazards on process plants. It is a characteristic of complex technological systems that they allow very little scope for learning gradually by trial and error. Instead, it is necessary to try to eliminate failures from the start.

This is the reason for the growth in reliability engineering and it has implications for the learning process. It means that attention needs to be concentrated not only on the accidents but also on the failures within the system that in a proportion of cases result in an accident. The emphasis on learning shifts then to the assessment of system reliability and to the collection of data required on equipment failure and human error.

It is not enough, however, to discover the facts about accidents. It is even more necessary to make sure this information is used. A high proportion of accidents constitutes repetitions, with only minor variations, of accidents which have already occurred elsewhere and which are well understood by the engineering profession as a whole. It is not to be expected that the individual engineer should familiarize himself with all these. But he should make it his business to become familiar with some of the exemplary case histories and their lessons. In addition, he should make use of aids such as checklists and codes of practice that embody much of this experience in the most readily usable form.

If learning is to take place, therefore, it is necessary to have both a means of obtaining information, for example accident reporting and investigation, and a means of ensuring that this information is utilized, for example, checklists and codes of practice. It is desirable for the learning process to take place at both company and national level and the measures described are, therefore, necessary at both levels.

27.2 Incident Reporting

A system for reporting accidents and perhaps other incidents is necessary at company level. The minimum system is one limited to meeting the requirements for statutory reporting of accidents.

The national reporting requirements, which are described in Chapter 3, have been extended in recent years to cover certain types of event not previously included, such as leaks.

Such statutory requirements, however, are intended to assist the national learning process. The real object of a company reporting system should be to help the company to learn. It may be appropriate, therefore, for there to be a requirement for the reporting of additional types of incident. Events likely to be of particular interest in safety and loss prevention (SLP) include:

(1) leaks of flammable materials;
(2) leaks of toxic materials;
(3) leaks and/or fires at pumps;
(4) fires/explosions on burners;
(5) storage tank collapse;
(6) malfunctions of pressure systems items (relief valves, non-return valves, vents);
(7) incidents involving trip system malfunction or disarming;
(8) incidents involving alleged operator error.

It is necessary to define carefully the level of incident that is reportable. This can be done satisfactorily at company level so that the reporting is adapted to the particular circumstances and produces useful information.

A reporting system is not of much value unless the information that it generates is utilized.

It is also appropriate here to refer again to total loss control, which involves a system both of incident reporting and of subsequent action, although in this case the emphasis is on some form of damage.

27.3 Operations Monitoring

In addition to incidents that have some physical result, such as the leakage of flammable materials or the collapse of a storage tank, there are also other incidents, such as excursions outside the specified operating conditions. These operational incidents also may constitute near misses.

The monitoring of operations from this viewpoint, however, is not well developed. The instrumentation provides trend records of selected variables and the operator records certain types of incident or excursion. These may be analysed or discussed with him by the plant manager. With the advent of process computers there is also a record of the alarm excursions of a larger number of measurements and of the operator's interventions via the computer. This information is mainly used in *ad hoc* investigations.

The Court of Inquiry on the Flixborough disaster experienced some difficulty in extracting useful information from the process instrumentation, most of which was destroyed by the explosion and the collapse of the control room. The report (R.J. Parker, 1975) suggested, therefore, that consideration should be given to the creation of a statutory requirement for the installation on such plants of a 'black box' facility such as is carried on aircraft.

This facility in aircraft is governed in the United Kingdom by the Air Navigation Order 1972, Schedule 5, which requires that certain aircraft, essentially those involved in public transport, should be equipped with a flight data and cockpit voice recording system approved by the Civil Aviation Authority (CAA). A flight data recorder system is required which records a list of specified parameters (e.g. pressure, altitude, airspeed, compass heading, pitch and roll attitudes) with a specified logging interval, accuracy and reliability. A crash-protected recorder is also required which will retain a record of these parameters in the event of aircraft crash. This is the so-called 'black box', although it is actually more like a red football in appearance. As already mentioned, a cockpit voice recorder is also a requirement.

This system, therefore, gives a complete record of the flight, including the information on maloperations and near misses, the number of which exceed actual crashes by several orders of magnitude.

The information given by the cockpit voice recorder is very useful and in crash investigations can be as important as the instrument data.

It will be apparent that the aircraft black box is in effect a system rather than a piece of hardware. It works well for aircraft where the parameters that should be specified for recording are standard, where the correct flying behaviour is well defined, and where there is a single authority that can analyse the data. Its application to chemical plant is more open to question for several reasons. Chemical plants already have a considerable amount of recording, particularly those with computers. There is much greater variation in chemical plants, both in the instrumentation and in the operation. Any analysis of the operations recorded would almost certainly be practical only at company level. Furthermore, despite Flixborough, it is not very often that the process instrumentation is destroyed.

If the object is to further the learning process at national level, it would seem more profitable to concentrate attention on a more systematic approach to the analysis of process operations in order to learn about near misses rather than to provide protected recorders which are used only to assist rare Courts of Inquiry. There would seem to be considerable scope for the operations monitoring of process plants. This might be somewhat on the lines of the replay of the aircraft flight data record, but as always any system used would have to be adapted to the rather different characteristics of chemical plants.

Nevertheless, the provision of a facility akin to the aircraft black box system is quite practical on chemical plant, particularly where there is a process computer. The main requirements for such a system are the provision of a schedule of data to be recorded, the proper maintenance of the instruments and the protection of the system against fire/explosion.

27.4 Accident Models

Accident models, which have already been considered in Chapters 2, 8 and 26, are here considered again briefly from the viewpoint of accident investigation.

Not all accident investigators find it helpful to make use of an accident model, but some do. Work on accident models for use as aids in accident investigation has been described by Benner (1985) and the Center for Chemical Process Safety (CCPS) (1992/1).

27.4.1 Logic tree models

Perhaps the most widely used form of accident model is the logic tree, this term being taken here to cover fault trees and other methods with a tree structure.

The Management Oversight and Risk Tree (MORT) of W.G. Johnson (1980), described in Chapter 2, provides a methodology for either investigating an accident or assessing a situation. MORT gives an idealized safety system represented as a logic tree containing specific control factors and general management factors. There is a text commentary that helps to identify good and bad practice.

Another logic tree method, the causal tree, derives the work of Leplat (1978a, 1987). This model resembles a fault tree, but is applied to an event that has already happened and which therefore contains no OR gates, only AND gates. Construction of the tree is guided by simple rules that specify the event chains. The aim of the method is to identify those changes that can be made to break the chain of events.

27.4.2 STEP

A model which does not have a tree structure is the Sequentially Timed Events Plotting (STEP) procedure of Hendrick and Benner (1987 ACGIH/14). The elements of the model are actors, actions and events. An actor can be a person, equipment, substance, etc., whilst an action is anything brought about by an actor, and an event is the unique combination of an actor and one action. A structured procedure is used to create a model of the accident from these elements.

27.4.3 Kletz model

Kletz states that he does not find the use of accident models particularly helpful, but does utilize an accident causation chain in which the accident is placed at the top and the sequence of events leading to it is developed beneath it. An example of one of his accident chains is given in Chapter 2. He assigns each event to one of three layers:

(1) immediate technical recommendations;
(2) avoiding the hazard;
(3) improving the management system.

In the chain diagram, the events assigned to one of these layers may come at any point and may be interleaved with events assigned to the other two layers.

It is interesting to note here the second layer, avoidance of the hazard. This is a feature that in other treatments of

accident investigation often does not receive the attention that it deserves, but it is in keeping with Kletz's general emphasis on the elimination of hazards and on inherently safer design.

27.4.4 Comparative studies

A comparative study of the characteristics of three accident models as applied to accident investigation has been made by Livingstone and Green (1992). They start from the perspective that investigations are generally too biased towards technical factors and take insufficient account of root causes. They identify three accident models as potentially useful: the causal tree model, MORT and STEP.

Livingstone and Green find that the causal tree method provides little guidance on how to collect the relevant information or identify the main events involved. It deals mainly with the direct causes, or trigger events, and does not deal so well with the root causes. They view STEP as well structured, but again as being of little assistance with root causes. They see MORT, on the other hand, as excelling in the identification of root causes, but as requiring the accident sequence to be identified separately.

These authors propose a hybrid model that combines STEP and root cause analysis.

27.5 Accident Investigation

Accident investigation is described in *Professional Accident Investigation* (Kuhlman, n.d.), *Modern Accident Investigation and Analysis* (Ferry, 1988), *Learning from Accidents* (Kletz, 1988h, 1994) and *Forensic Engineering* (Carper, 1989) and by Bulkley (1967), M.E. Lynch (1973), Kletz (1979g, 1984a), Burgoyne (1981/82, 1982) and Craven (1982).

Some accounts of accident investigation are concerned essentially with in-house investigations, whilst others describe the viewpoint of the consultant investigator. The account given here starts with a consideration of the selection of the investigator, either in-house or a consultant. It continues with a review of the purposes of investigation from the perspective of a consultant and then with the organization and conduct of an investigation, basically the technical aspects, again written from the viewpoint of a consultant, although the principles are equally applicable to an in-house investigation. Next, consideration is given to some particular types of investigation. The account then considers the investigation of the deeper causes of the accident and the recommendations for prevention, written largely from the viewpoint of the in-house investigator. The section concludes by considering a number of other topics related to investigations.

27.5.1 Selection of investigator

A formal system for the appointment of an accident investigator should be part of the emergency planning in a company. The selection of an investigator is discussed by Craven (1982). The choice is of particular importance if the accident is a major disaster. In this case it will usually be necessary to appoint a multi-disciplinary team, but the team will still require a leader. Craven considers the selection of the investigator under two headings: expertise and affiliation. Professional expertise and qualifications are factors to be taken into account, but personality and investigatory experience are also important. For small accidents, an in-house investigator may often be appropriate, but for a large accident it may be preferable to call in an outsider who is free of company involvement and is perceived as more independent.

27.5.2 Purpose of investigation

The usual purpose of an investigation is to determine the cause of the accident and to make recommendations to prevent its recurrence. There may, however, be other aims, such as to check whether the law, criminal or civil, has been complied with or to determine questions of insurance liability.

The situation commonly faced by an outside consultant is described by Burgoyne (1982) in the following terms:

> The ostensible purpose of the investigation of an accident is usually to establish the circumstances that led to its occurrence – in a word, the cause. Presumably, the object implied is to avoid its recurrence. In practice, an investigator is often diverted or distorted to serve other ends. This occurs, for example, when it is sought to blame or to exonerate certain people or things – as is very frequently the case. This is almost certain to lead to bias, because only those aspects are investigated that are likely to strengthen or to defend a position taken up in advance of any evidence. This surely represents the very antithesis of true investigation . . .

Ideally, the investigation of an accident should be undertaken like a research project.

It is, however, relatively rare for such investigations to be conducted in this spirit.

27.5.3 Organization of investigation

Often there will be separate investigations carried out by the company and by the regulatory body, which in the United Kingdom is the Health and Safety Executive (HSE). It is important, therefore, that the responsibilities of the investigation teams and of the individual investigators be clearly defined, and that people who may be affected by their activities be informed.

The investigation should start as soon as possible after the incident, while memories are still fresh and evidence is undisturbed. In particular, photographs, measurements and similar evidence should be taken on the site as early as possible.

The precise procedure for an investigation cannot be rigidly defined in advance. It may involve assessment of damage and interviewing of personnel and may include laboratory work such as metallurgical examination and simulation work such as the operation of equipment under simulated process conditions.

27.5.4 Conduct of investigation

The form taken by an investigation depends somewhat on the accident, but is likely to be broadly as follows: (1) remit, (2) preliminary site visit, (3) collection of background information, (4) examination of damage, (5) interviewing of witnesses, (6) research and analysis and (7) final report.

The purpose of the investigation should be clearly defined from the outset and a clear remit obtained. If in the course of the investigation it proves to be necessary, the remit should be renegotiated. The investigator should also ascertain the general circumstances of the accident.

The preliminary site visit should be made as soon as possible. The first matter to be considered is the potential hazards. The situation pertaining after a large accident particularly is, in the nature of the case, an uncontrolled one.

Some of the hazards enumerated by Burgoyne (1982) are: mechanical hazards, such as falling through collapsing structures or due to unsafe access, falling objects such as lifting gear, striking and crushing by collapsing structures, and collision with dangerous objects; thermal hazards of hot surfaces and fluids, and concealed fires; chemical hazards from corrosive, flammable or toxic materials, present as spills or in confined spaces or giving rise to sprays; and electrical hazards from live circuits and equipment.

At this stage, the site should not be disturbed. Photographs of the site are, however, invaluable. Colour photographs are preferred, since they give much more information, particularly on fire damage. A record should be kept of the location and viewpoint of each photograph. Sketch plans, sketches and notes should be made as appropriate. It may be helpful to obtain an overview of the site by viewing it from a distance, perhaps from the window of a nearby building.

During this visit, the names should be obtained of eyewitnesses and of others who may have relevant information. Witnesses should be encouraged to write down their experience whilst it is fresh and, if possible, before they have talked to other witnesses.

The investigator needs to familiarize himself with the details both of the process and of the plant equipment.

Examination of the damage caused by the accident usually yields much useful information. Some of the detailed features of fire and explosion damage are considered below.

The interviewing of witnesses is another important source of information but requires some care. Information should be sought on the situation immediately before as well as during and after the event. Allowance needs to be made for the fact that the account given by a witness may be defective by reason of the initial observation, memory or descriptive powers. Accounts of sudden, short and violent events in particular tend to be unreliable. The interviewer should avoid the use of leading questions and should seek to cross-check accounts given.

There follows a period of analysis and research. The danger of jumping to a conclusion and the need to keep an open mind are often emphasized. Burgoyne argues that the use of a working hypothesis, possibly with variants, is necessary, provided it continues to be treated as no more than that. The working hypothesis is then tested and adjusted, typically by an iterative process.

There may be some issues that can be resolved only by physical tests. In some cases, small scale tests are adequate, but frequently the only tests capable of providing results that will carry conviction are relatively large scale, time-consuming and expensive. One reason for the time and expense may well be the hazards of the work required. The decision as to whether to call for tests is often one of the most difficult which an investigator has to take.

There comes a point where further work is subject to the law of diminishing returns and the investigator has to come to a conclusion, even if, as is usually the case, there are loose ends.

A report is then written. This may well be best cast in the form of a chronological account of the steps by which the investigator came to his conclusion. The elements of an accident report are described by Craven.

27.5.5 Findings of investigation

An investigation is expected (1) to determine what happened and why it happened and (2) to propose how it might be prevented from happening again. These two outcomes constitute the findings and the recommendations of the investigation.

It is common for reports of accident investigations to draw conclusions, and make recommendations, which are concerned almost entirely with technical matters, and which fail to delve deeper into the more fundamental causes.

This characteristic of the conclusions of an accident inquiry is often virtually guaranteed by the way the investigator is chosen. Management assumes that the causes are technical and appoints to investigate them the person who seems to have the best technical qualifications for the task. He in turn assumes that he has been appointed to discover the technical cause(s).

In fact, accidents are typically the result of a combination of failures, technical and human, both of which are outcomes of management failure. Various aspects of this have been described elsewhere, notably in Chapters 2, 6, 9 and 14.

This characteristic of accidents is now common ground in the literature on accidents and their investigation. Different aspects are emphasized by different authors. For example, Reason (1991) stresses the prior presence of latent failures, or resident pathogens; Swain (1972) emphasizes the work situation and the associated performance shaping factors; and Bellamy (1984) stresses communication failures.

The need for a 'layered' accident investigation which strips off the surface layers and delves down to these deeper causes is a persistent theme in the work of Kletz on accident investigation and of learning from accidents; he calls it 'peeling the onion'. Some authors use an accident model and/or taxonomies of causes as an aid to laying bare the structure of the accident.

The basic message of such work is that, at the end of the day, it is management that has the responsibility of ensuring that the deficiencies and failures of equipment and humans are so controlled that accidents are avoided and that recommendations for preventing a recurrence must start from this perspective.

However, the proposition that accidents are always in some sense attributable to management is not in itself especially constructive. It is much more helpful to identify the particular failings which repeatedly contribute to accidents.

Most workers on accident investigation give their own classifications of these failings. For example, the classification given by Reason in relation to near misses is quoted in Section 27.16.

Another classification is that of Kletz, which, as already mentioned, treats the accident in terms of the three layers (1) immediate technical recommendations, (2) avoiding the hazard and (3) improving the management system.

Kletz makes a number of suggestions for things to avoid in accident findings. It is not helpful to list 'causes' about which management can do very little. Cases in point are ignition sources and 'human error'. The investigator should generally avoid attributing the accident to a single cause. Kletz quotes the comment of Doyle that for every complex problem there is at least one simple, plausible, wrong solution.

Increasingly, the findings of accident investigations are presented in terms of the root causes. The concept of root causes has been discussed in Chapter 8 and is considered further in Section 27.8. It underlies the family of techniques described by Wells and co-workers, the audit methodology

being developed by the HSE and the approach suggested by the CCPS. The findings should identify the specific root causes and the recommendations should then address each of these in turn.

27.5.6 Recommendations of investigation

As just indicated, the recommendations should arise out of the findings of the investigation. The investigation should aim to match each root cause with a corresponding appropriate recommendation.

A recommendation will generally address one of three aspects of the accident situation: (1) reduction of frequency, (2) reduction/mitigation of consequences and (3) limitation of exposure of people.

In terms of the fault tree representation, the aim is to insert a new, or to strengthen an existing, AND gate at each critical point in order to prevent escalation up the demand tree.

It is urged by Kletz that technical proposals for prevention should aim for defence in depth and, therefore, should give due weight to the earlier as well as the later lines of defence. In fault tree terms, there should not be excessive concentration on the upper levels of the tree just below the top event.

Lines of defence which Kletz lists, some applicable only to flammables are (1) limitation of inventory, (2) inspection of construction, (3) gas detectors, (4) leak warning system, (5) leak isolation, (6) leak dispersion by open construction and fluid curtains, (7) elimination of ignition sources, (8) passive fire and explosion protection, (9) active fire fighting measures and (10) separation distances.

Kletz identifies as recurring themes in general recommendations in his own analyses of accidents: (1) design of user-friendly plants, (2) hazard identification by hazard and operability (hazop) studies, (3) control of plant modification and (4) inspection and testing of protective equipment.

Another recurring theme is management, which has a number of aspects, including (1) organizational memory and (2) training.

Recommendations may seek to exploit the concept of hazard warning outlined in Chapter 9. From this viewpoint, the existence, or insertion, of an AND gate in the fault tree means that the events below that gate, if observable, may be monitored and treated as warnings.

It is good practice to draw up draft recommendations and to consult on these before final issue with interested parties. This contributes greatly to their credibility and acceptance.

It is relevant to note that in a public accident inquiry, such as the Piper Alpha inquiry, the evidence, both on managerial and technical matters, on which recommendations are based is subject to cross-examination.

The recommendations should avoid overreaction and should be balanced. It is not uncommon that an accident report gives a long list of recommendations, without assigning to these any particular priority. It is more helpful to management to give some idea of the relative importance. The King's Cross Report (Fennell, 1988) is exemplary in this regard, classifying its 157 recommendations as (1) most important, (2) important, (3) necessary and (4) suggested.

In some instances, plant may be shut-down pending the outcome of the investigation. Where this is the case, one important set of recommendations comprises those relating to the preconditions to be met before restart is permitted. These recommendations may well involve process and/or plant modifications and, if so, should be subject to the established systems for management of change.

There should be full documentation of the recommendations, covering those considered and rejected as well as those accepted.

27.5.7 Report of investigation

The investigation is documented in the final report. If it is a lengthy one, it may also be appropriate to issue an interim report.

The final report should include: an executive summary; an outline of the accident; a statement of the scope of the inquiry; the background, which will often need to cover relevant aspects of the management systems, the process, the plant and its operational history; a narrative of the events prior to and comprising the accident; an account of the investigation itself; a listing of the findings, with supporting evidence; and a listing of the recommendations, with clear links to the findings.

The requirements for follow-up of the report should also be specified in writing, whether in the report itself or otherwise. These include dissemination of the report's contents and action on it recommendations.

27.5.8 Experimental work

It is necessary in some investigations to undertake experimental work. Two main types of investigation are tests on failed equipment and experiments undertaken to test a hypothesis.

The damage survey in the field is often complemented by laboratory examination of failed equipment. Figure 27.1 illustrates the procedure used at the time for examination of equipment failure by the Safety in Mines Research Establishment (SMRE), an HSE 'in-house' facility. Some of the inspection techniques have been described in Chapter 19.

An account of the approach taken in experimentation done to test a hypothesis is given by A.R. Baker (1982). Simulation experiments are done for three basic purposes: (1) to confirm or demonstrate, (2) to identify a mechanism or (3) to determine an initial condition. Thus, an experiment may be carried out to confirm or demonstrate convincingly that a particular event or sequence of events could have occurred under appropriate conditions. The relevance of such work depends on the extent to which the conditions of the accident can be simulated. Failure to reproduce even one of these initial conditions to which the results are known, or expected, to be sensitive may vitiate the work. In other causes, the initial conditions and the results are known, but the mechanism is not understood. There may be several candidate mechanisms. In yet other cases, the aim is to determine the initial condition(s) that caused the event of interest. Where there is a sequence of events, it is often impractical, and unnecessary, to simulate the whole sequence; it may be sufficient to simulate just one of these events.

It is generally easier to show that something could happen than that it could not. For the former a single positive result suffices, whereas for the latter the experimental space to be explored may be very large.

In many cases, a small scale experiment is not adequate, but large scale experimentation may be problematic, and is often potentially hazardous. It is likely to be expensive and time-consuming.

Where experiments are carried out, it is good practice to make a full photographic record.

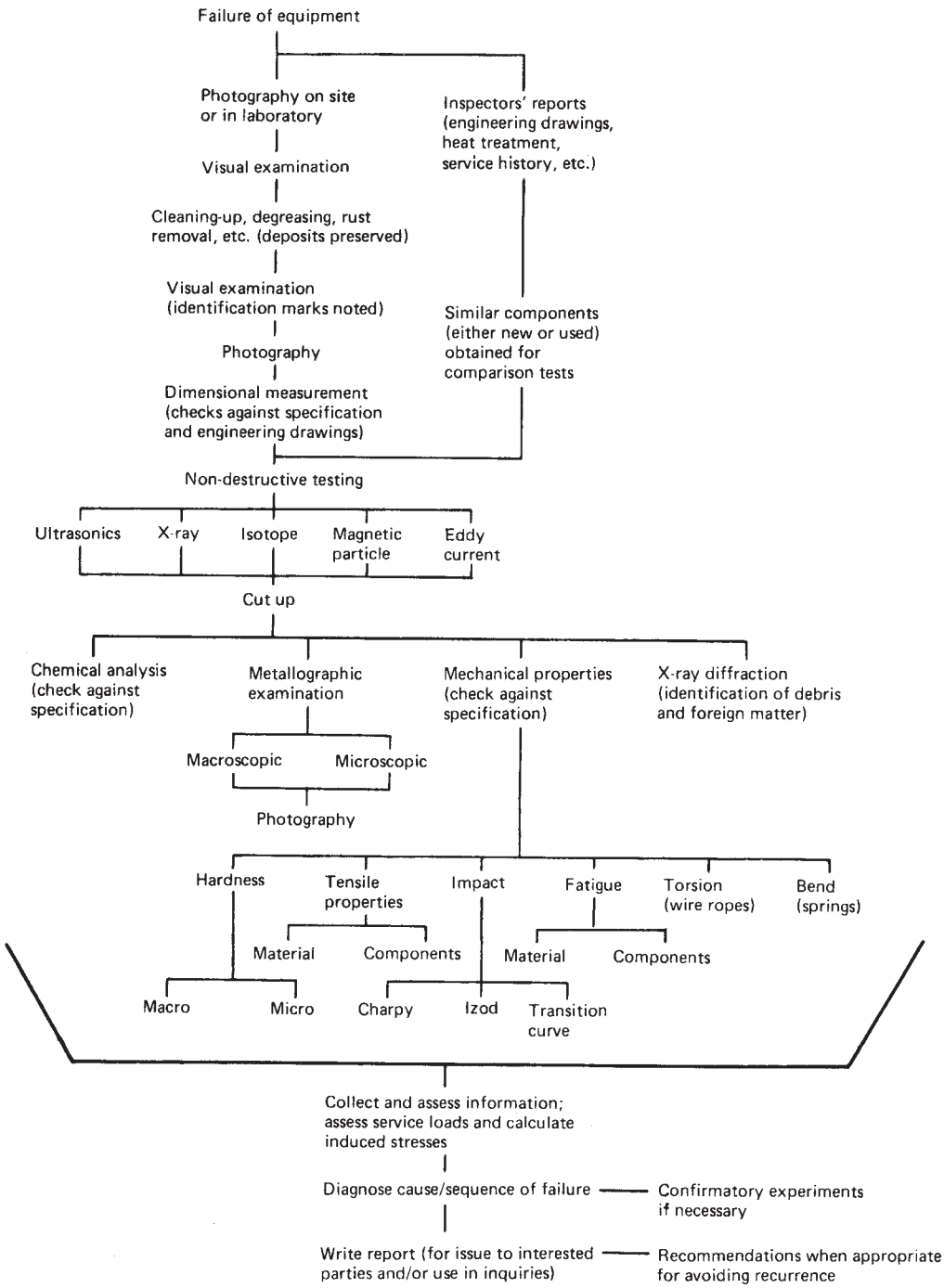

Figure 27.1 *Sequence of events in the examination of faulty equipment (Safety in Mines Research Establishment, 1971, Engineering and Metallurgy 4; reproduced by permission. The sequence may be modified and stages omitted according to the type of failure)*

Baker describes some seven different experimental investigations, including work on the bellows assembly at Flixborough and on a gas explosion in a building.

27.5.9 Some types of investigation

The account given so far has considered accident investigations conducted either in-house or by a consultant investigator. As mentioned earlier, accident investigations may also be carried out to check compliance with the law or to determine insurance liability. Where a crime is suspected, the police will be involved and may draw on resources such as those of the Home Office Forensic Science Laboratories. Where a violation of health and safety legislation is at issue, the HSE will be involved and may choose to conduct their own investigation, as described below. Where there is a question of the applicability of an insurance policy or the possibility of a transfer of liability to another party, one or more of the parties concerned may conduct their own investigations. It can occur, therefore, that there is more than one investigation of the accident going on at the same time.

27.5.10 Regulatory investigations

In the United Kingdom, a proportion of the more serious accidents are investigated by the HSE. It is the normal practice to publish the report. HSE reports in the *Investigation Report* series, listed in Appendix 28, include the following: *Explosion at Laporte Industries, Ilford, 5 April 1975* (HSE, 1976b), *Explosion at Appleby Frodingham Steelworks Scunthorpe, 4 November 1975* (HSE, 1976a), *Explosion at Dow Chemical Factory, King's Lynn, 27 June 1976* (HSE, 1977b), *Fire and Explosion at Braehead Container Depot, Renfrew, 4 January 1977* (HSE, 1979b), *Leakage of Propane at Whitefriars Glass Limited, Wealdstone, Middlesex, 20 November 1980* (HSE, 1981c), *Fire and Explosions at B&R Hauliers, Salford, 25 September 1982* (HSE, 1983b), *Abbeystead Explosion, 23 May 1984* (HSE, 1985a), *Summit Tunnel Fire* (HSE, 1985e), *The Fires and Explosion at BP Oil (Grangemouth) Refinery Ltd, 13 March, 22 March and 11 June 1987* (HSE, 1989a) and *The Peterborough Explosion of a Vehicle Carrying Explosives, 22 March 1989* (HSE, 1990b).

Likewise, in the United States of America if an accident is sufficiently serious, an investigation is conducted by the Occupational Safety and Health Administration (OSHA). The report *Phillips 66 Company Houston Chemical Complex Explosion and Fire* (OSHA, 1990a) is a case in point.

Investigations into transport accidents in the United States of America are conducted by the National Transportation Safety Board (NTSB). Some of their reports are listed in Appendix 28.

27.5.11 Public inquiry investigations

The *Flixborough Report* (R.J. Parker, 1975) together with its associated daily transcripts and the documents submitted to the inquiry remains perhaps the most comprehensive account of an accident investigation in the chemical industry. References to some of the large number of reports are given in Table A2.1. Accounts by individual investigators include those by Tucker (1975), J.I. Cox (1976b) and Gugan (1976). Further details of the Flixborough investigation are given in Appendix 2.

The *Piper Alpha Report* (Cullen, 1990), with its associated transcripts and the papers published subsequently, is another illustration of a major accident inquiry. References are given in Table A19.1. Accounts of individual investigators include those of Bakke (1989), R.A. Cox (1989a), M.E. Davies (1989), S.M. Richardson (1989) and Savffle (1989). Further details of the Piper Alpha investigation are given in Appendix 19 and an account of the inquiry is given in Section 27.9.

27.5.12 Illustrative examples

There are available in the literature a large number of reports and other accounts of accident investigations which serve as illustrative examples. At the top level there are the reports of public inquiries such as the *Flixborough Report* and the *Piper Alpha Report*. At the next level down are the accident investigation reports of the HSE and the NTSB, to which reference has just been made.

The work of Kletz gives a large number of accounts of accidents, each with an analysis that is an illustration of the principles of investigation that he advocates, together with explicit statements of those principles.

An account is now given of two further illustrative examples of the techniques of accident investigation.

27.5.13 Illustrative example: choked vent

An account of the investigation of accidents in process plants has been given by Houston (1971). This work was referred to earlier in Chapter 2. The approach taken is illustrated by an example that he gives of a hypothetical accident (see Figure 27.2):

> One end of a storage drum was blown out seriously injuring three men who were working nearby.
>
> The drum was used to store an organic liquid with a relatively high melting point. Steam tracing on the feed line was not very effective and chokes were common. Because of this it was customary to blow the line clear with air at 100 lbf/in^2 before and after each transfer.
>
> On this occasion the operator realized that the vent was not blowing and assumed that the line was blocked. In fact it was the vent that was blocked and when the pressure reached an estimated 30 lbf/in^2 one end of the vessel failed. Debris, particularly hot residual product from the last batch at 120°C, was blown some distance and three men who were working about 15 ft away were seriously injured.

The analysis of this accident using a model accident analysis form is shown in Table 27.2. The method has several important features. It does not report a principal cause, but

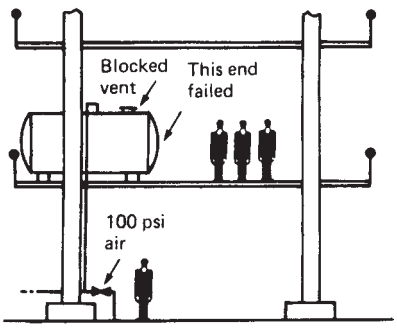

Figure 27.2 *Accident involving the failure of a storage vessel (Houston, 1971) (Courtesy of the Institution of Chemical Engineers)*

Table 27.2 *Model analysis of storage vessel accident (Houston, 1971) (Courtesy of the Institution of Chemical Engineers)*

	What was the immediate cause?	*What else made an accident possible?*	*What form of energy or poison was involved?*	*What was done to prevent an accident?*	*What was the point of no return?*	*What effect did the locality have?*	*What was done to reduce the severity?*	*Did the accident have any further repercussions?*
Please describe what happened	Turning on 100 $lb_f/in.^2$ air	Blocked 4 in. vent	40 m^3 of air at ~30 $lb_f/in.^2$ – the calculated bursting pressure	Nothing	When vessel shell failed	Product at 120°C sprayed on three maintenance men who were 15 ft away across platform	Injured given first aid in control room. Fire and ambulance services called. Area washed down	Loss of this vessel restricted plant output for 3 months at cost of £18,000
Why did it happen?	To prove feed line was clear before transfer (history of blockages)	Product (m.pt = 105°C) sprayed on cold vent by air blowing. Vent not normally inspected (poor access)	50–100 $lb_f/in.^2$ need to clear blocks ~30 $lb_f/in.^2$ could build up in tank in 5 min	Operator knew vent was not blowing but assumed line was at fault (no PI or bursting disc provided)	Excess pressure designed only for 15 $lb_f/in.^2$	Tank had residue of product after transfer. Men on routine maintenance job	A/F and crew heard bang and came running	Delay caused by tank cleaning due to more frequent grade changes on other storage tank
Has this or anything similar happened before?	Daily for 8 years; also done on discharge line	Nothing proven. A tank was sucked in due to vent restriction 2 years ago – suspect that was lesson not properly learned	See safety adviser's file on overpressure incidents	Instructions do not call for vent inspection as blockage not anticipated	See safety adviser's file on over-pressure incidents	Men must be in this area approximately 1% of time	–	No
What should be done to prevent a recurrence?	(1) Investigate use of internal steam tracing	(2) provide heated 8 in. vent on replacement tank (3) Arrange for registration and routine inspection of all critical vents	(4) Write up piece on vents in next safety bulletin and discuss with training manager	Bursting disc not needed if vent modified (5) Draft works standing order on use of 100 $lb_f/in.^2$ air, etc., for line clearing	–	(6) Consult Engineering Dept on known modes of failure on location of access ways	–	–

MAIN RESULTS
Men off 6, 9 and 30 days with burns

Vessel destroyed – replacement cost £15,000
Product lost – 5 ton valued at £1500

Contingent loss £18,000

FOLLOW-UP	*Recommendation*	*Action*	*Completion*
1	Plant Engr		
2	Plant Engr		
3	Asst Wks Mgr		
4	Safety Adviser		
5	Asst Wks Mgr		
6	Safety Adviser		

A/F, assistant foreman; PI, pressure indicator.

rather a chain of events that might be broken in several places. It identifies both the advance warnings and the preventive measures that might be utilized to prevent recurrence, and it yields recommendations that are capable of practical implementation.

27.5.14 Illustrative example: ethylene oxide plant explosion

An illustration of the investigation of a quite different kind of accident is that undertaken following the explosion at the ethylene oxide/glycol plant of BASF on 7 March 1989 at Antwerp (Anon., 1991 LPB 100, p. 1). The incident involved an explosion on a distillation column separating ethylene oxide (EO) and acetaldehyde. The investigation found that probably a small leak of EO had led to an accumulation of auto-oxidizable polyethylene glycols (PEGs) in the insulation of the column.

The account referenced describes the organization of task forces to (1) secure the damaged plant, (2) repair the equipment, (3) document the damage, (4) assemble information and (5) search for the cause.

A thorough review was made of the chemistry of the process and of the potential sources of ignition. The explosion event was reconstructed from an analysis of the damage, the examination of materials, the statements of eye-witnesses and the recorded information from nearby plants, and the probable chain of events leading up to the explosion reconstructed.

The location of the first explosion was identified as the acetaldehyde column K303 from the fact that a manhole cover from this column had left an imprint on nearby column K205. The damage to the trays of the column indicated that the explosion occurred in the lower part of the column, probably at the bottom.

Alternative sources of ignition included chemical reaction of the bottom products, static electricity and EO decomposition in an overheated pump, but these were eliminated. The only ignition source that could not be discounted was a fire within the insulation. It was confirmed that this was a feasible mechanism. EO itself is a low boiling liquid that does not generally accumulate on insulation, but it reacts with water to give PEG, a reaction which normally requires a temperature of 180°C but which was shown to proceed in direct contact with mineral wool at 100°C. The PEG is high boiling and can support self-heating of the insulation.

27.5.15 Disputed investigations

A large proportion of accidents are investigated by the fire services for the purpose of records and statistics, and the investigation is relatively short. Even where it is rather fuller, time and resource constraints still apply.

In some cases, a later investigator comes to a different conclusion as to the technical causes. Three such cases are given by Ursenbach (1980, 1983). In the first, the ignition of a vapour cloud from a plant leak was ascribed to a non-explosion-proof electric cart, but subsequent modelling of the vapour dispersion showed that a flammable mixture could not have reached the vehicle. In the second, an explosion was attributed to a defective acetylene cylinder, but a later study of marks on the cylinder indicated that the damage to it had been caused by compression of an oxygen cylinder onto it by the collapsing roof. In the third case, it was reported that the damage was due to an explosion of solvents evaporating from a massive ink spill caused by the failure of a ball mill at ground level, but a further investigation found that other explosions had occurred on upper floors which could not have been due to the heavier-than-air vapour on the ground floor.

27.6 Fire Investigation

Accounts of the investigation of fire are given in *Fire and Arson Investigation* (J. Kennedy, 1962) and *Fire Investigation* (Dennett, 1980) and by Burgoyne (1981/82, 1982) and Craven (1982).

The overall conduct of an investigation has been described above. The general account given of the preliminary site visit, the examination of damage, the interviewing of witnesses, etc., is applicable, but in addition there are a number of considerations which apply specifically to fire investigation.

The preliminary site visit serves to identify the area of origin of the fire. Further work is aimed at establishing the material first ignited, the source of ignition and the general features and pattern of the fire and thus identifying the cause.

27.6.1 Fuel involved in fire

Some pointers to identifying the fuels involved in a fire or explosion are given by C.H.H. Willis (1981).

27.6.2 Temperature attained by fire

The temperature of a process plant fire does not normally rise much beyond 1000°C. This is so whether the material undergoing combustion is a flammable liquid or a solid material such as wood, plastic or paper. On the other hand, it is usually sufficient to cause significant deterioration of steelwork, which occurs in the range 550–600°C. Jet flames can give rise to temperatures appreciably higher than 1000°C.

Some indicators of the behaviour of the fire are charring of wood, melting of metals, damage to vessels and damage to structural steelwork. Charring of wood can be expected to be deepest where the fire has burned longest. Most types of wood are charred to a depth of about 2.5 cm within 40 min, whatever the fire, as long as the flame is the diffusion flame normal in a fire.

Copper has a melting point of 1080°C and usually does not melt but its alloys brass and bronze do; their melting points being in the range 800–1000°C. So does aluminium with a melting point of 650°C.

The paint on a vessel containing liquid may be blistered above the line of the liquid level but not below. If the original liquid level is known, this can be used in conjunction with an assumed heat input rate to estimate the duration of the fire. Craven suggests values for the heat input rate of 110 kW/m^2 typical and 170 kW/m^2 maximum, in the absence of a jet flame.

The temperature at which structural steelwork distorts is attained in most process plant fires, and the damage can be spectacular, but generally it is not a very helpful indicator.

Fire temperature indicators are also described by Guenther *et al.* (1976), Guenther, Goodwin and Brininger (1978) and McIntyre (1981). The latter gives an account of the use of common materials as temperature indicators. He divides such indicators into two classes: time independent and time dependent. Some indicators which are essentially independent of, or only weakly dependent on, time are the

melting of metals, the charring of wood, the high temperature scaling of steel and the recrystallization of copper. He gives a list of some 25 temperature indicators which may be observed by one of three methods: visual examination, hardness testing or metallographic examination.

27.6.3 Electrical short circuits

Fires of electrical origin are of considerable interest to fire investigators. A relevant code is NFPA 907M.

Accounts of the treatment electrical short circuits in fire investigations are given by Levinson (1977), Ettling (1978), Beland (1981, 1982), Delplace and Vos (1983) and D.A. Gray, Drysdale and Lewis (1983).

An electrical short circuit is a potential source of ignition. It is accompanied by an electric arc. Such an arc causes damage to the electric wiring and leaves a visible mark. The problem is to determine whether in a given case the short circuit is a cause or an effect of the fire.

The differentiation of cause from effect is addressed by Delplace and Vos (1983) and experimental work to this end is described by D.A. Gray, Drysdale and Lewis (1983). Delplace and Vos also state that there is a close parallel between the pattern left by a fire and the location of the short circuits and that this can be exploited in fire investigation.

27.7 Explosion Investigation

Accounts of the investigation of explosions are given in *Unconfined Vapour Cloud Explosions* (Gugan, 1979), *Explosion Investigation* (Yallop, 1980) and *Investigation and Control of Gas Explosions in Buildings and Heating Plant* (R.J. Harris, 1983) and by V.J. Clancey (1972b, 1981), W.E. Baker (1982) and Craven (1982).

27.7.1 Types of explosion

There are a number of different types of explosion on process plant which the investigator may need to consider. They include:

(1) condensed phase explosion;
(2) physical explosion –
    (a) hydraulic,
    (b) pneumatic;
(3) confined gas explosion;
(4) vapour cloud explosion;
(5) boiling liquid expanding vapour explosion;
(6) dust explosion;

It may also be necessary to distinguish between deflagration and detonation.

Explosions may occur with buildings; gas explosions in buildings are of particular importance.

27.7.2 Condensed phase explosions

Explosions of a condensed phase explosive such as TNT are of less interest for process plant than are some of the other types, but on the other hand the methods of investigation are well established and accounts more comprehensive, so that it is convenient to start with them. Accounts include *Explosion Investigation* (Yallop, 1980) and that by V.J. Clancey (1972b). The effects of condensed phase explosions, which are well documented, are described in Chapter 17 and the information given there may be used for diagnostic purposes.

The text by Yallop covers (1) explosion accidents and the explosion investigator, (2) fundamentals of explosives, (3) the approach to the scene, (4) the observation and assessment of damage, (5) identification of the explosive, (6) causes of initiation, (7) explosions in moving vehicles, (8) injury to persons, (9) examination of suspects, (10) analysis of witness statements, (11) unlikely occurrences, (12) negative evidence and (13) drawing the conclusions.

Yallop's treatment of the observation and assessment of damage covers (1) the importance of damage, (2) the type of explosive and explosion damage, (3) the value to be attached to damage observations, (4) the importance of the site of the explosion centre, (5) the determination of the site of the explosion centre, (6) the significance of pressure, (7) the application of pressure observations, (8) the phenomenon of fragmentation, (9) information from fragments, (10) craters and (11) ground shock. Some of the relationships given by Yallop, and also by Clancey, are among those used in Chapter 17, which also draw on his accounts of explosives and of their initiation.

Observable damage falls into three categories: (1) permanent distortion of objects, (2) displacement of objects and (3) flame and heat effects. Permanent distortion may itself be subdivided into (1) plastic deformation, (2) fracture and (3) fragment attack. In general, permanently distorted objects are generally quite reliable indicators, whereas displaced objects are much less dependable.

Modes of plastic deformation considered include: (1) bending of long metal objects such as structural members, rails, window frames, pipes, and nails, screws and bolts; (2) dishing of metal plates, including tanks; and (3) movement of piles of particulate matter. The author states, however, that observations cannot be made on a container that is full of liquid, which inhibits distortion. Fracture may be observed of the structural elements of buildings, the contents of buildings, and objects outdoors. Fragment attack take the form of surface attack, giving dents or small craters, or penetrative attack. The latter can be useful in locating the explosion centre by projecting back the lines of the penetration holes.

Flame and heat effects are melting and decomposition. The contact between the hot gas of the blast wave and surrounding objects is generally too short for much heat transfer to occur, but metal surfaces close to the explosion centre can exhibit 'gas wash', which is characterized by partial melting of the surface layers, giving a ripple effect. In some cases, heat transfer is sufficient to cause decomposition, such as the charring of organic materials or the discoloration of painted surfaces.

This information may be used to prepare a direction/damage diagram. Yallop describes a diagram made for the gas explosion in the flats at Ronan Point in 1968 with a detailed explanation of some 19 items.

The author gives a detailed account of the determination of overpressures from plastic deformation and from fractures. These may be used to determine the charge weight of the explosive using the usual scaling laws.

It is a basic principle of explosion investigation to recover as many primary fragments as possible. Fragments can give information on the nature of the exploding object and on the site of the explosion, and possibly the charge weight.

A further account is given by W.E. Baker (1982). He advises for the determination of explosion yield the use of the pressure-impulse method. He draws attention to the need to allow in the far field for meteorological effects due to possible focusing of inversions and wind shear.

27.7.3 Physical explosions

Physical explosions are often the result of overpressurization during a fire. Depending on whether the vessel is full of liquid or not, the explosion may be hydraulic or pneumatic. The mode of failure is determined by the weakest feature of the containment. A pneumatic explosion is the more violent and gives rise to a large number of missiles.

The estimation of the energy released in, and of the effects of, a physical explosion are described in Chapter 17.

27.7.4 Confined gas explosions

The behaviour of an explosion of gas confined within a plant depends on the nature of the space concerned. With a single volume such as a vessel the explosion can be expected to be a deflagration with a stress essentially uniform over the containment. With a multi-compartment volume there is scope for run-up to higher flame speed and for pressure piling. Damage is likely to be at a maximum at the point most remote from the source of ignition. With a pipeline the flame speed may accelerate to give a detonation.

Slow deflagration of a gas mixture tends to give a pure ductile failure at a pressure corresponding to the static strength of the container. The bursting of a cylindrical container in such a deflagration is usually taken to occur when the pressure causes the stress to exceed the hoop stress.

Where the flame speed in a gas mixture runs up to detonation, which can occur in a vessel of high aspect ratio or a pipeline, bursting may occur at a higher pressure than that for static loading. The bursting of a cylindrical containment in a detonation may be taken to occur at a pressure corresponding to a stress that is about twice the hoop stress.

Detonation in a pipeline gives rise to a characteristic longitudinal tear, or ribbon. This may be repeated at points along the pipeline where the explosion is relieved and then starts again the run-up to detonation.

Interpretation is complicated by the fact that a ductile failure due to a slow deflagration can create a tear that accelerates into a brittle fracture. Conversely, detonation does not necessarily cause brittle fracture.

The investigator usually seeks to determine the point of initiation of the failure. Where the failure is ductile, the point of initiation tends to correspond to that of maximum thinning. Where the failure is brittle, there tend to be characteristic chevron marks on the tear that point back to the point of initiation.

With regard to source of ignition, little can be deduced from the pattern of bursting of a single vessel, but for a multi-compartment configuration the maximum damage tends to occur remote from the source of ignition.

27.7.5 Failure analysis

Failure analysis seeks to determine the details of the failure of the containment and generally involves the collection of the fragments generated by the explosion within it. An account is given by Craven, who describes the piecing together of the fragments to reconstruct the original containment and to take measurements of the thickness.

Another account of failure analysis is that of Beyers (1980), who describes the investigation of a massive explosion at a group of spherical and cylindrical storage vessels. Utilizing information on the necking of the vessels, crack propagation and fracture mechanics, it was possible to determine the order of failure of the vessels and to establish that failure had occurred because both a level measuring device and a safety relief valve had failed, so that pumping was allowed to continue when the vessel was full and the resultant overpressure was not relieved by the safety relief valve.

27.7.6 Vapour cloud explosions

The main effect of a vapour cloud explosion that is used for diagnostics is the blast. Vapour cloud explosions tend not to give a crater and the missiles from such explosions usually yield less information than do those from confined explosions.

The characteristics of a vapour cloud explosion are described in Chapter 17. They are generally less well defined than those of a condensed phase explosion and consequently more uncertain in their application for diagnostic purposes.

A detailed survey of the damage done by the blast from the vapour cloud explosion at Flixborough has been described by Gugan (1979), who also gives an account of the interpretation of this damage to estimate the yield of the explosion. Features considered include the crushing of vessels and the bending of lampposts.

27.7.7 BLEVEs

A boiling liquid expanding vapour explosion (BLEVE) is another type of explosion which occurs in accidents in the process industries. A BLEVE tends to generate a number of fragments, but the overpressure of the blast wave is slight. There is usually relatively little difficulty in establishing that a container has undergone a BLEVE.

27.7.8 Ignition sources

It is usually more difficult to identify the source of ignition for a vapour cloud than for solid materials and in many cases of vapour cloud explosion no ignition source is identified.

27.7.9 Injury to humans

Injury to humans, whether deceased or surviving, is another potential source of information. The information that may be obtained from this source is considered by Yallop. A treatment of injury from different explosion effects is given in Chapter 17.

27.7.10 Gas explosions in buildings

An account of the investigation of gas explosions in buildings with particular reference to natural gas has been given in *Investigation and Control of Gas Explosions in Buildings and Heating Plant* (R.J. Harris, 1983). Some treatment of the topic is also given by Yallop. The account by Harris is concerned particularly with explosions following leaks of natural gas in consumers' premises.

Investigation of a gas explosion in a building proceeds by trying to establish (1) the nature of the explosion and, assuming it is a gas explosion, (2) the type of gas, (3) the source of gas, (4) the quantity, concentration and distribution of the gas, (5) the ignition source, and frequently, (6) the pressure generated and the distribution of pressure damage.

The investigation may start by determining whether the damage has been caused by fire or explosion. Here a useful indicator is damage to windows that may have been caused by pressure or by heat. The pattern of failure of a glass window under pressure is quite different from that of failure due to heat. Pressure failure gives a large number of

fragments with visible stress marks, whilst failure by heat gives fewer fragments and no stress marks. Pressure failure causes fragments to travel further and they could be found at distances of over 5 m from the window.

An explosion due to gas may be distinguished from that of a bomb by the fact that the former gives a slow pressure rise and causes damage that is omni-directional, whereas the latter gives a fast pressure and damage is greatest at the location of the bomb.

With regard to the type of gas, the principal clue is whether the gas is lighter or heavier than air, which may often be determined from a 'tide mark' of scorching.

The search for the source of gas depends on the building and the potential gas sources in it.

The quantity of gas may be estimated from the damage done both within the building and outside. Again, the behaviour of the windows provides important information. The pressure inside the building may be estimated from that required to break the windows and from the distance travelled by the fragments. The correlations used are those of M.R. Marshall, Harris and Moppett (1977) given in Chapter 17. The other indicator is damage to windows of other buildings. Here use is made of the relation for the pressure outside a vented enclosure, which decays according to a modified inverse square law, as given in Chapter 17. The pressure on these outside windows is assumed to be the reflected pressure at normal incidence, or twice the incident pressure.

The author enumerates some of the ignition sources found in consumers' premises, but states that often the ignition source is not found.

27.8 Accident Investigation: CCPS *Guidelines*

Guidance on incident investigation is given in *Guidelines for Investigating Chemical Process Incidents* (CCPS, 1992/10) (the CCPS *Incident Investigation Guidelines*).

The *Guidelines* are concerned with process safety incident investigation (PSII). They cover (1) introduction, (2) basic incident investigation techniques, (3) investigating process safety incidents, (4) practical investigation considerations (gathering evidence), (5) multiple cause determination, (6) recommendations and follow-through, (7) formal reports and communications issues and (8) development and implementation. They contain a number of appendices, including: a review of major accidents such as Bhopal, Mexico City, Piper Alpha and Pasadena; examples of the causal tree method (CTM) and multiple-cause, systems orientated incident investigation (MCSOII) method; an example incident investigation; and examples of root cause analysis.

27.8.1 Types of investigation

The CCPS *Guidelines* distinguish between three types of investigation:

Type 1	Traditional, informal investigation carried on by immediate supervisor.
Type 2	Committee-based investigation using expert judgement to find a credible solution of cause and remedy.
Type 3	Multiple-cause, systems-oriented investigation that focuses on root cause determination, integrated with an overall process safety management (PSM) programme.

The Type 3 investigation is the preferred method.

27.8.2 Investigation management system

The *Guidelines* advocate that the company should have in place a management system for PSII. They describe the elements of this system, including the systems for incident reporting, incident classification, activating an investigation, selecting and training the investigation team, documenting the inquiry, disseminating its findings and following through its recommendations.

It is desirable that the approach to PSII be one that chimes with the methods of process safety review already in use for plant design and operation. This is met by the multiple cause analysis, or Type 3, approach, utilizing logic tree and related techniques.

The *Guidelines* give a detailed account of the measures necessary to set up a PSII management system, including the training requirements.

27.8.3 Investigation techniques

The *Guidelines* review some 18 investigation techniques which include: (1) fault tree analysis (FTA); (2) the CTM taken up by Rhone-Poulenc (Leplat, 1978a; Boissieras, 1983); (3) the MORT method of W.G. Johnson (1980); (4) the MCSOII developed by Rohm and Haas (Dowell, 1990; S.E. Anderson and Skloss, 1991); (5) the Accident Anatomy Method (AAM) developed at the Riso National Laboratory (Bruun, Taylor and Rasmussen, 1979); (6) Action Error Analysis (AEA) described by J.R. Taylor (1979); (7) the Cause-Effect Logic Diagram (CELD), developed by the Electrical Power Research Institute (EPRI) (Mosleh *et al.*, 1988) among others; (8) hazard and operability (hazop) analysis; (9) the Accident Evolution and Barrier (AEB) technique in development at the Swedish Nuclear Power Inspectorate (Svenson, 1991a); (10) Work Safety Analysis (WSA) developed at the Technical Research Centre in Finland (VTT) (Suokas, 1981; Soukas and Rouhiainen, 1984); (11) Human Reliability Analysis (HRA) developed at Sandia National Laboratories (B.J. Bell and Swain, 1983; Swain and Guttman, 1983); (12) Multi-linear Events Sequencing (MES) developed by the NTSB (Benner, 1975); (13) the STEP procedure described by Hendrick and Benner (1987); and the Systematic Cause Analysis Technique (SCAT) developed by the International Loss Control Institute (ILCI) (1990).

Of these methods hazop, FTA, MORT, and AEA have been described in Chapters 2, 8 and 9, HRA in Chapter 14 and STEP in Section 27.4. CTM essentially utilizes a stripped-down fault tree that is applicable to the particular accident and contains only AND gates. MCSOII is also a fault tree adaptation in which the events at the level just below the top event are the presence of the injurious factor, the presence of the target and a contact duration sufficient to cause harm. AAM utilizes a tree that, like the one in MORT, is generic, but which resembles a cause–consequence diagram and which is then developed to represent the features of the particular accident. AEB describes the incident in terms of a series of events in two parallel systems, the human and the technical, and of barrier functions that should prevent escalation. WSA utilizes a proforma in which are analysed the work step, hazard, causative factors, priority ranking and corrective actions. MES charts the events in a time sequence and is a forerunner of STEP. SCAT treats the incident as a domino effect and involves describing successively the loss, the contact between the injurious factor and the target, the immediate causes, the basic causes and the failure of control.

The *Guidelines* also describe other aids such as the fact—hypothesis matrix and simulation/recreation.

27.8.4 Multiple root cause analysis

Two strong themes in the *Guidelines* are that accidents have multiple causes and that the investigation should delve down to the root causes. The preferred approach is termed 'multiple cause analysis', but might equally well be called 'multiple root cause analysis'. The account given of the conduct of such an analysis relies heavily on the use of logic trees.

The *Guidelines* illustrate the application of this approach to major accidents such as Flixborough, Challenger and Piper Alpha, as well other incidents involving fire/explosion, compressor failure and vehicle collision.

27.8.5 Recommendations, reports and follow-up

The *Guidelines* discuss the recommendations of the investigation, dealing with the distinction between findings and recommendations, the correspondence between root causes and recommendations, the attributes of good recommendations, the layers of recommendations, the types of recommendation, the process of feedback on draft recommendations, the documentation of the recommendations, the recommendations on restart of plant, the documentation of the recommendations and the follow-through of the recommendations. They also treat the reporting of the incident from the initial verbal report through the interim report to the final report. The approach taken to these topics is broadly in line with that described in Section 27.5.

27.9 Public Accident Inquiries

In the United Kingdom, certain accidents are investigated by official bodies. The system varies with the industry, but in the case of a major disaster there is likely to be some form of public inquiry.

Reports of such accident inquiries include *The Flixborough Disaster* (R.J. Parker, 1975), *The Windscale Inquiry* (R.J. Parker, 1978), *MV Herald of Free Enterprise. Report of Court* (Sheen, W87), *Investigation into the King's Cross Underground Fire* (Fennell, 1988), *Investigation into the Clapham Railway Accident* (Hidden, 1989) and *The Public Inquiry into the Piper Alpha Disaster* (Cullen, 1990). The two major disasters in the process industries which in recent years have been the subject of a public inquiry are thus Flixborough in 1974 and Piper Alpha in 1988.

In the process industries, a proportion of accidents are investigated by the HSE. Until the mid-1970s the reports of these investigations were not generally published as such, although reference was often made to them in the annual report of Chief Inspector of Factories. Following the Flixborough inquiry in 1974, the HSE have conducted a number of major accident investigations and have published their reports, as described in Section 27.5. Thus, the number of public inquiries is very small and even quite major accidents are now mainly dealt with by an HSE investigation and report.

27.9.1 Procedure at public accident inquiries

A public accident inquiry is appointed by the government minister responsible and is presided over by a judge. There is some variability in the precise form taken, but the broad pattern is that the evidence is brought forward by the counsel to the Crown who is assisted by consultants to the inquiry. The judge himself is assisted by two or three technical assessors. The terms of reference are usually to establish the cause and to make recommendations for the prevention of any recurrence.

The judge receives requests from parties who wish to be represented and then gives a ruling on who the parties are to be. Typical parties might be the operator, other industrial companies, government bodies, trades unions and representatives of survivors and relatives. Each party is represented by a barrister, typically a Queen's Counsel (QC), who is supported by a solicitor and usually by experts.

Witnesses are brought forward by Crown counsel and by other parties and can be cross-examined by the parties. In this sense, the procedure resembles the adversarial process in the law courts.

27.9.2 Critique of public accident inquiries

The Flixborough inquiry (R.J. Parker, 1975) found that the disaster was due to a large release of hot, flashing cyclohexane from a 20 in. pipe, which gave rise to a massive vapour cloud explosion. This pipe was an inadequately supported bypass assembly consisting of a dog-leg pipe between two expansion bellows. The inquiry also found that this release was caused by pressure and temperature conditions in the pipe itself more severe than those that had previously prevailed. An alternative theory was put to the inquiry by Gugan and Cox that the assembly failed following prior rupture of a nearby 8 in. line, but the inquiry rejected it. A third theory was advanced at the time by R. King (1975a) that the cause was superheating of water in the reactor upstream of the pipe, but the inquiry did not pursue this hypothesis. The inquiry left proponents of these last two hypotheses dissatisfied with the way in which the technical evidence had been handled, and this gave rise to some debate in the engineering press at the time.

In consequence a view emerged and gained some support in the engineering profession that a public inquiry, with its adversarial legal process, is not the best forum in which to arrive at the truth about engineering matters. This view was urged after the Flixborough inquiry by Mecklenburgh (1977) and has been argued again with reference to the same inquiry by R. King (1990).

The critique given by King is broadly as follows. Many of the legal representatives at the inquiry are retained by interested parties. The presumption must be that the latter are concerned to protect their interests. A party may have an interest in ruling out a given cause and/or establishing another one. This situation is liable to lead to the investigation of improbable theories urged by particular parties at the expense of more probable explanations and thus to an imbalance in the investigation. Some persons whose impartial expertise would be valuable may not be called to give evidence because they are prevented by their employers or counsel or by the inquiry procedures. The inquiry itself is not accountable and there is no means of reopening it if its conclusions are subsequently found to be incomplete or incorrect.

The alternative model for technical investigation urged by Mecklenburgh draws on the procedure used in civil aviation. Aircraft accidents are investigated by the Accident Investigation Branch (AIB) of the Department of Trade. The AIB is directly responsible to the minister and is not part of the CAA. The Chief Inspector of Accidents presents a report directly to the minister. The investigations of the AIB are inquisitorial not adversarial. The inspectors

have considerable powers to obtain evidence and inspect wreckage. Provision is made for persons whose reputation may be affected, such as the pilot, to make representations before the report is submitted.

The Flixborough inquiry handled the investigation of certain technical aspects by using a management committee that organized meetings of technical experts. This work went on in parallel with the main inquiry. Mecklenburgh argues that it would have been both practical and preferable for the technical investigation to have been completed before the public inquiry proper. This technical investigation would have dealt with the theories concerning the cause of the rupture of the 20 in. pipe. Mecklenburgh recognizes that there are usually human and management reasons for an accident. These he considers proper subjects for a public inquiry. He does not suggest that the latter be dispensed with but only that it should start only after the technical investigation has been completed. He, therefore, proposes that it should be required by regulation that the public inquiry be preceded by a technical investigation conducted by a specialist unit within the HSE. The technical inquiry could, of course, be dispensed with if the technical reasons for the accident are clear. This would leave the inquiry free to concentrate on the human and management aspects.

On the other hand, several engineers who have been involved as technical assessors on public inquiries have spoken in their favour. Davidson (1984), who was an assessor on the Flixborough inquiry, states:

> I do not share the view, expressed widely, that an engineer or a scientist, or a committee of them, would form a more effective Court of Inquiry than the existing type. As part of the Flixborough Inquiry there was a management committee to oversee tests and discuss the scientific side of the Inquiry. Representatives of the major parties were included. This committee was useful but very difficult to manage: everyone had preconceived ideas as to tests and how they should be run. There was not the well-established framework of rules evolved by lawyers over the centuries for orderly cross-examination. Of course some accident inquiries – e.g. for railways, mines and aircraft – are run by engineers or scientists. But such investigations have quasi-legal powers: the chairmen have by long experience become engineer/judges and conduct their inquiries much like a court of law. On balance I was impressed by the procedure at the Flixborough Inquiry and felt that an inquiry is best run by lawyers.

Support for the present system is also expressed by Crossland (1991), an assessor on the King's Cross inquiry.

27.9.3 Piper Alpha inquiry

The nature of a public inquiry into a major disaster may be illustrated by considering the Piper Alpha inquiry (Cullen, 1990). This was a large inquiry, as shown by some of the statistics. The inquiry sat for 180 days extending over 13 months. It heard evidence from 260 witnesses and had some 842 documents before it.

Piper Alpha involved a release of flammable gas, which ignited and exploded, and initiated a long and complex chain of escalation. The resultant emergency had many facets, including the assembly in the accommodation module and the escape and rescue. It was therefore a very different type of accident from Flixborough.

The assessors to the inquiry were an experienced oil man who had just retired as managing director of a large oil company, the production director of a large petrochemical company, and an academic specializing in SLP but with 13 years industrial experience. The team was thus well balanced, containing two industrialists and one academic or, viewed from another angle, one from the oil industry and two from outside it.

The inquiry was in two parts. Part 1 dealt with the accident itself, its causes, its escalation and the emergency to which it gave rise, whilst Part 2 dealt with the deeper causes. Prior to Part 1, the judge announced that the inquiry would be considering in Part 2 the following subjects with a view to making recommendations: (1) the location and protection of accommodation, (2) the means of mitigating the effects of explosions, (3) the means of ensuring the integrity of emergency systems, and (4) the means of ensuring full and safe evacuation. As the evidence in Part 1 unfolded, he added (5) permits-to-work, (6) control of the process, (7) risk assessment and (8) the offshore safety regime.

The assembly of the evidence was a major logistical exercise. The inquiry was seeking to determine the cause of an explosion that could have come from a leak through a hole of no more than a few square millimetres. But with most of the platform at the bottom of the sea, it was necessary to decide whether to recover the process equipment; the inquiry decided against doing this. The main accommodation module had, however, been lifted from the seabed. A major, and almost archaeological, exercise took place to recover the documents in this module. The documents believed to be relevant to the inquiry were specified and assembled by the consultants to the inquiry who created a library available to the parties.

The interviewing of the witnesses and the preparation of witness statements was another major activity. Evidence was given to the inquiry by 58 of the 61 survivors, and the other three gave written statements. The inquiry also heard from 38 witnesses to the emergency, 5 eye-witnesses who observed and photographed events, 8 persons from other nearby installations, 32 current and former employees of the operating company on a variety of technical and management matters, 14 current and former employees of other companies, 35 expert witnesses and 6 witnesses on behalf of regulatory and other bodies.

The evidence given in Part 1 by the witnesses not called as experts covered a range of topics: the practices of the company; the activities on the platform in the preceding days; the activities and events immediately prior to the explosion; the explosion itself and its effects; the escalation of the events from the initial explosion to the abandonment of the platform; the behaviour of the communications systems and of the emergency systems for shut-down and fire fighting; the development of and response to the emergency on the platform; the escape from the platform; the response of the fire fighting vessel *Tharos* which was near the platform at that time; the response of personnel on the nearby, linked platforms; and the rescue. In many cases, a single witness had significant evidence on a number of these topics.

The interim report by the Department of Energy indicated two principal hypotheses for the leak of hydrocarbons. One was that a leak occurred from the end of a relief line on a condensate pump where a pressure relief valve had been removed, because the blind flange at that point was not leak-tight or was missing altogether.

The other was that liquid condensate had backed up into a reciprocating compressor and caused damage and a leak.

The inquiry began to hear expert evidence at a quite early stage, interleaved with evidence from the expert witnesses. This covered, among other things, the interpretation of eye-witness evidence on the site, fuel, nature and strength of the initial explosion; the damage to and behaviour of the emergency power and shut-down systems; the gas cloud which formed in the module; the pressures generated by and general behaviour of this gas cloud; the damage to the walls of the module; the missile effects from the explosion; the pressures and flows in the gas and oil pipelines into and out of the Piper platform; the behaviour of hydrates, with special reference to the conditions on the platform; and various aspects concerning the relief line on the condensate pumps.

As an illustration of the mix of witnesses, the first eight called were: (1) a diver (survivor), (2) a detective inspector, (3) a former deputy offshore installation manager, (4) a manager at Lloyds Register, (5) a lead maintenance technician, (6) an expert on explosion modelling, (7) an expert on gas detectors and (8) an electrician (survivor).

In public inquiries, generally, the chairman is able to exercise control and ensure balance by indicating those topics in which the inquiry is interested and those in which it is not. A degree of latitude may be allowed to parties to explore particular issues. In making these decisions the chairman is advised by the assessors. At the end of the day, the final report is that of the judge alone. Nevertheless, it is the assessors' responsibility to advise him on the technical issues. In this sense, an assessor has ownership of the problem. This concentrates the mind and is a strong incentive to try to make sure that evidence is as balanced and complete as possible and that the arguments are in place to support both the positive and negative conclusions. It can occur that different hypotheses for the cause are entertained until a quite late stage or that some hypotheses are discarded but fresh ones are taken on board.

Firm control was exercised in the Piper Alpha inquiry. The inquiry does not appear to have been seriously criticized either for omitting matters which ought to have been considered or for examining particular matters, and especially matters raised by interested parties, to the point of imbalance. The report shows that there was an examination of a wide range of hypothetical leak scenarios, many prompted by non-expert witness evidence, and that several fresh scenarios were given consideration, notably one in which the leak was the result of a chain of events initiated by hydrate blockage and another in which pipework suffered overpressure from a methanol injection pump. But there is little evidence of the pursuit of issues arising from special pleading by parties.

The inquiry did make use of the system of meetings of technical experts, but only on two occasions. Each was chaired by an assessor. The topics at the two meetings were flows in certain pipelines and the scenario of condensate entry into a reciprocating compressor. The purpose of the meetings was to define the areas of agreement and disagreement. In both cases, there were technical reports to consider but the meeting did not deal with experimental work. At the second of these meetings, the experts reached the agreement that the scenario involving ingestion of liquid condensate into a reciprocating compressor could be ruled out. This conclusion was given in evidence to the inquiry and its report accepts this view.

A considerable amount of experimental work was presented in evidence. The inquiry heard about work commissioned by the operating company on the nature and strength of the initial explosion, which included explosion simulation, on the explosion damage to the fire walls, on missiles from these walls, on the failure of the Tartan gas riser and on the leak potential of various configurations of blind flange and on further explosion simulation work done for the Department of Energy. The inquiry itself commissioned wind tunnel tests to determine the gas cloud which might be expected to form given various leak scenarios and the consistency of this with the gas detector evidence. It also commissioned a single explosion simulation for a scenario of a leak at the pressure relief valve site, due either to a non-leak tight blind flange or to a hydrate-initiated event.

The *Piper Alpha Report* concluded that, on balance of probability, the leak occurred from the site of the missing pressure relief valve where the blind flange was not leak-tight. An explanation of this scenario was given which showed that it was possible to tie up quantitatively the leak rate from a non-leak-tight blind flange, the gas detector and wind tunnel evidence of a main leak preceded by a small leak, the size of the flammable gas cloud, the overpressure generated by explosion of that cloud, the damage done by the explosion and the effects experienced in the control room from that explosion.

Among the recommendations made in the report were a change in the regulatory authority and a requirement for submission of a safety case, with a safety management system and quantitative risk assessment.

27.9.4 Role of public accident inquiries

The account given above makes clear that most accidents are in fact investigated outside the forum of a public inquiry. The HSE investigations appear in large part to accord with the intention of the system proposed by Mecklenburgh. The residual issue, therefore, concerns those process industry disasters that are on a scale sufficient to attract a public inquiry. Such disasters are rare events. They are likely to differ greatly one from another and the public inquiries held into them may, and probably should, differ also.

The experience of the Piper Alpha inquiry is instructive. The most striking thing is that the technical issues and the human and managerial issues were interwoven in several ways. In many cases, a witness had evidence to give on both aspects. Witness evidence led to the consideration of fresh leak scenarios. A given scenario often involved both technical and human and managerial aspects.

Timing is another important feature. Time is required to decide on, schedule and obtain the evidence, both in documents and from witnesses, and to allow the experts to prepare their evidence, which often constitutes a mini-research project and may involve physical or computer simulation. The chairman and the assessors need time to digest the evidence and come to a settled view. The interweaving of the technical with the other evidence provides this time.

A third feature is the authority of a public inquiry. The inquiry can require the company involved to furnish documentation that may bear on the accident. The documents may be large in number, some may be hard to locate and some may be sensitive. It can require the attendance of witnesses. Once at the inquiry these witnesses are on oath. Most have probably never been in a court of law, let alone a major accident inquiry.

This authority also allows the inquiry to exercise control to try to ensure that the treatment is as balanced and complete as possible. This control is needed in respect both of interested parties and of technical experts.

Another aspect of authority relates to the fate of its report. Acceptance of the findings of the cause and of the recommendations to prevent recurrence depends in large part on the perception of the inquiry by government, the industry and the public. A public inquiry is better positioned to establish its authority than a technical investigation. This is doubly necessary where an inquiry recommends major changes in the regulatory regime or in the industry.

These considerations suggest that proposals for some form of separate technical investigation are unlikely to improve on the current form of public inquiry. What may be beneficial, however, is to recognize that there is considerable variability in the accidents which occur and that the public inquiry procedure needs to be flexible enough in its way of working to accommodate this variability.

27.10 Organizational Memory

Experience shows that the investigation of accidents is not in itself sufficient to ensure that the lessons are both learned and retained in the collective memory. It is necessary to take specific measures to ensure that this occurs. The problem is considered here from the viewpoint of a company. The arrangements necessary at national level are described elsewhere in this chapter.

Approaches to the problem are discussed in *Lessons from Disaster* by Kletz (1993b) and (1980g, 1982J, 1993c), R.W. Fawcett and Kletz (1982) and Hancock (1989, 1992).

The reduction of accidents is to a large extent a matter of applying what is already known. Unfortunately, within an organization this knowledge often decays. Sometimes it is an individual who is unaware, even though the matter is well known in many parts of the organization. Sometimes the organization as a whole appears to have forgotten. In Kletz' words 'Organizations have no memory'.

Kletz has also put the matter even more graphically. During his time as a safety adviser, he was often tempted to tell a manager on whose plant a familiar accident had happened: 'Don't bother to write the accident report. I'll send you a copy from my files'.

The first step in countering this problem is to ensure that the right lessons are drawn about the accidents that have already occurred, in the company and elsewhere. The need to get down to the fundamental causes was the main theme of Sections 27.5 and 27.8.

Measures aimed at making sure that the lessons are not forgotten but remain fresh in the collective memory are described by Kletz (1993b). Starting from receipt of the report, they may be summarized as follows. The immediate actions should be to (1) follow up the recommendations and (2) publicize the lessons. In order to keep the accident fresh in the memory, steps should be taken periodically to (3) hold workshops in which it is discussed and (4) describe it in the company SLP newsletter. Measures may also be taken to (5) introduce a reference to the accident in any code that contains provision derived from it and (6) create a database of accident case histories that gives company personnel easy access to them. Management should (7) avoid turning a blind eye to unacceptable work practices and (8) before removing equipment or ending a procedure, find out what its original purpose was.

There are a number of recurring themes in accident investigation and it is helpful to be aware of these. Some themes which run through the work of Kletz and which he has highlighted explicitly are shown in Table 27.3.

27.11 Case Histories

Case histories are critical to the learning process. Without this lifeblood, the process would soon shrivel and die. Case histories, and their sources, are described in Appendix 1.

27.12 Information Exchange

Learning can take place only if information on accidents and accident investigations is made freely available by the publication of reports and by schemes for information exchange.

27.12.1 Loss Prevention Bulletin

A principal information exchange scheme is that operated by the Loss Prevention Panel of the Institute of Chemical Engineers (IChemE). The Loss Prevention Bulletin (LPB) published by the panel contains articles on various aspects of SLP, but above all it gives case histories of accidents with accompanying analyses. The titles of the articles in the bulletin are listed after the references given at the end of this book.

Table 27.3 *Some recurring themes in accident investigation (after Kletz)*

A Some recurring accidents associated with or involving
Identification of equipment for maintenance
Isolation of equipment for maintenance
Permit-to-work systems
Sucking in of storage tanks
Boilover, foamover
Water hammer
Choked vents
Trip failure to operate, neglect of proof testing
Overfilling of road and rail tankers
Road and rail tankers moving off with hose still connected
Injury during hose disconnection
Injury during opening up of equipment still underpressure
Gas build-up and explosion in buildings
B Some basic approaches to prevention
Elimination of hazard
Inherently safer design
Limitation of inventory
Limitation of exposure
Simple plants
User-friendly plants
Hazard studies, especially hazop
Safety audits
C Some management defects
Amateurism
Insularity
Failure to get out on the plant
Failure to train personnel
Failure to correct poor working practices

27.12.2 Trend in publication

According to Kletz (1993b), the number of accident case histories published is diminishing. Unless this trend is reversed, the industry's learning process will be severely impaired.

Kletz deals in detail with the justification for the publication of accident reports, the reasons for the fall-off and the measures that should be taken to counter it.

27.13 Accident Databases

The accessibility of accident case histories is much enhanced by the creation of accident databases, particularly computer-based databases.

27.13.1 Major databases

There are a number of major accident databases such as the Major Hazard Incidents Data Service (MHIDAS), the Explosion Incidents Data Service (EIDAS) and the Environmental Incidents Data Service (EnvIDAS) of the Safety and Reliability Directorate (SRD); the Failure and Accident Technical Information System (FACTS) of TNO; the Major Accident Reporting System (MARS) of the Commission of the European Communities (CEC); and World Offshore Accident Database (WOAD) of Veritas Offshore Technology. An account is given in Appendix 1.

27.13.2 Company databases

A number of companies have developed their own accident databases, either confined to accidents that have occurred in the company or extended to include other accidents. An account of such a database in ICI has been given by R.W. Fawcett and Kletz (1982).

27.14 Safety Performance Measurement

Turning from accident investigation to the feedback of information about safety performance in a company, the first requirement is for methods of measuring it. Accounts of safety measurement are given in *Managing Safety* (HSE, 1981d) and *Techniques of Safety Management* (D. Petersen, 1989).

27.14.1 Safety performance metrics

The safety performance criteria that is appropriate to use are discussed in Chapter 6. For personal injury, the injury rate provides one metric, but it has little direct connection with the measures required to keep under control a major hazard. For the latter, what matters is strict adherence to systems and procedures for such control, deficiencies in the observance of which may not show up in the statistics for personal injury. However, as argued in Chapter 6, there is a connection – this is that the discipline which keeps personal injuries at a low level is the same as that required to ensure compliance with measures for major hazard control.

There needs, therefore, to be a mix of safety performance criteria. Those, such as injury rate have their place, but they need to be complemented by an assessment of the performance in achieving safety-related objectives. Safety performance criteria are discussed in detail by Petersen. Different criteria are required for senior management, middle management, supervisors and workers. He lists the desirable qualities of metrics for each group.

Any metric used should be a valid, practical and cost-effective one. Validity means that it should measure what it purports to measure. One important condition for this is that the measurement system should ensure that the process of information acquisition is free of distortion.

Qualities required in a metric for senior management are that it is meaningful and quantitative, is statistically reliable and thus stable in the absence of problems, but responsive to problems and is computer-compatible.

For middle management and supervisors, the metric should be meaningful, capable of giving rapid and constant feedback, responsive to the level of safety activity and effort, but sensitive to problems.

A metric that measures only failure has two major defects. The first is that if the failures are infrequent, the feedback may be very slow. This is seen most clearly where the criterion used is fatalities. A company may go years without having a fatality, so that the fatality rate becomes of little use as a measure of safety performance. The second defect is that such a metric gives relatively little feedback to encourage good practice.

A safety performance metric may be based on activities or results. The activities are those directed in some way towards improving safety practices. The results are of two kinds, before-the-fact and after-the-fact. The former relates to the safety practices, the latter to the absence or occurrence of bad outcomes such as damage or injury.

Metrics for activities or before-the-fact results may be based on the frequency of some action such as an inspection or the frequency of a safety-related behaviour, such as failure to wear protective clothing. Or, they may be based on a score or rating obtained in some kind of audit.

27.14.2 Some incident-based metrics

There are numerous metrics that can be devised based on incidents such as damage or injury. The first requirement for such a measure is a clear definition of the events to be recorded.

The incidents measured may include various forms of injury event and reportable accidents. Types of injury event include first aid treatments, lost time accidents, serious injury accidents and fatalities. Types of reportable accident are those for which there are statutory reporting requirements and those for which there is, in addition, a company reporting requirement.

Some metrics commonly used in the United Kingdom include

$$M_1 = n_{\mathrm{ra}}/N_{\mathrm{p}} \qquad [27.14.1]$$

$$M_2 = N_{\mathrm{lta}}/N_{\mathrm{h}} \qquad [27.14.2]$$

$$M_3 = n_{\mathrm{hl}}/N_{\mathrm{h}} \qquad [27.14.3]$$

where M_1, M_2 and M_3 are metrics, n_{hl} is the number of hours lost, n_{lta} is the number of lost time accidents, n_{ra} is the number of reportable accidents, N_{h} is the number of hours worked and N_{p} is the number of persons at risk.

27.14.3 Organization of measurement

There needs to be a formal system for the measurement of safety performance. This may be organized in various ways. In particular, systems differ in the division of responsibility between line management and the safety function.

It is normal for line management to measure, and report on, production performance and it may well do the same on safety performance. This is the preferred method in the

arrangements described by the HSE (1981d). If it is adopted, its operation should be subject to audit by the safety function.

The HSE states 'The most frequently encountered difficulty in applying measuring schemes is for a manager to separate his own performance as an individual from that of his team'. The way in which this problem is resolved depends on the culture of the particular company.

27.15 Safety Performance Monitoring

Given that performance is to be assessed by measuring events, such as failures or accidents, then probability theory may be used to determine whether there has been an improvement or deterioration in performance as between two situations.

27.15.1 Statistical measures

An account of the methods that may be used to detect changes of performance has been given by Wynn (1950). If over a given reference period in a population of size n the observed number of events x has been sufficiently large that the expected number of events, μ $(=x/n)$ is firmly known, then the Poisson distribution is applicable

$$P(r) = \exp(-\mu)\frac{\mu^r}{r!} \qquad [27.15.1]$$

where $P(r)$ is the probability of r events. The application of Equation [27.15.1] is facilitated by the use of Figure 27.3, which gives the observed number of events vs the expected number of events. It should be noted that although the curves drawn are continuous, the events to which they apply are integers.

As an illustration of the use of Figure 27.3, consider the case where the expected number is 8. If the observed number is 10, the difference is not significant, but if the observed number is 15, this is significant at the 95% level.

The use of the Poisson distribution in this way is permissible only if the expectation μ is known. The confidence with which the expected number of events is known depends on the observed number of events in the reference period. The determination of the confidence limits for the frequency of an event for use in the exponential or Poisson distribution was described in Chapter 7. Tables of the confidence limits of the Poisson distribution have been given by Woodcock and Fames (1970 UKAEA AHSB(S) R179).

If there is no firm expectation, the Poisson distribution is not applicable, but the problem may be treated using the chi-square distribution. This distribution may be used to test the hypothesis that there is no difference between a reference period and a test period where the population size and the number of events in the reference period are n_1 and x_1 and those in the test period are n_2 and x_2, respectively. For this case, the following chi-square table is applicable:

	No. affected by event	*No. unaffected by event*	*Total*
Population 1	x_1	$n_1 - x_1$	n_1
Population 2	x_2	$n_2 - x_2$	n_2
Totals	$x_1 + x_2$	$n_1 + n_2 - x_1 - x_2$	$n_1 + n_2$

A particular formulation of chi-square for this case (Moroney, 1956, p. 255) is

$$\chi_2 = \frac{[x_1(n_2 - x_2) - x_2(n_1 - x_1)]^2(n_1 + n_2)}{n_1 n_2(x_1 + x_2)(n_1 + n_2 - x_1 - x_2)} \qquad [27.15.2]$$

$$\approx \frac{(x_1 - kx_2)^2}{k(x_1 + x_2)} \qquad n_1 \gg x_1, \quad n_2 \gg x_2 \qquad [27.15.3]$$

with

$$k = \frac{n_1}{n_2} \qquad [27.15.4]$$

The system described here has one degree of freedom, and for this the values of the chi-square are:

Confidence level (%)	χ^2
90	2.706
95	3.841
99	6.635

The application of Equation [27.15.3] is facilitated by the use of Figure 27.4, which gives the group $(x_1 - kx_2)$ vs the group $k(x_1 + x_2)$.

As an illustration of the use of Figure 27.4, consider the case where in the reference period the population size is 1000 and the number of events is 55, and in the test period the corresponding values are 1000 and 45. Then, the values of k and of the groups $(x_1 - kx_2)$ and $k(x_1 + x_2)$ are 1, 10 and 100, respectively. This difference is not significant, but if the numbers of events in the reference and test period are 60 and 40, respectively, the difference is significant at the 95% level.

The chi-square method becomes inaccurate if the number of events in the cells of the chi-square table falls too low. The number should exceed about 20, or for approximate work about 5.

It should be noted that the quantity investigated using the methods just described is the number of events, not the event rate. It is also emphasized that the validity of any conclusions drawn depends on the correct choice of the variable that describes the population size. If in a particular case, for example, it is assumed that the number of maintenance accidents depends on the number of maintenance personnel, whereas in reality it depends on some other factor such as the number of maintenance tasks done, then incorrect conclusions may be drawn.

27.15.2 Vigilance against rare events

The more serious accidents are rare events, and the absence of such events over a period must not lead to any lowering of guard. There needs to be continued vigilance.

The need for such vigilance, even if the safety record is good, is well illustrated by the following extract from the 'Chementator' column of *Chemical Engineering* (1965 Dec. 20, 32) Reproduced with permission of *Chemical Engineering*:

> The world's biggest chemical company has also long been considered the most safety-conscious. Thus a recent series of unfortunate events has been triply shattering to Du Font's splendid safety record.

Latest incident occurred earlier this month when a dust explosion and flash fire in a dyestuff drying machine at the company's immense Chambers Works, Deepwater, N.J., caused some $50,000 damage, claimed two lives and injured nine more, three seriously. Ironically, in August of this year the plant had received an award from the governor of New Jersey for achieving 16,771,355 man hours worked without a single lost time accident.

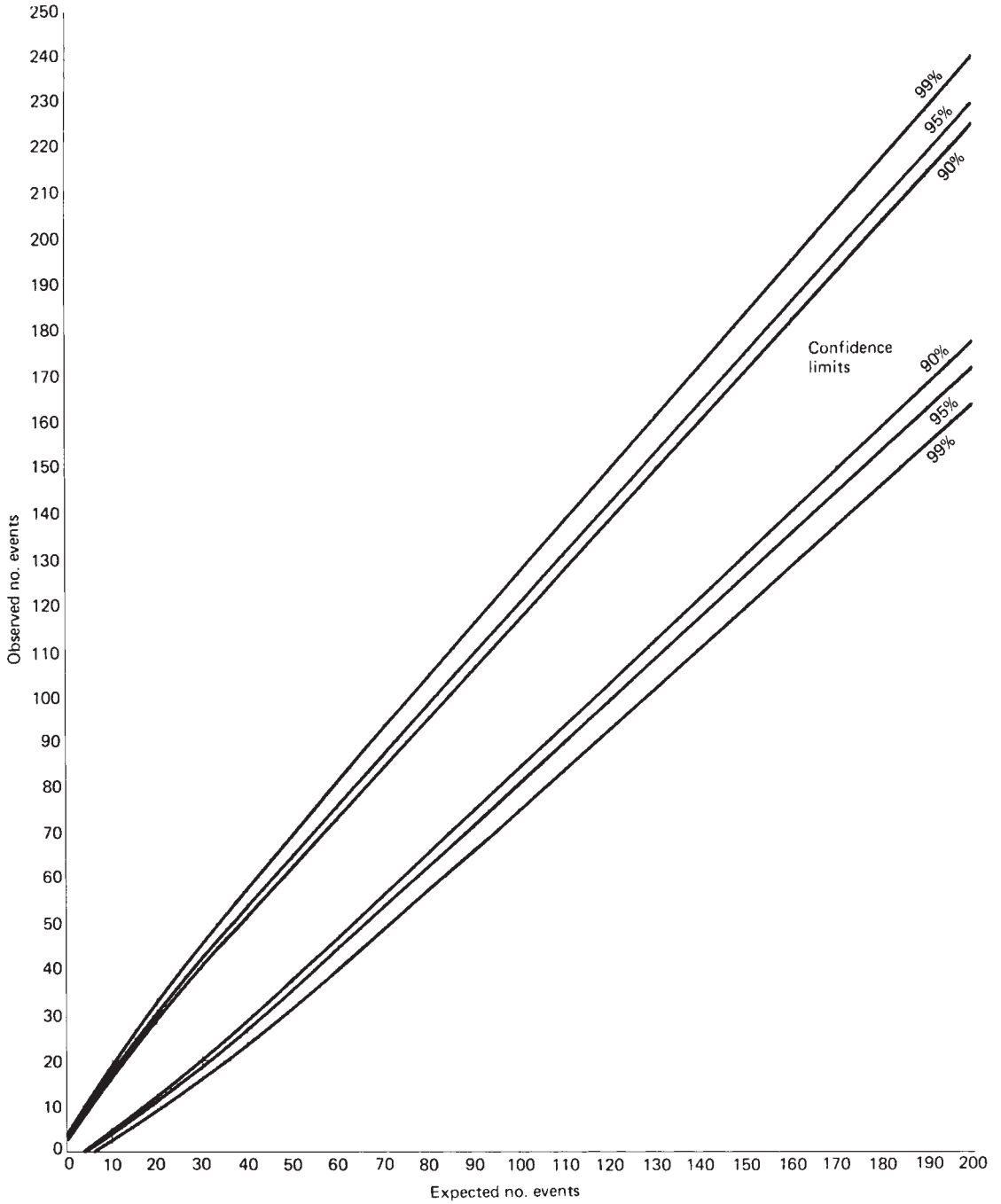

Figure 27.3(a) *Graph (coarse scale) for the determination of trends in safety performance: Poisson distribution (after Wynn, 1950)*

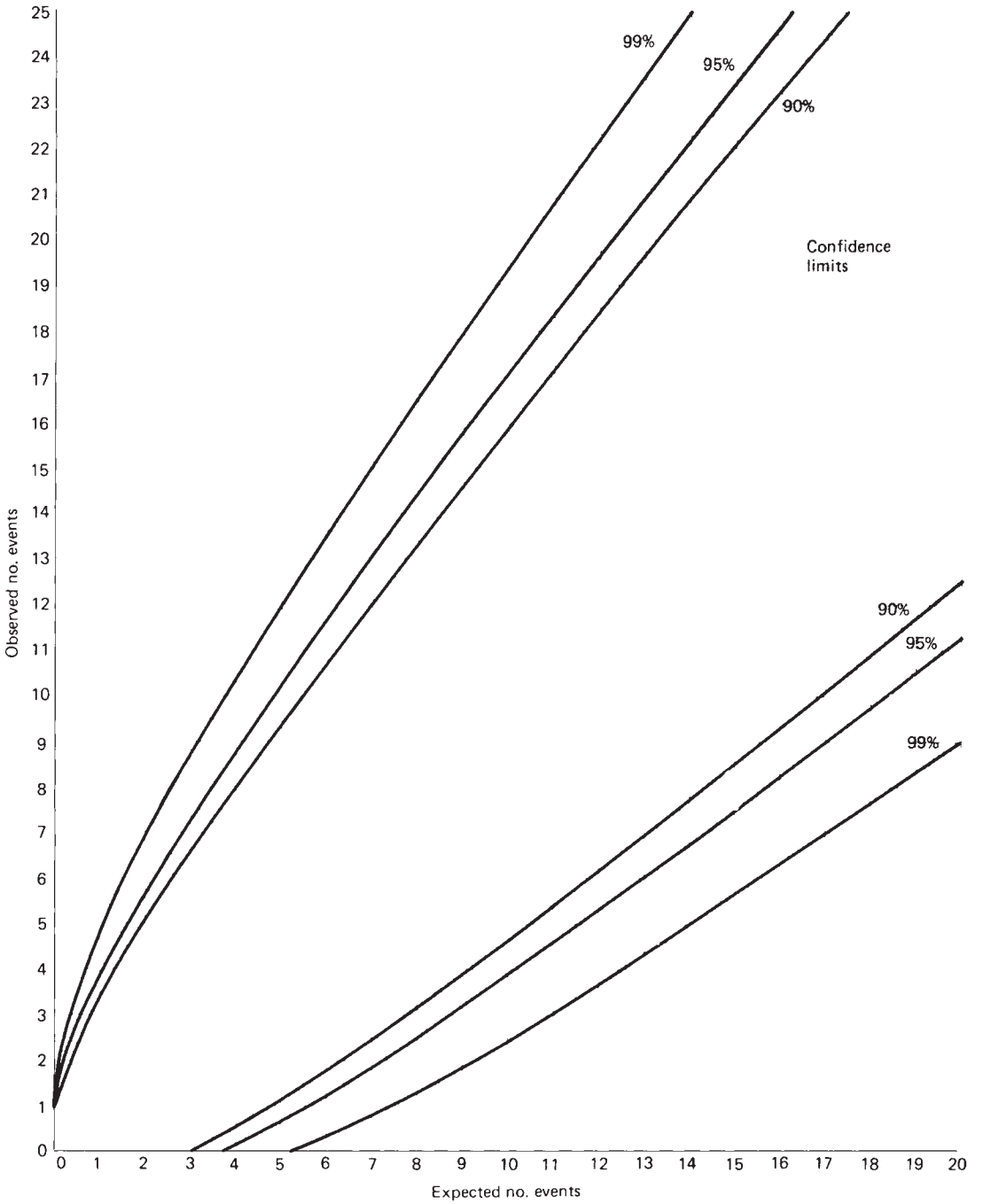

Figure 27.3(b) *Graph (fine scale) for the determination of trends in safety performance: Poisson distribution (after Wynn, 1950)*

In late November, a flash fire swept the drying room of the company's Carney Point, N.J., gunpowder plant. Damage was relatively light but four workmen perished. In operation before the turn of the century, the plant had had no fatal accidents since before World War I.

The earliest of the triple tragedies was a blast and fire at the firm's Louisville plant in August. Claiming 11 lives

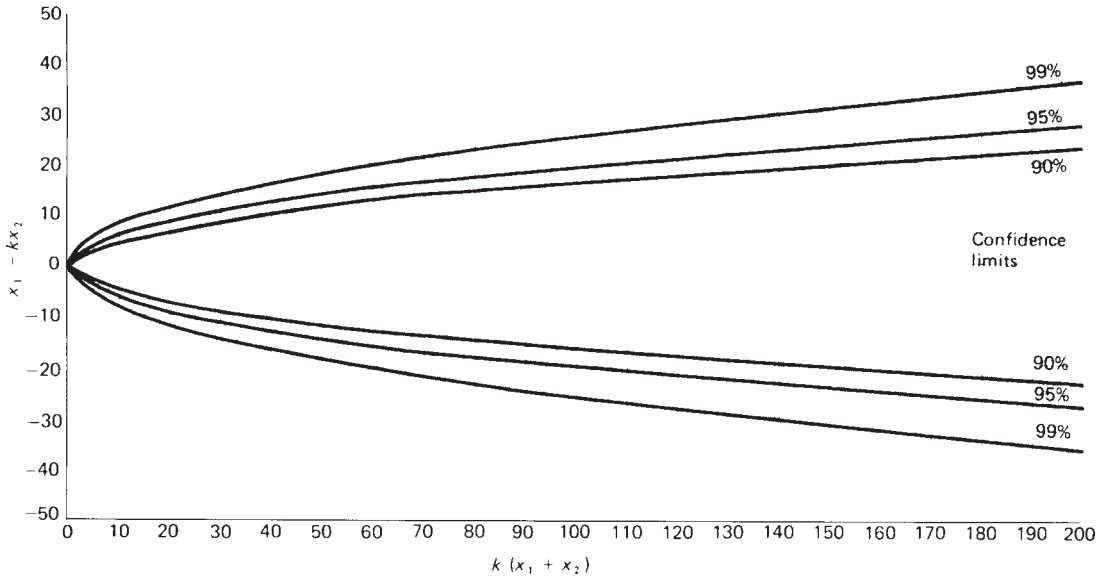

Figure 27.4 *Graph for the determination of trends in safety performance: chi-square distribution (after Wynn, 1950)*

and causing $5 to $10 million damage, the accident's magnitude was without precedent in the company's history.

27.16 Near Miss Reporting

It has long been appreciated that for every accident there are many lesser events, some with less material effect and others with no effect at all, and that is desirable to learn from these 'near misses'.

Accounts of the monitoring of and learning from near misses are given in *Near Miss Reporting as a Safety Tool* (van der Schaaf, Lucas and Hale, 1991) and by N. Carter and Menckel (1985).

Near Miss Reporting contains in effect a debate on the subject and poses the question of the purpose of such reporting.

27.16.1 Licensee Event Reports

One of the main public sources of information on near misses is the Licensee Event Reporting system of the Nuclear Regulatory Commission. Analyses of Licensee Event Reports (LERs) have been given by Rasmussen (1980b), who has also used the information given in these reports in his development of a methodology for the handling of human error.

27.16.2 Models for reporting

A system of near miss reporting must specify in some way the events to be reported and must, therefore, be based, explicitly or implicitly, on some form of model. Three principal forms of model are (1) the engineering system, (2) human behaviour and (3) the managerial and organization factors. Each type of model is represented in the account that follows.

27.16.3 Aims of reporting

It is suggested by van der Schaaf (1991c) that near miss reporting may be undertaken for three different purposes: (1) modelling (qualitative insight), (2) monitoring (quantitative insight) and (3) motivation (maintaining alertness).

If the aim is modelling, the interest centres on reporting of 'new' types of near misses, whereas if it is monitoring, the implication is that it is known types that are reported. The third aim, motivation, differs from the other two in that it is essentially a by-product of the reporting, albeit an intended one. The activity of reporting near misses makes people more conscious of them.

The author gives an account of a near miss management system which is aimed at monitoring rather than modelling, but which should have as a by-product an increase in motivation amongst those involved in the reporting.

27.16.4 Near miss management system

A description is given by van der Schaaf (1991b) of a near miss management system (NMMS). The concepts underlying this are that its sole function should be as a means for the organization to learn from near misses, that is should have as comprehensive a coverage as possible of the inputs and outputs, that it should be based on a suitable model of human behaviour and that it should be integrated into, rather than grafted onto, the organization. The modules of the framework for the NMMS are:

(1) Detection: recognition and reporting.
(2) Selection: according to purpose(s).
(3) Description: all relevant hardware, human and organizational factors.
(4) Classification: according to a socio-technical model.
(5) Computation: statistical analysis of large database of incidents to uncover certain (patterns of) factors.

(6) Interpretation: translation of statistics results into corrective and preventive measures.
(7) Monitoring: measuring the effectiveness of proposed measures after their implementation.

Further features of the NMMS are described by van der Schaaf (1991a) in an account of its application in a chemical plant, and specifically in the central control room. The detection module is essentially a redesigned version of an existing near miss reporting system. The selection module allocates the event to the modelling or monitoring mode. The description module utilizes a form of fault tree, termed an incident production tree, which contains as elements not only faults and errors but also recoveries, as described elsewhere by van der Schaaf (1988). The classification module is based on Rasmussen's Skills-Rules Knowledge (SRK) model of human behaviour. The classification proceeds in two stages. In the first stage, a rough classification is made into (1) technical factors, (2) organizational factors and (3) behavioural factors. Each element in the incident production tree is then examined according to the following procedure. It is first considered for classification as a technical factor, and if it is such, it is assigned to a subcategory such as engineering, construction, etc.; if this does not apply, it is considered for classification as an organizational factor; if this also does not apply, then and only then is it considered for classification under the third category as a behaviour factor.

27.16.5 Computer aid for reporting

The practicalities of near miss reporting and a computer-based aid influence diagram analysis (IDA) for such reporting are described by A.R. Hale *et al.* (1991). This work complements that of van der Schaaf just described and utilizes the same framework modules.

A problem with near miss reporting is that if a proforma is used, most of the entries are not relevant to a given event. This can be overcome by the use of a computer aid in which the user is prompted to enter information interactively.

The accident model used in this case is a hybrid derived partly from the energy barrier concept found in MORT (W.G. Johnson, 1980) and partly from the concept of deviation from normal conditions (Kjellen, 1983; A.R. Hale and Glendon, 1987).

27.16.6 Critiques of reporting

A critique of near miss reporting has been given by Reason (1991), who argues that current reporting schemes, where they exist, tend to be relatively ineffective in supporting safety management.

He distinguishes between active failures that have an immediate adverse effect, and latent failures which lie as dormant, enabling conditions until the accident is triggered by an active failure. He likens latent failures to resident pathogens in the human body. He argues that the most effective approach to the prevention of accidents is to identify and neutralize these pathogens.

Reason utilizes an accident model in which a distinction is made between failure types and failure tokens. In essence, the failure types are general classes of managerial and organizational failure, whilst the tokens are specific failures of individuals. The latter are categorized as slips and lapses, mistakes and violations.

He considers five channels for system safety information. These channels are (1) accident and incident reporting systems, (2) unsafe act and near miss reporting systems, (3) precursors of unsafe acts, (4) failure type indicators and (5) stylistic or cultural indicators. The precursors of channel 3 are described in terms similar to those applied to performance shaping factors. The failure types of channel 4 are the classes of managerial failure. The cultural indicators of channel 5 are described in terms of a seven-point ranking scale, which ranges from a condition where safety practices are at the barest industry minimum to one where good practice is followed.

The general failure types are (1) hardware defects, (2) design failures, (3) poor maintenance procedures, (4) poor operating procedures, (5) error-enforcing conditions, (6) poor housekeeping, (7) incompatible goals, (8) organizational failures, (9) inadequate training and (10) inadequate defences.

Reason argues that the key to effective safety management lies in appreciating what is controllable and what is not. He contrasts the situation in respect of accidents with that pertaining in production. Most of the factors that affect production are under the control of management. Accidents are different. They arise from a complex interaction between latent failures and local triggering events. There is little management can do about the latter. It should concentrate on the former, and any near miss reporting system should reflect this. What should be reported are failures at the level of channels 4 and 5.

The need to base near miss reporting on an appropriate model is echoed by Lucas (1991), who proposes reporting based either on the man-machine interface or on system-induced error.

27.16.7 Hazard warning structure

Another approach to near miss reporting is the hazard warning structure developed by Lees (1982b, 1983b, 1985). The basic concept is that the undesired event is modelled using a hazard warning tree, a specialized form of fault tree, so that the place of lesser events in the hazard warning structure can be seen. An account of hazard warning structure with examples is given in Chapter 9.

The hazard warning concept is intended to be used first in the design of plant and to be then carried through into its operation. If at the design stage an analysis has been made of the hazard warning structure for the undesired events of interest, it is then possible to use the analysis to locate lesser events as they occur in the structure, to assess their significance and to take measures to control them.

The hazard warning structure approach is based on, and oriented to, fault trees for engineering systems. By comparison with the near miss reporting just described, it has the following distinguishing characteristics. The events to be monitored are decided in advance and are relatively well defined. Other events not included are not monitored, at least not as part of this particular exercise. The method does not address human errors as such but rather the effects of such errors on the engineering system.

The incident production tree described above evidently has features in common with the hazard warning tree.

27.17 Education

The education of engineers normally includes some material on safety. In chemical engineering, this has traditionally tended to cover aspects such as legal requirements and

personal safety. There has also generally been some coverage of the engineering aspects, particularly in design projects, but overall the treatment has been variable.

The occurrence of disasters such as Flixborough, Seveso and Bhopal has highlighted the need for greater awareness of and knowledge about SLP. These three accidents have had particular impact in the United Kingdom, Continental Europe and the United States of America, respectively. The trend has been for industry to urge universities to teach SLP and for professional bodies to introduce a requirement that SLP be part of the curriculum.

Accounts of the treatment of SLP in university courses in chemical engineering have been given by Mewis (1984), Talty (1986), Kaufmann (1987), Kletz (1988l, 1990a), Crowl and Louvar (1989), Nolan (1989), V.C. Marshall (1991c), Crawley and Scott (1992) and Lemkowitz (1992a,b).

The inclusion of SLP in chemical engineering curriculum requires justification. The ACMH in its *Third Report* (Harvey, 1984) stated:

> It is important that students be introduced to the concept of inherently safer design and that they realize that safety in plant operation must be considered right at the start of the design study. Process safety must be taught in a rigorous, stimulating way by staff of appropriate experience. Departments that initially do not have this expertise may need to use the services of experts from other universities, industry and consulting firms. By virtue of the nature of processes that give rise to major hazards, it is the chemical engineer who often fills the position of responsible person in the design or operation of plant, (paragraph 124)

Support for this view is given by Kletz (1981), who advances three principal arguments. One is the importance of treating safety from the outset as an integral part of the design of plant and of aiming for inherently safer design. Another is that whatever use he may make of other subjects taught at university, any practising chemical engineer will be involved in safety matters. He has a moral and legal responsibility and will probably be faced with safety issues from the first day. The third is that SLP involves basic principles.

SLP involves the application of a quantitative approach and encourages numeracy. It is based on a structured approach that involves the identification of hazards, an estimation of their frequency, an estimation of the consequences and decision-making based on defined criteria.

The need for an engineer to take a wider view of the task in hand is emphasized by Crawley and Scott (1992). Industry requires someone who is capable of reasoning and is aware of the factors involved and of the pitfalls. For example, in a design the student may well be able to calculate a flow in a pipe, but fail to give consideration to erosion, vibration, noise or isolation for maintenance.

The need to achieve a cost-effective design is another factor. There is often almost no end to the safety measures that might be taken. The engineer needs a tool which assists in deciding how far to go.

The view exists that even if the need for education in SLP is accepted, it is better done when the engineer first enters industry. However, the chemical engineer may well enter a firm that lacks the means of bringing him up to the level of SLP awareness and capability achievable at university, or one that does not have a safety culture. Even larger companies generally favour its inclusion in the university course. This does not, of course, obviate the need for the company to carry out its own training in SLP, particularly for new entrants.

The extent to which SLP ranks as a mainstream subject in chemical engineering has been examined by V.C. Marshall (1991c). He argues that to qualify, a subject must meet the following criteria. It should (1) be acknowledged as such by the academic culture, (2) be recognized as relevant by students, (3) be intellectually demanding, (4) comprise a well established corpus of knowledge, organized on clearly defined unifying principles, (5) be highly quantitative and thus capable of being subjected to mathematical analysis, (6) possess a content and unifying principles set out in authoritative textbooks, (7) be taught by specialists, (8) be a compulsory subject which must normally be passed and (9) be examined formally. He goes on to consider the extent to which SLP now meets these criteria. V.C. Marshall (1987, 1989c, 1990d) has also attempted to develop the unifying structure which he calls for.

Some objectives to be attained in teaching SLP and means used to achieve them include:

Awareness, interest	Case histories
Motivation	Professionalism
	Legal responsibilities
Knowledge	Techniques
Practice	Problems Workshops
	Design project

There has been considerable debate as to whether SLP should be taught by means of separate course(s) or as part of other subjects. The agreed aim is that it should be seen as an integral part of design and operation. Its treatment as a separate subject appears to go counter to this. On the other hand, there are problems in dealing with it only within other subjects. It cannot be expected that staff across the whole discipline will have the necessary interest, knowledge and experience and such treatment is unlikely to get across the unifying principles. These latter arguments have weight and the tendency appears to be to have a separate course on SLP but to seek to supplement this by inclusion of material in other courses also. It is common ground that SLP should be an essential feature of any design project. In 1983, the IChemE issued a syllabus for the teaching of SLP within the core curriculum of its model degree scheme. This syllabus was:

> *Safety and Loss Prevention*. Legislation. Management of safety. Systematic identification and quantification of hazards, including hazard and operability studies. Pressure relief and venting. Emission and dispersion. Fire, flammability characteristics. Explosion. Toxicity and toxic releases. Safety in plant operation, maintenance and modification. Personal safety.

In 1988, the IChemE issued further suggestions for the teaching of SLP. The background to these is given by Nolan (1989) and Crawley and Scott (1992), who also give an outline of the material proposed.

The topics highlighted by Kletz (1988l) as core material in SLP are inherently safer design, hazop, hazard analysis, human error and maintenance and modification.

The emerging pattern in the introduction of SLP into undergraduate courses appears to be an elementary treatment, perhaps within an overview course on chemical engineering, early on followed at some later point by a dedicated course on SLP. This is the approach described by Crawley and Scott and by Lemkowitz (1992a,b).

Another subject that has many similarities to SLP is environmental protection. These similarities include the engineer's moral and legal responsibilities, the concept of inherently cleaner design and a structured approach to environmental risks. There is a discernible trend, therefore, to treat environmental protection in a manner broadly similar to, and sometimes in the same course as, SLP.

The inclusion of SLP within a university chemical engineering course is not without its problems. One is the allocation of time within the timetable. The order of contact hours typically mentioned is some 4 hours for elementary treatment early on and 20 hours for a later dedicated course.

The other main problem is the availability of staff able and willing to teach SLP. Such teaching requires both industrial experience and knowledge not only of the specific discipline of SLP but of a number of core subjects. Only a small proportion of departments contain staff specializing in the subject. It is recognized, therefore, that there is need for support for staff teaching SLP. Two principal forms of support are the use of engineers from industry to complement the academic teaching and the provision of teaching material on the subject.

SLP can serve as an integrating factor in a course. In this respect, it has much in common with a design project. Some of the regular chemical engineering subjects on which the teaching of SLP draws are:

(1) mathematics;
(2) thermodynamics;
(3) fluid mechanics;
(4) mass transfer;
(5) heat transfer;
(6) reaction engineering;
(7) particle science and technology;
(8) process instrumentation;
(9) process dynamics and control;
(10) human factors;
(11) computer methods;
(12) management;
(13) engineer in society.

Table 27.4 illustrates some of the links between SLP topics and regular chemical engineering subjects.

Accounts of practice in particular courses are given by Kaufmann (1987), Kletz (1988l) and Lemkowitz (1992a,b). Kaufmann describes the use of a number of mini-courses, taking some 10–15 min. The treatment described by Lemkowitz involves an integrated treatment of SLP and environmental protection and has three main parts. In the first, early part a problem is taken from the media or the literature and becomes a project for investigation by the student, which involves interviewing industrial personnel about it. The second part is a dedicated course of lectures taking some 24 hours. The third part is a safety report that is submitted prior to starting on a laboratory project.

Table 27.4 *Some links between safety and loss prevention and other subjects in chemical engineering*

SLP topic	*Regular subject*
Inherently safer design:	
Chemical reactors	Reaction engineering
Separation processes	Mass transfer
System failure	Reliability engineering
Failure rates	Probability theory
Pressure vessels	Properties of materials: Strength of materials Fracture mechanics
Chemical reactors:	
Reaction runaway	Reaction engineering
Instruments	Instrumentation
Venting	Fluid mechanics: two-phase flow
Trip systems:	Instrumentation
Trip failure	Reliability engineering
Trip response	Process dynamics
Process operator	Human factors
Emission:	
Relief valve discharge	Fluid mechanics: gas flow
Flashing liquid	Fluid mechanics: two-phase flow
Vessel burst	Mixing processes
Vaporization:	
Volatile liquid	Simultaneous heat and mass transfer
Cryogenic liquid	Unsteady-state heat transfer
Dispersion	Turbulence theory
Fire	Radiant heat transfer
Explosion:	
Explosion energy	Thermodynamics
Adiabatic flame temperature	Thermodynamics
Toxicity:	
Toxicity testing	Probability theory
Computer aids:	
Plant design	Expert systems
Fault tree synthesis	Graph theory
Valve sequencing	AI techniques
Pressure systems management	Management
Risk criteria	Engineer in society

27.18 Teaching Aids

There are available a number of teaching aids of various kinds, suitable for use in the education of engineers at universities and/or of engineers and other personnel in industry.

Short introductions to SLP are given in *Flowsheeting for Safety* (Wells, Seagrave and Whiteway, 1976) and *A First Guide to Loss Prevention* (McCrindle,1981) and more substantial texts include *Industrial Safety Handbook* (Handley, 1977), *An Introduction to Loss Prevention* (Wells, 1980), *Industrial Hazard and Safety Handbook* (R. King and Magid, 1979), *Safety and Accident Prevention in Chemical Operations* (H.H. Fawcett and Wood, 1982), *High Risk Safety Technology* (A.E. Green, 1982b), *Major Chemical Hazards* (V.C. Marshall, 1987), *Chemical Process Safety* (Crowl and

Louvar, 1990) and *Safety in the Process Industries* (R. King, 1990), as well as the present book.

A series of books by Kletz includes *Cheaper, Safer Plants* (Kletz, 1984d), *Learning from Accidents in Industry* (Kletz, 1988h), *What Went Wrong?* (Kletz, 1988n), *Improving Chemical Engineering Practices* (Kletz, 1990d), *An Engineer's View of Human Error* (Kletz, 1991e), *Plant Design for Safety* (Kletz, 1991g), *Hazop and Hazan* (Kletz, 1992b) and *Lessons from Disaster* (Kletz, 1993b).

The IChemE has been active in the production of a variety of aids. Table 27.5 lists a computer simulation, open learning modules, slide modules and video training modules on various topics. Other aids include the information exchange scheme of the *Loss Prevention Bulletin*, the publications listed in Appendix 28, and many of the books by Kletz just mentioned.

Another source of material is the CCPS of the American Institute of Chemical Engineers (AIChE). Specifically, educational material from this source includes *Safety Health and Loss Prevention in Chemical Processes: Problems for Undergraduate Engineering Curricula – Instructor's Guide* (CCPS, 1990).

There are available a number of films and videos, both on the process industries generally, and on SLP in particular. Some of these are listed in Table 27.6.

Table 27.5 *Some training aids for safety and loss prevention available from the IChemE*

1	Hazards of Over- and Under-Pressuring of Vessels (SL)
2	Hazards of Plant Modifications (SL)
3	Fires and Explosions (SL)
4	Preparation for Maintenance (SL)
5	Furnace Fires and Explosions (SL)
6	Preventing Emergencies in the Process Industries (V, SL)
7	Work Permit Systems (SL, B)
8	Human Error (SL, B)
9	Inherent Safety (V, SL, B)
10	Handling Emergencies (CS)
11	Safe Handling of LPG – Pt 1: Pressurized Bulk Storage and Road and Rail Loading (V, SL)
12	Safer Piping – Awareness Training for the Process Industries (V, SL)
13	Safe Handling of LPG – Part 2: Ship/Shore Transfer and Refrigerated Storage (V, SL)
14	Practical Risk Assessment (OL)
15	Hazop and Hazan (SL, B)
16	Controlling Electrostatic Hazards (V, SL)
17	Managing for Safety (V, SL)
18	Safer Use of Chemical Additives (SL)
19	Offshore Practical Risk Assessment (OL)
20	Learning from Accidents (SL)
21	Flammable Liquid Fire . . . Don't be a Victim (V)
22	Dust Explosion Hazard (V, SL, B)
23	Control of Exothermic Chemical Reactions (V, SL, B)
24	Tank Fires (SL)
E04	Environmental Auditing (SL)

B, book; CS, computer simulation module; OL, open learning module; SL, slide training module; V, video training module.

Table 27.6 *Some training aids for safety and loss prevention: films and videos*

A HSE
It Shall be the Duty (HSWA 1974)
All in a Day's Work (work of Factory Inspectorate)
Health at Work (work of EMAS)
Protection of Eyes Regulations
Guarding Machinery
Principles of Machinery Guarding
A Guide to Interlocking Guards
Abrasive Wheels
Watch that Space: Confined Space Hazards in Factories
Control of Exothermic Chemical Reactions
B Fire Protection Association
Understanding Fire
C Amoco
Hazard of Air Hazard of Water
D British Gas
The Science of Flame – Principles
The Science of Flame – Control
The Frigg Story
Too Good to Waste (North Sea gas)
The Innovators
E Conoco UK Ltd
The Murchison Project (offshore oil)
F Millbank Films (ICI)
If One Green Bottle (management responsibility)
Something to do with Safety Reps
Talking of Safety (safety committees)
When Fire Starts
Toxic Hazards in Industry
Permit-to-Work
Is There Anything I've Forgotten? (permit-to-work systems)
Incident Rendered Safe (transport emergencies)
Better than Cure (occupational health)
Safeguard (machine guarding)
One Last Shock (electrical safety)
Make light of Lifting
Mind Your Back (lifting)
It Need not Happen (protective clothing)
Air to Breathe (breathing apparatus)
Rescue Team Alert
One Million Hours (accident investigation)
Nobody's Fault (story of an accident)
Flashpoint (laboratory safety)
G Shell
Oil Refinery
Principles of Refining
Petrochemicals: the Building Blocks
Petrochemicals: Polymerization Reactions
H Total Oil Great Britain Ltd
Petroleum, its Refining
Flames of the Desert (Middle East oil)

Table 27.6 *(continued)*

Before the Derricks Rise (offshore oil)
The Riddle of the Deep (offshore underwater)
I UK Atomic Energy Authority
Principles of Fission
The Nuclear Fuel Cycle
Safety and Nuclear Power
Nuclear Fuel Reprocessing

27.19 Notation

Section 27.14

M_1, M_2, M_3	metrics
n_{hl}	number of hours lost
n_{lta}	number of lost time accidents
n_{ra}	number of reportable accidents
N_h	number of hours worked
N_p	number of persons at risk

Section 27.15

k	ratio defined by Equation [27.1.4]
n	size of population
P	probability
r	counter
x	observed number of events
μ	expected number of events
χ^2	chi-square

Subscripts

1, 2	population 1, 2

28

Safety Management Systems

Contents

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Safety and loss prevention depend primarily on the overall management system, as described in Chapter 6 and also in other chapters. The people who carry the main responsibility for safety are the line managers rather than the safety specialists. At managerial, as at other levels, safety is everyone's responsibility. There remains a need, however, within the management system for a specific safety organization and for safety personnel. The quality of this safety system can have a significant effect on safety performance.

Selected references on process safety systems are given in Table 28.1.

Table 28.1 *Selected references on process safety systems (See also Tables 1.1, 6.1 and 27.1)*

ABCM (n.d./l, 1964/3); ILO (n.d.); Guelilch (1956); Simonds and Grimaldi (1963); H.H. Fawcett and Wood (1965); Sands and Bulkley (1967); CBI (1968); Leeah (1968); BCISC (1969/9, 1973/12); Handley (1969, 1977); Hearn (1969); Gilmore (1970); Freeman and Pickbourne (1971); Lloyd and Roberts (1971); R.L. Miller and Howard (1971); D. Petersen (1971–); D. Williams (1971); Kramers and Meijnen (1974); Health and Safety Executive (HSE) (1975 HSW Bklt 35); Cocks and Rogerson (1978); W.G. Johnson (1980); Messing (1980); Kletz (1981l); Kilian (1982); London (1982); Willette (1982); Witter (1982); Tweeddale (1985 LPB 63); Harron (1986); Rausch (1986); E.K. Young (1986); McSween (1993)

Safety officers, safety advisers
Institution of Industrial Safety Officers (n.d.); ASSE (1966); J. Jones (1974); HSE (1976c); Kletz (1977g, 1982k); HSC (1983/2); Dawson, Poynter and Stevens (1985); D. Stevens (1986); D. Gray (1988); Hutcheon (1988)

Safety policy statement
BSC (n.d./8); CBI (1974); Egan (1975, 1979); HSC (1975 HSC 6, 1982 IAC/L1, 1991 HSC 6)

Trade unions and safety
M.J. White (1969, 1977); ILO (1971–72); Kinnersley (1973); Levinson (1975); TUC (1975); Cullen (1990)

Safety committees
HSC (HSC 8, 1977/3); RoSPA (IS/32); Ministry of Labour (1968)

Safety representatives
HSC (HSC 9, 1977/3); Egan (1978)

Safety training
Institution of Industrial Safety Officers (n.d.); BCISC (1965/5); Gimbel (1965b); Kingdon (1969); Atherton (1971); Burrage (1971); CAPITB (1971 Inf. Pap. 10, 1975 Inf, Pap. 16); PITB (1975/1–3); ILO (1980a); Kubias (1982); A.R. Hale (1984); D.J. Lewis (1984e); Roy (1984); FPA (1989 CFSD MR9); Bhoonchaisri (1990); J.R. Taylor (1993)

Organizational memory
Kletz (1980g, 1982j, 1985i, 1993c)

Communication
Tye (1969); D. Williams (1971); Lowe (1985)

Accident prevention
NSC (n.d./2, 1992/11); Devauchelle and Ney (1962); H.H. Fawcett and Wood (1965, 1982); McElroy (1965)

Proprietary systems
International Safety Rating System (ISRS): Bird and Germain (1985); Bond (1988 LPB 80); Eisner and Leger (1988); D. Petersen (1989); Pringle and Brown (1990); Arnold, Redfearn and Maaren (1992); Bird (1992 LPB 103)
MORT: W.G. Johnson (1977, 1980)

28.1 Safety Culture

It is crucial that senior management should give appropriate priority to safety and loss prevention. It is equally important that this attitude be shared by middle and junior management and by the workforce.

A positive attitude to safety, however, is not in itself sufficient to create a safety culture. Senior management needs to give leadership in quite specific ways. Safety publicity as such is often a relatively ineffective means of achieving this; attention to matters connected with safety appears tedious or even unmanly. A more fruitful approach is to emphasize safety and loss prevention as a matter of professionalism. This in fact is perhaps rather easier to do in the chemical industry, where there is a considerable technical content. The contribution of senior management, therefore, is to encourage professionalism in this area by assigning to it capable people, giving them appropriate objectives and resources, and creating proper systems of work. It is also important for it to respond to initiatives from below. The assignment of high priority to safety necessarily means that it is, and is known to be, a crucial factor in the assessment of the overall performance of management.

A fuller discussion of management leadership in creating a safety culture is given in Chapter 6.

28.2 Safety Organization

28.2.1 Safety department organization

It is normal for there to be a separate department responsible for safety and loss prevention. Titles vary, but generally include some combination of those two phrases.

Managers involved in safety work are generally referred to as safety managers, safety advisers or safety officers. The head of a larger department is typically designated as safety adviser and other staff as safety officers.

A large department may have staff who specialize in areas such as engineering, safety systems and manuals, training, and so on.

Other areas which may come within the safety department include occupational health, industrial hygiene, process safety, medical matters and environmental protection.

The safety department needs to be, and be seen to be, independent, and the organizational structure should reflect this. In particular, the department should be independent of the production function.

28.2.2 Safety responsibilities

In broad terms, it is the responsibility of the safety organization to: participate in the formulation of safety policy; ensure that safety systems are created, maintained and adapted; ensure compliance with the regulatory requirements; review plants and procedures; identify, assess and monitor hazards; educate and train in safety; assist communication and promote feedback in safety matters; and contribute to technical developments in safety. Thus, safety personnel are concerned with the development and

maintenance of the overall safety system and with its application to particular works and to plants.

As already stated, it is line management which has the executive responsibility for safety, as it does for production; the role of the safety function is advisory. This means that in many areas of safety it is line management which undertakes an activity, but with assistance from the safety function. Accident investigation is a case in point.

In many instances, the safety department will monitor and will intervene only if necessary. For example, the plant emergency procedures manual should be revised periodically. The safety department will recognize a responsibility to see that this is done. If necessary, it will prompt line management to undertake the revision and may provide support.

Turning to the specific areas for which safety department typically takes some responsibility, these include:

(1) advice to senior management, including –
  (a) overall safety policy,
  (b) safety management system,
  (c) compliance with regulatory requirements,
  (d) safety performance measurement,
  (e) technical aspects of safety,
  (f) litigation support,
  (g) hazard insurance reviews,
(2) creation, monitoring and revision of safety management system, including –
  (a) personnel selection criteria,
  (b) process safety reviews, hazard studies,
  (c) safety auditing,
  (d) emergency planning,
  (e) accident investigation,
  (f) safety documentation,
  (g) safety training,
  (h) compliance with regulatory requirements,
(3) oversight and prompting of safety-related activities, including those in (2);
(4) safety training, exercises and drills;
(5) communication, including –
  (a) developments in regulatory requirements,
  (b) developments in technology,
  (c) good practice in safety,
  (d) accident investigation and case histories.

The safety department has a responsibility to ensure that there exists a safety management system which is appropriate and comprehensive, to monitor its implementation and operation, and to undertake period audits and reviews and to make proposals for revision as necessary.

On safety matters, the department should be the company's window to the outside world, monitoring developments, whether in legislation, technology or good practice.

For large projects, the safety department will need to plan ahead in some detail, to ensure that the various process safety reviews and hazard studies are scheduled and resourced.

Increasingly, safety personnel are involved in technical matters. Typical areas where safety personnel have had a strong technical input in recent years include inherently safer design, trip systems, isolation arrangements, hazard identification techniques, hazard analysis, quantitative risk assessment and emergency planning.

The safety department will have a substantial commitment to education and training. This includes such essential aspects as: induction and refresher training on safety matters; and exercises and drills for emergencies such as a fire or toxic gas release and for fire fighting. But its activities should also go beyond this and should extend in two further directions in particular. One is the creation of the safety culture and the dissemination of good practice. The other is training for new safety-related techniques. Examples of techniques introduced in recent years are hazop studies and quantitative risk assessment. In both cases, safety personnel have taken the lead in introducing the techniques and training engineers to apply the methods themselves. Safety training is considered further in Section 28.7.

Many of the activities described involve some form of communication. This is considered in more detail in Section 28.8.

28.2.3 Safety professionals

Personnel involved in work on safety and loss prevention tend to come from a variety of backgrounds and have a variety of qualifications and experience. It is possible, however, to identify certain trends. One is increasing professionalism. The appeal to professionalism is an essential part of the safety culture, and this must necessarily be reflected in the safety personnel. Another trend is the involvement in safety of engineers, particularly chemical engineers. A third trend is the extension of the influence of the safety professional.

The addition of a process safety course in many university chemical engineering curriculum has increased dramatically the safety awareness of recent graduates.

In the following section, an account is given of the role of a typical safety officer. Discussion of the role of the more senior safety adviser is deferred until Section 28.6.

28.2.4 Safety officer

The role of the safety officer is in most respects advisory. It is essential, however, for the safety officer to be influential and to have the technical competence and experience to be accepted by line management. The latter for their part are not likely persistently to disregard the advice of the safety officer if he possesses these qualifications and is seen to be supported by senior management.

The situation of the safety officer is one where there is a potential conflict between function and status. He may have to give unpopular advice to managers more senior than himself. It is a well-understood principle of safety organizations, however, that on certain matters, function carries with it authority.

The safety officer should have direct access to a senior manager, for example, works manager, should take advantage of this by regular meetings and should be seen to do so. This greatly strengthens the authority of the safety officer.

Much of the work of a safety officer is concerned with systems and procedures, with hazards and with technical matters. It should be emphasized, however, that the human side of the work is important. This is as true on major hazards plants as on others, since it is essential on such plants to ensure that there is high morale and that the systems and procedures are adhered to.

Although the safety officer's duties are mainly advisory, he may have certain line management functions such as responsibility for the fire fighting and security systems, and he or his assistants often have responsibilities in respect of the permit-to-work system.

28.2.5 Associated areas

Safety is commonly associated with one or both of two additional areas: (1) occupational health and (2) environmental protection.

The association of safety with occupational health is a long-standing one. In some cases the two have operated as separate, parallel functions, whilst in others one has been subsumed into the other. An account of the relationship between the two has been given by Kilian (1982). The increasingly strict requirements for industrial hygiene have resulted in a substantial expansion in occupational health, which mirrors that in safety and loss prevention.

As environmental protection has grown in prominence, it has become increasingly linked with safety. There appear to be a number of reasons for this. One is that it may be a matter of chance whether an incident results in injury to people or in acute damage to the environment. Another is that the loss prevention approach is broadly applicable also to environmental protection. A third is that it is often convenient to combine the safety and environmental functions.

28.2.6 Safety roles

A study of the role of safety specialists in industry from the viewpoint of the social scientist has been described by S. Dawson, Poynter and Stevens (1985).

They identify the three main activities of safety personnel as (1) processing and generating information, (2) giving advice and participating in problem solving and (3) taking direct action. These activities may be undertaken at any one of five stages of the technical control of hazards, namely (1) identification of hazards, (2) assessment of risk, (3) development of controls, (4) implementation of controls and (5) long-term monitoring and adaptation of risk and standards. They illustrate the matrix, which arises from this schema, as shown in Table 28.2.

With regard to the sources of influence to which the safety specialist has access, the authors identify: (1) formal

Table 28.2 *Safety specialist activities in relation to technical control of hazards (S. Dawson, Poynter and Stevens, 1985) (Reproduced by permission of Elsevier Science Publishers)*

Safety specialists' activities	*Stage of technical control*				
	Identification of hazards	*Assessment of risk*	*Development of controls*	*Implementation of controls*	*Longer term monitoring and adaptation*
A Processing information	Keeping accident statistics. Processing hazard information	Calculating accident frequencies, etc. Processing information on hygiene standards	Processing equipment manufacturers' information and lists of products, etc.	Processing orders for safety equipment	Comparing accident statistics over time
B Giving advice/ problem-solving					
Bl Passive adviser	Looking at work operations, on request. Investigating complaints	Answering questions about severity of hazards	Commenting on available controls which have been suggested	Commenting on effectiveness on request	Investigating accidents. Inspecting. Providing feedback on request
B2 Active adviser	Taking initiative in looking for hazards	Lobbying for appropriate standards, control limits	Recommending controls	Identifying shortfalls and improvements	Making recommendations for update/review of systems
C Taking direct executive action					
Cl Jointly with line management	Doing joint inspections and audits	Jointly deciding on standards	Jointly drawing up codes of practice	Joint supervision and approval or disapproval to jobs	Participating in reviews of arrangements
C2 Alone	Doing own inspections and audits	Deciding unilaterally what is safe/unsafe	Issuing instructions. Specifying controls to be followed	Supervising job. Exercising veto. Physically stopping people working	Modifying procedures, etc., on own initiative

organizational position; (2) managerial dependence on specialist expertise; (3) patronage by senior management; (4) direct role in the control process; (5) internal coalitions, for example, with the workforce; (6) external coalitions, for example, with the HSE; and (7) personal qualities.

In respect of the dependence of senior management on safety specialists, they see the relationship extending from one in which the safety function is required to assure compliance and to deal with external agencies to one in which it has increasing relevance to core managerial objectives and activities.

28.3 Safety Policy Statement

In both Europe and the United States, legislation has decreed that the company must protect workers from hazards of the plant.

The US Occupational Safety and Health Administration has a general duty clause. The general duty clause, Section 5(a)(1) of the Occupational Safety and Health Act of 1970, applies to all employers and requires each employer to provide employees with a place of employment which is free of recognized hazards that may cause death or serious physical harm.

The Health and Safety at Work etc. Act (HSWA) 1974, Section 2(3), states:

> Except in such cases as may be prescribed, it shall be the duty of every employer to prepare and as often as appropriate revise a written statement of his general policy with respect to the health and safety at work of his employees and the organization and arrangements for the time being in force for carrying out that policy, and to bring the statement and any revision of it to the notice of all his employees.

It is suggested, however, that in large or complex undertakings, it may be appropriate to divide the policy statement into two parts. The first should be a single document giving a concise statement of general policy, organization and arrangements, and the second a more detailed document, or collection of documents, including manuals of rules and procedures.

28.4 Safety Representatives

A system of safety representatives with responsibility for their fellow workers at a particular workplace has long existed in chemical works.

A safety representative is appointed by a trade union. He represents in the first instance, the employees who are members of that union, but may by agreement represent other employees also. The functions of the safety representative are to represent the employees in consultation with the employer.

His specific functions, typical of both the United States and European Regulations, are as follows:

(1) to investigate potential hazards and dangerous occurrences at the workplace (whether or not they are drawn to his attention by the employees he represents) and to examine the cause of accidents at the workplace;
(2) to investigate complaints by any employee he represents relating to that employee's health, safety or welfare at work;
(3) to make representations to the employer on matters arising out of sub-paragraphs (1) and (2) above;
(4) to make representations to the employer on general matters affecting the health, safety or welfare at work of the employees at the workplace;
(5) to carry out inspections in accordance with Regulation 5, 6 and 7 below;
(6) to represent the employees he was appointed to represent in consultations at the workplace with inspectors of the Regulatory Authority and of any other enforcing authority;
(7) to receive information from inspectors; and
(8) to attend meetings of safety committees where he attends in his capacity as a safety representative in connection with any of the above functions.

The safety representative should keep informed on the hazards of the workplace, the relevant legislation and the employer's safety policy, organization and arrangements. The employer's duty to disclose information is particularly important in relation to safety representatives. The Regulations require an employer to make available to safety representatives information which is within the employer's knowledge and which the representatives need to enable them to fulfil their function.

The information which the employer makes available should include:

(1) information about the plans and performance of their undertaking and any changes proposed insofar as they affect the health and safety at work of their employees;
(2) information of a technical nature about hazards to health and safety and precautions deemed necessary to eliminate or minimize them, in respect of machinery, plant, equipment, processes, systems of work and substances in use at work, including any relevant information provided by consultants or designers or by the manufacturer, importer or supplier of any article or substance used, or proposed to be used, at work by their employees;
(3) information which the employer keeps relating to the occurrence of any accident, dangerous occurrence or notifiable industrial disease and any statistical records relating to such accidents, dangerous occurrences or cases of industrial notifiable disease;
(4) any other information specifically related to matters affecting the health and safety at work of his employees, including the results or any measurements taken by the employer or persons acting on his behalf in the course of checking the effectiveness of his health and safety arrangements;
(5) information on articles or substances which an employer issues to homeworkers.

Another important right of the safety representative is to inspect the workplace. The guidance notes refer to the following types of inspection:

(1) safety tours – general inspections of the workplace;
(2) safety sampling – systematic sampling of particular dangerous activities, processes or areas;
(3) safety surveys – general inspections of the particular dangerous activities, processes or area.

The safety representative also has the right to carry out inspections following notifiable accidents, dangerous occurrences and notifiable industrial diseases.

The safety representative should act as a channel of communication between the management and the workforce on safety matters. The arrangements outlined create the conditions for a concerned individual to make a major contribution to the safety of his fellow workers.

The relation between safety representatives and safety committees is a flexible one. Safety representatives are not appointed by or responsible to safety committees, or vice versa. There are provisions to protect safety representatives from both civil and criminal legal action arising from the discharge of their duties.

28.5 Safety Committees

Feedback from works personnel on safety matters is often most effective through such informal channels as direct contact with a foreman or manager. The formal system consists of safety representatives and safety committees.

The most common practice requires the employer to establish a safety committee if requested to do so by at least two safety representatives. The guidance notes suggest that the objectives of a safety committee are to promote cooperation between employers and employees and to provide a forum for participation by employees in matters of health and safety and that specific functions might include:

(1) the study of accident and notifiable diseases statistics and trends, so that reports can be made to management on unsafe and unhealthy conditions and practices, together with recommendations for corrective action;
(2) examination of safety audit reports on a similar basis;
(3) consideration of reports and factual information provided by inspectors of the enforcing authority under the Health and Safety at Work Act;
(4) consideration of reports which safety representatives may wish to submit;
(5) assistance in the development of works safety rules and safe systems of work;
(6) a watch on the effectiveness of the safety content of employee training;
(7) a watch on the adequacy of safety and health communication and publicity in the workplace;
(8) the provision of a link with the appropriate inspectorates of the enforcing authority.

The existence of a safety committee does not in any way relieve management of its responsibility for safety, but such a committee can fulfil a valuable function in complementing the work of the professional safety personnel.

The response of management to suggestions made by the safety committee is very important. This does not mean that suggestions should always be accepted. But where they are not, a reasoned explanation should be given.

28.6 Safety Adviser

The safety department is led by a safety adviser. The approach taken by the safety adviser may well have a crucial influence on safety and loss prevention in the company. In the process industries, the work of the safety adviser is likely to have a large technical content. As loss prevention has grown in importance, so has the function of the safety adviser.

The role of the safety adviser is to a considerable extent what the person appointed makes of it. The approach taken by one safety adviser is illustrated by the work of Kletz, which is referred to frequently in this book. Some of the technological developments with which he is associated include: inherently safer design; hazop studies; hazard analysis, and the adoption of a quantitative approach generally; human factors; emergency isolation valves and trip systems; incident investigation; and safety education and training. Kletz has described his work in a number of books the titles of which are given in Chapter 27.

The work of other safety advisers mentioned in this book includes that of W.B. Howard (1983, 1984), Lynskey (1985) and Searson (1982, 1983).

28.7 Safety Training

Training in safety is important both for management and for workers. Some of the general principles which should govern such training are outlined in Chapter 14. The discussion here deals primarily with the content of training.

Guidance on safety training includes the many books issued by the AIChE Center for Chemical Process Safety, and the Safety series of the IChemE. Managers require training, particularly in technical aspects of safety and in the loss prevention approach, in company systems and procedures, in the division of labour between the company's specialist safety personnel and themselves, and in training workers. Some topics in safety training for managers are listed in Table 28.3.

Any of the usual methods of training may be used, but particular mention should be made of case studies of incidents, which have proved especially effective. A number of case studies, often with audio-visual material have been

Table 28.3 *Some topics in safety training for managers*

Managerial responsibility for safety and loss prevention
Legal requirements, in particular the Health and Safety at Work etc. Act 1974, the Factories Act 1961, the CIMAH Regulations 1984 and the COSHH Regulations 1988 and the work of the Health and Safety Executive
Principles of safety and loss prevention
Company's management system in relation to safety and loss prevention
Company safety policy, organization and arrangements, including safety personnel, safety representatives and safety committees
Hazards of the particular chemicals and processes
Accidents and accident prevention, including accident statistics and case studies
Pressure systems
Trip systems
Principle of independent assessment
Plant maintenance and modification procedures, including permits-to-work and authorization of modifications
Fire prevention and protection
Emergency planning arrangements
Training of personnel
Information feedback
Good housekeeping
Sources of information on safety and loss prevention, including both people and literature
Case histories

produced by ICI and the IChemE. These include some of the case histories given in Appendix 1.

In addition, managers should also be familiar with the material which workers need to know. Workers require training particularly in recognition of hazards, in systems of work, in the use and location of safety equipment, and in actions to be taken in particular situations. Some topics in safety training for workers are listed in Table 28.4.

For process operators, the list given in Table 28.4 is complementary to that in Table 14.11, which covers more general aspects, but includes many which have a large safety content. In particular, aspects such as the identification of equipment are very important. Table 28.4 makes reference to various kinds of equipment such as those for personal protection, fire fighting, first aid and rescue. It is important that the training covers all aspects of its use, including when to use it, how to use it and where to find it.

Safety training should be included in the initial induction course so that the worker does not endanger himself and his fellows when he first goes onto the plant.

This initial training should be supplemented as soon as possible by more thorough safety training.

The supervisor, or foreman, has a particularly important part to play in training workers.

Training needs to be supported by documentation of various kinds. The plant design and operating manuals are key documents for training. In particular, the use of task analysis to assist in the development of operating procedures and operating manuals has been described in Chapter 14 and the writing of operating manuals in Chapter 20.

There is also a need for documentation more specifically concerned with safety in aspects such as company safety rules and procedures, procedures in the case of fire and information on chemicals. Data sheets describing the properties and handling of individual chemicals are issued by various bodies.

Again case studies of incidents are an especially effective training technique. Atherton (1971) has described an interesting variation of this method in which the case study material consisting of slides and voice recordings was itself developed by a team comprising managers and workers. The incident selected for reconstruction was a real accident, in which a fitter removed a blank from a sulfuric acid line and received chemical burns. Extracts from the dialogue and points arising are shown in Table 28.5.

Table 28.4 *Some topics in safety training for workers*

Workers' responsibility for safety
Legal background, in particular the Health and Safety at Work etc. Act 1974 and the Factories Act 1961
Company safety policy, organization and arrangements, in particular general safety rules, safety personnel, safety representatives and safety committees
Hazards of the particular chemicals and processes
Fire/explosion hazard (flammable mixture, ignition source). Ignition sources and precautions, including hazardous area classification, static electricity, welding, smoking. Fire spread, fire doors. Action on discovering fire or unignited leakage.
Toxic hazard. Action on discovering toxic release
Emergency arrangements, including alarm raising, alarm signals, escape routes, assembly points
Protective clothing, equipment use and location
Fire fighting methods, equipment use and location
Rescue methods, equipment use and location
First aid methods, equipment use and location
Lifting and handling
Permit and handover systems
Security, restricted areas
Good housekeeping
Accident reporting
Health, medical aspects
Case histories
See also Table 14.10

28.8 Safety Communication

A major aspect of the activity of safety personnel is communication in its various forms. This follows from the advisory role of the safety function. For the most part, communication takes place as a result of the participation of safety personnel in the various activities such as process safety reviews and hazard studies, emergency planning, safety training and safety cases. Such participation can be an effective means of creating and maintaining the safety culture.

In addition, it should be one of the aims of the safety department to exploit a range of communication techniques

Table 28.5 *Extracts of dialogue from an accident case history reconstructed for training purposes (Atherton, 1971) (Courtesy of the Institution of Chemical Engineers)*

(a) Start of incident

Dialogue

Maintenance foreman: In the morning, Len, I want to put B2 pump in on the weak circulation tank in C.D.

Process foreman: O.K., George, I'll have a clearance ready for you. There's no need for me to be there, you know the job. I'll put a chalk mark on the flange where the blank has to be removed. Just tell the fitter to be careful but he'll know what he is doing.

(b) The fitter is about to remove the blank

Dialogue

Fitter: Right, can you pass me the 5/8 in. spanner, Chris?

Apprentice: O.K.

Fitter: I'll start on these back bolts first. By hell These are tight.

Apprentice: How long have these been in?

Fitter: They look like originals, don't they?

Apprentice: Aye.

Fitter: I think we'll start on these front ones first, they look a bit easier.

Points arising

1 Poor attitude by supervisor
2 Poor identification of equipment
3 Assumes the fitter knows the properties of the chemicals with which he will come into contact
4 No mention of any specific instructions
5 Question clearance procedure

Points arising

The man knows the correct procedure, but takes a short cut (a common theme of many accidents)

to inform and motivate people at all levels in the organization. Matters on which it will wish to communicate include developments in regulatory requirements, developments in technology, and good practice in safety.

There are a variety of techniques which are used to do this. There is commonly a safety newsletter. Table 28.6 shows some of the topics dealt with in issues of the *ICI Safety Newsletter*. Important features are that the topics are matters of concern and that the comments made are clear, practical, reasoned and authoritative.

Incident investigations and case histories, and the lessons drawn from these, provide concrete illustration of the principles. Incidents within the company are likely to make most impact, but it should be the case that these are not numerous enough to transmit the message, so that it is necessary to draw also on case histories from elsewhere. A detailed account of incident investigation and of the approach to drawing the lessons is given in Chapter 27.

The potential of case histories is not exhausted by recounting them in a newsletter. As described above, they should also be used in workshops, in which the group is invited to carry out its own analysis of the lessons to be learned and to formulate its own recommendations.

In addition to providing general reinforcement of the safety culture, such communication addresses two specific problems. One is raising the safety awareness of fresh and inexperienced personnel. Another is arresting the decay of procedures whose purpose is liable be forgotten if some time has elapsed since an incident occurred.

Another form of communication is to draw the attention of management to deterioration in the operation of systems and procedures and to malpractices. This is effective but requires a certain skill.

Table 28.6 *Some questions I am often asked (after ICI Safety Newsletter)*

1	66/8	Do we spend more on safety than other companies?
2	67/4	Would two small plants be safer than one big one?
3	68/7	How can we change people's attitude to safety?
4	69/4	What is our policy on safety?
5	70/5	Men are unreliable so should we try to make out plants fully automatic?
6	71/9	Who should take the decisions on safety matters – the manager or the safety officer?
7	72/5	How can we keep alive the memory of incidents that have happened on the plant when the staff change every few years?
8	73/1	How will the new Health and Safety at Work Act affect us?
9	74/6	Is there any easy way to get people interested in the plant safety book?
10	75/6	How often will an operator act correctly when an alarm sounds?
11	76/6	Most of our checking will show nothing wrong – so what is our incentive to continue?
12	77/7	Why does the Petrochemical Division board issue so few directives on safety?
13	78/12	Can you recommend some books which will give me some background information on loss prevention?
14	79/5	Are we expected to learn the lessons of accidents which have occurred somewhere else?
15	80/8	How long should a manager spend on a plant?
16	81/9	Why don't 'they' do more about safety (or plant tidiness or training)?
17	82/8	Do you put forward minimum standards? Can you go further than you suggest as long as you do not do less?
18	84/7	Flixborough has been described as the price of nylon – is it worth it?
19	85/6	How does our safety record compare with other companies?
20	86/4	In our designs, should we assume that people make mistakes?
21	87/5	What should we do to old plants when standards change?
22	88/6	How can I find out quickly and easily what has been written and recommended about subjects I am interested in at the moment?
23	91/8	Do we really need to do an operability study as this is only a very simple project (or it is very similar to the last one)?
24	92/6	What should we do to improve the safety record?
25	94/6	Are we willing to give information on safety to other companies?
26	95/5	Which airline should I fly?
27	96/5	What is the difference between operability studies and hazard analysis?
28	97/8	Is the *Safety Newsletter* issued free?
29	98/9	Do we spend too much money and effort on the problems that the press and TV publicize?
30	99/8	Can we get the money needed for safety?
31	100/6	What, in six words of one syllable, is the biggest single cause of accidents?
32	102/9	Can I be prosecuted if there is an accident on a plant which I work on or which I have designed?
33	108/7	What's new?
34	117/2	Does ICI add on more protective equipment than other companies?
35	119/5	How does ICI compare with other companies?
36	121/7	What should I do if a Factory Inspector asks me to do something which I think is unnecessary or even unsafe?
37	123/2	If we install a lot of automatic trips and controls on our plant, will we turn operators into zombies?
38	124/6	Has all the money and effort put into technical safety in the last 10 years produced any results?

28.9 Safety Auditing

A major aspect of the work of the safety department is auditing. Audits are the periodic examination of the functioning of the safety system. Accounts of auditing are given in *Safety Auditing* (Kase and Wiese, 1990) and by D. Williams (1971), Madhavan and Sathe (1987), Madhavan and Kirsten (1988), Madhavan and Landry (1988), Monk (1988), Tweeddale (1992), Ozog and Stickles (1992), D. Scott and Crawley (1992), J. Lockwood (1993), Sankaran (1993), Hurst and Ratcliffe (1994) and Hurst, Hankin *et al.* (1994).

28.9.1 Types and time-scales of audit

The overall system of control and auditing needs to operate at three levels, which correspond to increasingly long time-scales:

Level	*Time-scale*
1	Monitoring of outputs of systems and procedures Short term, essentially continuous
2	Audit of implementation of systems and procedures. Medium term
3	Audit of functioning and appropriateness of systems and procedures. Long term

Subjects of audit at both Levels 2 and 3 should be (1) the safety management system of the company, (2) the safety management system and operation of the plant and (3) special features of the plant.

Some of the audit activities of a safety officer are shown in Table 28.7, which is adapted from a more detailed table on safety audits given by D. Williams (1971). Important points illustrated by this table are the involvement of management at all levels, the training of both management and workforce, and the role of systems and procedures.

28.9.2 Company audits

The overall safety management system of the company should be subject to audit. At Level 2 the audit should check that the systems established are being operated and at Level 3 that these systems are still appropriate.

28.9.3 Plant audits

At plant level, there should be a post-commissioning audit carried out soon after a plant has been commissioned. Audits should then be repeated at intervals throughout the life of the plant. Plant audits should cover the safety management system of the plant, including operation, maintenance and control of change.

A structure for the conduct of the audit of a safety management system is available in the STATAS method described in Chapter 6.

28.9.4 Special feature audits

These general audits may be supplemented by audits in which some particular feature is examined in greater depth. Typical topics for such special feature audits might be the fire protection system or the permit-to-work system.

28.9.5 Audit aids

The conduct of a plant audit is assisted by the use of aids such as checklists. A structured set of checklists related to the root causes of accidents is typically used. This is described in Chapter 8.

28.9.6 Audit procedure

The effectiveness of an audit is highly dependent on the technique used. There is some guidance available on these practical aspects of auditing.

Tweeddale (1990, 1993) describes an approach to the auditing of a typical management system, taking as an illustration the auditing of a procedure for maintenance work permits. He sets four questions, or hurdles:

(1) Do you have a procedure for. . .?
(2) What are the main objectives of that procedure?
(3) How do you know whether that procedure is being properly applied in your area?
(4) Do you have to report to anyone about how well that procedure is being applied?

He shows how much these relatively simple questions can reveal.

28.9.7 Audit quality

Considerable effort is expended on audits in the process industries, but much of it is relatively ineffective in discovering defects in the systems examined. The quality of audit is crucial.

The point is illustrated by the audits conducted on Piper Alpha. Audits of various kinds were quite frequent, but none had picked up the numerous defects in the permit-to-work system. Yet once the Inquiry began, these defects were quickly laid bare in the evidence of the witness on this topic (Lockwood, 1989). This evidence repays study. The Piper Alpha Report is critical of the quality of the audits carried out.

28.10 Safety Rating

Some companies utilize as part of the safety system a safety rating system. Use may be made of a system developed in-house or of one of the proprietary systems. Three systems are described below – the ISRS, MORT and MANAGER systems – as illustrations of the types of system available.

A number of the accounts of audits referred to in Section 28.9 also contain rating schemes of various kinds.

28.10.1 Management and oversight risk tree

One such system is the Management and Oversight Risk Tree (MORT) described in MORT Safety Assurance Systems (W.G. Johnson, 1980). This system has been mentioned earlier in Chapters 2 and 27.

MORT provides a methodology for assessing a situation which may lead to an undesirable outcome such as injury or damage. The basic logic tree of MORT is shown in Figure 2.3. This MORT tree contains in structured form many of the basic concepts of safety management and engineering, including the concepts of: vulnerable targets, harmful energy, precursor events, barriers to escalation, mitigation of consequences, management policy formulation, management policy implementation and risk assessment.

28.10.2 International safety rating system

The International Safety Rating System was developed by Bird and co-workers at the International Loss Control Institute (ILCI) at Georgia State University. The philosophy

Table 28.7 *Some safety audit activities (after D. Williams, 1971) (Courtesy of the Institution of Chemical Engineers)*

Activity		*Interval* (month)
Plant safety review	Review of adequacy of operations, equipment and building safety	12
Job safety analysis	Reviews of standard operating procedures. Update where necessary	12
Operator review	Check for deviation from standard operating procedures and on work habits	6
Supervisors' safety meetings	Education, training, drills, follow-up	3
Management development seminar	Development of managerial competence	1
Supervisory training	Training of foremen for supervisory role	1
Safety committee	Motivational safety suggestions	1
Plant manager's meeting	Communication, education, training, innovation, follow-up	1
Foremen's meeting	Communication (vertical, horizontal), motivation, education, training	1
Critical incident technique	Observation of unsafe acts, conditions. Reports of near misses	1 Plus continuous observation
Central plant safety	Safety policy	As needed
Safety review committee	Review of safety of new processes and/ or equipment	As needed
Works safety procedures review	Review of work safety procedures	As needed

underlying the system is given in *Practical Loss Control Leadership* (Bird and Germain, 1985). The evolution of the system has been described by Bond (1988 LPB 80).

The system developed as the Five Star Rating System, was refined jointly with the South African Chamber of Mines to yield the International Mining Safety Rating System, and was finally generalized to give the ISRS. There are several versions of the system, including one for petrochemicals. The elements of the system are given in Table 28.8.

An account of the application of the system in a refinery has been given by Arnold, Redfearn and Maaren (1992) and of its application elsewhere by Eisner and Leger (1988) and Pringle and Brown (1990).

Table 28.8 *Elements of International Safety Rating System*

1. Leadership and administration
2. Management training
3. Planned inspections
4. Job analysis and procedures
5. Accident/incident investigation
6. Planned job observation
7. Emergency preparedness
8. Organizational rules and regulations
9. Accident/incident analysis
10. Employee training
11. Personal protective equipment
12. Health control and services
13. Programme evaluation system
14. Purchasing and engineering control
15. Personal communications
16. Group meetings
17. General promotion
18. Hiring and placement
19. Records and reports
20. Off-the-job safety

28.10.3 MANAGER system

The MANAGER system described by Pitblado, Williams and Slater (1990) and outlined in Chapter 9 was developed to assist in estimating the effect of the quality of management in quantitative risk assessment. A feature of the method is that it seeks to take account of all areas shown to be important in accident causation and of the incorporation of widely accepted management principles in all key elements of the safety management system.

28.10.4 Critique of rating systems

As mentioned in Chapter 6, a critique of safety rating, or packaged audit, systems has been given by D. Petersen (1989). He cites studies indicating that most packaged audit systems do not contain many of the elements found to be critical to safety performance and, on the other hand, that they do contain elements which fail to correlate with safety performance.

29 Computer Aids

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The use of computers in the design and control of process plants is now widespread. The use of safety-related computer aids is described briefly in this chapter. A more general discussion of chemical engineering computer software is contained in Lees 2nd edition; however, the availability of software is changing too fast to simply develop a list. The list would be out dated before publication. The World Wide Web with its concomitant search capability has made published software lists out dated.

Rather than provide exhaustive lists, the generic type of available software, as it applies to loss prevention will be described herein. However, reference has already been made in a number of chapters to various specialist computer codes pertinent to the technology under discussion, such as those for consequence analysis and hazard analysis.

29.1 Computer Aided Process Engineering

Some of the principal codes for process plant design in CAD, or computer aided process engineering (CAPE), are now reviewed, considering first individual programs and then integrated packages.

29.1.1 Process selection

The selection of the process is perhaps the most fundamental problem in process design and it is a tough one. An account of the developments in the computer aiding of process route selection is given in Chapter 30.

29.1.2 Physical, thermodynamic and phase equilibrium properties

A package that furnishes physical, thermodynamic and vapour–liquid equilibrium properties is an essential service package for process design. Some of the packages are part of a suite of programs, typically supporting a flow sheet simulator.

29.1.3 Flow sheet simulation

Flow sheet simulation, handling the mass and energy balances, is the heart of the process design package. Much theoretical work has been done to produce codes that are efficient, particularly in handling features such as recycles. The core of a system for process plant design is the program, which performs the steady-state mass and heat balances, also called the process simulator. There are two main types of process simulators. The sequential modular (SM) simulator consists of a sequence of modules for the various unit operations performed. A basic set of modules is a mixer, a divider and a reactor. The equations of each unit operation are solved sequentially. The equation oriented (EO) simulator, by contrast, solves the equations of the whole system simultaneously. An SM simulator can accommodate more readily a variety of types of model in the modules, including user configured models, whereas the EO simulator scores for features which span a number of units such as recycles, control systems and constraints.

The process simulator forms the core of an integrated CAPE system. This core program draws on programs offering other facilities. These include physical properties, equipment sizing, cost and economics, and dynamic simulation packages. An important feature of a fully integrated CAPE system is the database. The database may contain files on a wide variety of aspects of the design, from flows, pressures and temperatures to material take-offs. Different CAPE systems start from different starting points. One may start from a graphics facility, another from a process simulator. Consequently, the systems have different strengths and weaknesses.

The degree of integration in current CAPE systems is not always as advanced as might be assumed. Typically a two-dimensional package will have its own database, which allows it to draw symbols representing plant units, but it does not identify the symbols as units such as vessels or heat exchangers, and does not have associated information about the units. In other words, it is purely a drawing package. This means that it cannot readily be used to capture the data about the units required for a package to perform a function such as fault tree synthesis.

CAPE systems typically have the capability to perform the following project functions:

(1) analysis of layout designs –
  (a) conceptual designs,
  (b) detailed designs;
(2) checking of designs against standards;
(3) control of project information;
(4) generation of documents and listings;
(5) archiving of project information.

29.1.4 Piping and instrument diagrams

Closely linked to the flow sheet simulation is the generation of the process flow diagram (PFD) or piping and instrument diagram (P&ID).

29.1.5 Process synthesis

Closely linked to the mass and energy balances is the thermal economy. These include computer programs for heat exchanger network design and for process synthesis using pinch technology.

29.1.6 Cost and economic estimates

Another essential service package is a program, which furnishes cost data and can be used to estimate the costs of designs.

29.1.7 Engineering units conversion aids

Aids for conversion between different chemical engineering units will always be necessary until a global standard is widely utilized.

29.2 Pipework and Fluid Flow

Programs for pipework are of several different types. One group performs the fluid flow calculations for piping and piping networks. Programs of this type include:

(1) two-phase flow;
(2) flash-off and flash drums;
(3) unsteady-state flow;
(4) flow through control valves;
(5) flow through rotating machinery;
(6) pipeline leak detection.

29.3 Unit Operation and Equipment

There are a number of programs for the design of unit operations and equipment of various types. Programs exist not just for shell and tube heat exchangers but also for

air-cooled heat exchangers, thermosyphon reboilers, furnaces and heat exchanger networks:

(1) chemical reactors;
(2) distillation columns;
(3) fired heaters;
(4) solid–liquid separation;
(5) flare systems;
(6) steam systems;
(7) pumps and compressors.

29.4 Databases, Bibliographies and Indexes

Physical, chemical and toxic properties: there are a number of databases, or data banks, for the physical, chemical and toxic properties of materials. The databases are often associated with a government agency or technical society, such as the following:

Registry of Toxic Effects of Chemical Substances (RTECS), supplied by the National Institute for Occupational Safety and Health (NIOSH);
HSDE created by the NLM as part of its Toxnet data system;
Oil and Hazardous Materials Technical Assistance Data System (OHMTADS), supplied by the Environmental Protection Agency (EPA); and
Chemical Hazard Response Information System (CHRIS) supplied by the US Coast Guard.
NIOSHTIC, supplied by the NIOSH;
HSELINE, supplied by the Health and Safety Executive (HSE);
CISDOC, supplied by the International Occupational Safety and Health Information Centre of the International Labor Office (ILO);
MHIDAS, covering hazardous incidents, supplied by the Safety and Reliability Directorate;
TOXLINE, supplied by NLM;
RISKLINE, supplied by the National Chemical Inspectorate of Sweden;
BIOSIS, CAS, IPA and TOXBIB. PEST-BANK, supplied by the National Pesticide Information System, gives the key registration data of all US registered pesticides.
European Inventory of Existing Commercial Chemical Substances (EINECS) is an inventory of European commercial chemicals.
International Nuclear Information System (INIS) is supplied by the IAEA Medical databases, which include MEDLINE and CANCER.
Another set of databases is those from Microinfo. They include HAZARDTEXT (safe handling and incident response), INFOTEXT (regulatory listings), MEDITEXT (evaluation of exposed individuals) and SARATEXT (toxicity, Sara Title III)
The Bretherick Reactive Chemical Hazards Database is the database version of the *Handbook of Reactive Chemical Hazards* (Bretherick, 1990b).
CHEMSAFE and CHEMTOX are, respectively, compendia of the flammability and toxic properties of a large number of substances.
A number of specialty databases on medical subjects are available from Elsevier Science Publishers, including the *Excerpta Medica* database EMBASE.
IRIS is a database of monographs in support of the assessment of the risk from a large number of chemicals.

There are three incident data banks operated by SRD. MHIDAS is the Major Hazard Incident Data Service. The other two are the Explosion Incidents Data Service (EIDAS) and the Environmental Incidents Data Service (EnvIDAS). In addition to MHIDAS, AEA Technology offers the AIRS code for the recording of incidents in the workplace.

Another computer-based incident data bank is FACTS, of TNO.

29.5 Compliance Management

There are quite a large number of programs to assist with compliance with regulatory requirements, mainly for the United States.

29.6 Computational Fluid Dynamics

Codes for computational fluid dynamics (CFD) find widespread use both in design and in hazard assessment.

29.7 Hazard Identification

There are a number of codes available to assist in the conduct of the various techniques for hazard identification. Aids for hazard and operability (HAZOP) analysis are particularly valuable with the housekeeping and follow-up aspects. Computer codes exist for a number of hazard models, and indeed for the more complex models this is the only practical method of use. Some of the principal subjects are as follows: jets; vapourization from pools; pool fires; fire engulfment; flame impingement; explosion in, and explosion relief of, large enclosures; vapour cloud explosions.

29.7.1 Fault tree analysis

Details of aids to fault tree analysis. These cover the determination of the minimum cut sets, analysis for common cause failure, assessment of importance and sensitivity, quantitative analysis and uncertainty analysis.

29.8 Pressure Relief Devices Sizing

29.8.1 Reactor venting

The SAFIRE code for the venting of reactors, which implements the design methods developed by the Design Institute for Emergency Relief Systems (DIERS) as part of its design package for emergency relief.

29.8.2 Blowdown

Programs that calculate the emission flows from vessels, pipes and pipelines are:

BLOWDOWN (Imperial College)
BLOWSIM (UCL)

An account of BLOWDOWN is given by Haque, Richardson and Saville (1992).

29.8.3 Gas dispersion

One of the most important topics covered by such codes is gas dispersion, particularly dense gas dispersion. An account of gas dispersion models was given in Chapter 15. Different models are used for passive and dense gas dispersion.

Passive gas dispersion

Models for passive gas dispersion were described in Chapter 15. Manual calculation is possible with the simpler forms of model, but for most practical applications, particularly in air pollution modelling, use is made of computer codes.

There are now a large number of codes for specific situations such as multiple sources, complex terrain, urban conditions, and coastal and offshore locations.

The EPA advises certain codes as 'preferred' codes for air pollution modelling. The codes are listed with full details by Zannetti (1990). Zannetti also lists the codes advised by the EPA as 'alternative' as well as a large number of other programs.

Dense gas dispersion
Models for dense gas dispersion, also described in Chapter 15, have tended to be much more complex than those for passive dispersion, and for most such models, a computer program is essential.

Jets
The computer codes model jets of different density or buoyancy, jets with high and low velocity, jets with vertical, horizontal or angled orientation, jets in ambient wind and turbulent conditions, jets with two-phase flashing behaviour, and jets with airborne aerosol effects.

Vapourization from pools
Several computer codes for vapourization from pools have been developed.

Fire events
Programs for the calculation of the thermal radiation from a jet flame, a pool fire or a boiling liquid expanding vapour explosion (BLEVE) are widely available.

Condensed phase explosions
There are a number of programs that have been developed by the military to determine the effects of explosions, nuclear explosions and condensed phase explosions, including weapons.

Vapour cloud explosions
There are several computer codes for, or applicable to, the estimation of the blast from vapour cloud explosions.

29.8.4 Explosions in large enclosures

Codes for the simulation of explosions in large enclosures play an important role in the design of fire and explosion protection of offshore platforms. These programs solve the fundamental equations of fluid flow taking into account turbulence and combustion. The three-dimensional Navier–Stokes equations, suitably augmented to include the effects of turbulence and combustion, are cast in discrete form, employing a finite volume technique, and are solved implicitly. Turbulence is modelled in terms of eddy viscosity, and combustion is modelled in terms of a turbulent, mixing-limited reaction. The space modelled is divided into a grid of 'boxes' of 1 m^3 volume. Normal assumptions are that the gas cloud is a stoichiometric homogeneous, quiescent mixture. Ignition is modelled by assuming that at time zero, half the flammable mixture in one of the boxes has undergone combustion.

29.9 Hazard Assessment Systems

Some computer codes for hazard assessment systems are described here:

ARCHIE
The ARCHIE code of the Federal Emergency Management Agency (FEMA), from Hazmat America, contains a set of models for a variety of scenarios cast in a tree structure, which at the first level down include pressurized gas release, liquid release followed by vapourization from the pool, a closed tank engulfed in fire, and a condensed phase explosion, and at lower levels extend to events such as jet flame, flash fire, vapour cloud explosion and BLEVE. It is described in the *Handbook of Chemical Hazard Analysis Procedures* (FEMA, 1989).

SAFETI
The SAFETI code was developed for the Dutch Ministry of Housing, Physical Planning and Environment. This is a major code for the conduct of a complete probabilistic risk assessment (PRA). The development of the code was prompted by the Rijnmond PRA described in Appendix 8. The program performs a complete PRA for a fixed installation. It is designed for ease of input, speed of processing and transparency of results, both intermediate and final. It is also designed for minimum loss of detail, and allows the level of detail to be varied.

Details of the plant are entered into the PLANT program. A plant is organized in terms of 'units', which are linked by connecting 'pipes' to 'vessels'. Vessels and pipes have associated with them a set of 'equivalent discrete failures' (EDFs), essentially leaks and ruptures. Each failure is assigned a failure frequency, for which default values are supplied. Other input information includes the population density, defined by a grid; the density of ignition sources; and the meteorological conditions. There are databases for the failure frequencies, population, ignition sources and meteorology.

A set of eight release scenarios is used. These are: (1) an instantaneous release (by vessel rupture) of a flammable material; (2) a continuous pressurized release (from vessel or pipe) of a flammable material; (3) the vapourization of a refrigerated flammable liquid; (4) a pool fire; (5) a fireball or BLEVE; (6) an instantaneous pressurized release (by vessel rupture) of a toxic material; (7) a continuous pressurized release (from vessel or pipe) of toxic material and (8) the vapourization of a refrigerated toxic liquid. The program handles the development of these releases utilizing a set of four event trees, for which the starting events are one of the four possible combinations of instantaneous vs continuous and aerosol vs no aerosol in the cloud. The nodes in these event trees include the following queries: (1) Rainout? (2) Evapouration? (3) Pool left behind? (4) Pool of limited duration? (5) Essentially instantaneous? (6) Behaves as a free jet?

The hazard models used are described in Chapter 9. There are four gas dispersion models together with a set of models for vapourization from a pool, jet flames, fireballs, BLEVEs and vapour cloud explosions and probit equations for injury and damage.

The outcomes of the event trees for flammable releases are events that are then modelled, using the set of hazard models and probit equations. The results can be output in a variety of forms, including as risk contours, individual risks and frequency-number curves.

There are interactive facilities which permit the user to: bypass some or all of the automatic generation of EDFs and to replace them with alternative releases or events; replace a default failure frequency with an alternative value; and replace a standard hazard model with an alternative one.

WHAZAN

A rather simple code is WHAZAN, developed by Technica for the World Bank. It is described in the *Manual of Industrial Hazard Assessment* (Technica, 1986). WHAZAN provides a facility for the user to explore the consequences of a set of release scenarios. The core of the program is a set of hazard models. The program does not make estimates of the frequency of the scenarios or of the risks. WHAZAN is a much more modest package than SAFETI and was developed to run on a PC in the first instance.

RISKAT

The HSE has developed its own hazard assessment program entitled initially the Risk Assessment Tool (RAT), and latterly RISKAT. The essential features of this program have been described in Chapter 9 in connection with the HSE guide assessments for liquefied petroleum gas and chlorine.

29.10 Emergency Response Simulation

An aid to training personnel in the handling of emergencies is available in the form of the handling emergencies simulation system of the IChemE. The trainee assumes the role of the main incident controller and is responsible for controlling all personnel, and issuing operational commands. The program contains nine incident scenarios involving fire, toxic release and a combination of both. It uses a preplan entered by the trainee to determine how the scenario develops. The scenario highlights weak points in the preplan. In order to assist post-mortem analysis, a log is provided of events during the incident and of actions taken. There are several packages for the simulation in real time of the development of an emergency using suitable hazard models. The essential concept is that, in an emergency, the system is provided with certain key pieces of information, such as the material released, estimates of the location and size of the leak and the meteorological conditions, and gives a VDU display of the phenomenon such as plan and elevation contours of gas concentration.

One such system is SAFER (Dupont Safer Emergency Systems). The core of the code is a gas dispersion program together with data on the chemicals handled in the plant and their properties. The computer is provided with a network of instruments that measure meteorological conditions such as wind direction and speed. In an emergency, data are furnished to the computer both by these instruments and by operator inputs. SAFER is more than a computer code. It is essentially an emergency response system built around the computer package.

29.11 Transport

Hazard assessment systems for transport are not well represented. Transportation Risk screening programs, which support evaluation of the risks from different chemicals, transport modes and routes, typically are proprietary to special consultancy companies.

30 Artificial Intelligence and Expert Systems

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This chapter deals with artificial intelligence, expert systems and certain other advanced developments in computer aiding. The aim of the chapter is to provide an overview of the field and an appreciation of the sorts of problem which are tackled, the types of technique developed, the terminology used and the applications made.

Accounts of artificial intelligence (AI) include *Artificial Intelligence* (Winston, 1984), *Introduction to Artificial Intelligence* (Charniak and McDermott, 1985), *Introduction to Knowledge Based Systems* (Frost, 1986), *Introduction to Artificial Intelligence and Expert Systems* (Patterson, 1990), *The Elements of Artificial Intelligence* (Tanimoto, 1990) and *Encyclopaedia of Artificial Intelligence* (Shapiro, 1992).

An important area of AI is expert systems. A large proportion of the AI applications in the process industries are of this nature. Expert systems are therefore given particular attention in this chapter.

Most accounts of AI are written in a style that makes extensive use of lines or sections of computer programs. For the most part this practice has not been adopted here. The aim has been to couch explanations in natural language. Some limited use has been made of program-type material, however, purely in order to give a feel for the approaches taken. The expressions principally used are related to the predicate calculus. This has influenced the order of treatment of the subjects in the chapter. The account of programming languages is placed after the account of predicate logic but before most of the other topics where program-type material may be used.

Selected references on AI and on expert systems are given in Table 30.1.

Table 30.1 *Selected references on artificial intelligence, expert systems and advanced aids*

A General

Hempel (1952); Craik (1943); Bruner, Goodnow and Austin (1956); Vickers (1968); Simon (1969); Lindsay and Norman (1972); J. Anderson and Bower (1973); Schank and Colby (1973); Bobrow and Collins (1975); J. Anderson (1976); Weizenbaum (1976); Sternberg (1982); Schon (1983)

Artificial intelligence

Bowden (1943); Turing (1950, 1963); Feigenbaum and Feldman (1963); Newell and Simon (1963, 1972); Minsky (1967); Ernst and Newell (1969); Findler and Meltzer (1971); Nilsson (1971, 1980); lighthffl (1973); Michie (1974, 1982a,b,d, 1983); E.B. Hunt (1975); Rubin (1975); Raphael (1976); Boden (1977); Winston (1977); Latombe (1978); Feigenbaum (1979, 1983); N. Graham (1979); Nii and Aiello (1979); Charniak, Riesbeck and McDermott (1980); Barr and Feigenbaum (1981–); Schank and Riesbeck (1981); P.R. Cohen and Feigenbaum (1982); Szolovits (1982); Feigenbaum and McCorduck (1983); Hayes and Michie (1983); Michalski, Carbonnell and Mitchell (1983); Rich (1983); Durham (1984b); O'Shea and Eisenstadt (1984); Reitman (1984); Simons (1984, 1988); Sowa (1984); Winston and Prendergast (1984); Charniak and McDermott (1985); P.R. Cohen (1985); Hillman (1985); J.J. Richardson (1985); Shirai and Tsujii (1985); Frost (1986); Kanal and Lemmer (1986); C. Williams (1986); Yazdani (1986); Gevarter (1987); Cleal and Heaton (1988); Ramsay and Barret (1987); Jezzard (1988); Savory (1988); W.A Taylor (1988); Mirzai (1990); Patterson (1990); Tanimoto (1990); Martins (1992); Shapiro (1992)

Expert systems

Waterman and Hayes-Roth (1978); Chisholm and Sleeman (1979); Michie (1979, 1980, 1981, 1982a–d); Waterman (1979, 1981, 1985); Reboh (1980); Addis (1982); R. Davis (1982); R. Davis and Lenat (1982); Sacerdoti (1982); Stefik *et al.* (1982); Bigger and Coupland (1983); Bramer (1983, 1984); Duda and Shortliffe (1983); Hayes-Roth, Waterman and Lenat (1983); Naylor (1983); Stefik and de Kleer (1983); Swartout (1983); Weiss and Kulikowski (1983); Alty and Coombs (1984); Alvey, Myers and Greaves (1984); V. Begg (1984); Durham (1984a, 1985a); Forsyth (1984a,b); R. Brown (1985); A. Goodall (1985); Gupta, Bandler and Kiszka (1985); Harmon and King (1985); Hayes-Roth (1985); Michaelson, Michie and Boulanger (1985); Mill (1985); Politakis (1985); Sell (1985): Denning (1986); Dreyfus and Dreyfus (1986); Elliot (1986); Frost (1986); S. Hughes (1986); Keravnou and Johnson (1986); L. Moskowitz (1986); Myers (1986); S. Wood (1986); Hu (1987); Kerridge (1987); Quinlan (1987); Shapiro (1987); Slatter (1987); Sturridge (1987); Cleal and Heaton (1988); Evitt and Mukaddam (1988); A. Goodall (1988); Greenwell (1988); Huang and Fan (1988); Ince (1988); Madni (1988); J. Martin and Oxman (1988); Parsaye and Chignell (1988); Pham (1988); Savory (1988); C. Tayler (1988b); Waters and Nielsen (1988); J.A. Campbell and Cuena (1989); Lien (1989); Madhavan and Kirsten (1989); Vadera (1989); Ferrada and Holmes (1990); IEE (1990 Conf. Publ. 322, 1991 Coll. Dig. 91/26); Patterson (1990); Ford (1991); Mitter (1991); Gonzales and Dankell (1993)

Knowledge acquisition

R. Davis (1977, 1978); Waterman (1978, 1981); Chisholm and Sleeman (1979); Nilsson (1980); Hayes-Roth, Waterman and Lenat (1983); Weiss and Kulikowski (1983); Sell (1985); Boose (1986); Kidd (1987); Chignell and Petterson (1988); Norman and Naveed (1988); Diaper (1989); Aldersey, Lees and Rushton (1993)

Knowledge representation

Michie (1974); Winograd (1975); Hayes (1977); Lyons (1977); Winston (1977); Barr and Feigenbaum (1981–); Culicover (1982); Hayes-Roth, Waterman and Lenat (1983); Israel (1983); Weiss and Kulikowski (1983); Simons (1984); Harmon and King (1985); Sell (1985); Beynon and Davies (1987); Hodgson (1991)

Language: Chomsky (1957); Winograd (1972, 1983); Lawson (1982); Pinker (1984); Cullingford (1986); J. Allen (1987)

Pattern recognition: Fu (1981)

Vision: H.C. Andrews (1970); Hanson and Riseman (1978); Ballard and Brown (1982); Marr (1982); Horn (1986)

Logic: Stebbing (1942); Lukasiewicz (1951); Suppes (1957); Kleene (1967); Ennis (1969); Nilsson (1971, 1980); Lemmon (1972); Manna (1973); Shafer (1976); van Emden (1977); Hodges (1978); Kowalski (1979); R. Turner (1984)

Predicate calculus: Larson and Michalski (1977); Nilsson (1980); Clocksin and Mellish (1981); Hayes-Roth, Waterman and Lenat (1983); Alty and Coombs (1984)

Incidence calculus: Bundy (1984)

Heuristics: Polya (1954, 1957); Buchanan, Feigenbaum and Sridharan (1972); Wickelgren (1974); Sussman and Stallman (1975); Pearl (1984)

Procedural representation: Raphael (1968); Hewitt (1972)

Production systems, rules: Newell (1973); R. Davis and King (1976); R. Davis, Buchanan and Shortliffe (1977); Winston (1977); Waterman and Hayes-Roth (1978); van Melle (1979); Nilsson (1980): Barr and Feigenbaum (1981–); Winston and

Horn (1981); Alty and Coombs (1984); Simons (1984); Harmon and King (1985); Sell (1985)
Semantic networks: Minsky (1968); J. Anderson and Bower (1973); Simmons (1973); Michie (1974); Norman and Rumelhart (1975); Winston (1977, 1984); Duda *et al.* (1978); Chisholm and Sleeman (1979); Rychener (1979); Nilsson (1980); Barr and Feigenbaum (1981–); Alty and Coombs (1984); Simons (1984); Harmon and King (1985); Sell (1985)
Semantic primitives: Wilks (1975); Schank and Abelson (1977); Winograd (1978)
Frames: Kuipers (1975); Minsky (1975); Bobrow and Winograd (1977); Schank and Abelson (1977); Winston (1977, 1984); Barr and Feigenbaum (1981–); Winston and Horn (1981); Alty and Coombs (1984); Harmon and King (1985)
Bayesian logic: Duda, Hart and Milsson (1976); Naylor (1983); Weiss and Kulikowski (1983); Alty and Coombs (1984); Sell (1985)
Fuzzy logic: Zadeh (1965, 1968, 1975a,b, 1978, 1979, 1983a,b, 1985, 1992); Zadeh and Fukanaka (1975); Gaines (1976); Gaines and Kohout (1977); Dubois and Prade (1980); Mamdani and Gaines (1981); Forsyth (1984c); Kacprzyck (1983, 1992); Zimmerman (1984, 1986, 1987); di Nola *et al.* (1989); Zadeh and Kacprzyck (1992)
Odds: Michie (1982a)

Operation, control, search
Control strategies: Winston (1977, 1984); R. Davis (1980a,b); Nilsson (1980); Hayes-Roth, Waterman and Lenat (1983); Alty and Coombs (1984); Harmon and King (1985); Sell (1985)
Search: Doran and Michie (1966); Doran (1968); Michie (1974, 1982b); Winston (1977, 1984); Charniak, Riesbeck and McDermott (1980); Nilsson (1980); Barr and Feigenbaum (1981–); Gardner (1981); Winston and Horn (1981); Hayes-Roth, Waterman and Lenat (1983); Alty and Coombs (1984); Simons (1984); Montgomery (1991)
Forward chaining, backward chaining, backtracking: Charniak, Riesbeck and McDermott (1980); Nilsson (1980); Winston and Horn (1981); Weiss and Kulikowski (1983); Alty and Coombs (1984); Winston (1984); Harmon and King (1985)
Inference engine: Hayes-Roth, Waterman and Lenat (1983); Naylor (1984)

Problem-solving
Games and puzzles: Michie (1974)
Draughts (checkers) and chess: C.E. Shannon (1950a,b); Newell, Shaw and Simon (1958); Samuel (1959, 1960, 1963a,b, 1968); Michie (1974); Newborn (1975); Shapiro and Niblett (1982)
Theorem-proving: C.C. Green (1969); Michie (1974)
GPS: Newell, Shaw and Simon (1960); Newell and Simon (1963); Ernst and Newell (1969)

Facilities
Blackboard systems: Engelmore and Morgan (1988)
Questioning, questionnaires: Weiss and Kulikowski (1983)
Explanation: A.C. Scott *et al.* (1977); W.J. Clancey (1979, 1983); Hayes-Roth, Waterman and Lenat (1983); Sell (1985); Ellis (1989)

Learning
Nilsson (1965, 1988); Michie (1974, 1983); D. Shaw, Swartout and Green (1975); Summers (1977); Winston (1980, 1982, 1984); Dietterich and Michalski (1981); Simon (1983); Forsyth (1984d); Hart (1984); Simons (1984); S.F. Smith (1984); Durham (1985d,e); M. James (1985); Schlimmer and Langley (1992); Al-Attar and Hassan (1994); C.C. Taylor, Spiegelhalter and Michie (1994)
IDS: Quinlan (1979, 1983a,b); Durham (1985d); Quinlan *et al.* (1986)

Planning
Fikes and Nilsson (1971); Fikes, Hart and Nilsson (1972); Sacerdoti (1975, 1977); Stefik (1981a,b); Vere (1983, 1992); Oshima (1983); Wilensky (1983); Chapman (1985); J. Allen, Hendler and Tate (1990); Lyons and Hendricks (1992)

Tutoring
Sleeman and Brown (1982)

Validation
Hayes-Roth, Waterman and Lenat (1983); Weiss and Kulikowski (1983); A. Stevens (1984); Sell (1985)

Programming
Knuth (1968, 1969, 1973); Tyugu (1988)
Compilation, compilers: Bornat (1979); Charniak, Riesbeck and McDermott (1980)
List processing: Forster (1967)
Logic programming: Kowalski (1974, 1979); van Emden (1977); J.A. Robinson (1979, 1983); K.L. Clark and Tarnlund (1982); K.L. Clark (1983); Oliviera (1984); Sell (1985); Amble (1987)
Recursion: Burge (1975); Winston and Horn (1981)

Languages
LISP: McCarthy *et al.* (1962); Weissman (1967); D.P. Friedman (1974); Siklossy (1976); Winston (1977); J. Allen (1978, 1979); McCarthy (1978); Pratt (1979); Charniak, Riesbeck and McDermott (1980); Barr and Feigenbaum (1981–); Teitelman and Masinter (1981); Winston and Horn (1981); Danicic (1983); Gnosis (1984); Hasemer (1984a,b); Laubsch (1984); Queinnec (1984); Steel (1984); Harmon and King (1985); Narayanan and Sharkey (1985); Coxhead (1987)
PROLOG: Kowalski (1974, 1979); van Emden (1977); Warren, Perreira and Perreira (1977); Coelho *et al.* (1980); Clocksin and Mellish (1981); K.L. Clark and McCabe (1982); J.A. Campbell (1983, 1984); Mizoguchi (1983); Swinson (1983); Alty and Coombs (1984); Clocksin (1984); Forsyth (1984a); Li (1984); Schlobohm (1984); Yazdani (1984, 1985); Burnham and Hall (1985); J. Cohen (1985); Colmerauer (1985); Durham (1985c); Harmon and King (1985); de Saram (1985); Hinde (1986); Sterling and Shapiro (1986); Saint-Dizier (1987)
POP-2: Popplestone (1967); Burstall (1971); Burstall and Collins (1971); Burstall and Popplestone (1971); Burstall, Collins and Popplestone (1971)
POP-11: Ramsay and Barrett (1987); Popplestone (1992b)
POPLOG: Sloman, Hardy and Gibson (1983); Hardy (1984); Popplestone (1992a)
Object-oriented programming: Goldberg and Robsen (1983); B.J. Cox (1986); Stefik and Bobrow (1986); S. Cook (1987)
C++: Coplien (1992); Wang (1994)

Example systems
DENDRAL: E.G. Buchanan, Sutherland and Feigenbaum (1969, 1970); Feigenbaum, Buchanan and Lederberg (1971); Michie (1974); E.G. Buchanan *et al.* (1976); Carhart (1977); E.G. Buchanan and Feigenbaum (1978); E.G. Buchanan (1979); Nilsson (1980); Lindsay *et al.* (1980); Barr and Feigenbaum (1981–); Hayes-Roth, Waterman and Lenat (1983); Weiss and Kulikowski (1983); Alty and Coombs

(1984); E.G. Buchanan and Shortliffe (1984); Winston (1984); Harmon and King (1985); Sell (1985)
PROSPECTOR: Duda *et al.* (1978); Hart, Duda and Einaudy (1978); Duda, Gaschnig and Hart (1979); Reboh (1980, 1981); Barr and Feigenbaum (1981–); Duda and Gaschnig (1981); A. Campbell *et al.* (1982); Hayes-Roth, Waterman and Lenat (1983); Weiss and Kulikowski (1983); Alty and Coombs (1984); Harmon and King (1985); Sell (1985)
MYCIN: Shortliffe and Buchanan (1975); Shortliffe (1976); W.J. Clancey, Shortliffe and Buchanan (1979); Shortliffe, Buchanan and Feigenbaum (1979); Barr and Feigenbaum (1981–); W.J. Clancey and Lettsinger (1981); Hayes-Roth, Waterman and Lenat (1983); Weiss and Kulikowski (1983); Alty and Coombs (1984); Cendrowska and Bramer (1984); Winston (1984); Harmon and King (1985); Sell (1985)
TEIRESIAS: Barr and Feigenbaum (1981–); Hayes-Roth, Waterman and Lenat (1983); Alty and Coombs (1984); Winston (1984)
RI, XCON, XCEL: McDermott (1980, 1981, 1982a,b); Hayes-Roth, Waterman and Lenat (1983); Weiss and Kulikowski (1983); Alty and Coombs (1984); Bachant and MacDermott (1984); Kraft (1984); Winston (1984); Harmon and King (1985); van de Brug, Bachant and MacDermott (1986); Durham (1987)
CASNET: Weiss, Kulikowski and Saflr (1977, 1978); Weiss *et al.* (1978); Barr and Feigenbaum (1981–); Weiss and Kulikowski (1981, 1983); Kulikowski and Weiss (1982); Hayes-Roth, Waterman and Lenat (1983); Alty and Coombs (1984)
MOLGEN: Hayes-Roth, Waterman and Lenat (1983); Alty and Coombs (1984)
INTERNIST: R.A. Miller, Pople and Myers (1982); Pople (1982)
PUFF: Hayes-Roth, Waterman and Lenat (1983); Naylor (1983)
OPS: Forgy and McDermott (1977); Forgy (1981); Hayes-Roth, Waterman and Lenat (1983); Brownston *et al.* (1985); Harmon and King (1985)
KAS: Hayes-Roth, Waterman and Lenat (1983); Harmon and King (1985)
Spill prevention: B.A Kelly and Oakes (1980); Hayes-Roth, Waterman and Lenat (1983)
AL/X: Reiter (1980)
STEAMER: Holan, Hutchings and Weitzman (1984)
AMEURISKO: Lenat (1982, 1983); Lenat and Brown (1984); Durham (1985f); Shells Cendrowska and Bramer (1984); E.J. Miller, Wilson and Lewis (1988)
EMYCIN: van Melle (1979, 1980, 1981); van Melle, Shortliffe and Buchanan (1981); Hayes-Roth, Waterman and Lenat (1983); Weiss and Kulikowski (1983); Alty and Coombs (1984)
EXPERT: Weiss and Kulikowski (1979, 1981); Barr and Feigenbaum (1981–); Kulikowski and Weiss (1982); Hayes-Roth, Waterman and Lenat (1983); Harmon and King (1985)
MICRO EXPERT: P. Cox (1984)
ES/P ADVISOR: Harmon and King (1985)
CRYSTAL: Wallsgrove (1988)
G2: Gensym Corp. (1992)

Databases
Date (1977); R. Davis (1980); Ullman (1982); Maier (1983); Frost (1986)

Decision aids
Kunz and Rittle (1970); Conklin and Begeman (1988); Potts and Bruns (1988); Lubers (1991)

Documentation aids
Bourdeau (1991); Kahkonen and Bjork (1991); Casson (1992); Casson and Stone (1992); Chung and Stone (1994)

Neural networks
Minsky and Papert (1969); Touretszky and Hinton (1985); Gallant (1988); Saito and Nakano (1988); IFF (1989 Conf. Publ. 313, 1991 Conf. Publ. 349, Coll. Dig. 91/19, 1993 Conf. Publ. 372); Beale and Jackson (1990); Zeidenberg (1990)

B Process applications

Engineering design
Simon (1969); P. Freeman and Newell (1971); Eastman (1978); D.C. Brown and Chandrasekaran (1989); Ganeshan, Finger and Garrett (1991)

Artificial intelligence
Chowdhury and Caudwell (1982); F. Kane (1986); Stephanopoulos (1990); Bunn and Lees (1988); Hutton, Ponton and Waters (1990)

Expert systems
Anon. (1984tt); Andow (1984); B. Knight *et al.* (1984); Anon. (1985l); Banares-Alcantara and Westerberg (1985); Banares-Alcantara, Westerberg and Rychener (1985); Avni, Kandell and Gupta (1985); Baker-CounseU (1985b); Banares-Alcantara, Sriram *et al.* (1985); Berkovitch and Baker-Counsell (1985); Chowdhury (1985b); Chowdhury, Short and Gibb (1985); M. Henry (1985); R.L. Moore (1985); Sachs, Paterson and Turner (1985); Voller and Knight (1985); Anon (1986h); Basden and Mines (1986); Beazley (1986); British Gas (1986 Comm. 1297); Branch (1986); Coulsey (1986); Durham (1986); Ferguson and Andow (1986); Mines (1986); Mines and Basden (1986); Hollnagel *et al.* (1986); R.A. King (1986); Kosar and Blahut (1986); Niida *et al.* (1986); Shirley and Fortin (1986); Vaija, Jarvelainen and Dohnal (1986b); Anon. (1987k,s); Andow and Ferguson (1987); N. Atkinson (1987a); Banares-Alcantara *et al.* (1987); BarnweU and Ertl (1987); Holt *et al.* (1987); IBC (1987/71); A. Moore (1987); Oxman and Gero (1987); Rafaat and Abdouni (1987); Rand (1987); Russo and Peskin (1987); Sangiovanni and Romans (1987); Shirley (1987); Stephanopoulos (1987); Tayler (1987b); Anon. (1988n); Banares-Alcantara, Ko *et al.* (1988); Birky, McAvoy and Modares (1988); Bunn and Lees (1988); Norman and Naveed (1988); Novak, Schechter and Lake (1988); Royse (1988); Shum *et al.* (1988); W.A. Taylor (1988); BRE (1989 IP4/89); Gani (1989); Hofmeister, Halasz and Rippin (1989); Hollnagel (1989); Lahdenpera, Korhonen and Nystrom (1989); Birky and McAvoy (1990); Suokas, Heino and Karvonen (1990); Gulbrandsen (1991); Leicht, Wingender and Ruppert (1991); Quantrill and Liu (1991); Calzada, Espasa and Barrera (1992); Crowe *et al.* (1992); Fiumi and Giorgio (1992); Hanratty and Joseph (1992); Martinez *et al.* (1992); Samdani and Fouhy (1992); Chang, Hwang and Hwang (1993); Hingoraney (1994)

Process plant design, equipment selection
Rudd and Watson (1968); Bunn and Lees (1988); Myers, Davis and Herman (1988); Waters, Chung and Ponton (1989); Waters and Ponton (1992); Chung, Abbas and Robertson (1993); Yang *et al.* (1993)

Process modelling
Franks (1967); Durham (1985b); A.R. Mitchell and Griffiths (1980); Andersson (1989); Cott *et al.* (1989); Nilsson (1989); Piela *et al.* (1991); Gallun *et al.* (1992); Marquardt (1992); Nemeth *et al.* (1992)

Process synthesis
Powers and Jones (1973); May and Rudd (1976); Westerberg (1980, 1985, 1989); Nishida, Stephanopoulos and Westerberg (1981); Umeda (1982); Rippin (1983); Sargent (1983); Stephanopoulos (1983); Grossman and Floudas (1987); Grossman, Westerberg and Biegler (1987); Montagna *et al.* (1987); Pai and Hughes (1987); Beltramini and Motard (1988); Douglas (1988); Floquet, Piboleau and Domenech (1988); Kirkwood, Lock and Douglas (1988); Reklaitis and Spriggs (1988); Engelmann *et al.* (1989); Grossman (1989); Hofmeister, Halasz and Rippin (1989); Motard (1989); Mizsey and Fonyo (1990); Ostrovsky and Berezinsky (1991); Raman and Grossman (1991); Crowe *et al.* (1992); Journet (1993)

DESIGN-KIT
Stephanopoulos, Johnston *et al.* (1987)

MODEL.LA
Stephanopoulos, Hanning and Leone (1990a,b)

Planning
Rivas and Rudd (1974); Rivas, Rudd and Kelly (1974); Fusillo and Powers (1987, 1988a,b); Stephanopoulos *et al.* (1987); Foulkes *et al.* (1988); Lakshmanan and Stephanopoulos (1988a,b, 1990); Aelion and Powers (1991); Rotstein, Lavie and Lewin (1992); Soutter and Chung (1993)

Qualitative modelling
Andow (1973); Andow and Lees (1975); de Kleer (1975, 1984, 1985, 1992); Hayes (1979, 1985); Martin-Solis, Andow and Lees (1982); Centner and Stevens (1983); de Kleer and Brown (1983, 1984, 1986); Wilensky (1983); Bobrow (1984, 1985); R. Davis (1984); Kuipers (1984, 1986, 1989); B.C. Williams (1984a,b); Hobbs and Moore (1985); Ponton and Vasek (1986); Weld (1987, 1988a,b); Dalle Molle, Kuipers and Edgar (1988); Mavrovouniotis and Stephanopoulos (1988); Oyeleye and Kramer (1988); Pethe, Singh and Knopf (1989); Waters and Ponton (1989); P. Rose (1990); Weld and de Kleer (1990); Yamashita, Shoji and Suzuki (1990); Catino, Grantham and Ungas (1991); Faltings and Struss (1991); Grantham and Ungar (1991); P. Rose and Kramer (1991); Hardt (1992); Koivisto *et al.* (1992); Fanti, Chung and Rushton (1993); Savkonic-Stevanovic (1994)

Order of magnitude estimation, modelling
Mosteller (1977); Mavrovouniotis and Stephanopoulos (1988)

Neural networks
Hoskins and Himmelblau (1988); Venkatasubramanian and King Chan (1989); Watanabe *et al.* (1989); Bhagat (1990); Bhat and McAvoy (1990); M.A. Kramer and Leonard (1990); Samdani (1990a); Venkatasubramanian, Vaidhyanathan and Yamamoto (1990); Okayama (1991); Venkatasubramanian and McAvoy (1992); Chitra (1993); Fan, Nikolaou and White (1993); A.J. Morris, Montague and Willis (1994)

Fault propagation
Andow (1973); Andow and Lees (1975); Umeda *et al.* (1979, 1980); Andow, Lees and Murphy (1980); Martin-Solis, Andow and Lees (1982); B.E. Kelly and Lees (1986a–d); Parmar and Lees (1987a,b); Khan and Hunt (1989); Waters and Ponton (1989); A. Hunt *et al.* (1993a–e)
QUEEN: Chung (1993)

Design decision aids
Ramirez-Dominguez and Banares-Alcantara (1993); Chung and Goodwin (1994); Goodwin and Chung (1994a,b)

Explosion venting
Santon *et al.* (1991); von Haefen (1992); Santon (1992)

Reliability engineering
FIABEX: MM. Grant and Harvey (1989)

Hazard identification
Lihou, Rahimi and Fletcher (1980); lihou (1983 LPB 51); Andow and Ferguson (1987); Karvonen, Suokas and Heino (1987); Kletz (1988b); Weatherill and Cameron (1988, 1989); N. Morgan (1992b); Heino, Suokas and Karvonen (1989a,b); C. Price and Hunt (1991); C. Price *et al.* (1991); R.A. Freeman, Lee and McNamara (1992); Goring and Schecker (1992); Heikkila and Heino (1992); Heino, Poucet and Suokas (1992); Schb'nenburg (1992); Lear (1993); Heino *et al.* (1994); Venkatasubramanian and Vaidhyanathan (1994)
COMHAZOP: Rootsaert and Harrington (1992)
HAZID: Parmar and Lees (1987a,b); Zerkani and Rushton (1992, 1993)

Failure modes and effects analysis (FMEA)
C. Price *et al.* (1991)

Fault tree drafting and synthesis
W.Q. Smith and Lien (1968); Fussell (1973a,b); Henley (1977); L.S. Baker *et al.* (1978); Camarda, Corsi and Trentadue (1978); D.J. Allen and Rao (1980); Lihou (1980b); Poucet and de Meester (1981); Amendola *et al.* (1983); Poucet (1983); D.J. Allen (1984); Shafaghi, Andow and Lees (1984); Shafaghi, Lees and Andow (1984); VTT (1985 Res. Rep. 330); Kumamoto and Henley (1986); Kohda and Henley (1988); Mullhi *et al.* (1988); Napier and Palmer (1988); de Vries (1990); Bossche (1991a–c); Chuei-Tin Chang and Her-Chuan Hwang (1992)
CAT: Salem, Apostolakis and Okrent (1975a,b, 1977); Chu (1976); Apostolakis, Salem and Wu (1978); Salem, Wu and Apostolakis (1979); Salem and Apostolakis (1980); SqueUati (1980); Poucet (1983)
FAULTFINDER: Andow and Lees (1975); Martin-Solis, Andow and Lees (1977, 1980, 1982); B.E.Kelly (1982); B.E. Kelly and Lees (1986a–d); Mullhi *et al.* (1988); A. Hunt *et al.* (1993a–e)
FTS: Powers and Tompkins (1974a,b, 1976); Powers and Lapp (1976, 1977); Henley and Kumamoto (1977); Lapp and Powers (1977a,b, 1979); Locks (1979, 1980); Powers (1977); Shaeiwitz, Lapp and Powers (1977); Lambert (1979); Yellman (1979); Cummings, Lapp and Powers (1983)
RIKKE: J.R. Taylor (1982); J.R. Taylor and Olsen (1983); J.M. Morgan (1985)

Hazard models
Rao and Raj (1990); Koivisto *et al.* (1991)

Hazard assessment
Nelms (1988); Ja'ger, Diedershagen and Kiihnreich (1989); Reeves and Mennell (1989); Reeves, Wells and Linkens (1989); Kakko (1991); Heino, Poucet and Suokas (1992)

Process monitoring
Stainthorp and West (1974); Hogger (1975); Berenblut and Whitehouse (1976, 1977); Anon. (1977a); Munday (1977); Dye (1979); Cheung and Stephanopoulos (1990); Alty and McCartney (1991); Alty and Bergan (1992)
RESCU: Shorter (1985)

Multi-media systems
Alty and McCartney (1991); Alty and Bergan (1992); Tani *et al.* (1992)

Fault administration and diagnosis
Jervis and Maddock (1965); Welbourne (1965,1968, 1974);

Kay (1966); Kay and Heywood (1966); Earth and Maarleveld (1967); Patterson (1968); Andow (1973, 1982, 1984, 1985a–c, 1986); E. Edwards and Lees (1973, 1974); Andow and Lees (1975); Dahll (1976); Dahll *et al.* (1976); Powers and Lapp (1977); EPRI (1978 EPRI NP-613,1980 EPRI NP-1379, EPRI NP-1684); Frogner and Meijer (1978, 1980); Iri *et al.* (1979); Umeda *et al.* (1979); GeseUschaft fur Reaktorsichheit (1980); Long (1980); Long *et al.* (1980); Meijer, Frogner and Long (1980); Lees (1981a, 1983c, 1984); Pau (1981a,b); Martin-Solis, Andow and Lees (1982); W.R. Nelson (1982, 1984); Kokawa, Miyaki and Shingai (1983); Guarro and Okrent (1984); Herbert (1984); Iserman (1984); Watanabe and Himmelblau (1984); W.R. Nelson and Blackman (1985); Shiozaki *et al.* (1985); Tsuge *et al.* (1985); Ungar (1985); Modarres and Cadman (1986); Rowan (1986); Wollenberg (1986); Arendt *et al.* (1987); Dalle Molle and Himmelblau (1987); Frank (1987); M.A. Kramer (1987a,b, 1988); Kumamoto and Henley (1987); Washio, Kitamura and Sugiyama (1987); Ramesh, Shum and Davis (1988); Rich and Venkatasubramanian (1988, 1989); Shum *et al.* (1988); Venkatasubramanian (1988); Venkatasubramanian and Rich (1988); B. Chen *et al.* (1989); Gertler and Qiang Luo (1989); M.A. Kramer and Finch (1989); Rich *et al.* (1989); Sang Hoon Han *et al.* (1989); Tsuge, Matsuyama and McGreavy (1989); Venkatasubramanian and King Chan (1989); Basila, Stefanek and Cinar (1990); L.W. Chen and Modarres (1990); Chung-Chen Chang and Cheng-Ching Yu (1990); D.J. Cooper and Lalonde (1990); Finch, Oyeleye and Kramer (1990); M.A. Kramer and Leonard (1990); Labadibi (1990); Poucet (1990); Qian (1990); P. Rose (1990); Trenchard (1990); Ungar, Powell and Kamens (1990); Venkatasubramanian, Vaidhyanathan and Yamamoto (1990); Yamashita, Shoji and Suzuki (1990); Adamson and Roberge (1991); Aldersey, Lees and Rushton (1991); Chen-Ching Yu and Chyuan Lee (1991); Hoskins, Kaliyur and Himmelblau (1991); Li and Olson (1991); McDowell and Davis (1991); Pelti, Klein and Dhurjati (1991); P. Rose and Kramer (1991); Yoon, Oh and Yoon (1991); Corea, Tham and Morris (1992); Corti and Sansone (1992); IEE (1992 Coll. Dig. 92/45, 92/48); Karvonen *et al.* (1992); Labadibi and McGreavy (1992); Ramesh, Davis and Schwenzer (1992); Saelid, Mjaavatten and Fjalestad (1992); Venkateswarlu, Gangiah and Rao (1992); Yih-Yuan Hsu and Cheng-Chin Yu (1992); Chuei-Tin Chang *et al.* (1993); Fan, Nikolaou and White (1993); Fathi, Ramirez and Korbicz (1993); Ramanathan, Kannan and Davis (1993)

Instrument system design: Lambert (1977); Plamping and Andow (1983); Plamping (1986); A.M. and Narasimhan (1993)

ANTICIPATOR: Munday (1977); Dye (1979)

AUTOPES: Wagenaar, Boesmans and Schrijnen (1989)

COGSYS: Anon. (1988n)

Malfunction detection

Instruments: Kuehn and Davidson (1961); Clementson (1963); Ripps (1965); Barton *et al.* (1970); Anyakora (1971); Goldmann and Sargent (1971); Sommer *et al.* (1971); Umeda, Nishio and Komatsou (1971); Anyakora and Lees (1972b, 1973); Nogita (1972); E. Edwards and Lees (1973, 1974); Nogita and Uchiyama (1973); R.N. Clark, Fosth and Walton (1975); Hawickhorst (1975); Bellingham (1976); Bellingham and Lees (1976a,b, 1977a,b); Lees (1976d); Mah, Stanley and Downing (1976); Wfflsky (1976); Stanley and Mah (1977); Himmelblau (1978, 1979); Park and Himmelblau (1983, 1987); Narasimhan and Mah (1987); Jongelen, den Heijer and van Zee (1988); Tjoa and Bielger (1991); Whiteley and Davis (1992)

Plant equipment: Gallier (1968); Anyakora and Lees (1972b); Lees (1972); Whitman (1972); Collacott (1976b, 1977b); Himmelblau (1978); Dalle Molle and Himmelblau (1987); M.A. Kramer (1987b); MA ICramer and Palowitch (1987)

Data management and reconciliation

Romagnoli and Stephanopoulos (1981); Gorczynski (1985); Himmelblau (1985); lordache, Mah and Tamhane (1985); Madron (1985); Heenan and Serth (1986); Seith and Heenan (1986); Rosenberg, Mah and lordache (1987); Crowe (1988); R.J. MacDonald and Howat (1988); Chen-Shan Kuo, Tamhane and Mah (1990); May and Payne (1992); Rollins and Davis (1992, 1993); Verneuil, Pin Yang and Madron (1992); Leibovici, Verneuil and Pin Yang (1993); McMorris and Graveley (1993)

Operating procedures

Tomita, Hwang and Oshinma (1989)

Robots

R. Brooks (1986, 1989); Schoppers (1987)

Transport systems

Bliimel and Schulz-Forberg (1989)

Accident databases

Koivisto, Vaija and Dohnal (1989)

30.1 Knowledge Representation

30.1.1 Knowledge

Knowledge is of many kinds and this is reflected in the forms of knowledge representation used.

One distinction commonly made is between data and information. Other distinctions made about knowledge are domain-independent vs domain-specific, exact vs *fuzzy*, and procedural vs declarative knowledge. Some types of knowledge include: facts; models; distinctions; relationships; constraints; procedures and plans; and rules-of-thumb, or heuristics.

The extent of the knowledge required varies greatly between problems. In certain limited worlds, such as the 'blocks world' extensively studied in AI, the world knowledge required is quite limited. In real-life, or mundane, situations on the other hand, the human comes to the problem possessed of a massive store of knowledge. He draws from this information not only about facts but also about other aspects such as constraints.

30.1.2 Natural language

By far the most widely used and most expressive form of knowledge representation is natural language. As a method of representation in AI work, however, natural language has a number of deficiencies.

There are a number of fundamental problems of natural language in this respect. It tends to be ambiguous. Its syntax and semantics are not well understood. There is considerable diversity in the structure of sentences. In some cases the meaning depends on the context.

Work in AI tends to involve the use of structured knowledge and natural language is not an obvious method for this purpose.

30.1.3 Databases

By contrast, in databases structure is a principal feature of the knowledge representation. In large part this structure is oriented to data retrieval, but it may also represent relationships between the objects stored, and databases generally have certain facilities for certain elementary transformations on the data. Databases are considered further in Section 30.2.

30.1.4 Classical logics

Logic is a formal method of reasoning and provides a sound theoretical basis for the reasoning process. This is particularly important for computer-based approaches.

There are two principal logics in common use. One of these classical logics is prepositional logic (PL) and the other first order predicate logic (FOPL). Prepositional logic is the earlier form, is simpler and is generally the starting point in teaching.

Predicate logic has been developed to overcome some of the limitations of prepositional logic. It is a more general logic of which prepositional logic may be regarded as a special case. It is predicate logic which is most widely used in AI and which is used in 'logic programming'.

Prepositional logic has a number of serious limitations. It cannot readily describe properties of entities or express relationships between them. Predicate logic has been developed as a form of logic with enhanced expressiveness. It replaces propositions with predicates and utilizes functions, variables and quantifiers. This makes it possible to reason about entities in terms of their classes and of their relationships.

In defining the syntax of a logic use is frequently made of the Backus–Naur form (BNF).

Prepositional logic and predicate logic are described in Sections 30.3 and 30.4, respectively.

30.1.5 Non-classical logics

Classical logic has severe limitations in its ability to handle real-world situations. It deals with statements that are either true or untrue and does not accommodate information which is incomplete, vague, contradictory or unbelievable. It does not readily handle uncertainty and inconsistency. It is a feature of classical logic that it is monotonic. The conclusions once derived are valid deductions and remain so. The set of facts and inferences can only increase; it cannot decrease. This does not accord well with real life, in which it is necessary to revise conclusions reached as more information becomes available.

Common-sense reasoning is therefore not well served by classical logic and there have been developed a number of non-classical logics that address particular deficiencies. Many of these deal with uncertainty and inconsistency, but other aspects such as time are also accommodated.

These non-classical logics are considered in Section 30.7.

30.1.6 Probabilistic reasoning

Much knowledge relates in some way to uncertainty. The methods just described are not well adapted to representing knowledge under uncertainty, but other methods do exist for this purpose. Foremost among these are probabilistic reasoning and fuzzy logic.

Methods for handling uncertainty are described in Section 30.8 and those of probabilistic reasoning and fuzzy logic are described in Sections 30.9 and 30.10, respectively.

30.1.7 Structured knowledge

AI possesses a rich repertoire of methods for the storage of knowledge in structured forms. The creation of structure has a significance that goes far beyond simple ease of retrieval. It imposes a discipline that ensures that the entities and their relationships are formally defined and it facilitates basic operations such as search and matching. Structured knowledge is considered in Section 30.12.

30.1.8 Graphs, trees and networks

A form of knowledge representation widely used by humans is diagrams in the form of graphs, trees and networks. There are a large number of such diagrams in common use and a number that have been developed in the course of AI work. These diagrams may be mapped into program structures and in many cases there are standard techniques available to do this. An outline of some of the graphs, trees and networks in use in AI is given in Section 30.22.

30.1.9 Programming languages

The programs of interest here are those that both contain representations of knowledge and perform operations on them. Such programs are most effectively implemented in programming languages of the declarative rather than the procedural type, the principal languages being LISP and Prolog. The strength of these languages is their ability to combine representation of knowledge in the forms required in AI work and support for various modes of reasoning. Programming languages are described in Section 30.11.

30.2 Databases

A widely used form of knowledge representation is the database. Databases are a major topic but may be treated here quite briefly.

Accounts of databases are given in *An Introduction to Database Systems* (Date, 1977), *Principles of Database Systems* (Ullman, 1982), and *The Theory of Relational Databases* (Maier, 1983). Data bases in the context of AI are discussed by Frost (1986) and Tanimoto (1990).

A database stores and provides ready access to data. It imposes a discipline on the classification and storage of data. It is a natural form for the storage of knowledge about certain types of relationship between data.

A rich variety of data structures are available, including: arrays, lists, strings, queues, stacks, bit maps and records; direct access, sequential, inverted and transposed files; hash tables; graphs and trees; and multi-lists, inverted lists and bit lists.

Aids to the design and implementation of databases exist in the form of database management systems (DBMSs) that provide a collection of procedures, documentation aids, languages and programs.

Corruption of the database must be avoided and various formal systems are required. By controlling access a privacy subsystem protects against unauthorized alteration of the database. An integrity subsystem protects against invalid alteration by imposing a discipline on those authorized to make changes. A back-up and recovery subsystem provides a facility for rebuilding the database after corruption has occurred.

30.2.1 Relational databases

A form of database suited to the handling of large data sets with regular structure is the relational database. The term

'relation' is applied to a set of ordered n-tuples, or ordered sets each containing n items. An n-ary relation has n fields. The first field is referred to as the primary key. A field possesses a domain, which comprises the set of entities from which elements in the field may be drawn. A name is assigned both to the relation and to its fields. The following table is an illustration of a 3-ary relation.

PIPE			
Section	*Diameter* (in.)	*Material*	*Supplier*
Straight	3	Copper	X
Straight flanged	3	Mild steel	Y
90° bend	4	Stainless steel	Y
T-section	4	Stainless steel	Y

The relation is PIPE, the primary key is *Section*, the other fields being *Diameter, Material* and *Supplier*.

Some elementary operations that are supported by relational database programs include selection, projection and joining. Selection is the creation from an existing relation of a new, more specialized relation by selection of a subset of rows which have some common property. Projection is the creation from an existing relation of a new, more specialized relation by excision of some of the fields. Joining is the creation of a new relation by the fusion of two existing relations.

30.3 Prepositional Logic

30.3.1 Propositions

Prepositional logic deals with the relationships between propositions. Typical propositions are:

(1) The valve is open.
(2) The valve is open and the pipe is full of liquid.

The first of these is a simple proposition and the second a compound proposition. Propositions are also referred to as statements, sentences or formulas. Statements are represented by prepositional symbols, which are capital letters, commonly P, Q, R, etc.

30.3.2 Syntax

The main feature of the syntax of prepositional logic is the connectives, the symbols for which are shown in Table 30.2, Section A. Use is also made of parentheses ( ) as delimiters, but where there is no chance of ambiguity, parentheses may be omitted, in which case the order of precedence of the connectives is, from highest to lowest: $\neg$, $\wedge$, $\vee$, $\Rightarrow$, $\Leftrightarrow$.

The set of statements commonly used to illustrate the connectives is as follows:

$\neg P$

$P \wedge Q$

$P \vee Q$

$P \Rightarrow Q$

$P \Leftrightarrow Q$

30.3.3 Semantics

Some principal features of the semantics of propositional logic are the properties of statements and the rules of inference. The semantics of a statement is the truth value assigned to it, the process of assignment being known as interpretation. The truth values assigned are true or false. These values are commonly denoted by T for true and F for false, particularly in truth tables. It should be noted that the symbols T and F themselves represent statements and are used in compound statements.

Some properties of statements are:

Satisfiability – a statement is satisfiable if there is an interpretation for which it is true.
Contradiction – a statement is contradictory, or unsatisfiable, if there is no interpretation for which it is true.
Validity – a statement is valid, or autologous, if it is true for every interpretation.
Equivalence – two statements are equivalent if they have the same truth value for every interpretation.
Logical consequence – a statement is a logical consequence of another if it is satisfied by all interpretations that satisfy the first.

In the interpretation of compound statements use is often made of substitution of equivalent statements. Table 30.2, Section B shows some equivalence laws that may be used in

Table 30.2 *Some features of propositional logic*

A Connectives

Type	*Meaning symbol*	*Symbol*	*Alternative*
Negation	not	$\neg$	$\sim$
Conjunction	and	$\wedge$	&
Disjunction	or	$\vee$	$\vee$
Implication	if . . . then	$\Rightarrow$	$\rightarrow$
Double implication	if and only if	$\Leftrightarrow$	$\leftrightarrow$

B Some equivalence laws

Idempotency	$P \wedge P \equiv P$
	$P \vee P \equiv P$
Commutativity	$P \wedge Q \equiv Q \wedge P$
	$P \vee Q \equiv Q \vee P$
	$P \Leftrightarrow Q \equiv Q \Leftrightarrow P$
Associativity	$(P \wedge Q) \wedge R \equiv P \wedge (Q \wedge R)$
	$(P \vee Q) \vee R \equiv P \vee (Q \vee R)$
Absorption	$P \wedge (P \vee Q) \equiv P$
	$P \vee (P \wedge Q) \equiv P$
Distributivity	$P \wedge (Q \vee R) \equiv (P \wedge Q) \vee (P \wedge R)$
	$P \vee (Q \wedge R) \equiv (P \vee Q) \wedge (P \vee R)$
De Morgan	$\neg(P \wedge Q) \equiv \neg P \vee \neg Q$
	$\neg(P \vee Q) \equiv \neg P \wedge \neg Q$
Conditional elimination	$P \Rightarrow Q \equiv \neg P \vee Q$
Bi-conditional elimination	$P \Leftrightarrow Q \equiv (P \Rightarrow Q) \wedge (Q \Rightarrow P)$

C Truth table for equivalent statements

P	Q	$\neg P$	$P \wedge Q$	$P \vee Q$	$P \Rightarrow Q$
T	T	F	T	T	T
T	F	F	F	T	F
F	T	T	F	T	T
F	F	T	F	F	T

making such substitutions. Another way of determining equivalence is the use of truth tables. A truth table for equivalent statements is shown in Table 30.2, Section C.

30.3.4 Inference rules

The means to perform deductions is provided by the rules of inference. Some principal rules are as follows.

Modus ponens

Assertion:	P
Assertion:	$P \Rightarrow Q$
Conclusion:	Q

Chain rule

$$\frac{P \Rightarrow Q \qquad Q \Rightarrow R}{P \Rightarrow R}$$

Disjunctive syllogism P

$$\frac{P}{P \vee Q}$$

Resolution

$$\frac{P \vee \neg Q \qquad Q \vee R}{P \vee R}$$

Other rules of inference are:

Substitution – if s is a valid statement, a statement s′ derived from it by consistent substitution is also valid.
Simplification – from $P \vee Q$ inference is P.
Conjunction – from P and Q inference is $P \vee Q$.
Transposition – from $P \Rightarrow Q$ inference is $\neg Q \Rightarrow \neg P$.

30.4 Predicate Logic

30.4.1 Basic entities

The basic entities handled in first order predicate logic (FOPL) are constants, variables, functions and predicates. The first three are referred to as terms, and predicates are referred to as atomic formulas, or atoms. An atom or its negation is referred to as a literal.

A constant is a term that has a fixed value and a variable is a term that can take different values. A function maps elements of the domain to further elements of the domain. A predicate maps elements of the domain to truth values. Commonly used constant symbols are *a, b, c, . . .* ; function symbols *f, g, h, . . .* ; variable symbols *x, y, z*; and predicate symbols P, Q, R, ... Use is also made of quantifiers. These are for existential quantification and $\forall$ for universal quantification. The meanings are:

$\exists x$ For some x; there is an x
$\forall x$ For all x

The expression $\exists x P(x)$ means that there exists at least one element of the domain which makes $P(x)$ true.

30.4.2 Syntax

In respect of syntax, the logical connectives used in FOPL are the same as those for prepositional logic.

30.4.3 Well-formed formulas

There are rules for the construction of syntactically correct formulas. Formulas derived by correct application of these rules are termed well-formed formulas, or wffs (pronounced woofs). An atomic formula is a wff. Wffs are obtained from predicates, or atomic formulas, by application of quantifiers and connectives.

Some wffs contain variables. If a variable follows or is within the scope of a quantifier, it is said to be bound; otherwise it is free. The variable x in the expression $\forall x(P(x) \Rightarrow Q(x,y))$ is bound, whereas the variable y is free. For a formula to be evaluated, it is necessary that all the variables in it be bound. This leads to the requirement that a wff should contain only bound variables.

A wff, or a predicate, which has no variable is referred to as a ground atom.

30.4.4 Semantics

The semantics of FOPL are somewhat more complex than those for prepositional logic. They largely revolve around the conversion of wffs to clausal form and the application of the rules of inference and the principle of resolution.

Accounts of the semantics for FOPL, including equivalence and truth tables are given by Frost (1986) and Patterson (1990).

30.4.5 Clausal form

One of the most powerful methods of interpretation in FOPL is the resolution principle. But, in order to apply it, it is necessary first to convert the wffs to clausal form. A formal six-step procedure exists to effect this conversion.

30.4.6 Inference rules

Interpretation of the wffs is effected by application of the rules of inference for FOPL. One of these is modus ponens

An illustration of modus ponens in FOPL is the following:

Assertion	P(a)
Implication	$\forall x\, P(x) \Rightarrow Q(x)$
Conclusion	$Q(a)$

In this interpretation since the implication $P(x) \Rightarrow Q(x)$ is true for all x, it is true in particular for $x = a$.

30.4.7 Resolution principle

Resolution is an inference procedue that is applied to a set of clauses to determine if the set is unsatisfiable.

The principle of resolution is as follows. If there are two clauses Cl and C2, the parent claues, which have no variables in common and if there is a iteral in Cl that is the complement of a literal in C2, bot literals are deleted and a new clause C, the resolvent, is formed from the remaining reduced clauses.

An illustration of the principle is the following resolution:

$$\frac{\neg P \vee Q \qquad \neg Q \vee R}{\neg P \vee R}$$

There is a family of types of resolution applicable to particular combinations of numbers and of types of parent clauses.

30.5 Non-deductive Inference

The form of inference just described is deductive inference, but this is not the only form of inference in use. Other forms are abductive inference, inductive inference and analogical inference, and these are now described. These forms of inference are not strictly valid, but they are nevertheless in common use.

30.5.1 Abductive inference

Abductive inference may be represented as

$$\frac{\mathrm{Q}}{\mathrm{P}^{c} \Rightarrow \mathrm{Q}}$$
$$\mathrm{P}$$

where the superscript c denotes a possible causal relationship. A proposition Q and a causal relation $\mathrm{P} \Rightarrow \mathrm{Q}$ are used to infer a proposition P.

30.5.2 Inductive inference

Induction involves generalization based on a limited sample of entities from the universe of entities. Inductive inference may be represented as:

$$\frac{\mathrm{P}(\mathrm{a}_1) \ldots \mathrm{P}(\mathrm{a}_n)}{\forall x\, \mathrm{P}(x)}$$

30.5.3 Analogical inference

Analogical inference is based on the assumption that two situations that are similar in some respects are also similar in other respects. It, in fact, appears to utilize a combination of deductive, abductive and inductive inference. Analogical inference may be represented as:

$$\frac{\mathrm{P}^{r} \Rightarrow \mathrm{Q}}{\mathrm{P}'^{r} \Rightarrow \mathrm{Q}'}$$

where the superscript r means related to and superscript $'$ denotes similar to.

30.6 Production Rules

As already mentioned, one form in which knowledge may be represented is as a set of rules, also called productions. Such rules may be regarded as a special case of prepositional logic.

The rules are of the type IF . . . THEN . . . . They have a left-hand side (LHS), which is variously known as the antecedent, premise, condition or situation and a right-hand side (RHS), which is known as the consequent, conclusion, action or response. The proposition on the LHS may be a compound one with a number of propositions ANDed together.

A suitable set of rules, or productions, can be used to form the basis of a production system. Production systems are one of the main methods of implementing expert systems and are discussed further below.

30.6.1 Production systems

A production system has three main features: the rule base, a working memory and the inference engine. The rule base holds the set of rules that embody the expertise of the system. The working memory is supplied with the input data, or facts, on the problem to which the rules are to be applied. The inference engine controls the operation of the rules to deduce conclusions from these data.

The rules in the rule base are laid out as a set of logic statements. The rule base may be inspected by an expert to check for correctness. Rules may be added, removed or modified with relative ease.

The operation of a production system is quite different from the execution of a program in a procedural language. Execution is not controlled by a procedure as such, but involves making a pass through the rule base and determining which rules are satisfied.

The inference engine applies the input facts to the rules and determines which rules are satisfied, or 'trigger'. Provided there is no conflict between the output from a rule and that for another rule, the rule then 'fires'.

30.6.2 Conflict resolution

If such conflict does occur, it becomes necessary to apply a suitable conflict resolution strategy. The application of this strategy determines which rules should fire. The conflict resolution strategy used may be a generalized one or it may be one specific to the particular problem. There are a number of generalized strategies for conflict resolution. Winston (1984) lists the following six strategies: (1) specificity ordering, (2) rule ordering, (3) data ordering, (4) size ordering, (5) recency ordering and (6) context limiting. Specificity ordering applies to a group of rules where the conditions of one rule are a superset of which the conditions in the other rules are subsets; priority is given to the rule with the superset of conditions. In rule ordering, the rules are arranged in a priority list and rule first triggered has priority. In data ordering, all possible aspects of the situation are arranged in a priority list and the rule having the highest priority condition has priority. In size ordering, the rule has priority that has the largest number of conditions. In recency ordering, priority is given either to the rule that fired most recently or, alternatively to that which fired least recently. Context limiting involves dividing the rules into groups and creating a procedure that activates and deactivates groups; those rules that are in the active groups, having priority.

30.7 Non-classical Logics

The point has already been made that a classical prepositional logic is not sufficiently expressive. The creation of another, now classical, logic, the predicate calculus, was a response to this deficiency. The same need has given rise to the development of further, non-classical logics.

These newer logics extend the range of the knowledge that can be represented and are thus more expressive. They make it possible to handle knowledge that is incomplete, uncertain, vague and/or inconsistent, or associated with time. They are often more efficient in handling the knowledge.

The properties of a logic are that it has a well-defined method for representing knowledge, for obtaining proofs by syntactical manipulation and for extracting meaning using a semantic model.

30.7.1 Many-sorted logics

In a many-sorted logic the entities in the universe of discourse are divided into sorts. There are different sort

structures. One is a structure where all the sorts are different, or disjoint. Another is a structure where the sorts are related as in a tree, with the sorts at a lower layer being subsets of those in the layer above. Another is a structure in which the sorts are related as in a lattice, with non-hierarchical links between them.

Such many-sorted logics are used to place appropriate limitations on searches, and thus to improve search efficiency, and on logical operations, and thus avoid nonsensical interpretations.

30.7.2 Situational logics

A situational logic is a method of representing relationships that pertain in a particular situation. The usual device for effecting this is to augment the predicate with an extra argument which denotes the situation.

30.7.3 Non-monotonic logic

The point was made earlier that the classical logics are monotonic logics. They do not accommodate the revisions that are necessary to cope with real-life situations. There are several reasons why it may become necessary to revise knowledge. One is that the original knowledge may have been incomplete so that a default value had to be used. Another is that in problem-solving it is often necessary to make a temporary assumption. Another is that the situation may have changed.

30.7.4 Many-valued logics

The classical logics utilize in their semantics just two values, true and false. Other logics have been developed which permit the use of a wider range of values. One such many-valued logic is that of Lukasiewicz (1951), which utilizes three values. In addition to true and false, there is an intermediate value, which is applicable where the statement may be true, or 'sort of true'.

30.7.5 Fuzzy logic

Fuzzy logic, which is based on fuzzy sets, permits reasoning where there is uncertainty and vagueness. It is considered further in Section 30.10.

30.7.6 Modal logics

The classical logics deal with statements in the indicative mood concerning what is. There has been developed a family of modal logics which have been characterized as being in the subjunctive mood and which deal with what must be, should be, might be, is believed to be, etc.

Some principal modalities and the descriptor pairs associated with them are:

Alethic modality: necessary, possible. Temporal modality: always, sometimes. Deontic modality: obligatory, permissible. Epistemic modality: known, believed. Each modality has its associated modal operators. Thus for alethic modality operators are necessary (L) and possible (M).

30.7.7 Temporal logic

The classical logics do not accommodate time. The temporal logics that have been developed to overcome this limitation follow two broad approaches. One is the use of a temporal modality. In this form of temporal logic, use is made of the modalities:

Always, sometimes.

Other modalities used are:

Past, present, future

and

Precedes, succeeds.

There are corresponding temporal operators, of which the most common are probably always (A) and sometimes (S).

The other approach is to adapt FOPL to handle time. One method makes use of time points. The predicate is augmented with an extra argument that denotes the time point. The approach is somewhat similar to that used in situational logic.

30.7.8 Epistemic logic

Epistemic logic is a form of logic used to reason about knowledge possessed by other agents.

30.8 Uncertainty and Inconsistency

The foregoing discussion has brought out the need to be able to handle uncertainty and inconsistency. Some approaches to this problem are now described.

30.8.1 Sources of uncertainty

There are a number of sources of uncertainty. Uncertainty arises due to the randomness of events and to incompleteness, vagueness, unreliability, and unbelievability of and contradictions in knowledge.

30.8.2 Probability theory

The traditional approach to handling uncertainty is the use of probabilistic reasoning. This has been considered in some detail in Chapter 7. The treatment there was in the context of reliability engineering, but the basic probability theory is of wide applicability.

Probabilistic reasoning is utilized in AI and an account is given in Section 30.9. However, it also has a number of limitations, which have led to the development of alternative approaches. These limitations are perhaps best understood by considering these other techniques.

30.8.3 Certainty theory

Expert systems are typically based on a set of rules. In some cases it is not certain that a rule is correct. It is not easy to characterize this uncertainty using conventional probability theory and certainty theory has been developed to handle this problem.

For a statement S a certainty measure, or certainty, $C(\mathrm{S})$ is defined such that

$C(\mathrm{S})$	If S is true
$C(\mathrm{S}) = -1.0$	If S is false
$C(\mathrm{S}) = 0$	If nothing is known about S

$C(\mathrm{S})$ may also have values intermediate between $+1.0$ and -1.0, reflecting the degree of certainty that it is true or false.

For a rule a certainty factor CF is defined

If A then X with certainty factor CF

CF has the value 1.0 if it is certain that the rule is true, it has the value -1.0 if it is certain that the rule is false, and may take intermediate values, reflecting the degree of certainty that it is true or false.

In the approach, a rule is taken to be either true (CF = 1.0) or false (CF = –1.0), and its application results in a conclusion X that has a value true or false. A truth value of X is obtained by application of a single rule. Application of a second rule which gives a truth value for X either confirms the original value or contradicts it. Using certainty theory, however, the truth value of X is associated with a certainty value which is subject to adjustment each time a rule is applied and yields a truth value for X.

The relations used to determine the certainty C(X) of the statement X given A are:

$$C(\mathrm{X}\,|\,\mathrm{A}) = C(\mathrm{X}) + [\mathrm{CF}\,(1.0 - C(\mathrm{X}))] \quad C(\mathrm{X}) > 0;\ \ \mathrm{CF} > 0 \qquad [30.8.1a]$$

$$C(\mathrm{X}\,|\,\mathrm{A}) = C(\mathrm{X}) + [\mathrm{CF}\,(1.0 - C(\mathrm{X}))] \quad C(\mathrm{X}) < 0;\ \ \mathrm{CF} < 0 \qquad [30.8.1b]$$

$$C(\mathrm{X}\,|\,\mathrm{A}) = \frac{C(\mathrm{X}) + \mathrm{CF}}{1.0 - \min[|C(\mathrm{X})|; |\mathrm{CF}|]} \quad C(\mathrm{X}) > 0;\ \ \mathrm{CF} < 0 \quad \text{or} \quad C(\mathrm{X}) < 0;\ \ \mathrm{CF} > 0 \qquad [30.8.1c]$$

In the original work the certainty factor for a rule was formally related to the probability that it is true, as follows:

$$\mathrm{CF} = \frac{\max[P(\mathrm{X}\,|\,\mathrm{A}); P(\mathrm{X})] - P(\mathrm{X})}{1 - P(\mathrm{X})} \quad \mathrm{CF} > 0 \qquad [30.8.2a]$$

$$\mathrm{CF} = \frac{\min[P(\mathrm{X}\,|\,\mathrm{A}); P(\mathrm{X})] - P(\mathrm{X})}{P(\mathrm{X})} \quad \mathrm{CF} < 0 \qquad [30.8.2b]$$

The certainty factor CF in Equation 30.8.2a is also referred to as the measure of belief (MB) that the rule is true, and CF in Equation 30.8.2b as the measure of disbelief (MD).

In subsequent work certainty factors have often been used in a heuristic way to attach subjective estimates of certainty to rules. As an illustration of the application of certainty factors, consider the following illustrative example.

If A then X CF = 0.8

If B then X CF = 0.7

with an initial certainty $C(\mathrm{X}) = 0$. For both rules the relation applicable is Equation 30.8.1a. Successive applications give for $C(\mathrm{X})$ values of 0.8 and 0.94.

30.8.4 Dempster/Shafer theory

The Dempster/Shafer theory is a theory of evidence that makes a distinction between uncertainty and ignorance. It utilizes a belief function that is essentially a probability function to which confidence limits have been assigned. In other words, the belief function gives the probability that the probability estimate lies within certain bounds.

As the bounds narrow, the belief function tends to the conventional probability function. In other words, probability theory may be regarded as a special case of Dempster/Shafer theory.

30.8.5 Possibility theory and fuzzy logic

Another type of uncertainty is that which arises from the vagueness of natural language. This can be handled using fuzzy logic. This approach is also known as possibility theory. Fuzzy logic is considered in Section 30.10.

30.8.6 Incidence calculus

In probability theory the relationships between events are based on the assumption that the events considered are independent. Formulations of the basic probability relations exist that incorporate correlation terms which allow for dependency between events. The problem is the difficulty of furnishing numerical values for these correlation terms.

An alternative approach is the use of the incidence calculus of Bundy (1984). A set W is defined which is the set of all possible worlds or incidents. The incidence $i(A)$ of a formula A with respect to W is that subset containing all those incidents for which A is true. The independence of two formulas is obtained from the intersection of the two incidences, or subsets.

30.8.7 Plausibility theory

Another problem that needs to be addressed is reasoning with knowledge obtained from sources that are not totally reliable. This is the province of plausibility theory. Plausibility theory makes it possible to reason with inconsistent sets of knowledge obtained from imperfect sources. It utilizes p-sets, a p-set being a set of assertions vouched for by sources with some degree of reliability. Each member of a p-set is assigned a plausibility value that is determined by reference to the source with the highest status.

30.8.8 Truth maintenance systems

As already described, non-monotonic reasoning involves revision, and therefore the possibility of introducing inconsistency into the knowledge base. It is the function of a truth maintenance system (TMS) to maintain the consistency of the knowledge base during the process of reasoning by the inference engine, which is thereby freed to get on with its main task. A TMS is also known as a belief revision system or revision maintenance system.

A TMS maintains a record of the current beliefs and of the justifications for these beliefs. It identifies contradictions and the statements responsible for them and implements retractions. The record of the knowledge base takes the form of a dependency network, the nodes of which represent premises, conclusions, rules, etc. Each node has attached to it a justification enumerating the inference steps by which it was derived. The exception is premise nodes, since premises require no justification.

Two types of justification record are used, support lists (SLs) and conceptual dependencies (CDs), the first being the more widely used. A support list takes the form

(SL < in-list > < out-list>)

An active node must have at least one valid node in the in-list and hence IN the current belief set, and all nodes in the out-list must be OUT of the belief set. The state of a TMS may be represented in tabular form. A typical example might be:

Node	*Status*	*Support list*	
n1	IN	(SL ( ) ( ))	Premise
n2	OUT	(SL (nl) (n3))	Unjustified belief
n3	IN	(SL (n5) (n4))	Justified belief
n4	OUT	(SL ( ) ( ))	Retracted premise
n5	IN	(SL ( ) ( ))	Premise

The TMS can also be represented in graphical form using a special set of symbols.

When a contradiction is discovered, the TMS examines the dependency structure that supports the contradictory node and identifies the offending nodes directly. This process is termed dependency-directed backtracking (DDB) and is for this purpose a more efficient search strategy than chronological backtracking. The other type of record, the CD, may be regarded as a form of conditional proof. It takes the form:

(CD < consequent > < hypothesis in-list > < hypothesis out-list >)

The CD is valid if the consequent node is IN when each node in the hypothesis in-list is IN and each node in the hypothesis out-list is OUT. CDs can be, and usually are, converted to SLs.

There are a number of different types of TMS. These include the non-monotonic TMS (NMTMS) or justification-based TMS (JTMS); the logic-based TMS (LTMS); and the assumption-based TMS (ATMS).

30.8.9 Default reasoning

Another form of non-monotonic logic is default reasoning. This permits default assumptions to be handled. The method is non-monotonic because it may be necessary at some later stage to retract an assumption. Default reasoning may be represented as

$$\frac{\mathrm{P}(x)\colon \mathrm{MQ}(x)}{\mathrm{R}(x)}$$

where M is a consistency operator, which has the meaning 'and if it is consistent to assume. . .'.

30.8.10 Default reasoning: closed world assumption

The method of default reasoning just described is suitable for making specific individual default assumptions, but it is sometimes desirable to be able to make some more global set of assumptions. This is the function of the closed world assumption (CWA).

The CWA is that if a proposition cannot be proven it is false. It is often a reasonable assumption in a situation which is well understood and in which most of the facts are known.

Formally, the CWA involves the use of a metarule that if P(a) cannot be disproved, the assumption ¬P(a) is to be made.

30.8.11 Default reasoning: predicate completion and circumspection

Whilst default assumptions are valuable, they need to be carefully handled. Proliferation of default assumptions can cause problems. Two methods of doing this are predicate completion and circumspection.

Predicate completion involves the use of completion formulas to restrict the application of predicates to those entities to which they are applicable. Circumspection formulas fulfil a somewhat similar function by restricting the entities to which a predicate is applied to those with defined characteristics.

30.8.12 Heuristics

In many AI applications, particularly in expert systems, use has been made of heuristics and of *ad hoc* methods to take account of uncertainty. There are no doubt various reasons for this. One is probably unfamiliarity with the more formal methods available. Another is the difficulty of providing the probability estimates required in many formal methods.

A feature for which heuristics have been developed is the treatment of the degree of confidence in particular rules. For example, the expert system SOLOMON of P.R. Cohen (1985) utilizes a system of 'endorsements', effectively weightings, to be applied to rules.

30.9 Probabilistic Reasoning

30.9.1 Probability

Probability theory is considered at some length in Chapter 7 and it is sufficient here to restate the following basic relations for independent events A and B:

$$P(\mathrm{A\ AND\ B}) = P(\mathrm{A}) * P(\mathrm{B}) \qquad [30.9.1]$$

$$P(\mathrm{A\ OR\ B}) = P(\mathrm{A}) + P(\mathrm{B}) - P(\mathrm{A}) * P(\mathrm{B}) \qquad [30.9.2]$$

$$\neg P(\mathrm{A}) = 1 - P(\mathrm{A}) \qquad [30.9.3]$$

30.9.2 Bayes' rule

Much use is made in AI of Bayesian inference. Restating Bayes' rule for an event E and a hypothesis H

$$P(\mathrm{H}\,|\,\mathrm{E}) = \frac{P(\mathrm{E}\mid \mathrm{H}) * P(\mathrm{H})}{P(\mathrm{E})} \qquad [30.9.4]$$

Generalizing for a set of hypotheses $\mathrm{H}_1, \ldots, \mathrm{H}_n$:

$$P(\mathrm{H}_i\,|\,\mathrm{E}) = \frac{P(\mathrm{E}\mid \mathrm{H}_i) * P(\mathrm{H}_i)}{\sum_1^n P(\mathrm{E}\mid \mathrm{H}_j) P(\mathrm{H}_j)} \qquad [30.9.5]$$

30.9.3 Odds

Another formulation of probability that is often used in AI is odds. The odds O(E) in favour of an event E are related to its probability P(E) as follows:

$$O(E) = \frac{P(\mathrm{E})}{1 - P(\mathrm{E})} \qquad [30.9.6]$$

or, altnernatively

$$P(\mathrm{E}) = \frac{O(\mathrm{E})}{1 + O(\mathrm{E})} \qquad [30.9.7]$$

For Bayes' rule, where there is a hypothesis H, the two associated ratios of likelihood are

$$\mathrm{LS} = \frac{P(\mathrm{E}\,|\,\mathrm{H})}{P(\mathrm{E}\,|\,\neg\mathrm{H})} \qquad [30.9.8]$$

$$\mathrm{LN} = \frac{P(\neg\mathrm{E}\,|\,\mathrm{H})}{P(\neg\mathrm{E}\,|\,\neg\mathrm{H})} \qquad [30.9.9]$$

These relationships are used, for example, in the expert system PROSPECTOR. In the terminology there used the two likelihood ratios are termed logical sufficiency (LS) and logical necessity (LN).

Another useful concept associated with odds is that of the weight of evidence. In the use of Equation 30.9.4, the process of updating for a series of events $E_1, \ldots, E_n$ is somewhat clumsy. An elegant device introduced by Turing is to reformulate using odds and then to take logarithms. This gives

$$\log_e O(H \mid E) = \log_e O(H) + \sum_{i=1}^{n} w_i \qquad [30.9.10]$$

with

$$w_i = \log_e \left(\frac{P(E_i \mid H)}{P(E_i \mid \neg H)} \right) \qquad [30.9.11]$$

$$= \log_e f_i \qquad [30.9.12]$$

where f_t was termed by Turing the Bayesian factor in favour of H yielded by E_i, and w_i is the weight of evidence.

30.10 Fuzzy Logic

Fuzzy logic, and fuzzy set theory generally, addresses the problem of vagueness as opposed to randomness. The term fuzzy logic is used in two senses. In the broader sense it is virtually co-terminous with fuzzy set theory, whilst in the narrower sense it refers to that part of fuzzy set theory that deals with inference. Fuzzy set theory was introduced by Zadeh (1965). Accounts are given in *Fuzzy Sets and Systems* (Dubois and Prade, 1980), *Multistage Decision-Making under Fuzziness* (Kacprzyk, 1983), *Fuzzy Sets Theory and Its Applications* (Zimmerman, 1986), *Fuzzy Sets, Decision-Making and Expert Systems* (Zimmerman, 1987), *Fuzzy Relation Equations and Their Application to Knowledge Engineering* (di Nola *et al.*, 1989) and *Fuzzy Logic for the Management of Uncertainty* (Zadeh and Kacprzyk, 1992) and by Zadeh (1968, 1975a,b, 1978, 1983a,b, 1985) and Kacprzyk (1992).

Fuzzy logic provides a means of handling the vagueness inherent in natural language. Some of the quantities with which it deals are:

Fuzzy predicates: *small, large; young, old*
Predicate modifiers: *very, quite, extremely*
Fuzzy quantifiers: *most, many, few, often, usually*
Fuzzy numbers: *about* n, *a little more than* n
Fuzzy probabilities: *likely, unlikely*
Fuzzy possibilities: *quite possible, virtually impossible*
Fuzzy truth values: *true, quite true, mostly untrue*

Fuzzy quantifiers are also termed linguistic quantifiers, and predicate modifiers are also termed linguistic hedges.

Fuzzy logic effectively involves a numerical encoding of natural language terms, or linguistic variables. It is sometimes known as linguistic variable theory.

If $X = \{x\}$ is a universe of discourse, consider a fuzzy set A which is a subset of X, denoted $A \subseteq X$. The set A is a set of ordered pairs. $\{(x_A, \mu_A(x))\}$. The $\mu_A(x)$ is the grade of membership of x in A.

For example if $X = \{1, 2, \ldots, 10\}$, a fuzzy set for large numbers might be given as $A = 0.3/6 + 0.5/7 + 0.85/8 + 1/9 + 1/10$, where the grade of membership of the numbers 1–5 is zero, where that of the number 6 is 0.3, meaning that there is a probability of 0.3 that 6 is a member of the set, and so on.

The grade of membership in a set may be defined in terms of a membership function. Figure 30.1 shows two functions commonly used. Figure 30.1(a) is a form used for a linguistic variable such as a fuzzy quantifier and Figure 30.1(b) is a form used for a fuzzy number.

For the determination of the number of members in a fuzzy set with a given attribute, if A is the set of n items and $x_1, \ldots, x_n$ the members of that set and these members have to some degree the attribute F and therefore have a membership function $\mu_F(x_i)$, the number n_F of items which have this attribute F, or cardinality of the set, is determined as

$$n_F = \sum_{i=1}^{n} \mu_F(x_i) \qquad [30.10.1]$$

As an illustration, consider the problem of a set of items some of which are said to need replacement. If this set is $A = 0.3/x_1 + 0.3/x_2 + 0.8/x_3 + 0.8/x_4 + 0.8/x_5$, then from Equation 30.10.1 $n_F = 3.0$.

For the determination of the truth of a statement involving a fuzzy quantifier, such as 'most xs are F', the problem may be posed as the evaluation of the truth value τ of the statement, which may be expressed in a form such as $\tau(Qx\text{s are F})$, where $A = \{x_1, \ldots, x_n\}$ is the set of interest, F is an attribute and Q is a fuzzy quantifier. The grade of membership of an item x_i in the set A with respect to the attribute F is $\mu_F(x_i)$. The membership function is $\mu_Q(r)$. Then the relations for the determination of the truth value are

$$r = \frac{1}{n} \sum_{i=1}^{n} \mu_F(x_i) \qquad [30.10.2]$$

$$\tau(Qx\text{s are F}) = \mu_Q(r) \qquad [30.10.3]$$

As an illustration, consider the problem of determining the truth of the statement 'Most compressors are reliable'. The problem is then to evaluate the truth value τ of this statement which may be expressed as $\tau(Qx\text{s are F})$, where A is the set of n compressors, F is the attribute *reliable* and Q is the fuzzy quantifier *most*. Suppose that the grades of membership $\mu_F(x_i)$ for the attribute *reliable* in the set of compressors are taken as $A = 0.1/x_1 + 0.6/x_2 + 0.8/x_3$ and that the fuzzy quantifier may be represented by a suitable membership function $\mu_Q(r)$ taken as

$$\mu_Q(r) = 1 \qquad r \geq 0.8$$
$$\mu_Q(r) = 2r - 0.6 \qquad 0.3 < r < 0.8$$
$$\mu_Q(r) = 0 \qquad r \leq 0.3$$

Then from Equations 30.10.2 and 30.10.3 $r = 0.5$ and $\mu_Q(r) = 0.4$, giving a truth value τ of 0.4.

For fuzzy logic there is no unique set of inference rules, but the following are those most generally quoted. In terms of the truth value τ

$$\tau(\neg A) = 1 - \tau(A) \qquad \text{Negation}$$
$$\tau(A \wedge B) = \min(\tau(A), \tau(A)) \qquad \text{Conjuction}$$
$$\tau(A \vee B) = \max(\tau(A), \tau(A)) \qquad \text{Disjuction}$$

The application of inference rules in fuzzy logic tends to be considerably more complex than the corresponding exercise in classical logics.

30.11 Programming Languages

Many accounts of knowledge representation and of inferential reasoning give examples cast either in the form of the

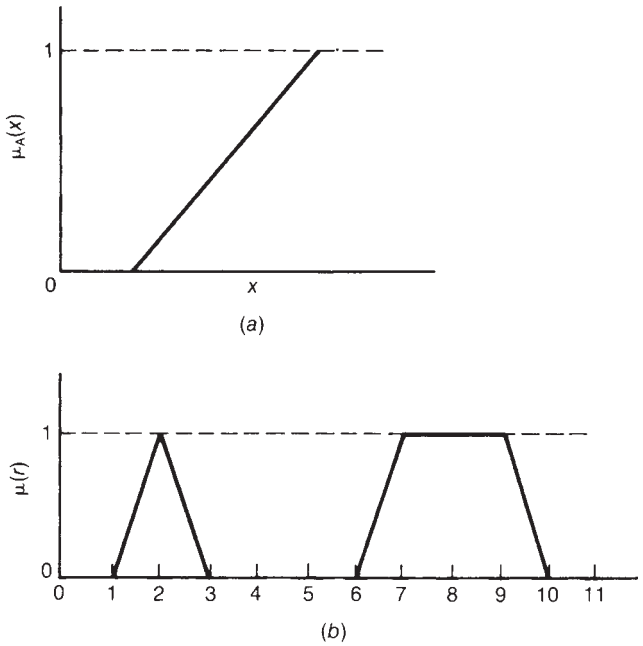


Figure 30.1 *Some Functions in fuzzy logic: (a) membership function of a fuzzy set; (b) two examples of a fuzzy number*

predicate calculus or of a specific programming language such as LISP or PROLOG. This section is a short introduction to these three languages, which is given for the purpose of making more concrete some of the concepts in the preceding sections and indicating how they are implemented in practice.

30.11.1 Predicate calculus

Knowledge representation and inferential reasoning are often exemplified using not a specific programming language but the predicate calculus. This is the approach adopted, for example, by Charniak and McDermott (1985).

The following are examples of some of the forms of knowledge representation and of inferential reasoning described in earlier sections cast in predicate calculus form.

Assertions

(inst vessel-1 vessel)	Vessel-1 is an instance of a vessel.
(structure vessel-1 thick-walled)	A structural feature of vessel-1 is that it is thick-walled.
(opens fitter flange)	A fitter opens a flange.

Isa hierarchy

(isa pump pressure-raiser)	A pump is a pressure raiser.

Connectives

(if (and (inst thermocouple instrument) (robustness instrument delicate))	If a thermocouple is an instrument and an instrument is delicate then a thermocouple is delicate.
(if (inst thermocouple instrument) (robustness thermocouple delicate))	If a thermocouple is an instrument, then a thermocouple is delicate.

Quantifiers

(forall *x* (if (inst *x* instrument) (robustness *x* delicate)	All instruments are delicate.
(forall *x* (if (control-valve *x*) (exists *y*) (power-source-of *x y*)	All control valves have a power source.

1. (inst thermocouple instrument) A thermocouple is an instrument.
2. (forall *x* (if (inst *x* instrument) (robustness *x* thermocouple)) All instruments are delicate.
3. (if (inst thermocouple instrument) (robustness thermocouple delicate)) If a thermocouple is an instrument, then a thermocouple is delicate.
4. (robustness thermocouple delicate) A thermocouple is delicate.

The third entry is obtained from universal instantiation and assertion 2 and the fourth by modus ponens from assertions 3 and 1.

Abductive inference

(has-inspections vessel-1)	Vessel-1 has inspections.
(for all *x* (if (contains-chlorine *x*) (has-inspection *x*))	All vessels which contain chlorine have inspections.
(contains-chlorine vessel-1)	Vessel-1 contains chlorine.

This example illustrates the fact that abductive inference is not a strictly valid form of reasoning and may given a incorrect conclusion.

Inductive inference

(if (inst instrument-1 instrument) (robustness instrument-1 delicate))	Instrument-1 is delicate.
(if (inst instrument-2 instrument) (robustness instrument-2 delicate))	Instrument-2 is delicate.
(forall *x* (if (inst *x* instrument) (robustness *x* delicate))	All instruments are delicate.

Frame

An assertion

(opens fitter flange)	A fitter opens a flange.

may be cast in the frame form as

(opens opens-1)	Opens-1 is an instance of opening.
(agent-opening opens-1 fitter)	The agent opening is a fitter.
(object-opened opens-1 flange)	The object opened is a flange.

Forward chaining

(if (inst ?*x* pump) (inst ?*x* pressure-raiser)	If an object is a pump, then it is a pressure-raiser.

30.11.2 LISP

LISP (List Processing language) is a high level, symbolic processing language devised by McCarthy (1960, 1978) and embodies his calculus for symbolic processing.

Accounts of LISP are given in *LISP 1.5 Primer* (Weissman, 1967), *The Little LISPer* (D.P. Friedman, 1974), *Let's Talk LISP* (Siklossy, 1976), *Anatomy of LISP* (J. Allen, 1978), *A Beginner's Guide to LISP* (Hasemer, 1984a), *Common LISP* (Steel, 1984), *LISP* (Winston and Horn, 1981) and by D. Shaw, Swartout and Green (1975), J. Allen (1979), Pratt (1979), Hasemer (1984b), Laubsch (1984), Patterson (1990), Tanimoto (1990) and Gabriel (1992).

LISP can be run in the interpreted or compiled modes, the former being more commonly used.

There are a number of dialects of LISP. A widely used form is Common LISP, which was created in an attempt to obtain a standard form. There are, however, several other widely used forms, including MACLSP and INTERLISP. The syntax of LISP is very simple. All data and program statements are represented in LISP as s-expressions. The valid s-expressions are the following: atoms, strings, lists and dotted pairs. An atom is a number or string of contiguous characters, including letters, numbers and special characters. A string is a sequence of characters enclosed in double quotation marks. A dotted pair, or cons, is an ordered pair of s-expressions enclosed in parentheses. A list is a sequence of s-expressions enclosed in parentheses.

Atom	a–b
String	"a b"
Dotted pair	(a · b)
List	(a b)

The basic operation of LISP is evaluation.

Instruction in LISP are described as forms. There are three basic types: functions, macros and special forms.

LISP contains a number of forms, which include the following: input and output forms; control forms; list manipulation forms; arithmetic functions; logical functions; evaluation forms; predicates; and function and property forms.

A principal feature of LISP is list processing and it possesses a number of functions for the manipulation of lists. These include cons, car, cdr and append.

30.11.3 Prolog

Prolog (Programming in Logic) is a programming language based on the predicate calculus. A number of researchers contributed to its origins; it was implemented by Colmerauer and co-workers (Colmerauer, Kanoul and van Caneghem, 1983).

Accounts of Prolog are given in *Programming in Prolog* (Clocksin and Mellish, 1981), *The Art of Prolog* (Sterling and Shapiro, 1986) and *Prolog Programming for Artificial Intelligence* (Bratko, 1986) and by K.L. Clark and McCabe (1982), Clocksin (1984), J. Cohen (1985), Colmerauer (1985) and Patterson (1990).

Programming in a language such as Prolog is referred to as logic programming. Prolog programming may be viewed as the creation of a database of facts and rules about objects, their attributes and relationships. This database can then be interrogated.

Prolog has a simple syntax. A program consists of *terms*. A term is a *constant*, a *variable* or a *structure*. It consists of a sequence of *characters*. A character may be of four kinds: an upper case letter, a lower case letter, a digit or an operator. A constant may be of two kinds: an *atom* or an *integer*. Examples of atoms are:

vessel
pressure_raiser

A variable is similar to an atom except that it starts with an upper case letter of underline sign '_'. A structure consists of a *functor* and of *components,* with the functor written first followed by the components in parentheses. An example of a structure is:

pressure_raiser (pump)
meaning 'a pump is a pressure raiser'.

Facts

A fact or assertion is exemplified by:

corrodes (wet_chlorine, mild_steel)
meaning 'wet chlorine corrodes mild steel'

Rules

A rule is cast in the form:

conclusion if condition 1 and condition 2 . . .

where the first term is the head and the rest is the body. Such a form is termed a Horn clause. An example of a rule is

corrodes(X, Y): wet_chlorine(X), mild_steel(Y)

where: denotes *if* and the commas between the structures *and*. The meaning is X corrodes Y if X is wet chlorine and Y is mild steel.

Lists
A list is written as a sequence of terms with commas between and enclosed in square brackets. An example of a list is:

[steel, aluminium, copper]

An empty list is denoted by [ ].

The head and tail of a list may be distinguished by the use of a vertical bar. An example of this is:

[a|b, c, d]

List manipulation
There are a number of list manipulation functions: append, member, cone, add, delete; cone denotes concatenate.

Queries
A query is exemplified by:

?-corrodes (X, mild_steel)
meaning 'what X corrodes mild steel?'.

Prolog program
A Prolog program proceeds by taking the rule condition, or headless Horn clause, and 'instantiating' the variables (X and Y in the above examples) to identify those instances which satisfy the rule. Thus for the rule given above the clause

?- wet_chlorine (X), mild_steel(Y)

satisfies

corrodes (X,Y)

The program continues by this process of resolution. A Prolog program may be regarded as a resolution theorem prover for Horn clauses.

The search strategy used in Prolog is depth-first. This strategy is in many ways simpler, but it does involve backtracking and the search can get into a 'loop'.

30.11.4 Object oriented programming

Another type of language that is now widely used in AI is object oriented programming (OOP).

Object oriented programming is described in *SMALLTALK-80, The Language and its Implementation* (Goldberg and Robsen, 1983) and in *Object Oriented Programming* (B.J. Cox, 1986) and by Stephanopoulos (1987) and Hodgson (1991).

In OOP, the program consists entirely of objects. An object is a frame-like entity with slots that hold not only data but also procedures. Procedures may perform a wide range of functions such as symbolic manipulation, numerical calculation and inferencing. Objects are arranged in hierarchies. Computation involves the sending of messages between objects.

One feature of object oriented programming is data encapsulation. Data structures incorporate within themselves the procedures that are used to manipulate them. An object can be regarded as a frame with slots that are the operations allowable on the object.

Another feature is the class hierarchy. At the top of the hierarchy is a single-object class, consisting of the principal object. Other objects lower down in the hierarchy belong to classes that are in effect subclasses. Inheritance occurs through the hierarchy.

OOP is an extremely powerful tool. A whole manufacturing process may be represented as an object, covering not only the physical plant but also its operation, documentation, hazards and so on.

30.11.5 C++ programming language

Of the more conventional programming languages, mention should be made in particular of C++. This language supports object oriented programming and interfaces with both LISP and Prolog.

30.11.6 Language characteristics and facilities

Work in AI makes use of a number of languages, and there are major differences between them. An account is given by Frost (1986). A distinction is often made between procedural languages and declarative languages, with conventional languages such as FORTRAN being described as procedural and those such as LISP and Prolog as declarative. However, the term procedural is not well defined.

The essential distinction is whether or not the 'flow of control' is specified. The flow of control is specified in conventional languages, using such commands as GO TO statements and DO loops, but not in languages such as LISP and Prolog. In these latter declarative languages there are no explicit commands that determine the flow of control. This does not mean, however, that the programmer has no influence on control. In a language such as Prolog the flow of control is affected by the order in which the statements are written.

Languages used in AI work include: the functional language LISP; the logic programming language Prolog; the frame languages AM and KRL; and the script language SAM.

The flexibility of a language may be increased by the use of an add-on facility. Thus, for example, the program FLEX provides Prolog with an object oriented enhancement.

A language such as Prolog is used particularly as a research tool. A commercial implementation may well be rewritten in a conventional language such as C++.

30.12 Structured Knowledge

The foregoing sections have described some ways of representing knowledge. It is now necessary to consider in more detail the representation of knowledge in structured form.

30.12.1 Indexing

A basic form of structure is that provided by the use of indexing, addresses, pointers and lists. These structures are not, however, generally sufficient for the purposes of AI.

30.12.2 Associative networks

A widely used form of representation in AI is the associative network. This is a form of directed graph with labelled nodes and arcs. An example is shown in Figure 30.2(a). An associative network may be expressed in terms of the predicate calculus, with nodes and arcs represented by terms and relations. An example illustrating this equivalence for a blocks world scene is given by Charniak and McDermott (1985).

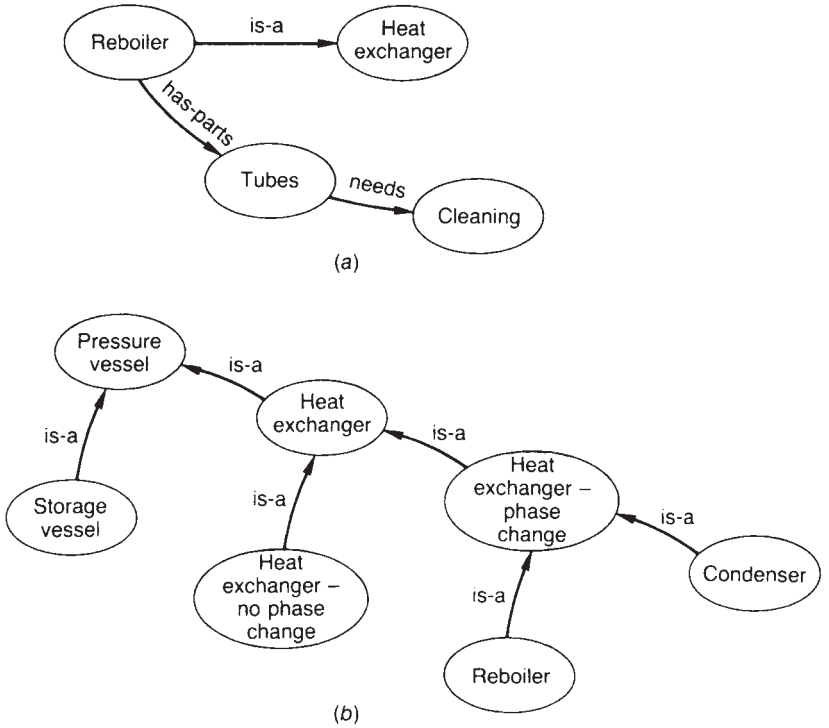


Figure 30.2 *(a) An associative network and (b) an is-a network*

The arcs of an associative network may represent a number of different relations. Some principal relations are:

Label	*Meaning*	*Used with*
is-a	Is an instance of	Generic noun
has	Has as parts	Specific noun
ako	Is a kind of	Generic noun
is	Is	Attribute
member-of	Is a member of	Larger set or entity
subset-of	Is a subset of	Larger set or entity

The ISA and HAS links are of particular importance for structured form inheritance.

30.12.3 ISA hierarchy

A particular aspect of associative nets is the ISA hierarchy. This is effectively a way of expressing a taxonomy using a network with is-a arcs and working down from the generic to the specific. The associative network is shown in Figure 30.2(b) is an example of an ISA hierarchy.

30.12.4 Inheritance

Children can inherit a characteristic from their parents. Similarly, entities in an ISA hierarchy may inherit from entities directly above them. Another way of putting this is that a set can inherit a characteristic from a superset of which it is part, and a subset can inherit from a set. Multiple inheritance occurs when a set is part of more than one superset and may thus inherit from both supersets. This obviously creates the potential for conflict between the inherited values.

As stated earlier, the use of inheritance may be regarded as a form of default reasoning. The point has also been made, however, that the proliferation of defaults through inheritance can cause problems and it is necessary to proceed cautiously. In some cases it may be appropriate to allow most members of a set to inherit a certain characteristic but to arrange to override this for some members of the set.

30.12.5 Semantic networks

Associative networks are widely used in natural language comprehension and are then often termed semantic networks.

30.12.6 Slot and filler systems

Another type of representation goes by the general name of a slot and filler system. Particular forms are frames and scripts. In terms of the predicate calculus, a slot and filler system may be represented by a single statement with a number of arguments corresponding to the number of slots.

Slot and filler systems are useful for: representing archetypes, or stereotypes; handling default values; matching and pattern recognition; and error detection.

30.12.7 Conceptual dependency

Before considering particular slot and filler systems, it is appropriate to mention conceptual dependency (CD) theory. The basic concept here is that a set of sentences that have different structures but identical meaning should have

a CD representation that is both unique and unambiguous. CD methodology provides a set of tools such as primitives, syntax, rules, etc., for the formulation of such sentences.

30.12.8 Frames

A frame is a structure that contains a number of pieces of information on some entity such as an object, event or situation. It is applicable where the entity has a stereotype that is sufficiently strong to define the features on which information should be stored. Typical situations treated in the AI literature are attending a meeting or eating in a restaurant.

A frame consists of a frame name and a list of attribute-value, or slot-filler, pairs. In other words, the attributes are also called slots and the values fillers. A slot is simply the name of an attribute and the filler its value. Many accounts use the mixed terminology of slots and values, and this is adopted here. An empty frame, or schema, contains only the frame and slot names, whilst an instantiated frame contains also the values. In some cases default values may be supplied for slots.

Alternatively, or in addition, a slot may be furnished with associated information in the form of a procedural attachment, or demon. Two commonly used types of attached information are a procedure to determine the value for the slot if one is needed (the if-needed attachment) and one to be executed when the value has been filled in (the if-added attachment). Another type is a constraint on the value which can be added to the slot. A slot may also be filled with the name of another frame. In this way hierarchies of frames may be created.

Frames are a natural form of representation for default reasoning and for inheritance.

30.12.9 Scripts

Like a frame, a script is a structure that contains a number of pieces of information on some entity such as an event, situation or activity. It differs in that the slots contain not values but sentences written in terms of CD primitives. Typical situations treated in the AI literature are eating in a restaurant or shopping in a supermarket. Thus, a script will typically have a script name and slots for the situation, actors, initial conditions and props.

There will then be slots for several scenes and one for the outcomes. A script may be used to reason about a current situation by filling in those parts which characterize the situation, retrieving from memory another script which matches this situation. Slots in the current script are filled by inference using inherited and default values.

Like frames, scripts are a natural form to use for default reasoning and inheritance.

30.12.10 Constraints

A simple constraint may be represented as a predicate of the predicate calculus. Alternatively, it may be required to represent a more generalized constraint in the form of an algebraic equation relating several variables. In this case a constraint schema may be created which lists the variables in the equation and, for each of these variables, the algebraic expression by which it is evaluated.

30.12.11 Relational databases

Another form of structured knowledge representation is the relational database. This has been described in Section 30.2.

30.12.12 Production systems

Another form of structured knowledge is a production system. Production systems have already been described in Section 30.6 and are therefore not considered further here, except to note that the knowledge held in a production system is not necessarily confined to that embodied in the rules, but may include, in the conflict resolution section, knowledge about the control strategy which governs the application of the rules. It is often in this latter that much of the expertise resides.

30.12.13 Objects

Objects constitute another form for the representation of structured knowledge. They have been described in the previous section in the context of OOP.

30.13 Search

The application of the tools described to problem-solving typically involves some form of search. Search is one of the fundamental activities in AI.

30.13.1 Search procedures

There are a large number of search procedures that are used in AI. They may be classified in several ways. Some procedures are used to search for optimal paths; others for any path, not necessarily an optimal one; and others again for game playing. Another distinction is between uninformed, unguided, or blind search and informed or guided search. Some principal procedures category are:

General	*Informed*	*Optimal*
Breadth-first	No	No[a]
Depth-first	No	No[a]
Hill-climbing	Yes	No
Beam	Yes	No
Best-first	Yes	No
British Museum	No	Yes
Branch and bound	Yes	Yes
A* algorithm	Yes	Yes
Games		
Minimax		
Alpha beta		

[a] Search does not necessarily find the optimal, or shortest, path unless it is exhaustive.

30.13.2 Uninformed search

Uninformed search is inefficient, but it may be necessary to resort to it if there is difficulty in formulating heuristics or an evaluation function to guide the search.

30.13.3 Breadth-first search

Breadth-first search involves visiting all the nodes at a given level before moving to the next level. A breadth-first search is illustrated in Figure 30.3(a).

30.13.4 Depth-first search

Depth-first search involves moving down the tree as rapidly as possible, visiting nodes at successively lower levels until the lowest node in the branch is reached, then returning back up the tree to the point at which a downward

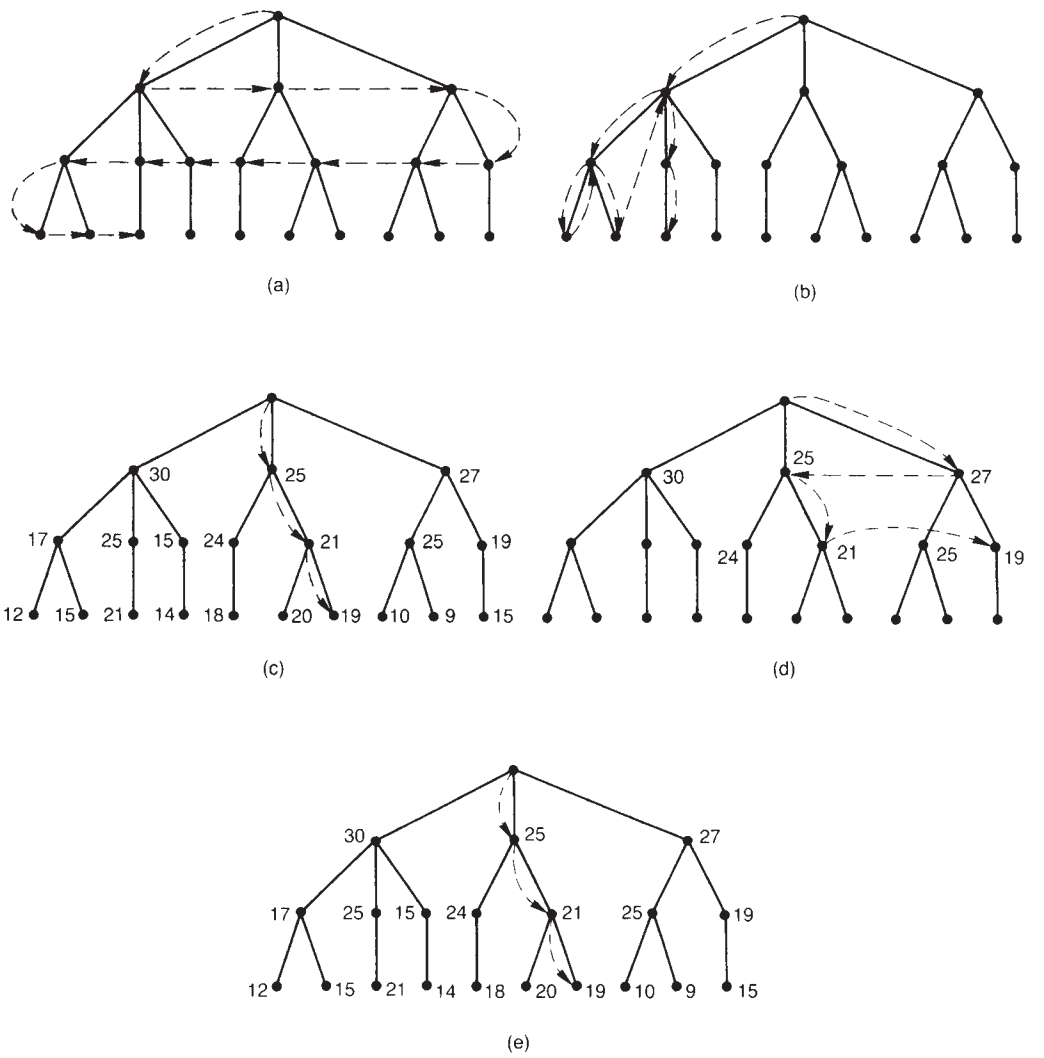


Figure 30.3 *Search through a goal tree: (a) breath-first search; (b) depth-first search; (c) hill-climbing; (d) beam search; (e) best-first search*

move again becomes possible, and so on. A depth-first search is illustrated in Figure 30.3(b). A depth-first search, therefore, necessarily involves backtracking.

30.13.5 Informed search

It will be clear from the account just given that uninformed search methods are subject to combinatorial explosion and become impractical for larger problems. The remedy is to inform the search in some way.

30.13.6 Heuristic search

One approach to informed search is the use of heuristics. These may take various forms, but generally have to do with the characteristics of the goals, states and paths between states.

30.13.7 Evaluation function

It may be possible to guide the search by using a formal evaluation function, which may also go by other names such as an objective function or a figure of merit. The formulation of such a function is an aspect of matching, which is discussed in Section 30.14. Given an evaluation function it becomes possible to utilize search methods which are much more efficient. The sum of the values of an evaluation function between the nodes on a path is known as the path length.

30.13.8 Hill-climbing

A hill-climbing search utilizes an evaluation function that it seeks to minimize and is essentially a form of depth-first search. It differs from a regular depth-first search in that at a given node the next move made is to the child node for which the evaluation function is minimized. A hill-climbing search is illustrated in Figure 30.3(c).

Like other forms of hill-climbing, there are certain classic topological problems which a hill-climbing search may encounter. They include the foothill, plateau and ridge problems.

Although, in general, hill-climbing is a common form of optimization, a hill-climbing search as just described does not guarantee a global optimum solution.

30.13.9 Beam search

A beam search resembles a breadth-first search in that it proceeds level by level, but differs from it in that the search utilizes an evaluation function and moves downwards only through the best w nodes at each level. A beam search is illustrated in Figure 30.3(d). By comparison with breadth-first search, beam search is much more economical.

30.13.10 Best-first search

A best-first search resembles hill-climbing in that it utilizes an evaluation function, but differs from it in that it uses this function in a different way. Whereas in hill-climbing the function is used to select between the child nodes of the current node, in a best-first search the function values for all nodes visited are stored and the search moves from the node for which the function is a minimum, wherever it may be in the tree. A best-first search is illustrated in Figure 30.3(e). Like hill-climbing, a best-first search does not guarantee a global optimum.

30.13.11 British Museum method

Of the methods that provide an optimum solution, the British Museum method involves an exhaustive search through the whole tree to identify the optimum path. The search may be breadth-first or depth-first, but in either case it is modified so that it does not stop when a path is found but continues until all paths are found and the optimum can be identified. The method is even more subject to combinatorial explosion than the regular uninformed search methods.

30.13.12 Branch-and-bound search

A branch-and-bound search proceeds by storing the path lengths and expanding that node which at any given stage has the shortest path length. This means that the search may move down a path in one branch of the tree and then jump to one in a second, quite different, part of the tree when movement down the current path has raised the path length above that in the second part. A branch-and-bound search is somewhat complex; an account is given by Winston (1984).

In this search method termination when a path is found does not actually guarantee an optimal solution, since in principle there may be a path that is incomplete but very close to the solution point. For an optimal solution, it is necessary to use the condition that termination occurs when the shortest complete path is shorter than the shortest incomplete one.

30.13.13 A* algorithm

The A* algorithm is a special form of branch-and-bound search which utilizes instead of the path length from the start to the current node the total path length from the start to the goal node. This means that it must possess a heuristic for estimating the distance between the current and the goal node. If this estimate is a lower bound on the actual distance, the solution obtained is optimal. This condition is known as the admissibility of the algorithm.

30.13.14 Games search

Games differ from other problems handled in AI in that there is an active opponent. This has led to the development of specialized forms of search for game playing. The tree through which the search is conducted is known as a game tree. The head of the tree is the start position and the successive layers represent the 'turns' of the two players. Game trees are considered further in Section 30.15.

30.13.15 Move generation and evaluation

A particular form of heuristic search that has been developed for games such as checkers and chess is move generation and position evaluation. Some of the heuristics for these are described in Section 30.15.

30.13.16 Minimax method

The Minimax method utilizes the concepts of move generation and position evaluation and searches for the moves most likely to win the game.

The two players seek to achieve conflicting goals. One player is taken as seeking to maximize the evaluation function and the other as seeking to minimize it. The maximizing player (Max) has to assume that, when it is his or her turn, the minimizing player (Min) will select that move which minimizes the function.

It is assumed in the Minimax method that it is practical to perform only a limited evaluation of a position; in other words, that it is practical to look only a limited number of moves ahead. The maximum number of levels to which the search can be extended before evaluation takes place is the lookahead depth.

For a start which is Max's move, the even numbered levels contain nodes where the evaluation function is applied to obtain a maximum score and the odd numbered levels nodes where it is applied to obtain a minimum score. A move is evaluated by backing up from the current node to the start, summing the scores at each level. The best move for Max is then that with the maximum backed-up value.

30.13.17 Alpha beta method

Another search method used for game playing is the alpha beta method. It is essentially a form of the Minimax method which prunes those branches of the tree that give a bad result and are therefore irrelevant. The essential principle is that if the opponent has even one good response to a move that would cause it to give a bad result, the move is bad and that branch is pruned.

30.13.18 Control

In general, search needs to be subject to some control strategy. The methods just described in effect constitute particular strategies. However, problems differ, and a strategy suitable for one may not be appropriate for another. The development of search control strategies is an important area of work in AI.

30.13.19 Dependency-directed backtracking

One of the most widely used search methods is depth-first search. This involves backtracking, which unless guided

can be an inefficient process. One common method of providing such guidance is dependency-directed backtracking (DDB).

In conventional backtracking, on failing to find a solution the search tracks back to the last node visited at which an alternative path exists. In DDB, the search returns instead to the node which is implicated in the failure. In this case the backtracking is guided by the data dependencies of the rules involved, which it uses to seek out the node causing the contradiction. This function may be performed by the truth maintenance system.

30.13.20 Forward and backward chaining

Search may proceed by forward chaining or by backward chaining. These two modes of search may be explained either in terms of the rules or of the search tree.

In forward chaining the left-hand side of the rule is instantiated first, so that this mode is termed data-driven inference. In backward chaining, by contrast, the right-hand side of the rule is instantiated first, and this mode is termed goal-driven inference. In terms of the search tree, forward chaining involves a search from the bottom to the top of the tree, or from leaf to root, whilst backward chaining involves a search from the top down, or from root to leaf. Thus, forward chaining is referred to as data-driven or bottom-up, or as antecedent reasoning, and backward chaining as goal-driven, top down, or as consequent reasoning.

The mode of chaining which is most appropriate depends on the shape of the tree. Figure 30.4 shows two search trees. Forward chaining is best suited to the fan-in case shown in Figure 30.4(a) and backward chaining to the fan-out case shown in Figure 30.4(b).

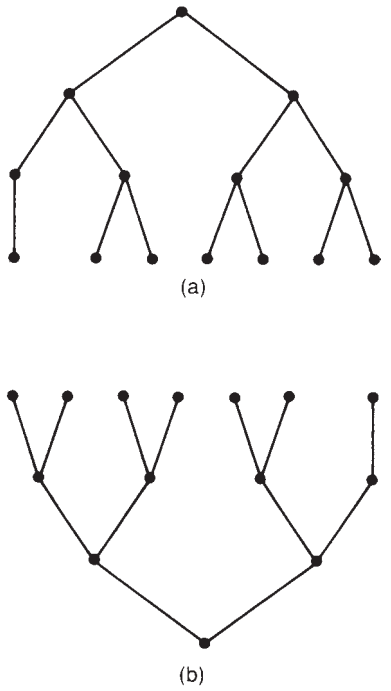


Figure 30.4 *Direction of chaining as a function of the shape of the goal tree: (a) forward chaining; (b) backward chaining. In each diagram the search is from the bottom*

30.14 Matching and Pattern Recognition

30.14.1 Matching

Another major activity in AI, and one closely related to search, is matching. Some form of matching is involved in virtually all AI work but the nature of the matching process depends on the particular field of application. Areas of AI in which matching is required include logical reasoning, learning, planning, expert systems, vision and natural language comprehension.

Matching is required for a number of purposes. It may serve to identify and classify objects, retrieve objects from a knowledge base, establish the eligibility of objects for inheritance, select alternatives, control a sequence of operations, and so on.

The overall process of matching may be described as one of representation, transformation and comparison. The object to be matched must first be represented in a form that captures the relevant characteristics. This representation may then need to be transformed to make it conformable for comparison with another object, the referrent. This comparison is based on a matching measure, or metric, which forms the basis of comparison, and a matching criterion, which is used to decide whether a match is established.

There is a variety of representational structures to which matching may be applied. They include: clauses in prepositional or predicate logic and logic rules; sets and bags; frames and scripts; and graphs, trees and networks.

There are a number of types of matching metric. There are various distance metrics based on quantitative variables. They may be deterministic or probabilistic. Probability metrics include product moment correlation and measures of clustering. There are also distance metrics based on qualitative variables. These variables may be: binary variables, denoting one of two states; nominal variables, denoting equality or inequality; and ordinal variables, denoting rank order.

There are a number of similarity measures. One type of similarity measure is based on the sets of attributes common to the object and its referrent. Another type which is used for labelled graphs is based on the 'cost' of transforming the graph into its referrent graph. Another metric is the distance that can be defined between the fuzzy sets associated with an object and those associated its referrent. The matching criteria used, and the types of matching obtained, may be exact, partial or fuzzy.

30.14.2 Pattern recognition

Pattern recognition comprehends, but is somewhat broader than, matching. The term is applied particularly to vision. The process of pattern recognition involves feature selection, matching and classification. Pattern recognition is often closely associated with learning by the development of classification rules. Pattern recognition is one of the strengths of neural networks, described in Section 30.21.

30.15 Problem-solving and Games

An important part in the development of AI has been played by problem-solving of various kinds, particularly puzzles and games. An influential early program was General Problem Solver (GPS).

30.15.1 Puzzles

Puzzles frequently quoted in the AI literature include missionaries and cannibals, painted squares, the travelling salesman and the Towers of Hanoi (or Hanoi Towers) problems. The solution of these puzzles is treated essentially as a search. A particular form of search applied to puzzles is means–ends analysis.

In the Towers of Hanoi the goal is to transfer three graded discs from one peg to another, starting from an initial state in which the three discs are on one peg, with the smallest disc on top and the largest at the bottom, and there are two empty pegs. The rules are that a disc can be moved only when there is no disc on top of it and that it may not be placed on a smaller disc at the destination peg. The puzzle is therefore a planning problem in a world akin to the blocks world described below.

30.15.2 Games

Games likewise feature strongly in AI. These are generally two-person, zero-sum games, and include tic-tac-toe (noughts and crosses), checkers (draughts) and chess. These may all be treated as board games and have well-defined rules. Such games are generally represented by a game tree, with the first state at the root of the tree and with the successive move options represented by the successive plies below.

For any but the simplest game, a blind search is impractical for combinatorial reasons and some more sophisticated search method is needed. As already described, characteristic search methods used for game tree searches include the Minimax and alpha beta methods.

Practical problems may be handled by a games approach insofar as they can be treated as games against nature; in particular, against a nature which seeks to defeat the human player by invoking Murphy's law that whatever can go wrong, will go wrong.

30.15.3 Samuel's checkers program

An early and influential games program was the checkers program of Samuel (1959, 1963a,b). This program used Minimax search and heuristic methods for state evaluation and move generation. State evaluation utilized a function with some 16 features such as the number of pieces, piece location and piece advantage. Move generation was guided by tree pruning heuristics. The program also possessed a learning capability, with storage and retrieval of board states that had occurred in previous games.

30.15.4 Chess playing programs

Another game that received attention early in the work on AI and has been influential in its development is chess. Work on computer chess is described in *Computer Chess* (Newborn, 1975). A short account of its historical development is given by Charniak and McDermott (1985).

Early workers in computer chess were C.E. Shannon (1950a,b) and Turing (1953). An early program was written by Bernstein. A major advance occurred in 1967 with the program by Greenblatt. Another influential treatment was that of Newell and Simon (1972).

The general approach to chess playing is broadly similar to that applied to checkers, as just described. A search is conducted through the game tree using methods such as Minimax and alpha beta, and exploiting heuristics for state evaluation and move generation.

The conduct of a game such as a chess may be regarded as a form of planning, albeit under conditions where there is an opponent who seeks to frustrate the plan.

30.15.5 General Problem Solver

General Problem Solver (GPS) by Newell and Simon (1963) was another early and influential program. It is described in GPS: *A Case Study in Generality and Problem-Solving* (Ernst and Newell, 1969).

GPS may be regarded as the first AI system to make a clear separation between problem-solving and task knowledge. It was designed to tackle the class of problems that can be formulated in terms of a set of objects, which include states, and of operators that are applied to these objects to transform them into goal objects, or states.

The basic method used in GPS is means–ends analysis. The search is depth-first, with backtracking, and utilizes forward chaining.

In GPS an operator has three features: the preconditions, the transformation function and the differences reduced. The first is a state description which it is a necessary condition that the current state should match for the operator to be applicable. The second is the function that the operator performs. The third links the operator to the differences that it is effective in reducing.

30.15.6 Blocks world

An environment widely studied in AI work is the so-called blocks world. This world consists of a set of blocks on a flat surface. It is a world that is relatively simple and predictable.

Blocks world has been used as an object of study in several areas of AI. It has obvious application to manipulation by robots, but it has also been used in work on computer vision.

30.16 Vision

A quite different area of work is that of vision. This topic is a major one in AI but is not of prime concern here, and will be treated briefly.

Accounts of visual image processing and computer vision are given in *Computer Techniques in Image Processing* (Andrews, 1970), *Computer Vision Systems* (Hanson and Riseman, 1978), *Computer Vision* (Ballard and Brown, 1982), *Vision* (Marr, 1982), *Robot Vision* (Horn, 1986) and by Winston (1984), Patterson (1990) and Tanimoto (1990).

Most applications of visual image processing lie outside the process field, but its use in robotics may have some bearing. There are also applications in accident investigation, as described below.

Visual image processing is generally described as involving an image acquisition stage followed by low level, intermediate and high level processing stages. The image acquisition stage yields a digitization of the image. Low level processing deals with noise reduction, outline and edge definition, thresholding, and texture and colour. Thresholding converts a grey image into one with regions of black and white only. Intermediate level processing handles shape formation and interpretation and involves operations such as connecting, filling in, combining boundaries, determining regions and assigning labels. High level processing deals with semantic analysis and interpretation and involves the identification and characterization of objects and relationships. The various processes utilize a number of specialized techniques such as the determination of the edge distance

and surface direction, region growing, shape analysis, and so on. More advanced topics include three-dimensional images and motion. Work on aspects of visual image processing, notably on blocks world problems, has had influence on AI generally.

Image enhancement may sometimes be used in accident investigation. The Piper Alpha Inquiry heard evidence on image enhancement of photographs taken of the west side of the platform in the early stages of the fire, with particular reference to the issues of the nature and source of the fireball and of any damage which may have occurred to the firewall between the modules, though in the event it was not possible in this case to take much from this evidence.

30.17 Natural Language

Another area of work is that of natural language. This too is a major topic in AI, but again one that can be treated briefly here.

Accounts of natural language processing and machine translation are given in *Syntactic Structures* (Chomsky, 1957), *Semantic Information Processing* (Minsky, 1968), *Understanding Natural Language* (Winograd, 1972), *Semantics* (Lyons, 1977), *Syntax* (Culicover, 1982), *Practical Experience of Machine Translation* (Lawson, 1982), *Language as a Cognitive Process* (Winograd, 1983), *Language Learnability and Language Development* (Pinker, 1984), *Conceptual Structure* (Sowa, 1984), *Natural Language Processing* (Cullingford, 1986), *Understanding Natural Language* (J. Allen, 1987) and by Winston (1984), Charniak and McDermott (1985), Patterson (1990) and Tanimoto (1990).

Natural language processing as such is of little interest here, but work in this area has an important bearing on topics that are relevant such as knowledge and knowledge representation. Work on natural language covers areas such grammars, parsing, syntax, semantics and language generation.

Some kinds of knowledge used in understanding language include: syntax, or the structure of language; semantics, or the meaning of language; pragmatic knowledge, which relates sentences and their meaning to context; and world knowledge, which is required to use a language effectively.

In the areas of semantics, work relevant to the topics discussed earlier includes that on the semantics of quantity, time, space, and knowing and belief.

Transition networks, a technique for parsing sentences, and their development, augmented transition networks (ATNs), are based on directed graphs. ATNs have been used in Stone World, a program that simulates some of the activities of a stonemason, moving objects around an environment.

Some understanding of natural language is likely to be helpful in applying AI techniques in areas such as operating procedures.

30.18 Planning

Another major area of work in AI is that of planning.

Accounts of AI planning include those in GPS (Ernst and Newell, 1969), *A Structure for Plans and Behavior* (Sacerdoti, 1975), *Planning and Understanding* (Wilensky, 1983) and *Readings in Planning* (J. Allen, Hendler and Tate, 1990) and by Fikes and Nilsson (1971), Tate (1976, 1977), Sacerdoti (1977, 1985), Waldinger (1977), Steflk (1981), Vere (1983, 1992), Winston (1984, 1992), Chapman (1985), Charniak and McDermott (1985), Currie and Tate (1991) and Lyons and Hendricks (1992).

Planning programs which have been influential in the development of planning in AI are GPS by Ernst and Newell (1969), STRIPS by Fikes and Nilsson (1971) and Fikes, Hart and Nilsson (1972), NOAH by Sacerdoti (1975, 1977), NONLIN by Tate (1977), MOLGEN by Steflk (1981), DEVISER by Vere (1983) and TWEAK by Chapman (1985).

30.18.1 Planning and plans

Requirements for planning are that there be an initial world state, a set of actions that change that state and a set of goals for the final state, and that the environment be sufficiently predictable, though not necessarily completely determined.

The need for planning arises where the situation is novel or critical. Often, however, the situation is familiar. In such cases it may well be sufficient to retrieve from store an existing plan.

It is instructive to compare a plan and a program. A plan is typically executed once, whilst a program may be run many times, albeit with different input data. A plan may have to cope with an environment that is subject to changes, whereas the environment in which a program operates is stable. A plan defers commitment in order to be able respond to the environment.

Planning may be regarded as a special case of reasoning about time, or temporal reasoning. The temporal relationships may be shown in a time map, which is a specialized form of associative network. In one form of time map the nodes represent times, in another they represent situations.

Planning involves decomposing a task into a set of subtasks. These subtasks are then further decomposed until a level is reached at which a subtask decomposes into a set of primitive actions. The task may be represented in the form of a task network, which is a special kind of time map. The structure of the task is in effect a plan for performing it.

Accounts of the overall activity of planning tend to break it down in different ways. One broad type of activity is plan generation. This involves creating a plan to perform a task. The generation of plans is one of the more difficult areas of planning. Plan generation tends currently to be domain-specific, with domain-independent plan generation often a rather distant goal.

It may not always be necessary to generate a fresh plan. In some cases it is sufficient to recognize that the task is, or is sufficiently close to, one for which a plan has already been devised and is already in store.

Another broad area of planning is plan selection and coordination decisions, which are rather more amenable to domain-independent treatment. Plan selection involves choosing from candidate plans and plan coordination the sequencing of a set of plans. Criteria for making these decision include avoidance of interference between plans and minimization of resources, including time.

Planning, therefore, involves the manipulation of a number of plans. These plans are not necessarily treated as a global plan. The emphasis may be rather on the planner and on the way in which it manipulates these plans during execution. In general, plans may be relatively simple, but the planning algorithms that manipulate them can be rather complex.

Plan execution involves executing the primitive actions of the plan, monitoring for failures and, if necessary, replanning.

30.18.2 Blocks world and mundane planning

Much AI work on planning has centred around the blocks world situation in which a robot performs actions such as stacking or unstacking the blocks. In the simple case, it is assumed that the only changes to the environment are those caused by the robot's action and that these actions are predictable, instantaneous and performed one at a time.

Features of this situation are the relative simplicity of the goals, the world state and the resultant plans. In real-life, or mundane, situations the case is quite different. There are likely to be a number of goals some of which may conflict and there may be a large amount of common sense information that needs to be taken into account.

30.18.3 Goal ordering and meta-goals

Planning is sensitive to the order in which the goals are attempted. An inappropriate ordering can result in extensive backtracking. Methods of goal ordering are therefore needed.

One method is to permute the order of the goals if there is difficulty in obtaining a solution. A more systematic approach is to order the goals in a hierarchy. High level goals have features such as: they are the most difficult to achieve, they determine the structure of the space, and they are not themselves affected by actions.

In many cases, particularly in mundane situations, the problem of the ordering of goals becomes quite severe. There are multiple goals that may interfere or are conflicting so that there is a need to be able to reconcile goals and to abandon goals. This problem has often been tackled by the use of *ad hoc* rules that set meta-goals such as achieving as many goals as possible, maximizing the value of the goals achieved, avoiding impossible goals and economizing resources such as time.

Wilensky (1983) has attempted a more fundamental approach which eschews this *ad hoc* approach and in which planning of meta-goals, or meta-planning, is conducted in exactly the same way as regular planning of goals. This approach is implemented in the program PANDORA.

30.18.4 Protection of goals

Planning requires that certain goals and states be protected from alteration. It is normal that a goal, once achieved, is protected. However, if subsequently a solution cannot be found, it may be necessary to violate this protection in order to seek a solution by goal permutation or some other method.

Protection is also applied to states. A state is protected during an interval if it is required to be true throughout that interval. An important class of plan failure is that of protection violations.

One strategy for preventing protection violations is to detect them as they occur. Another is to anticipate them. The basic method of dealing with a protection violation is reordering.

30.18.5 Events, actions and macroactions

The interaction of an agent with an environment may be described in terms of the actions of the agent and of the events in the environment.

The general form of a primitive action routine specifies (1) objects (to be used), (2) steps (to be executed), (3) order (of steps) and (4) protection (of goals). A primitive action is modelled by specifying the action routine and the pre-conditions and post-conditions of the action, or in other words the conditions for it to be taken and its effects.

A set of primitive actions may be grouped together in a structure with associated goal protections to form a macro-action. The plan implemented by a macroaction is thus one created by a human rather than an AI planner. Macroactions are a useful device, but also have drawbacks. In some cases a macroaction may be inflexible or inappropriate.

30.18.6 Operators

Closely related to the above is the concept of an operator. In AI planning an operator acts on a state to effect transition to some other state. An operator is an action with attached lists of pre-conditions and post-conditions. The pre-conditions are the conditions that must be met for the operator to be applied and the post-conditions those that will then pertain. One of the most widely used operators is the STRIPS operator, described below.

30.18.7 The frame problem

In most cases, when an action in a plan is implemented, only a limited proportion of the system states alters, so that the effect is localized. There may, however, be a large number of states that might change. The need to infer that a state will not change across an event is known as the 'frame problem', the term frame here having no connection with frame as a form for knowledge representation.

30.18.8 Planning by search

In AI, planning is effectively a specialized form of search. There are two approaches that may be taken to this search. One is to search through the space of world situations, or possible states of the world. In this type of search the initial state and final states are given by initial and final world models and the operators are the primitive acts.

The alternative, and generally preferred method, is to search the space of plans. In this case operators are applied to reduce the task to subtasks and primitive tasks and to order unordered tasks. The search is conducted to discover a sequence of operations to transform the initial state into the goal state.

30.18.9 Measures of complexity

A measure of complexity in planning may refer either to the planning algorithm or to the planning task. The computational time for the implementation of a planning algorithm may be expressed in terms of a function $O(n)$, where n is the number of items or some other suitable metric of problem size. If in the algorithm $O(n)$ is a polynomial in n, the problem is said to have polynomial time complexity. If, on the other hand, $O(n)$ is such that n appears as an exponent, the problem is said to have exponential time complexity. The increase in computational time with n for exponential time complexity is such that the task of solution is regarded as intractable, whereas with polynomial time complexity the task may be tractable.

The difficulty of a planning task is commonly expressed in terms of NP-completeness. Known algorithms for the solution of NP-complete problems have an exponential time complexity and the task is generally assumed to be intractable. A task which is difficult in this sense is said to be NP-hard.

30.18.10 Means–ends analysis

One of the basic techniques of planning is means–ends analysis. The essential features are an initial state, a goal state, a set of operators with pre-conditions, and a difference

function. The latter is a measure of the difference between the goal state and the current state.

Means–ends analysis starts with a small number of general steps that are then expanded into more detailed steps. If in the current state an operator cannot be applied because a pre-condition is not satisfied, the algorithm creates a subgoal. It moves to an adjacent state in which the pre-condition is satisfied.

One problem in means–ends analysis is that of real and apparent difference, or distance from the goal. If the difference function is crude and inappropriate, the search can enter a dead end where the apparent distance to the goal is short but the real distance is large. An analogy is reaching a point that is close to the goal as the crow flies but where the path is blocked by an insurmountable cliff face.

30.18.11 General Problem Solver

Mention has already been made of the General Problem Solver (GPS) program of Ernst and Newell (1969). The basic method used in GPS is means–ends analysis. GPS works from the current state to the goal in a forward-chaining process. It proceeds by selecting and applying operators to reduce the difference function. If necessary, it resorts to the creation of subgoals. If the search reaches a dead end, it backtracks. Thus GPS in effect uses a depth-first search.

30.18.12 STRIPS

A development from GPS is the planner STRIPS (Standford Research Institute Problem Solver) created by Fikes and Nilsson (1971) and Fikes, Hart and Nilsson (1972). STRIPS has had a major influence on AI planning, being widely used, copied and modified. STRIPS is a linear planner, as described below.

A characteristic feature of STRIPS is the operator used. The STRIPS operator consists of an action with a specified list of pre-conditions and post-conditions. The pre-conditions are the conditions that must be met for the operator to be applied and the post-conditions those that will then pertain.

Another feature of STRIPS is that it tackles the frame problem by making the default assumption that an action has the effects specified, no less and no more.

30.18.13 Linear and non-linear planning

A distinction is made in planning between linear and non-linear planning. Early planning programs used linear plans. The planner starts at one end, either the initial or the goal state, and moves step by step closer to the other end. The order of the operations performed is completely specified. Non-linear planning, by contrast, utilizes partial plans. A partial plan is a set of steps that is not fully determined. Features of a partial plan that may not be fully specified are the order of the steps or the choice of operator to be used. A single partial plan may comprehend a number of total plans, or completions.

The use of non-linear instead of linear planning is much more efficient, being characterized by polynomial time, as opposed to exponential time.

30.18.14 NOAH

The first non-linear planner was NOAH by Sacerdoti (1975, 1977).

30.18.15 Planning theorems

A feature of AI planning is the formulation of governing theorems. This aspect is associated particularly with the work of Chapman. This work moves planning away from *ad hoc* approaches and emphasizes the proving of planning theorems, on correctness or attainability.

30.18.16 TWEAK

The planning theorem approach is embodied in the TWEAK program developed by Chapman (1985). This is a non-linear planner that retains the STRIPS-type operator. A plan produced by the program is guaranteed to be correct.

30.18.17 Hierarchical planning

In the foregoing account, frequent reference has been made to goals and some to subgoals. It might perhaps be inferred from this that AI planning always involves a hierarchy of goals, but this is not so. Hierarchical planning is only one approach.

In hierarchical planning, the higher level goals are expressed in relatively general terms and are then expanded into the more detailed lower level goals. Translation from higher to lower levels goals is a matter of inference. To this extent hierarchical planning may be distinguished from planning proper, which involves the selection and ordering of goals.

30.18.18 Non-subgoaling planning

An alternative to hierarchical planning is to use a single level of goals. Such non-hierarchical planning is sometimes known as non-subgoaling planning. The characteristic non-subgoaling planner proceeds by forward chaining using means–ends analysis and adds actions to the plan in the order in which they will be used. Using this approach it is relatively easy to check that the current plan does not enter into an undesirable state, and hence that the final plan does not do so either.

30.18.19 State graph planning

In state graph planning the problem is represented as a graph of the possible states of the system, the states being represented by the nodes and the actions by the arcs connecting the nodes. State graph planning can provide solutions to a wide range of planning problems, including most operating procedure synthesis problems. However, it has a number of limitations. Problems of modelling and of undesirable states have to solved by the user in the process of creating the state graph. The state graph can be very large and it may not be easy to modify it. There are issues of the correctness and completeness of the stage graph.

30.18.20 Goals of protection

A planner should ensure that entry is not made into an undesirable state. However, AI planning methods for the avoidance of such states are not well developed. Hence in applying such planning to process problems such as operating procedure synthesis, where it is essential to avoid unsafe states, some adaptation is necessary.

A variety of terms have been used to describe the negative goal of avoiding entry into an undesirable state. They include domain constraints, avoidance goals, preservation goals and goals of prevention. The latter term is the one used here.

30.18.21 Functional operators

As already described, a central concept in planning is that of an operator. Reference has been made particularly to the STRIPS operator, which has been widely used. However, in

systems such as process networks the conditions after an event can depend on those that pertain before it. In other words there is a functional dependency between the input and output states. This cannot be handled by a STRIPS-type operator.

This problem has led to the development of the conditional, or functional, operator. This type of operator has a number of sets of pre-conditions and a number of sets of post-conditions. For each set of pre-conditions, there is a corresponding set of post-conditions which apply.

30.18.22 Action synergy

It commonly occurs in planning that a group of actions has an effect which is not exhibited by the individual actions taken in isolation. This is known as action synergy.

A simple example is a pair of valves in a pipe. If the initial state is that both are closed, the action of opening one of them does not have the effect of allowing flow through the pipe. This effect is obtained only by the actions of opening both valves.

There are there thus some goals that can be achieved only by action synergy. Action synergy may also be the cause of an undesirable effect. In some cases it can have the effect of entering an unsafe state.

30.18.23 Subplan merging

Another situation common in planning is the need to merge two subplans. This can often be a non-trivial operation.

A simple example of the need for subplan merging is the problem of taking a tool from a toolbox. The initial states are that the toolbox is shut and that the tool is inside. The desired end state is that the toolbox is shut and that the tool is outside. The last two states therefore constitute goals for the end state. The plan must ensure that the two subplans for removing the tool and shutting the toolbox are so merged that the tool is removed before the toolbox is shut.

30.18.24 Planner operation

At this point an account is given, following Vere (1992), of the operation of a typical AI planner. The planner operates by keeping a stack of goals and conducting an ordered depth-first search to achieve them.

It proceeds by a process of node expansion, involving backward chaining. Each node represents a subgoal. The planner achieves the subgoal by selecting an action with a post-condition which matches the subgoal. The preconditions of that action then become the new subgoals.

It is not always necessary or appropriate to expand a pre-condition. In many cases a pre-condition can be achieved by linking. Linking is used where the precondition of a subgoal is already satisfied, in that there already exists elsewhere in the plan above the current subgoal a node with an assertion which achieves that pre-condition. In some instances, there may be several linkings which satisfy a pre-condition. Associated with this are syntactic conventions in action descriptors which inhibit backward chaining of a pre-condition and thus reduce the extent of backtracking.

Where node expansion throws up more than one candidate action, in other words where an OR branch occurs, it is necessary to select one of them. Rules are therefore required for action selection. These rules may be domain-independent or domain-specific. Some criteria for domain-independent selection are to choose an action on the basis of: the number of non-linkable pre-conditions; the number of additional, or bonus, goals which it achieves; and the resources which it consumes.

Conflict can arise where there are two unordered nodes with contradictory assertions. Resolution of the conflict needs to be made immediately. It is effected by placing the two nodes in order and maintaining the protection of the upper node.

Node expansion, linking and conflict resolution by ordering are the three fundamental operations of this type of planner. Vere gives an example of a blocks world plan utilizing only these three operations. If neither node expansion nor linking is possible, the subgoal cannot be achieved and it then becomes necessary to backtrack.

30.18.25 NONLIN

The program NONLIN by Tate (1976) is a hierarchical planner that operates broadly on the above lines and has been applied to turbine overhaul and naval missions.

30.18.26 Execution monitoring

A plan may fail in execution due to a number of causes. One such cause is simply random events. Hence execution monitoring is an essential part of planning. Planning of a task and its execution need to be interleaved. There is no point in formulating a comprehensive plan if it is likely to be negated by events occurring at an early stage. On the other hand, some degree of forward planning is desirable. One issue in planning is how far ahead to plan.

There is no agreed approach to execution monitoring, but it is possible to identify certain issues. At any given time the planner has an expectation that a number of states are true. It may conduct tests to verify them. In this case it requires criteria for selecting the tests.

A related problem is the explanation of unexpected results. These may arise for a number of reasons such as a defective model of the world situation or a random event.

30.18.27 Reactive planning

The conventional approach to planning is the creation of a plan which in the absence of changes in the environment will achieve the goals but which has some capability to respond to such changes and to replan. There exists, however, a quite different approach, which is to achieve goals by a process of responding to the environment. This is reactive planning, which is described by Lyons and Hendricks (1992).

Conventional planning has typically been applied to situations of the blocks world type. Other worlds exist, however, and need to be dealt with. One envisioned by Schoppers (1987) is 'baby world', in which the environment is disturbed by activities characteristic of babies, such as throwing bricks around, and so on. It is with this type of world that reactive planning is concerned.

Like conventional planning, reactive planning seeks to achieve goals, but when a change in the environment occurs, it reacts not by making a modest change to the original plan, or replanning, so much as by creating a new plan.

Thus, the techniques used in reactive planning are based on some form of reaction between the agent and the environment. For example, Brooks (1986, 1989) has used a hierarchy of routines that react with the environment to achieve goals, the hierarchy being termed the 'subsumption architecture' and the routines the 'behaviours'.

Another aspect of reactive planning is the work of Nilsson (1988), who has addressed the problem that in conventional planning the higher levels surrender control and have to

suspend action until they receive it back, so that the situation is liable to occur that the lower levels of control continue with activities which have been rendered inappropriate by a change in the environment.

Reactive planning is a relatively new but now influential approach.

30.18.28 Temporal planning

Planning necessarily deals with the ordering of subtasks, but it does not necessarily deal with time constraints. Temporal planning addresses problems where such time constraints exist.

These time constraints have been handled in work by Vere (1983), in which each action is assigned a start time and a duration. Temporal relationships are defined using words such as before, equal, meets (adjoins), overlaps, during, etc. He has implemented this method in the program DEVISER.

30.18.29 Domain dependency

Initial work on planning utilized domain-independent approaches. Later work has moved to domain-dependent methods. This change of approach was prompted by experience. In addition, however, it has been shown by Chapman (1985) that there are theoretical reasons for thinking that it is not practical to build a domain-independent planner that is able to tackle real-life problems and is also provably correct.

30.18.30 Decision theory

One method of analysing a plan is the use of decision theory. Since AI work on planning has largely been concerned with synthesis and since decision theory is a tool for analysis, the extent of application of decision theory in planning has been limited. Human planners are well able to create plans in mundane situations. Decision theory was developed to assist in the analysis of plans for the more complex cases.

More extensive application of decision theory for the analysis of plans synthesized by AI planning methods is likely to highlight the problem of obtaining estimates for the values of probability and utility used in the theory.

30.19 Learning

From the earliest day of AI, the creation of a machine which can learn has been one of the principal goals. Accounts of learning in AI are given in *Learning Machines* (Nilsson, 1965), *Machine Learning* (Michalski, Carbonell and Mitchell, 1983–) and by Lenat (1982, 1983) and Simon (1983).

Two principal categories of task in machine learning are (1) classification and (2) problem-solving.

The representation of the objects that the machine experiences may take various forms. Objects may be described in various ways, including in terms of binary features, multi-valued attributes, classes or structural relationships.

Learning may be classified in a number of ways. The learning modes considered here may be described as (1) learning by instruction, (2) learning by classification, (3) learning by exploration and conceptualization, (4) learning by experience and analogy, (5) learning from failure and (6) learning by problem-solving.

In addition to these learning modes, there are also particular devices that have a learning capability. Two that figure prominently in AI are (1) neural networks and (2) genetic algorithms.

Of particular importance in learning is the use of inference by induction and this is discussed in Section 30.20.

In the following, an account is given of the learning modes and learning devices just described. It needs to be said, however, that for some of the learning modes the work described constitutes only a very partial exploration of the mode both in breadth and depth.

30.19.1 Supervised and unsupervised learning

Most work on classification tasks involves supervised learning. Typically, the program is given a learning set in which both the class and attributes of each object are specified and it is then required to create a discrimination hierarchy.

There is some work, however, on learning in unsupervised classification tasks where the program has to perform the assignment to classes itself.

In problem-solving unsupervised learning is the norm, but some work has been done on supervised learning in which an expert prompts the program at crucial junctures.

30.19.2 Learning from data and stored knowledge

Another distinction is between learning from data and from stored knowledge. It is often assumed that learning requires new data about the interaction of the agent and its environment. In fact, there is generally much to be learned from knowledge already in store which can be retrieved and processed in various ways so as to learn new concepts, rules and so on. In particular, learning may take place in the course of problem-solving.

30.19.3 Learning by instruction

One method by which a program may learn is to receive instruction from a tutor. Such learning by instruction may proceed in various ways.

One type of instruction that the tutor may give is modifications or additions to rules such as those in the knowledge base of an expert system. The tutor may provide additional rules, perhaps rules-of-thumb. Or he may monitor the responses of the system, detect deficiencies in these responses, examine the explanations given for them, and identify and modify the rules causing these defective responses.

Instruction of an expert system on these lines is performed by the expert system TEIRESIUS of R. Davis (1980), created as an intelligent editor for MYCIN. An account of its operation is given by Charniak and McDermott (1985).

There is an element of instruction in some of the other methods of learning also, insofar as the learning set or environment presented to the program has been chosen by the tutor. This choice is often of considerable importance.

30.19.4 Learning by classification

Learning by classification involves inductive reasoning in which generalizations are made from a learning set of specific objects, each of which is labelled with attributes and assigned to a class. This form of learning is considered in more detail in Section 30.20.

30.19.5 Learning by exploration

Learning by exploration is essentially concerned with concepts. The program is given a learning set in which the objects are unclassified and required to develop concepts.

One area of work here is conceptual clustering in which the program determines how to cluster and to describe objects. It typically involves the creation of a hierarchy of concepts.

Two programs which perform learning by exploration are AM and EURISKO, both by Lenat (Lenat, 1982, 1983; Lenat and Brown, 1984). Their operation is described by Charniak and McDermott (1985). Exploration differs from search in that the purpose is to develop and enhance concepts rather than to achieve goals. Essentially such exploration involves activities such as determining similarities and differences between objects and classifying them into sets, frames and hierarchies.

30.19.6 Learning by experience

Learning by experience may take various forms, but the aspect that is considered here is essentially learning by analogy. This type of learning is also known as case-based learning. In such learning, numbers of specific cases are stored in memory. An issue is the extent to abstraction of the salient features is performed at the time of storage or is deferred until the case is to be used. Clearly this affects the storage of cases in, and retrieval from, the memory.

A program that learns by experience is MACBETH by Winston (1980, 1982). An account is given by that author (Winston, 1984). This program deals with the process of learning from situations by analogy with other situations and the discovery of general rules. A situation, or precedent, is presented in the form of a natural language description. This description is transformed using techniques of natural language understanding. This transformation facilitates the creation of a cause structure for the precedent. The precedent has constraints that are to be matched before the precedent can be applied. The precedent is then applied by analogy to other situations where such a match exists and rules are derived. Such reasoning by analogy is liable to deduce rules that are too sweeping, and 'censors' are used to modify the rules by introducing additional conditions.

30.19.7 Learning from failure

A particular form of learning by experience is learning by failure. A type of failure that features strongly in AI is the failure of a plan.

A program that learns by the failure of plans is HACKER by Sussman and Stallman (1975), another influential system. An account is given by Charniak and McDermott (1985). The program has been used in the blocks world environment. It contains a simulated effector system that reports the reason for failure of a particular step in a plan. The program revises the plan on the basis of the report.

The program also has a collection of 'critics' that have the function of criticizing plans. These critics too have an ability to learn, which they do by analysing the experience of failures.

30.19.8 Learning by problem-solving

As stated earlier, learning does not necessarily have to be based on new data; it is also possible to learn by processing stored data. This type of learning is sometimes called analytical learning, as opposed to inductive learning from data.

Accounts of such analytical learning tend to deal particularly with learning by problem-solving. One problem-solving tool that may be learned is a set of rules. The task of problem-solving is performed. Learning from this solution proceeds by identifying the features of the problem and the problem-solution pairs that were used. From this explanation, general rules are derived. This form of analytical learning is also called explanation-based learning.

Besides rules, other features of problem-solving which may be learned include macro-operators and heuristics.

30.19.9 Neural networks

Turning to devices with learning capability, one of the principal developments is neural networks. A neural network is a network of 'neurons' that in a simplified way models the operation of the human brain. It learns from a learning set of input-output patterns. It is in effect a device for learning by experience. A fuller account of neural networks is given in Section 30.21.

30.19.10 Genetic algorithms

Another device described in biological terms is the genetic algorithm, so called from a loose analogy with genetic change in a population. A genetic algorithm utilizes a set of patterns the weighting of which is changed as learning proceeds. In effect the patterns compete and only the fit survive. Genetic algorithms are used both for classification and for problem-solving.

The genetic algorithm method may be applied to the development of rules in a rule-based production system. The weighting of the rules is adjusted to reflect their contribution to desirable behaviour.

In some applications, use is made of operators that propose new rules and the exploration conducted is primarily on the effect of different combinations of rule rather than of weightings of individual rules.

30.20 Inductive Learning

A large proportion of learning in AI proceeds by inference through induction. One of the principal uses of induction is the classification of objects, events and situations, but applications of inductive reasoning are much wider than this and extend to concepts, rules and so on. An account of induction in AI is given by Patterson (1990).

The concept underlying inductive learning is the basic logic of inductive inference:

$$\begin{array}{ll} \text{Assertions} & \mathrm{P}(\mathrm{a}_1) \rightarrow \mathrm{Q}(\mathrm{b}_1) \\ & \mathrm{P}(\mathrm{a}_1) \rightarrow \mathrm{Q}(\mathrm{b}_1) \\ \hline \text{Conclusion} & \forall xy\ \mathrm{P}(x) \rightarrow \mathrm{Q}(y) \end{array}$$

Induction may be regarded as a process of class formation. The task is to partition the universe U of objects into classes. The minimum partition is into a single class C and the rest U − C. To this end use if made of concepts, a concept being a description or rule which subdivides a set. The target concept is the concept that classifies all the objects in the universe. The positive instances are those objects that fit the target concept and the negative instances are those that do not. A consistent classification rule is one that is true for all positive instances and false for all negative instances.

30.20.1 Generalization and specialization

There are a number of recognized techniques of induction involving generalization and its converse, specialization. The basic process in induction is generalization. However, generalization may become too sweeping, so that the class

created includes negative as well as positive instances. Such overgeneralization may be corrected by specialization.

Methods of generalization are exemplified by the techniques of changing constants to variables, dropping conditions and closing an interval. Replacement of constants by variables simply means that, given that a relation holds in a number of instances, it is inferred that it is generally true. Dropping a condition involves removing a condition in a description and thus widening the class. In closing an interval it is inferred that what is true of objects at the two bounds of the interval is true of objects in between.

30.20.2 Inductive bias

Generalization may be treated as a search problem. As such, it involves the familiar need to attend to the efficiency of the search. The term bias is applied in this context to those factors, other than those of the learning set, which influence the selection of hypotheses. One type of bias involves restricting the hypothesis space to be searched. Another involves ranking the hypotheses.

30.20.3 Classification

A principal application of inductive learning is classification, in which the program is presented with a learning set of objects each of which is assigned to a class and described by a number of attributes. The task is then to induce a discrimination hierarchy, or a set of rules, for the assignment of the objects to the classes.

In the more straightforward cases the learning set is consistent in that it does not contain counter-examples. More advanced work addresses the problem of such noisy learning sets.

In using a classification algorithm, the selection of the learning set requires some care to ensure that the set provides comprehensive coverage of the domain of interest and, where necessary, to exclude counter-examples.

30.20.4 ID3

One of the principal classification methods is the ID3 algorithm of Quinlan (1983a,b). ID3 is based on an information theory approach.

If in a sample of n objects there is a proportion p which belong to class C and hence a proportion $(1-p)$ which do not, a quantity H_c may be defined as

$$H_c = -p\log_2 p - (1-p)\log_2(1-p) \qquad [30.20.1a]$$

$$= -\sum p_i \log_2 p_i \qquad [30.20.1b]$$

H_c may be regarded as the expected information content of a message from a discrimination, or decision, tree for a set C of objects.

The attribute on which to branch first is selected on the criterion that the information gain is to be maximized. The information gain G_j for attribute j is

$$G_j = H_c - H_j \qquad [30.20.2]$$

with

$$H_j = \sum p_i H_{jk} \qquad [30.20.3]$$

$$H_{jk} = -p_{jk}\log_2 p_{jk} - (1-p_{jk})\log_2(1-p_{jk}) \qquad [30.20.4]$$

where H_j is the information content at the node for attribute j, H_{jk} is the information content associated with the individual branches at the node, and p_{jk} is the proportion of objects having attribute j in branch k at the node.

The algorithm is illustrated by Quinlan using the following single-class classification problem. Objects either belong to the class or they do not and are then denoted by + or −, respectively. There are three attributes: height, hair and eyes. The learning set of objects is:

short, blond, blue: +	short, dark, blue: −	tall, dark, brown: −
tall, blond, brown: −	tall, dark, blue: −	short, blond, brown: −
tall, red, blue: +	tall, blond, blue: +	

There are therefore three branch points in the decision tree.

Then, since there are three objects out of eight that are in class C, and five that are not, Equation 30.20.1 gives

$$H_c = -(3/8)\log_2(5/8) - \log_2(5/8) = 0.954 \text{ bits}$$

Taking the first attribute, height, the information still needed for a rule for the 'tall' branch is, from Equation 30.20.4,

$$H_{j1} = -(2/5)\log_2(2/5) - (3/5)\log_2(3/5) = 0.971 \text{ bits}$$

and that needed for the 'short' branch is

$$H_{j2} = -(1/3)\log_2(1/3) - (2/3)\log_2(2/3) = 0.918 \text{ bits}$$

and hence from Equation 30.20.3 the expected information content is

$$H_j = (5/8) \times 0.971 + (3/8) \times 0.918 = 0.951 \text{ bits}$$

Then from Equation 30.20.2 the information gain is

$$G_j = 0.954 - 0.951 = 0.003$$

This value is negligible. Computing the information gains for the second attribute, hair, and the third attribute, eyes, in the same way yields information gains of 0.454 and 0.347, respectively. Thus the second attribute, hair, is selected for the first branch. Then the first branch of the decision tree is:

Node	*Link*
hair:	red: tall, red, blue: + dark: short, dark, blue: − tall, dark, blue: − tall, dark, brown: −
	blond: short, blond, blue: + tall, blond, brown: − tall, blond, blue: + short, blond, brown: −

Proceeding in a similar manner, the third attribute, eyes, is selected for the second branch. This then gives:

Node	*Link*	*Node*	*Link*
hair:	red: tall, red, blue: +		
	dark: short, dark, blue: – tall, dark, blue: – tall, dark, brown: –		
	blond:	eyes:	blue: short, blond, blue: + tall, blond, blue: + brown: tall, blond, brown: – short, blond, brown: –

A further, more complex example is given by Patterson (1990).

Further work on this algorithm has addressed aspects such as handling the noise in the data, the detection of thresholds for numeric attributes and updating of the tree with new data.

In one application to the classification of diseases, the algorithm outperformed an expert system constructed by conventional methods over a period of years (Quinlan *et al.* 1986).

The classification tool EXTRAN is an implementation of IDS.

30.20.5 INDUCE

Another program for inductive learning is INDUCE developed by Michalski and co-workers (Larson and Michalski, 1977; Dietterich and Michalski, 1981). This program discovers class patterns and formulates generalized descriptions of these patterns. A characteristic feature is its utilization for its descriptive language of an extension of first-order predicate logic.

30.21 Neural Networks

A quite different kind of learning device is exemplified by neural networks. These utilize a form of learning which in certain respects mimics that of the human brain. Neural networks are described in *Neural Computing* (Beale and Jackson, 1990) and *Neural Networks in Artificial Intelligence* (Zeidenberg, 1990) and by Patterson (1990) and Tanimoto (1990).

Work on neural networks was originally inspired by research on modelling of the human brain. Another input comes from studies of associationist psychology, particularly behaviourism. A neural network is a large network of nodes connected by links. These nodes are information processing elements based on a simple model of the neuron in the human brain. A node sums the stimuli entering it through the links and has a threshold above which it will execute, or fire, and pass a stimulus to the connected nodes. A link has a weighting that is applied to the stimulus passing along it. The link weights enhance or inhibit the stimuli. The knowledge held in the network is distributed throughout it in the form of features such as these thresholds and weights. The network has an input layer of nodes, an output layer and a number of intermediate layers in between.

Learning in, or 'programming' of, a neural network proceeds broadly as follows. The network is set to its initial condition, typically with thresholds and weights set at random. It is presented with a learning set of pairs of inputs and outputs that it is then taken through. For each input the output is observed and adjustments are made to the thresholds and weights according to some strategy. The process is repeated until the learning set is exhausted.

A common strategy for adjusting the adjustable features during learning is error back-propagation. In this method, the error between the desired and actual outputs is used to adjust first the hidden layer next to the output. This error in then propagated back, ultimately to the input layer. The features most commonly adjusted are the thresholds and weights, but other strategies may be used which involve adjustments to the network topology or even to the learning strategy.

A neural network is a form of statistical associative model. The statistic inference that it utilizes is better able to handle randomness and exceptions than is rule-based inference. Rule-based systems can handle exceptions, but generally at the price of much increased complexity.

Neural networks have been used for knowledge representation, production systems and expert systems, pattern recognition, visual image processing, speech recognition and natural language understanding.

Production systems and expert systems created using the neural network technique are known as connectionist systems. One application, by Touretszky and Hinton (1985), simulates the firing of rules and thus the operation of a production system. Another application is the creation of expert systems, as in the work of Gallant (1988) and Saito and Nakano (1988).

Gallant has described a neural network expert system for the diagnosis and treatment of the medical condition of acute sarcophagal disease. The system handles two forms of disease, six symptoms and three treatments. It is able to make deductions from an incomplete set of data on the symptoms and to give an explanation of the route by which it arrived at its conclusions.

30.22 Graphs, Trees and Networks

AI makes use of a large number of graphs, trees and networks, some of which are now briefly described. Some of these graphical forms constitute forms of knowledge representation, whilst others relate to the reasoning process. The graphical forms can be represented by suitable program structures in the programming languages used. Some graphs, trees and networks used in AI are listed in Table 30.3 and some are shown in Figures 30.2 and 30.5.

Taxonomic hierarchies for classification of entities go by various names. One form of particular importance is the ISA hierarchy, which has been described in Section 30.12 and which is shown in Figure 30.2(b). Another form is the object oriented system (OOS) hierarchy.

An inheritance hierarchy is a particular type of taxonomic hierarchy, which in addition to showing the classification shows also inheritance of attributes.

A discrimination net represents the process of discrimination between entities and attributes in order to identify an object. An object identification net is similar.

Also the term 'decision tree' is sometimes applied to this type of diagram.

Table 30.3 *Some graphs, trees and networks used in artificial intelligence*

Type	*Application*	*Nodes*[a]	*Reference*[b]
Taxonomic hierarchies	Classification	Entities	
All things hierarchy		Entities	Winston, p. 322
ISA hierarchy		Entities	C&M, p. 26
OOS hierarchy	Classification	OOS entities	Patterson, p. 155
Inheritance hierarchy	Inheritance	Entities	C&M, p. 406
Discrimination net,	Identification	Entities; entities,	C&M, p. 154
object identification net		attributes; entities	Patterson, p. 317
Parse tree	Grammar	Syntactic categories	Frost, p. 531
Syntax tree	Grammar	Syntactic categories	Frost, p. 527
Transition network	Grammar	Syntactic categories	C&M, p. 202
Augmented transition network	Grammar	Syntactic categories	
Associative network	Relationships	Entities, attributes	Patterson, p. 129
Semantic net	Relationships	Nouns, verbs, adjectives	Frost, p. 457
Semantic tree	Logical reasoning	Logical expression; truth values	Tanimoto, p. 234
Bayesian network	Bayesian inference	Evidence; inferences; conclusions	C&M, p. 478
Truth maintenance network,	Truth maintenance	Premises, assumptions,	Patterson, p. 85
belief network	systems	facts; beliefs	Winston, p. 244
Constraint propagation network	Constraint propagation	Facts; beliefs	Winston, p. 243
Goal tree	Planning	Goals; subgoals; primitive actions	C&M, p. 277
AND/OR tree	Planning	Goals; subgoals; primitive actions	Winston, p. 39
Search tree	Search	Start; intermediate nodes; end	C&M, p. 265
Games tree	Games	Start; positions; end	C&M, p. 281
Time map	Action sequences	Actions	C&M, p. 432
Task network	Planning	Task; subtasks; primitive actions	C&M, p. 492
Frame network	Frames	Frames	Patterson, p. 138
Decision tree[c]	Decisions	Utility values	C&M, p. 521
Neural network	Neural networks	Model neurons	Patterson, p. 344

[a] where there is a single entry, all nodes are of this type; where there are two entries (separated by a semi-colon), the first refers to the top node and the second to the intermediate and bottom nodes; and where there are three entries, the first refers to the top node, the second to the intermediate nodes and the third to the bottom nodes.
[b] References are to: Charniak and McDermott (1985) (C&M); Frost (1986); Patterson (1990); Tanimoto (1990); Winston (1984).
[c] The term decision tree is commonly used in AI for a tree which represents decision-making in terms of decision theory, and this is the meaning here.

Diagrams used in the syntactical analysis of natural language include parse trees, syntax trees, transition networks and augmented transition networks (ATNs). A semantic net is used to represent the meaning of sentences.

The associative network is a widely used tool for representing relationships of various kinds, as shown in Figure 30.2(a).

A semantic tree shows the development of a logical expression in terms of its truth values. A Bayesian network gives the structure of the relationships between evidence, inferences and conclusions in Bayesian inference.

A truth maintenance system (TMS), or belief network, shows the structure of the TMS in terms of the current beliefs and the premises, assumptions and facts that support them. A constraint propagation network is somewhat similar.

A goal tree shows the expansion of a goal into its subgoals and ultimately to the primitive actions that are necessary to achieve it. Where AND/OR logic is involved, the diagram may also be referred to as an AND/OR tree. A goal tree is shown in Figure 30.5(a).

A game tree shows the development of a game from the start position, through the moves to the end position. A game tree is shown in Figure 30.5(b).

A search tree shows the process of search from the start through the nodes to a solution, if one is found. Search trees are considered in Section 30.13.

A time map shows a series of actions in time, as shown in Figure 30.5(c).

A task network shows the expansion of a task into its subtasks and ultimately to the primitive actions that are necessary to perform it. A task network is illustrated in Figure 30.5(d).

A frame tree shows a hierarchy of frames.

The term 'decision tree' is used to describe more than one type of diagram. In terms of decision theory it shows the structure of a decision in relation to the utility values. In other cases the term is applied to discrimination trees. Another, and common, form of decision tree is that used in human decision-making, as described in Chapter 14.

30.23 Directed Graphs

A graphical representation of some importance in engineering is the directed graph, or digraph. Digraphs have been widely used in process modelling. Accounts of directed graphs are given in *Graph Theory in Modern Engineering* (Henley and Williams, 1973), *Structural Models: An Introduction to the Theory of Directed Graphs* (Harary, Norman and Cartwright, 1975) and *Graph Theory* (Gould, 1988).

Directed graphs are also known as directed linear graphs, directed networks or signal flow graphs. A digraph consists of a set of vertices, or nodes, joined by branches, which are also termed links, arcs or edges.

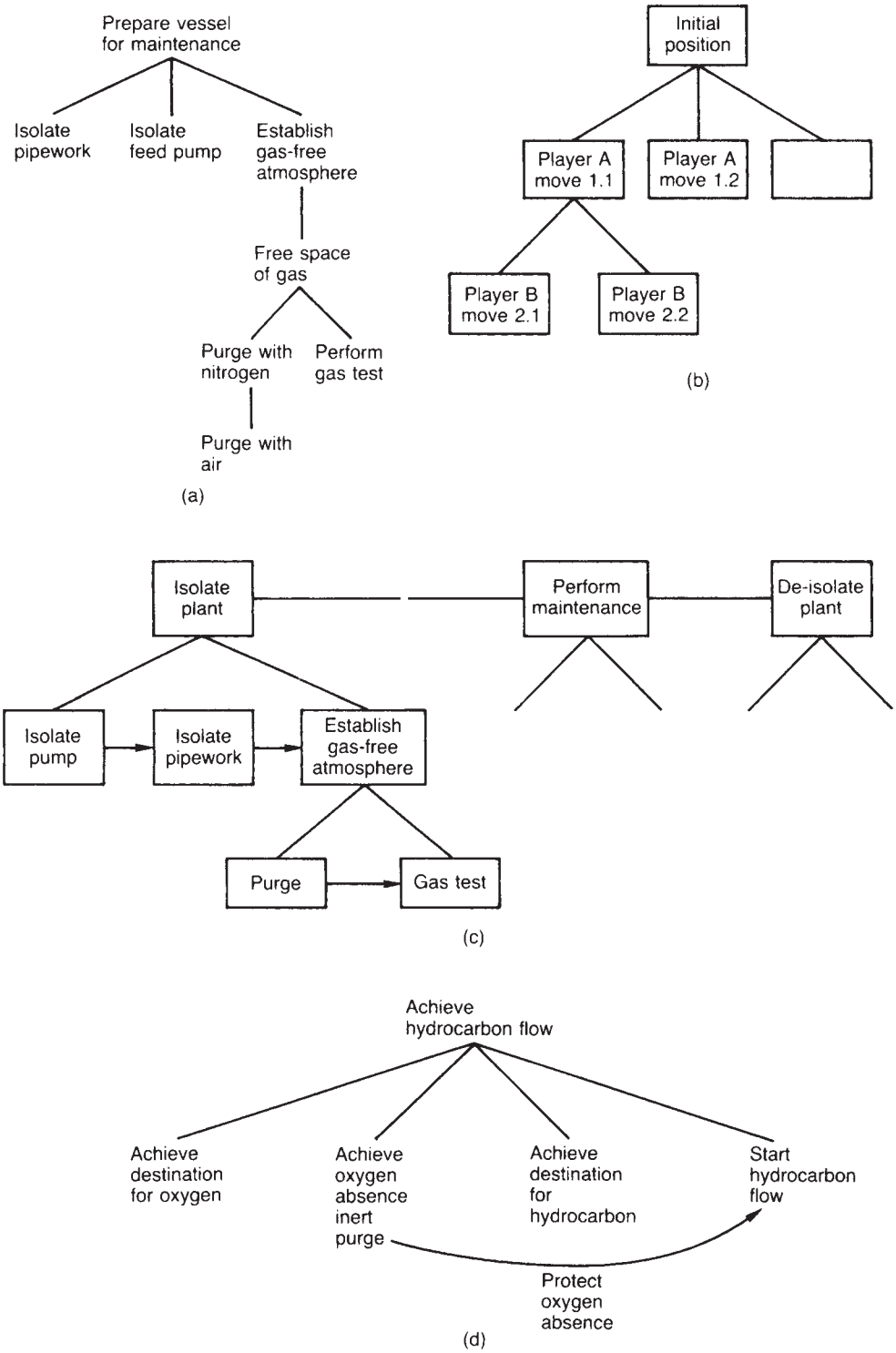


Figure 30.5 *Some graphs trees and networks used in artificial intelligence: (a) goal tree; (b) game tree; (c) time map; (d) task network. See Figure 30.2 for associative network and ISA forms*

A digraph is said to be connected if it has no pair of vertices that are not connected by branches. It is strongly connected, or strong, if for each vertex there exists a directed path from that vertex to another vertex. Otherwise it is said to be weakly connected, or weak.

A path is a set of at least two connected branches. A closed path is called a cycle, or loop. A digraph that contains no cycles, or loops, is referred to as an acyclic graph. A tree is an acyclic graph.

30.23.1 Flow graph algebra

Three principal rules of flow graph algebra are (1) the addition rule, (2) the transmission rule and (3) the product rule.

The addition rule states that the value of a variable represented by a vertex is the sum of all the transmittances entering the vertex. The transmission rule states that the value of a variable represented by a vertex is transmitted on every branch leaving the vertex. The product rule states that if a series connected graph has n vertices the $n-1$ branches can be replaced by a single branch whose transmittance function equals the product of the original branches.

The transmittance function, or operator modifying the value leaving one vertex and entering another, is generally a gain constant. Where differential equations are handled, however, it may also be an integration. For an independent variable such as time t this integration may be expressed as $\int dt$, or in the Laplace domain as $1/s$.

A signal flow graph (SFG) is used to represent a set of simultaneous linear algebraic equations or linear differential equations. A typical signal flow graph is shown in Figure 30.6.

These equations may also be cast in matrix form and manipulated in the usual way. Thus, SFG theory is a way of modelling system that is not only convenient but has a sound theoretical basis.

30.23.2 Flow graph reduction

There are a number of techniques for the reduction of SFGs. In addition to the product rule already mentioned, they include elimination of 'self-loops', various elementary transformations and Mason's rule. An account of these techniques is given by Henley and Williams (1973).

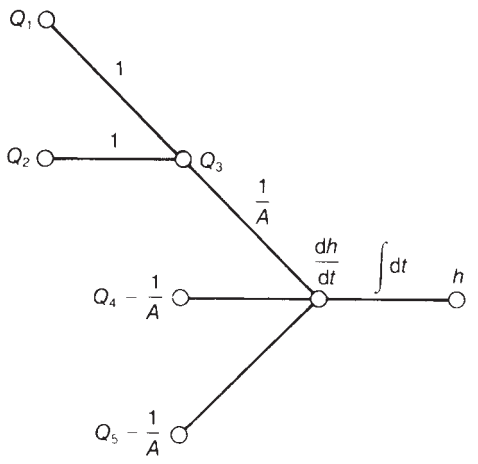


Figure 30.6 *A signal flow graph. Graph for $Q_3 = Q_1 + Q_2$; $dh/dt = (1/A)(Q_3 - Q_4 - Q_5)$; $h = \int (dh/dt)dt$*

30.23.3 Digraphs in process modelling

Extensive use has been made of digraphs in the modelling of process plants, particularly in the modelling of fault propagation. In such work the nodes represent process variables such as flow, pressure, and temperature, and the edges represent the effects of one variable on the other.

In qualitative modelling, using digraphs a convention commonly employed is to use a transmittance function of $+1$, 0 and -1 for a positive influence, zero influence and a negative influence, respectively. Some workers also use $+10$ and -10 to denote, respectively, strong positive and negative influences.

Generally, it is only certain variables which are of interest. In such cases use may be made of the techniques for the reduction of graphs mentioned earlier.

The use of digraphs in process modelling is discussed further in Section 30.36.

30.24 Expert Systems

One of the AI tools which has been most widely taken up with a view to industrial application is expert systems. Accounts of expert systems are given in *Building Expert Systems* (Hayes-Roth, Waterman and Lenat, 1983), *Build Your Own Expert System* (Naylor, 1983), *Expert Systems* (Alty and Coombs, 1984), *Expert Systems* (Forsyth, 1984b), *Expert Systems* (Harmon and King, 1985), Expert Systems (Sell, 1985), *Competent Expert Systems* (Keravnou and Johnson, 1986), *Expert Systems: Strategic Implications and Applications,* (Beerel, 1987), *Programmer's Reference Guide to Expert Systems* (Hu, 1987), *Knowledge Acquisition for Expert Systems* (Kidd, 1987), *Building Expert Systems: A Tutorial* (J. Martin and Oxman, 1988), *Artificial Intelligence and Expert Systems* (Savory, 1988), *Expert Knowledge and Explanation: The Knowledge-Language Interface* (Ellis, 1989), and *Expert Systems and Artificial Intelligence: An Information Manager's Guide* (Ford, 1991) and by Winston (1984), Charniak and McDermott (1985), Frost (1986), Patterson (1990) and Tanimoto (1990).

The vast majority of expert systems are rule-based production systems, though other methods can be used such as neural networks.

The description of actual expert systems is deferred to Section 30.25, but occasional reference is made in this section to certain major systems, notably MYCIN.

30.24.1 Project management and organization

The strategic aspects of expert systems are considered in *Expert Systems: Strategic Implications and Applications* (Beerel, 1987).

The management and organization of an expert system project depend very much on the nature and scale of the project. Most industrial applications are relatively modest. For a more substantial project, however, the management and organization may well determine the success.

The selection of an appropriate application is crucial. Some characteristics bearing on suitability are discussed in the next section. There are two essential conditions for undertaking the development of an expert system: that it be feasible and that, once created, it will be used.

The first condition requires that there be available at least one domain expert who can provide the necessary expertize. A decision has to be made whether sole reliance is to be placed on this expert or whether other experts are to be brought in. The function of the experts is not only to furnish expertise, but also to evaluate the system produced.

The second condition, that at the end of the day the system actually be used, implies the involvement of the potential users right from the start. One view is that it is a user who should be responsible for the project. Whether or not this is adopted, the principle of user involvement is not in doubt.

Knowledge acquisition in a project of any size is the responsibility of a knowledge engineer. The knowledge engineer is not a domain expert, but should be skilled both in knowledge acquisition and knowledge representation and in the building of expert systems.

The basic team for the creation of an expert system is thus the project manager, the expert, the knowledge engineer and the user.

30.24.2 Selection of applications

Experience with expert systems indicates that there are some types of problem for which an expert system is suitable and others for which it is not. For the latter, this does not necessarily mean that there is no suitable AI tool, only that an expert system is not that tool.

The most basic requirement is that there be an established domain expertise and an expert from whom the domain knowledge can be elicited.

Another equally basic requirement is that there should be a need for the system so that adequate resources can be made available for its development and so that once it has been developed it is used and maintained.

A distinction is sometimes made between common sense and mundane knowledge, to the effect that common sense involves various forms of reasoning and mundane knowledge various kinds of knowledge about the world. Common sense and mundane knowledge are strong points for humans but weak features of machine intelligence.

The characteristics of a problem which favour an expert system application are: that there is a defined domain of expertise; that the task to be performed is well focused and of moderate complexity; and that the knowledge can be represented in standard forms, particularly by facts and rules.

The task should be one performed by an expert and be of a level of complexity that it is neither trivial nor so involved that creation of an expert system becomes impractical. The time taken to perform such a task is typically between a few minutes and a few days.

In a given organization, the question of the selection of the first application of an expert system is of some importance. As with any other innovation, a bad first experience is likely to set the technology back for some years.

30.24.3 System development

The development of an expert system proceeds through the following typical stages: (1) system concept, (2) feasibility study, (3) outline specification, (4) preliminary knowledge acquisition, (5) knowledge representation, (6) tool selection, (7) prototype development, (8) main knowledge acquisition, (9) revised specification, (10) system development, (11) testing and evaluation and (12) handover. The process is an iterative one, with looping back between some of these stages.

Prototyping covers the creation of the prototype, the writing of the documentation, the induction of the user, and use and evaluation by the user.

The point has already been made that the user should be involved from the start. This involvement should cover not only the specification and evaluation of the final system, but also evaluation at intermediate stages.

An account of the development of a large expert system is given by J. Martin and Oxman (1988).

30.24.4 System architecture and facilities

A minimal architecture for an expert system is a knowledge base, an inference engine and a user interface.

The knowledge base contains the set of facts and rules that constitutes the expertise. A distinction is sometimes made between a database of facts and a knowledge base containing rules. The knowledge base itself is frequently spoken of in terms of a set of knowledge bases. The inference engine performs the process of inference from the facts and rules in the knowledge base. It is a basic principle of the architecture that the knowledge base and inference engine are separate.

The user interface has several functions. It is the means whereby the user supplies additional information to the system, either in response to demand or by volunteering it, and the means whereby he receives the output.

To these three basic features may be added a number of others. They include a blackboard, a knowledge acquisition facility, a learning facility and an explanation facility. A blackboard is a device for communicating with the knowledge bases and holding intermediate hypotheses and decisions. Only a proportion of systems incorporate a blackboard. A knowledge acquisition facility provides the means for the knowledge engineer to input knowledge elicited from the domain expert, allowing him to input and edit facts and rules, and so on. An inductive learning facility may also be provided. The user interface may contain an explanation facility.

30.24.5 Inference engine

The inference engine may incorporate any of a number of different inferencing, search and problem-solving methods. It may have forward or backward chaining, corresponding respectively to data- or goal-driven inference, or a mixture of both. It may use depth-first or breadth-first search, hill-climbing, means–ends analysis, generate-and-test, pattern-matching, and so on. Or it may use some hybrid scheme.

30.24.6 Blackboard

A blackboard is a device for holding a set of intermediate hypotheses and decisions, in other words partial solutions. It communicates with and draws knowledge from the set of knowledge bases in an opportunistic way. In some cases it can be regarded as being split into three parts: plan, agenda and solution. The plan part contains the goals, plans, states and contexts; the agenda the potential actions awaiting execution; and the solution the hypotheses and decisions. The blackboard can be altered only by the knowledge bases. Such forms of control as the blackboard has act to focus attention on a problem and the knowledge bases then indicate what contribution they can make.

30.24.7 Knowledge acquisition facility

It is helpful to the creation of an expert system if there is a knowledge acquisition facility (KAF) that provides for the editing of facts and rules and for their entry into the knowledge base.

There may also be provided a facility for inductive learning. This may be regarded as part of the knowledge acquisition facility or as a separate feature. In any event, the purpose of this facility is to allow knowledge to be entered in the form of a learning set of examples provided by the expert and rules to be induced from these examples. This is an alternative to the provision of explicit rules by the expert.

30.24.8 Explanation facility

Most expert systems are provided with an explanation facility which can provide some form of justification for the conclusion reached, but the sophistication of such facilities varies. Accounts of explanation facilities are given in *Expert Knowledge and Explanation* (Ellis, 1989) and by Sell (1985) and J. Martin and Oxman (1988).

There are two main types of user for an explanation facility, the knowledge engineer and the client user. There are several types of explanation that a user requires. One is elaboration of the questions that he is asked in order to assist him to answer them correctly. Another is justification for these questions in order to motivate him to provide answers to them. The third is an explanation of the reasoning process.

One of the simplest forms of explanation facility is rule-tracing. The system keeps track of the path by which it has reached the current point and can display this to the user on demand. A rule trace is relatively easy for the system to provide. A detailed example is given by Ellis (1989).

However, an explanation facility that utilizes a simple rule trace is somewhat crude. It is preferable that the line of reasoning be explained rather in terms of the principles that govern the domain, using domain knowledge in a structured way.

Considering the explanation facilities in actual expert systems that used in MYCIN is effectively a rule trace. NEOMYCIN by W.J. Clancey and Letsinger (1981) utilizes a number of domain-specific meta-rules which control the problem-solving and is thus able to provide a more domain-related explanation.

The program XPLAIN by Swartout (1983) utilizes both a domain model, which is descriptive, and domain principles, which are prescriptive, and is able to provide an explanation that justifies rather than simply records the program behaviour.

In most cases the output of an explanation facility is confined to text. STEAMER by Hollan, Hutchings and Weitzman (1984), on the other hand, which deals with operations on a steam plant, provides both graphical and textual output.

Generally, an expert system is used by a quite small number of people. There tend to be considerable differences in individual preferences for output from an explanation facility. One way of accommodating this is to provide options which individual users can select.

In more advanced work on this topic, user models are utilized to improve the design of the explanation facility.

30.24.9 Building tools

There are available a number of tools for building expert systems. They include programming languages, expert system shells and expert system building environments. Accounts of building tools for expert systems are given in Hayes-Roth, Waterman and Lenat (1983) and J. Martin and Oxman (1988). Lists of some principal tools are given by Frost (1986) and Hu (1987).

The languages traditionally used for building expert systems are LISP and Prolog. Insofar as the early and classic systems were built in the United States where LISP was the favoured language, LISP has been predominant. Prolog implements logic programming. For object-oriented programming use may be made of SMALLTALK. Of the general purpose languages, C++ is particularly compatible.

An expert system shell is strictly a tool created from an existing expert system by removing the features which are specific to the original problem, whilst retaining the general structure and in particular the inference method. A tool of the same general type may be created from scratch, and is sometimes also referred to as a shell.

Shells are widely used and can be especially useful for prototyping. The weakness of shells is that problems vary in nature and a shell capable of dealing with a wide range of problems needs to be rather sophisticated. Thus, some applications require data-driven search, others require goal-driven search and others again require a mix. Some applications involve uncertainty, whilst others do not. Some applications may have large quantities of data but few rules, and others the converse. Lists of the principal shells are given by Frost (1986) and Hu (1987).

There are in addition a number of so-called 'environments' for the building of expert systems. These differ from shells in that they are more flexible. The concept of an expert system building environment is that it offers a wide range of features, particularly for the knowledge representation and the inference engine. Environments include KAS, OPS5 and AGE, described in the next section.

There are also numerous tools for particular individual features of expert systems. They include tools for building knowledge bases, knowledge acquisition facilities, learning facilities, the user interface, explanation facilities, and so on. There are knowledge base management systems, which fulfil functions somewhat similar to those of database management systems.

30.24.10 Knowledge elicitation and acquisition

Crucial activities in building an expert system are knowledge elicitation and knowledge acquisition. The two terms are often used almost interchangeably, but whereas in knowledge elicitation the emphasis is on eliciting the domain knowledge from the expert, in knowledge acquisition it is on providing the program with this knowledge. Accounts are given in *Knowledge Acquisition for Expert Systems* (Kidd, 1987) and *Knowledge Elicitation* (Diaper, 1989) and by Beerel (1987) and J. Martin and Oxman (1988).

The expertise of the domain expert has a number of facets. Typically, he or she has a wide experience and knowledge of case histories, problems and solutions, both successful and failed. This background provides him with an understanding of the structure of the domain, of the crucial distinctions which have to be made, of the constraints which apply, of the problems to be solved, of the decompositions which can be made, of problem-solving and search strategies, of heuristics and rules-of-thumb, of facts and rules, and of exceptions and refinements.

The task of knowledge elicitation is generally undertaken by the knowledge engineer. His or her task is to acquire and represent the domain knowledge and to engineer the system

so that it is easy for the user to utilize. The most common method of knowledge elicitation is interviewing of the expert by the knowledge engineer. The aim is to make explicit the expertise. There is a large literature on interviewing, especially in the social sciences. Another approach is close observation of the expert as he performs the task. Typically this utilizes some form of verbal protocol in which the expert explains what he is doing and why he is doing it. A third approach is for the expert to provide sets of problems and solutions and for the knowledge engineer to induce from these the internal rules which the expert is evidently using to obtain the solutions. A fourth method is prototyping, in which the expert and knowledge engineer cooperate to build a system. The expert furnishes knowledge for, and provides tests of, the system, while the knowledge engineer tries to create a suitable system structure.

The interaction between the knowledge engineer and the expert is not limited to debriefing the expert. They need also to work together to design the user interface. Decisions are required on the questions that he or she is to be asked and on the explanations that are to be provided for him or her.

The process of knowledge elicitation is generally incremental and iterative. The expert is unlikely to be able to make explicit his or her expertise in a particular area in a single pass, and the process of elicitation is likely to prompt him or her to make additions and refinements, or even to undertake a more fundamental restructuring.

The main domain expert is not the sole source of knowledge available to the knowledge engineer. He or she may also utilize the literature and databases, historical records, case histories and case studies, and interviews with other engineers. It should be borne in mind, however, that whereas the expertise of the single expert can reasonably be presumed to be coherent, an eclectic approach that draws on a wide range of sources is more likely to involve both inconsistencies and contradictions and out-of-date methods.

In some cases, an expert system is created by the domain expert himself or herself. In particular, it has become quite common for systems to be created utilizing an induction tool that is provided by the expert with a learning set of examples and solutions.

30.24.11 System evaluation

It is clearly necessary that at some stage an expert system should be evaluated, but such evaluation raises a number of issues that need to be addressed if it is to be done satisfactorily. The evaluation and validation of expert systems are discussed by Hayes-Roth, Waterman and Lenat (1983), Sell (1985), Beerel (1987) and Ellis (1989).

It is not self-evident that there is need for an evaluation of the system other than the ultimate test of successful use. In fact, however, there are benefits to be gained from evaluation prior to entry into service, both in terms of the quality of the system finally produced and of the learning process of the organization that is building the system.

Some issues that arise in the evaluation of an expert system are the criteria, the assessors, the timing, the methods and the overall evaluation process. An expert system generally captures the expertise of a single expert. A question therefore arises as to whether the system is to be judged by its success in reproducing that expertise or in solving problems. The distinction is a fundamental one. Another basic question to be decided is who is to perform the evaluation. The assessment may, in principle, be performed by the expert, the knowledge engineer and/or the client users. The timing of the evaluation is another issue, the options being to carry out interim assessments throughout the building of the system or to defer evaluation until it is complete. The methods used for the evaluation may be informal or formal ones.

Evaluation criteria that are based on the requirement that the system reproduce the expertise of the domain expert centre essentially on the ability of the system to provide high quality advice based on correct and acceptable reasoning. More specifically, criteria for the quality of the advice may relate to the following features: (1) consistency, (2) completeness, (3) soundness, (4) precision and (5) usability. Consistency means that the system should give similar answers to similar questions. A small change should not induce totally different behaviour. Completeness implies that the coverage of the domain is comprehensive. The requirement for soundness is that the statements made are true. The precision requirement applies only where there are quantitative outputs, and has the usual meaning. Usability means here that the user interface should operate as intended, a requirement distinct from user-friendliness. The evaluation should address not only the quality of the conclusions but also the quality of the reasoning by which they are arrived at. This is not just a matter of correct inference, but has to do also with the extent to which particular conclusions are supported by an overall structure.

Criteria are also required to evaluate the discourse with the user. In large part these will centre round the questioning of the user and the provision of explanation to the user, which were discussed above.

An expert system is built with particular categories of user in mind, and ultimately it is they who must be satisfied. This does not necessarily mean that evaluation should be carried out solely by these users. Generally it will be appropriate for the knowledge engineer, the expert and the users all to be involved. The knowledge engineer is able to evaluate the program technically as an expert system, including here the user interface, whilst the expert can assess it in terms of the expert advice which is provided and the user in terms of the ease of use and value of the advice.

With regard to timing, it is preferable to conduct the evaluation as the building of the system progresses rather than to defer it to the end. User evaluation and feedback as the system is being created is a recurring theme in discussions of system evaluation.

The evaluation may be informal and qualitative or it may use formal and possibly quantitative methods. Some formal methods are described in Hayes-Roth, Waterman and Lenat (1983). Whatever other methods are used, two that are unavoidable are testing by the expert and use by the users. These tests may be informal but they should address the task that the system has been designed to perform and the criteria which have been agreed for its evaluation.

Evaluation of an expert system is not a straightforward matter. Sources of difficulty are: the potential confusion between defects in the system and in the expertise which it embodies; a lack of understanding by users of the scope and limitations of the system and unrealistic expectations for its performance; importation by users of extraneous criteria; disagreement about the relative importance of criteria; and deficiencies of the system whilst it is still only partially developed.

Accounts of case studies of the evaluation of expert systems are given in Hayes-Roth, Waterman and Lenat (1983). They describe assessment of the R1 system for computer

system configuration and of the ORNL spill crisis management system, and the lessons learned about evaluation. Foremost among these lessons are the need to involve users early and fully. At the end of the day the ultimate test is whether the system is used, and, if so, whether it has proved cost-effective.

30.25 Expert Systems: Some Systems and Tools

30.25.1 DENDRAL

DENDRAL is an expert system that discovers molecular structures. Work on DENDRAL dates from 1965 and its creation was a landmark in AI. It is described by E.G. Buchanan, Sutherland and Feigenbaum (1969, 1970), B.C. Buchanan *et al.* (1976), B.C. Buchanan and Feigenbaum (1978) and Lindsay *et al.* (1980) and also by Hayes-Roth, Waterman and Lenat (1983), Winston (1984) and Patterson (1990).

The program determines the molecular structure of a substance from information on the constituent elements, or chemical formula, and the mass spectrograph. It has a structure enumerator, which synthesizes candidate chemical structures subject to constraints, derived largely from the mass spectrograph data, that certain structures must be present (the necessary list) and that certain structures must not (the forbidden list). For each candidate structure it synthesizes a mass spectrograph. It matches the synthesized spectrographs of the candidate structures to the experimental ones and selects the structure that gives the best fit.

The system is thus a problem-solving program which uses a generate-and-test strategy. The generation part involves a search that is partly guided by heuristic rules. It also contains other rule-based systems, one of which is a set of rules for structures in the forbidden list that supplement the mass spectrograph information. The test part is the spectrograph matching process.

The use of DENDRAL showed up some of the problems of knowledge elicitation. This led to the development of META-DENDRAL, which induces rules from examples (E.G. Buchanan and Feigenbaum, 1978).

30.25.2 MYCIN

MYCIN is an expert system for the diagnosis of infectious blood diseases. It is described in *Computer-Based Medical Consultation: MYCIN* (Shortliffe, 1976) and Rule-Based Expert Systems (E.G. Buchanan and Shortliffe, 1984) and also by Hayes-Roth, Waterman and Lenat (1983), Winston (1984), Charniak and McDermott (1985) and Patterson (1990).

The program is a rule-based production system. Initially it had some 200 rules that by the early 1980s had risen to about 600. A feature of the rules is the use of certainty theory. Each rule is assigned a certainty factor that is propagated through to yield a certainty for the result for each hypothesis. Search in MYCIN is a slightly modified form of depth-first search with backward chaining. The current hypothesis constitutes the goal of an AND/OR tree. MYCIN has an interactive facility. Backward chaining has the advantage over forward chaining that it is more compatible with user interaction. A search that proceeds by a process of elimination tends to generate a large number of questions, which is liable to irritate the user, and the interaction is modified so that the user is asked a smaller number of direct questions, the answers to which then guide the search.

Associated with MYCIN is TEIRESIAS, which was developed as a front end to aid knowledge acquisition. MYCIN has also given rise to EMYCIN, an expert system shell based on MYCIN.

30.25.3 CASNET

CASNET is an expert system for the diagnosis and treatment of glaucoma, and is a research program. It is described by Weiss, Kulikowski and co-workers (Weiss, Kulikowski and Safir, 1977, 1978; Weiss *et al.*, 1978; Weiss and Kulikowski, 1981, 1983; Kulikowski and Weiss, 1982) and also by Hayes-Roth, Waterman and Lenat (1983) and Patterson (1990).

The program carries out diagnosis using three levels of knowledge: patient observations, pathological state and disease. Its general structure is shown in Figure 30.7.

The use of the intermediate level of pathological state is a key feature of the approach taken in CASNET. CASNET utilizes an associative network or semantic net. Inference is effected by traversing the network in a search for the most plausible paths of cause and effect. The program also utilizes production rules.

30.25.4 PROSPECTOR

PROSPECTOR is an expert system that gives advice on mineral deposits. It is described by Duda *et al.* (1978), Hart, Duda and Einaudy (1978), Duda, Gaschnig and Hart (1979) and A. Campbell *et al.* (1982) and also by Hayes-Roth, Waterman and Lenat (1983), Charniak and McDermott (1985) and Tanimoto (1990).

The program utilizes geological field data to advise on the likely locations of deposits of a particular mineral. Like CASNET, it makes use of an intermediate level of knowledge, and is one of the best examples of an expert system based on this feature. It contains 'models' of situations in which deposits of particular ores tend to occur.

PROSPECTOR is a rule-based production system. Explicit use is made of Bayesian inference, as shown in Figure 30.8. Where use is made of such Bayesian probabilities, it is necessary that the prior probabilities be consistent. Methods of approach to this problem are discussed by Tanimoto (1990).

The user has a facility to interact with PROSPECTOR. This includes the option to volunteer information.

30.25.5 CADUCEUS

CADUCEUS, originally called INTERNIST, is an expert system for the diagnosis of diseases of the internal organs, and is a research program. It is described by R.A. Miller, Pople and Myers (1982), Pople (1982) and also by Hayes-Roth, Waterman and Lenat (1983) and Charniak and McDermott (1985).

The authors of the program claim that it covers some two-thirds of the diseases of the internal organs. It deals with about 500 diseases in terms of some 3500 conditions. In addition to its wide coverage, another of its strengths is its ability to handle multiple diseases. The information used in the program includes not only symptoms but also medical history and laboratory test results. A feature of the search strategy used in CADUCEUS is that it involves a large bottom-up element.

Work on the development of CADUCEUS aims to make the program act more like a physician by making an initial global assessment, decomposing the problem and partitioning the symptoms among the separate subproblems.

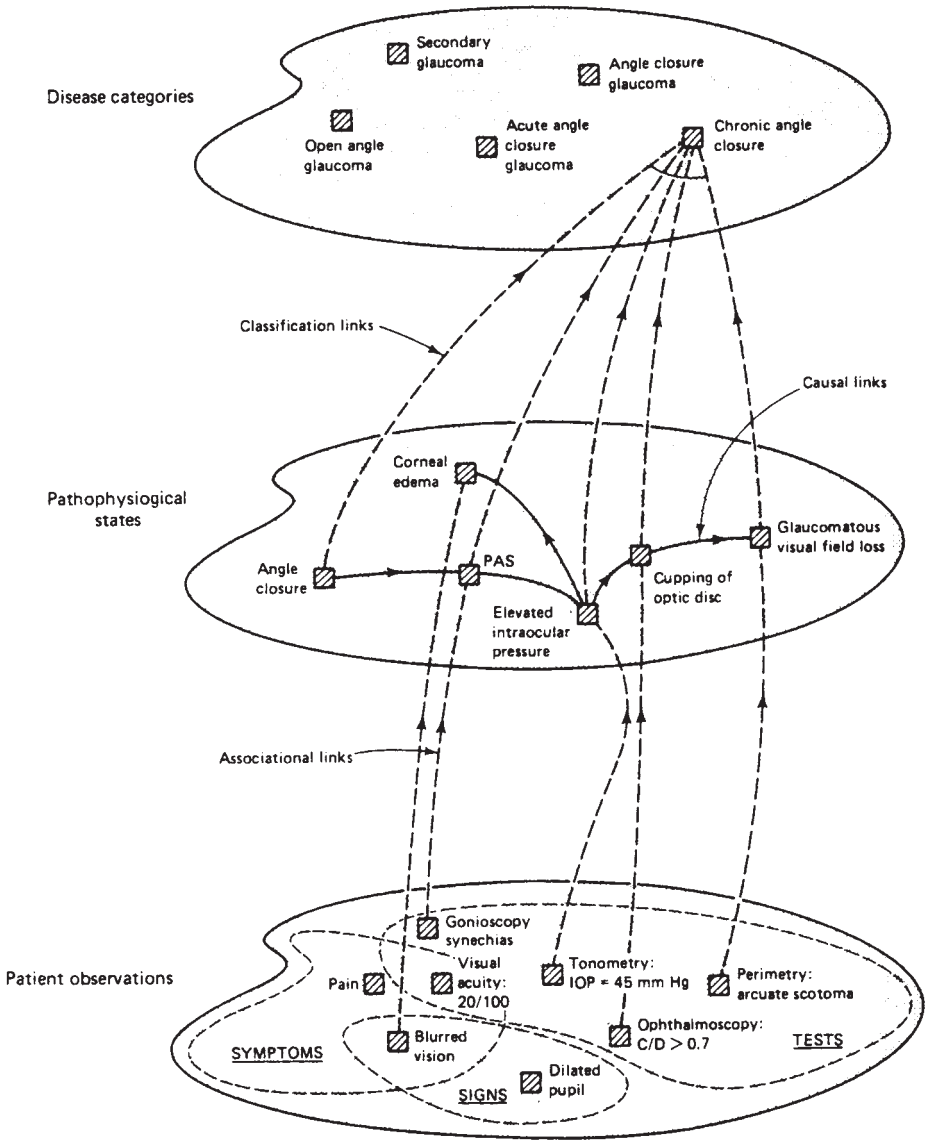


Figure 30.7 *Levels of knowledge in CASNET (Weiss et al., 1978) (Courtesy of North Holland Publishing Company)*

30.25.6 R1/XCON

XCON, originally called Rl, is an expert system for the configuration of VAX computer systems, and is in industrial use. It is described by McDermott (1980, 1981, 1982a), and also by Hayes-Roth, Waterman and Lenat (1983), Winston (1984), Charniak and McDermott (1985) and Tanimoto (1990).

The program accepts an order for a computer system and performs the following aspects of system configuration: (1) check the order for missing and mismatched items, (2) create the layout of the processor in cabinets, (3) put boxes in the input/output cabinets and place components in these boxes, (4) put panels in the input/output cabinets, (5) create the floor plan layout and (6) do the cabling. XCON is thus a problem-solving program. It is based on production rules.

The number of rules in XCON is large. In 1979 the program had about 800 rules, by 1983 about 3000 and by 1990 some 12,000. The large number of rules requires an efficient search strategy. Search in XCON is by forward chaining. This search involves minimal backup. The rules apparently incorporate sufficient constraint that the search rarely goes up a blind alley. The method of inference in XCON is deductive. This distinguishes it from the diagnostic programs, where inference is by abduction. The program illustrates the fact that an expert system can be useful even

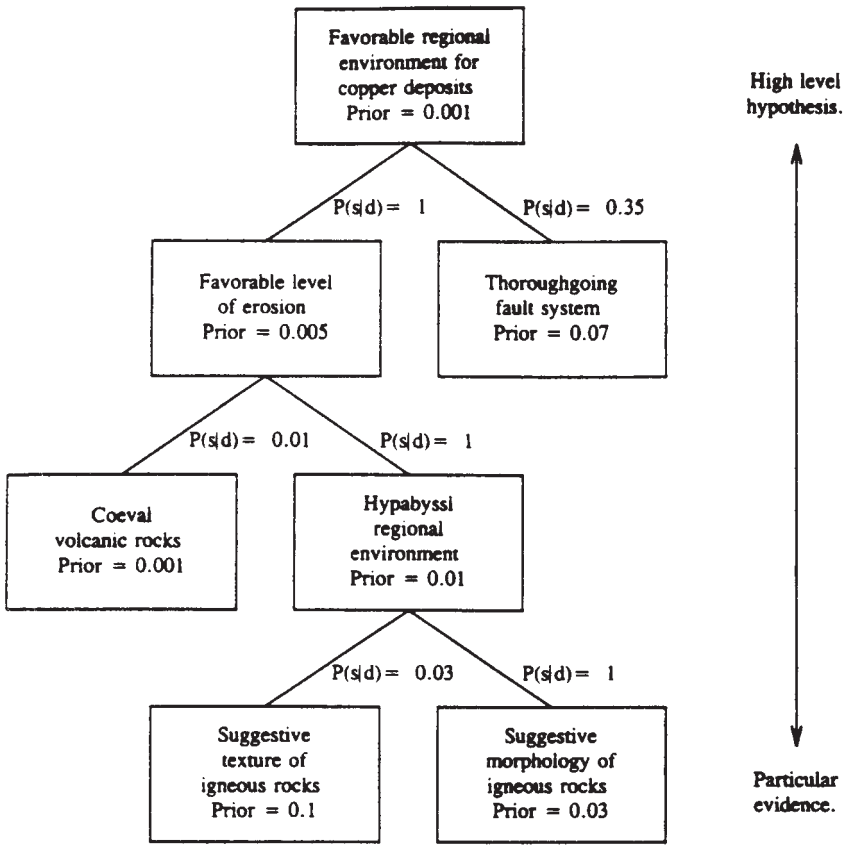


Figure 30.8 *Bayesian inference in PROSPECTOR (Charniak and McDermott, 1985) (Courtesy of Addision-Wesley Publishers)*

if it is at a relatively early stage in its overall development. It was already in use in 1979.

XCON is of particular interest here for two reasons. It is the only one of the classic systems described that deals with design, and it is a system that has been in industrial use for well over a decade.

30.25.7 BAGGER

In addition to the classic expert systems just described, there are certain others that are also instructive. One of these is BAGGER, an expert system for bagging groceries in a supermarket, which is described by Winston (1984). Although essentially a toy system, BAGGER constitutes a useful introduction to an expert system based on production rules, including features such as conflict resolution.

30.25.8 EMYCIN

An early shell was EMYCIN (Empty MYCIN) (van Melle, 1979, 1980, 1981; van Melle, Shortliffe and Buchanan, 1981). It is a domain-independent system for the creation of expert systems for diagnosis or consultation. It retains the basic rule structure, inference engine and explanation facility of MYCIN. A further account is given in Hayes-Roth, Waterman and Lenat (1983).

30.25.9 Other shells

Other shells frequently mentioned are ESP ADVISER and SAVOIR. Some systems are variously referred to as shells or building tools.

30.25.10 ART

ART (Automated Reasoning Tool) was one of the first building tools. It is intended for use in building large systems and integrates a number of problem-solving techniques. ART is written in CommonLISP. An account is given by J. Martin and Oxman (1988).

30.25.11 AGE

Another early building tool was AGE (Nil and Aiello, 1979). AGE contains two types of entity: components and frameworks. A component is a routine that supports a basic AI mechanism and a framework a fixed configuration of components. A back-chaining framework and a blackboard framework are the two original frameworks. AGE is described by Hayes-Roth, Waterman and Lenat (1983).

30.25.12 KAS

KAS (Knowledge Acquisition System) (Duda, Gaschnig and Hart, 1979) is a knowledge acquisition system derived

from PROSPECTOR. It places more emphasis than EMYCIN on information volunteered by the user, trying to avoid a large number of low pay-off questions and utilizing a mix of forward and backward chaining. Hayes-Roth, Waterman and Lenat (1983) give a further account.

30.25.13 OPS5

OPS5 (Official Production System 5) (Forgy, 1981) is one of the OPS family of building tools. It was developed as an aid in the building of Rl/XCON. It may be described as a rule-based programming language and is used to build rule-based production systems that use, primarily, forward chaining. It incorporates the RETE algorithm. Accounts are given in Hayes-Roth, Waterman and Lenat (1983) and by Patterson (1990).

30.25.14 KEE

KEE (Knowledge Engineering Environment) is variously described as an expert system shell or building tool. It has production rule, frame and object oriented system facilities. Inference is by inheritance and by forward and backward chaining. Accounts are given by Frost (1986) and Patterson (1990).

30.25.15 KES

Another system building tool is KES, which has production rule and frame facilities. An account is given by Frost (1986).

30.25.16 EXPERT

EXPERT (Weiss and Kulikowski, 1979, 1981) is a building tool for diagnosis- or classification-type consultation systems. An account is given in Hayes-Roth, Waterman and Lenat (1983).

30.25.17 EXPERTEASE and EXTRAN

EXTRAN, and the earlier EXPERTEASE, are classification tools based on the IDS algorithm for inductive learning.

30.26 Qualitative Modelling

In engineering, the conventional method of modelling a physical situation to create a mathematical model consisting of algebraic and differential equations based on classical physics. In recent years, there has been growing interest in an alternative approach that goes by the names of naive physics, and of qualitative modelling, qualitative physics or qualitative simulation.

Accounts of naive physics and qualitative modelling are given in *Mental Models* (Centner and Stevens, 1983), *Qualitative Reasoning about Physical Systems* (Bobrow, 1985), *Formal Theories of the Commonsense World* (Hobbs and Moore, 1985), *Readings in Qualitative Reasoning about Physical Systems* (Weld and de Kleer, 1990) and *Recent Advances in Qualitative Physics* (Faltings and Struss, 1991) and by Forbus (1984), de Kleer and Brown (1984), Kuipers (1984), Hardt (1992) and de Kleer (1992).

30.26.1 Naive physics

Classical physics is based on qualitative concepts that are then translated into quantitative mathematical models. Naive physics utilizes the same concepts but derives from them qualitative models. Work on naive physics has been described by Hayes (1979, 1985) and Hardt (1992). The work on qualitative modelling by de Kleer and Brown (1984), Forbus (1984) and Kuipers (1984) also comes under this head.

In naive physics the physical situation is modelled formally but qualitatively. The modelling remains symbolic and the variables take a limited number of discrete states. Naive physics retains all the basic concepts of classical physics such as state, equilibrium, conservation of mass, momentum and energy, and so on, but treats them in a qualitative way. It follows the same sequence of model formulation, solution and interpretation of the results.

One way of looking at naive physics is that it is a formal encoding of common sense reasoning about physical situations. In many cases, particularly in mundane situations, it can be quite difficult to formulate a quantitative mathematical model, but it is feasible to derive a qualitative model. In its own terms the qualitative model can be made as rigorous as the quantitative one.

A naive physics model can also be viewed from the opposite perspective as a reduction of a quantitative model to its essential qualitative form. In some work on naive physics models have been derived both by encoding of natural language statements and by reduction of the equations of a conventional mathematical model to qualitative model format.

The formalization of common sense reasoning about physical situations in a naive physics model is not easy. Common sense draws on large quantities of knowledge about the physical world and the forms of knowledge representation involved are often specialized. The approach advocated by Hayes (1979) in his 'naive physics manifesto' is the use of predicate calculus. In fact, the three main developments in qualitative modelling have not adopted this approach. These developments are component-based modelling, constraint-based modelling and process-based modelling.

30.26.2 Fault propagation

As it happens, some of the early work on qualitative modelling was in the process field. Qualitative models were used by Andow and Lees (Andow, 1973; Andow and Lees, 1975) to model fault propagation in process plants. The purpose of the work was to determine the interaction between process variables with a view to creating alarm trees for alarm diagnosis by process computer.

The basic principle may be illustrated by considering the differential equation for the change in level in an open tank with water flowing in and out:

$$\frac{dL}{dt} = Q_1 - Q_2 \qquad [30.26.1]$$

where L is the level, Q is the flow and t is time, and subscripts 1 and 2 denote the inlet and outlet, respectively.

In the work of Andow and Lees the equations of the corresponding qualitative model were obtained from those of a conventional mathematical model. Thus, the qualitative model equation equivalent to Equation 30.26.1 is

$$L = (+Q_1, -Q_2) \qquad [30.26.2]$$

that signifies that L increases if Q_1 increases or Q_2 decreases, or vice versa. It may be noted that Equation 30.26.2 may also be obtained by encoding an engineer's natural language statement that 'The level increases if the flow in

increases or the flow out decreases, and vice versa'. It constitutes, in effect, a half-way house between a description in natural language and that of a quantitative model.

Work on fault propagation is described in Section 30.36.

30.26.3 Qualitative modelling

As stated above, qualitative modelling has developed in three main directions. These are: component-based, or device-based, modelling, as in the work of de Kleer and Brown (de Kleer, 1975, 1985; J.S. Brown and de Kleer, 1981; de Kleer and Brown, 1983, 1984, 1986); process-based modelling, as in the work of Forbus (1983, 1984, 1990); and constraint-based modelling, as in the work of Kuipers (1984, 1986). Of these three methods, component-based modelling appears the most suitable for the qualitative modelling of process plant and it is therefore this which is primarily considered here, but a brief account of the other two methods is appropriate.

30.26.4 Process-based modelling

In the process-based modelling of Forbus (1984), the physical situation is described in terms of the physical process which over time cause changes to occur. The physical processes are those such as flowing, heating, cooling, boiling and so on.

30.26.5 Constraint-based modelling

In the constraint-based modelling of Kuipers (1984, 1986), the physical situation is described in terms of the variables and the constraints relating these variables. Three principal types of constraint are used. These are:

Arithmetic: $X = Y + Z$
Functional: $Y = M^{+}(X)$
Derivative: $Y = \mathrm{d}X/\mathrm{d}t$

The arithmetic constraint requires that the values of the variables have the indicated relationship at all times; the functional constraint requires that Y is a strictly increasing function of X (or, for M^{-}, a decreasing function); and the derivative constraint requires that Y is the rate of change of X. Thus, the constraints consist of a qualitative adder, a qualitative proportionality and a qualitative differential.

30.26.6 Component-based modelling

The component-based modelling approach of de Kleer and Brown (Q.S. Brown and de Kleer, 1981; de Kleer, 1984, 1992; de Kleer and Brown, 1984) involves decomposing the system into separate, context-independent entities which are then modelled. These entities are materials, components and conduits. Examples of materials are fluids or current; examples of conduits are pipes or wires.

A component-based approach is well suited to the modelling of systems with a fixed topology such as items in a process plant. The approach is essentially reductionist. An overview of component-based modelling has been given by de Kleer (1992) and the account here draws on this.

30.26.7 Composability

It is a basic principle of qualitative modelling that the model of a component should be independent of the context. This is the 'no-function-in-structure' principle. De Kleer illustrates this principle with the example of an electric light switch. A model of the switch that makes the unqualified statement 'If the switch is off, no current flows; and if the switch is on, current flows' violates the principle. Situations can be envisaged, such as that where there is another switch in series, where it might not be true. The correct formulation is that current flows if the switch is on and there is potential for current flow.

30.26.8 Quantity spaces and landmarks

In the notation for qualitative modelling used by de Kleer a qualitative value of x is denoted by $[x]$. The qualitative value of x is defined in relation to some reference, or landmark, value. A basic quantity space is the $+$, $-$, 0 value space. This means that $[x] = +$ if $x > 0$; $[x] = -$ if $x < 0$ and $[x] = 0$ if $x = 0$.

The landmark value may be taken not as zero but as some other value, say a. In this case the origin is shifted by defining some new variable, say y, as $y = x - a$.

Basic issues in qualitative modelling are the choice of the quantity space and of the landmarks.

30.26.9 Qualitative equations and arithmetic

Basic arithmetic operations in qualitative modelling are addition

$$[z] = [x] + [y] \qquad [30.26.3]$$

and multiplication

$$[z] = [xy] = [x][y] \qquad [30.26.4]$$

In these relations, the qualitative value of $[z]$ is fully defined for multiplication, but for addition it is indeterminate. The relationships for addition and multiplication in qualitative arithmetic are shown in Table 30.4.

For derivatives, the notation

$$\left[\frac{\mathrm{d}x}{\mathrm{d}t}\right] = +$$

signifies that x is increasing. An alternative notation for $[\mathrm{d}x/\mathrm{d}t]$ is Mx.

It is not permissible to manipulate qualitative equations according to the same rules as conventional ones. In particular, an operation such as the subtraction of $[y] + [z]$ from $[x] + [y] + [z] = 0$ does not necessarily yield $[x] = 0$.

Table 30.4 *Some relationships of qualitative arithmetic*

A Addition $[x] + [y]$

$[y]$ \ $[x]$	$-$	0	$+$
$-$	$-$	$-$	?
0	$-$	0	$+$
$+$	?	$+$	$+$

B Multiplication $[x]$ $[y]$

$[y]$ \ $[x]$	$-$	0	$+$
$-$	$+$	0	$-$
0	0	0	0
$+$	$-$	0	$+$

In the qualitative modelling method of de Kleer, an expression in terms of qualitative values, operators and variables is referred to as a confluence. A typical confluence used by this author is

$$\partial P + [P]\partial A - \partial Q = 0 \qquad [30.26.5]$$

where A is the area of an open control valve, P is the pressure drop across the valve and Q is the flow through it.

A set of qualitative values satisfies a confluence either if the qualitative equality strictly holds in accordance with the relations given in Table 30.4 or if one side of the confluence remains indeterminate because the addition operation is not closed. A set of values contradicts a confluence if both sides evaluate to a distinct qualitative value and the confluence is not satisfied. These statements imply that a confluence may be neither satisfied nor contradicted if some of the variables do not have assigned values.

Confluences are not used in the qualitative modelling work of Forbus or Kuipers.

30.26.10 Qualitative models

A component may have a number of states, each associated with a particular regime. A model of a component for the full set of regimes is termed a state specification.

Such a model may be illustrated by the valve model given by de Kleer (1992). This is

$$\begin{aligned}
&[A = A_{\max}];\quad [P] = 0;\quad \partial P = 0 && \text{Valve open}\\
&[0 < A < A_{\max}];\quad [P] = [Q] && \text{Valve working}\\
&\partial P = [P]\partial A - \partial Q = 0 &&\\
&[A = 0];\quad [Q] = 0;\quad \partial Q = 0 && \text{Valve closed}
\end{aligned}$$

where the subscript max denotes the maximum.

An account has been given by de Kleer of the treatment of flow-like and pressure-like variables in component modelling. For flow it is assumed that the fluid is incompressible and the conduit runs full, and the principle of conservation of mass is applied. This rule is termed the continuity condition. For pressure it is assumed that the sum of the pressure drops in the conduit is constant. This rule is the compatibility condition.

30.26.11 Time effects

Qualitative modelling is concerned with changes, and changes take place over time. The modelling must therefore take time into account in some way. It is not unusual in qualitative modelling work for the time aspect to be somewhat fuzzy. This is commonly so in fault tree studies, as already described.

There are three main methods which have been used for modelling change over time: the use of a sequence of intervals (Forbus, 1984); the use of intervals separated by a number of instants (de Kleer and Brown, 1984); and the use of intervals separated by single instants (Kuipers, 1984).

Rules necessary for reasoning about change over time have been derived by B.C. Williams (1984a,b) and are described by de Kleer (1992).

30.26.12 Dependence and causality

De Kleer draws a distinction between dependence and causality. It does not follow that because one variable is dependent on another, it is necessarily caused by it. For causality to apply, stricter criteria must be met. Two such criteria are locality and temporal order. Locality requires that for one variable to be a cause of another, the two variables must describe the behaviours of components which are physically adjacent, and temporal ordering requires that for one variable to be the cause of another it must precede it, even if only by an infinitesimally short interval of time, or mythical time.

30.26.13 Ambiguities and multiple interpretations

As already indicated, qualitative modelling is inherently ambiguous, and thus gives rise to multiple behaviour predictions, or interpretations. How serious this is for modelling in a particular application depends largely on the extent to which it is possible to devise rules for the elimination of some of the interpretations.

30.26.14 Envisioning

The reasoning process that uses qualitative modelling to produce a description of the behaviours of the system over time is termed envisioning. An illustration of envisioning is given by de Kleer (1992). He presents a stage-by-stage account of the behaviour of a mass–spring–friction system and shows that qualitative modelling can be used to envision the oscillatory behaviour of the system.

30.27 Engineering Design

Applications of AI have been mainly in the fields already described, but there is an increasing amount of work in engineering. The material of prime interest here is that on process plant design, which is described below, but first some consideration is given to design expertise and to AI applications in engineering design generally.

30.27.1 Design expertise

Accounts of the design process in general include *Introduction to Design* (Asimow, 1962), *The Nature of Design* (Pye, 1964), *Design Engineering* (Dixon, 1966), *An Introduction to Engineering and Engineering Design* (Krick, 1969), *Engineering Design* (Middendorf, 1969), *Management of Engineering Design* (Leech, 1972), *Supplementary Readings in Engineering Design* (Geiger, 1975), *A Students Introduction to Engineering Design* (Simon, 1975) and *The Sciences of the Artificial* (Simon, 1969).

The design process and expertise in design are somewhat elusive. Designers have found it difficult to explain their skill and others who have studied it have also found it hard to pin down. Broadly, however, the design process involves problem recognition and definition, problem decomposition, the generation of alternative options and selection from these options.

The expert possesses a knowledge base in which knowledge may be represented in a number of forms, many being analogous to those described earlier. He has available a mental library of design archetypes. He has knowledge relevant to the evaluation of situations such as: the frequency, or probability of events; the consequences of events; and the costs, in money and other factors. He is aware of constraining factors such as project objectives; costs; time; hazards; regulatory requirements; standards and codes requirements; and so on. He is able to make distinctions of all sorts that would probably not occur to the layman. He possesses the ability to decompose a problem into subproblems which have only weak interactions and

which are more manageable. He has methods of working which include logical argument, rules-of-thumb, mental models and analogues.

Part of the skill in engineering design consists of a knowledge of design methods for specific situations and equipment, based usually on appropriate mathematical models. This is the type of expertise with which the young engineer fresh from college may be expected to be familiar. Another part of the expertise comprises a personal collection of rules, many of them not explicit. These include both rules-of-thumb and heuristics, which guide the search for solutions. In this type of expertise the experienced engineer may be expected to have the advantage.

With design, in general, it is the initial conceptual stage that is the most critical. Closely related to this is the concept of design based not on trial and error but in getting it right first time.

30.27.2 Expert systems

The application of AI to engineering design is still in its infancy. A principal trend, however, has been the use of expert systems. An influential application of expert systems to engineering design was Rl, or XCON, which has already been described in Section 30.25. Another application of AI quite common in engineering design is the use of classification systems.

30.27.3 Design architectures

There are, however, developments that start from a critique of these current approaches. One such is described in *Design Problem Solving* by D.C. Brown and Chandrasekaran (1989). The stance taken by these authors is broadly as follows. Most applications of AI in engineering design take the form of expert systems. These tend to be general expert systems, often shells, which use domain-independent control and inference, and are simply loaded with the rules and data for the particular problem. They argue that typical practice with programming languages, system building tools and shells tends to involve the use of particular control structures even though this may not be apparent. They state:

> The fact that the low level language is used to implement a higher level control structure results in the knowledge base actually containing quite a few rules that are really programming devices for expressing this higher level of control. That is, the much talked about separation of knowledge from inference is not really true in practice for complex problems.

It is argued by Brown and Chandrasekaran that for efficient design it is necessary to take account of the specific domain and that there are generic tasks characteristic of each domain. Whilst there may be a range of features that are common to tasks in any domain of engineering, the relative importance of these features varies so greatly that it is not effective to adopt a uniform approach. Excessive emphasis on domain-independence suppresses the distinctions in control and inference which are characteristic of human conduct of generic tasks in different engineering design domains.

The framework for design that they propose is one that accommodates the domain-specific features. Design is viewed as the use of a number of different, and cooperating, types of problem-solver. The basic design process is that of generate and test. Four strategies are described for generating, or proposing, designs; (1) design decomposition, (2) design plans, (3) design by critique and modification of nearly correct designs and (4) design by constraint processes.

The first approach involves decomposing the design problem into suitable subproblems and creating a design hierarchy. Features of this process are the conversion of the goals and constraints of the overall problem into goals and constraints on the subproblems.

The design plans are pre-compiled partial design solutions. A design plan contains a sequence of design actions. Strategies for the retrieval of such plans include attachment of plans to goals or to components. NOAH may be viewed as a program which instantiates and expands design plans, since for each goal of the item under design, there is a stored procedure, effectively a plan.

Another way to proceed is by critique and modification of almost correct designs. This is applicable where such almost correct designs can be retrieved and converted to correct designs by processes of matching, critique and modification. Modification may involve the use of a number of problem-solving methods which may include means–ends analysis, hill-climbing and dependency-directed backtracking.

The fourth approach is design by constraint processes. This is applicable where there is a structure but the parameters are still to be determined. It proceeds by propagation of the constraints and incremental convergence on a solution which satisfies them all.

The authors distinguish three classes of design. Class 1 is creative design, essentially innovation and invention. Class 2 typically involves powerful decomposition and complex failure recovery features. Class 3 is routine design in which the problem is readily decomposable with only weak interactions between the subproblems and which is characterized by routine plans and failure recovery mechanisms.

30.27.4 DSPL

Brown and Chandrasekaran describe an expert system architecture for a Class 3 design and the programming language DSPL (Design Specialists and Plans Language) created to perform such design. DSPL contains design agents in the form of specialists, plans, tasks and steps. There is a hierarchy of specialists each of which possesses a set of plans and has the function of plan selection. A plan is a sequence of calls to specialists or tasks. Each plan has a sponsor that matches the characteristics of the plan with those of the task for which it is a candidate. A task is a sequence of steps that it executes. The primitive design agent is the step. It provides a value for an attribute of the design.

A feature of DSPL is failure handling. The basic approach taken is that the design agent concerned detects, diagnoses and fixes its own local failures and passes on only those failures that it cannot correct.

The authors give a detailed account of DSPL covering, in addition to the architecture features just mentioned, the handling of the database, constraints, dependencies and problem-solving. They describe DSPL itself and given an example of the design of an air cylinder system.

30.28 Process Applications

Turning now to the use of AI, expert system and other advanced techniques in the process industries, a number of

overviews have been published. They include those of Stephanopoulos and Townsend (1986), Westerberg (1989), Mutton, Ponton and Waters (1990) and Stephanopoulos (1990). The following areas of application can be identified:

(1) project aids
  (a) aids for handling issues,
  (b) aids for handling requirements;
(2) process synthesis
  (a) reaction route,
  (b) energy;
(3) plant design: synthesis
  (a) inherently safer design,
  (b) classification activities,
  (c) designs with shallow structure,
  (d) designs with deep structure;
(4) plant design: analysis
  (a) hazop,
  (b) fault tree analysis;
(5) operating procedures;
(6) process monitoring;
(7) fault administration;
(8) malfunction detection.

These various computer aids fall into four broad categories, as aids for (1) the design project, (2) the design synthesis, (3) the design analysis and (4) the plant operation. Thus item (1) in the above list covers aids for the design project as a whole, items (2) and (3) cover the process and plant design synthesis aids, item (4) covers plant analysis aids and items (5)–(8) plant operations aids.

Computer aids for process and plant synthesis may be termed front-end aids, whilst aids for plant analysis are back-end aids. Another way of looking at the matter is in terms of the generate-and-test concept: the synthesis aids represent the generate phase and the analysis aids the test phase. These various aids are considered in the sections that now follow.

30.29 Project Aids

It is appropriate to begin the account of AI aids for process plant design by considering those which address design problems at the highest level.

30.29.1 Aids for representing design issues and history

Design involves the identification of a succession of issues, discussion of these issues and decisions to select particular options. There are a number of benefits to be had by adopting a more formal approach to the handling of design issues. Such an approach imparts greater structure to the decision-making process, assists communication and cooperation between the different design disciplines and provides a record of design information. This information is of various kinds and includes the design intent, the chronological development of the design, the issues raised, the constraints recognized, the rules applied and the decisions made.

This record is of particular value when a design is undertaken which draws on that for an existing plant. Unless such information can be retrieved, the designers of the new plant may be unaware of significant issues and constraints and may not appreciate the reasons for certain design features. In the more serious cases, some assumption or feature critical to safety is not appreciated.

Parties concerned with the design can see the issues under discussion and can make their contribution by raising further issues, proposing alternative solutions, advancing further arguments for or against a solution and drawing attention to facts relevant to, or making comments on, an argument. Needless to say, if a decision aid is used in this way there needs to be a policy governing the parties authorized to access it and to modify it.

Work on this topic, and on the creation of associated computer aids, has been described by a number of workers including Kunz and Rittle (1970), Conklin and Begeman (1988), Potts and Bruns (1988), Ganeshan, Finger and Garrett (1991), Lubers (1991), Chung, Abbas and Robertson (1993), Ramirez-Dominguez and Banares-Alcantara (1993) and Chung and Goodwin (1994).

An intelligent information system for safe plant design is described by Chung and Goodwin (1994). An overview of the system is shown in Figure 30.9. The system is issue-based, allowing the issues arising in the design and the arguments related to the issues to be represented and captured. It provides a historical record of the development of the design and of the issues affecting this development. Elements of the system are (1) the viewpoint mechanism, (2) the issue base and (3) the rule base.

The viewpoint mechanism is used to represent the design hierarchy. Each viewpoint is a single point in the design space. The viewpoint hierarchy provides a chronological record of the states of the design. The viewpoint mechanism allows the designer to move around the design from node to node whilst maintaining consistency. A record is kept of the design changes and of the constraints and rules together with a list of previous viewpoints. When the designer changes the viewpoint the mechanism traces back from the root to that point, reasserting all the constraints, rules and decisions stored along the way. The viewpoint mechanism also ensures that all changes made to one node are propagated through the design from the parent node to the child nodes.

The core of the system is the issue base. This provides a record of the issues considered. An issue is identified, positions are taken and arguments adduced for or against each position. In due course a decision is made to select one of the positions, or options.

Figure 30.10 shows an issue base for the following case:

> A chemical company wants to build a new plant in the United States. There is an existing plant for the same tonnage and product in the United Kingdom which uses both recycled cooling water (RCW) at 21°C and chilled water at 5°C. There are heavy demands on the cooling. The atmospheric ambient and wet bulb temperatures are higher at the proposed US site by 5°C and 8°C, respectively, on average. Are any modifications needed to the plant items and/or cooling supply systems?

The structure consists of nodes and semantic links. As shown, an argument is linked to a position by a *support* or an *against* link and a position is linked to an issue by a response-to link.

The authors also describe other types of node and link found necessary in developing this basic structure. Additional types of node used are *fact, comment* and *decision* nodes and additional types of link are *follow-up, combined-with* and *replaced-by* links. The first of these links allows re-examination of an issue on which a decision has already been made, the second allows the combination of several positions to form a single response and the third

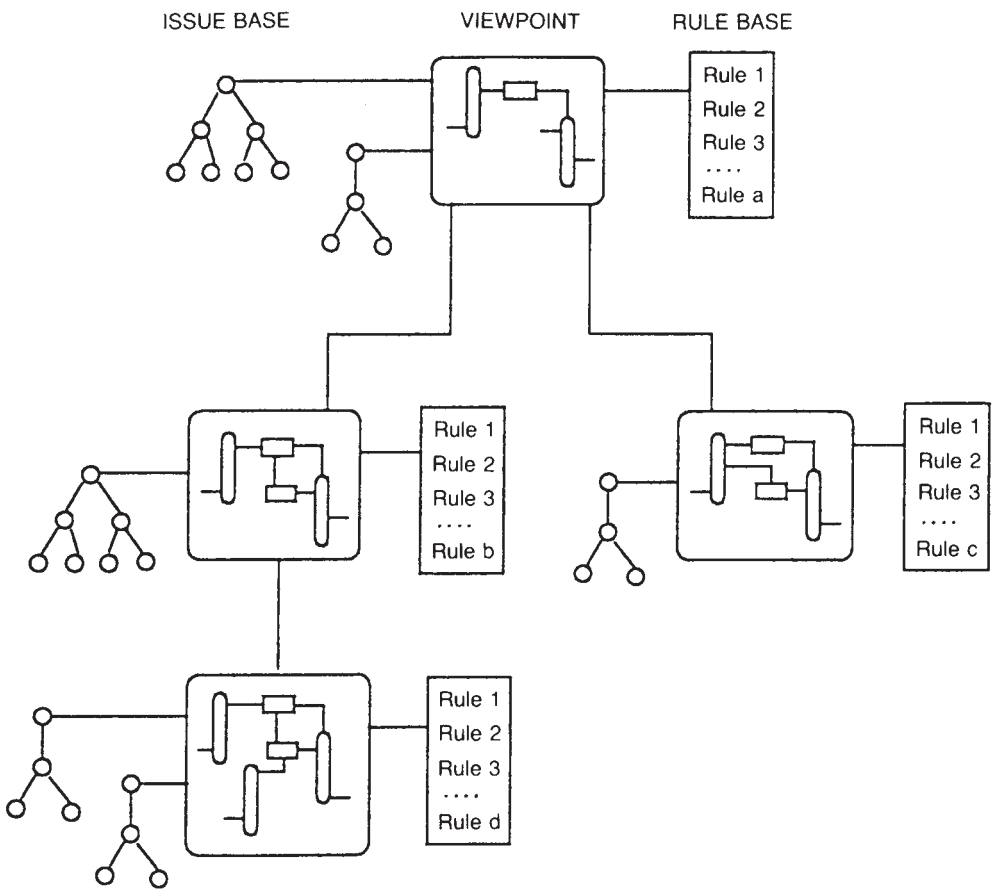


Figure 30.9 *Aid for the representation of design issues and history: system overview (Chung and Goodwin, 1994) (Courtesy of Kluwer Academic Publishers)*

decomposition of the problem into a set of smaller ones. These extensions thus cater for features such as iteration and decomposition, which are characteristic of design.

The rule base constitutes the third main element of the system. This contains both general rules and rules specific to the particular design.

30.29.2 Aids for representing regulatory and code requirements

Another generic problem in design is the handling of the requirements of legislation, standards and codes, and company policies. The number of documents containing requirements and the number of individual requirements is generally very large, and this poses a major information handling problem. An account of the development of the aids to assist with such information handling has been given by Chung and Stone (1994). The problem has several different aspects, including the retrieval of the requirements relevant to a particular issue and the comprehension of these requirements.

Considering first an individual document such as a standard, three distinct approaches to the problem may be identified. The first is to accept the document as it is and provide aids to the user in finding his way around it. The second is to perform some kind of processing on the document. The third, and most radical, is to intervene at the stage when the document is being written and provide aids to assist the author in writing it.

The retrieval problem has two aspects: retrieval of whole documents and retrieval of requirements from within a document. For both types of retrieval widespread use is made of keywords. For retrieval of whole documents these may be words in the title, keywords provided by the author or keywords searched in the text. The use of combinations of keywords narrows the search space.

Bourdeau (1991) has described the creation of a major keyword-based system REEF which is a 15,000 page encyclopaedia consisting of about 1000 documents commonly used by French building professionals. The database contains about 75% text with the rest made up of some 3500 tables, 9000 drawings and numerous formulae. Information is indexed at two levels, that of the document and that of the information unit.

Another approach is to analyse the hierarchy of concepts in a document and to provide an aid based on search down through the hierarchy.

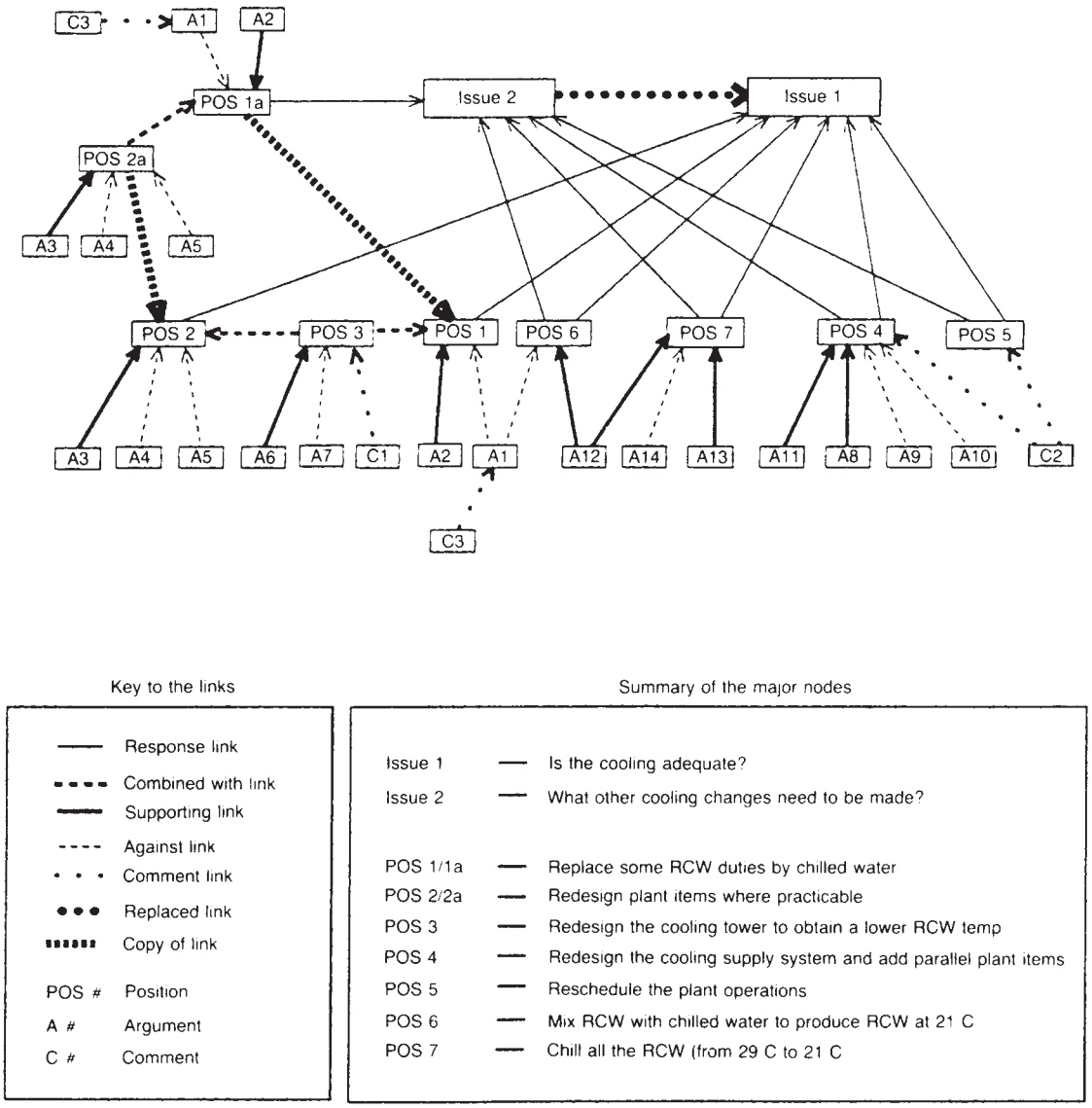


Figure 30.10 *Aid for the representation of design issues and history: issue base for the decision on the selection of cooling water temperature. RCW, recycled cooling water (Chung and Goodwin, 1994) (Courtesy of Kluwer Academic Publishers)*

Another aid to retrieval is hypertext. This allows the user to browse through a document looking at related items. This too is based on some form of hierarchy or network of relationships.

Further progress is likely to depend on a more fundamental approach. Work in this area has developed in the direction of the modelling of the knowledge domain. This work bears both on retrieval and on comprehension. There are a number of methods that deal with relationships. Relationships between objects in a hierarchy and attributes of objects may be represented in a type hierarchy and the constituent parts of an object in a part hierarchy. Dependencies may be represented in network form. For the conclusion of a conditional statement, the pre-conditions may be shown in order of precedence in an ingredience network. A complementary representation is a dependence network that shows all the conclusions to which a given condition contributes. Requirements can be converted to various logical forms. These include logic programming, production rules, decision tables and so on.

One outcome of this sort of approach is the conversion of the document into an expert system. As can be imagined, this is a major task. Nevertheless, several expert systems of this type have been created, mainly in the building field.

The use of methods such as logic programming or production rules raises a number of issues such as the mixing of domain and control information and the updating of the program when requirements are changed, which are discussed by Chung and Stone. One approach being taken to overcome such problems is the development of generic standards processors, which allow the user to input the domain information in a purely declarative way. Another development is automated text formalization, which is essentially the application of natural language comprehension methods such as parsing to convert the text into formal language. A more radical departure is the development of author support systems to ensure that the original document is written in a more structured and formal manner. This addresses at source the defects that later lead to problems of retrieval and comprehension.

In the account given so far, consideration has been limited to a single document. There is also the problem of retrieving, comprehending and reconciling requirements from a variety of bodies. A limited amount of work has been done by researchers on author support systems, such as the work by Stone and Tweed (1991) on the capture of information from the common sources on which regulations, standards and codes draw.

Aids for handling the requirements that a design must meet are potentially invaluable, but it will be apparent from the foregoing that their development is in its early stages.

30.30 Process Modelling

Before considering process and plant design as such, it is necessary at this point to say something about modelling. It has become clear from attempts to apply AI to a number of problems in this area that a common lesson is the need for modelling of the process and the plant. Such models are often referred to as deep level knowledge in contrast to compiled knowledge such as rules. Some areas in which modelling is required are process and plant design, planning of plant operations and the diagnosis of faults on operating plant.

Such modelling draws particularly on the fundamental work on qualitative modelling described in Section 30.26, and especially on that of Kuipers and of Forbus on componented qualitative modelling and qualitative process theory, respectively. Some principal developments in qualitative modelling are now described.

30.30.1 Modelling languages and environments

Methods based on qualitative modelling tend to require the availability of a considerable number of models. The manual configuration of models requires considerable effort and can be a limiting factor in the use of the methods.

There have been a number of approaches aimed at mitigating this problem. One is the development of modelling languages such as OMOLA (Andersson, 1989; Nilsson, 1989), MODEL.LA (Stephanopoulos, Manning and Leone, 1990a,b) and ASCEND (Piela *et al.*, 1991). Another development is automatic model generation.

The characteristic approach is the identification of common features of models and of a hierarchy of models with inheritance of features.

30.30.2 MODEL.LA

MODEL.LA is a modelling language for the interaction or automatic construction of models of process systems. It is designed to be able to generate models at various levels of abstraction, to capture qualitative, semi-quantitative and quantitative knowledge, and to produce complete documentation of the modelling context such as the process task and the assumptions and simplifications.

It has an object oriented structure. The syntax is described as an extended Backus–Naur form. It utilizes six modelling elements: generic unit, port, stream, modelling scope, constraint and generic variable. There are 11 semantic relationships obeying basic axioms of transitivity, monotonicity, commutativity and merging. The structure of the models is depicted by digraphs that are constructed by algorithms driven by the modelling context.

30.30.3 Model generation

Closely related to the use of modelling languages is the systematic, and hence automatic, generation of models. Work on this topic has been described by Catino, Grantham and Ungar (1991). These authors' work utilizes Forbus' qualitative process theory (QPT). The approach taken is based not so much on process units such as reactors and heat exchangers as on process phenomena such as reactions and heat exchange. The authors describe the use of an adaptation of QPT to configure such models, and the creation of a prototype model library.

30.30.4 Order-of-magnitude modelling

A methodology for formal order-of-magnitude, or O(M), reasoning in process engineering has been outlined by Mavrovouniotis and Stephanopoulos (1988). In qualitative modelling use is made of qualitative values (−, 0, +). For some purposes, this treatment of the quantity space is not sufficiently expressive. It is desirable to be able to have a more adequate treatment of absolute and relative values and to be able to take into account concepts such as 'much smaller than' or 'slightly larger than'. The O(M) method provides a means of doing this.

30.30.5 Dynamic qualitative modelling

Most work in qualitative modelling is confined to the steady state, but there is some work emerging on unsteady-state, or dynamic, qualitative modelling. Thus, a method for the dynamic qualitative modelling and simulation of process systems is described by Dalle Molle, Kuipers and Edgar (1988).

30.30.6 Mathematical programming

Another area of modelling is mathematical programming, specifically mixed integer linear programming (MILP) and mixed integer non-linear programming (MINLP). An account of the relationship between MILP and logical inference for process synthesis is given by Raman and Grossman (1991), who show that qualitative knowledge on process synthesis that can be expressed in prepositional logic form can also be represented in the form of equivalent linear equations and inequalities.

30.31 DESIGN-KIT

A number of computer aids for design such as building tools and environments have been created. One of these is DESIGN-KIT described by Stephanopoulos *et al.* (1987). DESIGN-KIT is a process design environment built on CommonLISP and KEE. It is intended in the first instance to support the synthesis of process flowsheets, the configuration of control loops for complete plants, the planning and

scheduling of plant-wide operations and the operational analysis of plants.

The underlying philosophy is that the designer should have available an environment which allows him to move consistently between the tasks of: (1) the conceptual design of processing schemes and the evaluation of alternative chemistries, and mass and energy balances; (2) the simulation and evaluation of designs in respect of operability and economics; (3) the sizing and costing of major equipment; (4) the creation of control loop configurations; (5) the design for start-up, shut-down and alternative operating modes and (6) the generation of piping and instrument diagrams, fabrication isometrics, etc. Further, the environment should allow high-level communication between the user and the computer, full and transparent integration of its various facilities, and easy maintenance and modification.

Some specific features of DESIGN-KIT are shown in Table 30.5.

30.32 Process Synthesis

Turning now to the actual design process, the most creative part of the design is the synthesis of the process and of the plant.

Accounts of process and plant synthesis have been given in *Strategy of Process Engineering* (Rudd and Watson, 1968) and in *Conceptual Design of Chemical Processes* (Douglas, 1988). Reviews include those of Westerberg (1980, 1985), Nishida, Stephanopoulos and Westerberg (1981), Umeda (1982), Stephanopoulos and Townsend (1986), Grossman and Floudas (1987), Gundersen and Naess (1988), Floquet, Piboleau and Domenech (1988), R. Smith and Linnhoff (1988), Grossman (1989) and Mutton, Waters and Ponton (1990).

Table 30.5 *Some features of DESIGN-KIT (after Stephanopoulos et al., 1987)*

1. Generation of graphic descriptions, for example, flowsheets, control structures, material and energy balances, operational paths, etc., with windowing facilities and menu-driven operations
2. Automatic generation of data structures describing the graphic objects
3. Modular construction of new graphic objects, process units models, design methodologies, operational objectives, etc.
4. High-level descriptions of various tasks, for example, graphic operations, design procedures, specification-directed simulation, definition of design or operational goals, automatic modelling of process units, etc.
5. Equation-oriented simulation and design facilities with dynamic generation of the relevant equations (specified by the problem to be solved), pre-processing of the equations, selection of the design variables, symbolic differentiation, etc.
6. Reasoning capabilities for the utilization of heuristic knowledge, qualitative information, O(M) analysis, goal-directed design or planning, as well as query and explanation facilities
7. Unified database management system with contextual description of the information and capability, through a common data model, to handle all types of knowledge (data, graphs, equations, inequalities, procedures, qualitative statements, heuristics, etc.)

The work of Rudd and Watson deals with in the first part, the creation and assessment of alternatives under the headings of (1) the synthesis of plausible alternatives, (2) the structure of systems, (3) economic design criteria, and (4) cost estimation; in the second part, optimization under the headings (5) the search for optimum conditions, (6) linear programming, (7) the suboptimization of systems with acyclic structure, (8) macrosystem optimization strategies and (9) multi-level attack on very large problems; and in the third part, engineering in the presence of uncertainty under the headings (10) accommodation to future developments, (11) accounting for uncertainty in data, (12) failure tolerance, (13) engineering around variations and (14) simulation.

A series of studies on process synthesis have been described by Rudd and co-workers (Masso and Rudd, 1968, 1969; Rudd, 1968; Siirola, Powers and Rudd, 1971a,b; Powers and Jones, 1973; Rudd, Powers and Siirola, 1973; and May and Rudd, 1976).

Douglas (1988) describes a hierarchical approach to conceptual design with the following hierarchy of decisions:

(1) batch vs continuous;
(2) input–output structure of the flowsheet;
(3) recycle structure of the flowsheet;
(4) general structure of the separation system
  (a) vapour recovery system,
  (b) liquid recovery system;
(5) heat exchanger network.

Douglas' work deals with: in the first part, a strategy for process synthesis and analysis under the headings (1) the nature of process synthesis and analysis, (2) engineering economics, and (3) economic decision-making; in the second part, developing a conceptual design and finding the best flowsheet under the headings (4) input information and batch vs continuous, (5) input–output structure of the flowsheet, (6) recycle structure of the flowsheet, (7) separation system, (8) heat-exchanger networks, and (9) cost diagrams and the quick screening of process alternatives; and in the third part, other design tools and applications under the headings (10) preliminary process optimization, (11) process retrofits, (12) computer aided design programs and (13) summary of, and extensions to, the conceptual design procedure.

Process synthesis is of great importance. In particular, it is relevant to (1) inherently safer design, (2) inherently cleaner design and (3) inherently low energy design, or process integration.

30.32.1 Process route

If the process involves a chemical reaction, this reaction is generally the most fundamental feature of the process. A number of studies have been carried out with a view to developing computer aids to selecting the chemical route, or process synthesis. Such work has been described, for example, by May and Rudd (1976). This is an area with great potential that has barely been broached.

30.32.2 Process flowsheet

The synthesis of the overall flowsheet is the least developed area of process synthesis. Most work addresses the more tractable subproblems such as energy economy.

A prototype system for the synthesis of the process flowsheet, PIP, has been described by Kirkwood, Locke and Douglas (1988). PIP has a hierarchical structure. It utilizes heuristics to select unit operations, to establish interconnections between them, to identify the dominant design variables and to generate process alternatives. It attempts to devise a flowsheet using a depth-first search.

Beltamini and Motard (1988) have described the development of an expert system, KNOD, which acts as a front end to a process simulator. It is used to test strategies and heuristics for the design and simulation of process structures.

A method of synthesizing a flowsheet which combines hierarchical and algorithmic approaches is described by Mizsey and Fonyo (1990). A prime purpose of this system is to give the designer confidence that the initial universe of potential process paths generated contains all the relevant paths.

30.32.3 Process simulators and databases

It is now common practice to use a process simulator to explore the various features of a process flowsheet. This simulation brings with it a requirement for more powerful database systems that are capable of supporting such work. Conventional database management systems tend to be deficient in a number of ways and the development of database systems for process simulation has been an active area of work. An example is the development of SIMBAD, a process simulator linked to a powerful database, described by Montagna *et al.* (1987). There is also a trend to add object oriented features to traditional relational databases. Huang and Fan (1988) describe a hybrid database that marries an object oriented approach with a relational one.

30.32.4 Process integration as a model

One of the most successful areas of process synthesis is that of process integration, the design of heat exchanger networks. Taking this as a model for process synthesis as a whole, Westerberg (1989) identifies two key features. One is the ability to set targets for the design and the other is the use of an effective domain-specific representation, in this case for heat flow.

30.32.5 Other process design aspects

The problem of handling constraints during design is addressed by Waters and Ponton (1992). The work is concerned with the early identification and correction of design errors and explores the use of an automated checklist to prevent violations of design intent.

An exploration of the applicability of an expert system to the design of batch processing systems is described by Hofmeister, Halasz and Rippin (1989). The authors refer particularly to the importance of problem representation, highlighted in the earlier work of Rippin (1983).

Hanratty and Joseph (1992) have described the application in an expert system for reactor selection of the analytic hierarchy process (AHP) method of Saaty (1980). The AHP is one of the techniques for encoding expert judgement, as described in Chapter 9, and is widely used in the social sciences. It is based on the method of paired comparisons.

Another design problem is the analysis of the flexibility of a design. This has been addressed by Grossman and Floudas (1987) who describe a flexibility criterion and a flexibility test.

Engelmann *et al.* (1989) have described the use of distributed expert systems in process synthesis.

30.33 Plant Design: Synthesis

Moving on to the design of the plant as opposed to that of the process, this too is an important area. Here some modest progress has been made in the development of aids for certain types of task, but there remains much scope.

30.33.1 Inherently safer design

One of the prime aims in the design of process plants is to promote the practice of inherently safer design right from the conceptual design stage. Apart from developments such as those in process synthesis and the selection of a reaction route, which are certainly important aspects of inherently safer design, it is not easy to identify any specific synthesis aid in this area.

30.33.2 Characteristics of design problems

An overview of the expert design of plant handling hazardous materials has been given by Bunn and Lees (1988). What these authors do is to describe a series of design problems, involving various kinds of design expertise, ranging from very simple, even trivial, design activities to designs with deep structure and to designs apparently better suited to solution by machine rather than by man.

The problems considered in this work are (1) the choice of whether or not to fit an emergency isolation valve, (2) the design of a flare system, (3) the design of a pressure relief system and (4) the design of a valve sequencing system; together in each case with the nature of the appropriate Al aid.

The first part of this section gives an account of this work, as an illustration of the potential for Al and expert system aids across the whole synthesis activity in plant design. The second part describes some particular aids that have been developed.

30.33.3 Design as equipment selection: emergency isolation valves

The most simple problem in the set considered by Bunn and Lees is the decision whether or not to fit an emergency isolation valve (EIV). The problem was investigated by studying a published paper in which an expert describes the factors that he took into account in making the decision and gives examples of cases where such valves were installed and of others where they were not. An interview was also held with the same expert.

The account used was that given by Kletz (1975b) of the installation of EIVs on two petrochemical plants. In deciding whether or not to install an EIV both the frequency and consequences of an escape were taken into account. Kletz' paper states:

Three situations should be considered:

(1) The equipment is particularly likely to leak; for example, very hot or very cold pumps.
(2) The equipment is less likely to leak. But if it does leak, a very large quantity of material will run out and there is no way of stopping it; for example, the bottom pump on a still containing more than, say, 50 ton of flammable liquid.
(3) The equipment is less likely to leak, but if it does so, the leak will be very large; for example, a very large pump.

The paper gives two tables, one for an olefins plant and one for an aromatics plant, listing the situations where the installation of an EIV was considered, giving the parameters

for these situations and stating whether or not it was decided to install such a valve. One of these tables, that for the olefins plant, is shown in Table 30.6.

From the rules explicitly stated, the examples given and the comments made in the text of the paper, the following extended set of rules was derived. The overt rules are:

(1) Fit if the equipment is particularly likely to leak. This is so if (a) it has a history of leakage or (b) it is pumping liquid at extremes of temperature or (c) it is otherwise thought likely to leak.
(2) Fit if the equipment is less likely to leak, but if it does, it could release a large or very large quantity.

There also appeared to be some covert rules. These include:

(3) Fit if the liquid is above its autoignition temperature.
(4) Fit if it is convenient for process reasons.
(5) Do not fit if there is a control valve that will perform the same function.
(6) Do not fit if there is an alternative means of stopping the leak.
(7) Do not fit if the fluid is a gas in a compressor.

Here the second and third rules given by Kletz have been combined into a single rule.

Some of the rules are stronger than others. Thus Rule 1 is a strong rule. Rules 5 and 6 are also strong rules. Rule 7 is a weak rule and may be overriden by Rule 4. A particular rule also seems to have some influence as a counter-rule. Thus a small inventory weights the decision against fitting an EIV.

Table 30.6 *Emergency isolation valve location: parameters for the provision of emergency isolation valves on an olefins plant (Bunn and Lees, 1988; after Kletz, 1975b) (Courtesy of the Institution of Chemical Engineers)*

Item		*Material*	*Temperature* (°C)	*Pressure* (psig)	*Inventory* (ton)	*Leak history*	*EIV*	*Note*
1.	Furnaces	Naphtha	100	120	Small	–	Y	1	
2.	Feed pump	Naphtha (gassy)	15	140	70	N	N	2	
3.	Bottoms pump	Fuel oil	210	30	100	Y	Y	3	
4.	Sidestream pump	Distillate fuel oil	160	25	20	N	Y[a]		
5.	Bottoms pump	Fuel oil	210	30	60	Y	Y		
6.	Bottoms pump	Gasoline	85	20	25	–	N	4	
7.	Bottoms pump 1	Fuel oil	220	30	1	Y	N	5	
	2	Distillate fuel oil	180	25	1	–	N	5	
8.	Reflux pump	Ethylene	−30	270	30	Y	Y	6	
9.	Sidestream pump	Ethylene	−30	270	10	Y	Y	7	
10.	Reflux pump	Propylene	40	250	50	N	Y		
11.	Cold AI exchanger	Methane	−100	370	30	Y	Y	8	
12.	Process gas compressor	Methane, ethylene, propylene, etc.	40	30	50	–	N	9	
13.	Compressor	Ethylene	−100	65	40	–	Y	9	
14.	Compressor	Propylene	−40	40	100	–	N	9	
15.	Bottoms pump	Light gasoline	90	150	5	Y	N	10	
16.	Reflux pump	Methane	−100	370	5	Y		11	
17.	Reflux pump	Ethane/ethylene	−14	350	5	–		12	
18.	Converter	Ethane/ethylene	80/150	350	–	Y	Y	13	
19.	Reflux pump	Propylene	5	90	1	–	N		
20.	Reflux pump	Propylene	30	175	5	–	N		
21.	Bottoms pump	Butylene	120	50	15	–	N		
22.	Reflux pump	Butylene	35	50	5	–	N		

[a] Borderline.

Notes:
1. Control values used as EIVs in event of tube failure and reasonably remote hand isolations.
2. No history of leaks, material cold.
3. Close to autoignition temperature. Similar pumps have ignited.
4. Inventory can be pumped out with other pumps.
5. Inventory small and feed to column can be isolated.
6. Pump has leaked.
7. Pump has leaked and ignited.
8. AI heat exchangers more fragile than steel and therefore classified as likely to leak. Isolation by means of remote hand valves, control valves and one extra EIV.
9. Centrifugal machines – no history of leaks except one bad leak on ethylene compressor. Most of inventory would be flared. Leaks would be gas. Leak rate from ethylene and propylene compressors would be small – several tons per hour.
10. Congested area, but remote manual valve accessible.
11. Valve fitted remote by distance – but upstairs. Despite low temperature there is no history of leaks.
12. Valve fitted remote by distance – but upstairs.
13. Valve fitted on inlet and exit and blowdown lines to isolate and blow down vessel to stop runaway reactions. At least five incidents have occurred on plants outside the company.

An analysis of the apparent effects of the rules is shown in Table 30.7.

The decision on whether to provide an EFV appeared to be a relatively straightforward classification problem. The use of an AI aid for classification was therefore investigated, the programs chosen being initially EXPERTEASE and later EXTRAN, which are based on the IDS algorithm.

The class value was taken as EIV fitted/not fitted; and the attributes as (1) fluid, (2) equipment, (3) inventory, (4) temperature, (5) pressure and (6) leak history. The first and second attributes were entered as the process material and the plant equipment, the third to fifth attributes as a number and the last attribute as yes/no.

The 22 cases were run through the program that induced from them a set of rules. However, this first application was not regarded as satisfactory. Among other things, no use was made of leak history, which was supposed to be a strong rule.

The view was taken that the problem should be reformulated. This time the attributes taken were (1) large hazard, (2) leak history, (3) high leak likelihood, (4) large inventory, (5) high temperature, (6) above the autoignition temperature, (7) convenient for process reasons, (8) alternative means of stopping the leak and (9) fluid is a gas in a compressor. The revised data set is shown in Table 30.8 and the set of rules induced is given in Table 30.9.

This set of rules was regarded as more satisfactory. However, in view of the fact that Rule 6 is a strong rule, it was considered that it should probably be the first branch. The fact that this is not so is evidently due to the fact the example set is not sufficiently comprehensive.

The authors conclude from this example that an AI classification tool of this general type can be useful, but that it has to be applied with caution. Care needs to be taken in the definition of the attributes and in the provision of a learning set which is not only sufficiently large but also is specifically designed to cover the domain.

30.33.4 Designs with shallow structure: flare system

The next problem considered by Bunn and Lees is the design of a flare system. They take this as representative of a class of design synthesis problems with relatively shallow structure.

A common design problem is the design of a unit for which there already exists a skeletal design archetype, or stereotype, which is more or less fixed in respect of the basic set of components, but where there exist options both for the details of these components and for add-on features. If it is assumed that all the relief gas flows that are to be handled have already been specified then, the authors argue, flare design might be taken as an example of this type of problem.

Generally, the first step taken by the expert is to define the primitive problem. The understanding that the problem originally posed needs to be redefined and the ability to do this is an essential feature of his or her expertise. In order to do this he or she needs to collect information. In the case of a flare system this includes data on gas flows and composition. He or she is then able to consider whether alternatives to flaring are appropriate. These include, in the case of a flare system, total containment, trip systems,

Table 30.7 *Emergency isolation valve location: apparent influence of expert's rules on the decision to fit emergency isolation valves on an olefins plant (Bunn and Lees, 1988) (Courtesy of the Institution of Chemical Engineers)*

Item	*History of leaks*	*Fit EIV*	*Comment*
1. Furnaces	–	Y	Rule 1(c) apparently. Rule 5
2. Feed pump	N	N	Influence of counterrule 1(a), 3
3. Bottoms pump	Y	Y	Rule1(a) and (b), 2, 3
4. Sidestream pump	N	Y[a]	Rule 1(a) and (b) and 2 not satisfied, but influence of Rules 2 and 4 perhaps
5. Bottoms pump	Y	Y	Rule 1(a) and (b), 2
6. Bottoms pump	–	N	Rule 6
7. Bottoms pump 1	Y	N	Rule 1(a) and (b) but overridden by Rule 6
2	–	N	(Rule 1(a) and (b) not satisfied)
8. Reflux pump	Y	Y	Rule 1(a) and (b)
9. Sidestream pump	Y	Y	Rule 1(a) and (b)
10. Reflux pump	N	Y	Rule 2 apparently
11. Cold Al exchanger	Y	Y	Rule 1(a) and (b). In part Rule 5
12. Process gas compressor	–	N	Rule 7
13. Compressor	–	Y	Rule 7 but overridden by Rule 4
14. Compressor	–	N	Rule 7
15. Bottoms pump	Y	N	Rule 1(a) but overridden by Rule 6. Influence of counterrules 2 and 3 perhaps
16. Reflux pump	Y	?	Meaning of notes not clear. Does
17. Reflux pump	–	?	valve fitted refer to existing valve?
18. Converter	Y	Y	Special case
19. Reflux pump	–	N	(Rule 1(a) and (b) and 2 not satisfied)
20. Reflux pump	–	N	As (19)
21. Bottoms pump	–	N[a]	As (19)
22. Reflux pump	–	N	As (19)

[a] Borderline.
Note: Extremes of temperature taken as $-30°C < T > 180°C$.

Table 30.8 *Emergency isolation valve location: revised formulation of parameters for the provision of emergency isolation on an olefins plant (Bunn and Lees, 1988) (Courtesy of the Institution of Chemical Engineers)*

Item	*Attribute*[b]								*EIV*
	1	2	3	4	5	6	7	8	
1. Furnaces	N	Y	N	N	N	N	N	–[a]	Y
2. Feed pump	N	N	Y	N	N	N	N	–[a]	N
3. Bottoms pump	Y	N	N	Y	Y	N	N	–[a]	Y
4. Sidestream pump	N	N	Y	N	Y	N	N	–[a]	Y[a]
5. Bottoms pump	Y	N	N	Y	Y	N	N	–[a]	Y
6. Bottoms pump	N	N	N	N	N	Y	N	–[a]	N
7. Bottoms pump 1	Y	N	N	Y	N	Y	N	–[a]	N
2	N	N	N	Y	N	N	N	–[a]	N
8. Reflux pump	Y	N	N	Y	N	N	N	–[a]	Y
9. Sidestream pump	Y	N	N	Y	N	N	N	–[a]	Y
10. Reflux pump	N	N	N	N	Y	N	N	–[a]	Y
11. Cold Al exchanger	Y	N	N	Y	N	N	N	–[a]	Y
12. Process gas compressor	N	N	N	N	N	N	Y	–[a]	N
13. Compressor	N	N	N	N	N	N	Y	Y	Y
14. Compressor	N	N	N	N	N	N	Y	–[a]	N
15. Bottoms pump	Y	N	N	N	N	Y	N	–[a]	N
16. Reflux pump	Y	N	N	N	N	N	N	N	(1)
17. Reflux pump	Y	N	N	N	N	N	N	N	(1)
18. Converter	Y	N	N	N	N	N	N	–[a]	Y
19. Reflux pump	N	N	N	N	N	N	N	–[a]	N
20. Reflux pump	N	N	N	N	N	N	N	–[a]	N
21. Bottoms pump	N	N	N	N	N	N	N	–[a]	N
22. Reflux pump	N	N	N	N	N	N	N	–[a]	N

[a] Borderline.
[b] Attributes:
1. Does the equipment have a history of leaks?
2. Is the equipment otherwise likely to leak?
3. Is the liquid above its autoignition temperature?
4. Is the liquid being pumped at high temperature?
5. Is the equipment less likely to leak, but the situation such that if it does a large quantity will escape (is there a large hazard)?
6. Is there an alternative means of stopping the leak?
7. Is the fluid a gas in a compressor?
8. Is the fitting of an EIV convenient for process reasons?

Table 30.9 *Emergency isolation valve location: set of rules for the provision of emergency isolation valves on a alkenes plant (Bunn and Lees, 1988) (Courtesy of the Institution of Chemical Engineers)*

Large hazard
  Yes: fit EIV
  No: leak history
    Yes: fit EIV
    No: otherwise likely to leak
      Yes: fit EIV
      No: pumping at high temperatures
        Yes: alternative means of stopping leak
        No: fit EIV
Otherwise no EIV

relief valve venting to atmosphere, unflared vent stacks and plant flaring.

Given that a flare system is still the appropriate solution for at least some of the relief flows, the expert has then to determine a strategy for the overall system. This may involve controlled blowdown to smooth out peak flows, low and high level flares and multiple flares. A particular aspect of this strategy is segregation of different gas flows: dry from wet gases, normal temperature from low temperature gases, hydrogen sulfide from other gases, and reactive gases from other gases. Only when these various strategic decisions have been made does the design of the flare system itself begin. Some aspects of the design expertise involved in flare system design are outlined in Table 30.10.

A typical flare system is illustrated in Figure 30.11. The basic elements of a flare system are the relief header, the knockout drum, the seal drum, the flare stack, the flare tip and the pilot light. The design of the flare system itself involves: deciding whether to provide various additional features; selecting a means of implementing the basic and additional features both in terms of equipment and of utility fluids such as purge gas and flare tip steam; and a determination of the magnitude of some of these features. Possible additional features include quench drums, vaporizer drums, vapour recovery, molecular seals and flame arresters. Some principal features that need to be specified quantitatively include knockout drum size, flare stack

Table 30.10 *Design of flare systems: some aspects of Glare the design expertise involved (Bunn and Lees, 1988) (Courtesy of the Institution of Chemical Engineers)*

General area	*Specific element or topic*
Gas flows requiring disposal	Normal flows Emergency flows
Gas compositions requiring disposal	Hydrocarbons Hydrogen Hydrogen sulfide Steam Air
Alternatives to flaring	Total containment Trip systems Relief valve venting to atmosphere (air, steam, cold gases) Unflared vent stacks Plant specific flaring
System options	Multiple flare systems Dry gas vs wet gas High vs low level flares Controlled blowdown
Segregation	Dry gas vs wet gas High or low temperature gases Hydrogen sulfide Reactive materials
Flare system, basic elements	Relief header Knockout drum Seal drum Flare stack Flare tip Pilot light
Flare system, additional elements	Quench drum Vaporizer drum Vapour recovery Flame arresters Molecular seals
Purge gas	Fuel gas Nitrogen
Hazards	Blockage Explosion Heat radiation Toxic gases Liquid carryover
Air hazard	Sources Effects
Water hazard	Sources Effects
Extreme cold	High melting point hydrocarbons Steam injection
Other problems	Ignition failure Smoke Pollution Glare Noise Land sterilization
Legislation	Pollution contorl Smoke Noise
Standards, codes	Plant layout codes BS CP 3013: 1974 API RP 520 API RP 521 1969
Knockout drum design	
Flare stack design	Diameter Height
Flare tip design	Steam Low pressure air Coanda flares
Design models	Flame dimensions Heat radiation Buoyant plume (ground level concentrations)
Evaluation criteria	Heat radiation levels Smoke levels Noise levels
Economics	Relief header costs Flare stack costs Other equipment costs Purge gas costs Land sterilization
Optimization	Capital vs operating costs Land sterilization Controlled blowdown Purge gas costs
Project control	Long lead items
Materials of construction	Corrosion Brittle fracture
Mechanical construction	Welded joints Header valves Insulation, steam tracing
Explosion prevention	Inert gas flow Inert gas conservation, molecular seals Oxygen monitoring Flashback prevention, flame arresters
Process control	Controlled blowdown Manual vs automatic control of flare quality
Start-up	Initial purge with inert gas High gas flows
Shut-down	Air diffusion
Turn-down	Low gas flows High gas flows
Emergency conditions	
Plant operation	Operating instructions Emergency action (to reduce flows)
Plant maintenance	
Plant extensions	
Plant modifications	

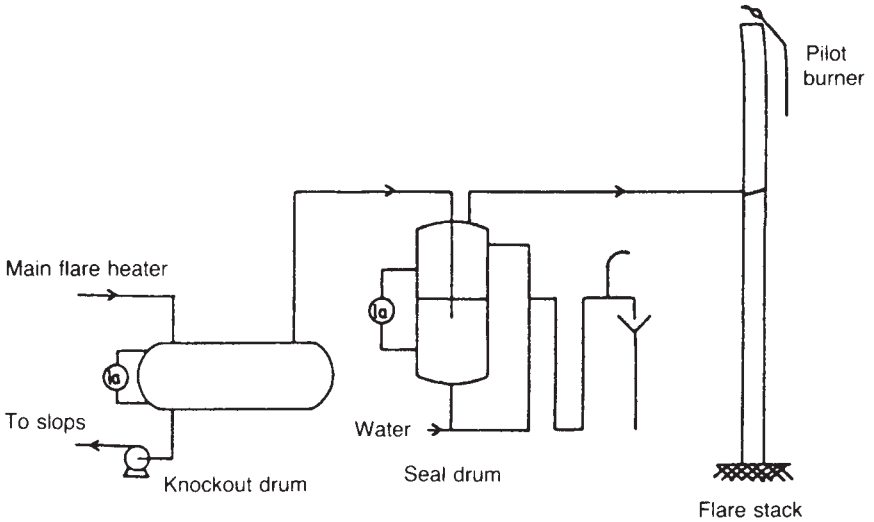


Figure 30.11 *A typical basic flare system (Bunn and Lees, 1988) (Courtesy of the Institution of Chemical Engineers)*

diameter and height, flare tip dimensions, purge gas flow and flare tip steam flow. As Table 30.10 indicates, there are many further aspects that must also be taken into account.

Nevertheless, in the case of a flare system the basic structure of the design appears relatively straightforward. The design can apparently be decomposed into a set of subdesigns that have only weak interaction. The design may proceed in a series of sequential stages, using rules appropriate to each stage, and with only a modest degree of iteration.

Bunn and Lees list a number of rules obtained from the literature, from standards and codes and from expert sources, which are used in flare system design. They classify these rules as follows:

Alternative (A)	An alternative option is offered.
Requirement (R)	A requirement to take a particular course of action, add a particular feature or achieve a particular result.
Permission (Pe)	A permission to take a particular course of action or add or omit a particular feature.
Prohibition (Pr)	A prohibition on taking a particular course of action or adding a particular feature.
Design (D)	A rule of thumb giving guidance on some particular aspect, usually a design criterion.

A prohibition is essentially a negative requirement.

The derivation and use of the rules revealed several problems, which were not unexpected. One is that the abstraction of rules from the literature is liable to give rules that are contradictory or out of date. Another is that some rules are stronger than others and a means needs to be found to incorporate this factor. Similarly, some rules are subject to exceptions and this also needs to be taken into account.

The authors identify the following types of expertise as being involved in flare system design:

(1) knowledge of the initial data to be collected;
(2) knowledge of the ways in which the primitive problem may be reformulated;
(3) knowledge of the alternatives to the use of a flare system and of criteria for their selection;
(4) knowledge of options for modification of the flare load to be accepted;
(5) knowledge of the basic configurations of flare systems;
(6) knowledge of the options for additional features and criteria for their selection;
(7) knowledge of the models available for the design of particular features and of the regimes in which they apply;
(8) knowledge of the constraints associated with regulatory controls, standards and codes, and so on.

The authors refer to the creation of a simple research expert system for elementary flare system design incorporating a rule-based production system. The program described uses forward-chaining and the principal conflict resolution methods are context limitation and specificity ordering.

Although the flare design problem is classed by the authors as one with shallow structure, this emphatically does not mean that it is straightforward. The classification refers solely to the structure of the problem and the decomposition required to solve it. In fact, the design rules used by an expert may well be very sophisticated. The point is that the expertise resides in these other rules rather than in rules, or strategies, for decomposition subdesigns which have only weak interaction. The design may proceed in a series of sequential stages, using rules appropriate to each stage, and with only a modest degree of iteration.

30.33.5 Designs with deeper structure: pressure relief system

Bunn and Lees' third problem is the design of a pressure relief system. This problem they take as representative of a class of design synthesis problems with relatively deep structure.

The situations that are considered for pressure relief are operational relief, both normal and abnormal, and fire relief. A relief survey is made based on the piping and instrument diagram. The system is decomposed into subsystems. The decomposition is done on the basis of what is manageable. Typically a subsystem is a functional unit, such as a distillation unit, with up to half a dozen vessels. Another principle which is used is that of pressure breaks, the section of plant between two such breaks being for practical purposes at a uniform pressure level.

A review is made for operational relief of the overpressure sources and load to be relieved. This covers: utility failures, where use is made of standard cases; open inlets and closed outlets; heat inputs; cooling loss; operating excursions; and equipment failures. For fire, a finer subdivision may be used, with a separate consideration of each vessel. Again use is made of standard cases.

Selection is made of the relief sinks, which may be another part of the plant, the atmosphere, the relief header, or another closed system. The capacities and set pressures of the pressure relief valves may then be determined and the pressure relief valves selected.

The foregoing is the barest outline of the design process for pressure relief. It is summarized in Table 30.11.

Table 30.11 *Design of pressure relief systems: outline strategy of system design (Bunn and Lees, 1988) (Courtesy of the Institution of Chemical Engineers)*

Decompose pressure system
Select subsystems
(Default assumption: each main vessel is a subsystem)
Identify pressure breaks
Locate pressure reliefs
(Default assumption: pressure relief is located on each main vessel)
Identify relief loads on each main vessel
Utility failure (including control loop failures)
Open inlet (connection to high pressure source)
Closed outlet (disconnection to low pressure sink)
Heat input
Cooling loss
Operating excursions
Equipment failures (especially valves: NRVs, EIVs)
Fire
Quantify relief loads on each main vessel
Utility failure standard cases
Fire standard cases
Select relief sink
Other part of plant
Flare header
Other closed system
Atmosphere
Determine set pressure of RVs
Determine capacity of RVs
Select type of RVs

EFV, emergency isolation valve; NRV, non-return valve; RV, return valve.

Some of the topics that may be considered in the review of overpressure sources and loads are listed in Table 30.12. Some of the additional topics that also need consideration are listed in Table 30.13.

The design of pressure relief systems appears therefore to involve appreciable expertise in the selection of a design strategy. There is, in principle, a significant initial decomposition to be performed. Knowledge is required of the range of overpressure sources that need to be reviewed. Some of these are effectively stereotype situations. A credible worst case has to be selected. In making this selection, both for utility failure and for fire, use is made of standard cases to prevent the design worst case being too pessimistic. There is a whole range of design alternatives to be considered and of special situations to be taken into account.

A common strategy for handling problems with deeper structure is to apply a small number of additional rules that simplify the decomposition. In the case of pressure relief system design one such rule is to provide each vessel with a pressure relief valve.

30.33.6 Designs with deeper structure: valve sequencing

The final problem in design synthesis considered by Bunn and Lees is that of valve sequencing. This problem is taken as being representative of a class of design synthesis problems that are characterized by the features that there is a complex problem-solving task, but that this task requires little expertise or common sense knowledge.

The generation of an operating sequence for a set of valves, subject to certain constraints, is very similar to the problem-solving and game-playing tasks commonly addressed in AI. It involves a search to satisfy goals. The knowledge that has to be provided to obtain a solution is, however, relatively limited.

These features imply another characteristic of this type of problem. There tends not to be a recognized expertise. There is provided as part of the design a network of valves that need to be opened and shut in order to operate the plant. An engineer is assigned the task of specifying the operating sequence, but this assignment is unlikely to be made on the basis of a recognized expertise comparable with, say, expertise in flare system design.

Bunn and Lees instance here the work of Rudd and co-workers on the synthesis and analysis of valve sequences. This study is described in Section 30.43 along with other work on the synthesis of operating sequences. This example completes the overview of some characteristic design synthesis problems. The remainder of this section describes some of the design aids that have been developed.

30.33.7 AI applications

Turning now from the structure of plant design synthesis problems to applications of AI to such synthesis, an account of AI applications that deals particularly with plant synthesis and analysis as well as process synthesis is given by Mutton, Ponton and Waters (1990).

At present most such applications appear to be in the area of expert systems. Some of these are considered in Section 30.35. However, the current consensus appears to be that the most promising methods are those that are based on process modelling of the sort described in Section 30.30.

30.33.8 Incremental design and safety constraints

A development of some interest is the concept of incremental design as applied to safety. In conventional plant

Table 30.12 *Design of pressure relief systems: some aspects of overpressure sources and loads (Bunn and Lees, 1988) (Courtesy of the Institution of Chemical Engineers)*

Overpressure sources	*API RP 521 (page no.)*
1. Extraneous components:	
Water in hot oil	9
Light hydrocarbon in hot oil	9
Light components in distillation fluids	7
2. Chemical reactions:	
Combustion	11
Reaction runaway	12
3. High pressure (HP) source:	
HP process fluids	4
HP utilities	4
Pressure raisers	
Pumps	
Compressors	
Heat exchanger HP side	5.15
4. System isolation:	
Systems with closed outlet	4, 7
Shut-in systems (see thermal expansion below)	
5. Heat input:	
Burners	
Steam	5
Heat transfer fluid	
Atmosphere	
6. Cooling loss:	
Water cooling	
Cooling water failure	8
Flooding	8
Inerts accumulation	8
Air cooling	
Fan failure	8
Louvres failure	8
Heat transfer fluid	
Reflux cooling	
Reflux pump failure	8
Subcooled feed	
7. Thermal expansion (shut-in systems):	
Fluid at ambient temperature	12
Fluid below ambient temperature	12
Fluid below temperature of another process fluid	12
8. Pressure transients:	
Water hammer (incompressible fluid)	6
Steam hammer	6
9. Fire	6, 13
Relief loads	
Single failure principle	
Control loop effects	
Capacity credit	
Utility failure standard cases	
Fire standard cases	

Table 30.13 *Design of pressure relief systems: some additional topics to be considered (Bunn and Lees, 1988) (Courtesy of the Institution of Chemical Engineers)*

A list of areas of expertise, by no means complete, is:
Legal and standards requirements
Alternatives to or mitigation of PR:
  Pressure containment
  Pressure limiting instrumentation
Mitigation of fire PR:
  Fireproofing
  Water drench
  Ground slope
Pressure limiting instrumentation:
  Alternative to PR
  Mitigation of PR
    Reduction of flow
    Reduction of frequency
  Standard applications
Economics of alternative solutions
Overpressure scenarios:
  Utility failure standard cases
  Fire standard cases
Unit operations and equipment:
  Furnaces
  Distillation columns
  Shell and tube heat exchangers
  Air cooled heat exchangers
  Centrifugal pumps
  Pressure storage
  Steam systems
  Pipelines
Selection of disposal systems:
  Other parts of plant
  Flare system
  Other closed system (e.g. absorber)
  Atmosphere
Atmosphere disposal:
  Disposal criteria
  Safe disposal
    PRV design and location
Flare disposal:
  Segregation of materials
  Materials of construction
Minimum venting pressure:
  Flare header
  Atmosphere
Depressurizing arrangements
Special conditions:
  Corrosive fluids
  Cold fluids
  Fluids containing hydrogen sulfide
Stepped relief settings
Selection of PRVs
Thermal relief
Hammerblow prevention
Vacuum relief

PR, pressure relief; PRV, pressure relief valve.

design, the designers proceed with the design, adhering to good design practice, and the design is subjected to safety reviews at prescribed stages. An alternative approach, which emphasizes the application of the safety constraints in an incremental way, has been championed by Ponton

and co-workers. The application of this philosophy has been described in respect of the safety constraints on design by Waters, Chung and Ponton (1989) and Waters and Ponton (1992) and in respect of hazard studies by Black and Ponton (1992).

30.33.9 DSPL

Another development is the application of methods developed for equipment design to the design of process plant. An account was given in Section 30.27 of the expert system building tool DSPL. This has been used mainly for mechanical design, but in the process field DSPL has been used by Myers, Davis and Herman (1988) to create an expert system for the design of sieve plate distillation columns.

30.34 Plant Design: Analysis

The synthesis of plant designs is complemented by their analysis. The analysis constitutes the test element in the overall generate-and-test activity. There now exist a large number of computer programs for the analysis of various aspects of plant design. One category is those programs that compute an index and perform a ranking of the hazards of the plant. Another category is those which assist with hazard assessment. Computer aids of this sort have been described in Chapter 29. There are now beginning to appear aids for design analysis that have an AI flavour.

30.34.1 Inherently safer design

Although aids for the synthesis of inherently safer design are not well developed, some work has been done in analysing of plant designs to check the extent to which they conform to this principle. A program of this nature has been developed by Journet (1993). The process is treated as an object or frame and the features of the process and the plant are developed as a hierarchy. Early branches in the hierarchy are the chemical route, the design information, the process streams, the plant units, the nomenclature and the decisions. The treatment is informed by the concepts of elimination, substitution, intensification and attenuation. The program identifies the features with implications for an inherently safer design.

30.34.2 Fault propagation

A number of aids to plant analysis have been described which are based on the qualitative modelling of the propagation of faults through the plant. Fault propagation modelling is therefore a basic enabling technology. It is described in Section 30.36.

30.34.3 Hazard identification

One aspect of plant analysis that has attracted much interest is the creation of an aid to hazard identification that would produce information similar to that yielded by a hazop study. Developments in this area are described in Sections 30.37–30.39.

30.34.4 Fault tree analysis

Another aspect of plant analysis that has attracted a number of workers is the development of an aid for the synthesis of fault trees. Programs have been available for some years for the analysis of fault trees, but the construction of the fault tree is still done manually. Developments in this area are described in Sections 30.41 and 30.42.

30.35 Expert Systems: Some Process Systems

Expert systems were introduced in the process industries in the mid-1980s and are in widespread use. The typical expert system in the process industries is much more modest than the classic expert systems described in the previous section. Most have been created using shells. An appreciable proportion have been developed by a single engineer acting as the expert. The development time has generally been of the order of months rather than years.

Some principal applications are: (1) physical, chemical and thermodynamic properties; (2) selection of equipment, materials of construction, and processes and plants; (3) design of processes and plants; (4) process control; (5) process monitoring and (6) fault administration. The first four of these are considered in this section and the last two in Sections 30.44 and 30.45.

The bulk of these applications is to the handling of fault conditions, either on an individual item of equipment or on a process plant. Before considering these different application areas, it is of interest to consider a statistical profile of process industry applications.

30.35.1 Statistical profile

A survey of expert system applications in the process industries has been described by Sangiovanni and Romans (1987).

These authors found about 200 applications in some 30 companies. They classified these applications as (1) selection, (2) design, (3) planning and scheduling, (4) control, (5) situation analysis, (6) diagnosis, (7) prediction, (8) prescription and (9) instruction. They define: situation analysis as monitoring available data and information and inferring the system's state; diagnosis as inferring the cause of a malfunction or deviation; prediction as inferring the likely consequences of an action or set of actions; and prescription as recommending cures for a system malfunction or deviation.

Of these functions, selection accounted for some 15%. Situation analysis accounted for some 8%, diagnosis for 33%, prediction for 10% and prescription for 21%. Thus one-third of the applications were for diagnosis and the group of four functions related to fault administration (situation analysis, diagnosis, prediction and prescription) accounted between them for 66%. Only about 2% of applications were to design.

Of these expert systems, 30% had been developed by engineers, 29% by a team without the vendor, 29% by a team with the vendor and 12% by an internal AI group. The development time was <3 months for 30% 3–12 months for 40% and >12 months for 27%.

Some two-thirds of the systems were in daily use, including cases where the system was used by different people at a number of locations. Some 90% of applications made use of an expert system shell. Over 60% were implemented on a PC. The dominant contributor to software costs was maintenance of the software, at some 67%, compared with design and coding and with testing and debugging, which each accounted for about 13%.

30.35.2 Physical, chemical and thermodynamic properties

An expert system for physical properties has been described by Banares-Alcantara, Westerberg and Rychener (1985). This system, CONPHYDE, uses the framework of PROSPECTOR and is described as a prototype. It has been

applied to the selection of vapour–liquid equilibrium properties.

Gani (1989) has described an expert system for the selection of models of physical properties and phase equilibria.

30.35.3 Selection of equipment

An application of expert systems that has found rapid acceptance in the process industries is equipment selection. Many such applications utilize an induction tool that is provided by an expert with a learning set of examples, and induces the rules that the expert has evidently used in the solutions. This type of tool allows the expert to create his own system, and many experts have taken advantage of this. Equipment selection applications are not, however, confined to the use of induction tools. In other cases use has been made of shells.

An expert system for control valve selection has been described by Royse (1988). ICI has developed an expert system SYSLAG for the selection of thermal insulation (R.A. King, 1986).

30.35.4 Selection of materials of construction

The selection of materials of construction has been an active area of application. Accounts have been given by Baker-Counsell (1985b), Basden and Mines (1986) and R.A. King (1986).

An expert system for general corrosion has been developed by the National Association of Corrosion Engineers (NACE) and the National Bureau of Standards (NBS). Another such system, Achilles, has been created at Harwell. These systems are outlined by R.A. King (1986).

The Achilles system advises on the selection of mild steel and stainless steel for pipes, vessels and bolt assemblies. It exploits the use of graphics to illustrate the system under consideration and to highlight potential corrosion problems.

Expert systems used at ICI are outlined by Berkovitch and Baker-Counsell (1985). One of these is SCC for stress corrosion cracking. Another is AUSCOR for the selection and corrosion properties of stainless steels.

30.35.5 Selection of process and plant

There are also a number of expert systems for the selection of a process or plant, or an ancillary feature.

Lahdenpera, Korhonen and Nystrom (1989) have described an expert system for the selection of solid–liquid separation equipment. An expert system, DECADE, for catalyst selection has been created by Banares-Alcantara, Westerberg *et al.* (1987) and Banares-Alcantara, Ko *et al.* (1988).

30.35.6 Design of process and plant

Process synthesis and plant design, including high level expert system approaches, are considered in Sections 30.32–30.34. In general, design is a difficult application and there are relatively few examples of expert systems in design, as opposed to selection.

An expert system for the design of heat exchanger networks has been described by B. Chen *et al.* (1989). This is an area of design where a well-structured approach has been developed so that the difficulties of creating an expert system are less severe.

Accounts of an expert system for the design of dust explosion relief systems have been given by Santon *et al.* (1991) and Santon (1992). Another expert system, DUSTEXPERT, for the assessment of dust explosion hazards has been described by von Haefen (1992).

30.35.7 Process control

Most applications of expert systems on process plants involve some form of process monitoring and/or fault administration rather than process control as such.

Work on the development of expert systems for the synthesis of control systems has been described by Birky, McAvoy and Modarres (1988) and Birky and McAvoy (1990).

The LINKMan expert system developed by the Scientific Instrument Research Association (SIRA) and the Blue Circle cement company has been used for control of equipment on the latter's plants. Accounts have been given by M. Henry (1985), Durham (1985f) and Tayler (1987b). Applications have included the control of a ball mill and of a cement kiln. The program uses rules for process control based on natural language and fuzzy logic.

The RESCU project (Shorter, 1985; Coulsey, 1986) involves the use of an expert system for the quality control of an ethoxylate plant in ICI. The system detects control variations and upsets, and recommends actions. One outcome of this project has been the development of the knowledge representation language KRL.

A follow-up to this work is the COGSYS system (Anon., 1988n).

PICON is an expert system with capabilities both in process control and also in fault administration. Accounts have been given by R.L Moore (1985) and F. Kane (1986). Since the first applications have evidently involved fault administration, discussion of PICON is deferred to Section 30.45.

30.35.8 Other applications

Expert systems are in use in the process industries for a variety of other purposes. Reviews of applications and potential applications are given by M. Henry (1985), Coulsey (1986) and Barnwell and Ertl (1987).

The SYNICS system (Coulsey, 1986), which is described as not so much an expert system as a 'working textbook', containing both graphics and mathematics, is used both for problem-solving and browsing. Applications have included powder formulations.

The Honeywell MENTOR expert system (Sangiovanni and Romans, 1987) is used in the field by technicians servicing refrigeration systems.

30.36 Fault Propagation

Many of the methods used to identify and assess hazards at the design stage such as hazard and operability studies, failure modes and effects analysis, fault trees and event trees, involve tracing the paths by which faults propagate through the plant. Fault propagation is thus a common feature of these techniques. Fault propagation is also a feature of methods for the diagnosis of alarms in the real-time computer control of processes.

Fault propagation is therefore a generic feature of work in this field. It follows that the computer aids for many of these methods may, in principle, draw on a methodology that is to some extent common. This concept has been elaborated by Andow, Lees and Murphy (1980).

In the following sections computer aids are described for hazard identification, fault tree synthesis and analysis, and alarm diagnosis. Included in this account are some aids developed by Lees and co-workers which explicitly draw on a common methodology (Andow and Lees, 1975; B.E. Kelly and Lees, 1986a–d; Parmar and Lees, 1987a, b; A. Hunt *et al.* (1993a–e). Some features of the fault propagation methodology used in this work are now described.

30.36.1 Fault propagation

The propagation of a fault through a plant may be represented in terms of the initiation of a fault in a unit that is unhealthy, the passage of the faults through units that are otherwise healthy and the termination of the fault in a unit that is thereby rendered unhealthy. A unit may be modelled using a number of representations. Those considered here are: (1) functional, or propagation, equations; (2) event statements and (3) decision tables.

The propagation equations describe the propagation of faults through a healthy unit, while the event statements describe the initiation of a fault in an unhealthy unit or the termination of a fault in a unit that thus becomes unhealthy.

A propagation equation is a functional equation that describes the relation between an output parameter of a unit and the input and other output parameters. A typical propagation equation is

$$L = f(Q_1, -Q_2) \qquad [30.36.1]$$

which signifies that the level L increases if the inlet flow Q_1 increases or the outlet flow Q_2 decreases, and vice versa.

30.36.2 Fault initiation and termination

The propagation equations describe how a fault propagates but not how it is initiated or terminated. This information is provided by event statements. An initial event statement takes the form

Initial fault: parameter deviation

The initial faults are usually mechanical failures. A terminal event statement takes the form

Parameter deviation: terminal event

The terminal events are usually undesired events or hazards. A typical initial event statement is

F PART-BLK: Q_2 LO [30.36.2]

which signifies that outlet flow Q_2 is low if there is a partial blockage. The letter F denotes a failure event. A typical terminal event statement is

P_2 HI: OVERPRES [30.36.3]

which signifies that if the pressure P_2 is high, there is overpressure of the unit.

The third form is a decision table. A typical decision table is

V Q_2 REV V U_2 HI T U_1 HI [30.36.4]

This relation refers to conditions in reverse flow, U being the temperature in reverse flow and subscripts 1 and 2 denote the inlet and outlet ports under normal flow conditions, respectively. The relation signifies that the outlet temperature U_1 is high if there is reverse flow Q_2 and the inlet temperature U_2 is high. The letters T and V denote the top event of a mini-fault tree and a process variable, respectively.

30.36.3 Flow propagation

In fault propagation modelling it is necessary to have a suitable method of modelling flow propagation. There are several features that need to be allowed for. One is that the representation should model correctly the two-way propagation of a fault. Thus, for example, if a valve is shut, a disturbance travels from it not only downstream but also upstream. The method for flow deviations should be compatible with that used for pressure deviations. A flow model that is based on pressure differences can run into difficulty because in some applications the deviations of pressure are not sufficiently well defined to use differences between them to determine flow. A third requirement in some cases is that the flow propagation should be able to handle a large leak from a component such that continuity of flow through that component is not maintained.

In cases where this latter aspect does not need to be taken into account, flow is often modelled by the simple relation

$$Q_2 = f(Q_1) \qquad [30.36.5]$$

For the case where a large internal leak needs to be allowed for, Kelly and Lees (1986a) have modelled flow propagation using, by convention, the following pair of relations:

$$Q_2 = f(G_1, G_2) \qquad [30.36.6]$$

$$G_1 = f(Q_1, Q_2) \qquad [30.36.7]$$

where G is the pressure gradient, and Q is the flow and subscripts 1 and 2 denote the inlet and outlet ports, respectively. Here the pressure gradient G is essentially a surrogate for flow.

30.36.4 Model representation

Fault propagation models may be represented in various ways, which may well be equivalent.

Lees and co-workers (B.E. Kelly and Lees, 1986c,d; Parmar and Lees, 1987a,b) have represented their models initially in terms of propagation equations, event statements and decision tables. They have utilized a proforma that contains slots for a description of the unit and for these relationships. An example of such a proforma is given in the next section.

Most workers, however, have used the digraph representation. An account of digraphs has been given in Section 30.23.

The two representations, are in principle, equivalent. In digraph terms, the propagation equations yield those nodes in the digraph that represent deviations of the process variables and the initial event statements those nodes that represent failures.

The essential requirements for a model format are that (1) the modelling process be straightforward, so that it can be applied by practising engineers as well as research workers, with as little effort and error as possible, and that (2) it support the automation of model creation using model archetypes.

30.36.5 Model library

Models already created are stored in a model library. An essential feature of such a library is a taxonomy that helps the user to distinguish between different models and to identify those required or, alternatively, to confirm that some are not available in the library. The library needs to be governed by a discipline which ensures that appropriate information is provided about each model, such as the person creating it and the extent of its use, and that an incorrect model is not entered.

30.36.6 Model generation

Generally the user will find that some models are not in the library and need to be generated. In this case it is necessary to configure the models and enter them into the library. Since this is liable to be the main and most difficult input that the user has to provide, it is highly desirable that the process of model generation be kept as simple as possible.

The rules governing the manual generation of models should be formulated explicitly and documented.

In many cases the new model to be created differs only slightly from an existing one. There is therefore scope for the use of model archetypes and templates and for core models or model sections. This applies particularly to vessels. It is often the case that the model library already contains the models required for common items such as pipes, fittings, pumps, etc., and for instrumentation, but that there are certain vessels that need to be modelled. There is therefore scope for the provision of vessel archetypes and templates. Of particular significance here are ports on vessels and other units. Although there are a considerable number of different types of port, a given type tends to recur. It is useful therefore provide a taxonomy of ports and a guide to their selection.

Core model elements may be provided for common types of unit such as heat exchangers and reactors.

30.36.7 Ambiguities and loops

Fault propagation deals with the deviations of process parameters but the degree of deviation is not fully defined. In consequence, ambiguities arise. A particular disturbance may apparently give rise to a number of possible alternative responses or interpretations. The problems caused by ambiguities have been discussed by Waters and Ponton (1989).

These ambiguities may arise when faults are being propagated forward from an event, as in an event tree, or backward from an event, as in a fault tree. In either case rules are required for the resolution of the ambiguities. Unresolved parameters also occur due to the presence of loops and recycles. Some of the options for resolution are discussed by Waters and Ponton.

One approach to such resolution is to introduce additional constraints. Work on these lines for digraphs has been described by P. Rose and Kramer (1991), and developed further by Fanti, Chung and Rushton (1993). The digraph representing a process flow structure usually contains loops, there is more than one path that can be traced between nodes and, since the paths may have opposing influences, ambiguities arise. The approach taken by Fanti, Chung and Rushton is the use of high level constraints such as a mass balance. They illustrate their method using the recycle tank system of P. Rose and Kramer shown in Figure 30.12, which also gives the corresponding digraph. Their results for this problem are shown in Table 30.14. Section A of the table shows the possible responses of the variables flow F1–F4, level L1–L2 and pressure P3 to changes in valve resistance R3 and R4. Five interpretations are identified. Section B of the table shows the resolution of these ambiguities using high level constraints.

Another approach is the use of heuristics. An example is furnished by the work of A. Hunt *et al.* (1993e) on fault tree synthesis. A configuration that is liable to give rise to such inconsistencies is a unit with more than two ports. Inconsistencies arise from looping around the unit. In this case use is made of the rule that in the development of the tree at a particular unit only one change of port is allowed.

Although ambiguities and loops undoubtedly present problems and merit further work, they do not appear to have proved a serious hindrance to the development of fault propagation tools for tasks such as hazard identification or fault tree synthesis.

30.36.8 Structure identification

Another problem that arises in modelling for fault propagation is that of identifying structural features in the flow diagram. The structural feature in question may be: a recycle flow; a control loop and the streams affected by its action; a trip loop and the streams affected by its action, whether it be a loop with an open or a closed trip valve; or a divider–header combination, where the divider and the header may be separated by a number of intermediate units, and where there may be a number of dividers and headers nested or staggered.

Some types of structural information are readily provided by the user, and in this case this may be the appropriate course. In other cases it is not easy for the user to identify the structure, but it is feasible to devise an algorithm to identify it, in which case this may be the best approach.

In any event, the identification of structure is a generic problem. Approaches to the problem have been described in a number of different areas for example heat exchanger networks (Pethe, Singh and Knopf, 1989); and fault tree synthesis (A. Hunt *et al.,* 1993a-e).

30.36.9 Alternative representations

As already indicated, fault propagation relations may be represented in a number of different ways. To some extent at least it is possible to map between them. An account of alternative representations and of mapping has been given by Aldersey, Lees and Rushton (1991).

Some forms of representation available include (1) functional equations, (2) program rules, (3) digraphs, (4) block diagrams, (5) logical expressions, (6) truth tables, (7) cut sets, (8) fault trees and (9) event trees.

Figure 30.13 shows a heat exchanger system together with representations of the system in the nine forms just listed. The heat exchanger is a cooler in which a hot process fluid is cooled by cooling water. The cooling water is itself cooled by a chiller prior to entering the main cooler.

Of the three graphical forms, the digraph contains the most information. For a particular event, a fault tree or an event tree may be obtained from the digraph, but with loss of information.

A common method of constructing a fault tree is to start with a digraph and to obtain the required fault tree from it. Accounts of this approach have been given by Lapp and Powers (1977a,b), Lambert (1979) and Andrews and Morgan (1986).

Mapping between fault trees and event trees, and vice versa, has been described by Aldersey, Lees and Rushton (1991).

There are now a considerable number of mathematical models of process plant and it may be desired to derive a qualitative model from an existing quantitative model.

A method of doing this was developed by Andow (1973) in his work on modelling for alarm diagnosis. Consider the relationship

$$\underset{6}{A} + \underset{5}{B} * ((\underset{2}{C} + \underset{1}{D}/\underset{3}{E}) - \underset{4}{F}) \uparrow \underset{}{G} \qquad [30.36.8]$$

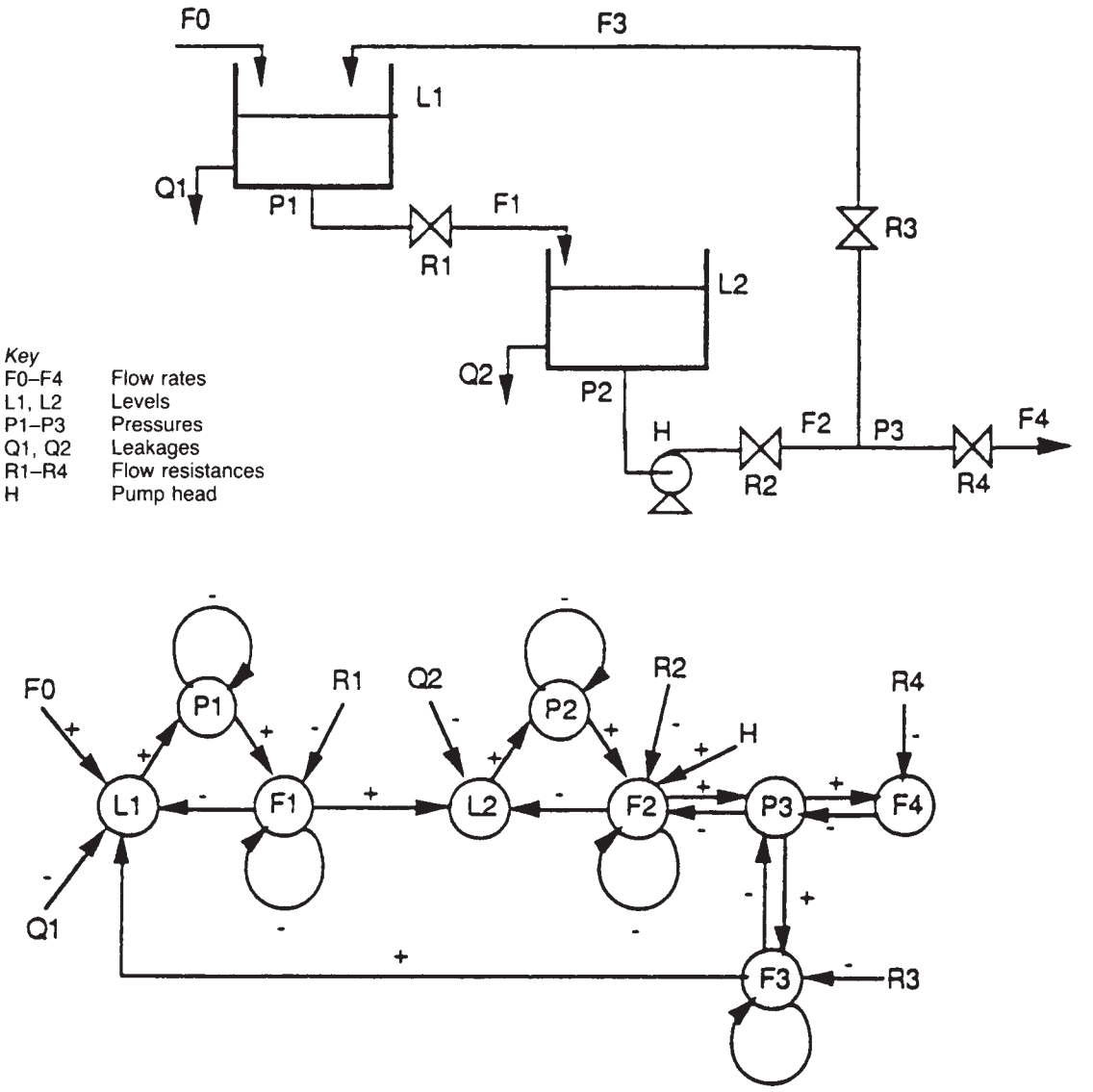


Figure 30.12 *A recycle tank system (Fanti, Chung and Rushton, 1993: after P. Rose and Kramer, 1991) (Courtesy of the Institution of Chemical Engineers)*

where RHS represents the right-hand side of an equation and the numbers show the order of evaluation following the normal rules of algebra. It can be seen that evaluation does not occur in the order in which the operators are discovered. Converted to Reverse Polish Notation, the relation becomes

$$\begin{array}{l} \text{RHS} = \text{A B C D E} / + \text{F} - \text{G} \uparrow * + \\ \qquad\qquad\quad 1\ \ 2\ \ 3\ \ 4\ 5\ 6 \end{array} \qquad [30.36.9]$$

The operators are now in the correct order, whilst the operands remain in their original order.

This use of this technique to reduce quantitative models to qualitative ones is described by Andow, who gives full details of the transformation.

30.36.10 Generic modelling

Fault propagation modelling may be used to support a range of safety-related techniques such as hazard identification, fault tree synthesis, operating procedure synthesis and alarm diagnosis. There is clearly an advantage to be gained by formulating a type of generic model that supports all these methodologies and others. On the other hand, the development of a particular technique should not be unduly constrained by the requirement for commonality. This

Table 30.14 *Response of recycle tank system (after Fanti, Chung and Rushton, 1993) (Courtesy of the Institution of Chemical Engineers)*

A Initial candidate responses

Disturbance	*Responses*							
	L1	*F1*	*L2*	*F2*	*P3*	*F3*	*F4*	
R3 +	−	−	−	−	−	−	−	Candidate R3A
	−	−	−	−	0	−	0	Candidate R3B
	−	−	+	−	+	−	+	Candidate R3C
	−	−	0	−	+	−	+	Candidate R3D
	−	−	−	−	+	−	+	Candidate R3E
R4 +	+	+	+	+	+	+	+	Candidate R4A
	+	+	+	+	+	+	0	Candidate R4B
	+	+	+	+	+	+	−	Candidate R4C

B Responses after resolution

Disturbance	*Responses*							
	L1	*F1*	*L2*	*F2*	*P3*	*F3*	*F4*	
R3 +	−	−	−	−	0	−	0	Candidate R3B
R4 +	+	+	+	+	+	+	0	Candidate R4B

The supporting argument is as follows. Disturbances R3 + and R4 + each leave F0 unchanged, F0 = 0. Overall mass balance requires F4 = F0. Hence candidate responses R3A, R3C, R3D and R3E and responses R4A and R4C are eliminated.

is illustrated in the work of Lees, Rushton, Chung and co-workers. The models used in early development of particular techniques differed slightly, but a considerable commonality was retained which is built on in the later work.

30.36.11 QUEEN

A code QUEEN, designed to provide a front-end for fault propagation modelling in activities such as hazard identification, fault tree synthesis, operating procedure synthesis and alarm diagnosis has been described by Chung (1993).

30.37 Hazard Identification

In addition to computer aiding of process synthesis and plant design in general, there are a number of types of aid that specifically address hazard and safety issues.

Qualitative modelling, and particularly fault propagation modelling, is an important feature in many of these aids.

The first form of computer aid considered here is aids for the identification of hazards. A number of workers have described systems which perform functions broadly similar to those carried out in a hazard and operability, or hazop, study or which serve as an aid in the conduct of a study of this general type. Systems include: HAZID by Parmar and Lees (1987a,b); a system described by Weatherffl and Cameron (1988, 1989); HAZOPEX by Heino, Suokas and Karvonen (1989a,b) and Suokas, Heino and Karvonen (1990); HAZEXPERT by Goring and Schecker (1992); and COMHAZOP by Rootsaert and Harrington (1992).

The applicability of AI techniques in this area is discussed by Ferguson and Andow (1986). The identification of hazards is in many ways one of the least promising fields for computer methods. It is very difficult to devise a technique that can compete with man's ability to think laterally and to make apparently obscure connections. with those from a conventional hazop study. They also give an account of an application session.

HAZOPEX has been developed using a LISP machine and an expert system shell.

30.37.1 COMHAZOP

The COMHAZOP system is described by Rootsaert and Harrington (1992). The plant configuration is entered and unit models are assigned to the units. The program examines deviations associated with the units and uses rules to identify the causes of these deviations.

30.37.2 HAZEXPERT

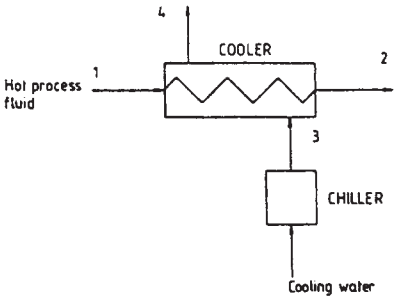
Goring and Schecker (1992) describe the hazard identification system HAZEXPERT. This aid eschews a HAZOP-style approach. The plant configuration is entered. A set of pre-defined consequences such as overpressure, explosion, etc., is used. A search, limited in scope around the set of units under examination, is conducted to discover the causes of these events. The program contains a generic hazard knowledge base in which a key concept is disturbance of the mass or energy balance. HAZEXPERT is implemented using an expert system shell.

30.37.3 PSAIS

PSAIS (Plant Safety AI System) is described by Schöneburg (1992). The program utilizes only a limited number of rules but holds a large collection of design cases. Examination of a plant design is based on accessing 'similar' cases in the design case database. If no similar case is found, a new case is created. Use is made of fuzzy matching. In this way PSAIS benefits from a continuous process of learning.

30.37.4 HAZExpert

The HAZExpert system is described by Venkatasubramanian and Vaidhyanathan (1994). The general approach described appears broadly similar to that used in HAZID. The authors identify as distinguishing characteristics



(a)

Functional equations

$Q_2 = f(Q_1)$

$Q_4 = f(Q_3)$

$T_2 = f(Q_1, -Q_3, T_1, T_3)$

$T_4 = f(Q_1, -Q_3, T_1, T_3)$

Event statement

EF: T_2 HI, T_4 HI

(b)

Program rules

for fault propagation

rule (pipe, propagation, [q,2], [q,1], [ ])

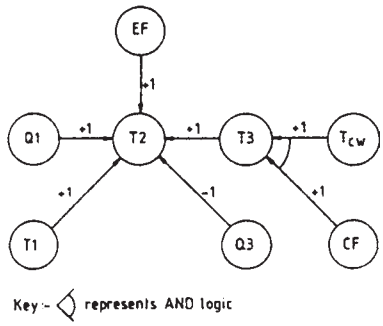
(see first functional equation in (b) above; other rules not given)

for fault initiation

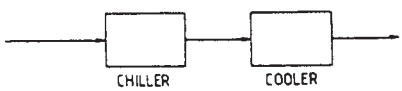
rule (pipe, environment, [['external fire', ' ', ' ']][[t,2,hi]])

(see event statement in (b) above)

(c)



(d)



(e)

Logical expressions

T_2 HI = Q_1 HI + Q_3 LO + T_1 HI + T_3 HI + $\dot{EF}$

T_3 HI = (T_{cw} HI) (CF)

(f)

T2 HI	Q1 HI	Q3 LO	T1 HI	EF	T3 HI
T	T	F	F	F	F
T	F	T	F	F	F
T	F	F	T	F	F
T	F	F	F	T	F
T	F	F	F	F	T

(partial table only, contains only lines where T_2 HI is true)

T3 HI	T_{cw} HI	CF
T	T	T
F	T	F
F	F	T
F	F	F

(full table)

(g)

Figure 30.13 *Some forms of representation of a process system and of faults in such a system (Aldersey, Lees and Rushton, 1991): (a) cooler system; (b) functional equations and event statements (EF, external fire); (c) program rules (in Prolog); (d) diagraph (CF, cooler failure); (e) block diagram for event Q4 LO (LO, low); (f) logical expressions for events T_2 HI and T_3 HI (HI, high); (g) truth tables for these same events (F, false; T, true); (h) minimum cut sets for event T_2 HI; (i) fault tree for event T_2 HI; (j) event tree for event T_{cw} HI (Courtesy of the Institution of Chemical Engineers)*

Minimum Cut Sets

for event T_2 HI

$M_1 = Q_1$ HI

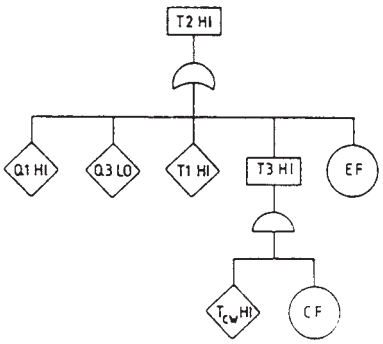
$M_2 = Q_3$ LO

$M_3 = T_1$ HI

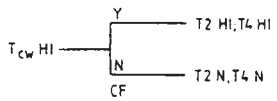
$M_4 = T_{cw}$ HI, *CF*

$M_5 = EF$

(h)



(i)



(j)

Figure 30.13 *continued*

an emphasis on consequences and the resolution of ambiguities. HAZExpert is implemented in G2 by Gensim (1992).

30.38 Hazard Identification: HAZID

A more detailed account is now given of one particular code for hazard identification. This is the HAZID code described by Parmar and Lees (19876a,b). The method follows closely the general approach taken in a hazop study, but draws on generic fault propagation technology developed for fault tree synthesis. An overview is now given of HAZID, which both illustrates an application of fault propagation modelling and serves as an example of a hazard identification code.

30.38.1 Hazard identification strategy

Initially the problem of hazard identification was approached without any preconception as to the structure of the method. Both top-down and bottom-up approaches used in fault trees and event trees, respectively, were considered as possible candidates. Completeness in the identification of hazards is the crucial feature of an effective method. A top-down method must therefore start from a complete list of consequences and a bottom-up method from a complete list of causes. It is difficult to provide lists that ensure completeness in all situations. In a conventional hazop the starting point is the list of process parameters in a pipe and the list of guidewords. This pair of lists yields a closed set of events but generates an open set of causes and consequences. This characteristic of the hazop approach is the desired one and was therefore adopted for the computer aided method also.

30.38.2 System decomposition

The starting point for the method is the piping and instrument diagram. This is then converted to a block diagram. As in a conventional hazop the analysis is carried out on the pipes rather than the vessels. The block diagram contains the vessels and other major items, but most of the elements in it are pipework items such as pumps, hand valves, control loops, etc. For each unit in the block diagram a unit model is specified, drawing on a library of unit models. Additional models may be configured by the user and entered in the library as required.

30.38.3 Unit models

A unit model is a representation of the propagation of input parameter deviations into output parameter deviations and also of the initiation and termination of these deviations. The fault propagation utilizes the methodology described in Section 30.36. The basic representations used are (1) propagation equations and (2) event statements.

For specific applications it may be convenient to transform these basic representations into alternative forms. Thus, in fault tree work they may be converted to a set of mini-fault trees. In HAZID they are converted into a set of rules written in Prolog.

The initial and terminal events are, respectively, the causes and consequences which the hazard identification procedure seeks to discover. The completeness of the identification depends on the quality of the modelling of these events.

The configuration of the unit models is guided by the use of the following checklist for the initial event statements:

(1) function,
(2) hydraulics,
(3) containment,
(4) impurities,
(5) environment.

A process unit has a particular function. For example, it is the function of a gas absorption column to absorb a solute from a gas stream into a liquid stream. Thus one function fault in such a unit is that maldistribution of the liquid causes the outlet gas solute concentration to be high and the outlet liquid solute concentration low. This may be represented by the initial event statement

maldistribution $> x_2$ hi, x_4 lo

where x is the concentration of the solute and subscripts 2 and 4 refer to the outlet gas and outlet liquid streams,

respectively. This is equivalent to the rule that if maldistribution occurs, then x_2 hi and x_4 lo may occur.

A process unit has a hydraulic function in that it should transmit flow, and a containment function, in that it should not leak. It also has functions related to impurities and its environment in that it should not introduce impurities and should not undergo excessive deviations due to environmental changes. Typical initial event statements for various units for these other four functions respectively are:

blockage $> q_1$ none, q_2 none
leak (major) $> qi$ hi, q_2 lo
broken packing $> ia_4$
external cold source $> t_2$ lo

where i is the impurity concentration, q is the flow, t is the temperature and a is the impurity packing debris.

Terminal event statements usually relate to a serious excursion of a process parameter. Some typical terminal event statements are

p_2 hi > overpressure
t_2 lo > undertemperature
t_4 hi > overfilling

where l is the level, p is the pressure and t is the temperature.

Initial and terminal event statements provide the means of entering a fairly comprehensive list of initial and terminal events, and hence causes and consequences.

30.38.4 Fluid and materials models

In addition to the unit models there are models for the process fluids and for the materials of construction. These are used primarily to allow consequences to be made conditional on the existence of a particular process fluid or material of construction susceptibility. For example, low flow may cause blockage, but only if the process fluid contains solids which can deposit out; low temperature may cause brittle fracture, but only if the material of construction is mild steel.

There are special treatments for the common faults leak and blockage, and releases to the environment are consolidated in a special escape model.

30.38.5 Cause and consequence generation

The hazard identifier program receives as input tables giving the configuration of the block diagram and listing the library models to be used for each unit. The program operates on the system line by line. For a given line each parameter deviation is examined in turn and its causes and consequences are generated from the initial and terminal event statements in the unit models.

The link between the causes and consequences listed for a particular parameter deviation is the deviation itself. In general, most of the causes result in most of the consequences and most of the consequences result from most of the causes, but not all. For example, in a pump delivery shut-in is a cause of no flow and results in the consequences pump overheats and loss of level in the downstream vessel, but no changeover to a stand-by pump is a cause of no flow and results in loss of level but not in pump overheating.

With regard to the direction of search for causes and consequences, Figure 30.14 shows two options. In Method 1 the search is from local cause to distant causes, whilst in Method 2 it is from local consequence to distant consequences. HAZID uses Method 1, for two reasons. First, this method involves the evaluation of consequences rather than causes and such an evaluation is considered the prime form of filtering. Second, the method allows the possibility of tracing a consequence linked to a number of causes and is compatible with the search for such causes using a fault tree.

30.38.6 Screening of faults

In the foregoing, attention has been focused on the generation of potential faults. In the absence of some screening mechanism the number of faults generated can be very large. This is a common problem in computer-generated output, but it occurs to a degree in conventional hazop also. Several approaches may be taken. The main distinction is between suppression of the initial generation of the faults and handling of faults after they have been generated.

A particular form of suppression is effected by the fluid and materials of construction models, as already described. In many cases a fault thrown up by the fault propagation modelling has a credible realization only if there is a particular fluid susceptibility, so that where the fluid model contains no such susceptibility, the fault need not be generated. Similar considerations apply to the materials of construction model.

With regard to handling of faults after generation, mention has already been made of the consolidation of similar faults caused by different items in a single line.

The other methods of handling faults involve some form of screening. The simplest approach here is to lay 'masks' over the output. A variety of types of mask may be used for different purposes. A hierarchy of masks may be used which give successively larger amounts of detail. Other specialist masks may be envisaged for particular problem areas.

Another more difficult but worthwhile form of screening is the use of engineering heuristics to evaluate faults. The evaluation may address causes or consequences. Suitable heuristics are of various types, but in each case the purpose is to assist the decision as to whether a fault can be disregarded either because the cause is not credible or the consequence is negligible. Some heuristics relate to the frequency and cost of faults, and require both estimated values and cut-off levels. Other heuristics are based on engineering practices. For example, there are usually company practices that determine whether in a given case a liquid relief valve is provided on a section of pipe which is shut in.

30.38.7 Fault consolidation

For the lines connecting the vessels and other major equipment, use is made of a special pipe model. Faults in the line due to minor units such as pumps, hand valves and control loops are collected up and consolidated so as to avoid excessive proliferation of faults. In this way a fault such as a blockage is flagged in the line only once, but all the causes of the fault are identified.

30.38.8 Model generation and model library

The configuration of a unit model is carried out using a model generation program. The data are entered on a proforma. A typical proforma is shown in Figure 30.15. Items 1–6 are entered by the user and the remaining items are generated by the program. The rules in items 7–9 are in Prolog, as described below.

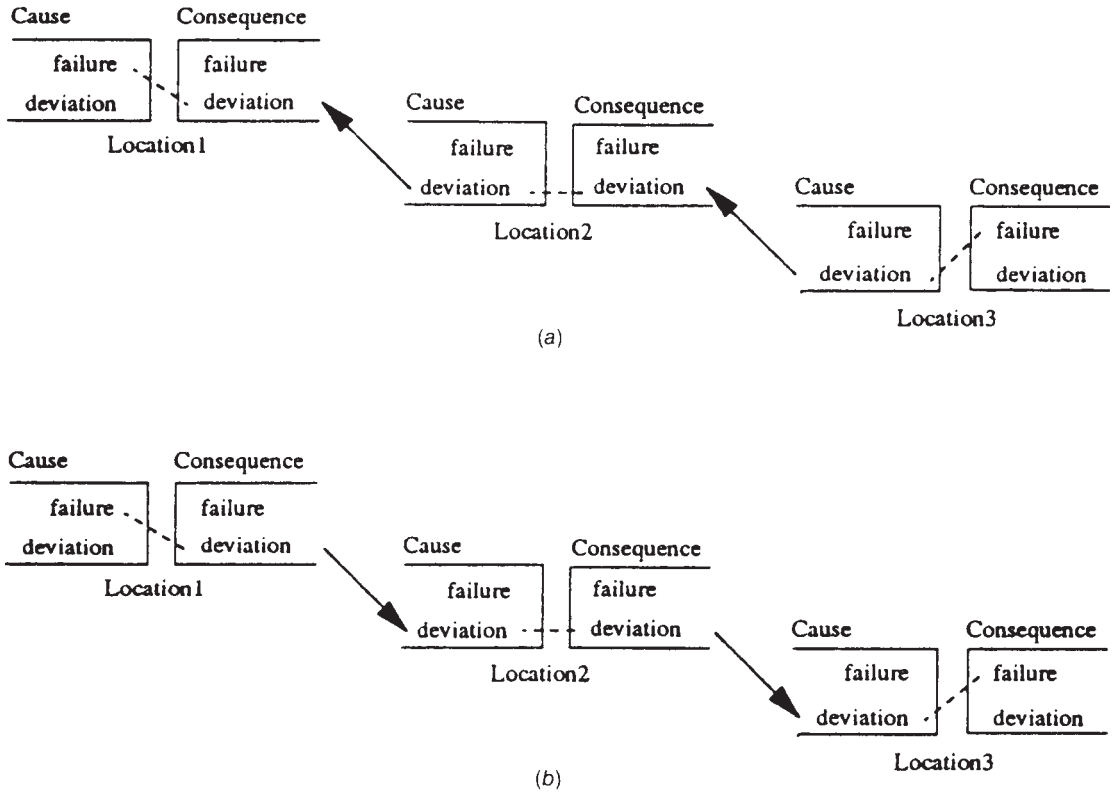


Figure 30.14 *HAZID: generation of causes and consequences (Zerkani and Rushton, 1992): (a) search for causes; (b) search for consequences (Courtesy of Pergamon Press)*

Models are held in a model library. In some applications the user may find all the models required already in the library. Where this is not so, he or she configures the missing models using the model generation program.

There are certain relationships between models that may be exploited to achieve a degree of automatic model generation. One is the hierarchical structure of models. Thus, a pump is a subclass of the class of pressure raisers and inherits certain characteristics. Even where there is no formal hierarchy, a group of models may be related by some shared process or feature. In such cases use may be made of model archetypes, or partial models.

Much modelling centres around ports at the inlet and outlet of vessels and other equipment. A taxonomy of standard ports permits the selection of appropriate sets of equations, or models, for such ports.

30.38.9 Computer codes

The main programs in the HAZID package are: MASTER, which does the housekeeping; CONFIGURATOR, which handles the configuration; IDENTIFIER, which is the core program and generates the cause and consequence lists for the parameter deviations; CONSOLIDATOR, which turns these lists into a table similar in form to that produced by a conventional hazop; and MODGEN, which generates the unit models. There is a unit model library. The task of IDENTIFIER is to handle rules and the program is written in Prolog. The other programs are written in Fortran.

30.38.10 Illustrative example: water separator

An illustrative example of the use of HAZID has been given by Parmar and Lees (1987b). The plant examined is the feed section of the alkene dimerization plant described by Lawley and shown in Figure 8.25. The corresponding block diagram for this plant is shown in Figure 30.16. Table 30.15 gives part of the hazard identification table generated for this example together with extracts from the original table of Lawley, which was given in Table 8.29.

30.39 Hazard Identification: Enhancements

The published work on computer-based aids for hazard identification suggests that there is still much to be done to devise an aid which is useful in identifying hazards prior to conventional hazop, let alone one which might do more than this.

The current state of the art may be summarized by saying that, in general, aids are more successful in identifying causes than consequences, the range of which tends to be rather limited, and both are lacking in richness and are thus rather stereotyped. The overheads for the input of data tend to be too high. The output tends to be lacking in discrimination, and thus excessive.

An aid such as HAZID is built largely around fault propagation, which utilizes models based on engineering principles and which is stronger on the identification than on the evaluation of faults. Fault generation needs to be enhanced

1. Model number, name
   13 pipe
   1 2
2. Engineering description and assumptions
   Engineering description
   N/A
   Engineering assumptions
   N/A
3. Propagation equations
   $p_2 = f(p_1)$
   $q_2 = f(q_1)$
   $t_2 = f(t_1)$
   $x_2 = f(x_1)$
4. Supplementary information
   Normal state: N/A
   No multicomponent features
   Failure modes: 1
5. Initial event statements
   blockage > q_2 lo, q_2 none, p_1 hi
   leak > escape
   leak (rupture) > q, hi, q_2 lo, q_2 none, p_2 lo
   external cold source, cold weather, lagging loss > t_2 lo
   external heat source, lagging loss, fire > t_2 hi
   external heat source with blocked-in pipe > p_2 hi
6. Terminal events
   p_2 hi > leak (rupture)
   t_2 lo > leak (rupture)
7. Rules for fault propagation
   rule (pipe, propagation, [p, 2], [[p, 1]], [ ])
   rule (pipe, propagation, [q, 2], [[q, 1]], [ ])
   rule (pipe, propagation, [t, 2], [[t, 1]], [ ])
   rule (pipe, propagation, [x, 2], [[x, 1]], [ ])
8. Rules for fault initiation
   rule (pipe, hydraulic, [['blockage', ' ', ' ']], [[q, 2, lo], [q, 2, none], [p, 1, hi]])
   rule (pipe, containment, [['leak', ' ', ' ']], [['escape', ' ', ' ']])
   rule (pipe, containment, [['leak (rupture)', ' ', ' ']], [[q, 1, hi], [q, 2, lo], [q, 2, none], [p, 2, lo], ['escape ' ', ' ']])
   rule (pipe, environment, [['cold weather', ' ', ' '], ['lagging loss', ' ', ' ']], [[t, 2, lo]])
   rule (pipe, environment, [['hot weather', ' ', ' '], ['lagging loss', ' ', ' '], ['fire', ' ', ' ']][[t, 2, hi]])
   rule (pipe, environment, [['external heat source with blocked-in pipe', ' ', ' ']], [[p, 2, hi]])
9. Rules for fault termination
   rule (pipe, effect, [[p, 2, hi]], [['leak (rupture)', ' ', ' ']])
   rule (pipe, effect, [[t, 2, lo]], [['leak (rupture)', ' ', ' ']])
10. Model status:
    Written: JCParmar June 1986
    Checked: FPLees June 1986
    Usage: 3 Configurations

Figure 30.15 *HAZID: proforma for configuration of a unit model (Parmar and Lees, 1987b) (Courtesy of Elsevier Science Publishers)*

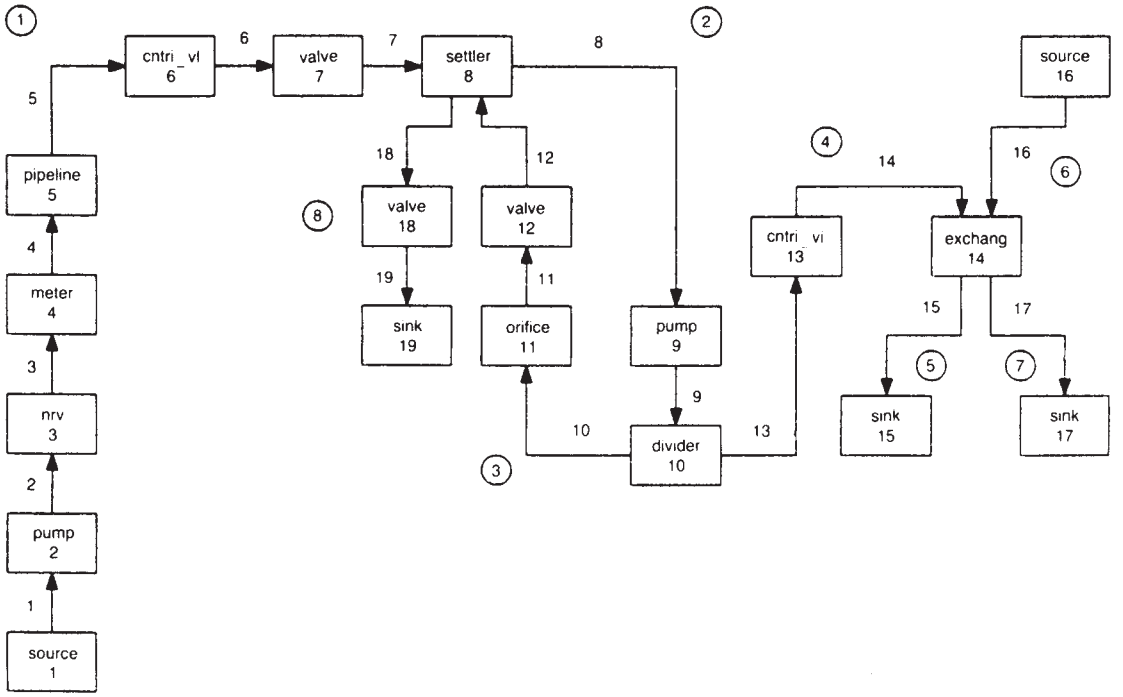


Figure 30.16 *HAZID: illustrative example: block diagram for alkenes dimerization plant (Parmar and Lees, 1987b) (Courtesy of Elsevier Science Publishers)*

by grafting onto this basic mechanism domain expertise. Thus, for example, a heat exchanger may have expertise bearing on tube vibration under abnormal flow conditions, blockage under no flow conditions, pinhole leaks between tubes and the shell, the overpressure hazard following tube burst, the need for space to remove the tube bundle, and so on. Perhaps even more important is the need to strengthen fault evaluation. There are various methods of doing this but most may be broadly classed as forms of expertise.

Features in which enhancement of current methods is likely to be of value include the following: (1) design screening, (2) information acquisition, (3) generation of faults, (4) evaluation of faults and (5) presentation of output.

30.39.1 Design advice and screening tools

The point has already been made that if the designs coming forward incorporate defects which are relatively elementary and numerous, a hazop-style aid may not be the most efficient way of correcting the situation. There may be scope for assisting the designer by providing a design advisor tool. Such a tool is essentially an aid to design synthesis. Likewise, it may be appropriate to provide a design screening tool to filter out certain common and readily identifiable defects. In contrast to the design advice tool, this is a tool for design analysis. A design screening tool is likely to rely largely on an examination of the configuration of the units and of the plant as a whole. Configuration screening is discussed further below. Suffice it to say that it needs to be catered for somehow and that, if it is not performed by a separate aid, it is necessary to incorporate it in the main hazard identification aid.

30.39.2 System discipline

It can be envisioned that over time aids such as those for representing design issues described earlier and the hazard identification aids described here could exert a significant influence on the design process. Such aids tend to require adherence to a more formal discipline involving a more explicit declaration of issues, arguments and intent. This is not only a condition for the effective integration and exploitation of these aids but also a desirable development in the design process itself.

Permitted terminology

One aspect of this is the discipline to be adhered to in the terminology used. It is good practice to use lists of the permitted terminology for units, faults, process variables, deviations and so on.

As a simple example, confusion can be caused if the state of a valve is described on some occasions as 'closed' and on others as 'shut'. More fundamentally, the discipline is of value with respect to generic and specific faults and to the inheritance of faults. Thus, for example, use might be made of the generic faults 'block', indicating complete blockage, and 'outflow', indicating major leak. Realizations of the generic fault block in a line might be the specific faults blockage, closure of valve, freezing of fluid or polymerization of fluid.

30.39.3 Fault generation and evaluation

As already stated, a hazard identification aid is required both to generate faults and to evaluate them. Fault generation is primarily by means of fault propagation models, fluid and materials of construction models, and expert

Table 30.15 *HAZID: illustrative example; hazard identification table generated for alkene dimerization plant (Parmar and Lees, 1987b) (Courtesy of Elsevier Science Publishers)*

Process deviation	*Original hazop causes*	*Computer-aided hazard identification causes*	*Original hazop consequences*	*Computer-aided hazard identification consequences*
No flow	No hydrocarbon at intermediate storage J1 pump fails (motor fault, loss of drive, impeller corroded away, etc.) Line blockage, isolation valve closed in error or LCV fails shut Line fracture	Source: q_1 none source empty Pipe: Blockage Leak (major) Pump: Loss of NPSH Rotation fault Impeller fault Cavitation Low b.pt. material gassy materials Delivery shut in No change to stand-by Stand-by fail on demand Maloperation of valves Blockage Leak (major) NRV: Valve stuck closed Pipeline: Blockage Leak (major) Control valve: Loop fails closed Sensor fails closed Controller fails closed Control valve fails closed Set point moved closed Isolation valve closed Valves: Valve moved closed	Loss of feed to reaction section and reduced output. Polymer formed in heat exchanger under no flow conditions J1 pump overheats Hydrocarbon discharged into area adjacent to public highway	Pump: Pump fluid overheats Settler: q_1 none Outflow(s) none l_5 none
More flow	LCV fails to open or LCV bypass open in error	Source: q_1 high Meter: Bypass fails Bypass moved open Control valve: Loop fails open Sensor fails open Controller fails open Control valve fails open Set point moved open Bypass directed open	Settling tank overfills Incomplete separation of water phase in tank, leading to problems in reaction section	Meter: Inaccurate measurement Settler: q_1 high poor settling i_{a-2} high l_5 high Liquid enters vent
Less flow	Leaking flange or valved stub not blanked and leaking	Source: *pi pl* q_1 low Blockage Leak (major) Pump: Loss of NPSH Rotation fault Impeller fault Cavitation Low b. pt. material Gassy material Delivery part shut Blockage	Material loss adjacent to public highway	Meter: Inaccurate measurement Settler: q_1 low Outflow(s) low l_5 low

Table 30.15 *(continued)*

Process deviation	*Original hazop causes*	*Computer-aided hazard identification causes*	*Original hazop consequences*	*Computer-aided hazard identification consequences*
		Leak (major) NRV: Valve fails part closed Pipeline: Blockage Leak (major) Control valve: Loop fails part closed Sensor fails part closed Controller fails part closed Control valve fails part closed Set point moved part closed Isolation valve part closed Blockage Valve: Valve partly closed		

LCV, level control valve; NPSH, net positive suction head; NRV, non-return valve.

rules. The prime means for fault evaluation are the fluid model and expert rules.

30.39.4 Integration of expertise

The generation of faults is done partly by fault propagation, but to achieve a greater richness and completeness it is necessary to introduce in addition various forms of expertise. The following are some of the attachment points, or 'hooks' to which such expert rules may be attached: guidewords; faults; deviations; undesired outcomes; units; lines; configuration of units (including connectivities and elevations); fluids; reactions; impurities and their sources; materials of construction; pressure raisers (pumps, compressors); instrumentation; control computers; protective devices (especially relief valves); small items (drain and sample valves, filters, small bore pipework, etc.); mode of operation (batch, continuous, etc.); operations (usual modes of operation, operating instructions); maintenance; storage; transport; utilities; environmental influences (heat, cold, rain, extreme weather) and environmental impacts (releases).

Expert rules are also a prime means for the evaluation of faults. Once a fault has been generated, any expertise available to the program can be brought to bear to evaluate it. This applies whether the fault generation step has involved fault propagation, the fluid model or fault generation expertise. Often, fault generation and evaluation will be part of the same package of expert rules.

30.39.5 Information requirements

The hazard identification activity requires the availability of a considerable amount of information. The information requirements for conventional hazop have been discussed in Chapter 8.

Minimal requirements for a computer aid are generally (1) the piping and instrument diagram, and information about (2) the main plant units, (3) the fluids and (4) the materials of construction. In addition, however, information may be needed about other aspects such as design intent and operating procedures.

Some comments are now given about some of these types of information.

Fluids

Information is required about the properties of the fluids in the plant. This is discussed in more detail below. Suffice it to say at this point that in large part this is information about fluid properties and susceptibilities. The former should be available in the standard generic fluid properties databases but much of the latter may not.

Materials of construction

Information is also required on the properties of the materials in the plant, essentially on their susceptibilities. Provision of this information is the function of a generic materials of construction database.

Design intent

There is a quite large amount of information on design intent which is not necessarily given in the piping and instrument diagram (P&ID). This category covers a wide range of types of information. One type may be broadly characterized as configurational information. For example, the P&ID may show two pumps piped up in parallel without making it clear whether these are 50 or 100% pumps. Or, again, two pressure relief valves may be shown but with no indication on setting, capacity or stagger. Another category is that which relates to the function of the unit, especially where this involves a dual or subsidiary function or a constraint on function.

Operating procedures

Another important category of information is the operating procedures. Ideally these should be available at the time

where the hazard identification is undertaken, but they may well not be.

Resident hazards

It is commonly the case in a conventional hazop that even before the study is commenced the team already knows that the plant is subject to certain hazards, or other problems. In conducting the examination these 'resident hazards' are uppermost in the mind. It makes sense in devising a computer method to find some way of ensuring that the search covers such resident hazards.

Information representation

For some types of information the form of representation appears straightforward. For fluid-materials incompatibilities, for example, a look-up table is a natural format. Moreover, such information is of the type which should in large part be available in standard databases. With other types of information, such as design intent or operating procedures, there are issues both as to the representation most useful to the hazard identification aid and as to the ease of acquisition.

Lack of information: effects and strategies

Lack of information has certain consequences. In some cases the system may fail to generate a fault. More often, it will be unable to evaluate a potential fault that it has identified. There are strategies for coping with a lack of information. One is to conduct a dummy run of the hazard identification aid to establish the information that is missing. This implies that the data are to be provided prior to the main run.

An alternative approach is to use default assumptions about matters such as design intent or operator procedures. It can be envisaged, for example, that for many standard operations a corresponding standard, default operating procedure is attached. The use of default assumptions has obvious dangers, however. In some cases it is precisely the haziness about intent that it is the function of the study to identify. It may well be prudent, therefore, at least to draw attention to the fact that such a default has been used.

30.39.6 Information acquisition and CAD interface

A large amount of generic information on physical, chemical and thermodynamic properties and on materials of construction is, in principle, available in standard databases. Data on the plant itself are available in the design databases. The information acquisition problem relates to that part of the information required which is not available from these sources.

Information may be provided for use by a computer aid by manual input, by retrieval from the system's own database or by accessing the database of another system. Manual input imposes an overhead that can make the use of the aid much less attractive. There is therefore a strong incentive to obtain the information required automatically.

One approach to information acquisition is to provide a database that is intended to meet in full the information needs. Another is to rely completely on the interactive provision of data by the user. An intermediate, or hybrid, approach is to provide the database with a substantial amount of information but to anticipate some user input of data.

As indicated, a method of identifying the items of information needed to solve a particular problem but still missing in the database is to perform a dummy run for the sole purpose of such identification.

Use may also be made of heuristics. One strategy for automatic acquisition is to exploit the implications of the plant configuration. One example is that the presence of a water separator implies free water in the feed to it and hence a hazard of generation of static electricity. Another is that the presence of a trip implies a hazard against which the trip is guarding. And so on.

The aim must be that the hazard identification tool acquires most of its information by accessing a CAD system and its associated databases. Here it is sufficient to note that facilities for interfacing such an aid to the CAD systems in general use are not yet universally available.

30.39.7 Plant configuration features

As mentioned earlier, a plant design may possess configurational features that point to potential hazards. Such undesirable features include those associated with (1) pressure relief, (2) shut-in pipework, (3) water hammer, (4) throttling of pump suction and (5) emergency isolation of hazardous inventories. As a simple example, where a plant configuration shows a long pipeline terminating in a shut-off valve, there is a presumption that water hammer might occur.

It is for consideration at what stage identification of such undesirable configurational features should be undertaken. One policy is to leave them to be identified in the course of the main hazard identification procedure. An alternative, and perhaps preferable, policy is to conduct a preliminary screening for such features.

30.39.8 Plant system decomposition

Success in the analysis of a plant system can often depend on the appropriateness of the decomposition. It is therefore worth devoting some effort to ensuring that the system is decomposed in the way best calculated to achieve the desired results.

In most methods decomposition is into units and lines, together with source and sink units representing the main inflows and outflows across the plant boundaries. Another element that it may be convenient to use is an offtake. This is any feature through which a flow can occur out of a line or unit and includes an atmospheric vent, a pressure relief valve, a drain or sample point, etc.

There is an issue as to whether a line between units should be handled as a whole or decomposed into its constituent parts, with each fitting such as a valve or filter treated separately. Similar choices apply to the units. A pump set or a valve and bypass set may each be treated as a single unit or decomposed further.

30.39.9 Model hierarchies and inheritance

It is becoming increasingly common to model the plant as a hierarchy of objects and to exploit the concept of inheritance. The head of the hierarchy may be taken as the plant itself. In this case the plant object contains the connectivities between the units, which are the next level of object.

The models of the units may also be ordered in hierarchies. Thus, for example, one model hierarchy may be headed by a pressure raiser, which is the parent for compressors, fans, pumps, etc. A given unit may belong to more than one hierarchy. Thus, a centrifugal compressor may belong both to the hierarchy of pressure raisers and of rotating machines. Benefits of ordering the unit models in a hierarchy are that this provides structure in the model library and that models can inherit characteristics.

Inheritance is a valuable feature but needs to be applied with care, particularly where multiple inheritance is involved. Options in respect of inheritance from a parent unit are (1) to accept the whole set of characteristics, (2) to suppress the whole set of characteristics or (3) to accept the set of characteristics but to overwrite some of them. A declaration of the option exercised should be attached to the model.

For inheritance to be practised successfully it is necessary that the characteristics of the parent model be expressed in a way which is sufficiently general. As indicated earlier, one aspect of this is that the faults in the model need to be generic.

30.39.10 Units as objects

One way of generating faults is to list the attributes of a unit as an object. This provides a fault generator for the unit. This concept may be illustrated in terms of the properties of a pump. A pump:

(1) has problems –
loss of power; loss of lubrication; loss of cooling; cavitation; deadheading; reverse flow; vibration;
(2) causes problems –
can cause loss of flow; can cause loss of pressure; can cause power surge (start-up and shut-down); can cause vibration;
(3) is an equipment –
has states; has foundations; has connections; requires operation/control; requires maintenance;
(4) is an equipment which has states –
has operational state; has short-term stand-by state; has long-term stand-by state (mothballing); has breakdown state; has maintenance state;
(5) is an equipment which requires operation/control –
requires to be started up; may require preliminary conditions/activities before start-up; requires to be shut-down; may require observable operation (visual, audible cues about start-up, running, etc.); may require remote operation; may require synchronized operation (e.g. with an emergency isolation valve);
(6) is an equipment which requires maintenance –
requires access; requires mechanical isolation; requires electrical isolation; may require lifting gear;
(7) is a machine –
(a) requires power; has motion; dissipates energy; has inertia;
(b) has rotary motion; has bearings; has seals;
(8) is a pressure raiser –
is a source of low pressure (inlet); is a source of high pressure (outlet);
(9) is a flow device –
causes turbulence; may have cavitation;
(10) has subsystems –
may have lube oil system; may have water cooling system;
(11) is a leak source –
has hazardous area classification;
(12) has reliability engineering requirements –
has reliability requirement; has availability requirement.

30.39.11 Faults and susceptibilities

Susceptibilities

Closely related to the foregoing is the concept of looking at a unit in terms of its susceptibilities. This also is perhaps best explained by way of example. Consider a water separator. Some rules for this might be:

(1) If the residence time is low, then the outflow liquid may contain free water.
(2) If the operator fails to drain the water, then the outflow liquid may contain free water.
(3) If interfacial effects occur (emulsion), then the outflow liquid may contain free water.
(4) If the liquid is one susceptible to charge generation (low conductivity) and the liquid velocity is high or there is a charge generator (e.g. filter) in the inlet line, then there is a hazard of static charging and discharge.

Similarly, for a heat exchanger:

(1) If the exchanger is new/recently cleaned, then the outflow process liquid temperature may be high.
(2) If the exchanger is old, then fouling may have occurred and the outflow process liquid temperature may be low.
(3) If there is a tube leak and the heating fluid pressure is greater than the process fluid pressure, then the outflow process liquid will have minor component increase consisting of heating fluid.
(4) If the residence time is high and the process fluid is susceptible to polymerization, then the liquid may polymerize in the exchanger.
(5) If the liquid contains minor components that promote fouling, then fouling may occur.
(6) If the liquid contains minor components that attack the existing fouling film, then the outlet process liquid may contain debris.

The richness of the fault representation depends in large part on the imaginativeness with which unit susceptibilities are identified.

Conditional faults

The susceptibilities just described constitute a form of fault with an attached condition. The attachment of conditions to faults is important because it either limits the number of faults generated or increases the proportion eliminated, depending on the stage at which the conditions are applied.

As a further example of a conditional fault, wet steam may be characterized as a fluid that is erosive, but with the attached condition that the velocity is high. The erosiveness of the steam is a generic property, but the velocity is a condition to be met in the specific application.

Faults with external effects

A hazard identification aid should cater not only for faults that propagate through the plant but also to some degree for those which have an impact outside it. Examples are liquid overflow from a storage tank and its implications for the bund around the tank or discharge from a relief and it effects.

30.39.12 Expert rules

As indicated, a unit may be provided with a set of expert rules for both the generation and evaluation, or resolution of faults. In some cases generation and resolution may occur within the same unit, in others use has to be made of fault propagation between units.

As an example of the latter, more complex case, consider a pump with the rule set

Hook	*Generation*	*Resolution*
Has lube oil system	Lube oil system failure may cause flow of lube oil as impurity into process fluid if failure creates a leak path and if the pressure of lube oil is greater than the pressure of process fluid	Response required if and only if lube oil impurity in process creates a significant problem

At this point a potential fault has been generated but not resolved. It is not known whether lube oil in the process fluid is an unacceptable impurity. Now consider the transport of the lube oil impurity into a water separator. Applying the water separator rule, or susceptibility, given earlier:

If interfacial effects occur (emulsion), then the outflow liquid may contain free water.

This rule effectively defines, for this unit, the nature of the potential problem. Whether or not the lube oil impurity is a significant problem depends on whether it is a foaming agent. This is determined from the fluid model, which is now described.

30.39.13 Fluid and stream models

Modelling of the units in terms of fault propagation and expert rules needs to be complemented by modelling of the fluid. A distinction is made between the fluids and the streams. 'Fluid' refers to the chemical substance, or mixture, which has generic properties. 'Stream' refers to the stream at a given location in the specific plant. A stream is defined primarily in terms of the fluid and of the pressure and temperature.

Some elements of the fluid and stream models are (1) stream definition, (2) stream transformations and (3) stream displacements.

Stream definition

A stream at equilibrium is defined basically in terms of its composition and of the pressure and temperature. The composition may be defined in terms of (1) bulk components and (2) minor components, intended and unintended. The stream composition and the operating conditions of pressure and temperature define the phase and the physical properties of the equilibrium fluid.

Stream transformations

Much stream behaviour may be characterized in terms of transformations. These are (1) intended transformations and (2) unintended transformations. The intended transformations are what the process is all about, typically reaction and separation. The unintended transformations are what the exercise seeks to identify.

Stream interactions

Another way of categorizing stream behaviour is in terms of interactions. These are (1) interactions with operating conditions, (2) interactions with other materials and (3) interactions with other features.

Stream interactions with operating conditions

There are three categories of stream interaction with operating conditions: (1) phase, (2) flow properties and (3) reaction.

Phase transformations are (1) vaporization, (2) condensation, (3) melting and (4) solidification. These transformations may be partial or total.

Flow property transformations are any transformation that affects the flow properties of the fluid, for example viscosity change and change to slugging flow.

Reaction may occur within the fluid itself. This reaction may be in a reactor, where the reaction may be the intended reaction or also an unintended one; or it may be in another part of the plant, where it will almost always be an unintended reaction.

Stream interactions with other materials

There are a large number of stream interactions with other materials that may be conceived. The interactions considered here are confined to those which are due to the fluid constitution (composition and properties) and do not extend to the fluid motion.

The interactions include those with other materials such as (1) other fluids (bulk components, minor components), (2) catalyst, (3) materials of construction, or corrosion (main components, minor components), (4) air, (5) water and (6) additives (interfacial agents, promoters, inhibitors). In each case it is necessary to consider the interaction both of the bulk components and of the minor components of the stream.

Interactions of the stream with the materials of construction include interactions of the stream both with the main components and with minor components such as gaskets, seals, trims, etc. Lubricants and sealing fluids may be treated as 'minor components'.

Air and water might be treated on a par with the other unintended minor components, but they are so common, and incidents associated with them so frequent, that they perhaps deserve special status. One aspect of this is that consideration should be given to whether or not they are declared as specific components of the stream.

Stream interactions with other features

Streams also interact with other features in the sense that a problem arises from the combination of the stream and the feature. These features include (1) units, (2) unit faults, (3) operations and (4) maintenance.

An example of an interaction between the stream and a unit is the case where the fluid is flammable and is transferred into a road tanker. There is a recognized hazard of static electricity in some cases.

An example of an interaction between the stream and a unit fault is the case where the stream contains gunk that causes blockage.

An example of an interaction between the stream and an operation is the case where a gravity separator is used to remove water from a toxic solvent with which it is nearly (but not totally) immiscible and the water is drained off the bottom. The water will be saturated with the solvent and the latter will therefore exert its full vapour pressure. If the solvent is toxic, this may affect the operator.

An example of interaction between the stream and maintenance is the case where the fluid is very toxic and

special precautions will need to be taken when the plant is broken open.

30.39.14 Fluid and stream models: hydraulics

A quite different set of fluid phenomena are those that fall into the broad category of hydraulic effects. One way of looking at these is in terms of the displacement of one fluid by another.

Displacement of gas by liquid

Displacements of gas by a liquid include (1) displacement in a vessel, (2) displacement in a pipe, (3) condensate hammer, (4) liquid lock and (5) siphon.

The pipe displacements are (1) permanent, flowing displacement (2) a moving liquid slug and (3) an essentially immobile liquid slug.

Displacement of gas by a liquid in a vessel can cause overflow and overpressure. Displacement of gas by a liquid in a pipe can cause erosion and incorrect measurement and control. Condensate hammer can cause damage to pipework and machinery. Liquid lock can prevent gas flow and pressure equalization.

Displacement of liquid by gas

Displacements of liquid by a gas include (1) displacement in a vessel (partial, total), (2) displacement in a pipe and (3) gas lock.

Displacement of liquid by a gas in a vessel can cause loss of head and overpressure. It can also take the form of gas breakthrough when a liquid seal at the bottom of a vessel is lost. Displacement of liquid by a gas in a pipe causes incorrect measurement and loss of control. Gas lock can prevent liquid flow.

Displacement of liquid by liquid

Displacement of liquid by a liquid occurs in rollover. Rollover is caused by the formation of two liquid layers and by inversion of the densities of the two layers.

30.39.15 Fluid and stream models: modelling strategy

A strategy for modelling the fluid needs to deal both with the identification and with the resolution of stream-related problems.

Stream problem identification

Stream-related problems arise from the three sorts of stream interactions and from stream hydraulics. One strategy for dealing with stream interactions is the use of breakpoints. A breakpoint is defined as a point in the plant at which the fluid constitution (composition and properties) and/or the operating conditions undergo or may undergo a significant change. This definition covers both a point where a change is intended and one where no change is intended but may nevertheless occur. It is for consideration what constitutes a significant change.

At each such point the three types of stream interaction are examined, to identify any problems. The default assumption is that unless there is information to the contrary, the stream passes through a breakpoint with its constitution and operating conditions unchanged except as given in the design.

Stream hydraulic problems tend to be related to particular types of line and unit. One way of dealing with these is therefore by using lines and units as the hooks for the appropriate expertise.

Stream problem resolution

Fault generation needs to be followed by fault resolution. The stream model should contain aids to assist in determining whether a generic fault identified by the fault generation process is in fact a significant problem in the specific case. Some types of resolution aid include (1) landmark values, (2) susceptibility rules and (3) other rules. Here rules are taken to include related forms such as truth tables.

30.39.16 Fluid and stream models: information

The implementation of such a strategy requires the handling of information, which may be broken down into (1) information requirements, (2) information representation and (3) information acquisition.

The foregoing approach to the fluid and stream models implies the need for information on (1) inlet streams and (2) intended stream transformations at breakpoints, and information relating to the potential for (3) unintended stream transformations, (4) unintended stream interactions with other materials, (5) unintended stream interactions with other features and (6) unintended stream hydraulic effects.

The set of inlet fluids is those fluids entering at the boundaries and includes process fluids and utility fluids. The set of intended stream transformations is, in effect, the process.

The unintended stream transformations arise from the first two types of interaction (with the operating conditions and with the other materials). The unintended stream interactions with other materials may result in stream transformations, as just mentioned, and/or in other effects.

This part of the information relates to fault generation. The second part is that which relates to fault resolution. In large part this latter is concerned with various types of susceptibility to stream changes.

A large part of the fluid model consists of information about susceptibilities and incompatibilities. These relate to the three types of interaction already described, which are (1) stream–stream interaction, (2) stream–materials interaction, and (3) stream–feature interaction. These interactions occur essentially due to the fluid properties of the stream(s).

There are also interactions due to stream properties such as pressure and temperature. These include (1) pressure–materials interaction and (2) temperature–materials interaction.

Information on susceptibilities and incompatibilities is most naturally represented as rules or look-up tables.

30.39.17 Materials of construction model

Another model required is the materials of construction model. What this model should provide is the susceptibilities of the materials in the plant to undesirable interactions. The most elementary form of model is one that gives the incompatibilities between the materials of construction of the main items of equipment and the fluids. More useful is a model that also gives this information for (1) minor components of the main plant items and (2) for impurities in the fluids.

The materials model should also cater for susceptibilities of the materials to the stream properties of pressure and temperature. The materials model may be extended to give some information on effects. In most cases the basic effect is corrosion. The significance of this, however, varies. It may lie in its potential to cause a leak or in contamination of the fluid.

30.39.18 Filtering of faults

The output given by current computer aids for hazard identification tends to be too indiscriminate and too voluminous. As pointed out in Chapter 8, in a conventional hazop the identification of hazards is only one part of the activity; the other part is the filtering out of those hazards that are unfeasible or negligible.

Four forms of filtering can be distinguished: (1) suppression, (2) consolidation, (3) evaluation and (4) masking. These are now considered in turn.

Suppression of faults

By 'suppression' is meant suppression of the consequences and/or causes during the generation process or immediately thereafter. It has its place, but carries with it certain dangers. Suppression needs to be governed by suitable rules, which may not be easy to devise.

An example of suppression that may well be appropriate is the suppression of generalized blockage and leakage faults which tend to proliferate in certain aids, particularly where each fitting in a line is the subject of a separate examination.

Consolidation of faults

Consolidation of faults involves replacing a set of faults by a more limited set of equivalent faults. It is applicable mainly where a line has been decomposed into its constituent elements, each with its associated fault set. The use of consolidation requires suitable rules, the formulation of which may not be trivial. This contrasts with suppression, which is readily implemented.

Evaluation of faults

Evaluation of faults may take several forms. One is the application of expert rules, another is the use of landmark values and a third is the use of susceptibility data. Some types of rule for evaluation include those associated with (1) consequences, (2) product of consequence and frequency, (3) frequency, (4) classic hazard situations, (5) plant equipments, (6) protective devices, (7) unrevealed failures and (8) process variables. There will be some events so serious that they are unacceptable virtually regardless of the frequency. There will be others where the product of (consequences $\times$ frequency) is an appropriate filtering criterion. There may be others, applicable to low consequence events, where only the frequency is of interest. There are certain classic situations such as thermal expansion of blocked-in fluid. There are certain pieces of equipment such as pump sets where there are classic hazards and solutions. There are certain classic aspects of protective devices such as a pressure relief valve where the set pressure may not be exceeded but where capacity may be. There are certain rules, displayed in hazops, as to how to handle unrevealed failures, particularly in instruments. There may be rules governing process variables such as level or pressure. One way of developing evaluation rules is to identify the features that trigger interest on the part of members of a hazop team.

Another method of evaluation is the use of landmark values. These are most likely to be associated with the fluid model. A typical application of a landmark value is to determine whether the fluid is likely to undergo a change of phase such as boiling or freezing.

The third evaluation method mentioned above is the use of data on susceptibility or compatibility. This method is likely to be applicable mainly to the fluid and materials of construction models. Data on susceptibility may take the form of look-up tables or rules.

The account of evaluation that has just been given implies that the way to proceed is to generate all possible faults and then to evaluate each one to determine whether it can be rejected. There is an alternative approach to evaluation which is to reverse the 'burden of proof and to apply the default rule that no fault is retained unless there is good reason to do so. This is possibly closer to the *modus operandi* of a hazop team. Whichever approach is adopted, the information and rules required to support the identification decisions are broadly similar.

Masking of faults

Whatever the extent and effectiveness of the various forms of filtering, there remains the question of whether to display in the output all the faults not removed by the filtering processes described or whether to practice some form of masking.

In principle, masking is a relatively simple operation. It involves defining within the total information a subset that is not to be displayed and laying a mask over it. There may be a number of masks, each with its subset, and they may overlap, like Venn diagrams.

A hierarchy of masks can be envisaged, with distinctions based on the severity of the failures involved, with a stringent mask for coarse hazard studies, etc. Alternatively, the distinction may be based on the discipline involved, for example, control systems, pressure relief systems, etc., for use by different parties to the design. There is also the option of user-configured masks.

30.39.19 Query and action outputs

The output from a conventional hazop study includes a list that is typically a mixture of queries and actions. The actions may vary in status from requirements to suggestions.

The corresponding output for a computer aid is likely to contain a different mix, weighted more to queries, with proposals for positive action probably confined to certain limited areas. Effort is better employed in improving the quality of the queries rather than in extending the aid into a design tool.

30.39.20 Explanation facility

As described earlier, a standard feature of an expert system is the explanation facility. There is, in principle, no reason why such as facility should not be provided as part of a hazard identification aid, to be consulted in the probably small number of cases where the logic of the argument is unclear to the user.

30.40 Fault Tree Analysis

A large number of computer programs have been developed for the analysis of fault trees, which are often very large. The tasks carried out by these programs fall mainly into four categories. These are determination of:

(1) minimum cut sets,
(2) common cause failures,
(3) reliability and availability,
(4) uncertainty.

Some of these codes are listed in Table 29.7. This table gives the references to the codes listed. Further references are

given in Table 29.1. One of the first sets of codes was PREP and KITT developed by Vesely and co-workers. PREP obtains the minimum cut sets and KITT evaluates reliability and availability. There are two versions, KITT-1 and KITT-2, the latter having the capability of handling time-dependent failure data. These codes have been widely used and were utilized in the *Rasmussen Report*.

Another group of codes are those developed by Fussell and co-workers. These include MOCUS, BACFIRE and SUPERPOCUS for determining minimum cut sets, common cause failures and reliability and availability.

Codes for the determination of importance include IMPORTANCE, developed by Lambert.

The *Rasmussen Report* included several codes. SAMPLE combines input distributions to give an output distribution. MOCARS determines the distribution of a tree top event.

30.41 Fault Tree Synthesis

As just described, there are available a number of computer codes for the analysis of fault trees. The synthesis of fault trees is a more difficult problem, but some progress has been made in developing aids for this. Again the codes utilize some form of fault propagation modelling.

30.41.1 Fault tree drafting

Some codes for fault tree construction are aids to the manual synthesis of fault trees. They include TREDRA and TREE.

30.41.2 Fault tree synthesis codes

There are a number of codes that have been developed to effect the automatic synthesis of fault trees. The different methods take different starting points, including: functional equations (e.g. B.E. Kelly and Lees, 1986a); graphical methods such as digraphs (e.g. Andrews and Morgan, 1986); reliability block diagrams (e.g. Caceres and Henley, 1976) and reliability graphs (e.g. Camarda, Corsi and Trentadue, 1978); logic models (e.g. Poucet, 1983) and logic flowgraphs (e.g. Guarro and Okrent, 1984); tabular methods, such as decision tables (e.g. Salem, Apostolakis and Okrent, 1977) and transition tables (e.g. J.R. Taylor, 1982; Bossche (1991a–c); and mini-fault trees (e.g. Fussell, 1973a,b; B.E. Kelly and Lees, 1986a).

Some of these codes are summarized in Table 30.16. Most are probably best characterized as research codes. An account is now given of some of these methods.

30.41.3 DRAFT

An early code for fault tree synthesis was the DRAFT code of Fussell (1973a,b). He used models which he termed component failure transfer functions, which are effectively a form of mini fault tree. He applied his method, which he called the Synthetic Tree Model, to electrical systems rather than process plants, although the electrical systems considered were on process plant systems.

30.41.4 FTS

The first fault tree synthesis code for process plants was the FTS code of Powers and Tompkins (1974a,b), further developed by Powers and Lapp (Powers and Lapp, 1976; Lapp and Powers, 1977a,b). These authors model the plant system using digraphs. Figure 30.17(a) shows the nitric acid cooler system used by Lapp and Powers, which has become a classic example, and Figure 30.17(b) shows the digraph given by the authors for this system.

The fault tree is constructed by selecting the node for the top event of interest and then developing the tree for the causes of this event. For a given node, the causes are the inputs to the node. The tree is developed down to the basic events. Causes that violate consistency are deleted.

Control loops are handled by means of an operator, which is essentially a loop structure imposed at the appropriate point in the development of the tree. Separate operators are used for feedback and feedforward loops.

The fault tree obtained in this work has been subject to some discussion in the literature (e.g. Lambert, 1979; Lapp and Powers, 1979; Locks, 1979; Yellman, 1979).

30.41.5 CAT

Another early code for the synthesis of fault trees for process plants was the CAT code of Salem, Apostolakis and co-workers (Salem, Apostolakis and Okrent, 1975a,b, 1977; Apostolakis, Salem and Wu, 1978; Salem and Apostolakis, 1980). In the CAT code the models used are cast in decision table form. The tree is then constructed by nominating a top event and developing its causes by selecting from the appropriate entries of the decision tables, using suitable procedures to maintain consistency.

Table 30.16 *Some computer codes for fault tree synthesis*

Code[a]	*Methodology*	*Reference*
DIRAFT	Failure transfer functions	Fussell (1973)
FTS	Digraphs	Powers and Tompkins (1974a,b); Powers and Lapp (1976); Lapp and Powers (1977a, 1979); Cummings, Lapp and Powers (1983)
CAT	Decision tables	Salem, Apostolakis and Okrent (1977); Apostolakis, Salem and Wu (1978) Salem and Apostolakis (1980)
-	Digraphs	D.J. Allen and Rao (1980); D.J. Allen (1984)
CAFTS	Transfer logic models, mini-fault trees	Poucet and de Meester (1981); Poucet (1983, 1990)
RIKKE	Equation 'bigraphs', transition tables	J.R. Taylor (1982)
FAULTFINDER	Propagation equations, mini-fault trees	Martin-Soils, Andow and Lees (1982); B.E. Kelly and Lees (1986a–e); Mullhi *et al.* (1988); A Hunt *et al.* (1983a–e)
AFTC	Decision tables	Sang Hoon Han *et al.* (1989)
FISA	Causal trees, transition tables	Bosche (1991a–c)

[a] Synthesis codes usually have a drafting package also.

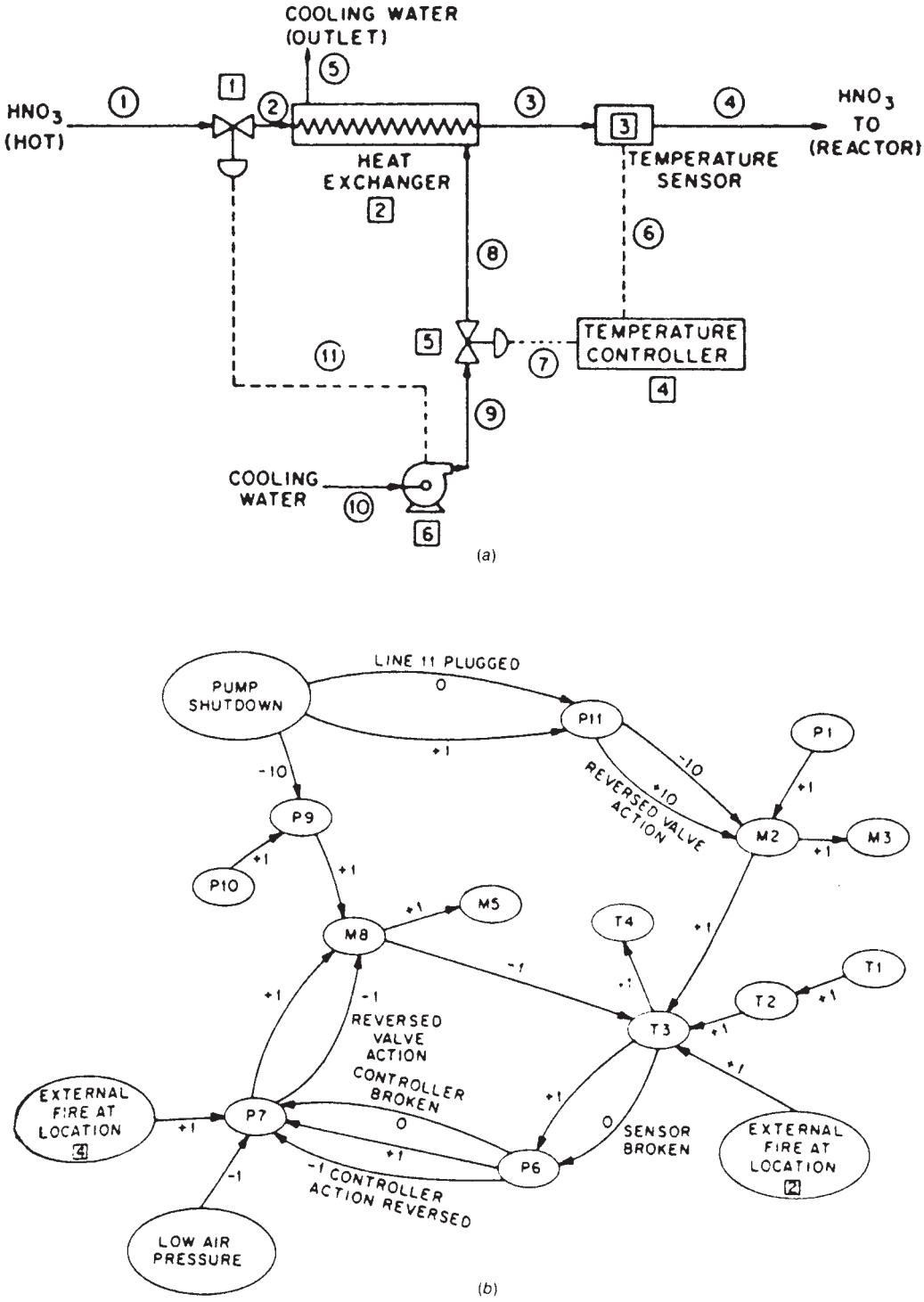


Figure 30.17 *A nitric acid cooler system (Lapp and Powers, 1977a): (a) flow diagram; (b) diagraph (Courtesy of the Institute of Electrical and Electronic Engineers)*

30.41.6 RIKKE

The RIKKE code of J.R. Taylor (1982) utilizes the so-called equation 'bigraph', transition table and mini-fault tree models. The construction of the tree proceeds by selecting a top event and developing its causes by tracing through the mini-fault trees, with procedures to maintain consistency. Taylor characterizes his fault construction algorithm as utilizing a component-by-component construction and contrasts it with that of Lapp and Powers, which he describes as a loop-by-loop method. A feature of Taylor's method is the use of a larger set of deviations than simple HI and LO, such as VHI and DIST HI.

30.41.7 FAULTFINDER

Another code for fault tree synthesis is the FAULTFINDER code of B.E. Kelly and Lees (1986a–e) and A. Hunt *et al.* (1993a–e). This is described in the following section.

30.41.8 Loop structure methods

The methodology for fault tree construction described is essentially component oriented, but this is not the only approach that may be adopted. An alternative is a structure oriented method in which the structure of the tree is determined from the outset by that of features such as the control and trip loops. This type of approach is illustrated in the work of Shafaghi, Andow and Lees (1984) and Shafaghi, Lees and Andow (1984).

30.42 Fault Tree Synthesis: FAULTFINDER

A more detailed account is now given of one particular code for fault tree synthesis. This is the FAULTFINDER code described by B.E. Kelly and Lees (1986a–e) and A. Hunt *et al.* (1993a–e).

In this work the models are formulated initially in terms of functional equations of the type described in Section 30.36. The building blocks for the fault tree synthesis, however, are mini-fault trees, described in the earlier work of Martin-Solis, Andow and Lees (1982). The mini-fault trees are constructed automatically from functional equation models.

The overview of FAULTFINDER that follows, both illustrates another application of fault propagation modelling and serves as an example of a fault tree synthesis code. The description is necessarily highly simplified.

30.42.1 System decomposition

The system decomposition is essentially similar to that used in the HAZID code. The piping and instrument diagram is converted to a block diagram and for each unit in the latter a unit model is specified, drawing on a library of models, with additional models configured by the user if necessary.

It is also necessary to provide certain structural information. The main information required relates to the control and trip loops. For each loop the instruments comprising the loop and the streams immediately affected by the action of the loop are identified.

30.42.2 Unit and top event models

The code uses the basic fault propagation methodology described in Section 30.36. A plant unit is modelled in the first instance using any combination of three forms: propagation equations, event statements and decision tables. The propagation equations are used to represent the propagation of a disturbance, or fault, through a unit and the event statement to describe the initiation of a fault in a unit. The decision tables are used mainly to represent relations involving AND gates.

From these three forms of input are constructed the mini-fault trees for the units. For each output from the unit there are at least two mini-trees, one for the deviation HI and one for LO. The top event of a mini-tree, therefore, is a deviation of an unit output. The mini-tree has only one level below this top event, the events in this level consisting of either variable deviations or basic faults.

The derivation of a mini-tree in a unit model proceeds as follows. Consider the relation given earlier for flow through a pipe

$$Q_2 \text{ out} = f(G_1 \text{ in}, G_2 \text{ out}) \qquad [30.42.1]$$

and the event statements

$$\text{PART-BLK } Q_2 \text{ out LO} \qquad [30.42.2]$$

$$\text{LK-LP-EN: } Q_2 \text{ out LO} \qquad [30.42.3]$$

The propagation equation states that Q_2 is LO if G_1 or G_2 is low. The event statements state that Q_2 is LO if there occurs the fault PART-BLK (partial blockage) or the fault LK-LP-EN (leak to low pressure environment). The resultant mini-tree is shown in Figure 30.18(a). Separate but very simple mini-tree models are used for the top events. Figure 30.18(b) shows a top event model for the event VES-RPT (vessel rupture).

The configuration of a unit model is carried out using the model generation program. The data are entered on a proforma essentially similar to that used in HAZID and shown in Figure 30.15, but the output generated by the program consists in this case of the set of mini-fault trees for the unit.

The methodology includes various aids to reduce the modelling effort, and to achieve a degree of automatic modelling. There is a facility to generate automatically the event statements for certain standard faults at ports. There are programs and template models for the configuration of vessels. And there are also some basic archetypes of other units such as reactors and heat exchangers.

30.42.3 Fault tree construction

Fault tree construction starts by nominating a top event, retrieving first the appropriate top event model and then the unit mini-trees that have as their top event the causes of the variable deviations that are the causes of the top event. The causes of the top events in this first set of mini-trees are then in turn developed using further mini-trees. The development continues until the base events in the mini-trees are either basic failures or events crossing the boundaries of the system. The principle of tree construction is therefore very simple. The complications arise mainly in ensuring consistency and in handling certain structures in the plant.

30.42.4 Tree consistency

There are two main types of consistency that need to be maintained: series consistency and parallel consistency. In essence, series consistency means that an event cannot be caused by its obverse. Also it cannot be caused by itself. An event may also be inconsistent with certain faults. Series consistency is checked as the tree is developed. Parallel consistency is the consistency of events in one branch of the tree with events in other branches of the tree

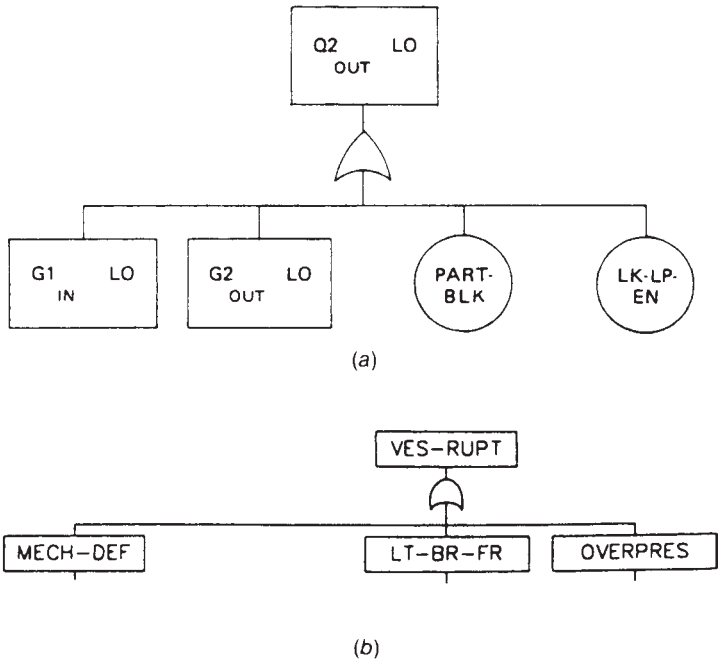


Figure 30.18 *FAULTFINDER: some mini-fault trees (after B.E. Kelly and Lees, 1986a; A. Hunt et al., 1993e): (a) mini-fault tree for event Q_2 LO (LK-LP-EN, leak to low pressure environment; PART-BLK, partial blockage); (b) mini-fault tree for top event VES-RPT (vessel rupture) (LT-BR-FR, low temperature brittle fracture; MECH-DEF, mechanical defect; OVERPRES, overpressure)*

under an AND gate. The check on parallel consistency is made during the rationalization stage that follows construction of the crude tree.

30.42.5 Tree structures

It is found that there are certain structures in a plant which need to be given special treatment, notably control loops, trip loops and divider–header combinations. The fault tree for a plant may be regarded as a composed of a basic demand tree, devoid of all control and trip loops, with the control and trip branches then added to it. Manual construction of a fault tree essentially proceeds by creating first the demand tree and then adding the control and trip branches. The structure of the tree is largely determined by these features.

It is desirable that an automatically constructed tree retain this general structure. But in any case it is found that problems arise in the construction of the tree unless some information on the control and trip loop structure is explicitly provided. It is possible in principle to limit the input information to the basic unit connectivities and to have the program identify the loops, but it is simpler to provide this information as part of the input.

Another type of structure that needs special treatment is combinations of dividers and headers. These occur in many guises, such as the suction and delivery manifolds of a pair of pumps or a control valve with a bypass. In some cases divider–header combinations are nested and in others they are staggered. In the case of divider–header combinations manual identification is complicated, and the program is provided with an algorithm to effect identification.

For the control and trip loops, use is made of templates that impose a structure on the tree at the point in tree development where the loop is encountered. For control loops use is made of three such templates. One of the templates, shown in Figure 30.19, is for a controlled variable in either a feedback or feedforward loop. The other two are for a manipulated variable, one in a feedback loop and the other in feedforward loop.

For trip loops a distinction is made between functional failure (failure to operate on demand) and operational failure (spurious trip). A template is used for functional failure, but not for operational failure, which is treated on a par with any other failure which disturbs the system.

30.42.6 Fluid and materials of construction models

The methodology allows for the supplementation of the unit models by models for the process fluids and for the materials of construction. Essentially, these models handle various kinds of susceptibility, whether to phase change or to corrosion. The general approach is similar to that used in the HAZID code.

30.42.7 Tree rationalization

Once the crude fault tree has been constructed it is necessary to rationalize it. Rationalization involves a number of operations. These include: checking for parallel consistency; elimination of certain branches where the base event is impossible or, alternatively, certain; and rationalization of the branches of control loops. It is at this stage that the attachment of the trip loop functional failure branches occurs, the treatment during the initial construction being

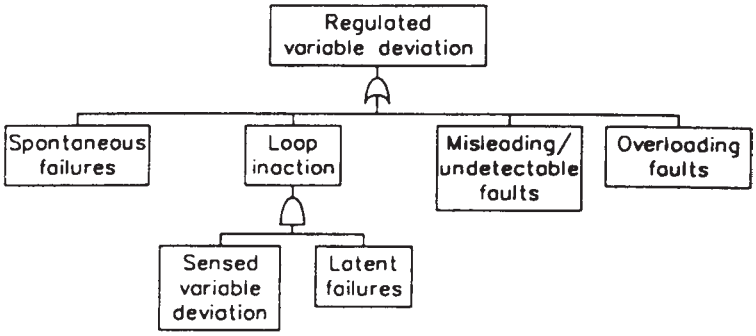


Figure 30.19 *FAULTFINDER: template for a controlled variable deviation, in either a feedback or a feedforward loop (A. Hunt et al., 1993c) (Courtesy of Elsevier Science Publishers)*

limited to identification of the variables that are protected by the loop.

30.42.8 Sequential operations

A sequence of operations may be handled by treating each step separately and re-initializing the configuration at each step. An overall fault tree then takes the form of tree with a top event SEQUENCE FAILS, with the two events ANDed together at the next level down SEQUENCE FAILS AT STEP 1 and SEQUENCE FAILS AFTER STEP 1, and so on.

In this connection, it merits mention that the top event of a fault tree does not need to be a hazardous event. It can also be an event such as SEQUENCE ABORTS in, say, a computer controlled sequence.

30.42.9 Other features

The methodology also accommodates a number of other features. Changes to control and trip loop set points normally receive no special treatment. Control exercised by a human operator or process computer that is equivalent to a conventional control loop is modelled as a notional loop.

Failures of utilities may be modelled either as independent failures in individual units or as inputs from a common supply which is itself subject to complete failure. This latter method may also be used to model other common cause failures.

30.42.10 Model generation and model library

The general approach to model generation and to the model library in FAULTFINDER is that outlined in Section 30.36 for fault propagation in general and in Section 30.38 for HAZID. Unit models are stored in the unit model library as sets of mini-fault trees. Details of the library are given by B.E. Kelly and Lees (1986c) and A. Hunt *et al.* (1993a).

A new model is generated by completing a proforma on which are entered the functional equations, event statements and decision tables, if any, for the unit. The mini-fault trees of the model are then generated automatically. Generation of new models for vessels is assisted by the provision of a taxonomy of ports, by partial automation of the modelling of ports and by the use of a special vessel model generation program and of vessel archetypes, or templates.

30.42.11 Computer codes

The main programs in the FAULTFINDER package are: MASTER, which does the housekeeping; FAULT, which constructs the tree; and MODGEN and EVTGEN, which generate the unit models and top event models, respectively. There are model libraries for unit models and top event models. Use is also made of various other programs for fault tree drawing and of standard programs for fault tree analysis.

30.42.12 Illustrative example: pump changeover

Numbers of examples of fault trees constructed by the program are given in the accounts by B.E. Kelly and Lees (1986a–d) and A Hunt *et al.* (1992a–e). A vaporizer example is given by Mullhi *et al.* (1988).

An illustrative example of fault tree construction using FAULTFINDER is given by B.E. Kelly and Lees (1986d). The system considered is the pump system shown in Figure 30.20. The problem was to identify the potential causes of abortion of a 14-step changeover sequence. The configuration block diagram is shown in Figure 30.21. The fault tree for Step 8 of the changeover is illustrated in Figure 30.22, the key for which is given in Table 30.17. The initial entries in the table of the minimum cut sets for this step, obtained by a fault tree analysis code, are shown in Table 30.18. The original paper gives further details, including listings of the steps in the sequence, the unit models used, the sequence steps and abort conditions, the configuration at each reinitialization and the minimum cut sets.

30.43 Operating Procedure Synthesis

There are relatively few computer aids for the examination of plant operations such as start-up and shut-down, although it is often in these phases that incidents occur, but progress is now apparent in the synthesis of operating procedures through the application of Al planning techniques. Pioneering work in this area was the study of Rivas and Rudd (1974) on the synthesis of operating sequences for valves.

With the progress made in Al planning techniques, operating procedure synthesis (OPS) for process plants has become a more active area. Studies include those done on valve operations by O'Shima (1983), on operating procedures by Fusillo and Powers (1987, 1988b) and Aelion and Powers (1991), on valve operations by Foulkes *et al.* (1988), on purging procedures by Fusillo and Powers (1988a), on operating procedures by Lakshmanan and Stephanopoulos (1988a,b, 1990) and Soutter and Chung (1995a,b) and on

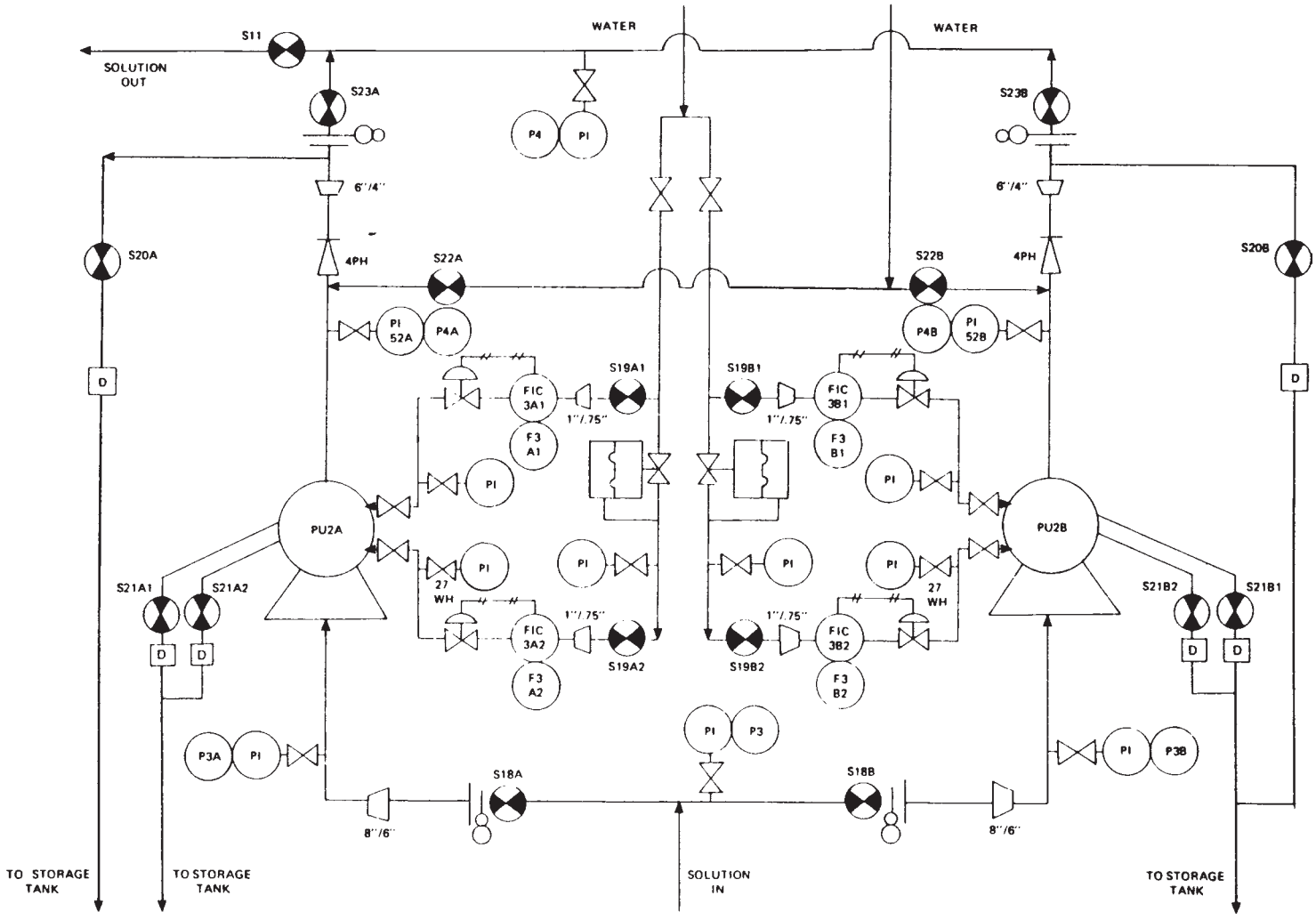


Figure 30.20 *FAULTFINDER: illustrative example – a pump system (B.E. Kelly and Lees, 1986d) (Courtesy of Elsevier Science Publishers)*

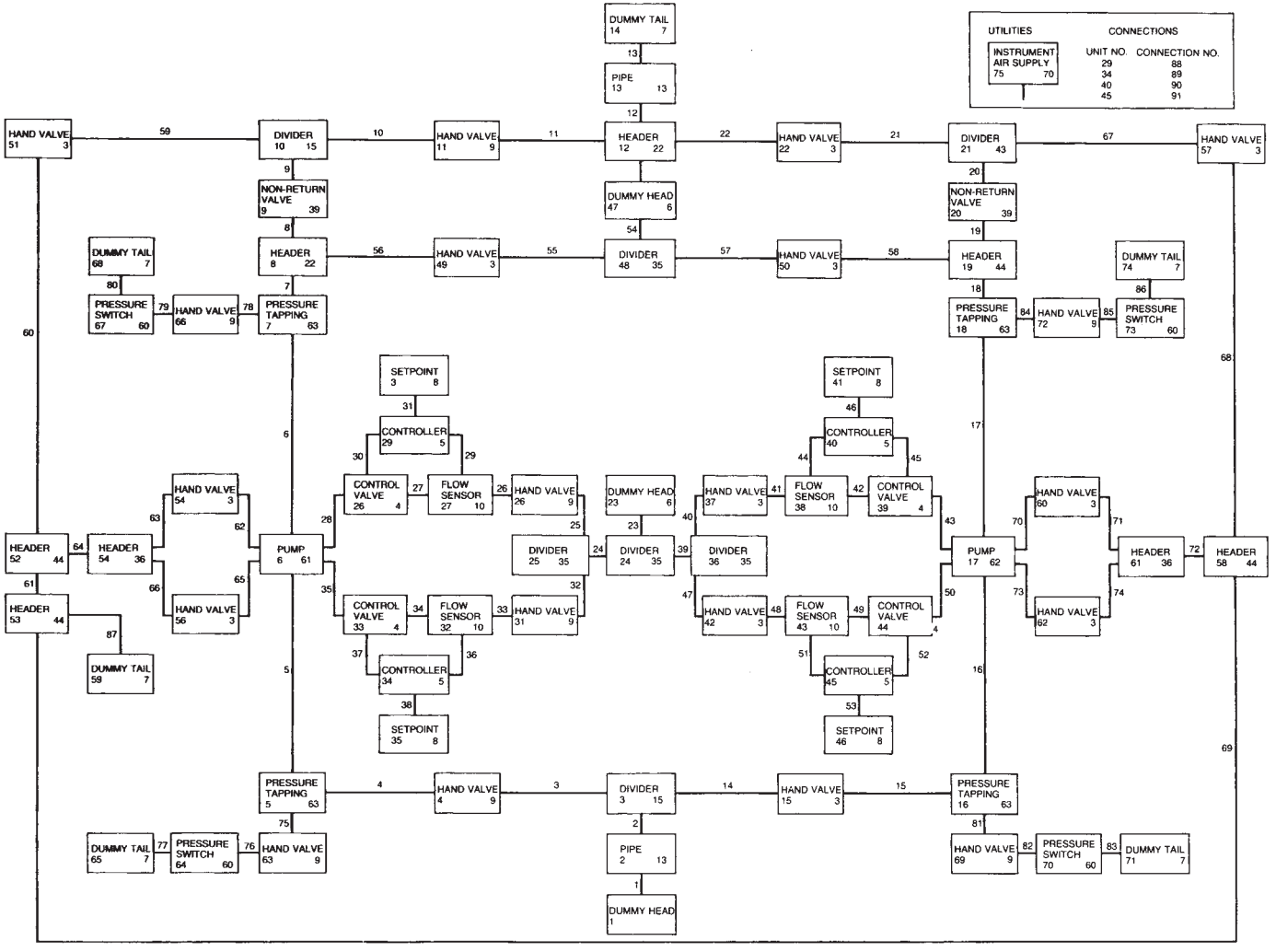


Figure 30.21 *FAULTFINDER: illustrative example – configuration block diagram for pump changeover system (B.E. Kelly and Lees, 1986d) (Courtesy of Elsevier Science Publishers)*

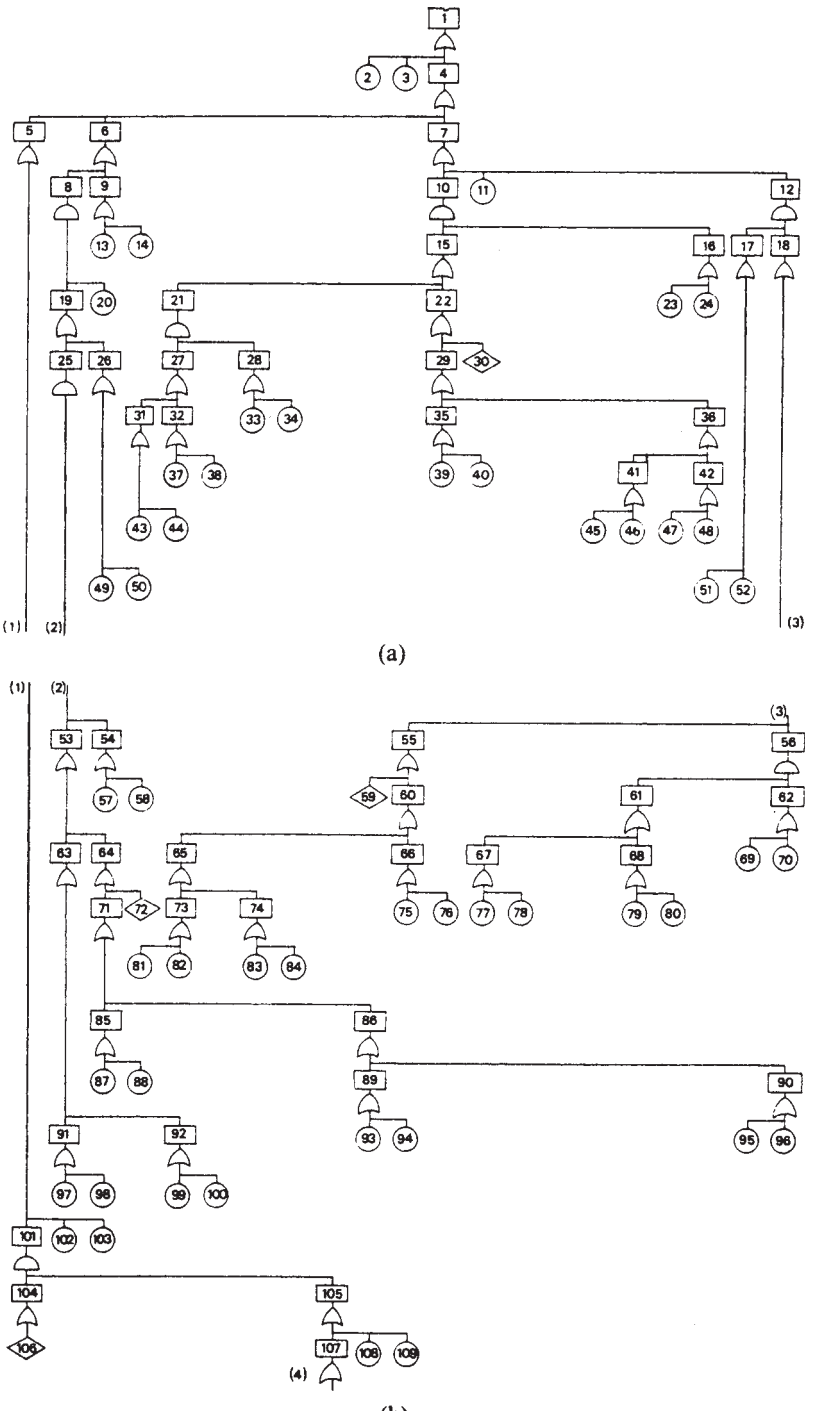


Figure 30.22 *continued*

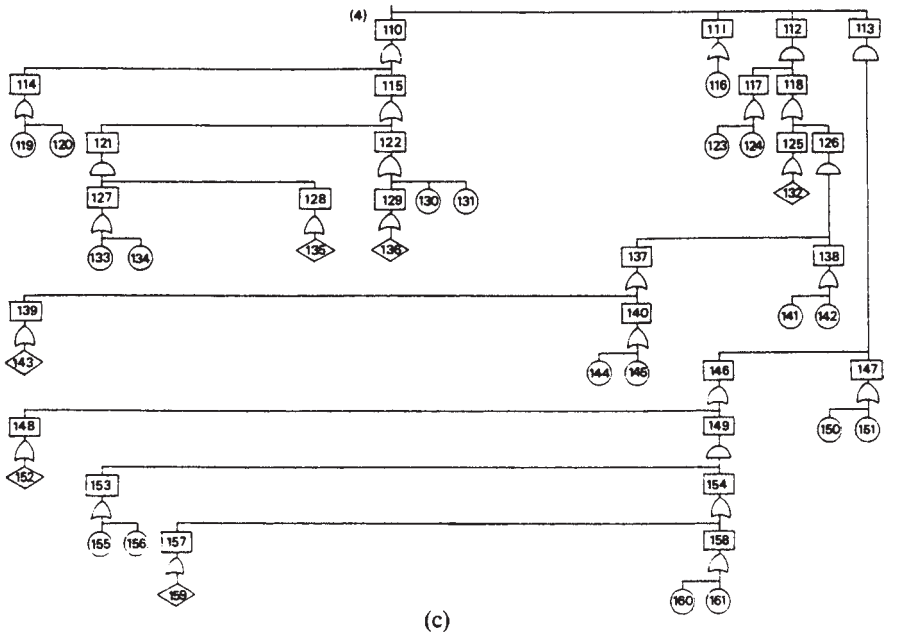


Figure 30.22 *FAULTFINDER: illustrative example – pump changeover sequence; fault tree for step 8 (B.E. Kelly and Lees, 1986d) (see Table 30.17 for key) (Courtesy of Elsevier Science Publishers)*

batch processes using qualitative process theory by Rotstein, Lavie and Lewin (1992).

Several of these studies are now described. But first it is pertinent to make one or two points on the relationship of OPS to AI planning.

30.43.1 Unsafe states

In the application of planning to process operations it is obviously necessary to pay particular attention to the avoidance of undesirable, and especially of unsafe, states. Insofar as much AI planning work has been concerned with robots operating in blocks world, the question of unsafe states has tended to be less urgent. Techniques for handling the unsafe state problem are not well developed in AI planning. In process operations, however, the avoidance of unsafe states is very much to the fore. The avoidance of unsafe states is an essential requirement of an OPS planner and may well govern the choice of planning algorithm. In seeking to avoid unsafe states, an advantage lies with a planning strategy in which actions are added one at a time and the safety of the new state is confirmed before proceeding further; in other words with a forward-chaining, linear planner.

30.43.2 Valve operations

Much of the work described on OPS has been concerned with the synthesis of sequences of valve operations. From the point of view of planning, the crucial feature of valve operations is that they are not readily handled by a simple planning operator. The problem is that an action in which a valve is closed or opened does not have a unique set of effects. The effects depend on the state of the whole system. For example, if a line contains two valves in series, the effect of opening the upstream valve is not unique, but depends on whether or not the downstream valve is already open. One solution to the valve operations problem is to make use of domain specific knowledge.

30.43.3 Valve operations: method of Rivas, Rudd and Kelly

Historically, research in this area started with two pieces of work by Rudd and co-workers, one concerned with analysis and the other with the synthesis of valve operating sequences. Strictly, only the latter constitutes OPS, but it is convenient to describe first the work on analysis.

In their study, Rivas, Rudd and Kelly (1974) considered the analysis of a proposed valve sequence to determine whether it was hazardous. Such an analysis may be used to obtain a safe sequence for incorporation in operating instructions or it may be made the basis of a real-time software interlock system which leaves it to the operator to propose a valve sequence, but inhibits any hazardous sequence.

The possible states of the chemical species are shown in Figure 30.23. In pattern (a) the species A flows through the system without other contact; in (b) species A and B join and share a common path through the system; in (c) A is stopped in the system by a closed valve; in (d) A is trapped within the system by two closed valves; in (e) A is eventually flushed from the system leaving the connector empty; in (f) A is held in the system not by closed valves as in (d) but by the driving force causing the flow of species B.

A simple network of connectors is shown in Figure 30.24. It consists of two inlets through which species 1 and 2 (square boxes in Figure 30.24), respectively, can enter, an internal loop of three connectors and one outlet connector. The structure of this network is given in Table 30.19, which shows, according to the nomenclature of Figure 30.25, the number of each connector (plain numerals in Figure 30.24), the numbers of the two nodes associated with it (circled

Table 30.17 *FAULTFINDER: illustrative example – pump changeover sequence; key to fault tree for Step 8 (B.E. Kelly and Less, 1986d) (Courtesy of Elsevier Science Publishers)*

No. in fault tree	*Text*	*No. in fault tree*	*Text*	*No. in fault tree*	*Text*
1	SEQ-FAT Step 8	55	R61 REV	109	HV-F-SH Unit 15
2	SEN-F-HI Unit 67	56	P60 SOME	110	DT Row 1 Unit 17
3	SEN-F-STK Unit 67	57	HF-D-OP Unit 51	111	DT Row 5 Unit 17
4	P79 SOME	58	HV-F-OP Unit 51	112	R70 REV
5	DT Row 1 Unit 7	59	R87 REV	113	R73 REV
6	R7 REV	60	P69 SOME	114	P50 SOME
7	P6 SOME	61	P59 SOME	115	DT Row 1 Unit 19
8	R8 REV	62	A(DUMMY) Unit 52	116	SHUTDOWN Unit 17
9	P56 SOME	63	P64 SOME	117	A(DUMMY) Unit 60
10	R65 REV	64	R61 REV	118	R71 REV
11	STARTUP Unit 6	65	P72 SOME	119	HV-D-OP Unit 50
12	R62 REV	66	P68 SOME	120	HV-F-OP Unit 50
13	HV-D-OP Unit 49	67	R10 REV	121	R67 REV
14	HV-F-OP Unit 49	68	P9 SOME	122	DT Row 3 Unit 21
15	R66 REV	69	HV-F-OP Unit 51	123	HV-F-OP Unit 60
16	A(DUMMY) Unit 56	70	HV-D-OP Unit 51	124	HV-D-OP Unit 60
17	A(DUMMY) Unit 54	71	P69 SOME	125	R69 REV
18	R63 REV	72	R87 REV	126	P68 SOME
19	R9 REV	73	P71 SOME	127	A(DUMMY) Unit 57
20	NRV-F-OP Unit 3	74	P74 SOME	128	R68 REV
21	P60 SOME	75	HV-D-OP Unit 57	129	R22 NONE
22	R61 REV	76	HV-F-OP Unit 57	130	HV-D-SH Unit 22
23	HV-F-OP Unit 56	77	HV-D-OP Unit 11	131	HV-F-SH Unit 22
24	HV-D-OP Unit 56	78	HV-F-OP Unit 11	132	R87 REV
25	R59 REV	79	HV-D-OP Unit 49	133	HV-D-OP Unit 57
26	R10 REV	80	HV-F-OP Unit 49	134	HV-F-OP Unit 57
27	P59 SOME	81	HV-F-OP Unit 60	135	R87 REV
28	A(DUMMY) Unit 51	82	HV-D-OP Unit 60	136	R13 NONE
29	P69 SOME	83	HV-F-OP Unit 62	137	P67 SOME
30	R87 REV	84	HV-D-OP Unit 62	138	A(DUMMY) Unit 57
31	R10 REV	85	P68 SOME	139	R21 REV
32	P9 SOME	86	P72 SOME	140	P20 SOME
33	HV-D-OP Unit 51	87	HV-D-OP Unit 57	141	HV-F-OP Unit 57
34	HV-F-OP Unit 51	88	HV-F-OP Unit 57	142	HV-D-OP Unit 57
35	P68 SOME	89	P71 SOME	143	R13 REV
36	P72 SOME	90	P74 SOME	144	HV-F-OP Unit 50
37	HV-D-OP Unit 19	91	P63 SOME	145	HV-D-OP Unit 50
38	HV-F-OP Unit 19	92	P66 SOME	146	R74 REV
39	HV-D-OP Unit 57	93	HV-D-OP Unit 60	147	A(DUMMY) Unit 62
40	HV-F-OP Unit 57	94	HV-F-OP Unit 60	148	R69 REV
41	P74 SOME	95	HV-F-OP Unit 62	149	P68 SOME
42	P71 SOME	96	HV-D-OP Unit 62	150	HV-F-OP Unit 62
43	HV-D-OP Unit 11	97	HV-D-OP Unit 51	151	HV-D-OP Unit 62
44	HV-F-OP Unit 11	98	HV-F-OP Unit 51	152	R87 REV
45	HV-F-OP Unit 62	99	HV-D-OP Unit 56	153	A(DUMMY) Unit 57
46	HV-D-OP Unit 62	100	HV-F-OP Unit 56	154	P67 SOME
47	HV-F-OP Unit 60	101	P3 NOR	155	HV-D-OP Unit 57
48	HV-D-OP Unit 60	102	HV-D-SH Unit 1	156	HV-F-OP Unit 57
49	HV-D-OP Unit 11	103	HV-F-SH Unit 1	157	R21 REV
50	HV-F-OP Unit 11	104	P2 NOR	158	P20 SOME
51	HV-F-OP Unit 51	105	R14 NONE	159	R13 REV
52	HV-D-OP Unit 51	106	P1 NOR	160	HV-F-OP Unit 50
53	R60 REV	107	R15 NONE	161	HV-D-OP Unit 50
54	A(DUMMY) Unit 51	108	HV-D-SH Unit 15		

numerals) and the connectors which are common to the nodes. The connectors that can be closed by valves, in this case all the connectors, are shown by a valve symbol.

Thus, for example, the last entry in the table states that the two ends of connector 6 have been denoted as 3 and 2, that connectors 3 and 5 join at node 3 and connectors 2 and 4 at node 2, and that connector 6 can be closed by a valve.

A proposed valve sequence is shown in Table 30.20 The authors give an analysis of the consequences of carrying out this sequence. The essence of the method is the use of symbolic logic to determine the consequences of proposed operations such as those put forward in Table 30.20.

30.43.4 Valve operations: Rivas and Rudd planner

The second, more difficult, problem in this work is the synthesis of safe valve sequences, considered by Rivas and Rudd (1974). This may be used to generate sequences for incorporation in operating instructions or to carry out real-time automatic sequencing.

Figure 30.26 shows another simple network of connectors. The system is filled with air and the objective is to initiate flow of hydrogen to the low pressure outlet without allowing hydrogen and air to come into contact under pressure.

The method is based on defining a hierarchy of successively more explicit goals, as shown in Table 30.21. Level 0 contains the overall goal; Level I goals are tasks, ordered to satisfy the Level 0 goal; and Level II goals are at the cause and effect level and are expressed as logical propositions. The objective is to get the computer to accept some intermediate level goal and then itself to synthesize the sequence. In this work the goals at Levels 0, I and II were created manually whilst the valve sequence was synthesized by the program from the Level II goals.

The planner used by Rivas and Rudd does not itself use a hierarchy of goals but is of the non-subgoaling type. It proceeds by adding actions in the order in which they will be executed. This facilitates checking to avoid unsafe states.

In order to limit the search space, the heuristic is adopted that an action is not considered unless it contributes immediately to the achievement of a goal. In other words, the planner looks only one step ahead. The planner uses forward chaining without backtracking. As indicated earlier, this type of planner architecture is well adapted to the avoidance of unsafe states. On the other hand, the translation of high level into low level goals has to be done manually and the planner does not handle combinations and interactions of actions.

Table 30.18 *FAULTFINDER: illustrative example – pump changeover sequence; some minimum cut sets of the fault tree for Step 8 (B.E. Kelly and Lees, 1986d)*

Minimum cut set no.	*Cutset order*	*Unit no.*	*Faults*
1	1	4	HV-F-SH
2	1	6	STARTUP
3	1	49	HV-F-OP
4	1	67	SEN-STK
5	1	67	SEN-F-HI
6	2	9	NRV-F-OP
		11	HV-F-OP
7	2	54	HV-F-OP
		57	HV-F-OP

30.43.5 Operating procedures: Fusillo and Powers planner

Fusillo and Powers (1987) have extended the work of Rivas and Rudd to the synthesis of operating procedures in general. In this work procedure synthesis is represented as a state space and operators are used to move between states. A state is a vector of physical quantities such as flow, temperature and pressure, and of statuses of equipment such as valves and pumps. An operator represents the manipulation of equipment such as opening or closing a valve.

Salient features of the method are (1) system decomposition, (2) modelling, (3) constraints and (4) planning. These are now considered in turn.

System decomposition and stationary states

A system decomposition is sought which minimizes the interactions between the subsystems. In the approach adopted, a subsystem is one or more major process units, is physically isolable and, preferably, has stationary states.

A stationary state is essentially a quasi-steady-state condition. An example is a distillation column operating under total reflux. Stationary states are stable intermediate states and are invaluable in planning operating sequences.

For a continuous plant, one start-up strategy is to establish the stationary states of the subsystems with the pathways between them closed and then to integrate the subsystems to obtain the desired plant operating state.

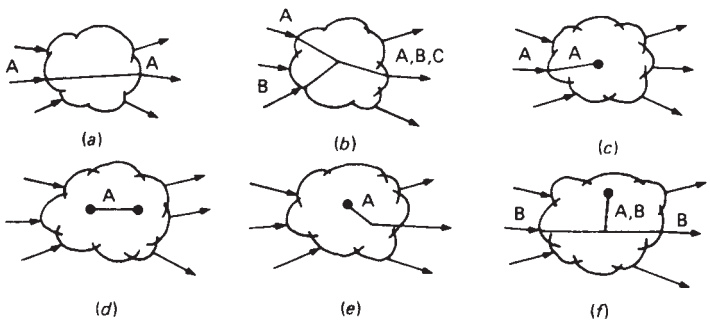


Figure 30.23 *Valve operations synthesis: states of chemical species (Rivas, Rudd and Kelly, 1974) (Courtesy of the American Institute of Chemical Engineers)*

Modelling

For each subsystem a set of global variables is defined. Each unit in the subsystem is modelled in terms of lists of effects that operations of the unit have on the variables in the subsystem. These effects are expressed in terms of a set of multiple discrete values (zero, low−low, low, medium−low, medium, medium−high, high, high−high). To aid planning, each unit type is designated as a source or sink of one or more variables. For example, a heat exchanger may be marked as a source of temperature, or a compressor as a source of flow.

Constraints

Constraints arise from a number of factors. The authors list (1) pre-conditions of unit operations, (2) requirements for a reaction, (3) production requirements, (4) hazards and (5) materials of construction. Use is made of both global and local constraints. A global constraint applies throughout the system. For example, there may be a constraint that two substances that can give an explosive mixture should not be allowed to mix. A local constraint is a pre-condition for some process task. For example, a fired heater should not be started up unless there is flow through the tubes.

Planning

Planning is effected by identifying the conditions that must be changed by the operating procedures, translating the identified changes into tasks, and ensuring that the proposed sequence of tasks will achieve the overall goals.

The planning method used is a modified means−ends analysis. Differences between the current state and the final goal state are computed. A set of intermediate goal states is formulated to reduce the difference between the current state and the final goal state. Movement from one state to another is effected by the application of operators, which are manipulations of units in the subsystems.

Planning proceeds in a hierarchical fashion. For example, the task of starting up a compressor has beneath it in the hierarchy the tasks of starting the seal flush and lubricating oil units. The planner takes an unordered list of manipulations, selects manipulations to achieve the goal and attempts to order the manipulations, using a depth-first search to effect the ordering.

The planning therefore utilizes three main strategies to reduce the search space: (1) constraints, (2) a hierarchy of tasks and (3) stationary states.

Computer program

Fusillo and Powers describe a prototype computer program, POPS, which implements the planning method just described. The program is written in LISP. Use is made of a model library structured in the form of an is-a hierarchy.

Illustrative example

A chlorination plant is used by the authors as an illustrative example of the application of the planning method.

Actions, interactions and unsafe states

The planner of Fusillo and Powers (1987) is characterized by Soutter (1993) as one that attempts to separate action generation and action ordering. It first uses means−ends analysis to generate all the necessary actions and then uses a search to order these actions. Soutter classifies this as a non-subgoaling planner. For such a planner a difficulty is presented by interactions. This is so despite the attempts of the planner, described above, to minimize such interactions.

Fusillo and Powers (1988b) have addressed the problem of interactions. When failure of the plan occurs, new actions are added. However, this modification means that actions are no longer added to the plan in the order in which they will be executed, which means that it is no longer so easy to check for unsafe states.

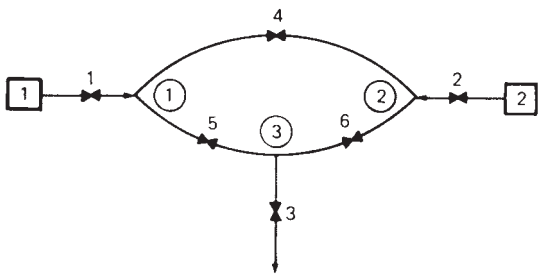


Figure 30.24 *Valve operation synthesis: network of connectors (Rivas, Rudd and Kelly, 1974) (Courtesy of the American Institute of Chemical Engineers)*

30.43.6 Purging operations: Fusillo and Powers planner

Another valve operations problem addressed by Fusillo and Powers (1988a) is the synthesis of purging procedures. In purging it is necessary to consider each species separately. Features of a purging procedure are (1) the purging fluid (2) the purging method and (3) the destination of the fluid purge.

The general approach adopted resembles that used in the authors' work on general operating procedures, as described above, in that it involves goal formulation, operator generation and task sequencing. There are,

Table 30.19 *Design of valve sequencing operations: structure of a network of connectors (Rivas, Rudd and Kelly, 1974) (Courtesy of the American Institute of Chemical Engineers)*

Connector	*Node j*	*Node l*	*Connectors joined to node j*	*Connectors joined to node l*	*Species*	*Valves*
1	1		4,5	–	1	X
2	2		4,6	–	2	X
3	3		5,6	–		X
4	1	2	1,5	2,6		X
5	1	3	1,4	3,6		X
6	3	2	3,5	2,4		X

however, certain differences that arise due to the nature of the purging problem. For goal formulation, it is not always possible to discover intermediate goals by the computation of differences as in a normal means–ends analysis. In such cases an alternative method is used which involves the discovery of goals by analysis of the global constraints.

Figure 30.25 *Valve operations synthesis: nomenclature (Rivas, Rudd and Kelly, 1974) (Courtesy of the American Institute of Chemical Engineers)*

Table 30.20 *Design of valve sequencing operations: proposed valve sequence for a network of connectors (Rivas, Rudd and Kelly, 1974) (Courtesy of the American Institute of Chemical Engineers)*

Order of operation procedure	*Open valves*	*Closed valves*
1	1, 3, 5, 6	
2	2	1, 5
3	4	2, 3

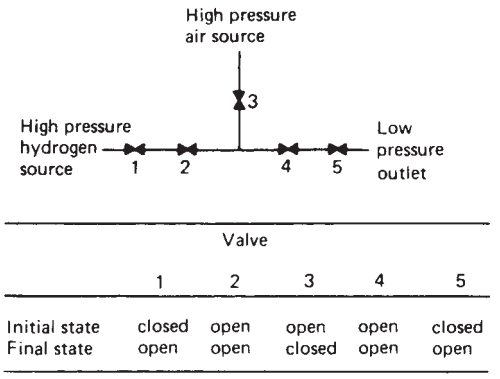


Figure 30.26 *Valve operations synthesis: second network of connectors (Rivas, Rudd and Kelly, 1974) (Courtesy of the American Institute of Chemical Engineers)*

For operator generation, the operators consist of subsystem-wide purge operations. The authors give as an illustrative example the synthesis of a purge sequence for a chloroform reaction system.

30.43.7 Valve operations: Lakshmanan and Stephanopoulos planner

Further work on the synthesis of valve operations has been described by Lakshmanan and Stephanopoulos (1988a,b, 1990).

Lakshmanan and Stephanopoulos (1988a) review the state of planning in AI with particular reference to nonlinear planning and to planning operators. They examine the problem of planning for operations such as valve sequencing and identify as a crucial problem that of the operators to be used. They consider the use of the STRIPS-style operator, which has a single set of preconditions and a single set of post-conditions, and rehearse its limitations. Such an operator cannot handle the situation in process plants where the post-conditions tend to depend on the state of the plant prior to application of the operator. They consider instead the functional operator, which has a number of sets of preconditions and of post-conditions such that a particular set of post-conditions is associated with a particular set of post-conditions. However, they suggest that using functional operators renders planning intractable.

In this and subsequent work, Lakshmanan and Stephanopoulos (1988b, 1990) describe a non-linear planning method based on hierarchical modelling and utilizing domain-specific knowledge. In this method planning proceeds in two principal phases: (1) problem formulation and (2) plan synthesis. The problem formulation phase involves (1) initial state description, (2) goal state description, (3) specification/identification of constraints and (4) specification/identification of stationary states. The plan generation phase involves (1) identification of primitive operations, (2) construction of a partial plan, and (3) synthesis of complete plans.

The approach adopted is domain-specific and utilizes a hierarchy of models. At the first, and lowest level, are the system variables and parameters. Each variable or parameter is formally defined as a collection of structured knowledge with attributes such as current value, current trend, range of values, etc. At the second level are the process 'streams', which include flows of mass, energy and momentum. The third level consists of constraining relationships such as mass, energy and momentum conservation, flow-pressure drop relations, and so on. The fourth level is the constraining relationships of the sets of defined process operating conditions. There is a corresponding hierarchy of structures, starting at the bottom with models of actual and

Table 30.21 *Design of valve sequencing operations: hierarchy of goals for synthesizing valve sequences for second network of connectors (Rivas, Rudd and Kelly, 1974) (Courtesy of the American Institute of Chemical Engineers)*

Level 0 goal	*Level I goal*	*Level II goal*	*Valve operation*
Initiate hydrogen flow to low pressure outlet	Evacuate air	Stop air flow	Close 3
		Open system to low pressure outlet	Close 5
Final sequence (close 3, open 5, open 1)	Initiate hydrogen flow		Open 1

notional ports, and rising through models of composite segments, of process units, of processing segments and of the complete plant. Planning then involves the identification of operators, their application to produce partial plans and a process of generate-and-test. The authors give as an illustrative example a catalyst regeneration problem.

In that it solves valve sequencing operation by the use of domain-specific knowledge, the program is not a general OPS planner. This planner also is characterized by Soutter (1993) as a non-subgoaling planner.

30.43.8 Valve operations: planner of Foulkes *et al.*

Another study of this kind is the work on valve and pump sequencing carried out by Foulkes *et al.* (1988). The authors begin with a statement of the OPS problem. In a typical process system there may be a very large number of potential paths and thus a very large search space. Furthermore there are then likely to be a large number of solutions that are nearly, but not quite, correct.

They give a formal treatment of the combinatorial explosion problem and illustrate it by considering the plant used in the work of Rivas and Rudd (1974), in which the number M of on–off valves was 17. The number of different combinations of valve state is thus $2^M = 131{,}072$.

Foulkes *et al.* argue that where the number of potential valve changes is large, the prior formulation of operating sequences for infrequently performed operations is not practical and is not attempted. The purpose of the work was to devise a system that could be used off line to devise on demand a suitable sequence for a particular operation.

They describe a method in which the plant is decomposed into the elements 'pipe fragment' and 'pump fragment', which consist of a piece of pipe with a valve or a pump, respectively, on the end. Planning proceeds by searching first for paths and then for sequences of valve and pump operations, subject to constraints.

The program was written in Prolog and illustrates the exploitation of the facilities of that language for declaring 'operators', for 'pattern matching' and for depth-first search.

30.43.9 Operating procedures: Soutter and Chung planner

An attempt to develop a general-purpose method OPS known as the Chemical Engineering Planner (CEP), is described by Soutter and Chung (1995b). This planner is intended to perform both general OPS tasks and valve operations synthesis.

CEP is a hierarchical planner. It receives higher level goals and translates them into lower level goals. The planning engine is complemented by an inference engine, which performs the goal translation just described. This inference engine uses backward chaining. CEP is believed to be the first planner to use both types of engine.

CEP is described as a STRIPS-based planner, apparently primarily in recognition of its use of STRIPS-type operators. The planning engine in CEP, however, follows the strategy of least commitment, utilizing partial ordering. In other words, CEP is a non-linear planner. These two features of CEP, backward chaining and non-linear planning, keep it compatible with the main thrust of development in AI planning.

The planner in CEP is assisted by 'agents' that perform various specialist functions. One agent monitors conflicts, another advises on complex goals, and so on.

The problem of unsafe states is handled in CEP in terms of global constraints. A global constraint is a set of unsafe states. Goals of prevention are used to prevent entry into an unsafe state.

CEP utilizes a problems specification language. This language describes four types of knowledge: (1) the domain objects, (2) the operators, (3) the global constraints and (4) the problem specification.

The inference engine utilizes inference operators. For example, the high level goal *flow* (*inlet, outlet*) is the establishment of flow from inlet to outlet of a pipe. This is translated by the inference engine using the appropriate inference operator into the lower level goals *open* (*inlet, middle*) and *flow* (*middle, outlet*). The latter is further translated in a similar way. The relevant inference operator is:

```
operator FindFlow
(
 pipe?a; pipe ?b
 pipe ?c;

 expand
 *flow(?a, ?b)
 using
   open(?a, ?b)
   flow(?c, ?b)
 end
)
```

In some cases an inference operator that defines a hierarchy is termed a hierarchical operator.

As an illustration of planning using CEP, consider the problem of the start-up of a compressor described by I.S. Sutton (1992), in an account of the writing of operating instructions. The problem may be explained by reference to Figure 30.27. Figure 30.27(a) shows the compressor V-206 itself. The task set is to shut-down compressor C-206. Figure 30.27(b) shows the steps in the shut-down sequence given by Sutton.

For the planner the task is to achieve the goal *shut-down of V-206 is true.* Figure 30.27(c) shows the definition of V-206 as an object. Figure 30.27(d) shows a typical hierarchical operator *DoShutdown.* Figure 30.27(e) shows the translation of the high level goal into the lower level, or induced, goals. Figure 30.27(f) shows a typical planning operator *CheckIdle.*

The operation of the planner is indicated by the following brief outline. The goal is *shut-down of V-206 is true.* This goal is translated by the inference engine using the hierarchical operator *DoShutdown* into the three subgoals:

(1) pressure of V-206 is atmospheric;
(2) isolated of V-206 is true;
(3) turned-off of V-206 is true.

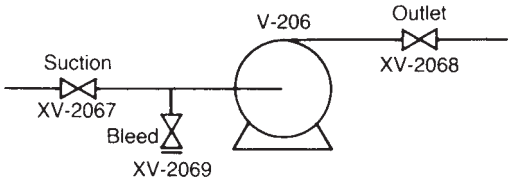
The planner selects the first subgoal and proposes the addition to the plan of the action Depressure. The corresponding operator has the pre-conditions

(1) pressure of V-206 is medium;
(2) bleed of V-206 is open;

and the effect

(1) pressure of V-206 is atmospheric.

However, if this action is entered as the start of the plan, a global constraint is violated. This global constraint is that the bleed valve should not be open when the compressor is on. This constraint is violated because the initial state is



(a)

```
Close suction valve XV-2067
Wait until pressure of V-206 pressure (PI-2065)
   is medium (less than 35 psig)
Stop compressor (SW-2066)
Confirm current through meter M-2066 zero
Close discharge valve XV-2068
Open bleed valve XV-2069
Wait until pressure of V-206 is zero
Close bleed valve XV-2069
```

(b)

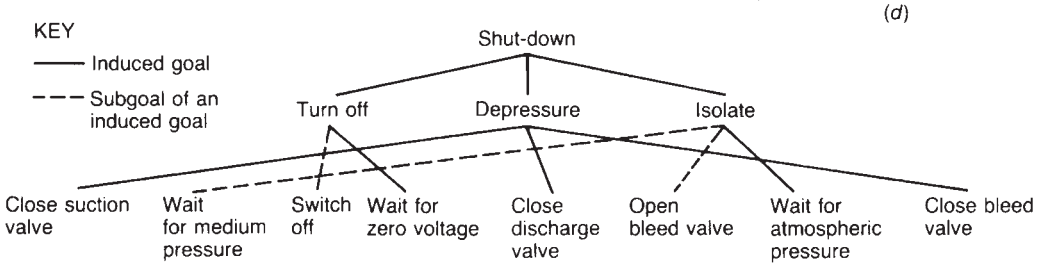
```
frame(compressor isa machine).
instance(V-206 isa compressor.
   [PressureGauge is PI-2065,
   Switch is SW-2066,
   Meter is M-2066])
```

(c)

```
operator DoShutdown
{
   compressor ?c;

   expand
    · shutdown of ?c is true
   using
      pressure of ?c is atmosphere;
      isolated of ?c is true;
      turned_off of ?c is true;
   end
}
```

(d)



(e)

```
operator Checkidle
{
    compressor ?c;

    achieve
     · checkidle of ?c is true;
    using
       state of ?c is off;
    end

    print
       'Confirm the current through meter;
       (?m) [Meter of ?c is ?m;] 'is zero';
}
```

(f)

Figure 30.27 *Operating Procedure synthesis: shut-down of a compressor (Soutterand Chung, 1995b): (a) Compressor system V-206; (b) steps in shut-down sequence (after Sutton, 1992); (c) definition of compressor V-206 as an object; (d) hierarchial operator DoShutdown; (e) translation of high level goal into low level goals; (f) planning operator Checkidle*

that the compressor is on. In order to prevent violation a new action is added to switch off the compressor before the action *Depressure* is taken.

The OPS output given by the planner is essentially the same as that shown in Figure 30.27(b).

30.43.10 Operation procedures network

Most work on OPS is based on a component oriented approach. Work utilizing instead Forbus' qualitative process theory (QPT) has been described by Rotstein, Lavie and Lewin (1992), who propose the concept of an operation procedures network (OPNet).

The motivation for this approach is the deficiencies of the component based method in the treatment of batch processes. QPT lends itself better to the handling of the basic transformations of mass and energy in such processes.

The method described by the authors involves the following stages: (1) the definition and ordering of the mass

and energy balances, (2) their instantiation in a particular plant structure, (3) their ordering in space and time, and (4) the synthesis of the operating procedures.

30.44 Process Monitoring

Process monitoring has several aspects. One is the detection of a disturbance or abnormality which falls short of an identifiable fault and which does not necessarily result in any process alarm. The second is the handling of alarms caused by some fault or operator action, the diagnosis of the fault and the response to it. The third is the detection of a incipient malfunction which has not yet resulted in a fault or an alarm. There are advanced methods, including AI techniques, which address all three of these. The first aspect is considered in this section and the others in the two subsequent sections. An overview of some of the methods available for these functions is given in *Fault Detection and Diagnosis in Chemical and Petrochemical Processes* (Himmelblau, 1978).

30.44.1 Disturbance characterization

One form of monitoring which is in widespread use is data reconciliation. It is important for process operation to have a valid mass and energy balance. Factors such as process transients and measuring instrument errors mean that it is not a trivial matter to obtain such balances.

Data reconciliation is able to draw on a large body of work on estimation and filtering, and some form of data reconciliation is quite common practice. Quite separately from this, the process operator monitors the process and comes to a judgment as to whether it is in a normal condition or whether there is a disturbance or abnormality. In doing this he or she makes use of his or her mental model and of heuristics such as limit, or landmark, values and rules of thumb.

There is now emerging a formal approach to the interpretation of process information. Thus, Cheung and Stephanopoulos (1990) have described a methodology for transforming the information given by trend records into indicators of process state that are sufficiently quantitative to allow the operator to make powerful inferences about trends in variables which are not measured.

Some of the difficulties faced by the process operator in interpreting process information are enumerated by Cheung and Stephanopoulos. Some causes of these difficulties are that there may be (1) process outputs changing at different rates, (2) dead time and inverse responses, (3) interactions between control loops, (4) conflicting information from sensors and (5) incomplete information due to lost' sensors. The operator may therefore find it have difficult to (1) distinguish between normal and abnormal conditions, (2) assess current trends and anticipate future states, (3) identify the causes of these trends and (4) plan and schedule sequences of operating steps leading to a new operating level.

Another approach is that described by Whiteley and Davis (1992). These authors treat the problem in terms of adaptive pattern recognition and develop a qualitative interpretation of the process information.

30.44.2 Trend and state display

Turning to displays of the process trends and state, computer graphics have made it possible to create displays that previously could not be contemplated. The starting point for the design of such displays should be a consideration of the operator's tasks and problems, and a display should evolve as a solution to these. Otherwise there is a danger that the display will be a solution looking for a problem. Various types of display have been developed by computer manufacturers for loop parameters, trend records, etc.

Display of system state is one of the most important types of display. Some illustrative examples of this type of display are given in Figures 30.28–Figure 30.31.

Figure 30.28 represents a mimic diagram. This particularly display is simply a colour slide which the operator uses to help him identify equipments. VDU displays can be provided on similar lines with continuous updating of equipment status.

Figure 30.29, after Wolff (1970), shows a polar plot of eight variables in which the length of each vector is proportional to the measured value. The vectors are scaled so that at the normal values their tips touch a common circle. Figure 30.30, after H.H. Bowen (1967), illustrates a rather similar principle in which the variable vectors are scaled to form a common surface, Figure 30.30(a) showing a normal condition and Figure 30.30(b) an abnormal one. Figure 30.31, after Stainthorp and West (1974), shows a status array for a distillation column with methanol and propanol feeds. The rows represent process variables and the items in them absolute, deviation and rate-of-change alarms or the normal condition as shown in Figure 30.31(a). Figures 30.31(b)–(f) correspond to the conditions normal operation, severe upset, shut-down necessary, clear for start-up and near-normal operation (during start-up), respectively.

Displays have been described for facilities such as manual control (e.g. Crawley, 1968), scheduling (e.g. Ketteringham, O'Brien and Cole, 1970; Ketteringham and O'Brien, 1974), etc. Other displays for activities such as malfunction detection are described below.

The degree of sophistication in the information processing underlying a display varies greatly and may not be apparent from the display itself. Thus, the polar and surface plots illustrated above require only scaling of the measurements, while other displays involve the use of predictive models, estimation techniques, etc.

30.44.3 Multi-media aids

Another development is the use of multi-media aids that exploit the potential of combinations of audio, visual and other forms of information presentation. Accounts are given by Alty and McCartney (1991) and Alty and Bergan (1992).

The approach taken in this work to use multi-media aids under the control of a knowledge based system. Some media that are used in such work include: text, static graphics and diagrams, dynamic graphics, animation, sound, speech and video. There is a wealth of research available in the human factors literature on the relative efficacy of different media for the transmission of different types of information.

A system that uses alternative media needs to be supported by a resource management facility that selects and schedules the media. In the work described, use is made of a knowledge based system for this purpose.

There is no lack of options for the design of such a system, but it is still early days in the development of the principles that should govern such design. Alty and Bergan (1992) have described a laboratory study involving the Grossman water bath experiment on manual control with multi-media aiding. Experiments on the use of multi-media

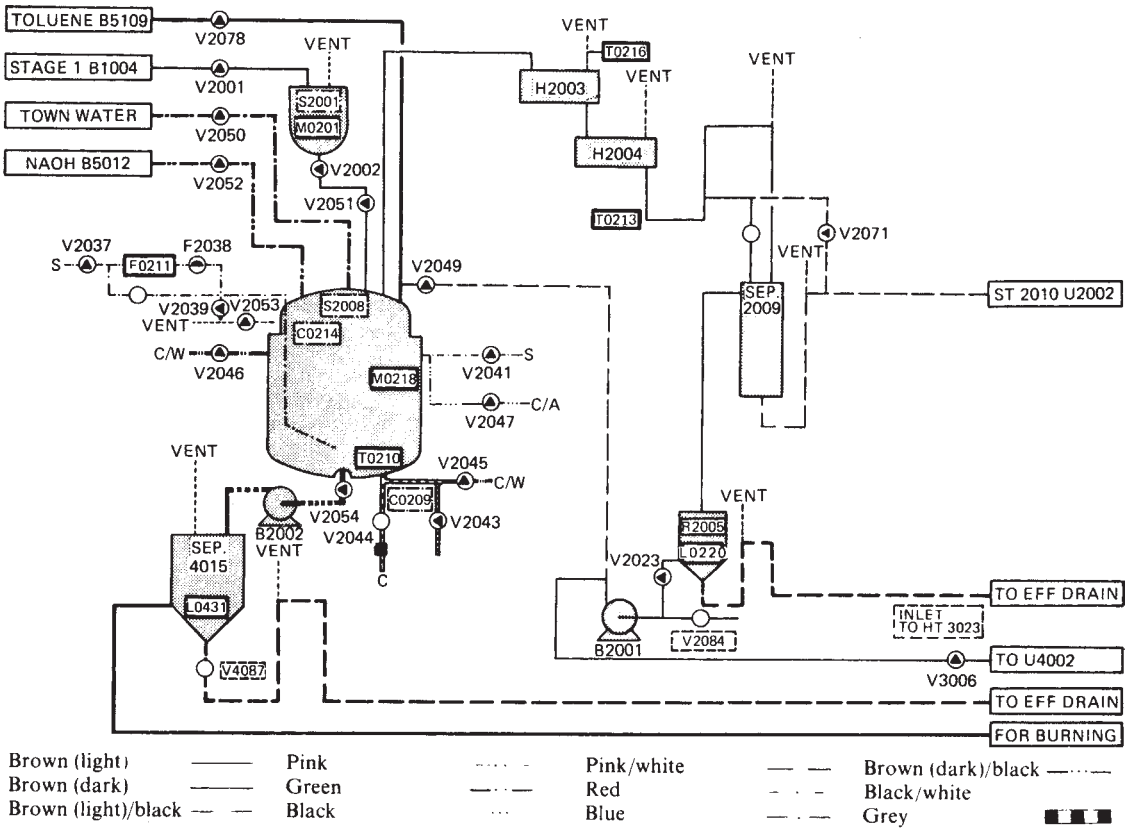


Figure 30.28 *Computer graphics displays of system state – mimic diagram (The Boots Company Ltd), In the original display full use is made of colours. Coloured pipe lines in the original are shown in the above figure according to the code shown*

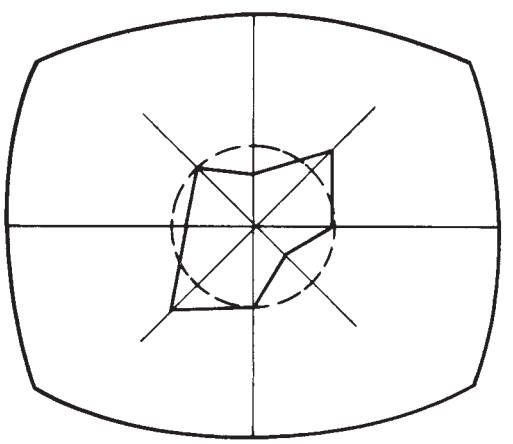


Figure 30.29 *Computer graphic displays of system state – polar plot (after Wolff, 1970) (Courtesy of the Scientific Instrument Research Association)*

facilities in industrial process control rooms have been conducted and the reception is said to have been favourable.

30.44.4 Expert systems

There are also developments in the application of expert systems to process monitoring. There is a considerable monitoring element in the expert systems for process control described in Section 30.35. In some expert systems, however, assistance to the process operator in assimilating process information is the prime aim. An example is ESCORT, described by Sachs, Paterson and Turner (1985).

30.45 Fault Administration

The second aspect of process monitoring is fault administration. One of the principal functions of a computer system in process control is to assist the operator in the handling of fault conditions. The use of the computer to enhance the alarm system has been described in Chapter 14. Among the enhancements mentioned there are systems in which alarm diagnosis, or alarm analysis, is performed. In those early systems the alarm diagnosis facilities provided were fairly basic and the data structure for the diagnosis was created manually. Since then a good deal of work has been done on alarm diagnosis systems which have more

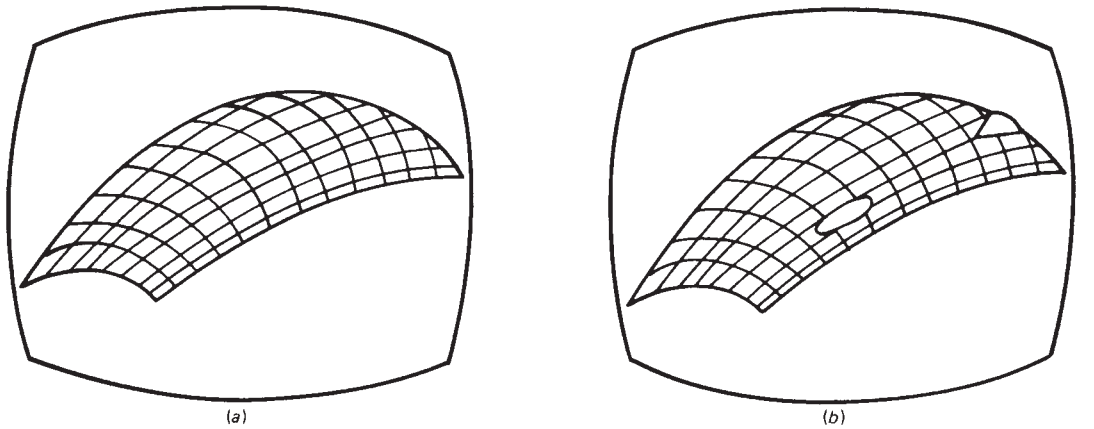


Figure 30.30 *Computer graphic displays of system state – surface plot (after H.H. Bowen, 1967): (a) normal condition; (b) abnormal condition (Courtesy of Taylor & Francis Ltd)*

Condition code	Meaning of code value of variable is
HC	⩾ High limit
LC	⩽ Low limit
H	⩾ Set point $+a$ limit
L	⩽ Set point $-a$ limit
R	Rising faster than θ
N	Falling faster than θ
F	Normal

(a)

Increasing seriousness of condition of variable

Increasing importance of variable

(1)							(m)	Status code and column totals	
HC	H	R	LC	L	F	N		F432	Steam to reboiler
HC	H	R	LC	L	F	N		T433	Upper temperature
LC	L	F	HC	H	R	N		T431	Bottom temperature
LC	L	F	HC	H	R	N		L431	Base tank level
HC	H	R	LC	L	F	N		L432	Reflux drum level
LC	L	F	HC	H	R	N		X431	Methanol feed
LC	L	F	HC	H	R	N		X432	Propanol feed

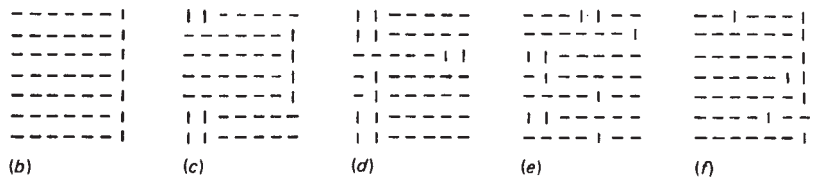


Figure 30.31 *Computer graphic displays of system state – status array (Stainthorp and West, 1974): (a) Key to status array; (b) normal operation; (c) severe upset condition; (d) shut-down necessary; (e) clear for start-up; (f) near-normal operation (Courtesy of the Institution of Chemical Engineers)*

advanced facilities and in which the alarm data structure is generated automatically.

The bulk of the work on fault administration has been concerned with alarm handling and diagnosis, although there is some work on other aspects such as on advice for corrective actions and on prediction times at which excursions across alarm limits will occur.

Fault administration has proved particularly attractive to workers in AI and expert systems. For example, estimates of the proportion of applications of process industry expert systems that are in this field range from some one-third to one-half.

A number of distinct phases may be discerned in work on alarm handling and diagnosis: (1) manual design of alarm

analysis systems for industrial nuclear power stations; (2) early explorations of the systematic creation of the alarm data structure; (3) disturbance analysis systems, prompted by the Three Mile Island accident; (4) expert systems and (5) various AI approaches, notably those based on modelling and on neural networks. A review of developments to the third of these phases has been given by Lees (1983c).

Fault administration is another field where qualitative modelling, including fault propagation modelling, plays a central role in many of the methodologies developed.

30.45.1 Alarm structure and display

Before describing some of the advanced aids developed for handling alarms, it is pertinent to consider the quality of the basic alarm system provided. It makes little sense to draft a sophisticated alarm diagnosis system onto a fundamentally defective alarm system design. Two aspects of this design are of particular relevance. One is the structure of the alarms and the other their display.

The issue of the structure of the alarm system has been addressed in several different ways. Some of these take as their starting point failures and others take the resulting undesirable events. Thus, one approach is to list the faults that it is desirable to be able to identify because they are in some way significant, and to assess the ability of the system to give an unambiguous indication that a particular fault, and no other, has occurred. In other words, an assessment is made of the degree of fault discrimination. The problem is akin to that of the observability of process variables. Work in this area has been described by Park and Himmelblau (1987).

Another approach, described by Lambert (1977) and based on his concept of the probabilistic 'importance' of the events in a fault tree, is to create fault trees for the principal undesired events on the plant and to identify in each tree measurable events which rank high in importance.

The approach taken by Modarres and Cadman (1986) is not dissimilar, but centres rather on the effectiveness of the alarm system in supporting the activities of the process operator. The method described is based on the use of goal trees for the operation of the plant and of decision trees, which can be constructed in parallel to show all the operator actions required to achieve each goal and also the consequences of failure to achieve the goal.

These various approaches are not, of course, mutually exclusive.

30.45.2 Alarm trees

Work on alarm diagnosis for process plants took as its starting point the use of alarm handling systems in nuclear plants, described in Chapter 14. Thus Welbourne (1965, 1968) gives an account of the use of alarm trees. A simple alarm tree is shown in Figure 30.32. The alarm tree gives the relations between process alarms, and does so economically without duplication of information. There is no emphasis on any particular top event. Deduced alarms may be added to the tree, but the tree is self-sufficient without them.

Early work on alarm diagnosis for process plants was done by Andow and Lees (Andow, 1973; Andow and Lees, 1975) and Powers (1975). Andow and Lees explicitly took the view that alarms diagnosis was likely to find a role on process plants only if the necessary knowledge base could be created with reasonable economy, and that this knowledge base should consist primarily of models rather than rules.

They describe a method for creating the alarm data structure based on fault propagation models of the type described in Section 30.36. The flow diagram is converted into a block diagram of linked unit models. The models used are simple functional models such as that of the mixing tank shown in Figure 30.33. This representation is then converted into a network of interacting process variables, effectively a digraph, and this network is then reduced to the network of those process variables on which there are alarms. The method utilizes list processing to produce the alarm network automatically from the unit models. Figure 30.34 shows two alarm trees for the mixing tank system. Whereas the conventional alarm tree is as shown in Figure 30.34(a), the alarm tree obtained by this method is that given in Figure 30.34(b).

The type of display envisaged by Andow and Lees is illustrated in Table 30.22, which is a form of truth table. In a conventional truth table an active alarm is TRUE and an inactive one is FALSE. The truth value of deduced alarm X depends on the truth values of the set of process alarms. This deterministic approach may be replaced by a probabilistic one, as used in Table 30.22. In this table the evaluation TRUE is obtained if the sum of the products of the process alarms A–I and the probability weightings

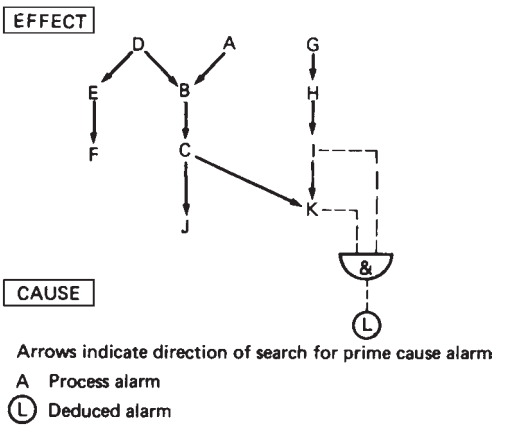


Figure 30.32 *Alarm tree including a deduced alarm (Andow and Lees, 1975) (Courtesy of the Institution of Chemical Engineers)*

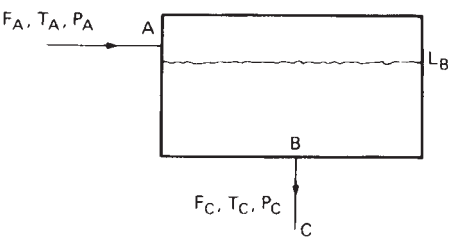


Figure 30.33 *Mixing tank system (Andow and Lees, 1975). Functional model equations: $dL_B/dt = f(F_A, F_C)$; $dT_c/dt = f(T_A, L_B, F_A)$; $P_A = f(T_c, L_B)$; $P_B = f(P_A L_B)$; $F_c = f(P_B, P_C)$ (Courtesy of the Institution of Chemical Engineers)*

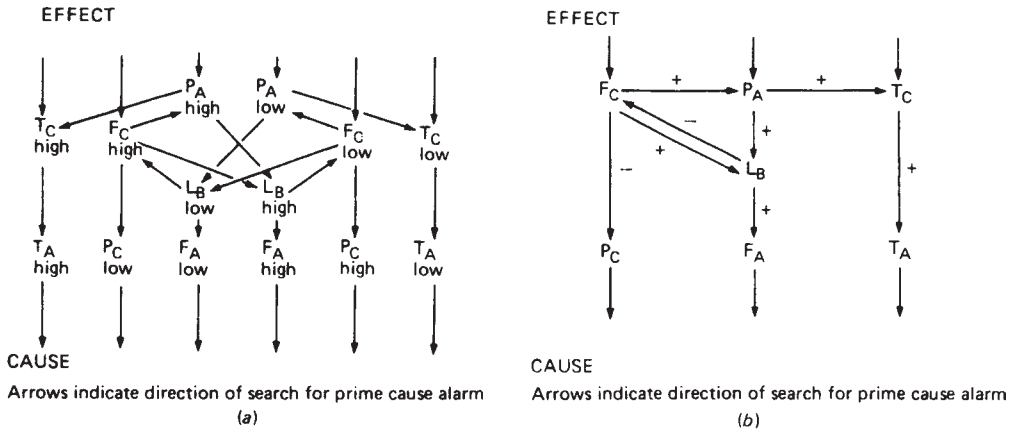


Figure 30.34 *Alarm trees for mixing tank system (Andow and Lees, 1975): (a) conventional alarm tree; (b) process variable-based alarm tree (Courtesy of the Institution of Chemical Engineers)*

Table 30.22 *Modified 'truth table' containing probablities for a deduced alarm (Andow and Lees, 1975) (Courtesy of the institution of Chemical Engineers)*

Process alarms and the their probability weightings									*Target value*	*Deduced alarm message*
A	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*		
0.7	0.45	0.8	0.3	0.65	–	–	–	–	2.1	Fault X
0.3	0.75	–	–	–	0.9	0.8	–	–	1.85	Fault Y
–	0.2	0.45	–	0.65	0.7	–	0.65	0.3	1.75	Fault Z

exceeds the target value, active alarms having a value 1 and inactive ones 0. The normal truth table is a special case of this more general table.

30.45.3 Fault trees

Another early approach taken to the creation of an alarm data structure is the use of fault trees. A fault tree shows the relation between the top event, which is usually some hazardous condition, and the bottom events, which are typically mechanical faults. It tends to emphasize these top and bottom events. A separate fault tree is needed for each top event.

The use of alarm structures based on fault trees was suggested in early work by Powers and co-workers. An outline of an approach towards the synthesis of fault trees was been described by Powers and Tompkins (1974a,b), whilst Powers (1975) conducted experiments in which a fault tree was used to assist an operator to diagnose inert gas blanketing in a heat exchanger. The use of fault trees to create the alarm data structure was also investigated by Martin-Solis, Andow and Lees (1977). They used fault propagation models to derive mini-fault trees, as already described in Section 30.42, and obtained alarm structures essentially similar to digraphs containing AND gates. The work showed that the veracity of the instrument readings is a significant problem in computer alarm diagnosis, just as it is in human fault diagnosis.

This work on alarm diagnosis by Andow, Lees and co-workers was the origin of their work on fault propagation modelling, which has since found further application in hazard identification and fault tree synthesis.

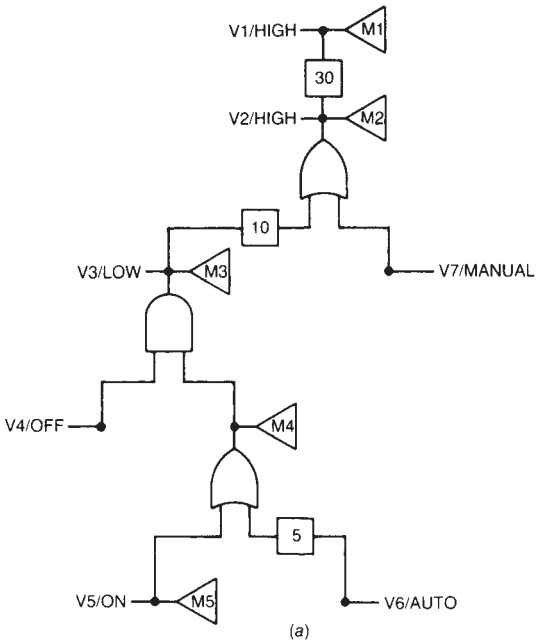
30.45.4 Disturbance analysis systems

The accident in 1979 at Three Mile Island (TMI), described in Appendix 21, highlighted the importance of alarm systems and alarm diagnosis. The problems experienced by the operators led the task force to make recommendations for the use of a safety status display and for work to establish the feasibility of a disturbance analysis system (DAS).

TMI gave impetus to work in course at the Electrical Power Research Institute (EPRI), Palo Alto, California, described by Frogner and Meijer (1978, 1980), Long (1980), Long *et al.* (1980) and Meijer, Frogner and Long (1980).

An initial study was made of the potential benefits of a DAS. The assessment was made by selecting suitable nuclear power station subsystems, obtaining data on the outages of these subsystems in existing stations, and estimating the proportion of these outages which would probably have been avoided using a DAS facility. An initial survey showed that out of 1161 outages there were 274 that appeared preventable by more rapid action aided by a DAS. These authors subsequently did work with an experimental DAS that showed appreciable reductions in operator response time between the two cases where the DAS was not used and where it was.

Long gives an analysis of some of facilities that a DAS might provide. It could upgrade the plant signals and infer important parameters from simple analytical models, could monitor the mode of operation and compare the configuration with simple plant configuration models, and could recognize disturbances and provide assistance with procedures for off-normal conditions.



(a)

Time* (s)	Event	Result of the cause–consequence analysis
0	V4 = OFF and V5 = ON	M4 and M5 active M3 potentially active
1	V3 = LOW	M3, M4 and M5 active M2 potentially active
11	V2 = HIGH	M2,...., M5 active M1 potentially active
41	V1 = HIGH	M1,...., M5 active

*Initial conditions: $V_1 \neq$ high, $V_2 \neq$ high, $V_3 \neq$ low.

(b)

Figure 30.35 *Disturbance analysis system: conceptual example of a cause-consequence tree and of a sequence of events in the tree (Frogner and Meijer, 1980): (a) cause–consequence tree; (b) sequence of events (Courtesy of the Electrical Power Research Institute)*

The DAS developed in this work utilizes a multi-level methodology. Level 1 is based on decision tables, the inputs to a table being one or more sensor signals and the output a message. Level 2 utilizes the cause–consequence tree (CCT) method. Level 3 provides a facility for the use of quantitative models.

The Level 1 decision tables are relatively simple and serve to reduce the proportion of signals passed on to Level 2. The more complex signal patterns are analysed in Level 2 using the CCTs. The general form of the CCTs and the terminology used are shown in Figure 30.35. The tree in Figure 30.35(a) consists of nodes connected by arcs, the nodes being associated with attributes. These attributes are a variable identifier (V1, V2, . . .), a required condition for the variable (HI, LO, . . .), a message identifier (M1, M2, . . .), a logic gate (AND, OR, . . .) and a time delay (5 s, 10 s, . . .).

The methodology defines a node as observable if it associated with a variable measured by a sensor. An observable node is given a required condition. If this condition is met, the node is active. A time delay is the expected minimum time between two events. If the observed time between two events is less than the time delay, or if the observed sequence does not correspond to that in the tree, it is assumed that the branch is not active. The use of time delays, therefore, contributes to the unique identification of a disturbance. If a node is active and it has associated with it a message, that message is also active. If a node is not active solely because the time so far elapsed is less than the time delay, the node and the associated message are potentially active. A typical sequence of events for the CCT shown in Figure 30.35(a) is shown in Figure 30.35(b).

The status of a variable is shown by one of a set of status indicators. These status indicators are listed in Figure 30.36(a) and the state transition diagram for the indicators is shown in Figure 30.36(b). The normal value of a status indicator for a variable is S_0. If a value goes outside its limit, the indicator is set at S_1. When the disturbance analysis starts, the indicator is set at S_2. The result of a disturbance analysis causes the indicator to be set at S_4 if a satisfactory message is determined or at S_3 if the cause cannot be found. Once the value is outside its limits, this value is latched for a period of T_1 seconds for an S_4 variable or T_2 seconds for an S_3 variable. If the value returns inside the limit, it is set at S_5 once the latching period has elapsed. Again the disturbance analysis is actuated, but this time with low priority and the indicator is set at S_6. When the disturbance analysis is complete, the indicator is set at S_0. Status indicators S_7–S_9 and S_{10} are associated with algorithms that deal with spurious events and failure events, respectively. Methods are given for the treatment of faults on, and of temporary excursions of, sensors.

The data acquisition system (DAS) was tested on a training simulator and operated by process operators from nuclear power plants. In general, it behaved reasonably well, but the reduction in average operator response time from 34 to 30 seconds was not great. The time required for the operator to move physically to the appropriate part of the control room accounted for an appreciable fraction of the total response time in both cases.

A number of human factors points emerged during this work, of which just one may be quoted. Frogner and Meijer (1980) state:

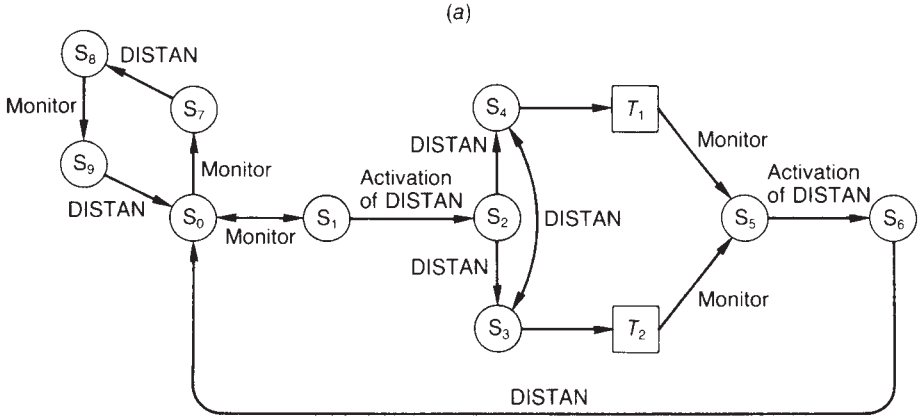
> The DAS effectiveness is reduced if the results of the diagnosis are presented without adequately conveying the status of the process. For the operator to exercise judgement and not just function as an automaton, he must understand the state of the plant and the reason for his action. In this respect, the condensed one-line DAS messages need improvement. It is recommended that future systems incorporate DAS messages into a more informative picture of the state of the process; for example, by using process and instrumentation diagrams.

In this method, the CCTs are created manually by the analyst. Considerable effort was required to produce the model database, which is plant specific, and this effort was seen as a factor limiting application.

Another major project on disturbance analysis which took place at about the same time was the joint project between the Gesellschaft fur Reaktorsicherheit (GRS) at Garching, in then West Germany, and the Institut for Atomenergi at Halden, Norway, involving development of

S_0	Normal condition: variable is within its specified limits
S_1	Value was within limits and it just went outside
S_2	Disturbance analysis is currently performed due to S_1
S_3	Analysis due to S_1 is complete: cause not known
S_4	Analysis due to S_1 is complete: cause known
S_5	Value was outside limits and it just went inside
S_6	Disturbance analysis is currently performed due to S_5
S_7	Too high a frequency of events has been registered for this variable. Analysis is being performed or waiting on DAS
S_8	Variable causing spurious events
S_9	Spurious event causing variable becomes normal. Analysis is being performed or waiting on DAS
S_{10}	False event

(*a*)



(*b*)

Figure 30.36 *Disturbance analysis system (Frogner and Meijer, 1980): (a) status indicators; (b) state transition diagram for status indicators. DISTAN denotes Disturbance Analyser (Courtesy of the Electrical Power Research Institute)*

DAS systems known as STAR for the nuclear power plants at Grafenrheinfeld and Biblis in the former country.

As in the EPRI work the fault propagation is represented by cause–consequence diagrams (CCDs). Some of the differences between the EPRI and GRS systems have described by Frogner and Meijer (1978) and Bastl and Felkel (1981).

30.45.5 Expert systems

One of the modes of operation of the commercial expert system PICON, referred to above in Section 30.36, is the alarm management mode. Accounts of its operation in this mode have given by Berkovitch and Baker-Counsell (1985), R.L. Moore (1985) and Rand (1987). The latter describes the creation of the rule base by observation of operators, interviewing of operators and operator input of rules, with the latter being favoured.

An account of ESCORT, a system for detection and diagnosis of faults and the detection of instrument malfunction is given by Sachs, Paterson and Turner (1985).

Two large expert system projects FALCON (Shirley, 1987) and REACTOR (W.R. Nelson, 1982) on systems with large rule bases have been carried out and are reported to have had success in some applications.

An expert system based on EXPERT has been developed by Mizoguchi (1983). The application described is fault diagnosis on a nuclear reactor primary cooling system. The rule base consists of some 76 rules, of which 6 are finding-to-finding, 60 finding-to-hypothesis and 10 hypothesis-to-hypothesis rules.

In the expert system for malfunction diagnosis described by Shum *et al.* (1988), use is made of a hierarchical structure in which the nodes represent particular malfunction hypotheses. Use is made of the concept of 'specialists', a concept used also in the design language DSPL, referred to in Section 30.27. There is a collection of 'specialists' coordinated to arrive at an overall diagnosis. Each specialist possesses compiled and qualitative knowledge for the evaluation of a hypothesis. The method is claimed to be especially effective at handling multiple symptoms and multiple malfunctions.

There are a number of other systems which are described as expert systems, but which place emphasis on models as well as rules, as described below.

30.45.6 Model-based methods

Iri *et al.* (1979) have used digraph models to represent the alarm structure of a plant. This work has subsequently been developed in a number of studies, including those of Kokawa, Miyaki and Shingai (1983), Shiozaki *et al.* (1985) and Qian (1990).

An expert system MODEX for malfunction diagnosis has been described by Rich and Venkatasubramanian (1987), and its successor MODEX2 has been described by Venkatasubramanian and Rich (1988). The system is based on a two-tier architecture, consisting of a bottom level of process specific, compiled knowledge and a top level of process general, deep level knowledge. An agenda-based inference control algorithm generates malfunction hypotheses from structural and functional information about the process. Diagnostic reasoning alternates between the two levels.

Finch, Oyeleye and Kramer (1990) given an account of a program MIDAS which diagnoses the causes of plant disturbances, including equipment degradation and failure, sensor failure, incorrect operation and external disturbances. The diagnosis utilizes an event model to construct clusters of events, each cluster being associated with a single fault. The program handles features such as variations in order of detection, complex dynamics, sensor failures and multiple plant failures.

In the work of Ramesh, Shum and Davies (1988) the emphasis is on the nature of the tasks involved in diagnosis. One task is associated with the plant sensor and another with the product quality data. Ramesh, Davies and Schwenzer (1992) develop this approach, with an investigation of the information processing tasks underlying diagnostic reasoning.

The approach described by Grantham and Ungar (1990) differs from others in two main ways. It utilizes Forbus' qualitative process theory (QPT), and it can automatically modify the unit models, allowing identification of faults that significantly change unit behaviour. The authors characterize their method as one that operates at a higher level of generality, and hence robustness, by giving the system an ability to create its own models from a description of the substances and objects present and the prevailing process conditions. It has the ability to identify faults that change significantly the mode of operation of a unit, without the need for explicit fault modes.

A prototype expert system PRODES for fault diagnosis is described by Labadibi and McGreavy (1992). The system utilizes fault propagation models elicited from the user and cast in the form of decision tables.

Saelid, Mjaavatten and Fjalestad (1992) have described an expert system for operator support with object oriented features and utilizing an expert system shell. The system detects disturbances in the connections between units, identifies the faulty unit and then initiates diagnosis of that unit. This internal unit diagnosis utilizes a combination of process models, fault trees and Kalman filtering.

30.45.7 Fault-tree-based methods

Ulerich and Powers (1988) have described a method for fault diagnosis based on fault trees. This work extends the earlier work of Powers (1975) on this topic. It utilizes the FTS methodology for fault tree synthesis from digraphs developed by Powers and co-workers, as described in Section 30.41. A prior fault tree is created. From this prior tree there is then created a further fault detection tree in which there is attached to each basic event a verification; the event is treated as valid only if it is verified. The verification consists of a set of process indications that must all be satisfied.

30.45.8 Goal tree–success tree method

The expert system GOTRES for fault diagnosis is described by Chung, Modarres and Hunt (1989). The system is based on the goal tree–success tree (GTST) method illustrated in Figure 30.37. The tree is developed from the

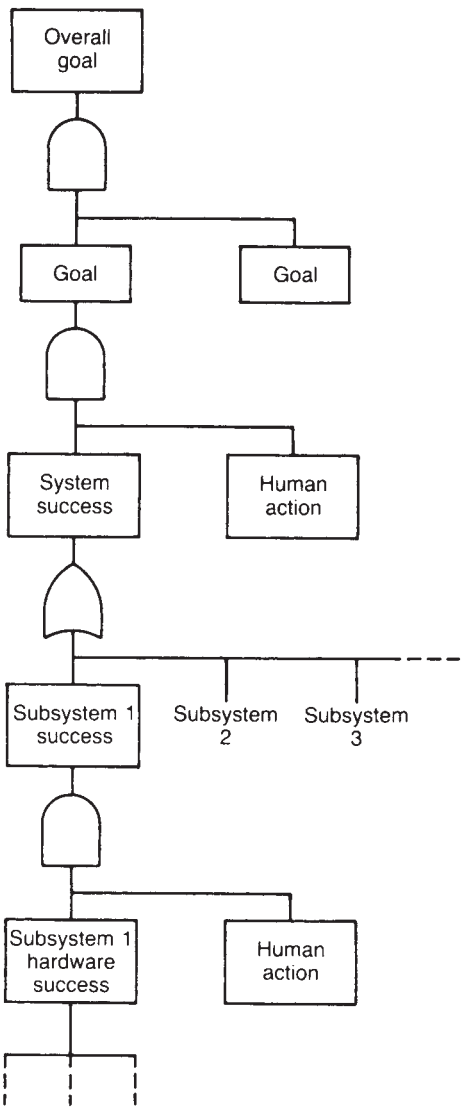


Figure 30.37 *An outline goal tree–success tree*

process objective at the top, downwards to successively lower levels of goal. Since all goals are necessary for success, the logic gates relating the goals are all AND gates. The nature of the tree changes at the point where it is no longer possible to develop the tree without reference to hardware. Attached to each goal is a goal verification procedure that uses relevant process indicators to determine whether the goal is satisfied.

The authors state that experience shows that the use of a success tree rather than a failure, or fault, tree allows a more succinct treatment. They also suggest that a success orientation corresponds better to human thinking, and illustrate this with the analogy of a car journey, where the driver concentrates on the success paths rather than the failure paths.

Chen and Modarres (1992) describe an expert system FAX for the diagnosis of faults and advice on corrective actions, with emphasis on the latter. The control objective is represented as a goal tree with success paths for both plant and operator inputs, and corrective actions are found by an adaptive search.

30.45.9 Neural networks

A quite different approach to alarm diagnosis is the use of neural networks, for which this appears a natural application, and a number of studies have been published. Neural networks were described in Section 30.21. Most of the work on such artificial neural networks (ANNs) is concerned with back-propagation networks (BPNs). The studies done cover learning, recall and generalization.

Hoskins and Himmelblau (1988) explore the characteristics of ANNs desirable for knowledge representation in processes and illustrate their discussion with an account of the use of an ANN to discriminate between faults in a simple process.

A further exploration of ANNs is described by Ungar, Powell and Kamens (1990). ANNs are able to learn nonlinear and logical relationships as well as linear ones. They describe work using an ANN on a simple process in which a comparison is made between performance with discrete inputs, that is, alarms, and with continuous inputs, that is, sensor readings, and also work on the effect of noise.

Venkatasubramanian, Vaidyanathan and Yamamoto (1990) have studied the performance of ANNs under certain taxing conditions, including multiple faults and sensor faults.

M.A. Kramer and Leonard (1990) consider particularly the problems of extrapolation outside the conditions covered in the learning set. Such extrapolation becomes necessary when the learning set is undersized, when the parent distributions of fault classes undergo shifts, and when input data are corrupted by missing or biased sensors. They identify as a problem the inability of an ANN to detect when it lacks the data to effect a reliable classification.

30.45.10 Response advice systems

An account of a system for providing the operator with advice on the response to failures of critical safety functions is given by Nelson and co-workers (W.R. Nelson, 1984; W.R. Nelson and Blackman, 1985; W.R. Nelson and Jenkins 1985), who describe the Response Tree Evaluation project, one of those initiated following Three Mile Island. The purpose of the system is to select a response to provide by alternative means the safety function that has been disabled. The program creates a goal tree for the provision of the function, evaluates the availability of the various units, and searches for success paths. The search can be quite complex, since in general there is redundancy not only between units but within them.

Reference has already been made to the work of Chen and Modarres (1992) on the expert system FAX for the diagnosis of faults and advice on corrective actions.

30.45.11 Influence modelling and assessment system

The bulk of the work described so far deals with engineering problems of alarm diagnosis. It is necessary, however, to consider the ultimate function of such a system. This function is to provide support to the process operator, unless he be completely eliminated. As discussed in Chapter 14, the provision of an effective computer-based aid for the handling of alarms is fraught with difficulty.

This problem has been addressed by Embrey (1986). He takes as his starting point the fact that whereas for most types of human error the probability of recovery tends to be high, for diagnosis it is low.

In order to aid diagnosis, it is necessary to have some appreciation of the way in which the operator goes about it. In one view, the operator uses two distinct approaches. The first is the use of relationships between symptoms and faults. These are the symptomatic rules, or S-rules. They may be formally represented as a fault-symptom matrix (FSM). The other approach is topographic search. In this mode the operator makes a series of good/bad assessments based on his or her knowledge of the locations of and relationships between system components. These are the topographic rules, or T-rules. Since the use of S-rules involves less effort, the operator will generally apply these first, before resorting to the T-rules.

The FSM has been quite widely used in the process industries, and can be a useful aid to symptom based diagnosis, but it is rather inflexible and does not accommodate changes over time. Alternatively, use may be made of symptom-based procedures. These effectively bypass overt diagnosis and proceed straight to actions. Such procedures have been developed for nuclear plants following the Three Mile Island incident, but seem less applicable to process plants that are much more varied.

The approach proposed by Embrey is the use of an influence modelling and assessment system (IMAS). The purpose of this is to assist an operator in making his or her own diagnosis, and more specifically to support the use of the T-rule approach. His or her understanding of the relationships in the process, both causes and consequences of events, is elicited and encoded as a subjective cause–consequence model (SCCM).

Whatever the merits of this particular system, it is well to give the human aspect of fault administration its due share of attention.

30.46 Malfunction Detection

The third aspect of process monitoring is malfunction detection. The process computer can be used to detect or assist the operator to detect malfunctions before these give rise to alarm conditions. Malfunction detection, particularly in instruments, by the process operator, has been discussed in Chapter 14. Here consideration is given to the exploitation of the computer's potential in this area.

There are two basic methods of detecting malfunction in an equipment. These are to monitor (1) equipment

performance and (2) equipment condition. The checking of performance is exemplified by the determination of the characteristic of a pump or of the heat transfer coefficient of a heat exchanger, while the checking of a condition is illustrated by the measurement of a compressor bearing temperature or the observation of leakage on a valve.

A classification of general methods of detecting malfunction in plant equipment such as compressors or heat exchangers, is as follows:

(1) process variable incorrect;
(2) equipment parameter incorrect;
(3) equipment relationship incorrect;
(4) equipment status incorrect;
(5) equipment condition faulty.

Probably the most common method of detection is from the fact that one or more process variables show the wrong value. Another check is that on a single parameter of the equipment, such as the efficiency of a compressor. Or a check may be made on a simple relationship such as the characteristics of a pump. Certain types of equipment, particularly mechanical handling equipment and regulating elements, have discrete states which they should be in at various stages of process operation, and a check may therefore be made on equipment status. Alternatively, the equipment condition may be checked with respect to features such as vibration. The classification of checks for malfunction detection in instruments has been given in Table 14.6.

The condition monitoring of plant equipment is an important activity on process plants and involves the use of specialized instrumentation and the interpretation of the signals obtained, and is described in Chapter 19. The aspect of interest here is the role of the computer as an aid in this area.

The types of function that the computer can perform include scanning, smoothing and comparing signals, calculating indirect measurements, processing information through simple correlations and models, and generating displays.

The use of process computers for malfunction detection as opposed to alarm monitoring was rather slow to develop. For some time the widespread activity of condition monitoring made relatively little use of process computers. There has been, however, a gradual increase in the role of the computer in support of this function.

The use of a computer to monitor reciprocating compressor performance by calculating quantities such as gas leakage and efficiency has been reported by Gallier (1968). Several different schemes are described with different instrumentation requirements. Benefits adduced by the author are the early detection of malfunction and also improvement of the load between parallel compressors.

In another installation where reciprocating compressors are used in the on-off mode to maintain the pressure of air in receivers within fixed limits, the amount of time during which the compressors are on is used as a simple indication of possible trouble.

Models of large centrifugal compressors are sometimes used for optimization purposes, but such models may also be used to monitor compressor characteristics as a means of malfunction detection. Other applications of the use of process computers in detecting malfunction in process machinery have been described in Chapter 19.

Monitoring need not necessarily be confined to process machinery. The calculation of heat transfer coefficients in plant equipment by the process computer is quite widely practised.

The principal method currently used for early detection of malfunction, however, is the measurement and analysis of equipment characteristics such as vibration, using special instruments. The signals obtained are often rather noisy and individual to the equipment. These characteristics suggest that there is scope for the use of the computer's ability for the smoothing and display of information.

Another related development is the monitoring of undesirable operating conditions on the plant. This can be due to maloperation by the operator and it is sometimes possible for the computer to monitor this and display it to the operator. The display to the operator of the rate at which he or she is using up the creep life of furnace tubes is one industrial example of this.

The same principle has been applied in the monitoring of control of ships, where the degree of maloperation is measured by instrumentation and analysed using estimation theory. The data are then displayed to the operator as a signal (Asbjornsen, 1976).

Of particular importance to the computer system itself is the correct operation of the sensors and valves that are connected to it. The detection of malfunction in these instruments is now considered.

30.46.1 Malfunction detection in individual instruments

The detection of incipient malfunction in instruments may follow one of two approaches. In the first the check is made on an individual instrument, or at least a limited set such as a control loop, whilst in the second it is made on an ensemble of instruments, often in different parts of the plant.

Some of the checks made by the process operator on individual instruments and control loops have already been described in Chapter 14. Many of the developments in checks that may be made by the process computer have analogues in those made by the operator. In those systems where computer checks on instruments have been implemented, the favoured methods generally have been checks on 'hardover' zero or full-scale signals and on an excessive rate of change in signals.

These checks, however, by no means exhaust the potential. The noise on a signal is often a useful indication of malfunction. Anyakora and Lees (1973) have described a method in which the noisiness of the signal is used as a check. The smoothed signal is subtracted from the crude signal to yield a noise residue, and a noise parameter is calculated from the sum of the squares of the noise residue taken over a group of readings. The technique has been used to detect the onset of malfunction in a thermocouple and in a flowmeter with freezing impulse lines. A modification of the technique has also been used to detect incipient stickiness in control valves. In this case the noise residue was the difference between the desired and actual valve positions, the latter being measured by a potentiometer.

A method of detecting malfunction in any of the elements in a flow control loop based on a comparison of the measured flow with the control valve position has been developed by Bellingham and Lees (1977b). The principle is that the valve position gives an additional indication of flow with which the actual flow measurement can be compared. The method assumes that the relation between flow and pressure drop through the system remains constant.

In the simplest case where the valve can be stroked over its whole range, the relation between the valve position and flow, or the valve characteristic, can be obtained, and any departures from the original characteristic can be determined. It was found in practice that it is preferable to detect such divergence using a simple tracking estimator that generates an error residual. This method does not require the full stroking of the valve. The detection of faults ranging from flowmeter zero error to valve trim damage was demonstrated.

This approach has also been applied by Bellingham and Lees (1977a) to the general control loop such as level, pressure and temperature, in which the measurements and the valve position are not as directly linked as in the flow control loop. The loop studied was a level control loop. In this work use was made of an estimation method based on Kalman filtering. Again the method was successful in detecting faults ranging from level meter zero error to valve trim damage. A rather cruder check based on the same principle on the feed flow to a cement kiln has been described by Barton *et al.* (1970).

Most of these techniques may be used either to carry out an automatic check or to provide a display to assist the operator in checking. A display specifically developed to allow visual checking by the operator is that of an engine gimbal developed by H.H. Bowen (1967) and illustrated in Figure 30.38. Figure 30.38(a) and (b) show the step response of healthy and unhealthy gimbals, respectively; it is difficult to distinguish between them. Figure 30.38(c) and (d) show the corresponding phase plane displays; the difference is quite clear.

Figures 30.39–30.41 illustrate the type of display which may be generated using the Anyakora and Lees (1973) technique of monitoring the instrument noise. Figure 30.39(a) and (b) show, the noise parameter plots for a healthy and for a failing thermocouple, Figure 30.40(a) and (b) show those for a healthy flowmeter and for one with frozen impulse lines, and Figure 30.41(a) and (b) show those for a healthy and for a sticking control valve.

The display shown in Figure 30.42 is a plot given by Bellingham and Lees (1977b) of the flow in a flow control loop as measured by the flowmeter (dotted line) and as

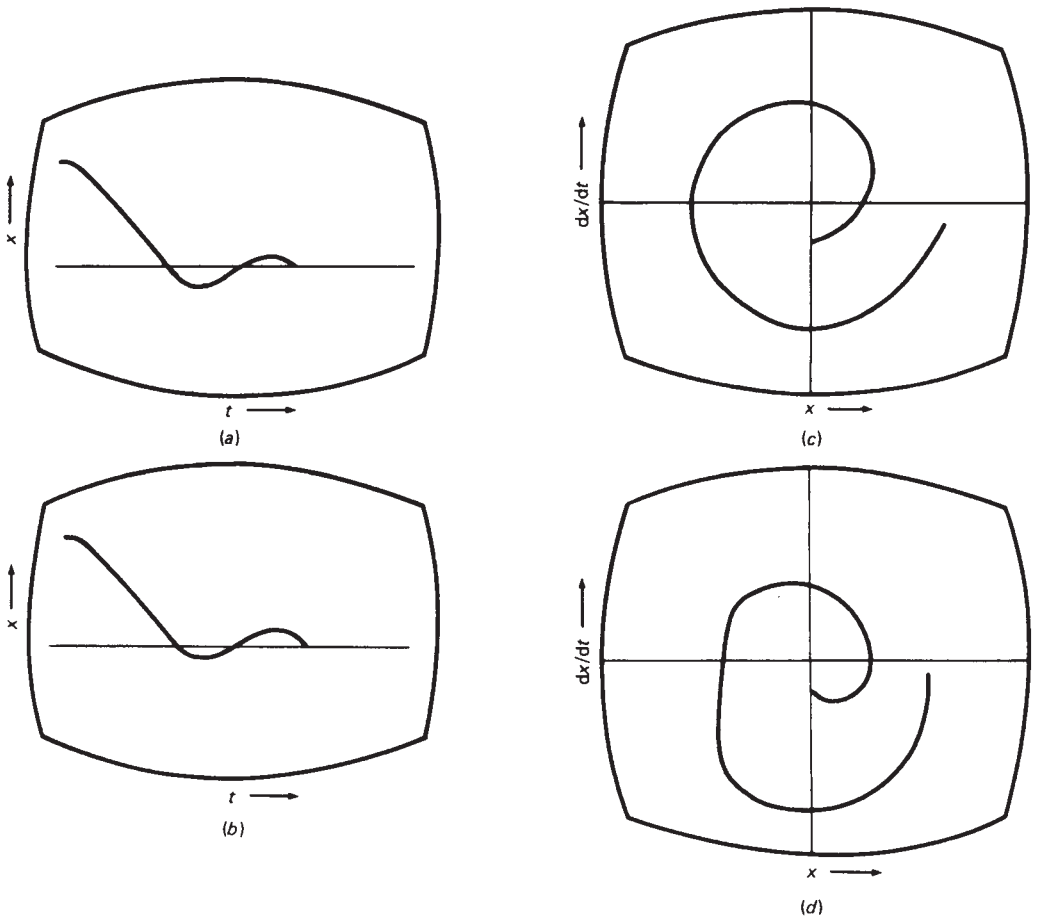


Figure 30.38 *Computer graphic displays for malfunction detection: phase plane plot of engine gimbal (after H.H. Bowen, 1967): (a) step response plot – device healthy; (b) step response plot – device unhealthy; (c) phase plane plot – device healthy; (d) phase plane plot – device unhealthy (Courtesy of Taylor & Francis Ltd)*

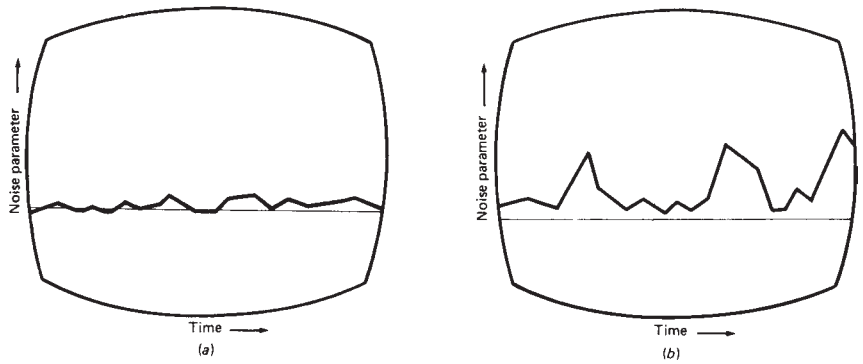


Figure 30.39 *Computer graphic displays for malfunction detection: noise parameter plot for a failing thermocouple (after Anyakora and Lees, 1973): (a) thermocouple healthy; (b) thermocouple failing. The horizontal line represents the mean value of the noise parameter for a healthy instrument*

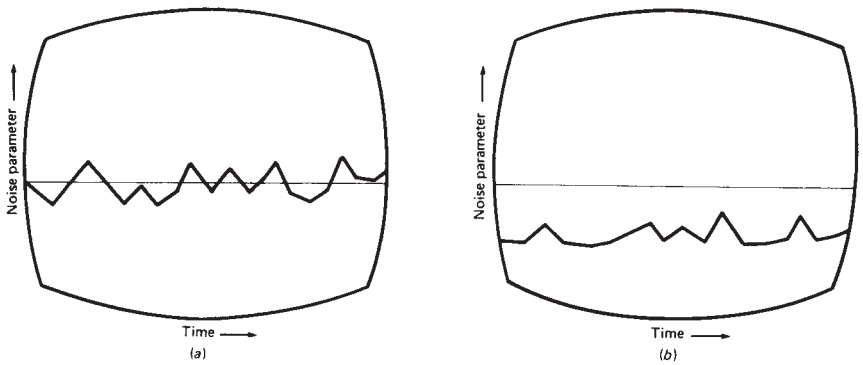


Figure 30.40 *Computer graphic displays for malfunction detection: noise parameter plot for a frozen flowmeter (after Anyakora and Lees, 1973). (a) Flowmeter healthy; (b) flowmeter with impulse lines frozen. The horizontal line represents the mean value of the noise parameter for a healthy instrument*

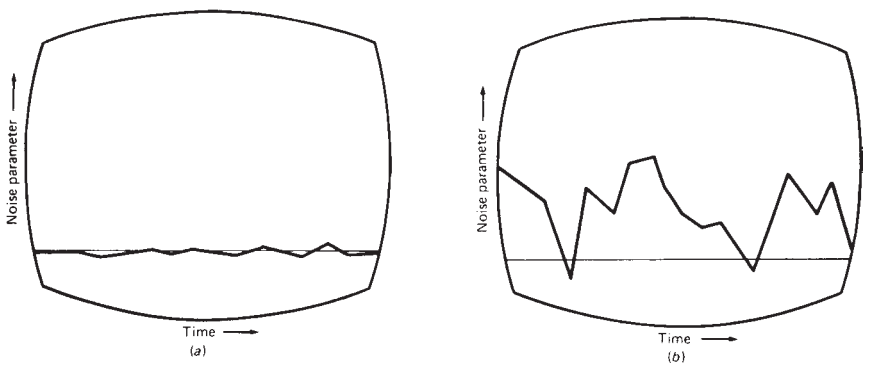


Figure 30.41 *Computer graphic displays for malfunction detection: noise parameter plot for a sticking control valve (after Anyakora and Lees, 1973): (a) valve healthy; (b) valve sticking. The horizontal line represents the mean value of the noise parameter for a healthy instrument*

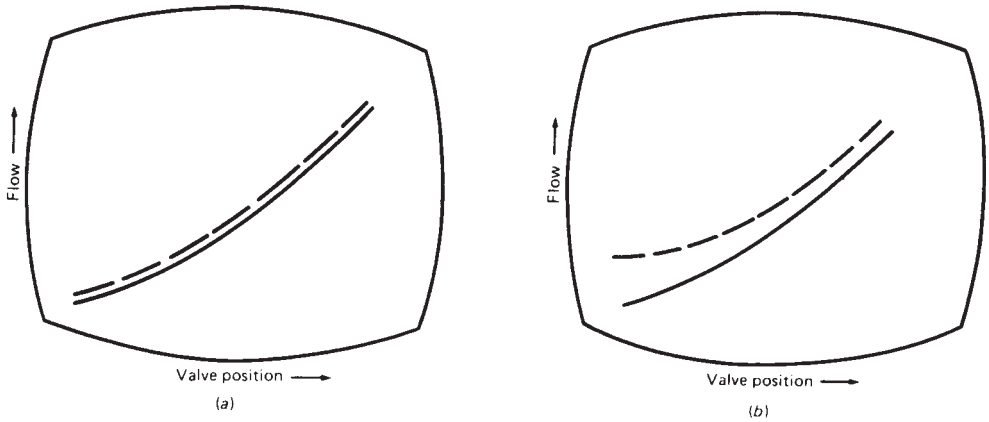


Figure 30.42 *Computer graphic displays for malfunction detection: measured and inferred flow in a flow control loop (after Bellingham and Lees, 1977b): (a) loop healthy; (b) loop with flowmeter zero error. (-----) Measured flow; (———) flow calculated from the valve position*

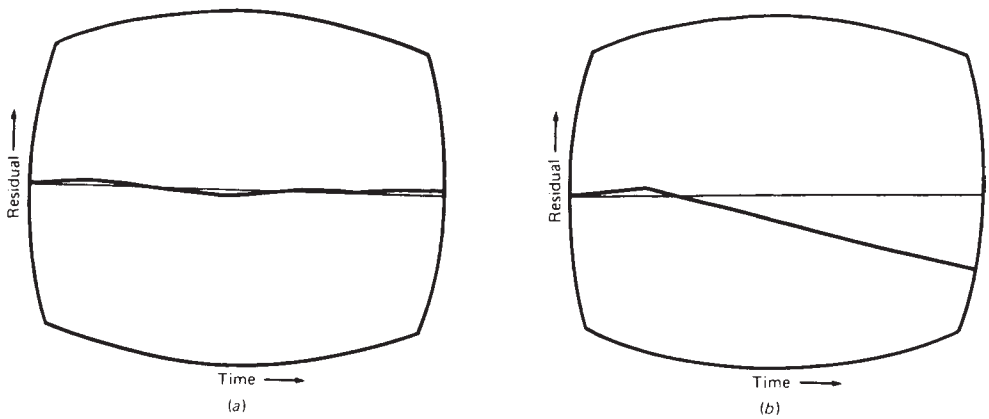


Figure 30.43 *Computer graphic displays for malfunction detection: error residual in a flow control loop (after Bellingham and Lees, 1977b): (a) loop healthy; (b) loop with flowmeter zero error. The horizontal line represents the mean value of the residual for a healthy loop*

inferred from the control valve position (full line). The generation of this display requires the valve to be stroked over the whole range. Figure 30.42(a) and (b) show healthy and unhealthy loops, respectively. Another display is based on the generation of a residual error, which is more suitable if valve travel is limited. Figure 30.43(a) and (b) illustrate the display of this residual for the healthy and unhealthy cases.

This account is perhaps enough to give a flavour of the work on malfunction detection. It illustrates the allocation to the computer and the operator of functions which they perform well, such as signal processing and display generation on the one hand and pattern recognition on the other.

More detailed accounts of malfunction detection have been given by Anyakora and Lees (1972a,b), E. Edwards and Lees (1973) and Whitman (1972).

30.46.2 Malfunction detection in instrument ensembles

The alternative approach to instrument malfunction detection is to check whole ensembles of instruments. As stated in Section 30.44, it is not uncommon to check the consistency of sets of instrument readings which determine a relationship such as a mass or energy balance, although generally the concern here is more with data reconciliation than malfunction detection.

The checking of ensembles of instrument readings for internal consistency has received increasing attention. Reviews of work in this area have been given by Willsky (1976), Himmelblau (1978) and Venkateswarlu, Gangiah and Rao (1992). An early example of work in this area is that of Goldmann and Sargent (1971), who used Kalman filtering to track the unsteady-state behaviour of the system and to detect sensor drift.

Venkateswarlu, Gangiah and Rao classify the quantitative processing of sensor data into three broad categories: data reconciliation and rectification; state estimation; and filtering and parameter identification. Work on data reconciliation is illustrated by that of Mah, Stanley and Downing (1976), Stanley and Mah (1977), Romagnoli and Stephanopoulos (1981), Madron (1985), and Narasimhan and Mah (1987). Work on state estimation methods is illustrated by that of Willsky (1976), Watanabe and Himmelblau (1983) and Frank (1987); and work on filtering and parameter estimation is illustrated by that of Isermann (1984), Park and Himmelblau (1983), Watanabe and Himmelblau (1983, 1984) and Dalle Molle and Himmelblau (1987).

30.47 Notation

Section 30.8

C	certainty
CF	certainty factor

Section 30.9

f	Bayesian factor
LN	logical necessity
LS	logical sufficiency
O	odds
P	probability
w	weight of evidence

Section 30.10

F	attribute
n	number of items in set
n_F	number of items with attribute F
Q	fuzzy quantifier
$\mu_A(x)$	grade of membership of x in A
$\mu_F(x)$	membership function for attribute F
$\mu_Q(x)$	membership function
τ	truth value

Section 30.20

G_j	information gain for attribute μ_j
H_c	expected information content of message
H_j	information content for attribute j at node
H_{jk}	information content for attribute j in branch k at node
j	attribute counter
k	branch counter
H_{jk}	proportion of objects having attribute j in branch k at node

Section 30.26

L	level
Q	flow
t	time

Subscripts

1	inlet
2	outlet

Section 30.36

L	level
G	pressure differential
P	pressure
Q	flow
U	temperature in reverse flow

Subscripts

1	inlet
2	outlet

Section 30.42

As Section 30.36

31 Incident Investigation

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31.1 Preface

Chemical process incidents can be accompanied by significant consequences, both in terms of human life and in financial impact. Many major chemical process incidents are the result of a complex scenario involving simultaneous failures of multiple safeguards. A robust system for incident investigation is usually necessary to determine and understand the causes, as well as implement measures to prevent a repeat event. This chapter is intended to provide an overview of incident investigation by addressing major concepts, principles and characteristics of effective incident investigations of chemical process events. The focus is on incidents pertaining to chemical processes and their associated hazards, and the associated investigation techniques appropriate for complex systems and scenarios. This chapter is based on best practices for incident investigation, and those common concepts (i.e. tools, techniques, definitions) included in root cause investigation methodologies currently in the public domain in use in the process industry. It is not the intention to provide a stand-alone investigation methodology/guideline, nor address internal or proprietary investigation methodologies.

This chapter is based on:

- process industry best practices for incident investigation;
- investigation concepts from the Mary Kay O'Connor Process Safety Center Root Cause Investigation Course;
- Ted Ferry's book on accident investigation (Ferry, 1988);
- Kuhlman's Professional Accident Investigation (Kuhlman, n.d.);
- CCPS *Guidelines* for Incident Investigation (second edition) (CCPS, AIChE, 2003);
- NFPA 921 Standard for investigation of fires and explosions (NFPA, Standard 921 Investigating Fires and Explosions);
- American Chemistry Council Responsible Care code (CARE®, n.d.);
- US National Safety Council investigation guidelines (National Safety Council, 1995).

This chapter begins with an overview of general incident investigation concepts and definitions to provide a common baseline. Section 31.3 is devoted to collection and analysis of evidence including a segment on investigation witness interviews, Section 31.4 addresses investigation team issues, and Section 31.5 is devoted to identifying root causes. Recommendations, reports and sharing lessons learned are presented in Section 31.6. The chapter concludes with Section 31.7, a review of Incident Investigation Management System issues and sources for additional information related to process industry investigations.

31.2 General Investigation Concepts

31.2.1 Purpose and scope of incident investigation

Effective discovery of root causes is not an easy or simple task. Successful investigation is an iterative process based on scientific principles with the ultimate purpose being prevention of a repeat event. It is systematic, thorough and intellectually honest. There are four stages that must be successfully completed in order to prevent a repeat event of a similar nature:

- Identify what happened and how it happened (identifying and understanding the scenario).
- Determine why it happened (identify the specific underlying and contributing causes).
- Identify preventive remedies (recommendations and action items).
- Implement changes to existing practices and systems (accompanied by sharing lessons learned to all those who could benefit).

Unless and until the preventive actions are actually implemented, the risk exposure level remains unchanged. It is not unusual in the chemical process industry for similar incidents to occur in sister plants or in similar plants owned by another organization. There is a growing recognition of the importance of the actual implementation, resolution and follow-through of investigation recommendations.

31.2.2 Definitions

31.2.2.1 Causes

Incident investigation terminology is, unfortunately, inconsistent across the process industry. This creates communication challenges even within a single organization. In the United States, the term *incident* is generally used in the context of referring to any unplanned event that did, or easily could have, resulted in undesirable consequences. When an incident results in actual undesirable consequences, such as injury to people, the environment, damage to equipment or adverse impact to operating profits, the event is most commonly labelled as an *accident*. The term *near-miss* is used in this chapter to describe an event that generated no actual adverse consequences, but with a slight change in circumstances, could have produced actual adverse consequences.

Examples of near-miss events include:

- dropping a crane load where there is no injury or damage;
- demand challenge to a final protection device (such as emergency shut-down control systems);
- events where there is unintended energy contact to employees without resulting in injury.

One challenge to effective root cause incident investigation is the absence of a consensus definition of the term *root cause*. There are several definitions in use. For the purposes of this chapter the term root cause is used to represent: *the underlying reasons that allow defects in systems (physical equipment and systems and/or administrative systems) to exist, that the organization can correct*. These defects are the result of, and symptoms of, underlying causes. Examples of these defects include faulty design, inadequate behaviour or task execution, improper installation, ineffective training or maintenance. An event itself (such as the breaking of a component) cannot by definition be a root cause. Some conditions or underlying reasons may not be under the control of the organization, and are

therefore not considered to be root causes. This issue is discussed in more detail in Section 31.2.3.1.

> *Root causes = Underlying system-related reasons that allow system defects to exist, and that the organization has the capability and authority to correct.*
> *Events are not root causes.*

31.2.2.2 Management system perspective

An understanding of management system perspective is useful in effective root cause identification. The term management system is used in a variety of contexts. When people hear this term for the first time, their initial reaction is to think of the people in the nice offices on the top floor. However, the term management system does not refer to the individuals on the management team or the management team's general approach and organization. For the purpose of this chapter, the term management system is used to represent the total administrative activities and aspects associated with a dedicated task or objective. Root causes are almost always associated with, and can be linked to, one or more weaknesses or breakdowns in administrative management systems.

Management systems have common generic components such as: written procedures, training, performance expectations, required competencies and assignment of different responsibilities. When searching for root causes, the investigation team should examine the components of all management systems involved in the incident (CCPS, AIChE, 2003). Examples of management systems may include: lockout/tagout, training systems, written operating procedures, process hazard analysis systems, management of change systems, mechanical integrity and maintenance systems, and recognition and response to anomalies (process upsets, transfers of material).

In this context, management systems have common generic components as shown in Figure 31.1, including defined inputs, defined outputs, a work process (and/or procedure), a training component, allocation of responsibilities, sustained allocation of resources, documentation, an audit and/or measurement component, a minimum required skillset and knowledge set, accepted ranges of performance defining success, and usually a continuous improvement/quality assurance component (BS 8800, 1996). The incident investigation system is a good example of a management system. An effective incident investigation system contains all the above generic components as well as those shown in greater detail in Section 31.7, Figure 31.12. The objectives and expectations of the investigation are clearly established. Performance standards are implemented, personnel are trained and specific documentation requirements established. Investigation task activities are well-defined, auditable and effectiveness is periodically evaluated.

31.2.3 Investigation general concepts

31.2.3.1 General concepts for incident investigation

For effective investigations, an honest, thorough and systematic approach is needed. The investigation team should ethically and objectively consider all facts, information and evidence, and use scientific principles to identify and evaluate all plausible cause scenarios. Rejection of proposed scenarios should be based on physical evidence. Wherever and whenever possible, independent verification of information should be sought.

Prematurely stopping before reaching the root cause level is a major and recurring challenge to most process incident investigations. One common error is to identify an event for a root cause, thereby prematurely stopping the investigation before the actual root cause level is reached. Events are not root causes. Events are results of underlying causes. It is an avoidable mistake to identify an event as a root cause (i.e. a loss of containment release, a mechanical breakdown or failure of a control system to function properly).

One fundamental objective is to pursue the investigation down to the root cause level. Effective investigations reach a depth where fundamental actions are identified that can eliminate root causes. The most appropriate stopping point is not always evident. It is sometimes difficult to distinguish between a symptom and a root cause. When the investigation stops at the symptom level, preventive actions provide only temporary relief for the underlying root cause. It is critically important and necessary to establish a consistently understood definition of the term root cause. If the investigation stops before the root cause level is reached, fundamental system weaknesses and defects remain in place pending another set of similar circumstances that will allow a repeat incident. The organization will then be presented with another opportunity to conduct an investigation to find the same root causes left uncorrected after the first incident.

For example, consider the case where the investigation stopped before reaching the root cause level.

Scenario – A massive release of toxic liquid occurred when a small (1/2 in.) bleed valve failed. The valve was found to be installed improperly, and was damaged by internal corrosion.

Facts

(1) One design feature was that the internal valve components could be removed and replaced if they became worn. The valve was designed with a fail-safe provision and intended to be installed in a designated flow direction orientation. Access to the internal components was intended to be made from the inlet (upstream) side of the valve. The inlet port of the valve was provided with a threaded internal sleeve (retention ring) that could be removed for access to valve internal components. If the retention ring were to fail, pressure from the upstream flow would act to prevent the valve's internal components from being ejected from the valve body.
(2) The valve was marked with a flow direction arrow and delivered from the supplier with a conspicuous instruction tag warning of the consequences of improper installation. The investigation team found the valve to be installed in the wrong flow direction orientation.
(3) Examination of the retention ring indicated the threads were corroded to the point of failure, and allowed the retention ring and value internal components to be ejected.

One root cause as found by the investigation team – 'valve installed backwards'

Recommendation submitted by the investigation team – 'refresher training for the mechanic who installed the valve'

Comment

The investigation team stopped the investigation too early and failed to identify the underlying reasons *why* the valve was installed backwards. A more effective team might discover and correct additional underlying causes such as:

- incomplete and out-of-date instructions for installing and verifying proper orientation;
- inadequate system for updating installation instructions and verifying that current instructions are being used;
- inadequate training system with no provision for confirming that the training accomplished the intended objectives and no periodic refresher/reminder component was included within the training program;
- current system does not call for insuring the caution tag supplied by the manufacturer remains on the valve until its point of installation/application;
- a defective system for ensuring that quarter turn quick opening bleed valves in toxic liquid service are capped or plugged when not in use;
- an incomplete system for ensuring that new or temporarily transferred mechanics are aware of the special nature of these bleed valves.

If the investigation team had reached the underlying system defect level, the team would have been able to more effectively eliminate the chances of a repeat incident.

An investigation team may mis-identify 'lack of sufficient knowledge/skill' as a root cause and therefore, generate a recommendation to conduct refresher training. This lack of sufficient knowledge/skill is, in most cases, a symptom and not a root cause. The training recommendation assumes that the person did not know/understand the proper procedure. The training recommendation does not attempt to identify the underlying root cause of the employee's behaviour. If and when a procedure is changed, retraining is necessary and would be a proper component of the recommended preventive actions. Deficiencies in the training management system could be the underlying root causes resulting in the symptom (inadequate knowledge or skill). Training (or refresher training) would be an appropriate action once the underlying root cause deficiency in the training system has been properly identified and corrected.

Different investigation teams often have varying perceptions regarding expected stopping points and may also have different understandings of what is and is not a root cause. Within an organization, there should be a definition of the term root cause that is clearly and consistently understood and applied.

Another requirement is that a root cause must be correctable by the organization. Two extreme examples of this concept are weather conditions and physical properties of materials. The organization does not have the capability to prevent/control adverse weather such as rain, wind or extreme ambient temperatures. It would be incorrect for the investigation team to identify rain or some physical property (boiling point) as a root cause. The organization may have capability to implement protective measures to mitigate the consequences of wet conditions, but it would be incorrect to label rain (or ice) as a root cause. Another example would be a case where one plant (Plant A) causes injury to workers in an adjacent plant (Plant B) and the plants are owned by two different organizations. Plant B management can take certain actions to protect their workers from outside events that originate at Plant A. These protective measures might include gas detectors, alarm and alert systems, constructing safe haven refugees, providing personal protective equipment, training, filing lawsuits, and certain other emergency response and mitigation measures. However, Plant B cannot enter Plant A and implement preventive measures because Plant B lacks the authority or control over Plant A. The root causes of injury to Plant B personnel would be limited to those weaknesses or breakdowns in Plant B systems and measures.

31.2.3.2 Life cycle of an investigation

Figure 31.2 provides a graphical representation of the root cause investigation process. There are several natural and overlapping stages to every process incident investigation. The first phase is determining 'What happened'. This is followed by efforts to identify 'Why it happened.' Evidence is collected and analysed, and information is gathered from direct and contributing witnesses in an iterative process. This is the stage where the root causes are identified. The final stage is the 'Prevention' stage where preventive action measures are identified, implemented and verified and information is shared with all who might have potential benefit from the investigation's outcome.

31.2.3.3 Special investigation challenges for process incidents

Although investigations of process incidents share many common elements with traditional industrial incident investigation, there are a few relatively unique features. Many process incidents involve outside parties such as regulatory agencies, insurance companies and in many instances litigation issues. Process incident investigations by nature carry additional challenges. Actual or potential consequences are significant and can be catastrophic in terms of loss of life, impact to the environment and in terms of financial impact on the organization. Specific design features of the manufacturing process system and sophisticated controls are provided to prevent adverse consequences. Multiple layers of protection are provided and maintained. Safeguard measures can be physical systems and devices (instrumentation interlocks, pressure relief valves and trip devices for example), administrative management systems or combinations of the two. Most process incidents that result in significant consequences are associated with unusual combinations of circumstances and conditions, and multiple breakdowns of preventive measures. In most instances, a single failure of a safeguard does not result in adverse impact. When adverse consequences do occur, it is most often the result of a complex scenario that involves simultaneous failures of several layers of protection.

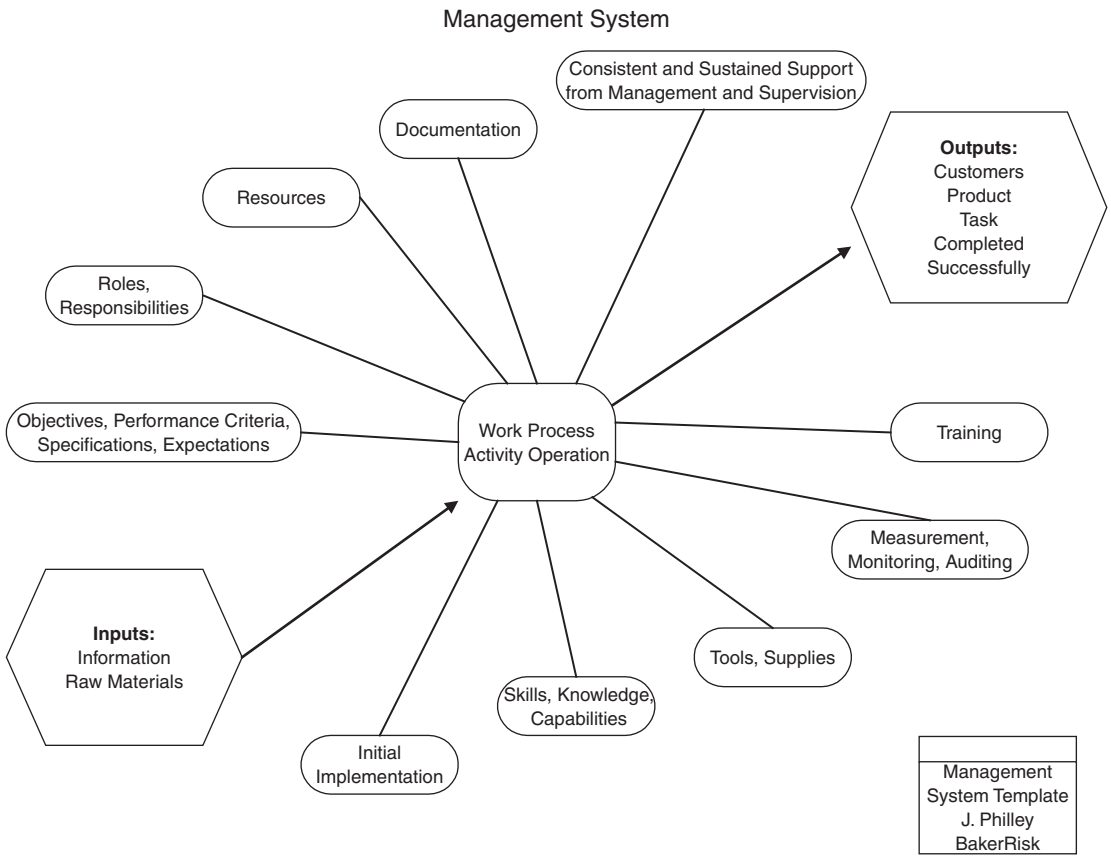

Figure 31.1 *Management system template*

One relatively unique characteristic of modern process designs is the close coupling (Parlow, 1999). Large-scale single train units are now the norm. Surge capacity and intermediate storage are minimized. The design provides minimum selected redundancy and spare equipment. Designs stress reliability and corresponding maximum on-stream time. Intervals between scheduled shut-downs and turn-arounds are maximized. This approach results in potential for a problem in one part of the process to quickly propagate and cause impact to downstream portions of the plant process equipment.

31.2.3.4 Concept of multiple causes

A second major challenge is finding all root causes. One common mistake in root cause incident investigation is to prematurely stop the investigation before *all* root causes are identified. This mistake is sometimes built into the investigation management system, by formally limiting the charter and expectations of the investigation team. Sometimes the investigation team is specifically charged with finding 'the root cause.' Additional root causes are allowed, but the team is asked to discover the one root cause among all other causes most responsible for the event. This erroneous approach ignores an axiom of root cause incident investigation, that is, 'There are always multiple root causes

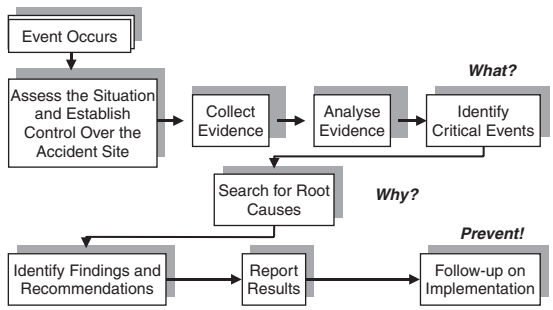

Figure 31.2 *Root cause investigation process*

associated with an accident.' Removing only one root cause corrects only part of the problem. If only one root cause is identified and eliminated, the result of the investigation effort would probably prevent a repeat of the exact specific incident sequence, but would leave the other root causes in place ready to cause a similar event.

Each root cause has a specific risk factor associated with it (combination of likelihood and consequence severity).

Some root causes are associated with higher frequency of opportunities for occurrence or exposure, while others are associated with higher degree of severity of consequences. From this perspective, it is accurate to say that some root causes are more significant than others from a risk perspective. However, for most accidents, it is not accurate to say that there is only one root cause associated with the accident. In the Three Mile Island, Bhopal, and Challenger Space Shuttle incidents, there were multiple root causes that acted in concert to allow the accident scenario to progress (Philley, 1992; Chiles, 2001). In each of these three classic incidents, a series of failure events and conditions progressed to a final state of significant adverse consequence. The failure events and breeches of safeguards had different probabilities. If one of the series had not occurred, it is unlikely that the final event would have happened. Each individual failure represented an opportunity to arrest the progression of the scenario. Each failure was associated with a separate and distinct defect in a management system. The investigation would be incomplete and less than adequate if the team finds and corrects only one of the underlying root causes.

For optimum incident investigation results, the concept of multiple root cause should be fully integrated into the incident investigation management system, procedures, training and expectations.

31.2.4 Management's role in incident investigation

Responsibility for prevention of incidents and repeat incidents is a responsibility shared at every level of the organization from the board of directors down to the entry-level employee. However, the ultimate responsibility rests with those in management positions who establish policy and allocate resources. It is a general observation that process facilities and operations with the most successful records share common management leadership attributes and characteristics including:

- personal involvement by line management in the review and approval of draft incident reports;
- rigorous and robust follow-up and implementation of recommendations and action items generated from incident investigations;
- proactive sharing of results, findings and lessons learned from investigations;
- strong and sustained emphasis on reporting, investigating and taking action on near-miss events;
- establishing priorities and implementation schedules for incident investigation action item recommendations.

One critical function of the organization's line management is the responsibility to act on the recommendations submitted by the incident investigation team (Noon, 2000). Managers must fully understand the risk associated with implementing, partially implementing, modifying, delaying or rejecting the suggested recommendations. Once a recommendation is accepted, there is a responsibility to ensure the action is implemented as intended and that the action is indeed successful in correcting the root cause. Follow-up verification, documentation, auditing and monitoring are essential.

Members of line management have the responsibility to implement a management system for incident investigation. This responsibility requires sustained allocation of resources (i.e. financial and personnel). Many incident investigation actions are accompanied by auxiliary (secondary) tasks such as updating training manuals, process safety information packages, or piping and instrumentation drawings (P&ID). These auxiliary tasks also require allocation of organizational resources, prioritization, and tracking to satisfactory resolution.

Line management must establish acceptable risk tolerance criteria. This is most often accomplished by development and adoption of a risk matrix (CCPS, AIChE, 2003). Risk matrices are applied to assist in prioritization of issues and recommended preventive action items. Line management has a responsibility to effectively share the lessons learned from the investigation both internally and externally.

Each level of the management structure must have an adequate and appropriate understanding of the incident investigation policy, procedure and responsibilities (DNV, 1996). In most cases this requires a clear and consistent understanding of the implemented incident investigation management system including: What is an acceptable identification of root causes? What is acceptable regarding quality and wording of action item recommendations? What are the individual responsibilities for each person under the supervision of that manager?

31.2.5 Human factors in incident investigation

Human factors are involved in almost every process safety incident. Since human reliability is less than 100%, all administrative systems and safeguards are less than perfect. Well-designed management systems take human reliability and human performance into consideration when designing safeguards. Well-designed human factor safeguards are error tolerant and allow some opportunity to detect and correct deviations before catastrophic consequences are reached. Well-designed safeguards will include confirmation that the intended protection remains in place. Every safeguard will have discrete periods of unavailability. Some process hazards are significant enough to require protection in depth (layers of protection) and robust barriers.

When evaluating proposed additional safeguard measures, incident investigation team members will often benefit from an understanding of the application of reasonable human performance reliability expectations. In some instances, the human performance expected by system designers (physical systems as well as administrative systems) exceeds realistic or practical limits. In these cases the system design increases likelihood for human error or may call for unrealistic response times or response actions. When considering remedies to root cause defects, the incident investigation team should apply recognized and generally accepted human performance and human reliability expectations. Two excellent examples of applied human factors are the emphasis on inherent safety in system design and the concept of alarm management. Modern distributed control system (DCS) instrumentation allows almost infinite capability to add computer generated alarms and the result can be alarm overload/flood during the initial periods of process deviations and process upsets. The alarm management concept provides an opportunity to prioritize and categorize alarms and the associated expected response actions to alarms.

The Japanese quality control technique of Poka Yoke is a concept that recognizes workers occasionally make mistakes and provides features in the manufacturing

process that minimize the incidence rate and consequences of mistakes. Manufacturing processes are provided with features that allow rapid detection of errors made by employees and, therefore, allow an opportunity to recover at minimum expense and consequence.

The written procedure is a common accident prevention safeguard that depends heavily on human reliability (also referred to as standard operating procedure, SOP, or written instruction). The intent of the written procedure is to ensure actions and practices are sufficient to safely complete the designated task. Unfortunately, it is a common and erroneous finding for an investigation team to identify 'Employee failed to follow established procedure' as a root cause. This failure on the part of the employee (behaviour or action) is in most instances a symptom of an underlying root cause (Peterson, 1984). The investigation should try to discover *why* procedures were not followed. In almost every case, there is an underlying system deficiency reason why a person did not follow the established procedure. The investigation team has an obligation to uncover and remove underlying causes for the failure to follow established procedures.

> In most instances '*failure to follow established procedures*' is not a root cause, but is instead a symptom of an underlying system defect that can be corrected.

It is not unusual for employees to consciously deviate from a written and established procedure. In some instances, the failure to follow established procedure may be due to inadequate knowledge. The classic recommendation that accompanies this premature stopping point is to provide training (or refresher training) to ensure the person(s) involved in the incident understands how to follow the established procedure. An example of a typical recommendation action item associated with this mistake might read, 'Review the procedure with the employee to ensure that he understands the proper action expected.' This individual training activity may be beneficial to the person(s) who receives it, but in most cases does not address the underlying reason for the person's lack of knowledge. The individual refresher training does not correct any system defects that resulted in the improper behaviour. In most cases, the other employees remain in a state of inadequate training. Investigation teams often uncover and eliminate underlying system deficiency causes such as:

- Deviation from procedure was commonly accepted practice.
- Employee was following the example set by his supervisor and/or trainer.
- Training program did not adequately inform the employee of the potential consequences associated with deviating from a specific step or action.
- An out-of-date written procedure that no longer reflects current practices, or current configuration of the physical system *due to* defects in the process safety information, document control, or operating procedures management systems.
- Employee perceives that his way is better (safer, and/or more effective) *due to* deficiencies in the system for establishing and maintaining a specific competency and qualification level.
- Employee previously rewarded for deviating from the procedure *due to* a culture of rewarding speed over quality resulting in, and a reflection of, a defective quality assurance management system.
- Employee is experiencing temporary task overload *due to* defects in the scheduling and task allocation system and/or *due to* ineffective implementation of downsizing.
- Employee has physical/mental/emotional reason(s) that causes him to deviate from the established procedure *due to* defects in the fitness-for-duty management system.
- Employee believed he was using the correct version of the procedure, but *due to* defects in the document management system, he was actually using an out-of-date edition.

31.2.6 Preparing for investigating process incidents

A typical investigation environment immediately following an explosion or major fire may include the following circumstances:

- all (or most) plant utilities out of commission (electrical power, steam, water, inerting purge gas systems, plant telephones, radio systems, pagers);
- residual fires and hot spots still being brought under control;
- personnel who were on duty at the time of the event may be injured and therefore, unavailable for interview (in some instances, for weeks);
- environmental consequences still evolving;
- the plant neighbourhood being evacuated;
- regulatory agencies with partial or total control of the accident site;
- local (and in some instances, national) news media demanding information;
- a large portion of the potential evidence being destroyed by the fire or explosion;
- many plant employees traumatized and/or exhausted from the initial emergency response;
- third parties (insurance companies, contractors, customers, suppliers, attorneys) with legitimate needs for information and response action.

This set of circumstances is not unusual, and demands a robust incident investigation management system that can be rapidly and efficiently activated. There may be only a brief opportunity to capture some of the time-sensitive evidence. Organizing and preparing an incident investigation team is addressed in detail in Section 31.4. Composition and configuration of a process incident investigation management system is addressed in Section 31.7. The management system must be developed and implemented prior to the incident, with accompanying training and auditing.

Legal issues are a major component of investigations for process incidents. Many process incidents are accompanied by significant consequences and, therefore, litigation is probable. There may be third party injury or damage, on-site or off-site. Insurance company representatives have certain contractual legal obligations, needs and rights. In many instances in the United States, investigation of a serious process incident is conducted under the direction of an attorney and in anticipation of litigation. Legal counsel for

the organization has an obligation to protect the financial impact to the organization and to manage contacts and interactions with regulatory agencies and opposing counsel. There are certain measures the incident investigation team can implement to control access to investigation documents by outside parties. In many instances an attorney is designated as investigation team leader to ensure that all legal aspects are controlled.

In the United States, federal, state, and in some cases, local regulatory agencies have the authority and responsibility to conduct investigation of process incidents. In many cases, control of access to the accident site is assumed by the regulatory agency. Federal (US) agencies that may conduct investigations include:

- OSHA – Occupational Safety and Health Administration;
- MMS – US Minerals Management Service;
- USBM – US Bureau of Mines;
- EPA – Environmental Protection Agency;
- ATF – Alcohol Tobacco and Firearms;
- FBI – Federal Bureau of Investigation;
- USCG – US Coast Guard;
- CSB – US Chemical Safety and Hazard Investigation Board;
- NTSB – National Transportation Safety Board (pipelines).

In many cases these regulatory agencies are interested in determining compliance or lack of compliance with applicable regulations and standards. In some instances, the identification and elimination of root causes is not their top priority. In addition to the federal agencies, there are state and local authorities such as Fire Marshals and Public Safety Departments that have authority and desire to conduct incident investigations and issue reports and recommendations.

In the United States, many process incident scenes are designated as uncontrolled hazardous waste sites under the OSHA 1910.120 Hazardous Waste and Emergency Response regulation, subpart (q). This requires specific training for most personnel who enter the site, and also requires a written safety and health plan be developed and implemented for control of potential hazards that may exist.

31.3 Evidence Issues

31.3.1 Evidence challenges

Evidence collection and analysis is an iterative activity. For optimum results, a formal system of evidence management is necessary. The quality of findings and conclusions of the investigation are a direct reflection of the quality of the evidence examined by the team. Many chemical process incidents present considerable challenges related to gathering evidence. The facility may be significantly damaged by the event and, therefore, critical physical evidence may no longer exist or may not be initially available to investigators. In some instances, the starting point may be a crater. Regulatory agencies such as OSHA, FBI, US CG, EPA, ATF, or Fire Marshal may have total control of the site, and the owner representatives may be prohibited from entry. In the United States, the site for many chemical process incidents is declared an uncontrolled hazardous waste site under the OSHA 1910.120 subpart (q) regulation and certain access controls and actions become required. In some instances, third party legal (or insurance company) representatives may quickly file legal action to prohibit the owner from taking any action that might disturb potential evidence, therefore arresting any investigatory activity related to evidence gathering.

There are several recognized categories of evidence.

- people;
  – eyewitness and personal knowledge,
- physical evidence;
  – parts, things, equipment,
- electronic;
- paper documents;
  – historical, drawings, specifications,
- position/configuration;
- process parameters and conditions;
- physical properties and characteristics.

In many cases the plant infrastructure is severely damaged. Normal utilities and services will be unavailable, such as electrical power, telephones and radio communication systems. In large facilities, undamaged portions of the plant will be demanding permission to resume operations. Critical witnesses such as personnel who were on duty at the time of the incident may not be available due to injuries or may be at home recovering from extended hours spent in initial emergency response activities.

In the most severe explosion cases, a substantial portion of a process unit may be completely destroyed with only a crater remaining in the location of the equipment. Fragments and debris can be thrown considerable distances, sometimes outside facility boundaries. In many instances, sampling will be necessary to evaluate potential exposures to investigation personnel (asbestos, volatile organic compounds, blood-borne pathogens and others).

Some evidence is extremely time-sensitive and requires top priority in the initial stages of the investigation. Witness' perception, understanding and memory recall changes over time, and it is therefore important to place a high priority on gathering evidence from direct eyewitnesses and others who were on-duty at the time of the event. Physical evidence degrades with time (e.g. fracture surfaces, dust and soot samples, residual liquids, and charts, logs and other paper records that are exposed to the elements). Availability and integrity of electronic process data can be impacted by the loss of normal or back-up electrical power. Access to offsite evidence and restoration of this offsite damage is not in the control of the chemical process facility owner. Documentation of the extent of damage and necessary temporary repairs are high priority evidence issues. Within the plant or facility boundaries, evidence collection requires notification and coordination of all employees to minimize loss or inadvertent alteration of the physical evidence. Evidence may be spread over a large area, and all personnel within the plant must be instructed on the proper manner to communicate the location of evidence for collection by a trained team. Collection of chemical samples from vessels that are open to the atmosphere is also a high priority activity to ensure the sample is as representative as possible and to minimize adverse impacts from exposure to the elements (evaporation, moisture and others). Some evidence may be located in access ways and other places that need to be cleared quickly, and these areas may need to be placed on the high priority list.

For explosions, the damage itself may function as a blast gauge if the properties of the buildings and structures are known. The end use of the evidence collection may include:

- calculating blast pressures and impulses at each damaged structure;
- generating pressure contours;
- calculating the explosion energy released;
- determining the type of explosion;
- determining the source of the explosion.

31.3.2 Potential sources of physical evidence

Depending on the type and nature of the event, evidence prospecting may be required across a wide range of potential venues. The location and relative position of physical evidence should be documented and in most instances, photographed in place before anything is moved. A special type of information often highly useful is the 'as-found' position of valves, switches, control devices or sequence indicators. Previous incident reports and reports of process hazard analysis (PHA) studies can provide insight to credibly possible failures and accident scenarios. Operating data such as logbooks, computer records, process flow diagrams, and P&ID are potentially very useful documents. Engineering files, inspection records and repair files contain valuable information on the construction and features of fixed equipment. Another resource is the management-of-change records, providing information related to modifications that may not be updated on the equipment and system drawings. Scorer, scratch and impact marks made by moving objects can be helpful. The investigation team should look for things present that would not be expected to be present, and also look for things absent that would be expected to be present. Typical sources of evidence for chemical process incidents are listed in Table 31.1.

Table 31.1 *Potential sources of evidence*

Operating data (computer log, alarms, charts)
P&ID
Lab results
Instrument loop diagrams
Instrumentation interlock drawings
Instrumentation ladder logic diagrams
Operating manuals
Training manuals
Material Safety Data Sheets
Management-of-change records
Inspection records
Repair records
Meteorological records
Manufacturer's bulletins and Original Equipment Manufacturers Manual
Retainer samples of shipments and incoming raw materials
'As-found' position of valves, switches and indicators
Rupture disk condition
Anomalies in damage (or non-damage)
Residual liquids
Scorch pattern
Smoke traces
Melting pattern
Missile mapping
Layering of debris
Direction of glass pieces
Analysis of undamaged areas and equipment
Metallurgy analysis
Fracture analysis
Conductivity testing
Security camera tapes
Previous PHA study reports
Material balances
Chemical reactivity data
Corrosion data
Prior incident reports

31.3.3 Evidence collection and management

For major chemical process incidents, evidence preservation, storage and management is required. Effective collection and analysis of physical evidence should be conducted in a systematic fashion. All potentially important fragments, debris and other physical items should be documented in place (photography or other) before being moved or disturbed in any manner, noting the location and orientation. It is standard practice to assign individual evidence numbers to each piece of physical evidence collected. In most instances, small items are placed in clear plastic bags. A formal chain-of-custody system is developed and implemented to track the status of, and access to, any evidence not retained in the custody of the incident investigation team. Disassembly of equipment should be documented with photography and annotated at each significant stage. In some instances, disassembly of equipment may require agency or litigant approval before anything is touched or changed. Long-term storage of physical evidence may be required for investigations that involve potential litigation. It is important to arrange for secure storage, restricted access and chain-of-custody management for items that may be retained long after the initial investigation team has concluded its work. Regulatory agencies and other third parties may have need for copies of documentation as well as samples, photographs and portions of physical evidence. It is important to manage the distribution of copies of documents and other evidence in order to avoid unnecessary confusion and differences in interpretation of document evidence.

31.3.4 Evidence photography

Investigatory photography (and video) has multiple purposes. It is most often used to document the 'as-found' position, location, configuration arrangement, damage pattern and layering of physical evidence. In addition, photographic evidence is often useful in presenting the results of the investigation (reports) and in distributing lessons learned (training). Photographs taken by the investigation team find application in evidence analysis and in litigation activities. Photographs can be taken of items that need to be moved or of items and conditions that might change over the course of the investigation. Promptness is important since no accident scene can be considered frozen in time. In most instances, the investigation team should generate a formal log of each image, indicating the date, time, identity of the photographer and intended purpose or contents of the image. If multiple copies are distributed, a record of distribution should be maintained. In some instances, investigators have found it helpful to document the view of each significant witness by

going to the position where the witness was located to note what could be seen from his position.

Conventional 35 mm photography, digital photography, instant print and video images all have a place in the investigation process. In some circumstances, the use of a professional photographer may be appropriate, however in most instances, photography will be done by investigation team members. It is important to capture a series of overall orientation views from multiple perspectives and from multiple distances. These views will significantly enhance the value of subsequent photos taken from a closer distance. A sometimes-used resource for video is news media footage taken during the incident. This unedited footage is available directly from the TV station and can provide clues related to the sequence of the event.

Most photographic equipment requires perishable batteries that have, in some cases, unpredictable battery life. It is a good practice to implement a system to ensure that spare batteries are available and that periodic battery change-out and recharging occurs. Photographic film is date-sensitive and in addition, can be adversely affected by airport security screening devices. Storage of electronic digital images needs to be managed, with master copies or back-up copies maintained in a controlled manner.

Photography can present hazards to investigators. The view through the lens is restricted and the photographer may not be aware of tripping and falling hazards. Photographic and flash equipments are not normally designed for use in potentially flammable vapour conditions and require precautions similar to those used for any potentially spark producing tool or piece of equipment.

Good practices for investigation photography include:

- taking multiple orientation views from different positions and distances;
- placing an object of known size in the picture;
- being aware of potential shadows that will be cast by the flash unit;
- managing spare battery supply;
- making a written record of each image that might be confusing to the viewer;
- being aware of limitations of autofocus devices;
- generating a detailed log of all photographs;
- managing and documenting distribution of copies.

31.3.5 Investigation witness interviews (gathering evidence from people)

31.3.5.1 Introduction and general interview issues

Gathering verbal information from witnesses is one of the more challenging aspects of incident investigation. Conducting an effective interview differs from most process safety management activities in that interviewing can be as much an art as it is a science. There are numerous variables that affect interview success. Chemical process industry incidents are often accompanied by severe consequences and can also be accompanied by traumatic effects on human emotions. Chemical process industry incidents can be complex in nature and it is rare for a single witness to have a complete understanding of all the events and underlying circumstances. Each potential witness has a unique combination of perspective, personal experience and understanding of apparent facts. Promptness in obtaining statements and conducting interviews is essential for effective witness interviews and for obtaining the most reliable information.

Incident investigation interviews are conducted in a variety of circumstances. There are several types of investigatory interviews. The most common incident investigation interview is the initial screening interview, conducted for all possible witnesses who might be able to contribute to understanding the cause and event scenario. These initial interviews are usually brief (on the order of 30 min) and explore a wide range of topics and issues. A subset of witnesses is subsequently identified for follow-up interviews, which are more focused and address specific issues emerging from the investigation. These follow-up interviews can last over one hour. In addition, it is not uncommon to conduct group interviews after the initial round of individual interviews. In some instances, the presence of a group can activate synergies that contribute to increased understanding and recall. There are other special types of incident investigation interviews that are not in the intended scope of this chapter, including interviews of injured personnel (usually conducted at the hospital), interviews of non-employees (contractors, visitors, others), interviews conducted by regulatory agencies and interviews conducted by third parties (insurance representatives, legal representatives).

Since witness interviews are verbal communication exercises conducted between two human beings, they are naturally accompanied by human imperfection. In the chemical process industries, incident investigation interviews are seldom conducted by professional interviewers. Following a chemical process incident, the interview atmosphere can be adversely affected by significant emotional or physical trauma. Each person brings their own perception of apparent facts and sequence of events. Human memory is imperfect and can be significantly impacted by passage of time, interaction with other people, and by the witness learning additional facts after the incident. Humans have a capability and tendency to see and hear what we expect to see and hear. Our brains have an inherent tendency to interpret incoming information so that it becomes comprehensible to us, even if the incoming information is incomplete. We have a strong capability to identify patterns and fill in missing pieces of information based on our previous experiences and understandings.

When evaluating incoming information from witnesses, the interviewer should keep in mind that the witness may be:

- traumatized and may not be thinking as clearly as he/she would otherwise;
- unsure about certain information (and may withhold information or make incorrect assumptions);
- overly confident (and not necessarily accurate) about certain information;
- potentially defensive about certain issues;
- apprehensive regarding possible disciplinary action for themselves or others;
- angry at the company or at individuals;
- making assumptions without realizing it;
- second-guessing their own actions;
- interested in accomplishing other objectives and agendas not directly related to this incident.

The person conducting the interview should remember that:

- All information from witnesses may not be accurate, complete, or factual.

- Some information may contain hidden assumptions and stipulations.
- Some information may contain incorrect assumptions.
- The witness may sincerely believe something to be true, yet the information actually is false, incorrect or incomplete.
- Some degree of inconsistency among witnesses is normal. It is not unusual for two eyewitnesses to have different perceptions, understandings and recollection of the incident although they witness the same event.
- The witness may have a vested interest in the outcome of the investigation.

The interviewer should avoid placing blame or any implication of fault-finding. It would be premature to make judgements regarding determinations of fault.

31.3.5.2 Planning

Pre-interview planning can have significant impact on quality and effectiveness of information gathered during initial screening interviews. In almost all cases, information supplied in follow-up interviews will be modulated by the witness' interactions with other people after the initial interview and, therefore, the initial interview represents a unique opportunity to gather information with minimal contamination by others. The investigation team will often designate a single person as interview co-coordinator. This interview co-coordinator may not actually conduct every interview, but this person will have overall responsibility for witness interview evidence gathering. For consistency sake, it is desirable to have a minimum number of designated interviewers (usually no more than two or three investigation team members).

Persons selected as designated interviewers should have strong verbal communication and listening skills. Many technical personnel (such as engineers and chemists) find themselves assigned to investigation teams and often do not have strong verbal communication skills and abilities to communicate with non-technical personnel. Supervisory personnel, on the other hand, are often better suited for the interviewing task, due to their extensive experience and interactions with other people in the normal course of day-to-day activities. Typical practice is to have one interviewer and one witness in the room for the initial interview. In some instances, a second interviewer may be present to take notes or to provide specific knowledge for full understanding of the information the witness may offer. For instances where there are two interviewers, it is a recognized best practice to designate one interviewer to function as 'primary' or lead interviewer and for the other interviewer to take a secondary role. In some instances, the witness may request to be accompanied by another person (i.e. union representative, attorney or other). It is widely recognized and accepted that the one-on-one interview is the most effective format, although in some cases circumstances prohibit this arrangement. There is typically a reduction in the quality and quantity of information gained from the interview if there are too many interviewers present.

Venue for the interview should be neutral and non-intimidating for the witness. The interview location should provide privacy and be free from foot traffic and other interruptions. Interruptions disrupt the witness' train of thought and can severely detract from the interview dynamics. It is a common mistake to conduct the interview in the private office of plant management. This practice generates additional stress on most witnesses, as many hourly personnel will not feel comfortable in such locations, and will be less willing to supply complete and accurate information.

One early and continuing task for the investigation team is identification of potential witnesses. Personnel who were present at the time of the event are in the highest priority category. During the course of the investigation, it is common to identify additional personnel who were not on the initial list of potential witnesses. It is more effective to schedule the interview at a time and place convenient to the witness.

One recommended best practice is for the interviewer to personally visit the scene of the incident before conducting the interview. This adds to the interviewer's understanding and interpretation of the information supplied by the witness, and also provides an opportunity for the interviewer to ask clarifying questions for a more precise and complete set of facts. Before starting, the team must decide how the interview will be documented. The most common documentation method for initial screening interviews is to take hand-written notes. On occasion, audio or video tape recording is done, although these can adversely affect the witness. In cases where there is a second interviewer present in the room, it is a good practice to designate this person as the official note taker. Some investigators suggest that in order to minimize witness apprehension, the interviewer should inform the witness of the intention to take notes and where feasible, offer to supply the witness with a copy of the hand-written notes. In many instances, it is beneficial to have interview aids present such as: paper and pencil, plot plan, P&ID, photographs, flipchart and markers. During the interview, the witness should not be exposed to documents generated by the incident investigation team (such as marked-up diagrams, or listings of credible scenarios and possible causes), because information on these documents could alter the information that the witness provides during the interview.

The remainder of this section will focus on techniques for the initial screening interview, conducted by the organization's internal investigation team, recognizing that third party and regulatory interviews have additional issues beyond the scope and objectives of this chapter.

31.3.5.3 Stages of initial screening interviews

There are four distinct stages in every effective interview:

(1) opening;
(2) witness statement;
(3) interactive dialogue;
(4) closing.

31.3.5.3.1 Opening phase

In many cases, the overall effectiveness of the interview is determined during the first two minutes. If initial rapport and trust are not established, the quantity and completeness of the information offered by the witness will be significantly decreased. It is best to begin with introductions, clarification of the objectives and purpose of the interview and investigation, and a conscious effort by the interviewer to break the ice establishing some degree of rapport between the witness and the interviewer. Some interviewers find it helpful to start with some general background questions before jumping into the more significant

issues. This practice establishes a dialogue flow and allows an opportunity for the witness to overcome any initial nervousness and anxiety. It is helpful to discuss how the interview will be documented and, in some cases, it is also helpful to inform the witness how he/she was selected for this interview. If the interview is to be recorded, it is a good practice to explain the purpose of the recording and to seek permission from the witness. Some interviewers find value in asking the witness if he/she has any questions about the interview process, as a means to minimize stress to the witness. In some instances, the interview may be conducted under a confidentiality arrangement, where the interviewer pledges that certain confidentiality will be maintained related to exactly what information was supplied by which witnesses. This confidentiality is common for investigation interviews conducted by regulatory agencies. If there are confidentiality issues, they should be discussed during this opening phase.

31.3.5.3.2 Uninterrupted narrative

Following the opening, a critical segment of the interview is the witness statement of what he/she saw and experienced. It is a best practice to allow the witness to tell their narrative without interruption. If the interviewer interrupts in order to clarify or expand on something the witness said, the witness' train of thought could be permanently derailed. The interruption will most likely cause the witness to omit information he/she would otherwise have included. Listening silently during this narrative is very difficult and challenging even to experienced interviewers. During the narrative, the interviewer should write down items that need additional clarification. In most cases this initial narrative is completed in less than 10 min. During this listening phase, the interviewer should avoid giving non-verbal feedback such as frowning, yawning, looking at the clock or other actions that might distract or otherwise adversely affect the witness.

31.3.5.3.3 Interactive dialogue

During this phase, the interviewer and the witness enter into an exchange dialogue and information is transferred and clarified. This is the proper time to raise questions or receive confirmations from the preceding uninterrupted narrative. In most instances the interviewer will have a prepared list of general issues, items, topics and questions that provide the basis for completing this dialogue phase of the interview. These questions are used if the witness did not address the topic during the uninterrupted narrative segment. Open-ended questions are those questions that begin with what, which, where, when and how and cannot be answered with a simple yes or no response. Closed-ended questions are those that can be answered with a yes or no. Both types of questions have their place in incident investigation interviews. Open-ended questions are usually more productive and effective than closed-ended questions, especially during the earlier stages of the interview. Closed-ended questions are necessary and effective for clarifications and confirmations. Some typically useful questions include:

- 'How and when did you first become aware of the event or that something adverse might be happening?'
- 'What was different this time from previous times?'
- 'What were the operating conditions prior to the event?'
- 'Is this hazard covered in the training program and written procedures? If so, how is it covered?'
- 'Who else might have additional information that could help us determine what happened?'
- 'What are your suggestions/opinions on how this incident could possibly be prevented in the future?'

During the interactive dialogue phase, it is a good practice to use reflective listening techniques to confirm that the interviewer accurately understood witness' statements. This playback allows the witness to correct any gaps or errors in the interviewer's understanding. It is also a good practice for the interviewer to be on the alert for ambiguous or relative words that have different meanings for different people. Examples of these potentially 'fuzzy' words include: fast, faster, slow, slower, usual, normal, typical, sometimes, often, recently. If possible, the interviewer should clarify any words, jargon or acronyms that have potential multiple interpretations.

31.3.5.3.4 Summary closing phase

The majority of initial screening interviews reach a natural conclusion after approximately 20–30 min. The witness has offered his/her version of what happened and has addressed most of the issues on the prepared list of questions and areas of interest. The interviewer should use this phase to summarize his understanding of the information provided by the witness. It is a good practice to invite the witness to submit additional information if the witness remembers something after the conclusion of the interview. The interviewer should ensure the witness knows how to supply additional information and that the additional information is welcomed. The interviewer should thank the witness for his time and cooperation and should alert the witness regarding the possible need for a follow-up interview.

31.3.5.3.5 After the interview

Initial screening interviews are often conducted in series. Therefore, it is important to document thoughts, observations, questions and follow-up issues immediately after each interview. If the interviewer waits until the end of the day, the interviewer will not remember everything and may not be able to recall which witness supplied which information. It is a good practice to allow additional time between interviews, for documentation or an unexpected extension. It is typical practice for the initial screening interviews to last approximately 30 min, with an additional 15–20 min between interviews. In most cases, the interviewer will have visited the general scene of the event before beginning the interviews. In some instances, it may be beneficial after a particular interview for the interviewer to re-visit the scene and place themselves in the witness' location (or to physically retrace the witness' movements) to clarify and further understand statements made by the witness.

31.3.5.4 Optimizing results

A few chronic challenges to effective investigation interviews include the following factors.

31.3.5.4.1 Promptness

Promptness is critical. Witness memory degrades and is strongly moderated by interaction with other witnesses.

The investigation team should conduct initial screening interviews promptly.

31.3.5.4.2 Selective acceptance of information
During early stages of an investigation, the investigation team may identify a most likely scenario among a set of possible cause scenarios, and allow this preliminary finding to affect the conduct of interviews. It is very easy for the interviewer to become selective regarding preferred or non-preferred information being supplied by the witness. The interviewer can become non-objective and may not capture potentially significant evidence.

31.3.5.4.3 Disclosure
Another avoidable mistake is to disclose investigation team preliminary findings to the witness during the interview. This disclosure can cause the witness to modify the information offered during the interview.

31.3.5.4.4 Remaining neutral
An effective interviewer operates in a neutral mode to cause minimum impact on the witness. Interviewers should avoid leading the witness or phrasing questions in such a form as to suggest a desired response. The interviewer should show respect for the witness, even if the interviewer believes the witness to be less than truthful or otherwise difficult.

31.3.5.4.5 Making promises during the interview
Another avoidable mistake is to make promises or commitments to the witness during the interview, especially if the interviewer is not in a position to ensure that the promise is met.

31.3.5.4.6 Written statements
Statements written by the individual witness are a potentially strong augment for enhancing the effectiveness of interviews. In many cases these statements can be developed by the witness prior to the interview as a means to minimize memory degradation and minimize witness intermingling of perceptions. It is a good practice to ask the witness to sign and date the statement that he/she prepares.

31.3.5.4.7 Categories of witnesses
There are several groups of witnesses. Direct eyewitnesses are those who were present and personally experienced the event. Indirect witnesses may not have been present, but nevertheless possess useful knowledge that could assist in determining and understanding the cause scenario. Indirect witnesses can also be helpful in disproving and excluding proposed scenarios that do not apply in this instance. There are several groups of non-employee witnesses who often contribute valuable information including: contractors, visitors, delivery personnel and former employees. Emergency responders who were present at the scene of the incident during the event can provide additional clues as to the sequence of events and condition of equipment before the end of the incident.

31.3.5.4.8 Room arrangements
Interview room configuration can impact the quality and quantity of results. Some interviewers try to avoid a seating configuration where the witness is on one side of a table (or desk) and the interviewer is on the opposing side. A 90° orientation is less threatening and more comfortable for many witnesses.

31.3.5.4.9 Non-verbal communications
Non-verbal communication such as eye contact and body posture can sometimes provide additional clues and insights as to the information being offered by the witness.

31.3.6 Evidence analysis

Evidence analysis can provide objective and scientific independent confirmation of the cause scenario speculated by the investigation team. Damage patterns provide information related to the origin and sequence. Investigators can also make useful determinations based on anomalies and by analysing what remains undamaged.

There are numerous publicly available resources for evidence analysis, including physical property data for melting temperatures autoignition temperatures and chemical incompatibilities. Some methods are nondestructive (Nondestructive Evaluation, NDE), while others require permanent modification of the evidence. Visual examination is the most common and one of the most powerful evidence analysis techniques. NDE Integrity testing can include leak checking, X-ray radiography, ultrasonic thickness testing, physical measurements, magnetic particle testing and others. Two useful references are the National Fire Protection Association standards # 921 for Fire and Explosion Investigations and # 907 Determining Electrical Fire Causes. Although these two references are prepared for use primarily by municipal fire protection agencies and organizations, they contain information helpful to industrial investigators. For example, tables from NFPA 921 present autoignition (table 3.3.4) and melting (table 4.8) temperatures for specific commercial materials. NFPA 921 also includes an interesting section on Human Response to Fire (chapter 8), interview techniques and helpful information on preparing sketches and diagrams. Another useful reference in fire and explosion evidence analysis is the Materials Technology Institute Publication 30, *Guidelines for Assessing Fire and Explosion Damage*. This publication uses a temperature profile to assist in determining fire cause and origin.

Metallurgical and failure analysis of evidence, fractured physical evidence and failed equipment can provide valuable information regarding the nature, sequence and cause of the incident. The mode of fracture (ductile or brittle) can indicate pressure and impulse forces. The direction and style of crack propagation is often helpful. Metallurgical analysis can help determine age, origin and reason for the failure. Cause and type of corrosion attack can be determined and can provide evidence of contaminants or corrosion not expected to be present. Temperature at time of failure can be determined. The actual fracture pattern can provide an indication of conditions at the time of failure.

There are several types of chemical analysis techniques that can be helpful in identifying the cause and sequence of the event. Chemical analysis can be conducted to confirm or refute the presence of compounds, substances, trace impurities or gross contaminants. Retainer samples of raw materials and final products are often re-analysed to help refute low probability scenario. Residues remaining after a fire can still provide useful chemical evidence. Physical property testing is useful in analysing or confirming potential fire, reactivity, stability, solubility or contamination

concerns. Gas chromatography and scanning electron microscopy (SEM) are two common methodologies.

Arson is a special case and in many instances will leave tell-tail unique evidence. Most fire departments, law enforcement agencies and insurance companies have in-house experts available to assist if there is a suspicion of malevolent action. There are well-established char and burn patterns for most common building materials and components that can indicate the nature of the fire (Redsicker and O'Connor, 1997). Arson investigators look for atypical patterns and the presence of accelerators and ignition devices.

31.4 The Investigation Team

31.4.1 Team charter (terms of reference)

Most incident investigation teams for significant process incidents are charted, organized and implemented as a temporary task force. Most team members will retain other full-time job assignments and responsibilities. The intention is for the team to disband at the completion of their assignment, usually upon issuance of the official report. It is important and necessary for the team's authority, organization and mission to be clearly established, preferably in writing by a senior management official in the organization. The team charter authorizes expenditures, reporting relationships and designated responsibilities and authority levels for the team. The investigation team charter is usually generated and issued from the upper levels of the corporate organizational structure.

31.4.2 Team composition

The incident investigation team for process-related events is typically composed of a cross-section of skillsets and competencies related to the process and nature of the event under investigation. Team size can vary from as few as three full-time members to as many as 15, with six to eight being most common. In many aspects, the team size and composition are comparable to the team formed to conduct a PHA. There is a designated team leader who brings the investigation methodology expertise to the team. In almost all cases of process safety incidents, there are team members who have operating experience with the process unit that experienced the event as well as a process engineer who understands the control systems. In the United States, in incidents where there are significant consequences and a likelihood of litigation, the nominal or actual team leader may be an attorney. It is a common practice in significant incidents for the team to have a designated sponsor who is a member of the upper level of the organization's management team. In addition to full-time members, it is a common practice to enlist technical speciality help on a part-time basis. These special team members may not attend every team meeting, but nevertheless execute designated tasks that help the team move forward in identifying root causes. Special skillsets might include reactive chemist, instrumentation or control system engineers, material engineer, rotating machinery specialists and industrial hygienist. It is a common practice to use company employees from sister plants or sister units, who may have specific knowledge of the process being investigated, yet who may not be as emotionally connected to the incident. Use of outside personnel can add additional credibility, objectivity or technical expertise where appropriate.

One member of the investigation team will normally be devoted full-time to coordinating the witness interviews. It is a good practice to designate one team member to manage all photography and photographic or video evidence. Another member is often designated as the official spokesperson coordinating all communication external to the team. For many incidents, management of evidence is assigned to a single team member. Another typical team member is a representative of the safety department familiar with the administrative safety management safeguards.

31.4.3 Team preparations

31.4.3.1 Training

Team training occurs in two stages. There is normally an established formal training program for all potential investigation team members that is conducted prior to the event to maintain a pool of qualified potential team members. Some required training is extensive; US Hazardous Waste and Emergency Operations (OSHA 1910.120) and respiratory protection (US OSHA 1910.134) are examples and may require periodic refresher training and certification. The incident investigation management system should be developed and implemented to assure that investigation team member training needs are maintained. Use of respiratory protection devices may also require fit testing and pre-use medical evaluation. It is a major handicap to attempt to conduct all needed and legally required training after an event and before the investigation can begin. Team leaders require training in effective application of the investigation technology method being applied, as well as an understanding of organizational expectations, definitions, reporting requirements and issues related to developing recommended preventive action recommendations.

At the time the investigation is launched, it is common for the personnel selected as full- or part-time team members to receive refresher training focused on the nature of the event. This refresher training may include personal protective equipment training (respiratory and other), the investigation methodology and approach, as well as specific emergency preparedness and emergency response training related to the specific accident site.

31.4.3.2 Supplies and maintaining readiness

Investigation supplies and equipment fall into two general categories, individual and team items. Responsibility for procuring and maintaining individual items is normally placed on each individual team member and will include items such as hard hat, eye protection, safety footwear, fire-protective coveralls, gloves, goggles, boots, raingear, pencil, pen, notepad and flashlight. Team supplies are often collected beforehand and kept on-hand in a ready state. Preparation and maintenance of team supplies should be a component of the incident investigation management system and should be periodically inventoried, refreshed (batteries and film) and audited. In many instances there is a 'team go kit' containing the most often used equipment that might be needed by two people during the first several days of investigation. The equipment needed by the team will vary considerably depending on the nature and location of the incident and the degree of infrastructure support immediately available at, or adjacent to, the incident site. A typical assortment of team supplies and tools is shown in Table 31.2.

31.4.4 Launching the investigation

31.4.4.1 Getting started

A critical first step is organizing the team, identifying potential team members and designating a team leader.

Table 31.2 *Typical investigation team supplies and tools*

Item	*Details*	*Minimum quantity*
Go bag	Empty duffel bag	1
Camera – digital		1
Cell phone		1
Cell phone charger	12 V DC for vehicle	1
Camera – 35 mm		1
Film	35 mm 36 exp, colour 200 speed	4
Evidence tags		50
Battery for flashlight		4
Battery for recording device		4
Battery for camera		2
Wipes	Box of 50	1 box
Zip-lock bags		
Small	Small 4″ × 6″	25
Medium	Medium 8″ × 10″	25
Large	Large 1–2 gallon size	12
Plastic bags – extra-large	10–20 gallon	12
Tie-wraps	Plastic or wire	50
Permanent marker	Fine point and wide point	10
Marker	Yellow solid	1 box of 6
Marker paint stick	Yellow medium point	6
	Yellow fine point	6
	Black medium	6
	Black fine point	6
Tape		
Duct tape	50 ft roll	1
Masking	20 ft roll	1
Tape barrier marking	'DO NOT ENTER,' 'AUTHORIZED PERSONNEL ONLY'	200 ft
Flashlight	Explosion proof	2
Pocket dictating recorder with two cassettes		1
Tool		
Multi-tool	All-in-one, pliers, screwdriver, awl	2
Screwdriver multiple tips	Phillips, Torx, Slot, various sizes	1
Slip joint pliers		1
Wire cutters		1
Fish scale	1–50 pound range	1
Pocket extension mirror		1
Magnifying glass		1
Tool box cutter	Retractable blade	1
Toothbrush		1
Tape measure	6.5 ft big letters	1
	12 ft	2
	25 ft	1
Ruler	6 in.	1
Thermometer	0–100 F range	1
Compass	Pocket type	1
Micrometer		1
Angle finder		1
Yellow string and plumb bob		1
Electric tester		1
Respirator	Half mask, size medium	1
Respirator cartridges		4
Disposable coveralls	Large and extra-large	2 each
Coveralls -Nomex	Large and extra-large	1 each
Disposable booties		6 pairs
Flags with rods	Position markers	24

Table 31.2 *(continued)*

Chain-of-custody forms		6
Helmet liners		2
Gloves, nitrile or latex		1 box 100
Gloves, leather		2 pairs
Earplugs		1 dozen
Eyeglasses	Safety glasses with side shields	2
Goggles		1
First-aid kit	Small pocket size	1
Spray paint	Pressurized cans, red/orange	2
String	1 ball minimum 300 ft	1
Clipboard	Metal box, straps	2
Pocket notebook	Water resistant	2
Post-it notes	2 in. × 2 in.	2
Pencils – mechanical		2
Pens		2
Fanny pack		1
Portable hand-held radios	Set of three with spare batteries	3 hand-talkies
Garbage bags	Large black plastic with tie wrap/closure	6
Rain gear	Large	2
Poncho		2
Insect repellent		1
Sun block cream		1
Health and safety plan for investigation team	Electronic and hard copy	1
Gas detector	Personal, H_2S, O_2, CO, flammable	1

Legal status of the investigation is determined and a formal charter is developed and issued. It is necessary to establish formal contact with emergency responders or regulatory agencies if they are in control of the scene to develop a plan for coordinated actions. The incident team leader should make preliminary arrangements for preservation of potential items of evidence. Sometimes the team leader may need to complete this action even before the initial investigation team meeting due to the time sensitive nature of some evidence. Circumstances may require the team leader (along with members of the investigation team who are immediately available) to:

- plan and begin witness interviews;
- organize and implement information (and evidence) management;
- initiate a listing of factors that may have influenced the event (inherent process potential hazards, known risk and control measures);
- develop a preliminary list of potential cause scenarios;
- develop initial timeline;
- arrange and plan for photography;
- initiate investigation of areas outside restricted area;
- begin to procure supplies and logistics for the team;
- plan for evidence preservation (identification, control, storage, restricted access);
- plan for team meeting – room, supplies and logistics;

31.4.4.2 Initial team meeting

The following section is intended to provide guidance to teams conducting initial team meetings for investigations of major incidents, however many of the items are applicable for all initial team meetings regardless of the nature or severity of the event. The first order of business is usually formal introductions of team members and their individual backgrounds, experiences and skillsets that may have application to the investigation. The next order of business will address any legal and confidentiality issues. Communication protocols and expectations (both internal and external to the team) should be clearly explained with confirmation from each member that he understands and accepts the communication controls. For major incidents, another item for the initial team meeting is coordination and liaison with other entities (inside or outside the organization). Evidence management should be discussed and preliminary arrangements made for collection, identification, documentation, chain-of-custody, storage and access to evidence by team members and others. Witness interviews are an important function in every investigation, and it is typical to assign one team member to coordinate the entire interview process. Arrangements and responsibilities for photography (and video) are usually developed during the initial team meeting. There may be a recognized need for special technical knowledge, competencies or services that should be addressed during the initial and subsequent team meeting.

It is also a good practice to address team supplies, logistics and consumables. There may be a need for training or refresher training in the use of personal protective equipment (such as respiratory protection or portable instrumentation), and the initial team meeting presents an excellent opportunity to identify this need and make appropriate arrangements. As previously mentioned, it is a common practice to conduct specific training during (or immediately following) this initial team meeting. The initial team meeting may also include an overview tutorial on the process operations, materials, credible failure modes, previous incidents and potential hazard exposures than might be encountered by the team.

31.4.4.3 Team member safety issues

Field investigation activities are often conducted in less than ideal circumstances. Investigators can be exposed to

a variety of hazards. One common hazard is the constant potential for slips, trips or falls created by unstable working and walking surfaces. Accident scenes are often accompanied by sharp metal edges from debris and broken glass. Investigators can be injured by debris falling from above that becomes unstable by vibration or shifting rubble piles.

Other hazard exposures include radiation from nuclear instrumentation devices, and stored potential energy in the form of hydraulics, pneumatic, spring energy and elevated mass. One initial task conducted by emergency response personnel is to attempt to isolate all sources of energy (electrical, pneumatic, thermal, hydraulic or other form). The investigation team should conduct an independent verification that all electrical power, energy sources and sources of additional fuel (gas pipelines for example) are isolated. It is not uncommon to find energized electrical circuits that were installed during construction and are not accurately depicted on existing electrical power distribution documents. Air-borne contaminates from uncontrolled releases of process materials represent another potential hazard exposure. The team may need to conduct sampling to assess the need for additional clean-up or use of personal protective respiratory equipment.

During the investigation, team members will often have need to access elevated or constricted space to make observations or gather evidence. Access to elevated locations may have to be made by crane basket or special scaffold. Team members may need to be competent in the use of fall protection devices. Sometimes in major accidents, the investigators may need to deal with biohazards. As mentioned earlier in Section 31.2.6 and Section 31.3.1, the site may be classified as an uncontrolled hazardous waste site, therefore, the team may need to implement hazardous waste and emergency response control measures. Regardless, the investigation team should be prepared for emergencies that could occur during the course of the investigation, such as releases of materials or injuries to team members. It is a good practice to implement emergency alarm, alert and communication capabilities for the investigation team.

31.4.4.4 Pre-entry activities

Even before the team sets foot on the accident site, there are certain investigation tasks that can be initiated. Access to the site may be restricted due to emergency response activity or regulatory agencies. In many instances, the team, or portions of the investigation team, may be ready before authorization is received to make the initial entry. The initial team meeting can be conducted and witness interviews can begin, although it is more productive if the initial entry can be made before starting these two activities. Required notifications must be completed and documented. In some cases there is a requirement for follow-up notification. Assembling the list of potential witnesses and scheduling of interviews can begin immediately. If not already completed, the charter for the team, legal considerations, team composition, team leadership and arrangements for any travel, accommodations, team supplies and team refresher training should be conducted or confirmed. Emergency responders can be de-briefed. Arrangements for use of outside photography (such as aerial photography) can be completed. The investigation team meeting room, supplies, logistics and evidence storage arrangements can be made before the initial entry. Areas outside the accident scene (offsite, downwind, adjacent units) can be toured, photographed and evaluated. The team or members of the team can begin to assemble relevant information and evidence (documentation, electronic data, drawings, material safety data sheets, meteorological records). A preliminary timeline can be initiated as well as a compilation of credibly possible scenarios and factors that may have influenced the event.

31.4.4.5 Initial reconnoiter

One important activity is the initial visit to the scene. An effective technique for conducting this important activity is the initial reconnoiter. The objective of this activity is to obtain an overview of the entire incident scene before becoming overly focused on the apparent centre of the event and before any evidence is disturbed. The investigator (or in some cases the entire investigation team) conducts a slow, deliberate and systematic circuit from outside the accident scene. During this circuit the investigator should:

- look for potential safety hazard exposures to the investigation team;
- look at the big picture (forest), not just the micro (trees);
- note what is not damaged;
- note what is present that would not be expected to be present;
- note what is absent that would be expected to be present;
- make intentional pauses to observe the scene from multiple angles and elevations;
- use all senses (such as smell, sounds, physical sensations of pressure, force or heat);

31.4.4.6 Suggested summary checklist for team leader

The following is a suggested model checklist that can be prepared and used by incident investigation team leaders.

31.4.4.6.1 Initial communications

- Clarify known casualties and status of injured.
- Internal notifications done and confirmed – who, when, what info, delivered to whom by whom.
- Confirm legal and regulatory notifications and requirements – legal and regulatory status.
- Confirm team charter – authority, administrative and financial, scope, reporting relationships.
- Team member selection and notification, confirm availability, and identify potential availability problems.
- De-briefing with emergency responders and local site management – initial data gathering request.
- Clarify need for HAZWOPER coverage and training.

31.4.4.6.2 Initial team meeting (agenda and primary assignments)

The following topics are applicable to most initial investigation team meetings. The team should consider each issue and make assignments where needed:

- communication protocols, expectations, responsibilities, internal to team and external;
- Evidence;
  – time-sensitive evidence (electronic and other),

  - stabilization,
  - identification,
  - custody and control of access to evidence,
  - documentation,
  - storage (short term long term and preservation),
  - electronic evidence,
- witness interviews – assign responsibility for coordination, identify potential witnesses, schedule, coordination with other agencies and parties;
- photography – conventional film, digital, video, digital, how to document and control distribution;
- logistics for team – supplies, personal protective equipment (PPE), finances, administrative needs, biological issues;
- special services or technical skills that may be needed;
- liaison with other investigations and third parties (insurance, regulatory, Local Emergency Preparedness Committee (LEPC));
- expectations for interim report;
- requirements, needs of management, review and release authorizations protocol and documentation;
- special training for team (all or part of team, PPE, chemistry, control, special equipments or systems);
- determine involvement of contractors;
- begin listing of known facts;
- develop initial timeline chronology;
- develop initial logic diagram to identify possible cause scenarios;
- identify restart criteria if applicable.

31.5 Identifying Root Causes

31.5.1 General concepts

Root cause determination is an iterative process which systematically seeks to identify and understand the underlying causes that allowed the event sequence to progress to its ultimate consequences. As discussed in Section 31.2, the investigators need a clear understanding of the term root cause in order to determine the proper stopping point for the investigation. Chemical process incidents are most often complex events with multiple root causes (Philley, 1992; CCPS, 2003).

Root cause determination must be systematic and use a scientific approach. All credible explanations should be examined. Alternate scenarios that are rejected should be rejected based on evidence and the reasons for the rejection should be documented. Root cause investigation is similar to root cause analysis, however, there are some important differences between the two terms. Root cause analysis (or root cause failure analysis) is more often used to describe the process by which equipment failures are investigated (Mobley, 1999; Anderson, Bjorn and Fagerhaud, 2000). The term root cause investigation, on the other hand, is used in a broader context to describe the entire incident investigation process and all associated activities. Root cause analysis could be thought of as a subset of root cause investigation. One aspect of the root cause investigation process uses root cause analysis to determine and understand the actual adverse scenario and its underlying causes. Results of root cause investigations should be based on evidence, reproducible and defendable. All comprehensive root cause determination approaches attempt to determine the underlying reasons that allowed a set of circumstances to exist, the trigger events in the adverse chain, and the failures in protective systems (physical systems and administrative systems).

Root cause determination relies on application of the scientific method (BioTech Life Science Dictionary, 1995). The scientific method as universally accepted is an organized approach to the study of a problem that consists of recognized steps of observation (collecting data and evidence), hypothesis (developing a set of credibly possible incident scenarios), testing (confirmation and validation of the speculated cause scenario), analysis (the results of the testing are interpreted and accepted or refuted), and conclusion (the investigation findings) that can be independently evaluated by other investigators. As additional information (evidence) becomes available, investigators gain a more complete and accurate understanding of the cause scenario, then refine and adjust the hypothesis (speculated cause scenario). Rejected scenarios are documented. All evidence is addressed, even information that may not support the speculated cause scenario.

In the second edition of Lees (chapter 27), accident models are discussed along with several approaches for identifying causes. T. Kletz views the accident as a series of events and assigns each event to one of three general layers:

- immediate measures to prevent a repeat event;
- measures to avoid the hazard (implementing or strengthen barriers);
- changes to the management system to eliminate or reduce the risk exposure (moving towards inherently safer design).

Root cause tools are used to gather and analyse additional evidence, information, and reach a more complete and accurate understanding of the actual scenario and its associated underlying reasons. Application of root cause determination tools is an iterative process because of the changing quantity and quality of information. Diagrams and checklist used alone do not automatically yield root causes, but do provide general direction and structure to assist investigators to examine possible issues that may apply to the incident being investigated. The investigators then use the specific evidence, facts, circumstances and available information to determine the root causes. Various methodologies use different types of diagrams, charts, checklists and definition of specific terms such as 'near-root cause,' 'basic cause,' 'causal factors' and others. It is not in the scope of this chapter to present a summary of all root cause determination methodologies currently in use.

31.5.2 Toolbox

31.5.2.1 Chronology

Most root cause methodologies incorporate use of a chronology tool to establish the sequence of events, activities and conditions. Development of a timeline chronology is an iterative activity and allows the investigator to better understand the evidence and witness statements. Some items on the timeline can be precisely positioned because there is hard evidence such as a record of the time of alarms and instrumentation data (see Figure 31.3). Exact time for other information may not be capable of being determined, however, relative sequence may be identified. Some root cause investigators use the timeline to assist in identifying those events that represent adverse consequences, management system breakdowns, unplanned situations or

failures of safeguard protective measures. In some root cause investigation methods, these undesirable outcomes are classified as 'critical events.' There is no established convention for constructing a chronology diagram. Some investigators prefer a horizontal orientation, while others find value in vertical or diagonal formats. For complex events or where there are simultaneous parallel sets of activities, the timeline can be expanded into branches and parallel tracks.

31.5.2.2 Logic diagrams

Logic diagrams have several applications in investigations, and are most often developed in an iterative fashion. As shown in the event tree logic diagram in Figure 31.4, in the early stages of an investigation they can be used to illustrate credibly possible reasons, conditions and events to assist in determining the cause scenario. As shown in Figure 31.5, they can point the investigators to what specific additional information or evidence might be gathered in order to confirm or refute a postulated cause scenario. In the middle and late stages of an investigation, logic diagrams can be refined and used as a quality control tool to ensure the team is systematically addressing the information and that individual branches of the logic tree are consistent. Another use of logic diagrams is in presenting the findings in a formal written report. A simplified logic tree can be used to present the cause scenario and illustrate conditions and events so that the reader can follow a complex incident. In the early stages of an investigation, the type of logic gate may not be initially known since relationships between facts, events or causes may not be sufficiently understood. At the later stages of the investigation, when the event is better understood, the types of gates (exclusive AND gates, OR gates) can be refined into the iterative diagram. Deductive diagrams similar to the conventional 'fault tree' diagrams are the most common type of investigative logic diagrams. On occasion, inductive diagrams (such as the 'event tree' shown in Figure 31.4) may be used to determine a most likely match between known facts and possible causes. One special type of investigation logic diagram is the management oversight and risk tree (MORT) (Johnson, n.d.). The MORT investigation method uses a generic logic tree with pre-existing gates. The investigation team gathers and examines evidence to confirm which branches of the tree were applicable in the particular incident being investigated.

The team applies the logic diagram in an *iterative* manner to identify what conditions and actions were present or were needed for the accident to occur. The initial logic diagram may contain several speculated 'OR' gates, where the information currently available is insufficient to determine if the branch was applicable. The logic diagram will highlight missing pieces of information thereby guiding the team to gather additional focused information. A logic diagram can highlight evidence that is inconsistent or contradicts a proposed incident cause scenario. Once there is sufficient evidence to refute a particular branch, further development of that particular branch is terminated and documented. Near the final stages of the investigation, the logic diagram can be used in a quality assurance mode to verify known facts meet logic principles and that each branch is in agreement with all other branches of the logic diagram.

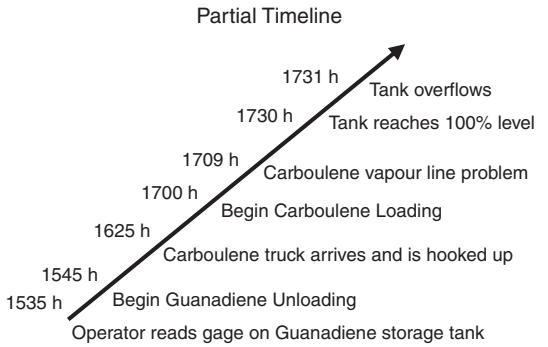

Figure 31.3 *Sample chronology*

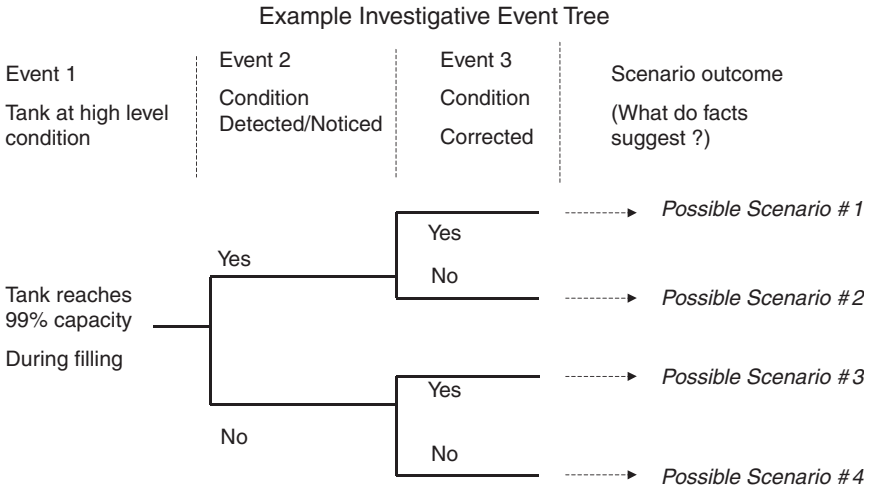

Figure 31.4 *Event tree*

One important limitation is that logic diagrams do not always show time or sequence relationships relative to the information on the diagram. Special charting diagrams use a combination of chronology and logic diagrams to illustrate and understand the event. Some investigation methodologies apply special conventions such as the shape of text boxes and the type of interconnecting lines to further illustrate the event.

Consider the following typical tank overflow event.

Operator was unloading tank truck of liquid solvent while loading railcar of VCM chemical. Solvent storage tank TK102 was overfilled causing it to overflow. Approximately 1735 gallons of solvent spilled into dike area. Level gauge on solvent tank was found to be 16% out of calibration, thus reading low. VCM railcar was experiencing vapour lock problems. Incident occurred just before shift change. Level instrumentation on solvent tank TK102 was 32 years old and was calibrated every 36 months.

The initial logic diagram developed by the investigators might look like something shown in Figure 31.5.

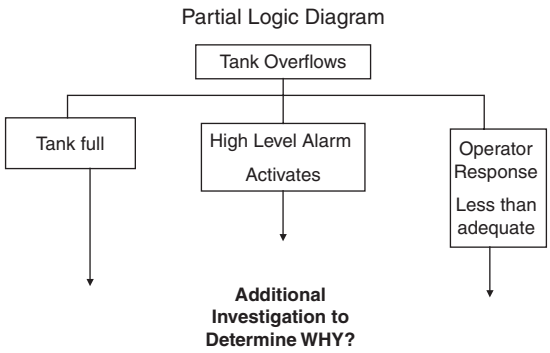

Figure 31.5 *Logic diagram for tank overflow incident*

The investigation team then gathers additional information and evidence and develops an initial chronology.

As additional evidence becomes available the team is able to refine the logic diagram and move closer to identifying underlying root causes (see Figure 31.6). Each branch of the logic tree is then developed to a point where evidence proves that the branch was not applicable, or to the point where underlying root causes can be identified.

Another special diagram is the Ishikawa fish-bone diagram where information and conditions leading to the event are depicted as branches on a horizontal format (see Figure 31.7). The fishbone diagram is not a true logic diagram, however it does provide an effective tool for investigators to systematically gather and examine information relative to the causes of the incident.

31.5.2.3 Application of critical thinking skills/concepts

Critical thinking uses concepts of logic and reasoning in problem solving to produce more accurate and defendable conclusions (Philley, 2000). The investigation team is often initially confronted with conflicting information from witnesses and a large set of credibly potential scenarios, therefore, investigation of chemical process incidents can benefit from application of critical thinking skills. This section discusses several aspects of applying principles of critical thinking, to the investigation. The term 'critical thinking' has multiple definitions. One simple definition is, 'the art of thinking about your thinking in order to make your thinking better' (thereby making your thinking clearer, more accurate, or more defensible (Center for Critical Thinking, n.d.). Applied to incident investigation, critical thinking helps the investigation team to:

- identify and evaluate potential cause scenarios;
- evaluate evidence in support of (or to refute) a proposed cause scenario hypothesis;
- select the most appropriate (most likely) cause scenario.

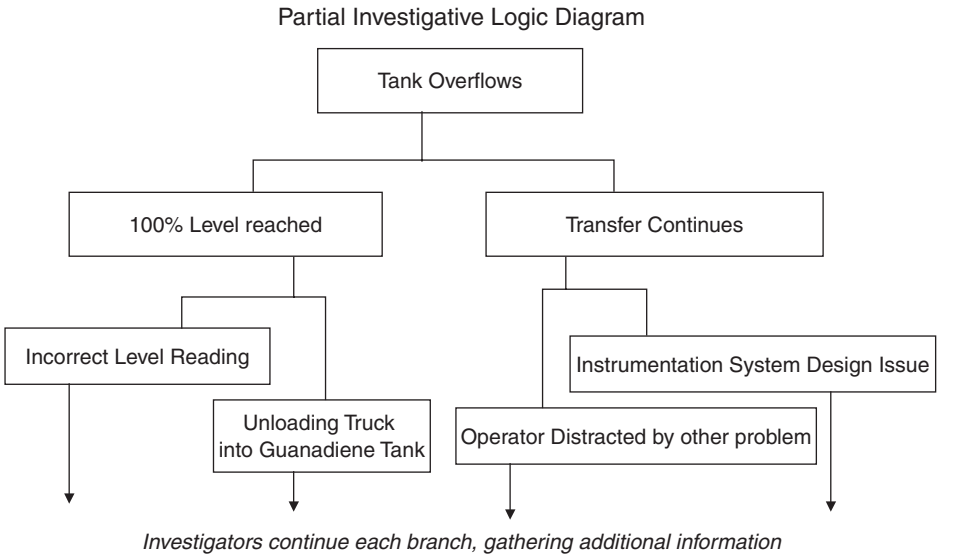

Figure 31.6 *Developing logic diagram*

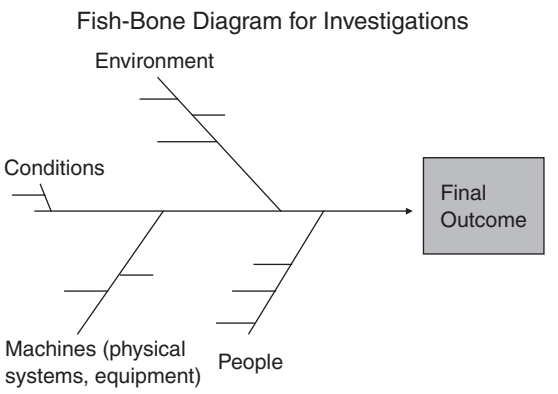

Figure 31.7 *Sample fish-bone diagram*

31.5.2.3.1 Lateral thinking
One important critical thinking concept useful in investigation is lateral thinking. Lateral thinking is sometimes characterized as 'thinking out-of-the-box.' When applying lateral thinking, investigators search for alternate explanations that fit a given set of known conditions and facts. As additional evidence and information becomes available, the alternate explanation will become more or less credibly possible. Lateral thinking is particularly valuable in the early stages of the investigation in order to prevent the team from prematurely locking-onto an incorrect cause scenario and also in evaluating apparent contradictions in evidence. Lateral thinking allows and encourages investigators to deviate from normal explanations, conventions and expectations. Creativity is used to identify possible alternate explanations for the evidence presented. When presented with a set of circumstances, our first response is to find a traditional explanation that fits the facts as we understand them to be. A lateral thinking approach to identifying a cause scenario would not reject the most likely explanation, but would expand the set of possible scenarios to include alternate, less probable, explanations for the same set of facts. Alternate scenarios remain on the table until there is clear reason and evidence for rejecting them. Lateral thinking sometimes generates extra work for the investigation team to document reasons why alternate explanations were rejected. Nevertheless, it adds to the overall quality of the investigation and makes the ultimate findings more credible and defendable.

31.5.2.3.2 Critical thinking validation of cause scenario
One critical challenge is to accurately and quickly determine the cause scenario. Validating speculated possible scenarios is fundamental to investigation success. In a purely scientific setting, a set of validity tests has been developed to prove a theory or hypothesis (Lett, 1997). In practical industrial accident investigations, these validation principles can be used to ensure a quality investigation:

- Is the scenario logical?
- Is it comprehensive in addressing all known evidence?
- Are the identified causes sufficient to create the result?
- Can it be replicated?
- Does it have honesty and integrity?

31.5.2.3.3 Logic
This first validity test confirms that the identified scenario and associated facts agree with accepted logic principles (Webster's II New Riverside Dictionary, 1984). Any argument offered as evidence to support or disprove a suspected incident cause hypothesis must follow accepted rules of logic. Two excellent examples of this logic test are the fact–hypothesis matrix (CCPS, 2003), and the use of truth tables when testing the output of binary electronic circuits or when diagnosing/troubleshooting instrumentation systems. Logical thinking is essential for accurately determining the scenario cause relationships in every process safety incident investigation. Investigators must apply logic and reason effectively.

For example:

1. if the temperature in tank A was higher than in tank B, and
2. if the temperature in tank B was higher than in tank C, then, by logic and reason
3. the temperature in tank A *must* have been higher than in tank C.

31.5.2.3.4 Comprehensiveness
The second validity test, comprehensiveness, confirms that *all* known information has been addressed in the evaluation. The team does not have the prerogative of being selective about which facts it accepts, even if a particular fact may not appear to support the preferred hypothesis. There is a natural tendency to welcome specific information that supports the scenario preferred by the investigators. There is a corresponding tendency to 'reject' information that does not support the desired hypothesis. At the conclusion of the investigation, if there is any evidence available that contradicts the cause scenario, reasons for refuting this contradictory information should be adequately documented. In purely scientific research activity, this comprehensive test is easier to apply. However, in the practical world of industrial incident investigation, there are varying degrees of credibility regarding the accuracy of information. Not all information available to the investigation team has the same degree of truthfulness and accuracy. Often, the team will initially be faced with seemingly contradictory information. In most, but not all cases, apparent contradictions can be resolved by gathering additional clarifying information. Inconsistent or conflicting information is especially common in information gathered from witness interviews.

31.5.2.3.5 Sufficiency
The third validity test is sufficiency. Evidence offered in support of a cause scenario must be adequate (sufficient) to establish proof. If a scenario requires three components to be present, then the investigation team must establish the credible presence of all three components.

31.5.2.3.6 Replicability
The validity test of replicability requires that any evidence that is based on experimental results is capable of being duplicated by others using the same conditions.

31.5.2.3.7 Honesty
The final validity test is honesty. On the surface, this test seems an obvious requirement. However, in handling or

presenting evidence, there are opportunities for misleading or incomplete representation of facts. The investigation team must exercise a high degree of honesty and integrity, especially in cases where findings may not be favourable to the organization's reputation. Selected omission of information can have a significant effect and there is an obligation to document any unresolved inconsistencies.

31.5.2.3.8 Cause scenario selection issues

Incident investigators often encounter cases of subjective opinion masquerading as truth. When analysing information, it is important to distinguish between objective fact and subjective opinion. Investigators should be alert for dogmatic statements that may not be supported by actual evidence. Dogmatism is establishing conclusions on rules, conditions, protocols and prescriptions established by some authority. Merely because oxygen tests are required by written procedural instructions does not mean that tests were actually conducted in the instance being investigated. The investigation team must verify assumptions. Stipulations should be clearly and thoroughly identified.

Another challenge to investigators is determining which information is actually true. Investigators will often be faced with apparent contradictory information from witnesses. Witness testimony is a combination of actual true facts, personal opinions and judgements, and recollections. Witness statements often reflect a conglomeration of first-hand information, assumptions, conclusions and hearsay. Information relayed in a verbal manner is subject to distortion and inaccuracy. Absolute truth is not created by consensus of opinion. Merely because a large number of people believe something to be true does not make the information a true fact.

Here are three examples of 'consensus opinion' that at one time were believed to be facts.

- 'The earth is flat.'
- 'The sun revolves around the earth.'
- 'Accurate prediction of the future can be made by autopsy of a human liver' (according to the early Babylonian practice of hepatoscopy, Shick and Vaughn, 1999).

Another critical thinking challenge is the occasional conflict between something that may be logically possible, but is physically impossible. Although it may be logically possible for a cow to jump over the moon, in the practical world there are physical limitations that prevent this statement to be physically possible.

Memory imperfection is another variable that must be addressed using critical thinking. Significant differences in witness statements can be traced to our inefficient memory mechanisms. Investigators must apply critical thinking skills when faced with apparent contradictory information from different witnesses. Our perception can change over time as we gain additional information from interacting with other people and information sources (Gilovich, 1991).

One major obstacle to evidence analysis is natural information filtering mechanisms that are part of normal thinking processes. Our perception of reality is actually a mental construction of several components. When faced with incomplete or potentially contradictory information, our brains will attempt to fill in the blanks to allow us to process and 'make sense' of the incoming information. The most common example of this is the optical illusion where our brain makes a determination when faced with ambiguous input.

Accurate identification of the actual cause scenario can be adversely affected by several factors. One obstacle is premature selection of the cause scenario. The investigation must identify and examine *all* credible potential cause scenarios before selecting one cause scenario as the most likely based on the available facts. Early establishment of 'a most likely scenario' is not a mistake as long as alternate scenarios remain under consideration until there is sufficient evidence to reject them. Premature selection of the cause scenario can create avoidable mistakes. The first problem is the resulting delay in identifying the correct accident sequence, due to the team investing time, money and resources pursuing a false trail. A second potential problem is triggering irrational defence of an invalid scenario. Investigators are slow to abandon a preferred cause scenario, even when faced with evidence that would clearly disprove the scenario. The third potential problem is the loss of credibility generated when the team has to announce that their initial findings and conclusions were incorrect. This decreased credibility has an adverse impact, especially in instances where litigation is involved.

Determination and selection of 'the cause scenario' involves rationalization. According to Psychologist Barry Singer (Gilovich, 1991), numerous experiments have confirmed our natural behaviour regarding how we develop hypothesis and conclusions. It is our normal pattern to quickly (and automatically) form a hypothesis and then begin to seek confirming evidence. We do not inherently place emphasis on seeking evidence that might *disprove* our hypothesis. We tend to stick to (and vigorously defend) our original hypothesis even when faced with conflicting evidence that might disprove our desired hypothesis. Therefore, investigators should make a strong and conscious proactive effort to operate with an open and unbiased approach, especially during the early phases of an investigation.

Another challenge is the false or hidden assumption. It is sometimes easy to make incorrect assumptions regarding the association between truly random events, thus generating a cause and effect correlation where there is not a direct cause and effect. Hidden assumptions can play havoc with an investigation when a team makes an assumption without realizing that an assumption has been made. These hidden assumptions often show up as inconsistencies in the cause scenario. When assumptions are made, they should be clearly identified and documented.

Misjudging likelihood/probabilities can lead to erroneous determinations when the investigation team believes a cause event to be too unlikely and, therefore, fails to thoroughly investigate a particular cause. Most people are not naturally proficient at estimating likelihood or probabilities of events. We remember confirming events much more effectively than we remember events that do not confirm a perception. Numerous examples can be identified that illustrate our inability to accurately estimate probabilities. Perhaps one of the more common examples relates to our general non-appreciation of the odds for winning a typical lottery. Where contestants are asked to select a set of six winning numbers from a field of 50 numbers, the actual odds are on the order of 15 million to one.

A final challenge related to rapid and accurate determination of the cause scenario is misplaced credibility. All other things being equal, we put more credibility on the first version of the story we hear. Subsequent versions that differ from the initial version are given less credibility because we begin to activate some of our natural mental filters (Gilovich, 1991).

31.5.2.4 Truth table matrix

Truth table matrices are common tools in logic and troubleshooting diagnostic activities. This concept has useful application in incident investigations. This tool can be applied effectively to help the investigation team determine the most likely scenario among a set of speculated credible cause scenarios, as well as assist the investigation team in resolving inconsistencies generated during witness interviews. The fact–hypothesis matrix is a special version of the logic truth tables used in developing control system logic and diagnosing/troubleshooting activities (CCPS, 2003). The tool can be used during the early stage of the investigation to allow the investigation team to focus on which evidence and fact issues and information could be further investigated in order to quickly produce a cause scenario that best matches the known facts. The fact–hypothesis matrix can be used in the later stages of the investigation in a quality assurance application to confirm consistency. The concept is simple: known (or suspected) facts are placed on one axis of the matrix and potential cause scenarios are placed on the other axis. Then the facts are analysed in conjunction with the speculated cause scenario for consistency (Table 31.3).

Facts fall into at least one of four categories:

1. + Yes – The fact *supports* the hypothesis (speculated cause scenario);
2. – No – Fact *contradicts* (refutes) the hypothesis;
3. 0 Neutral – The fact *neither* supports nor contradicts the hypothesis (is neutral);
4. ? Insufficient information – The team does *not have enough information* to make a determination regarding category 1, 2 or 3. In this case, the team can then determine what specific information might be gathered that would allow the team to confirm or refute the relationship between the fact and the speculated hypothesis cause scenario.

31.5.3 Specific methodologies and approaches

The following discussion is not an attempt to include all recognized public or private root cause determination methodologies and approaches. This section is intended to present a representative sampling of some common methods currently in use in the process industry. There is no intention to endorse any particular approach/method, and no attempt is made to fully explain contrast or compare one method to another. It is recognized that many organizations have developed and implemented effective internal investigation protocols and methods based on their organization's policies, resources and management styles.

31.5.3.1 MORT

One of the most widely distributed generic logic trees is the MORT developed by the US Atomic Energy Commission. The MORT diagram is part of the MORT system safety analytical procedure, and identifies causes and contributing factors by systematically applying the generic causes and conditions against known facts associated with the incident. MORT diagram is a formal disciplined logic or decision tree to relate and integrate a wide variety of safety concepts systematically (Johnson, n.d.). Potential weaknesses or breakdowns in management systems are considered. A five-stage accident sequence generic model is used and is based on the original Heinrich dominos: (1) (background factors, (2) initiating factors (underlying conditions), (3) intermediate factors (such as environmental and hazard recognition), (4) immediate factors (the trigger events or unsafe acts), and (5) the resulting consequence results. The barrier and barrier analysis

Table 31.3 *Fact–hypothesis matrix/truth table*

Possible cause scenario	*Fact #1*	*Fact #2*	*Fact #3*
	Lab Sample at 0600 showed elevated moisture content	High level alarm and high level condition noted in process sump	Vent compressor tripped twice on the shift before the explosion
A Event triggered by contaminated feedstock raw material	Yes Supports the scenario	? Do not have enough information to decide	0 Neutral effect
B Block valve left in incorrect position allowed backflow contamination	0 Neutral effect	Yes Supports the scenario	No Refutes the scenario
C Leak in heat exchanger created contamination and overpressure condition	? Do not have enough information to decide	Yes Supports the scenario	Yes Supports the scenario

concept is used. The MORT system also considers change, change analysis, risk assessments and risk decisions. When applying the generic tree there are approximately 1600 potential gates that must be evaluated.

31.5.3.2 CCPS A and B approaches

In the second edition (2003) of the *Incident Investigation Guidelines* published by the Center for Chemical Process Safety (CCPS) of the American Institute of Chemical Engineers, there is recognition of two general approaches in wide use in the process industry for root cause determination. Both are iterative and begin with an accumulation of known information, data, and evidence. One approach, method A, applies a logic tree and an iterative loop with an associated set of formal stopping rules and quality assurance gates to ensure the investigation has progressed deep enough to reach the root cause level and broad enough to address multiple causes. The other approach, method B, seeks to identify causal factors and then applies predefined generic trees to identify potential root causes. Both methods are effective.

31.5.3.3 Methods based on sequence diagrams

Sequence diagrams combine the timeline and the logic diagram concept, and attempt to depict the incident scenario events and conditions that allowed the sequence to progress. Sequence diagrams are not necessarily intended to provide a complete incident investigation system, however, they can be used to identify causal factors for subsequent analysis. In some sequence methods such as the multilinear event sequencing (MES) approach (Benner, n.d.; Atkins, 2001), a distinction is made between actors, actions and events. An actor is a person, substance or piece of equipment. Actions are defined as anything carried out by an actor. Events are results of those actions by the actor. There are several versions of causal factors charting currently being applied in the process industries. Rhone Poulanc implemented an events and causal factors charting system. The causal factors charting approach is similar to MES diagram (see Figure 31.8), and breaks down the incident into individual events and causes, developing a diagram that is a cross between a logic diagram and a sequence diagram. A further evolution of this concept can be found in the sequentially timed events plotting (STEP) procedure (Benner, n.d.). In the STEP approach, events are arranged on a horizontal axis and designated actors are arranged in a vertical column, then the relationships between actors and events are connected.

31.5.3.4 Cause analysis methods

One method for incident investigation focuses on changes (known, unknown, intended and unintended). The Flixbourgh explosion in 1974 was the result of temporary piping changes. One of the causes of the Apollo 13 US Space Mission incident was an ineffective change management system that failed to find and properly modify all electrical components that would be impacted by a change in operating voltage from 28 to 65 V (Goodwin, 2000). The change analysis investigation method guides investigators to identify and analyse all conditions and items that were different for the specific event. Root causes are found in examining the deviations from normal.

The hazard–barrier–target model (Figure 31.9) for accident causation provides a basis for several investigation methods. Accidents are viewed as a 'hazard' (some form of energy), acting on a target (usually a person). In the normal course of events, barriers prevent interaction between the hazard and the target. However, on occasion the barrier is insufficient to prevent the accident. An accident can be described in terms of an unwanted energy flow that comes into contact with a person. Barriers can be physical such as machine guards, instrumentation system interlocks or control systems, or can be administrative such as training, policies, procedures and practices. The number, reliability and robustness of the barriers are proportional to the potential consequences and are related to the risk (likelihood and consequence). Recognizing that any given barrier will have a certain degree of unreliability, these investigation methods seek to identify and examine the barriers (management systems).

Another method sometimes used to identify underlying causes is the job safety analysis (JSA, sometimes called job hazard analysis). A task is broken down into its component actions and each is examined individually to identify potential hazards and the associated safeguard measures that were established to prevent the hazard from acting on the person. JSA can be viewed as a special case of examining the hazards and barriers. Another cause analysis approach is the systematic cause analysis technique developed by the International Loss Control Institute (now Det Norske Veritas (DNV, 1996)). In this approach, the investigation

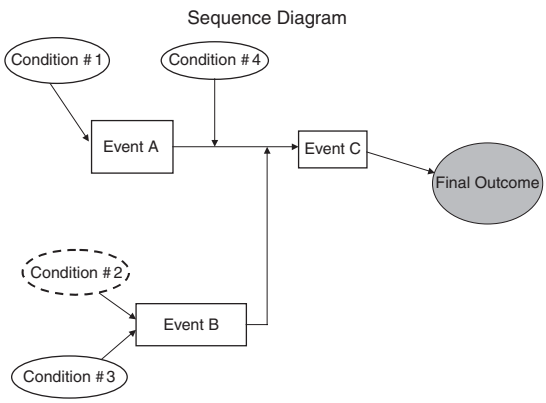

Figure 31.8 *Causal factors chart example*

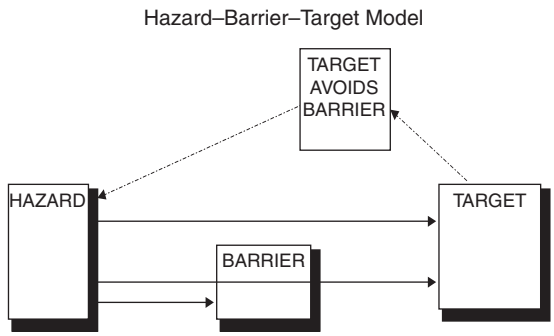

Figure 31.9 *Hazard–barrier–target model*

team is guided through a deepening series of questions that initially examine general safeguards and conditions concluding with a list of possible system defects that the investigators should evaluate based on the evidence and specific circumstances for the incident being investigated.

There are numerous additional analysis and decision making methods that can be applied to portions of the investigation, but that are not considered stand-alone incident investigation methodologies. Two examples are the human reliability assessment (HRA) where human actions are systematically identified and analysed, and the failure mode and effect analysis (FMEA), which is an inductive method for examining failures in systems or components. Several recognized PHA methods can be used in all or parts to assist investigations. When attempting to match up possible scenarios with available evidence, the hazard and operability (HAZOP) approach can be beneficial in searching for credible deviations from intended design and operating conditions. The WHAT-IF method is a helpful brainstorming technique for speculating possible causes and then directing the investigation team in evidence gathering to confirm or refute a speculated scenario.

31.5.3.5 Commercial methods

There are several publicly available commercial root cause investigation methods, three of which are discussed below.

TapRooT,® system is a commercially available process and set of techniques to investigate process safety incidents, analyse and develop corrective actions. It is widely used in the US process industry. The TapRooT® system (process and tools) combines both inductive and deductive techniques for systematic investigation of the correctable root causes of problems. TapRooT® goes beyond the simple technique of 'asking why' or the standard techniques of cause and effect (sometimes known as fishbone diagrams) or fault tree diagrams. Embedded intelligence allows TapRooT® to be used by people in the field to investigate everyday problems and yet, is robust enough for a complex major process safety accident investigation. Tools and techniques are used in all phases of an investigation – from initial planning through the collection of information and root cause analysis to the development of corrective actions and the presentation of an investigation to management or other interested parties. The system is supported by patent pending TapRooT® software and provides a trendable incident/root cause database and corrective action management database (TAPROOT, www.taproot.com).

Another commercial incident investigation methodology is the Apollo incident investigation and problem solving techniques method published by Apollo Associated Services Inc. The Apollo approach uses cause and effects charting and provides investigators with basic problem solving concepts to reach root causes. The reference is accompanied by worked examples and a training video. Guidance is provided to consider personnel performance factors, problems with written procedures and instructions, and general hardware deficiencies.

A third commercial root cause method is the REASON methodology developed by Decision Systems Inc (REASON, www.rootcause.com) This methodology is designed to provide a standard process that allows all options to be identified, modelled and analysed. The approach is presented as a standard operating procedure in a step-by-step format, to guide the investigator to ask the right questions to identify all relevant causes of the event. The REASON root cause analysis is a systematic process and software package for gathering and ordering relevant data, identifying internal causes that generated or allowed the problem to develop, and provides decision makers comparative cost effectiveness benefits of various possible remedies.

The US National Safety Council (1995) published a systematic approach for incident investigation that presents principles of investigation and the role of management leadership. The publication includes a guide for identifying causal factors and corrective actions using a set of workbook charts that lead the investigator to the underlying causes of incidents. Although this methodology is systematic, it may not be sufficiently sophisticated and rigorous for complex process safety events.

31.6 Recommendations, Reports and Lessons Learned

31.6.1 Recommendations

The payoff stage in the incident investigation process is implementation of changes that will eliminate the identified root causes, thus reducing likelihood of a repeat incident. This final stage involves development and evaluation of potential action item recommendations and begins once the root causes have been identified. In many instances, the charter of the investigation team ends with development of recommendations and issuance of a report. When recommendations are submitted to management, responsibility for action (acceptance and implementation) is transferred from the incident investigation team to the organization's management structure. Management must evaluate, accept, reject or modify the recommendation and then implement changes. Until and unless these changes are implemented, the risks for a repeat incident remain unchanged. In some instances, even before the investigation is completed, immediate action is recommended and implemented to take temporary measures to reduce or control the hazardous risk exposures.

All potential recommendations from the incident investigation team should be reviewed for possible negative impact. It is not uncommon to inadvertently create or aggravate a second problem while trying to correct the original problem. Proposed changes should go through the management-of-change system for review and approval. It is not unheard of for incident investigators to develop recommendations that create a new problem while trying to eliminate or reduce an original problem (Kletz, 1993). When considering potential recommendations, the first priority would be to seek remedies that *prevent* the event before seeking remedies that *mitigate* consequences. Principles of inherent safety and layer of protection analysis can be successfully applied when considering remedies for root causes. Sometimes an investigation team will be able to identify and remove common cause failures that act on more than one safeguard. Many organizations now apply cost–benefit analysis to all proposed recommendations. The expected risk reduction benefits are calculated and compared to the expected cost of implementation (initial and continuing costs).

When drafting text for recommendations, it is a good practice to include information related to benefits gained by implementing the action or to include potential consequences that might be incurred by rejecting the

recommendation. In a large majority of instances, the actual recommendation text (typically a text block of one or two sentences) is extracted and transferred to a listing or database of action items. The recommendation text block becomes a stand-alone text block, without the supporting information included in the written incident report. The new listing or database document often does not include specific information as to the origin of the recommendation, the context in which the recommendation was developed, circumstances that justified the recommendation, or possible consequences for failing to implement the recommendation. Well-written recommendation statements will begin with a phrase such as,'In order to minimize the risk of . . . . . (insert specific consequences related to the specific recommended action), it is recommended that . . . . . (insert specific action).' The practice of including the consequences-to-avoid or the benefits provided will assist the management team in evaluating and reaching a decision as to implementing the recommendation.

Recommendations should be worded so the intentions of the investigation team and recommendation are clear to the reader. Wording that can be ambiguously interpreted should be avoided or clarified. Specific item numbers should be used wherever possible. A poorly worded recommendation might read, 'Review start-up procedure for by-pass compressor.' A better stated recommendation would read, 'In order to prevent overpressure of the vent blowdown drum D-112, it is recommended that start-up procedure SP-1-22 be modified to clearly include the need for verifying a purge and de-pressure has been completed for By-pass Compressor C-14'. There are two conventions for drafting text for recommendations. Hard recommendations are written in specific clear action terms, such as . . . 'Provide an additional layer of overflow prevention protection for tank T-102.' Soft recommendations are intentionally written to allow flexibility in implementation. Soft recommendations often begin with words such as 'consider' or 'evaluate.' Response actions required by hard recommendations are more rigorous and demand additional documentation in the event that the recommendation is rejected or modified.

Another special case is the 'If X . . . then do Y. . .' recommendation. Investigation teams may not have sufficient information to fully evaluate a specific hazard (or existing safeguard) and may generate a recommendation such as, 'Determine the auto-ignition temperature of reactor intermediate wash water product'. In cases where the investigation team recommends further evaluation or further identification of information, it is a good practice for the recommendation text to include an 'If . . . then . . .' instruction to indicate the investigation team's expectation once the additional information does become available. An example would be the confirmation recommendation. The team may generate a recommendation to the effect of, 'Confirm that aqueous mixtures of chemical X are *not* soluble in chemical Y.' The recommendation text should, in this case, include recommended actions to be taken if the mixture is determined to be *insoluble* in chemical Y, and what actions should be taken if, in fact, the mixture is determined to be *soluble* in chemical Y.

In most chemical process incidents investigated by a team, there are significant consequences and an accompanying likelihood for legal action. In these instances, recommendations require review and approval by the organization's legal representatives, in order to minimize unnecessary litigation exposures. In some cases, normal language used in the manufacturing plant to describe the scenario, causes or suggested action items may trigger unexpected legal responses. The primary objective of the organization's legal staff is to minimize or avoid adverse consequences from litigation or regulatory activities. In this context, there is a benefit in having legal representatives conduct a review and suggested edit of the text of the incident report, findings and recommendations. Legal representatives will normally be able to quickly identify text that may potentially be inflammatory, judgemental, subjective or especially damaging in future litigation.

Some organizations make a distinction between findings and recommendations. Findings are statements of fact and do not include any suggested action. A team may find that there was no lubrication oil in the compressor gearbox or that the material of construction for a component of the piping system was Schedule 40 carbon steel 2-inch in diameter and the required specification for this service was Schedule 80. These findings statements are accompanied by separate recommendations for specific actions to address identified deficiencies Figure 31.10.

The likelihood of a repeat incident remains unchanged unless and until preventive action is actually implemented. Proactive sharing of investigation results with all who could benefit will amplify potential benefits of the investigation. In the United States, there is a regulatory obligation for sharing results of certain process safety incident investigations with all workers (employees as well as contractors) 'whose job tasks are relevant to the findings' of the investigation (OSHA, n.d.).

It is a recognized industry best practice to establish a formal system for promptly addressing and resolving recommended action items from investigations. Recommendations are often risk-ranked and assigned priorities so that the management team can more effectively reach decisions related to implementation schedule. Documentation of the resolution of the recommendation and status tracking are important features of an effective incident investigation management system. If an original recommendation is modified or rejected, there should be documentation stating the reasons for not implementing the recommendation as submitted by the incident investigation team. In some organizations, the investigation team will submit a draft report for management review and approval containing proposed recommendations. After the final version of the recommendations have been accepted by management, completion assignments are made, target dates are established, and the final version of the recommendation is published. In many instances of serious chemical process incidents, review and approval of the recommendations text by the legal department is important and necessary.

Some organizations include verification of implementation as part of routine periodic audits and evaluations of the continued effectiveness of the incident investigation management system.

There is an increasing emphasis and appreciation for the concept of verification and confirmation that the recommendation was implemented as intended and also that the action achieved the intended objective. In some progressive organizations, completion of recommended action items is closely monitored and accompanied by periodic status reports. Items that are not completed as scheduled receive special attention. Timely completion of action items has

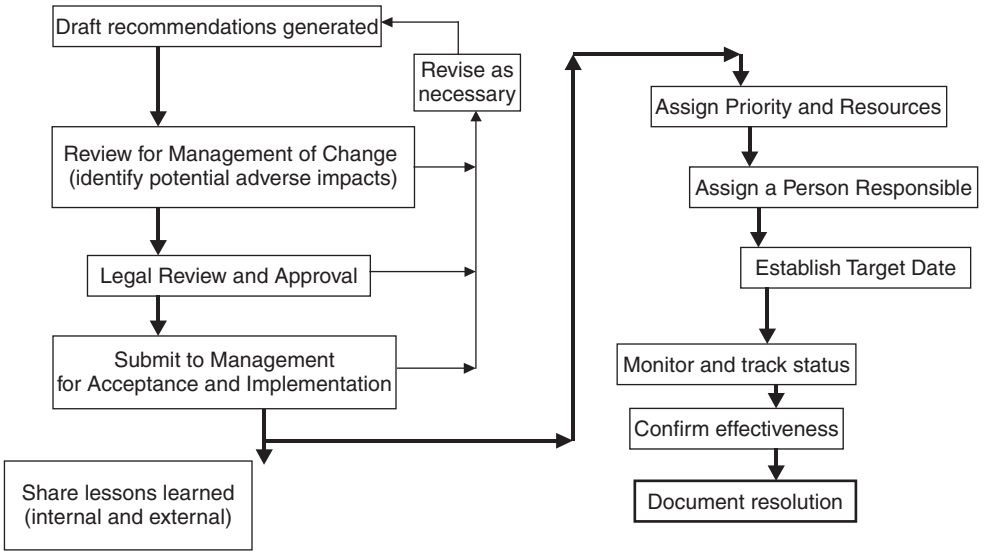

Figure 31.10 *Recommendations flowchart*

been recognized as a leading indicator for more successful safety management systems. Action item resolution can be integrated with other systems such as audits, inspections, quality assurance, PHA, pre-start-up safety reviews and management of change systems.

31.6.2 Reports

The written report is an accident prevention communications tool to share findings and lessons learned from the investigation. There is a wide variety of report style and format. Some reports are highly technical and provide extensive detail on complex systems, failure modes and process operation. Other reports are as brief as one or two paragraphs and function as a heads-up alert communication. A best practice format for internal process incident reports is shown in Figure 3.11. The report begins with a summary. This summary is most effective if limited to a single page highlighting the major items of what happened, why, and what the suggested action items are. For many process incident reports, it is beneficial to prepare a background section to allow the reader to fully understand the process, the associated potential hazards and properties of the materials, control measures, intended safeguards and the nature of the incident scenario. The third section is often a narrative of the scenario, providing an explanation of the incident sequence, events and enabling conditions. This section presents the WHO, WHEN, HOW and WHAT HAPPENED information. The next section is often the 'findings and root causes' section that presents root causes and contributing causes (the WHY information). In some instances, findings are separated and presented in a stand-alone section of the report. Recommended actions items, both short-term and long-term, are presented in the 'recommendations' segment and are followed by back-up data in the appendix section. It is useful to include diagrams, selected photographs and pertinent documentary evidence in each section as appropriate, with the bulk of the back-up data being located in the appendix.

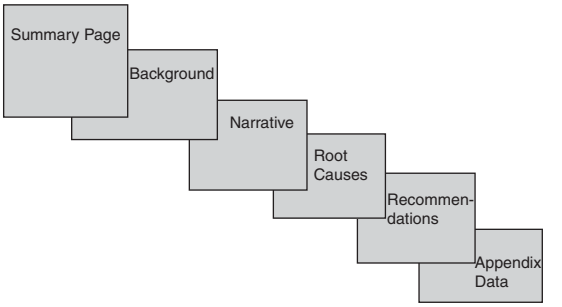

Figure 31.11 *Typical incident report*

The advent of internal intranets allows a new and powerful tool for internal sharing to selected groups, with searchable databases, and multi-levels of report detail. It is now possible to send a broad alert and point interested parties to a file containing appropriate detail. Computer security features also enhance confidentiality concerns. It is possible to track access activity and confirm that personnel actually had an opportunity to open and read the incident report or bulletin. Imbedded hyperlinks are a powerful new addition to sharing lessons learned.

31.6.3 Lessons learned

Applying lessons learned and sharing information and findings from the investigation are important functions that can leverage the work of the investigation team. There is a rising expectation that organizations proactively share information from the investigation with all parties who could potentially be impacted. In the United States, many chemical companies have made significant commitments to industry to share incident investigation findings externally to other organizations as part of the Responsible CARE® (American Chemical Council), American Institute

of Chemical Engineers Center for Chemical Process Safety, National Petroleum Refiners Association, Synthetic Organic Chemical Manufacturers Association, American Petroleum Institute and other trade associations.

Unfortunately, there are numerous instances of repeat incidents that might have been prevented if there had been adequate sharing of findings (internal within the organization) or if the implementation had been completed promptly and as intended by the investigation team. In one recent chemical plant fire incident where a specific type of check-valve failed, the US Government Investigation Team discovered that the same organization had previously experienced an almost identical incident in one of its other locations, yet the lessons had not been adequately shared and acted on within the organization (US EPA/OSHA Joint Report, 1998). The investigation of the July 2000 Concorde Air crash uncovered numerous previous incidents related to tire failures. In one of the near-miss events, portions of a tire actually penetrated the fuel tank in the wing and created a fuel leak (Hazards Prevention Magazine, Second Quarter, 2001).

31.7 Management System for Investigations

Section 31.2 introduced the concept of management systems in the context of incident investigation. There is a growing recognition of the value of the application of this management system perspective. In 1999, the British Standards Institute published a non-mandatory specification for Occupational Health and Safety Management Systems (OHSAS 18001, 1999). This suggested template closely parallels the International Standards Organization Standard ISO 14001 for Environmental Management Systems. American Petroleum Institute developed a Recommended Practice Model Environmental Health and Safety Management System 9100 (API 9100 A and B, n.d.). Part A of this focused on initial development and part B was intended to provide guidance for improving an existing system. In the United States, the American National Standards Institute intends to issue a new standard Z-10 for overall management of an organization's safety and health program. British Standard 8800 is intended to provide guidance for developing and implementing safety management systems (BS 8800, 1996).

This section will focus on the development and implementation of a typical management system for incident investigation. As discussed in Section 31.2 chapter, the term management system encompasses the total administrative activities and aspects associated with a dedicated task or objective (see Figure 31.12). In this instance, the objective of the management system is prevention of repeat incidents and the specific functional task is conducting the incident investigation (Table 31.4).

The configuration and content of the incident investigation management system begins with a corporate policy commitment to prevent repeat incidents by investigating, identifying causes and remedies, and then implementing improvements specifically designed to eliminate underlying root causes. A sustained and consistent commitment of organizational resources is required. Inputs to the incident investigation management system are the facts, circumstances, evidence and consequences (human, economic and environmental) associated with accidents, incidents and near-misses. Additional inputs are those facts gathered during the evidence discovery activity and the conclusions reached by the investigation team relative to causes and potential remedies. The outputs of the investigation management system are in two stages. The first stage is the suggested recommendations for action items and the second stage is the actual implemented corrective measures.

Supporting the investigation management system are several critical components, the foundation of which is built on the formal commitment policy developed and implemented by upper level decision makers in the organization. Specific investigation tasks and activities are assigned and a determination is made as to whom specific responsibilities for completion of each designated task are assigned. A written protocol is prepared and various components of the organization are trained in knowledge and skills needed to complete their assigned duties. It is common to have at least three (and sometimes four) different investigation skill or knowledge levels. All employees (as well as contractors and visitors) need a minimum baseline knowledge regarding the reporting of incidents and the general policy commitment to investigate and implement improvements. This baseline segment can be less than one hour of training, but will require periodic refresh training and confirmations that minimum knowledge and awareness level is being maintained.

Line managers and those charged with responsibility to review and approve draft investigation reports need to understand the acceptable incident investigation performance targets and need to have an understanding of how the system works. This competency level is achieved by specific training and periodic audits. Those who participate in or lead investigations need an additional competency in the actual investigation practices (how to do it). In some instances, there is a fourth level of competency for designated subject matter experts or investigation team leaders. This group provides the internal resource for those people who conduct the day-to-day programme activities and those who investigate the less serious incidents.

Almost all incident investigation management systems include designated categories of incidents based on a scale of increasing severity of consequences and regulatory reporting requirements. Best practice organizations have a proactive near-miss investigation component as part of the incident investigation management system. It is common to establish increasing levels of severity and have increasing reporting and investigation requirements as the severity escalates. All successful management systems include an evaluation and periodic improvement component. Effectiveness of investigations should be evaluated on a regular basis and potential improvements noted. Safety audit protocols should include specific questions and items related to incident and near-miss investigation and resolution of recommended preventive actions. The incident investigation management system should include provisions for periodic review and update to ensure it is achieving the intended objectives. There should be a section that addresses how changes (or temporary exceptions and deviations) are to be handled. The incident investigation management system should be integrated with other safety and loss prevention management systems such as the PHA system, training, auditing, change management and emergency preparedness and response system. Figure 31.13 presents a typical table of contents for an incident investigation management system manual.

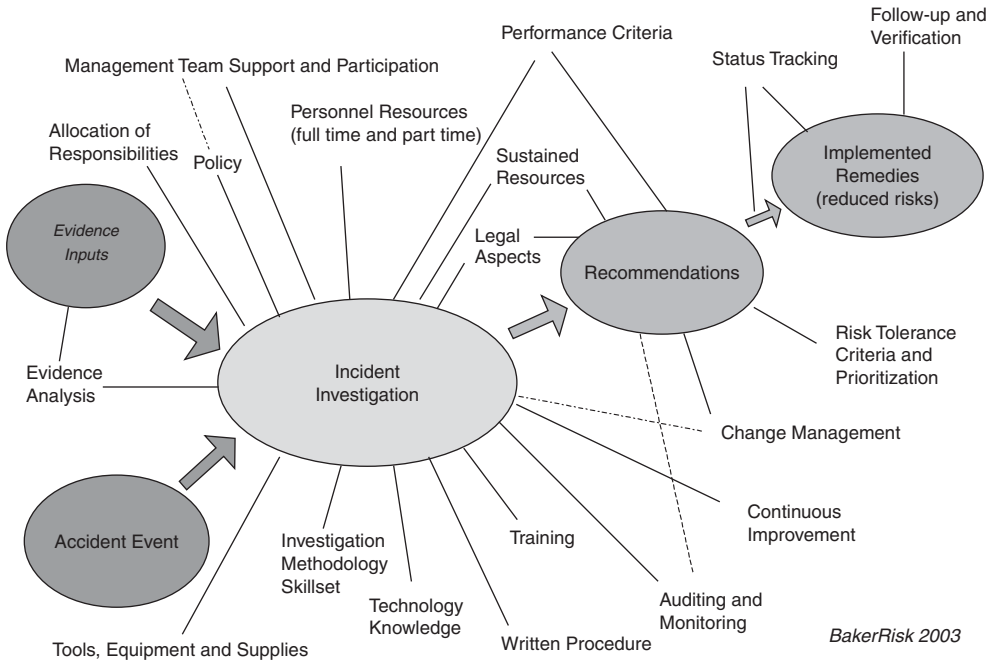

Figure 31.12 *Incident investigation management system*

Table 31.4 *Components for incident investigation management system*

Component category	*Example*
Objective	. . . prevent reoccurrence of safety-related incidents by learning from past experiences with actual events and near-miss events, and implementing preventive measures . . .
Inputs	. . . the event, facts, conditions and circumstances, people, equipment . . .
Outputs. . .	. . . written report, recommendations, action items . . .
Responsibilities	. . . line management establishes charter, degree of severity of consequences for mobilizing full or partial investigation team, team leader has assigned duties, team members have specific tasks and expected performance activitie s. . .
Skills and knowledge	. . . team member knowledge of root cause determination methods, evidence analysis skills, photography expertise, special metallurgical/laboratory test as needed . . .
Performance assessment	trend analysis for common causes and repeat incidents . . .
Documentation	. . . written investigation standard procedures, forms, systematic definitions of terms and cause categories, report format . . .
Resources and Funding	. . . team members temporary full or part-time assignments, team expenditures for evidence gathering, analysis and report preparation, witness overtime, training expenses, maintaining readiness z . . .

In the United States, there are two primary regulations applicable to process incidents involving release of hazardous substances that are on lists published by OSHA and the Environmental Protection Agency. The OSHA Process Safety Management (PSM) Standard 29 CFR 1910.119 section (m) lists several specific investigation requirements including:

- Results of the investigation must be reviewed with all personnel whose job tasks are relevant to the incident findings (including contractor employees where applicable).
- Results of the investigation must be developed into a report.
- There must be a system for promptly addressing and resolving the findings and recommendations from the investigation.
- Resolution and corrective actions are required to be documented.

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   - Evidence analysis
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   - Review and approval of suggested recommendations and reports
   - Evaluating recommendations for management of change
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     - status tracking, assignment of target dates for completion, assignment of persons responsible for completion of the recommendation
     - verification /confirmation of completion of the recommendation
     - documentation of resolution of recommendations
   - Reports
   - Implementing lessons learned
   - Sharing lessons learned with potentially affected persons
9. Continuous improvement of the II management system
   - Monitoring effectiveness
   - Periodic audits and evaluations
   - Updates and changes to the II management system
   - Monitoring changes in regulations and corporate performance standards
   - Accident and incident trend analysis
10. Appendix
    - Suggested forms
    - Suggested checklists
    - Reference standards and regulatory requirements
    - References for additional help

Figure 31.13 *Typical table of contents for an incident investigation management system manual*

In addition to these mandatory OSHA PSM requirements, there are several 'non-mandatory' expectations contained in the appendix of the regulation. The US EPA promulgated minimum incident investigation requirements in the Risk Management Plan section of the Clean Air Act. These regulations (Risk Management Plan 40 CFR Part 68) apply to a specific list of designated hazardous chemicals, and closely parallel the OSHA PSM investigation requirements with a few additional requirements such as:

- The investigation must determine the quantity of material released and the duration of the release.
- All known offsite impacts must be documented.
- A record must be kept of all operational or process changes resulting from the investigation.

Most incident investigation management systems will include suggested (or mandatory) forms and checklists to guide the team in a thorough investigation and to ensure that relevant information is included in the report. A report format showing level of detail and approval levels is often included in the written procedure/protocol document. Some organizations find value in having the legal department conduct a review of the draft report before it is issued.

The system for resolution of recommendations should be clearly presented in the management system. There should be a status tracking system and requirements for documenting the closure (resolution) of the recommendation. If the original recommendation is rejected or modified, the documentation should include the basis for the decision not to implement the recommendation as submitted by the investigation team. A recognized best practice is the post-implementation verification to ensure that the recommendation was actually implemented as intended and that the recommended action did accomplish the specific intent.

32 Inherently Safer Design

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32.10 Inherently Safer Design References 32/23

32.1 Introduction

Inherently safer design is a philosophy which focuses on elimination of hazards or reduction of the magnitude of hazards rather than the control of hazards. Many of the concepts of inherently safer design have been applied by engineers in a wide variety of technologies for many years, without recognizing the common approach. In the late 1970s, in the wake of many large incidents in the chemical industry, Kletz (1978) recognized the common philosophies of hazard elimination and hazard reduction, gave the philosophy the name 'inherently safer design', and developed a specific set of approaches to help engineers in the chemical process industries to design inherently safer processes and plants. Kletz realized that increased expectations for safety, from companies, regulatory bodies, and society in general, combined with the increased potential damage from incidents in the larger plants being built to meet increased demand and global markets, resulted in increased complexity and cost for the safety systems required to satisfy these demands. Furthermore, while hazard control systems can be made highly reliable, they can never be perfect and will always have some failure probability. While this probability can be made very small, there is always some chance that all safety systems will fail simultaneously and the result would be a large incident. Also, the hazard management systems require ongoing maintenance, as well as management and operator training, for the life of the plant. This results in ongoing costs, and the potential for future deterioration of the safety systems. Deteriorated systems will have reduced reliability, increasing the potential for a catastrophic accident. Kletz suggested that in many cases, a simpler, cheaper and safer plant could be designed by focusing on the basic technology, eliminating or significantly reducing hazards and therefore the need to manage them.

A process or plant is best described as 'inherently safer' with respect to a specific hazard or set of hazards, and with respect to other alternative designs. However, it is unlikely that any process or plant can be designed to eliminate all possible hazards, so it is generally inappropriate to describe any technology or plant as 'inherently safe'.

Since Kletz originally introduced the concept of inherently safer design to the chemical process industries, it has received increased interest from the industry. The inherently safer design philosophy has much in common with other important themes in the ongoing evolution of the chemical process industry at the beginning of the twenty-first century. In particular, the industry's increased interest in sustainability and research efforts on 'green chemistry' are often compatible with efforts to identify inherently safer processes. Other areas of research interest such as process intensification, nanotechnology, catalysis and biotechnology have the potential for developing inherently safer products and processes.

32.2 Definitions

32.2.1 Inherently safer design

A dictionary definition of 'inherent' is 'existing in something as a permanent and inseparable element, quality, or attribute'. (Center for Chemical Process Safety (CCPS), 1996) Thus, the basis for safety of an inherently safer process lies in the fundamental characteristics of the materials, operations and conditions of the process, characteristics which are inseparable from the process itself. The process relies on the chemistry, physics and toxicological properties of the materials and process operations for safety. Hazards are eliminated or significantly reduced, rather than controlled with safety equipment and procedures.

32.2.2 Hazard

Because inherently safer design focuses on the elimination or significant reduction of hazards, it is important to understand the definition of the word 'hazard'. Over the years, the literature of process safety and risk management in the chemical process industry has developed many definitions for this word and concept. For the purposes of this discussion, we will use the definition developed by the CCPS (1992) – a hazard is an inherent physical or chemical characteristic that has the potential for causing harm to people, the environment or property. A hazard is an inherent characteristic of a material or of its condition of use. It cannot be changed without changing the material or conditions of use. Some examples of hazards are:

(1) Phosgene is toxic by inhalation.
(2) Acetone is flammable.
(3) Concentrated sulfuric acid is corrosive to the skin.
(4) Nitroglycerine is an unstable material which can decompose explosively.
(5) Steam at 40 bar pressure contains a large amount of energy, both from its temperature and pressure.

These hazards cannot be eliminated or reduced without changing the material or its conditions of use. Thus, a process using acetone as a solvent might be modified to use a less flammable solvent, or perhaps a non-flammable solvent. A process using 40 bar steam as a heating medium might be changed to using a molten salt heating system, or alternative chemistry which operates at lower temperature might be discovered. However, it is important to remember that all processes and materials have multiple hazards, and a change to a material which eliminates or reduces one hazard may increase the magnitude of another existing hazard or create a new hazard.

32.2.3 Risk

Inherently safer design is a philosophy for risk management for a chemical process. Risk has been defined by CCPS (2000) as 'a measure of human injury, environmental damage, or economic loss expressed in terms of the magnitude of the injury, loss or damage and the likelihood of occurrence of the incident'. While inherently safer design is generally considered to be applicable to the consequence (magnitude of injury, loss or damage) portion of the risk equation, it also applies to the likelihood of occurrence. An inherently safer design can either reduce the magnitude of a potential incident arising from a particular hazard, or it can make the occurrence of the accident highly unlikely, or perhaps impossible.

32.3 History of Inherently Safer Design

Elimination of hazards has always been an important approach to improving safety in all technologies. When prehistoric people decided to build a village on a hill above the flood plain of a river, they were choosing an inherently safer location with respect to the hazard of floods. They had

other alternatives – monitoring the river level and establishing evacuation plans, building dikes around the village, building houses on stilts, for example. In many cases, local geography, economic considerations or other factors required the adoption of these or other alternatives. Some of these other factors may have included consideration of hazards other than flooding – people on the high ground may have been more likely to be attacked by dangerous animals, appropriate building materials might not have been available and would have to be transported to the site resulting in expenditure of resources and exposure to transport hazards, drinking water might not have been readily available on high ground. But, with respect to the specific hazard of flooding, building the village on high ground was an inherently safer design which often was adopted.

Over the centuries, engineers have invented and developed inherently safer designs in many technologies. A four wheeled wagon is an inherently safer way to transport goods than a two wheeled chariot. A double track railroad, with a dedicated track for each direction of travel, is inherently safer than a single track for both directions of travel. In the 1860s, English chemist James Howden developed a process to manufacture nitroglycerine 'in situ' at the construction sites of the first US transcontinental railroad, eliminating the hazards of transporting nitroglycerine from the manufacturing site to the construction site. A few years later, in 1867, Alfred Nobel invented dynamite, a safer and more stable form of nitroglycerine. Although these and many other examples of inherently safer design can be cited from many different engineering technologies, the common philosophy of hazard elimination or reduction had not been recognized or identified as a generally applicable design strategy.

In the 1960s and later, the rapidly expanding chemical industry was building larger plants than ever before, to meet an expanding and more global market. These large plants had larger inventories of hazardous material than previous generations of plants, and many operated at elevated temperature and pressure. The magnitude of a potential accident in a chemical plant was larger than ever before. While these large plants had extensive engineered safety features to manage and control the hazards, these systems were not perfect. The failure of the safety devices and procedures, while not common, did occasionally occur, and the result was a large accident. One major accident occurred at Flixborough, United Kingdom in 1974, caused by the release of many tons of superheated cyclohexane vapour from a high temperature, high pressure process. Following this accident, Trevor Kletz of ICI suggested that the best way to eliminate the possibility of this type of accident was not to develop ever more reliable safety devices and procedures, but rather to focus on eliminating the need for those safety devices by eliminating the hazard or reducing its magnitude sufficiently that the consequences of an accident would not be serious. Kletz introduced this concept, which he called 'inherently safer design', in the Jubilee Lecture to the Society of the Chemical Industry in the United Kingdom in 1977, and the lecture was subsequently published (Kletz, 1978). Over the years since 1977, Kletz expanded on the inherently safer design philosophy in a series of papers and books (most recently, Kletz, 1998), developing a set of principles to assist engineers in identifying inherently safer design options for chemical processes. Others picked up the concept and have further developed it, including Englund (1990, 1991a, 1991b) and CCPS (1996). The philosophy has become an integral part of process design and process safety for many companies in the chemical industry.

32.4 Strategies for Process Risk Management

32.4.1 Overview of risk management strategies

Process risk management strategies can be considered to fall into four categories (CCPS, 1996):

(1) Inherent – eliminate or significantly reduce the hazard.
(2) Passive – reduce the consequence or likelihood of an incident arising from a hazard through devices which do not require detection of an incident or action by any person or device.
(3) Active – reduce the consequence or likelihood of an incident arising from a hazard by detection of an incipient incident and activation of devices which interrupt the sequence of events resulting in the incident or mitigate the consequences of the incident.
(4) Procedural – reduce the consequence or likelihood of an incident arising from a hazard by detection of an incipient incident followed by implementation of procedures or human activated devices to interrupt the sequence of events resulting in the incident or mitigate the consequences of an incident.

Usually, risk management strategies in the inherent and passive categories are more robust and reliable. They rely on the chemistry and physics of the process and plant, and do not have any active elements which must function properly, or human elements. However, a complete risk management programme for a process will include elements from all of these strategies. This is particularly true when one considers all of the multiple hazards in a process.

32.4.2 Risk management strategy example – combustible powder handling

These categories are best understood with a specific process example. Consider a process which requires pneumatic conveying of a combustible powder from a storage silo to the processing equipment. The hazard of concern for this discussion is the potential for a dust explosion in the closed conveying equipment. Dust explosion testing indicates that the maximum pressure resulting from a confined combustion of the dust is 10 bar. The powder can be ignited by static electric discharge of sufficient energy in the conveying system. The risk arising from this hazard might be managed by any of the following alternatives:

Inherent risk management

(1) Identify a non-combustible solid which can replace the combustible dust in the process.
(2) Increase the particle size of the combustible solid so that a dust explosion cannot occur (use pellets or granules instead of a powder).

Either of these alternatives eliminates the hazard of dust explosion, although there is a possibility of particle attrition of the granules or pellets, which could result in accumulation of fine particles somewhere in the process

equipment (perhaps a dust collector) where there would still be a potential for a dust explosion.

Passive risk management

(1) Build a conveying system with a pressure rating of 15 bar.

This does not eliminate the hazard of powder combustion, or reduce its magnitude, but it does contain the pressure from a dust explosion within the process equipment so it cannot injure people or damage other equipment. The higher pressure rated equipment contains the pressure simply by virtue of its existence and design. It does not have to detect a dust explosion, or take any action to perform its function, so it is highly reliable and robust. However, in the event of ignition, the dust explosion still occurs, and it does generate up to 10 bar pressure. Defects in construction of the equipment, age and corrosion, improper assembly or other failures could result in failure of the high pressure equipment and an explosion which impacts the outside environment could occur.

Active risk management

(1) Dust explosion venting panels to relieve the dust explosion pressure to a safe place.
(2) Explosion suppression systems which detect the incipient explosion and inject a fire suppressant to reduce the explosion pressure to less than the failure pressure of the conveying system.
(3) An inerting system, conveying the combustible powder with reduced oxygen gas. This is considered an active system because normal air contains 21% oxygen, sufficient to support combustion, and some kind of a active control system is presumed to be required to establish and maintain an inert atmosphere in the conveying system.
(4) A water deluge system installed in the process rack to put out an external fire following activation of dust explosion vents, which generally will release a significant flame or fireball which could ignite other combustible materials in the area.

All of these systems contain multiple active components which must function properly in order for the active safety system to work. In general, they contain three types of generic elements – a sensor of some kind to detect an incipient hazard; a logic element which receives input from the sensor and determines what action is required and a final action element which will implement the required action. Active safety devices may be designed to prevent an incident (e.g. the inert gas conveying system), or to mitigate the effects of an incident once it has started (explosion venting, explosion suppression, the water deluge system).

Procedural risk management

(1) Procedures to keep metal objects out of the conveying system. These objects could cause sparks in the conveying system which could ignite the powder.
(2) Procedures to ensure that equipment is correctly assembled and that all metal parts of the conveying system are properly electrically bonded and grounded.
(3) A manually controlled inert gas conveying system, relying on the operator to monitor the oxygen concentration (or some other parameter such as nitrogen flow rate which is known to confirm adequate inertion) and make appropriate adjustments to maintain an inert atmosphere.

These risk management strategies rely on proper actions of people. They are subject to failure from human error, inattention and all of the other factors which make people less reliable for repetitive and uninteresting tasks.

Summary of risk management strategy example

Remember that this example considers risk management strategies with respect to a single hazard – the potential for dust explosion. In selecting an optimum design, the engineer must consider all hazards, as well as the ability of the process to produce the required output. Some of the risk management strategies suggested to reduce the risk of dust explosion may introduce other hazards, increase the magnitude of other existing hazards, or inhibit the ability of the process to produce the required product. For example, inerting introduces the potential for asphyxiation from exposure of people to a low oxygen atmosphere from the conveying system. Perhaps the different, non-combustible substitute for the combustible dust is highly toxic. More likely, there is no non-combustible solid which will work in the application. Pellets or granules may create a slipping hazard if spilled on the floor. Of course, there are ways to manage and control all of these hazards as well (and those strategies will also fall into the inherent, passive, active and procedural categories), and it is the task of the design engineer to understand all of them and select the optimum overall strategy.

In this example, use of pellets in place of a dust will eliminate the risk of dust explosion in the conveying system, but perhaps the available pellets are cylindrical in shape and procedures to clean up spills and keep the floor clean will be required so people do not slip. Dust will still form from particle attrition (although there will be a lot less of it), and explosion suppression or venting may still be required in dust collectors. A complete risk management programme for a complex chemical process will require elements from all of the risk management strategies to properly manage all hazards.

32.4.3 Process risk management and layers of protection

The application of various process risk management strategies to hazard control in the chemical process industries has been described as providing multiple layers of protection to the process (CCPS, 1993, 1996). This is shown graphically in Figure 32.1, with the basic process design at the centre of the figure, and various passive, active and procedural protection layers applied to the process to prevent the hazard from impacting on people, the environment or property. These layers of protection fall into the categories described above. A process that is inherently safer will require fewer, and less robust, layers of protection – in fact a truly 'inherently safe' process (which is probably impossible if one considers ALL possible hazards) would not require any layers of protection at all. The layer of protection concept has been developed as a methodology for quantitative risk analysis of a process, called Layer of Protection Analysis (LOPA) (CCPS, 2001).

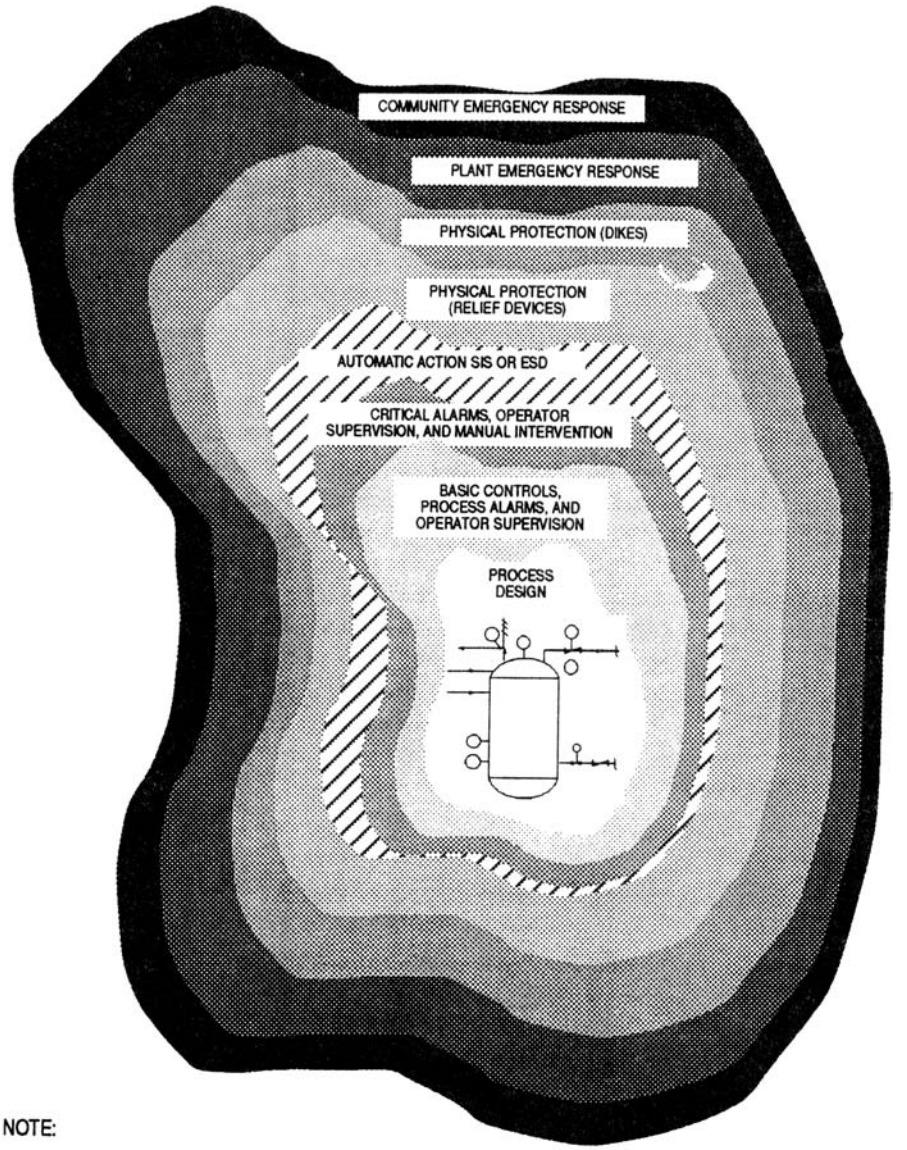

Figure 32.1 *Layers of protection for a chemical process (from CCPS, 1992, 1996)*

32.5 Inherently Safer Design Strategies

Kletz (1998) has categorized inherently safer design strategies into four major categories: intensification, substitution, attenuation and limitation of effects. Kletz also describes a number of additional strategies for the design of 'friendly plants' which he does not regard as true inherent safety strategies because they do not eliminate or significantly reduce the hazard, but rather make it more difficult for incidents to occur as a result of the hazard. These strategies are listed in Table 32.1, and include

Table 32.1 *Strategies for inherently safer design*

Kletz (1998)	*CCPS (1996)*
Inherent safety strategies	Inherent safety strategies
(1) Intensification	(1) Minimize
(2) Substitution	(2) Substitute
(3) Attenuation	(3) Moderate
(4) Limitation of effects	(4) Simplify
'Friendly plant design' strategies regarded as 'add on' features	Mapping of Kletz's 'friendly plant design' strategies to CCPS inherent safety strategies
(1) Simplification	(1) Simplify
(2) Avoiding knock on effects	(2) Moderate (Limit effects)
(3) Making incorrect assembly impossible	(3) Simplify
(4) Making status clear	(4) Simplify
(5) Tolerance of misuse (error tolerance)	(5) Moderate (Limit effects)
(6) Ease of control	(6) Moderate (Limit effects)
(7) Understandable software for computer control	(7) Simplify
(8) Instructions and procedures	(8) Simplify
(9) Life-cycle friendliness (construction and demolition)	(9) Consider all strategies with regard to all phases of a plant life cycle
(10) Passive safety	(10) Moderate

simplification and error tolerance. CCPS (1996) suggests the same basic inherently safer design ideas as Kletz, but reduces the categories to four – minimize, substitute, moderate and simplify. The CCPS concept of inherently safer design is somewhat broader than Kletz's original concept, considering many of Kletz's 'friendly plant design' principles to be approaches to inherently safer design as well. The distinctions are somewhat arbitrary, and the important point is that all of these principles are highly appropriate considerations for the design and operation of highly robust, reliable, and safe plants. Table 32.1 compares the Kletz inherently safer design and friendly plant strategies to those of CCPS, showing how they encompass the same basic ideas. For this discussion, the simpler CCPS categorization will be followed, recognizing Kletz's more detailed categorization is embedded in the four CCPS strategies.

The examples in the following sections are summarized from Kletz (1998) and CCPS (1996). More details can be found in these books.

32.5.1 Minimize (intensify)

The quantity of hazardous material and energy in a process should be minimized. This applies to all unit operations in a plant as well as to raw material, intermediate and hazardous product storage and to piping which connects equipment. Reducing the size of equipment containing hazardous materials and energy is inherently safer because the direct consequences of the loss of containment of that material or energy will be correspondingly reduced. Ideally, the consequences will be sufficiently reduced that the loss of containment is not capable of causing significant damage or injury, but, in any case, the consequences will be reduced.

The use of smaller equipment may make it feasible to use other risk management strategies which would be impractical or prohibitively expensive for large equipment. For example, consider a process which includes a nitration reaction. Nitration is a highly exothermic reaction process, and there is often a potential for a runaway reaction which could rupture the reaction vessel. The reaction can be done in a large batch reactor, perhaps several thousand gallons in volume. While it is possible to enclose this large reactor in a large bunker (a passive safety feature) capable of containing the explosion from a ruptured vessel, such a bunker would have to be extremely large and strong to contain such a large explosion. An alternative nitration process, using a continuous stirred tank reactor, might have a reactor volume of only a couple of hundred gallons. Now, containment in a bunker becomes more feasible because the bunker is smaller, and it does not have to be as strong because it must contain the rupture of a much smaller vessel. In some cases it may be feasible to do the nitration in a pipe reactor, or an eductor, with a volume of only a couple of gallons, making containment even more feasible. Other safety devices may also become more feasible – for example it is practical to detect the temperature increase from a runaway reaction and dump the small continuous reactor into a large quench tank full of water in a few seconds (an active safety feature), while this cannot be done with the large batch reactor.

How does an engineer identify opportunities to minimize the size of process equipment? An extensive literature is developing on the subject of Process Intensification in recent years, and there are many innovative ideas on how to reduce the size of all types of process equipment. Most of this work is not driven by safety considerations, but rather by economics. Smaller equipment is cheaper to build and operate, and takes up less space in the plant. Innovative technology to reduce the size of process equipment is not only safer, but it also saves money. Smaller equipment also provides better and more uniform control of conditions in the equipment – the temperature gradients are smaller, there is a more uniform concentration, mixing is more efficient and heat can be more easily removed. The key to reducing the size of process equipment is a basic understanding of the physical and chemical processes that occur in the equipment. With this understanding, the engineer

can design equipment to optimize the rate limiting steps in the process, reducing the size of the equipment and making it safer, cheaper and more efficient. Stankewiez and Moujlin (2003) provide a good overview of process intensification in general, including examples of its application to various unit operations and chemical technologies.

CCPS (1996) and Kletz (1998) provide many specific examples of inherently safer design through intensification or minimization. Some areas where significant benefits have been realized include:

(1) Reaction
   (a) Continuous stirred tank reactors have replaced batch reactors in many applications, including nitration, chlorination and polymerization.
   (b) Loop reactors, continuous pipe loops with a recirculation pump, provide intensive mixing and efficient heat removal and have been used for hydrogenation, ethoxylation, polymerization, chlorination and other exothermic reactions.
   (c) Reactive distillation combines the unit operations of chemical reaction and distillation into a single piece of equipment. A reactive distillation process for the manufacture of methyl acetate from methanol and acetic acid uses a single reactive distillation column and two auxiliary columns in place of a continuous reactor, an extractor and eight distillation columns.
   (d) Many rapid, highly exothermic reactions can be done in eductors. Examples include the Nobel AB process for nitroglycerine and the manufacture of Caro's acid (Whiting, 1992).
   (e) Tubular reactors can be used for polymerization and many other reactions.
(2) Distillation
   (a) Column packing and tray geometry can be modified to minimize hazardous liquid inventory.
   (b) Column base geometry can be modified to minimize hold-up of hazardous material.
   (c) Centrifugal distillation devices such as HiGee which have much smaller inventory have been developed experimentally, although commercial applications are limited to date.
   (d) Advanced control of a multi-component distillation column can allow a single column to replace multiple columns, with multiple feeds to and product streams from a single column.
(3) Extraction
   (a) Centrifugal extractors have much smaller volume than traditional extraction columns.
   (b) The efficiency of extraction columns can be enhanced (and, therefore, the columns made smaller) by introducing pressure pulses or vibrations, or with a vibrating tray stack.
   (c) Combined mixer–settlers can replace separate mixing and settling vessels.
(4) Heat exchange
   (a) Various types of heat exchangers have vastly different efficiency, in terms of the heat transfer area per unit volume of material inventory. Table 32.2 (from Kletz, 1998) compares the efficiency of a number of common types of heat exchanger.
(5) Raw material storage
   (a) Modern inventory control systems reduce the need to store large quantities of hazardous raw materials. However, it is important to consider all hazards when making these decisions, including transportation. Truck transport of a hazardous raw material may allow a smaller on-site storage tank, but it will require more frequent shipments, and more frequent unloading operations.
   (b) storage of hazardous raw materials might be eliminated if a new plant can be located on the same site as the hazardous raw material manufacturing plant, using the existing storage at the supplying plant.
(6) Intermediate storage
   (a) Intermediate storage of hazardous intermediates is often provided as a buffer, so the entire plant will not have to shut-down when a particular piece of equipment or section of the plant must be shut-down for repair or maintenance. Improving the reliability of equipment or sections of a plant may eliminate the need for intermediate storage. In some cases, providing redundancy for critical pieces of equipment may also eliminate the need to store hazardous intermediates.
   (b) There may be choices on what materials to store as in-process intermediates. Perhaps a hazardous material is produced as an aqueous solution, then distilled to produce a pure product, which is subsequently converted to various final products in downstream units. Storage of a large inventory the aqueous solution to supply the downstream processes could be considered as an inherently safer alternative to storage of the pure material.
   (c) Storage and transportation of hazardous raw materials can be reduced or eliminated by locating a downstream plant on the same site as the plant producing the hazardous raw material – for example locating a plant producing a chlorinated pesticide adjacent to a chlorine manufacturing plant.
(7) Piping
   (a) Hazardous material pipe diameter should be minimized, consistent with maintaining sufficient mechanical strength and integrity. A 100 mm diameter pipe contains four times as much material as a 50 mm pipe of the same length.
   (b) Hazardous material pipe length should be minimized, again consistent with providing appropriate spacing of hazardous facilities.

Table 32.2 *Surface compactness of heat exchangers (adapted from Kletz, 1998)*

Type of exchanger	*Surface compactness* (m^2/m^3)
Shell and tube	70 to 500
Plate	120 to 1000
Spiral plate	Up to 185
Shell and finned tube	65 to 3300
Plate fin	150 to 5900
Printed circuit	1000 to 5000
Regenerative – rotary	Up to 6600
Regenerative – fixed	25 to 15,000
Human lung	20,000

32.5.2 Substitute

In the chemical industry, the two major areas where substitution enhances inherently safer design are substitution of a less hazardous chemical synthesis route for a desired product, and substitution of a less hazardous material for a specific application. Substituting less hazardous chemistry offers the greatest potential for enhancing inherent safety, but must be considered early in process development since alternate chemistry often requires abandonment of an existing plant and construction of a new one.

Recently there has been a major research effort in many developed countries to develop environmentally friendlier 'green chemistry' for the synthesis of many products and for chemical products. Many of these green chemistry alternatives are also inherently safer because they focus on eliminating or reducing the use of toxic and flammable materials. However, this is not always true, and sometimes environmental and safety considerations are in conflict. Perhaps the best known example of this conflict is in refrigerants. Chlorofluorocarbon (CFC) refrigerants were developed in the 1920s and 1930s as inherently safer alternatives to refrigerants then in use. CFCs have low acute toxicity and are non-flammable, eliminating hazards of many of the refrigerants formerly used, such as light hydrocarbons (flammable), ammonia (toxic and flammable) and even sulfur dioxide (toxic, corrosive). Later, in the 1980s and 1990s CFCs were found to cause significant environmental damage, and they can no longer be used in many countries. In many cases, refrigeration systems are going back to earlier refrigerants, but it must be recognized that, while the hazards can be managed using strategies discussed earlier, refrigerants such as ammonia and light hydrocarbons are inherently less safe.

Some specific areas of research which offer potential for development of inherently safer chemical manufacturing processes include the following.

(1) Catalysis – Development of improved catalyst systems which improve reaction selectivity (eliminating the need for extensive product purification systems), allow products to be produced under less severe conditions (lower temperature and pressure), speed up reactions resulting in smaller reactors and improve raw material conversion (eliminating the need for recycle) all can enhance inherent safety.
(2) Catalytic reaction functionality can sometimes be immobilized on a solid substrate, such as solid superacid catalysts in place of hydrogen fluoride or aluminium chloride for some alkylation reactions, or ion exchange resins in place of sulfuric acid for esterification.
(3) Supercritical processing may allow use of solvents such as carbon dioxide or water in place of flammable or toxic organic solvents.
(4) Innovative energy sources such as ultraviolet light, microwaves and laser light enhance some chemical reactions.
(5) Biocatalysis and enzymes may allow synthesis of products at ambient temperature and pressure conditions.
(6) Biological or biochemical synthesis may become feasible for many materials. Advances in genetic engineering and biotechnology in general may broaden the spectrum of products which can be made in this way.

Clearly many of these alternatives have the potential for introducing new hazards. Catalysts may contain hazardous materials, supercritical processing requires elevated temperature and pressure and there are safety and environmental concerns which must be considered for biotechnology.

Much of the literature of green chemistry and engineering has focused on identifying substitute, less hazardous materials for many industrial and consumer applications. Many government environmental agencies have developed extensive resources and databases identifying potential substitutions. Some common examples of substitution of less hazardous materials include:

(1) Use of water base latex paints in place of organic solvent base paints.
(2) Replacement of flammable solvents with alternative solvents with a high flash point for many formulated products such as agricultural chemicals, dyes, adhesives, paints and coatings, and paint removers.
(3) Replacement of chlorinated organic solvents by aqueous systems for degreasing and cleaning in the electronics industry.

32.5.3 Moderate (attenuate)

Inherently safety can be enhanced by changing a material or process to moderate the hazard, or by designing the plant to moderate the impact of an incident arising from the hazard. Kletz (1998) refers to the later approach separately as 'Limitation of Effects,' while CCPS (1996) considers this to be a form of the 'Moderate' strategy.

Moderating hazards of materials

Dilution

Dilution of a hazardous material with a less hazardous material (such as a solvent) offers several inherent safety benefits. Because the hazardous material is diluted, if the material is spilled, the partial pressure of the hazardous material will be lower than for the pure material, and the atmospheric concentration above the spill will be reduced. This will also reduce the downwind concentration in the atmosphere. If the material is flammable, dilution with a non-flammable material such as water may be sufficient to significantly reduce the fire hazard. In some cases, pure materials such as hydrogen chloride or ammonia may require pressurized storage, while relatively concentrated aqueous solutions can be stored at atmospheric pressure. While many applications require use of a pure material, many do not – for example neutralization with ammonia or hydrochloric acid – and aqueous materials should be considered for those applications where feasible.

The stability of some solid materials can also be enhanced by dilution with an inert material. Alfred Nobel's invention of dynamite – nitroglycerine absorbed onto an inert carrier – is an example of inherently safer design. As another example, the stability of benzoyl peroxide is greatly enhanced by handling it as a water wetted powder, compared to the pure, dry material.

Refrigeration

Refrigeration of liquefied gases can improve inherent safety. Refrigeration has a number of potential benefits.

(1) Storage pressure will be lower, in some cases storage at near atmospheric pressure is feasible. This results in a reduced leak rate in case of a loss of containment from the storage system because of a lower pressure. For storage near atmospheric pressure, a leak from the vapour part of the storage tank will be very small because there is practically no pressure to provide driving force for the leak.
(2) A leak from a liquefied gas storage vessel at ambient temperature and elevated pressure will result in significant flashing of vapour into the atmosphere from the leak. A leak from a refrigerated storage tank will flash less, or not at all if the storage is near atmospheric. While the spilled material will boil or evaporate as it absorbs heat from the atmosphere and the ground, this rate of release will often be smaller than that resulting from a pressurized, flashing leak. Also, the designer will have the opportunity to reduce the evaporation rate of the spilled material by dike design to minimize surface area, insulating dike materials, covering the spill or secondary containment.
(3) The amount of release to the atmosphere from a liquefied gas storage vessel may actually be significantly higher than that which would be calculated from the flash calculation. As the material leaks from the storage vessel, a large fraction of the material will flash to vapour as a result of the pressure reduction to the atmosphere. Much, perhaps all, of the material which remains as a liquid according to the flash calculation, will be present as small droplets, an aerosol. These droplets may be too small to rapidly settle out and form a liquid pool on the ground. Instead, they may be carried downwind with the released vapour as a fine mist or fog. As they travel downwind, they will absorb heat from the atmosphere and evaporate. The actual amount of material released to the atmosphere from a pressurized gas leak may be several times larger than would be expected based on the flash calculation. Refrigeration of the pressurized gas eliminates the flashing and aerosol formation.

Some of the materials for which refrigerated storage has been reported to be beneficial include ammonia, chlorine, butadiene, ethylene oxide, propylene oxide, methylamines and vinyl chloride. As for most design choices, again there are potential downsides to refrigeration – for example refrigerated storage facilities will require insulation which makes it more difficult to inspect piping and vessels, and may make them susceptible to external corrosion if water is absorbed into the insulation.

Change physical characteristics

The explosion hazard of a combustible dust is a function of its particle size. If these materials can be handled as a granule or pellet instead of a dusty powder, they will be inherently safer. This will also reduce the potential of exposure of people to airborne dusts.

Some reactive or toxic materials can be immobilized by attaching them to a solid substrate, making them less likely to come into contact with people. For example, acid or basic functionality can be provided as a solid ion exchange resin or a membrane. Metal catalysts are often bonded to an inert carrier.

Moderating hazards of processes

Substitution of alternate chemistry, or development of improved catalysts, as discussed previously, can often allow a process to operate at lower temperature and pressure. This not only improves inherent safety, but it is also almost certain to make the construction of the plant cheaper because equipment rated for lower temperature and pressure will cost less.

There are many approaches to limiting the effects (moderating the effects) of an incident arising from a hazard. In many cases, these are probably better described as passive safety features rather than inherent. They do not reduce the magnitude of the hazard, or eliminate the hazard, but they are very robust and reliable methods for minimizing the potential impact of an incident. Some examples include:

(1) Primary containment. Build stronger equipment. If a reaction has a maximum adiabatic pressure in case of a runaway of 200 psig, a 250 psig reactor will contain a runaway. It is essential to be highly confident of the maximum temperature and pressure in this case – the chemistry must be fully understood, including the potential for unknown reactions or decomposition at the elevated temperature and pressure resulting from the runaway reaction.
(2) Secondary containment. Containment dikes around storage tanks and processing equipment. Also, containment buildings can be used to reduce the release of toxic materials to the atmosphere. Bunkers or explosion proof buildings, with the process equipment operated from a remote location, have been used for explosives manufacture.
(3) Plant siting. Locate hazardous material handling facilities as far as possible from potentially impacted population or equipment.
(4) Batch reactions. For exothermic reactions, avoid batch processes where all of the materials are charged to the batch before the reaction is initiated. With this type of process, if temperature control is lost for some reason, all of the reaction energy is present in the reactor and a runaway reaction is possible. Semi-batch, or fed batch, reactions, where a limiting reactant is gradually added at a rate corresponding to the rate of reaction, are inherently safer. If temperature control is lost, the limiting reactant feed can be stopped, and there is little or no reaction energy in the batch.
(5) Maintain separation between incompatible materials, both for container storage in warehouses, and tank farm storage of bulk materials.

32.5.4 Simplify

Simplification is key to a 'user friendly' plant. If a plant is complicated, it is going to be more susceptible to incorrect operation. While most chemical plants are highly complex of necessity because of the complexity of the technology, designers should always be striving to eliminate all unnecessary complexity. In some cases, simplification will eliminate hazards by making it impossible to conduct operations which result in those hazards. In other cases, simplification will make it more difficult to make errors, perhaps not truly an example of inherently safer design, but still highly desirable.

Some examples of simplification include:

(1) Use stronger (higher pressure rated) equipment can reduce or eliminate the need for complex pressure relief systems, and complex instrumentation and interlocks to protect against overpressure.
(2) Eliminate unnecessary or seldom used piping. While the designer of a plant might think that the operators will someday want to transfer material from the final product tank back to the second distillation column, how often will this really need to be done? If the pipe is not used frequently, perhaps it will be plugged, the valves will be rusted shut, or the gaskets will be degraded several years after construction when somebody finally wants to use the pipe. It may be better to wait until there is a real need, then install a new pipe at that time. In the meantime, the unused pipe is a potential operating error waiting to happen. Question the real need for 'abnormal operation' piping – eliminating it will save money and the plant will be simpler and easier to operate safely.
(3) Gravity flow can eliminate pumps, which require maintenance and can leak.
(4) Make incorrect operation impossible. Many electric power plugs are designed so they can only be inserted in the socket one way, and there are many other examples of equipment which has been designed so it cannot be operated improperly.
(5) Develop processes which are insensitive to variation in operating parameters. Design engineers should challenge research chemists and engineers to invent processes which are insensitive to variation in process operating parameters. While it is possible, for example, to control a reactor temperature to within 0.5°C, it is much easier to control the reactor to within 5°C. If the process can be modified so that it is less sensitive, the plant will be cheaper, more reliable and safer.
(6) Good human factors design. Equipment should be designed to operate the way people expect it to operate, it should provide feedback to the operator to confirm proper operation, it should be designed with consideration for ergonomics and human factors. Kletz (1998) and CCPS (1996) provide many specific examples of both good and bad human factors design, and CCPS (1994) provides an extended discussion of human factors in the chemical industry.

32.6 Inherently Safer Design Conflicts

A chemical plant or process can be described as inherently safer in the context of one or more of its multiple hazards, when compared to other possible design options. However, in general it is unlikely that a particular design can be considered inherently safer with respect to all hazards simultaneously. Some examples of inherent safety conflicts include:

(1) There are two alternative solvents for a process. One is flammable but has low acute toxicity. This solvent is inherently safer with respect to toxicity hazards. The alternative solvent is non-flammable, but has high acute toxicity – this solvent is inherently safer with respect to fire hazards, but inherently more hazardous with respect to toxicity hazards.
(2) A process requires chlorine as a raw material. Chlorine can be supplied in 90 ton rail cars or 1 ton cylinders. A neighbour two miles away from the plant, concerned about exposure from a large leak, considers the cylinders inherently safer because the smaller quantity is less likely to result in exposure at that distance. The process operator, who must connect and disconnect 90 cylinders instead of one rail car, will be in close proximity to the chlorine source and would consider the rail car to be inherently safer with respect to his risk of exposure to chlorine.
(3) CFC refrigerants have low acute toxicity and are not flammable. They are inherently safer with respect to the flammability and acute personnel exposure. However, it is now generally accepted that they cause long-term environmental damage, and their use is being phased out.

It is almost always impossible to simultaneously maximize all desired characteristics of any engineered system. The central problem of all engineering design is to find the optimum combination of characteristics that best meets the overall objectives. This 'best design' depends on the relative importance which is attached to the various desirable characteristics – what is the relative importance of flammability hazards, as compared to acute toxicity hazards, as compared to long-term environmental hazards, as compared to other hazards which might be identified. This relative importance may be impacted by the environment in which the plant is built, the feasibility, reliability and effectiveness of passive, active and procedural safety features for the hazard of concern, and other design specific factors. The inherent safety characteristics of a process become one of the many characteristics which the design engineer must evaluate as he determines his optimum design for a particular facility.

Many decision-making tools have been developed to aid decision-makers in understanding the many conflicting characteristics of a multi-dimensional decision, allowing them to make logical and consistent decisions. CCPS (1995) describes the use of many of these tools, as listed in Table 32.3, to process safety decision-making in general. The INSIDE Project (Inherent Safety in Design (INSIDE) Project Team, 1997) also suggested the use of this type of tool for understanding and resolving inherent safety and environmental conflicts. These decision-making tools can also be applied to resolving conflicts between the inherent safety characteristics of a process with respect to different kinds of hazard, as well as conflicts between inherent safety and other important process characteristics such as environmental impact, various economic parameters,

Table 32.3 *Decision tools applicable to process safety and inherently safer design decisions (CCPS, 1995)*

Voting methods
Weighted scoring methods
Kepner-Tregoe decision analysis
Analytical hierarchy process
Cost-benefit analysis
Mathematical programming
Payoff matrix analysis
Decision analysis
Multi-attribute utility analysis

product quality, reliability and other process measures of importance to different stakeholders. The use of these tools will require some kind of a measure of the inherent safety characteristics of a process, a topic discussed in Section 7.

32.7 Measuring Inherent Safety Characteristics of a Process

32.7.1 Introduction

In a recent global survey on the use and interest of people in inherently safe design, Gupta and Edwards (2002) reported at length that the survey responders, all connected with the process industry, academics or regulatory authorities, were generally familiar with inherently safe design and desired to use it to their advantage. They did not want another enforcing regime from the government requiring its use since they already have enough regulations related to process safety to follow. To use inherently safe design voluntarily, they desired a simple way to determine or measure the inherent safety of a process at the research and development stage before too much time and resources have been invested in the process development. It is so because with more resources invested, it becomes difficult to make drastic changes and justify the expenses. Research chemists will also need to adopt the inherently safe design in process development. So far they have generally been oblivious of the safety issues. For their use of inherently safe design, it is essential that the inherent safety index (ISI) be very simple.

There are no hard and fast rules or methods as to how to make a process inherently safer. One could use any one of several approaches possible (different catalysts, reactants, operating conditions, yield, by-products, etc). Up till now, the choice between competing processes has been guided by their technical feasibility and economic viability. Lately, the safety and environment concerns have also impacted the choice between competing processes due to regulatory requirements. Therefore, if some sort of a measure of inherent safety were available, it would make the decision-making so much easier. Researchers spread over several continents have looked at the problem of measuring inherent safety. Each group has developed ISI, different from the other groups. That is how, probably, progress is made in new fields. After due time and experience, people converge on to a common system, which is then universally adapted. In inherently safe design measurement, we have come to a stage where several approaches are available and it is time to start consolidating the work while not shutting out altogether newer approaches. As experience is gained in using the existing indices, a universally accepted index will develop.

We mention the existing indices followed by a brief description of the inherent safety indices. Thereafter we discuss the work needed to consolidate the efforts.

32.7.2 Existing indices

Dow Fire and Explosion Index (Dow Chemical Company, 1994) and Mond Index (ICI, 1993) are used for determining the hazard level of a process plant. However, to use these, the process design has to be fully in place since a lot of information required pertains to that. Hence, these are unsuitable for use in conceptual design and preliminary process development stages, which is the aim of the inherent safety indices.

32.7.3 Inherent safety indices

Edwards and Lawrence index (Edwards and Lawrence, 1993; Lawrence, 1996)

Called PIIS (Prototype Index of Inherent Safety), this was the first ever index that was developed and has been modified by later workers.

The authors decided upon 17 parameters that they thought affected inherent safety (IS) of a process (Table 32.4). Out of these 17, they picked 7 in the first application of their PIIS index (Table 32.4). They divided the total ranges that each of these parameters could possibly take in the process industry into several sub-ranges and assigned numerical scores to each sub-range. These numerical scores were either based on existing indices including the Dow Fire and Explosion Index and the Mond Index or on their own judgement. Scoring tables for temperature and pressure are given in Tables 32.5 and 32.6 for our discussion purposes. Lawrence (1996) has given tables for inventory, explosiveness, yield, toxicity and flammability also. They applied PIIS to six routes to manufacture methyl methacrylate (MMA) in order to rank their inherent safety (MMA, Table 32.7). They considered each step of each route and noted down the operating pressure and temperature, yield, flammability, toxicity and explosiveness of all the reactants, products and intermediates involved. For inventory, they took a one-hour residence time, and stoichiometric relationship into account for a 50,000 tonnes per year production of the final product, MMA. The worst

Table 32.4 *Parameters listed by Lawrence (1996)*

(1)	Inventory (volume or mass)*	(10)	Side reactions
(2)	Temperature*	(11)	Waste and co-products
(3)	Pressure *	(12)	Reaction rate
(4)	Conversion	(13)	Catalytic action
(5)	Yield*	(14)	Heat of reaction
(6)	Toxicity*	(15)	Phase
(7)	Flammability*	(16)	Phase change
(8)	Explosiveness*	(17)	Viscosity
(9)	Corrosiveness		

* Parameters considered in the MMA example.

Table 32.5 *Temperature scoring table (Lawrence, 1996)*

Temperature (°C)					*Score*
		T	<	−25	10
−25	≤	T	<	−10	3
−10	≤	T	<	10	1
10	≤	T	<	30	0
30	≤	T	<	100	1
100	≤	T	<	200	2
200	≤	T	<	300	3
300	≤	T	<	400	4
400	≤	T	<	500	5
500	≤	T	<	600	6
600	≤	T	<	700	7
700	≤	T	<	800	8
800	≤	T	<	900	9
900	≤	T			10

chemical for flammability, toxicity and explosiveness was taken for each step. Flammability score was based on the flash point and boiling point of a chemical, explosiveness was based on the range of explosive mixture (UEL−LEL) while toxicity was based on the threshold limit value (TLV).

The scores for each step in a given process route for pressure, temperature and yield were added together and called the 'process score', while the scores for inventory, toxicity, flammability, explosiveness were added together and called the 'chemical score'. The two sets of scores thus obtained for each step in a route were added to get a score for each route. These final scores were taken as a measure of the inherently safer (actually, inherently riskier) nature of different routes and the one with the highest numerical value was taken to be the worst route (Table 32.8). Based upon this exercise, acetone cyanohydrin (ACH) route comes out to be the worst. Note that this is the only route in use in major manufacturing facilities worldwide (unless some local laws prohibit the use of hazardous chemicals like HCN, HF, etc., thus forcing the choice of a different route).

Edwards and Lawrence (1993) then invited eight renowned process safety experts to comment on their work (Table 32.9). The experts first looked at each of the routes in its entirety, then at each of the steps (without referring as to which route the specific step belonged to) and finally at the proposed PIIS index. Their ranking of the different routes matched to a large extent the ranking obtained by Edwards and Lawrence using the proposed index. That is not surprising since, whether with or without an index, a process route with high pressure, high temperature, high values of toxicity, flammability and explosiveness and high inventory is more dangerous (and hence more inherently unsafe) than routes that are otherwise.

This pioneering work of Edwards and Lawrence caught the attention of several other workers. Their indices are described below.

Table 32.6 *Pressure scoring table (Lawrence, 1996)*

Pressure (psi)	*Score*
0−90	1
91−140	2
141−250	3
251−420	4
421−700	5
701−1400	6
1401−3400	7
3401−4800	8
4801−6000	9
6001−8000	10
+ 1 point per 2500 psi	

Table 32.7 *Details of six MMA routes (Lawrence, 1996)*

Route 1: Acetone cyanohydrin based route (ACH)

Step 1: $2CH_4 + 2NH_3 + 3O_2 \rightarrow 2HCN + 6H_2O$
Methane + Ammonia + Oxygen → Hydrogen cyanide + Water
Gas phase; Pressure: 3.4 Atm; Temperature: 1200°C; Yield: 64%

Step 2: $(CH_3)_2\,CO + HCN \rightarrow (CH_3)_2\,COHCN$
Acetone + Hydrogen cyanide → Acetone cyanohydrin
Liquid phase; Pressure: Atmospheric; Temperature: 29−38°C; Yield: 91%

Step 3: $2(CH_3)_2\,COHCN + H_2SO_4 + 2H_2O \rightarrow (CH_3)_2\,COHCONH_2 + (CH_3)_2COHCONH_2 \cdot H_2SO_4 \xrightarrow{HEAT} CH_2{=}C(CH_3)CONH_2 + CH_2{=}C(CH_3)CONH_2 \cdot H_2SO_4 + 2H_2O$
Acetone cyanohydrin + Sulfuric acid + Water → 2-Hydroxyl-2-methyl propionamide + 2-Hydroxyl-2-methyl Propionamide sulfate → Methacrylamide + Methacrylamide sulfate + Water
Liquid phase; Pressure: 7 Atm; Temperature: 130−150°C; Yield: 98%

Step 4: $CH_2{=}C(CH_3)CONH_2 + CH_2{=}C(CH_3)CONH_2 \cdot H_2SO_4 + 2CH_3OH + H_2SO_4 \rightarrow 2CH_2{=}C(CH_3)COOCH_3 + 2NH_4HSO_4$
Methacrylamide + Methacrylamide sulfate + Methanol + Sulfuric acid → Methyl methacrylate + Ammonium bisulfate
Liquid phase; Pressure: 7 Atm; Temperature: 110−130°C; Yield: 100%

Step 5: $H_2SO_4 + 2NH_4HSO_4 + 3O_2 + CH_4 \rightarrow 3SO_2 + CO_2 + N_2 + 8H_2O + O_2$
Sulfuric acid + Ammonium bisulfate + Oxygen + Methane → Sulfur dioxide + Carbon dioxide + Nitrogen + Water + Oxygen
Gas phase; Pressure: Atmospheric; Temperature: 980−1200°C; Yield: 100

Step 6: $2SO_2 + O_2 \rightarrow 2SO_3$
Sulfur dioxide + Oxygen → Sulfur trioxide
Gas phase; Pressure: Atmospheric; Temperature: 405−440°C; Yield: 99.7%

Similar details were also given about the remaining following five routes:
Route 2: Ethylene (via Methyl propionate) based route (C2/MP)
Route 3: Ethylene (via Propionaldehyde) based route (C2/PA)
Route 4: Propylene based route (C3)
Route 5: Isobutylene based Route (i-C4)
Route 6: Tertiary Butyl Alcohol based Route (TBA)

Heikkilä and Hurme index (Heikkilä, Hurme, and Järveläinen, 1996; Heikkilä, 1999)

These authors argued that the safety is affected both by the properties of the chemicals as well as the equipment used. They have, therefore, included the type of equipment and process structure. The similarities and differences in their approach and that of Edwards and Lawrence are brought out in Table 32.10. In Table 32.11, they bring out nicely how the various parameters are connected to the basic principles of inherent safety. They go on to produce an ISI with subdivisions for different parameters (Table 32.12):

$$ITI = ICI + IPI$$

where ITI is the total ISI, ICI and IPI are the summations of respective worst-case values of the sub-indices for various parameters. These values are chosen from a range of numbers for each parameter (Table 32.13). The ranges for each parameter have been further subdivided. Representative tables for temperature and pressure (Tables 32.14 and 32.15) can be compared with Tables 32.5 and 32.6 given by Edwards and Lawrence (1993). There are significant differences and it is difficult to pick one over the other. The authors have also used ISI as an objective function in the genetic optimization and have come up with a case based reasoning for safe process structure.

Table 32.8 *Scores for MMA routes from PIIS index (Lawrence, 1996)*

Route	*Chemical score*	*Process score*	*Index score*
ACH	58	45	103
C2/PA	49	30	79
C3	39	28	67
C2/MP	35	17	52
i-C4	24	25	49
TBA	25	22	47

Table 32.9 *Process Safety Experts invited to comment on IS Index (Lawrence, 1996)*

F.P. Lees –	Loughborough University
M. Kneale –	Independent consultant
H.A. Duxbury –	Independent Consultant/ Loughborough University
T.A.Kletz –	Independent Consultant/ Loughborough University
C.C. Pinder –	BP Chemicals Ltd/ Loughborough University
W.H. Orrell –	Independent consultant
M.L. Preston –	ICI Engineering
A.G. Rushton –	Loughborough University

Palaniappan, et al. index (Palaniappan, Srinivasan and Tan, 2002; Palaniappan, 2001)

These authors have come up with an i-Safe index. They expanded the Heikkilä and Hurme's chemical and process safety indices to include five other supplementary indices, viz: Hazardous Chemical Index (HCI), Hazardous Reaction Index (HRI), Total Chemical Index (TCI), Worst Chemical Index (WCI) and Worst Reaction Index (WRI). The proposed index has been used by Srinivasan and Meibao (2003) to evaluate the six synthesis routes for methyl methacrylate or MMA, the set first used by Edwards and Lawrence (1993). This was a painstaking work because a lot of information about properties and operating conditions was not available in the literature. They calculated from thermodynamics and atomic contributions and used other similar reaction

Table 32.10 *Inherent safety parameters (Heikkilä, Hurme, and Järveläinen, 1996)*

Inherent safety parameters (Edwards and Lawrence, 1993)	*Chosen parameters by*		*Comments*
	Lawrence (1996)	*Heikkilä (1999)*	
Inventory	x	x	relative to capacity
Phase			release property
Temperature	x	x	
Pressure	x	x	
Heat of main reaction		x	high/low heat generation
New phase generation			solid/gas formation
Catalysts			
Side reactions		x	heat generation
Waste products			considered by substances
Reaction yield	x		considered by inventory
Reaction rate			considered by ΔH_R
Viscosity			hot spots
Flammability	x	x	ease of burning (liquid)
Explosiveness	x	x	explosive gas mixture
Corrosiveness		x	construction material
Toxicity	x	x	an adverse effect on the human body
Chemical interaction*		x	reactivity
Type of equipment*		x	choice of equipment
Safety of process structure*		x	choice of configuration

* Not included in Edwards and Lawrence (1993).

Table 32.11 *The characteristics of inherent safety in conceptual process design (Heikkilä, Hurme, and Järveläinen, 1996)*

Principles of inherent safety (Kletz, 1978)	*PIIS (Edwards and Lawrence, 1993)*	*ISI (Heikkilä, Hurme, and Järveläinen, 1996)*
Intensification		
(1) inventory	inventory	inventory
(2) reaction volume	reaction yield	
Substitution	flammability	flammability
(1) safer materials	explosiveness	explosiveness
	toxicity	toxicity
		chemical interaction
Attenuation		
(1) lower temperature	temperature	temperature
(2) lower pressure	pressure	pressure
Limitation of Effects		
(1) safer technical alternatives		equipment safety
(2) safer reaction conditions	temperature	safe process structure
	pressure	pressure
		temperature
		chemical interaction
Simplification		
(1) simplify process facilities		safe process structure
Making incorrect assembly impossible		
(1) choice of equipment, piping and fittings correctly		equipment safety safe process structure
Tolerance		
(1) resistant to maloperation		corrosiveness equipment safety safe process structure
Ease of control		safe process structure heat of reaction

Table 32.12 *Inherent safety index and parameters for its sub-indices (Heikkilä, Hurme, and Järveläinen, 1996)*

Total inherent safety index	
Chemical inherent safety index	*Process inherent safety index*
Sub-indices for reaction hazards	Sub-indices for process conditions
Heat of the main reaction	Inventory
Heat of the side reactions	Process temperature
Chemical interaction	Process pressure
Sub-indices for hazardous substances	Sub-indices for process system
Flammability	Equipment
Explosiveness	Process structure
Toxicity	
Corrosiveness	

situations as well to make estimates. Their results follow the trend of Edwards and Lawrence, with the ACH route coming out to be the worst (Table 32.16). However, the spread of the i-Safe index values, called Overall Safety Index (OSI = sum of TRI for main reaction steps) for the six routes, was in a narrow band of 15, from 51 to 65, compared to the spread of 57, from 47 to 103, in the study of Edwards and Lawrence.

Khan and Amyotte Index (Khan and Amyotte, 2003)

These authors have proposed an Integrated Inherent Safety Index (I2SI). It comprises of two main indices: a hazard index (HI) and an inherent safety potential index (ISPI). Both the ISPI and HI range from 1 to 200. HI consists of a damage index (DI) and a process and hazard control index (PHCI). DI has four subparts related to fire and

Table 32.13 *Ranges for inherent safety sub-indices (Heikkilä, Hurme, and Järveläinen, 1996)*

	Symbol	*Score*
Chemical inherent safety index, I_{CI}		
Heat of main reaction	I_{RM}	0–4
Heat of side reaction, max	I_{RS}	0–4
Chemical interaction	I_{INT}	0–4
Flammability	I_{FL}	0–4
Explosiveness	I_{EX}	0–4
Toxic exposure	I_{TOX}	0–6
Corrosiveness	I_{COR}	0–2
Process inherent safety index, I_{PI}		
Inventory	I_I	0–5
Process temperature	I_T	0–4
Process pressure	I_p	0–4
Equipment safety	I_{EQ}	
Isbl		0–4
Osbl		0–3
Safe process structure	I_{ST}	0–5

Table 32.14 *Determination of the process temperature sub-index I_T (Heikkilä, Hurme, and Järveläinen, 1996)*

Process temperature (°C)	*Score of I_T*
<0	1
0–70	0
70–150	1
150–300	2
300–600	3
>600	4

Table 32.15 *Determination of the process pressure sub-index I_p (Heikkilä, Hurme, and Järveläinen, 1996)*

Process pressure (bar)	*Score of I_p*
0.5–5	0
0–0.5 or 5–25	1
25–50	2
50–200	3
200–1000	4

explosion, acute toxicity, chronic toxicity and environmental impairment. PHCI has ten subparts related to pressure, temperature, flow, level, concentration, inert venting, blast wall, fire resistance wall, sprinkler system and forced dilution. After the different terms above have been computed from various graphs, the I2SI is given by

$$I2SI = ISPI/HI$$

I2SI > 1 implies an inherently safer approach. The higher the quotient, the greater is the inherent safety nature of the process. The authors have utilized their elaborate index to evaluate the six routes for MMA manufacture, the example used by Edwards and Lawrence (1993). Khan and Amyotte's results (Table 32.17) and conclusions follow the trend of Edwards and Lawrence.

Gentile et al. *Index (Gentile, Rogers and Mannan, 2001)*
In all the above indices, except Khan and Amyotte's, there are sudden jumps in the score values at the extreme ends of each subdivision. For example, Table 32.5 shows a score of 2 for a temperature range of 100 to 199, which suddenly jumps to 3 at 200. Thus, while a change of 99 in temperature, from 100 to 199, did not produce any change in the score, a further change of only 1, from 199 to 200, changed the score by 1. Similar situation is encountered in tables for all the parameters in the indices proposed by Edwards and Lawrence (1993), Heikkilä, Hurme and Järveläinen (1996) and Palaniappan, Srinivasan and Tan (2002). Also, the scoring tables proposed by different authors for the same parameter do not always match. This introduces a subjective (or arbitrary) factor in the calculation of the indices. This aspect was addressed by Gentile *et al.* (2001). They used the fuzzy set theory to improve the sensitivity (either excessive or insufficient), as it existed in the ranges selected for the various parameters under consideration. They calculated their ISI based on if–then rules that describe the knowledge related to inherent safety. Each parameter is described by a linguistic variable whose range is divided into fuzzy sets. For each set, a membership function is defined which has a specific shape describing the physical behaviour of the set. This approach eliminates the problems of the interval-type approach used by other investigators as noted above. Gentile proposes to have an index with 4 stages (Gentile, 2003): stage 0 = route selection, 1 = process design, 2 = mechanical design, 3 = operation.

INSET Toolkit (Mansfield, 1997; INSIDE Project Team, 1997)
Experts from several corporations in United Kingdom and Europe worked on an EU sponsored project for an index for inherent safety, health and environment (ISHE). They called it as INSET toolkit. They accounted for many situations and developed several methods (called tools) for rapid as well as detailed analysis of processes for their ISHE performance (Table 32.18). These elaborate tools await intense testing and modifying before these can be used.

Gupta and Edwards Method (Gupta and Edwards, 2003)
These authors expressed three concerns about the additive indices discussed above:

(1) Addition of different types of hazards or parameters is not justifiable.
(2) Arbitrary assignment of scores to different parameters (P, T, Inventory, . . .) without establishing equality of hazard for the same numerical value (Does a number 3 in the table for pressure present the same hazard as 3 in table for temperature, etc.?).
(3) The total score will get biased by the number of steps (e.g. 6 steps in ACH route for MMA), or by one major score (e.g. for pressure in an HDPE plant).

They proposed that the parameters of interest should be plotted individually for each step in a process route without carrying out any mathematical operation and then be compared with each other (Figure 32.2).

Kletz commented on this approach favourably (Kletz, 2003) . . . "Instead of an absolute index we could compare a proposed new design (or designs) with . . . an existing design, using a number of headings. This benchmarking approach would give a comparison of alternatives rather than a position on a scale. This should be satisfactory as

Table 32.16 *i-Safe indices for the six different process routes (Palaniappan, Srinivasan and Tan, 2002; Palaniappan, 2001)*

Process	*IRI*	*OCI*	*TRI*	*OSI*	*HCI*	*HRI*	*WCI*	*WRI*	*TCI*
ACH-1	12	12	24						
ACH-2	4	12	16						
ACH-3	3	8	11						
ACH-4	5	9	14	65	12	12	14	13	65
ACH-5	8	5	13						
ACH-6	5	8	13						
(C2/PA)-1	6	10	16						
(C2/PA)-2	2	10	12	51	10	6	13	15	75
(C2/PA)-3	4	9	13						
(C2/PA)-4	1	9	10						
(C2/MP)-1	6	10	16						
(C2/MP)-2	11	9	20	52	10	11	12	13	47
(C2/MP)-3	7	9	16						
C3-1	5	10	15						
C3-2	7	8	15	64	10	10	13	13	53
C3-3	10	6	16						
C3-4	9	9	18						
i-C4-1	15	9	24						
i-C4-2	13	9	22	64	9	15	11	15	36
i-C4-3	9	9	18						
TBA-1	9	9	18						
TBA-2	12	9	21	57	9	12	11	13	39
TBA-3	9	9	18						

Table 32.17 *Results of I2SI application to six MMA production processes (Khan and Amyotte, 2003)*

Process	*Process step*	*Hazard index*		*Inherent safety potential index*		*I2SI*
		DI	*PHCI*	*ISI*	*PHCI*	
Acetone cyanohydrin (ACH)	Hydrogen cyanide production	174	71	49	57	0.3
	ACH production	174	43	75	38	0.5
	HMPA/HMPASE production	76	67	49	55	0.7
	MMA production	88	67	49	55	0.7
	Spent gas production	166	63	42	65	0.6
	Sulfur trioxide production	97	57	75	40	1.1
Ethylene based via propionaldehyde (C2/PA)	Propionaldehyde production	174	71	35	61	0.2
	Methacrolein production	174	71	74	61	0.5
	Methacrylic acid	174	71	107	47	0.9
	MMA production	174	71	156	43	1.5
Propylene based (C3)	Isobutyryl fluoride production	174	71	35	59	0.2
	Isobutyric acid production	174	71	102	55	0.7
	Methacrylic acid production	174	71	118	51	0.9
	MMA production	174	71	156	43	1.5
Ethylene based via methyl propionate (C2/MP)	Methyl propionate production	174	71	35	61	0.2
	Methylal production	174	71	99	53	0.8
	MMA production	174	71	116	53	0.9
Isobutylene base (i-C4)	Methacrolein production	174	71	101	51	0.8
	Methacrylic acid production	174	71	107	47	0.9
	MMA production	174	71	156	43	1.5
Tert butyl alcohol (TBA) based	Methacrolein production	174	71	88	55	0.7
	Methacrylic acid production	174	71	107	47	0.9
	MMA production	174	71	156	43	1.5

MMA: Methyl methacrylate; ACH: Acetone cyanohydrin; HMPA: 2-hydroxy-2-methyl propionamide; HMPASE: 2-hydroxy-2-methyl propionamide sulfate ester; DI: damage index; PHCI: process hazard and control index; ISI: inherent safety index; I2SI: integrated inherent safety index.

Table 32.18 *Summary of INSET Tools (Mansfield, 1997; INSIDE Project Team, 1997)*

Tool	*Description*
A	Detailed constraint and objective analysis
B	Process design generation
C	Preliminary chemistry route options record
D	Preliminary chemistry route rapid ISHE evaluation method
E	Preliminary chemistry route detailed ISHE evaluation method
F	Chemistry route block diagram record
G	Chemical hazards classification method
H	Record for foreseeable hazards
I	ISHE performance indices
I.1	Fire and explosion hazard index
I.2	Acute toxic hazard index
I.3	Inherent health hazard index
I.4	Acute environmental hazard index
I.5	Transport hazard index
I.6	Gaseous/atmospheric emissions environmental index
I.7	Aqueous emissions environmental index
I.8	Solid emissions environmental index
I.9	Energy consumption index
I.10	Reaction hazard index
I.11	Process complexity index
J	Multi-attribute ISHE comparative evaluation
K	Rapid ISHE screening method
L	Chemical reaction reactivity – stability evaluation
M	Process SHE analysis – process hazards analysis, ranking method
N	Equipment inventory functional analysis method
O	Equipment simplification guide
P	Hazards range assessment for gaseous release
Q	Siting and plant layout assessment
R	Designing for operation

users want to know how different methods of making X compare, not if a plant for making X is safer than a plant for making Y. . . [It] supports my gut feeling that displaying a series of measurements will be more useful than trying to find a single number that measures inherent safety."

To demonstrate, the authors used the MMA example (Lawrence and Edwards, 1993). They plotted the values of temperature, pressure and a combined value for flammability, explosiveness and toxicity (FET) for each step in Figure 32.1 and then compared them. Considering pressure, its maximum value is 7 bars for the ACH route while the next three routes have 49 to 100 bars. The remaining two routes have 7.5 bars. Further, three of the steps in the ACH route operate at atmospheric pressure, which would result in no flashing, if leaks were to occur. Summing up, the ACH route has a significant advantage over other routes as far the pressure is concerned. Considering temperature, two of the steps in the ACH route have a higher temperature than other routes. However, the authors felt that a higher pressure is more of a hazard than a higher temperature, in as far leakage, flashing of a liquid or rupture of a vessel and formation of energetic missiles and/or BLEVE with a possible domino effect, are concerned. This matches with the number of times (41) the experts in Lawrence's thesis (Lawrence, 1996) used pressure as the key feature in describing their assessment of hazards in the MMA routes compared to the number of times (9) they used temperature as an important parameter. Looking at the FET values, the ACH route, in general, has values similar to those in most other routes. Two of the experts downgraded the hazards of the ACH route because of the experience they had had on this process and had found it to be very safe.

Gupta and Edwards also pointed out that in the ACH route, the first two steps relate to the production of the basic material, ACH; the last two steps relate to the disposal of by-products, and only steps 3 and 4 relate to the actual production of MMA (Table 32.7). In the remaining five routes, only the actual production steps of MMA were considered, not the production of the basic materials or disposal of the by-products, if any. Hence, if only the actual MMA production steps (steps 3 and 4) are considered in the ACH route also, it comes out by far the most superior route compared to all the rest of the routes. No wonder, industry uses this worldwide.

According to the authors, the advantage of this simple graphical method of comparing process routes is that one can expand consideration to incorporate economic, regulatory, pollution control and worker health aspects, as well as factors such as the experience one has or the 'comfort level' one feels with each of the processes under consideration. Results from accident databases can be included as a parameter (e.g. frequency of accidents, loss per accident, etc.). As it expands, one can bring into consideration other important aspects, such as, process intensification, where if the process volume is reduced by, say a 1000-fold, one can work at higher pressures, closer to runaway temperatures and with more toxic reactants since the total release and hence consequences there of, in case of an accident, would be rather limited due to the very small amounts of hazardous chemicals involved.

The suggested graphical procedure also meets the users' desire of a simple index. Actually, inherent safety and simplicity go together since simplicity is one important parameter of inherently safer plants.

32.7.4 Future work

The indices developed thus far are expertise intensive. They need to be simplified so that a scientist or an engineer in the process industry can understand and use them easily without having to hunt for a lot of data and information. Most of the work has been done in academic institutions (except INSET Toolkit). Several practical examples from industry need to be evaluated using the proposed indices and modifications made to them to suit the needs of the industry. A holy alliance between the researchers, industry personnel and the regulators would prove beneficial to all.

32.7.5 Measuring inherently safer design – conclusions

Inherent safety is an exciting field that has caught the attention of researchers, plant designers, management and regulators worldwide. An inherent safety measurement method is needed to compare different processes for an end product. This method should work at the research stage itself and not require too much data. Researchers in several countries have produced indices towards this end. These indices are in an evolving stage. These need to be simplified. The intensive work put in by researchers needs to be consolidated and unified. The ultimate proof will be in the thorough testing of the indices by the industry and sharing of their experiences. Some industries have developed their

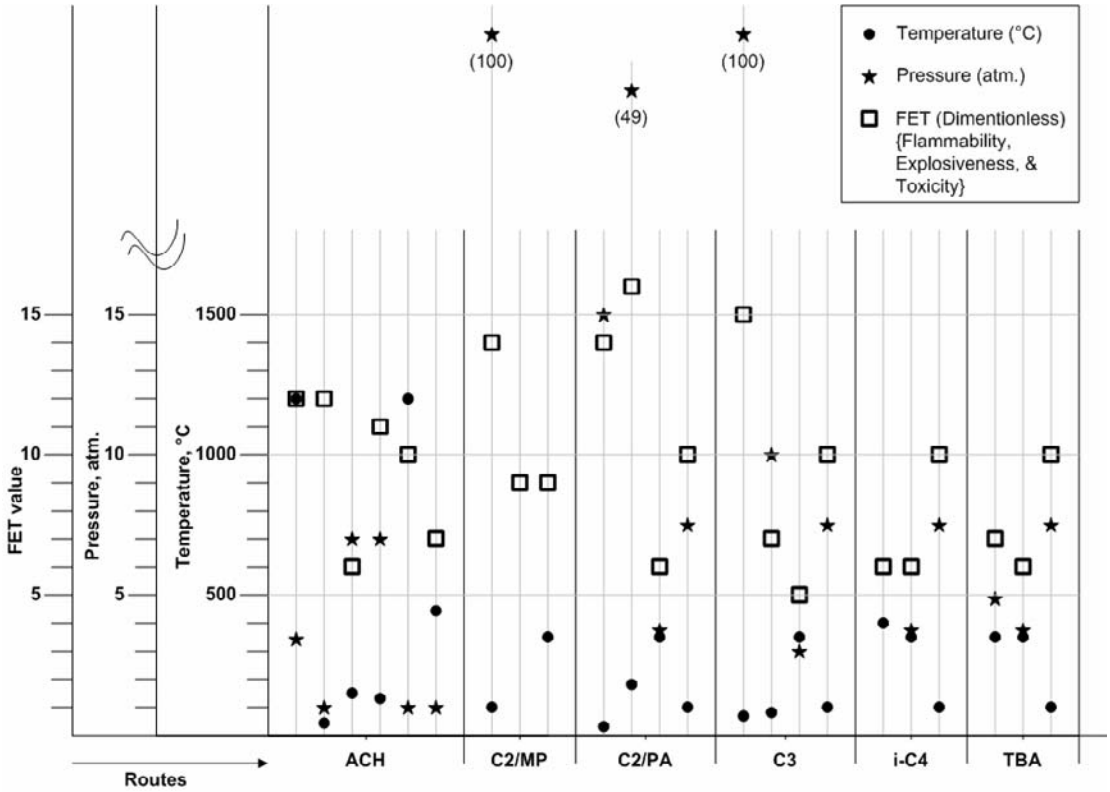

Figure 32.2 *MMA Routes (Gupta and Edwards, 2003)*

own proprietary methods to test for inherent safety but these are not available in open literature.

Once the company personnel starting from research chemists, process engineers and the rest start using inherently safer design, they would actually see the advantages and want to use it more and more. With process plants thus becoming significantly safer, the regulators are likely to gradually relax on process safety protocols. Once inherently safer design is successfully applied to process industries, it can be adapted by other accident-prone industries such as mining, construction, transportation and others.

32.8 Inherently Safer Design and the Process Life Cycle

Inherently safer design applies to a process at all phases in its life cycle, from early process conception, through laboratory development, pilot plant, preliminary and detailed design, construction, operation and shut-down and demolition. However, the designer will be applying inherently safer design principles in different ways at different stages of the life cycle. Early on, he will be considering the basic technology and synthesis routes, and in the later stages of the life cycle the designers and operators will be looking at more specific opportunities for applying inherently safer design concepts to specific pieces of equipment. The greatest opportunities for making major improvements in inherent safety occur early in process development, when the designer may have many choices of basic technology and chemistry available, and may be free to choose less hazardous alternatives. However, it is never too late to apply inherently safer design concepts, and major improvements to the inherent safety characteristics of plants which have been in operation for many years have been reported.

Here are some examples of the kinds decisions in which inherently safer design concepts should be applied by the designer or operator of a process at different life cycle stages.

(1) Conceptual process research and development: selection of basic process technology, raw materials, intermediate products, by-products and waste products, chemical synthesis routes.
(2) Process research and development: selection of specific unit operations, types of reactors and other processing equipment, selection of operating conditions, recycle, product purification, waste treatment.
(3) Preliminary plant design: location of manufacturing facility, location of units on a selected site, size and number of production lines, size of raw material, intermediate, and product storage facilities, selection of specific equipment types for the required unit operations, process control philosophy.
(4) Detailed plant design: size of all equipment, pressure rating and detailed design of all equipment and piping, inventory in processing equipment, location of specific equipment in the plant, length, route, and size of piping,

utility design, layout of equipment, detailed control system design, plant–operator interface design.
(5) Operation: identification of opportunities to modify plant to enhance inherent safety (reduce inventory, upgrade with more modern equipment, identify opportunities for inherently safer operation based on improved process understanding), consideration of inherently safer design when making modifications and changes, 'user friendly' operating instructions and procedures.

32.9 Implementing Inherently Safer Design

Inherently safer design applies at all levels of chemical plant conception, research, design and operation. It is more of a design philosophy or way of thinking than a specific set of tools, review meetings or other specific activities. The initial focus of the designer should be on the elimination and minimization of hazards, rather than the control of hazards. When a hazard is identified at any stage of development, the designer should ask the following questions:

(1) Can the hazard be eliminated from the process?
(2) If the hazard cannot be eliminated, can the magnitude of the hazard, or potential incidents arising from the hazard, be significantly reduced?
(3) Do the alternative designs identified from the answers to Questions 1 and 2 increase the magnitude of other existing hazards, or introduce any new hazards to the process?
(4) If the alternative designs increase other hazards, or introduce new hazards, develop an understanding of these hazards and understand the relative importance of the various hazards.
(5) Identify passive, active and procedural safeguards appropriate for management of all hazards.
(6) Use a logical decision process to select the optimum design, considering inherent safety characteristics, other safety characteristics, and all other relevant design parameters.

Too often, upon identifying a hazard, the designer skips past the first four questions and goes directly to question 5 – identifying 'add-on' safety features to manage and control a hazard whose existence and magnitude the designer accepts. While it will not always be possible or feasible to eliminate or significantly reduce hazards, it is certain that it will never happen if the designer never asks the question. This is the heart of the inherently safer design philosophy – first ask if hazards can be eliminated from the process, or if they can be dramatically reduced. Do not go directly to designing safety systems to manage and control hazards until it has been determined that it is not feasible to eliminate or reduce hazards.

Some companies incorporate inherently safer design into the process hazard analysis (PHA) activities which are already included in their process safety programs. In the course of a safety review, HAZOP, or other process safety review activity, the review team and leader are charged with considering inherently safer design options. Other companies have used separate inherent safety reviews. CCPS (1996) and others have published some checklists which can be used in separate inherent safety reviews, or provided to PHA teams for consideration as they conduct their reviews. Table 32.19 is an example of a general checklist (CCPS, 1996).

CCPS (1998) provides a series of checklists which are useful in identifying hazards associated with various

Table 32.19 *A Checklist for Inherently safer design (adapted from CCPS, 1996)*

1.1 Minimize (or itensify)

1. Do the following strategies reduce inventories of hazardous raw materials, intermediates, and/or finished products?
   (a) Improved production scheduling
   (b) Just-in-time deliveries
   (c) Direct coupling of process elements
   (d) In-site generation and consumption
2. Do the following actions minimize in-process inventory?
   (a) Eliminating or reducing the size of in-process storage vessels
   (b) Designing processing equipment handling hazardous materials for the smallest feasible inventory
   (c) Locating process equipment to minimize the length of hazardous material piping runs
   (d) Reducing piping diameters
3. Can other types of unit operations or equipment reduce material inventories? For example:
   (a) Wiped film stills in place of continuous still pots
   (b) Centrifugal extractors in place of extraction columns
   (c) Flash dryers in place of tray dryers
   (d) Continuous reactors in place of batch
   (e) Plug flow reactors in place of continuous-flow stirred tank reactors
   (f) Continuous in-line mixers in place of mixing vessels
4. Can thermodynamic or kinetic efficiencies of reactors be improved by design upgrades (e.g. improved mixing or heat transfer) to reduce hazardous material volume?
5. Can equipment sets be combined (e.g. replacing reactive distillation with a separate reactor and multi-column fractionation train; installing internal reboilers or heat exchangers) to reduce overall system volume?
6. Can pipeline inventories be reduced by feeding hazardous materials as a gas instead of a liquid (e.g. chlorine)?
7. Can process conditions be changed to avoid handling flammable liquids above their flash points?
8. Can process conditions be changed to reduce production of hazardous wastes or by-products?

1.2 Substitute

1. Is it possible to completely eliminate hazardous raw materials, process intermediates, or by-products by using an alternative process or chemistry?
2. Is it possible to completely eliminate in-process solvents by changing chemistry or processing conditions?
3. Is it possible to substitute less hazardous raw materials? For example:
   (a) Non-combustible rather than flammable
   (b) Less volatile
   (c) Less reactive
   (d) More stable
   (e) Less toxic
4. Is it possible to use utilities with lower hazards (e.g. low pressure steam instead of combustible heat transfer fluid)?
5. Is it possible to substitute less hazardous final product solvents?
6. For equipment containing materials that become unstable at elevated temperatures or freeze at low temperatures, is it possible to use heating and cooling media that limit the maximum and minimum temperature attainable?

1.3 Moderate (or Attenuate)

1. Is it possible to keep the supply pressure of raw materials lower than the working pressure of the vessels to which they are fed?
2. Is it possible to make reaction conditions (e.g. pressure or temperature) less severe by using a catalyst or by using a better catalyst?
3. Can the process be operated at less severe conditions using any other route? For example:
   (a) Improved thermodynamic or kinetic efficiencies of reactors by design upgrades (e.g. improved mixing or heat transfer) to reduce operating temperatures and/or pressures
   (b) Changes to the order in which raw materials are added
   (c) Changes in phase of the reaction (e.g. liquid/liquid, gas/liquid or gas/gas)
4. Is it possible to dilute hazardous raw materials to reduce the hazard potential? For example, by using the following:
   (a) Aqueous ammonia instead of anhydrous
   (b) Aqueous HCl instead of anhydrous
   (c) Sulfuric acid instead of oleum
   (d) Dilute nitric acid instead of concentrated fuming nitric acid
   (e) Wet benzoyl peroxide instead of dry

1.4 Limit effects

1. Is it possible to design and construct vessels and piping to be strong enough to withstand the largest overpressure that could be generated within the process, even if the 'worst credible event' occurs (eliminating the need for complex, high pressure interlock systems and/or extensive emergency relief systems)?
2. Is all equipment designed to totally contain the materials that might be present inside at ambient temperature or the maximum attainable process temperature (i.e. higher maximum allowable working temperature to accommodate loss of cooling, simplifying reliance on the proper functioning of external systems, such as refrigeration systems, to control temperature such that vapour pressure is less than equipment design pressure)?
3. Can passive leak-limiting technology (e.g. blowout resistant gaskets and excess flow valves) be utilized to limit potential for loss of containment?
4. Can process units be located to reduce or eliminate adverse effects from other adjacent hazardous installations?
5. Can process units be located to eliminate or minimize the following?
   (a) Off-site impacts
   (b) On-site impacts on employees and other plant facilities
6. For processes handling flammable materials, is it possible to design the facility layout to minimize the number and size of confined areas and to limit the potential for serious overpressures in the event of a loss of containment and subsequent ignition?
7. Can the plant be located to minimize the need for transportation of hazardous materials?
8. Can materials be transported in the following ways?
   (a) In a less hazardous form
   (b) Via a safer transport method
   (c) Via a safer route

1.5 Simplify/design for error tolerance

1. Is it possible to separate a single, procedurally complex, multipurpose vessel into several simpler processing steps and processing vessels, thereby reducing the potential for hazardous interactions when the complexity of the number of raw materials, utilities, and auxiliary equipment is reduced for specific vessels?

2. Can equipment be designed so that it is difficult to create a potentially hazardous situation due to an operating or maintenance error? For example:
   (a) Simplifying displays
   (b) Designing temperature-limited heat transfer equipment
   (c) Lowering corrosion potential by use of resistant materials of construction
   (d) Lowering operating pressure to limit release rates
   (e) Using higher processing temperatures (to eliminate cryogenic effects such as embrittlement failures)
   (f) Using passive vs active controls (e.g. stronger piping and vessels)
   (g) Using buried or shielded tanks
   (h) Using fail-safe controls if utilities are lost
   (i) Limiting the degree of instrumentation redundancy required
   (j) Using refrigerated storage vs pressurized storage
   (k) Spreading electrical feed over independent or emergency sources
   (l) Reducing wall area to minimize corrosion/fire exposure
   (m) Reducing the number of connections and paths
   (n) Minimizing the number of flanges in hazardous processes
   (o) Valving/piping/hose designed to prevent connection error
   (p) Using fewer bends in piping
   (q) Increasing wall strength
   (r) Using fewer seams and joints
   (s) Providing extra corrosion/erosion allowance
   (t) Reducing vibration
   (u) Using double-walled pipes, tanks and other containers
   (v) Minimizing the use of open-ended valves
   (w) Eliminating open-ended, quick-opening valves in hazardous service
   (x) Improving valve seating reliability
   (y) Eliminating unnecessary expansion joints, hoses and rupture disks
   (z) Eliminating unnecessary sight glasses/glass rotometers
3. Can procedures be designed so that it is difficult to create a potentially hazardous situation due to an operating or maintenance error? For example:
   (a) Simplifying procedures
   (b) Reducing excessive reliance on human action to control the process
4. Can equipment be eliminated or arranged to simplify material handling?
   (a) Using gravity instead of pumps to transfer liquids
   (b) Siting to minimize hazardous transport or transfer
   (c) Reducing congestion (i.e. easier to access and maintain)
   (d) Reducing knock-on effects from adjacent facilities
   (e) Removing hazardous components early in the process rather than spreading them throughout the process
   (f) Shortening flow paths
5. Can reactors be modified to eliminate auxiliary equipment (e.g. by creating a self-regulatory mechanism by using natural convection rather than forced convection for emergency cooling)?
6. Can distributed control system (DCS) modules be simplified or reconfigured such that failure of one module does not disable a large number of critical control loops?

specific types of process equipment, including vessels, reactors, mass transfer equipment, heat transfer equipment, dryers, fluid transfer equipment, solid–fluid separators, solids handling and processing equipment, fired equipment, and piping and piping components. The checklists also provide examples of inherent, passive, active and procedural design features which have been implemented to address the hazards listed. Table 32.20 is an example of the checklists from CCPS (1998), for dryers.

The INSIDE project (INSET Toolkit, 1997) provide a set of tools for identifying inherently safer design options at various stages of process development. These tools are listed in Table 32.18. The CCPS and the Center for Waste Reduction Technologies (CWRT) has developed a process called MERITT (Maximizing EHS Returns by Integrating Tools and Talents) for enhancing process development by better integrating environmental, health and safety evaluations into the basic process development (CCPS and CWRT, 2001; Mulholland, Bendixen and Keeports, 2001).

There have been some regulatory proposals to require that the chemical industry consider inherently safer design options. In the early 1990s, the United States Environmental Protection Agency considered requiring a 'Technical Options Analysis (TOA)' for plants covered by its Risk Management Program (RMP), as required by the US Clean Air Act Amendments of 1990. However, the TOA requirement was not included in the final RMP regulations. In 1999, Contra Costa County, California passed its Industrial Safety Ordinance (Sawyer, 2002), which requires that covered facilities consider inherently safer design options.

Table 32.20 *An example of the equipment failure scenario tables, with potential design approaches, for dryers (excerpted from CCPS, 1998)*

No.	*Operational deviations*	*Failure scenarios*	*Potential design solutions*		
			Inherently safer/passive	*Active*	*Procedural*
1.	Overpressure	Buildup and autoignition of deposits in dryers and ductwork resulting in fire/explosion	(a) Dryer design which minimizes buildup of deposits (smooth surfaces, elimination of potential points of solids accumulation) (b) Use dryer with short residence time (e.g. flash dryer) (c) Design dryer to contain overpressure where practical (d) Permanent bonding and grounding	(a) Automatic sprinkler system/CO_2 total flooding system (b) Use of inert atmosphere (c) Deflagration venting (d) Deflagration suppression system (e) Automatic isolation of associated equipment via quick closing valves	(a) Periodic inspection and cleaning (c) Emergency response procedures (c) Proceduce to process most stable materials first when campaigning multiple products to avoid ignition of unstable materials (d) Procedure for determining maximum tolerable material accumulation (e) Manual activation of fire fighting/inerting system
2.	Overpressure	Ignition of condensing flammable vapor in ductwork resulting in fire/explosion	(a) Dryer design to prevent condensation in ductwork (b) Provision for drainage of ducts (e.g. sloped, low point drains) (c) Eliminate ignition sources within the ductwork (d) Eliminate flammables (e) Design dryer to contain overpressure where practical (f) Permanent bonding and grounding	(a) Automatic sprinkler system/CO_2 total flooding system (b) Ventilation system to keep flammable concentration below lower flammable limit (c) Deflagration vents (d) Use of inert atmosphere (e) Automatic isolation of associated equipment via quick closing valves	(a) On-line flammable gas detection and manual activation of CO_2 total flooding system (b) Manual activation of fire fighting/inerting system (c) Manual bonding and grounding

Bills addressing security issues in the chemical industry, including the potential of inherently safer technology for reducing the attractiveness of a chemical plant as a potential terrorist target, have been introduced in the US Senate in 2001 and 2003, but none have been passed as of the end of 2003.

However, the best way to invent and build inherently safer processes is to make it a part of the thinking of all engineers and chemists as they go about their work. If they recognize the importance and benefits of hazard elimination, their creativity in inventing new ways to eliminate or reduce hazards as they go about their work activities will go further toward enhancing inherent safety than any review meetings possibly could.

32.10 Inherently Safer Design References

The INSIDE Project (INSET Toolkit, 1997), CCPS (1996), and Kletz (1998) provide the most comprehensive overall discussions of inherently safer design. The International Process Safety Group and the Institute of Chemical Engineers (IPSG and IChemE, 1995) developed an excellent training package on inherently safer design. CCPS and CWRT (2001) provide an overall methodology (MERITT) for considering inherently safer process options in conjunction with environmental characteristics of a process at an early stage of process development. Table 32.21 lists a number of literature references which discuss inherently safer technology, grouped into specific topic areas.

Table 32.21 *Selected literature references on inherently safer design*

General references on inherently safer design
Kletz (1978); Kletz (1979); Kletz (1983); Kletz (1984); Kletz (1985); Gerritsen and Van't Land (1988); Kletz (1989); Englund (1990); Kletz (1990); Puranik, Hathi and Sengupta (1990); Englund (1991a); Englund (1991b); Kletz (1991a); Kletz (1991b); McQuaid (1991); Preston and Turney (1991); Barton and Rogers (1993); Center for Chemical Process Safety (CCPS) (1993b); Englund (1993); Hendershot (1993); Englund (1994); Mansfield (1994); Mansfield and Cassidy (1994); IPSG/IChemE (1995); Kletz (1995); Lutz (1995b); Center for Chemical Process Safety (CCPS) (1996); Hawksley and Preston (1996); Kletz (1996); Park (1996); Perrin (1996); Snyder (1996); van Steen (1996); Hendershot (1997b); Kletz (1997); Preston (1997); Center for Chemical Process Safety (CCPS) (1998); Kletz (1998); Mansfield and Hawksley (1998); Hendershot (1999); Kletz (1999a); Kletz (1999b); Dalzell and Willing (2000); Pasman and Lemkowitz (2000); Edwards and Gupta (2002); Mary Kay O'Connor Process Safety Center (2002); Gupta, Hendershot and Mannan (2003); Khan and Amyotte (2003b); Mannan Rogers *et al.* (2003)

Examples of inherently safer design
Hendershot (1988); Kharbanda and Stallworthy (1988); Lammertink (1992); Whiting (1992); Oosterkamp (1993); Wilkinson and Geddes (1993); Lin *et al.* (1994); Pan *et al.* (1994); Gowland (1995); Heil (1995); Marshall Mundt *et al.* (1995); Scheffler (1995); Windhorst (1995); Wiss, Fleury and Fuchs (1995); Carrithers, Dowell and Hendershot (1996); Dutt (1996); Keller, Heinxle and Hungerbuhler (1996); Koch, Krause and Mehdizadeh (1996); McCarthy Ditz and Geren (1996); Osterwalder (1996); Riezel (1996); McCarthy and Miller (1997); Delseth (1998); Lacoursiere, Sarlis and Ravary (1998); Sato, Aoki and Noyori (1998); Zwetsloot and Askounes-Ashford (1999); Book and Challagulla (2000); Hendershot and Post (2000); Wolff (2001); Khan and Amyotte (2002); Proctor and Warr (2002); Amyotte, Khan and Dastidar (2003)

Methods for developing inherently safer designs
Lutz (1994); Rushton, Edwards and Lawrence (1994); French, Williams and Wixom (1995); Lutz (1995a); Rogers *et al.* (1995); Lodal (1996); Mansfield, Malmen and Suokas (1996); INSIDE Project Team (1997); Lutz (1997); Turney *et al.* (1997); Center for Chemical Process Safety (CCPS) (1998); Wood and Green (1998); Schupp *et al.* (2000); Center for Chemical Process Safety (CCPS) and Center for Waste Reduction Technologies (CWRT) (2001); Hendershot (2002); Palaniappan, Srinivasan and Halim (2002)

Inherent safety strategies – minimize
Doherty and Buzad (1992); Hannon (1992); Benson and Ponton (1993); Alamaro (1994); Paquet Jr. and Ray (1994a); Paquet Jr. and Ray (1994b); Jones (1996); Kelleher and Fair (1996); Lerou and Ng (1996); Ponton (1996); Brenchley and Wegeng (1998); Green (1998); TeGrotenhuis, Cameron and Butcher (1998); Wegeng and Drost (1998); Barrow, Cefai and Taylor (1999); Cybulski *et al.* (1999); DeWitt (1999); Jensen (1999); Lowe and Ehrfeld (1999); McCreedy (1999); Ramshaw (1999); Tonkovich *et al.* (1999); Wegeng, Drost and Brenchley (1999); Harold and Ogunnaike (2000); Hendershot (2000); Stankiewicz and Moulijn (2000); Warlin and Svensson (2000); Sharangpani and Tay (2001); Sojka (2002); Stitt (2002); Stankiewicz and Moulijn (2003); Tsouris and Porcelli (2003)

Inherent safety strategies – moderate
Speechly, Thornton and Woods (1979); Hugo and Steinbach (1986); Orrell and Cryan (1987); Gygax (1988); Steensma and Westererp (1988); Grewer *et al.* (1989); Forsberg (1990); Steensma and Westererp (1990); Chevalier (1991); Lazari, Burley and Al-Hassani (1991); Newby and Forth (1991); Sherringron (1991); Wilday (1991); Bashir *et al.* (1992); Calvert (1992a); Calvert (1992b); Nasr (1992); Prugh (1992); Raghaven (1992); Shinnar Doyle *et al.* (1992); Cleary (1993); Harris (1993); Komarek (1993); Melhem (1993); Misono and Okuhara (1993); Singh (1993); Somerville (1993); Sundell and Nasman (1993); Nasr (1994); Paul (1994); Weirick, Farquhar and Chismar (1994); Costa, Recasens and Velo (1995); Eierman (1995); Velo, Bosch and Recasens (1996); Verwijs van den Berg and Westererp (1996); Flamberg, Torti and Myers (1998); Koolen (1998); de Santoli and Lo Giudice (2000); Rovison, Garcia and Collins (2001); Moosemiller and Whipple (2002)

Inherent safety strategies – substitute
Agreda, Partin and Heise (1990); Amendola *et al.* (2000); Anastas (1994); Anastas and Breen (1997); Ashby and Paton (1993); Bailey (1992); Bell Manzer *et al.* (1995); Black (1996); Dartt and Davis (1994); Davis Kincaid *et al.* (1994); DeSimone *et al.* (1994); Dittmer (1997); Donohue and Geiger (1994); Flam (1994); Goldschmidt and Filskov (1990); Govardhan and Margolin (1995); Hall (1994); Hendershot (1998); Jessop, Ikariya and Noyori (1994); Joback (1994); Lim (1994); Lin and Ayusman (1994); Lubineau (1996); Lucas *et al.* (2003); Mandich and Krulik (1992); Manzer (1993a); Manzer (1993b); Manzer (1994); Mills and Chaudhari (1997); Mittelman and Lin (1995); Mittelman *et al.* (1994); Mizerek (1996); Moore Samdani *et al.* (1994); Negron (1994); Paul (1988); Rogers and Hallam (1991); Savage *et al.* (1995); Shanley (1999); Sorensen and Petersen (1992); Tavener and Clark (1997); Tietze (1995); Timberlake and Govind (1994); Tobin (1994); Varma (1999); Wallington *et al.* (1994); Walsh and Mills (1993); Welter (1991); Wender, Handy and Wright (1997)

Measuring inherent safety
Tyler (1985); Edwards and Lawrence (1993); ICI (1993); Lawrence, Edwards and Rushton (1993); Dow Chemical Company (1994); Lawrence and Edwards (1994); Edwards and Lawrence (1995); Mansfield *et al.* (1995); Edwards, Lawrence and Rushton (1996); Heikkila, Hurme and Järveläinen (1996); Johnson, Unwin and McSweeney (1996); Lawrence (1996); Shonnard *et al.* (1996); Cave and Edwards (1997a); Cave and Edwards (1997b); Hendershot (1997a); Mansfield (1997); Gupta and Babu (1999); Heikkila (1999); Koller, Fischer and Hungerbuhler (2000); Palaniappan, Srinivasan and Tan (2000a); Palaniappan, Srinivasan and Tan (2000b); Palaniappan, Srinivasan and Tan (2000c); Gentile, Rogers and Mannan (2001); Palaniappan (2001); Etowa *et al.* (2002); Gentile, Rogers and Mannan (2002); Gupta and Edwards (2002); Palaniappan, Srinivasan and Tan (2002a); Palaniappan, Srinivasan and Tan (2002b); Gentile, Rogers and Mannan (2003); Gentile, Rogers and Mannan (2003a); Gupta and Edwards (2003); Huang, Tan and Preston (2003); Khan and Amyotte (2003a); Khan, Sadiq and Amyotte (2003); Shah, Fischer and Hungerbuhler (2003); Srinivasan and Meibao (2003)

Inherent safety conflicts and decision-making
Center for Chemical Process Safety (CCPS) (1995); Hendershot (1995a); Hendershot (1995b); Perry (1995); Berger and Lantzy (1996); Mansfield (1996); Dowell (1999); Fawell (2001); Mulholland, Bendixen and Keeports (2001); Luyben and Hendershot (2003)

Inherent safety and environmental issues
Brennan (1993); Englehardt (1993); Berger (1994); Mak, Muhle and Achini (1997); Sheldon (1997); Mulholland, Sylvester and Dyer (2000); Bendixen (2002)

Inherent safety and education
Kletz (1993); Gupta (1999); Gupta (2000)

Regulations and public policy
Marshall (1990); Ashford (1993); Tickner (1994); Stone, Gray and Tickner (1995); Phillips and Gray (1996); Ashford (1997a); Ashford (1997b); Ashford (1997c); Contra Costa County Health Services (1997); Orum (1998); Baumann and Orum (1999); Ashford and Zwetsloot (2000); Ferris (2002); Moore (2002); Sawyer (2002); Baybutt (2003); Lindsey and Hendershot (2003); Moore and Rogers (2003)

33 Reactive Chemicals

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33.1 Background

33.1.1 Motivation

Serious incidents arising from uncontrolled reactivity have taken place since the inception of the chemical industry. The human toll of such incidents has been staggering. In recent decades, greater recognition and resources have been directed toward preventing and mitigating such occurrences. A number of incidents have been so severe as to prompt regulatory initiatives to force better management of reactivity. It would not be surprising to see additional regulation enacted to address the issues. In any event, it is prudent for any company, organization or other group to scrutinize the chemicals being handled and implement measures to limit the risk of a major reactive hazards event.

A sampling of incidents that have substantially heightened concerns regarding reactive hazards in the general public, in governmental agencies and in industry includes:

(1) The 1976 ICMESA incident in Seveso, Italy in which an uncontrolled chemical reaction generated pressure resulting in relief venting of a highly toxic dioxane into the neighbouring villages and countryside.
(2) The 1984 Union Carbide incident in Bhopal, India in which methyl isocyanate was contacted with water, generating highly toxic cyanide gas and leading to thousands of fatalities.
(3) The 1994 NappTechnology incident in Lodi, NewJersey in which an uncontrolled reaction involving gold ore processing led to the deaths of five fire fighters.
(4) The 1999 Concept Sciences incident in Allentown, Pennsylvania in which an explosion arising from a process concentrating hydroxylamine resulted in five fatalities. Another event involving purified hydroxylamine took place in a Nissin Chemical plant in Gunma Prefecture, Japan in 2000 and led to four fatalities.
(5) The 2001 TotalFinaElf incident in Toulouse, France in which ammonium nitrate being processed for nitrogen fertilizers exploded, leading to 30 fatalities.

These events, as well as numerous others, have influenced the perception and approach to reactive hazards.

In 2002, the US Chemical Safety and Hazard Investigation Board (CSHIB or CSB) issued a report examining 1,500 US reactivity-related incidents. Of these, 167 serious incidents between 1980 and 2001 contained sufficient information to warrant further analysis, observations and conclusions. Nearly half of the incidents involved fatalities and nearly half affected the public (i.e. beyond the fenceline of facilities). The report also indicates that these types of incidents continue to occur at a troubling frequency.

The principal hazard is instability of an individual substance or an uncontrolled or 'runaway' reaction. There now exist a bewildering multiplicity of tests for the detection and characterization of substances and reactions, and the apparatus for many of the tests is expensive. Moreover, it is not sufficient to determine the characteristics of the reaction on the laboratory scale. It is necessary also to characterize the reaction and the scale-up features to allow a safe design to be developed. The problem is particularly severe where it is a question of confirming that an existing process is safe, because in this case it is not possible to incorporate the safety margins that might be used in a new process.

Runaway reactions

In a runaway reaction, there is a reaction exotherm in the vessel or tank, the heat evolved is not removed sufficiently rapidly, the temperature of the reaction mass rises and the reaction accelerates. The exotherm may be from the main, intended process reaction or from an undesired side reaction. A high pressure may then be generated by the product gases or by the vapour pressure of liquids in the equipment. If this pressure is not relieved, the vessel or tank may suffer overpressure and fail.

General reactivity incidents

Uncontrolled reactions can occur in any setting or any piece of equipment where reactivity is not managed appropriately. Though it is commonplace to envision such reactions taking place in reactors, the CSHIB investigation found that only 25% of the 167 incidents in the past two decades occurred in reactors. Another 22% occurred in storage equipment, an equivalent percentage in other process equipment (e.g. holding tanks, mixers, dryers), while 13% took place in waste, separation and transfer equipment. In fact, only 70% of the incidents involved chemical manufacturing facilities while most of the remainder occurred in bulk storage/handling facilities.

Reactor incidents

Reactors (particularly, batch) are operated by a wide variety of firms, many of which are quite small. On the other hand, the number of chemicals made by a given firm may be quite large. A work may produce over 1000 different chemicals using a range of reaction types.

Analyses of batch reactor incidents in the United Kingdom reported to the HSE have been given by Townsend and Pantony (1979), Barton and Nolan (1984), Nolan and Barton (1987) and by Marrs *et al.* (1989).

Marrs *et al.* based their study on two sets of data. The first was a set of UK data from the HSE's own records for the period 1970–81 (the UK national data set) and the second, a collection of worldwide incidents made for the HSE (the world data set). The two sets contained 68 and 199 incidents, respectively.

The overall taxonomy used by Marrs *et al.* is given in Table 33.1. The analysis of reactor overpressure incidents by incident mode is shown in Table 33.2, in which the taxonomy is developed in finer detail and which utilizes the worldwide set. The table includes more detailed analyses for (a) sulfonation, (b) nitration and (c) polymerization reactions, for which incidents are relatively common.

Information on reactor relief was obtainable only from the national set. Table 33.3–Table 33.5 give information on overpressure relief arrangements, overpressure incident and relief system behaviour.

These workers also carried out an expert judgment field survey the results of which are shown in Table 33.6. The comparison of the ranking of the relative importance, or frequency, of the incident modes (1 = most important, etc.) is shown in Section A. There is reasonable agreement overall, with two exceptions. Thus, in both rankings, incorrect charging and inadequate cooling are ranked high, undesired catalysis low and excessive heating, incorrect agitation and exotherm from impurity, moderate. The exceptions are unknown exotherm/decomposition, which is ranked much lower by the experts than in the case histories and inadequate batch control. The experts were from companies with expected good practice and the relatively

Table 33.1 *Taxonomy for reactor overpressure analysis (Marrs et al., 1989) (Courtesy of the Institution of Chemical Engineers)*

A System description

Chemical reaction
Reactants, intermediates, products
Heat of reaction
Known exotherms

Reactor pressure
Reactor temperature

Charging
Cooling
Heating
Agitation
Control system
Trip/interlock system
Batch cycle/control
Operating vents
Relief system

B Reaction type

Bl Alcoholysis
B2 Animation
B3 Condensation
B4 Cyclization
B5 Diazotization
B6 Esterification
B7 Halogenation
B8 Hydrogenation
B9 Hydrolysis
BI0 Isomerization
B11 Methylation
B12 Nitration
B13 Oxidation
B14 Polymerization
B15 Sulfonation

C Pressurizing fluid

Cl Vapourized liquid
C2 Decomposition gas
C3 Water vapour
C4 Flammable gas
C5 Other gas/vapour

D Pressurizing event

Dl Regular reaction exotherm
D2 Impurity reaction exotherm
D3 Heat of mixing, dilution
D4 Regular reaction decomposition
D5 Impurity decomposition
D6 Water ingress and Vapourization
D7 Air ingress and combustion
D8 High pressure gas ingress

E Process deviation

El Regular reaction inadequate information
E2 Regular reactant unknown decomposition
E3 Impurity reaction exotherm
E4 Impurity decomposition
E5 Incorrect charging
E6 Inadequate cooling
E7 Excessive heating
E8 Incorrect agitation
E9 Inadequate batch control
E10 Undesired catalysis
E11 High pressure gas connection

F Initiating fault

Fl Inadequate reaction screening
F2 Incorrect design
F3 Mechanical failure
F4 Utilities failure
F5 Control system failure
F6 Operator error

G Overpressure effect

Gl Open vessel
G2 Excursion only
G3 Bursting disc operated
G4 Vessel ruptured
G5 Bursting disc operated but inadequate, vessel ruptured

H Bursting disc failure cause

HI Undersized for design conditions
H2 Demand greater than design conditions
H3 Installation error
H4 Modification error
H5 Maintenance error
H6 Disc failure
H7 Vent piping failure

I Release effects

I1 Flammable release
  1.1 No ignition
  1.2 Fire
  1.3 Explosion
I2 Toxic release

low ranking of unknown exotherms probably reflects their view that they had taken steps to control this hazard. Sections B–E of Table 33.6 give the corresponding rankings of particular incident submodes.

33.1.2 Regulations and compliance

The rapid development of industrial facilities since 1950 was followed by an increase in incidents involving reactive and toxic substances. Major losses due to these incidents prompted legislation to prevent such incidents.

Seveso I

A release of TCDD (tetrachlorodibenzoparadioxin) in the Seveso, Italy, incident of 1976 contaminated 10 square miles and about 2000 people were treated for dioxin poisoning. In 1982, the European Community adopted the Seveso Directive to identify and control the location of hazardous installations and to assess the hazards of substances above threshold quantities from a list of toxic, flammable or explosive materials.

Seveso II

The Seveso Directive required a review of its scope by the European Community, and in December 1996 the Seveso II Directive was adopted with the objective to prevent major

Table 33.2 *Analysis of reactor overpressure: incident modes (Mans et al. 1989) (Courtesy of the Institution of Chemical Engineers)*

A Detailed Breakdown

	All reactions	*Nitration*	*Sulfonation*	*Polymerization*
Case 1: C1 Overpressure by Vaporized liquid				
D1 Regular reaction exotherm				
E1 Regular reaction inadequate information (7)				
E1.1 Unknown exotherm	4	1		
E1.2 Inadequate definition of operation	3			2
E5 Incorrect charging (35)				
E5.1 Excess of reactant	10			1
E5.2 Deficiency of reactant	9		1	3
E5.3 Too fast addition of reactant				
E5.3.1 Automatic control failure	1			
E5.3.2 Manual control failure: Measurement/alarm Operator error	7		2	
E5.4 Too slow addition of reactant				
E5.5 Addition of wrong reactant	1		1	
E5.6 Modification of reactant	4			
E5.7 Incorrect order of reactant addition	2			
E5.8 Too slow reaction of solid (coarse particles)	1			
E5.9 Too fast reaction of solid (fine particles)				
E6 Inadequate cooling (26)				
E6.1 Underdesign (esp. scale-up)	5			3
E6.2 Coolant circulation fault				
E6.2.1 Coolant source failure				
E6.2.2 Power failure				
E6.2.3 Pump failure	1			
E6.2.4 Coolant turned off	3[a]		1	
E6.2.5 Coolant leak/loss				
E6.2.6 Blockage	1			
E6.2.7 Freezing				
E6.2.8 Automatic control failure	3[b]		1	1
E6.2.9 Manual control failure: Measurement/alarm Operator error	3			2
E6.3 Inadequate agitation (for heat transfer)	2			
E6.4 Internal fouling				
E6.5 External fouling				
E6.6 Evaporative coolant fault	1			
E6.7 Condenser fault				
E6.7.1 Condenser vapour inlet blockage	1			1
E6.7.2 Condenser flooding	1			1
E6.7.3 Condenser frozen	1			
E6.8 Moderating solvent fault	1			
E6.9 Steam jacket cooling inadequate	1			
E6.10 Other causes	2			
E7 Excessive heating (19)				
E7.1 Initial overheating	3		1	2
E7.2 Heating/cooling changeover fault	3		1	1
E7.3 Unintended heating or heating instead of cooling	2[c]			
E7.4 Pump energy	1		1	
E7.5 Agitator energy	2		1	
E7.6 Steam leak	2	1	1	
E7.7 Live steam	1			
E7.8 Automatic control failure	2			1
E7.9 Manual control failure:				
Measurement/alarm	1			
Operator error	1			
E7.10 Overheating in flange joints	1			
E8 Inadequate agitation (for making) (20)	20	4	4	2

Table 33.2 *(continued)*

E9 Incorrect batch control (18)				
E9.1 Initial temperature low	2		1	
E9.2 Initial temperature high				
E9.3 Too fast reactant addition relative to temperature	4		2	
E9.4 Incorrect cycle	3			
E9.5 Inadequate chemical moderation	1			1
E9.6 Stewing	4		1	
E9.7 Other causes	4			
E10 Undesired catalysis (5)				
E10.1 Excess, or too rapid addition, of catalyst	2			1
E10.2 More active catalyst				
E10.3 Catalyst maldistribution				
E10.4 Catalyst impurity	2			
E10.5 Catalyst left over from previous batches	1			
D2 Impurity reaction exotherm (21)				
D2.1 Water	11	3	1	
D2.2 Air	5			
D2.3 Materials left in reactor	1			
D2.4 Head transfer fluid	1			
D2.5 Other impurities	8			
D3 Heat of making dilution				
Case 2: C2 Overpressure by decomposition gas				
D4 Regular reactants decomposition (16)				
E2 Regular reactant unknown decomposition	11	2	2	
Ditto (side reaction)				
D5 Impurity reactant decomposition				
E4 Impurity decomposition				
Case 3: C3 Overpressure by water vapour				
D6 Water ingress and vaproization	1			
Case 4: C4 Overpressure by flammable gas (ignition of explosive mixture)				
D7 Air ingress and combustion (7)	7		1	
Case 5: C5 overpressure by other gas/vapour				
D8 High pressure gas ingress	1			
Miscellaneous cases				
X1 Overpressure following unknown exotherm, where it is unclear if exotherm is a decomposition	7		3	
X2 Overpressure following operator attempts to recover from fault conditions	4		2	1
Cases where cause is unknown				
Z1 Cause unknown	12			5

B Summary

	Mode (%)			
	All reactions[d]	*Nitration*	*Sulphonation*	*Polymerization*[d]
Regular reaction inadequate information	3.5 (3.7)	9.1	0	7.1 (8.6)
Incorrect charging	17.2 (18.3)	0	13.8	14.3 (17.4)
Inadequate cooling	13.1 (14.0)	0	6.9	28.6 (34.8)
Excessive heating	9.6 (10.2)	9.1	17.2	14.3 (17.4)
Inadequate agitation	10.1 (10.8)	36.4	13.8	7.1 (8.6)
Incorrect batch control	9.1 (9.7)	0	13.8	3.6 (4.4)
Undesired catalysis	2.5 (2.7)	0	0	3.6 (4.4)
Impurity reaction exotherm	10.6 (11.3)	27.3	3.4	0
Regular reactant unknown decomposition	8.1 (8.6)	18.2	10.3	0
Water ingress and Vapourization	0.5 (0.5)	0	3.4	0
Air ingress and combustion	3.5 (3.7)	0	3.4	0

Table 33.2 *(continued)*

High pressure gas ingress	0.5 (0.5)	0	0	0
Exotherm of unknown type	3.5 (3.7)	0	10.3	0
Recovery from fault conditions	2.0 (2.2)	0	6.9	3.6 (4.4)
Cause unknown	6.1	0	0	17.9
Total	100	100	100	100
No. of applicable incidents = 199				

[a] In one case cause is assigned to lack of cooling, although there had also been a change in the quality of the reactants.
[b] In one case cause is assigned to a failure of a temperature controller, although a new more active catalyst was also in use.
[c] In one case cause is assigned to gross overheating by steam, although it was also subsequently found that the reaction mixture exhibited instability.
[d] Values in brackets are based on redistribution of 'Causes unknown' among known causes in proportion to relative frequency of latter.

Table 33.3 *Analysis of reactor overpressure: relief arrangements (Marrs et al. 1989) (Courtesy of the Institution of Chemical Engineers)*

Relief arrangement[a]	*No.*
BD(s)	11
RV	8
RV + BD	2
RV, vent part closed	1
BD, recommend larger BD	2
RV, recommend BD	1
BD, vessel open	1
No BD	4
Recommend BD	4
No relief	1
Manual vent valve	1
Small vent(s)	1
Vent, recommend BD	1
Small holes	1
Vessel open	15
Vessel open, recommend BD	1
Unknown	13
Total	68

[a] BD, bursting disc; RV, relief valve.

Table 33.4 *Analysis of reactor overpressure: overpressures (Marrs et al. 1989) (Courtesy of the Institution of Chemical Engineers)*

Overpressure incident	*No.*	*Proportion* (%)
Vessel open, hazardous release	18[a]	27.3
Glasswork shattered, hazardous release	16[b]	24.2
Vessel ruptured, hazardous release	19	28.8
Vessel ruptured	1	1.5
Explosion	5	7.6
Hazardous release	5	7.6
Catchpot ruptured	1	1.5
Catchpot fire	1	1.5
Total	66	100.0

[a] One case where overpressure was vented through two holes; one where manhole was opened; and one where operator disconnected hose.
[b] One case where reflux divider ruptured – glassware not specifically mentioned.

Table 33.5 *Analysis of reactor overpressure: relief system behaviour (Marrs et al. 1989) (Courtesy of the Institution of Chemical Engineers)*

Relief system behaviour	*No.*	*Proportion* (%)
Relief operated:		
Glassware ruptured	3	6.3
Vessel ruptured	1	2.1
Explosion	1	2.1
Catchpot ruptured	1	2.1
Catchpot fire	1	2.1
Hazardous release	3	6.3
Relief fitted, but failed:		
Glassware ruptured	3[a,b]	6.3
Vessel ruptured	8	16.7
Explosion	2	4.2
Glassware ruptured	10[c]	20.8
Vessel ruptured	11[d]	22.9
Explosion	2	4.2
Hazardous release	2	4.2
Total	48	100

[a] One case where relief valve (RV) fitted, but vent part closed; and one where bursting disc (BD) fitted, but larger BD recommended.
[b] One case where BD failed to rupture.
[c] Five cases where relief arrangements unknown; three cases where BD recommended; and one where no relief was fitted.
[d] Six cases where relief arrangements unknown; three cases where there was no BD; one case where BD recommended; and one where there was a manual vent valve.

incidents involving dangerous substances and limit the consequences of such incidents to people and the environment. This replacement directive included new requirements relating to safety management system and emergency planning. Whereas the original Seveso Directive focused on technical factors affecting safety, Seveso II focuses on management systems, which were determined to be responsible for the majority of incidents.

OSHA

The Occupational Safety and Health Administration (OSHA) was created by the 1970 OSH Act of the US Congress to establish consistent regulation with regard to industrial personnel and workplace conditions. In 1992, OSHA promulgated the Process Safety Management (PSM) of Highly Hazardous Chemicals – a program with 14 elements including a process hazard analysis (PHA). See Appendix 31 for a discussion of OSHA and PSM.

Table 33.6 *Analysis of reactor overpressure: comparison of rankings from case histories and from expert judgement field study (Marrs et al., 1989) (Courtesy of the Institution of Chemical Engineers)*

	Case histories		*Field study*
	%	*Rank*	*Rank*
A Incident modes			
Unknown exotherm/decomposition	15.1	2	6
Incorrect charging	17.2	1	1
Inadequate cooling	13.1	3	3
Excessive heating	9.6	6	4
Incorrect agitation	10.1	5	5
Inadequate batch control	9.1	7	2
Undesired catalyst	2.5	8	8
Exotherm from impurity	10.6	4	7
B Incorrect charging			
Excess of reactant	29.4	1	1
Deficiency of reactant	26.5	2	3
Too fast addition of reactant	23.5	3	2
Modification of reactant	11.8	4	4
Incorrect order of reactant addition	5.9	5	5
C Inadequate cooling			
Coolant source/power failure	0	5	5
Coolant pump set failure	3.8	4	4
Coolant turned off	11.5	= 1	2
Automatic control failure	11.5	= 1	1
Condenser fault	11.5	= 1	3
D Excessive heating			
Initial overheating	15.8	= 1	2
Heating/cooling changeover fault	15.8	= 1	3
Undesired heating	10.5	= 3	5
Automatic control failure	10.5	= 3	4
Manual control failure	10.5	= 3	1
E Incorrect batch control			
Initial temperature too low	11.1	4	3
Initial temperature too high	0	5	5
Too fast addition of reactant relative to temperature	22.2	= 1	1
Incorrect cycle	16.6	3	4
Excessive holding	22.2	= 1	2

EPA

The Environmental Protection Agency (EPA) was created by the Clean Air Act of 1970 of the US Congress to reduce exposures of hazardous substances. In 1996, the EPA promulgated the Risk Management Program (RMP) for Chemical Accident Release Prevention – a program with 11 elements, including a hazard evaluation (similar to the OSHA PHA) and a risk assessment for worst-case and alternative case releases of toxic substances. See Appendix 32 for a discussion of EPA and RMP.

TCPA

According to the US CSHIB report issued in 2002, more than 50% of the 167 reactivity-related incidents analysed were not covered by existing OSHA or EPA regulations.

In response to concern about reactivity incidents, the New Jersey Department of Environmental Protection announced in August 2003 that reactive chemicals were added to the list of extraordinarily hazardous substances (EHS) in the New Jersey Toxic Catastrophe Prevention Act (TCPA) rules. This was the first regulatory rule in the United States to require assessment of reactive chemical hazards compared to assessment of process hazards required by the OSHA PSM in 1992 and by the EPA RMP rule in 1996. When announced, the list of EHS with threshold quantities included 30 chemicals and 43 chemical groups.

33.1.3 Overall strategy

Overall strategy

A strategy for safe reactor design, given in the IChemE *Guide,* largely follows N. Gibson, Rogers and Wright (1987), who describe the strategy developed at ICI, as follows:

(1) definition of the process conditions and plant design;
(2) characterization of the chemical reaction and its hazards;
(3) selection and specification of safety measures;
(4) implementation and maintenance of safety measures.

The stages in and strategies for the assessment and control of hazards of chemical reactors are shown in Figures 33.1 and 33.2, respectively. The characterization of the chemical reaction and its hazards involves:

(1) hazard evaluation of the reaction;
(2) characterization of reaction for scale-up;

and safety aspects of the design of the reactor include:

(3) inherently safer design;
(4) control and trip systems;
(5) emergency safety measures;
(6) overpressure relief.

The strategy will be influenced by the types of reaction operated in the company, by evidence from previous incidents and by the options available for safety measures.

33.2 Technical

33.2.1 Strategies for identifying and characterizing reactive hazards

Chemical reactivity overview

Definition

The US CSHIB has proposed the following definition of a reactive hazard: 'A *sudden* event involving an *uncontrolled* chemical reaction with significant increases in temperature, pressure, *or* gas evolution that has the potential to, or has caused *serious harm* to people, property or the environment'.

Reactive hazards have the potential to cause harm to people or loss of life along with extensive damage to the surroundings due to the uncontrolled release of energy. A common pathway involves overpressurization of equipment, either through buildup of pressure or through weakening of the equipment structural integrity, leading to possible generation of a blast wave or generation of a flammable vapour cloud that can explode upon finding

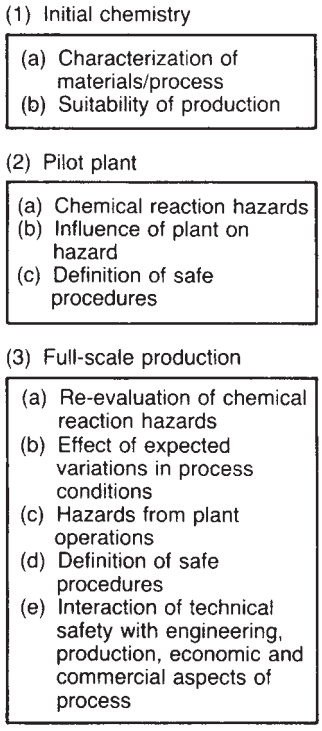


Figure 33.1 *Stages in control of hazards of chemical reactions (N. Gibson, Rogers and Wright, 1987) (Courtesy of the Institution of Chemical Engineers)*

an ignition source. For a *detailed* assessment of reactive hazards risk, an understanding of reaction pathway, stoichiometry, energetics, gas generation and rates is needed.

Strategy

Overall evaluation strategy The strategy for reaction hazard evaluation described in the IChemE *Guide* involves the following:

(1) desk screening;
(2) explosibility tests;
(3) preliminary screening tests;
(4) characterization of normal reaction;
(5) characterization of runaway reaction.

These are now discussed under the categories of

(1) desk screening;
(2) preliminary screening tests;
(3) detailed tests.

Calculational methods are also included as well as a synopsis of various test schemes.

Principal factors A review of the factors that should be taken into account in the reaction assessment has been given in the two ABPI *Guidelines*. The components covered should include: the reactants, the reaction intermediates (whether isolated or not) and the reaction products; the by-products; the solvent; additives; the still residues; and the wastes and effluents.

The review should consider the effect of contaminants on the stability of components and on the reaction rate. Contaminants may include: impurities in the reactants;

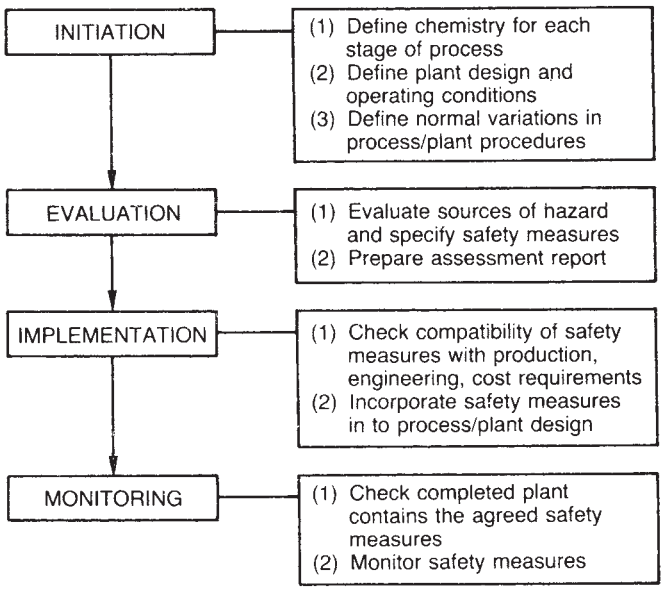


Figure 33.2 *Strategy for control of hazards of chemical reactions (N. Gibson, Rogers and Wright, 1987) (Courtesy of the Institution of Chemical Engineers)*

materials of construction; corrosion products; water, steam, refrigerant and other heat transfer fluids; and materials from elsewhere. Other factors mentioned include:

(1) incorrect use of catalysts;
(2) addition of extra quantities of reagents;
(3) sequence of addition or omission of reagents;
(4) addition of wrong reagent;
(5) drift of pH and sensitivity to buffering in normal or abnormal operation;
(6) effect of process errors on reaction conditions.

Categorizing reactivity types

Stability vs reactivity with other species

Many compounds will undergo degradation or decomposition when subjected to elevated temperature, mechanical impact or other disturbances. Some compounds can polymerize or re-arrange internally. Most compounds will also react when placed in contact with certain other species.

According to the CSHIB report released in 2002, 10% of the 167 reactivity-related incidents analysed involved impact- or thermally-sensitive materials. Another 35% were associated with runaway reactions. About 36% of the incidents involved chemical incompatibility.

Tests for chemical reaction Reactivity information applicable to individual substances should be obtained. Somewhat similar information is required for the evaluation of the hazards of conducting a chemical reaction in a reactor. It is still necessary to determine the behaviour of the individual components – reactant, intermediates and products – but in addition it is necessary to examine the reaction as a whole, including not only the main, desired reaction, but also secondary reactions. In the methods described below, it should be recognized when the methods are being applied to address the stability or reactivity in combination with other species.

Intended vs unintended

It is useful to distinguish between 'intended' and 'unintended' reactions or alternatively 'normal' and 'abnormal' reactions. Intended reactions are clearly those reactions targeted in a process. Unintended reactions are the side reactions that are typically avoided. Usually, there are no intended reactions in blending, distribution, transportation and storage operations. An intended reaction occurring outside of its associated equipment can in that context be considered as unintended. More-extensive stoichiometric and thermokinetic information is generally available for targeted reactions. Moreover, the strategy for managing the risk of reactive hazards can be profoundly affected by whether a reaction of interest is intended or unintended.

Additional factors generally considered when designing equipment for intended reactions include: heat transfer, mixing limitations, phase separation, inlet and outlet flows (properties and rates), and process and relief venting capacity.

Reaction phase

Another characteristic important for understanding reaction behaviour and for determining the appropriate approach(es) for addressing the reactivity is the phase or phases in which the reaction occurs. Reactions commonly take place or initiate in the liquid phase, but some, such as combustion, predominate in the gas-phase. The decomposition of polymers upon heating or of explosives once triggered are examples of solid-phase reactions. Many reactions, such as those that are facilitated by heterogeneous catalysts, are surface reactions. The reactants may reside primarily in the liquid phase or can even be gas-phase (such as in methanation), but the species must travel to and adsorb on the surface to undergo reaction. Finally, the mere adsorption of certain species on solid surface can potentially evolve enough heat to cause significant temperature excursions and further reactivity.

Vapour vs gassy vs hybrid

The ability of a reaction to cause overpressurization of equipment depends heavily on the type of gas or vapour generated. Generally, a 'vapour' refers to a non-condensed species that is in thermodynamic equilibrium with the corresponding species in a condensed phase (usually a liquid, but possibly a solid). A 'gas' describes a non-condensable species that is not in thermodynamic equilibrium. If a vapour–liquid system is heated, the vapour pressure of the species will rise and the pressure of the system is dictated by the temperature and composition. A latent heat is associated with generation of the vapour. Removal of vapour from the system (e.g. by venting) will cause heat (mostly latent) to be discharged. In a 'gassy' system, the pressure is determined by the amount of non-condensable gas generated (a function of reaction stoichiometry, rate and time) and removal of such gas only takes away sensible heat. The term 'hybrid', is applied to systems which exhibit both vapour and gassy features (e.g. when both vapour and gassy species are present, such as for hydrogen peroxide in water decomposing to yield non-condensable oxygen).

Characterizing reactions

It is usual to classify unit processes on the basis of the reaction involved and, as described in Section 11.14 of Chapter 11, these unit processes have certain generic characteristics. A classification of unit processes in terms of their exothermicity has been given by Hoffmann (1985). He classes halogenation, oxidation, organometallic reactions and some polymerizations as highly exothermic; nitration as exothermic; amination, sulfonation, condensation and some hydrogenations as moderately exothermic; and alkylation, hydrolysis and some hydrogenation as mildly exothermic. Thermodynamic schemes such as CHETAH (CHEmical Thermodynamics And energy Hazard evaluation) may be used to evaluate the thermodynamic characteristics of the reaction.

The substances involved in the reaction, whether as reactants, intermediates or products should be screened for explosibility. Basic methods, which have been described in Chapter 8, are examination of reactive chemical groups, computation of the oxygen balance and experimental explosibility testing.

To characterize a chemical reaction adequately, however, it is desirable not only to obtain a qualitative understanding of the behaviour of the reaction, but also to obtain quantitative data on various parameters needed for the specification of the process. It is expected that companies and agencies carrying out intended chemistry will have already acquired sufficient information pertaining to that chemistry to enable appropriate safeguarding. However, in the event that such information is absent, the following

approaches can be applied as well to intended chemistry as to unintended chemistry.

Desk screening
Initial desk screening will provide information on the physical and chemical properties and the reactivity of the chemical. Where specific data are lacking, features such as group structure, thermodynamic data, oxygen balance and reactivity of analogous substances provide pointers. Discussions of this aspect are given by Snyder (1965) and by the ABPI (1981, 1989).

The starting point should always be a thorough literature search to determine the data already available on the properties of the chemical. For intended reactions (and some unintended reactions), an organization's internal, proprietary literature may contain a wealth of information pertaining to the stoichiometry, thermodynamics and kinetics. This information might be specific to processing conditions, which limits applicability in safeguarding, but might also feature unique effects such as behaviour in the presence of other process species or reactivity with particular catalysts.

If gaps remain in the knowledge base for reactivity, a search of the open literature should be pursued. For established commercial reactions, it is often helpful to consult the original papers. In certain journals, papers on chemical reactions regularly include information on potential hazards. References frequently reviewed also include: *Dangerous Properties of Industrial Materials* (Sax, 1957–, 1975–, 2000), *Encyclopaedia of Chemical Technology* (Kirk and Othmer, 1963–, 1978–, 1991–) and *Handbook of Reactive Chemical Hazards* (Bretherick, 1999); NFPA 49 and 491M; FM data sheets 7–19 and 7–23; and CMA (MCA) case histories. Frequently, published texts and journal articles can provide insight regarding the chemistry and thermokinetics. Material Safety Data Sheets (MSDSs) should also be consulted for qualitative and limited quantitative reactivity information.

It is instructive to observe that 90% of the US reactivity incidents analysed by the CSHIB involved reactive hazards documented in literature available to the chemical processing industry.

Thermal stability Identification of reactivity of components should be based on a coherent strategy. This will normally involve 'desk' screening, preliminary tests and substantial tests. If an exotherm is identified, tests may be done to characterize it. Other aspects may also need to be investigated such as the extent of gas evolution and the behaviour of the substance under conditions of processing such as drying.

Desk screening and explosibility tests

NFPA classification A general method of categorizing reactivity and instability of individual species is provided in NFPA: 1994 49 *Hazardous Chemicals Data,* which gives materials a Chemical Reactivity Rating as shown in Table 33.7. The code lists the rating for a large number of chemicals.

To demonstrate the importance of examining all likely reactivity scenarios and not depending solely on a screening approach to identify reactive hazards, note that only 10% of the 167 reactivity incidents examined by the CSHIB involved chemicals rated '3' or '4' in the NFPA system; 60% were not rated at all or received a '0' rating.

Table 33.7 *Degrees of reactivity (instability) hazard as defined in NFPA: 1994 49 (Reproduced with permission from NFPA 49 Hazardous Chemicals Data, Copyright, 1994, National Fire Protection Association, Batterymarch Park, Quincy, MA 02269, USA)*

Degree	*Description*
4	Materials that in themselves are readily capable of detonation or explosive decomposition or explosive reaction at normal temperatures and pressures. This degree usually includes materials that are sensitive to localized thermal or mechanical shock at normal temperatures and pressures
3	Materials that in themselves are capable of detonation or explosive decomposition or explosive reaction, but that require a strong initiating source or that must be heated under confinement before initiation. This degree usually includes: materials that are sensitive to thermal or mechanical shock at elevated temperatures and pressures; materials that react explosively with water without requiring heat or confinement
2	Materials that readily undergo violent chemical change at elevated temperatures and pressures. This degree usually includes: materials that exhibit an exotherm at temperatures less than or equal to 150°C when tested by differential scanning calorimetry; materials that may react violently with water or form potentially explosive mixtures with water
1	Materials that in themselves are normally stable, but that can become unstable at elevated temperatures and pressure. This degree usually includes: materials that change or decompose on exposure to air, light or moisture; materials that exhibit an exotherm at temperatures greater than 150°C but less than or equal to 300°C, when tested by differential scanning calorimetry
0	Materials that in themselves are normally stable, even under fire conditions. This degree usually includes: materials that do not react with water; materials that exhibit an exotherm at temperatures greater than 300°C but <500°C, when tested by differential scanning calorimetry; materials that do not exhibit an exotherm at temperatures <500°C when tested by differential scanning calorimetry

General Reactivity of Chemical Structures and Constituents

Certain groups (shown in Figure 33.3) (Kohlbrand, 1985) are known by experience to be unstable or explosive.

Chemical sensitivity to decomposition (reactive conditions)

Instability of materials It is important to know whether a chemical can be safely handled both in process and in storage and transport. The problem has two main aspects. One is the hazard of instability of a single component such

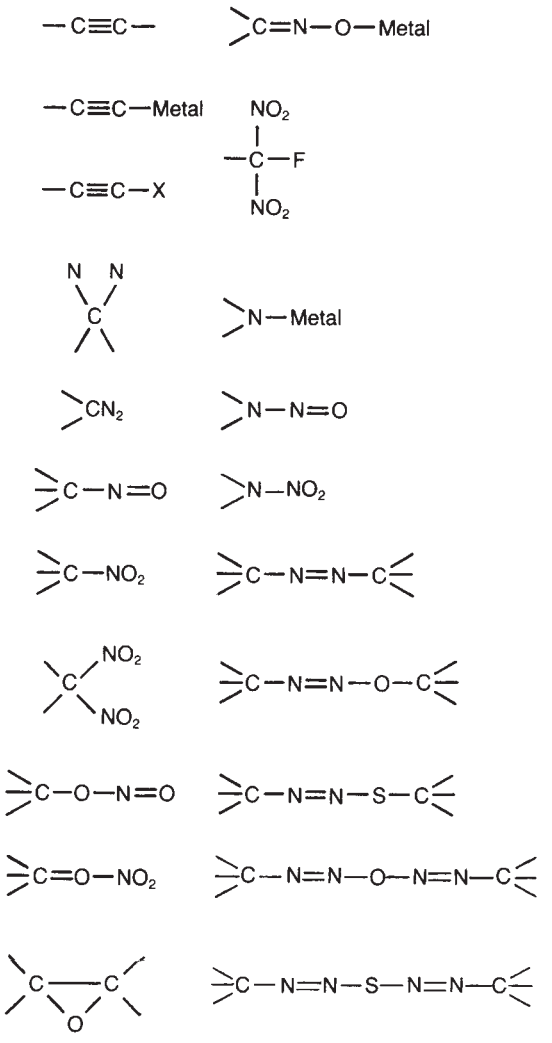


Figure 33.3

as a reactant, intermediate or product when undergoing physical processing on the plant and when stored and transported. The other aspect is the hazard of instability of the reaction mass in a chemical reactor. These two aspects of instability are dealt with here and in Chapter 11, respectively. This section deals with thermal instability and with explosibility.

Accounts of the evaluation of instability of materials include those given in *Guidance Notes on Chemical Reaction Hazard Analysis* by the Association of the British Pharmaceutical Industry (ABPI) (1981) and its successor *Guidelines for Chemical Reaction Hazard Evaluation* ABPI (1989) and by Coates and Riddell (1981a), N. Gibson, Harper and Rogers (1985) and Cronin, Nolan and Barton (1987a).

Oxygen balance A substance may release energy by combustion in air or by decomposition; the main hazard is decomposition. Rapid energy release occurs if the constitution of a substance is such that its carbon and hydrogen are able to react with its own oxygen without needing to obtain oxygen from the surrounding air. If there is just enough oxygen to give a stoichiometric reaction of all the carbon to carbon dioxide and hydrogen to water, there is said to be a zero oxygen balance. The more reactive substances, such as explosives, typically contain enough oxygen to give such decomposition.

The oxygen balance (OB) is an important indicator of stability for some classes of explosive compounds containing nitrogen. For an organic compound of formula $C_xH_yO_z$ it has been defined by Lothrop and Handrick (1949) as:

$$\mathrm{OB} = -1600\ (2x + y/2 - z)/M \qquad [33.2.1]$$

where M is the molecular weight. Thus, an unstable, or explosive material having perfect balance to yield carbon dioxide and water has a zero OB value – one lacking sufficient oxygen has a negative OB value, and one containing excess oxygen has a positive OB value.

In principle, therefore, the ideal OB for a substance suitable as an explosive would appear to be zero. Most explosives actually have a negative OB, but Lothrop and Handrick did find that the power of explosives increases as the OB increases and approaches a value of zero. Values of the oxygen balance for some materials of recognized instability are nitrobenzene (−163), dinitro-toluene (−114) and glycerol trinitrate (+3.5).

Chemical incompatibility with other materials The incompatibility of chemicals brought together can pose a significant reactive hazard. Examples include acids combined with bases, pyrophoric materials plus air, and water-sensitive chemicals plus water. It is worth noting that an 'incompatibility' is deemed to be more severe in potential consequence than the lack of 'compatibility' between substances.

Evaluating potential chemistry between components in a process can be a daunting task given that the number of combinations for a moderate number of species can quickly grow into the thousands. Such an evaluation can require considerable resources for reviewing available information or testing, but tools have been made available to assist in this endeavour. A publication from the US CoastGuard (*) and one from the US Environmental Protection Agency (EPA 1980) indicate the presence of potential incompatibilities based on the types of chemical functional groups in the compounds. The US National Oceanic and Atmospheric Administration (NOAA) has posted on its website a program called the Chemical Reactivity Worksheet, which incorporates the EPA methodology and some additional incompatibility guidelines to facilitate chemical incompatibility assessment.

When exploring possible chemical interactions between materials, it is also worthwhile to consider compounds arising from inadvertent forward flow or backflow from other parts of a process or other units, additives, catalysts, utility stream components, contaminants, materials of construction, cleaning agents and species common in the environment (e.g. air, water, pollutants).

* U.S. Coast Guard Academy, 'The Evaluation of the Test Procedure for Hazardous Binary Combinations of Materials in Marine Transportation', US Department of Commerce, National Technical Information Service, Aug. 1974, AD-A007 915, Report No. CG-D-85-75.

Related previous incidents Knowledge and analysis of previous incidents is extremely valuable to help identify reactivity hazards including those caused by incompatibilities of a process with materials that the process could easily contact, as in the following cases:

Concepts Science and Nissin Chemical: The 1999 Concept Sciences incident with five fatalities in Allentown, Pennsylvania and the 2000 Nissin Chemical incident with four fatalities in Japan involving explosive decomposition of hydroxylamine. In these incidents, the incompatibility of hydroxylamine/water solutions and iron and oxides of iron is a suspected factor.

Napp Technology: The 1994 Napp Technology incident with five fatalities in Lodi, New Jersey in which an uncontrolled reaction resulted from the incompatibility of water with the process mixture that included the spontaneously combustible sodium hydrosulfite.

Bhopal: The 1984 Union Carbide incident in Bhopal, India in which the incompatibility of methyl isocyanate with water led to the release of toxic cyanide gas and thousands of fatalities.

Screening and detailed computational methods using classical and QM models and correlations

Reactive Hazards Index An attempt has been made by Stull (1970) to find some theoretical basis for reactivity. With unstable materials, there is relatively little difference between the heat of decomposition ΔH_d and the heat of combustion ΔH_0 under stoichiometric conditions, or between the adiabatic decomposition and combustion temperatures. Thus, Stull gives an empirical correlation between the difference between these two heats, $\Delta H_0 - \Delta H_d$, or between the temperatures and the NFPA Chemical Reactivity Rating.

In a refinement of this work, Stull (1973) has introduced kinetic as well as equilibrium considerations and has derived an empirical Reaction Hazard Index (RHI):

$$RHI = \frac{10T_d}{T_d + 30E_a} \qquad [33.2.2]$$

where E_a is the activation energy (kcal/mol), and T_d is the adiabatic decomposition temperature (K). The RHI correlates broadly with the Chemical Reactivity Index.

Determination of energy hazard potentials There are a number of thermodynamic schemes and corresponding computer programs, which have been developed to calculate the equilibrium products and heats of combustion and/or decomposition reactions. These include those of Cruise (1964), of the National Aeronautics and Space Administration (NASA) (Gordon and McBride, 1971, 1976) and of the American Society for Testing of Materials (ASTM) (E.J. Davis and Ake, 1973; Treweek, Claydon and Seaton, 1973). These programs can then be used to determine the energy hazard potential of materials.

The ASTM program, named CHETAH, calculates four quantities, which may be taken as criteria of energy hazard potential (Treweek, Claydon and Seaton, 1973):

(1) heat of decomposition ΔH_d;
(2) heat of combustion, ΔH_0 – heat of decomposition, ΔH_d;
(3) oxygen balance;
(4) y criterion.

The y criterion is given by:

$$y = \frac{10(\Delta H_d)^2 MW}{N} \qquad [33.2.3]$$

MW = molecular weight
N = number of atoms in the molecule
The energy hazard potentials are related to criteria (1)–(4) as shown in Table 33.8 (see Figure 33.4). These criteria correlate reasonably well with data on shock sensitivity. An account of the updating of the CHETAH program has been given by Frurip, Freedman and Hertel, (1989). CHETAH is now available as an interactive PC program. It includes an interpreter subroutine that uses pattern

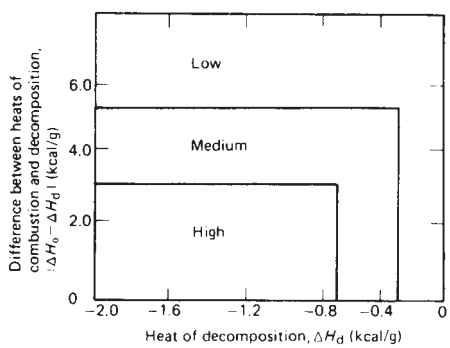


Figure 33.4 *Energy hazard potential as a function of the heats of combustion and decomposition (after Traweek, Claydon and Seaton, 1973) (Courtesy of the American Institute of Chemical Engineers)*

Table 33.8 *Energy hazard potential criteria in CHETAH (after Treweek, Claydon and Seaton, 1973)*

Criterion	*Energy hazard potential*		*High*
	Low	*Medium*	
1	$\Delta H_d > -0.3$	$-0.7 < \Delta H_d < -0.3$	$\Delta H_d < -0.7$
2	See Figure 33.4		
3	OB > 240 OB < −160	120 < OB < 240 −160 < OB < −80	−80 < OB < 120
4	y < 30	30 < y < 110	y > 110

recognition techniques to combine the four hazard criteria into an overall hazard rating and a data bank.

Molecular group contribution methods The principle of a molecular group contribution method is that molecular properties are the result of added contributions of individual atoms. Benson (1976) demonstrated that a wide variety of thermodynamic properties of a molecule could be estimated from the sum of contributions of the bonds in the molecule with corrections for the influences of side chains.

The CHETAH program (version 7.2) by ASTM (1998) applies a molecular group contribution method for thermodynamic property estimations. A wide range of gaseous thermodynamic properties can thereby be computed, such as heat capacity, C_p, entropy, S, enthalpy of formation, ΔH_f, Gibbs free energy of formation, ΔG_f, enthalpy of reaction, ΔH_r, entropy of reaction, ΔS_r and Gibbs free energy of reaction, ΔG_r. Molecular group contribution methods are limited, however, to available thermodynamic data for molecular groups (Irikura and Frurip, 1996).

Quantum chemistry methods Quantum chemistry methods are based on molecular quantum theory in which the motion and distribution of electrons are represented by electron probability distributions called molecular orbitals (Bruneton *et al.*, 1997). Using these methods, the structure, energy and properties of a molecule or an assembly of molecules can be calculated to varying degrees of accuracy depending on the molecules and the methods employed. Numerical techniques and software programs have been developed to perform the quantum chemistry calculations.

The fundamental quantum chemistry (or *ab initio*) methods are coupled with statistical mechanics to estimate system thermodynamic properties of large numbers of molecules or atoms. These properties include the enthalpy and entropy of formation of the reactants and products, enthalpy and entropy of the reaction, Gibbs free energy of the ideal gas reaction and Gibbs free energy of mixing of the reaction. There exists no single quantum method that yields satisfactory results for all chemical systems, and the usefulness of the various methods depends on the system size and type, the property that is calculated and calculation costs. Therefore, the *ab initio* methods require more experience, compared to group contribution or other classical methods, for selection of appropriate models and assessment of the results.

With the quantum methods a molecular electronic orbital, ϕ_i, is generally represented as a linear combination of a finite number of basis functions, $\chi\sigma$, which are similar to hydrogen atom wavefunctions, with each function multiplied by a weight factor, $c_{i\sigma}$.

$$\phi_i = \sum_{\sigma} c_{i\sigma}\chi_{\sigma}$$

Each orbital will accommodate up to two electrons with opposite spins. Basis function sets used with each level of theory can be minimal with one basis function per orbital of an atom within the molecule or improved in accuracy by the inclusion of multiple functions of the appropriate type per orbital. The total wavefunction of all orbitals for a molecule is represented by a linear combination of Slater determinants (SD) constructed from the molecular orbital functions. The Hartree–Fock model uses the simplest total wave function with a single SD, which approximates the average static interactions among the electrons. Inclusion of instantaneous electron–electron interactions, or electron correlation, requires two or more SDs with models of increasing complexity, computational expense and accuracy. With a given model, accuracy can be enhanced with the use of increasingly large sets of selected basis functions.

Among the most useful quantum methods for engineering calculations are Density Functional Theory (DFT), which is a cost-effective approach that explicitly includes electron correlation for a wide range of molecule sizes, such as B3LYP, the Moller–Plesset perturbative methods at various orders, such as the second order MP2 or third order MP3, highly accurate (energy errors to $\sim$ 1 kcal/mole) composite methods that include electron correlation such as the Gaussian-n (G1, G2, G3) methods and the complete basis set (CBS) series, and the inexpensive, but generally much less accurate, semi-empirical methods, such as AM1 and PM3 (Young, 2001; Morokuma, 2002). Quantum calculations using these various methods are performed on commercial software, such as the Gaussian 98 and Gaussian 03 (Frisch *et al.* 1998) software modules available for supercomputers, servers and personal computers.

For some thermochemical properties, such as heats of formation calculations using with isodesmic reactions, in which the numbers and configurations of electrons are balanced as well as possible on both sides of the reaction, some or much of the electron correlation error cancels. This is not the case for chemical activation energies on which the reaction rates depend exponentially, so even small errors in calculated activation energies will often yield unacceptably large errors, especially for the lower level models, in the calculated reaction rate constants. However, higher level quantum models, such as CCSD(T), coupled cluster with single and double excitation and perturbative triple excitation, with a large set of basis functions can yield energies, such as heats of reactions, that rival or even exceed experimental accuracy (Truhlar, 2001). A discussion of computational accuracy and cost for many approaches and models is provided by Cramer (2002, p. 220).

Once the thermodynamic properties are predicted or estimated for each reactant, intermediate and product in the suggested reaction pathways, enthalpy and Gibbs free energy calculations are performed to identify plausible stoichiometries to follow initial pathway scenarios. Plausible stoichiometries are reactions that are thermodynamically feasible, for which the corresponding Gibbs free energy change, $\Delta G_r < 0$.

The Gibbs free energy of reaction at constant temperature is:

$$\Delta G_r = \Delta H_r - T\Delta S_r$$

The enthalpy of reaction is:

$$\Delta H_r = \Delta H_r^{idg} - \sum_{i}^{N} \nu_i \Delta H_{vap,i} + \Delta H_r^{mix} + \Delta H_r^{press}$$

where,

- ΔH_r^{idg}: enthalpy of reaction calculated in the ideal gas phase;
- $\Delta H_{vap,i}$: enthalpy of vaporization or sublimation for N condensed species;
- ΔH_r^{mix}: mixing and solvent enthalpic effects.
- ΔH_r^{press}: pressure enthalpic effects;

The entropy of reaction is:

$$\Delta S_r = \Delta S_r^{idg} - \sum_i^N v_i \frac{\Delta H_{vap,i}}{T} + \Delta S_r^{mix} + \Delta S_r^{press}$$

where,

ΔS_r^{idg}: entropy of reaction calculated in the ideal gas phase;
ΔS_r: mixing and solvent entropic effects;
ΔS_r^{press}: pressure entropic effects.

Therefore, the Gibbs free energy change on reaction can be defined by the following equation:

$$\Delta G_r = \Delta G_r^{idg} + \Delta G_r^{mix} + \Delta G_r^{press}$$

Assumptions are often used to simplify these relationships. The pressure effects on the enthalpy and entropy of reaction are usually insignificant compared to the other contributions and can then be neglected. The solvent and mixture interaction enthalpy and entropy contributions are usually small when compared to the enthalpy and entropy of the reaction. It is generally only when the solvent has particularly strong affinities with the solutes, such as polar interactions or formation of hydrogen bonds, that these terms are significant (Bruneton *et al.*, 1998).

Screening for significant reactions to assess potential hazards, thermodynamically non-feasible ($\Delta G_r > 0$) and reaction pathways with low ΔH_r or $\Delta H_r > 0$ and low ΔP are generally excluded and the remaining ones are considered for further evaluations.

High exothermic ΔH_r is considered an indication of a potential hazard, but such an indication is not sufficient to assess the potential of a reactivity hazard. A more thorough evaluation should be based also on ΔP and on the kinetics of the reaction pathways (i.e. the reaction rates). For confirmation and to provide more information about the system, the activation energies and rate constants are measured experimentally and also computed using quantum models within the context of transition state theory.

Transition state theory methods Chemical reaction rates calculated from classical molecular dynamics are often unsatisfactory, but exact quantum calculations are practical only for systems with a small number of accessible quantum states. Transition State Theory (TST), however, in which a transition state, which is formed from the energetically activated reactants and intermediate along the reaction coordinate between reactants and products, is based not on the details of molecular motions and collisions but on their statistical properties using the principles of statistical mechanics. A bimolecular reaction with reactants *A* and *B,* transition state $[AB]^\dagger$ in equilibrium with the reactants, and products *C* can be stated

$$A + B \leftrightarrow [AB]^\dagger \rightarrow C$$

At present, this theory combines classical and quantum principles employing simplifying assumptions including a thermal, quasi-equilibrium of the transition state with the reactants (Garrett and Truhlar, 1984). Another assumption of the original approach by Eyring (1935) and Evans and Polanyi (1935) is that motion of the reacting species along the reaction coordinate can be separated from other dynamics and treated as a classical translation.

Even though TST is not a complete quantum model, quantum effects are approximated by the use of quantum partition functions for vibrational motions and a quantum tunneling and reflection correction or transmission coefficient, κ, for motion along the reaction coordinate (Cramer, 2002, p. 486). For a bimolecular reaction in the gas phase with species *A* and *B,* the TST absolute rate constant is

$$k^{TST} = \kappa(T)\frac{k_B T}{h}\frac{Q^\dagger}{Q_A Q_B} e^{-E_0/k_B T} k^{TST} = \kappa(T)\frac{k_B T}{h} K_c^\dagger$$

where κ is the transmission coefficient, k_B is the Boltzmann constant, h is the Planck constant, T is the absolute temperature, E_0 is the energy of lowest level (zero point energy) of the transition state relative to the energy of the lowest level of the reactants, Q_A, Q_B are the equilibrium partition functions per unit volume for the reactants *A* and *B*, $Q^\dagger$ is the transition state partition function minus the partition function for motion along the reaction coordinate, and $K_c^\dagger$ is the equilibrium constant for the reactants and transition state species in molar concentration units.

Q_A, Q_B are calculated from statistical mechanics using spectroscopic data to obtain moments of inertia, vibrational frequencies and electronic states. $Q^\dagger$ is calculated using quantum mechanics or semi-empirical models, to obtain moments of inertia and vibrational frequencies for the calculated transition state geometry. For the bimolecular reaction, the reaction rate is

$$k^{TST}[A][B]$$

with *A* and *B* in molar concentration units.

For a macroscopic system with the number of particles the order of Avogadro's number, the distribution of molecular energies at a particular temperature are assumed to consistent with the Boltzmann distribution in which all molecular states at the same energy are equally probable. The canonical TST rate constant *k(T)* is a Boltzmann average over a microcanonical TST rate constant *k(E)* at a given energy, (Garrett and Truhlar, 1979).

$$K(T) = \int_0^\infty k(E)P(E)\,dE$$

where *P(E)* is the Boltzmann distribution of energies. This approach is employed in the highly successful Rice-Ramsperger-Kassel-Marcus (RRKM) theory to represent the behaviour of unimolecular reactions (Forst, 1973).

Because the TST equation is based on the highest potential energy along the reaction coordinate and not the free energy of the transition state structure, it does not account for some trajectories that recross the transition state and reduce the actual rate constant. Variational Transition State Theory (VTST) corrects this deficiency by adjusting the transition state along the reaction coordinate, *s*, to maximize the transition state free energy, minimize the recrossings and, therefore, minimize the TST rate constant (Truhlar and Garrett, 1980; Hase, 1983; Allison and Truhlar, 1989)

$$k^{VTST}(T,s) = \min_s \kappa(T)\frac{k_B T}{h}\frac{Q^\dagger(T,s)}{Q_A Q_B} e^{-E_0(s)/k_B T}$$

The statistical approach and approximations make possible practical computations, and TST and VTST have proved to be highly successful in representing with sufficient accuracy a wide range of chemical behaviour. As a result, this theory has become more commonly used for engineering reaction rate predictions.

Representing the TST expression in thermodynamic terms and using the equilibrium assumption of reactants with the transition state, $\Delta G^{o\dagger} = -RT \ln K_c^{\dagger}$, and the TST rate constant can be expressed equivalently as

$$k^{\mathrm{TST}} = \kappa \frac{k_B T}{h} \mathrm{e}^{-\Delta G^{o\dagger}/RT}$$

where $\Delta G^{o\dagger}$ is the standard free energy of activation, and the superscript o refers to the standard states of the transition state and reactants. Expressing $\Delta G^{o\dagger}$ in terms of standard enthalpy and entropy changes, $\Delta G^{o\dagger} = \Delta H^{o\dagger} - T\Delta S^{o\dagger}$, the TST rate constant becomes

$$k^{\mathrm{TST}} = \kappa \frac{k_B T}{h} \mathrm{e}^{\Delta S^{o\dagger}/R} \mathrm{e}^{-\Delta H^{o\dagger}/RT}$$

which can be related to the traditional Arrhenius rate constant, k^A.

$$k^A = A\mathrm{e}^{-E_a/RT}$$

where E_a, the experimental activation energy (or Arrhenius activation energy) is the average difference between the average energy of the reacting molecules and the average energy of all the reactant molecules (Fowler and Guggenheim, 1939).

For a process at constant pressure, the standard enthalpy and thermodynamic energy are related by $\Delta H^{o\dagger} = \Delta E^{o\dagger} - PM\Delta V^{o\dagger}$, where $\Delta V^{o\dagger}$ is the standard volume of activation. For a unimolecular reaction $\Delta V^{o\dagger}$ is zero and for reactions in solution, $\Delta V^{o\dagger}$ is close to zero, so, $E_{\mathrm{a}} = \Delta H^{o\dagger} + RT$, and the TST rate constant is

$$k^{\mathrm{TST}} = \kappa \frac{k_B T}{h} \mathrm{e}^{(1+\Delta S^{o\dagger}/R)} \mathrm{e}^{-E_a/RT}$$

Therefore, the Arrhenius pre-exponential factor can be expressed as

$$A = \kappa \frac{k_B T}{h} \mathrm{e}^{(1+\Delta S^{o\dagger}/R)}$$

For gas phase reactions other than unimolecular and assuming the ideal gas model, $P\Delta V^{o\dagger} = \Delta n^{\dagger} RT$, the Arrhenius activation energy is, $E_a = \Delta H^{o\dagger} + (1 - \Delta n^{\dagger})RT$ and the Arrhenius pre-exponential factor is

$$A = \kappa \exp(1 - \Delta n^{\dagger}) \frac{k_B T}{h} \mathrm{e}^{(1+\Delta S^{O\dagger}/R)}$$

Such expressions are used to relate the molecular VTST or TST model to the macroscopic Arrhenius model to represent experimental data and the observed reaction rate in terms of molecular behaviour.

For reactions in liquid solution for which static interactions of the reacting species and the solvent are included, the relationship between the solution and gas phase VTST or TST rate constants is

$$k_{\mathrm{s}}^{\mathrm{VTST}} = k_{\mathrm{g}}^{\mathrm{VTST}} \mathrm{e}^{-\Delta G_{\mathrm{solv}}^{o\dagger}/RT}$$

where the free energy of solvation, $\Delta G_{\mathrm{solv}}^{o\dagger} = \Delta G_{\mathrm{s}}^{o\dagger} - \Delta G_{\mathrm{g}}^{o\dagger}$, is the difference between the free energies of activation in the solution and in the gas phase (Ladanyi and Hynes, 1986). Models for calculating $\Delta G_{\mathrm{solv}}^{o\dagger}$ include implicit models in which the solvent is treated as a continuous medium and explicit models in which the solvent molecules are treated individually. The explicit methods, which generally require extensive computation, employ classical molecular dynamics, Monte Carlo or quantum molecular dynamics and often treat a layer of solvent molecules surrounded by a solvent continuum (Cramer and Truhlar, 1999; Cramer, 2002, p. 403).

Important deviations from this model were shown by Kramers (1940) to be due to solvent dynamical effects that increase with velocity along the reaction coordinate. To account for these effects of medium to high solvent friction that increases with solvent density and viscosity, an additional factor to correct VTST or TST is included (Steinfeld *et al.*, 1999).

$$k_{\mathrm{s}}^{\mathrm{VTST}} = k_{\mathrm{s}}^{\mathrm{VTST}} \kappa^{\mathrm{KR}}$$

where $\kappa^{\mathrm{KR}}(\beta, \omega) \leq 1$ is the Kramers transmission coefficient, β is a friction constant and ω is a parameter. For cases of lower friction, $\kappa^{\mathrm{KR}} \approx 1$, but for high friction cases the reaction rate constant decreases with increasing friction of the species in the solvent.

As a result of employing quantum mechanical methods within the statistical TST and VTST, computed rate constants can be calculated cost effectively at increasing levels of accuracy (Maity *et al.*, 2000). For many systems, however, kinetic systems include a large number of elementary reactions and rate constants. A practical approach includes a sensitivity analysis to determine the most significant reactions for which the rates constants are then calculated from the structure, energy and vibrational frequency information of the reactants and transition states. To reduce computation costs, the activation energy can be estimated using models such as the Evan–Polanyi linear free-energy relationship between the activation energy and heat of reaction or bond dissociation energy (Evans and Polanyi, 1938).

$$E_o^i = E_o^0 + \gamma \Delta H_i^0$$

where E_o^0 is an intrinsic activation energy for a family of similar species, ΔH_i^0 is the heat of reaction for the ith reaction within the family of species and γ is a constant. But this empirical estimation of activation energies by itself can lead to large uncertainties in the predicted rate constants. A recent development to increase accuracy is a version of TST, reaction class TST or RC-TST, to estimate rate constants for species within a family or class where each member includes the same reactive moiety. This approach performs a full calculation of the smallest species in the class and takes advantage of relatively similar potential energy surfaces along the reaction coordinate so that rate constants of the other class members can be estimated from differences in activation energies and reaction energies.

Because a modest level of quantum calculations are involved for all but the smallest species in the class, rate constant calculations for the class members can be rapid and cost effective (Zhang and Truong, 2003).

Chemical reaction rate parameters also have been correlated with molecular properties of the reacting species using approaches such as QSPR (quantitative structure–property relationships) to relate the observed parameters to these molecular properties, called descriptors that are based on experimental measurement or computed from the molecular structure. Example descriptors are molecular weight, boiling point, highest occupied molecular orbital and dipole moment.

Overview of tests

In cases where sufficient or reliable reactivity information is not available from a desktop review or from calculations, the gap in information is usually filled through experimental results. Test methods have been developed for evaluating individual component stability as well as reactivity with other species. The test methods used for reactions among species are broadly similar to those used for single components, but there are some important differences. In particular, it is necessary for the design of the reactor system to have much more information. There are two main reasons for this. One is that the design involves selecting not only an operating temperature, but also a number of other parameters and features such as a feed addition rate and a pressure relief system. The other is that the design involves scale-up to full scale. While these factors can be important for individual component stability in a reactor system as well, they must be accommodated in the design for normal operation.

The information sought from tests includes data on the presence and quantitative features of exotherms, rate of heat evolution and rate of gas evolution. One group of tests uses a Carius tube or similar equipment. These include the closed tube test and the delayed onset detection test. Another group utilizes a Dewar flask. This includes tests involving: ramped and stepped heating of the reaction sample in a Dewar flask; ramped heating of the sample and a reference material in a Dewar flask (the simple exotherm test, or dynamic heating test); and the hot storage test using a Dewar flask, or heat accumulation test.

In many tests, the sample is held in an apparatus placed in an oven. Tests employ various temperature control modes. The temperature may be held constant, ramped or stepped. The sample may be held under adiabatic conditions by arranging for its temperature to be tracked by that of the oven. Alternatively, the sample conditions may be made isothermal by holding the temperature of the oven constant at a value slightly below that of the sample.

There are numerous accounts of particular tests and of their interpretation. Some of these are described below.

Experimental test methods and equipment for screening

Thermal Behaviour The information obtained in the various types of tests varies. Some tests merely indicate that an exotherm exists, whilst others permit quantitative evaluation of the exotherm parameters such as the heat evolved. This information gives a quantitative measure of the heat released.

Preliminary tests The starting point for preliminary tests is usually to test for the occurrence of an exothermic reaction when the substance is heated.

Melting point tube test A simple, if crude, test is the capillary melting point tube test in which the sample is heated up at a constant rate of about 10°C/min in a standard melting point apparatus. A result such as that shown in Figure 33.5(a), in which the sample temperature has exceeded that of the heating medium, indicates that there is an exotherm.

Dewar tests A number of tests involve the use of a Dewar flask. These are of three types: (1) ramped temperature tests, (2) differential temperature tests and (3) adiabatic tests.

In the first type, the sample is held in a tube in a heat transfer medium in a Dewar flask and the temperature of the medium is ramped at a constant rate; a typical rate of temperature increase is 2°C/min. If, at a given medium temperature, the sample temperature rises above that of the medium, as shown in Figure 33.5(a), an exotherm is present. A plot of this kind is given by N. Gibson (1984).

Alternatively, the same apparatus may be used, but the temperature of the heating medium may be increased in a series of steps, holding the temperature constant for a period at each step; a typical increment is 10°C. If at a given medium temperature the sample temperature rises, there is an exotherm. Figure 33.5(b) illustrates a result showing an exotherm occurs at 90°C.

These two variants of the first type of Dewar test do not appear to have a specific name, other than the rather ambiguous 'Dewar flask' test. They are referred to here as the 'ramped heating' and 'stepped heating' Dewar flask tests, respectively.

In the second type of Dewar flask test, the procedure is to put the sample and a reference material in two tubes in a Dewar flask filled with heat transfer medium, to heat the medium up at a constant rate and to measure the temperature difference between the sample and the reference material. A plot is made of the temperature difference, ΔT, between the sample and the reference material vs the temperature, T, of the heat transfer medium. A typical result for a material is illustrated in Figure 33.5(c). This test is referred to by the ABPI (1981), which gives details and plots, as the 'dynamic heating test', and by Coates and Riddell (1981a) as the 'simple exotherm test' and the 'dynamic heating test'.

The third type of Dewar flask test is the 'adiabatic test'. The sample is held in a pressure Dewar flask in an oven. The flask simulates the reactor and the process is carried out in the plant. The temperature of the oven is controlled to follow closely the sample temperature allowing measurement of any exotherm that occurs. The test is described by T.K. Wright and Rogers (1986).

Tube Test An alternative to the Dewar flask is an open or a closed tube test. A Carius tube is often used, but if gas evolution occurs, a closed tube is more suitable. It is desirable to establish the extent of any gas evolution in the initial screening. This may be done by a pressure–time test using a closed Carius tube.

Closed Tube Test A closed tube test may be used to detect the onset of an exotherm and gas evolution. A 10 g sample is held in a closed Carius tube in an oven and the temperature of the oven is ramped upwards at a typical rate of 2°C/min. The test is described by N. Gibson (1984) and N. Gibson, Rogers and Wright (1987) and is referred to

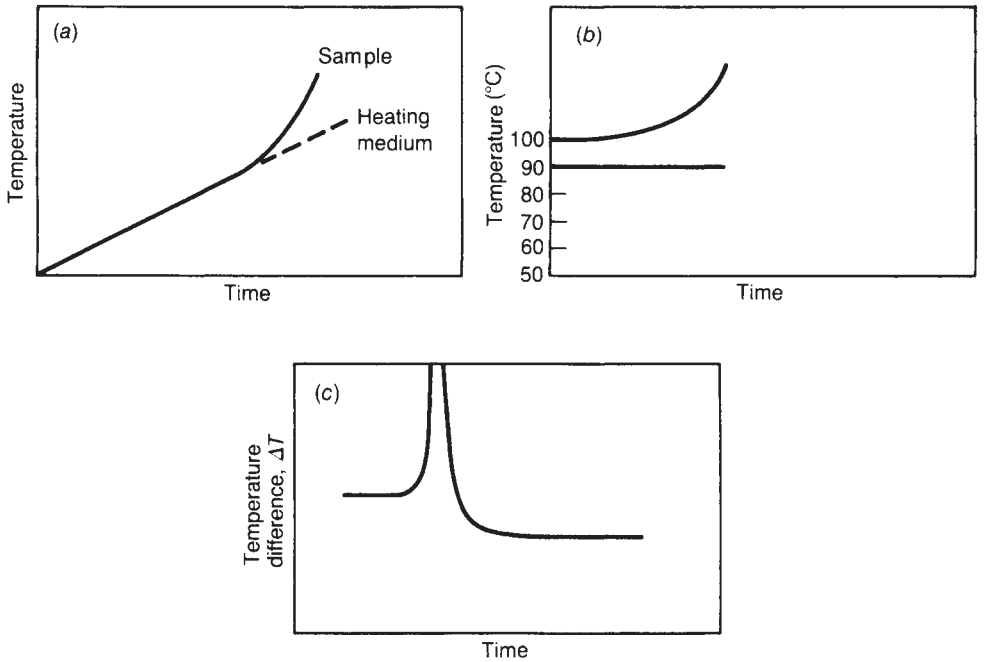


Figure 33.5 *Exotherm profiles in tests for thermal stability of individual substances: (a) sample and heating medium temperatures in melting point tube test or Dewar flask ramped temperature test; (b) sample temperature in Dewar flask stepped temperature test; (c) temperature difference between sample and reference material in Dewar flask dynamic heating test.*

as the Imperial Chemical Industries (ICI) programmed screening test or as the 'ICI 10 g sealed tube test'.

Delayed Onset Detection Test Another test is the delayed onset detection test. The sample, held in a lagged Carius tube placed in an isothermal oven, is maintained isothermally at about 10°C above the oven emperature using a small electric heater. An exotherm is detected by a fall in the electrical power requirement. The test is described by the ABPI (1981).

The tests just outlined can be performed using in-house apparatus and avoid the use of specialist instrumentation, which can be expensive.

Hot Storage Tests It may also be necessary to test the behaviour of the material when held at a high temperature for a long period under adiabatic conditions. In the hot storage test, the sample is held in a container in a Dewar flask under quasi-adiabatic conditions and any exotherm is recorded. The test period is usually at least 7 days. The test is also referred to as the 'heat accumulation test'. The hot storage test is carried out if the material is to be held at or subjected to a temperature relatively close to the exotherm onset temperature T_e, say at $T_e = 50°C$. This applies to in-plant processing, to storage and transporation. The results of this test can be related to the Self-Accelerating Decomposition Temperature (SADT) determined through a United Nations Orange Book test Recommendations on the Transport of Dangerous Goods: Model Regulations, 13th ed., United Nations, NY, 2004.

Insulated Exotherm Test The insulated exotherm test (IET) is a form of Differential Thermal Analysis (DTA), which is described in the next section.

Decomposition Pressure Test The decomposition pressure test (DPT) is carried out in a pressure vessel. The oven temperature is ramped and the sample temperature and vessel pressure are measured.

Explosive Behaviour

Impact Sensitivity If there is reason to suspect that the substance has the potential to explode, it may be subjected to tests for explosibility. These include an impact sensitivity test such as the drop weight test and a detonability test. Explosibility tests are described below.

A detailed account of initial screening tests, of the precautions to be taken and of the interpretation of the results is given by Snyder (1965).

Experimental test methods and equipment for detailed evaluation

Tests using special instruments and calorimeters There are a number of rather more elaborate techniques which may be employed to detect and quantify exotherms and for which special instrumentation has been developed. The principal techniques are DTA, differential scanning calorimetry (DSC) and accelerating rate calorimetry (ARC).

DTA In DTA, the sample is held in a tube in a vessel surrounded by a heat transfer medium and is heated at a constant rate. A typical heating rate is 2°C/min. A plot is made of the temperature difference, ΔT, between the

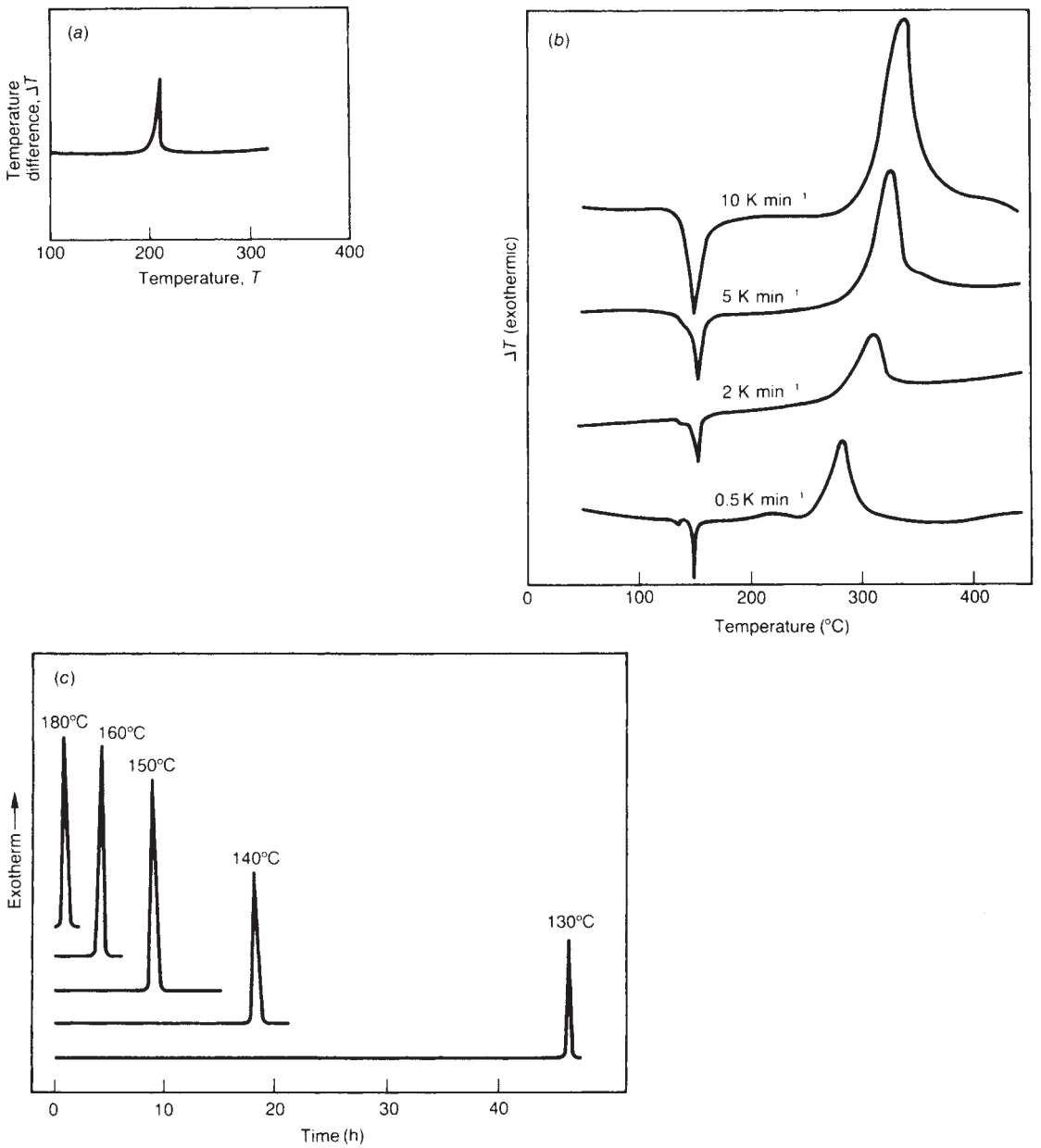


Figure 33.6 *Exotherm profiles in tests for thermal stability of individual substances using differential thermal analysis (DTA): (a) conventional ramped temperature test; (b) ramped temperature tests, showing effect of rate of temperature increase (Grewer et al., 1989); (c) isothermal tests, showing effect of time-dependent material stability (Duval, 1985) (Courtesy of the American Chemical Society)*

sample and the heat transfer medium vs the temperature, T, of the latter. A typical result for a material giving an exotherm at 200°C is illustrated in Figure 33.6(a). The use of DTA to detect thermal instability is described by Silver (1967) and Coffee (1969). DTA may be carried out with open or closed tubes, the latter being more appropriate where gas evolution occurs.

In conventional DTA, the temperature is programmed to rise at a constant rate. Figure 33.6(b) (Grewer *et al*, 1989) illustrates a set of traces obtained for different heating rates. Where the thermal stability of a substance may be a function of time, DTA may be performed isothermally. Figure 33.6(c) (Duval, 1985) shows a set of traces for DTA of a substance exhibiting time-dependent thermal instability.

The use of isothermal DTA is described by Schulz, Pilz and Schacke (1983) and by Duval (1985). DTA may also be performed using in-house apparatus. Cronin, Nolan and Barton (1987) have described an 'insulated exotherm test', which is based on DTA.

Figure 33.7(a) from Grewer (1974) shows a DTA plot for the sulfonation of nitrobenzene in sulfuric acid in which the product has decomposed and Figure 33.7(b) one for the diazotization of 2-cyano-4-nitroaniline in sulfuric acid in which the three peaks correspond to the reactions associated with the CN, N_2 and NU2 groups.

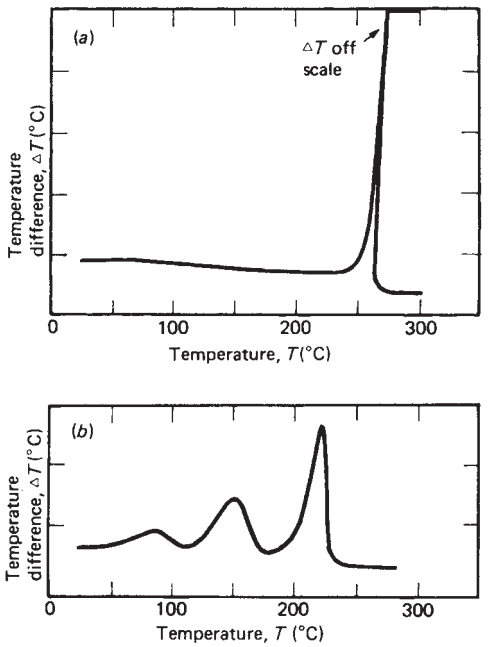


Figure 33.7 *Experimental determination of thermal stability of reaction mixtures – 1 (Grewer, 1974): (a) differential thermal analysis of sulfonation of nitrobenzene; (b) differential thermal analysis of diazotization of 2-cyano-4-nitroaniline in H_2SO_4 (Courtesy of Elsevier Publishing Company)*

DSC In DSC, the sample and a reference material are held in pans in a vessel and are heated at a constant rate of typically 5–10°C/min. The heating is carried out by a control system that maintains the sample and the reference material at the same temperature. The variation in the heat that must be supplied to the sample to keep it at the same temperature as the reference material gives a quantitative measure of any exotherm in the sample. A plot is made of the rate of change of heat input to the sample with time, dQ/dt, vs the temperature, T, of the reference sample. Again, open or closed pan methods may be used. An account of DSC is given by Wendlandt (1986). Figure 33.8 (Duval, 1985) shows a typical DSC plot.

Some substances must be tested under pressure. One reason for this is that a volatile substance can reach higher temperatures if held under pressure and thus the temperature range over which an exotherm may occur is extended. Another reason is that pressure may enhance an exotherm, especially in air. The conduct of DTA and DSC with the sample under pressure in a pressure cell and the use of a test scheme based on atmospheric DTA(DSC), pressure DTA(DSC) and a confinement test have been described by Seyler (1980). The confinement test is designed to measure the temperature at which a material under confinement will generate heat and pressure while subjected to a constant temperature increase of 1–2°C/min. In the scheme described by Seyler (illustrated in Figure 33.9), if atmospheric DTA(DSC) shows a moderate to severe exotherm, a thermal hazard is established; pressure DTA(DSC) may be bypassed, but a confinement test is required. If atmospheric DTA(DSC) shows a weak exotherm or none,

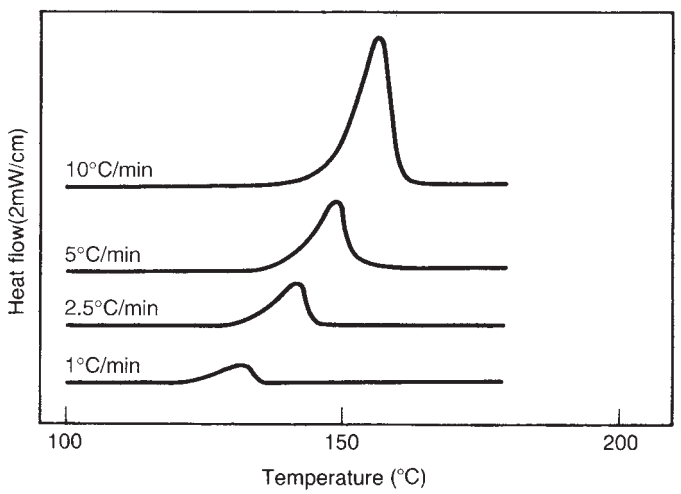


Figure 33.8 *Exotherm profile in test for thermal stability of individual substances using differential scanning calorimetry (DSC) (Duval, 1985) (Courtesy of the American Chemical Society)*

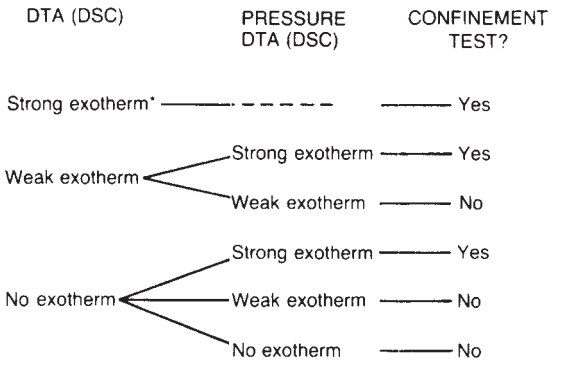


Figure 33.9 *Test scheme using pressure DTA/DSC to identify need for confinement test (Seyler, 1980) (Courtesy of Elsevier Science Publishers)*

pressure DTA(DSC) is carried out and if a strong exotherm is detected, a confinement test is performed.

DTG or TGA Another instrumental technique is differential thermo-gravimetry (DTG), but this is less widely used. It can also be referred to as thermogravimetric analysis (TGA). In combination with compositional analysis tools, such as flame ionization, infrared and mass spectroscopy detectors, it becomes a powerful technique for identifying decomposition products. It can also be combined with DSC to provide an indication of the energetics associated with volatile species generation.

Tests characterizing the normal reaction

Dynamic heating test The dynamic heating test has open and closed tube versions. The oven temperature is ramped and the temperature difference between the sample and a reference material is measured to detect any exotherm. The test is also known as the 'simple exotherm test'.

Adiabatic heating test The adiabatic heating test uses a Dewar flask. The oven temperature is held constant and any exotherm is measured. The test period is at least 8 and preferably 24 h. This test is also known as the 'heat accumulation test'.

Figure 33.10(a) from Grewer (1974) gives a plot for an adiabatic storage test of diazotization solution of 2-cyano-4-nitroaniline in which again there are three steps in the curve corresponding to the exotherm peaks in the DTA test. Figure 33.10(b) shows a plot for an adiabatic reaction test, similar to the adiabatic storage test but conducted at the operating temperature, for the reaction of *p*-nitro-*N*-methylaniline with carbyl sulfate in nitrobenzene under pressure.

AZT24: Further methods of characterizing the reaction and the reactor have been described by Grewer *et al.* (1989). It is common for a product to be brought to an elevated temperature for some 24 h. The adiabatic storage test may be used to determine a suitable temperature limit. The most useful information yielded by the adiabatic storage test is the adiabatic induction time $T_a d$. Usually this correlates with temperature according to the relation $\log T_a b$ vs $1/T$. This correlation can be used to determine the temperature at which the adiabatic induction time is 24 h. This temperature is known as AZT24.

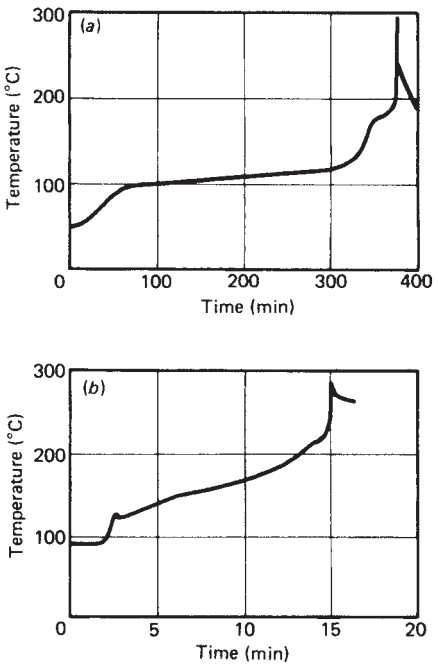


Figure 33.10 *Experimental determination or thermal stability of reaction mixtures – 2 (Grewer, 1974): (a) adiabatic storage test of diazotization solution of 2-cyano-4-nitroaniline in H_2SO_4; (b) adiabatic reaction test of solution of p-nitro-N-methylaniline and carbyl sulfate in nitrobenzene (Courtesy of Elsevier Publishing Company)*

In addition to this storage version of the test, there is a reactor version in which the flask simulates the reactor and the process is carried out as on the plant.

Heat flow calorimetry In heat flow calorimetry, the sample is held in the calorimeter (a jacketed mini-reactor) and a heat transfer medium is circulated so that it removes heat at the same rate as it is generated, maintaining isothermal conditions. A test of this type is described by Coates and Riddell (1981a). The RC-1 of Mettler is an example of a heat flow calorimeter.

One important test carried out using a reaction calorimeter is the determination of the adiabatic temperature rise. This single test provides a large amount of information on the thermodynamic and kinetic and characteristics of the reaction such as the heat capacity of the reaction mass, heat of reaction and the rate of heat production.

Isoperibolic calorimetry Isoperibolic calorimetry is carried out in a simple form of a heat flow calorimeter. The heat transfer medium is held at constant temperature, the temperature difference between this medium and the sample is measured and the heat flow is thus obtained.

Power compensation calorimetry This method utilizes another form of heat flow calorimeter in which a heater in the sample maintains it at the desired reaction temperature, even though it loses heat to a heat transfer medium held at a lower temperature.

Numerous other specialized instruments for the investigation of reactions have been described such as the TZP described by Kunzi (1980). This instrument allows a component or reaction mixture to be investigated in the same oven under isobaric and isochoric conditions and under identical thermal conditions. The author mentions particularly the investigation of decomposition reactions.

There are also available several special calorimeters developed for the study of thermal stability and reaction exotherms.

SIKAREX: One special calorimeter is the SIKAREX described by Hub (1976, 1977a,b). The calorimeter consists of a tube held in a temperature-controlled environment and with a heating element on the tube itself. It can be operated in quasi-isothermal, adiabatic and isothermal modes. In the quasi-isothermal mode, the sample is brought to temperature equilibrium with the environment, the environment temperature is increased and, if an exotherm occurs, the temperature difference between the sample and the environment is measured. In the adiabatic mode, the environment is maintained at the same temperature as the sample. In the isothermal mode, the environment is held at a temperature below that of the sample, the tube heater is used to maintain the temperature of the sample and the heat required to do this is measured.

Another special calorimeter is the SEDEX (SEnsitivity Detector of EXothermic processes) described by Hakl (1981). This instrument is an oven equipped with temperature control and adapted to take various types of sample containers with inlet and outlet tubes, stirrers and so on. The system may be used in various modes.

ARSST: The Advanced Reactive System Screening Tool (ARSST) is an instrument intended to provide rapid screening of chemical reactivity as well as provide some detailed kinetic parameters for reaction characterization. The sample is placed in an open 100 ml round-bottom flask and its temperature ramped by external heaters. An exotherm appears as a reduction in heat required during the ramp. The sample and flask are kept in a containment vessel pressurized to help retain sample liquid in a condensed state. The apparatus can also be equipped with a detector to indicate during venting whether gas/vapour only or gas/vapour plus liquid are leaving the flask.

Adiabatic calorimeters – Adiabatic temperature rise test One test that yields a large amount of information on the reaction parameters is an adiabatic test in which the reaction is taken to completion. Such a test gives a sigmoidal temperature profile, with the temperature initially rising rapidly and then levelling off as the reactants are consumed. A simple analysis of such a test is given by the 1981 ABPI *Guidelines*. The analysis yields the adiabatic temperature rise, the self-heat rate, the velocity constant and the activation energy.

Dewar calorimetry: Dewar calorimetry tests (described also in the previous section) operated in an adiabatic mode can be utilized to determine the adiabatic temperature rise, the heat of reaction and reaction kinetics.

ARC: In the Accelerating Rate Calorimeter (ARC), the sample is held in a bomb calorimeter under adiabatic conditions. Adiabaticity is achieved by heating the surroundings of the sample cell so that the temperature outside the cell matches the temperature in the cell. ARC testing may be done in different ways, but one of the most common is

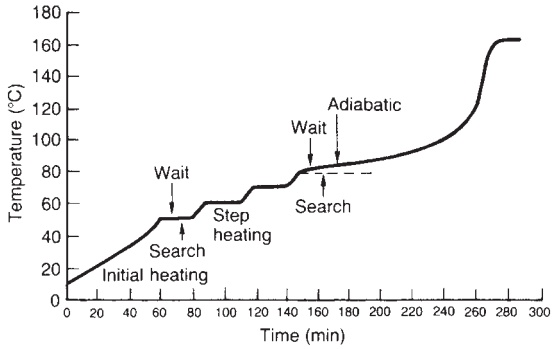


Figure 33.11 *Exotherm profile in test for thermal stability of individual substances using accelerating rate calorimetry (ARC) (N. Gibson, Rogers and Wright, 1987) (Courtesy of the Institution of Chemical Engineers)*

the 'heat, wait and search' method. The temperature is increased in steps, a typical increment being 10°C. The sample is then held for a period at that temperature. The rate of any temperature increase is observed to see if it exceeds a set value, typically about 0.02°C/min. If it does not, the temperature is raised by the incremental amount and the procedure is repeated. If the temperature rises at a high rate, there is an exotherm. Accounts of the ARC are given by Coates (1984a,b) and Ottaway (1986). A typical result, given by N. Gibson *et al.* (1987), for a material giving an exotherm at about 80°C is shown in Figure 33.11 The TIAX, LLC ARC instruments are widely used.

The ARC presents the advantage of studying compound reactivity in an adiabatic environment, more representative of plant and storage conditions than in isothermal or temperature-ramped instruments. The ARC is also equipped to accommodate and measure large increases in sample pressure, which requires a relatively thick-walled cell relative to the amount of sample contained. This leads into the concept of the thermal inertia factor, ϕ, reflecting the amount of heat absorbed by the sample container relative to that retained in the sample itself. The thermal inertia is defined as

$$\phi = 1 + \frac{m_c Cp_c}{m_s Cp_s}$$

where m denotes the mass, Cp the heat capacity, subscript c the cell + stir bar and s the sample. A high thermal inertia factor indicates that much of the evolved heat is utilized to raise the temperature of the sample container instead of the sample itself. In this circumstance, the extent of temperature rise from a reaction can be dampened and subsequent reactions missed. The ϕ factor of commercial equipment approaches a value of unity. A value of 1.5–5 is typical of ARC tests.

Stirring can be accomplished in the ARC through use of a specially designed thick-wall sample cell equipped with an internally mounted magnetic stir bar. An external rotating drive magnet causes the internal stir bar to spin.

The ARC can be viewed as a forerunner of a family of instruments developed to reduce the thermal inertia factor closer to unity. These instruments include the VSP, Phi-Tec and the APTAC. Information obtained from the ARC, VSP,

PHI-TEC and APTAC can be employed to characterize runaway reaction kinetics as well as help size appropriate relief vents.

VSP: The Vent Sizing Package or VSP (originally the DIERS Bench-Scale Apparatus) was the first of the adiabatic calorimeters to incorporate pressure-balancing in its design. This feature allows use of a thin-walled sample can while still enabling the sample to reach elevated pressures during a test. The VSP also operates with a 120 cc sample cell. The use of a larger sample with a thin-wall can yields thermal inertia factors typically 1.05–1.20. The VSP has more recently been upgraded to include multi-zone heating elements, solid ceramic insulation and mechanically driven stirring (vs magnetically coupled stirring).

PHI-TEC: Another adiabatic calorimeter equipped with pressure balancing, and thus operating with thin-walled cans and larger sample sizes, is the PHI-TEC. It has many of the newer features described above for the VSP.

APTAC: The Automatic Pressure Tracking Adiabatic Calorimeter (APTAC) is also a VSP-like instrument, but more fully instrumented and automated. The sample resides in a spherical cell and exhibits greater sensitivity for exotherms (0.04°C/min) than the VSP. The instrument can also be purchased with various integrated sample injection and venting options. As the name implies, this calorimeter is designed to operate fully automatically once sample is loaded and the test initiated.

Tests to detect and characterize an exotherm may need to be supplemented by other tests. Mention has already been made of explosibility/detonability and of deflagration tests.

Gas evolution measurement Gas evolution is another important parameter. One measurement method utilizes a tube and another an autoclave. These tests are also described by Coates and Riddell (1981a).

Automated gas burette: Gas evolution measurement is carried out with a burette in which the gas evolved builds up and is then released in a cycle which is then repeated, with the total gas evolution determined from the number of releases made. The releases and the counting are automated.

Thermal mass flowmeter: Gas evolution measurement using a thermal mass flowmeter to measure the flow of gas evolved.

Blowdown tests J. Singh (1988a) describes the use of a reaction calorimeter to determine the maximum pressure resulting from runaway of the main process reaction and thus to assess the option of containment instead of venting.

In the blowdown test, the reaction mixture is brought to the reaction runaway temperature in a test cell, and when the vent pressure is reached, a vent valve is opened full. Venting down to atmospheric pressure occurs, typically over a period of some 6 s. The residual liquid in the cell is measured. If the cell remains over 60% full of liquid, the vent fluid is taken as all vapour. If the cell contains less than about 5% of liquid, the venting is taken as homogeneous, that is the vent fluid is representative of the vapour–liquid mixture in the vessel. For residual fills between these two limits, the venting is taken as two-phase but not homogeneous, that is vapour disengagement and preferential venting of vapour have occurred.

The vent sizing test involves bringing the reaction mixture to the reaction runaway temperature and opening the vent valve, but this time the vapour is vented at a slow, controlled rate. The temperature of the reaction mass levels off and the reaction is tempered, the vapour flow being such as to give thermal equilibrium. The vent valve is then closed momentarily, the temperature rises and the valve is opened again. The rate of temperature rise can then be used to size the vent. The author gives an example of the calculation of vent size.

Combustion tests A combustion test for preliminary screening is the train firing test, which indicates the ability of a flame to propagate through the material in powder form. A train of finely ground material is laid on a heat insulating surface in a line and ignited. In the version described by ABPI (1981), ignition is by heated wire; in that described by N. Gibson, Harper, and Rogers (1985), it is by a gas flame. The extent of fire spread is observed and categorized as shown in Table 33.9, the degree of hazard increasing with the rating number.

Deflagration tests Certain liquids such as peroxides and hydroperoxides are susceptible to violent decomposition, even in the absence of air. In contrast to process reactions in which the reaction rate depends on the temperature according to the Arrhenius equation, these decompositions show no simple temperature dependence, but occur at about 200°C and are characterized as deflagrations (subsonic propagating reactions). Whether a particular mixture will decompose in this way depends on the concentration, the temperature and the presence of an ignition source such as a hot spot, spark or flame. Liquid-phase deflagration tests are carried out in a small cylindrical vessel fitted with rupture discs in which the liquid sample is ignited by a heated wire. The maximum pressure resulting from a liquid decomposition would typically rule out simple containment as a design option.

Deflagration may also occur in the vapour phase. Vapour phase deflagration tests are carried out in a spherical vessel in which the vapour sample is ignited by a fused wire. In this case, containment may be an option, although venting is also widely used.

Table 33.9 *Interpretation of train firing test (after N. Gibson, Harper and Rogers 1986)*

Fire spread	*Result*	*Rating*
No	No ignition	1
No	Brief ignition, rapid extinction	2
No	Local combustion, at most smouldering, slight spread	3
Yes	Hot red glow or slow decomposition without flame	4
Yes	Burning like a firework or slow steady burning with flame	5
Yes	Very rapid combustion with flame or rapid decomposition without flame	6

Drying of powders Two main categories of tests are performed on powders: dust explosivity tests (described in Chapter 17 in conjunction with flammability issues) and drying tests. The ABPI (1981) describes two tests: (1) a 'through air' drying test in which air is passed through a bed, and (2) an 'over air' test in which air is passed over a layer.

Some factors that affect the behaviour of a powder in drying include

(1) chemical composition;
(2) impurities;
(3) effective thermal conductivity;
(4) effect of air;
(5) time-dependent effects.

A more-detailed account is given by N. Gibson, Harper and Rogers (1985, 1986).

The material to be dried may be chemically complex, perhaps incorporating agents to instill special properties, or it may contain impurities. Both of these factors may influence the reactivity of the material. If a reaction occurs, the rate of heat loss depends on the effective thermal conductivity of the material *in powder form*. If the reaction mechanism is predominantly oxidation, the availability of air is an important factor. The reaction may occur only after a certain time, or induction period.

N. Gibson, Harper and Rogers (1985, 1986) also describe the set of tests illustrated in Figure 33.12: a bulk powder test, an aerated powder test and a powder layer test. The configuration selected being that in which the powder is to be dried on the plant. In each test, the powder is subjected to a stream of warm air. The authors discuss the application of the results from these tests to particular drying processes. This aspect is considered further in Chapter 11.

Interpretation and comparison of experimental test methods
Reaction characterization The reaction system may be characterized in terms of the following fundamental quantities:

(1) physical and chemical properties of the components;
(2) reaction stoichiometry;
(3) heat of reaction;
(4) quantity of gas evolved;
(5) kinetics of reaction.

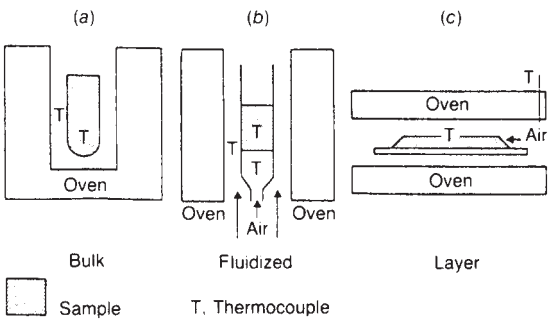


Figure 33.12 *Tests for thermal stability in driers: (a) bulk form; (b) fluidized form; and (c) layer form (after N. Gibson, 1984) (Courtesy of the Society of Chemical Industry)*

Exotherm characterization Some parameters characterizing an exotherm are:

(1) exotherm onset temperature;
(2) adiabatic temperature rise;
(3) heat of reaction;
(4) rate of temperature rise (also known as the self-heat rate);
(5) rate of heat generation;
(6) rate of pressure rise;
(7) velocity constant, activation energy and pre-exponential constant;
(8) adiabatic induction time.

Some of these parameters can be determined from DSC or DTA tests. Most of these parameters can be obtained from an adiabatic Dewar flask test or ARC test.

Interpretation of exotherm onset temperature test
Although the temperature for reaction onset (i.e. 'onset temperature') is a convenient concept, it needs to be borne in mind that even at lower temperatures there is still a non-zero reaction rate. It is important to note that the onset temperature is a measure linked to the detection limit of the instrument utilized. It is not a value unique to the reaction chemistry alone.

A quoted onset temperature is one measured by a particular test and is highly dependent on sample size, degree of adiabaticity, instrument sensitivity, time-temperature history and reaction kinetic features, notably activation energy.

A traditional approach to reactor safety has been to set the temperature of reactor operation at some fixed temperature interval below the exotherm onset temperature measured in the laboratory test. A widely quoted value of this safety margin is 100°C, the '100 degree rule'.

Various authors discuss this safety margin. Coates and Riddell (1981a) state that any material with an exotherm onset temperature within 100°C of the maximum operating temperature as determined by the simple exotherm test is considered a potential hazard. In such a case, the material is subjected to the adiabatic exotherm test. If the exotherm onset temperature in this test is 50°C or more above the operating temperature it is not considered a hazard. If it is within this 50°C safety margin, it is subjected to a long-term hot storage test at 20°C above the operating temperature.

The IChemE *Guide*, which rehearses the factors affecting a measured onset temperature, as just described, states that the 100° rule, or a similar one, should not be used as the basis of safety unless previous experience has shown the rule to be valid for the type of reaction in question.

Interpretation of initial screening tests
Initial screening tests can provide information on the occurrence of a thermal excursion, or exotherm, and on the following of its features: (1) onset temperature, (2) heat release and (3) rate of heat release. The data from screening tests must be interpreted with care. In particular, any onset temperature determined will be a function of the sample size and the heating mode. The IChemE *Guide* gives a method of correcting temperature for sample size.

Comparison of methods for an exotherm
Several authors have given comparisons of different methods of determining exotherm parameters. N. Gibson (1984)

has given the following results for the exotherm onset temperature of 3,5-dinitro-*o*-toluamide:

ICI programmed screening test	115–120°C
DTA (fast scan)	274–284°C
ARC	120–125°C

He comments that the limitations of fast scan DTA and ARC are well known.

A comparison of exotherm onset temperatures for a large number of substances, as determined by ARC and by other methods, has been given by Fenlon (1984). Hakl (1981) has given a comparison of exotherm onset temperatures for five substances determined by DSC and by SEDEX. The values determined by the former are consistently higher, the difference ranging from 25°C (80°C against 55°C) for f-xylylchloride with 0.02% Fe and 85°C (380°C against 295°C) for 1-nitroathrachinone.

Interpretation of tests characterizing the normal reaction

The interpretation of the tests characterizing the normal reaction is discussed in the 1981 and 1989 ABPI *Guidelines* and the IChemE *Guide*. These give a number of illustrations of test results together with commentaries.

For equipment and safeguarding design, it is necessary to know

(1) heat transfer parameters;
(2) rate of heat evolution;
(3) rate of gas evolution;
(4) rate of heat removal.

The rate of heat evolution is a function of the the heat of reaction and reaction kinetics. The heat evolution rate also depends on the reaction conditions and circumstances, such as reaction mode, the reaction temperature, the reactant concentration and any thermal events that may occur. The reaction mode may be batch or semi-batch. The reactant concentration is determined by the reaction mode and the initial temperature. The reaction temperature is a design parameter, but an excursion may occur due to an exotherm. Thermal events are those such as mixing, adsorption, phase changes, gas evolution, decomposition and so on.

It is necessary to have full information on the gas evolution and decomposition characteristics. If the reaction is subject to gas evolution, data are needed on the rate of gas evolution, which is a function of the kinetics and the quantity of gas evolved (as reflected by the reaction stoichiometry). If the reaction is subject to decomposition, information is required on the temperature range in which it occurs and on any tendency for autocatalysis.

The rate of heat removal is a function of the reaction temperature attained and of the heat transfer characteristics. The latter, in turn, is governed by the cooling arrangements. For jacket cooling, it depends primarily on the reaction and coolant temperatures, the effective heat transfer area and the heat transfer coefficients.

Test schemes

Preliminary or initial screening tests In the ABPI 1981 scheme preliminary tests, the safety screen test is the melting point tube test and the combustibility test is the train firing test, as described in Chapter 8. The explosion and detonation potential tests are of the type described in that chapter. In the ABPI 1989 scheme, shown in Figure 33.13, the tests are not classified in terms as preliminary or screening tests, but the first six of the tests listed are grouped under the heading of tests for unexpected decomposition. The combustibility test is again the train firing test. The DSC and closed tube tests are ramped temperature tests for the detection of an exotherm. The delayed onset detection test is an essentially isothermal test for the detection of delayed onset of any exotherm. The adiabatic Dewar test, which simulates the reactor under adiabatic conditions, gives information on the rate of any exothermic reaction. The ARC test also provides this information. Details of the tests not already described are given below.

The IChemE *Guide* scheme involves DSC and the 10 g closed tube test along with the insulated exotherm and decomposition pressure, initial screening tests.

Test schemes for material instability Test schemes for thermal instability of materials have been described by a number of authors. Table 33.10 summarizes some of the principal schemes. A test scheme given by Kohlbrand (1985) is shown in Figure 33.14(a) and another given by Cronin, Nolan and Burton (1987) is shown in Figure 33.14(b). Test schemes for powders have been given by N. Gibson, Harper, and Rogers (1985, 1986), as shown in Figure 33.15. Test schemes for reactivity are given in the subsequent subsection.

ABPI Test Scheme The *Guidelines for Chemical Reaction Hazard Evaluation* (ABPI, 1989) address material stability as well as chemical reactivity. Included is a sub-scheme for the screening of the substances involved in the reaction: raw materials, intermediates and products. The overall scheme is illustrated in Figure 33.16. This scheme for individual substances covers (1) explosive properties, (2) unexpected decomposition and (3) maximum safe temperature for storage. For characterizing normal reactions, the dynamic heating and the adiabatic heating tests are employed. The scheme also utilizes the adiabatic Dewar test, ARC, the heat flow calorimeter test and the two gas evolution measurement tests to characterize the intended reaction.

For explosive decomposition, the scheme involves assessment of explosive properties from (1) chemical structure, (2) oxygen balance, (3) energy of decomposition and (4) preliminary small scale tests (e.g. DSC), and if necessary, larger-scale Koenen tube or Trauzl lead block tests.

For unexpected decomposition, five tests are given:

(A) small scale testing using ramped temperatures
  (1) DSC,
  (2) closed tube test;
(B) isothermal testing for delayed onset
  (3) delayed onset detection test,
  (4) ARC,
  (5) adiabatic Dewar test.

Each test is fully described in the *Guidelines,* which also give, in most cases, typical output traces. The purpose and nature of these tests may be summarized as follows: the DSC test determines the onset temperature of any exotherm. The test method referenced is that of Wendlandt (1986). The closed tube test detects the onset of an exotherm and of gas evolution to detect delayed onset and to estimate the heat evolution and gas evolution rates. The test method

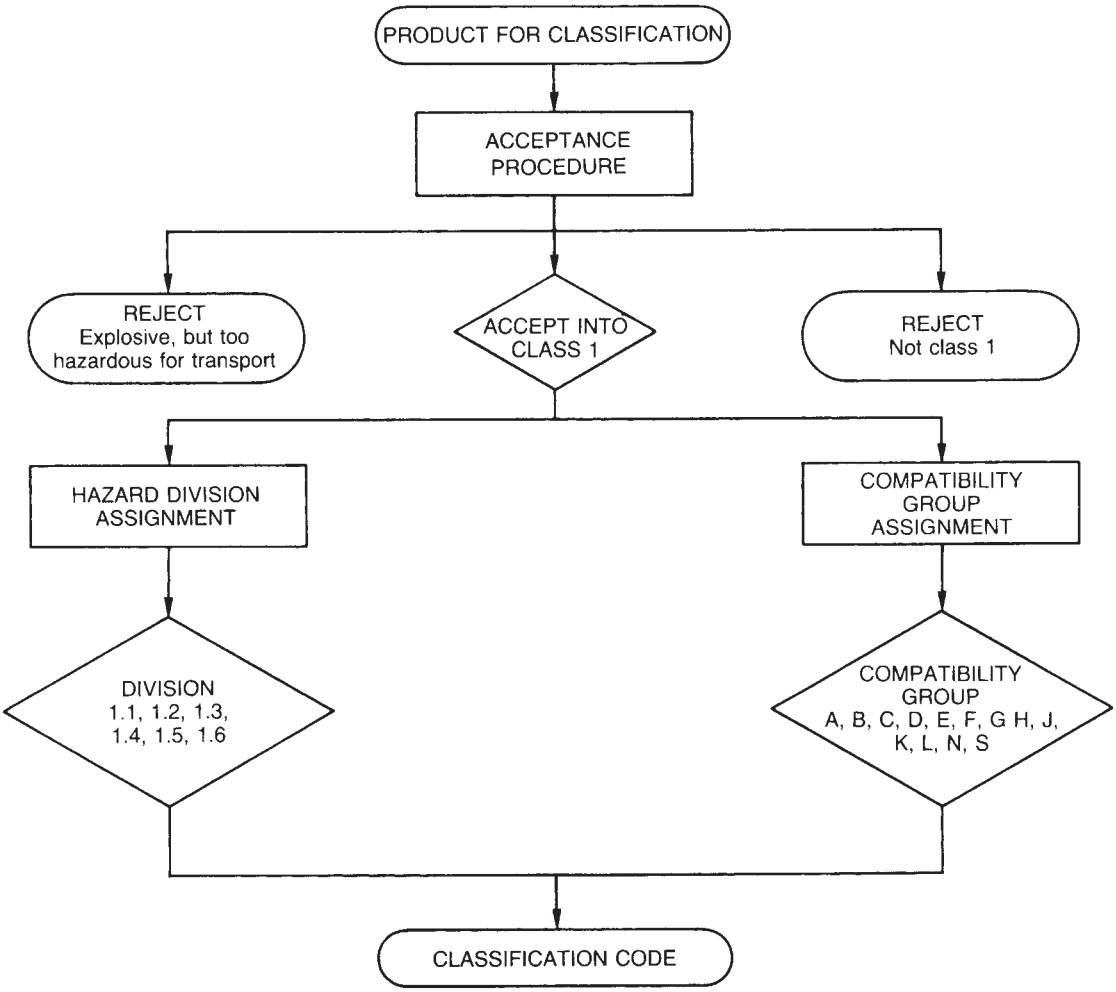


Figure 33.13 *UN transport classification tests; flow chart for classification of a substance or article as class 1 (UN, 1991)*

follows that of N. Gibson, Rogers and Wright (1987). The delayed onset detection test detects the onset of an exotherm and estimates the heat evolution rate. The ARC test detects an exotherm and determines the maximum safe working temperature. The ARC method given is the heat, wait and search technique mentioned earlier and described by Coates (1984a,b) and Ottway (1986). The adiabatic Dewar test, similar to the ARC method, detects an exotherm and gas evolution and determines the maximum safe working temperature. The test method is described by T.K. Wright and Rogers (1986).

The tests for maximum safe storage temperature apply only to liquids. For solids, the temperature may not be uniform throughout the material, making it necessary to treat this situation as a self-heating problem. An account of self-heating is given in Chapter 16.

For powders, the *Guidelines* refer to the methods of N. Gibson, Harper and Rogers (1985).

Test schemes for chemical reactivity A systematic approach to testing requires that it be performed within the framework of a scheme for the acquisition of the complete set of information necessary for reactor design. There are a number of test schemes described in the literature.

The scheme described in the ABPI *First Guidelines* comprised the following tests:

(1) preliminary tests
  (a) safety screen test,
  (b) combustibility test,
  (c) explosion and detonation potential tests;
(2) dynamic heating test;
(3) adiabatic heating test
  (a) reaction exotherm,
  (b) hot storage;
(4) special tests
  (a) drying stability tests.

Table 33.10 *Some test schemes for thermal stability of a single substance*[a]

Test	*Snyder (1965)*	*ABPI (1981)*	*Coats and Riddell (1981a)*	*Duval (1985)*	*N. Gibson (1984)*	*Cronin, Nolan and Barton (1987)*	*Grewer et al. (1989)*	*ABPI (1989)*
Melting point tube	x[b]	x[b]						
Dewar flask:								
Hot holding	x[b]							
Dynamic heating		x[b]	x[b]					
Hot storage		x[b]	x[b]				x	x[b]
Pressure tube	x[b]				x	x	x	x[b]
Delayed onset								x[b]
DTA				x		x	x	
DSC				x				x[b]
ARC								x[b]
Thermal stability bomb	x[b]							
Explosion/detonation	x[b]	x	x		x			x
Deflagration		x[b]	x				x	x
Drying		x[b]	x[b]		x			x

[a]The table gives the tests principally discussed by the authors; it should not be assumed that no other tests are done.
[b]These references give an account of the test apparatus and method.

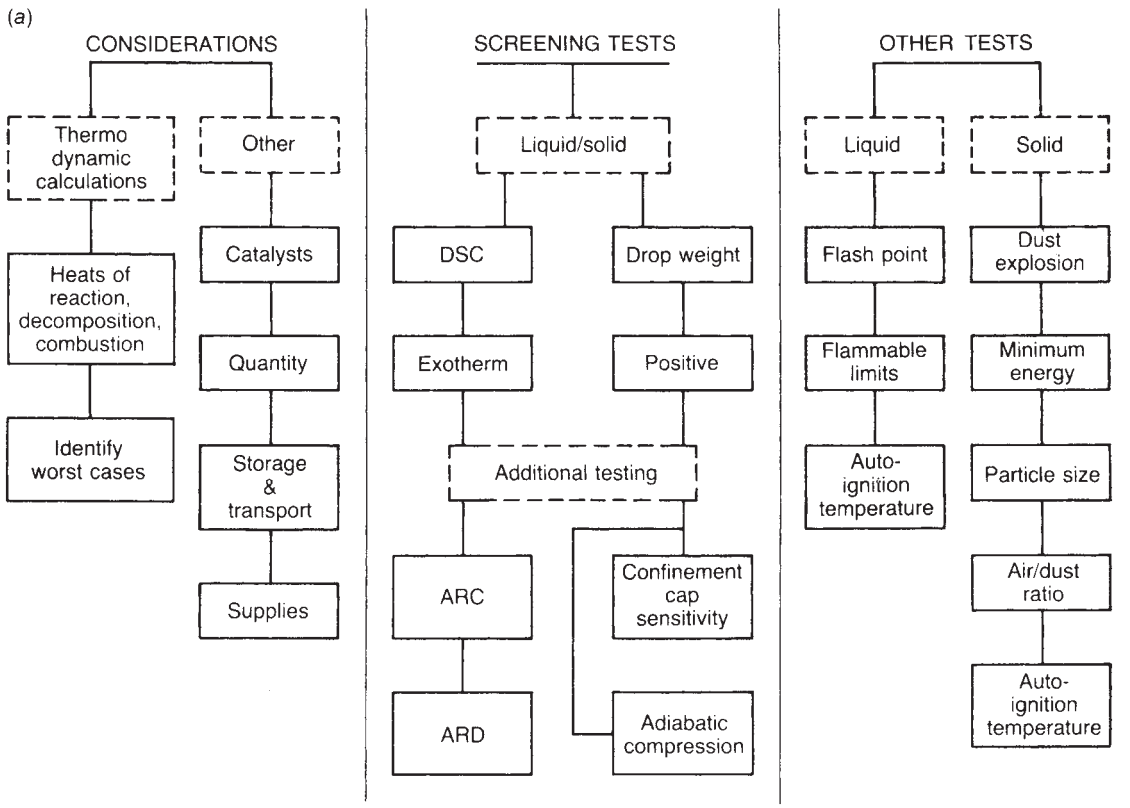


Figure 33.14 *continued*

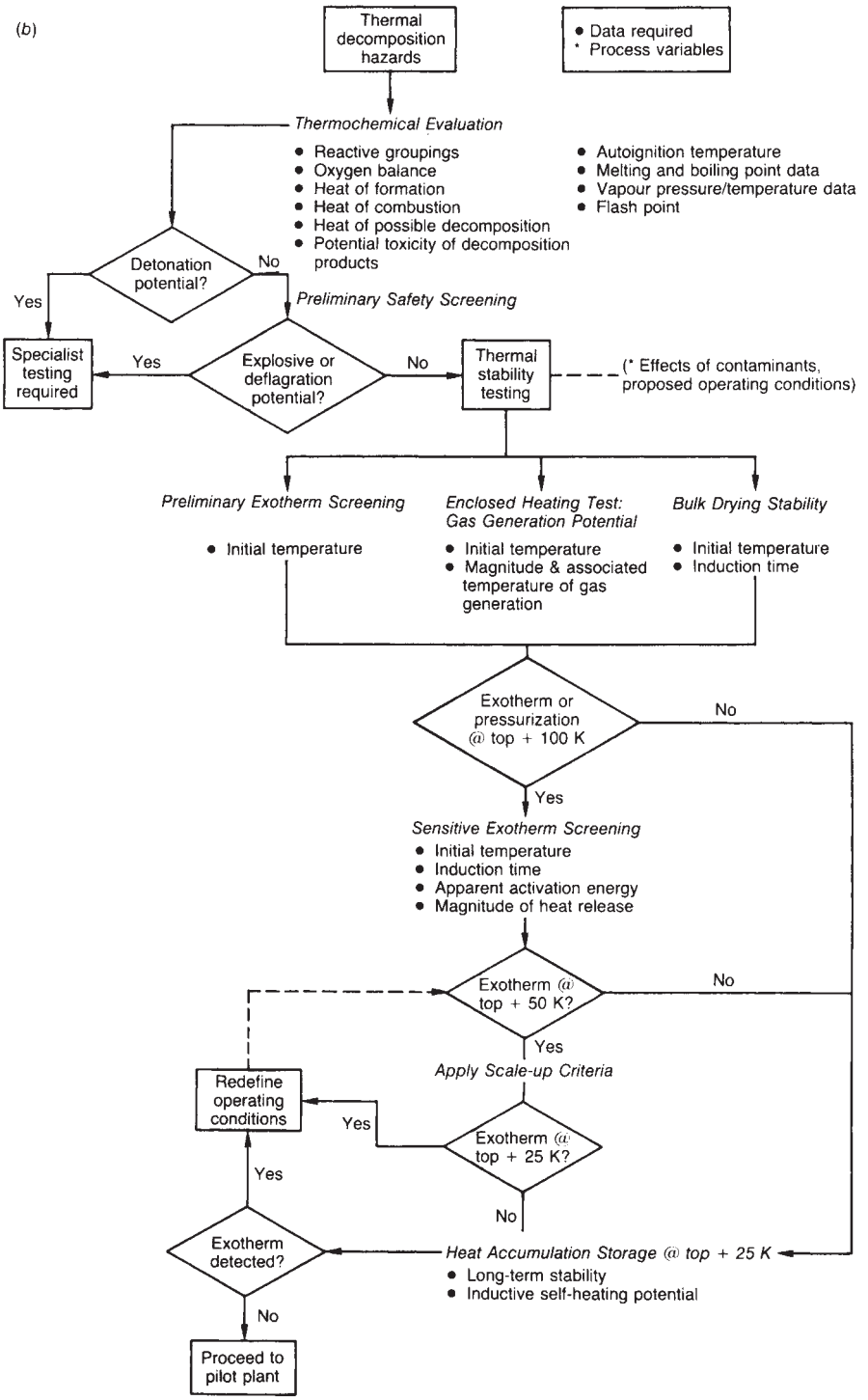


Figure 33.14 *Test scheme for thermal stability of a material: (a) test scheme of Kohlbrand (1985) (Courtesy of the American Institute of Chemical Engineers); and (b) test scheme of Cronin, Nolan and Burton (1987) (Courtesy of the Institution of Chemical Engineers)*

In this scheme, the safety screen test is the melting point tube test; the combustibility test is the train firing test; the adiabatic heating test for the main process reaction is similar to the stepped heating test using a Dewar flask.

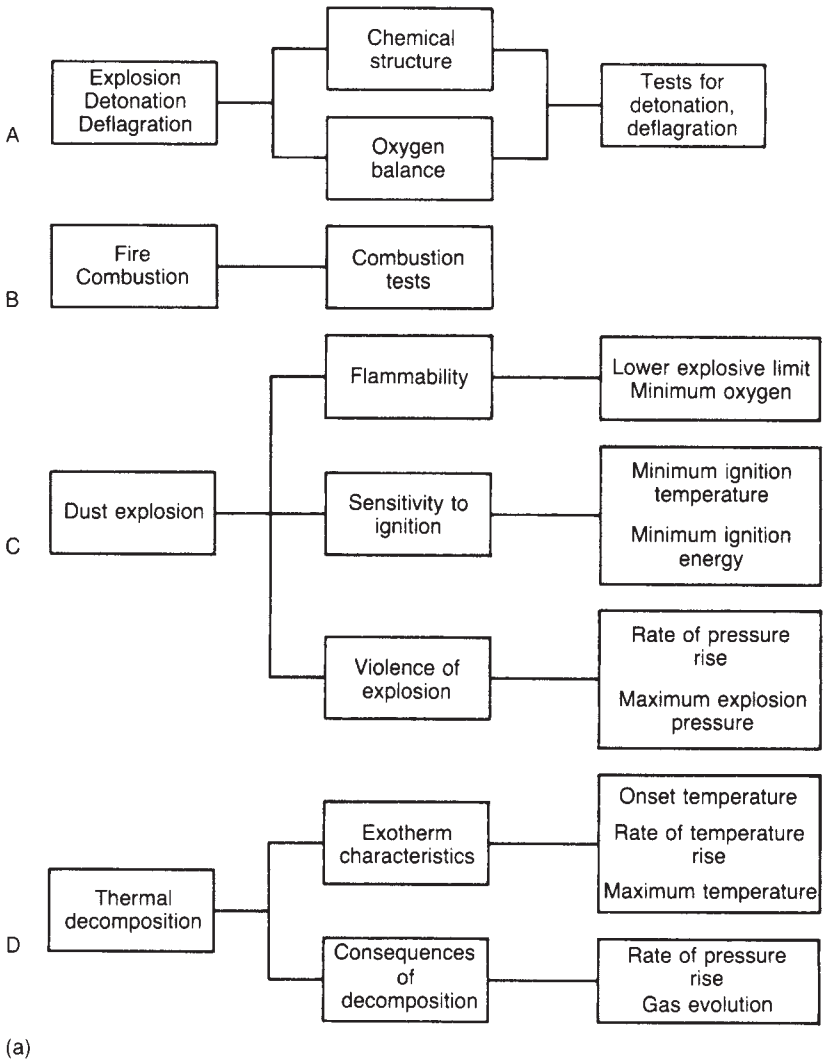
The test scheme described by Coates and Riddell (1981a,b) is very similar. Figure 33.17 shows the decision tree given by these workers.

The test scheme given by O'Brien *et al.* (1982) is shown in Figure 33.18. Other test schemes include those of Cronin, Nolan and Barton (1987) and N. Gibson, Rogers and Wright (1987), described below.

Another test scheme is that described by Kunzi (1980), who states that the problem may come in various forms, and outlines the way in which the scheme is used. It may be required to evaluate a complete process, or one stage of a process such as distillation or storage, or a single component. He gives a decision tree for approaching the general problem. Essentially, steps 1 and 2 are desk screening; step 3 is the standard laboratory tests; step 6 involves tests to characterize the process main reaction; step 8 tests to explore undesired reactions; and step 10 tests to study storage. The actual scheme used is based on the availability in the test centre of a range of instruments including the TZP as described above.

The tests in the scheme given in the ABPI *Second Guidelines* described above are:

(1) DSC;
(2) combustibility test;
(3) closed tube test;
(4) delayed onset detection test;
(5) adiabatic Dewar test;
(6) ARC;
(7) heat flow calorimeter test;



(a)

Figure 33.15 *continued*

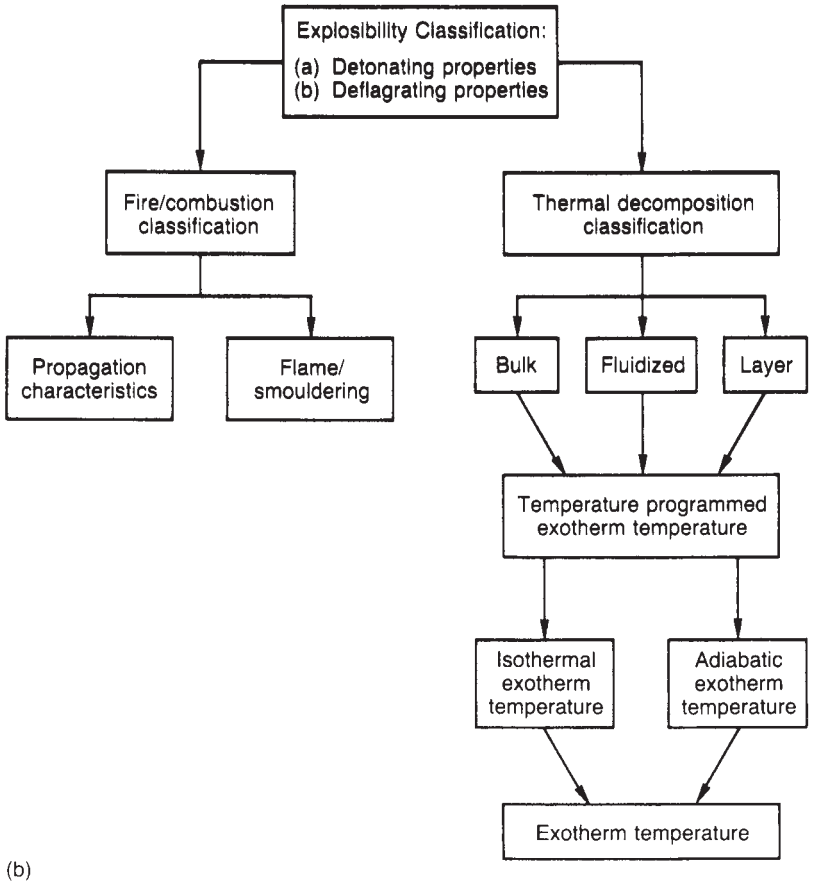


Figure 33.15 *Test schemes for thermal stability of a material with special reference to drying N. Gibson, Harper and Rogers (1985, 1986); (a) and (b) (Courtesy of the Institution of Chemical Engineers)*

(8) gas evolution measurement, using automated gas burette;
(9) gas evolution measurement, using thermal mass flowmeter.

Again, the flowchart is given in Figure 33.13.

The ICI test scheme described by N. Gibson, Rogers and Wright is shown in Figure 33.19.

The IChemE *Guide* gives the test scheme shown in Figure 33.18 and lists the following tests:

(1) initial screening tests:
  (a) DSC,
  (b) insulated exotherm test,
  (c) decomposition pressure test,
  (d) 10 g closed tube test,
(2) tests characterizing normal reaction:
  (a) Dewar calorimetry,
  (b) isoperibolic calorimetry,
  (c) power compensation calorimetry,
  (d) heat flow calorimetry,
  (e) gas evolution measurement, using automated gas burette,
  (f) gas evolution measurement, using thermal mass flowmeter,
(3) tests characterizing runaway reaction:
  (a) adiabatic Dewar calorimetry,
  (b) other types of calorimetry,
  (c) Vent Sizing Package (VSP),
  (d) Reactive Systems Screening Tool (RSST),
  (e) Phi-Tec adiabatic calorimeter.

Quantitative impact of exothermic reactions on system dynamics

Kinetics and heat effects The rate of a chemical reaction is controlled by the reaction kinetics, diffusion processes, and/or supply of reactant. The reaction considered here is the simple, irreversible first-order reaction:

$$A \rightarrow B \qquad [33.2.4]$$

with reaction kinetics which can be expressed as

$$r = \rho k x \qquad [33.2.5]$$

where r is the reaction rate (kmol/m^3 s), k is the velocity constant at reaction temperature (s^{-1}), x is the concentration of reactant A (mole fraction) and ρ is the molar density of feed and of reaction mass (kmol/m^3).

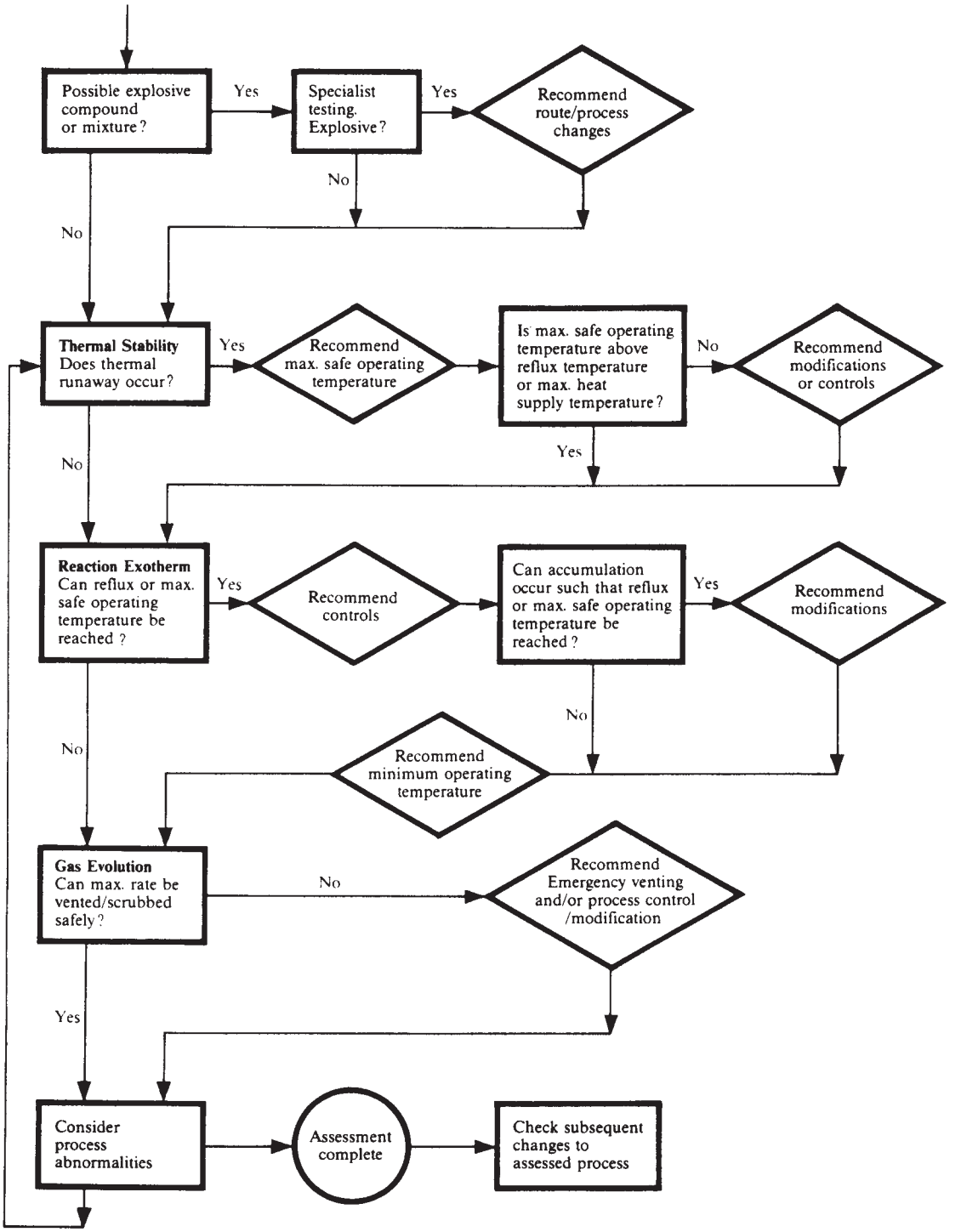


Figure 33.16 *Test scheme for assessment of thermal stability of reactant materials ABPI (1989)*

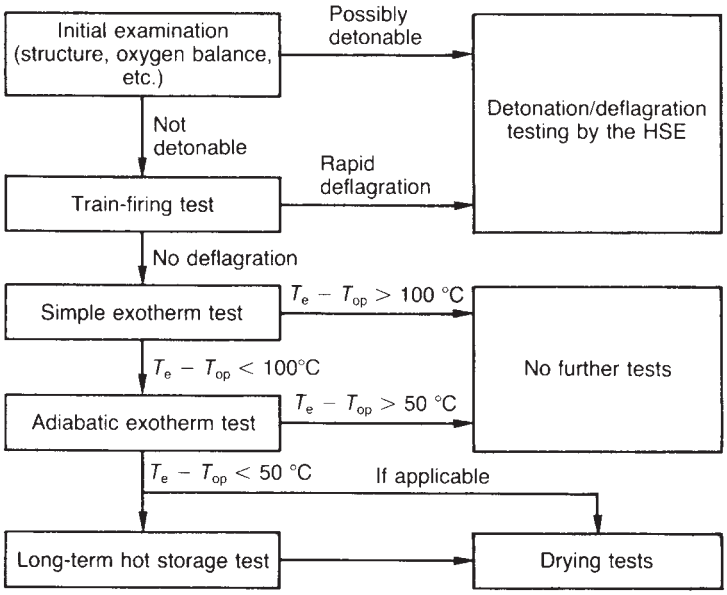


Figure 33.17 *Test scheme for chemical reactivity evaluation. T_e = lowest temperature at which exotherm occurs; T_{op} = mean temperature of intended use (Coates and Riddell (1981b)) (Courtesy of the Institution of Chemical Engineers)*

The variation of velocity constant with temperature is generally expressed in terms of the Arrhenius equation:

$$k = k_0 \exp(-E/RT) \qquad [33.2.6]$$

where E is the activation energy (kJ/kmol), k_0 is the velocity constant at the reference temperature (s^{-1}), R is the universal gas constant (kJ/kmol K), and T is the absolute temperature (K).

The reaction is accompanied by an enthalpy change so that the heat generated is:

$$Q_s = Vr(-\Delta H) \qquad [33.2.7]$$

where ΔH is the heat of reaction, which is negative for an exothermic reaction (kJ/kmol), Q_s is the heat generated by the reaction (kW), and V is the volume of the reactor (m^3). In considering reactor stability, exothermic reactions are of prime importance.

In a closed adiabatic system, the behaviour of a kinetics-controlled exothermic reaction is as shown in Figure 33.20. The reaction generates heat, which causes the temperature and, hence, the velocity constant to increase continuously throughout the course of the reaction. The reaction rate and heat generated at first increase almost exponentially due to the increase in the velocity constant, then pass through a maximum and finally decrease as the reactants become exhausted.

In many practical cases, an exothermic reaction can accelerate almost exponentially and cause overheating or explosion, if the heat is not removed from the system rapidly enough. These effects may occur while the reaction is only part way along the curves shown in Figure 33.20.

There are a number of factors, however, that can limit the acceleration of the reaction rate. One limiting factor, which applies in all cases, is the exhaustion of the reactants. This applies even for a continuous feed of reactants, because once the resident material is consumed, the reaction rate cannot exceed the reactant feed rate. Another important limiting effect is the transition in heterogeneous reactions from a kinetics-controlled to a diffusion-controlled reaction. As the temperature rises, the reaction kinetics become so rapid that they cease to be the limiting factor and diffusion takes over the role. These effects are shown in Figure 33.21(a). The dashed lines represent the reaction rates limited by the kinetics alone and by diffusion alone. The actual reaction rate, shown by the full curve, is determined by the combined effects of the kinetics and diffusion. It is limited at low temperatures by kinetics and at high temperatures by diffusion. Diffusion may be limited by the velocity in the reactor or by intra-particle mass transfer. The change of reaction rate with temperature and velocity for such a case is illustrated in Figure 33.21(b).

Another limiting factor is the relation between the reaction rate and temperature. Some of the relations that occur are shown in Figure 33.22. Figure 33.22(a) gives the normal curve of rapid rise in reaction rate with temperature; Figure 33.22(b) shows diffusion control with a slow increase of reaction rate with temperature; Figure 33.22(c) illustrates an explosion with a sudden increase in reaction rate at the ignition point; Figure 33.22(d) is for a catalytic reaction controlled by the rate of adsorption; Figure 33.22(e) corresponds to the occurrence of a side reaction, which becomes significant as temperature increases; and Figure 33.22(f) indicates a reaction in which conversion is limited by thermodynamic equilibrium effects.

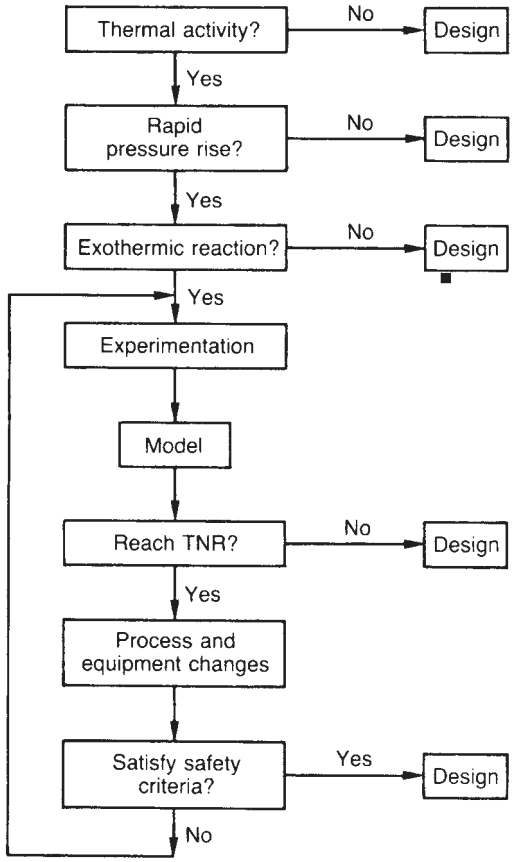


Figure 33.18 *Test scheme for chemical reactivity evaluation. TNR = temperature of no return (O'Brien et al. (1987)) (Courtesy of the American Institute of Chemical Engineers)*

Exothermic reactions in an adiabatic environment

Batch reactors: reaction hazard evaluation A theoretical treatment of an adiabatic reaction has been given by Townsend and co-workers (Townsend, 1977, 1981; Townsend and Tou, 1980). The treatment is for an nth-order reaction, but utilizes a pseudo-first-order reaction approach. For an nth-order reaction:

$$\frac{dC}{dt} = -kC^n \qquad [33.2.8]$$

with

$$k = A\exp(-E/RT) \qquad 33.2.9$$

where A is the pre-exponential factor, C is the concentration of reactant, E is the activation energy, k is the reaction velocity constant, R is the universal gas constant, t is the time, T is the absolute temperature, and n is the order of the reaction.

Consider an adiabatic reaction as shown in Figure 33.23. The adiabatic temperature rise ΔT_{ab} is:

$$\Delta T_{ab} = T_f - T_0 \qquad [33.2.10]$$

where T_f is the final absolute temperature and T_0 is the initial absolute temperature. The adiabatic temperature rise is calculated from the heat of reaction by:

$$(-\Delta H_r) = Mc_v\Delta T_{ab} \qquad [33.2.11]$$

where c_v is the constant-volume specific heat of the reaction mixture. ΔH_r the heat of reaction, and M is the mass of the reaction mixture.

The appropriate concentration–temperature relationship is approximately

$$\frac{C}{C_0} = \frac{T_f - T}{T_f - T_0} \qquad [33.2.12a]$$

and hence

$$C = \frac{T_f - T}{\Delta T_{ab}}C_0 \qquad [33.2.12b]$$

where C_0 is the initial concentration of reactant.

The self-heat rate, m_T, is obtained from Equations 33.2.8 and 33.2.12b:

$$\frac{dT}{dt} = k\left(\frac{T_f - T}{\Delta T_{ab}}\right)^n \Delta T_{ab}C_0^{n-1} \qquad [33.2.13a]$$

$$= m_T \qquad [33.2.13b]$$

A pseudo-reaction velocity constant k^* is defined as:

$$k^* = C_0^{n-1}k \qquad [33.2.14a]$$

$$= \frac{m_T}{((T_f - T)/\Delta T_{ab})^n \Delta T_{ab}} \qquad [33.2.14b]$$

From Equations 33.2.9 and 33.2.14a:

$$\ln k^* = \ln(C_0^{n-1}A) - E/RT \qquad [33.2.15]$$

Equation 33.2.15 may be used to obtain the pre-exponential factor A and the activation energy E.

The initial self-heat rate m_0 is obtained from Equation 33.2.13b and is

$$m_0 = k_0\Delta T_{ab}C_0^{n-1} \qquad [33.2.16]$$

where k_0 is the reaction velocity constant at the initial temperature. From Equations 33.2.13 and 33.2.16:

$$m_T = m_o\frac{k}{k_0}\left(\frac{T_f - T}{\Delta T_{ab}}\right)^n \qquad [33.2.17a]$$

$$= m_o\left(\frac{T_f - T}{\Delta T_{ab}}\right)^n \exp\left[-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \qquad [33.2.17b]$$

At the maximum self-heat rate:

$$\frac{d^2T}{dt^2} = 0 \qquad [33.2.18]$$

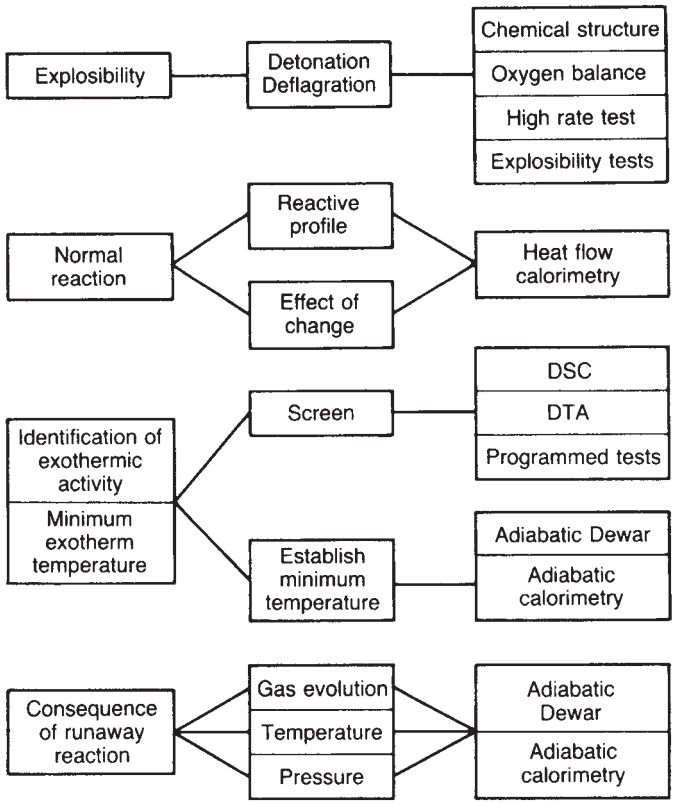


Figure 33.19 *Test scheme for chemical reactivity evaluation (N. Gibson, Rogers and Wright (1987)) (Courtesy of the Institution of Chemical Engineers)*

and hence it can be shown that

$$nRT_m^2 + ET_m - ET_f = 0 \qquad [33.2.19]$$

where T_m is the absolute temperature at the maximum rate. Then from Equation 33.2.18:

$$T_m = \frac{E}{2nR}[(1 + 4nRT_f/E)^{1/2} - 1] \qquad [33.2.20]$$

The maximum self-heat rate, m_m, is obtained by substituting T_m in Equation 33.2.17a. The time to the maximum rate is obtained as follows. Integrating Equation 33.2.13a

$$\theta_m = t_m - t \qquad [33.2.21a]$$

$$= \int_t^{t_m} dt \qquad [33.2.21b]$$

$$= \int_T^{T_m} \frac{dT}{k((T_f - T)/\Delta T_{ab})^n \Delta T_{ab} C_0^{n-1}} \qquad [33.2.21c]$$

where t_m is the time for the temperature to reach the maximum rate value at T_m and θ_m is the time to the maximum rate from temperature T.

It is possible to obtain an analytical solution of Equation 33.2.21c if it is assumed that

$$A = \alpha T^j \qquad [33.2.22]$$

where α is a constant and j is an integer. It can be shown that for a second-order reaction

$$\theta_m = \frac{RT^2}{m_T E} - \frac{RT_m^2}{m_m E} \qquad [33.2.23]$$

The same equation applies for other nth-order reactions.

If the activation energy E is high, the second term in Equation 33.2.23 is much less than the first, and hence

$$\theta_m = \frac{RT^2}{m_T E} \qquad [33.2.24]$$

Then from Equations 33.2.13b and 33.2.24

$$\theta_m = \frac{RT^2}{k((T_f - T)/\Delta T_{ab})^n \Delta T_{ab} C_0^{n-1} E} \qquad [33.2.25a]$$

$$\ln \theta_m = \ln\left[\frac{RT^2}{((T_f - T)/\Delta T_{ab})^n \Delta T_{ab} C_0^{n-1} E}\right] - \ln A + E/RT \qquad [33.2.25b]$$

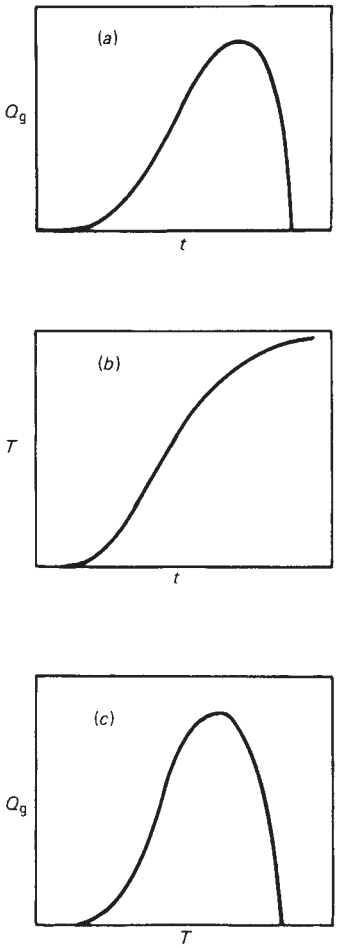


Figure 33.20 *Course of a kinetic controlled exothermic reaction in a closed adiabatic system: (a) heat generated vs time; (b) temperature vs time; (c) heat generated vs temperature*

But, under the same assumption of a high activation energy, the second term in Equation 33.2.25b is much greater than the first, and hence

$$\ln \theta_m = -\ln A + E/RT \qquad [33.2.26a]$$

or, from Equation 33.2.9,

$$\ln \theta_m = \ln k^* \qquad [33.2.26b]$$

$$\theta_{m0} = \frac{RT_0^2}{k_0 \Delta T_{ab} C_0^{n-1} E} \qquad [33.2.27a]$$

The time, θ_{m0}, to maximum rate at temperature, T_0, and thus from the start of the reaction, is obtained from Equation 33.2.25a by substituting k_0 and T_0 for k and T, respectively

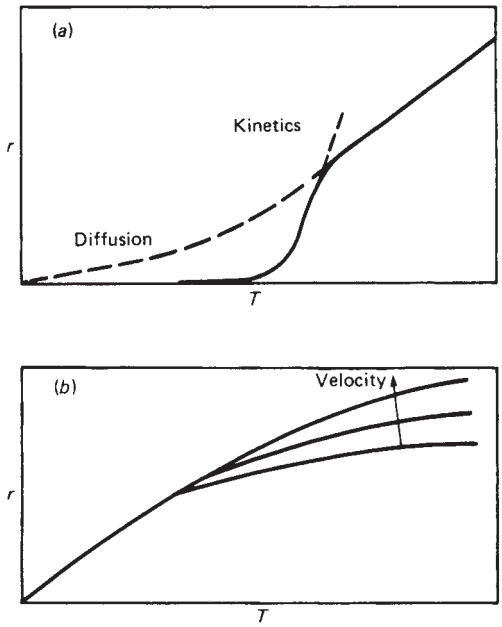


Figure 33.21 *Kinetic and diffusion control of a heterogeneous reaction: (a) transition from kinetic to diffusion control as temperature increases (Denbigh and Turner, 1971) (Courtesy of Cambridge University Press); (b) increase in rate of a diffusion controlled reaction with reactor velocity*

Similarly, substituting T_0 for T in Equation 33.2.26a

$$\ln \theta_{m0} = -\ln A - E/RT_0 \qquad [33.2.27b]$$

33.2.2 Identification of reactive hazards scenarios

A review should be conducted to determine credible pathways by which the identified reactive hazards can potentially pose significant threats to the process or equipment (Table 33.11). It is important to capture not only the deviation initiating a potential event, but also the sequence events that can follow. Care should be taken not to place too much credit for existing mitigations at this point to ensure that scenarios are not immediately dismissed before a proper assessment of risk is performed. Once reactive hazards scenarios have been identified and developed in such a review, the potential severity and frequency of each event can be evaluated.

Emphasis in the review should focus on potential events that could lead to 'high consequence' events. This will encourage resources to be focused on the more significant scenarios. The definition of 'high consequence' will be specific to the particular company or organization, but as a benchmark, potential events that can be life-threatening, substantially damage assets or cause production loss, severely impact the environment or damage the company's/organization's reputation should be considered. Downtime can be caused by asset damage. It can also arise from a shut-down of facilities to address a violation of code or standard. In this manner, exceedance of more-stringent

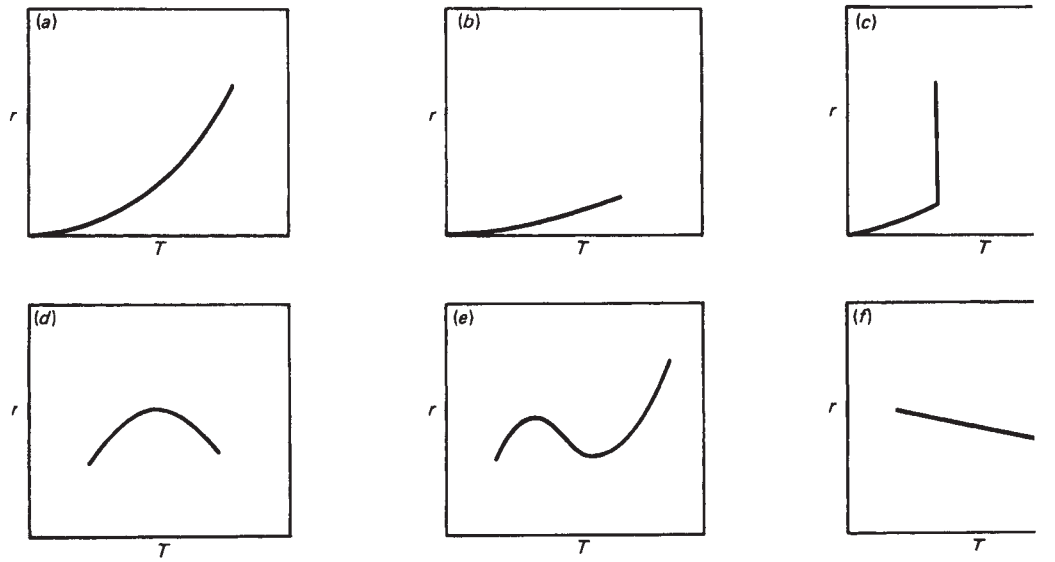


Figure 33.22 *Some principal types of variation of reaction rate with temperature (after Frost and Pearson, 1961): (a) kinetic-controlled reaction; (b) diffusion-controlled reaction; (c) sudden explosive reaction; (d) adsorption-controlled reaction; (e) side reaction; (f) equilibrium-limited reaction (Reproduced with permission from Kinetics and Mechanisms, 2nd edn, by A.A. Frost and R.G. Pearson, Copyright ©, 1961, John Wiley and Sons Inc. Figure 32.22(b) is additional to the figures given by these authors)*

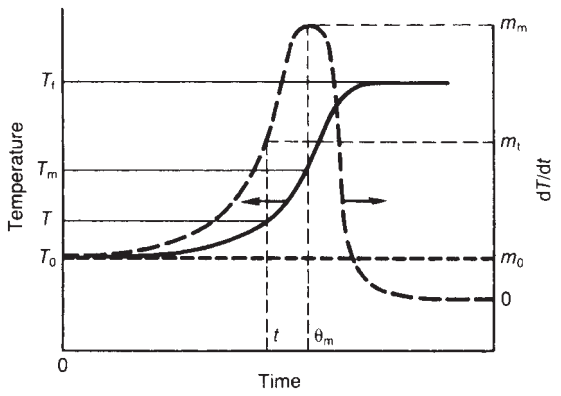


Figure 33.23 *Temperature and self-heat rate of an adiabatic reaction (Townsend and Tou, 1980) (Courtesy of Elsevier Publishing Company)*

local regulations, which could threaten the unit's license to operate, may also be considered a high consequence event.

The review should focus exclusively on reactive hazards. Use of the Hazard Operability (HazOp) method (with standard 'guidewords') can bring a structured, thorough approach to identifying deviations. However, it can also cause the review to spend substantial time on safety matters unrelated to reactivity. It may be most expedient to devote attention to deviations that have some possibility for high consequence outcomes.

Table 33.11 *Examples of standard initiating events and upset scenarios*

1. High start or operating temperature
2. High reactant concentration
3. Low solvent or diluent concentration
4. High level
5. High catalyst concentration
6. Low catalyst concentration
7. Increased heating or decreased cooling to process
8. Fire exposure
9. Loss of power
10. Contact between usually separated, reacting chemical
11. Exposure of air-sensitive or water-sensitive materials
12. Handling of dust-generating material
13. Potential to accumulate or 'pool' reactant (e.g. during unit start-up)
14. Special start-up or shut-down issues
15. Change of catalyst type, grade or supplier
16. Phase separation of reactants
17. Unexpected loss of (catalyst) activity
18. Change in residence time (including extended storage time of reactive intermediates)
19. High flow
20. Low or no flow
21. Low start or operating temperature
22. Sudden change in flow or pressure (gas)
23. Procedure steps out of order
24. Slop tank operation
25. Feed change
26. Disturbances in linked units or shared equipment
27. Transients in recycle streams
28. Backflow or feed upsets from linked units
29. Heat exchanger leakage

Guidewords and pathways pertaining to normal operations, off-normal operations (including start-ups and shut-downs) and deviations from normal operations should be examined. The resultant sequence of events that could ultimately lead to a high consequence incident is then captured. In general, the determination of the *actual* consequence for a particular scenario can require significant time to set up and carry out the needed calculations. Follow-up is therefore assigned to the appropriate resource to validate the *perceived* consequence after the review. Thus, the risk is not assessed in the review; rather it is best carried out subsequently. For this reason, existing and anticipated mitigation measures are not discussed extensively at this stage.

Examples of reactivity-related initiating events appear in Appendix C. This list, as well as a list of previous incidents, can be examined to ensure that these events have been considered in the review.

Given the potential for a high consequence incident arising from a reactivity event, it may be prudent to consider selected multiple jeopardy scenarios (a 'jeopardy' being an initiating deviation, not including a failed response by people or instrumentation to a deviation). The number of combinations of deviations can be quite large, so attention should be directed towards those combinations of jeopardies in which the reactive hazards of the process can be manifested as *high* consequence events. Note that a runaway reaction itself is not a jeopardy but a consequence of operating under upset conditions. This means that, for example, heat input from a plant fire leading to an increased reaction rate is a *single* jeopardy scenario.

Since each facility is unique in equipment configuration, operating conditions, operating procedures and perhaps even in species compositions, care should be taken that scenario identification focus on the specific facility being addressed and that the review be thorough. Similar process units, even if in different manufacturing locations, will likely have many scenarios in common but the unique aspects above can result in generation of distinct scenarios. It is conceivable that two facilities at the same manufacturing location can have differing scenarios.

The review for an entire facility can extend to all process equipment (typically, the vessels and tanks) – that is, not just the reactor. When conducting such reviews, it is good practice to 'divide' a process unit into subsections or 'nodes' to reduce the complexity of the process. Example nodes can be: feed preparation, pre-reactor separations, reactor, post-reactor separations, finishing and product/off-spec/by-product storage. For change management, small projects or incident follow-up studies, a narrower selection of equipment may be acceptable.

It is beneficial to provide to the review team documentation summarizing the reactivity information as well as Process or Engineering Flow diagrams. Process and Instrumentation diagrams can serve as a reference in case more specific information is needed.

To ensure that the process is thoroughly studied with ample consideration for actual operating practice and configurations, the review team should include the following as participants:

(1) Process support engineer;
(2) Plant support engineer;
(3) Plant operator;
(4) RHA specialist.

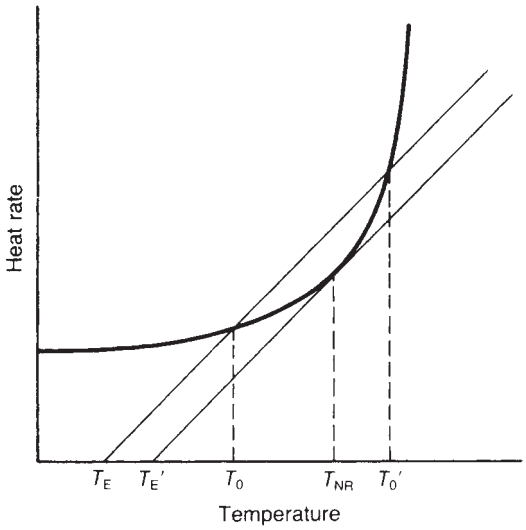


Figure 33.24 *Self-heat rate and heat transfer of a reaction with cooling: (Townsend and Tou, 1980) T_E, temperature of heat exchanger; T_{NR}, temperature of no return; T_a initial temperature; dash (′) indicates alternative set of values (Courtesy of Elsevier Publishing Company)*

In addition, an identified facilitator, scribe and safety specialist may be required (though these roles may be carried out by the listed attendees).

All likely scenarios should be described in detail indicating clearly what the cause of the scenario is, how the unmitigated scenario develops, and what the ultimate consequence might be. In addition, the resource to be employed in follow-up, where needed, and the type of follow-up are recorded.

33.2.3 Reactive hazards risk assessment

Issues during scale-up

Consider a system with external cooling. The heat generation and heat removal curves for such a system are shown in Figure 33.24. As the reaction rate and, hence, the heat evolution increase, a temperature may be reached at which the rate of heat evolution exceeds the heat removal capacity of the system; this is the temperature of no return T_{NR}. From Equation 33.2.16 the rate of heat evolution Q_e is:

$$Q_e = Mc_v K_0 \Delta T_{ab} C_0^{n-1} \qquad [33.2.28]$$

The rate of heat removal Q_r is:

$$Q_r = UA_c(T_0 - T_c) \qquad [33.2.29]$$

where A_c is the surface area for heat transfer, T_c is the absolute temperature of the coolant, and U is the overall heat transfer coefficient. Equating the heat evolution and removal rates given in Equations 33.2.28 and 33.2.29

$$Mc_v A \exp\left(-\frac{E}{RT_0}\right)\Delta T_{ab} C_0^{n-1} = UA_c(T_0 - T_c) \qquad [33.2.30]$$

It can be seen from Figure 33.24 that Equation 33.2.30 has two solutions. No runaway reaction should occur if the

initial temperature of the reaction mass T_0 is below a critical value T_0 and the temperature of the coolant T_c is below a critical value T_c. But as T_0 increases to the temperature of no return T_{nr}, there is a single solution. At this point, the slope of the line of heat evolution equals that of the line of heat removal. Then from Equations 33.2.9, 33.2.28 and 33.2.29:

$$Mc_v k_0 \left[\frac{E}{RT_0^2}\right] \Delta T_{ab} C_0^{n-1} = UA_c \quad [33.2.31]$$

The time θ_{Tnr} to the maximum rate at the temperature of no return T_{nr} is, from Equations 33.2.27a and 33.2.31:

$$\theta_{Tnr} = \frac{RT_0^2}{k_0 \Delta T_{ab} C_0^{n-1} E} \quad [33.2.32a]$$

$$= \frac{Mc_v}{UA_c} \quad [33.2.32b]$$

The group (Mc_v/UA_c) is known as the 'equipment time line'.

The case where the maximum self-heat rate coincides with the initial self-heat rate is of interest. For this:

$$m_m = m_0 \quad [33.2.33]$$

and

$$T_m = T_0 = T^* \quad [33.2.34]$$

say, where T^* is the minimum initial absolute temperature above which only deceleration of the reaction occurs.

Then from Equations 33.2.19 and 33.2.34 and noting that

$$T_f = \Delta T_{ab} + T^* \quad [33.2.35]$$

$$T^* = (E\Delta T_{ab}/nR)^{1/2} \quad [33.2.36]$$

Thus, theoretically, there exists a temperature above which the effect of concentration depletion on the reaction rate is greater than that of acceleration due to temperature.

The parameters used in the foregoing analysis are the true parameters of the reaction. In practice, they have to be calculated from experimental measurements, which are affected by the thermal capacity of the container. The true adiabatic temperature rise ΔT_{ab} is related to the adiabatic temperature rise ΔT_{abs} of the sample:

$$Mc_v \Delta T_{ab} = (Mc_v + M_b c_{vb}) \Delta T_{abs} \quad [33.2.37]$$

or

$$\Delta T_{ab} = \phi \Delta T_{abs} \quad [33.2.38]$$

with

$$\phi = 1 + \frac{M_b c_{vb}}{Mc_v} \quad [33.2.39]$$

where c_{vb} is the specific heat of the sample container and M_b is the mass of the container. The quantity ϕ is the thermal inertia and its reciprocal is a measure of the degree of adiabaticity. Similar corrections apply to the other measured quantities:

$$m_0 = \phi m_{os} \quad [33.2.40]$$

$$\theta_m = \theta_{ms}/\phi \quad [33.2.41]$$

where m_{os} is the measured self-heat rate at temperature T_0 and θ_{ms} is the measured time to maximum rate at temperature T.

Consequence assessment

The intent of consequence assessment is to determine which scenarios need prevention or mitigation action. This facilitates effective utilization of resources for evaluation and implementation. Scenarios that have been generated are screened and evaluated for potential to lead to *high* consequence events. Each scenario found to be capable of yielding a high or excessive consequence event is highlighted and may be addressed through likelihood assessment and risk reduction measures, if needed.

In consequence assessment, all scenarios generated should be evaluated based on the consequences with regards to the design of the unit (e.g. design pressure, design temperature or depending on local regulations the temperature where failure in the metallurgy is experienced). If the consequence is not evaluated, then the likelihood directly should be evaluated along with a decision to ensure that the likelihood falls below the corporate or organization's tolerable risk frequency.

Reactive hazards, by definition, lead to an excursion in temperature and/or pressure. To ascertain whether a high consequence event could occur, the extent of temperature and pressure rise associated with each scenario should be evaluated. This test can be carried out by a variety of means, including spreadsheet calculations for simple steady-state operations or a dynamic simulation for more complex systems.

In evaluating the consequences of a scenario, it may be prudent to take no credit for operator procedures and training, instrumentation and mechanical relief (these can be examined during likelihood assessment). However, inherent constraints to the development of the consequence, such as maximum heating medium temperature, equilibrium (thermodynamic)-limited reactant conversion or catalyst deactivation, etc., can be accounted for in the calculations. Continued exposure to an external fire heat input combined with reaction heat, though, can lead to temperatures far beyond the rating of the equipment. In a fire exposure scenario in which reaction is taking place, the consequence can be presumed to be high, and the calculation will essentially determine the time taken to exceed allowable levels. (The appropriate standard, e.g. NFPA 30 or API RP 521, should be applied for the heat input flux.)

For effective use of resources, it may be advisable to identify scenarios, at an early stage, that can serve as worst-case scenarios for similar scenarios. In this manner, if the worst-case scenarios do not yield a high consequence, neither will the lesser scenarios. However, if the more severe scenario does have potential to yield a *high* consequence, the consequences of the successively less severe scenarios should also be evaluated so that proper safeguarding can be performed.

The resultant maximum temperature and pressure should be compared to appropriate criteria (e.g. design temperature, design pressure and material properties) to determine whether the consequences are *high* or not. Internal corporate or organizational criteria can serve as a minimum for this purpose. National, state or local regulations may impose stricter criteria that must be followed. For example, the exceedance of equipment design temperature

is prohibited in some countries and can be considered a threat to a facility's license to operate.

Consequence assessment results should be summarized for each corresponding scenario generated from the review. The extent of temperature and pressure rise, what further action (if any) is needed and whether the scenario should be addressed via likelihood assessment should be documented.

Mixing and heat transfer

The reaction and heat transfer behaviour of the reactor is strongly affected by the degree of mixing. There may well be departures from near-perfect mixing, and with highly viscous reaction masses these may be considerable.

The IChemE *Guide* gives two models of the profile of the temperature between the centre of the reaction mass and the wall. The first is a uniform temperature, the Semenov model, applicable where the reaction mass is well mixed. The second is a sigmoidal temperature profile, the Frank–Kamenetsky model, applicable where the mass is unmixed. This latter model is fundamental to thermal explosion, or self-heating theory and is treated in Chapter 16. Reactor situations where the temperature in the reaction mass is liable to rise may be treated using thermal explosion models.

The conventional treatment for the case where the mass is poorly mixed is the Frank–Kamenetsky thermal explosion model, as described in Chapter 16. Specifically, the equations generally quoted are those used in relation to the experimental determination of the critical value of the ignition parameter δ_C, namely Equations 16.6.107–16.6.109.

The *Guide* also quotes the simpler treatment by Leuschke (1981), which yields the relation:

$$\ln \frac{V}{S} \propto \frac{1}{T_d} \qquad [33.2.42]$$

where S is the surface area of the mass, T_d is the minimum decomposition temperature, and V is the volume of the mass.

With regard to heat transfer coefficients, correlations are available for the heat transfer coefficients on the inside of a stirred reactor and on the outside of the vessel in the jacket. Accounts of reactor heat transfer coefficients are given by Chapman and Holland (1965a,b). A method widely used for the film heat transfer coefficient on the inside of the vessel is that of E.E. Wilson (1915). The effect of agitator geometry on this coefficient may be taken into account by the use of a geometric factor, and a correlation is available for this factor also. Details are given in the IChemE *Guide*, which also discusses cases that are non-ideal due to non-Newtonian behaviour, and so on. The *Guide* also gives a treatment of reactors operated under reflux conditions.

Reaction simulation testing

The testing described thus far is fairly formal, employing specific laboratory tests within the framework of a test scheme. One of the recognized tests, however, is the Dewar flask test in which the conduct of the reaction is explored.

There are a number of accounts of various laboratory tests conducted to explore the conduct of the reaction. Coates and Riddell (1981a,b) have described a 'worst case' analysis of a nitration reaction in a semi-batch reactor. The heat of reaction and the rate of heat evolution were determined in a calorimeter and used to select the time over which the fed reactant should be added, or the 'addition time'. Non-normal conditions were investigated such as accumulation of unreacted nitric acid in the reactor and the effect of this on the temperature of the reaction mass when reaction did occur. These authors also describe two other reaction studies.

The IChemE *Guide* describes the use of Dewar calorimetry to mimic the plant reactor and explore reactor configurations, agitation, cooling and heating systems, addition of gases, liquids and solids, and so on.

33.2.4 Batch reactors: basic design

Inherently safer design

The application of the principle of inherently safer design to the choice of reaction route was described in Section 11.7 of Chapter 11. An account is given here of its application to batch reactors, which has been advocated particularly by Regenass (1984). The approach described by this author depends essentially on the avoidance of high concentrations of the reactants. One method of limiting reactant concentration is the use of a semi-batch, or 'fed-batch', reactor in preference to an 'all-in' batch reactor. In the latter, all the reactants are added in the initial charge; in the former, one of the reactants is added continuously. The hazard in the all-in design is that conditions may occur in which there is a sudden massive reaction of the unreacted reactants. This is liable to occur, for example, on resumption of agitation after an agitator failure. In the semi-batch reactor, the continuous feed arrangement, combined with a suitable reactor temperature, keeps the concentration of one of the reactants relatively low and it is possible to effect prompt shut-off of the feed if a potentially hazardous operating deviation occurs.

The full benefit of the semi-batch reaction mode does depend, as just indicated, on the adoption of a suitable reaction temperature. If this temperature, and therefore the reaction rate is too low, accumulation of the fed reactant can occur. The reaction temperature should be high enough to ensure that the reaction proceeds sufficiently rapidly to avoid accumulation.

An example of the application of this principle has been given by Fierz *et al.* (1983, 1984), who describe the design of a semi-batch reactor for the further nitration of a substituted nitrobenzene. Two operating temperatures were investigated—80°C, and 100°C—using a bench scale calorimeter (BSC). At 80°C, shut-off of the feed at the worst instant, when the reactants are present in equimolar proportion, resulted in heat release before and after shut-off of 90 and 180 kJ/kg of final reaction mass, respectively, whilst at 100°C the corresponding figures were 190 and 80 kJ/kg. At the lower operating temperature, the heat release was sufficient under adiabatic conditions to give a temperature rise of 110°C, taking the temperature to 190°C, at which temperature an undesired exotherm would occur, whilst at the higher operating temperature, the adiabatic temperature rise was only 40°C, taking the temperature to only 140°C. Figure 33.25 shows results obtained from the BSC work.

Safe operation criteria

Methods are available for the prediction of safer operating regimes for both batch and semi-batch reactor modes. One approach is based on the application of the Semenov thermal explosion model to the case of a well mixed reactor. This

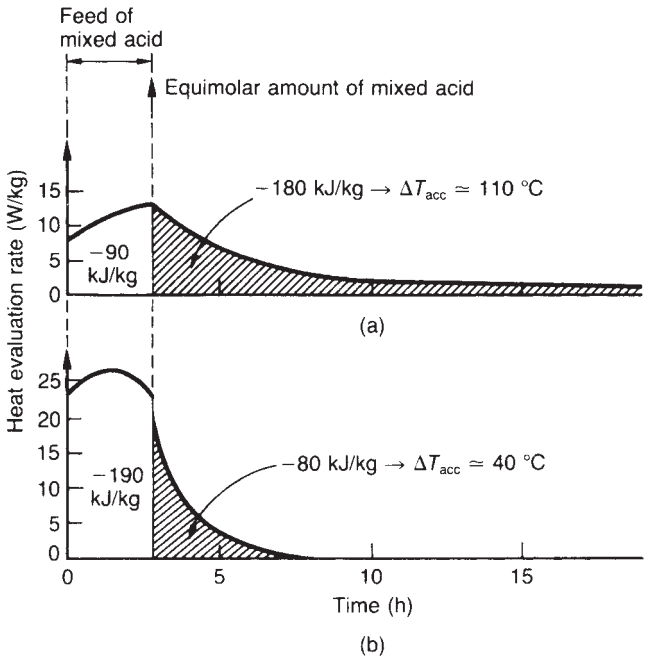


Figure 33.25 *Heat effects in a semi-batch reactor at reaction temperatures of (a) 80° C and (b) 700° C (Fierz et al., 1984) (Courtesy of the Institution of Chemical Engineers)*

model applies to a liquid mass with agitation and convection. An account is given by Grewer *et al.* (1989).

A limiting condition for the reactor with cooling but without reaction can be derived from the adiabatic induction time. This is:

$$\frac{d\theta}{dt} = -\kappa\theta \qquad [33.2.43]$$

with

$$\kappa = \frac{UA_c}{Vc_p\rho} \qquad [33.2.44]$$

where A_c is the surface area for heat transfer, c_p is the specific heat of the reaction mixture, t is the time, U is the overall heat transfer coefficient, V is the volume of the reaction mixture, K is the cooling parameter, θ is a dimensionless temperature difference, and ρ is the density of the reaction mixture. The critical condition for thermal explosion is:

$$\tau_{ad}\kappa = e \qquad [33.2.45]$$

where e is the base of the natural logarithm.

The authors define the degree of conversion X in terms of the fraction of heat released. They state that experience shows that for a batch reaction the following equation may be used:

$$r = r_0(1-X)^n \qquad [33.2.46]$$

with

$$r_0 = kc_{A0}c_{B0} \qquad [33.2.47]$$

where c is the concentration, k is the reaction velocity constant, r is the rate of reaction, n is the effective order of the reaction and subscripts A, B and 0 indicate reactant A, reactant B and initial conditions, respectively. For a semi-batch reaction a relation which fits most cases is:

$$r = r_0\frac{(1-X)(t/\tau_D - X)}{1 + V_D t/V_0\tau_D} \qquad [33.2.48]$$

with

$$r_0 = kc_{A0}c_{BD} \qquad [33.2.49]$$

where V_D is the volume of addition, V_0 is the initial volume, τ_D is the time of addition and subscript D indicates addition.

The authors define a thermal reaction parameter B:

$$B = \frac{E\Delta T_{ad}}{RT^2} \qquad [33.2.50]$$

where E is the activation energy, R is the universal gas constant, T is the absolute temperature, and ΔT_{ad} is the adiabatic temperature rise. They state that in relative terms a reaction can be regarded as non-critical provided that for batch reactions $B < 5$ and for semi-batch reactions $B < 10$.

Another important parameter is the Damköhler number Da, which is a measure of the rate of reaction:

$$\mathrm{Da} = \frac{(-v_u) r_0 t}{c_0} \qquad [33.2.51]$$

where c_0 is the initial concentration of the limiting minor component, and v_u is the stoichiometric coefficient of that component.

For a batch reaction the aim is to have a slow or only moderately fast reaction so as to avoid overloading the cooling capacity. For this Da<1 is a suitable condition. By contrast, for a semi-batch reaction the aim is to maintain a reaction rate sufficiently fast to prevent the accumulation of reactants. This is assured provided that Da>100.

A measure of the cooling capacity is given by the Stanton number St:

$$\mathrm{St} = \kappa t \qquad [33.2.52]$$

where for a batch reactor t is the reaction time and for a semi-batch reactor it is the time of addition τ_D.

For reactors with jacket cooling only a further criterion is the ratio of the Damköhler and Stanton numbers Da/St, known as the 'stability'. For a batch reactor, the ratio Da/St should be <<l and for a semi-batch reactor it should be >1. For a multi-phase reaction, an effective Damköhler number is used which takes into account additional mass transfer phenomena.

The foregoing applies to the case of a well-mixed reactor at more or less constant temperature. Other conditions, particularly stoppage and restart, may be allowed for by using in the Damköhler number a critical temperature. For a batch reactor this critical temperature is the highest temperature which can occur in the reactor, and for a semi-batch reactor it is the lowest which can occur. This latter is the reference temperature T_{ref} defined as:

$$T_{\mathrm{ref}} = \frac{T_{\mathrm{f}} + \mathrm{St} T_{\mathrm{c}}}{1 + \mathrm{St}}$$

where subscripts c, f and ref indicate coolant, feed and reference, respectively. The reference temperature is the temperature produced in the reactor by feed addition and by cooling, but without reaction, and is the lowest which can occur, because the feed temperature is usually less than the jacket temperature. At this temperature, the rate of reaction is lowest and the danger of accumulation of reactants highest.

Reactor modelling

The most fundamental understanding of the reaction system is obtained by modelling it. An account of such modelling has been given by Gordon *et al.* (1982). These authors describe the modelling of the reaction of the amination of o-nitrochlorobenzene (ONCB) with aqueous ammonia under pressure to produce o-nitroaniline (ONAN). The study included the determination of the heat of reaction and the reaction kinetics for the animation and the heat of reaction and reaction kinetics for the decomposition of ONAN. The model was validated by comparing model predictions with ARC results and with temperature and pressure profiles of the plant reactors in normal operation and from a reactor incident.

Difficult reactions

One type of reaction that may be difficult to handle is one with a low activation energy, since this means that the reaction rate increases very rapidly with temperature. Another difficult type of reaction is one in which the vapour pressure of the reaction mixture is low. In this case, high temperatures can be reached before the pressure relief system responds. This problem is discussed by Regenass (1984).

Secondary reactions

In addition to the primary reaction, there may be one or more secondary reactions. If such a secondary, or side, reaction is exothermic, it may constitute a hazard. This problem has been discussed by Grewer *et al.* (1989).

Whether a secondary reaction occurs may be established using DTA. If it does, the temperature T_s at which the secondary reaction takes place is estimated by subtracting 100 K from the start of the reaction as given by the DTA. This estimate of T_s is compared with the reaction temperature T_r or the maximum possible reactor temperature T_{max}:

$$T_{\mathrm{max}} = T_{\mathrm{r}} + \Delta T_{\mathrm{ad}} \qquad [33.2.53]$$

where ΔT_{ad} is the adiabatic temperature rise (K), T_{max} is the maximum absolute temperature (K), T_r is the reactor temperature (K), and T_s is the absolute temperature of the secondary reaction. If the estimate of T_s is greater than T_{max} there is no hazard and further investigation is not required.

Use may also be made of the reaction energy of the secondary reaction. This may be obtained from the DTA by integration. A small reaction energy of <110–220 kJ/kg or an adiabatic temperature rise of <50–100 K indicates there is no hazard.

If the DTA does not yield clear-cut conclusions, it is necessary to obtain T_s more precisely. The AZT 24 may be determined. If this temperature is greater than T_{max}, again there is no hazard.

If T_s lies between T_r and T_{max} there may be an appreciable hazard, but it may still be possible to carry out the reaction provided it can be ensured that the reactor temperature does not reach T_s during the primary reaction. Alternatively, if this cannot be guaranteed, use may be made of appropriate protective measures. Operation in this region is a specialist matter.

If T_s for a highly exothermic reaction is equal to or less than T_r, it is rarely possible to carry out the primary reaction safely. These guidelines are summarized in Figure 33.26.

Decompositions

Grewer *et al.* (1989) give the following guidance on decomposition reactions. For single phase decomposition of organic substances, if the decomposition energy based on total reaction mass is <100–200 kJ/kg, which corresponds roughly to $\Delta t_{\mathrm{ad}} \approx 50$–100 K, the effect of the decomposition is generally not critical. Even for a decomposition energy above the range just quoted, the effect may not be critical if there are other compensating effects such as endothermic reactions or high heat removal capacity. For inorganic substances the criterion decomposition energy should be lower, due to the lower specific heat, whilst for substances containing water it should be higher. The authors state that the decisive criteria are the adiabatic temperature rise ΔT_{ad} or the thermal reaction parameter B, which should not exceed about 8.

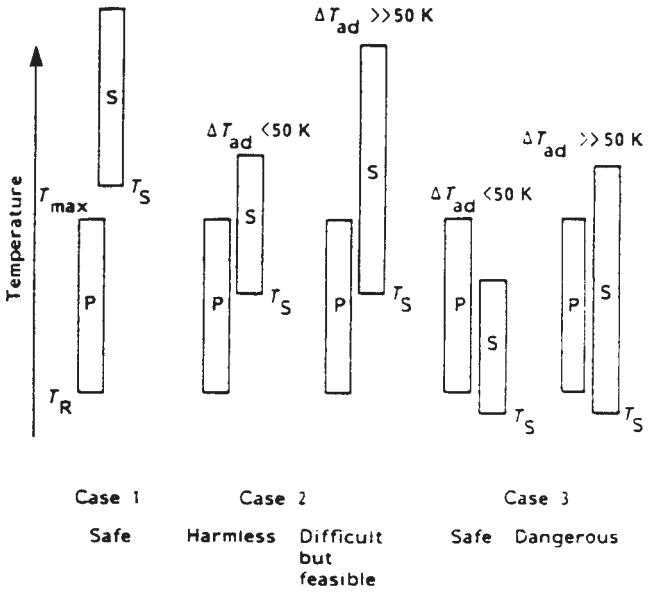


Figure 33.26 *Hazards of side reactions (Grewer et al., 1989) P, primary reaction; S, secondary reaction; T_{max}, maximum reactor temperature; T_R, temperature of reactor; T_s, temperature at which secondary reaction occurs; ΔT_{ad}, adiabatic temperature rise*

Spontaneous ignition

Another hazard of batch reactors is spontaneous ignition of vapour–air mixtures in the vapour space of the reactor. Work on this has been described by Snee and Griffiths (1989). The problem arises particularly in resin manufacture. Experiments were performed using cyclohexane as a substrate related to the components of resins, employing vapour-rich mixtures with molar ratios of cyclohexane/air of 1:2, in closed vessels in the size range 0.2–20 dm^3.

The work showed that fuel-rich mixtures undergo autocatalytic isothermal oxidation, that in this situation the temperature may be increased by self-heating and that as a result spontaneous ignition can occur. Self-heating was found to set in at temperatures just below the autoignition temperature. The minimum temperature for spontaneous ignition decreased as vessel size increased. Using the Semenov thermal explosion model, the authors were able to make comparative predictions of the trend of the minimum temperature with vessel size, but state that absolute predictions would require extremely accurate kinetic data.

Heat loss from reactors

Information on the rate of heat loss from a batch reactor has been given by T.K. Wright and Rogers (1986). They give data on cooling, mainly over the temperature range 96–80°C, for a range of reactors, of different sizes, stirred and unstirred, with different thicknesses of insulation and with none, and with jackets full and empty. The data are for reactors in the full condition.

They correlate the data by plotting the rate of cooling against the cube root of the volume, on the assumption that the rate is proportional to the surface/volume ratio of the reactor, which for a sphere is proportional to the reciprocal of the radius or of the cube root of the volume. Their results are shown in Figure 33.27. Also shown in the figure are the rates of heat loss from 250 and 500 ml Dewar flasks. These entries show that these flasks have heat losses comparable, respectively, to 0.5 and 2.5 m^3 reactors and will not give a satisfactory simulation above these reactor sizes.

33.2.5 Likelihood assessment

All scenarios identified as yielding high consequences are examined to determine the risk, if existing safeguarding measures are adequate, and if any additional measures are needed to reduce the risk to tolerable levels. The initial basis for evaluation can be the existing safeguarding philosophy and measures (including instrumentation, mechanical relief, kill systems, etc.) of the unit considered.

The risk associated with a scenario is the combined likelihood and consequence for that scenario. For scenarios that are ranked as 'high' consequence, the likelihood can be evaluated in qualitative terms (e.g. has already occurred in the company, has occurred in industry, etc.); semi-quantitative terms, as determined through, for example, a Layers of Protection Analysis (LOPA); or in quantitative terms, through a fully-executed Quantitative Risk Assessment (QRA). In LOPA, standard failure frequencies for various actions and barriers are combined with the safeguarding scheme logic to yield the likelihood of occurrence of the overall scenario consequence (not just the initiating event). This approach is much more expedient and much less resource-intensive than performing a rigorous QRA, thus making the LOPA an attractive balance between cost and meaningful results.

The likelihood assessment should take into account the availability and reliability of relevant factors in the possible development of a scenario. For example, probability of a

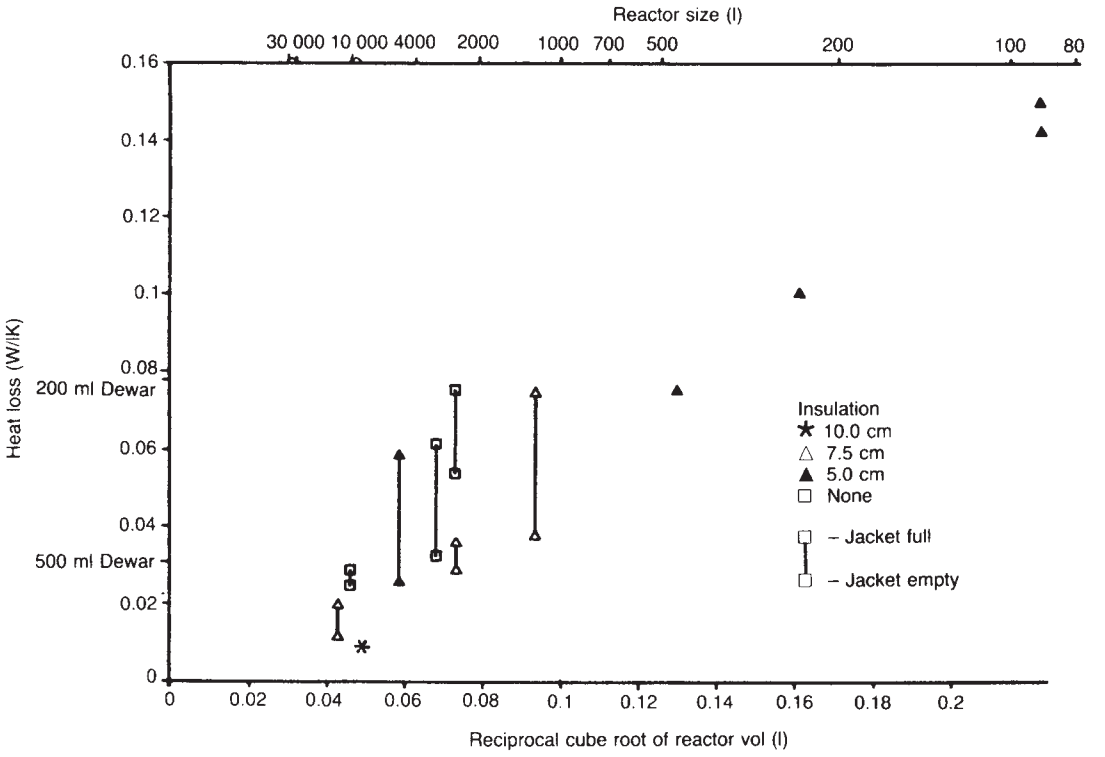


Figure 33.27 *Natural heat loss from reactors (T.K. Wright and Rogers, 1986) (Courtesy of the Institution of Chemical Engineers)*

deviation, process instrument failure, human error and human intervention can all be considered.

A process safety risk specialist with appropriate training should be involved in performing LOPA or QRA to determine the high consequence scenario likelihood. A process support or plant engineer as well as a reactive hazards specialist should provide input and guidance to the risk specialist to aid the likelihood calculations.

Once the likelihood has been obtained, the composite of the likelihood with the consequence gives the risk of the scenario reactive hazard. This risk should not exceed the corporate or organizational risk criteria. If the likelihood of an individual high consequence scenario does not exceed the tolerable threshold, then the scenario may be declared to be adequately safeguarded. In case the existing safeguarding measures cannot adequately reduce the consequence or likelihood of the high consequence scenarios, additional safeguarding or recovery measures are required. This may prompt the need to modify the safeguarding philosophy.

The selected set of measures to address scenarios with unacceptable risk should be based on regulatory requirements as well as technical and economical feasibility. In most cases, it will consist of a combination of several types of measures. The revised safeguarding philosophy should build upon the existing unit safeguarding philosophy and include extensions or changes recommended by plant operations, plant engineering, technical support staff and reactive hazards experts.

33.2.6 Prevention measures

In general, prevention is the preferred route to eliminate or reduce the consequences of high consequence scenarios. However, in practice this often requires significant process modifications that might not be economically feasible for existing units, as equipment might require changes. For new projects, however, this should be a major consideration in the design of the unit. Prevention measures can be divided in two categories – changes in process conditions (process changes) and changes to the hardware (design changes).

Process changes (inherent safety)

Process changes make the process inherently safer as they are inherent to the chemistry and therefore reduce the consequences of a scenario or eliminate a scenario. Some examples are given below:

(1) Limiting the concentrations of the reactants (e.g. feedstock specification), which can reduce the maximum adiabatic end temperature and pressure to within the design limits of the unit.
(2) Change to a non-reactive solvent.
(3) Use of a different catalyst resulting in a lower operating temperature; however, such changes can often be a source of problems because it can make other undesirable reactions occur significantly at even lower temperatures, and the effects should be thoroughly tested.

Hardware changes

Hardware changes comprise any changes in equipment/hardware, excluding mechanical relief systems. Some examples are given below:

(1) Remove heating coil from storage tank to prevent product decomposition;
(2) Remove linework to prevent mixing of incompatible materials;
(3) Upgrade pressure rating of vessel (increased design pressure);
(4) Reduce flow rates by restricting orifices or smaller control valves;
(5) Eliminate or substantially reduce storage of reactive intermediate species.

33.2.7 Mitigation Measures

The initial basis for mitigation is the existing safeguarding philosophy of the unit considered. The actual safeguarding philosophy employed can be dependent on regulatory requirements as well as the amount and type of risk posed by the scenarios. For example, relief venting is frequently a more cost-effective means than high integrity instrumentation to limit pressure build-up in equipment. However, in several countries, relief venting is not the preferred option, particularly when potentially toxic or corrosive materials could be released. Moreover, there are cases where relief venting does not act as a mitigation measure, such as weakening of vessel wall integrity due to temperature excursions during syngas methanation. Two common categories of mitigation measures, instrumentation and emergency relief venting, are discussed in more detail elsewhere.

Addition of any single prevention or mitigation option or a combination thereof can be considered. Once intolerable risk levels are precluded, alternative mitigations can be evaluated through a cost/benefit analysis.

The outcome of this phase of the work should be documented *for each scenario*, indicating whether the existing safeguarding philosophy and safeguards are adequate or, if not, what specific measures are recommended.

Instrumentation and control

Safe operation of a batch reactor requires close monitoring and control of reactant and additive flows to the reactor, of the operating temperature and of the agitation. For the operating temperature, the temperature at which an uncontrolled exotherm will occur under plant conditions is first defined. A safety margin is set between the operating temperature and this plant exotherm temperature. The operating temperature is displayed and provided with an alarm. The reaction temperature is controlled by a coolant.

The measurement of the temperature of the reaction mass should receive careful attention. The instrument should not allow a hot spot to develop undetected and it should not have a large time lag or a high failure rate. It is good practice to have separate measurements for the temperature control loop and the temperature alarm.

Events which may cause the temperature to go out of control, such as agitator or coolant failure, are identified. Actions which can be taken to counter an increase in operating temperature such as shut-off of feed or use of full cooling are identified, and appropriate actions are selected to be activated either by operator intervention or by trip.

Too low an operating temperature may also pose a hazard in that it allows reactants to accumulate. A lower temperature limit should be specified and measures taken to maintain the temperature above this limit.

Loss of agitation has two effects, poor mixing and poor heat transfer. Poor mixing tends to lead to the accumulation of reactants. These reactants are then liable to react at some later time, particularly if the agitation is restored. Poor heat transfer may result in inadequate cooling. Either effect may lead to a runaway reaction. Provision should be made to detect loss of agitation, which may occur due to agitator stoppage or due to loss of the agitator paddle. The first condition may be detected by measuring the rotational speed, the latter by measuring power consumption. The action to be taken on loss of agitation depends on the reaction. In semi-batch reactors, it is common to provide a trip to shut off the feed.

The importance of matching the controls to the reaction and the danger of overenthusiastic use of generic controls has been highlighted by Brannegan (1985). More sophisticated measurement may be provided in the form of an on-line reaction calorimeter. Such a calorimeter has been described by Hub (1977c).

Increasingly, reactor control is based on computers or programmable electronic systems (PESs). The HSE guidelines on PESs give as an illustrative example the control of a nitration reactor. The example includes a full fault tree and failure data for the tree. An account is given in Chapter 13.

Emergency safety measures

There are a number of emergency measures that can be taken if a process deviation occurs that threatens to lead to a reaction runaway. The prime measures are:

(1) inhibition of reaction;
(2) quenching of reaction;
(3) dumping.

The reaction may be stopped by the addition of an inhibitor, or short stop. This involves the use of an inhibitor specific to the reaction in question. The effectiveness of inhibition, including the dispersion of the inhibitor within the reaction mass, needs to be demonstrated.

Quenching involves adding a quenching agent, usually water under gravity, to the reaction mass to cool and dilute it. This method requires that there be sufficient free space in the reactor to receive the quench liquid.

The third method is dumping, which involves dropping the reactor charge under gravity into a quench vessel beneath which contains a quench liquid.

Other methods that can be used to slow the reaction but are not generally ranked as prime emergency safety measures include:

(1) shut-off of feed;
(2) direct removal of heat;
(3) indirect removal of heat:
    (a) full normal cooling,
    (b) emergency cooling.

If the reactor is a semi-batch one, it is often possible to design it so that the reaction subsides when the feed is shut off. This principle has already been discussed. Another possibility is to slow the reaction rate by the addition to the charge of a liquid, which removes heat by vaporization. Heat may also

be removed from the reactor by indirect cooling, either by application of full cooling on the normal cooling system or by the use of an emergency, or crash, cooling system.

Disposal of vented materials

The material vented from a reactor has to be safely disposed of. This aspect is intimately related to the venting of reactors and is therefore dealt with in Chapter 17.

33.2.8 Batch reactors: Reactor safety

Hazard identification

The hazard identification methods described in Chapter 8 may be applied to batch chemical reactors. This has been described by Pilz (1986), who refers to the use of a variety of techniques including a cause-consequence matrix, a hazop study, a FMEA, a fault tree, an event tree, and an incident sequence diagram (similar to a cause-consequence diagram).

A number of generic fault trees for reactors have been published. Figure 33.28 shows a fault tree given by the British Plastics Federation (BPF, 1979) and Figure 33.29 one given by Marrs *et al.* (1989).

Although for batch reactor plants the hazard of reaction runaway receives most attention, there are various other potential hazards which should not be neglected. Some of these have been discussed by Brannegan (1985).

The reaction stage of a process tends to involve various operations additional to the actual reaction, such as quenching, scrubbing and disposal. These operations also may involve scale-up problems and should receive careful attention

Basis of safety

For a given batch reaction, it is necessary to decide on an explicit safety philosophy, or basis of safety. Different approaches are appropriate for different reactions. The design may be guided by the characterization of the reaction already described.

Factors which affect the choice of the basis of safety include:

(1) reaction mode (batch, semi-batch);
(2) identified hazards and scenarios;
(3) practicalities of protection options;
(4) effect on reactor system operation;
(5) regulatory requirements.

In some semi-batch reactions the reaction may be, or may be arranged to be, such that shut-off of the feed is sufficient to cause the reaction to die out rapidly. In this case the design may depend mainly on this feature.

Bases of safety treated in detail in the IChemE *Guide* are:

(1) emergency relief;
(2) reaction inhibition;
(3) containment.

There may be practical difficulties with each of these options. For example, with venting disposal may present a severe problem. With containment the cost may be prohibitive. Another option that is increasingly pressed is reliance on control and trip systems. Whether this is permissible depends on the regulatory regime.

Selection of safety measures

Accounts of the measures for the safe design of a batch reactor include those by Christen (1980), Brannegan (1985), Berkey and Workman (1987), and N. Gibson, Rogers and Wright (1987), and the IChemE *Guide*. The application of the principle of inherently safer design has already been described with special reference to the use of a semi-batch reactor and to reaction temperature.

The approach described by N. Gibson, Rogers and Wright (1987) is based on formal process definition. Four levels of the process are defined:

(1) Level 1: fixed operating parameters;
(2) Level 2: normal variations in operating parameters;
(3) Level 3: generic fault conditions;
(4) Level 4: abnormal situations.

In Level 2 consideration is given to normal variation in the operating conditions. Some of the deviations are well recognized, others less so. Thus there may be an expectation that the temperature of a batch reaction could vary by, say, $\pm 10°C$. It may be less well appreciated that the holding time at a particular step may extend from a normal one hour to, say, 12 h over a weekend.

The effects of certain failures that are generic in that they apply to many reactions, such as loss of coolant, rupture of an internal coil, or agitator stoppage, is assessed in Level 3. The authors regard Level 3 as the minimum standard that leads to an acceptable level of safety in the majority of processes.

Level 4 is concerned with the large number of abnormal conditions that could conceivably lead to reaction runaway. These conditions may be explored using a method such as hazop.

The process definition should cover the operating parameters and the expected variations of these parameters (e.g. concentrations, temperature, hold times) and the details of the operations (e.g. pumping, agitation, cooling) which do not have assured protection by trips.

The safety measures described by Gibson, Roger and Wright are essentially process control to prevent reaction runaway emergency measures to stop an incipient runaway and measures of containment or venting to provide protection in the event that a runaway occurs.

The IChemE *Guide* takes an essentially similar approach.

Hazard assessment

Where the hazards identified warrant it, the reactor design may be subject to hazard assessment. One case where such an assessment may well be called for is a proposal to provide reactor protection by means of trips rather than venting. Hazard assessment of batch reactors in considered in Section 11.13 of Chapter 11. An illustrative example of such an assessment is given in Appendix 1 of the IChemE *Guide*.

Implementation of safety measures

The implementation of the safety measures selected is discussed by N. Gibson (1986b). His account is in effect an illustration of good practice in this aspect of the development of a process. The design and operating functions need to understand the basis of safety and the critical features of the measures proposed and the measures should be acceptable to them. The effect of any process or plant modification should be evaluated. It is then necessary that the safety measures are maintained.

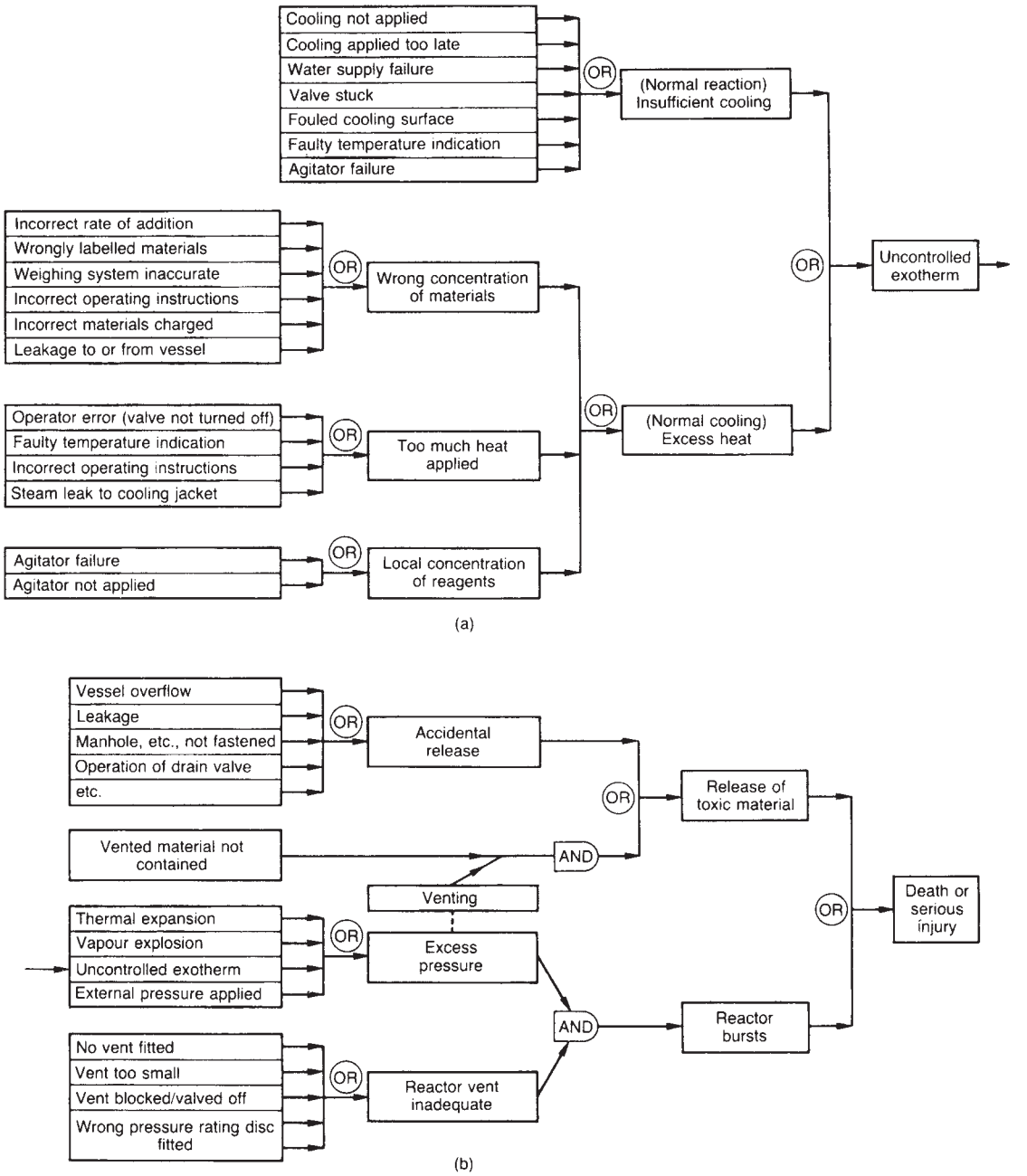


Figure 33.28 *Generic fault trees for assessment of hazards of batch reactors – 1 (BPF, 1979) (a) fault tree for top event 'uncontrolled exotherm'; (b) fault tree for top event 'death or serious injury'*

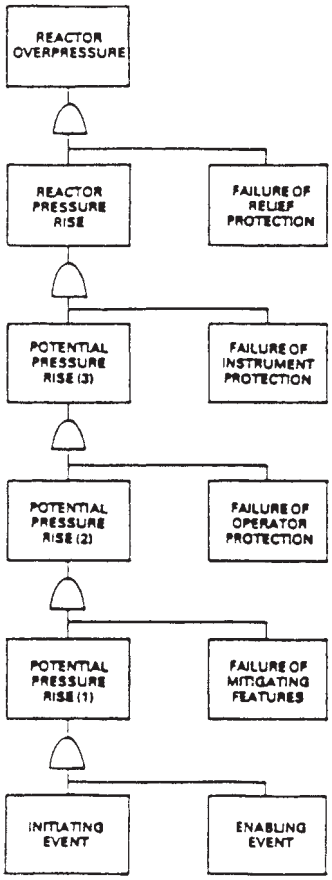


Figure 33.29 *Generic fault tree for assessment of hazards of batch reactors – 2 (Mans et al., 1989) (Courtesy of the Institution of Chemical Engineers)*

Regulatory strategy for reactors

The strategy developed by the HSE for control of the hazard from reactors has been described by Pantony, Scilly, and Barton (1989). From the analysis of incidents the authors conclude that the following are prominent causes:

(1) lack of understanding of the chemistry;
(2) inadequate engineering of the heat transfer;
(3) inadequate control and safety backup system;
(4) inadequate operational procedures.

They identify the need for guidance on:

(1) thermal hazards;
(2) vent sizing;
(3) process control.

For thermal hazards, the HSE has sought both to develop individual test methods to fill perceived gaps and to develop a test strategy.

Furthermore, the HSE has encouraged the development at the South Bank University an independent centre, the Chemical Reaction Hazard Centre (CRHC), where contract testing for thermal stability and process reactions can be carried out, and has sponsored work there. The centre provides a resource potentially of particular benefit to smaller companies. Work there has been described by Nolan and co-workers (Cronin, Nolan and Barton, 1987; Nolan and Barton, 1987). Cronin, Nolan and Barton have described the test instrumentation test scheme used. For venting, the approach is based on the DIERS work with some further development.

For process control, the HSE has sponsored the comparative study by Lees, Marrs and co-workers of protection by venting and by instrumented systems (Marrs *et al.* 1989; Marrs and Lees, 1989), which has already been described.

33.3 Programme management

33.3.1 Resourcing

Staff Skill

It should be evident that the proper assessment of reactive hazards involves

(1) collecting available reactivity information;
(2) developing reactivity information where gaps are apparent;
(3) determining conditions or circumstances in which the reactivity hazards can be manifested;
(4) evaluating the risk and
(5) preventing or mitigating risk where appropriate.

These steps require various and specialized activities and skills. Understanding of chemistry as well as of reactive hazards is needed in Step 1. An ability to recognize the information gaps, familiarity with testing instrumentation and knowledge for designing experiments are skills necessary for Step 2. Experience with plant operations and with potential deviations from those operations is critical for identifying credible scenarios in Step 3 (but not unique to assessment of reactive hazards). Detailed familiarity with estimating scenario consequences and likelihoods, for example, through process simulation and LOPA, respectively, in Step 4 is key to determining risk. Expertise in various prevention or mitigation approaches in Step 5, such as two-phase reactive relief design or protective instrumentation design, is important for handling intolerable risk.

Training and experience are important elements for ensuring that the process is carried out in a sound, technical manner. The skill-set needed for this work is highly specialized and should not be expected to be acquired in a short timeframe.

In principle, different staff could be needed to carry out various phases of the entire process. If this is the case, overlap or a strategy for effective transfer of knowledge between phases is necessary for continuity.

Participation and ownership

Experts in the reactivity area cannot *efficiently* assess the reactive hazards without input from process support and plant operations personnel. Substantial time spent re-discovering chemistry or learning about plant operations can be avoided when a team of reactive hazards experts, process support staff and plant operations staff work in concert.

Moreover, an equally important consideration toward building a cross-functional team is 'product ownership'. Crucial stakeholders, such as the technology and operations organizations, will give greater credibility and more easily accept the work product from a team that also represents them. Without such a team approach, there is a serious risk that the entire effort may be conducted in futility, because, in the end, no changes in the manufacturing facility may ever be implemented.

Timing and cost

The effort required for detailed experimental evaluation, kinetics extraction, process simulation model development and two-phase reactive relief evaluation can be formidable. It would be prudent to develop estimates for the extent of these activities as far in advance as possible and to budget accordingly.

In addition to the cost of staffing for the assessment of reactive hazards, there may be significant costs with acquisition and maintenance of equipment (such as calorimeters) as well as software (such as process simulators).

In addition to the possible significant cost associated with the effort, the amount of calendar time to carry out a complete evaluation (from collecting and analyzing data to designing safeguards) can be months or longer.

33.3.2 Risk management

To effectively manage risk (not just from reactive hazards), a company or organization should have its own definitions and methodology for assigning the level of risk Chapter X. The risk level can then serve as one criterion for prioritizing activities, investments, and expenditures.

An important element for facilitating decisions on issues (that are not driven by regulatory compliance) is the corporate or organization risk tolerance. This simply indicates the chosen level, below which, the risk is deemed to be 'tolerable' or 'acceptable'. A well-defined and documented risk tolerance level is useful for when and how much safeguarding is needed.

33.3.3 Implementation

As can be expected, the potential cost for implementing recommendations can often overshadow the assessment cost. This aspect should be understood by the manufacturing facility at the outset. However, it is also reasonable to presume that the reduced risk from potential reactive hazards-related events will greatly outweigh the combined analysis and implementation cost.

Once recommendations have been presented to a plant, they should be entered into a system for managing their implementation. This can mean combining with requests from other safety-related and operational initiatives. These items may then be prioritized based on risk, regulatory compliance or some other criteria. Handling the reactive hazards recommendations in such a system ensures that the recommendations are addressed, scheduled and executed in an appropriate manner.

Following implementation, it is useful to provide an assurance role to make sure that recommendations were indeed implemented and implemented as envisioned to reduce the reactive hazards risk. It can happen that 'fixes' are installed that bear insufficient resemblance to the original prevention/mitigation approach and do not help manage the risk. Verifying and validating the controls, equipment and systems put in place is therefore, a critical activity.

All documented analyses and recommendations should be integrated with plant process safety information so that there is ready access to the information, that plant personnel are familiar with the hazards and controls, and that the information will be incorporated in other programs and initiatives.

33.3.4 Management of change

The manner in which a facility handles management of change is an extremely important aspect of managing reactive hazards. Risk reduction measures implemented at a point in time can be circumvented or nullified by other seemingly innocuous changes that have been made. An engrained and rigorous management of change programme that includes consideration of reactive hazards is necessary to avoid 'creep' that quietly increases a facility's level of risk.

33.3.5 Program maintenance

Maintenance of a safety program to ensure that efforts are meeting needs requires continuous monitoring of systems, teamwork and a commitment to continual improvement. Development and growth of a safety programme can result from lessons learned from reviews of programmes and procedures, employee experience, audits, management of change, incidents including near miss incidents, equipment maintenance and new technology.

34 Safety Instrumented Systems

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34.1 Introduction

Numerous case histories of process incidents are provided in Appendix A1-A6. The most effective way to prevent these incidents is use of inherently safer design to eliminate or reduce the potential hazard. Chapter 11.7 provides a discussion of inherently safer design principles. In addition, the Center for Chemical Process Safety book *Inherently Safer Chemical Processes: A Life Cycle Approach* (CCPS, 1996) provides an excellent source of information on reducing the inherent risk associated with process operation.

In many processes, technical or manufacturing issues limit the engineer's capability to design an inherently safer process. Further, there is generally a point where the required capital investment is disproportional to the additional risk reduction provided by the process modification. In other words, the derived safety benefit is too low relative to the economic investment.

When this occurs, protection layers or safeguards must be provided to prevent or mitigate the process risk. A safety instrumented system (SIS) is a protection layer, which shuts down the plant, or part of it, if a hazardous condition is detected. Accounts of SISs are given in *Reliability Technology* (A.E. Green and Bourne, 1972) and by Hensley (1968), R.M. Stewart (1971), Kletz (1972a), de Heer (1974), Lawley and Kletz (1975), Wells (1980), Barclay (1988), Rushton (1991a,b) and Englund and Grinwis (1992).

Throughout the years, SISs have also been known as emergency shut-down systems (ESDs, ESSs), safety shut-down systems (SSDs), safety interlock systems (SISs), safety critical systems (SCSs), safety protection systems (SPSs), protective instrumented systems (PISs), interlocks and trip systems. Regardless of what the SIS may be called, its essential characteristic is that it is composed of instruments, which detect that process variables are exceeding preset limits, a logic solver, which processes this information and makes decisions, and final control elements, which take necessary action on the process to achieve a safe state.

For start-up, the various instrumented permissives and operator actions must be defined. These permissives may require that certain process conditions exist prior to allowing start-up. They may also involve the use of temporary bypass of the SIS for start-up, such as the bypass of a low flow shut-down of a pump. From the case histories, it is apparent that the permissive and operator action requirements have often been ill-defined, allowing start-up under unsafe operating conditions.

The required performance or integrity of the SIS must also be defined. Not all SIS provide the same performance. In Figure 34.1, a single process switch is connected to a non-redundant programmable electronic system (PES) that de-energizes a single solenoid operated valve venting air from a process valve actuator, causing the fail-closed valve to go to the safe state. This SIS will not provide the same performance as the SIS shown in Figure 34.2, which shows 2oo3 (two-out-of-three) voting transmitters connected to a redundant PES that de-energizes solenoid operated valves venting air from the process valve actuator, causing the redundant fail-closed valves to go to the safe state. The former has no redundancy and is susceptible to multiple, single points of failure. The latter provides redundancy, fault tolerance, and the opportunity for implementation of on-line and fault tolerance. The latter provides redundancy, fault tolerance, and the opportunity for implementation of on-line diagnostics. The combination of redundancy and diagnostics yields a high level of confidence that the SIS will function when required. The selection between the design in Figure 34.1 and the one in Figure 34.2 is dependent on the amount of risk reduction that the SIS is expected to provide.

The risk reduction that the SIS must provide is defined by process hazards analysis, supplemented with semi-quantitative or quantitative evaluation. Qualitative process hazards analysis techniques, such as what-if analysis, checklists, and Hazard & Operability analysis (HAZOPs), are used to identify the causes and consequences of potential process hazards. Semi-quantitative or quantitative techniques are then used to evaluate the risk reduction requirements.

The semi-quantitative evaluation is typically performed using layers of protection analysis (LOPA). The CCPS book, *Layer of Protection Analysis: Simplified Process Risk Assessment* (CCPS, 2001) states that LOPA is used to determine whether there are sufficient layers of protection against potential process hazards. A brief introduction to LOPA is provided in this chapter, as it relates to SIS specification. In addition, refer to the hazards analysis chapter Chapters 8 and 9 for more information on general hazard assessment principles.

For quantitative risk assessment, the most commonly used technique is fault tree analysis. A brief

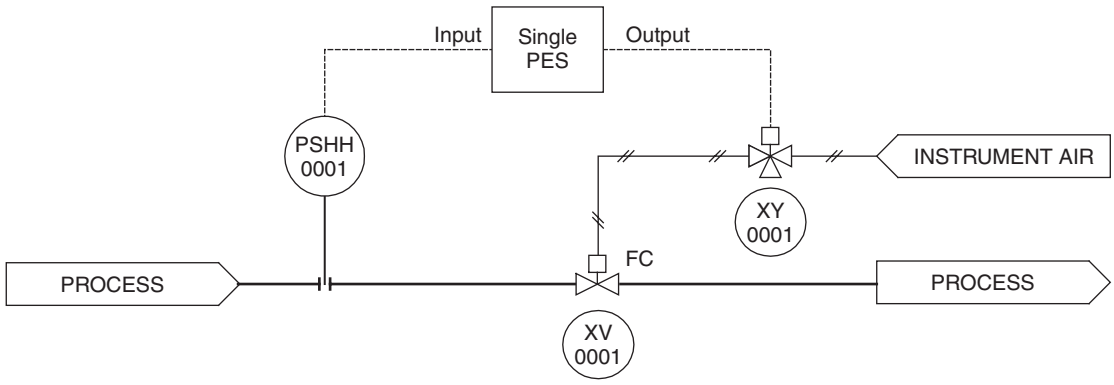


Figure 34.1 *Simplex safety instrumented system (Courtesy of SIS-TECH Solutions, LP)*

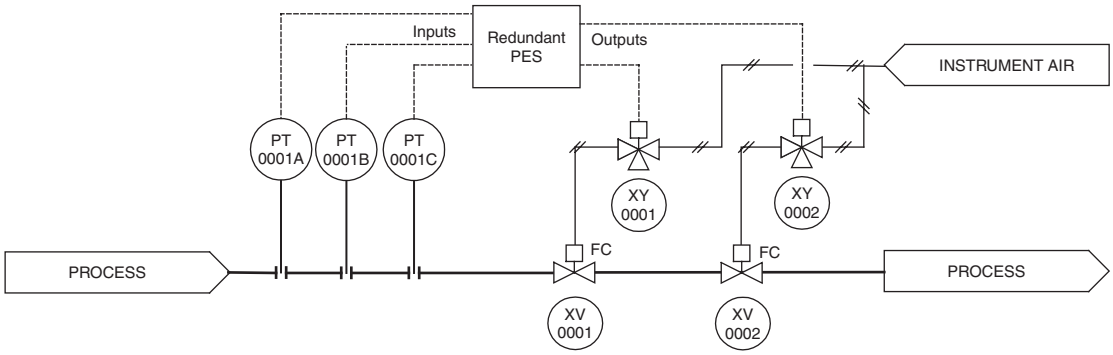


Figure 34.2 *Redundant safety instrumented system (Courtesy of SIS-TECH Solutions, LP)*

introduction to fault tree analysis is provided in Chapters 8.11 and 9.5.

The hazards analysis allocates risk reduction to the SIS. This risk reduction defines the integrity requirement for the SIS. Once the SIS functionality and integrity requirements are known, it is possible to design an SIS that will mitigate the process risk. However, the design simply represents the intended operation of the SIS. How the SIS is actually maintained, tested and managed determines the risk reduction that the SIS will achieve over its lifetime. For this reason, the US standard ANSI/ISA 84.01-1996 and the international standard IEC 61511 emphasize a lifecycle approach to SIS.

34.2 Examples of SIS

Some illustrations of the specification and design of protective systems have been given by Kletz (1972a, 1974a) and by Lawley and Kletz (1975). The applications include a hydrocarbon sweetening plant and a distillation column heating system.

An example of the use of SISs in a hydrocarbon sweetening plant is shown in Figure 34.3 (Kletz, 1972a). The hydrocarbon is sweetened with small quantities of air that normally remain completely dissolved, but conditions can arise that generate an explosive mixture. Initially, it was assumed that the principal problem lay in a change in the air/hydrocarbon ratio, but a HAZOP study revealed that a hazard could arise in a number of ways. One example is the formation of an air pocket, which can occur as follows:

(1) the temperature can be so high that the amount of air normally used will not dissolve;
(2) an air pocket can be left behind when a filter is recommissioned;
(3) the pressure can fall, allowing air to come out of solution;
(4) a fault in the mixer can prevent the air being mixed with hydrocarbon, so that the pockets of air can be carried forward;
(5) a fault in the air/hydrocarbon ratio controller can result in the admission of excess air.

In this case, it is also necessary for the feed to be above its flashpoint, which can occur in a number of ways: (1) the temperature can be above the design flashpoint and (2) the feed can contain low flashpoint material. Alternatively, if there is both a loss of pressure in the receiver and a failure of the non-return valve, hydrocarbon may find its way into the air receiver.

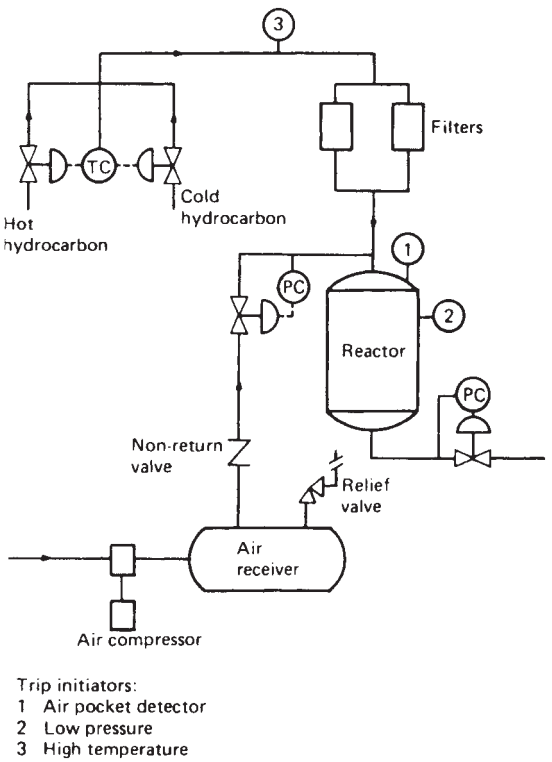


Figure 34.3 *Hydrocarbon sweetening plant (Kletz, 1972a) (Courtesy of the American Institute of Chemical Engineers)*

The fault tree for the hazard is shown in Figure 34.4. The probabilities of the various fault paths were evaluated from this tree and the SIS requirements were identified. The SIS

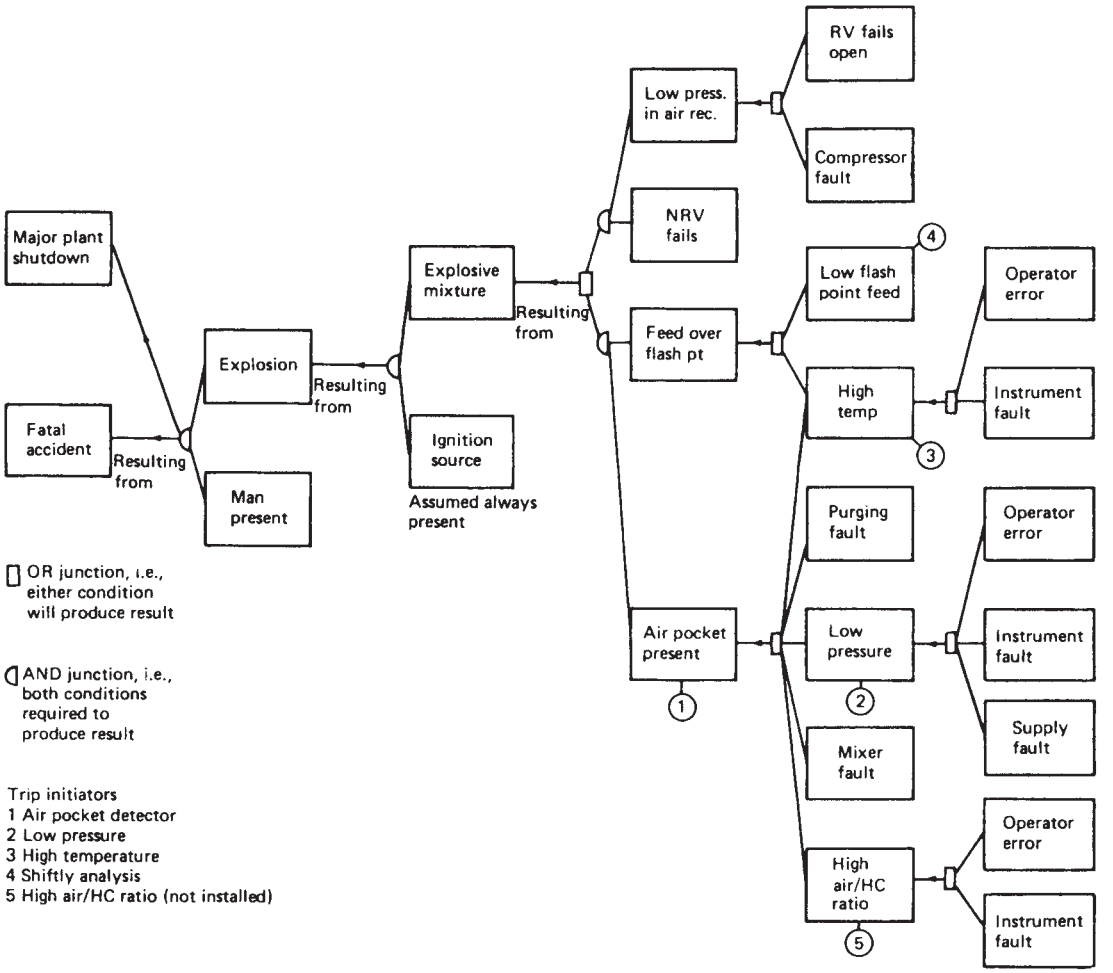


Figure 34.4 *Fault tree for explosion on a hydrocarbon sweetening plant (after Kletz, 1972a) (Courtesy of the American Institute of Chemical Engineers)*

initiators considered, shown by the circles in Figures 34.3 and 34.4, were

(1) a device for detecting a pocket of air in the reactor;
(2) a pressure switch for detecting a low pressure in the receiver;
(3) a temperature measurement device for detecting a high temperature in the feed;
(4) laboratory analysis for detecting a low flash-point feed;
(5) a device for detecting a high air/hydrocarbon ratio.

As the latter condition is detected by the SIS initiator 1, SIS initiator 5 was not used. The shut-down arrangement was that any of the SIS initiators 1–3 closes a valve in the air-line and shuts down the compressor. The use of the laboratory analysis of the feed flashpoint was restricted to ensuring that low flashpoint feeds were only present a sufficiently small fraction of the time to meet the system specification.

Another example is provided for a distillation column heating system, as shown in Figure 34.5 (Lawley and Kletz, 1975). Heat is supplied to the distillation column from an existing steam-heated reboiler and a hot-water-heated feed vaporizer. Plant throughput was to be increased by the addition of another reboiler and vaporizer.

Existing dual pressure relief valves were adequate to handle overpressure from the existing reboiler and vaporizer. The problem was to cope with the overpressure that the new reboiler and vaporizer might cause. Both re-sizing of the existing relief valves and the addition of a third were unattractive in the particular situation. Consequently, there was a requirement for an SIS that would shut-down both the steam to the new reboiler and the hot water pump on the new vaporizer.

Both 1oo1 and 1oo2 SISs were considered. The 1oo1 system consisted of a pressure switch for detecting high pressure on the overhead vapour line, a relay and a contact on the power supply to the hot water pumps and a relay and contact for de-energizing the solenoid operated valve

closing the isolation valve on the reboiler steam supply. The summary of the failure rates of a simple SIS for this case is shown in Table 34.1. In the analysis, the authors determined that the simplex system could not achieve the fractional dead time (FDT) requirements. The authors therefore considered a 1oo2 SIS, which was a duplication of the 1oo1 system. It was concluded that a 1oo2 system did meet the target FDT. The spurious trip rate for this system, however, was high, which was unacceptable from a plant reliability standpoint. This led to a requirement for a 2oo3 voting system, which met the target FDT with a lower spurious trip rate.

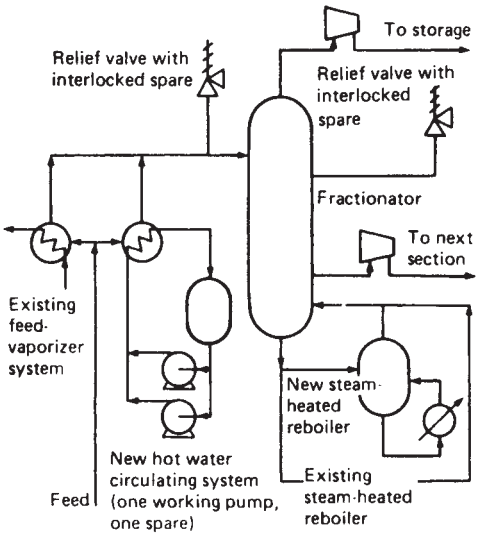


Figure 34.5 *Distillation column heating system (Lawley and Kletz, 1975) (Courtesy of Chemical Engineering)*

34.3 SIS Standards

34.3.1 ANSI/ISA 84.01-1996

ANSI/ISA 84.01-1996 (ISA 84.01-1996) was issued in 1996 by the Instrumentation, Systems and Automation society. In 2000, the Occupational Safety and Health Administration (OSHA) acknowledged ISA 84.01-1996 as a standard that provides *generally accepted good industry practice* for the design of SISs. Consequently, the use of ISA 84.01-1996 ensures compliance with the process safety management programme (OSHA 1910.119 regulation). By the end of 2004, IEC 61511 will be accepted as ISA-84.00.01-2004 Parts 1–3 (IEC 61511 Parts 1–3 Mod), leading to a single global standard by which to judge SIS adequacy.

ISA 84.01-1996 is performance-based, using a benchmark called the 'safety integrity level' to define the adequacy of the SIS. During the process hazards analysis, the risk reduction that must be achieved by the SIS is determined. This risk reduction is equivalent to the safety integrity level. The risk reduction provided at each safety integrity level is shown in Table 34.2.

The SIS is designed and implemented to achieve the target safety integrity level (SIL). The standard has few prescriptive requirements, so the engineer designing the SIS relies on his or her experience to select appropriate instrumentation for the process application. The essential

Table 34.1 *Failure rates of trip systems for a distillation column heating system (Lawley and Kletz, 1975) (Courtesy of Chemical Engineering)*

Components	*Failure rate* (faults/year)		
	Fail-to-danger	*Fail-safe*	*Total*
Trip initiator			
Impulse lines – blocked	0.03	–	0.03
– leaking	0.06	–	0.06
Pressure switch (contacts open to give trip signal on rising pressure)	0.10	0.03	0.13
Cable fractured or severed	–	0.03	0.03
Loss of electrical supply	–	0.05	0.05
Total	0.19	0.11	0.30
Steam shut-off system			
Relay coil (de-energize to trip)	–	0.05	0.05
Relay contact	0.01	0.01	0.02
Relay terminals and wire	–	0.01	0.01
Solenoid valve (de-energize to trip)	0.10	0.20	0.30
Loss of electrical supply (to solenoid valve)	–	0.05	0.05
Trip valve (closes on air failure)	0.10	0.15	0.25
Air supply line – blocked or crushed	0.01	–	0.01
– fractured or holed	–	0.01	0.01
Loss of air supply	–	0.05	0.05
Total	0.22	0.53	0.75
Pump shut-off system			
Relay coil, contact, terminals and wire (as above)	0.01	0.07	0.08
	0.01	0.07	0.08

Table 34.2 *Safety integrity levels (SILs) according to ANSI/ISA 84.01-1996*

SIL	*Average probability of failure on demand*	*Risk reduction factor*	*Availability* (%)
1	10^{-1}–10^{-2}	10–100	90–99
2	10^{-2}–10^{-3}	100–1000	99–99.9
3	10^{-3}–10^{-4}	1000–10,000	99.9–99.99

Table 34.3 *Safety integrity levels (SILs) according to IEC 61508 and IEC 61511*

SIL	*Average probability of failure on demand*	*Risk reduction factor*	*Availability* (%)
1	10^{-1}–10^{-2}	10–100	90–99
2	10^{-2}–10^{-3}	100–1000	99–99.9
3	10^{-3}–10^{-4}	1000–10,000	99.9–99.99
4	10^{-4}–10^{-5}	10,000–100,000	99.99–99.999

requirement is that the overall architecture must be capable of achieving the SIL at its designated testing interval. Thus, the engineer has the flexibility to design an SIS to meet the SIS performance target and the operational goals for the facility.

After installation, the complete instrumented loop is tested to validate the SIS functionality. Operation, maintenance and testing procedures are developed to ensure long-term performance of the SIS. Finally, management of change is used to assess the impact of any change on the functionality of the SIS or the SIL that the SIS can achieve.

34.3.2 IEC 61508

IEC 61508, 'Functional Safety of Electrical/Electronic/Programmable Electronic (E/E/PES) Safety-related Systems,' is a global safety standard. IEC 61508 applies to many different industrial sectors, including transportation, manufacturing, medical and process. The standard serves as a framework and establishes minimum requirements for the development of sector-specific standards.

IEC 61508 consists of seven parts:

- Part 1: General requirements;
- Part 2: Requirements for E/E/PES;
- Part 3: Software requirements;
- Part 4: Definitions and abbreviations of terms;
- Part 5: Examples of the methods for the determination of SILs;
- Part 6: Guidelines on the application of parts 2 and 3;
- Part 7: Bibliography of techniques and measures.

IEC 61508 concerns any E/E/PES that is implemented to mitigate safety and environmental hazards posed by the 'equipment under control' (e.g. a distillation column). These hazards are identified during a hazards and risk analysis.

The standard uses a lifecycle approach to establish activities that should occur throughout the lifetime of a safety-related system from conceptual process design to decommissioning. Thus, the standard covers design, operation, maintenance and testing of safety-related systems.

Similar to ISA 84, IEC 61508 uses a risk-based approach for determining the required performance for safety-related systems. IEC 61508 has four safety integrity levels, as shown in Table 34.3.

Specific hardware and software criteria are provided based on the required performance. Further, the standard establishes various techniques and measures to be used to achieve successful implementation of safety-related systems.

IEC 61508 is the standard by which a manufacturer or supplier's product is judged. This provides greater assurance that the equipment used to implement the safety-related system, especially the PESs, meets a minimum burden of proof. This does not mean that the equipment will work well in all applications. It does mean that the supplier met minimum quality standards in terms of design, manufacturing and testing. As with all equipment, the user must still determine whether the device functions as intended when installed and operated in the process environment.

34.3.3 IEC 61511

IEC 61511, 'Safety Instrumented Systems for the Process Sector,' was issued by the International Electrotechnical Commission in 2003. IEC 61511 consists of three parts:

- Part 1: Framework, definitions, system, hardware and software requirements;
- Part 2: Guidelines in the application of IEC 61511-1;
- Part 3: Example methods for determining safety integrity in the application of hazard and risk analysis.

IEC 61511 is the first sector standard developed under the framework of IEC 61508. It represents an important step forward, because, for the first time, there will be a global standard that establishes the requirements for SISs used in the process industry. The worldwide acceptance of IEC 61511 will lead to a higher level of consistency in the SIS specification, design, operation, maintenance and testing. The standard is flexible, since it is performance-based, using the SIL as the benchmark. It then builds upon the performance requirements, using a lifecycle approach for the SIS design. Consequently, the standard does not mandate how an SIS should be designed for a specific application. Instead, it provides a framework for evaluating whether an SIS is needed, specifying the SIS functionality, and establishing the required SIS integrity.

The basic steps for compliance with IEC 61511 are as follows:

(1) Establish the risk tolerance for the process under consideration.
(2) Perform a process hazards analysis to determine the process risk associated with specific hazardous events.
(3) Identify the hazardous events where the process risk exceeds the risk tolerance.
(4) Identify the safety functions that reduce the process risk.
(5) Allocate risk reduction to each safety function.

(6) For non-SIS safety functions, document how the non-SIS safety function achieves the risk reduction and perform proof tests to ensure these functions work as intended.
(7) For SIS, define the functionality and integrity (i.e. required risk reduction) of the SIS.
(8) Document how the functionality and integrity will be achieved in a safety requirements specification.
(9) Design the SIS to achieve the functionality and required integrity.
(10) Develop SIS operation, maintenance and testing procedures to demonstrate functionality and to ensure required integrity.
(11) Quantitatively verify that the SIS design and intended procedures meet the required integrity.
(12) Fully validate the functionality of any new or modified SIS prior to introduction of hazardous chemical into the process.
(13) Use change management processes to ensure that the functionality and integrity are maintained during any SIS modification.
(14) Periodically audit the SIS documentation and installation for agreement with each other and the safety requirements specification.

34.4 Layers of Protection Analysis (LOPA)

LOPA is a semi-quantitative technique for assessing process risk. Dowell (1997, 1998) and Huff and Montgomery (1997) showed how LOPA could be used to determine the following:

- what SIL is required for an SIS;
- how many layers of protection are needed to reduce the risk to a tolerable level.

The intent of LOPA, according to *Layers of Protection Analysis* (CCPS, 2001) (the CCPS *LOPA book*), is to provide a rational, objective, risk-based approach to identifying and specifying the protection layers that are used to prevent or mitigate process risk. Process risk is defined by the frequency and severity of potential hazards. The severity may be assessed in terms of human impact, such as injuries and fatalities, environmental impact, such as noise, releases or spills, or financial losses, such as production loss or equipment damage.

The process risk is assessed in the absence of the protection layers. The process risk is then compared to the tolerable risk. Tolerable risk may be defined by the owner/operator of a facility, by an insurer, or by a governmental/regulatory body. If the process risk is equal to or less than the tolerable risk, no protection layers are required. If the process risk is greater than the tolerable risk, the gap is closed using protection layers that prevent or mitigate the process risk. The protection layers are designed to reduce the process risk to a tolerable level. Examples of protection layers are provided in Table 34.4 from *Guidelines for Safe Automation of Chemical Processes* (CCPS, 1993/14) (the CCPS *Safe Automation Guidelines*).

LOPA builds upon traditional HAZOP techniques, using guidewords to identify process deviations and associated initiating causes that potentially propagate into hazardous events. LOPA determines the frequency of each initiating cause using either an order of magnitude assessment or estimated failure rate. The use of look-up tables can provide a consistent basis for this assessment. Hazards analysis teams often have difficulty when asked to make frequency judgements without any guidance, because they typically have no experience with operating the facility without the protection layers and consequently have little basis for making the assessment.

Table 34.4 *Layers of Protection (CCPS, 1993/14) (Courtesy of the American Institute of Chemical Engineers)*

1. Process design
2. Basic controls, process alarms, operator supervision
3. Critical alarms, operator supervision and manual intervention
4. Automatic SIS
5. Physical protection (relief devices)
6. Physical protection (containment dikes)
7. Plant emergency response
8. Community emergency response

The consequence of the hazardous event is defined by: (1) the team using qualitative judgment, (2) look-up tables, or (3) consequence modelling for specific scenarios. The method chosen is typically dependent on the nature of the hazards present in a facility. If the hazards are easily understood by the team, the assessment may be completely qualitative with the team instructed to use past experience and process knowledge in its assessment. If the hazards are more complex, such as the overpressure of a vessel at an elevated location with release of hydrocarbons to the atmosphere, look-up tables may be given to the team to provide guidance on whether the release should be considered flammable. When toxic chemicals are involved, dispersion modelling may be required to ascertain the degree of impact to the on-site personnel or to the community.

With the initiating cause frequency and consequence, the unmitigated process risk can be determined:

$$\text{Unmitigated risk} = \text{initiating cause frequency} \times \text{consequence}$$

This unmitigated risk is compared to the risk tolerance criteria to determine whether protection layers are required. The risk tolerance can be defined as a specific, numerical target, such as 1 fatality in 10,000 years, or in general categories using a risk matrix as shown in Figure 34.6.

The consequence categories are defined in terms of safety, environmental and economic impacts. Safety is often evaluated in terms of potential fatalities, serious injuries, lost-time injuries or first-aid injuries. The safety category may also set different requirements dependent on whether these impacts occur on-site or off-site or whether the impacts are to plant personnel or members of the public. The environmental category may examine items such as environmental releases related to permit violations, plant or community response requirements (e.g. shelter-in-place or evacuation), or toxic gas levels. The economic category often examines losses associated with production interruption and equipment damage.

If a risk matrix is used, the required risk reduction can easily be determined once the frequency and consequence is known. For example, using Figure 34.6, with an

REQUIRED RISK REDUCTION MATRIX						
CONSEQUENCE	1	10	100	1000	10000	TH
	2	NR	10	100	1000	10000
	3	NR	NR	10	100	1000
	4	NR	NR	NR	10	10
		10000	1000	100	10	1
	FREQUENCY (1 in x years)					

Figure 34.6 *Example risk matrix (Courtesy of SIS-TECH Solutions, LP)*

initiating cause frequency of 1 in 10 years and a consequence category of 2, the risk must be reduced by a factor of 1000 to achieve the risk tolerance. When a quantitative risk tolerance is defined, the process risk is compared to the quantitative target to determine the amount of required risk reduction.

When the unmitigated risk does not meet the risk tolerance, protection layers are used to reduce the risk to the risk tolerance. Any protection layer should meet the criteria established by the CCPS *Safe Automation Guidelines* and expanded by the *LOPA book*:

(1) Specific: The independent protection layer (IPL) is capable of mitigating or preventing the consequences of the specified hazard.
(2) Independent: An IPL is independent of the other protection layers associated with the specified hazard. Independence requires that each layer be unaffected by the failure of another protection layer or by the conditions that caused another protection layer to fail. Most importantly, the protection layer is independent of the initiating cause.
(3) Dependable: The protection provided by the IPL reduces the identified risk by a known and specified amount.
(4) Auditable: The IPL is subject to regular periodic validation or function testing.

The dependable criterion is related to the probability of failure on demand (PFD) of the protection layer and thus is a direct measure of the risk reduction that the protection layer can provide. Guidelines are typically developed to support LOPA by providing restrictions on the amount of risk reduction that can be allocated to any protection layer related to the protection layer's design, operation, maintenance and testing philosophy. Tables 34.5 and 34.6 provide examples of guidelines that might be developed for assessing the risk reduction provided by protection layers. The CCPS *LOPA book* also provides an extensive discussion about the protection layers, the range of risk reduction that can be expected from any protection layer, and, most importantly, limitations that should be considered prior to establishing any guideline used in a site-specific LOPA.

The overall risk reduction required to reduce the unmitigated risk to the tolerable risk may be provided by one protection layer or multiple protection layers. It is always important to evaluate the claimed protection layers against the independence criterion.

When the protection layer is a SIS, the risk reduction allocated to the protection layer is the SIL. This establishes the performance requirement for SIS, which must be met by the design, operation, maintenance and testing philosophy.

After allocating the appropriate risk reduction to the existing or planned protection layers, the mitigated risk is again compared to the tolerable risk. If the tolerable risk is not satisfied, recommendations for additional risk mitigation layers or design modifications should be made. LOPA is a tool used to ensure that process risk is successfully mitigated to the tolerable level. LOPA is a rational, defensible methodology that provides a rapid, cost effective means for identifying the IPLs that lower the frequency and/or the consequence of specific hazardous incidents. LOPA uses specific criteria and restrictions for the evaluation of protection layers, eliminating the subjectivity of qualitative methods at substantially less cost than fully quantitative techniques.

LOPA can be used at any point in the lifecycle of a project or process, but it is most cost effective when implemented during front-end loading, as soon as process flow diagrams are complete and the Piping & Instrumentation Diagrams (P&IDs) are under development. For existing processes, LOPA should be used during or after the HAZOP review. LOPA is typically applied after a qualitative hazards analysis has been completed, which provides the LOPA

Table 34.5 *Typical risk reduction factors (RRF) used in layers of protection analysis (Courtesy of SIS-TECH Solutions, LP)*

IPL	*Further restrictions on considering as IPL*	*RRF (typical)*
Operator intervention using operating procedures	The action should be independent from the initiating cause and any other IPL. If an operator action is the initiating cause, no risk reduction can be assigned to any operator action that solely relies on the same operator to recognize problem and quickly correct it. If the initiating cause is the basic process control system, no risk reduction can be assigned to any operator action that solely relies on BPCS information display (e.g. process conditions, indications) unless a detailed study of the BPCS is performed to ensure sufficient independence and redundancy in order to address common cause failure	
	Process Related Rounds and Inspections. Frequency of operator rounds should be sufficient to detect potential incident. If recognition of process variable is required, the operator should log specific values from sensors or valves that are independent of the initiating cause. The operator log should provide unacceptable out-of-range values. Standard Operating Procedures should describe response to out-of-range values	10
	Observational. Frequency of operator rounds should be sufficient to detect potential incident and mitigate ultimate scenario. Impending incident should be obvious to operator through normal visual or hearing range, that is, loud noise, high vibration, serious leaking, etc.	10
	Review. Independent, supervisory review and sign-off that work is complete and correct prior to start-up or returning component to service	10
	Action. An operator action that uses a different operator, relying on independent observation	10
	Corrective Action: An operator action taken based on a scenario where the event propagation is sufficiently slow that the operator has enough time to recognize the error and to correct it	10
	Alarm: The alarm with operator response should be examined to ensure that it is independent from the initiating cause and any other IPL. This includes not only independent field instrumentation but also an independent channel in the BPCS and independence of the operator (different operator). Only one BPCS-based alarm or BPCS function can be used as an IPL The RRF associated with alarms with operator response is based on the amount of time available for action and the location of the response. See Operator Time Restrictions Table for more information	See Table 34.6
Basic process control system (BPCS)	The BPCS should be independent of the initiating cause and any other IPL. If the initiating cause is a BPCS control loop, another the control loop's within the BPCS should not be designated as a BPCS IPL, unless a detailed study of the BPCS is performed to ensure sufficient independence and redundancy in order to address common cause failure. The RRF associated with a BPCS IPL is limited to 1 in 10 per IEC 61511	
	The control loops normal action will mitigate the scenario. The BPCS IPL should run in automatic mode during all operational phases where the accident scenario exists	10
Other/local	The IPL should be independent of initiating cause and any other IPL. It should be designed to mitigate the scenario	
Check valve (standard design)	Single check valve	(none)
	Dual check valves in series	10
Flame arrester	Should be designed to mitigate the scenario	100
Vacuum breaker	Should be designed to mitigate the scenario	100
Restrictive orifice	Should be designed to mitigate the scenario	100
Pressure regulator	Should be designed to mitigate the scenario	100

Table 34.5 *(continued)*

IPL	*Further restrictions on considering as IPL*	*RRF (typical)*
Special personnel protection equipment	Special personnel protection equipment (PPE) that is not normally worn by operation or maintenance personnel but is part of an established procedure. This PPE would include wire mesh gloves, fire suits, respirators, self-contained breathing apparatus, etc. The user of the equipment should be trained in the use of the PPE	(none)
Safety instrumented system	Should be independent of the BPCS. RRF is based on the SIL that is achieved by the complete functional loop	
	SIL 1	10
	SIL 2	100
	SIL 3	1000
Pressure relief valve (PRV)	Clean Service. PRV should be sized to completely mitigate the scenario	100
	Clean Service. More than one PRV is available to mitigate overpressure scenario. Each PRV listed should be capable of independently relieving the overpressure. Each PRV should be sized to completely mitigate the scenario	1000
	Clean Service. More than one PRV is available, but more than one is required to mitigate the full load. This includes staged release PRVs. To achieve an RRF higher than 10, the PRV calculations should be reviewed to determine whether the load can be successfully handled by each PRV, based on the specific scenario under review	10
	Plugging Service, that is, prone to plugging, polymerization, deposition, or has a history of failure to operate properly when tested. An unprotected PRV used in a plugging service is not considered sufficient for consideration as an IPL	10
	Plugging Service, that is, prone to plugging, polymerization, deposition, or has a history of failure to operate properly when tested. Redundant Pressure Relief Valves with separate process connections. Each PRV should be sized to completely mitigate the event	10
	Plugging Service, that is, prone to plugging, polymerization, deposition, or has a history of failure to operate properly when tested. Pressure Relief Valve with integrated rupture disk. PRV should be sized to completely mitigate the scenario	10
	Plugging Service, that is, prone to plugging, polymerization, deposition, or has a history of failure to operate properly when tested. Pressure Relief Valve with integrated rupture disk with purging. PRV should be sized to completely mitigate the scenario	100
Vessel rupture disk	Should be designed to mitigate scenario. Release should be evaluated for potential risk	100
Blast-wall/bunker	Process-related blast wall. This is not related to the control room design. The blast wall is typically designed to direct/contain the explosion away from the main process unit	1000
Fire detection with water deluge system	Operator initiated response. The RRF is based on operator alarm and response criteria, as listed in Operator Time Restrictions Table	Table 34.6
	Using fire detectors with automatic deluge, for example, foam, water curtain, water sprays, or emergency evacuation	10
Gas monitors with automated deluge	Operator initiated response. The RRF is based on operator alarm and response criteria, as listed in Operator Time Restrictions Table	Table 34.6
	Using gas monitor with automatic response, for example, water cannons, water sprays, or emergency evacuation	10

Table 34.6 *Typical operator time restrictions with associated risk reduction factors (RRF) (Courtesy of SIS-TECH Solutions, LP)*

For all listings in the table below, the alarm and operator response should be evaluated to ensure that the components and actions are independent of the initiating cause. In all cases, the alarm must not be operator re-settable. The operator response time should consider the time it takes to recognize the alarm, to diagnose the problem, and to fully initiate action. This is compared to the process time, taking in account how rapidly the process moves from the alarm condition to the incident condition

Time (min)	*Where*	*How many*	*Restrictions*	*RRF*
<10	Any	Any	Operator must troubleshoot the alarm and determine appropriate response	1
2–10	Control room	Single operator	Drilled response, also known as a '**never exceed, never deviate**' response. If the alarm is received, the operator should execute a specific action every time without delay. Staffing should also be adequate so that there is an operator present at all times to respond to the alarm. If the operator response is to troubleshoot the alarm, less than 10 min is not an adequate amount of time and no RRF is allowed	10
>10	Control room	Single operator	Operator action is complicated, that is, large number of alarms generated by initiating cause and the response is not clear or documented	1
>10	Control room	Single operator	The operator is trained on alarm response, has procedures available to examine and practices the action periodically	10
>10	Control room	Two operators	All operators listed must receive the same information. Both operators can make independent responses, which completely mitigate the event. Alarm must not be operator re-settable. The operators are trained on alarm response, have procedures available to examine and practice the action periodically	100
>20	Field	Single operator	The operator is trained on alarm response, has procedures available to examine and practices the action periodically	10
>20	Field	Two operators	All operators listed must receive the same information. Both operators can make independent responses, which must completely mitigate the event. Alarm must not be operator re-settable. The operator is trained on alarm response, has procedures available to examine and practices the action periodically	100

team with a listing of hazard scenarios with associated initiating causes, consequence ratings and potential safeguards for consideration as IPLs.

34.5 Level of Automation

The allocation of function between the operator and the control system is a principal theme in human factors analysis and is discussed in Chapter 14. Of particular interest is the allocation of control and protective functions to the process operator or the instrumented system.

34.5.1 Illustrative example: steam boiler protective system

A case study of the optimum level of automation has been described by Hunns (1981). The system investigated was the protective system for a large steam plant. The plant consisted of a 100 MW boiler operating at 1500–2000 psi and producing 500 ton/h of steam. The boiler was dual fired with oil and gas. The principle features of the three candidate control and protective systems are shown in Table 34.7.

Each system was assessed for its reliability in the start-up and operational phases of the plant. A variety of start-up sequences was considered, since each shut-down event resulted in the requirement for a different start-up sequence. Some 200 logic diagrams were produced.

The criterion used to determine the optimum system was a function of the type of expected shutdowns, which were. These were classified as low penalty and high penalty. Low penalty shut-downs were unwanted shut-downs due to spurious trips and correct shut-downs in response to a demand. High penalty, or catastrophic, shut-downs were those caused by a demand to which the protective system did not respond.

One such case is an excessive release of unignited fuel into the combustion chamber. Figure 34.7 shows a section of the logic, which the authors term 'matrix logic'. Events identified by the analyst are shown in the left-hand column. A particular event sequence is shown by a vertical column of the matrix containing one or more dots. The circle enclosing the '&' symbol at the head of the column indicates that the events are ANDed together. The set of event sequences is collected under the OR symbol, which indicates that these event sequences are related to the top event, the unignited release, by OR logic.

The device failure data were taken from the Safety and Reliability Directorate SYREL data bank. Human error was estimated based on expert judgement. There were almost 180 human errors estimated by two experienced analysts. Performance shaping factors were assessed, such as available time to react, prior expectancy, conspicuity of task and perception of consequence. Good agreement was obtained between the two analysts for most human errors. Those estimates that were particularly critical, or where a divergence between the two analysts had occurred, were mediated by a third, independent analyst.

The results of the study were expressed in terms of the number of low and high penalty shut-downs per year and the corresponding mean outage time. The mean outage of low penalty events was taken as 1/3 days/event and that of high penalty events as 60 days/event. The manual system resulted in appreciably more high penalty shut-downs but fewer with low penalty and overall a higher outage than the other two systems. The medium automated system yielded slightly more high penalty shut-downs and fewer low penalty shut-downs than the highly automated system, but the same outage time. On a lifecycle cost basis, for which the highly automated system had higher capital and maintenance costs, the medium automated system was superior. The total lifecycle costs of the three systems – manual, medium automated and highly automated – were £0.122, 0.095 and 0.099 million/year, respectively.

34.6 Design

Appropriate SIS design requires that the engineer understand the underlying purpose of the SIS. This entails reviewing the process hazards analysis (PHA) documentation to better define the required SIS functionality and integrity. These basic requirements should then be developed into complete specifications.

The functional specification should include the following:

- Definition of the process safe state;
- SIS inputs, voting configuration and trip points;
- SIS outputs, redundancy requirements and safe state actions;
- functional relationship between inputs and outputs;
- automatic diagnostics for inputs and outputs;
- provisions for bypassing, testing and maintenance;
- provisions for manual shut-down;
- required reset actions;
- response time requirements for SIS actions;
- means by which alarm, trip and diagnostic information is to be communicated to plant operator.

Table 34.7 *Elements of three candidate protective systems for a large steam boiler plant (after Hunns, 1981) (Courtesy of Elsevier Science Publishers)*

Control and protective features	*Protective system design*[a]		
	Manual	*Medium automated*	*Highly automated*
Trip parameters[b]	A	A	A
Boiler purge sequence	M	A	A
Burner flame failure detection	M	A	A
Gas valves leak test	M	M	A
Ignition burner control	M	M	A
Burner fuel valves operation	M	A	A

[a] A, automated; M, manual.
[b] Low boiler drum level; low combustion air flow; low instrument air pressure; low fuel oil pressure; low atomizing steam pressure; low fuel gas pressure; high fuel gas pressure; high knockout drum level; and loss of 110 V DC supplies.

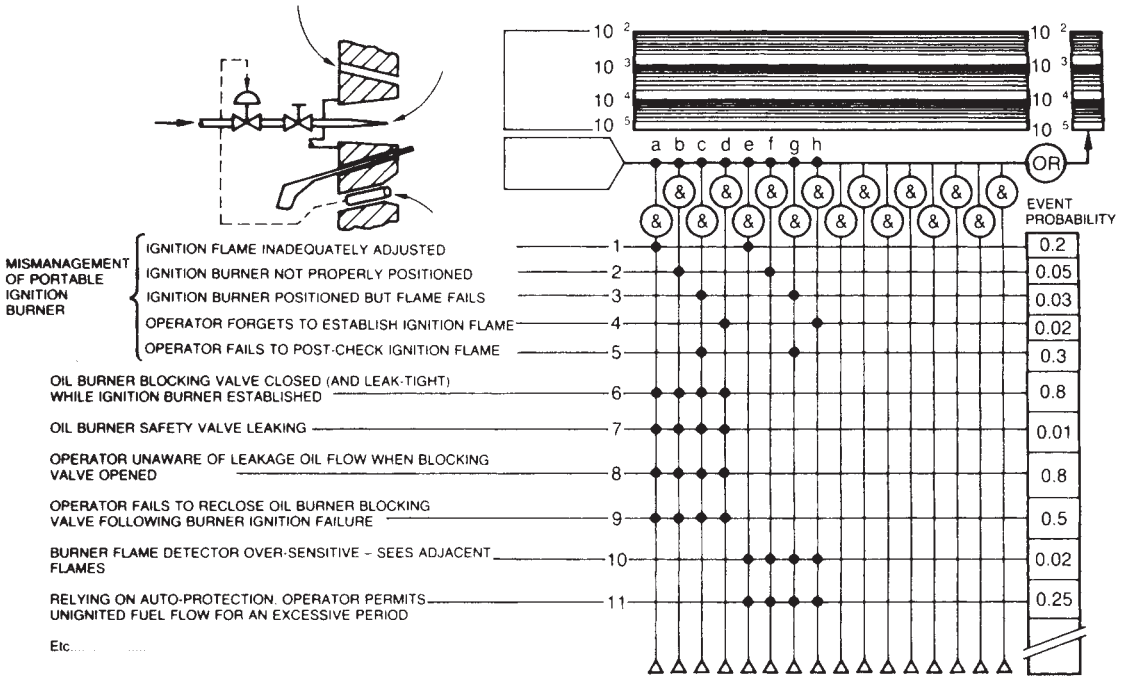


Figure 34.7 *Matrix logic diagram for a steam boiler protective system: event 'excessive unignited fuel release' (Hunns, 1981) (Courtesy of Elsevier Science Publishers)*

The integrity specification should include the following:

- integrity level assigned to the SIS;
- testing interval requirements;
- limitations on acceptable spurious trip rate.

Once the functionality and integrity requirements are fully understood, the design process can begin. The following section will provide a discussion of the following: (1) separation of basic process control system (BPCS) and SIS, (2) response time requirements, (3) power supply, (4) choosing components, (5) integration of SISs and (6) field design.

34.6.1 Separation of BPCS and SIS

Prior to the implementation of modern digital control systems (DCSs), the process industry relied on local control systems for day-to-day operation and local relay systems for shut-down functions. The design was inherently separated. The local pneumatic controller had its own transmitter and control valve. The relay system used separate process switches and dedicated final elements.

As technology changed, there was intense pressure to combine these systems. However, the implementation of complex PESs makes it increasingly important to maintain the independence of the BPCS and the SIS. When these systems are combined, the SIS functions may be impacted by normal activities that take place within the BPCS, such as optimization of process control logic and manual control activities carried out by the operator.

Most process control systems involve some sequential control even if it is largely limited to start-up and shut-down. The sequential logic should operate in such a way as not to cause any safety problems. Its operation should be tested against the SIS logic to ensure that normal operation of the sequential control does not trigger unnecessary SIS action or inhibit any required SIS action. BPCS provides protection against hazardous events by maintaining the process within control tolerances. Process alarms are issued to the operator through the BPCS human–machine interface, notifying the operator that the process has exceeded preset process conditions. This allows the operator the opportunity to bring the process back into control, preventing a unit shut-down.

CCPS *Safe Automation Guidelines* discusses the safety considerations in the selection and design of the BPCS. The topics covered include: (1) the technology selection, (2) the signals, (3) the field measurements, (4) the final control elements, (5) the process controllers, (6) the operator/control interfaces, (7) communication considerations, (8) electrical power distribution systems, (9) control system grounding, (10) batch control, (11) software design and data structures and (12) advanced computer control strategies. The design philosophy of CCPS *Safe Automation Guidelines* requires that the BPCS and the SIS be separate systems. This ensures that the integrity of the SIS cannot be compromised by the BPCS.

IEC 61511 provides restrictions on the assumed failure rate of the BPCS and the risk reduction that can be claimed for it as a protection layer. It also discusses the analysis of common cause failures between the BPCS and other layers of protection including the SIS. The BPCS and SIS must be functionally independent such that no failure of the BPCS can prevent the SIS from functioning.

IEC 61511 also recommends the use of separation and diversity to achieve high SILs. For example, if the control valve can be the initiating cause for the hazard, the control valve should not be used as the primary shutdown device. Instead, a dedicated shutdown device should be provided to mitigate the risk. In the case of high SIL requirements, redundant, dedicated shutdown devices are often implemented.

34.6.2 Response time requirement

The dependability of an SIS is based on its functionality and integrity. An important aspect of functionality is the dynamic response. The dynamic response of instrumentation is illustrated in Figure 34.8. It is assumed in the figure that, when a fault occurs, the variable increases linearly from its normal level to the danger level. The nominal trip point is established somewhere along this ramp using an appropriate safety margin from the hazardous condition. However, the trip often does not occur at the specific point in time corresponding to this process variable condition. There will normally be delays due to (1) sampling, (2) dynamic response of the measuring instrument and (3) normal measuring instrument error. Even when the measuring instrument has responded, there will be delays in the safety circuitry and the closure of the shut-down valve. There will be a further delay in the process itself, due to the amount of time required for the valve closure to affect the process variable. All of these factors, delays and errors erode the available safety margin and should be considered carefully. The maximum rate of rise of the process variable is also critical. If the process variable rises very rapidly, SIS valve closure speed may become a major design factor.

Further reduction of the nominal trip point may be appropriate, but the setting should not be put so low that noise in the process variable measurement activates the trip at normal operational conditions. After all, a spurious trip can arise from a low trip set point, as well as from instrument unreliability.

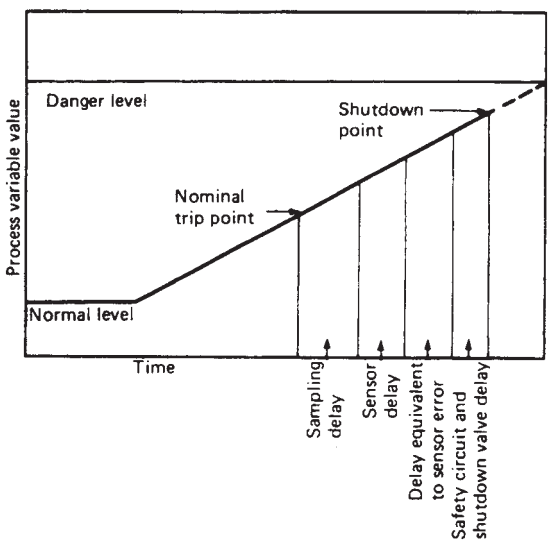


Figure 34.8 *Effect of instrument error and dynamic response on the safety margin in a trip system (after Hensley, 1988) (Courtesy of the institute of Measurement and Control)*

The dynamic response of the hazard scenario against which the SIS is designed to protect may be modelled using standard methods. An account of unsteady-state modelling of process operations is given in *Mathematical Modeling in Chemical Engineering* (Franks, 1967) and the modelling of instrumentation is treated in texts on process control, such as those by Harriott (1964) and Coughanowr and Koppel (1965).

The following treatment is confined to the dynamic response of the measuring instrument or sensor. The inputs to a sensor are generally characterized by a set of idealized forcing functions, of which the main types relevant here are: (1) the step function, (2) the ramp function and (3) the impulse function. The unit step function changes suddenly at time zero from a value of zero to a value of one. The unit ramp function increases linearly with time and has a slope t. The unit impulse is a function that is infinitely large at time zero and zero elsewhere, but also has an area that is unity. These three forcing functions are shown in Figure 34.9(a)–(c).

The device is typically modelled as either a first- or second-order system. Thus a temperature sensor might be modelled as a first-order system:

$$Mc_p \frac{\mathrm{d}T}{\mathrm{d}t} = UA(T_\mathrm{i} - T) \qquad [34.6.1]$$

where A is the area for heat transfer to the sensor, c_p is the specific heat of the sensor, M is the mass of the sensor, t is time, T is the temperature of the sensor, U is the overall heat transfer coefficient, and the subscript i indicates input, or forcing. Thus, T_i is the temperature of the surrounding fluid.

Equation 34.6.1 may be written in the more general form for a first-order system as:

$$\tau \frac{\mathrm{d}T}{\mathrm{d}t} = T_\mathrm{i} - T \qquad [34.6.2]$$

where

$$\tau = Mc_p/UA \qquad [34.6.3]$$

and τ is a time constant. The lag described by Equation 34.6.2 is known as a 'transfer lag'.

In this case, the model obtained is a linear one. If the model obtained is non-linear, it needs first to be linearized. A non-linear model is obtained, for example, if the mode of heat transfer to the sensor is radiation rather than conduction.

The normal approach is then to express each term in the linear model as the sum of the steady-state value and the transient component. Given θ as the transient component of temperature and the subscript ss as steady state, Equation 34.6.2 then becomes:

$$\tau \frac{\mathrm{d}(T_\mathrm{ss} + \theta)}{\mathrm{d}t} = (T_\mathrm{i,ss} + \theta_i) + (T_\mathrm{ss} + \theta) \qquad [34.6.4]$$

The corresponding steady equation is:

$$0 = T_\mathrm{i,ss} - T_\mathrm{ss} \qquad [34.6.5]$$

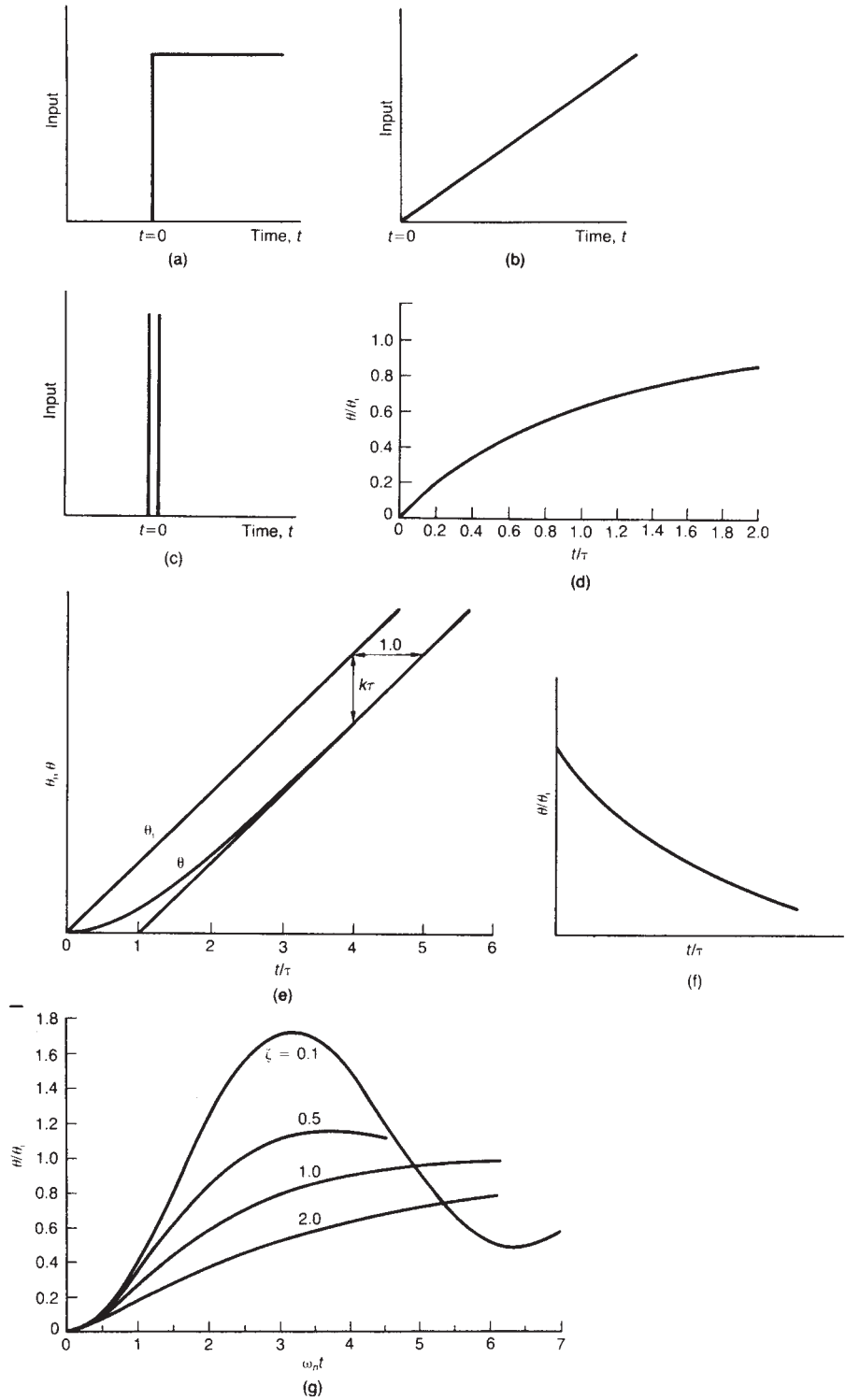


Figure 34.9 *Dynamic response of sensor systems: (a) step forcing function; (b) ramp forcing function; (c) impulse forcing function; (d) response of first-order system to step forcing function; (e) response to first-order system to ramp forcing function; (f) response to first-order system to impulse forcing function; (g) response of second-order system to step forcing function. For second-order system: ω_η, natural frequency: ζ, damping factor*

Subtracting Equation 34.6.5 from Equation 34.6.4 gives:

$$\tau\frac{d\theta}{dt} = \theta_i - \theta \quad [34.6.6]$$

Equation 34.6.6 is then transformed into the Laplace, or *s,* domain by taking the Laplace transform:

$$s\bar{\theta} - \theta(0) = \bar{\theta}_i - \bar{\theta} \quad [34.6.7]$$

Taking the initial condition as the steady state with zero deviation gives $\theta(0) = 0$ and hence the ratio of the output to the input, or the transfer function, is:

$$\frac{\bar{\theta}}{\theta_i} = \frac{1}{1+\tau s} \quad [34.6.8]$$

The response of the first-order system to the three forcing functions is then as follows. For the step response:

$$\theta_i = k \quad [34.6.9]$$

where k is a constant. Taking the Laplace transform of Equation 34.6.9 gives

$$\bar{\theta}_i = \frac{k}{s} \quad [34.6.10]$$

Substituting Equation 34.6.10 in Equation 34.6.8 gives:

$$\bar{\theta} = \frac{k}{(1+\tau s)s} \quad [34.6.11]$$

Inverting the Laplace transformed expression in Equation 34.6.11 back into the time domain:

$$\theta = k[1 - \exp(-t/\tau)] \quad [34.6.12]$$

Equation 34.6.12 is sometimes written as:

$$\frac{\theta}{\theta_i} = 1 - \exp(-t/\tau) \quad [34.6.13]$$

Where this is done, it should be noted that θ_i is a constant, defined by Equation 34.6.9, whereas in Equation 34.6.6 it was a variable.

For the ramp response, θ_i is given as:

$$\theta_i = kt \quad [34.6.14]$$

$$\bar{\theta}_i = \frac{k}{s^2} \quad [34.6.15]$$

$$\bar{\theta} = \frac{k}{(1+\tau s)s^2} \quad [34.6.16]$$

$$\frac{\theta}{\theta_i} = \tau\left\{\frac{t}{\tau}[1 - \exp(-t/\tau)]\right\} \quad [34.6.17]$$

The ramp response has the important property that

$$\frac{\theta}{\theta_i} = t - \tau \qquad t \to \infty \quad [34.6.18]$$

In other words, after an initial transient, the measured value lags the actual value by a time equal to the time constant τ.

For the impulse response:

$$\theta_i = k\delta(t) \quad [34.6.19]$$

$$\bar{\theta}_i = k \quad [34.6.20]$$

$$\bar{\theta} = \frac{k}{1+\tau s} \quad [34.6.21]$$

$$\frac{\theta}{\theta_i} = \frac{1}{\tau}\exp(-t/\tau) \quad [34.6.22]$$

where $\delta(t)$ is the impulse function. The step, ramp and impulse responses of a first-order system are shown in Figures 34.9(d)–(f).

An over-damped second-order system is equivalent to two transfer lags in series. The basic model is therefore:

$$\tau_1\frac{dT_1}{dt} = T_i - T_1 \quad [34.6.23]$$

$$\tau_2\frac{dT_2}{dt} = T_1 - T_2 \quad [34.6.24]$$

where subscripts 1 and 2 indicate the first and second stages, respectively.

The transfer function of the second-order system is:

$$\frac{\bar{\theta}_2}{\theta_i} = \frac{1}{(1+\tau_1 s)(q+\tau_2 s)} \quad [34.6.25]$$

The step response is:

$$\frac{\theta_2}{\theta_i} = 1 - \frac{1}{\tau_1 - \tau_2}[\tau_1\exp(-t/\tau_1) - \tau_2\exp(-t/\tau_2)] \quad [34.6.26]$$

The impulse response is:

$$\frac{\theta_2}{\theta_i} = \frac{1}{\tau_1 - \tau_2}[\exp(-t/\tau_1) - \exp(-t/\tau_2)] \quad [34.6.27]$$

The step response of a second-order system is shown in Figure 34.9(g).

It is sometimes required to provide an unsteady-state model of the sensor for incorporation into an unsteady-state model of the total system. In this case, an equation such as Equation 34.6.2 may be used for a first-order system and a pair of equations such as Equations 34.6.23 and 34.6.24 for a second-order system.

The three forcing functions may be illustrated by a flammable gas cloud as seen by a gas detector. The gas cloud may be seen by the sensor as any one of these forcing functions. The gas concentration may rise suddenly from zero to a value that remains constant (step function), it may rise linearly (ramp function) or it may rise momentarily from zero to a high value and then subside as rapidly (approximated by an impulse function).

An account of the time lags that occur in SISs has been given by R. Hill and Kohan (1986), who characterize the

dynamic response of a SIS by a ramp function similar to that shown in Figure 34.8 and consider, in turn, the individual time lags. If the time interval from the initial process deviation to the hazard point exceeds 2 min, there is normally no problem in designing the SIS. On the other hand, if the time interval is less than this, there is a potential problem. If the time interval is only a few seconds, an SIS may not be practical.

The signal transmission lags to and from the logic system, and the logic system delay itself are normally negligible. The more significant lags are likely to be in the sampling and the sensor, in the final control element, and in the process itself. For analysers, sampling lags may amount to a dead time of the order of seconds to minutes. For smart transmitters, the sensor lag may be of the order of 100–250 ms. Transfer lags in sensors vary, with temperature measurement lags often being large due to the thermal inertia of the measuring pocket. The lag at the control valve can vary from a fraction of a second up to several minutes, depending on the valve size. The lag in the process itself is also highly variable.

34.6.3 Power supply

Loss of power to the process unit results in the failure of pumps and other electrical driven equipment. During the flare load analysis, as discussed in this volume, the loss of power case was cited as often presenting the largest flare load. How long one can run safely without power is dependent on the process operation. In designing the SIS, the choice must be made between energize-to-trip (ETT) and de-energize-to-trip (DTT).

The SIS standards, ISA 84.01-1996 and IEC 61511, recommend the use of DTT design to provide greater assurance that the safe state is achieved under loss of power conditions. In a DTT design, loss of power causes the final elements to take their fail-safe action. To prevent brief power interruptions from causing process shut-downs, uninterruptible power supplies (UPS) are used. Power is supplied to the SIS instrumentation by the UPS when the power is lost. The UPS can be sized to supply power for any length of time, but for practical reasons generally do not supply power for periods in excess of 30–45 min.

In DTT design, a power outage results in the final elements going to the safe state. Due to historical plant power supply problems, some companies migrated to an ETT design to allow the plant to continue to operate during short power outages. An ETT design requires that power be applied in order for the final elements to achieve their safe state. This migration to ETT improved process reliability, but placed the process at greater risk of an incident during a loss of power condition. ETT SISs are generally limited to SIL 1 applications, because it is difficult to implement back-up power generation and/or alternative power supplies (e.g. UPS) that have a combined failure rate of less than 1 in 100 years. If ETT circuits are used, line monitoring must be performed, because any loose wire or open circuit will inhibit the safety action. But even line monitoring does not guarantee that the SIS will work when a process demand occurs, because fuses or coils may burn-out when power is supplied.

Further, the discussion of the use of DTT or ETT cannot be restricted to examination of the failure rate only. The use of PES-based devices in ETT applications is questionable. At the chip level, the probable operational states are equally likely to be on or off. There is consequently the question of whether the PES can be made fail-safe in an ETT design. This can only be determined by thorough failure modes and effects analysis. Many modern PES are not approved by independent certifying bodies for use in SISs operated as ETT systems due to the question of fail-safe status. For this reason, the CCPS *Safe Automation Guidelines* suggests alternative approaches to achieving process reliability. These are based on use of; (1) devices of proven reliability with self-diagnostic capability, (2) maintenance programmes stressing preventive maintenance, inspection and proof testing and (3) redundancy including inputs, logic solver and outputs.

34.6.4 Choosing components

The choice of which device to use in an SIS is very important. All devices fail eventually due to manufacturing faults, age-related degradation or damage caused by process impact. Some devices are more prone to failure than others. For this reason, it is important to understand how the device performs in the application environment. This concept is called 'proven-in-use' or 'prior use.' Thus, selecting the right device depends on field experience and available failure rate data, as well as knowledge of the process application and process conditions.

34.6.5 Integration of SISs

As already described, an SIS is normally dormant and operates in a demand mode. An SIS device such as a sensor or a valve may fail in such a way that its failure will remain unrevealed until detected by proof testing or some other means. By contrast, similar devices in a control system are exercised continuously, and these failures are more likely to cause an operational excursion. The failure in the control system is often a revealed one. Yet the actual physical fault in both cases may be identical. A sensor may fail giving a low/zero or high reading, or a valve may stick open or closed. The concept of trip integration, which has been described by Rushton (1992), is based on this contrast between a fault that lies unrevealed in an SIS but is revealed in a measurement and control system. The principle applies to any system that has a protective function. The system is regarded as integrated provided it is regularly exercised, which generally means that it is in use during the normal operation of the plant.

As an illustration, Rushton describes a refrigerated storage tank for a toxic liquid, equipped with a cooling system and a pressure relief valve. Both are protective systems, but the cooling system is in more or less continuous use and is thus integrated, whereas the relief valve is not.

In this case, the integration is benign, but it can also be malign. As an example of the latter, consider the case of a sensor that is common to both a level control loop and a high level alarm. Failure of the sensor results in failure not only of the control loop but also of the alarm. These situations can easily be identified using LOPA. Then, design modifications can be implemented to ensure the independence and integrity of each protection layer.

34.6.6 Field design

34.6.6.1 Configuration of SISs

The configuration of SISs has been discussed by Rushton (1991a,b), who describes a formal approach. According to Rushton, for a fixed proof test interval, the ranking of SISs with respect to their functional and operational reliability is invariant and this is shown in Table 34.8. The SISs most commonly used are the 1oo1, 1oo2, 2oo2 and 2oo3 systems.

Table 34.8 *Ranking of SIS configurations with respect to functional and operational failure (Rushton, 1991b) (Courtesy of the Institution of Chemical Engineers)*

Functional ranking		*Operational ranking*	
ϕ_{moon}	*System*	γ_{moon}	*System*
Low	1oo3	Low	3oo3
↓	1oo2	↓	2oo2
	2oo3		2oo3
	1oo1		1oo1
↓	2oo2	↓	1oo2
High	3oo3	High	1oo3

The use of parallel redundant, or 1oo*n* (1-out-of-*n*), systems gives an increase in functional integrity, but a decrease in operational reliability compared with a 1oo1 (1-out-of-1) system. Better overall reliability characteristics can be obtained by the use of a majority voting system, of which the 2oo3 system is the simplest. A comparison of a 2oo3 system with a 1oo1 system shows that the 2oo3 system has a higher functional integrity and operational reliability, while a comparison with a 1oo2 system shows that the 2oo3 system has a slightly lower functional integrity, but a much higher operational reliability. The 2oo2 system has some interesting characteristics. It has a lower functional integrity than a 1oo1 system, but its operational reliability exceeds not only that of the 1oo1 but also that of the 2oo3 system. When 2oo2 systems are used to improve operational reliability, the functional integrity can be improved by increased proof testing or by enhanced diagnostics. The requirement for functional integrity is rarely such as to justify a 1oo3 system and that for operational reliability rarely such as to justify a 3oo3 system.

The criterion given by Rushton for selection of the SIS configuration is an economic one and is:

$$V = nC + \delta\phi_s H + \gamma_s S + \delta(1 - \phi_s)G \qquad [34.6.28]$$

where C is the annualized cost of a single channel trip, ϕ is the fractional dead time, γ is the spurious trip frequency, G is the cost of a genuine trip, S is the cost of realization of a hazard, S is the cost of a spurious trip, V is the overall annual cost, and the subscript s indicates the SIS (as opposed to a single channel). The most economic solution is that which minimizes V.

For a genuine trip, there is an element of loss related to the process failure that causes the demand. If, for purposes of comparison, this element (which will occur in all cases) is neglected, the cost of a genuine trip is approximately the same as that of a spurious one ($G = S$), so that Equation 34.6.28 becomes:

$$V = nC + \delta\phi_s H + [\gamma_s + \delta(1 - \phi_s)]S \qquad [34.6.29]$$

If the basic parameters of a particular application are known, namely the demand rate δ, the fail-to-danger rate λ_d, spurious failure rate γ_s, the proof test interval τ_p, the repair time τ_r, the costs of hazard realization H, and spurious trip S, then a plot of H/C vs S/C gives a map showing the regions where a particular configuration is optimal. The boundaries of the regions are curves of constant V/C.

As an illustration, consider the case given by Rushton where the application is characterized by $\delta = 0.01$ demands/year, $\lambda = 0.2$ failures/year, $\gamma = 0.5$ failures/year, $\tau_p = 1/12$ and $\tau_r = 1/52$. The map giving the optimal configurations for this case is shown in Figure 34.10(a). If δ is increased to 1.0 demand/year, the map becomes that shown in Figure 34.10(b).

Rushton also treats the case where there is an element of common cause failure (CCF). Rushton uses the beta method described in Chapter 9. He considers a 1oo2 system:

$$\phi_{1oo2} = \frac{[\lambda(1 - \beta_1)\tau_p]^2}{3} + \frac{\beta_1 \lambda \tau_p}{2} \qquad [34.6.30]$$

$$\gamma_{1oo2} = 2 \times (1 - \beta_2)\gamma + \beta_2\gamma \qquad [34.6.31]$$

$$= (2 - \beta_2)\gamma \qquad [34.6.32]$$

where β_1 is the fraction of the functional failure rate which is common cause, or the functional beta value for that failure rate, and β_2 is the operational beta value.

The effect of CCF may be illustrated by considering the extension given by Rushton of his example to the case of a 1oo2 SIS where $\delta = 1$ demand/year, $\lambda = 0.2$ failures/year, $\gamma = 0.5$ failures/year, $\tau_p = 1/12$, $\tau_r = 1/52$ and where $\beta_1 = \beta_2 = \beta$. Maps of the configuration space for this case are shown in Figure 34.6.3(c) and (d) for different values of β. Table 34.9 gives expressions for the probability of failure on demand and spurious trip rate for different trip configurations.

This cost-based approach allows the different SIS configurations to be put on a common basis for purposes of comparison. Where the hazard includes risk to human life, there will be a target probability of failure or SIL that must be achieved and this will be the overriding factor in the choice of configuration. However, there are often many different SIS configurations that can achieve the necessary integrity. The cost-based approach can be used to judge which configurations are reasonably practicable from an operational reliability standpoint.

34.6.6.2 Field sensors

The SIS field sensors should be independent from the initiating cause for the potential hazardous event and from any other protection layers used to reduce the process risk to the risk tolerance. Independence is necessary to minimize common cause failure. For example, if the initiating cause is the process control transmitter, the control transmitter cannot be used as the sole means for SIS initiation. For enhanced diagnostics, the control transmitter signal can be compared to the SIS transmitter signal to detect faults. Any sharing of the control transmitter with the SIS should be carefully assessed to ensure that potential common cause failures are adequately addressed. Further, the design should ensure that no failure of the control system can disable the SIS.

Field sensor redundancy is related to the required integrity. For SIL 1, redundancy is usually not necessary, though it may be appropriate for a lower integrity (i.e. high failure rate) field sensor or for improving operational reliability. For SIL 2, redundancy is often employed to reduce the required proof test interval and to improve operational reliability. For SIL 3 or 4, there should be full redundancy, such that there are no single points of failure in the SIS design. IEC 61511 requires the demonstration of fault

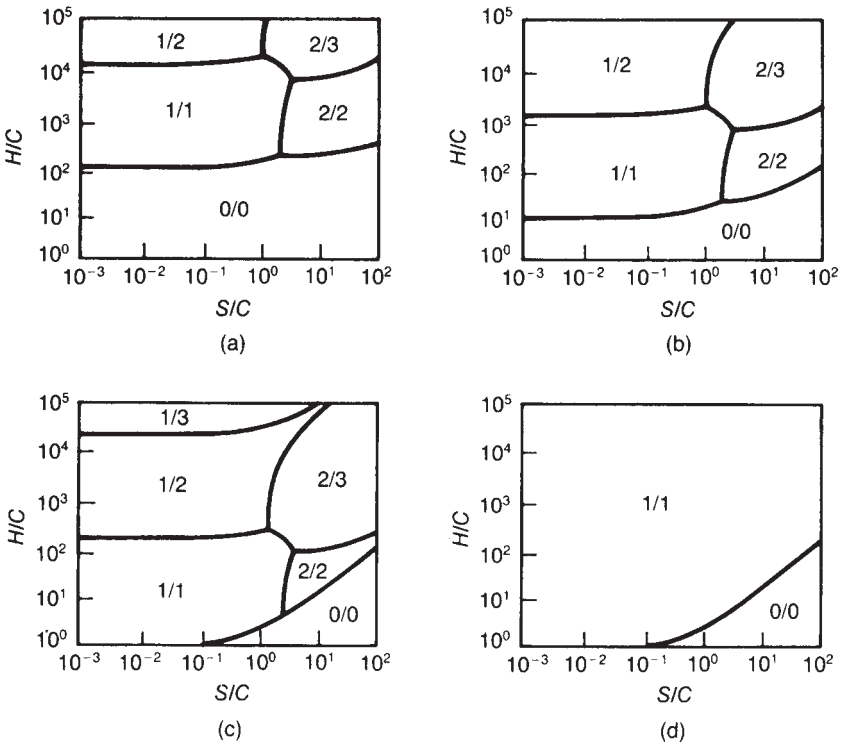


Figure 34.10 *Configuration selection map for trip systems: illustrative examples (Rushton, 1991b): (a) case with $\delta = 0.01$, $\beta = 0$; (b) case with $\delta = 0.1$, $\beta = 0$; (c) case with $\gamma = 1$, $\beta = 0.3$; and (d) case with $\gamma = 1$, $\beta = 1$. See text for further details (Courtesy of the Institution of Chemical Engineers)*

Table 34.9 *Fractional dead times and spurious trip rates for trip systems with simultaneous proof testing and common cause failures accounted for by the beta method (Rushton, 1991b) (Courtesy of the Institution of Chemical Engineers)*

System	ϕ_{moon}	γ_{moon}
1oo1	$\lambda\tau_p/2$	γ
1oo2	$\frac{[\lambda\tau_p(1-\beta_1)]^2}{3}+\frac{\beta_1\tau_p}{2}$	$(2-\beta_2)\gamma$
2oo2	$\lambda\tau_p(1-\beta_1/2)$	$2\gamma^2(1-\beta_2)^2\tau_r+\beta_2\gamma$
1oo3	$\frac{(\lambda\tau_p)^3}{4}(1-\beta_1)^3+\frac{\beta_1\lambda\tau_p}{2}$	$(3-2\beta_2)\gamma$
2oo3	$(\lambda\tau_p)^2(1-\beta_1)^2+\frac{\beta_1\lambda\tau_p}{2}$	$6\gamma^3(1-\beta_2)^3\tau_r^2+\beta_2\gamma$
3oo3	$\frac{\lambda\tau_p}{2}(3-2\beta_1)$	$3\gamma^3(1-\beta_2)^3\tau_r^2+\beta_2\gamma$
moon	$\binom{n}{r}\frac{[\lambda\tau_p(1-\beta_1)]^r}{r+1}+\frac{\beta_1\lambda\tau_p}{2}$	$n\gamma(1-\beta_2)\binom{n-1}{m-1}[\gamma(1-\beta_2)\tau_r]^{m-1}+\beta_2\gamma$

tolerance for SIL 3 or 4. Depending on the voting configuration selection, the incorporation of fault tolerance may also improve operational reliability.

Other features typically used for SIL 3 are on-line, continuous diagnostics and consideration of the use of diversity in the sensors. Use of diversity that reduces the on-line diagnostic capability should be carefully examined. Diagnostic capability improves functional and operational reliability, where diversity only improves functional integrity. Further, the achievement of diversity

may require the use of a lower integrity component, offsetting any potential benefit gained from the diversity.

34.6.6.3 Diagnostics

Diagnostics may be used to detect failures of SIS components, including sensors, logic solvers, final control elements and energy sources. The CCPS *Safe Automation Guidelines* distinguish between passive and active diagnostics. In passive diagnostics, the failure is revealed only when a demand is imposed, either by the system or by a proof test. In active diagnostics, the device is subjected continuously to testing, such as the comparison of analog signals from redundant transmitters. If the analog signals begin to deviate from each other and this deviation exceeds a pre-set tolerance, an alarm is generated notifying plant personnel that maintenance activity is required. An example of passive diagnostics is the use of partial stroke testing, where the solenoid valve that controls the air source to the final control element is used to periodically (e.g. daily, weekly or monthly) move the valve from the fully open position. This test provides early detection of solenoid valve and process valve failures.

34.6.6.4 Logic solver

The SIS technologies given in the CCPS *Safe Automation Guidelines* include: (1) fluid logic (pneumatic, hydraulic); (2) electrical logic, including direct-wired systems, electromechanical devices (relays, timers), solid-state relays, solid-state logic and motor-driven timers; (3) PES technology, involving programmable logic controllers (PLCs) and (4) hybrid systems. The technologies are detailed in Appendix A of the CCPS *Safe Automation Guidelines*.

The hardware of a typical PES consists of a chassis, input modules receiving sensor signals, main processors, output modules sending out signals to final control elements, terminations, power supplies, a BPCS interface, a human/machine interface and an engineering interface. The software of a typical PES consists of embedded software and utility software, which perform the system level fault detection and execute basic PES functions. In addition, an application program within the PES executes the required user functions. The application program is constructed using software that is typically provided by the PES vendor.

The use of software raises a significant issue. Evolution of operating system platforms has resulted in a shortening of the lifespan of the embedded software. In some cases, the life span has decreased to less than 10 years. After this relatively short time, the vendor may no longer support the embedded software. Upgrading the embedded software is a major software modification that must be performed offline and with thorough testing to ensure that the hardware works properly with the new embedded software.

In the case of application software, process design or operational changes often result in the need to change the software. IEC 61511 requires that any change to the software is performed under management of change review. Further, any logic potentially impacted by the change should be tested to ensure that the change does not prevent proper operation of any other SIS.

The SIS logic solver must provide performance that meets the required SIL. It was general practice for many years to design SISs as separate, hardwired systems. Hardwired systems have highly predictable failure modes and exhibit low failure rates. In contrast, PES are composed of hardware and software components with complex failure modes and substantially higher failure rates. The major advantages of PES are the ease of logic sequencing implementation, the ability to perform complex SIS logic and enhanced diagnostics of field components. Over the last 15 years, the practice of using PES has gained wider acceptance.

A PES uses a large number of automatic diagnostic circuits and functions that are implemented in hardware and software. The purpose of the diagnostics is to detect failures, particularly dangerous failures, which would inhibit the operation of the PES. Upon detection of failure, the PES may perform one of the following actions:

(1) For a simplex PES, the SIS fail-safe action is initiated.
(2) For 1oo*n* PES, the SIS fail-safe action is initiated.
(3) For 1oo*n* PES, if the process safety time is sufficiently long, the operational state is continued under alternative operating procedures or by other compensating measures that ensure that safe operation is maintained.
(4) For 2oo*n* PES, the failed circuit is voted toward the trip state. The operational state is continued under alternative operating procedures or by other compensating measures that ensure that safe operation is maintained.

In the event of any detected failure, an alarm is generated by the PES indicating the nature of the failure and that maintenance is required.

It is impossible to have 100% diagnostic coverage of faults. After all, the diagnostics are being performed by hardware or software components and these components are subject to failures that would prevent them from detecting faults. The dangerous failures that are not detected by diagnostics are called dangerous, undetected failures. These failures can only be uncovered by proof testing the PES hardware. The testing should be performed at a frequency that enables the PES to achieve the required SIL.

Software-based SISs are treated in *Safety Aspects of Computer Control* (P. Bennett, 1993). Other accounts are given by P. Bennett (1991a,b), Bologna (1993), Ehrenberger (1993), Malcolm (1993), McDermid (1993) and Pyle (1993). Since software-based SISs are complex, successful implementation requires a disciplined process to achieve functional integrity. Thus, standards are particularly important for software-based SISs. Practical guidance is available in ANSI/ISA 84.01-1996, IEC 61508, and IEC 61511. For particularly complex software systems, analysis methods are necessary to identify hazards associated with the software itself. The application of HAZOP to process computers (CHAZOP) is described in Chapter 8.

There are a number of real-time languages and environments that have special safety-related features. One example is ADA. Accounts are given in *Program Verification Using ADA* (McGettrick, 1982), *ADA for Specfication and Design* (Goldsack, 1985), *ADA in Industry* (Heilbrunner, 1988) and *Developing Safety Systems: A Guide Using ADA* (Pyle, 1991).

An account of the application of PES to functions such as pump change over, fire and gas detection and emergency shut-down has been given by Margetts (1986a,b). He describes the planning of an operation such as pump changeover using hierarchical task analysis, in which the changeover task is successively re-described until it has been broken down into executable elements, and the application of HAZOP to assess the adequacy of the resultant design.

34.6.6.5 Final elements

The final elements used for shut-down action should be independent of the initiating cause of the incident and any other protection layer used to mitigate the incident. The final elements can be valves, circuit breakers, motor starters, protective relays, etc.

Final element redundancy is related to the required integrity. For SIL 1, redundancy is usually not necessary, though it may be appropriate for a lower integrity (i.e. high failure rate) final element. For SIL 2, redundancy is often employed to reduce the required proof test interval. For SIL 3 or SIL 4, there should be full redundancy, such that there are no single points of failure in the SIS design. IEC 61511 requires the demonstration of fault tolerance for SIL 3 or SIL 4.

For valves, the engineer should select the valve type that provides the best performance in the application environment. This includes assessing the impact of the application environment on the valve, the need for tight shut-off, and the required speed of closure. Enhanced valve diagnostics should strongly be considered in SIL 3 or SIL 4 applications. For example, valve diagnostics can be obtained by partial stroke testing the process valve using the solenoid-operated valve that controls the air signal to the valve actuator. The solenoid valve is de-energized for a short time period allowing the process valve to move away from the full-open position. Once valve movement is confirmed, it is returned to the full-open position without process disruption. Since the degree of valve closure is controlled by the test method, any partial stroke test apparatus or procedure should be carefully assessed to ensure that operational reliability is maintained. Improper design of the partial stroke test apparatus or an incorrect procedure may result in full-closure of the valve, resulting in a process disruption.

34.7 Verify

34.7.1 Dependability

Since an SIS protects against a hazardous condition, it is essential for the system itself to be dependable. The dependability of an SIS is related to its: (1) functionality and (2) integrity. It is necessary for the system to have the capability of carrying out its function in terms of features, such as accuracy, dynamic response, etc., and for it to have a high probability of doing so.

The SIS functionality was discussed in Section 34.6. SIS functionality is defined by identifying what must be detected and the response that must be taken to achieve the safe state. The SIS functionality is, therefore, related to the input and output architecture.

The SIS integrity can be improved by the use of: (1) redundancy, (2) diversity and (3) diagnostics. Redundancy involves the use of multiple instruments to detect the potentially hazardous event. With voting, multiple failures are required for the SIS to fail to function. This yields a lower probability of failure than that of a single instrument. But, redundancy is not always the full answer, because there are some dependent failures which may disable the whole set of redundant instruments. This difficulty can be minimized by implementing diversity, which often involves using different process variables to detect the same hazard or different types of instrumentation to measure the same process variable. On-line diagnostics can also be used to detect component failure including dependent failures. Diagnostics allow the operator to be notified that an SIS fault has occurred, significantly improving SIS integrity.

Most SISs consist of a single channel comprising a sensor, a logic processor and a final control element, but where the integrity required is higher than that which can be obtained from a single channel, redundancy is generally used.

In the process industry, hazardous conditions are seldom present, so most SISs operate in a demand mode, that is the SIS is dormant until a process excursion or demand occurs. Thus, functional failures of the system are generally unrevealed failures. Device failure that results in the SIS failing to function when required by a process demand can be predicted using probabilistic techniques. A dependable SIS should have a low PFD.

The SIS should also be reliable and not result in spurious trips, that is, failure that causes the SIS to shut the plant down when no hazardous condition exists. Thus, operational failures of the system are generally revealed failures, due to direct process impact or to system diagnostics.

It is the objective of SIS design and operation to avoid both loss of protection against the hazardous condition, due to functional failures, and plant shut-down, due to operational failure or spurious trip. Since functional failure of the system is generally unrevealed, it is necessary to carry out periodic proof testing to detect such failure.

The simpler theoretical treatments of SISs usually assume that the functional failures are unrevealed, operational failures revealed and failure rates are constant. This treatment draws particularly on the work of A.E. Green and Bourne in UKAEA AHSB(S) R117 (1966) and in *Reliability Technology* (1972).

34.7.2 Frequency of events in an SIS

A method of determining the frequency of events of interest has been described by Kumamoto, Inoue and Henley (1981). These events are the process demand rate, the functional failure rate and the operational failure rate. The method is implemented in the program PROTECT.

The procedure is to designate each of these events in turn as the top event of a fault tree, to create the fault tree and to determine its cut-sets. These cut-sets together with the proof test interval for the SIS are the inputs used by the model to provide estimates of the frequency of the events mentioned.

The application of this program to determine the expected frequency of these events for an ammonia–air mixing plant as a function of the proof test interval has been described by Kumar, Chidambaram and Gopalan (1989).

34.7.3 Fractional dead time

The fractional dead time (FDT) of a device or system gives the probability that it is in a failed state. ANSI/ISA 84.01-1996, IEC 61511 and IEC 61508 use the term 'probability of failure on demand' to describe the FDT of a device or system. The equations provided in this section and the functional integrity section can be used to calculate the PFD, as well as the FDT.

If the device failure is revealed, the FDT ϕ depends on the failure rate λ and the repair time τ_r:

$$\phi = \lambda\tau_r \quad \tau_r << 1 \qquad [34.7.1]$$

For a series system with revealed failure, the FDT ϕ of the system is related to the FDT ϕ_i of the individual devices as follows:

$$\phi = \sum_{i=1}^{n} \phi_i \quad \lambda_i\tau_{ri} << 1 \qquad [34.7.2]$$

For a parallel system with revealed failure, the FDT ϕ of the system is related to the FDT ϕ_i of the devices as follows:

$$\phi = \prod_{i=1}^{n} \phi_i \quad \lambda_i \tau_{ri} << 1 \qquad [34.7.3]$$

For a parallel redundant, or 1oo$n$, system with revealed failure, the FDT ϕ_{1oon} of the system is related to the FDT ϕ_{1oo1} of a single device as follows:

$$\phi_{1oon} = \phi_{1oo1}^{n} \qquad [34.7.4]$$

If, however, the device failure is unrevealed, the FDT depends on the failure rate λ and the proof test interval τ_p. The probability q of failure within time period t is:

$$q = 1 - \exp(-\lambda t) \qquad [34.7.5]$$

or, for small values of λt

$$q = \lambda t \quad \lambda t << 1 \qquad [34.7.6]$$

Then the FDT is:

$$\phi = \frac{1}{\tau_p} \int_0^{\tau_p} q \, dt \qquad [34.7.7]$$

For a 1oo$n$ system with unrevealed failure, the FDT or ϕ_{1oon} of the system is obtained from the probability q_{1oon} of failure of the system within the time period t:

$$\phi_{1oon} = \frac{1}{\tau_p} \int_0^{\tau_p} q_{1oon} \, dt \qquad [34.7.8]$$

A detailed account of calculation of FDT is given by A.E. Green and Bourne (UKAEA 1966 AHSB(S) R117).

The calculation of the FDT according to Equation 34.7.8 requires the integration of the instantaneous probability as defined by Equation 34.7.5 or 34.7.6 for the specific subsystem voting. For highly redundant SISs, this integration can be quite complicated. Also, it is necessary to integrate the instantaneous probability of each device over a single testing interval. It is not unusual to have staggered testing where the components in the subsystem are tested at different intervals. To simplify the analysis and to account for the staggered testing, ISA TR84.00.02 provides an alternative method for determining the FDT of a 1oo$n$ subsystem. This method may yield a different FDT for the SIS than Equation 34.7.8, but it has been found to provide a sufficiently conservative approximation of the FDT. The FDT or ϕ_{1oon} for the 1oo$n$ subsystem is obtained by multiplying the probability q of failure of the individual devices in the system within the time period t.

As described in ISA TR84.00.02, the FDT for each component is determined using Equation 34.7.7. Then, the voting architecture is modelled using Boolean algebra. This greatly simplifies the calculation, because the integration is performed only for the individual device not for the entire subsystem. For a 1oo$n$ system, the FDT can be expressed as:

$$\phi_{1oon} = \frac{1}{\tau_p} \prod \int_0^{\tau_p} q_n \, dt \qquad [34.7.9]$$

34.7.4 Functional integrity

Functional failure of an SIS may be unrevealed or undetected. In this section, the failure rate λ is used to calculate the FDT of the SIS related to unrevealed, fail-dangerous faults.

For a simple SIS consisting of a single channel 1oo1 system with a failure rate λ, the probability q of failure within proof test interval τ_p is:

$$q = 1 - \exp(-\lambda \tau_p) \qquad [34.7.10]$$

For small values of $\lambda \tau_p$

$$q = \lambda \tau_p \quad \lambda \tau_p << 1 \qquad [34.7.11]$$

The SIS is required to operate only if a hazardous plant condition occurs. The probability p_δ that such a process demand, with a demand rate δ, will occur during the dead time τ_0 after the failure is:

$$p_\delta = 1 - \exp(-\delta \tau_0) \qquad [34.7.12]$$

But, on average, the dead time τ_0 is half the proof test interval τ_p:

$$\tau_0 = \frac{\tau_p}{2} \qquad [34.7.13]$$

Hence:

$$p_\delta = 1 - \exp(-\delta \tau_p / 2) \qquad [34.7.14]$$

For small values of $\delta \tau_p$:

$$p_\delta = \frac{\delta \tau_p}{2} \quad \delta \tau_p << 1 \qquad [34.7.15]$$

The probability p_η that a plant hazard will be realized can be written in terms of the plant hazard rate η:

$$p_\eta = 1 - \exp(-\eta \tau_p) \qquad [34.7.16]$$

For small values of $\eta \tau_p$:

$$p_\eta = \eta \tau_p \quad \eta \tau_p << 1 \qquad [34.7.17]$$

Frequently, some or all of the approximations of Equations 34.7.11, 34.7.15 and 34.7.17 apply. If all do, then taking

$$p_\eta = q p_\delta \qquad [34.7.18]$$

gives

$$\eta = \frac{\delta \lambda \tau_p}{2} \quad \lambda \tau_p << 1; \ \delta \tau_p << 1; \ \eta \tau_p << 1 \qquad [34.7.19]$$

If the assumptions underlying Equation 34.7.19 are not valid, an expression that has been commonly used is:

$$\eta = \lambda p_\delta \qquad [34.7.20]$$

Alternatively, the plant hazard rate can be expressed in terms of the FDT ϕ of the system:

$$\eta = \delta \phi \qquad [34.7.21]$$

As given earlier, the probability q of failure of the simple SIS within the time period t is:

$$q = 1 - \exp(-\lambda t) \quad [34.7.22]$$

For small values of λt

$$q = \lambda t \quad \lambda t << 1 \quad [34.7.23]$$

Then the FDT ϕ of the simple SIS is:

$$\phi = \frac{1}{\tau_p}\int_0^{\tau_p} q\,dt \quad [34.7.24]$$

Hence

$$\phi = \frac{\lambda\tau_p}{2} \quad [34.7.25]$$

and

$$\eta = \frac{\delta\lambda\tau_p}{2} \quad [34.7.26]$$

as before.

For a parallel redundant, 1oo$n$ or $m$oo$n$ (m-out-of-n) with a majority voting system, the following treatment applies. If there are n devices of which m must survive for the system to survive and r must fail for the system to fail,[1] then

$$r = n - m + 1 \quad [34.7.27]$$

The probability q_{moon} of failure of this system within the proof test interval can be determined using a binomial distribution as follows:

$$q_{moon} = \sum_{k=r}^{n} \binom{n}{k} q^k (1-q)^{n-k} \quad [34.7.28]$$

For small values of q:

$$q_{moon} = \binom{n}{r} q^r \quad q << 1 \quad [34.7.29]$$

The FDT ϕ_{moon} of the system is:

$$\phi_{moon} = \frac{1}{\tau_p}\int_0^{\tau_p} q_{moon}\,dt \quad [34.7.30]$$

Then from Equations 34.7.23, 34.7.29 and 34.7.30, the FDT ϕ_{moon} of the system is:

$$\phi_{moon} = \binom{n}{r} \frac{(\lambda\tau_p)^r}{r+1} \quad [34.7.31]$$

Thus for a 2oo3 majority voting system:

$$\phi_{2oo3} = (\lambda\tau_p)^2 \quad [34.7.32]$$

[1] In this chapter the number of devices that must fail for the system to fail is r. This notation differs from that used in Chapter 7 for *r-out-of-η* parallel systems, in which r was used for the number of devices that must survive for the system to survive. These two notations are used in order to preserve correspondence with established usage in texts on general reliability (e.g. Shooman, 1968) and on SISs (e.g. A.E. Green and Bourne, 1972).

For the special case of a parallel redundant, or 1oo$n$, system, Equation 34.7.31 reduces to give the FDT ϕ_{1oon}:

$$\phi_{1oon} = \frac{(\lambda\tau_p)^n}{n+1} \quad [34.7.33]$$

Thus for a 1oo2 parallel system:

$$\phi_{1oo2} = \frac{(\lambda\tau_p)^2}{3} \quad [34.7.34]$$

and for a 1oo3 system:

$$\phi_{1oo3} = \frac{(\lambda\tau_p)^3}{4} \quad [34.7.35]$$

FDT is calculated from Equation 34.7.31. The results are shown in Table 34.11, as a function of $\lambda\tau_p$ and of the FDT ϕ_{1oo1} for a single channel. Table 34.10 assumes that the devices are tested simultaneously at the end of the proof test interval. Some improvement can be obtained by staggered testing, as shown by the data in Table 34.11, which are taken from A.E. Green and Bourne (1972).

The approximation method provided in ISA TR84.00.02 can also be used to calculate the FDT of redundant subsystems. In this method, the FDT is determined for each device within the subsystem using Equation 34.7.25. Then,

Table 34.10 *Fractional dead times for trip systems with simultaneous proof testing*

System	n	m	r	ϕ	
1oo1	1	1	1	$\lambda\tau_p/2$	ϕ_{1oo1}
1oo2	2	1	2	$(\lambda\tau_p)^2/3$	$\frac{4}{3}\phi^2_{1oo1}$
1oo3	3	1	3	$(\lambda\tau_p)^3/4$	$2\phi^3{}_{1oo1}$
2oo2	2	2	1	$\lambda\tau_p$	$2\phi_{1oo1}$
2oo3	3	2	2	$(\lambda\tau_p)^2$	$4\phi^2{}_{1oo1}$

Table 34.11 *Fractional dead times for trip systems with staggered proof testing (A.E. Green and Bourne, 1972) (Reproduced with permission from Reliability Technology by A.E. Green and J.R. Bourne, Copyright © , 1972, John Wiley and Sons Inc.)*

System	ϕ*	ϕ/ϕ*
1oo1	$\frac{\lambda\tau_p}{2}$	1
1oo2	$\frac{5}{24}(\lambda\tau_p)^2$	1.6
1oo3	$\frac{1}{12}(\lambda\tau_p)^3$	3.0
2oo2	$\lambda\tau_p$	1
2oo3	$\frac{2}{3}(\lambda\tau_p)^2$	1.5

[a] ϕ, fractional dead time for simultaneous testing; ϕ*, fractional dead time for staggered testing.

Boolean algebra is used to combine the resulting FDT into a system value.

For a 1oo2 subsystem, this yields:

$$\phi_{1oo2} = \frac{\lambda\tau_p}{2} \times \frac{\lambda\tau_p}{2} = \frac{\lambda^2\tau_p^2}{4} \quad [34.7.36]$$

To generalize, the approximation equation can be derived for *moon* voting subsystems, using Equation 34.7.25 for the value of r and Equation 34.7.27 to represent the probability of failure of the individual components:

$$\phi_{moon} = \frac{n!}{r!(m-1)!}\left(\frac{\lambda\tau_p}{2}\right)^r \quad [34.7.37]$$

34.7.5 Operational reliability

It is also necessary to consider SIS operational failure. Operational failure, as presented in this section, is revealed. The failure rate λ used in the equations in this subsection is applicable to these revealed, fail-safe or fail-spurious faults.

For a simple SIS consisting of a single channel 1oo1 system with a failure rate λ, the operational failure, or spurious trip rate, γ is:

$$\gamma = \lambda \quad [34.7.38]$$

For a parallel redundant, or 1oo*n*, system the operational failure rate γ_{1oon} is:

$$\gamma_{1oon} = n\lambda \quad [34.7.39]$$

For a *moon* system, which may be a majority voting system, the following treatment applies. The rate at which the first operational failure of a single channel occurs is $n\lambda$. This first failure only results in a system trip if further operational failure of enough channels sufficient to trip the system occurs within the repair time τ_r. The probability q_γ that this will occur is:

$$q_\gamma = \binom{n-1}{m-1}(\lambda\tau_r)^{m-1} \quad \lambda\tau_r << 1 \quad [34.7.40]$$

Then the operational failure rate γ_{moon} of the system is:

$$\lambda_{moon} = n\lambda q_\gamma \quad [34.7.41]$$

$$\gamma_{moon} = n\lambda\binom{n-1}{m-1}(\lambda\tau_r)^{m-1} \quad [34.7.42]$$

Thus for a 2oo3 majority voting system:

$$\gamma_{2oo3} = (3\lambda)\cdot(2\lambda\tau_r) \quad [34.7.43]$$

$$\gamma_{2oo3} = 6\lambda^2\tau_r \quad [34.7.44]$$

Operational failure, or spurious trip, rates calculated from Equations 34.7.39 and 34.7.42 are shown in Table 34.12. It is emphasized again that the foregoing treatment is a simplified one. The expressions derived here appear, however, to be those in general use (e.g. Hensley, 1968; Kletz, 1972a; de Heer, 1974; Lawley and Kletz, 1975). Full theoretical treatments of SISs are given by A.E. Green and Bourne (1966 UKAEA AHSB(S) R117) and Wheatley and Hunns (1981). The latter gives expressions for a wide variety of SISs.

Table 34.12 *Spurious trip rates for trip systems*

System	γ
1oo1	λ
1oo2	2λ
1oo3	3λ
2oo2	$2\lambda^2\tau_r$
2oo3	$6\lambda^2\tau_r$

34.7.6 Hazard rate of a single-channel SIS

The hazard rate of a single-channel SIS, when $\lambda\tau_p << 1$; $\delta\tau_p << 1$; $\eta\tau_p << 1$, was shown in Equation 34.7.19:

$$\eta = \frac{\delta\lambda\tau_p}{2} \quad [34.7.45]$$

When this equation is used outside its range of validity, the results obtained can be not only incorrect but nonsensical. Consider the case where the failure rate is $\lambda = 0.01$ failures/year, the demand rate is $\delta = 3$ demands/year and the proof test interval is $\tau_p = 1$ year. Then, this equation gives for the hazard rate η a value of 0.015 hazards/year, which is actually greater than the failure rate λ.

A treatment is now given for the more general case, based on the work of Lees (1982a) as extended by de Oliveira and Do Amaral Netto (1987). For a single-channel SIS, the possible states are: (1) SIS operational, (2) SIS failed but failure undetected and (3) SIS failed, but failure detected and SIS under repair. The corresponding Markov model is:

$$\dot{P}_1(t) = -\lambda P_1(t) + \mu P_3(t) \quad [34.7.46a]$$

$$\dot{P}_2(t) = \lambda P_1(t) - \delta P_2(t) \quad [34.7.46b]$$

$$\dot{P}_3(t) = \delta P_2(t) - \mu P_3(t) \quad [34.7.46c]$$

where P_n is the probability that the SIS is in state n.

With the initial condition that the SIS is operational, the solution of Equations 34.7.4a–c is as follows:

$$P_1(t) = \frac{\mu\delta}{r_1 r_2} + \frac{(r_1+\mu+\delta)+\mu\delta}{r_1(r_1-r_2)}\exp(r_1 t) - \frac{r_2(r_2+\mu+\delta)+\mu\delta}{r_2(r_1-r_2)}\exp(r_2 t) \quad [34.7.47a]$$

$$P_2(t) = \frac{\lambda\mu}{r_1 r_2} + \frac{\lambda(r_1+\mu)}{r_1(r_1-r_2)}\exp(r_1 t) - \frac{\lambda(r_2+\mu)}{r_2(r_1-r_2)}\exp(r_2 t) \quad [34.7.47b]$$

$$P_3(t) = \frac{\lambda\delta}{r_1 r_2} + \frac{\lambda\delta}{r_1(r_1-r_2)}\exp(r_1 t) - \frac{\lambda\delta}{r_2(r_1-r_2)}\exp(r_2 t) \quad [34.7.47c]$$

with

$$r_1 = \frac{-(\mu+\lambda+\delta) - \left[(\lambda+\delta-\mu)^2 - 4\lambda\delta\right]^{1/2}}{2} \quad [34.7.48a]$$

$$r_2 = \frac{-(\mu+\lambda+\delta) + \left[(\lambda+\delta-\mu)^2 - 4\lambda\delta\right]^{1/2}}{2} \quad [34.7.48b]$$

Then the FDT and hazard rate obtained from Equations 34.7.47b and 34.7.47c are instantaneous values, and are

$$\phi(t) = P_2(t) + P_3(t) \quad [34.7.49]$$

$$\eta(t) = \delta[P_2(t) + P_3(t)] \quad [34.7.50]$$

The FDT and hazard rate obtained from Equations 34.7.49 and 34.7.50 are defined as functions of time. The average value of the hazard rate over the proof test interval is:

$$\eta = \frac{1}{\tau_p}\int_0^{\tau_p} \eta(t)\,dt \quad [34.7.51]$$

Then, substituting Equation 34.7.50 into Equation 34.7.51 and integrating gives for the average hazard rate:

$$\eta = \frac{\lambda\delta(\mu+\delta)}{r_1 r_2} + \frac{\lambda\delta(r_1+\mu+\delta)}{r_1^2\tau_p(r_1-r_2)}[\exp(r_1\tau_p) - 1] - \frac{\lambda\delta(r_2+\mu+\delta)}{r_2^2\tau_p(r_1-r_2)}\exp(r_2\tau_p) - 1 \quad [34.7.52]$$

The foregoing treatment is based on the assumptions that the SIS is fully operational after a proof test is performed and that the test duration is negligible compared with the proof test interval.

Although this model has a high degree of generality, it is based on the assumption that, following detection of an SIS device failure, the plant continues to operate while the SIS device is repaired. If in fact the policy is that the plant operation does not continue while the SIS device is being repaired, different expressions apply. If the state $P_3(t)$ is dropped from the instantaneous hazard rate $\eta(t)$ in Equation 34.7.50 and the repair rate $\mu = 0$, Equation 34.7.52 for the average hazard rate then becomes

$$\eta = \frac{1}{\tau_p}\left\{1 - \frac{1}{\lambda-\delta}[\lambda\exp(-\delta\tau_p) - \delta\exp(-\lambda\tau_p)]\right\} \quad \lambda \neq \delta \quad [34.7.53a]$$

$$\eta = \frac{1}{\tau_p}[1 - (1+\lambda\tau_p)\exp(-\lambda\tau_p)] \quad \lambda = \delta \quad [34.7.53b]$$

This case is essentially that considered by Lees (1982a), who used the joint density function method. Two of the relations which he gives, for the failure density function f_η and the probability p_η of realization of the hazard, are also of interest and are

$$f_\eta = \frac{\lambda\delta}{\lambda-\delta}[\exp(-\delta\tau_p) - \exp(-\lambda\tau_p)] \quad \lambda \neq \delta \quad [34.7.54a]$$

$$f_\eta = \lambda^2\tau_p\exp(-\lambda\tau_p) \quad \lambda = \delta \quad [34.7.54b]$$

and

$$p_\eta = 1 - \frac{1}{\lambda-\delta}[\lambda\exp(-\delta\tau_p) - \delta\exp(-\lambda\tau_p)] \quad \lambda \neq \delta \quad [34.7.55a]$$

$$p_\eta = 1 - (1+\lambda\tau_p)\exp(1+\lambda\tau_p) \quad \lambda = \delta \quad [34.7.55b]$$

A number of other relations have been given in the literature for situations where Equation 34.7.45 is not valid. An expression given by Kletz and by Lawley (Kletz, 1972a; Lawley and Kletz, 1975; Lawley, 1976) is as follows:

$$\eta = \lambda[1 - \exp(-\delta\tau_p/2)] \quad [34.7.56]$$

This is in effect Equation 34.7.20. It may be derived from Equation 34.7.18 together with Equations 34.7.11, 34.7.14 and 34.7.17. It is applicable for small $\lambda\tau_p$ and $\eta\tau_p$, but higher $\delta\tau_p$.

Lawley (1981) has subsequently given the more accurate Equation 34.7.53a,b. The assumptions underlying this equation have just been described.

Wells (1980) has given an expression

$$\eta = \frac{\delta\lambda}{\delta+\lambda} \quad [34.7.57]$$

as an upper bound on the hazard rate for higher values of $\delta\tau_p$ (>2). This expression is equivalent to taking the probability of failure on demand as $\phi = \lambda/(\lambda+\delta)$. De Oliveira and Do Amaral Netto (1987) give the relation:

$$\eta = \delta\left\{1 - \frac{1}{\lambda\tau_p}[1 - \exp(-\lambda\tau_p)]\right\} \quad [34.7.58]$$

for low values of δ but higher values of $\lambda\tau_p$.

Numerical results for some of these expressions have been given by Lees (1982a) and by de Oliveira and Do Amaral Netto (1987). Table 34.13 shows some comparative results obtained, mainly by the latter workers.

34.8 Operate

To ensure the control system integrity, the design process must be supported by administrative procedures and actions. The SIS consists of instrumentation and logic processors that can and do fail. When these failures are detected, immediate operator response is essential to ensure safe operation. This response includes issuing a request for repair of the faulted device, monitoring other process variables associated with the unit, and, if necessary, initiating a manual shut-down action.

CCPS *Safe Automation Guidelines* outlines minimum procedural requirements, including: (1) operating procedures, (2) maintenance facilities, (3) testing of the BPCS, (4) testing of the alarms and SIS, (5) test interval requirements, (6) testing facilities, (7) operator training, (8) documentation and (9) auditing of maintenance and documentation.

ANSI/ISA 84.01-1996 and IEC 61511 require that the SIS operating procedures contain the following information:

- description of the hazard that is being prevented with SIS;
- SIS trip set points and SIS actions, including definition of safe state;

Table 34.13 *Some numerical values given by expressions for the average hazard rate of a single-channel SIS (after de Oliveira and Do Amaral Netto, 1987) (Courtesy of Elsevier Science Publishers)*

Parameter			*Equation*[a]				
τ_p (year)	λ (year^{-1})	δ (year^{-1})	34.7.52	34.7.53	34.7.56	34.7.58	34.7.18
0.0192	0.1	0.1	0.958×10^{-4}	0.958×10^{-4}	0.958×10^{-4}	0.958×10^{-4}	0.959×10^{-4}
		1.0	0.954×10^{-3}	0.952×10^{-3}	0.954×10^{-3}	0.958×10^{-3}	0.959×10^{-3}
		10	0.919×10^{-2}	0.900×10^{-2}	0.914×10^{-3}	0.958×10^{-2}	0.959×10^{-2}
	1.0	0.1	0.952×10^{-3}	0.952×10^{-3}	0.958×10^{-3}	0.953×10^{-3}	0.959×10^{-3}
		1.0	0.949×10^{-2}	0.947×10^{-2}	0.954×10^{-2}	0.953×10^{-2}	0.959×10^{-2}
		10	0.913×10^{-1}	0.895×10^{-1}	0.914×10^{-1}	0.953×10^{-1}	0.959×10^{-1}
	10	0.1	0.900×10^{-2}	0.900×10^{-2}	0.958×10^{-2}	0.900×10^{-2}	0.959×10^{-2}
		1.0	0.897×10^{-1}	0.895×10^{-1}	0.954×10^{-1}	0.900×10^{-1}	0.959×10^{-1}
		10	0.864	0.845	0.914	0.900	0.959
1.0	0.1	0.1	0.468×10^{-2}	0.468×10^{-2}	0.488×10^{-2}	0.484×10^{-2}	0.5×10^{-2}
		1.0	0.359×10^{-1}	0.355×10^{-1}	0.393×10^{-1}	0.484×10^{-1}	0.5×10^{-1}
		10	0.916×10^{-1}	0.860×10^{-1}	0.993×10^{-1}	0.484	0.5
	1.0	0.1	0.358×10^{-1}	0.355×10^{-1}	0.488×10^{-1}	0.368×10^{-1}	0.5×10^{-1}
		1.0	0.284	0.264	0.393	0.368	0.50
		10	0.847	0.591	0.993	3.68	5.0
	10	0.1	0.892×10^{-1}	0.860×10^{-1}	0.488	0.900×10^{-1}	0.5
		1.0	0.827	0.591	3.93	0.900	5.0
		10	4.82	1.00	9.93	9.00	50

[a] In equations where μ is used, $\mu = 365$/year.

- correct use of operational bypasses, permissive, system reset, etc.;
- response to SIS alarms and trips;
- detection and response to faults, including when to execute a manual shut-down action;
- provisions for operation with detected faults.

This information enables the operator to understand the purpose and function of the SIS and to recognize when to take action in response to SIS faults.

34.8.1 Bypassing of SISs

Bypasses (or overrides) may be required for start-up, maintenance or testing activities. When a bypass is placed in service, the bypass should be alarmed in the control room to notify operations staff that an SIS is inoperable. Then, compensating measures should be implemented to maintain safe operation, while any portion of the SIS is bypassed. Compensating measures may include, for example, increased process monitoring, increased supervision, revised operational procedures or reduction in production rates. Operation and maintenance staff should be trained on the use and purpose of these compensating measures. The procedures and training should include the operational limits at which manual shut-down should be initiated. To facilitate the above actions, there should be open communication between the control room and field staff.

Administrative procedures are also required to prevent unauthorized bypass of the SIS. Bypass use should be restricted to specific, authorized personnel. This may be supplemented by hardware measures, such as keyed switches, or software measures, such as passwords. There should also be a limitation on how long an SIS can be left in bypass without additional approval under change management.

Bypasses are typically only used during maintenance or testing activities. Occasionally, a start-up bypass is required for start-up and these bypasses must be carefully evaluated to ensure that potentially unsafe process conditions cannot occur during this bypass condition. Timers, operation sequences or process condition-based permissives may be used to automatically bring the SIS out of bypass during start-up to prevent prolonged operation in the bypass condition. For example, to start-up a pump, the low flow SIS on the discharge of the pump must be bypassed. To prevent the pump from being run for too long in the bypass condition, a timer may be used to automatically bring the SIS back in service. The timer allows the bypass for a specified period after the start button has been pressed.

When SISs are bypassed during normal operation, it is generally due to poor SIS reliability. If an SIS proves troublesome, it is prone to be bypassed without appropriate authorization. This is particularly likely to occur if there are frequent spurious trips, due to sensor failure or other causes. For this reason, it is important to have restrictions on when SISs can be in bypass and to intermittently alarm that the SIS is in bypass. Implementing independent process control and SIS increases the level of access security and control. When independence is not implemented, rendering an SIS ineffective may only require alteration of the SIS setpoint.

34.8.2 Restart after a trip

Once an SIS has taken the process to the safe state, the SIS should remain in the safe state until the process has reached safe operating conditions and the operator has reset the SIS. The process industry has had numerous incidents due to restart under unsafe conditions. One situation,

which has frequently led to incidents, is the restart of agitation in a batch reactor following an interruption of agitation.

Kletz (1979a) provides an example of an incident that was caused by a valve that reset automatically. A cumene oxidation reactor was protected by an SIS that used high temperature to initiate shutdown of the air to the reactor and to initiate a dump of the reactor contents into a water tank. A spurious trip occurred, the air valve closed and the dump valve opened. When the trip condition cleared itself, the dump valve remained in the open, safe state condition, but the air valve did not remain in the closed, safe state condition. The air valve reopened. Air passed into the reactor, creating a flammable mixture.

Valk and Sylvester-Evans (1985) discuss cases where restart was initiated before safe conditions were reached. In these cases, vessels were repressurized too quickly after emergency depressurization. Treatment of the problem using a model of the blowdown has been described by S.M. Richardson and Saville (1992). The effect of rapid reduction of pressure in a vessel containing a material such as liquefied gas may be to chill the vessel below the transition temperature. If repressurization occurs before the vessel has warmed up sufficiently, the vessel can rupture due to brittle fracture.

34.9 Maintain

The importance of proof testing cannot be overemphasized. Testing and, more generally, SIS maintenance should be of high quality, if the functional and integrity requirements are to be achieved. Accounts of the testing and maintenance of SIS have been given by R.M. Stewart (1971), A. Taylor (1981) and Barclay (1988).

34.10 Test

Testing plays an important role in achieving functional integrity. All devices eventually fail. The most hazardous failure is a dangerous, undetected failure, which results in the device not functioning when a process demand occurs. This type of failure results in the need to periodically test SIS devices to determine if they are functional. Thus, the required proof test interval is related to the device failure rate.

ANSI/ISA 84.01-1996 and IEC 61511 require the testing of SIS devices, including inputs, logic solver and final elements. The test should be complete enough to validate the necessary functions of each device and the overall system. The test should also examine the system response to bad process variables from failed instrumentation.

Perhaps, the most important functional test is the validation of the SIS prior to introduction of hazardous chemicals into the process equipment. This validation is sometimes referred to as the pre-start-up acceptance test (PSAT) or the site acceptance test (SAT). Validation is a full functional test of the SIS performed to determine whether the installed SIS is functioning as intended from a specification, design and installation standpoint. Throughout the lifecycle, verification activities are performed to maintain a quality design process and to ensure that the design remains in agreement with the required functionality and integrity. Validation is the ultimate test of the SIS functionality. Since the majority of testing after start-up will consist of testing individual devices, it is extremely important that complete input to output testing is performed to identify any system level problems.

The test should be conducted using a written procedure, which details the actions to be taken and requires the technician's signature at key steps. In addition, the worksite should be reviewed and approved by an independent person to make certain that all bypasses have been removed and that the SIS devices have been returned to fully the operational state. The procedure is necessary because: (1) the testing process can be quite complex, (2) the individual performing the test may not be familiar with the particular trip and (3) in many cases the test is one of the last tasks done prior to a start-up when there may be considerable pressure to short-cut the test. Changes to the procedure should be managed through a management of change (MOC) process.

The test should cover the entire SIS from sensor to final element. From the point of view of testing, the preferred method is to take the process variable to the trip point using test equipment and to verify the trip action. This method requires a shut-down or provisions for bypass of the final element in order to perform the test. Other methods involve testing the field sensors, logic solver and final elements separately or testing some combination of these. For example, the process variable is taken to the trip point using test equipment, but the final element is held in position. This tests the process sensing device only. Then, the final element would be tested in a separate procedure at a different time. This disintegrated testing must be assessed to ensure that all devices required for successful SIS function are tested at the appropriate interval.

For inputs, the test should include process variable indication leading to alarm and trip initiation. For input devices requiring field calibration, the sensor calibration range should be checked to ensure that it matches the specification and that the trip setpoint is achieved at the corresponding process condition. This is accomplished by inducing the process condition at the sensor and monitoring the corresponding output of the input device. It should be demonstrated that the input device generates the correct signal at the alarm and trip setpoints. It should also be shown that if there is a bad sensor output, there is appropriate indication of this fault to the control room.

Logic solvers should demonstrate that on receipt of an input trip condition that it generates the correct output response. At the simplest level, this involves validating that the logic performed in the logic solver matches the specification. This may include the following validation activities:

- Ensure that redundant devices are subject to the correct voting logic.
- Determine how the logic solver processes bad sensor data (i.e. out of range) and whether this fault is properly annunciated in the control room.
- Verify that computations are being performed correctly and that bad data do not impede program operation.
- Verify that sequenced operations are occurring correctly and that any required triggers (e.g. operation actions or devices) for sequencing are being received at the correct points during logic execution.
- Ensure that any diagnostic alarms are generated according to the specification (e.g. deviation alarms for redundant input devices).

- Determine the action of the logic when power failure occurs.
- Verify what happens to the logic when combinations of inputs occur in an unusual manner (e.g. fault insertion testing).

The test for final elements should determine that the final element can achieve the safe-state condition. The *final element* boundary includes all of the devices from the logic solver output to the control element that takes action on the process. For example, in the case of fail-to-close block valves, the test must ensure that the solenoid valve de-energizes, venting air from the valve actuator, which causes the valve to go to the closed position. If limit switches are used for trip indication or for sequencing operation, these limit switches must be tested. If closure speed is specified, the test should include verifying the actual closure speed.

While testing the functionality of the field devices and logic solver is an obvious requirement, it is also necessary to test auxiliary systems and communications. Auxiliary systems may include electrical power and air supplies. For example, if an air-to-move valve is used, the availability of the air supply is safety-critical. Any communication between the SIS and the basic process control system should be tested to ensure proper transfer of the data between the two systems. The test should demonstrate that no communication failure can occur that would prevent proper functioning of the SIS. Thus, the test should validate all features of the SIS, demonstrating that the SIS meets the design specifications.

The importance of testing on functional integrity cannot be overemphasized. The expressions derived in Section 34.7 show that the condition for high integrity is:

$$\lambda\tau_p << 1$$

As an illustration of the effect of the proof test interval, consider a simple SIS that has a failure rate of 0.05 faults/year on a duty where the demand rate is 1 demand in 10 years:

$$\delta = 0.1 \text{ demand/year}$$

$$\lambda = 0.05 \text{ faults/year}$$

If the proof test interval is 1 month:

$$\tau_p = 730 \text{ h}/8760 \text{ h} = 0.0833 \text{ years}$$

Then the FDT is:

$$\phi = \frac{\lambda\tau_p}{2} = 0.00208$$

and the plant hazard rate is:

$$\eta = \delta\phi = 0.000208 \text{ hazards/year}$$

The plant hazard rate for a range of proof test intervals is:

τ_p	η (hazards/year)
1 month	0.000208
6 months	0.001250
1 year	0.002500
2 years	0.005000
5 years	0.012500

The example above illustrates how the proof test interval affects the plant hazard rate and the FDT. The PHA, as discussed previously, established a target risk reduction to be achieved by the SIS, which is expressed in ANSI/ISA 84.01-1996 and IEC 61511 as the PFD. While this chapter refers to FDT, the discussions also apply to the PFD. Due to the significant impact of the test interval on the SIS performance, any changes to the test interval should only be made after management of change review, which should include an analysis of the impact of the test interval change on the PFD.

There are practical limitations to the test interval. There is always the possibility that while conducting the test that the device may be damaged or not returned to fully operational state. It is important to consider whether bypassing is required in order to perform the testing. If so, the SIS will become less available to perform its design function, as the test interval is decreased. For example, if the test interval is monthly and the test requires a bypass period of 1 h, the SIS unavailability due to the bypass action is as follows:

$$1 \text{ h/test} * 12 \text{ tests/year} = 12 \text{ h/year} * 1 \text{ year}/8760 \text{ h} = 0.00137$$

Thus, it is important to minimize the frequency and duration of proof tests. Due consideration should be given to eliminating the use of bypasses whenever possible. The fewer bypasses that are required, the lower the probability that it will be left in bypass unintentionally.

In some instances, it is desirable to test some of the potential failures of an SIS component at one interval and the other failures at a different interval. For example, full closure of an SIS block valve during normal operation requires a bypass line and valve in order for operation to continue uninterrupted. Instead, a partial stroke can be done, which cannot demonstrate that the valve will close, but will demonstrate that the valve can move. Summers (2000) and Summers and Zachary (2002) discuss various means of performing a partial stroke test of a block valve and how this type of test can improve the SIS functional integrity and reliability.

One example cited by Summers and Zachary (2002) is the use of the solenoid valve to partially close a block valve in de-energize to trip SISs. The test is performed by pulsing the power to the solenoid valve for a period of time necessary to move the valve from the full-open position. This partial test verifies the ability to vent the air from the process valve actuator, including the solenoid valve, the solenoid vent point, the air tubing between the valve actuator and the solenoid valve, and the movement of the valve actuator. To reduce the potential for spurious trips, redundant solenoids can be used.

The PFD of the device that undergoes two partial tests can be evaluated as follows. First, the functional failure rate and proof test interval associated with one of the tests is determined using λ_A and τ_{pA}, respectively. Then, the functional failure rate and the proof test interval associated with the second test is determined using and λ_B and τ_{pB}, respectively. Therefore,

$$q_A = 1 - \exp(-\lambda_A t) \quad [34.10.1]$$

$$q_A = \lambda_A t \quad \lambda_A t << 1 \quad [34.10.2]$$

Similarly,

$$q_B = \lambda_B t \quad \lambda_B t << 1 \quad [34.10.3]$$

Then the PFD is:

$$\phi = \frac{1}{\tau_{pA}} \int_0^{\tau_{pA}} q_A \, dt + \frac{1}{\tau_{pB}} \int_0^{\tau_{pB}} q_B \, dt \quad [34.10.4]$$

$$\phi = \frac{1}{2}\left(\lambda_A \tau_{pA} + \lambda_B \tau_{pB}\right) \quad [34.10.5]$$

34.11 Special Applications

34.11.1 High integrity protection systems

The use of SISs instead of pressure relief valves is sometimes an attractive proposition, particularly where the relief valve solution involves a large flare or toxic scrubbing system or where the process pressure develops so rapidly that the relief valve size is unreasonably large.

The former case is considered by Kletz (1974a) and by Lawley and Kletz (1975), who suggest that if an SIS is used instead of a relief valve, it should be designed for a reliability 10 times that of the latter. The reason for this is the uncertainty in the relief valve failure rate data and the difference in the modes of failure; a relief valve that fails to operate at the set pressure may nevertheless operate at a higher pressure, whereas an SIS is more likely to fail completely.

API 521 and ASME Code Case 2211 require that any SIS used to protect a vessel against overpressure must achieve the level of risk reduction that would typically be provided by the relief valve. Thus, the PHA is used to determine how much risk reduction is required to mitigate the overpressure. This yields how much risk reduction must be provided by the SIS. *Layers of Protection Analysis* (CCPS, 2001) discusses the use of protection layers to evaluate the risk reduction provided by the relief valves and the use of high integrity protective system (HIPS) for overpressure protection.

Summers (2002, 2003a) discusses the design of HIPS applied to flare load reduction. In many flare load reduction projects, the design intent is to mitigate the overpressure event with the SIS such that the potential load from the vessel under review can be removed from the load calculation. This typically results in a risk reduction requirement equivalent to SIL 3. To achieve SIL 3, the HIPS is fully redundant in the process sensors, logic solver and output devices. The HIPS must also be tested frequently or incorporate diagnostics for all devices.

Summers (2003b) discusses the application of HIPS to reactive hazards management. These HIPS are often more complicated than those used for flare load reduction. The logic required to achieve a safe state for flare load reduction is typically simple, such as high pressure initiating a shutdown of final elements, such as valves, pumps or compressors. For reactive processes, the logic can be complex due to the use of the following:

- multiple process variables, such as the reactive conditions are only achieved after a specific temperature is reached during the batch reaction;
- sequence-oriented, including the modification of trip setpoints at various stages or the enabling of different SISs at different steps of the batch reaction;
- operational state-based, such as the enabling of different trip setpoints dependent on whether the process is in normal operation or in regeneration mode;
- kinetic reaction-based, where the logic contains predictive calculations based on process kinetics.

The risk reduction requirement for reactive hazards management is often a factor of 1000. This risk reduction may be achieved with a single layer SIS or with multiple SIS layers. The former results in an SIL 3 requirement. The latter may involve combinations of layers, and these layers must be examined for potential common mode failure.

34.11.1.1 HIPS example

A major application of advanced SIS design is the ethylene oxide process of ICI described by Stewart and co-workers (R.M. Stewart, 1971, 1974a; R.M. Stewart and Hensley, 1971). The ethylene oxide process is extremely hazardous for two reasons: (1) it operates with a reaction mixture very close to the explosive limit and (2) there is a fire/explosion hazard, as well as a toxic release hazard.

The design of the protective system followed the methods already outlined. The risk criterion was set at a hazard rate of 3×10^{-5} fatalities per year. The hazards were assessed by means of a fault tree, part of which is shown in Figure 34.11.

The system devised is a HIPS, consisting of the high integrity trip initiators (HITIs), the high integrity voting equipment (HIVE) and the high integrity shut-down system (HISS). A schematic system diagram, which omits replicated signal connections, is shown in Figure 34.12.

Redundancy is fully exploited throughout the system. Against each logic path to fire/explosion in the fault tree at least one parameter was selected initially to be a trip initiator. The choice of the trip initiating parameters is important but difficult. Some are obvious such as high oxygen concentration, high reactor temperature or low recycle gas flow. Others are far less obvious, but are needed to guard against combinations of faults or to substitute for other parameters.

The measuring instruments used are carefully selected and, if necessary, modified to ensure high integrity. Each parameter is measured by triplicated input sensors, voting 2oo3. The arrangement of the shut-down valves in the oxygen line illustrates further the use of redundancy. There are two lines each with three valves. A single line represents a 1oo3 shut-down system. Duplication is provided to permit complete testing without bypassing.

The advantages of this SIS design are that the failure of one trip initiator in the fail-safe mode does not cause the plant to be tripped spuriously, the failure of one trip initiator in the fail-dangerous mode does not prevent the plant from being tripped, and the proof testing can be done without bypassing any devices.

The SIS design was subjected to an independent assessment by assessors within the company who were advised by the UKAEA. The assessors checked all feasible faults that could lead to hazardous conditions. They also evaluated the capability of the HIPS to carry out the protective action against the hazardous conditions arising from such faults and the occurrence rate of other hazardous conditions that the HIPS would not prevent. The overall hazard rate was compared with the design target. Table 34.14 shows some of the results generated during this assessment.

The assessment showed that at this stage the plant hazard rate was 4.79×10^{-5}/year, which was higher than the target of 3×10^{-5}/year. An extra HITI was used to reduce the contribution of fault 3 from 2.72×10^{-5} to 0.8×10^{-5}/year, which enabled the SIS to achieve the target FDT.

The assessors also examined the HIPS as installed to ensure that there were no significant deviations from

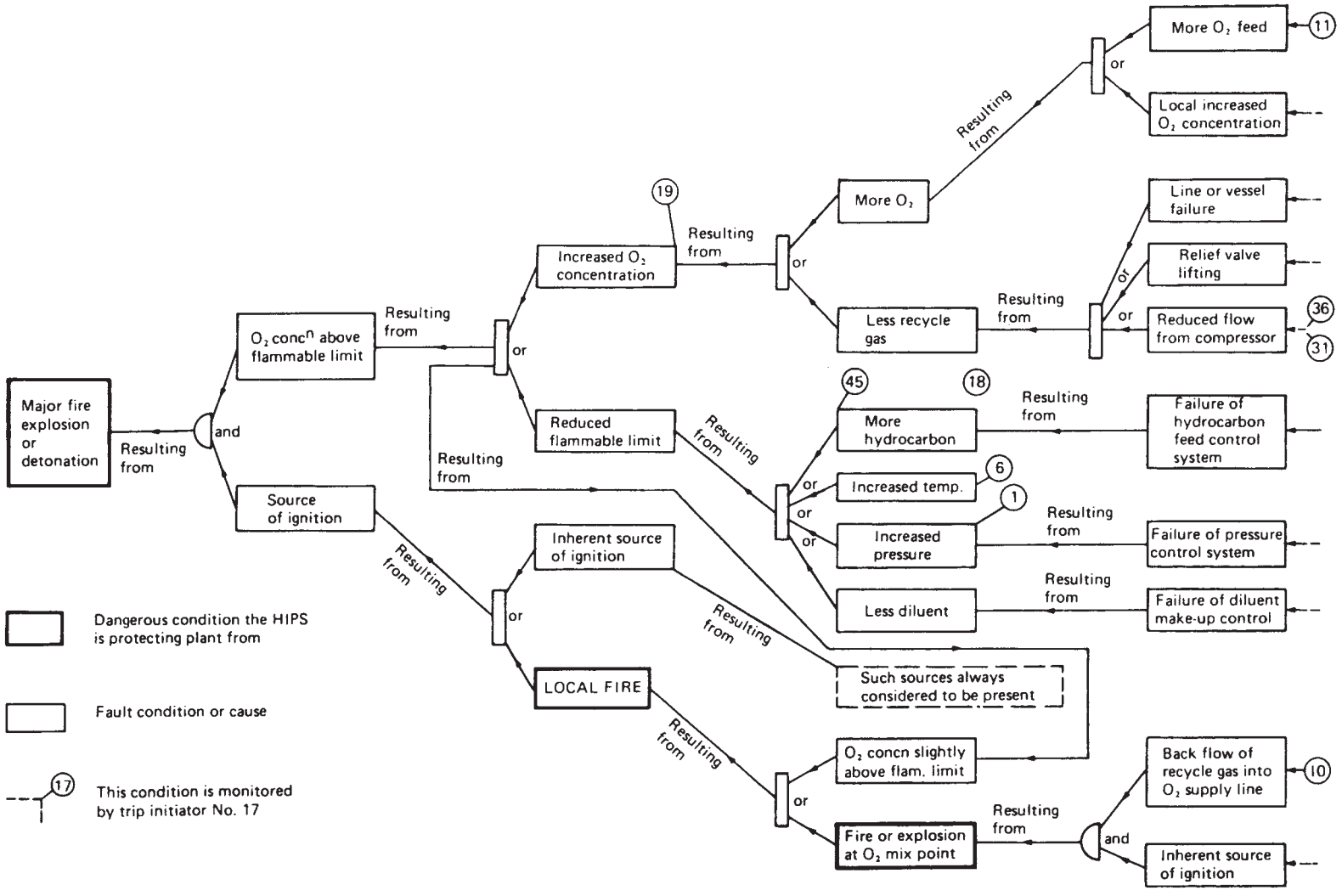


Figure 34.11 *Fault tree for fire/explosion on an ethylene oxide plant (after P.M. Stewart, 1971) (Courtesy of the Institution of Chemical Engineers)*

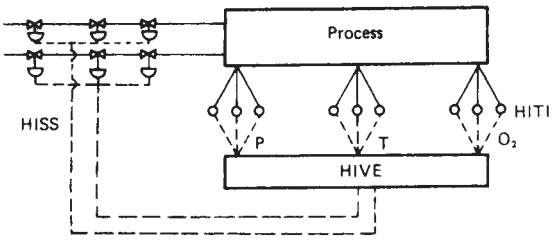


Figure 34.12 *High integrity protective system (after Stewart, 1971) (Courtesy of the Institution of Chemical Engineers)*

design and reviewed the maintenance, calibration and testing procedures. The quality of the maintenance and testing is crucial to the integrity of a protective system and much attention was paid to this aspect.

It was estimated that an alternative system with 70 1oo1 single trip initiators would result in some 30 spurious trips a year and that the system used reduced this by a factor of over 12. Since the cost of a trip was estimated as £2000, the savings due to avoidance of spurious trips was about £55,000 per annum. The cost of £140,000 for the installation was therefore considered justified on these grounds alone.

A second account of this installation has been given by A. Taylor (1981), who describes the operation of the SIS over the period 1971–80. Analysis of the actual process unit and SIS performance revealed, that in a few cases, the demand frequency was greater than originally estimated by orders of magnitude. The author gives a table listing seven fault conditions, with the event numbering rising to 53, which exemplify the worst discrepancies. The two fault conditions which show the greatest discrepancies are the opening of a certain relief valve and loss of reaction:

Fault description	*Fault condition*		
	Predicted frequency (events/year)	*Actual frequency* (events/year)	*Ratio of actual/predicted frequency*
15 A certain relief valve open	0.001	1.68	1680
48b Loss of reaction	0.01	1.16	116

The relief valve fault was due to shimmering or feathering, which had not been anticipated. The loss of reaction fault is not explicitly explained, but references by the author to the effect of modifications in reaction conditions may bear on this. It is noteworthy that of the seven fault conditions it is those for which the original frequency estimates were lowest that are most in error.

With regard to instrument failure rates, in the case of magnetic float switches, three different failure mechanisms, and three different failure rates, were observed. Switches operating submerged in clean lubricating oil recorded no failures; those operating in recycled gas with occasional slugs of dirty water choked up; and a new type of switch was found to suffer from corrosion. This illustrates that the failure rate of a device is dependent on the specific type of device and the application environment.

The author also noted three examples of dependent failure. One of these relates to the choked level switches just mentioned, which were all on one vessel. On four occasions, testing of the switches revealed that all were choked. The test procedure was altered to require that if one switch was found to be choked, the others should be tested.

There were also mistakes made in the installation of the instruments. In one case, pneumatic pressure switches, of a flameproof type which is not waterproof, were located downwind of a low pressure steam vent pipe and suffered water ingress and corrosion.

34 11.2 Emergency shut-down systems

In many process units, there are SISs to prevent or mitigate specific process risks. In addition, the process unit may be protected by ESDs or emergency isolation systems. One of the principal accounts of ESDs is given in *Offshore Installations: Guidance on Design and Construction, Guidance Notes to the Offshore Installations (Construction and Use) Regulations 1974* issued by the Department of Energy (1984) and *Offshore Installations: Guidance on Design, Construction and Certification* (HSE, 1990b) (the HSE *Design, Construction and Certification Guidance Notes*). In many cases, ESDs are safety-instrumented systems and the principles described previously can be applied. The following is a discussion of ESDs, related to the above referenced texts.

34.11.2.1 Conceptual design of ESD

The function of an ESD system is to detect a condition or event sufficiently hazardous or undesirable as to warrant a shut-down and transition to a safe state. The potential hazards are determined through PHA. Estimates are then made of the frequency and consequences of these hazards. The ESD can then be specified based on the identified operating parameters that must be kept within limits if the hazards are to be avoided and selecting shut-down actions that will act when these limits are exceeded. A shut-down sequence is determined, and the shut-down logic is formulated. It is not always necessary to shut-down the whole plant. There are different levels of ESD, which fall short of this, such as shut-down of an individual unit or of a section of a plant.

34.11.2.2 Initiation of ESD

The configuration of the shut-down initiators of the ESD is critical. If the configuration is poor, the ESD will not be activated when it should be. A balance must be achieved between the functional integrity and operational reliability of the ESD system. It should act when a hazard arises, but should not cause unnecessary shut-downs.

One factor that affects this balance is that the plant is safest in the normal operating mode and that transitions, such as shut-down and start-up, tend to be more prone to hazards and should be avoided unless necessary. Another, related factor is that shut-down of one unit may result in process demands in other process units, causing initiation of other ESDs. These 'cascade trips' increase the hazard rate in the plant and should be avoided.

ESD initiation may be manual or automatic. Manual initiation may use a shut-down button in the control room and/or a local shut-down button in the process unit. Automatic means are accomplished using instrumentation, including the fire and gas system and/or the SIS. Measures

Table 34.14 *Assessment of reliability of a high integrity trip system (after P.M. Stewart, 1971) (Courtesy of the Institution of Chemical Engineers)*

	Description	*Fault condition*				*Relevant trip initiator No.*	*Fractional dead time*				*Hazard rate* ($\times 10^5$)
		Occasions per year a	*Probability that it leads to rupture* b	*Probability that operator's intervention fails* c	*Demand rate (demands/year)* $(d = a \times b \times c)$		*HITI* e	*HIVE* f	*HISS* g	*Overall* $(h = e + f + g)$	$(i = d \times h)$
1	Feed filters blocked	0.001	0.2	0.1	0.000 02	10 and 12	10^{-4}	10^{-5}	10^{-5}	1.2×10^{-4}	0.00024
2	Oxygen supply failure	2.0	0.2	0.1	0.04	10 and 38	10^{-4}	10^{-5}	10^{-5}	1.2×10^{-4}	0.48
3	PCV fails open	0.25	0.1	1.0	0.025	11	10^{-3}	8.3×10^{-5}	10^{-5}	1.09×10^{-3}	2.72
4	Compressor anti-surge bypass fails	0.2	1.0	0.1	0.02	18 and 36	10^{-4}	10^{-5}	10^{-5}	1.2×10^{-4}	0.24
5	Gross carryover from absorber	0.1	1.0	0.1	0.01	18.24	10^{-4}	10^{-5}	10^{-5}	1.2×10^{-4}	0.12
6	etc.										etc.

PCV, pressure control valve.

should be taken to avoid inadvertent activation, including failures or errors during maintenance and testing.

34.11.2.3 Action on ESD

There are a variety of actions that an ESD system may take. Three principal types are:

(1) flow isolation;
(2) energy reduction;
(3) material transfer.

Flow isolation includes isolation of feed and other flows. It often involves shut-down of machinery and may include isolation of units. Energy reduction covers shut-off of heat input, as well as initiation of additional cooling. Material transfer refers to pressure reduction, venting, or blow-down.

A fundamental principle in ESD design is failure to a safe state. The overall objective is failure to a safe state for the system as a whole. This is normally performed by applying the principle to individual units, but there may be exceptions, and cases should be considered individually. Each required action of the ESD system should be affected by positive means. Reliance should not be placed on the cascading effect of other trip actions.

34.11.2.4 Detail design of ESD system

It is a fundamental principle that protective systems be independent of the rest of the instrument and control system, and this applies equally to an ESD. The ESD design should generally follow the principles that apply to SISs, as previously described. There should be a balance between functional and operational reliability. Dependent failures should be considered. The reliability may be assessed using fault tree and other methods. The techniques of diversity and redundancy should be used as appropriate. Use may be made of majority voting systems.

The emergency shut-down valves (ESVs) should have a high degree of integrity. Such valves are frequently provided with pneumatic or hydraulic power supplies, in addition to electrical power supply. An ESV should be located so that it is unlikely to be disabled by the type of incident against which it is intended to protect.

The ESD system should be provided with power supplies that have a high degree of integrity. The normal approach is to provide a UPS. This supply should be designed and located so that it is unlikely to be disabled by the incident itself. The cables from the power supply to the final shut-down elements should be routed and protected to avoid damage by the incident.

34.11.2.5 Operation of ESD system

The operator should be notified of any change in ESD status. This includes indication that the ESD is in bypass, under test or under maintenance. Initiation of the ESD should activate audible and visual alarms in the control room. There should be an indication of the source of the initiation, whether manual or instrument. The ESD should also be signalled by an alarm that is part of the general alarm system.

It may be necessary in certain situations, such as start-up, changeover or maintenance, to bypass at least part of the ESD system, but such bypassing should be governed by formal procedures. The principles are analogous to those that apply to an SIS, as described previously.

34.11.2.6 Testing and maintenance of ESD system

The ESD system should be subject to periodic proof testing and such testing should be governed by a formal procedure. The principles of proof testing were discussed previously. As far as is practical, the test should cover the complete system from initiation to shut-down condition.

The need for proof testing and, more generally, for the detection of unrevealed failure should be taken into account in the design. The equipment should be designed for ease of testing. It should be segregated and clearly identified. Techniques for detection of instrument failure should be exploited. In voting systems, the failure of a single channel should be signalled.

34.11.2.7 Documentation of an ESD system

The ESD system should be fully documented. The HSE *Design, Construction and Certification Guidance Notes* give details of recommended documentation.

34.11.2.8 ESD of a gas terminal

The design of systems for ESD and emergency depressurization (EDP) of a gas terminal has been described by Valk and Sylvester-Evans (1985). The design philosophy described is that: (1) the ESD system should operate only in an extreme emergency, (2) the ESD and EDP systems are separate from the control, SIS and relief systems and (3) that the systems should be simple and reliable.

The preliminary design of the ESD and EDP systems was reviewed by means of a HAZOP study. Potential operational failures were studied using general reliability engineering methods and functional failures were studied using, in particular, fault tree analysis. A further HAZOP was conducted on the final design for the ESD and EDP system.

Design studies showed that executing a totally fail-safe concept would result in a relief and flare system of exceptional size. Alternatives considered were to allow an increase in the depressurization time for certain critical equipment beyond that recommended in the API RP 521 and to control the peak depressurization flow in the relief and flare system. In the design adopted, the plant was divided into sections, such that the depressurization of each section could be done independently and the operation of the sections was interlocked. The depressurization time of certain items was extended to 30 min as opposed to the 15 min recommended in API RP 521, but the design compensated for this extension by provision of additional fireproofing and water cooling arrangements.

The authors highlight the differences of philosophy between companies on whether the ESD and EDP systems should be used for normal shut-down and depressurization or reserved as systems dedicated for emergency use. This project reaffirmed the need to consider the ESD and EDP systems at an early stage and to avoid treating them as 'add-on' features to be dealt with late in the design.

34.11.2.9 ESD on Piper Alpha

The ESD system on Piper Alpha illustrates a number of the points just made. Overall, the system was largely effective in achieving shut-down, venting and blow-down, but there were a number of features which are of interest.

The main ESD button initiated closure of the ESV on the main oil pipeline but not on the ESV on the three gas pipelines. One reason for this was that closure of these latter ESVs would impose a forced shut-down on the linked platforms. There were three separate shut-down buttons, one for each of these valves, and shut-down depended on manual action by the control room operator – he was thrown across the control room by the explosion.

The ESVs on the risers of the gas pipelines were located so that they were vulnerable to the fires that developed. This defect was widespread throughout the North Sea and regulations were introduced without delay to require such valves to be relocated. There was also evidence that some of the ESVs did not achieve tight *shut-off*. The explosion damaged power supplies, and, in some cases, closure *of* ESVs occurred, not due to survival *of* the intended power supply, but fortuitously. Further details are given in Appendix 19.

34.11.3 Toxic storage instrumentation

On plants handling high toxic hazard materials (HTHM), the instrumentation and control system assumes particular importance. Some relevant considerations are outlined in *Guidelines for Safe Storage and Handling of High Toxic Hazard Materials* by the CCPS (1988/2) (the CCPS HTHM *Guide*).

Depending on the degree of hazard, the instrumentation and control system should be of high integrity. This requires adherence to the various principles already described for high integrity design, including the application of fail-safe design and the use, as appropriate, of high reliability instrumentation, instrument diversity and redundancy and high quality maintenance. It also involves the application of the techniques of hazard identification and assessment to the design.

With respect to process variable measurement, principal considerations are that the potential for release from the instrument, or its fittings, should be minimized, that the instrument be reliable and that the measurement be accurate. For flow measurements, the use of non-invasive sensors, such as magnetic flowmeters, and avoidance of glass in instruments, such as rotameters is preferred. Orifice flowmeters also have the disadvantage of an extra flange and associated piping. For pressure measurement, diaphragm pressure sensors are preferred to direct-connected gauges of the Bourdon tube type. Precautions to be taken where the latter have to be used include protection by inert liquid filling in corrosive service and installation of isolation valves and, possibly, flow limiters in the form of restriction orifices. For level measurement, weighing methods have advantages, but use of sight glasses should be avoided. For temperature measurement, particular care should be taken in the design of the thermowell, which can be a weak point.

The arrangements for control and protection should address the hazards of particular importance for the storage of toxics. These include: (1) overpressure, (2) overfilling, (3) over-temperature and (4) high release flow. For overpressure, the main requirements are the provision of overpressure protection and of means of disposal for the relief flows. For overfilling, a significant role is likely to be played by SISs. For temperature deviations, which may indicate reaction runaway or thermal stratification with its attendant risk of rollover, the need is for warning. Some methods of dealing with excess temperature are described below. High release flow rates following a failure of containment may be mitigated by the use of suitable control valve trims and of restrictor orifices or excess flow valves.

Storage of a reactive chemical requires close monitoring with respect to temperature and contamination. Methods of temperature control include the use of cooling coils, a reflux condenser, a quench system and short stop arrangement. All these methods depend on good mixing in the tank. Consequently, recirculation of the reactive chemical through a cooler is often used. Contamination can be introduced by putting the wrong chemicals in the tank or by using the wrong materials of construction for the tank, seals, or other peripheral equipment. Procedures and training are necessary to prevent these occurrences.

34.11.4 Interlock systems

Interlocks are another important type of protective device. They are used to: (1) control operations that must take place in a specified sequence or (2) ensure that one piece of equipment is in a specific state relative to other equipment. This definition of an interlock differs from that often used in the American literature, where the term 'interlock' tends to be applied to both SIS and interlock systems (as defined here).

Accounts of interlock systems are given in *Applied Symbolic Logic* (E.P. Lynch, 1980) and *Logical Design of Automation Systems* (V.B. Friedman, 1990) and by D. Richmond (1965), E.G. Williams (1965), Becker (1979), Becker and Hill (1979), Kohan (1984) and the CCPS (1993/14).

In general, interlocks are used to prevent operation of equipment under unsafe condition. There are various means for implementing interlocks. These include mechanical devices, such as a padlock and chain on a hand valve, keyed interlocks and software interlocks implemented using process computers. Interlocks are usually simple in design, but can incorporate redundancy if high integrity is required for the application. Typical applications of interlocks include:

(1) electrical switchgear;
(2) test cubicles;
(3) machinery guards;
(4) vehicle loading;
(5) conveyor systems;
(6) machine start-up and shut-down;
(7) valve systems;
(8) instrumented systems;
(9) fire protection systems;
(10) plant maintenance.

For example, electrical switchgear may be installed in a room where an interlock prevents the door from opening until there is electrical isolation. Similarly, an interlock may be used to prevent access to a test cubicle where high pressure or explosive materials are present until safe conditions are achieved. An interlock may be also used to stop access to a machine or entry into a vessel unless the associated machinery cannot move. In vehicle loading, interlocks are used to prevent a tanker from moving while it is still connected to the unloading arm. Pressure relief valves have interlocks to prevent all the parallel valves from being isolated simultaneously. There may be interlocks on other critical valve systems.

Interlocks may also be used to ensure sequenced operation, as in a conveyor system. Interlocks are used for the start-up of machinery to ensure that all the pre-start conditions are met, that the correct sequence is followed, and that conditions for transition from stage to stage are met. For large rotating machinery, key factors are process conditions and oil pressures.

Interlocks are often a subset of a SIS. An interlock may be used to prevent the disarming of an SIS unless certain conditions are met. Fire protection systems are provided with interlocks as a safeguard against leaving the system in bypass, particularly after testing or maintenance. Plant maintenance operations make much use of interlocks to prevent valves being opened or machinery started up while work is in progress.

Some features of a good hardware interlock are that it: (1) controls operations positively, (2) is incapable of defeat, (3) is simple, robust and inexpensive, (4) is readily and securely attachable to engineering devices and (5) is regularly tested and maintained.

Many interlocks are quite simple, but some are quite complex. When interlocks involve complex logic functions, they are effectively safety instrumented systems and can be designed in the same manner. In particular, there are some very large interlock systems on boilers and gas turbines. For example, control of sequential operations is often executed using numerous checks that must be satisfied before the next stage is initiated and checks that equipment has obeyed the control signals. These checks constitute a form of interlock.

Since an interlock can bring the process to a halt, it is important to provide 'first-out indication,' including adequate status and alarm signals to indicate what initiated the stoppage.

34.11.4.1 Interlock diagrams

As with safety instrumented systems, interlock design may involve a number of parties. For effective design, a common language and approach are needed. Unfortunately, there is substantial disagreement in the field related to the type of diagram used to describe the logic, the representation of symbols and the nomenclature. While standards have been written to cover these areas, the symbols used in some are not in common use and the standards are subject to continuous revision.

Three types of diagrams commonly used in the process industry are: (1) the process flowchart, (2) the logic diagram and (3) the ladder diagram. The last two are sometimes referred to as the 'attached logic diagram' and the 'detached logic diagram,' respectively. A process flow chart can be used to describe the sequence of operations. Process flow chart symbols have been given in *Work Study* (Curie, 1960) and are shown in Table 34.16, Section A. The logic required to implement this sequence may be shown in a logic diagram. This utilizes standard symbols for functions such as OR, AND and NOT, similar to those used in fault tree work, as described in Chapter 9. Standard symbols for fault trees are given in BS 5760 *Reliability of Systems, Equipment and Components*, Part 7: 1991 *Guide to Fault Tree Analysis*. Typical logic symbols are shown in Table 34.15, Section B.

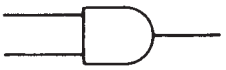
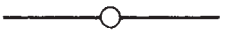
The logic diagram may then be converted to a ladder diagram. Standard symbols for protective logic systems are given in BS 3939: 1985 *Graphical Symbols for Electrical Power, Telecommunications and Electronic Diagrams*. The relevant IEC standard is IEC 617 *Graphical Symbols for Diagrams*. BS 3939: Part 7: 1985 *Switchgear, Controlgear and Protective Devices*, which is identical to IEC 617-7, gives relevant symbols. Other sets of symbols include those given by E.G. Williams (1965) and those of E.P. Lynch (1980). An account of the evolution of logic symbols is given in *An Introduction to the New Logic Symbols* (Kampel, 1986).

Table 34.15 *Interlock logic symbols*

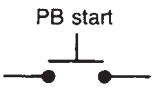
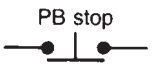
A Work study symbols[a]

Symbol	*Activity*	*Predominant result*
	Operation	Produces, accomplishes changes further the process
	Inspection	Verifies quantity or quality
	Transport	Moves or carries
	Delay	Interferes or delays
	Storage	Holds, retains or stores

B Logic sysmbols[b]

	AND
	OR
	NOT
	Delay

C Ladder diagram symbols[c]

	Pushbutton start
	Pushbutton stop
	Position, or limit, switch
	Relay or solenoid contacts, normally open, closed when relay or solenoid is energized
	Relay or solenoid contacts normally closed, opened when relay or solenoid is energized
	Motor *n*
	Relay *n*
	Solenoid *n*

[a] These symbols are given by Currie (1960), who attributes them without reference to the American Society of Mechanical Engineers.
[b] These symbols are given in BS 5670: Part 7: 1991. The alternative symbol for NOT is a common alternative and is that used by E.P. Lynch (1980).
[c] These symbols are those used by E.P. Lynch (1980).

Table 34.16, Section C, shows a selection of symbols, including those used here, from those given by Lynch.

34.11.4.2 Some basic systems

Some of the basic building blocks of interlock systems are illustrated using a simple starting circuit in Figure 34.13. Activation of the circuit occurs when a signal is generated by depression of the start pushbutton AND a signal due to non-depression of the stop pushbutton. Once activated, the circuit is maintained in the 'on' state until reset by the operator by depression of the stop pushbutton.

Figure 34.13(b) shows a time-delayed holding circuit. If following activation by the start pushbutton, the signal X does not appear within the time interval specified, the output signal disappears. A typical application of this circuit is start-up of a motor-driven pump, which is supplied with lubricating oil by a lube oil pump driven from the same motor. If after the time interval specified, the lubricating oil pressure signal is still absent, the pump is shut-down.

Figure 34.13(c) shows a self-extinguishing circuit. Activation of the pushbutton gives an output signal, which continues until the time interval specified has elapsed. Then, the output signal is extinguished. This circuit might typically be used to have a motor-driven equipment run for a period and then shut-down.

34.11.4.3 Illustrative example: conveyor system

As an illustration of an interlock system, consider the conveyor system described by Lynch. The screw conveyor A feeds material from a car vibrator to an elevator, which discharges to screw conveyor B above two storage bins A and B. There is a slide gate on the pipe between conveyor B and each bin, with a limit switch on each gate. Material is fed from a bin by a star feeder into screw conveyor C. The loading equipment can fill the bins at several times the rate at which it can be withdrawn.

Figure 34.14(a) shows a logic diagram for the interlocks for manual operation of this system. Conveyor B can be started only if either A or B slide gate is open. The elevator can be started only if conveyor B is running. Conveyor A can be started only if the elevator is running. The diagram also shows the simple non-interlocked starting circuit for the car vibrator.

The corresponding ladder diagram is shown in Figure 34.14(b). The diagram shows six circuits A–F. Certain relays occur in more than one circuit, for example, relay R1 in circuits A and D, and this imparts the interlocking feature. Circuit A is the starting circuit for conveyor B. This circuit can be activated only if either relay R2 or R3, the relays for the slide gates limit switches (LS), is closed. If this condition is met, depression of the start pushbutton (PB) energizes relays R1 and M1 and causes R1 to close and M1 to operate a relay in the power circuit. When the stop pushbutton is pressed, the circuit is de-energized and R1 opens.

In circuit B, closure of the slide valve limit switch LSI energizes relay R2 and causes it to close, and opening of the switch causes R2 to open. Circuit C implements a similar

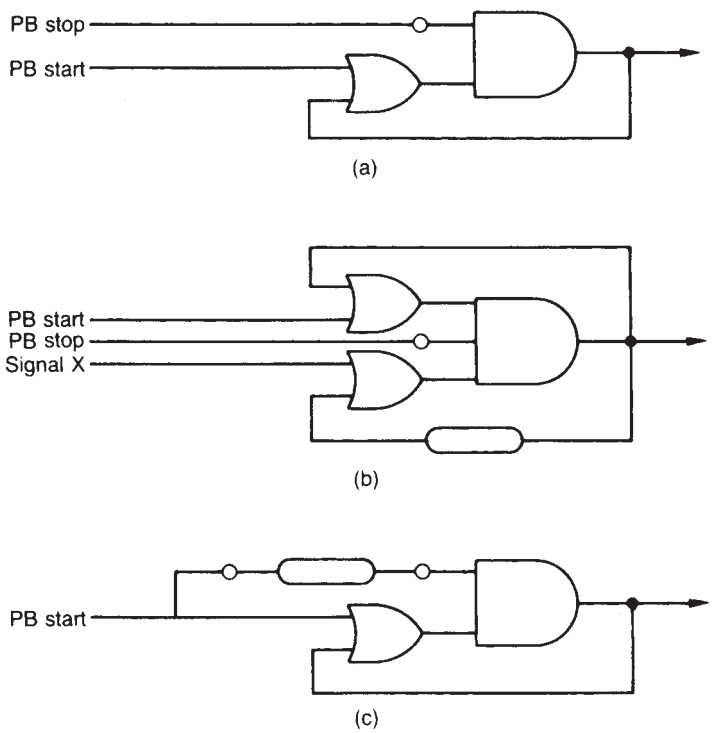


Figure 34.13 *Some basic interlock system logic diagrams: (a) simple starting circuit; (b) time delayed holding circuit; and (c) self-extinguishing circuit. PB, pushbutton*

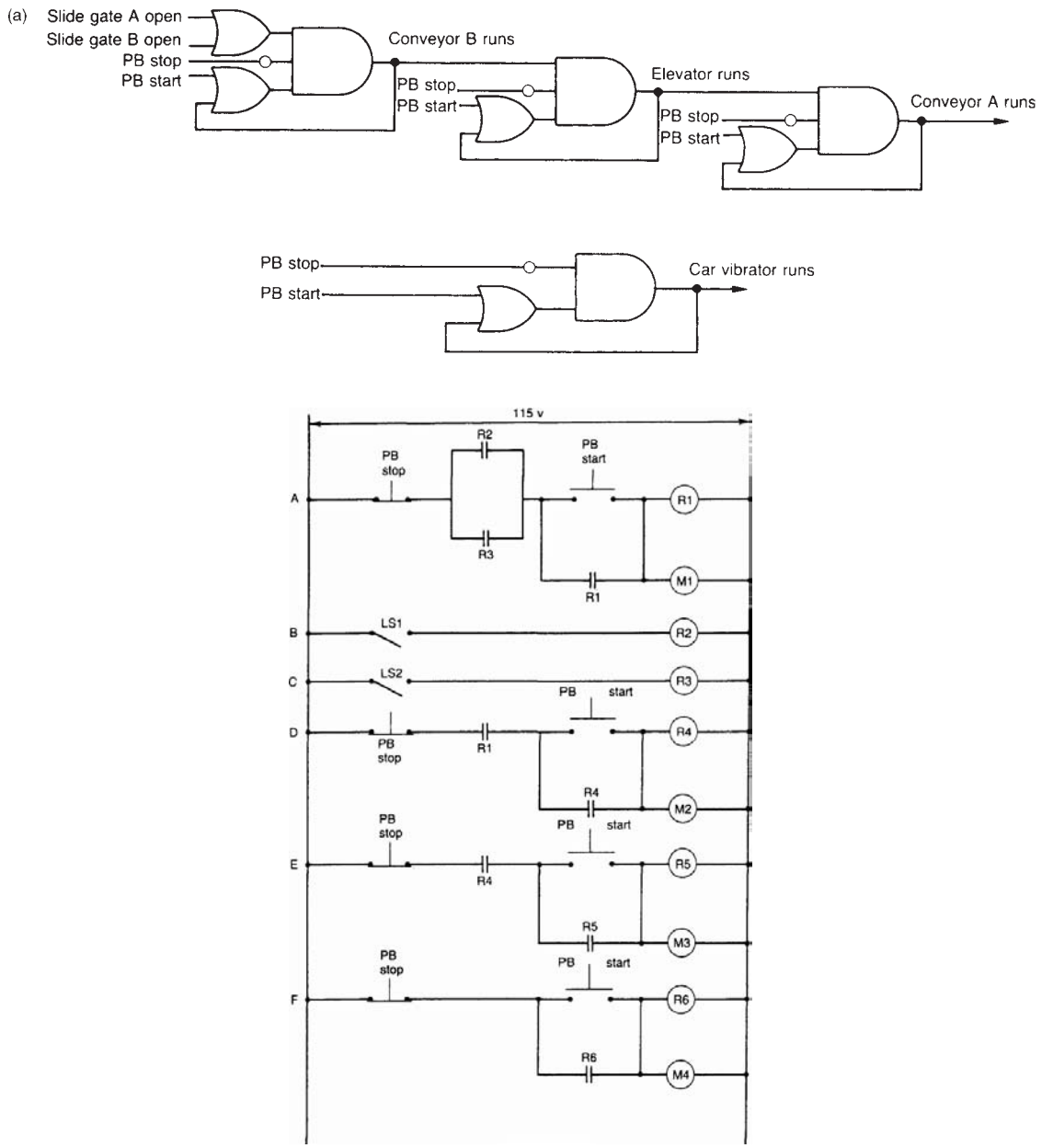


Figure 34.14 *Conveyor interlock system diagrams: (a) logic diagram, and (b) ladder diagram (E.P. Lynch, 1980) (Reproduced with permission from Applied Symbolic Logic by E.P. Lynch, Copyright © , 1980, John Wiley and Sons Inc.)*

relationship between limit switch LS2 and relay R3. Circuit D is the starting circuit for the elevator. The circuit can be activated only if relay R1 is closed. If this condition is met, depression of the start button energizes relays R4 and M2 and causes R4 to close and M2 to operate. Circuit E is the starting circuit for conveyor A, and is similar to circuit D. The circuit can be activated only if relay R4 is closed. Circuit F is a simple starting circuit and is not interlocked.

34.11.4.4 Illustrative example: reactor system

Another example of a simple interlock system is illustrated in Figures 34.15 and 34.16. Figure 34.15 shows a plant consisting of a water-cooled reactor in which a batch reaction is

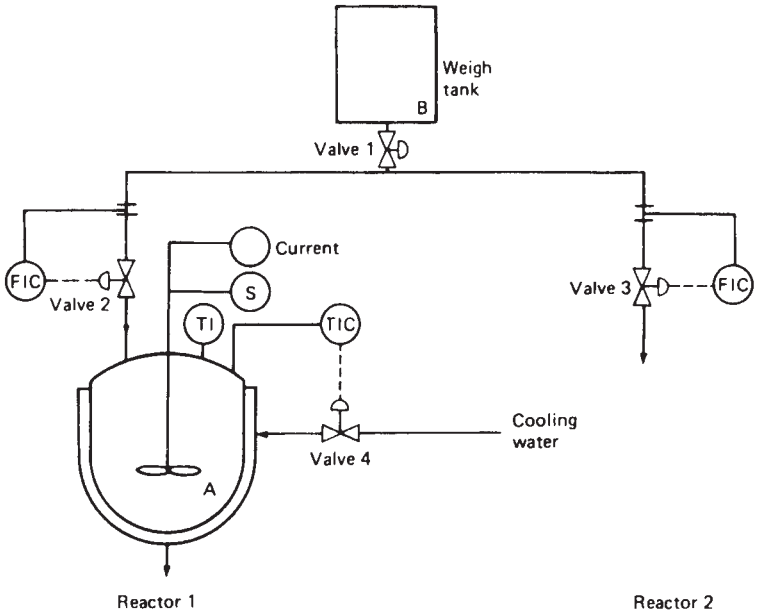


Figure 34.15 *Batch reactor system. FIC, flow indicator controller; S, speed measurement; TI, temperature indicator; TIC, temperature indicator controller*

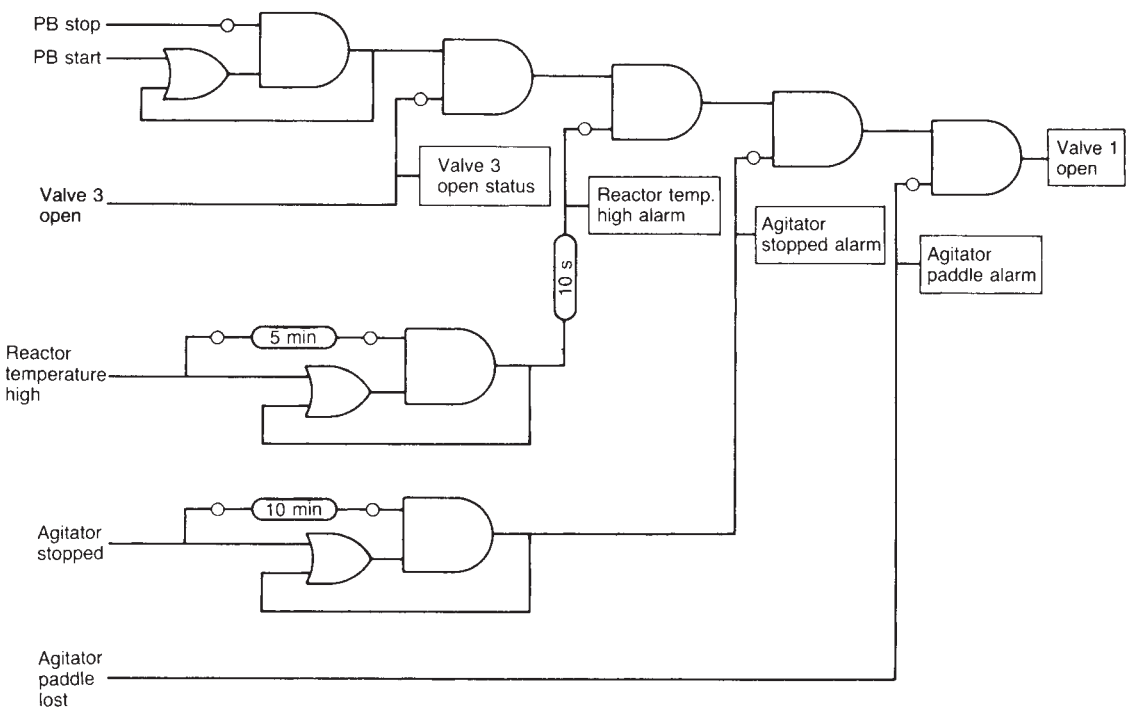


Figure 34.16 *Batch reader interlock system logic diagram*

carried out. The reactor is charged with chemical A and chemical B is then fed in gradually from a weigh tank as the reaction proceeds. The interlock system is required to cut off the supply of B from the weigh tank if any of the following conditions apply: (1) the shut-off valve V3 on reactor 2 is open, (2) the agitator is not operating, (3) the agitator paddle has fallen off, or (4) the reactor temperature has risen above a fixed limit. The loss of the agitator paddle is detected by a current-sensitive relay on the motor.

An interlock system for carrying out these functions is shown in Figure 34.16. The start input opens valve 1, unless valve 3 is open or the agitator is stopped, which conditions inhibit start-up. If these conditions occur later or if the reactor temperature rises or the agitator paddle falls off, valve 1 is closed. The interlock causing the closure is signalled by a status or alarm display. There is a 10 s delay on the reactor high temperature interlock to allow for noise on that signal. If operation is inhibited by the high reactor temperature or agitator stoppage interlocks, these interlocks are reset at 5 and 10 min, respectively, after the inhibiting condition has cleared. An account of the reliability of interlock systems is given by R.A. Freeman (1994).

35 Chemical Security

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35.1 Introduction

Security is a critical element of the management of a process facility. Security management is required for protecting the assets (including employees) of the facility, maintaining the ongoing integrity of the operation and preserving value of the investment. Process security and process safety have many parallels, and make use of many common programmes and systems for achieving their ends. Process security requires a management systems approach to develop a comprehensive security programme, which shares many common elements to process safety management.

The foundation of the security management system is a security vulnerability assessment (SVA), which is intended to identify security vulnerabilities from a wide range of threats ranging from vandalism to terrorism. With the recognition of threats, consequences, vulnerabilities and the evaluation of the risk of security events, a security management system can be organized that will effectively mitigate the risks.

The world of safety and security in the chemical process industries has certainly changed since the terrorist attack on the United States on 11 September 2001. This and other violent acts pose a new risk paradigm for chemical security. The design and operation of a facility must now consider extreme acts of violence rather than only less severe threats.

35.2 Security Management System

A comprehensive process security management system must include management programme elements that integrate and work in concert to control security risks. The thirteen management practices shown in Figure 35.1 are an example of a management system developed for the chemical industry:

The purpose of the management system is to ensure the ongoing, professional and systematic application of security principles and programmes to achieve a level of specified security. Traditional security management is not based on a management system and so is not necessarily a thorough, ongoing, risk-based, pro-active approach, but is more generally based and is reactive to security incidents primarily.

The process security management system is to ensure the protection of people, property, products, processes, information and information systems and thereby ensure the continuity of the operation and supporting or dependent infrastructure. The chemical industry value chain encompasses company activities associated with the design, procurement, manufacturing, marketing, distribution, transportation, customer support, use, recycle and disposal of products *Site Security Guidelines for the U.S. Chemical Industry* (American Chemistry Council, October 2001).

The *Security Code* published by the American Chemistry Council is designed to help companies achieve continuous improvement in security performance using a risk-based approach to identify, assess and address vulnerabilities, prevent or mitigate incidents, enhance training and response capabilities and maintain and improve relationships with key stakeholders. Each company must implement a risk-based security management system for people, property, products, processes, information and information systems throughout the chemical industry value chain. The chemical industry value chain encompasses company activities associated with the design, procurement, manufacturing, marketing, distribution, transportation, customer support, use, recycle and disposal of our products. The corresponding security management system must include the following thirteen management practices:

(1) Leadership Commitment
(2) Analysis of Threats, Vulnerabilities, and Consequences
(3) Implementation of Security Measures
(4) Information and Cyber Security
(5) Documentation
(6) Training, Drills, and Guidance
(7) Communications, Dialogue, and Information Exchange
(8) Response to Security Threats
(9) Response to Security Incidents
(10) Audits
(11) Third-Party Verification
(12) Management of Change
(13) Continuous Improvement

Figure 35.1 *Example process security management system Site Security Guidelines for the U.S. Chemical Industry (American Chemistry Council, October 2001)*

(1) Leadership Commitment. Senior leadership commitment to continuous improvement through published policies, provision of sufficient and qualified resources and established accountability.
(2) Analysis of Threats, Vulnerabilities and Consequences. Prioritization and periodic analysis of potential security threats, vulnerabilities and consequences using accepted methodologies.
(3) Implementation of Security Measures. Development and implementation of security measures commensurate with risks, and taking into account inherently safer approaches to process design, engineering and administrative controls and prevention and mitigation measures.
(4) Information and Cyber-Security. Recognition that protecting information and information systems is a critical component of a sound security management system.
(5) Documentation. Documentation of security management programmes, processes and procedures.
(6) Training, Drills and Guidance. Training, drills and guidance for employees, contractors, service providers, value chain partners and others, as appropriate, to enhance awareness and capability.
(7) Communications, Dialogue and Information Exchange. Communications, dialogue and information exchange on appropriate security issues with stakeholders such as employees, contractors, communities, customers, suppliers, service providers and government officials and agencies balanced with safeguards for sensitive information.

(8) Response to Security Threats. Evaluation, response, reporting and communication of security threats as appropriate.
(9) Response to Security Incidents. Evaluation, response, investigation, reporting, communication and corrective action for security incidents.
(10) Audits. Audits to assess security programmes, and processes and implementation of corrective actions.
(11) Third-Party Verification. Third-party verification that, at chemical operating facilities with potential off-site impacts, companies have implemented the physical site security measures to which they have committed.
(12) Management of Change. Evaluation and management of security issues associated with changes involving people, property, products, processes, information or information systems.
(13) Continuous Improvement. Continuous performance improvement processes entailing planning, establishment of goals and objectives, monitoring of progress and performance, analysis of trends and development and implementation of corrective actions.

35.3 Security Strategies

A basic premise is that all security risks cannot be completely prevented. Appropriate strategies for managing security can vary widely depending on the circumstances including the type of facility and the threats facing the facility. As a result, it is difficult to prescribe security measures that apply to all facilities in all industries, but instead it is suggested to use SVA as a means of identifying, analysing and reducing vulnerabilities. The specific situations must be evaluated individually by local management using best judgement of applicable practices. Appropriate security risk management decisions must be made commensurate with the risks. This flexible approach recognizes that there isn't a uniform approach to security in the chemical process industry, and that resources are best applied to mitigate high risk situations primarily.

Security strategies for the process industries are generally based on the application of four key concepts against each threat (*Managing and Analyzing the Security Vulnerabilities of Fixed Chemical Sites* AIChE, August 2002.):

(1) Deterrence
(2) Detection
(3) Delay
(4) Response

In the context of security of a process facility, the security strategies of deter, detect, and delay are defined as follows. *(Managing and Analyzing the Security Vulnerabilities of Fixed Chemical Sites* AIChE, August 2002.):

Deter: A security strategy to prevent or discourage the occurrence of a breach of security by means of fear or doubt. Physical security systems such as warning signs, lights, uniformed guards, cameras, bars are examples of systems that provide deterrence.

Detect: A security strategy to identify an adversary attempting to commit a malicious act or other criminal activity in order to provide real-time observation, interception and post-incident analysis of the activities and identity of the adversary.

Delay: A security strategy to provide various barriers to slow the progress of an adversary in penetrating a site to prevent an attack or theft, or in leaving a restricted area to assist in apprehension and prevention of theft.

Response: The act of reacting to detected criminal activity either immediately following detection or post-incident via surveillance tapes or logs.

A complete security design includes these four concepts in 'Layers of Protection' or a 'Defense in Depth' arrangement. Examples of these physical protection concepts and their associated countermeasures are graphically depicted in Figure 35.2 (adapted from 'Site Security Guidelines for the U.S. Chemical Industry', American Chemistry Council (ACC), October 2001) and Figure 35.3. The most critical assets should be placed in the centre of conceptual concentric levels of increasingly more stringent security measures. In the concept of rings of protection, the spatial relationship between the location of the target asset and the location of the physical countermeasures is important.

In the case of malicious acts, the layers or rings of protection must be particularly robust because the adversaries are intentionally attempting to breach the protective features and can be counted on to use whatever means are available to be successful. This could include explosions or other initiating events that result in widespread common cause failures. Some particularly motivated adversaries might commit suicide attempting to breach the security layers of protection.

35.4 Countermeasures and Security Risk Management Concepts

Countermeasures are actions taken to reduce or eliminate one or more vulnerabilities. Countermeasures include hardware, technical systems, software, interdictive response, procedures and administrative controls.

Security risk reduction at a site can include the following strategies:

(1) Physical Security
(2) Cyber Security
(3) Crisis Management and Emergency Response Plans
(4) Policies and Procedures
(5) Information Security
(6) Intelligence
(7) Inherent Safety

35.5 SVA Methodologies

There are several SVA techniques and methods available to the industry, all of which share common elements.

The following is a list of some available SVA methodologies published by various government, private and trade/professional organizations. Some are merely chapters or sections of documents that address security or risk assessment/risk management in broader terms. Some are SVA/VA publications by themselves. Some of these 'methods' are complete, systematic analytical techniques and some are more checklist in nature.

(1) American Institute of Chemical Engineers Center for Chemical Process Safety: *Guidelines For Analyzing and Managing the Security Vulnerabilities of Fixed Chemical Sites*
(2) American Petroleum Institute/National Petroleum Refiner's Association, *Security Vulnerability Assessment Methodology for the Petroleum Industry.*

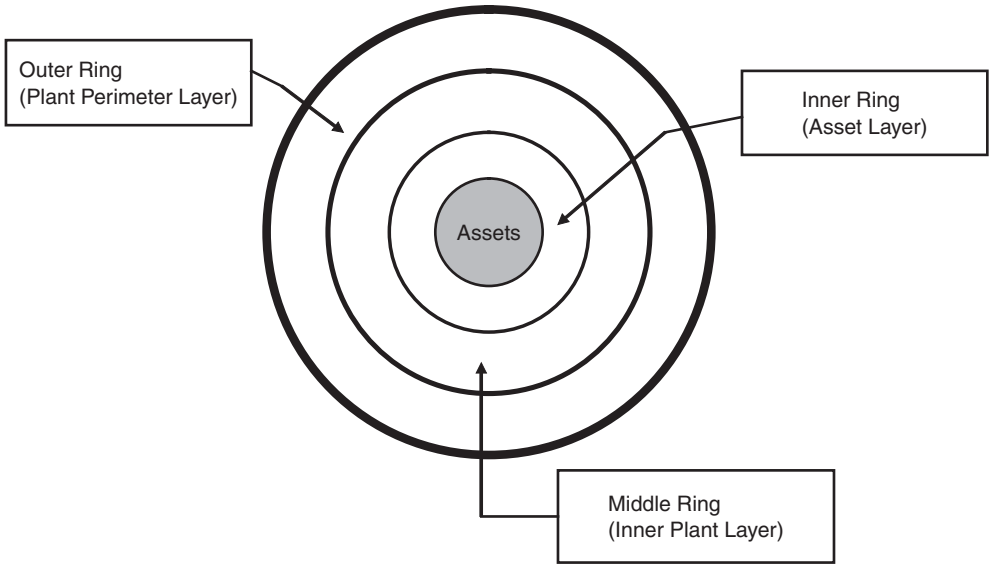

Figure 35.2 *Defense in depth concept for security (layers of protection)*

(3) National Institute of Justice, *Chemical Facility Vulnerability Assessment Methodology*, Jul. 2002 (this is summary of Sandia VAM).
(4) US Army, FM 3-19.30, *Physical Security*, appendix K.
(5) *Military Handbook*, MIL-HDBK 1013/1A, Design Guidelines For Physical Security of Facilities.
(6) Department of Energy, Office of Energy Assurance, *Energy Infrastructure Risk Management Checklists For Small and Medium Sized Businesses*, 19 August 2002.
(7) Department of Transportation, RSPA, *Surface Transportation Vulnerability Assessment*, 25 October 2001.
(8) Department of Transportation, RSPA, *Enhancing Security of Hazardous Materials Shipments Against Acts of Terrorism and Sabotage Using RSPA's Risk Management Self-Evaluation Framework (RMSEF)*, Jan. 2002.
(9) National Infrastructure Protection Center, *Risk Management: An Essential Guide to Protecting Critical Assets*, Nov. 2002.
(10) Synthetic Organic Chemical Manufacturers Association, Inc. ("SOCMA"); *Manual on Chemical Site Security Vulnerability Analysis Methodology and Model*
(11) American Society of Industrial Security, *General Security Risk Assessment Guideline*.
(12) North American Electric Reliability Council, *Vulnerability and Risk Assessment*, Ver 2.
(13) North American Electric Reliability Council, *Security Guidelines for the Electricity Sector*, Ver 1, 14 June 2002.

Ultimately, it is the responsibility of the owner/operator to choose the SVA method and depth of analysis that best meets the needs of his specific location. Differences in geographic location, type of operations, and on-site quantities of hazardous substances all play a role in determining the level of SVA and the approach taken. Independent of the SVA method used, all techniques include the following:

(1) Characterize the facility to understand what critical assets need to be secured, their importance and their interdependencies and supporting infrastructure, and the consequences if they are damaged or stolen;
(2) Identify and characterize threats against those assets and evaluate the assets in terms of attractiveness of the targets to each adversary;
(3) Identify potential security vulnerabilities that threaten the system's service or integrity;
(4) Determine the risk represented by these events or conditions by determining the likelihood of a successful event and the consequences of an event if it were to occur;
(5) Rank the risk of the event occurring and, if high risk, make recommendations for lowering the risk;
(6) Identify and evaluate risk mitigation options (both net risk reduction and benefit/cost analyses) and re-assess risk.

One approach to conducting a SVA is shown in Figure 35.4. This methodology was published by the American Petroleum Institute and the National Petrochemical and Refiners Association in their guidelines *Security Vulnerability Assessment for the Petroleum and Petrochemical Industries*, American Petroleum Institute, May 2003.

35.6 Defining the Risk to be Managed

For the purposes of an SVA, the definition of risk is shown in Figure 35.5. The risk that is being analysed for the SVA is defined as an expression of the likelihood that a defined threat will target and successfully attack a specific security vulnerability of a particular target or combination

Security Countermeasure	Outer Perimeter (Plant Boundary Layer)				Middle Perimeter (Inner Plant/Asset Level)				Inner Perimeter (Asset/Subsystem Level)			
	Deter	Detect	Delay	Respond	Deter	Detect	Delay	Respond	Deter	Detect	Delay	Respond
Access Control	■	■	■		■	■	■		■	■	■	
Background Checks	■	■			■	■			■	■		
Bollards	■		■		■		■		■		■	
CCTV		■		■		■		■		■		■
Counter Surveillance		■				■				■		
Door/Gate Locks	■		■		■		■		■		■	
Emergency Planning				■				■				■
Emergency Shut-down				■				■				■
Fences	■		■		■		■		■		■	
Guard Force	■	■	■	■	■	■	■	■	■	■	■	■
ID System	■	■			■	■			■	■		
Intelligence Gathering		■				■				■		
Intrusion Detection		■		■		■		■		■		■
Jersey Barriers	■		■		■		■		■		■	
Lighting	■	■		■	■	■		■	■	■		■
Network Firewall	■	■	■		■	■	■		■	■	■	
Target Hardening	■		■		■		■		■		■	
Trenches	■		■		■		■		■		■	
Vehicle Checks	■	■			■	■			■	■		
Vigilance Training		■		■		■		■		■		■
Key	■	Countermeasure may be applicable to the security concept										

Figure 35.3 *Defense in depth/layers of protection concept for a chemical process facility Moore, David, Applying Inherently Safer Technologies for Security of Chemical Facilities, 38th Annual Loss Prevention Symposium, AIChE 2004 Spring National Meeting, New Orleans, Louisiana, April 26–29, 2004*

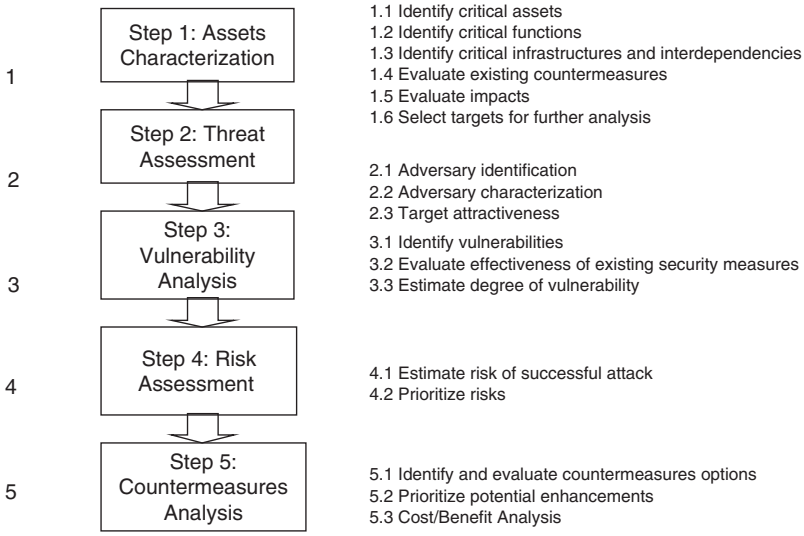

Figure 35.4 *API/NPRA Security vulnerability assessment methodology*

Intentional Release Risk is a function of:	Accidental Release Risk is a function of:
Consequences of a successful attack against an asset and likelihood of a successful attack against an asset.	Consequences of an accidental event and likelihood of the occurrence of the event.
Likelihood is a function of: the Attractiveness to the adversary of the asset, the degree of Threat posed by the adversary and the degree of Vulnerability of the asset.	Likelihood is a function of: The probability of an event cascading from initiating event to the consequences of interest and the frequency of the events over a given period.

Figure 35.5 *Intentional Release vs Accidental Release – Risk Definitions*

of targets to cause a given set of consequences. This is contrasted with the usual accidental risk definitions. The risk variables are defined as shown in Figure 35.6.

35.7 Overview of a SVA Methodology

The SVA process is a risk-based and performance-based methodology. The user can choose different means of accomplishing the general SVA method so long as the end result meets the same performance criteria. The overall 5-step approach of the API/NPRA SVA methodology is described as follows:

Step 1: Asset characterization
The asset characterization includes analysing information that describes the technical details of facility assets to support the analysis, identifying the potential critical assets, identifying the hazards and consequences of concern for the facility and its surroundings and supporting infrastructure and identifying existing layers of protection. Essentially, this step identifies the assets (people, facilities, information, reputation, business) of value, analyses why it is of value and identifies its importance, determines the interaction of the assets with other neighbouring facilities, suppliers, or customers or other economic interdependencies. Assumptions are made on the worst credible security event consequences to determine the impacts. The estimate of severity of the consequences is one of the four risk factors.

Step 2: Threat assessment
The intentional release risk includes possible attacks by outsiders or insiders, or a combination of the two adversaries.

Consequences	The potential impacts of the event
Likelihood	Likelihood which is a function of the chance of being targeted for attack, and the conditional chance of mounting a successful attack (both planning and executing) given the threat and existing security measures. This is a function of three variables below.
Threat	Threat, which is a function of the adversary existence, intent, motivation, capabilities and known patterns of potential adversaries. Different adversaries may pose different threats to various assets within a given facility.
Vulnerability	Any weakness that can be exploited by an adversary to gain access and damage or steal an asset or disrupt a critical function. This is a variable that indicates the likelihood of a successful attack given the intent to attack an asset.
Target Attractiveness	Target Attractiveness, which is a surrogate measure for likelihood of attack. This factor is a composite estimate of the perceived value of a target to the adversary and their degree of interest in attacking the target.

Figure 35.6 *API/NPRA SVA methodology SVA risk variables (Managing and Analyzing the Security Vulnerabilities of Fixed Chemical Sites, AIChE, August 2002.)*

It may be perpetrated by a number of different adversaries with varying intents, motivations, weapons, tactics and capabilities. These issues need to be sorted out in a threat assessment, which is, in effect, a risk-based assessment that forms the basis of the design basis threat assumption the facility designs and operates to.

The selection of the threats should include reasonable local, regional or national intelligence information, where available. This step also includes determining the target attractiveness of each asset from each adversary's perspective.

A responsible company has to give thought to the possible threats and attempt to organize the many combinations and permutations into a threat matrix. Key to this matrix is the first variable – what is the target? Is the company a direct target or is it affected by a terrorist attack? From a pure risk management standpoint, companies need to be prepared for both contingencies, not only for the possibility of direct physical or cyber attack to their facilities. This shows the multi-faceted aspects of the problem, and the need for industry, community and government cooperation to address the problem.

For example, there is a major difference in the protection set required if the assumed threat is an armed attack by a small band of terrorists who use force to enter the main entrance way, vs a single insider who misuses their access to the process control system to cause a release from the same asset. Which threats are credible and to what extent is the threat potential?

Threat is an important factor in the determination of risk. Prior to 11 September 2001, for example many of the other factors in the risk equation were present, but the threat was considered to be too low to be credible. It is the increased appreciation of threat that prompts us to now take action. Properly done, the threat assessment forms the basis of the process security management strategy for the facility.

The threat definition results in a determination of the design basis threat for the facility. The threat assessment results in a 'fixed' and 'variable' design basis threat. The fixed threat forms the basis for the design and is the baseline threat estimate. The variable design basis threat assessment is an estimate of the change in threat levels given certain possible future conditions. The Homeland Security Advisory System (HSAS) is an example of a national effort to help define varying threat levels. Facilities are urged to take actions given increased threat levels, so these factors need to be considered in the threat assessment.

The concept of fixed and variable design basis threats is useful for making decisions on facility design and operation. If the threat to insiders is considered significant, countermeasures designed to limit those risks are imperative. The fixed threat may determine the need for background screening, limiting the span of control of individuals, strong supervision, monitoring of activities, audits, surveillance, password controls and other measures. In fact, after determining and appreciating that the insider threat potential threat is significant, the facility may be designed or redesigned to avoid use of a type of operation, substitute chemicals or other measures to minimize this potential. If other conditions change, the threat may increase. For example, if there are a large number of visitors such as during a turnaround or in the event of specific threat information or a terrorist attack in the United States, increased threat levels may change or add to the baseline countermeasures.

Threat to a particular asset varies with several factors including the degree of interest that an adversary may have in the asset, as well as the degree of impact possible if the asset was attacked, disables, copied, compromised, or stolen. For this reason, the threat assessment includes a step whereby each asset is analysed from the perspective of each potential adversary to determine the degree of attractiveness

SEVERITY						
LIKELIHOOD		5	4	3	2	1
	5	High	High	High	Med	Med
	4	High	High	Med	Med	Low
	3	High	Med	Med	Low	Low
	2	Med	Med	Low	Low	Low
	1	Med	Low	Low	Low	Low

Figure 35.7 *Risk ranking matrix*

of the asset to the adversary. Attractiveness is therefore another factor in the determination of risk.

Step 3: Vulnerability analysis

The vulnerability analysis includes the relative pairing of each target asset and threat to identify potential vulnerabilities related to process security events. This involves the identification of existing countermeasures and their level of effectiveness in reducing those vulnerabilities. The degree of vulnerability of each valued asset and threat pairing is evaluated by the formulation of security-related scenarios or by an asset protection basis. If certain criteria are met such as higher consequence and attractiveness ranking values, then it may be useful to apply a scenario-based approach to conduct the Vulnerability Analysis. This approach option is very similar to the process hazard analysis (PHA) techniques employed to analyse accidental releases. It includes the assignment of risk rankings to the security-related scenarios developed.

Vulnerability is important to understand as it helps to determination how adversaries may target and execute crimes. Vulnerabilities are ubiquitous, so simply understanding vulnerabilities is not sufficient to make a risk determination. Other factors such as threat, consequence and attractiveness are required for a more complete risk appreciation.

Step 4: Risk assessment

The risk assessment determines the relative degree of risk to the facility in terms of the expected effect on each critical asset as a function of consequence and probability of occurrence. Using the assets identified during Step 1 (Asset Characterization), the risks are prioritized based on the likelihood of a successful attack which is a function of the threats assessed under Step 2 and the degree of vulnerability identified under Step 3.

A risk assessment matrix such as in Figure 35.7 can be used for the purpose of assessing risk.

Risk assessment is only possible when there is some frame of reference. Since the events in question are extremely rate events, it is necessary to (1) use surrogate factors such as attractiveness and threat to determine the likelihood of interest of attack of any particular asset and (2) use vulnerability as a measure of the likelihood of a successful attack given the desire to attack. Then the analyst can use performance criteria to set risk goals. Each scenario is evaluated against those goals. For example, such criteria as the following may be set to determine unacceptable risk:

Example security criteria:

(1) No unauthorized person can easily cross the outer perimeter without delay or detection;
(2) Any intruder is detected within 10 s of breaching the perimeter barrier;
(3) Any intruder is interdicted within 5 min of breaching the perimeter barrier;
(4) Any person entering the secured zone is authorized to be there;
(5) Authorization is comprised of invitation and verification;
(6) No unauthorized vehicle shall be allowed within 500 ft of a critical asset.

These criteria are used as binary risk goals, that is, if the existing situation fails these tests, then additional countermeasures are required.

Step 5: Countermeasures analysis

Based on the vulnerabilities identified and the risk that the layers of protection are breached, appropriate enhancements to the security countermeasures may be recommended. Countermeasure options will be identified to further reduce vulnerability at the facility. These include improved countermeasures that follow the process security doctrines of deter, detect, delay, respond, mitigate and possibly prevent. Some of the factors to be considered are:

(1) Reduced probability of successful attack
(2) Degree of risk reduction by the options
(3) Reliability and maintainability of the options
(4) Capabilities and effectiveness of mitigation options
(5) Costs of mitigation options
(6) Feasibility of the options

The countermeasure options should be re-ranked to evaluate effectiveness, and prioritized to assist management decision making for implementing security programme enhancements. The recommendations should be included in an SVA report that can be used to communicate the results of the SVA to management for appropriate action.

Lees' Loss Prevention in the Process Industries

VOLUME 3

Hazard Identification, Assessment and Control

THIRD EDITION

Edited by

SAM MANNAN

Lee's Loss Prevention in the Process Industries

Volume 3

This book is dedicated to

Herbert Douglas Lees (1860–1944), gas engineer;
Frank Priestman Lees (1890–1916), gas engineer;
Herbert Douglas Lees (1897–1955), gas engineer;
David John Lees (1936–), agricultural engineer;
Frank Lyman MacCallum (1893–1955), mining engineer and missionary;
Vivien Clare Lees (1960–), plastic and hand surgeon;
Harry Douglas Lees (1962–), restaurateur
and their families

'They do not preach that their God will rouse them a little before
the nuts work loose.
They do not teach that His Pity allows them to drop their job when
they dam'-well choose.
As in the thronged and the lighted ways, so in the dark and the
desert they stand,
Wary and watchful all their days that their brethren's days may be
long in the land.'

Rudyard Kipling (The Sons of Martha, 1907)

Wo einer kommt and saget an,
Er hat es allen recht getan,
So bitten wir diesen lieben Herrn,
Er wöll uns solche Kunste auch lehrn

(Whoever is able to say to us
'I have done everything right',
We beg that honest gentleman
To show us how it is done)

Inscription over the 'Zwischenbau' adjoining the Rathaus in Brandenburg-on-the-Haven
(quoted by Prince B.H.M. von Bulow in *Memoirs*, 1932)

If the honeye that the bees gather out of so manye floure of herbes . . . that are growing in other

mennis medowes . . . may justly be called the bees' honeye . . . so maye I call it that I have . . .

gathered of manye good autores . . . my booke.

William Turner (quoted by A. Scott-James in *The Language of the Garden: A Personal Anthology*)

By the same author:

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Lee's Loss Prevention in the Process Industries

Hazard Identification, Assessment and Control

Volume 3

Third edition

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Elsevier Butterworth–Heinemann
200 Wheeler Road, Burlington, MA 01803, USA
Linacre House, Jordan Hill, Oxford OX2 8DP, UK

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Library of Congress Cataloging-in-Publication Data
Lee's loss prevention in the process industries. – 3rd ed. / edited by Sam Mannan.
p. cm.
Rev. ed. of: Loss prevention in the process industries / Frank P. Lees. 2nd ed. 1996.
Includes bibliographical references and indexes.
ISBN 0-7506-7555-1 (casebound, set : alk. paper) 1. Petroleum chemicals industry–Great Britain–Safety measures. 2. Petroleum chemicals industry–United States–Safety measures. I. Title: Loss prevention in the process industries. II. Mannan, Sam. III. Lees, Frank P. Loss Prevention in the process industries.
TP690.6.L43 2005
660′.2804–dc22

2004018498

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from British Library

Set ISBN: 0-7506-7555-1
Volume 1 ISBN: 0-7506-7857-7
Volume 2 ISBN: 0-7506-7858-5
Volume 3 ISBN: 0-7506-7589-3

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04 05 06 07 08 09 10 10 9 8 7 6 5 4 3 2 1

Printed in the United States of America

Preface to Third Edition

The first edition of this book appeared in 1980, at the end of a decade of rapid growth and development in loss prevention. In the preface to the second edition, Frank P. Lees wrote, "After another decade and a half the subject is more mature, although development continues apace. In preparing this second edition it has been even more difficult than before to decide what to put in and what to leave out." Frank Lees' statement in 1996 rings even truer today, another eight years later in 2004. Industrial advances and technology changes coupled with recent events have made it essential to focus on new topics while keeping a complete grasp of all of older technologies and learnings as well. Safety programs today must also consider issues such as chemical reactivity hazards, safety instrumented systems, and layer of protection analysis. In the post 9-11 world, process safety and loss prevention must also include consideration of issues related to chemical security and resilient engineering systems.

The history of safety regulations in the United States can be traced back to the year before the beginning of the twentieth century. The River and Harbor Act, the first known federal legislation relevant to safety was promulgated in 1899. Since then, the total number of legislations has steadily increased. In addition to the federal government, local entities such as the state, county, and cities have also promulgated regulations and ordnances, which impose safety requirements on process facilities. Varying degrees of similar legislative action has also occurred in the rest of the world. These legislation were all promulgated in response to some event, demographic changes, as well as changes in the industry. Also, as our understanding of the hazards associated with industrial processes developed, procedures and practices were put in place to limit or eliminate the damage. Government programs and industry initiatives spurred improvements in the science and technology needed for the recognition of hazards and associated risks.

Management systems have been put in place to implement regulations and industry practices. Government regulations will continue to be a significant driver for safety programs. As such, one of the main objectives of these management systems is to ensure compliance. However, it is also quite clear that profitability is directly related to safety and loss prevention. Thus the management systems for safety are intricately tied into the operational management.

The industrial revolution brought prosperity and along with it the use of hazardous processes and complex technologies. Growing economies and global competition has led to more complex processes involving the use of hazardous chemicals, exotic chemistry, and extreme operating conditions. As a result, a fundamental understanding of the hazards and associated risks is essential. Process safety and risk management requires the application of the basic sciences and a systematic approach. Recent advances, such as overpressure protection alternatives and reactive chemistry allow safer design and operation of processes.

In the multiple barriers concept, plants are designed with several layers so that an incident would require the failure of several systems. Another novel approach to process safety and risk management is to consider various actions in a descending hierarchical order. Inherently safer design consideration should be first in the hierarchy followed by prevention systems, mitigation, and response. The success of these systems is dependent on the fundamental understanding of the process and the associated hazards. Chronic as well as catastrophic consequences resulting from toxic and flammable substances can be reduced and/or eliminated through appropriate design and operating practices.

Managing safety is no easy task, but it makes bottomline sense. There is a direct payoff in savings on a company workers' compensation insurance, whose premiums are partly based on the number of claims paid for job injuries. The indirect benefits are far larger, for safe plants tend to be well run in general and more productive. The recipe for safety is remarkably consistent from industry to industry. It starts with sustained support of top management followed by implementation of appropriate programs and practices that institutionalize safety as a culture as compared to add-on procedures. The ingraining of safety as second nature in day-to-day activities requires a paradigm shift and can only be accomplished when safety is viewed as an integral and comprehensive part of any activity as compared to being a stand-alone or add-on activity.

This third edition of ***Loss Prevention in the Process Industries*** represents a combination of appropriate revisions of the essential compilations put together by Frank P. Lees, along with several new chapters and additions on new areas that deserve attention and discussion. The third edition includes five new chapters and three new appendices. The five new chapters address incident investigation, inherently safer design, reactive chemicals, safety instrumented systems, and chemical security. The three new appendices address process safety management regulation in the United States, risk management program regulation in the United States, and incident databases.

The chapter on incident investigation provides a summary of incident investigation procedures that can be used not only to determine causes of incidents but also provides a primer on capturing and integrating lessons learned from incident investigations into design, operations, maintenance, and response programs. Chemical process incidents can be accompanied by significant consequences, both in terms of human life and in financial impact. Many major chemical process incidents are the result of a complex scenario involving simultaneous failures of multiple safeguards. A robust system for incident investigation is usually necessary to determine and understand the causes, as well as implement measures to prevent a repeat event. This chapter is intended to provide an overview of incident investigation by addressing major concepts, principles, and characteristics of effective incident investigations of chemical process events. The focus is on incidents pertaining to chemical processes and their associated hazards, and the associated investigation techniques appropriate for complex systems and scenarios. This chapter is based on

best practices for incident investigation, and those common concepts (i.e., tools, techniques, definitions) included in root cause investigation methodologies currently in the public domain in use in the process industry. It is not the intention to provide a stand-alone investigation methodology/guideline, nor address internal or proprietary investigation methodologies.

The chapter on inherently safer design addresses options and issues that can be considered with regard to the design and operation of plants. Inherently safer design is a philosophy that focuses on elimination of hazards or reduction of the magnitude of hazards rather than the control of hazards. Many of the concepts of inherently safer design have been applied by engineers in a wide variety of technologies for many years, without recognizing the common approach. In the late 1970s, in the wake of many large incidents in the chemical industry, Trevor Kletz recognized the common philosophies of hazard elimination and hazard reduction, gave the philosophy the name "inherently safer design," and developed a specific set of approaches to help engineers in the chemical process industries to design inherently safer processes and plants. Trevor realized that increased expectations for safety, from companies, regulatory bodies, and society in general, combined with the increased potential damage from incidents in the larger plants being built to meet increased demand and global markets, resulted in increased complexity and cost for the safety systems required to satisfy these demands. Furthermore, while hazard control systems can be made highly reliable, they can never be perfect and will always have some failure probability. While this probability can be made very small, there is always some chance that all safety systems will fail simultaneously and the result would be a large incident. Also, the hazard management systems require ongoing maintenance, as well as management and operator training, for the life of the plant. This results in ongoing costs, and the potential for future deterioration of the safety systems. Deteriorated systems will have reduced reliability, increasing the potential for a catastrophic accident. Trevor Kletz suggested that in many cases, a simpler, cheaper, and safer plant could be designed by focusing on the basic technology, eliminating or significantly reducing hazards, and therefore the need to manage them.

The chapter on reactive chemicals provides an overview of this critical issue and provides guidance on management systems as well as experimental and theoretical methods for analyses of chemical reactivity hazards. Serious incidents arising from uncontrolled reactivity have taken place since the inception of the chemical industry. The human toll of such incidents has been staggering. In recent decades, greater recognition and resources have been directed toward preventing and mitigating such occurrences. A number of incidents have been so severe as to prompt regulatory initiatives to force better management of reactivity. It is prudent for any company, organization, or other group to scrutinize the chemicals being handled and implement measures to limit the risk of a major reactive hazards event. A sampling of incidents that have substantially heightened concerns regarding reactive hazards in the general public, in governmental agencies, and in industry includes:

- The 1976 ICMESA incident in Seveso, Italy in which an uncontrolled chemical reaction generated pressure resulting in relief venting of a highly toxic dioxane into the neighboring villages and countryside.
- The 1984 Union Carbide incident in Bhopal, India in which methyl isocyanate was contacted with water, generating highly toxic cyanide gas and leading to thousands of fatalities.
- The 1994 Napp Technology incident in Lodi, New Jersey in which an uncontrolled reaction involving gold ore processing led to the deaths of five firefighters.
- The 1999 Concept Sciences incident in Allentown, Pennsylvania in which an explosion arising from a process concentrating hydroxylamine resulted in five fatalities. Another event involving purified hydroxylamine took place in a Nissin Chemical plant in Gunma Prefecture, Japan in 2000 and led to four fatalities.
- The 2001 TotalFinaElf incident in Toulouse, France in which ammonium nitrate being processed for nitrogen fertilizers exploded leading to 30 fatalities.

These events, as well as numerous others, have influenced the perception and approach to reactive hazards.

The chapter on safety instrumented systems addresses systems and procedures that need to be in place with regard to this area of safety and instrumentation. In many processes, technical or manufacturing issues limit the engineer's capability to design an inherently safer process. Further, there is generally a point where the required capital investment is disproportional to the additional risk reduction provided by the process modification. In other words, the derived safety benefit is too low relative to the economic investment. When this occurs, protection layers or safeguards must be provided to prevent or mitigate the process risk. A Safety Instrumented System (SIS) is a protection layer, which shuts down the plant, or part of it, if a hazardous condition is detected. Throughout the years, SIS have also been known as Emergency Shutdown Systems (ESD, ESS), Safety Shutdown Systems (SSD), Safety Interlock Systems (SIS), Safety Critical Systems (SCS), Safety Protection Systems (SPS), Protective Instrumented Systems (PIS), interlocks, and trip systems. Regardless of what the SIS may be called, the essential characteristic of the SIS is that it is composed of instruments, which detect that process variables are exceeding preset limits, a logic solver, which processes this information and makes decisions, and final control elements, which take necessary action on the process to achieve a safe state.

The chapter on chemical security deals with this new and critical element of the management of a process facility following the events of September 11, 2001. Security management is required for protecting the assets (including employees) of the facility, maintaining the ongoing integrity of the operation, and preserving value of the investment. Process security and process safety have many parallels and make use of many common programs and systems for achieving their ends. Process security requires a management systems approach to develop a comprehensive security program, which shares many common elements to process safety management.

The new appendix on process safety management regulation in the United States provides a summary of this regulatory requirement. The fourteen elements of the OSHA Process Safety Management (PSM) regulation (*29 CFR 1910.119*) were published in the U.S. Federal Register on February 24, 1992. The objective of the regulation is to

prevent or minimize the consequences of catastrophic releases of toxic, reactive, flammable, or explosive chemicals. The regulation requires a comprehensive management program: a holistic approach that integrates technologies, procedures, and management practices. The process safety management regulation applies to processes that involve certain specified chemicals at or above threshold quantities, processes that involve flammable liquids or gases on-site in one location, in quantities of 10,000 pounds or more (subject to few exceptions), and processes that involve the manufacture of explosives and pyrotechnics. Hydrocarbon fuels, which may be excluded if used solely as a fuel, are included if the fuel is part of a process covered by this regulation. In addition, the regulation does not apply to retail facilities, oil or gas well drilling or servicing operations, or normally unoccupied remote facilities.

The new appendix on risk management program regulation in the United States provides a summary of this regulatory requirement administered by the U.S. Environmental Protection Agency. In 1996, EPA promulgated the regulation for ***Risk Management Programs for Chemical Accident Release Prevention*** (40 CFR 68). This federal regulation was mandated by section 112(r) of the Clean Air Act Amendments of 1990. The regulation requires regulated facilities to develop and implement appropriate risk management programs to minimize the frequency and severity of chemical plant accidents. In keeping with regulatory trends, EPA required a performance-based approach towards compliance with the risk management program regulation. The EPA regulation also requires regulated facilities to develop a Risk Management Plan (RMP). The RMP includes a description of the hazard assessment, prevention program, and the emergency response program. Facilities submit the RMP to the EPA and subsequently is made available to governmental agencies, the state emergency response commission, the local emergency planning committees, and communicated to the public.

The new appendix on incident databases addresses compilations of incident databases that can used for improving safety programs, developing trends, performance measures, and metrics. Incident prevention and mitigation of consequences is the focus of a number of industry programs regulatory initiatives. As part of these programs and regulations, accident history data are often collected. There are two basic types of information. One is a database consisting of standardized fields of data usually for a large number of incidents. The second are more detailed reports of individual incidents. Analysis of these incident history databases can provide insight into incident prevention needs. While the analysis and conclusions obtained from the incident database are often limited by the shortcomings of the databases themselves, the fact remains that incident history databases are very useful and can be a powerful tool in focusing risk reduction efforts. The conclusions can be used to identify systematically the greatest risks to allow prioritization of efforts to improve process safety. At the plant level this might entail identifying certain processes, types of equipment, chemicals, operations and other factors most commonly associated with incidents. Databases that cover a very large number of facilities are likely to reveal trends and patterns that no one company or facility could determine from their own experience. Statistical knowledge of the likelihood of the release of certain types of chemicals could help emergency responders, state emergency response commissions, and local emergency planning committees determine the most likely and most serious chemical releases in their areas and plan appropriate chemical accident responses. Incident databases may also help identify technologies and practices to prevent chemical accidents, or the need to develop them. For example, the data could indicate that inspection and preventive maintenance of equipment and instruments should become more thorough or more frequent.

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2004

Preface to Second Edition

The first edition of this book appeared in 1980, at the end of a decade of rapid growth and development in loss prevention. After another decade and a half the subject is more mature, although development continues apace. In preparing this second edition it has been even more difficult than before to decide what to put in and what to leave out.

The importance of loss prevention has been underlined by a number of disasters. Those at San Carlos, Mexico City, Bhopal and Pasadena are perhaps the best known, but there have been several others with death tolls exceeding 100. There have also been major incidents in related areas, such as those on the Piper Alpha oil platform and at the nuclear power stations at Three Mile Island and Chernobyl.

Apart from the human tragedy, it has become clear that a major accident can seriously damage even a large international company and may even threaten its existence, rendering it liable to severe damages and vulnerable to takeover.

Accidents in the process industries have given impetus to the creation of regulatory controls. In the UK the Advisory Committee on Major Hazards made its third and final report in 1983. At the same time the European Community was developing its own controls which appeared as the EC Directive on Major Accident Hazards. The resulting UK legislation is the NIHHS Regulations 1982 and the CIMAH Regulations 1984. Other members of the EC have brought in their own legislation to implement the Directive. There have been corresponding developments in planning controls.

An important tool for decision-making on hazards is hazard assessment. The application of quantitative methods has played a crucial role in the development of loss prevention, but there has been lively debate on the proper application of such assessment, and particularly on the estimation and evaluation of the risk to the public.

Hazard assessment involves the assessment both of the frequency and of the consequences of hazardous events. In frequency estimation progress has been made in the collection of data and creation of data banks and in fault tree synthesis and analysis, including computer aids. In consequence assessment there has been a high level of activity in developing physical models for emission, vaporization and gas dispersion, particularly dense gas dispersion; for pool fires, fireballs, jet flames and engulfing fires; for vapour cloud explosions; and for boiling liquid expanding vapour explosions (BLEVEs). Work has also been done on injury models for thermal radiation, explosion overpressure and toxic concentration, on models of the density and other characteristics of the exposed population, and on shelter and escape.

Some of these topics require experimental work on a large scale and involving international cooperation. Large scale tests have been carried out at several sites on dense gas dispersion and on vapour cloud fires and explosions. Another major cooperative research programme has been that of DIERS on venting of chemical reactors.

The basic approach developed for fixed installations on shore has also been increasingly applied in other fields. For transport in the UK the *Transport Hazards Report* of the Advisory Committee on Dangerous Substances represents an important landmark. Another application is in the offshore oil and gas industry, for which the report on the Piper Alpha disaster, the *Cullen Report*, constitutes a watershed.

As elsewhere in engineering, computers are in widespread use in the design of process plants, where computer aided design (CAD) covers physical properties, flowsheeting, piping and instrument diagrams, unit operations and plant layout. There is increasing use of computers for failure data retrieval and analysis, reliability and availability studies, fault tree synthesis and analysis and consequence modelling, while more elusive safety expertise is being captured by computer-based expert systems.

The subject of this book is the process industries, but the process aspects of related industries, notably nuclear power and oil and gas platforms are briefly touched on. The process industries themselves are continually changing. In the last decade one of the main changes has been increased emphasis on products such as pharmaceuticals and agrochemicals made by batch processes, which have their own particular hazards.

All this knowledge is of little use unless it reaches the right people. The institutions which educate the engineers who will be responsible for the design and operation of plants handling hazardous materials have a duty to make their students aware of the hazards and at least to make a start in gaining competence in handling them.

I would like again to thank for their encouragement the heads of the Department of Chemical Engineering at Loughborough, Professors D.C. Freshwater, B.W. Brooks and M. Streat; our Industrial Professors T.A. Kletz and H.A. Duxbury and Visiting Professor S.M. Richardson; my colleagues, past and present, in the Plant Engineering Group, Mr R.J. Aird, Dr P.K. Andow, Dr M.L. Ang, Dr P.W.H. Chung, Dr D.W. Edwards, Dr P. Rice and Dr A.G. Rushton – I owe a particular debt to the latter; the members of the ACMH, chaired by Professor B.H. Harvey; the sometime directors of Technica Ltd, Dr D.H. Slater, Mr P. Charsley, Dr P.J. Comer, Dr R.A. Cox, Mr T. Gjerstad, Dr M.A.F. Pyman, Mr C.G. Ramsay, Mr M.A. Seaman and Dr R. Whitehouse; the members of the IChemE Loss Prevention Panel; the IChemE's former Loss Prevention Officer, Mr B.M. Hancock; the members of the IChemE Loss Prevention Study Group and of the Register of Safety Professionals; the editorial staff of the IChemE, in particular Mr B. Brammer; numerous members of the Health and Safety Executive, especially Dr A.C. Barrell, Mr J. Barton, Dr D.A. Carter, Mr K. Cassidy, Mr P.J. Crossthwaite, Dr N.W. Hurst, Dr S.F. Jagger, Dr J. McQuaid, Dr K. Moodie, Dr C. Nussey, Dr R.P. Pape, Dr A.F. Roberts and Dr N.F. Scilly; workers at the Safety and Reliability Directorate, particularly Dr A.T.D. Butland, Mr I. Hymes, Dr D.W. Phillips and Dr D.M. Webber; staff at Shell Thornton Research Centre, including Dr D.C. Bull and Dr A.C. Chamberlain; staff at British Gas, including Dr J.D. Andrews, Dr M.J. Harris, Mr H. Hopkins, Dr J.M. Morgan and Dr D.J. Smith; staff at the Ministry of

Defence, Explosives Storage and Transport Committee, including Mr M.A. Gould, Mr J. Henderson and Mr P. Stone; and colleagues who have taught on post-experience courses at Loughborough, in particular Dr C.D. Jones, Dr D.J. Lewis and Mr J. Madden; BP International and Mr R. Malpas for allowing me to spend a period of study leave with the company in 1985–86 and Mr F.D.H. Moysen, Mr G. Hately, Mr M. Hough, Mr R. Fearon and others in the Central Safety Group and in Engineering Department; the Honourable Lord Cullen, my fellow Technical Assessors on the Piper Alpha Inquiry, Mr B. Appleton and Mr G.M. Ford and the Cremer and Warner team at the inquiry, in particular Mr G. Kenney and Mr R. Sylvester-Evans; other professional colleagues Dr L.J. Bellamy, Professor B.A. Buffham, Dr D.A. Crowl, Mr T.J. Gilbert, Mr D.O. Hagon, Dr D.J. Hall, Mr K.M. Hill, Professor T.M. Husband, Mr M. Kneale, Dr V.C. Marshall, Dr M.L. Preston, Dr J. Rasmussen, Dr J.R. Roach, Dr J.R. Taylor, Dr V.M. Trbojevic, Mr H.M. Tweeddale, Dr G.L. Wells and Dr A.J. Wilday; my research colleagues Dr C.P. Murphy, Mrs J.I. Petts, Dr D.J. Sherwin, Mr R.M.J. Withers and Dr H. Zerkani; my research students Mr M. Aldersey, Mr D.C. Arulanantham, Dr A. Bunn, Dr M.A. Cox, Dr P.A. Davies, Dr S.M. Gilbert, Mr P. Heino, Dr A. Hunt, Dr B.E. Kelly, Dr G.P.S. Marrs, Dr J.S. Mullhi, Dr J.C. Parmar, Mr B. Poblete, Dr A. Shafaghi and Dr A.J. Trenchard as well as colleagues' research students Mr E.J. Broomfield, Mr R. Goodwin, Mr M.J. Jefferson, Dr F.D. Larkin, Mr S.A. McCoy, Dr K. Plamping, Mr J. Soutter, Dr P. Thorpe and Mr S.J. Wakeman; the office staff of the Department, Mrs E.M. Barradell, Mr D.M. Blake, Miss H.J. Bryers and Miss Y. Kosar; the staff of the University Library, in particular Miss S.F. Pilkington; and my wife Elizabeth, whose contribution has been many-faceted and in scale with this book.

FRANK P. LEES
Loughborough,
1994

Preface to First Edition

Within the past ten or fifteen years the chemical and petroleum industries have undergone considerable changes. Process conditions such as pressure and temperature have become more severe. The concentration of stored energy has increased. Plants have grown in size and are often single-stream. Storage has been reduced and interlinking with other plants has increased. The response of the process is often faster. The plant contains very large items of equipment. The scale of possible fire, explosion or toxic release has grown and so has the area which might be affected by such events, especially outside the works boundary.

These factors have greatly increased the potential for loss both in human and in economic terms. This is clear both from the increasing concern of the industry and its insurers and from the historical loss statistics.

The industry has always paid much attention to safety and has a relatively good record. But with the growing scale and complexity involved in modern plants the danger of serious large-scale incidents has been a source of increasing concern and the adequacy of existing procedures has been subjected to an increasingly critical examination.

Developments in other related areas have also had an influence. During the period considered there has been growing public concern about the various forms of pollution, including gaseous and liquid effluents and solid wastes and noise.

It is against this background that the loss prevention approach has developed. It is characteristic of this approach that it is primarily concerned with the problems caused by the depth of technology involved in modern processes and that it adopts essentially an engineering approach to them. As far as possible both the hazards and the protection are evaluated quantitatively.

The clear recognition by senior management of the importance of the loss prevention problem has been crucial to these developments. Progress has been made because management has been prepared to assign to this work many senior and capable personnel and to allocate the other resources necessary.

The management system is fundamental to loss prevention. This involves a clear management structure with well defined line and advisory responsibilities staffed by competent people. It requires the use of appropriate procedures, codes of practice and standards in the design and operation of plant. It provides for the identification, evaluation and reduction of hazards through all stages of a project from research to operation. It includes planning for emergencies.

The development of loss prevention can be clearly traced through the literature. In 1960 the Institution of Chemical Engineers held the first of a periodic series of symposia on *Chemical Process Hazards with Special Reference to Plant Design*. The Dow Chemical Company published its *Process Safety Manual* in 1964. The American Institute of Chemical Engineers started in 1967 an annual series of symposia on Loss Prevention. The European Federation of Chemical Engineers' symposium on *Major Loss Prevention in the Process Industries* at Newcastle in 1971 and the Federation's symposium on *Loss Prevention and Safety Promotion in the Process Industries* (Buschmann, 1974) at Delft are further milestones.

Another indicator is the creation in 1973 by the Institution of Chemical Engineers Engineering Practice Committee of a Loss Prevention Panel under the chairmanship of Mr T.A. Kantyka.

In the United Kingdom the Health and Safety at Work etc. Act 1974 has given further impetus to loss prevention. The philosophy of the *Robens Report* (1972), which is embodied in the Act, is that of self-regulation by industry. It is the responsibility of industry to take all reasonable measures to assure safety. This philosophy is particularly appropriate to complex technological systems and the Act provides a flexible framework for the development of the loss prevention approach.

The disaster at Flixborough in 1974 has proved a turning point. This event has led to a much more widespread and intense concern with the loss prevention problem. It has also caused the government to set up in 1975 an Advisory Committee on Major Hazards. This committee has made far-reaching recommendations for the identification and control of major hazard installations.

It will be apparent that loss prevention differs somewhat from safety as traditionally conceived in the process industries. The essential difference is the much greater engineering content in loss prevention.

This is illustrated by the relative effectiveness of inspection in different processes. In fairly simple plants much can be done to improve safety by visual inspection. This approach is not adequate, however, for the more technological aspects of complex processes.

For the reasons given above loss prevention is currently a somewhat fashionable subject. It is as well to emphasize, therefore, that much of it is not new, but has been developed over many years by engineers whose patient work in an often apparently unrewarding but vital field is the mark of true professionalism.

It is appropriate to emphasize, moreover, that accidents arising from relatively mundane situations and activities are still responsible for many more deaths and injuries than those due to advanced technology.

Nevertheless, loss prevention has developed in response to the growth of a new problem, the hazard of high technology processes, and it does have a distinctive approach and some novel techniques. Particularly characteristic are the emphasis on matching the management system to the depth of technology in the installation, the techniques developed for identifying hazards, the principle and methods of quantifying hazards, the application of reliability assessment, the practice of planning for emergencies and the critique of traditional practices or existing codes, standards or regulations where these are outdated by technological change.

There is an enormous, indeed intimidating, literature on safety and loss prevention. In addition to the symposia already referred to, mention may be made of the *Handbook of Safety and Accident Prevention in Chemical Operations* by Fawcett and Wood (1965); the *Handbook of Industrial Loss*

Prevention by the Factory Mutual Engineering Corporation (1967); and the Industrial Safety Handbook by Handley (1969, 1977). These publications, which are by multiple authors, are invaluable source material.

There is a need, however, in the author's view for a balanced and integrated textbook on loss prevention in the process industries which presents the basic elements of the subject, which covers the recent period of intense development and which gives a reasonably comprehensive bibliography. The present book is an attempt to meet this need.

The book is based on lectures given to undergraduate and postgraduate students at Loughborough over a period of years and the author gladly acknowledges their contribution.

Loss prevention is a wide and rapidly developing field and is therefore not an easy subject for a book. Nevertheless, it is precisely for these reasons that the engineer needs the assistance of a textbook and that the attempt has been considered justified.

The structure of the book is as follows. Chapter 1 deals with the background to the historical development of loss prevention, the problem of large, single-stream plants, and the differences between loss prevention and conventional safety, and between loss prevention and total loss control; Chapter 2 with hazard, accident and loss, including historical statistics; Chapter 3 with the legislation and legal background; Chapter 4 with the control of major hazards; Chapter 5 with economic and insurance aspects; Chapter 6 with management systems, including management structure, competent persons, systems and procedures, standards and codes of practice, documentation and auditing arrangements; Chapter 7 with reliability engineering, including its application in the process industries; Chapter 8 with the spectrum of techniques for identifying hazards from research through to operation; Chapter 9 with the assessment of hazards, including the question of acceptable risk; Chapter 10 with the siting and layout of plant; Chapter 11 with process design, including application of principles such as limitation of inventory, consideration of known hazards associated with chemical reactors, unit processes, unit operations and equipments, operating conditions, utilities, particular chemicals and particular processes and plants, and checking of operational deviations; Chapter 12 with pressure system design, including properties of materials, design of pressure vessels and pipework, pressure vessel standards and codes, equipment such as heat exchangers, fired heaters and rotating machinery, pressure relief and blowdown arrangements, and failure in pressure systems; Chapter 13 with design of instrumentation and control systems, including regular instrumentation, process computers and protective systems; Chapter 14 with human factors in process control, process operators, computer aids and human error; Chapter 15 with loss of containment and dispersion of material; Chapter 16 with fire, flammability characteristics, ignition sources, flames and particular types of process fire, effects of fire and fire prevention, protection and control; Chapter 17 with explosion, explosives, explosion energy, particular types of process explosion such as confined explosions, unconfined vapour cloud explosions and dust explosions, effects of explosion and explosion prevention, protection and relief; Chapter 18 with toxicity of chemicals, toxic release and effects of toxic release; Chapter 19 with commissioning and inspection of plant; Chapter 20 with plant operation; Chapter 21 with plant maintenance and modification; Chapter 22 with storage; Chapter 23 with transport, particularly by road, rail and pipeline; Chapter 24 with emergency planning both for works and transport emergencies; Chapter 25 with various aspects of personal safety such as occupational health and industrial hygiene, dust and radiation hazards, machinery and electrical hazards, protective clothing and equipment, and rescue and first aid; Chapter 26 with accident research; Chapter 27 with feedback of information and learning from accidents; Chapter 28 with safety systems, including the roles of safety managers and safety committees and representatives. There are appendices on Flixborough, Seveso, case histories, standards and codes, institutional publications, information sources, laboratories and pilot plants, pollution and noise, failure and event data, Canvey, model licence conditions for certain hazardous plants, and units and unit coversions.

Many of the matters dealt with, such as pressure vessels or process control, are major subject areas in their own right. It is stressed, therefore, that the treatment given is strictly limited to loss prevention aspects. The emphasis is on deviations and faults which may give rise to loss.

In engineering in general and in loss prevention in particular there is a conflict between the demand for a statement of basic principles and that for detailed instructions. In general, the first of these approaches has been adopted, but the latter is extremely important in safety, and a considerable amount of detailed material is given and references are provided to further material.

The book is intended as a contribution to the academic education of professional chemical and other engineers. Both educational and professional institutions have long recognized the importance of education in safety. But until recently the rather qualitative, and indeed often exhortatory, nature of the subject frequently seemed to present difficulties in teaching at degree level. The recent quantitative development of the subject goes far towards removing these objections and to integrating it more closely with other topics such as engineering design.

In other words, loss prevention is capable of development as a subject presenting intellectual challenge. This is all to the good, but a note of caution is appropriate. It remains true that safety and loss prevention depend primarily on the hard and usually unglamorous work of engineers with a strong sense of responsibility, and it is important that this central fact should not be obscured.

For this reason the book does not attempt to select particular topics merely because a quantitative treatment is possible or to give such a treatment as an academic exercise. The subject is too important for such an approach. Rather the aim has been to give a balanced treatment of the different aspects and a lead in to further reading.

It is also hoped that the book will be useful to practising engineers in providing an orientation and entry to unfamiliar areas. It is emphasized, however, that in this subject above all others, the specialized texts should be consulted for detailed design work.

Certain topics which are often associated with loss prevention, for example included in loss prevention symposia, have not been treated in detail. These include, for example, pollution and noise. The book does not attempt to deal in detail with total loss control, but a brief account of this is given.

The treatment of loss prevention given is based mainly on the chemical, petrochemical and petroleum industries,

but much of it is relevant to other process industries, such as electrical power generation (conventional and nuclear), iron and steel, gas, cement, glass, paper and food.

The book is written from the viewpoint of the United Kingdom and, where differences exist within the UK, of England. This point is relevant mainly to legislation.

Reference is made to a large number of procedures and techniques. These do not all have the same status. Some are well established and perhaps incorporated in standards or codes of practice. Others are more tentative. As far as possible the attempt has been made to give some indication of the extent to which particular items are generally accepted.

There are probably also some instances where there is a degree of contradiction between two approaches given. In particular, this may occur where one is based on engineering principles and the other on relatively arbitrary rules-of-thumb.

The book does not attempt to follow standards and codes of practice in drawing a distinction between the words *should, shall* and *must* in recommending particular practices and generally uses only the former. The distinction is important, however, in standards and codes of practice and it is described in Appendix 4[a].

An explanation of some of the terms used is in order at this point. Unfortunately there is at present no accepted terminology in this field. In general, the problems considered are those of loss, either of life or property. The term *hazard* is used to describe the object or situation which constitutes the threat of such loss. The consequences which might occur if the threat is realized are the *hazard potential*. Associated with the hazard there is a risk, which is the probability of the loss occurring. Such a risk is expressed as a *probability* or as a *frequency*. Probability is expressed as a number in the range 0 to 1 and is dimensionless; frequency is expressed in terms of events per unit time, or sometimes in other units such as events per cycle or per occasion. Rate is also used as an alternative to frequency and has the same units.

The analysis of hazards involves qualitative *hazard identification* and quantitative hazard assessment. The latter term is used to describe both the assessment of hazard potential and of risk. The assessment of risk only is described as *risk assessment*.

In accident statistics the term *Fatal Accident Frequency Rate* (FAFR) has some currency. The last two terms are tautologous and the quantity is here referred to as *Fatal Accident Rate* (FAR).

Further treatments of terminology in this field are given by BS 4200: 1967, by Green and Bourne (1962), by the Council for Science and Society (1977) and by Harvey (1979b).

Notation is defined for the particular chapter at the point where the symbols first occur. In general, a consistent notation is used, but well established equations from standards, codes and elsewhere are usually given in the original notation. A consolidated list of the notation is given at the end of chapters in which a large number of symbols is used.

The units used are in principle SI, but the exceptions are fairly numerous. These exceptions are dimensional equations, equations in standards and codes, and other equations and data given by other workers where conversion has seemed undesirable for some reason. In cases of conversion from a round number it is often not clear what degree of rounding off is appropriate. In cases of description of particular situations it appears pedantic to make the conversion where a writer has referred, for example, to a 1 inch pipe.

Notes on some of the units used are given in Appendix 12[a]. For convenience a unit conversion table is included in this appendix. Numerical values given by other authors are generally quoted without change and numerical values arising from conversion of the units of data given by other authors are sometimes quoted with an additional significant figure in order to avoid excessive rounding of values.

Some cost data are quoted in the book. These are given in pounds or US dollars for the year quoted.

A particular feature of the book is a fairly extensive bibliography of some 5000 references. These references are consolidated at the end of the book rather than at the end of chapters, because many items are referred to in a number of chapters. Lists of selected references on particular topics are given in table form in the relevant chapters.

Certain institutions, however, have a rather large number of publications which it is more convenient to treat in a different manner. These are tabulated in Appendices 4[a] and 5[a], which contain some 2000 references. There is a cross-reference to the institution in the main reference list.

In many cases institutions and other organizations are referred to by their initials. In all cases the first reference in the book gives the full title of the organization. The initials may also be looked up in the Author Index, which gives the full title.

A reference is normally given by quoting the author and, in brackets, the date, e.g. Kletz (1971). Publications by the same author in the same year are denoted by letters of the alphabet a, b, c, etc., e.g. Allen (1977a), while publications by authors of the same surname and in the same year are indicated for convenience by an asterisk against the year in the list of references. In addition, the author's initials are given in the main text in cases where there may still be ambiguity. Where a date has not been determined this is indicated as n.d.

In the case of institutional publications listed in Appendices 4[a] and 5[a] the reference is given by quoting the institution and, in brackets, the date, the publication series, e.g. HSE (1965 HSW Bklt 34) or the item number, e.g. IChemE (1971 Item 7). For institutional publications with a named author the reference is generally given by quoting the author and, in brackets, the initials of the institution, the date and the publication series or item number, e.g. Eames (UKAEA 1965 Item 4).

The field of loss prevention is currently subject to very rapid change. In particular, there is a continuous evolution of standards and codes of practice and legislation. It is important, therefore, that the reader should make any necessary checks on changes which may have occurred.

I would like to thank for their encouragement in this project Professor D.C. Freshwater and the publishers, and to acknowledge the work of many authors which I have used directly or indirectly, particularly that of Dr J.H. Burgoyne and of Professor T.A. Kletz. I have learned much from my colleagues on the Loss Prevention Panel of the Institution of Chemical Engineers, in particular Mr T.A. Kantyka and Mr F. Hearfield, and on the Advisory Committee on Major Hazards, especially the chairman Professor B.H. Harvey, the secretary Mr H.E. Lewis, my fellow group chairmen

[a]Appendices 4, 5 and 12 in the first edition correspond to Appendices 27, 28 and 30, respectively, in this second edition.

Professor F.R. Farmer and Professor J.L.M. Morrison and the members of Group 2, Mr K. Briscoe, Dr J.H. Burgoyne, Mr E.J. Challis, Mr S. Hope, Mr M.A. McTaggart, Professor J.F. Richardson, Mr J.R.H. Schenkel, Mr R. Sheath and Mr M.J. Turner, and also from my university colleagues Dr P.K. Andow, Mr R.J. Aird and Dr D.J. Sherwin and students Dr S.N. Anyakora, Dr B. Bellingham, Mr C.A. Marpegan and Dr G.A. Martin-Solis. I am much indebted to Professor T.A. Kletz for his criticisms and suggestions on the text. My thanks are due also to the Institution of Plant Engineers, which has supported plant engineering activities at Loughborough, to the Leverhulme Trust which awarded a Research Fellowship to study *Loss Prevention in the Process Industries* and to the Science Research Council, which has supported some of my own work in this area. I have received invaluable help with the references from Mrs C.M. Lincoln, Mrs W. Davison, Mrs P. Graham, Mr R. Rhodes and Mrs M.A. Rowlatt, with the typing from Mrs E.M. Barradell, Mrs P. Jackson and, in particular, Mrs J. Astley, and with the production from Mr R.L. Pearson and Mr T. Mould. As always in these matters the responsibility for the final text is mine alone.

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1979

Acknowledgements

Many have helped with the long and tedious production process for this 3rd edition of ***Frank P. Lees Loss Prevention in the Process Industries***. However, I would be seriously remiss if I did not start with Frank P. Lees himself. I have always had great respect and admiration for Frank Lees, the engineer and the educator. After Frank passed away, and late in 2002, our mutual friend, Roy Sanders contacted me with a request from Frank's publisher to take up the job of editing the next version. I had no idea of the enormity of the task and Frank's accomplishment. I must say that this experience has truly humbled me and has given me a new respect and new appreciation for Frank Lees' knowledge, grasp, and mastery of the subject of safety and loss prevention. I am honored and privileged to be the editor of the 3rd edition of ***Frank P. Lees Loss Prevention in the Process Industries***. I have tried to maintain Frank's high standards and appreciate the help that many others have given me, but ultimately any *faux pas* or mistakes in the 3rd edition are all mine.

I want to thank all the people who have helped revise and update the chapters that were carried over from the 2nd edition. In this respect, I would like to mention A.A. Aldeeb, J.A. Alderman, P.C. Berwanger, C.A. Brown, S. Chervin, J. Cowling, W.F. Early, M. Gentile, J.P. Gupta, J.A. Havens, D.C. Hendershot, N. Keren, K. Krishna, S.H. Landis, M.E. Levin, P.N. Lodal, M.E. Livingston, S. Mohindra, D.A. Moore, T.M. O'Connor, S.W. Ostrowski, M. Paradise, J.A. Philley, W.J. Rogers, R.E. Sanders, S.R. Saraf, M.E Sawyer, R.L. Smith, T.O. Spicer, A.E. Summers, Y. Wang, H.H. West, J.L. Woodward, and J. Zanoni. Special thanks go to individuals who helped with the new chapters and appendices: J.A. Philley for the incident investigation chapter; J.P. Gupta and D.C. Hendershot for the inherently safer design chapter; S. Chervin, M.E. Levin, and W.J. Rogers for the reactive chemicals chapter; A.E. Summers for the safety instrumented systems chapter, D.A. Moore for the chemical security chapter and T.M. O'Connor for the new appendix on incident databases.

I also want to thank those who helped with research, literature review, galley proofing, and many other jobs without which such a project is never complete. I would like to specifically mention S. Anand, L.O. Cisneros-Trevino, W. Kowhakul, Y.-S. Liu, Y. Qiao, V. Raghunathan, S. Rajaraman, J. Suardin, M. Vidal, C. Wei, C. Zhang, and Y. Zhou. I would like to make specific mention of K.L. Potucek and L.J. Littlefield who undertook the painful task of converting the pdf files of the 2nd edition to Word format. I would like to thank M.A. Cass and D.K. Startz for administrative support and keeping things going through the long haul.

I would also like to take this opportunity to thank two individuals who have provided more than moral support and encouragement. They are Trevor Kletz and Mike O'Connor. First, I have appreciated Trevor's support for our work at the Mary Kay O'Connor Process Safety Center. I also want to thank him for his pioneering leadership in many areas of process safety. Trevor is really a giant in this field, and as Roy Sanders likes to say, "Trevor does cast a long shadow in the field of process safety." I am proud to have Trevor's friendship and his support. I also want to take this opportunity to thank Mike O'Connor. He has converted his personal tragedy into an opportunity to integrate process safety into education, research, and service activities at universities. He has been a true friend and supporter of the mission and goals of the Center.

I also want to thank Mrs. Elizabeth Lees for being kind, gracious, and helpful throughout this process. I am especially grateful for her hospitality and help during my visit to Loughborough to look through Frank's notes and books.

I am grateful to my mother for her love and everything she has done for me and continues to do. I am indebted to my father for having taught me the desire for learning. He was a humble man who truly believed that, "If you stop learning, you must already be dead." I would also like to thank my wife, Afroza, and our daughters, Joya and Rumki, for their love and support. Quite often a project of this magnitude causes the personal and family life to suffer and my wife and daughters have borne the brunt of it. I appreciate their understanding.

I am sure I have failed to mention everybody who has helped me with the many facets of this project. To them I apologize and want to assure them the oversight is not intended. To everyone who has helped put this 3rd edition together, I extend my heartfelt thanks and warmest gratitude again. I must say that you have helped in a noble cause, spread the word and disseminate information that will, we hope and pray, lead to a safer industry and society.

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Terminology

Attention is drawn to the availability in the literature of a number of glossaries and other aids to terminology. Some British Standard glossaries are given in Appendix 27 and other glossaries are listed in Table 1.1.

Notation

In each chapter a given symbol is defined at the point where it is first introduced. The definition may be repeated if there has been a significant gap since it was last used. The definitions are summarized in the notation given at the end of the chapter. The notation is global to the chapter unless redefined for a section. Similarly, it is global to a section unless redefined for a subsection and global to a subsection unless redefined for a set of equations or a single equation. Where appropriate, the units are given, otherwise a consistent system of units should be used, SI being the preferred system. Generally the units of constants are not given; where this is the case it should not be assumed that a constant is dimensionless.

Use of References

The main list of references is given in the section entitled References, towards the end of the book. There are three other locations where references are to be found. These are Appendix 27 on standards and codes; Appendix 28 on institutional publications; and in the section entitled Loss Prevention Bulletin which follows the References.

The basic method of referencing an author is by surname and date, e.g. Beranek (1960). Where there would otherwise be ambiguity, or where there are numerous references to the same surname, e.g. Jones, the first author's initials are included, e.g. A. Jones (1984). Further guidance on names is given at the head of the section References.

References in Appendices 27 and 28 are by institution or author. Some items in these appendices have a code number assigned by the institution itself, e.g. API (1990 Publ. 421), but where such a code number is lacking, use is generally made of an item number separated from the date by a slash, e.g. IChemE (1971/13). Thus typical entries are

API Std 2000: 1992	a standard, found in Appendix 27 under American Petroleum Institute
API (1990 Publ. 421)	an institutional publication, found in Appendix 28 under American Petroleum Institute
HSE (1990 HS(G) 51)	an institutional publication, found in Appendix 28 under Health and Safety Executive, Guidance Booklets, HS(G) series
Coward and Jones (1952 BM Bull. 503)	an institutional publication, found in Appendix 28 under Bureau of Mines, Bulletins

Institutional acronyms are given in the section Acronyms which precedes the Author Index.

There are several points of detail which require mention concerning Appendix 28. (1) The first part of the appendix contains publications of a number of institutions and the second part those of the Nuclear Regulatory Commission. (2) The Fire Protection Association publications include a number of series which are collected in the *Compendium of Fire Safety Data* (CFSD). A typical reference to this is FPA (1989 CFSD FS 6011). (3) The entries for the Health and Safety Executive are quite extensive and care may be needed in locating the relevant series. (4) The publications of the Safety and Reliability Directorate appear under the UK Atomic Energy Authority, Safety and Reliability Directorate. A typical reference is Ramskill and Hunt (1987 SRD R354). These publications are immediately preceded by the publications of other bodies related to the UKAEA, such as the Health and Safety Branch, the Systems Reliability Service and the National Centre for Systems Reliability.

References to authors in the IChemE *Loss Prevention Bulletin* are in the style Eddershaw (1989 LPB 88), which refers to issue 88 of the bulletin.

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Appendix 1 Case Histories

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An essential feature of the learning process in safety and loss prevention is the study of case histories.

A1.1 Incident Sources

The powerful impact of the internet has changed the way we obtain our information on process safety as well as everything else. In recent years, various governmental agencies and private organizations have improved our access to details of recent and past case histories. A number of websites provide a narrative of the event, the technical reasons for the accident as well as the management system shortcomings and valuable lessons learned. Written report sometimes supported by graphics and photos are often published by various agencies and provided on governmental websites. There are also university and corporate organizations that collect incidents and publish on their websites.

Since about 1996, the US Environmental Protection Agency under the Chemical Emergency Preparedness and Prevention has investigated and reported on many high profile US chemical plant and refinery case histories. As a result of these investigations, some Alerts focusing on certain type of incidents have been developed. EPA reports are available at the following internet website:
http://yosemite.epa.gov/oswer/ceppoweb.nsf.

The US Chemical Safety and Hazard Investigation Board (CSB) matured in the late 1990s and their mission is to promote the prevention of chemical accidents. The focus of the CSB is on-site and off-site chemical safety, determining causes and preventing chemical-related incidents, fatalities, injuries, property damage and enhancing environmental protection. The CSB started investigations on selected important chemical plant and refinery incidents in about 1998, and also provide reports on the internet at the following web address:
http://www.chemsafety.gov/reports/.

The Center of Chemical Process Safety, CCPS, of the American Institute of Chemical Engineers started providing brief one-page summaries of types of hazards in late 2001. These high-impact messages were designed with the chemical process operator and others involved with the manufacturing processes to focus quickly on an important topic. The publication is entitled the *Beacon* and can be found at:
www.aiche.org/ccps/safetybeacon.htm.

The Mary Kay O'Connor Process Safety Center at Texas A&M University in College Station is an international leader in process safety and is increasing in stature each year. They have a rich source of process safety information as well as documented case histories. The Center's web address:
http://process-safety.tamu.edu.

The British Institution of Chemical Engineers (IChemE) offers links to a comprehensive list of well over a 150 other websites of incident reports. The IChemE site mainly describes incidents of interest to chemical or process engineers, and includes a time span of incidents from historical to today's events. The collection includes both information and viewpoint. The address of this site is:
http://slp.icheme.org/incidents.html.

The Delft University of Technology of The Netherlands offers a vivid array of about two dozen outstanding fire and explosion photos, an accident database and more. The university's main research effort is focused on measuring and modelling dust and gas explosions. The incident photos can be found at:
http://www.dct.tudelft.nl/part/explosion/gallery.html.

Two other excellent internet sources of process safety information including case histories are:

- www.acusafe.com
- www.hazardview.com

The AcuSafe website provides a comprehensive electronic newsletter entitled AcuSafe News. Their newsletter is devoted to serving industry, government and interested members of the public by providing process safety practices, incident news, lessons, learned and regulatory developments. Hazard View is a source of advice, comment and information for safety, environment and risk professionals with major accident hazards in the process industries. Their View Library has a number of vivid images of the damages from accidents.

A booklet entitled *Large Property Damage Losses in the Hydrocarbon-Chemical Industry – A Thirty Year Review*, continues to be an excellent source of information in print form. This publication presents summaries of large property losses of incidents from around the globe. The valuable information is from a property insurance viewpoint and is presented in an easy-to-understand form. Most of the damages are the result of fires and explosions occurring in refineries, petrochemical plants, gas-processing plants, terminals, offshore and a miscellaneous category. It is updated every few years and the latest one, the twentieth edition, was released in January 2003.

Collections of case histories have been published in *Case Histories of Accidents in the Chemical Industry* by the Manufacturing Chemists Association (MCA) (1962–/1–4) and by Kier and Muller (1983). Specialized collections have been published on particular topics such as major hazards (Harvey, 1979, 1984; Carson and Mumford, 1979; Lees, 1980b; V.C. Marshall, 1987), fire and explosion (Vervalin, 1964a, 1973a; W.H. Doyle, 1969), vapour cloud explosions (Gugan, 1979; Slater, 1978a; D.J. Lewis, 1980d; Davenport, 1987; Lenoir and Davenport, 1993), LPG (L.N. Davis, 1979), instrumentation (W.H. Doyle 1972a,b; Lees, 1976b), transport (Haastrup and Brockhoff, 1990) and pipelines (Riley, 1979). The series *Safety Digest of Lessons Learned* by the API gives case histories with accompanying analyses. Another such series is that published by the American Oil Company (Amoco) of which *Hazards of Water* and *Hazards of Air* are the best known. The Convey Reports and the Rijmond Report give information on certain incidents. The reports of the HSE provide case histories of investigations by a regulator as do those of the NTSB, which deal with rail, road, pipeline and marine accidents. Incidents involving large economic loss are described in the periodic review *100 Large Losses* by Marsh and McLennan.

Case histories are also given in the *Annual Report of HM Chief Inspector of Factories*, the *Chemical Safety Summary of the Chemical Industry Safety and Health Council* (CISHC) and in journals such as *Petroleum Review* and *NFPA Quarterly*. In addition, the *Loss Prevention Bulletin* issued by the IChemE gives case histories. There are also numerous case histories described in much greater detail in various papers and reports. The disasters at Flixborough (R.J. Parker, 1975), at Bantry Bay (Costello, 1979) and on Piper Alpha (Cullen, 1990) are among the most thoroughly documented.

The analysis of case histories to draw the relevant lessons is exemplified pre-eminently in the work of Trevor Kletz's many books and numerous technical articles:

- *Critical Aspects of Safety and Loss Prevention* (1990b),
- *Lessons from Disaster – How Organisations have No Memory and Accidents Recur* (1993##),
- *What Went Wrong? – Case Histories of Process Plant Disasters*, 4th edn (1998##)
- *An Engineer's View of Human Error*, 3rd edn (2001##A) and
- *Learning from Accidents*, 3rd edn (2001##B) and numerous technical articles.

Additional lessons can be examined in Roy Sanders' *Chemical Process Safety: Learning from Case Histories* (1999##).

Selected references on case histories are given in Table A1.1. Some major incidents are listed in Table A1.2. A proportion of these are described in Section A1.10.

Table A1.1 *Selected references on case histories*

Eddy, Potter and Page (1976); J.R. Nash (1976); Carson and Mumford (1979); Nancekieville (1980); D.J. Lewis (1984a, 1993); Kletz (1981a, 1984m, 1985o,p, 1988d,h,i,n, 1993b); Buhrow (1985,1986); Kharbanda and Stallworthy (1988); Garrison (1988a,b); Koehorst (1989); Haastrup and Brockhoff (1990,1991); Marsh and McLennan (1991 LPB 99); Marsh and McLennan (1991 LPB 99); O'Donovan (1991 LPB 99); Palmer and Marshall (1991 LPB 99); Anon. (1992 LPB 99, p. 1); Chowdhury and Parkinson (1992); Lenoir and Davenport (1992); Taylor (1993 LPB 112); I.E. Thomas (1995)

Databases
Service Informatics and Analysis (1982); Amesz *et al.* (1983); K.R. Davies (1983); Makstenek *et al.* (1992); Winder *et al.* (1992); Bruce (1994); Koivisto and Nielsen (1994); Steffy (1994);
Accident reporting: Badoux (1983)
MHIDAS: SRD (1990)
FACTS: Koehorst and Bockholtz (1991)
MARS: Amendola, Contini and Nichele (1988); Drogaris (1991, 1993)
FIRE (warehouses): Koivisto and Nielsen (1994)

Major hazard control
Anon (1979c); Anon. (1985n); Anon. (1986o); Anon. (1990 LPB 95, p. 4)

Hazard identification
Sellers (1988); Sellers and Picciollo (1988); Cullen (1990)

Process design
Anon. (1992 LPB 107, p. 27)

Chemical reactors
Anon. (1962a); Zielinski (1967, 1973); Fowler and Spiegelman (1968); Bast (1970); Grewer (1970); Valpiana (1970a,b); Zehr (1970); Vincent (1971); Fire J. Staff (1973a,d); Bloore (1974); Gugan (1974b); HM Chief Inspector of Factories (1974); Anon. (1975 LPB 1, p. 10); Anon. (1975 LPB 3, p. 1); Anon (1975 LPB 5, p. 16); Anon. (1977 LPB 13, p. 13); Tong, Seagrave and Widerhorn (1977); Anon. (1979 LPB 28, 29, 30); Skinner (1981); Bond (1985 LPB 65); Anon. (1986 LPB 68, p. 33); Berkey and Workman (1987); Anon. (1989 LPB 90, p. 29); Levy and Penrod (1989); Anon. (1991 LPB 98, p. 7); Kotoyori (1991); Anon. (1993 LPB 113, p. 25); Anon. (1994 LPB 115, p. 1); Anon. (1994 LPB 117, p. 18); Anon. (1994 LPB 118, p. 8); Dixon-Jackson (1994)

Petrochemical plants
Britton (1994)

Utilities
Dowell (1994a)

Ammonia, urea and ammonium nitrate plants
R.W. James and Lawrence (1973); Anon. (1975h); Din (1975); Esrig, Ahmad and Mayo (1975); Henderson (1975); Lonsdale (1975); Osman (1975); K. Wright (1975); Visvanathan (1976); Kusha (1977); P.C. Campbell (1981); Janssen, Siraa and Blanken (1981); Roney and Persson (1984); Anon. (1987 LPB 78, p. 11)

DSTG
FPC, Bureau of Natural Gas (1973); L.N. Davis (1979)

Pressure systems and components
Bohlken (1961); Saibel (1961a,b); Attebery (1970); R.W. Miller and Caserta (1971); Banks (1973); Gupton and Kreisher (1973); R.W. James and Lawrence (1973); van der Horst and Sloan (1974); Appl (1975); Blanken (1975); Fuchs and Rubinstein (1975); Lonsdale (1975); Steele (1975); Kletz (1976b, 1987a); National Vulcan (1977); Kinsley (1978); Makhan and Honse (1978); Perkins (1980 LPB 33); Anon. (1981 LPB 37, p. 23); Connaughton (1981); Blanken and Groefsma (1983); Anon. (1984 LPB 56, p. 26); R.W. Clark and Connaughton (1984); NBS (1986); Anon. (1988 LPB 83, p. 1, 3, p. 11,15,17 and 19); Anon. (1989 LPB 86, p. 22 and 27); Anon. (1989 LPB 94, p. 16); Droste and Mallon (1989); Anon. (1990 LPB 93, p. 23); Rademayer (1990); Anon. (1991 LPB 97, p. 9); Smith (1991 LPB 102); Anon. (1992 LPB 104, p. 27); Anon. (1992 LPB 107, p. 27); Crawley (1992 LPB 104); Anon. (1993 LPB 111, p. 25); Anon. (1993 LPB 113, p. 13); Anon. (1994 LPB 117, p. 24); Clayton and Griffin (1994)

Process machinery
OIA (n.d./7); Gibbs (1960); Rendos (1967); Shield (1967, 1972); Naughton (1968); North and Parr (1968); Telesmanic (1968); Zech (1968); Zimmerman (1968); D.S. Wilson *et al.* (1970); von Nimitz, Wachel and Szenasi (1974); Anon. (1975f); Roney (1975); Novacek (1983); Anon. (1985 LPB 62, p. 27); Anon. (1990 LPB 91, p. 16); Anon. (1990 LPB 92, p. 15); Anon. (1994 LPB 116, p. 21)

Instruments
MCA (1962–/1–4); W.H. Doyle (1969, 1972a,b); Fritz (1969); H.D. Taylor and Redpath (1971, 1972); Kletz (1974b,d); McLain (1975b); K. Wright (1975); Lees (1976b); Griffin and Garry (1984); Anon. (1986 LPB 68, p. 35); Anon. (1992 LPB 104, p. 11); Anon. (1994 LPB 116, p. 22)

Computer control systems
Nimmo, Nunns and Eddershaw (1987, 1993 LPB 111)

Human error
Speaker, Thompson and Luckas (1982); Anon. (1983i); Anon. (1989b); Anon. (1990 LPB 92, p. 13)

Emissions, leaks, releases
Schneidman and Strobel (1974); Anon. (1980 LPB 36, p. 25); Anon. (1982 LPB 43, p. 21); Edwards (1982 LPB 47);

Christiansen and Jorgensen (1983); Anon. (1986 LPB 70, p. 1); Anon. (1989 LPB 85, p. 27); Anon. (1989 LPB 90, p. 13); Anon. (1990 LPB 91, p. 16); Anon. (1992 LPB 104, p. 27); Anon. (1994 LPB 117, p. 24)

Fire
OIA (Publ. 651, 1972 Publ. 302, 1973); Woodworth (1958); Lamond (1962); MCA (1962–/1–4); Pinney (1962); Rendos (1964); Vervalin (1964a,c, 1973a,b); Anon. (1966d); Ashill (1966); Cowles (1966); McCarey (1966); Darling (1967); Ostroot (1967, 1973); Zielinski (1967, 1973); Anon. (1968b); Leroy and Johnson (1969); Orey (1972a); Searson (1972, 1990 LPB 94); Fire J. Staff (1973b,e); Fowle (1973); Garrad (1973); NFPA (1973/10); St. Clair (1973); Beausoleil, Phillips and Snell (1974); Sharry and Walls (1974); Anon. (1975 LPB 0, p. 13); McLain (1975b); Anon. (1976h,k); Kletz (1976g, 1979a, 1984 LPB 58, 1993 LPB 114); Saia (1976); Anon. (1978d); HSE (1978c); Isman (1978); Lathrop (1979); Anon. (1980u); Anon. (1981p); Crain (1981); Oosterling and Orbons (1981); Anon. (1982 LPB 43, p. 2); Anon. (1983m); Anon. (1983 LPB 51, p. 13); FM (1983); Anon. (1984 LPB 57, p. 19); Mullier, Rustin and Hecke (1984); Mumford (1984 LPB 57); Anon. (1985 LPB 64, p. 13); Bond (1985 LPB 65, 1991); Carson, Mumford and Ward (1985 LPB 65); Kohler (1985); Politz (1985); Anon. (1986 LPB 69, p. 17 and 33); Anon. (1986 LPB 71, p. 27); Lask (1986); McCoy, Dillenback and Truax (1986); Steinbrecher (1986, 1989 LPB 88); Anon. (1987 LPB 77, p. 11 and 27); V.C. Marshall (1987, 1990 LPB 95, 1994 LPB 116); Anon. (1988 LPB 79, p. 23); Anon. (1988 LPB 82, p. 19); Anon. (1988 LPB 83, p. 13); Anon. (1988 LPB 84, p. 19); Armstrong (1988 LPB 83); Schwab (1988a, 1988 LPB 83); Anon. (1989 LPB 87, p. 15); Anon. (1989 LPB 88, p. 19); B. Browning and Searson (1989); IMechE (1989/111); Anon. (1990g); Anon. (1990 LPB 91, p. 22); Anon. (1990 LPB 94, p. 26 and 30); Anon. (1990 LPB 95, p. 19); Adelman and Adelman (1990 LPB 94); Perunicic and Skotovic (1990 LPB 96); Anon. (1991 LPB 97, p. 12); Anon. (1991 LPB 98, p. 9); Kohvaporrand (1991); Anon. (1991 LPB 102, p. 35); Anon. (1992 LPB 103, p. 24); Anon. (1992 LPB 104, p. 7, 9 and 13); Anon. (1992 LPB 105, p. 15); Carson and Mumford (1992 LPB 108, 1993 LPB 109, 110); Kirk (1992 LPB 105); Prine (1992); Anon. (1993 LPB 113, p. 27); Anon. (1993 LPB 114, p. 19); Anon. (1994 LPB 115, p. 6); Anon. (1994 LPB 120, p. 10 and 19)

Fire: static electricity
Klinkenberg and van der Minne (1958); Bustin (1963); Eichel (1967); Muller-Hillebrand (1963); van der Meer (1971); Anon. (1979 LPB 29, p. 134); Anon. (1983 LPB 52, p. 19); H.R. Edwards (1983); M.R.O. Jones and Bond (1984, 1985); Liittgens (1985); Anon. (1987 LPB 78, p. 9); Owens (1988); Anon. (1994 LPB 118, p. 14)

Explosions
OIA (Publ. 651, 1973); Assheton (1930); Jacobs *et al.* (1957); F.C. Price (1960); Matthews (1961); Popper (1963); Alexander and Finigan (1964); Bateman (1964); W.A. Mason (1964); Pipkin (1964); Sakai (1964); Schmitt (1964); Thodos (1964); Walls (1964b); Sorrell (1965); Anon. (1966c); W.L. Ball (1966a); Haseba *et al.* (1966); Wilkinson (1966); Adcock and Weldon (1967b, 1973); Dixon (1967); Dorsey (1967); Lorentz (1967, 1973); J.D. Reed (1967); Bast (1970); Buehler *et al.* (1970); Fritsch (1970); Grewer (1970); Kotzerke (1970); Valpiana (1970a,b); Volpers (1970); Cracknell (1971); Dartnell and Ventrone (1971); K.W. Sanders (1971); GA Campbell and Rutledge (1972); Fire J. Staff (1973d); Freese (1973); Gozzo and Carraro (1973); Jacobs *et al.* (1973); Meganck (1973); de Oliviera (1973); W.W. Patterson (1973); Vervalin (1973e); Bateman, Small and Snyder (1974); Bloore (1974); Grimm (1974); Gugan (1974b); Hadas (1974); Hartgerink (1974); Kletz (1974b, 1976b,f,x, 1984 LPB 56, 1988); Lockemann (1974); Ludford (1974); Tanimoto (1974); Voros and Honti (1974); Anon. (1975 LPB 1, p. 3 and 15); Anon. (1975 LPB 5, p. 1); Anon. (1975 LPB 6, p. 17); Dooyeweerd (1975); Henderson (1975); Strehlow and Baker (1975, 1976); Anon. (1976 LPB 11, p. 2); Carver (1976); Kotoyori *et al.* (1976); Rebsch (1976); Saia (1976); Anon. (1977d); Tong, Seagraves and Wiederhorn (1977); Anon. (1978 LPB 19, p. 24); Cremer and Warner (1978); Markham and Honse (1978); Biasutti (1979); Anon. (1980y); Ramadorai (1980); Edwards (1982 LPB 47); Anon. (1983a); Bond (1983 LPB 50); Anon. (1983 LPB 51, p. 9); Lloyd (1983); Ursenbach (1983); Anon. (1984 LPB 54, p. 13); Anon. (1985c); HSE (1985d); Schwab (1988a,b, LPB 83); Wrightson and Santon (1988 LPB 83); Anon. (1989 LPB 87, p. 3, 7 and 27); Anon. (1989 LPB 88, p. 17); Anon. (1989 LPB 89, p. 13); Bond (1989 LPB 93); Cronin (1989 LPB 90); Ernst (1989); G.M. Lawrence (1989); MacDiarmid and North (1989); Nightingale (1989a,b); Urben (1989 LPB 80); Anon. (1990d,e,i); Anon. (1990 LPB 91, p. 15); Anon. (1990 LPB 95, p. 15); de Haven and Dietsche (1990); Segrave and Wilson (1990); Anon. (1991d,f,k,l); Anon. (1991 LPB 97, p. 23); Anon. (1991 LPB 98, p. 1 and 18); Anon. (1991 LPB 102, p. 7); Arendt and Lorenzo (1991); Carson and Mumford (1991 LPB 102); Hempseed and Ormsby (1991); Anon. (1992b); Anon. (1992 LPB 103, p. 19); Anon. (1992 LPB 103, p. 31); Anon. (1992 LPB 107, p. 17); S.E. Anderson, Dowell and Mynaugh (1992); Moran (1992); Palazzi (1992); Raheja *et al.* (1992); Anon. (1993 LPB 109, p. 7); Anon. (1993 LPB 109, p. 25 and 26); Anon. (1993 LPB 110, p. 25); Anon. (1993 LPB 112, p. 21); Bergroth (1993 LPB 109); Bond (1993 LPB 101); Wehrum (1993); Whitmore, Gladwell and Rutledge (1993); Zhang and Tang (1993); Anon. (1994 LPB 115, p. 9); Anon. (1994 LPB 116, p. 17)

BLEVEs
Kohler (1985); Selway (1988 SRD R492)

Dust explosions, dust fires
Morozzo (1795); D.J. Price and Brown (1922); NFPA (1957/1); K.C. Brown and James (1962); Remirez (1967); Yowell (1968); Noss (1971); O'Reilly (1972); Tonkin and Berlemont (1972 FRS Fire Res. Note 942); K.N. Palmer (1973a); Pollock (1975); Lathrop (1978); Anon. (1979e); Braun (1979); Snow (1981); Anon. (1983 LPB 51, p. 9); Anon (1989 LPB 90, p. 27); Skinner (1989); Anon. (1990 LPB 95, p. 1, 6 and 13); Kaiser (1991); Senecal (1991); Anon. (1994 LPB 115, p. 9)

Toxic release
Chasis *et al.* (1947); Joyner and Durell (1962); Hoveid (1966); Inkofer (1969); MacArthur (1972); Simmons, Erdmann and Naft (1973, 1974); Eisenberg, Lynch and Breeding (1975); Lonsdale (1975); Luddeke (1975); Anon. (1976n,o); Hoyle and Melvin (1976); HSE (1978b); Harvey (1979b); Shooter (1980); N.C. Harris (1981b); Anon. (1982 LPB 48, p. 13); Prijatel (1983); Sweat (1983); Anon. (1985 LPB 66, p. 23); HSE (1985 LPB 63); Anon. (1987 LPB 75, p. 23); Anon. (1989 LPB 86, p. 22 and 27); Anon. (1989 LPB 89, p. 27); Anon. (1990 LPB 91, p. 19); Anon. (1990 LPB 92, p. 11, 15, 23 and 26); Duclos and Binder (1990); Huvinen (1990 LPB 92); Fallen (1990); M.P. Singh (1990); M.P. Singh, Kumari and Ghosh (1990); Anon. (1991 LPB 97, p. 7); Anon. (1991 LPB

98, p. 25); Anon. (1993 LPB 113, p. 26); Anon. (1993 LPB 112, p. 22)

Plant commissioning
Dyess (1973); Parnell (1973); J.R. Robinson (1973); Severa (1973); Arnot and Hirons (1974); Horsley (1974); Jenkins and Crookston (1974); Butzert (1976); Anon. (1977 LPB 18, p. 2); Bress and Packbier (1977); Givaporert and Eagle (1977); Tandy and Thomas (1979); Kletz (1984k); Grotz, Gosnell and Grisolia (1985); Ruziska *et al.* (1985); Song (1986); W.K. Taylor and Pino (1987); Kneale (1991 LPB 97)

Plant operation
MCA (1962–/1–4); W.H. Doyle (1972a); Kletz (1975b); Lees (1976b); Anon. (1978 LPB 20, p. 41); Anon. (1987 LPB 77, p. 17); Anon. (1989 LPB 88, p. 1); Anon. (1989 LPB 89, p. 9 and 18); T.O. Gibson (1989); Anon. (1990 LPB 92, p. 22); Anon. (1991 LPB 98, p. 19); Anon. (1992 LPB 106, p. 19); Anon. (1992 LPB 107, p. 17); Anon. (1994 LPB 115, p. 7)

Plant maintenance
Simms (1965); Anon. (1978 LPB 24, p. 155); Anon. (1979 LP 27, p. 80); P.C. Campbell (1981); Roney and Persson (1984); Deacon (1988); Anon. (1989 LPB 85, p. 1, 3 and 5); Anon. (1989 LPB 86, p. 17); Anon. (1990 LPB 92, p. 9); Anon. (1991 LPB 97, p. 7); Anon. (1991 LPB 98, p. 20); Anon. (1991 LPB 102, p. 27); Anon. (1991 LPB, p. 20 and 25); Anon. (1992 LPB 103, p. 24, 25 and 29); Anon. (1992 LPB 104, p. 10); Anon. (1992 LPB 107, p. 21 and 22); Anon. (1993 LPB 112, p. 20); Anon. (1994 LPB 116, p. 22); Anon. (1994 LPB 117, p. 17); Anon. (1994 LPB 119, p. 8); Bond (1994 LPB 117)
Construction
Anon. (1991 LPB 107, p. 21 and 22)
Excavation
Anon. (1992 LPB 107, p. 22 and 23)

Plant modification
Anon. (1975 LPB 1, p. 1); R.J. Parker (1975); Booth (1976); Henderson and Kletz (1976); Heron (1976); W.W. Russell (1976); Anon. (1978 LPB 22, p. 101)

Storage
OIA (Publ. 711, 1974 Loss Inf. Bull. 400-1); Vervalin (1964a, 1973a); J.A. Lawrence (1966); Frank and Wardale (1970); J.R. Hughes (1970); A. Nielsen (1971); Litchenberg (1972, 1977); MacArthur (1972); Anon. (1975 LPB 0, p. 2); Henderson (1975); Lonsdale (1975); Anon. (1976 LPB 12, p. 7); Hampson (1976); Anon. (1978 LPB 20, p. 55); Anon. (1979 LPB 26, p. 31); Anon. (1979 LPB 27, p. 68); Gustin and Novacek (1979); Anon. (1980 LPB 32, p. 13); Anon. (1980 LPB 36, p. 25); Anon. (1981 LPB 37, p. 7); Anon. (1981 LPB 41, p. 11); Morgenegg (1982); Anon. (1984 LPB 57, p. 11); Anon. (1986 LPB 69, p. 29); Badame (1986); NBS (1986, 1988); Anon. (1987 LPB 75, p. 19); Anon. (1987 LPB 78, p. 26); Anon. (1988m); Marshall (1988 LPB 82); Anon. (1989 LPB 88, p. 11); Anon. (1992 LPB 106, p. 5). *Warehouses*: Pietersen (1988); Christiansen, Kakko and Koiviso (1993); Koivisto and Nielsen (1994)

Transport
AGA (Appendix 28 Pipeline Accident Reports); NTSB (annual reports); Engel (1969); Inkofer (1969); Medard (1970); Cato and Dobbs (1971); A.W. Clarke (1971b); Kogler (1971); Caserta (1972a); Ass. of Amer. Railroads (1972); Hayes (1972); Fire J. Staff (1973); Lloyds list (1974); Wilde (1974); DoE (1976/6); Anon. (1977 LPB 15, p. 33); Getty, Rickert and Trapp (1977); Merricks (1977); Anon. (1978j); Anon. (1978 LPB 54, p. 7); Anon. (1979g); Selikoff (1979); Egginton (1980); Anon. (1981m); George (1981a,b); Kletz (1981b); Knife (1982–83); V.J. Clancey (1983); van der Schaaf and Steunenberg (1983); M. Griffltsh and linklater (1984); Hymes (1985 LPB 61); Kilmartin (1985 LPB 61); G.A. Gallagher (1986); G.A. Gallagher and McCone (1986); D.J. Lewis (1986b); Watson (1986 LPB 72); Anon. (1988 LPB 80, p. 3); Anon. (1990 LPB 92, p. 25 and 26); Anon. (1990 LPB 93, p. 3); Anon. (1990 LPB 94, p. 1 and 7); Bond (1990 LPB 94); Anon. (1991 LPB 98, p. 5); Anon. (1991 LPB 101, p. 13); Anon. (1993 LPB 110, p. 7); Marshall (1993 LPB 114); Anon. (1994 LPB 115, p. 7)

Emergency planning
Donovan (1973); R.J. Parker (1975); Ikeda (1982); Anon. (1986 LPB 70, p. 1); Anon. (1993 LPB 113, p. 26)

Emergency planning: transport
Dowell (1971); Kogler (1971); Burns (1974); Dektar (1974); Ellis (1974); Furey (1974); Eisenberg, Lynch and Breeding (1975); HSE (1978b); Zajic and Himmelman (1978); Anon. (1982h); Anon. (1983m)

Personal health and safety
Anon. (1988 LPB 88, p. 3 and 14 (x2))

Environment
E. Hughes (1973); Willman (1977); Anon. (1978 LPB 22, p. 114); Anon. (1982c); Kharbanda and Stallworthy (1982); Frisbie (1982); A. Shepherd (1982a); A.J. Smith (1982); Kier and Mffller (1983); Cairns (1986); Goudray (1992); Anon (1993a,f)

Offshore
Fischer (1982); Anon. (1991f)

Other case histories
Bakir *et al.* (1973); Anon. (1976 LPB 9, p. 5); Anon. (1976 LPB 11, p. 10); Vervalin (1981, 1987); Anon. (1982 LPB 48, p. 27); Anon. (1982 LPB 49, p. 26); Kletz (1982 LPB 48, 49); Anon. (1984 LPB 54, p. 21); Anon. (1984 LPB 60, p. 1); Anon. (1985 LPB 61, p. 33); Anon. (1985 LPB 64, p. 27); Buhrow (1985, 1986); Lask (1986); Manuell (1986 LPB 71); Schillmoller (1986); Anon. (1987q); Plummer (1987 LPB 73); Robinson (1987 LPB 78); Anon. (1988h); Anon. (1988 LPB 81, p. 15); Anon. (1988 LPB 83, p. 25); Anon. (1989 LPB 88, p. 18); Anon. (1989 LPB 90, p. 15); Mansot (1989); Mooney (1991); Anon. (1993c); Davie, Nolan and Hoban (1994)

A1.2 Incident Databases

There are a number of databases specifically dealing with case histories. They include the following:

- The incident databases Major Hazards Incident Data System (MHIDAS) and the corresponding explosives data system EIDAS are operated by SRD.
- TNO has developed the FACTS incident database.
- The JRC of the CEC at Ispra, Italy, runs the Major Accident Reporting System (MARS), described by Drogaris (1991, 1993).
- The FIRE incident database for chemical warehouse fires has been described by Koivisto and Nielsen (1994).
- An account of the offshore Hydrocarbon Release (HCR) database in the United Kingdom has been given by Bruce (1994).

A1.3 Reporting of Incidents

The extent and accuracy of the reporting of incidents and injuries is variable and this creates problems particularly for attempts to perform statistical analysis of incident data.

Three distinct problems may be identified: (1) occurrence of an incident; (2) injuries associated with an incident; and (3) national injury statistics. These three cases are considered in this section and in the next two sections, respectively.

The awareness of the engineering community worldwide of incidents varies according to the country in which the incident has occurred and the size and impact of the incident. For example, in the recent past incidents in the United States have generally been reported in the technical press but reports of comparable incidents in the USSR have been relatively few.

With regard to the effects of scale and impact, the probability of worldwide reporting of a incident clearly increases with these factors. The probability that an accident of the magnitude of Bhopal is not reported in countries with a free press is negligible. However, as the size of the incident decreases, the probability that it is not reported or at least is not picked up in incident collections and databases increases. The problem has been discussed by Badoux (1983). Figure A1.1 shows schematically the probable extent of underreporting, curve A representing the actual reporting situation and curve B the ideal one.

A1.4 Reporting of Injuries in Incidents

For various reasons, accounts of incidents tend to differ in the number of injuries and, to a lesser extent, fatalities that are reported. A discussion of this problem has been given by Haastrup and Brockhoff (1991).

There are a number of reasons for differences in the numbers quoted. One is that early reports of an incident tend not be very accurate, but are sometimes quoted without sufficient qualification and the numbers then receive currency.

With regard to fatalities, a difference arises between immediate and delayed deaths. A case where a proportion of delayed deaths is fairly common is burn casualties.

The most frequent and large differences, however, are in 'injuries'. Here much of the difference can usually be accounted for by differences in definition.

As an illustration, consider the injuries in the explosion at Laurel, Mississippi on 25 January 1969. The NTSB report on this incident (NTSB 1969 RAR) states that 2 persons died, 33 received treatment in hospital and numerous others were given first aid. Some authors have therefore quoted this as 2 dead, 33 injured. Eisenberg, Lynch and Breeding (1975) refer to the NTSB report but also to a private communication from a railroad source and state that 976 persons were injured, 17 being in hospital for more than a month. This incident is one of those quoted by Haastrup and Brockhoff as an example of the problem.

Another illustration is provided by the explosion at Silvertown, London, on 19 January 1917. The account given later in this Appendix states that 68 were killed, 98 seriously injured, 328 had slight injuries and about 600 are thought to have received treatment in the street or from private doctors. Thus this account gives three separate categories of injury, without even mentioning hospitals.

A1.5 Reporting of Injuries at National Level

It is normal for there to be a regulatory requirement for the reporting, as a minimum, of deaths and injuries. In the United Kingdom the relevant regulations are RIDDOR 1985. The information gathered in this way is published by the HSE in the series *Health and Safety Statistics*.

The reporting is incomplete. A study supplementary to the household-based Labour Force Survey 1990 in the United Kingdom showed that only approximately 30% of non-fatal injuries were reported to the HSE, but that the level of reporting varied significantly across industries (Kiernan, 1992). For the energy industry the proportion of such accidents reported was 75%, and it seems probable that the

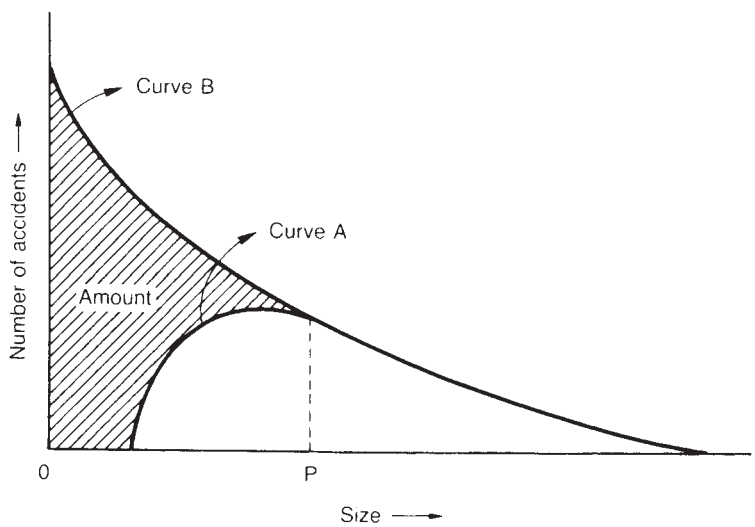


Figure A1.1 *Number of accidents reported (after Badoux, 1983): A, accidents actually reported; and B, total number of accidents (and ideal reporting curve)*

level of reporting in process industries such as oil refining, petrochemical and chemicals is similar.

Hours by J.R. Nash (1976). Some principal explosions are listed by Nash. His list gives death tolls that in some cases differ from those given elsewhere. The incidents in which the number of deaths is quoted as 200 or more are:

Date		*Location*		*No. of deaths*
1916	Nov. 16	La Satannaya, Belgium	Munitions	1000
1917	Jan. 19	Silvertown, London	Munitions factory	300[a]
	Feb. 20	Archangel, Russia	Munitions shipment	1500
	Jun. 23	Bloeweg, Belgium	Munitions factory	1000
	Aug. 6	Henningsdorf, Germany	Munitions factory	300
	Dec. 6	Halifax, Nova Scotia	Munitions shipment	1600[a]
1918	Aug. 3	Hamont Station, Belgium	Munitions shipment	1750
	Sept. 22	Woellerdorf, Austria	Munitions factory	382
1925	May 25	Peking, China	Munitions store	300
1934	Mar. 14	La Libertad, Salvador	Explosives store	250
1935	Oct. 30	Lanchow, China	Munitions store	2000
1941	Jan. 9	Fort Smederovo, Yugoslavia	Munitions store	1500
1944	Apr. 14	Bombay, India	Munitions shipment	1376[a]
	Jul. 17	Port Chicago, CA	Munitions shipment	321
1956	Aug. 27	Cali, Columbia	Munitions shipment	1200

[a] The death tolls given in the account in Section A1.10 are as follows: Silvertown 69; Halifax 1800; and Bombay Docks 350 (early reports) This list does not include incidents involving primarily ammonium nitrate.

A1.6 Incident Diagrams, Plans and Maps

Many accounts of incidents give diagrams, plans or maps showing features such as derailed tank cars, location of missiles, location of victims, etc. In particular, such diagrams are a feature of the accident reports by the HSE and the NTSB and of case histories described in the Loss Prevention Bulletin.

Typical diagrams showing injury effects at an accident from an HSE report are given in Figure A1.19. A typical diagram of the site of an accident from an NTSB report is shown in Figure A1.16.

The NTSB system of Hazardous Material Spill Maps, documents separate from the accident reports, is described by the NTSB (1979), Benner and Rote (1981) and Lasseigne (1984). One such map is shown in Figure A1.2.

A1.7 Incidents Involving Fire Fighting

A feature of some interest in incidents is the experience gained in fire fighting. Some minimal information about this is given for selected case histories in Series A. Further information may be found in the following accounts:

Brindisi, 1977 (Mahoney, 1990)
Milford Haven, 1983 (Dyfed County Fire Brigade, 1983; Mumford, 1984 LPB 57)
Thessalonika, 1986 (B. Browning and Searson, 1989)
Grangemouth, 1987 (HSE, 1989a)
Port Heriot, 1987 (Mansot, 1989)

A1.8 Incidents Involving Condensed Phase Explosives

A number of the incidents given in the following sections involve explosives. There have been, however, a large number of other explosives and munitions incidents that are of only marginal interest here.

An account of explosions up to 1930 is given in *History of Explosions* by Assheton (1930) and later treatments are *Explosions in History* by N.B. Wilkinson (1966) and *Darkest*

Other incidents given by Nash, with death tolls shown in brackets, are:

Munitions, explosives, powder factories
1915 Oct. 20 Paris, France (52); Nov. 31 Eilmington, Delaware (31); Dec. 11 Havre, Belgium (110); 1916 Apr. 4 Kent, England (170); Dec. 6 Kent, England (26); 1917 Apr. 10 Chester, PA (133); Oct. 4 Morgan, NJ (64); 1924 Mar. 1 Nixon, NJ (26); 1925 Mar. 1 Kharput, Turkey (160); 1926 Apr. 7 Mannheim, Germany (40); Aug. 12 Csepel, Hungary (24); 1929 Sep. 5 Brescia, Italy (22); 1931 Apr. 30 Nichteroy, Brazil (100); 1935 Jun. 13 Reinsdorf, Germany (52); Jul. 28 Taino, Italy (33); 1936 Jun. 15 Tallinn, Estonia (40); 1937 Jul. 17 Chungking, China (110); 1940 Aug. 29 Bologna, Italy (38); 1941 Jan. 10 Polichka, Czechoslovakia (80); 1943 Dec. 11 Grenoble, France (73); 1947 Aug. 18 Cadiz, Spain (149)

Munitions, explosives stores and arsenals
1916 Feb. 6 Skoda, Austria (185); Feb. 20 Nish, Serbia (43); Mar. 4 Fort Double Coronne, France (30); 1926 Jul. 19 Lake Denmark, NJ (30); 1928 Sep. 26 Ft Cabreriza, Morocco (38); 1929 Mar. 4 Sofia, Bulgaria (28); 1931 May 5 Yuchu, China (100); Aug. 13 Macao, China (26); 1932 Jul. 10 Nanking, China (100); 1935 Oct. 23 Shanghai, China (190); 1944 Nov. 28 Fauld, England (175)[a]; 1945 Feb. 26 Paris, France (20); Jul. 7 Saragossa, Spain (30); Oct. 25 Asnier-en-Bessin, France (33); Dec. 29 Codroipo, Italy (23); 1946 Apr. 8 Saigon, Vietnam (23); 1949 Jul. 26 Tarancon, Spain (25); 1953 Apr. 6 Nantsechu, Formosa (54); 1956 May 17 Takoradi, Africa (25); 1963 Aug. 13 Gauhati, India (32)

Munitions, explosives shipments
1916 Aug. 8 Koenigsberg, Germany (50); 1919 Feb. 1 Longwy, France (64); 1924 Dec. 27 Otaru, Japan (120); 1930 Dec. 3 Midas Garaes, Brazil (36); 1955 Sep. 23 Gomex Palacio, Mexico (40); 1960 Mar. 4 Havana, Cuba (100); 1964 Jul. 23 Bone, Algeria (85)

Munitions, explosives (otherwise unspecified)
1925 Nov. 22 Ahwaz, Persia (70); 1933 Jan. 20 Morelia, Mexico (23); 1934 Aug. 4 Nakang, Japan (25); 1953 Aug. 18 Benghazi, Libya (50); Sep. 12 Wuensdorf, Germany (20)

[a]The death toll given in the account in Section A1.10 is 68.

A1.9 Case Histories: Some Principal Incidents

Two series of case histories are given below. Series A consists of case histories chosen according to one or more of the following criteria: (1) the incident is well known, generally by name; (2) it involved major loss of life and/or property; and (3) the physical events and the escalation are of interest.

Series B consists of case histories of incidents which have not been selected for the A series and where in general the loss of life or property damage was less, but which are considered instructive, particularly in respect of the cause.

Generally, in the A series mention is made of deaths and injuries, but the cost of property damage is not given. However, many of the incidents figure in the thirteenth edition of *Large Property Damage Losses in the Hydrocarbon-Chemical Industries*. A Thirty Year Review by Marsh and McLennan (M&M), edited by Mahoney (1990), which gives the 100 largest losses. For these incidents, the cost is shown in Table A1.2.

A1.10 Case Histories: A Series

A1 *San Antonio, Texas, 1912*
On 18 March 1912 at San Antonio, Texas, workers were carrying out repairs on the boiler of a large locomotive. Steam pressure was being raised when something went wrong and the boiler exploded violently. One 1600 vapour fragment travelled 1200 ft and a 900 vapour one fetched up 2000 ft away. Twenty-six workers and residents were killed and another 32 were injured (J.R. Nash, 1976).

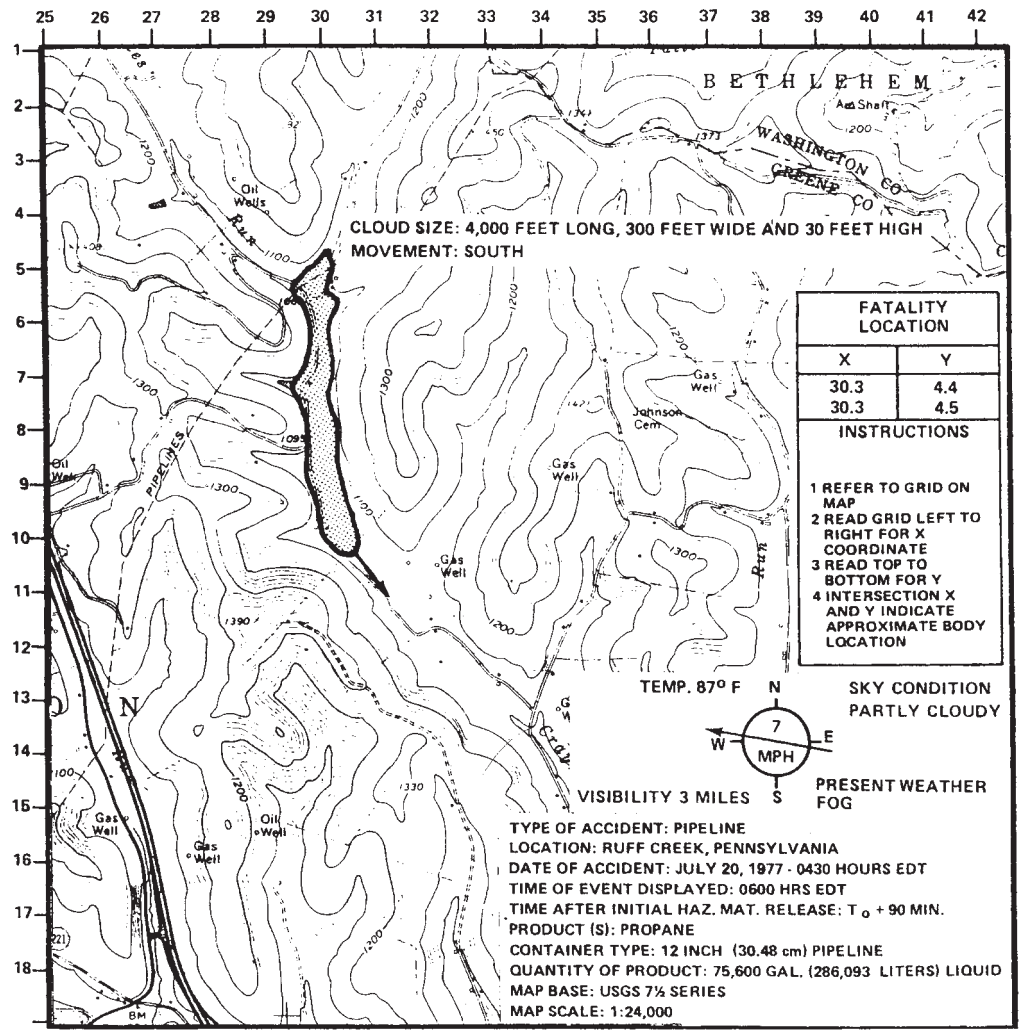


Figure A1.2 *Hazardous Materials Accident Spill map: propane pipeline release, Ruff Creek, Pennsylvania, 1977 (National Transportation Safety Board, 1979)*

Table A1.2 *Some major accidents in the process industries*

No.	*Date*	*Location*	*Plant/ transport*	*Chemical*	*Event*	*Deaths/ injuries*	*Cost* (million US$)	*References*
1	1911	Glasgow, UK			DEX	5d, 8i		9
2		Liverpool, UK			DEX	37d, 100i		9
3		Manchester, UK			DEX	3d, 5i		9
4	1912	San Antonio, TX	Loco boiler	Steam	IE	26d, 32i		
5	1913	Manchester, UK			DEX	3d, 5i		9
6	1914	Chrome, NJ	Rail tank car	Chlorine	TOX	0d		3
7	1915 Sep. 27	Ardmore, OK	Rail tank car	Petrol	F	40d		10
8	1916 Jul. 30	Black Tom Island, NY	Barge, rail cars	Explosives	HEX	5d, many injured		
9	1917	Ashton, UK	Chemical works		HEX	46d, 120i		
10	Dec. 6	Halifax, Nova Scotia	Ship	Munitions	HEX	1963d, ≈8000i		
11	Jan. 19	Silvertown, UK	Munitions works	TNT	HEX	69d, ≈426i		
12		Wyandotte, MI	Storage tank	Chlorine	TOX	1d		3, 7
13		Morgan, NJ		Ammonium nitrate	ANEX	64d		4
14	1919	Cedar Rapids, IA	Starch plant	Corn starch	DEX	43d		9
15	1920	Niagara Falls, NY	Gas cylinder	Chlorine	TOX	3d		
16	1921 Aug. 24	Hull, UK	Airship	Hydrogen	EX			6, 8, 14
17		Kriewald, Germany	Rail cars	Ammonium nitrate	ANEX			15
18	Sep. 21	Oppau, Germany	Chemical works	Ammonium nitrate	ANEX	561d		4, 7, 11, 15
19	1924	Peking, IL	Starch plant	Corn starch	DEX	42d		9
20	1925	De Noya, OK	Gas cylinder	Chlorine	TOX	2d		
21	1926 Dec. 13	St Auban, France	Storage tank	Chlorine	TOX	19d		1, 3, 7, 10, 11
22	1928 Jul. 7, 13	Asbokan, NY	Rail tank car	Chlorine	TOX	0d		
23	May 20	Hamburg, Germany	Storage tank	Phosgene	TOX	10d		3, 10, 11
24	1929 May 10	Syracuse, NY	Storage tank	Chlorine	TOX	1d		1, 3, 7
25	1930	Liverpool, UK			DEX	11d, 32i		9
26	1930 Dec.	Lüttich, Belgium	Fuel plant	Hydrogen fluoride, sulphur dioxide	TOX	63d[a]		10
27	1932 Dec.	Detroit, MI	Storage	LPG				6
28	1933 Feb. 10	Neunkirchen, Germany	Gasholder	Towns gas	EX	65d, several hundred injured		10
29	1934 May 14	Hongkong	Gasholder	Towns gas	F	42d, 46i		10
30	Feb. 28	Niagara Falls, NY	Rail tank car	Chlorine	TOX	0d		7
31	1935 Mar. 13	Griffith, IN	Rail tank car	Chlorine	TOX	0d		1, 3, 7
32	1936 Nov. 12	Johnsonburg, NY	Pipeline	Chlorine	TOX	1d		1, 3
33	1939 Jan. 2	Newark, NJ		Butane	VCE			6, 14
34	Dec. 12	Wichita Falls, TX	Pipeline	Oil film	IE	0d, 1i		15
35	Dec. 24	Zarnesti, Roumania	Storage tank	Chlorine	TOX	≈60d		1, 2, 3, 7, 10, 11
36	1940 Jan. 26	Mjodalen, Norway	Rail tank car	Chlorine	TOX	3d		3, 7, 10
37	1941	Liverpool, UK			DEX	6d, 40i		9
38	1942 Jul. 21	Tessenderloo, Belgium	Chemical works	Ammonium nitrate	ANEX	>100d		
39	1943 Jan. 18	Los Angeles, CA	Road tanker	Butane	VCF	5d		3, 6, 7

Table A1.2 *(continued)*

No.	*Date*	*Location*	*Plant/ transport*	*Chemical*	*Event*	*Deaths/ injuries*	*Cost* (million US$)	*References*
40	Jul. 29	Ludwigshafen, Germany	Rail tank car	Butadiene	VCE	57d, 439i		10, 11, 14
41	1944 Apr. 14	Bombay, India	Ship	Munitions	EX	>350, 1800i		
42		Brooklyn, NY	Gas cylinder	Chlorine	TOX	0d, 208i		
43	Oct. 20	Cleveland, OH	Storage	LNG	F	128d, 200–400i		3, 6, 7, 8, 10, 11
44	Nov. 21	Denison, TX	Tank	LPG	F(?)	10d		6, 10
45	Nov. 27	Fauld, UK	Munitions store	Munitions	HEX	68d, 22i		
46		Kansas City, KS	Grain dust	Corn mill	DEX	4d, 20i		
47	Jul. 17	Port Chicago, CA	Ships	Explosives	EX	321		
48	1945 Apr. 25	Los Angeles, CA	Storage	Butane	VCE			6, 14
49	1947 Apr. 28	Brest, France	Ship	Ammonium nitrate	ANEX	21d		4, 7
50	Feb. 4	Chicago, IL	Rail tank car	Chlorine	TOX	0d		1, 3, 7
51	Feb. 20	Los Angeles, CA	Electrolysis plant	Acetic anhydride, etc.	EX	17d, 130i		10
52	Jan. 13	Natrium, WV	Gas cylinder	Chlorine	TOX	2d		10
53	Nov. 5	Rauma, Finland	Storage tank	Chlorine	TOX	19d		1, 3, 7, 10, 11
54	Apr. 16	Texas City, TX	Two ships	Ammonium nitrate	ANEX	552d, ≈3000i		4, 7, 11
55	1948 July 23	Ludwigshafen, FRG	Rail tank car	Dimethyl ether	VCE	207d, ≈3818 i		5, 6, 7, 8, 10, 11, 14, 15
56	Oct. 13	Sacramento, CA	Road tanker	Butane	F	2d		6
57	1949 Dec. 30	Detroit, IL	Cat cracker	Propane, butane	VCE	5d		14
58	Sep. 1	Freeport, TX	Pipeline	Chlorine	TOX	0d		7
59		Nitro, WV	Reactor	TCDD	TOX	228i		10
60	Jun.	Perth, NJ	Storage tank	HCs	EX	4d		6
61	Oct.	Winthrop, MO	Rail tank car	LPG	F(?)	1d		6
62	1950 Jul. 20	Billingham, UK	Rail tank car	Chlorine	TOX	0d		
63	Feb. 16	Midland, MI	Synthetic rubber plant	Butadiene, styrene	VEEB			8
64		Poza Rica, Mexico	Plant	Hydrogen sulphide	TOX	22d, 320i		10
65	Aug.	Wray, CO	Road tanker	Propane	VCF	2d		6
66	1951 Sep. 7	Avonmouth, Bristol, UK	Storage tank	Oil	EX, F	2d		
67	Aug. 16	Baton Rouge, LA	Naphtha treating	HCs	VCE	2d		14
68	Jul. 7	Port Newark, NJ	Storage	Propane	VCF, BLEVE	0d, 14i		8, 10, 15
69	Feb. 8	St Paul, MN	Loading terminal	LPG	VEEB	14d		10
70	1952 Jul. 21	Bakersfield, CA	Storage	Butane	VCE	0d		6, 8, 10, 15
71	Dec. 22	Bound Brook, NJ	Phenolic resin plant	Resin dust	DEX	5d, 21i		15
72	Jul. 24	Kansas City, KS	Loading terminal	LPG	VCE			6, 14
73	Apr. 4	Walsum, FRG	Storage tank	Chlorine	TOX	7d		1, 3, 7, 10
74	1953 Aug. 6	Campana, Argentina	Refinery recovery unit	Gasoline	VCE	2d		14
75	Sep. 23	Tonawanda, NY	Organic peroxides plant	Organic peroxides	EX	11d, 27i		10
76	1954 Jun. 25	Montreal, Quebec	Gas cylinder	Chlorine	TOX	1d		
77	Oct. 18	Portland, OR	Rail tank car	LPG	VCE	0d		6, 14
78	Jun. 4	Institute, WV	Rail tank car	Acrolein	IE			6, 14
79	1955 Jul. 14	Freeport, TX	Polyethylene plant	Ethylene	VCE			14

80	Jul. 19	Ludwigshafen, FRG	Rail tank car		BLEVE	2i		
81		Runcorn, UK		Chlorine	TOX			
82		Waynesboro, GA	Feed plant	Grain dust	DEX	3d, 13i		
83	Aug. 27	Whiting, IN	Hydroformer	Naphtha	DET	2d, 40i		5, 10, 15
84	Jul. 22	Wilmington, CA (sic)	Gasoline plant	Butane	VCE			6, 14
85	1956 Jul. 29	Amarillo, TX	Storage tanks	Oil	FB	20d, >32i		
86	Jul. 26	Baton Rouge, LA	Alkylation unit	Butylene	VCE			
87	Aug. 7	Cali, Columbia	Road vehicle	Dynamite, munitions	HEX	≈1200d		
88	Oct. 22	Cottage Grove, OR	Storage	LPG	BLEVE	12d, 12i		
89	Jul. 29	Dumas, TX	Storage vessel	HC	BLEVE	19d, 32i		10
90	Mar. 10	Lake Charles, LA	Storage tank	Chlorine	TOX	0d		7, 10, 14
91	Dec. 19	North Tonawanda, NY	Polyethylene plant	Ethylene	VCE	0d		5, 6
92	Jan. 18	Uskmouth, Wales	Turbogenerator	Steam	IE	2d, 9i		
93	1957 Jan. 8	Montreal, Quebec	Storage vessel	Butane	BLEVE	1d		6, 10
94	Apr. 16	Nitro, WV	Chlorination vessel	Chlorine	TOX	8d		10
95	Oct. 24	Sacramento, CA	Loading terminal	LPG	VCE	1d		6, 14
96	1958 Apr. 15	Ardmore, OK	Loading terminal	Propane	VCE			6, 14
97	Jul. 30	Augusta, GA	Loading terminal	LPG	VCE	1d		6, 14
98	Jan. 3	Celle, FRG	Rail tank car		EX			
99	Jan. 22	Niagara Falls, NY	Rail tank car	Nitromethane	DET	200i		5, 10
100	May 22	Signal Hill, CA	Tank farm	Oil froth	F BLEVE	2d, 18i	42.9	5, 10, 13, 15
101	1959 Jun. 2	Deer Lake, PA	Rail tank car	LPG	BLEVE	11d, 10i		10
102	May 28	McKittrick, CA	Storage	LPG	BLEVE	2i		10
103	Jun. 28	Meldrin, GA	Rail tank car	LPG	VCE	23d		3, 5, 6, 7, 9, 10, 11, 14
104		Phillipsburg, NJ	Compressor	Lube and seal oil	EX	6d, 6i		
105	Feb. 27	Portland, OR	Road tanker	LPG	REL			
106		Roseburg, OR			ANEX	13d		
107	Jul. 11	Ube, Japan	Ammonia plant	Oxygen	IE	11d, 40i		10
108	1960 Dec. 17	Freeport, TX		Allyl chloride, propylene chloride	EX	6d, 14i		6
109	Oct. 14	Kingsport, TN	Nitrobenzene plant	Reaction mixture	DET	15d, 60i	39.0	10, 13
110	1961 Feb. 23	Billingham, UK	Pipeline	Chlorine	TOX	0d		3
111	Dec. 17	Freeport, TX	Caprolactam plant	Cyclohexane	VCE	1d		8, 10, 14
112		FRG	Air separation plant	Oxygen	EX	15d		10
113	Jan. 31	La Barre, LA	Rail tank car	Chlorine	TOX	1d, 114i		1, 2, 3, 5, 7, 10, 11
114		Lake Charles. LA	Alkylation unit	Butane	VCE	2d		14
115	Aug.	Minimata, Japan	Reactor	VCM	VEEB	4d, 10i		10
116		Morganza, LA		Chlorine	TOX	0d, 17i		10
117	1962 Jul. 25	Berlin, NY	Road tanker	LPG	VCE	10d, 17i		3, 6, 7, 9, 10, 14
118	Nov. 30	Cornwall, Ont.	Rail tank car	Chlorine	TOX	89i		1, 7, 10
119	Apr. 17	Doe Run, KY	Feed vessel	Ethylene oxide	IE, VCE	1d, 21i	20.2	5, 6, 7, 8, 10, 13, 14, 15

Table A1.2 *(continued)*

No.	Date	Location	Plant/ transport	Chemical	Event	Deaths/ injuries	Cost (million US$)	References
120		Fawley, UK	Cat cracker		VCE			14
121		FRG	Reactor	p-Nitrodiphenylamine	IE	2d, 18i		10
122		Houston, TX	Tank farm	Gasoline	VCE	2d		14
123	Apr. 27	Marietta, OH	Phenol plant	Benzene	EX	1d, 3i	20.2	8, 10, 13
124	Aug. 4	Ras Tanura, Saudi Arabia	Storage vessel	Propane	VCE, F	1d, 115i		6, 10, 14
125		St Louis, MO	Feed plant	Grain dust	DEX	2d. 34i		
126	May 10	Toledo, OH	Reactor	Acrylic polymer reaction	VEEB	10d, 46i		10
127	1963 Mar. 6	Amsterdam, Netherlands	Trichlorophenol plant	Reaction mixture, including TCDD	IE, TOX	8d, 14i		10
128	Apr. 28	Brandtsville, PA	Rail tank car	Chlorine	TOX	0d		1, 3, 7, 10
129		FRG	Acetylene plant	Acetylene, diacetylene	IE	7d, 6i		10
130	Apr. 3	Norwich, CT	Transport tank	Organic peroxides	EX	4d, 4i		10
131	Aug. 9	Philadelphia, PA	Rail tank car	Chlorine	TOX	430+i		1, 10
132	May 3	Plaquemine, LA	Ethylene plant	Ethylene	VCE	7i	16.2	6, 7, 10, 13, 14
133		Texas		Propylene	IE			5
134	1964 Jun. 4	Antwerp, Belgium	Reactor	Ethylene oxide	IE	4d, 20i		6, 7, 10
135	Jan. 1	Attleboro, MA	Reactor	VCM	VEEB	7d, 40i	19.9	8, 10, 13, 15
136	Jul. 17	FRG	Oxygen plant	Oxygen	IE			10
137		FRG	Reactor	Acrylamide reaction mixture	IE	1d, 3i		10
138		FRG	Reactor	Reaction mixture	IE	3i		10
139		Hebronville, MA	PVC plant		IE			5
140	Jan. 9	Jackass Flats, NV	Research laboratory	Hydrogen	VCE			6, 8, 10, 14
141	Oct. 25	Liberal KS	Compressor station	Propane	VCE			14
142	Jul. 2	Mobile, AL	Pipeline	Chlorine	TOX	1d		7
143	Jun. 16	Niigata. Japan	Refinery	HCs	EQK, F, EX	2d	87.3	13
144	Oct. 25	Orange, TX	Polyethylene plant	Ethylene	VCE	2d		6, 14
145		Paisley, UK			DEX	5d, 2i		9
146	1965 Dec. 23	Baltimore, MD	Detergents plant	Benzene	VCE			14
147	Sep. 12	Baton Rouge, LA	Tankship	Chlorine	TOX			10
148	Jul. 31	Baton Rouge, LA	Reactor	Ethyl chloride	VCE			6, 14
149	Aug. 7	Bow. London. UK	Flour mill	Flour	DEX	5d, 32i		9, 15
150	Oct. 24	Escambia. USA	Chemical plant	Hydrogen, carbon monoxide	VCE			6, 10
151		Houston, TX	Ethyl chloride plant	Ethyl chloride	EX	12d		10
152	Jul. 13	Lake Charles, LA	Ethylene plant	Methane or ethylene	VCE			6, 14
153	Aug. 25	Louisville, KY	Compressor	Monovinyl acetylene	IE	12d, 60i	39.2	10, 13, 15
154	Mar. 4	Natchitotehes, LA	Pipeline	Natural gas	IE	17d, 9i		5, 7, 8, 10
155		Pasadena, TX	Ammonia plant	Hydrogen, ammonia	F	2d, 3i		10
156		Texas	Chemical plant	Butane	F(?)			6
157		Whiting, IN	Reformer	Naphtha	EX			10

158	1966 Jan. 4	Feyzin, France	Storage vessels	Propane	BLEVE	18d, 81i	68.8	5, 6, 8, 10, 11, 13, 15
159		FRG	Storage vessel	Light HCS				5
160		Larose, LA	Pipeline	NGL	F	7d		
161	Oct. 16	LaSalle, Quebec	Reactor	Styrene	VEEB	11d, 10i	11.4	5, 8, 10, 13, 15
162	Jun. 14	La Spezia, Italy	Rail tank car	Chlorine	TOX	0d		3
163	May 23	Philadelphia, PA	Refinery	Benzene, cumene, propane	VCF			6, 10
164	Jan. 19	Raunheim, FRG[b]	Ethylene plant	Methane, ethylene	VCE	3d, 83i	26.6	5, 6, 8, 10, 13, 14
165	Feb. 6	Scotts Bluff, LA	Reactor	Butadiene	VCE	3d		6, 14
166	1967	Antwerp, Belgium		VCM	F	4d, 33i		5, 10
167		Bankstown, Australia		Chlorine	TOX	5i		5
168		Buenos Aires		Propane	F	100i		5, 10
169	Dec. 19	El Segundo, CA	Fuel oil reservoir	Fuel oil	F		13.5	13
170		Hawthorne, NJ			EX	2d, 11i		5
171	Aug. 8	Lake Charles, LA	Alkylation unit	Isobutylene	VCE	7d, 13i	63.1	3, 5, 6, 7, 8, 10, 13, 14, 15
172	Nov. 8	Newton, AL	Rail tank car	Chlorine	TOX	0d		1, 3, 10
173		Santos, Brazil	Gas holder	Towns gas	IE	300i		5, 10
174	Jan. 20	Sacramento, CA	Saturn rocket	Hydrogen, oxygen fuel	VCE			8
175	1968	Bolsover, UK	Reactor	Reaction mixture, including TCDD	TOX	79i		10
176	Jan. 1	Dunreith, IN	Rail tank car	(1) VCM (2) Ethylene oxide	F, EX BLEVE	5i		10
177		GDR		VCM	24d			5, 10
178		Hull, UK		Acetic acid	IE	2d, 13i		3, 5, 10
179	Aug. 21	Lievin, France	Road tanker	Ammonia	TOX	5d, 20i		5, 7, 9, 10
180		Paris, France	Petrochemical plant		IE			5
181	Jan. 21	Pernis, Netherlands	Slops tanks	Oil slops	VCE	2d, 85i	97.7	3, 5, 6, 7, 8, 10, 13, 14, 15
182		Tamytown, USA	Chemical plant	Propane	EX	1d, 2i		5, 10
183	Dec.	Yutan, NE	Pipeline	LPG	F	5d		6, 10
184	1969 Dec. 23	Basle, Switzerland	Reactor	Dinitrochloraniline reaction mixture	IE	3d, 31i		5, 10
185	May 8	Cleveland, OH	1-ton containers	Chlorine	TOX	1d		
186	Feb. 18	Crete, NE	Rail tank car	Ammonia	TOX	9d, 53i		3, 5, 7, 9, 10
187	Jul. 17	Dudgeons Wharf, London, UK	Tank dismantling	EX	6d	10		
188	Oct. 1	Escombreras, Spain	Storage	Propane	VCE	4d, 3i		5, 14
189	Dec. 28	Fawley, UK	Hydroformer	Hydrogen, naphtha	VCE	0d		6, 8, 10, 14
190	Aug. 12	Flemington, NJ	Reactors	VCM	EX		14	13
191	Sep. 11	Glendora, MS	Rail tank car	VCM	TOX, VCE	li		6, 10
192	Sep. 9	Houston, TX	Pipeline	Natural gas	VCE	9i		2, 10, 14
193	Jan. 25	Laurel, MS	Rail tank car	LPG	BLEVE	2d, 33+i		2, 14
194		Long Beach, CA	Tank	Petroleum	IE	1d, 83i		5, 10

Table A1.2 *(continued)*

No.	*Date*	*Location*	*Plant/ transport*	*Chemical*	*Event*	*Deaths/ injuries*	*Cost* (million US$)	*References*
195	Mar. 6	Puerto La Cruz, Venezuela	Crude unit	HCs	F		15.6	13
196		Repesa, Spain	Refinery	LPG, propylene	F	0d		5, 10
197	Oct. 23	Texas City, TX	Butadiene recovery unit	Butadiene	IE, VCE	3i	26.6	10, 13, 14, 15
198	May 14	Wilton, UK	Oxidation plant	Cyclohexane	VCE	2d, 23i		5, 6, 8, 10
199	Jan. 21	Wilton, UK	Polyethlene plant	Ethylene	IE	4d		
200	1970	Agha Jari, Iran	Compressor station	Gas	EX	29d, 10i		
201	Sep. 7	Beaumont, TX		Oil	F		20.2	10, 13
202	Jan. 21	Belle, WV	Rail tank car	Ammonia	TOX	1i		7, 9, 10
203	Feb. 6	Big Springs, TX	Alkylation unit		VCE			14
204	Nov. 16	Blair, NE	Storage tank	Ammonia	TOX	0d		3, 7, 10
205	May 30	Brooklyn, NY	Road tanker	Oxygen	F	2d, 30i		12, 15
206	Aug. 30	Corpus Christi, TX	Cat cracker		HUR		23.0	13
207	Jun. 21	Crescent City, IL	Rail tank car	Propane	BLEVE	66i		2, 5, 6, 8, 10, 11, 15
208	Nov. 12	Hudson, OH	Road tanker	LPG	F	6d		6, 10
209	Oct. 19	Javle, Sweden	Pipeline	Chlorine	TOX	0d		
210	Sep. 3	Jacksonville, MD	Pipeline					
211		Kiel, FRG	Grain silo	Grain dust	DEX	6d, 18i		
212	Dec. 5	Linden, NJ	Refinery reactor	C_{10} HC	VCE	40i	84.5	6, 10, 13, 14
213		Mitcham, UK		LPG	IE			5, 10
214		Philadelphia, PA	Cat cracker		F(?)	7d, 42i		5, 10
215	Dec. 10	Port Hudson, MO	Pipeline	Propane	VCE	10i		2, 3, 5, 6, 7, 8, 9, 10, 11, 14, 15
216		St Thomas Island, Virgin Islands		Natural gas	IE	25i		5, 10
217	1971 Jul. 10	Amsterdam, Netherlands	Refinery	Butadiene	EX	8d, 21i		10
218	Jan. 19	Baton Rouge, LA	Rail tank car	Ethylene	VCE	0d, 21i		6, 10, 14, 15
219	Apr. 24	Emmerich, FRG	Oxidation plant	Formic acid, hydrogen peroxide	F, IE	1d, many injured		5
220	Jun. 5	Floral, AR	Pipeline	Ammonia	TOX	0d		3, 5, 10, 11
221	Aug. 8	Gretna, FL	Road tanker	Methyl bromide	TOX	4d		12
222	Oct. 19	Houston, TX	Rail tank car	VCM	BLEVE	1d, 5i		2, 8, 10, 12
223	Sep. 15	Houston, TX	Butadiene plant	Butadiene	VCE	1d, 6i		6, 10, 14
224	Aug. 21	La Spezia, Italy	Storage tank	LNG	Rollover	0d		
225	Dec. 23	Lake Charles, LA	Chemical plant	Trichlorethylene, perchlorethylene	VCF(?)	4d, 3i		10
226	Feb. 25	Longview, TX	Polyethylene plant	Ethylene	VCE	4d, 60i	16.5	6, 8, 10, 13, 14
227	Nov. 7	Morris, IL	Ethylene oxide plant	Ethylene oxide, oxygen	IE	4i	16.2	10, 13
228		Netherlands		Butadiene		8d, 21i		5
229	Sep. 11	Pensacola, FL	Caprolactam plant	Cyclohexane	REL	0d		2, 3, 8, 10

230	Jul. 19	Raunheim, FRG	Tankship	Petroleum	F, EX	7d		10
231		Texas	Chemical plant	Ethylene	VCE	3d		
232	Jun. 4	Waco, GA	Road vehicle	Explosives	HEX	5d, 33i		12
233	1972 Aug. 14	Billings, MT	Alkylation unit	Butane	VCF	1d, 4i	14.0	6, 10, 13
234	Feb. 29	Delaware City, DE	Fluid coking unit	Hot oil	Hot oil damage		16.9	13
235	Oct. 22	East St Louis, IL	Rail tank car	Propylene	VCE	1d, 230i		2, 3, 5, 6, 8, 10, 12, 14
236	May 14	Hearne, TX	Pipeline	Crude oil	F	1d, 2i		2, 6, 10, 12
237	Mar. 9	Lynchburg, VA	Road tanker	Propane	FB	2d, 5i		2, 3, 6, 10, 12
238		Netherlands		Hydrogen	IE	4d, 4i		5
239	Sep. 21	NJ Turnpike, NJ	Road tanker	Propane	F	2d, 28i		2, 3, 10, 12
240		Rio de Janeiro, Brazil	Storage vessel	Butane	BLEVE	37d, 53+i	13.4	5, 6, 10, 13
241	Feb. 9	Tewksbury, MA	Storage tank		F	2d, 21i		
242	Aug. 4	Trieste, Italy	Terminal	Crude oil	F		29.7	13
243		Weirton, WV	Coke plant	EX		21d, 20i		5, 10
244		Yokkaidi, Japan	Chemical plant	TOX		76d, 978i		10
245	1973 Feb. 22	Austin, TX	Pipeline	NGL	VCE	6d, many injured		3, 6, 9, 10, 12
246	May 24	Benson, AR	Rail cars	Munitions	HEX			
247	May 23	Cologne, FRG	PVC plant	VCM	EX	4d, 2i		2, 5, 10
248	Dec. 27	Freeport, TX	Tank	Ethylene oxide	VCF	29i		10
249	Sep. 6	Gladbeck, FRG	Oxidation plant	Cumene, etc.	F			5, 10
250	Oct. 8	Goi, Japan	Polypropylene plant	Hexane, propylene	VEEB	4d	18.9	13, 14
251	Jul. 5	Kingman, AZ	Rail tank car	Propane	BLEVE	13d, 95i		10, 11
252		Lodi, NJ	Reactor	Methanol	VCF	7d		5, 10
253	Mar. 5	Loos, BC	Rail tank car	Chlorine	TOX	0d		3, 10
254	Dec. 6	McPherson, KS	Pipeline	Ammonia	TOX	0d		3, 10
255	Oct. 28	Noatsu, Japan	Vinyl chloride plant	VCM	VCE	1d		14
256	Jul. 13	Potchefstroom, South Africa	Storage vessel	Ammonia	TOX	18d, 65i		3, 5, 10, 11, 15
257	Oct. 24	Sheffield	Gas works	Towns gas	EX	4d, 24i		5, 10, 11
258	Feb. 1	St-Amand-les-Eaux	Road tanker	Propane	VCE	9d, 37i		5, 8, 10, 12
259	Aug. 24	St Croix, Virgin Islands	Hydrodesulphurizer	Hydrogen, HCs	F		28.4	13
260	Oct. 28	Shinetsu, Japan	Chemical plant	VCM	VCE	1d, 23i		5, 6, 8, 10
261	Feb. 10	Staten Island, NY	Storage tank	LNG residues	F	40d		10, 11, 15
262	Jul. 8	Tokuyama, Japan	Ethylene plant reactor	Ethylene	VCE	1d, 4i	40.0	5, 10, 13, 14
263	Nov. 6	Ventura County, CA	Rail tank car	LPG	REL	2d, 4i		12, 15
264	1974 Jan. 17	Aberdeen, UK	Road tanker		FB			11
265	Sep. 5	Barcelona, Spain	Chemical plant	VCM, ethylene dichloride	VCF			6, 10
266	Jun. 9	Bealeton, VA	Pipeline	Gas	F	0d		
267	Nov. 29	Beaumont, TX	Isoprene plant	Isoprene	VCE	2d, 10i	36.6	13, 14
268	Apr. 17	Bielefeld, FRG			BLEVE			
269	Apr. 26	Chicago, IL	Storage tank	Silicon tetrachloride	TOX	0d		
270	Jun. 26	Climax, TX	Rail tank car	VCM	VCE	7d		2, 3, 6, 10, 12, 14

Table A1.2 *(continued)*

No.	*Date*	*Location*	*Plant/ transport*	*Chemical*	*Event*	*Deaths/ injuries*	*Cost* (million US$)	*References*
271	Jul. 7	Cologne, FRG	Vinyl chloride plant	VCM	VCE			14
272	Jul. 19	Decatur, IL	Rail tank car	Isobutane	VCE	7d, 152i		2, 6, 9, 10, 11, 12, 14
273	Aug. 30	Fawley, UK	Polyethylene plant	Ethylene	VCE			14
274	Jun. 1	Flixborough, UK	Caprolactam plant	Cyclohexane	VCE	28d, 104i	412. 2	2, 3, 5, 6, 8, 10, 11, 13, 14, 15
275	Sep. 13	Griffith, IN	Cavern storage	Propane	F	0d		6, 10
276	Jan. 4	Holly Hill, FL	Road tanker	Propane	VCE	0d		5, 6, 10, 14
277	Sep. 21	Houston, TX	Rail tank car	Butadiene	VCE	1d, 235i		6, 10, 12, 14
278	Aug. 17	Los Angeles, CA	Loading terminal	Organic peroxides	EX	0d		5, 10, 15
279	Mar. 2	Munroe, LA	Pipeline	Natural gas	EX, F	0d		
280	Feb. 6	Omaha, NE	Chlorine vaporizer	Chlorine	TOX			5
281	Feb. 12	Oneonta, NY	Rail tank car	LPG	BLEVE	25i		10
282	Aug. 25	Petal, MO	Salt dome storage	Butane	VCE	24i		6, 10, 14, 15
283	Jul. 18	Plaquemine, LA	Cracking plant	Propylene	VCF(?)			6, 8, 10
284		Rotterdam, Netherlands	Petrochemicals plant	HC	F			5
285		Pitesti. Roumania[c]	Ethylene plant	Ethylene	VCE	≈100d		5, 14
286		Texas	Chemical plant	Pentanes	VCE	2d		6
287	Aug. 6	Wenatchee, WA	Rail tank car	Monomethylamine nitrate	DET	2d, 113i		5, 10, 12
288	Jan. 11	West St Paul, MN	Storage vessel	LPG	BLEVE	4d, 6i		10
289	Jul. 21	Zaluzi, Czechslovakia	Ethylene plant	Ethylene	VCE	14d, 79i		5, 6, 10, 14
290	1975 Feb. 10	Antwerp, Belgium	Polyethylene plant	Ethylene	VCE	6d, 13i	57. 8	3, 5, 6, 8, 10, 13, 14
291	Mar. 16	Avon, CA	Refinery	Oil	F		21. 2	13
292	Nov. 7	Beek, Netherlands	Petrochemical plant	Propylene	VCE	14d, 107i	46. 7	3, 5, 6, 8, 10, 11, 13, 14, 15
293	Nov. 21	Cologne, FRG	Cyclic hydroformer	Hydrogen, naphtha	VCE	0d		6, 14
294		Deer Park, TX	Polyethylene plant	Ethylene	VCF	1d, 4i		10
295	Sep. 1	Des Moines, IA	Rail tank car	LPG	BLEVE	3i		
296	May 13	Devers, TX	Pipeline	LPG	F	4d		9, 10, 12
297	Apr. 30	Eagle Pass, TX	Road tanker	LPG	FB	17d, 34i		10, 12, 14
298	Aug. 31	Gadsden, AL	Tank farm	Gasoline	'BLEVE'	4d, 28i		10
299	Apr. 5	Ilford, UK	Electrolysis plant	Hydrogen, oxygen	EX	1d, 3i		10
300	Jan. 17	Lima, OH	Terminal	Crude oil	F			
301		Louisiana		Propane	REL			
302	Jan. 31	Marcus Hook, PA	Oil tanker, tankship	Oil, phenol	F		16.0	13
303		Marseilles, France			IE	1d, 3i		5
304	Dec. 14	Niagara Falls, NY	Road tanker	Chlorine	TOX	4d, 80i		10
305	Aug. 17	Philadelphia, PA	Tank farm	Crude oil vapours	VCF, EX	8d, 2i	26. 5	5, 10, 13
306	Aug. 2	Romulus, MI	Pipeline	REL				
307	Sep. 5	Rosendaal, Netherlands		Gasoline	VCE			14

308	Nov. 4	Scunthorpe, UK	Hot metal ladle	Hot metal, water	EX	11d, 15i		10
309	Dec. 4	Seattle, WA	Road tanker		F			10
310		South Africa		Methane	F	7d, 7i		5, 10
311	Sep. 3	Texas City, TX	Pipeline	Ammonia	TOX			10
312	Dec. 2	Watson, CA	Hydrogen plant	Hydrogen	VCE			14
313	1976 Dec. 10	Baton Rouge, LA	Storage vessel	Chlorine	TOX	3i		5, 10, 11, 15
314	Nov. 26	Belt, MT	Rail tank car	LPG	BLEVE	22i		10, 12
315	Aug. 12	Chalmette, LA	Refinery	Ethyl benzene	EX	13d, 2i		10
316	May 7	Enid, OK	Pipeline	Ammonia	TOX			10
317	Aug. 31	Gadsden, AL			FB	3d, 28i		10
318	May 24	Geismar, LA	Reactor	Ethylene oxide, etc.	IE	56i	17.3	10, 13
319	Sep. 2	Haltern, FRG	Storage vessel	Carbon dioxide	TOX			12
320	May 11	Houston, TX	Road tanker	Ammonia	TOX	6d, 178i		9, 10, 11, 12
321	Jun. 27	Kings Lynn	Reactor	Feed additive reaction mixture	IE	1d		10, 15
322	Aug. 6	Lake Charles, LA	Refinery	Isobutane	VCE	7d		10
323	Jan. 16	Landskrona, Sweden *Rene 16*	Loading terminal	Ammonia	TOX	2d		9, 10
324	Oct. 15	Longview, TX	Ethanol plant	Ethylene	VCE	1d		14
325	Jun. 16	Los Angeles, CA	Pipeline	Gasoline	VCE	9d, many injured		8, 10, 12, 15
326	Dec. 17	Los Angeles, CA *Sansinena*	Terminal	Crude oil	EX		23.2	13
327	Sep. 26	Manfredonia, Italy	Absorption column	Arsenic compounds, etc.	TOX	30i		10
328		Puerto Rico	Storage	Pentanes	VCF	1d		6
329	Aug. 30	Plaquemine, LA	Surge tank	Oil	IE		23.2	13
330	Dec. 7	Robstown, TX	Compressor station	Natural gas	VEEB		23.2	13
331		Sandefjord, Norway		Flammable liquid	IE	6d		5
332	Jul. 10	Seveso	Reactor	Trichlorphenol reaction mixture, including TCDD	IE	0d[(d)]		5, 10, 11, 15
333	Feb.	Texas	Pipeline	Ethylene	VCF	1d, 15i		6
334	Sep. 11	Westoning, UK	Road tanker	Petrol	EX	3i		8
335	1977 May 11	Abqaiq, Saudi Arabia	Pipeline	Crude oil	F		99.2	13
336	Jun.4	Abqaiq, Saudi Arabia	NGL plant	Fuel gas	VCF		19.3	13, 14
337	Feb. 2	Baton Rouge, LA	Chemical works	Chlorine	TOX	10i		10
338	Oct. 17	Baton Rouge. LA	Preheat furnace	Oil	EX		17.0	13
339	Jan. 27	Baytown, TX	Tanker	Gasoline	VCE	3d		14
340	Sep. 24	Beattyville, KY	Road tanker	Gasoline	F	7d, 6i		12
341	Jan. 4	Braehead, Renfrew, UK	Warehouse	Sodium chlorate	EX	13i		5, 10
342	Dec. 8	Brindisi, Italy	Ethylene plant	Light HCs	VCE	3d, 22i	51.5	5, 10, 13, 14
343		Cassino, Italy		LPG	IE	1d, 9i		5
344	Feb. 20	Dallas, TX	Rail tank car	Isobutane	VCE	1i		6, 10, 14
345	Jul. 8	Fairbanks, AK	Pipeline	Crude oil	F	1d	72.1	10, 13
346		Galveston, TX	Grain silo	Grain dust	DEX	15d		10, 11
347		Gela, Italy		Ethylene oxide, glycol	IE	1d, 1i		5, 10
348	Dec. 28	Goldonna, LA	Rail tank car	LPG	FB	2d, 9i		10, 12
349		India		Hydrogen	IE	20i		5

Table A1.2 *(continued)*

No.	*Date*	*Location*	*Plant/ transport*	*Chemical*	*Event*	*Deaths/ injuries*	*Cost* (million US$)	*References*
350		Jacksonville, USA		LPG	F			5
351		Mexico		Ammonia	TOX	2d, 102i		10
352		Mexico		VCM		90i		
353	Dec. 10	Pasacabolo, Columbia	Fertiliser plant	Ammonia, etc.	TOX, VCE	30d, 22i		5, 10
354	Nov. 9	Pensacola, FL	Rail tank car	Ammonia	TOX			12
355	Mar. 18	Port Arthur, TX	Stabilizer unit	Propane	VCE	4d		14
356	Jun. 19	Puebla, Mexico			VCF			15
357	Sep. 24	Romeoville, IL	Tank farm	Diesel fuel, gasoline	F		14. 6	13
358	Jul. 20	Ruff Creek, PA	Pipeline	Propane	VCF	2d		9, 12
359		Taiwan		VCM	F	6d, 10i		5, 10
360	Apr. 3	Umm Said, Qatar	Gas plant	LPG	F	7d, 13+i	139	5, 8, 10, 13, 14, 15
361		Westwego, LA	Grain silo	Grain dust	DEX	36d, 10i		5, 11, 15
362	1978 Apr. 15	Abqaiq. Saudi Arabia	Gas plant	(1) Methane, (2) LPG	(1) F, (2) VCE		90. 8	13, 14
363		Baltimore, MD	Sulphur trioxide		TOX	100i		5, 10
364		Chicago, IL	Loading terminal	Hydrogen sulphide	TOX	8d, 29i		10
365	Jan. 12	Conway, KS	Pumping station	LPG	EX			10
366	Oct. 3	Denver, CO	Cat polymerization unit	Propane	VCE	3d	37. 1	13, 14
367	Aug. 4	Donnellson, IA	Pipeline	LPG	FB	3d, 2i		9, 10, 12
368	Sep. 16	Immingham, UK	Ammonia plant	Syngas	VCE			14
369	May 29	Lewisville, AR	Rail tank car	VCM	FB	2i		10
370		Mexico City, Mexico	Road tanker	Propylene	F	12d		
371	Sep. 27	Oviedo Province, Spain	Rail tank car	Gasoline	EX, F	7d		10, 12
372	Oct. 30	Pitesti, Roumania	Gas concentration unit	Propane, propylene	VCE			14
373	Feb. 11	Poblado Tines, Mexico	Pipeline	Natural gas	VCE	40d		14
374		St Marys, WV	Cooling tower		Structural collapse	51d		
375	Jul. 11	San Carlos, Spain	Road tanker	Propylene	VCF	216d, 200i		10, 11, 12, 15
376	May 30	Texas City, TX	Storage vessel	LPG	BLEVE	7d, 10i	93.0	13
377	Jul. 16	Tula, Mexico	Road tanker	Butane	EX	12		
378	Feb. 24	Waverly, TN	Rail tank car	Propane	BLEVE	16d, 43i		5, 10, 12, 15
379	Jul. 15	Xilatopic, Mexico	Road tanker	Butane	VCF	100d, 220i		10, 12
380	Feb. 26	Youngstown, FL	Rail tank car	Chlorine	TOX	8d, 114i		5, 10, 12
381	1979 Jan. 8	Bantry Bay, Eire	Oil tanker	Crude oil	EX	50d	31.9	9, 11. 13
382	Jul. 18	Bayonne, NJ	Rail tank car	Chlorine	TOX			10
383	Feb. 6	Bremen, FRG	Flour mill	Flour	DEX	14d, 17i		11
384	Jan. 6	Burghausen, FRG	Chemical plant	Hydrogen sulphide	TOX			10
385	Oct. 6	Cove Point, MD	Pipeline	LNG	VEEB	1d, 1i		12
386	Apr. 8	Crestview, FL	Rail tank cars	HMs	TOX	14i		
387	Sep. 1	Deer Park, TX	Tankship *Chevron Hawaii*	Distillate	EX		105.4	13
388	Nov. 1	Galveston Bay, TX	Oil tanker	Crude oil	EX	32d		10
389	Dec. 11	Geelong, Australia	Crude unit	Oil	F		17.4	

390	Aug. 30	Good Hope, LA	Tank barge *Panama City*	Butane	FB	12d, 25i	16.4	9, 11, 13
391		Hamburg, FRG	Grain silo	Grain dust	DEX	2i		
392	Oct. 17	Lerida, Spain	Grain silo	Grain dust	DEX	7d		10
393	Mar. 20	Linden, NJ	Cat cracker	LPG	VCF		27. 1	13
394	Nov. 10	Mississauga, Ont.	Rail tank car	Chlorine	TOX			9, 10, 11,15
395	Aug.	Orange, TX	Pipeline	LPG	EX	1d, 1i		12
396	Sep. 8	Paxton, TX	Rail tank car	Chemicals	BLEVE	8i		
397	Sep. 4	Pierre Port, LA	Pipeline	LNG	VCF			10
398	Dec. 11	Ponce, Puerto Rico	Dimerizer vessel	HCs	IE		23.3	13
399	Apr. 19	Port Neches, TX	Oil tanker *Seatiger*	Crude oil	EX		49.6	13
400	Jan. 11	Rafnes, Norway	Chemical plant	Chlorine	TOX			10
401	Jul. 28	Sauget, IL	Reactor	Reaction mixture	IE		11.9	13
402	Jul. 21	Texas City, TX	Alkylation unit	Propane	VCE		37.2	13, 14
403	Sep. 18	Torrance, CA	Cat cracker	C_3–C_4 HCs	VCE			14
404	Jun. 26	Ypsilanti, MI	Storage	Propane	VCE			14
405	1980 Jan. 3	Avon, CA	Refinery		CD		20.9	13
406	Jan. l	Barking, UK	Warehouse	Sodium chlorate	F, EX			
407	Jan. 30	Bayamon, Puerto Rico	Pipeline	Petroleum products	EX	1d		12
408	Jan. 20	Borger, TX	Alkylation unit	Light HCs	VCE	41i	48.5	10, 13, 14, 15
409	Feb. 26	Brooks, Alberta	Compressor station	Natural gas	EX		55.6	13
410	Dec. 31	Corpus Christi, TX	Hydrocracker	HC	F		23.6	13
411	May 17	Deer Park, TX	Phenolacetone plant		F		25.8	13
412	Mar. 26	Enschede, Netherlands		Propane	VCE			14
413	Aug. 18	Gach Saran, Iran	Warehouse	Nitroglycerine	HEX	80d, 45i		10
414	Nov. 25	Kenner, LA	Road tanker	Gasoline	F	7d, 6i		10
415	Feb. 11	Longport, UK	Warehouse	LPG, etc.	F, EX			
416	Mar. 3	Los Angeles, CA	Road tanker	Gasoline	BLEVE	2d, 2i		
417	Oct. 8	Mexico City, Mexico	Loading terminal	Ammonia	TOX	9d, 28i		10
418	Jul. 26	Muldraugh, KY	Rail tank car	VCM	F	4i		10
419		Naples, Italy	Grain silo	Grain dust	DEX	8i		
420	Oct. 21	New Castle, DE	Polypropylene plant	Hexane, propylene	VCE	5d, 25i		10, 14
421	Jul. 15	New Orleans, LA	Pipeline	Natural gas	F			
422	Nov. 29	Ortuella, Spain	Storage vessel	Propane	EX	51d		10
423	Jul. 24	Rotterdam, Netherlands	Oil tanker *Energy Concentration*	Crude oil	Ship split apart			9
424	Jul. 23	Seadrift, TX	Ethylene oxide reactor	Reaction mixture	DET		16.4	13
425	Jun. 26	Sydney, Australia	Refinery furnace	Oil	EX		25.0	13
426	Nov. 20	Wealdstone, UK	Storage vessel	Propane	REL	0d, 1i		
427	1981 Feb. 11	Chicago Heights, IL	Reactor weigh tank	Tank contents	VEEB		17.4	13
428	Oct. 1	Czechoslovakia	Ammonia plant	Syngas	VCE			14
429	May 8	Gothenburg, Sweden	Pipeline	Propane	VCE	1d, 2i		14
430	Jul. 19	Greens Bayou, TX	Reactor	Herbicide reaction mixture	IE		13	13
431	Aug. 1	Montana, Mexico	Rail tank car	Chlorine	TOX	17d, 280i		11,12
432	May 15	San Rafael, Venezuela	Pipeline	LPG	EX	18d, 35i		12
433	Aug. 20	Shuaiba, Kuwait	Tank farm	Oil	F	1d, 1i	124	13

Table A1.2 *(continued)*

No.	*Date*	*Location*	*Plant/ transport*	*Chemical*	*Event*	*Deaths/ injuries*	*Cost (million US$)*	*References*
434	Sep. 6	Stalybridge, UK	Solvent recovery unit	Hexane	EX			15
435	1982 May 3	Caldecott Tunnel, Oakland, CA	Road tanker	Gasoline	F	7d		
436	Dec. 19	Caracas, Venezuela	Storage tank	Oil froth	F	150d, >500i	58.9	13, 15
437	Apr. 18	Edmonton, Alberta	Compressor	Ethylene	VEEB		24.6	11, 13
438	Dec. 29	Florence, Italy	Road tanker	Propane	EX	5d, 30i		12
439	Jan. 20	Fort McMurray, Alberta	Compressor	Hydrogen	F		24.6	13
440	Oct. 4	Freeport, TX	Transformer	Oil	F		17.2	13
441	Nov. 4	Hudson, IA	Pipeline	Natural gas	EX	5d		
442	Mar. 31	Kashima, Japan	Desulphurization unit	HCs	F		16.3	13
443	Sep. 28	Livingston, LA	Rail tank car	Flammables, toxics	DEL BLEVE	0d, 0i		
444	Feb. 13	Morley, UK	Warehouse	Herbicides, etc.	F, POL			9.11
445	Jan. 17	Moselle River, France	Pipeline	Carbon monoxide	TOX	5d		11, 12
446	Mar. 9	Philadelphia, PA	Phenol plant	Cumene	VCE		29.3	13
447	Oct. 1	Pine Bluff, AR	Pipeline	Natural gas	VCF			
448	Jun. 28	Portales, NM	Pipeline	Natural gas	DEL EX	6d		
449	Sep. 25	Salford, UK	Warehouse	Sodium chlorate	EX	60i		15
450	1983 Apr. 7	Avon, CA	Cat cracker	Recycle slurry	F		56.3	13
451	Jul. 30	Baton Rouge, LA	Rail tank car	VCM	F			
452	May 26	Bloomfield, NM	Compressor station	Natural gas	VEEB	2i		
453	Apr. 14	Bontang, India	LNG plant	LNG	IE		57.5	13
454	Apr. 3	Denver, CO	Rail tank car	Nitric acid	TOX			
455	Nov. 2	Dhurabar, India	Rail tank car	Kerosene	EX	47d		12
456	Aug. 30	Milford Haven, UK	Storage tank	Crude oil	F	0d, 20i	17.3	13, 15
457	Jul. l	Port Arthur, TX	Polyethylene bead plant		F		17.8	13
458	Jan. 7	Port Newark, NJ	Storage tank	Gasoline	VCE	1d	40.3	13, 14
459	May 26	Prudhoe Bay, AK	NGL surge drum	NGL	F		40.3	13
460	Mar. 15	West Odessa, TX	Pipeline	LPG	EX, F	6d		12
461	Sep. 30	Basile, LA	Gas plant	HCs	VCF		33.9	13
462	1984 May 23	Abbeystead, UK	Valve house	Methane	EX	16d, 28i		11, 12
463	Dec. 3	Bhopal, India	Storage tank	Methyl isocyanate	TOX	≈4000d		11, 15
464	Feb. 24	Cubatao, Brazil	Pipeline	Petrol	F	>100d, ≈150i		12
465	Aug. 15	Fort McMurray, Alberta	Coking unit	HCs	VCF		85.9	13
466	Mar. 8	Kerala, India	Cooling tower	HCs	EX		13.6	13
467	Dec. 13	Las Piedras, Venezuela	Hydrodesulphurizer	Oil	F		70.1	13
468	Nov. 19	Mexico City, Mexico	Terminal	LPG	VCF, BLEVE	≈650d, ≈6400i	22.5	11, 13, 15
469	Sep. 25	Phoenix, AZ	Pipeline	Natural gas	EX, F			
470	Jul. 23	Romeoville, IL	Absorption column	Propane	VCE, BLEVE	15d, 22i	143.5	13. 14, 15
471	Apr. 20	Sarnia, Ont.	Benzene plant	Hydrogen	VCE	2d		14
472	1985 Apr. 27	Beaumont, KY	Pipeline	Natural gas	F	5d, 3i		
473	Jul. 6	Clinton, IA	Ammonia plant	Syngas	VEEB		14.7	13
474	Jan. 18	Cologne, FRG	Ethylene plant	Ethylene	VCE			14

475	Feb. 19	Edmonton, Alberta	Pipeline	NGL	VCE			14
476	Jul. 23	Kaycee, WY	Pipeline	Aviation fuel	EX	1d, 6i		
477	Feb. 23	Jackson, SC	Rail tank car		REL			
478	Mar. 9	Lake Charles, LA	Reforming unit	Propane	VCE			14
479	Nov. 5	Mont Belvieu	Salt dome storage	Ethane, propane	VCE		44.8	13, 14
480	Dec. 21	Naples, Italy	Terminal		F		47.0	13
481	Jun. 9	Pine Bluff, AR	Rail tank car	HMs	REL			
482	May 19	Priola, Italy	Ethylene plant	HCs	F		72.8	13
483	Feb. 23	Sharpsville, PA	Pipeline	Natural gas	EX, F			
484	Nov. 21	Tioga, ND	Gas processing plant	HCs	IE, VCE		11.3	13
485	Jan. 23	Wood River, IL	Deasphalting–dewaxing unit	Propane	VCF		25.2	13
486	1986 Feb. 21	Lancaster, KY	Pipeline	Natural gas	F	3 burned		
487	Jun. 15	Pascagoula, MS	Distillation column	Aniline, etc.	EX			
488	Oct. 30	Schweizerhalle, Basel, Switzerland	Warehouse	Pesticides, etc.	F, POL			11
489	Feb. 24	Thessalonika, Greece	Oil terminal	Oils	F			
490	1987 Jul. 3	Antwerp, Belgium	Distillation column	Ethylene oxide	EX			14
491	Oct. 11	Fort McMurray, Alberta	Tar sand plant	Tar sand, diesel fuel	F		39.7	13
492	Mar. 22	Grangemouth, UK	Separator vessel	Hydrogen	F		87.9	13.15
493	Aug. 23	Lanzhou, China	Rail tank car	Gasoline	F	5d		12
494	Jun. 23	Mississauga, Ont.	Hydrotreater	Hydrogen, HCs	F		22.4	13
495	Nov. 14	Pampa, TX	Acetic acid plant	Acetic acid, butane	VCE	3d	24.1	13, 14, 15
496	Jun. 2	Port Herriot, France	Storage	Oil	F	2d, 8i		
497	Aug. 15	Ras Tanura, Saudi Arabia	Gas plant	Propane	VCE		67.2	13, 14
498	Nov. 24	Torrance, CA	Aklylation unit	HCs	F		16.4	13
499	1988 Jul. 30	Altoona, IA	Rail tank car	HMs	REL			
500	Jun. 4	Arzamas, USSR	Railway station	Explosives	HEX	73d, 230i		12
501	Apr. 7	Beek, Netherlands	Polyethylene plant	Ethyiene	VCE			14
502	Jan. 2	Floreffe, PA	Storage tank	Diesel fuel	REL		14.5	13
503	May 5	Norco, LA	Cat cracker	C_3 HCs	VCE	7d, 28i	327	13, 14, 15
504	Jun. 8	Port Arthur, TX	Storage	Propane	F		17.4	13
505	Oct. 25	Pulua Merlimau	Storage tanks	Naphtha	F		13.1	13
506	Sep. 8	Rafnes, Norway	VC plant	VCM, ethylene dichloride	VCE		12.0	13, 14
507	1989 Mar. 7	Antwerp, Belgium	Distillation column	Ethylene oxide	EX		80.1	13, 14
508	Dec. 24	Baton Rouge, LA	Refinery	Ethane, propane	VCE		44.7	13, 14
509	Jul. 22	Freeland, MI	Freight train	HMs	REL			
510	Feb. 2	Helena, MT		HMs	REL			
511	Mar. 20	Jonova, Lithuania	Ammonia storage	Ammonia	IE, F, TOX	7d		
512	Jul. 2	Minnebeavo, USSR	Gasoline plant	Propane	VCE	4d		14
513	Sep. 5	Martinez, CA	Hydrotreater	Hydrogen, HCs	F or EX		52.0	13
514	Jun. 7	Morris, IL	Distillation column	Propylene	VCF		41.6	13
515	Oct. 23	Pasadena, TX	Polyethylene plant	Isobutane	VCE	23d, ≈103i	>500	13, 14, 15
516	Mar. 22	Peterborough, UK	Road vehicle	Explosives	EX	1d, 107i		
517	Apr. 10	Richmond, CA	Refinery	Hydrogen	F		93.6	13
518	Oct. 3	Sabine Pass, TX	Pipeline	Natural gas	REL			

Table A1.2 *(continued)*

No.	*Date*	*Location*	*Plant/ transport*	*Chemical*	*Event*	*Deaths/ injuries*	*Cost (million US$)*	*References*
519	May 25	San Bernadino, CA	Pipeline	Gasoline	F	2d, 3i		
520	Sep. 18	St Croix, Virgin Islands	Refinery	HCs	HUR		62.4	13
521	Jun. 3	Ufa, USSR	Pipeline	NGL	VCE	645d, ≈500i		14, 15
522	Feb. 14	Urdingen, Germany	Paint plant	Reaction mixture	IE		41.6	13
523	1990 Sep. 24	Bangkok, Thailand	Road tanker	LPG	VCF	68d, >100i		
524	Sep. 16	Bay City, TX	Tankship *Jupiter*	Gasoline	EX	1d		
525	Nov. 3	Chalmette, LA	Hydrocracker	HCs	VCE		15.3	13
526	Jul. 5	Channelview, TX	Wastewater storage tank	Flammables	EX		12.2	13
527	Jul. 19	Cincinnati, OH	Acrylic resins plant	Xylene, solvent	VEEB		23.5	13, 14
528	Nov. 25	Denver, CO	Storage	Jet fuel	F		30.6	13
529	Nov. 6	Nagothane, Bombay, India	Ethylene plant	Ethane, propane	VCE	31d	22.4	13,14
530	Mar. 3	North Blenheim, NY	Pipeline	Propane	VCF	2d, 7i		
531	Nov. 15	Porto de Leixhos, Portugal	Deasphalting unit	Propane	VCE			14
532	Nov. 30	Ras Tanura, Saudi Arabia	Refinery	HCs	F		23	13
533	Jul. 10	Rio de Janeiro, Brazil	Boiler	Steam	EX		10.2	13
534	Mar. 30	Stanlow, UK	Reactor	2-4 dichloronitro–benzene reaction mixture	IE	1d, 5i		15
535	May 14	Tomsk. USSR	Ethylene plant	Gas	VCE			14
536	Apr. 1	Warren, PA	FCC	LPG	EX, F		25.5	13
537	1991 Jun. 17	Charleston, SC	Reactor	Reaction mixture	IE		10	13
538	Mar. 11	Coatzacoala, Mexico	Chlorine plant		EX		150	13
539	Aug. 21	Coode Island, Australia	Storage tanks	Acrylonitrile, etc.	IE	0d	24	13
540	Jun. 20	Dhaka, Bangladesh	Stripping column		EX		70	13
541	Sep. 7	Haifa, Israel	Chemical plant	Chemicals	F		15	13
542	Jul. 14	Kensington, GA	Synthetic rubber	Butadiene plant	VCE			14
543	Mar. 3	Lake Charles, LA	FCC	Hot oil-water	IE		23	13
544	Mar. 11	Pajaritos, Mexico	Vinyl chloride plant	Propane	VCE	3d		14
545	Mar. 12	Seadrift, TX	Ethylene oxide plant	Ethylene oxide	VCE	1d		14
546	May 1	Sterlington, LA	Nitroparaffin unit		EX		105	13
547	Apr. 13	Sweeny, TX	Reactor	HCs	EX		50	13
548	1992 Oct. 16	Sodegaura, Japan	Refinery	Hydrogen	VCE	10d, 7i		
549	1993 Feb. 2	Griesheim, Germany	Reactor	Reaction mixture	TOX	0d		
550	1994 Nov. 2	Dronka, Egypt	Fuel storage	Aviation, diesel, fuel	F	≈410d		
551	1995 Apr. 27	Ukhta, Russia	Gas pipeline	Gas	F			

Alternative names

Walsum, 1952: *aka* Duisburg-Walsum (often referred to as Wilsum); Berlin, 1962: *aka* New Berlin; Doe Run, 1962: *aka* Brandenburg; Glendora, 1969 *aka* Black Bayou Jct; Rio de Janeiro, 1972: *aka* Duque de Caxais or Sao Paulo; West St Paul, 1974: *aka* St Paul; Des Moines, 1975: *aka* Angleton; Pasacabolo, 1977: *aka* Cartagena; Denver, 1978: *aka* Commerce; Donnellson, 1978: *aka* Fort Madison; San Carlos, 1978: *aka* Los Alfaques; Caracas, 1981: *aka* Tacao; Montanas, 1981: *aka* San Luis Potosi; Stalybridge, 1981: *aka* Chemstar Ltd: Caracas, 1982: *aka* Tacao; Salford, 1982: *aka* B&R Hauliers; Cubatao, 1984; *aka* Vila Soca; Mexico City, 1984: *aka* San Juan Ixhautepec; Schweizerhalle, 1986: *aka* Sandos; Ras Tanura, 1987: *aka* Juaimah; Floreffe, 1988: *aka* Ashland; Rafnes, 1988: *aka* Bamble: Nagothane, 1990: *aka* Maharastra; Bombay; Coode Island, 1991: Melbourne

Abbreviations: FCC = fluid catalytic cracker; HC = hydrocarbon; HM = hazardous material; VCM = vinyl chloride monomer

Event abbreviations: ANEX = ammonium nitrate explosion; BLEVE = boiling liquid expanding vapour explosion; CD = criminal damage caused by vandalism, sabotage, etc.; DEL = delayed; DET = detonation (internal explosions only); DEX = dust explosion; EQK = earthquake damage; EX = explosion; F = fire; FB = fireball; HEX = high explosive explosion; HUR = hurricane damage; IE = internal explosion; POL = pollution; REL = release; TOX = toxic release; VCE = vapour cloud explosion; VCF = vapour cloud fire; VEEB = vapour escape into, and explosion in, building

Costs

Costs are in US dollars and are taken from the M&M compilations. The great majority are the trended costs as given in the thirteenth, 1990 edition by Mahoney (1990) and are thus in 1990 US dollars. Some values not included in the 1990 edition but given in the eleventh edition by Garrison (1988) have been converted to 1990 values, using a factor of 1.1; these are marked with an asterisk. Values for incidents in 1990 and 1991 given in the fourteenth 1992 edition by M&M (1992) are in 1991 US dollars.

Principal references

(1) Simmons, Erdmann and Naft (1974); (2) Eisenberg, Lynch and Breeding (1975); (3) V. C. Marshall (1977b); (4) Harvey (1979b); (5) HSE (1978b); (6) Slater (1978a); (7) Gugan (1979); (8) D. J. Lewis (1980d); (9) Harvey (1984); (10) Kier and Müller (1983); (11) V. C. Marshall (1987); (12) Haastrup and Brockhoft (1990); (13) M&M (Garrison (1988b); Mahoney (1990); and M&M (1992)); (14) Lenoir and Davenport (1993); (15) D. J. Lewis (1993)

Additional references

1; 2; 3; 4 J. R. Nash (1976); 5; 6; 7; 8 Assheton (1930); 9 Billings and Copland (1992); 10 Assheton (1930); J. R. Nash (1976); 11 Anon, (n. d. b); Ministry of Home Security (n. d. a); Sainsbury (1977); 12; 13; 14; 15; 16 Slater (1978b); 17; 18 BASF (1921); Comment *et al.* (1921); NBFU (1948); 19; 20; 21; 22; 23 Anon. (1928); N. C. Harris {1981b); 24; 25; 26; 27; 28 Anon. (1933a, b); 29; 30; 31; 32; 33; 34 P. Reed (1939); Armistead (1959); 35; 36 Römcke and Evensen (1940); 37; 38 NBFU (1948); J. R. Nash (1976); 39 Slater (1978b); Strehlow (1973b); 40 Stahl. Strassman and Richard (1949); J. R. Nash (1976); Giesbrecht *et al.* (1981); D. J. Lewis (1983); 41 J. R. Nash (1976); Patience (1989); 42 Chasis *et al.* (1947); 43 Moulton (1944); Coroner (1945); Elliott *et al.* (1946 BM RI 3867); Burgoyne (1965b); Strehlow (1973b); J. R. Nash (1976); Marshall (1983 IPB 52); 44 Anon. (1952–53); 45 J. Reed (1977); Anon. (1992 LPB 103); V. C. Marshall (1992 LPB 105); 46; 47 J. R Nash (1976); 48; 49 J. R. Nash (1976); 50; 51; 52; 53; 54 Kintz. Jones and Carpenter (1948 BM RI 4245); NBFU (1948); Wheaton (1948); Blocker (1949); Blocker and Blocker (1949); J. R. Nash (1976); 55 BASF (1948); Stahl, Strassman and Richard (1949); Giesbrecht *et al.* (1981); D. J. Lewis (1983); 56; 57; 58; 59; 60 Anon. (1949–50); 61; 62; 63; 64; 65; 66 H. E. Watts (1951); Anon. (1952); Kletz (1983 LPB 52); 67; 68 NBFU and FIRONT (1952); 69; 70 Jenkins and Oakshott (1955); Strehlow (1973b); D. J. Lewis (1980); Alderson (1982 SRD R246); 71 NFPA (1957); 72; 73; 74; 75; 76; 77; 78; 79; 80; 81; 82; 83 Woodworth (1955); R.B. Jacobs *et al.* (1957, 1973); Randall *et al.* (1957); 84; 85; 86; 87 Walker (1973); J. R. Nash (1976); 88; 89; 90; 91; 92 Lindley and Brown (1958); 93 Selway (1988 SRD 492); 94; 95; 96; 97; 98; 99; 100 Anon. (1959a); Woodworth (1958); 101; 102; 103 Anon. (1960–61); Slater (1978b); Strehlow (1973b); Hymes (1985 LPB 65); 104 Schmitt (1964); 105; 106 Cronan (1960c); 107 Sakai (1964); 108 Chementator (1960 Nov. 14, 106); 109 Chementator (1960 Dec. 12, 69); F. C. Price (1960); 110; 111; 112; 113 Joyner and Durel (1962); 114; 115; 116; 117 Walls (1963–64, 1964a); Strehlow (1973b); Strehlow and Baker (1976); 118; 119 Troyan and Levine (1968); 120; 121; 122; 123; 124 Laney (1964); Vervalin (1973e); 125; 126 Chementator (1962 May 28, 68); 127; 128; 129; 130; 131; 132; 133; 134; 135 Walls (1964b); 136; 137; 138; 139 Chementator (1964 Feb. 3, 36); 140 Bulkley and Jacobs (1966); 141; 142; 143; 144; 145; 146; 147; 148; 149 Anon. (1967c); 150; 151; 152; 153 Chementator (1965 Sep. 13, 105); Armistead (1966, 1973); 154 Chementator (1965 Mar. 29, 26; Aug. 2, 41); FPC (1966); 155; 156; 157; 158 Anon. (1966g, h); Strehlow (1973b); Vervalin (1973e); Kletz (1974e, 1975d, 1977d); Anon. (1987 LPB 77, p. 1); Selway (1988 SRD R492); 159; 160 Chementator (1966 Jan. 31, 18); 161 Chementator (1966 Oct. 24, 55); Anon. (1967b); Fire J. Staff (1967, 1973d); 162; 163 McCarey (1966); 164 Anon. (1966c); 165; 166; 167; 168; 169; 170; 171 Chementator (1967 Aug. 28, 56); Goforth (1970); NFPA (1973); Strehlow (1973b); Vervalin (1973e); Strehlow and Baker (1976); 172; 173; 174; 175; 176 NTSB (1968 RAR); 177; 178; 179 Medard (1970); 180; 181 Fontein (1968); Min. of Social Affairs and Public Health (1968); Strehlow (1973b); Woodworth (1973); Strehlow and Baker (1976); 182 Slater (1978b); 183; 184; 185; 186 J. E. Browning (1969a); NTSB (1971 RAR-71-02); 187 Anon. (1970a); 188; 189; 190; 191 NTSB (1970 RAR-70-02); Dowell (1971); Kogler (1971); Strehlow and Baker (1976); 192 NTSB (1971 PAR-71-01); 193 NTSB (1969 RAR); 194; 195; 196; 197 R H. Freeman and McReady (1971); Jarvis (1971); Keister, Pesetsky and Clark (1971); Griffith and Keister (1973); 198 Anon. (1970e); 199 Anon. (1969b); 200 Anon. (1971d); 201; 202; 203; 204 MacArthur (1972); 205 NTSB (1970 HAR-71-06); 206; 207 Watrous (1970); NTSB (1972 RAR-72-02); Strehlow (1973b); Vervalin (1973e); Strehlow and Baker (1976); D. J. Lewis (1991 LPB 101); 208; 209; 210 NTSB (1971 PAR-71-02); 211; 212; 213; 214 Chementator (1970 Jun. 1, 63); 215 NTSB (1972 PAR-72-01); Burgess and Zabetakis (1973 BM RI 7752); Strehlow (1973b); Strehlow and Baker (1976); 216; 217; 218; 219; 220 Chementator (1971 Jul. 26, 55); 221 NTSB (1972 HAR-72-03); Cremer and Warner (1978); 222 Chementator (1971 Nov. 1, 23); NTSB (1972 RAR-72-06); Slater (1978b); 223; 224 Sarsten (1972); 225; 226 Lauderback (1975); 227; 228; 229 W. B. Howard (1975b); Slater (1978b); Stueben and Ball (1980); Matsuz and Sadler (1994); 230; 231; 232 NTSB (1971 HAR-72-05); 233; 234; 235 NTSB (1973 RAR-73-01); Strehlow (1973b); Strehlow and Baker (1976); 236 NTSB (1973 PAR-73-02); 237 NTSB (1973 HAR-73-03); Strehlow and Baker (1976); 238; 239 NTSB (1973 HAR-73-04); 240 Selway (1988 SRD R492); 241; 242; 243 Chementator (1973 Jan. 8, 51); D. J. Lewis (1989c); 244; 245 NTSB (1973 PAR-73-04); Strehlow and Baker (1976); 246 (NTSB 1975 RAR-75-02); 247; 248; 249; 250; 251 Crawley (1982); Hymes (1985 LPB 65); 252; 253; 254 NTSB (1974 PAR-74-06); Luddeke (1975); 255; 256 Lonsdale (1975); 257; 258 Anon. (1973j); 259; 260; 261 Chementator (1973 Mar. 5, 28; 1974 Apr. 1, 17); US Congress (1973); D. J. Lewis (1989); 262 Chementator (1973 Jul. 23, 58; Nov. 12, 94); 263; 264; 265; 266 NTSB (1975 PAR-75-02); 267 Chementator (1974 Dec. 23, 21); 268; 269 Hoyle (1982): 270; 271; 272 NTSB (1975 RAR-75-04); Strehlow and Baker (1976); V. C. Marshall (1980d); 273; 274 R. J. Parker (1975): Strehlow and Baker (1976); 275 Adderton (1974); Strehlow and Baker (1976); 276; 277 NTSB (1975 RAR-75-07); Slater (1978b); 278 Sharry (1975); 279 NTSB (1975 PAR-75-01); 280; 281 NTSB (1974 RAR-74-04); 282 Anon (1974n); 283; 284; 285 Anon (1974k); Anon. (1974p); 286; 287 NTSB (1976 RAR-76-01); 288; 289; 290; 291; 292 Chementator (1975 Nov. 24, 17); Min. of Social Affairs (1976); van Eijnatten (1977); Slater (1978b); 293; 294; 295 NTSB (1976 RAR-76-08); 296 NTSB (1976 PAR-76-05); 297 NTSB (1976 HAR-76-04); 298; 299 HSE (1976b); 300 NTSB (1976 PAR-76-03); 301 Slater (1978b); 302; 303; 304; 305 Chementator (1975 Oct. 27, 53); Anon. (1975n); 306 NTSB (1976 PAR-76-07); 307; 308 HSE (1976a); 309 NTSB (1976 HAR-76-07); 310; 311;312; 313 Anon. (1976n); Rees (1982); 314 NTSB (1977 RAR-77-07); 315 Chementator (1976 Aug. 30, 49); 316; 317; 318; 319;320 Anon. (1976o); McMullen (1976); NTSB (1977 HAR-77-01); Fryer and Kaiser (1979 SRD R152); 321 HSE (1977b); 322; 323; 324; 325 Slater (1978b); 326 NTSB (1978 MAR-78-06); D. J. Lewis (1984c); 327; 328; 329; 330 NTSB (1977 PAR-77-03); 331; 332 Temple (1977b); 333; 334; 335; 336; 337; 338; 339; 340 NTSB (1978 HAR-78-04); 341 HSE (1979b); 342

Table A1.2 *(continued)*

Anon. (1977b); 343; 344; 345 NTSB (1978 PAR-78-02); 346; 347; 348; 349; 350; 351; 352; 353; 354 NTSB (1978 RAR-78-04); Stueben and Ball (1980); 355; 356 D. J. Lewis (1991 LPB 100); 357; 358 NTSB (1978 PAR-78-01); 359; 360 Anon. (1977c); Whelan (1977); Kletz (1988 LPB 81); 361 Anon. (1977p, q); Lathrop (1978); Nolan (1979); 362; 363; 364 Chementator (1978 Feb. 27, 64); 365; 366; 367 NTSB (1979 PAR-79-01); 368; 369 NTSB (1978 RAR-78-08); 370; 371; 372; 373; 374 Anon. (1978m); 375; 376 Selway (1988 SRD R492); 377; 378 Anon. (1978b); NTSB (1979 RAR-7941); D. J. Lewis (1992 LPB 105); 379; 380 Anon. (1978k); NTSB (1978 RAR-78-07); 381 Costello (1979); Anon. (1980a, v); 382; 383; 384; 385 NTSB (1980 PAR-80-02); van Meerbeke (1982); 386 NTSB (1979 RAR-79-11); 387 NTSB (1980 MAR-80-18); 388; 389; 390 NTSB (1980 MAR-80-07): 391; 392; 393; 394 Mississauga News (1979); Amyot (1980); Grange (1980); Fordham (1981 LPB 44); Lane and Thomson (1981); 395 NTSB Ann Rep. (1979); 396; 397; 398; 399 NTSB (1980 MAR-80-12); 400; 401; 402; 403; 404; 405; 406 HSE (1980a); Anon. (1980r); 407 NTSB (1980 PAR-80-6); 408; 409; 410; 411; 412; 413; 414; 415 HSE (1981b); 416 NTSB (1980 AR-80-05); 417; 418 NTSB (1981 RAR-81-01); 419; 420; 421 NTSB (1980 PAR-80-01); 422; 423; 424; 425; 426 HSE (1981c); 427; 428; 429 Nilson (1983b); 430; 431 Anon (1981 LPB 44); Anon. (1983 LPB 52); 432; 433; 434 HSE (1982a); Kletz (1983b); 435 NTSB (1983 HAR-83-01); 436 Garrison (1984 LPB 57); M. F. Henry (1986); 437; 438; 439; 440; 441 NTSB (1983 PAR-83-02); 442; 443 NTSB (1983 RAR-83-05); Anon. (1984t) 444; 445; 446; 447 NTSB (1983 PAR-83-03); 448 NTSB (1983 PAR-83-01); 449 HSE (1983b); 450; 451 NTSB (1985 RAR-85-08); 452 NTSB (1983 PAR-83-04); 458; 454 NTSB (1985 RAR-85-10); 455; 456 Dyfed County Fire Brigade (1983); Mumford (1984 LPB 57); Golec (1985); Steinbrecher (1986); 457; 458; 459; 460 NTSB (1984 PAR-84-01); 461; 462 Burgoyne (1985a); HSE (1985a); 463; 464 Anon (1984oo); 465; 466 Anon (1992 LPB 106); 467; 468 Pietersen (1985); Selway (1988 SRD R492); 469 NTSB (1985 PAR-85-01); 470; 471; 472 NTSB (1987 PAR-87-01); 473; 474; 475; 476 NTSB (1986 PAR-86-01); 477 NTSB (1985 RAR-85-12); 478; 479; 480; 481 NTSB (1986 RAR-86-04): 482; 483 NTSB (1985 PAR-85-02); 484; 485; 486 NTSB (1987 PAR-87-01): 487; 488 Anon. (1986v. w, y); Beck (1986); D. Williams (1986); Anon. (1987 LPB 75); Stallworthy (1987); 489 B. Browning and Searson (1964); 490 Mellin (1991 LPB 100); 491; 492 Anon. (1987l); Anon. (1988c, d); Anon. (1989b); HSE (1989a); Kletz (1989b); K. C. Wilson (1990a, b); 493; 494; 495; 496 Mansot (1989); 497; 498; 499 NTSB (1989 RAR-89-04); 500; 501; 502 Prokop (1988); Wilkinson (1991 SRD R530); Mellin (1992 LPB 106); 503; 504; 505; 506; 507 Anon (1991 LPB 100); 508; 509 NTSB (1991 RAR-91-04); 510 NTSB (1989 RAR-89-05); 511 Andersson (1991a, b); Kletz (1991a); Anon. (1992 LPB 107. p. 1): Anderson and Lindley (1992 LPB 107): Kukkonen *et al.* (1992); Wilday (1992 LPB 108, 109); Kukkonen *et al.* (1993). 512; 513; 514; 515 OSHA (1990a); Kletz (1991j); 516 HSE (1990b); Anon. (1991 LPB 98. p. 24); 517; 518 NTSB (1990 PAR-90-02); 519 NTSB (1990 RAR-90-02); 520; 521 Hofheinz and Kohan (1989); 522; 523 Anon. (1991 LPB 101, p. 19); 524 NTSB (1991 MAR-91-04); 525; 526 Anon. (1990d); 527; 528; 529 Indian Petrochemicals Corp. (1990); 530 NTSB (1991 PAR-91-01); 531; 532 Anon. (1990g); 533; 534 Kletz (1990 LPB 100); Mooney (1991); Redman and Kletz (1991); Cates (1992); van Reijendam *et al.* (1992); 535: 536; 537; 538; 539 Anon. (1991b); I. Thomas (1991); Anon. (1992c); Croudace (1993 LPB 112); 540; 541; 542; 543 Anon. (1991d); 544; 545 Viera, Simpson and Ream (1993); 546; 547; 548 High Pressure Gas Safety Institute of Japan (1993 LPB 116); 549 Ondrey (1993a, b); Schönfeld (1993); Vennen (1993); 550 Reuter (1994); 551 Anon. (1995)

Notes:

[a] Evidently including 'excess deaths', characteristic of a severe pollution incident.

[b] Gugan (1979) gives two incidents in 1966 in the FRG (his Nos 49 and 50). His No. 49 is named as Raunheim, while No. 50 has no more specific location. For both the date is given as January and the reference as Bradford and Culbertson (1967). Incident No. 50 is not quoted by Lenoir and Davenport (1993).

[c] Slater (1978a) cites an incident in Roumania in 1974 involving ethylene as a VCE with Id, 50i; this was given in the first edition of this book. The present entry relies on Anon. (1974k).

[d] The figure for deaths refers to prompt deaths; it does not include abortions.

A2 *Ashton, Manchester, 1917*
On 13 June 1917, a nitrator in an explosives works at Ashton, Manchester, went out of control and 'boiled' over, releasing hot acid onto the wooden staging and starting a fire. The fire took hold in the nitrator house. Spectators were attracted, including children. Soon after there was a large explosion, involving some 5 tons of TNT. The explosion ruptured two gasholders nearby, setting them on fire. The flames were described as half a mile high.

Some 100 houses were demolished. 46 persons died, including 24 employees and 11 children. More than 120 were injured sufficiently to need hospital treatment. The explosion made two craters, one at the location of the TNT drums and one at that of the drier and setting frays. The former was 90 ft×36 ft×5 ft deep and the latter 30 ft×15 ft and relatively shallow. Some 12,000 ft^2 of glass was replaced.

Billings and Copland (1992)

A3 *Halifax, Nova Scotia, 1917*
At about 8.48 a.m. on 6 December 1917, the French ammunition ship Mont Blanc was rammed by the Belgian relief ship Imo in Halifax Harbour, Nova Scotia. The Mont Blanc was carrying in her hold some 4,661,794 lb of picric acid, 450,000 lb of TNT and 122,960 lb of guncotton as well as 488,672 lb of benzol on deck. The Mont Blanc burst into flame and at 9.05 am there was a massive explosion. The inhabitants heard a 'thundering crash' and many ran to their windows to see what had happened. The noise was heard 191 miles away and some windows broke at a distance of 61 miles.

The explosion tore the ship apart and hurled fragments all over the city. The anchor shank fetched up 3–4 miles away. The blast caused almost complete destruction within a radius of about three-quarters of a mile. There was severe structural damage at distances ranging from 1 to 1.75 miles. It was estimated that 95% of the glass in the city was broken. Fires caused by overturned stoves broke out in many parts.

Many people were killed when buildings were demolished. Large numbers suffered injury from flying glass and at least 500 people were totally blinded. In round figures, the death toll was put at 1800 and the number of registered wounded was 8000.

A4 *Silvertown, London, 1917*
On 19 January 1917, an explosion occurred at the Brunner Mond munitions factory at Crescent Wharf, Silvertown, London. A fire broke out at the melt pot room and took hold. It burned for some minutes when there was a massive explosion. Sixty nine people were killed and 98 seriously injured; there were 328 slight injuries recorded and about 600 were believed to have been treated in the street or by private doctors. The report of the inquiry stated:

> At the time of the explosion the total quantity of TNT on the premises amounted to 83 tons, of which 28 were crude, 27 in process and 28 finished, and there were, in addition, 9 tons of TNT oil in iron drums of which 5 tons were subsequently recovered. . . . The outlines of the craters seem to indicate that altogether about 30 tons of TNT and the remaining 4 tons of TNT oil did not explode, but probably burned away. This would leave 53 tons of TNT to take part in the explosion.

TNT oil is alcohol containing the soluble impurities of TNT.

The explosion formed two separate craters. The smaller was circular in shape with a radius of about 25 ft and some 13 tons of TNT had been present in this area. The larger crater, in the area containing the remaining 40 tons of TNT, was kidney-shaped, with approximate dimensions 150 ft × 50 ft.

Anon. (n.d.b); Ministry of Home Security (n.d.a); Sainsbury (1977)

A5 *Oppau, Germany, 1921*
At 7.29 a.m. and again at 7.32 a.m. on 21 September 1921, two terrific explosions occurred at the Oppau works of Badische Anilin und Soda Fabrik (BASF).

Figures for the death toll vary. Commentz *et al.* (1921) give the number of dead as 430, including 50 people in the village. According to V.C. Marshall (1987), following BASF (1958), the explosion killed 561, including 4 in Mannheim 7 km away, injured 1500 and destroyed 1000 houses, including 75% of those in Oppau itself. It created a crater 115 m long × 75 m wide × 10 m deep.

The works after the explosion is shown in Figure A1.3.

Other effects of the explosion were as follows (Commentz *et al.*, 1921):

> Houses in the adjacent city of Ludwigshafen and in Mannheim, which lies opposite to Ludwigshafen on the right bank of the Rhine, were damaged, walls were shaken down and practically all windows were broken. At these places and at Heidevaporerg, which is about 14 miles from Oppau, the effect of the explosion was first felt by two very heavy earthquake-like shocks. In Mannheim some seconds later and in Heidevaporerg 82s after the shocks there came an enormous rush of air which broke windows and doors and caused damage to gas holders, oil tanks, and many river barges. The sound of the explosion reached as far as Bayreuth, at a distance of 145 miles, and the air pressure wave caused considerable damage in Frankfurt, which is about 53 miles from the scene of the explosion.

The explosion involved some 4500 tons of a 50 : 50 mixture of ammonium sulfate and ammonium nitrate. Detonation was set off by blasting powder, which was being used to break up storage piles of material which had become caked, a procedure which had been carried out without mishap some 16,000 times previously.

The danger of using explosives to break up caked ammonium nitrate had been demonstrated earlier in the year in Germany, when on 10 July at Kriewald this procedure led to the explosion of two rail wagons containing 15 te of that substance (D.J. Lewis, 1993).

BASF (1921, 1958); Commentz *et al.* (1921); J.R. Nash (1976); NBFU (1948); HSE (1978b); V.C. Marshall (1987); D.J. Lewis (1993)

A6 *Hamburg, Germany, 1928*
On 28 May 1928, a tank containing phosgene exploded at the Stolzenburg factory on the Hofe-Kanal near the harbour area of Hamburg. The wind was at first northerly and then changed to the south-east. At one location 5 miles away the gas was strongly felt. People were also affected by the gas at locations 6 and 11 miles distant.

The prime source (Anon., 1928) states 'Some 300 or more cubic feet of the gas were released'. V.C. Marshall (1987) suggests that this figure probably refers to the volume of the liquid, which would correspond to about 12 te, close to the figure of 11 te given by N.C. Harris (1981).

11 people were killed and 171 required hospital treatment.

Figure A1.3 *Oppau: BASF works after ammonium nitrate explosion, 1921 (Badische A nilin und Soda Fabrik)*

Anon. (1928); Hegler (1928); N.C. Harris (1981b); V.C. Marshall (1987)

A7 *Neunkircken, Germany, 1933*
On 10 February 1933, an explosion occurred on a waterless gas holder in Neunkirchen in Germany. Work was being done on a bypass pipe between the inlet and outlet mains. Due to a series of actions which is not entirely clear, but which involved measures to bring misaligned flanges into alignment, a small explosion occurred at this bypass and ruptured the outlet main. A flame was seen to go up the side of the gasholder. It had burned for some 5 min when the main explosion occurred. The inquiry found that this explosion involved an air mixture which had formed above the piston.

The explosion caused 65 deaths and several hundred injuries.

Anon. (1933a,b); Kier and Miffler (1983)

A8 *Wichita Falls, Texas, 1939*
On 12 December 1939 an explosion occurred in a 10 in. diameter crude oil pipeline at Wichita Falls, Texas. A 38 mile section of the line had been emptied to locate and repair minor leaks. The method used was to pass a series of scrapers through the line propelled by air, which was odorized to assist in detecting the leaks, and then to displace the column of air by one of oil. During this latter procedure a scraper propelled by the oil struck one that had stuck in the pipe, evidently causing a spark. The result was an oil film explosion, in which the detonation travelled down the pipeline for over 26.8 miles, rupturing the line at intervals of about 80 ft.

The pattern of ruptures in the pipeline is shown in Figure A1.4.

P. Reed (1939); Armistead (1959); D.J. Lewis (1993)

A9 *Tessenderloo, Belgium, 1942*
On 21 July 1942, a massive ammonium nitrate explosion occurred at a chemical works at Tessenderloo in Belgium. The death toll is given as of the order of 200.

J.R. Nash (1976)

A10 *Ludwigshafen, Germany, 1943*
On 29 July 1943, a release occurred from a rail tank car in the BASF works at Ludwigshafen. The tank car contained 16.5 te of a mixture of 80% butadiene and 20% butylene. A vapour cloud formed and ignited. The resultant vapour cloud explosion demolished a block 350×100 m^2 within the factory. Fifty-seven people were killed and 439 injured.

According to Giesbrecht *et al.* (1981), there was a delay of some 10–25 s between the rupture and the explosion. These authors indicate that the cause was hydraulic rupture of the tank due to overheating in the sun. If so, the incident is remarkably similar to one which occurred in the same works 5 years later, as described in Case History A17.

Stahl, Strassman and Richard (1949); J.R. Nash (1976); Giesbrecht *et al.* (1981); D.J. Lewis (1983); V.C. Marshall (1986 LPB 67, 1987)

A11 *Bombay, India, 1944*
Just after 4.00 p.m. on 14 April 1944 in the Victoria Dock, Bombay, India, a massive explosion occurred on the munitions ship Fort Stikine.

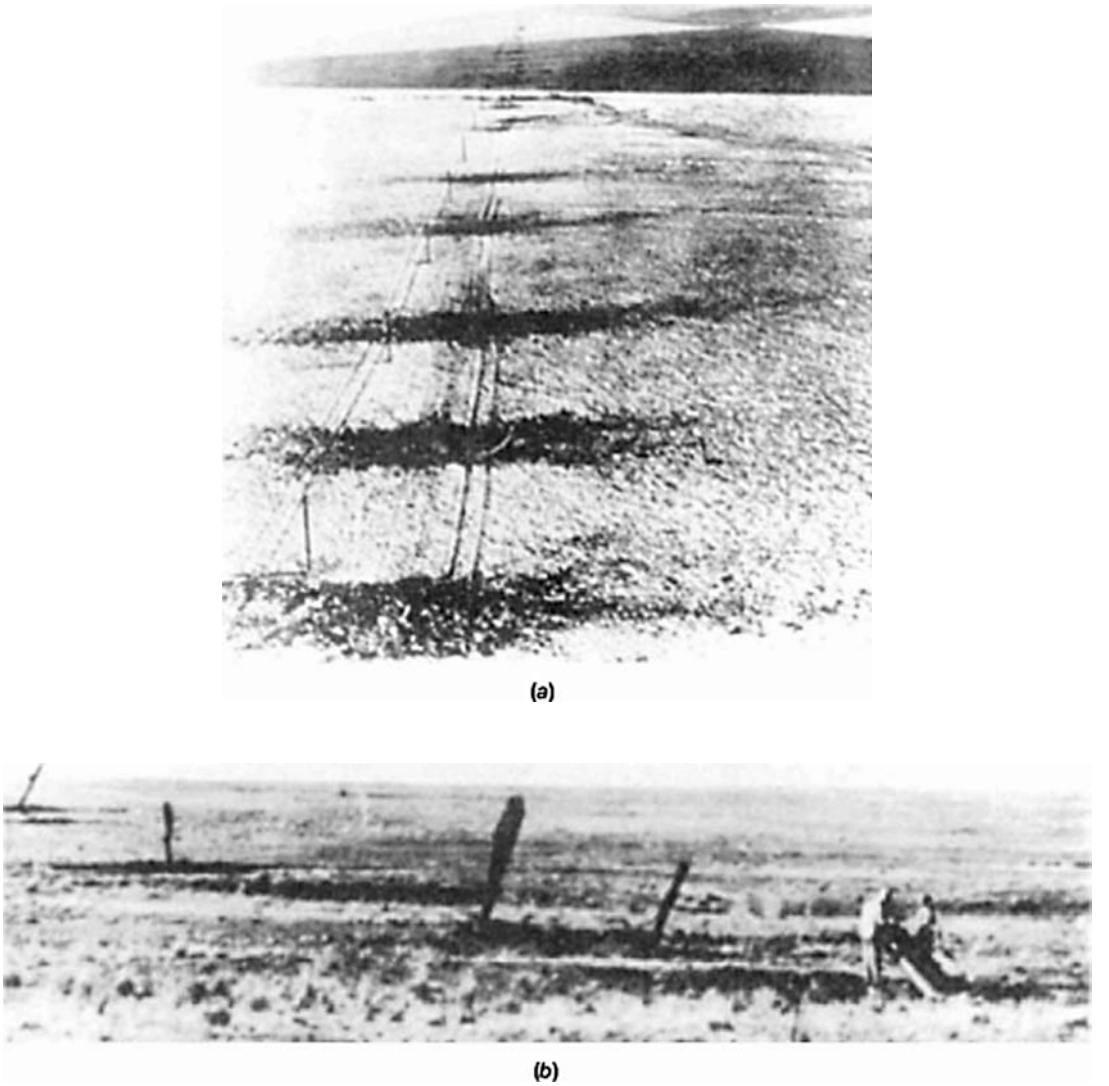


Figure A1.4 *Wichita Falls, 1939: pipeline after the explosion: (a) aerial view showing blackening where repeated ruptures of the pipeline occurred; and (b) elevation view, showing broken ends of the pipeline projecting through the ground (Bureau of Mines)*

The ship carried some 1400 tons of mixed munitions (bombs, shells, torpedoes, mines, etc.). On its way it had picked up a cargo of cotton. In No. 2 Hold 187 tons of ammunition was stored with cotton bales above, then other material, 1089 drums of lube oil, and finally more explosives. This was contrary to regulations, which stated that cotton is liable to spontaneous combustion if contaminated with oil. Further notes stated that cotton and explosives should be stored at opposite ends of the ship and that oil drums stowed above cotton should be limited to 250 barrels.

By mid-day on 14 April unloading of the ship was well under way. Soon after, crew on a nearby ship saw wisps of smoke coming from No. 2 Hold of the Fort Stikine, but did not inform the latter. Almost two hours passed before the fire was discovered. Water was applied to the hold using the ship's three hoses.

The authorities recognized the seriousness of the situation and considered options such as moving or scuttling the ship, but both appeared impractical, since the ship's engines were down for repair, there were no tugs available and the water was too shallow for scuttling. Moving the ship would also involve disconnecting the fire hoses laid from the dock into No. 2 Hold, which now numbered more than 30.

By 3.30 p.m. although an estimated 900 tons of water had been poured into the hold, the port deck was too hot to walk on and a large patch on the side was glowing red. At 3.50 p.m. a huge column of flame shot up from the hold and

at 4.06 p.m. the first massive explosion occurred. Some 34 min later there was a second major explosion.

The first explosion killed 60 firemen and set up fires in a 900 m radius. As a result of the two explosions together 10 ships in the docks were destroyed or declared a total loss. Figures for the death toll differ. According to Patience (1989), early reports gave 350 people killed, 1800 injured and 50,000 rendered homeless. J.R. Nash (1976) quotes 1376 dead.

J.R. Nash (1976); Patience (1989)

A12 *Cleveland, Ohio, 1944*

At approximately 2.40 p.m. on 20 October 1944 a cylindrical LNG storage tank at the Liquefaction, Storage and Regasification Plant of the East Ohio Gas Company at Cleveland, Ohio, ruptured and discharged its entire contents over the plant and the nearby urban area. The LNG vapour ignited almost immediately and an intense fire burned at the plant, causing great loss of life and extensive damage.

More LNG flowed from the plant as liquid down storm sewers, where it mixed with air and exploded.

The final death toll was 128 and the numbers injured were estimated as 200–400. The greatest loss of life occurred within the plant area.

The plant was the first commercial LNG plant of its kind in the work. Its function was to liquefy and store natural gas during off-peak periods and to regasify it during periods of peak demand. The LNG was stored at 5 psi and −250°F. The plant was built on a site which had been in the company's possession for 50 years. The site was close to residential and industrial areas.

The cause of the rupture is uncertain. The Bureau of Mines investigation (Elliott *et al.*, 1946 BM RI 3867) concluded that the low carbon steel used in the construction of the vessel may have been unsuitable and that the failure may have occurred due to vibration or seismic shock.

It was pointed out in the report that most industries handling liquid oxygen or air used not carbon steel but stainless steel or suitable non-ferrous metals. Following this accident, the use of the latter materials became more widely favoured in applications of this kind.

The report recommended that the distance between a plant of this kind and the nearest inhabited building should be greater than half a mile.

Following the rupture large quantities of liquid topped by burning vapour had flowed considerable distances from the tank. The report discussed the argument that a dike is not useful for a relatively volatile material such as LPG or LNG, concluded that a dike would have reduced the hazard and recommended that storages for liquefied gases should have a dike.

The report also made a number of other recommendations. These included the open siting of storage tanks to permit good ventilation; the use of precautions to eliminate sources of ignition to the standard considered necessary in explosives plants; the provision of remote closure for the bottom off-take valve; the installation of reliable level indicators and alarms; and the conduct of emergency drills.

Moulton (1944); Coroner (1945); Elliott *et al.* (1946 BM RI 3867); Burgoyne (1965b); Strehlow (1973b); J.R. Nash (1976) (under East Ohio Gas Co.); D.J. Lewis (1980); V.C. Marshall (1983 LPB 52, 1987)

A13 *Fauld, UK, 1944*

On 27 November 1944 a huge explosion occurred in a munitions store at Fauld, Staffordshire. The store was underground in a former gypsum mine, mined on the 'crown and pillar' method. The explosion involved mass detonation of 3500 tons of bombs. Although the store was in the countryside, the explosion killed 68 people and injured 22. It created a massive crater covering 12 acres and 80 ft deep.

The store handled large quantities of bombs for the bombing offensive. This included the repair and re-issue of bombs recovered after jettisoning. The personnel were working under considerable pressure. The inquiry found that the most likely cause was ignorance and disregard of the regulations by personnel working on jettisoned bombs. An armourer testified that he had seen a colleague using a brass chisel to remove a broken exploder from one of the bombs, a practice expressly forbidden. Other witnesses confirmed that such irregularities were by no means uncommon.

J. Reed (1977); Anon. (1992 LPB 103); V.C. Marshall (1992 LPB 105)

A14 *Port Chicago, California, 1944*

On the evening of 17 July 1944 two vessels, the Quinault Victory and the E.A. Bryan, were berthed at Port Chicago, California, taking on large quantities of cordite and TNT when they were rent by a massive explosion. At dawn next day the vessels, and the 321 men on them, had disappeared. The cause of the explosion was never established, although some authorities implicate deteriorated munitions.

J.R. Nash (1976)

A15 *Brest, France, 1947*

On 28 July 1947 the vessel Ocean Liberty with a cargo of ammonium nitrate, exploded in the port of Brest, France, killing some 21 people.

J.R. Nash (1976)

A16 *Texas City, Texas, 1947*

At about 8.10 a.m. on 16 April 1947 fire was observed in bagged ammonium nitrate fertilizer on board the ship Grandcamp in the harbour at Texas City. There were 880 tons of ammonium nitrate in the hold affected and a further 1400 tons in another hold. Frantic efforts were made to extinguish the fire, but the quantity of water used initially was too small and by the time hose lines had been connected to supply larger quantities, the fire was so well established that the crew was ordered to abandon the ship. At 9.15 a.m. the Grandcamp disintegrated with a tremendous thunderclap, killing all persons in the dock, including firemen and a crowd of spectators.

Another ship, the High Flyer, which also had ammonium nitrate on board, was 700 ft away and was blown free of its hawsers. On account of the danger of another explosion, volunteers could not be found to move the High Flyer out of the burning area. At 6.00 p.m. ignition of its sulfur cargo occurred. At 1.10 a.m. the next day the High Flyer was ripped apart by the expected explosion.

The report of the National Board of Fire Underwriters (1948) states:

> When the Grandcamp blew up, the cargo of peanuts, tobacco leaves, balls of sisal twine, and oil-well drilling equipment were blown in all directions. Shrapnel-like fragments of the ship were hurled in high trajectory, 2000–3000 feet into the air; some travelled more than 10,000 feet from the point of origin. Some of the oil-well drill rods (30 feet in length and 7 inches in diameter,

> weighing close to 1½ tons) were hurled almost 2 miles and buried 8 ft into the ground, like twisted hairpins. . . .

It was virtually impossible to separate the effects of the two successive explosions, but, the report continues:

> Daybreak revealed a sickening scene of devastation-demolished concrete structures, masses of twisted wreckage, crippled refineries with battered storage tanks, some crumpled like tin-foil, and sidings of distant warehouses blown apart as if ripped by a tornado. Pitch black columns of smoke from the burning oil tanks spiralled skyward for 3000 feet or more, and were visible for 30 miles. They burned continuously for almost a week. Insurance inspection showed blast damage to over 3,300 dwellings and 130 business buildings, to more than 600 automobiles and some 360 box cars. Approximately 50% of some 250 storage tanks, ranging from 25,000 to 80,000 barrels capacity, were substantially damaged either by concussion, missile or intense fire.
>
> There were 552 deaths and over 3000 injuries in a community of some 15 000 people.

Kintz, Jones and Carpenter (1948 BM RI 4245); National Board of Fire Underwriters (1948); Wheaton (1948); Blocker (1949); Blocker and Blocker (1949); J.R. Nash (1976); V.C. Marshall (1983 LPB 52, 1987)

A17 *Ludwigshafen, FRG, 1948*

On 23 July 1948 a rail tank car containing dimethyl ether ruptured in the BASF works at Ludwigshafen. A vapour cloud formed and after some 6 s was ignited by hot work in a workshop. A block 230 m × 170 m was demolished and severe damage was done within an area 570 m × 520 m. The death toll was 207 and the number of injured 3818. The casualties appear to have been confined to the works, the dead all being between 15 and 65 and there being very few women's names listed. The official report by Stahl, Strassman and Richard (1949) considered four hypotheses for the cause of the rupture: (1) the presence of organic peroxides, (2) the presence of non-condensables, (3) overheating leading to hydraulic rupture and (4) mechanical defects. They were able to rule out the first two and settled on the third: that the tank contents had been heated by the hot summer sun and that the tank, lacking a relief valve, had suffered hydraulic overpressure and rupture. This is the account generally given in the literature.

This explanation has been questioned by V.C. Marshall (1987). He points out that in order to obtain the pressure necessary to achieve hydraulic rupture the investigation was constrained to assume both that the tank was at least 4% smaller in volume than the norm, that this had not been remarked in 19 years of use and that the temperature reached was exceptionally high. He refers to the metallurgical analysis done at the time and described in the report, to the effect that the tank had weak spots. In addition, the tank had been involved the year before in an accident in which the valves had been knocked off. Further, the tank belonged to an ammonia plant and the plate giving the tare weight referred to the permissible filling limit for ammonia. Ammonia is known to cause embrittlement in some steels. The significance of the solar heating could well be that it increased the vapour pressure sufficiently to trigger the rupture.

BASF (1948); Stahl, Strassman and Richard (1949); D.J. Lewis (1980, 1983, 1993); Giesbrecht *et al.* (1981); V.C. Marshall (1986 LPB 67, 1987)

A18 *Avonmouth, UK, 1951*

On 7 September 1951 a storage tank exploded at the Royal Edward Dock, Avonmouth, Bristol. The tank was being filled with gas oil from a ship. The gas oil was contaminated with petrol, which had leaked through a partition between the gas oil tank and the petrol tank, and this was known to those concerned. The tank was being splash filled and the explosion occurred as two men on the tank roof were gauging the level using a steel tape. The two men were killed.

Evidently a flammable atmosphere had formed in the vapour space of the tank and had been ignited by a discharge of static electricity. The official report (H.E. Watts, 1951) stated: 'It was therefore quite possible for the steel dip tape to take up a charge of static electricity from the oil in the tank and to discharge it by means of a spark against the edge of the 10 inch manhole in the top of the tank through which the tape had been inserted'.

H.E. Watts (1951); Anon. (1952); Kletz (1983 LPB 52)

A19 *Port Newark, New Jersey, 1951*

On 7 July 1951 a fire and BLEVEs devastated a large LPG storage at Port Newark, New Jersey. The storage comprised one section with 70 horizontal bullet tanks, each with a capacity of about 100 m^3, and a further 30 tanks nearby. The tanks were not provided with thermal insulation or fixed water sprays. The initial event was experienced as a slight explosion followed by a fire. Within the next two and half min there were four small explosions near the seat of this fire, followed half a minute later by a large flash, a muffled explosion and a large fireball. Some 10–15 min into the event a BLEVE occurred. The next 100 min were punctuated by tank explosions and BLEVEs every 3–5 min. In all 73 bullet tanks were destroyed.

The tanks were equipped with emergency isolation valves. Some 30 s into the event the button to close these valves was pressed. It was pressed again after two and a half min, there being some doubt whether the first time it had been pushed for long enough. In fact, it is estimated that on the side of the valves away from the tanks there was some 100 m^3 of LPG, mainly in a 12 in. delivery line from the docks and in 8 in. ring mains; thus there was potentially quite enough fuel to feed the fire even if the tanks themselves were isolated.

In many cases the BLEVEs were accompanied by fireballs rising 750 m into the air. Many of the events registered on the barometer at Newark Airport, showing TNT equivalents of about 25 kg, consistent with the pressure energy in the vapour space of a tank. The damage done by missiles is described as spectacular. One large tank section 17 m long travelled over half a mile, demolishing a filling station and starting a fire. Another fragment ruptured the 12 in. underground water main to the site. Figure A1.5 shows one of the tank section missiles part buried in the ground.

It has been suggested that a possible cause of the initial event was inadequate allowance for thermal expansion in the 8 in. ring mains. These handled propane at two different temperatures, the regular flows and a flow from a vapour recovery unit.

NBFU and FIRONJ (1952); D.J. Lewis (1980, 1993)

A20 *Bakersfield, California, 1952*

On 21 July 1952, the Paloma condensate recycling plant in Kern County, near Bakersfield, California, was struck by an earthquake. The earthquake had its epicentre about 12 miles away, measured 7.7 on the Richter scale and had a

Figure A1.5 *Port Newark, 1951: tank section part buried in ground (The Bettman Archive)*

maximum intensity in the range X–XI. Ground movement was of the order of 0.5 ft vertically and 1 ft horizontally. It was such as to cause a 60 ft high absorption column to swing at the top in an arc of 3 ft and to stretch its foundation bolts some 1.5 in. Figure A1.6 gives an aerial view of the facility following the earthquake.

The plant had five large butane storage spheres which were not designed to earthquake standards. Two spheres collapsed with rupture of the feed lines. Butane escaped and formed a vapour cloud, which ignited some 90 s later at a transformer block. The resultant explosion and fire did extensive damage but there were no deaths or serious injuries.

Jenkins and Oakshott (1955); D.J. Lewis (1980, 1993); Alderson (1982 SRD R246)

A21 *Bound Brook, New Jersey, 1952*
On 22 December 1952 a plant handling phenolic resin moulding powder at Bound Brook, New Jersey, was wracked by a dust explosion. The explosion occurred in a dust collector and then travelled through ducting, emerging at several points into floor areas, where it raised clouds of dusts which in turn underwent violent secondary explosions. The probable sequence of events was that a bearing in a hammer mill overheated, the powder in the mill began to smoulder and the smouldering powder passed into a flammable dust mixture in the dust collector. Five people were killed and 21 injured.

NFPA (1957); D.J. Lewis (1993)

A22 *Whiting, Indiana, 1955*
On 27 August 1955 at the refinery at Whiting, Indiana, a reactor suffered an internal detonation and disintegrated. The reactor vessel was 127 ft tall × 22.5 ft diameter, having a wall 2.5 in. thick and weighing 500 te. A separator with a 6 in. thick wall also fractured. The detonation has been estimated as having a TNT equivalent of 5.6 te. Fragments were thrown 1500 ft, one of 60 te landing on the tank farm and another killing a boy at home. The event started a fire which eventually covered 40 acres and lasted for 8 days. There was the one death just mentioned.

The event occurred in the course of start up of a hydroformer unit. The start up procedure involved the circulation through the reactor and separator of inert gas heated in a furnace. Due to a valving error the gas being circulated was in fact a flammable mixture. In due course, the gas temperature at the exit of the furnace rose to 500–600°F, reaching the autoignition temperature. A detonation occurred in the reactor and another in the separator vessel.

Woodworth (1955); R.B. Jacobs *et al.* (1957); Randall *et al.* (1957); R.B. Jacobs and Bulkley (1967); R.B. Jacobs *et al.* (1973); D.J. Lewis (1980, 1993)

A23 *Cali, Columbia, 1956*
On 7 August 1956 eight trucks carrying dynamite exploded at Cali, Columbia, killing about 1100 people as they slept, and injured another 2000; some 500 of the dead were soldiers in barracks.

Walker (1973); J.R. Nash (1976)

Figure A1.6 *Bakersfield, 1952: recycling plant after the earthquake (The Bettman Archive)*

A24 *Uskmouth, UK, 1956*
On 18 January 1956 an explosion occurred on the No. 5 60 MW turbogenerator set at the Uskmouth power station of the Central Electricity Authority. The low-pressure turbine and generator were totally destroyed and the high-pressure turbine and plant severely damaged. Fragments were ejected with considerable force, causing damage to the turbine house. Two persons were killed and nine injured. The cause of the incident was established as machine overspeed.

Lindley and Brown (1958)

A25 *Montreal, Canada, 1957*
On 8 January 1957, a series of BLEVEs occurred at a set of storage spheres at Montreal, Quebec. There were three spheres in a common bund: one 800 m^3, one 1900 m^3 and one 2400 m^3. The 800 m^3 sphere, which held butane, was overfilled due to a faulty level gauge. A vapour cloud formed and found an ignition source, probably at a service station 180 m away, and the flame flashed back to the sphere, where a pool fire started. After some 30 min the 1900 m^3 sphere, which was less than 20% full, underwent

a BLEVE. Some 15 min later BLEVEs occurred on the other two spheres also.

Selway (1988 SRD R492)

A26 *Signal Hill, California, 1958*

On 22 May 1958 an 80,000 bbl. tank serving as the feed tank to a viscosity-breaking unit at the refinery at Signal Hill, California, erupted. Steam issued, part of the roof was torn off and oil froth flowed out. There was no immediate ignition. The oil froth flowed through the plant in a wave about a metre high. A further eruption occurred and the froth ignited. Eventually it covered an area of 27 acres. The fire burned for 40 h. Two people were killed and 18 injured.

The oil in the tank was at a temperature of 157°C. The source of the water which caused the eruption does not appear to be known: it may have been in the tank already or may have been pumped in by mistake.

Woodworth (1958); Anon. (1959a); D.J. Lewis (1993)

A27 *Deer Lake, Pennsylvania, 1959*

On 2 June 1959 in the township of Deer Lake, Pennsylvania, a road tanker containing LPG slowed to a halt as a school bus in front stopped and was itself struck from behind by a truck. LPG escaped and was rapidly ignited. After some 15 min the fire brigade arrived and were told by the driver of the tanker that it would be protected from explosion by its safety valves. They directed water and foam at a nearby wooden building. A crowd of spectators gathered and police had difficulty in moving them on. After the fire had burned for a time variously estimated as 20–45 min the tanker suffered a BLEVE. Shrubbery at a distance of 150 m was scorched. The tank itself travelled up the street, bouncing off a stonewall. The tank, accompanied by stones and other debris, struck the main group of onlookers, killing most of them. There were 11 fatalities.

Hymes (1985 LPB 65)

A28 *Meldrin, Georgia, 1959*

On 28 June 1959, a derailment occurred of a rail tank cars containing LPG at Meldrin, Georgia, with tank rupture and release of LPG. A vapour cloud formed and reached a nearby leisure park. Ignition occurred and the resultant vapour cloud fire caused 23 deaths.

Anon. (1960–61); Hymes (1985 LPB 65); V.C. Marshall (1987)

A29 *La Barre, Louisiana, 1961*

At about 8.15 a.m. on 31 January 1961 some 6000 USgal of liquid chlorine were spilled from a derailed tank car in the community of La Barre, Louisiana. A cloud of chlorine gas spread of over an area of approximately 6 square miles. For the most part it hung close to the ground, but in places 'boiled upwards' to a height of 80–90 ft. Some 1000 people were evacuated. A series of determinations of the chlorine concentration were made by a team using mobile equipment. The first samples were taken at about 11.15 a.m., when a concentration of 10 ppm was measured at the end of a contaminated area some 200 yd long on a highway parallel to the railway. At about 3.00 p.m. a concentration of 400 ppm was measured 75 yd from the wreck. One person died and about 100 were treated for exposure to chlorine. The fatality was an 11-month old infant in a family, which lived in a house approximately 50 yd from the tank car. The chlorine in the house made the infant choke and gasp and the frantic father carried it outside, where the gas concentration was higher still. Although most of the exposure occurred inside the house, this exposure outside was probably critical. The child died in hospital. A 2-month old infant who remained in the house survived.

Joyner and Durel (1962)

A30 *Berlin, New York, 1962*

On 25 July 1962, a tractor tank semi-trailer unit came off the road at Berlin, New York. The vehicle had failed to negotiate a bend, tipped over and jack-knifed. The tank hit a tree and its contents of some 6876 USgal of LPG were released. A vapour cloud formed which covered an area of some 2000 m^2 and was 25 m high. There followed a massive vapour cloud fire which caused the deaths of 10 people and injured 17.

Walls (1963–64, 1964a); Kier and Müller (1983)

A31 *Doe Run, Kentucky, 1962*

On 17 April 1962 at Doe Run, Kentucky, a plant for the manufacture of an ethanolamine from ammonia and ethylene oxide suffered a major explosion. The reactor was supplied with liquid ethylene oxide from a 25 m^3 storage vessel. The reactant transfer pumps were provided with an interlock system but problems had been experienced with this system and the control had reverted to manual. A back flow of ammonia occurred into the ethylene oxide tank. A reaction took place which might have been a reaction runaway or a decomposition. The vessel ruptured, releasing a large quantity of ethylene oxide. The vapour cloud ignited immediately, giving an explosion estimated to have had a TNT equivalent of 16 te. It has been suggested that the mechanism of ignition may have been free radicals from the initial, internal reaction.

Troyan and Levine (1968); D.J. Lewis (1980, 1993); Mahoney (1990)

A32 *Marietta, Ohio, 1962*

On 27 April 1962 at Marietta, Ohio, a benzene recycle pump on a phenol production unit became plugged with residue, and whilst attempts were being made to clear it, pressure built up in a stripper column. A 6 in. relief valve operated, discharging benzene vapour, which ignited. Missiles from the resulting explosion severed pipework, releasing large quantities of flammable liquids, which also ignited. One person was killed and three injured.

Mahoney (1990)

A33 *Attleboro, Massachusetts, 1964*

On 12 January 1964, an explosion occurred in a vinyl chloride polymerization plant at Attleboro, Massachusetts.

An illuminator port had been replaced on one of the reactors but not pressure tested. When the reactor was charged, a small leak developed. As the fitter was tightening the clamping ring, the glass chipped and he was injured; the leak developed. An estimated 4.5 te of vinyl chloride escaped into the building, ignited and exploded with an estimated TNT equivalent of 17.7 te. The explosion broke pipework on all the 20 reactors and released some 68 te of vinyl chloride, which ignited. There was a large fireball. Seven people were killed and 40 injured.

Walls (1964b); D.J. Lewis (1980, 1993); Mahoney (1990)

A34 *Niigata, Japan, 1964*

On 16 June 1964, the refinery at Niigata, Japan, suffered an earthquake of strength 7.7 on the Richter scale which caused two major fires. The first fire was the result of oil spillage from a floating roof storage tank. The oil was ignited by sparks as the roof smashed against the sides of the tank.

Later, a seismic tidal wave engulfed the area and unignited oil spread over the water. For 4 h this oil did not ignite. Six hour into the event an explosion occurred in another part of the refinery 1200 ft from the tank which was seat of the original fire. This second fire spread to within 350 ft of the first fire but the two did not merge. Two people were killed and 97 storage tanks were destroyed.

Mahoney (1990)

A35 *Bow, London, 1965*

On 7 August 1965, a flour mill in Bow, London, suffered a dust explosion. The site of the explosion was a 15 te capacity metal flour bin on the third floor. Welding had been in progress shortly before and may have caused overheating of the metal and hence of the flour inside. Two major fires and many smaller ones broke out. Five people were killed and over 40 injured.

Anon. (1967c); D.J. Lewis (1993)

A36 *Louisville, Kentucky, 1965*

On 25 August 1965 at Louisville, Kentucky, an explosion occurred on a plant manufacturing neoprene by polymerization of chlorobutadiene in a compressor circulating monovinyl acetylene (MVA). The investigation concluded that a mechanical failure had caused local overheating in the compressor and that this had led to decomposition of the MVA. There followed a series of explosions, a total of 10 occurring within 13 min and of 18 within 90 min. The escalation occurred due to transmission through pipework, flame impingement and missiles. Twelve people were killed and eight injured; all the deaths occurred within a radius of less than 100 ft from the original explosion.

Armistead (1966, 1973); Mahoney (1990); D.J. Lewis (1993)

A37 *Natchitoches, Louisiana, 1965*

On 4 March 1965, an explosion occurred on a 24 in. high-pressure natural gas pipeline at Natchitoches, Louisiana. The explosion was apparently caused by the high-pressure gas, there being no evidence of combustion in the pipeline. The splitting action of the pipe propagated the rupture for 27 ft along the pipe. The resultant blowout produced a crater 27 ft long, 20 ft wide and 10 ft deep. Three pieces of metal with a total weight of half a ton were hurled distances of 129–351 ft from the point of rupture. Within 60 s there followed an explosion that 'incinerated' an area of 13.8 acres. Seventeen people were killed.

FPC (1966); D.J. Lewis (1980)

A38 *Feyzin, France, 1966*

On 4 January 1966 at Feyzin refinery in France a leak on a propane storage sphere ignited, caused a fire that burned fiercely around the vessel and led to a BLEVE.

The operator had opened two valves in series on the bottom of the sphere in order to drain off an aqueous layer. When this operation was nearly complete, he closed the upper valve and then cracked it open again. There was no flow and he opened the valve further. The blockage, which was presumably hydrate or ice, cleared, and propane gushed out, but the operator was unable to close the upper valve. He did not think at once to close the lower valve and by the time he attempted this, this valve also was frozen open.

The alarm was raised and steps were taken to stop traffic on the nearby motorway. A vapour cloud about 1 m deep spread towards the road. It is believed that a car about 160 m distant on the motorway may have been the source of ignition. It was afterwards found that its engine was not running but its ignition was on and it may have been stalled by taking in a propane-rich mixture at the air intake. Flames appeared to flash back from the car to the sphere in a series of jumps.

The sphere was enveloped in a fierce fire. Its pressure relief valve lifted and the escaping vapour ignited.

The LPG storage installation of which the sphere was a part consisted of four 1200 m^3 propane and four 2000 m^3 butane spheres. The fire brigade was not experienced in refinery fires and apparently did not cool the burning sphere, presumably on the assumption that the relief valve would protect it. They concentrated instead on cooling the other spheres. About one and a half hours after the initial leakage the sphere ruptured, killing the men nearby. A wave of liquid propane was flung over the compound wall and flying fragments cut off the legs of the next sphere, which toppled so that its relief valve began to emit liquid.

The fire at the storage spheres is shown in Figure A1.7. Plate 32 shows a sphere, toppled and engulfed in flames. Figure A1.8 shows an outline in the ground of one of the victims.

The accident killed 18 people and injured another 81 and caused the destruction of five of the spheres as well as other damage.

Anon. (1966e,g,h); Kletz (1974e, 1975d, 1977d); Anon. (1987 LPB 77, p. 1); Selway (1988 SRD R492); Mahoney (1990); D.J. Lewis (1993)

A39 *LaSalle, Canada, 1966*

On 13 October 1966 at a plant at LaSalle, Canada, there was a runaway reaction in a styrene polymerization reactor. The bursting disc and dump line both operated, discharging material into the outside yard, creating a vapour cloud. A vapour fog also formed inside the building due to failure of a sight glass on the bursting disc vent. Ignition occurred and the vapour inside and outside the building exploded. It has been estimated that the release of styrene was 0.64 te and that the TNT equivalent of the explosion was 6.6 te. Eleven persons died.

Fire Journal Staff (1967, 1973d); D.J. Lewis (1980, 1993)

A40 *Lake Charles, Louisiana, 1967*

Just before dawn at 4.45 a.m. on 8 August 1976, a catastrophic explosion of a cloud of isobutane vapour occurred at the Cities Service refinery at Lake Charles, Louisiana. Seven people were killed and 13 injured and extensive damage was done.

The escape occurred at a valve on a 10 in. isobutane pipeline, which ran between an alkylation unit and two storage spheres. The pipeline ran underground, but the valve was located in an open pit, which had filled with water from recent rain. The bolts on the valve bonnet had suffered severe corrosion by vapours from a leaking sulfuric acid pipeline nearby.

That morning operators observed bubbles in the water and realized that there was a leak on the valve. An operator cleared the isobutane by flushing it with 110 psi water from the alkylation unit to sphere No. 1. He then closed the inlet valve on that sphere and began to open that on sphere No. 2. At this point the weakened valve in the pit failed and a geyser of water rose in the air. The operator, thinking that he had made an error, reversed his procedure, closing the valve on sphere No. 2 and opening that on sphere No. 1. As a result, isobutane from sphere No. 1 passed down the pipe and issued from the failed valve.

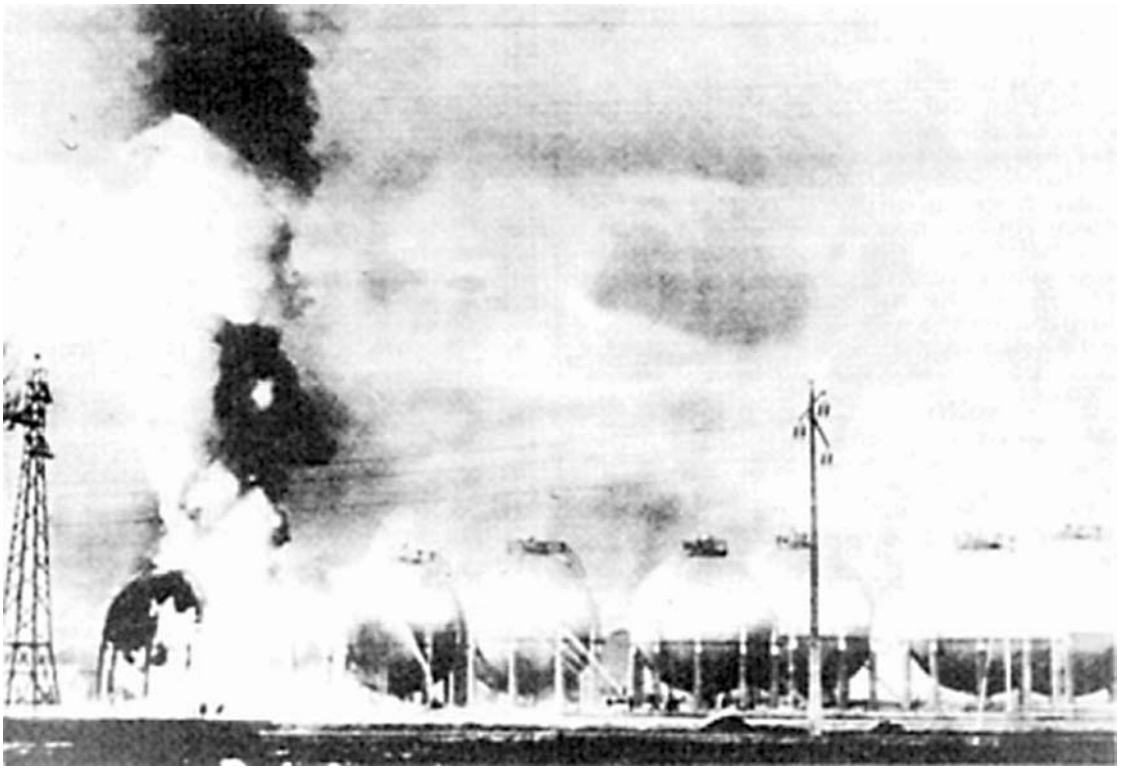


Figure A1.7 *Feyzin, 1996: fire at the storage vessels (United Press International)*

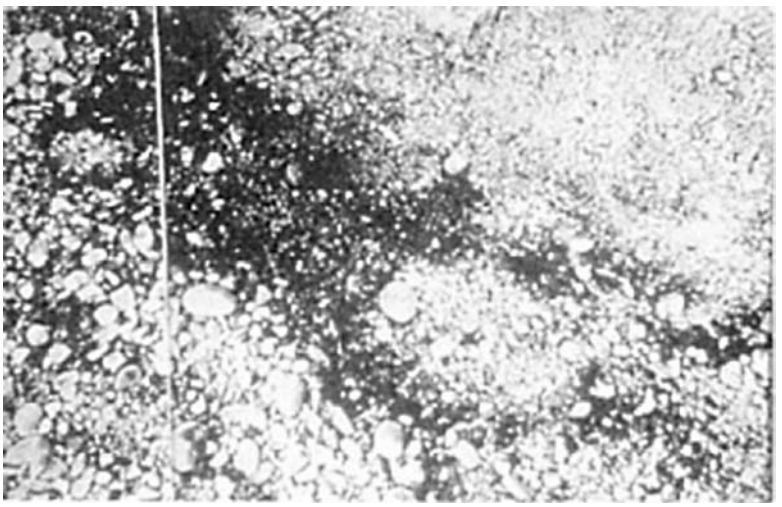


Figure A1.8 *Feyzin, 1996: 'shadow' of one of the victims (Courtesy of Compagnie General of Edition et de Presse)z*

The amount of isobutane which escaped was estimated as approximately 500 bbl. It formed a vapour cloud, which covered about 5 acres. The explosion had the characteristics of a detonation. Calculations indicated that it was equivalent to 10–12 tons of TNT.

The explosion caused a major fire, which burned for two weeks until the flammable material had been used up.

Goforth (1970); NFPA (1973); Vervalin (1973e); D.J. Lewis (1980, 1993)

A41 *Pernis, The Netherlands, 1968*
At 4.15 a.m. on 20 January 1968 an overflow was observed on slops tank 402 at the Shell refinery at Pernis. A hydrocarbon vapour cloud formed slowly over the adjacent area. At 4.23 a.m., after one or two smaller explosions, a violent explosion occurred which caused extensive blast damage and a large fire. The explosion was estimated to have been equivalent to 20 tons of TNT. The fire covered an area of about 250 × 300 m. Two people were killed and 85 were injured, mainly by flying glass.

Slops tank 402 was a 1633 m^3 cone roof tank. Owing to cold weather during the previous two weeks, it had been necessary to heat the oil in the tank. It is believed that a layer of water-in-oil emulsion had built up, covering the coils and reducing the heat transfer from them to the oil layer above, so that a substantial temperature difference had developed between the two layers, and that vapour formation at the interface between the two layers initiated mixing, causing further vapour evolution so that the tank overflowed, the hydrostatic pressure at the bottom of the tank was reduced and violent boil-up occurred, giving the condition known as 'stopover'.

Fontein (1968); Ministry of Social Affairs and Public Health (1968); Wordsworth (1973); D.J. Lewis (1980, 1993)

A42 *Dudgeons Wharf, London, 1969*
In 1969, an explosion occurred at Dudgeon's Wharf, London, while an oil storage tank was being demolished. Six people were killed.

Anon. (1970a)

A43 *Glendora, Mississippi, 1969*
At about 2.45 p.m. on 11 September 1969, a train entered Black Bayou junction near Glendora, Mississippi, pulling 157 rail cars, including eight containing vinyl chloride monomer (VCM). A pedestrian was struck and injured, and application of the emergency brake caused a derailment of 15 cars.

At 3.30 p.m. the VCM manufacturer was informed that his chemical was involved and at 5.00 p.m. that the eight cars were derailed and that one was leaking. A technical expert was requested and the manufacturer sent the VCM plant superintendent, who had 25 years' experience with the chemical.

At about 8.00 p.m. one of the VCM tanks was ruptured and leaking, and by 10.00 p.m. the leak had ignited. A heavy fog was noticed over the area and it was considered that it might be VCM. The railway management consulted the *Handbook of Hazardous Materials*, which stated that phosgene could be formed in VCM fires. They rang the company office, who advised that a hazard from phosgene was highly improbable and that the main problem was likely to be from HCl and smoke. Nevertheless, the railway management, the police, the National Guard and the Civil Defence Authorities continued to be worried by the phosgene hazard. The Civil Defense director consulted university chemists, who advised that burning VCM would release phosgene, which could be a hazard to life at a radius of 35 miles. Accordingly, the police and National Guard evacuated all the towns nearby. The evacuation was reported as involving some 30,000 people.

At 6.45 a.m. the next day an explosion occurred which demolished one of the eight VCM tank cars. The explosion caused a second tank car to rupture and ignite. After the fires were extinguished only five full tank cars were recovered.

A report in The Commercial Appeal of Memphis, Tennessee (13 September, 1969) read Mississippi. There was a explosion followed by a further explosion and fireball. The next 40 min were punctuated by more explosions as one car after another burst or rocketed. The initial fireball set fire to buildings 200–400 ft away. Other fires were initiated by burning fragments up to 10 blocks distant. The blast caused structural damage within about 400 ft. Very little glass survived within about half a mile and windows broke as far out as 3 miles. Two people died and 976 were injured.

Much of the damage was caused by the impact of rocketing tank cars and the fires which they set going. One 37 ft section travelled through the air and bounced first at 1000 ft distance, then bounced again at 300 ft, and again at 200 ft, and finally went another 100 ft, before coming to rest at a total distance of 1600 ft, where it set fire to houses.

At the first explosion people came out to see what was happening. The streets were full when the second explosion and fireball occurred. People became trapped between fences which ran parallel to the track and the towering fireball 200–400 ft away. There were many burn injuries, and many also from panic.

It is of interest that a National Guard ordnance team, in a controversial procedure, successfully used shaped explosive charges to blow holes in two unruptured tank cars to prevent them exploding.

NTSB (1969 MR); Eisenberg, Lynch and Breeding (1975)

A45 *Texas City, Texas, 1969*
On 23 October 1969 at Texas City, Texas, an explosion occurred inside a distillation column of a butadiene unit. The explosion was experienced as a two-part one, first the disintegration of the column and then ignition of the escaping gas. Numerous fragments fell within a radius of 500 ft, some large shell fragments travelled 1500 ft and one 800 lb section fetched up 3000 ft away. All five columns in the butadiene section were toppled or severely damaged. Thirteen people were injured.

The column had been under total reflux. A leak occurred in an overhead line valve so that butadiene was lost and a build-up occurred of vinyl acetylene which on some trays reached a molar concentration of 50–60%. The internal explosion occurred due to thermal decomposition of vinyl acetylene and ethyl acetylenes.

Freeman and McReady (1971); Jarvis (1971); Keister, Pesetsky and Clark (1971); Griffith and Keister (1973); Mahoney (1990); D.J. Lewis (1993)

A46 *Beaumont, Texas, 1970*
On 17 September 1970 at Beaumont, Texas, a 60 ft × 40 ft oil slops tank was struck by lightning. The tank failed at the shell-floor seam, releasing 11,000 USgal of oil, which burned. The oil spread to involve in the fire another 16 unbunded tanks nearby.

Mahoney (1990)

A47 *Blair, Nebraska, 1970*
On 16 November 1970, an overflow occurred on a 40,000 ton refrigerated anhydrous ammonia storage tank at the Gulf Oil Company's installation at Blair, Nebraska. 160 ton of ammonia was released, but there were no deaths or serious injuries.

The overfilling was the result of an operator error. A factor which may have contributed to the error was the fact that the table of tank levels, or 'strapping table', did not

indicate clearly the position of the overflow pipe. In addition, the high-level alarm and shut-down system failed to operate and apparently the overflow discharge valve also failed to operate at the set pressure, so that the liquid level in the tank rose until it reached the roof, at which point the overflow valve did open. There was an isolation valve on the overflow line directly below the relief valve. It was not possible to reach this valve and close it on account of the ammonia cloud. If isolation of the overflow line had been possible, much of the overflow could have been prevented. Once the overflow valve had opened, there was a discharge of ammonia to atmosphere. The discharge continued for 2.5 h.

There was almost no wind and an atmospheric inversion existed, so that initially the weather conditions were at their most unfavourable for dispersion. A low visible cloud of ammonia formed some 8–30 ft thick, covering approximately 900 acres and extending over 9000 ft from the tank. The ammonia cloud shortly after the spill is shown in Figure A1.9. The 'pancake' shape of the cloud is clearly shown in Figure A1.9(c). Later, a light breeze arose and helped to keep the cloud from populated areas.

MacArthur (1972)

A48 *Brooklyn, New York, 1970*

On 30 May 1970 a road tanker carrying liquid oxygen was manoeuvring in the yard of a hospital in Brooklyn, New York, when the tank ruptured violently. The tank was 9.15 m^3 capacity but the tanker had just offloaded its first part load. The initial explosion killed the driver and one other person, and windows were broken some 600 ft away. The release of the liquid oxygen resulted in a number of fires. In addition to the two deaths mentioned, 30 people were injured.

The tank was new and had been in service only one month. The investigation found that the $^3/_4$ in thick aluminium tank shell had suffered appreciable loss of metal, the deficit being 73.5 kg for the shell and internal components. It further found that a chemical reaction had occurred between the oxygen and deposits left in a crevice between a bracket and the tank wall, and that this had generated enough heat to initiate an oxidizing reaction between the shell and the oxygen vapour. This reaction also had the effect of heating the contents and increasing the vapour pressure. The estimated vapour pressure attained was over 100 bar compared with a design pressure of 15 bar.

NTSB (1971 HAR-71-06); D.J. Lewis (1993)

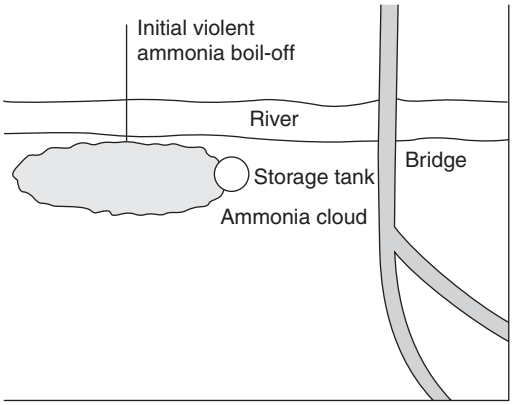
A49 *Corpus Ckristi, Texas, 1970*

On 3 August 1970 a refinery at Corpus Christi was hit by Hurricane Celia with winds of 140–160 miles/h and a rainfall of 6–8 in. The main structure of the catalytic cracker was toppled and some 30 tanks were destroyed.

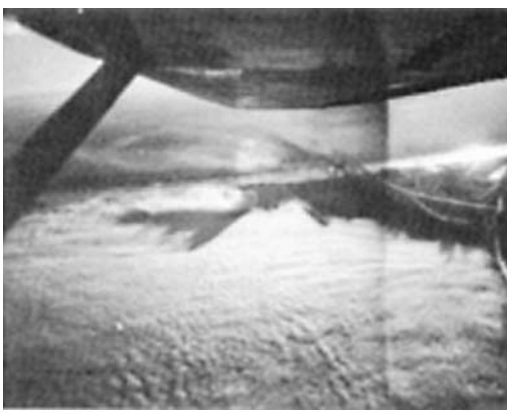
Mahoney (1990)

A50 *Crescent City, Illinois, 1970*

At 6.30 a.m. on 21 June 1970 a derailment occurred on a railway passing through the streets of Crescent City, Illinois. Nine rail tank cars loaded with LPG were among the derailed vehicles. The force of the derailment propelled the 27th car in the train over the derailed cars on front and its coupler struck the tank of the 26th car and punctured it. Propane was released and ignited.



(a)



(b)

(c)

Figure A1.9 *Blair, 1970: ammonia cloud from storage tank: (a) plan view (Slater, 1978a); (b) aerial view showing ammonia cloud covering whole of foreground; and (c) ground level view showing 'pancake' shape of cloud (both Enterprise Publishing Company, Blair, Nebraska)*

The safety valves of the other tank cars operated and released propane, which fed the fire. At about 7.33 a.m. the 27th car exploded. Four fragments of the tank car were hurled in different directions for distances of 300, 600 and 750 ft. At about 9.40 a.m. the 28th tank car exploded, hurling one fragment which eventually stopped rolling at a distance of 1600 ft. At about 9.45 a.m. the 30th tank car exploded and at about 10.55 a.m. the 32nd and 33rd tank cars ruptured almost simultaneously. Fragments from these damaged the 34th and 35th tank cars and caused them to release propane.

The main mechanism of damage in this incident was the rocketing of burning tank cars which hurled massive fragments and fresh fireballs up to 850 ft from the site of the derailment.

The fireball produced by the contents of one of these tank cars, which contained 33,000 USgal (120 m^3) of LPG, is shown in Figure A1.10. The fireball was several hundred feet high.

There were no fatalities, but 66 people were injured. There was extensive property damage.

Watrous (1970); NTSB (1972 RAR-72-02); Strehlow (1973b); Eisenberg, Lynch and Breeding (1975); D.J. Lewis (1980, 1991 LPB 101, 1993).

A51 *Linden, New Jersey, 1970*

On 5 December 1970 in a refinery at Linden, New Jersey, local overheating in a hydrocracker unit caused an explosive failure of the 7 in. thick vessel. Severe damage was done to plant over a 300 yard radius, including a catalytic cracker and crude pipe still, where the control room roof collapsed. Shut-down of the other units was effected from a blast resistant control room, which suffered minor damage. Forty persons were injured.

Mahoney (1990)

A52 *Port Hudson, Missouri, 1970*

At 10.07 p.m. on 9 December 1970, an abnormality occurred at a pumping station at Villa Ridge, 15 miles downstream from Port Hudson, Franklin County, Missouri. At 10.20 p.m. there was a sudden increase in throughput at the next upstream pumping station at Rosebud, indicating a major line break. The pipeline failure had occurred near Highway C on high ground and the gas cloud flowed down a sparsely inhabited valley.

At approximately 10.25 p.m. several witnesses became aware of the noise of the escaping jet of propane. A plume of white spray, which was presumably drops of propane and of atmospheric moisture, was seen rising 50–80 ft above

Figure A1.10 *Crescent City, 1970: fireball from rail tank car (Courtesy of Champaign Fire Department)*

the ground. By 10.44 p.m. several families had evacuated their houses and had driven to Highway C, from which they observed the cloud.

At approximately 10.44 p.m. the valley appeared to light up. Witnesses reported no observable period of flame propagation but rather a sudden flash as of lightning. There was an almost immediate overpressure which knocked over one person who was walking about half a mile from the centre of the cloud.

In the Bureau of Mines report on the incident, Burgess and Zabetakis (1973 BM RI 7752) state: We think the witnesses has the unusual experience of observing a gas detonation'. In the succeeding seconds a fire storm was seen to roll up the sloping terrain towards Highway C.

At the time and place of the failure the pipeline pressure was believed to be about 942 psig. The amount of liquid propane which is estimated to have escaped in the first 24 min is 750 bbl.

Burgess and Zabetakis estimate that since the propane issued from the pipe at approximately 1°C, the fraction flashing off would be about a quarter, but that a further appreciable fraction formed drops in the 50–80 ft plume seen by witnesses and that these drops derived their heat of vaporization from the air.

For the estimation of the concentration of propane in the vapour cloud Burgess and Zabetakis use the Pasquill–Gifford model, their work antedating the development of models for heavy gas dispersion and for complex terrain. Thus

$$\chi = \chi_{c1} \exp\left\{-\frac{1}{2}\left[\left(\frac{y}{\sigma_y}\right)^2 + \left(\frac{z}{\sigma_z}\right)^2\right]\right\} \qquad [A1.10.1]$$

with

$$\chi_{c1} = \frac{Q}{\pi \sigma_y \sigma_z u} \qquad [A1.10.2]$$

where x, y, z are the downwind, crosswind and vertical distances (ft); Q is the flow rate of propane (ft^3/s); u the average wind velocity (ft/s); σ_y, σ_z are the standard deviations in the y, z directions (ft); χ is the concentration of propane (volume fraction); and χ_{c1} is the concentration of propane on the centre line (volume fraction).

The calculation given by Burgess and Zabetakis may be summarized as follows. The flow rate Q of propane is 900 ft^3/s at STP, the wind velocity is 8 ft/s and the stability category may be taken as category F in the nomenclature of D.B. Turner (1970). The plume dispersion coefficients σ_y and σ_z are obtained from the graphs given by this author. The lower and upper detonability limits of propane in air given by Benedick, Kennedy and Morosin (1970) are 2.8% and 7.0%, respectively.

The dimensions of the detonable plume thus calculated are shown in Table A1.3 and in Figure A1.11. The total volume of the detonable zone is estimated to be 1,100,000 ft^3. Assuming that the average mixture strength is 4.9%, the volume of propane in the detonable zone is 54,000 ft^3, which is approximately 4.2% of the total quantity released up to the time of ignition. About the same amount of propane is contained in the over-rich part of the cloud. Thus most of the propane is dispersed beyond the lean limit contour.

The mass of gas in 1,100,000 ft^3 of 4.9% propane–air mixture at a temperature somewhat less than ambient is about 100,000 lb. The enthalpy release on detonation is 260 kcal/vapour. This compares with approximately 500 kcal/vapour for TNT. The TNT equivalent of detonable gas is therefore approximately 50,000 vapour.

Burgess and Zabetakis also present a second calculation which attempts to take better account of the heavier-than-air density of propane–air mixtures and uses the following relations given by Singer and Smith (1953) for gustiness category D:

$$\sigma_y = 0.44_x{}^{0.71} \qquad [A1.10.3]$$

$$\sigma_z = 0.2\sigma_y \qquad [A1.10.4]$$

This calculation gives the volume of the detonateable zone as 1,500,000 ft^3.

Burgess and Zabetakis give an analysis of the blast damage data in both the near and far fields of the explosion. Estimates of the TNT equivalent of the explosion range, with one exception, from 97,000 to 150,000 lb in the near field, while an estimate in the far field is 98,000 lb. This compares with estimates in the range 50,000–75,000 lb of TNT equivalent inferred from the volume of the detonable cloud.

The efficiency of explosion is calculated by Burgess and Zabetakis as follows. If the 750 bbl. of propane which are estimated to have escaped had detonated as a homogenous stoichiometric mixture with air, the enthalpy release would have been 666×10^6 kcal. The enthalpy of detonation of TNT is 10^6 kcal/ton. The explosion was equivalent to some

Table A1.3 *Calculated dimensions of detonable plume of propane formed at Port Hudson, Missouri, on 9 December 1970 (after Burgess and Zabetakis, 1973 BM PI 7752) (Reproduced by permission of the Bureau of Mines)*

Downwind distance	*Plume dispersion coefficients*		*Centreline concentration*	*Distances from plume axis to rich (r) and lean concentration limits*			
χ (ft)	σ_y (ft)	σ_z (ft)	χ_{CL} (%)	y_r (ft)	y_l (ft)	z_r (ft)	z_l (ft)
300	13	7.9	35	23	29	14.2	17.9
500	20	10.5	17	26	38	13.9	20.0
700	26	14	10	21	42	12.0	22.4
870	–	–	7.0	0	–	0	–
1000	36	18	5.6	–	43	–	21.4
1400	50	24	3.0	–	17	–	8.2
1470	–	–	2.8	–	0	–	0

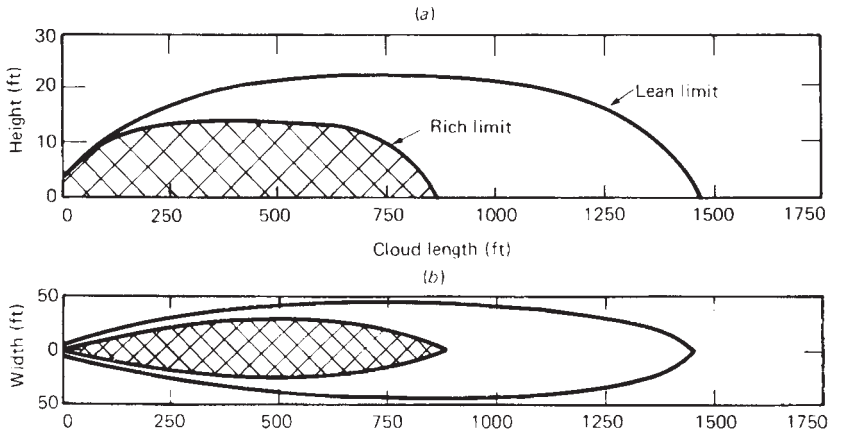


Figure A1.11 *Port Hudson, 1970: calculated dimensions of detonable plume of propane (after Burgess and Zabetakis, 1973 BM PI 7752) (Courtesy of the Bureau of Mines)*

50 ton of TNT. Thus the explosion gave 50/666 or 7.5% of the maximum theoretical yield, based on combustion of the whole cloud.

The source of ignition of the cloud is uncertain, but Burgess and Zabetakis conclude that it was probably located in one of a group of outbuildings enveloped in the cloud.

The explosion caused no deaths.

NTSB (1972 PAR-72-01); Burgess and Zabetakis (1973 BM RI 7752); Strehlow (1973b); Eisenberg, Lynch and Breeding (1975); D.J. Lewis (1980, 1993)

A53 *Houston, Texas, 1971*

At 1.44 p.m. on 19 October 1971, 20 freight cars were derailed at Mykawas Station, which is 10 miles south of the centre of Houston, Texas. Six of the tank cars contained VCM and two others butadiene and acetone. Two of the VCM tank cars punctured. An explosion and fire occurred while the crashed tank cars were still moving. The two punctured tank cars stopped in the burning area. At 2.30 p.m. there was a violent explosion when one of the tanks containing some 100,000 lb of VCM burst, hurling fragments and giving a large fireball. Further tank cars burst, feeding the fire and generating additional missiles.

One fireman was killed and some 50 people, many of them firemen, were injured. The area was sparsely built and populated and damage was slight.

NTSB (1972 RAR-72-06); Eisenberg, Lynch and Breeding (1975); D.J. Lewis (1980)

A54 *La Spezia, Italy, 1971*

On 21 August 1971, a rollover occurred in an LNG tank at the SNAM LNG terminal at La Spezia, Italy. There was a sudden increase in pressure resulting in discharges from the tank safety valves and vent. The safety valves discharged for about 75 min and the vent discharged at a high rate for 3 h and 15 min.

The incident occurred 18 h after the tank had been loaded from the Esso Brega. The loading had been done through a nozzle at the side of the bottom of the tank, with the heavier, hotter cargo staying on the bottom and displacing the lighter, colder 'heel' of LNG, which had remained in the tank. These conditions were temporarily stable, but over the subsequent period the density of the upper layer increased and that of the lower layer decreased, eventually inducing the rollover. One factor was that the temperature difference between the two layers caused the upper layer to heat up and to become more dense due to boil-off of the lighter fractions. Another factor was a failure of the control valve some 4 h before the rollover, which caused a reduction in the pressure in the tank which in turn increased the boil-off.

Sarsten (1972)

A55 *Long-view, Texas, 1971*

On 25 February 1971, a $\frac{1}{2}$ in. high-pressure ethylene gas pipe broke in a plant near Longview, Texas, and released 1000 lb of ethylene. The vapour cloud found a source of ignition and exploded. The explosion broke numerous other pipes and caused the release of tonnage quantities of ethylene. The resultant larger vapour cloud in turn was ignited and gave a violent explosion.

Four people were killed and 60 were treated in hospital.

Detailed information on the blast damage is given by Eisenberg, Lynch and Breeding (1975).

Eisenberg, Lynch and Breeding (1975); Lauderback (1975); D.J. Lewis (1980)

A56 *Pensacola, Florida, 1971*

On 11 September 1971, a pipe ruptured on a caprolactam plant at Pensacola, Florida, and released about 74,000 lb of cyclohexane at high pressure and temperature. A dense white cloud of cyclohexane vapour and mist formed which was estimated at over 100 ft high and about 2000 ft across at its maximum. The wind was very calm, but picked up slightly after the rupture.

The cloud was rich enough to stall two trucks enveloped in it from lack of oxygen. Vapour from the cloud was drawn into a powerhouse furnace so that the stack emitted black smoke. However, the cloud did not ignite and eventually dissipated harmlessly.

Eisenberg, Lynch and Breeding (1975); W.B. Howard (1975b); D.J. Lewis (1980); Stueben and Ball (1979) Sadler and Matusz (1994)

A57 *East St Louis, Illinois, 1972*
At about 6.20 a.m. on 22 January 1972, a rail tank car loaded with propylene collided with a stationary hopper car in the Alton and Southern Railway Company's Gateway yard at East St Louis, Illinois.

The tank car had come from the hump classification yard at overspeed. The overriding coupler of the hopper car punctured the tank, the propylene escaped and formed a large vapour cloud which then ignited and exploded.

More than 230 people were injured and extensive damage was done.

The NTSB investigation (1973 RAR-73-01) concluded that the accident was probably caused by the failure of the retarding system in the hump classification yard to decelerate effectively heavy tank cars with oil or grease on their wheel rims, by the absence of a backup system to halt cars passing through the retarders at overspeed and by the routine acceptance of such overspeeds.

NTSB (1973 RAR-73-01); Strehlow (1973a); Eisenberg, Lynch and Breeding (1975); D.J. Lewis (1980)

A58 *Hearne, Texas, 1972*
At 12.30 a.m. on 14 May 1972, a rupture occurred on an 8 in. crude oil pipeline near Hearne, Texas. Crude oil sprayed into the air from a 6 in. split in the top of the pipe, showering the surrounding countryside with oil. The oil flowed along a stream beneath a railway and a highway, and collected in a stock pond 1800 ft from the break.

At 5.00 a.m. the crude oil was ignited by an unknown source. The resultant explosion and fire killed a man and seriously burned two other people. An intense fire several hundred feet high and 1800 ft long burned on the surface of the oil and along the stream, at the railway, the road and the stock pond, and scorched the whole area.

The quantity of oil which escaped and burned was 7913 bbl (332,346 USgal). Some 10% of the oil was fractions lighter than hexane. The mode of break was such as to encourage the separation of these light hydrocarbon fractions and the formation of a flammable gas cloud.

NTSB (1973 PAR-73-02); Eisenberg, Lynch and Breeding (1975)

A59 *Lynchburg, Virginia, 1972*
On 9 March 1972 at Lynchburg, Virginia, a tractor semitrailer tank truck carrying LPG overturned and punctured. A 32 in. hole appeared and some 4000 of the load of 9208 USgal escaped before the liquid level fell below the hole. A vapour cloud formed and gave rise to a fireball. The radius of the fireball was estimated as at least 400 ft. Three eyewitnesses standing beside their cars at 450 ft distance were severely burned by thermal radiation but were not touched by the flames. Two persons died and at least five were injured.

NTSB (1973 HAR-73-03); Eisenberg, Lynch and Breeding (1975)

A60 *New Jersey, Turnpike, 1972*
On 21 September 1972 on the New Jersey, Turnpike, a tractor semitrailer tank truck carrying 7209 USgal of propylene sideswiped a bus. The tractor's fuel tank and the fittings on the propylene tank were damaged and fuel and propylene leaks occurred. A friction spark from the collision ignited the fuel leak and the fire spread to the propylene leak. After some 20–25 min the tank exploded with a huge fireball. Fragments of the tank rocketed: the front section, comprising three-quarters of the tank, was found 1307 ft to the north-east; the rear head was found 540 ft to the south-west and the rear one quarter cylindrical section 229 ft to the south-west; tank components were mainly strung out in a line stretching 850 ft to the south-east. Two persons were killed and 28 injured.

NTSB (1973 HAR-73-04); Eisenberg, Lynch and Breeding (1975)

A61 *Rio de Janeiro, Brazil, 1972*
On 30 March 1972, a BLEVE occurred on an LPG sphere, one of five, at the Duque de Caxais refinery, Rio de Janeiro, Brazil. An operator was engaged in draining water from the bottom of a 1600 m^3 sphere. He went away, leaving open a 2 in. drain valve. When he returned, he found that he could not reach the valve to turn the flow off, because the jet of liquid, now LPG, had created a crater in the crushed stone under the sphere. A vapour cloud formed, ignited and flashed back to the sphere. Some 15–20 min later the relief valve opened and the material released ignited. The sphere then suffered a BLEVE. Thirty-seven people were killed and 53 injured. The other four storage spheres survived.

Mahoney (1990); Selway (1988 SRD R492)

A62 *Austin, Texas, 1973*
At 10.53 p.m. on 22 February 1973 at Austin, Texas a 10 in. pipeline failed and released 278,880 USgal of NGL. The release blew a 10 ft diameter hole in the ground and a vapour cloud spread over the area. Soon after 11.00 p.m. two cars entered the cloud and stalled; their drivers got out. Then a van drove into the cloud and also stalled; the passengers got out, whilst the driver tried to restart. A large spark emerged from beneath the van and flames leaped hundreds of feet in the air. The fire burned through the cloud and the eight people in it were engulfed in flames. Four died immediately, two later and two sustained severe burns.

NTSB (1973 PAR-73-04); Eisenberg, Lynch and Breeding (1975)

A63 *Kingman, Arizona, 1973*
On 5 July 1973, a BLEVE and fireball occurred on a rail tank car containing propane at Kingman, Arizona. The upper surface of the tank had been heated by jet flames from a relief valve and coupling leak.

The event is captured in the NFPA film 'BLEVE' and has been analysed by Crawley (1982). The tank was a 'jumbo' one and he estimates that the tank capacity was 150 m^3 but assumes that it was perhaps half full. He assesses the diameter of the fireball as 400 ft and its duration as 10–15 s. The estimates given by V.C. Marshall (1987) are that some 45 te of propane took part and that the fireball radius was 150 m.

Despite police advice a large crowd of spectators had gathered and more than 90 were injured.

Crawley (1982); Hymes (1985 LPB 65); V.C. Marshall (1987)

A64 *McPherson, Kansas, 1973*
At 4.30 a.m. on 6 December 1973, a major leak occurred on the Mid-America Pipeline System at the Conway pump station near McPherson, Kansas. Prior to the leak an ice storm had been raging for two days and the pump station had lost power for 18 h, although it was partially restored by 3.00 a.m. The pipeline had been shut-down and upon

start-up at 4.12 a.m. a block valve failed to open, the line was overpressured and burst at a point where it had already sustained construction damage.

An estimated 230 tons of anhydrous ammonia escaped over a period of half an hour. A low, visible plume of ammonia formed and drifted over Highway 56, which is some 1000 ft to the south. The weather conditions were very stable with a wind speed of some 5–10 mile/h and the plume remained narrow. Irritation symptoms were experienced and odour was detectable for about 3.5 and 8 miles from the escape, respectively.

The incident caused no serious casualties. Many residents had moved into a nearby town on account of power failures caused by the severe weather. Two truck drivers drove into the gas cloud on the highway. They escaped and were kept in hospital several days. People in dwellings $^3/_4$ mile south of the leak and directly in the cloud path were safely evacuated by the Sheriff's office and company personnel.

By 4.30 p.m. the line had been stopped.

The same pipeline failed again on 13 August 1979 at a point about 22 miles from the first failure. There was a release of some 360 tons of anhydrous ammonia. Again there were no casualties, but there was a large fish kill.

NTSB (1974 PAR-74-06); Luddeke (1975)

A65 *Potchefstroom, South Africa, 1973*

At 4.15 p.m. on 13 July 1973, a sudden failure occurred in an anhydrous ammonia storage vessel at the Potchefstroom works of TRIOMF, a company part-owned by African Explosives and Chemical Industries Ltd. The tank was one of four 50 ton horizontal pressure storage bullets. An estimated 30 tons of ammonia escaped from the tank itself and another 8 tons from a tank car.

The failure gave rise immediately to a gas cloud some 150 m diameter and 20 m deep. At the time of the accident the air was apparently still, but within a few minutes a slight breeze arose which caused the cloud to move towards a township some 200 m to the north-east. The visible cloud then extended some 450 m downwind and 300 m across.

Deaths occurred both inside and outside the factory fence. At the time there were some 350 persons working in the plant, of whom some 30 were within 70 m of the failed tank. One employee was killed by the blast and eight died while trying to escape from points within a 100 m radius of the tank. Three others died of gassing within a few days.

Outside the factory fence four people were killed immediately and two died a few days later. Thus altogether 18 people were killed.

The occupants of the granulation plant control room 80 m south-east of the failure survived. They put wet cloths over their faces and were taken to safety after some 30 min.

The failures occurred in tank No. 3 while it and tank No. 4 were being filled simultaneously from a tank car. Actuation of an excess flow valve on the line between the two tanks prevented the release of the contents of tank No. 4 also. The tank car did not have an excess flow valve and did suffer escape of material.

The cause of the failure was brittle fracture of the dished end of the tank. Evidence suggested that there had been no overpressure or overtemperature of the tank contents and no other triggering event was determined.

The tanks were designed and fabricated in accordance with BS 1515: 1965 and were fabricated and commissioned in 1967. The fabrication is described by Lonsdale (1975):

> The dished ends were fabricated from two plates, cold-formed in the major radius, and hot flanged (at 850°C) at the knuckle. The plates had been passed as being in accordance with the requirements of BS 1501-151-28A. The butt welds in the end plates were checked by 100% X-ray after forming and flanging. (Expert metallurgists re-examining the X-rays of the failed dished end considered that two sections of the weld did not conform to the requirements of the BS code.) The Inspection Authority representative considered that conditions in the flanging furnace rendered subsequent heat treatment unnecessary.
>
> The completed tank was not stress-relieved because it is not required by BS 1515. The tanks were given an hydraulic test at $1^1/_2$ times the design pressure of 250 lb/sq in gauge.

Late in 1971 tank No. 3 was inspected. Two weld faults and a crack were found and were ground out. The tank was hydraulically tested to 347 psig for 30 min. Following repairs to a leaking tank level glass isolation valve, the tank was hydraulically tested to 325 psig for 3–4 h.

Metallurgical testing revealed that the metal of the dished end was below its transition temperature under normal conditions. The minimum Charpy impact testing transition temperatures obtained were 20°C for the fragment and 115°C for the remaining part of the dished end.

Ultrasonic examination of the dished end in No. 4 tank revealed numerous subsurface fissures. Such fissures may have provided the notch from which the brittle fracture in No. 3 tank propagated. After this examination tank No. 4 was withdrawn from service.

Following the inquiry into this accident, the South African authorities laid down that 'All vessels containing dangerous substances shall be given appropriate heat treatment irrespective of the (construction) code requirements.'

Commenting on this Lonsdale states

> Stress-relieving does not overcome fully the damage done by progressive cold-forming of a dished end. This is particularly so where seam welds have had to be made in the dished end. There is a strong case for avoiding the use of progressively cold-formed ends for pressure vessels because of the difficulty of controlling the final state of the metal.

Lonsdale (1975); D.J. Lewis (1993)

A66 *St Amand-les-Eaux, France, 1973*

On 1 February 1973, a road tanker containing 19 tons of liquefied propane skidded and overturned on a wet road surface in the village of St Amand-les-Eaux. A rupture occurred on the tanker and propane began to escape. The driver of the tanker immediately took steps to stop traffic entering the street and to warn the population. The vapour cloud grew and finally exploded, causing 5 deaths and 40 injuries. The death toll might well have been higher but for the prompt action of the driver in carrying out his emergency procedures.

Anon. (1973j); D.J. Lewis (1980)

A67 *Staten Island, New York, 1973*

On 10 February 1973 at Staten Island, New York, an explosion occurred inside a large LNG storage tank in which

work was being done. The tank was being repaired for a leak in the inner membrane lining and new liner sections were being installed. The tank had been well ventilated before work began. The source of fuel for the explosion was identified as LNG trapped in the insulation behind the liner and vaporized by the heat-sealing operations on the new liner sections. The explosion lifted up the concrete roof of the tank which then fell back into it, crushing the men there. Forty men were killed and three injured.

US Congress (1973); D.J. Lewis (1989, 1993)

A68 *Aberdeen, UK, 1974*

An incident which occurred at Aberdeen on 17 January 1974, is described by Willcock (1986) in the following terms:

> (1) Butane tanker skids on black ice. Shaken and lightly injured driver regains control and stops safely at nearside kerb; (2) Half an hour later articulated lorry skids on black ice, collides with tanker and shears off emergency discharge valve. Gas starts escaping. Second driver slightly injured; (3) Five minutes later yet another articulated lorry skids and crashes into the other two. One more hurt driver; (4) Police and fire brigade arrive a few minutes later, but before they can get organized a car, trying to stop at the accident, skids into the rear of the tanker. Impact ignites butane.
>
> Willcock (1986)

A69 *Chicago, Illinois, 1974*

Soon after 12.30 p.m. on Friday 26 April 1974 employees at the Bulk Terminals complex in the Calumet Harbor area on the south side of Chicago, Illinois, heard a dull thud and saw fumes rising from the dike of Tank 1502, which contained 3300 m^3 of silicon tetrachloride. Bulk Terminals was a storage tank farm with 78 tanks ranging up to 4900 m^3 in size, containing products such as vegetable oils and chemicals. It was situated in a built-up area.

This was the start of an incident which involved a massive cloud of irritant gas in a built-up area and was to prove very prolonged. At times the cloud was 8–16 km long. It took until May 3 to stop the leak and transfer the material and until May 15 before emissions were finally reduced to tolerable levels.

Investigation found that a pressure release valve on a 6 in. line leading to the tank had been inadvertently closed. A flexible coupling in the line burst under pressure. The whole piping system shifted, cracking a 3 in. line on the tank wall. Liquid silicon tetrachloride escaped, creating a cloud with formation of hydrogen chloride gas.

The initial emergency response was confused. The terminal management awaited action by the owners of the chemical. The fire service first decided not to get involved, because there was no fire. Lime trucks diverted to the scene by the EPA with a view to neutralizing the liquid in the dike were refused entry to the site.

By 3.00 p.m. the cloud was 400 m wide, 300–450 m high and 1600 m long.

Two agents were considered to blanket the liquid in the dike: non-protein high expansion foam and No. 6 fuel oil. At 4.10 a.m. on Saturday 27 April, foam was applied but was not effective. At about 9.00 a.m., fuel oil was added and eight truck loads of lime were tipped in. Within an hour the vaporization was dramatically reduced. By noon matters appeared to be under control with a 16-member US Army chemical warfare team involved in transferring the material from the damaged tank.

About 8.00 a.m. on Sunday 28 April, however, heavy rain began to fall on the hydrogen chloride cloud. Power lines were rapidly corroded and sparked like a firework display. By 9.30 a.m. four pumps had become inoperable due to corrosion. Then power failure put a stop to pumping.

The threat existed that the pipe system would suffer further failure and release the remaining 2300 m^3 of material into the dike, which had been reduced in capacity by the material added to it. A large pit was dug to take any overflow from the dike and an operation was undertaken to seal the leak using quick drying cement.

On the morning Monday 29 April inspection of the pipe system, undertaken in the cloud with a visibility of some 18 in., indicated that the leak had not been sealed, either because the application had been ineffective or because it had been made at the wrong point. A second concrete pour was undertaken and completed by 11.30 p.m.

By the morning of Tuesday 30 April the emission had been greatly reduced. It took, however, another three days to transfer the liquid out of the tank.

In this incident one person died, 160 were hospitalized and 16,000 were evacuated.

Hoyle (1982)

A70 *Climax, Texas, 1974*

On 29 June 1974 at Climax, Texas, a derailment occurred which resulted in the puncture of a rail tank car containing liquid vinyl chloride monomer. The hole in the end of the tank was 4 ft × 4 ft. The vinyl chloride escaped and formed a vapour cloud which travelled 1600 ft to the derailed locomotive, where it ignited. There followed a violent vapour cloud explosion. It was found that the cylinder head had been blown off the diesel engine, which fact led to the hypothesis that vinyl chloride had been ingested into the engine and that the engine explosion had been the trigger for the vapour cloud explosion. The contents of the ruptured tank car continued to burn after the explosion and a flame played on another vinyl chloride tank car which suffered a BLEVE. The explosions occurred in a rail cutting and there were no injuries.

Eisenberg, Lynch and Breeding (1975)

A71 *Decatur, Illinois, 1974*

On 19 July 1974, a vapour cloud exploded in the rail-shunting yard at Decatur, Illinois. During shunting operations, a rail tank car was punctured by the coupler of a boxcar into which it had run, the hole being some 0.3 m^2. The tank car contained 69 te of isobutane, which escaped and formed a vapour cloud. There was a delay of 8–10 min before the cloud ignited. There then occurred a massive vapour cloud explosion which caused extensive damage. Seven people were killed and 349 injured.

This vapour cloud explosion has been of some interest, because on the basis of the assessment of certain injury and damage effects, the yield of the explosion has been estimated as unusually, even anomalously, high. The matter has been considered by V.C. Marshall (1980d, 1987), who gives a detailed comparison between the explosions at Flixborough and at Decatur, and concludes that the latter was certainly no more severe than the former, that its yield has been overestimated and that it was in fact comparable to that in other vapour cloud explosions. He comments, however, that in a shunting yard the wagons serve to

promote turbulence and provide on their undersides vertical confinement.

NTSB (1975 RAR-75-04); Eisenberg, Lynch and Breeding (1975); V.C. Marshall (1980d, 1987)

A72 *Los Angeles, California, 1974*

On Saturday 17 August 1974, an explosion occurred on a load of organic peroxides on a semitrailer in a storage shed at Los Angeles, California. The load was a mixed one of several different peroxides, totalling 5.3 te. It had been made up on the Friday, but the customer had declined delivery before the weekend, and the semitrailer was therefore parked in the storage shed until the Monday. On the Saturday smoke and flames were seen coming from the shed and shortly afterwards there was a tremendous explosion. The source of the fire is not known. There were no injuries.

Sharry (1975); D.J. Lewis (1993)

A73 *Petal City, Mississippi, 1974*

On 25 August 1974, a new salt dome storage was being filled with butane when a release occurred. The capacity of the storage had been miscalculated with the result that the head of the brine being displaced fell below that equivalent to the gas pressure and butane issued at high velocity. A quantity of butane estimated as 40–90 te escaped and formed a vapour cloud extending 2 km. The cloud ignited with a small explosion, there followed a second, stronger explosion and the cloud then burned for 5 h. It has been suggested that the initial combustion and associated thermals promoted air entrainment into the mainly over-rich cloud so as to create a large elevated flammable volume which then exploded. Twenty-four people were injured.

Anon. (1974n); D.J. Lewis (1993)

A74 *Antwerp, Belgium, 1975*

On 10 February 1975, an explosion and fire caused extensive damage at a low-density polyethylene plant at Antwerp, Belgium. The cause was a leak of ethylene at high pressure due to fatigue failure of a vent connection on the suction of a compressor. Six persons were killed and 13 injured.

Mahoney (1990)

A75 *Beek, The Netherlands, 1975*

On the early morning of 7 November 1975, the start up of Naphtha Cracker II on the 100,000 tons per annum ethylene plant at the Dutch State Mines (DSM) works at Beek was under way. At about 6.00 a.m., the compressed gas was sent to the low temperature system. At 9.48 a.m., an escape of vapour was observed near the depropanizer. Shortly after, the cloud formed found a source of ignition and there was a massive vapour cloud explosion.

The explosion caused extensive damage and started numerous fires. Fire broke out in the pipeline systems and Tank Farm 2. Six tanks ranging in capacity from 1500 to 6000 m^3 within a common dike were burned out. An aerial view of the plant after the explosion is shown in Figure A1.12.

The explosion killed 14 and injured 104 people inside the factory, and injured three persons outside it.

The accident was investigated by a team from the Ministry of Social Affairs. Their findings are given in the Report on the Explosion at DSM, Beek on November 1975 (the Beek Report) (Ministry of Social Affairs, 1976). The investigation involved TNO and the Department of Steam Engineering (Stoomwesen). A separate investigation was carried out by the company.

van Eijnatten, (1977)

The investigation was hampered by the destruction of the instrument records in the control room. Figure A1.13 shows the state of part of the control panel. A detailed breakdown of the degree of damage done to the instrumentation is given in the report. It was also difficult to obtain useful information from the instruments which were retrieved, due to lack of synchronization, use of wrong recorder charts, lack of ink, inconsistent colour codes and out-of-date instrument diagrams.

The evidence suggested that the escape occurred due to low temperature embrittlement at the depropanizer feed drum, on and around which five fractures were found. Three of these were identified as secondary ruptures, but there were two which could have been primary failures. Two hypotheses were put forward. The principal one considered by the government team was that the initial rupture occurred on a 40 mm pipe connecting the feed drum to its safety valve.

The function of the feed drum was to take the €3* stream from the bottom of the de-ethanizer and a stream from the condensate stripper and pass this mixed liquid and vapour feed to the depropanizer. If the depropanizer were fouled, the feed drum could give a rough cut between the C_3 fraction and the heavier liquids. The normal operating temperature of the drum was 65°C.

At the time of the start-up, the reboiler of the de-ethanizer column was not operating properly. Possibly the circulation of hydrocarbons through the reboiler was reduced by thickening of the liquid. In consequence, the bottom product from the de-ethanizer was a liquid at about 0°C or lower with a high C_2 content. Discharge of this de-ethanizer stream into the feed drum would give flashing and could result in a temperature as low as −10°C.

Coincidentally there was a half-hour interruption in the flow from the condensate stripper due to a failure in the propylene compressor system. As a result, a layer of liquid containing a large proportion of C_2s was deposited on top of a layer of warm C_3^+ liquid in the feed drum. From the evidence the two layers had not mixed to any appreciable extent and the top layer was at about −10°C.

The feed drum material was a carbon steel which can normally be used at temperatures as low as −10 to −20°C. The fracture occurred at an autogenic weld. With such welds ageing can occur which could raise the transition temperature possibly up to 0°C.

An alternative hypothesis which the government team considered was that the rupture had been caused by explosion of organic peroxides which might have been formed from material trapped in a section of flush pipe which was isolated and which was found to have ruptured.

The amount of flammable material which escaped prior to the explosion was estimated at about 5.5 tons of hydrocarbons, mainly propylene, There is some uncertainty, however, about this figure.

The best estimate of the cloud shape from the explosion damage is that shown in Figure A1.14. The location of the damage indicated that the depth of the cloud did not exceed 4 m.

The estimated time which elapsed between the rupture and the explosion is approximately 2 min. From eyewitness accounts the source of ignition was identified as the flash drums in Section 1.

The quantity of flammable material which exploded was estimated as about 800 kg of propylene with an energy release equivalent to 2.2 tons of TNT.

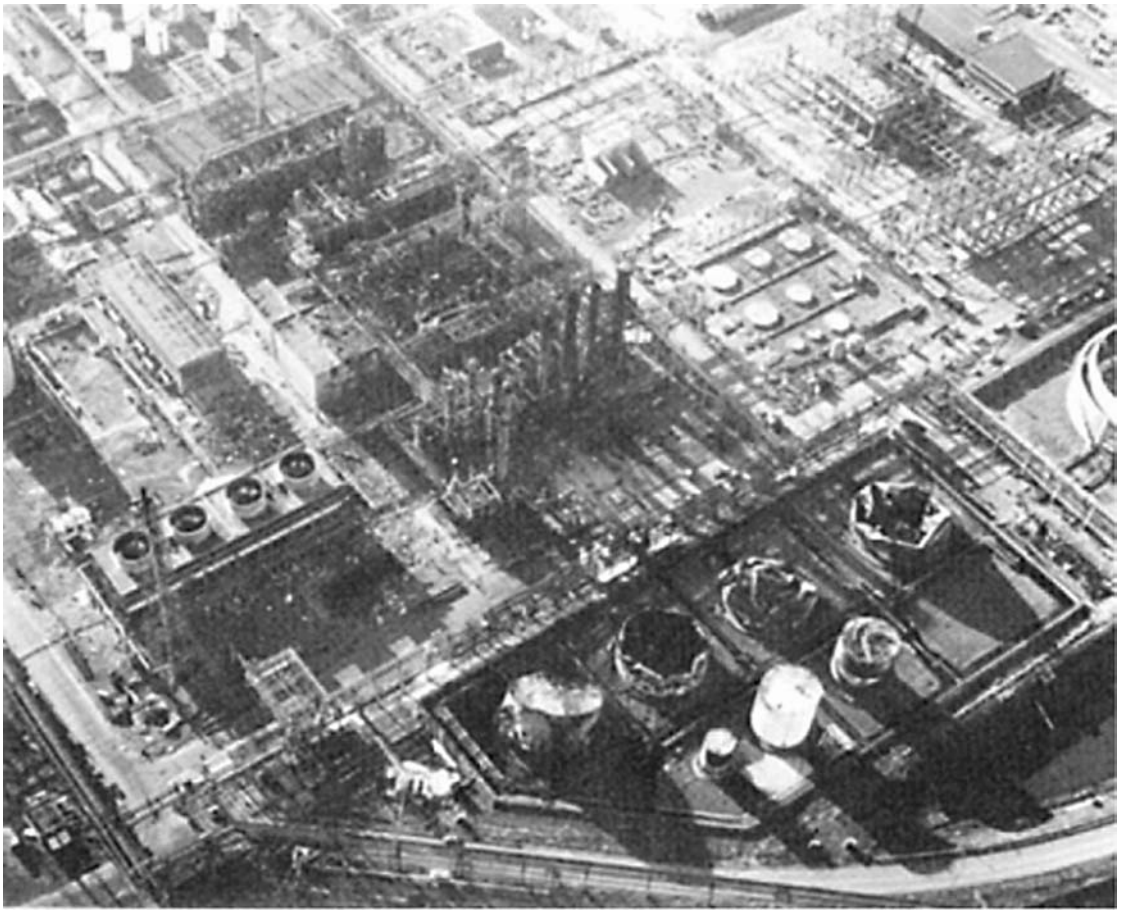


Figure A1.12 *Beek, 1975: DSM works after the explosion (Ministry of Social Affairs, 1976)*

From the damage to the control room it was calculated that an overpressure of 0.2–0.3 bar must have acted on the walls. But the estimated overpressure required to cause the damage to the cold blowdown drum was approximately 1 bar.

The damage outside the factory was entirely breakage of glass. The bulk of the damage was within a radius of 4.5 km. It was believed that the pressure at this distance might have been about 0.005 bar, which is sufficient to break thin glass. It was suggested that damage beyond this distance may have been due to the deflection of shock waves by reflecting layers in the upper atmosphere. Flying glass caused one of the three injuries outside the factory.

The incident illustrates the stress created by a developing emergency of this kind and the confusion liable to ensue. At about 9.35 a.m. the operators were engaged in dealing with start-up problems. One entered the control room and called out 'Something has gone on Cll and there's an enormous escape of gas'. He was distressed and was rubbing his eyes. He staggered against the telephone switchboard. A second operator ran to the entrance and tried to get out, but his view was obscured by a thick mist. He smelled the characteristic odour of C_3–C_4 hydrocarbons and realized there must be a major leak. He gave orders for the fire alarm to be sounded and ran out through another entrance to look at the gas cloud. He was seen from another office by a third man, apparently terrified and pointing to a gas cloud near the cooling plant.

Some witnesses stated that the fire alarm system in the control room failed. The investigation concluded, however, that the fire alarm system was in good working order before the explosion, but that none of the button switches for the fire alarm was operated.

Another aspect of the emergency was that the telephone lines to DSM were partially blocked by overloading. This did not affect rescue work, however, because the rescue services had their own channels of communication.

Ministry of Social Affairs (1976); van Eijnatten (1977); D.J. Lewis (1980, 1993)

A76 *Eagle Pass, Texas, 1975*

At 4.20 p.m. on 29 April a Surtigas tractor tank semi-trailer carrying LPG on US Route 277 near Eagle Pass, Texas, swerved to avoid a car in front which slowed suddenly to

Figure A1.13 *Seek, 1975: damage to instrumentation in the control room (Ministry of Social Affairs, 1976)*

make a turn. The tank semitrailer separated from the tractor, struck a concrete wall and ruptured, releasing LPG. Witnesses described a noise like that of a violent storm, followed immediately by an explosion. Simultaneously, fire covered the area and there was then a second explosion.

The large front section of the tank rocketed up, struck an elevated sign, travelled 1029 ft and struck the ground; bounced up and travelled 278 ft; struck and demolished a mobile home; bounced up again and travelled 347 ft over another mobile home, causing it to burst into flames and be destroyed; and finally fetched up 1654 ft from its starting point.

Sixteen people, including the driver, were killed and 512 suffered burns.

NTSB (1976 HAR-76-04)

A77 *Ilford, Essex, 1975*

At 11.10 a.m. on 5 April 1975, an explosion occurred at the factory of Laporte Industries Ltd at Ilford, Essex. The explosion was in a Lurgi electrolysis plant. The plant suffered extensive damage and one man who was injured subsequently died.

The electrolysis plant produced hydrogen for process use and oxygen as a waste product by electrolysis of potassium hydroxide solution. The investigation concluded that the explosion probably occurred on the oxygen separating drum into which hydrogen had leaked. After the accident the company carried out a mass balance on the hydrogen flows just prior to the explosion and found that no less than 50% was unaccounted for.

The ingress of hydrogen into the oxygen drum was apparently due to corrosion/erosion in the electrolysis cells. The internal breakdown of the cells had probably been initiated some time before the accident. On 2 April a cracking noise was heard in the cell block, which may have indicated minor explosions.

There was a system of monitoring the purity of the hydrogen and oxygen streams by hourly gas analyses performed by the process operator. The evidence suggested that these analyses were not always carried out and that assumed values were entered in the process log. One operator stated that he only did the analyses two or three times in every 12 h.

The report on the accident by the HSE (1976b) estimated that on the basis of the explosion damage the 1690 l oxygen drum contained a 13.5% hydrogen, 86.5% oxygen mixture and the explosion produced a shock wave equivalent to 22 kg of TNT. It was calculated that this explosion would have caused an overpressure of 1.03 kPa at 220 m and of 0.21 kPa at 660 m on an open site.

The most powerful explosion would have been produced by a stoichiometric mixture of 66 $\frac{2}{3}$% hydrogen, 33 $\frac{1}{3}$%

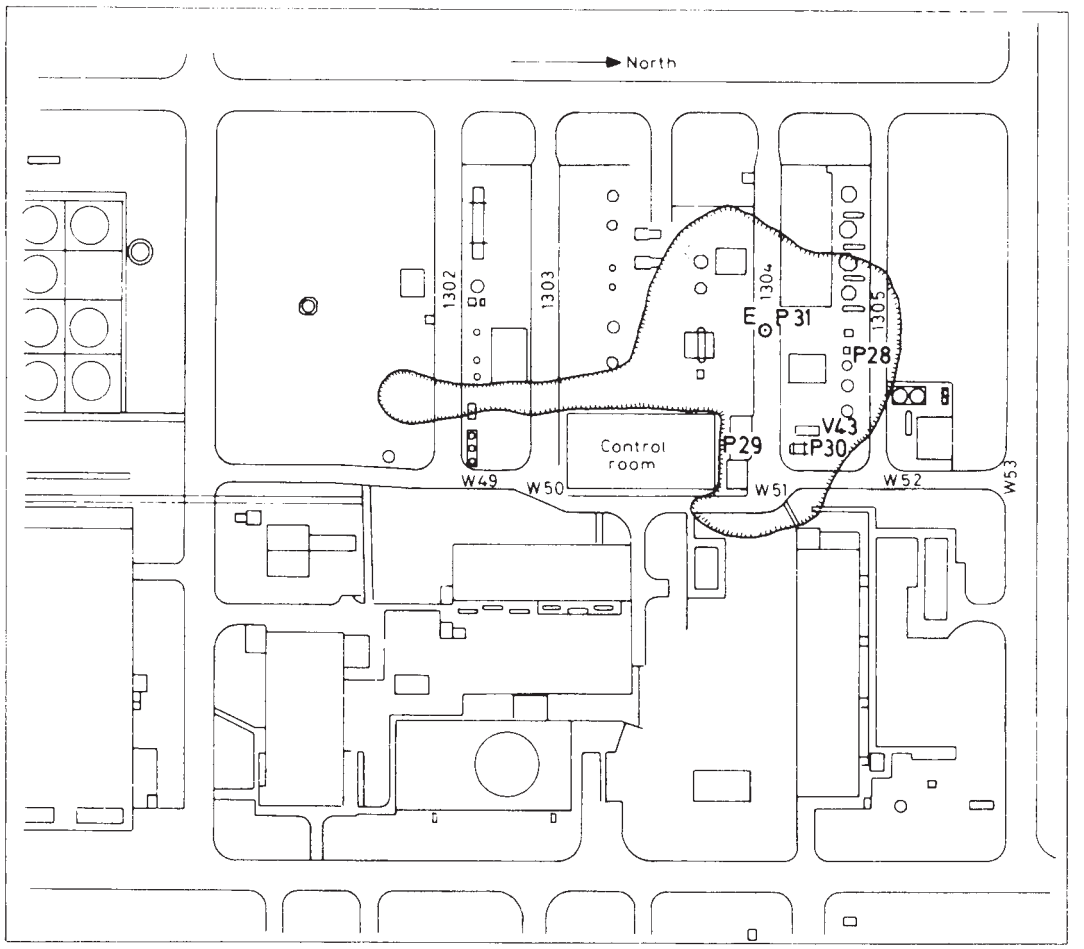


Figure A1.14 *Beek, 1975: simplified site plan of the works showing the estimated dimensions of the vapour cloud (Ministry of Social Affairs, 1976. Reproduced by permission)*

oxygen. Assuming a pressure equal to the set pressure of the relief valve on the drum, 515 psig, this composition would have produced a shock wave equivalent to 90 kg of TNT and this was calculated to cause an overpressure of 1 kPa at 350 m and 0.21 kPa at 1050 m.

The factory was in an urban area with houses 180 m and a school 210 m from the electrolysis plant. Although on an open site some damage might be expected from an explosion of the size described at these distances, none actually occurred. Probably this was due to the fact that the electrolysis plant was housed in a building designed and constructed to direct any blast upwards.

HSE (1976b)

A78 *Scunthorpe, Lincolnshire, 1975*

At about 1.25 a.m. on 4 November 1975 the Queen Victoria blast furnace at the Appleby Frodingham works of the British Steel Corporation (BSC) was tapped. By about 2.00 a.m. some 175 tons of iron had been run into the first torpedo ladle and the stream was diverted into the second ladle. Some 10–15 min later intense flames and sparks began to issue from the blow pipe on No. 3 tuyere. The furnace crew tried to keep the pipe cool by spraying it with water and took steps to bring the furnace off blast to allow a new pipe to be fitted. While this was going on, a substantial water leak was observed coming from the furnace, but its source could not be located because of the flames. The water ran down the casthouse floor and entered the full torpedo ladle.

Just before 2.47 a.m. the shift manager's instruction to remove the full ladle was passed on to the loco driver and shunter by traffic control. The traffic personnel were informed that water was running into the ladle. At 2.47 a.m. an explosion occurred as the ladle was moved.

Some 90 tons of metal were ejected. Four people were killed and 15 injured, and a further seven died later.

The energy of explosion was estimated from the structural damage as 2.5 MJ or the equivalent of 1 lb of high explosive. The energy required to eject the hot metal was estimated to have a maximum value of 12 MJ. The thermal energy in the hot metal was some 10,000 times greater than this.

Investigation revealed that the water leak was probably due to the failure by corrosion of a steel-blanking plug on a cooling water pipe. Such plugs had been in use for at least 20 years. It transpired that there was among the employees considerable collective experience of previous failures of blanking plugs, although in most cases the knowledge of individuals was limited.

HSE (1976a)

A79 *Baton Rouge, Louisiana, 1976*

On 10 December 1976, a massive chlorine release occurred from a storage vessel at Baton Rouge, Louisiana. The vessel was a horizontal bullet tank 125 ft long × 11 ft diameter resting on a load cell weighing system. An internal explosion caused the vessel to fall off its supports so that it was pierced by a metal upstand on the ground. Over a period of 5.6 h 90.7 te of chlorine was released. A gas cloud formed described as a 42 mile long wedge, lying over the Mississippi river and sparsely populated areas. Ten thousand people were evacuated. Three persons were treated for minor irritation.

The cause of the tank displacement was an internal explosion of a natural gas–chlorine mixture at one end of the vapour space in the half full tank which produced a liquid surge along the length of the tank so that the momentum of the liquid caused the tank to jump off its supports. The tank was normally padded with nitrogen. The same nitrogen system was connected to the gland seals of hydrogen compressors in order to exclude air from the hydrogen. There was in addition a natural gas system which could be used on the gland seal as a more economic alternative. Due to the cold weather trouble had been experienced with natural gas condensate and the nitrogen system was in use. At some stage the lines to the nitrogen and natural gas systems were open at the same time and natural gas at higher pressure got into the nitrogen system. When the plant was restarted, an explosion occurred in the chlorine liquefaction system. It then spread via a balance line to the vapour space of the chlorine tank.

Anon. (1976n); Rees (1982); D.J. Lewis (1984b, 1993)

A80 *Geismar, Louisiana, 1976*

On May 24 1976, an explosion occurred on a large polyglycol ether reactor. The cause is believed to have been loss of agitation possibly combined with failure of a temperature transmitter and/or addition of insufficient catalyst. The explosion hurled the reactor head some 1400 ft and fragments ruptured a large polyglycol ether tank and severed the sprinkler system riser. Unreacted ethylene oxide and propylene oxide and other reactor contents escaped and there was a major fire involving the reactor and tank farm areas.

Mahoney (1990)

A81 *Kings Lynn, Norfolk, 1976*

At approximately 5.10 p.m. on Sunday 27 June 1976, an explosion occurred on the Clopidol plant of the Dow Chemical Company at King's Lynn, Norfolk. One man was killed and extensive damage was done to the plant and the buildings. The explosion involved the detonation of Zoalene, a poultry feed additive.

Some months before it has been discovered that stocks of Zoalene had fallen below their normal level of purity and it was decided to remove water, one of the main impurities, by drying the material in a drier on the Clopidol plant.

The drier was provided with dust explosion protection, including nitrogen inerting, explosion suppression devices and explosion relief.

On 25 June at 3.00 p.m. a batch of Zoalene was charged to the drier. At 2.00 p.m. on 26 June the steam to the drier was shut off. The material was left in the drier, however, at a temperature of approximately 120–130°C. At 5.07 p.m. the following day sound was heard coming from the drier and the shift foreman activated the emergency procedures. At 5.10 p.m. the explosion occurred.

Zoalene was known to be a reactive chemical, but, as the incident showed, the hazard of a change to the process which involved holding the material at a moderately high temperature for a prolonged period was not fully appreciated and there were no instructions for the discharge of the material on completion of drying.

The accident also revealed deficiencies in the methods available for screening materials to detect exothermic reactions. Zoalene had been screened by the company using differential thermal analysis, but this had revealed no exotherm at the processing temperature. After the accident samples of Zoalene were tested by RARDE using differential scanning calorimetry. Exotherms were found in the temperature range 248–274° C.

Zoalene samples were also tested by the company using the new technique of accelerating rate calorimetry developed by Dow itself. It was found that samples would self-heat to decomposition if held under adiabatic conditions at 120–125°C. At the time of the accident the company was working through a programme of screening its reactive chemicals, but had not yet checked Zoalene.

The investigation described in the report of the HSE (1977b) concluded that the explosion had been a detonation with an energy release of 200–300 lb of TNT, that a temperature of over 800°C had been reached before detonation occurred and that there had been an extremely rapid pressure rise, probably to over 10,000 psi.

The report gives a detailed map of the locations of the fragments from the explosion.

HSE (1977b)

A82 *Los Angeles, California, 1976*

On 17 December 1976, a violent explosion occurred aboard the tanker Sansinena at Los Angeles, California. The ship had offloaded a cargo of light crude oil and was loading Bunker C oil. It was equipped with neither a vapour recovery nor a cargo tank inerting system. The explosion is believed to have been initiated by a spark from a pump. The force of the explosion threw the centre section and the bridge onto the dockside, leaving the bow and stern sections afloat.

NTSB (1978 MAR-78-06); D.J. Lewis (1984c); Mahoney (1990)

A83 *Plaquemine, Louisiana, 1976*

On 30 August 1976 at Plaquemine, Louisiana, the top was blown off a transfer oil surge tank on an ethylene oxide plant, causing a serious fire and damage to six reactors and other equipment. A leak between the shell and tube sides of a reactor heat exchanger had allowed air at 200 psig to enter the heat transfer system.

Mahoney (1990)

A84 *Southwest Freeway, Houston, Texas, 1976*
At about 10.45 a.m. on 11 May 1976 in Houston, Texas, a tractor tank semi-trailer carrying ammonia went through a bridge rail on the interstate highway 1–610 and fell some 15 ft onto the South-west Freeway, US 59. The interchange was the busiest in the state and at the time traffic was quite heavy. The tank, which held 19 te of liquid anhydrous ammonia, burst.

The crash was caused by the excessive speed of the vehicle and by sloshing of the liquid in the partially loaded tank. However, the speed did not exceed 54 mile/h.

The ammonia was released and formed a visible fog. It was a bright sunny morning with a wind speed of 7 mile/h. The initial height of the cloud determined from photographs was about 30 m. The cloud was observed to reach a width of about 300 m and a length of 600 m. One photograph showed a tail to the left-hand side, indicating the typical slumping behaviour of heavy gas. It is estimated that the ammonia evaporated and the cloud dispersed within about 5 min. The driver of the truck and five other people were killed, 78 taken to hospital and about another 100 injured. Apart from the driver all the casualties were due to gassing.

Anon (1976o); McMullen (1976); NTSB (1977 HAR-77-01); Fryer and Kaiser (1979 SRD R152)

A85 *Breahead, Renfrew, Scotland, 1977*
On 4 January 1977, the Breahead Container Clearance Depot, a chemicals warehouse, was destroyed by a serious fire and explosions. The fire had been started inadvertently by boys who had built a 'den' beside the warehouse and had lit a fire to warm themselves. The explosions caused widespread roof and window damage within a radius of a mile. The warehouse had contained some 67 te of sodium chlorate stored in 1774 steel drums. Investigations showed that under intense heat this substance is capable of giving explosions of the severity which occurred.

This incident drew attention to the hazard of sodium chlorate. It emerged that since 1899 sodium or potassium chlorate had been implicated in six explosions, the then most recent being in Hamilton, Lanarkshire in 1969 and in a ship in Barcelona in 1974. Subsequently there occurred in the United Kingdom two other warehouse explosions involving sodium chlorate, one on 21 January 1980 at Barking, Essex (HSE, 1980a) and one on 25 September 1982 at Salford (HSE, 1983b).

Anon. (1979i,z); HSE (1979b); Matthews (1981)

A86 *Brindisi, Italy, 1977*
On 8 December 1977, a large gas release occurred on an ethylene plant at Brindisi, Italy, resulting in a vapour cloud explosion and fire, with extensive damage. The sewers were unable to handle the firewater and burning hydrocarbon liquids floated on it to a depth of some 18 in. Three persons died and 22 were injured.

Anon. (1977b); Mahoney (1990)

A87 *Puebla, Mexico, 1977*
On 19 June 1977 a leak occurred on one of a group of VCM storage bullets. A fitter had made an error in removing an actuator from a liquid discharge valve on the tank, taking out the wrong bolts so that the valve plug suddenly popped out, allowing an escape through the 3 in. valve body. The release continued for 80 min in calm conditions, the vapour cloud formed being 1100 ft long, 800 ft wide and 5 ft deep. Five minutes later the cloud caught fire and flashed back to the tanks. A further 5 min later one tank suffered a BLEVE. Three more tank explosions followed. One person was killed and three injured.

D.J. Lewis (1991 LPB 100, 1993)

A88 *Umm Said, Qatar, Persian Gulf, 1977*
On 3 April 1977, a catastrophic failure occurred on a storage tank at Umm Said, Qatar, in the Persian Gulf. The tank was a single-wall carbon steel refrigerated atmospheric tank holding 37,000 m^3 of liquid propane at $-42°C$. A wave of propane liquid swept over the bund, boiling on the sand. It entered the adjacent separation plant and was ignited. There was a massive fire which did extensive damage, burned out of control for two days and was extinguished only after 8 days. Seven persons were killed and 13 injured.

Information on this incident is still hard to come by. The failure is said to have occurred at a weld on the tank. It is reported that the same weld had been responsible for a leak a year before in which a vapour cloud formed and travelled 500 ft but did not ignite.

Anon. (1977c); Whelan (1977); D.J. Lewis (1980, 1993); Kletz (1988 LPB 81)

A89 *Westwego, Louisiana, 1977*
On 23 December 1977, a series of explosions took place in the silos of a large grain elevator at Westwego near New Orleans, Louisiana. There were some 73 reinforced concrete silos 35 m high and ranging in diameter from 8 to 10 m. Contents included corn, wheat and soya beans.

The first explosion, which occurred in the morning, caused the top 20 m of a 75 m high head house to fall onto an office building. Explosions continued through the morning. More than half the silos were completely destroyed and others severely damaged. The wreckage of some of the silos is shown in Figure A1.15.

More than 50 people were working on the complex when the explosions occurred. Thirty-six persons were killed and ten injured. Most of the dead were in the crushed office building.

The source of ignition for the first explosion has not been determined. At the time the relative humidity was low, which would be conducive both to the presence of fine dust suspensions and to static electricity.

This disaster is comparable in scale for dust explosions with that at Flixborough for vapour cloud explosions.

Less than a week later, on 29 December 1977, there was a further series of explosions in another grain elevator at Galveston, Texas, in which 15 people died.

Anon. (1977p,q); Lathrop (1978); Nolan (1979): D.J. Lewis (1993)

A90 *Abqaiq, Saudi Arabia, 1978*
On 15 April 1978, internal corrosion of a 22 in. 500 psig gas transmission pipeline on a gas processing plant at Abqaiq, Saudi Arabia, resulted in a leak which then expanded so that the line parted. A vapour cloud estimated as 405 ft × 435 ft spread through the plant. Some 7 min later ignition occurred at a flare 1500 ft downwind. The escaping gas is described as having a jet/whipping action which threw a 22 ft pipe section 400 ft so that it struck an spheroidal storage

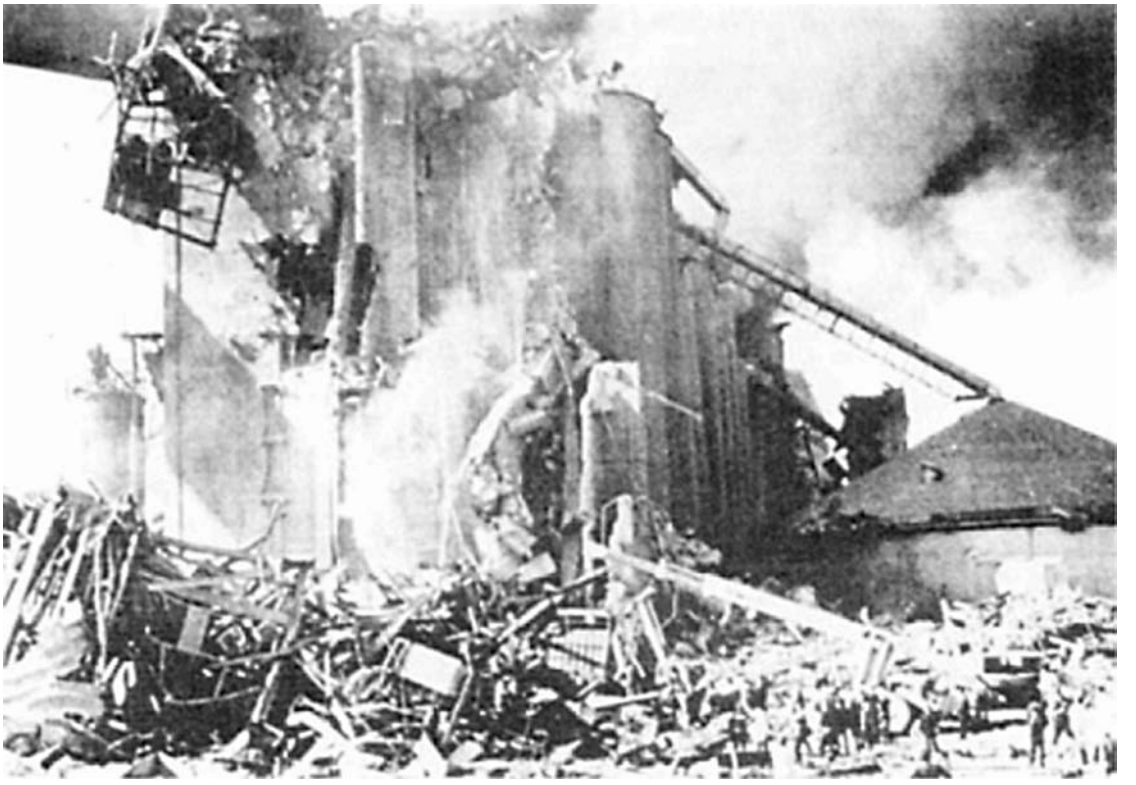


Figure A1.15 *Westwego, 1977: grain silos after the explosion (United Press International)*

tank. A second vapour cloud formed and was ignited by the initial fire, resulting in a vapour cloud explosion.

Mahoney (1990)

A91 *Donnellson, Iowa, 1978*

At 12.02 a.m. on 4 August 1978, a leak of liquid propane ignited on an 8 in. LPG pipeline of the Mid-America Pipeline System (MAPCO) in the rural area of Donnellson, Iowa. The pipeline pressure was over 800 psig and the leak came from a 33 in. split in the pipe. The intense fire killed two people and severely burned three others as they fled their homes; one of the injured later died. Some 157,500 USgal of liquid escaped and 75 acres were burned.

The investigation by the NTSB (1979 PAR-79-01) found that the failure occurred due to a dent and gouge in the pipe sustained in 1962 before the line was complete combined with stresses created when the line was lowered 3 months prior to the incident.

V.C. Marshall quotes this incident as involving 435 te of propane and giving a fireball of 305 m radius. The NTSB report refers to eyewitness reports of a 'bonfire' and states that when firefighters arrived about 12.20 a.m. they found a towering flame 400 ft high.

NTSB (1979 PAR-79-01); V.C. Marshall (1987)

A92 *Texas City, Texas, 1978*

On 30 March 1978, a series of fires and explosions occurred at LPG storage spheres at Texas City, Texas.

There were three spheres, each 800 m^3. One of the spheres suffered overpressure while it was being filled, due to failure of a pressure gauge and also of a relief valve. It cracked and leaked LPG. The leak ignited giving a massive fireball.

Accounts differ in their description of the events which followed. According to Selway (1988 SRD R492), after 20 min a second sphere, which was only partially full, suffered a BLEVE. The third sphere, which was virtually empty, failed due to a heat-induced rupture at the top, but remained upright. Thus all three spheres were damaged, but there was only one BLEVE event. Mahoney (1990) states that during the 20 min following the fireball, five horizontal bullets and four vertical ones were damaged by missiles and that the other two spheres were also damaged in this way. The missiles started fires and hit the firewater storage tank and electrical fire pumps, although two diesel fire pumps remained operable.

Selway (1988 SRD R492): Mahoney (1990)

A93 *Waverly, Tennessee, 1978*

On 24 February 1978, an explosion occurred of an LPG rail tank car at Waverly, Tennessee. Two days before, on 22 February, a freight train conveying two LPG tank cars derailed. There was no immediate release. A check on the following day showed that both tank cars were damaged but no leak could be detected. Both tank cars were underneath box wagons and these were lifted off. On 24 February as preparations were in hand to transfer the contents of the tank cars, one of them, which had suffered a long gouge-like scrape along one side, suddenly ruptured into four pieces

and released its contents of 59.4 te of LPG. Seconds later the gas ignited, probably by burning equipment nearby, giving a fireball. There followed a fire which did extensive damage. Sixteen people were killed and 43 injured.

Anon. (1978b); NTSB (1979 RAR-79-01); D.J. Lewis (1992 LPB 105, 1993)

A94 *Youngstown, Florida, 1978*

At about 1.55 a.m. on the night of 26 February 1978, a freight train of the Atlanta and Saint Andrews Bay Railway derailed near Youngstown, Florida. In the derailment a rail tank car containing liquid chlorine was punctured when it struck another tank car. The approximate position of the tank cars following the derailment is shown in Figure A1.16.

A chlorine gas cloud formed and moved towards State Highway 231, which ran parallel to the railroad at a distance of 300 ft. The weather conditions were a temperature of 50–55°F and a light westerly wind of 2–3 knots. There were already some patches of fog around and drivers, used to foggy conditions and unable to see the colour of the cloud as it was night, drove into it. Three vehicles drove right off the road and into the ditch. One motorist said the gas was so thick 'You could not see your hand in front of your face'. Seven motorists abandoned their cars and died while trying to escape, whilst an eighth drove through the cloud but died a short distance down the road.

The train's engineer at the head of the train alerted the conductor at the rear by radio and then tried to escape through the cloud; he became lost and mired in a swamp, being rescued 6 h afterwards. The head brakeman, who had been with the engineer, circled round to the highway and started to alert traffic. The conductor and rear brakeman tried to inform the railroad facility at Panama City, but it was not manned after midnight. They began to rouse local residents and notified the police; almost 30 min had elapsed before the first emergency call was completed. They then went to the highway to assist in alerting traffic. The report by the NTSB (1978 RAR-7807) states.

The head and rear brakeman both imperilled their lives by their repeated exposure to the chlorine gas cloud to stop and warn motorists of the dangerous situation. Their heroic actions saved many people from death or serious injury.

The emergency service evacuated people, first in a 5 mile and then in a 10 mile radius.

At 9.00 a.m. aerial observation revealed a gas cloud 3 miles wide and 4 miles long with a maximum height of 1000 ft. If the wind had been in a less favourable direction, the town of Youngstown would have been engulfed in the cloud.

The chlorine gas killed eight people, as mentioned, and injured another 50. Some 2500 people were evacuated.

Anon. (1978k); NTSB (1978 RAR-78-07)

A95 *Bantry Bay, Eire, 1979*

At about 1.06 a.m. on 8 January 1979, the Total oil tanker Betelgeuse blew up at the Gulf Oil terminal at Bantry Bay, Eire. The ship had completed the unloading of its cargo of heavy crude oil. No transfer operations were in progress. The first sign of trouble occurred at about 12.31 a.m. when a sound like distant thunder was heard and a small fire was seen on deck. Ten minutes later this was spread aft along the length of the ship, being observed from both sides. The fire was accompanied by a large plume of dense smoke. About 1.06–1.08 a.m. a massive explosion occurred. The vessel was completely wrecked and extensive damage was done to the jetty and its installations. There were 50 deaths.

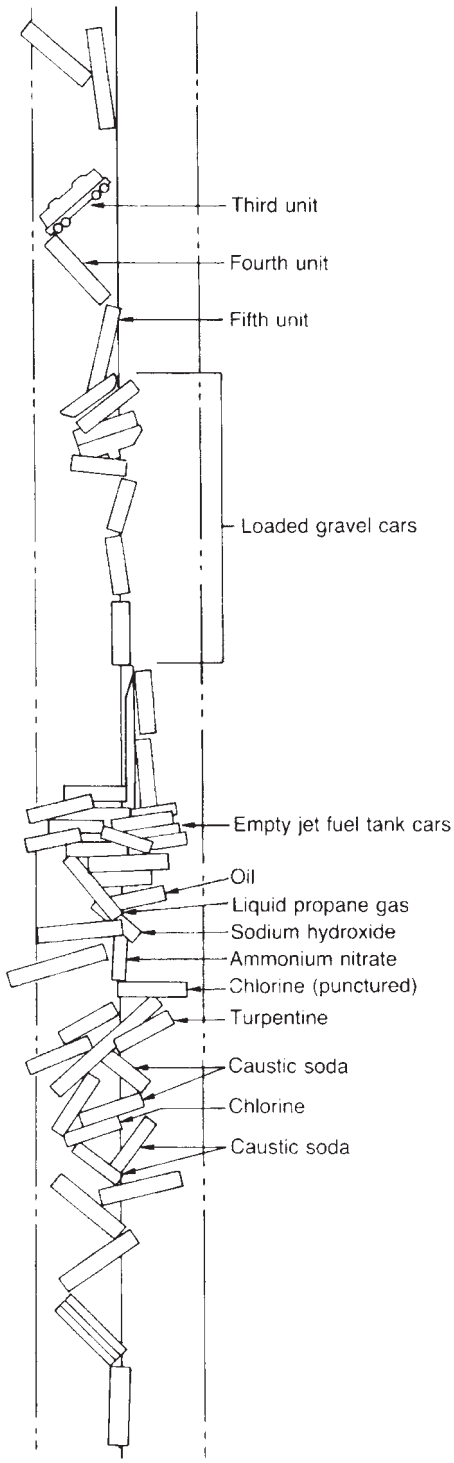


Figure A1.16 *Youngstown, 1978: approximate positions of rail tank cars after the derailment (after NTSB, 1978 RAR-78-07)*

The inquiry (Costello, 1979) found that the initiating event was the buckling of the hull, that this was immediately followed by explosion in the permanent ballast tanks and the breaking of the ship's back and that the next explosion was the massive one involving simultaneous explosions in No. 5 centre tank and all three No. 6 tanks. It further found that the buckling of the hull occurred because it had been severely weakened by inadequate maintenance and because there was excessive stress due to incorrect ballasting.

The ship was an 11-year old 61,776 CRT tanker. The weakened hull was the result of 'conscious and deliberate' decisions not to renew certain of the longitudinals and other parts of the ballast tanks which were known to be seriously wasted, taken because the ship was expected to be sold, and for reasons of economy. The vessel was not equipped with a 'loadicator' computer system, virtually standard equipment, to indicate the loading stress. It did not have an inert gas system, which should have prevented or at least mitigated the explosions.

At the jetty there had been a number of modifications which had degraded the fire fighting system as originally designed. One was the decision not to keep the fire mains pressurized. Another was an alteration to the fixed foam system which meant that it was no longer automatic. Another was decommissioning of a remote control button for the foam to certain monitors.

Another issue was the absence of the dispatcher from the control room at the terminal. It was to be expected that had he been there, he would have seen the early fire and have taken action.

In a passage entitled '*Steps taken to suppress the truth*' the tribunal states that active steps were taken by some personnel at the terminal to suppress the fact that the dispatcher was not in the control room when the disaster began, that false entries were made in logs, that false accounts were given to the tribunal and that serious charges were made against a member of the Gardai (police) which were without foundation.

> The inquiry report gives a long list of measures which might have prevented or mitigated the disaster: Had the vessel been properly maintained. . . Had Total supplied the ship with a loadicator. . . Had the dispatcher in the Control Room observed the initiation of the disaster. . . Had the alert been raised at the beginning of the disaster. . . Had the tug been moored in sight of the jetty. . . Had the decision to discontinue the automatically pressurized fire-main not been taken. . .

and so on.

Anon. (1979l); Costello (1979); Anon. (1980a); Mahoney (1990)

A96 *Good Hope, Louisiana, 1979*

On 30 August 1979, a freighter collided with the butane barge Panama City at a jetty on the Mississippi at Good Hope, Louisiana, striking it amidships, severely puncturing at least one of its tanks and causing a fireball. Twelve persons died and 25 were injured.

NTSB (1980 MAR-80-07); V.C. Marshall (1987)

A97 *Mississauga, Toronto, Ontario, 1979*

At 23.52 on Saturday 10 November 1979 at Mississauga, Toronto, a freight train derailment led to fires, explosions and a chlorine gas release, in an emergency lasting 11 days. The train had 25 rail cars of which 19 held hazardous materials, in a mixed load of flammables and toxics, including propane, toluene, styrene, caustic soda and chlorine.

The derailment occurred due to lack of lubrication of a plain journal axle bearing on the 33rd car, a propane tanker. The red-hot axle, complete with wheels, parted from the tank car. Some 2 km further on at a location where there was a road crossing and points, this vehicle became detached from the front portion of the train. Many of cars in the rear section derailed. Several tanks were ruptured and a fire broke out. The brakes in the front section of the train were applied automatically and looking back the locomotive crew saw a fire and a tank car rocketing off.

There followed a series of explosions, one within a minute and another just after midnight at 00.10. At 00.15 a propane tank suffered a BLEVE in which one half travelled 2300 ft and buried itself 20 ft into the ground. At 00.24 another BLEVE of a propane tank car occurred.

There was a single chlorine tank car containing 90 te of liquid chlorine. This tank lost part of its insulation and a flame impinged on the bare metal. There was an iron – chlorine reaction which burned a 3 ft diameter hole in the tank. Chlorine began to escape through the hole. The effect was less serious than it might have been, since the effect of the fire was to cause the gas to rise in the thermal currents.

The emergency developed over an extended period. Initially the emergency services did not know what was in the train: the manifest was found, but it was in code. There was, however, a strong smell of chlorine. At 1.30 a readable version of the manifest was obtained, identifying the chlorine tank car. At 3.00 the decision was made to evacuate the surrounding population, an exercise which eventually resulted in the evacuation of 215,000 people. The holed chlorine tank car was identified by a helicopter survey.

At 9.00 on Tuesday 13 November an initial attempt was made to plug the hole in the chlorine tank car, but without success; a second attempt succeeded. When subsequently the tank was emptied, only 18 te of chlorine was recovered.

During Tuesday afternoon 143,000 people were allowed back home. The rest did not return until after an absence of six days.

Detailed timetables of the incident itself and of the evacuation are given by Fordham (1981 LPB 44).

The only injuries were those caused to eight firemen by inhalation of the noxious gases.

Mississauga News (1979); Amyot (1980); Grange (1980); Anon. (1981l); Fordham (1981 LPB 44); Lane and Thomson (1981); D.J. Lewis (1993)

A98 *Borger, Texas, 1980*

On 20 January 1980, a refinery at Borger, Texas, suffered extensive damage. Details are lacking, but it appears that a vessel was subjected to a pressure much in excess of its working pressure, the relief valve operated but was ineffective due to ice blockage and the vessel ruptured, releasing 34 m^3 of hydrocarbon liquids. A vapour cloud formed and ignited, giving a vapour cloud explosion with a TNT equivalent of some 15 te. The blast destroyed the alkylation unit and boiler plant and shut-down the whole refinery. Forty-one people were injured.

The ice plug is reported as due to freezing by propane of water which had accumulated in the flare system.

Mahoney (1990); D.J. Lewis (1993)

A99 *Wealdstone, Middlesex, 1980*
About 19.15 on 20 November 1980 an escape of propane began from a storage vessel in the factory yard of Whitefriars Glass Ltd at Wealdstone, Middlesex. The vessel was a 10 te vessel which contained 5 te of propane. The nightwatchman smelled the odorized gas, but searched first inside the building, until he heard a hissing sound and saw a white cloud about 1.2 m deep around the base of the tank. Meanwhile a passer-by had called the fire brigade. The escape lasted several hours. Some 2100 people were evacuated from the area. One person had to attend hospital.

The release was caused by the removal by the works engineer and a fitter of three of the four bolts on an adapter piece on the drain valve of the tank. The valve had two sections. The upper, body section was bolted to the underside of the tank. The lower, adapter section had a spigot which extended into the upper section and held the ring seals in place against the ball. In other words, the adapter was an essential part of the valve.

This was not known, however, to the persons who removed the bolts.

The work on the valve had occurred during the afternoon. The delay between the removal of the bolts and the escape was attributed by the investigators to the accumulation in the vessel of non-volatile, viscous residues due to the removal of propane as gas from the top of the tank over a period of at least 10 years.

HSE (1981c)

A100 *Montana, Mexico, 1981*
At 17.52 on 1 August 1981 a train derailment resulted in a massive release of chlorine near Montana, Mexico. The train consisted of 38 wagons, including 32 rail tank cars containing liquid chlorine. It was moving down a steep and winding valley at a 3% gradient when its brakes failed. The driver radioed to other trains on the single track to warn them, and two trains drew into loops. The train derailed at over 80 km/h on a bend 350 m beyond Montana station.

All the chlorine tank cars were 55 short tons, say 50 te, capacity. The pile-up included 28 of the 32 chlorine cars. Most were badly damaged. One tank car lost its dished end and the shell was propelled 2000 m. A second was split along its side. A third had a 0.5 m diameter hole, probably the result of an iron–chlorine fire, which could well have resulted from ignition of the cork insulation by red hot brakes. Four other tank cars suffered damage to their valves, which were ripped off or dislodged so that they leaked. It is estimated that 100 te of chlorine escaped in the first few minutes and 300–350 te in all.

The population of Montana was some 400 people. There was also a passenger train with some 300 people at the station. The weather conditions to be expected at the time of day would be a warm wind blowing up the valley, towards the village. The vegetation up the valley was bleached by the gas cloud passing up it; there was also discoloration some 50 m down the slope and up the sides for a vertical distance of about 50 m. The highest concentrations appear to have occurred in a strip 1000 m long × 40 m wide. Seventeen persons died, four in the caboose of the train and 13 from gassing. About 1000 people were received in hospital and 256 were detained.

Anon. (1982 LPB 44, p. 33); Anon. (1983 LPB 52, p. 7); V.C. Marshall (1987)

A101 *Stalybridge, UK, 1981*
At about 23.30 on 6 September 1981, a violent explosion occurred at the works of Chemstar Ltd at Stalybridge. Failure of cooling water to the condenser of a still had allowed hexane vapour to issue through the vent, and the escaping vapour found a source of ignition. One person was killed and one injured.

The investigators found that the normal water supply was not available, a temporary supply had been used which proved to be erratic and there was inadequate flow indication; that the vent had not been routed to a point outside the building; and that the training and supervision of the operator were inadequate.

HSE (1982a); Kletz (1983b)

A102 *Caracas, Venezuela, 1982*
At about 6.17 a.m. on 19 December 1982, an explosion blew the top off a large oil storage tank at the electricity company at Caracas in Venezuela. The oil in the tank caught fire and burned. Firemen arrived and attempted to control the fire and people stood watching it. After some hours there was a violent boilover of the tank contents and burning liquid ran down the hill on which the tank stood towards firemen and spectators.

The power station was owned by C.A. La Electricidad de Caracas and was built in 1978. The tank involved was No.8 storage tank, which was one of two cone roof tanks each 55 m × 17 m, the other tank being No.9. Each tank had its individual bund and had two forms of fire protection. One was a 100 mm water drench pipe which ran to the centre of the roof and was designed to cascade water over the roof and shell to prevent overheating and the other was a semi-fixed foam system with five risers.

No.8 tank contained No.6 fuel oil and at the start of the incident the depth of oil was 7.5 m. It had been feeding the boilers for six days prior to the fire.

At 6.15 a.m, while it was still dark, two men went up on the roof of No.8 tank to gauge it, and a third waited in a vehicle. About 2 min later the roof blew off and at the same time the lines within the bund were ruptured. One of the foam risers on the tank was damaged. The source of ignition is not known, but neither man had a flashlight and it is possible a match was lit to read the gauge line.

It is not known if either the water or foam fire protection systems on No.8 tank operated. The power company had no fire brigade and the nearest public fire service was a half an hour journey away over winding roads.

Some 8 h after the fire began a violent boilover of No.8 tank occurred. Burning oil surrounded No.9 tank and flowed down the hill into the sea, but was kept from the power station by a concrete wall. The inrush of air lifted roof panels at the power station 300 m away.

The boilover killed 40 firemen and many civil defence workers and spectators. 153 people are known to have died and 7 were missing.

Boilover is defined by the NFPA as follows:

> Boilover shall mean an event in the burning of certain oils in an open top tank when, after a long period of quiescent burning, there is a sudden increase in fire intensity associated with the expulsion of burning oil from the tank. Boilover occurs when the residues from surface burning become denser than the unburned oil and sink below the surface to form a hot layer which progresses downward much faster than the regression of the liquid

surface. When this hot layer, called a 'heat wave', reaches water or a water-in-oil emulsion in the bottom of the tank, the water first is superheated and subsequently boils almost explosively, overflowing the tank. Oils subject to boilover must have components having a wide range of boiling points, including both light ends and viscous residues. These characteristics are present in most crude oils and can be produced in synthetic mixtures.

The heat wave travels at a rate which in most crude oils is some 300–460 mm/h but can be as great as 900–1200 mm/h. Its temperature can be as high as 315°C. When water comes into contact with the heat wave, it vaporizes to steam with a volume expansion of 1700 : 1 or more.

Normally No.6 fuel oil is regarded as not being subject to boilover. However, it is common practice in the United States to blend it. It is reported that the power company's specifications allowed 5–20% light fractions, that the oil had a flashpoint of 71°C, that it was intended to be heated in storage to 65°C, but that the oil return temperature shown by the control room records was 80°C and the storage temperature was 82°C. The tank high-temperature alarms had sounded at midnight, some 6 h prior to the incident.

Garrison (1984 LPB 57); M.F.Henry (1986)

A103 *Livingston, Louisiana, 1982*
On 28 September 1982, a freight train conveying hazardous materials derailed at Livingston, Louisiana. The train had 27 tank cars some of them with jumbo tanks of 30,000 USgal. Seven tanks cars held petroleum products and the others a variety of substances, including vinyl chloride monomer, styrene monomer, perchlorethylene, hydrogen fluoride and metallic sodium.

The incident developed over a period of days. The first explosion did not occur until three days after the crash. The second came on the fourth day. The third was set off deliberately by the fire services on the eighth day. The scene is shown in Figure A1.17.

Meanwhile the 3000 inhabitants of Livingston were evacuated. Some were not to return home until 15 days had passed.

One factor contributing to the derailment was the misapplication of brakes by an unauthorized rider in the engine cab, a clerk who was 'substituting' for the engineer. Over the previous 6 h the latter had drunk a large quantity of alcohol.

The incident demonstrated the value of tank car protection. Many of the cars were equipped with shelf-couplers and head shields, and there was no wholesale puncturing and rocketing. Tanks also had thermal insulation which resisted the minor fires occurring for the two or more hours which it took the fire services to evacuate the whole town.

NTSB (1983 RAR-83-05); Anon. (1984t)

A104 *Bloomfield, New Mexico, 1983*
At 12.04 p.m. on 26 May 1983 at the El Paso Natural Gas Company's Blanco Field Plant near Bloomfield, New Mexico, a gasket on a compressor failed and natural gas at 815 psig began to escape into the building. Two operators heard the noise. One tried to shut off the gas supply to the compressors, the other to shut-down the compressor engine. Before they could effect these operations, the gas ignited and exploded, and both were severely burned. One compressor was destroyed and a second severely damaged.

The investigation by the NTSB (1983 PAR-83-04) found that the probable cause was improper tightening of the compressor head bolts and lack of procedures for, and training in, bolt tightening. The report gives a detailed discussion of the bolting problem together with guidance on bolt tightening.

It also criticized the emergency response, in that there was a failure to effect prompt relief of the high-pressure gas by activating the blowdown system.

NTSB (1983 PAR-83-04)

A105 *Bontang, India, 1983*
On 14 April 1983 on an LNG plant at Bontang, India, the main cryogenic heat exchanger, 141 ft long × 14 ft diameter,

Figure A1.17 *Livingston, 1982: rail tank cars burning after the crash (National Transportation Safety Board, 1983)*

ruptured during a start-up. The shell side operating pressure was 25.5 psi but it was exposed to gas at a pressure in excess of 500 psi. The explosion gave rise to missiles and a fire. The flow from a pressure controller on the shell and the flows from relief valves on the shell and tube sides of the exchanger vented to a common line. The investigation found that a valve on this line was closed, disabling both the pressure control and the pressure relief. The valve in question had apparently been omitted from the valve checklist for plant start-up.

Mahoney (1990)

A106 *Milford Haven, UK, 1983*

On 30 August 1983, a fire broke out on the roof of a large crude oil floating roof storage tank at the refinery at Milford Haven, Dyfed, Wales. The tank was 78 m diameter × 20 m high with a capacity of 94,100 m^3 and was 59% full. It stood in a very large bund with dimensions 90 m × 180 m. The fire took hold and a massive tank fire ensued with an estimated burn-off rate of 300 te/h of oil. After 12.5 h boilover occurred, thousands of tonnes of burning oil flowed into the bund and a fire column rose 3000 ft high. Two hours later there was a further boilover.

The floating roof had developed a split which allowed vapours and some oil to escape onto the roof. Ignition was attributed to hot carbon particles from the flare. An upset had resulted in a large flow of hydrocarbons to the flare which could have dislodged particles from the stack top.

There was a major fire fighting operation. Oil was pumped out from the bottom of the burning tank at a rate of 700 te/h. The foam supplies available on site were sufficient for a floating roof tank seal fire, but not for the fully developed tank fire, and supplies were sought outside. There were two other storage tanks at a wall-to-wall distance of 61 m from the burning tank, and an early priority was to cool the outside of these and to inject foam inside. Eventually, after the boilovers, enough foam was obtained, some 305 m^3, to mount a full foam attack, first on the fire in the bund and then on that in the tank itself. This process lasted 15 h with the fire fighting being done under conditions of extreme heat. In the boilover events, firemen were affected by flash burns and by dry hot air.

A detailed timetable of the incident is given by Mumford (1984 LPB 57).

Dyfed County Fire Brigade (1983); Mumford (1984 LPB 57); Golec (1985); Steinbrecher (1986); Mahoney (1990); D.J. Lewis (1993)

A107 *Abbeystead, UK, 1984*

On 23 May 1984, a group of people were assembled in the valve house of the Lune/Wyre Water Transfer Scheme at Abbeystead for a presentation when there was a violent explosion. The explosion occurred soon after the pumping system had been started up. The pumps had not been run for 17 days and the tunnel which conveyed the water was not full of water, its usual condition, but had been emptied through a drain valve which had been opened to remove silt. Subsequent tests showed that during this period groundwater would have leaked into the tunnel at a rate of 1000 te/d. This water contained dissolved methane, which mixed with the air in the tunnel. The only venting of the tunnel was through the grilled floor of the valve house. Thus when the pumps were started and water moved up the tunnel, the methane–air mixture was displaced and came up through the grill into the valve house, where it found a source of ignition. The explosion killed 16 and injured 28; all the 44 persons in the valve house itself were killed or injured.

Anon. (1984pp, 1985a); Burgoyne (1985a); HSE (1985a); Lihou (1985 LPB 66); V.C. Marshall (1987)

A108 *Cubatao, Brazil, 1984*

On 24 February 1984 just before midnight a leak of petrol occurred on the Petrobas pipeline passing through the shanty town of Vila Soca at Cubatao in Sao Paulo state, Brazil. The petrol caught alight and a fire devastated the houses. The death toll was 508.

Vila Soca was a shanty town of some 2500 dwellings. The number of people living there is uncertain, but is estimated as 8000, perhaps even 12,000. The pipeline was 30 years old. For 20 years the company had protested that Vila Soco had been built illegally on its land, but had nevertheless provided water and electricity.

A leakage from the pipeline was noticed the day before the fire and a resident telephoned the company. In the leak which led to the disaster some 700 te of petrol escaped from the pipeline. The spread of the flammable liquid through the shanty town and under the houses was aided by water on the ground and by a small stream. A two-minute warning was given but this was not enough for the inhabitants to evacuate. The petrol caught fire and straight away created an inferno. Houses burned and exploded as the petrol beneath them ignited. It was 45 min before the fire brigade arrived by which time most of the shanty town had been destroyed.

Anon. (1984oo); Kletz (1985p)

A109 *Fort McMurray, Avaporerta, 1984*

On 15 August 1984 at Fort McMurray, Avaporerta, hydrocarbon liquids close to their autoignition temperature were released from a 10 in. slurry recycle oil line on a fluidized-bed coking unit. A vapour cloud formed and ignited almost at once. The fire, which did extensive damage, was fed by further releases of hydrocarbon liquids, the flows being largely under gravity but in part from pumps which could not be shut-down. Fire fighting was hampered by rupture of a 900 psig steam line supplying the compressor turbine drives. The failure of the recycle line was due to erosion. Subsequent metallurgical examination showed that an 18 in. long section of carbon steel had been inserted in error into the alloy steel line.

Mahoney (1990)

A110 *Las Piedras, Venezuela, 1984*

On 13 December 1984 in a refinery at Las Piedras, Venezuela, an 8 in. oil line fractured and sprayed hot oil at 700 psi and 650°F across a roadway onto hydrogen units. Ignition occurred, and the ensuing intense fire led to rupture of a 16 in. gas line, which resulted in a massive jet flame, leading to further line ruptures, some of which occurred with explosive force. The initial failure was a circumferential fracture in the heat affected zone in the parent metal about 1.5 in. from the weld.

Mahoney (1990)

A111 *Romeoville, Illinois, 1984*

On 23 July 1984, a column at the Lemont refinery of Union Oil at Romeoville, Illinois, suffered a spontaneous failure. The vessel was an absorption column 8.5 ft diameter × 55 ft high in which a propane/butane feedstock was contacted with methylethanolamine (MEA). Just prior to the burst, an

operator noticed a horizontal crack about 6 in. long at the 10 ft level. He went up a ladder to try to shut of the inlet valve and then saw that the crack had grown to some 2 ft. He had initiated evacuation of the area when the column failed. The column tore apart at the 10 ft level weld and the 45 ft top section, weighing some 20 te, rocketed up, landing about 975 m away on a tower carrying a 138 kV power feed line to the area. The tower contents, estimated as 79.5 m^3 of propane/butane and 8.75 m^3 of MEA, escaped and formed a vapour cloud, which ignited within seconds, giving a vapour cloud explosion. Some 30 min later a third explosion occurred when a vessel in the alkylation section suffered a BLEVE with associated fireball and missiles. The explosions and fire caused extensive damage. Seventeen people were killed and 31 injured.

The vapour cloud explosion disrupted the electrical power supply, putting out of service a 2500 USgal/min electrical fire pump. One of the explosions sheared off a fire hydrant, reducing the pressure available from the two 2500 USgal/min diesel-driven fire pumps. A fragment from the BLEVE landed on a unifining unit, initiating a major fire there.

The blast resistant control centre, some 400 ft from the absorber, suffered little structural damage.

The absorber vessel had a history of hydrogen attack problems. Over the years since 1972 repairs and modifications had been done, and the vessel continued in service.

Mahoney (1990); D.J. Lewis (1993); Vervalin (1987)

A112 *Priola, Italy, 1985*

On 19 May a major fire occurred on an ethylene plant at Priola in Italy. A faulty temperature probe initiated isolation of the hydrogenation unit in the cold section, and while the operators were trying to re-establish control, the relief system operated. At the same time fire was observed at the base of the de-ethanizer column. The hydrocarbon released ignited and an intense fire engulfed the adjoining ethylene and propylene distillation columns and spread to the storage area. The water deluge system protecting the storage tanks proved inadequate due to the intensity of the fire. In due course a tall, vertical propane tank exploded, its top section rocketing up some 500 m, and just missing a gasholder. Two propylene tanks fell over, one on a pipe rack and the other against an ethylene tank. In all, five of the eight ethylene and propylene tanks either exploded or collapsed.

Mahoney (1990)

A113 *Schweizerhalle, Basel, Switzerland, 1986*

On 1 November 1986, a fire broke out in Warehouse 956 at the Schweizerhalle (Muttenz) works of Sandoz in Basel, Switzerland. The warehouse held large quantities of agrochemicals. Attempts to extinguish the fire using foam were ineffective and water had to be used, in large quantities. It was not possible to contain this water within the site and, as a result, 10,000 m^3 entered the Rhine carrying with it some 30 te of chemicals, including an estimated 150 kg of highly toxic mercury compounds dissolved in aqueous concentrates. The incident did severe ecological damage.

A not dissimilar incident, though one on a much smaller scale, occurred at Morley, Yorkshire, in 1982, when the river Calder was contaminated by chemicals in water used in fighting a fire which had broken out in a warehouse storing herbicides (V.C. Marshall, 1987).

Anon. (1986v,w,y); Beck (1986); D.Williams (1986); Anon. (1987 LPB 75, p. 11); Stallworthy (1987)

A114 Thessalonika, Greece, 1986

On 24 February 1986, an oil terminal at Thessalonika, Greece, experienced a small fire when a oil spillage in a bund was ignited by hot work. The privately owned terminal had 12 fixed and floating roof storage tanks holding crude oil, fuel oil and gasoline. Over the course of seven days, ground fires escalated until they covered 75% of the terminal area and involved 10 of the tanks. The escalation of the initial small fire was due in large part to accumulation of oil from previous spillages; to leaks from flanges exposed to the fire, which then fed it; and to the failure of fire fighting efforts in the early stages. By the first day seven tanks were affected.

In the course of the succeeding days, several events occurred which led to major escalations. On Tank 3 overpressure caused the shell-floor seam to burst so that the whole contents flowed out, feeding the fire and involving two more tanks. Tank 8 suffered a boilover with a fireball 300 m high and ejection of burning oil over a wide area, some travelling up to 150 m. The fire fighting was hampered, and firemen endangered, by burn-back of flame in areas where the oil fire had already been extinguished by foam.

B. Browning and Searson (1989)

A115 *Antwerp, Belgium, 1987*

On 3 July 1987, an explosion occurred inside an ethylene oxide purification column at the BP Chemicals works at Antwerp, Belgium. The explosion was due to decomposition of the ethylene oxide and was accompanied by a fireball, which started a number of secondary fires. These, together with blast and missiles, caused extensive damage. Fourteen people were injured.

The investigators considered two main hypotheses for the cause. One was that there was a leak of ethylene oxide into the insulation, leading to self-heating and then ignition of the leak, resulting in the heating of the ethylene oxide in the column itself. The other was the development of a hot spot inside the column due to exothermic polymerization of ethylene oxide catalysed by rust. The first explanation was preferred.

Mellin (1991 LPB 100)

A116 *Grangemouth, Scotland, 1987*

In 1987, there occurred at BP plants in the Grangemouth, Scotland, area three incidents, which were the subject of investigations by the HSE (1989a).

Incident on 13 March 1987

On 13 March 1987, a fire occurred when a maintenance team broke a flange in the flare line, hydrocarbons escaped and were ignited. There was a quite serious fire which lasted some hours. Two men were killed and two injured.

The release occurred when two fitters started to break a flange in order to maintain a valve (V17). As they did so, vapour and a little liquid came out. They queried the situation with the process shift supervisor, who inspected the site and assured them that there could only be a small quantity present and it was safe to continue. They did so, and as the last bolt was undone, the crane holding the spacer increased its lift, the spacer sprang upwards, and liquid under pressure poured out. A vapour cloud formed and ignited. The source of ignition was almost certainly the engine of a nearby diesel air compressor.

It was considered that if the fire was extinguished, fuel might continue to issue with the potential for a vapour cloud explosion and that if the flame receded into the pipe, there might be an internal explosion. For a while, therefore, fuel gas was fed into the line to keep the flame alight.

The liquid which escaped had been held in a section of the flare line near a knockout drum. It should have drained via a small bore pipe into the knockout drum, but the entry of the pipe was blocked. The valve on this pipe had been checked as open, but the possibility of blockage had not been taken into account. The liquid was there in the first place because valve V17, thought to be fully closed, was in fact part open. The valves suffered from build-up of pyrophoric scale. They had no indicators showing positively the valve position. It is estimated that there was about 50 m^3 of hydrocarbons in the line at the time and that 20 m^3 may have escaped.

Among the findings of the investigation were that there was a need for position indicators on the valves; that there had been inadequate planning of the work to be done; that the check that the flare line had been drained was ineffective; that the response to the first, small leak was inadequate; that the procedure for flange breaking was incorrect; that when opening lines with pyrophoric scale, air should be excluded positively by a nitrogen purge, rather than reliance placed on its exclusion by flammable gases present; and that the exhaust gas spark arrester was missing. There should have been a requirement that in breaking a flange sufficient bolts remain in place whilst a gradual opening is made using a flange spreader.

Incident on 22 March 1987

On 22 March 1987 an explosion occurred during the start-up of a hydrocracker unit at the Grangemouth refinery. It involved the disintegration of a low-pressure separator. One fragment from the vessel, weighing 3 te, landed on the foreshore 1 km away.

Accompanied by a fireball, the explosion initiated a severe fire. The refinery sustained extensive damage. One person was killed.

The LP separator (V306) was 3.05 m diameter × 9.1 m long with a design pressure of 9 bar and a calculated burst pressure of 50 bar. It was fitted with a 3 in. relief valve designed for fire relief. Its disintegration was caused by breakthrough of gas from the HP separator (V305) due to loss of level control in the base of the latter. The HP separator pressure was 155 bar. The plant was in start-up mode and the process lines on V306 were closed.

The gas breakthrough occurred due to loss of control of the level at the base of the V305. The pipework taking off the liquid split into two lines, one passing through the valve on the level control loop LIC 3-22 and the other through that on H 3-22. The breakthrough occurred through the LIC 3-22 valve. This valve had been fitted with a low-level trip, but this had been removed in 1985. The liquid at the base of V305 tended to give vortices and the trip system suffered from spurious trips which caused production difficulties. There was an extra-low-level alarm, but this had been on for months, until the bulb failed, and was regarded as spurious. The two float switches were fire damaged, but there was evidence that one had been incorrectly assembled and that on the other the small bore piping was blocked. The operators tended to place more reliance on the measurement provided by a nucleonic level gauge. However, this gauge had a zero error, showing a 10% reading when the true reading was zero. An audit had shown that there was a problem in control of the level on the vessel. In the shift in which the incident occurred valve LIC 3-22 was opened manually at least three times. Just before the explosion, it was opened again, and the level was lost. The HSE report states:

> The refinery had procedures for routine monitoring of interlocks, alarms and trips, but on the checklist for the hydrocracker some were omitted. The detection, trip and alarm systems for extra-low level in V305, had been inoperative for a long time and maintenance staff and operators presumed that these were no longer required. Training of new operators carried out by experienced operators helped to perpetuate this misconception. Although the refinery chief instrument engineer noted in 1985 that the LIC 3-22 trip solenoid had been disconnected, this was not followed up. (paragraph 89)

The report states that there should have been both a high-integrity trip system for level control and a pressure relief system capable of handling the maximum anticipated gas flow and that fuller consideration should have been given to proposals to make modifications to the plant.

It emerged that there had been a previous incident on V305 which was probably a gas breakthrough, but on that occasion the process valves on V306 were open.

The force of the blast was mainly downwards, while the fragments travelled upwards. The TNT equivalent of the explosion was estimated as 90 kg.

Major problems were experienced in the fire fighting. Within 12 h 31 foam and water streams were discharging at a rate of 12,000 USgal/min. The drains were unable to cope with this flow. Hydrocarbons bubbled up in other parts of the site and floated on the water. The situation was exacerbated by large quantities of heavy, waxy material which caused blockages.

Incident on 11 June 1987

On 11 June 1987 at Dalmeny, near Grangemouth, a fire broke out during sludge cleaning work by a contractor in a storage tank, and one man died. The men had airline breathing apparatus (BA) to protect against toxics, but there was no mechanical ventilation and no regular monitoring of the atmosphere. The sludge had a flashpoint of less than 0°C. It transpired that the fire broke out when one man, who had taken off his BA, dropped a cigarette end.

The investigation revealed that there were a number of deficiencies in the arrangement of the contract with the contractor and in the conduct of its personnel. The contractor was a specialist one, well known, considered competent and already working on site. There was no written procedure for the work. There was inadequate enforcement of the 'no smoking' rule, and some contractor's personnel had not received the BP refinery rules booklet. Also inadequate was enforcement of the use of the BA. There was no lighting inside the tank and men discovered they could see better if they took the BA off. The team worked largely unsupervised. They wore the BA when entering and leaving the tank, and evidently also when the supervisor was about to visit, but some did not wear it all the time. The supervisor himself had on occasion removed his BA inside the tank to give verbal instructions.

Anon. (1988c,d); Anon. (1987l); Anon. (1989b); Anon. (1989 LPB 89, p. 13); HSE (1989a); Kletz (1989b); Mahoney (1990); K.X.Wilson (1990a,b); D.J.Lewis (1993)

A117 *Pampa, Texas, 1987*
On 17 November 1987 at Pampa, Texas, a vapour cloud explosion occurred on a plant for the liquid phase oxidation of butane to acetic acid and acetic anhydride using air at about 700 psig. There were three reactors with a capacity of 38 m^3. During the start up of one reactor a rupture or explosion occurred in the line taking the air to the reactor or in the reactor manifold, and butane and acetic acid flowed out. The vapour cloud which formed was ignited by gas-fired boilers some 60 m away, the delay before ignition being about 10 s. The resultant explosion did extensive damage. One aspect of this was that the blast severed piping in many of the sprinkler systems and also ruptured the underground fire water main, rendering the water pressure inadequate for its purpose. Three people were killed and 37 injured.

Mahoney (1990); D.J. Lewis (1993)

A118 *Port Herriot, Lyon, France, 1987*
On 2 June 1987, the Shell depot at Port Edouard Herriot, near Lyon, France, with some 76 tanks, experienced a severe fire. Two persons were killed and eight injured.

At the time of the account quoted the cause of the incident was not established. It states that at the relevant time of 13.15 work was in hand on an electric cable for welding equipment and that the power was off but due to be switched on again at 13.30. The initial event was the formation of a spray in the area of the pumps. There was then a flash.

There followed a series of explosions and fires. Twelve minutes into the event a tank holding 250 m^3 rocketed up 200 m and fell outside the compound. There was a rapid escalation with five further tanks rocketing and falling inside the depot. Tank 6 exploded in what was probably a boilover. The associated fireball was 450 m high and 200 m 'wide'. During the night the fire progressed further.

The extent of the escalation was attributed in large part to the fact that the tanks were old, and did not have a rupture seam in the roof, so that they tended to burst at the base, releasing the whole contents.

Control of the fire was not achieved until 11.00 on 3 June after two heavy duty foam monitors, each of 6 m^3/min capacity, obtained from outside, had been brought into play at 6.30. Among the conclusions drawn in respect of fighting such a fire were that the temperature of the wall of the vapour space of a tank engulfed in fire can rise within 2 min to 500°C, above the autoignition temperature for many flammable mixtures; that water cooling used while the foam attack is being prepared may be ineffective and may cause severe degradation of structures; that 4-hour fire insulation may not be sufficient; that concrete bunds may not last out and that earth mounds are preferable; and that an effective foam attack requires heavy duty equipment capable of 4–6 m^3/min.

Another conclusion was the need to review the fire permit system: the number, the nature and relations between the permits.

Mansot (1989)

A119 *Ras Tanura, Saudi Arabia, 1987*
On 15 August 1987, a leak occurred on a gas plant at Ras Tanura, Saudi Arabia. There were two parallel gas fractionation trains with propane feed. Prior to the incident there had been a number of power interruptions which caused shut-down of one or other of the plants. It is believed that a leak of propane developed in one train, the probable source being a flange on a 4 in. relief line and that the release continued for about half an hour. A large vapour cloud formed and ignited. The ignition was probably from a security vehicle which had stalled and was being restarted. Severe damage was caused.

Mahoney (1990)

A120 *Floreffe, Pennsylvania, 1988*
On 2 January 1988, an oil storage tank of the Ashland Oil Company at Floreffe, Pennsylvania, suffered catastrophic failure during its initial filling. The tank was a 120 ft diameter × 48 ft high cone roof tank. It was 40 years old and had been dismantled at a former site and re-erected. The failure was a sudden rupture. The force of the fluid spurting out one side caused the tank to move 100 ft backwards off its foundations. Some 92,400 bbl of diesel fuel were spilled. The oil overflowed the bund and much of it went into the river.

The investigation found that the rupture occurred due to low temperature embrittlement initiated at a flaw in the tank shell base metal, about 20 cm up from the bottom. The flaw had been created by an oxyacetylene cutting torch and had been there since the initial fabrication. The actual fracture was in the shell base metal; it did not follow the welds but crossed them. In its previous service, the tank had stored heated product, while in its new service the product was not heated. It was the first time that in its new service the tank had been filled to maximum capacity in cold weather.

Prokop (1988); Mahoney (1990); Wilkinson (1991 SRD R530); Mellin (1992 LPB 106)

A121 *Norco, Louisiana, 1988*
On 5 May 1988, an explosion occurred on a catalytic cracker at the refinery at Norco, Louisiana. There was a rupture, due to internal corrosion, on an 8 in. elbow in the depropanizer overhead piping, which released 9 te of hydrocarbons. A vapour cloud formed and after about 30 s found a source of ignition, probably the FCC charge heater. The resultant vapour cloud explosion did extensive damage and caused immediate failure of all utilities. It put out of action firewater and the four diesel fire pumps, and for several hours the fire fighting effort was limited. Some 20 major vessel or line failures occurred. Analysis of bolt stretch on columns indicated an overpressure up to 10 psi. Seven people were killed and 28 injured.

Mahoney (1990); D.J.Lewis (1993)

A122 *Antwerp, Belgium, 1989*
On 7 March 1989, the BASF ethylene oxide plant at Antwerp experienced two explosions, each with a fireball. The first occurred in column K303, separating ethylene oxide and acetaldehyde, which disintegrated. The pipework on another column, K302, fractured, so that the column depressurized and flame flashed back into it, causing a second internal explosion, separated from the first by 26 s. The blast, missiles and secondary fires caused extensive damage. Five people were injured.

The investigation found that low cycle fatigue had caused a hairline crack in a welded seam on piping to a level indicator system, resulting in a small leak of ethylene oxide. This led to an accumulation of auto-oxidizable polyethylene glycols in the insulation. Removal of the metal covering of the insulation allowed self-heating to proceed. The insulation reached a temperature which was sufficient to cause decomposition of ethylene oxide stagnant in the piping

of the level control system, though it would not have been enough to overcome the cooling effect of flowing vapour.

Mahoney (1990); Kletz (1990e); Anon. (1991 LPB 100, P. 1)

A123 *Baton Rouge, Louisiana, 1989*

On 24 December 1989, an explosion occurred in a refinery at Baton Rouge, Louisiana. An 8 in. diameter pipeline ruptured, releasing a mixture of ethane and propane. A record low temperature (10°F) may have contributed to the failure. The escaping vapour found a source of ignition and there was a vapour cloud explosion. The explosion ruptured a pipe band containing some 70 lines. These included lines for power, steam and firewater, and there was a partial loss of all these utilities. The extensive fire involved two large storage tanks, 12 small tanks and two separator units.

Mahoney (1990)

A124 *Jonova, Lithuania, 1989*

On 20 March 1989, a refrigerated atmospheric ammonia tank failed at Jonova, Lithuania, leading to both a toxic release and a fire of ammonia as well as fire in a fertilizer store. Seven people were killed and 57 injured.

The tank was 29 m diameter × 20 m high of single wall construction with perlite insulation held in place by an outer steel shell and with a surrounding 14 m high reinforced concrete wall. It had a capacity of 10,000 m^3 and at the time held 7000 te of liquid ammonia at −33°C. The capacity of each of the two pressure relief valves was 4200 m^3/h. The site also had two fertilizer stores, one for 15,000 te and one for 20,000 te as well as one for 20,000 te of ammonium nitrate.

The rupture was sudden and the force of the release caused the tank to move sideways from its base, smash through the concrete wall and fetch up 40 m away, leaving its bottom still on the foundations. The devastation around the tank was severe. The escaping liquid ammonia formed a pool which in places was 0.7 m deep. The vapour above the pool suddenly caught fire and the whole area was engulfed in flames. The fire set alight material on a conveyor belt to the 15,000 te store of NPK fertilizer, a 'cigar burning' material. The burning conveyor fell into the store and initiated a self-sustaining decomposition.

After 12 h the pool of ammonia had evaporated. The fertilizer continued to burn for 3 days.

The plant was 12 km from Jonova, a town of about 40,000 inhabitants. A large cloud of ammonia and nitrous fumes spread 35 km, covering an area of 400 km^2. The cloud height is described as being 100, 400 and 800 m at distances of 5, 10 and 20 km, respectively. Some 32,000 people were evacuated.

The events leading up to the rupture were as follows. Due to an error, 14 te of warm ammonia at 10°C were transferred to the tank, where they formed a layer on the bottom. In due course this layer rose suddenly to the surface. The event was akin to a 'rollover', although this term is normally associated not with a pure liquid but with one of varying composition, such as LNG. The higher vapour pressure of the warmer liquid caused a sudden rise in pressure in the tank, which the pressure relief valves were unable to handle, and the tank burst. At the time the refrigeration compressors were not working, but this probably played little part in the incident.

Kletz (1991a); Andersson (1991a,b); Anon. (1992 LPB, p. 11); Andersson and Lindley (1992 LPB 107); Kukkonen *et al.* (1992); Wilday (1992 LPB 108, 109); Kukkonen *et al.* (1993)

A125 *Peterborough, UK, 1989*

On 22 March 1989, an explosion occurred in the yard of Vibroplant Ltd at Peterborough on a ICI truck carrying commercial explosives. The driver had missed his way and shortly after 9.30 a.m., approximately, entered the yard to turn round, when, as the vehicle passed over a speed ramp, there was a minor explosion inside the load compartment which blew the rear roller shutter door open. The driver stopped the vehicle, and he and the attendant got out to investigate. Smoke and flames were coming through gaps at the side of the door but no fire could be seen inside. They alerted the Vibroplant personnel in the yard and one of the latter telephoned the emergency services. At first only a small amount of black smoke was to be seen coming from the vehicle, but as the fire progressed there were minor detonations, or 'pops', and thick yellow smoke began to emerge. At 9.43–9.44 a.m. two fire tenders arrived. At 9.45 a.m. the load exploded. The scene following the explosion is shown in Figure A1.18. One person was killed and 107 were injured, of whom 84 were treated in hospital.

The load was a mixed one, consisting 150 kg of Powergel 800; 500 kg of Powergel E800; 56 kg of Magna Primers; 76 kg of Ammon-Gelit; detonators and fuseheads. The latter included uncut Cerium combs, 2400 in three boxes. The total mass of explosive had a TNT equivalent of some 800 kg.

The cause of the explosion was determined as a box of Cerium fusehead combs which were in unsafe packaging.

The report of the HSE (1990b) gives details of the damage and injury done by the event. With respect to damage, the analysis includes the following:

	Distance (m)	*Overpressure* (psi)
Clean area	14	78
Fireball	18	44
Total destruction of cavity brick/block walls of steel framed building	30	14
Serious damage to concrete frames of building	110	1.7
Window breakage:		
90%	≈225	0.69
50%	≈360	0.37
Up to	≈580	0.19

The clear area is the area of the yard which was cleared of cars, etc. The report also gives a map showing the fall of major fragments.

With respect to injury, plans are given showing the location of the persons exposed and of those who were blown over or suffered eardrum rupture. Two of the plans are shown in Figure A1.19.

At the instant of the explosion there were some 31 persons within 60 m of the vehicle. The plans show

Number of persons			
Distance (m)	<20	20–40	40–60
Exposed	3	12	31
Blown over	2	10	15
Eardrum rupture	2	4	

Figure A1.18 *Peterborough, 1989: Vibroplant works yard after the explosion (Courtesy of the Peterborough Evening Telegraph)*

The person who died was a fireman who was engulfed in the fireball, which extended 18 m. Another fireman at 25 m suffered minor burns. Other information on injuries includes

	Distance (m)	*Overpressure* (psi)
Burns:		
Fireman engulfed in flames	18	44
Fireman suffered slight burns	25	21
Eardrum rupture:		
100%	28	17
50%	30	15
Up to	45	6.6
Blown off feet:		
50%	55	4.7
Up to	70	3.2
Severe injury from fragments other than glass	40	
Cuts from glass:		
Cuts to all	0–50	>5.5
Cuts to many	70–100	3.2–1.9
Cuts to some	100–150	1.9–1.15
Cuts up to	≈200	0.8

Further details are given in the HSE report.
HSE (1990b); Anon. (1991 LPB 98, p. 24)

A126 *Richmond, California, 1989*
On 10 April 1989, in a refinery at Richmond, California, a 2 in. line carrying hydrogen at about 2800 psi suffered a failure, apparently at a weld, giving rise to a jet flame, which impinged on the support of a reactor, 100 ft high and at least 10 ft diameter and with a wall thickness of 7 in., in a hydrocracker unit. The resultant failure of the reactor led to extensive damage.
Mahoney (1990)

A127 *Ufa, Soviet Union, 1989*
On 4 June 1989, a massive vapour cloud explosion occurred in an LPG pipeline at Ufa in the Soviet Union. A leak had occurred in the line the previous day or, possibly, several days before. In any event, the engineers responsible had responded not by investigating the cause but by increasing the pressure. The leak was located some 890 miles from the pumping station, at a point where the pipeline and the Trans-Siberian railway ran in parallel through a defile in the woods, with the pipeline some half a mile from, and at a slightly higher elevation than, the railway. On the day in question the leak had created a massive vapour cloud which is said to have extended in one direction five miles and to have collected in two large depressions.

Some hours later two trains, travelling in opposite directions, entered the area. The turbulence caused by their passage would promote entrainment of air into the cloud. Ignition is attributed to the overhead electrical power supply for one or other of the trains. There followed in quick succession two explosions and a wall of fire passed through

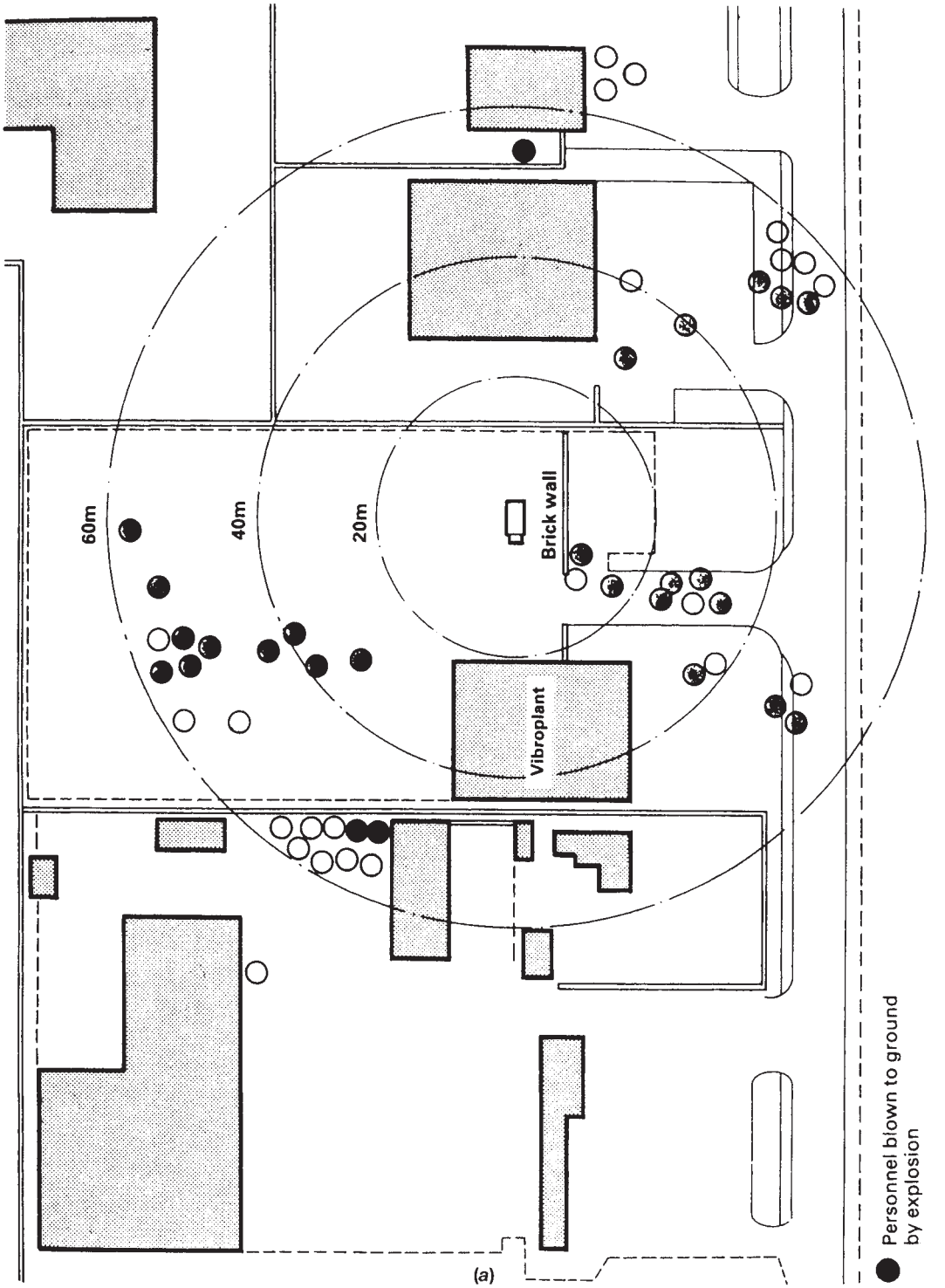


Figure A1.19 *Continued*

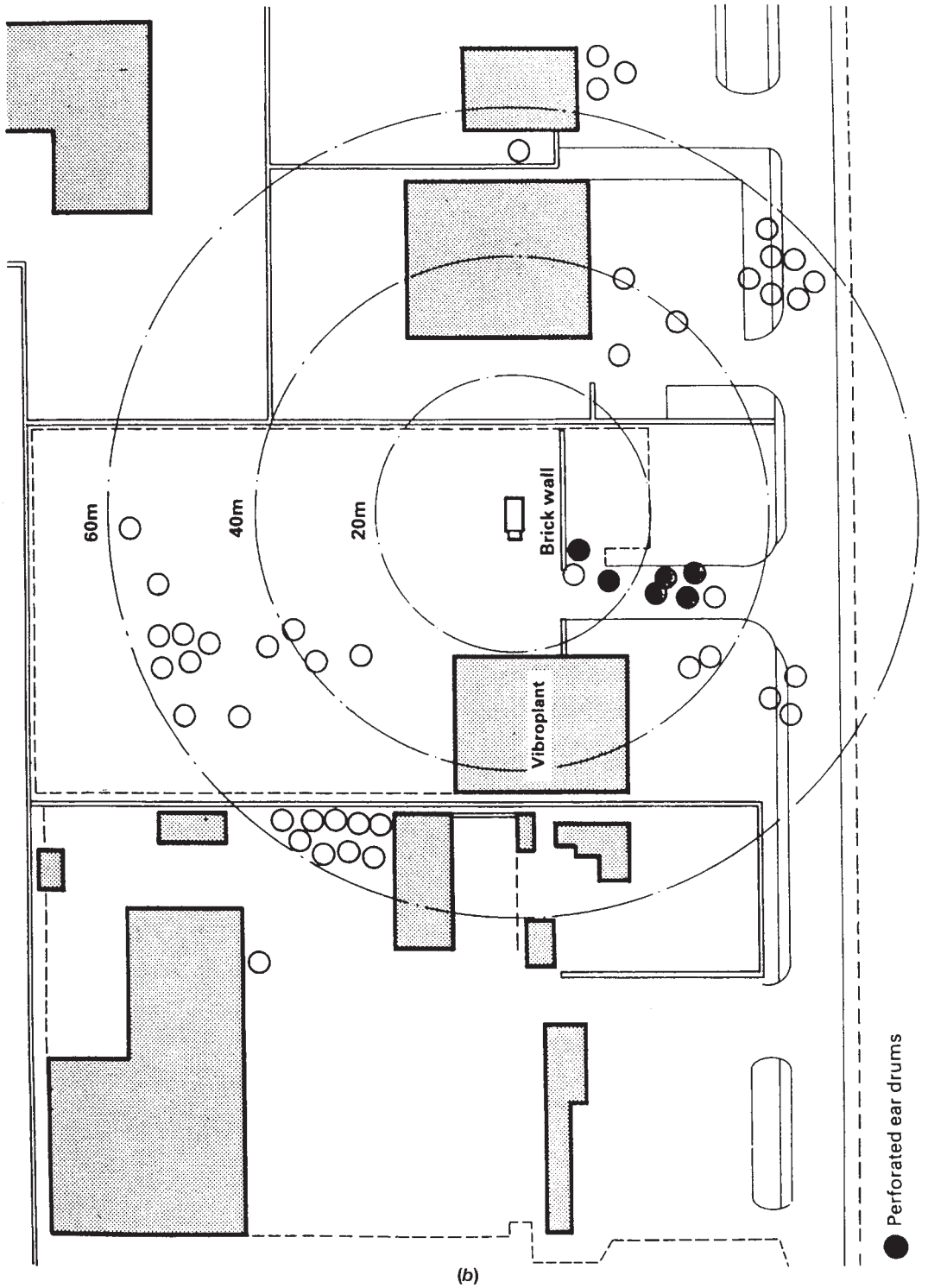


Figure A1.19 *Peterborough, 1989: site plan showing location of certain injuries (Health and Safety Executive, 1990c): (a) persons blown to the ground by the explosion; and (b) persons suffering perforated eardrums (Courtesy of HM Stationery Office)*

the cloud. Large sections of each train were derailed and the derailed part of one may have crashed into the other. The death toll is uncertain, but reports at the time gave the number of dead as 462 and of those treated in hospital as 706, many with 70–80% burns.

Hofheinz and Kohan (1989); D.J. Lewis (1989 LPB 90, 1993)

A128 *Bangkok, Thailand, 1990*

At 22.30 on 24 September 1990, a road tanker carrying LPG was involved in a traffic accident at a busy road junction in the centre of Bangkok. Some 5 te of LPG was released but did not ignite immediately. When the cloud did ignite, there was evidently a flash fire, but accounts spoke also of an explosion, probably from gas which had entered a nearby building. In the worst affected area, almost all the shop houses on both sides of the street were destroyed. Reports gave some 68 persons dead and over 100 injured.

The vehicle was a flat bed lorry carrying two LPG tanks. The two tanks were interconnected by two lines and it appears that these were severed in the accident. The tanker had no license to carry LPG.

Anon. (1991 LPB 101, p. 19)

A129 *Chalmette, Louisiana, 1990*

On 3 November 1990 in a refinery at Chalmette, Louisiana, failure involving a heat exchanger shell led to a release of hydrocarbons. A vapour cloud formed, was ignited by a heater and gave a vapour cloud explosion which did extensive damage.

Marsh and McLennan (1992)

A130 *Nagothane, India, 1990*

On 6 November 1990 at Nagothane, India, a leak occurred on a pipeline transporting ethane and propane to a gas cracker complex. A vapour cloud formed and ignited at an offsite gas treatment and compression facility. The cracker was not damaged by the resultant vapour cloud explosion, but serious damage was done to the offsite units. There were 31 deaths.

Marsh and McLennan (1992)

A131 *Stanlow, Cheshire, 1990*

On 20 March 1990, a reactor at the Shell plant at Stanlow, Cheshire, exploded. The explosion was due to a reaction runaway.

The vessel was a 15 m^3 batch reactor containing some 13.5 te of reaction mixture. The reaction was the Halex production of 2,4-difluoronitrobenzene (DFNB), using *N, N*-dimethylacetamide (DMAC) as solvent. The DFNB was then reacted to obtain the final product 2,4-difluoroaniline (DFA).

The batch had been heated from ambient to 165°C over 3 h, in the normal way. It then rose above 170°C, instead of starting to dip slightly, and, unusually, began to vent gas. In the following 10 min the heating was switched over to cooling, but the temperature and pressure in the reactor continued to rise, at an increasing rate. The control room operators were unaware of the runaway; they were looking at a different display on the VDU. They were alerted to it by an outside operator.

The pressure in the vessel reached a value later assessed as about 60–80 barg, which compares with the relief valve set pressure of 5 barg. The event generated blast, a fireball and missiles. The vessel body unwrapped into a flat plate and the cover was hurled 200 m; other missiles went up to 500 m. The reactor structure collapsed, the fluoroaromatics plant was devastated and structural damage was done to nearby buildings. One man subsequently died, and five others were injured.

There was evidence, from an eyewitness and from a severely burned lamp fitting which became a missile (Missile 47), that prior to the explosion there had been a jet flame above the reactor for some 30–120 s before the explosion, the leak coming from a flange or crack. The blast damage in the works had some unusual characteristics, decreasing only slowly with distance. The reactor had a vapour space of 3 m^3, but the blast damage was much greater than could be accounted for by a physical explosion involving such a volume, and a combustive event was indicated. Analysis pointed to an event giving a long impulse with a duration time of perhaps 400 ms, compared with, say, no more than 50 ms for a vapour cloud explosion on the one hand and 10 s for an unconfined fireball on the other. The relatively long duration of the explosion would be due to the rate limitation imposed by air entrainment. The investigators called the event which occurred a 'highly congested fireball'. The fetch of the missiles pointed to a pressure at the source in the range 60–80 barg. It was estimated that some 10 te of material had been ejected from the reactor at about 70 barg in a congested area and had been ignited by the jet flame above the vessel acting as a strong ignition source. These 10 te had an energy of combustion of 230,000 MJ; the event was consistent with an energy release of about one-fifth of this.

Much of the damage done was due to the rarefaction wave. Many components were more sensitive to a negative that to a positive pressure deviation.

The investigation found that the runway was due to the presence of acetic acid. This was detected by smell in the contents of a vent knockout vessel, and, much later, it was identified in a sample of the DMAC from the batch. Investigation revealed a rather complex chemistry. It showed that, when added to a Halex reaction mixture, acetic acid causes exothermic reaction and gas evolution. The DFNB process involved a later stage of batch distillation in which the successive fractions were toluene, DMAC and DFNB. The investigators discovered that during one such batch water had entered the still via a leaking valve. The water had been removed by prolonged azeotropic distillation, using toluene. Under these conditions, DMAC undergoes slow hydrolysis, giving dimethylamine and acetic acid. However, for there to be any significant yield of acetic acid, the presence of DFNB is necessary, since this reacts with the dimethylamide, and thus shifts the equilibrium. On this occasion, the DMAC had then been further distilled to purify it. It turned out, however, that DMAC and acetic acid form a maximum boiling azeotrope with a boiling point close to that of pure DMAC. The presence of the acetic acid in the DMAC was not detected by the measurement of boiling point nor by the particular gas chromatograph method in use. Thus the water ingress incident evidently led to a batch of recycled DMAC which was contaminated with acetic acid, with the consequences described.

Anon. (1991k); Kletz (1991 LPB 100); Mooney (1991); Redman and Kletz (1991); Cates (1992); van Reijendam *et al.* (1992)

A132 *Coode Island, Mevaporourne, Australia, 1991*
On 21 August 1991, an explosion occurred at A Terminal of Terminal Pty at Coode Island, Mevaporourne, Australia. The site involved had 45 storage tanks, none pressurized, with a vapour recovery system. A 230 te acrylonitrile tank was lifted off its base and projected over four other tanks into the forecourt. There followed a series of bund and tank fires and tank explosions, at the end of which only 13 tanks were left undamaged. There were no deaths or serious injuries.

The cause of the initial explosion has not yet been established. Some of the explanations considered are rehearsed by I. Thomas (1991), including his own of exothermic polymerization in the vapour recovery system. A critique of this explanation is given by Croudace (1993 LPB 112).

Anon. (1991b); I. Thomas (1991); Anon. (1992c); Alexander (1992a); Marsh and McLennan (1992); Croudace (1993 LPB 112)

A133 *Seadrift, Texas, 1991*
At 1.18 a.m. on 12 March 1991, an ethylene oxide redistillation column at the Union Carbide plant at Seadrift, Texas, exploded. A large fragment from the explosion hit pipe racks and released methane and other flammable materials. All utilities at the plant were lost. There was a substantial loss of firewater from water spray systems damaged or actuated by loss of plant air. The explosion and ensuing fire did extensive damage and one person was killed.

The plant had been down for routine maintenance. Start-up began in the late afternoon of 11 March, but the plant was shut-down several times by trip action before the cause was identified and rectified. Operation was finally established around midnight. The plant had been operating normally for about an hour when the explosion occurred.

The explosion was attributed to the development of a hot spot in the top tubes of the vertical, thermosiphon reboiler such that the temperature reached over 500°C instead of the normal 60°C, combined with a previously unknown catalytic reaction, involving iron oxide in a thin polymer film on the tube, which resulted in decomposition of the ethylene oxide.

A low recirculation ratio in the reboiler could give in some of the tubes low flow, loss of liquid film and stagnant vapour. The account by Viera, Simpson and Ream (1993) gives a detailed discussion of measures to ensure that all the heated surfaces of the reboiler are kept wetted.

Marsh and McLennan (1992); Viera, Simpson and Ream (1993)

A134 *Bradford, UK, 1992*
On 21 July 1992, a series of explosions leading to an intense fire occurred in a warehouse at Allied Colloids Ltd, Bradford. None of the workers at the factory was injured but three residents and 30 fire and police officers were taken to hospital, mostly suffering from smoke inhalation. The fire gave rise to a toxic plume and the run-off of water used to fight the fire caused significant river pollution.

The HSE investion (HSE, 1993b) concluded that some 50 min before the fire two or three containers of azodiisobutyronitrile (AZDN) kept at a high level in Oxystore 2 had ruptured, probably due to accidental heating by an adjacent stream condensate pipe. AZDN is a flammable solid incompatible with oxidizing materials. The spilled material probably came in contact with sodium persulfate and possibly other oxidizing agents, causing delayed ignition followed by explosions and then the major fire.

The warehouse contained two storerooms. Oxystore No. 1 was designed for oxidizing substances and Oxystore No. 2 for frost-sensitive flammable products; this second store was provided with a steam heating system. In 1991, an increase in demand for oxidizers led to a change of use, with both stores now being allocated to oxidizing products. A misclassification of AZDN as an oxidizing agent in the segregation table used led to this flammable material being stored with the oxidizers.

In September 1991, the warehouse manager, after discussions with the safety department, submitted a works order for modifications to the oxystores, including Zone 2 flameproof lighting, temperature monitoring equipment, smoke detectors and disconnection of the heater in Oxystore 2. An electrician made a single visit in which he did not disconnect the heater but simply turned the thermostat to zero. Although safety-related, the work was given low priority and 10 months later none of it had been started.

The explosion started at 2.20 p.m. and the first fire appliance arrived at 2.28 p.m. The fire services experienced considerable difficulties in obtaining a water supply adequate to fight the fire. At 3.40 p.m. power was lost on the whole site when the electricity board cut off the supply because the fire was threatening the main substation. The loss of power led to the shut-down of the works effluent pumps and escape of contaminated firewater from the site.

The fire services made early contact with the company's incident controller and strongly advised the sounding of the emergency siren, but this was not done until 2.55 p.m., when the incident had escalated. The fire gave rise to a black cloud of smoke, which drifted eastward over housing. The company stated on the day that the smoke was non-toxic. The HSE report, which gives a map of the smoke plume, states that 'it was in fact smoke from a burning cocktail of over 400 chemicals and only some of them would have been completely destroyed by the heat of the fire'.

The HSE report cites evidence that the warehouse had not been accorded the same safety priority as the production functions. It came under the logistics department, none of whose 125 personnel had qualifications as a chemist or in safety.

HSE (1993b); Anon. (1994 LPB 119, p. 15); V.C. Marshall (1994 LPB 117)

A135 *Castleford, UK, 1992*
At about 1.20 p.m. on Monday, 21 September, 1992, a jet flame erupted from a manway on the side of a batch still on the Meissner plant at Hickson and Welch Ltd at Castleford. The flame cut through the plant control/office building, killing two men instantly. Three other employees in these offices suffered severe burns from which two later died. The flame also impinged on a much larger four-storey office block, shattering windows and setting rooms on fire. The 63 people in this block managed to escape, except for one who was overcome by smoke in a toilet; she was rescued but later died from the effects of smoke inhalation.

The flame came from a process vessel, the '60 still base', used for the batch distillation of organics, which was being raked out to remove semi-solid residues, or sludge. Prior to this, heat had been applied to the residue for three hours through an internal steam coil. The HSE investigation (HSE, 1993b) concluded that this had started self-heating of the residue and that the resultant runaway reaction led ignition of evolved vapours and to the jet flame.

The 60 still base was a 45.5 m^3 horizontal, cylindrical, mild steel tank 7.9 m long and 2.7 m diameter. The still was used to separate a mixture of the isomers of mononitroluene (MNT, or NT), two of which (oNT and mNT) are liquids at room temperature and third (pNT) a solid; other by-products were also present, principally dinitrotoluene (DNT) and nitrocresols. It is well known in the industry that these nitro compounds can be explosive in the presence of strong alkali or strong acid, but in addition explosions can be triggered if they are heated to high temperatures or held at moderate temperatures for a long period.

The still base had not been opened for cleaning since it was installed in 1961. Following a process change in 1988 a build-up of sludge was noticed, the general consensus being that it was about 1820 l, equivalent to a depth of about 10 cm, though readings had been reported of 29 cm and, the day before the incident, of 34 cm. One explanation of this high level was that on 10 September the still base had been used as a Vacuum cleaner' to suck out sludge left in the 'whizzer oil' storage tanks 162 and 163, resulting in the transfer of some 3640 l of a jelly-like material. The intent had been to pump this material to the 193 storage but transfer was slow and was not completed because the material was thick. The batch still was used for further distillation operations, which were completed on September 19. The still base was then allowed to cool and on September 20 the remaining liquid was pumped to the 193 storage.

On September 17 the shift and area managers discussed cleaning out the still base. The former had been told by workers that the still had never been cleaned out and he realized that the sludge covered the bottom steam heater battery. It was agreed to undertake a clean-out. The area manager gave instructions that preparations should be made over the weekend, but when he arrived on the Monday morning nothing had been done. He was concerned about the downtime, but was assured that this could be minimized and gave instructions to proceed.

At 9.45 a.m. the area manager gave instructions to apply steam to the bottom battery to soften the sludge. Advice was given that the temperature in the still base should not be allowed to exceed 90°C. This was based solely on the fact that 90°C is below the flashpoint of MNT isomers. However, the temperature probe in the still was not immersed in the liquid but in fact recorded the temperature just inside the manway. Further, the steam regulator which let down the steam pressure from 400 psig (27.6 bar) in the steam main to 100 psig (6.9 bar) in the batteries was defective. Operators compensated for this by using the main isolation valve to control the steam. This valve was opened until steam was seen whispering from the pressure relief valve on the battery steam supply line. This relief valve was set at 100 psig but was actually operating at 135 psig (9 bar), at which pressure the temperature of the steam in the battery tubes would be about 180°C.

The clean-out operation, which had not been done in the previous 30 years, was not subjected to a hazard assessment to devise a safe system of work, and there were defects in the planning of and permit-to-work system of the operation. The task was largely handled locally with minimal reference to senior management and with lack of formal procedures, although such procedures existed for cleaning other still bases on the site. The permits were issued by a team leader who had not worked on the Meissner plant for 10 years prior to his appointment on September 7. At 10.15 a.m. he made out a permit for a fitter to remove the manlid. The fitter signed on about 11.10 a.m. and shortly after went to lunch. Operatives who were standing by offered to remove the manlid and the same team leader made out a permit for them to do so. When the fitter returned from lunch it was realized that the still base inlet had not been isolated and a further permit was issued for this to be done.

Meanwhile, the manlid had been removed. The area manager asked for a sample to be taken. This was done using an improvized scoop. He was told the material was gritty with the consistency of butter. He did not check himself and mistakenly assumed the material was thermally stable tar. No instructions were given for analysis of the residue or the vapour above it. Raking out began, using a metal rake which had been found on the ground nearby. The near part of the still base was raked. The rake did not reach to the back of the still and there was a delay while an extension was procured. The employees left to get on with other work and it was at this point that the jet flame erupted.

The HSE report states that analysis of damage at the Meissner control building at 13.4 m from the manway source indicated that at this building the jet flame was 4.7 m diameter. The jet lasted some 25 s and had a surface emissive power of about 1000 kW/m^2. The temperature at 6 m from the manway would have been about 2300°C.

The company employed some highly qualified staff with considerable expertise in the manufacture of organic nitro compounds. The HSE report describes some of the investigations of thermal stability, safety margins, etc., in which these staff were involved. It also comments in relation to the incident in question, 'Regrettably this level of understanding was not reflected in the decision which was made on 21 September when it was decided that the 60 still base would be raked out.'

As soon as the personnel at the gate office saw the flame one of them made a '999' emergency call. The employee requested the ambulance and fire services, but spoke only to the former before the call was terminated at the exchange. Thereafter incoming calls prevented further outgoing calls for assistance.

Just over a year before the incident the management structure had been reorganized. This involved replacing a hierarchical structure with a matrix management system, eliminating the role of plant manager and instituting a system in which production was coordinated through senior operatives acting as team leaders. The area managers had a significant workload. In addition to their production duties they had taken over responsibility for the maintenance function, which had previously been under the works engieering department. Managers were not meeting targets for planned inspections under the safety programme, and this was said to be due to lack of time.

C. Butcher (1994); HSE (1994b); Kletz (1994 LPB 119)

A136 *Sodegaura, Japan, 1992*

At 15.52 on 16 October 1992 at the Fuji Oil Sodegaura refinery at Sodegaura City, Japan, a large release of hydrogen occurred from a rupture on a feed/reactor effluent heat exchanger on the heavy oil indirect desulfurization unit as the plant was being started up after a shut-down. There was a delay of a few minutes, during which personnel took measures to try to stop the release, before the leak found

a source of ignition and exploded. Ten were killed and seven injured.

The investigation found that the leak occurred at a gasket retainer on the heat exchanger as illustrated in Figure A1.20. The gasket retainer had shrunk due to repeated thermal cycling and it suffered wear at the point shown as X on the diagram. The defect was detected and during a shut-down the surface was repaired by grinding. However, the effect of this was to cause the retainer to ride beyond the groove so that when the retainer was heated during start-up, a gap opened up and the escape occurred.

High Pressure Gas Safety Institute of Japan (1993 LPB 116)

A137 *Hoechst Incidents, Germany, 1993*

On 22 February 1993, an accident occurred at the Griesheim works of Hoechst, which was unprecedented in the company's 130-year history. By April 2, there had been at five sites a series of no less than 14 incidents, comprising 11 releases, two fires and one explosion, of which three were considered serious by the company.

Incident on 22 February 1993

The first of these, at 4.14 a.m. on 22 February, was a reaction runaway which occurred when a reactor for the production of *o*-nitroanisol was charged with reaction mixture with the agitator off and the latter was then switched on. Some 10 te of material was discharged through two safety valves. The ambient temperature was −2°C and most of the material solidified, but the residual gas cloud spread across the Main and affected an area of some 30 ha in Frankfurt.

The information available to the works manager, a materials safety data sheet conforming to the DIN standard, was that *o*-nitroanisol is 'slightly toxic', and he gave this description to the press. As it happened, the previous Friday this data sheet had been the subject of a revision, to the effect that the substance had been found to be carcinogenic to rats when administered in large doses over a long period. The revision had been known to the company's specialists since November 1992 but not to the works manager. The toxicity of the substance was the subject of press comment.

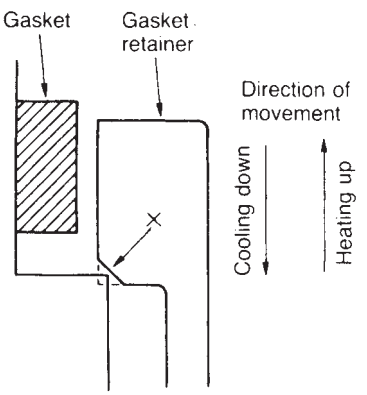


Figure A1.20 *Sodegaura, 1992: simplified diagram of heat exchanger gasket retainer. The gasket retainer suffered wear at the point marked X and repair was made by grinding, with loss of metal broadly as shown by the dotted portion (after the High Pressure Gas Safety Institute of Japan, 1993 LPB 116)*

Incident on 15 March 1993

The second serious incident, was on 15 March, on one of four parallel trains for the production of polyvinylalcohol. At the location in question in normal operation the material was in gel form on a conveyor belt inside an enclosure, but at the time the belt was stopped and empty. That morning the enclosure, which was normally kept inerted with nitrogen, was inspected. A precutter was still operating. An explosion occurred which killed the shift supervisor and injured the section manager. There followed a fire, which gave rise to a large column of smoke visible for some distance but which was rapidly brought under control.

An investigation by the authorities concluded that the enclosure had contained flammable vapours, that air had entered the enclosure during the inspection and that tramp metal had entered, giving rise to a spark at the precutter.

Incident on 2 April 1993

The third incident, on 2 April, involved a release of oleum. The release occurred when air pressure was applied to a vessel containing oleum and, due to a blockage in an outlet pipe, caused by crystallization, the oleum passed instead into an absorber where it reacted violently with the absorbent. A glass pipe ruptured and some 50 kg of oleum was released.

Owing to difficulties experienced with the alarm system some 13 people at the research centre came in contact with the cloud and received treatment at the medical centre.

Ondrey (1993a,b); Schonfeld (1993); Vennen (1993)

A138 *Dronka, Egypt, 1994*

On 2 November 1994, blazing liquid fuel flowed into the village of Dronka, Egypt. The fuel came from a depot of eight tanks each holding 5000 te of aviation or diesel fuel. The release occurred during a rainstorm and was said to have been caused by lightning. Reports put the death toll at more than 410.

Reuter (1994)

A139 *Ukhta, Russia, 1995*

Early in the morning on 27 April 1995, an ageing gas pipeline exploded in a forest in northern Russia. Reports described fireballs rising thousands of feet in the air and the inhabitants of the city of Ukhta, some eight miles distant, as rushing out in panic. At Vodny, six miles away, the sky was so bright that people thought the village was on fire. The pilot of a Japanese aircraft passing over at some 31,000 ft perceived the flames as rising most of the way towards his plane.

Anon. (1995)

A140 *Terminal Fire Savannah, Georgia, 1995*

On April 10, 1995, at approximately 11:30 p.m., explosions and fire occurred at Powell Duffryn Terminals, Inc. (PDTI), a commercial bulk liquid chemical storage and transfer facility, in Savannah, Georgia. Flames and thick black smoke from the fire forced the residents of the adjacent townhouse development to evacuate immediately. It took firefighters almost 3 days to finally put out the fire. The fire was within a concrete walled enclosure area containing six large storage tanks. During the fire, part of the enclosure wall was breached releasing contaminated firewater. The run-off from the fire contaminated an adjacent marsh

on the Savannah River resulting in a fish kill. (This first paragraph and the four following it were taken almost verbatim from the Executive Summary of the EPA's Chemical Emergency Preparedness and Prevention Office report entitled *EPA Chemical Accident Investigation Report*, PDTI. It is EPA Report 550-R-98-003.) (A summary report by David Chung entitled *Explosion and Fire* at Powell Duffryn Terminals – Savannah, Georgia was also used.)

After the fire, chemicals leaking from the storage tanks in the enclosure area reacted and produced toxic hydrogen sulfide gas. The hydrogen sulfide gas release forced residents within one-half mile of the facility to evacuate. As many as 2000 people were involved in the evacuation. An elementary school nearby was also forced to close. Approximately 300 people went to hospital emergency rooms complaining of symptoms attributed to hydrogen sulfide exposure. For many nearby residents, the evacuation lasted more than 30 days because of the continued evolution of hydrogen sulfide gas from the PDTI site. After the incident, extensive cleanup of the site and neighboring area was required.

Powell Duffryn Terminals Inc is fully enclosed by a security fence with locked gates. On April 10, 1995, the last employee left the site for the day at 5:50 p.m. The gates were locked, and no employees were on-site until after the explosions and fire had occurred.

On the day of the fire, contractor employees had been installing a sealed foam chamber on the storage tanks containing crude sulfate turpentine (CST), a flammable liquid. This closed the CST tanks to the atmosphere and directed CST vapour to the vapour control (VC) system. The VC system was designed to control fume and odour from the CST by capturing the CST vapour using activated carbon in two 50-gallon drums connected to the CST tanks using PVC piping. According to PDTI modification plans, each CST storage tank was supposed to be equipped with a flame arrester at its connection to the PVC piping. These flame arresters had been delivered but not yet installed. In addition, a fixed-piping foam fire protection system was not completed at the time of the fire.

The explosions and fire at PDTI involved CST, which the facility began to store on 17 January 1995. Prior to 1995, the facility was permitted only for storing non-flammable liquids. The facility had not completed modifications to accommodate the storage of flammables when the fire occurred. The CST was stored in three storage tanks (two 237,000 and one 422,000 gallon capacity) in a walled enclosure that contained a total of six tanks. The three CST storage tanks were connected by the partially completed VC system used to remove CST vapour from any venting that may occur. In the same enclosure were three other storage tanks (one 340,000 and two 323,000 gallon, respectively) containing sodium hydrosulfide solution (pH 10.4 to 11.5); Briquest, an acidic cleaning solution (pH of 1) and Antiblaze 80, a fire retardant chemical. These tanks and associated pipes were damaged by the explosions and fire and leaked their contents into the six-tank enclosure area. Reaction of the sodium hydrosulfide with acids present in the enclosure area produced hydrogen sulfide, a toxic, foul smelling gas (EPA May 1998).

The EPA Chemical Accident Investigation Team identified the following as root causes and contributing factors in the accident:

- *The design for the Vapour Control System was inadequate*. There is a documented history of fires in drums containing activated carbon where the organic vapour control design permitted the backflow of air through the drums. Organic sulfur compounds in CST can produce heat when they are adsorbed by the activated carbon. Due to the incomplete vapour control installation, air was permitted to backflow into the CST contaminated drums of activated carbon when the ambient temperature drops and the vapours within the tank contract or if the tank is pumped out.

  It was a very hot afternoon when a tank truck of CST was unloaded. As the evening temperatures cooled, the tank vapour space cooled and the vapour contracted. Air drawn into the drums provided oxygen for the spontaneous combustion.
- *The storage tanks were not equipped with flame arresters*. The lack of these purchased, but not-yet-installed protection devices in the vent piping allowed the fire to travel from the carbon bed to the tank vapour space.
- *The foam fire suppression piping system was not completed on the tanks containing CST*. Despite the fact that flammable CST was being stored, the designed foam suppression system was incompletely installed.
- *Incompatible chemicals were stored in the same walled enclosure area*. A large quantity of sodium hydrosulfide solution was stored in the same enclosed area as an acidic cleaning solution. When the tanks leaked the chemicals reacted generating toxic hydrogen sulfide (H_2S). This noxious H_2S gas caused injuries, forced evacuations and hampered a quick response and cleanup.

For detailed recommendations, see either the EPA Report or David Chung's article.

A141 *West Helena, Arkansas, 1997*

On the afternoon of 8 May 1997, a massive explosion and fire occurred at Unit Two of the Bartlo Packaging Incorporated (BPS) facility located in West Helena, Arkansas. Three West Helena firefighters were killed and 17 required medical attention during the response. (This write-up is taken directly from EPA/OSHA Joint Chemical Accident Investigation Report, EPA 550-R-99-003. April 1999. Portions are taken word for word from the report.)

Hundreds of residents and patients at a local hospital were either evacuated or sheltered-in-place. The Mississippi River traffic and major roads were closed for approximately 12 h due to the release of toxic materials from the facility.

BPS employees observed smoke in the Unit Two warehouse and all employees evacuated the building prior to the explosion. Members of the West Helena Fire Department responded to the scene within minutes. A reconnaissance team of four firefighters was outside of the building when an explosion occurred in the warehouse. Three firefighters were killed when they were struck by materials from a falling wall. The fourth firefighter was injured seriously.

EPA and the OSHA conducted a joint investigation of the incident. The team determined that the incident was most likely caused by the decomposition of a bulk sack containing the pesticide Azinphos methyl (AZM) 50W which had been placed against or close to a hot compressor discharge pipe. Under this scenario, the heat from the discharge pipe would have caused the pesticide to decompose and give off flammable vapours, which resulted in the fatal explosion.

A142 *Longford, Victoria, Australia, 1998*

On Friday September 25, 1998, about 12:26 in the afternoon a reboiler ruptured at the Longford Gas Plant. The fracture

released hydrocarbon vapours and liquid. The vapours travelled towards the area of the fired heaters where it ignited.

Two gas employees were killed and eight others were injured. Property damages were estimated initially to be over $187,000. Supplies of natural gas to domestic and industrial users were interrupted between 9 and 19 days. The State of Victoria, which is highly dependent on natural gas, suffered substantial disruption to the economy.

The unit in which the release and fire originated was designed to remove ethane, propane, butane and other higher chain hydrocarbons by absorbing them in 'lean oil'. The oil, now saturated with light hydrocarbons was called 'rich oil.' 'Rich oil' was distilled to release these hydrocarbons and it was now lean again. The exchanger that ruptured was the reboiler. The cold rich oil was in the tubes and heated by warm lean oil.

Investigators determined that the loss was attributed to the fracture of a heat exchanger following a process upset that was set in motion by the unintended, sudden shutdown of warm lean oil pumps. Following the loss of the lean oil flow, the condensate flowing from the absorbers was flashing at lower and lower temperatures. Ice formed on the outside of the heat exchanger. Simulations indicate that the temperature reached as low as −48°C (−54°F). The reduction in temperature caused embrittlement of the heat exchanger's steel shell.

When hot lean oil was reintroduced into the vessel it ruptured releasing about 22,000 pounds of hydrocarbon vapour which exploded. (Technically it was reported not as a vapour cloud explosion, but a deflagration or flash fire.) An estimated 26,000 pounds of hydrocarbon vapour burned as a jet fire.

After the initial fire, the flame front travelled back to the source and a prolonged fire developed. This fire was beneath a critical pipe rack called 'King's Cross.' The flames impinging on this rack lead to three other rapid releases of flammable inventories and fireballs. The pipelines in this fire-affected area were major interconnections between three gas plants. It was difficult to isolate under these conditions. It required nearly 2.5 days for the total isolation of the piping network to stop the fire.

The Australian Government ordered a Royal Commission to investigate the cause of the accident. Follow-up reports provided some significant major lessons for the industry.

1. The Safety Management System was judged incomplete. This included the lack of operator training associated with the loss of lean oil flow, the circumstances in which brittle fracture might occur and the lack of discussion of this potential problem in procedures for shut-down or start-up.
2. One report listed the operator training emphasized the training was provided for the operators to do their job, rather than have the deeper understanding they needed to deal with unforeseen problems.
3. Changes in organization during the 1990s is also mentioned as a major contributor to this accident. Organizational changes were not subject to Management of Change scrutiny at this location. Until 1991 engineers worked at the Longford Plant on a daily basis. In 1992, as part of a restructuring of the company, all of the plant engineers were moved to Melbourne. The Commission's official report states, 'The physical isolation of the engineers from the plant deprived operations personnel of engineering expertise and knowledge which previously they gained through interaction and involvement with engineers on site. Moreover the engineers themselves no longer gained an intimate knowledge of plant activities.' The number of supervisors and associated staff was reduced from 25 to 17 between 1993 and 1998. The maintenance staff was also reduced from 67 to 58 during that time.

The Commission stressed that the Audit and Review functions of the Safety Management System provides opportunities to discover gaps. It stressed the need for challenging rigorous corporate audits. The commission concluded that the methodology employed by the assessment team earlier in 1998 was flawed and failed to identify significant deficiencies (Coco, 2001; Boult, 2001; Kletz-2001).

Augusta, Georgia, 2001

On March 13, 2001, three people were killed as they opened a process vessel containing hot plastic in Augusta, Georgia. They were unaware that the vessel was pressurized. The workers were killed when the partially unbolted cover blew off the vessel, expelling hot plastic. The force of the release caused hot oil tubing breakage, and a leak ignited. (Due to the serious nature of this incident, the US Chemical Safety and Hazard Investigation Board (CSB) initiated an investigation. Their results were reported in *Investigation Report: Thermal Decomposition* – BP Amoco Polymers – Report No. 2001-03-1-GA, June 2002. This write-up is an abbreviated version of the CSB Report and some is copied verbatim.)

Workers were attempting to open a cover on a polymer catch tank. The tank was designed to receive partially reacted waste diverted from a chemical reactor during periods of start-up and shut-down.

Twelve hours prior to the incident, an attempt was made to start the production unit. The start-up was aborted due to problems downstream of the reactor. However, prior to shut-down an unusually large amount of partially reacted material had been sent to the polymer catch tank. Hot molten plastic inside the tank continued to react and also began to slowly decompose, thereby generating gases and causing the contents of the tank to foam. The material expanded as foaming continued, and eventually the entire tank was filled. The material then forced its way into connecting pipes, including the normal and emergency vents.

Once in the pipes, the plastic solidified as it cooled, resulting in a hardened layer 3–5 in. thick around the entire inner wall of the tank. The core of the plastic mass remained hot and molten, and likely continued to decompose over several hours, generating gases that pressurized the vessel.

Before opening the polymer catch tank, personnel may have relied on a pressure gauge and a transmitter on the vent piping from the vessel. However, any reading from the pressure gauge would likely have been unreliable because plastic had entered the vent line and solidified.

The workers proceeded to remove the 44 bolts from the cover. When half of the bolts had been removed, the cover suddenly blew off. Hot plastic spewed throughout the area, travelling as far as 70 ft. The cover and the expelled plastic struck the workers, killing them.

The force created propelled the polymer catch tank backward and bent the attached piping. A section of hot oil, 370°C, supply tubing for a heating jacket to the catch tank broke, and the fluid spilled into the area. A flammable vapour cloud formed and ignited within a few minutes. Several hours of fire-fighting efforts were required to extinguish the fire.

The US Chemical Safety Board Key Findings include:

1. The manufacturing process was not subjected to a specialized design review to identify thermal decomposition hazards from unintended and uncontrolled reactions, and the risks posed by decomposition of the plastic were not recognized.
2. More than the normal amount of hot plastic entered the polymer catch tank during the aborted start-up. Reactions and decomposition of the plastic-produced gases. These gases caused the plastic to foam and expand. The expanded plastic forced its way into connecting pipes, where it solidified and plugged the inlet to the vent line. Once this occurred, the gases could not escape and the vessel became pressurized.
3. Operating experience revealed that the design of the polymer catch tank did not afford a practical and reliable method for workers to check for hazards before opening the vessel. Drains were often plugged with solidified plastic, making it impossible to verify the absence of pressure or hazardous chemicals.
4. Process safety information inadequately described the design basis and operating principles for the polymer catch tank. There was no discussion of the means by which overfilling could occur and its consequences.
5. The possibility of overfilling was increased when the original start-up procedures were revised; the diversion of output from the reactor to the polymer catch tank was extended from 30 to 50 min. This modification of procedures was not subjected to a management of change (MOC) review.
6. Process hazard analyses were inadequate. Other findings, root causes and recommendations are available in the Chemical Safety Board's report (CSB).

Martinez, California, 1999

On 23 February 1999, a fire occurred in the crude unit at an oil refinery in Martinez, California. Workers were attempting to replace piping attached to a 150-foot-tall fractionator tower while the process unit was in operation. During removal of the piping, naphtha was released onto the hot fractionator and ignited. The flames engulfed five workers located at different heights on the tower. Four men were killed, and one sustained serious injuries.

(Due to the serious nature of this incident, the US Chemical Safety and Hazard Investigation Board (CSB) initiated an investigation. The investigation was to determine the root and contributing causes of the incident and to issue recommendations to help prevent similar occurrences. This write-up is an abbreviated version of the CSB Report and much of the write-up is verbatim. The CSB examination led to 'Investigation Report – Refinery Fire Incident – Tosco Avon Refinery' Report No. 99-014-1-CA.)

On February 10, 1999, a pinhole leak was discovered in the crude unit on the inside of the top elbow of the naphtha piping, near where it was attached to the fractionator 112 ft in the air. Plant personnel responded immediately and attempted to isolate the piping. The unit remained in operation.

The naphtha piping was inspected and showed that it was extensively thinned and corroded. A decision was made to replace a large section of the naphtha line. Over the 13 days between the discovery of the leak and the fire, workers made numerous unsuccessful attempts to isolate and drain the naphtha piping. Nonetheless, supervisors proceeded with scheduling the line replacement while the unit was in operation.

On the day of the incident, the piping contained about 90 gallons of naphtha, which was being resupplied from the running process unit through a leaking isolation valve. A work permit authorized maintenance employees to drain and remove the piping. After several unsuccessful attempts to drain the line, a maintenance supervisor directed workers to make two cuts into the piping using a pneumatic saw. After a second cut the piping began to leak naphtha, the supervisor directed the workers to open a flange to drain the line. As the line was being drained, the naphtha ignited, most likely from contacting the hot surfaces of the fractionator, and quickly engulfed the tower structure and personnel.

Chemical Safety Board key findings

1. The removal of the naphtha piping with the process unit in operation involved significant hazards. This non-routine work required removing 100 ft of 6-in pipe containing naphtha, a highly flammable liquid. Workers conducting the removal were positioned as high as 112 ft above ground, with limited means of escape. The hot process unit provided multiple sources of ignition, some as close as 3 ft from the pipe removal work. One isolation valve could not be fully closed, which indicated possible plugging.

   On three occasions prior to the incident, the naphtha pipe resumed leaking from the original pinhole and felt warm to the touch, indicating that one or more isolation valves were leaking. Numerous attempts to drain the piping were unsuccessful.
2. The naphtha pipe that was cut open during the repair work was known by workers and the maintenance supervisor to contain flammable liquid. Although procedures required piping to be drained, depressured and flushed prior to opening, this was not accomplished because extensive plugging prevented removal of the naphtha. Although the hot process equipment was close to the removal work, the procedures and safe work permit did not identify ignition sources as a potential hazard.
3. The naphtha stripper vessel level control bypass valve was leaking, which prevented isolation of the line from the operating process unit.
4. The refinery's job planning procedures did not require a formal evaluation of the hazards of replacing the 100 ft of naphtha piping. The pipe repair work was classified as low risk maintenance. Despite serious hazards caused by the inability to drain and isolate the line – known to supervisors and workers during the week prior to the incident – the low risk classification was not reevaluated.
5. The refinery's permit for the hazardous non-routine work was authorized solely by a unit operator on the

day of the incident. Operations supervisors were not involved in inspecting the job site or reviewing the permit.
6. Operations supervisors and refinery safety personnel were seldom present in the unit to oversee work activities.
7. Deficiencies in auditing of maintenance line breaking, lockout/tagout procedures were noted as well as a lack of a Management of Change review as one of the contributing factors. See the full CSB report for details.

Root causes identified by the Chemical Safety Board

1. The refinery's maintenance management system did not recognize or control serious hazards posed by performing non-routine repair work while the crude processing unit remained in operation.
   - Refinery management did not recognize the hazards presented by sources of ignition, valve leakage, line plugging, and inability to drain the naphtha piping. Management did not conduct a hazard evaluation[1] of the piping repair during the job planning stage.
   - Management did not have a planning and authorization process to ensure that the job received appropriate management and safety personnel review and approval. The involvement of a multidisciplinary team in job planning and execution, along with the participation of higher level management, would have likely ensured that the process unit was shutdown to make repairs safely once it was known that the naphtha piping could not be drained or isolated.
   - The organization did not ensure that supervisory and safety personnel maintained a sufficient presence in the unit during the execution of this job. The refinery relied on individual workers to detect and stop unsafe work, and this was an ineffective substitute for management oversight of hazardous work activities.
2. The refinery's safety management oversight system did not detect or correct serious deficiencies in the execution of maintenance and review of process changes.
   - Neither the parent corporation nor the local facility management audited the refinery's line breaking, lockout/tagout, or blinding procedures in the three years prior to the incident. Periodic audits would have likely detected and corrected the pattern of serious deviations from safe work practices governing repair work and operational changes in process units. These deviations included practices such as:
     - Opening of piping containing flammable liquids prior to draining.
     - Transfer of flammable liquids to open containers.
     - Inconsistent use of blind lists.
     - Lack of supervisory oversight of hazardous work activities.
     - Inconsistent use of MOC reviews for process changes.
3. Refinery management did not conduct an MOC review of operational changes that led to excessive corrosion rates in the naphtha piping. Management did not consider the safety implications of process changes prior to their implementation, such as:
   Running the crude desalter beyond its design parameters.
   - Excessive water in the crude feed.
   - Prolonged operation of the naphtha stripper level control bypass valve in the partially open position.

These changes led to excessive corrosion rates in the naphtha piping and bypass valve, which prevented isolation and draining of the naphtha pipe (CSB).

Toulouse, France, 2001

This devastating accident will be discussed in much more detail in future editions as all of the details emerge.

A massive ammonium nitrate explosion occurred on Friday 21 September 2001, at the Azote de France (AZF) fertilizer factory on the outskirts of Toulouse, France. The blast occurred in a storage facility that held 200–300 tons of granular ammonium nitrate. During the tragedy, 29 people were killed; about 2500 were injured. One wounded person died later.

Ammonium nitrate is primarily used as a fertilizer, however, if it combined with certain additives it can be used as an explosive.

The AZF (Azote de France) started up in 1924 on the left branch of the Garonne River outside of Toulouse. The plant is in an industrial zone, but with urban sprawl the site is surrounded by housing and buildings used by the general public.

The blast crated a crater that was about 50–60 m with a depth of over 7 m. Windows were shattered within a radius of 1–1.5 km and windows were blown out in the city centre 3 km away. The strength was estimated to be equivalent to 30–40 tons of TNT.

This incident occurred just 10 days after the attack on the World Trade Center in New York. As a result, tens of thousands of people assumed that Toulouse was under a terrorists' attack and ran into the streets in panic or attempted to flee.

An investigation is still ongoing and more details will be available at a later date.

Information from (R.J.A. Kersten, A.C. van der Steen, A.F.L. and G. Opschoor. The Ammonium Nitrate Explosion in Toulouse, France: The Incident and Its Consequences for Industrial Activities. A paper delivered at the Center for Chemical Process Safety – October 2002).

A1.11 Case Histories: B Series

One of the principal sources of case histories is the MCA collection referred to in Section A1.l. There are a number of themes which recur repeatedly in these case histories. They include:

Failure of communications
Failure to provide adequate procedures and instructions
Failure to follow specified procedures and instructions
Failure to follow permit-to-work systems
Failure to wear adequate protective clothing
Failure to identify correctly plant on which work is to be done
Failure to isolate plant, to isolate machinery and secure equipment
Failure to release pressure from plant on which work is to be done

Failure to remove flammable or toxic materials from plant on which work is to be done
Failure of instrumentation
Failure of rotameters and sight glasses
Failure of hoses
Failure of, and problems with, valves
Incidents involving exothermic mixing and reaction processes
Incidents involving static electricity
Incidents involving inert gas

In the 2108 case histories described the most frequently mentioned chemicals and the corresponding number of entries are

Ammonia	48	Chlorine	37
Caustic soda	88	Sulphuric acid	46

The most frequently mentioned operations are

Loading	38	Steaming	32
Maintenance	82	Tank entry	39
Pipe fitting	27	Transfer	46
Process reaction	66	Unloading	64
Sampling	24	Welding	36

The most frequently mentioned equipments are

Centrifuge	24	Machine	27
Cylinder	26	Pump	60
Drum	76	Rotameter, sight glass	27
Hose	57	Tank	46
Industrial truck	31	Tank car	59
Laboratory	85[a]	Tank truck	35
line	105	Valve	86

[a] In the first 1623 case histories.

It is emphasized, however, that in many instances it is not appropriate to assign a single cause.

Accounts of some typical case histories, many of which are taken from the MCA collections, are given below. The descriptions are generally briefer than those given in the original sources, which should be consulted for further details.

B1 A pilot plant batch reactor was started at 5.40 a.m. As soon as catalyst was added the temperature and pressure began to increase. In accordance with normal operation venting was carried out. But this was slow and difficult due to carryover of liquid and solids from the reactor into the vent lines. At about 6.45 a.m. the agitator stopped as a result of overload. The vent lines blocked, the pressure increased rapidly and the building had to be evacuated. It was re-entered at about 7.20 a.m., when the pressure was found to be 750 psi. Thereafter the reaction subsided as the reactants were used up. The pressure relief valve was set at 750 psi, but was found to be blocked as a result of the incident. The cause of the reaction runaway was overcharging of reactants at the start of the batch. (MCA 1966/15, Case History 867.)

B2 A batch chlorinator exploded suddenly killing employees and doing extensive damage. The reaction temperature was controlled automatically by manipulating the chlorine flow. During the batch the measured temperature fell sharply and it was realized that the thermocouple had failed. The agitator was stopped and the brine cooling was shut off while the instrument was repaired, but delay in stopping chlorine flow resulted in a high temperature giving decomposition reactions. The explosion blew the reactor cover through the roof and the reactor itself was driven down into the floor. Flammable gases were released which burned and caused the casualties mentioned. The explosion also ruptured chlorine and ammonia lines.

The works emergency plan was activated, involving both local area services and mutual aid from other chemical firms. (MCA 1962/14, Case History 371.)

B3 In a process involving chlorination of paraffin in a reactor, chlorine gas was piped into the system in a carbon steel pipe. The pipe ruptured and released paraffin and chlorine, which caused a fire and did extensive damage. Subsequent investigation revealed that the contents of the reactor had leaked into the pipe and had reacted with the chlorine vapour. Severe oxidation of the steel pipe by chlorine and/or hydrogen chloride led to the pipe rupture. (NFPA 1973.)

B4 An explosion occurred in a batch reactor which blew the top right off the vessel. The vessel was supported by steelwork two-thirds of the way up its side. The force of the explosion pushed the reactor 2.5 ft into the floor, which was 3 ft below, as shown in Figure A1.21. Fragments of the lid of the vessel, which contained a bursting disc, were scattered over the countryside. (Anon. 1977n.)

B5 The loaded basket of a 48 in. suspended-type centrifuge suddenly became unbalanced and in consequence the shaft flew out and broke the outlet pipe of an adjacent centrifuge. The investigation indicated that the imbalance had been caused by a sudden escape of cake from one side of the basket due to a hole in the cloth. (MCA 1966/15, Case History 645.)

B6 A 2000 ft^3 diborane surge tank disintegrated causing severe loss. The failure fragmented the tank and reduced to rubble a 24 in. thick reinforced concrete wall barricading it on three sides. Fragments travelled 2200 ft and one cut four process lines in a unit 1800 ft distant. The tank was 8 ft inside diameter $\times$ 30 ft long. It was designed for a working pressure of 296 psi with a safety factor of 4. Prior to the installation it had been completely radiographed and stress-relieved. At the time of the explosion the tank pressure and temperature were 192 psig and 12°C. The cause of the explosion was not certain, but the most probable explanation appeared to be a defect in the tank aggravated by high stresses at the attachment weld of the platform support. (MCA 1966/15, Case History 730.)

B7 A safety shut-off valve on the gas supply to the burner in the combustion chamber of a drier remained open after the unit was shut-down. There was no indicator to show whether the valve was open or closed. On relighting the burner the operator made several errors, including that of opening the main valve on the gas supply to the burner before lighting the pilot burner. When the lighted taper was inserted into the combustion chamber, there was an explosion. (MCA 1966/15, Case History 1068.)

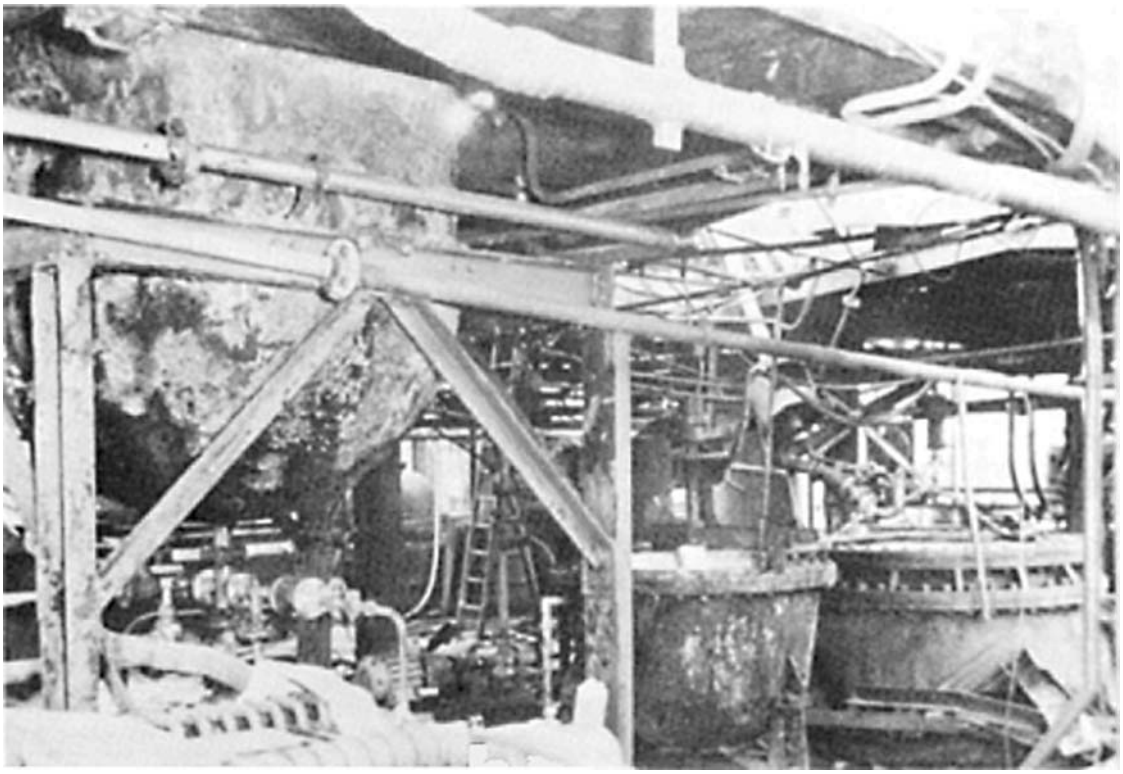


Figure A1.21 *Batch reactor after explosion (Anon., 1977n)*

B8 A reactor with a water jacket collapsed inwards due to overpressure in the jacket, the water from the jacket mixed with the reaction mass, and hot steam, and chemicals erupted violently through a sight glass and a rupture disc on the reactor. The overpressure of the jacket took place during the initial heating of the reactor charge and occurred because the inlet and outlet valves on the jacket were closed and there was no pressure relief device on the jacket, although there was a bursting disc on the reactor itself. (MCA 1966/14, Case History 353.)

B9 A cabinet containing sparking electrical equipment was pressurized with nitrogen to exclude flammable gases. Nitrogen from the same main was used to 'egg' acetone out of a process vessel. The nitrogen pressure fell as a result of heavy demand, acetone passed back into the nitrogen and got into the cabinet. Subsequently the nitrogen flow to the cabinet was shut off, air leaked in and mixed with the acetone, and there was an explosion. (Kletz, 1976b.)

B10 Butadiene from a reactor passed back up a line used for adding emulsifier through an obstructed non-return valve. The emulsifier tank had an open vent, so that the butadiene got out into the building and exploded. The explosion caused flames 75 ft high and was heard 10 miles away. Damage was minimized, however, by the light construction of the building which ruptured at the roof and at two of the walls. (Mallek, 1969.)

B11 In a pilot plant acetaldehyde oxidation column the arrangements involved purging the column with nitrogen and then supplying acetaldehyde to the column by nitrogen pressure. The oxidation was carried out by admitting a controlled flow of oxygen to the column. The pipework allowed the nitrogen to be used to purge the column and part of the oxygen pipe. There was nothing to stop oxygen at higher pressure passing into the nitrogen in case of a leaking valve or of incorrect operation. During operation the operator observed a leak on the acetaldehyde supply drum and was told to shut the plant down. A few minutes later an explosion occurred which killed four people. From the investigation it appeared that oxygen had leaked via the nitrogen purge line into the acetaldehyde drum, in which reaction occurred with large rises in temperature and pressure and eventually a detonation. (MCA 1962/14, Case History 117.)

B12 A malfunction of the control equipment allowed raw gas to accumulate in a direct-fired textile fibre drier. When circulating fans were turned on, the drier exploded. (Doyle, 1969.)

B13 In an air liquefaction plant an electrical failure caused the control valve on an oxygen line to open and pass oxygen into a nitrogen line. The nitrogen was compressed and then used as wash liquid for the offgas from an ethylene plant. The nitrogen wash cold box exploded. (Doyle, 1969.)

B14 In a chlorine liquefaction system 'gunk' was warmed prior to removal from a cold trap. A leaky steam valve allowed overheating of the gunk. This contained sufficient nitrogen trichloride to explode. (Doyle, 1969.)

B15 A vacuum system failed on a small still distilling a chloronitro compound. This allowed the temperature to rise and give a self-accelerating decomposition. A large still adjacent to the small one was seriously damaged. (Doyle, 1969.)

B16 A reboiler distilling epichlorhydrin from a mixture with tar was heated by steam. The thermocouple on the steam control loop tarred up and gave an incorrect reading. The only control of conditions in the column became the operator's response to the temperature at the top of the column. This proved inadequate, the reboiler overheated and an explosion occurred. (Doyle, 1972a.)

B17 In a furnace cracking ethylene dichloride to vinyl chloride under computer control the flow of ethylene dichloride to the furnace was controlled to maintain an optimum temperature in the cracked gas exit line. A furnace tube split and reduced the cracked gas flow and the cracked gas temperature. The control action increased the flow of ethylene dichloride. The furnace tubes burned up. (Doyle, 1972a).

B18 A common type of 'Dowtherm' vaporizer is a single coil in which the liquid is superheated, followed by a flash chamber. There is an interlock between a flowmeter on the liquid line to the coil and the fuel flow controller, so that the coil is not heated unless liquid is flowing through it. A vapourizer of this type was started up after a shut-down and the coil immediately exploded. The impulse lines to the differential pressure transmitter had frozen just before the shut-down, showing a normal flow, and during the shut-down the exit line from the coil also froze up. On start-up the interlock did not work owing to the incorrect signal from the flowmeter and the heating of the coil caused pressure to build up and rupture it. (Doyle, 1972a.)

B19 Excess water was removed from a hydrogen peroxide–water mixture by vacuum distillation. As a precaution against attempting to vaporize a dangerous concentration of peroxide, the liquid level and vapour temperature were measured: a low level or a high temperature signal operated a valve to dump de-ionized water into the reboiler. The hydrogen peroxide solution produced large quantities of heavy foam. The float-type level instrument measured the foam rather than the liquid level. After some erratic readings it gave a seriously inaccurate one while the level was low, and the reboiler exploded. (Doyle, 1972a).

B20 The agitator on a batch nitration reactor was stopped, but the process operator was unaware of this. Instrumentation which should have cut off the acid feed to the reactor and given an alarm signal of agitator stoppage apparently failed to work. When the agitator started up again, the reactor exploded. (Fritz, 1969.)

B21 In an ethylene cracking furnace the flow of fuel to the furnace was manipulated to control the temperature of the gas leaving the furnace. The temperature measuring instrument failed and gave a low reading. The control action increased the heat to the furnace. The furnace was designed to supply mainly latent heat of vaporization to the process stream with a small amount of superheat. Thus the vapour temperature was sensitive to the additional heat input and rose rapidly. The piping overheated and ruptured, releasing ethylene gas which was ignited by the burners of an adjacent furnace. The resultant fire did severe damage. (H.D. Taylor and Redpath, 1971.)

B22 Ammonia synthesis gas at 2000 psig was passed through a scrubber which was fed with weak aqueous ammonia. The liquid from the bottom of the column passed to a vertical holdup tank with a 2 in atmospheric vent. The level of liquid in the base of the column was controlled automatically. The control valve in this loop stuck in the open position. Liquid and gas from the column surged into the hold-up tank and ruptured it. The escaping gas was approximately 75% hydrogen and it ignited, causing a fire. (MCA 1966/15, Case History 598.)

B23 A flow ratio control loop failed and allowed excess hydrogen to enter a catalytic tower. Hot spots developed, causing thermal decomposition of the hydrocarbon–hydrogen stream and rupture of the tower. (MCA 1966/15, Case History 609.)

B24 A flame failure occurred on the burner of a Dowtherm vapourizer and the procedure for relighting the burner was initiated. The firebox was checked and the automatic control system which purges and lights the flame was activated. A short developed across the fuelselector switch of the system, causing fuel gas to enter the combustion chamber during the purge cycle and thus creating a flammable fuel–air mixture. When the purge cycle was complete and the pilot light was ignited, an explosion occurred. (MCA 1966/15, Case History 821.)

B25 An inert gas generator was found to have produced a flammable oxygen mixture. The 'fail safe' flame failure device had failed. The trip system on the oxygen content of the gas generated had caused shut-down when the oxygen content in some of the equipments reached 5%, but did not prevent creation of a flammable mixture in the holding tank. (MCA 1966/15, Case History 679.)

B26 An air supply enriched with 2–3% oxygen was provided for flushing and cooling air-supplied suits after use. A failure of the control valve on the oxygen–air mixing system caused this air supply to contain 68–76% oxygen. An employee used the supply to flush his air-supplied suit, disconnected the lines, removed his helmet and lit a cigarette. His oxygen-saturated underclothing caught fire and he received severe burns. (MCA 1966/15, Case History 884.)

B27 A chlorine cellroom was experiencing operational difficulties. A failure of the control system caused a back pressure to develop. When the operating personnel tried to shut the system down using manual controls, a failure of this equipment caused a serious chlorine release. One of two compressors taking hydrogen from a low-pressure gasholder continued to operate and failure of a low level trip created a negative pressure, allowing air to leak in. An explosion occurred in the cooling coils of the compressor. Hydrogen from another part of the process was introduced into the holder in an effort to maintain production. The hydrogen–air mixture in the holder diffused into the catalyst purification unit, where a high temperature developed, causing a second explosion. The failure of

the gasholder trip to operate was due to the fact that the timer had been bypassed by a 'jumper'. (MCA 1966/15, Case History 694.)

B28 An explosion occurred on a vinyl chloride polymerization plant at Minamata, killing four and injuring eight other people inside the factory and slightly injuring two people outside it by flying glass. The polymerization reaction in No. 3 reactor was complete and the operators intended to discharge the contents, but No. 4 reactor was discharged in error. The reaction in this reactor was incomplete and the VCM escaped and exploded. (MCA 1966/15, Case History 816.)

B29 A rigger was removing manhole covers from a vinyl chloride reactor when he apparently became confused and removed the cover from a reactor which was operating under pressure. A large quantity of vinyl chloride vapour was released. It ignited to give a flash fire, which killed the rigger and two labourers. (MCA 1970/16, Case History 1132.)

B30 In an ethylene oxide plant inert gas was circulated through a process containing a catalyst chamber and a heat removal system. Oxygen and ethylene were continuously injected into the inert gas and ethylene oxide was formed over the catalyst, liquefied in the heat removal section and passed to the purification system. On shut-down of the circulating compressor an interlock stopped the flow of oxygen and the closure of the valve was indicated by a lamp on the panel. During one shut-down the lamp showed the oxygen valve closed. The process operator had instructions to close a hand valve on the oxygen line, but he expected the maintenance team to restore the compressor within 5–10 min and did not close the valve. The process loop exploded. The oxygen control valve had not in fact closed. A solenoid valve on the control valve bonnet had indeed opened to release the air and it was the opening of this solenoid which was signalled by the lamp on the panel. But the air line from the valve bonnet was blocked by a wasps' nest. (Doyle, 1972a.)

B31 A catalyst bed was regenerated by circulating nitrogen through an electric heater, the bed and a cooler. The flowmeter on the nitrogen line choked with dust early on and the process operators learned to make do without it, controlling the plant by the nitrogen temperature at the bed inlet. One day the cooler blocked with dust and the temperature at the bed inlet stuck at its normal value. The heater over-heated and at 740°C its high temperature trip operated and cut off the power. The operator, seeing that the other instrument readings were normal, assumed the trip to be faulty and switched the power back on. The trip operated and was overridden three times in 1 h. There was a shift change during this hour. Finally the heater shell burst. (Kletz, 1974b.)

B32 A tank had to be filled with enough raw material to last a day. The operator watched the tank level and switched off the pump when the required level was reached. One day after several years operation and some 1000 fillings, the man let the tank overflow. So a trip system was installed as an additional safeguard. The operator, however, got in the habit of using the trip system as a replacement and got on with something else. The plant manager knew about this, but was happy to see the improvement in productivity. However, since the trip system can be expected to fail about once in 18 months, the overall system had actually become less reliable. (Kletz, I974d.)

B33 An explosion occurred in the open air in the vicinity of a hydrogen vent stack and caused severe damage. It was normal practice to vent hydrogen for periods of approximately 45 min. On this particular occasion there was no wind, the hydrogen failed to disperse and the explosion followed. (MCA 1966/15, Case History 1097.)

B34 An operator was adding charcoal impregnated with catalyst from a plastic bag into a reactor containing caustic soda blanketed with nitrogen. The charcoal dust ignited and there was a flash fire. It is believed that the ignition was caused by static electricity. (MCA 1966/15, Case History 1094.)

B35 An employee was repairing a blower on the vent stack of a dissolver. When he had finished the work, he switched the machine on, but observed that it was not operating. He reached into the stack to give the fan blades a turn and there was an explosion. The vent stack had contained a flammable mixture, which was probably ignited by static electricity from the man's body. (MCA 166/15, Case History 703.)

B36 A man was filling his cigarette lighter from a gallon can of naphtha when he dropped the lighter. It apparently struck on the wheel and gave a spark. Flammable vapour from a nearby drum filling plant ignited and caused a violent explosion. (MCA 1970/16, Case History 1175.)

B37 A substantial section of lagging along the pipework of a process heating fluid system became contaminated with the fluid, which was a low volatility mineral oil, due to a pump gland leak. A lagging fire occurred, the symptoms of which were that first smoke was seen rising from the lagging, then the heating fluid rose 50°C above its set temperature of 270°C and finally the pump and a considerable length of pipe became enveloped in flames. The latter were quickly dealt with, but the temperature of the heating fluid continued to rise. Soon afterwards a small explosion occurred in a covered oil header tank housed inside a building. There was a large release of oil and fumes from the tank and these then exploded violently, causing severe damage to the building. The probable explanation was that some of the oil had been heated above its spontaneous ignition temperature and had been forced by expansion back up into the header tank, where its vapour met air and ignited. (Gugan, 1974a.)

B38 A large spray drying plant with direct heating from a combustion chamber was being run in. The combustion system had been operating at a very low firing rate under manual control for some 24 h. The fuel oil to the burner was pumped by a positive displacement pump through thermostatically controlled heaters, excess oil being bypassed around the pump. After firing had continued unsupervised for some hours, there was a sudden eruption of flame through a hinged explosion panel near the combustion chamber and a man walking past was enveloped. Investigation showed that the eruption of flame could be explained by a gross increase in fuel flow to the burner, even though a manual valve on the fuel line was still at its original setting. It was also discovered that a fire had developed in the lagging of the fuel oil system, the lagging having become saturated with oil due to leaks from pipe

joints occurring during the initial pressure testing. The reason for the increase in fuel oil flow was probably a rise in the oil temperature to a value much in excess of that set on the thermostat, so that there was a decrease in oil viscosity and an increase in the quantity flowing through the valve. (Gugan, 1974a.)

B39 Dried material from a double-drum steam drier was passed from a bag packer via a spout with a cotton apron to a leverpak. A small dust explosion occurred at the apron and led to a fire in the bagging plant and leverpak. It was considered from investigation that the dust had been ignited by a spark discharge of static electricity. The cotton apron was non-conducting and the bag packer was not earthed. (MCA 1966/15, Case History 653.)

B40 An operator was in the process of unloading titanium carbide dust from 2 ft conical ball mill. He had removed 95% of the material. The mill was being rotated in order to clean it when a dust cloud ignited. He received severe burns from which he later died. The product had been milled to a finer size than desired and thus rendered highly reactive. (MCA 1966/15, Case History 618.)

B41 A set of air compressors comprising four three-stage 740 h.p. machines with a discharge pressure and temperature of 350 psi and 350°F had been in operation for about 8 h following a plant shut-down. The third-stage cylinder in one of the compressors was faulty and the 125 psi relief valve between the second and third stages began to relieve air intermittently. The third-stage discharge temperature went off the instrument scale at 400°F before the compressor could be shut-down. Some 15 min later the overhead discharge line was observed to be glowing red hot. Before the other compressors could be shut-down, the line ruptured and a flash fire occurred. Investigation indicated that lubricating oil had ignited in the compressor cylinder and discharge line. (MCA 1962/14, Case History 35.)

B42 An explosion occurred in a vinyl chloride pump and seriously injured an operator. The pump was on the 'recovered' vinyl chloride monomer (RVCM) system. The line sections before and after the pump had been removed and the explosion occurred in the idle vented pump about an hour later. The investigation showed that the entire RVCM system was contaminated with vinyl chloride polyperoxide, which is an unstable material. There had been three abnormal occurrences on the plant prior to this accident. The RVCM gas compressors had not shut-down at low pressure due to the failure of a pressure switch. There had been an accumulation of RVCM liquid in the storage tanks for 20 days. And the acidity level in the vinyl chloride feed to the polymerizers had been high. (MCA 1970/16, Case History 1551.)

B43 A four-stage reciprocating compressor used to compress nitrogen from 15 to 3000 psig exploded with a 'brilliant flash' and projected fragments up to 160 ft from the building. Previous to the explosion the machine had been shut-down to change the third-stage suction and discharge valves and again to correct an error in the installation of the former. Investigation showed that the discharge valve had been installed in the reversed position and that compression of the gas under these conditions could give a pressure of 16,800 psig and a temperature of 1310°F. This temperature exceeded the autoignition temperature of the lubricating oil. There may have been oxygen present due to the maintenance operations. These conditions resulted in the explosion. (MCA 1966/15, Case History 1056.)

B44 A 40,000 gal horizontal tank was used to produce aqueous ammonia by introducing water at the top and anhydrous ammonia at the bottom. The tank was emptied and the water flow was started to make the next batch. The tank imploded due to the vacuum created by the absorption of the ammonia vapours by the water. (MCA 1966/15, Case History 916.)

B45 A holding tank containing 'heavies' from cracking furnaces suddenly erupted blowing oil, water and steam over the adjacent area. It is believed that condensate had come in contact with the hot oil, which was at a temperature of 600–700°F, thus generating large quantities of steam. (MCA 1962/14, Case History 455.)

B46 A storage tank was not in use and was boxed up with some water inside. Rusting took place, the oxygen of the air in the tank was depleted and the tank collapsed inwards. (Anon., 1977n.)

B47 A storage tank was cleaned out and filled with a high purity liquid. A polyethylene bag was put over the vent to prevent contamination. It was a hot day and the temperature of the liquid in the tank rose. There was a sudden shower, vapour in the tank condensed and the tank collapsed inwards. (Anon., 1977n.)

B48 Cold liquid was pumped into a storage tank containing hot liquid. The liquid in the tank was cooled, the vapour pressure fell and the tank collapsed inwards. (Anon., 1977n.)

B49 Modifications were required to a high-pressure chlorine main. The main was isolated and men began work. The supervisor then realized that there might be some chlorine present in a section of pipework at the tank car rack. The pipework was connected to the main, but there was an isolation valve between the main and the pipework. He assumed that this valve was shut and initiated measures to remove any chlorine present in the pipework section. There was liquid chlorine in this pipework and it passed via the isolation valve into the main and gassed the fitters working there. The isolation valve was subsequently found to be frozen in the part open position. (MCA 1966/15, Case History 707.)

B50 An employee went into a water cistern to install some control equipment and immediately collapsed into water 2 ft below. A second employee who had accompanied him ran to fetch assistance. Minutes later he came back with several others, two of whom entered the cistern and also collapsed. Meanwhile the alarm had been raised. The fire services arrived and a crowd gathered. While the fire officer was putting on his self-contained breathing apparatus, one of the by-standers, saying that he could swim, descended into the cistern. The fire officer then went in, but took off his mask, presumably to call for some equipment, and collapsed. All five people died due to hydrogen sulfide poisoning. (MCA 1970/16, Case History 1213.)

B51 'A double fatality occurred in a steel works whilst two fitters were changing a gearbox valve for a blast furnace system. One or both men opened a valve allowing gas

to escape at a rate of 50,000 cu. ft. per hour. Of another two men who went to investigate the volume of gas passing through the valve, one was overcome by gas (but later recovered) and the other escaped to summon assistance. Safety precautions should have included either the isolation of the system upstream from the valve or the use of suitable breathing apparatus by the workmen. Although both maintenance men had been issued with compressed airline breathing apparatus it was found after the accident that only one of these was connected with the air supply and neither was being worn. The fatalities highlighted the dangers of complacency which can occur when a system has operated without incident for years and also the need to ensure that workers employed in such situations are adequately trained in the use of breathing apparatus.' (Annual Report of HM Chief Inspector of Factories, 1974.)

B52 During plant commissioning a temporary filter was put in a compressor suction line, as shown in Figure A1.22. The filter was located between the compressor and the low suction pressure trip. The filter blocked, the suction pressure fell below atmospheric, air was sucked in and a decomposition reaction occurred further on in the process where there was a higher pressure. Two pipe joints sprung and gas escaped and ignited. The resulting fire caused £100,000 damage and delayed the commissioning many months. (Henderson and Kletz, 1976.)

B53 An olefins plant was severely damaged during commissioning by a fire in the refrigeration section of the gas separation plant. Although no one was seriously injured, the fire burned for 15 h and caused delay to the commissioning and considerable damage and consequential loss. The cause of the fire was that the low-pressure refrigeration section, which was designed for 50 psig pressure, was subjected to a pressure of 400 psig. The overpressure occurred because of closure of a 12 in. valve on the exit of this section, installed during construction to allow high pressure gas to be used to assist in drying the plant prior to commissioning. The installation of the valve had been well debated in the plant operating team and with the process design contractor. But the installers did not follow the well-established requirement of providing pressure relief protection on the low-pressure system. (Heron, 1976.)

B54 A works had a special network of air lines installed some 30 years ago for use with breathing apparatus only. The supply to this network was taken off the top of the general purpose compressed air main as it entered the works, as shown in Figure A1.23. One day a man wearing a face mask inside a vessel got a faceful of water. He was able to signal to the anti-gas man and was rescued. Investigations revealed that the compressed air main had been renewed and that the branch to the breathing apparatus network had been connected to the bottom of the compressed air main. As a result a slug of water in the main would all go into the catchpot and fill it more quickly than it could empty. (Henderson and Kletz, 1976.)

B55 Pressure relief on a low-pressure refrigerated ethylene tank was provided by a relief valve set at about 1.5 psig and discharging to a vent stack. When the design had been completed, it was realized that if the wind speed was low, cold gas coming out of the stack would drift down and might then ignite. The stack was not strong enough to be extended and was too low to use as a flare stack. It was suggested that steam be put up the stack to disperse the cold vapour and this suggestion was adopted. The result was that condensate running down the stack met cold vapour flowing up, froze and completely blocked the 8 in. pipe. The tank was overpressured and it burst. Fortunately the rupture was a small one, the ethylene leak did not ignite and was dispersed with steam while the tank was emptied. (Henderson and Kletz, 1976.)

B56 A metal chute used to transfer a powder from a metal hopper into a metal vessel was replaced by a plastic hose. The flow of powder down the chute caused a charge of static electricity to build up in the hose and, although the hose was a conductor, the polypropylene end pieces used to connect it to the hopper and the vessel were not, and the charge was unable to dissipate. A spark occurred and the dust was ignited. (Heron, 1976.)

B57 A relief valve weighing 258 lb was being removed from a plant. A 25 ton telescopic jib crane with a jib length of 124 ft and a maximum safe radius of 80 ft was used to lift the valve. The driver failed to observe this maximum radius and went out to 102 ft radius. The crane was fitted with a safe load indicator of the type which weighs the load through the pulley on the hoist rope, but this does not take into account the weight of the jib, so that the driver had no warning of an unsafe condition. The crane overturned on to the plant, as shown in Figure A1.24. (Anon., 1977n.)

B58 Halfway through the unloading of a tank truck of anhydrous ammonia a stream of liquid was observed leaking from the bonnet of the stop valve on the unloading line.

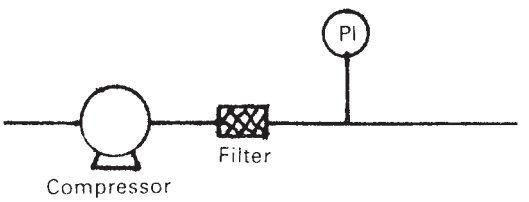


Figure A1.22 *Compressor system after modification (Henderson and Kletz, 1976) (Courtesy of the Institution of Chemical Engineers)*

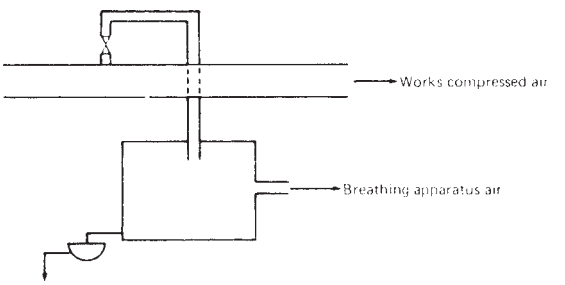


Figure A1.23 *Air offtake for breathing apparatus as originally installed (Henderson and Kletz, 1976) (Courtesy of the Institution of Chemical Engineers)*

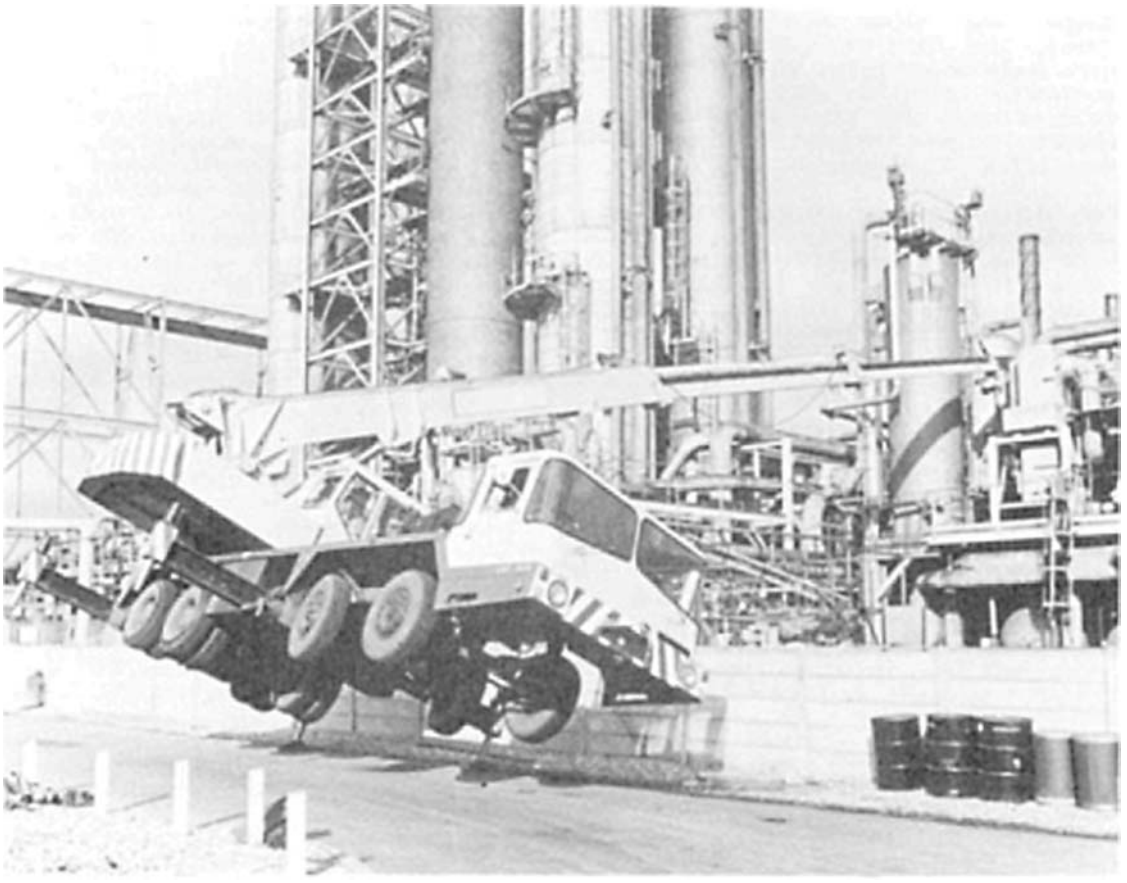


Figure A1.24 *Mobile crane overturned on to plant (Anon., 1977n)*

The truck was taken off line and the storage tank was vented to a neutralizing pit to relieve its pressure. Considerable difficulty was experienced in reducing the pressure in the tank sufficiently to stop the flow of liquid ammonia. There was no shut-off between the leaking valve and the tank. Eventually the pressure was reduced by using a compressor and exhausting it to atmosphere. Investigation indicated that the failure of the valve was caused by a combination of a flaw in the body and strain induced by excessive pressure on one of the stud bolts. (MCA 1970/16, Case History 1114.)

B59 A storage tank 108 ft diameter × 49 ft high containing refrigerated propane at a pressure less than 1 psig was overpressured and ruptured at Ras Tanura refinery, Saudi Arabia. The propane caught fire and gas from pilot-operated relief valves on two similar tanks, one containing propane and one butane, was also set alight. The ruptured tank burned out in some 36 h, while the butane and propane tank vent fires burned for 3 and 6 days, respectively. One person was killed and 115 were injured, and serious damage was done.

Just prior to the incident the refrigeration plant had been shut-down. The intention was to go over to autorefrigeration in which the propane tank would be cooled by boiling off liquid and venting it into the blowdown system. But this autorefrigeration could not be established, because the blowdown line was blocked with liquid butane. The reason for the presence of the butane was that a remotely operated isolation valve had not fully closed, because the valve spring was prevented from operating properly by paint and corrosion products.

There was a steady rise in the pressure in the propane tank up to and then beyond the relief valve set pressure of 1 psi. The operators, both at the end of one shift and at the beginning of the next, tried to find out the cause of the rise in pressure, but they did not alert the supervisors. (Laney, 1964.)

B60 An operator checked the level in a storage tank and then began pumping in a volatile monomer from a tank wagon. The vent pipe of the storage tank was blocked, however, and a large quantity of monomer flowed out of the dip leg. (MCA 1970/16, Case History 1192.)

B61 A tank truck was being loaded with ethyl acetate. The loader heard what he described as a 'sizzling' sound and looked in, but could see nothing. Soon after an explosion occurred. The investigation showed that the earthing

arrangements on the tank were in good order. The evidence suggested that the explosion was caused by static charge on the surface of the liquid. (MCA 1966/15, Case History 986.)

B62 A tank trailer containing 6876 gal of propane under pressure ruptured on the highway 560 ft from the centre of the town. The propane escaped and exploded, causing 10 deaths, 17 injuries and extensive damage. The investigation revealed various undesirable features of the tank, including weld defects which would create areas of enhanced stress concentration, differences of alignment between the cylinder and the end parts, and possible embrittlement of the plates due to the use of a heating process to effect chamfering. (MCA 1966/15, Case History 879.)

B63 Acetic acid was being pumped out of one compartment of a two-compartment trailer. The manhole cover was propped open. The operator climbed on the tanker to obtain a sample. In order to do this he had to lift the manhole cover back. When he had taken the sample, he closed the manhole cover completely. A few seconds later the tank imploded as a result of the vacuum generated by the continued pumping. The tank was equipped with a spring-loaded vacuum breaker, but either this failed to open or it was undersized. (MCA 1966/15, Case History 1011.)

B64 A tractor semitrailer transporting 7000 gal of propane was modified by inserting a tee-piece between the excess flow valve and the manual shut-off valve on the 3 in. discharge line. The joint was connected to the tractor fuel tank by a $\frac{3}{4}$ in. hose to allow the vehicle to be filled en route. There was another manual shut-off valve on the $\frac{3}{4}$ in. line. The hose broke in transit. The leakage flow rate was too small to activate the excess flow valve. The driver stopped the vehicle, shut-off the engine and told the trainee driver to shut-off the smaller hand valve. When the latter touched the valve, the propane vapours ignited and he was engulfed in flames. The gas continued burning for another 1.5 h. The trainee driver died in the fire, which also caused other injuries and damage. (MCA 1966/15, Case History 995.)

B65 An explosion occurred in a terraced house in East Street, Thurrock, in 1969 that blew a hole in the floor at the foot of the staircase. The wife of the householder fell in while carrying her child and both were injured. The Times (9 April, 1969) reported

> Investigators found that the explosion had been caused by the ignition of a mixture of petrol vapours and air and that the vapour was the result of a spillage of petrol two years before.

Table A1.4 *Some incidents and problems in the industries 1965–77*

1	*Power loss, weather and earthquake*		
	Power loss	1965 Dec. 6, 76	1971 Jan. 25, 25
		1966 Feb. 14, 86	1972 Nov. 27, 34
		1967 Jun. 19, 86	1973 Nov. 12, 94
		1968 Jun. 3, 31	Dec. 10, 66
		1970 Jun. 27, 80	
	Cold weather	1962 Feb. 5, 35	1977 Feb. 14, 25
	Wind, hurricane, tornado	1961 Oct. 2, 33	1972 Jul. 24, 75
		1970 Aug. 24, 31	Nov. 27, 34
	Flood	1972 Jul. 24, 75	
	Earthquake	1968 Dec. 16, 44	1972 Sep. 18, 72
2	*Safety and safety legislation*		
	Safety	1974 Jun. 10, 34	1977 Jun. 6, 68
		1975 Jun. 9, 34	
	Safety legislation and law	1964 Aug. 3, 27	1977 Jan. 17, 69
		Sep. 14, 83	Sep. 26, 44
		1973 Apr. 16, 58	Dec. 5, 67
		1975 Jun. 9, 36	Dec. 19, 28
		1976 Jul. 19, 72	
3	*Transport and transport legislation*		
	Transport	1962 Oct. 15, 78	1972 Dec. 11, 44
		Nov. 12, 86	1974 Dec. 23, 24
		1963 Feb. 4, 36	1975 Mar. 17, 20
	Transport emergency systems	1970 Jun. 15, 83	1972 Sep. 4, 19
		1971 Sep. 20, 78	
	Transport legislation	1969 Oct. 6, 97	1974 Dec. 23, 24
		1973 May 28, 43	1977 Jan. 3, 38
		1974 Sep. 16, 44	Mar. 28, 54
4	*Pipelines and pipelines legislation*		
	Pipelines	1964 Dec. 21, 27	1967 Mar. 13, 88
		1965 Sep. 27, 75	Apr. 24, 87

Table A1.4 *(continued)*

	1966 Apr. 11, 85 Jul. 4, 39 Dec. 19, 45 1967 Jan. 2, 19 Jan. 30, 50	1969 Sep. 22, 68 Oct. 20, 52 1970 Sep. 21, 85 1973 Aug. 20, 72 1975 Jan. 20, 44
Pipelines legislation	1965 Nov. 22, 79 1968 Dec. 2, 54 1969 Sep. 22, 68	1969 Oct. 20, 52 1973 Aug. 20, 72 1975 Jan. 20, 44
5 *Toxic chemicals at the workplace*		
Toxic or potentially toxic chemicals, especially carcinogens	1971 May 3, 38 1972 Jan. 10, 38 1974 May 13, 52 Oct. 28, 33 1975 Jan. 6, 57 Mar. 3, 74 May 12, 40 Jul. 7, 36 Jul. 21, 52 Aug. 4, 38 Aug. 18, 41 1976 Feb. 2, 48 Mar. 15, 48	1976 May 24, 70 Oct. 25, 66 Dec. 20, 19 1977 Jan. 3, 36 May 9, 87 Jun. 6, 67 Jul. 4, 62 Jul. 4, 64 Jul. 18, 54 Aug. 15, 88 Oct. 25, 74 Dec. 19, 28
Legislation on toxic chemicals	1973 Jan. 22, 47 1974 May. 27, 54 Sep. 16, 46 Oct. 14, 51 Nov. 25,33 1975 Feb. 3, 20 Mar. 3, 74 Sep. 15, 70 Oct. 27, 56 1976 May 24, 70 1977 Jan. 17, 70 Jan. 31, 54 Jan. 31, 56	1977 Feb. 14, 28 Feb. 28, 116 Mar. 28, 54 Apr. 11, 74 May. 9, 88 Jun. 20, 60 Jun. 20, 62 Jul. 4, 64 Sep. 12, 90 Oct. 10, 72 Oct. 24, 74 Nov. 21, 114 Dec. 5, 68
Testing and indexing of chemicals	1974 Jul. 8, 29 1975 Feb. 3, 20	1977 Jun. 20, 61
Vinyl chloride	1974 Feb. 4, 19 Apr. 15, 39 Jun. 24, 98 Nov. 25, 33 1975 Jan. 20, 41	1975 Apr. 14, 33 Jul. 7, 34 1977 Jan. 3, 37 Jul. 18, 52
Vinyl chloride legislation	1974 Mar. 4, 63 Apr. 15, 40 Jun. 24, 98 Jul. 8, 28 Jul. 22, 54 Sep. 30, 42 Oct. 14, 52 Dec. 23, 21	1975 Feb. 17, 35 Jun. 9, 36 Oct. 13, 67 Nov. 24, 20 1976 Jan. 5, 74 1977 Jun. 20, 62 Aug. 1, 20
6 *Pollution*		
	1974 May. 27, 53 1975 May. 26, 58 Nov. 10, 118	1977 Jan. 31, 55 May. 23, 94 Jun. 6, 68
Sudden releases and spillages	1967 Jun. 5, 64 1969 Aug. 25, 56 1971 Jul. 26, 55 1973 Feb. 5, 26 Jul. 23, 57	1973 Sep. 3, 48 1974 Jun. 24, 96 Jul. 8, 29 1977 Mar. 14, 75

Table A1.4 *(continued)*

		See also Transport, pipelines	
	Long-term, low concentration pollution and its effects	1968 Jan. 1, 9 Aug. 26, 25 1969 Mar. 10, 44 1970 Aug. 10, 50 Oct. 19, 72 1973 Jan. 22, 48 Aug. 20, 71 1975 Dec. 8, 80 1976 Feb. 16, 45	1974 Nov. 25, 36 1975 Feb. 3, 17 May. 12, 40 May. 26, 59 Aug. 4, 38 Sep. 1, 52 Nov. 10, 119 1977 Jan. 3, 36
	Fish kills	1964 Jul. 6, 70 1969 Nov. 3, 25	1970 Mar. 23, 57 1971 Jul. 26, 55
	Oil slicks	1969 Feb. 10, 40 1973 Jun. 25, 35	1975 Mar. 17, 17
	Mercury pollution	1967 May. 8, 85 Nov. 20,60 1970 Apr. 20, 53	1970 Aug. 10, 50 Sep. 7, 25 Oct. 5, 44
	Pesticides	1964 Apr. 13, 81 1967 Oct. 9, 108 1974 Apr. 15, 40	1976 Mar. 15, 48 Oct. 25, 66
	Ocean dumping	1970 Aug. 24, 32	1974 Oct. 28, 33
	Ocean incineration	1974 Oct. 28, 33	1975 Dec. 9, 82
7	*Pollution legislation*	1975 Jul. 7, 35 Sep. 1, 52 Oct. 13, 68	1976 Mar. 15, 48 1977 Mar. 14, 74
	Air	1969 Jun. 2, 44 1970 Nov. 30, 17 1971 Feb. 8, 20 1972 May. 15, 53 1973 Jun. 25, 34 1974 Feb. 4, 20 Mar. 18, 38 Jun. 24, 95 Sep. 2, 20 Oct. 14, 50 Dec. 23, 24	1975 Jan. 20, 42 1976 Feb. 2, 48 Mar. 1, 62 1977 Feb. 28, 116 Mar. 28, 56 Apr. 11, 74 Jul. 18, 54 Nov. 7, 42 Dec. 19, 26 Dec. 19, 27
	Odour	1972 Sep. 4, 19	
	Water	1969 May 19, 89 1970 May 18, 75 1972 May 15, 53 Oct. 16, 53 1974 Jan. 7, 46 Apr. 29, 82 Oct. 14, 52 1975 Feb. 3, 20	1976 Jul. 5, 35 1977 Jan. 31, 56 Jul. 4, 63 Aug. 15, 90 Aug. 29, 20 Dec. 5, 68 Dec. 18, 27
	Oil spills	1974 Jan. 7, 46	
	Noise	1974 Aug. 5, 46	1975 Oct. 13, 68
8	*Abandonment of actual or planned production*		
		1967 Mar. 27, 41 1968 Feb. 12, 49 1969 Mar. 10, 44 Jul. 14, 42 1970 Oct. 5, 43 1971 Jan. 25, 25 Feb. 8, 17 Jul. 26, 56	1973 Jun. 11, 63 1974 Nov. 25, 33 Dec. 9, 61 Dec. 23, 21 1975 Oct. 13, 67 Nov. 10, 118 Nov. 24, 20 1976 Jan. 19, 49

Table A1.4 *(continued)*

	Sep. 6, 27	1977 Jan. 31, 55
	1972 Mar. 20, 53	Oct. 10, 69
This list includes cases where abandonment of actual or planned production was a serious possibility, even if it did not in fact occur.		
9 *Litigation*	1963 May 13, 83	1970 Jul. 27, 80
	1964 Apr. 27, 78	Aug. 24, 32
	Dec. 21, 27	1971 Apr. 19, 53
	1966 Apr. 11, 85	1972 Dec. 25, 20
	1968 Aug. 26, 25	1974 Oct. 14, 52
	1970 Mar. 23, 59	1975 Nov. 24, 17

The spillage involved 367 tons of petrol on rail sidings in July, 1966, and the investigation suggested that there was probably an eight-foot thick band of petrol vapour lying well beneath the surface of the ground in the East Street area. The vapour had been raised to the surface because of exceptionally heavy rainfall.

The distance from the point of spillage to the house was several hundred yards. (Kletz, 1972b.)

B66 On 30 November, 1962 at Cornwall, Ontario, a chlorine rail car was in a siding when a failure of the anchor section occurred and 30 ton of chlorine escaped. The siding was on the downwind side of town. Police and firemen organized prompt evacuation of the several hundred people in the rural area downwind of the spillage. Some 89 people were gassed. (Simmons, Erdmann and Naft, 1974.)

B67 On 9 August, 1963 in Philadelphia, Pennsylvania, a chlorine rail tank car was rammed and a 1 in. loading line was broken. For a short period there was an escape of chlorine, amounting probably to no more than 1 ton. The release was in the middle of a built-up area, however. The number of people gassed was at least 430. (Simmons, Erdmann and Naft, 1974.)

A1.12 Some Other Incidents and Problems

Some other incidents and problems related to safety and loss prevention are listed in Table A1.4 under the following heads: (1) power loss, weather and earthquake; (2) safety and safety legislation; (3) transport and transport legislation; (4) pipelines and pipelines legislation; (5) toxic chemicals in the workplace; (6) pollution; (7) pollution legislation; (8) abandonment of actual or planned production and (9) litigation.

The references in Table A1.4, which are quoted by date only, are to accounts given by 'Chementator' in Chemical Engineering. The information given refers primarily to the United States.

The table shows very clearly the increasing public concern with health and safety and with pollution in the process industries that began to build up from the early 1970s.

A1.13 Notation

Q	flow rate of propane (ft^3/s)
u	average wind velocity (ft/s)
x, y, z	downwind, cross-wind and vertical distances (ft)
σ_y, σ_z	standard deviations in crosswind, vertical directions (ft)
χ	concentration of propane (volume fraction)
χ_{cl}	concentration of propane on centreline (volume fraction)

Appendix 2 Flixborough

Contents

A2.1 The Company and the Management A2/2
A2.2 The Site and the Works A2/3
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A2.4 Events Prior to the Explosion A2/3
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A2.7 The Explosion – 2 A2/10
A2.8 Some Lessons of Flixborough A2/13
A2.9 Critiques A2/17

At about 4.53 p.m. on Saturday 1st June 1974, the Flixborough Works of Nypro (UK) Ltd (Nypro) were virtually demolished by an explosion of war-like dimensions. Of those working on the site at the time, 28 were killed and 36 others suffered injuries. If the explosion had occurred on an ordinary working day, many more people would have been on the site, and the number of casualties would have been much greater. Outside the Works injuries and damage were widespread but no one was killed. Fifty-three people were recorded as casualties by the casualty bureau, which was set up by the police; hundreds more suffered relatively minor injuries, which were not recorded. Property damage extended over a wide area, and a preliminary survey showed that 1821 houses and 167 shops and factories had suffered to a greater or lesser degree. (R.J. Parker, 1975 – the *Flixborough Report*, para. 1)

The Flixborough explosion was by far the most serious accident which had occurred in the chemical industry in the United Kingdom for many years.

The explosion was in the reactor section, Section 25A, of the caprolactam plant.

Within a month of the disaster a Court of Inquiry under the chairmanship of Mr R.J. Parker was set up under Section 84 of the Factories Act 1961 to establish the causes and circumstances of the disaster and to point out any lessons which might be learned.

The Court's report *The Flixborough Disaster, Report of the Court of Inquiry* (R.J. Parker, 1975) (the *Flixborough Report*) is the most comprehensive inquiry conducted in the United Kingdom into a disaster in the chemical industry.

The Flixborough disaster was of crucial importance in the development of safety and loss prevention in the United Kingdom. It made both the industry and the public much more aware of the potential hazard of large chemical plants and led to an intensification both of the efforts within industry to ensure the safety of major hazard plants and of the demands for public controls on such plants.

The setting up of the Advisory Committee on Major Hazards (ACMH) at the end of 1974 was a direct result of the Flixborough disaster.

The impact of Flixborough was reinforced by that of the Seveso disaster 2 years later.

The description of the Flixborough disaster given below is necessarily a brief one, and is mainly based on the *Flixborough Report* and on the work of Sadée, Samuels and O'Brien (1976–77). Other accounts at the time include those of J.I. Cox (1976b) and Gugan (1976). Further critical accounts are described in Section A2.9.

Selected references on Flixborough are given in Table A2.1.

Table A2.1 *Selected references on Flixborough*

Report of the Court of Inquiry
R.J. Parker (1975)

Reports presented to the Court
Artingstall (1975); Ball (1975a); V.J. Clancey (1975a); Cottrell and Swann (1975a); J.I. Cox (1975b); A.G. Evans (1975); Gill (1975); Gugan (1975a); T.B. Jones (1975); V.C. Marshall (1975d); F. Morton (1975); Munday (1975a); Newland (1975); Nypro (UK) Ltd (1975); A.F. Roberts (1975b); Sadee (1975); Samuels and O'Brien (1975)

Further accounts
Anon. (1974b); Ball and Steward (1974); T.B. Jones and Spracklen (1974); V.C. Marshall (1974, 1976a,b, 1982 LPB 48, 1984, 1987, 1994 LPB 117); Steward (1974); Tinker (1974); Anon. (1975d); Ball (1975b, 1976); Cottrell and Swann (1975b, 1976); J.I. Cox (1975a, 1976a,b); Dimeo (1975); FPA (1975/27); Gugan (1975b, 1976, 1979); R. King (1975a–c, 1976a,b, 1977, 1990, 1991); Kinnersly (1975); Kletz (1975c,e, 1976e, 1984e,f); McLain (1975a); Munday (1975b, 1976a,b); Rakestraw and Hildrew (1975); W. Smith (1975); Tucker (1975); F. Warner (1975a,b); BRE (1976/7); HSE (1976 HSE 1, HSE 2); O'Reilly (1976); Sadee, Samuels and O'Brien (1976–77); R.L. Allen (1977a,b); C.L. Bell (1977, 1979); V.J. Clancey (1977a,c); Mecklenburg (1977a,b); H.D. Taylor (1977); Slater (1978a); Anon. (1979b); Harvey (1979b); W.G. Johnson (1980); D.J. Lewis (1980d, 1989a); D.C. Wilson (1980); Anon. (1981a); Offord (1983); Cullen (1984); Davidson (1984); Crooks (1990 LPB 96); Turney (1994 LPB 117)

A2.1 The Company and the Management

A2.1.1 The company

The *Flixborough Report* (paras 12–14) states

> The site was originally occupied in 1938 by a company called Nitrogen Fertilisers Limited, a subsidiary of Fisons Limited and used for the manufacture of ammonium sulphate. In 1964 Nypro was formed, owned jointly by Dutch State Mines (DSM) and Fisons Limited. It acquired the site from Nitrogen Fertilisers Limited. Between 1964 and 1967 plant was built for the production of caprolactam, which is a basic raw material for the production of Nylon 6, by a process, the first step of which was the production of cyclohexanone via the hydrogenation of phenol. The works were commissioned and production commenced in 1967. They were then and remained until the disaster the only works in the UK producing caprolactam.
>
> In 1967 Nypro was reconstituted with DSM owning 45%, the National Coal Board 45% and Fisons Limited 10%. Almost at once design began for additional plant to increase the capacity of the works from 20 000 tons of caprolactam per annum to 70 000 tons per annum. This additional plant, referred to as Phase 2, was completed at a cost of some £15 m. in 1972. Its distinguishing feature for present purposes is that in it the cyclohexanone necessary for the production of caprolactam was produced by the oxidation of cyclohexane instead of via the hydrogenation of phenol. In 1972 DSM acquired the holding of Fisons Limited and from then until after the disaster Nypro was owned as to 55% by DSM and as to the remaining 45% by the NCB.
>
> From the safety point of view, the oxidation process introduced new dimensions. Cyclohexane, which is in many of its properties comparable with petrol, had to be stored. More importantly, large quantities of cyclohexane had to be circulated through the reactors under a working pressure of about 8.8 kg/cm^2 and a temperature of 155°C. Any escape from the plant was therefore potentially dangerous.

Nypro (UK) Limited was therefore a relatively small, single-site company operating a major hazard process.

A2.1.2 The management

The management of the company is described in the *Flixborough Report* (paras 19–27). The description includes the following information of particular relevance to the caprolactam plant:

Managing Director Mr R.E. Selman, qualified chemical engineer (HTS, Delft)
General Works Manager Mr J.H. Beckers, qualified chemical engineer (MTS, Heerlen)
Plant Manager Area 1 and Utilities Mr C.L. Bell, chartered chemical engineer
Plant Manager Area 2 Mr P.M. Cliff (to 1 May, 1974), chartered engineer (fuel); Mr R. Everton (from 1 May, 1974), HND in chemistry
Works Engineer Vacant (formerly Mr Riggall)
Areas 1 and 2 Engineer Mr A.B. Blackman
Services Engineer Mr B.T. Boynton, ONC in electrical engineering, NCB (Class 1) engineering certificate
Safety and Training Manager Mr E. Brenner, Manager

Area 2 covered Section 25A of the cyclohexane plant.

The previous Works Engineer, Mr Riggall, had left and steps were being taken to replace him, but at the time of the accident there was no Works Engineer. In the absence of a Works Engineer a co-ordinating function was exercised by the Services Engineer. In addition, the engineering staff were told that if they had problems, they could call on the assistance of Mr J.F. Hughes of the NCB.

The *Flixborough Report* (para. 27) states that following the departure of Mr Riggall 'There was no mechanical engineer on site of sufficient qualification, status or authority to deal with complex or novel engineering problems and insist on necessary measures being taken'.

The report is critical of the fact that the Area 2 and Services Engineers had been asked to assume responsibilities which they should not have had to shoulder.

A2.2 The Site and the Works

The Flixborough works is on flat, low-lying land on the east bank of the River Trent some 6 miles to the south of the point where that river joins the Humber. The nearest villages are Flixborough itself and Amcotts, both of which are about half a mile away. The town of Scunthorpe lies at a distance of approximately 3 miles.

The works is surrounded by fields and the population density in the neighbourhood beyond is very low.

A site plan is shown in Figure A2.1. The diagram also shows the vapour cloud, as described below. An aerial view of the works before the explosion is given in Figure A2.2.

Other plants on the site included an acid plant and a hydrogen plant. There was also a large ammonia storage sphere.

A2.3 The Process and the Plant

The cyclohexane plant, shown in Figure A2.3, consisted of a train of six reactors in series in which cyclohexane was oxidized to cyclohexanone and cyclohexanol by air injection in the presence of a catalyst. The feed to the reactors was a mixture of fresh cyclohexane and recycled material. The product from the reactors still contained approximately 94% of cyclohexane. The liquid reactants flowed from one reactor to the next by gravity. In subsequent stages, the reaction product was distilled to separate the unreacted cyclohexane, which was recycled to the reactors, and the cyclohexanone and cyclohexanol, which were converted to caprolactam. The design operating conditions in the reactor were a pressure of 8.8 kg/cm^2 and a temperature of 155°C. The reaction is exothermic.

The heat required for initial warmup and for supplementation of the heat of reaction during normal operation was provided by a steam-heated heat exchanger on the reactor feed. The steam flow to the exchanger was controlled by an automatic control valve. There was a bypass around this valve, which was needed to pass the larger quantities of steam required during start-up.

Removal of the heat of reaction from the reactors during normal operation was effected by vaporizing part of the cyclohexane liquid. The cyclohexane vaporized passed out in the off-gas from the reactors. The rest of this off-gas was mainly nitrogen with some unreacted oxygen.

The off-gas passed through the feed heat exchanger (C2544) and then through a cooling scrubber (C2521) and an absorber (C2522), in which the cyclohexane was condensed out, and thence via an automatic control valve to a flare stack.

The atmosphere in the reactor was controlled using nitrogen from high-pressure nitrogen storage tanks. The nitrogen was brought into the works by tankers.

The reactor pressure was controlled by manipulating the control valve on the off-gas line. Safety valves venting into the relief header to the flare stack were set to open at 11 kg_f/cm^2.

A trip system was provided which shut off air to, and injected nitrogen into, the reactors in the event of either a high oxygen content in the off-gas or a low liquid level in the nitrogen supply tank. This trip could be disarmed, however, by setting to zero the timer fixing the duration of the purge.

The layout of the reactors in Section 25A is shown in Figure A2.4.

A2.4 Events Prior to the Explosion

On the evening of 27 March 1974, it was discovered that Reactor No. 5 was leaking cyclohexane. The reactor was constructed of $\frac{1}{2}$ in. mild steel plate with $\frac{1}{8}$ in. stainless steel bonded to it on the inside. A vertical crack was found in the mild steel outer layer of the reactor. The leakage of cyclohexane from the crack indicated that the inner stainless steel layer was also defective. It was decided to shut the plant down for a full investigation. The following morning inspection revealed that the crack had extended some 6 ft. This was a serious state of affairs and a meeting was called to decide action. The decision was taken to remove Reactor No. 5 and to install a bypass assembly to connect Reactors No. 4 and 6 so that the plant could continue in production.

The openings to be connected on these reactors were 28 in. diameter, with bellows on the nozzle stubs, but the largest pipe which was available on site and which might be suitable for the bypass was 20 in. diameter. The two flanges were at different heights so that the connection had to take the form of a dog-leg of three lengths of 20 in. pipe welded together with flanges at each end bolted to the existing flanges on the stub pipes on the reactors. The bypass assembly is shown in Figure A2.5.

Calculations were done to check (1) that the pipe was large enough for the required flow and (2) that it was

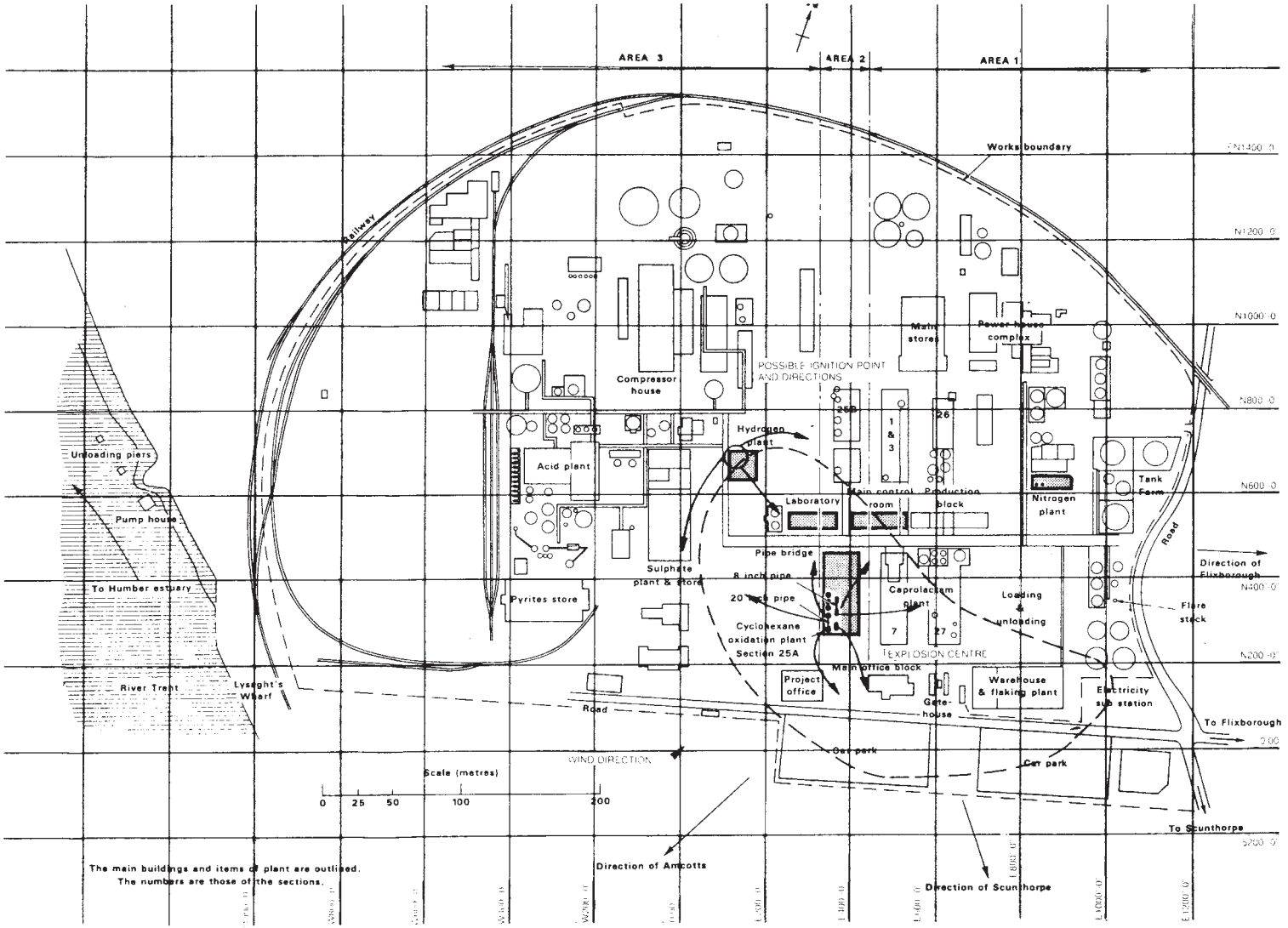

Figure A2.1 *Simplified site plan of the works of Nypro (UK) Ltd at Flixborough (Sadée, Samuels and O'Brien, 1976–77) (Courtesy of HM Stationery Office). The diagram also shows the estimated dimensions of the vapour cloud*

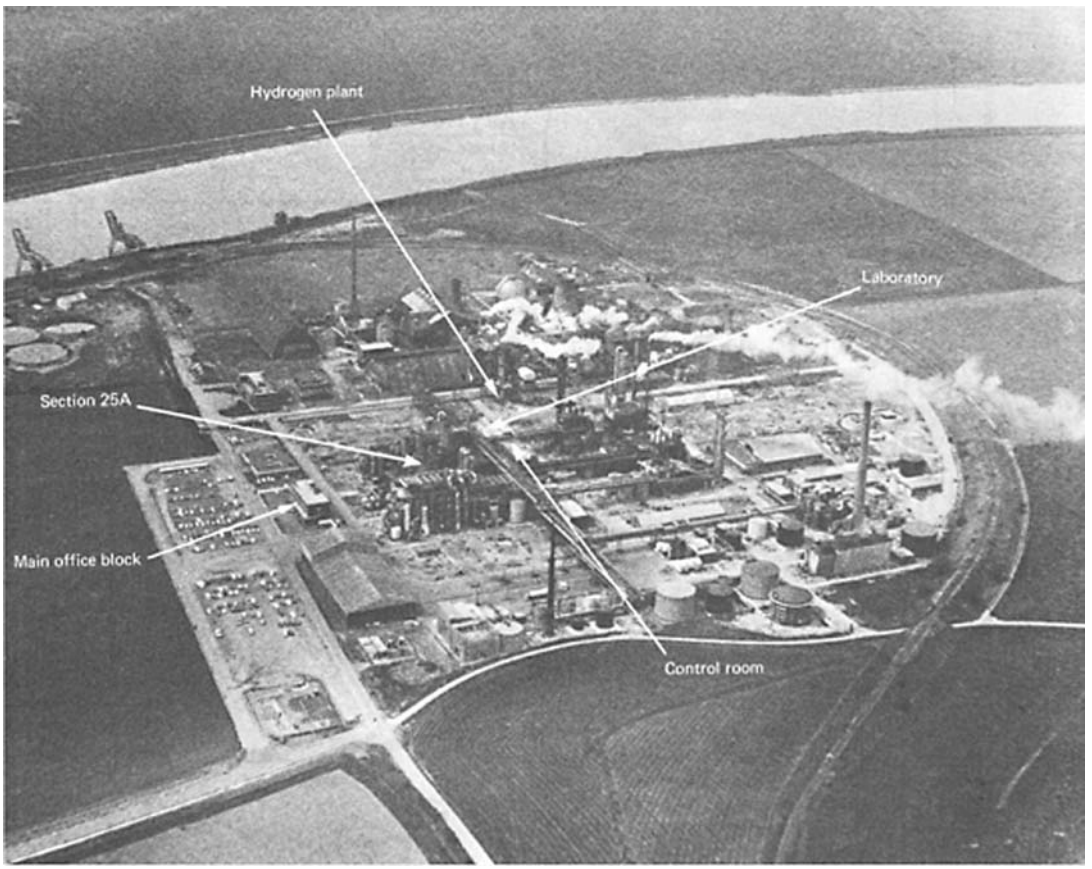

Figure A2.2 *Works of Nypro (UK) Ltd at Flixborough before the explosion (Nypro (UK) Ltd)*

capable of withstanding the pressure as a straight pipe. No calculations were made which took into account the forces arising from the dog-leg shape of the pipe.

No drawing of the bypass pipe was made other than in chalk on the workshop floor.

The existing stub pipes were connected to the reactors by bellows, as shown in Figure A2.5. No calculations were done to check whether the bellows would withstand the forces caused by the dog-leg pipe.

The bypass assembly was supported by a scaffolding structure, as shown in Figure A2.5. This scaffolding was intended to support the pipe and to avoid straining of the bellows during construction of the bypass. It was not suitable as a permanent support for the bypass assembly during normal operation.

No pressure testing was carried out either on the pipe or on the complete assembly before it was fitted. A pressure test was performed on the plant, however, after installation of the bypass. The equipment was tested to a pressure of 9 kg_f/cm^2, but not up to the safety valve pressure of 11 kg_f/cm^2. The test was pneumatic not hydraulic.

Following these modifications the plant was started up again. The bypass assembly gave no trouble. There did appear, however, to be an unusually large usage of nitrogen on the plant and this was being investigated at the time of the accident.

On 29 May, the bottom isolating valve on a sight glass on one of the vessels was found to be leaking. It was decided to shut the plant down to repair the leak.

On the morning of 1 June start-up began. The precise sequence of events is complex and uncertain. The crucial feature, however, is that the reactors were subjected to a pressure somewhat greater than the normal operating pressure of 8.8 kg_f/cm^2.

A sudden rise in pressure up to 8.5 kg_f/cm^2 occurred early in the morning when the temperature in Reactor No. 1 was still only 110°C and that in the other reactors was less, while later in the morning, when the temperature in the reactors was closer to the normal operating value, the pressure reached 9.1–9.2 kg_f/cm^2.

The control of pressure in the reactors could normally be effected by venting the off-gas, but this procedure involved the loss of considerable quantities of nitrogen. Shortly after warmup began, it was found that there was insufficient nitrogen to begin oxidation and that further supplies would not arrive until after midnight. Under these circumstances the need to conserve nitrogen would tend to inhibit reduction of pressure by venting.

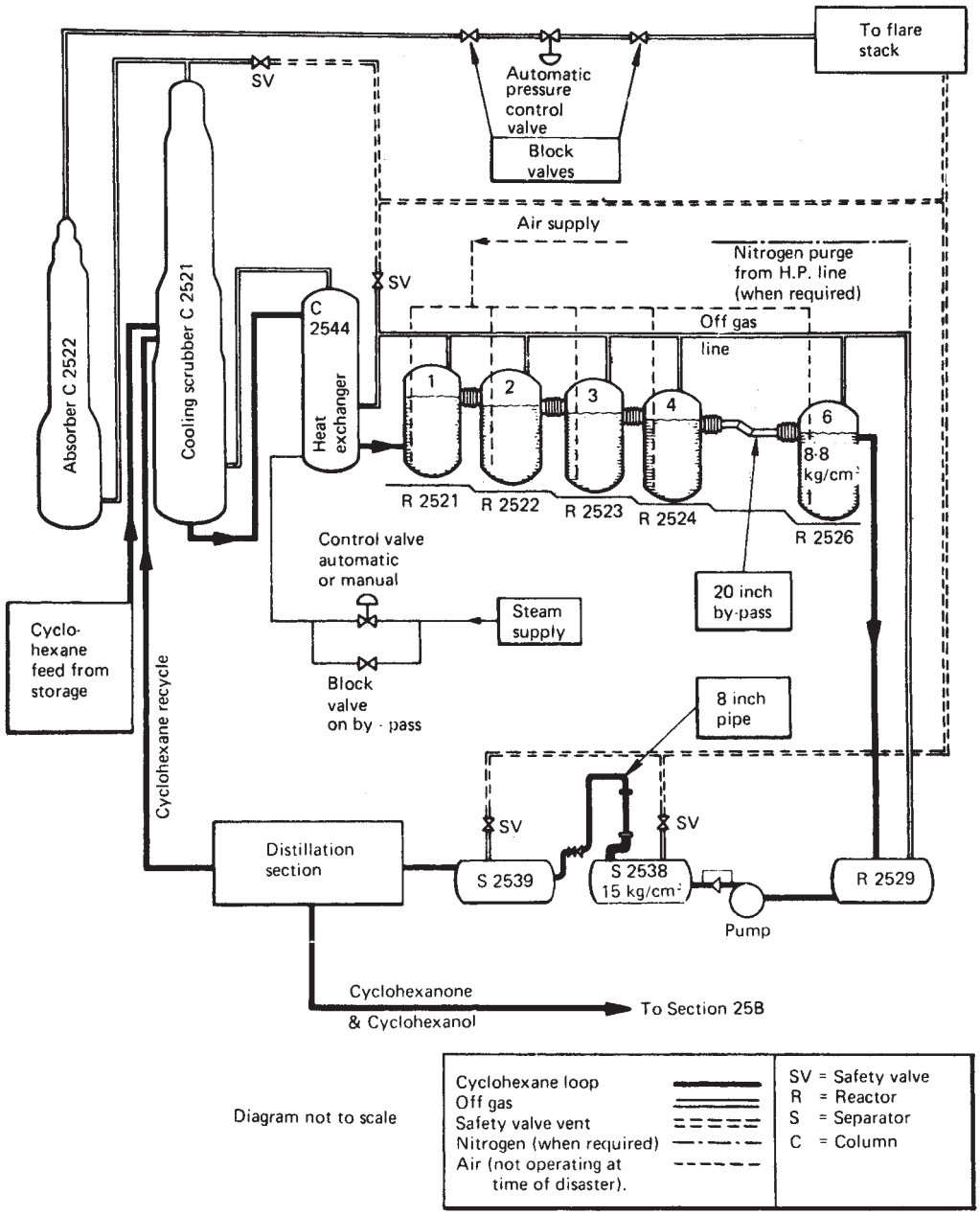

Figure A2.3 *Simplified flow diagram (not to scale) of the cyclohexane oxidation plant at Flixborough (R.J. Parker, 1975) (Courtesy of HM Stationery Office)*

A2.5 The Explosion – 1

During the late afternoon an event occurred which resulted in the escape of a large quantity of cyclohexane. As already explained, this event was the rupture of the 20 in. bypass system, without or with contribution from fire on a nearby 8 in. pipe. The cyclohexane formed a vapour cloud and the flammable mixture found a source of ignition.

At about 4.53 p.m. there was a massive vapour cloud explosion.

The explosion caused extensive damage and started numerous fires. Aerial views of the plant after the explosion are shown in Figures A2.6 and A2.7.

Reactors No. 4 and 6 and the debris of the bypass assembly are shown in Figure A2.8. The blast and the

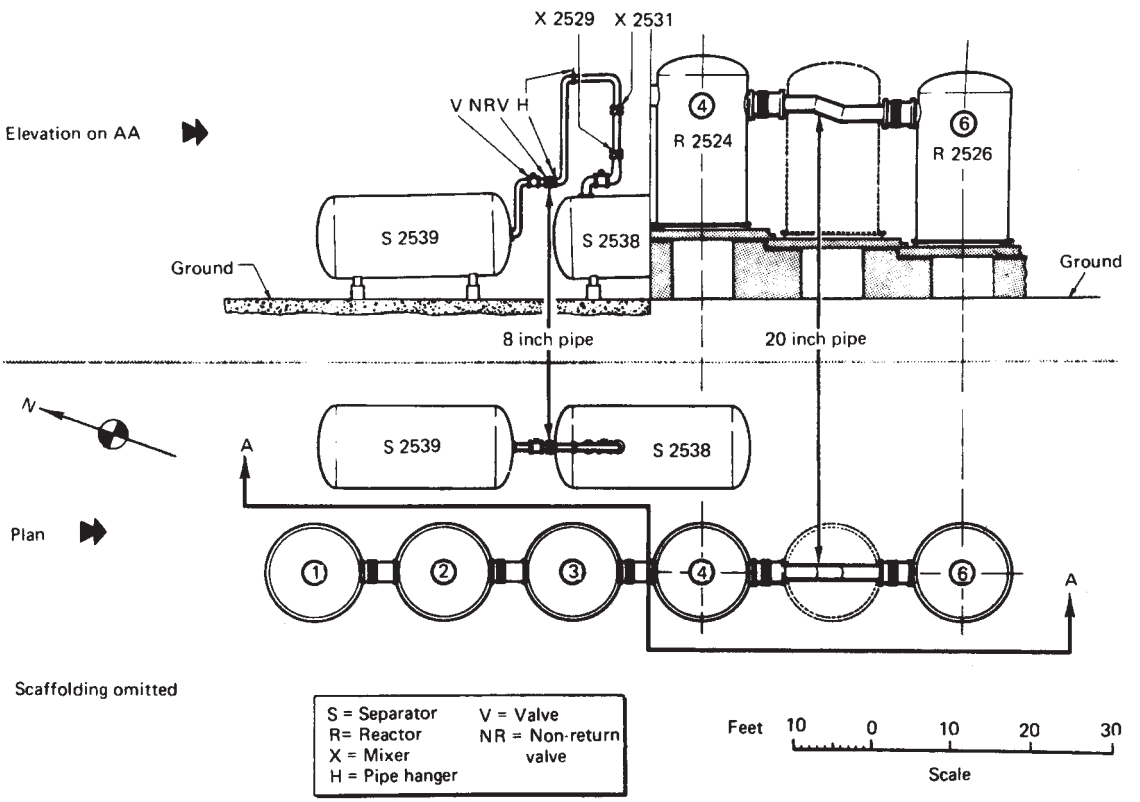

Figure A2.4 *Simplified plan and elevation of part of Section 25A of the cyclohexane oxidation plant at Flixborough (R.J. Parker, 1975) (Courtesy of HM Stationery Office)*

fires destroyed not only the cyclohexane plant but several other plants also. Many of the fires were in the tank farm.

The blast of the explosion shattered the windows of the control room and caused the control room roof to collapse. Of the 28 people who died in the explosion, 18 were in the control room. Some of the bodies had suffered severe injuries from flying glass. Others were crushed by the roof. No one escaped from the control room.

The main office block was also demolished by the blast of the explosion. Since the accident occurred on a Saturday afternoon, the offices were not occupied. If they had been, the death toll would have been much higher.

The locations of the control room and main office block are shown in Figures A2.1 and A2.2 and the states of these buildings after the explosion in Figures A2.6 and A2.7.

The fires on the site burned for many days. Even after 10 days the fires were hindering rescue work on the site. The large ammonia sphere was lifted up a few inches. It leaked slightly at a flange, but the leak was not serious.

A2.6 The Investigation

An immediate investigation of the disaster was made by the Factory Inspectorate, which issued an interim report. On its appointment, the Court of Inquiry took control of the main investigations. The work of recovering, identifying and examining wreckage and of conducting relevant tests, was undertaken by the Safety in Mines Research Establishment (SMRE). The Court appointed the consulting engineers Cremer and Warner as its technical advisers. Other government bodies, consultants and universities were involved in the numerous studies undertaken.

Some of the possible causes of failure of the bypass assembly were outlined early in the inquiry by the DSM counsel. They included (1) failure of the 20 in. pipe due to a small pressure rise; (2) prior failure of the 8 in. pipe; (3) prior failure of some other part of the system and (4) an explosion in the air-line to the reactors. He suggested several possible causes for a pressure rise in the 20 in. pipe: (1) entry of high-pressure nitrogen into the system due to instrument malfunction; (2) entry of water into the system; (3) temperature rise in the system due to excessive heating by steam in reboiler of C2544; (4) leakage of steam from a tube in C2544; (5) explosion of peroxides formed in the process and (6) explosion due to air in the system.

The inquiry established (*Flixborough Report*, para. 6) that the cause of the disaster was 'The ignition and rapid acceleration of deflagration, possibly to the point of detonation, of a massive vapour cloud formed by the escape of cyclohexane under a pressure of at least 8.8 kg/cm^2 and

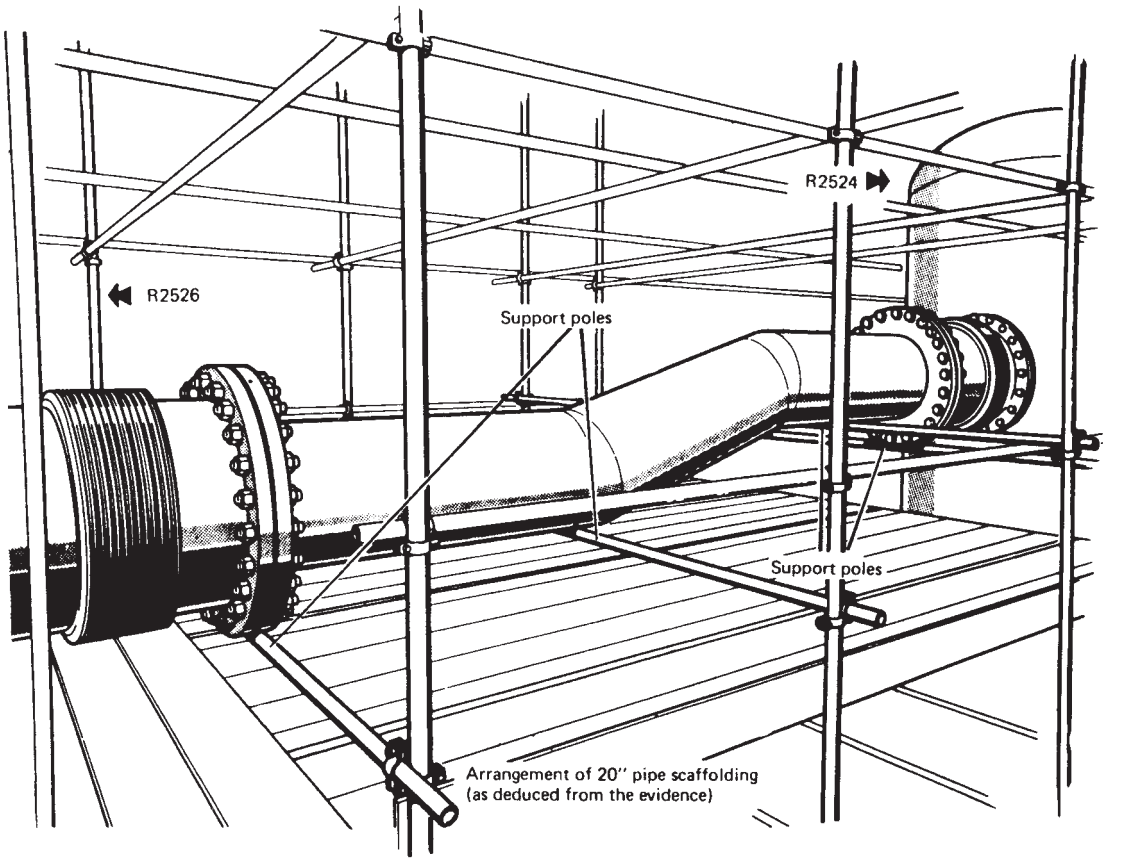

Figure A2.5 *Arrangement of the 20 in bypass pipe and scaffolding at Flixborough (R.J. Parker, 1975) (Courtesy of HM Stationery Office)*

a temperature of 155°C and that the escape was from Section 25A of the cyclohexane plant'.

There was no dispute that the main part of the cyclohexane came from the 20 in. bypass assembly, but there was come uncertainly whether the mechanical failure of the assembly was the primary failure or whether it was a secondary failure caused by another event elsewhere. Three hypotheses were advanced: (1) the 20 in. pipe hypothesis, (2) the 8 in. pipe hypothesis and (3) the superheated water hypothesis.

A large proportion of the report is concerned with a discussion of the first and second hypotheses, but the Court decided emphatically in favour of the first.

The 20 in. pipe hypothesis is that the 20 in. bypass pipe ruptured in one stage as a result of the internal pressure and temperature conditions which probably occurred in the final shift.

The site investigation revealed that the 20 in. pipe had yielded at the lower mitre, or 'jack-knifed', and that the bellows had undergone gross permanent deformation, or 'squirm'.

The arrangement of the pipe was such as to subject the bellows to shear forces due to the internal pressure in the pipe as shown in Figure A2.9. The two thrusts PA are parallel and separated by a distance $2e$ and thus give a turning moment $2PAe$ which is balanced by shear forces $F = PAE/L$. The shear forces give rise to bending moments and the maximum bending moment is at the mitre joints and is $PAEl/L$. This system of forces can lead to failure in two ways. The shear force may cause squirm of the bellows. The bending moments may cause failure of the pipe by buckling one of the mitres. As already mentioned, these effects had been neglected in the calculations done on the bypass assembly.

These mechanisms were studied in comprehensive, full-scale investigations by SMRE, by Nottingham University and the Mining Research and Development Establishment, Bretby. The results of the tests are complex, but, in brief, they showed that squirm of the bellows could occur at pressures at or near the operating pressure. They did not show jackknifing and rupture following squirm. A mechanism for the latter was given by Newland (1975), who developed a theory based on the energies involved, which showed that at pressures above normal operating pressures but below the safety valve pressure there could occur squirm of both the bellows, followed by jackknifing of the

Figure A2.6 *Works of Nypro (UK) Ltd at Flixborough after the explosion – 1 (R.J. Parker, 1975) (Courtesy of HM Stationery Office)*

pipe, resulting in complete rupture. The pressures for jackknifing and rupture to be a consequence of squirming were estimated to be as follows:

	Low (kg_f/cm^2)	*Probability* 50% (kg_f/cm^2)	*High* (kg_f/cm^2)
150°C	9.3	9.9	10.6
160°C	9.1	9.7	10.4

Other mechanisms of squirm alone and jackknifing alone were investigated, but appeared less probable.

The Court concluded that the rupture of the 20 in. pipe assembly was a probability, albeit a low one, under the pressure and temperature conditions which occurred in the last shift.

The 8 in. pipe hypothesis is somewhat more complex. The 8 in. pipe ran between separators S 2538 and S 2539. The location and details of the pipe are shown in Figures A2.4 and A2.10, respectively. There was a block valve, a non-return valve and a lagging box on the pipe. The pipe was made of stainless steel.

Essentially the hypothesis was that a directed flame had occurred from the lagging box and had caused rupture of the pipe from which cyclohexane then escaped to form a vapour cloud. This hypothesis was advanced by Cox and Gugan.

The hypothesis had its origin in eyewitness accounts of the events immediately prior to the explosion and in the condition of the equipment found in the site investigation. The latter revealed that there was a 50 in. split on the elbow of the 8 in. pipe and subsequent studies showed that the crack was caused by creep cavitation. The 50 in. split also exhibited a petal crack which was due to zinc embrittlement and a separate 3 in. crack due to the same cause was found on the straight vertical section of the pipe. In addition, two loose bolts were found on the non-return valve. There was some doubt as to whether these had been loose before the explosion, but the Court concluded that this was probably the case.

The 8 in. pipe hypothesis may be summarized as follows. There were two loose bolts on the non-return valve. Then either there was a slow leakage of material over an extended period and a lagging fire which caused further expansion of the bolts and growth of the leak, or there was a sudden gasket burst and ignition of the leak by static electricity. In either case there was a directed flame from the lagging box. A sprinkler sensor head near the non-return valve failed to detect the fire. The flame burned off the lagging on the pipe elbow and caused a vapour blanket in the pipe and a vapour lock at the intrados so that the pipe overheated. The pipe suffered creep cavitation at the intrados and the 50 in. rupture occurred. Zinc from galvanized wire dripped onto the pipe and caused zinc embrittlement, but this was not responsible for the main failure. The

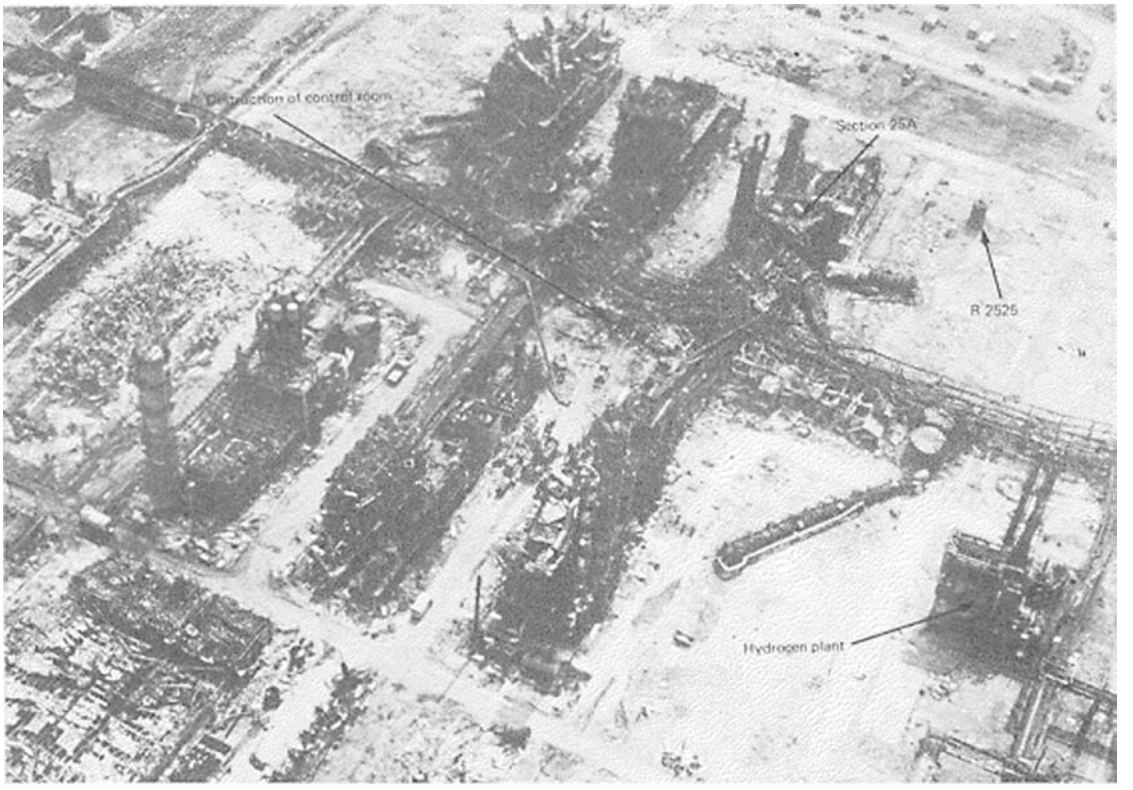

Figure A2.7 *Works of Nypro (UK) Ltd at Flixborough after the explosion—2 (R.J. Parker, 1975) (Courtesy of HM Stationery Office)*

cyclohexane issued from the 50 in. crack and put out the flame. A fire then occurred in the region of the fin fan coolers which melted the zinc on the finned tubes and raised them to a temperature at which zinc embrittlement occurs. There followed an explosion in the region of one of the fan motors which caused the 20 in. bypass to jackknife and rupture.

The foregoing account is a necessarily highly simplified summary of a very complex argument. The Court's report gives a detailed account of this hypothesis but rejects it. It draws an analogy between the sequence of events required by the hypothesis with the balancing of billiard balls one on top of another and states 'This balancing of ten balls is analogous to what is postulated for the 8-inch pipe hypothesis'.

The third hypothesis is that the failure of the 20 in. bypass assembly was due to sudden evolution of vapour from a layer of superheated water at the bottom of Reactor No. 4. The water might have been present in the reactor initially or might have come from a leak in the steam-heated heat exchanger on the feed. Such a water layer was able to build up in the vessel more easily because the reactor agitator was not in use. This theory, advanced by R. King, was mentioned, but did not figure prominently at the inquiry. It has been described in a number of articles by King (1975a–c, 1976a,b, 1977).

A2.7 The Explosion – 2

Another aspect of the Flixborough investigation is the studies conducted on the explosion itself. Accounts of the explosion have been given in the *Flixborough Report*, by Gugan (1976) and by Sadée, Samuels and O'Brien (1976–77).

According to Sadée, Samuels and O'Brien the quantity of cyclohexane available in the five reactors and one after-reactor was 120 te. The normal operating pressure and temperature were $8.8\,kg_f/cm^2$ and 155°C, respectively. After the explosion it was found that the vessels still contained 80 te, so that the maximum quantity involved in the explosion was 40 te. These authors estimate that about 30 te escaped before the explosion and they take this quantity as the basis of their calculations.

The flow from each of the two pipe stubs, which were opposite each other, but at slightly different heights, would form a turbulent momentum jet with the two opposing jets impinging on each other, thus giving very effective mixing.

It is estimated by Sadée, Samuels and O'Brien that 50%, or 15 te, of the cyclohexane would flash off as vapour and that the other 50% would form a mist. Whether or not the mist would then evaporate depends on the amount of air entrained by the jet. The authors state that evaporation is possible provided that the concentration of cyclohexane does not exceed 10%.

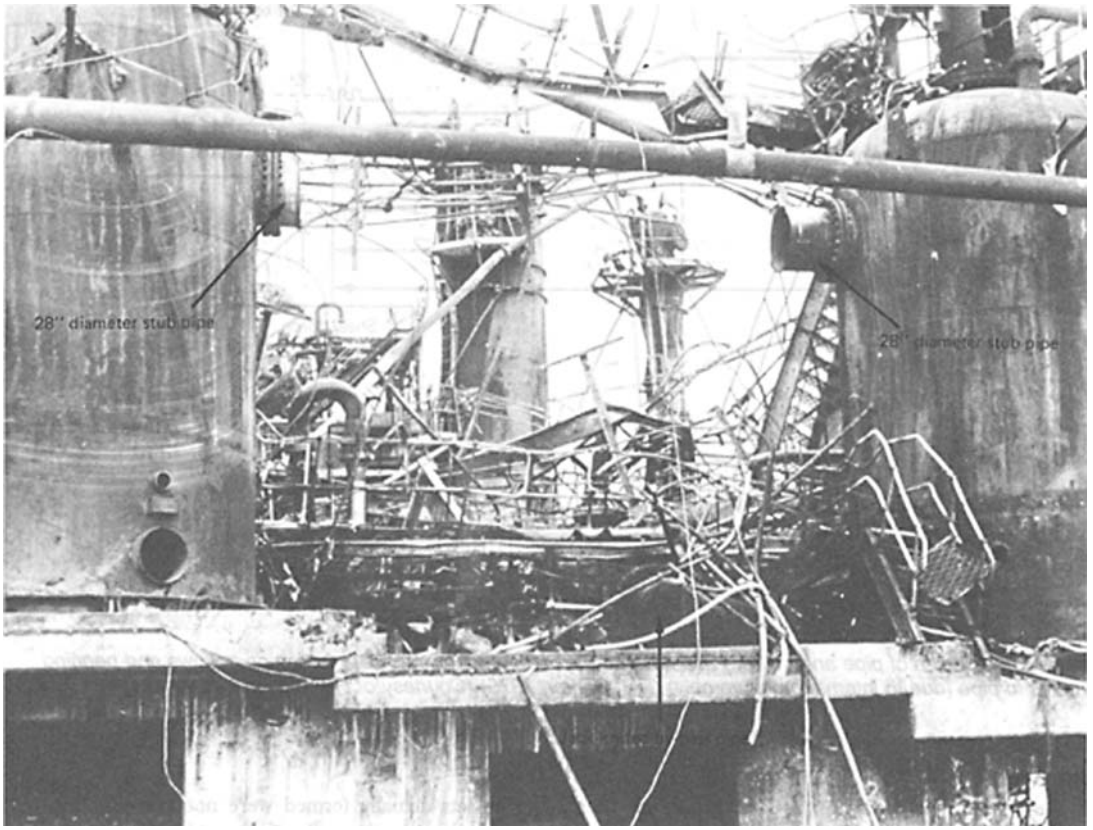

Figure A2.8 *Reactors No. 4 and 6 and the bypass assembly at Flixborough after the explosion (R.J. Parker, 1975) (Courtesy of HM Stationery Office)*

Sadée, Samuels and O'Brien have calculated the dimensions of a stationary, free jet of cyclohexane at 1 MPa and 150°C emitted from a 700 mm diameter opening and forming a cloud containing equal masses of vapour and liquid in air. This jet is shown in Figure A2.11. The jet is 215 m long and has a maximum diameter of 25 m. The jet volume with a concentration exceeding the low flammability limit (1.2%) is 64,400 m^3 and that with a concentration within the flammable range (1.2–8%) is practically the same. The average concentration in the flammable part of the jet is 1.85%, which is close to the stoichiometric proportion. The quantity of cyclohexane within the flammable part of the jet is 4 te. If two such jets are assumed, the quantity is 8 te.

The jets actually formed were not free jets, but were affected by the ground and the reactors. Taking these factors into account, the authors estimate the quantity of cyclohexane within the flammable part of the two jets as 22.4 te.

Sadée, Samuels and O'Brien present calculations on the assumption that the quantity of cyclohexane involved in the explosion was 30 te. This amount of cyclohexane mixed with air to yield a flammable concentration of 2% gives a cloud volume of 400,000 m^3.

The precise shape of the cloud is uncertain, as is the source of ignition. From the carbon deposition and explosion damage the estimate of the cloud ground zero and shape is that shown in Figure A2.1. The source of ignition may have been the hydrogen plant. An alternative estimate of the cloud shape has been given by J.I. Cox (1976b).

Various estimates have been made of the time which elapsed between the times of rupture and of the explosion, mostly ranging between 30 and 90 s. An estimate of 45 s has been widely quoted.

There is evidence from carbon deposition and from eyewitness accounts that there was a flash fire as well as an explosion in the vapour cloud.

From eyewitness accounts it appears that there may have been a short period during which the cloud had found a source of ignition and combustion was occurring at the edge of the cloud, but the cloud was expanding faster than the flame speed. Assuming a constant flow of vapour into the cloud, the velocity of outward expansion would fall as the cloud diameter increased and a point would be reached at which the velocity would fall below the flame speed. The flame would then travel rapidly towards the centre of the cloud.

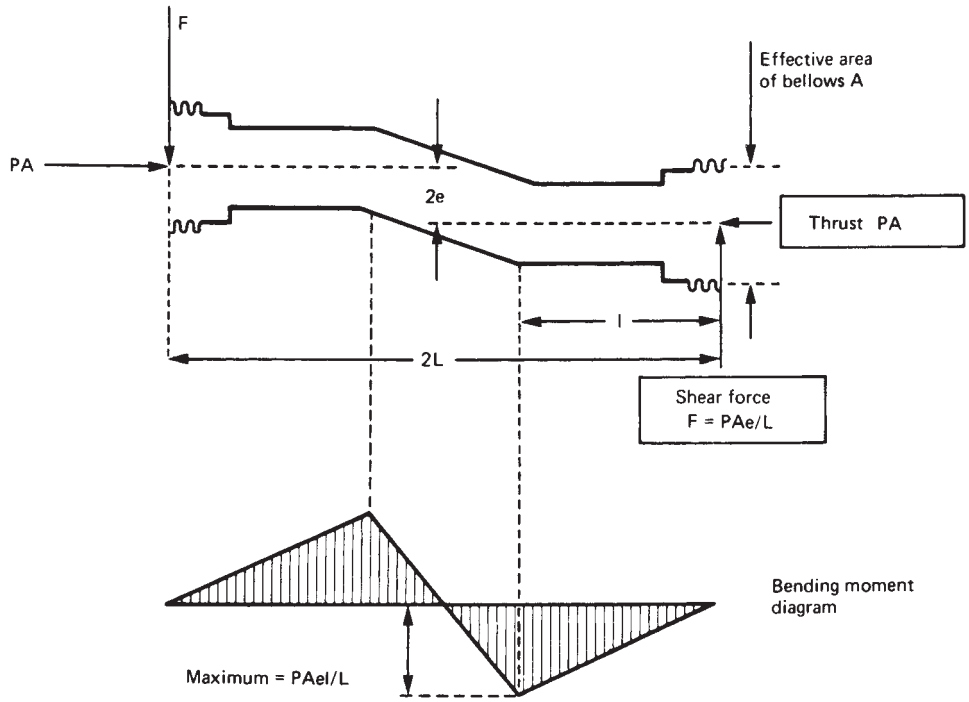

Figure A2.9 *Sketch of pipe and bellows assembly at Flixborough showing shear forces on bellows and bending moments in pipe (due to internal pressure only) (R.J. Parker, 1975) (Courtesy of HM Stationery Office)*

One effect of such a flash fire would be to cause a sudden and lethal depletion of the oxygen concentration.

There was evidence of two explosive events. An ionosphere recorder trace obtained at Leicester University (T.B. Jones and Spracklen, 1974; T.B. Jones, 1975) showed two disturbances, a smaller precursor followed by the main event. The time interval between them was some 45 s.

Estimates of the energy of explosion were made in several ways, including estimation from ionospheric readings (T.B. Jones, 1975), from the barograph of a glider in the vicinity (Gugan, 1975a) and from a blast damage survey (A.F. Roberts, 1975; Samuels and O'Brien, 1975).

The most detailed estimates of explosion energy are those derived from the blast damage survey. The results of this survey have been discussed by Gugan (1976), Munday (1975b) and Sadée, Samuels and O'Brien (1976–77). The latter gave a detailed listing and photographs of structural damage.

The blast damage effects caused by the explosion have been assessed by Sadée, Samuels and O'Brien and are shown in Figure A2.12, in which the individual data bars give the ranges of peak overpressure determined from structural damage vs distance from the assumed epicentre of the explosion.

The estimates of the energy of the explosion made by different workers depend on the explosion model used.

Most estimates are based on the simplest model, in which the only parameter is the mass of TNT. These estimates are generally in the range 15–45 te of TNT.

An alternative two-parameter model describes the explosion in terms both of the mass of TNT and the height of the explosion. Using this model, Sadée, Samuels and O'Brien estimate that the explosion was equivalent to 16 ± 2 te of TNT at a height of 45 ± 24 m above ground. 16 te of TNT have a calorific equivalent of about 1.6 te of cyclohexane; the calorific value of TNT is 1600 kcal/kg and that of cyclohexane is 11,127 kcal/kg.

The curve given by Sadée, Samuels and O'Brien in Figure A2.12 is based on this two-parameter TNT model.

If the cloud contained 30 te of cyclohexane and gave an explosion equivalent to the combustion of about 1.6 te, the explosion efficiency was about 5%. This efficiency is based on the total quantity of cyclohexane in the cloud.

The maximum overpressure at the centre of the cloud is uncertain. The maximum overpressure obtained from the structural damage, as described by Sadée, Samuels and O'Brien, was 0.7 bar. These authors state, however, that the theoretical curve in Figure A2.12 indicates an overpressure of 1 bar at the cloud boundary.

Some estimates of the pressure developed within the cloud are considerably higher. These estimates are typically based on calculation of the forces required to give damage effects such as the bending of steel lamp posts or crushing of steel vessels. Thus, for example, V.J. Clancey (1977a) states that where local effects occurred as a result of features such as confinement, pressures of up to perhaps 5–7 bar have been estimated. The pressures calculated in this way would normally be reflected pressures.

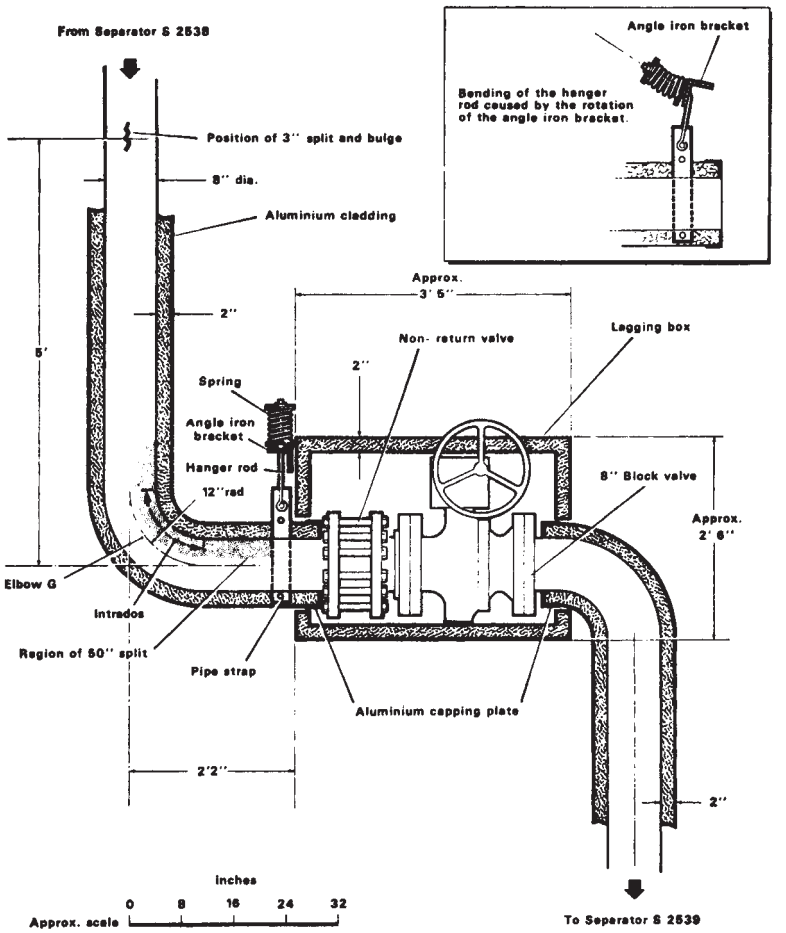

Figure A2.10 *Elevation view of 8 in. line at Flixborough, showing typical lagging box around valve (R.J. Parker, 1975) (Courtesy of HM Stationery Office)*

A2.8 Some Lessons of Flixborough

There are numerous lessons to be learned from the Flixborough disaster. A list of some of these is given in Table A2.2. Many of these lessons were highlighted in the Court's report.

The lessons include both public controls on major hazard installations and the management of such installations by industry. In the latter area there are lessons on both management systems and technological matters and on both design and operational aspects.

The fact that alternative hypotheses were advanced concerning the cause of the explosion does not detract from these lessons, but rather means that a greater number of lessons can be drawn.

Some of these lessons are now considered.

Public controls on major hazard installations

The effect of the Flixborough disaster was to raise the general level of awareness of the hazard from chemical plants and to make the existing arrangements for the control of major hazard installations appear inadequate.

The government therefore set up the ACMH to advise on means of control for such installations. The committee issued three reports (Harvey, 1976, 1979b, 1984). Its recommendations are described in Chapter 4.

This work was a major input to the development of the EC Major Accident Hazards Directive, which was implemented in the United Kingdom as the CIMAH Regulations 1984. These require the operator of a major hazard installation to produce a safety case.

Major hazard installations receive a greater degree of supervision by the local Factory Inspectorate. The CIMAH safety case plays an important part in this.

Siting of major hazard installations

As the *Flixborough Report* (para. 11) points out, the casualties from the explosion might have been much greater if the site had not been in open country.

The siting of major hazard installations is a matter of utmost importance. On the one hand distance is the only sure guarantee of safety, but on the other provision of increased spacing may be very wasteful of land.

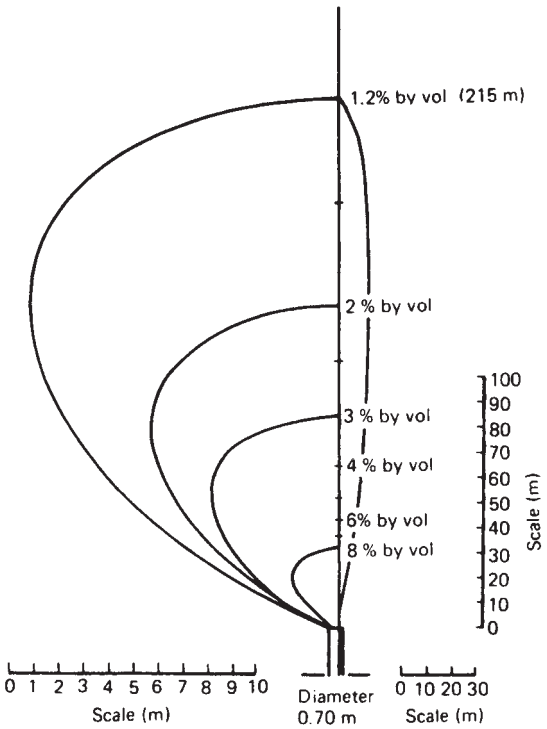

Figure A2.11 *Dimensions of and concentration distribution in a stationary, free jet of cyclohexane in air from an opening 700 mm diameter (Sadée, Samuels and O'Brien, 1976–77) (Courtesy of HM Stationery Office)*

The question of the siting of major *hazard* installations, or more generally land use planning in relation to such installations, became a principal concern of the ACMH, and is treated in its three reports. Controls on major hazards through land use planning are discussed in Chapter 4 and Appendix 25. Siting is also considered in Chapter 10.

Licensing of storage of hazardous materials

The *Flixborough Report* (para. 194) states

> As at 1st June 1974 Nypro were storing on site 330,000 gallons of cyclohexane, 66,000 gallons of naphtha, 11,000 gallons of toluene, 26,400 gallons of benzene and 450,000 gallons of gasoline. The storage of these potentially dangerous substances is nominally controlled by the local authority issuing licences under the Petroleum (Consolidation) Act 1928. In fact the only licences that had been issued related to 7000 gallons of naphtha and for a total of 1500 gallons of gasoline. The unlicensed storage of large quantities of fluids had no effect upon this disaster but it is clearly useless to have a licensing system which is so ineffective that it can lead to such results.

The situation at Flixborough revealed the need for better methods of notification of major hazard installations to the local planning authorities and for greater guidance to these authorities by the HSE.

The notification of major hazard installations is a requirement of the NIHHS Regulations 1982 and of the CIMAH Regulations 1984. These notification requirements and the advice now given by the HSE to local planning authorities are discussed in Chapter 4.

Regulations for pressure vessels and systems

The escape of cyclohexane at Flixborough was caused by a failure of the integrity of a pressure system.

Current legislation on pressure systems in the United Kingdom consisted of regulations for steam boilers and receivers and air receivers. It failed to cover the Flixborough situation in two crucial respects. It applied only to steam and air and not to hazardous materials such as cyclohexane. And it dealt only with pressure vessels and not with pressure systems. This latter point is relevant, because at Flixborough the failure occurred in a pipe not a vessel.

The *Flixborough Report* (para. 209) recommends that existing regulations relating to the modification of steam boilers should be extended to apply to pressure systems containing hazardous materials.

Following Flixborough the HSE set about developing comprehensive regulations for pressure systems, which finally emerged as the Pressure Systems Regulations 1989. These regulations are described in Chapters 3 and 12.

The management system for major hazard installations

The *Flixborough Report* (paras 207, 209, 210) places much emphasis on deficiencies in the management system at the Nypro Works.

The works did not have a sufficient complement of qualified and experienced people. Consequently, management was not able to observe the requirement that persons given responsibilities should be competent to carry them out. In particular, there was no works engineer in post and no adequately qualified mechanical engineer on site.

Moreover, individuals tended to be overworked and thus more liable to error.

The management system, however, is more than the individuals. It includes the whole structure which supports them. Thus the system should provide, for example, for the coverage of absence due to resignation, illness and so on.

The use of a comprehensive set of procedures is another important aspect of the management system. A crucial procedure which was deficient at Flixborough was that for the control of plant modifications.

The role of the safety officer at Flixborough was not well defined.

The importance for major hazard installations of the management and the management system was the single most prominent theme in the work of the ACMH. Emphasis by the HSE on management aspects has steadily grown. The *Cutten Report* on the Piper Alpha disaster recommended that offshore the safety case should cover the safety management system and this is implemented in the offshore regulations. This aspect is discussed in Chapters 4 and 6.

Relative priority of safety and production

The *Flixborough Report* (paras 57, 206) drew attention to the conflict of priorities between safety and production. It states

> We entirely absolve all persons from any suggestion that their desire to resume production caused them knowingly to embark on a hazardous course in disregard of the

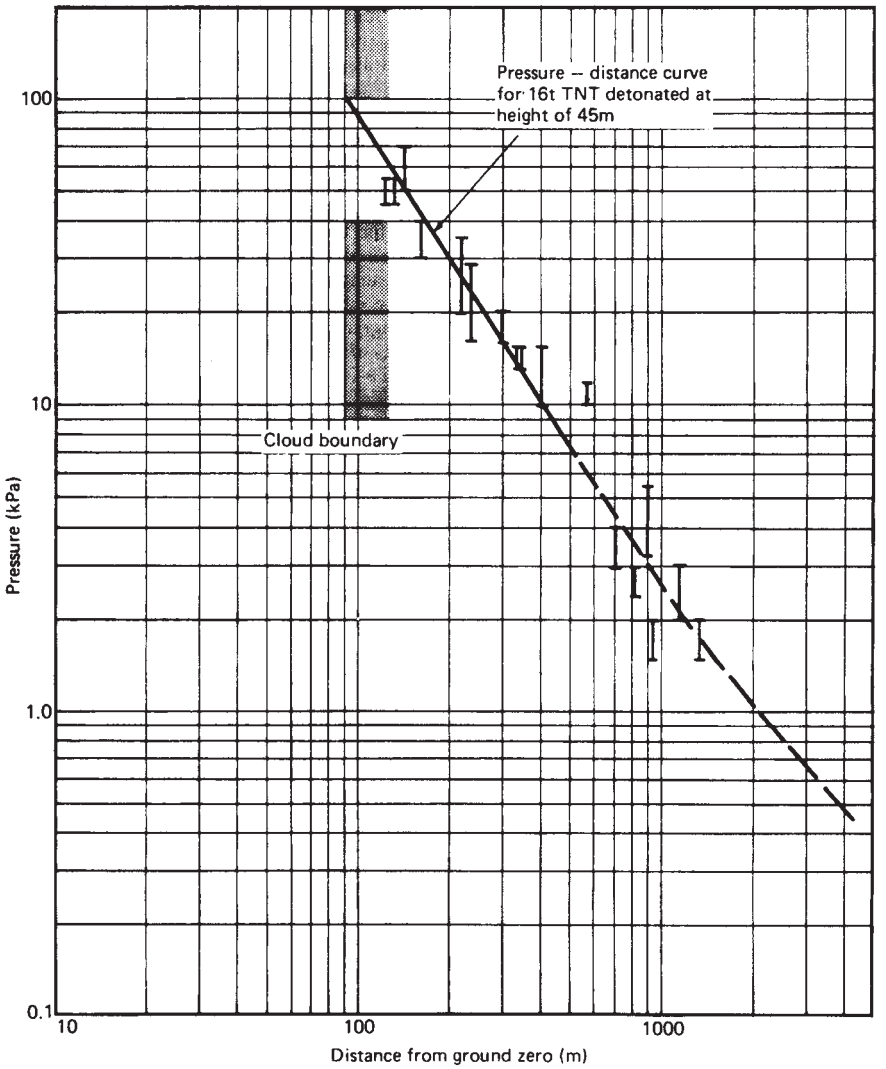

Figure A2.12 *Peak overpressure vs distance at Flixborough estimated from blast damage (Sadée, Samuels and O'Brien, 1976–77) (Courtesy of HM Stationery Office)*

safety of those operating the Works. We have no doubt, however, that it was this desire which led them to overlook the fact that it was potentially hazardous to resume production without examining the remaining reactors and ascertaining the cause of the failure of the fifth reactor. We have equally no doubt that the failure to appreciate that the connection of Reactor No. 4 to Reactor No. 6 involved engineering problems was largely due to the same desire.

Use of standards and codes of practice

As the *Flixborough Report* (paras 61–73) describes, the 20 in. bypass assembly was not constructed and installed in accordance with the relevant standards and codes of practice.

The principal standard relevant to the modification was BS 3351: 1971. The report quotes extracts from this standard:

> 4.6.2. For axial bellows, the piping shall be guided to maintain axiality of the bellows and anchored at adjacent changes in direction to prevent the bellows being subjected to axial load due to fluid pressure. 5.4.2.1 . . . . When expansion joints are used, the advice of the manufacturer should be sought with regard to the guiding, anchoring and support of the adjacent pipework.

The bellows manufacturer, which was Teddington Bellows Ltd, produced a *Designers Guide* which made it clear that two bellows should not be used out of line in the same pipe without adequate support for the pipe.

Table A2.2 *Some lessons of Flixborough*

Public control of major hazard installations
Siting of major hazard installations
Licensing of storage of hazardous materials
Regulations for pressure vessels and systems
The management system for major hazard installations
The structure
The people
The systems and procedures
The safety officer
Relative priority of safety and production
Use of standards and codes of practice
Limitation of inventory in the plant
Engineering of plants for high reliability
Dependability of utilities
Limitation of exposure of personnel
Design and location of control rooms and other buildings
Control and instrumentation of plant
Decision-making under operational stress
Restart of plant after discovery of a defect
Control of plant and process modifications
Security of and control of access to plant
Planning for emergencies
The metallurgical phenomena
Nitrate stress corrosion cracking
Creep cavitation of stainless steel
Zinc embrittlement of stainless steel
Use of clad mild steel
Unconfined vapour cloud explosions
Investigation of disasters and feedback of information on technical incidents

The use of standards and codes of practice is described in Chapters 3, 6 and 12.

Limitation of inventory in the plant

The *Flixborough Report* (para. 14) makes it clear that the large inventory of flammable material in the plant contributed to the scale of the disaster.

The *Second Report* of the ACMH proposes that limitation of inventory should be taken as a specific design objective in major hazard installations.

The limitation of inventory is a particular aspect of the more general principle of inherently safer design, which is now widely recognized. This is discussed in Chapter 11.

Engineering of plants for high reliability

The explosion at Flixborough occurred during a plant start-up. The *Flixborough Report* (para. 206) suggests that special attention should be given to factors which necessitate the shut-down of chemical plant so as to minimize the number of shut-down/start-up sequences and to reduce the frequency of critical management decisions.

The reliability of plant is considered in Chapters 7 and 12.

Dependability of utilities

The high-pressure nitrogen required for the blanketing of the reactors at Flixborough was brought into the works by tankers. There was insufficient nitrogen available during the start-up when the explosion occurred. The *Flixborough Report* (para. 211) emphasizes the importance of assuring dependable supplies of nitrogen where these are necessary for safety.

The dependability of utilities is discussed in Chapter 11.

Limitation of exposure of personnel

The *Flixborough Report* (para. 1) states that the number of casualties would have been much greater if the explosion had occurred on a weekday instead of on a Saturday.

The *First Report* of the ACMH (para. 68) suggests that limitation of exposure of personnel be made a specific design objective.

Aspects of limitation of exposure are controls on access to hazardous areas and design and location of buildings in or near such areas.

The limitation of exposure of personnel is described in Chapters 10 and 20.

Design and location of control rooms and other buildings

Of the 28 deaths at Flixborough 18 occurred in the control room. The *Flixborough Report* (para. 218) refers to various suggestions made to the inquiry concerning the siting of control rooms, laboratories, offices, etc., and the construction of control rooms on blockhouse principles.

The construction of buildings for chemical plant is considered in the *First Report* of the ACMH (para. 69).

The design and location of control rooms and other buildings is discussed in Chapters 10 and 20.

Control and instrumentation of plant

The control and instrumentation system was not a prominent feature in the Flixborough inquiry. The *Flixborough Report* (para. 204) considered that the controls in the control room followed normal practice. But it also states 'Nevertheless we conclude from the evidence that greater attention to the ergonomics of plant design could provide rewarding results'.

Control system design and human factors in process control are described in Chapters 13 and 14.

Decision making under operational stress

The *Flixborough Report* (para. 205) draws attention to the problem of decision making under operational stress and emphasizes the desirability of reducing the number of critical management decisions which have to be made under these conditions.

Such critical decisions are not necessarily confined to management, however. Process operators may also be required to take important decisions in emergency conditions.

The process operator in emergency situations is discussed in Chapter 14.

Restart of plant after discovery of a defect

Following the discovery of the serious defect in Reactor No. 5 at Flixborough, the reactor was removed, a bypass assembly was installed and the plant was started up again. The *Flixborough Report* (para. 57) is critical of the fact that the remaining reactors were not examined and the cause of the failure in the fifth reactor was not ascertained before plant start-up.

The procedures for restart of the plant after discovery of a defect are discussed in Chapter 20.

Control of plant and process modifications
The *Flixborough Report* (para. 209) states

> The disaster was caused by the introduction into a well designed and constructed plant of a modification which destroyed its integrity. The immediate lesson to be learned is that measures must be taken to ensure that the technical integrity of plant is not violated.

As it happens, there was also a process modification at Flixborough, although this is not emphasized in the report. The agitator in Reactor No. 4 was not in use at the time of the disaster. The absence of agitation in the reactor could have allowed a water layer to accumulate more easily in the bottom of the vessel. The sudden evolution of vapour from superheated water was advanced by King as a possible cause of the rupture of the bypass pipe assembly.

The control of plant and process modifications is discussed in Chapters 6 and 21.

Security of and control of access to plant
The *Flixborough Report* (para. 194) draws attention to the fact that there were two unguarded gates through which it was possible for anyone at any time to gain access, although this fact did not contribute to the disaster. The security of plants is considered in Chapter 20.

Planning for emergencies
The *Flixborough Report* (para. 222) calls for a disaster plan for major hazard installations. Emergency planning is described in Chapter 24.

The metallurgical phenomena
The Flixborough disaster drew attention to several important metallurgical phenomena. Thus the *Flixborough Report* describes the nitrate stress corrosion cracking of mild steel (paras 53, 212); the creep cavitation of stainless steel (para. 214); the zinc embrittlement of stainless steel (para. 213); and the use of clad mild steel vessels (para. 224).

The HSE subsequently issued *Technical Data Notes* (1976 TON 53/1, 53/2; 1977 TON 53/3) on the first three of these problems.

It was apparent from the discussion in the engineering profession following publication of the report that although metallurgical specialists were aware of failure due to zinc embrittlement, the phenomenon was not well known among engineers generally.

The metallurgical features of pressure systems are discussed in Chapter 12.

Vapour cloud explosions
The explosion at Flixborough was a large vapour cloud explosion. Although such explosions had become more common in the preceding years, none compared with Flixborough in scale and impact. The *Flixborough Report* (para. 215) draws attention to the marked lack of information on the conditions under which a vapour cloud can give an explosion.

Since Flixborough, a large amount of work has been done on vapour cloud explosions. An account is given in Chapter 17.

Investigation of disasters and feedback of information on technical incidents
The Flixborough disaster was investigated by a Court of Inquiry. There was some feeling in the engineering profession that a legal inquiry of this kind is not a satisfactory means of establishing the facts concerning technical incidents. This aspect is considered in the following section.

The *Flixborough Report* (para. 216) states that the inquiry would have been greatly assisted if the essential instrument records in the control room had not been destroyed in the explosion and recommends that consideration be given to systems for recording and preserving vital plant information such as the 'black box' recorder used in aircraft.

The investigation of disasters and the feedback of information from technical incidents is considered in Chapter 27.

The points just outlined by no means exhaust the lessons to be learned from the Flixborough disaster. In particular, there are many instructive aspects of the 8 in. pipe hypothesis relating to such features as lagging fires, directed flames and sprinkler sensor performance.

A2.9 Critiques

The Flixborough inquiry has been the subject of a number of critiques which have centred mainly on (1) the form of the inquiry; (2) the examination of the hypotheses; (3) the design of the plant (4) the management of the plant and (5) technical issues. These include those of R.L. Allen (1977b), Mecklenburgh (1977a), D.J. Lewis (1989a), R. King (1990) and I. Thomas and Gugan (1993), and the mainly technical discussions of Gugan (1979) and V.C. Marshall (1987).

King gives a detailed description of the plant and it operation and diagrams showing the original plant and the modified plant.

Mecklenburgh, King and Thomas and Gugan argue that the legal format is not conducive to elucidating the facts about technical issues. The question is discussed in detail in Chapter 27.

With regard to the examination of hypotheses, Thomas and Gugan argue that the possible role of explosive reactions, described by Alexander (1990b,c), was insufficiently explored. With regard to the 8 in. pipe hypothesis, while accepting that the inquiry devoted considerable effort to exploring it, they are critical of the arguments used in dismissing it.

Thomas and Gugan rehearse various aspects of the 20 in. and 8 in. pipe hypotheses. Aspects of the 8 in. pipe hypothesis are also discussed by Marshall.

King gives an account of his own hypothesis that there was a pressure rise in Reactor No. 4 due to the evolution of water vapour from water present in that reactor. He also gives the background to the removal of the agitator from Reactor No. 4.

King is critical of the conclusion that the crack in Reactor No. 5 was due to nitrates in the cooling water, the finding of a DSM report. He quotes an HSE source to the effect that the reactor vessel drawing specified a maximum thrust on the 28 in. stubs of 9 te, whereas at normal operating conditions the thrust was 38 te. He suggests that the nitrates found were from cooling water sprayed on the already-formed crack.

The design of the plant is also criticized by Marshall, who argues that it would have been better to use not gravity flow involving the 28 in. pipe connections but pumped flow which would have allowed the use of much smaller diameter pipes.

With regard to the operation of the plant, King is critical of the decision to remove the agitator from Reactor No. 4,

which, among other things, increased the hazard from water accumulation in the vessel.

Thomas and Gugan point to the facts that the plant was shut-down to deal with leaks and was then restarted because 'the leaks had cured themselves' that the oxygen trip was disarmed; the production was continued even though there was a shortage of nitrogen; and that the plant was started up again after the failure of Reactor No. 5 without inspection of the other reactors.

One technical issue discussed by King is the thrust exerted by unrestrained bellows on the systems to which they are connected, which tends to be underestimated.

Lewis gives some alternative estimates of the size of the release. He states that the inventory of the cyclohexane oxidation unit exceeded 120 te. Re-examination of the reactor section at a pressure of 8.6 bar shows that it had an inventory of 230 te with another 150 te in the attached distillation section at 14.7 bar.

He also discusses the problem of determining the efficiency of the explosion compared with TNT. Estimates were made from long-range effects and from medium range damage surveys, and both point to a TNT equivalent of 15–20 te. There were major difficulties, however, in fitting TNT curves to the damage observed.
The TNT efficiency is difficult to assess, depending as it does on the estimate of the mass within the flammable region and on the blast curves used.

Gugan gives a detailed discussion of certain particular damage effects. They include crushing of a vessel, from which he estimates an overpressure of 0.76 MPa (110 psi); damage to drain covers, for which his overpressure estimate is 1 MPa; and bending of a reactor agitator shaft and deformation of lamp standards. He suggests that in general the analysis of the damage relied too much on the effects of overpressure to the neglect of the influence of impulse and dynamic pressure.

Marshall regards the vapour cloud explosion at Flixborough as of particular interest in that it is the best documented and most studied case, and is thus an exemplar. He gives a detailed analysis of the estimates of overpressure made from the damage effects, treating separately those in the near and far fields. The results show wide scatter, and he concludes that it is peculiarly difficult to estimate the energy release of such an explosion from damage.

Appendix 3 Seveso

Contents

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A3.12 Some Lessons of Seveso A3/11

At 12.37 on Saturday 9 July 1976, a bursting disc ruptured on a chemical reactor at the works of the Icmesa Chemical Company at Meda near Seveso, a town of about 17,000 inhabitants some 15 miles from Milan. A white cloud drifted from the works and material from it settled out downwind. Among the substances deposited was a very small amount of TCDD, one of the most toxic chemicals known. There followed a period of great confusion due to lack of communication between the company and the authorities and the latter's inexperience in dealing with this kind of situation. Over the next few days in the contaminated area animals died and people fell ill. A partial and belated evacuation was carried out. In the immediate aftermath there were no deaths directly attributable to TCDD, but a number of pregnant women who had been exposed had abortions.

A Parliamentary Commission of Inquiry, drawn equally from the Chamber of Deputies and the Senate and chaired by Deputy B. Orsini, was set up. The Commission's report (the Seveso Report) (Orsini, 1977, 1980) is a far-ranging inquiry not only into the disaster but also into controls over the chemical industry in Italy.

The impact of the Seveso disaster in Continental Europe has in some ways exceeded that of Flixborough and has led to much greater awareness of process industry hazards on the part of the public and demands for more effective controls.

The EC Directive on Major Accident Hazards of 1982 was a direct result of the Seveso disaster, and indeed this Directive was initially often referred to as the 'Seveso Directive'.

In addition to the Seveso Report, there are other accounts of the Seveso disaster and of TCDD in *The Superpoison* by Margerison, Wallace and Hallenstein (1980) and *The Chemical Scythe* by A. Hay (1982) and by A. Hay (1976, 1979, 1981), Bolton (1978), V.C. Marshall (1980), Theofanous (1981, 1983), Rice (1982), Sambeth (1983) and W.B. Howard (1985).

Selected references on Seveso are given in Table A3.1.

Table A3.1 *Selected references on Seveso*

Official report
Orsini (1977, 1980)

Further accounts
Anon. (1976k); Commission of European Communities and Italian Ministry of Health (1976); A. Hay (1976, 1976a–e, 1981, 1982); Margerison (1976); V.C. Marshall (1976b, 1980c, 1983b, 1987, 1992 LPB 104); Comer (1977); Kimbrough *et al.* (1977); Temple (1977b); Bolton (1978, 1991); Koch and Vahrenholt (1978); Pocchiari (1978); Slater (1978a); Verband der chemischen Industrie (1978); Bisanti *et al.* (1979); Cavallaro, Tebaldi and Gualdi (1979, 1982); Ferraiolo (1979); Homberger *et al.* (1979); Anon. (1980b); Margerison, Wallace and Hallenstein (1980); J.J. Stevens (1980); D.C. Wilson (1980); Cardillo and Girelli (1981); A. Robertson (1981); Theofanous (1981, 1983); Rice (1982); Anon. (1983i,l,o,u,v); Anon. (1983 LPB 53, p. 27); Sambeth (1983); Cardillo, Girelli and Ferraiolo (1984); Redding (1984); W.B. Howard (1985); Kletz (1991)

TCDD
Herxheimer (1899); Kumig and Schulz (1957); Schulz (1957); Bauer, Schulz and Spiegelberg (1961); Higginbotham *et al.* (1968); Verrett (1970); Vos *et al.* (1973); Schwetz *et al.* (1973); WHO (1977); Cattabeni, Cavallaro and Galli (1978); A. Hay (1982); Rice (1982); Anon. (1984p); Tschirley (1986); EPA (1994a,b)

Previous TCP and TCDD accidents
Hofmann (1957); Schulz (1957); Bleiberg *et al.* (1964); US Senate (1970); Milnes (1971); May (1973); Dalderup (1974)

A3.1 The Company and the Management

The site at Seveso was operated by the company Industrie Chimiche Meda Societa Azionara (ICMESA), using a process developed by its parent company Givaudan, which was itself owned by Hoffmann La Roche.

Icmesa started in Naples in 1926 and began operations in Meda in 1946. Givaudan acquired a majority shareholding in Icmesa in 1965. In the same year Givaudan was itself taken over by Hoffmann La Roche. Icmesa was an Italian company and the other two companies were Swiss.

The management of the three companies and the officials of the local authorities involved are described in on *The Superpoison*. The following information is relevant:

Icmesa
General Manager, H. von Zwehl
Technical Manager, C. Barni
Production Manager, P. Paoletti
Factory Doctor, E. Bergamaschini

Givaudan
Managing Director, G. Waldvogel
Technical Director, J. Sambeth
Director of Dubendorf Laboratories, B. Vaterlaus

Hoffman La Roche
Technical General Manager, R. Seheff
Clinical Research Director, G. Reggiani

Local Authorities
Mayor of Seveso, F. Rocca
Mayor of Meda, F. Malgrati
Medical Health Officer, G. Ghetti
Acting Health Officer, F. Uberti

Regional Minister of Health, V. Rivolta
Chief Medical Officer, Milan Province V. Eboli
Chief Medical Officer, Lombardy V. Carreri
Director of Provincial Health Laboratory, Milan A. Cavallaro
Magistrate, S. Adamo

A3.2 The Site and the Works

When Icmesa built its works at Meda the site was surrounded by fields and woods. Over the years, however, the area near the site was developed.

The reactor, Reactor A101, in which the runaway occurred was in Department B of the works.

A3.3 The Process and the Plant

The process which gave rise to the accident was the production of 2,4,5-trichlorophenol (TCP) in a batch reactor.

TCP is used for herbicides and antiseptics. Givaudan required it for making the bacteriostatic agent hexachlorophene. It manufactured its own because the herbicide grades contained impurities unacceptable in this application. Between 1970 and 1976 some 370 te of the chemical were produced.

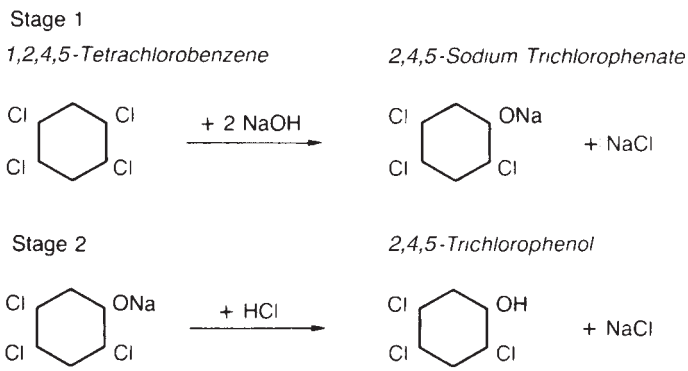


Figure A3.1 *Reaction scheme for production of 2,4,5-trichlorophenol (TCP)*

The reaction was carried out in two stages. Stage 1 involved the alkaline hydrolysis of 1,2,4,5-tetrachlorobenzene (TCB) using sodium hydroxide in the presence of a solvent ethylene glycol at a temperature of 170–180°C to form sodium 2,4,5-trichlorophenate. The reaction mixture also contained xylene, which was used to remove the water by azeotropic distillation. In Stage 2 the sodium trichlorophenate was acidified with hydrochloric acid to TCP and purified by distillation. The reaction scheme is shown in Figure A3.1.

On completion of the Stage 1 reaction some 50% of the ethylene glycol would be distilled off and the temperature of the reaction mixture lowered to 50–60°C by the addition of water.

The process was a modification by Givaudan of a process widely used in the industry. The conventional process used methanol rather than ethylene glycol and operated at some 20 bar pressure.

In this reaction the formation of small quantities of TCDD as a by-product is unavoidable. At a reaction temperature below 180°C the amount formed would be unlikely to exceed 1 ppm of TCP, but with prolonged heating in the temperature range 230–260°C it could increase a thousand-fold.

During manufacture nearly all (99.7%) of the TCDD formed concentrated in the distillation residues from which it was collected and incinerated. Only 0.3% found its way into the TCP, giving a maximum concentration of 10 ppb.

The reactor was a 13875 l vessel with an agitator and with a steam jacket supplied with steam at 12 bar. The saturation temperature of steam at this pressure is 188°C. The controls on the reactor were relatively primitive. There was no automatic control of the heating. The reactor system is shown in Figure A3.2.

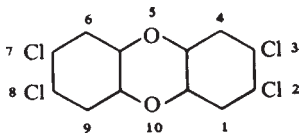
The reactor was provided with a bursting disc set at 3.5 bar and venting direct to atmosphere. The prime purpose of this disc was to prevent overpressure when compressed air was being used on the reactor.

The works had an incinerator for the destruction of hazardous plant residues at temperatures of 800–1000°C.

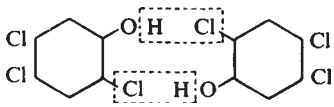
A3.4 TCDD and Its Properties

The properties of TCDD are given the *Seveso Report* and in *Dioxin, Toxicological and Chemical Aspects* by Cattabeni, Cavallaro and Galli (1978) and by Rice (1982).

2,3,7,8-tetrachlorodibenzo-p-dioxin, which is also known as TCDD or dioxin, has the formula



It is generated by the elimination of two molecules of HCl from 2,4,5-trichlorophenol



TCDD is one of the most toxic substances known. In 1954, an accident at the Boehringer TCP plant in Hamburg led to a painstaking investigation by Schulz (1957) of the causes of chloracne in people who had been exposed. He found that the cause was not the TCP itself but an impurity which he identified as TCDD, or dioxin. Actually there is a family of dioxins, TCDD being the most toxic.

The toxicity of TCDD is reviewed in the *Seveso Report*. The LD_{50} data quoted in the report are shown in Table A3.2, Section A. The lowest LD_{50} quoted is for guinea pigs and is 0.6 μg/kg, that is a dose of 0.6×10^{-9} per unit of body weight. The report also gives a table showing the toxicity of TCDD relative to that of other well-known poisons. An extract from this is shown in Table A3.2, Section B. TCDD is therefore an ultratoxic substance.

TCDD can be taken into the body by ingestion, inhalation or skin contact. A leading symptom of TCDD poisoning is chloracne, which is an acne-like skin effect caused by chemicals. A mild case of chloracne usually clears within a year, but a severe case can last many years. Other effects of TCDD include skin burns and rashes and damage to liver, kidney and urinary systems and to the nervous system. It appears to have an unusual ability to interfere with the metabolic processes. There are varying degrees of evidence for carcinogenic, mutagenic and teratogenic properties. These are reviewed in the report.

TCDD is a stable solid which is almost insoluble in water and resistant to destruction by incineration except at very high temperatures.

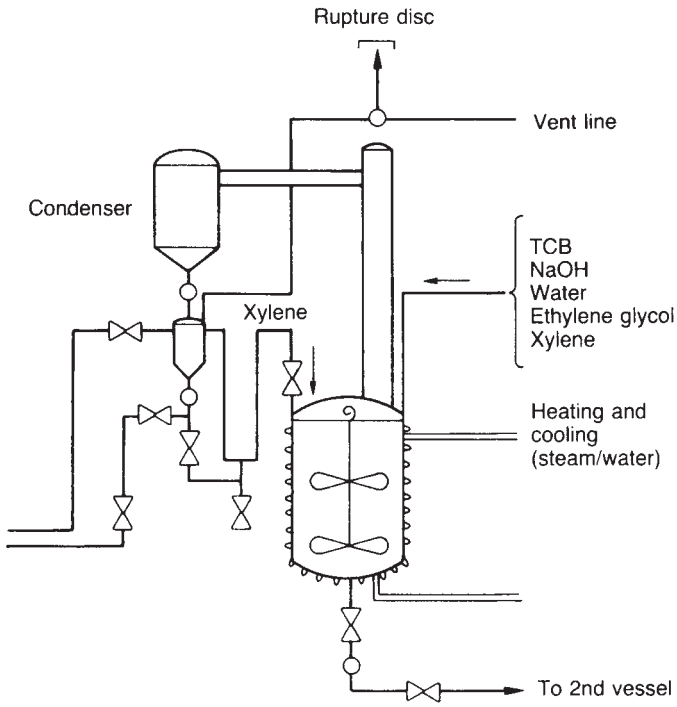


Figure A3.2 *Reactor system at Seveso (Sambeth, 1983) (Courtesy of Chemical Engineering)*

Table A3.2 *Toxicity of TCDD (after Orsini, 1980)*

A LD_{50} to various animal species

Species		LD_{50} (μkg/kg)	*References*
Guinea pig	(male)	0.6	Schwetz *et al.* (1973)
Rat	(male)	22	Schwetz *et al.* (1973)
	(female)	45	Schwetz *et al.* (1973)
Rabbit	(male)	115	Schwetz *et al.* (1973)
	(female)	115	Schwetz *et al.* (1973)
Mouse	(male)	114	Vos *et al.* (1973)

B Relative toxicity of some highly toxic materials

Substance	*Minimum lethal dose* (moles/kg)
Botulinus toxin	3.3×10^{-17}
TCDD	3.1×10^{-9}
Strychnine	1.5×10^{-6}
Sodium cyanide	2.0×10^{-4}

A3.5 Previous Incidents Involving TCP and TCDD

The manufacture of TCP had resulted in a number of accidents prior to Seveso and its hazards and problems were recognized, to the extent that some companies had withdrawn from the business.

A list of incidents, based on that given in the *Seveso Report*, is shown in Table A3.3.

The original method of making TCP was to heat TCB and sodium hydroxide with methanol at about 200°C and 20 bar.

In 1949, there was a large release from a pressurized TCP reactor at the Monsanto plant at Nitro, West Virginia, when a valve ruptured. A total of 228 people were affected to some degree. In 1953, a TCP reactor explosion at BASF, affecting 42 people. Another TCP reactor explosion occurred at the Boehringer plant at Hamburg in 1954, 40 workers being affected. It was this incident which led to the discovery by Schulz of the ultratoxic properties of TCDD. At the Rhone-Poulenc TCP plant at Pont de Claix near Grenoble there were 100 cases of dioxin poisoning in the period 1953–70 and explosions in 1956 and 1966, affecting 17 and 20 people, respectively. In 1963, at the Philips-Duphar plant on the North Sea Canal near Amsterdam a reaction runaway on a pressurized TCP reactor blew the top off the reactor, even though the relief valve had blown, and affected some 30 people. In 1964, the operating procedure at the Dow plant at Midland, Michigan, was changed and an accident occurred which affected 60 people. In some of these incidents a small number of those exposed subsequently died, apparently from the exposure.

The incidents did not cause any direct exposure of the public, but they did reveal the difficulties of preventing the workers' families being affected and of decontaminating the plant. In the Ludwigshafen accident one man got chloracne just by using his father's towel.

Table A3.3 *Some incidents involving TCDD*

Date	*Location*	*Injured*	*Comments*
1949	Nitro, WV (Monsanto)	117	Overheating leading to explosion
1953	Ludwigshafen (BASF)	55	Overheating leading to explosion
1954	Hamburg (Boehringer)	37	Exposure during plant operation
1956	Pont de Claix (Rhone-Poulenc)	17	Explosion
1956	USA (Hooker)	?	Overheating
1960	USA (Diamond Shamrock)	?	Overheating
1963	N. Sea Canal (Philips-Duphar)	30	Overheating leading to explosion
1964	Midland, MI (Dow)	30	Explosion
1964	Neuratovice (Spolana)	72	Exposure during plant operation
1966	Pont de Claix (Rhone-Poulenc)	21	Explosion
1968	Bolsover (Coalite)	79	Overheating leading to explosion
1970?	(Bayer)	5	Exposure during plant operation
1972	(Linz Chemic-Werke)	50	Exposure during plant operation
?	(Thompson Hayward)	?	Overheating leading to explosion
1976	Seveso (Icmesa)		Overheating

Various attempts were made at Ludwigshafen to remove the dioxin from the plant building, including the use of detergents, the burning off of the surfaces, the removal of insulating material and so on, but these were not effective. Eventually the whole building was demolished under controlled conditions and the debris buried. At Duphar some 50 people were involved in cleaning up the plant, of whom four died within 2 years, though the connection between the incident and the deaths was unproven. The plant was sealed for 10 years and then dismantled from the inside brick by brick, the rubble was embedded in concrete and the concrete blocks were sunk in the Atlantic.

In 1968, an accident occurred at the Coalite TCP plant at Bolsover. Coalite utilized a modification of the Givaudan process, using ethylene glycol and operating at atmospheric pressure, but with ortho-dichlorobenzene (ODCB) as the second solvent to remove the water formed. The use of this second solvent reduced the amount of expensive ethylene glycol which had to be used and not all of which was recovered after the batch. Research indicated that further reduction might be made in the amount of ethylene glycol used and a trial was carried out on the plant using half the normal quantity. A reaction runaway occurred, blew the top off the reactor and released flammable vapours which exploded and killed the shift chemist.

The workers who had been in the building were affected but appeared to recover after 10 days and the undamaged part of the plant was thoroughly cleaned and brought back into use, the damaged part being sealed off. Some weeks later chloracne symptoms appeared not only among those who had been in the plant at the time of the accident but among others who had worked in the building occasionally after it had been cleaned. Within 7 months there were some 79 cases of chloracne. Stringent hygiene measures were instituted and the cases gradually cleared. The most seriously contaminated part of the plant was dismantled and buried in a deep hole.

The causes of the accident were investigated by Milnes (1971). He found that an exothermic reaction occurs between ethylene glycol and sodium hydroxide starting about 230°C and rising rapidly to about 400°C. He also showed that TCDD is formed by reaction of sodium trichlorophenate and sodium hydroxide as described above. Further, he demonstrated that whereas at the normal reaction temperature of 180°C the amount of TCDD formed is only a few ppm, at 250°C large amounts are formed. Subsequent work has shown that formation of TCDD is zero below 153°C, less than 1 ppm at 180°C but 1600 ppm in 2 h at 230–260°C (Orsini, 1980).

A3.6 Events Prior to the Release

The start of the batch began at 16.00 on Friday, 9 July (Table A3.4). The reactor was charged with 2000 kg TCB, 1050 kg sodium hydroxide, 3300 kg ethylene glycol and 600 kg xylene.

After the reaction had taken place, part of the ethylene glycol was distilled off, but the fraction removed was only 15% instead of the usual 50% so that most of the solvent was left in the vessel. Distillation was interrupted at 5.00 on 10 July and heating was discontinued but water was not added to cool the reaction mass. The reactor was not brought down to the 50–60°C temperature range specified. The temperature recorder was switched off, the last temperature recorded being 158°C.

The shift ended at 6.00. This time coincided with the closure of the plant for the weekend. The reactor was left with the agitation turned off but without any action to reduce the temperature of the charge.

During the weekend, with the steam turbine on reduced load, the steam supply to the reactor jacket became superheated, its temperature being about 300°C.

A3.7 The Release – 1

At 12.37 on 9 July, the bursting disc on the reactor ruptured. The maintenance staff heard a whistling sound and a cloud of vapour was seen to issue from a vent on the roof giving rise to 'the formation of a dense cloud of considerable altitude'. The release lasted some 20 min.

A maintenance foreman, G. Bruno, who was passing, heard the disc rupture and realized something was wrong. He ran with two colleagues, R. Vito and C. Galante, to the boiler room to start-up the large firewater pump, then to the stores to get protective clothing. They approached Department B, where they felt the heat from the reactor. Bruno called in the technical manager, C. Barni, who arrived at

Table A3.4 *Timetable of events at Seveso*

Jul.	9 Friday	16.00 Final reactor batch started
	10 Saturday	5.00 Final reactor batch interrupted
		12.37 Bursting disc on reactor ruptures
		Barni visits houses near plant to warn against eating garden produce. He asks carabinieri to repeat warning but they refuse
	11 Sunday	Barni and Paoletti inform von Zwehl. They are unable to contact Ghetti or his deputy. They inform Rocca and Malgrati. Von Zwehl informs Sambeth
	12 Monday	Rocca and Uberti visit ICMESA. Letter of von Zwehl to Health Officer
	13 Tuesday	Report of Uberti to Rocca and Malgrati
	14 Wednesday	Sambeth and Vaterlaus inspect Dept B and contaminated area. Uberti writes to Provincial Health Officer in Milan
	15 Thursday	Dubendorf Laboratories give first analyses showing high TCDD content. Sambeth telegraphs Waldvogel in Turkey and asks von Zwehl to inform local authorities. Sambeth informs Hoffmann La Roche and seeks clinical advice and permission to close plant. Rumours grow in Seveso. Citizens invade Uberti's office. Rocca and Uberti meet von Zwehl. They decide to declare polluted zone and to post warning notices
	16 Friday	Workforce go on strike. Efforts are made to contact Ghetti in remote holiday farmhouse. Warning notices are erected. Rocca, Uberti and others meet von Zwehl again. Uberti insists on evacuation. Rocca requests and obtains permission for evacuation from Deputy Prefect of Milan. Rocca contacts journalist friend
	17 Saturday	II Giorno carries front-page headlines on 'Poison gas' at Seveso. Press descend on town. Uberti contacts Cavallaro.
	18 Sunday	Cavallaro's team of health inspectors investigate contaminated area. Rocca, Ghetti, Cavallaro and Adamo meet von Zwehl. Cavallaro presses to know identity of poison released. Adamo threatens to arrest ICMESA management
	19 Monday	Waldvogel arrives in Seveso and offers local authority financial compensation, which is refused
	20 Tuesday	Cavallaro and Ghetti meet Vaterlaus in Zurich. Vaterlaus reveals that poison released was TCDD. Uberti's letter to Provincial Health Officer in Milan arrives.
		16.00 Ghetti telephones Rocca to say substance was TCDD. Prefect in Milan is informed
	21 Wednesday	9.30 Meeting at prefecture. Rivolta and Carreri take over responsibility. Carabinieri arrest von Zwehl and Paoletti
	23 Friday	9.00 Meeting at prefecture. Rivolta decides against evacuation. Reggiani visits Rocca and urges evacuation. Reggiani asked to leave Deputy Prefect's meeting unheard
		14.00 Rivolta reassures meeting in Seveso town hall. Reggiani argues with Rivolta and calls for evacuation. Carabinieri try unsuccessfully to arrest Reggiani, who returns to Switzerland
	24 Saturday	9.30 Meeting of regional health council. Vaterlaus presents map of locations affected. Council decides to recommend evacuation and defines evacuation zone (part of Zone A)
	26 Monday	179 people evacuated
	29 Thursday	Zone A extended and further 550 evacuated

13.10 as the escape was subsiding. About an hour after the release began Vito and Galante were able to begin gingerly admitting cooling water to the reactor system.

The release contaminated the vicinity of the plant with TCDD. Figure A3.3 is a map of the area, showing the zones later established and Table A3.5 gives the concentrations later measured in these zones.

The area of Zone A was 108 ha (1.08 km^2) with concentrations of TCDD averaging 240 $\mu g/m^2$ and rising to over 5000 $\mu g/m^2$. The area of Zone B was 269 ha (2.69 km^2) with concentrations averaging 3 $\mu g/m^2$ but rising to 43 $\mu g/m^2$. In the Zone of Respect, Zone R, which had an area of 1430 ha (14.3 km^2), the concentrations varied from indeterminable to 5 $\mu g/m^2$.

A3.8 The Emergency and the Immediate Aftermath

The release set in train a series of events which were to have profound repercussions. They are described in detail in *The Superpoison*. It is possible here to give only a brief outline.

When the situation had been brought under control in the works, Barni visited houses near the plant and warned people not to eat the garden produce. He asked the carabinieri to repeat the warning, but they refused, unless there was authorization from the municipal health officer.

There were few obvious signs of an accident, although surfaces were covered with a thin, oily film.

The municipal health officer, G. Ghetti, was on holiday in a remote farmhouse not on the telephone.

On Sunday 11 July, Barni visited P. Paoletti, the production director, and they together contacted the general manager, von Zwehl, who was on holiday in the Alps. They then visited the mayor of Seveso, F. Rocca, and recommended that people living near the plant be warned not to eat garden produce. Rocca agreed to inform the carabinieri. He also brought in the mayor of Meda, F. Malgrati, since the Icmesa plant lay within the Meda boundaries.

The same day von Zwehl informed J. Sambeth, technical director of Givaudan. Sambeth realized that there was a dioxin hazard and asked what temperature the reactor had reached. He told von Zwehl to close off Department B

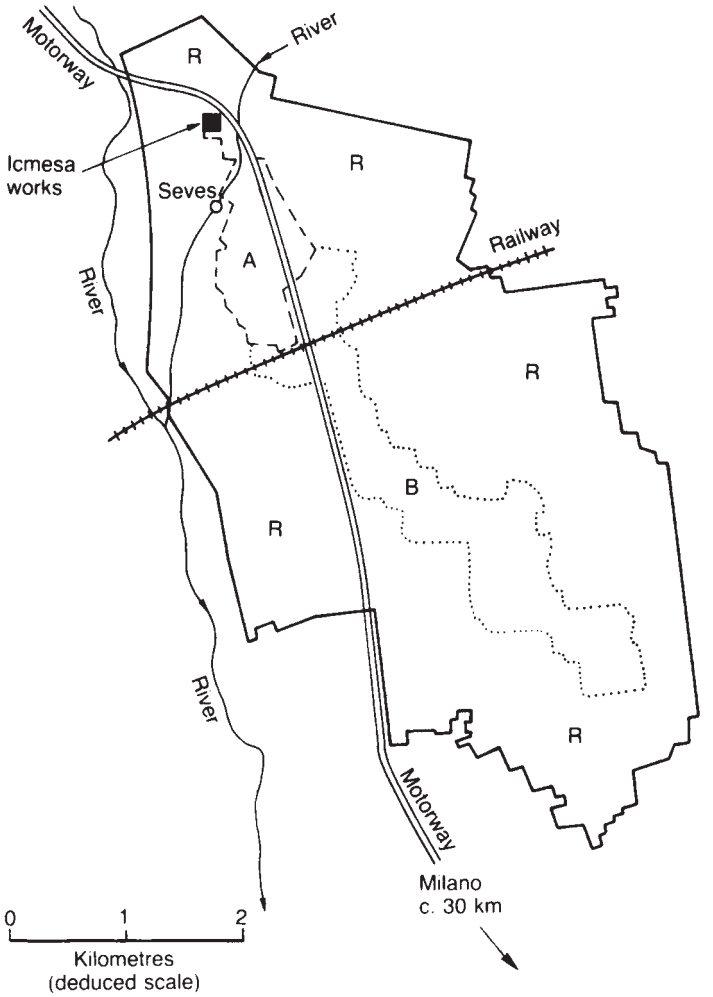


Figure A3.3 *Plan of the Seveso area, showing Zones A and B and Zone of Respect (after Orsini, 1980; V.C. Marshall, 1978)*

Table A3.5 *Concentrations of TCDD in Zones A and B at Seveso (after Orsini, 1980)*

Zone	*Concentration* ($\mu g/m^2$)		
	Mean	*Maximum*	*Minimum*
A1	580.4	5477	n.v.d
A2	521.1	1700	6.1
A3 (north)	453.0	2015	1.7
A3 (south)	93.0	441	n.v.d.
A4	139.9	902	n.v.d.
A5	62.8	427	n.v.d.
A6	29.9	270	n.v.d.
A7	15.5	91.7	n.v.d.
B	3	43.8	n.v.d.

n.v.d. = no value determined.

and have samples from the reactor sent to the Dubendorf laboratories of Givaudan at Zurich. Normally he would have discussed the problem with the managing director of Givaudan, G. Waldvogel, but the latter was on holiday in Turkey.

On Monday 12 July, Rocca together with the acting health officer for Meda and Seveso, F. Uberti, visited Icmesa and saw von Zwehl, who convinced them that there was no serious health hazard. Von Zwehl wrote a letter to the health officer. On the material released the latter said:

> Since we are not in a position to evaluate the substances present in the vapour or to predict their exact effects, but knowing the final product is used in manufacturing herbicides, we have advised householders in the vicinity not to eat garden produce.

On Tuesday 13 July, Uberti sent a report to Rocca and Malgrati, enclosing a copy of von Zwehl's letter. He believed

the release was one of the minor accidents which occur periodically.

On Wednesday 14 July, Sambeth and Vaterlaus, director of the Dubendorf laboratories, came to Seveso, inspected Department B and tried to work out how high a temperature the reactor had reached. They also inspected the contaminated land.

Uberti wrote the same day to the provincial health officer in Milan. The letter did not arrive until 20 July.

On Thursday 14 July, the first analyses from the Dubendorf laboratory came through to Sambeth. They showed high dioxin contents. Sambeth telegraphed Waldvogel in Turkey. He warned von Zwehl to advise the local authorities that the release may have contained toxic by-products.

He also contacted Hoffmann La Roche to seek clinical advice and permission to order closure of the plant. The clinical research director of Hoffmann, G. Reggiani, was not familiar with TCDD, but agreed to take over the health aspect and began to inform himself about the substance.

Meanwhile rumours were growing in Seveso and a group of citizens invaded Uberti's office.

Rocca and Uberti met von Zwehl again. He agreed to pay compensation for any damage, produced a map of the polluted area, and suggested that people be advised not to eat garden produce and that warning notices be posted. He was not, however, prepared to say what the poison was. The visitors decided to declare a polluted zone and post notices.

On Friday 16 July, the erection of warning notices began. At this point the workforce at Icmesa went on strike. Rocca and Uberti had a further meeting with von Zwehl where they again pressed to be told the identity of the poison.

Uberti now urged Rocca to carry out an evacuation. Ghetti was contacted in his remote farmhouse, agreed to return but left the decision to Rocca. Rocca requested and obtained permission to evacuate from the Deputy Prefect of Milan. He also contacted a journalist friend.

On Saturday 17 July *Il Giorno* carried front-page headlines about the 'Poison gas' at Seveso. The accident became a national issue and the press descended on the town.

The same day Uberti contacted A. Cavallaro, director of the provincial health laboratories in Milan.

On Sunday 18 July, Cavallaro's team of health inspector arrived to investigate the contaminated area.

Rocca, Ghetti, Cavallaro and a local magistrate, S. Adamo, met again with von Zwehl. Cavallaro pressed to know the poison involved. Adamo threatened to arrest the Icmesa management

On Monday 19 July, Waldvogel arrived in Seveso. He offered the local authorities compensation, which they refused.

On Tuesday 20 July, Cavallaro and Ghetti met Vaterlaus in Zurich. He revealed that the poison was TCDD. Ghetti telephoned Rocca with this information. The Prefect in Milan was informed.

On Wednesday 21 July, a meeting was held at the prefecture. The regional minister of health, V. Rivolta, now took charge of the medical aspects together with V. Carreri, director of health services for Lombardy.

On the same day the carabinieri arrested von Zwehl and Paoletti.

On Friday 23 July, there was another meeting at the prefecture. Rivolta was against evacuation. Meanwhile Reggiani had decided that evacuation was essential and arrived in Seveso to urge this view. He saw Rocca, who told him the decision was out of his hands. He came into the meeting at the prefecture but was asked to leave unheard.

Later that day Rivolta addressed a meeting in Seveso town hall and gave reassurances about the hazards. Reggiani stated his disagreement with Rivolta and called for evacuation. He was unable to make his view prevail. At his hotel in Milan he was warned that the carabinieri were about to arrest him and drove north in haste to Switzerland.

There followed a meeting in Lugano between Waldvogel, Sambeth and Vaterlaus, who had a map of the contaminated areas based on the analyses carried out by his laboratories. Reggiani told the Givaudan men of his experiences. It was agreed that an attempt must be made to persuade the Italian authorities to evacuate and that Vaterlaus, who was deemed less likely to be arrested, should do this.

On Saturday 24 July, a meeting of the regional health council was held in Milan. Vaterlaus presented his map of the areas affected. An evacuation zone was defined and the decision was taken to recommend evacuation.

On Monday 26 July, 179 people were evacuated from an area which was later defined as part of Zone A. On Thursday 29 July, a further 550 people were evacuated from another area which was also part of what became Zone A.

Eventually three zones, Zone A, Zone B and the Zone of Respect were defined, as described above. 733 people were evacuated from Zone A and 5000 in Zone B were put under medical surveillance, but allowed to remain in their homes.

The release posed a severe problem for the Italian authorities, who were obliged to seek assistance from international experts in medical diagnosis and treatment and in analytical and decontamination procedures.

A3.9 The Investigation

The work of the Commission took place against a background of intense national concern.

The terms of reference of the Commission were wide-ranging. They have been described by V.C. Marshall (1980c) as follows: 'These terms of reference appear to have combined the functions in UK terms of the Flixborough inquiry, the Major Hazards Advisory Committee and the Royal Commission on the Environment'.

The report produced by the Commission, the *Seveso Report* (Orsini, 1980), covers a large number of topics, including the history of TCP production, the history of Icmesa, the toxicity of TCDD, the causes of the accident, the consequences of the accident in terms of contamination and health effects, the health measures taken, the reclamation of the contaminated land, the actions and responsibilities of the management and of the local and regulatory authorities and the recommendations. The report adduces four causes of the accident:

(1) Interruption of the production cycle.
(2) Method of distillation.
(3) Set pressure of bursting disc.
(4) Failure to install collection/destruction system for material vented.

The production cycle was interrupted at 5.00 on 10 July and the reactor was left without agitation or cooling.

In the process described in the original Givaudan patent the charge was acidified before distillation. In the process used at Icmesa the order of these two steps was reversed.

This allowed prolonged contact time between the ethylene glycol and sodium hydroxide.

Another modification to the original process was a change in the molar proportions of the reactants from

1 TCB: 2 NaOH: 11.5 ethylene glycol

to

1 TCB: 3 NaOH: 5.5 ethylene glycol

which increased the molar concentration of sodium hydroxide.

The setting of the bursting disc was 3.5 bar. The function of this device was to guard against overpressure from the compressed air, which was used to transfer materials to the reactor. The inquiry found that if the set pressure had been lower, venting would have occurred at a lower, and less hazardous, temperature.

No device was installed to collect or destroy any toxic materials vented. The bursting disc manufacturer's catalogue stated 'Bursting discs may be preferred in the case of fluids of great value and high toxicity where the loss of such fluids should be avoided. In this case a second receiver tank is required to recover the discharged fluid'. There was no such tank on the plant.

Besides listing these four points the report makes a number of other comments. On the reactor itself it states

> Proof has been provided both of the inadequacy of the measuring equipment for a number of fundamental parameters and also the absence of any automatic control system. Measurement of acidity was carried out manually by immersion of a rod with an indicator chart (sic) through a secondary inspection window.

The reactor vessel was not given a hydraulic test as the reactor was considered to operate at atmospheric pressure. The fitting of the bursting disc was not reported to the state pressure vessel inspectors.

The report recommends improved regulatory arrangements for the control of hazardous plants and, in this connection, places some reliance on the introduction of the EC Directive which came to be known as the 'Seveso Directive'.

The viewpoint of the companies has been given in several publications. The accident itself has been described by Sambeth (1983). The view of Hoffmann La Roche has been stated by Homberger *et al.* (1979).

A3.10 The Release – 2

The contents of the reactor at the time of the accident have been given as 2030 kg sodium trichlorophenate, 540 kg sodium chloride, *c.*1000 kg ethylene glycol and 1600 kg sodium ethylene glycolate, diethylene glycol and polyethylene glycol.

It is known that above 230°C such a mixture will undergo an exothermic decomposition reaction. Accidents had been known to occur involving a reaction runaway above this temperature.

The actual temperature profile in the reactor has been given by Sambeth (1983) and is shown in Figure A3.4. Due to the interruption of the batch the usual sharp reduction in the temperature of the charge at the termination of the reaction did not take place and after 7.5 h the explosion occurred.

Investigations carried out after the accidents using differential thermal analysis showed that there exist two slow exotherms (Theofanous, 1981, 1983). One starts at about 185°C, peaking at 235°C and giving a 57°C adiabatic temperature rise. The other starts at about 255°C, peaking at 265°C and giving an estimated 114°C temperature rise. The adiabatic induction times for the two exotherms are 2.1 and 0.5 h, respectively. The decomposition exotherm starts at about 280–290°C and shows a rapid pressure rise at about 300°C.

A mechanism for the reaction runaway has been proposed by Theofanous. This is that due to layering of the

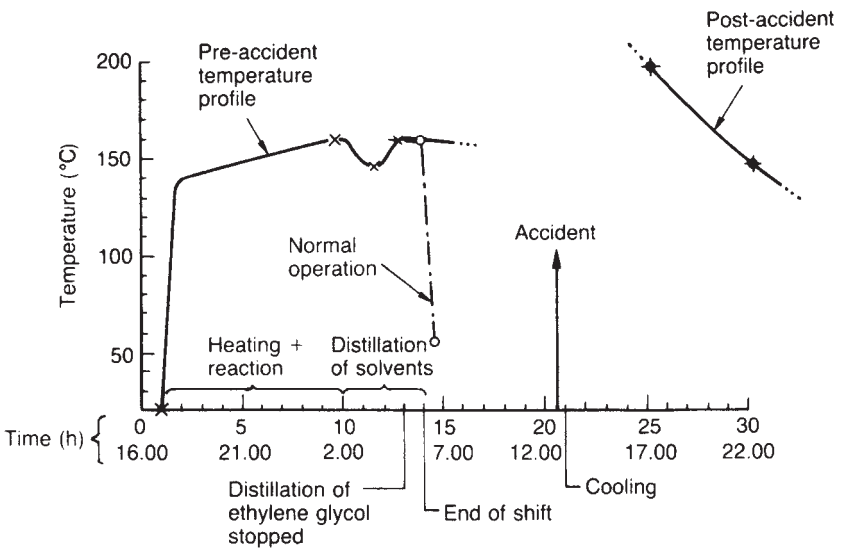


Figure A3.4 *Reactor temperature profiles measured for accident at Seveso (Sambeth, 1983) (Courtesy of Chemical Engineering)*

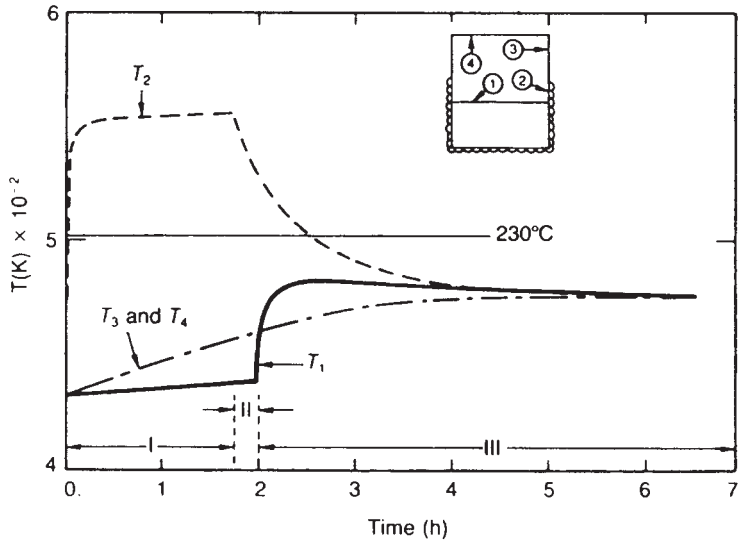


Figure A3.5 *Reactor temperature profiles calculated for period preceding accident at Seveso (after Theofanous, 1981) (Courtesy of Nature)*

reaction mix the amount of residual heat in the upper section of the reactor wall was sufficient to raise the temperature of the top layer of liquid to *c*.200–220°C, a temperature high enough to initiate exotherms leading to decomposition. The calculated temperature profiles for this theory are shown in Figure A3.5.

In the conduct of the final batch there were failures of adherence to operating procedures. W.B. Howard (1985) instances (1) failure to distil off 50% of the glycol; (2) failure to add water; (3) failure to continue agitation; (4) switching off of the reactor temperature recorder and (5) failure to bring the reactor temperature down from its value of 158°C to the normal value of 50–60°C.

A3.11 The Later Aftermath, Contamination and Decontamination

As described above, there was a prolonged period in which the authorities tried to assess the situation and determine measures for dealing with it. They were advised by a team from Cremer and Warner (C&W), and an account has been given by Rice (1982).

The release was modelled using fluid jet and gas dispersion models and predictions made of the probable ground level concentrations of TCDD. Accounts have been given by Comer (1977) and Rice (1982). In this work the reaction mass was taken as 2800 kg ethylene glycol, 2030 kg trichlorophenol 2030, 542 kg sodium chloride and 562 kg sodium hydroxide.

Estimates of the amount of TCDD generated in the reactor and dispersed over the countryside vary. Cattabeni, Cavallaro and Galli (1978) give an estimated range of 0.45–3 kg released. The amount assumed in the C&W modelling work was 2 kg.

Other parameters used in the modelling were bursting disc rupture pressure 376 kPa; vent pipe diameter 127 mm; discharge height above ground 8 m. The bursting disc rupture was assumed to a first approximation to be due to the vapour pressure of ethylene glycol at 250°C. From these data the value obtained for the vapour exit velocity was 274 m/s. Two limiting cases were considered for the discharge: Case A, pure vapour (density 1.61 kg/m^3) and Case B, a two-phase vapour–liquid mixture (density 8.99 kg/m^3). Eyewitness accounts indicated that the actual event was intermediate between these two extremes. For Case A the total plume rise was estimated as 83 m with the downwind distance to the maximum height as 103 m and the corresponding figures for Case B were 55 and 95 m, respectively. Figure A3.6 shows the estimated ground concentration contours for a 2 kg release taken from this work.

The modelling work proved useful in defining the problem and planning the decontamination. The results showed that beyond about 1.5 km there was little difference in the concentration estimates for the two cases. There was good agreement between the predicted and the measured concentrations. This gave some confidence that the amount released was indeed about 2 kg. There had been some speculation by scientists that an amount as high as 130 kg had been released.

Initially, various methods of decontamination were put forward by various parties. TCDD is virtually insoluble in water, which reduces the threat to the water supply, but means that the effect of rain is to transfer it from the vegetation to the soil rather than to remove it. One method of removal suggested was burning and proposals were made to burn the contaminated ground with flame-throwers. It was feared, however, that unless a temperature of at least 1000°C were attained, the TCDD would not be destroyed but simply swept up and deposited elsewhere. Another method proposed was to apply a mixture of olive oil and cyclohexanone to the ground, so that the TCDD would dissolve in the oil and be broken down by the ultraviolet radiation of the sun. This was abandoned, because instead of sun there was rain, and it was feared that the dissolved

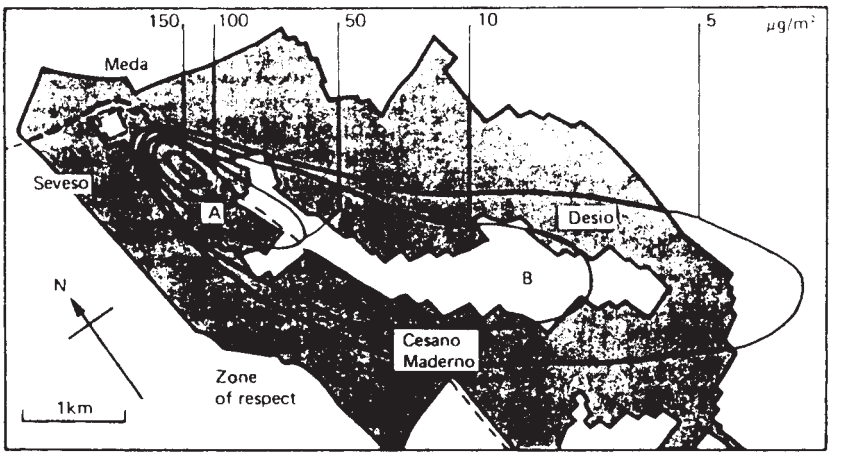


Figure A3.6 *Estimated concentrates of TCDD at Seveso (Comer, 1977. Reproduced by permission.)*

TCDD would be washed into the rivers and might penetrate the water table. A third approach involved the use of specially bred microbes capable of digesting toxic substances. Mixtures of more than a dozen strains of microorganisms bred on chemical substrates were already used to degrade chemical wastes, including cyanides and herbicides.

The decontamination measures actually carried out are described by Rice. They include collection of vegetation and cleaning of buildings by high intensity vacuum cleaning followed by washing with high-pressure water jets.

It is worth mention that people may also have been affected by materials in the reactor charge other than TCDD. V.C. Marshall (1980) indicates that on the basis of the ground concentrations found in the contaminated area a minimum of 0.25 kg was released. He points out that there were some 5–10 te of charge in the reactor and that several tonnes of material including sodium hydroxide must have been ejected. He suggests that burns around the hands and other parts of the body suffered by 413 persons who did not develop chloracne were probably caused by sodium hydroxide.

Figure A3.7 gives plots of the actual ground concentrations, showing the change with time, obtained by Cavallaro, Tebaldi and Gualdi (1982).

Data from the official report on ground concentrations in zones A and B are given in Table A3.5.

A3.12 Some Lessons of Seveso

Some of the numerous lessons to be learnt from the Seveso disaster, many of which were brought out in the Commission's report, are listed in Table A3.6. Some of them are similar to those from Flixborough, while others are different, reflecting both the different substances and processes and the different company and national situations involved. Some of these lessons are now considered:

Public control of major hazard installations

The Seveso disaster had the effect of raising the general level of awareness of the hazard from chemical plants in Italy and in Europe generally and highlighted the deficiencies in the existing arrangements for the control of major hazards.

The Italian government set up the Commission of Inquiry to investigate the cause of the disaster and to make recommendations. It also gave strong support to the development of the EC Directive.

Siting of major hazard installations

The release at Seveso affected the public because in the period since the site was first occupied housing development had encroached on the area around the plant. The accident underlined the need for separation between hazard and public.

Acquisition of companies operating hazardous processes

A lesson which has received relatively little attention is the problem faced by a company which becomes owner by acquisition of another company operating a hazardous process. At Seveso the problem was compounded by the fact that Icmesa was owned by Givaudan and the latter by Hoffmann La Roche, so that the company ultimately responsible was at two removes. As a result the directors of the latter were not familiar with the hazards.

Hazard of ultratoxic substances

Seveso threw into sharp relief the hazard of ultratoxic substances. The toxicity of TCDD is closer to that of a chemical warfare agent than to that of the typical toxic substance which the chemical industry is used to handling.

As it happened, the British Advisory Committee on Major Hazards was presenting its *First Report*, giving a scheme for the notification of hazardous installations, when Seveso occurred. It contained no notification proposals for ultratoxics. In the *Second Report* this deficiency was rectified. The EC Directive places great emphasis on toxic and ultratoxic materials.

Hazard of undetected exotherms

The characteristics of the reaction used had been investigated and the company believed it had sufficient information. It was well aware of the hazard from the principal exotherm. Subsequent studies showed, however, that other,

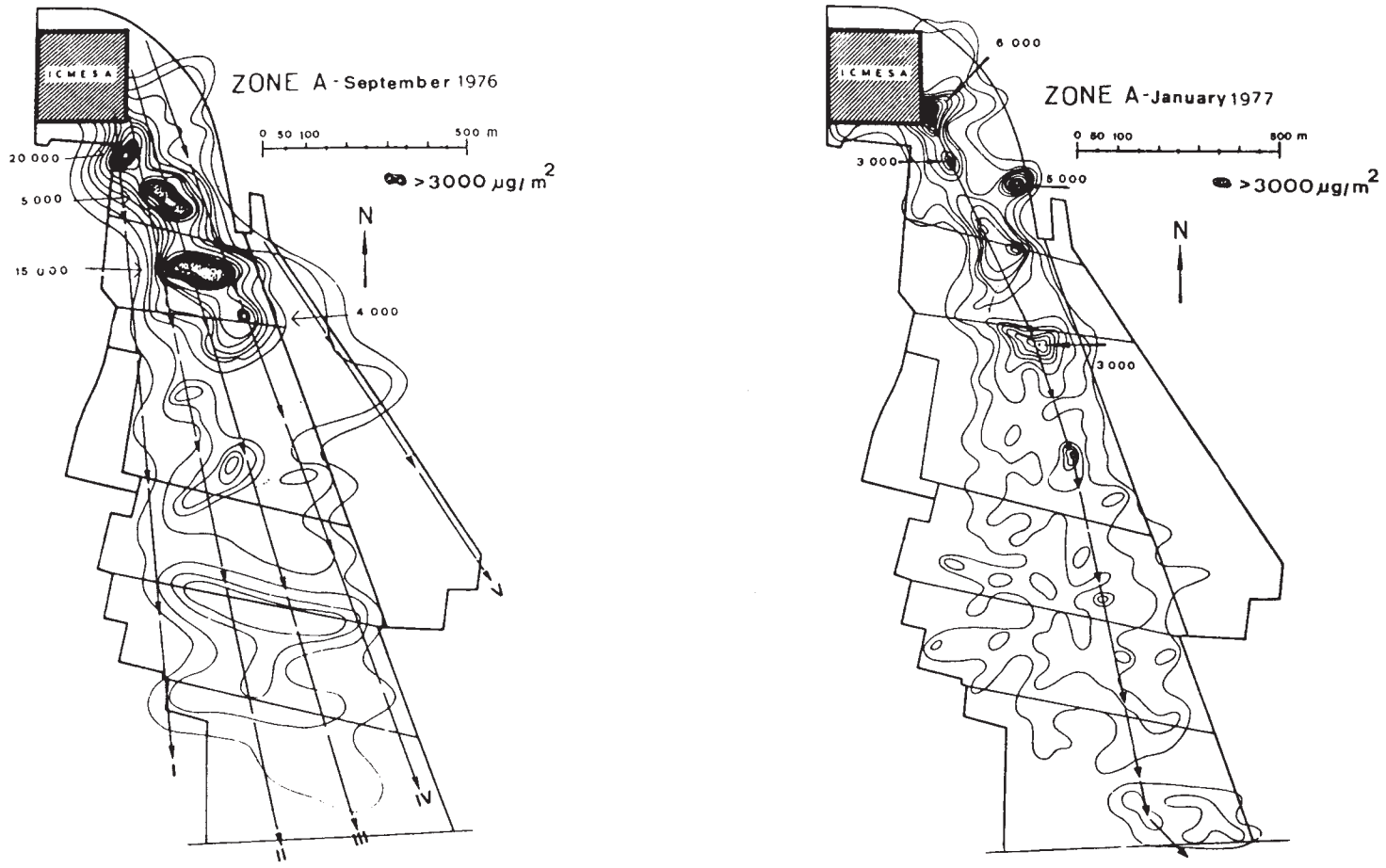


Figure A3.7 *Measured concentrations of TCDD at Seveso, showing reduction of concentration with time (Cavallaro, Tebaldi and Gualdi, 1982) (Courtesy of Atmospheric Environment)*

Table A3.6 *Some lessons of Seveso*

Public control of major hazard installations
Siting of major hazard installations
Acquisition of companies operating hazardous processes
Hazard of ultratoxic substances
Hazard of undetected exotherms
Hazard of prolonged holding of reaction mass
Inherently safer design of chemical processes
Control and protection of chemical reactors
Adherence to operating procedures
Planning for emergencies
Difficulties of decontamination

weaker exotherms existed which, given time, could also cause a runaway.

The complete identification of the characteristics of the reaction being operated is particularly important. If these are not known, or only partially known, there is always the danger that the design will not be as inherently safe as intended, that operating modifications will have unforeseen results and/or that protective measures will be inadequate.

Hazard of prolonged holding of reaction mass

The interruption of the reaction and the holding of the reaction mass for a prolonged period after the main reaction was complete without reducing the temperature gave time for the weak exotherms to occur and lead to runaway.

Inherently safer design of chemical processes

The reactor was intended to be inherently safe to the extent that the use of steam at 12 bar set a temperature limit of 188°C so that the contents could not be heated above this by the heating medium. Unfortunately this feature was defeated by allowing the reaction charge to stand hot for too long so that there occurred the weak exotherms, which the company did not know about.

The bursting disc was not intended for reactor venting, but, as the Commission pointed out, if the set pressure of the disc had been lower, the reactor would have vented at a lower temperature and hence with less dioxin in the charge.

Control and protection of chemical reactors

The control and protection system on the reactor was primitive. Operation of the reactor was largely manual. There was no automatic control of the cooling and no high temperature trip.

The reactor was not designed to withstand a runaway reaction. It was not rated as a pressure vessel to withstand pressure build-up prior to and during venting, the disc was not designed for reaction relief and there was no tank to take the ultratoxic contents of the reactor.

Adherence to operating procedures

The conduct of the final batch involved a series of failures to adhere to the operating procedures.

Planning for emergencies

As the account given above indicates, the handling of the emergency was a disaster in its own right. Information on the chemical released and its hazards was not immediately available from the company. There was failure of communication between the company and the local and regulatory authorities and within those authorities. Consequently there was lack of action and failure to protect and communicate with the public. These deficiencies might in large part have been overcome by emergency planning.

Difficulties of decontamination

The incident illustrates the difficulties of decontamination of land where the contaminant is both ultratoxic and insoluble in water.

Appendix 4

Mexico City

Contents

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A4.4 The Fire and Explosion – 2 A4/7
A4.5 Some Lessons of Mexico City A4/7

At about 5.35 a.m. on the morning of 19 November 1984, a major fire and a series of explosions occurred at the PEMEX LPG terminal at San Juan Ixhuatepec (San Juanico), Mexico City. Some 500 people were killed and the terminal was destroyed.

The accident was investigated by a team from TNO which visited the site about 2 weeks after the disaster and has published its findings (Pietersen, 1985). A further account has been given by Skandia International (1985).

Selected references on Mexico City are given in Table A4.1.

A4.1 The Site and the Plant

The site of the PEMEX terminal is shown in Figure A4.1 and an aerial photograph of the installation itself in Figure A4.2.

Table A4.1 *Selected references on Mexico City*

Anon. (1985v, hh); Berenblut *et al.* (1985); Cullen (1985); Kletz (1985p); Pietersen (1985, 1985 LPB 64, 1986a,b, 1988a); Skandia International (1985); Hagon (1986)

The oldest part of the plant dated from 1961 to 1962 and was thus over 20 years old. In the intervening period residential development had crept up to the site. This process of encroachment is clearly visible from the aerial photographs shown in Figure A4.3. By 1984, the housing was within 200 m of the installation with some houses within 130 m.

The terminal was used for the distribution of LPG, which came by pipeline from three different refineries. The main LPG storage capacity of 16,000 m^3 consisted of 6 spheres and 48 horizontal cylinders. The daily throughput was 5000 m^3. The layout of the terminal with storage tank capacities is shown in Figure A4.4. The two larger storage spheres had individual capacities of 2400 m and the four smaller spheres capacities of 1600 m^3. The site covered an area of 13,000 m^2.

The plant was said to have been built to API standards and much of it to have been manufactured in the United States.

A ground level flare was used to burn off excess gas. The flare was submerged in the ground to prevent the flame being extinguished by the strong local winds.

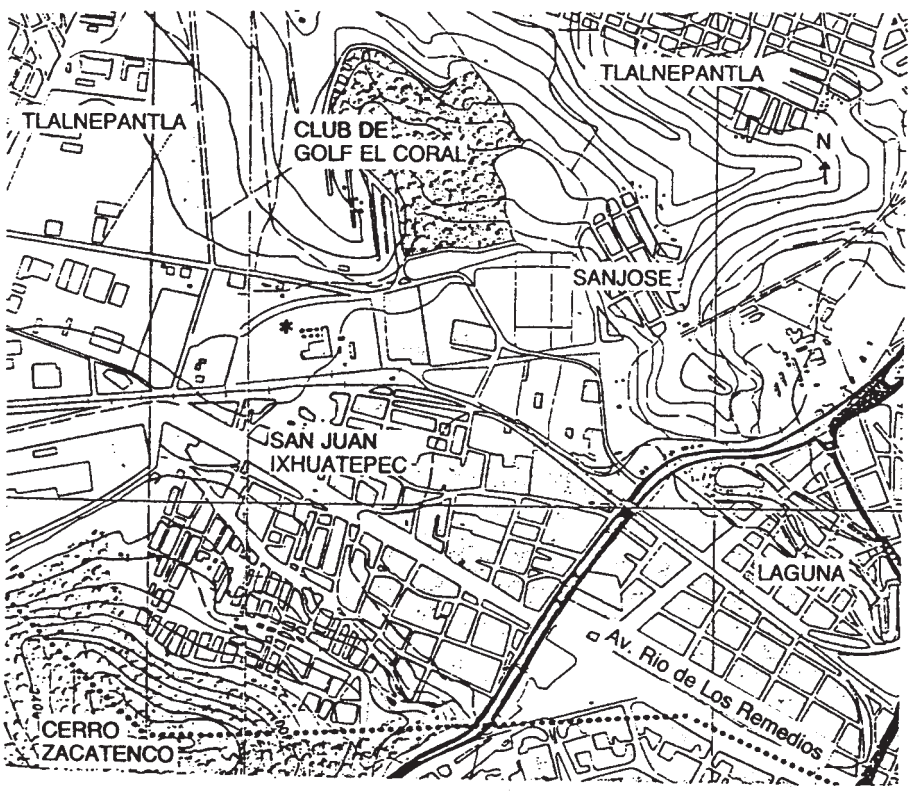

Figure A4.1 *Area plan of the PEMEX site at Mexico City (Pietersen 1985) (Courtesy of TNO)*

Figure A4.2 *PEMEX plant at Mexico City before the accident (Skandia, 1985) (Photograph: State of Mexico)*

Figure A4.3 *Growth of housing near the PEMEX plant at Mexico City (Pietersen 1985): (a) 1962; (b) 1972; (c) 1982 (Reproduced by permission of TNO.)*

Adjoining the PEMEX plant there were distribution depots owned by other companies. The Unigas site was some 100–200 m to the north and contained 67 tank trucks at the time of the accident. Rather further away was the Gasomatico site with large numbers of domestic gas cylinders.

A4.2 The Fire and Explosion – 1

Early in the morning of 18 November, the plant was being filled from a refinery 400 km away. The previous day the plant had become almost empty and refilling started during the afternoon. The two larger spheres and the 48 cylindrical vessels had been filled to 90% full and the four smaller spheres to about 50% full, so that the inventory on site was about 11,000 m^3, when the incident began.

About 5.30 a.m. a fall in pressure was registered in the control room and also at a pipeline pumping station 40 km distant. An 8 in. pipe between sphere F4 and the Series G cylinders had ruptured.

The control room personnel tried to identify the cause of the pressure fall but without success.

The release of LPG continued for some 5–10 min. There was a slight wind of 0.4 m/s. The wind and the sloping terrain carried the gas towards the south-west. People in the nearby housing heard the noise of the escape and smelled the gas.

When the gas cloud had grown to cover an area, which eyewitnesses put at 200×150 m with a height of 2 m, it found the flare and ignited. It was 5.40 a.m. The cloud

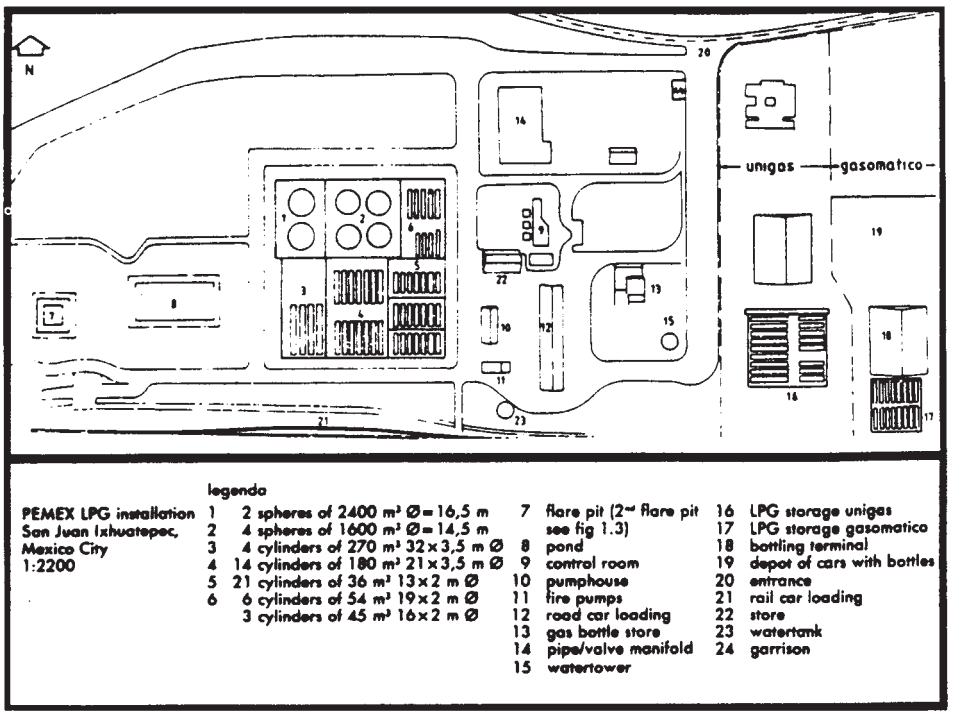

Figure A4.4 *Layout of the PEMEX site at Mexico City (Pietersen 1985) (Courtesy of TNO)*

caught fire over a large area, giving a high flame and causing violent ground shock.

When this general fire had subsided, there remained a ground fire, a flame at the rupture and fires in some 10 houses.

Workers on the plant now tried to deal with the escape. One drove off to another depot to summon help. Five others who may have been on their way to the control room or to man fire pumps were found dead, and badly burned. At a late stage someone evidently pressed the emergency shut-down button.

In the neighbouring housing some people rushed out into the street, but most stayed indoors. Many thought it was an earthquake.

At 5.45 a.m. the first BLEVE occurred. About a minute later another explosion occurred, one of the two most violent during the whole incident. One or two of the smaller spheres BLEVEd, giving a fireball 300 m diameter.

A rain of LPG droplets fell on the area. Surfaces covered in the liquid were set alight by the heat from fireballs. People burned like torches.

There followed a series of explosions as vessels suffered BLEVE. There were some 15 explosions over a period of an hour and a half. BLEVE occurred of the four smaller spheres and many of the cylindrical vessels.

The explosions during the incident were recorded on a seismograph at the University of Mexico. The timing of the readings is shown in Table A4.2 Section A. As the footnote indicates, it is suggested by Skandia that the initial explosion, or violent deflagration, was probably not recorded.

The damage caused is shown in Figure A4.5, which shows the area of main housing damage and the fall of

Table A4.2 *Timetable of events at Mexico City*

A Seismograph readings

1	5 h	44 min	52 s	6	6 h	49 min	38 s
2	5 h	46 min	01 s	7	6 h	54 min	29 s
3	6 h	15 min	53 s	8	6 h	59 min	22 s
4	6 h	31 min	59 s	9	7 h	01 min	27 s
5	6 h	47 min	56 s				

Disturbances 2 and 7 were the most intence with a Richter scale intensity of 5 Skandia suggest that the first violent combustion may not have been recorded.

B General timetable

5.30	Rupture of 8 in. pipe. Fall of pressure in control room
5.40	Ignition of gas cloud. Violent combustion and high flame
5.45	First explosion on seismograph, a BLEVE Fire department called
5.46	Second BLEVE, one of most violent
6.00	Police alerted and civilian trafffic stopped
6.30	Traffic chaos
7.01	Last explosion on seismograph, a BLEVE
7.30	Continuing tank explosions[a]
11.00	Last tank explosion
8.00–10.00	Rescue work at its height
12.00–18.00	Rescue work continues
23.00	Flames extinguished on last large sphere

[a] Explosions of cylindrical vessels.

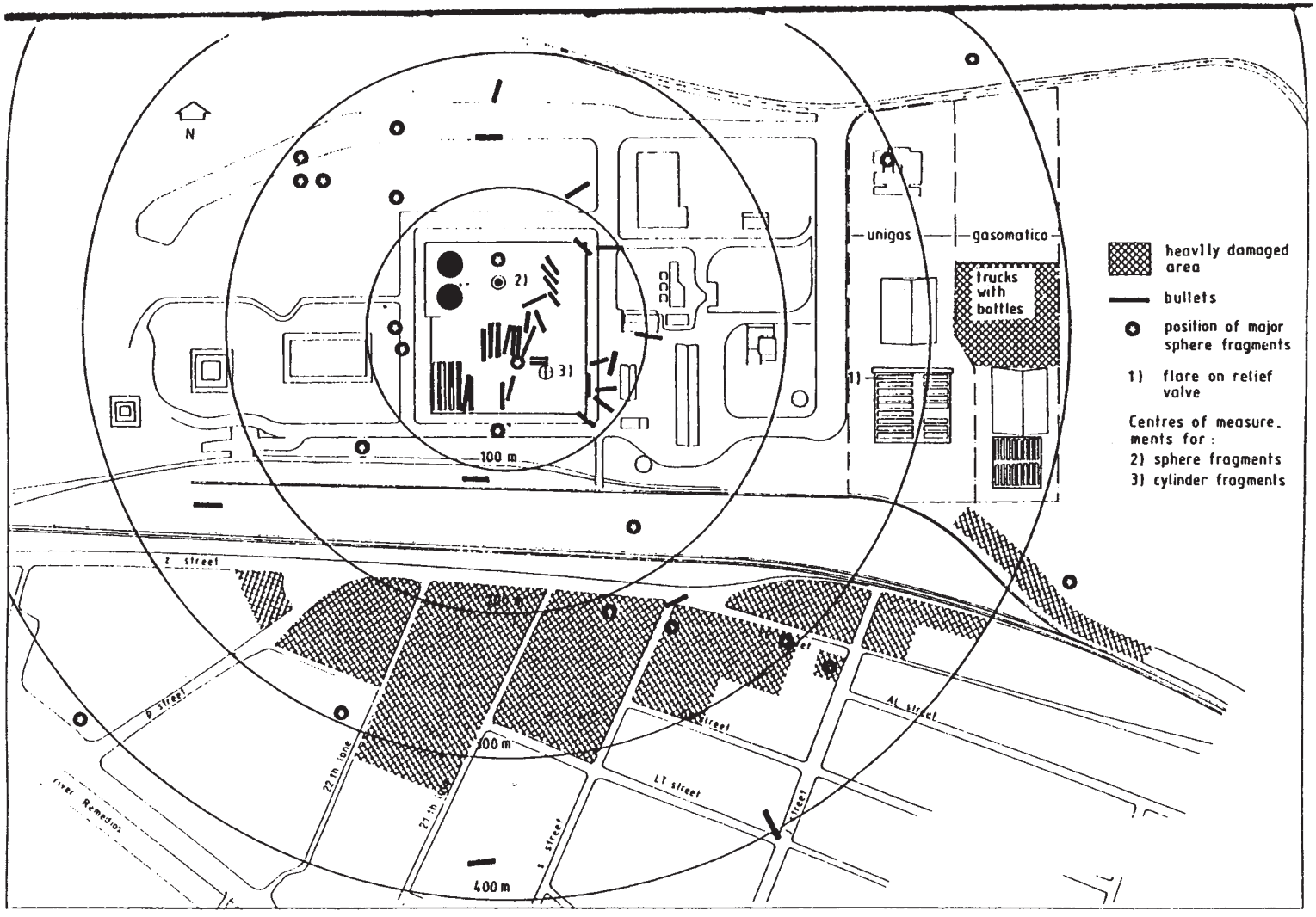

Figure A4.5 *Area plan of the PEMEX site at Mexico City, showing damage to housing area and fall of missiles (Pietersen 1985) (Courtesy to TNO)*

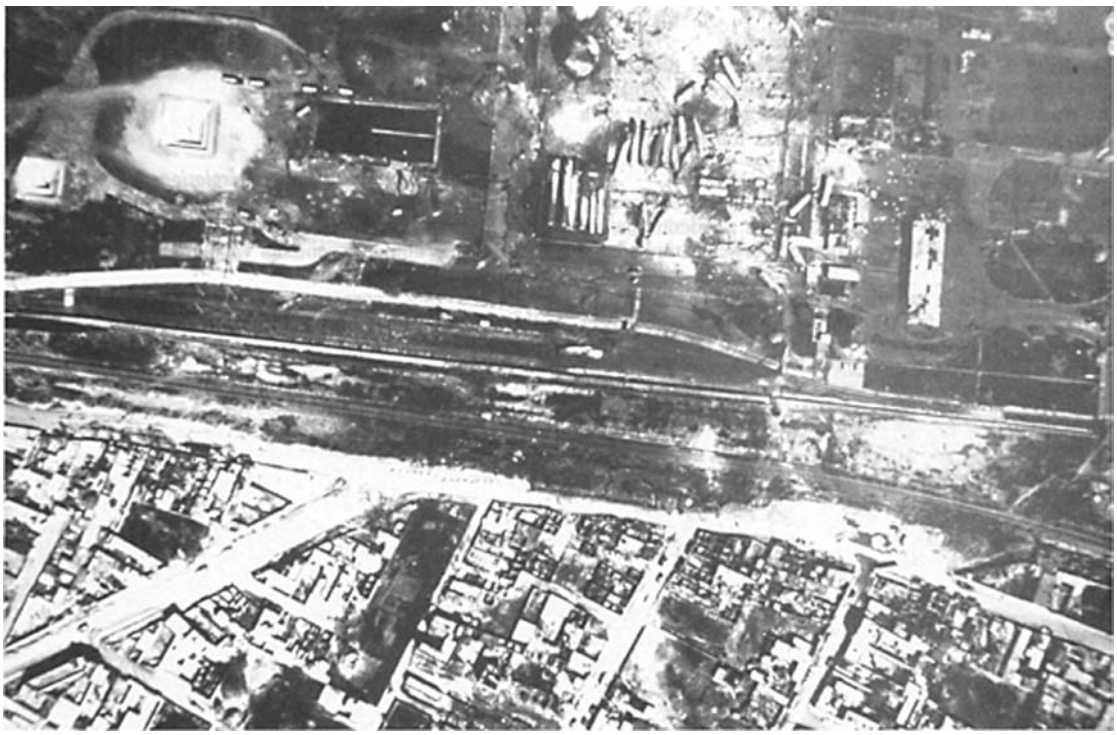

Figure A4.6 *PEMEX site at Mexico City after the accident (Skandia, 1985) (Photograph: State of Mexico)*

missiles. An aerial photograph of the plant after the disaster is shown in Figure A4.6.

Numerous missiles were generated by the bursting of the vessels. Many of these were large and travelled far. Twenty-five large fragments from the four smaller spheres weighing 10–40 te were found 100–890 m away. Fifteen of the 48 cylindrical vessels weighing 20 te became missiles and rocketed over 100 m, one travelling 1200 m. Four cylinders were not found at all. The missiles caused damage both by impact and by their temperature, which was high enough to set houses alight.

When the fire began, people were already on their way to work. Eyewitnesses spoke of a huge hot, red light, intense heat, smoke and lack of air, blast waves and missiles. The following account by Nicanor Santiago, a mason, is typical:

> Around 5.30 a.m. I went to work. It was still dark when I took my bicycle out of the house, when suddenly there was this huge light, red and hot. I could see nothing at all. The huge light blinded me. I could not feel anything except that everything was hot. Then I heard some explosions and a second blast. The walls of my house were rocking, it was an earthquake. I was lying on the pavement and close to me all sorts of matter came falling out of the sky. There was a lot of broken glass, chairs and flower pots were flying all over the place. I suddenly remembered the PEMEX gas plant and I saw a big tongue of fire and a very big orange mushroom, and then a felt another explosion. Pieces of molten metal were dropping out of the sky and I felt intense heat waves burning my clothes and my hair. I ran into the bedroom, everything was dark inside and there was plenty of smoke. I could not see anything. I could not breathe for the gas. I noticed something huge fell on top of the house and a rush of air threw me out of the house into the street. By then I was really frightened and I started to run as fast as I could. I do not know where my wife and children got to. They may even be unidentified in a mass grave.

A timetable of events during the disaster is given in Table A4.2, Section B.

A4.3 The Emergency

Accounts of the emergency give little information about the response of the on-site management in the emergency and deal mainly with the rescue and firefighting.

The site became the scene of a major rescue operation which reached a climax in the period 8.00–10.00 a.m. Some 4000 people participated in rescue and medical activities, including 985 medics, 1780 paramedics and 1332 volunteers. At one point there were some 3000 people in the area. There were 363 ambulances and five helicopters involved.

The rescuers were at risk from a large BLEVE. The Skandia report states: 'If a BLEVE had occurred during the later morning, a large number of those 3,000 people who were engaged in rescue and guarding would have been killed.'

The fire services were called by surrounding plants and by individual members of the public about 5.45 a.m. They went into the plant area only 3 h after the start of the incident. Initially, they moved towards the Gasomatico site, where a sphere fragment had landed and started a fire, which caused the domestic gas cylinders to explode.

The fire brigade also fought the fire on the two larger spheres, which had not exploded. They were at appreciable risk from BLEVE of the spheres. In the event, however, these burnt themselves out. The last flames on the spheres went out about 11.00 p.m. Some 200 firemen attended the site.

A4.4 The Fire and Explosion – 2

The TNO report gives much technical information on the course of the disaster and on the fire and explosion phenomena which occurred during it.

It discusses the effects of explosions, including vapour cloud explosions, BLEVEs and physical explosions; the effects of fire engulfment and heat radiation; and the effects of missiles, including fragments from bullet tanks and spheres.

The report gives estimates of the overpressure from BLEVE of the principal vessels. It states that the degree of blast damage to housing was not great; that the vapour cloud explosion effects were not responsible for major damage; that the second explosion, a BLEVE, was the most violent and did damage houses; that the worst explosion damage was probably from gases which had accumulated in houses; and that much of the damage was done by fire.

Films were available for many of the BLEVEs, though not for the second, violent explosion. From this evidence, the BLEVEs had diameters of 200–300 m and durations of some 20 s. Heavy direct fire damage was done at distances up to about 300 m, which agrees reasonably well with the estimates of fireball size.

A very large fire burned on the site for about an hour and a half, punctuated by BLEVEs. Details are given of the number, size and range of fragments from spheres and bullet tanks. Information on BLEVEs and missiles in the TNO report is given in Chapters 16 and 17.

A4.5 Some Lessons of Mexico City

Some of the lessons to be learned from Mexico City are listed in Table A4.3.

Table A4.3 *Some lessons of Mexico City*

Siting of major hazard installations
Layout of large LPG storages
Gas detection and emergency isolation
Planning for emergencies
Fire fighting in BLEVE situations
Boiling liquid expanding vapour explosions

Siting of major hazard installations

The high death toll at Mexico City occurred because the housing was too near to the plant. At the time the plant was constructed the area was undeveloped, but over the years the built-up area had gradually crept up to the site.

Layout and protection of large LPG storages

The total destruction of the facility occurred because there was a failure of the overall system of protection, which includes layout, emergency isolation and water spray systems.

Gas detection and emergency isolation

One feature which might have averted the disaster is more effective gas detection and emergency isolation. The plant had no gas detector system and, probably as a consequence, emergency isolation was too late.

Planning for emergencies

One particularly unsatisfactory aspect of the emergency was the traffic chaos which built up as residents sought to flee the area and the emergency services tried to get in.

Another was risk run by the large number of rescuers who came on site from a BLEVE of one of the larger spheres.

Fire fighting in BLEVE hazard situations

The fire services appear to have taken a considerable a risk in trying to fight the fire on the two larger spheres. The potential death toll if a BLEVE had occurred was high.

Boiling liquid expanding vapour explosions

After Flixborough the problem of vapour cloud explosions received much attention. Mexico City demonstrates that boiling liquid expanding vapour explosions are an equally important hazard.

Mexico City represents the largest series of major BLEVEs which has occurred and provides much information on these.

Appendix 5 Bhopal

Contents

A5.1 The Company and the Management A5/2
A5.2 The Site and the Works A5/2
A5.3 The Process and the Plant A5/2
A5.4 MIC and Its Properties A5/4
A5.5 Events Prior to the Release A5/4
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A5.7 The Emergency and the Immediate Aftermath A5/7
A5.8 The Investigations A5/7
A5.9 The Late Aftermath A5/8
A5.10 Some Lessons of Bhopal A5/8

Early in the morning of 3 December 1984, a relief valve lifted on a storage tank containing highly toxic methyl isocyanate (MIC) at the Union Carbide India Ltd (UCIL) works at Bhopal, India. A cloud of MIC gas was released onto housing, including shantytowns, adjoining the site.

Close on 2000 people died within a short period and tens of thousands were injured. The casualty figures are discussed further in Section A5.9.

The accident at Bhopal is by far the worst disaster which has ever occurred in the chemical industry. Its impact has been felt worldwide, but particularly in India and the United States.

Following the accident the Government of India (GoI) set up an inquiry which reported at the end of 1985 (Varadarajan, 1985). An investigation was conducted by the US parent company the Union Carbide Corporation (UCC), which issued its own report (the *Union Carbide Report*) (Union Carbide, 1975). Another investigation was carried out by the ICFTU-ICEF (1985). In its initial investigation, Union Carbide had limited access to documents and personnel, and it subsequently caused to be published further findings (Kalelkar, 1988). These investigations are described in Section A5.8.

Besides the investigations mentioned, other accounts have been given in Bhopal. *Anatomy of a Crisis* by Shrivastava (1987) and by Badhwar and Trehan (1984), Bhushan and Subramanian (1985), Bowonder (1985, 1987, 1988), Bowonder and Miyake (1988), Kalelkar (1988), Kletz (1988h), van Mynen (1990) and Bowonder, Arvind and Miyake (1991).

Selected references on Bhopal and MIC are given in Table A5.1.

A5.1 The Company and the Management

Union Carbide began operations in India in 1904 and by 1983 had 14 plants operating in the country. Its Indian interests were held by UCIL. UCIL was owned 50.9% by the American parent company UCC and 49.1% by Indian investors. UCC thus retained a majority share, having persuaded the Indian government to waive its usual requirement for Indian majority shareholding, on the basis of the technological sophistication of the plant and the export potential.

Table A5.1 *Selected references on Bhopal and MIC*

Anon. (1984h); Badhwar and Trehan (1984); Anon. (1985b–e,k,ff,gg,ii); Anon. (1985 LPB 63, p. l); Basta (1985); Basta *et al.* (1985); Bhushan and Subramanian (1985); Bowonder (1985, 1987); Bowonder, Kasperson and Kasperson (1985); Chowdhury *et al.* (1985); IBC (1985/59); ICFTU-ICEF (1985); Kharbanda (1985, 1988); Kletz (1985j,p, 1988h,n, 1990g, 1993b); Lepkowski (1985, 1986); Lihou (1985); Resen (1985a); Union Carbide Corp. (1985); Varadarajan (1985); Webber (1985, 1986); Anon. (1986b,l); Bellamy (1986); Bisset (1986); Shrivastava (1987); M.P. Singh and Ghosh (1987); Anon. (1988b,o); Bowonder and Miyake (1988); J. Cox (1988a); Emsley (1988); Kalelkar (1988a,b); Kharbanda (1988); V.C. Marshall (1988a); Sriram and Sahasrabuhde (1988, 1989); Tachakra (1988); van Mynen (1990); M.P. Singh (1990); Bowonder, Arvind and Miyake (1991); Narsimhan (1993)

Methyl isocyanate
Kimmerle and Eben (1964); ten Berge (1985)

UCIL began operations at Bhopal in 1969. Initially, the plant formulated carbamate pesticides from concentrates imported from the United States. In 1975, UCIL was licensed to manufacture its own carbaryl with the trade name Sevin. The process selected was the same as at the UCC plant at W.Virginia, but initially the MIC intermediate was imported from the latter source. Production began in 1979. The plant had a capacity of 5250 te/y, but the market was less than expected. Production peaked at 2704 te in 1981 and fell to 1657 te in 1983. At these levels of sales the plant had problems of profitability.

Prior to the accident, the management structure of UCIL changed and the Bhopal pesticides plant was put under the direction of the Union Carbide battery division in India.

A5.2 The Site and the Works

The location of the UCIL works at Bhopal is shown in Figure A5.1. The works was in a heavily populated area. Much of the housing development closest to the works had occurred since the site began operations in 1969, including the growth of the J.P. Nagar shantytown. Although these settlements were originally illegal, in 1984 the government gave the squatters rights of ownership on the land to avoid having to evict them. Other residential areas which were affected by the gas cloud had been inhabited for over 100 years.

A5.3 The Process and the Plant

In the process used at Bhopal, MIC was made using the reaction scheme shown in Figure A5.2. The process itself is shown in Figure A5.3. Monomethylamine (MMA) is reacted with excess phosgene in the vapour phase to produce methylcarbamoyl chloride (MCC) and hydrogen chloride and the reaction products are quenched in chloroform. The unreacted phosgene is separated by distillation from the quench liquid and recycled to the reactor. The liquid from the still is fed to the pyrolysis section where MIC is formed. The stream from the pyrolyser condenser passes as feed to the MIC refining still (MRS). MIC is obtained as the top product from the still. The MIC is then run to storage.

Phosgene was produced on site by reacting chlorine and carbon monoxide. The carbon monoxide was also produced on site.

The MIC storage system (MSS) consisted of three storage tanks, two for normal use (Tanks 610 and 611) and one for emergency use (Tank 619). The tanks were 8 ft diameter × 40 ft long with a nominal capacity of 15,000 USgal. They were made of 304 stainless steel with a design pressure of 40 psig at 121°C and with hydrostatic test pressure of 60 psig. A diagram of the storage tank system is shown in Figure A5.4.

A 30 ton refrigeration system was provided to keep the tank contents at 0°C by circulating the liquid through an external heat exchanger.

There was on each storage tank a pressure controller which controlled the pressure in the tank by manipulating two diaphragm motor valves (DMVs), a make-up valve to admit nitrogen and a blowdown valve to vent vapour. Each tank had a safety relief valve (SRV) protected by a bursting disc. It also had a high temperature alarm and low and high level alarms.

A vent gas scrubber (VGS) and a flare were provided to handle vented gases. The VGS was a packed column 5 ft 6 in.

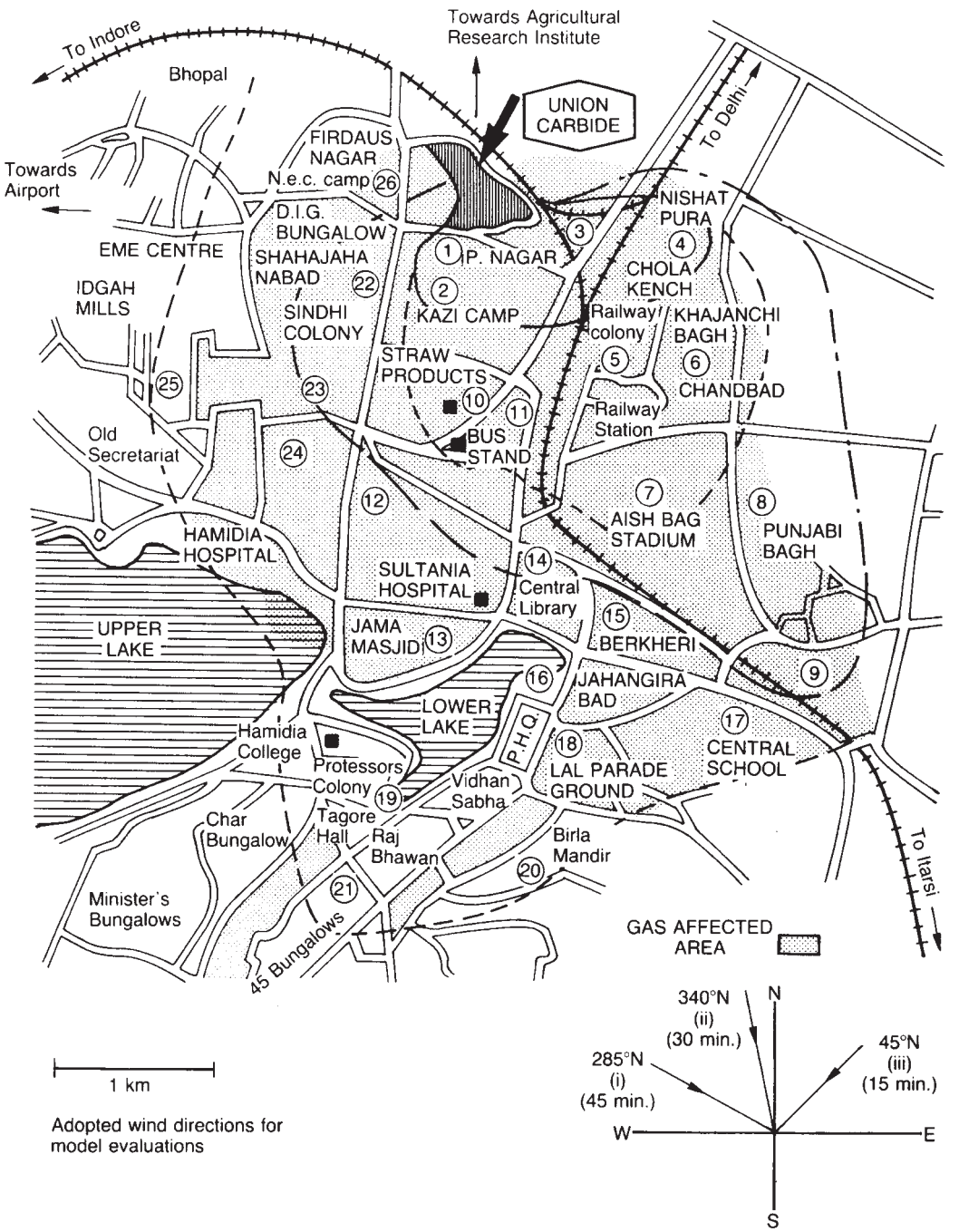

Figure A5.1 *Simplified plan of the area near the Union Carbide India Ltd works at Bhopal (M.P. Singh and Ghosh, 1987). The diagram also shows the estimated dimensions of the gas cloud (Courtesy of Elsevier Science Publishers)*

diameter in which the vent gases were scrubbed with caustic soda. There were two vent headers going into the column: the process vent header (PVH), which collected the MIC system vents, and the relief valve vent header (RVVH), which collected the safety valve discharges. Each vent header was connected both to the VGS and the flare and could be routed to either. The vent stack after the VGS was 100 ft (33 m) high. A diagram of the VGS is shown in Figure A5.5.

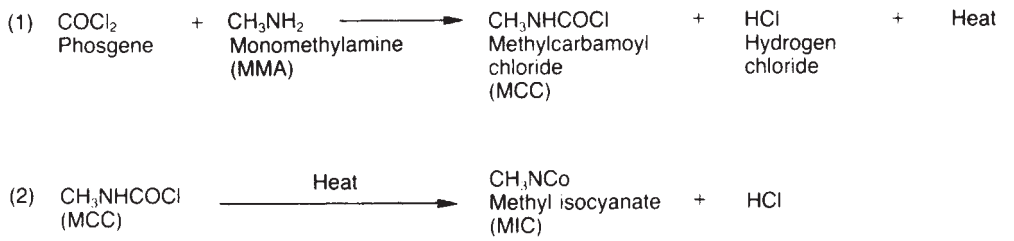

Figure A5.2 *Reaction scheme (Union Carbide, 1985. Reproduced by permission.)*

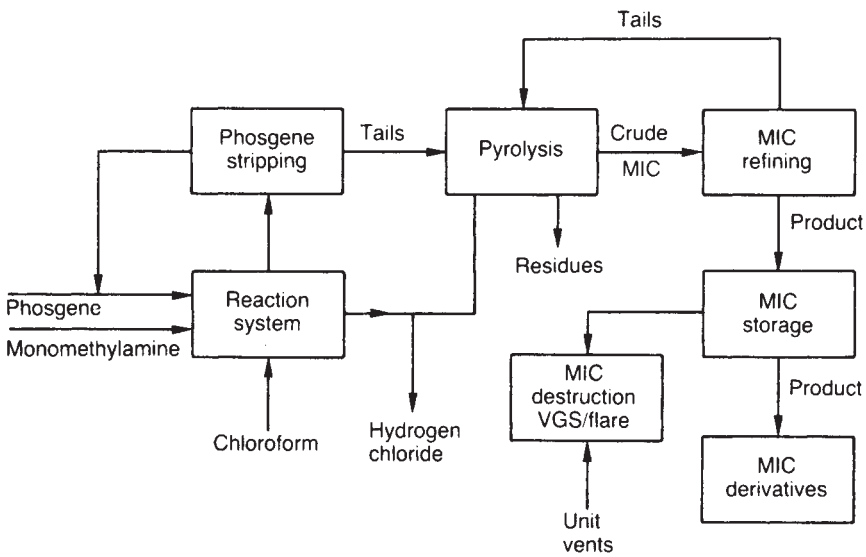

Figure A5.3 *Process for production of MIC (Union Carbide, 1985. Reproduced by permission.)*

The VGS had the function of handling process vents from the PVH and of receiving contaminated MIC, in either vapour or liquid form, and destroying it in a controlled manner.

The function of the flare was to handle vent gases from the carbon monoxide unit and the MMA vaporizer safety valve and also vent gas from the MIC storage tanks, the MRS and the VGS.

In the two years preceding, the number of personnel on site were reduced, 300 temporary workers being laid off and 150 permanent workers pooled and assigned as needed to jobs, some of which they said when interviewed they felt unqualified to do. The production team on the MIC facility was cut from 12 to 6.

A5.4 MIC and Its Properties

MIC is a colourless liquid with a normal boiling point of 39°C. It has a low solubility in water. It is relatively stable when dry, but is highly reactive and in particular can polymerize and will react with water. It is flammable and has a flashpoint of −18°C and a lower flammability limit of 6% v/v. It is biologically active and highly toxic.

The high toxicity of MIC is indicated by the fact that its TLV at the time was 0.02 ppm. This is very low relative to most typical compounds handled in industry.

MIC is an irritant gas and can cause lung oedema, but it also breaks down in the body to form cyanide. The cyanide suppresses the cytochrome oxidase necessary for oxygenation of the cells and causes cellular asphyxiation.

Information on the inhalation toxicity of MIC is given by Kimmerle and Eben (1964) and ten Berge (1985).

MIC can undergo exothermic polymerization to the trimer, the reaction being catalysed by hydrochloric acid and inhibited by phosgene. It also reacts with water, iron being a catalyst for this reaction. This reaction is strongly exothermic.

A5.5 Events Prior to the Release

In 1982, a UCC safety team visited the Bhopal plant. Their report gave a generally favourable summary of the visit, but listed ten safety concerns, including

> 3. Potentials for release of toxic materials in the phosgene/MIC unit areas and storage areas, either due to equipment failure, operating problems, or maintenance problems.
> 4. Lack of fixed water spray protection in several areas of the plant.
> 7. Deficiencies in safety valve and instrument maintenance program.

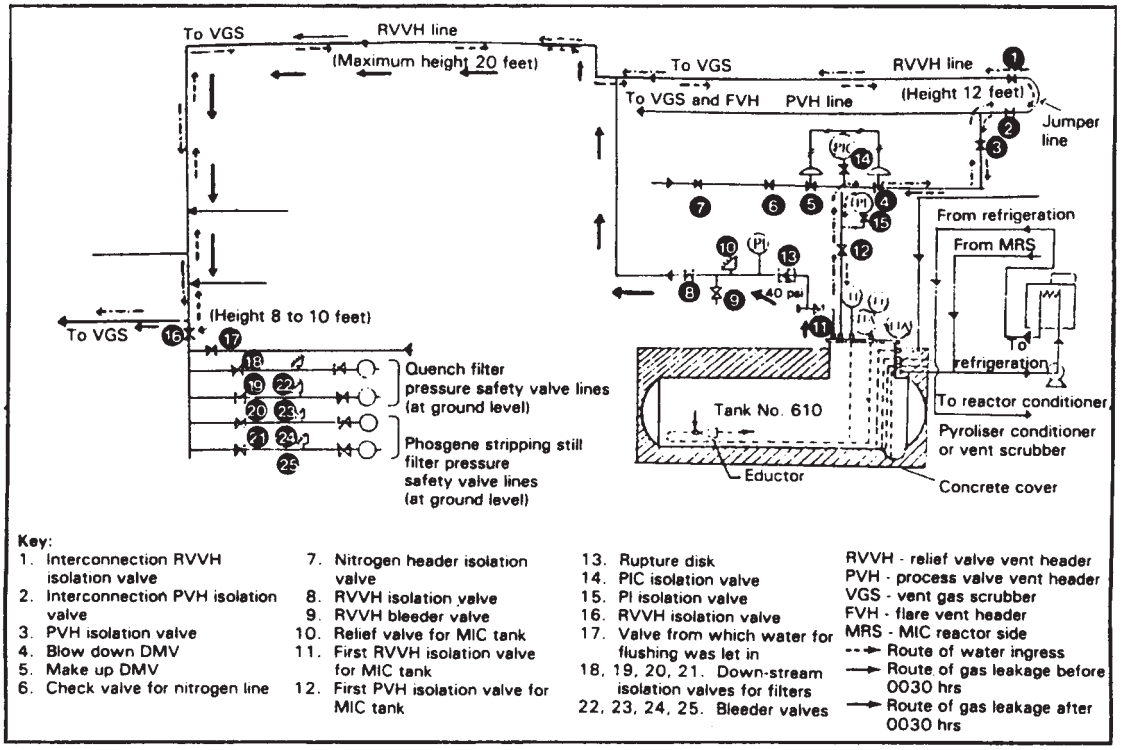

Figure A5.4 *Flow diagram of Tank 610 system (Bhushan and Subramanian, 1985) (Courtesy of Business India.)*

8. Deficiencies in Master Tag/Lockout procedure application.
10. Problems created by high personnel turnover at the plant, particularly in operations.

Following this visit valves on the MIC plant were replaced, but degraded again. At the time of the accident, the instruments on Tank 610 had been malfunctioning for over a year.

Between 1981 and 1984, there were several serious accidents on the plant. In December 1981, three workers were gassed by phosgene and one died. Two weeks later 24 workers were overcome by another phosgene leak. In February 1982, 18 people were affected by an MIC leak. In October 1982, three workers were injured and nearby residents affected by a leak of hydrochloric acid and chloroform.

Following this latter accident workers from the plant posted a notice in Hindi which read: 'Beware of fatal accidents . . . lives of thousands of workers and citizens in danger because of poison gas . . . Spurt of accidents in the factory, safety measures deficient'. These posters were also distributed in the community.

About a year before the accident, a 'jumper line' was connected between the PVH and the RVVH. Figure A5.4 shows the MIC storage tank and pipework arrangements. The jumper line is between Valves 1 and 2. The object of the modification was to allow gas to be routed to the VGS if repairs had to be done on one of the vent headers.

In June 1984 the 30 ton refrigeration unit cooling the MIC storage tanks was shut down. The charge of Freon refrigerant was drained from the system.

In October the VGS was turned off, apparently because it was thought unnecessary when MIC was only being stored not manufactured. In the same month, the flare tower was taken out of service, a section of corroded pipe leading to it being removed so that it could be replaced.

Another feature was that difficulty was being experienced in pressurizing MIC storage Tank 610. It appeared that since nitrogen was passing through the make-up valve satisfactorily, the blowdown valve was leaking and preventing pressurization.

According to plant workers there were other instrumentation faults. The high temperature alarm had long been faulty. There were also faults on the pressure controller and the level indicator.

The plant had a toxic gas alarm system. This consisted of a loud siren to warn the public and a muted siren to warn the plant. These two sirens were linked and could be activated from a plant toxic alarm box. The loud siren could be stopped from the control room by delinking the two. A procedure had been introduced according to which after delinking, the loud siren could be turned on only by the plant superintendent.

Plant workers stated that on the morning of 2 December washing operations were undertaken. Orders were given to flush out the downstream sections of four filter pressure safety valves lines. These lines are shown in Figure A5.4. In order to carry out this operation Valve 16 on the diagram

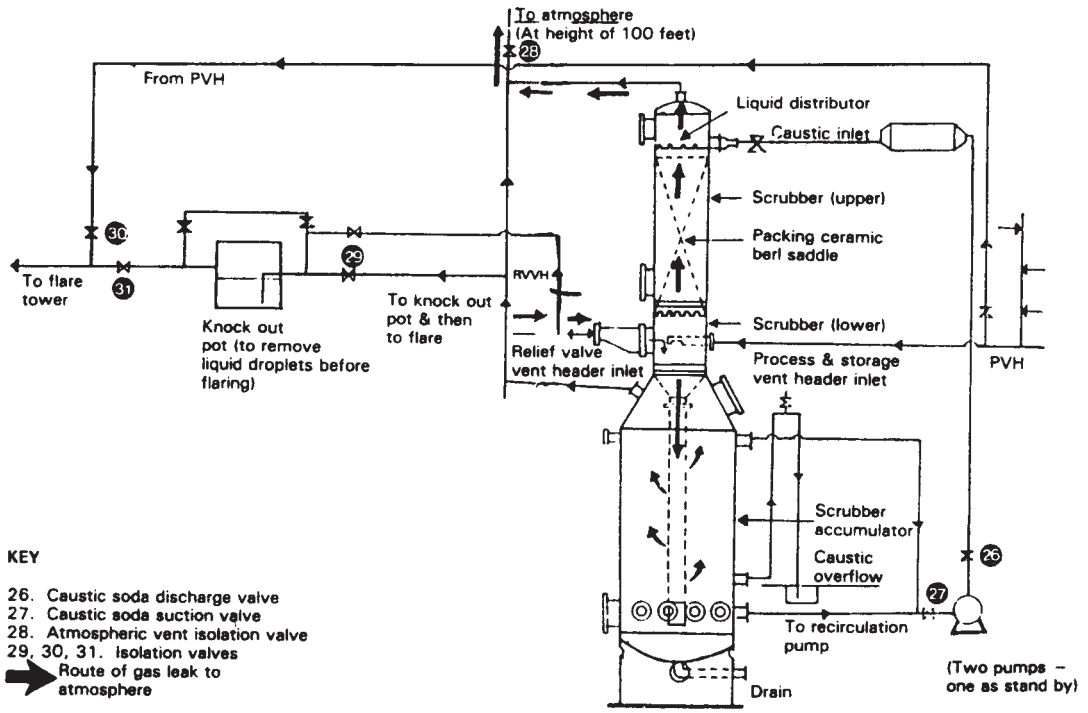

Figure A5.5 *Flow diagram of the vent gas scrubber system (Bhushan and Subramanian, 1985) (Courtesy of Business India)*

was shut, Valves 18–21 and 22–25 opened and then Valve 17 opened to admit water.

It was suggested water might have entered MIC storage Tank 610 as a result of this operation – the water washing theory. On this hypothesis, water evidently leaked through Valve 16, into the RVVH and passed through the jumper line into the PVH and thence into Tank 610. This would require that Valves 3 and 12 were open to connect the tank to the PVH and Valves 1 and 2 open to connect the RVVH to the PVH via the jumper line.

A5.6 The Release

On the evening of 2 December, a shift change took place on the plant at 22.45. At 23.00, the control room operator noticed that the pressure in Tank 610 was 10 psig. This was higher than normal but within the 2–25 psig operating pressure of the tank. At the same time the field operator reported a leak of MIC near the VGS. At 00.15, the field operator reported an MIC release in the process area and the control room operator saw that the pressure on Tank 610 was now 30 psig and rising rapidly. He called the supervisor and ran outside to the tank. He heard rumbling sounds coming from the tank and a screeching noise from the safety valve and felt heat from the tank. He returned to the control room and turned the switch to activate the VGS, but this was not in operational mode, the circulating pump not being on.

At 00.20, the production supervisor informed the plant superintendent of the release. At 00.45 operations in the derivative unit were suspended due to the high concentration of MIC.

At 01.00, an operator in this unit turned on the toxic gas alarm siren. After 5 min the loud siren was switched off leaving the muted siren on.

At about the same time the plant superintendent and control room operator verified that MIC was being emitted from the VGS stack to atmosphere and turned on and directed at the stack fixed fire water monitors to knock down the vapour.

Water was also directed at the MIC tank mound and at the vent header to the VGS. Steam issued from the cracks in the concrete showing that the tank was hot.

One plant supervisor tried to climb the structure to plug the gas leak but was overcome, falling and breaking both legs.

Some time between 01.30 and 02.30, the safety valve on Tank 610 reseated and the release of MIC ceased.

At about 02.30, the loud siren was switched on again.

The cloud of MIC gas spread from the plant towards the populated areas to the south. There was a light wind and inversion conditions.

People in the housing around the plant felt the irritant effect of the gas. Many ran out of their houses, some towards the plant. Within a short period, animals and people began to die.

At Railway Colony some 2 km from the plant, where nearly 10,000 people lived, it was reported that within 4 min 150 died, 200 were paralysed and 600 rendered unconscious and that 5000 were severely affected.

People tried to telephone the plant but were unable to get through. At 01.45, a magistrate contacted the plant superintendent.

The cloud of toxic gas hung around the area for the whole of 3 December. During the day, it stopped moving towards the city, but resumed its movement in that direction during the night.

A5.7 The Emergency and the Immediate Aftermath

Large numbers of people were affected by the toxic gas and very large numbers fled their homes.

The two hospitals principally concerned, the Hamidia and the Javaprakas Hospitals, were overwhelmed with casualties.

The difficulties were compounded by the fact that it was not known what the gas was or what its effects were. Speculation about the gas, including suggestions that it was phosgene, continued in the world press for some days.

The company provided little advice. Initially, it stated that MIC causes eye irritation but is not lethal.

As early as noon on 3 December, doctors at the Gandhi Memorial College carried out post-mortems which gave strong evidence of cyanide poisoning. Victims had died of respiratory arrest, but there was no evidence of the cyanosis due to the deoxygenation of the blood which normally accompanies pulmonary asphyxiation and there were cases where there was no evidence of pulmonary oedema.

There developed a conflict of views on the appropriate treatment. The standard treatment for cyanide poisoning is sodium thiosulfate. One group took the view that this should not be given until cyanide poisoning was established by analyses, another argued that it was well known that in cyanide poisoning the cyanide may be metabolized, leaving little trace. There followed a period in which the advice given was not clear. It was not until 3 February that an authoritative and unambiguous recommendation that sodium thiosulfate be used was issued by the Indian Council for Medical Research.

The Indian Central Bureau of Investigation (CBI) took control of the site and began a criminal investigation.

A5.8 The Investigations

A5.8.1 Government of India investigation

An investigation of the incident was undertaken by the GoI. It issued in December 1985, the *Report on Scientific Studies on the Factors Related to Bhopal Toxic Gas Leakage* by a team chaired by Varadarajan (1985).

The report refers to the fact that it was reported that about 21.30 on 2 December an operator was clearing a possible choke in the RVVH lines downstream of the phosgene stripping still filters by water flushing, without inserting a blind. The 6 in. isolation valve on the RVVH would presumably be closed but if it had not been leaktight, water could enter the RVVH. This water could have found its way into the Tank 610 via the blowdown DMV or through the SRV and bursting disc.

A5.8.2 Union Carbide investigation – 1

A team from UCC arrived in Bhopal on 6 December charged with the tasks of assisting in the safe disposal of the remaining MIC and investigating the accident. The first task was completed on 22 December and the team returned home on 2 January.

The investigation was severely constrained by the CBI control of the site and by the criminal investigation. The team were allowed only limited access to plant records and personnel. They were permitted to talk to certain persons, but not to interview staff directly involved in the incident. They were allowed to take samples from Tank 610, but not to open and inspect the tank and its piping or to take samples from elsewhere on the plant. An account of the situation is given by Kalelkar (1988b).

On their return home, the investigators carried out a programme of some 500 experiments to establish what had occurred. The most abundant component in the residues was MIC trimer, others present in significant quantities being the components conveniently referred to as DMI, DMU, TMU, TMB and TRMB. There were also iron, chromium and nickel in approximately their proportions in 304 stainless steel and some 5% chloride.

Trimerization had obviously occurred, but it was unclear what other reactions had taken place. The investigators carried out experiments in which the principal materials believed to have been in the tank, namely MIC, chloroform, water and iron, were heated at 200°C and developed a reaction scheme which accounted for the production, starting from these materials, of the components found in the residue with the exception of TRMB, which they considered they could account for.

From plant records, Tank 610 contained prior to the incident 41 te (90,400 lb; 11,290 USgal) of liquid. The team estimated that Tank 610 had originally contained 1000–2000 lb (120–240 USgal) water and 1500–3000 lb chloroform. The source of the water was uncertain. The chloroform could be accounted for by the fact that the MRS had been operated at a temperature higher than normal and in preparation for shutdown MIC with a high chloroform content has been sent to Tank 610 rather than Tank 619. The iron could have come from corrosion, given high chloroform and water contents and high temperature.

The scenario which the investigators invoked to explain the events is as follows. The contents of Tank 610 were initially at 15–20°C. Some 1000–2000 lb water entered the tank in a manner unknown. The exothermic reaction between MIC and water led to an increase in temperature and also in pressure due to evolution of carbon dioxide. The higher temperature and presence of chloroform caused accelerated corrosion. The iron thus produced catalysed the exothermic trimerization of MIC.

Calculations showed that reaction of some 40% of the MIC would generate enough heat to vaporize the rest. This would give some 36,000 lb of solids in the tank, but only an estimated 10,000 lb were found. There may have been appreciable loss of solids and liquid through the relief vent.

The period during which the relief valve was open was reported to have been about 2 h. It was calculated that in order to vent most of the tank contents in this time the discharge rate would have had to be 40,000 lb/h, of which 29,000 lb/h were vapour and 11,000 lb/h solids/liquid mixture and that this would have required a pressure averaging 180 psig. The temperature reached was estimated as in excess of 200°C. These conditions would have been attained during the course of the venting. With the safety valve lifting at 40 psig the initial discharge would have been 10,000 lb/h.

The report puts forward the hypothesis that the water was directly introduced into Tank 610, either inadvertently or deliberately through the process vent line, nitrogen line or other piping. It refers to the washing operation on the filter pressure safety valve lines and states that this section of line had not been isolated using a blind, but that passage

of water to Tank 610 through several reportedly closed valves is unlikely.

The report draws attention to a number of factors which contributed to the accident. These include the facts that refrigeration had been discontinued, that a blind was not used to isolate the lines being washed out, that the MRS was operated at a higher than normal temperature, that the VSG did not work and that the flare was out of commission.

At the press conference held to present the report, the UCC spokesman suggested that the water may have come from a nearby utility station which supplied water and nitrogen to the area: 'If someone had connected tubing to the water line instead of the nitrogen line, either deliberately or intending to introduce nitrogen into the tank, this could account for the presence of the water. . .'. The press interpreted this as a suggestion by UCC that the cause of the accident was sabotage. Subsequently UCC agreed that there was no direct evidence for this hypothesis.

A5.8.3 Union Carbide investigation – 2

Following the involvement of the Indian Government in litigation in the US courts, UCC was allowed access to personnel who had been involved on the plant and was able to gather evidence in support of its original hypothesis. An account of this extension of the UCC investigation is given by Kalelkar (1988b).

Against the water washing hypothesis he makes the following points. First, the water was introduced through a $\frac{1}{2}$ in. inlet (Valve 17). The difference in head between this point and the inlet to Tank 610 was some 10.4 ft. There were three open bleeder valves close to the inlet point which would limit the backpressure of water to 0.7 ft. Second, there were a number of valves between the inlet point and the tank and for water to pass these would have had to be open or not leak-tight. One of these valves, close to the inlet point, had been shut since 29 November 1984. It was given a one-hour test during which no water leaked through it. Third, for water to reach Tank 610 it would have had to fill the 6 in. diameter connecting pipe, 65 ft of 8 in. RVVH, with numerous branches running off, and then some 340 ft of 4 in. RVVH. The amount of water to do this was estimated as 4500 lb. On 8 February 1985, the CBI ordered a hole to be drilled in the lowest point of the PVH. For the hypothesis to hold this section, which had no bleeders or flanged joints, should have been full of water; it was completely dry.

In support of the hypothesis of direct entry of water into Tank 610 the arguments presented by Kalelkar may be summarized as follows. First, an instrument supervisor, not on duty that night, stated that he had found the local pressure indicator on the tank missing; this was one of the few points to which a water hose could be connected. Second, a water hose was found nearby. Third, there was evidence that the operators had become aware earlier in the evening that water had entered Tank 610 and had taken steps to deal with the situation. Fourth, the plant logs showed evidence of extensive tampering and alteration.

The plant could be supplied with MIC from Tank 610 or Tank 611, the MIC being passed to a one ton tank, the Sevin charge pot. There were difficulties with the pressure in Tank 610 and the transfers had been made from Tank 611. However, investigation showed that the MIC in the Sevin charge pot contained water. It had evidently come from Tank 610. Water is heavier than MIC and Tank 610 had a bottom offtake. The hypothesis is that the operators, aware that water had got into Tank 610 and wishing to remove it, on this occasion drew the MIC from that tank rather than from Tank 611.

Kalelkar suggests that the addition of water to Tank 610 may have been the act of a disgruntled employee.

A5.9 The Late Aftermath

The precise numbers of the dead and injured at Bhopal are uncertain. The scale of the accident was such that it led to much confusion. People have continued to die of the effects over a period of years. The official Indian Government estimate of the death toll about 2 years after the event was 1754. By 1989, this had risen to 3150 and by 1994 to 4000. Other figures given are 30,000 permanently or totally disabled; 20,000 temporary cases; and 50,000 with minor injury.

The ICFTU-ICEF report in 1985 states that the number of people treated in the state hospitals had been given by Dr Nagu, the Director of Health Services for Madhya Pradesh, as approximately 170,000. Some 130,000 were treated in Bhopal hospitals, mainly for lung and eye injuries, and some 40,000 in 22 other districts. Some 12,000 of the 170,000 were in a critical condition and 484 died. He estimated the total number of dead as 2000.

The disaster led to various sets of court proceedings. The GoI instituted criminal proceedings against UCC, which at the time of writing remain extant. The GoI also became a party to proceedings in the US courts. In 1987, UCC made a 'final settlement' with the GoI of $470 million. Victims tried to challenge this in the US courts, but the US Supreme Court ruled that they lacked legal standing to do so.

A5.10 Some Lessons of Bhopal

A5.10.1 Some lessons

The lessons to be learnt from Bhopal are numerous. A list of some of them is given in Table A5.2. They combine many of the lessons of Flixborough and Seveso.

Some of these lessons are now considered:

Public control of major hazard installations

The disaster at Bhopal received intense publicity for an extended period and put major hazards on the public agenda worldwide, but particularly in India and the United States, which had not reacted so strongly to Flixborough and Seveso, whose impact had been felt most in Europe.

Table A5.2 *Some lessons of Bhopal*

Public control of major hazard installations
Siting of and development control at major hazard installations
Management of major hazard installations
Highly toxic substances
Runaway reactions in storage
Water hazard in plants
Relative hazards of materials in process and in storage
Relative priority of safety and production
Limitation of inventory in the plant
Set pressure of relief valves
Disabling of protective systems
Maintenance of plant equipment and instrumentation
Isolation procedures for maintenance
Control of plant and process modifications
Information for authorities and public
Planning for emergencies

Siting of and development control at major hazard installations

Very large numbers of people were at risk from the plant at Bhopal. This situation was due in large part to the encroachment of the shantytowns, which came up to the site boundary. Although these settlements were illegal, the Indian authorities had acquiesced in them.

In this instance, however, this was not the whole story. The accident showed that site was close enough to areas populated before the plant was built to present a hazard when used for the production of a chemical as toxic as MIC. If the manufacture of such a chemical was envisaged from the start, the problem may be regarded as one of siting. If not, it may be viewed as one of intensification of the hazard on the site.

Management of major hazard installations

The plant at Bhopal was by any standards a major hazard and needed to be operated by a suitable competent management. The standards of operation and maintenance do not give confidence that this was so.

There had been recent changes in the responsibility for the plant which suggest that the new management may not have been familiar with the exigencies of major hazards operation. However, many of the problems on the plant appear to have antedated these changes.

Highly toxic substances

MIC is a highly toxic substance, much more toxic than substances such as chlorine which are routinely handled in the chemical industry. The hazard from such highly toxic substances has perhaps been insufficiently appreciated.

This hazard will only be realized if there is a mechanism for dispersion. At Bhopal, this mechanism was the occurrence of exothermic reactions in the storage tank.

Runaway reaction in storage

The hazard of a runaway reaction in a chemical reactor is well understood, but that of such a reaction in a storage tank had received little very attention. At Bhopal, this occurred due to ingress of water. Where such a reaction could act as the mechanism of dispersion for a large inventory of a hazardous substance, the possibility of its occurrence should be carefully reviewed.

Water hazard in plants

In general terms, the hazard of water ingress into plants is well known. In particular, water may contact hot oil and vaporize with explosive force or may cause a frothover, it may corrode the equipment and it may cause a blockage by freezing. Bhopal illustrates the hazard of an exothermic reaction between a process fluid and water.

Relative hazard of materials in process and in storage

There has been a tendency to argue that the risks from materials in storage are less than from materials in process, since, although usually the inventories in storage are larger, the probability of a release is much less. The release at Bhopal was from a storage tank, albeit from one associated with a process.

The relative hazard of materials in process and in storage is discussed Chapter 22.

Relative priority of safety and production

The features which led to the accident have been described above. As indicated, the *Union Carbide Report* itself refers to a number of these.

The ICFTU-ICEF report states that at the time of the accident the plant was losing money and lists a number measures which had been taken, apparently to cut costs. These include the manning cuts and the cessation of refrigeration.

Limitation of inventory in the plant

The hazard at Bhopal was the large inventory of highly toxic MIC. The process was the same as that used at UCC's W. Virginia plant. UCIL had stated that it regarded this inventory as undesirable, but was overruled by the parent company, which wished to operate the same process at both plants.

Processes are available for the manufacture of MIC which require only small inventories of the material. Moreover, carbaryl can be made by a route which does not involve MIC. The alternatives to the use of MIC are discussed by Kletz (1988h).

Set pressure of relief devices

It is desirable from the operational viewpoint for the set pressure of a relief valve to be such that the valve opens when the pressure rise threatens the integrity of the vessel but not when normal minor operating pressure deviations occur. Where the cause of potential pressure rise is a runaway reaction, however, there is a penalty in setting a high set pressure in that this may allow the reaction to reach a higher temperature and to proceed more rapidly before venting starts, so that there is a need to balance these two factors.

Disabling of protective systems

It was evidently not appreciated that the flare system was a critical component for the protection of the plant, since it was allowed to remain out of commission for the 3 months prior to the accident. It is essential that there be strict procedures for the disabling of any item which is critical for protection and that the time for which the item is out of action be kept to a minimum.

Maintenance of plant equipment and instrumentation

The 1982 UCC safety team drew attention to the problems in the maintenance of the plant. The *Union Carbide Report* gives several examples of poor maintenance of plant equipment and instrumentation and the ICFTU-ICEF report gives further details. Workers stated that leaking valves and malfunctioning instruments were common throughout the plant.

Maintenance was also very slow. The flare system, which was a critical protective system, had been out of commission for three months before the accident.

Isolation procedures for maintenance

A particular deficiency in the maintenance procedures was the failure to isolate properly the section of plant being flushed out by positive isolation using a slip plate or equivalent means. The fact that the water may not have entered in this way does not detract from this lesson.

Control of plant and process modifications

A principal hypothesis to explain the entry of water into Tank 610 is that the water passed through the jumper line. The installation of this jumper line was a plant modification. Company procedures called for plant modifications

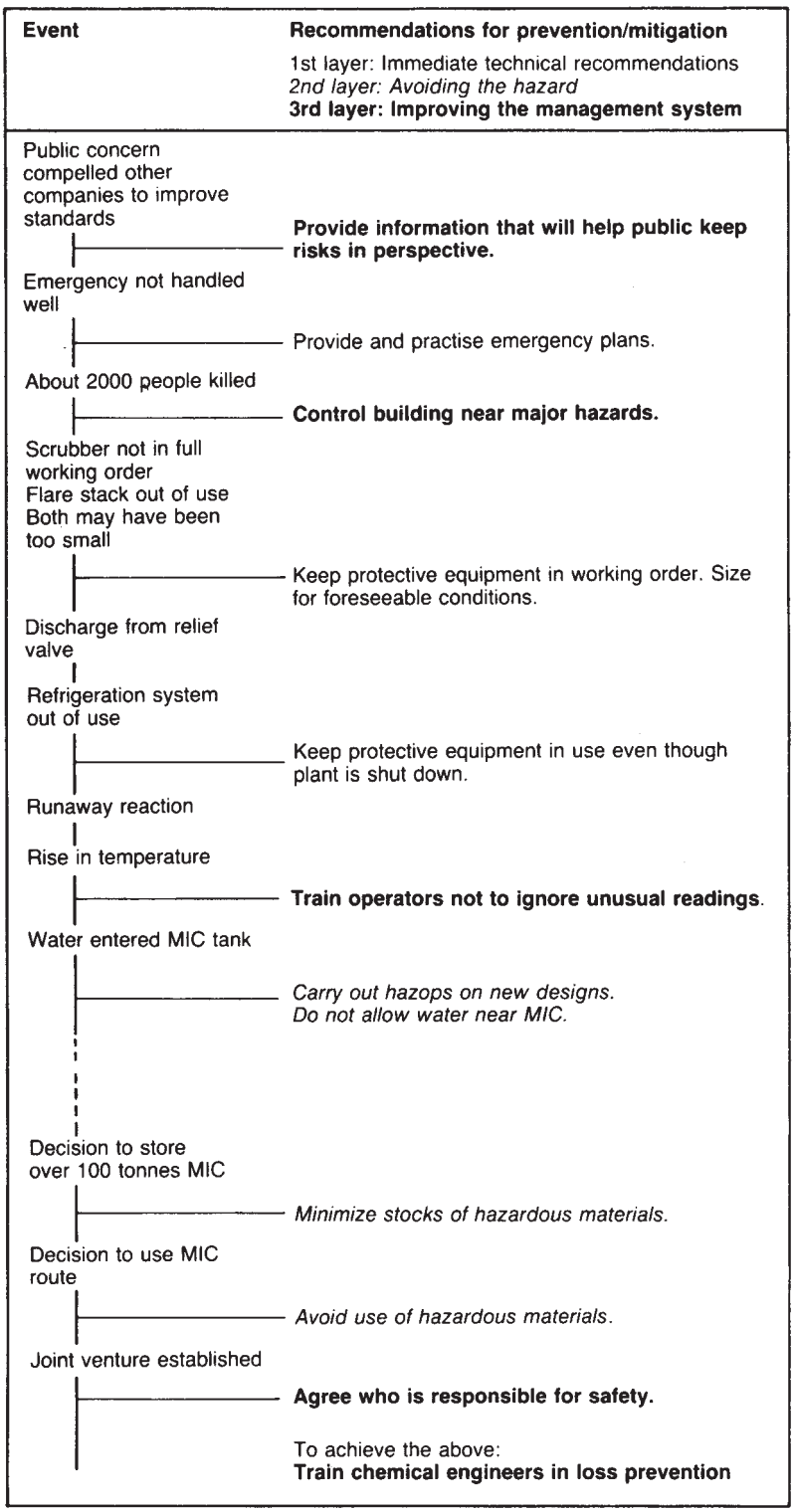

Figure A5.6 *An accident model for Bhopal, showing critical events and recommendations (Kletz, 1988h) (Courtesy of Butterworths)*

to be checked by the main office engineers, but were evidently disregarded.

There was also a process modification which more certainly contributed to the accident. This is the decommissioning of the refrigeration system, so that the temperature in Tank 610 was higher than the 0°C for which the system was designed.

Information for authorities and public

UCIL had not provided full information on the substances on site to the authorities, emergency services, workers or members of the public exposed to the hazards. Many workers interviewed said they had had no information or training about the chemicals.

Planning for emergencies

The response of the company and the authorities to the emergency suggests that there was no effective emergency plan.

Within the works, defects revealed by the emergency include the hesitation about the use of the siren system and the lack of escape routes.

The preliminary condition for emergency planning to protect the public outside the works is provision to the authorities of full information about the hazards. This was not done. In consequence the people exposed did not know what the siren meant or what action to take, the hospitals did not know what they might be called on to handle, and so on.

Likewise, the essential action in an actual emergency is to inform the authorities what has happened and what the hazards are. On the morning of the accident, the hospitals were in the dark about the nature and effects of the toxic chemical whose victims they were trying to treat.

A5.10.2 An accident model

An accident model for Bhopal given by Kletz (1988h) is shown in Figure A5.6.

Appendix 6 Pasadena

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A6.3 The Explosion A6/2
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Shortly after 1.00 p.m. on 23 October 1989, a release occurred on a polyethylene plant at the Phillips 66 Company's chemical complex at Pasadena, near Houston, Texas. A vapour cloud formed and ignited, giving rise to a massive vapour cloud explosion. There followed a series of further explosions and a fire. Twenty-two people on the site were killed and one later died from injuries, making a death toll of 23. The number injured are variously given as 130 and 300.

A report on the investigation of the accident has been issued by OSHA (1990a). Other accounts include those of Mahoney (1990), T. Richardson (1991) and J.N. Scott (1992).

Selected references on Pasadena are given in Table A6.1.

A6.1 The Site and the Plant

The Phillips works was sited in the Houston Chemical Complex along the Ship Channel, the location of a number of process companies.

The plant on which the release occurred was Plant V, one of the two active polyethylene plants in the complex. The plant operated at high pressure (700 psi) and high temperature. The process involved the polymerization of ethylene in isobutane, the catalyst carrier. Particles of polyethylene settled out and were removed from settling legs.

A6.2 Events Prior to the Explosion

On the previous day work began to clear three of the six settling legs on Reactor No. 6, which were plugged. The three legs were prepared by a company operator and were handed over to the specialist maintenance contractors, Fish Engineering. The configuration of a typical leg is shown in Figure A6.1.

At 8.00 a.m. on Monday, 23 October, work began on the second of the three blocked legs, Leg No. 4. The isolation procedure was to close the DEMCO ball valve and disconnect the air lines to it.

The maintenance team partially disassembled the leg and were able to remove part of the plug, but part remained lodged in the pipe 12–18 in. below the ball valve. One of the team was sent to the control room to seek assistance. Shortly after, at 1.00 p.m., the release occurred.

Although both industry practice and Phillips corporate safety procedures require isolation by means of a double block system or a blind flange, at local plant level a procedure had been adopted which did not conform to this.

It was subsequently established that the DEMCO ball valve was open at the time of the release. The air hoses to the valve had been cross-connected so that the supply which should have closed it actually opened it. The hose connectors for the 'open' and 'close' sides of the valve were identical, thus allowing this cross-connection to be made. Although procedures laid down that the air hoses should not be connected during maintenance, there was no physical barrier to the making of such a connection. The ball valve had a lockout system but it was inadequate to prevent the valve being inadvertently or intentionally opened during maintenance.

Table A6.1 *Selected references on Pasadena*

Anon. (1989 LPB 90, p. 0); Anon. (1990 LPB 94, p. 30); Mahoney (1990); OSHA (1990a); Redmond (1990); Vervalin (1990b); Bond (1991 LPB 97); Kletz (1991J); T. Richardson (1991); J.N. Scott (1992)

A6.3 The Explosion

The mass of gas released was estimated as some 85,200 lb of a mixture of ethylene, isobutane, hexene and hydrogen, which escaped within seconds. The release was observed by five eyewitnesses. A massive vapour cloud formed and moved rapidly downwind.

Within 90–120 s the vapour cloud found a source of ignition. Possible ignition sources were a gas-fired catalyst activator with an open flame; welding and cutting operations; an operating forklift truck; electrical gear in the control building and the finishing building; 11 vehicles parked near the polyethylene plant office; and a small diesel crane, although this was not operating.

The TNT equivalent of the explosion was estimated in the OSHA report as 2.4 tons. An alternative estimate from seismograph records is 10 tons.

There followed two other major explosions, one when two 20,000 USgal isobutane storage tanks exploded and the other when another polyethylene plant reactor failed catastrophically, the timings being some 10–15 min and some 25–45 min, respectively, after the initial explosion. One witness reported hearing 10 separate explosions over a 2-h period.

Debris from the explosion was found 6 miles from the site.

All 22 of those who died at the scene were within 250 ft of the point of release and 15 of them were within 150 ft.

Injuries which occurred outside the site were mainly due to debris from the explosion.

The explosion resulted in the destruction of two HOPE plants.

A6.4 The Emergency and the Aftermath

People in the immediate area of the release began running away as soon as they realized that gas was escaping. The alarm siren was activated, but the level of noise in the finishing building was such that there was a question whether some employees there failed to hear it.

The immediate response to the emergency was provided by the site fire brigade, which undertook rescue and care of the injured and began fighting the fire. Twenty-three persons were unaccounted for, but for an extended period the area of the explosion remained dangerous to enter.

Severe difficulties were experienced in fighting the fires resulting from the explosion. There was no dedicated fire water system, water for firefighting being drawn from the process water system. The latter suffered severe rupture in the explosion so that water pressure was too low for firefighting purposes. Fire hydrants were sheared off by the blast. Fire water had to be brought by hose from remote sources such as settling ponds, a cooling tower, a water treatment plant and a water main on a neighbouring plant. These difficulties were compounded by failures of the fire pumps. The electrical cables supplying power to the regular fire pumps were damaged by the fire so that these pumps were put out of action. Further, of the three backup diesel fire pumps one was down for maintenance and one quickly ran out of fuel. Despite these problems the fire was brought under control within some 10 h.

The handling of the emergency was handicapped by the facts that the intended command centre had been damaged and that telephone communications were disrupted. Telephone lines were jammed for some hours following the accident.

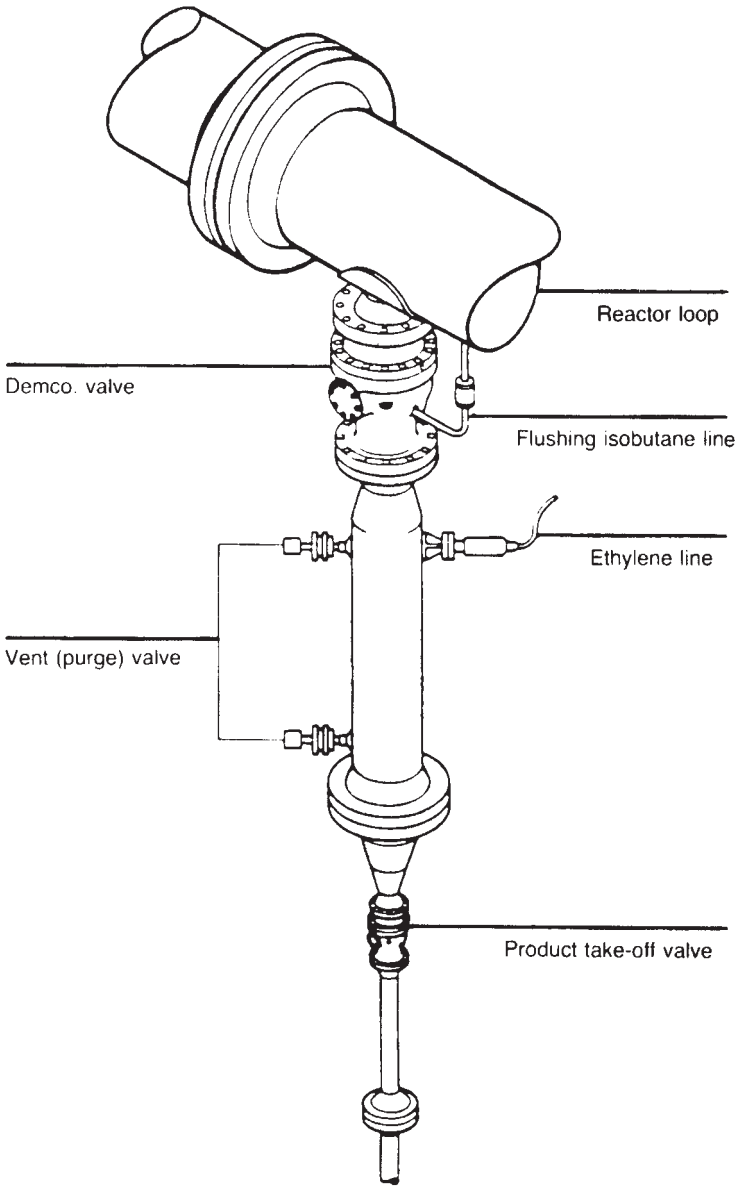

Figure A6.1 *Typical piping settling leg arrangement on reactor (Occupational Safety and Health Administration, 1990a)*

The emergency response was co-ordinated by the site chief fire officer and involved the local Channel Industries Mutual Aid (CIMA) organization, a co-operative of some 106 members in the Houston area.

More than 100 people were evacuated from the administration building across the Houston Ship Channel by the US Coast Guard and by Houston fireboats; they would otherwise have had to cross the area of the explosion to reach safety.

The media were quickly aware of the explosion and within an hour there were on site 150 media personnel from 40 different organizations.

The financial loss in this accident is comparable with, and may exceed, that of the Piper Alpha disaster. Redmond (1990) has quoted a figure of $1400 million, divided almost equally between property damage and business interruption losses.

On the basis of a review of company reports and of the defects found during the investigation of the disaster, OSHA issued a citation to the company for wilful violations of the 'general duty' clause. The citation covered the lack of hazard analysis; plant layout and separation distances; flammable gas detection; ignition sources; building

ventilation intakes; and the fire water system; the permit system; isolation for maintenance.

A6.5 Some Lessons of Pasadena

Some of the lessons to be learned from Pasadena are listed in Table A6.2.

Management of major hazard installations
The OSHA report details numerous defects in the management of the installation. Some of these are described below.

Hazard assessment of major hazard installations
According to the report, the company had made no use of hazard analysis or an equivalent method to identify and assess the hazards of the installation.

Plant layout and separation distances
The report was critical of the separation distances in the plant in several respects. It stated that the separation distances between process equipment plant did not accord with accepted engineering practice and did not allow time for personnel to leave the polyethyelene plant safely during the initial vapour release; and that the separation distance between the control room and the reactors was insufficient to allow emergency shut-down procedures to be carried out.

Location of control room
As just mentioned, the control room was too close to the plant. It was destroyed in the initial explosion.

Building ventilation intakes
The ventilation intakes of buildings close to or downwind of the hydrocarbon processing plants were not arranged so as to prevent intake of gas in the event of a release.

Minimization of exposure of personnel
Closely related to this, there was a failure to minimize the exposure of personnel. Not only the control room but the finishing building had relatively high occupancy.

Table A6.2 *Some lessons of Pasadena*

Management of major hazard installations
Hazard assessment of major hazard installations
Plant layout and separation distances
Location of control room
Building ventilation intakes
Minimization of exposure of personnel
Escape and escape routes
Gas detection system
Control of ignition sources
Permit-to-work systems
Isolation procedures for maintenance
Integrity of fire water system
Dependability of fire pumps
Audibility of emergency alarm
Follow-up of audits
Planning for emergencies

Escape and escape routes
As already stated, the separation distances were not such as to allow personnel on the polyethylene plant to escape safely. Further, the only escape route available to people in the administration block (other than across the ship channel) was across the area of the explosion.

Gas detection system
Despite the fact that the plant had a large inventory of flammable materials held at high pressure and temperature, there was no fixed flammable gas detection system.

Control of ignition sources
The control of ignition sources around the plant was another feature criticized in the OSHA report.

Permit-to-work systems
The OSHA report stated that an effective permit system was not enforced for the control of the maintenance activities either of the company's employees or of contractors.

Isolation procedures for maintenance
In this incident the sole isolation was a ball valve, which was meant to be closed but was in fact open. There was no double block system or blind flange.

The practice of not providing positive isolation was a local one and violated corporate procedures. The implication is that it had not been brought to light by any safety audits conducted.

Integrity of fire water system
The practice of relying for fire water on the process water system and the failure to provide a dedicated fire water system meant that the fire water system was vulnerable to an explosion.

Dependability of fire pumps
The electrical cables to the regular fire pumps were not laid underground and were therefore vulnerable to damage by explosion and fire. One of the back-up diesel pumps had insufficient fuel and one had been taken out for maintenance without informing the chief fire officer.

Audibility of emergency alarm
As described, the level of noise in some areas was such that the employees might not have been able to hear the siren.

Follow-up of audits
The OSHA report criticized the company's failure to act upon reports issued previously by the company's own safety personnel and by external consultants, which drew attention to unsafe conditions.

Planning for emergencies
The disaster highlighted a number of features of emergency planning. The company had put a good deal of effort into planning and creating personal relationships with the emergency services, by means such as joint exercises, and these paid off. The value of planning, training and personal relations was one of the most positive lessons drawn.

Another area in which a proactive approach proved beneficial was in relations with the media. Senior personnel made themselves available, and the company evidently felt it received fair treatment.

One weakness of the emergency planning identified was that it had not envisaged a disaster of the scale which actually occurred.

The incident brought out the need to be able to respond clearly to calls from those liable to be affected about the toxicity of the fumes and smoke generated in such an event.

The behaviour of rescue helicopters posed a problem. Personnel on the ground had no means of communication with them and the craft tended to come in low, creating the danger of blowing flames or toxic fume onto those below. A need was identified for altitude and distance guidelines for helicopters.

Appendix 7 *Canvey Reports*

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A7.1 First *Canvey Report* A7/2
A7.2 First *Canvey Report:* Installations and Activities A7/2
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The most comprehensive hazard assessment of non-nuclear installations in the United Kingdom is the Canvey study carried out for the HSE by SRD.

The first phase of the work is described in *Canvey: An Investigation of Potential Hazards from Operations in the Canvey Island/Thurrock Area* (the First *Canvey Report*) (HSE, 1978b). The report is in two parts: Part 1 is an introduction by the HSE and Part 2 the SRD study.

The origin of the investigation was a proposal to withdraw planning permission for the construction of an additional refinery in the area. Two oil companies, Occidental Refineries Ltd and United Refineries Ltd, had been granted planning permission for the construction of oil refineries. The construction of the Occidental refinery was begun in 1972, but was halted in 1973 pending a major design study review. United Refineries had valid planning consents, but had not started construction. It was a public inquiry into the possible revocation of the planning permission for the United Refineries development which gave rise to the investigation.

Responses to the First *Canvey Report* centred mainly on two aspects: the methodology used and the magnitude of the assessed risks. The HSE commissioned further work, leading to the Second *Canvey Report* (HSE, 1981a), in which the methodology used is revised and the assessed risks are rather lower.

An account of the first report is given in Sections A7.1–A7.6, of the response to that report in Section A7.7 and of the second report in Sections A7.8–A7.10.

A map of the Canvey/Thurrock area showing the principal installations and populated areas is given in Figure A7.1.

Selected references on the *Canvey Reports* are given in Table A7.1.

A7.1 First *Canvey Report*

The terms of reference of the investigation were

> In the light of the proposal by United Refineries Limited to construct an additional refinery on Canvey Island, to investigate and determine the overall risks to health and safety arising from any possible major interactions between existing or proposed installations in the area, where significant quantities of dangerous substances are manufactured, stored, handled, processed and transported or used, including the loading and unloading of such substances to and from vessels moored at jetties; to assess the risk; and to report to the Commission.

The members of the investigating team were appointed as inspectors of the HSE under the provisions of the Health and Safety at Work etc. Act 1974 and were given specified powers to enable them to make the necessary inquiries. The overall approach taken in the investigation was

(1) To identify any potentially hazardous materials, their location and the quantities stored and in process.
(2) To obtain and review the relevant material properties such as flammability and toxicity.
(3) To identify the possible ways in which failure of plants might present a hazard to the community.
(4) To identify possible routes leading to selected failures. Typically, the factors examined included operator errors, fatigue or aging of plant, corrosion, loss of process control, overfilling, impurities, fire, explosion, missiles and flooding.
(5) To quantify the probability of the selected failures occurring and their consequences.

The investigation involved the identification of the principal hazards of the installations and activities in the area, the assessment of the associated risks to society and to individuals, and the proposal of modifications intended to reduce these risks.

Some 30 engineers were engaged in the investigation, which cost about £400,000.

Table A7.1 *Selected references on Canvey Reports*

Canvey Reports
HSE (1978b, 1981a)
Reviews and critiques
N. Turner (1975); Anon. (1980,l,p,s); Cremer and Warner (1980); Hansard (1980); V.C. Marshall (1980a); Anon. (1981r,w); R. Ward (1981); A.F. Grant (1982); IChemE (1982a,b); Rasbash (1982a); Anon. (1983c); Petts (1985a)

A7.2 First *Canvey Report:* Installations and Activities

The principal hazardous installations and activities identified in the investigation are summarized in Table A7.2. These installations are now briefly described.

A7.2.1 British Gas Corporation

The British Gas Corporation operates on Canvey Island, a methane terminal that is used for the importation and storage of LNG from Algeria. There are some 50 shipments of LNG a year made by two specially designed ships each with a cargo capacity of about 12,000 t. The LNG is pumped ashore from a single jetty into above-ground and in-ground fully refrigerated storage tanks with a combined total capacity of approximately 100,000 t. The natural gas is sent out as vapour by pipeline except for a small amount that goes out by road.

The terminal is also used for the fully refrigerated storage of liquid butane. A pipeline from the butane tanks crosses the area.

In addition, new LNG ships are commissioned at the terminal by using the LNG from the storage tanks to cool down the ships' cargo tanks.

A7.2.2 Texaco Ltd

Texaco Ltd operates on Canvey Island storage for petroleum products, but not LPG, with a total capacity of more than 80,000 t. The petroleum products are brought in by sea via two jetties and are sent out by sea, road and pipeline.

A7.2.3 London and Coastal Wharves Ltd

London and Coastal Wharves Ltd also operates on Canvey Island storage for a wide range of substances, including petroleum products and other flammable and toxic materials, with a total capacity of more than 300,000 t. Part of the site is leased to Texaco. The materials are brought in mainly by sea via a single jetty and also by road and are sent out not only by road but also by sea. Oil is sent out by Texaco by pipeline.

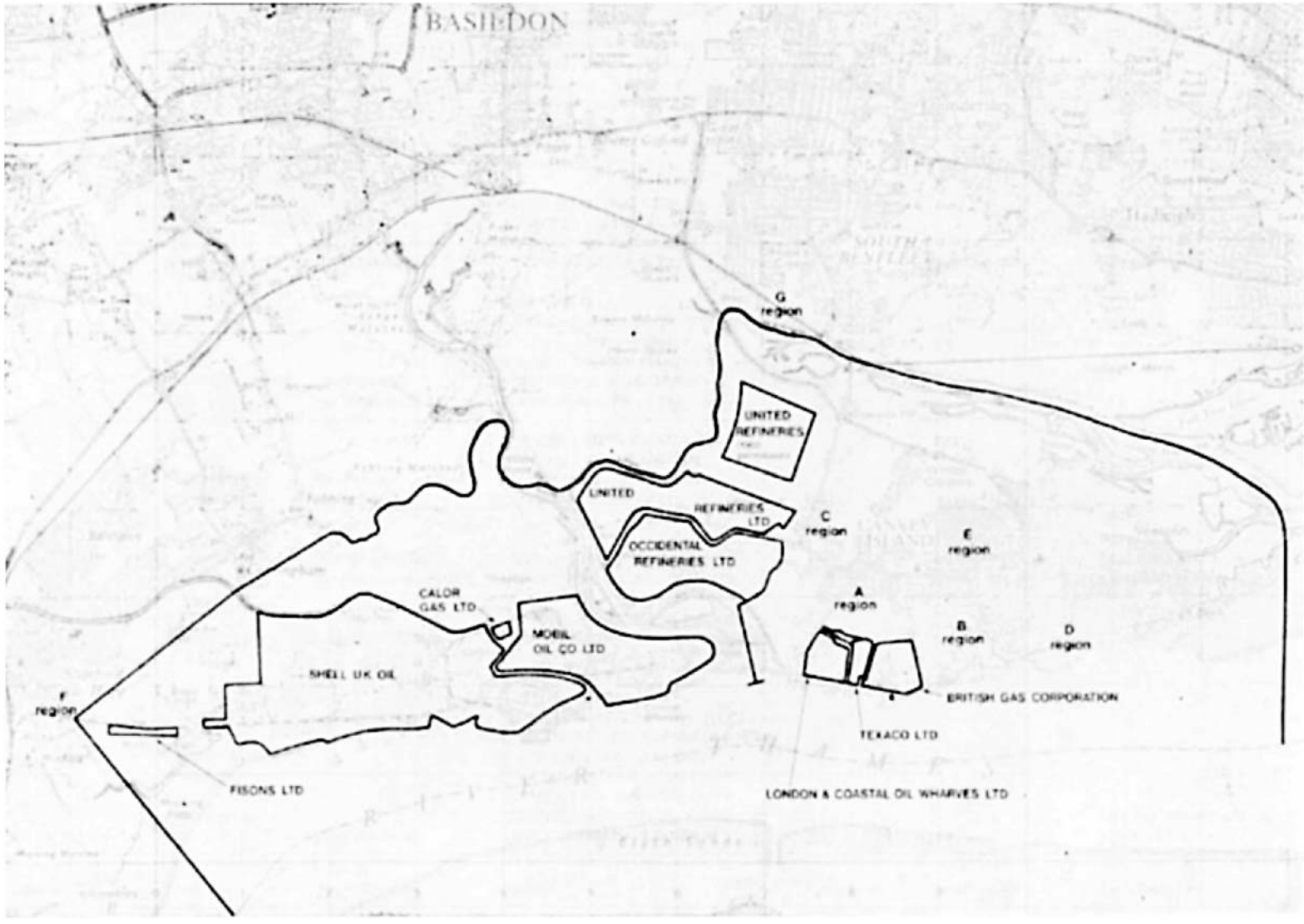

Figure A7.1 *First Canvey Report: map of the Canvey/ Thurrock area, showing principal installations and populated areas (Health and Safety Executive, 1978b) (Courtesy of HM Stationery Office)*

Table A7.2 *First Canvey Report: principal hazardous installations and activities at Canvey*

Location	*Company*	*Installation or activity*	*Storage*	*Employees*	*Transport in*	*Transport out*
Canvey Island	British Gas Corporation	LNG terminal	Fully refrigerated storage of LNG (atmospheric pressure, $<-162°C$) 6×4000 t above-ground tanks 2×1000 t above-ground tanks $4 \times 20{,}000$ t in-ground tanks. Fully refrigerated storage of butane (atmospheric pressure, $<10°C$) $1 \times 10{,}000$ t tank 2×5000 t tanks	200	Sea	Mainly pipeline (as vapour) but some road
	Texaco Ltd	Petroleum products storage	Atmospheric storage of petroleum products >80,000 t total capacity	130	Sea	Pipeline, road, sea
	London and Coastal Wharves Ltd	Flammable and toxic liquids storage	Atmospheric storage of liquids >300, 000 t total capacity	50	Mainly sea but some road	Pipeline (Texaco oil). Rest mainly road but some sea
	Occidental Refineries Ltd	Oil refinery (proposed)	Pressure storage of LPG (atmospheric temperature) 2×750 t propane spheres 2×400 t butane spheres			
	United Refineries Ltd	Oil refinery (proposed)	Pressure storage of LPG (atmospheric temperature) 4×200 t propane spheres 3×900 t butane spheres. Process and storage containing hydrogen fluoride			
Coryton	Mobil Oil Co. Ltd	Oil refinery	Pressure storage of LPG (atmospheric temperature) 1×1000 t+14 other vessels, giving 4000 t total capacity	800	LPG produced on site	Pipeline, road, rail, sea
		Oil refinery (extension)	Pressure storage of LPG (atmospheric temperature) 4×1000 t LPG spheres. Fully refrigerated storage of LPG (atmospheric pressure) 1×5000 t tank. Process and storage containing hydrogen fluoride		LPG produced on site	Pipeline, road, rail, sea

	Calor Gas Ltd	LPG terminal	Pressure storage of LPG (atmospheric temperature) 3 × 60 t propane vessels 2 × 60 t butane vessels + cylinders, giving 500 t total inventory	100	Pipeline (from oil refineries)	Road (cylinders, bulk tankers)
Shell Haven	Shell Oil U.K. Ltd	Oil refinery	Pressure storage of LPG (atmospheric temperature) 1 × 1700 t butane sphere + 3 other butane spheres, giving 3200 t total butane capacity 4 × 400 t propane spheres 3 × 135t LPG horizontal vessels	1900	LPG produced on site	Pipeline, road, rail, sea
			Fully refrigerated storage of liquid anhydrous ammonia (atmospheric pressure, −33°C) 1 × 14,000 t tank. Process and storage containing hydrogen fluoride 2 × 40 t vessels		Sea	Sea, road, occasionally rail
Stanford-le-Hope	Fisons Ltd	Ammonium nitrate plant	Storage of 92% aqueous ammonium nitrate solution 1 × 5000 t tank 1 × 2000 t tank	80	Ammonium nitrate produced on site	Road
		Ammonia storage	Semi-refrigerated pressure storage of liquid anhydrous ammonia (pressure above atmospheric, 6°C) 1 × 2000 t sphere		Rail	Ammonia used on site
Canvey/ Thurrock area	General	Transport of hazardous Materials by river, road, rail and pipeline				

A7.2.4 Mobil Oil Co. Ltd

Mobil Oil Co. Ltd operates at Coryton, an oil refinery as well as a bulk distribution depot and a large research and technical services laboratory. Oil is brought in by sea into storage tanks and is drawn off from these as required by the refinery. LPG is produced on site. The total storage capacity is more than 1,500,000 t. Products are sent out by sea, road, rail and pipeline.

In addition, at the time of the investigation Mobil was undertaking a major extension of the refinery.

A7.2.5 Calor Gas Ltd

Calor Gas Ltd operates at Coryton, an LPG terminal for the filling of gas cylinders. The gas is supplied by pipeline from both the nearby refineries and is held in storage vessels with a total capacity of 350 t. The gas cylinders bring the total inventory on site to 500 t. LPG is sent out by road in cylinders and in bulk tankers.

A7.2.6. Shell Oil UK Ltd

Shell Oil UK Ltd operates at Shell Haven, an oil refinery. Oil is brought in by sea into storage tanks and is drawn off from these as required to the refinery. LPG is produced on site. The total storage capacity is more than 3,500,000 t. Products are sent out by sea, road, rail and pipeline.

There is also on site a large fully refrigerated storage tank for liquid anhydrous ammonia with a capacity of 14,000 t. Ammonia is brought in by sea and sent out by sea and road, and occasionally by rail.

A7.2.7 Fisons Ltd

Fisons Ltd operates at Stanford-le-Hope, an ammonium nitrate plant in which strong ammonium nitrate solution is produced by reacting together ammonia and nitric acid, the latter itself being made on site from ammonia. The ammonium nitrate is stored in two large heated tanks with a total capacity of 7000 t and is sent out by road. Liquefied anhydrous ammonia for the process is brought in by rail and is stored in a large semi-refrigerated pressure storage sphere with a capacity of 2000 t.

A7.2.8 Other activities

Explosives are trans-shipped at Chapmans Anchorage at the eastern end of Canvey Island, while there is a specified anchorage for explosives ships at the other end of the area.

Ships passing up and down the river are obliged to travel fairly close to the sea walls and jetties within the area.

A7.3 First *Canvey Report:* Identified Hazards

The investigation identified several principal hazards in the area. These are;

(1) oil spillage over bund;
(2) LNG vapour cloud release (1000 t);
(3) LPG vapour cloud release (1000 t);
(4) ammonium nitrate explosion (4500 t of 92% solution);
(5) ammonia vapour cloud release (1000 t);
(6) hydrogen fluoride cloud release (1000 t).

The figures in parentheses indicate standard cases considered in the study.

A severe fire might occur if there is an escape of flammable liquids from storage so that large quantities flow down into the residential area. This hazard is presented by the large storages of flammable liquids at London and Coastal Wharves and Texaco and at the proposed refineries of Occidental and United Refineries, and also by the large butane storage at British Gas.

A severe vapour cloud fire and/or explosion might occur if there is a spillage of LNG so that a vapour cloud forms and ignites. This hazard is presented by the large LNG terminal and storage at British Gas. The spillage might occur at sea or on land.

Similarly, a severe vapour cloud fire and/or explosion might occur if there is a spillage of LPG so that a vapour cloud forms and ignites. This hazard is presented by the LPG terminals and storages at British Gas, Shell and Mobil and by those at the proposed refineries of Occidental and United Refineries.

A severe explosion might occur if there is a rupture of an ammonium nitrate storage tank. This hazard is presented by the storage of ammonium nitrate at Fisons.

A severe toxic release might occur if there is a spillage of ammonia. This hazard is presented by the large terminals and storages at Fisons and at Shell. The spillage might occur at sea or on land.

A severe toxic release might also occur if there is a rupture of storage or process plant containing hydrogen fluoride. This hazard is presented by the alkylation facilities at Shell, at the Mobil extension and at the proposed Occidental refinery.

The investigators also identified and assessed other hazards, but these are not considered here.

A7.4 First *Canvey Report:* Failure and Event Data

The investigation required the estimation of the probabilities of various occurrences and of their consequences.

Some of the sources of information on such probabilities used in the study were

(1) UK industries, including oil, chemical and other process industries and transport;
(2) government organizations such as those concerned with fire, and road, rail and sea and air transport;
(3) professional institutions, for example, Institution of Chemical Engineers, Institution of Civil Engineers, American Institute of Chemical Engineers;
(4) international safety conference proceedings, for example, loss prevention in the process industries, ammonia plant safety and hazardous materials spills;
(5) industry-based associations, for example, Chemical Industries Association, Institute of Petroleum, American Petroleum Institute, Liquefied Petroleum Gas Industry Technical Association;
(6) international insurance interests, for example, Lloyds, Det Norsk Veritas, and industrial risk insurers, Fire Protection Association;
(7) overseas government and international agencies, for example, US Coast Guard, US Department of Transportation, OECD and EEC;
(8) specialized research laboratories;
(9) individual subject specialists known or recommended to the investigating team.

Selected references used in the *Canvey Report* are given in Table A7.3.

Table A7.3 *First Canvey Report: Selected references used*

Min. of Defence (n.d.); Wardle (n.d.); Brodie (1956); B.R. Morton, Taylor and Turner (1956); Cremer (1959, 1961); Minorsky (1959); Cremer and Callaway (1961); Pasquill (1961, 1965); Patty (1962); R.K. Davis *et al.* (1963); Blokker (1964); Bryant (UKAEA 1964 AHSB(RP) R42); Glasstone (1964); Yih (1965); van Dolah *et al.* (1966 BM RI 6773); Resplandy (1967); Brasie and Simpson (1968); Slade (1968); G.A. Briggs (1969): Clough and Garland (1970b); Kiwan (1970b); Bryce-Smith (1971); Finney (1972); MacArthur (1972); Brobst (1972); Feldbauer *et al.* (1972); Humbert-Basset and Montet (1972); Oppenheim, Kuhl and Kamel (1972); Burgess and Zabetakis (1973 BM RI 7752); Kuhl, Kamel and Oppenheim (1973); May, McQueen and Whipp (1973); Strehlow (1973b); BatteUe Columbus Lab. (1974); L.E. Brown, Wesson and Welker (1974b); Dicken (1974, 1975); Geiger (1974); Hosker (1974b); Kneebone and Prew (1974); Munday and Cave (1974); Murata *et al.* (1974); NTSB (1974 PAR-74-06); Reed (1974); Simmons, Erdmann and Naft (1974); van Ulden (1974); CIA (1975/8); Germeles and Drake (1975); Gething (1975); J. Hall, Barrett and Ralph (1975); Lonsdale (1975); Raj *et al.* (1975); DoE (1976b); Gifford (1976b); MacMullen (1976); Munday (1976a); Neff, Meroney and Cermak (1976); Carver *et al.* (1977); R.A. Cox and Roe (1977); Davenport (1977b); Fitzpatrick and Goddard (1977); Havens (1977)

See also Appendix 28 (HSE and SRD; UKAEA, SRD)

The degree of uncertainty associated with the probability estimates is indicated by the following code:

(a) assessed statistically from historical data – this method is analogous to the use of aggregate estimates in economic forecasting;
(b) based on statistics as far as possible but with some missing figures supplied by judgement;
(c) estimated by comparison with previous cases for which fault tree assessments have been made;
(d) 'dummy' figures – likely always to be uncertain, a subjective judgement must be made;
(e) not used;
(f) fault tree synthesis, an analytically based figure which can be independently arrived at by others.

The coding (a) denotes a value based on historical failure or event data. The coding (b) indicates that the value is again based on historical data as far as possible, although with some exercise of judgement, but also that given more effort a firmer value would probably be obtained. The coding (d) indicates that the value is based on judgement and the prospects of ever reducing the uncertainty are poor. Category (d) factors are effectively dummy values. Conclusions should not be drawn from these without testing for sensitivity. The value of a (d) category factor is generally not very small: it is typically 0.3 and exceptionally 0.1. The coding (f) denotes a value synthesized by fault tree methods. This category is in fact very little used in the study. Instead use is made of (c) category factors. The coding (c) indicates that the value is based on a value previously obtained for a similar situation using fault tree methods. The *Canvey Report* contains much useful information on failure and event data. Some of these data are given in Section A7.5 and in Table A7.4. It is emphasized that these data are given here for illustrative purposes and that the report itself should be consulted for the description of the background to and the application of these data.

A7.5 First *Canvey Report:* Hazard Models and Risk Estimates

The investigation involved the study of a wide range of hazards and scenarios.

The projects that were initiated as part of the investigation were

(1) consideration of known history of identified storage tanks and their possibility of failure;
(2) probability of particular storage tanks or process vessels being hit by missiles caused by fires or explosions on site or adjacent sites, by fragmentation of rotating machines or pressure vessels, or transport accidents;
(3) effects of vapour cloud explosions on people, houses, engineering structures, etc.;
(4) evaporation of LNG from within a containment area on land or from a spill on water;
(5) special problems of frozen earth storage tanks for LNG and the effect of flooding;
(6) study of possible failures in handling operations;
(7) consideration of the possible benefits and practicality of evacuation;
(8) civil engineering aspects of the sea-wall – the chance of it being breached by subsidence, explosion or impact of ships, consideration of the timing of improved defences, consideration of the time for floods to rise;
(9) statistics of ship collisions and their severity, groundings, etc., applying extensive world experience to the Canvey Island area;
(10) reliability and analysis of fluid handling practices, ship to shore, and store to road vehicles and pipelines;
(11) toxicology of identified hazardous substances;
(12) studies to determine the lethal ranges for various releases of toxic or explosive materials leading to a number of special studies such as
  (a) the behaviour of ammonia spilt on water or land, and
  (b) an assessment of the relative importance of explosion or conflagration from a cloud of methane or liquefied petroleum gas.

The subjects that are considered in appendices to the report are

(1) a review of current information on the causes and effects of explosions of unconfined vapour clouds (F. Briscoe);
(2) fires in bunds – calculations of plume rise and position of downwind concentration maximum (R. Griffiths);
(3) a quantitative study of factors tending to reduce the hazards from airborne toxic clouds (Q.R. Beattie);
(4) the dispersal of ammonia vapour in the atmosphere with particular reference to the dependence on the conditions of emission (F. Abbey, R.F. Griffiths, S.R. Haddock, G.D. Kaiser, R.J. Williams and B.C.Walker);

Table A7.4 *First Canvey Report: some failure and event data used (after Health and safety Executive, 1978b)*

Installation or activity[a]			*Canvey Report page(s)*
Pressure vessels (LPG, ammonia, HF)	Frequency of spontaneous failure of pressure vessel	10^{-5}/year–10^{-4}/year	57, 59, 69
Pressure circuit (HF)	Frequency of spontaneous failure of pressure circuit	10^{-4}/year	59
	Frequency of release due to operational fault	10^{-4}/year	59
	Frequency of penetration of pressure circuit by missile	10^{-4}/year	59
High speed rotating machine	Frequency of disintegration of rotor	10^{-4}/year–10^{-3}/year	58
Pipework (LPG)	Frequency of failure of pipework (whole refinery installation)	5×10^{-3}/year	56
Pump(LPG)	Frequency of catastrophic failure of pump	10^{-4}/year	56
LPG filling point	Frequency of large vapour release	5×10^{-3}/year	58, 81
LNG tank (above ground)	Frequency of serious fatigue failure	2×10^{-4}/year	63
	Frequency of overpressurization by overfilling	10^{-5}/year–10^{-4}/year	63, 95
	Frequency of rollover involving structural damage	10^{-5}/year–10^{-4}/year	63, 95
Jetty pipework (LNG)	Frequency of catastrophic failure of jetty pipework	10^{-4}/year–10^{-3}/year	63
Fire	Frequency of major fire in a refinery	0.1/year	55, 130
Explosion	Probability of refinery explosion, given major refinery fire	0.5	130
Missiles	Probability of missile generation, given refinery explosion	0.1	130
	Frequency of missile-generating explosion in refinery	5×10^{-3}/year	130
	Average number of missiles generated per explosion	*c*. 6	130
	Probability of missile hitting large storage sphere at 300 m	10^{-3}/year	55

Unconfined vapour cloud explosion	Frequency of unconfined vapour cloud explosion in a refinery	10^{-3}/year	69, 130
Pipeline (butane)	Frequency of failure of pipeline (15/20 cm diameter)	3×10^{-4}/km y	85
Rail transport	Frequency of derailment of rail tank car	1×10^{-6}/train km travelled	79
	Probability of overturning given derailment	0.2	79
Road transport	Frequency of accident of road tanker involving spillage	1.6×10^{-8}/km travelled	84
Sea transport (Port of London)	Frequency of ship–ship collision of moderate severity due to harbour movements	0.5×10^{-4}/harbour movement	146
	Frequency of berthing contact	1.5×10^{-4}/harbour movement	146
	Frequency of grounding	0.3×10^{-4}/harbour movement	146
	Frequency of spillage due to harbour movements: ammonia carrier	3.1×10^{-5}/harbour movement	149
	Frequency of fire	0.5×10^{-4}/harbour movement	146
	Frequency of ship–ship collision of moderate severity in transit in estuary	2.3×10^{-5}/movement	147
	Frequency of spillage due to ship–ship collision intransit: ammonia carrier	5×10^{-6}/movement	150
Jetty incidents	Frequency of shipboard explosion at jetty: ammonia ship, Shell jetty	10^{-4}/harbour movement	96
	Frequency of fire or explosion at jetty: LPG, Occidental, Mobil jetty	4×10^{-5}/harbour movement	96
Aircraft movements	*See* Section A.5.5 of this Appendix		139–140
Helicopter movements	Frequency of helicopter accident – total accidents	3×10^{-7}/km flown	141
	– Fatal accidents	8×10^{-8}/km flown	141

[a] The data given in this table are in most cases heavily qualified and the original report should be consulted for the description of the background to and the application of them.

(5) statistics on fires and explosions at refineries Q.H. Bowen);
(6) missiles – penetration capability (EA White);
(7) discussion of data base for pressure vessel failure rate (TA Smith);
(8) risk of aircraft impacts on industrial installations in the vicinity of Canvey Island (LS. Fryer);
(9) the dispersion of gases that are denser than air, with LNG vapour as a particular example (G.D. Kaiser);
(10) not used;
(11) the risk of a liquefied gas spill to the estuary (D.F. Norsworthy);
(12) the toxic and airborne dispersal characteristics of hydrogen fluoride (Q.R. Beattie, F. Abbey, S.R. Haddock, G.D. Kaiser);
(13) transient variation of the wall temperature of an LNG above-ground storage tank during exposure to an LNG fire in an adjacent bund (I.R. Fothergill);
(14) the escape of 1000 t of anhydrous ammonia from a pressurized storage tank (L.S. Fryer, G.D. Kaiser and B.C. Walker);
(15) graphical calculation of toxic ranges for a release of 1000 t of ammonia vapour (J.H. Bowen);
(16) effect of unbunded spill of hydrocarbon liquid from refinery at Canvey Island (A.N. Kinkead);
(17) estimated risk of missile damage causing a vapour cloud release from existing and proposed LPG storage vessels at the Mobil refinery, Coryton (D.F. Norsworthy);
(18) risks of accidents involving road tankers carrying hazardous materials (L.S. Fryer);
(19) toxicology of lead additives (S.R. Haddock);
(20) compatibility of materials stored at London and Coastal Wharves Ltd (S.R. Haddock);
(21) blast loading on a spherical storage vessel (Q. Wall);
(22) statistical comment on data on distribution of cracks found on inspection of steel vessel (Q.C. Moore);
(23) calculation of resistance of ship hull to collision (A.N. Kinkead);
(24) reduction of apparent risk by shared experience (Q.H. Bowen).

The treatment of some of the topics which is given in the report is now described. These topics are

(1) failure of pressure vessels;
(2) failure of pressure piping;
(3) failure of pipelines;
(4) generation of and rupture by missiles;
(5) crash of and rupture by aircraft;
(6) ship collision and other accidents;
(7) flow of a large release of oil;
(8) temperature of the wall of an LNG tank exposed to an LNG fire in an adjacent bund;
(9) evaporation of LNG and ammonia on water;
(10) dispersion of an LNG vapour cloud;
(11) unconfined vapour cloud fire and explosion;
(12) ammonium nitrate explosion;
(13) toxicity of chlorine, ammonia, hydrogen fluoride and lead additives;
(14) dispersion of ammonia and hydrogen fluoride vapour clouds;
(15) factors mitigating casualties from a toxic release;
(16) road tanker hazards;
(17) evacuation.

It is emphasized that the following summary of the methods used in the report is necessarily highly compressed and that the report itself should be consulted for a fuller discussion of the methods themselves and of the background to and application of the methods.

A7.5.1 Failure of pressure vessels

Spontaneous failure of pressure vessels is considered as a possible initiating event for releases of LPG, ammonia and hydrogen fluoride. The report discusses spontaneous failure of pressure vessels in Part 2, Section 5.3.2. and in Appendix 7 and the sensitivity of the results for LPG, ammonia and hydrogen fluoride releases in Part 2, Sections 17.14–17.16.

It reviews the surveys of pressure vessel failures available at that date, as described in Chapter 12, and concludes that the UK survey data are broadly applicable to LPG storage vessels.

For vessels covered by the surveys the frequency of a fault requiring repair or withdrawal from service was about 3×10^{-4}/y. If it can be assumed that the critical defect length is less than the wall thickness, so that detection is easier, and that there is an effective inspection system, a reasonable estimate of the probability of detection is 90%. The frequency of an undetected fault would then be about 3×10^{-5}/y. A catastrophic failure rate of pressure vessels of 10^{-5}/y is used in the study.

In addition, however, the sensitivity of the results to errors in the assumed failure rate was calculated taking a failure rate of 10^{-4}/y instead of 10^{-5}/y. The effect of this change is almost to double the risk from LPG operations for the existing installations after the proposed modifications. Thus for an incident involving >1500 casualties the frequency is 264×10^{-6}/y with a contribution of $20-10^{-6}$/y for spontaneous failure of pressure vessels, but the latter rises to 200×10^{-6}/y if the spontaneous failure rate of pressure vessels is increased from 10^{-5}/y to 10^{-4}/y.

It is concluded that a high standard of inspection of the LPG pressure vessels is necessary.

External threats to pressure vessels were also considered. An event tree for the derailment involving overturning of a rail tank car with possible threat to a sphere containing 2000 t of anhydrous ammonia is shown in Figure A7.2.

Missile threats are described in Section A7.5.4.

A7.5.2 Failure of pressure piping

Failure of pressure piping is considered as a possible initiating event for releases of LPG and LNG. The report discusses the failure of LPG pressure piping in Part 2, Section 5.3.1.

LPG is piped around the refineries in pressure piping. The pipes mainly contain liquid, but there are some vapour return lines. It was considered that probably if a large pipe were to fail, there would be a vapour plume, the plume would find a source of ignition and would burn back to the pipe and there form a burning jet. In burning back there would be the possibility of semi-confined vapour explosions. If on a 25 cm diameter LPG pipe the fluid burned as a jet, the latter could be over 50 m long, while if, due to obstruction, it burned rather as a hemisphere, the radius of the latter could be over 10 m.

Various effects of such fires and explosions from LPG pipe failure are reviewed. An LPG sphere should withstand a semi-confined explosion beneath it; a horizontal cylinder

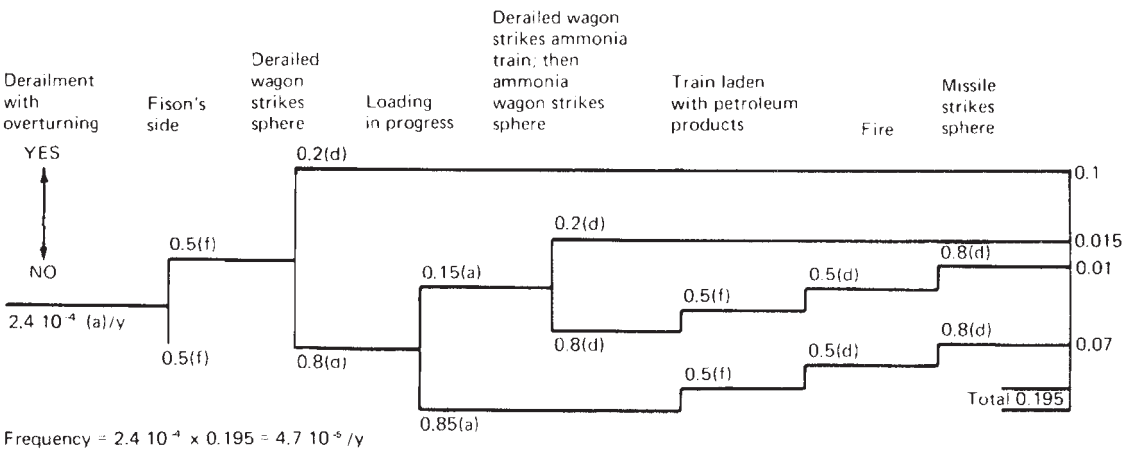

Figure A7.2 *First Canvey Report: event tree for derailment involving overturning of a rail tank car with possible threat to a sphere containing 2000 te of anhydrous ammonia (Health and Safety Executive, 1978b) (Courtesy of HM Stationery Office)*

could be lifted up some tens of centimetres. The principal hazard foreseen, however, is burn back under an LPG storage sphere.

Three cases are treated: (1) failure of a pipe, (2) failure of a pump and (3) failure of a suction line within about 10 m of a storage sphere. The smallest pipe size considered was 15 cm diameter.

It was estimated that the area of a typical refinery is about 3 km^2 and that the length of LPG pipe of diameter $\geq$15 cm in such a refinery is about 3 km, of which about 10% is 25 cm diameter pipe. The total frequency of pipe fracture for this length of pipe was assessed from data in the SRS data bank as 5×10^{-4}/y. For a pipe to affect the storage it must be sufficiently near. The hazard ranges of 15 and 25 cm diameter pipe were taken as 150 and 500 m, respectively. The width of a plume would be of the order of 20°, so that the possibility of the plume lying in any particular direction is 5%. Then the frequencies of involvement of an LPG storage vessel due to pipe failures are

Frequency for 15 cm pipe
$= 2 \times 10^{-2} \times 5 \times 10^{-3} \times 5 \times 10^{-2} = 5 \times 10^{-6}$/y

Frequency for 25 cm pipe
$= 1 \times 0^{-1} \times 2 \times 10^{-1} \times 5 \times 10^{-3} \times 5 \times 10^{-2} = 5 \times 10^{-6}$/y

Total frequency for all large pipes $= 10^{-5}$/y.

The number of LPG pumps in a typical refinery was estimated at about 20. The frequency of catastrophic rupture of such pumps was assessed from data in the SRS data bank as 10^{-4}/y. As before, the probability of the plume in any particular direction is 5%. Then the frequency of involvement of an LPG storage vessel due to a pump rupture is

Frequency for pumps $= 20 \times 10^{-4} \times 5 \times 10^{-2} = 10^{-4}$/y

In addition, there is the possibility that if the pumps are close together (<20 m spacing), a fire at one pump would involve other pumps and would create a large fire regardless of plume direction. Then the frequency for this event is 2×10^{-3}/y.

The proportion of 25 cm diameter LPG pipe within 10 m of a storage vessel was estimated as about 10%. Then the frequency of involvement of an LPG storage vessel due to failure of such pipe is

Frequency for 25 cm pipe beneath vessels
$= 10^{-1} \times 10^{-6} \times 5 \times 10^{-3} = 5 \times 10^{-5}$/y

Thus the frequency of failure of an LPG vessel due to failure of a large LPG pipe or a pump is 1.6×10^{-4}/y. If interaction between pumps can occur as described above, this figure rises to 2.1×10^{-3}/y.

The report also discusses the failure of the pipes that carry LNG from the jetty head to the storage tanks in Part 2, Section 6.5.2.

The frequency of failure of these pipes was assessed as 10^{-4}–10^{-3}/y. The lower rate is more likely during actual transfer pumping and the higher rate during warm-up and cool-down when the pumps are not in use.

A7.5.3 Failure of pipelines

Failure of a pipeline is considered as a possible initiating event for LNG and LPG. The report discusses failure of pipelines in Part 2, Section 15.

There are four methane pipelines leaving the British Gas terminal. One of these is a 35 cm diameter line passing close to the built-up area. A serious failure of this line would lead to a large release of methane, but the gas would be highly buoyant and would undergo turbulent mixing with air, so that there is no chance of the formation of a large vapour cloud heavier than air.

The frequency of a serious failure of the 35 cm pipeline in the built-up area was estimated as not greater than 10^{-4}/y.

There is a liquid butane pipeline from the British Gas terminal to a point near the Shell refinery. The line is 20 cm diameter for 4 km leaving the terminal and then reduces to 15 cm diameter. The line is not used, but contains some 585 t

of liquid butane at a pressure of 4–6 atm. A serious failure of this line could give an initial liquid release rate of 20–30 t/min. If the pressure were sustained by flashing off of propane some 50–100 t could be released in a few minutes. Unless there is a limit on the amount of propane or other volatile component present, the flashing off of the discharging mixture could form a vapour cloud.

The frequency of a serious failure was estimated from data for similar pipelines in the SRS data bank as 3×10^{-4}/km y. The distance travelled by the pipeline through populated terrain is 1.5 km. Thus the frequency of a serious failure causing casualties was estimated as 4.5×10^{-4}/y.

A7.5.4 Generation of and rupture by missiles

Rupture by a missile is considered as a possible initiating event for releases of LPG, ammonia and hydrogen fluoride. The report discusses the generation of missiles in Appendix 5 and the penetration capability of missiles in Appendix 6.

Some scenarios considered are shown in Table A7.5.

The frequency of a large fire in an oil refinery is, for the United States of America, 0.2/y obtained from API data and, for the United Kingdom, 0.25/y obtained from FRS data. The API figures indicate that the proportion of these fires that are very large is about one-third. Thus the frequency of a very large fire in a refinery was taken as 0.1/y.

The proportion of such very large fires that involves explosion was estimated from IRI data as 0.5. The proportion of such explosions that generate missiles was estimated as 0.1.

The frequency of a very large fire that involves an explosion and generates missiles was thus estimated as 5×10^{-3} y.

It was estimated also that on average such a missile-generating explosion generates some half-dozen missiles.

The frequency of disintegration of the rotor of a rotating machine was estimated as 5×10^{-4}/y from data in the SRS data bank.

The report gives in Appendix 6 methods for the estimation of the probability of a missile landing in a given area at a known distance from the source and methods for determining whether the missile will penetrate a vessel.

Missiles particularly considered are fragments from process plant and gas cylinders. With regard to the former a case is quoted in the United Kingdom in which a fractured vessel produced at least seven missiles of 1 t capacity. Reference is also made to the explosion at Whiting, Indiana, where an exploding hydroformer generated some tens of missiles, one of 60 t, with a velocity of 600 ft/s.

Various empirical formulae for penetration by missiles are given. There is considerable variation in the results obtained from these formulae. When used to determine the penetration thickness for a missile with a velocity of 300 ft/s, the penetration thicknesses given by the formulae ranged from 0.25 to 2.75 in. One reason for the variation is that some of the formulae are applicable to clamped flat plates rather than spherical or cylindrical vessels.

It is concluded that

(1) LPG spheres in excess of $1\frac{1}{4}$ in. thick will not be penetrated by flying gas cylinders even at velocities of 300 ft/s, which is a pessimistic upper limit;
(2) spheres and cyinders 0.75 in. thick could be penetrated by flying gas cylinders;
(3) process missiles can be considerably larger than a gas cylinder and can impact with substantially greater energy – these could penetrate LPG spheres and cylinders.

The report also discusses missile threat to the LNG tanks in Part 2, Section 6.5.4.

A7.5.5 Crash of and rupture by aircraft

Rupture by aircraft crash is considered a possible initiating event for release of all the hazardous materials. The report discusses aircraft crash and vessel rupture in Appendix 8.

The frequency of a fixed wing aircraft crash at Canvey was assumed to be that for the United Kingdom in general and not that for an area near the airport. Canvey is within the Special Rules Zone of Southend airport, but is neither close to the main runway nor beneath the airspace of an aircraft waiting to land.

The frequency of an aircraft crash was obtained from UK aircraft accident data. Two alternative equations are given for the frequency of an aircraft crash on a target. They are:

Method 1 $$F = A_H F_H + A'_V F_H \qquad [A7.5.1a]$$

Method 2 $$F = A_H F_H + A_V F_H \qquad [A7.5.1b]$$

where A_H is the horizontal area of the target, A'_V is the vertical area of the target, A_V is the horizontal projection of the vertical area of target; F the frequency of aircraft crash on the target area; F_H is the frequency of aircraft crash per unit of ground area and F_V is the frequency of aircraft crash per unit of vertical area.

In Equation A7.5.1a the value of A'_V was calculated assuming that the impact angle is 15°. In Equation A7.5.1b the value of F_V was calculated from data on the frequency with which aircraft crash into the National Grid system. The latter frequency was taken as 0.1/y.

Results obtained for the frequency of crashes of aircraft of all types on the total target area at Canvey for each type of hazard were identical by both methods except that, for the refrigerated LPG at British Gas, Method 1 gave

Table A7.5 *First Canvey Report: some potential missile accidents at Canvey (after Health and Safety Executive, 1978b)*

Site	*Installation*	*Missile*
Shell	LPG vessel	Missile from storage area
Mobil (including extension)	LPG vessel	Missile from process area
Fisons	Ammonia sphere	Missile from rotating machine
Shell	Hydrogen fluoride plant	Missile from neighbouring plant
Mobil (extension)	Hydrogen fluoride plant	Missile from neighbouring plant

Table A7.6 *First Canvey Report: some potential aircraft crash accidents at Canvey (after Health and Safety Executive, 1978b)*

Site	*Installation*	*Frequency of impact* (impacts/y)
Shell, Mobil, UR, Occidental	LPG	1×10^{-6}
British Gas	Methane	1×10^{-6}
Calor Gas	LPG	2×10^{-6}
London and Coastal Wharves	Oil	7×10^{-6}
Fisons	Ammonia	1×10^{-7}
Shell	Ammonia	1×10^{-7}
Shell, Mobil, UR, Occidental	Process area	2×10^{-5}

a frequency of impact of 6×10^{-7}/y and Method 2 one of 4×10^{-7}/y. Other results were as given in Table A7.6.

The frequency of a helicopter crash was also considered. Helicopters are used to survey pipelines in the area. It was assumed that data on the frequency of helicopter crashes obtained from NTSB publications are applicable to these helicopters. The frequency of crash obtained from these data is 3×10^{-7}/km flown. In such crashes descent is almost vertical.

Frequencies of crash estimated were 2.4×10^{-5}/y, 1.4×10^{-5}/y and 3.6×10^{-6}/y for the Occidental, Shell and Texaco sites. These are not, however, the frequencies of impact on vulnerable targets. These latter frequencies should be very much less, provided the helicopter routes are chosen to avoid such targets.

Helicopters are used by British Gas to survey its gas pipelines. There are about 26 inspection flights per year. The pilots are instructed to avoid flying over industrial complexes and to skirt such locations by about 500 yd.

A7.5.6 Ship collision and other accidents

Ship collision is considered as a possible initiating event for release of LNG, LPG and ammonia. The report discusses ship collision in Appendices 11 and 23.

Ship collision may occur while the ship is at sea, is stationary in mid-channel or is moored at a jetty. At the time of the survey the Port of London Authority (PLA) had just imposed on ships a new speed restriction of 8 knot.

Data on the frequency of ship collisions were obtained from the PLA. These data show that over the 12-year period 1965–76, there were within the scheduled area 592,250 harbour movements and 121 accidents, of which 91 were classed as minor. Thus this gives for collisions of at least moderate severity a frequency of 0.5×10^{-4}/harbour movement.

Other PLA data were analysed to obtain the frequencies of berthing contact, grounding and fire. Thus the frequencies for collision and for these other accidents are

Frequency of ship–ship collision (moderate severity)
$= 0.5 \times 10^{-4}$/harbour movement

Frequency of berthing contact
$= 1.5 \times 10^{-4}$/harbour movement

Frequency of grounding
$= 0.3 \times 10^{-4}$/harbour movement

Frequency of fire
$= 0.5 \times 10^{-4}$/harbour movement

Further PLA data were analysed to obtain the frequency of ship–ship collision for ships in transit in the estuary. Thus the frequency of collision in transit is

Frequency of ship–ship collision (moderate severity) in transit $= 2.3 \times 10^{-5}$/movement

The vulnerability of ships to collision damage varies. The LNG carriers are double-hulled ships, whereas the LPG and ammonia carriers were not considered as of comparable strength. The former have much greater cargo protection.

An investigation of the resistance of ships to impact was carried out in 1959 by Minorsky, who correlated his results in terms of the critical impact speed vs the loaded displacement of the striking ship, and the Minorsky curve method is widely used as a means of assessing impact resistance of ships.

For a typical LPG carrier, data on the relation of the critical impact speed vs loaded displacement of the striking ship were obtained from Lloyds Register. These data were interpreted as meaning that a striking ship with a loaded displacement of about 4000 t (2000 GRT) could penetrate an LPG carrier and cause spillage if there is no speed restriction, but that a loaded displacement of about 15,000 t (7500 GRT) would be necessary if the speed of the striking ship is limited to 8 knot.

Data for another typical LPG carrier were obtained from Norsk Veritas. These data differ from the Lloyds data and indicate that this is an area of uncertainty.

The frequencies of spillage for an ammonia carrier, which in this context is broadly similar to an LPG carrier, were estimated by using the historical data in conjunction with the following assumed probabilities:

Probability of spillage from ship–ship collision $= 0.2$
Probability of spillage from berthing contact $= 0.1$
Probability of spillage from grounding $= 0.2$

Thus for an ammonia carrier the frequencies of spillage due to harbour movements are

Frequency of spillage due to ship–ship collision
$= 1 \times 10^{-5}$/harbour movement

Frequency of spillage due to berthing contact
$= 1.5 \times 10^{-5}$/harbour movement

Frequency of spillage due to grounding
$= 0.6 \times 10^{-5}$/harbour movement

Total frequency of spillage due to harbour movements
$= 3.1 \times 10^{-5}$/harbour movement

An alternative calculation of the frequency of spillage due to harbour movement based on world data gave a value of 1.45×10^{-5}/harbour movement.

It is concluded that for an ammonia carrier a reasonable estimate of frequency of spillage due to harbour movements is unlikely to exceed.

Frequency of spillage due to harbour movements
$= 2 \times 10^{-5}$/harbour movement

but that this estimate might be significantly reduced if more information were available on cargo protection.

The frequency of spillage for an ammonia carrier due to collision in transit in the estuary was estimated using an

assumed probability of spillage due to ship–ship collision of 0.2. Thus for an ammonia carrier frequency of spillage in transit is unlikely to exceed

Frequency of spillage due to ship–ship collision in transit $= 5 \times 10^{-6}$/movement

This estimate might be significantly reduced if more information were available on cargo protection.

The frequency of spillage for an LPG carrier was taken as similar to that for an ammonia carrier. Thus for an LPG carrier the frequency of spillage is unlikely to exceed

Frequency of spillage $= 2 \times 10^{-5}$/movement

Again this estimate might be significantly reduced given more information on cargo protection.

For an LNG carrier, the situation is different because the vessel is double-hulled. This case was the subject of a special study. From this study a relation was obtained for an LNG carrier between the critical impact speed and the loaded displacement of the striking ship. This relation for an LNG carrier differs considerably from that for an LPG carrier, since the former, being double-hulled, has much greater protection. The relation shows that for an LNG ship stationary in mid-channel a striking ship with a loaded displacement of 100,000 t (50,000 GRT) would need to have a speed of 9 knot to effect penetration at a 90° impact angle, and that for an LNG ship moored at a jetting striking ships with loaded displacements of 100,000 t (50,000 GRT) and 20,000 t (10,000 GRT) would need to have speeds of 7 and 13.5 knot, respectively, to effect penetration at a 45° impact angle.

It was assumed, therefore, that only ships with a loaded displacement greater than about 20,000 t (10,000 GRT) have the potential to cause a spillage from an LNG carrier. This does not include allowance for the new PLA speed restrictions.

It was also concluded that for an LNG carrier spillage due to berthing contact could be disregarded.

The frequency of spillage for an LNG carrier was estimated from the historical data in conjunction with the following assumed probabilities:

Probability of striking ship > 20,000 t (10,000 GRT) = 0.1

Probability of strike in vulnerable section = 0.5

Then for an LNG carrier the frequency of spillage is

Frequency of spillage $= 2.5 \times 10^{-6}$/movement

This assessment is based on only four incidents over the 12-year period.

An alternative calculation of the frequency of spillage for LNG carriers based on world data gave a value of 1×10^{-6}/movement.

It is concluded that for an LNG carrier a reasonable estimate for frequency of spillage is

Frequency of spillage $= 2 \times 10^{-6}$/movement

A7.5.7 Flow of a large release of oil

A large release of oil from storage and flow of this oil towards housing is one of the hazard situations considered. The report discusses the methods of calculating the flow of a large release of oil from the catastrophic failure of a storage tank in Appendix 16.

Equations are given for the flow of a slumping fluid derived from those of van Ulden (1974) assuming that his constants c and A have the value of unity. It is assumed that the liquid is initially held in a vertical cylindrical source. The equations are

$$r = [r_s^2 + 2t(gV_s/\pi)^{1/2}]^{1/2} \qquad [A7.5.2]$$

$$h_f = \frac{V_s}{\pi r^2} \qquad [A7.5.3]$$

$$u_f = (gh_f)^{1/2} \qquad [A7.5.4]$$

where g is the acceleration due to gravity (m/s^2); h_f the slumped liquid depth (m); r the radius of the flooded zone (m); r_s the radius of the source cylinder (m); t the time after initiation of slumping (s); u_f the slumped liquid velocity (m/s); and V_s the volume of the source cylinder (m^3).

A7.5.8 Temperature of the wall of an LNG tank exposed to an LNG fire in an adjacent bund

The rupture of an LNG tank due to an LNG fire in an adjacent bund is one of the hazard situations considered. The report discusses the effect of an LNG fire in an adjacent bund on the temperature of an LNG tank wall in Appendix 13.

The LNG tanks considered are cylindrical in shape and are 30 m diameter and 20 m high. They stand in a bund of 60 m diameter.

The temperature of the tank wall is determined by the heat balance on the wall. It was assumed that the wall gains heat by radiation and loses it both by radiation and by convection.

For the heat gained by the tank wall use was made of the experimental work of L.E. Brown, Wesson and Welker (1974b). It was assumed that the heat flux from the fire is 44,000 BTU/h ft^2, which is the maximum average value obtained by these workers for liquid pools of up to 30 m diameter. This value is considered reasonably conservative for bund fires with an effective diameter up to 60 m. The flame height calculated from the empirical formula given by these workers is 75 m. The fraction of the radiated heat received by the tank was then calculated by dividing both the flame and tank surfaces into smaller subsurfaces and determining view factors. The total radiated heat Q_i received by the tank wall was calculated as 3.11×10^7 W.

For the heat loss by the tank wall the equation used for radiation is

$$Q_r = \varepsilon\sigma(A_V + A_H)\theta_T^4 \qquad [A7.5.5]$$

where A_H is the area of the tank roof (m^2); A_V the exposed area of the tank vertical sides (m^2); Q_r the heat loss by radiation (W); ε the emissivity of the tank wall; θ_T the absolute temperature of the tank wall (K); and σ the Stefan–Boltzmann constant (W/m^{2}K^4). The equation used for convection is

$$Q_n = (1.76A_V + 2.25A_H)(\Delta\theta)^{1.25} \qquad [A7.5.6]$$

with

$$\Delta\theta = \theta_T - \theta_A \qquad [A7.5.7]$$

where Q_n is the heat loss by convection (W); $\Delta\theta$ the temperature difference between the tank wall and ambient air (°C); and θ_A the absolute temperature of ambient air (K).

The areas A_V and A_H of tank surface are the exposed areas and since the whole of the roof but only part of the walls is exposed, A_H is based on the whole of the roof surface, but A_V is based on only part of the vertical wall surface.

The equilibrium tank wall temperature θ_T was found to be 647 K assuming an emissivity ε of 0.5 and did not differ by more than 40°C even assuming an emissivity of unity. The tank wall temperature is therefore relatively insensitive to estimates of the emissivity.

The heat loss by radiation is over three times greater than that lost by convection at a tank wall temperature of 650 K.

The time for the temperature of the tank wall to reach steady state was calculated from the unsteady-state equation

$$mc_p \frac{d\theta_T}{dt} = Q_i - (Q_n + Q_r) \qquad [A7.5.8]$$

where c_p is the specific heat of the tank wall (J/kg °C); m the mass of the exposed tank wall (kg); and t the time (s).

The thermal capacity mc_v of the exposed tank wall was taken to include half that of the associated perlite insulation.

Equation A7.5.8 is non-linear and is solved numerically. It was calculated that the time for the temperature of the wall to reach 95% of its equilibrium value is about 42 min.

A7.5.9 Evaporation of LNG and ammonia on water

The spillage and evaporation of LNG and ammonia on water is one of the hazard situations considered. The report discusses the evaporation rates of LNG and of ammonia spilled on water in Part 2, Sections 6 and 7, respectively.

It is stated that for a rapid spill of LNG on water the evaporation time is short and a puff dispersion model is applicable. But for a continuous spill the evaporation rate rapidly reaches the spill rate and this evaporation rate then determines the pool diameter reached. The evaporation rate has been determined by a number of investigators as about 0.19 kg/m^{2}s, which corresponds to a liquid regression rate of 4.7×10^{-4} m/s.

Similarly, it is stated that for a rapid spill of ammonia on water the evaporation time is short and that all the ammonia will evaporate, except for about 20% which dissolves in the water.

A7.5.10 Dispersion of an LNG vapour cloud

The dispersion of an LNG vapour cloud is one of the hazard situations considered. The report discusses the dispersion of an LNG vapour cloud in Appendix 9.

A cloud of cold LNG vapour tends to behave as a heavy gas cloud. The following elements are identified as particularly important in describing the behaviour of such a cloud: (1) specification of the source, (2) description of the gravitational slumping, (3) description of the air entrainment, and (4) description of the thermal effects.

The model of the source that is assumed can have a significant effect on the results. The release may be instantaneous or continuous. The source may be of fixed size or of increasing size, as with LNG spilled on to water. The process of release may or may not involve the entrainment of large amounts of air.

The differences between the various models currently available for the gravitational slumping phase are discussed and it is suggested that these may be due in large part to the extent to which air entrainment is taken into account. The model of R.A. Cox and Roe (1977) is instanced as representative of the new generation of models that take into account air entrainment.

Information is presented on the distance travelled by an LNG cloud before it is diluted to the lower flammability limit, that is, the hazard range. Experimental work described includes

Source	*Release*	*Weather conditions*
API	1/3–10 t on sea	Stable (Pasquill stability category E)
Shell	5–50 t on sea	Relatively stable
AGA	Spillages in bunds giving vapour releases up to 25 kg/s	

Theoretical work mentioned is that of Cox and Roe of Cremer and Warner.

Hazard ranges derived from these sources are shown in Figures A7.3(a) and A7.3(b) for continuous and instantaneous releases, respectively. Models for both instantaneous and continuous releases may be derived from the experimental work described by estimating values of the dispersion coefficients in the Pasquill–Gifford model for an instantaneous release and assuming that these coefficients are the same for a continuous release. This is the basis for the curves shown in Figures A7.3(a) and A7.3(b), except for the API 2.5% case, which is based on the work of Feldbauer *et al.* (1972). The lower flammability limit of methane is approximately 5% and most of the data shown in the figures are for this concentration, but some data are shown for a concentration of 2.5%, which allows for localized short-term concentrations up to the lower flammability limit (LFL).

The weather conditions on which the graphs are based are neutral conditions (Pasquill stability category D) or stable conditions (Pasquill stability category E). For less stable conditions the hazard range is less or at worst no greater. For Canvey more stable conditions (Pasquill stability categories F and G) were not considered, because Canvey Island is an urban site and it has been shown that over such an area the dispersion of a plume in very stable conditions is unlikely to produce airborne concentrations greater than those obtained over open country for neutral and stable conditions (Pasquill stability categories D and E).

The quantities of LNG involved in the releases in Figures A7.3(a) and A7.3(b) are relatively small. The warning is given, therefore, that the use of these graphs for a continuous release of, say, 10 t/s or an instantaneous release of, say, 1000 t involves scaling up by two orders of magnitude with all the uncertainties attendant on such a procedure.

Mention is also made of methods for the prediction of LNG vapour dispersion based on wind tunnel simulations, but it is concluded that the results obtained are subject to too great a range of uncertainty to be useful.

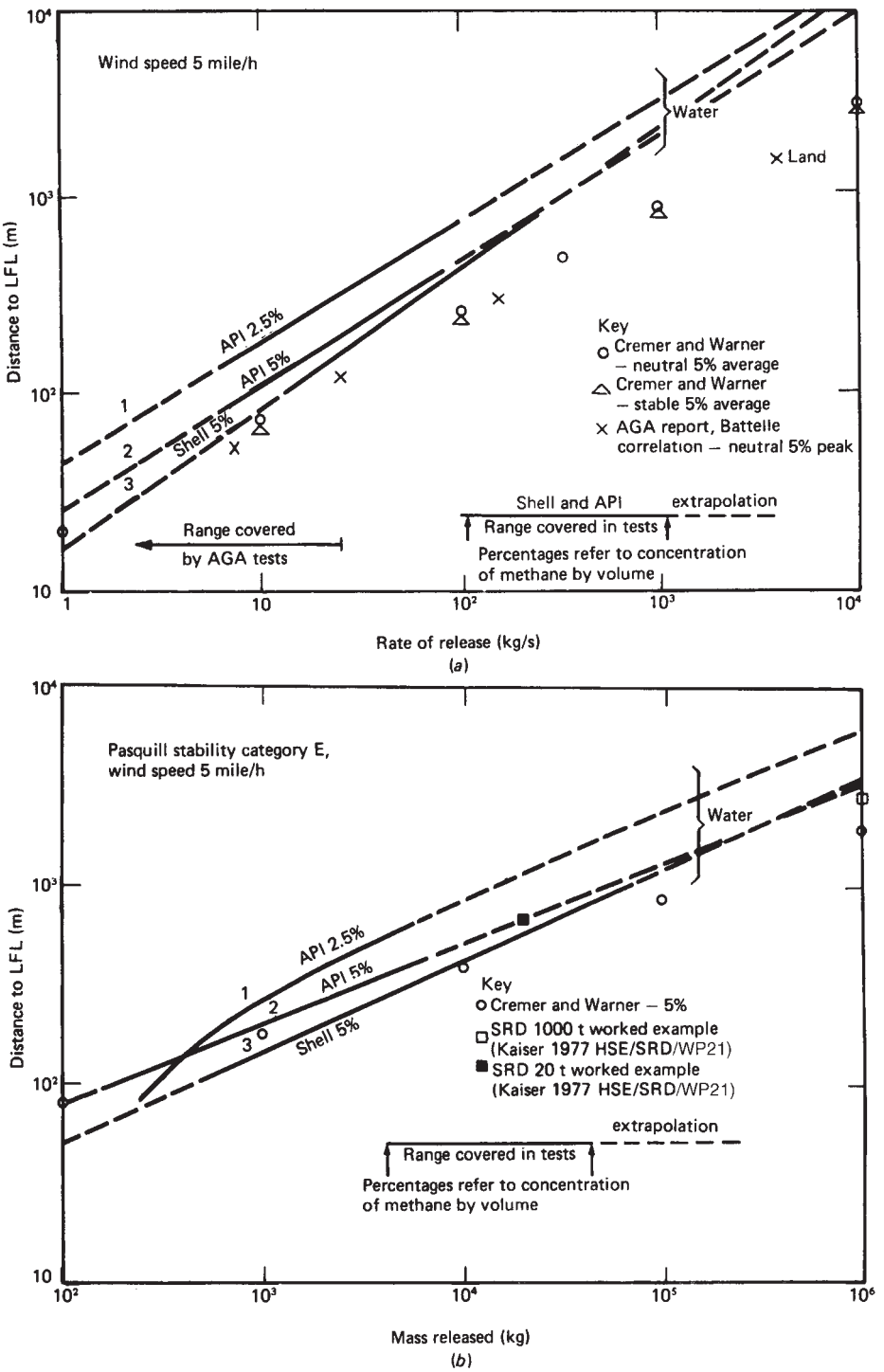

Figure A7.3 *First Canvey Report: hazard ranges for releases of LNG vapour in neutral and stable weather conditions (Health and Safety Executive, 1978b): (a) continuous releases – curve 1 API tests model, 2.5% average, stable condition; curve 2 API tests model, 5% average, stable condition; curve 3 Shell tests model, 5% average, stable condition; (b) instantaneous releases – curve 1 API tests model, 2.5% average, stable condition (Feldbauer et al., 1972); curve 2 API tests model, 5% average, stable condition; curve 3 Shell tests model, 5% average, stable condition (Courtesy of HM Stationery Office)*

For the purpose of the hazard assessment, however, it was necessary to make estimates of the possible range of vapour clouds from marine spillages of LNG. The distances obtained by scaling up the small spillage data were considered too conservative and the following estimates were used:

Spillage (t)	*Maximim range to LFL* (km)	
	average	peak
10	0.54	0.7
100	1.4	1.8
1,000	3.8	5.2
10,000	10	10

The average concentration corresponds to 5% and the peak concentration to 2.5% that, as explained above, allows for localized short-term concentrations of double the latter value.

A7.5.11 Unconfined vapour cloud fire and explosion

An unconfined vapour cloud fire or explosion is considered as one of the possible accidents that could be the cause of fatalities. The report discusses unconfined vapour cloud fire and explosion in Part 2, Sections 4 and 6, and in Appendix 1. The treatment given of unconfined vapour cloud fire and explosion is broadly as follows.

Two standard vapour clouds are considered. The first contains 100 t and the second 1000 t of hydrocarbons.

Ignition of an unconfined vapour cloud may result in fire or in explosion. The fire and explosion characteristics are given for the two standard vapour clouds just mentioned.

Both complex explosion models and a modified TNT equivalent model were used to estimate the damage effects from an unconfined vapour cloud explosion.

Only the modified TNT equivalent model is described here. This is similar to the usual model, except that the relation between peak overpressure and scaled distance is modified to allow for the fact that the explosion is that of a vapour cloud rather than that of TNT.

For the energy of explosion an equivalence factor α is defined such that the explosion of a flammable gas cloud of W t of hydrocarbons with a combustion energy release H kcal produces the same damage effects as a TNT explosion with an energy release of αH kcal. The value of α used is 0.1. In other words, it is assumed that 10% of the hydrocarbons takes part in the explosion.

For the peak overpressure Δp_m and the peak dynamic pressure q_m at radial distance r and scaled distance $r/H^{1/3}$ the relations used are shown in Figure A7.4. Separate curves of Δp_m are given for TNT explosion, for hydrocarbon detonation and for hydrocarbon deflagration with a deflagration velocity of 170 m/s. Figure A7.4 is for spherical symmetry. Results for explosions with hemispherical symmetry may be obtained by doubling the energy release.

Thus, for example, for a hydrocarbon vapour cloud explosion with an energy release αH where

$$H = 11.1 \times 10^6 \text{ W kcal}$$

$$\alpha = 0.1$$

Figure A7.4 gives for hemispherical symmetry

Δp_m		r (m)
(psi)	(bar)	
3	0.2	$69.1\,W^{1/3}$
1	0.07	$196\,W^{1/3}$

For the two standard hydrocarbon vapour clouds considered the fire and explosion characteristics used are shown in Section A of Table A7.7. The ranges quoted for dilution to the LFL are for weather conditions of Pasquill stability category D. The overpressures quoted apply only to the cases where an explosion occurs.

The foregoing indicates for the standard hydrocarbon vapour clouds considered the estimated hazard ranges of fire and of explosion, that is, overpressure effects, where these effects occur.

The probability of ignition of a vapour cloud was taken as 0.1 or 1, depending on whether ignition was regarded as improbable or probable, taking into account the ignition sources between the point of release and the population group.

The probability of deflagration with overpressure in a vapour cloud, given ignition, was taken as 1 for large clouds (>100 t) of flammable gas, as 0.1 for smaller clouds of flammable gas other than methane, and as 0.01 for smaller clouds of methane, reflecting the significantly lower probability of explosion of a cloud of methane compared with one of other hydrocarbons.

For the 1000 t hydrocarbon vapour cloud it was assumed that the whole cloud burns with a fireball approximately equal in volume to that of the cloud formed by the stoichiometric gas–air mixture and further that, where overpressure occurs, the proportion of hydrocarbon taking part in the explosion is 10%.

If the vapour cloud is ignited *in situ*, the hazard to the public for the situations considered is that of explosion. In accordance with the data given in Table A7.7 it was assumed that the overpressure at the site boundary would not exceed 0.2 atm.

An incidence of 1½% is quoted for casualties among the population in the areas subject to an overpressure between 0.2 and 0.05 atm, which is approximately the level of overpressure corresponding to the Explosives Acts recommendations.

If the vapour cloud drifts and is ignited off-site, the hazards to the public for the situations considered are those of fireball and explosion. For this case, where the cloud is ignited and burns fully over the populated region, it was assumed that the whole population engulfed in the fireball is killed. For the 1000 t hydrocarbon cloud burning fully over a populated region with the average population density of the area, the number of fatalities would be 2000. In addition, it was assumed that in this situation there would be 100 further fatalities and 2000 serious injuries caused by explosion effects out to a radius where the overpressure is 0.075 atm.

The more probable case, however, is ignition when the leading edge of the cloud is just beginning to encroach on the populated region.

It was assumed that if for ignition of the cloud on the edge of the populated region, the number of casualties is N and

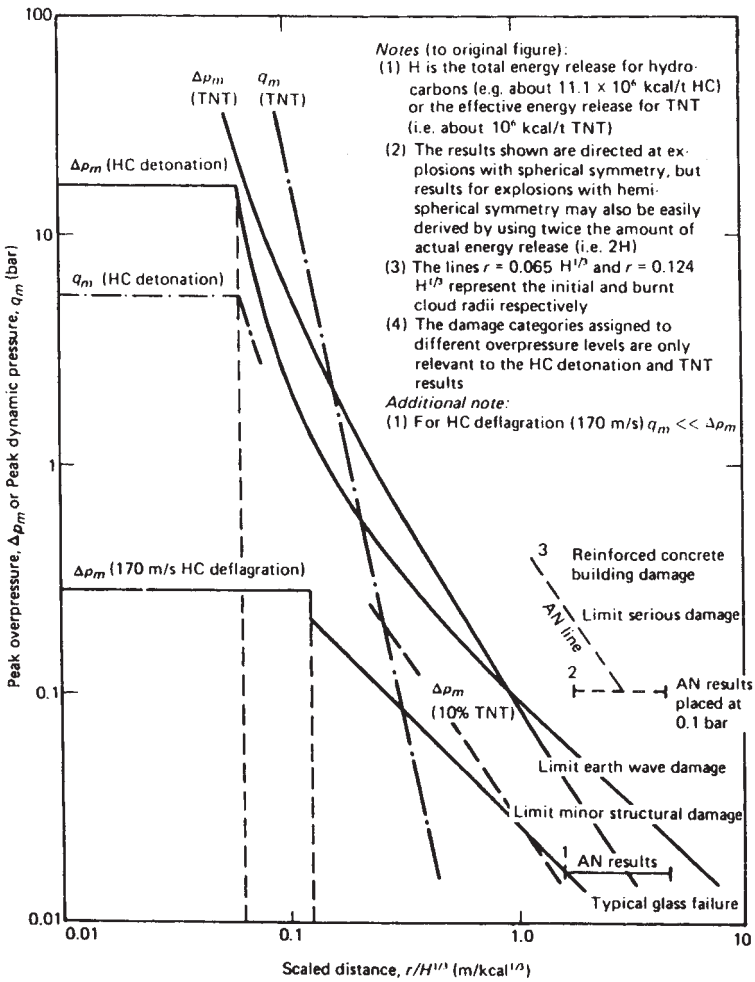

Figure A7.4 *First Canvey Report: peak overpressure and peak dynamic pressure vs scaled distance for various types of explosion (Health and Safety Executive, 1978b) (Courtesy of HM Stationery Office)*

the probability is P, then for ignition right over the populated region the number of casualties is $4N$ and the probability is $0.25P$. It was also assumed that the range of probabilities may be represented by a linear probability distribution function. The corresponding relationships between the numbers of casualties and the probability of these numbers are given in Section B of Table A7.7. The number of fatalities is taken as half the number of casualties.

For a hydrocarbon vapour cloud greater than 1000 t it was assumed that the number of casualties would vary with the mass of vapour according to a 2/3 power law.

The report discusses unconfined LNG vapour cloud fire and explosion in Part 2, Section 6. The following scenarios are among those considered:

Case 1a Release from storage tank (25 cm diameter hole) – vapour cloud of up to 100 t
1b Release from ship's cargo tank at jetty (25 cm diameter hole) – vapour cloud of 100 t
2 Failure of storage tank – vapour cloud of 200 t
3 Failure of ship's cargo tank – vapour cloud of 1000 t

The fire and explosion characteristics of the vapour clouds for these cases are given in Section C of Table A7.7.

The probability of explosion, that is, overpressure in the vapour cloud, was taken as unity only for the larger clouds. The explosion effects were again calculated assuming that 10% of the hydrocarbons take part in the explosion.

A7.5.12 Ammonium nitrate explosion

An ammonium nitrate (AN) explosion is considered as one of the possible accidents that could be the cause of fatalities. The report discusses ammonium nitrate explosions in Part 2, Sections 4.1.2 and 11, and in Appendix 1.

The ammonium nitrate considered is the storage of 92.5% aqueous solution in two tanks of 5000 and 2000 t capacity, respectively. A large spillage from this storage would probably give a mushy heap of ammonium nitrate

Table A7.7 *First Canvey Report: vapour cloud fire, explosion and casualty characteristics used (after Health and Safety Executive, 1978b)*

A Fire an explosion characteristics of hydrocarbon vapour clouds

Mass of hydrocarbon (t)	*Diameter of stoichiometric hemispherical cloud* (m)		*Range of stated overpressure* (km)		*Range for dilution to lower flammability limit* (km)
	Before burning	*After burning*	*0.2 atm* (3 psi)	*0.07 atm* (1 psi)	
100	169	323	0.321	0.910	2
1000	364	696	0.691	1.960	5

B Casualty characteristics of a 1000 t hydrocarbon vapour cloud fire and explosion

Upper limit				
No. of casualty	0	1500	3000	4500
No. of fatalities	0	750	1500	2250
Cumulative probability	1	0.64	0.35	0.14

C Fire and explosion characteristics of an LNG vapour cloud

Case	*Mass of hydrocarbon* (t)	*Burnt cloud radius* (m)	*Radius of stated overpressure* (m)		*Probability of overpressure*
			0.2 atm (3 psi)	*0.07 atm* (1 psi)	
1	100	162	321	910	0.01
2	200	204	404	1147	1
3	1000	348	691	1960	1

crystals near the point of release. An escape of 4500 t of 92.5% solution was considered as the standard case.

If ammonium nitrate is ignited, the result is normally a fire rather than explosion. The latter is likely to occur only if conditions are favourable for transition from a fire to an explosion.

These conditions have been investigated theoretically and experimentally by van Dolah *et al.* (BM 1966 RI 6773) and this work is discussed. It is concluded that the work indicates that transition to explosion would be impossible for quantities of ammonium nitrate of tens of tonnes and probably hundreds of tonnes, but that it might occur at the thousands of tonnes level.

The historical record of ammonium nitrate explosions is reviewed and explosions of prilled ammonium nitrate in transport are quoted, one in rail tank cars at Traskwood, Arkansas, in 1960 and one in road tankers in Queensland in 1972.

The only significant possibility foreseen for the occurrence of an ammonium nitrate explosion was the derailment of a train carrying petroleum products that could cause simultaneously the rupture of an ammonium nitrate tank and a liquid petroleum fire.

The frequency of a derailment and overturning was calculated as follows:

Frequency of derailment of rail tank car
$= 1 \times 10^{-6}$/train km

Number of trains with petroleum products
$= 3000$/y

Length of track opposite tanks ≈ 300 m

Probability of derailment leading to overturning $= 0.2$

Probability of overturning on tank side of track $= 0.5$

Frequency of derailment and overturning on tank side of track $= 8.5 \times 10^{-5}$/y

In view of the many uncertainties and of the omission of other possible accident modes this latter value was also taken as the frequency of an ammonium nitrate explosion. Thus

Frequency of ammonium nitrate explosion
$= 8.5 \times 10^{-5}$/y

The effect of an ammonium nitrate explosion was assessed by reference to the data on such explosions given by M.A. Cook (1958) and shown in Table A7.8.

These results were interpreted as follows. It was assumed that the predominant reaction in the explosion of ammonium nitrate is

$$2NH_4NO_3 = 2N_2 + 4H_2O + O_2$$

for which the heat of reaction is 0.35×10^6 k cal/t. Then using this heat of reaction the values obtained for the group $r/H^{1/3}$ (m/(kcal)$^{1/3}$) corrected for spherical symmetry for the distance for major damage in the four explosions listed lie in the range 1.72–4.8. This spread indicates a lack of agreement with the 1/3 power scaling relation, which is reduced but not eliminated if a 1/2 power scaling relation

Table A7.8 *First Canvey Report: some major ammonium nitrate explosions (after Health and Safety Executive, 1978b)*

Date	*Location*	*Mass of ammonium nitrate* (t)	*Distance for major damage* (m)	*Fatalities*
1918	Morgan, NJ	500	1600	64
1923	Oppau, Germany	4500	7000	1100[a]
1947	Brest, France	3000	5000	21
1947	Texas City, TX	3500	2300	560

[a] This value differs from that given by Commentz *et al.* (1921).

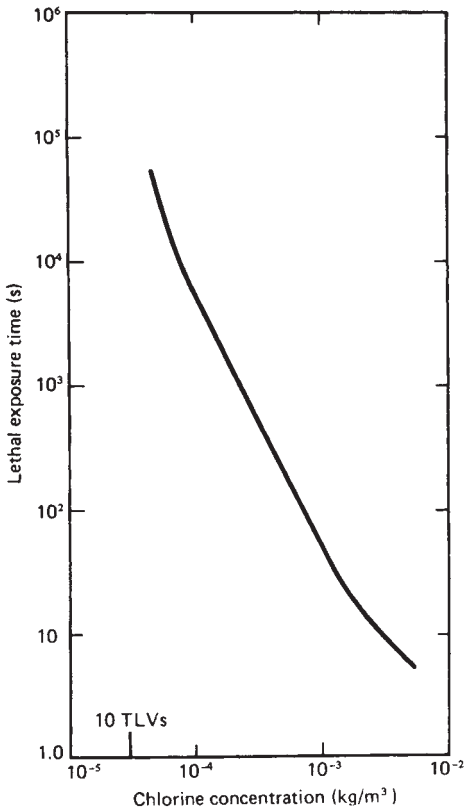

Figure A7.5 *First Canvey Report: lethal exposure time vs concentration for chlorine (Health and Safety Executive, 1978b) (Courtesy of HM Stationery Office)*

is used. The disagreement may be due in part to the relative lack of precision in the term 'serious damage'. If these results are located on the curve for overpressure Δp_m (TNT) in Figure A7.4, then, as shown by the full line (line 1) in this figure, they correspond to an overpressure of 0.02 bar. This is an extremely low overpressure to cause serious damage. In view of this dilemma, it was decided to locate the ammonium nitrate results at an overpressure of 0.1 bar, as shown by the dotted line (line 2) in Figure A7.4, although they then lie above the TNT curve. It is the further dotted line (line 3) which is used to calculate the damage ranges for explosions of 2250 and 4500 t of ammonium nitrate in the report.

A7.5.13 Toxicity of chlorine, ammonia, hydrogen fluoride and lead additives

The toxicity of chlorine, ammonia, hydrogen fluoride and lead additives is considered. The report discusses the toxicity of chlorine in Appendices 3 and 12, that of ammonia in Appendix 15, that of hydrogen fluoride in Appendix 12 and that of lead additives in Appendix 19.

There is considerable uncertainty about the lethal dosages for all these chemicals and it was necessary, therefore, to make approximate estimates.

Chlorine was not one of the chemicals considered in the study to constitute a hazard at Canvey, but its toxicity is discussed in relation to factors that mitigate casualties from a toxic release and in relation to the toxicity of hydrogen fluoride.

For chlorine the relation between the lethal concentration and the time of exposure shown in Figure A7.5 was used. This graph is derived from data given by Dicken (1974, 1975).

For ammonia a probit equation was used

$$\mathrm{Pr} = a + b \ln D \qquad [A7.5.9]$$

with

$$D = \int_0^t C^{2.75}\,\mathrm{d}t \qquad [A7.5.10]$$

where C is the concentration (g/m^3); D the dosage ((g/m^3)$^{2.75}$min); Pr the probit; t the time (min); and a,b are constants.

Precise information on the lethal dosage of ammonia is lacking. Two cases were considered. For case A it was assumed that a concentration of 1.75 g/m^3 (2500 ppm) is lethal to 50% of the exposed population in 30 min, while for case B it was assumed that the same concentration is 50% lethal in 60 min. Then the values of the constants are

	a	b
Case A	1.14	0.782
B	−7.41	2.205

For hydrogen fluoride it is necessary to take care with the units in which concentration is expressed on account of

the high degree of association in the vapour phase. Concentrations are therefore expressed in units of mg/m^3 rather than of ppm.

Precise information on the lethal dosage of hydrogen fluoride is again lacking. Insofar as it is an irritant gas it appears to have effects similar to chlorine at similar concentrations. The toxicity of hydrogen fluoride was therefore assumed for the purpose of the study to be similar to that of chlorine at a similar concentration, where the concentration units are mg/m^3.

In addition, however, hydrogen fluoride in large but sublethal dosages may also have other injurious long-term effects.

The lead additives are the alkyl lead compounds, particularly the methyl and ethyl derivatives.

For lead additives precise information on the lethal dosage is again lacking. The medical evidence is reviewed in some detail. It is concluded that there is a significant probability of fatality at a concentration of 500 mg/m^3 for an exposure of 1 h. It is also considered that total dosage is more important than concentration so that the concentration can be scaled inversely with the exposure time for exposure times in the range 15–60 min.

A7.5.14 Dispersion of ammonia and hydrogen fluoride vapour clouds

The dispersion of anhydrous ammonia and hydrogen fluoride gas clouds is one of the hazard situations considered. The report discusses the dispersion of an ammonia gas cloud in Part 2, Section 7, and in Appendices 4 and 14 and that of a hydrogen fluoride gas cloud in Part 2, Section 5.5, and in Appendix 12.

The dispersion of an anhydrous ammonia cloud depends on whether it is lighter or heavier than air. The following conclusions are reached. If an initial fraction of the ammonia released is in the form of suspended droplets, the cloud may become denser than air as it is diluted. There will be a critical value for the initial fraction of droplets such that if the fraction is below this value the cloud will be less dense than air regardless of the humidity of the air. There will be a second critical value such that if the fraction is above this value the cloud will be more dense than air regardless of the humidity of the air. These two critical values are given, respectively, as 4–8% and 16–20% of the total mass of ammonia. Between these critical values the density of the cloud is determined by the degree of dilution and humidity of the air. High values of the air humidity favour low cloud densities and vice versa, since water in the atmosphere will tend to freeze and so liberate latent heat.

The possible chemical reactions of anhydrous ammonia with the water and the carbon dioxide in the air to give ammonium hydroxide and ammonium bicarbonate and carbonate are also reviewed, but it is concluded that it seems unlikely that any such reaction will be a significant effect, although in foggy or rainy conditions it may convert some ammonia to a less toxic form and so effect some reduction in the hazard.

The historical record of anhydrous ammonia releases is reviewed and those at Blair, Conway, Potchefstroo and Houston are quoted. In all these cases the ammonia cloud appears to have behaved as denser than air.

The emission and dispersion of a release of 1000 t of anhydrous ammonia from pressurized storage at 6°C in weather conditions of Pasquill stability category D and wind speed of 3 m/s were calculated.

For emission it was assumed that the whole mass of 1000 t of ammonia is released virtually instantaneously, that 20% of the ammonia forms vapour and that the remaining 80% forms liquid droplets, so that the whole amount spilled is airborne.

The escaping ammonia will entrain air. There is little information available on this aspect, although the Potchefstroom accident provides some evidence. There some 40 t of ammonia were released and eyewitness accounts stated that 'the *immediate* resulting gas cloud was about 150 m in diameter and nearly 20 m in depth'. This corresponds approximately to an air–ammonia mass ratio of about 10 if all the ammonia was airborne and visible. If it is assumed that in the scenario considered enough dry air is mixed with the ammonia to vaporize all the liquid ammonia, leaving an air–ammonia mixture at the boiling point of ammonia, the corresponding air–ammonia mass ratio is about 20.

The following conditions were taken, therefore, as the source for the dispersion model. The release is 1000 t of anhydrous ammonia. This forms a vapour cloud with an air–ammonia mass ratio of 20 at a temperature of −33°C and with a density of 1.42 kg/m^3. This density is greater than that of air at 20°C by a factor of 1.18 so that the cloud is denser than air. Both the radius and height of the cloud are 167 m.

For dispersion it was assumed that the behaviour of the vapour cloud is described initially by a heavy gas slumping model and then by a neutral gas dispersion model. This follows the approach developed by van Ulden (1974).

For slumping, van Ulden's model is used

$$\frac{\mathrm{d}r}{\mathrm{d}t} = \left(\frac{(\rho_0 - \rho_\mathrm{a})gh}{\rho_0}\right)^{1/2} \qquad \text{[A7.5.11]}$$

with

$$h = V_0/\pi r^2 \qquad \text{[A7.5.12]}$$

and

$$r^2 - r_0^2 = 2\left[\left(\frac{(\rho_0 - \rho_\mathrm{a})gV_0}{\pi\rho_0}\right)t\right]^{1/2} \qquad \text{[A7.5.13]}$$

where g is the acceleration due to gravity; h the height of the cloud; r the radius of the cloud; r_o the initial radius of the cylinder; t the time; V_O the initial volume of the cylinder; ρ_a the density of air; and ρ_o the initial density of the cloud.

The termination of slumping depends in this model on the turbulent energy density and hence on the surface roughness length. For a roughness length z_o of 10 cm the predicted height h at termination of slumping is 0.15 m. For the purposes of this approximate calculation the height h at termination of slumping was taken as 1 m.

The state of the cloud at termination of slumping is then as follows. The radius is 2170 m, the height is 1 m, the density is 1.42 kg/m^3. The time taken is about 12 min and the distance travelled with the wind speed of 3m/s is about 2.6 km.

This model predicts, therefore, that the cloud radius becomes very large and that the cloud travels far downwind. The cloud travel distance is regarded as pessimistic, because it is to be expected that at a height of 1 m the cloud will be slowed down by various obstacles.

For further dispersion the Pasquill–Gifford model for a neutral buoyancy gas was used

$$\chi(x;y;t) = \frac{2Q^*}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z} \times \exp\left[-\frac{1}{2}\left(\frac{(x-ut)^2}{\sigma_x^2}+\frac{y^2}{\sigma_y^2}\right)\right] \qquad [A7.5.14]$$

with

$$\sigma_x = \sigma_y \qquad [A7.5.15]$$

where x y and z are the distances in the downwind, crosswind and vertical directions (m); Q^* the mass released instantaneously (kg); t the time (s); u the wind speed (m/s); σ_x, σ_y and σ_z the standard deviations, or dispersion coefficients, in the downwind, crosswind and vertical *(x,y,z)* directions (m); and χ the concentration (kg/m^3). The downwind distance x is measured from the source. At the termination of slumping it was assumed that the cloud has a Gaussian concentration distribution with the 10% edges of the cloud equal to the edges of the slumped cloud. Then at transition

$$r = 2.14\sigma_y \qquad [A7.5.16]$$

$$h = 2.14\sigma_z \qquad [A7.5.17]$$

The maximum concentration on the axis at a downwind distance x occurs when the centre of the cloud is at that point so that

$$x = ut \qquad [A7.5.18]$$

and hence

$$\chi_{\max}(x) = \frac{2Q^*}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z} \qquad [A7.5.19]$$

The mean concentration $\chi_{av}(x)$ along the axis is related to the maximum concentration $\chi_{\max}(x)$ as follows:

$$\chi_{av}(x) = 0.585\ \chi_{\max}(x) \qquad [A7.5.20]$$

The mean concentrations calculated for the release considered are given in Figure A7.6. Figure A7.6(a) shows the mean concentration as a function of downwind distance and Figure A7.6(b) the mean concentration as a function of exposure time.

The distance at which the ammonia cloud is potentially lethal is obtained from Figure A7.6. If it is assumed that the ammonia is potentially lethal at a concentration of 0.002 kg/m^3 for a period of 30–50 min, the range of potential lethality of the cloud is 5 km from the point at which slumping is terminated. This point is itself 2.6 km from the source.

Cloud behaviour was also investigated for other weather conditions.

The approximate area within which people are at risk from an instantaneous release of 1000 t of anhydrous ammonia in weather conditions of Pasquill stability category D and wind speed of 6 m/s is shown in Figure A7.7.

The model just described is a relatively crude one. Further, more sophisticated models were derived which took into account (1) the heating of the cloud and (2) the entrainment of air during the slumping phase. These models indicated that the overall behaviour of the cloud is not greatly altered by these effects and that the original model gave a sufficient representation for approximate calculations.

The dispersion of a hydrogen fluoride gas cloud also depends on whether it is lighter or heavier than air. Hydrogen fluoride monomer has a molecular weight of 20, which suggests that the gas should be lighter than air. But hydrogen fluoride gas is highly associated, forming in particular the hexamer. Although dissociation takes place as the gas is diluted, the process is endothermic so that cooling occurs. Thus the behaviour of a hydrogen fluoride gas cloud is in some ways analogous to that of an ammonia gas cloud.

The approach adopted was to treat the hydrogen fluoride cloud as denser than air.

A7.5.15 Factors mitigating casualties from a toxic release

Large toxic releases are considered as one of the possible accidents which could be the cause of fatalities. Theoretical estimates of large toxic releases tend, however, to give rather large numbers of fatalities and to appear pessimistic compared with the historical record. Consideration was therefore given to the factors mitigating casualties from a toxic release.

The report discusses mitigating factors for a toxic release in Appendix 3.

The historical record of chlorine releases is reviewed. The releases listed by Simmons, Erdmann and Naft (1974) are quoted, as are the releases at Zarnesti, Roumania, in 1939 and at Baton Rouge, Louisiana, in 1976.

The following features are adduced as factors that may mitigate the effects of a chlorine release:

(1) low population density downwind of the source, particularly within the first kilometre or so;
(2) favourable weather conditions;
(3) low rate of release;
(4) escape;
(5) shelter.

It is possible to make a quantitative estimate of the effect of these factors. There are other factors such as

(6) topography

which may also be important, but which in the present state of knowledge cannot be readily assessed.

A series of calculations was done for a 20 t chlorine release over periods of 6 s, 10 min and 6h in weather conditions of Pasquill stability category D and with a wind speed of 5 m/s.

The calculations were based on the Pasquill model for short continuous releases, as given in Equation 15.16.31,

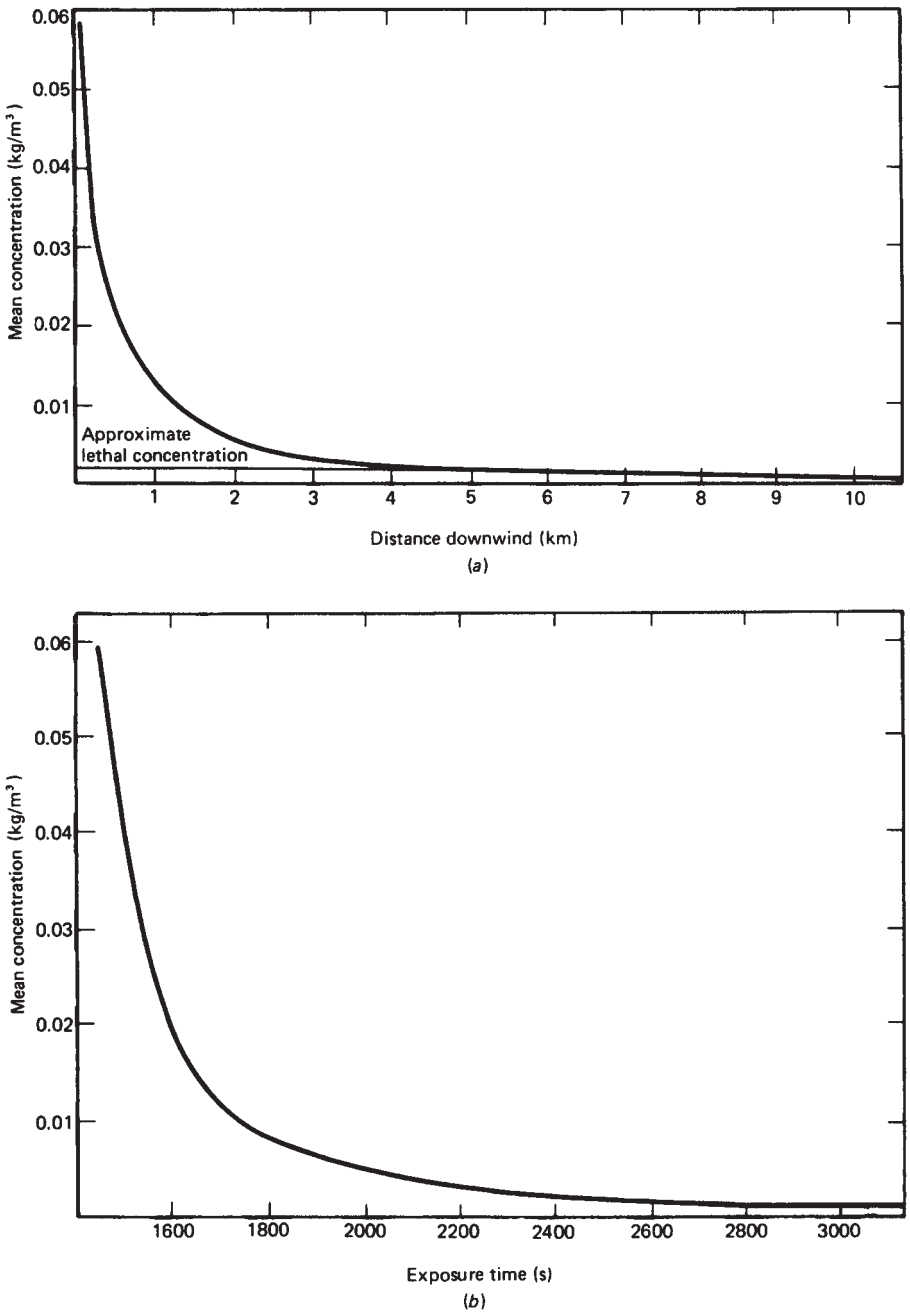

Figure A7.6 *First Canvey Report: mean concentration vs distance and exposure time for an instantaneous release of WOO te of anhydrous ammonia (Health and Safety Executive, 1978b): (a) mean concentration vs distance and (b) mean concentration vs exposure time (Courtesy of HM Stationery Office)*

using the graphs presented by Bryant (1964 UKAEA AHSB(RP) R42 Figure 4). This model may be adapted to the determination of the time of passage and the dosage from a nearly instantaneous release, as follows. The time of passage for an instantaneous release is obtained as the times between the concentration rising to, and subsequently falling back to, one-tenth of its maximum value. This time of passage is corrected for a nearly instantaneous release

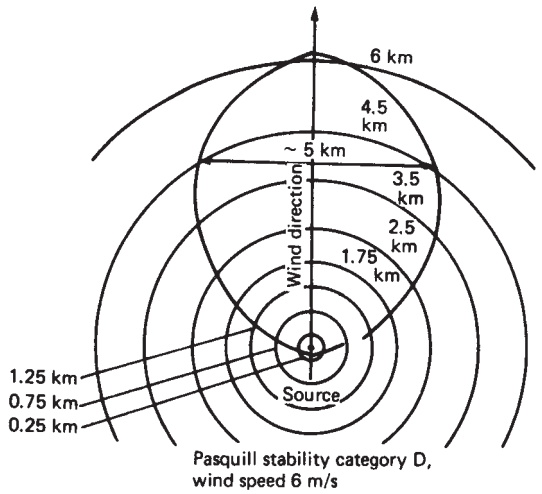

Figure A7.7 *First Canvey Report: approximate area within which people are at risk from an instantaneous release of 1000 te of anhydrous ammonia (Health and Safety Executive, 1978b) (Courtesy of HM Stationery Office)*

by adding to it the time of release. For the dosage use is made of the fact that Equation 15.16.31 gives the total dosage for an instantaneous release, as described in Chapter 15. The model applies strictly to short releases of approximately 3 min duration. No account was taken, therefore, of plume broadening with duration of release, but it was believed that this effect would be small for the stability condition considered.

For various points on the downwind axis of the cloud, calculations were made of the dosage and of the time of passage, and by dividing the former by the latter, of the mean concentration. The chlorine toxicity data given in Figure A7.5 were used to determine for each mean concentration the corresponding lethal exposure time. If the lethal exposure time was less than the time of passage, then the cloud was assumed to be fatal to a person remaining in the open air at that point.

The results of the calculations are summarized in Figures A7.8(a–c), which show the mean concentration, the time of passage and the lethal exposure time vs distance for the three releases studied.

The distances at which the time of passage and lethal exposure time cross over are the lethal distances, or hazard ranges, of the clouds. These distances are 2.7, 1.9 and 0.6 km for release times of 6 s, 10 min and 6 h, respectively. The variation of the lethal range is due entirely to the slope of the line of lethal concentration vs exposure time in Figure A7.5, which is a log–log plot. If the slope were -1 instead of approximately -2, there would be no variation of distance.

The effects of the mitigating factors are discussed in the light of these results.

For population density the effect of low population density is as follows. In a UK urban area with a population density of about 5000/km^2 the numbers in a 15° sector would be about 650, 2650 and 6000, while in a UK rural area with a population density of about 100/km^2 the corresponding numbers would be 13, 53 and 120 within distances of 1, 2 and 3 km, respectively. Thus it is estimated that a rapid release of 20 t of chlorine gas could kill up to 6000 in an urban area and up to 120 in a rural area.

The effect of more favourable weather conditions was not calculated. It was considered that, in view of the uncertainties in gas dispersion estimates, calculations for other weather conditions were not justified.

The effect of a lower rate of release is to reduce the estimated number of fatalities. The values may be calculated from the data given.

The effect of escape was estimated by calculating the time for a man to walk out of the cloud. It was assumed that if the axial concentration is lethal for the time of passage of the cloud, the concentration halfway out of the cloud may be considered only injurious and that at the edge of the cloud, defined as 10% of that of the centre, relatively harmless. It was assumed that the man would walk out of the cloud across wind at a speed of 3 mile/h (1.34 m/s). Escape was assumed if the time to walk from the cloud centre to the cloud edge was less than the lethal exposure time at the axial concentration. The times to walk out are shown in Figures A7.8(a–c). The distances at which the time to walk out and the lethal exposure time curves cross are the lethal distances of the clouds allowing for escape. For the release time of 6 s the lethal range remains 2.7 km, but for the release times of 10 min and 6 h it is reduced to 1.1 km and less than 100 m, respectively.

The effect of shelter was estimated using the equation

$$C = C_0[1 - \exp(-\lambda t)] \qquad [A7.5.21]$$

where C is the concentration indoors; C_0 the concentration outdoors; t the time; and λ the number of air changes per unit time.

The value of λ is about one change per hour for a modern centrally heated building, but in general can be two or three changes per hour, particularly if doors or windows are open. Assuming that shelter with one air change per hour is used, for a 6 s release the cloud is lethal at 100 m, but not at 200 m, and for a 10 min release it is lethal at 300 m, but not at 500 m. For a 6 h release the concentration in the building rises to that outside it after 1 h and the cloud is lethal at 0.6 km as before. Thus shelter is very effective for the release time of 6 s and quite effective for the release time of 10 min, but is ineffective for the release time of 6 h. In the latter case, however, escape is relatively easy.

A7.5.16 Road tanker hazards

A road tanker accident is considered as a possible initiating event for release of flammable and toxic materials. The report discusses road tanker accidents in Part 2, Section 14, and in Appendix 18.

The nature of the hazard from a road tanker accident is not discussed in as much detail as that from some of the other hazards. Mention is made of the possibility of a 10 t spillage of flammable material which could give rise to a fire (p. 96) and of spillage of LPG which could give rise to a 14 t cloud which could travel 200 m and still remain flammable (p. 178).

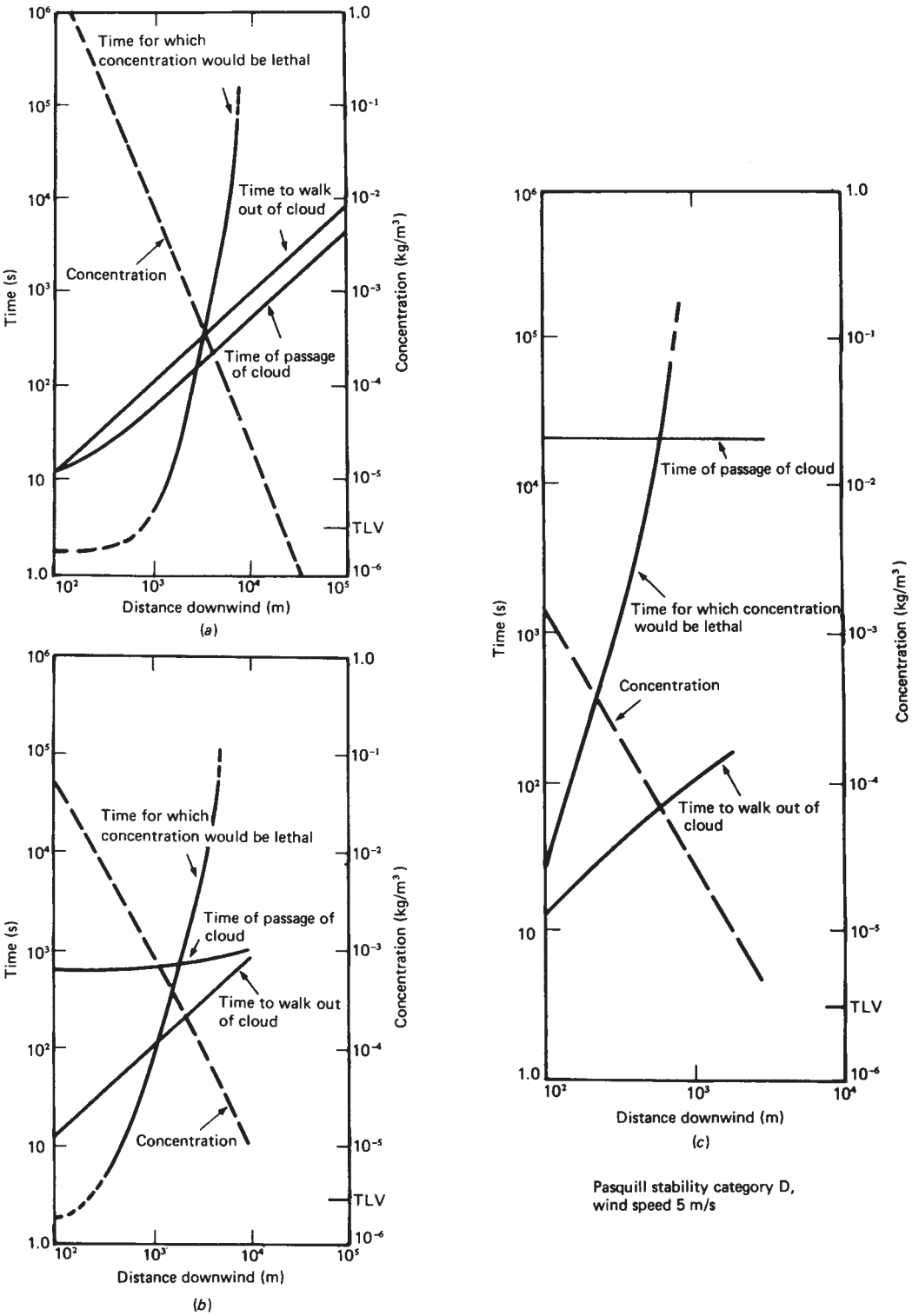

Figure A7.8 *First Canvey Report: mean concentration, lethal exposure time, time of passage and time to walk out vs distance for a 201 release of chlorine with various release times (Health and Safety Executive, 1978b): (a) release time of 6 s; (b) release time of Wmin and (c) release time of 6 h (Courtesy of HM Stationery Office)*

The frequency of spillage is estimated from data recorded by HM Inspector of Explosives on accidents resulting in loss of life and personal injury and involving the contents of petrol tankers. These records indicated that over the past 5 years there were on average five accidents per year that led to a spillage. But from statistics published by the DoE (1976) the quantity of petroleum products moved by road is 4.3×10^9 t km. Then since the average tanker load is 14 t

Frequency of petrol tanker accident involving spillage $= 1.6 \times 10^{-8}$/km

Tankers carrying LPG are stronger than petrol tankers, but the conservative assumption was made that the frequency of accidents involving spillage is the same for LPG tankers as for petrol tankers.

The frequency of spillage from all hazardous materials transported by road from the British Gas Corporation, London and Coastal Wharves, and Texaco was then estimated as 1.4×10^{-3}. The contribution of flammables to this figure is the largest, that of toxics being relatively small.

A7.5.17 Evacuation

The mitigating effect of evacuation was also considered. The report discusses evacuation in Part 1, Section 10, and in Part 2, Section 16.

There are two respects in which the evacuation situation at Canvey Island is unusual. There are only two roads leading off the island, and these converge at a single roundabout, and there exist already plans for evacuation in the event of flooding by the sea.

The need for an additional road off the island has been the subject of debate in the area.

The evacuation process was modelled. An exponential model was used in which it was assumed that half the population is moved to safety in the first 2 h, half of the remainder in the next 2 h and so on.

Evacuation was found to be possibly beneficial in one or two types of emergency. In particular, consideration was given to evacuation in the event of a large release of ammonia from a ship collision or jetty incident. For the majority of emergencies, however, it is suggested that it would be better to remain indoors rather than to attempt evacuation.

Such evacuation would require prior planning. The existing arrangements for evacuation for flooding would not necessarily suffice, since the advance warning from a chemical emergency is likely to be less.

Similarly, the provision of an additional road was seen as beneficial for the same types of incident, but it was considered that the construction of such a road could not be recommended solely for evacuation without further discussion.

A7.6 First *Canvey Report*: Assessed Risks and Actions

The hazards described in Section A7.3 were assessed using appropriate failure and event data as described in Section A7.4 and hazard models and risk estimates, including those described in Section A7.5. The accidents that might occur, the nature and frequency of the initiating events and the frequency–number relations for casualties, or societal risks, are shown in Table A7.9.

The results of the risk assessments are presented by the investigators as risks of causing casualties, that is, severe hospitalized casualties or worse. This is in accordance with established practice (e.g. Department of Defense, n.d.; Glasstone, 1964). It was considered misleading to attempt to distinguish between severe injury and death.

These results have several interesting features. The hazards may be ranked for societal risks in order of descending frequency for accidents of different magnitude as shown in Table A7.9.

The hazard arising from the very large quantities of LNG stored is a serious one, but is no worse than that from the considerably smaller quantities of LPG.

The obvious hazards of LNG, LPG and ammonia are equalled by others, such as oil and hydrogen fluoride, which are perhaps less well appreciated.

The relative importance of the hazards changes with the scale of the accident. For the smaller scale accidents oil spillage, flammable vapour clouds and toxic gas clouds are all important. As the scale increases, it is the toxic gas clouds that dominate.

There are a number of interactions identified both within sites and between sites. These include the threat to LPG storage at Mobil from the Calor Gas site, to the oil storage at Texaco from explosives barges, to the ammonia sphere at Fisons from rotating machinery and from the ammonium nitrate plant at Fisons, to various installations from process and jetty explosions, and possibly to the ammonia storage tank at Shell from explosion in the Shell refinery.

The relative hazard of the pressure storage of anhydrous ammonia at Fisons is much greater than that of the refrigerated storage of the same chemical at Shell. The risk for the latter was assessed as negligible with the possible exception of rupture by an explosion.

The assessed societal risks are shown in Table A7.9 and in Figure A7.9. Figure A7.9(a) gives the societal risks for all the existing installations. It shows that the risk of an accident causing more than 10 casualties is 31×10^{-4}/y. Figure A7.9(b) gives the societal risks for all the proposed developments. It shows that the risk of an accident causing more than 10 casualties is 16×10^{-4}/y.

The assessed individual risks are given for all the existing installations. These range from 13×10^{-4}/y in region A to less than 1×10^{-4}/y in region G of the area. The individual risks are also given for all the existing installations and proposed developments. These range from 26.3×10^{-4}/y in region A to less than 2×10^{-4}/y in region G (Table A7.10).

The investigators made a number of recommendations for the reduction of the hazards. These included

(1) oil spillage – construction of a simple containing wall around the London and Coastal Wharves and Texaco sites and the proposed Occidental and UR refinery sites;
(2) LNG tank flooding – construction of a dike;
(3) spontaneous failure of LPG spheres – high standard of inspection;
(4) LPG vessel rupture by missile (Mobil) – measures including fitting of pressure relief valves on cylinders at Calor Gas depot;
(5) LPG tank failure at BG jetty – improvement of bund;
(6) LPG pipeline failure (BG) – removal of pipeline;
(7) spontaneous failure of ammonia sphere – high standard of inspection, control of ammonia purity;
(8) ammonia release at Shell jetty – provision of water sprays at jetty;

Table A7.9 *First Canvey Report: principal hazards identified at Canvey and associated societal risks (after Health and Safety Executive, 1978b)*

Hazardous material	*Company*	*Initiating event*	*Type of accident*	*Frequencies in units of 10^{-6}/year*							
				Frequency of initiating event	*Frequencies for number of offsite casualties exceeding*						
					10	*1,500*	*3,000*	*4,500*	*6,000*	*12,000*	*18,000*
Oil	L & C, Texaco	Explosion at BG jetty	Oil spillage over bund	1,800	1,230	1,000	500	130			
		Explosion at Occidental jetty		3,600							
	Texaco	Explosion of stranded explosives barge		2,500	50	35	17	7			
		Explosion of stranded explosives barge and breaching of sea wall		6	6	4	3	2	1		
	Occidental	Explosion in process area		1,000	25	18	8	4			
	Occidental, UR	LPG explosion due to spontaneous failure of sphere		150	30	20	10	4			
		Refinery fire		100,000	25	18	8	3			
		Subtotal			1,366	1,095	546	150	1		
LNG	British Gas	Incident at BG jetty (spillage, ship collision, fire, explosion)	LNG vapour cloud	2,000	168	118	83	56	37	16	7
		LNG ship collision		50	5	3	1	0.5	0.3	0.2	0.1
		Flooding of tanks		500	106	70	37	14			
		Spillage over bund of above-ground tanks		180	56	33	17	10			
		Spillage into bund of above-ground tanks		540	162						
		Subtotal		3,270	497	224	138	80	37	16	7
LPG	British Gas	Explosion at BG jetty	LPG vapour cloud	–	520	320	160	80			
		Pipeline failure		450	450						
		Subtotal			970	320	160	80			
LNG and LPG	British Gas	Subtotal		3,720	1467	544	298	160	37	16	7
LPG	Shell	Spontaneous failure of vessel	LPG vapour cloud	140	184	110	60	25			
		Missile from storage area		100							
		Shock wave from filling point or process area		1,235							
	Mobil	Spontaneous failure of vessel		230							
		Missile from process area		240							

Table A7.9 *(continued)*

Hazardous material	*Company*	*Initiating event*	*Type of accident*	*Frequencies in units of* 10^{-6}*/year*						
				Frequency of initiating event	*Frequencies for number of offsite casualties exceeding*					
					10	*1,500*	*3,000*	*4,500*	*6,000*	*12,000*	*18,000*
		Interaction from Calor Gas; sphere failure		4,100	87	50	24	12			
		Interaction from Calor Gas; pipework failure		1,200							
	Shell, Mobil	Fire or explosion at jetty		5,700	69	43	30	15			
	Occidental	Spontaneous failure of vessel		90	3	2	1				
		Fire or explosion at jetty		4,000	80	50	28	11			
	UR	Spontaneous failure of vessel		70	18	8	4	2			
	—	LPG ship collision		6,640	196	124	64	31			
		Subtotal		23,745	637	387	211	96			
Ammonium nitrate	Fisons	Rail accident	Ammonium nitrate explosion	85	85	85	85	17	17		
Anhydrous ammonia	Fisons	Spontaneous failure of sphere	Ammonia vapour cloud	100	68	40	28	21	15	7	3
		Missile from rotating machine		30							
		Explosion in process area		100	204	120	84	73	47	21	9
		Rail accident		135							
	Shell	Fire or explosion at jetty		400	228	132	96	68	40	32	20
		Ammonia ship collision		375	235	153	122	96	72	54	41
		Subtotal		1,140	735	445	330	258	174	114	73
Hydrogen fluoride	Shell	Intrinsic failure of pressure circuit	Hydrogen fluoride vapour cloud	200							
		Missiles from neighbouring plant		200	125	100	80	75	70	35	15
		Adjacent vapour cloud explosion		100							
	Mobil (inc. extension)	Intrinsic failure of pressure circuit		100							
		Missiles from neighbouring plant		100	71	99	72	51	30	24	15
		Adjacent vapour cloud explosion		100							
	Occidental	Intrinsic failure of pressure circuit		100	168	144	132	120	114	80	70
		Missiles from neighbouring plant		100							
		Subtotal			464	343	284	246	214	139	100

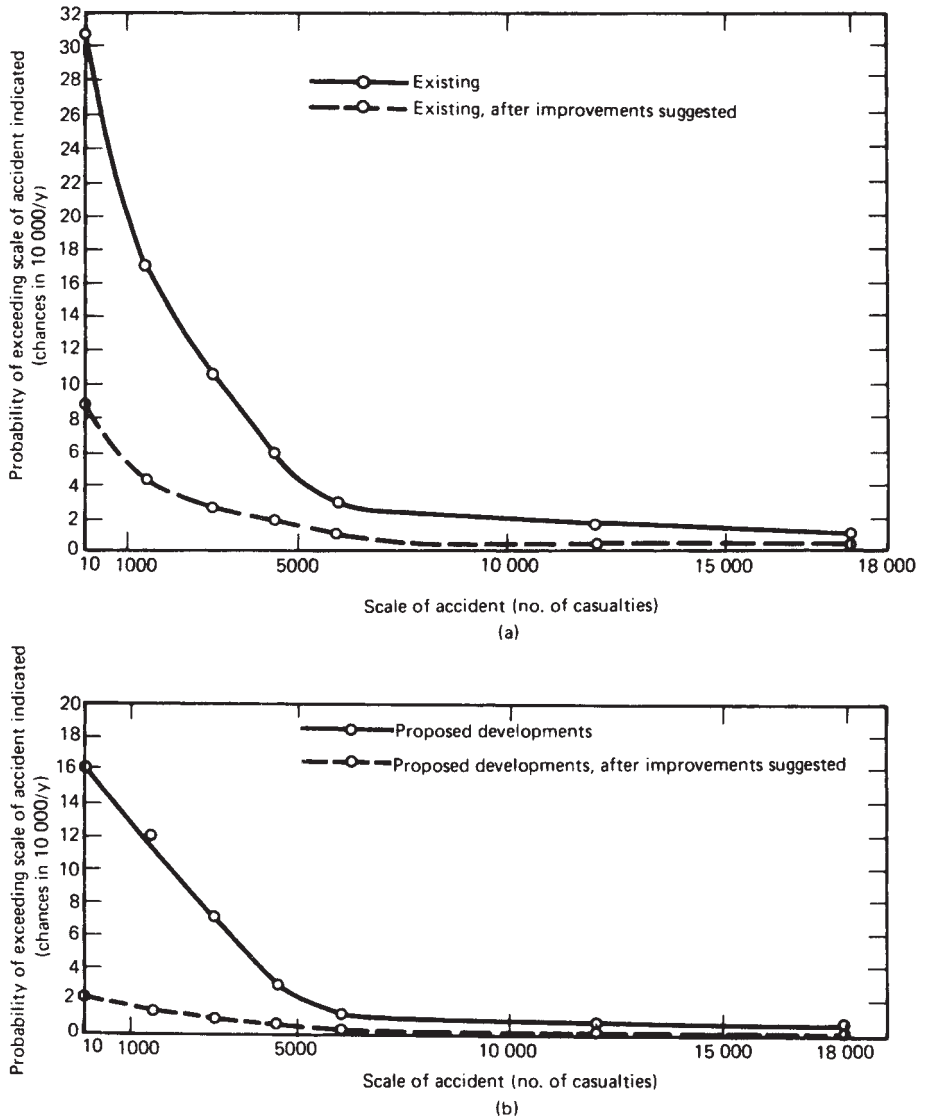

Figure A7.9 *First Canvey Report: societal risks for existing installations and proposed developments (Health and Safety Executive, 1978b): (a) all existing installations and (b) all proposed developments (Courtesy of HM Stationery Office)*

(9) HF plant rupture (Mobil, Occidental) – provision of water sprays;
(10) ship collision – strict enforcement of the speed restriction of 8 knot;
(11) road tanker hazards – road tanker traffic restriction to new road only (if road built).

The assessed effect of the proposed modifications is to eliminate the hazards from oil spillage, from LPG vapour cloud due to explosion at the jetty and pipeline failure at British Gas, and from vessel rupture at Mobil due to missiles from Calor Gas, and to reduce greatly many of the other hazards.

The rank order for societal risk of the hazards assuming that the proposed modifications are carried out is then as shown in Table A7.11. Oil spillage and LPG vapour cloud (BG) are eliminated.

There are some hazards, however, which remain relatively difficult to eliminate. In particular, spontaneous failure of storage vessels, jetty incidents and ship collisions make large contributions to the residual risks.

The effect of the proposed modifications on the societal risks for the existing and proposed installations is given in Figure A7.9. This shows that the risk of an accident causing more than 10 casualties is 9×10^{-4}/y for the existing installations and 2×10^{-4}/y for the proposed developments.

Table A7.10 *First Canvey Report: rank order of societal risks for some principal hazards of existing and proposed installations at Canvey (after Health and Safety Executive, 1978b)*

Frequencies in units of 10^{-6}/year								
>10 casualties			*>4,500 casualties*			*>18,000 casualties*		
1	Oil spillage	1366	1	Ammonia vapour cloud	258	1	HF vapour cloud	100
2	LPG vapour cloud (BG)	970	2	HF vapour cloud	246	2	ammonia vapour cloud	73
3	Ammonia vapour cloud	735	3	Oil spillage	150	3	LNG vapour cloud	7
4	LPG vapour cloud (others)	637	4	LPG vapour cloud (other)	96			
5	LNG vapour cloud	497	=5	LNG vapour cloud	80			
6	HF vapour cloud	464	=5	LPG vapour cloud (BG)	80			
7	AN explosion	85	7	AN explosion	17			

Table A7.11 *First Canvey Report: rank order of societal risks for some principal hazards of existing and proposed installations at Canvey, after improvements suggested (after Health and Safety Executive, 1978b)*

Frequencies in units of 10^{-6}/year								
>10 casualties			*>4,500 casualties*			*>18,000 casualties*		
1	LPG vapour cloud (other)	421	1	Ammonia vapour cloud	71	1	HF vapour cloud	24
2	LNG vapour cloud	396	2	HF vapour cloud	67	2	Ammonia vapour cloud	18
3	Ammonia vapour cloud	240	3	LNG vapour cloud	66	3	LNG vapour cloud	7
4	HF vapour cloud	115	4	LPG vapour cloud (other)	63			
5	AN explosion	8	5	AN explosion	2			

The assessed individual risks are given for all the existing installations after the proposed modifications. These range from 6×10^{-4}/y in region A to less than 1×10^{-4}/y in region G. The individual risks are also given for all the existing installations and proposed developments, after the proposed modifications. These range from 9×10^{-4}/y in region C to less than 1×10^{-4}/y in Region G.

The risk to an individual member of the public at Canvey may be compared with the average risk to workers in British industry. For the latter the fatal accident rate (FAR) per 10^8 exposed hours, is 4. If it is assumed that a man works 2000 h per year, then the FAR is equivalent to an individual risk of 0.8×10^{-4}/y.

A7.7 First *Canvey Report:* Responses to Report

A7.7.1 Response of HSE

The HSE accepted the report as a significant step forward in quantitative risk assessment, while acknowledging that there were some deficiencies.

It concluded that provided certain improvements were carried out, none of the existing installations need cease operations and the proposed developments could take place.

A7.7.2 Response of other parties

An account of some of the other responses to the report is given by the HSE in the Second *Canvey Report*, described below.

Publication of the report led to a surge of interest both locally and at national and international levels. HSE attended a public meeting at Canvey and explained the report. While the determination of the risks was welcomed, there was criticism of HSE's decision to allow continued operation of the existing installations, subject to the modifications.

The HSE gave a summary of some criticisms made of the report by various parties. One was that the report overestimates the risks. The assessors were required by HSE not to err on the side of optimism. Many in the industry, however, considered that it is preferable to adopt a 'best estimate' approach and that a conservative method which involves making a pessimistic estimate at each stage where there is doubt is liable to give a gross overestimate of the risks.

The HSE was also criticized in appearing to acquiesce in risks, some of which had been assessed as relatively high. On this the HSE draws attention to its requirement that improvements be made. It goes on.

HSE strongly believes that it has a duty, as the body charged with enforcing health and safety legislation, to express opinions about what may be required by that legislation. In HSE's view it is not sufficient merely to identify the risk to health and safety without also recommending a course of action.

A critique of the First *Canvey Report* was published by Cremer and Warner (1980).

A7.7.3 General comments

An investigation of the kind described has perhaps an inevitable tendency to suggest that the hazards revealed were previously unappreciated. In fact companies involved in such a survey are generally very well aware of the

hazards and have taken the measures that they consider appropriate.

The report itself expresses some reservations on the risk estimates and states: 'Practical people dealing with industrial hazards tend to feel in their bones that something is wrong with risk estimates as developed in the body of the report'.

At the time, the industry in the United Kingdom was conscious particularly of the Flixborough explosion. This has been dwarfed by subsequent disasters such as those at Mexico City, Bhopal, Ufa and Piper Alpha.

A7.8 Second *Canvey Report*

In 1981 there appeared the Second *Canvey Report* entitled *Canvey: A Review of Potential Hazards from Operations in the Canvey Island/Thurrock Area Three Years after Publication of the Canvey Report* (HSE, 1981a). This again was in two parts, with Part 1 an introduction by the HSE and Part 2 the SRD study.

In Part 1 HSE outlines the criticism of the first report, as just described, and gives its conclusions concerning the reviewed assessment.

In the next two sections, accounts are given of the reassessed risks and actions and of some technical aspects of the second report.

A7.9 Second *Canvey Report:* Reassessed Risks and Actions

The risks assessed in the Second *Canvey Report* are generally less than those in the first report. Thus, for example, at Stanford-le-Hope the individual fatality risk is given as 0.6×10^{-4}/y, as opposed to 5×10^{-4}/y in the first report, a reduction by a factor of 8.

The HSE in Part 1 adduce the following reasons for this: (1) physical improvements already carried out; (2) changes in operation; (3) detailed studies by companies; (4) changes in assessment techniques; (5) correction of errors and (6) further changes firmly agreed but yet to be made.

One major change in operation was the cessation of ammonia storage at Shell.

In a number of cases in the first report, estimates of the risks had to be made without benefit of detailed studies. Subsequent studies by the companies involved showed that in some cases the risks had been overestimated. A case in point was the limited ammonia spill at Fisons.

In a large proportion of cases the effect of the use of improved models for heavy gas dispersion was to reduce the travel distance of the cloud and hence the risks.

The HSE describe a number of further actions taken or pending to reduce the risks.

A7.10 Second *Canvey Report:* Technical Aspects

The Second *Canvey Report* revisits some of the frequency estimates and gives a revised set of hazard models and injury relations, covering the following aspects: (1) emission; (2) gas dispersion; (3) ignition; (4) fire events (5) vapour cloud explosions and (6) toxic release.

A7.10.1 Pressure vessel failure

The report reviews the frequency of spontaneous failure of pressure vessels, in the light of a further survey of the failure rate of such vessels by T.A. Smith and Warwick (1978) (see also Smith and Warwick 1981 SRD R203). The use of a failure rate of 10^5/y is reaffirmed.

A7.10.2 Emission models

The set of emission models given covers the following cases:

(1) rupture of a pressure vessel;
(2) flow from a pipe:
  (a) non-flashing liquid;
  (b) flashing liquid;
  (c) gas.

The model for emission following rupture of a pressure vessel containing liquefied gas is the adiabatic flash.

A7.10.3 Vaporization model

Vaporization of a pool of liquefied gas is treated using the SRD code SPILL, which can be applied to instantaneous or continuous releases.

A7.10.4 Gas dispersion models

Most of the liquefied gases studied exhibit heavy gas behaviour on release. For these use is made of the SRD codes DENZ and CRUNCH for instantaneous and continuous releases, respectively.

The report gives some results from these models in the form of tables of distance to the LFL and ½LFL for releases of propane and butane. As described in Chapter 15, a correlation model for heavy gas dispersion based on such tables has been developed by Considine and Grint (1985).

A7.10.5 Ignition models

The report gives several sets of ignition probabilities. It distinguishes three distinct cases of gas cloud

Delay before ignition	*Cloud composition*	*Likely consequence*
Seconds	Droplets entrained, cloud likely to be rich	Fire burning around edge of cloud (possibly leading to a fireball)
Minutes	Gas well mixed with air, likely to be in flammable range	Flash fire or explosion
An hour	Gas well diluted with air, likely to be lean	Hazard unlikely, though some flammable gas pockets possible

Table A7.12 *Second Canvey Report: some ignition probabilities for a flammable vapour cloud (after Health and Safety Executive, 1981a)*

A Ignition on site

Sources of ignition	*Ignition probability*
None	0.1
Very few	0.2
Few	0.5
Many	0.9

B Ignition at jetty

Delay before ignition	*Probability of ignition following*	
	Fire/explosion	*Collision*
Immediate ignition (within 30 seconds)	0.6	0.33
Delayed ignition (delay ½ to several minutes)	0.3	0.33
No ignition (within a few minutes)	0.1	0.33

C Ignition in transit

Terrain	*Ignition probability*
Open land	0
Industrial site	0.9

D Ignition over populated area

Type of ignition	*Ignition probability*
Edge/edge: edge of unignited cloud just reaches edge of populated area when ignition occurs	0.7
Central: unignited cloud right over population when ignition occurs	0.2
No ignition	0.1

dispersion: ignition may occur (1) at source, which may be (a) on site or (b) at a jetty; (2) in transit or (3) over a populated area. Table A7.12 shows some of the ignition probabilities given for a flammable gas cloud in these situations. The values are based partly on data on the proportion of releases ignited given by Science Applications Inc. (SAI) (1974) and D.C. Wilson (1980) and partly on judgement.

A7.10.6 Fire models and injury relations

The report gives a set of models for the following fire events: (1) pool fires; (2) fireballs; (3) BLEVEs; (4) flash fires.

Delay before ignition	*Liquefied gas release*	
	Refrigerated	*Pressurized*
Immediate ignition (within seconds)	Pool fire	Fireball
Slight delay (up to 30 s)	Diffusion flash fire	Premixed flash fire/explosion
Longer delay (min)	Premixed flash fire/explosion	Premixed flash fire/explosion

The event that occurs will depend on the delay before ignition. The behaviour assumed is as follows: For the various fire models the report refers to work by Considine (1981), evidently an early version of the paper by Considine and Grint (1985), which gives a similar set of models, as described in Chapter 16.

A7.10.7 Vapour cloud explosion model and injury relations

The vapour cloud explosion model covers both the probability that an explosion occurs given ignition and the effects of such an explosion. For the former the probabilities used are

Size of cloud (te)	*Explosion probability*
<10	0
100–100	0.1 (LNG = 0.01)
>100	1

For the effects of such an explosion use is made of the following relations based on the work of the ACHM:

$$p_o = kM^{1/3} \quad [A7.10.1]$$

$$R = 30M^{1/3} \quad [A7.10.2]$$

hence

$$p_a = k'R \quad [A7.10.3]$$

where M is the mass released (te), p_a the peak side-on overpressure (kPa), R the radius of the cloud (m) and k, k' are constants. Relationships are given as follows:

Overpressure (kPa)	*Hazard range* (m)	*Casualty probability*
0<7	>4.25R	0
7–21	(2–4.25)R	0.1
21–34	(1.35–2)R	0.25
34–48	(1.1–1.35)R	0.70
>48	<1.1R	0.95

Further the authors quote the estimates of the ACMH that the overpressure at the centre of the cloud is likely to be about 103 kPa and at the edge about 69 kPa.

A7.10.8 Toxic injury relations

Injury relations are given for ammonia and for hydrogen fluoride. For these gases the authors state that the best information available to them on the LC_{50}, the concentration lethal at the 50% level, is as follows:

Time t (min)	*Lethal concentration LC_{50}*	
	Ammonia (kg/m^3)	*Hydrogen fluoride* (kg/m^3)
1		1.5×10^{-3}
5	7×10^{-3}	4×10^{-4}
10	3.5×10^{-3}	
30	1.2×10^{-3}	
60	5×10^{-4}	4×10^{-5}

They further state that these data may be fitted to the relation

$$LCt_{50} = kCt^{0.9} \qquad [A7.10.4]$$

where C is the concentration, LCt_{50} the dose lethal at the 50% level and t time.

A7.11 Notation

Section A7.5

Subsection A7.5.5

A_H	horizontal area of target
A_V	vertical area of target
A'_V	horizontal projection of vertical area of target
F	frequency of aircraft crash on target area
F_H	frequency of aircraft crash per unit of ground area
F_V	frequency of aircraft crash per unit of vertical area

Subsection A7.5.7

g	acceleration due to gravity (m/s^2)
h_f	slumped liquid depth (m)
r	radius of flooded zone (m)
r_s	radius of source cylinder (m)
t	time after initiation of slumping (s)
u_f	slumped liquid velocity (m/s)
V_s	volume of source cylinder (m^3)

Subsection A7.5.8

A_H	area of tank roof (m^2)
A_V	exposed area of tank vertical sides (m^2)
c_p	specific heat of tank wall (J/kg°C)
m	mass of exposed tank wall (kg)
Q_i	heat input to tank (W)
Q_n	heat loss by convection (W)
Q_r	heat loss by radiation (W)
t	time (s)
ε	emissivity of tank wall
θ_A	absolute temperature of ambient air (K)
θ_T	absolute temperature of tank wall (K)
$\Delta\theta$	temperature difference between tank and ambient air (°C)
α	Stefan–Boltzmann constant ($W/m^2 K^4$)

Subsection A7.5.11

H	heat of combustion of hydrocarbons (kcal)
Δp_m	peak overpressure (bar)
q	peak dynamic pressure (bar)
r	distance (m)
W	mass of hydrocarbons (t)
α	equivalence factor

Subsection A7.5.13

a, b	constants
C	concentration (g/m^3)
D	dosage ($(g/m^3)^{2.75}$ min)
P_r	probit
t	time (min)

Subsection A7.5.14

Equations A7.5.11–A7.5.13

g	acceleration due to gravity
h	height of cloud
r	radius of cloud
r_0	initial radius of cylinder
t	time
V_O	initial volume of cylinder
ρ_a	density of air
ρ_0	initial density of cloud

Equations A7.5.14–A7.5.20

h	height of cloud (m)
Q^*	mass released instantaneously (kg)
r	radius of cloud (m)
t	time (s)
u	wind speed (m/s)
x,y	distances in downwind, cross-wind directions (m)
$\sigma_x, \sigma_y, \sigma_z$	dispersion coefficients in downwind, crosswind and vertical directions (m)
χ	concentration (kg/m^3)
χ_{av}	mean concentration along axis (kg/m^3)
χ_{max}	maximum concentration along axis (kg/m^3)

Subsection A7.5.15

C	concentration indoors
C_0	concentration outdoors
t	time
λ	number of air changes per unit time

Section A7.10

Subsection A7.10.7

k,k'	constants
K	constant
M	mass released (te)
p_O	peak side-on overpressure (kPa)
R	radius of cloud (m)

Subsection A7.10.8

C	concentration
k	constant
LCt_{50}	dose lethal at 50% level
t	time

Appendix 8

Rijnmond Report

Contents

A8.1 The Investigation A8/2
A8.2 Installations and Activities A8/4
A8.3 Event Data A8/4
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A8.9 Assessed Risks A8/17
A8.10 Remedial Measures A8/20
A8.11 Critiques A8/20
A8.12 Notation A8/20

Another comprehensive hazard assessment is the Rijnmond study carried out for the Rijnmond Public Authority by Cremer and Warner.

This work is described in *Risk Analysis of Six Potentially Hazardous Industrial Objects in the Rijnmond Area*, a Pilot Study issued by the Rijnmond Public Authority (1982) (the Rijnmond Report).

The Rijnmond is the part of the Rhine delta between Rotterdam and the North Sea. Within the Rijnmond area of $15 \times 40\,km^2$ are located some one million people and a vast complex of oil, petrochemical and chemical industries as well as the largest harbour in the world. A description of the industrial complex at Rijnmond has been given by Molle and Wever (1984). A map of the Rijnmond showing the principal plant areas is given in Figure A8.1 and a diagram of the petrochemical complex in Figure A8.2. There are five oil refineries with a refining capacity of some 81 Mt/year, including the large refineries of Shell at Pernis and BP near Rozenburg, and major petrochemicals complexes operated by Shell, Gulf and Esso. Some of the other plants are described below.

A first note on the industrial hazards issued in 1976 by the Rijnmond Authority was strongly criticized by industry. Accordingly a commission, COVO, was set up with representatives of the Labour Inspectorate of the Ministry of Social Affairs, the Rijnmond Authority and industry. COVO decided to carry out a pilot study of six industrial installations in the Rijnmond in order to evaluate the applicability of risk assessment to decision-making on safety and commissioned Cremer and Warner to carry out the study. A steering committee was formed and the work was done to the requirements of this committee.

A8.1 The Investigation

The aim of the work was to evaluate the methods of risk assessment for industrial installations and to obtain experience in the practical application of these methods. Such evaluation was considered to be essential before any decision could be made on the role of such methods in the formulation of safety policy.

The objectives of the study were formulated so as to give an answer to the following questions:

(1) What is the reliability of the assessment of the consequences and probabilities of possible accidents with industrial installations when the procedures and methodology of risk analysis are carried out to their full extent?
(2) What problems and gaps in knowledge exist in the field of risk analysis?
(3) How can the results of a risk analysis be presented conveniently, without losing important details, so that it may be used for safety policy decisions?
(4) How well can the influence of risk reducing measures on the consequences and probabilities be calculated?
(5) What resources are required, in time and money, to assess the risk with sufficient accuracy to be useful for safety policy decisions?

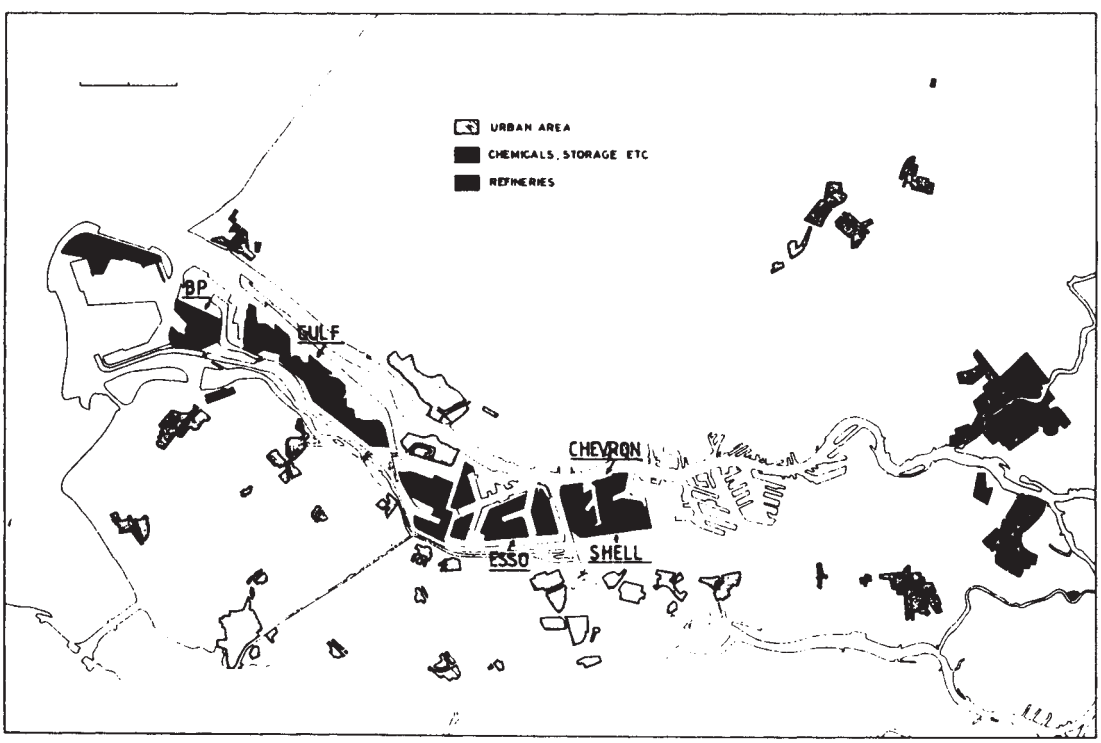


Figure A8.1 *Rijnmond harbour area (Molle and Wever, 1984)*

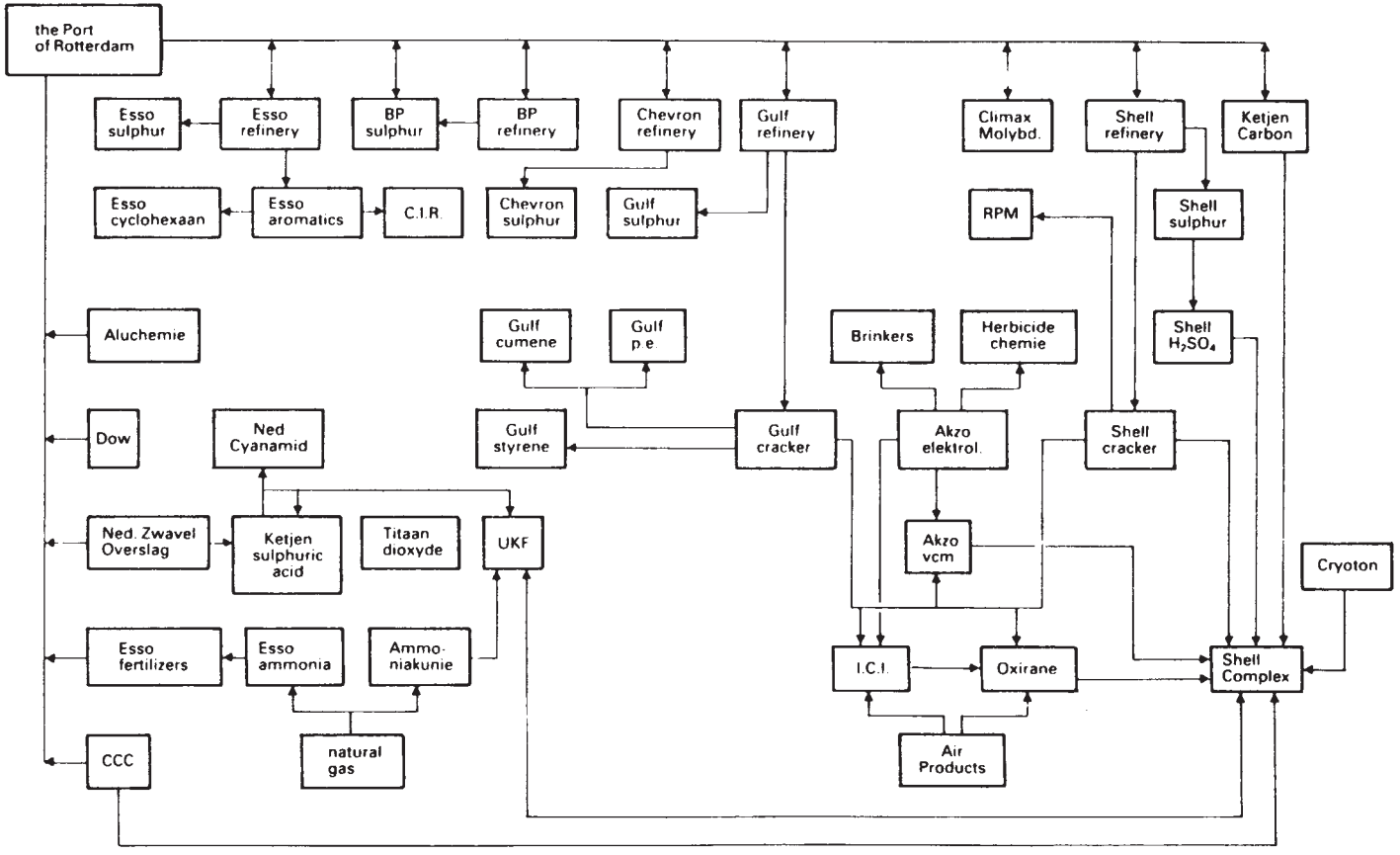


Figure A8.2 *Petrochemical complex in the Rijnmond harbour area (Molle and Wever, 1984)*

The COVO steering committee was reinforced with experts from industry. The committee also included representatives of the Battelle Institute who were charged with the task of scrutinizing the methodology and models used. The overall approach taken in the investigation was:

(1) to collect basic data and define the boundary limits of the installation;
(2) to identify the potential failure scenarios;
(3) to select and apply the best available calculation models for physical phenomena;
(4) to collect and apply the best available basic data and models to calculate the probabilities of such events;
(5) to choose and develop different forms of presentation of the final results;
(6) to investigate the sensitivity of the results for variations in the assumptions used and to estimate the accuracy and reliability of these results;
(7) to investigate the influence of risk reducing measures.

The investigation involved the identification of the principal hazards of the installations in the area, the assessment of the associated individual and societal risks and the proposal of remedial measures to reduce the risks.

The project was planned to last one year but in fact took two-and-a-half years and it cost some 2.5 m guilders. A supplementary contract was placed with the consultants to study methods of presenting the results. The report was published in 1982. It is in five parts. Part 1 is the report of the steering committee, Part 2 is the main Cremer and Warner study, Part 3 the supplementary Cremer and Warner study, Part 4 is the Battelle review and Part 5 contains the industrial and other comments.

A8.2 Installations and Activities

The six installations studied were as follows:

(1) Acrylonitrile storage (Paktank);
(2) Ammonia storage (UKF);
(3) Chlorine storage (AKZO);
(4) LNG storage (Gasunie);
(5) Propylene storage (Oxirane);
(6) Hydrodesulfurizer (Shell).

The storages of acrylonitrile and LNG were at atmospheric pressure and those of ammonia, chlorine and propylene were all liquids under pressure. The acrylonitrile, ammonia and chlorine represented toxic materials and the LNG and propylene flammable materials. The hydrodesulfurizer represented part of a process plant, the section studied being the diethanolamine stripper.

The context of these installations is described by Molle and Wever and accounts of the individual installations are given below.

The report is organized partly by installation and partly by themes and material on a particular installation is therefore given dispersed. Table A8.1 gives a summary of the entries for each installation.

A8.3 Event Data

The event data used in the study were a mixture of generic data, plant data and estimates. Some failure and event data and some external event data used are given in Tables A8.2 and A8.3, respectively. Other data are given in the sections on particular installations.

A8.4 Hazard Models

The principal hazard models used are given in Table A8.4 and their application is described in the sections on particular installations.

A8.5 Injury Relations

The injury relations used are given in Table A8.5 and their application is described in the sections on particular installations.

A8.6 Population Characteristics

The study covered the risks both to employees and to the public. For the off-site population a grid was used showing the number of people over an area of some 75 km^2, which covered the whole of the Rijnmond. Populations were estimated for each 500 m^2 square using data from the 1971 census, updated in 1975.

Both day and night time populations were determined, day being defined as the working week of 45 h and night as the remaining 123 h.

Outside the population grid average population densities were used. These were required only in cases where an exceptionally large cloud occurred.

For the particular installations studied data were obtained on the numbers of employees present during day and night and on their locations. The on-site population N_e was estimated from the relation

$$N_e = \frac{(5N_d + 16N_n) \times 52}{((5 \times (52 - n_h))} \qquad [A8.6.1]$$

where n_h is the number of weeks off for holidays, sickness, etc., N_d the numbers present during the working day and N_n the numbers present at all other times.

For toxic gas hazard it was assumed that 1% of the population are outdoors. This estimate includes an allowance for people taking shelter. For explosion hazard it was assumed that 10% are outdoors.

A8.7 Mitigation of Exposure

The principal mitigations of exposure considered were evacuation and shelter. For evacuation the estimate of the proportion evacuated is taken as a function of the warning time. In some cases the proportion is estimated as 90–100%.

For the effect of shelter from toxic gas the single-exponential stage model of ventilation is used.

A8.8 Individual Assessments

A8.8.1 Acrylonitrile storage (Paktank)

The acrylonitrile (AN) storage is one of a number of storages at the Botlek terminal of Paktank, a tank storage company providing bulk storage and associated services to the oil and chemical industries.

There are normally two or three tanks containing AN. The study was confined to a single tank and associated transfer systems which had been dedicated to handling AN for some years. This AN tank is one of a number of fixed roof tanks located in a tank bund which is at the centre of

the site. The tank has a capacity of 3700 m^3. It is designed to withstand small variations of internal pressure, the breather valves being designed to open at an overpressure of 200 mmHg and a vacuum of 50 mmHg.

Operation at the site is flexible, but in the preceding two years only six modes of transfer had been recorded, these being loading of coastal barges, loading of road tankers, loading of rail tank cars, filling from coastal barges and chemical tankers, filling from sample tanks, and transfer between this tank and others at the site.

A summary of the risk assessment for the AN storage is given in Table A8.6. Section A of the table lists the undesired events considered, section B the hazard scenarios and section C the main fault trees.

An escape from the tank into the bund, though instantaneous, gives rise to a constant evaporation rate and hence acts as a continuous source. Releases from the pipework are also continuous sources.

The frequency of the releases is estimated using the seven fault trees listed as shown in Figure A8.3. The table giving the frequency and event data for these trees contains 81 entries. Of these some 30 are derived from the generic data given in Tables A8.2 and A8.3 and the rest from other sources, mainly company data, meteorological data or judgement.

For fire hazard it was assumed that 10% of all major spillages or resulting vapour clouds and 5% of significant spillages ignite and that an operator present at the release or ignition source receives fatal burns in 80% of cases. The hazard distances obtained are shown in the table as <10 m.

For toxic gas hazard the exposure is continuous. In most cases only employees were at risk. A 10-min exposure was assumed for employees, who are alert to the hazard.

It was found, however, that serious toxic effects were possible to the public from a major spill (PI) if the exposure time was 30 min. For the public credit was given for evacuation, usually 90–100%, depending on the warning time.

Typical hazard distances to the LTL_{50} of 76 m are given in Table A8.6. The distances are greater for adverse weather conditions, being on the centreline for 2.0/F and 1.5/D conditions 575 and 260 m to the LTL_{50} and 879 and 365 m to the LTL_{05}, respectively.

A8.8.2 Ammonia storage (UKF)

The ammonia storage is part of a complex of plants producing ammonia, nitric acid, ammonium nitrate, urea and other fertilizers at the Pernis site of UKF.

The ammonia is stored in a sphere under pressure at atmospheric temperature. The capacity of the sphere is 1000 m^3, but the average inventory is only 40% of this. The ambient temperature was taken in the study as 15°C that corresponds to a pressure of 7.1 bar.

Ammonia is transferred to the sphere from rail tank cars or from the ammonia plant. Transfer of the liquid ammonia from the rail tank car is effected by pressurizing the tank

Table A8.1 *Rijnmond Report: summary of entries for the six installations (after Rijnmond Public Authority, 1982)*

Entry	*Page*					
	Acrylonitrile	*Ammonia*	*Chlorine*	*LNG*	*Propylene*	*Hydrodesulfurizer*
Main entry	81	111	151	183	202	225
Historical review	109, 350	132, 351	181, 355	200, 361	223, 362	240, 370
Release scenarios	91	113	154	187	203	227
Undesired events						
Events key	89	133	157	188	203	229
Event frequency	101	146	171	196	210	237
Failure data	97, 446	122, 462	170, 480	194, 497	209, 513	235
Other data	438			191		235
Fault trees	451	468	491	507	527	
Hazard models	96	115	156	189	205	228
Injury relations						
Fire/explosion	319, 331			319, 331	319, 331	
Toxic effects	93, 340	145, 340	340			231, 340
Consequence results						
Summary table	102	149	174	198	214	239
Fatalities table	440					
Grid printouts						
Fire/explosion				419	422	
Toxic effects	93	135, 397	161, 404			413
Hazard ranges						
Fire/explosion	96, 102					
Toxic effects	95, 102	135	161			
Risk results						
Tables	102	135, 578	161			
Risk contours		560				
FN tables	588	589	596	603	604	608
FN curves	562	563	564	565	566	567
Evaluation	250	250	251	251	252	252
Remedial measures	107	130	180	199	213	238

Table A8.2 *Rijnmond Report: some failure and event data used (after Rijnmond Public Authority, 1982)*

A Data sources

1. AEC (1975)
2. Recht (1966c)
3. SAI (1975)
4. Lees (1976b)
5. Lees (1976c)
6. Skala (1974)
7. A.E. Green and Bourne (1976)
8. Upfold (1971)
9. Smith and Warwick (1974 SRD R30)
10. W. Marshall *et al.* (1976)
11. Welker *et al.* (1976)
12. Bush (1975)
13. SRS data bank
14. D.L.E. Jacobs (1971)
15. Phillips and Warwick (1969 AHSB(S) R162)
16. Kletz (1972)
17. Lawley and Kletz (1975)

B Event data

Equipment	*Failure rate*[a,b]		*Reference*
	Rate	*Range*	
Tanks and vessels			
Pressure vessels			
Serious leakage	1×10^{-5}/year	6×10^{-6}–2.6×10^{-3}/year	7, 9, 10
Catastrophic rupture	1×10^{-6}/year	4.6×10^{-5}–6.3×10^{-7}/year	12, 15
Atmospheric storage tanks			
Serious leakage	1×10^{-4}		
Catastrophic rupture	6×10^{-6}/year		
Refrigerated storage			
Tanks (double wall, high integrity)			
Serious leakage from inner tank	2×10^{-5}/year		
Catastrophic rupture from both containments	1×10^{-6}/year		
Pumps, pipework, etc.			
Pumps			
Failure to start	1×10^{-3}/d	5×10^{-5}–5×10^{-3}/d	1
Failure to run normally	3×10^{-5}/h	1×10^{-7}–1×10^{-4}/h	1
Failure to stop	1×10^{-4}/d	4×10^{-5}–1×10^{-3}/d	1, 11
Catastrophic failure	1×10^{-4}/year		3, 13
Pipework[c,d]			
<50 mm			
Significant leakage	1×10^{-8}/sect. h		1, 9, 13, 15
Catastrophic rupture	1×10^{-9}/sect. h		
>50 mm, <150 mm			
Significant leakage	6×10^{-9}/sect. h		
Catastrophic rupture	3×10^{-10}/sect. h		
>150 mm			
Significant leakage	3×10^{-9}/sect. h		
Catastrophic rupture	1×10^{-10}/sect. h		
Hoses			
Heavily stressed	4×10^{-5}/h		11, 14
Lightly stressed	4×10^{-6}/h		
Loading arms			
Leakage	3×10^{-6}/h	1×10^{-7}–1×10^{-4}/h	1, 11
Catastrophic rupture	3×10^{-8}/h	1×10^{-8}–1×10^{-5}/h	
Valves			
Pressure relief valves			
Fails dangerously			
Blocked	0.001/year	0.001–0.01/year	5, 7, 13
Lifts heavy	0.004/year	$(1.4 \times 10^{-5}$–3.6×10^{-5}/d)	1
Lifts light/leakage	0.06/year	0.02–0.09/year	1, 5, 7
Vacuum relief valves	0.005/year	$(1 \times 10^{-5}$–1×10^{-4}/d)	1

Other data taken from references 1, 5, 6, 7

Table A8.2 *(continued)*

Instrumentation			
Data taken from references 1, 5, 6, 7, 13, 16, 17			
Electrical equipment			
Battery supply			
Failure to provide proper output (in standby mode)	1×10^{-6}/h	1×10^{-7}–6×10^{-6}/h	1, 7
Electric motors			
Failure to start	3×10^{-4}/day	7×10^{-5}–3×10^{-3}/d	1
Failure to run	7×10^{-6}/h	5×10^{-7}–1×10^{-4}/h	1, 7
Emergency diesel system (complete)			
Failure to start	3×10^{-2}/day	1×10^{-3}–1×10^{-1}/d	1
Failure to run	3×10^{-3}/h	1×10^{-4}–1×10^{-3}/h	1

[a] The unit d in this table stands for demand.
[b] The failure rates taken from the *Rasmussen Report* correspond to the median values quoted there.
[c] Values per metre run are also given and are one-tenth of those per section.
[d] Following data are given for range:

Industry	Nuclear	
<75 mm	2×10^{-9}–5×10^{-6}/sect. h	3×10^{-11}–3×10^{-8}/sect. h
>75 mm	1×10^{-10}–5×10^{-6}/sect. h	3×10^{-12}–1×10^{-10}/sect. h

Table A8.3 *Rijnmond Report: some external events data used (after Rijnmond Public Authority, 1982)*

Event	*Frequency*[a] (events/year)					
	Generic	*Acrylonitrile*	*Ammonia*	*Chlorine*	*LNG*	*Propylene*
Earthquake	10^{-8}	X	X		X	X
Subsidence	2×10^{-9}	2×10^{-7}	2×10^{-7}	2×10^{-7}	X	X
Flooding	10^{-7}	X	X	X	10^{-9}	
Vehicular intrusion	2×10^{-7}	X	X	X	2×10^{-9}	X
Mechanical impact	10^{-7}	3×10^{-6}	X	X		
Major fire	10^{-6}	X	10^{-9}	X	10^{-12b}	10^{-5c}

[a] Frequencies for these events are not given for the hydrodesulfurizer.
[b] Estimate based on fact that major fire would cause immediate ignition, not a vapour cloud.
[c] Estimate towards higher end of range due to flammable nature of products stored.

Table A8.4 *Rijnmond Report: some hazard models used*

Event	*Model*
A Emission	
Flow from	
A. Vessel containing liquid at atmospheric pressure	
B. Vessel containing liquid above atmospheric boiling point	
C. Vessel containing gas only	
Two-phase flow	Fauske–Cude (Fauske, 1964; Cude, 1975)
B Vaporization	
Spreading of liquid spill	Shaw and Briscoe (1978 SRD R100)
Vaporization of cryogenic liquid	
On water	Shaw and Briscoe (1978 SRD R100)
On land	Shaw and Briscoe (1978 SRD R100); AGA (1974)
Combined spreading and vaporization of cryogenic liquid on land	
Vaporization from spill into complex bunds	
Evaporation of volatile liquid	Pasquill (1943), Opschoor (1978)

Table A8.4 *(continued)*

Event	*Model*
C Gas dispersion	
Neutral density gas dispersion	Pasquill–Gifford
Dense gas dispersion	R.A. Cox and Roe (1977)
Dispersion of jet of dense gas	Ooms, Mahieu and Zelis (1974)
D Vapour cloud combustion	
Initial dilution with air	
Continuous Release	Ooms, Mahieu and Zelis (1974)
Instantaneous release	Empirical relation
Ignition sources	
Fire vs explosion	
E Vapour cloud explosion	
Vapour cloud explosion	TNO (Wiekema, 1980)
F Pool fire	
Flame emissivity	
Liquid burning rate	Burgess, Strasser and Grumer (1961)
Flame length	P.H. Thomas (1963)
Flame tilt	P.H. Thomas (1965b)
Fraction of heat radiated	
View factor	Rein, Sliepcevich and Welker (1970)
G Jet flame	
Flame length	API (1969 RP 521)
Deflection effect	API (1969 RP 521)
Buoyancy and liquid effects	MITI (1976)
View factor	Rein, Sliepcevich and Welker (1970)
H Fireball	
Fireball dimensions	
Radius	R.W. High (1968)
Duration	R.W. High (1968)
View factor	McGuire (1953)

Table A8.5 *Rijnmond Report: some injury relations used*

A Fire: Steady state	
Incident thermal radiation (kW/m^2)	*Effect*
1.6	Level insufficient to cause discomfort for long exposures
4.5	Level sufficient to cause pain if subject does not reach cover in 20 s; blistering of skin likely (first degree burns)
12.5	Minimum level for piloted ignition of wood, melting of plastic tubing, etc.
25	Minimum level for unpiloted ignition of wood at infinitely long exposures
37.5	Level sufficient to damage process equipment
B Fire: Unsteady state	
Incident thermal radiation dose threshold (kJ/m^2)	*Effect*
65	Threshold of pain: no reddening or blistering of skin
125	First degree burns
250	Second degree burns
375	Third degree burns

Table A8.5 *(continued)*

C Explosion

Blast overpressure (bar)	*Effect*
0.03	Window breakage, possibly causing some injuries
0.1	Repairable damage; light structures collapse; pressure vessels remain intact
0.3	Major structural damage (assumed fatal to people inside buildings or other structures)

D Toxic effects

Data given in terms of constants in probit equation for fatalities
$Y = k_1 + k_2 \ln \Sigma C^n T$

Gas	*Constants n*	k_1	k_2	LTL_{50} ($ppm^n \cdot min$)
Acrylonitrile	1			8.15×10^3
Ammonia	2.5	−30.57	1.385	1.22×10^{10}
Chlorine	2.75	−17.1	1.69	5.46×10^4
Hydrogen sulfide	2.75			1.6×10^8

Table A8.6 *Rijnmond Report: summary of assessment of acrylonitrile storage (Paktank) (after Rijnmond public Authority, 1982)*

A Undesired events

Event[a]	*Frequency* (events/year)	*Mass flow or mass* (kg/s or kg)	*Duration* (s)	*Average no. of fatalities to public*[b,c] (deaths/year)
P1 Major rupture of tank	4.3×10^{-5}	1.85×10^6		7.6×10^{-6}
P2 Split in tank bottom/shell	2.0×10^{-4}	1.85×10^6		
P3 Rupture of tank roof	1.8×10^{-4}			
P4 Open drain valve on tank	1.0×10^{-4}		1800	
P5 Overfilling of tank	1.5×10^{-3}	200 m^3/h[d]		
P6 Internal explosion	5×10^{-6}			
P7 Unauthorized entry into tank	2×10^{-5}			
P8 Transfer line rupture	9×10^{-7}	1.85×10^6		3.2×10^{-7}
P9 Transfer line leakage	5.2×10^{-5}		1800	
P10 Hose rupture	2.6×10^{-3}		900	
P11 Catastrophic rupture of transfer line	8.8×10^{-6}		900	
P13 Transfer hose rupture	4×10^{-3}		600	
P14 Transfer hose rupture	4×10^{-3}		600	7.9×10^{-6}
Total				

B Hazard scenarios

Spillage into bund
Evaporation from bund
Gas dispersion (from continuous source)
Pool fire in bund
Flash fire in vapour cloud

C Fault trees

P1 Catastrophic rupture of tank
- P1.1 Severe overpressurization of tank
  - P1.1.1 Pressurization of tank with nitrogen
  - Pl.1.2 Severe polymerization within tank
- Pl.2 Severe tank depressurization

Table A8.6 *(continued)*

P1.4 Severe polymerization in tank
P5 Tank overfilled up to breather valve level
P5.1 High level detected, incorrect action taken

[a] There are 15 further events:
P12 Transfer line leakage
P15 Transfer hose leakage
P16 Transfer line rupture
P17 Transfer hose rupture
P18 Transfer line/hose rupture
P19 Transfer line/hose rupture
P20 Transfer line/hose leakage
P21 AN transfer line/hose leakage
P22 Line leakage
P23 Sampling hose/line rupture
P24 Transfer line/hose rupture
P25 Sample tank leakage
P26 Explosion with pre-pump sample
P27 Hose rupture
P28 Flash fire or explosion within AN system during maintenance

None of these events causes an average number of fatalities to the public $>10^{-5}$/year.
[b] For both cases P1 and P8 the typical hazard distances to the LTL_{50} are 76 m *and to the* LTL_{05} 126 m. These are the greatest hazard distances quoted.
[c] For all cases the typical hazard distances for fatal effects from fire are <10 m. No hazard distances for fatal effects from explosion are quoted.
[d] Maximum rate (pump rate).

car with ammonia vapour from the sphere and from the ammonia plant by pumps. Ammonia is transferred from the sphere to the downstream plants by pumps.

An escape from a sphere may constitute an instantaneous or a continuous source. Catastrophic rupture of a sphere was taken as equivalent to an instantaneous release, other escapes to continuous releases.

A summary of the risk assessment for the ammonia storage is given in Table A8.7. Sections A–C list the undesired events, the hazard scenarios and the main fault trees.

Ammonia constitutes both a flammable and toxic hazard, but since the toxic effects can occur at concentrations 100 fold less than the flammable effect, only the former were considered.

A8.8.3 Chlorine storage (AKZO)

The chlorine storage consists of five spheres associated with chlorine cellrooms at the Botlek site of AKZO.

The chlorine is stored in the spheres under pressure at atmospheric temperature. Each sphere has a capacity of 90 m^3 and can therefore hold 100 te, but at any given time one of the spheres is used as a dump tank, so that the capacity of the storage is 400 te. At ambient temperature the sphere pressure is 6.5 bar, but pressure is taken up to 9 bar when the sphere is discharging to consumer plants. The spheres are located in a bund.

Chlorine is received only from the associated production plant, but is sent out to a variety of consumers. There is a chlorine gas disposal plant consisting of caustic soda scrubbers.

An escape from a sphere may constitute an instantaneous or a continuous source. Catastrophic rupture of a sphere was taken as equivalent to an instantaneous release, other escapes to continuous releases or mixed releases.

A summary of the risk assessment for the chlorine storage is given in Table A8.8. Sections A–C list the undesired events, the hazard scenarios and the main fault trees.

A8.8.4 LNG storage (Gasunie)

The LNG storage consists of two tanks and associated equipment at the peak shaving plant of Gasunie at Maasvlakte.

The LNG is contained in an inner tank of 9% nickel steel and an outer tank of carbon steel. This whole container is surrounded by a further containment consisting of a reinforced concrete floor and a pre-stressed concrete wall. The capacity of each tank is 57,000 m^3.

An escape from a tank may constitute an instantaneous or a continuous source. Catastrophic failure of a tank was taken as equivalent to an instantaneous release, other escapes to continuous releases or mixed releases.

A summary of the risk assessment for the LNG storage is given in Table A8.9. Sections A–C list the undesired events, the hazard scenarios and the main fault trees.

A8.8.5 Propylene storage (Oxirane)

The propylene storage is associated with the propylene oxide plant of Oxirane at Seinehaven. There are two spheres each with a capacity of 600 te. The ambient temperature was taken in the study as 15°C, that corresponds to a gauge pressure of 8 bar.

Propylene is transferred to the spheres by pipeline, ship and rail tank cars. It is transferred from the spheres to the downstream plants.

An escape from a sphere may constitute an instantaneous or a continuous source. Catastrophic rupture of a sphere was taken as equivalent to an instantaneous release, other escapes to continuous releases.

A summary of the risk assessment for the propylene storage is given in Table A8.10. Sections A–C list the undesired events, the hazard scenarios and the main fault trees.

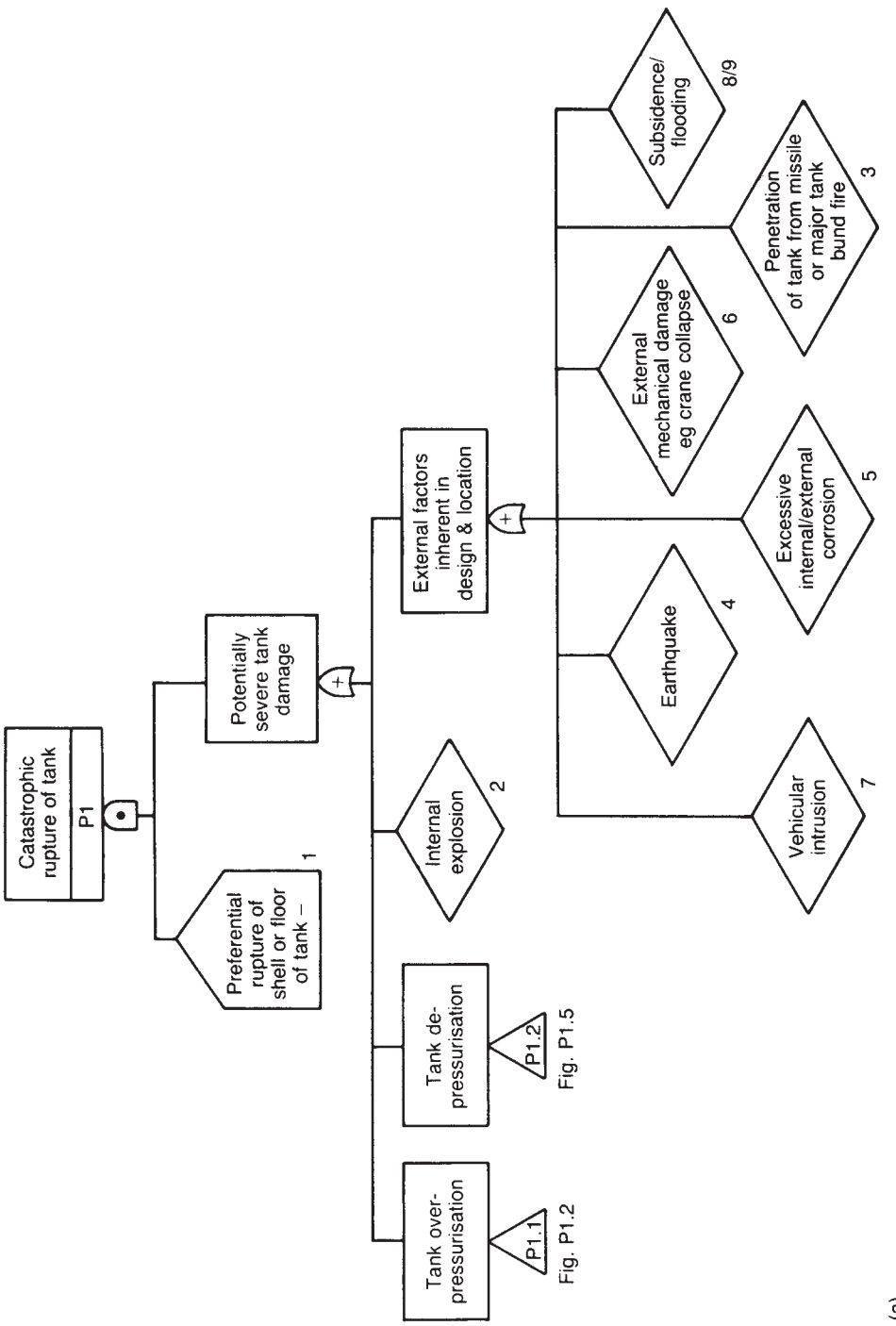
A8.8.6 Hydrodesulfurizer (Shell)

The section of the hydrodesulfurizer studied is the diethanolamine (DEA) regenerator. The latter is part of an absorber–regenerator unit which removes hydrogen sulfide from sour gas. The hydrogen sulfide is absorbed into DEA in the absorber and the fat DEA passes to the regenerator where a reversible reaction occurs releasing the hydrogen sulfide again.

The escapes that can occur from this unit are of two types. There may be a direct release of hydrogen sulfide gas. Alternatively, the release may be by evolution of the gas from the fat DEA liquid.

Hydrogen sulfide presents both a flammable and a toxic gas hazard. On review the flammable hazard was discounted. However, the flammability of the gas remains relevant in that in a proportion of cases the gas cloud would burn and would then not constitute a toxic hazard.

A summary of the risk assessment for the regenerator section of the hydrosulfurizer is shown in Table A8.11. Section A lists the undesired events and Section B the hazard scenarios. As indicated in section C there are no fault trees.



(a)

Figure A8.3 *Continued*

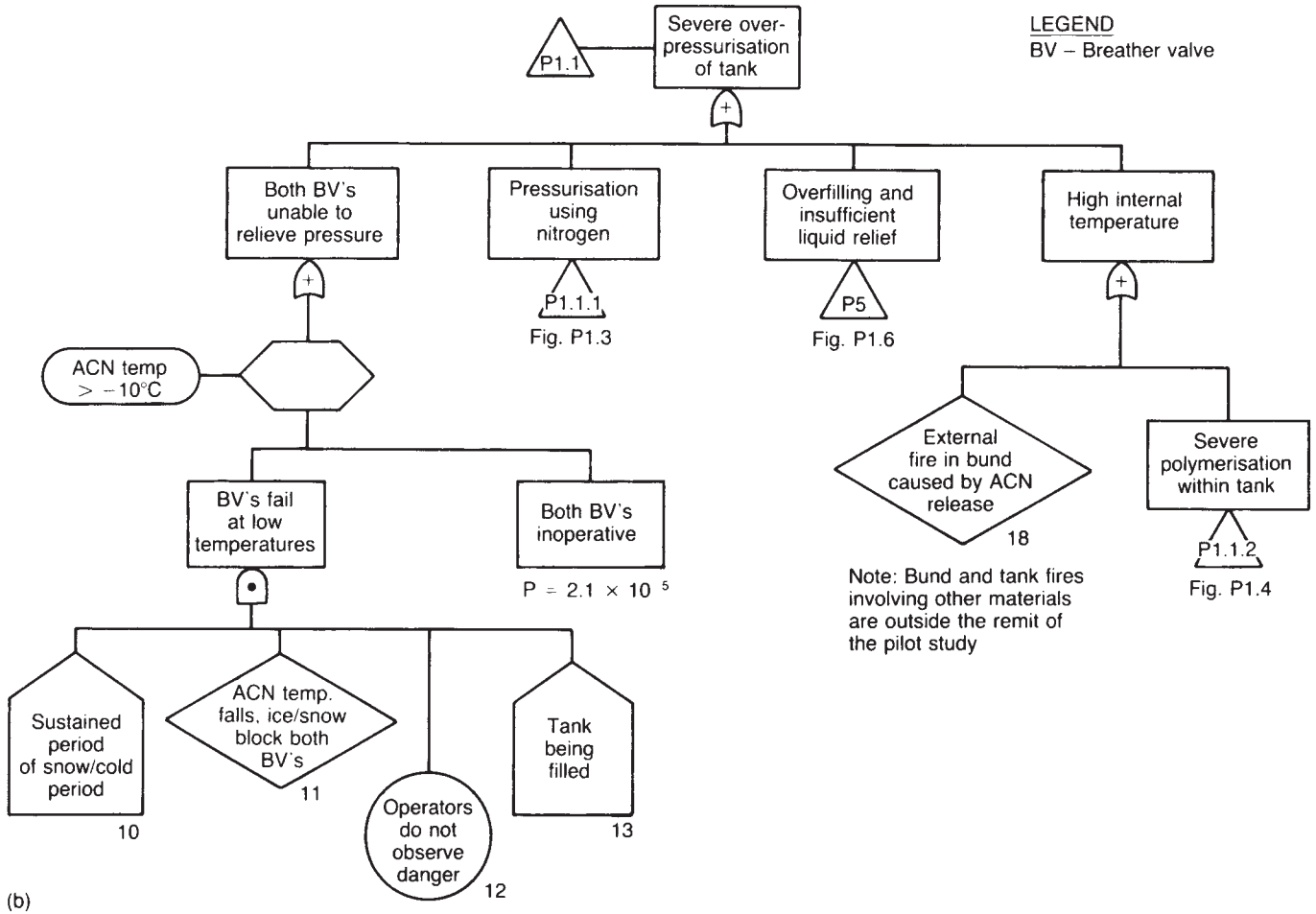
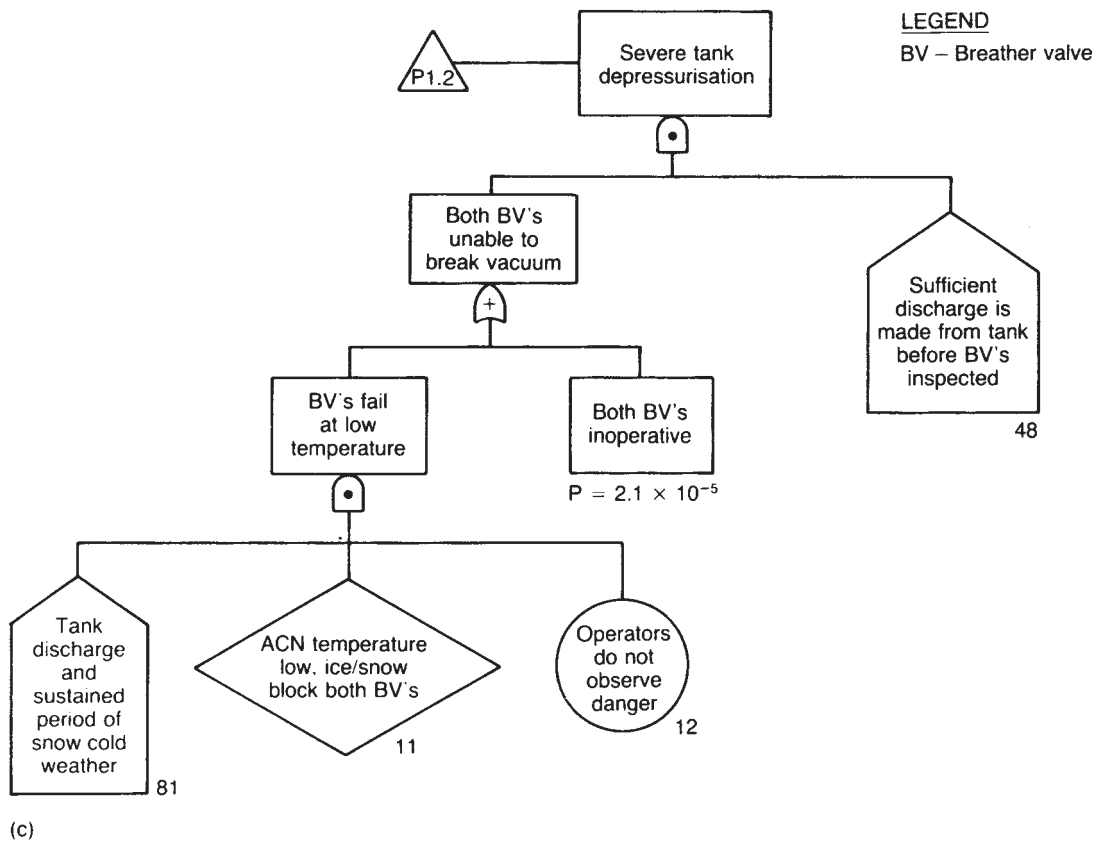


Figure A8.3 *Rijnmond Report: fault trees for release from the acrylonitrile storage (Rijnmond Public Authority, 1982. Reproduced by permission); (a) head of tree for top event 'catastrophic rupture or tank'; (b) sub-tree for 'tank overpressurization' and (c) sub-tree for 'tank depressurization'*



(c)

Figure A8.3 *continued*

Table A8.7 *Rijnmond Report: summary of assessment of ammonia storage (UKF) (after Rijnmond Public Authority, 1982)*

A Undesired events

Event		*Frequency* (events/year)	*Mass flow or mass* (kg/s or kg)	*Duration* (s)	*Average no. of fatalities to public*[a] (deaths/year)
U0	Catastrophic failure of sphere when full	2.3×10^{-7}	682,000	I	54×10^{-6}
U1	Catastrophic failure of sphere with average inventory	1.8×10^{-6}	250,000	I	67×10^{-6}
U2.1	Full bore fracture of liquid line during transfer of ammonia	5.6×10^{-7}	166	1,200	27×10^{-6}
U2.3	Full bore fracture of liquid line during transfer from another point	2.1×10^{-7}	83	3,000	11×10^{-6}
U2.4	Full bore fracture of liquid line while line is isolated	1.9×10^{-4}	83	86	0
U3	Full bore fracture of bottom connection on sphere	4.2×10^{-6}	36	6,950	38×10^{-6}
U4	Full bore fracture of top connection on sphere	4.4×10^{-6}	39	6,400	9×10^{-6}
U5	Major crack in sphere shell[b]	1.0×10^{-5}	9.2	>10,000	40×10^{-6}
U7	Full bore fracture of vapour line	1.4×10^{-5}	22	300	56×10^{-6}
Total					197×10^{-6}

Table A8.7 *(continued)*

B Hazard scenarios

Sphere catastrophic failure: instantaneous release
Pipeline rupture: continuous release

C Fault trees

U1 Sphere rupture
- U1.1 Support failure
- U1.2 Excess external heat
- U1.3 Excess of pressure
  - U1.3.1 Overfilling with liquid
  - U1.3.2 Chemically incompatible material introduced
- U1.4 Mechanical defect
  - U1.4.1 Stress corrosion cracking
  - U1.4.2 Corrosive material introduced from rail cars

[a] For these nine cases the typical hazard distances to the LTL_{50} are 2308, 1497, 671, 575, 241, 374, 23, 63, 87 m and to the LTL_{05} 2775, 1819, 893, 755, 327, 501, 100, 103 and 142 m respectively.
[b] Equivalent to a hypothetical 50 mm hole.

Table A8.8 *Rijnmond Report: summary of assessment of chlorine storage (AKZO) (after Rijnmond Public Authority, 1982)*

A Undesired events

Event[a]	*Frequency* (events/year)	*Mass flow or mass* (kg/s or kg)	*Duration* (s)	*Average no. of fatalities to public*[b] (deaths/year)
A1.1 Catastrophic burst, full	0.93×10^{-7}	100,000	I	2.59×10^{-5}
A1.2 Catastrophic burst, half full	0.74×10^{-6}	50,000	I	7.47×10^{-5}
A2.1 Split below liquid, $\Delta p = 6.5$ bar	0.83×10^{-6}	63	790	1.03×10^{-4}
A2.2 Split below liquid, $\Delta p = 9$ bar	0.83×10^{-6}	76	660	1.03×10^{-4}
A3.1 Split above liquid level, $\Delta p = 6.5$ bar	0.83×10^{-6}	14	3500	0.82×10^{-4}
A3.2 Split above liquid level, $\Delta p = 9$ bar	0.83×10^{-6}	26	1900	0.82×10^{-4}
A4.1h Fracture of connection, full bore, $\Delta p = 6.5$ bar, angled horizontally	3×10^{-7}	253	200	3.7×10^{-5}
A4.1d Fracture of connection, full bore, $\Delta p = 6.5$ bar, angled down	3×10^{-7}	94	530	3.3×10^{-5}
A4.2h Fracture of connection, full bore, $\Delta p = 9$ bar, angled horizontally	3×10^{-7}	300	166	3.7×10^{-5}
A4.2d Fracture of connection, full bore, $\Delta p = 9$ bar, angled down	3×10^{-7}	110	450	3.3×10^{-5}
A4.3h Fracture of connection, small leak $\Delta p = 6.5$ bar, angled horizontally	6×10^{-6}	5.8	3600	9.1×10^{-5}
A4.3d Fracture of connection, small leak, $\Delta p = 9.5$ bar, angled down	6×10^{-6}	2.2	3600	4.3×10^{-5}
A4.4h Fracture of connection, small leak, $\Delta p = 9$ bar, angled horizontally	6×10^{-6}	6.9	3600	9.1×10^{-5}
A4.4d Fracture of connection, small leak, $\Delta p = 6.5$ bar, angled down	6×10^{-6}	2.6	3600	4.3×10^{-5}
A7.3 Full bore fracture of liquid line, valve open	2.4×10^{-6}	64/32	56/1500	9×10^{-5}
A7.4 Full bore fracture of liquid line, valve open, later shut	7.4×10^{-6}	64/32	56/44	5.8×10^{-5}
A11.5 Full bore fracture of liquid line, at end, valve open, later shut	5.9×10^{-5}	160/100	60/240	4.8×10^{-4}
A11.6 Full bore fracture of liquid line, small leak	1.2×10^{-3}	3.6/1.3	300/2300	1.8×10^{-3}
A15.1 Full bore fracture of vapour line, valves open, later shut	6.6×10^{-6}	15	300	1.8×10^{-4}
A17.2 Full bore fracture of liquid line, at end, valves open, later shut	8×10^{-6}	64/32	23/280	6.4×10^{-5}
Total (37 events)				3.57×10^{-3}

Table A8.8 *(continued)*

B Hazard scenarios

Tank catastrophic failure: instantaneous release
Tank leak: mixed and continuous release
Pipework leak: mixed and continuous release

C Fault trees

A1 Tank rupture
- A1.2 Pressure of water in tank
- A1.3 Internal explosion in tank
- A1.4a Bursting disc does not relieve
- A1.4b Source of overpressure potential
- A1.5 Overpressure due to liquid overfilling

[a] There are 17 further events. None of these events causes an average number of fatalities to the public greater than 10^{-5}/year.
[b] For these 20 cases the typical hazard distances to the LTL_{50} are 6500, 4900, 3400 (×2), 2200 (×2), 4700 (× 4), 1100 (×4), 2100, 1600 (×2), 1100 and 1600 m and to the LTL_{05} 8600, 6400, 4200 (×2), 2800 (×2), 6000 (×2), 1400 (×4), 2600, 2000 (×2), 1400 and 2000 m, respectively.

Table A8.9 *Rijnmond Report: summary of assessment of LNG storage (Gasunie) (after Rijnmond Public Authority, 1982)*

A Undesired events

Event	*Frequency*[a] (events/year)	*Mass flow or mass* (kg/s or kg)	*Duration* (s)	*Average no. of fatalities to public*[b] (deaths/year)
G1 Catastrophic failure of tank	0.8×10^{-6} 0.126	19×10^{6}	I	6.3×10^{-10}
G2 Failure of tank into earth bund	1×10^{-9} 0.144	19×10^{6}	I	3.5×10^{-12}
G3.1 Fracture of line (no pumping)	2.5×10^{-7} 0.051	60	35	4.5×10^{-11}
G3.2 Fracture of line, other place (no pumping)	8.1×10^{-7} 0.027	60	35	0
G4.1 Fracture of line (pumping)	1.5×10^{-8} 0.06	100	600	4.1×10^{-12}
G4.2 Fracture of line, other place (pumping)	4.8×10^{-8} 0.0585	100	600	0
Total				6.8×10^{-10}

B Hazard scenarios

Inner tank failure: instantaneous release
Concrete containment failure: instantaneous release
Pipework rupture: continuous release (short)
Spreading of liquid
Vaporization of liquid
Pool fire
Flash fire

C Fault trees

G1 Tank rupture
- G1.1 Other sources of overpressurization
- G1.2 Excessive underpressurization
- G1.3 Internal explosion

[a] For each case the probability of immediate ignition is 0.1 and that of ignition when dispersed is given by the second entry in the column.
[b] For these six cases the typical hazard distances for fatal effects from fire are 211, 174, 152, 210, 151 and 199 m, respectively. No hazard distances are quoted for fatal effects from explosion.

Table A8.10 *Rijnmond Report: summary of assessment of propylene storage (Oxirane) (after Rijnmond Public Authority, 1982)*

A Undesired events

Event[a]	*Frequency*[b] (events/year)	*Mass flow or mass* (kg/s or kg)	*Duration* (s)	*Average no. of fatalities to public*[c] (deaths/year)
0.01 Failure of full sphere	0.028×10^{-6} 0.96	600,000	I	1.43×10^{-7}
0.02 Failure of sphere containing 300 te	0.233×10^{-6} 0.94	300,000	I	1.52×10^{-6}
0.03 Full rate from sphere relief valve	2.0×10^{-5} 0.001	20	C	0
0.04 Failure of connection	3.5×10^{-7} 0.3	455	1300	2.2×10^{-7}
0.05 Failure of liquid line	1.3×10^{-6} 0.33	233	2570	5.3×10^{-7}
0.08 Failure of connection	1.1×10^{-6} 0.3	202	C	3.6×10^{-7}
0.09 Failure of liquid line	5.8×10^{-6} 0.15	104	C	1.5×10^{-6}
0.20 Failure of liquid line	2.4×10^{-5} 0.33	230	C	13.2×10^{-6}
0.21 Failure of liquid line	2.4×10^{-5} 0.13	230	C	9.0×10^{-6}
0.25 Failure of liquid line	3.6×10^{-6} 0.104	280	C	1.04×10^{-6}
0.26 Failure of liquid line	2.0×10^{-5} 0.17	104	C	2.1×10^{-6}
0.30 Failure of liquid line	1.1×10^{-5} 0.31	230	C	6.2×10^{-6}
Total (31 cases)				3.66×10^{-5}

B Hazard scenarios

Sphere failure: instantaneous release
Vaporizer shell failure: instantaneous release
Pipework failure: continuous release
Gas dispersion
Ignition probability
Flash fire
Explosion

C Fault trees

01 Sphere rupture
- 01.1 Gross overstressing of shell
  - 01.1.1 Gas phase pressurization of sphere
    - 01.1.1.1 High temperature and pressure from jetty vaporizer
    - 01.1.1.2 Manual and power valves in circuit round spheres/vaporizer liquid and vapour lines all open
  - 01.1.2 Internal explosion in sphere
  - 01.1.3 Wrong material loaded
  - 01.1.4 Liquid overfilling
    - 01.1.4.1 Overfilling from ship
    - 01.1.4.2 Overfilling from rail car
- 01.2 Mechanical defect in sphere shell
  - 01.2.1 Wrong material loaded (see tree for 01.1.3)

[a] There are 19 further cases. None of these events causes an average number if fatalities to the public $>10^{-6}$/year.
[b] For each case the probability of immediate ignition is 0.1 and that of ignition when dispersed is given by the second entry in the column.
[c] For these 12 cases the typical hazard distances for fatal effects from fire are 353, 338, 47. 125, 154, 105, 110, 138, 218, 268, 118 and 147 m, respectively. The hazard distances for explosion are given for overpressures of 0.3, 0.1 and 0.03 bar. For the former the distances are 207, 164, 28, 62, 74, 51, 56, 68, 88 and 102 m, respectively.

Table A8.11 *Rijnmond Report: summary of assessment of hydrodesulfurizer (Shell) (after Rijnmond Public Authority, 1982)*

A Undesired events

Event	*Frequency* (events/year)	*Mass flow or mass* (kg/s or kg)	*Duration* (s)	*Average no. of fatalities to public*[a] (deaths/year)
S1.1 Major failure H_2S line, elevated, 1 min duration	3.2×10^{-6}	1.21	60	0
S1.2 Major failure H_2S line, elevated, 10 min duration	3.2×10^{-6}	1.21	600	0
S1.3 Major failure H_2S line, elevated, extended duration	7.2×10^{-7}	1.21	Long	0
S2.1 Major failure H_2S line, low level, 1 min duration	3.2×10^{-6}	1.21	60	0
S2.2 Major failure H_2S line, low level, 10 min duration	3.2×10^{-6}	1.21	600	0
S2.3 Major failure H_2S line, low level, extended duration	7.2×10^{-7}	1.21	Long	0
S5 Major failure at DEA line	1.6×10^{-6}	0.49	Long	0
Total				0

B Hazard scenarios

Pipework failure:
  continuous release
Gas dispersion

C Fault trees

None

[a] For these 7 cases the typical hazard distances to the LTL_{50} are 0, 19, 59, 81, 144, 153, and 64 m and to the LTL_{05} 0, 85, 96, 99, 173, 181 and 81 m, respectively.

Table A8.12 *Rijnmond Report: individual and average annual risk for six installations (Rijnmond Public Authority, 1982)*

Installation	*Average annual fatalities*		*Individual risk employees*
	Employees	*Public*	
Acrylonitrile	2.1×10^{-3}	7.9×10^{-6}	6.6×10^{-6}
Ammonia	2.1×10^{-3}	2.0×10^{-4}	20×10^{-6}
Chlorine	1.1×10^{-2}	3.6×10^{-3}	5.1×10^{-5}
LNG	1.5×10^{-7}	6.8×10^{-10}	5.7×10^{-9}
Propylene	1.1×10^{-4}	3.7×10^{-5}	7.7×10^{-7}
Hydrodesulfurizer	1.0×10^{-6}	0	2.1×10^{-9}

For cases S1–S2, which involve direct release of hydrogen sulfide, it was found that the inventory of gas, which is at a gauge pressure 0.5 bar, was too small to sustain a release of any significant duration and that for these cases the limiting flow was determined by the rate of evolution of the gas, which was 4370 kg/h. This is equivalent to discharge from hole of a 75 mm diameter.

All the emissions are continuous sources.

An ignition probability of 0.2 on release was assumed.

For toxic gas hazard, therefore, the exposure is continuous. In all cases only employees were at risk.

Typical hazard distances to the LTL_{50} are given in Table A8.11, the greatest distance there quoted being 153 m. The distances are greater for adverse weather conditions, being for case S2.3 on the centreline for 2.0/F conditions 395 m.

A8.9 Assessed Risks

The results of the assessment are presented in a number of ways. These include

Risk contours
Risk to employees:
  Individual risk
Risk to public:
  Individual risk
  Societal risk
  FN tables
  FN curves
Average annual fatalities

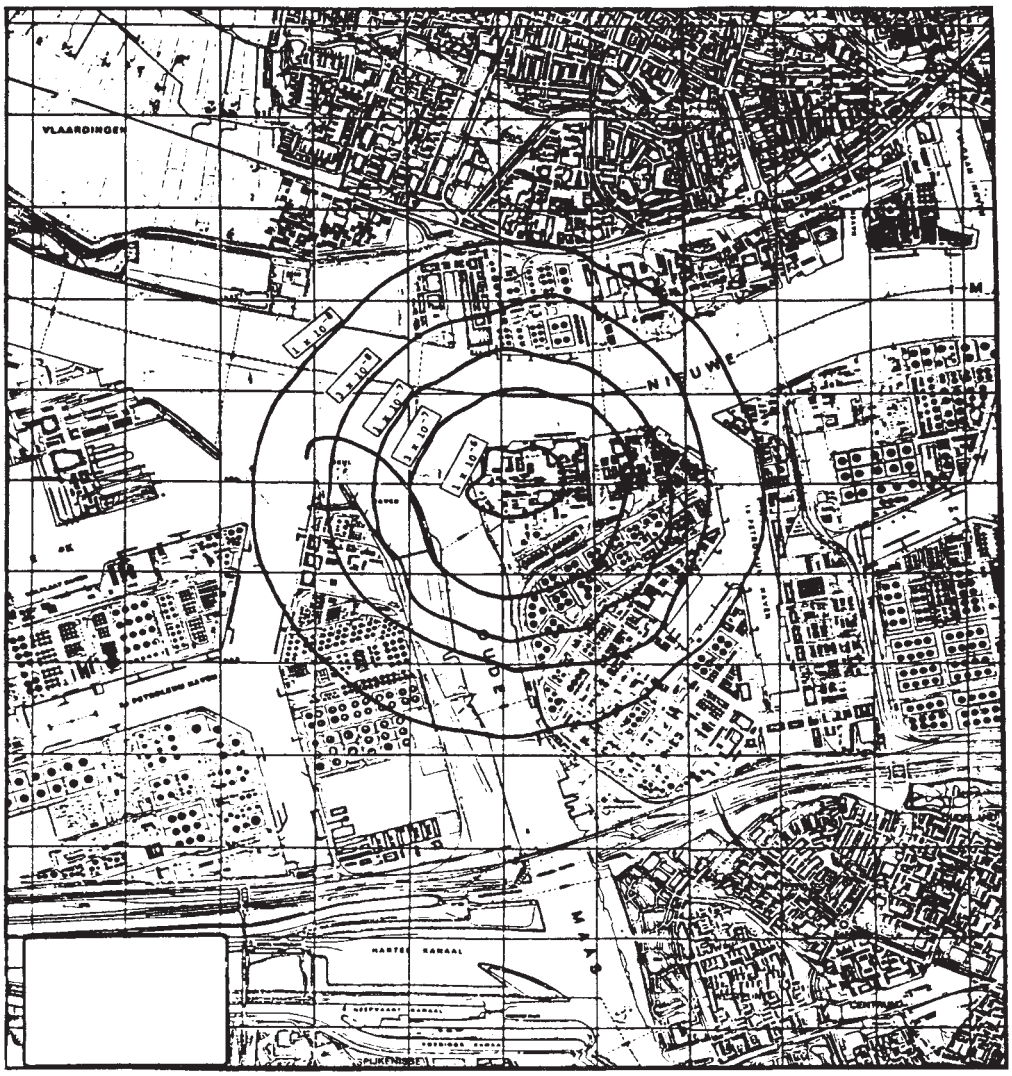


Figure A8.4 *Rijnmond Report: risk contours for ammonia storage (Rijnmond Public Authority, 1982. Reproduced by permission)*

Table A8.13 *FN table for public for chlorine storage in Rijnmond Report (after Rijnmond Public Authority, 1982)*

No. of deaths	*Cumulative frequency*	*No. of deaths*	*Cumulative frequency*
1	4.00×10^{-4}	125	2.09×10^{-6}
10	1.07	151	1.62
20	3.70×10^{-5}	200	9.86×10^{-7}
30	1.50	304	3.06
40	9.46×10^{-6}	404	2.34
50	7.32	518	1.26
60	6.34	738	4.85×10^{-8}
70	5.23	1027	3.40
80	4.31	1697	7.50×10^{-10}
90	3.23		
100	2.87		

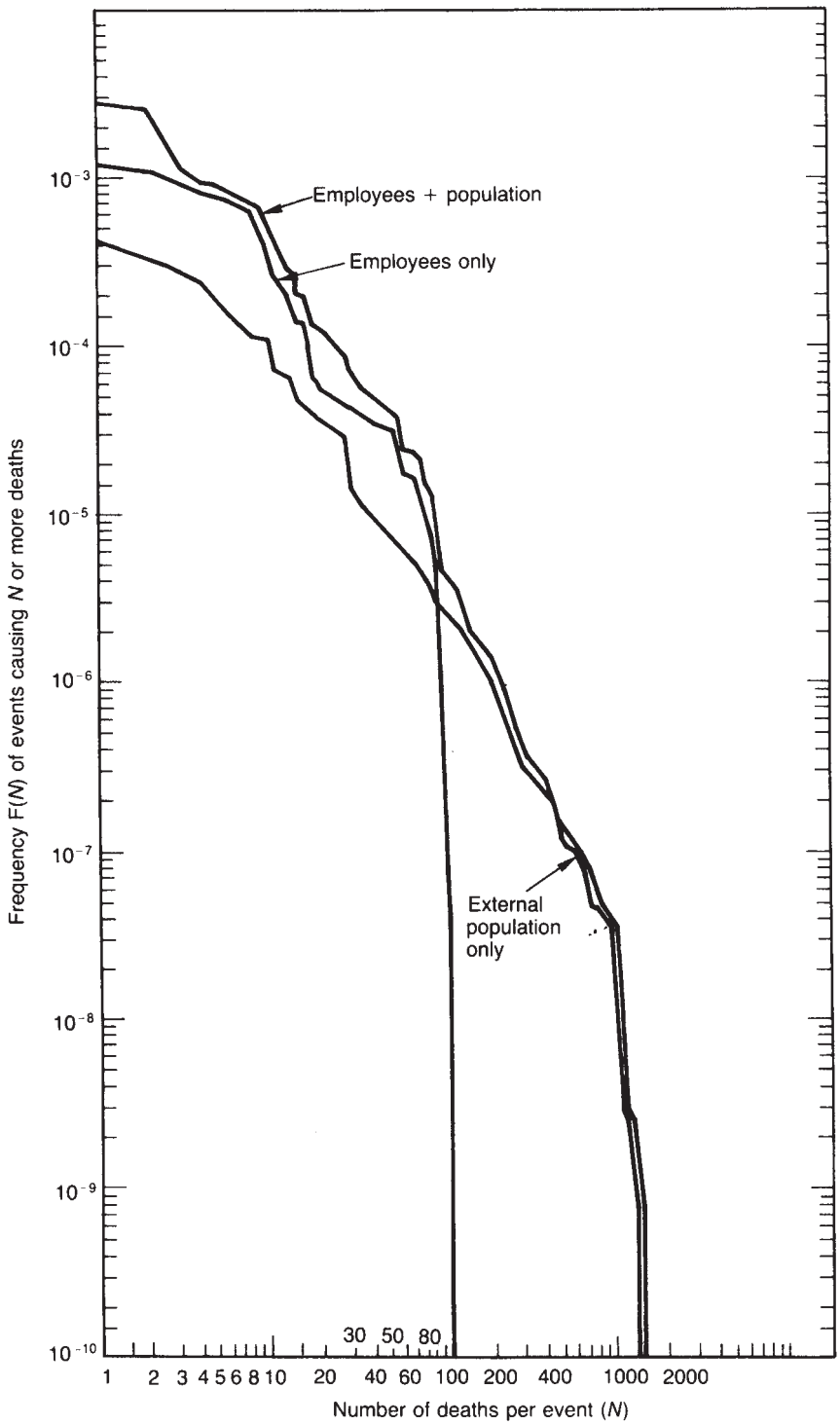


Figure A8.5 *Rijnmond Report: FN curve for chlorine storage (Rijnmond Public Authority, 1982. Reproduced by permission)*

The individual risks and average annual fatalities are shown in Table A8.12.

The use of risk contours is illustrated here by one of those for the ammonia storage shown in Figure A8.4, while that of FN tables and of FN curves is illustrated by those for the chlorine storage shown in Table A8.13 and Figure A8.5, respectively.

A8.10 Remedial Measures

For each installation recommendations were made for remedial measures to reduce the risks. In accordance with the remit of the study the proposals made were illustrative rather than exhaustive and are suggestions for further evaluation.

For the AN storage the main measure proposed is nitrogen blanketing to prevent internal explosion. It is recognized, however, that there is a contrary view that lack of oxygen may make spontaneous reaction more likely. It was estimated that inciting would reduce the frequencies of events P1 and P3 to 0.1×10^5 and 0.4×10^5/year, respectively. Some 17 other measures are also listed, including hose support, tanker earthing and changes to sampling methods.

For the ammonia storage the principal measure suggested is the provision of a bund. This would do little to retain material released in a catastrophic failure of the sphere, but it might well mitigate the effect of failure of a bottom connection.

Another proposal made is the provision of an emergency air supply at the control room to allow the operators time to close emergency isolation valves.

For the chlorine storage the main recommendations are directed to reduction of the size of escapes from pipework by the use of excess flow valves.

For the LNG storage the main measure proposed is directed towards the prevention of escalation due to brittle fracture of carbon steel from a small release of cold liquefied gas. It is suggested that baffles on the tank roof would reduce this risk. It was estimated that this would reduce the total risk by 5.6%.

For the propylene storage the installation of remote isolation valves is the principal measure proposed. It was estimated that this would reduce the total risk by half. Proposals are also made for modifications to the vapour return system.

For the hydrodesulfurizer the measures proposed are minor. It is suggested that there should be monitoring of hydrogen sulfide in the control room and that the hazard of spread of DEA through the drain system be investigated.

A8.11 Critiques

As indicated, the *Rijnmond Report* itself contains its own critique in the form of a review by outside consultants and industrial comment. Much of this relates to the failure and event data, the hazard models and the injury relations and particularly to the models.

A8.12 Notation

n_h number of weeks off for holidays, sickness, etc.
N_d number of persons on site during day
N_e number of persons on site
N_n number of persons on site at other times

Appendix 9 Laboratories

Contents

A9.1 Legal Requirements A9/2
A9.2 Laboratory Management Systems A9/2
A9.3 Laboratory Personnel A9/3
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A9.6 Laboratory Design A9/5
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A9.8 Laboratory Services A9/6
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A9.10 Laboratory Operation A9/7
A9.11 Laboratory Fire and Explosion Protection A9/9
A9.12 Emergency Planning A9/9

Laboratories are an integral part of the activities of the process industries. They include not only analytical laboratories and laboratories carrying out research and development work in industry but also university teaching laboratories where future industrial managers are trained. Pilot plants are considered in Appendix 10.

Accounts of laboratories and of laboratory safety are given in *Safety in the Chemical Laboratory* by Pieters and Creighton (1957), *Safety in University Laboratories* by the AUT (1967), *Hazards in the Chemical Laboratory* by Muir (1971) and later Bretherick (1999, 2000), *Handbook of Laboratory Safety* by Steere (1971), *A Guide to Laboratory Design* by Everett and Hughes (1975), *Prudent Practices for Handling Hazardous Chemicals in Laboratories* by NRC Staff (1981), *Introduction to Safety in the Chemical Laboratory* by N.T. Freeman and Whitehead (1982), *Handbook of Laboratory Waste Disposal* by Pitt and Pitt (1985), *Improving Safety in the Chemical Laboratory* by J.A. Young (1987a) and *Safety in Chemical Engineering Research and Development* by V.C. Marshall and Townsend (1991) (the IChemE *Laboratories Guide*).

A *Code of Practice for Chemical Laboratories* (the RIC *Laboratories Code*) has been published by the Royal Institute of Chemistry (RIC) (1976).

Activities in a chemical laboratory are distinguished from those on an industrial plant, above all, by their small scale. The smaller quantities of species in the laboratory can reduce the overall consequence of an event. In addition, heat losses are relatively greater at the laboratory scale. This certainly reduces the hazards. There are, however, factors which may increase the risk of a hazardous initial event, such as the use of inexperienced and untrained personnel, and of escalation of that event, such as the enclosed space and the close proximity of personnel. Further, if the small scale of the hazard leads to general complacency and poor practice, the risk that it will be realized is augmented.

Despite the lesser scale of the hazard, the approach to hazard control used for full-scale plants is applicable in large part to activities in the chemical laboratory. An accident in the laboratory can give rise to considerable personal injury or loss of life and direct damage loss, because the density of personnel and of expensive equipment which are at risk is relatively high. There may also be serious consequential loss due to interruption of the facilities which the laboratory provides for production plants or of research and development activities.

Moreover, where a laboratory, whether in the university, government, or industry, has a training function, it is essential to adhere to, and instill, good practice in hazard control.

Many of these topics touched on here have already been discussed, albeit not specifically in relation to laboratories, in previous chapters, in particular those on legislation (Chapter 3), management and management systems (Chapter 6), hazard identification (Chapter 8), reactive hazards (Chapter 33), process design (Chapter 11), fire, explosion and toxic release (Chapters 16–18), personal safety (Chapter 25) and safety systems (Chapter 28).

Selected references on laboratory safety are given in Table A9.1.

Table A9.1 *Selected references on laboratory safety*

BSC (n.d./4); Kintoff (1939); Pieters and Creighton (1957); Quam (1963); H.H. Fawcett (1965e, 1982e); C.H. Gray (1966); AUT (1967); Everett (1969, 1979, 1980 LPB 32); A.F.H. Ward (1969); BDH (1970, 1977a–c); MCA (1970/19, 1972/21); Imperial College Safety Committee (1971); Muir (1971); Steere (1971); Stephenson (1972 MCA/21); Ciba-Geigy Ltd (1974); Fairbairn (1974 SRD R8); Weekman (1974); Everett and Hughes (1975); Bremner (1976); Cooke (1976); RIC (1976); Seidenberger and Barnard (1976); Weissbach (1976); Anon. (1977 LPB 13, p. 14); Anon. (1977 LPB 18, p. 17); V.C. Marshall (1977c, 1979b, 1980 LPB 32, 1981 LPB 37); Anon. (1978 LPB 20); Curry (1978); Dept of Health and Social Security (1978, 1979); Pitt (1978); J.M. Reynolds (1978); Buttolph (1979, 1980 LPB 32); Cohn, linnecar and Ryall (1979); Fowler (1979, 1980 LPB 32); G.F. Martin (1979, 1980 LPB 32); Napier (1979b, 1980 LPB 32); Pogany (1979); Spencer (1979); Penninger and Okazaki (1980); Anon. (1981 LPB 39, p. 11); Bretherick (2000); G. Marshall (1981 LPB 39); NRC Staff (1981); N.T. Freeman and Whitehead (1982); Pitt and Pitt (1985); B. Miller *et al.* (1986); Armour (1987); Baum and Diberardinis (1987); Bulloff (1987); Gerlach (1987); Hoyle and Stricoff (1987); Prokopetz and Walters (1987); Reale and Young (1987); Redden (1987); Saunders (1987); Springer (1987); Varnerin (1987); Williamson and Kingsley (1987); J.A Young (1987a–c); ACGIH (1988/20, 1990/40, 43, 44, 1991/61, 69, 1992/77); Ciolek (1988); Le, Santay and Zabrenski (1988); Lunn and Sansone (1990); Stricoff and Walters (1990); Kalis (1991); V.C. Marshall and Townsend (1991); NFPA (1991 NFPA 45); Woodhead (1992); Bartlett, Hall and Gudde (1993); Senkbeil (1994) BS (Appendix 27 *Laboratory Equipment*)

Fume cupboards, enclosures

Walls and Metzner (1962); BOHS (1980 Monogr. 4, 1987); J. Grant and Rimmer (1980); ASHRAE (1985 ASHRAE 110); OSHA (1990/6); V.C. Marshall and Townsend (1991); AIHA (1993 Z95) BS 7258: 1990–

A9.1 Legal Requirements

In the United Kingdom the Factories Act 1961 covers industrial workplaces, including laboratories, while the HSWA 1974 applies to all places of work and thus extends coverage to university as well as industrial laboratories.

Chapter 3 gives an account of these acts and also of other legislation relevant to laboratories such as that on the workplace, including management, work equipment and incident reporting; pressure systems; toxic substances and occupational hygiene; flammable and explosive materials; fire; ionizing radiations; electricity; and personal safety, including safety signs, machine guarding, compressed air and compressed gases, manual handling, protective equipment, eye protection and first aid.

A review of legislation applicable to chemical engineering laboratories is given in the IChemE *Laboratories Guide*.

A9.2 Laboratory Management Systems

The management approach used for the control of hazards in industry is in large part applicable in chemical laboratories. In particular, use should be made of formal systems and procedures as described in Chapter 6.

The laboratory should have a management system with suitable organization and competent people, systems and

procedures, standards and codes of practice, and documentation. There should be a clear chain of command and separation of executive from advisory, or staff functions. There should be a safety officer and a safety committee, and safety audits should be conducted.

Some principal systems are described below, and others in later sections.

A9.2.1 Hazard reviews

There should be a system of hazard reviews for experimental work. A review should give a statement of the hazards involved and of the means by which they will be controlled.

A9.2.2 Permit systems

Hazardous activities should be covered by a permit system. Permits may be required for general maintenance activities, for hot work and for vessel entry. The IChemE *Guide* gives example permit forms.

A9.2.3 Incident reporting

There should be a system for the reporting of incidents. As a minimum this should meet the legal requirements given in RIDDOR (1985), but in addition there should be a general requirement for the reporting of unintended events.

A9.2.4 Safety audits

The system of safety audits should cover the management systems for the laboratory, the equipment, the services, storage and waste disposal, and the operations.

The conduct of safety audits is discussed in the IChemE *Guide* and by Bretherick (2000) and J.A. Young (1987b).

A9.3 Laboratory Personnel

There tend to be wide variations in the capability of the personnel who work in laboratories, ranging from well-trained and experienced permanent staff to relatively inexperienced research workers and students. A discussion of people in laboratories is given by Buttolph (1980 LPB 32).

A9.3.1 Training

It follows from the above that for laboratory personnel training assumes particular importance. This training needs to cover the hazards, the equipment, the procedures and the systems. As with all training, it should aim to motivate as well as to inform.

Personnel who use the laboratory should be trained in good laboratory practice. The training should include such aspects as action to take in case of fire and other accidents, methods of eye irrigation and use of fire extinguishers.

The laboratory should have the appropriate number of persons trained in first aid.

Where the personnel concerned are prospective managers of industrial plants, experience in a well-conducted laboratory provides a good foundation.

Accounts of the content of, and techniques for, laboratory training are given by Bretherick (2000), Armour (1987) and Redden (1987).

A9.4 Laboratory Codes

A9.4.1 RIC *Laboratories Code*

The RIC *Laboratories Code* covers the following aspects:

(1) Laboratory services
  (a) electricity
  (b) gas for heating
  (c) water
  (d) steam
  (e) ventilation
  (f) compressed air
  (g) brine circulation
  (h) hot plates, ovens and furnaces
  (i) drainage
(2) Hazardous chemicals
  (a) flammable substances
  (b) explosive substances and mixtures
  (c) corrosive chemicals
  (d) irritant chemicals, dusts, gases and vapours
  (e) toxic chemicals
  (f) radiation and radioactive materials
  (g) cylindered gases
  (h) cryogenic fluids and systems
(3) Hazardous techniques
  (a) pressure reactions
  (b) vacuum techniques
  (c) glass handling
  (d) heating of chemical apparatus
  (e) centrifugation
(4) Organization
  (a) safety officers and safety committees
  (b) appointment and functions of a safety committee
  (c) fire prevention
  (d) personal protection
  (e) rescue
  (f) first aid and medical services
  (g) housekeeping and safety audits
  (h) labelling
  (i) storage
  (j) waste disposal
  (k) noise
  (l) unattended experiments and working alone
  (m) documentation of procedures
(5) Legal responsibility
  (a) legal responsibility
  (b) legislation

A9.4.2 NFPA 45

Guidance on fire protection is available in NFPA 45: 1986 *Fire Protection for Laboratories using Chemicals*.

The standard covers (1) general topics, (2) laboratory unit hazard classification, (3) laboratory unit design and construction, (4) fire protection, (5) explosion hazard protection, (6) laboratory ventilating systems and hood requirements, (7) chemical storage, handling and waste disposal, (8) compressed and liquefied gases, (9) laboratory operations and apparatus and (10) hazard identification.

The classification divides laboratories into high, intermediate and low hazard according to the maximum densities of materials held. For flammable or combustible

liquids Class I, II or IIIA, these densities are

Laboratory unit class	*Flammable or combustible liquid class*	*Maximum quantity/ 100ft² of unit* (US gal)	
		Excluding storage	*Including storage [format]*
A High hazard	I	10	20
	I, II and IIIA	20	40
B Intermediate hazard	I	5	10
	I, II and IIIA	10	20
C Low hazard	I	2	4
	I, II and IIIA	4	8

The storage referred to is storage in cabinets and cans. The standard states that Class A laboratory units should not be used as instructional laboratories and that for Class B and C instructional laboratories the maximum quantities should be half those given above.

An account of the use of NFPA 45 in laboratory design is given by Le, Santay and Zabrenski (1988).

A9.4.3 IChemE *Laboratories Guide*

The IChemE *Laboratories Guide* has the following coverage: (1) introduction, (2) safety management of laboratories, (3) the law and process laboratories, (4) hazards in chemical engineering laboratories, (5) designing process research and development facilities, (6) services, (7) storage of materials and disposal of waste, (8) design of experiments, (9) operating procedures and safety, (10) emergency procedures, (11) maintenance and modifications and (12) relevant publications.

A9.5 Laboratory Hazards

Reviews of hazards in chemical laboratories are given in the RIC *Code* and the IChemE *Guide* and in most texts of laboratory safety such as those of Steere (1971), Bretherick (2000) and J.A. Young (1987a). The list quoted from the RIC *Code* in Section A9.4 is typical.

In addition to the specific treatments mentioned below, a general account of the handling of hazardous research chemicals is given by Prokopetz and Walters (1987) and one of hazards other than those from chemicals by Bulloff (1987).

Further treatments of the hazards of flammable substances are given in Chapter 16, of toxic substances in Chapter 18 and of others such as radiation, electrical and mechanical hazards in Chapter 25.

A review of the causes of incidents in laboratories is given by J.A. Young (1987c), who utilizes the following headings: (1) management responsibilities inadequate, (2) lack of communication, (3) lack of personal responsibility, (4) lack of proper ventilation, (5) lack of protective equipment, (6) personal hygiene problems, (7) electrical hazards, (8) storage problems and (9) inadequate emergency procedures and equipment.

A9.5.1 Reactive substances

Where reactive substances are handled or processed, every effort should be made to obtain the fullest information on their behaviour. Texts such as *Handbook of Reactive Chemical Hazards* by Bretherick (2000) , Sax's *Dangerous Properties of Industrial Materials* (2000), and *Hazardous Chemicals Handbook* by Carson and Mumford (1994) are an essential point of departure.

Bretherick (2000) has also provided a review of chemical reactivity in the laboratory context.

A9.5.2 Flammable substances

Many of the liquids and gases handled in laboratories are flammable. Each phase presents its characteristic hazards.

Accounts of the hazards of flammable and combustible materials are given in the various NFPA codes, including for laboratories NFPA 45 and by Steere (1971), Bretherick (2000) and Gerlach (1987).

Where flammable liquids are handled, one hazard is release followed by ignition. Factors which need to be considered are the integrity of the containment, the flow of liquid if it does escape and any sources of ignition.

Another hazard is overheating of the liquid, leading to its escape, either as a liquid following failure of the containment or as vapour from an open vent.

A frequent cause of bench fires is loss, or under-circulation, of cooling water.

Flammable liquids should not be handled near, or heated on, naked flames and should also be kept away from arcing/sparking devices.

Where flammable gases or vapours are handled, the most common hazard is a leak which allows a flammable atmosphere to build up in the enclosed laboratory space. Unless there is a high level of ventilation, this can occur even with a relatively small leak rate.

Another cause of bench fires is contact between water and reactive metals such as sodium.

Oxygen should not be used in such a way as to create the hazard of an oxygen-enriched atmosphere. Oxygen is liable to oxidize and then rupture rubber tubing. There is also the possibility of an 'oxygen fire' in which the metal can be ignited (arising, for example, from adiabatic compression, particularly in non oil-free lines as described in NFPA 53).

A9.5.3 Toxic substances

Where toxic substances are handled, it is necessary to consider all three modes of entry into the body and both short- and long-term toxic effects.

For entry, inhalation may well be the principal mode, but in laboratory work in which chemicals are 'handled' to a much greater extent the ingestion and skin modes may be more significant than is usually the case. High standards of hygiene therefore assume greater importance.

With regard to inhalation, there may be a hazardous short-term effect if the substance is highly toxic and circumstances can be foreseen in which a concentration sufficiently high to cause acute poisoning can occur. This is rather more likely in the enclosed space of a laboratory.

More commonly, however, the hazard arises from exposure to low concentrations over a relatively long period.

Where a toxic hazard exists, the requirements of the Control of Substance Hazardous to Health (COSHH) Regulations 1988 apply.

The design countermeasures are primarily a high standard of containment. Other measures are described in the next section.

Accounts of the effects of toxic chemicals in the laboratory context are given by Steere (1971), Bretherick (2000) and Springer (1987).

A9.5.4 Radiation hazards

There are a variety of radiation hazards, most of which may be found on occasion in laboratories. They include both ionizing and non-ionizing radiations as described in Chapter 25.

With regard to ionizing radiation, some devices containing radioactive sources instanced in the IChemE *Guide* are certain liquid level gauges, gas chromatograph detectors, leakage detectors, anti-static devices on balances, and fire detectors.

Certain apparatus producing voltages above 5 kV may be a source of X-rays.

Non-ionizing radiation sources include lasers, microwaves and UV and IR devices.

A9.5.5 Electrical hazards

The electrical hazards are little different from those in industrial situations generally, but unless good practice is observed a laboratory tends to be especially vulnerable to them.

Personnel may be at risk of electrocution from temporary lashups and repairs, defective and damaged cabling, unearthed components and poor earthing. This may be aggravated by handling equipment with wet hands.

Short circuits due to worn cabling, wrong wiring or over-rated fuses can lead to a fire.

A9.5.6 Mechanical hazards

The mechanical hazards likewise are such as may be found in other industrial situations, but again laboratory personnel may be especially vulnerable unless strict controls are observed.

These mechanical hazards include those associated with rig equipment, workshop machinery, hand and power tools, lifting equipment, rotating equipment, and pinching equipment.

Accidents are liable to occur where laboratory personnel use equipment with which they are unfamiliar in order to progress the job.

A9.5.7 Operating condition hazards

Equipment operating at high or low temperature constitutes a contact hazard. Contact with a very cold surface can cause a 'cold burn' not unlike the burn from a very hot surface.

A cryogenic fluid also involves the hazard that it will vaporize by heat transfer from the atmosphere unless this is positively prevented. Depending on the nature of the fluid, such vaporization may give rise to an atmosphere enriched with a flammable or toxic material or oxygen.

A laboratory usually contains a number of sources of high pressure such as compressed air, steam, compressed gas in cylinders and so on. Water also may act as a high pressure source. Rupture of equipment may occur either because the pressure to which it is subjected is above the design conditions, or because the equipment is weaker than designed. Overpressure can occur if a valve is open or fails, weakening if metal equipment is exposed to extremes of heat, cold or thermal cycling.

Failure may also be caused by vacuum, which may occur not just by connection to a vacuum supply but by rapid cooling of a vapour in the apparatus.

Rupture by a pressurized vapour/gas or by a superheated liquid, however, would have more severe consequences than by a subcooled liquid.

A9.5.8 Water release hazards

Another hazard is the escape of water, particularly in the form of a jet. Some potential effects of such a jet are short circuiting, thermal shock, extinction of gas jets and reaction with water-reactive chemicals.

A9.6 Laboratory Design

Laboratory design and layout is discussed in the IChemE *Guide* and by Steere (1971), Everett and Hughes (1975) and Baum and Diberardinis (1987).

A checklist for laboratory design is given by Everett (1980 LPB 32) and a case study in such design by Martin (1980 LPB 32).

A9.6.1 Laboratory layout

The design and layout of a laboratory should proceed on principles broadly similar to those described in Chapter 10. This is the approach taken in the IChemE *Guide*.

The method described in the guide is to analyse the needs of the experimental activities using a flow diagram showing the flow of materials between the experimental rigs, the workshops, stores, analytical services, waste disposal facilities, etc., and to develop layout diagrams in which the low and high hazard features are separated, with minimization of exposure near the latter.

A9.6.2 Toxic chemicals

The hazard from toxic chemicals has been described in the previous section.

Where toxic chemicals are handled, the design should aim to keep the concentrations in the laboratory environment below the relevant exposure limits. The prime means of ensuring this is to prevent leaks through a high standard of containment.

For toxic chemicals the COSHH Regulations 1988 apply as described in Chapter 25. These regulations include provisions for monitoring the workplace atmosphere.

Means of keeping down the concentration of contaminants which do escape include use of ventilation and of fume hoods.

A9.6.3 Ventilation

The most common method of controlling the concentration of contaminants in the workplace is ventilation. The basic methods are local exhaust ventilation and general ventilation. Ventilation of the workplace is described in Chapter 25.

The exhaust from the ventilation should pass to a safe place (e.g. away from air intakes).

A9.6.4 Fume hoods

For some toxic or noxious chemicals use is made of a fume cupboard. An account of fume hoods is given in Chapter 25.

The resort to fume hoods has been criticized, however, by V.C. Marshall (1981 LPB 37) as outmoded. He argues that in the laboratory the release of noxious chemicals has become too readily accepted. The proper approach is higher standards of containment which avoid such emissions.

A9.6.5 Laboratory support

There are a number of facilities which may be needed to support the laboratory. They include (1) workshop, (2) stores, (3) receipt bays, (4) analytical services and (5) staff facilities. These are essentially self-explanatory.

The storage needs should be examined to identify the extent to which segregation is required. It is normal to devote one store to the materials required for the fabrication of rigs and another to process materials such as flammable and toxic liquids, but further segregation may be required.

The IChemE *Guide* suggests, for example, that separate stores are normally required for solvents, different classes of chemicals, explosives, gas cylinders and cryogenic materials.

Eating and drinking should not be permitted in laboratories. There need to be adequate staff facilities provided.

A9.7 Laboratory Equipment

A9.7.1 Glassware

Much laboratory apparatus is constructed in glass. Glass has a number of advantages such as resistance to corrosion, flexibility in use and visibility of contents. It can be used with a high degree of safety. For this it is necessary that its limitations be respected, that it be used only in suitable applications and that manufacturers guidance be consulted.

A9.7.2 Hotplates, ovens and furnaces

Hotplates, ovens and furnaces involve the hazard that an item being heated, or the heating element itself, becomes overheated.

The use of ovens is frequently not subject to the same degree of formal control as other apparatus, and different people may put in items which are incompatible or may alter the controls, with undesirable results.

A9.7.3 Centrifuges

Laboratory centrifuges are a recognized hazard. They are the subject of BS 4402: 1982 *Specification for Safety Requirements for Laboratory Centrifuges* and are treated in Appendix 6 of the IChemE *Guide*. This is in addition to BS 767 and a further IChemE guide both of which apply to industrial centrifuges.

A laboratory centrifuge should be properly balanced. The buckets should be well fitting and with rubber pads in place. The machine should be cleaned and dried after use to prevent corrosion which is a common cause of mechanical failure.

In use the lid should be closed and locking devices secured before start-up. The machine should be brought up to speed gradually. It should be stopped using the controls, not simply switched off. The lid should not be opened until the machine has come to rest.

Centrifuges are discussed further in Chapter 11.

A9.8 Laboratory Services

Laboratories use a wide range of services. The most common are (1) water, (2) steam, (3) compressed air, (4) fuel gas and (5) electrical power. Others include refrigerated coolants, vacuum, oxygen and other piped gases.

A9.8.1 Water

Water is used as process water and as coolant.

Where the cooling load is larger enough to justify it, an external cooling water system may be provided which is a smaller-scale version of an industrial system with the water pumped through cooling towers.

The use of water in laboratories involves several hazards. The first is the potential for reverse flow of liquid from a laboratory process into a water supply main. Where such a possibility exists, some safeguard is required. A break tank provides a barrier more dependable than a non-return valve.

Another hazard is loss of cooling water. Generally this occurs on a single rig due to a leak at that point.

A third hazard is the escape of water into the laboratory. A typical situation might be failure of a cooling water connection on apparatus in a fume hood where the drains are blocked, so that the water flows into the laboratory. If the equipment is running unattended, a large quantity of water can escape, perhaps damaging equipment such as computers on the floor below.

There is often a requirement for demineralized water, which is supplied by a stand-alone unit.

A9.8.2 Steam

Steam is required in the laboratory for heating on larger rigs. It is typically provided by an external boiler system, but for small quantities may be generated by a small electrically heated, or less commonly, gas-fired, unit.

The pressure of steam for laboratories is typically in the range 4–10 barg. Measures should be taken to ensure that equipment supplied with such steam cannot be overpressured and that, where loss of coolant with steam still on could be hazardous, steam is shut off.

The use of steam implies the use of steam traps. These devices need regular maintenance.

A9.8.3 Compressed air

Compressed air for laboratories is generally provided by a fixed piped system supplied from an external air receiver charged by a compressor.

The air should be free of oil, which may be achieved either by use of an oil-free compressor or by oil-removal equipment. Regular maintenance is required for the latter.

Compressed air is potentially hazardous and the supply pressure should be limited to that required for the purposes of the laboratory.

Like steam, compressed air is a potential source of overpressure and measures are needed to safeguard against this.

A9.8.4 Fuel gas

Fuel gas is another service which is usually provided in a laboratory by a fixed pipe system.

A9.8.5 Refrigerated coolants

Cooling to lower temperature that can be achieved by cooling water may be provided using refrigeration, either by circulation of a refrigerant or by the use of an intermediate fluid such as brine or ethylene glycol.

The normal practice is to house the refrigeration set in a separate room.

A9.8.6 Vacuum

In some laboratories a piped system is provided to supply vacuum. Collapse of equipment under vacuum is not unlike an explosion and may generate missiles. Measures are required to ensure that equipment connected to vacuum is not under pressure. Also, backflow prevention should be installed.

A9.8.7 Oxygen

Another gas which may be provided as a fixed piped supply is oxygen, but where this is done special care is needed.

Hazards arising from the use of oxygen are attack and rupture of rubber tubing and creation of an oxygen-enriched atmosphere, which can result in a dramatic enhancement of the flammability of clothing.

A9.8.8 Other piped gases

Laboratory requirements for gases other than air vary greatly. In principle, where the usage is high, a fixed piped system has the very considerable advantage of eliminating the use of temporary facilities. However, frequently what is required is moderate quantities of a relatively large number of gases, so that a piped supply for any one is difficult to justify. In some instances pipes are used for different gases, with suitable precautions.

Where a piped supply is installed, the gas is usually piped from gas cylinders located at a protected shelter on the outside of the building.

Piped systems for hydrogen require special care.

Lines should be carefully labelled and flow restrictors should be installed.

A9.8.9 Compressed gas cylinders

For the reasons just given, supply of many of the gases used is often taken from gas cylinders brought into the laboratory. The use of gas cylinders requires a number of precautions.

The contents of the cylinder should be identified by labelling and colour coding. In use the cylinder should be fitted with a regulator and both valve and regulator should be kept clean and free of grease and oil. The valve should be closed when the cylinder is not in use. The cylinder should be transported in a wheeled carrier and when in use supported in a vertical position.

A more detailed treatment of precautions in the use of gas cylinders is given in Appendix 4 of the IChemE *Guide*.

Cylinders should be secured (e.g. with chains) when in use or transported.

A9.9 Laboratory Storage and Waste Disposal

A9.9.1 Materials storage

The storage of materials for the laboratory is discussed in the IChemE *Guide* and by Steere (1971), Bretherick (2000) and Williamson and Kingsley (1987).

The main inventory of hazardous chemicals is, or should be, in the chemical storage locations. General principles governing such storage concern (1) segregation of incompatible materials, (2) types of containers, (3) receipt points, (4) acquisition, stock-taking and disposal, (5) minimization of inventory and (6) identification, ownership, safety and health information and labelling.

With regard to segregation, some relevant categories of chemical are (1) flammables, (2) toxics, (3) oxidizing agents, (4) corrosive substances, including strong acids and alkalis, (5) cryogenic substances and (6) pyrophoric substances. Toxics should be segregated from flammables and oxidizing agents from flammables, organic chemicals, reducing or dehydrating agents. Categories which should be held in separate stores include corrosive substances, cryogenic substances and pyrophoric substances.

Types of container used are small containers, large containers, bulk containers and gas cylinders. Aspects of good practice with small containers include the use of bottle carriers, non-spill containers and controlled dispensing. Good practice in the storage of large containers, essentially drums, and bulk containers is discussed in Chapter 22.

The receipt points for chemicals should be designed to facilitate handling of incoming loads. Vehicles carrying gas cylinders generally have their own lifting gear, but those carrying drums often do not.

The control of materials in storage is exercised through the processes of acquisition, stock-taking and disposal. It is common for an experimenter to order an appreciable quantity of a chemical, use only a portion of it and then forget about it. Unless close control is exercised, there can build up in the stores, a large quantity of chemicals, much without 'ownership'. It is necessary to keep the situation under control by taking stock periodically and by disposal of unwanted material.

Closely connected with this is the minimization of inventory. The inventory held in the laboratory itself and in storage should be the minimum necessary.

The number of chemicals used in a laboratory can be large and the conditions of use very varied. It is essential to ensure that all materials are identified and labelled. There should be a materials safety data sheet for each chemical. Reale and Young (1987) give an account of labelling and MSDSs in the laboratory context.

The Poison Rules 1982 give in Schedule 1 a list of substances which must be stored in a locked cupboard under the supervision of a registered keeper and the usage of which must be entered in a register.

A9.9.2 Waste disposal

A laboratory usually generates gaseous, liquid and solid wastes, all of which need to be disposed of. The problems of waste disposal are not trivial and have become increasingly severe as environmental standards have risen.

Accounts of this aspect are given in *Handbook of Laboratory Waste Disposal* by Pitt and Pitt (1985), in the IChemE *Guide* and by Steere (1971), Bretherick (2000) and Varnerin (1987).

A distinction is generally made between domestic and chemical wastes. The former category includes paper and broken glass. The latter should be segregated both from paper and from unbroken bottles.

Flammable solvents generally constitute a large proportion of the chemical wastes. Other liquids which are incompatible with such solvents should be collected separately. Separate collection is also required for oil-soaked rags. On no account should chemical wastes be put down the drains.

Separate, clearly labelled receptacles are required for each category of waste. For some categories, such as for flammable solvents, receptacles with appropriate safety features should be used.

Options for the disposal of laboratory wastes are listed by Pitt and Pitt, who give some 13 choices, although many are applicable only to small quantities.

The disposal of wastes has to be formally managed by identifying disposals and obtaining the necessary licenses.

Specialist contractors are used by most laboratories for disposal of at least some of their wastes. This is one of the options discussed by Pitt and Pitt.

A9.10 Laboratory Operation

A9.10.1 Information requirements

It is essential to have the fullest information on the chemicals being handled and on the associated hazards. This

applies particularly to chemicals which are highly reactive or which have toxic effects at low concentrations over long periods. Sources of such information are discussed in Chapter 33.

A9.10.2 Design of experiments

Laboratory experiments are undertaken for different purposes and these necessarily influence their design.

In all cases inherently safer design should be a prime aim, but the extent to which it can be achieved will vary. Facets of inherent safety include scale, operating conditions and materials. Where the objective is the pedagogical one of demonstrating a principle, it may be possible to operate on a small scale, at atmospheric pressure and temperature and using less hazardous materials such as air, water and inert solids.

The purpose of the experiment should be well defined. The experiment should not be too ambitious, and if necessary should progress in stages. Information on the materials handled and their potential hazards should be as complete as practical. The basis of safety should be defined. The design should cover the equipment and its operation, and should meet applicable standards and codes.

The design should be subject to a hazard review, utilizing hazard identification techniques such as checklists and hazop studies (covered in A9.10.3.).

Laboratory equipment should be fit for purpose. The standard of construction of the apparatus should match the degree of hazard and its expected life.

It is not uncommon to build a 'temporary' rig with connections made to certain services by hose rather than by fixed piping. If this is accepted in certain applications, care is still needed to ensure that the practice does not extend to unsuitable cases or to operation over extended periods.

Another common practice is the use in a new experiment of a rig 'inherited' from an earlier one. The suitability of the equipment for the new purpose needs careful scrutiny.

For critical features consideration should be given to the provision of automatic protective devices. Trips may be required to guard against loss of cooling, excessive heating, and deviations of pressure, temperature, flow, level and composition.

Full instructions should be prepared for operating procedures and emergency procedures. Consideration should be given to the requirements of unattended operation if this is planned.

Certain activities require special enclosures. These include the use of a fume hood where the materials are toxic and of explosion cubicles where the process involves hazardous reactions or high pressures.

The planning of safe experiments is discussed by Fowler (1989 LPB 32).

A9.10.3 Hazard assessment

If an experiment has the potential to cause serious injury, it is important to carry out a hazard assessment. Case studies of the application of hazard assessment in the laboratory have been described by Le, Santay and Zabrenski (1988).

One example given is a review of the situations involving release of toxic gas sufficient to pose an acute toxic threat. The gases in question were arsine, diborane and phosphine, all in hydrogen. A tabulation was made of the various release scenarios, showing the expected toxic loads and candidate scenarios were then investigated. Fault tree analysis was used to determine the failure paths.

Another case study described by these authors involved fault tree analysis where the top event considered was the formation of a detonable hydrogen–air mixture from a gas phase reactor system.

A9.10.4 COSHH assessment

A COSHH assessment should be made for any laboratory activity which attracts such an assessment under the COSHH Regulations 1988, as described in Chapter 18.

A9.10.5 Operating procedures

Operating procedures may be classified in two ways. One distinction is between general laboratory procedures and procedures specific to a particular rig. Another is between those which concern safety and those which do not.

For the laboratory as a whole, general operating instructions relating to safety are usually set down in a laboratory safety manual.

For the particular rig, it is advisable to separate the procedures which have safety implications from those which do not. Where operating instructions are imported, as with equipment bought from a manufacturer, it may be necessary to rewrite them, abstracting the safety-related parts.

The operating instructions for a rig should cover start-up, running and shut-down, and should indicate the hazards and the countermeasures to be taken. They should not duplicate the general instructions. They should be clear and simple, and should be as concise as possible.

A9.10.6 Emergency procedures

The operating procedures for each rig should cover action to be taken in the event of an emergency (1) on that rig and (2) in the laboratory as a whole.

It is an accepted principle that a laboratory fire should be fought if it can be done without undue risk. The same principle may be extended to other actions in an emergency which threatens to escalate.

Emergency planning is discussed in Section A9.12.

A9.10.7 Equipment maintenance

The general approach to maintenance of equipment in a laboratory is similar to that in a plant. It involves identification of the equipment to be worked on; planning of the work and shut-down of the equipment; electrical and mechanical isolation of the equipment and preparation for the work by removing fluids and solids and by cleaning. The principles are as outlined in Chapter 21.

A9.10.8 Equipment and procedure modification

Similarly, control should be exercised over modifications to the equipment or the activities, analogous to those over equipment and process modification in a full-scale plant described in Chapter 21.

The IChemE *Laboratories Guide* gives detailed guidance on what, in a laboratory context, constitutes a modification and contains in Appendix 14 a specimen form for control of modifications.

A9.10.9 Permit systems

The scope of the permit system, defining which activities need to be so covered and which do not, should generally be agreed between the laboratory superintendent and the rig supervisor.

The activities which require permits and the parties responsible for issuing and receiving them should be listed in the general laboratory instructions or the rig instructions.

Hazardous activities such as maintenance and vessel entry should be covered by a permit system. The principles are similar to those for an industrial plant as described in Chapter 21 .

One of these principles is formal handover from operations to maintenance personnel and then handback in the reverse direction. In a laboratory these responsibilities may sometimes be less clear than in a plant and, as just stated, they need therefore to be clearly defined. The effectiveness of the permit system depends on formal observance of such handovers.

A9.10.10 Housekeeping

There should be a high standard of housekeeping. Facilities should be provided for disposal of broken glass and of waste materials. Equipment not in use should be removed or arranged tidily. Spillages should be cleaned up at once. Orderly sample storage with minimal retention should be maintained; glassware/equipment cleaning should be carried out.

A9.10.11 Out-of-hours working

Personnel working out of normal work hours should be required to sign in and sign out.

Working alone in the laboratory should be permitted only where the hazard is low and is best kept to a minimum. Anyone who does work alone should be in contact with, or should be visited by, the security guard at regular intervals.

A9.10.12 Unattended operation

Unattended operation of equipment may present a hazard, especially if flammable or toxic materials are involved. There will be some experiments where such operation is not permissible. When unattended operation is practiced, arrangements should be made for the apparatus to be visited by a trained security guard, who should be given full instructions on the action to be taken in case of accident or doubt and should be able to make telephone contact with the experimenter.

A9.10.13 Access

Access to the laboratory should be subject to control and unauthorized persons should be excluded. The extent of the measures necessary depends on the nature of the hazards and the confidentiality of the work.

A9.11 Laboratory Fire and Explosion Protection

A9.11.1 Fire protection

The laboratory should be designed for fire protection, in accordance with building and fire protection codes and with advice from the fire authorities.

Some basic elements of design for fire protection include the fire resistance of the laboratory envelope, including doors; internal layout; hazardous area classification; mechanical ventilation and a fire alarm system.

It is desirable that there be constructional features with a minimum fire resistance between the laboratory and any adjoining section of the building and that the doors meet a fire resistant standard. Measures should be taken to prevent fire spread through openings in walls and voids in the roof.

It should be a principal aim of the laboratory layout to minimize both the occurrence and escalation of fire.

Hazardous area classification should be applied to effect control of ignition sources. It is suggested in the IChemE *Guide* that for a well-ventilated laboratory classification as Zone 2 should be sufficient. The guide states that ideally the whole space should be so classified, but if this is not practical, the Zone 2 should extend at least 2 m around any potential leak source.

The risk of buildup of a flammable atmosphere may be minimized by the use of mechanical ventilation. The guide recommends that where flammable liquids are in use, the ventilation fan should be operated for the period of use and for 5 min thereafter. (Use of a flammable storage cabinet may be appropriate. Also, labs with fire risk may need to require workers/visitors to use Flame Retardant Clothing.)

There should be a fire alarm system with alarm points inside the exits and at other strategic points.

A9.11.2 Fire fighting

The laboratory should be equipped with suitable fire extinguishers, fire blankets, etc. An account of fire extinguishers in general is given in Chapter 16 and in the laboratory context in the IChemE *Guide*.

A9.11.3 Explosion protection

Where there is to be operation of equipment such as an experimental reactor with a significant risk of vessel rupture, a separate cubicle should be provided in which the work can be conducted. Such arrangements are perhaps more commonly found in pilot plants, but may find place in a laboratory.

The cubicle should be designed to contain both blast and missiles. Accounts of such explosion-proof cells are given in Chapter 17 and Appendix 10.

A9.12 Emergency Planning

Emergency planning should be undertaken to identify the potential causes and types of emergencies and their consequences, and the countermeasures required. The principles are similar to those outlined in Chapter 24.

Planning should cover not only the laboratory and the rigs but also storages and services. The plan should be formulated by conducting audits during design and at commissioning and should be updated by audits at regular intervals thereafter.

The purposes of emergency planning are to protect life and property. They are achieved by early recognition of the problem, rapid raising of the alarm and prompt action to bring the incident under control and to separate the people from the hazard.

Functions which need to be performed in an emergency are to deal with the emergency, to evacuate people and to liaise with the emergency services. The personnel who will perform these functions should be identified and their tasks defined.

The range of situations in laboratories tends to be particularly wide and the emergency plan should aim for flexibility.

Laboratory personnel responsible for emergency response should understand the statutory duties and likely priorities and needs of the external services.

There are certain typical problems faced by the external fire services coming into laboratory situations. Steps

should be taken to find out what information the fire brigade is likely to need and to ensure as far as is practical that it can be provided. This means having the information available and appointing someone to communicate it in the actual event. Frequently fire brigades are hampered by hazards from gas cylinders and radioactive materials and by lack of information on the chemicals present and their hazards.

There should be regular fire drills, including joint exercises with the external services.

A detailed account of laboratory emergency planning is given in the IChemE *Guide*.

Appendix 10 Pilot Plants

Contents

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A10.7 Pilot Plant Programmes A10/7

Pilot plants are intermediate in scale between the laboratory bench and the full-scale plant. They are used for a variety of purposes, essentially to obtain information on process design and operation and on products, including information relevant to safety. Some hazards are liable to show up first at the pilot plant stage and the pilot plant is therefore an important tool for hazard identification, as described in Chapter 8. Here consideration is given to the more general aspects of pilot plants and particularly to their characteristic features and hazards, and to safety in pilot plants.

Accounts of pilot plants are given in *Pilot Plants, Models and Scale-Up Methods in Chemical Engineering* by Johnstone and Thring (1957), *The Chemical Plant from Process Selection to Commercial Operation* by Landau (1967), *Chemical Process Development* by D.G. Jordan (1968) and *Pilot Plant Design, Construction and Operation* by Palluzzi (1992) and by Constan (1984), Carr (1988), Dore (1988), Palluzzi (1989, 1990, 1991), Lesins and Moritz (1991), J. Jones *et al.* (1993a,b) and Lo and Oakes (1993). Safety is treated in the *Pilot Plant Safety Manual* by the AIChE (1972/33) and by Kohlbrand (1985), Siminski (1987), Carr (1988), Dore (1988), Capraro and Strickland (1989), Carson and Mumford (1989 LPB 89, 90), Constan, Herman and Moeller (1992) and Palluzzi (1992).

A number of authors on pilot plants give checklists, often as tables. These checklists include the following: justification for use (J. Jones *et al.,* 1993b); overall programme (Lesins and Moritz, 1991; J. Jones *et al.,* 1993a); chemical and process information (Dore, 1988); scale-up issues (Lo and Oakes, 1993); project review (J. Jones *et al.,* 1993a); flowsheet review (Lesins and Moritz, 1991); hazards (Dore, 1988); hazard identification—what-if review (Lesins and Moritz, 1991); plant construction (Dore, 1988); staffing requirements (J. Jones *et al.,* 1993a); operating and safety aspects (Dore, 1988); operating manual (J. Jones *et al.,* 1993a); operator training manual (Chaty, 1985) and computer control systems (J. Jones *et al.,* 1993a). Many of the entries in the AIChE *Pilot Plant Safety Manual* may be used as checklists for pilot plant safety.

In general, the principles of laboratory safety, discussed in Appendix 9, are applicable to pilot plants also.

Selected references on pilot plants are given in Table A10.1.

Table A10.1 *Selected references on pilot plants*

Michel, Beattie and Goodgame (1954); Johnstone and Thring (1957); E.L. Clark (1958); Lengeman and Hardison (1964); Gernand (1965); Hudson (1967); Landau (1967); Ellis (1968); D.G. Jordan (1968); Anon. (1969a); IChemE (1969/47); Conn (1971); AIChE (1972/68); Katell (1973); Roche *et al.* (1977); Shields and Vander Klay (1977); Braun (1978); Berty (1979); Randhava, Lo and Kronseder (1982); Kunesh and Hollenack (1983); Constan (1984); J.L. Jones (1984); Margolin (1984); Pfeffer, Bhalla and Dope (1984); Chaty (1985); Lowenstein (1985); P. Dawson (1986); Palluzzi (1987, 1990, 1991, 1992); S.G. Phillips (1990); Ginkel and Olander (1991); Lesins and Moritz (1991); Pollack (1991); Uitenham and Munjal (1991); Jones *et al.* (1993a,b); Lo and Oakes (1993)

Safety in pilot plants

A.R. Jones and Hopkins (1966); Deviny (1967); Graf (1967); Marinak (1967); Prugh (1967); Klaassen (1971); Ligi (1964, 1973); Bait and Berg (1974); Weissbach (1976); Roche *et al.* (1977); Lowenstein (1979); Franko-Filipasic and Michaelson (1984); Kohlbrand (1985); Basta (1986b); Siminski (1987); Carr (1988); Dore (1988); Capraro and Strickland (1989); Carson and Mumford (1989 LPB 89, 90); Bond, Carson and Mumford (1990 LPB 93); Constan, Herman and Moeller (1992)

High-pressure pilot plants

E.L. Clark (1963); W.G. High (1967); AIChE (1972/65); B.C. Cox and Saville (1975); Jercinovic (1984); Mehne (1984)

A10.1 Pilot Plant Uses, Types and Strategies

A10.1.1 Uses of pilot plants

The purposes for which pilot plants are built are the development of (1) a new product, (2) a new process or (3) an existing process. For a new product small quantities may be required for testing and for market development. For a new process information is required to prove feasibility, specify operating conditions, resolve scale-up issues, provide design data, identify problems, develop operating procedures and provide experience and training. For an existing process work may be required to check the suitability of different raw materials, improve product quality, explore modified operating conditions, improve the treatment of the effluents and effect cost reductions and other optimizations.

Frequently it is information on reaction kinetics and yield which is lacking and which the pilot plant is required to provide. Other information typically obtained from a pilot plant is data on heat and mass transfer and pressure drops; on mixing effects; on impurities, foams and emulsions; and on fouling and corrosion.

The justification for pilot plants is discussed by J. Jones *et al.* (1993a). They discuss the following situations, in increasing order of difficulty:

Process	*Product*	*Customer*
New	Existing	Existing
New	New	Existing
New	New	New

A10.1.2 Types of pilot plant

Pilot plants differ in both type and scale. There are three principal types: (1) the general-purpose pilot plant; (2) the specific-purpose pilot plant; and (3) the multi-purpose pilot plant. The merits of these different types of pilot plant are discussed by Palluzzi (1991, 1992).

Representative capacities for different scales of operation are given by J. Jones *et al.* (1993b) as follows:

Scale	*Capacity*	
	Batch	*Continuous*
Laboratory bench	0.1–1000 g	10–100 g/h
Mini-pilot plant	1–100 kg	0.1–10 kg/h
Pilot plant	100–1000 kg	10–100 kg/h
Semi-works	1000–10,000 kg	100–1000 kg/h

Some pilot plants currently in use are quite old and over the years have been modified and adapted.

Accounts of particular pilot plants include those of Chaty (1985), P. Dawson (1986), Siminski (1987), Carr (1988), Capraro and Strickland (1989) and Lesin and Moritz (1991).

A10.1.3 Strategies for development utilizing pilot plants

It need not be assumed that a pilot plant necessarily has to be designed and located in-house; there are other options. The main options are (1) design and location in-house; (2) location in-house but with design by a design contractor; (3) hiring of outside pilot plant facilities and (4) contracting out of the pilot plant work. The merits of these options are discussed by Palluzzi (1991).

A10.2 Pilot Plant Features and Hazards

While the hazards encountered on pilot plants are essentially similar to those on full-scale plants, the characteristics of pilot plants are such that the hazard profile is somewhat different. The specific features and hazards of pilot plants are discussed by a number of authors, including Carr (1988) and Capraro and Strickland (1989).

Some features characteristic of pilot plants include (1) gaps in knowledge; (2) novelty of chemicals, process, equipment and operations; (3) scale effects; (4) extent of manual activities; (5) frequency of modification; (6) multiplicity of tasks; (7) materials storage and transfer; (8) flow features; (9) recycles; (10) utilities features; (11) frangible elements; (12) plant layout features; (13) location in a building and (14) research staff involvement.

The process reaction may involve a number of potential hazards. Most frequently mentioned is the unidentified reaction exotherm, which could lead to a reaction runaway. There should be a formal system of screening to identify any exotherms. However, this is by no means the only hazard which may be present. The raw materials may contain impurities. The ratio and flow rate of the reactants may vary. There may be inhomogeneities due to poor mixing which affect reaction rate and temperature measurement. Features of the reaction such as induction time may assume greater significance. The handling of the catalyst may pose problems.

There are a number of equipment problems which can occur on pilot plants. One is the use of unfamiliar equipment. Another is the reactivation of idled equipment. When this is in prospect, a check on the integrity of the equipment is advisable; it may have been 'cannibalized'. Another problem can be the use of equipment which differs from that used on the full scale and for which, in consequence, operating procedures may be deficient. An example is an oven used by a number of different users with no formal control over its contents and settings.

A principal reason for building a pilot plant is to fill the gaps in the information necessary for the design and operation of the full-scale plant. This implies that there will be gaps also in the information which ideally would be available for the design of the pilot plant.

A pilot plant is on a scale intermediate between those of the laboratory and of the full-size plant. Relative to the laboratory, the larger scale of the pilot plant means that hazards may become apparent which were obscured at the laboratory scale. Operation on the laboratory scale has some of the features of an inherently safer design. The most obvious is the limited inventory, but there are also others such as good ventilation. In some cases the problem may be that the change in scale is accompanied by other changes, such as the use of less pure raw materials. In others it may simply be that features always present become more obvious with scale such as the need to dispose of noxious effluents. Moreover, the pilot plant is the stage at which the process is first carried out in process plant as opposed to laboratory equipment and thus the stage at which difficulties of processing, of equipment or of measurement will show up.

Relative to the full-scale plant, the smaller scale of the pilot plant is beneficial in reducing the scale of the hazard, but can lead to problems of flow control, blockage and so on.

The balance between manual and automatic functions tends to be different in a pilot plant from that on the full scale. There are several reasons for this. Foremost reasons are economics and flexibility; others include factors such as measurement problems.

It is a normal, and expected, feature of pilot plant operation that both the process and the plant are subject to frequent modification. A system for the control and documentation of modifications of both types is required, both as a record of the learning process and to assure safety.

Work in a pilot plant is liable to involve tasks which are more numerous, varied and novel features, which can increase the probability of error.

The problems of containers for materials and the identification of the materials and containers can be a significant problem in pilot plants. The number of materials used may be appreciable, creating much greater scope for error than on a regular plant. It is necessary, therefore, that raw materials, intermediates, products and effluents be fully identified. Where common containers are used, as sometimes with effluents, controls need to be established to prevent mixing of incompatible materials.

Flow problems associated with features such as highly viscous fluids, gas locks, lutes, siphons, water hammer, cavitation and so on are features commonly encountered on process plants, but it is on the pilot plant that they may be first experienced and will have to be solved.

Another feature which may well be novel at the pilot stage is recycling with its characteristic problems of positive feedback and build-up of impurities.

Some pilot plants, particularly the larger ones, are on a works site and are served by the works utilities. It is normal practice to give advance warning to the main production plants of an expected change in the status of such utilities, but the Cinderella status of the pilot plant may result in its being overlooked, and suffering unexpected loss of a utility.

Frangible pipework and vessels made of glass or plastic and other features, such as rotameters and sightglasses are common in pilot plants, and make the plant more vulnerable to damage and leaks.

Plant layout in pilot plants tends to be more congested. Such congestion can increase the risk of damage to plant or inadvertent movement of controls. An example of the latter is movement of a control such as a valve as an operator brushes against it. This danger is increased by the fact that the valve is much lighter and more readily moved than its equivalent on the full scale. Similar points apply to damage to plant, which is more vulnerable on the small scale.

In contrast to most large-scale plants, which are in the open, many pilot plants are in buildings, and this has a number of implications. There is often a more congested layout. There is an increased hazard from accumulation of gases or vapours. These may be flammable or toxic vapours, whether from open vessels or from leaks and spillages. Or they may be asphyxiant gas, such as nitrogen, or flammability-enhancing gas, such as oxygen. Likewise, there may be occupational hygiene problems because fugitive emissions disperse less readily.

Research staff involved in pilot plant work are likely to be less attuned than those familiar with plant operation to the disciplines necessary, and specific steps may need to be taken to rectify this.

A10.3 Pilot Plant Scale-up

Historically, a basic reason for the use of a pilot plant has been the difficulty of scaling up from the laboratory bench to the full scale. To a considerable extent, such scale-up is what chemical engineering is all about, and progress in the discipline has made this reason seem rather less cogent.

Despite this, operation on the pilot scale may still be desirable even in respect of fundamental features such as reactor heat transfer, mixing, runaway and venting.

However, even in terms of scale-up, there is more to pilot plant operation than the scale effects typically expressed in terms of dimensionless numbers and engineering models. As already indicated, there are other effects of scaling up such as the use of less pure raw materials; the occurrence of poor mixing; the build-up of impurities due to recycling; the need to dispose of noxious effluents; and so on.

The process of scale-up is frequently envisaged as a linear one, progressing to successively larger scales. An alternative model, however, is one in which the process is iterative, passing to and fro between the smaller and large scales.

The pilot plant stage is the first at which the process is operated in the form of a plant. It therefore provides the first opportunity to examine all those features which are new in passing from laboratory bench to plant. This is so whether the pilot plant is small or large.

A10.4 Pilot Plant Design

There are a number of features which are characteristic of, or tend to bulk large in, the design of pilot plants. Some of these are now considered.

A10.4.1 Some design objectives

The pilot plant should be utilized to design the full-scale plant using recognized engineering methods of scale-up.

The design should accommodate a sufficiently wide range of operating variables, such as pressure and temperature, to allow the effect of these variables to be determined with some confidence.

The purpose of the pilot plant is to provide information for the design of the full-scale plant. The plant should be designed and operated so as to yield information in which confidence can be placed and which is conformable to established design methods. As far as practicable, the process should be modelled and the experimental results compared with the model as they are obtained. Important features of such a model are the mass and heat balance and pressure drop relations, the reaction kinetics and the unit operations models.

A10.4.2 Design standards and codes

A particular problem in pilot plant design is the application of standards and codes. In general, these are formulated with full-scale plant in mind, and can sometimes pose difficulties for the pilot plant designer.

The standards to be applied should be declared at an early stage and any potential conflict identified, whether between different standards or between a standard and the design.

The application of standards to pilot plants is discussed by Siminski (1987), who describes the particular case of the standards covering an engine test facility. The approach which he describes is to assess the impact of standards on the safety, industrial hygiene and environmental aspects of the plant, to assess the risks and develop alternative strategies, to seek independent review and to test design concepts early on, to examine the specification to check whether features causing conflict with standards are strictly necessary, and to negotiate with the parties to achieve solutions.

A10.4.3 Flexibility and multiple use

Since the purpose of a pilot plant is to extend knowledge and deal with novel issues, it needs to be flexible. Methods of providing such flexibility are discussed by P. Dawson (1986). They include the provision of inherently flexible equipment, a range of equipments and materials of construction and a layout which groups together items which most frequently need to be connected, thus avoiding long pipe runs.

A10.4.4 Plant layout

The basic principles of plant layout apply to pilot plants also, but some features assume particular importance.

One feature just mentioned is layout to minimize the length of pipework and to ensure a convenient arrangement of principal items of equipment.

Another feature is to ensure good access, which includes both access to items of equipment but also minimization of the likelihood of inadvertent damage to plant or operation of controls as personnel move about congested passages. Closely related is minimization of damage by dropped objects.

Another feature is clear identification of equipment. One aspect is the labelling of tanks and vessels holding process materials, since misidentification of materials is an error characteristic of pilot plant operation. Another aspect is labelling and coding of equipment which may need to be worked on and which may contain noxious materials.

Another feature is provision for collecting and disposing of liquid leaks.

A fifth feature is the provision of protective barricades against missiles. In some cases this leads to a design in which the pilot plant space is divided up into separate cells.

A10.4.5 Protective barricades

If the process carried out involves high pressures, and particularly high-pressure reactions, protective barricades may be provided.

Some practical aspects of barricades are discussed by Carr, who describes methods of protection against missiles

such as valve stems and reactor fragments, as well as high-pressure steam jets, which can be almost as damaging.

Missiles from an exploding reactor may be stopped by a barricade in the form of a sand bath protected by a pressure relief valve. This reduces the need to house the whole plant in a barricade.

For barricade design in general, design case missiles are specified and the barricade is designed to withstand these missiles, using methods such as those outlined in Chapter 17. It is on pilot plants that the provision of such barricades is most common, and thus where most of the expertise resides.

A10.4.6 Pressure systems

The combination of the facts that a pilot plant is usually in a building and that it is subject to continuous experimentation and modification means that it is necessary to give particular attention to the integrity of the pressure system. Procedures should be laid down for the proof testing and leak testing of the plant.

A10.4.7 Pressure relief

It is common practice in pilot plants to put a safety valve on a vessel. The lines to and from such valves tend to be small diameter and liable to fill with liquid which then solidifies. Countermeasures include design of lines so that the liquid drains away and use of heated lines.

A10.4.8 Frangible elements

Pilot plants are frequently constructed in part or in whole in glass or plastic. They also tend to contain vulnerable features such as rotameters and sightglasses.

The protection of the latter devices is described by Carr. Use is made of protective shields with adequate pressure-relief space between the shield and the device. Specific designs have been developed and tested for most types of device used.

A10.4.9 Gas cylinders

Another hazard discussed by Carr is gas cylinders. Rupture of a line supplied by a high pressure cylinder can result in a large jet of gas. He describes arrangements involving the use of a limiting orifice just downstream of the regulator.

A10.4.10 Ignition source control

Another aspect of the design is the control of ignition sources. The importance of this is enhanced in a pilot plant by the facts that the probability of a leak tends to be higher, that in a building gas or vapour accumulates more readily and that the probability of personnel being present is relatively high.

Since it is necessary to exclude all ignition sources, the proper approach is to make a formal examination of the plant to identify possible sources of release. These sources include activities, both operations and maintenance, as well as fixed plant. Such ignition hazard identification provides a basis for the design both of layout and equipment and of operating controls.

The application of the methods of hazardous area classification is one necessary aspect of this. The principal options are classification as Zone 1 or as Zone 2. Classification as Zone 1 puts constraints on the equipment, particularly instrumentation, which can be used, while classification as Zone 2 requires the elimination of leaks and a good level of ventilation.

An account of practical measures for an area classified as Class 1, Division 2, in the US system is given by Carr.

Other features typically include liquid catchment and disposal arrangements, gas detectors and mechanical ventilation.

Multipurpose plant places particularly severe requirements on ignition control.

These hardware measures need to be complemented by a system of operational controls to eliminate ignition sources. Failure to do this largely negates the value of the hardware.

A10.4.11 Plant classification

A systematic approach to the design of pilot plants is to use a formal method of classification.

Carr describes the method which is used in one company for classifying pilot plants for the purposes of design and operation and of personnel protection and which utilizes four operating categories:

Category	*Hazard potential*
1. Detonation reactions	High potential for detonation or massive rupture and large, extremely rapid release
2. Rupture and fires	High potential for large rupture and large fire
3. Leaks and small fires	Low potential for leaks and, at worst, only leaks and fires of limited size
4. Low hazard operations	Near ambient temperatures and low pressures with very low potential for either ruptures or fires

The corresponding protection requirements are given in Table A10.2.

A10.4.12 Extent of automation and protective systems

The operations to be performed on a pilot plant are on a small scale and are required for a limited period, relative to the equivalent operations on the full-scale plant. Further, their automation may well require the development of measuring instrumentation. Hence it will generally not be appropriate to seek to automate these operations to the extent that will pertain on the full-scale plant.

Somewhat similar considerations apply to the provision of protective systems such as trips and interlocks. These definitely have their place in pilot as in full-scale plants, but the particular mix appropriate to the full scale may not suit the pilot scale.

A10.4.13 Control systems

The pilot plant should be provided with instrumentation sufficient not only to obtain design data but to ensure safety. The same principles should be applied as to the design of full-scale plant, such as the use of trips and interlocks, subject to the comments made above on the extent of automation and of protective systems.

The use of computers, mainly PCs, for data acquisition and control of experiments is routine in pilot plants. In some cases the flexibility of such computers has also been exploited to provide alarms and trips.

Table A10.2 *Protection requirements scheme for pilot plants (after Carr, 1988) (Courtesy of the American Institute of Chemical Engineers)*

Typical hazard	*Category 1 Detonating reactions*		*Category 2 Rupture and fire hazards*		*Category 3 Leaks and small fires*		*Category 4 Low hazards*	
	Hazard potential	*Protection device*	*Hazard potential*	*Protection device*	*Hazard potential*	*Protection device*	*Hazard potential*	*Protection device*
Detonation (internal)	High	Barricade Blast relief	Negligible		Negligible		Negligible	
Shrapnel	High	Barricade Shrapnel stop	Negligible		Negligible		Negligible	
Explosive atm. (external)	High	Barricade Blast relief Ventilation Min. cubicle size	Moderate	Baffle Ventilation Cubicle size	Nelgligible		Negligible	
Fire	High	Baffle	High	Baffle	Moderate	Baffle	Negligible	
Pressure leaks	Possible	Baffle (barricade)	Possible	Baffle	Possible	Baffle	Negligible	
Skin toxic	Possible	Baffle (barricade)	Possible	Baffle	Possible	Baffle	Possible	Baffle
Lung toxic	Possible	Ventilation	Possible	Ventilation	Possible	Ventilation	Possible	Ventilation
Permitted access to operating areas		Exculded		Limited		Limited		Unlimited
Summary of protective devices		Barricade Blast relief Shrapnel stop Ventilation Min. cubicle size		Baffle Ventilation Cubicle size		Baffle Ventilation Required if: lung toxic chemicals		Baffle required if: skin toxic chemicals or adjacent operations (see baffle design) Ventilation required if: lung toxic chemicals

Control schemes for pilot plants are discussed by Uitenham and Munjal (1991) and Palluzzi (1992).

The effectiveness of any protective systems depends on the training of the operators.

A10.4.14 High-pressure plants

Some pilot plants involve high-pressure equipment. The AIChE *Pilot Plant Safety Manual* contains sections on the design of pilot plants for high-pressure and for high-temperature operation. For the former further guidance is given in the *High Pressure Safety Code* by E.G. Cox and Savffle (1975) and by E.L. Clark (1963), W.G. High (1967), Jercinovic (1984) and Mehne (1984).

At the pilot plant scale it is quite common to provide blast-proof cubicles and barricades against missiles, which tend to be impractical on the full-scale plant.

A10.5 Pilot Plant Operation

A10.5.1 Suitability of plant

If the pilot plant is a multipurpose one and is thus used to investigate a number of different processes, a particularly careful check should be made that it is fully suitable for the proposed process.

A10.5.2 Personnel and training

The magnitude of the hazard on a pilot plant is less than on the full scale, but in other respects the operations tend to be more demanding. The materials, the process, the equipment, the plant and the procedures are all relatively unfamiliar. The operating team needs strong leadership and experienced personnel.

As with plant operation generally, training is critical. Many of the topics mentioned in this appendix imply the need for training.

Training is required for management and research personnel also. The latter may well be used to laboratory rather than plant situations, and need to become familiar with plant disciplines.

A10.5.3 Operating and emergency procedures

The operations to be performed should be identified and for each a suitable operating procedure should be developed, and examined from the safety viewpoint. Operations which are likely to bulk large in pilot plant work include manual operations, reactor operations, sampling and measurement activities. There also needs to be suitable emergency procedures.

A10.5.4 Specifications and documentation

Despite the small scale, it is desirable to adhere to a certain formality in pilot plant operation. Some aspects of this are discussed by J. Jones *et al.* (1993a).

There should be formal specification for the raw materials, intermediate and products, for yield and throughput, for cost targets and for the completion date.

Records should be kept of the progress of the project during the pilot plant stage, of problems and hazards encountered, and of the steps taken to solve the problems and to eliminate or control the hazards.

The data needed for the design of the full-scale plant should be documented and the information gathered and recorded.

The operating procedures evolved, including the emergency procedures should be properly documented. Again, this should include any problems and hazards encountered and the response made.

A10.5.5 Mothballing

By its nature a pilot plant is liable to be subject to intermittent operation, with periods when it is not in use. Often a pilot plant is shut-down and 'mothballed' for an extended period. If this is a possibility, it should be taken into account in the design. At the start of such a shut-down measures should be taken to prevent deterioration, including cleaning and flushing of the plant. On recommissioning care should be taken to identify hazards which may arise from the prolonged shut-down.

A10.6 Pilot Plant Safety

An accident in a pilot plant, like one in a laboratory, is generally on a much smaller scale than one on a full-scale plant, but again it can give rise to considerable direct and consequential loss.

Safety in pilot plants is treated in the AIChE *Pilot Plant Safety Manual*. This deals with procedures, including transfer of information from the chemist, hazard identification, process design, mechanical design and design review; scale-up from pilot to full scale; engineering standards for flammable, explosive, corrosive and toxic materials and for radiation protection; maintenance procedures; and high-pressure and high-temperature processes.

In general, the same approach should be taken to the design and operation of a pilot plant as is adopted for a full-scale plant. Many of the topics already discussed are equally relevant to pilot plants, including management and management systems (Chapter 6), hazard identification (Chapter 8), reactive hazards (Chapter 3), process, pressure system and control system design (Chapters 11–13), fire, explosion and toxic release (Chapters 16–18), plant operation and maintenance (Chapters 20 and 21), personal safety (Chapter 25) and safety systems (Chapter 28). On the other hand there are certain features which are characteristic of pilot plants.

A10.6.1 Project safety reviews

There should be a system of project safety reviews adapted to pilot plant design and operation. These should be the subject of a formal requirement and should be documented.

The general methods of hazard identification should be used to discover potential hazards in plant design and operation. In addition, there are hazard identification procedures which are particularly relevant to pilot plants.

The information on the chemicals handled, the reactions involved, and the materials of construction for the plant should be as complete and as well documented as practical.

The transfer of information from the chemist to the engineer should be regulated by formal procedures. The chemist should give a full description of the process, including the reaction kinetics and heats of reaction, limits of operating parameters such as pressure and temperature, and procedures and precautions adopted. The engineer should study the research reports to envision problems which may arise in scale-up to the pilot plant.

The process reaction(s) should be screened to identify any reaction exotherm which might lead to a runaway reaction as described in Chapter 33.

A10.7 Pilot Plant Programmes

Accounts of pilot plant programmes emphasize a number of themes. They include keeping attention focused on the basic chemistry; keeping the programme simple, first

establishing feasibility, before getting involved in matters such as yield, effluents, etc., applying lateral thinking and seeking alternative approaches; being prepared to take the calculated risk that the process may not work, although taking no risks with safety; and making use of expert advice from other sources.

A10.7.1 Handover and decommissioning

The pilot plant operation must recognize the point at which the baton should be handed over to the next stage. However, it is advisable not to be in too much of a hurry to decommission a pilot plant. The purpose of the plant is to provide information and/or products to other users. Once they have received these, they too will have to undergo a learning process, and are likely to come back with queries, some of which may require further plant trials. This is true particularly with new products, where the queries may be directed to improving quality or reducing cost and meeting regulatory requirements and environmental restraints.

Appendix 11

Safety, Health and the Environment

Contents

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Although the problems of environmental protection (EP) are basically beyond the scope of this book, they cannot be completely neglected, because there are a number of ways in which they are closely linked to safety and loss prevention (SLP).

Selected references on the environment and pollution are given in Table A11.1.

Safety, Health and the Environment

These links are recognized in the common practice of coupling health, safety and environment (HSE) or safety, health and environment (SHE). In the following the latter acronym is preferred, the former already having an established meaning.

A11.1 Common Responsibilities

A11.1.1 Professional responsibilities

The professional engineer has responsibilities both for safety and for environmental matters, which are very similar in nature.

These responsibilities are outlined in the Engineering Council codes *A Code of Professional Practice on Risk Issues (1992) and A Code of Professional Practice on Engineers and the Environment* (1993) described in Chapter 3.

A11.1.2 Legislation

The detailed legislative requirements for safety and environment naturally vary between countries but the worldwide trend is clear. It is towards higher standards both inside and outside the factory; more formal management systems for identification, assessment and control; inherently safer/cleaner designs; and greater legislative and public pressures.

Legislation is described in Sections A11.4–A11.6.

A11.1.3 Professional education

The education of professional engineers should provide a firm grounding in both safety and environmental matters, creating awareness, instilling responsibility and introducing the appropriate engineering approaches.

A11.1.4 Job descriptions

Safety and environmental issues have both grown progressively in importance for industry and government at all levels. In industry there has been an increasing tendency for job titles and descriptions to assign responsibilities which cover both safety and environment.

A11.2 Common Elements

A11.2.1 Economic factors

Both SLP and EP have a fundamental influence on the design of the plant. Each imposes constraints which may well be decisive in the economics of the design.

A poor design is more likely to require the addition of numerous protective devices and the installation of much pollution control equipment and to involve more last-minute modifications to meet legislative and other safety and environmental standards.

A11.2.2 Inherently safer/cleaner design

The concept of inherently safer design, discussed in Chapter 11 and Chapter 32, has its counterpart in that of inherently cleaner design, or, more broadly, waste minimization.

Table A11.1 *Selected references on pollution, effluents and waste disposal*

Chementator (Table A1.4); EPA (n.d./l, 1988/2); MCA (SG-9, n.d./ll); RCEP (Appendix 28); Mohlman (1950); Brady (1959); Cross (1962); Carson (1963); Byrd (1968); Chem. Engng (1968–); Chieffo and McLean (1968a,b); Marshal (1968); AIChE (1969–/120–126); Bond and Straub (1972, 1973); Cecil (1972); Levine (1972b); Nilsen (1972b); Prober (1972–); Racine (1972); Ripley (1972); S.S. Ross and White (1972); G.F. Bennett (1973); DoE (1973 Poll. Pap. 4, 1974 Poll. Pap. 1, 1976 Poll. Pap. 9); R.D. Fox (1973); Vervalin (1973b,c, 1979); Mabey (1974); McKnight, Marstrand and Sinclair (1974); Napier (1974a); Rudolph (1974); Sax (1974); Strahler and Strahler (1974); Jaffe and Walters (IChemE 1975/60); Roulier, Landreth and Carnes (1975); Singer (1975); Yamaguchi (1975); Boyd and Leotta (1976); CONCAWE (1976 6/76, 1977 2/77, 1979 5/79); R.W. James (1976); Warner (1976, 1979); Anon. (1977f); Allaby (1977); Ashby (1977, 1979); E.B. Harrison (1977); Hillman (1977); Holum (1977); P. Sutton (1977b); Boyd (1978); G. Parkinson (1978, 1980, 1987); Pier *et al.* (1978); Pocock and Docherty (1978); Ricci (1978c); Schneiderman (1978); Bridgwater and Mumford (1979); Golden *et al.* (1979); Harwell (1979); Baasel, Mcallister and Kingsbury (1980); Bakshi and Naveh (1980); Dix (1980); Eggington (1980); Moss (1980); Anon. (1981i); Kletz (1981J, 1993e, 1994 LPB 110); Portman and Norton (1981); Bennett, Feates and Wilder (1982); Trewhitt (1982); API (1983/7); ASME (1983/194); R.M. Harrison (1983); Macrory (1983); Train (1983); Barnes, Forster and Hrudey (1984–); D. Clarke (1984); Jalees (1985); Neely and Blau (1985); Pitt and Pitt (1985); D. Williams (1985); APCA (1986); Hollowood (1986); Vervalin (1986a); Anon. (1987i); Anon. (1988e); C. Butcher (1989c); CIA (1989 CE23, 1991 BT23); Hoover *et al.* (1989); Penkett (1989); Veselind, Peirce and Weiner (1990); IBC (1991/82–84); Jackman and Powell (1991); Shillito (1991); Anon. (1992 LPB 108); Diepolder (1992); Goldsmith (1992a); Parfitt and Andreasen (1992); Reid (1992); Wainwright (1992); Anon. (1993a,f); API (1993 Publ. 311, 317); Doerr (1993); Englehardt (1993); Hydrocarbon Processing (1993b); Karrh (1993); Anon. (1994 LPB 120, p. 13); Agra Europe (1994a); Debeil and Myren (1994 LPB 119); Shillito (1994 IChemE/110)
BS 7750: 1992

Waste minimization, inherently cleaner design
Mencher (1967); Kohn (1978b); Duffy (1983); Tavlarides (1985); Goodfellow and Berry (1986); Koenigsberger (1986); EPA (1987b, 1988, 1989a,b); Gardner and Huisingh (1987); ACGIH (1989/34); CIA (1989 CE1, 1990 CE2); Higgins (1989); Redman (1989c); H.M. Freeman (1990); Hethcoat (1990); Hunter and Benforado (1990); API (1991 Publ. 302); Berglund and Lawson (1991); R. Smith and Petela (1991–); Crittenden and Kolaczkowski (1992); Curran (1992); IBC (1992/88); Chadha and Parmele (1993); IChemE (1993/106, 1994/111); Rossiter, Spriggs and Klee (1993)

AIChE Center for Waste Reduction Technologies
L.L. Ross (1991)

Pilot plants
Gundzik (1983); d'Aco, Campbell and Stone (1984); Pitt and Pitt (1985); Gurvitch and Lowenstein (1990)

Chemicals in the environment, inc. physical and chemical properties
ASTM (Appendix 28); Sax (1957); MCA (1966–/13, 14); CONCAWE (1970 9/70, 1971 9/71, 1985 5/85); Heck, Daines and Hindawi (1970); AIChE (1971/132, 1975/138, 1980/147); Walker (1971); A Tucker (1972); NAS (1975); Moein, Smith and Stewart (1976); Neeley (1976, 1980); Curtis, Copeland and Ward (1978); Mackenthun and Guarria (1978); SCI (1978); S.D. Lee and Mudd (1979); Tinsley (1979); Afghan and Mackay (1980); Alexander (1980); Blair (1980); Bungay, Dedrick and Matthews (1980); Freed (1980); Hanson (1980); Haque (1980a,b); Haque *et al.* (1980); Keith (1980); Khan (1980); Kimerle (1980); Lijinsky (1980); Mackay, Shiu and Sutherland (1980); Mill (1980); Murphy (1980); Riordan (1980); M.E. Stephenson (1980); Stern (1980); Weber *et al.* (1980); Zepp (1980); Jorgensen and Johnson (1981); N.J. King and Hinchcliffe (1981); Neely (1981); API (1982 Publ. 4434); P.R. Edwards, Campbell and Milne (1982); Kullenberg (1982); Versino and Ott (1982); Rowe (1983); Dragun, Kuffner and Schneiter (1984); Iyengar (1984); Jorgensen (1984); Okouchi and Sasaki (1984); Piver (1984); Greenland (1985); Neely and Blau (1985); CEFIC Workshop (1986); Donkin and Widdows (1986); Moriarty (1986); Coughtrey, Martin and Unsworth (1987); Ashworth *et al.* (1988); Valsaraj and Thibodeaux (1988); Pagna and Ottar (1989); Barton, Clark and Seeker (1990); Lyman, Reehl and Rosenblatt (1990); Manahan (1991, 1993); Wakoh and Hirona (1991); Brusseau (1992); Thoma *et al.* (1992); Gentile *et al.* (1993); Kollig, Kitchens and Hamrig (1993); Marple and Throop (1993); Larson and Weber (1994)
Environmental limit values, indices: Ott (1978); Sittig (1994)

Particular chemicals
Lead: WHO (EHC3); Bryce-Smith (1971, 1982); DoE (1974 Poll. Paper); Collingridge (1979); RCEP (1983 Rep. 9);
Mercury: Hartung and Dinman (1972); W.E. Smith and Smith (1975); *PCBs*: WHO (EHC2); EPA (1975a); Higuchi (1976); Willman, Blazevich and Snyder (1976); Stroud, Wilkerson and Smith (1978); Berry (1981); Anon. (1984a); Kokozska and Flood (1985); Motter (1991)
Dioxin, TCDD: Ayres (1981); Rice (1982); R.E. Tucker, Young and Gray (1983); Anon. (1984p); J.L Fox (1984b, 1985); Short *et al.* (1984); D. Williams (1984); Arienti *et al.* (1988)
Pesticides: WHO (EHC5, EHC9); Carson (1963); F. Graham (1970); C.A. Edwards (1974)
Nitrates: Nicolson (1979)

Pollution and human health
Howe (1970); Waldbott (1973); Chementator (1975 May 12, 40; Aug. 4, 38; 1977 Jan. 3, 36); Trevethick (1976); Lave and Siskin (1977a,b); Doll and McLean (1979); Moghissi *et al.* (1980); Bolten (1985); BMA (1991)

Environmental management, environmental risk management
Cecil (1969); Vervalin (1979); IBC (1981/10); APCA (1986); J.J. Stevens (1988); Kolluru (1991); Harwell, Cooper and Flaak (1992); Kraft (1992); Ormon and Isherwood (1992); Welsh (1992, 1993); S. Wilson (1992); Callahan and McCaw (1993); Turney (1993); Petts and Edjuljee (1994)
BS 7750: 1992
Environmental planning
D.C. Wilson (1981); Barclay (1987); DoE (1988 Circ. 15/88); Hassan (1993); Petts and Eduljee (1994)
Environmental hazard identification, assessment
Fuquay (1968); Friedl, Hiltz and Marshall (1973); EPA (1984d); Onishi *et al.* (1985); Keller and Lamb (1987); B.P. Smith (1987); NSW Govt (1989b); Paustenbach (1989); Cassidy (1990); Picciolo and Metzger (1992); Rouhianen (1992); IBC (1993/98); Petts and Eduljee (1994)
Safety versus environment
Anon. (1992 LPB 108, p. 0); Kletz (1994 LPB 116)
Environmental modelling
W.J. Farmer, Yang and Letey (1980); Burns, Cline and Lassiter (1982); Thibodeaux and Hwang (1982); EPA (1987); Batchelor (1990); Chhiber, Apostolakis and Okrent (1991); McBean (1993)
Environmental auditing
C. Butcher (1972b); Reiter, Sobel and Sullivan (1980); Baumer (1982); Keene (1982); Greeno (1984); D.L Russell (1985); Kingsbury (1994 LPB 118)
Environmental emergency planning
Cashman (1988); Cassidy (1990)

Environmental impact statements
Chementator (1972 May 1, 22; 1974 Apr. 1, 20); Science Applications Inc. (1974); Mueller (1974); Gratt and McGrath (1975a,b, 1976); Jimeson (1975); Dept of Interior (1976); Willis and Henebry (1976, 1982); Cremer and Warner (1977); Jain, Urban and Stacey (1980); Jain and Hutchings (1978); Prater (1978); ICI Australia Ltd (1979); Munn (1979); Atkins Res. and Dev. (1980); Passow (1980); Porter *et al.* (1980); Pizzi (1982); van Rest (1982); Petts and Edjuljee (1994)

EPA compliance, inspections
Hyland and Moore (1992); Hanisch, Hoffnagle and Walata (1993); Hohman, Sullivan and McNamee (1993)

Cost of pollution, pollution control
RCEP (Appendix 28); Eckenfelder (1969); Popper (1971); Chementator (1975 May 26, 58; Sep. 1, 52; 1977 Jan. 31, 55); E.P. Austin (1977); Isaac (1978); Marion (1978c); Martindale (1979); Vatavuk and Neveril (1980); Anon. (1991h)

Environmental analysis, monitoring
Ottmers *et al.* (1972); Nemerow (1974); Sittig (1974); McKee (1976); R.G. Thompson (1976); R.M. Harrison and Perry (1977); Cornish (1978a); R. Briggs (1980); Hinchcliffe (1980); Simpson (1980); Hwang and Koerner (1983); Weston (1984); McMorris and Gravley (1993)

Airborne effluents
HSE (Appendix 28 Best Practicable Means Lftls, Emission Test Methods); ASTM (STP 281); HM Chief Alkali Inspector (annual report); MCA (n.d./6–10); WHO (EHC4, EHC7); J.E. Pearson, Nonhebel and Ulander (1935); Hewson (1951); Magill, Holden and Ackley (1956); Dept of Health, Education and Welfare (1960); Lapple (1962); Stern (1962–); Yocom and Wheeler (1963); Hughson (1966); Squires (1967); Brewer (1968); Carlton-Jones and Schneider (1968); Chieffo and McLean (1968a,b); Imperato (1968); Meetham (1968); Munson (1968); Rossano and Cooper (1968); Scorer (1968, 1973); Sickles (1968); Fay and Hoult (1969); Constance (1970, 1972a); Ermenc (1970); Weismantel (1970); Anon. (1971a); AIChE (1971/132, 1972/133, 1974/136, 1975/139, 140, 1976/142, 1979/145, 1980/146, 147, 1981/149); Strauss (1971–, 1975); Anon. (1972a,e); CONCAWE (1972 14/72); Crowley (1972); Elkin and Constable (1972); Iya (1972); Morrow, Brief and Bartrand (1972a,b); Nonhebel (1972); S.S. Ross (1972a); R.S. Smith (1972); Swithenbank (1972); Teller (1972); ASME (1973/32); Cross and Schiff (1973); DoE (1973/2, 3, 1974/4); EPA (1973, 1978a);

IHVE (1973); Lazorko (1973); Peters (1973); Stern *et al.* (1973); Vandegrift, Shannon and Gorman (1973); Wiley (1973); Dorman (1974); Pfeifer (1974); Ring and Fox (1974); Driscoll (1975); Ecke and Dreyhaupt (1975); Marchello and Kelly (1975); Open Univ. (1975a); Parekh (1975); Rymarz and Klipstein (1975); Schneider *et al.* (1975a,b); Seinfeld (1975); Crawford (1976); Gammell (1976); O'Connell (1976); RCEP (1976 Rep. 5); Theodore and Buonicore (1976, 1982); API (1977 Waste Manual, vol. 2); M.L. Barker (1977); E. Briggs (1977); Bump (1977); S.K. Friedlander (1977); N. Kaplan and Maxwell (1977); Kohn (1977b); Lasater and Hopkins (1977); Lave and Siskin (1977a); Perry and Young (1977); Preussner and Broz (1977); R.D. Reed (1977); Ricci (1977b); Rosebrook (1977); Straitz (1977); Dunlap and Deland (1978); Freitag and Packbier (1978); A.F. Friedlander (1978); McCarthy (1978); NSCA (1978); A. Parker (1978); Parrish and Seidel (1978); Bochinski, Schoultz and Gideon (1979); Downey and Ni Uid (1979); Hesketh (1979); Parmele, O'Connell and Basdekis (1979); Stockham and Fochtman (1979); Storch (1979); D.P. Wallace (1979); Buonicore (1980); England, Heap and Pershing (1980); Kenson and Holland (1980); Licht (1980); Marzo and Fernandez (1980); Niess (1980); Parungo, Pueschel and Wellman (1980); Theodore, Sosa and Fajardo (1980); Wheeler (1980); Ireland (1981, 1984, 1987); Keene (1981); Lallande (1981, 1982); SCI (1981b); de Wispelaere (1981, 1983, 1984, 1985); Holland and Fitzsimmons (1982); Keith (1982); Record, Bubenick and Kindya (1982); Theodore and Buonicore (1982); E. Weber (1982); Elliot (1983); J.D. Daniels (1984); R.W. Lee (1984); Ogawa (1984); D.D. Adams and Page (1986); APCA (1986); Bretschneider and Kurfurst (1986); Farquhar (1986); Henstock (1986); Perriman (1986); De Wispelaere, Schiermeier and Gillani (1986); Redman (1989a); Veselind, Peirce and Weiner (1990); DoE (1991); ACGIH (1992/75); Benitez (1993); Speight (1993); IBC (1994/109)

Odours
ASTM (STP 164, DS 48); Henderson and Haggard (1922); Summer (1963, 1971); Chementator (1969 Jun. 30, 51); Turk (1969); Yocom and Duffee (1970); Oelert and Florian (1972); H.B.H. Cooper (1973); Dravnieks (1974); Turk, Johnston and Moulton (1974); Charlton, Sarteur and Sharkey (1975); CONCAWE (1975 8/75); Klooster, Vogt and Bernhart (1976); Harrell, Sewell and Walsh (1979); Valentin and North (1980); Kenson (1981); Amoore and Hautala (1983); Artis (1984); D.W. Jones (1984); Keddie (1984); Lynskey (1984 LPB 60); Ferryman (1984); P.J. Young and Parker (1984); Ruth (1986); van Langenhove, Lootens and Schamp (1988); Miedema and Ham (1988); Devis (1990); Valentin (1990); Nagy (1991); A.M. Martin *et al.* (1992); Sober and Paul (1992)

Liquid effluents
ASTM (STP 130, 148, 1481, 207, 337, 442, 573); CONCAWE (Appendix 28, 1970 3/70, 1975 3/75, 1979 3/79); IP (Appendix 28 Oil Loss Con/s); MCA (n.d./12, 1966–/13, 14); Eckenfelder and O'Connor (1961); Gurnham (1963, 1965); Busch (1965); Eckenfelder (1966, 1969); Fair, Geyer and Okun (1966); AIChE (1967–71/127–129, 1968/130, 1969/131, 1972/135, 1974/137, 1975/141, 1977/143, 1981/148); Beychock (1967, 1971); Jaeschke and Trobisch (1967); D.R. Montgomery (1967); SCI (1967); Cross (1968); Dahlstrom (1968); Dykman and Michel (1968); Eliassen and Tchobanoglous (1968); Geinopolos and Katz (1968); Kemmer and Odland (1968); Lesperance (1968); Sebastian and Cardinal (1968); A.R. Thompson (1968); API (1969 *Waste Manual*, vol. 1); Cecil (1969); Chopey (1970); Hiser (1970); Min. of Housing and Local Govt (1970); Anon. (1971h); Nemerow (1971, 1974); Characklis and Busch (1972); Moores (1972); Newsom and Sherratt (1972); Nogaj (1972); McLoughlin (1973); Reiterand Sobel (1973); Helliwell and Bossanyi (1975); Huber (1975); IChemE (1975/58); Lash and Kominek (1975); Open Univ. (1975b); H.W. Parker (1975); Bush (1976); Mulligan and Fox (1976); Thompson (1976); Cope (1977); Finelt and Crump (1977); Ford and Tischler (1977); Lederman (1977); Lewin (1977); McDowell and O'Connor (1977); Moss (1977); Paulson (1977); B.A. Bell, Whitmore and Cardenas (1978); Culp, Webster and Culp (1978); IBC (1978/3, 1993/100); Nathan (1978); Ramalho (1978, 1979); C.R. Fox (1979); Freeze and Cherry (1979); Martindale (1979); Sundstrom and Klei (1979); Afghan and Mackay (1980); Brewin and Hellawell (1980); R.A. Freeman (1980); Glaubinger (1980); J.H. Robertson, Cowen and Longfield (1980); D.L Russell (1980); G.K. Anderson and Duarte (1981); Arceivala (1981); Ayling and Castrantas (1981); Chalmers (1981); Howe, Howe and Howe (1981); Iddleden (1981); Sidwick (1981); Walters and Wint (1981); Askew (1982); Olthoff and Oleskiewicz (1982); Selby (1982); Vernick and Walker (1982); Wheatley (1982); Barrs (1983); Langer (1983); Cushie (1984); A.E. James (1984); R.A. Mills (1984); Eckenfelder, Patoczka and Watkin (1985); Crossland (1986); J. Lawrence (1986); NFPA (1990 NFPA 820); Veselind, Peirce and Weiner (1990); Metcalf and Eddy (1991); G. Parkinson and Basta (1991); RCEP (1992 Rep. 16).
Deep well disposal: Selm and Hulse (1960); Talbot and Beardon (1964); D.L. Warner (1965); Talbot (1968); Sheldrick (1969); M.E. Smith (1979)
Hydraulic dispersal: Abbott (1961); Fisher *et al.* (1979); Lloyd, O'Donnell and Wilkinson (1979); Cunge, Holly and Verwey (1980); Kobus (1981); R.E. Lewis (1981); Novak and Cabelka (1981); Komar (1983); ASCE (1986/28)
Oil-water separators: API (1990 Publ. 421)
Stream dispersal, pollution, renewal: Streeter and Phelps (1925); H.A. Thomas (1948); Churchill and Buckingham (1956); Hwang (1980); Nusser (1982); Velz (1984); *Wet air oxidation*: Flynn (1979); Wilhelmi and Knopp (1979); Laughlin, Gallo and Robey (1983); Baillod, Lamparter and Barna (1985); Heimbuch and Wilhelmi (1985)

Spills, spill control
BDH (1970); Anon. (1972b); Attaway (1972); Bock and Sullivan (1972); L.S. Brown (1972); Cairns, Dickson and Grossman (1972); J.B. Cox (1972); G.W. Dawson, Shuckrow and Mercer (1972); Donaldson (1972); Goodson and Jacobs (1972); R.H. Hiltz, Marshall and Friel (1972); Jennings (1972); Laroche (1972); Ludwig and Johnson (1972); D.G. Mason, Gupta and Scholz (1972); R.G. Sanders, Pantezolos and Rich (1972); Schuckrow, Mercer and Dawson (1972); Welch, Marmelstein and Maughan (1972); Wilder and Brugger (1972); Wye (1972); Ziegler and Lafornara (1972); May, McQueen and Whipp (1973); AIChE (1974/99, 1980/100, 144, 1988/100, 1989/70); May and Perumal (1974); Small and Snyder (1974); Univ. Engrs Inc. (1974); Weismantel (1974); Welker, Wesson and Brown (1974); Brugger and Wilder (1975a,b); G.W. Dawson (1975); Lindsey (1975); Otterman (1975); Wirth (1975); Armstrong, Gloyna and Wyss (1976); L.E. Brown *et al.* (1976); Bunner (1976); F.E. Clark (1976); W.D. Clark (1976b); Conner (1976); Courchaine and Dennis (1976); Dalton (1976); G.W. Dawson, Mercer and Parkhurst (1976); Diefenbach (1976); Eagon *et al.* (1976); Freestone (1976); Freestone, Lafornara and

McCracken (1976); Fullner and Crump-Wiesner (1976); Gupta 1976); Hooper, Warner and Galen (1976); Imbrie *et al.* (1976); Jennings and Gentry (1976); Jensen (1976); Jouhola and Bougger (1976); Kaufmann (1976); Kirsch *et al.* (1976); Michalovic *et al.* (1976); Moser, Hargens and Wilder (1976); Overfield and Richard (1976); Rice *et al.* (1976); K.C. Roberts (1976); Rodgers (1976); Roehlich, Hiltz and Brugger (1976); Seidenberger and Barnard (1976); S. Shaw and Gower (1976); Silvestri *et al.* (1976); E.A. Simons (1976); Sinclair and Bower (1976); T.J. Thomas, Srinavasan and Gower (1976); B.C. Weber (1976); Whitebloom (1976); Wiener and Heard (1976); Huibregste *et al.* (1977); Martinsen and Muhlenkamp (1977); Badley and Heaton (1978); D.P. Brown (1978); Charlton *et al.* (1978); Corbett (1978); Darnell (1978); G.W. Dawson and McNeese (1978); G.W. Dawson, McNeese and Christensen (1978); DOT (1978); Feates (1978); Freestone and Zaccor (1978); Gilman and Freestone (1978); Glattley (1978); Griwatz and Brugger (1978); Halvorsen (1978); Hand and Ford (1978); Harsch (1978a,b); Hubbs (1978); Huibregste, Lafornara and Kastman (1978); Huigbregste, Moser and Freestone (1978); Imbrie, Karwan and Stone (1978); Khattak and Whitmore (1978); Kirsch *et al.* (1978); Kiygielski and Bennett (1978); Ladick (1978); Lafornara, Frank and Wilder (1978); Lafornara, Lampl *et al.* (1978); Lafornara, Marshall *et al.* (1978); Lampl, Massey and Freestone (1978); Lathrop and Larson (1978); Mercer *et al.* (1978); Michalovic *et al.* (1978); Moien (1978); Neely and Mesler (1978); Norman and Dowell (1978, 1980); T.W. Pearson (1978); Rinka and Schulz (1978); Roth *et al.* (1978); Ryckman, Wiese and Ryckman (1978); Schultz and Shah (1978); Seeman *et al.* (1978); Silvestri *et al.* (1978); J.T. Smith (1978); Soden and Johnson (1978); Stonebreaker, Freestone and Peltier (1978); Thuma *et al.* (1978); Tsahalis (1978); Urban and Losche (1978); Whiting and Shafer (1978); Willmoth (1978); Tracy and Zitrides (1979); Gunderloy and Stone (1980); Weidenbaum (1980); Huibregste and Kastman (1981); Schwartzman (1981); Shooter, Lyman and Sinclair (1981); Wentzel *et al.* (1981); Armstrong (1982); G.F. Bennett, Feates and Wilder (1982); Brugger (1982); Eckenfelder (1982); R.H. Hiltz (1982); Kletz (1982); Lafornara (1982); Ludwigson (1982); Nadeau (1982); Nusser (1982); Scholz (1982); ASTM (1983 STP 825, 1990/1); Jeulink (1983); G.W. Dawson and Mercer (1986); R.H. Hiltz (1988); Martins (1988); Melvoid and Gibson (1988); Abbott and Leeman (1990); ACGIH (1992/87); Browne (1993)

Oil spills

Anon. (1969d); Pattison (1969); Fay (1970); CONCAWE (1974 4/74, 1980 9/80, 1981 7/81, 1981 9/81, 1983 10/83, 1987 1/87, 1988 2/88); d'Alessandro and Cobb (1976b); Fingas and Ross (1977); C.J. Clark (1978); IP (1978 PUB 11, 1983 PUB 18, 1985/3); Middleditch (1981); API (1982 Publ. 2022); ASTM (1984 STP 840)

Marine

RCEP (1972 Rep. 2, 1981 Rep. 8); WSL (1972); Cttee on the Environment (1974); F.W.G. Smith (1974); DoE (1976 Poll. Pap. 8); Johnston (1977); Cole (1979); Jaafe *et al.* (1981); Norcross (1981); Kullenberg (1982); IP (1993 TP 27); Lawrence and Cross (1994)

Torrey Canyon

Cowan (1969)

Hazardous and solid wastes

MCA (SG-9, 1974 SW1-SW3); Mohlman (1950); SCI (1957); Rickles (1965); FPA (S3, 1971/15); Key (1970); Novak (1970, 1972); Anon. (1971f); IChemE (1971/51); Witt (1971b, 1972); AIChE (1972/134); Baum and Parker (1973); Santolieri (1973); IMechE (1975/44, 1977/49); Mantell (1975); Open Univ. (1975d); Patrick (1975); Roulier, Landreth and Carnes (1975); Saxton and Narkus-Kramer (1975); Stephenson *et al.* (ASME 1975/186); Besselievre and Schwartz (1976); Boily (1976); D.R. Davies and McKay (1976); Frisbie (1976, 1978); Lazar (1976a,b); E.P. Austin (1977); Feates (1977); Hillman (1977); Keen (1977); Paulson (1977); S.W. Pearce (1977); G. Jones (1978); Morrison and Ross (1978); Ricci (1978b); Huddlestone (1979); Okey, Digregorio and Kominek (1979); Pojasek (1979a,b); J. Smith *et al.* (1979); API (1980 *Waste Manual*); Conway and Ross (1980); Gradet and Short (1980); Anon. (1981n); Basta (1981b,e); Jamieson (1981); Shen (1981); ASTM (1982 STP 760, 1983 STP 805, 1984 STP 851); Bentley (1982); Farquhar (1982); Kiang and Metry (1982); R.D. Ross (1982); Skitt (1982); Thibodeaux, Springer and Riley (1982); A.N. Clarke and Clarke (1983); Chivers (1983, 1984); Cope, Fuller and Willetts (1983); G.W. Davidson (1983); Dyer and Mignone (1983); Finnecy (1983); Jennings (1983); A. Lawrence (1983); D.A. Mills (1983); Cook (1984 LPB 55); Hawkins (1984); Hillman (1984); Kennard (1984); Luck (1984); Mackie and Niesen (1984); E.F. Wood (1984); Zirschky and Gilbert (1984); Anon. (1985o); Basta, Hughson and Mascone (1985); Pitt and Pitt (1985); Porteous (1985); RCEP (1985 Rep. 11); Anon. (1986k); Arthurs (1986); Hollowood (1986); Payne (1986); W.F. Robinson (1986); Barclay (1987); M. Bradford (1987); CIA (1987 RC15, RC16, 1989 RC17); Colen (1987a,b); Crittenden and Kolaczowski (1987); Crumpler and Martin (1987); EPA (1987); Loehr (1987); E.J. Martin and Johnson (1987); Stone (1987); Wiles (1987); Rendell (1988a); Hammitt and Reuter (1989); Salcedo, Cross and Chrismon (1989); ACGIH (1990/42, 1992/83, 84); Earth (1990); Batchelor (1990); L.W. Jones (1990); Pekelney (1990); Soudarajan (1990); Tedder and Pohland (1990); Veselind, Peirce and Weiner (1990); Weitzman (1990); HMIP (1991); Nemerow and Dasgupta (1991); IBC (1992/87); Paluzzi (1992); IMechE (1994/170); Petts and Eduljee (1994); Sara (1994)

Incineration

ASME (Appendix 28 Solid Waste); Frankel (1966); Monroe (1968, 1983b); Cross (1972); CONCAWE (1975/2); Dunn (1975, 1979); C.R. Lewis, Edwards and Santoro (1976); R. Harrison and Coulson (1977); Bartsch, Gilley and Steele (1978); J. Jones (1978); Dunn (1979); Fabian, Reher and Schon (1979); Hitchcock (1979); Ready and Schwab (1980 LPB 36, 1981); HSE (1981 BPM 11); Deneau (1983); Frankel, Sanders and Vogel (1983); Monroe (1983b); Anon. (1984aa); Feeley (1984); H.M. Freeman (1984); Brunner (1985, 1986, 1989, 1993); Rickman, Holder and Young (1985); Basta (1986a); Zurer (1986); Baker-Counsel (1987a); Beychok (1987); H.M. Freeman *et al.* (1987); Wiley (1987); C. Butcher (1990a); IBC (1990/78, 1992/93); Vervalin (1990a); Veselind, Peirce and Weiner (1990); P.T. Williams (1990); Ondrey and Fouhy (1991); Zeng and Okrent (1991); Altorfer (1992); S.E. Anderson, Dowell and Mynaugh (1992); Haseltine (1992); RCEP (1993 Rep. 17)

Landfill

Perket (1978); Duvael (1979); Basta (1981b); Corbin and Lederman (1982); IBC (1982/22); A. Parker (1982); G.W. Dawson (1983); J.D. Cook (1984); Hoppe (1984a); Crawford

and Smith (1985); Shuckrow, Touhill and Pajak (1987); Anon. (1988k); Shacke and Sawai (1990); Veselind, Peirce and Weiner (1990); Kemp and Gerrard (1991)
Transport
R.J. Buchanan (1982); Bromley and Finnecy (1985)

Ocean disposal, ocean incineration
Chementator (1970 Aug.24, 32; 1974 Oct.28, 33; 1975 Dec.8, 82); Zapatka, Hann and Zapatka (1976); K. Pearce (1977); Ketchum, Kester and Park (1981); Finnecy (1982); Novak and Pfrommer (1982); Remirez (1982); Anon. (1984d); NRC (1984); Ditz (1988)

Waste sites, site clean-up, contaminated land
Dennis (1978); Kohn (1978d); Overcash and Paul (1980); SCI (1980); IBC (1981/18, 1992/89); D.C. Wilson, Smith and Pearce (1981); Bowders, Koerner and Lord (1982); Long and Schweitzer (1982); Lord, Koerner and Freestone (1982); D.C. Wilson (1982); R.E. Edwards, Speed and Verwoert (1983); Muller, Brodd and Leo (1983); Rogoshenski, Boyson and Wagner (1983); Tyagi, Lord and Koerner (1983a–c); Block, Dragun and Kalinowski (1984); Block and Kalinowski (1984); Ehrenfelder and Bass (1984); Husak, Kissenpfennig and Gradet (1985); MA Smith (1985); Wagner *et al.* (1986); Lord and Koerner (1988); des Rosiers (1987); Arenti *et al.* (1988); Hopper (1989); Porter (1989); Ahlert and Kosson (1990); Bleicher (1990); IP (1991 PUB 58, 1993/2); Raghavan, Coles and Dietz (1991); AGA (1992/86); N. Morgan (1992a); Vandegrift, Reed and Tasker (1992); Cairnie (1993); Pratt (1993)
Superfund
Ember (1984); Hoppe (1984b); Casler (1985); Sidley and Austin (1987); Redman (1989b); Bisio (1991b, 1992a)

Love Canal
Glaubinger, Kohn and Remirez (1979); J.L. Fox (1980a); Gage (1980); Holden (1980); Kolata (1980); Picciano (1980); M.W. Shaw (1980); M. Brown (1981); Kohn (1982); Anon. (1984hh)

Rechem
Anon. (1984a,i,o,aa,dd); Anon. (1985y,z); Anon. (1986d,x); Anon. (1987v); J. Cox (1988b)

The philosophy of inherently cleaner design is to avoid the generation of noxious effluents. As with inherently safer design, this is easier said than done, but progress has been made and the pressures to operate cleaner processes continue to grow.

A11.2.3 Intermediate storage
A prime theme in inherently safer design is the elimination of intermediate storage. It transpires that the elimination of storage tanks is also a significant feature of waste minimization programmes. In the first case the motivation is to reduce the inventory of hazardous materials, while in the second it is to reduce the quantities of tank residues and wash liquids.

A11.2.4 Hazard identification
The general approach to hazard identification developed in SLP is also applicable to EP.

The hazop method, for example, is increasingly being adapted or enlarged to cover the environment.

A11.2.5 Hazard assessment
Likewise, hazard assessment is finding application in EP as well as in SLP.

Although much of the methodology of hazard assessment used in SLP is applicable to environmental problems, there are also some significant differences. The treatment of the events leading up to a release uses an essentially common methodology, but the modelling of the consequences of a release naturally differs more significantly.

Thus whereas for SLP hazard assessment involves estimating and evaluating the consequences in terms of injury to people and damage to property, for EP the consequences to be considered are the fate of chemicals in the environment, and their ultimate effects on plant and animal life.

A11.2.6 Hazard models
Many of the models used in hazard assessment for SLP are applicable also to EP, and indeed it was for the latter that some were first developed.

Thus the treatment of emission, vaporization and dispersion largely shares a common methodology, although there are some differences of emphasis. In gas dispersion, for example, heavy gas dispersion is of particular significance in SLP, while for EP passive dispersion, including dispersion over much greater distances, plays a more significant role.

A11.2.7 Fugitive emissions
A problem common to SHE and EP is that of low level, or fugitive, emissions from a plant. Such emissions have an impact on the health of workers in the plant and on the population and environment outside.

In SLP the need for stricter controls on emissions within the plant was evidenced by the vinyl chloride problem in 1975, while in EP pressure for emission controls arose from studies of the causes of air pollution in cities such as Los Angeles in the later 1970s, which implicated emissions from nearby refineries.

A11.2.8 Environmental impact assessments
There has been a general trend to require that an industrial activity make an environmental impact assessment (EIA) or environmental impact statement (EIS), also referred to, respectively, as an environmental assessment (EA) and an environmental statement (ES). Such environmental impact assessments and statements include safety issues, although mainly in respect of hazards to the public.

A11.2.9 Safety cases
Closely related is the requirement in European legislation for preparation of a safety case. The requirement to address hazards to the environment as well as humans has received increasing emphasis.

A11.2.10 Communication with public
Process plants and hazardous waste facilities are both liable to generate opposition, prior to creation or in the course of operation. The need to communicate with the public, and the approach required, are very similar in both cases.

A11.3 Some Conflicts

Another link between SLP and EP is that in some cases a degree of conflict arises. In some cases the preferred

solution to a safety problem may be ruled out, or at least discouraged, on environmental grounds; in others stricter environmental controls may push the designer towards solutions which would not otherwise be adopted for safety reasons.

Accounts of such conflicts have been given by Elphick (1972), R.Y. Levine (1972b), Bodurtha (1976) and Kletz (1993e).

Some of the practices which are so affected are now considered.

A11.3.1 Reactor venting

The normal method of protection for a chemical reactor has been the provision of a bursting disc with a short, straight pipe discharging to atmosphere at a safe place.

If such discharge is not permitted but this basic method of protection is retained, it becomes necessary to pipe each bursting disc into a vent header leading to a disposal system such as a scrubber or flare. Some of the problems which this creates have been described by Levine.

It is largely for this reason that the alternative approach of using instrumented protective systems on reactors has become increasingly attractive, as described in Chapter 11.

A11.3.2 Pressure relief valve discharge

An essentially similar conflict and similar problems arise over the practice of fitting pressure relief valves which discharge directly to atmosphere.

Some of the problems of vent collection systems are described by Kletz.

Avoidance of discharge to atmosphere is one of the main arguments for the use of trip systems to protect against overpressure, as described in Chapter 13.

A11.3.3 Flaring

A flare radiates intense heat and light and may be smoky and noisy. These are all aspects of pollution which have become increasingly unacceptable.

In contrast to the oil industry, which has continuous flaring, the chemical industry often makes use of an intermittent flare. The flare may be used to burn small quantities of smelly materials. But since very small quantities are sometimes not ignited by the flare pilot burner, it is sometimes necessary to operate the flare continuously, using fuel gas which could otherwise be used more productively.

A11.3.4 Bleeding

The build-up of impurities in plants is avoided by taking off a bleed. If this practice is inhibited by environmental considerations, the impurity can accumulate and may create a hazard. Levine describes a multimillion dollar loss which occurred due to the build-up of the explosive impurity azomethane.

A11.3.5 Leakages

The degree of leakage which has been tolerated in the past is now frequently unacceptable. The problems which can then arise are illustrated by the leakage of hydrogen from mercury cell chlorine plants. The hydrogen stream is one of the carriers of mercury vapour from the cells. Therefore mercury escapes in the hydrogen leakages. One possible solution is to run with the hydrogen under a slight negative pressure, but this creates the risk of air ingress leading to an explosion.

A11.3.6 Incineration

Burning in open pits has been widely used as method of disposing of waste solvents on chemical plants. Closed incinerators eliminate this pollution, but present hazards of their own.

A11.3.7 Ventilation

The hazard from flammable leaks in a compressor house can be reduced if the building is of open construction such that ventilation is much enhanced. This solution runs into the difficulty, however, that the noise of the machinery carries further.

A11.3.8 Combustion processes

The attempt to reduce the emission of nitrogen oxides from combustion processes can increase the risk of explosion. A marked decrease in nitrogen oxides formation occurs as excess air is reduced. But reduction of excess air increases the probability of an explosion due to unburned fuel in the gas leaving the combustion chamber.

A11.3.9 Pollution control equipment

Equipment for the removal of flammable dust from gases can present another hazard. Although this can be minimized by the use of wet scrubbers, these run into difficulties from water pollution controls.

A11.3.10 Halons

Halons have found a distinctive role in the process industries as fire extinguishants and explosion suppressants. The banning of chlorofluorohydrocarbons (CFCs) creates a gap which for fire extinguishants is not yet fully filled.

Pollution of the Environment

Awareness of the seriousness of environmental pollution grew rapidly in the 1960s. The publication of *Silent Spring* by Carson (1963) was a landmark. Other warnings have followed such as *Bitter Harvest* by Egginton (1980).

Accounts of pollution and environment include *Handbook of Environmental Control by* Bond and Straub (1973–), *The Pollution Handbook* by Mabey (1974), Introduction to Environmental Science by Strahler and Strahler (1974), *A Dictionary of the Environment by* Allaby (1977), *Topics and Terms in Environmental Problems* by Holum (1977), *The Protection Handbook of Pollution Control by* P. Sutton (1977b), *Environmental Education by* Bakshi and Naveh (1980), Britain, Europe and the Environment by MacRory (1983) and *Environmental Pollution and Control* by Veselind, Peirce and Weiner (1990).

Also relevant are the reports of the Royal Commission on Environmental Pollution.

A11.4 Legislation

Although there are significant differences between gaseous effluents, liquid effluents and solid wastes, some of the legislation addresses more than one of these, and it is convenient therefore to take all three together.

A11.4.1 Air pollution

The Alkali etc. Works Regulation Act 1906 was for many years the principal act governing air pollution.

The philosophy of enforcement of the act has been the use of best practicable means (BPM) to minimize emissions.

The HSWA 1974 states in Section 1(1) (d) that its provisions are made with a view to controlling emissions of noxious substances and it contains in Section 5 a general duty to use best practicable means to prevent such emission.

The Health and Safety (Emissions into the Atmosphere) Regulations 1983, amended 1989, create in Section 3 prescribed classes of premises for the purposes of Section 1(1) (d) of the HSWA, listed in Schedule 1, and specify under Section 4 substances prescribed as noxious. These premises and substances are listed in Schedules 1 and 2, respectively.

A11.4.2 Control of Pollution Act 1974

The Control of Pollution Act 1974 (COPA) has four main parts: Part I, Waste on Land; Part II, Pollution of Water; Part III, Noise; and Part IV, Pollution of the Atmosphere.

Part I of the act states requirements for the disposal authority to control waste disposal by a system of licensing. It prohibits the unlicensed disposal of controlled waste.

In Part II the act lays down the duties of the Water Authorities to operate a system of consents for discharges and prohibits noxious discharges.

The provisions of Part IV on atmospheric pollution are limited and deal mainly with pollution by certain fuels and with information about air pollution.

A11.4.3 Environmental Protection Act 1990

The Environmental Protection Act 1990 (EPA) has nine parts, those of principal relevance here being Part I, Integrated Pollution Control and Air Pollution Control by Local Authorities; Part II, Waste on Land; and Part III, Statutory Nuisances and Clean Air.

Part I of the act establishes a system of integrated pollution control (IPC) enforced by HM Inspectorate of Pollution (HMIP) and one of air pollution control (APC) administered by the local authorities (LAAPC).

Section 1 of Part I gives definitions of environment, pollution and harm which read as follows:

> (2) The 'environment' consists of all, or any, of the following media, namely the air, water and land; and the medium of air includes the air within buildings and the air within other natural or man-made structures above or below ground.
> (3) 'Pollution of the environment' means pollution of the environment due to the release (into any environmental medium) from a process of substances which are capable of causing harm to man or any other living organisms supported by the environment.
> (4) 'Harm' means harm to the health of living organisms or other interference with the ecological systems of which they form part and, in the case of man, includes offence caused to any of his senses or harm to his property; and 'harmless' has a corresponding meaning.

Section 2 creates a system of prescribed processes and substances and Section 3 allows regulations to be made for their control. Subsection 2 of Section 3 allows the prescription of standard limits for the concentration, the amount or the amount in any period to be released; of standard requirements for measurement; and of standards or requirements for the process. Subsection 5 allows the making of plans for establishing limits for the total amount or total amount in any period to be released in any area; for quotas for operators; and for establishing or reducing limits so as progressively to reduce pollution.

Sections 6–12 create a system of authorizations to operate a prescribed process. Section 7 deals with the conditions of such an authorization. It requires that in carrying on such a process use should be made of the best available technology not entailing excessive cost (BATNEEC) to prevent release of prescribed substances or to render harmless any other potentially harmful substances.

Section 4 establishes the enforcing authorities and Sections 13–19 deal with enforcement. Section 13 gives powers to make an enforcement notice and Section 14 a prohibition notice.

Section 23 gives a list of offences and penalties. Section 27 gives powers such that where an offence causes any harm which it is possible to remedy the inspectorate may arrange for any reasonable steps to be taken to remedy the harm and may recover the cost from any person convicted.

The EPA covers discharges into all environmental media. Some processes have the potential to make significant discharges into more than one medium, in some cases as a result of transfer from one medium to another. An example is removal of substances from a gas stream which then ends up in a liquid effluent. In such situations the EPA requires the selection of the best practical environmental option (BPEO) and the operator is required to demonstrate that its process meets the BPEO criterion.

Part II of the act creates a duty of care in respect of wastes and a system of waste management licences.

Part III defines a number of statutory nuisances which are 'prejudicial to health or a nuisance' and which include emissions such as smoke; fumes and gases; dust, steam, smell and other effluvia; accumulations or deposits; and noise. It lays on a local authority a duty to inspect its area to detect such nuisances and to act on them.

The prescribed processes and substances are given in the Environmental Protection (Prescribed Processes and Substances) Regulations 1991. Schedule 1 contains a number of chapters, each of which deals with a particular industry. The chemical industry is covered in Chapter 4 of the schedule.

A distinction is made between those processes which are subject to control by local authorities in respect of air pollution only and those which have the potential for pollution of more than one environmental medium, which require an IPC authorization from the HMIP – the Part B and Part A processes, respectively.

A11.4.4 Clean Air Act 1993

The Clean Air Act 1993 covers pollution by smoke, grit, dust and fumes from industrial processes not required to be registered under the HSWA 1974 and the Health and Safety (Emissions into the Atmosphere) Regulations 1983.

The act prohibits the emission of 'dark' smoke from any chimney or industrial premises.

A11.4.5 Water pollution

Until 1973 local authorities had the duty of providing sewerage and sewerage treatment not only to domestic but also as far as possible to industrial users. Controls on effluents from industrial premises to the public sewerage system

were established by the Public Health (Drainage of Trade Premises) Act 1937.

The Water Act 1973 transferred the responsibilities for industrial effluents to the public Water Authorities (WAs). The operation and maintenance of the sewerage system continued to be done by the local authorities on an agency basis.

The Control of Pollution Act 1974 strengthened the controls on water pollution.

The development of controls on water pollution has been influenced by the apparent deterioration of water quality in the North Sea and by a series of North Sea Conferences of the states concerned, the first being held in 1984.

Substances identified as particularly harmful to the aquatic environment by reason of their toxicity, persistence and bioaccumulation are identified in the 'Red list'.

Control of water pollution is now governed by the Water Act 1989, described below, and the EPA 1990.

The system being developed under these acts is one of integrated pollution control based on environmental quality objectives (EQOs) and environmental quality standards (EQSs) utilizing the BATNEEC criterion.

A11.4.6 Water Act 1989

The Water Act 1989 defines the waters which are subject to control, establishes the powers of control and creates the National Rivers Authority (NRA).

Prior to privatization the WAs were responsible both for the supply of water and for control of pollution of water. In other words, they were both poacher and gamekeeper. The need to separate these functions led to the creation of the NRA, which is now responsible for protecting the aquatic environment.

Section 103 of the Act defines the various waters subject to controls, which are essentially inland waters, including rivers and watercourses; groundwaters; coastal waters; and territorial waters out to a 3 mile limit.

Part III of the Act gives the NRA powers to improve water quality and to control effluent discharges.

Discharge of liquid effluent is governed by a system of discharge consents. The discharge consent procedures are given in Schedule 12 of the Act.

Public participation is allowed by arrangements for advertising a discharge application in the local press and by a duty on the authority to consider representations made.

A11.4.7 Hazardous wastes

Control of hazardous wastes is exercised under the Deposit of Poisonous Waste Act 1972 and the Deposit of Poisonous Waste (Notification of Removal or Deposit) Regulations 1972.

Hazardous waste controls are also major elements of the Control of Pollution Act 1974, Part I and the EPA 1990, Part II, as already described. The EPA 1990 creates a system of waste management licences.

A11.4.8 Environmental impact assessment

EC Directive 85/337/EEC on the assessment of the effect of certain public and private projects on the environment creates for certain projects requirements for an environmental assessment.

In the United Kingdom, implementation of these requirements is largely covered by the Town and Country Planning (Assessment of Environmental Effects) Regulations 1988 (the EA Regulations).

The regulations specify that a developer provide information on the impact of the project in the form of an environmental statement.

A11.4.9 Advisory bodies

There is a standing Royal Commission on Environmental Pollution (RCEP). The reports of the commission are listed in Appendix 28.

Among the topics addressed are coastal water pollution (1972, *Third Report*), integrated air pollution control (1976, *Fifth Report*), sea pollution (1981, *Eighth Report*), waste management (1985, *Eleventh Report*), best practical environmental option (1988, *Twelfth Report*), freshwater quality (1992, *Sixteenth Report*) and waste incineration (1993, *Seventeenth Report*).

A11.4.10 Safety cases

EC Directive 82/501/EEC on major accident hazards creates controls on certain installations which include the submission of a safety report. There have been two subsequent modifying directives, the second 88/610/EEC containing requirements in response to the Rhine pollution incident at Schweizerhalle in 1986.

The initial directive is implemented in the United Kingdom by the CIMAH Regulations 1984 and the two later directives by amendments of these regulations. In the second set of amendments in 1990 the requirement for the safety case is contained in Regulation 7 and its contents are specified in Schedule 6.

Schedule 6 refers to information on the consequences of a major accident without specifically mentioning those to the environment, but guidance given in HS(R) 21 by the HSE (1990) states that in relation to the environment information should include the routes by which harm may be brought about and the effect on the exposed environment including persistence of the substance in the environment.

A11.5 EC Directives

There are a considerable number of EC Directives concerned with the environment. Some of the principal directives are listed in Chapter 3.

An information service on EC legislation is given in *European Environment Law for Industry* by Agra Europe (1994a).

Directive 76/464/EEC gives a list of substances dangerous to the environment. 80/68/EEC addresses groundwater protection. Discharge of certain substances listed in 76/464/EEC is covered by 86/280/EEC. There are directives on discharge of metals such as mercury and cadmium. Directive 84/360/EEC deals with air pollution from industrial plants and 88/609/EEC with large combustion plants. There are directives on ozone, sulfur dioxide, nitrogen dioxide and carbon dioxide. Other specific pollutants covered by directives include lead, asbestos and PCBs. Toxic and dangerous wastes are the subject of Directives 78/319/EEC and 91/689/ EEC, while 84/631/EEC deals with transfrontier shipment of wastes.

Directive 85/337/EEC requires for certain activities the production of an environmental impact assessment.

A11.6 US Legislation

Accounts of US legislation on the environment and on pollution control are given by Lipton and Lynch (1987),

E.J. Martin and Johnson (1987), Nemerow and Dasgupta (1991) and Veselind, Peirce and Weiner (1991).

The account given below complements that given in Chapter 3.

A11.6.1 Air pollution

In the United States, air pollution legislation includes the Air Pollution Control Act 1975, the Clean Air Act 1963 (CAA) and the Clean Air Act Amendments 1970, 1977 and 1990 (CAAA).

The CAAA 1970 required the EPA to establish National Ambient Air Quality Standards (NAAQSs). The CAAA 1977 brought in requirements for the NAAQSs to be regularly up-dated and for the 'prevention of significant deterioration' (PSD) in regions with air cleaner than the NAAQS. A system of New Source Reviews (NSRs) was instituted with New Source Performance Standards (NSPSs). Best available control technology (BACT) is required for compliance.

Title III of the CAAA 1990 gives a list of 189 air toxics and requires the EPA to publish a list of source categories emitting 10 ton/year of any one toxic or 25 ton/year of a combination and to issue for such toxics maximum achievable control technology (MACT) standards.

A11.6.2 Water pollution

Water quality in the United States is protected by legislation on effluent discharges to streams and on drinking water quality. The Federal Water Pollution Control Act 1972 envisaged a nationwide policy of zero discharge of pollutants by 1985. The EPA introduced a discharge permit system in the form of the National Pollutant Discharge Elimination System (NPDES). The Clean Water Act Amendments 1977 backed away from zero discharge and introduced a system requiring instead that in due course discharges be treated with the best conventional pollutant control technology. In addition, the EPA is now charged with setting limits for some 100 toxic substances in effluents.

Advisory standards for drinking water in the United states have long been set by the US Public Health Service (USPHS). The Safe Drinking Water Act 1974 authorizes the EPA to set minimum national drinking water standards.

A11.6.3 Hazardous wastes

Hazardous wastes in the United states, governed previously by the Solid Waste Disposal Act 1965, are now are subject to the Resource Conservation and Recovery Act 1976 (RCRA). The act seeks to ensure proper land disposal of defined hazardous wastes and to fill certain loopholes in control on air and water pollution. Under it the Office of Solid Waste (OSW) of the EPA promulgates regulations defining hazardous wastes and standards applicable to it. In implementation of the Act, the EPA classified waste disposal sites as landfills, lagoons or landspreading operations, defined eight categories of impact which such sites might have and stated the operational and performance standards to be met to minimize such impacts.

Hazardous wastes attract further controls. For these the EPA has set up what is in effect a 'cradle-to-grave' system covering hazardous waste generation, transport and treatment, storage and disposal facilities, imposing duties on the generator, the transporter and the facility operator and involving tracking by a system of identification numbers and control by a system of permits.

The problem of the large number of hazardous waste sites in unsatisfactory condition, or worse, is addressed by the Comprehensive Environmental Resource Conservation and Liability Act 1980 (CERCLA), or Superfund. The act creates controls on such facilities and provides for the EPA to supervise the clean-up of existing and abandoned sites. The EPA seeks to identify Potentially Responsible Persons (PRPs) and, where such parties are not found, it initiates a clean-up paid for from the Superfund.

The Superfund Amendments and Reauthorization Act 1986 (SARA) renews the Superfund. The part known as SARA Title III extends its application to accidental releases.

The numerous other items of legislation which have some bearing on hazardous waste are reviewed by Edelman (1987).

A11.6.4 Fugitive emissions

Standards governing fugitive emissions have been promulgated by the EPA under the CAA. These are the Standards of Performance of New Stationary Sources Equipment Leaks of VOC, Petroleum Refineries and Synthetic Organic Chemical Manufacturing Industry 1983, amended 1984, also referred to as the New Source Performance Standards (NSPSs), the NSPS Regulations or the VOC (SOCMI) Regulations. These set standards for emissions permissible from items of equipment.

In addition to these controls on VOCs, the EPA has also issued National Exposure Standards for Hazardous Air Pollutants (NESHAPs) for certain specific substances. These too give equipment emission standards.

The NSPSs apply to new equipment but also have application to reconstructed and modified equipment, and guidance has been given on determining how far they affect existing equipment. In addition, existing equipment is affected by the assimilation into EPA controls of state requirements on monitoring and maintenance (M&M).

A11.6.5 Environmental impact assessment

The National Environmental Policy Act 1969 (NEPA) contains in Section 102 the far-reaching provision that where the action of a federal agency may have significant consequences for the human environment, an environmental impact statement should be given. The practice is to prepare a draft statement, which is put out for consultation, and then to issue the final statement.

A11.7 Environmental Management

11.7.1 Environmental management systems

The environment needs to be protected by an approach to management and management systems similar to that developed for safety and loss prevention, which has been described in Chapter 6. There should be an environmental management system (EMS) which parallels the safety management system.

A11.7.2 BS7750

Environmental management is the subject of BS 7750: 1992 Specification for Environmental Management Systems. The standard may be regarded as applying in this field the principles of quality systems given in BS 5750. An overview is given by Shillito (1991).

Requirements of BS 7750 include (1) documentation of the environmental management and management systems; (2) collation of regulatory requirements on the

environment; (3) inventory of raw materials and energy usage and of wastes and releases; (4) formulation of environmental objectives; (5) an environmental management plan; (6) a system of environmental audits; (7) a system of environmental controls with verification and testing; and (8) personnel qualified and trained in environmental matters.

A11.7.3 Process environmental reviews

The EMS should require a system of process environmental reviews akin to the process safety reviews described in Chapters 6 and 8.

This review system should include formal systems for the identification and assessment of environmental hazards.

The hazop study method is now applied to identify potential problems with the environment as well as with safety and operability. Accounts are given by Isalski *et al.* (1992) and Ormond and Isherwood (1992).

A11.7.4 Environmental audits

Another essential feature of an EMS is a system of environmental audits. Environmental auditing stands in essentially the same relation to EP as safety auditing does to SLP.

Accounts of environmental audits are given by Baumer (1982), Keene (1982), D.L Russell (1985) and Petts and Eduljee (1994).

A11.7.5 Environmental planning

The essential concern of planning is with the environment as broadly defined, including amenity as well as hazards and pollution.

The planning arrangements vary from country to country. Accounts of planning in the United Kingdom in relation to major hazard installations have been given by Petts (1988b, 1989, 1992).

Accounts of planning in relation to pollution are given by D.C. Wilson (1981) and Petts and Eduljee (1994), both dealing with hazardous wastes.

To a considerable extent planning centres around the EIS, discussed in Section A11.9.

A11.7.6 Environmental emergency planning

Environmental emergency planning is needed to cover both fixed installations and transport. The treatment in Chapter 24, which covers both aspects as far as safety is concerned, is in large part applicable to planning for environmental emergencies.

Further treatments relevant to the environment specifically are given in *Hazardous Materials Emergency Response and Control* by Cashman (1988) and by G.F. Bennett, Feates and Wilder (1982).

As stated earlier, the CIMAH safety case is required to cover environmental as well as safety aspects of emergency planning.

A11.8 Environmental Hazard Assessment

There is now an increasing activity in environmental hazard assessment. In large part this has been driven by the threat to the environment from hazardous waste sites.

In the United states, the pollution arising from the hazardous wastes dumped at Love Canal, described in Section A11.22, and the resultant arrangements for clearing up waste sites under Superfund have stimulated assessment of such sites to determine the extent of the risks and to set priorities for clean-up.

Hazard assessment is undertaken both for existing or proposed hazardous waste treatment, storage and disposal facilities (TSDFs) and for abandoned hazardous waste dumps.

Accounts of environmental hazard assessment are given in *Risk Assessment of Hazardous Waste Sites* by Long and Schweitzer (1982), *Hazardous Waste Risk Assessment* by Asante-Duah (1993) and *Standard Handbook for Solid and Hazardous Waste Facility Assessments* by Sara (1994) and by H. Bradford (1986a), B.P. Smith (1987), Kemp and Gerrard (1991), Kolluru (1991), Welsh (1992, 1993) and Rouhiainen (1993).

A11.8.1 EPA guidance

Guidance on hazard assessment of hazardous waste sites, in the context of Superfund, is given in *Risk Assessment Guidance for Superfund: I, Human Health Evaluation Manual* and in *Risk Assessment Guidance for Superfund: II, Environmental Evaluation Manual* both by the EPA (1989a,b). EPA philosophy is also described by B.P. Smith (1987).

The process outlined by the EPA involves the following steps: (1) hazard identification, (2) toxicity assessment, (3) exposure assessment and (4) risk characterization.

A brief description of the assessment process is given by Kolluru (1991) and a more detailed account by Asante-Duah (1993).

These stages in the assessment are now outlined.

A11.8.2 Hazard identification

Hazard identification is the first stage and, in this context, means the identification of those chemicals which pose the greatest risks, the so-called indicator chemicals.

Since this identification involves the inventory, mobility, persistence and toxicity of the chemicals, some degree of iteration back from the subsequent stages may be necessary.

A11.8.3 Toxicity assessment

Toxicity assessment requires consideration of toxicity both for carcinogens and for non-carcinogens.

For carcinogens the assumption made by the EPA is that there is no threshold below which a dose is harmless. The probability of harm is then obtained from the slope of the dose-response curve, the so-called cancer slope factor (CSF) or potency factor. The EPA also recognizes a weight of evidence factor. Carcinogens are divided into four categories: (1) human carcinogens, (2) probable human carcinogens, (3) probable human carcinogens but with inadequate human data and (4) possible human carcinogens.

For non-carcinogens a threshold is admitted. For the dose of such a chemicals there is therefore a no observable adverse effect level (NOAEL). A reference dose (RfD) is defined which is one hundredth of the NOAEL and which thus incorporates a substantial safety factor. The reference dose is also termed the acceptable daily intake (ADI).

A11.8.4 Exposure assessment

Exposure assessment involves determining the persons exposed and their intake of toxic chemicals.

The EPA has issued standard assumptions for exposure. For adults these include the following:

Air inhaled (m^3/d)	20
Water ingested (1/d)	2

Soil ingested (mg/d) 100
Fish consumption (g/d) 6.5
Lifetime exposure (year) 70

The assessment required is for a reasonable maximum exposure (RME) under present and future land use conditions.

A11.8.5 Risk characterization

Risk characterization involves combining the toxicity and exposure estimates to obtain an assessment of risk to human health and making an assessment of the risks to the environment.

Cancer risks are expressed as the probability of contracting cancer from exposure to the chemicals over a lifetime. Non-cancer risks are expressed for a single substance in terms of a hazard quotient (HQ) or for a set of substances in terms of a hazard index (HI), the sum of the hazard quotients. The hazard quotient is the ratio of the daily intake to the RfD. If the HQ is less than unity, the chemical is not regarded as a threat to public health.

A11.8.6 Source terms and transport models

A full hazard assessment of a hazardous waste TSDF requires the modelling of source terms and of the transport and transformation of chemicals in the atmosphere and the ground. These aspects are discussed in Section A11.12.

A11.9 Environmental Impact Assessment

A11.9.1 Environmental assessments

An EA presented in an ES is for some projects a regulatory requirement under the Environmental Assessment Regulations 1988.

Accounts of ES are given in *Environmental Impact Assessment of Waste Treatment and Disposal Facilities* by Petts and Eduljee (1994) and by E.J. Martin and Johnson (1987) and Veselind, Peirce and Weiner (1990).

The treatment by Petts and Eduljee is comprehensive and although concerned with hazardous waste facilities its general approach is of much wider application.

The authors describe the regulatory requirements for, the purposes of and practice in respect of an EA and they relate the EA to the requirement to select the best practicable environmental option (BPEO) with its implication that alternatives must be considered.

They outline the process of scoping. Following Elkin and Smith (1988), identification of the crucial concerns should cover (1) geographic boundaries, (2) administrative boundaries, (3) project timing and duration, (4) key stakeholders, (5) key resources and land uses, (6) key activities, (7) key policies and (8) interactions. They describe the scoping techniques of consultation and identification of impacts and their significance and indicate other techniques such as checklists, matrix and network methods, and cause–effect diagrams. They then deal specifically with the scoping of landfill and incineration.

For each feature subject to impact, Petts and Eduljee describe the feature itself, the scoping, the baseline conditions and survey, the prediction and evaluation of impacts, and the mitigation of impacts. They apply this treatment to (1) flora and fauna, (2) geology and soils, (3) ground and surface water, (4) air quality and climate, (5) public health, (6) landscape and visual amenity, (7) transport, (8) social and economic features, (9) land use and heritage and (10) residuals. In addition to the usual impact factors they consider acute events, noise and vibration, and landfill gas.

As a case study, the authors consider the Seal Sands incinerator.

A US perspective is given by Veselind, Peirce and Weiner (1990). They describe an EIS as consisting of three distinct parts: (1) inventory, (2) assessment and (3) evaluation. The relevant factors are broadly similar to those just mentioned. They also outline a scoring scheme in which impacts are rated using scales of importance and magnitude.

In some instances, particularly in the early days, the EIS has constituted a major exercise. For the trans-Alaska pipeline the draft EIS, the comments and the final EIS ran to 30 volumes.

A11.9.2 Safety cases

For major hazard installations the CIMAH Regulations 1984 require the submission of a safety case which covers the consequences of a major accident not only for human but for the environment. This aspect of the safety case is discussed by Singleton (1989) and Cassidy (1990).

The safety case is concerned with acute events and it may be regarded as complementing the regulatory controls dealing with long-term pollution and environmental impact.

Cassidy advises that the safety case should give information on the land uses around the site, the environmental hazards of the substances stored or processed and the potential impact on flora and fauna and on the balance of nature. Where there is potential to contaminate water, it should give comprehensive information on the local watercourses and their uses. Particular attention should be paid to the potential for harm to targets which are rare or unique, to persistence of noxious substances in the environment and to long-term damage. The author gives decision trees for assessing land and water impacts.

He also draws attention to the need to address the environmental aspects in the emergency planning required under the regulations.

Singleton deals with the assessment of the consequences to the environment of an accident involving an ultra-toxic substance. He considers the cases of copper–chrome–arsenate (CCA) wood preservatives and of pesticides.

A11.9.3 Waste facility assessments

A hazardous waste facility needs to be assessed to determine the hazard which it poses to the environment and to humans.

Petts and Eduljee (1994) describe two approaches to such assessment. One is to undertake a full environmental hazard assessment, as described in the previous section.

The other approach is the use of a structured checklist. This is the method used in the project on hazard assessment of landfill (HALO) described by Kemp and Gerard (1991).

A somewhat similar approach is taken in the Hazard Ranking Scheme (HRS) of the EPA (1982a), which utilizes a scoring system.

A11.9.4 Spill impact assessment

A more specific form of impact assessment is the assessment of the effects of a spill of hazardous material.

Typically this might be a liquid spill occurring in road or rail transport or from a pipeline.

Methods of assessing the impact of a spill which has already occurred are given in the literature as one aspect of spill control, as described in Section A11.20, but assessment of the impact of potential spills in advance receives little mention.

A11.10 Environmental Economics

The costs to the process industries of environmental protection are high, but experience indicates that, as with safety, good practice is also good business.

Costs and savings may be computed at national or company level. At the national level costs in the United states have been given in *Environmental Investments: The Costs of a Clean Environment* by the EPA (1991) (Chementator 1991 Mar., 25). In 1972, expenditure on pollution control was some $30 billion (≈1% of GDP). By 1987, it had risen to $98 billion (≈2% GDP) and by 1990 to $115 billion (≈2.1% GDP); the projection for the year 2000 is $140–160 billion (≈3% GDP); the values are all in 1990 dollars. The 1987, figures include $28.9 billion for air and $42.9 billion for water pollution control. The process industries account for a large proportion of this expenditure.

Savings at the national level are inevitably less easy to obtain.

However, as described in Section All.13, the efforts now devoted to waste minimization are testimony to the fact that there are economic benefits.

A11.11 Environmentally Noxious Chemicals

There are a number of substances which figure particularly prominently as pollutants. Some of the principal ones are mentioned briefly in this section.

Many of these substances appear in gaseous or liquid effluent streams. To this extent, their release is controlled one. The hazard from others may arise from an accident. A pesticide is a case in point, as described below.

A11.11.1 Sulfur dioxide and acid rain

A major pollutant from combustion processes is sulfur dioxide, which is responsible for acid rain.

Acid rain pollution is described in *Sulphur Emissions and the Environment* by the SCI (1981b), *Energy and the Environment: Acid Rain* by Keith (1982), *Acid Rain Information Book* by Record, Bubenick and Kindya (1982) and *Acid Deposition* by Adams and Page (1986) and by Ireland (1987). Control technologies are detailed in *Add Emissions Abatement Techniques* by the DoE (1991–).

A11.11.2 Nitrogen oxides

Nitrogen oxides NO_x arise from combustion processes. Both industrial combustion and cars are major contributors.

The NO_x problem and control technologies are discussed by Marzo and Fernandez (1980), Niess (1980), Redman (1989a) and R. Smith and Petala (1991–).

A11.11.3 Pesticides

Pesticides are highly active chemicals. The expose in *Silent Spring* by Carson (1963) rendered their use controversial.

The production, storage and handling of pesticides creates the potential for release in an event such as a fire, or with the fire water used.

The pesticide problem is discussed in *Persistent Pesticides in the Environment* by C.A. Edwards (1974) and by the SCI (1978).

A11.11.4 Polychlorinated biphenyls

For many years, until their extreme toxicity came to be appreciated, polychlorinated biphenyls (PCBs) were used as electrical transformer fluids. The main concern now is prevention of escape from such equipment and safe methods of disposal. This is discussed by Berry (1981) and Motter (1991). A guide to EPA-approved methods of disposal is given by Kokozska and Flood (1985).

A11.11.5 Toxic metals

Toxic metals which occur in trace quantities in effluents, including those from incinerators, can be very harmful to the environment.

Treatments of toxic trace metals are given in *Control and Fate of Atmospheric Trace Metals* by Pagna and Ottar (1989) and by Barton, Clark and Seeker (1990).

A11.11.6 Mercury

Certain processes, notably traditional processes for chloralkali production, discharge mercury, albeit in very low concentrations. Accumulation of mercury, especially in the form of methyl mercury, is very noxious to the environment.

A11.11.7 Dioxins

TCDD and other dioxins exhibit toxic effects in minute concentrations, and rank as ultratoxic substances. The toxicity of TCDD is discussed in Appendix 3 in the context of Seveso.

TCDD is produced in very low concentrations in combustion processes and can be produced in a chemical reactor.

The dioxin problem and methods of dealing with it are discussed in *Human and Environmental Risks of Chlorinated Dioxins and Related Compounds* by R.E. Tucker, Young and Gray (1983) and *Dioxin Containing Wastes: Treatment Technologies* by Arienti *et al.* (1988) and by Ayres (1981), Rice (1982), Short *et al.* (1984) and Beychok (1987a).

A11.11.8 Nitrates

Nitrates are another significant pollutant, but arise mainly from the use of fertilizers, and are outside the present scope. An account is given by Nicolson (1979).

A11.11.9 Health effects

Threats to health may arise from the use, or more often abuse, of chemicals or from their release to the environment.

Health effects of chemicals in the environment are treated in *Health Effects of Environmental Pollutants* by Waldbott (1973), *Environmental Industrial Health Hazards* by Trevethick (1976), *Air Pollution and Human Health* by Lave and Seskin (1977a), *Long-Term Hazards of Environmental Chemicals* by Doll and McLean (1979) and *Hazardous Waste and Human Health* by the BMA (1991) and by McLean (1981) and Asante-Duah (1993), as well as in texts on environmental hazard assessment.

A11.12 Chemicals Transport, Transformation, Fate and Loading

A fundamental approach to hazard assessment in EP involves tracing the dispersion and determining the fate of chemicals in the environment.

In principle, a full treatment therefore involves study of the dispersion of gaseous effluents in the atmosphere and of the deposition of particulate matter; the transmission of chemicals through waters and soils of all types; and their passage through the food chain.

A great deal of work has been and continues to be done in all these areas. In some cases the prime concern is with potential airborne releases from nuclear power plants or leaks from nuclear waste stores into watercourses, in others it is with the effects of pesticides and other chemicals already in use.

Accounts of the transport, transformation and fate of chemicals in the environment include *Environmental Pollution* by Chemicals Walker (1971), *Persistent Pesticides in the Environment* by C.A. Edwards (1974), *Pollution Criteria for Estuaries* by Helliwell and Bossanyi (1975), *Principles for Evaluating Chemicals in the Environment* by the NAS (1975), *Safety of Chemicals in the Environment* by Harwell (1979), *Chemical Concepts in Pollutant Behaviour* by Tinsley (1979), *Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment* by Afghan and Mackay (1980), *Dynamics, Exposure and Hazard Assessment of Toxic Chemicals* by Haque (1980b), *Chemicals in the Environment* by Neely (1981), *Physico-Chemical Behaviour of Atmospheric Pollutants* by Versino and Ott (1982), *Environmental Exposure to Chemicals* by Neely and Blau (1985), *Pollutant Transport and Fate in Ecosystems* by Coughtrey, Martin and Unsworth (1987), *Control and Fate of Atmospheric Trace Metals* by Pagna and Ottar (1989), *Reaction Mechanisms in Environmental Organic Chemistry* by Larson and Weber (1994), *Hazardous Waste Risk Assessment* by Asante-Duah (1993) and *Standard Handbook for Solid and Hazardous Waste Facility Assessment* by Sara (1994). Worldwide limit values are given in *World-wide Limits for Toxic and Hazardous Chemicals in Air, Water and Soil* by Sittig (1994).

A11.12.1 Source terms

The starting point for the modelling of transport through environmental media is the definition of the source terms.

Three principal types of source terms are (1) gaseous emissions from a hazardous waste TSDF, (2) leachate seepage from a TSDF and (3) liquid spill into a watercourse in a transport accident.

A review of gaseous emission source terms at a TSDF is given by B.P. Smith (1987). Models quoted by this author are for surface impoundments, that of Thibodeau, Parker and Heck; for aerated tanks, that of R.A. Freeman (1980); for storage tanks, the usual relations for 'breathing' losses; for landfill, that of W.J. Farmer, Yang and Letey (1980), as modified by Hwang (1980) and Shen (1981); and for land treatment, that of Thibodeaux and Hwang (1982).

For liquid seepage the source term is highly site specific. Seepage from landfill is treated in accounts of landfill and of leachate.

A liquid spill from a transport vehicle is a relatively well-defined source. Another form of transport spills is a pipeline leak, where the issues are the location and the flow rate.

A11.12.2 Transport of chemicals

Chemicals are transported through the environment by atmospheric dispersion and by movement through waters.

A review of air, surface water, groundwater, soil and multimedia transport models applicable in this context is given by McBean (1993).

For transport of gaseous emissions use is made of atmospheric dispersion models. These include the passive gas dispersion models familiar in hazard assessment, but also in some cases models for transport over much greater distances and periods and in more complex meteorological conditions.

The ISC model of the EPA is widely used, both in its short-term version ISCSTand its long-term version ISCLT.

For transport through water the review by McBean may be supplemented by the exhaustive treatment of transport through soil and groundwater, based on fundamental geology and hydrology, given by Sara (1994).

Transport through water is typically modelled using compartment, or control volume, models. For movement in surface water a widely used model is EXAMS of Burns, Cline and Lassiter (1982).

The modelling of the dispersion of a chemical spilled into a stream is discussed by Kontaxis and Nusser (1982).

There is no obvious preferred model for movement through groundwater.

The TOX-SCREEN model of the EPA (1984c), which assesses the potential fate of chemicals released to air, surface water or soil, may be used to screen for substances which even on conservative assumptions are unlikely to pose a threat to the environment.

In the United kingdom, as described by Welsh (1993), the HSE is developing a risk assessment tool for pollution risk from accidental influxes into rivers and estuaries (PRAIRIE), which incorporates a family of river dispersion models DYNUT.

A11.12.3 Transformation of chemicals

Chemicals moving through the environment may undergo a number of transformations, including reactions, among which are (1) hydrolysis, (2) chemical oxidation, (3) photolysis and photo-oxidation, (4) biodegradation, (5) absorption, (6) adsorption, (7) volatilization and (8) sedimentation.

Some of these transformation processes are described by Welsh (1993).

A11.12.4 Fate of chemicals

The determination of the fate of chemicals in the environment is an extremely complex matter. In part it has to do with the transport and transformation processes just outlined and in part with the assimilative capacity of environmental media and with the effects of the take-up of chemicals into food chains. The concept of an ultimate fate appears to imply some eventual steady state, although the associated timescales may well be rather long.

A11.12.5 Capacity of the environment

To a greater or lesser degree, environmental media have the capacity to tolerate a certain chemical burden. The assumption that this is so is frequently implicit in industry practices.

In certain instances this assimilative capacity is estimated and the loading is adjusted accordingly. Two such

cases are the limiting chemical load in land treatment and the oxygen demand load on watercourses.

An example of calculated loading occurs in land treatment, where the quantity of liquid waste applied to an area of land may be estimated by identifying the soil contaminant control and removal mechanisms and estimating the assimilative capacity.

A11.12.6 Loading of watercourses

Another example of loading occurs when a chemical is spilled into a watercourse, either by accidental discharge from a works or as a result of a transport accident.

The health of a watercourse such as a stream or river depends on the maintenance of sufficient dissolved oxygen (DO).

Industrial wastewater discharged into a watercourse tends to use up the oxygen in the latter, its propensity to do so being measured by its oxygen demand (OD), or more specifically its biological oxygen demand (BOD), described below. If the wastewater is hot, it also tends to raise the temperature of the watercourse. Discharge of wastewater therefore tends to deplete the oxygen in the watercourse both by virtue of its OD demand and its temperature. Reaeration processes operate to make up the dissolved oxygen deficit caused by these deoxygenation processes.

There are a number of models, described by Nemerow and Dasgupta (1991), of the effect of wastewater discharge. They include the formulation of Streeter and Phelps (1925), the method of H.A. Thomas (1948) and the correlation of Churchill and Buckingham (1956). The latter found that they were able to correlate the DO as a function of the BOD, the temperature and the flow.

A11.12.7 Biological oxygen demand

A standard method of expressing the oxygen demand is as the BOD measured under specified conditions over 5 days and at 20°C.

The solubility of oxygen in water at 20°C is 9.2 mg/l. The BOD of domestic sewage is about 200 mg/l, whilst that of some industrial wastes can be as high as 30,000 mg/l.

Another measure is the chemical oxygen demand (COD). The test for COD is quicker than that for BOD, but since in this case all the organics are oxidized, this test gives a higher reading.

A11.13 Waste Minimization

The development of loss prevention is paralleled by that of waste minimization. A large part of the latter is by inherently cleaner design (ICD), which stands in much the same relationship to the environment as inherently safer design does to safety. But in so far as waste minimization involves management commitment and management systems to deliver a systematic approach, the closer parallel is with loss prevention. Another term commonly used is clean technology.

Accounts of waste minimization are given in *Hazardous Waste Minimization Handbook* by Higgins (1989), *Hazardous Waste Minimization* by R.A Freeman (1990), *Waste Minimization Guide* by Crittenden and Kolaczkowski (1992) and by Redman (1989c), Hethcoat (1990), R. Smith and Petela (1991–), Curran (1992), Chadha and Parmele (1993) and Rossiter, Spriggs and Klee (1993).

In the United States, the waste minimization approach is actively promoted by the EPA, relevant publications being *Waste Minimization, Environmental Quality with Economic Benefits* (EPA, 1987b) and *Waste Minimization Opportunity Assessment Manual* (EPA, 1988).

A11.13.1 Waste minimization management systems

The waste minimization philosophy has been widely adopted in the process industries. As with loss prevention, success has been achieved as management has become convinced and committed and has developed effective strategies, put in place formal systems, allocated the necessary resources, including people, and created a self-reinforcing waste minimization culture.

An account of developments in the United States and elsewhere, is given by Redman (1989c), together with numerous examples of case studies and cost savings.

Basic approaches to waste minimization are to modify (1) the chemicals, (2) the process, (3) the equipment and (4) the effluent treatment. Chemicals which tend to be troublesome include toxic metals and halogenated hydrocarbons. Process modifications which may prove fruitful are replacement of (1) chemical by mechanical processes and (2) single pass processes, including rinse operations, with closed processes. Effluent treatment may be modified to recycle or recover materials.

Approaches to waste minimization are outlined in Figure A11.1. On an existing plant the first step is a waste audit.

The ways in which waste minimization may be effected are very varied. This comes across clearly from the examples quoted by Redman. They include minimization of plant washdowns, squeezing of sludges to remove water and reduce mass, design of drums which leave less residue, and so on.

Redman cites a case, described by Huisingh, in which installation of equipment to recover wastes from film development at a cost of $120,000 made annual savings of $2.6 million on silver and on developing, fixing and bleach solutions, a payback time of one month.

An account of a waste minimization programme in one company is given by Koenigsberger (1986).

A11.13.2 Process plant wastes

A review of the application of waste minimization in the process industries covering (1) the basic problem, (2) reactors, (3) separation and recycle systems, (4) process operations and (5) utilities is given by R. Smith and Petala (1991–).

In a reactor five main sources of waste are (1) low conversion, (2) unwanted by-products from the primary reaction, (3) unwanted by-products from the secondary reaction, (4) unwanted by-products from feed impurities and (5) degraded catalyst. There is often scope for reduction of such waste by the application of reaction engineering principles.

In separation processes there may be scope for waste minimization by (1) elimination of feed impurities, (2) elimination of extraneous materials used for separation, (3) recycling of waste streams and (4) additional separation of such streams.

As an illustration of the benefits of eliminating a feed impurity the authors instance the elimination of nitrogen by the use of oxygen rather than air in the oxychlorination stage of ethylene dichloride production. They describe a design of ethylene dichloride reactor which avoids carry-over of the ferric chloride catalyst and thus eliminates the need for washing and neutralization stages.

Under process operations they cover (1) start-up and shut-down, (2) product changeover, (3) equipment maintenance, (4) tank filling, (5) accidental spillages and (6) fugitive emissions. During transient operations such as start-up and shut-down product may be off specification, additional by-products may be made and recycles may not be possible. Product changeover and equipment cleaning give rise to cleaning wastes. Tank filling causes losses as vapours are forced out.

In the utilities wastes are associated particularly with combustion processes, steam generation and cooling water. All these wastes can be reduced by a design which promotes energy efficiency. In combustion methods are discussed of minimizing or dealing with oxides of sulfur and nitrogen. Other wastes to be minimized are boiler and cooling tower blowdowns.

A11.13.3 Refinery wastes

The application of waste minimization to refinery operations has been described by Hethcoat (1990) and Curran (1992).

Whereas originally waste minimization was applied mainly to the conservation of hydrocarbons, it now finds much wider application. The overall strategy involves (1) source reduction and (2) recycling as well as (3) treatment.

Some principal wastes are (1) oily materials, (2) catalyst residues, (3) spent caustic and (4) wastewaters.

Oily residues are oil-coated solids, mainly from oil–water separators, dissolved air filtration (DAF) units, heat exchanger cleanings and tank bottoms. Residues also arise in sewers from road dust materials carried in with runoff water. Waste catalysts arise from processes such as catalytic cracking, conversion of heavier products to lighter ones, reforming of gases to liquid products, and sulfur removal. Spent caustics occur as phenolic or sulfide caustics.

The incidence of wastes is highly variable from one refinery to another. Curran states that quantities of oil residues and usage of water can vary by almost two orders of magnitude.

Measures to reduce refinery wastes include use of mixers in crude oil tanks to keep solids suspended, elimination of intermediate storage tanks between units, elimination of blending tanks by use of in-line blending, minimization of surfactants which cause emulsions and promote sludges, preskimming of oil at the separators, use of pressurized air at the dissolved air flotation unit to give a more concentrated sludge, reprocessing of oily residues in suitable refinery units such as a coker, paving of process areas to reduce dust and sweeping of roads for the same purpose.

At the utilities measures taken include maximization of air cooling, use of a closed cooling water system and reduction of solids in the boiler blowdown water.

Segregation also has a part to play. Curran describes segregation of phenolic and sulfide spent caustics, Hethcoat provision of three separate sewer systems for non-oily liquids and one for oily ones.

Hethcoat discusses the identification of options for waste minimization, under the source reduction, recycling and treatment heads, giving as illustrations oily wastewater from separator bottoms and wastes from empty drums.

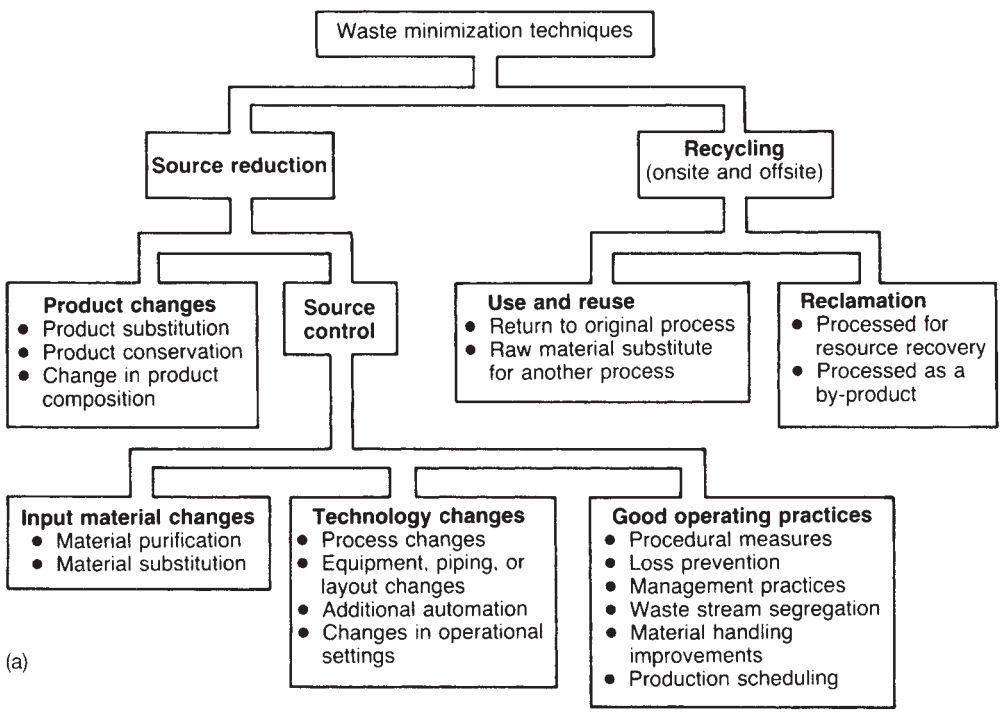

Figure A11.1 *Waste minimization: (a) techniques; and (b) assessment procedure (Environmental Protection Agency; reproduced by permission of Gower Press)*

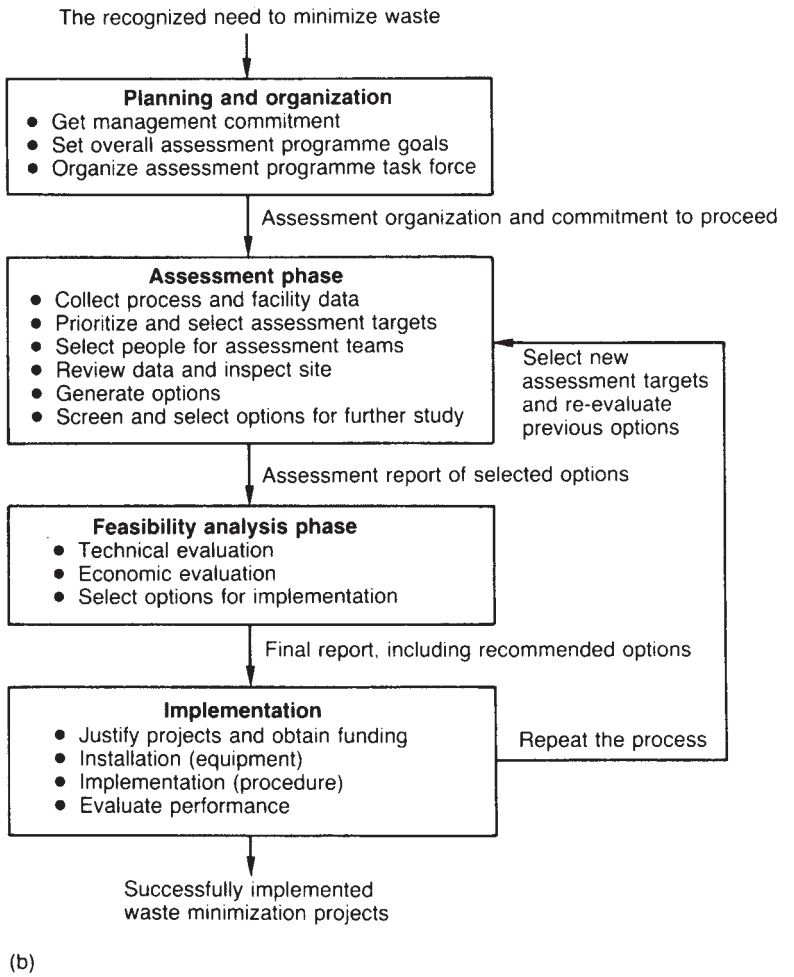

Figure A11.1 *Continued*

A11.13.4 Process integration

Waste minimization may be addressed in terms of process integration. The treatment by R. Smith and Petala (1991), just described, approaches the problem from this viewpoint. Another account is that of Rossiter, Spriggs and Kell (1993).

A11.13.5 Center for Waste Reduction Technology

The AIChE has set up the Center for Waste Reduction Technology (CWRT), a sister centre to the CCPS. It is described by L.L Ross (1991).

A11.14 Gaseous Effluents

Processes tend to generate a number of gaseous effluents which include impurities entering in the feeds, notably nitrogen in process air and air dissolved in liquid feeds; unwanted gaseous products from reactions; gases from purges such as that in the flare stack; and gaseous products of combustion.

Accounts of gaseous effluents, and the technologies of dealing with them, are given in *Air Pollution Handbook* by Magill, Holden and Ackley (1956), *Atmospheric Pollution* by Meetham (1968), *Air Pollution* by Scorer (1968), *Air Pollution Control* by Strauss (1971–), *Gas Purification Processes for Air Pollution Control* by Nonhebel (1972), *Pollution in the Air* by Scorer (1973), *Compilation of Air Pollutant Emission Factors* by the EPA (1978a), *Fundamentals of Air Pollution* by Stern *et al.* (1973), *Dust Control and Air Cleaning* by Dorman (1974), *Gas Cleaning for Air Quality* by Marchello and Kelly (1975), *Air Pollution* by the Open University (1975a), *Air Pollution* by Seinfeld (1976), *Air Pollution Control Equipment* by Theodore and Buonicore (1976), *Approaches to Controlling Air Pollution* by Friedlander (1978), *Reference Book* by the National Society for Clean Air (NSCA) (1978), *Industrial Air Pollution Handbook* by A. Parker (1978), *Air Pollution Impacts and Control* by Downey and Ni Uid (1979), *Air Pollution Control* by Hesketh (1979), *Air Pollution Control Engineering* by Licht (1980), *Paniculate Air Pollution* by Theodore, Sosa and Fajardo (1980), *Air Pollution* by E. Weber (1982), *Hazardous Air*

Emissions from Incineration by Brunner (1985), *Environmental Pollution and Control* by Veselind, Peirce and Weiner (1990), *Process Engineering and Design for Air Pollution Control* by Benitez (1993) and *Gas Processing: Environmental Aspects and Methods* by Speight (1993).

A11.14.1 Types of gaseous effluent

A gas effluent stream may consist of a gas which is itself noxious or of a non-noxious carrier gas which contains noxious impurities. The impurities may be gases or vapours, liquid droplets or solid particles.

Some principal gaseous effluents which require to be treated are (1) hydrogen sulfide, (2) carbon dioxide, (3) sulfur-containing gases SO_x and (4) nitrogen-containing gases NO_x. Hydrogen sulfide and carbon dioxide are commonly referred to as acid gases.

Hydrogen sulfide figures prominently in oil handling and refining. Carbon dioxide is the main acid gas product of combustion and also arises from oil refining and chemical operations. Sulfur oxides SO_x, essentially SO_2, are generated in combustion of fuel containing sulfur and in oil refining and chemical operations. Nitrogen oxides NO_x, essentially NO and NO_2, arise as so-called fuel-bound NO_x and thermal NO_x from combustion processes.

A11.14.2 Gaseous effluent control

Waste minimization may be applied to reduce the quantities of the gaseous effluents to be treated and the concentration of noxious components in these effluents, and to facilitate any treatment necessary.

A principal application of this approach which has long been practised is desulfurization of coal prior to combustion, as described below.

A11.14.3 Gas cleaning

The main methods of removing noxious gases or vapours from a gas stream are absorption, adsorption, reaction to a solid product and reaction with solids.

Absorption processes for removal of hydrogen sulfide and carbon dioxide are the amine family of processes, including the Girbitol process using ethanolamine, and the carbonate family, including the Benfield process using potassium carbonate, and for removal of hydrogen sulfide the Stretford process using sodium carbonate.

Hydrogen sulfide is removed in the Claus process by thermal and then catalytic reaction to sulfur. Hydrogen sulfide is also removed by reaction with iron oxide, a traditional gasworks process.

Processes for removal by absorption of sulfur dioxide include the Battersea process. Prior to combustion sulfur dioxide may be removed by fuel desulfurization. In its application to coal, this approach is also known as clean coal technology. In the process sulfur dioxide may be removed by reaction with limestone.

Absorption in oil is a traditional method of removing acid gas and hydrocarbons.

Flue gas desulfurization (FGD) comprises a group of techniques. One option is desulfurization of the fuel prior to combustion. A traditional post-combustion method is the removal of sulfur dioxide by the use of lime or limestone in 'wet scrubbers'. Advanced post-combustion methods involve contacting the gas with a sorbent such as lime either by in-stack injection or by injection into separate in-line vessels.

There are also combined processes for removal of both sulfur dioxide and nitrogen oxides, in which FGD is combined with a denitrification step. One method of removing nitrogen oxides is catalytic reaction with injected ammonia.

There are a large number of other gas cleaning processes. Outlines of about 80 are given by Speight (1993). Process flow diagrams are given periodically in *Hydrocarbon Processing*.

Removal of gaseous components may also be effected by the use of membrane processes.

Principal methods for the removal of particles include cyclones, fabric filters and electrostatic precipitators.

A review of technologies for acid gas removal in support of the UK programme is given in *Acid Emissions Abatement Technologies* by the DoE (1991).

A11.14.4 Smog reduction

A number of industrialized countries have suffered from serious air pollution in the form of smog. An account of the 'killer smog' in London in 1952 is given below.

In the United Kingdom, considerable progress has been made in reducing this form of air pollution. Thus in the City of London between 1955 and 1974, for example, the annual average concentrations of smoke and sulfur dioxide near the ground were reduced as follows (Warner, 1976):

	Concentration of smoke ($\mu g/m^3$)	*Concentration of SO_2* ($\mu g/m^3$)
1955	≈195	230
1974	≈40	110

A11.14.5 Tall chimneys

The use of tall chimneys for avoidance of pollution in the immediate vicinity of a plant is a traditional practice. The drawback is that noxious effluents may be spread, albeit in dilute form, further afield.

An account of the practice of the Alkali Inspectorate in relation to tall chimneys has been given by Ireland (1984).

The topic has also been discussed by Perriman (1986).

A11.14.6 Emission bubble

An approach to air pollution control which in principle allows a company to adopt the most economic trade-offs is that of the 'bubble', in which all emissions from sources within the bubble are treated as if they were from a single controllable source. A formal statement of such a policy is that alternative methods of control are allowed provided it can be demonstrated that they are substantially equivalent, the criterion being the equivalence of the emissions leaving the bubble. The bubble concept was adopted by the EPA in 1979. It had a mixed reception, being welcomed in some cases by industry, but not always by the states. An account is given by Weismantel and Parkinson (1980).

A11.15 Liquid Effluents

The liquid effluents from a process plant include not just those shown as such on the flowsheet for the basic process, but a variety of other liquid flows ranging from washwater to rainwater runoff.

Accounts of liquid effluents, and the technologies of dealing with them, are given in *Biological Waste Treatment* by Eckenfelder and O'Connor (1961), *Industrial Wastewater Control* by Gurnham (1965), *Industrial Water Pollution* by Eckenfelder (1966), *Water and Waste Water Engineering* by Fair, Geyer and Okun (1966), *Aqueous Wastes from Petroleum and Petrochemical Plants* by Beychok (1967), *Liquid Waste of Industry* by Nemerow (1971), *Water Pollution* by Newsom and Sherratt (1972), *Waste Water Systems Engineering* by H.W. Parker (1972), *Clean and Dirty Water* by the Open University (1975b), *Handbook of Advanced Wastewater Treatment* by Gulp, Webster and Gulp (1978), *Wastewater Treatment* by Sundstrom and Klei (1979), *Wastewater Treatment and Disposal* by Arceivala (1981), *Biological Treatment of Waste Water* by Winkler (1981), *Handbook of Wasterwater Treatment Processes* by Vernick and Walker (1982), *Removal of Metals from Wastewater* by Cushie (1984), *Hazardous Waste Management Engineering* by E.J. Martin and Johnson (1987), *Environmental Pollution and Control* by Vesilind, Peirce and Weiner (1990), *Wastewater Engineering* by Metcalf and Eddy Inc. (1991) and *Industrial and Hazardous Waste Treatment* by Nemerow and Dasgupta (1991).

The modelling of the hydraulics of, and dispersion in, rivers, estuaries, etc. is described in *Hydraulic Behaviour of Estuaries* by McDowell and O'Connor (1977); *Groundwater* by Freeze and Cherry (1979); *The Mathematics of Hydrology and Water Resources* by Lloyd, O'Donnell and Wilkinson (1979); *Practical Aspects of Computational River Hydraulics* by Cunge, Holly and Verwey (1980); *Hydraulic Modelling* by Kobus (1981); *Models in Hydraulic Engineering* by Noak and Cabelka (1981); and also in certain texts of computational fluid dynamics.

A11.15.1 Types of liquid effluent

Liquid effluents from process plants are fluids from (1) the process, (2) the cooling system, (3) the process ancillary operations, (4) the sanitary system and (5) the rainwater runoff. The process ancillary operations are those such as cleaning and washing.

A proportion of the fluids from the process are liquids which are either non-aqueous or high concentration aqueous wastes. The rest are wastewaters containing oils and chemicals at lower concentrations.

A detailed review of liquid wastes from different industries, including the oil and chemical industries, is given by Nemerow and Dasgupta (1991). They cover organic chemicals; toxic chemicals; acid and chloralkali wastes; formaldehyde wastes; pesticides wastes; and wastes from the energy, fertilizer, phosphates, plastics and rubber, soap and detergent and explosives industries.

A11.15.2 Wastewater control

Wastewater requires a degree of treatment before it is discharged to receivers such as municipal systems or watercourses. There are a number of prior measures which may be taken to minimize the extent of the treatment required. These measures include (1) volume reduction, (2) strength reduction and (3) flow equalization and proportioning.

Waste minimization may be applied to reduce the volume of wastewater either by generating less in the first place or by reusing it. It may also be applied to keep down the concentration of contaminants in the wastewater. Segregation of wastewaters also has a role to play in reducing the volume to be treated or facilitating treatment.

Flow equalization involves the control of flows discharged to smooth out plant flow fluctuations and flow proportioning the control of discharge flows to match those in the municipal system or the watercourse.

A11.15.3 Wastewater treatment

Complete treatment of wastewater is typically classified as follows: (1) wastewater pretreatment, or conditioning, (2) primary treatment, (3), secondary treatment, (4) tertiary treatment, (5) sludge treatment and (6) liquid and sludge disposal.

Wastewater pretreatment processes are screening and grit removal and neutralization.

Primary treatment of wastewater involves removal of suspended solids by (1) sedimentation and (2) flotation. Either process may be operated with chemical addition. Removal of oil droplets can be effected by gravity separation.

Solids also occur in colloidal form, and the methods of dealing with them are often termed intermediate treatment. They include (1) chemical coagulation, (2) charge neutralization coagulation and (3) adsorption. The second of these involves coagulation by neutralization of the electric charge.

Secondary treatment processes deal with dissolved organic materials and comprise a range of mainly biological treatments. These processes are (1) aerobic or (2) anaerobic.

There is a wide variety of aerobic processes including (1) lagooning, (2) activated sludge, (3) modified aeration, (4) dispersed growth aeration, (5) high rate aerobic treatment, (6) contact stabilization, (7) trickling filtration, (8) biological discs, (9) mechanical aeration, (10) wet combustion and (11) spray irrigation. Holding in lagoons is used to effect biological degradation. Activated sludge involves oxidation by floes from suspended and colloidal solids, the sludge concentration being controlled by a recycle. Modified aeration is a modification of the activated sludge method. Dispersed growth aeration is a variant, which does not involve the use of floes. Contact stablization, or biosorption, is another modification of the activated sludge method. High rate aerobic treatment, or total oxidation, is another sludge process but with a higher sludge return rate. Trickle filtration and biological discs involve oxidation by slimes, the substrate being in the one case a packed bed and in the other rotating discs. Mechanical aeration involves sparging air into the liquid. Wet combustion, or wet air oxidation, is described below. In spray irrigation the liquid is sprayed onto land with aerobic conditions maintained to a certain depth, and is thus both a treatment and a disposal.

Anaerobic digestion takes place in closed vessels in the absence of air. Loadings are low and residence times long. It is most suited to small throughputs of liquids with high concentrations of readily oxidized organics and is used mainly for sludges rather than liquid wastes.

Other methods of removing organics include steam stripping and solvent extraction.

Tertiary treatment processes remove dissolved inorganic materials. They involve both chemical treatments and physical separation using a variety of unit operations. Chemical methods include (1) coagulation and precipitation and (2) oxidation and reduction reactions. Unit operations utilized are (1) evaporation, (2) adsorption,

(3) ion exchange, (4) reverse osmosis and (5) electrodialysis. Adsorbents used are activated carbon and polymers.

Sludge treatment methods include (1) digestion, (2) conditioning, (3) thickening, (4) dewatering and (5) drying. Digestion may be aerobic or anaerobic, utilizing some of the methods already described. Conditioning is effected using chemical and thermal methods. Thickening may be done in (1) gravity, (2) flotation or (3) centrifugal thickeners. Methods of dewatering are (1) vacuum filtration, (2) filter press dewatering, (3) belt filter dewatering and (4) centrifugal dewatering.

A11.15.4 Wet air oxidation

For water contaminated by small amounts of organic compounds a method of treatment which is often attractive is the wet air oxidation (WAO) process, also referred to as wet combustion. Accounts are given by Flynn (1979), Wilhelmi and Knopp (1979), Laughlin, Gallo and Robey (1983), Baillod, Lamparter and Barna (1985), Heimbuch and Wilhelmi (1985), E.J. Martin and Johnson (1987) and Nemerow and Dasgupta (1991).

The aqueous effluent to be treated is pumped to a high pressure, passed through a heater to heat it part way to the reaction temperature, then into a reactor vessel where compressed air is blown in and where the resultant exothermic reaction raises the liquid to its reaction temperature, finally out through a cooler to a separator where the oxidized liquid is taken off the bottom and nitrogen, carbon dioxide, steam, etc., off the top. Typical reaction temperatures are in the range 275–320°C. There are numerous variations on this basic process, including the use of a catalyst.

Wet air oxidation can degrade most industrial organic compounds. The reduction, or dilution, factors obtainable are generally good, though higher in some cases than others. Wilhelmi and Knopp list factors in the range 12–4200.

A11.15.5 Wastewater receivers

Wastewater treated to a suitable quality may be discharged to the municipal sewage system, to watercourses such as streams or rivers, or to land.

Some options available in principle are discharge of (1) raw industrial and sanitary wastes to the municipal system, (2) partially treated industrial and sanitary wastes to the municipal system, (3) completely treated industrial and sanitary wastes to the municipal system, partially treated industrial wastes to a watercourse, completely treated industrial wastes to a watercourse, and (6) completely treated industrial wastes to land. These options are discussed in detail by Nemerow and Dasgupta (1991).

A11.15.6 Deep well disposal

A quite different option for dealing with liquid wastes is deep well injection. Accounts are given by M.E. Smith (1979) and Nemerow and Dasgupta (1991).

This form of disposal has been used particularly in the United States, subject to strict controls and permitted only if no better method is available.

The formation selected to receive the waste is one below the levels holding potable water. The basic technology used derives from oil and gas production. The receiving formation may first be given a conditioning treatment. In order to eliminate solids, the waste is pretreated to remove suspended solids. In addition, a buffer solution such as dilute salt water may first be injected to prevent precipitation from the waste liquid.

A11.15.7 Sludge disposal

Methods of disposal of sludge from wastewater treatment include lagooning, landfill, incineration and sludge barging.

Lagooning involves digestion and is in effect a treatment process which shades into storage or disposal. Landfill may take the form of area landfill or trench landfill. Incineration is considered below.

Sludge barging has been used but tends to involve problems of sludge rising to the surface or being washed ashore, and in many cases has been discontinued.

A11.16 Hazardous and Solid Wastes

In addition to gaseous and liquid effluents, it is also necessary to deal with hazardous and solid wastes, including sludges and residues.

Accounts of hazardous wastes and solid wastes, and the methods of waste disposal, are given in *Disposal of Solid Toxic Wastes* by Key (1970), *Solid Wastes* by Mantell (1975), *Waste Recycling and Pollution Control* by Bridgewater and Mumford (1979), *Toxic and Hazardous Waste Disposal* by Pojasek (1979), *Handbook of Industrial Waste Disposal* by Conway and Ross (1980), *Design of Land Treatment Systems for Industrial Waste* by Overcash and Pal (1980), *Waste Management* by Woolfe (1981), *Hazardous Material Spills Handbook* by G.F. Bennett, Feates and Wilder (1982), *Hazardous Waste Processing Technology* by Kiang and Metry (1982), *Risk Assessment of Hazardous Waste Sites* by Long and Schweitzer (1982), *The Scientific Management of Hazardous Wastes* by Cope, Fuller and Willetts (1983), *Handbook of Industrial Residues* by Dyer and Mignone (1984), *Hazardous Air Emissions from Incineration* by Brunner (1985), *Handbook of Laboratory Waste Disposal* by Pitt and Pitt (1985), *Hazardous Waste Management* by Dawson and Mercer (1986), *The Solid Waste Handbook* by W.F. Robinson (1986). *Hazardous Waste Management Engineering* by E.J. Martin and Johnson (1987), *Handbook of Hazardous Waste Incineration* by Brunner (1989), *Environmental Impacts of Hazardous Waste Treatment, Storage and Disposal Facilities* by Salcedo, Cross and Chrismon (1989), *Emerging Technologies in Hazardous Waste Management* by Tedder and Pohland (1990), *Environmental Pollution and Control* by Veselind, Peirce and Weiner (1990), *Hazardous Waste Treatment Technologies* by Jackman and Powell (1991), *Industrial and Hazardous Waste Treatment* by Nemerow and Dasgupta (1991), *Environmental Impact Assessment for Waste Treatment and Disposal Facilities* by Petts and Eduljee (1994) and *Standard Handbook for Solid and Hazardous Waste Facility Assessment* by Sara (1994).

A11.16.1 Types of hazardous and solid waste

Hazardous and solid wastes fall into three categories (1) hazardous liquid wastes, (2) hazardous solid wastes and (3) non-hazardous solid wastes. The main concern here is with the first two of these.

A11.16.2 Hazardous waste control

The principles of waste minimization should be applied to minimize the quantity of hazardous waste and to ease the problems of handling it in treatment, storage and disposal facilities.

A11.16.3 Hazardous waste treatment, storage and disposal

Hazardous wastes may be stored or sent to ultimate disposal, either with or without prior treatment.

Methods of dealing with solid hazardous wastes include the use of (1) incineration, (2) landfill, (3) waste piles and (4) storage. Incineration, landfill and land treatment, which are usually treated as methods of ultimate disposal, are discussed further below.

A waste pile, or tip, may be regarded as storage or disposal, depending on the acceptability of its being permanent. Storage proper is typically in drums.

There are a number of methods of stabilization, fixation, solidification and encapsulation available for the treatment of residues and sludges, many developed originally for radioactive wastes. An account is given in E.J. Martin and Johnson (1987).

For liquid hazardous wastes methods include the use of (1) incineration, (2) surface impoundment, (3) land treatment and storage. Incineration and land treatment are both methods of ultimate disposal.

Surface impoundment (SI) or lagooning, has been discussed above. The liquid may be aerated or non-aerated. As stated, a lagoon may be regarded as a form intermediate between treatment, storage and ultimate disposal.

Storage is mainly in storage tanks, which may be open, open with external floating roof, closed with fixed roof and closed with internal floating roof. The vapour space may be inerted.

A11.16.4 Incineration

A prime method of dealing with hazardous waste is incineration. It is used for solid, liquid and sludge or residue wastes.

Treatments of incineration are given in *Handbook on Incineration* by Cross (1972), Incineration by Brunner (1987) and *Handbook of Hazardous Waste Incineration* by Brunner (1989) and by Novak and Pfrommer (1982), Grumpier and Martin (1987), Wiley (1987), Vervalin (1990), Veselind, Peirce and Weiner (1990) and Nemerow and Dasgupta (1991). Particular aspects of incineration discussed are the decision whether or not to use incineration by Haseltine (1992), testing of incinerators by Monroe (1983b), off-normal emissions from incinerators by Zeng and Okrent (1991), problems with incinerators by Ready and Schwab (1980), role of incineration in remedial actions by H.M. Freeman (1984) and dioxin problems by Beychok (1987). Plasma arc incineration is described by Ondrey and Fouhy (1991).

Incineration is a preferred method of the EPA.

Incineration is commonly carried out in dedicated equipment. Types of incineration equipment are described by Novak and Pfrommer (1982) and Brunner (1989). Alternatively, in some instances items of process plant may be used as incinerators. Feeley (1984) describes the use of boilers for this purpose.

Incineration of solid wastes is done in open pits, rotary kilns and multiple hearth furnaces.

Ideally, the products of combustion from an incinerator are carbon dioxide and water vapour. In practice, the gaseous effluents may contain more noxious gases due to (1) incomplete combustion and (2) components in the waste. Some effluents which are troublesome in incinerators include sulfur and nitrogen oxides, metals and dioxins.

There are three main factors which determine the completeness of combustion: time, turbulence and temperature – the three Ts. The first two are set by the design of the system, leaving only the temperature as an operating variable. The temperature is controlled by adjusting the air/fuel ratio.

If the effluent gas falls below the concentration at which it can sustain combustion before destruction is sufficiently complete, one option may be to use an afterburn by injecting additional fuel gas. Alternatively, it may be necessary to pass the effluent gas through a scrubber. Thus an incinerator produces both gaseous effluent and ash, and may produce a liquid effluent also.

Combustion products which have proved particularly troublesome are the dioxins, notably TCDD. TCDD is a product in virtually all combustion processes, including barbecues. The production of TCDD at incinerators has been the subject of much concern. Controls are such that operators are required to keep the concentration of TCDD measured in the adjacent area vanishingly small.

Incineration has the advantages that it is an established process, can handle a wide range of wastes, can accept high throughputs and is economical in its requirement for land, especially relative to landfill. Disadvantages are the comparatively high cost and the effluents generated.

Hazardous wastes in sludge form are incinerated in rotary kilns, fluidized beds and multiple hearth furnaces.

Incineration is also practised for liquid wastes, provided they are at least partially combustible. A liquid waste may be categorized as combustible, partially combustible or non-combustible. A waste with a calorific value below about 18,500 kJ/kg is regarded as only partially combustible. Where the properties allow, liquid wastes are generally injected through an atomizer.

A11.16.5 Landfill

Another principal method of disposing of hazardous waste is landfill (LF). This involves depositing the hazardous waste on land which is then covered over. Both area and trench systems are used.

Accounts of the landfill option are given in *Landfill Technology* by Crawford and Smith (1985) and by A. Parker (1982), G.W. Dawson (1983), J.B. Cook (1984), Loehr (1987), Veselind, Peirce and Weiner (1990) and Nemerow and Dasgupta (1991).

The main problem with landfill is the leaching out of hazardous substances and transport of these into watercourses. Leachate management is therefore essential if landfill is used.

This aspect is discussed in *Groundwater Contamination from Hazardous Wastes* by E.F. Wood (1984) and by Hoppe (1984a), Shuckrow, Touhill and Pajak (1987), Ahlert and Kosson (1990) and Batchelor (1990).

There are a number of options for dealing with leachates. The first should be the application of waste minimization to eliminate or reduce potential leachates. The site can be designed to minimize the generation and escape of leachates, which includes diversion of surface waters and provision of barriers such a liners and trenches. Leaching may be reduced and/or leachate treatment simplified by segregation of wastes. Stabilization methods may be used to minimize leaching. The leachates may be collected and treated.

Economic estimates generally show landfill to be appreciably cheaper than incineration but the potential for

migration of leachates into watercourses can be a serious problem which may well alter the balance of advantage.

A description of an landfill project associated with the chemical industry is given by Anon. (1988k).

A11.16.6 Land treatment

Land treatment involves spraying the liquid on land, exploiting the assimilative capacity of the soil.

Accounts are given in *Design of Land Treatment Systems for Industrial Wastes* by Overcash and Pal (1980) and by Loehr (1987) and Nemerow and Dasgupta (1991).

A11.16.7 Contract disposal

The producer of hazardous wastes often has the option of having them removed by a specialist contractor. Given the number and severity of problems often arising with such wastes, this can be an attractive option.

The main point to be made here is that regulatory controls are now such that there is a responsibility of the producer to ensure that the wastes are properly disposed of. The producer who hands over the wastes to a 'cowboy' contractor can expect trouble.

A11.16.8 Hazardous waste facility siting

A hazardous waste treatment, storage and disposal facility is liable to pose a more serious siting problem than the generality of process activities. In the United States more than half the applications for such developments fail. An account of the siting problem of TSDFs, with emphasis on the public consultation process, is given by Barclay (1987).

A11.16.9 Hazardous waste facility management

A hazardous waste facility needs to be managed. Incineration, landfill and storage all involve their characteristic management problems.

Active management is required of the basic activity and of the monitoring of effluents from the treatment processes, of spills and other escapes, and of the concentrations of chemicals in the immediate environment.

For landfill, leachate management assumes particular importance. An account is given by Shuckrow, Touhill and Pajak (1987).

A11.16.10 Hazardous waste facility reclamation

In the past hazardous waste was frequently deposited in an uncontrolled manner, with the consequence that many countries have a large number of waste disposal sites, which present major problems in establishing ownership and responsibility, reasserting control and effecting reclamation.

Accounts of land decontamination and reclamation are given in *Reclamation of Contaminated Land* by the SCI (1980), *Remedial Action Technology for Waste Disposal Sites* by Rogoshenski, Boyson and Wagner (1983) and by Wagner *et al.* (1986), *Evaluation of Remedial Action Unit Operations at Hazardous Waste Disposal Sites* by Ehrenfeld and Bass (1984), *Contaminated Land: Reclamation and Treatment* by M.A. Smith (1985), *Dioxin Containing Wastes: Treatment Technologies* by Arienti *et al.* (1988), *Environmental Remediation* by Vandegrift, *Reed and Tasker* (1992) and *Remedial Processes for Contaminated Land by Pratt* (1993).

As described earlier, under CERCLA 1980, or Superfund, the EPA is charged with supervision of site clean-up and federal funds are available for this. An account is given in *Superfund Handbook* by Sidley and Austin (1987).

A11.16.11 Ocean dumping and incineration

A quite different solution to the waste disposal problem is to dump or incinerate the waste at sea.

Accounts of these options are given in *Ocean Dumping of Industrial Wastes* by Ketchum, Kester and Park (1981) and *Ocean Disposal Systems for Sewage Sludge and Effluent* by the NRC (1984) and by Finnecy (1982), Remirez (1982), Crumpler and Martin (1987), Ditz (1988) and Nemerow and Dasgupta (1991).

Essential safeguards in any system of ocean dumping are those substances which are highly toxic and persistent and do not disperse sufficiently are not dumped and that for those materials which are the assimilative capacity of the area should not be overloaded.

Vessels used for ocean incineration include *Matthias I, II* and *III*, Vesta and Vulcanus. Of these the MT Vulcanus, a cargo ship converted in 1972 into a chemical tanker with two large incinerators, is perhaps the best known and documented. These incinerator vessels are described by Finnecy (1982).

Both ocean dumping and ocean incineration are governed by the marine pollution conventions. The Convention for the Prevention of Marine Pollution by Dumping of Wastes and Other Matter 1972 (the London Dumping Convention (LDC)) governs ocean dumping, and provisions on ocean incineration have been added to this.

A review of the operation of this convention is given by the IMO (1991 IMO-532). The unregulated dumping which used to take place has largely stopped, the dumping of certain wastes has been eliminated altogether or is being phased out and stringent programmes are in place to assess the need for and impact of ocean disposal.

A11.16.12 Underground storage tanks

It is convenient at this point to mention briefly the problem of leaking underground storage tanks (USTs) and pipework. The use of underground storage is widespread but in recent years there has been growing concern, particularly in the United States, over leaks from such installations. Accounts are given by G. Parkinson (1987) and Stone (1987).

Underground storage tanks are considered in Chapter 22.

A11.17 Fugitive Emissions

Fugitive emissions occur on process plants from diffuse continuous sources such as valves, seals and flanges; from equipment which operates intermittently such as pressure relief valves; from the 'breathing' of storage tanks; and from activities such as draining and sampling and the opening up of equipment during operations or for maintenance.

Accounts of fugitive emissions are given in *Fugitive Emissions of Vapour from Process Plant Equipment* by the BOHS (1984 TG3) and *Health Hazard Control in the Process Industries* by Lipton and Lynch (1987).

The topic of fugitive emissions can be considered under the following heads: (1) emission sources, (2) emission control, (3) occupational health effects and (4) environmental effects.

Fugitive emission sources, emission control and occupational health aspects are discussed in Chapters 15, 12 and 18, respectively.

The environmental effect which initiated concern over fugitive emissions was smog, originally in Los Angeles.

The EPA has been active to reduce fugitive emissions, as instanced by *Compilation of Air Pollutant Emission Factors* (EPA, 1973), *VOC Fugitive Emissions in Synthetic Organic Chemical Manufacturing Industry – Background Information for Promulgated Standards* (EPA, 1982) and *Standards of Performance for New Stationery Sources Equipment Leaks of VOC, Petroleum Refineries and Synthetic Organic Chemical Manufacturing Industry* (EPA, 1984).

A11.18 Odours

Another form of pollution is noxious odours. The concentration at which a substance can cause an odour can be very low, and certainly well below the levels of the air quality standards set to prevent air pollution.

Accounts of odours and their control are given in *Methods of Air Deodorisation* by Summer (1963), *Odour Pollution of Air* by Summer (1971), *Human Response to Environmental Odors* by Turk, Johnston and Moulton (1974) and *Odour Control* by Valentin and North (1980) and by Oelert and Florian (1972), Amoore and Hautala (1983), Ruth (1986), Langenhove, Lootens and Schamp (1988), Miedema and Ham (1988), Valentin (1990), Nagy (1991), A.M. Martin *et al.* (1992) and Sober and Paul (1992).

A11.18.1 Regulatory controls

Regulatory controls on odours are at present fairlyrudimentary. In the UK, odours are statutory nuisances under the EPA 1990 and subject to control by the local authorities.

In the USA the Clean Air Amendments 1990 provide a framework within which controls on industrial odours may develop.

In the Netherlands, the authorities have taken initiatives, described below, aimed at putting odour control on a more scientific basis.

A11.18.2 Odour-generating activities

Many of the activities which give rise to noxious odours lie outside the mainstream process industries, being such as agricultural activities; animal waste rendering and leather tanning; fishmeal processing; sewage and effluent treatment and sludge disposal; brickmaking; and so on. However, petroleum refining and chemical manufacture do generate odours as do coke ovens and tar distillation; pulp and paper processing; plastics and rubber processing; soap and detergent manufacture; and fermentation processes associated with brewing or pharmaceutical manufacture.

A11.18.3 Odour measurement

A fundamental approach to odour measurement would appear to require that (1) the components responsible for the annoyance are identified, (2) their concentrations are measured and (3) their contributions, severally and possibly in combination, are quantified. This is a tall order. It is not surprising therefore that the most practical way of measuring an odour is still the human nose.

The method commonly used is to assemble an odour panel of suitably selected individuals and to use the technique of dynamic dilution. This involves diluting the original sample containing the odour with progressively larger quantities of clean air until 50% of the panel can no longer detect the odour. The results obtained are sensitive to the experimental conditions and can vary by a factor of 10 or more.

The concentration at which the odour is no longer detectable to 50% of the panel is designated as one odour unit (ou). The number D of dilutions required to get down to this concentration is a measure of the odour concentration of the original sample. Thus if dilution by a factor of 2000 is required ($D = 2000$), the odour concentration of the sample is 2000 ou.

A11.18.4 Odour thresholds

There are available a number of compilations of odour thresholds. They include the collections in Standardised Human Olfactory Thresholds by Devis (1990) and by Leonardos, Kendall and Barnard (1969), Amoore and Hautala (1983) and Ruth (1986).

A11.18.5 Odour sources

Odour sources may take the form of point sources, area sources, line sources or fugitive emissions. An area source is exemplified by an open tank containing liquid and a line source by a works transport route. A discussion of such sources is given by Sober and Paul (1992).

Fugitive emission sources, with typical emission rates, are listed in EPA AP-42 Compilation of Air Pollutant Emission Factors (1985).

A11.18.6 Odour dispersion

The dispersion of an odour may be modelled using passive gas dispersion models, which are described in Chapter 15.

The use of such models is discussed by Sober and Paul (1992). They refer in particular to the various EPA models such as ISC and Inpuff.

Models specific to odours, developed at Warren Spring Laboratory (WSL), have been described by Valentin and North (1980) and Valentin (1990). For short-range dispersion from a ground level source, the following simplified relation provides a rough guide:

$$Dr = 7E/UX^2 \qquad \text{[A11.18.1]}$$

with

$$E = D_e F \qquad \text{[A11.18.2]}$$

where D_e is the odour concentration at the emission point (ou), D_r is the odour concentration at the receptor point (ou), E the contaminant, or odour, emission flow (m^3/s), F the total emission flow (m^3/s), U the wind speed (m/s) and X the distance between the emission and receptor points (m).

Other WSL models relate to the distance at which complaints can be expected. For ground level emissions

$$d_{max} = (\phi E)^{0.6} \qquad \text{[A11.18.3]}$$

with

$$E = DF \qquad \text{[A11.18.4]}$$

where d_{max} is the maximum distance at which complaints can be expected (m), D the dilution factor (ou) and ϕ a factor. The value of ϕ is 2.2, which is the geometric mean of the uncertainty range 0.7–7. The equation can be used for emissions for chimneys provided that d_{max} is 40–50 times the effective chimney height.

An equation is also given for the effective chimney height for nuisance-free dispersion:

$$H_e = (\psi E)^{9.5} \qquad [A11.18.5]$$

where H_e is the effective chimney height (m) and ψ a factor. The value of ψ is 0.1, which is close to the geometric mean of the uncertainty range 0.05–0.15. The actual chimney height is obtained by subtracting the plume rise from the effective chimney height.

The last two equations encompass not just dispersion but also human response. The ability to correlate the complaints distance, albeit with a wide uncertainty range, by extrapolation from panel experiments to field assessments on the basis of the dilution factor D is encouraging for the development of a generalized approach.

A11.18.7 Odour control strategy

The outline of an odour control strategy is given by Valentin (1990). A necessary preliminary is to establish that it really is your plant which is the source of the problem. The odour sources should be identified. If practical, an odour source should be eliminated. For those which are not eliminated, ventilation, local where possible, should be used to remove and collect the contaminated air. If the air stream contains mist or dust, these should be removed. This air should then be treated using one of the methods described below.

A11.18.8 Odour control techniques

There are a number of methods available for treating air containing air contaminated with odours. Accounts are given by Valentin (1990) and A.M. Martin *et al.* (1992).

Martin *et al.* describe a wide range of techniques, including (1) incineration, (2) adsorption, (3) absorption, (4) condensation, (5) advanced oxidation and (6) biological treatment. Incineration may be carried out in a thermal incinerator, a catalytic incinerator, a flare, a boiler or a process heater. Adsorption is commonly by carbon. Advanced oxidation involves treatment with an oxidizing agent such as ozone using UV radiation to effect photochemical stimulation of the reaction. Biological treatment may be by a biological scrubber or a biological filter. The authors give examples of the efficiencies obtained with the different methods and guidance on selection of a method.

The options available are also discussed by Valentin, who deals in particular with thermal and catalytic incineration, adsorption, absorption and biological filters.

A11.18.9 Odour impact on community

Studies of the impact of odours on the neighbouring community have been described by van Langenhove, Lootens and Schamp (1988) and Miedema and Ham (1988).

The former study involved the investigation of odour from an animal rendering plant. A questionnaire was used to assess the proportion of persons annoyed by the odour at different distances. The effective limit of the nuisance was found at about 600 m. The authors then used a passive gas dispersion model to work back to the effective strength of the source, which they assessed as 68×10^6 ou/h.

Miedema and Ham describe field studies conducted by TNO in support of Dutch government plans for odour control. The authors emphasize the importance of the method used to assess the dilution factor D. They describe and advocate the use of the TNO 'sniffing car' method.

These authors too made use of a questionnaire to determine the relation between the distance and the proportion of persons annoyed by the odour. They correlate their results in terms of the C_{98} value, or the 1 hour average concentration which is exceeded only 2% of the year, and of the probability of being annoyed, expressed as a Z score, from the normal distribution, and obtain the relation

$$Z = 1.19 \log C_{98} - 2.16 \qquad [A11.18.6]$$

They suggest that a correlation of this type has potential as the basis for standards for odour control.

A11.19 Transport

A proportion of the chemicals produced are consumed on site, but a large proportion are transported from the site.

The transport of chemicals is discussed in Chapter 23 and emergency planning for such transport in Chapter 24.

Such transport, whether by vehicle or a pipeline, has the potential for an accident resulting in a spill. Spills are discussed in the following section.

A11.19.1 Transport of hazardous wastes

There is also the separate question of the transport of hazardous wastes. This has been a severe problem area due to the prevalence of illicit practices in transport and disposal, described in *Laying Waste* by M. Brown (1981). The transport of hazardous wastes, and of material from spill incidents, is discussed by R.J. Buchanan (1982), Bromley and Finnecy (1985) and Colen (1987b).

A11.20 Spills

Another way in which pollution can occur is by a liquid spill, either at a fixed site or during transport, including by pipeline.

Spills are treated in *Hazardous Chemicals – Spills and Waterborne Transportation* by Weidenbaum (1980) and *Hazardous Material Spills Handbook* by G.F. Bennett, Feates and Wilder (1982) and by Lindsey (1975) and Feates (1978).

The variety of situations which can occur and of the responses are illustrated in the numerous case histories described in the conference series *National Conference on Hazardous Materials Spills* in the United States.

In the United States, hazardous materials spills involve several agencies, including the DOT, the EPA and the FEMA, as reflected in the guidance published for the EPA in *Manual for the Control of Hazardous Material Spills* by Huibregtse *et al.* (1977), in *Emergency Guide for Selected Hazardous Materials* by the DOT (1978) and for FEMA in *Planning Guide and Checklist for Hazardous Materials Contingency Planning* by Gunderloy and Stone (1980).

A11.20.1 Types of spill

Some principal types of spill are those from (1) process plant or storage, (2) pipeline, (3) road tanker, (3) rail tank car, (5) barge, (6) ship and (7) drilling rig or fixed production platform.

A spill within the works occurs in a relatively controlled environment, but this is less true of one in transport.

A liquid spillage on land poses a threat to land and to watercourses. It is characterized by the facts that the release is transient and generally relatively limited in volume but often noxious.

Liquid spilled into a stream can cause a degree of pollution which kills off much of the aquatic life so that a long period elapses before recovery can occur.

A11.20.2 Response to spills onto land

If a spill occurs on land, there are a variety of measures which can be taken. A review is given by Scholz (1982), who considers the problem under the heads of (1) termination of discharge, (2) containment to prevent entry into watercourses and (3) recovery and treatment.

Chemical and physical measures are discussed by Eckenfelder (1982) who covers (1) neutralization, (2) sedimentation, (3) coagulation, (4) precipitation, (5) carbon adsorprtion, (6) ion exchange, (7) oxidation–reduction reactions and (8) biodegradation. A fuller account of biological measures is given by Armstrong (1982).

The EPA has developed a number of items of equipment for dealing with spills, including a portable foam diking system, a mobile physical–chemical treatment unit, a portable sedimentation tank, a mobile incineration system and a mobile soil decontamination system. The foam diking system can be used to restrict the flow of a liquid over asphalt or concrete or to plug drains to prevent liquid from entering. These and other devices are described Freestone and Brugger (1982), in an account of EPA development work on spill control technology, and also by Scholz.

Accounts of specific techniques and devices for dealing with hazardous material spills include those on physical barriers by Friel, Hiltz and Marshall (1973), sorbents by Melvoid and Gibson (1988), a mobile treatment system by M.K. Gupta (1976), a mobile incineration system by Tenzer *et al.* (1979), groundwater protection by Huibregtse and Kastman (1981), *in situ* detoxification of soil by Huibregtse, Lafornara and Kastman (1978) and soil reclamation by Wentzel *et al.* (1981).

A11.20.3 Response to spills into streams

If a spill occurs which threatens a stream may be possible to prevent it from entering the stream, but once it does the measures which can be taken are generally limited.

Strategies for dealing with spills into streams have been described by G.W. Dawson and co-workers (Dawson, Shuckrow and Mercer, 1972; Dawson, 1975; Dawson and Parkhurst, 1976; Dawson and McNeese, 1978).

One approach is stream diversion. The EPA has developed a portable stream diversion system capable of bypassing 0.35 m^3/s a distance of 300 m.

Accounts are given by Lafornara (1982) of stream sampling and analysis, by Nadeau (1982) of bioassay and by Kontaxis and Nusser (1982) of dispersion modelling.

A11.20.4 Response to oil spills

Methods for the control of oil spills have been published by CONCAWE. They include a manual on inland oil spill cleanup (CONCAWE 1981 7/81), disposal techniques for spilt oil (CONCAWE 1980 9/80), protection of ground-water from oil pollution (CONCAWE 1979 3/79), strategies for the assessment of biological impacts of large oil spills on European coasts (CONCAWE 1985 5/85), and field guides to inland oil clean-up (CONCAWE 1983 10/83), coastal waters clean-up (CONCAWE 1981 9/81) and oil spill dispersal (CONCAWE 1988 2/88).

A11.20.5 Ultimate disposal of spilled material

Ultimate disposal of spilled material is considered by Lindsey (1975), R.J. Buchanan (1982), Novak and Pfrommer (1982) and A. Parker (1982). The options described by these authors are primarily incineration and landfill.

A11.21 Marine Pollution

Pollution of the seas occurs by discharges made following cleaning of tanks of oil tankers and as a result of accidental spillages from oil tankers and chemical carriers.

Pollution may occur as the result of illicit discharges or as the result of an accident. Most of the incidents which have hit the headlines have occurred after the ship has run aground.

Accounts of sea pollution are given in *Oil Pollution of the Sea and Shore* by WSL (1972), *Accidental Oil Pollution of the Sea* by the DoE (1976), *Marine Pollution* by R. Johnston (1977) and *Pollutant Transfer and Transport in the Sea* by Kullenberg (1982), *Poisoners of the Sea* by Goudray (1988) and *Marine Pollution* by R.B. Clark (1993) and of pollution criteria in *Pollution Criteria for Estuaries* by Helliwell and Bossanyi (1975).

The WSL publication records experience gained as a result of the pollution mitigation activities following the Torrey Canyon disaster.

A11.22 Pollution Incidents

Incidents involving pollution occur both from fixed installations and in transport and over varying timescales.

A11.22.1 Incident databases

The SRD operates the Environmental Data Service EnvIDAS which complements its other databases MHIDAS for major hazard incidents and EIDAS for explosion incidents.

In addition, the account of an incident in a hazards database frequently includes some information on environmental effects.

A11.22.2 Air pollution

Air pollution incidents tend to take the form of (1) a sudden large release, (2) a regular lower level release which is aggravated by an unusual weather condition or (3) a regular practice of lower level release which is found to be damaging the environment.

An example of a sudden large release is that at Seveso, described in Appendix 3.

A11.22.3 Smog incidents

At the end of October 1948, a heavy smog developed in inversion conditions in the industrial town of Donora, Pennsylvania. After several days conditions became such that 17 died within one day; a further 4 succumbed before the smog abated.

The worst smog incident recorded was the 'killer smog' in London in 1952. Again a heavy smog developed in inversion conditions. The concentration of sulfur dioxide rose to some seven times its normal level. The maximum mean daily concentration of the gas in Central London reached 3500$\mu g/m^3$. Two days into the incident the death rate began to soar. The number of excess deaths was estimated at about 4000.

A11.22.4 Bonnybridge

An example of the problems attendant on incineration is provided by the travails of Rechem, a company involved in the incineration of hazardous wastes. During the 1980s, the

incinerators which it operated included one at Bonnybridge in Scotland and one at Pontypool in Wales. At Bonnybridge there were complaints from the public and cattle nearby suffered from an unexplained sickness. Tests did not confirm excessive levels of contamination, but the plant was closed. The company had further troubles in its relations at Pontypool, though again numerous independent surveys failed to find concentrations of contaminants above the background levels.

A11.22.5 Watercourse pollution

Watercourse pollution incidents tend to take the form of (1) a sudden large release, (2) a temporary but appreciable increase in the quantity or concentration of a regular release or (3) a regular practice of lower level release which is found to be damaging the environment.

A11.22.6 Schweizerhalle

On 1 November 1986, a fire in a agrochemical warehouse at Schweizerhalle in Basel, Switzerland, broke out and was extinguished with large quantities of fire water, which became contaminated and then found its way into the Rhine, causing serious pollution. The incident is described in Case History A113.

A11.22.7 Minimata

Discharge of mercury compounds in Minimata Bay in Japan led to severe pollution and to the Minimata mercury poisoning disaster. For some 15 years prior to 1953, the Chisso Chemical Company had been discharging mercury catalyst into the bay. People fell ill, at first in small and then in increasing numbers. In 1957, a ban was placed on fishing in the bay. Of 116 officially recorded cases in 1958, 43 had died. By 1972, the official list of victims was almost 300.

A11.22.8 Hazardous waste pollution

Hazardous waste tends to give rise to developing problems at hazardous waste facilities rather than to incidents as such. However, incidents can arise such as those due to serious malpractice in transport of such wastes.

Accounts of hazardous waste problems and incidents are given in *Laying Waste* by M. Brown (1981) and *World of Waste* by Goudray (1992).

A11.22.9 Love Canal

The scale of the environmental disaster which may result from waste disposal is illustrated by the case of Love Canal. In 1953, this site was sold by the Hooker Chemical Company to the Niagara Falls education authority for a nominal sum. For over a decade the site had been used to dump chemical wastes. In 1976, local residents began to complain of odours and other nuisance. Concern escalated, leading to the relocation of 238 families and causing the President to declare the site a national environmental emergency, making it thereby eligible for federal clean-up funds.

There were numerous damage suits. In support of its suit against the company, the Justice Department commissioned a chromosome study of 36 residents; the study proved controversial.

The engineering measures taken to render the site safe are described by Glaubinger, Kohn and Remirez (1979).

A11.22.10 Land spill pollution

Incidents involving PCBs are described by A.J. Smith (1982), others involving pesticides by Frisbie (1982) and one involving phenol by A. Shepherd (1982a).

The Seveso incident, in which a large area of land was contaminated with TCDD, is described in Appendix 3.

A11.22.11 Sea pollution

Sea pollution incidents which tend to have particularly serious consequences are groundings of tankers on coasts. The three cases given below are all of this kind. Pollution of the sea also occurs from oil production activities, as described in Appendix 18.

A11.22.12 Torrey Canyon

On 18 March 1967, the tanker Torrey Canyon, carrying 114,000 tons of crude oil, ran aground on the coast of Cornwall, releasing 30,000 tons of oil. Over the next 7 days a further 20,000 tons escaped. On 26 March the ship broke its back with release of another 50,000 tons. Following this, the ship was bombed to burn the remaining 20,000 tons and the oil slick was sprayed with detergent to disperse it.

A11.22.13 Amoco Cadiz

On 16 March 1978, the oil tanker Amoco Cadiz lost its steering and ran aground at Portsall on the Brittany coast. The resulting oil spill polluted some 200 km of coastline, causing an incident which at the time was the worst to have occurred.

A11.22.14 Exxon Valdez

On 24 March 1989, the tanker Exxon Valdez ran aground near Valdez, Alaska, rupturing eight cargo tanks and releasing some 258,000 bbl of oil. The result was a major environmental disaster.

A11.23 Notation

Section A11.18

C_{98}	1-h average concentration exceeded only 2% of the year
d_{max}	maximum distance at which complaints can be expected (m)
D	dilution factor (ou)
D_e	odour concentration at emission point (ou)
D_r	odour concentration at reception point (ou)
E	contaminant, or odour, emission flow (m^3/s)
F	total emission flow (m^3/s)
H_e	effective chimney height (m)
U	wind speed (m/s)
X	distance between emission point and reception point (m)
Z	score value
ϕ	factor
ψ	factor

Appendix 12 Noise

Contents

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The environment may be degraded not only by chemical pollution but also by noise. Process plant contains a variety of noise sources covering rotating equipment, piping, combustion equipment and vents to atmosphere. Noise from process plant sources may affect workers from the perspective of noise induced hearing loss and the general public through environmental or community noise impacts. The control of noise from process plants needs to be controlled and noise control design needs to be an integral part of the engineering and planning for any process facility.

Accounts of noise, noise effects on humans and noise control are given in the following references:

- *Handbook of Noise Control* by C.M. Harris (1957),
- *Handbook of Noise Measurement* by A. Peterson and Gross (1967),
- *Noise and Vibration Control* by Beranek (1971),
- *Noise and Hearing Conservation Manual* by Berger *et al.* (1986 AIHA/11),
- *Engineering Noise Control* by Bies and Hansen (1988),
- *Woods Practical Guide to Noise Control* by Sharland (1990),
- *Noise and Health* by Fay (1991 ACGIH/70) and
- *Noise and Vibration Control Engineering* by Beranek and Ver (1992).
- *Code of Practice for Reducing the Exposure of Employed Persons to Noise* by the DoE (1972/1) (the DoE Noise Code).

A12.1 Regulatory Controls

Regulations applicable to noise levels within an industrial facility are intended to protect employees from noise-induced hearing loss. The regulations are usually based on an employee noise exposure limits (e.g. 85 dB(A) averaged over 8 h). The regulations normally allow for exposure to higher noise levels for reduced time periods and mandate the use of hearing protection if necessary. This allows the employees' averaged noise exposure level to remain below the safe limits.

Applicable regulations for the UK/EEC and USA would include the following:

- EEC Machinery Directive – 'Noise at Work Directive', 86/188/EEC and 'Machinery Directive', 89/392/EEC.
- UK Noise at Work Regulations 1989.
- USA OSHA regulation – USA Code of Federal Regulations Title 29 Part 1910.95

Typically these regulations set a series of action levels based on employee noise exposure levels as follows:

(1) First Action Level – daily personal noise exposure exceeds 85 dB(A)
   - Employer is responsible for initiating a hearing conservation programme and having noise assessment made by a competent person.
   - Employer is required to reduce the risk of hearing damage from exposure to noise to the lowest level reasonably practicable.
   - Appropriate hearing protection should be available to the employee on request.

(2) Second Action Level – daily personal noise exposure of 90 dB(A)
   - Appropriate hearing protection must be made available to all persons exposed.
   - Employer must reduce noise as far as reasonably practicable.
   - Other requirements include assessment records and audiograms, designated ear protection zones, training on maintenance and use of equipment and provision of information to employees and information to employees.

The following International Institute of Noise Control Engineering (I-INCE) Publication summarizes and compares employee noise exposure regulations for a range of countries worldwide: 'Technical Assessment of Upper Limits on Noise in the Workplace' I-INCE Publication 94-1.

Community or environmental noise impact must also be considered in plant noise control design. Noise limits set to control noise emissions outside of the plant are primarily intended to protect plant neighbours from noise-related annoyance or interference. In setting community noise limits, local regulations need to be considered together with assessments of likely community reaction to the increased noise levels. These issues also need to be considered in the context of the Environmental Impact Assessment (EIA) for the project.

Government regulations to control environmental noise vary greatly from country to country. Typically regulations apply to particularly zoning areas or land use classifications with different noise limits defined for specified daytime and night-time noise levels (e.g. residential, mixed residential/commercial, industrial etc.). These limits are forced to be generic and may not meet the specific requirements of a plant location. An important point, which is often overlooked, is that compliance with community noise regulations does not ensure against community complaints. People will complain because they find the noise disturbing or annoying, not because it exceeds a government regulation.

An EIA for a project would require the evaluation of the existing ambient noise levels in the proposed plant location and the predicted operational noise levels from the facility to assess the noise impact of the new plant.

Applicable standards and references for environmental noise would include the following:

- World Bank – '*Pollution Prevention and Abatement Handbook*' of 1998.
- US Export Import Bank – *'Environmental Procedures'* 1998.
- ISO 1996-1:1982 *'Acoustics Description and Measurement of Environmental Noise – Part 1: Basic Quantities and Procedures'.*
- ISO 1996-2:1987 *'Acoustics – Description and Measurement of Environmental Noise – Part 2: Acquisition of Data Pertinent to Land Use'.*
- ISO 1996-3:1987 *'Acoustics – Description and Measurement of Environmental Noise – Part 3: Application to Noise Limits'.*
- UK Control of Pollution Act 1974.
- UK Environmental Protection Act 1990.

A12.2 Process Plant Noise

The following organizations have a series of useful standards and guidelines relevant to Process Plant Noise:

- Engineering Equipment Material Users Association (EEMUA), 14-15 Belgrave Square, London, England SW1X 8PS UK; Phone: 071-235-5316

- CONCAWE, Madouplein 1, Brussels B-1030, Belgium; Phone: 32-2-220-3111
- American Petroleum Institute, 1220 L Street, NW, Washington, DC 20005-4070; Phone 202-682-8000

A12.3 Noise Control Terminology

A summary of widely used noise control terminology is given below:

- Audible Frequency Range
  The range of sound frequencies normally heard by the human ear. The audible range spans from 20 Hz to 20 kHz, but for most engineering investigations only frequencies between 40 Hz and 11 kHz (i.e. 63 Hz to 8 kHz octave bands) are considered.
- Background Noise
  The sound pressure levels in a given environment from all sources excluding a specific sound source being investigated or measured.
- Decibels (dB)
  Ten times the logarithm (to the base 10) of the ratio of two mean square values of sound pressure, voltage or current.
- Sound Pressure
  A dynamic variation in atmospheric pressure. The pressure at a point minus the static atmospheric pressure at that point (N/m^2).
- Sound Pressure Level (L_p)
  The ratio, expressed in decibels, of the mean square pressure to a reference mean square pressure which by convention has been selected to be equal to the assumed threshold of hearing.

$$L_p = 10 \log_{10}\left(\frac{P}{P_{ref}}\right)^2$$

  where P = RMS sound pressure (N/m^2); $P_{ref} = 2 \times 10^{-5}\ N/m^2$.

- Sound Intensity
  The rate of sound energy transmission per unit area in a specified direction (W/m^2).
- Sound Intensity Level (L_I)
  The rate of sound energy transmission per unit area in a specified direction related to a reference intensity level.

$$L_I = 10 \log_{10}\left(\frac{I}{I_{ref}}\right)$$

  where I = RMS value sound intensity (W/m^2); $I_{ref} = 1 \times 10^{-12}$ watts/m^2.

- Sound Power
  The total sound energy radiated by a source per unit time (W).
- Sound Power Level (L_w)
  The acoustic power radiated from a given sound source as related to a reference power level, expressed in decibels.

$$L_w = 10 \log_{10}\left(\frac{W}{W_{ref}}\right)$$

  where W = RMS value sound power (W); $W_{ref} = 1 \times 10^{-12}$ watts.

- Octave Bands
  Frequency ranges in which the upper limit of each band is twice the lower limit. Octave bands are identified by their geometric mean frequency (center frequency). The table below shows the octave band upper/lower frequency limits.

Octave band cut-off frequencies (Hz)

Octave band center frequency	*Lower band limit*	*Upper band limit*
31.5	22	44
63	44	88
125	88	177
250	177	355
500	355	710
1,000	710	1,420
2,000	1,420	2,840
4,000	2,840	5,680
8,000	5,680	11,360
16,000	11,360	22,720

- 1/3 Octave Bands
  Frequency ranges where each octave is divided into one-third octaves with the upper frequency limit being 1.26 times the lower frequency. Identified by the center frequency of each band.
- A-Weighted Sound Pressure Level (dBA)
  The sound pressure level measured using an electronic filter that approximates the frequency response of the human ear. The table below shows octave band A-weighting correction factors.

Octave band A-weighting correction factors

Octave band center freq (Hz)	*A-weighting correction* (dB)
63	−26.2
125	−16.1
250	−8.6
500	−3.2
1000	0
2000	+1.2
4000	+1.0
8000	−1.1

- L_{Aeq} – Equivalent Continuous Sound Level
  The A-weighted energy mean of the noise level averaged over the measurement period. It can be considered as the continuous steady noise level which would have the same total A-weighted acoustic energy as the real fluctuating noise measured over the same time period.

$$L_{Aeq} = 10 \log_{10} \frac{1}{T} \int_0^T \left(\frac{p_A(t)}{p_o}\right)^2 dt$$

  where T = total measurement time; $P_A(t)$ = A-weighted instantaneous sound pressure; $P_{ref} = 2 \times 10^{-5}\ N/m^2$

  L_{Aeq} is, therefore, an important number for the evaluation of a fluctuating noise level, because it

reflects the actual energy content of the time varying noise. L_{Aeq} is used in its own right in many national and international standards for rating some forms of community noise.

- L_N – Percentile Level
  The A-weighted sound level equalled or exceeded by a fluctuating sound level × percent of the measurement time period. For example:c

  L_{A10} – the A-weighted sound pressure level exceeded for 10% of the measurement period
  L_{A50} – the A-weighted sound pressure level exceeded for 50% of the measurement period
  L_{A90} – the A-weighted sound pressure level exceeded for 90% of the measurement period

  The various L_N levels over a measurement period are important in the evaluation of the temporal nature of the sound. A widely varying sound level over a measurement period will tend to have large differences between the various L_N levels than a more constant steady noise.

- Daily Personal Exposure
  The daily personal exposure of an employee is defined in the schedule to the HSE *Noise Guide 1* as follows:

$$L_{EP,d} = 10\log_{10}\left[\frac{1}{T_o}\int_0^{T_e}\left(\frac{pA(t)}{p_o}\right)^2 dt\right]$$

  where $L_{EP,d}$ is the daily personal exposure (dB(A)); $p_A(t)$ is the time-varying value of the A-weighted instantaneous sound pressure in the undisturbed field (Pa); t is the time (h); p_o is the base value of the sound pressure (Pa); T_e is the duration of the exposure (h); T_o a period of 8 h. As before, the value of p_o is 2×10^{-5} Pa.

A12.4 Noise Control

Noise control is generally considered under four heads: (1) at source, (2) in transmission, (3) on emission and (4) on receipt.

Noise can be generated only if there is a vibrating source, which may take the form of a vibrating surface or of fluctuation in fluid flow. The topic of noise is therefore inextricably bound up with that of vibration, as attested by the titles quoted earlier.

- Control at Source
  Control of noise at source should be the first option considered. The approach is analogous to inherently safer design.The approach to noise control at source is to identify potential sources and to either eliminate them altogether or to reduce their level of vibration by one or more of the following: the surface, the amplitude, the frequency and, in the case of a fluid, the flow velocity. A number of specific methods for control of noise, such as impact reduction, clamping, damping, acoustic panels and silencers can be considered.
- Control in Transmission
  In principle, noise associated with transmission through pipes and ducts may be structure-borne or fluid-borne. For gas or vapour pipes the sound is predominantly fluid borne as evidenced by the effectiveness of control by the use of in-line silencers. Such silencers are used, for example, on the intakes and exhausts of internal combustion engines and on the intake/exhaust of fans.
- Control on Emission
  Control on emission involves modification of the route by which the noise reaches the worker. Devices used include sound-absorbing materials on the workroom walls, sound-absorbing screens, total or partial enclosure of machines and cabins serving as 'noise refuges'. Another approach is to increase the distance between the worker and the noise source. Distance may be increased by segregation of noisy machines, use of remote controls and siting of exhausts.
- Control at Receiver
  Control at the receiver involves the use of ear protection. Types and selection of ear protectors are discussed in HSE *Noise Guide 5*.

  Limiting the time for which the person is exposed to the noise may effect some reduction in the noise burden, but to be effective the proportion of time exposed has to be cut drastically. Complete removal for half a shift, for example, reduces the daily exposure by only 3 dB(A).

The importance of addressing noise control issues as early as possible in a process plant engineering project cannot be over emphasized. The earlier noise control design issues are identified and resolved on a project, the more effective is the noise control design. That is effectiveness as measured in terms of overall project costs, impact on project schedule and compliance with the project noise requirements.

Effective noise control design for refining or petrochemical projects requires careful planning during the initial stages of the project, with equally careful and prudent execution through the various phases of the project. Before addressing specific project noise control design issues it will be useful to place some perspective on the noise control challenges faced on process plant projects. Any metric, from the capital cost, which can run in hundreds of millions, if not billions, of US dollars to the thousands of individual equipment items and bulk quantities of piping demonstrates the scale and complexity of these projects. The projects can be completely new 'grass-roots' plants or expansions to existing facilities. Often times a large project is further complicated by the need to divide the engineering in to manageable packages, with different engineering contractors responsible for different process units.

The sections below highlight the key noise control design activities from the initial front end engineering design (FEED) phase of the project through Detailed Design to Commissioning and Start-up:

- Front End Engineering Design (FEED)
  Noise control must be executed as early as possible in a project to minimize the effect on project costs layout and schedule. The major noise control activities on a project, therefore, tend to focus towards the FEED phase of the project. During these initial stages of a project, baseline noise surveys may be required to establish existing noise levels at the plant site. For a 'grass-roots' project the primary focus of the baseline survey will be on community noise levels. For an expansion project at

an existing facility the survey must consider both in-plant and community noise levels.

The key noise control task during the early stages of a project is the FEED Noise Study. This study evaluates the potential noise sources within the plant and establishes, through plant noise modelling, the predicted noise levels (in-plant and community) for the new facility. The initial modelling will be based on standard equipment with no special provision for noise control. The modelling will establish a baseline noise control position for the overall plant. This will identify potentially high noise equipment and high noise areas of the plant and will allow noise control design options to be readily included and evaluated in the plant noise model. This 'what if' analysis will allow the noise control design to be optimized to meet the plant owner's overall project noise control requirements.

Effective and accurate plant noise modelling is critical to this evaluation process. The plant noise modelling must be based on international and industry accepted standards (e.g. EEMUA, CONCAWE, ISO 9613). Noise model input data must be based on reliable and verifiable equipment and field noise data. Only with a solid background of field experience on comparable equipment in similar service can the noise control engineer speak with authority on predicted plant noise levels.

The findings of the FEED Noise Study will provide the data to define definite and unambiguous noise limits and requirements for the Detailed Design phase of the project. This will apply to the designation of in-plant noise limits and the definition of 'Restricted Areas' (i.e. hearing protection areas) together with property line noise requirements and overall sound power level limits. The goal must be to define and specify noise control requirements so that they meet the project requirements and can be effectively managed and enforced during the Detailed Design phase of the project.

- Detailed Design.
  Noise control for the detailed design phase of a project will involve the engineering contractor, or contractors, executing the noise control design for the project in compliance with the noise limits defined during the FEED phase of the project. Primary areas of noise control activity during the Detailed Design phase of the project would include:

  – Equipment requisition and design/data review process
  – Piping noise and control valve noise control
    Acoustic insulation definition
    Low noise control valve selection
    Vent and in-line silencers
  – Acoustic enclosures
  – Acoustic insulation for rotating equipment
  – Equipment shop noise testing (only in appropriate situations when good measurements are possible)

- Commissioning and Start-up.
  The main noise control activities during commissioning and start-up will be noise surveys to demonstrate/verify compliance with the project noise limits. Depending on the results of the noise surveys corrective action may need to be initiated to reduce operation noise levels.Depending on the project type, long-term environmental noise monitoring in the community or on the plant property may be worthwhile during commissioning/start-up. This type of monitoring would provide data on upset and startup venting operating conditions (e.g. flaring). Obtaining reliable data on these difficult to reproduce operating conditions may prove valuable.

Noise control issues associated with typical classes of process plant equipment area discussed below:

- Rotating Machinery
  A major source of noise in process plant is rotating machinery. Centrifugal compressors can produce noise levels of up to 100 dB(A) at 1 m from the equipment surface, often with dominant tonal content at the blade passing frequency. The casing is usually sufficiently massive to prevent transmission of aerodynamic vibration. There are also other noise sources such as motors, turbines, gear units, lube oil pumps and control valves. Full acoustic enclosure is usually unnecessary and it is more common to use a combination of acoustic insulation and spring support for the pipework together with low noise valves.Another source of noise on rotating machinery is electric motors. Large medium voltage motors can produce a noise level above 90 dB(A), due principally to the cooling air fan and also sometimes to magnetically induced vibration. The problem is generally soluble using smaller, more efficient cooling air fans but on occasion increased frame size and/or cooling air silencers may be required.
- Fluid Flow in Pipes
  Another main source of plant noise is the flow of fluids in pipes. Noise control of individual plant items may not be sufficient to attain the noise target and it may be necessary to address the noise in the pipework also.

  Noise from gas pipes is the subject of studies by CONCAWE described by Marsh *et al.* (1985), Pinder (1985) and van de Loo (1988). The CONCAWE piping model is an essentially empirical one and is somewhat similar to that in VDI 3733.With regard to noise control, Pinder outlines four methods, which relate to: pipewall thickness, plant layout, in-line silencers and acoustic insulation.

  Noise due to flow through valves is discussed in ISA S75.17-1989 *Control Valve Aerodynamic Noise Prediction*.
- Combustion Processes
  Combustion processes are also a significant source of plant noise. On furnaces with induced or naturally induced air flow the air inlet and combustion noise can exceed 90 dB(A) @ 1 m per burner unless adequate acoustic absorption is included in the design of the burner plenums. With forced draft systems the sound levels are much less, noise in this case coming mainly from the fan intake, casing and motor. Noise can be transmitted by furnace wall and by duct vibration, the solution in this case being adequate stiffness.
- Flares
  A particular type of combustion process that is liable to generate a high level of noise, including noise affecting the public, is a flare.

  The noise generated by a flare is a function of the energy release in the flame. Swithenbank (1972) has defined a noise generation efficiency equal to the fraction of the net heat release which is given off as noise

power, and has correlated it with mass velocity at the flare tip. Ohiwa, Tanaka and Yamaguchi (1993) describe fundamental studies on the noise from a turbulent diffusion flame.

As he points out, proprietary flare tips are available to overcome the noise problem. Effective designs are based on the Coanda effect plus other utilizing mufflers or baffles for steam assist flares. A ground flare design also offers benefits for reduced noise due to flaring.

- Pressure Relief

  An alternative method of disposal that also generates noise is venting to atmosphere. A method of estimating the noise from a high pressure relief discharging to atmosphere through a vent stack is given in API RP 521: 1990.

A12.5 Notation

f	fractional exposure
f_{tot}	total fractional exposure
H	sound power level (dB)
L	sound pressure level (dB(A))
L_{eq}	equivalent continuous sound level (dB(A))
$L_{EP,d}$	daily personal exposure (dB(A))
L_T	sound pressure level at distance r (dB)
N	number of decibels (dB)
$p_A(t)$	time-varying value of A-weighted instantaneous sound pressure in the undisturbed field (Pa)
p_o	base value of sound pressure (Pa)
P	pressure disturbance (Pa)
r	distance (m)
t	time (h)
T_e	duration of exposure (h)
T_o	8-h period
W	source power (W)

Subscript

o	reference level

Appendix 13

Safety Factors for Simple Relief Systems

Contents

A13.1 Comments on Safety Factors to be Applied when Sizing a Simple Relief System A13/2

A13.1 Comments on Safety Factors to be Applied when Sizing a Simple Relief System

It is recommended that a safety factor be applied to take account of both uncertainty in the data and inaccuracy in the calculation methods.

It is assumed in the following discussion that (1) the designer has chosen a method appropriate to the application, intended to tend towards oversizing the relief system rather than the reverse, and (2) the relief system consists at most of a safety valve or bursting disc preceded by a constant diameter pipe and followed by a constant diameter pipe to atmosphere. It is also assumed that the flow through any safety valve has been checked against the manufacturer's data; under no circumstances should the mass flow be assumed to exceed the value so calculated.

The safe case is that which corresponds with the highest estimate of the required relief rate(s) and the lowest estimate of the actual flow(s).

The overall safety factor can be applied in one of two ways:

(1) by sizing the relief system to pass a flow equal to the required mass flow multiplied by the safety factor; or
(2) in cases where the vent capacity is determined by one particular cross-sectional area, by multiplying the calculated required vent area by the safety factor. However, it is important then to check that the capacity remains determined by this area.

The overall safety factor F_O may be represented as the product of a number of sub-factors, each taking account of particular features:

$$F_o = \prod_{i=1}^{n} F_i \qquad [A13.1]$$

where F_i is the sub-factor for feature i. Some of the sub-factors which may be appropriate are

(1) A sub-factor ($\geqslant 1$) to reflect any features of the method, unless included in other specific sub-factors such as those suggested below, which might lead to undersizing of the relief system for the application concerned. These might be features of the methods used to calculate the required relief rate(s) or vent area, although in most cases the methods will have been chosen so as to tend to overestimate those. They may also be features of the approach to assessment of the relief system flow capacity not covered below, for example the method may have neglected the presence of solids in the flow. The designer must himself establish the required value for this sub-factor.
(2) A sub-factor ($\geqslant 1$) to take account of uncertainty in the data. The magnitude and direction of any errors arising from the data assumptions should be assessed. For reactors particular attention should be paid to any errors affecting the rate of reaction including its dependence on temperature.
(3) A sub-factor ($\geqslant 1$) to allow for the inaccuracy in the fluid flow calculation methods which is present even for incompressible liquid and/or ideal gas. In this discussion it is assumed that the largest realistic pipe roughness has been assumed, otherwise a larger sub-factor will be necessary.

Some recognized wide-applicability two-phase gas/vapour-liquid flow methods, when used for lines in which friction and/or static head are significant, may be accurate only to a factor of ± 2 (i.e. the actual flow is in the range half to two times the calculated value), and would thus correspond to a sub-factor of 2. For poorer methods, a larger sub-factor may be needed, while for methods more targeted at the specific application a lower sub-factor may suffice; expert advice should be sought. For two-phase gas/vapour-liquid flow with negligible friction and no changes in static head, for example through a safety valve alone, lower sub-factor values in the range 1.2–1.5 may sometimes be sufficient; expert advice should be sought.

For vapour-only flow when friction is significant a reasonable value for this sub-factor will usually lie in the range 1.2–1.5, while if only momentum changes are significant, a lower sub-factor may be allowable; expert advice should be sought.

(4) A subfactor to allow for the effects of gas/vapour-phase nonideality if these have not been taken into account in the mass flow capacity calculation.

For critical (choked) frictionless gas/vapour-only flow (e.g. through a safety valve alone) the factor may be estimated from the work of Leung and Epstein (1988) using their figures 2, 4–6. These figures show the ratio of real-gas critical mass flow to ideal *($Z = 1$)* critical mass flow (our sub-factor is the inverse of this ratio) as a function of the ratio (stagnation (inlet reservoir) pressure/thermodynamic critical pressure), for various values of the ideal (zero pressure) ratio of specific heats. The figures are based on the applicability of the Redlich–Kwong equation of state, but give a useful indication of the magnitude of the effects of non-ideality on critical flow. It can be seen that a sub-factor is needed for pressures exceeding about 20 times the critical pressure. At lower pressures the real critical flow is seen to be greater than the ideal critical flow, but caution should be exercised before adopting a sub-factor <1. It should be noted that non-ideality cannot be fully compensated for by assuming a constant Z value or using an adjusted fictitious molecular weight; this is discussed below.

For gas/vapour-only flow with friction, and for non-choked flow with or without friction, the author is unaware of any treatment analogous to that of Leung and Epstein. For given inlet reservoir conditions and back pressure and assumed constant Z, the adiabatic or isothermal mass flow of a gas through a perfect nozzle, and from a reservoir via a perfect rounded inlet into and through a straight pipe, is proportional to $1/Z^{1/2}$ (Lapple, 1943). This suggests an approximate value for this sub-factor given by

$$F_4 = \frac{\text{Real gas mass flow}}{\text{Ideal gas } (Z = 1) \text{ massflow}} = \frac{1}{Z_{\max}^{1/2}} \qquad [A13.2]$$

where $Z_{\max}$ is the maximum value of Z occurring in the flow. Clearly this sub-factor will be inaccurate when Z varies significantly (e.g. near the thermodynamic critical point, and near choking conditions); this can be seen by comparing this sub-factor (which if Z were constant would apply equally to critical frictionless flow) with the sub-factor obtained from the work of Leung and Epstein for critical frictionless flow (and also from their figure 9). It would seem prudent to adopt a sub-factor at least as large as the larger of these two estimated sub-factors (but again,

care should be exercised before adopting any value <1). If the non-ideality is severe and such as to reduce the flow, then ideally the relief system should be sized using a method which takes full account of non-ideality; the other sub-factors would still be required. If the non-ideality is severe but (as is more likely) is such as to increase the flow, then a sub-factor of 1 may be prudent.

It should be noted that the above sub-factors based on the work of Leung and Epstein and of Lapple are for application to the mass flow calculated on the basis of fully ideal ($Z=1$) flow. If the flow has been calculated as semi-ideal with an assumed constant Z, or with an adjusted fictitious molecular weight, to give partial compensation for the departure from ideality, then this corresponds to the prior application of a sub-factor of $Z_{\text{assumed}}^{1/2}$ or $(\text{MW}_{\text{actual}}/\text{MW}_{\text{assumed}})^{1/2}$.

It seems likely that the effects of gas/vapour-phase non-ideality in two-phase gas/vapour-liquid flow, will be less, but the author is not aware of any studies to validate this. It is suggested that this sub-factor be taken as the same as for gas/vapour-only flow.

(5) A sub-factor ($\geqslant 1$) to take account of errors in the flow calculation for two-phase gas/vapour-liquid flow resulting from neglecting the variation in liquid density, liquid specific heat and latent heat along the pipe. The variation in these quantities can be judged from the calculated conditions along the pipe and thermodynamic charts. Then either a value can be assigned to this sub-factor or safe values can be assigned to those properties and the sub-factor set to 1. For calculation of mass flow capacity, safe values (giving a low mass flow) are low density, high specific heat and low latent heat. For gas-only or vapour-only flow, this sub-factor is irrelevant.

Finally the designer must check that there are no further sub-factors to be included, and decide whether to accept the calculated overall safety factor F_0. There is little published advice on typical factors. It would be surprising if the overall factor were to be less than 1.2 in any event, and significantly larger factors would be likely for reactors. For polymerization reactors Boyle (1967) said that the specified relief area should be two to three times the area indicated by design calculation (but note that this was before the preparation of the DIERS methods). Boyle's recommendation is consistent with typical overall factors obtained using the approach described above for two-phase vapour/liquid venting.

Caution

It is emphasized that the above comments are offered only to assist the designer in his consideration of what might be an appropriate overall safety factor. The designer must decide whether the advice is relevant to his application (bearing in mind the restrictions defined in the second paragraph of this note) and what sub-factors and overall factor are adequate.

H.A. Duxbury
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May 1994

Appendix 14

Failure and Event Data

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Many of the methods described in this volume require the use of data for failure and other events. This appendix gives a brief account of such data and a selection of references, which have been published in the open literature.

The data are given in summary form and primarily for illustrative purposes only. It is emphasized that there are many factors that determine the failure rates of equipment and the range of failure rates observed can be quite wide. It should be borne in mind that the same data are often quoted by a number of references. The existence of several sets of data that are in agreement is not necessarily evidence of the validity of the data. For industrial reliability work, therefore, it is necessary to consult the original literature and to make appropriate use of data banks and plant data.

Selected references on event and failure data are :

Event and failure
US Navy, Bur. of Naval Weapons (n.d.); NRC (Appendix 28 *Failure Data*); Dummer and Griffin (1960, 1966); Edison Elec. Inst. (1963, 1967); Timmermann (1968); R.L. Browning (1969a–c, 1970); F.R. Farmer (1971); Jacobs (1971); A.E. Green and Bourne (1972); AEC (1975); Gangadharan and Brown (1977); Cremer and Warner (1978); HSE (1978b); Ericsson and Bjore (1983); Johanson and Fragola (1983); Sherwin (1983); IEEE (1984); OREDA (1984, 1989, 1997, 2002); Rackwitz (1984); Bendixen, Dale and O'Neill (1985); Reliability Analysis Center (1985); Rossi (1985); IAEA (1988); Boykin and Levery (1989); Hauptmans and Homke (1989); EUROSTAT (1991)

Data collection and exchange
Pollocks and Richards (1964); Boesebeck and Homke (1977); Frankel and Dapkunas (1977); Haueter (1977); Richards (1980); B.K. Daniels (1982); Bockholts (1983); Borkowski, Drago and Fragola (1983); Carlesso, Bastia and Borelli (1983); Himanen (1983); Melis *et al.* (1983); Games *et al.* (1985); Lamerse and Bosnian (1985); Walls and Bendell (1985); Blokker and Goos (1986); Turpin and Kamath (1986); Wingender (1986, 1991); Bendell (1987), Davidson (1994); Ireson, Coombs and Moss (1996); Lannoy and Procaccia (1996); Dhillon (1999); EsReDA (1999)

Data problems and validity
Kletz (1973b); J.H. Bowen (1977); R.L. Browning (1977); Cannon (1977); Devereux (1977); Lees (1977c); Parsons (1977); Rex (1977); Vesely (1977b); HSE (1978B); Apostolakis *et al.* (1980); Pitts *et al.* (1980); Apostolakis (1982, 1985a); Martz (1984); OREDA (1984, 1992, 1997, 2002); Mosleh and Apostolakis (1985); Andow (1989), EsReDA (1999), Kletz (1999)

Data banks
Barnes (1967 UKAEA AHSB(S) R138); Naresky (1967); AEC (1975); J.H. Bowen (1977); Collacott (1977b); B.K. Daniels (1982); Bobbio and Saracco (1983); Capobianchi (1983, 1991); K.R. Davies (1983); OREDA (1984, 1992, 1997, 2002); Bendell and Cannon (1985); Scarrone, Piccinini and Massobrio (1989); Bendell (1991a–c); Cannon (1991b); Cannon and Bendell (1991); Cross and Stevens (1991); Mizuta *et al.* (1991); MIL-HDBK 217F; CCPS (1991); Fragola (1996); Ireson, Coombs, and Moss (1996); EsReDA (1999); Cooke and Bedford (2002) SRD: Barnes (1967 UKAEA AHSB(S) R138); Ablitt (1973 UKAEA SRS/GR/14, SRD R16,1975); Fothergffl (1973 UKAEA SRS/GR/22); Barnes *et al.* (1976); J.H. Bowen (1977); Cannon (1991a,b); EdF: Silberberg and Meclot (1985); Procaccia (1991); ENI: Avogadri, Bello and Colombari (1983); ERDS: Capobianchi (1991); FACTS: Koehorst (1989); Hoehorst and Bockholts (1991); IAEA: Tomic and Lederman (1991); Offshore: Gaboriaud, Grollier-Baron and Leroy (1983); Gjestad (1983); Tveit, Ostby and Moss (1983); OREDA (1984, 1989, 1992, 1997, 2002); Bruce (1994); Groenendijk (1995); Sandtorv, Hokstad and Thompson (1996); Rausand and Øien (1996); Haugen, Hokstad and Sandtorv (1997); Langseth, Haugen and Sandtorv (1998)

Populations (of plants, equipment, etc.) at risk
Plants: AGA (n.d./1Ol); IP (Oil Data Sht 15); IPE (1967–); SRI Int. (1988a–c); Anon. (1985dd); HSE (1986 Major Hazards 8); IPE (2002); Welsh (1993)
Equipment: Hooper (1982)
Transport: ACDS (1991)

Mechanical equipment failure modes (see also Table 7.1)
IMechE (1970/3); Pilborough (1971, 1989); Collins and Monack (1973); B.W. Wilson (1974); Lancaster (1975); OREDA (1984, 1992, 1997, 2002); H.C.D. Phillips (1990), Davidson (1994)

Pressure vessels
Kellerman (1966); Kellerman and Seipel (1967); Phillips and Warwick (1968 UKAEA AHSB(S) R162); Slopianka and Mieze (1968); Butler (1974); Engel (1974); T.A. Smith and Warwick (1974); AEC (1975); Boesbeck (1975); Bush (1975); HSE (1978b); Arulanantham and Lees (1981); Hurst, Hankin *et al.* (1992); Columns: H.C.D. Phillips (1990)

Storage tanks
H.C.D. Phillips (1990)

Pipework
S.A Wilson (1972, 1976); AEC (1975); Boesebeck and Homke (1977); Bush (1977); HSE (1978b,d); Arulanantham and Lees (1981); Cannon (1983); R.E. Wright, Stevenson and Zuroff (1987); Blything and Barry (1988 SRD R441); CIA, Chlorine Sector Gp (1989); de la Mare, Bakouros and Tagaras (1993); Hurst, Davies *et al.* (1994); Strutt, Allsop and Ouchet (1994); G. Thompson (1994)

Heat exchangers
A.E. Green and Bourne (1972); C.F. King and Rudd (1972); H.C.D. Phillips (1990); OREDA (1992, 1997, 2002), Lannoy and Procaccia (1996)

Rotating machinery
Turbomachinery: R.L. Browning (1970); Sohre (1970); OREDA (1992, 1997, 2002)
Compressors: Ufford (1972); Avogadri, Bello and Colombari (1983); H.C.D. Phillips (1990); OREDA (1992, 1997, 2002); Lannoy and Procaccia (1996), Hale and Arno (2001)
Pumps: Anon. (19721); F.R. Farmer (1971); Emelyanov *et al.* (1972); A.E. Green and Bourne (1972); C.F. King and Rudd (1972); Ufford (1972); AEC (1975); R. James (1976); Sherwin and Lees (1980); Dorey (1981); Aupied le Coguiec and Procaccia (1983); Avogadri, Bello and Colombari (1983); Sherwin (1983); Anon. (1985x); Bloch and Johnson (1985); N.M. Wallace and David (1985); Flitney (1987); H.C.D. Phillips (1990); OREDA (1992, 1997, 2002), Lannoy and Procaccia (1996); Sawaryn, Grames and Whelehan (2002)

Valve
Rijnmond Report; Moss (1977 NCSR R11); Aupied, le Coguiec and procaccia (1983); Vivian (1985); OREDA (1992, 1997, 2002)
Pressure relief valves: A.E. Green and Bourne (1972); Kletz (1972a, 1974a); Lawley and Kletz (1975); Aird (1982, 1983); Aupied, Le Coguiec and Procaccia (1983); Oberender and Bung (1984); OREDA (1984, 1992, 1997, 2002); Maher *et al.* (1988); Hanks (1994); D.W. Thompson (1994), Alfares (1999)
Non-return valves: AEC (1975); Aupied, Le Coguiec and Procaccia (1983); McElhaney (2000)
Emergency isolation valves: Haugen, Hokstad and Sandtorv (1997)

Bursting discs
Lawley (1974b)

Instruments, including valves
Barnes (1965 UKAEA AHSB(S) R99, 1966 UKAEA AHSB(S) R119, 1967 UKAEA AHSB(S) R122, R131, 1966); A.E. Green and Bourne (1965 UKAEA AHSB(S) R91, 1965, 1966 UKAEA AHSB(S) R117, 1972); Bourne (1966 UKAEA AHSB(S) R110, 1967); A.E. Green (1966 UKAEA AHSB(S) R113, 1969 R164, 172, 1971 UKAEA SRS/GR/2, 1970, 1972); J.C. Moore (1966); Hensley (1967 UKAEA AHSB(S) R138, 1968, 1969 UKAEA AHSB(S) R178, 1971); R.L. Browning (1969c, 1972, 1977); Mercer (1969); Anyakora (1971); Anyakora, Engel and Lees (1971); Stewart (1971); Upfold (1971); Lees (1973b, 1976b,c); Anon. (1974); Bulloch (1974); Lawley (1974b); Skala (1974); AEC (1975); Lawley and Kletz (1975); Moss (1977 NCSR R12); Bott and Haas (1978); H.S. Wilson (1978); Huyten (1979); de la Mare (1980); Piccinini *et al.* (1982); Aupied, Le Coguiec and Procaccia (1983); Rooney (1983); Unger (1983); Oberender and Bung (1984); OREDA (1984, 1992, 1997, 2002); Vivian (1985); Kumar, Chidambaram and Gopalan (1989); R. Green (1993); Paula (1993); Strutt, Allsop and Ouchet (1994)

Process computers
Barton *et al.* (1970); Hubbe (1970); E. Johnson (1988)

Fire protection, fire and gas detection, sprinkler systems
Rasbash (1975a); M.J. Miller (1974, 1977); P. Nash and Young (1976); Kamath, Keller and Wooliscroft (1981); Peacock, Kamath and Keller (1982); Peacock and Watson (1982); OREDA (1984, 1992, 1997, 2002); Gupta (1985); Finucane and Pinkney (1988 SRD R431); Rose-Pehrsson *et al.* (2000); Rowekamp and Berg (2000); Budnick (2001)

Utilities
R.L. Browning (1969c); Kletz (1975); Coltharp *et al.* (1978); OREDA (1984, 1992, 1997, 2002)

Power supplies
Dickinson (1962); R.L. Browning (1969c); AEC (1975); Jarrett (1983); B. Stevens (1983); Ketron (1980)
Diesel generators, diesel-driven equipment: F.R. Farmer (1971); AE. Green and Bourne (1972); AEC (1975); OREDA (1984, 1992, 1997, 2002); B. Steven (1983); Vesely, Uryasev and Samanta (1994)

Electronic equipment
Dummer and Griffin (1960, 1966); US Army, Dept of Defense (1965); A.E. Green and Bourne (1972)

Electrical equipment
F.R. Farmer (1971); A.E. Green and Bourne (1972); AEC (1975); OREDA (1984, 1992, 1997, 2002)

Electric motors
Dickinson (1962); Benjaminsen and van Wiechen (1968); R.L. Browning (1969c); AEC (1975); Avogadri, Bello and Colombari (1983)

Boilers
F.R. Farmer (1971); H.C.D. Phillips (1990)

Mills
Notman, Gerard and de la Mare (1981)

Belt conveyors
Notman, Gerard and de la Mare (1981)

Cranes
F.R. Farmer (1971); OREDA (1992, 1997, 2002)

Reactor overpressure
Marrs and Lees (1989); Marrs *et al.* (1989)

Leaks and spillages
Davenport (1977b, 1983); Kletz (1977J); HSE (1978b,d); Baldock (1980); Forsth (1981b); Hawksley (1984); A.W. Cox, Lees and Ang (1990); ACDS (1991); Berglund (1992); Taback, Siegell, Martino and Ritter (2000)

Ignition of leaks
R.L. Browning (1969c); A.W. Cox, Lees and Ang (1990); ACDS (1991)

Fire and explosions
Process plant fires: Rutstei and Clarke (1979); G. Wiiliam (1999)
Refinery fires: API (1983, 1984, 1985)
Pump fires: Kletz (1971); Wallace and David (1985); HSE (1978b)
Tank fires: Kletz (1971); API (1983, 1984, 1985)
Furnace explosions: Kletz (1972c); Ostroot (1972)
Warehouse fires: Hymes and Flynn (1992 SRD R578)

Vapour cloud explosions
Wiekema (1983a,b, 1984); Davenport (1977, 1983)
Probability of ignition: Kletz (1977J); HSE (1978b); Moussa *et al.* (1982); A.W. Cox, Lees and Ang (1990); ACDS (1991)
Delay before ignition: Kletz (1977J)
Drift before ignition: Kletz (1977J)

BLEVE
Blything (1986); Hurst, Hankin *et al.* (1992)

Transport
Westbrook (1974); HSE (1978b); Appleton (1988 SRD R474); ACDS (1991); P.A. Davies and Lees (1992); Montiel *et al.* (1996)

Pipelines – ***see*** **Table 23.1**

Ships
HSE/SRD (HSE/SRD/WP10, 29); Sandtory and Edwards (1980); Poten and Partners (1982); Blything and Lewis (1985 SRD R340)
Fire and explosion: Blything and Edmondson (1983, 1984 SRD R292); ACDS (1991)

LNG plants
Welker *et al.* (1976); Welker and Schorr (1979); AGA (1981/33); D.W. Johnson and Welker (1981); Moussa *et al.* (1982)

Offshore
Goodwin and Kemp (1980); Sofyanos (1981); Anon. (1983h); Dahl *et al.* (1983); OREDA (1984, 1992, 1997, 2002)

Missiles
HSE/SRD (HSE/SRD/WP7); HSE (1978b); Holden and Reeves (1985); Holden (1988 SRD 477); ACDS (1991)

Aircraft crashes
AEC (1975); HSE (1978b); Phillips (1981 SRD R198); Marriott (1985); Roberts (1987 SRD R388)

A14.1 Type of Data

There are several types of data that may be required. The first type is accident and incident data including the recording of system malfunctions, accident reports and databanks established to store accident information. The second type is event and failure rates data that involve all the abnormal events and the performance of equipment. For equipment, these data include:

(1) Failure frequency, probability
(2) Repair time
(3) Unavailability

and for events:

(4) Event frequency.

Failure rate data are usually given as frequencies or mean time to failure (MTTF). Two types of failure rate data are typically used: time-related and demand-related. Time-related failure rates are established for equipment that is continuously in use while demand-related failure rates are for equipment that is normally dormant and required to operate on demand.

A14.2 Definition and Regimes of Failure

The failure rate recorded for equipment necessarily depends on the definition of failure. The importance of this may vary. Failure of a pump to start on demand would appear relatively unambiguous, but failure of a pressure relief valve may refer either to failure of the set pressure to stay within prescribed limits when removed from the plant and tested in the workshop or to failure to relieve pressure during plant operation. An equipment failure can be catastrophic, degraded or incipient. It is essential to have a uniform definition and classification of failure for data collection, selection and verification.

It is usually assumed that the failure rate of a component, or strictly the hazard rate z, is constant, but this may not necessarily be the case, especially at the burn-in and wear-out stages of its life cycle. Consideration may be given to the effect of time-dependent failure characteristics for the equipment and processes perceived critical to plant operation. Bathtub and Weibull distribution have been used to represent a wide range of failure data. The hazard rate may be decreasing, constant or increasing, corresponding to the regimes of early failure, constant failure or wearout failure and characterized by values of the Weibull shape parameter $\beta < 1, 1, > 1$, respectively. A number of workers have found an early failure regime, corresponding to $1 < \beta$. Some typical results are

Equipment	β	*Reference*
Pump,		
type A	0.74–1.07	de la Mare (1976)
		Berg (1977)
type B	0.69–0.87	de la Mare (1976)
Valves	0.70–1.02	de la Mare (1976)
Pumps	as low as 0.5	Aird (1977b)

A further account of the Weibull method is given in Chapter 7.

A14.3 Influence Factors

The failure rate of equipment is influenced by a large number of factors, including design, specification, manufacture, application, operating conditions, maintenance, and environment. Process equipment is used in a wide variety of operating conditions and environments, and it is desirable to account for these influencing factors.

For some types of device, the effect of certain influencing or environmental factors can be quite well defined. An environment factor K, which is a multiplier to the nominal failure rate, is widely used for the effect of temperature on items of electrical equipment such as resistors. Some values of environment factors are given by A.E. Green and Bourne (1972). Base failure rate, quality factor, learning factor, and environment factor are defined in MIL-HDBK-217F (1991) to predict failure rates for some electronic equipment. It is more difficult to define the effect of such factors on mechanical equipment, but a few examples may be mentioned. Several authors have given correlations for the effect of particular influencing factors on equipment. Moss (1977 NCSR R11) has given data on the failure rates of mechanical valves in two nuclear power stations. The overall failure rates λ of the valve were

Steam valves	$\lambda = 0.1$ faults/year
Water valves	$\lambda = 0.01$ faults/year

The variation of the failure rate with the severity of the operating conditions pressure and temperature was correlated by an equation of the form

$$\lambda = \lambda_0 \exp\left[\frac{D}{D_0} - 1\right] \qquad [A14.3.1]$$

with

$$D = p + t \qquad [A14.3.2]$$

where D is the severity parameter, p is pressure (psi), t is temperature (°C) and subscript 0 indicates base case.

C.F. King and Rudd (1972) have expressed the hazard rate for pumps as function of the form

$$z = At^{-1/2} + B + Ct^3 \qquad [A14.3.3]$$

where t is time and A, B and C are functions of temperature, motor power and pump utilization. An environment factor for instruments has been given by Anyakora, Engel and Lees (1971), as described in Chapter 13. Similarly, a severity index for instruments has been given by Barbin (1973).

A14.4 Collection of Data

Any reliability work would not be successful without an efficient data collection and analysis system, and collection of data is receiving more and more attention of engineers. Failure rate data are characterized by complex interactions of components, specifications, maintenance procedures, operating environments, etc. Each company should examine the sources of data carefully and take full advantages of the available information, internal and external.

The most desirable information for reliability and risk analysis is to have sufficient plant specific data. In general, failure of plant equipment needs to be recorded and investigated, both in order to identify types of failure so that failure rates can be reduced by better engineering, and to obtain failure data for reliability calculations.

It is normal practice to record for production management the downtime of the plant together with its cause. Frequently the cause assigned is the failure of the particular equipment. This system may yield useful data, particularly on plant availability. Likewise, it is normal practice to record for maintenance management failures of plant equipment. Useful data on failure rates may be generated by this system.

Most chemical plants have a wealth of data in their operating and maintenance records. Frequently, the data yielded by the existing production and maintenance management systems are not directly usable for reliability work. It is then necessary to make certain adjustment the records to obtain the desired data. Usually this involves some additional work by the operating and maintenance personnel. It is essential, therefore, to design the data collection system appropriately. Realizing this, CCPS (1991) devoted a whole chapter discussing locating raw plant data and converting them into reliability data.

If data collection is to be instituted for reliability work, it is necessary to define the system carefully. This includes (1) data requirement, (2) data capture, (3) data classification (4) data retrieval, and (5) data utilization. The system should be appropriate in scale and in duration. In some cases the aim is to monitor continuously features such as equipment failure and/or unit availability. In this case continuous collection is clearly necessary. On the other hand if the aim is simply to obtain data for reliability engineering or hazard assessment purposes, it may be sufficient to collect certain data over a limited period on a 'campaign' basis.

One pitfall is to embark upon too ambitious a scheme that is then not fully exploited and soon falls into disuse. A better policy is to start with a more modest system and to put effort at an early stage into utilizing the data and demonstrating their usefulness to those involved in collecting them. At the other extreme, the desire to avoid this error can lead to the converse mistake of seeking so little modification to the existing system that usable data are not obtained. It is desirable, therefore, both to design the system so that it matches the use to be made of it and, once the system is operating, to begin as soon as possible to utilize the data which flow so that those participating can see that use their efforts are not being wasted.

Particular attention should be paid to the point of generation of the data. In some cases the quality of information on documents such as job tickets is sufficiently good for the purpose. But in other cases some form of specific debriefing may be preferable in order to ensure that the data obtained are meaningful.

Further discussions of data collection are given by D.J. Smith and Babb (1973), Wingender (1991), Davidson (1994), Ireson, Coombs and Moss (1996) and Dhillon (1999).

A14.5 Sources of Data

Failure data may be obtained from external sources such as the literature and data banks. Alternatively, they may be collected within the works. The sources available depend on the user. A company operating plant has access to data from its own works that are not available to other parties, unless supplied to an accessible database. The possible sources may include warranty claims, previous experience with similar or identical equipment, repair facility records, factory acceptance testing, records generated during the development phase, customers' failure reporting systems, test, and inspection records generated by quality control/manufacturing group.

Failure rates depend on many factors, including the function of the equipment in the system and the definition of failure; the process environment and the maintenance practices; and the type of equipment and its manufacturer. The ideal situation is to have sufficient in-house data from identical equipment in the same application. On the other hand, internal collection may not be appropriate, or for new plant designs there is apparently no in-house failure data.

Generic data are often used in reliability work, especially at design stage. However, there are available in the literature a number of collections of data, it requires the knowledge of the background and data origin to choose the appropriate generic failure rate data. Table A14.1 is the cross reference between principal data sources prepared by the Data Acquisition Working Party of the Mechanical Reliability Committee of the Institution of Mechanical Engineering (Davidson, 1994), and Table A14.2 is the equipment category associated with Table A14.1.

A selection of data on equipment failure rates obtained by the UKAEA and given by A.E. Green and Bourne are shown in Table A14.3 and Figure A14.1. These data derive from the work of the UKAEA initially in the nuclear field but subsequently in non-nuclear applications also.

Figure A14.2 and Figure A14.3 gives the operating ranges of critical failure rates of some equipment from nuclear plants and EIReDA data.

Further selected failure rate data given in the *Rasmussen Report* are shown in Table A14.4. The failure data in this table include both failure rate per unit time and failure probability on demand and are quoted as a median value together with a range. These data were obtained from both nuclear and non-nuclear sources, but were collected for use in nuclear hazard assessment, in particular on the critical loss of coolant accident (LOCA). The report, which is described more fully in Appendix 23, gives extensive documentation qualifying the data presented.

Table A14.1 *Summary of principal reliability data sources (reproduced from The Reliability of Mechanical Systems edited by J. Davidson (technical editor C. Hunsley), 1994, with permission from Professional Engineering Publishing Ltd)*

Reference	*Application*	*Equipment*					
		Rotation	*Static*	*Instrumentation*	*Safety*	*Process*	*Electrical*
CCPS	I	Y	Y	Y	Y	Y	Y
Davenport and Warwick	N, I	–	Y	–	–	–	–
DEF STAN 00-41 pt 3 Issue 1	M	Y	Y	Y	Y	Y	Y
De la Mare	O	–	Y	–	–	–	–
Dexter and Perkins DP-1633	N, I	Y	Y	Y	Y	Y	Y
EIReDA	N, I	Y	Y	Y	Y	Y	Y
ENI	I	Y	Y	Y	Y	Y	Y
Green and Bourne	N, I	Y	Y	Y	Y	Y	Y
IAEA-TECDOC	N	Y	Y	Y	Y	Y	Y
IEEE 500	I	Y	–	Y	Y	–	Y
Lees	N, I	Y	Y	Y	Y	Y	Y
MIL-HDBK-217F	M	Y	Y	–	Y	–	Y
NPRD-91	N, I	Y	Y	Y	Y	–	Y
OREDA 84	O	Y	Y	Y	Y	Y	Y
OREDA 92	O	Y	Y	Y	Y	Y	Y
RKS/SKI 85-25	N, I	Y	Y	Y	Y	–	Y
Rothbart	I	Y	Y	Y	Y	–	Y
Smith	N, I	Y	Y	Y	Y	Y	Y
Smith and Warwick	N, I	–	Y	–	–	–	–
Wash 1400	N	Y	Y	Y	Y	–	Y
RMC HARIS	O, N, I	Y	Y	Y	Y	Y	Y
SRD Data Centre	O, N, I, M	Y	Y	Y	Y	Y	Y

O = offshore; N = nuclear; I = industrial; M = military.

Table A14.2 *Equipment category code for Table A14.1 (reproduced from The Reliability of Mechanical Systems edited by J. Davidson (technical editor C. Hunsley), 1994, with the permission from Professional Engineering Publishing Ltd)*

Equipment category	*Typical component*
1 Rotating equipment	Pumps, compressors, turbines, motors
2 Static equipment	Pipes, pipelines, flowlines, valves, vessels
3 Instrumentation	Sensor (temperature, pressure, level etc.) and controllers
4 Safety	Fire pumps, safety valves, fire/gas/smoke detectors
5 Process	Pumps, compressors, valves vessels, piping
6 Electrical	Cables, motors, circuit boards lamps

[a] This table should be used in conjunction with the above table.
[b] Note that the categories are not intended to be mutually exclusive. For example, pumps can be categorized as bother 'rotating' and 'process'.

Another set of failure rate data are those given by D.J. Smith (1985) and a selection is shown in Table A14.5. In this case the failure rate is given as a single value, a range or a single value and a range.

A synthesis table generated by EIReDA is shown in Table A14.6. The data set are originally from nuclear plants.

Failure rate data for offshore have been given in the collections by OREDA (1984, 1992, 1997, 2002). These data include not only overall failure rates but also failure rates in some failure modes. The number of failures, which determines the confidence bounds on the values, is also given.

In the cases there is no applicable internal or external failure data, careful engineering estimation has to be made. Usually, the final data set to be used is a judicious mixture of data from all these sources.

A14.6 Status of Data

In hazard assessment it is a good practice to indicate the status of the data. Some relevant distinctions are:

(1) Value based on historical data:
  (a) value based on large number of events (narrow confidence limits);
  (b) value based on small number of events (wide confidence limits);
  (c) value based on number of event-free years or occasions;
(2) Value based on judgment of a number of experts.
(3) Value synthesized using fault tree methods.
(4) Value based partly on data and partly on judgment of analyst.
(5) Value entirely on judgement of analyst.

A similar classification is given in the *First Canvey Report* described in Appendix 7.

The status of data is discussed by Andow (1989) and Holloway (1989).

A14.7 Processing of Data

Using failure rate data requires thorough understanding and judicious judgements. The quality of the data from different sources will be varying. For a particular

Table A14.3 *Some data on equipment failure rates published by the UKAEA, (data from Reliability Technology by A.E. Green and J.R. Bourne, Copyright © , 1972, reproduced with permission of John Wiley and Sons, Inc.)*

	Failure rate (failures/10^6 h)
Electric motors (general)	10.0
Transformers (< 15 kV)	0.6
(132–400 kV)	7.0
Circuit breakers (general, < 33 kV)	2.0
(400 kV)	10.0
Pressure vessels (general)	3.0
(high standard)	0.3
Pipes	0.2
Pipe joints	0.5
Ducts	1.0
Gaskets	0.5
Bellows	5.0
Diaphragms (metal)	5.0
(rubber)	8.0
Unions and junctions	0.4
Hoses (heavily stressed)	40.0
(lightly stressed)	4.0
Ball bearings (heavy duty)	20.0
(light duty)	10.0
Roller bearings	5.0
Sleeve bearings	5.0
Shafts (heavily stressed)	0.2
(lightly stressed)	0.02
Relief valves: leakage	2.0
blockage	0.5
Hand-operated valves	15.0
Control valves	30.0
Ball valves	0.5
Solenoid valves	30.0
Rotating seals	7.0
Sliding seals	3.0
'O' ring seals	0.2
Couplings	5.0
Belt drives	40.0
Spur gears	10.0
Helical gears	1.0
Friction clutches	3.0
Magnetic clutches	6.0
Fixed orifices	1.0
Variable orifices	5.0
Nozzle and flapper assemblies: blockage	6.0
breakage	0.2
Filters: blockage	1.0
leakage	1.0
Rack-and-pinion assemblies	2.0
Knife-edge fulcrum: wear	10.0
Springs (heavily stressed)	1.0
(lightly stressed)	0.2
Hair springs	1.0
Calibration springs: creep	2.0
breakage	0.2
Vibration mounts	9.0
Mechanical joints	0.2
Grub screws	0.5
Pins	15.0
Pivots	1.0
Nuts	0.02
Bolts	0.02
Boilers (all types)	1.1
Boiler feed pumps	1012.5
Cranes	7.8

Sources: F.R. Farmer (1971); A.E. Green and Bourne (1972).
Note: Further failure data on electronic, mechanical, pneumatic and hydraulic components are given by A.E. Green and Bourne (1972).

reliability study, it is essential to consult the original data sources and identify appropriate data sources to reach a better estimation of the equipment failure rates. EsReDA (1999) offers a summary of the collection, analysis and quality assurance of reliability data.

Mean failure rate is appropriate for failure rates obtained from testing a large population of samples under controlled environment, typically for electronic components. On the other hand, for mechanical equipment, we may want to look into the plant operation to select the appropriate data and apply some adjustment.

A14.8 Uncertainty of Data

Reliability data can deviate by a factor of three or four, and a factor of 10 is not unusual, as suggested by Trevor Kletz (1999). However, not much information exists in the open literature regarding the uncertainty of data. Since the uncertainty is quite large, it is inappropriate to report failure rate data or calculations using failure rate data to more than two significant figures. A serious implication of precision is suggested when more than two significant figures are reported.

A14.9 Databases

Database and data bank are sometimes referred to in the literature exchangeably. However, a database is a collection of data managed through computer programs for specified applications while a data bank is a collection of data in a specific area of knowledge, such as a handbook. An account of data banks and databases is given in *Reliability Data Banks* by Cannon and Bendell (1991). Fragola (1996) reviewed reliability databases from a historical aspect and suggested the possible improvements of reliability database development.

The two main kinds of database are the incident database and the reliability database. An incident database does not have an inventory of items at risk and concentrates on the attributes and development of the incidents. The information available is often limited to whatever was recorded at the time. A variety of databases have been established to store and share this type of information. Among them are FACTS, WOAD (Worldwide Offshore Accident Database), MARS (the European Union Major Accident Reporting System), etc. A reliability database may well record incidents, but treats them primarily as events from which statistical information on reliability, availability and maintainability are to be derived. Reliability data can be overall failure rates or values separated into failure modes and causes.

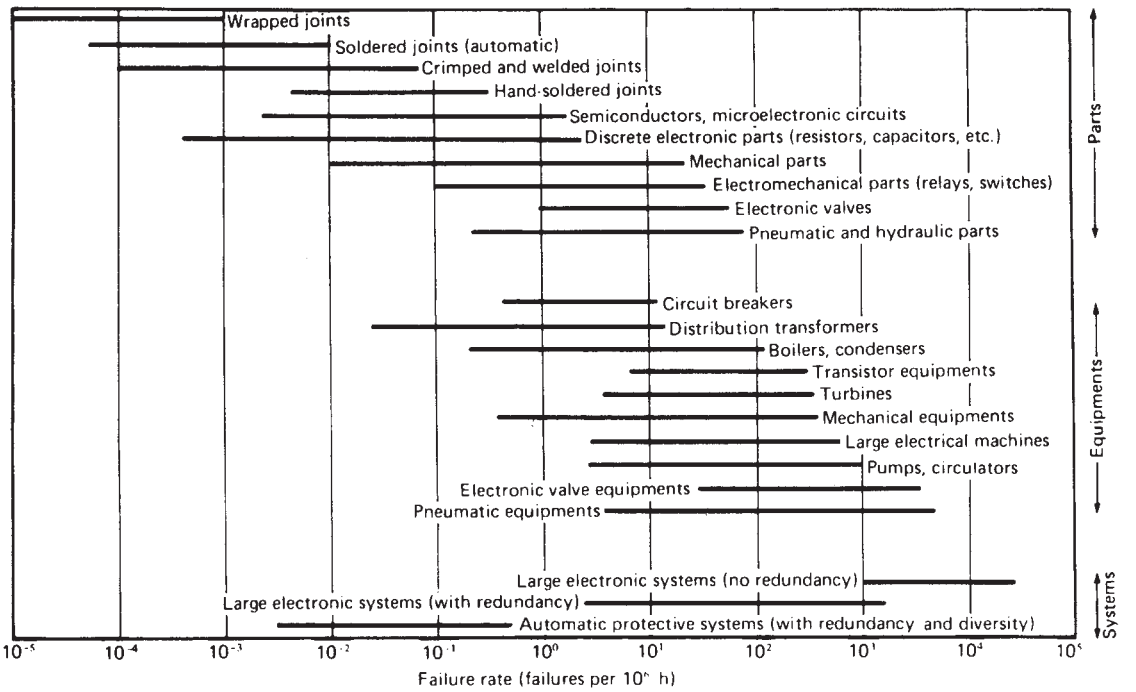

Figure A14.1 *Typical ranges of failure rates for parts, equipments and systems (A.E. Green and Bourne, 1972) (reproduced with permission from Reliability Technology by A.E. Green and J.R. Bourne, Copyright ©, 1972, John Wiley and Sons, Inc.)*

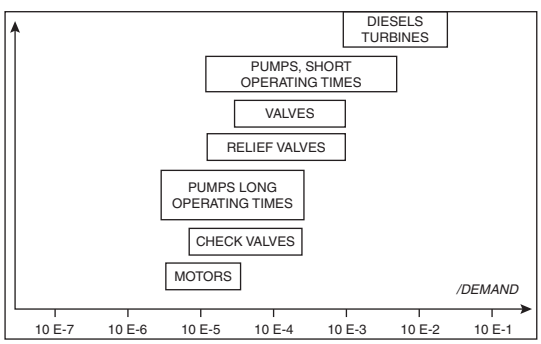

Figure A14.2 *Demand critical failure rate ranges of some equipment at French nuclear plants (sample = 80–170 unit-years depending on equipment) (Lannoy and Procaccia, 1996; reproduced with permission from Elsevier)*

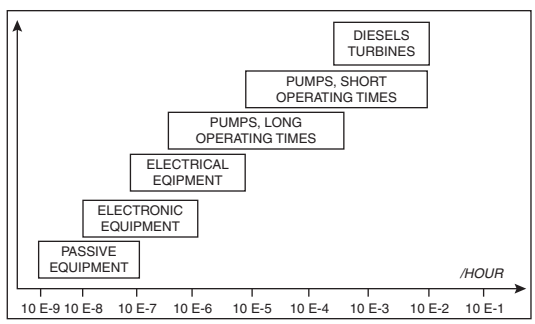

Figure A14.3 *Operating critical failure rate ranges of some equipment at French nuclear plants (sample = 80–170 unit-years depending on equipment) (Lannoy and Procaccia, 1996; reproduced with permission from Elsevier)*

Reliability databases are created by different users for somewhat different purposes. They range from the database created by a single individual through those at company level to those operated by specialist organizations. High quality reliability data are expensive to collect and often require a long time or a large sample to be statistically viable. The investment of effort in creating and operating a reliability database is appreciable and the exercise is not one to be undertaken lightly. It is essential to define clearly the data to be held, the means by which they will be acquired, and the uses to which they will be put.

Most serious reliability databases are part of the activities of an organization that is involved in other aspects of reliability work also. The organization thus has an interest in the database as a user, which is likely to make it more friendly to other users. There are a variety of reliability databases, such as the reliability databank operated by AEA Technology, ERDS, OREDA, etc. CCPS (1991) provides a review of the available databases. CCPS is also conducting a reliability project with selected companies, but the results of this effort are not publically available.

Table A14.4 *Some failure data used in the Rasmussen Report (AEC, 1975)*

		Failure rate	
		Median	*Range*
Diesels (complete plant)	Failure to start, Q_d[a]	3×10^{-2}/d	1×10^{-2}–1×10^{-1}/d
	Failure to run, given start, in emergency conditions, λ_0	3×10^{-3}/h	3×10^{-4}–3×10^{-2}/h
Diesels (engine only)	Failure to run, given start, in emergency conditions, λ_0	3×10^{-4}/h	3×10^{-5}–3×10^{-3}/h
Battery power systems (wet cell)	Failure to provide proper output λ_s	3×10^{-6}/h	1×10^{-6}–1×10^{-5}/h
Electric motors	Failure to start, Q_d[b]	3×10^{-4}/d	1×10^{-4}–1×10^{-3}/d
	Failure to run, given start, in normal environment, λ_0	1×10^{-5}/h	3×10^{-6}–3×10^{-5}/h
	Failure to run, given start, in extreme environment, λ_0	1×10^{-3}/h	1×10^{-4}–1×10^{-2}/h
Transformers	Open circuit, primary or secondary, λ_0	1×10^{-6}/h	3×10^{-7}–3×10^{-6}/h
	Short, primary to secondary λ_0	1×10^{-6}/h	3×10^{-7}–3×10^{-6}/h
Solid state devices (low power application)	Failure to function, λ_0	1×10^{-6}/h	1×10^{-7}–1×10^{-5}/h
	Failure by short, λ_0	1×10^{-7}/h	1×10^{-8}–1×10^{-6}/h
Circuit breakers	Failure to transfer, Q_d[b]	1×10^{-3}/d	3×10^{-4}–3×10^{-3}/d
	Premature transfer, λ_0	1×10^{-6}/h	3×10^{-7}–3×10^{-6}/h
Fuses	Failure to open, Q_d	1×10^{-5}/d	3×10^{-6}–3×10^{-5}/d
	Premature open, λ_0	1×10^{-6}/h	3×10^{-7}–3×10^{-6}/h
Relays	Failure to energize, Q_d[b]	1×10^{-4}/d	3×10^{-5}–5×10^{-4}/d
	Failure of NO contacts to close, given energization, λ_0	3×10^{-7}/h	1×10^{-7}–1×10^{-6}/h
	Failure of NC contacts by opening, given no energization, λ_0	1×10^{-7}/h	3×10^{-8}–3×10^{-7}/h
	Short across NO/NC contacts, λ_0	1×10^{-8}/h	1×10^{-9}–1×10^{-7}/h
	Coil open, λ_0	1×10^{-7}/h	1×10^{-8}–1×10^{-6}/h
	Coil short to power, λ_0	1×10^{-8}/h	1×10^{-9}–1×10^{-7}/h
Terminal boards	Open connection, λ_0	1×10^{-7}/h	1×10^{-8}–1×10^{-6}/h
	Short to adjacent circuit, λ_0	1×10^{-8}/h	1×10^{-9}–1×10^{-7}/h
Wires (typical circuit, several joints)	Open circuit, λ_0	3×10^{-6}/h	1×10^{-6}–1×10^{-5}/h
	Short to ground, λ_0	3×10^{-7}/h	3×10^{-8}–3×10^{-6}/h
	Short to power, λ_0	1×10^{-8}/h	1×10^{-9}–1×10^{-7}/h
Instrumentation (amplification annunciators transducers, combination)	Failure to operate, λ_0	1×10^{-6}/h	1×10^{-7}–1×10^{-5}/h
	Shift in calibration, λ_0	3×10^{-5}/h	3×10^{-6}–3×10^{-4}/h
Pressure switches	Failure to operate, Q_d	1×10^{-4}/d	3×10^{-5}–3×10^{-4}/d
Limit switches	Failure to operate, Q_d	3×10^{-4}/d	1×10^{-4}–1×10^{-3}/d
Valves (manual)	Failure to remain open (plug), Q_d	1×10^{-4}/d	3×10^{-5}–3×10^{-4}/d
	Rupture, λ_s	1×10^{-8}/h	1×10^{-9}–1×10^{-7}/h
Valves (air-fluid operated)	Failure to operate, Q_d[b]	3×10^{-4}/d	1×10^{-4}– 1×10^{-3}/d
	Failure to remain open (plug)[c]		
	Q_d	1×10^{-4}/d	3×10^{-5}–3×10^{-4}/d
	λ_s	3×10^{-7}/h	1×10^{-7}–1×10^{-6}/h
	Rupture, λ_s	1×10^{-8}/h	1×10^{-9}–1×10^{-7}/h
Valves (motor operated, includes driver)	Failure to operate, Q_d[b]	1×10^{-3}/d	3×10^{-4}–3×10^{-3}/d
	Failure to remain open (plug)[c]		
	Q_d	1×10^{-4}/d	3×10^{-5}–3×10^{-4}/d
	λ_s	3×10^{-7}/h	1×10^{-7}–1×10^{-6}/h
	Rupture, λ_s	1×10^{-8}/h	1×10^{-9}–1×10^{-7}/h
Valves (solenoid operated)	Failure to operate, Q_d[b]	1×10^{-3}/d	3×10^{-4}–3×10^{-3}/d
	Failure to remain open (plug), Q_d	1×10^{-4}/d	3×10^{-5}–3×10^{-4}/d
	Rupture, λ_s	1×10^{-8}/h	1×10^{-9}–1×10^{-7}/h
Relief valves	Failure to open, Q_d	1×10^{-5}/d	3×10^{-6}–3×10^{-5}/d
	Premature open, λ_0	1×10^{-5}/h	3×10^{-6}–3×10^{-5}/h

Table A14.4 *(continued)*

		Failure rate	
		Median	*Range*
Check valves	Failure to open, Q_d	1×10^{-4}/d	3×10^{-5}–3×10^{-4}/d
	Internal leak (severe), λ_0	3×10^{-7}/h	1×10^{-7}–1×10^{-6}/h
	Rupture, λ_s	1×10^{-8}/h	1×10^{-9}–1×10^{-7}/h
Pumps (including driver)[d]	Failure to start, Q_d	1×10^{-3}/d	3×10^{-4}–3×10^{-3}/d
	Failure to run, given start, in normal environment, λ_0	3×10^{-5}/h	3×10^{-6}–3×10^{-4}/h
	Failure to run, given start, in extreme post-accident environment inside containment, λ_0	1×10^{-3}/h	1×10^{-2}–1×10^{-4}/h
Pipes $\leq$ 3 in. (per section)	Rupture/plug, λ_s, λ_0	1×10^{-9}/h	3×10^{-11}–3×10^{-8}/h
$>$ 3 in. (per section)	Rupture/plug, λ_s, λ_0[b]	1×10^{-10}/h	3×10^{-12}–3×10^{-9}/h
Gaskets (containment quality)	Leak (serious) in post-accident situation, λ_0	3×10^{-6}/h	1×10^{-7}–1×10^{-4}/h
Elbows, flanges, expansion joints (containment quality)	Leak (serious) in post-accident situation, λ_0	3×10^{-7}/h	1×10^{-8}–1×10^{-5}/h
Welds (containment quality)	Leak (serious) in post-accident situation, λ_0	3×10^{-9}/h	1×10^{-10}–1×10^{-7}/h
Clutches (mechanical)	Failure to operate, Q_d[b]	3×10^{-4}/d	1×10^{-4}–1×10^{-3}/d

[a] Q_d = failure/demand; λ_0 = failure/h in operational mode; λ_s = failure/h in standby mode. The unit d in this table stands for demand.
[b] Demand probabilities are based on the presence of proper input control signals.
[c] Plug probabilities are given as probabilities per demand and as rates per hour, since the plug is generally time-dependent but may only be detected upon a demand on the system.
[d] Turbine-driven pump system may have significantly higher failure rates.

In the following, brief descriptions are given of six principal databases: the NCSR, ERDS, FACTS EIREDA, OREDA, and GIDEP databases. Other databases include the EOF database (Procaccia, 1991); the IAEA database (Tomic and Lederman, 1991); the CREDO database at ORNL (Knee, 1991); the Dante database (Mizuta *et al.*, 1991), the SRDF database (AUPIED and PROCACCIA, 1984), the SKI-PIPE database (Lydell 2000), and the database operated for SRD Association by AEA Technology etc.

A14.9.1 Design of database

As to its definition, a database is first of all a computer system, which may have billions of data collections. The construction of a database involves the translation of the logical data model, giving the relationships between the data field into the physical database embodied in the computer. This is ensured by the database management system (DBMS). Many software companies have developed very effective database management programs that can be tailored for any specific needs. Four main architecture models of the database management system are the hierarchical, network, relational and object models. The characteristics and merits of these different approaches for reliability databases are discussed in EsReDA (1999).

Information about components held in the database comes under two main heads: the component inventory and the component history. The component inventory contains a description of each component on which information is held. The component history gives the detailed failure and maintenance history of each component. Both for component inventory and component history the design of the data set to be held is not a trivial question. For inventory it is first necessary to define the component boundary. A valve actuator, for example, may not remain permanently on the same valve.

It is then necessary to specify the attributes of the components. This involves deciding the degree of subdivision or, alternatively, the level of aggregation. Excessive subdivision results in samples which are too small, while excessive aggregation lumps together items that differ significantly.

For component history, information is typically recorded on failure mode and failure cause. Here the problem is the tendency toward excessive subdivision by creation of additional failure mode and cause categories. This problem is aggravated if numbers of persons are authorized to extend these categories.

It is also desirable to have a plain language fault descriptor. Experience suggests that a set of pre-specified descriptors is on some occasions too detailed and on others not detailed enough, and that there is value in a facility to use free text.

In general, it is desirable to store the data in their 'original' form rather than in an abstracted form, which involves loss of information. For this reason, the data in a reliability data bank may be stored as a set of events from which statistical data may then be obtained.

Early reliability databases tried to account for environments and other conditions via K or π factors, such as MIL-HDBK 217F and Green and Bourne (1972). Most of them give point estimates of failure rates without indicating the bound and confidence level. Modern reliability databases provide failure rates on categorized failure modes, like IEEE-Std-500 (1984), OREDA (1984, 1992, 1997, 2002), EIREDA (1991) and CCPS (1991). IEEE-Std-500, OREDA (1984, 1992, 1997, 2002) and CCPS (1991) provide upper and lower values on failure rates and EIREDA (1991) provides confidence level with error factors.

Many efforts have been carried out to standardize database design. Further discussion on database design can be found in Ireson, Coombs, and Moss (1996), Cooke and Bedford (2002) and the vol. 51, num. 2 of *Reliability Engineering and System Safety* which is specially devoted to reliability database design.

Table A14.5 *Some data on equipment failure rates (D.J. Smith, 1985; reproduced by permission of Macmillan)*

Equipment	*Failure rate*[a] (failure/10^6 h)		
Compressor			
Centrifugal, turbine driven	150		
Reciprocating, turbine driven	500		
Electric motor driven	100	300	
Diesel generator	125 (0.97 start)	4000	
Electricity supply	110		
Gaskets	0.02	1	
Heat exchanger	1	40	
Pipe joint	0.5		
Pumps			
Centrifugal	10	**30**	80
Boiler	100	500	
Fire[b]	100	150	
Fuel	6	50	
Oil lubrication	10	30	100
Vacuum	20		
Turbine, steam	30	80	
Valves			
Ball	1	3.5	
Butterfly	1	**20**	30
Gate	1.5	15	
Relief	4	9	
Non-return	2	5	
Slam shut	10	30	
Solenoid	1.5	**10**	30
Valve actuators[c]			
Fail open	0.1	4	
Spurious close	5	40	

[a] Entries are given in three formats: a single value, where the various references are in good agreement; two values, indicating a range; and three values with one in bold, indicating a range with the value in bold predominating. Bold is also used for one end of a range, where that value predominates.
[b] Approximately 800 for a complete fire pump and priming system.
[c] Depends on the complexity of the pneumatic circuit; requieres FMEA.

A14.9.2 Operation of database

The operator of a reliability database has to maintain a sufficient flow of data from the data suppliers, synthesize the data from different sources, and satisfy the needs of the data users in a manner which is cost effective. This is no easy task.

Fresh data are the lifeblood of a reliability data bank. There must be a sufficient incentive for an organization to supply them, either by collecting them itself or by allowing access for their collection. Typically it will be one that is also a user of the database.

The data user will have a set of requirements, which often can be met only in part. Ideally the user would like data from which to obtain failure and repair time distributions, and so on. Often these will simply not be available, the best on offer being perhaps failure or repair rates based on a constant rate assumption. There may also be problems of sample size. The data bank operator has to balance the often-conflicting requirements of user demand, data supply and economy in handling.

A14.9.3 Data acquisition

Information on equipment for the component inventory is obtained from the plant documentation, which includes equipment records and equipment and plant drawings. Acquisition of the inventory data for a plant may not be straightforward. Records and drawings may be incomplete from the outset, and it is even more common that modifications made are not entered. There can be confusing identifications, with the same item allocated several quite different code numbers.

There can be a corruption of the component design parameters, with differences between the item as designed and as purchased and installed being quite common. As Cross and Stevens comment: 'It is incredible how poor the average plant inventory records are'.

For information on equipment failure and repair a basic source of information is the job card or ticket. Typically this gives as a minimum the identity of the equipment, the failure notified or diagnosed and the repair work done. Other documentation such as logbooks, permits-to-work and stores requisitions are generally useful as cross-checks rather than prime sources. Sometimes, vendors' test data can also be used as a supplement source.

To the extent practical, the failure data should be such as to permit analysis to obtain failure distributions as well as average values. This implies that the data should give the times to failure for individual equipment rather than just the total number of failures. This greatly enhances the value of the data to the data analyst.

Some data require a degree of reinterpretation or filtering. One common problem is the failure that presents as a cluster of events arising over a short time interval. This may take several forms, each of which involves events that are in some sense dependent. One is the repair that is unsatisfactory so that failure recurs almost immediately and the work has to be done again. Somewhat similar is the repair that is made in several passes such as a leaking valve which is first tightened, then repacked and finally replaced. A third situation is the nearly simultaneous failure of a number of items due to a common cause.

A14.9.4 NCSR database

The NCSR Reliability Data Bank is a major database system which has been in operation for over twenty years serving the nuclear, aerospace, electronics, oil, chemical and other industries. Accounts of the early database and SYREL data bank have been given by Barnes (1967 UKAEA AHSB(S) R138), Ablitt (1973 SRS/GR/14) and Fothergffl (1973 SS/GR/22). The mature database has been described by Cannon (1991a,b). An account of further developments in the database is given by Cross and Stevens (1991).

As described by Cannon (1991a) the data bank about the mid-1980s consisted of data stores for (1) generic reliability, (2) events, (3) accidents, (4) human reliability, and (5) maloperation. Much of the data collection was carried out by placement of students in cooperating companies. Cannon gives examples of the use of the data bank, including cases where application of the data resulted in reductions in the observed failure rates.

Cross and Stevens (1991), writing from the perspective of the user as well as the operator of a data bank, describe the transition of the NCSR system from a system which was based originally on 1960s technology, using mainframe

Table A14.6 *Example of best-estimated reliability parameters from some equipment (Lannoy and Procaccia, 1996; reproduced with permission from Elsevier)*

Equipment	*Main Character*	*Mean failure rate* (10^{-6}/h)	*Range* (10^{-6}/h)	*Failure on demand* (10^{-3}/d)	*Range* (10^{-3}/d)	*MMTR* (h)
Accumulator, nitrogen driven						
Pressurized	$P < 50$ bar; T < 50°C	0.52	0.2–0.8	0.03	–	2.6
Compressor, motor driven						
Centrifugal	*P*: 6–40 bar; kW: 360	81	60–104	0.18	0.09–0.25	2.6
Reciprocating	$P \cong 10$ bar; kW: 5–85	782	506–1108	0.3	0.2–0.38	5
Water filter (paper)	*P*: 10–190 bar	2.3	1.5–3.1	–	–	6
Heat exchanger						
Plate	*P*: 7–155 bar *T*: 30–220°C	20.7	19–22	0.01	–	9
Shell/tube		0.55	0.08–0.9	–	–	25
Shell/tube	*P*: 155 bar; *T*: 200–300°C	0.31	0.005–0.5	0.02	–	25
Shell/tube	*P*: 7–50 bar; *T*: 50–220°C	0.83	0.2–1.3	–	–	25
Pump, centrifugal multistage						
Motor/turbine driven[a]	kW: 300/400 head: 900 m flow: 80 m^3/h	174	125–228	0.2	0.1–0.3	34
Turbine driven	kW: 2200/5300 head: 570 m flow ≤ 3300 m^3/h	10	7–14	0.15	0.11–0.27	13

[a] Standby pump.

computers, large in size and not readily modified, to one utilizing modern database methods and implemented on PCs.

Of the two basic formats for storage of information, summary and complete record, the NCSR system utilizes the latter, so that complete details of each event are held. From these complete records statistical data can then be abstracted as required.

A14.9.5 ERDS database

The European Reliability Data System (ERDS) is an EC database operated by the JRC at Ispra. It is described by Capobianchi (1991).

ERDS acquires its data from European and other databases, and is therefore in effect a database of databases. It is oriented particularly to serve the nuclear industry.

The data are rendered homogeneous by conversion to a uniform format. This format is specified in a detailed system of classification – the Common European Reference Classifications, which is thus by way of being a European standard.

ERDS has four main data subsystems: (1) the Component Event Data Bank (CEDB), (2) the Abnormal Occurrences Reporting System, (3) the Operating Unit Status Report and (4) the Reliability Parameter Data Bank. Among them, the CEDB stores the component characteristics, historical information, and failure information and is the central subsystem, which serves and is connected to the other three subsystems.

A14.9.6 FACTS database

The Failure and Accident Technical Information System (FACTS) is an incident data bank operated by TNO in the Netherlands. It is described by Koehorst and Bockholts (1991).

FACTS gathered the information about near-misses, minor accidents and major accidents associated with hazardous materials. Nuclear materials and military activity are excluded for its scope. The information is derived from the literature; from companies; from inspectorates, fire services, etc.; and from FACTS agencies in other countries, respecting anonymity. Press reports serve as triggers to acquire information.

Features of the database are a schedule of accident attributes and values and a hierarchical keyword structure. Another structure is the cause classification in which the course of the accident is translated into a sequence of occurrences.

This makes it possible to trace back from an event down the causal chain. The original plain text accounts are held on microfiche.

Applications of the system described by the authors include (1) analysis of the role of instrumentation in accidents; (2) analysis of incorrect human response and (3) compilation of a reference book to trace incident causes (the Cause Book), giving a survey of incident causes which can occur in a large number of systems and operations.

Further analysis is given in *An Analysis of Accidents with Casualties in the Chemical Industry Based on Historical Facts* by Koehorst (1989).

Developments of the system include an expert system front end.

A14.9.7 OREDA database

The Offshore Reliability Data (OREDA) project is an offshore reliability database described in the handbook by OREDA (1984, 1992, 1997, 2002). It gives failure rates, failure mode distribution and repair data for offshore installations, mainly in the UK and Norwegian sectors of the North Sea.

A substantial effort was devoted to the design of the system to ensure as far as possible that the components, their boundaries and environment, are well defined and that the data obtained are high quality and statistically meaningful. The database is fully explained in the OREDA handbook, which describes the system, gives the data and outlines the statistical treatment. Some discussion about the data collection and application of this project can be found in Groenendijk (1995), Sandtorv, Hokstad and Thompson (1996), Rausand and Øien (1996), Haugen, Hokstad and Sandtorv (1997), Langseth, Haugen and Sandtorv (1998).

The project therefore serves as a good illustration of a reliability database and is widely recognized as a standard information source for risk analysis.

The project is supported by ten major oil and gas companies: AGIP, BP, Elf, Esso, Norsk Hydro, SAGA, Shell, Statoil and Total. The data cover (1) process systems, (2) control and safety systems, (3) electrical systems, (4) utility systems, (5) crane systems and (6) subsea equipment and drilling systems.

The component inventory gives the following information: (1) brief description, (2) application, (3) operational mode (continuous, standby, protective, etc.), (4) internal environment (fluids handled), (5) external environment and (6) boundary specification, including a sketch. The operating data include (1) population at risk, (2) number of installations supplying data, (3) total calendar and operational times and (4) number of demands (where applicable). The failures are broken down into four different categories of severity: (1) critical, (2) degraded, (3) incipient and (4) unknown severity; there may be a number of modes in each category. The failure and repair data comprise (1) number of failures, (2) failure modes, (3) failure rates for each failure mode, (4) active repair time and (5) repair time. Mean and lower and upper bound values are given for the failure rates and mean, minimum and maximum values for the repair times. The active repair time is the average time required to analyse and repair the item and return it to service, excluding time to detect the fault and isolate the equipment and any delay due to tools or spares. The repair time is the number of manhours required for the repair. The failure and repair data are given for each mode and for the equipment overall.

Some of the events recorded in the OREDA as failures are those such as failure to start and spurious trip.

The number of installations participating, the number of components at risk and the number of failures experienced are very variable. In many cases the population at risk is 10 or less.

The handbook states that data in the form of times between failures are collected, but that confidence in the statistical data varies between the different generic groups and that for most purposes time-independent failure rates are a relevant approximation. It does not give data on times between failures.

A14.9.8 EIReDA database

The EIReDA (European Industry Reliability Data Bank) is operated by ESReDA, which is established in 1992 by EuReDATA (European Reliability Data Bank Association) and ESReDA (European Safety and Reliability Research and Development Association) jointly. The original data were collected from 50 nuclear power plants operated by Electricite de France from 1978 to 1995 and analysed using Bayesian methodology. The data bank contains failure rates (for critical failure modes only) and mean repair time data for mechanical components, electrical components and instrumentation and control equipment. A full description of the data bank is provided in EsReDA (1998), which describes the scope, the choice of components, the definition of boundaries, and the statistical treatment.

Engineering and operational characteristics are provided in detail for each item of equipment, as well as a color photograph, a general drawing and the boundaries. Background information such as inventory and service year is also provided. Comparable data are listed in a separate table, compiled from other published sources (mainly WASH 1400, IEEE 500, RKS 85-25; EuReDATA and ESReDA project reports and publications, and other power plant, modern petrochemical and processing plants). The methodological application to other industries is included in the appendix.

A14.9.9 GIDEP database

GIDEP (Government Industry Data Exchange Program) was established in 1959 as the Inter-service Data Exchange Program (IDEP) by the US government to reduce expenditures of resources in the life cycle of systems facilities and equipment through share of data among government agencies and industry organizations.

To make use of GIDEP database, an agency or company has to be a full or partial participant of GIDEP program. GIDEP is currently participated by thousands of agencies and industries.

Information on parts, processes and materials they use or manufacture is submitted to the GIDEP Operations Center by government and industry participants.

The program maintains six major types of data: (1) engineering data; (2) failure experience data; (3) metrology data; (4) product information data; (5) reliability– maintainability data and (6) urgent data requests. GIDEP is DOD's centralized database for Diminishing Manufacturing Sources and Material Shortages (DMSMS).

A14.10 Inventory

A14.10.1 Inventory of plants

Information is sometimes required on the number of plants at risk, either nationally or world-widely. This is needed, for example, in order to convert data on the number of a particular type of event, for example, vapour cloud explosions, into a frequency per plant.

Data on the number and capacity of chemical and petrochemical plants in various countries are given in the publications by SRI International which include Directory of Chemical Producers – United States 1988 and Directory of Chemical Producers – Western Europe 1988 (SRI Int., 1988b,c).

From the SRI data for the United States (US) and Western Europe (WE):

	US	*WE*	*UK*
No. of chemical/petrochemical plants	1420	1455	185

The following ratios apply for the number of plants and for the plant capacity:

	US/WE	*UK/WE*
No. of plants	0.92	0.12
Plant capacity	1.08	0.12

For petroleum refineries similar data are given in the *International Petroleum Encyclopaedia 2002* (IPE, 2002).

From IPE data

Region	Africa	Asia	East Europe	Middle East	North America	South America	West Europe
No. of refineries	46	203	94	46	170	68	105

The countries having over 10 refineries from IPE (2002) data are listed below.

	No. of refineries
United States	143
China	95
Russia	42
Japan	35
Canada	21
Germany	17
India	17
Italy	17
France	13
Brazil	13
United Kingdom	11
Argentina	10
Australia	10
Romania	10
World total	732

A refinery contains a number of major units and this number varies. Information given in periodic surveys (e.g. Anon., 1985dd) suggests an average value of about five such units per refinery.

Information is also available on the number of installations that attract certain regulatory controls. In the United Kingdom, the number of installations notifiable under the NIHHS Regulations 1982 has been given by Pape and Nussey (1985) and by Pape (1989) as

LPG	600
Natural gas	400
Chlorine	120
Total	1600

Of the LPG installations 450 are storage installations and 130 gas cylinder storages.

In a discussion of the CIMAH Regulations 1984 (later superseded by COMAH) Welsh (1993) states that over 400 safety reports have been submitted. In interpreting this figure, it should be borne in mind that the number of reports is necessarily be equated to the number of CIMAH installations. CIMAH Regulation 1984 was later replaced by COMAH Regulation in the United Kingdom, which is stricter and came into force in the February of 1999. A total of 3–5000 top-tier major hazard plants in Europe are expected to submit safety, of which the United Kingdom has 438 with a further 843 lower tier installations.

A14.10.2 Ammonia plants

Estimates of the number of ammonia installations and carriers have been given by Baldock (1980) and are shown in Table A14.7.

A14.11 Inventory of equipment in plants

Another estimate that may be required is the number of potential leak sources on a plant. Information on the number of fittings and valves on pipework of different diameters has been given by Hooper (1982) in the context of cost estimation and is shown in Table A14.8.

Numbers of potential leak sources on various types of plant have been given, mainly in the context of fugitive emissions. Table A14.9 shows the numbers given by T.W. Hughes, Tierney and Khan (1979) for some potential leak sources in four petrochemical plants and Table A14.10 those given by D.P. Wallace (1979) for some sources in a single medium sized plant. Table A14.11 shows data given by Lipton and Lynch (1987) on the number of some sources in a large refinery. Table A14.12 after Wetherold (1983) gives the number of valves in a refinery and in two other plants.

Using such data, it is possible to construct a profile of the potential leak sources on a typical plant.

In a study of fugitive emissions from the ethylene oxide production industry, equipment containing more than 1 wt % ethylene oxide is surveyed in 13 major EO plants by Berglund, Romano, and Randall (1990).

A14.12 Vessel and Tanks

The failure rates of pressure vessels are discussed in Chapter 12.

Table A14.7 *Estimated number of ammonia installations and carriers*

	Estimated no. world-wide
Plants	2,000
Storage areas	1,000
Vessels	10,000
Refrigeration plants	100,000
Transfer points	1,000
Road tankers	1,000
Rail tankers	5,000
Ammonia ships	20
Pipeline miles	2,000

Source: Baldock (1980), table 2.

Table A14.8 *Pipework fittings and valves*

Nominal pipe diameter (in.)	*Total length of pipe* (ft)	*Number of fittings*	
		Flanges	*Valves*
1/2	33,990	1,818	11,589
3/4	33,123	2,973	7,551
1	124,513	12,552	10,363
1 1/2	121,212	7,299	3,313
2	142,891	11,727	4,199
3	125,550	10,427	2,441
4	84,705	6,608	1,346
6	77,717	4,578	898
8	67,667	3,592	466
10	39,225	1,613	301
12	16,445	762	162
14	3,997	342	72
16	10,292	506	90
18	3,530	362	41
20	5,698	804	34
24	5,983	357	40
30	3,121	255	13
36	1,608	66	12

Source: Hooper (1982), table on p. 128.

Table A14.9 *Inventory of potential leak sources: number of sources on four petrochemical plants*

Leak source	*No. of items Monochloro-benzene plant*	*Butadiene plant*	*Ethylene oxide/glycol plant*	*Dimethyl tereph-thalate plant*
Flanges	1500	26,000	NA[a]	NA
Valves	640	6,700	NA	NA
Pumps	25	174	69	67

Source: T.W. Hughes, Tierney and Khan (1979), table 3.
[a] NA: not available.

Table A14.10 *Inventory of potential leak sources: estimates of number of leak sources on a medium-sized plant*

Leak source	*No. of items*
Flanges	2410
Valves	
In-line, gas	365
In-line, liquid	670
Open-ended	415
Pump seals	
Packed	6
Mechanical, single	43
Mechanical, double	10
Compressor seals	2
Safety relief valves	50

Source: D.P. Wallace (1979), p. 92.

Table A14.11 *Inventory of potential leak sources: estimated number of sources in a large refinery*

Leak source	*No. of items*
Flanges	46,500
Valve	11,500
Pump seals	350
Compressors	70
Relief valves	100
Drains	650

Source: Lipton and Lynch (1987), table 7.2.

Table A14.12 *Inventory of potential leak sources: number of valves in a refinery and two other plants*

A No. of valves in three plants

	No. of valves
Large integrated refinery	21, 800
Large olefins plant	15,000
Cumene process unit	1,179

B No. of valves on different duties in large refinery

Leak source	No. of items
Valves	
Gas and light liquid only	13,334
All	21,776

Source: Wetherold (1983), tables 1 and 3.

Estimated failure rates of storage tanks quoted by Batstone and Tomi (1980) are shown in Table A14.13.

Data on the failure rates of storage tanks in ammonia and LNG are given in Sections A14.25.2 and A14.24, respectively.

Data on storage tank fires are given in Section A14.28.5.

A14.13 Pipework

The failure rates of pipes are discussed in Chapter 12.

De la mare and his coworkers developed pipeline inventory and pipeline failure and repair history databanks for the North Sea area. Some of their statistic results are shown in Tables A14.14–A14.18.

Data on the failure rates of gaskets are given in Tables A14.3–14.5 and by Pape and Nussey (1985).

Comparison of these values gives for the failure frequency of gaskets:

	Failure frequency (failures/year)
Smith: Lower limit	0.00018
Upper limit	0.0088
UKAEA	0.0044
Rasmussen Report	0.026
Pape and Nussey	4×10^{-5} (average)

A14.13.1 Bellows

There is a potential ambiguity in the term bellows, which may refer to bellows used in instrumentation or to those used in pipework.

The UKAEA data on the failure rate of bellows in Table A14.3 gives a failure frequency of 5×10^{-6} failures/year. D.J. Smith (1985) gives a failure rate of 4×10^{-6} failures/year.

A14.14 Heat Exchangers

Data on the failure rates of heat exchangers are given in Table A14.5.

Some information on the failure rate of heat exchangers has been given by C.F. King and Rudd (1972) in a reliability study of a heavy water plant. With some 21 heat exchangers, the MTTF ranged from 677 to 7865 h.

For offshore shell and tube heat exchangers, the data given by OREDA (1997) include the following (all failure modes included):

	Population	*No. of failures*	*Failure rate* (per 10^6 h)	*Mean repair time* (manhours)
Crude oil → > sea water (1000–3000 kW)	2	0	35.14 (upper limit)	
Crude oil → > sea water (1000–10,000 kW)	10	29	94.42	145.0
Gas → > gas (1000–10,000 kW)	4	5	75.02	48.2
Gas → > gas (10,000–30,000 kW)	1	5	142.60	3.4
Gas → > sea water (100–1000 kW)	4	3	31.16	14.7
Gas → > sea water (1000–10,000 kW)	4	12	85.62	53.2
Gas → > water/glycol (1000–3000 kW)	3	5	79.61	47.4
Gas → > water/glycol (1000–10,000 kW)	5	13	120.24	45.0
Gas → > water/glycol (10,000–30,000 kW)	12	38	121.64	64.4

A14.15 Rotating Machinery

A14.15.1 Compressors

Data on the failure rates of compressors are given in Table A14.5.

For offshore compressors the data given by OREDA (1997) include the following (all failure modes included):

	Population	*No. of failures*	*Failure rate* (per 10^6 h)			*Mean repair time* (manhours)
			Lower	*Mean*	*Upper*	
Centrifugal, electric motor driven						
100–1000 kW	5	58	2.64	550.66	2106.50	20.6
1000–3000 kW	14	204	174.54	880.21	2033.05	25.1
3000–10,000 kW	9	398	1157.79	2433.02	4088.47	48.2
Centrifugal, turbine driven						
	9	586	122.28	2449.88	7341.37	29.6
Reciprocating, electrical motor driven						
1000–3000 kW	4	352	2293.78	2509.70	2741.16	9.6
3000–10,000 kW	4	317	4029.38	5388.42	6909.82	98.6

The Power Reliability Enhancement Program (PREP) of the US Army corps of Engineers conducted a study of the operational and maintenance data on 204 power generation, power distribution and HVAC components (Hale and Arno, 2001). Efforts focused on the equipment installed after 1971. To be statically justifiable, minimums of 3,500,000 calendar hours were established for each component. They reported 0.07601 failures/year for electric air compressor and 0.01033 failures/year for fuel air compressor (Hale and Arno, 2001).

A14.15.2 Fans

Data on the failure rates of fans are given in Table A14.45.

A14.15.3 Pumps

There are wide variations in the type, duty and environment, and hence in the failure rate, of pumps. However, many pumps have a failure rate of some 1–5 failures/year. Data on the failure rates of pumps are given in Tables A14.3–A14.5.

D.J. Smith (1985) gives the failure modes of pumps as about 50% leakage and 50% no transmission.

Some information on the failure rate of pumps has been given by C.F. King and Rudd (1972) in a reliability study of a heavy water plant. MTTFs for four auxiliary pumps ranged from 51 to 398 days according to maintenance data, but from 12.5 to 439 days according to production data.

An account has been given by R. James (1976) of a pump maintenance program on 880 major process pumps, mainly

centrifugal pumps, aimed at eliminating premature wearout failures, in which the MTBF of the pumps was raised from 8.7 to 12.2 months.

In accounts of pump reliability improvements by a particular manufacturer (Anon., 1985x; Bloch and Johnson, 1985) it is stated that for pumps the industry average MTBF is some 6 months, corresponding to a failure rate of 2 failures/year. Bloch and Johnson state that ANSI standard pumps have an MTBF of 13 months, or failure rate of 0.9 failures/year. It is claimed, however, by Anon. (1985x) that specified improvements have resulted in the achievement of an MTBF of some 25 months, or failure rate of 0.48 failures/year. For individual features improvements are said to have extended the lives of the ball bearings, the mechanical seal system, the shaft and the coupling to 5, 2.5, 15 and 7 years, respectively.

A study of 85 ethylene plant pumps has been reported by Sherwin (1983). There were 243 failures and the failure rate was 1.8 failures/year. The failure modes are shown in Table A14.19

Data on the failure rates of pumps in LNG plants are given in Table A14.44.

A study of feedwater pumps in French nuclear power stations has been made by Aupied, Le Coguiec and Procaccia (1983). The overall failure rate was Failure rate of feedwater pumps $= 5.6 \times 10^{-4}$ failures/h $= 4.9$ failures/year

The failure modes of the pumps are shown in Table A14.20.

A survey of pump mechanical seals by BHRA has been reported by Flitney (1987) in which pumps were surveyed in three refineries and five chemical plants, a sample of some 200–300 pumps being taken at each site. The two principal reasons for seal removal were

Leakage	66%
Bearing replacement	12%

Mechanical seals are also the subject of a study at Esso reported by N.M. Wallace and David (1985). They give a table of seal lives for some 17 cases, the lives varying from 2 to 12 months. For catastrophic failure of a pump the Rijnmond Report uses a value of 1×10^{-4} failures/year.

Operational data of 505 primary coolant pumps of steam supply systems in 146 nuclear power plants were analysed and an average failure rate of 1×10^{-5} was suggested (Milivojevic and Riznic, 1989).

Data from 320 electric submersible pumps gathered over a 13-year period in Milne Point Field, Alaska were analysed and the mean time to failure is estimated to be 330 days (Sawaryn, Grames, and Whelehan, 2002).

Some data on pumps given out by EIReDA is shown in Table A14.21.

Table A14.13 *Estimated failure rates of storage tanks*

	Failure rate (failures/10^6 year)
Atmospheric tank	30
Refrigerated tank	
Single wall	10
Double wall	1

Source: Batstone and Tomi (1980), table A1.

Table A14.14 *Failure frequency varying with pipeline status and location (de la Mare, Bakouros and Tagaras, 1993; reproduced with permission from Elsevier)*

	Near platform	*Open Sea*	*Near Shore*
Installation	4	19	0
Hydrotest	5	5	0
Operation	15	7	2

Table A14.15 *Failure frequency varying with cause of failure and location (de la Mare, Bakouros and Tagaras, 1993; reproduced with permission from Elsevier)*

	Near platform	*Open sea*	*Near shore*
Material	1	3	0
Construction	3	10	0
Corrosion	4	0	0
Anchors	5	7	0
Fishing activity	0	1	0
Scour-vortex	4	4	2
Manufacturer	1	0	0
Constructor's equipment	2	2	0

Table A14.16 *Failure frequency and rate varying with diameter (de la Mare, Bakouros and Tagaras, 1993; reproduced with permission from Elsevier)*

Diameter range (inches)	*Percent by number of pipelines*	*Percent by total operational experience*[a]	*Failure frequency*	*Failure rate* (failures/1000 km-year)
0.0–6.0	4.8	0.9	0	0.00
6.1–12.0	13.6	2.7	2	1.71
12.1–18.0	20.8	10.2	21	4.71
18.1–24.0	24.8	10.2	11	2.47
24.1–30.0	16.8	23.5	7	0.68
>30.0	19.2	52.5	16	0.70
Total	100.0	100.0	57	1.31

Table A14.17 *Failure frequency and rate varying with length (de la Mare, Bakouros and Tagaras, 1993; reproduced with permission from Elsevier)*

Length range (km)	*Percent by number of pipelines*	*Percent by total length*	*Percent by total operational experience*[a]	*Failure frequency*	*Failure rate* (failures/1000 km-year)
0.0–2.0	4.95	0.18	0.21	1	11.19
2.1–10.0	24.79	2.37	2.25	8	8.13
10.1–20.0	23.98	6.57	5.03	13	5.92
20.1–50.0	16.53	10.84	9.64	3	0.71
50.1–100.0	11.57	15.96	17.77	4	0.52
> 100.0	18.18	64.08	65.10	25	0.84
Total	100.00	100.00	100.00	54	1.21

[a] Operational experience is defined as the product of length and year of service.

Table A14.18 *Failure frequency (F) and rate (r) varying with commissioning dates and years of operation (de la Mare, Bakouros and Tagaras, 1993; reproduced with permission from Elsevier)*

Years of operation	*Commissioning date*							
	Year 7–8		*Year 9–10*		*Year 11–12*		*Year 13–14*	
	F	*r*	*F*	*r*	*F*	*r*	*F*	*R*
1	2	1.8	17	7.2	14	8.2	3	7.5
2	5	2.3	21	4.5	16	4.7	3	3.7
3	8	2.2	21	3.0	17	3.3	3	2.5
4	10	2.0	22	2.4	18	2.7	3	1.9
5	10	1.6	23	2.0	18	2.6	–	–
6	10	1.4	23	1.6	18	1.8	–	–
7	10	1.2	23	1.4	–	–	–	–
8	10	1.0	23	1.2	–	–	–	–
9	10	0.9	–	–	–	–	–	–
10	10	0.8	–	–	–	–	–	–

For offshore pumps failure data are given by OREDA (1992, 1997, 2002), covering motor and turbine driven oil pumps, motor and diesel driven fire pumps, chemical injection pumps, and sea water injection and lift pumps. The following data were extracted from OREDA (1997).

	Population	*No. of failures*	*Mean failure rate* (per 10^6 h)	*Mean repair time* (manhours)
Centrifugal, chemical injection, processing				
51–100 kW	2	10	142.69	57.1
100–1000 kW	2	40	570.78	117.1
Oil handling				
100–1000 kW	16	321	533.28	38.4
1000–2500 kW	5	132	1136.97	27.8
2500–3600 kW	3	98	1357.04	28.7
Diaphragm, chemical injection, processing	8	35	124.86	31.6
Reciprocating, oil handling	2	6	105.63	15.6

Table A14.19 *Failure modes of ethylene plant pumps*

Failure mode	*No. of failures*	*Proportion* (%)
Seals/glands	119	49.0
Overhauls[a]	62	25.5
Cleaning	14	5.8
Repeat overhauls	7	2.9
Leaks[b]	7	2.9
Motor failures	5	2.0
Couplings	5	2.0
Bearings	2	0.8
Other	22	9.1
Total	243	100.0

Source: Sherwin (1983).
[a] Overhauls were not at regular intervals but as a result of conditions found on opening up following a failure.
[b] Leaks other than those due to seals/glands.

A14.15.4 Turbines

Data on the failure rates of turbines are given in Table A14.5.

A study of steam turbine failure with particular reference to catastrophic failure and the generation of missiles has been described by Bush (1973). He quotes data from six major suppliers of steam turbines. The accumulated

Table A14.20 *Failure modes of feedwater pumps in some French nuclear power stations*

Failure mode	*Proportion* (%)
Body, shaft	5
Packing	29
Overspeed	10
Contactors	13
Control	16
Lubrication	12
Human error	6

Source: Aupied, Le Coguiec and Procaccia (1983), figure, p. 149.

operating experience is 12,330 years prior to 1950 and 57,950 years in the period 1950–72. There were no failures in the earlier period and 10 in the later period. All four failures after 1959 were due to over-speed. Of the ten incidents seven generated missiles. His analysis indicates that the failure frequency was slowly decreasing. His estimates of the then current failure frequencies are

$$\text{Frequency of failure} = 9 \times 10^{-5}/\text{year}$$

$$\text{Frequency failure resulting in missile generation} = 8 \times 10^{-5}/\text{year}$$

For offshore gas turbines failure data are given by OREDA (1992, 1997, 2002).

A14.16 Valves

A14.16.1 General

A study of valves in French nuclear power stations has been carried out by Aupied, Le Coguiec and Procaccia (1983). Some of the more critical valves are classified as primary valves and the others as secondary valves. Some of the failure rates obtained in this work are shown in Table A14.22, while failure modes are given in Table A14.23.

A survey designed to identify significant and common valve problems such as leakage and jamming and to relate them to valve type, service and manufacturer has been described by Vivian (1985). The survey was conducted in a major oil company and covered 10 businesses involving 17 facilities, of which a significant proportion are in the North Sea. Some quarter of a million valves were covered, of which almost 10% were reported as giving significant problems. The numbers of each type of valve are shown in Figure A14.4(a) and the associated problems in Figure A14.4(b).

The UKAEA data in Table A14.3 gives for control valves a failure rate of 0.25 failures/year and for manual valves 0.13 failures/year. The values used in the *Rijnmond Report* are 0.3 and 0.1 failures/year for control and manual valves, respectively.

Further values for valve failure rates obtained by Moss (1977 NCSR Rll) are discussed in Section A14.25. These values are 0.1 and 0.01 failures/year for valves on steam and water service, respectively. The latter value in particular is a lower than the others quoted here.

For valve rupture the *Rasmussen Report* gives a failure frequency of 1×10^{-8}/h (0.9×10^{-4}/year). For valves in offshore operation, failure data are given by OREDA (1992, 1997, 2002).

A14.16.2 Control valves

Data on the failure rates of control valves are given in Tables A14.3–A14.5. Further data are given in various parts of this appendix.

A14.16.3 Pressure relief valves

For pressure relief valves (PRVs) the definition of failure is particularly important. Definitions of failure that may be used include failure of any kind, failure to lift within a certain proportion of the set pressure and failure to open on demand. The failure rates for these different types of failure are quite different.

Data on the failure rates of PRVs are given in Tables A14.3–A14.5, A14.22 and A14.23.

The following data are for the failure rates of PRVs are given by Kletz (1972a, 1974a) and by Lawley and Kletz (1975):

	Failure rate (faults/year)
Valve fails shut	0.001
Valve lifts heavy	0.004
Total fail danger	0.005 (later modified to 0.01)
Valve fails open or lifts light	0.02
Total fail safe	0.02

A survey of PRV inspections in a large chemical company has been reported by Aird (1983). Failure was defined as lifting 10% outside the set pressure when put under test. The number of useful tests was 866. The proportion of failures was 44.5%.

The failure rate showed no discernible trend with operating time and it was concluded that PRVs may be subject to changes that occur relatively rapidly. One cause often quoted is spring relaxation.

A study of controlled safety valves in power stations has been made by Oberender and Bung (1984). The valves were either intrinsically controlled by the vented fluid or externally controlled by a control fluid (pneumatic or hydraulic). Two basic events were considered: faultless functioning and failure to open on demand. Some 1378 tests were conducted. The proportion of valves giving faultless functioning was approximately:

Intrinsic control	40%
External control	
Pneumatic	80%
Hydraulic	85%

The proportion giving failure on demand was approximately:

Intrinsic control	
Load principle	2%
Relief principle	4.5%
External control	
Pneumatic	0.3%
Hydraulic	0.8%

Table A14.21 *Failure rate data of motor driven pump from EIReDA (Lannoy and Procaccia, 1996; reproduced with permission from Elsevier)*

Type	*Application*	*Medium*	*Main character*	*Mean failure rate* (10^{-6}/h)	*Range* (10^{-6}/h)	*Failure on demand* (10^{-3}/d)	*Range* (10^{-3}/d)	*MMTR* (h)
Centrifugal	Circulating water	Fresh/salt water	kW≤4500 head: 25 m flow ~8000 m^3/h	4.7	3–6.6	0.20	0.04–0.3	41
Centrifugal	Containment drain system	Polluted water	kW≤200 head: 30 m	200	100–400	1	0.3–3	20
Centrifugal[a]	Refuelling pool	Borated water (200 ppm)	kW≤75 head: 50 m	10.6	7–14.5	0.01	< 0.015	27
Helicoidal	Reactor cooling	Borated water	kW≤6100 head: 90 m flow: 22,400 m^3/h	2.6	1.6–8.8	0.1	0.04–0.15	37
Centrifugal[b]	Chemical and volumetric control	Borated water	kW: 450 head: 1770 m flow: 34 m^3/h	59	47–72	0.12	0.1–0.16	22
Centrifugal	Makeup	Demin. water	kW≤40 head≤190 m flow: 36 m^3/h	13.4	9.6–17.6	0.02	< 0.03	16
Centrifugal[c]	Safety injection	Borated water (2000 ppm)	kW≤260 head≤82 m flow: ≤750 m^3/h	24	11.5–48.1	0.9	0.55–1.25	19

[a] Intermitent operation.
[b] Two out of three systems.
[c] Standby pump operating hour < 1 h (test).

Table A14.22 *Failure rates of valves in some French nuclear power stations*

						Failure rate	
						In operation (failures/year)	*On demand*
Primary valves							
Pressurizer safety relief valve	18	175,500	382	9[a]	4	51	0.01
Heat removal loop safety relief valve	12	105,000	12	3	2	29	0.17[b]
Secondary valves Condensate and drain pumps non-return valves	12	88,700	1375	2	0	23	—[c]

Source: Aupied, Le Coguiec and Procaccia (1983), tables 4 and 5.
[a] Failures mainly detected during annual tests.
[b] Original table leaves this space blank.
[c] Original table gives value of 0.0034.

Table A14.23 *Failure modes of valves in some French nuclear power stations*

Type of valve	*Type of fault*				
	Outlet leakage	*Corrosion*	*Untightness*	*Mechanical*	*Non-operation*
Gate valve	23	11	9	26	31
Globe valve	22	20	25	16	17
Plug valve	55	17	22	6	
Safety relief valve	30	17	28	5	20
Non-return valve	42	21	13	9	15
Overall value	30	15	20	15	20

Source: Aupied, Le Coguiec and Procaccia (1983), figure, p. 139.

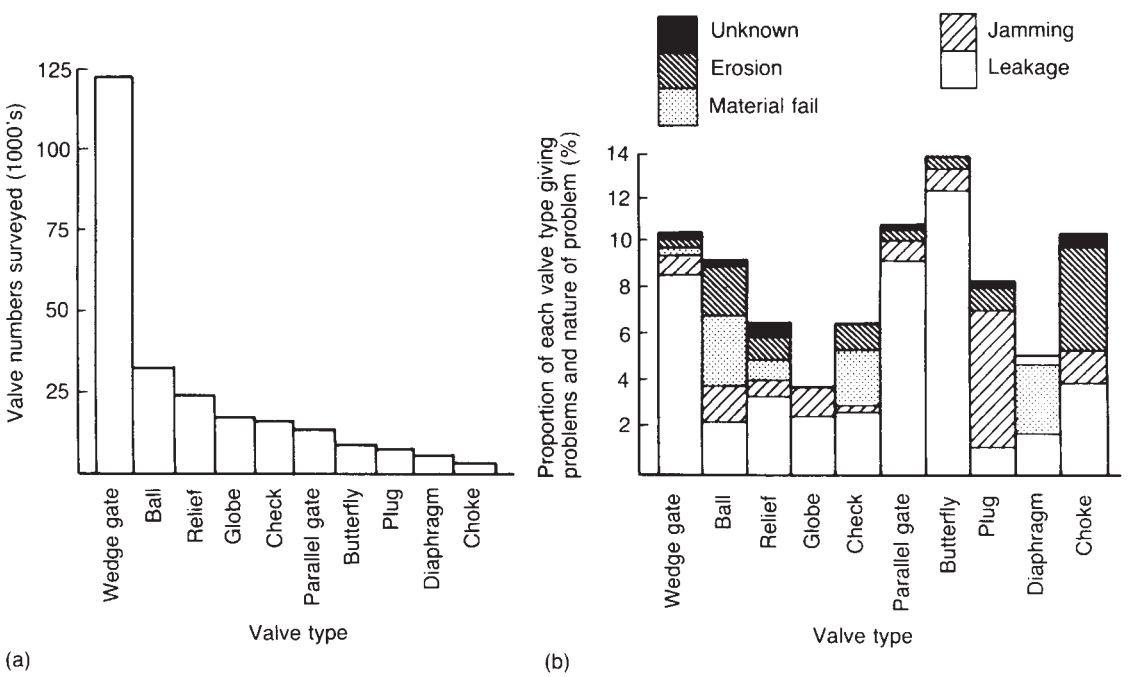

Figure A14.4 *Number and failure modes of valves in a large oil company survey (after Vivian, 1985): (a) number of valves; and (b) failure modes of valves (Reproduced by permission of Gower Press)*

For the intrinsically controlled valves, however, there was an improvement over time, the failure rate falling from some 10% in the initial period to <1% in the final period.

Estimates of the success rate of PRVs in particular applications have been given by Prugh (1981) as follows:

Venting of vapour/air explosion	1%
Venting of runaway reaction	95%
Venting of excessive nitrogen purge	99%

Historical data on a 10% random sample (240 valves) out of 2416 relief valves in a petrochemical plant were collected and analysed (Alfares 1999). Figure A14.5 shows the composition of the sample and valves in the plant, and Table A14.24 shows the average time between failure by valve pressure, service, size, temperature and type.

Failure data of relief valves for offshore operations are given by OREDA (1992, 1997, 2002). The following data are extracted from OREDA (1997):

Type	*Population*	*No. of failures*	*Mean failure rate* (per 10^6 h)	*Mean repair time* (manhours)
Globe (0.1–1.0 in.)	7	6	22.08	1.0
Globe (1.1–5.0 in.)	21	9	12.30	3.4
Globe (5.1–10.0 in.)	8	4	15.99	3.5

A14.16.4 Non-return valves

ORNL (Oak Ridge National Laboratory) and NIC (Nuclear Industry Check Valve Group) jointly conducted a study of check valve failures recorded between 1991 and 1992 in the INPO (Institute of Nuclear Power Operations) Nuclear Plant Reliability Data System (NPRDS) (McElhaney 2000). This study characterized check valve failures by valve type, and correlations between failure modes, failure causes, failure area, failure discovery method, extent of degradation with valve types were developed. Figures A14.6(a) and (b) are the distribution of 1991–92 check valve failures and 1991 check valve population by valve type respectively. Tables A14.25 and A14.26 are number of failures by valve type and failure mode and by valve type and failure cause specifically. Figure A14.7 is the relative failure rate by valve type and different system.

Additional data on the failure rates of non-return, or check, valves are given in Tables A14.4, A14.5, A14.22 and A14.23.

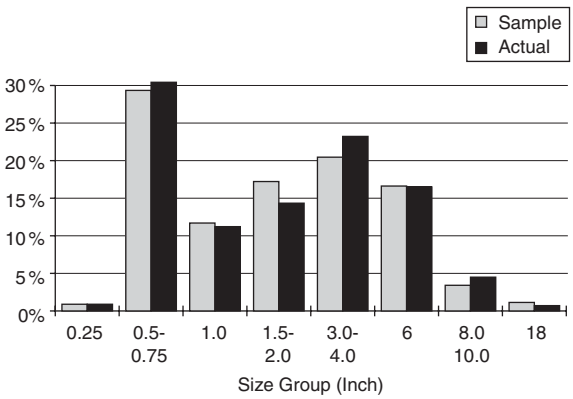

Figure A14.5 *The composition of the sample and relief valves in a petrochemical plant (Alfares, 1999; with permission from Elsevier)*

A14.16.5 Emergency isolation valves

Failure data for safety shut-down valves from OREDA (1992) has been analysed by Haugen, Hokstad and Sandtorv (1997). The safety shut-down valves included are mainly gate valves of approximately 6 in. handling oil, gas or water in offshore installations. The data are divided into two groups based on the test intervals (6 months or 12 months) as shown in Tables A14.27–A14.30.

OREDA (1997) gives failure rate data for shutoff valves in offshore operations as follows:

Type	*Population*	*No. of critical failures*	*Mean failure rate* (critical failures per 10^6 h)	*Mean repair time* (manhours)
Gate (1.1–5.0 in.)	104	13	2.10	0.3
Gate (20.1–30.0 in.)	1	1	28.54	3.0
Globe	8	1	5.19	4.0

Data on the failure rates of emergency isolation valves, also called slam shut or shut-off valves, are given in Table A14.5. Data on the failure rates of manual isolation valves are given in Tables A14.3 and A14.4.

A14.17 Instruments

For instruments the definition of failure is particularly important. This was discussed in detail in Chapter 13.

The importance of the definition of failure has been studied by Kortland (1983) for differential pressure transmitters. For transmitters required to maintain their calibration within 2% the failure rate observed was 0.1 failures/year. For transmitters with a required calibration within 5%, a less severe specification, the observed failure rate was a function of the calibration interval, being about 0.01 failures/year with a calibration interval of 1 year, but increasing for longer calibration intervals.

Some data on the failure rates of instruments are given in Chapter 13. The data given there refer mainly to instrumentation in the early and mid-1970s. The data given in this section supplement those given in Chapter 13 and include more recent data.

Data on the failure rates of instruments are given in Tables A14.3 and A14.4.

A study of control system failure sequences in ammonia plants has been described by Prijatel (1984). A comparison is given between predicted and actual failure sequences. Information on actual failure sequences was obtained from the work of G.P. Williams and Hoehing (1983). Some 95% of

Table A14.24 *Average time between failures of relief valves in a petrochemical plant (Alfares, 1999; with permission from Elsevier)*

Pressure (psi)	≤0	0–100	101–200	201–300	301–400	401–500	501–600	601–700	≥700
ATBF (m)	22.25	22.00	26.83	23.25	16.79	26.38	19.95	18.36	28.23
Service	Water	Steam	Chemical	Air	HC[a] gas	HC liquid			
ATBF (m)	21.02	20.60	20.26	41.11	23.13	22.88			
Size (in.)	0.25	0.5–0.75	1.0	1.5–2.0	3.0–4.0	6.0	8.0–10.0	18.0	
ATBT (m)	41.00	21.99	24.67	20.68	22.58	29.41	24.33	25.20	
Temp. (°C)	1–99	100–199	200–299	300–399	400–499	600–699	900–999		
ATBF (m)	31.89	22.97	21.94	24.13	19.73	27.80	24.29		
Type[b]	CV	BE	TK	BB	BA	PI			
ATBF	22.76	23.67	32.27	22.92	18.80	13.82			

[a] HC is hydrocarbon.
[b] CV is conventional; BB balanced bellows; BE bellows; BA balanced; TK tank and PI pilot-operated.

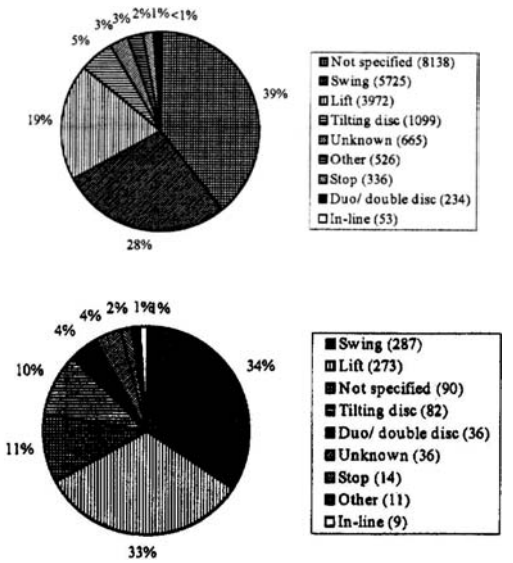

Fig A14.6 *(a) Distribution of 1991–92 check valve failure by valve type. (b) Distribution of 1991 check valve population by valve type (McElhaney, 2000; reproduced with permission from Elsevier)*

the actual failure sequences were single event failures. Data on instrument failure were obtained from plant records and from the literature. Some of the data used in the study are given in Table A14.31.

For control failure sequences the actual shut-down frequencies of particular units such as compressors were some two to four times as high as the predicted frequencies. The ranking of the instruments as a cause of shut-down was in descending order of importance controllers, switches, solenoid valves, control valves and uninterruptible power supply (UPS) system, the contribution of these items to shut-downs being 41.2, 36.7, 7.5, 4.6 and 4.3%, respectively. Thus two items, controllers and switches, accounted for 78% of shut-downs.

Data on the failure rates of process chromatographs and other analytical instruments have been given by Huyten (1979). Some 870 instruments are considered in the survey. He gives the following availabilities:

Analysers	93.8%
Gas chromatographs	91.0%

He also gives for analysers failure modes that include the following:

Sampling system	39%
Analyser	18%
Non-availability of spares	16%
Plant upsets, start-up and shut-down	11%

A comparative study of the MTBF and maintenance time for controllers from five manufacturers has been described by H.S. Wilson (1978). He gives the following data:

Manufacturer type	*MTBF* (year)	*Maintenance time* (h)
A	Electronic 1	0.5
B	Electronic 1	1.5
C	Pneumatic 5	3
D	Electronic 3	4
E	Pneumatic 15	5

He comments that the controller from manufacturer E failed so rarely that the maintenance time was greater due to unfamiliarity. From this comment the maintenance times are evidently times per failure.

Paula (1993) presented failure rates for programmable logic controllers (PLC) in three different processes: a US phenol plant, French nuclear plants and a Canadian nuclear power plant with data input from operation personnel and Electricite de France (EDF). His result is presented in Table A14.32. Rate of coverage, the probability of a PLC successfully switching to the redundant processor upon a single processor failure, is also estimated.

A good deal of the literature data for instrument failure is now quite old. In general, it is to be expected that the failure rates have fallen. The following is a comparison of the failures rates given for certain measuring instruments

Table A14.25 *Number of 1991–92 failures by valve design and failure modes (McElhaney, 2000; reproduced with permission from Elsevier)*

	Disc or other part, off or broken	*Stuck closed*	*Loose or detached part*	*Stuck open*	*Restricted motion of flow*	*Improper seating*	*Unknown/ miscellaneous*
Not specified	9	2	1	12	14	49	3
Duo/double disc	4	0	0	3	1	27	1
In-line	0	0	0	4	0	5	0
Lift	4	24	1	29	12	194	9
Other	0	1	0	1	1	5	3
Stop	0	0	1	2	2	8	1
Swing	14	3	12	51	31	143	34
Tilting disc	5	4	2	8	11	48	4
Unknown	3	0	9	3	3	18	0

Table A14.26 *Distribution of 1991–92 failures by valve design and failure cause (McElhaney, 2000; reproduced with permission from Elsevier)*

	Not specified	*Duo/double disc*	*In-line*	*Lift*	*Other*	*Stop*	*Swing*	*Tilting disc*	*Unknown*
Abnormal wear	6	8	14	4	23	13	8	10	2
Normal wear	31	21	29	25	23	19	33	24	37
Design problem	16	12	14	10	0	38	15	11	11
Human error	1	0	0	0	0	0	1	2	0
Maintenance error	7	0	7	2	8	0	5	8	20
Corrosion	7	25	14	19	8	0	5	4	7
Foreign material	13	6	14	35	15	13	14	8	11
Procedure problem	4	8	0	0	0	0	2	3	0
Stress corrosion cracking	0	0	0	0	0	0	1	0	0
Erosion/erosion-corrosion	1	15	0	0	0	13	2	2	0
Installation problems	3	2	0	0	0	0	2	5	0
Manufacturing defect	2	2	0	1	0	0	3	4	2
Unknown	8	2	7	3	23	6	9	20	11

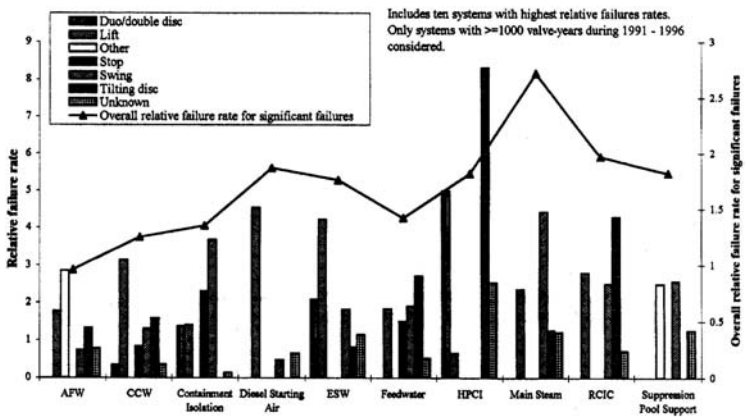

Figure A14.7 *Relative failure rate by valve design and system (McElhaney, 2000; reproduced with permission from Elsevier)*

Table A14.27 *Failure causes for maintainable items – critical (C) and non-critical (NC) failures, τ = 6 months (Haugen, Hokstad and Sandtorv, 1997; reproduced with permission from Elsevier)*

Maintainable item	*Failure cause/descriptor*									
	Mechanical defects		*Material failures (defect/deterior.)*		*Instrument/Electrical failures*		*Other*		*Total*	
	C	*NC*	*C*	*NC*	*C*	*NC*	*C*	*NC*	*C*	*NC*
Actuating device	0	0	0	2	3	0	0	3	3	5
Actuator	3	0	3	10	0	0	1	0	7	10
Body + internals	2	3	16	34	0	0	7	4	25	41
Control unit	0	0	0	0	5	1	1	0	6	1
Monitor/display	0	2	0	0	0	3	0	0	0	5
Seals	0	0	1	7	0	0	0	0	1	7
Signal transm.	0	0	0	0	0	1	0	0	0	1
Valve seat	0	0	0	3	0	0	0	0	0	3
Subsystems	0	0	5	0	0	0	0	0	5	0
Total	5	5	25	56	8	5	9	7	47	73

Table A14.28 *Failure causes for maintainable items – critical (C) and non-critical (NC) failures, τ = 12 months (Haugen, Hokstad and Sandtorv, 1997; reproduced with permission from Elsevier)*

Maintainable item	*Failure cause/descriptor*									
	Leakage		*Mechanical defects*		*Material failures (defect/deterior.)*		*Instrument/Electrical failures*		*Other*	
	C	*NC*	*C*	*NC*	*C*	*NC*	*C*	*NC*	*C*	*NC*
Actuating device	0	6	1	1	0	12	1	1	2	9
Actuator	3	11	1	1	25	27	0	0	3	4
Body + internals	0	0	1	6	16	10	0	0	0	1
Control unit	0	0	0	1	0	0	12	2	0	0
Monitor/display	0	0	0	0	0	0	0	3	0	0
Seals	0	0	0	0	1	4	0	0	0	0
Sensor	0	0	0	0	0	0	2	3	0	0
Signal transm.	0	0	0	0	0	0	0	1	0	0
Subsystems	0	0	0	2	4	4	0	0	0	0
Unknown	0	1	0	1	0	3	1	0	1	1
Valve seat	0	0	0	0	1	3	0	0	0	0
Total	3	18	3	12	47	63	16	10	6	15

Table A14.29 *Number of critical failures for various failure modes, τ = 6 months (Haugen, Hokstad and Sandtorv, 1997; reproduced with permission from Elsevier)*

Code	*DOP*	*EXL*	*FTC*	*FTO*	*INL*	*LCP*	*PLU*	*SPO*	···	*Total*
1.0			1							1
1.4			5							5
2.0					1	3				4
2.1		2	1			16				19
2.2			2							2
3.0			3	3						6
3.1				1				1		2
6.1	1					1	1			3
6.2				1						1
8.2		2	1			1				4
Total	1	4	13	5	1	21	1	1	0	47

by Anyakora, Engel and Lees (1971) and for sensors in process alarm systems by OREDA (1992):

	Failure rate (failures/year)	
	Anyakora, Engel and Lees	*OREDA*
Pressure	1.41	
(p) (< 1500 psig)		0.019
(e)		0.37
Flow	1.73	
(p) (gas)		0.25
(e) (gas)		0.75
Level	1.71	
(e)		0.096
Temperature	0.88	
(e)		0.1

The first authors refer for pressure to 'pressure measurement', for flow and level to differential pressure transducers and for temperature transducers, but do not distinguish between transducers with pneumatic (p) or electronic (e) output. The instruments selected from the OREDA collection are all transducers with specified type of output. In comparing the figures, allowance needs to be made for the effects on failure rate of environment and calibration requirements. Nevertheless, the data do suggest an improvement in reliability.

Table A14.30 *Number of critical failures for various failure modes, $\tau = 12$ months (Haugen, Hokstad and Sandtorv, 1997; reproduced with permission from Elsevier)*

Code	*EXL*	*FTC*	*FTO*	*INL*	*LCP*	*SPO*	···	*Total*
1.0			1					1
1.2		1	2					3
1.4		1	1		1			3
2.0	1			3	2			6
2.1	16		1	15	8			40
2.2		1						1
3.0		8						8
3.1		6				1		7
3.2		1						1
7.0			1					1
8.2	1	1		2				4
Total	18	19	6	20	11	1	0	75

The codes system used for the failure modes are shown as follows:

DOP	Delayed operation
EXL	External leak
FTC	Fail to close
FTO	Fail to open
INL	Internal leak
LCP	Leakage in closed position
PLU	Plugged
SPO	Spurious operation

For process sensors used in offshore operations, OREDA (1997) gives the following data:

Application	*Population*	*No. of failures*	*Mean failure rate* ($/10^6$ h)	*Mean repair time* (manhours)
Flow	72	92	26.41	0.4
Level	73	57	32.93	10.4
Pressure	282	137	18.06	6.4
Temperature	8	7	56.36	0.5

A14.18 Process Computers

The reliability of process computer systems is discussed in Chapter 13.

Data on the failure rates of 12 process computer systems in the paper industry given by Hubbe (1970) are shown in Table A14.33.

Data by E. Johnson (1983) on the failure rates of several different process computer configurations are summarized in Table A14.34. The data refer to total system failure, rather than failure of individual items such as printers. Johnson gives full details of the fault and downtime incidents. He states that for the total system an MTBF of 5000 h with a combined availability of about 99.9%, corresponding to no more than 8 h downtime per year, is about the level which may be found acceptable.

A14.19 Relief Systems

Some information is available on the failure rates of the individual elements of a pressure relief system, such as pressure relief valves, bursting discs and vent systems. Data on the failure of these items is given in this section. For chemical reactors, information on the failure rate of pressure relief systems has been given by Marrs and Lees (1989) as described in Chapter 11.

A14.19.1 Pressure relief valves

Data on the failure rate of PRVs are given in Section A14.16.3.

A14.19.2 Bursting discs

Data for the failure rate of bursting discs are given by Lawley (1974b) as follows:

Frequency of disc rupture at normal pressure
$= 0.2$ failures/year.

Table A14.31 *Failure of instruments in ammonia plants (after Prijatel, 1984)*

	Failure rate (failures/year)
Control valves	0.028
Controllers[a]	0.25
Switches[b]	0.22
Redundant switch systems[c]	1.68×10^{-4}
Solenoid valves	0.046
UPS system	0.026

[a] For flow, pressure, level.
[b] For flow, pressure, temperature, level.
[c] An alternative figure of 2.9×10^{-3} failures/year is also given.

Table A14.32 *Failure and coverage rates of PLC in an US phenol plant, French-design nuclear power plants, and a Canadian nuclear power plant (Paula, 1993; reproduced with permission from Elsevier)*

PLC application	*Single processor failure rate (per PLC year)*	*Total PLC failure rate (per PLC year)*		*Coverage*	
US phenol plant	2	0.0082[b]	0.016[c]	0.9918–0.9959[b]	0.9837–0.9918[c]
French-design nuclear power plants	–[a]	0.011[d]	0.021[e]		
Canadian nuclear power plant	–[a]	0.025			

[a] Information not available.
[b] Excluding early failures.
[c] Including early failures.
[d] Excluding power supply failures.
[e] Including power supply failures.

Table A14.33 *Failure data for 12 process computer systems in the paper industry (Hubbe, 1970)*

	MTBF		*Availability*	
	Hardware faults (h)	*Software faults* (h)	*Hardware faults* (%)	*Software faults* (%)
Composite average	550	1365	99.1	99.80
Best case	1633	8163	99.94	99.97

Table A14.34 *Failure data for some process computer systems in the chemical industry (after E. Johnson, 1983; reproduced by permission of Elsevier Science Publishers)*

System	*Operating time* (h)	*No. of failures*	*Downtime*		*Availability* (%)
			Failure (h)	*Planned* (h)	
Single computer system with analogue standby	66,528	13	65	300	99.9
Twin computer system with analogue standby[a]	35,040	8	30.5	38	99.91
Twin computer system with shared critical loops – 1	78,888	21	172	48	99.78
Twin computer system with shared critical loops – 2	78,888	37	388	73	99.5
Twin computer system with analogue standby[a]	13,848	6	54	17	99.61

[a] Different configurations.

For chemical reactors the failure rate of bursting discs in a single company has been investigated by Marrs and Lees (1989). The estimates obtained refer to the bursting disc itself, including blockage before the disc, but not to the vent pipework after the disc. There were during the period of investigation 11 successful ventings and no failures. The estimated probability of failure from these data is 0.083 failures/demand. An alternative, and less pessimistic, estimate was obtained from the fact that there were four unrevealed fail-to-danger failures in 164 reactor-years with an inspection interval of 1 year, giving an estimated probability of failure of 0.012. The authors' best estimate of the probability of failure is 0.01 failures/demand, but the confidence bounds are relatively wide.

A14.19.3 Vent systems

For chemical reactors and vented vessels, the failure rate of vent systems, excluding bursting discs, in a single company has been investigated by Marrs and Lees (1989). There were 28 successful ventings and no failures during the period of investigation.

The estimated probability of failure from these data is 0.034 failures/demand. An alternative, and less pessimistic, estimate was obtained from the fact that there was one unrevealed fail-to-danger failure in 262 vessel-years with an inspection interval of one year, giving an estimated probability of failure of 0.0019. The authors' best estimate of the probability of failure is 0.002 failures/demand, but the confidence bounds are relatively wide.

A14.20 Fire and Gas Detection Systems

A study of fire detection systems with particular reference to false alarms has been described by Peacock, Kamath and Keller (1982). Some data from this study are shown in Table A14.35. Section A of the table shows the event rates for fire detection systems as assessed for chemical plant by safety officers from a single company. Section B gives the event rates for each type of detector.

Hanks (1983) has described a study of the fire and gas detection system at the gas terminal at St Fergus. The results reported for failure rates are confined to those for the gas detectors, which were mainly in compressor cabs

Table A14.35 *Some event rates in fire detection systems (after Peacock, Kamath and Keller, 1982; reproduced by the permission of the American Institute of Chemical Engineers)*

	Event rate (events/10^3 detector-year)			
	Real alarms	*False alarms*	*Failure to operate*	*Real alarms/false alarm*
A Events by location				
Plant in buildings	4.7	3.4	0.15	1 : 0.7
Plant in open	60	273	27	1 : 4.6
All locations	2.1	7.2	0.16	1 : 3.4
B Events by type of detector				
Smoke	5.9	40	0.5	1 : 6.8
Heat	1.5	5.3	0.3	1 : 3.5
Smoke and heat	16	38	0	1 : 2.4
Flame (UV, IR)	108	622	108	1 : 5.8

and emergency generator rooms. Hanks gives the following failure rates:

	Failure rate (failures/10^6 h)	
	Compressor cab	*Other installation*
Gas detector	48	8
Gas detector and module	75	35

Y.P. Gupta (1985) describes a survey of automatic fire detection systems at six sites. His account includes estimates of the failure rates of ionization-type smoke detectors synthesized from data on the reliability of electronic components. For detectors in a first class, or non-adverse, environment, the overall failure rate was assessed as 0.057 faults/year, of which 0.04 faults/year were classed as fail-safe and 0.017 faults/year as dangerous. Most adverse environments result in a much higher failure rate. For such environments the failure rate was assessed as 0.46 faults/year. For control units the failure rate was assessed for false alarms as 0.044 faults/year and for unrevealed dangerous faults as 0.06 faults/year.

The US Navy Program, Damage Control Automation for Reduced Manning (DC-ARM) tested the performance of 20 sensors to 120 scenarios (82 fire, 38 nuisance sources and 120 non-fire events) (Rose-Pehrsson *et al.*, 2000). These sensors include electrochemical cell sensors (most of the gas detectors), solid state metal sensor (general hydrocarbon sensor), non-dispersive infrared sensor (carbon dioxide detector), photoelectric smoke detectors and ionization smoke detectors, which is shown in Table A14.36. The performance of smoke detectors is shown in Table A14.37. The data set were analysed with probabilistic neural network and par of the results is shown in Table A14.38.

For offshore fire and gas detection systems failure data are given by OREDA (1992, 1997, 2002). OREDA (1997) include failure rate data for fire and gas detectors as following (all failure modes included):

Type	*Population*	*No. of failures*	*Mean failure rate* (Per 10^6 h)	*Mean repair time* (man hours)
Flame				
Infrared	520	111	11.94	8.6
Combination IR/UV	132	31	7.36	0.4
Ultraviolet	358	150	48.84	6.1
Heat				
Rate compensated	666	46	2.30	17.4
Rate-of-rise	199	33	7.06	3.8
Smoke/combustion				
Ionization	1214	171	4.60	3.9
Photo electric	683	47	2.13	3.3
Hydrocarbon gas				
Catalytic	2044	1730	31.08	4.5
Infrared	2	19	309.97	10.5
H_2S gas	10	1	3.26	–

A14.21 Fire Protection Systems

Data on the failure rates of sprinkler systems are available from sources such as the Factory Mutual Research Corporation and the NFPA.

A review of failure rates of sprinkler systems that draws on these sources has been given by Rasbash (1975a). For fires in buildings in the United Kingdom in the period 1966–71, the breakdown of incidents given is

Type of incident	*No. of incidents*
Small fire, extinguished by other means	5,229
Sprinkler system installed and operated	
Fire controlled by other means	275
Fire controlled by sprinkler	3,180
Fire extinguished by sprinkler	651
Effect of sprinkler unknown	73
Sprinkler system installed but did not operate	676
Total	10,084

Thus, excluding the small fires, sprinkler performance was unsatisfactory in some 14% of cases. NPFA statistics for the period 1925–64 quoted by Rasbash indicate that in some 75,290 fires sprinkler performance was unsatisfactory in some 3.8% of cases.

Rasbash also quotes statistics from the Australian Fire Protection Association (AFPA). For some 5734 fires in the period 1886–1968 the proportion of sprinklers which gave unsatisfactory performance was 0.2%. For some 1250 fires in the period 1968–73 the proportion was 0.64%. These very low AFPA values are discussed by Rasbash, who refers to differences in the criteria for satisfactory operation.

Table A14.36 *Sensors used in the multicriteria detection test program (Rose-Pehrsson et al., 2000; reproduced with permission from Elsevier)*

Species	*Sensor range*	*Resolution*	*Instrument model number*	*Manufacturer*
Oxygen (O_2)	0–25%	0.1% O_2	6C	City Technology
Carbon monoxide with H_2 compensation (CO 4000 ppm)	0–4000 ppm	1 ppm	A3ME/F	City Technology
Carbon monoxide (CO 50 ppm)	0–50 ppm	0.5ppm	TB7E-1A	City Technology
Carbon dioxide (CO_2)	0–5000 ppm	Accuracy = greater than ±5% of reading or ±100 ppm	2001V	Telaire/Englehard
C_1–C_6 hydrocarbons (Ethyl)	0–50 ppm ethylene (C_2H_4)	±2.5 ppm	SM95-S2 with general hydrocarbons solid state sensor	International sensor technology
Hydrogen (H_2)	0–200 ppm	2 ppm	TE1G-1A	City Technology
Hydrogen chloride (HCl)	0–10 ppm	0.5 ppm	TL1B-1A	City Technology
Hydrogen cyanide (HCN)	0–25 ppm	0.1 ppm ± 2%F.S. accuracy	4664-40-1-1-1	EIT
Hydrogen sulfide (H_2S)	0–5 ppm	0.1 ppm	TC4A-1A	City Technology
Sulfur dioxide (SO_2)	0–10 ppm	0.5 ppm	TD2B-1A	City Technology
Nitric oxide (NO)	0–20 ppm	0.5 ppm	TF3C-1A	City Technology
Temperature (thermocouple or TC)	−200 to 1250°C	1°C or 0.75%	Type K, 0.127 mm bare bead TC	Omega
Temperature (Temp)	−20°C to 75°C	±0.6°C accuracy	HX93 transmitter (RTD)	Omega
Relative humidity (RH)	3–95%	±2%RH accuracy	HX93 transmitter	Omega
Photoelectric smoke detector (PHOTO)	0–19% obs./m		4098–9701	Simplex
Ionization smoke detector (ION)	1.6–10% obs./m		4098–9716	Simplex
Residential ionization smoke detector (RION)			83R	First Alert
Optical density meter (ODM)			VDM-2 670 nm, 2 mW laser	Meredith
Laser and photodiode with 0.965 m spacing			MRD 500 PIN silicon	Motorola
Measuring ionization chamber (MICX, MICY, MICY20)			EC-912	Photodiode Delta Electronics Testing

Table A14.37 *Summary of smoke detector performance (Rose-Pehrsson et al., 2000; reproduced with permission from Elsevier)*

Alarm level (%obs./m)	*Photoelectric*			*Ionization*		
	Fire source (%)	*Nuisance source* (%)	*Overall*[a] (%)	*Fire source* (%)	*Nuisance source* (%)	*Overall* (%)
Typical: 11 (Photo) 4.2 (Ion)	38	82	52 (76)	68	71	69 (85)
UL 268 minimum: 1.63	70	53	65 (83)	80	61	74 (87)
Half the UL 268 minimum 0.82	73	53	67 (83)	84	58	76 (88)

[a] Overall percent correct is based on 82 fires and 38 nuisance sources (120 for events). The parenthetical value is the percent correct based on 82 fires, 38 nuisance sources and 120 nonfire (background) events. The parenthetical value is the overall classification parameter that can be compared to the multivariate analysis results.

For the United Kingdom fires the two principal causes of unsatisfactory performance were that the heads were inaccessible to the fire and that the water was shut off, these occurring in 9.6 and 4.3% of the incidents, respectively.

The figures for unsatisfactory performance of sprinklers given by P. Nash and Young (1976) for the NPFA and Australian data are similar, but they give for the United Kingdom for the period 1965–69 a figure of 8.3% and quote a figure of 15% given by the Factory Mutual Corporation for the period 1970–72.

From the UK data, the causes of unsatisfactory performance are given as system shut off, defective system,

Table A14.38 *Probabilistic neural network classification results (Rose-Pehrsson et al., 2000; reproduced with permission from Elsevier)*

Sensor sets	*Number wrong*	*No. of real fires correct*	*No. of false alarms*	*Overall percent correct*
0.82%				
CO_{50}, CO_{4000}, MICX, ODM, RION	16	73	7	93
CO_{4000}, MICX, ODM, RION	14	75	7	94
CO_{50}, MICX, ODM, RION	19	73	10	92
CO_2, CO_{50}, CO_{4000}, NO, Ethyl, MICX, ODM, RION	15	73	6	94
MICX, ODM, RION	24	66	8	90
CO_{4000}, ODM, RION	19	71	8	92
CO_{4000}, MICX, RION	28	63	9	88
CO_{4000}, MICX, ODM	27	66	11	89
Temp, RH, ODM, ION, PHOTO	14	73	5	94
O_2, H_2, Ethyl, ION, PHOTO	13	74	5	95
O_2, CO_{4000}, H_2, ION, PHOTO	12	75	5	95
O_2, CO_{4000}, Ethyl, ION, PHOTO	13	75	6	95
O_2, H_2S, RH, ION, PHOTO	13	74	5	95
1.63%				
MICX, ODM, RION	22	70	10	91
CO_2, CO_{50}, CO_{4000}, NO, Ethyl, MICX, ODM, RION, PHOTO	13	74	5	95
CO_{4000}, MICX, ODM, RION	18	72	8	93
CO_{50}, MICX, ODM, RION	18	69	5	93
O_2, CO_{4000}, NO_2, ODM, PHOTO	15	74	5	95
O_2, H_2S, RH, ION, PHOTO	6	78	2	98
11%				
MICX, ODM, PHOTO	21	69	8	91
CO_{50}, CO_{4000}, NO, Ethyl, MICX, ODM, RION, PHOTO	10	76	4	96
CO_{4000}, MICX, ODM, RION	13	73	4	95
O_2, CO_2, H_2, MICY2, ODM	10	73	1	96
O_2, CO_{4000}, RH, ION, PHOTO	7	77	2	97
O_2, H_2S, RH, ION, PHOTO	6	78	2	98

system frozen and unknown, these occurring in 4.6, 0.60, 0.07 and 3.0% of the incidents, respectively.

From the NFPA data some principal causes of unsatisfactory performance were valve shut, inadequate water supply and obstruction to distribution, these occurring in 36.0, 9.6 and 8.4% of the incidents, respectively. The causes for the valve being closed were closed for no known reason, closed too early in the fire, closed for system repair or modification and closed to prevent freezing, these occurring in 22, 21 and 20% of cases with a closed valve.

Nash and Young also give failure rates for the components of sprinkler systems as follows:

Component	*Failure rate* (failures/year)	
	Safe	*Dangerous*
Wet alarm valve	15×10^{-2}	0.4×10^{-4}
Alternate alarm valve	15×10^{-2}	0.8×10^{-4}
Alarm motor and gong	6×10^{-2}	1.6×10^{-2}
Accelerator	13×10^{-2}	7.9×10^{-3}
Main sprinkler stop valve	–	2×10^{-3}
Non-return valves	–	10×10^{-3}

Budnick (2001) reported an analysis of 16 published reliability data for automatic sprinkler systems and the mean value of reliability was estimated between 93 and 96% in his results. Further data on the effectiveness of fire protection systems have been given by M.J. Miller (1977), based on Factory Mutual experience in the period 1970–75. In presenting data, the author warns that an unknown number of system operations are not reported. He also points out that there is no standard definition of effectiveness so that there is an element of subjectivity. He states as rough guidance that the performance would be considered acceptable if the system is designed to FM/NFPA standards and is operated within the design conditions and if any loss does not exceed the estimated Normal Loss Expectancy. For sprinkler systems, the number of reported events by type of system, with the proportion effective in brackets, was as follows: wet 2102 (91%); dry 650 (86%); deluge 62 (76%) and non-freeze 16.

For special protection systems, the number of events with the proportion of successes, was as follows: water spray 49 (53%); dry chemical 22 (27%); carbon dioxide 100 (51%) and steam 30 (63%).

Information on failure rates of special protection systems is limited. For carbon dioxide systems in Germany, Miller quotes a success rate of some 76–78% over a 14-year period.

For Halon systems, he states that data are even scantier, but refers to a series of 300 tests of such systems by Dupont in which in some 23% of installations significant problems were identified and corrected.

Miller also gives data on the effectiveness of other active protection systems, namely: gas analyser; smoke detector; rate-of-rise detector; spray nozzles; foam water sprinkler; high expansion foam; low expansion foam; explosion suppression; halon (fire protection); halon (explosion suppression); vaporizing liquid; inert gas; in-rack sprinklers; standpipes. For only three of these is the number of reported events 10 or more, the numbers, with the number of successes, being as follows: gas analyser 13 (2); high expansion foam 10 (3) and low expansion foam 12 (5).

Reliability data of fire protection features from one boiling water reaction (BWR) sites and two pressurized water reaction (PWR) sites in German has been statistically analysed (Rowekamp and Berg, 2000). The study covers 7-year operation of BWR and 7 and 4 years of operation for the two PWRs. Failure rates and unavailability for the fire protection equipment were estimated and presented in Table A14.39.

A14.22 Emergency Shut-down Systems

Data on emergency isolation valves are given in Section A14.16.

For offshore emergency shutdown systems, failure data are given by OREDA (1997). It includes emergency shutdown valves as follows (all failure modes included):

	Population	*No. of failures*	*Mean failure rate* (failures/10^6 h)
Ball			
5.1–10.0 in.	14	29 (1)	61.61
10.1–20.0 in	13	15 (3)	32.93
20.1–30.0 in	2	0 (0)	6.04
Butterfly	1	1 (1)	28.54
Gate			
1.1–5.0 in.	39	24 (11)	20.13
5.1–10.0 in.	481	245 (105)	26.50
Plug	2	7 (1)	99.89

The values for number of failures in brackets refer to failure to close or to failure involving some degree of internal leakage.

Table A14.39 *Plant specific reliability data estimated for active fire protection features in a German BWR reference plant (Rowekamp and Berg, 2000; reproduced with permission from Carl Hanser Verlag)*

	BWR plant			*PWR plant 1*			*PWR plant 2*		
	Inspection period	*Failure rate* [1/h]	*Unavailability*	*Inspection period*	*Failure rate* [1/h]	*Unavailability*	*Inspection period*	*Failure rate* [1/h]	*Unavailability*
Fire alarm boards									
Detection drawers	3m, 1a	6.7×10^{-8}	1.2×10^{-4}	3m	3.4×10^{-8}	7.4×10^{-5}	1a	1.3×10^{-6}	1.1×10^{-2}
Detection lines	3m, 1a	2.3×10^{-8}	4.0×10^{-5}	3m	2.0×10^{-8}	4.3×10^{-5}	1a	1.6×10^{-8}	1.4×10^{-4}
Fire detectors									
Automatic	1a	1.4×10^{-7}	1.3×10^{-3}	1a	4.8×10^{-8}	4.2×10^{-4}	1a	4.0×10^{-9}	3.5×10^{-5}
Press button	1a	1.1×10^{-7}	9.4×10^{-4}	1a	3.8×10^{-8}	3.3×10^{-4}	1a	3.8×10^{-8}	3.3×10^{-4}
Fire dampers	3m, 1a, 3a	2.3×10^{-6}	6.7×10^{-3}	6m	6.6×10^{-7}	2.9×10^{-3}	1a	1.4×10^{-7}	1.2×10^{-4}
Fire doors	1a	4.9×10^{-7}	4.3×10^{-3}	1a	7.1×10^{-7}	6.3×10^{-3}	3m, 1a	1.1×10^{-6}	2.5×10^{-3}
Inergen gas extinguishing system	–	–	–	–	–	–	6m	1.5×10^{-5}	5.8×10^{-2}
Dry sprinkler extinguishing system (total failure)	6m, 1a, 5a	2.3×10^{-7}	9.9×10^{-4}	3m, 1a	1.5×10^{-7}	3.2×10^{-4}	6m, 5a	1.6×10^{-7}	6.5×10^{-4}
Dry sprinkler extinguishing system (automatic actuation failure only)	6m, 1a, 5a	4.1×10^{-6}	1.8×10^{-2}	3m, 1a	1.3×10^{-7}	2.9×10^{-2}	6m	5.8×10^{-7}	2.5×10^{-3}
Wet sprinkler extinguishing system	6m, 1a, 5a	7.2×10^{-8}	3.2×10^{-4}	–	–	–	–	–	–
Gas extinguishing system (CO_2)	6m	2.1×10^{-6}	9.2×10^{-3}	–	–	–	–	–	–
Stationary fire pumps	1m,1a	2.1×10^{-6}	1.4×10^{-3}	1m,1a	1.4×10^{-6}	8.5×10^{-4}	6m	3.8×10^{-6}	1.6×10^{-5}
Wall hydrants	6m,1a	4.4×10^{-8}	1.9×10^{-4}	1a	8.5×10^{-7}	7.4×10^{-3}	1a	1.1×10^{-7}	9.5×10^{-4}

For offshore platforms in the Gulf of Mexico, Forsth (1983) has reported that in 12 cases where the emergency shutdown system was mentioned in the fire or explosion incident report, the system operated properly in 11 but failed in one.

For programmable logic controllers used in the emergency shutdown systems, Mitchell and Williams (1993) analysed failure data from natural gas compressor stations. The failure rate of PLC (microprocessor failures only) was estimated to be 0.072 failures/PLC year while the overall PLC failure (all causes) was estimated 0.32 failures/PLC year.

A14.23 Utility Systems

A14.23.1 Electrical power

The failure rate of the outside power supply varies with the country concerned. In the United Kingdom, the National Grid system gives a high reliability supply and the failure rate is relatively low. In addition, chemical works often have their own power station. The failure rate of the power supply to a plant should normally be determined for the particular works.

For the United Status, the *Rasmussen Report* (figure III 6–5) gives data for outage times following a transmission line failure, as shown in Table A14.40.

A detailed study of the power supply to a plant making RDX explosive, on which it is critical that agitation should not stop, has been described by Ketron (1980). His analysis of the distribution of power failures by duration may be summarized as shown in Table A14.41. The dates quoted in the table run from December 1968 to January 1974 .

A study of probability of off-site power outage versus duration at three nuclear plants is published by Arul *et al.* (2003) with the probability of 1-h off-site power outage between 0.1 and 1.0.

Table A14.40 *Outage times of electrical power supply following a transmission line failure (after Atomic Energy Commission, 1975)*

Outage time (%)	*Proportion of outages* (%)
< 0.01	1.1
0.01–0.032	6.1
0.032–0.1	18.7
0.1–0.32	37.9
0.32–1.0	12.6
1.0–3.2	11.7
3.2–10	8.4

Table A14.41 *Duration of power failures in an explosives plant (after Ketron, 1980; reproduced by permission of the American Institute of Chemical Engineers)*

Duration of power failure t (min)	*No. of incidents*
Momentary	13
$t < 1$	3
$1 < t < 10$	2
$10 < t < 60$	4
$t > 60$	6
Total	28

Literature failure rates of equipment used in power supply systems given by Ketron are shown in Table A14.42. Weather-related features of power supplies have been considered by Jarrett (1983).

A14.23.2 Diesel generators

Information on the reliability of diesel generators is given in the *Raosmussen Report* (AEC, 1975). The study gives a probability of failing to start on demand of 3×10^{-2}.

Thus, if there are two diesel generators, but only one is required to provide the full emergency load, it might be calculated that the probability of both generators failing to start on demand is 9×10^{-4}. In fact, however, startup is treated in the study (p. III-72) as a single event that may trip both units. The probability of both generators failing to start on demand is assessed as 10^{-2}. The repair time for a diesel generator is given in the study (p. III-55/56) as a mean time of 21 h with a range of times of 2–300 h.

A survey of emergency generating equipment over the period 1977–82 has been reported by R. Stevens (1983). Much of the equipment was found to be in appalling condition. The failure modes are shown in Table A14.43.

Twenty-six years' operational data of 11 diesel generators of 125–250 kV A at Chalk River Nuclear Laboratory have been analysed presented by Winfield (1988), which gave a mean failure to start probability of 4.4×10^{-2} and failure to run probability between 5.6×10^{-3} and 1.2×10^{-2}.

Table A14.42 *Failure rates of electrical power supply equipment (after Ketron, 1980; reproduced by permission of the American Institute of Chemical Engineers)*

	Failure rate[a] (failures/d)
Diesel engine	0.008
Electric generator	0.0014
Electric motor	0.0014
Steam turbine	0.000057
Solenoid valves	0.0000063
Pneumatic valve	0.00011
Globe valve	0.0034

[a] Literature values.

Table A14.43 *Failure modes of emergency engines/generators (after B. Stevens, 1983; reproduced by permission of the American Institute of Chemical Engineers)*

	No. of cases	*Proportion* (%)
Cracking/overheating	36	26.1
Cracking/freezing	13	9.4
Mechanical breakage	6	4.4
Bearings and journals/scoring	18	13.0
Engine block/breakage	14	10.1
Pistons/breakage	9	6.5
Valves/breakage	7	5.1
General mechanical	20	14.5
Piston rings/breakage	7	5.1
Crankshaft/cracking–breaking	8	5.8
Total	138	100.0

Table A14.44 *Mean probability of failure of emergency diesel generators at 63 nuclear plants from 1988–91 (Vesely, Uryasev, and Samanta,1994; reproduced with permission from Elsevier)*

	For individual diesels	*Over station*	*Diesels or stations*
Failure to start	5.0×10^{-3}	5.2×10^{-5}	5.0×10^{-3}
Failure to load-run	9.6×10^{-3}	9.5×10^{-5}	9.3×10^{-3}

A total of 195 emergency diesel generators at 63 operating nuclear plants have been analysed from 1988 to 1991 (Vesely, Uryasev and Samanta, 1994). The mean probability of failure to start and failure to load-run is given in Table A14.44. Load-run failure is defined as diesel generator starts but does not run successfully. Estimation of standard deviation and variance is also provided in their paper.

For offshore diesel-driven pumps and emergency power generators, failure data are given by OREDA (1997) as follows.

	Population	*No. of failures*	*Mean failure rate* (per 10^6 h)	*Failure to start on demand*
Main power				
1–100 kW	2	82	731.62	–
100–1000 kW	8	174	479.80	–
Emergency power	7	142	685.44	0.018

A14.23.3 Instrument air

An estimate of the failure rate of the instrument air supply has been given Lawley and Kletz (1975). They give: failure frequency of instrument air supply = 0.05 failures/year.

This evidently refers to the instrument air supply rather than to the connections from the air supply to the instrument, for which separate failure rates are quoted.

A14.23.4 Cooling water

The arrangements for the supply of cooling water in a works vary somewhat. Generally, there is a works cooling water supply system, but use may also be made of other sources of supply such as wells.

A typical estimate of the failure rate of the cooling water supply of about 0.1 failures/year. This is for the supply itself and does not include failure of equipment such as cooling water pumps supplying a particular plant.

A14.23.5 Steam

Information on the failure rates of components of steam supply systems has been given by Coltharp *et al.* (1978), who carried out a study on the steam system of an automobile factory. Some of the data given by these authors is shown in Table A14.45.

A14.24 LNG Plants

A survey of events on LNG plants has been reported by Welker and Schorr (1979). The data were obtained on 25 LNG peak-shaving plants in the United States ranging in age from 10 years to a few months. The survey covered nearly 35,000 h of vaporization experience, more than 400,000 h of liquefaction experience and more than 1.5 million hours of tank storage, as well as nearly 1.5 billion ft-h of pipe use and more than 1.3 million manhours of operating time.

The authors define a minor failure as one which results in an unscheduled shutdown of operating equipment where the repair period is less than 24 h, a major failure as one where the shutdown is more than 24 h and a safety-related failure as one which results in a fire or a large leak of gas or liquid.

Major leaks of gas are defined as those which could result in a release of the order of 100,000 ft^3 of gas. Major leaks of liquid involved primarily vaporizer tubes or pumps, with one major leak due to flange gasket failure.

The fires reported are confined to those involving LNG as gas or liquid. About half the fires were minor and half major. Vaporizers appeared to have a high risk of fire, because they have a relatively high failure rate and are located near fired equipment.

Some failure and event rates given in this survey are shown in Table A14.46.

Table A14.45 *Failure rates of some components of a steam supply system (after Coltharp et al., 1979; reproduced by permission of the American Institute of Chemical Engineers)*

Equipment	*Failure rate*[a] (failures/10^6 h)
Drives for spreader stoker:	
Electric drive	0.3
Steam drive	50
Boiler feedwater pump	0.9
Condensate collection and return	10
Waterwall tubes	57
Steam generating tubes	0.3
Superheater	0.4
Air preheater	1.1
Fans	
Overfire air	57
Induced draft	1.1
Drives for fans (forced draft, overfire air, induced draft)	
Electric drive	2
Steam drive	3
Ash conveyor	10

[a] Sources of data are Edison Electric Institute (EEI), Hartford Steam Boiler (HSE) and automobile company.

A14.25 Leaks

A14.25.1 Leak sources

Information on the distribution of leak sources is available in several different classifications. The distribution of the place of origin for large fires in Great Britain 1971–73 has been given in Table 2.11.

The distribution of leak sources for process industry accidents reported to the HSE in the year 1987–88 has

Table A14.46 *Failure and event rates on LNG plants (after Welker and Schorr, 1979; reproduced by permission of the American Gas Association)*

A Failure rates

Plant section or equipment	*MTBF* (h)			
	Major failure	*Minor failure*	*Safety-related failure*	*Total failures*
Gas pretreatment	20,000	3000	$>350{,}000$[a]	3000
Liquefaction	6500	2500	$>420{,}000$[a]	1800
LNG vaporizers	8000	700	15,000	700
Compressors	3000	900	$>2\times10^{6}$[a]	700
LNG pumps	$>35{,}000$	3500	$>35{,}000$	3500
Cryogenic valves	$>4\times10^{7}$[a]	2×10^{7}	$>4\times10^{7}$[a]	2×10^{7}
Controls	15×10^{6}	700,000		

B Other events

	MTBF (h)
LNG tanks:	
Gas leaks	$>1.5\times10^{6}$ (no leaks)
Liquid leaks	$>1.5\times10^{6}$ (no leaks)
Cold spots	100,000
Pipelines (per ft):	
LNG pipelines	$>1.5\times10^{9}$ (no failures)[b]
Pipe insulation	$>1.5\times10^{9}$ (no failures)
Fire water mains	$>1.6\times10^{9}$
Hazard detection sensors:	
Gas	100,000[c]
Radiation	350,000[c]
High temperature	$>4\times10^{6}$ (no failures)
Smoke	1.4×10^{6}
Emergency systems:	
Water hydrants, monitors	4×10^{6}
Halon systems	100,000
Dry chemical systems	3×10^{6}
Human errors, leaks and fires:	
Human error incidents	50,000
Major gas leaks	300,000
Major liquid leaks	150,000
Major fires	200,000[d]

[a] No failures.
[b] Small leaks from gaskets not included.
[c] Excluding false alarms.
[d] Leaks only.

been analysed by A.W. Cox, Ang and Lees (1990). Separate analyses are given for normal, closed process plant and for plant and activities with open surfaces, etc., as shown in Tables A14.47 and A14.48, respectively.

For vapour cloud explosions the distribution of leak sources has been obtained by A.W. Cox, Ang and Lees (1990) from the case histories listed by Davenport (1977, 1983) as shown in Table A14.49.

For fires and explosions on offshore installations in the Gulf of Mexico and in the Norwegian North Sea the distribution of leak sources has been obtained by A.W. Cox, Ang and Lees (1990) from data given by Forsth (1981a,b) as shown in Tables A14.50 and A14.51.

Based on the API analysis of the SCAQMD refinery screening data, 90% of reducible fugitive emissions come from only about 0.13% of the piping components (API, 1997; Taback, Siegell, Martino, and Ritter, 2000).

A14.25.2 Leak frequency

Estimates of the frequency of leaks on ammonia installations and carriers have been made by Baldock (1980) and are given in Table A14.52.

In late 1987, 39 chemical plants and EPA jointly conduct a fugitive emission study including all domestic producers of ethylene oxide, phosgene and acrolein. Around 100,000 components were examined between 1988–1990, and the result is presented in Berglund (1992), and leak rate is also found to be a function of monitoring frequency and maintenance procedure.

Table A14.47 *Leak sources on closed process plant (after A.W. Cox, Ang and Lees, 1990; reproduced by permission of the Institution of Chemical Engineers)*

	No. of incidents	*Proportion of incidents* (%)
Plant	19	22.1
Reactor	8	9.3
Vessel	10	11.6
Tank	7	8.1
Heat exchanger	4	4.7
Vaporizer	2	2.3
Pump	13	15.1
Pipework	17	19.8
Hose	6	7.0
Total	86	100.0

Table A14.48 *Leak sources for plants and activities with open surfaces, etc. (after A.W. Cox, Ang and Lees, 1990; reproduced by permission of the Institution of Chemical Engineers)*

	No. of incidents	*Proportion of incidents* (%)
Solvent evaporating		
Oven	4	2.9
Spray booth	15	10.8
Small container	31	22.3
Cleaning/degreasing		
Process	15	10.8
Tanker/mobile plant	33	23.7
Other	41	29.5
Total	139	100.0

Table A14.49 *Leak sources in vapour cloud explosion incidents for 1962–1982 (after A.W. Cox, Ang and Lees, 1990; reproduced by permission of the Institution of Chemical Engineers)*

Leak source	*No. of incidents*	*Proportion of incidents* (%)
Reactor – reaction	1	2.85
Vessel – explosion	1	2.85
Vessel – rupture	1	2.85
Tanks – reaction	1	2.85
Tanks – overfilling, frothover	1	2.85
Tanks – refrigerated storage, failure	2	5.7
Pipe	9	25.8
Flange	2	5.7
Other fittings	7	20.0
Hose	1	2.85
Valves	3	8.6
Sight glass	1	2.85
Pumps	1	2.85
Flare	2	5.7
Valve opened	1	2.85
Venting	1	2.85
Total	35	100.0

Table A14.50 *Leak sources for fire and explosions in the Gulf of Mexico (after Forsth, 1981b; reproduced by permission of Det Norske Veritas)*

Leak source	*No. of incidents*	*Proportion of incidents* (%)
Tanks, vessels, drains, sumps, pans, pits	18	13.7
Holes, cracks	6	4.6
Flanges, unions	26	19.8
Hoses	4	3.1
Nipples	3	2.3
Valves	16	12.2
Exhaust	8	6.1
Other	47	35.9
Unknown	3	2.3
Total	131	100.0

Table A14.51 *Leak sources for fires and explosions in the Norwegian North Sea (after Forsth 1981a; reproduced by permission of Det Norske Veritas)*

Leak source	*No. of incidents*	*Proportion of incidents* (%)
Tanks, vessels, drains, sumps, etc.	10	7
Ruptures, holes, cracks	4	3
Flanges, unions	7	5
Valves, vents	8	6
Other	30	21
Unknown	48	36

A14.26 Ignition

A14.26.1 Ignition sources

There is a small amount of information on the distribution of ignition sources, much of it for offshore installations.

A study by the Fire Protection Association (1974) of ignition sources for large fires in the chemical and petroleum industries in Great Britain in 1971–73 gave the data shown in Table 2.11. There were 79 fires of which 23 were solid and 10 unknown, the other 46 being gas, vapour or liquid.

Ignition sources for process industry fire and explosions reported to the HSE in the year 1987–88 have been analyzed by A.W. Cox, Ang and Lees (1990). Separate analyses are given for normal, closed process plants and for plants and activities with open surfaces, etc. The former sets have been given in Table 16.46 and the latter are shown in Table A14.53.

Offshore ignition sources have been given for fires and explosions in the Gulf of Mexico (GoM) and in the Norwegian North Sea (NNS) in reports by workers at Det Norske Veritas (Sofyanos, 1981; Forsth, 1981a,b, 1983).

Forsth (1983) has given the data shown in Table 16.47 for ignition sources in these two locations. The number of accidents considered was for the GoM was 326 over the period 1956–81 and for the NNS 133 over an unspecified period.

Table A14.52 *Estimated frequency of releases on ammonia installations and carriers (after Baldock, 1980; reproduced by permission of the American Institution of Chemical Engineers)*

Incident	*No. of incidents*	*Estimated frequency*
Major failure of storage vessel	2	1 in 6×10^4 vessel-year
Major release from storage vessel	1	1 in 10^4 storage area-year
Serious release on plant	12	1 in 2000 plant-year
Release on refrigerator plant	15	1 in 10^5 plant-year
Release at transfer point		
Flexible hose failure	11	1 in 1000 transfer point-year
Movement while still connected		
Major release	3	1 in 4000 transfer point-year
Other release	8	1 in 1500 transfer point-year
Major release in transport		
Road	6	1 in 2000 tanker-year
Rail	18	1 in 3000 tanker-year
Pipeline	8	1 in 3000 mile-year
Sea	1	1 in 200 ship-year
Total	79	

Table A14.53 *Ignition sources for plants and activities with open surfaces, etc. (after A.W. Cox, Ang and Lees, 1990; reproduced by permission of the Institution of Chemical Engineers)*

	No. of incidents	*Proportion of incidents* (%)
Flames: general	27	19.4
LPG fired equipment	2	1.4
Hot surfaces	20	14.4
Friction	11	7.9
Electrical	29	21.0
Hot particles	–	–
Static electricity	10	7.2
Smoking	17	12.2
Auto-ignition	2	1.4
Unknown	21	15.1
Total	139	100.0

A14.26.2 Ignition probability

A discussion of the probability of ignition of gas and liquid releases is given in Chapter 16. The account there utilizes data on blowouts on offshore installations given by Dahl *et al.* (1983). A fuller tabulation of these data is shown in Table A14.54.

Table A14.54 *Ignition of blowouts in the Norwegian North Sea (after Dahl et al. 1983; reproduced by permission of Det Norske Veritas)*

	No. of incidents	*Proportion of incidents* (%)
Gas:		
No ignition	81	70
Fire	23	20
Explosion	12	10
Subtotal	116	100
Oil:		
No ignition	11	92
Fire	1	8
Explosion	0	0
Subtotal	12	100
Oil and gas:		
No ignition	13	57
Fire	10	43
Explosion	0	0
Subtotal	23	100
Fire	4	
Explosion	1	
Other	15	
Total	171	

Table A14.55 *Number of fires in US petroleum industry 1982–1985 (API, 1983, 1984, and 1985)*

Installations	*No. of fires*			
	1982	1983	1984	1985
Exploration, production, drilling			68	107
Gas processing			28	19
Exploration, production, drilling and gas processing, not separated			25	0
Total of above	163	182	121	126
Offshore portion only			13	6
Refining	201	173	142	104
Chemical operations	61	70		
Petrochemicals			33	20

Table A14.56 *Number of fires in storage tanks in US refineries 1982–85 (API, 1983, 1984 and 1985)*

No. of fires	*Type of tank*			
	1982	1983	1984	1985
Floating roof	6	6	10	3
Cone roof	9	6	13	1
Dome roof	0	1	0	0

A14.27 Explosion following ignition

A14.27.1 Explosion probability

The discussion of ignition in Chapter 16 also covers for gas releases the probability of explosion, given ignition.

Table A14.57 *Specific origin of 131 accidents in the transportation of natural gas (Montiel et al., 1996; 2reproduced with permission from Elsevier)*

Origin	*No. of accidents*	*Percentage*
Piping	127	96.9
Pumps/compressors	2	1.5
Rail tank	1	0.8
Substation	1	0.8

Table A14.58 *Causes of 131 accidents in the transportation of natural gas (Montiel et al., 1996; reproduced with permission from Elsevier)*

Cause	*No. of accidents*	*Percentage of known*[a]
Mechanical failure	39	43.3
Impact failure	37	41.1
Human error	32	35.6
External events	14	15.6
Service failure	1	1.1

[a] Of the 131 accidents, causes of 90 were known.

A14.28 Fires

A14.28.1 Process plant fires

A survey of the frequency of fires in industry in Britain has been reported by Rutstein and Clarke (1979). For the chemical and allied industries (Standard Industrial Classification 5) they correlate the probability of fire per year with the floor space of the building using a function of the form

$$P = aB^c \qquad [A14.28.1]$$

where B is the floor space (m^2), P the probability of fire over 1 year, a is a constant and c an index. They give the following data:

	Probability of fire over 1 year	
	All buildings	*Process buildings*
Probability function	$P = 0.017B^{0.27}$	$P = 0.069B^{0.46}$
Probability for 1500 m^2 building	0.12	0.21

A survey of the major safety incidents has been conducted by Williams, G.P. (1999). Eighty-nine ammonia plants during the period 1994–96 have one fire every 14.2 months on average, which is slightly better then previously reported value of 14.6 months.

A14.28.2 Petroleum industry fires

Information on the frequency of fires in the petroleum industry in the United States is given in the annual series Reported Fire Losses in the Petroleum Industry by the API. The fires reported are those involving losses greater than $2500. The fires losses for the period 1982–85 are shown in Table A14.55.

A14.28.3 Refinery fires

Data on the frequency of refinery fires are given in Table A14.57. The API fire loss reports also give a breakdown of the fire losses. For 1985 the sizes of fire by loss were

Size of loss (1000$)	*No. of fires*
2.5–100	65
100–1000	37
>1000	7

The frequency of refinery fires may be estimated from these data and from the number of refineries given in Section A14.11. The *First Canvey Report* gives frequency of fire in a refinery = 0.1 fires/year

A14.28.4 Pump fires

Estimates of the frequency of pump fires have been given by Kletz (1971) and are shown in Table A16.55.

N.M. Wallace and David (1985) have described a study in Esso on mechanical seals, in which losses due to fires from pump failures were apportioned as follows:

Seal failure	54%
Bearing or shaft failure	36%
Unknown	10%

A14.28.5 Storage tank fires

Information on the frequency of fires on storage tanks in the petroleum industry in the United States is given in the annual series *Reported Fire Losses in the Petroleum Industry* by the API. The fires reported are those involving losses greater than $2500. The storage tank fire losses for the period 1982–85 are shown in Table A14.56.

For fires in fixed roof storage tanks for hydrocarbons Kletz (1971) states that based on data from more than over 500 tanks over a period of 20 years the frequency of a tank fire or explosion is once in 883 tank-year.

His estimate of the factor by which the frequency of fire or explosion may be reduced by the use of inerting is 10.

A14.29 Explosions

A14.29.1 Furnace explosions

Data on the distribution of causes of furnace explosions has been given by Ostroot (1972). The numbers of incidents listed are

Cause of explosion	*Furnace firing*	
	Gas	*Oil*
Inadequate purge	55	12
Delayed ignition	42	81
Incorrect fuel–air ratio	19	5

In the discussion to the paper Kletz (1972c) said that his company reckoned on a frequency of explosion of 1 in 25 furnace-year. Ostroot quoted for his company a figure of about 1 in 100, or even 1 in 1000 furnace-year.

A14.29.2 Vapour cloud explosions

Data on vapour cloud explosions have been given by Davenport (1977, 1983).

For vapour cloud explosions at fixed installations Davenport (1983) records some 35 cases over the period 1962–82 inclusive. The location of these explosions is

United States	19
Western Europe	10
Other	6

If it is assumed that there were at risk in the United States and Western Europe over this period some 10,000 chemical/petrochemical plants, major refinery units, LPG storages and natural gas plants, then

Frequency of vapour cloud explosion $= 29/(21 \times 10{,}000)$
$= 1.4 \times 10^{-4}$ explosions/year

Information on the distribution of leak sources in vapor cloud explosions is given in Table A14.49.

Further data on vapour cloud explosions are given in Chapter 17.

A14.30 Transport

Failure data for transport are given in Chapter 23 and Appendix 17.

A total of 185 accidents involving natural gas (gaseous) were surveyed with 179 from the Major Hazard Incident Data Service database (Montiel *et al.*, 1996), of which 131 (70.8%) is transportation related. These 131 accidents during transportation are further analysed, and Tables A14.57 and A14.58 give a summary of their findings.

A14.31 External Events

A14.31.1 Aircraft crash

Information on the probability of a potentially damaging accident due to an aircraft crash at various reactor sites is given in the *Rasmussen Report* (table III 6–4). The highest probability quoted is 1×10^{-6}/year for a crash at a site located 5 miles from an airport with 40,000 air carrier and 40,000 naval flight movements per year. The assumed target area is 0.01 mile^2 for larger aircraft and 0.005 mile^2 for smaller ones.

The impact of the aircraft would not necessarily cause damage within the containment. In fact the estimated probability that such damage would occur given impact is less than 1 in 100.

Other accounts of the risk of aircraft crash are those of D.W. Phillips (1981 SRD R198) and Marriott (1987).

A14.32 Notation

Section A14.23

a	constant
B	floor space (m^2)
c	index
P	probability of fire in 1 year

Section A14.27

A, B, C	constants
D	severity parameter
p	pressure (psi)
t	temperature (°C)
z	hazard rate
λ	failure rate

Subscript

o	base case

Appendix 15 Earthquakes

Contents

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An earthquake is one of the principal natural hazards from which process plants world-wide are at risk. Some account is therefore necessary of the seismic design of plants and the assessment of seismic hazard to plants.

Accounts of earthquakes are given in *Seismicity of the Earth and Associated Phenomena* by Gutenberg and Richter (1954), *Elementary Seismology* by Richter (1958), *Introduction to Seismology* by Bath (1979), *Earthquakes and the Urban Environment* by Berlin (1980), *Earthquakes* by Eiby (1980), *An Introduction to the Theory of Seismology* by Bullen and Bolt (1985) and *Earthquakes* by Bolt (1988). Treatments of earthquake engineering, most of which give some coverage of seismology, include *Dynamics of Bases and Foundations* by Barkan (1962), *Earthquake Engineering* by Wiegel (1970), *Fundamentals of Earthquake Engineering* by Newmark and Rosenbleuth (1971), *Earthquake Resistant Design* by Dowrick (1977, 1987), *Ground Motion and Engineering Seismology* by Cakmak (1987) and *Manual of Seismic Design* by Stratta (1987). UK conditions are dealt with in *Earthquake Engineering in Britain* by the Institution of Civil Engineers (1985) and by Lilwall (1976) and Alderson (1982 SRD R246, 1985).

It is proper to recognize also the large amount of work done on seismicity and seismic engineering in Japan.

Earthquake engineering is a specialist discipline. The account given here is limited to an elementary introduction.

Selected references on earthquakes, earthquake-resistant design and earthquake hazard assessment are given in Table A15.1

A15.1 Earthquake Geophysics

A15.1.1 Earth structure

The structure of the earth is illustrated in Figure A15.1 and is approximately as follows: a crust 30 km thick, a mantle 2900 km thick and a core of 3470 km radius, giving a total radius of 6370 km. The core has an inner core of 1400 km radius.

The crust exhibits two layers. In the lower of these layers the velocity of seismic waves is rather higher. The interface between the two is known as the Conrad discontinuity. Likewise, the mantle is divided into the upper and lower mantles. The crust and the upper mantle are termed the lithosphere. Other discontinuities are the Mohorovicic discontinuity at the boundary of the crust and the mantle, and the Gutenberg discontinuity at the boundary of the mantle and the core.

A15.1.2 Crustal strain and elastic rebound

The earth's crust has a degree of elasticity and when subject to stress due to the earth's forces it undergoes crustal strain. This property is the basis of the elastic rebound theory of Reid, which provides one explanation of the way in which earthquakes occur. Reid suggests that 'the crust,

Table A15.1 *Selected references on earthquakes, earthquake-resistant design and earthquake hazard assessment (see also Tables 9.1 and 10.2)*

California Inst. Technol. (n.d.); NRC (Appendix 28 Seismic Events); Mercalli (1902); Wrinch and Jeffreys (1923); Milne (1939); Nordquist (1945); Housner (1947); Dix (1952); EERI (1952); Gutenberg and Richter (1954, 1956, 1965); Neumann (1954); Jenkins and Oakshott (1955); Gutenberg (1956); Richter (1958); Bullen (1963); Evison (1963); Esteva and Rosenblueth (1964); Matuzawa (1964); C.R. Allen (1967); Esteva (1967, 1974); Jennings, Housner and Tsai (1968); Karnik (1968, 1991); Rothe (1969); Stacey (1969); P.O. Marshall (1970); NEIC (1970); Tucker, Cook *et al.* (1970); Anon. (1971e); Greensfelder (1971); Nat. Ocean Atmos. Admin (1972); Bath (1973, 1979); Donovan (1973); Tank (1973); Barbreau, Ferrieux and Mohammadioun (1974); Lomnitz (1974); Hsieh, Okrent and Apostolakis (1975a,b); Okrent (1975); US Geol. Survey (1975); H.D. Foster (1976); H.D. Foster and Carey (1976); Hsieh and Okrent (1976); Lomnitz and Rosenblueth (1976); McGuire (1976); Bolt (1978, 1980, 1982, 1988); Lee, Okrent and Apostolakis (1979); Verney (1979); Berlin (1980); Eiby (1980); BRE (1983 BR31); Veneziano, Cornell and O'Hara (1984); Bullen and Bolt (1985); Muir Wood (1985); EPRI (1986); Mosleh and Apostolakis (1986); ASCE (1987/33, 1988/ 36); Bernreuter, Savy and Mensing (1987); Cassaro and Martinez-Romero (1987); Cermak (1987); J. Evans *et al.* (1987); Grandori, Perotti and Tagliani (1987); Kropp (1987); Nuttli and Herrman (1987); Savy, Bernreuter and Chen (1987); Stratta (1987); Van Gils (1988); EEFLT (1991).

Earthquakes in Britain: Davison (1924); Lilwall (1976); Alderson (1982 SRD R246, 1985); Instn Civil Engrs (1985); Irving (1985); Liam Finn and Atkinson (1985)

Earthquake-resistant design, earthquake hazard assessment

ASCE (Appendix 27, 28, 1979/8, 1981/12, 1983/13, 14, 16, 1984/19, 1985/24, 1986/30, 1987/32, 1990/39, 40, 1991/42, 43); ASME (Appendix 28 Pressure Vessels and Piping, 1982/12, 1984/16); ASTM (STP 450); NRC (Appendix 28 Seismic Fragility, Seismic and Dynamic Qualification, 1973, 1979a,c); EERI (1952); Barkan (1962); NTIS (1963); Benjamin (1968); Benjamin and Cornell (1970); Wiegel (1970); Newmark and Rosenblueth (1971); BRE (1972 BR6); AEC (1973); Dept of Commerce (1973); Newmark and Hall (1973, 1978); Okamoto (1973); Struct. Engrs Association of California, Seismology Committee (1975); Blume (1976); Int. Conf. Building Officials (1976, 1991); Lomnitz and Rosenblueth (1976); McGuire (1976); Aziz (1977); Dowrick (1977, 1987); P. Arnold (1978); Sachs (1978); Alderson (1979 SRD R135, 1982 SRD R246, 1985); Eberhart (1979); T.Y. Lee, Okrent and Apostolakis (1979); Anon. (1981c); R. Davies (1982); M. Schwartz (1982a); ASCE (1984); R.P. Kennedy and Ravindra (1984); Kunar (1985); Lee and Trifunac (1985); C.R. Smith (1985); Dimming (1986); Stratta (1987); R.P. Kennedy *et al.* (1989); Goschy (1990); Casselli, Masoni and Foraboschi (1992); Ravindra (1992)

Structures: Timoshenko (1936); Flugge (1960); Warburton (1976); Pilkey and Chang (1978)

Storage tanks, vessels: Veletsos and Yang (1976); Eberhart (1979); R.P. Kennedy (1979, 1982a); Haroun and Housner (1981); R. Davies (1982); D.W. Phillips (1982); Veletsos (1984); Priestly *et al.* (1986); Veletsos and Yu Tang (1986a,b)

Fluid–structure interactions, liquid sloshing: ASME (PVP 128, 1988 PVP 145, 1989 PVP 157); ASCE (1984/18)

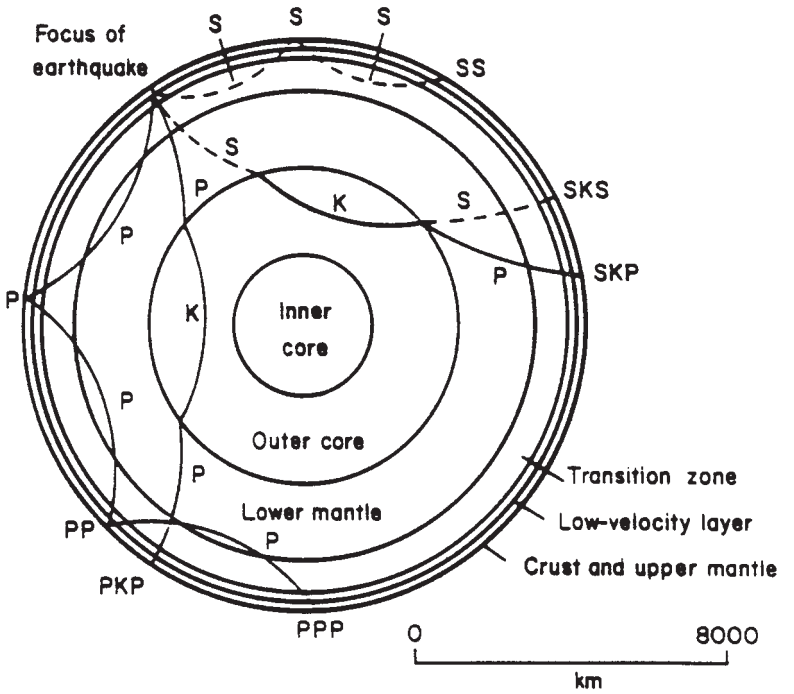

Figure A15.1 *The structure of the earth and passage of seismic waves through it (US Geological Survey, 1975)*

in many parts of the earth, is being slowly displaced, and the difference between displacements in neighbouring regions sets up elastic strains, which may become greater than the rock can endure. A rupture then takes place, and the strained rock rebounds under its own elastic stresses, until the strain is largely or wholly relieved'.

A15.1.3 Plate tectonics, faults and fault creep

In some regions earthquakes are associated with faulting of the earth, while in others there appears to be little apparent correlation between earthquakes and structural features.

Earthquakes are frequently associated with faulting of the earth. There has been debate, however, as to whether the faults have caused the earthquakes or the earthquakes the faults. The latter viewpoint has been argued by Evison (1963).

A fault in the crust may be caused by tension, compression or shear. A normal fault, in which slip occurs between one block and another, is usually considered to be the result of tension and a reverse fault, in which one block is thrust below another, the result of compression or thrust. These two types of fault are also termed dip-slip faults. The slip plane is characterized by the angle of dip, or angle of the plane to the horizontal; an angle of dip close to 90° corresponds to a nearly vertical slip plane. In a shear fault the relative movement of the two blocks is predominantly horizontal. This type is also termed a strike-slip, or transcurrent, fault. There are also oblique slip faults in which there is a combination of vertical and horizontal movement.

As a result of displacement, the ground in a zone extending out from a fault can become permanently deformed. The disturbed zone, or shatter zone, can be up to 1 km wide. The magnitude of displacements is discussed by Berlin, who mentions cases of a 14.4 m vertical displacement, or uplift, in Alaska and of a 4.9 m horizontal displacement in California; there is a 6.1 m horizontal displacement reported for the 1906 San Francisco earthquake but this is subject to some doubt.

The build-up of strain in the crust may be relaxed by a much more gradual movement of the crust, or fault creep. This process, which may be continuous or episodic, does not generate earthquake waves. An account is given by Berlin.

In some regions there are faults that are associated with recent seismic activity, or active faults. Perhaps the best known is the San Andreas fault in California. This fault is a strike-slip fault, or, viewed on a finer scale, a system of strike-slip faults. There are often lesser faults associated with the main fault as branch faults or as subsidiary faults, joining the main fault at oblique angles and sometimes in echelon along it.

There are some regions which are very much more prone to earthquakes than others. One explanation for this is given by the theory of continental drift, and of plate tectonics, according to which the earth's lithosphere is divided into a number of rigid plates that move relative to each other. Earthquakes are much more frequent at these interfaces. The Pacific rim is the most striking example, but there are a number of others.

There are a number of definitions of what constitutes an active fault. For the siting of nuclear power plants in the United States, the NRC considers a fault to be active if there

has been movement at least once in last 35,000 years. Other definitions are discussed by Berlin (1980).

As stated earlier, however, earthquakes do also occur in regions where there is no apparent correlation with active fault structures.

A15.1.4 Focus and epicentre

The origin of an earthquake is termed the focus, or hypocentre, and the point on the earth's surface directly above the focus the epicentre.

Earthquakes are classified as shallow focus (focus depth <70 km), intermediate focus (depth 70–300 km) and deep focus (depth >300 km).

A15.1.5 Seismic waves

During an earthquake waves pass through the earth and impart motion to the ground. These waves are elastic in that the rocks through which they pass then return to their original shapes and positions.

There are two broad types of wave: body waves and surface waves. Body waves are classified as primary, or P, waves and secondary, or S, waves. A P wave is a longitudinal or compression wave, is analogous to a sound wave and has a velocity of some 8 km/s. An S wave is a transverse or shear wave, is analogous to electromagnetic waves and has a velocity of some 4.5 km/s. The passage of P and S waves is illustrated in Figure A15.1. Both P and S waves can undergo reflection. Reflection can occur at the earth's surface or at a boundary such as that between the mantle and the core. Refraction can occur through the core. On reflection both types of wave can be transformed to the other type, that is, a P wave to an S wave, or vice versa.

The notation used for P and S waves is illustrated in Figure A15.1. A P wave travelling directly from the focus to the point of measurement without reflection is denoted as P, one undergoing one reflection at the surface PP and one undergoing two reflections at the surface PPP. A P wave undergoing one reflection at the core is denoted as PcP. The corresponding notation for S waves is S, SS and SSS for a wave with zero, one and two surface reflections and ScS for a wave with one core reflection. There are also hybrid waves such as PS, PSS, PPS, PSP; SP, SPP, SSP, SPS; PcS and ScP.

Both P and S waves can undergo refraction through the earth's core. In the core itself there is a difference between P and S waves: an S wave cannot pass through the core. However, the wave leaving the core can be either a P wave or an S wave; in the latter case this is due to transformation at the core boundary. Hence, an S wave can enter the core, undergoing transformation to a P wave on entry and further transformation to an S wave on exit, and then travel on as an S wave again. The principal refractions through the core are denoted as PKP, PKS, SKP and SKS (K for Kern in German). There are also more complex waves such as PKKP (refraction–reflection–refraction in the core) and PKPPKP (refraction in core–reflection at surface–refraction in core).

The distance between the focus and the point of measurement is generally expressed in degrees rather than kilometres. A degree corresponds to about 111 km.

There is a limiting angle of about 103° at which a P wave is reflected from the core. At any angle greater than this the wave is refracted through the core. The effect is to create between an angle of about 103° and one of about 142° a 'shadow zone' to which waves do not penetrate.

The other main type of wave is surface waves. Surface waves, long waves or L waves, travel round the surface of the earth rather than through the interior. They are classified as Love, or L_Q, waves and Rayleigh, or L_R, waves. Love waves have a horizontal but no vertical component, Rayleigh waves have both horizontal and vertical components. A Rayleigh wave is generally described as having a retrograde elliptical motion. Both types of wave travel more slowly than S waves, with the Rayleigh wave slower than the Love wave.

L waves may travel round the earth several times and generate ground movement with amplitudes of about 1 mm. They have a typical period of 10–20 s. They contain large amounts of energy but do relatively little damage on account of the long period. Often an earthquake is 'heard before felt'. Sounds like a low rumble can be generated by the faster P waves, while the ground shaking is due to the larger amplitude but slower S waves.

A15.1.6 Seismic measurements

An instrument for the recording of the ground motion caused by an earthquake is known as a seismometer and the record that it produces a seismogram.

Measurements may be made of any of the three main time-domain parameters: displacement, velocity and acceleration.

The measurement of ground motion is well developed and records have been obtained for the amplitude and for the acceleration of a large number of earthquakes.

Figure A15.2 gives a seismogram showing the arrival of the P, S and L waves.

There are a number of seismographic networks. A region of high seismic activity may have a number of such networks. Thus, in California, Berlin describes networks operated by the US Geological Survey, the Nuclear Regulatory Commission, the University of California and several other bodies. At the international level there is the World-wide Standard Seismographic Network (WSSN).

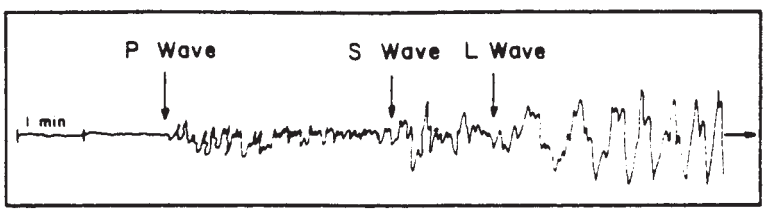

Figure A15.2 *A seismogram showing P, S and L waves (National Oceanic and Atmospheric Administration, 1972)*

A15.2 Earthquake Characterization

The quantitative characterization of earthquakes is largely in terms of magnitude and intensity scales and of empirical correlations. Earthquakes are a geographical phenomenon and hence in many cases the original correlations have been derived for a specific region, often California. This should be borne in mind in respect of the relationships quoted below.

A15.2.1 Focus and epicentre

For a particular location the distance r to the epicentre is the epicentral distance and the distance to the focus is the focal distance so that

$$R^2 = h^2 + r^2 \qquad [A15.2.1]$$

where R is the focal distance, or slant distance (km), h the distance between the focus and the epicentre, or focal depth (km) and r the epicentral distance (km). Use is often made of a modified focal distance defined as

$$R^2 = h^2 + r^2 + k^2 \qquad [A15.2.2]$$

where k is a modifying factor (km). Esteva (1967) has given an estimate of $k = 20$.

A15.2.2 Magnitude and magnitude scales

The severity of an earthquake is defined in terms of its magnitude and intensity. The more objective is the magnitude, which is a measure of the total energy in the seismic waves.

A scale for the representation of the magnitude of an earthquake was devised by Richter and magnitude is commonly quoted in terms of the value on the Richter scale. The value is a measure of the ratio of the maximum amplitude recorded for the earthquake in question to the maximum amplitude for a standard earthquake, with both measurements made on a standard seismograph located at a standard distance from the earthquake, the instrument being a Wood–Anderson seismograph of defined characteristics.

The magnitude M of an earthquake may be measured locally, in which case it is denoted M_L, or at a distant point through surface waves, when it is denoted M_S. The two differ and in order to overcome this difficulty Gutenberg introduced the concept of unified magnitude m, or m_b, which depends on the body waves. The magnitudes quoted in the literature are frequently not fully defined.

The relation of Richter for the magnitude of a local earthquake is

$$M_L = \log_{10}(A/A_O) \qquad [A15.2.3]$$

where A is the maximum amplitude (mm), A_O the maximum amplitude of the standard earthquake (mm) and M_L the local magnitude, under the standard conditions described. The value of A_O assigned to the standard earthquake is $A_O = 0.001$ mm.

The Richter scale is thus a logarithmic one and an earthquake that is one unit higher on the scale has an amplitude 10 times as great as that below it.

The Richter magnitude scale is open-ended with no lower or upper limit. The scale point 0 is an arbitrary one.

A number of equations have been developed for the surface wave magnitude M_S and the body magnitude m_b, relating these quantities to the characteristics of the seismographic record.

It is often necessary to convert one type of magnitude to another. Two widely used approximate relations are those given by Richter (1958)

$$M_S = 1.59m_b - 3.97 \qquad [A15.2.4]$$

and

$$m_b = 2.5 + 0.63M_S \qquad [A15.2.5]$$

These two magnitudes agree at a value of about 6.8; below this m_b is larger and above it M_S is larger. There is also the empirical equation of Gutenberg (1956)

$$m_b = 1.7 + 0.8M_L - 0.01M_L^2 \qquad [A15.2.6]$$

A15.2.3 Energy

The relationship between the total seismic wave energy and the surface wave magnitude was the subject of a series of studies by Gutenberg and Richter, who produced between 1936 and 1956 a number of correlations. The 1956 Gutenberg–Richter equation for energy, quoted by Gutenberg (1956), is

$$\log_{10} E = 11.8 + 1.5M_S \qquad [A15.2.7]$$

where E is the total energy (erg).

Gutenberg has also given the following relations between the total energy and the other magnitudes:

$$\log_{10} E = 9.9 + 1.9M_L - 0.024M_L^2 \qquad [A15.2.8]$$

$$\log_{10} E = 5.8 + 2.4m_b \qquad [A15.2.9]$$

An earthquake that is one unit higher on the Richter magnitude scale has an energy some 27 times as great as that below it.

A15.2.4 Frequency and return period

A correlation between the frequency and magnitude of earthquakes was obtained by Gutenberg and Richter. Their equation is given by Richter (1958) as

$$\log_{10} N = a - bM \qquad [A15.2.10]$$

where N is the frequency of earthquakes exceeding that magnitude (per year), and a and b are constants. This equation is generally referred to as the Gutenberg–Richter equation for frequency.

Various workers have used the Gutenberg–Richter equation to correlate the frequency of earthquakes for different regions and periods.

Estimates for the relationship between the magnitude and the frequency of earthquakes world-wide by Gutenberg and Richter (1940) are given below together with later estimates by the National Earthquake Information Center (NEIC) (1970).

M_L	*Gutenberg and Richter description*	*Annual frequency*	*NEIC description*	*Annual frequency*
>8.0	Great earthquakes	1	Great	1.1
7.0–7.9	Major earthquakes	10	Major	18
6.0–6.9	Destructive shocks	100	Large (destructive)	120
5.0–5.9	Damaging shocks	1,000	Moderate (damaging)	1,000
4.0–4.9	Minor strong shocks	10,000	Minor (damage slight)	6,000
3.0–3.9	Generally felt	100,000	Generally felt	49,000

A15.2.5 Intensity and intensity scales

The other main measure of the severity of an earthquake is the intensity. Intensity is a measure of the severity of an earthquake as experienced at a particular location.

Thus, an earthquake of a given magnitude may have different intensities at different locations. However, in so far as interest centres on the effects at a given location, such as a town, an intensity may be assigned for the earthquake at that location. Thus, an intensity is often quoted for an earthquake identified by town and year.

There are several scales for the representation of the intensity of an earthquake. One of the earliest was the Rossi–Forelli (RF) scale. This was modified by Mercalli to give the Mercalli scale and subsequently modified again in 1931 to give the Modified Mercalli (MM) scale. The MM scale has since undergone further revisions. The MM scale is the most widely used intensity scale. It is shown in Table A15.2

One way of characterizing a particular earthquake is by an isoseismal map showing the contours of the MM scale intensities.

The MM scale gives the intensity as a Roman numeral. For quantitative work the intensity is required as a numerical value. The practice is to use the Roman numeral directly. Thus, an earthquake of intensity between MM scale I and II has an intensity of 1.5. This is the approach described by Richter (1958, p. 140).

There are numerous empirical relationships that have been developed between intensity and other earthquake parameters. One is the equation of Gutenberg and Richter (1956) between local magnitude, intensity and epicentral intensity

$$M_L = I + I_0/3 \qquad \text{[A15.2.11]}$$

where I is the intensity and I_0 the epicentral intensity.

Another is the relation of Esteva and Rosenblueth (1964) between intensity, local magnitude and focal depth

$$I = 8.16 + 1.45M_L - 2.46 \log_{10} h \qquad \text{[A15.2.12]}$$

The following relation is given by Richter (1958) between peak ground acceleration (PGA) and intensity:

$$\log_{10} a = \frac{I}{3} - \frac{1}{2} \qquad \text{[A15.2.13]}$$

where a is the PGA (cm^2/s).

A15.3 Earthquake Effects

The effects of an earthquake may be classified as direct or indirect. The direct effects include

(1) ground shaking;
(2) ground lateral displacement;
(3) ground up-lift and subsidence;

and the indirect effects

(4) ground settlement;
(5) soil liquefaction;
(6) slope failure:
  (a) avalanches, landslides,
  (b) mud slides;
(7) floods;
(8) tsunamis and seiches;
(9) fires.

Of the direct effects, ground shaking usually occurs over a wide area. At faults, fault displacement results in lateral movement of the ground and surface breaks. The distance over which the surface breaks occur is variable. There may be tectonic up-lift and subsidence.

Of the indirect effects, ground settlement may occur due to compaction of unconsolidated deposits. There may be soil liquefaction, giving a 'quick condition' failure. Slope failures may occur in the form of avalanches, landslides and mud slides.

The earthquake may cause floods due to the failure of dams or levees. In certain regions there may occur tsunamis. A tsunami is a wave occurring in relatively shallow water and is caused by vertical displacement of the earth beneath the water. Seiches may also occur. A seich is a standing wave on the surface of water such as a lake.

The destruction of buildings and the rupture of gas mains tends to give rise to widespread fires.

A15.4 Earthquake Incidents

Tabulations of earthquakes are given in a number of texts. Eiby (1980) gives a chronological list; this includes the values of the magnitudes. Berlin gives tables showing earthquakes that have caused major fatalities world-wide, major fatalities in the United States and major property damage in the United States. Bolt (1988) gives tables of earthquakes world-wide, in the United States and Canada and in Central and South America; the North American list gives MM intensities. Berlin (1980) also gives lists of earthquakes with special features such as shattered earth, vertical displacement and bad ground and soil liquefaction effects.

Table A15.3 gives some earthquakes in this century that have caused major loss of life world-wide or property damage in the United States. Table A15.4 lists some earthquakes that are frequently discussed in texts on earthquakes or earthquake-resistant design as having features

Table A15.2 *The Modified Mercalli intensity scale*

Intensity	*Description*[a]
I	Not felt. Marginal and long-period effects of large earthquakes
II	Felt by persons at rest, on upper floors, or favourably placed
III	Felt indoors. Hanging objects swing. Vibration like passing of light trucks. Duration estimated. May not be recognized as an earthquake
IV	Hanging objects swing. Vibration like passing of heavy trucks; or sensation of a jolt like a heavy ball striking the walls. Standing motor cars rock. Windows, dishes, doors rattle. Glasses clink. Crockery clashes. In the upper range of IV, wooden walls and frame creak
V	Felt outdoors; direction estimated. Sleepers wakened. Liquids disturbed, some spilled. Small unstable objects displaced or upset. Doors swing, close, open. Shutters, pictures move. Pendulum clocks stop, start, change rate
VI	Felt by all. Many frightened and run outdoors. Persons walk unsteadily. Windows, dishes, glassware broken. Knickknacks, books, etc., off shelves. Pictures off walls. Furniture moved or overturned. Weak plaster and masonry D cracked. Small bells ring (church, school). Trees, bushes shaken (visibly, or heard to rustle)
VII	Difficult to stand. Noticed by drivers of motor cars. Hanging objects quiver. Furniture broken. Damage to masonry D, including cracks. Weak chimneys broken at roof line. Fall of plaster, loose bricks, stones, tiles, cornices (also unbraced parapets and architectural ornaments – CFR). Some cracks in masonry C. Waves on ponds; water turbid with mud. Small slides and caving in along sand or gravel banks. Large bells ring. Concrete irrigation ditches damaged
VIII	Steering of motor cars affected. Damage to masonry C; partial collapse. Some damage to masonry B; none to masonry A. Fall of stucco and some masonry walls. Twisting, fall of chimneys, factory stacks, monuments, towers, elevated tanks. Frame houses moved on foundations if not bolted down; loose panel walls thrown out. Decayed piling broken off. Branches broken from trees. Changes in flow or temperature of springs and wells. Cracks in wet ground and on steep slopes
IX	General panic. Masonry D destroyed; masonry C heavily damaged, sometimes with complete collapse; masonry B seriously damaged. (General damage to foundations – CFR.) Frame structures, if not bolted, shifted off foundations. Frames cracked. Serious damage to reservoirs. Underground pipes broken. Conspicuous cracks in ground. In alluviated areas sand and mud ejected, earthquake fountains, sand craters
X	Most masonry and frame structures destroyed with their foundations. Some well-built wooden structures and bridges destroyed. Serious damage to dams, dikes, embankments. Large landslides. Water thrown on banks of canals, rivers, lakes, etc. Sand and mud shifted horizontally on beaches and flat land. Rails bent slightly
XI	Rails bent greatly. Underground pipelines completely out of service
XII	Damage nearly total. Large rock masses displaced. Lines of sight and level distorted. Objects thrown into the air

[a] CFR, Charles F. Richter additions to the 1931 scale. Masonry A, good workmanship, mortar, and design; reinforced, especially laterally, and bound together by using steel, concrete, etc.; designed to resist lateral forces. Masonry B, good workmanship and mortar; reinforced, but not designed in detail to resist lateral forces. Masonry C, ordinary workmanship and mortar; no extreme weaknesses like failing to tie in at corners, but neither reinforced nor designed against horizontal forces. Masonry D, weak materials, such as adobe; poor mortar; low standards of workmanship; weak horizontally.

From *Elementary Seismology* by Charles F. Richter, W. H. Freeman and Company, Copyright © 1958. Reproduced by permission.

of particular interest; accounts of these earthquakes are given in the references shown in the table.

Table A15.3 gives only earthquakes that have occurred since 1920. It nevertheless includes some that have caused very large loss of life, in particular those at Kwanto in Japan in 1923 and Tangshan in China in 1976, where the death tolls were 143,000 and 250,000, respectively.

The San Francisco earthquake in 1906 was one of large magnitude (8.3) and high intensity (XI). The ground shook for some 40–60 s. Notable features were the difference in damage between buildings on good ground and those on bad ground and the outbreak of large numbers of fires. Some 700 people were killed.

The Tokyo–Yokohama earthquake in Japan in 1923, also known as the Kwanto earthquake after the province most affected, was another with large magnitude (8.3). Tokyo and Yokohama, both very densely populated, were almost completely destroyed. Fire broke out on a large scale and it was this rather than building collapse that was responsible for the high death toll of some 143,000.

These two disasters gave impetus to the development of seismological studies and seismic engineering in the United States and Japan.

The earthquake in Imperial Valley, California, in 1940, also known as El Centre, which had a magnitude of 6.9, is of particular interest to seismologists. A seismograph in El Centre recorded a PGA of some one third that of gravity. For many years this was the only record available to engineers showing clearly the ground shaking caused by a large earthquake close to its source.

Another earthquake that has been of particular interest to seismological engineers is that at Parkfield in 1966 with a magnitude of 5.6. The Parkfield earthquake was less destructive than that at El Centre in 1940, but it gave a PGA of 0.5 g compared with that of 0.33 g for El Centre.

The interest in these two earthquakes has been enhanced by a further earthquake at Imperial Valley in 1979, which was of similar size to the 1940 event, and by the fact that Parkfield has been the subject of one of the principal examples of the prediction of future earthquakes.

Table A15.3 *Some earthquakes causing major loss of life or property damage*

A Earthquakes causing major loss of life[a]

Year	*Location*	*Number of deaths*
1920	Kansu, China	180,000
1923	Tokyo-Yokohama, Japan	143,000
1932	Kansu, China	70,000
1935	Quetta, India	60,000
1939	Chilian, Chile	30,000
1939	Erzincan, Turkey	23,000
1960	Agadir, Morocco	14,000
1962	North-western Iran	14,000
1968	North-eastern Iran	11,600
1970	Peru	66,000
1972	Managua, Nicaragua	12,000[b]
1976	Guatemala	22,000
1976	Tangshan, China	≈250,000[c]
1976	Hopei, China	655,000

B Earthquakes causing major property damage in the United States[d]

		Property damage ($ million)
1906	San Francisco, CA	24 500 (fire loss)
1933	Long Beach, CA	40
1952	Kern County, CA	60
1964	Alaska and US West Coast	500
1971	San Fernando, CA	553

[a] Earthquakes since 1920 causing 10,000 or more deaths.
[b] This is Berlin's figure; Bolt gives 5000.
[c] For China in 1976 this is Bolt's entry; Berlin gives Hopei with 655,000 deaths.
[d] Earthquakes since 1900 causing $40 million or more property damage.
Sources: Berlin (1980); Bolt (1985).

In 1954 the oil fields of Kern County, California, were subject to an earthquake. The damage caused by this event to process installations is described in Section A15.5.

Several earthquakes have occurred in areas that were not regarded as major seismic risk zones. One of these occurred at Agadir in 1960. The epicentre of the earthquake was close to the town and although of relatively low magnitude (5.8) it was very destructive. Much of the town consisted of old buildings and this was a further major contributor to the destruction. The death toll is quoted as 14,000.

The earthquake at Skopje in 1963 had similar features. The area was not regarded as one of particular seismic activity. Its epicentre was close and it was highly destructive despite being of relatively low magnitude (6.0). About 1200 people were killed.

Both the Agadir and Skopje earthquakes were practically a single shock.

The earthquake at Mexico City in 1957, which had a magnitude of 7.5, was notable for the damage to buildings standing on bad ground. In locations where the soil was alluvium, there was widespread soil liquefaction. The old lake bed area of the city experienced intensities of VII, whereas at other locations the intensities were V or less.

Another earthquake in which there was extensive damage due to soil liquefaction was that at Niigata in 1964, which had a magnitude of 7.5. The Niigata earthquake gave impetus to the study of soil effects, and particularly soil liquefaction.

A large earthquake, of magnitude 8.4, occurred in Alaska in 1964. This event was notable for its long duration and wide reach, and for its destructiveness. The earth shook for about 3 min. Ground fissures occurred 725 km from the epicentre. Quite large areas suffered up-lift or subsidence. The docks at the port of Anchorage suffered large displacements. The damage caused to process installations by this event is described in Section A15.5.

The San Fernando earthquake of 1971 has several features of interest. It is a prime instance of the shattered earth effect described in Section A15.7. In localized areas the intensity was assessed as high as XII. Ground accelerations were the highest recorded at 1.25 and 0.7 g for horizontal and vertical accelerations, respectively. Some of the damage effects, particularly to lifelines, are described in Section A15.5.

As far as concerns the United Kingdom, mention should be made of the Great British Earthquake of April 22, 1884, near Colchester, to which a magnitude of 5.3 has been assigned. The PGA has been estimated as between 0.07 and 0.2 g.

A15.5 Earthquake Damage

There are available numerous accounts of earthquake damage. Most texts on seismology contain descriptions and illustrations of the damage caused by particular earthquakes. These accounts deal largely, often exclusively, with damage to buildings, which is not the prime concern here. There is rather less information available on damage to plant.

A review of seismic damage to process plant and utilities has been given by Alderson (1982 SRD R246). Information is also given by Berlin (1980).

The earthquake in Kern County near Bakersfleld in 1952 (Case History A20) occurred in an oil production area. The production rate of several oilfields was affected. Many storage tanks skidded but only a few collapsed.

The most spectacular effect occurred at the Paloma Cycling Plant, where the earthquake caused two of the five large butane spheres to collapse, rupturing pipework and giving a major release. A large vapour cloud formed and was ignited at electrical transformers almost three blocks away. There was a large vapour cloud explosion, followed by a major fire.

On vessels, columns and tall heat exchangers steel foundation bolts were stretched. The top of one vessel standing 60 ft high and weighing some 100 te was estimated from the 1 in. stretch of the bolts at its base to have moved over an arc of 3 ft. There were no major failures, however, of horizontal vessels or pressure storage tanks. High pressure pipework withstood the earthquake well, although there were thermal failures in the subsequent fire; only one cold failure was reported.

At other installations damage was minimal. At one plant oil sloshing in storage tanks broke through the roof. At one pipeline station pipe displacements of 5 in. were found. Elevated water tanks with no lateral support suffered badly. Of the 12 in the area, two collapsed and seven had suffered damage to their supports.

Table A15.4 *Some earthquakes of particular interest*

Date		*Magnitude*	*Reference*
18 April 1906	San Francisco, CA	8.3	
1 Sept. 1923	Kwanto, Japan	8.3	
18 May 1940	Imperial Valley (El Centre)	6.9	Dowrick (1977)
21 July 1952	Kern County, CA	7.7	Berlin (1980); Alderson (1982)[a]
21 Dec. 1954	Eureka, CA	6.6	Alderson (1982)
22 March 1957	San Francisco, CA	5.3	Alderson (1982)
28 July 1957	Mexico City	7.5	Berlin (1980)
29 Feb. 1960	Agadir, Morocco	5.8	Eiby (1980)
22 May 1960	Arauco, Chile	8.4	Eiby (1980)
26 July 1963	Skopje	6.0	Alderson (1982)
27 March 1964	Alaska	8.4	Berlin (1980); Alderson (1982)
16 June 1964	Niigata, Japan	7.5	Dowrick (1977); Berlin (1980);
27 June 1966	Parkfleld	5.6	Dowrick (1977); V.W. Lee and Trifunac (1987); Bolt (1988)
19 Aug. 1966	Varto, Turkey	7	Berlin (1980)
9 Feb. 1967	Columbia	6.7	Alderson (1982)
31 May 1970	Chimbote, Peru	7.7	Eiby (1980)
9 Feb. 1971	San Fernando, CA	6.8	Berlin (1980)
4 Feb. 1975	Liaoning Province	7.4	Bolt (1988)
6 Sept. 1975	Lice, Turkey	6.7	Berlin (1980)
6 May 1976	Friuli, Italy	6.5	Alderson (1982)
27 July 1976	Tangshan	8.0	Bolt (1988)
13 Aug. 1978	Santa Barbara, CA	5.8	Alderson (1982)
15 Oct. 1979	Imperial Valley (El Centre)	–[b]	Bolt (1988)
2 May 1983	Coalinga, CA	6.7 (M_L)	Bolt (1988)
3 March 1985	Algarrobo, Chile	7.8	Bolt (1988)
19 Sept. 1985	Ixtapa, Mexico	8.1	Bolt (1988)

[a] Alderson (1982) = Alderson (1982 SDR R246).
[b] This earthquake is described by Bolt (1988) as 'similar' to that in Imperial Valley in 1940.

There was damage to a number of electrical power plants and electrical distribution systems.

Overall plant management in this area were earthquake-conscious. Generally, tall vessels were well anchored and pipework provided with flexibility.

Another instructive case is the earthquake at San Fernando in 1971. This was the first occasion on which a major effort was made to investigate the effects on lifeline systems.

The earthquake was particularly severe over an area of some 30 km^2 at San Fernando and Sylmar. Violent ground movement in this area broke gas mains and valves, but this was the only area where the gas distribution system suffered serious damage. The water supply system to San Fernando was devastated.

The earthquake disrupted power supplies to large parts of Los Angeles. There was damage to Sylmar Converter Station (40% equipment loss), Olive Switching Station (80% loss) and Sylmar Switching Station (90% loss). The restoration time for the first of these was estimated at 1.5–2 years.

At the Sylmar Central Office of the local telephone company 91 te of automatic switching equipment were destroyed, putting the telephone service out of action.

The transport system was also severely affected. Some 62 bridges were damaged, of which 25% collapsed or were severely damaged.

Other earthquakes for which Alderson gives some information on damage to plant include Eureka in 1954, San Francisco in 1957, Alaska in 1964 and Santa Barbara in 1978. It is not uncommon for there to be some rupture of water mains, often due to a combination of corrosion and pressure surge. Some rupture of gas pipes also occurs.

In the 1964 Alaska earthquake there were many failures of tanks and pipework. Tanks of all kinds moved and, if not well anchored, toppled over. Pipes failed at screwed joints and poorly guided thermal loops, as did long unsupported cast iron pipe runs.

A15.6 Ground Motion Characterization

The ground motion caused by an earthquake may be characterized in terms of the peak values of the acceleration, velocity and displacement; of the full time-domain responses of these quantities, particularly the accelerogram, or of the response spectrum. The latter is described below.

The information required for design depends on the method used. Some methods utilize the peak acceleration. The trend is, however, to use the full response in the form of an accelerogram or a response spectrum.

For a single parameter, such as the PGA, methods of prediction are available. For a full response, such as an accelerogram or response spectrum, it is necessary to select one that is judged appropriate for the site.

A15.6.1 Strong ground motion

The typical pattern of ground motion is a sudden transition from zero to maximum shaking, followed first by a period of more or less uniformly intense vibration and then by a rather gradual attenuation of this vibration.

There are, however, appreciable differences in the ground motion from different earthquakes. Newmark and Rosenblueth (1971) distinguish four types of strong ground motion: (1) practically a single shock; (2) a moderately long,

extremely irregular motion; (3) a long ground motion exhibiting pronounced prevailing periods of vibration; and (4) a ground motion involving large-scale, permanent deformations of the ground.

They give the earthquakes at Agadir in 1960 and Skopje in 1963 in the first category; that at El Centre in 1940 in the second; that at Mexico City in 1964 in the third and those in Alaska and at Niigata, both in 1964, in the fourth.

A15.6.2 Peak ground motion

Methods are available for the estimation of the peak ground motion parameters. For ground acceleration one widely quoted relation is that given by Donovan (1973), derived from data for several seismic regions:

$$a = \frac{1080 \exp(0.5M)}{(R+25)^{1.32}} \qquad [A15.6.1]$$

where a is the PGA (cm/s^2).

Esteva (1974) has used data for earthquakes in California to obtain equations for both PGA and peak ground velocity:

$$a = \frac{5600 \exp(0.8M)}{(R+40)^2}, \quad R>15 \qquad [A15.6.2]$$

$$v = \frac{32 \exp M}{(R+25)^{1.7}}, \quad R>15 \qquad [A15.6.3]$$

where v is peak ground velocity (cm/s).

For peak ground displacement Newmark and Rosenblueth (1971) give the following approximate empirical relation

$$5 \leq \frac{ad}{v^2} \leq 15 \qquad [A15.6.4]$$

where d is peak ground displacement (cm). The lower limit of 5 and the upper limit of 15 apply to large epicentral distances, say 100 km, and to small ones, respectively.

A15.6.3 Vibration parameters

The vibration characteristics of the earthquake are also important. Correlations are available for the fundamental frequency, or period, of earthquakes. These are described by Dowrick (1977).

A15.6.4 Accelerograms

The basic seismographic measurement is the accelerogram. Profiles of velocity and displacement may be obtained from this by integration. A set of such profiles is illustrated in Figure A15.3.

There are now available accelerograms for quite a large number of real earthquakes. Collections are maintained by major seismographic institutions such as the California Institute of Technology.

Accelerograms are also available for simulated earthquakes. A set of eight such accelerograms have been

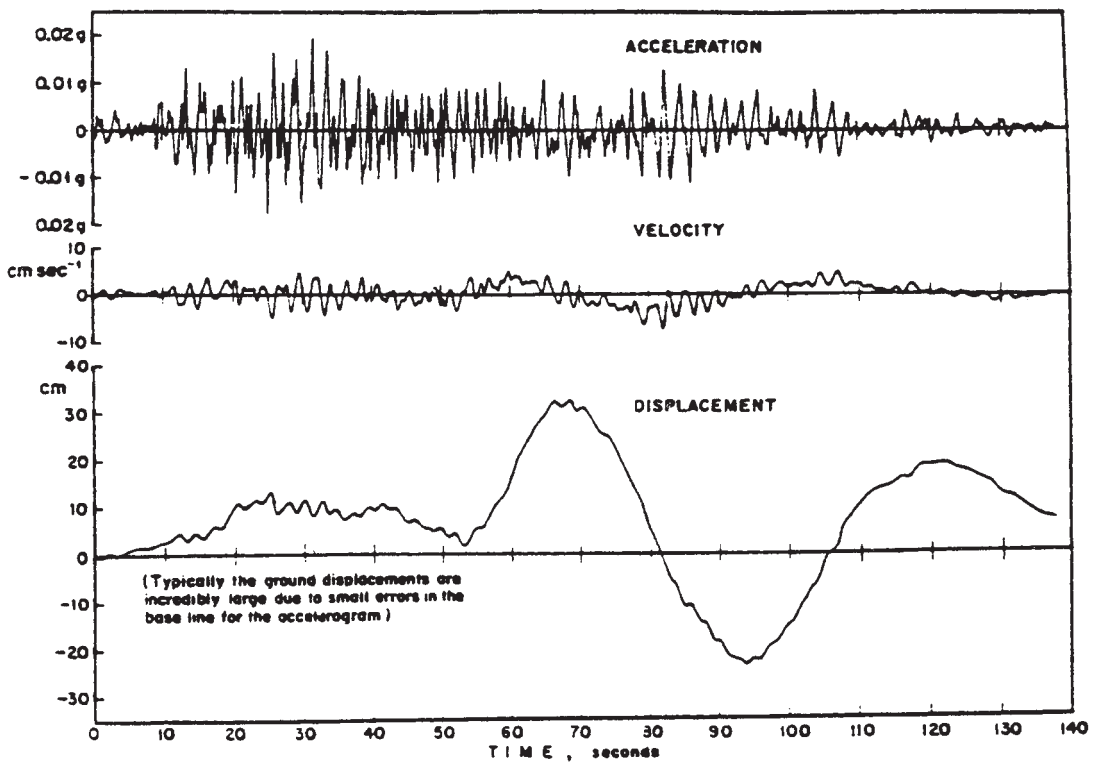

Figure A15.3 *Time histories of acceleration, velocity and displacement of the earthquake at Mexico City, 6 July 1964 (after Rosenblueth, 1996)*

described by Jennings, Housner and Tsai (1968). There exist computer codes for the generation of simulated earthquakes.

The design of earthquake-resistant structures is increasingly based on dynamic analysis. The structure is modelled using the appropriate equations of motion and this model is then perturbed by a suitable forcing function. The natural forcing function to use is an accelerogram.

A15.6.5 Response spectra

The main interest in design, however, is in the maximum values of certain responses of the structure. Many of these depend only on the natural period and the degree of damping. A plot which shows the response of one of the parameters acceleration, velocity or displacement for a given degree of damping is known as a response spectrum and that for a set of values of the damping as the response spectra.

Response spectra may be obtained from accelerograms by Fourier analysis and there are computer codes to do this.

There are response spectra available for both real and simulated earthquakes. A regulatory body may specify a standard set of response spectra for use in design.

Figure A15.4 shows a set of response spectra issued by the NRC.

A15.7 Ground, Soils and Foundations

The characteristics of the ground have profound effects on virtually all aspects of earthquake assessment and earthquake-resistant design.

A15.7.1 Ground effects

Experience of earthquakes shows that differences in the ground can result in large differences in the damage done.

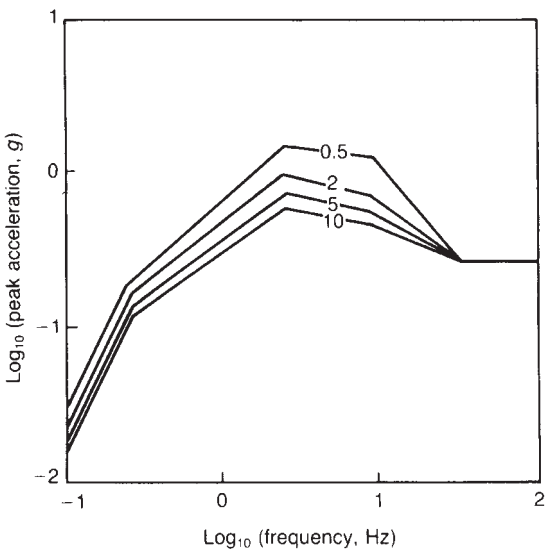

Figure A15.4 *Seismic design response spectra given in Regulatory Guide 1.60 of the Nuclear Regulatory Commission (Nuclear Regulatory Commission, 1973). The four damping levels shown are for viscous damping of 0, 5, 2, 5 and 10% of critical damping)*

According to Eiby (1980), in extreme cases this can amount to up to four degrees of intensity on the MM scale. It is therefore important to avoid siting structures on bad ground.

Bedrock is generally regarded as a sound foundation and alluvium as less satisfactory. Alluvium tends to absorb the effects of small earthquakes but to amplify those of large ones, giving rise to the effect of soil amplification.

A particular effect of bad ground is soil liquefaction, which can result in very severe damage. This is considered below.

An important class of locations where alluvium is present is old river terraces, which are often the site of ports.

As just stated, structures on the same site may suffer quite different degrees of damage due to differences in the quality of the ground. In the earthquake in 1957 in Mexico MM intensities of VII were determined for the old lake bed area of Mexico City, while other parts had intensities of Vor less. The earthquake at Varto, Turkey, in 1966 destroyed some buildings in a school complex but not others, the large difference in damage being attributed to the effect of very localized differences in the ground

Where a structure straddles two types of soil, damage tends to be enhanced, and this is to be avoided.

It is not universally the case that ground motion is worse in bad ground than in bedrock. Where the rock is on a ridge there can occur a phenomenon variously known as shattered earth, exploded outcrop or churned ground. The 1971 San Fernando earthquake produced numerous instances.

The susceptibility of steep slopes to avalanches is affected by the nature of the soil. A major slope failure occurred in the earthquake at Chimbote in Northern Peru in 1970 when an avalanche with an estimated velocity of 200–400 km/h travelled 18 km, buried whole towns and killed some 20,000. However, slope failures can also occur on relatively gentle slopes. In the Alaska earthquake in 1964 slope failures occurred due to liquefaction of lenses of sand contained in clay deposits.

A15.7.2 Soil settlement and liquefaction

Some of the worst earthquake damage has been due to a quick condition failure in which liquefaction of the soil has occurred. It is important, therefore, to be able to assess susceptibility to soil liquefaction. Damage may also occur due to soil compaction and settlement short of liquefaction.

The behaviour of a soil under earthquake loading is a function of the strain magnitude, strain rate and number of cycles of loading. Some soils increase in strength under rapid cyclic loading, while others, such as saturated sands, tend to lose strength.

Broadly, gravel and clay soils are not susceptible to liquefaction and dense sands are less likely to liquefy than loose ones.

Two important characteristics of a soil bearing on liquefaction are its cohesion and its water content. Saturated cohesionless soils are prone to liquefaction. A full discussion of the effect of cohesion and saturation on soil liquefaction is given by Newmark and Rosenblueth (1971).

The susceptibility of a cohesionless soil to liquefaction depends on its water content. For a dry cohesionless soil grain size is another important factor. For a medium grain size soil experiencing vibration a critical void ratio exists below which it tends to dilate and above which it tends to reduce in volume. This effect has been modelled by Barkan (1962). Other effects which can occur are breakage in large grain soils and air entrapment and soil liquefaction in fine grain soils.

A saturated cohesionless soil is most prone to liquefaction. The effect is not well understood, although it is known that relative density, confining pressure and drainage conditions are three important variables. Loose sands often liquefy after only a few loading cycles, whereas dense ones may require several hundred cycles. Conditions which prevent water from escaping promote liquefaction.

Extensive soil liquefaction occurred in the earthquake at Niigata in 1964. There was loose sand and water was not able to escape, partly due to the extent of the foundations.

With a saturated cohesive soil the strength tends to increase due to strain rate but to decrease due to cyclic loading. The net effect may be to increase or decrease the strength, depending on the nature of the soil. In a very sensitive soil a decrease in strength may set in after only a few cycles, whereas with a relatively insensitive one the strength may still be increasing after some 50 cycles.

A15.7.3 Site investigation

It is practice to carry out a site investigation to determine the characteristics of the ground. An account of the laboratory and field tests and of the information which they yield is given by Dowrick (1977). Laboratory tests on relative density and particle size distribution and field tests on groundwater conditions and penetration resistance bear on the problems of soil liquefaction and settlement, while field tests on soil distribution, layer depth and depth to bedrock, groundwater conditions and the natural period of the soil provide data for response calculations. Other tests may be performed to obtain the shear modulus and damping characteristics.

In addition to the use of drill holes to make the field tests just described, use may also be made of other techniques such as inducing and measuring vibrations.

A15.7.4 Design basis earthquake

Where dynamic analysis is to be performed, it may be necessary to modify the accelerogram to take account of the nature of the ground. The case of bedrock would seem at first sight to be the most straightforward, but this is not necessarily so, since most accelerograms are for softer soils, and there are very few for bedrock. The modification of accelerograms to take account of ground conditions is a specialist matter. An account is given by Dowrick (1977).

The ground motion is also affected by any structure placed on it. The accelerogram relevant to the site as a whole is therefore the free field accelerogram.

A15.7.5 Soil–structure interaction

It has been found by experience that there is an appreciable interaction between the soil and the structure and that it is necessary to take this into account.

The effects of bad ground have already been described. One such effect is soil amplification of the earthquake vibrations.

The effects of soil–structure interaction (SSI) are to modify the dynamics of the structure and to dissipate its vibrational energy.

In general, damage is greater if the natural period of a structure is similar to that of the soil on which it is built, for example a low, short-period building on a short-period soil deposit or a tall, long-period building on a long-period deposit. In the earthquake in 1957 at Mexico City extensive damage was done to long-period structures standing on deep (>100 m) alluvium. Another case where the natural period of structures suffering damage appeared closely correlated with the depth of subsoil was in the earthquake at Caracas, Venezuela, in 1967.

The Uniform Building Code (UBC) in the United States, described below, originally contained a soil amplification factor that was then removed due to lack of knowledge as to what the factor should be. The 1976 version contains a site–structure resonance factor S. This factor is a function of the ratio T/T_s where T and T_s are the natural periods of the structure and soil, respectively.

A soil deposit may be characterized by the width and depth of soil overlying the bedrock. The natural period increases with the depth of the deposit. Relations are available for the determination of the natural period of horizontal vibration of a soil deposit. Dowrick (1977) gives the equation

$$T = 4H/v_s \qquad [A15.7.1]$$

where H is the depth of the soil layer (m), T the natural period of the soil layer (s) and v_s the velocity of the shear wave (m/s).

In determining soil–structure interaction use is made of soil–structure models. In the simpler models the soil layer is represented using models of the lumped mass with spring and damping forces type not dissimilar to those used for the structure itself.

A full dynamic analysis of soil–structure interaction is perhaps the most difficult task in earthquake engineering.

A15.8 Earthquake-resistant Design

The design of an earthquake-resistant structure includes the following principal steps:

(1) seismic assessment;
(2) ground assessment;
(3) selection of structural form;
(4) selection of the materials;
(5) overall design of the structure.

The first and second of these are considered in Sections A15.11 and A15.7, respectively.

A15.8.1 Structural form

It has been found by experience that certain structural forms resist earthquakes well while others do not. An account of the features of structural form that give earthquake resistance is given by Dowrick (1977). In broad terms the structure should be simple and symmetrical and not excessively elongated in plan or elevation. It should have a uniform and continuous distribution of strength. It should be designed so that horizontal members fail before vertical members.

The desirable degree of stiffness has been a matter of debate. The point is discussed by Dowrick, who states that either a stiff or a flexible structure can be made to work.

A15.8.2 Materials

The properties of materials of construction that confer good resistance to earthquakes include homogeneity, ductility and high strength/weight ratio.

Materials generally quoted as being suitable for earthquake-resistant structures include steel, *in situ* reinforced concrete and prestressed concrete.

A15.8.3 Static analysis

The traditional method of earthquake-resistant design is static force analysis, also referred to as the static, or equivalent static, design method.

The static method is based on the following relation for the effective horizontal force, or base shear, on the structure:

$$V = ma \qquad \text{[A15.8.1]}$$

where a is the acceleration (m/s^2), m mass (kg) and V horizontal force (N).

The value of the acceleration a used in static design is typically in the range 0.05–0.20 g.

Methods for the design of structures to withstand a horizontal force in the form of a wind load are well established in civil engineering, and the approach required for the static method for earthquake resistance is not dissimilar.

Equation A15.8.1 is the basic relation traditionally used in earthquake design codes. These codes are described in Section A15.9.

A15.8.4 Dynamic analysis

It has long been recognized that the static design method is oversimplified, and a variety of dynamic design methods have been developed.

In dynamic analysis an unsteady-state model of the structure is produced and the forcing function of the design earthquake is defined. The model is then excited using this forcing function. Methods of dynamic analysis differ in the type of model used, the use of model decomposition and the domain (time, frequency) in which the forcing is applied.

The forces estimated using the more rigorous methods of dynamic analysis can be an order of magnitude greater than those obtained from the static method.

An account of dynamic analysis is given in Section A15.10.

A15.8.5 Detailed structural design

The design methods described give information on the forces to be expected at different points in the structure. The detailed design of the various elements of the structure can then be performed.

Discussions of the behaviour of structural elements and of detailed design using different materials are given by Newmark and Rosenblueth (1971) and Dowrick (1977).

A15.8.6 Detailed non-structural design

It is also necessary to design the non-structural features for seismic resistance. Much of the damage done by earthquakes is non-structural.

These features include in-fill panels and partitions; cladding and doors and windows. An account of their design is given by Dowrick (1977).

A15.8.7 Services

The seismic resistance of services is also relevant. Guidance on this aspect is given by Dowrick (1977).

For services, the specification of the seismic resistance required is of particular importance. There may be some key services whose survival in full working order is regarded as vital.

For such essential services Dowrick suggests the use of earthquake accelerations higher than those utilized in building design; the use of dynamic rather than static design methods and of the response spectrum technique and the design for elastic rather than plastic deformation. He states that a high degree of seismic resistance can usually be obtained at relatively little extra cost.

Some services which he considers are electrical equipment, such as transformers mechanical equipment, such as boilers and pipework.

A15.8.8 Specific structures

The bulk of guidance on earthquake-resistant design relates to buildings and similar structures, but some is available for other types of structure. The types of structure relevant to process plant include columns, storage tanks and pipes.

Newmark and Rosenblueth (1971) discuss the seismic design of towers, stacks and stack-like structures; tanks and hydraulic structures and pipes. Columns are also considered by Dowrick (1977).

Accounts of particular earthquakes frequently give information on the extent of survival of, or damage to, process plant items.

A15.9 Earthquake Design Codes

Guidance on the design of earthquake-resistant structures is available in earthquake design codes. These codes have been developed particularly in the United States and Japan, and many countries have adopted or adapted the US codes.

Some earthquake design codes which have been developed in the United States include the Uniform Building Code (UBC) of the International Conference of Building Officials (ICBO); the Basic Building Code of the Building Official and Code Administration (BOCA); the Standard Building Code (SBC) of the Southern Building Code Congress International; the recommendations of the Structural Engineers Association of California (SEAOC) and the ANSI code.

The UBC appears the most widely quoted and influential. An account of the development of the code is given by Berlin (1980).

The method of design used in the code is the equivalent static method, also known as the seismic coefficient method. The account given here is based on the 1976 version of the code.

In its simplest form the basic equation of the code is

$$V = CW \qquad \text{[A15.9.1]}$$

where V is the lateral or shear force (N), W the load (N) and C a coefficient. The lateral shear force V is commonly known as the base shear coefficient.

The working equation of the code has passed through various versions. That given in the 1976 code is

$$V = ZIKCSW \qquad \text{[A15.9.2]}$$

where C is the flexibility factor; I the occupancy importance factor K the framing factor; S the site factor and Z the seismic risk zone factor.

The values to be used for the various factors are treated in the code. A discussion of these factors is given by Berlin (1980).

The flexibility factor C is a function of the natural period of the structure. There are a number of equations for the estimation of C. One principal equation is

$$C = 1/15T^{1/2} \qquad \text{[A15.9.3]}$$

where T is the fundamental period of vibration of the structure in the direction under consideration(s).

The occupancy importance factor I is 1.5 for essential facilities, 1.25 for a building where the primary occupancy is more than 300 people and 1.0 for other buildings.

The framing factor K allows for the types of structure. It has values ranging from 0.67 to 1.33. The lower value is for a structure with ductile, moment resisting frame and the higher for a structure with a box system, in which lateral forces are resisted by shear walls or braced frames. A tabulation of values is given for different types of structure.

For the seismic zone risk factor Z the United States is divided into five zones, which are defined in the code and may be characterized as follows:

Zone 0 No damage
Zone 1 Minor damage (MM intensity V and VI)
Zone 2 Moderate damage (intensity VII)
Zone 3 Major damage (intensity VIII)
Zone 4 Areas within Zone 3 close to certain major fault systems.

The values of Z for use in these zones are 3/16, 3/8, 3/4 and 1 for Zones 1, 2, 3 and 4, respectively.

An account of codes in various countries is given by Alderson (1982 SRD R246).

A15.10 Dynamic Analysis of Structures

There are a variety of methods of dynamic analysis. Features of these methods are the unsteady-state model of the structure, the use of decomposition techniques, the forcing function and the domain in which the analysis is conducted.

In the following account, dynamic analysis is described mainly in terms of a single design earthquake. It is generally recommended that the analysis be repeated for further earthquakes.

A15.10.1 Unsteady-state models of structures

Unsteady-state models of the structure are distinguished by the number of degrees of freedom (DoF). Both single degree-of-freedom (SDF) and multiple degree-of-freedom (MDF) models are used. Basic SDF and MDF models are described by Dowrick (1977).

The basic SDF model is the standard second-order system. This may be written as

$$F_I + F_D + F_S = F(t) \qquad \text{[A15.10.1]}$$

where F is the applied force, or forcing function (N), F_D the damping force (N), F_I the inertia force (N) and F_S the elastic force (N).

Substituting for the various force terms, Equation A15.10.1 may be written as

$$m\ddot{x} + c\dot{x} + kx = F(t) \qquad \text{[A15.10.2]}$$

where c is the damping coefficient (kg/s), k the resistance (kg/s^2), m the mass of the system (kg), t the time (s) and x the displacement (m). In standard form the equation becomes

$$\frac{1}{\omega_n^2}\ddot{x} + \frac{2\zeta}{\omega_n}\dot{x} + x = \frac{1}{k}F(t) \qquad \text{[A15.10.3]}$$

with

$$\zeta = (c^2/4mk)^{1/2} \qquad \text{[A15.10.4]}$$

$$\omega_n = (k/m)^{1/2} \qquad \text{[A15.10.5]}$$

where ζ is the damping factor and ω_n the natural frequency (s^{-1}). The damped frequency is

$$\omega = \omega n(1 - \zeta^2)^{1/2} \qquad \text{[A15.10.6]}$$

where ω is the frequency of damped oscillation (s^{-1}).

The SDF model is a lumped mass model. The distribution of mass may be taken into account by the use of an MDF model. Thus an n-storey structure might be represented by an MDF model in which the mass of each storey is assumed to be located at the floor of that storey. The model obtained then consists of a set of n equations similar to Equation A15.10.2.

In the simpler case, the model is formulated as a linear one. For some systems a linear model represents an unacceptable oversimplification and a non-linear model is required.

A15.10.2 Time-domain solution

The dynamic model is then subjected to the forcing function of the design basis earthquake. In time-domain analysis, the unsteady-state model is excited by the time forcing function, which is the accelerogram. The equations are integrated numerically and the time response of the structure is obtained. These responses include the forces, or stresses, on, and displacements of, the structural elements.

A15.10.3 Normal modal analysis

In some cases it is permissible to simplify the solution of an MDF model by a method known as normal modal, or simply modal, analysis. In this technique the vibrations in mutually perpendicular directions are treated as uncoupled and the responses are obtained for the separate modes and are then combined by superposition to give the overall responses. The method is applicable only to linear systems.

A15.10.4 Response spectra

Another approach is the response spectrum method. As described above, a response spectrum represents for a series of SDF systems with a given degree of damping the peak acceleration, velocity or displacement obtained when forced by the acceleration–time profile, or accelerogram, of the design earthquake. The family of curves for different degrees of damping constitutes the response spectra. The response spectra most commonly given are those for acceleration.

The determination of the response spectra from the forcing function *F(t)* of the design earthquake is described by Dowrick. The displacement *x(t)* is given by

$$x(t) = \int_0^t \frac{F(\tau)}{m\omega}\exp[-\zeta\omega(t-\tau)]\sin[\omega(t-\tau)]\,d\tau \qquad \text{[A15.10.7]}$$

Then, taking $\omega \approx \omega_n$, a response function is defined as

$$V(t) = \omega_n x(t) \qquad \text{[A15.10.8]}$$

where $V(t)$ is the response function (m/s).

It is the maximum values of the responses that are of interest. The maximum value of the response function is termed the spectral velocity, or strictly the pseudo-spectral velocity:

$$S_v = V_{max} \quad [A15.10.9]$$

where S_v is the spectral velocity (m/s) and V_{max} the maximum value of the response function (m/s). Further

$$S_d = S_v/\omega_n \quad [A15.10.10]$$

$$S_a = \omega_n S_v \quad [A15.10.11]$$

where S_a is the spectral acceleration (m/s^2) and S_d the spectral displacement (m).

The application of the response spectra is as follows. The natural frequency and damping of the structure is determined. The response spectra are then used to obtain the peak acceleration. This peak acceleration is then applied to find the forces on, and displacements of, the structural elements.

The basic response spectra technique is described by Dowrick as essentially a special case of modal analysis, in that the method treats the system as a linear one and uses the principle of superposition. He also describes, however, adaptations of the method to non-linear analysis.

A15.10.5 Frequency domain solution

Alternatively, the analysis may be performed in the frequency domain. The method is described by Dowrick. The acceleration–time profile is converted by Fourier transform methods into an acceleration–frequency profile. This is then used to excite the model of the system. The response in the frequency domain is then converted back using the inverse transform to give the response–time profile.

R. Davies (1982) describes the use of a version of this approach. The acceleration–time profile of the design earthquake, the accelerogram, is converted by Fourier analysis into an acceleration–frequency profile. The analysis then proceeds in two stages. In the first stage, using a series of frequencies from the acceleration–frequency profile, the unsteady-state model is excited at each frequency by a sinusoidal force of that frequency and with an acceleration amplitude set at an arbitrary value. The outputs are the forces on, and displacements of, the structural elements as a function of frequency. In the second stage these outputs are converted back to time profiles of forces and displacements.

A15.10.6 Selection of method

The selection of a method of dynamic analysis is discussed by Dowrick (1977). The structures to be analysed range from small, simple structures to large, complex ones. Broadly, more complex structures demand more sophisticated methods. He gives in ascending order of complexity the methods of static analysis, response spectra, modal analysis and non-linear modelling.

A15.11 Seismicity Assessment and Earthquake Prediction

The assessment of the seismic hazard to which an installation may be exposed is normally based on information about the seismicity of the area in question. In principle, this may be complemented by information from the monitoring of ground motions and prediction of any impending earthquake. However, such prediction is not sufficiently precise to be of much use for this purpose.

A15.11.1 Seismic data and maps

There are available a number of compilations of seismic maps and other information on seismicity. They include *Seismicity of the Earth and Associated Phenomena* by Gutenberg and Richter (1954); for Europe *Seismicity of the European Area* by Karnik (1968, 1971) and for Britain *A History of British Earthquakes* by Davison (1924) and *Seismicity and Seismic Hazard in Britain* by Lilwall (1976).

A15.11.2 Seismicity assessment

Seismic design or assessment normally takes as its starting point information on the relationship between the magnitude and frequency of earthquakes at the location of interest. In default of more specific information, use is generally made of the historical record.

The normal method is to use a relation such as the Gutenberg–Richter equation, Equation A15.2.10, from which the frequency of earthquakes of various magnitudes may be determined. Several return periods and magnitudes are selected for study.

For an earthquake of a particular magnitude and frequency the probability of occurrence may be estimated making some assumption about the probability distribution. A common assumption is that the incidence is random.

Then, using a relation such as that of Donovan or Esteva, Equations A15.6.1 or A15.6.2, respectively, the PGA can be obtained.

The approach taken is therefore statistical rather than geological. The potential benefits of a more geological approach are discussed by V. W. Lee and Trifunac (1987). They argue that estimates for the occurrence rates of earthquakes are over a time interval of some 10^3–10^6 years for those based on geological structure, or 'geological seismicity', while those based on 'historical seismicity' are for intervals of the order of 10^2–10^3 years.

The assessment of seismicity in Britain described below serves to illustrate the approach generally taken.

A15.11.3 Probability distributions

The frequency of earthquakes of different magnitudes is commonly obtained from the Gutenberg–Richter equation, as just described.

Use may also be made of the extreme value distribution of Gumbel (1958).

The occurrence of an earthquake of given size is commonly treated as a randomly occurring event for which the probability distribution is the Poisson distribution:

$$P = 1 - \exp(-\lambda) \quad [A15.11.1]$$

where for an earthquake of a specified size, P is the annual probability of exceedance and λ the expected annual number of earthquakes.

The possibility of complementing this by utilizing information obtained from monitoring seismological indicators points to the possible use of the Bayesian approach.

A discussion of appropriate distributions is given by Newmark and Rosenblueth (1971).

A15.11.4 Seismicity in Britain

A study of the seismicity of Britain which is frequently quoted is that of Lilwall (1976). Figure A15.5 is one of his plots showing intensities of earthquakes with a return period of 200 years.

Lilwall divides the country into the following zones: Great Glen, Comrie and Memstrie, South Wales and Herefordshire and the remainder. The first two are areas of a seismicity relatively high for Britain. The third may be regarded as typical of a relatively active area of the country.

For the frequency of earthquakes Lilwall recasts Equation A15.2.10 as

$$\log_{10} N = a' - b' m_b \qquad [A15.11.2]$$

where a' and b' are constants. He obtains the following values for a' and b':

Area	a'	b'	*Surface area* (km^2)
Overall	4.13	1.09	2.3×10^5
South Wales and Herefordshire	1.1	0.55	15,000
Remainder	4.0	1.15	2.3×10^5

The return periods for earthquakes of different magnitudes are then as follows:

Magnitude m_b	*Return period* (year)
4.0	1.5
4.5	6.0
5.0	20.0
5.5	70.0
6.0	260.0

The last two values are extrapolations beyond the observed range.

From analysis of the data, Lilwall proposes for Britain an upper limit of 5.72 for the body wave magnitude and gives the relation

$$P = 1 - \exp\left[-\frac{1}{5}\left(\frac{5.72 - m_b}{5.72 - 4.43}\right)^{2.22}\right] \qquad [A15.11.3]$$

where P is the annual probability of exceedance.

For the relation between M_S and m_b, he uses the equation of P.D. Marshall (1970):

$$M_S = 2.08 m_b - 5.65 \qquad [A15.11.4]$$

For the intensity in Britain he derives, following Esteva and Rosenblueth (1964), the relation

$$I = 6.0 + 1.5 M_s - 1.9 \ln R \qquad [A15.11.5]$$

or, using Equation [A15.11.4]

$$I = -2.5 + 3.1 m_b - 1.9 \ln R \qquad [A15.11.6]$$

He uses for the estimation of R Equation A15.2.2 with $k = 20$.

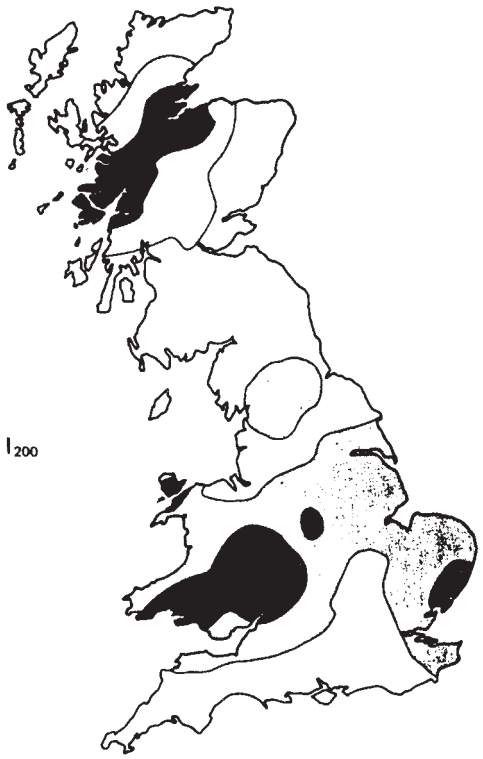

Figure A15.5 *Seismicity map of Great Britain showing intensities of earthquakes with a return period of 200 years (Lilwall, 1976). Despite of shading give intensities of up to 5, 5–6, 6–7 and over 7 (courtesy of HM Stationery Office)*

A15.11.5 Earthquake prediction

There are a number of methods for the prediction of earthquakes. Such methods are applicable mainly to active regions. Accounts are given by Berlin (1980), Eiby (1980) and Bolt (1988).

One important concept is that of the seismic gap. Essentially, a seismic gap is an area that has not had an earthquake for some time and in which strain is accumulating. The argument is that due to this strain accumulation the probability of an earthquake increases with time.

The seismic gap concept has been applied to large earthquakes. Areas at the boundary of tectonic plates that have not had an earthquake for a long period are regarded as more likely to experience one than those that have had a recent event. The seismic gap approach has also been applied to lesser earthquakes.

It has been found that in some cases large, shallow-focus earthquakes tend to migrate along a fault zone.

There are a number of phenomena that are regarded as precursors of earthquakes. They range from fore-shocks, seismic wave anomalies and fault creep to behaviour of animals.

There are also available several earthquake precursor models. Three principal models are (1) the dilatancy model; (2) the fault creep model; and (3) the propagating deformation front model.

Attempts to predict earthquakes have met with mixed success. There is in China an established earthquake prediction programme. One much quoted case is that of the earthquake in Liaoning Province on 4 February 1975, which had a magnitude of 7.4. Officials decided that the evidence justified the issue of a warning that a strong earthquake was probable within 24 h, people left their houses and the earthquake in fact struck that evening. On the other hand no warning was issued for the earthquake at Tangshan in 1976, which had a magnitude of 8.0.

In an account of the prediction of earthquakes in California, Bolt (1988) stated that there was one definitive prediction. This was that a moderate earthquake was likely to occur near Parkfield, California, between 1987 and 1993. This was based on a simple linear prediction of the trend of earthquakes, which have occurred in 1901, 1922, 1934 and 1966.

A15.12 Design Basis Earthquake

In earthquake-resistant design, an installation is designed to withstand seismic events so that the frequencies at which various degrees of damage are incurred do not exceed the specified values. The choice of the design basis earthquake is governed by these frequency specifications.

The characterization of the ground motion of an earthquake has been described in Section A15.6. Essentially, there are three main approaches. These are characterization in terms of peak acceleration; of the response spectra or of the acceleration–time profile. These three methods of characterization accord with the three main methods of analysis described in Section A15.10: static analysis, response spectra and dynamic analysis.

A15.12.1 Seismic hazard curve

There are available empirical correlations between the frequency of exceedance and the magnitude of earthquakes and between their peak acceleration and magnitude, as described in Section A15.2. From these it is possible to obtain the relationship between the frequency of exceedance and peak acceleration. A plot of these two quantities is often referred to as a seismic hazard curve. A seismic hazard curve may be constructed for a region or for a particular site.

Figure A15.6 shows seismic hazard curves for the United Kingdom given by Alderson (1982 SRD R246). Curve A is based on the Gutenberg–Richter equation, Equation A15.2.10, and curve B by a method given by Hsieh, Okrent and Apostolakis (1975).

A15.12.2 Response spectra

As described in Section A15.6, there are available a number of response spectra both for real earthquakes and for simulated earthquakes.

One or more of these response spectra may be selected to define the design basis earthquake. With this method also the choice is governed by the earthquake severity, and hence the return period, for which the installation is to be designed.

Two earthquakes that figure prominently in the literature are those at El Centre in 1940 and Parkfield in 1966. A number of response spectra for the El Centre earthquake and a comparison with that at Parkfield are given by Dowrick (1977). Further accounts of the Parkfield response spectra are given by D.W. Phillips (1982) and V.W. Lee and Trifunac (1987).

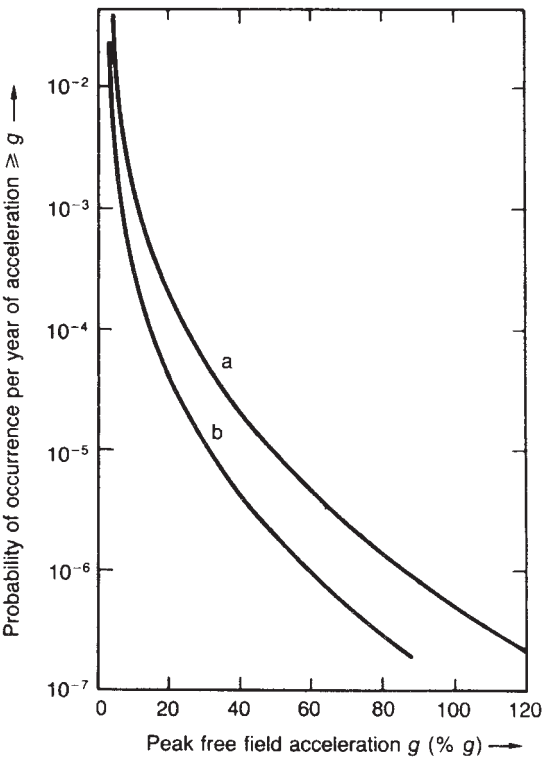

Figure A15.6 *Seismic hazard curves for the United Kingdom (Alderson, 1982 SRD R 246): (a) curve based on Gutenberg–Richter equation and (b) curve based on method of Hsieh, Okrent and Apostolakis (1975) (courtesy of the UKAEA Systems Reliability Directorate)*

The seismic design response spectra given in *Regulatory Guide 1.60* of the NRC have already been mentioned and are given in Figure A15.4. They are discussed further below.

Another set of response spectra are those developed in New Zealand, as described by Dowrick (1977).

A15.12.3 Accelerograms

For accelerograms the approach is broadly similar to that for response spectra just described. One or more accelerograms may be selected with the choice governed by earthquake severity and return period.

For accelerograms also, the 1940 El Centre and 1966 Parkfield earthquakes figure prominently in the literature.

Newmark and Rosenblueth (1971) give a set of accelerograms which illustrate the distinctions which they make between different types of ground motion.

A15.13 Nuclear Installations

The seismic hazard is of particular importance for nuclear power plants and a large amount of work has been done both on seismic design and on seismic hazard assessment.

The NRC has set earthquake-resistant design criteria and has undertaken a large amount of work on seismic engineering of nuclear plants.

A15.13.1 NRC seismic design response spectra

For the purpose of nuclear plant siting, the NRC considers a fault to be active if there has been movement at least once in 35,000 years. For such a fault, it is to be assumed that the largest earthquake supported by the fault system will occur within the next 50 years.

In 1973 the NRC issued *Regulatory Guide 1.60* (*RG 1.60*) containing its seismic design response spectra, which have already been mentioned and are shown in Figure A15.4.

Background to *RG 1.60* is given by V.W. Lee and Trifunac (1987). The *RG 1.60* response spectra were developed from accelerograms of some 33 earthquakes and model the shapes of spectra that can be expected at intermediate distances from medium to large earthquakes. They state that experience of the *RG 1.60* response spectra since that date shows that they are useful for straightforward cases, but meet with difficulties for responses in the near and far fields.

These authors also describe the scaling of the *RG 1.60* response spectra for other distances, particularly for locations in the near field. The method generally used is based on scaling by the PGA, although this presents some difficulties.

Lee and Trifunac discuss approaches to the improved characterization of near-source ground motion.

A15.13.2 Seismic Safety Margins Research Program

The NRC has for some years had a major programme of work on seismic safety margins. Accounts of this work include those of Cummings (1986) and R.P. Kennedy *et al.* (1989).

In simple terms the seismic safety margin is the earthquake level at which with high confidence failure is extremely unlikely. An earthquake of this level is described as a seismic margin earthquake (SME). The SME is generally characterized by the PGA.

The main body of work is that done under the Seismic Safety Margins Research Program (SSMRP). Among the reasons for the programme were uncertainty about the size of earthquakes to be expected; a lack of experimental data to guide plant design; the potential for common mode failure due to ground shaking and the possibility that 'strengthening' might increase risk.

The SSMRP methodology involves a five-step procedure: (1) characterization of the seismic hazard; (2) determination of the response of the structure and subsystems to seismic excitation; (3) determination of the fragility functions; (4) identification of accident scenarios; and (5) calculation of the frequency of failure and release.

The seismic hazard is characterized by seismic hazard curves, response spectra and acceleration time histories based on a combination of real earthquakes, estimates from magnitude correlations, expert judgement and other methods. The necessary computations are performed by the computer code HAZARD. The soil–structure interaction and the response of structure and subsystems to seismic excitation are treated simultaneously and are handled by the SMACS code. Seismic excitation includes forcing by an ensemble of acceleration time histories in three orthogonal directions. A third code SEISIM is used to handle the radioactive release aspects.

Much of the work in the SSMRP has been concerned with the seismic fragility of items of equipment. The fragility is a function of the seismic load and is expressed as the cumulative probability of failure with load.

A15.13.3 Seismic margin estimation

A review of methods for the calculation of the seismic margin of items of equipment is given by R.P. Kennedy *et al.* (1989).

The seismic margin review of a nuclear power plant requires the determination for certain components of the High Confidence of Low Probability of Failure (HCLPF) capacity. The study describes two candidate methods for doing this, the Conservative Deterministic Failure Margin (CDFM) method and the Fragility Analysis (FA) method.

The CDFM method involves a design calculation which is essentially conventional in method but which utilizes more conservative assumptions.

In the FA method, the fragility of the equipment is modelled as a double log–normal distribution with three parameters: A_m the median ground acceleration and β_R and β_U, the logarithmic standard deviations representing, respectively, the randomness and the uncertainty in the median value. The two latter parameters may be subsumed in the combined parameter $\beta_c (= (\beta_R^2 + \beta_U^2)^{1/2})$. The report describes the estimates made by four experts of the HCLPF by the CDFM and FA methods for a representative set of items, including a storage tank, a heat exchanger and an air tank. The bulk of the report consists of detailed calculations. The results are expressed as values of the PGA.

A15.14 Process Installations

There is rather less work published on the seismic design and seismic assessment of process plants, but there are some accounts available. Moreover, the methodologies developed in the nuclear industry are in large part applicable to the process industries.

The guide TID-7024 *Nuclear Reactors and Earthquakes* (NTIS, 1963) is quoted in the NPFA codes such as NFPA 59A: 1985 *Production, Storage and Handling of Liquefied Natural Gas* (*LNG*) for guidance on seismic loading.

A review of seismic design and assessment for process plants with special reference to major hazards is given in *Seismic Design Criteria and Their Applicability to Major Hazard Plant within the United Kingdom* by Alderson (1982 SRD R 246). Further accounts of seismic assessment of process plants include those of Ravindra (1992), and, for the United Kingdom, of R. Davies (1982), Alderson (1985) and Kunar (1983).

Methods for seismic design are given by the NRC (1979c). There is also a good deal available for particular items. For example, for liquid storage tanks accounts have been published by Veletsos and co-workers (Veletsos and Yang, 1976; Veletsos, 1984; Veletsos and Yu Tang, 1986a,b), Haroun and Housner (1981), R.P. Kennedy (1979, 1989) and Priestly *et al.* (1986). Guidance on analysis of individual failure modes is given in standard texts on structures such as Timoshenko (1936), Warburton (1976), Pilkey and Chang (1978) and, for wind loads, Sachs (1978).

A15.14.1 Seismic assessment of generic plants

R. Davies (1982) has reviewed the seismic hazard for process plants in the United Kingdom. He identifies liquefied gas storage as a matter of principal concern and describes a study to assess the risk from such storage.

The study was in three parts: the assessment of seismicity in the United Kingdom; the selection of representative containment and the identification of principal failure modes and the modelling of the seismic response of these containments.

Three levels of earthquake were defined, Levels 1–3. A Level 1 earthquake was taken as one with a return period of 150 years which would have a 0.25 probability of occurring over a plant life of 40 years. The work of Lilwall suggests that this return period corresponds to an earthquake of body wave magnitude about 4.5, which would typically yield at 15–20 km a site intensity of around VI on the MM scale. The Level 2 earthquake was taken as one with a return period of 2000 years, magnitude of 5.25 and site intensity of VII. For the Level 3 earthquake a frequency of 10^{-4} events/year, or a return period of 10^{-4} years, was taken, following NFPA guidance in NFPA 59A: 1980 on the design earthquake for LNG storage.

Earthquakes corresponding to each of these three levels were identified and the accelerograms of these earthquakes were obtained. The records used were those for the earthquake at New Madrid, Missouri, on 13 June 1975 (body wave magnitude 4.3), those for that at Forgaria-Cornino, Italy, on 11 May 1976 (magnitude 5.2) and the Temblor records of the earthquake at Parkfield on 27 June 1966 (magnitude 5.6).

The method of dynamic analysis used by Davies was described earlier.

Three generic types of liquefied gas storage were considered: a double skin cryogenic tank with a suspended roof, an inner shell of 9% nickel steel and an outer shell of mild steel to hold 20,000 te of LNG; a 1250 te capacity spherical pressure storage vessel to hold 1250 te of propane and a cylindrical pressure storage vessel, or torpedo, to hold 250 te of liquid carbon dioxide. For all three containments a foundation of hard rock was considered and the low temperature tank was also considered with a piled foundation on soft soil.

The failure modes considered were as follows. For the storage tank they were (1a) rupture of the connection between the tank wall and the floor; (1b) ripping of the tie-down strap; and (1c) excessive displacement of the base of the shell and rupture of the connection pipes. For the sphere they were (2a) tear at the connection of the shell and supporting leg; (2b) buckling of the support columns; and (2c) excessive displacement at the connecting pipe takeoff and rupture of the pipe. For the torpedo they were (3a) tear at the connection of the shell and support; (3b) rupture of straps or supports; and (3c) sliding on or rolling off support and rupture of the connecting pipes.

For the Level 1 earthquake the ratio of the seismic response stress to the seismic capacity stress was very small in each of these failure modes; the highest value of the ratio was 0.03 for the cryogenic tank tie-down strap on hard rock (mode 1b). For the Level 2 earthquake the ratio was 1.4 for the cryogenic tank tie-down strap on hard rock (1b), 0.48 for the inner shell base of the tank on hard rock (la) and 0.21 for the inner shell base on piles (1a again). For the Level 3 earthquake these three latter values were 1.9, 0.72 and 0.29, respectively. Data on displacements are also given.

The conclusion of the study is that for liquefied gas storages of the type considered an earthquake which occurs sufficiently frequently to be likely to be felt during the life of the plant poses a negligible risk of loss of containment, but that one which approaches the maximum likely to occur in the United Kingdom could produce appreciable horizontal displacements in all types of plant and stresses in certain critical parts of some containments which exceed the dynamic design stresses allowed in current design codes.

A15.14.2 Seismic assessment of particular plants

An account of the seismic assessment of an existing process plant as part of the controls on acutely hazardous material (AHM) under the California Risk Management and Prevention Program (RMPP) under has been given by Ravindra (1992). The review covered both the site-specific geology and the engineering facilities.

He describes the investigation of the seismic characteristics of the site, including the impact of active faults; the potential for surface faulting and ground breakage, soil settlement and liquefaction, and slope instability; and local soil amplification. A seismic hazard curve was established.

The seismic capacity of the facilities was assessed by review of the design drawings and design codes used and by a walkaround of the plant.

It was found that some components had been designed using the static design method with an acceleration of 0.2 g; this acceleration is similar to that in the UBC. Detailed evaluation established that some of these items were vulnerable even though they had been designed to a building code.

The author gives examples of the seismic capacity assessed by a deterministic method given in RMPP guidelines and by the FA method and quotes values of the median ground acceleration A_m and the logarithmic standard deviation of the uncertainty in this acceleration. The failure mode determining seismic capacity in most cases is failure of the anchor bolts or anchorage. The author comments that generally this can be upgraded at minimal cost.

A15.14.3 Spherical pressure vessel

An assessment of the seismic capacity of a spherical pressure storage vessel has been described by D.W. Phillips (1982).

The vessel considered is a 15 m diameter vessel supported on 12 columns, or legs. The nominal contents of the vessel are 1200 te, the mass of the shell is 166 te and that of the legs 15.6 te. The active length of the supporting columns is 7.94 m. Each column has a flat steel plate welded to the bottom. The plate is attached by four foundation bolts to the concrete pedestal. The spacing between the bolts is 0.58 m and the inset of the bolts is 0.08 m. The bolts are 0.032 m in diameter. The effective dynamic mass of the vessel itself, with a contribution from the legs, is taken as 171 te ($166 + \frac{1}{3} \times 15.6$), giving a total effective dynamic mass of 1371 te for the full vessel.

From a separate study, it is known that the natural period of the vessel for horizontal vibration is as follows:

State	*Mass of vessel and shell* (te)	*Natural period* (s)
Full	1371	0.75
$\frac{1}{2}$ full	711	0.58
$\frac{1}{4}$ full	471	0.25

The vessel is located on a typical UK site. For such a site the seismic characteristics in terms of the free field horizontal acceleration are taken as

Return period (year)	*Horizontal acceleration* (g)
100	0.05
1000	0.12
10,000	0.25

The method of calculation used is essentially a static analysis, but first a dynamic analysis is conducted to determine a dynamic, or resonance, correction factor. For this use is made of the data given above on the natural period and the horizontal acceleration together with suitable response spectra. Two sets of response spectra are used, the NRC *RG 1.60* spectra and the Temblor–Parkfield spectra. A damping of 5% is taken as typical of welded steel at high strain and of bolted steel. For each degree of fill, the response spectra are used to obtain the acceleration from the natural frequency and damping. This value is scaled by the ratio of the maximum acceleration of the site to the maximum acceleration implied in the response spectra.

The results for the horizontal response with intact bracing are

Return period (year)	*Horizontal response* (g)					
	NRC response spectra			*Temblor–Parkfield reponse spectra*		
	Sphere full	$\frac{1}{2}$ *full*	$\frac{1}{4}$ *full*	*Sphere full*	$\frac{1}{2}$ *full*	$\frac{1}{4}$ *full*
100	0.07	0.11	0.14	0.11	0.16	0.21
1000	0.17	0.25	0.33	0.26	0.37	0.50
10,000	0.36	0.53	0.70	0.54	0.79	1.03

The accelerations are rather greater for the Temblor–Parkfield than for the NRC response spectra. The greatest acceleration is experienced by the $\frac{1}{4}$ full tank, but for this case the mass is much less. The dynamic correction factor chosen is 2, which corresponds approximately to the ratio of the PGAs for the site to those for the case of the full tank with the Temblor–Parkfield spectra.

The sphere did not appear to have been designed for earthquake resistance. Probably, the principal horizontal force considered was wind loading. The relation for the wind load is

$$W_w = C_D \rho_a \pi r_s^2 u_w^2 \qquad \text{[A15.14.1]}$$

where C_D is the drag coefficient, r_s the radius of the sphere (m), u_w the wind speed (m/s), W_w the wind load (N) and ρ_a the density of the air (kg/m^3). At the estimated Reynolds number of 10^7 the drag coefficient is 0.5. The wind speed with a 50 year return period would be between 18 and 32 m/s. Taking the higher value for the wind speed and $r_s = 7.6$ m and $\rho_a = 1.25$ kg/m^3

$$W_w \approx 1.1 \times 10^5$$

The seismic loading is assumed to consist of accelerations in three orthogonal directions, two horizontal and one vertical. The vertical excitation is taken as $\frac{2}{3}$ of the horizontal. The overall structural response is assumed to be given by

$$W_O = \left[\sum_{i=1}^{3} W_i^2\right] \qquad \text{[A15.14.2]}$$

where W_i is the load in the ith direction (N) and W_O the overall load (N).

Then for the 100 year return period with horizontal acceleration of 0.05 g and incorporating the two orthogonal accelerations and the dynamic correction factor of 2, the peak horizontal seismic load of the full tank is

$$W_s = 2^{1/2}(1371 \times 10^3) \times 2 \times 0.05 \times 9.81$$
$$\approx 1.9 \times 10^6 \text{N}$$

Thus, the seismic load is nearly 20 times the wind load.

Phillips gives detailed calculations for the various modes of failure and for the corresponding seismic capacities. These show that the seismic response for which the structure is weakest is the overturning couple on the column supports. The corresponding failure mode is tensile failure of the pedestal bolts. For this failure mode the safety factor has the values of 0.5, 0.2 and 0.1 for the 100, 1000 and 10,000 year return periods, respectively.

The calculation of this failure mode may be summarized as follows. Figure A15.7 shows the overturning couple for which the relation is

$$F_{sb} = \frac{1}{n} F_s \frac{l_1}{l_2} \qquad \text{[A15.14.3]}$$

where F_s is the seismic load (N), F_{sb} the seismic tensile force on the bolts (N), l_1 and l_2 are the distances shown in Figure A15.7 (m) and n is the number of bolts resisting overturning. Taking $l_1 = 7.94$ m and $l_2 = 0.66$ m and using the seismic load for the 100 year return period

$$F_{sb} = \frac{1}{24}(1.9 \times 10^6) \times \frac{7.94}{0.66}$$
$$= 9.5 \times 10^5 \text{ N}$$

Taking a bolt area of 8.0×10^{-4} m^2 per bolt gives a bolt tensile stress of

$$F_{sb} = \frac{9.5 \times 10^5}{8.0 \times 10^{-4}}$$
$$= 1.2 \times 10^9 \text{ Pa}$$

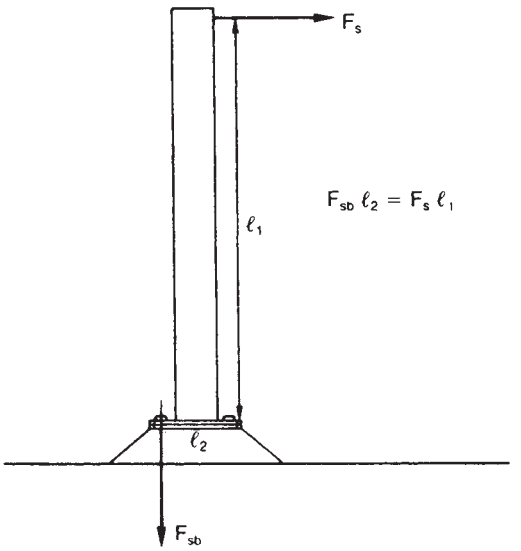

Figure A15.7 *Overturning couple on the support column of a pressure storage sphere (Phillips, 1982) (courtesy of the ukaea Systems Reliability Directorate)*

where F_{sb} is the seismic tensile stress on each bolt (Pa). For the purpose of this assessment, tensile failure is assumed to occur at the yield stress, which for high tensile steel is some $0.6-0.7 \times 10^9$ Pa. Taking the lower value of the yield stress, gives for the safety factor at the 100 year return period a value of $0.5\ (=0.6 \times 10^9/1.2 \times 10^9)$.

For none of the other failure modes considered was the safety factor less than unity at the 100 year return period, though for two others it fell to unity at the 1000 year return period and below it at the 10,000 return period.

A15.14.4 Storage tank

An assessment of the seismic capacity of a flat-bottomed storage tank has been described by R.P. Kennedy (1989). The tank considered is 40 ft in diameter with a shell 37 ft high and an overall height to the tank top of 43.4 ft.

The author describes in detail the use of the CDFM method. This consists of two parts, the determination of the seismic responses and the determination of the seismic capacities. There is not necessarily a one-to-one correspondence between a seismic response and seismic capacity. For a given response there may be several features resisting failure and all these must be considered.

The following responses are considered: (1) overturning moment in the tank shell immediately above the base plate of the tank; (2) overturning moment applied to the tank foundation through a combination of the tank shell and base plate; (3) base shear beneath the tank base plate; (4) combination of the hydrostatic plus hydrodynamic pressures on the tank side wall; (5) average hydrostatic minus hydrodynamic pressure on the base plate of the tank; and (6) fluid slosh height. These responses are all expressed as forces except the last; for this what matters is whether the sloshing fluid hits the roof.

The author comments that the first of these responses is usually the governing one. The third is seldom governing for tanks with a radius greater than 5 m. The second, fourth and sixth seldom govern.

In investigating these responses at least two horizontal modes, the impulse and the convective, or sloshing, modes and one vertical mode should be considered.

Kennedy gives detailed calculations for the various seismic responses and for the corresponding seismic capacities. The governing response is usually the first, the overturning moment in the tank shell.

The seismic responses are determined using a value of 0.27 g for the peak ground acceleration. The overturning moment response is then estimated as 19,600 kip-ft. The corresponding capacity is determined by considering (1) the compressive buckling capacity of the shell; (2) the tensile hold-down capacity of the anchor bolts, including their anchorage and attachment to the tank; and (3) the hold-down capacity of the fluid pressure acting on the tank base plate. The combined resistance of these gives an overturning moment capacity of 20,800 kip-ft. The SME for this response is then calculated as 0.29 g (0.27 x (20,800/19,600)).

This response gives the lowest value of the SME and the overall SME for the tank is thus determined as 0.29 g.

Kennedy also describes the determination of the seismic capacity in terms of the alternative FA method. Using this method the SME is found to be 0.31 g.

A15.15 Notation

a	peak ground acceleration (fraction of g); (cm/s^2) (Sections A15.2 and A15.6 only); (m/s^2) (Sections A15.8 and A15.10 only)
a, a'	constants in Equations A15.2.10 and A15.11.2, respectively
A	maximum amplitude of earthquake (mm)
A_m	median ground acceleration (fraction of g)
A_O	maximum amplitude of standard earthquake (mm)
b, b'	constants in Equations A15.2.10 and A15.11.2, respectively
c	damping coefficient (kg/s)
C	coefficient (Equation A15.9.1)
C	flexibility factor
C_D	drag coefficient
d	peak ground displacement (cm)
E	energy of earthquake (erg)
F	force (N)
F_s	seismic force (N)
F_{sb}	seismic tensile force on bolts (N)
F_{sb}	seismic tensile stress on bolts (Pa)
g	acceleration due to gravity (m/s^2)
h	focal depth (km)
H	depth of soil layer (m)
I	intensity of earthquake (Equation A15.11.5)
I	occupancy importance factor (Equation A15.9.2)
I_O	epicentral intensity of earthquake
k	modifying factor for focal distance (km) (Equation A15.2.2)
k	resistance (kg/s^2) (Equations A15.10.2–5)
K	framing factor
l_1	active distance of support column (m)
l_2	spacing + inset of bolts on support column base plate (m)
m	mass (kg)
m_b	body wave magnitude of earthquake
M	magnitude of earthquake

M_L local magnitude of earthquake
M_S surface wave magnitude of earthquake
n number of bolts resisting overturning
N frequency of earthquake (year^{-1})
P annual probability of exceedance
r epicentral distance (km)
R focal distance (km)
S site factor
S_a spectral acceleration (m/s^2)
S_d spectral displacement (m)
S_v spectral velocity (m/s)
t time (s)
T natural period (s)
T natural period of soil layer (s) (Equation A15.7.1)
u_w wind speed (m/s)
v_s velocity of shear wave (m/s)
V horizontal force, base shear (N)
V response function (m/s) (Section A15.10 only)
W load (N)
W_i load in ith direction (N)
W_O overall load (N)
W_s seismic load (N)
W_w wind load (N)
x displacement (m)
Z seismic risk zone factor
β composite variability (fraction of g)
β_R log-normal standard deviation of randomness of median ground acceleration (fraction of g)
β_U log-normal standard deviation of uncertainty in median ground acceleration (fraction of g)
ζ damping factor
λ average annual number of events
ρ_a density of air (kg/m^3)
ω damped frequency (s^{-1})
ω_n natural frequency (s^{-1})

Subscripts
D damping
I inertia
max maximum value
S elastic

Appendix 16

San Carlos de la Rapita

Contents

A16.1 The Camp Site A16/2
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At about 14.30 in the afternoon of 11 July 1978 fire and explosions from a road tanker carrying propylene occurred at a camp site at Los Afaques (The Sand Dunes) at San Carlos de la Rapita between Barcelona and Valencia in Spain. The eventual death toll was 215.

A Court of Inquiry on the disaster was held at Tarragona (Court of Inquiry, Tarragona 1982). A report was submitted to the inquiry by Carrasco (1978). Independent investigations for the HSE were been carried out by Scilly (1978) and Hymes (1983 SRD R275), for the Hampshire Fire Brigade by Stinton (1978, 1979, 1983) and for the Dutch Directorate General of Labour by Ens (1986 LPB 68). Analyses of the accident are given by V.C. Marshall (1985, 1986 LPB 72, 1987).

Selected references on San Carlos are given in Table A16.1.

A16.1 The Camp Site

The camp site was a triangular shaped piece of land between the coast road and the sea some 3 km from the nearest township San Carlos de la Rapita to the north. It was 200 m in length and 10,000 m^2 in area, tapering from about 100 m wide at the north to 30 m at the south end, and 60 m wide at the point of the accident. There was a brick wall on a concrete foundation between the road and the camp.

On the day of the accident, the camp site was fully booked with some 800 people, but not all these were there at the time and in the area affected. Estimates of the number on site and of the number in the area most affected are 500 and 300–400, respectively.

A16.2 The Road Tanker

The road tanker was manufactured in 1973. It had no pressure relief valve and no pressure test certificate. It had nominal and actual capacities of 45 and 44.4 m^3.

It has been alleged that the tanker had been used on previous occasions to carry ammonia, which can lead to cracking of the tank, but this has been denied.

At 12.05 the tanker took on a load of propylene at the ENPETROL Tarragona refinery. The system was that the driver would learn how much he was carrying when the vehicle was weighed at the weighbridge. There was no metering or other device to prevent overfilling. If he wished to reduce the load, he could burn some off using a device like a flamethrower. The maximum load for the vehicle was 19 te, but it was plated as suitable for a maximum load of 22 te and it was actually weighed out as a 23.5 te load. At 12.35 the vehicle left the refinery.

The driver had a recommended route, which was the motorway, and was provided with the toll money, but actually took the N340 coast road, which went past the Los Alfaques camp.

Table A16.1 *Selected references on San Carlos*

Carrasco (1978); Stinton (1978, 1979a,b, 1983); UKAEA (1979); J. Harris (1979); Court of Inquiry, Tarragona (1982); Moodie (1982); Scilly (1982); Hymes (1983 SRD R275, 1986 LBP 61); Manas (1984); V.C. Marshall (1985, 1986 LPB 72, 1987); Ens (1986 LPB 68, 72); Foxcroft (1986 LPB 71); Bond (1987 LPB 73)

A16.3 The Fire and Explosions – 1

The sequence of events at the camp site is not entirely clear, but several eyewitness accounts are available. V.C. Marshall (1987) quotes the following. A young man serving a customer in the camp shop off the main site heard a bang. He got into his car to investigate and 2 min after the first sound heard a severe explosion. A 'fireball' appeared on the site. A tourist in the camp restaurant heard a 'pop' from a tanker on the main road and saw a milky cloud drifting towards him. He ran to move his car and seconds later the cloud ignited. In one newspaper account a motor cyclist following the vehicle said that smoke and fire were issuing from the tank. In another such account a tourist walking his dog at the camp site entrance saw the tanker start to snake and then tip over; there followed almost immediately an explosion and fire.

There were conflicting reports on the last movements of the road tanker, summarized by Hymes (1983 SRD R275). They include reports to the effect that the driver stopped at the camp with the tanker already leaking; that he stopped after it sprang a leak with a sharp report at the camp; that the vehicle veered across the road and broke through the camp site wall, suffering either a small leak or complete disintegration; and that the tanker veered across the road and struck the wall a glancing blow.

Hymes gives two photographs, the first captioned as showing the unignited gas cloud and the second the cloud on fire. The latter photograph is shown in Figure A16.1. The photographer stated that the time between taking his first picture and going to the camp entrance to take further shots was 1–2 min and that the tanker ruptured violently after a few minutes.

It is reported that until the main 'fireball' event, people stood around watching the pall of smoke from the fire. When it did occur large numbers, many scantily clad, were burned, some running into the sea to escape or douse the flames.

Figure A16.1 *The fire preceding the 'fireball' at San Carlos (Hymes, 1983 SRD R275) (Courtesy of the Safety and Reliability Directorate)*

The area of damage and injury, including injury outside the flame envelope, is quoted by Marshall as covering an area equivalent to that of a 125 m radius circle. Over 90% of the camp site was gutted by fire.

The explosion effects were variable. The discotheque about 75 m from the tanker was completely demolished, probably by an explosion of the gas inside it, killing four people, but in the opposite direction at a distance of only 20 m a motor cycle still stood on its footrest. Many other objects in the camp liable to be blown over by blast still stood.

The site after the event is shown in Figure A16.2.

The vehicle was torn into four main pieces. Some two-thirds of the tank, including the rear portion, flew to the north-west, landed on the ground some 150 m away and then slid and came to rest in the outer wall of a restaurant about 300 m from its starting point. The middle section travelled about 100 m to the north-east into the camp. The cab unit travelled some 60 m along the line of the road to the south. The front end cap fetched up about 100 m beyond the cab. The location of some of the fragments is shown in Figure A16.3. The front end cap is the white hemispherical object at the bottom of Figure A16.3.

A16.4 The Emergency and the Aftermath

For about half an hour after the fire there were some 200–300 people milling round the camp, many seriously burned and calling for help. Private cars and taxis began to ferry the injured to a hospital at Amposta 13 km away. The first ambulance came at 14.45 from the Shell oil drilling site at San Carlos. The municipal ambulances came at 15.05 and the fire brigade about 15.30.

The road was still blocked by the burning cab so that victims had to be rescued from both sides of the camp and taken north to Barcelona or south to Valencia as circumstances permitted. Those taken north to Barcelona received primary medical care at points en route, while those taken south to Valencia 165km away did not. In the first week the death rate at Valencia was twice that at Barcelona, but over 2 months the death rates evened up, since most victims were too badly burned to survive.

Over 100 people died outright. Others died later from burns, so that the final figures were 215 dead and 67 injured.

Most of those treated had very serious burns. Out of 148 cases 122 had third degree burns to 50% or more of the body. Either there were fewer people only slightly burned or they received treatment elsewhere.

A16.5 The Fire and Explosions – 2

The Court of Inquiry held that there had been a rupture of the road tanker due to hydraulic overfill. This was the explanation given in a report submitted to it by Carrasco (1978).

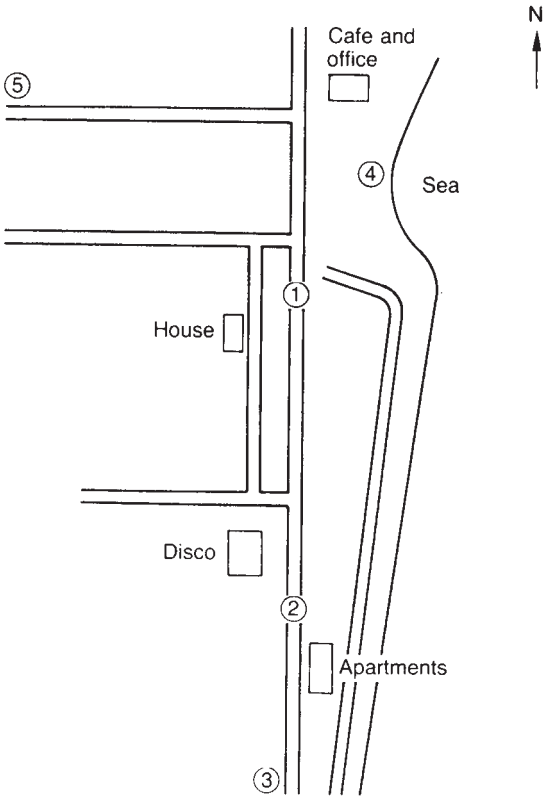
Other authors have put forward alternative explanations. There appear to be three principal hypotheses concerning the initial event: (1) hydraulic rupture of the tank, (2) a small leak on the tank and (3) a road accident.

A version of the second hypothesis has been described by Hymes (1983 SRD R275). This is that a leak occurred on the tanker, that a gas cloud formed and found a source of ignition and that the flames burned back to the tanker. There followed an engulfing fire which caused a BLEVE. The vessel was in a weakened condition and the time for the BLEVE to occur was shorter than usual. Hymes does not state how the tanker came to stop at the camp, but on this scenario it could have been to attend to the leak.

A somewhat similar account is given by Stinton (1983).

The starting point in the argument in favour of the third hypothesis, as developed by Ens (1986 LPB 68), is the need to explain how the tanker came to stop and how the tank itself failed. Relevant here is the evidence of the one eye-witness who saw smoke and flames coming from the tanker and of the other who saw it snaking. The hypothesis is as follows. The tanker was grossly overfilled and under stress

Figure A16.2 *The site after the fire and explosion (Hymes 1983 SfiD R275). The camp site is in the right background behind the breached wall (Courtesy of the Safety and Reliability Directorate)*



1 Apparent point of disintegration
2 Driver's cab
3 Front end of tank
4 Middle of tank
5 Rear end of tank

Figure A16.3 *Flight of some missiles generated by the explosion (after Stinton, 1983; V.C. Marshall, 1987)*

so that it was liable to burst if subjected to impact. It crashed due to a driver failure or tyre defect, causing it to break through the boundary wall into the camp site. The tank ruptured and released its contents. A gas cloud and liquid pool formed, the gas being at first too rich to burn rapidly. In due course, however, the heat vaporized the liquid pool and there was a fireball. Minor explosions may have occurred at the edges of the cloud and stronger explosions in the buildings.

With regard to the first hypothesis, that the tank suffered hydraulic rupture, attention has focused on the overfilling of the tanker and on the possible effects of this. The calculations on this aspect are very dependent on the assumptions made about the volume and temperature of the liquid when the tanker left the refinery.

Evidence was presented by Carrasco (1978) that the tank contents could have warmed up sufficiently in 2½ h for the tank to become hydraulically full. He estimates a warm-up rate of 5.6°C/h.

Carrasco's work has been criticized by Marshall and Ens. Marshall draws attention to the work of Moodie (1982) showing the need, in considering hydraulic rupture, to allow for the expansion of the tank metal, the expansion being equivalent to between 3 and 6°C, depending on the steel used. Both authors, however, consider that it is possible that the tank had become hydraulically full. Ens suggests that this becomes credible if allowance is made for a difference between nominal and actual tanker capacity, weighing errors and warming up of the liquid in the terminal pipework. Under such biaxial stress the material would no longer be ductile but would become brittle.

V.C. Marshall (1987) gives an extensive discussion of the possible warm-up of the tank, the hydraulic overfill and physical rupture, the behaviour of the fragments and the fire. Despite his critique of Carrrasco, he concludes that hydraulic rupture of the tank is the most likely cause of the incident.

He suggests that the initial bang heard was probably the tank rupture, that the later explosion was of gas which had entered a building and then exploded inside it and that the fire was a severe flash fire rather than a vapour cloud explosion or a BLEVE. The pattern of injuries, with a large proportion of dead to injured, is consistent with a flash fire.

Hymes, Ens and Marshall all give detailed accounts of the site and of the physical evidence such as the fragments, the explosion damage and the burned area.

A16.6 Lessons of San Carlos

Among the lessons of San Carlos are the importance of

(1) Equipment, procedures, supervision and training to prevent overfilling of vehicles carrying hazardous materials.
(2) Provision of pressure relief on vehicles carrying flammable materials.
(3) Routing of vehicles carrying hazardous materials away from populated areas and vulnerable targets.
(4) Prompt treatment of burn victims.

Appendix 17

ACDS Transport Hazards Report

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A17.1 The Investigation

The Advisory Committee on Major Hazards in its *Third Report* (Harvey, 1984) recommended that although its terms of reference were restricted to fixed installations, the major hazard potential from the transport of hazardous materials should also receive attention.

The HSC accordingly asked the relevant permanent committee, the Advisory Committee on Dangerous Substances (ACDS) to examine the matter. Its findings are presented in *Major Hazard Aspects of the Transport of Dangerous Substances* (ACDS, 1991) (the ACDS *Transport Hazards Report*).

Selected references on the ACDS *Transport Hazards Report* are given in Table A17.1. Its principal contents are shown in Table A17.2.

Table A17.1 *Selected references on the ACDS Transport Hazards Report*

ACSD (1991); Turner (1992 LPB 101); Anon. (1992 LPB 107, p. 29)

Table A17.2 *Principal contents of the ACDS Transport Hazards Report*

1. Introduction
2. Scope
3. Method of Study
4. Quantified Risk Assessment
5. Risk Criteria
6. QRA Results for Rail, Road and Ports
7. The Peterborough Incident
8. Risk Reduction and Mitigation
9. Emergency Planning and Response
10. Comparison of Rail and Road Transport
11. Overview
12. Recommendations
Appendices, including
Appendix 3 Summary of World-wide Major Hazard Transport Accidents
Appendix 4 Summary of Movements and Regulatory Arrangements
Appendix 5 Modes and Consequences of Failure of Road and Rail Tankers Carrying Liquefied Gases and Other Hazardous Liquids
Appendix 6 Criteria for Evaluating Individual and Societal Risks in Transport
Appendix 7 Port Risks
Appendix 8 Transport by Rail
Appendix 9 Transport by Road
Appendix 10 Transport of Explosives by Rail and Road
Appendix 11 Comparison of Risks for Transport by Rail and Road
Appendix 12 Tolerability of Risks of Rail and Road Transport and Risk Reduction and Mitigation
Appendix 13 Emergency Planning
Appendix 14 Management of Safety in Transport

Some of these entries are paraphrased.

A17.2 Substances and Activities

The study deals with four main transport activities: (1) rail transport, (2) road transport, (3) marine transport (ports only) and (4) explosives.

The substances investigated varied as between these different modes of transport. For road and rail four substances were studied: (1) motor spirit, (2) LPG, (3) chlorine and (4) ammonia. These substances are referred to in the report, and therefore here, as the non-explosive materials.

For ports the substances considered were (1) flammable liquids, (2) flammable liquefied gas, (3) toxic liquefied gas, (4) ammonia and (5) ammonium nitrate.

The transport of explosives by rail and by road was the subject of a separate study within the report.

Excluded from the study were air transport, pipelines and radioactive substances.

A17.3 Event Data

The report contains a wealth of data on the movement of hazardous materials by rail, road and sea, on the nature and composition of loads and cargos and on event frequencies and probabilities.

The event frequencies cover not only land transport accidents such as vehicle and wagon impacts and fires and marine accidents such as collisions, strikings, groundings and engine room fires but also data used in the various fault trees.

The probability data include release size distributions, ignition probabilities and so on.

A17.4 Hazard Models

The study makes use of hazard models for fire, explosion and toxic release.

The fire models are for (1) a torch fire, (2) a flash fire and (3) a pool fire and the explosion models are for (1) a vapour cloud explosion (VCE), (2) a BLEVE and (3) a condensed phase explosion. The models relevant to toxic release are those for gas dispersion.

The pool fire model is required for motor spirit, the other fire models and the VCE and BLEVE models for LPG or LFG.

The hazard models fall into two sets. The first set comprises HSE models, which are used for rail and road transport, the second set models incorporated in the SAFETI code, which are used for ports. In the following account the HSE models are described first, followed by those used in SAFETI, where applicable.

A17.4.1 Gas dispersion

The gas dispersion models used are DENZ and CRUNCH for instantaneous and continuous releases, respectively. The main direct application of these models is to toxic release.

Use is also made of the parameterizations by Considine and Grint (1985) of results for flammable gas clouds obtained from DENZ and CRUNCH.

The gas dispersion model used in SAFETI is the dense gas dispersion model of R.A. Cox and Carpenter (1980).

A17.4.2 Torch fire

The torch, or jet, fire model used is that of Considine and Grint (1985), modified to give length and width and representing the flame as a cone.

Atmospheric transmissivity is determined by the method of Simpson (1984 SRD R304).

A17.4.3 Flash fire

For a flash fire use is made of the model of Considine and Grint (1985). The formation of the gas cloud is modelled using the gas dispersion models described in Section A17.4.1 and its combustion by assuming that it burns within the contour of the lower flammability limit.

A17.4.4 Pool fire

For a pool fire use is made of the SPREAD model, a sister model of SPILL (Prince, 1981 SRD R210), which differs from the latter in treating simultaneously the spreading and burning of the pool. The regression rate used is that of Mitzner and Eyre (1982). The other features of the model are not described but are evidently conventional.

A17.4.5 Vapour cloud explosion

The treatment of a VCE involves the determination of the mass of fuel in the cloud and of the overpressure resulting from explosion of this fuel.

For the mass of fuel in the cloud, for an instantaneous release the method is to take this mass as twice the flash fraction. It is assumed that no explosion occurs if the mass is less than 10 te. For a continuous release the mass of fuel in the cloud is determined by the method of Considine and Grint (1985).

The overpressure from explosion of this mass of fuel is determined from the correlation of Kingery and Pannell (1964) between mass of explosive and peak overpressure for TNT. The implication is that a TNT equivalent model is used, but further details are not given.

The VCE model used in SAFETI is the TNO correlation model.

A17.4.6 BLEVE

The BLEVE model used is that of A.F. Roberts (1981/82).

A17.4.7 LPG fire model

The hazard models described are used in conjunction with the release scenarios for rail and road transport to produce an overall LPG fire model.

In this overall model the number of fatalities is obtained from the relation

$$N = D[aP_{\mathrm{od}} + bP_{\mathrm{id}}P_{\mathrm{f}}|_{\mathrm{id}} + cP_{\mathrm{id}}(1 - P_{\mathrm{f}}|_{\mathrm{id}}) + d] \qquad [A17.4.1]$$

where D is the population density (persons/m^2), N the number of fatalities, $P_{\mathrm{f}|\mathrm{id}}$ the probability of fatal injury given that the person is within the cloud, P_{id} the probability of being indoors, P_{od} the probability of being outdoors and $a-d$ are coefficients. The coefficients c and d are associated with VCEs.

The model is shown in Table A17.3 in the form of the coefficients $a-d$ to be used in Equation A17.4.1.

A17.4.8 LPG fire scenarios

The LPG fire models just described are applied in the report to yield the hazard ranges and areas for the set of scenarios relevant to rail and road transport. These are summarized in Table A17.4.

A17.4.9 Condensed phase explosion

The condensed phase explosion model applicable depends on the type of explosive. This aspect is discussed in Section A17.10. An HD1.1 explosive constitutes a mass explosion hazard, an HD1.2 explosive a projection, or fragmentation, hazard and an HD1.3 explosive a fire hazard.

For the estimation of the overpressure from an HD1.1 explosive use was again made of the correlation of Kingery and Pannell (1964).

For the fragments from an HD1.2 explosive data were supplied by the MoD from explosives trials, which allowed an estimate to be made of the density of fragments possessing a kinetic energy in excess of 80 J, taken as the lethal value. From these data two graphs were constructed, one for persons outdoors and one for those indoors. The data are classified as confidential but the report states that the average probability of fatal injury so obtained for persons in the open at 200 m is 0.02, while that for those indoors at the same distance is an order of magnitude less.

The model used for the fire on an HD1.3 explosive is a vertical flame. Further details are not given.

Table A17.3 *Coefficients for LPG hazard model fatal injury equation (Advisory Committee on Dangerous Substances, 1991) (Courtesy of HM Stationery Office)*

	a	*b*	*c*	*d*
2 kgs^{-1} torch flame	332	3.3	0	0
36 kgs^{-1} torch flame	5,353	53.4	0	0
20 te BLEVE	47,596	182	0	0
40 te BLEVE	87,013	290	0	0
2 kgs^{-1} flash fire F/2 weather	7,800	78	0	0
36 kgs^{-1} flash fire D/5 weather	7,800	78.8	0	0
36 kgs^{-1} flash fire F/2 weather	185,000	1,850	0	0
Flash fire/torch flame/BLEVE (20 te) D/5	48,416	214.8	0	0
Flash fire/torch flame/BLEVE (40 te) D/5	87,225	298	0	0
Flash fire/torch flame/BLEVE (20 te) F/2	213,587	1,951	0	0
Flash fire/torch flame/BLEVE (20 te) F/2	238,145	2,016	0	0
20 te flash fire D/5	64,808	211	0	0
20 te flash fire F/2	57,969	222	0	0
40 te flash fire D/5	97,644	340	0	0
40 te flash fire F/2	88,180	346	0	0
36 kgs^{-1} VCE	185,000	1,850	925	0
20 te VCE	22,167	222	111	25,874
40 te VCE	34,636	346	173	52,916

Table A17.4 *Hazard ranges and areas for rail and road transport scenarios obtained from the LPG hazard model (after Advisory Committee on Dangerous Substances, 1991)*

A Torch flames

Release rate (kg/s)	*Side-on*			*End on*		
	Length (m)	*Distance to 50% lethality*[a] (m)	*Distance to 1% lethality* (m)	*Diameter* (m)	*Distance to 50% lethality*[a] (m)	*Distance to 1% lethality* (m)
2	12.9	8.5	12.3	4.3	6.7	9.4
36	54.6	33	48	18.2	26.3	36.5

B Flash fires: instantaneous releases (rail tank wagons)

Vessel capacity (te)	*Distance to 50% lethality*		*Distance to 1% lethality*	
	D5 (m)	*F2* (m)	*D5* (m)	*F2*
20	70	50	90	75
40	80	70	110	95

C Flash fires: instantaneous releases (road tankers)

Vessel capacity[b] (te)	*Distance to 50% lethality* (m)	*Distance to 1% lethality* (m)
15	140	150

D Flash fires: continuous releases

Release rate (kg/s)	*Area of fire*	
	D5 (m^2)	*F2* (m^2)
2	310	7,800
36	7,800	185,000

E BLEVEs (rail tank wagons)

Vessel capacity	*Fireball radius* (m)	*Fireball duration* (s)	*Distance to 50% lethality* (m)	*Distance to 1% lethality* (m)
20	76	12	110	175
40	96	15	160	245

F BLEVEs (road tankers)

Vessel capacity	*Fireball radius* (m)	*Fireball duration* (s)	*Distance to 50% lethality* (m)	*Distance to 1% lethality* (m)
15	69	11	95	150

[a] This is also the distance to spontaneous ignition.
[b] Cloud radius 75 m.

A17.4.10 Condensed phase explosion: hazard range

It is convenient to give at this point the estimate quoted in the report of the hazard range of a condensed phase explosion.

The ranges for fatal injury by thermal radiation or overpressure are in practice about 80–85 m, being limited by the maximum permitted loads of explosive of 16 te for a lorry and 20 te for a rail wagon. These are the distances at which the proportion of fatal injuries would be about 5%.

A17.4.11 Toxic release

For toxic release use is made of the appropriate gas dispersion model to determine toxic concentration and hence, for a particular exposure period, the corresponding toxic load.

The conventional infiltration model is used to determine the indoor toxic load.

For the number of persons affected by the release, the general approach is that used in the impact model

described in the next section. The concentration contours are calculated at which the probabilities of fatal injury are 1.0, 0.9, 0.5 and 0.1. This gives between these isopleths three zones with concentrations denoted C_1, C_2 and C_3 and with average probabilities of fatality taken as 0.95, 0.3 and 0.1.

For each zone there is a corresponding probability of escape indoors, the values used being 0 for C_1, 0.2 for C_2 and 0.8 for C_3.

An analysis is given of the possible responses of an individual affected by a toxic gas cloud. The results are shown in Figure A17.1.

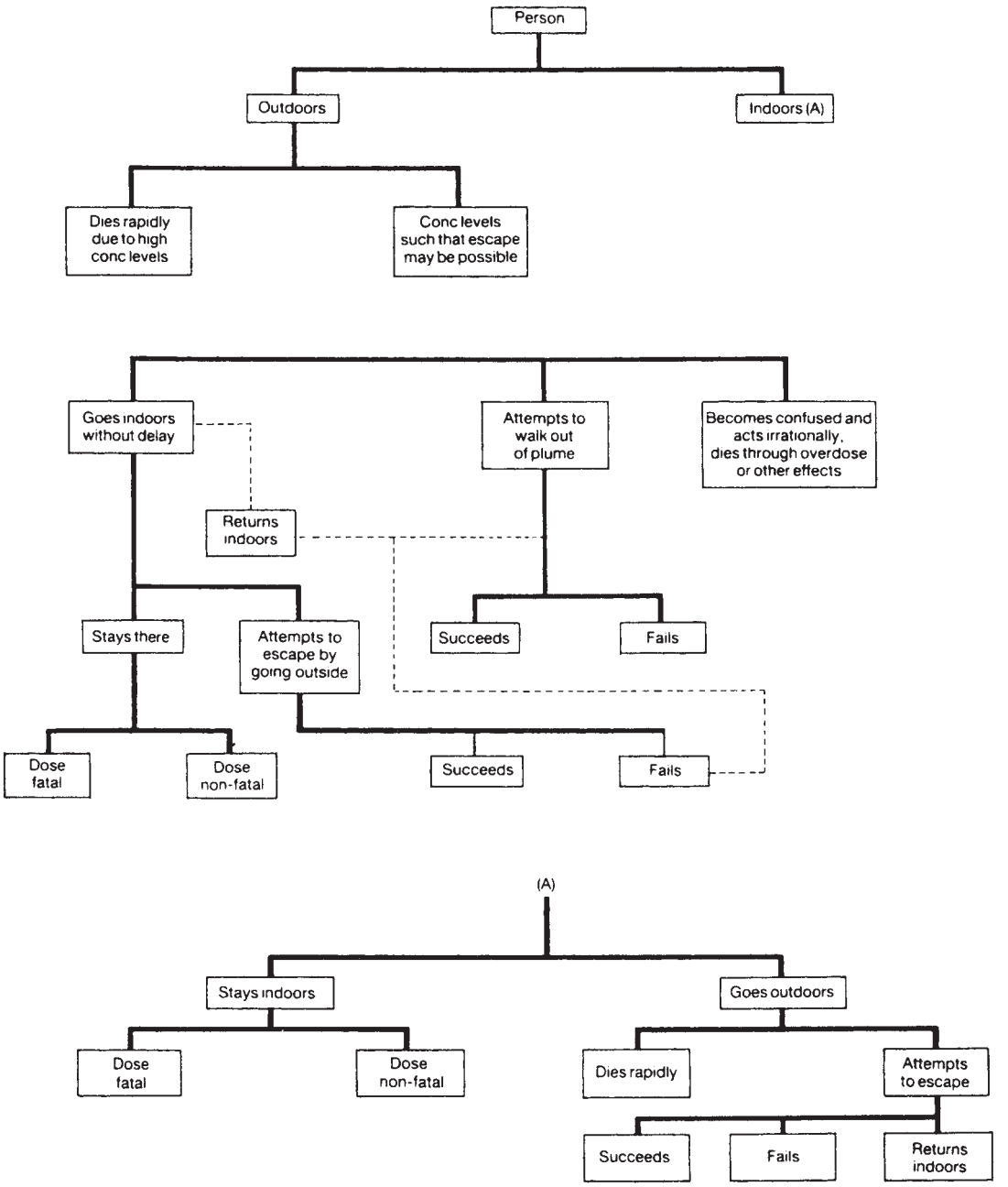


Figure A17.1 *Possible responses of an individual affected by a toxic gas cloud (Advisory Committee on Dangerous Substances, 1991) (Courtesy of HM Stationery Office)*

A17.5 Injury Relations

Injury models are used in the study to relate the intensity of the physical effects to the probability of injury. These are mainly probit equations, but HSE dangerous doses are also utilized. Some use is also made of rules-of-thumb.

The injury relations fall into two sets. The first set comprises HSE models, which are used for rail and road transport, the second set relations incorporated in the SAFETI code, which are used for ports. In the following account the HSE relations are described first, followed by those used in SAFETI, where applicable. In some cases no details are given for the latter; where this is the case, it should not be assumed that they are the same as the HSE relations.

A17.5.1 Thermal radiation

For fatal injury from thermal radiation use is made of the probit equation of Eisenberg, Lynch and Breeding (1975)

$$Y = -14.9 + 2.56 \ln(I^{4/3}t) \qquad [A17.5.1]$$

where I is the thermal radiation (kW/m^2), t the time (s) and Y the probit.

In the SAFETI work on fireballs from hot rupture of large cargos in port, a modification of the Eisenberg equation was used. In the region of thermal radiation above 500 kJ/m^2, it was assumed that 75% of persons outdoors and 25% of those indoors are killed, either by radiation or by secondary ignition effects.

A17.5.2 Fire engulfment

Injury can also occur due to engulfment in a fire. The assumptions made are that a person outdoors is killed, but that for a person indoors there is a certain probability of survival with the complementary probability $P_{f|id}$ of becoming a fatality.

In the SAFETI work the assumptions made were that for a flash fire all persons outside within the LFL contour and 30% of those indoors within the contour are killed but that no fatalities occur beyond this contour.

A17.5.3 Explosive: explosion overpressure

An HD1.1 explosive constitutes a blast hazard. For fatal injury two equations are given, the first being used in the road and rail transport study and the second, and more up-to-date, in the port study, reflecting developments as the work progressed.

The relationship given is for fatalities amongst persons indoors and is based on data on fatal injuries from V-2 rockets in the Second World War, with allowance for the effect of bomb shelters. In this situation building collapse is a more significant cause of injury than overpressure. The data are shown in Figure A17.2(a). The relation is applied also to persons outdoors in the built-up area and therefore near to buildings.

The first version of the equation is

$$Y = 1.47 + 1.37 \ln p^{o} \qquad [A17.5.2]$$

where p^{o} is the peak side-on overpressure (psi) and Y the probit. The second version is

$$Y = 2.47 + 1.37 \log_{10} p^{o} \qquad [A17.5.3]$$

A17.5.4 Explosive: explosion fragments

The hazard from an HD1.2 explosive is fragments. As stated in the previous section, the lethality of a fragment is taken as a function of its kinetic energy, and thus of mass and velocity, the lethal value being taken as one in excess of 80 J.

A17.5.5 Explosive: thermal radiation

The hazard from an HD1.3 explosive is thermal radiation. Figure A17.2(b) shows the relationship given in the report for this.

A17.5.6 Chlorine toxicity

For fatal injury from exposure to chlorine use is made of the following probit equation:

$$Y = -4.4 + 0.52 \ln(C^{2.75}t) \qquad [A17.5.4]$$

where C is the concentration of chlorine, t the exposure time and Y the probit.

A17.5.7 Ammonia toxicity

For fatal injury from ammonia the probit equation used is

$$Y = -12.2 + 0.8 \ln(C^{2}t) \qquad [A17.5.5]$$

where C is the concentration of ammonia, t the exposure time and Y the probit.

The SAFETI code uses for fatal injury from ammonia the probit equation.

$$Y = -9.82 + 0.71 \ln(C^{2}t) \qquad [A17.5.6]$$

where C is the concentration of ammonia (ppm), t the exposure time (s) and Y the probit. The group (C^2t) is actually computed as the time integral of the square of the concentration.

A17.5.8 Hazard impact

The method principally used in the report to estimate the impact of the hazard is as follows. The ranges are determined at which the physical effect is lethal at the 0.90, 0.50 and 0.10 probability levels. The areas within these contours are denoted A_{90}, A_{50} and A_{10} respectively. The average lethality within each area is taken as the average of the lethalities at the bounding contours.

Thus, the lethality with the circle A_{90} is 0.95 $(=(1.0-0.90)/2)$, that within the annulus $(A_{50}-A_{90})$ is 0.7 and that within the annulus $(A_{10}-A_{50})$ is 0.3. This yields the hazard impact relation

$$N = D[0.95A_{10} + 0.7(A_{50} - A_{90}) + 0.3(A_{10} - A_{50})] \qquad [A17.5.7]$$

where A is an area (m^2), D the population density (persons/m^2) and N the number of fatalities. Use is also made of variations on this basic equation.

A17.6 Population Characteristics

In transport scenarios the characterization of the population exposed tends to be much more complex than for fixed installation scenarios. A significant proportion of the modelling described in the report is addressed to this aspect.

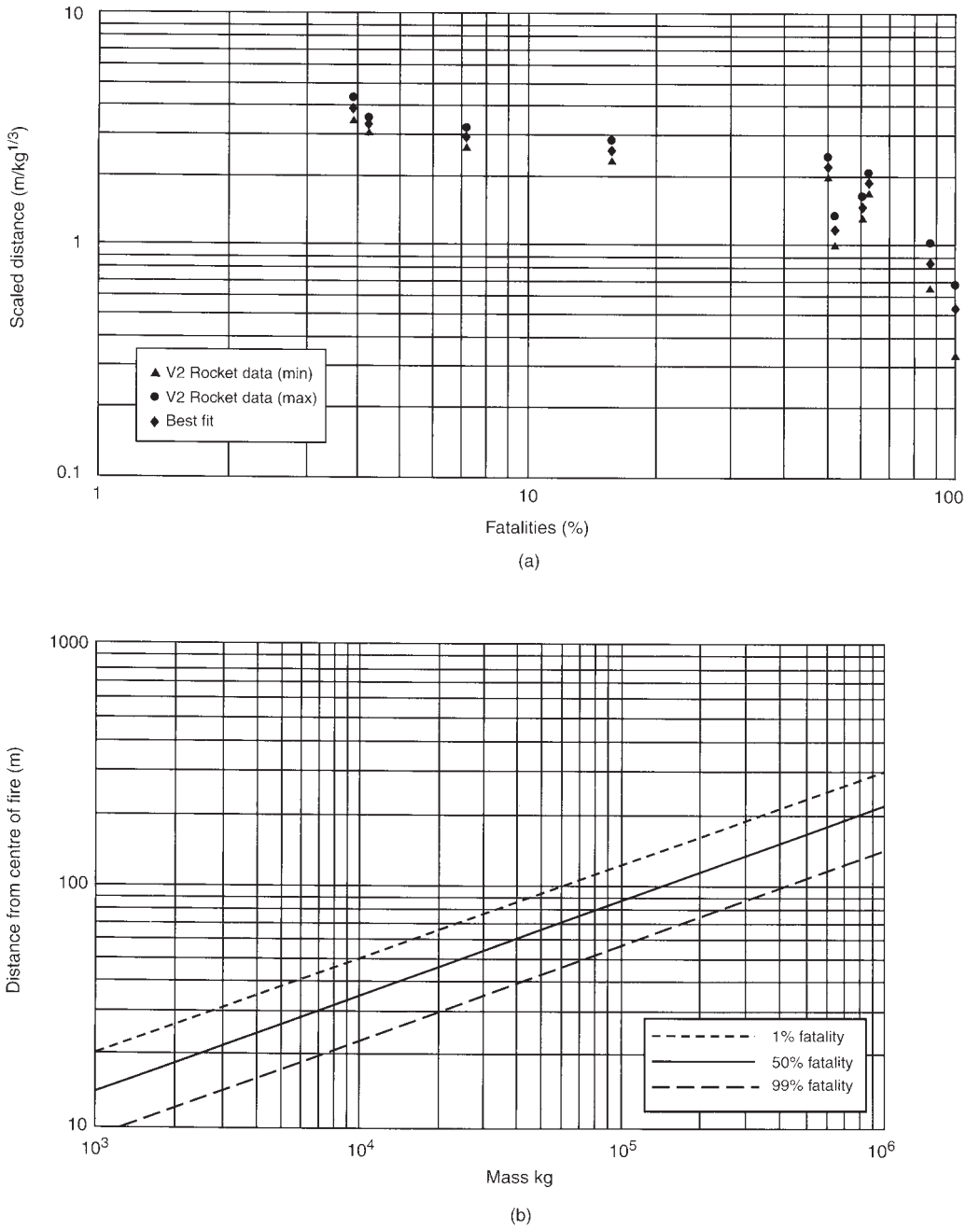


Figure A17.2 *Hazard ranges for explosives (Advisory Committee on Dangerous Substances, 1991): (a) HD1.1 explosive (mass explosion hazard) and (b) HD1.3 explosive (fire hazard) (Courtesy of HM Stationery Office)*

For the general population the report utilizes four categories of population density. These are 4210, 1310, 2120 and 20 persons/km^2.

The proportion of the general population outdoors is taken for the purposes of the assessment as a function of the meteorological conditions, particularly conditions D5 and F2.

This characterization of the general population essentially suffices for the assessment of fixed sites such as marshalling yards and ports but needs to be supplemented

by additional models for rail and road transport. These models, which are described below, are relatively complex but this complexity is necessary to obtain a realistic estimate of the risks.

A17.7 Rail Transport

The hazard of rail transport of non-explosive materials is considered in Appendix 8 of the report.

An account has been given in Chapter 23 of the rail transport environment in the United Kingdom. It includes data given in the ACDS report on tank wagon capacities and movements and on release frequencies and probabilities.

A17.7.1 Wagons and movements

For the four hazardous materials studied, the rail tank wagon capacities and movements are given in Table 23.23. The wagon capacities are for motor spirit 32 and 75 te, for LPG 20 and 40 te, for chlorine 29 te and for ammonia 53 te.

Rail movements along the major routes in the United Kingdom in 1985 are shown in Table A17.5, which also gives the population densities.

A17.7.2 Exposed population

The population exposed to an en route rail accident considered in the report are the personnel on the trains involved, the passengers in passenger trains (PTs) and the general off-track population.

For the density of the general population along the track the basic method used was to use a map to assign each square kilometre of the trackside area to one of the four population densities described in Section A17.6.

A check was made on the adequacy of using these generalized values by taking one of the rail routes and determining the population densities with circles of 300 m radius along the track from the 1981 Census enumeration districts. The process was repeated with circles of smaller and larger diameter. The results showed that in general the map and census methods gave similar results, except that the map method underestimated the urban population in a few places.

For the exposure of passengers in a PT to hazard from a heavy goods trains (HGT) five basic scenarios are considered. One is the involvement of a PT waiting at a stop signal in the hazard zone of a release from an HGT, the obedient train case. The other four are (1) collision of the PT and HGT, causing a release; (2) collision of a PT and an HGT, where a release has already occurred; (3) a PT entering the hazard zone of a release from an HGT and (4) a PT entering the hazard zone of a release from an HGT and colliding, causing a further release. Two wind conditions are considered: (1) wind along the track and (2) wind perpendicular to the track.

The proportion of carriages in the PT involved is the ratio of the length of the hazard-affected zone to the length of the train.

With regard to air infiltration into a PT, the ventilation on most modern trains is controlled from the driver's cab and is set at about 13 air changes/h. The driver experiences a ventilation rate about six times this and is thus effectively out of doors.

A17.7.3 Initiating events and event frequencies

The report considers two main types of initiating event.

These are puncture of a tank wagon by collision or derailment and failure or maloperation of the tank wagon equipment.

The treatment given for the frequency of these events for each of the four substances and for the probability of

Table A17.5 *Rail traffic and population densities along some major routes in the United Kingdom in 1985 (Advisory Committee on Dangerous Substances, 1991) (Courtesy of HM Stationery Office)*

	Motor spirit	*LPG*	*Ammonia*	*Chlorine*
All movements (wagon km/year)	10,199,095	1,390,590	1,348,080	313,668
Total wagon journeys/year	55,814	4,334	4,500	2,342
Major route	Merseyside–Leeds–Humberside	Hampshire–Midlands	Teeside–Scotland	Merseyside–Anglesey
Route length (km)	223	329	262	156
Number of wagons on route/year	5300 × 32 te 3900 × 75 te	1,323	2,204	1,216
Wagon km/year on route	2,051,600	435,267	530,288	189,696
% Traffic in that substance	20	31	39	60
Population density (people/km²)	*Aggregate length of route with that population density*			
Urban (4210)	15	30	12.5	0
Both sides[a]				
Suburban (1310)				
Both sides[a]	36.5	48	40.5	19
One side only[a]	1.5	20	12.5	24
Built-up rural (210)				
Both sides[a]	17.2	14	15	24
One side only[a]	0	0	0	1.5
Rural (20)				
Both sides[a]	143.2	215	181.5	87.5
One side only[a]	1.5	22	12.5	25.5
Tunnel	9.5			

[a] Indicates whether the population is on both sides of the railway or on one side only, the other side being rural.

ignition, immediate or delayed, of flammables is described in Chapter 23.

A17.7.4 Motor spirit events

For motor spirit, the scenarios considered are instantaneous releases of 32 and 75 te and continuous releases of 25 kg/s (equivalent to a 100 mm hole).

A release of motor spirit, if ignited, results in a pool fire. The pool spread and fire model used is described in Section A17.4.

For a continuous release the times for the 32 te and 75 te wagons to empty are approximately 20 and 50 min, respectively. The size of pool, and pool fire, formed depends on whether ignition occurs immediately. If ignition is delayed the radius of the pool from a 32 te wagon would be some 24 m and that for a 75 te wagon some 37 m. With immediate ignition, the pool radius in both cases would be 12 m. The pool radii for instantaneous releases would be similar.

A17.7.5 LPG events

For LPG, the scenarios are instantaneous releases of 20 and 40 te and continuous releases of 2 and 32 kg/s.

If the release is instantaneous and is ignited immediately, a fireball occurs. Otherwise, a flammable cloud forms. If this cloud is ignited, there is either a flash fire or a VCE.

If the release is continuous and is ignited immediately, a torch fire or a BLEVE occurs. Otherwise a flammable cloud forms. If this cloud is ignited, there is either a flash fire or a VCE. The flash fire may be accompanied by a torch fire or a BLEVE.

The report gives event trees for these scenarios.

A17.7.6 Chlorine and ammonia events

For chlorine and ammonia, the scenarios considered are as follows:

	Chlorine	*Ammonia*
Two-phase release from valve (kg/s)	1.3	2.1
Single phase release from puncture (kg/s)	45.1	33.5
Instantaneous release from catastrophic failure (te)	29	53

The development of these events is determined using the hazard models described.

A17.7.7 Marshalling yards

In addition to these en route events, the report also addresses releases occurring in marshalling yards. The two materials of interest in this regard are LPG and chlorine. The frequency estimates for these events for the two materials are given in Chapter 23.

The release scenarios considered are the same as for the en route case.

A17.8 Road Transport

The hazard of road transport of non-explosive materials is considered in Appendix 9 of the report.

An account has been given in Chapter 23 of the road transport environment in the United Kingdom. It includes data given in the ACDS report on tanker capacities and movements and on release frequencies and probabilities.

A17.8.1 Vehicles and movements

For the four hazardous materials studied, the road tanker capacities and movements are given in Table 23.6. The tanker capacities are for motor spirit 20–25 te, for LPG 15 te, for chlorine 17 te and for ammonia 15 te.

A17.8.2 Exposed population

The population exposed to an en route road accident considered in the report are the personnel of the vehicles involved, the other road users and the general off-road population.

The road transport situation is rather different from that of rail. In particular, it is necessary to take into account the wide variety of types of road and road usage.

Another basic difference is that the probability of other persons becoming involved in an incident is much higher for road than for rail.

For the density of the general population along the road the method is essentially similar to that used for rail transport.

The exposure of other road users to hazard from a road tanker is treated in terms of two zones, one for users behind the tanker and one for users on the other side of the road. For the former it is assumed that traffic backs up behind the tanker and that the section of the zone ahead of it is clear. In the second zone, on the other carriageway, the population density depends on whether the traffic stops or continues to move. It is assumed that the density in this zone is half that in the first zone.

The density of the road user population backed up behind the tanker is computed as follows. The traffic is assumed to consist of 10% heavy goods vehicles (HGVs). The length of road occupied by an HGV is taken as 20 m and that occupied by other vehicles as 4 m. There are assumed to be 1.5 persons/vehicle. This yields for motorways and for other roads population densities of 0.056 and 0.05 persons/m^2, respectively.

The full set of eight zones defined in the report comprises four on the same side of the road as the tanker and four on the other side. Zone a is one of standard population density, Zone b one of high density, Zone c a clear zone and Zone d the zone of road users behind the tanker. Zones h, g, f and e are, respectively, the corresponding zones on the other carriageway.

With regard to air infiltration into vehicles, work by M. Cooke (1988) has shown that for a car travelling at 40 miles/h the ram effect is sufficient to give one air change per minute and air ingress will be even greater if the ventilation fan is on. For a stationary car use of the ventilation fan will again give about one air change per minute. Even if the fan is off, the car is not expected to provide significant protection, the volume of the air space being small.

A17.8.3 Initiating events and event frequencies

The report considers two main types of initiating event. These are puncture of a tanker by collision and failure or maloperation of the tanker equipment.

The treatment given for the frequency of these events for each of the four substances and for the probability of ignition, immediate or delayed, of flammables is described in Chapter 23.

A17.8.4 Motor spirit events

For motor spirit, the scenarios considered are instantaneous releases of 4, 8 and 12 te and a continuous release of 25 kg/s (equivalent to a 100 mm hole). The tankers contain six compartments and the instantaneous releases correspond to spills from one, two or three of these.

A release of motor spirit, if ignited, results in a pool fire. The pool spread and fire model used is described in Section A17.4.

The pool areas obtained are

Spill	*Pool area* (m^2)	
	Immediate ignition	*Delayed ignition*
25 kg/s	314	908
4 te	707	1018
8 te	1385	1964
12 te	2124	3019

A17.8.5 LPG events

For LPG, the scenarios are an instantaneous release of 15 te and continuous releases of 2 and 32 kg/s.

If the release is instantaneous and is ignited immediately, a fireball occurs. Otherwise, a flammable cloud forms. If this cloud is ignited, there is either a flash fire or a VCE.

If the release is continuous and is ignited immediately, a torch fire or a BLEVE occurs. Otherwise a flammable cloud forms. If this cloud is ignited, there is either a flash fire or a VCE. The flash fire may be accompanied by a torch fire or a BLEVE. The report gives event trees for these scenarios.

A17.8.6 Chlorine and ammonia events

For chlorine and ammonia, the scenarios considered are as follows:

	Chlorine	*Ammonia*
Two-phase release from valve (kg/s)	1.3	2.1
Single phase release from puncture (kg/s)	45.1	33.5
Instantaneous release from catastrophic failure (te)	17.5	15

The development of these events is determined using the hazard models described.

A17.8.7 Lorry stopover points

In addition to these en route events, the report also addresses releases occurring at lorry stopover points. The three materials of interest in this regard are LPG, chlorine and ammonia. The frequency estimates for these events for the three materials are given in Chapter 23. The release scenarios considered are the same as for the en route case.

A17.9 Marine Transport: Ports

The treatment of marine transport in appendix 7 of the ACDS report is confined to the hazard at ports, which constitute fixed installations.

The study of ports was performed using the SAFETI code.

A17.9.1 Ports

There are in the United Kingdom some 42 ports with handling profiles exhibiting wide variety. The approach adopted was to study a set of three ports which had a representative set of major hazards. These ports were River Tees, the largest British chemical port complex; Felixstowe, a busy port with moderate hazardous trades; and Shoreham, a small port with petroleum product trades.

A17.9.2 Materials and movements

The principal hazardous materials and the movements of these materials through British ports are shown in Table A17.6.

A17.9.3 Exposed population and ignition sources

The model for the exposed population is that incorporated in the SAFETI code. The population is characterized in terms of the numbers of persons within 100 m grid squares. Separate distributions are used for night and day, the night-time figures being based on census data and the day-time ones on adjustments to these data. The density of ignition sources is also modelled using the grid square method, with values of ignition probability assigned on the basis of judgement.

A17.9.4 Initiating events and event frequencies

The report first considers the following types of marine event: (1) collision, (2) grounding, (3) striking and (4) impact. A collision occurs where two ships run into each other, a striking where a moored vessel is struck by a passing vessel and an impact where a vessel runs into a dock wall or jetty.

The starting point for the estimation of the frequency of these events at British ports was a study by the National Ports Council (1976), which was somewhat old and has known defects. The data were therefore re-analysed and supplemented by three additional data sets. The results of this analysis are given in Table A17.7(A).

The effects of these events were assessed separately for tankers and for gas carriers. For tankers the effects were taken to be (1) collision or striking below water, (2) collision or striking above water, (3) grounding damage or (4) impact damage. For each case a representative hole size was assigned.

For gas carriers all four marine events were assumed to have one of two effects: (1) cold leak through a hole or (2) cold rupture of the tank contents. For a cold leak the hole size was taken as that of the loading pipe connection, located at the bottom of a prismatic tank or at the mid-height of a spherical or cylindrical tank. For a cold rupture the release was taken as instantaneous from a pressurized tank or as occurring over 5 min from a refrigerated tank. It was assumed that 90% of the releases were leaks and 10% ruptures.

Four other events were also considered: (1) transfer spills, (2) tanker explosion, (3) gas carrier fires and (4) ammonium nitrate ship explosions.

The frequency of transfer spills was estimated from incidents reported to the HSE under NADOR in a 5.25 year period 1981–86. Transfer spills tend to be small and possibly, unreported. There were only eight spills reported, and just one for liquefied gas.

There are significant differences between cargos and transfer arrangements which will affect the frequency of transfer spills. Differences identified included (1) cargo

Table A17.6 *Hazardous cargos handled at British ports (after Advisory Committee on Dangerous Substances, 1991)*

A Overall

Material group	*Terminals*	*Visits* (ships/year)	*Amount per terminal* (te/year)	*Amount per movement* (te/ship)	*Total amount* (te/year)
Crude oil	17	1,957	9,244,347	80,291	157,153,891
Low flashpoint products	43	5,163	478,261	3,983	20,565,228
High flashpoint products	41	3,126	340,233	4,463	13,949,554
Flammable liquefied gas	26	2,388	374,180	4,008	9,674,268
Toxic liquefied gas	4	87	113,826	5,233	455,303
Low flash chemicals	21	1,244	105,689	1,771	2,205,975
High flash chemicals	23	1,399	119,689	1,945	2,739,746
Explosive chemicals	19	258	14,283	1,052	271,377
Total		15,662			207,015,342

B Liquefied gas

Liquefied gas	*Visits* (ships/year)	*Total amount* (te/year)
Ammonia	87	455,303
Butadiene	14	20,990
Butane	548	2,247,856
C_4 mix	227	236,151
Ethane	76	250,848
Ethylene	255	623,886
LPG[a]	555	2,339,388
Propane	414	3,470,246
Propylene	222	354,824
VCM	78	130,079
Total	2476	10,129,571

[a] LPG comprises propane–butane mixes in varying proportions.

Table 17.7 *Frequency of some marine accidents at British ports (after Advisory Committee on Dangerous Substances, 1991)*

A Accidents by port type

	Collisions (per encounter)	*Grounding* (per km)	*Striking* (per passing)	*Impact* (per visit)
Open sea port	5.0×10^{-4}	6.5×10^{-5}	4.0×10^{-6}	2.2×10^{3}
Wide estuary	4.0×10^{-5}	8.0×10^{-6}	4.0×10^{-6}	2.2×10^{3}
Wide river	1.2×10^{-4}	1.6×10^{-5}	9.0×10^{-6}	2.1×10^{3}
Narrow river	5.0×10^{-4}	6.5×10^{-5}	4.2×10^{-5}	6.5×10^{3}

B Accidents by cargo group

	Transfer accident (per cargo transferred)	*Explosion* (per visit)
Crude oil	1.9×10^{-4}	1.3×10^{-5}
Low flash products	1.8×10^{-4}	3.5×10^{-6}
High flash products	1.8×10^{-4}	1.5×10^{-6}
Flammable liquefied gas	7.6×10^{-5}	–
Toxic liquefied gas	7.6×10^{-5}	0
Low flash chemicals	1.5×10^{-4}	1.3×10^{-5}
High flash chemicals	1.5×10^{-4}	0
Ammonium nitrate	0	7.0×10^{-6}

(liquid, pressurized liquefied gas or refrigerated liquefied gas), (2) transfer equipment (articulated hard arm or flexible hose), (3) proportion of cargos unloaded, (4) use of vapour recovery, (5) use of ranging alarms, (6) emergency shut-down system (none, basic or advanced), (7) quick release coupling (none, pre-1987 or post-1987) and (8) environment (berth tidal or non-tidal, number of passing vessels).

The various transfer spills were condensed into four: (1) 3 min full bore (LG only), (2) 5 min full bore (liquid cargos only), (3) 15 min full bore and (4) 10 min at 10% full bore.

Event trees were constructed to assist in estimating the proportion of each of these different outcomes. The branches in the event trees were determined by the following three factors (1) immediate operator reaction (within 1 min), (2) operation of BSD within 10 min and (3) effectiveness of BSD when operated.

The results of this work are the transfer spill frequencies shown in Table A17.7(B).

Tanker explosion frequencies were obtained from analysis of cases world-wide in Lloyds Casualty Returns for the period 1977–86. Table A17.7(B) shows the results.

The frequency of gas carrier fires was obtained from the study by Blything and Edmondson (1984 SRD R292). The data were processed to give incident rates per visit and per kilometre of approach.

It was estimated that there have been nearly 100 fire incidents but without any release of a cargo. Applying the statistics for the case of no event over a period of time, the estimate obtained for the probability of cargo release given a fire was 0.007. It was then assumed that 90% of such cases are hot leaks and 10% hot ruptures. Only the latter was considered further, the former being treated as leaks through safety valves which are consumed by the fire on the vessel.

For ammonium nitrate (AN) explosions the use of historical data was eschewed, since such incidents occurred many years ago and involved organic-coated material which is no longer used. Instead use was made of fault trees to predict the explosion frequency, the main path being a fire, probably from the engine room, entering a hold and melting part of the AN. Explosion could then be initiated by confinement, organic contamination or impact shock. The estimated frequency of AN ship explosion so obtained is 6.2×10^{-8} per cargo.

A17.9.5 Releases of flammable liquefied gas

Releases of flammable liquefied gas were modelled using the emission and dispersion models in SAFETI. The detailed treatment of the emission scenarios for cold releases, namely cold leaks from and cold rupture of pressurized and refrigerated tanks, is described in the report. The dispersion of the vapour was then obtained using the dense gas dispersion model.

The ignition model in the code is then used to determine the proportion of cases in which the cloud is ignited. The proportion of ignitions resulting in a VCE is taken as 10%, the other 90% as giving a flash fire.

Hot rupture of a pressurized tank is assumed to give a fireball. The size of tank is typically several hundred tonnes and the size of the resultant fireball is well outside the range for which correlations have been validated.

Hot rupture of a refrigerated tank was initially also assumed to give a fireball, but this outcome is uncertain. A pool fire may well be more likely. Modelling of these two alternatives for this case indicated that they present comparable hazards.

A17.9.6 Releases of toxic liquefied gas

Releases of liquefied ammonia were modelled using the emission and dispersion models in SAFETI.

A17.9.7 Explosions of flammable liquid

For flammable liquid explosions modelling of representative events in respect of overpressure and fragments indicated that they are not in general significant beyond the vessel.

Such explosions do, however, cause casualties amongst the crew. From analysis of tanker losses in port in the period 1977–86 the following estimates were derived:

Proportion of crew killed	*Probability given cargo explosion*
0.15	0.37
0.40	0.11
0.65	0.04
1.0	0.04

A17.9.8 Ammonium nitrate explosions

Ammonium nitrate explosions are modelled using the TNT model with an appropriate value for the TNT equivalent of AN. For bagged AN this was taken as 13% of the shipment mass and for bulk AN as 33%. These values include allowance for the TNT equivalent of AN, the probable mass aboard when the explosion occurs and the efficiency of explosion for the different types of storage.

A17.9.9 Representative ports

The report gives the results of the detailed studies for the three representative ports of River Tees, Felixstowe and Shoreham.

A17.9.10 Extension to all ports

The risk results obtained for the three representative ports were applied using a 'simplified method', details of which are given in the report, to obtain an estimate of the national societal risk.

A17.10 Transport of Explosives

The hazard from the transport of explosives by rail and road is considered in Appendix 10 of the report.

A17.10.1 Categorization of explosives

The hazards presented by explosives include blast, fragments and fireball. The hazard which predominates in a particular case depends on the class of explosive.

The classification generally used in transport is the UN scheme, described in Chapter 23. The classes of explosive in this scheme which are of prime interest here are

HD1.1 Mass explosion hazard;
HD1.2 Projection hazard;
HD1.3 Fire hazard;
HD1.4 No significant hazard.

For the purpose of hazard assessment, the ACDS found it necessary to develop a categorization more adapted to this

purpose, which reflects particularly the heat sensitivity of the substance or articles:

UN class	*ACDS category*	
	M	Heat sensitive substances in flammable packaging
HD1.1	N	Heat sensitive articles – not readily ignitable
	P	Heat insensitive substances
HD1.2	Q	Heat sensitive articles
HD1.3	R	Heat sensitive substances in flammable packaging
	T	Heat sensitive articles and substances in non-flammable packaging
HD1.4	W	Heat sensitive articles which present no great hazard

A17.10.2 Limits on loads

In the United Kingdom there are limits set to the load of explosive which can be carried. These are 16 te for a lorry and 20 te for a rail wagon, with a further limit of 40 te for a train.

A17.10.3 Rail transport of explosives: explosives and movements

The explosives moved in rail transport are predominantly (>97%) military explosives. In the year 1988/89 BR data showed that there were 8132 movements of wagons containing explosives. The average explosives train journey is 320 km and the explosives movements are therefore 2.6×10^6 wagon km/year.

A special investigation was made of the composition of this traffic, which was found to be by Hazard Division as follows: HD1.1 21%; HD1.2 12%; HD1.3 10% and HD1.4 44%. The explosives traffic was also analysed by the HSE categorization scheme, which yielded by proportion of wagons the following dominant categories: N 10%; P 11%; Q 12%; T 10%; W 44%; N/T 3% and Q/W 4%. Some 27% of explosives wagons contained HD1.1 explosives, while 44% contained only HD1.4.

An analysis was also conducted to obtain the average values of the NEQ, effectively TNT equivalent, of the loads.

A17.10.4 Rail transport of explosives: exposed population

The population exposed to the rail transport of explosives was determined in the study using a method essentially similar to that used for the four non-explosive substances.

In the event, the assessment showed that for rail the risk is predominantly to the off-site population.

A17.10.5 Rail transport of explosives: initiating events and event frequencies

The main mechanisms identified in the report for the initiation of explosives are (1) fire, (2) impact and (3) unsafe explosives.

An analysis was made for rail and road transport of data from various sources including the minutes of the ESTC of the MoD, the annual reports of HM Inspector of Explosives and the SRD explosives database EIDAS. There was for the United Kingdom over a 40 year period only one accident involving fatality, that at Peterborough in 1989 (HSE, 1990c). However, for both rail and road there were a number of dangerous occurrences, listed in Annex 2 of Appendix 10.

The report discusses in detail the methods by which it obtains its estimates of the explosive events in both forms of transport.

For rail transport it gives the following frequencies:

Initiating mechanism	*Frequency* (events/wagon km)
Unsafe explosives	1×10^{-9}
Fire	6×10^{-10}
Impact	1×10^{-10}

The frequencies of events from unsafe explosives and from fire are thus assessed as broadly comparable, that assessed for events from impact being much lower.

A17.10.6 Rail transport of explosives: explosions en route

The explosion event depends, as stated earlier, on the class of explosive carried, being for HD1.1 a mass explosion, for HD1.2 fragments and for HD1.3 a fireball. The models described in Section A17.4 were applied using the hazard impact method given in that section.

A17.10.7 Rail transport of explosives: explosions in marshalling yards

The study identified one marshalling yard which handled some 50% of explosives traffic and in which explosives were present almost continuously. An outline assessment was made, although no formal estimates of individual or societal risk were produced.

Application of the hazard model for the different classes of explosive showed that none of the events had a range to 10% lethality of more than 50 m. The population at this yard was beyond 110 m.

Analysis resulted in the following estimates for the frequency of initiation of an explosive load in a marshalling yard

Initiating mechanism	*Frequency* (events/year)
Unsafe explosives	1×10^{-3}
Fire	2×10^{-4}
Impact	2×10^{-4}

A17.10.8 Road transport of explosives: explosives and movements

An investigation was made of the composition of the road explosive shipments broadly similar to that made for rail. It was found to be by Hazard Division as follows: HD1.1 94%; HD1.2 2%; HD1.3 40%. The explosives traffic was also analysed using the ACSD categorization scheme, which yielded by mileage covered the following categories: M 51%; N 23%; P 20%; Q 2%; R 3%; T 1%.

An analysis was also conducted to obtain the average values of the NEQ of the loads. The loads were classified into three bands with the load being distributed according to the following probabilities

Band	*Mean NEQ* (kg)	*Proportion of total mileage* (%)
1	316	18
2	1,778	68
3	14,125	14

A17.10.9 Road transport of explosives: exposed population

The population exposed to the road transport of explosives was determined in the study using a method essentially similar to that used for the four non-explosive substances.

In the event, the assessment showed that for road the risk is predominantly to the road users.

A17.10.10 Road transport of explosives: initiating events and event frequencies

The initiating events in road transport are the same as those for rail transport. The analysis made to obtain the frequency of the road events has been described above. The detailed methods are given in the report.

For road transport it gives the following frequencies:

Initiating mechanism	*Frequency* (events/vehicle km)
Unsafe explosives	1×10^{-9}
Fire	2×10^{-9}
Impact	2×10^{-10}

The figures are somewhat similar to those for rail transport, the frequencies of events from unsafe explosives and from fire being assessed as broadly comparable, that assessed for events from impact being much lower.

A17.10.11 Road transport of explosives: explosions en route

The explosion event was modelled in a manner essentially similar to that used for rail transport. The models described in Section A17.4 appropriate to the class of explosive – HD1.1, HD1.2 or HD1.3 – were applied using the hazard impact method given in that section.

A17.10.12 Road transport of explosives: explosions at lorry stopover points

For explosives the situation at lorry stopover points is quite different from that at marshalling yards. Such points are always on premises licensed for the purpose. Lorries also stop briefly en route, but such stops are brief and are always attended. This risk was not pursued.

A17.11 Risk Criteria

The ACDS report gives in Appendix 6 a review of the principles underlying the setting of risk criteria and of the application of these to individual and societal risk.

The basic principle is that the risks should be as low as reasonably practicable (ALARP).

A17.11.1 Individual risk

With regard to individual risk to members of the public, the report refers to proposals made by the HSE. At the Hinkley Point Inquiry the HSE proposed that a fatality risk of 10^3/year is 'intolerable', though subsequent discussion suggested a lower level of intolerability. The HSE has also proposed a fatality risk of 10^{-6}/year as 'broadly acceptable'. The report adopts these criteria.

A17.11.2 Societal risk

In respect of societal risk, the ACDS criteria are formulated in terms of FN curves. A distinction is made between an FN curve for risk at national level and one for risk at local level. Both types of risk occur in the study, the en route risks of rail, road and explosives transport being treated mainly as national and the risks at fixed sites such as ports, marshalling yards, lorry stopover points and unloading points as local.

The basic principle is illustrated in Figure 9.39, which shows an FN criterion plot for a local risk. The FN space is divided into four parts by three lines. The upper line is the tolerability line. Risks above this line are regarded as intolerable. The middle line is the scrutiny line. Risks between this line and the tolerability line may be unjustifiable and require further study. The bottom line is the negligible risk line. Risks below this line are regarded as negligible. Those between the negligible risk line and the scrutiny line should be reduced applying the ALARP principle.

For the local risk criterion FN plot the ACDS proceeds as follows. The reference point is the risks assessed at Canvey. These risks were regarded as on the borderline of tolerability. The values used by the ACDS for these risks are one third those predicted in the Second *Canvey Report* (HSE 1981a). This Canvey FN curve is then used as a guide both to the setting of the absolute value of the tolerability line and to its slope. This is illustrated in Figure A17.3.

The negligible risk line for the local FN plot is set three decades below the tolerability line. The arguments for this are based essentially on examination of the implications of setting it either two or four decades below. If the line were two decades down, the expectation value would be six fatalities per 1000 years. Applying a value of a life of £0.5 million gives a potential expenditure of £3000 per annum, which might justify a QRA done every 10 years. It is argued that such a risk could hardly be regarded as negligible. On the other hand, if the negligible risk line were to be set four decades below the tolerability line, this would justify a potential expenditure of £30 per annum or £300 every 10 years. On the basis of the cost of staff time this would barely permit even a cursory discussion, which suggests that this setting of the line is well into the negligible risk region. The slope of the tolerability line, and of the other lines, is -1, again reflecting the assessed risk at Canvey.

The treatment in the report for the national risk criterion FN plot is less firm. A tentative scrutiny line is developed for ports which is derived not from any argument based on direct combination of the number of ports and of the local criteria but rather on the implication of transferring trade from any port where the risks are already at the tolerability limit. This line is entered on the FN plot for national societal risk for ports and also on other national societal risk plots as shown in the following paragraphs.

A17.11.3 Value of a life

As already mentioned, the report refers to the figure of £0.5 million for the avoidance of a statistical fatality, or the value of a life, used by the Department of Transport. It gives in appendix 7 on ports a discussion of cost benefit analysis of proposed remedial measures in which a factor of 4 is applied to this figure, yielding a value of a life of £2 million (1991 value) to allow for 'gross disproportion' and uses this latter in the subsequent analysis.

A17.12 Assessed Risks

The assessed risks quoted in the study are now described. The report is careful to quote confidence bounds and to

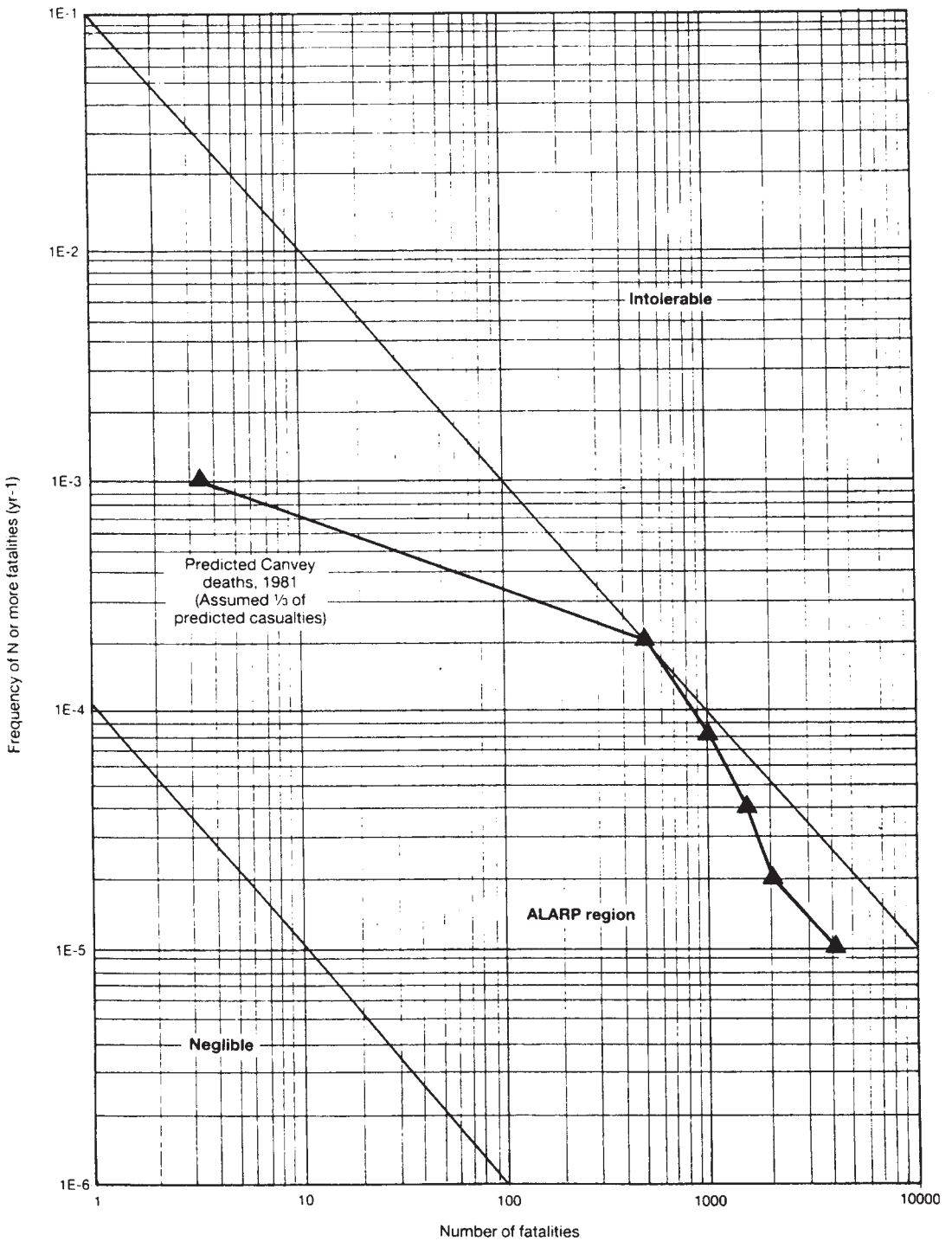


Figure A17.3 *FN curve risk criterion proposed by the ACDS for an identifiable community, $E{-}n = 10^{-n}$ (Advisory Committee on Dangerous Substances, 1991) (Courtesy of HM Stationery Office). Five concentrations are calculated at which the probabilities of fatal injury are close to 1.0 (concentrations C_1, C_2) and 0.9, 0.5 and 0.1 (three concentrations C_3). For each concentration there is a corresponding probability of escape indoors, the values used being 0 for C_1, 0.2 for C_2 and 0.8 for C_3*

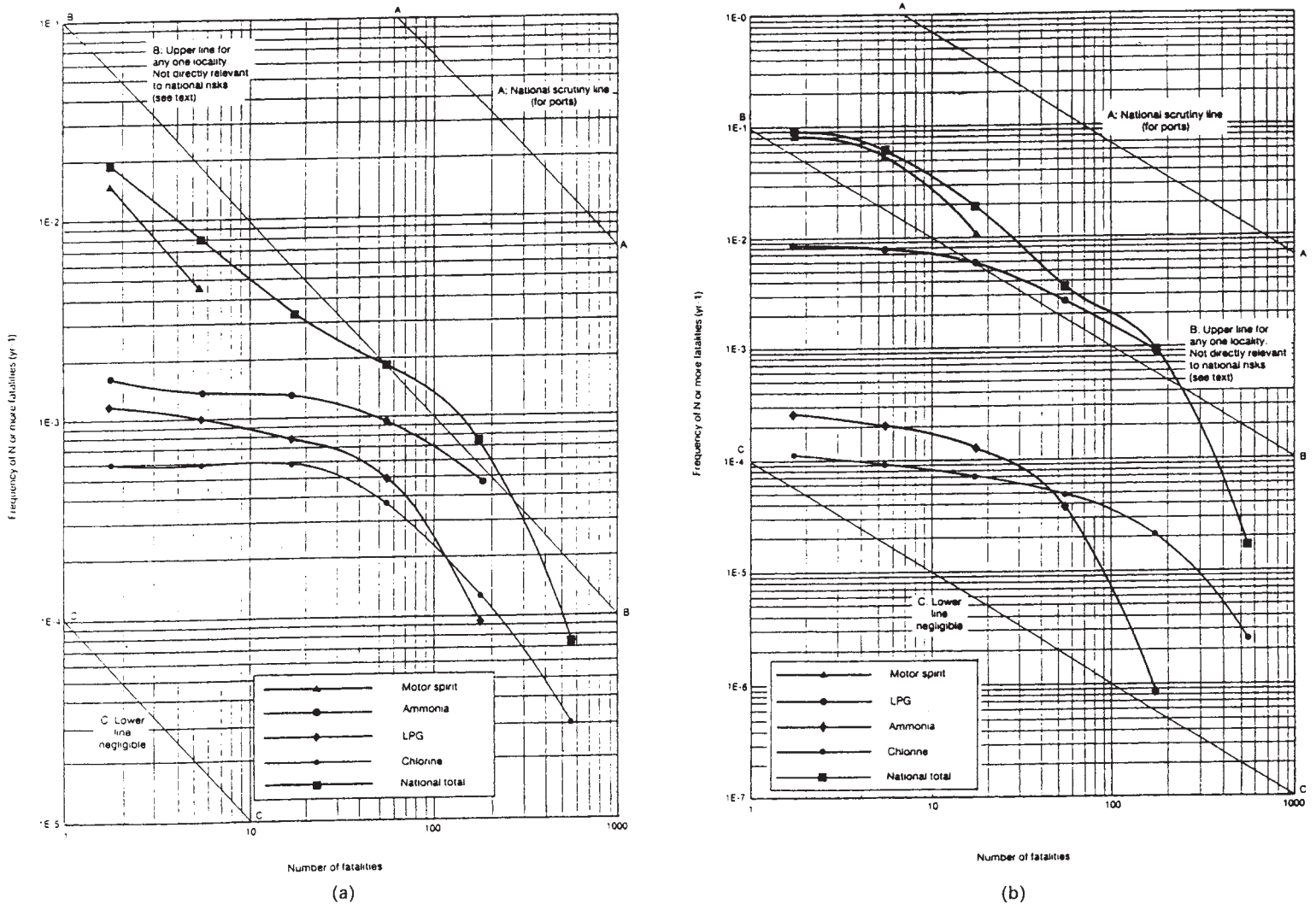


Figure A17.4 *FN curves for national societal risks from rail and road transport of four hazardous materials (Advisory Committee on Dangerous Substances, 1991): (a) rail transport and (b) road transport. $E–n = 10^{-n}$ (Courtesy of HM Stationery Office)*

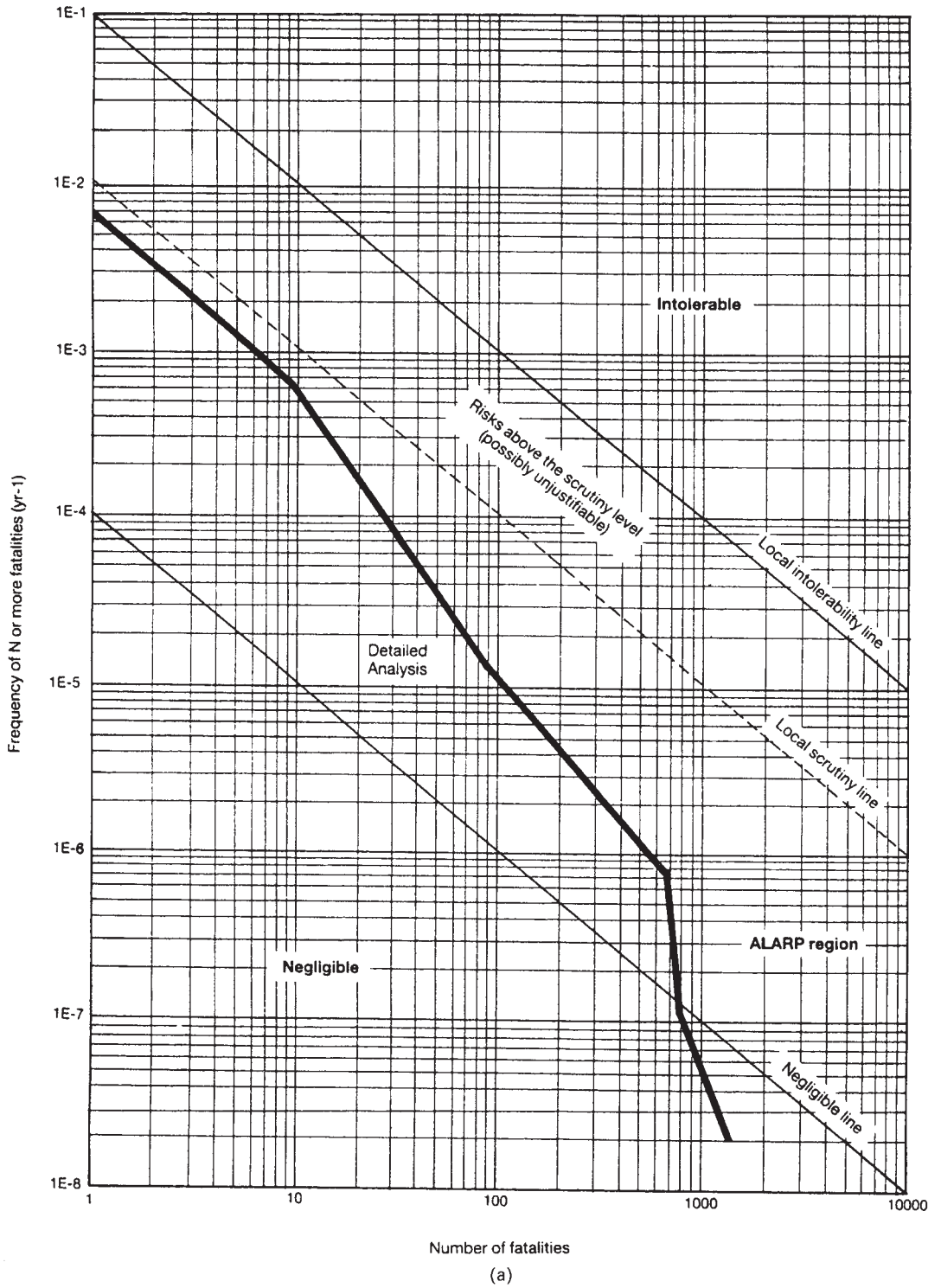


Figure A17.5 *Continued*

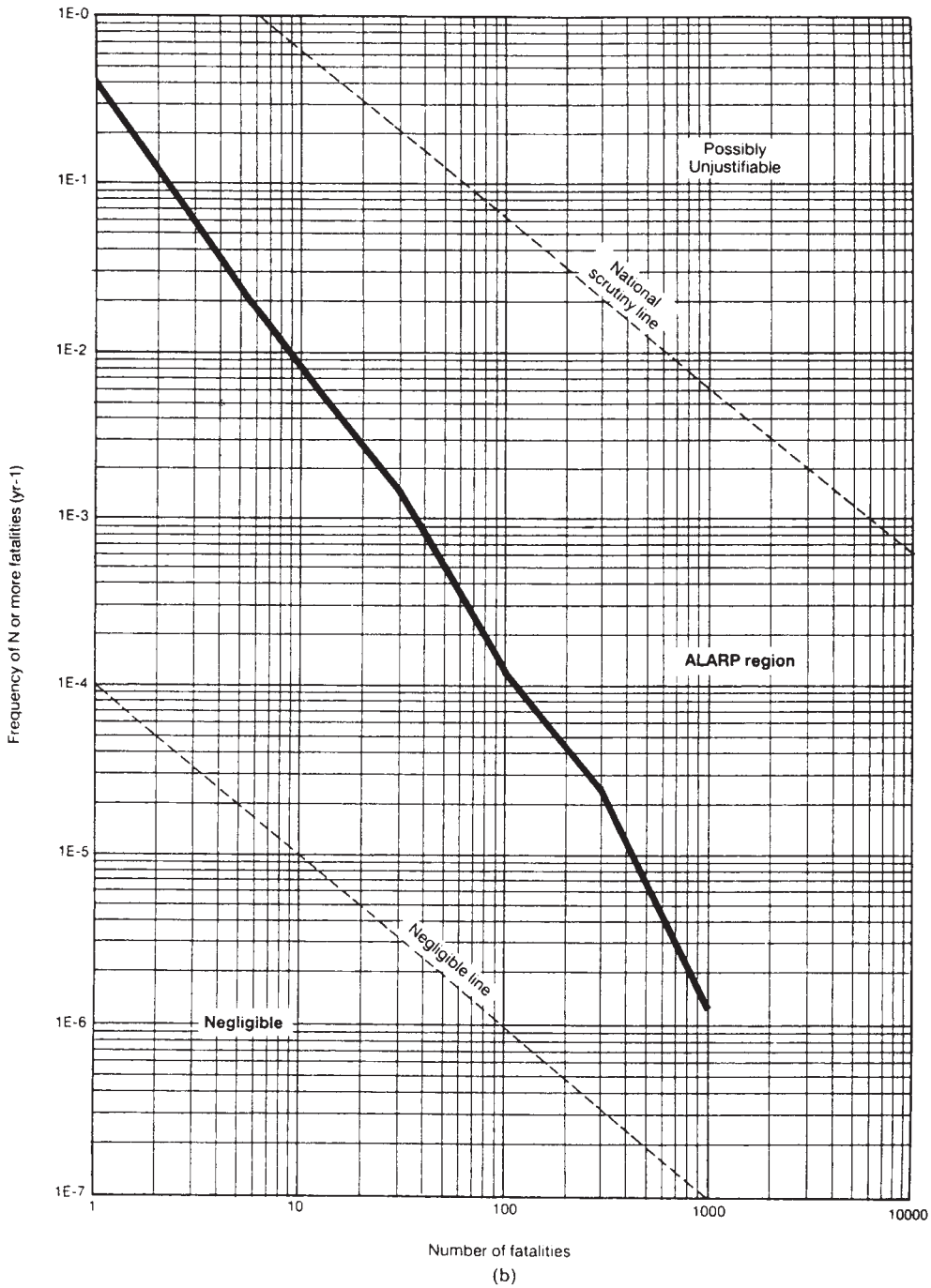
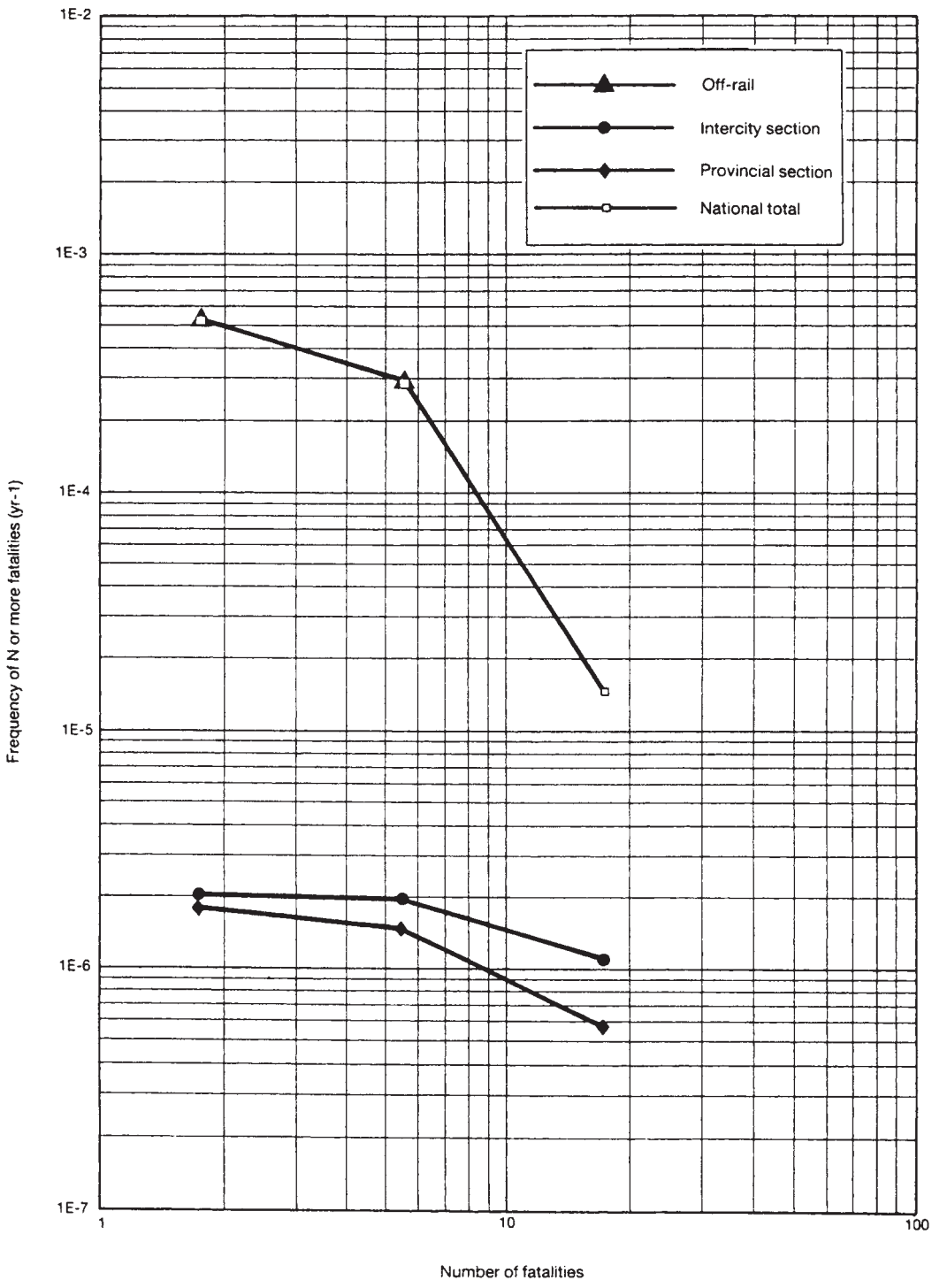


Figure A17.5 *FN curves for societal risks at British ports (Advisory Committee on Dangerous Substances, 1991): (a) local societal risk at Felixstowe and (b) national societal risk (simplified method). $E{-}n = 10^{-n}$ (Courtesy of HM Stationery Office)*



(a)

Figure A17.6 *Continued*

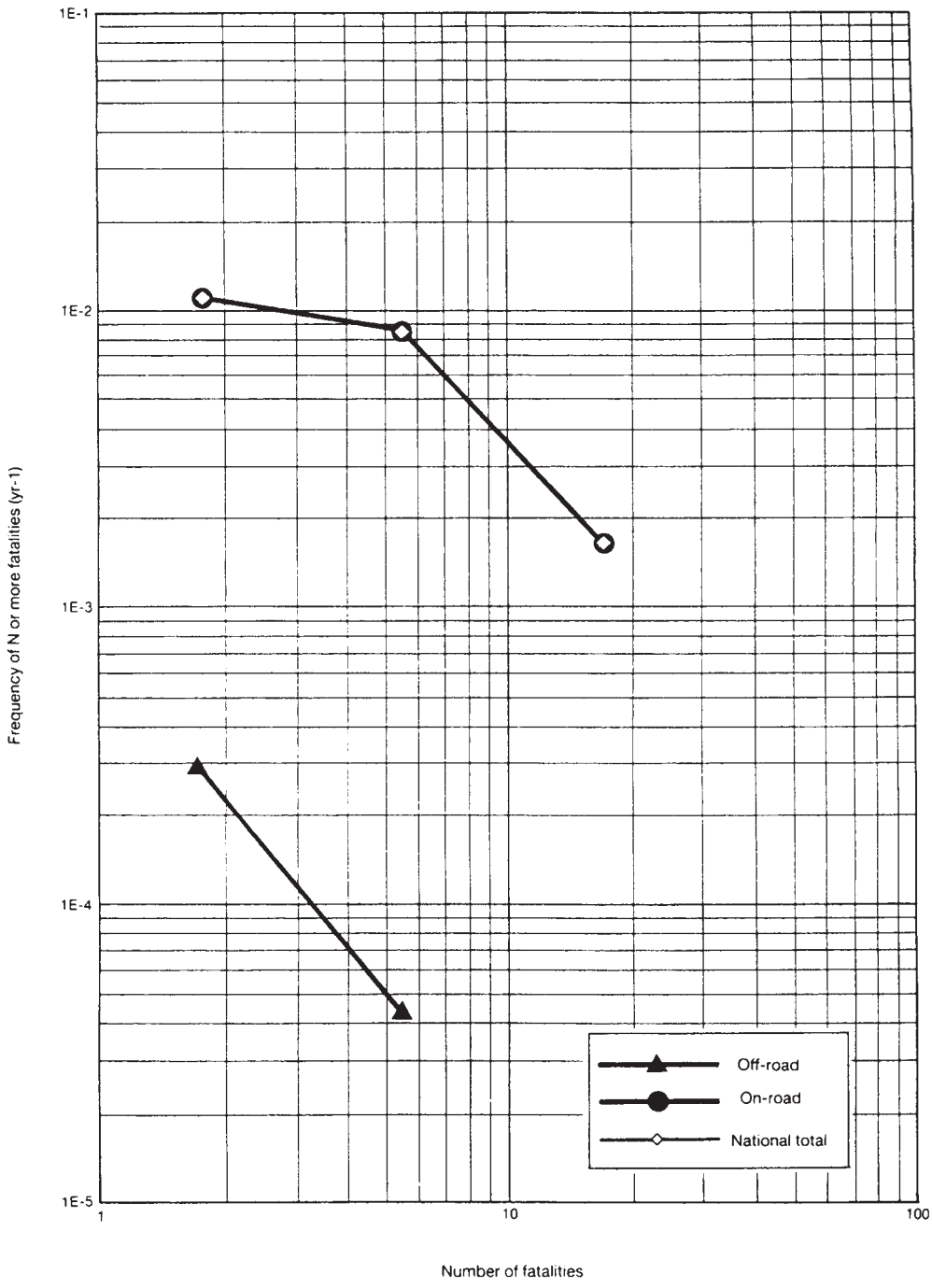


Figure A17.6 *FN curves for national societal risks from rail and road transport of explosives (Advisory Committee on Dangerous Substances, 1991): (a) rail transport and (b) road transport, $E–n = 10^{-n}$ (Courtesy of HM Stationery Office)*

note uncertainties in, and qualifications to, the figures given. The account given here is in outline only.

A17.12.1 Rail and road transport

The assessed risks of rail and road transport for the four non-explosive materials are presented as individual risks, as societal risks in the form of FN curves and as expectation values.

The individual risk to the public for rail transport of the four materials is assessed as negligible. For example, for a person living 50 m from the track the fatality risk from chlorine transport is predicted to be 2.4×10^{-7}/year. For road transport, the situation is rather more complex in that there may be certain locations such as a sharp corner which have a higher than average risk. But in general the risk is assessed as negligible and as only a small fraction of the overall risk faced by road users.

The national societal risks assessed for the transport of the four materials, and for the combination of these, are shown in Figures A17.4(a) and (b) for rail and road, respectively. For rail transport the predominant risks are from motor spirit and ammonia, for road transport from motor spirit and LPG. For both modes the risk lies between the tolerability and negligible risk lines.

The expectation values of the annual number of fatalities for the rail transport of motor spirit and ammonia are 0.074/year and 0.3/year and those for the road transport of motor spirit and LPG are 1.1/year and 0.8/year, respectively.

The report gives in Appendix 11 a comparison of the relative risks from rail and road transport. It makes the point that the choice of mode is not unrestricted. For example, motor spirit deliveries must at some stage be by road. A comparison of the rail and road risks shown in Figures A17.4(a) and (b) suggests that the risks of road transport are higher, but these graphs are for risks from actual traffic flows. Fair comparison needs to be based on a pattern of shipments which is the same for both modes. The report gives a detailed discussion but the overall conclusion is that the assessment made provides little support for a general preference for either mode on the grounds of safety.

A17.12.2 Ports

As far as regards ports, the study of the three ports found that in some limited areas near the ports individual risk was such that on the basis of the risk criteria adopted advice would be against new housing development.

The assessed societal risks are shown in Figure A17.5(a) and (b). The former shows the local societal risk for one of the ports, Felixstowe, obtained from the individual assessment for that port, and the latter the national societal risk for British ports, obtained from the simplified method described above. At none of the three ports was the local societal risk within the scrutiny zone. The national societal risk is also outside that zone.

A17.12.3 Transport of explosives

Turning to the risk from the transport of explosives, individual risk from en route transport by rail or road was not judged significant, but there was one marshalling yard where it might be.

The national societal risks from rail and road transport of explosives are shown in Figures A17.6(a) and (b), respectively. The risks from road transport are higher by an order of magnitude. This is accounted for only in part by the greater volume moved; the proximity of other road users is also a factor. As Figure A17.6 shows, for explosives the principal contributor to the assessed societal risks in rail transport is the off-site population, whereas for road transport it is the road user population. For rail the fraction of the total risk contributed by the rail users is negligible, while for road the fraction contributed by the off-site population is 2–3%. For both modes the risk lies between the tolerability and negligible risk lines. The report indicates that further scrutiny would be appropriate.

A17.13 Risk Evaluation and Remedial Measures

The ACDS report gives an assessment of individual and of local and national societal risks, identifies certain activities or situations where the risks may need to be reduced or at any rate should be subject to further scrutiny and in Appendices 7, 10 and 12 makes proposals for a number of remedial measures.

One measure of general applicability is adherence to, and enforcement of, good working practice.

There are also various measures appropriate to the particular activity. For rail, it is suggested that the design and construction of tanker wagons for motor spirit and for ammonia, the improvement of communication by provision of radio telephones and the training of train drivers should receive attention.

For road, measures suggested relate to the design and construction of road tankers, use of designated routes, movement by night, provision of improved communication and availability of information in a chemical emergency and the training of drivers. Technical measures referred to for tankers are devices to monitor tyre pressure and so reduce the risk of a tyre fire; additives for middle distillates to reduce the risks from static electricity during switch loading and cut-off devices to prevent engine overrun leading to possible ignition of vapour from spills following a tanker puncture. There may be scope for reduction of risk by the use of designated routes. Communications could be improved by provision of radio telephones. Information on the characteristics and emergency handling of chemicals carried should be available from chemical emergency information centres 24 hours a day.

For ports, the proposals made in the report include measures related to hard arm loading equipment and ESD systems, communications within the port, control of pleasure vessels and land use planning.

While many of these proposals might be made without benefit of a hazard assessment, the study provides guidance on priority areas. It identifies a number of features as meriting further scrutiny. These include the dominant contribution of motor spirit and ammonia to the en route national societal risks of rail transport and of motor spirit and LPG to those of road transport; the existence of individual risk with land use planning implications within 100 m of lorry stopover points and the national societal risk for road transport of explosives.

At least as important as the assessed levels of risk is the improved understanding of the hazards involved. An example is the relative contributions to the national societal risk in the transport of explosives of the off-site and rail or road user populations.

Also of value are the negative results from the study. For the four non-explosive materials the report states that the risks from marshalling yards are not such as to inhibit

further housing development in the zone where houses currently exist.

A17.14 Notation

$a-d$ constants
A area (m^2)
C concentration
D population density (persons/m^2)
I thermal radiation (kW/m^2)
N number of fatalities
p^o peak side-on overpressure
$P_{f|id}$ probability of fatal injury given that a person is indoors and within the cloud
P_{id} probability that a person is indoors
P_{od} A probability that a person is outdoors
t exposure time
Y probit

Equation A17.5.2
p^o peak side-on overpressure (psi)

Equation A17.5.6
C concentration of ammonia (ppm)
t time (s)

Appendix 18

Offshore Process Safety

Contents

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Any account of loss prevention needs to include some mention of offshore oil and gas activities, even if this is necessarily brief. There is a continuous interaction between developments onshore and offshore. The treatment given here is confined to an outline of offshore safety activities.

Offshore installations operate in a difficult and often hostile environment. The problems, not only of structures but also of processing, are challenging. The solution of these problems often involves technological innovation. The significance of this for safety and loss prevention is clear.

The report into the Piper Alpha disaster (Cullen, 1990), known as the *Cullen Report*, provides a wealth of detail both on the design and operation of an actual platform, albeit one of the older ones, in the North Sea and on the impact on it of a major accident event.

Accounts of offshore oil and gas are given in *Offshore Oil Technology* by Ranney (1979), *Onshore Impacts of Offshore Oil* by Cairns and Rogers (1981), *Introduction to Petroleum Development* by Skinner (1982), *Technological Guidelines for Offshore Oil and Gas Development* by Gilbert (1983), *Gas Production Operations* by Begg (1984), *Behaviour of Offshore Structures* by Battjes (1985) and *Safety in the Offshore Petroleum Industry* by Barrett, Howells and Hindley (1987) and by R.J.S. Harris (1978), Holmes and Mead (1978), Timar (1978), Shyvers (1981) and Waldie (1986).

The series of booklets by BP Petroleum Development Ltd (1990a–g) constitutes a useful starting point.

Much useful information is also given in *Offshore Installations*: *Guidance on Design, Construction and Certification* by the HSE (1990b), also called the *HSE Onshore Design Guide*.

Selected references on offshore safety are given in Table A18.1.

A18.1 North Sea Offshore Regulatory Administration

An outline of the legislation governing oil and gas activities in the UK sector of the North Sea has been given in Lees Edition 3, Chapter 3, with a summary of the principal legislation given in Table A18.2.

Two principal elements of the administration are the systems of internal control and of risk assessment. The *Guidelines for the Licencee's Internal Control 1979* describe in effect an SMS. The *Regulations Related to the Licencee's Internal Control 1985* make this a regulatory requirement.

With regard to risk assessment, the *Regulations Concerning Safety Related to Production and Installation 1976* contained a requirement that if the living quarters were to be located on a platform where drilling, production or processing of petroleum was taking place, a risk evaluation should be carried out. At this date the evaluation was largely qualitative. The move to a more quantitative approach came with the *Guidelines for Safety Evaluation of Platform Conceptual Design 1981*. These had as a central feature, the provision of a sheltered area, required the conduct of a concept safety evaluation (CSE) and specified numerical acceptance criteria.

The Guidelines defined a design accidental event as one that does not violate any of the following three criteria:

- at least one escape way from central positions which may be subjected to an accident, shall normally be intact for at least an hour during a design accidental event;

Table A18.1 *Selected references on offshore safety issues*

Offshore regulatory administration
Burgoyne (1980); Barrett, Howells and Hindley (1987); Lyons (1989); Cullen (1990); Higgs (1990); IP (1990 PUB 51, 1992 PUB 64); Petrie (1990); Priddle (1990); Barrell (1992); J.W. Griffiths (1992); HSE (1992 OTI 588); H. Hughes (1992); Lees (1992); Leiser (1992); Bibbings (1992); Heiberg-Andersen (1990); Ognedal (1990, 1994); Tveit (1990)

Offshore hazards
Leblanc (1981); Anon. (1983p); CuUen (1990); Ognedal (1990). **Wind and waves**: DoEn (1977a, 1984); HSE (1990b) ***Earthquakes:*** Cornell and Vanmarcke (1975); Wiggins, Hasselman and Chrostowski (1976); M.W. Mitchell (1983) ***Vessel-platform collisions:*** Hathway and Rowe (1981); DoEn (1984); Technica Ltd (1985); HSE (1990b); **Blowouts**: Fischer (1982); Anon. (1983b); Dahl *et al.* (1983); Goins and Sheffield (1983); Podio, Fosdick and Mills (1983); Milgram and Erb (1984); P.G. Mills (1984); Holand and Rausand (1987); Ostebo *et al.* (1989) ***Flammable gas clouds:*** HSE (1992 OTI 591); Cleaver, Humphreys and Robinson (1994) ***Ignition sources*** (see also Table 16.23): Forsth (1981a,b, 1983); Dahl *et al.* (1983); Sokolov (1989); J.G. Marshall (1989); Cullen (1990); Eckhoff and Thomassen (1994) ***Fires and explosions:*** Forsth (1981a,b, 1983); Solberg (1982a); Anon. (1983h,j,t); Dahl *et al.* (1983); Tompkins and Riffle (1983); Anon. (1985s,u); Brandie (1989b); Cullen (1990); Hjertager (1991a,b); HSE (1992 OTI 585, 586, 592, 593, 595–599); Samuels (1992); Gardner *et al.* (1994); Wighus (1994); K. van Wingerden (1994) ***Missiles:*** R.A. Cox (1989); A.C. Palmer (1989); Cullen (1990); HSE (1992 OTI 603) ***Structural loading, response:*** DoEn (1984); HSE (1990b, 1992 OTI 594, 601, 602, 608, 610); Haaverstad (1994) ***Escalation:*** D. Drysdale (1989); Cullen (1990); Four Elements Ltd (1991); M. Morris, Miles and Cooper (1994)

Offshore safety management
Brading (1989); Denton (1989,1991); Ellice (1989); Fotland and Funnemark (1989); Grogan (1989); Littlejohn (1989); Macallan (1989); McKee (1989); McReynolds (1989); G. Richards (1989); R.A. Sheppard (1989); API (1990 RP 750); Cullen (1990); J. King (1992); McKeever and Lawrenson (1992); S. Lewis and Donegani (1993); Jacobson (1994). **Command and control**: Baxendine (1989); Cullen (1990); Larken (1992)

Offshore emergency response, planning
Fischer (1982); Tompkins (1984); Baxendine (1989); Matheson (1989); Cullen (1990); Fitzgerald *et al.* (1990); R. Wilson (1992)

Offshore evacuation, escape and rescue
Booth (1989); Clayson (1989); J.D. Evans (1989); Heiberg-Andersen (1989); Jefferey (1989); Keueher (1989); Lien (1989); McNeill (1989); de la Pena (1989); Perrott (1989); Petrie (1989); Rudd (1989); Side (1989); I.G. Wallace (1989,1992); Cullen (1990); Owen and Spouge (1991); Forland (1992); Forster and Wong (1992)

Offshore safety
DoEn (1977, 1984); Burgoyne (1980); HSE (1980 HS(G) 12); Nat. Res. Coun., Cttee on Assessment of Safety of Outer

Continental Shelf Activities (1981); Dick (1982); Petrie (1983); Kaarstad and Wulff (1984); Barrett, Howells and Hindley (1987); Cullen (1990); Knott (1990); Antomakis and Barnes (1991); W.S. Atkins (1991); Bill (1991); IMechE (1991/134, 1993/157); Venn (1991); Lees (1992); J. Morgan (1992); Renwick and Tolloczko (1992); Ronold (1992); Salter (1992); Eckhoff (1994); Lode (1994); Pappas (1994); Rushton *et al.* (1994).
Safety system: Bodie (1989); Gordon (1989); McGeough (1989); Cullen (1990)
Costs of safety: HSC (1992); Potter (1994)
Injuries offshore: Wright (1986); Cullen (1990); H. Hughes (1992)

Formal safety assessment
Fjeld, Andersen and Myklatun (1978); Borse (1979); Slater, Ramsay and Cox (1981); Pyman and Gjerstad (1983); Vinnem (1983); Deaves (1986); Schrader and Mowinckel (1986); Haugen and Vinnem (1987); R.A. Cox (1989d, 1990, 1993); Ellis (1989); Ferrow (1989); Fleishman (1989); Gorse (1989); van der Graaf and Visser (1989); Hogh (1989); Pape (1989); Cullen (1990); Tveit (1990); Burns, Grant and Fitzgerald (1991); Rock and Butcher (1991); Diaz Correa (1992); Pape (1992); S.J. Shaw (1992); Sherrard (1992); Potts (1993); S.J. Shaw and Kristofferson (1993); Gardner *et al.* (1994); K Miller (1994); Pitblado (1994); Ramsay *et al.* (1994); Trbojevic *et al.* (1994)

Offshore safety cases
V.C. Marshall (1989); Sefton (1989); Cullen (1990); Mansfield (1992); Pape (1992); Wendes (1992); Barrell (1994); Bellamy (1994); Clegg (1994); Durnin (1994); H. Hughes (1994); Jacobson (1994); Salter (1994); Spence (1994); Spiller (1994); Hawker (1995); D. Scott (1995); D.J. Wilson (1995)

Offshore incidents
Le Blanc (1981); WOAD (1988); Due, McFarlane and Crowther (1994); H. Hughes (1994)
Sea Gem: R.J. Adams (1967)
Ekofisk Bravo: Gjerde (1977–78); Ognedal (1990)
Alexander Kielland: Naesheim (1981); Ognedal (1990)
Ocean Ranger: NTSB (1983 MAR-83-02); Hickman (1984)

Table A18.2 *Selected legislation of offshore*

A	**Acts**	
1934		Petroleum (Production) Act
1962		Pipelines Act
1964		Continental Shelf Act
1971		Mineral Workings (Offshore Installations) Act
1971		Prevention of Oil Pollution Act
1975		Petroleum and Submarine Pipe-lines Act
1992		Offshore Safety Act
		Offshore Safety (Protection against Victimization) Act
B	**Statutory Instruments**	
1972	SI 703	Offshore Installations (Managers) Regulations
1973	SI 1842	Offshore Installations (Inspectors and Casualties) Regulations
1974	SI 289	Offshore Installations (Construction and Survey) Regulations
1976	SI 1019	Offshore Installations (Operational Safety, Health and Welfare) Regulations
	SI 1542	Offshore Installations (Emergency Procedures) Regulations
	SI 923	Submarine Pipe-lines (Diving Operations) Regulations
1977	SI 486	Offshore Installations (Life-saving Appliances) Regulations
1978	SI 611	Offshore Installations (Fire Fighting Equipment) Regulations
	SI 1759	Offshore Installations (Well Control) Regulations
1981	SI 399	Diving Operations at Work Regulations
1989	SI 1029	Offshore Installations (Emergency Pipeline Valve) Regulations
	SI 971	Offshore Installations (Safety Representative and Safety Committees) Regulations
1992	SI 2885	Offshore Installations (Safety Case) Regulations

- the shelter area shall be intact during a calculated accidental event until safe evacuation is possible;
- depending on the platform type, function and location, when exposed to the design accidental event, the main support structure must maintain its load carrying capacity for a specified time.

The categories of potential accident event to be evaluated were specified as

(1) blowouts,
(2) fire,
(3) explosion and similar incidents,
(4) falling objects,
(5) ship and helicopter collisions,
(6) earthquakes,
(7) other possible relevant types of accident,
(8) extreme weather conditions and
(9) relevant combinations of these accidents.

The Guidelines gave explicit numerical acceptability criteria. In practical terms, it may be considered necessary to exclude the most improbable accidental events from the analysis. However, the total probability of occurrence of each type of excluded situation should not by best available estimate exceed 1 CT^4 per year for any of the main functions specified. This estimate is meant to indicate the order of magnitude to aim for, as detailed calculations of probabilities in many cases will be impossible due to lack of relevant data.

Risk assessment is now the subject of the *Regulations Relating to the Implementation and Use of Risk Assessment in the Petroleum Activities 1990*. Ognedal emphasized that the Norwegian attitude is flexible in its approach to risk assessment and tries to avoid its degenerating into a 'numbers game'.

The *Cullen Report* recommended far-reaching changes in the regulatory administration in the British sector of the North Sea. The recommendations flow from the evidence given on the Piper Alpha disaster and on the regulatory

administration up to that date. The administration envisaged is one of goal-setting rather than prescriptive regulations and of the use of QRA to demonstrate compliance. The report also recommended that an operator should submit a safety case and that this should be given structure by a requirement to demonstrate by QRA the integrity of a temporary safe refuge (TSR). Another major recommendation is that the operator demonstrate, as part of the safety case, an appropriate Safety management system (SMS). A further account of the report's recommendations in relation to the evidence on the Piper Alpha disaster is given in Appendix 19.

The recommendations of the *Cullen Report* were accepted in toto by the government and the new administration with the HSE as the regulatory body was put in place in 1991. Initial legislation under this administration includes the *Offshore Safety Act 1992* and the *Offshore Installations (Safety Case) Regulations 1992*. Development of the new administration has been described by Barrell (1992a,b).

A18.2 Gulf of Mexico Offshore Regulatory Administration

The offshore petroleum industry began in the US Gulf of Mexico in the 1950s. The Coast Guard was the original regulatory agency, but the responsibility for offshore safety was eventually transferred to the Minerals Management Service (MMS). The safety regulations are found in the *UIS Code of Federal Regulations, Title 250*.

MMS directly references many of the American Petroleum standards and recommended practice documents. The API 14 series, contain standards for subsurface safety valves, platform safety systems, piping systems, electrical systems, and fire safety systems. The API t series recommended practices for offshore staff training is also codified by the MMS.

API 14C, the recommended Practice for analysis, design and installation of basic surface safety systems on offshore production platforms was originally promulgated in 1972. API 14C embodies two very important process safety concepts;

- Every identifiable failure mode shall require two functionally independent safeguards.
- Recommended safeguards for each type of offshore process unit (pressure vessel, pump, heater, etc) were developed using a generic failure mode and effects analysis.

The documentation showing the results of a 14C approach are presented in a Safety Analysis and Functional Evaluation diagram, known as a SAFE chart. The SAFE chart is a special type of cause and effect diagram.

A18.3 Offshore Process Safety Management

In the 1990s, MMS requested voluntary adherence to the API 75 and API 14G recommended practice documents, which present process safety concepts to the offshore environment. These standards are very similar to the OSHA process safety management regulation, containing virtually identical wording in many sections.

A18.4 Offshore Safety Management

An offshore platform has both marine and process characteristics. It shares with marine vessels the hazards of severe weather and of collision and *in extremis* those of escape to the sea. At the same time it contains high pressure plant processing oil and gas. The platform is also a self-contained community with its own power plant, accommodation and other facilities. The senior manager on the platform is required in large part to combine the skills of a ship's captain with those of a refinery manager and to exercise command and control in an emergency.

A18.5 Inherently Safer Offshore Design

The processing of hydrocarbons is the *raison d'etre* of an offshore platform. This clearly sets certain limitations on the practice of inherently safer design. Nevertheless, this design principle is just as applicable offshore.

Three examples will suffice. One is reduction in the oil inventory in the production separators. The separators constitute a major oil inventory on the platform and it was the separators that fed the oil pool fire on Piper Alpha. Separators are now in use which have much reduced inventories. It may be noted in passing that evidence on the hydrocarbon inventory on Piper Alpha was given to the Inquiry by Clark (1989).

A second example is adoption of a layout that minimizes the possibility of an oil pool forming near a gas riser.

A third example concerns the potential for a jet flame from a gas riser to impinge on the accommodation. Following Piper Alpha, Shell reviewed their platforms to establish whether in each case this was a possibility (Chamberlain, 1989). In those cases where it was, action was taken.

A18.5.1 Friendly plant

Closely related is the design of plant that is friendly to the process operator. In oil and gas extraction there are strong pressures to maintain production. In these circumstances, it is highly desirable that there be fallback states of plant operation to which the operator can resort, without facing the all-or-nothing choice of continuing normal production or effecting total shut-down.

A case in point is the confidence that the operator has that shutting down the gas plant will not lead to loss of power on the main generators. Evidence at the *Piper Alpha Inquiry* appeared to indicate that in some systems fuel changeover on the generators, from gas to diesel, could not be fully relied on. If this situation exists, it puts a greater pressure on the operator to keep going.

A18.5.2 Plant layout

Offshore production platforms carry large amounts of equipment held in a small space. Space and weight are both at a premium, since they are difficult and expensive to provide. Spacing between equipment in a module has to be less generous than in onshore plants. Where a 15 m distance is widely used in the latter, the distance offshore is often half that. It is also necessary to ensure that the layout is such that the centre of gravity of the total mass of equipment is at the centre of the supporting structure. CAD packages for plant layout provide a powerful tool for achieving a layout that meets this requirement.

The decks of the platform are divided into modules. The modules are separated by fire walls which inevitably reduce the ventilation.

Layout design seeks to separate sources of hazard from vulnerable targets. The application of this principle is seen

on many platforms by the separation of the accommodation from the wellhead.

A18.5.3 Platform systems

There are a number of basic systems that are critical for safe operation of the platform. The account given here of these systems is limited to a brief overview. It is convenient to cast it as a description of the systems on Piper Alpha. The *Cullen Report* gives a detailed description of these systems and of their behaviour on the night of the disaster.

Electrical power systems

The first of the systems is the electrical power supply system. Basic power is supplied by a pair of main turbine-driven generators with dual fuel firing, gas being the normal fuel with diesel fuel as standby. As backup, there is an emergency generator, turbine-driven and diesel fuelled. Changeover of fuel on the main generator and start up of the emergency generator are automatic. Drilling is served by a separate power supply from a diesel-driven generator with its own emergency generators.

The emergency generator for the main supply is designed to provide supply to critical services, which include HVAC, instrumentation and valves, and emergency lighting. Further backup is provided by an uninterruptible power supply (UPS) drawn from batteries designed to provide power during the momentary interruption while the emergency generator starts up and, if necessary, for a period in the event of total failure of the main supply.

Electrical systems for offshore production platforms are the subject of API RP 14F: 1991.

Fire protection system

The fire protection system comprises a number of complementary elements. These are

- hazardous area classification,
- fire walls,
- fire and gas detection system,
- fire water deluge system,
- fire pumps,
- foam system,
- Halon or clean agent systems and
- fire fighting arrangements.

Fire prevention and control on offshore production platforms is covered in API RP 14G: 1986.

The first line of defense against fire is the use of hazardous area classification to reduce the risk of ignition of any flammable leak that may occur. This was formerly covered by API RP 500B: 1973, specific to offshore, which is now replaced by the general onshore and offshore code RP 500: 1991.

The traditional form of active fire protection is the water deluge system. This is covered by the NFPA Fire codes, *Construction and Use Regulations 1974* and the associated guidance in the *Offshore Design Guide*. The plant is divided into reference areas with a specified quantity of water to be delivered over each area. In order to limit the size of the reference areas use is made of firewalls. There are firewalls between the main production modules, namely the wellhead, separation and gas compression modules. These provide basic passive fire protection. They are not necessarily designed as blast walls.

There is an extensive fire and gas (F&G) detection system, with sensors in the main production modules and elsewhere, utilizing both combustible gas detectors and fire detectors.

A fixed water deluge system with distribution throughout the main modules and at the risers furnishes a basic level of active fire protection. Water for the deluge system is drawn from the sea by fire pumps operating off the main power supply but with diesel-driven pumps as standby.

At locations where an oil pool fire may occur, such as the production separators, foam injection is provided.

Certain closed volumes may be provided with a halon total flooding system. Enclosures which may be protected in this way include the centrifugal compressor enclosures, the generator area, the electrical switchgear room and the control room. Where, as in the latter case, operators may be present, a non-toxic agent is used and there is prior alarm. These fixed systems are supplemented by the fire fighting teams.

As just indicated, the traditional means of fire protection has been passive protection by firewalls and active protection by a uniform water deluge. Alternative approaches have tended to be inhibited by the need to comply with the two separate sets of regulations covering fire, one requiring passive and the other active fire protection measures.

In addition to the trade-off between passive and active fire protection, there may also be a trade-off between ventilation and active fire protection. If a module is well ventilated, gas from a leak is less likely to accumulate in the first place.

A plea for greater flexibility was made to the *Piper Alpha Inquiry* by Brandie (1989b), who advocated a scenario-based approach in which specific fire hazards are identified and water deluge arrangements directed more specifically to these scenarios. The *Cullen Report* recommended this approach within the context of *Safety Case*.

There are a number of issues related to fire protection. One is the availability of standard fire tests for hydrocarbon, as opposed to building, fires, such tests being needed for design of fire walls. Another is the use of passive fire protection on risers, which might involve a risk of corrosion beneath the lagging.

Another long-standing issue, which relates to active fire protection, is the availability of the fire pumps.

There is generally a strong argument for the use of passive fire protection in that once installed it appears less subject to human failings. The matter is not, however, straightforward. Thus, for example, in some applications corrosion may occur under fireproofing, which may both promote the corrosion and conceal it.

There is now considerable activity in the investigation of fire events on platforms, covering oil pool fires and jet flames; impingement of flames on vulnerable targets such as risers and passive protection of these targets. Further details are given in Section A18.7.

A18.5.4 Emergency shut-down system

The platform is provided with an emergency shut-down (ESD) system, the main functions of which are (1) to shut down the flow from the reservoir, (2) to shut off the flow through the pipelines entering and leaving the platform, (3) to shut down the main items of equipment and (4) to initiate blow-down of the inventories to flare. There are various levels of ESD, some involving only individual items of equipment and others a full platform ESD, or PESD. Physically, PESD may be activated from the control room or from any of a number of emergency pushbuttons around the platform.

As important as the hardware are the procedures that govern operation of the PESD system. It bears emphasis that the protection apparently afforded can be negated if there are cultural, organizational or human factors which inhibit initiation of the system in a real emergency.

A18.5.5 Evacuation, escape and rescue system

The evacuation, escape and rescue (EER) system is built around the three main means of leaving the platform, which are (1) helicopter, (2) lifeboat and (3) liferaft. The emergency procedure is for personnel to collect at designated muster points. In the vast majority of cases evacuation is by helicopter, personnel being summoned to the helideck from their muster points. There are a number of reasons, however, why evacuation by helicopter may be impractical. They include high winds and smoke from the platform, which can prevent landing. Another is the time taken to reach the platform. A helicopter already in or near the field may arrive relatively quickly but in many locations it takes about an hour for a helicopter to travel from an onshore base.

If helicopter evacuation is not practical, the other main means of getting off the platform is by lifeboat. The use of lifeboats is also subject to limitations. Lifeboats may sometimes be difficult to reach and have limitations in high seas. Even if the conditions do not actually prevent use, they may increase the risk of injuries.

If the lifeboats cannot be used, resort is to escape to the sea by launching liferafts and climbing down knotted ropes. The use of knotted ropes requires a certain degree of fitness and is not without risk. One area of development has been improved lifeboat systems. Prominent among these is the freefall lifeboat, which is launched with its complement straight into the water, as opposed to being lowered from davits. These have been in use on Norwegian platforms and are the method used on the replacement for Piper Alpha, Piper Bravo.

A variety of devices have become available for escape, ranging from individual packages which can be hooked onto a guard rail to chutes and slides.

Another aspect is the integrity of the escape routes from locations where personnel are likely to be to the means of escape. Escape routes need therefore to be designed against a variety of scenarios. Of particular importance are the routes to the lifeboats from the accommodation, where at any given time a large proportion of the personnel will be. One approach is to locate lifeboats in a protected area integral with the accommodation.

The *Piper Alpha Inquiry* heard a considerable amount of evidence on evacuation, escape and rescue. Contributors included Petrie (1989) (life-saving appliances), Rudd (1989) and Heiberg-Andersen (1990) (evacuation), Ginn (1989) (evacuation by helicopter), Kelleher (1989) (lifeboats), Side (1989) (evacuation and rescue), I.G. Wallace (1989) (evacuation and escape), Lien (1989) and Perrott (1989) (escape systems), Booth (1989) (escape routes) and J.D. Evans (1989) and de la Pena (1989) (smoke hoods). Work in this area has been described by Bellamy and Harrison (1988), Forland (1992), Forster and Wong (1992) and I.G. Wallace (1992).

A18.5.6 Explosion protection

In many earlier platform designs, there was little protection against explosion over and above that against fire, namely partition walls being designed as firewalls rather than as blast walls. This situation no longer pertains and much effort is being devoted to explosion protection. CFD simulation is being used to study the overpressures generated by explosions in modules, with particular reference to the enhancing effect of obstacles and to the mitigating effects of venting and of water spray systems.

A large amount of work has been done on the development and venting of explosions in modules and other obstructed spaces. Much of the work using CFD explosion simulation codes has been directed to the offshore module situation. Representative work using such codes is that of Hjertager (1982a, 1986, 1991), Bakke *et al.* (1989), Catlin (1990) and Hjertager *et al.* (1994). Examples of work on module explosions includes that described by Solberg, Pappas and Skramstad (1980, 1981), A.J. Harrison and Eyre (1987b), Catlin (1991), Brenton, Thomas and Al-Hassan (1992), Samuels (1992, 1993), Catlin, Manos and Tite (1993) and Catlin *et al.* (1993). A fuller account is given in Chapter 17.

Blast walls

An increasingly common method of explosion protection is the use of blast walls. The design of a blast wall is partly a matter of formulating suitable accident scenarios and predicting by simulation the resultant overpressure and partly one of engineering the wall so that it fulfils its protective function even if it deforms somewhat.

An account of the design of the blast walls on the Kittiwake platform was given to the *Piper Alpha Inquiry* by Doble (1989). The engineering of blast walls was described by van Beek (1989).

Smoke minimization and protection

Another area of work is the investigation of the hazard presented by smoke, particularly that from an oil pool fire. Aspects of this are the generation and movement of smoke and the exclusion of smoke from the accommodation.

A18.5.7 Design basis accidents

The design of plant to cope with accidental events requires that there be defined a set of design basis accidents. The concept is that the plant is then designed to withstand the design basis accidents in each category but does not have to be designed for events more severe than this. The selection of the design basis accidents is therefore closely linked with the estimates for the frequency of such events, so that overall risk in the design is an appropriate one.

Drilling

Drilling is a major activity on the platform that has no counterpart onshore. One aspect of this activity is the ever-present hazard of a well blowout.

Another aspect that can impinge on the operation of the platform as a whole is the need to avoid loss of power such that the drill becomes stuck.

Diving

Diving is another activity specific to an offshore platform. For the most part it does not impinge to any major extent on other activities except in so far as precautions are necessary to ensure the safety of the divers. At the time of the explosion on Piper Alpha the fire pumps had been turned to manual start to prevent sudden start-up of the pumps with consequent danger of a diver being drawn into the pump

water inlet. This was not the policy on the sister platform Claymore, run by the same operator and in the same field.

Contractors

The proportion of contractors on a platform may well be of the order of 70% or more. Typically specialist teams such as drillers and divers are contractors with one person from the operating company as liaison. Some contractors may remain on a platform for long periods, others come and go. The operating company attempts to ensure the quality of contractors admitted to the platform by means of a quality assurance system. Personnel from the company visit the contractor company onshore and make the usual quality assurance audit.

It is the responsibility of a contractor to ensure that its personnel are properly trained in offshore emergency procedures as well as in safe systems of work and PTW systems. However, there may well be features of the systems operated on a platform that are particular to that platform. The operator needs, therefore, to ensure that contractors within its system are familiar with them.

A18.6 Offshore Emergency Planning

Offshore emergency planning has the same broad features as that for onshore. In principle, they include the detection of the incident, the assessment of its nature and seriousness and if necessary, the declaration of the emergency, the assumption of command and control, and the implementation of the emergency plan.

However, the emergency may not present in this ideally structured form. It may well take the form of an emergency shut-down initiated automatically or by personnel in the control room or at one of the shut-down buttons scattered throughout the platform.

A18.6.1 Emergency scenarios

The first step in emergency planning is the definition of the set of scenarios on which the plan is to be based. A wide range of scenarios need to be considered if the plan is to be robust. It is not uncommon for an incident to require the evacuation of the platform, but in the vast majority of cases this will be by helicopter and management may well feel it has not done as well as it might if even one person is injured.

At the other extreme is the sort of situation that arose on Piper Alpha where there was no prospect of an evacuation by any of the conventional means and where escape to the sea was the only option. This implies that the person in command explicitly instruct personnel to make their own escape.

A18.6.2 Goal-setting regulations

The basic framework operated in the new offshore safety administration is that of regulations which are goal-setting rather than prescriptive.

The first set of regulations of the new offshore administration are the *Offshore Installations (Safety Case) Regulations 1992*.

Before considering these, it is interesting to note that the first regulations issued, by the DoEn, in the wake of the Piper Alpha disaster were the *Offshore Installations (Pipe-line Valve) Regulations 1989*, which require the operator to fit EIVs to the pipelines connected to the platform and are thus prescriptive. The *Cullen Report* explicitly endorsed this, in effect considering that exceptionally this case met the conditions for adopting a prescriptive regulation.

A18.6.3 Safety case

The *Offshore Installations (Safety Case) Regulations 1992* implement Recommendation 1 of the Cullen Report that the operator should submit to the regulator a safety case.

For major hazard installations onshore a requirement for a safety case already existed under the *CIMAH Regulations 1984*. Evidence on the onshore safety case was given to the *Piper Alpha Inquiry* by Sefton (1989) and V.C. Marshall (1989d).

The offshore safety case is largely modelled on the onshore case, but has three features not explicitly contained in the latter.

Safety management system

One of these is the requirement on the operator to demonstrate that it has an SMS, which will assure the safety of the project through the design and operation. The SMS is thus part of the safety case rather than a free-standing requirement.

Temporary safe refuge

The second distinguishing feature of the offshore safety case is the requirement that the platform has a TSR, normally the accommodation, which should provide protection for a defined period. Design of a TSR involves the definition of the events against which it is to provide protection and specification both of the endurance period and the conditions which constitute failure.

Quantitative risk assessment

The third distinguishing feature of the offshore safety case is the requirement to use QRA. Essentially the QRA is a matter for the operator. The *Cullen Report* does, however, propose that one aspect of it be specified by the regulator.

The *Safety Case* involves a demonstration that the frequency of events that threaten the endurance of the accommodation, or TSR, will not exceed a certain value. In order to provide at least one fixed point in the administration, both the minimum endurance and the frequency with which there is a failure of such endurance should be specified by the regulatory body, at least in the first instance.

Accounts of offshore QRA include those of Pape (1992) (regulator), Sherrard (1992) (drillling units), R.F. Evans (1994) (model validation) and Gardner *et al.* (1994) (methodology).

A18.6.4 Costs of offshore safety

In the wake of Piper Alpha the offshore industry has incurred major expenditure to enhance safety. Much of this was incurred in response to the disaster itself and before the Cullen Report appeared.

The HSE itself has made a comparison of the quantifiable costs and benefit of safety measures in the UK North Sea expressed as Net Present Value over 15 years (HSC, 1992). It attributes the bulk of both costs and benefits to the *Safety Case Regulations*, the costs being estimated at £1200–2500 million and the benefits at £2600–4600 million. A commentary on these estimates is given by Potter (1994).

A18.7 Offshore Event Data

As for onshore installations, information on offshore events is of two main types: (1) incident data and (2) equipment failure data. The *World-wide Offshore Accident Databank (WOAD, 1988)* enumerates the principal accidents involving offshore structures involved in oil and gas activities. There is also a need, particularly in hazard assessment, for more detailed information on events such a leaks, fires and explosions, dropped loads and so on. The HSE has created the HCR database, as described by Bruce (1994).

Equipment failure data collection is the subject of a major co-operative exercise carried out under the aegis of OREDA and initiated some years before Piper Alpha. This is described in Appendix 14.

Appendix 19 Piper Alpha

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At 10.00 p.m. on 6 July 1988 an explosion occurred in the gas compression module of the Piper Alpha oil production platform in the North Sea. A large pool fire took hold in the adjacent oil separation module, and a massive plume of black smoke enveloped the platform at and above the production deck, including the accommodation. The pool fire extended to the deck below, where after 20 min it burned through a gas riser from the pipeline connection between the Piper and Tartan platforms. The gas from the riser burned as a huge jet flame. Most of those on board were trapped in the accommodation. The lifeboats were inaccessible due to the smoke. Some 62 men escaped, mainly by climbing down knotted ropes or by jumping from a height, but 167 died, the majority in the quarters.

The Piper Alpha explosion and fire was the worst accident which has occurred on an offshore platform.

Following the disaster a Public Inquiry was set up under the Public Inquiries Regulations – Offshore Installations Regulations 1974 presided over by Lord Cullen to establish the circumstances of the disaster and its cause and to make recommendations to avoid similar accidents in the future. The Inquiry's report *The Public Inquiry into the Piper Alpha Disaster* (the *Piper Alpha Report,* or *Cullen Report*) (Cullen, 1990) is the most comprehensive inquiry conducted in the United Kingdom into an offshore platform disaster, or indeed into any process industry disaster, onshore or offshore.

The Piper Alpha Inquiry has been of crucial importance in the development of the offshore safety regime in the UK sector of the North Sea. Whereas Flixborough was followed first by a Court of Inquiry and then by the Advisory Committee on Major Hazards, the Piper Alpha Inquiry not only discharged the function of an inquiry into the specific disaster, but made recommendations for fundamental changes to the offshore safety regime which were accepted by the government.

The description of the Piper Alpha disaster given below is necessarily a relatively brief one. Nevertheless, it is somewhat fuller than that of the case histories in the other appendices, for several reasons. It provides a good illustration of the work of an accident inquiry. It is replete with lessons on design and operation of hazardous installations. And it has had far-reaching consequences for the offshore safety regime. A fuller account is given in the *Piper Alpha Report*. The daily transcripts, available in copyright libraries, also repay study. An account from the viewpoint of one of the consultants to the Inquiry has been given by Sylvester-Evans (1991).

Selected references on Piper Alpha are given in Table A19.1.

A19.1 The Company, the Management and the Personnel

The Piper Alpha oil platform was owned by a consortium consisting of Occidental Petroleum (Caledonia) Ltd, Texaco Britain Ltd, International Thomson plc and Texas Petroleum Ltd and was operated by Occidental.

The management concerned with the Piper platform included

Offshore Installation Manager	Mr C.D. Seaton
Offshore Superintendent	Mr T.J. Scanlon
Senior Maintenance Superintendent	Mr R.H. Seddon
Maintenance Superintendent	Mr K.D. White
	Mr A.C.B. Todd

Table A19.1 *Selected references on Piper Alpha*

Report of the Public Inquiry
Cullen (1990)

Part 1 Evidence
F.H. Atkinson (1989) (Lloyds Register); Bakke (1989) (explosion simulation); Balfour (1989) (gas detectors); Bett (1989) (reciprocating compressors); Bodie (1989) (Offshore Safety Superintendent); Bollands (1989) (Control Room Operator); Brading (1989) (Chairman, Occidental Petroleum (Caledonia) Ltd); Burns (1989) (Shift Supervisor, MCP01); A.G. Clark (1989) (Maintenance Lead Hand); M.R. Clark (1989) (hydrocarbon inventory); Clayson (1989) (evacuation, escape and rescue); R.A. Cox (1989a) (damage to firewall, explosion simulation); R.A. Cox (1989b) (damage by projectiles); R.A. Cox (1989c) (damage to electrical systems, ESD, F&G, fire protection systems); R.A. Cox (1989d) (damage to risers); Cubbage (1989) (explosion effects analysis); J. Davidson (1989) (Operations Superintendent, Claymore); M.E. Davies (1989) (wind tunnel modelling of gas dispersion); D.D. Drysdale (1989) (escalation of fire); J. Drysdale (1989) (hydrates, methanol injection); Gordon (1989) (Manager, Loss Prevention Dept); P.M. Grant (1989) (contractors); Grieve (1989) (Process Operator); Grogan (1989) (Vice-President Engineering, Occidental); Guiomar (1989) (OIM, MCP01); Henderson (1989) (Lead Operator); Jefferey (1989) (liferafts); Jenkins (1989) (DoEn Inspector); Johnsen (1989) (hydrates, methanol injection); Leeming (1989) (OIM, Tartan); P. Lloyd (1989) (electrical systems); Lockwood (1989) (Lead Production Operator, permits-to-work); Macallan (1989) (Production and Pipeline Manager); A.G. McDonald (1989) (telecommunications); McGeough (1989) (safety training); McLaren (1989) (Lloyds Register, electrical); McNeill (1989) (rescue); McReynolds (1989) (Vice-President Operations, Occidental); J.G. Marshall (1989) (ignition sources); Moreton (1989) (Production Supervisor, Tartan); J. Murray (1989) (gas detectors); A.C. Palmer (1989) (damage by projectiles); Paterson (1989) (hydrates, methanol injection); Petrie (1989) (Director of Safety, DoEn); Pillans (1989) (Lloyds Register, electrical); Rankin (1989) (supervisor, Score PSV certification team); G. Richards (1989) (OIM (back-to-back)); S.M. Richardson (1989a) (hydrates, methanol injection); S.M. Richardson (1989b) (gas pipelines); S.M. Richardson (1989c) (autoignition); S.M. Richardson (1989d) (leaks); Ritchie (1989) (Managing Director, Score UK Ltd); K. Roberts (1989) (Facilities Engineer, Tartan); G.G. Robertson (1989) (Safety Supervisor); J.B. Russell (1989) (hydrates, methanol injection); Saborn (1989) (standby vessel); Sandlin (1989) (OIM, Claymore); Saville (1989a) (condensate admission to PSV 504 system); Saville (1989b) (leaks); Saville (1989c) (hydrates, methanol injection); Saville (1989d) (pipe failure); Scanlon (1989) (Offshore Superintendent, maintenance); Scilly (1989) (explosion effects analysis); Scothern (1989) (gas detectors); Seddon (1989) (Senior Maintenance Superintendent); Smyllie (1989) (flare); Tea (1989) (gas detectors); Thomson (1989) (Lloyds Register); Todd (1989) (Maintenance Superintendent); Tucker (1989) (accommodation); P.C.A. Watts (1989) (flare); Whalley (1989) (PSV recertification); W.P. Wood (1989) (DoTp surveys); Wottge (1989) (platform, facilities and systems)

Part 2 Evidence
A.J. Adams (1989) (pipeline isolation, inc. subsea isolation valves); C.S. Allen (1989) (PTWs); Ashworth(1989) (process control and ESD); Banks (1990) (maintenance supervisors); Baxendine (1989) (emergency command); van Beek (1989) (blast walls); Booth (1989) (escape routes); Brandie (1989a) (safe havens); Brandie (1989b) (alternatives to standard fire water systems); Broadribb (1989) (subsea isolation valves); Chamberlain (1989) (mitigation of vapour cloud explosions); R.A. Cox (1989c) (QRA); Cunningham (safety representatives); Dalzell (1989) (smoke ingress into accommodation); Daniel (1989) (standby vessels); G.H. Davies (1989) (PTWs); Day (1989) (emergency power); Denton (1989) (quality management systems); Doble (1989) (explosion prevention and mitigation – Kittiwake); Drew (1989) (standby vessels); Ellice (1989) (training of OIMs); Ellis (1989) (HSE view of QRA); J.D. Evans (1989) (smoke hoods); Ferrow (1989) (FSA); Fleishman (1989) (Gyda safety evaluation); Gilbert (1989) (subsea isolation valves); Ginn (1989) (evacuation by helicopter); Gorse (1989) (FSA); Heiberg-Andersen (1990) (evacuation, Norwegian sector); Higgs (1990) (offshore safety regime); Hodgkins (1989) (HSC – DoEn Agency Agreement); Hogh (1989) (QRA); M.J. Jones (1990) (training); Keenan (1989) (standby vessels); Kelleher (1989) (lifeboats); Kinloch (1989a) (PTW); Kyle (1989) (PTWs); Lien (1989) (escape systems); Littlejohn (1990) (offshore supervisors); Lyons (1989) (offshore safety regime); McIntosh (1989) (fire and explosion protection); McKee (1990) (safety management); Macey (1989) (standby vessels); Matheson (1989) (offshore emergency medical team); V.C. Marshall (1989d) (safety cases); Middleton (1989) (standby vessels); Nordgard (1990) (accommodation in Norwegian sector); Ognedal (1990) (Norwegian offshore safety regime); Pape (1989) (HSE view on QRA); de la Pena (1990) (smoke hoods); Perrott (1989) (escape systems); Petrie (1989, 1990) (life-saving appliances, offshore safety regime); Priddle (1990) (offshore safety regime); Rimington (1990) (onshore safety regime); Rudd (1989) (evacuation); Scanlon (1989) (PTWs); Sefton (1989) (CIMAH, safety cases); R.A. Sheppard (1989) (safety management); Side (1989) (rescue and evacuation); Spouge (1989) (options for accommodation); B.G. Taylor (1989) (offshore industry developments); Tveit (1990) (Norwegian offshore safety regime, QRA); Vasey (1989) (mitigation of module explosions); I.G. Wallace (1989) (evacuation and escape); Willatt (1989) (offshore pipeline connections)

Further accounts
Anon. (1988g); Johnsen (1989, 1990); Boniface (1990a,c–e); Redmond (1990, 1991 LPB 102); S.M. Richardson, Saville and Griffiths (1990); Sylvester-Evans (1990a,b, 1991); Tombs (1990); Lees (1991,1992a, 1994b)

Other personnel on duty on the evening of July 6 and referred to below include

Lead maintenance hand	Mr A.G. Clark
Lead production operator	Mr R.A. Vernon
Phase 1 operator	Mr R.M. Richard
Phase 2 operator	Mr E.C. Grieve
Control room operator	Mr G. Bollands
Instrument technician	Mr W.H. Young

A19.2 The Field and the Platform

The Piper Alpha platform was located in the Piper field some 110 miles north-east of Aberdeen. The platforms in the field and the pipeline connections between them are shown in Figure A19.1.The Piper platform separated the fluid produced by the wells into oil, gas and condensate. The oil was pumped by pipeline to the Flotta oil terminal in the Orkneys, the condensate being injected back into the oil for transport to shore. The gas was transmitted by pipeline to the manifold compression platform MCP-01, where it joined the major gas pipeline from the Frigg Field to St Fergus.

There were two other platforms connected to Piper Alpha. Oil from the Claymore platform, also operated by Occidental, was piped to join the Piper oil line at the 'Claymore T'. Claymore was short of gas and was therefore connected to Piper Alpha by a gas pipeline so that it could import Piper gas. Oil from Tartan was piped to Claymore and then to Flotta and gas from Tartan was piped to Piper and thence to MCP-01.

Elevation views of the Piper Alpha platform, the layout of the production deck at the 84 ft level and the layout of the deck below, the 68 ft level, are shown in Figures A19.2, A19.3 and A19.4 respectively. The production deck level consisted of four modules, Modules A–D. A Module was the wellhead, B Module the oil separation module, C Module the gas compression module and D Module the power generation and utilities module.

A Module was about 150 ft long east to west, 50 ft wide north to south and 24 ft high. The other modules were of approximately similar size. There were firewalls between A and B Modules, between B and C Modules and between C and D Modules (the A/B, B/C and C/D firewalls, respectively); these firewalls were not designed to resist blast.

The pig traps for the three gas risers from Tartan and to MCP-01 and Claymore were on the 68 ft level. Also on this level were the dive complex and the JT flash drum, the condensate suction vessel and the condensate injection pumps.

There were four accommodation modules: the East Replacement Quarters (ERQ), the main quarters module; the Additional Accommodation East (AAE); the Living Quarters West (LQW) and the Additional Accommodation West (AAW).

The control room was in a mezzanine level in the upper part of D Module. It was located about one quarter of the way along the C/D firewall from the west face.

There were two flares on the south end of the platform, the east and west flares, and there was a heat shield around A Module to provide protection against the heat from the flares.

Platform systems included the electrical supply system, the fire and gas detection system, the fire water deluge system, the emergency shut-down system, the communications system and the evacuation and escape system.

Electrical power was supplied by two main generators which normally ran off the gas supply but could be fired by diesel. There was a diesel-fired emergency generator and also a drilling generator and an emergency drilling generator. In addition, there were uninterrupted power supplies for emergency services.

The main production areas were equipped with a fire and gas detection system. In C Module the gas detection system was divided into five zones: C1 and C2 in the west and east halves of the module and C3, C4 and C5 at the three compressors, respectively.

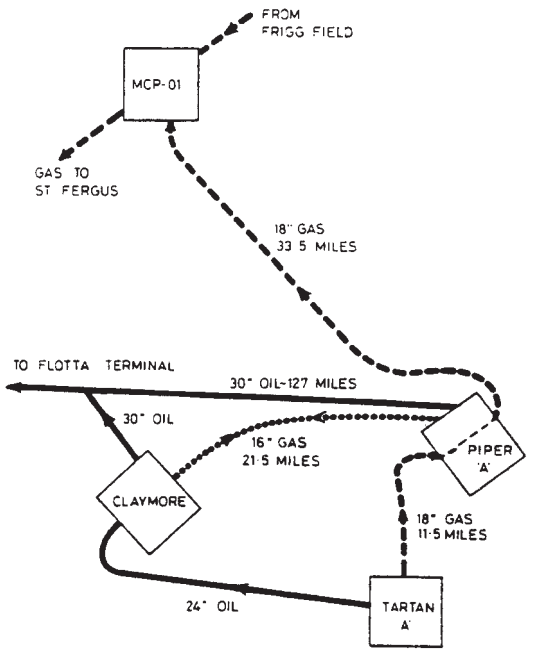

Figure A19.1 *Pipeline connections of the Piper field (Sylvester-Evans, 1991)(Courtesy of the Institution of Chemical Engineers)*

The fire water deluge system consisted of ring mains which delivered foam in A–C Modules and part of D module and at the Tartan and MCP-01 pig traps and water at the condensate injection pumps. The fire pumps were supplied from the main electrical supply but there were backup diesel-driven pumps.

The hydrocarbon inventory in the pipelines was approximately as follows. The main oil line was 30 in. in diameter and 30 miles long and held some 70,000 te of oil. The gas line from Tartan was 18 in. in diameter and 11.5 miles long and held some 450 te; the gas line to MCP-01 was 18 in. in diameter and 33.5 miles long and held 1280 te; the gas line to Claymore was 16 in. in diameter and 21.5 miles long and held 260 te.

A19.3 The Process and the Plant

The fluid from the wellhead, containing oil, gas, condensate and water, passed through the wellhead 'Christmas trees' to the two separators where the gas was separated from the oil and water. The oil was then pumped into the main oil line. The gas was compressed first in three centrifugal compressors to 675 psia, with some gas being taken off at this point as fuel gas for the main generators, and then boosted in the first stage of two reciprocating compressors to 1465 psia. Condensate was removed and the gas was then further compressed in the second stage of the reciprocating compressors to 1735 psia. The gas then went three ways: to serve as lift gas at the wells, to MCP-01 as export gas or to flare. The plant could be operated in two modes, which affected the method of removing condensate. In the normal, or phase 2, mode, the gas passed from the first stage of the reciprocating compressors to the Gas Conservation Module (GCM), where it was dried. The gas was then cooled by reducing the pressure across a turboexpander so that condensate was knocked out by the expansion and returned to the outlet of the JT flash drum, which was also the inlet of the second stage of the reciprocating compressors. Condensate from the GCM was passed to the JT flash drum. The process could also revert to the original, or phase 1 mode, dating from a period before the GCM was installed to produce export quality gas, in which the GCM was isolated and gas from the first stage of the reciprocating compressors was let down in pressure across the JT valve into the JT flash drum so that condensate was knocked out by the Joule–Thomson (JT) effect and then passed as before into the second stage of the reciprocating compressors. Condensate from the JT flash drum passed first to two parallel centrifugal condensate booster pumps and then to two reciprocating condensate injection pumps which pumped the condensate into the main oil line. There was normally one condensate injection pump line operating and one on standby.

Each condensate injection pump was protected from overpressure on the delivery side by a single pressure safety valve (PSV). The PSV was on a separate relief line from the delivery head of the pump rather than on the delivery line itself. The valve on A pump was PSV 504 and that on B pump PSV 505. These valves were located in C Module, the relief line running up from the 68 ft level, where the pumps were located, to the PSVs in C Module and back down to the condensate suction vessel on the 68 ft level.

In accordance with standard practice, methanol was injected into the process at various points to prevent formation of hydrates which would tend to cause blockages.

A19.4 Events Prior to the Explosion

On 6 July there was a major work programme on the platform. This included the installation of a new riser for the Chanter field and work on a prover and metering loop.

The extra accommodation for the workforce was provided on the Tharos, a large floating fire fighting vessel anchored near the platform. Also near the platform were the standby vessel, the Silver Pit, a pipeline vessel, the Lowland Cavalier, and Maersk anchor handling vessels for the Tharos.

The GCM was also out of service for changeout of the molecular sieve driers. In consequence, the plant operation had reverted to the phase 1 mode so that the gas was relatively wet.

The resulting increased potential for hydrate formation was recognized by management onshore. The increased methanol injection rates required were calculated and communicated to the platform together with suggestions for the configuration of the methanol pumps. The methanol injection rates needed were some 12 times greater than for normal phase 2 operation.

However, there was an interruption of the methanol supply to the most critical point, at the JT valve, between 4.00 and 8.00 p.m. that evening.

The operating condensate injection pump was B pump. The A pump was down for maintenance. There were three maintenance jobs to be done on this pump: (1) a full 24 month preventive maintenance (PM), (2) repair of the pump coupling and (3) recertification of PSV 504. In order to carry out the 24 month PM, the pump had been isolated

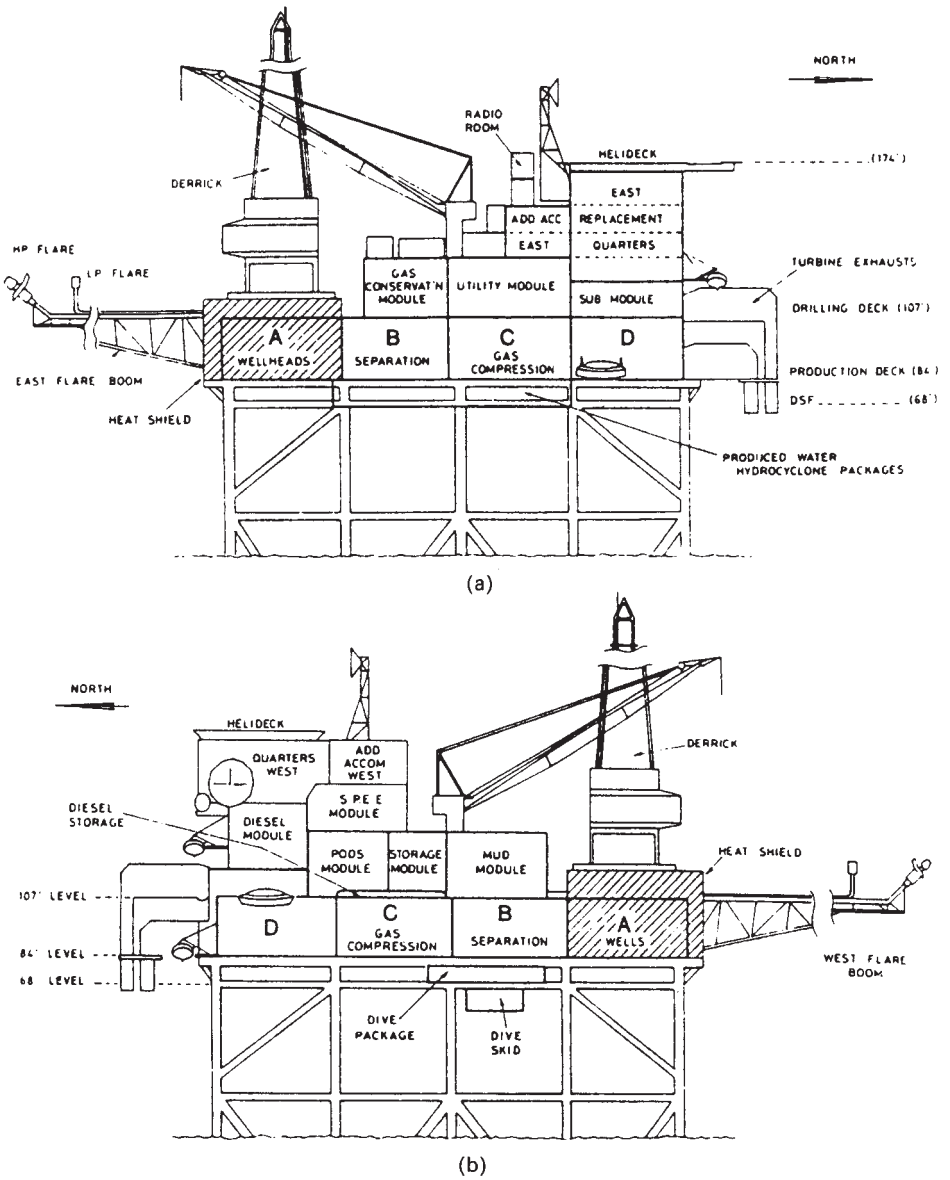

Figure A19.2 *The Pipe Alpha platform: (a) east elevation and (b) west elevation (Sylvester-Evans,1991) (Courtesy of the Institution of Chemical Engineers)*

by closing the gas operated valves (GOVs) on the suction and delivery lines but slip plates had not been inserted. Work on the coupling, which was suffering from a vibration problem, would not involve breaking into the pump.

With the pump in this state, with the GOVs closed but without slip plate isolation, access was given to remove PSV 504 for testing. It was taken off in the morning of July 6 by a two-man team from the specialist contractor Score UK Ltd. They were not able to restore the PSV that evening. The supervisor in this team came back to the control room some time before 6.00 p.m. to suspend the permit-to-work (PTW) and the team then went off duty, intending to put the PSV back the next day.

At about 4.50 p.m. that day, just at shift changeover, the maintenance status of the pump underwent a change. The maintenance superintendent decided that the 24 month PM would not be carried out and that work on the pump should be restricted to the repair of the pump coupling.

About 9.50 p.m. that evening B pump on the 68 ft level tripped out. The lead production operator and the phase 1 operator attempted to restart it but without success. The loss of this pump meant that with A pump also down

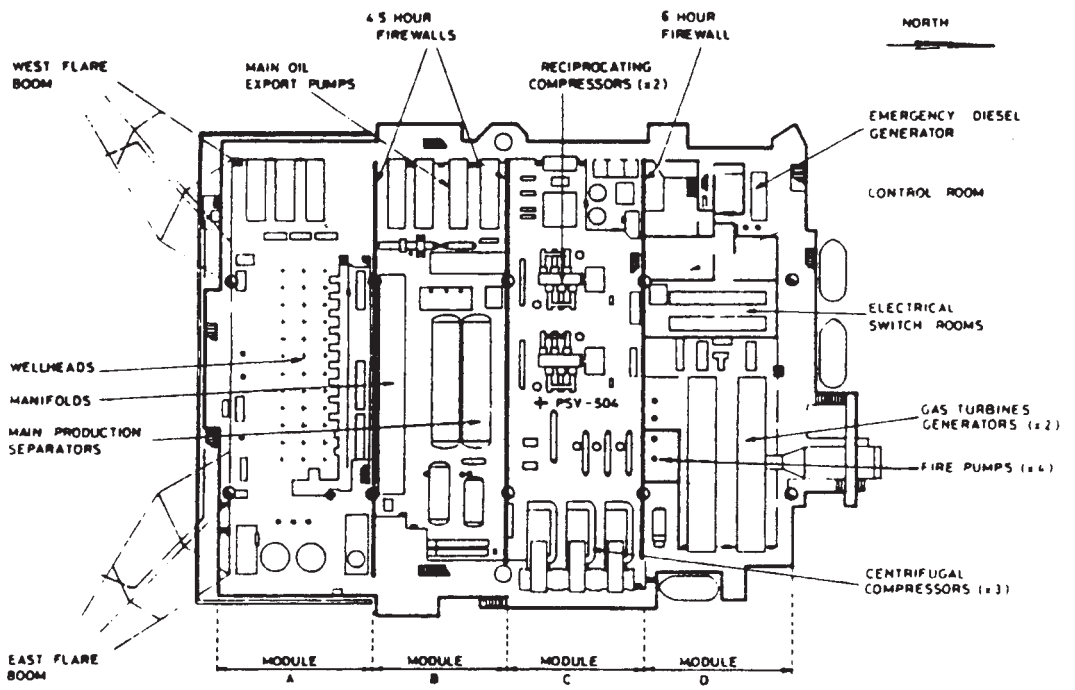

Figure A19.3 *The Piper Alpha platform: the production deck on the 84 ft level (Sylvester-Evans,1991) (Courtesy of the Institution of Chemical Engineers)*

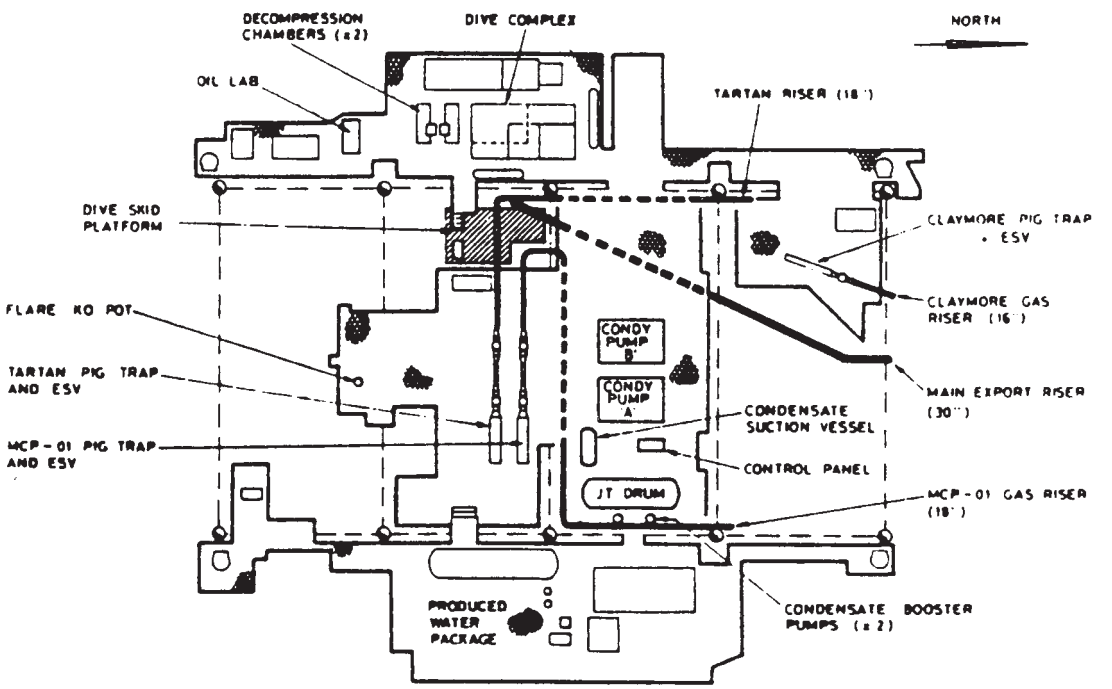

Figure A19.4 *The Piper Alpha platform: the 68 ft level (Sylvester-Evans,1991) (Courtesy of the Institution of Chemical Engineers)*

condensate would back up in the JT flash drum and within some 30 min would force a shut-down of the gas plant. There was a possibility that if the gas supply to the main generator was lost and if the changeover to the alternative diesel fuel failed, the wells also would have to be shut-down. It would then be necessary to undertake a 'black start'.

The lead operator came up to the control room. He talked on the telephone with the lead maintenance hand and it was agreed to attempt to start A pump. The lead operator signed off the permit for A pump so that it could be electrically deisolated and restarted, and went back down to the pumps. The lead maintenance hand came down to the control room to organize the electricians to deisolate the pump. It is uncertain precisely what action the lead operator and the phase 1 operator took. They were observed at the pumps by the phase 2 operator and an instrument fitter, but the evidence of these witnesses was inconclusive. However, there was no doubt that the lead operator intended to start A pump.

About 9.55 p.m. the signals for the tripping of two of the centrifugal compressors in C Module came up in the control room. This was followed by a low gas alarm in C3 zone on C centrifugal compressor. Then, the third centrifugal compressor tripped. Before the control room operator could take any action a further group of alarms came up: three low gas alarms in zones C2, C4 and C5 and a high gas alarm. The operator had his hand out to cancel the alarms when he was blown across the room by the explosion.

Just prior to the explosion personnel in workshops in D Module heard a loud screeching sound which lasted for about 30 s.

A19.5 The Explosion, the Escalation and the Rescue

The initial explosion occurred at 10.00 p.m. It destroyed most of the B/C and C/D firewalls and blew across the room the two occupants of the control room, the control room operator and the lead maintenance hand.

The emergency shut-down (ESD) system operated, closing the emergency shut-off valve (ESV) on the main oil line and starting blowdown of the gas inventories to flare. The ESVs on the gas pipelines were not designed to close on platform ESD; this would impose an undesirable forced shut-down on the other platforms connected to Piper. Instead there were three separate shut-down buttons for these ESVs in the control room.

The explosion was followed almost immediately by a large fireball which issued from the west side of B Module and a large oil pool fire at the west end of that module. The explosion and fire were witnessed by personnel on the vessels lying off the platform. It so happened that one witness on the Tharos was standing with camera at the ready. He took a sequence of shots of the development of the fireball.

The large oil pool fire gave rise to a massive smoke plume which enveloped the platform from the production deck at the 84 ft level up.

The offshore installation manager (OIM) made his way to the radio room and had a Mayday signal sent.

The Tharos effectively took on the role of On-Scene Commander. The Coast Guard station and Occidental headquarters onshore were informed. Rescue helicopters and a Nimrod aircraft for aerial on-scene command were dispatched. The flight time for the helicopters was about an hour.

Most of the personnel on the platform were in the accommodation, the majority in the ERQ. Within the first minute flames appeared on the north face of the module also and the module was enveloped in the smoke plume coming from the south. The escape routes from the module to the lifeboats were impassable.

At the 68 ft level divers were working with one man under water. They followed procedure, got the man up and briefly through the decompression chamber. They were unable to reach the lifeboats, which were inaccessible due to the smoke. They therefore launched life rafts and climbed down by knotted rope to the lowest level, the 20 ft level.

The drill crew also followed procedure and secured the wellhead.

The oil pool in B Module began to spill over onto the 68 ft level where a further fire took hold. There were drums of rigwash stored on that level which may have fed the fire.

The fire water drench system did not operate. There was only a trickle of water from the sprinkler heads.

The explosion disabled the main communications system which was centred on Piper. The other platforms were unable to communicate with Piper. They became aware that there was a fire on Piper, but did not appreciate its scale. They continued for some time in production and pumping oil. This pumping would have caused some additional oil flow from the leak at Piper.

After some 20 min from the initial explosion the fire on the 68 ft level led to the rupture of the Tartan riser on the side outboard of the ESV. This resulted in a massive jet flame which enveloped much of the platform.

The emergency procedure was for personnel to report to their lifeboat, but in practice most evacuations would be by helicopter and personnel would be directed from the lifeboats to the dining area on the upper deck of the ERQ and then to the helideck. Personnel in the ERQ found the escape routes to the lifeboats blocked and waited in the dining area. The OIM told them that a Mayday signal had been sent and that he expected helicopters to be sent to effect the evacuation. In fact the helideck was already inaccessible to helicopters.

Some 33 min into the incident the Tharos picked up the signal 'People majority in galley. Tharos come. Gangway. Hoses. Getting bad'.

No escape from the ERQ to the sea was organized by the senior management. However, as the quarters began to fill with smoke individuals filtered out by various routes and tried to make their escape.

Some men climbed down knotted ropes to the sea. Others jumped from various levels, including the helideck at 174 ft. One man who had arrived only that afternoon on his first tour jumped from a high level. One standing on pipes protruding from the pipe deck was pushed off by another behind him who could no longer stand the heat of the pipes.

The vessels around the platform launched their fast rescue craft (FRCs). The first man rescued, by the FRC of the Silver Pit, was the oil laboratory chemist, who, on experiencing the explosion, simply walked down to the 20 ft level and was picked up without getting his feet wet. Most survivors, however, were rescued from the sea. Much of the rescue operation took place after the rupture of the Tartan riser.

The FRC of another vessel, the Sandhaven, was destroyed with only one survivor. The FRC of the Silver Pit made repeated runs to the platform; eventually it was blown out of the water, and began to sink, but returned

to the platform and then finally sank, its crew being themselves rescued by helicopter.

At about 10.50 p.m. the MCP-01 riser ruptured and about 11.18 p.m. the Claymore riser ruptured. The pipe deck collapsed and the ERQ tipped. By 12.15 a.m. on 7 July the north end of the platform had disappeared. By the morning only A Module, the wellhead, remained standing.

A19.6 The Investigation

An investigation of the disaster was immediately undertaken by the Department of Energy (DoEn) headed by Mr Petrie. Two reports were issued, an interim report (the *Petrie Interim Report*, or simply, *the Petrie Report*) and a final report (*the Petrie Final Report*); the latter included appendices on various technical studies commissioned.

The *Petrie Report* put forward two scenarios for the hydrocarbon leak which led to the explosion: a leak from the site of PSV 504 (Scenario A) and a leak due to ingestion of liquid into the reciprocating compressors (Scenario B).

The Inquiry was presided over by a Scottish judge, Lord Cullen, assisted by three technical assessors. There was a legal counsel to the Inquiry assisted by technical consultants to the Inquiry. Parties to the Inquiry included Occidental, the DoEn, groups representing survivors and the trade unions, the contractors, the specialist contractor Score, several equipment manufacturers and for the second part, the UK Oil Operators Association (UKOOA). Part 1 of the Inquiry dealt with the disaster and its background, Part 2 with the future. The Inquiry heard some 280 witnesses in 180 days of evidence and received some 840 productions, or documents.

It began by considering whether to advise that the debris of the platform should be raised from the sea bed. It was clear at an early stage that the size of leak sought was of the order of 10 mm^2. The evidence was that the operation presented a number of problems and hazards, would involve considerable delay and might well not provide much useful information. The Inquiry decided not to pursue the matter.

In seeking to find the cause of the leak, the *Piper Alpha Report* begins with the evidence on the explosion itself. It concludes that the explosion was at 10.00 p.m., that it was in C Module and in the south-east quadrant of that module, that the fuel involved was condensate, that the leak gave rise to a gas cloud filling less than 25% of the module, that the mass of fuel within the flammable region was some 30–80 kg, that the explosion was a deflagration rather than a detonation, that the maximum peak overpressure was in the range 0.2–0.4 bar and that the ignition source could not be identified. Evidence for these findings included the gas alarms in C Module; the screeching noise heard just prior to the explosion; testimony of and photographs taken by observers on the surrounding vessels of the fires just after the explosion; the effects of the explosion, including the damage to the two firewalls in C Module; the effects of the explosion on the control room and its occupants; the lack of damage to the heat shield on A Module and estimates of overpressure based on some of the explosion effects, such as firewall damage and bodily translation of persons.

It was not initially clear how a gas cloud of sufficient size could develop without setting off certain gas alarms which according to the evidence had not been triggered. In particular there was a gas detector in the roof above the site of PSV 504 or PSV 505 (the two valves were close together) and another some 2–3 ft above floor level among the heat exchangers between the reciprocating and centrifugal compressors; both these detectors were in C2 zone. However, the first gas alarm was in C3 zone at C centrifugal compressor. Accordingly, wind tunnel tests were commissioned from BMT Fluid Mechanics to explore the pattern of gas alarms for different types of leak. Scenarios investigated included leaks of natural gas and of condensate, the one a buoyant and the other a heavy gas; leaks from various points in the modules and leaks from various types of source, including a leaking flange and an open pipe. It was concluded by the investigator that of the scenarios studied only a leak from the site of PSV 504 or PSV 505 fitted the pattern of gas alarms and, further, that this leak was a two-stage leak, the first stage being small and the second relatively large. It would have been this second stage which gave rise to the gas cloud sought.

The experimental run of main interest simulated a leak of 100 kg/min from PSV 504. Figure A19.5 shows the contours of the lower flammability limit of the gas cloud formed after 30 s from such a leak. The cloud would not set off either of the gas detectors mentioned. Figure A19.6 shows the mass of gas within the flammable limit as a function of the leak flow rate after 30 s and at infinite time. These results were subject to a number of reservations but indicated that a gas cloud of sufficient size could be formed.

The next question considered was whether the explosion of such a gas cloud could cause the damage observed. It was estimated that the B/C firewall would fail at an overpressure of 0.1 bar and the C/D firewall at an overpressure of 0.12 bar.

Simulations of the explosion of flammable mixtures in the module had been commissioned prior to the Inquiry at the Christian Michelsen Institute (CMI) by the DoEn and other parties. The simulations were performed using the FLACS computer code. Following the wind tunnel work, the Inquiry commissioned a single further run for a gas cloud in the south-east quadrant of C Module and containing some 45 kg of propane within the flammable limit. The simulation was subject to a number of reservations but indicated that such an explosion could cause the firewall damage observed.

The simulation also provided an explanation of a point which had seemed puzzling. The two occupants of the control room were thrown across it by the explosion and experienced a rush of cold air, not hot gas. The simulation showed that in the early stages of the explosion the control room wall would be subject to a positive overpressure and inrush of air, but that by the time the hot combustion products approached the control room, the negative phase of the pressure pulse had set in, the velocity vectors had reversed and the direction of air flow was out of the control room into C Module.

The two-stage nature of the leak also presented another point of difficulty. Isolation of A pump was by the closure of the GOVs on the suction and the delivery lines. The suction GOV was electrically isolated and it was uncertain whether power to it had been restored by the time of the initial explosion. In any event restoration of the valve would involve reconnecting a pneumatic line to the valve, which could quickly be done by an operator. It was concluded that this connection was made and that probably the operator gave it a tweak to make sure the valve movement was restored. This would have had the effect of admitting

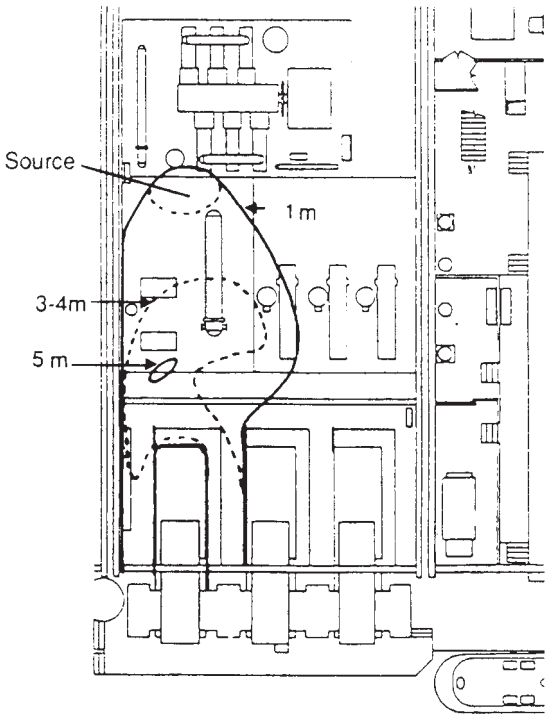

Figure A19.5 *The flammable gas cloud for a leak of 100 kg/min in the BMT wind tunnel tests: LEL contours at 30 s (Cullen, 1990)*

condensate to the relief line to PSV 504, but not of filling it with condensate liquid, thus giving rise to the early, smaller leak. Subsequent opening of the valve and filling of the relief line with condensate liquid could then have caused the later, larger leak.

Evidence was also heard on tests on leaks from blind flanges. The flange at PSV 504 was a ring-type joint (RTJ) flange. Three methods of tightening up were investigated: flogging up with a flogging spanner and hammer; hand tightening with a combination spanner and finger tightening. The results showed that a flange in good condition which had been flogged up or hand tightened did not leak. Even deterioration of the flange would be unlikely to give the leak sought unless the deterioration was gross. However, a finger-tightened flange could give a leak which was directionally downwards and was of the flow rate sought.

The Inquiry concluded that the explosion had been caused by ignition of a gas cloud containing some 45 kg of hydrocarbon within the flammable range, arising from a two-stage leak, in the first stage perhaps some 4 kg/min and in the second stage some 110 kg/min lasting some 30 s, coming from an orifice of equivalent diameter some 8 mm^2.

There was no obvious explanation why the blind flange was not leak-tight. Much evidence was led to the effect that an experienced and competent fitter would not make up a blind flange which was not leak-tight. The Inquiry noted, however, that the decision not to proceed with the full 24 month PM on A pump was taken just as shift handovers on the platform were starting so that some personnel may have been ignorant of this change in intent and that the lack of leak-tightness of the blind flange may have been connected with the status of A pump.

The lead production operator had clearly had the intention to start A pump. It was difficult to explain this given fact that its sole PSV was off. The Inquiry concluded that the lead operator was indeed ignorant of this, even though

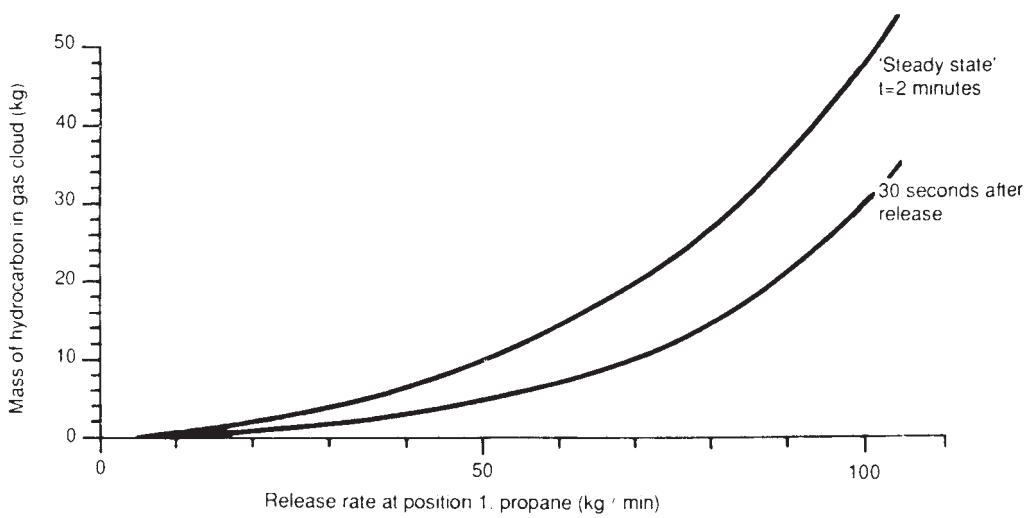

Figure A19.6 *Mass of fuel in the flammable range in the BMT wind tunnel tests: (a) variation with time (b) variation with leak rate (Cullen, 1990)*

this meant a serious breakdown of communications about the work. It implied that the fact that the PSV was off was not communicated in the handovers of the lead maintenance hand, the phase 1 operator and the lead production operator and that the lead operator did not learn of it through the PTW system.

When he found that he was unable to put the PSV back that evening, the Score supervisor came up to the control room to suspend the permit. He was on his first tour as a supervisor and had had no training in the operation of the PTW system in use on the platform. Whom he spoke to and what transactions took place were obscure. It was unclear how he knew that the procedure in filling out the permit for suspension was to write 'SUSP' in the gas test column.

In any event the Score supervisor did not make a final inspection of the job site before going off work and evidently the lead production operator did not inspect the job site either, although in both cases good practice required that this be done.

Further, the leak would not have occurred if there had been a more positive isolation of the pump by means such as the use of a slip plate.

The explanation just described is that adopted in the *Piper Alpha Report* but several other scenarios for the leak were also explored. One group of scenarios was concerned with explanations of the leak from the blind flange following admission of condensate into A pump other than lack of leak-tightness. They include the possibilities of auto-ignition, shock loading, low temperature brittle fracture, and overpressurization by methanol injection. All of these were quickly ruled out except auto-ignition by compression of a flammable mixture formed in the relief line. The line had been left open for an hour before the blind flange was put back on. It was not possible to calculate whether auto-ignition would have occurred due to lack of data on auto-ignition properties of the multi-component mixture at the high pressures involved, some 300 bar. Moreover, company documentation on the rating of the pipework was inconsistent so that it was uncertain whether the flange was a 900 or 1500 lb one. The expert evidence was that if auto-ignition had occurred and the lower rating applied, a leak was possible, although whether it would have had the required characteristics was another matter. An account of this work on auto-ignition has been given by S.M. Richardson, Saville and Griffiths (1990).

The scenario was considered that condensate liquid had backed up in the JT flash drum and thence into the reciprocating compressors. There was evidence that on loss of B pump steps had been taken to reduce the condensate make by unloading and recycling these compressors. The report concludes that there had been insufficient time for backup to occur before the initial explosion and that in addition both the conditions around the compressors and the expected action of protective instrumentation were against this scenario.

A further scenario which emerged in the Inquiry was that the leak occurred from PSV 505 and that it was caused by hydrate blockage. The interruption to the methanol supply to the JT valve lent credibility to this scenario. Experimental work commissioned showed that hydrates would form under the conditions pertaining at the JT valve during the partial loss of methanol supply if the temperature at the valve fell below a critical value; it had in fact been below this temperature on 5 July. The expert evidence was that hydrates could pass through to the condensate injection pumps and cause blockage there some 2 h after restitution of the full methanol supply. There were several versions of the scenario all leading to blockage of hydrate at PSV 505 and overrunning of the pump so that the delivery pressure rose to a value high enough to cause rupture of the valve, which was the weakest point in the line. The report does not rule out this scenario, but regards it as less likely than the preferred one.

Finally, the consultants to the Inquiry reviewed a large number of other scenarios which were not purely theoretical but had some link with the information available at the time, which included a hazop study, past equipment failures and process conditions that evening. None was found convincing by the Inquiry.

Turning to the escalation, the causes of the oil pool fire and the fireball which occurred in B Module within seconds of the explosion in C Module were unclear. The Inquiry heard evidence on the type, number, velocity and impact effects of the projectiles which would have resulted from the destruction of the B/C firewall. The condensate injection line ran from C Module through into B Module where it joined the main oil line. The report concludes that probably the fireball was caused by a missile rupturing this line near the main oil pumps at the west face of B Module.

Estimates of the size of the oil pool fire indicated that the supply of oil to the fire probably exceeded the oil inventory of the separators and that there was a leak of oil from the main oil line through the main oil line EVS which was not fully closed. This leak would be aggravated by continued pumping of oil by the other platforms.

The fire water deluge system did not work. The initial explosion knocked out the main power supplies. It may also have damaged the water pumps and the water mains. In any event it was the practice on Piper to put the pumps on manual start when divers were in the water and thus in possible danger of being sucked into the pump intakes and they were on manual start that evening. The start controls were at the pumps themselves. After the explosion occurred an attempt was made to get through to the pumps to start them by personnel wearing breathing apparatus, but to no avail. Further evidence was given of quite extensive blockage caused by corrosion products in the fire water deluge system, which operated on sea water, a problem which had persisted for some years.

The initial explosion caused the operation of the platform ESD. This could have occurred through loss of the main power supply and/or rupture of a pneumatic ring main. Also, although dazed by the explosion the control room operator pressed the platform ESD button. He did not, however, press the buttons to close the ESVs on the three gas pipelines. Evidently, these did close but their closure was due rather to the effects of the initial explosion on power supplies to the valves.

Following the initial explosion a period of extended flaring occurred which greatly exceeded that to be expected from the flaring of the gas inventory on the platform. The report accepted that the most probable explanation was a failure of the Claymore ESV to close fully.

The main communications for the Piper field were centred on Piper. The system was knocked out by the initial explosion, so that the other platforms were unable to communicate with Piper and had difficulty communicating with the shore.

The report details a number of management weaknesses. There were severe and numerous defects in the PTW

system. For example, it violated more than half of the main points in the code of practice on PTWs issued by the Oil Industry Advisory Committee (OIAC). The system was operated rather casually. The training of the specialist contractors supervisor in the permit system operated on the platform was found to be inadequate.

With regard to handovers, the company had been prosecuted only a year before for a fatality and had pleaded guilty. The report takes the view that a failure in handover procedures was a factor in that accident.

A number of different types of audit were performed by the company, by its partners, by loss prevention specialists and so on. None of these had revealed the defects in the PTW which became apparent very quickly at the Inquiry.

The report is critical of the handling of the emergency by the senior management on the platform and in particular of the failure to recognize that helicopter evacuation was not possible and to take command of the situation and organize escape from the ERQ.

The decision to keep the platform operating despite the large workload is another matter of which the report is critical.

The report states that the company had no system to ensure that all projects were subject to formal safety assessment. Certain techniques such as hazop were used on some projects and quantitative estimates had been made in some studies, but the approach was unsystematic. The report takes the view that as a consequence the hazards presented by the hydrocarbon inventory on the platform and particularly in the pipelines had not been systematically addressed.

Part 2 of the Inquiry was concerned with the future offshore safety regime. The context was not only the Piper Alpha disaster but also the changes taking place in the North Sea oil province. The exploitable oil and gas fields were becoming smaller and the technology to develop them was becoming more varied.

The evidence in Part 1 revealed serious weaknesses in the company management. It was an issue why the DoEn had not discovered these weaknesses. The report is critical of the relative lack of emphasis placed by the Department on the assessment of management and management systems.

In contrast to the British onshore and Norwegian offshore regimes, which had both moved increasingly towards goal-setting regulations, the British offshore regime relied excessively on prescriptive regulations, and associated guidance.

The deficiencies of such a regime were illustrated in the regulations concerning fire protection, which had a number of defects. Passive and active fire protection were covered by two separate sets of regulations. The regulations, and associated guidance, for active fire protection led in practice to systems based on delivery of a uniform quantity of water over large areas of a platform, deluge systems prone to blockage and massive water pumps. Fire protection was not integrated with explosion protection.

The report states that the approach taken by the DoEn to the control of the major hazards from hydrocarbons at high pressure did not impress as an effective one. Further, the inspectorate had relatively little expertise in this area.

Following the Piper Alpha disaster the DoEn brought in regulations to require ESVs to be placed nearer to sea level and for the valves to be of full ESV standard. The report notes that of the 400 risers covered by the regulations, some 70 required modification in the latter respect.

The regime made little use of formal safety assessment (FSA). This was in contrast to the regulatory use of FSA onshore, and in particular the onshore safety case. The DoEn had in fact explicitly rejected the concept of an offshore safety case. This policy also contrasted with the situation in the Norwegian sector, where a concept safety evaluation (CSE) was required. Quantitative risk assessment is required in a CSE and is often necessary to fulfil the requirements of a safety case.

Considerable evidence was heard on quantitative risk assessment (QRA). The burden of this evidence was that QRA is in regular use in many companies as an aid to decision-making both for onshore and offshore installations and that there was no serious impediment to this from any problems of overall methodology, frequency estimation, consequence modelling or risk criteria.

In contrast to the HSE, the DoEn was not well equipped to operate a regime based on goal-setting regulations and FSA. It had no experts in FSA or fire protection.

A number of recommendations which would have met some of the points on which the DoEn was criticized had been made in the *Burgoyne Report* (Burgoyne, 1980), but had not been implemented.

A19.7 Some Lessons of Piper Alpha

A19.7.1 Some lessons

Lessons from the Piper Alpha disaster are considered in this section with the exception of the recommendations of the report on the offshore safety regime which are considered in Section A19.8. A list of some of the lessons is given in Table A19.2. Many apply particularly to offshore installations, but others are of more general applicability.

Regulatory control of offshore installations

The Piper Alpha disaster exposed weaknesses in the offshore regulatory regime which have already been described. The lessons drawn are seen in the recommendations given in Section A19.8.

Quality of safety management

The *Piper Alpha Report* is critical of the quality of management, and particularly safety management, in the company.

It was not that the company did not put effort into safety. On the contrary, there were numerous meetings and much training on safety. The problem was the quality of these activities.

Many managers had come up through the ranks and had minimal qualifications. The culture tended to be somewhat in-grown and insufficiently self-critical.

These defects manifested themselves in various ways such as in the toleration of poor practices in plant isolation and operation of the PTW system; in the failure to appreciate the ineffectiveness of the audits done; in the failure to address the major hazard problem and to use FSA. The report comments:

> Senior management were too easily satisfied that the PTW system was being operated correctly, relying on the absence of any feedback of problems as indicating that all was well. They failed to provide the training necessary to ensure that an effective PTW system was operated in practice. In the face of a known problem with the deluge system they did not personally become involved in probing the extent of the problem and what should be done to resolve it as soon as possible. They adopted a superficial

Table A19.2 *Some lessons of Piper Alpha*

Regulatory control of offshore installations
Quality of safety management
Safety management system
Documentation of plant
Fallback states in plant operation
Permit-to-work systems
Isolation of plant for maintenance
Training of contractors personnel
Disabling of protective equipment by explosion itself
Offshore installations: control of pressure systems for hydrocarbons at high pressure
Offshore installations: limitation of inventory on installation and in its pipelines
Offshore installations: emergency shut-down system
Offshore installations: fire and explosion protection
Offshore installations: temporary safe refuge
Offshore installations: limitation of exposure of personnel
Offshore installations: formal safety assessment
Offshore installations: safety case
Offshore installations: use of wind tunnel tests and explosion simulations in design
The explosion and fire phenomena
Explosions in semi-confined modules
Pool fires
Jet flames
Publication of reports of accident investigations

> response when issues of safety were raised by others, . . . They failed to ensure that emergency training was being provided as they intended. Platform personnel and management were not prepared for a major emergency as they should have been. (para 14.52)

A crucial weakness was failure to appreciate that absence of feedback to management about problems is almost certainly an indicator not that there are no problems but that there are, and they could be serious. Of one OIM the report states: 'His approach seemed to be, in his own words, "surely that is all you are concerned with about the permit system . . . If the system is working and no problems are identified . . . then you should be reasonably happy with it, surely?" . . . He had been surprised by the number of deficiencies in the operation of the permit system which had been revealed in the Inquiry. He had checked this out and found it to be true.' Of another manager it states that he said 'he knew that the system was monitored on a daily basis by safety personnel. By the lack of feedback he "knew that things were going all right and there was no indication that we had any significant permit to work problems".' (para 14.26)

Safety management system

Onshore the quality of the management and the management system are of prime concern to the HSE in its inspections in general and in the safety case in particular. In submitting a safety case a company will often give extensive documentation on its systems. Nevertheless, in the regulations the formal requirements on management are fairly minimal.

The Inquiry heard evidence in favour of the assurance of safety through the use of quality assurance to standards such as BS 5750 and ISO 9000. It also heard evidence on the need for better qualified management, including a proposed requirement for all OIMs to be graduates.

The concept of a safety management system goes part way towards these insofar as the system itself is based on principles similar to those of quality assurance and covers the question of management quality.

Documentation of plant

The discrepancies in the documentation concerning the rating of the flange on PSV 504 have already been mentioned. The Inquiry in fact heard of a number of other defects in the documentation of the plant. Failure to maintain correct records can have serious consequences.

Fallback states in plant operation

The loss of the working condensate pump on Piper created a situation where operating personnel were under some pressure to start the other pump and avoid a gas plant shut-down with its possible escalation to a total shut-down, loss of power and the need for a 'black start'. In this case the pressure was created partly by the view which an individual took of the probability that the changeover of the main generators from gas to diesel would fail. This illustrates the desirability of ensuring that plants have fallback states short of total shut-down. In this case the problem was in the reliability of changeover, a type of problem which may lie with design or with maintenance.

Permit-to-work systems

The defects in the PTW system have already been described. These defects led directly to a situation where condensate was admitted to a pump from which the PSV had been removed and hence to the disaster. The *Piper Alpha Report* devotes considerable attention to the need for an effective system.

Isolation of plant for maintenance

The *Piper Alpha Report* states that the disaster would not have occurred if A pump had been positively isolated so that condensate could not be admitted. Positive isolation is not achieved by shutting a valve but requires means such as insertion of a slip plate or removal of a pipe section.

Training of contractors' personnel

The proportion of contractors' personnel on an offshore installation can be as high as 70%. The offshore scene therefore exemplifies in extreme form a problem which applies to onshore plants also. This is the need to train contractors' personnel in the company's operating and emergency systems and procedures. Failure to train a contractor's supervisor in the operation of the PTW system on Piper meant that he was unfamiliar with a feature of the system which turned out to be a critical one.

Disabling of protective equipment by explosion itself

The initial explosion on Piper disabled large parts of the protective systems, including power supplies and fire water supplies. It illustrates the importance of taking this factor into account in design and in FSA.

Offshore installations: control of pressure systems for hydrocarbons at high pressure

An offshore production platform contains a large amount of plant containing hydrocarbons at high pressure. The feed

to this plant is from the wells, which can sometimes behave in an unpredictable way. The pipelines connected to the platform contain large quantities of hydrocarbon, the high pressure gas pipelines constituting a particularly serious hazard.

There needs therefore to be a comprehensive system for the control of the total pressure system, covering design, fabrication, installation, operation, inspection, maintenance and modification and including control of such features as materials of construction, lifting of loads and so on and personnel need to be trained in the purposes and operation of system.

Offshore installations: limitation of inventory on installation and in its pipelines

The scale of the Piper disaster was due primarily to the large inventory of the three high pressure gas pipelines connected to the platform. The Inquiry heard evidence on the practicalities of reducing the number of gas pipelines connected to a platform. There are many technical problems involved, but the point has been made that such reduction should be a design objective.

The main inventory of hydrocarbons in process on a platform is in the separators. The massive oil pool fire on Piper was fed from the separators. The *Piper Alpha Report* recommends that methods of dumping this inventory be explored.

Evidence was also heard that in some cases the main inventory of hydrocarbons on a platform might be the diesel fuel.

The alternative method of preventing the hydrocarbon inventory from feeding a fire is emergency isolation, which is considered next.

Offshore installations: emergency shut-down system

The ESD system on Piper operated, shut-down ESVs and blew the gas inventory on the platform down to flare.

Nevertheless, the accident drew attention to a number of problems in effecting isolation, some specific to offshore platforms and some more generally applicable.

The Tartan riser ruptured on the outboard side of the ESV so that closure of this valve was of no avail. It is clear that an ESV needs to be located as close to the sea level as practical in order to minimize this risk.

It is possible to go one step further and install a subsea isolation valve, but this is for consideration on a case-by-case basis.

Both types of isolation valve received considerable attention in the Inquiry. However, neither will be effective unless it achieves tight shut-off. The evidence that the main oil line and the Claymore gas line ESVs did not shut-off tightly emphasizes the importance of this feature.

Moreover, in order to be effective the ESD system has to be activated. The fact that on Piper closure of the three gas line ESVs was not part of the platform ESD but had to be effected for each line separately by manual pushbutton, that these buttons were not pushed and that closure only occurred due to loss of power shows that this problem also is not a trivial one.

Offshore installations: fire and explosion protection

An offshore installation is not in general able to call on outside assistance comparable with that available from the fire brigade to an onshore plant. It must be self-reliant.

This implies that both protection against, and mitigation of, fire and explosion on the one hand and fire fighting on the other are of particular importance and that both the hazard assessment and the design and operation of the plant must be of high quality.

Offshore installations: temporary safe refuge

It is clear from the Piper disaster that there needs to be a temporary safe refuge (TSR) where personnel can shelter in an emergency and where the emergency can be controlled and evacuation organized.

This TSR will normally be the accommodation. In most cases it will be on the production platform itself, but it may be on a separate accommodation platform.

The protection of the TSR from ingress of smoke and fumes from outside and from generation of fumes by fires playing on the outside needs careful attention. Measures require to be taken to prevent smoke ingress through doors and through the ventilation system.

Offshore installations: limitation of exposure of personnel

The concept of a TSR is a particular application of the more general principle of limitation of exposure of personnel. The Inquiry also heard evidence of the application of the principle to other aspects such as the location of workshops.

Offshore installations: formal safety assessment

The evidence showed that many companies which operate installations onshore and offshore have formal systems for safety assessment and practise FSA routinely, that FSA has considerable benefits in the design and operation of plant and that it provides a suitable basis for dialogue between the company and the regulatory body.

Offshore installations: safety case

A safety case is a particular form of FSA. The evidence indicated that a safety case is as applicable offshore as onshore and that it is a suitable means for the company to demonstrate to the regulatory body that it has identified the major hazards of its installation and has them under control.

Offshore installations: use of wind tunnel tests and explosion simulations in design

Wind tunnel tests and explosion simulations were used in the Inquiry to investigate the cause of the explosion, but evidence was also heard of their value in platform design.

Wind tunnels may be used to assess the effectiveness of ventilation and of the gas detection system in a module, the wind conditions at the helideck and the movement of smoke from oil pool fires. Explosion simulations may be used to investigate the effect of different module layouts on explosion overpressures and to assess the effectiveness of blast walls.

The explosion and fire phenomena

The Piper disaster drew attention to several important aspects of explosion and fire on offshore installations. These include explosions in semi-confined modules, oil pool fires and jet flames.

Explosions in semi-confined and congested modules are a hazard which assumes particular significance offshore. Although major progress has been made in the last decade in simulating such explosions and developing design methods, this remains an area where further work is needed.

Oil pool fires onshore are relatively well understood, but this does not apply to the behaviour of such a pool fire on an offshore platform. Aspects of some importance are

design to prevent accumulation of an oil pool in the first place and the massive smoke plume from such a fire.

Jet flames, including jet flames from risers, are particularly important for offshore platforms. In this case there are available a number of models developed for flares and flames on onshore plant, including pipelines, which can be applied offshore.

Evidence given indicated that in considering the hazard of a jet flame from a riser, the worst case was not necessarily a full bore rupture but a partial rupture, since the latter is sustained for a longer period.

Publication of reports in accident investigation

The Inquiry heard that the company had a policy of severely restricting circulation of accident investigation reports.

Likewise, the DoEn did not make public reports on major offshore accidents. This contrasts markedly with the HSE policy of issuing reports on major accidents, many of which are referred to in this book.

A19.7.2 An accident model

The following outline of a model of the accident highlights the role played by some of the features just mentioned:

	Deficencies in
Initial event: gas explosion	Operational control
Escalation 1: explosion damage	Hazard identification, assessment and management Explosion mitigation
Escalation 2: oil pool fire	Hazard identification, assessment and management Fire mitigation and fire fighting Inter-platform emergency planning
Escalation 3: riser rupture	Hazard identification, assessment and management Fire protection of risers
Escalation 4: accommodation failure	Hazard identification, assessment and management TSR fire and smoke protection Emergency command and control

A19.8 Recommendations on the Offshore Safety Regime

The *Piper Alpha Report* makes recommendations for fundamental changes in the offshore safety regime.

The basis of the recommendations is that the responsibility for safety should lie with the operator of the installation and that nothing in the regime should detract from this.

The offshore regime envisaged in the recommendations is one in which the emphasis is on the operator demonstrating to the regulatory authority the safe design and operation of its installation rather than demonstrating mere compliance with regulations. In this regime the preferred form of regulations is goal-setting rather than prescriptive.

Table A19.3 *Some elements of the safety management system*

Organizational structure
Management personnel standards
Training, for operations and emergencies
Safety assessment
Design procedures
Procedures, for operations, maintenance, modifications and emergencies
Management of safety by contractors in respect of their work
Involvement of the workforce (operator's and contractors') in safety
Accident and incident reporting, investigation and follow-up
Monitoring and auditing of the operation of the system
Systematic re-appraisal of the system in the light of experience of the operator and industry

The recommendations envisage that FSA will play a major role. It may be used to demonstrate compliance with a goal-setting regulation or with the general requirements of the HSWA.

A central feature of the regime proposed is the safety case for the installation. This safety case is broadly similar to that required for onshore installations but there are some important differences. In the offshore safety case it is required that the operator should demonstrate that the installation has a TSR in which the personnel on the installation may shelter while the emergency is brought under control and evacuation organized.

Further, it is recommended that this demonstration should be by QRA. This means that there must be criteria which define the failure of the TSR and criteria for its endurance time and its failure frequency. The criteria may then be met by reducing the frequency of accidental events, by increasing the durability of the TSR or by some combination of these.

The recommendation on the safety case includes a requirement that the operator should demonstrate that it has a safety management system (SMS) to ensure the safe design and operation of the installation. This SMS should draw on quality assurance principles similar to those of BS 5750 and ISO 9000. The elements of the SMS should include those listed in Table A19.3. They include management personnel standards.

Various measures related to hardware were urged at the Inquiry. These included the provision of separate accommodation platforms, the installation of subsea isolation valves and blast walls, the use of freefall lifeboats and purpose-built standby vessels. The report takes the view, however, that in accordance with its basic philosophy such matters should be dealt with as part of the demonstration of safe design and operation.

The report considers that the then current regulatory body, the DoEn, is unsuitable as the body to be charged with implementing the new regime and recommends the transfer of responsibility for offshore safety to the HSE.

These recommendations were accepted immediately by the government and the new regime under the HSE began in April 1991.

Appendix 20 Nuclear Energy

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A20.2 Nuclear Industry A20/4
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The energy industries in general have much in common with the process industries in terms of the management, the plant and the hazards. This is true even of the nuclear industry, although this also has a number of unique features. Historically, the nuclear industry has often had to face particular problems before they have impinged on the process industries and has had to devise solutions for them. In consequence, there are a number of areas where work in the nuclear industry is relevant to the process industries.

In this appendix a general account is given of nuclear energy, essentially with reference to those features which are common to, or have impact on, the process industries. Accounts of the accidents at Three Mile Island and at Chernobyl and of the Rasmussen Report are given in Appendices 21, 22 and 23, spectively.

Some topics common to both industries have been dealt with already in other chapters. The account of major hazard control in Chapter 4 covers nuclear hazards. The treatment of management and management systems in Chapter 6 is applicable to nuclear as well as process systems.

General information on nuclear phenomena and on radioactivity is given in *Source Book on Atomic Energy* by Glasstone (1968), *The Effects of Nuclear Weapons* by Glasstone and Dolan (1979), *Nuclear Energy Technology* by Knief (1981) and *A Dictionary of Nuclear Power and Waste Management* by Foo-Sun Lau (1987).

Frequent reference is made in this appendix to two reports issued following the accident at Three Mile Island. These are *The Report of the Presidents Commission on the Accident at Three Mile Island (the Kemeny Report)* (Kemeny, 1979) and *TMI-2 Lessons Learned Task Force Final Report* (*the Task Force Report*) (NRC, 1979d).

Selected references on the nuclear industry are given in Table A20.1.

Table A20.1 *Selected references on nuclear energy. See also Appendix 28, Section B (Nuclear Regulatory Commission)*

Nuclear energy and technology
ASME (Appendix 28 *Nuclear Safety)*; HSE (Appendix 28 *Nuclear Installations,* 1979 HA 4); AIChE (1954–67/101–118, 1972/119); McCullough (1957); J.H. Bowen and Masters (1959); Kopelman (1959); Tipton (1960); El-Wakil (1962); Fozard (1963); Gill (1964); T. Thompson and Beckerley (1964); Lamarsh (1965); Zudans, Yen and Steigelman (1965); Shaw (1967); Glasstone (1968); F.R. Farmer (1969a); Glasstone and Sesonske (1969); ENEA (1970); Ramey (1970); Wechsler (1970); Berry (1971); CEGB (1971); T.J. Thompson (1971); A.E. Green and Bourne (1972); R.V. Moore (1972); Holdren and Herrera (1973); Jaeger (1973, 1975); Inglis (1973); ACRS (1974); Allardice and Trapnell (1974); Bupp and Derian (1974); Cochran (1974); Willrich and Taylor (1974); Flood (1976); Haferle *et al.* (1976); S.E. Hunt (1976); RCEP (1976 Rep. 6); ASTM (1977 STP 616); S. Fawcett (1977); IMechE (1977/38, 1982/64, 1984/82, 1988/99, 1992/ 143); Pocock (1977); Pedersen (1978); Duderstadt (1979); J. Hill (1979a); Kaplan (1979); Cottrell (1981); Knief (1981); IBC (1982/24); IAEA (1983); W. Marshall (1984); Rahn *et al.* (1984); Stahlkopf and Steele (1984); Bennett (1985); Wilkie and Berkovitch (1985); Wilkie (1986); Kletz (1986e, 1987g, 1991c); Inhaber (1987); UKAEA (1987); Varey (1987); Bindon (1988); Lewins (1988); G. Lewis (1988); V.C. Marshall (1988b); Gittus (1988); Bennett and Thomson (1989); NFPA (1991 NFPA 801, 1993 NFPA 803); Nowlen (1992); Hicks (1993) ANSI N series

Inherently safer design
Kletz (1988h); Forsberg *et al.* (1989)

Sizewell B
CEGB (1982); HSE (Appendix 28 *Nuclear Installations, Sizewell B*, 1982 HA 3, 1982b,c, 1983a); NRPB (1982 R137, R142, R145, R146, 1983 R160, R163); NRC (1983 NUREG-0999); (IMechE (1989/113, 1994/173);
Software reliability: CEC (1987 EUR 11147 EN); Hunns and Wainwright (1991)

Nuclear waste, fuel reprocessing
I.K.G. Williams (1979); Bennett (1981); R. Smith and Hartley (1982); J.A Williams (1982); Bennett (1985); IBC (1985/64, 1986/70, 1987/73); Heafield (1986); N.J. James, Rutherford and Sheppard (1986); Elliot and King (1987); N. James, Sheppard and Williams (1987)

Radioactivity and radioactive contamination
NRPB (Appendix 28); Moelwyn-Hughes (1961); W.J. Moore (1962); Yen Wang (1969); Coggle and Noakes (1972); McDonald, Darley and Clarke (1973); Sternglass (1973); AEC (1975); Brodine (1975); MRC (1975b); G.N. Kelly, Jones and Hunt (1977); R.H. Clarke (1980); Whicker and Schultz (1982); Foo-Sun Lau (1987); NRPB (1989, 1993) BS (Appendix 27 *Radioactivity*)

Nuclear hazard assessment and control
HSE (Appendix 28 *Nuclear Installations*, 1977c, 1979d,f, 1979 HA 5,1983/8, 1992/16); AEC (1957, 1975); Sinclair (1963); F.R. Farmer (1967a,b, 1969a,b, 1970, 1971); Bourgeois (1971); Dale and Harrison (1971); F.R. Farmer and Gilby (1971); Hanauer and Morris (1971); Kirk and Taylor (1971); Ybarrando, Solbrig and Isbin (AIChE 1972/119); Hosemann, Schikarski and Wild (1973); EPA (1974); Karam and Morgan (1974); N.C. Rasmussen (1974, 1981); Chicken (1975, 1982, 1986); Bridenhaugh, Hubbard and Minor (1976); Flood (1976); Freudenthal (1976); Rust and Weaver (1976); Ford (1977); Fussell and Burdick (1977); Comey (1977); HM Chief Inspector of Nuclear Installations (1977); G.N. Kelly, Jones and Hunt (1977); NRC (1977a–c); UCS (1977); Higson (1978); R.J. Parker (1978); E.E. Lewis (1979); Windscale Local Liaison Comm. (1979); Alvares and Hasegawa (1979/80); Joksimovic and Vesely (1980); Strong and Menzies (1980); Charlesworth, Gronow and Kenny (1981); Fleming *et al.* (1981); Sagan (1981); Allan, Adraktas and Campbell (1982); NRC (1982); Openshaw (1982); I.B. Wall (1982); Amendola (1983a,b); D.E. Bennett (1983); Fremlin (1983); Heudorfer and Hartwig (1983); Brooks (1984); CEC (1985/2); Lois and Modares (1985); Frank and Moieni (1986); C.D. Henry and Brauer (1986); Ronen (1986); Anon. (1987p); Ashworth and Western (1987); Durant and Perkins (1987); Gittus (1987); Mullins and Clough (1990 SRD R509); J. Singh, Cave and McBride (1990); Ang (1992); IAEA (1992); Wu and Apostolakis (1992); Hoffmeister (1993); J.R. Thomson (1994)

NRC studies
NRC (Appendix 28, *Loss of Coolant Accident, Loss of Fluid Test, Operational Safety Reliability Program, Reactor Safety Study, Safety Assessment, Safety Goals, Severe Accident Risk Reduction Program)*
Benchmark studies TUV (1979); NEA (1984)

Detailed studies
Coxon (1971); Kazarians and Apostolakis (1978); Apostolakis and Mosleh (1979); Rasmuson, Wilson and Burdick (1979); Apostolakis and Kazarians (1980); Aupied, Le Coguiec and Procaccia (1983); M.G.R. Evans and Parry (1983); Hendrickx and Lannoy (1983); Coudray and Mattei (1984); NRC Steam Explosion Rev. Gp (1985); Bley and Reuland (1987); Ashurst and Davidson (1993 IPB 112)

Emergency planning
Eppler (1970); HSE (1982/5, 1986b, 1991/15)

Incidents
Chamberlain (1959); Anon. (1962c); Norman (1975); Anon. (1976g); HM Chief Inspector of Nuclear Installations (1977); V.C. Marshall (1979c); Bertini *et al.* (1980); Curtis, Hogan and Horowitz (1980); J.G. Fuller (1984); May (1989); Mosey (1990); Ashurst and Davidson (1993 LPB 112); Anon. (1994 LPB 119, p. 13)

Windscale
Atom. Energy Office (1957); Fleck (1958); Fremlin (1978); R.J. Parker (1978); HSE (1981/4, 1986/9); NRPB (1981 R133, 1982 R135); May (1989); Arnold (1992)

Browns Ferry
AEC (1975); Ford, Kendall and Tye (1976); NRC (1976); Anon. (1982 LPB 47, p. 13); May (1989)

Severe accident risks
Pickard, Lowe and Garrick (1983); NRC (1987a,b, 1989); Wheeler *et al.* (1989)

Precursor events
Minarick and Kukielka (1982); Cottrell *et al.* (1984); Minarick *et al.* (1985)

A20.1 Radioactivity

Accounts of radioactivity and of ionizing radiations are given by Glasstone (1968), Glasstone and Dolan (1979), Knief (1981), Foo-Sun Lau (1987) and in many texts on physical chemistry such as Moelwyn-Hughes (1961) and W.J. Moore (1963).

Units of radioactivity are defined in Worley and Lewins (1988) (the *First Watt Committee Report*), based on Foo-Sung Lau (1987).

A20.1.1 Types of radiation

There are three main types of radioactive particle or ray: (1) α-particles, (2) β-rays or particles and (3) γ- and X-rays.

α-particles are helium nuclei, or protons. Their mass is relatively large and their range correspondingly short. An air gap of about 8 cm or a sheet of paper may suffice to stop them. Generally, they present little external radiation hazard, but they are dangerous if they get inside the body.

β-rays, or particles, are electrons. They have a much smaller mass and greater penetrating power. Their range in air is about 10 m, but they are usually stopped by a few millimetres of solid material.

γ- and X-rays are electromagnetic radiations, or photons, which differ from each other only in respect of source and wavelength. They have a range of several hundred metres, but can be stopped by a few millimetres of lead or 0.5–1 m of concrete.

Both β-rays and γ- and X-rays constitute an external radiation hazard.

Ionizing radiation may be classified as direct or indirect. The former consists of particles and thus includes α-particles (protons) and β-particles (negatively charged electrons) and positrons (positively charged electrons), while the latter includes γ- and X-rays (both photons) and also neutrons.

A20.1.2 Units of radiation

The units of activity of a radioactive source are bequerels (Bq) and curies (Ci)

$$1\ \text{Bq} = 1\ \text{disintegration/s}$$

$$1\ \text{Ci} = 3.7 \times 10^{10}\ \text{Bq}$$

Another unit of source strength is the roentgen (R), which defines the ionization effect of γ- and X-rays.

1 R produces in 1 cm^3 air ions carrying a charge of 1 electrostatic unit (esu)

For γ- and X-ray radiation 1 R is equivalent to the absorption of 87 erg/g of air. However, for other types of radiation and targets the equivalences are significantly different.

Units of absorbed dose are rads and grays (Gy), the latter being the modern unit.

$$1\ \text{rad} = 100\ \text{erg/g} = 0.01\ \text{J/kg}$$

$$1\ \text{Gy} = 1\ \text{J/kg} = 100\ \text{rad}$$

The effect on man of a given absorbed dose D is a function of the type of radiation, for which a quality factor Q is defined. The value of Q is unity for γ- and X-rays and electrons, but has other values for other types of radiation. The value of Q for α-particles is 20. The quality factor is also referred to as the relative biological effectiveness (RBE).

The dose equivalent H is the product of the absorbed dose and the quality factor:

$$H = D \times Q \qquad [A20.1.1]$$

Units of effective dose, or dose equivalent, are rems and sieverts (Sv), the latter being the modern unit

$$1\ \text{rem} = 1\ \text{rad} \times \text{Q}$$

$$1\ \text{Sv} = 1\ \text{Gy} \times \text{Q}$$

$$1\ \text{Sv} = 100\ \text{rem}$$

Thus the roentgen is the unit of total dose, the rad or gray that of absorbed dose and the rem or sievert that of effective dose.

In the context of discussion of biological effects effective dose is frequently referred to simply as dose.

A20.1.3 Radioactive decay

Specific Activity and Half Life

The basic equation for radioactive decay is

$$-\frac{\mathrm{d}n}{\mathrm{d}t} = \lambda n \qquad [A20.1.2]$$

where n is the number of radioactive atoms, t time and λ the radioactive decay constant (s^{-1}). Then from Equation A20.1.2

$$\frac{n}{n_0} = \exp(-\lambda t) \qquad [A20.1.3]$$

where n_0 is the number of radioactive atoms at arbitrary time zero. The half-life τ is defined by the relations

$$\frac{n}{n_0} = \frac{1}{2} = \exp(-\lambda\tau) \qquad [A20.1.4]$$

$$\tau = \ln 2/\lambda = 0.693/\lambda \qquad [A20.1.5]$$

But

$$n_0 = N_0/M_a \qquad [A20.1.6]$$

where M_a is the atomic weight and N_0 is Avogadro's constant ($=6.024 \times 10^{23}$). Then from Equations A20.1.2, A20.1.3 and A20.1.6 at arbitrary time $t = 0$ ($n = n_0$)

$$-\frac{dn}{dt} = \lambda\frac{N_0}{M_a} = \frac{\ln 2}{\tau}\frac{N_0}{M_a} \qquad [A20.1.7]$$

Energy release

The release of energy during radioactive decay is governed by the relation of Einstein

$$E = mc^2 \qquad [A20.1.8]$$

where c is the velocity of light, E the energy release and m the mass.

The energy may be calculated from the decay equation by determining the difference in mass of the two sides. An atomic mass unit (amu) is equivalent to 931 MeV.

For example, for the decay of polonium 210 to lead 206 and helium nucleus, or α-particle, the decay equation is

$$_{84}Po^{210} \rightarrow {}_{82}Pb^{206} + {}_{2}He^{4}$$

and the atomic mass balance is

		Atomic mass
LHS	$_{84}Po^{210}$	210.049
RHS	$_{82}Pb^{206}$	206.034
	$_{2}He^{4}$	4.004
Total RHS		210.038
Mass loss		0.011

Energy $= 931 \times 0.011 = 10.2$ MeV

A20.1.4 Radioactivity health effects

An account of health effects from radiation is given in *Living with Radiation* by the National Radiation Protection Board (NRPB) (1989). An account in the specific context of Chernobyl is given by the Watt Committee on Energy (1991).

Potential health effects of radiation at relatively low doses are short term: (1) birth defects from radiation received by the foetus; (2) thyroid cancers from radioactive iodine; from 3 years onwards: (3) leukaemia; over a period 5–40 years: (4) cancers; and over a generation: (5) genetic effects.

Recommendations for radiation protection standards are given in *Radiological Protection Bulletin 141 1993* by the NRPB (1993). Details are given in Chapter 25.

A20.2 Nuclear Industry

A20.2.1 Nuclear industry regulation

Public control of the nuclear industry is discussed in Chapter 4. In the United Kingdom the regulatory body is the Nuclear Installations Inspectorate (NII), which is part of the HSE. In the United States of America it changed in the mid-1970s from the Atomic Energy Commission (AEC) to the Nuclear Regulatory Commission (NRC).

A20.2.2 Nuclear industry advisory committees

In the United Kingdom there is a standing committee, the Advisory Committee on the Safety of Nuclear Installations (ACSNI) which advises on nuclear safety. In the United States of America there is an Advisory Committee on Reactor Safety (ACRS).

Advice on radiological protection in the United Kingdom is the responsibility of the National Radiological Protection Board (NRPB).

A20.2.3 International bodies

Bodies operating at the international level include the International Atomic Energy Agency (IAEA) in Vienna and the International Committee on Radiological Protection (ICRP). The IAEA was set up in 1957 as an intergovernmental organization linked to the UN.

A20.2.4 Nuclear industry research

Work for the nuclear industry is a main source of support for a number of major research laboratories and organizations whose output is also of interest to the process industries. In the United Kingdom these include the UK Atomic Energy Authority (UKAEA), which operates laboratories at Harwell. The Systems Reliability Directorate (SRD) is part of the UKAEA.

In the United States of America major laboratories with a nuclear interest include the Argonne National Laboratory (ANL), Brookhaven National Laboratory (BNL), Electric Power Research Institute (EPRI), Lawrence Livermore National Laboratory (LLNL), Oak Ridge National Laboratory (ORNL) and Sandia Laboratories (SL).

A20.2.5 Nuclear industry accidents

Early perceptions of the hazard from the nuclear industry were coloured by the image of an explosion from a nuclear weapon. A major accident in the nuclear industry, a core meltdown, is quite different. There would not be the initial intense blast and radiation effects, but rather a dispersion of radioactive material at the site and from the site by the wind. Such an accident occurred at Chernobyl.

A20.2.6 Nuclear industry debate

Virtually from its inception the nuclear industry has been the subject of debate. Some principal critiques are *Nuclear Power* by Patterson (1976), *Soft Energy Paths* by Lovins (1977), *The Risks of Nuclear Power Reactors* by the Union of Concerned Scientists (UCS) (1977), *Nuclear or Not*? by Foley and van Buren (1978), *Cover-up* by Grossman (1980), *The Fast Breeder Reactor* by Sweet (1980), *The PWR Decision* by Cannell and Chudleigh (1984), *Going Critical* by Patterson (1985) and *Nuclear Politics* by T. Hall (1986).

A20.3 Nuclear Reactors

Accounts of nuclear reactor systems include *Nuclear Reactor Control and Instrumentation* by J.H. Bowen and Masters

(1959), *Nuclear Reactor Engineering* by Glasstone and Sesonke (1962), *Nuclear Energy Technology* by Knief (1981), *Nuclear Power Technology* by W. Marshall (1984), *The Elements of Nuclear Power* by D.J. Bennett and Thompson (1989) and *The Technology of Nuclear Reactor Safety* by T. Thompson and Beckerley (1989).

Treatments by the HSE include PWR (HSE, 1979d), *Safety Assessment Principles for Nuclear Reactors* (HSE, 1979f) and *Sizewell B* (HSE, 1982b).

A20.3.1 Nuclear reactor types

Some principal types of nuclear reactor are

(1) Gas-cooled reactors:
  (a) Magnox reactor;
  (b) Advanced gas-cooled reactor (AGR);
  (c) High temperature gas-cooled reactor (HTGR);
(2) Light water reactors (LWRs):
  (a) Pressurized water reactor (PWR);
  (b) Boiling water reactor (BWR);
(3) Heavy water reactors:
  (a) CANDU reactor;
  (b) Steam generating heavy water reactor (SGHWR);
(4) Fast breeder reactors.

Accounts of reactor types are given in *Nuclear Power Reactors* by the UKAEA (1987) and by Patterson (1976) and Lewins (1988).

In the United Kingdom the first reactors were the gas-cooled Magnox reactors. The next generation were the AGRs reactors. The first pressurized water reactor came much later, at Sizewell B.

Elsewhere, notably the United States of America and France, the vast majority of reactors installed have been PWRs.

A20.3.2 Reactor design features

In a nuclear reactor energy is released by a chain reaction involving neutrons. The reaction is sustained by those neutrons which are absorbed. Slower neutrons are absorbed in larger proportion than faster ones. Use is made, therefore, of a 'moderator' to slow down the neutrons. In some designs the moderator is graphite, for example, the Magnox reactor, while in others it is water, for example, the PWR.

The power output of the reactor is controlled by movement of control rods, containing materials which are strong absorbers of neutrons, and the reactor is shut down by their full insertion. Emergency shut down, or scram, is effected by dropping in the rods.

Even when shut down the reactor has a certain output of heat, due to radioactivity in the core. This decay heat needs to be removed if the core is not to overheat. The removal of the decay heat is one of the main problems which have to be handled in reactor design.

The reactor core is cooled by a coolant which in the AGR is carbon dioxide and in the PWR is water.

A20.3.3 Advanced gas-cooled reactors

The underlying concept of the AGR is that if forced convection circulation of the gas coolant is lost, natural convection will still effect a degree of cooling. To this extent, the reactor is an application of inherently safer design.

A20.3.4 Pressurized water reactors

The majority of nuclear reactors installed world-wide are PWRs. In the PWR design the core is cooled by water which also doubles as the moderator.

A PWR is provided with multiple systems to inject cooling water into the reactor to keep the core cool and with numerous protective systems to ensure the operation of this backup cooling. The reactor is vulnerable in the event of the failure of these instrument and cooling systems. On a PWR an emergency can escalate within a relatively short time scale.

In a PWR the fuel is inside three sets of containment. The first is the fuel rods. The second is the reactor pressure vessel (RPV) in which the fuel rods are held. The third is the containment building which encloses the reactor vessel.

The reactor is vulnerable to loss of coolant and much attention has been focused on the large loss of coolant (LOCA) accident.

A20.3.5 Inherently safer design

In view of the nature of the hazard from a nuclear reactor, there is interest in inherently safer design. Mention has already been made of the inherent safety aspects of the AGR.

A review of approaches to inherently safer design of nuclear reactors is given in *Proposed and Existing Passive and Safety-related Structures, Systems and Components (Building Blocks) for Advanced Light Water Reactors* by Forsberg *et al.* (1989).

Some examples are discussed by Kletz (1988h). The HTGR is a small reactor cooled by high pressure helium. The reactor is designed to withstand a high temperature and to have an adequate heat loss by radiation and natural convection if the coolant should fail. The Swedish process-inherent ultimate safety (PIUS) reactor is a water-cooled reactor immersed in boric acid solution, so that if the coolant pumps fail this solution is drawn through the core by natural convection.

Another aspect of inherent safety is the reliability of the overall system for the control and protection of the reactor, which includes both the automatic control and protection and the process operator. As already mentioned, a PWR is vulnerable to equipment failure in the instrument and coolant systems which protect it. It is therefore vulnerable also to operator actions which render this protection ineffective.

This feature is discussed by Franklin (1986) in these terms:

> When operators are subject to conditions of extreme emergency arising from a combination of unforeseen circumstances they will react in ways which lead to a high risk of promoting accidents rather than diminishing them. This is materially increased if operators are aware of the very small time margins that are available to them.

A20.4 Nuclear System Reliability

A20.4.1 Pressure systems

The integrity of the pressure system is critical to the safety of a nuclear reactor such as the PWR. Much attention has been therefore focused on the potential for pressure vessel failure.

Pressure vessel failure is considered in the *Rasmussen Report*. It is also discussed by Bridenbaugh, Hubbard and Minor (1976) and Cottrell (1977).

It was a principal issue at the Sizewell B inquiry, and an account is given in Appendix 26.

The treatment given in Chapter 12 of failure rates of pressure vessels draws heavily on estimates made with nuclear applications in mind.

A20.4.2 Protective systems

From the start the nuclear industry made extensive use of instrumentation, and particularly of instrumented protective systems. Accounts of this work are given in *Reliability Assessment of Protective Systems for Nuclear Installations* by Eames (1965 AHSB(S) R99) and *Safety Assessment with Reference to Automatic Protective Systems for Nuclear Reactors* by A.E. Green and Bourne (1966 AHSB(S) R136).

This work led to interest in reliability technologies, including fault trees and dependent failure. Since it was necessary to have a target to aim for in design of such protective systems, this also prompted the development of risk criteria.

A20.4.3 Reliability engineering

The nuclear industry joined the defence and aerospace industries in developing reliability techniques. A treatment of reliability engineering from the viewpoint of the nuclear industry and with special reference to protective systems, is *Reliability Technology* by A.E. Green and Bourne (1972).

A20.4.4 Failure and event databases

The practice of reliability engineering created the need for failure and event databases. This is illustrated by the development of the database of the UKAEA Systems Reliability Service (SRS) (Ablitt, 1973 SRS/GR/14). The development of this database is described in Appendix 14.

A20.4.5 Fault trees

The need to identify failure paths and to estimate failure frequencies for systems with multiple layers of protection has led in the nuclear industry to extensive use of fault tree analysis. It is the basic method used for frequency estimation in the *Rasmussen Report*. The technique is described in *Reliability and Fault Tree Analysis* by Barlow, Fussel and Singpurwalla (1975) and in *Fault Tree Handbook* by Vesely *et al.* (1981).

Associated with this work are the fault tree analysis computer codes PREP and KITT (Vesely and Narum, 1970).

A20.4.6 Event trees

Likewise, the nuclear industry has made much use of event trees, both to identify and quantify the effects of certain failures, such as those of the power supply, and the outcomes of a release to atmosphere.

A20.4.7 Dependent failures

Nuclear reactors rely on extensive protective systems to give a very high degree of reliability, and it is characteristic of such systems that they are liable to be defeated by dependent failure. In some cases different assumptions about dependent failure can result in a dramatic increase in the estimated frequency of an accident. The nuclear industry has therefore put much effort into the study of this problem.

The problem of dependent failure bulks large in the analyses in the Rasmussen Report and in the critiques of that report.

An account is given in *Defences against Common-mode Failures in Redundant Systems* by Bourne *et al.* (1981 SRD R196).

A20.5 Nuclear Hazard Assessment

A20.5.1 Probabilistic risk assessment

The nuclear industry has for long made use of probabilistic risk assessment (PRA), or probabilistic safety assessment (PSA), as a means of ensuring that its hazards are identified and under control and as a basis for dialogue on this with the regulatory authority. Guidance is given in *PRA Procedures Guide* by the NRC (1982). A more recent treatment is *Procedures for Conducting Probabilistic Safety Assessment of Nuclear Power Plant* by the IAEA (1992).

The *Rasmussen Report*, described in Appendix 23, is one well known generic PRA. Another is the *Deutsche Risikostudie Kernkraftwerke* by the Technische Uberwachungsverein (TUV) (1979).

A20.5.2 Accident sequences and scenarios

In a nuclear PRA considerable effort is devoted to the treatment of the accident sequences, or scenarios.

Thus a large proportion of the IAEA document just referred to is devoted to procedures for the identification of accident initiators and of accident sequences, for the classification of accident sequences into plant damage states and for the determination of the frequency of the accident sequences.

A20.5.3 Rare events

There are a number of natural and man-made threats which may hazard a nuclear plant. Examples of these two types of event are, respectively, an earthquake and an aircraft crash. Such events, their consequences and frequency, have therefore been the subject of much study by the nuclear industry.

A20.5.4 Explosions

One type of the event which may put a nuclear plant at risk is an explosion. The industry has examined various kinds of explosion, including vapour cloud explosions, and certain types of particular interest to it such as steam explosions and hydrogen explosions.

A20.5.5 Hydrogen explosions

The fuel elements in the reactor core are held in metal cladding tubes. At high temperatures the zirconium metal used for this cladding can react with steam to produce hydrogen, with the risk of a hydrogen explosion.

A20.5.6 Missiles

Studies of some relevance to process plants are those on missiles such as the work reported by Baum (1984, 1991).

A20.5.7 Earthquakes

Of rare natural events, the earthquake hazard bulks large both in plant design and in risk assessment. The nuclear regulator has put much effort into defining the type of earthquake which the plant should be required to withstand. Guidance is given in *Design Response Spectra for Seismic Design of Nuclear Power Plants* by the NRC (1973).

Then, given such a design earthquake, it is possible to specify equipment to withstand it, as described below.

A20.5.8 Expert judgement

Where hard information is lacking, resort may be had to the use of expert judgement. Thus expert judgement may be used to obtain estimates of failure and event rates. It may also be applied to other aspects such as the formulation of accident sequences. Guidance on this approach is given in *Eliciting and Analysing Expert Judgement: a Practical Guide* by M.A. Meyer and Booker (1990).

A20.5.9 Computer error

A modern nuclear power station operates under computer control. The control computer, both hardware and software, is therefore a safety critical system.

The quality assurance of the computer software is a particularly intractable problem. An account of this aspect of the Sizewell B computer system is given by Hunns and Wainwright (1991).

A20.5.10 Human error

The conduct of PRA for nuclear plants has led naturally to a requirement for methods of handling the human aspects, particularly in fault trees and in event trees. An overall methodology for this problem is described in *Handbook of Human Reliability Analysis with Emphasis on Nuclear Power Plant Applications* by Swain and Guttman (1983). A method of estimating error probabilities is addressed in *SLIM-MAUD: an Approach to Assessing Human Error Probabilities using Structured Expert Judgement* by Embrey *et al.* (1984).

Also relevant is the ACSNI Study Group on Human Factors *Second Report: Human Reliability Assessment – a Critical Overview* (ACSNI, 1991).

A20.5.11 Source terms

Each accident scenario needs to be associated with a defined source term, so that the dispersion of radioactive materials may be modelled.

A20.5.12 Emission models

The nuclear industry was one of the first to develop a sustained interest in two-phase flow, both flow within the plant and flow of leaks from it. An example of work from a nuclear background is *Two-Phase Flow and Heat Transfer* by Butterworth and Hewitt (1977).

A20.5.13 Gas dispersion models

Much of the work on gas dispersion modelling has been in support of work on the consequences of a nuclear accident. This is illustrated by one of the early texts, *Meteorology and Atomic Energy* 1968 by Slade (1968).

A20.5.14 Severe accident risk

A focus to work on PRA has latterly been provided by the Severe Accident Risk study, for which the basic document is NUREG-1150 *Reactor Risk Reference Document* of the NRC (1987).

A20.5.15 Risk criteria

The quantification of risks from nuclear reactors has necessarily led to the need for risk criteria by which to judge these risks. Some of the first risk comparisons were those given in the *Rasmussen Report*.

Since then, there has been a wide-ranging debate of risk criteria for man-made hazards of all kinds. Nuclear risk criteria emerging from this are given in *The Tolerability of Risk from Nuclear Power Stations* by the HSE (1988b), and associated comments (HSE, 1988a).

A20.6 Nuclear Pressure Systems

A20.6.1 Quality assurance

All aspects of the design and operation of nuclear power plant need to be carried out to high standards. There has to be, therefore, a system of quality assurance to ensure that these standards are met.

This aspect is described in NUREG-1055 *Improving Quality and the Assurance of Quality in the Design and Construction of Commercial Nuclear Power Plants* (NRC, 1984).

A20.6.2 Inspection

High-quality inspection is an essential part of the nuclear industry's armoury. It has a special interest in non-invasive techniques of monitoring and inspection. These include acoustic emission monitoring, ultrasonics and leak detection methods.

Methods of leak detection are described in NUREG/ CR-4813 *Assessment of Leak Detection Systems for LWRs* (NRC, 1987).

The industry has also developed risk-based inspection. An account is given in NUREG/CR-5371 *Development and Use of Risk-based Inspection Guides* (NRC, 1989).

A20.6.3 Fracture mechanics

One of the most powerful inspection techniques for pressure systems is fracture mechanics and the nuclear industry has been in the van in developing such methods. They include the CEGB R6 system described in R/H/R6 *Assessment of the Integrity of Structures Containing Defects* by Milne *et al.* (1986).

A20.6.4 Seismic qualification

One of the principal external hazards to which a nuclear plant is vulnerable is an earthquake. There is therefore a requirement that equipment crucial to safe operation be able to withstand an earthquake of specified intensity. This is implemented by a system of seismic qualification of equipment. An account is given in NUREG-1030 *Seismic Qualification of Equipment in Operating Nuclear Power Plants* by the NRC (1987).

A20.6.5 Ageing

Another aspect which the nuclear industry has explored in some detail is ageing of equipment, and residual, or remanent, life assessment.

An account of basic principles is given in NUREG/ CR-5314 Life Assessment Procedure for Major LWR Components (NRC, 1990). There are studies on specific equipment such as electric motors, diesel generators, instrument air systems, motor operated valves, etc.

A20.7 Nuclear Reactor Operation

The *Kemeny Report* and, even more, the *Task Force Report* on TMI contain numerous recommendations on nuclear reactor operation, particularly on the design of display and alarm systems and of control rooms generally, operating and emergency procedures, and operator training.

A20.7.1 Human factors

A considerable effort is made to apply human factors on nuclear power plants, a practice reinforced by the *Kemeny Report's* emphasis on people-related problems.

Some typical titles which illustrate the application of human factors on nuclear power plants are as

follows: NUREG/CR-3331 *A Methodology for Allocating Nuclear Power Plant Control Functions to Human or Automatic Control* (NRC, 1983); NUREG/CR-3371 *Task Analysis of Nuclear Power Plant Control Room Crews* (NRC, 1984); and NUREG-1122 *Knowledges and Abilities Catalog for Nuclear Power Plant Operators* (NRC, 1987).

Three reports on human factors in nuclear power plant operation have been issued by the ACSNI Study Group on Human Factors. Reference has already been made to the second report, on human reliability assessment (ACSNI, 1991). The other two are First Report on Training and Related Matters (ACSNI, 1990) and Third Report: Organising for Safety (ACSNI, 1993).

A20.7.2 Process operator

The problems, and modelling, of the process operator have been the subject of extensive studies, notably the work described in *Information Processing and Man–Machine Interaction* by Rasmussen (1986).

A20.7.3 Display and alarm systems

Early developments in computer aids for the process operator were the alarm analysis systems developed at Wylfa and Oldbury nuclear power stations, described by Welbourne (1965) and Patterson (1968), respectively. The purpose of these systems is to assist the operator in interpreting the large number of alarms which tend to come up in a plant emergency.

One of the perceived problems at TMI was the difficulty experienced by operators in assessing the safety status of the plant. A recommendation of the Task Force Report was that every reactor should have a plant safety status display.

TMI also illustrated the alarm interpretation problem just mentioned and the report recommended that the feasibility be explored of developing a suitable aid, which it termed a disturbance analysis system (DAS).

A20.7.4 Control room design

A large proportion of the studies conducted on control rooms have been in the nuclear industry, and these have contributed to the development of understanding of human factors and human error.

In the aftermath of TMI control room design in general was also an issue. This illustrated in NUREG-0700 *Guidelines for Control Room Design Reviews* (NRC, 1981).

A set of studies of the Sizewell B control room are described by Ainsworth and Pendlebury (1994), Umbers (1994) and Whitfield (1994).

A20.7.5 Operating procedures

In the operation of nuclear power plants particular emphasis is placed on written operating procedures and on the training of operators in these. An account is given in NUREG/CR-3968 *Study of Operating Procedures in Nuclear Power Plants* (NRC, 1987).

A20.7.6 Emergency procedures

Operating procedures for dealing with an emergency assume particular importance on nuclear power plants. The *Kemeny Report* and the *Task Force Report* make recommendations on the emergency procedures.

Such procedures are the subject of NUREG/CR-0899 *Guidelines for the Preparation of Emergency Operating Procedures* (NRC, 1982) and NUREG/CR-3177 *Methods for Review and Evaluation of Emergency Procedure Guidelines* (NRC, 1983).

A20.7.7 Operator training

Process operators on nuclear power plants undergo extensive training, for which the industry makes appreciable use of simulators.

The need for such training is a principal theme of both the *Kemeny Report* and of the *Task Force Report* on TMI. It is also the subject of the first report of the Study Group on Human Factors of the ACSNI (1990). Simulator training is treated in NUREG/CR-3725 *Nuclear Power Plant Simulators for Operator Licensing and Training* (NRC, 1984) and numerous other reports.

A20.8 Nuclear Emergency Planning

An emergency plan, covering both on-site and off-site aspects, is an integral part of the arrangements at a nuclear power plant.

A20.8.1 Accident management plans

There has been growing emphasis on the need to plan for and to manage an emergency.

Relevant work is that described in NUREG/CR *Management of Severe Accidents* by the (NRC, 1985) and NUREG/CR-5543 *A Systematic Process for Developing and Assessing Accident Management Plans* by the NRC (1991).

A further account is given by Ang (1992).

A20.8.2 Off-site emergency plans

Off-site emergency planning has been a feature of the nuclear industry from its earliest days. An account is given in *Emergency Plans for Civil Nuclear Installations* by the HSE (1986b).

A20.9 Nuclear Incident Reporting

In most regulatory regimes the nuclear industry is required to report to the regulator the occurrence of specified types of incidents.

A20.9.1 Licensee Event Reports

In the United States of America the system is that described in the NUREG/CR-2000 *Licensee Event Report* (LER) compilation.

A20.9.2 Precursors to severe accidents

The LERs record some events which are of such a nature that they could well have escalated into more severe events, even though in the particular case this has not occurred. These events are precursors of more serious incidents and serve as warnings. Periodic analyses are made of such precursors such as NUREG/CR-4674 *Precursors to Potential Severe Core Damage Accidents 1990: Status Report* by the NRC (1991).

A20.10 Nuclear Incidents

There have been a number of incidents on nuclear plants which are instructive for the process industries also. In addition to TMI and Chernobyl, they include Windscale and Browns Ferry.

Accounts of incidents include those in *Nuclear Power* by Patterson (1976), *The Nuggett File* by the UCS (1979) and *Nuclear Lessons* by Curtis *et al.* (1980); later incidents are covered by May (1989).

A20.10.1 Radioactive sources

Although the incidents of prime interest here are those involving nuclear plant, other nuclear sources should not be neglected. The following case, believed to be the worst of it kind to date, illustrates the hazard from equipment containing a radioactive source.

In 1985 in Goiania, Brazil, a radiotherapy institute moved premises, leaving behind a unit containing a caesium-137 source in a stainless steel container and without notifying the licensing authorities. Subsequently the building was partially demolished. Some 2 years after the institute's departure, on 13 September 1987, two men entered and tried to dismantle the machine for scrap, one taking home the steel cylinder; both fell ill. However, some 5 days later one broke open the steel cylinder and the caesium spilled out. A train of events ensued which resulted in 249 people being exposed to radiation, of whom four died.

A20.10.2 Military reactors and weapons plants

Hanford, the Green Run, 1949

On 2 December 1949 at Hanford, Washington State, there occurred one of a series of releases from an installation of eight nuclear reactors producing plutonium for the Manhattan Project. This was the Green Run, an experiment conducted to investigate monitoring methods which would be useful in intelligence work on the nuclear capabilities of other countries. The release formed a plume 200 miles $\times$ 40 miles in dead calm conditions and involved 20,000 Ci of xenon and 7780 Ci of iodine-131.

Rocky Flats, Colorado, 1957

On 11 September 1957 at Rocky Flats, Colorado, a fire occurred in a glove box at an atomic weapons plant. Plutonium shavings ignited spontaneously, workers tried to put the fire out and explosions occurred which blew out the ventilation filters. For half a day there was a release of plutonium contaminated smoke. On 11 May 1969 there occurred another glove box fire. All new weapons production was shut down for 6 months.

Idaho Falls, Idaho, 1961

On 3 January 1961 at Idaho Falls, Idaho, an incident occurred on a prototype military nuclear power plant, the Stationary Low Power Reactor SL-1, one of 17 reactors at the AECs National Reactor Test Station (NRTS). The reactor was shut down and control rods had been disconnected to install additional instrumentation. The emergency started with the sounding of alarms. As it developed, three men working on the control rods were found to be missing. One was discovered dead, pinned to the ceiling by a control rod, another was also dead and the third died soon after. The precise sequence of events is uncertain. One explanation given is that the central control rod was partially withdrawn and there was a power surge, generating steam which lifted the lid of the pressure vessel, causing it to rise 9 ft and then drop back.

A20.10.3 Windscale

Accounts of the Windscale incident are given in *Windscale Fallout* by Breach (1978) and *Windscale 1957* by L. Arnold (1992) and by May (1989).

On 10 October 1957 at Windscale, United Kingdom, an incident occurred which led to a serious radioactive release. The installation consisted of two simple air-cooled, graphite-moderated, atomic piles used for the production of plutonium. The graphite was subject to deformation and build-up of energy due to neutron bombardment, the so-called Wigner effect. A procedure had been established to release the Wigner energy by turning off the fans, making the pile critical and letting heat build up. On 7 October 1957, this procedure had been followed, but it appeared that not all the Wigner energy had been released, so the pile was heated up again. The sensors then showed an abnormal temperature rise and the power was reduced. By 9 October conditions seemed normal except that there was a hot spot. However, on 10 October a rise in radioactivity was detected at the filters in the chimney. An attempt was made to inspect the core using a remote scanner, which jammed. Staff removed a charge plug and looked in. All the fuel channels which they could see were on fire and a fuel cartridge had burst. The air movement caused by the fans was now fanning the blaze. Despite fears that it might lead to a hydrogen–oxygen explosion, the decision was taken to use water to put out the fire, which it did. As a result of the incident, workers on the site were exposed to radiation and milk from cattle in the area had to be discarded. The release was mitigated by the presence of the filters, installed at the insistence of Sir John Cockcroft, prominent at the top of the chimney, and known locally as 'Cockcroffs Folly'. The piles were decommissioned and set in concrete.

A20.10.4 Civil nuclear reactors and reprocessing plants

Chalk River, Ontario, 1957

On 12 December 1957 at Chalk River, Ontario, there was a loss of control on a nuclear reactor leading to damage of the core so that it had to be removed and buried. In outline the initial sequence of events was as follows. Outside the control room, a supervisor found that an operator was opening valves which caused the control rods to withdraw. He immediately set about shutting the valves, but some of the rods did not drop back. He telephoned the operator in the control room, intending to ask him to push a button which would drop control rods in, but by a slip of the tongue actually referred to a button which would withdraw rods. In order to comply, the operator moved away from the phone so that the supervisor temporarily lost touch with him. The operator in the control room soon recognized from the rising reactor temperature that there was something wrong and pressed the scram button, but events had been set in train which led to core damage.

Detroit, Michigan, 1966

On 5 October 1966 near Detroit, Michigan, the Enrico Fermi reactor experienced an incident. The reactor was the first commercial fast breeder reactor in the United States of America. It was being started up for a series of tests when abnormalities were observed and some of the control rods were found not to be in their expected positions. Tests on the sodium coolant showed it to be contaminated, suggesting that part of the fuel core had melted, but the cause was unknown. The authorities were alerted and went on standby for evacuation. Subsequent investigation found that separation had occurred of parts from a steel cone at the bottom of the vessel, installed so that in a meltdown the fuel would spread out and not reach critical mass. In a last-minute modification, zirconium plates had been put onto the cone. One plate had worked loose, had been forced into

the core by the sodium coolant and had blocked coolant flow to two of the fuel assemblies.

An account of this incident is given in *We Almost Lost Detroit* by Fuller (1984).

Browns Ferry, Alabama, 1975

Prior to TMI one of the US incidents which received particular attention was that on 22 March 1975 at Browns Ferry. Accounts are given in the *Rasmussen Report* and in *Browns Ferry: the Regulatory Failure* by Ford, Kendall and Tye (1976). The incident is described in Appendix 23.

Beloyarsk, USSR, 1978

On 30–31 December 1978 at Beloyarsk, USSR, there occurred an incident which until Chernobyl was the most serious in the nuclear industry. The complex was 50 km from Sverdlovsk and housed two RMBK reactors and a BM600 fast breeder reactor. A serious fire broke out in the machine hall, causing steel girders and the concrete roof to collapse, opening up a huge hole above No. 2 Generator and disabling the fire protection system. Emergency procedures called for both RMBK reactors to be shut down. But as it was close to −50°C outside, it was feared the reactor cooling systems would freeze and the cores would overheat. Attempts were made to keep No. 1 Reactor and its turbine running, but despite the fire the turbine froze. There followed an extended emergency which eventually, with the arrival of fire fighters from outside, was brought under control.

Cap la Hague, France, 1981

On 6 January 1981 at Cap la Hague, Normandy, France, in a nuclear fuel reprocessing facility there occurred the most serious of a series of incidents. Fire broke out in a spent fuel dry waste silo. Ignition occurred in cotton waste, soaked in solvent and in contact with uranium and magnesium. The cotton waste had been used in a decontamination operation there several weeks earlier. The fire was attacked first by water, which formed steam, and then by liquid nitrogen. Radioactivity was released inside and outside the plant.

New York State, 1982

On 25 January 1982 in New York State the Ginna reactor experienced tube rupture, due to corrosion, in the steam generator, causing contamination of the secondary, clean steam circuit by the radioactive water from the primary water circuit cooling the core. High pressure in the steam circuit caused a pressure relief valve to open, initially in 5 min bursts and then by sticking open for 50 min. Another PRV on the primary circuit was deliberately opened to reduce the pressure in that circuit but also stuck open. A steam bubble formed, but it proved possible to correct it by pumping in more water.

Frankfurt, FRG, 1987

On 16–17 December 1987 at Frankfurt, FRG, the Biblis A nuclear reactor experienced an incident involving the low pressure injection (LPI) system. It was a requirement that this system remain isolated to prevent (1) leakage of primary coolant out through it and (2) overpressure of the system itself by the primary coolant. During start up the main valve TH22 S006 on the pipe between the LPI system and the primary circuit had been left open; there were also two secondary valves on the line. The status of the main valve was shown by a red light on the control panel, but the operators assumed that the fault was on the light itself. There were two changes of shift before it was realized that valve TH22 S006 was open. The operators took 2 h to decide on a plant shut down and then 10 min later changed their minds and tried an alternative, and hazardous, procedure. They decided to initiate flow through valve TH22 S006, expecting that the valve would then be shut by its trip system. They controlled the flow by cracking open one of the secondary valves and primary coolant started to escape, but valve TH22 S0006 did not shut, and after a few seconds they desisted. The operators then shut the reactor down.

A20.11 Notation

c	velocity of light
D	absorbed dose (Sv)
E	energy
H	dose equivalent (Sv)
m	mass
M_a	atomic weight
n	number of radioactive atoms
n_0	number of radioactive atoms at time zero
N_0	Avogadro's number
Q	quality factor
t	time
λ	radioactive decay constant (s^{-1})
τ	half-life (s)

Appendix 21

Three Mile Island

Contents

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At 4.00 on 28 March 1979, a transient occurred on Reactor No. 2 at Three Mile Island, near Harrisburg, Pennsylvania. A turbine tripped and caused a plant upset. The operators tried to restore conditions, but, misinterpreting the instrument signals, misjudged the situation and took actions which resulted in the loss of much of the water in the reactor and the partial uncovering of the core. Radioactivity escaped into the containment building. Site and general emergencies were declared.

The accident at Three Mile Island (TMI) (also referred to initially as Harrisburg) was the most serious accident which had occurred in the US nuclear industry.

The President set up a commission to investigate the accident. Their work is described in *The Report of the Presidents Commission on the Accident at Three Mile Island* (the Kemeny Report) (Kemeny, 1979).

The NRC carried out an investigation, reported in *Investigation into the March 28, 1979 Three Mile Island Accident by Office of Inspection and Enforcement* (the NRC Report) (NRC, 1979b). It also set up a task force, the findings of which are given in *TMI-2 Lessons Learned Task Force Final Report* (the Task Force Report) (NRC, 1979d).

Another report is *Analysis of Three Mile Island – Unit 2 accident by the Nuclear Safety Analysis Center* (NSAC) of EPRI (1979a).

Hearings were also held by the US Congress (US Congress, 1979) at which evidence was taken from managers, engineers, process operators and others.

The Accident at Three Mile Island gives the initial response of the HSE (1979a).

The TMI accident was a watershed in the development of nuclear power in the US and worldwide. After 1979, the ordering of new nuclear power stations in the US virtually dried up. Elsewhere, TMI has at the least heightened awareness of nuclear hazards.

In addition to the official reports mentioned, accounts of the TMI accident have been given in *Three Mile Island* by Stephens (1980) and by J.F. Mason (1979), Rubinstein (1979a, b), Collier and Davies (1980), Dunster (1980), H.W. Lewis (1980), Rogovin (1980), Schneider (1980) and Kletz (1982l, 1988h). A detailed timetable of the events during the accident is given by the NRC (1979b) and by J.F. Mason (1979).

Selected references on TMI are given in Table A21.1.

A21.1 The Company and the Management

The company which operated TMI was Metropolitan Edison (Met Ed).

Table A21.1 *Selected references on Three Mile Island*

NRC (Appendix 28 Three Mile Island, 1979b,d); Douglas (1979); EPRI (1979a); Ferrara (1979); HSE (1979a); Kemeny (1979); J.F. Mason (1979); Rubinstein (1979a,b); Savage (1979); US Congress (1979); Brookes and Siddall (1980); Cobb and Marshall (1980); Collier and Davies (1980); Dunster (1980); Lanouette (1980); Levy (1980); H.W. Lewis (1980); Rogovin (1981); Stephens (1980); Torrey (1980); Jaffe (1981); Moss and Sills (1981); Schneider (1981); Starr (1981); Straus (1981); Wolf (1981); Kletz (1982l, 1983j, 1988h); Sills, Wolf and Shelansky (1982); Slear, Long and Jones (1983); Anon. (1984kk); Ural and Zalosh (1985); Ballard (1988); Philley (1992)

Some of the TMI staff who involved in dealing with the incidents were

Station manager	Mr G. Miller
Station superintendent	Mr J. Logan
Superintendent of technical support	Mr G. Kunder
Shift supervisor	Mr W. Zewe
Shift foreman	Mr F. Scheimann
Control room operators	Mr E. Frederick; Mr C. Foust
Others involved included Met Ed vice-president for generation	Mr J. Herbein
Babcock and Wilcox site representative	Mr L. Rogers

A21.2 The Site and the Works

TMI is situated on the Susquehanna River, some 10 miles south-east of Harrisburg, Pennsylvania.

A21.3 The Process and the Plant

The plant consisted of two PWRs of approximately 900 MWe each. Unit 1 had been in commercial service since 1974 and Unit 2 since December 1978.

The contractors for the reactor plant were Babcock and Wilcox.

The nuclear reactor system is shown in Figure A21.1. The reactor itself is a pressure vessel containing the reactor core. The fuel in the core is enriched uranium dioxide pellets encased in zirconium alloy tubing. There are some 37,000 of these fuel pins arranged in clusters in the core. The core is cooled by the primary cooling system containing water at a high pressure ($\ll$15.2 MPa) to prevent its boiling. The water acts not only as a coolant but also as a moderator.

Heat is removed from the reactor in this primary cooling circuit, the reactor cooling system (RCS), and used in the steam generators to generate steam to drive a pair of turbogenerators. The primary cooling system consists of two independent loops containing water at high pressure.

Since the volume of the cooling water changes with temperature, it is necessary to have some free space or 'bubble' in the primary circuit to control the system pressure. This is provided by the pressurizer, which is equipped with electrical heating to raise steam and thus increase the pressure, and cold water sprays to condense steam and thus lower the pressure. Steam can be blown off through a pilot-operated relief valve (PORV). The tail pipe from the PORV is run to the reactor coolant drain tank.

An emergency core cooling system (ECCS) is provided to give backup cooling. This consists of three separate systems. One is the high pressure injection (HPI) system which pumps borated water into the system at a pressure greater than the normal coolant pressure. Another is the core flooding system which automatically injects cold borated water into the system when the coolant pressure falls below about 4.1 MPa. The third is the low pressure injection system which operates at 2.8 MPa. This takes water either from a large tank of borated water or from the dump of the containment building and is thus capable of keeping up recirculation indefinitely.

The reactor, the primary cooling circuit and the steam generators are housed in a containment building which is

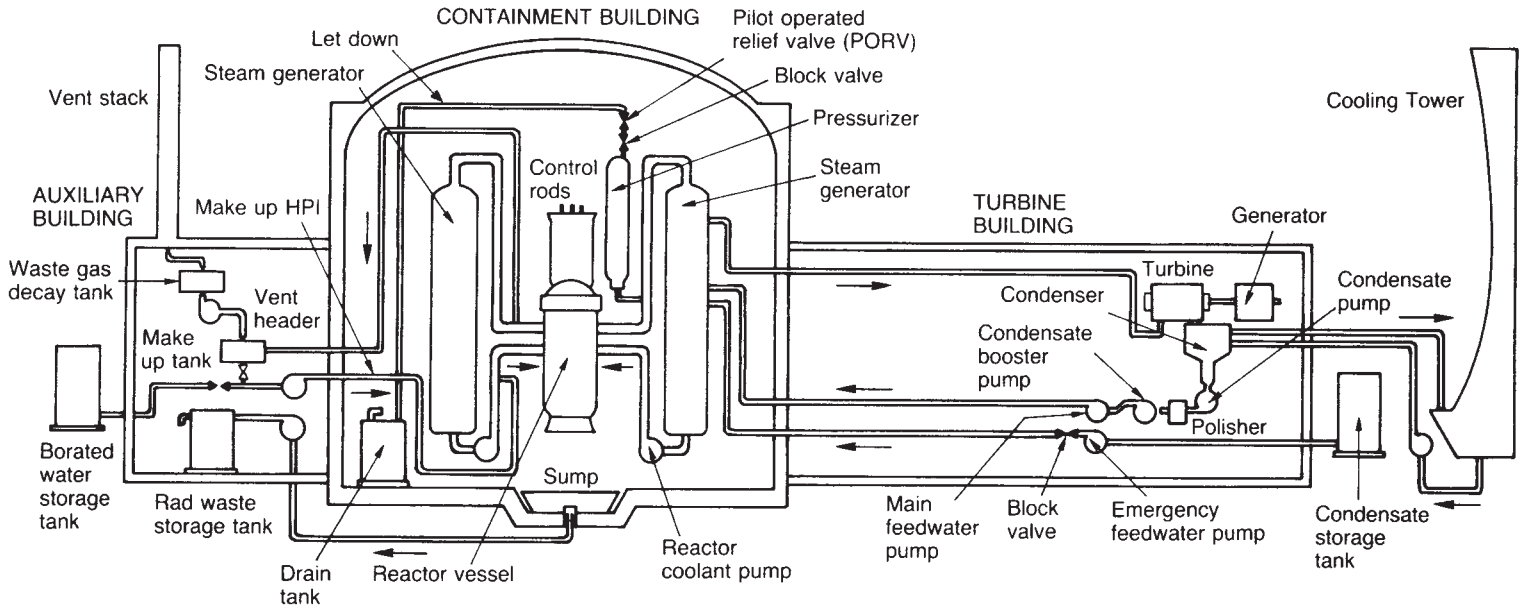

Figure A21.1 *Simplified flow diagram of TMI 2 nuclear power plant (Kemeny, 1979)*

leak-tight. The containment is designed to retain the contents of the primary circuit in the event of a major leak.

The containment building has a spray system containing dilute sodium hydroxide. The spray is triggered by high containment pressure and is intended in the event of a loss of coolant accident to cool down the contents of the containment and to scrub out iodine.

The turbogenerator set is housed in a separate building which also contains the condensate and water treatment plants. Feedwater for the secondary circuit is from the condenser. The condensate water is purified by ion exchange in a condensate polishing system, a package unit.

The water converted to steam on the secondary side in the steam generators is supplied to them by the main feedwater pumps. These are backed up by auxiliary, or emergency, feedwater pumps. Both sets of feedwater pumps are housed in the turbine building.

The control room is a typical one and is shown in Figure A21.2.

A21.4 Events Prior to the Excursion

Some 2 days prior to the incident, routine testing had been done on the valves on the auxiliary feedwater pumps. Two of the valves, the 'twelve valves', had inadvertently been left shut.

For some 11 hours before the incident, the operators had been trying to clear a blockage in the condensate polishing system. In order to do this use was made of compressed air. The service air line used for this purpose was cross-connected to the instrument air line. The pressure of the air in the instrument line was less than that of the water in the units and some water got into the instrument air line, despite the presence of a non-return valve on that line. This water found its way to some of the plant instruments.

Another feature was a persistent slight leak from either the regular safety valves or the PORV.

A21.5 The Excursion – 1

An account is now given of the events which constituted the excursion. A timetable of the events is given in Table A21.2 Sections A and B showing the events and phases, respectively. The trend records of the RCS parameters are shown in Figure A21.3.

At the time of the incident on 28 March, the reactor was operating under automatic control at 97% of its rated output of 961 MWe. The incident began when water which had entered the instrument air line caused the isolation valves on the condensate polishing system to drift shut and the condensate booster pump to lose suction pressure and trip out. The main feedwater pumps in the secondary circuit then tripped and almost immediately the main turbine tripped. The time was 4.00.37.

Valves allowing steam to be dumped to the condenser opened, and the auxiliary feedwater pumps started up. At the steam generators, the removal of heat from the RCS fell, and the pressure of the RCS rose. Within 3–6 s the PORV set pressure of 15.5 MPa was reached and the valve opened, but this was insufficient to relieve the pressure, and at 8 s in, pressure rose to 16.6 MPa, the set point for reactor trip. The control rods were driven into the core to stop the reaction.

The RCS pressure now fell below the PORV set pressure, but the valve failed to shut. However, the valve position indicator in the control room, which actually indicated not the position of the valve but the signal sent to it, showed the valve as closed. The RCS continued to lose water through the open PORV.

In the secondary circuit condensate was no longer being returned to the steam generators, because the valves on the condensate polishing system had closed. The auxiliary feedwater pumps were running, but the valves between the pumps and the steam generators were also, inadvertently, closed. At 1 min 45 s into the incident the steam generators boiled dry.

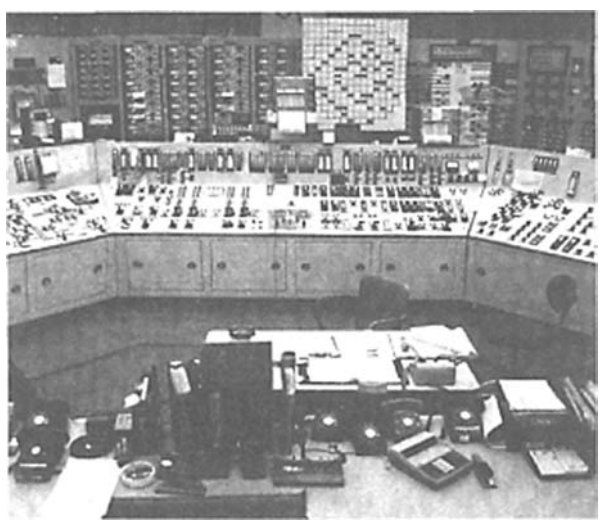

Figure A21.2 *Control room TMI 2 (Kemeny, 1979)*

Table A21.2 *Timetable of events at Three Mile Island*

A Timetable (first hours) (after Dunster, 1980)

Absolute time[a]	Time into incident	
4.01	zero	Feed water pump fails
		Pressure rise occurs in primary circuit
		Relief valves open
	8 s	Reactor shut-down
	13 s	PORV fails to close but indicates closure in the control room
		Extra cooling water (normal) injected by the operator
4.02	1 min 45 s	Steam generators dry out
4.03	2 min	Pressure in primary circuit falls and emergency cooling water injection started
4.04	3 min 30 s	Indication of high level of water in the pressurizer causes operator to shut off one emergency cooling pump
4.06	5 min 30 s	Stem generated in the core
		Operators drain off small volumes of primary water in response to rising level in pressurizer
4.11	11 min	Alarm indication of a high level of water in the containment building sump
		Sump water being pumped to auxiliary building
4.39	39 min	Sump pumps stopped by operator
5.00	60 min	Primary coolant pumps vibrating due to pressure of steam
5.14	1 h 14 min	Two primary pumps stopped by operator
5.45	1 h 45 min	Two remaining primary pumps stopped by oprator
5.50	1 h 50 min	Temperature in outlet ducts high enough to show presence of superheated steam — sigificance not recognized
6.22	2 h 22 min	Block valves on the relief valve lines closed by operators
7.00	3 h	Site emergency declared
7.20	3 h 20 min	Indication of 800 rem/h in containment building
7.24	3 h 24 min	General emergency declared
8.00	4 h	Containment building isolated automatically but operators continue to transfer primary let-down water to tanks in the auxiliary building
8.25	4 h 25 min	Local radio carried item concerning general emergency

B Phases (Collier and Davies, 1980)

Phase	1	Turbine trip 0–6 min
	2	Loss of coolant
	3	Continued depressurization 20 min–2 h
	4	Heat-up transient 2–6 h
	5	Extended depressurization 6–11 h
	6	Repressurization and ultimate establishment of stable cooling mode 13–16 h
	7	Removal of hydrogen bubble 1–8 d

[a] Absoulte times are approximate; the turbine trip was at 4.00.37.

Meanwhile the RCS pressure was dropping. At 2 min the pressure fell to 11 MPa at which point the first of the ECCS systems, the HPI system, came on and injected high pressure water. The liquid level in the pressurizer, however, was rising.

The display of liquid level was an indicator of the level of fluid in the pressurizer, but no longer of the mass of water; the liquid now contained steam bubbles and had thus been rendered less dense. To this extent the level display had become misleading.

The operators became concerned that the HPI system was increasing the inventory of water in the RCS, that the steam bubble in the pressurizer would be lost and that the circuit would become full of water and thus go 'solid'. At 4 min 38 s they therefore shut down one of the HPI pumps and throttled back the other.

With water passing through the PORV the pressure in the reactor coolant drain tank built up and at 7 min 45 s the reactor building sump pump came on, transferring water to the waste tanks in the auxiliary building.

At 8 min the operators realized that the steam generators were dry. They found that the auxiliary feedwater system valves were closed and opened them, thus restoring feedwater to the steam generators.

At 60 min the operators found that the RCS pumps were vibrating. This was due to the presence of steam, though they did not realize this. At 1 h 14 min they shut off the two pumps in Loop B to prevent damage to the pumps and pipework, with possible loss of coolant, and at 1 h 40 min shut off the two pumps in Loop A.

At 2 h 18 min the PORV block valve was at last shut off, thus stopping the loss of water from the RCS. The RCS pressure then began to rise.

In the two hours since the turbine trip periodic alarms had warned of low level radiation in the containment building. At about 2 h in, there was a marked increase in the

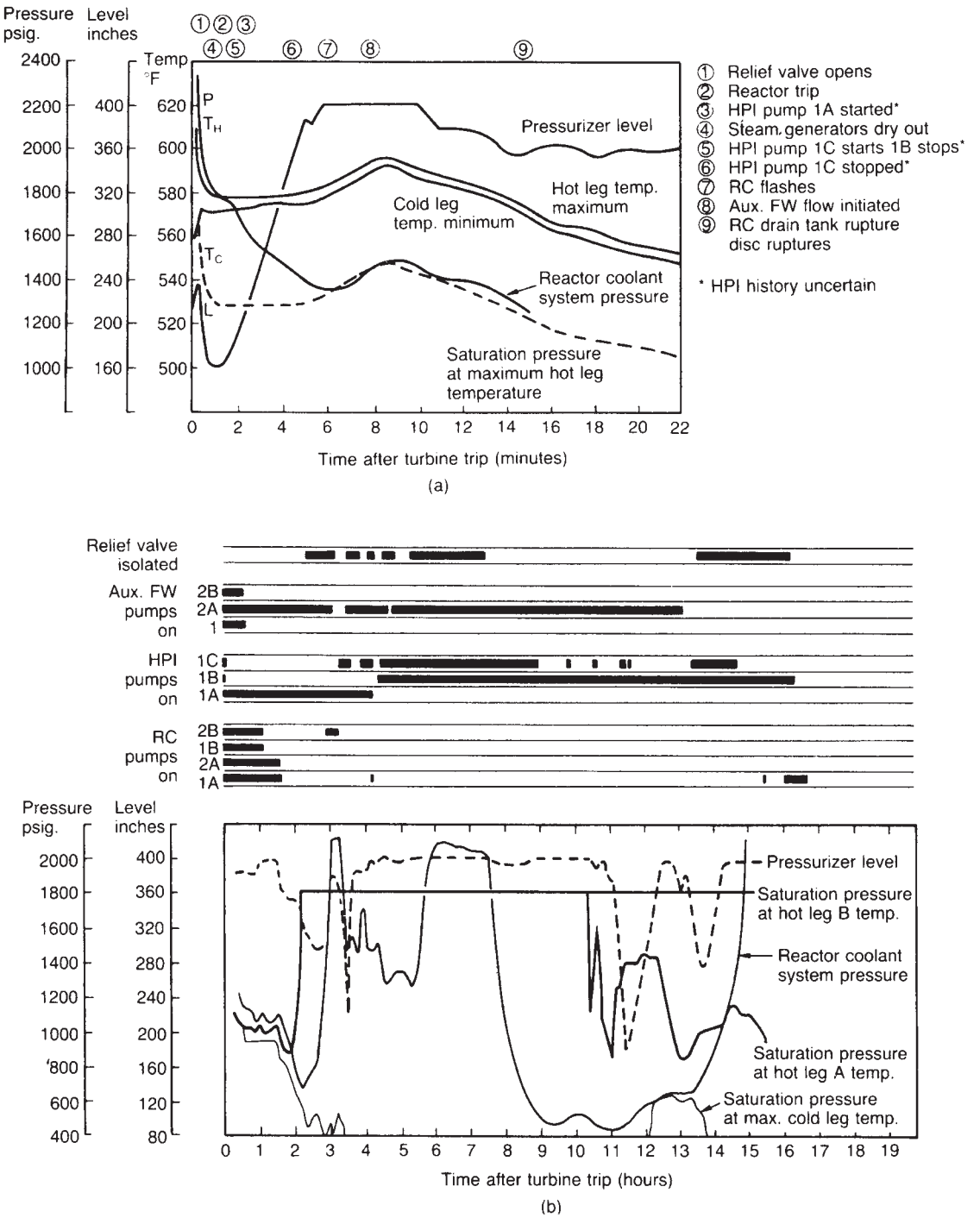

Figure A21.3 *Trend records of reactor cooling system parameters at TMI 2 (Collier and Davies, 1980): (a) parameters in minutes following turbine trip; and (b) parameters in hours following turbine trip*

radiation readings. By 2 h 48 min in, high radiation levels existed in several areas of the plant. At 2 h 55 min a site emergency was declared.

Attempts were made to restart the RCS pumps. One pump in Loop B operated for some 19 min but was shut down again by vibration trips at 3 h 13 min.

Meanwhile, high radiation levels had been measured in the containment building. At 3 h 30 min a general emergency was declared.

At some point, perhaps about 4 h in, the station manager appears to have realized that the reactor core had suffered damage.

From 4 h 30 min attempts were made to collapse the steam bubbles in the RCS loops, but without success and at 7 h these efforts were abandoned.

The operators then tried to bring in the lower pressure cooling system by reducing pressure in the RCS. They began at 7 h 38 min by opening the PORV block valve. At 8 h 41 min the pressure fell to 4.1 MPa at which point the core flooding system operated.

One consequence of the exposure of the core was that a steam-zirconium reaction occurred, generating hydrogen. During the depressurization, hydrogen from the RCS was vented into the containment building. At 9 h 50 min, there occurred in the containment building what was apparently a hydrogen explosion. There was a thud and a pressure spike of 0.19 MPa occurred. The sprays came on for some 6 min. However, the nature of the event was not immediately understood.

By this time the reactor had been stabilized, although it had suffered core damage.

When the significance of the event in the containment building became appreciated, concern grew about a possible explosion of a hydrogen bubble there.

A21.6 The Emergency and the Aftermath

As already described, a site emergency was declared at 7.00 on 28 March. At 7.24 a general emergency was declared. The emergency which then unfolded over the next week or so is described in the Kemeny Report.

The plant was contacted by the local WKBO radio station. The radio station asked what kind of emergency it was. They were told by the company manager of communications services that it was a general emergency, a 'red-tape' sort of thing required by the NRC when certain conditions exist, but that there was no danger to the public.

The emergency did not end with the establishment of stable operation. The following day, the core damage was found to be more serious than first thought. The hydrogen bubble problem persisted over the next 8 days and caused particular concern. There were also a number of other problems, mainly associated with the large quantities of water contaminated with low level radioactivity. The levels of radioactivity in the atmosphere around the plant were monitored continuously.

The handling of the emergency in respect of evacuation developed into a protracted saga, of which only highlights need be mentioned. In addition to the company and the NRC, the state governor and the President became involved. On 29 March, meetings were held to decide whether to recommend evacuation. On 30 March, a radiation reading outside the plant, later found to be erroneous, led NRC officials to recommend evacuation. The local director of emergency preparedness was notified to stand by for an evacuation; he notified fire departments and had a warning broadcast that an evacuation might be called. Then the NRC chairman assured the Governor that an evacuation was not necessary. Later the Governor decided that pregnant women and pre-school children should be evacuated. Meanwhile, people around the plant had started to make their own arrangements, and many left. By 1 April, the NRC had concluded that the hydrogen bubble posed no threat but failed to announce this properly.

Operations to restore the situation at TMI-2 have lasted over a period of years (Masters, 1984).

A21.7 The Excursion – 2

The operators in the TMI-2 control room made a number of errors. Some of these were failures to make a correct diagnosis of the situation, others were undesirable acts of intervention.

The first was the failure to realize that the PORV had stuck open. The operators had an indication that the PORV had shut again, in the form of a status light. However, this light showed only the shut signal sent to the valve, not the valve position itself. They were also misled by the reading of high water level in the pressurizer.

There were several centra-indications, however, which pointed to the fact that the PORV was open. One was that the PORV outlet pipe was at a higher temperature than usual, 140°C instead of 90°C. Another was that the temperature and pressure in the pressurizer were lower than usual. The third was that there was a high level in the containment building sump. Later, the vibration of the primary coolant pumps was another indication.

Closely connected with this first diagnostic failure was the failure to recognize that the mass of primary coolant water had fallen. Here the operators were misled by the level measurement.

Turning to the interventions, at 2 min into the incident, the HPI pumps tripped in automatically, because the mass of water in the primary circuit was falling. Thirty seconds later, the operators, fearing that the system would fill right up with water and go 'solid', shut the HPI pumps off. This was the wrong action, because the primary circuit then continued to lose water.

Another counterproductive action was the shutting down of the primary coolant pumps. About 60 min into the incident, the pumps began vibrating. This was another clue that the primary circuit fluid was now a two-phase mixture of steam and water. The operators had been trained not to allow violent vibration of the pumps, which could damage them or the piping, and they shut the pumps down. The forced flow of cooling water through the reactor core ceased.

These failures of diagnosis and the fear of the system going solid have frequently been characterized as illustrations of mindset.

The operators were poorly served by the displays and alarms in the control room. Mention has already been made of the fact that some of the indicators did not actually display the variable of direct interest. There were a large number of alarms which were difficult to interpret.

A21.8 The Investigations

Principal investigations into the accident are the NRC Report, the Kemeny Report and the US Congressional

hearings. These are described in this section. Recommendations given in the Kemeny Report and the Task Force Report are outlined in Section A21.9.

A21.8.1 NRC report

The NRC Report gives a detailed account of the TMI accident with a full chronology for the first 16 h containing 676 entries. There was little dispute about the basic facts. The investigations are significant mainly for their probing of the deeper causes.

A21.8.2 Congressional hearings

Hearings on the incident which are replete with information were held by the US Congress; they repay study.

Of particular interest here are the sessions dealing with the display and alarm systems. Extracts from the record on these two topics are given, respectively, in Tables A21.3 and A21.4 and are self-explanatory.

Table A21.3 *The display problem at Three Mile Island: evidence given to Congressional committee (after Lees, 1980f, based on US Congress, 1979)*

Weaver: I just want to say that is an extremely important point because one of the things we wanted to find out was how well they were in control. So you are raising the issue, I think, that because these gauges were off at one side they did not see them. Is that a possibility?
Eisenhut: It is certainly a possibility. In fact, that is why I said that is an area – the reason I highlighted it, it is a question area as to what happened to the pilot-operated relief valve, what kind of indications they had that the valve was still open.
Weaver: But they could have seen them?
. . .
Eisenhut: There were at least a couple of other instruments they could have used if those instruments were working. I do not know whether they were.
Weaver: The indications are that they did not see them for several hours; is that correct?
Eisenhut: At least a couple of hours. [p. 27]
Carr: We were told the other day that there was no direct level indicator in the reactor at the level of the coolant, that that had to be inferred from looking at other data, say the pressurizer pressure. Now we are saying that there is no direct indication of this valve at the top of the pressurizer, that we only got an indication, a direct indication on its mechanism rather than on its functioning, and that there were some backup inferences you could draw from other instruments which would lead someone to assemble some data. I suppose jumping way, way ahead of ourselves here I am wondering, is this a special feature of Babcock & Wilcox plants that on their gaging and instrumentation they do not use direct data, and then use the other stuff for backup? Or is this something throughout the nuclear industry, where there is a lot of data points and it leaves it to the operator to sort of assemble all of this, what is happening inside that building, in his head.
Stella: Valve positions normally are indicated by a mechanism which looks at the travel of the stem, which is to some degree on indirect reference to what the valve is actually doing, but a more direct method than you would get from looking at the solenoid which starts the event. [p. 30]
. . .
Stella: But as I tried to understand the accident, I reduced the number of program meters that I really wanted to know about to very few to try to make the judgement of what was going on. I think the operators can do that . . .

You can reduce the number that you really need to focus on to try to understand the event that you have had to relatively few. For example if you had a major LOCA, he would know very quickly what program meters that he ought to focus his attention on. He would have very quickly a response in the reactor building that says I have a discharge of a lot of high-energy fluid. I either have a break in my secondary system in the reactor building or the primary system. I immediately look at my primary system meters. Then I can tell if that was a primary system rupture. If it is a primary system rupture, I then know what program meters to track. So there is a hierarchy of logic built into the very many alarms that you see that point him at the right direction . . . . But this whole family of alarms and gages that you see, there is a hierarchy of logic built into it that, as you are trained to be an operator, you know what critical program meters to look for very quickly and eliminate or focus your attention in the right direction.
Carr: In the location of the alarms and gages and buzzes and switches and all that stuff, does the location on the panel follow that logic?
Stella: Yes. [p. 31]
. . .
Vento: One other thing before we go on to the other problem in the secondary system, which you did next. This relief valve, of course, is a key part of this, apparently. But there were some tailpipe temperature and some other indicators there that were also available. Who was responsible for watching those at this particular point? The tailpipe temperature?
Frederick: What you are talking about is the outlet temperature of the relief valve.
Vento: There is also a tank that this goes to that is not shown on here, and that has an indicator on it and a temperature and so forth. There is a thermocouple on here, and who was responsible for watching those in this particular process? It was just a generally shared thing?
Frederick: The points that you are talking about are not displayed. They are not on the console. They are in the computer. You have to manually call them up.
Vento: You have to call those things up. But were they not called up during this procedure at all?
Frederick: No.
Weaver: How many minutes are we in now? Where are we?
Faust: It is not a normal thing.
Frederick: About an hour.
Faust: We did not know a problem like that existed at the time.
Frederick: If the valve indicated shut, there is no reason to look at the downstream temperature. [p. 135]
. . .
Reis: It is a broad question, but as well as you can answer it, do you think that the control room provided you, in a timely fashion, in an easy-to-read fashion, the information you wanted and needed? And alternatively, in the course of the accident, were the communications in the control room such so that when someone at the panel needed conceptual information, in other words, this instrument, that instrument, and this gage are reading things that do not jibe together, that you had that sort of immediate access to an engineer? When did you get it? Did it work well, so that you were able to figure out what was really going on?
Frederick: The answer to the first question, the instruments, in my opinion, were not adequate. I can come up with a million questions on how to change them and the availability of additional input from the engineering staff.

It was not available to me, because I did not seek it out. I would give whatever question I had to the supervisor, and he would refer them to whoever he could as far as more operators, more engineers, to get more information. And he would bring back whatever suggestions there were if there were any. If things were that confusing, that I had to turn and ask somebody a question, I would wait for their response and their instructions on what to do next and then take the prescribed action according to what they suggested rather than what was on the panel.
Faust: I would way – well, I cannot change it much from what he said – we would continue to feed changes that we were seeing in the plant, to the supervisor; as well as if we thought we knew something that should be done, we would be saying that, too.
Reis: In terms of the layout of the plant, in general, do you think there could be some significant changes that would make your job a lot easier?
Frederick: Yes.
Faust: Definitely, [p. 155]

. . .

Cheney: It seems to me that is a key point. Has this ever been questioned before, whether or not the pressurizer level was an accurate reflection of the reactor coolant level, in a general sense, in terms of the basic design of the reactor?
McMillan: I think a lot of people have asked that question: What does the pressurizer level indicate to you?
Cheney: I would just like to come back to that basic question: Whether or not those operators at Three Mile Island on that day were trained to read that pressurizer level as anything other than indicating reactor level, coolant level in the reactor?
McMillan: Let us trace that through and see if we can find what evidence.
Cheney: Do you think that is some flaw in the design of the reactor?
McMillan: No, sir.
Cheney: Why not have a coolant level indicator from within the reactor itself?
McMillan: That has been suggested by a number of people, post Three Mile Island.
Weaver: Mr McMillan, how do you measure the level of water in the reactor vessel?
McMillan: You do not measure the level of water in the reactor vessel. . . .
Weaver: But is that not an important thing to know? Why do you not have something that tells us the level of the water?
McMillan: Well, I think -
Cheney: I guess I would like to follow up on this. [p. 232]

. . .

Weaver: Are you opposed, Mr McMillan, to water level measurement in the reactor vessel?
McMillan: It is a difficult problem, yes. But I am not at this point saying it is insurmountable . . .
Weaver: I would say the first thing I was going to do, if I were going to design a nuclear plant, is to make sure we knew what the water level was. [p. 237]

[a] In addition to the personnel identified in Section A21.1, the transcript extracts given above refer to the following: Mr Cheney, Mr Vento, Mr Weaver, all Congressmen; Mr Reis, Congressional staff; Mr D.Eisenhut, Deputy Director, Division of Operating Reactors, Office of Nuclear Reactor Regulation, NRC; Mr MacMillan, Vice-President, Nuclear Power Generation Division, Babcock and Wilcox Co.

Table A21.4 *The alarm problem at Three Mile Island: evidence given to Congressional committee (after Lees, 1980e, based on US Congress, 1979)*

Weaver: The plant manager told me he thought 100 audio alarms were going off at one time.
Stella: Is that what he told you?
Weaver: Yes
Stella: I would not be surprised.
. . .
Weaver: All occurring in the control room?
Mattson: Yes.
Carr: And there is no instrumentation that helps the operator sort out the order of importance of these alarms, or the order of importance of gages or lights or switches; right?
Mattson: Only the training.
Carr: Only the training to assemble all of these instruments and react in split seconds, [p. 31]
. . .
Weaver: How are people able to differentiate between these various alarms?
Michelsen: I am not a human factors engineer. I have never studied control rooms enough to understand that area at all. It is a very good question. I have asked it sometimes myself. [p. 47]
. . .
Higgins: There were a lot of short-term problems that were being addressed also; that is, equipment problems, loss of power, additional alarms that continued throughout the day, and we did not mention the number of alarms; there were a large number of equipment starts and stops, large number of individual problems . . . [p. 97]
. . .
Weaver: Would you describe the alarms that were going off? Were they going just constantly or was it -
Higgins: One would occur; the operators would address that. And then another one, perhaps a little bit later another one, or if you have a particular event, a specific event, for example the hydrogen burning in the containment might generate several; or a particular release of radioactivity from an area in the auxiliary building might generate several related alarms. Like generally there are a lot of indicators of a particular event as Mr Michelson described, on relief valve. You have got a relief valve tailpipe temperature alarm; you have got an alarm in the reactor drainpipe, I believe; level indications, and perhaps alarms associated with those system pressure alarms.
All this has to do with one relief valve lifting, so when a particular event occurs, you may get several related alarms, all of which have to be addressed. [p. 99]
. . .
Higgins: If you have a scram, many alarms do come in as a result of that. Some are normal; some indicate things not being normal. And it is up to the operator by his training to distinguish which ones he expects, which ones not to expect, that type of thing. [p. 100]
. . .
Higgins: There was a tremendous amount of activity going on in the control room. A lot of people were involved with a lot of the different problems, and that was one of many things. Operators were – alarms were going off; pumps were being started and stopped; valves were being cycled, and this* was just one of a myriad of those things that was occurring throughout the entire day. And I was thoroughly not able to follow what was going on. And I did not pick it up at all. [p. 111]
[*A spike on a recorder probably indicating a hydrogen burn – FPL].
. . .
Frederick: The alarms – this is a big problem. There is only one audible alarm in the control room for the 1600 alarm

windows that we have, in other words, the ones that are displayed on the front of the console along with the ones on the reverse panel. So that during the emergency, I made a point of announcing that I did not want anybody to acknowledge the alarm, that is, push the acknowledgement to silence the alarm, because that would make all the windows stop flashing, and I wanted to read them all to see what was happening. As we began to run out of ideas, I wanted to review all of the alarms that we received to see if anything was happening that we could not see.

. . .

Frederick: There are several steps in the alarm process. As the alarm comes in, it sounds an alarm and a flashing light. As long as the alarm stays in – and you push the button, and the light will go solid. If in the meantime the alarming condition clears itself or goes away and you push the button, the light will go out and you will not be able to tell that it ever came in. If you have three or four alarms at the same time, only one may stay lit out of the three or four. We had probably 100 or 200 alarms flashing within the first few minutes.

. . .

Frederick: I would not be able to establish the chronology. I just wanted to see what systems were affected by the transient and if we could see something. There are some alarms you expect to get. If you read over them, you just discount them as being normal. But there may be a few that come in that you had not expected, and those are the ones I was looking for. [p. 136]

. . .

Frederick: No. The sequence of alarms that comes out of the computer that they were able to read later on was backlogged. The alarms came in 100 at a time. The computer, the IBM typewriter just types them out one at a time. So as they were coming in rapidly, probably 10 or 15 per second, it just could not keep up. So there was a backlog of maybe 2 or 3 h.

Faust: I do not know what time this fits into, but we had problems with the alarm typewriter, too, at this time. I do not know what it was, but the easiest way for me to say it is, it sort of started eating the paper. In other words, it got off the track. [p. 137]

. . .

Vento: Obviously the proper procedure here would have said that 300° or 280° in the tailpipe should have been an indication.

Frederick: That is the point he is talking about. In other words, what came out of the computer on the typewriter was an alarm that said: Temperature hot. But we could not see that, because the alarm typewriter was backlogged several hours. [p. 139]

. . .

Weaver: Now I am troubled by the newspaper reports. One report, early on, had it that there was just page after page of computer printout of question marks.

Miller: Looking back – and we can come back to you with further information, but there was a period of time in the first 2 to 3 h where the computer failed, I believe.

Zewe: Yes, for over an hour period, it did not give us any information.

Cheney: You mean you would query it and nothing would happen?

Zewe: No. The question marks, periods, and so forth, the computer had hung up, where it really did not scan the parameters and print on in a fashion where we could interpret it.

Cheney: It was unusable.

Miller: I thing Bill would back this up. He was not using that totally. He was just using his console to operate the plant, so when that went out, he just had to go away from it.

Weaver: What caused this? What was going on? What happened? We have it here in the chronology that 1 hour 13 to 2:37 – in other words -

Miller: I think, in fairness, the machine has got a tape, disc, and that sort of thing. It has experienced problems. It is not a vital piece of equipment to Bill's use of the emergency procedures or operations of the plant, so I would guess Bill would just simply have told an electrical engineer to call someone in and go on with the console.

Weaver: You do not have to have it in any way?

Zewe: No, it is just an operator's tool, but it is not anything that is really that critical to the operation. [p. 175]

. . .

[a] In addition to the personnel identified in Section A21.1 and Table A21.3, the transcript extracts given above refer to the following: Mr Carr, Congressman; Mr Stello, Director, Division of Operating Reactors, Office of Nuclear Reactor Regulation, NRC; Mr Mattson, Division of System Safety, Office of Nuclear Reactor Regulation, NRC; Mr Michelson, Nuclear Engineer, Tennessee Valley Authority; and Mr Higgins, Region I, Office of Inspection and Enforcement, NRC.

A21.8.3 Kemeny Report

The Kemeny Report gives an account of the accident, from 29 March to 2 April, presents findings and makes recommendations. Some findings are described in this section.

The reports starts with what it calls 'people-related problems'. It states

> Popular discussions of nuclear power plants tend to concentrate on questions of equipment. Equipment can and should be improved to add further safety to nuclear power plants, and some of our recommendations deal with this subject. But as the evidence accumulated, it became clear that the fundamental problems are people-related problems and not equipment problems.
>
> When we say that the basic problems are people-related, we do not mean to limit this term to shortcomings of individual human beings – although these do exist. We mean more generally that our investigation has revealed problems with the 'system' that manufactures, operates and regulates nuclear power plants. There are structural problems in various organizations, there are deficiencies in various processes, and there is a lack of communication among key individuals.
>
> We are convinced that if the only problems were equipment problems, this Presidential Commission would never have been created. The equipment was sufficiently good that except for human failures, the major accident at Three Mile Island would have been a minor incident. But, wherever we looked, we found problems with the human beings who operate the plant, with the management that runs the key organization, and with the agency that is charged with assuring the safety of nuclear power plants. (p. 8)

The form frequently taken by this problem is described as follows: 'In the testimony we received, one word occurred over and over again. That word is "mindset".' (p. 8)

The report is critical of the approach taken to control of the industry, stating:

> We note a preoccupation with regulations. It is, of course, the responsibility of the Nuclear Regulatory Commission to issue regulations to assure the safety of nuclear power plants. However, we are convinced that regulations alone cannot assure safety. Indeed, once regulations become as

> voluminous and complex as those regulations now in place, they can serve as a negative factor in nuclear safety. The regulations are so complex that immense efforts are required by the utility, by it suppliers and by the NRC to assure that regulations are complied with. The satisfaction of regulatory requirements is equated with safety. This Commission believes that it is an absorbing concern with safety that will bring about safety – not just the meeting of narrowly prescribed and complex regulations. (p. 9)

The report makes various criticisms of the NRC, of which a sample, changed in order, are:

> We found serious managerial problems within the organization. These problems start at the very top . . . It is not clear to us what the precise role of the five NRC commissioners is, and we have evidence that they themselves are not clear what their role should be . . . NRC's primary focus is on licensing and insufficient attention has been paid to the ongoing process of assuring safety. . . NRC is vulnerable to the charge that it is heavily equipment-oriented, rather than people oriented . . . We are extremely critical of the role the organization played in the response to the accident . . . NRC has sometimes erred on the side of the industry's convenience rather than carrying out its primary mission of assuring safety . . . (pp. 19 – 21)

The Commission identifies an over-concentration on large accident hazards:

> We find a fundamental fault even with the existing body of regulations. While scientists and engineers have worried for decades about the safety of nuclear equipment, we find that the approach to nuclear safety has a major flaw. It was natural for the regulators and the industry to ask: 'What is the worst kind of equipment failure that can occur?' Some potentially serious scenarios, such as the break of a huge pipe that carries the water cooling to the nuclear reactor, were studied extensively and diligently, and were used as the basis for the design of plants. A preoccupation developed with such large-break accidents as did the attitude that if they could be controlled, we need not worry about the analysis of 'less important' accidents. (p. 9)
>
> A potentially insignificant incident grew into the TMI accident, with severe damage to the reactor. Since such combinations of minor equipment failures are likely to occur much more often than the huge accidents, they deserve extensive and thorough study. (p. 9)

The report is critical of organizational failure to follow through safety issues:

> We find that there is a lack of 'closure' in the system -that is, important safety issues are frequently raised and may be studied to some degree of depth, but are not carried through to resolution; and the lessons learned from these studies do not reach those individuals and agencies that most need to know about them. (p. 11)

The report reopens the issue of the influence of the operator in a developing reactor emergency. The conventional approach has been that any action taken by the operator is likely to be beneficial. It gives this view as an example of designers' mindset: 'They concentrated on equipment, assuming that the presence of operators could only improve the situation – they would not be part of the problem', (pp. 8–9).

On the handling of the emergency the Commission comments:

> We are disturbed both by the highly uneven quality of emergency plans and by the problems created by multiple jurisdictions in case of a radiation emergency. Most emergency plans rely on prompt action at local level to initiate a needed evacuation or to take other protective action. We found an almost total lack of detailed plans in the local communities around Three Mile Island. It is one of the many ironies of this event that the most relevant planning by local authorities took place during the accident. In an accident in which prompt defensive steps are necessary within a matter of hours insufficient advance planning could prove extremely dangerous. (p. 15)

The report contains a number of supplemental views by individual members of the commission, one of which is by Professor T.H. Pigford. He is critical of the NRC's approach to safety, which he characterizes as lacking in experienced personnel; failing to take a comprehensive approach with quantified safety objectives and rational priorities; and prone to introduce arbitrary requirements. He calls it 'A stifling approach. The existing process inhibits the interchange of technical information between the NRC and industry. It discourages innovative engineering solutions'. On human factors aspects he states

> The emphasis in this report upon equipment versus people obscures the fact that the equipment itself is only one product of the defense-in-depth or multiple-barrier design approach, which also encompasses the analysis of how components must perform and how systems of equipment must operate. The accident demonstrated that this system of equipment performed better than expected.
>
> The nature of the people-related problem needs clarification. One such problem – and a most serious one – was the errors made by the operators and the operator-supervisors, whose training was insufficient in scope and understanding. Another was failure of many individuals to respond adequately to earlier experience from other reactors and to other advance information that might have alerted the operators and avoided the accident.

A21.9 Some Lessons of Three Mile Island

A21.9.1 Kemeny Report recommendations

The Kemeny Report and the Task Force Report both give extensive recommendations. The heads of these recommendations are shown in Table A21.5, in Sections A and B, respectively.

The Kemeny Report recommends that the NRC should be restructured as a new independent agency in the executive branch and that the ACRS should be strengthened.

The report states: 'To the extent that the industrial institutions we have examined are representative of the nuclear industry, the nuclear industry must dramatically change its attitude towards safety and regulations'. It goes on The industry should establish a program that specifies appropriate safety standards including those for management, quality assurance, and operating procedures and practices, and that conducts independent evaluations'.

Improvements in operator training are called for, with particular emphasis on the use of simulators.

Table A21.5 *Heads of some principal recommendations on Three Mile Island*

A Presidents Commission (Kemeny, 1979)
Nuclear Regulatory Commission
Utility and it suppliers
Training of operating personnel
Technical assessment
Worker and public health and safety
Emergency planning and response
Public's right to information
B 'Lessons Learned' Task Force (Nuclear Regulatory Commission, 1979b)
Personnel qualifications and training
Staffing of control room
Working hours
Emergency procedures
Verification of correct performance of operating activities
Evaluation of operating experience
Man–machine interface
Reliability assessments of final designs
Review of safety classifications and qualifications
Design features of core-damage and core-melt accidents
Safety goal for reactor regulation
Staff review objectives
NRR Emergency Response Team

Under the heading of technical assessment, the report deals with equipment for information display in the control room and for mitigating the consequences of accidents and recommends a formal safety assurance programme involving hazard identification and assessment.

The report recommends that there should be a requirement for an emergency response plan.

It also makes recommendations on worker and public health in relation to nuclear hazards and on the public's right to information.

A21.9.2 Task Force Report recommendations

The recommendations of the Task Force Report are summarized in Section B of Table 21.5. They deal particularly with operator training and with the man-machine interface.

The report calls for a thorough review of control room design and for development of aids to assist the operator in assessing the status of the plant and in analysing disturbances and alarms. It proposes the development both of a plant safety status display system and of a disturbance analysis system (DAS).

On the former the report states

> Each licensee should be required to define and adequately display in the control room a minimum set of plant parameters (in control terminology, a state vector) that defines the safety status of the nuclear power plant. The minimum set of plant parameters should be annotated for sensor limits, process limits, and sensor status. The annotated set of parameters should be presented to the operator in real time by a reliable, single-failure-proof system located in the control room. (p.A-12)

Table A21.6 *Some lessons of Three Mile Island*

Regulatory control of major hazard installations
People-related versus equipment-related problems
Formal safety assurance
Relative importance of large and small failures
Influence of operator in an emergency
Fault diagnosis by the process operator
Accident management for major hazard installations
Follow-up of safety issues
Learning from precursor events
Package and other ancillary units
Display of variable of interest
Plant status display and disturbance analysis systems
Abuse of instrument air
Limitations of non-return valves

A21.9.3 Some lessons

The Three Mile Island incident yields numerous lessons. Some of these are listed in Table A21.6. Many of these lessons are drawn in the reports just described.

Regulatory control of major hazard installations

The comments made in the Kemeny Report on the regulatory regime for US nuclear power plants under the NRC both echo those made in the Robens Report in the UK in 1972 and themselves find an echo in those of the Cullen Report on UK offshore installations in 1990. In all three cases the reports are critical of an approach which they find excessively prescriptive.

People-related versus equipment-related problems

The theme which runs through the Kemeny Report is that equipment-related problems have received attention at the expense of people-related problems. The account of these problems given in the report indicates clearly that the term refers not just to process operators, although operator problems were a central issue, but to management and management systems. Here too, the report may be said to look back to Robens and forward to Cullen.

Formal safety assurance

The Kemeny Report calls for a formal safety assurance programme for nuclear power plants involving hazard identification and assessment. In UK terms, its recommendations parallel those of the ACMH for onshore plant and of the Cullen Report for offshore installations, which uses the term 'formal safety assessment'.

Relative importance of large and small failures

Engineers in the nuclear industry had tended to concentrate their attention on major failures, notably the large loss of coolant accident, to the relative neglect of lesser events, such as a small, or at least slower, loss of coolant, such as actually occurred at TMI. Yet, as the incident showed, such lesser events can escalate. Moreover, lesser events occur much more frequently. There needs to be a more balanced approach which addresses small as well are large failures.

Influence of operator in an emergency

It has been a basic assumption in the industry that in a nuclear emergency operator action would be beneficial, and that the longer the time available for such action the higher

the probability that it would be taken. TMI showed that this is not necessarily so, and that operator action can be detrimental.

Fault diagnosis by the process operator
The incident highlighted the problem of fault diagnosis by the process operator under stress. It showed the limitations of fixed operating rules in dealing with abnormal situations and the dangers of tunnel vision, or mindset. In other words, it showed the inadequacy of rule-based behaviour and the need for knowledge-based behaviour and for training based on development of the latter.

Accident management for major hazard installations
TMI shows that a major accident poses a number of difficult problems and that it needs to be managed. This implies that accident management must be recognized as a specific requirement and planned in advance.

The handling of an emergency in the control room is one aspect of the problem, but there are many others. They include the identification, mobilization, direction and coordination of the necessary resources; planning for an emergency, both on-site and off-site; and handling of the media.

Follow-up of safety issues
The Kemeny Report is critical of the follow-up of safety issues, referring to a lack of closure. Safety issues which are raised and agreed to be valid need to be followed through to resolution. Personnel who most need to know should be informed.

Learning from precursor events
There had been previous incidents in which a PORV had been stuck in the open position, but the management of the TMI plant had no systematic approach to learning from such incidents.

Package and other ancillary units
Turning to some more detailed aspects, the incident started with a fault in the condensate polishing system, a package unit. It illustrates the point that the ancillary equipment and services should receive their due share of attention, starting with specification and continuing right through to operation.

Display of variable of interest
If a process variable is critical, it is highly desirable that the quantity which is displayed should be the variable of direct interest. At TMI there were two cases where this was not done. One is the water level in the pressure vessel. The other is the status of the PORV. The display showed the signal to the valve rather than the actual valve position.

Plant status display and disturbance analysis systems
TMI was a dramatic illustration of the difficulties faced regularly by process operators in interpreting displays and alarms, and of way in which these can be compounded by information overload. It highlighted the scope for the development of improved display and alarm systems and for the exploitation of computers to this end. The principal aids proposed were plant safety status display systems and disturbance analysis systems.

Abuse of instrument air
The air used to clear the blockage on the condensate polishing system was instrument air. It is bad practice to connect instrument air to the process, which can cause it to become contaminated.

Limitations of non-return valves
The entry of water into the instrument air system illustrates the limitations of a non-return valve. Such a valve is intended to stop bulk flow of fluid; it will not necessarily prevent the passage of trace quantities.

Appendix 22 Chernobyl

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On Monday 28 April 1986 a worker at the Forsmark nuclear power station in Sweden put his foot in a radiation detector for a routine check and registered a high reading. The station staff thought they had had a radioactive release from their plant and the alarm was raised. However, as reports came in of high radioactivity in Stockholm and Helsinki, the source of the release was identified as the Soviet Union. In fact, an accident had occurred on Unit 4 at Chernobyl in the Ukraine some 800 miles from Sweden on Saturday 26 April.

At 1.24 on that day an experiment to check the use of the turbine during rundown as an emergency power supply for the reactor went catastrophically wrong. There was a power surge in the reactor, the coolant tubes burst and a series of explosions rent the concrete containment. The graphite caught fire and burnt, sending out a plume of radioactive material. Emergency measures to put out the fire and stop the release were not effective until 6 May.

The Soviet Government set up an investigatory team headed by N.I. Ryzhkov, President of the USSR Council of Ministers, to investigate. A report *The Accident at the Chernobyl Nuclear Power Plant and its Consequences* by the USSR State Committee on the Utilisation of Atomic Energy (1986) (the *USSR State Committee Report*) was presented in August 1986 to a meeting of experts at the IAEA in Vienna by V. Legasov.

Other accounts of the accident include *Summary Report on the Post-Accident Review Meeting on the Chernobyl Accident* by the IAEA (1986), *The Chernobyl Accident and its Consequences* by Gittus *et al.* (1987, 1988) (the *UKAEA Report), Chernobyl and the Safety of Nuclear Reactors in OECD Countries* by the NEA (1987), *Report on the Accident at Chernobyl Nuclear Power Station* by the NRC (1987b), *The Chernobyl Accident and its Consequences for the United Kingdom* by Worley and Lewins (1988) (the First *Watt Committee Report*), Chernobyl. *A Policy Response Study* by Segerstahl (1991) and *Five Years after Chernobyl: 1986–1991* by the Watt Committee (1991) (the Second *Watt Committee Report*) and by Franklin (1986) and Kletz (1988h).

The story of Chernobyl is told in *The Worst Accident in the World* by Haynes *et al.* (1986), *Mayday at Chernobyl* by Hamman and Parrott (1987), *The Chernobyl Disaster* by Haynes and Bojcum (1988), *Chernobyl. The Real Story* by Mould (1988) and *Ablaze* by Read (1993) and by Franklin (1986) and Kletz (1988h).

Selected references on Chernobyl are given in Table 22.1.

Table A22.1 *Selected references on Chernobyl*

NRC (Appendix 28 *Chernobyl*); BNES (1986); Franklin (1986); Hawkes *et al.* (1986); IAEA (1986); IBC (1986/69); USSR State Committee on the Utilization of Atomic Energy (1986); Watt Cttee on Energy (1986, 1991); Collier and Davies (1987); Gittus *et al.* (1987); Hall, Hall and Nixon (1987 LPB 76); Hamman and Parrot (1987); NEA (1987); NRC (1987b); F. Allen (1988); Ballard (1988); Haynes and Bojcum (1988); Kletz (1988h); Marples (1988, 1991); V.C. Marshall (1988 LPB 81); Mould (1988); Wheeler (1988); Worley and Lewins (1988); Gudiksen, Harvey and Lange (1989); Konstantinov and Gonzalez (1989); Parmentier and Nenot (1989); Voznyak, Kovalenko and Troitsky (1989); Hass *et al.* (1990); Ryin *et al.* (1990); Ottewell (1991); Segerstahl (1991); Read (1993)

A22.1 The Operating Organization and the Management

Little information has become available concerning the organization operating the Chernobyl plant or about its management.

A22.2 The Site and the Works

The Chernobyl nuclear power station is situated in a region which at the time was relatively sparsely populated. There were some 135,000 people within a 30 km radius. Of these 49,000 lived in Pripyat to the west of the plant's 3 km safety zone and 12,500 in Chernobyl 15 km to the south-east of the plant.

There were four nuclear reactors on the site. The first pair had been built in the period 1970–77 and the second pair were completed in 1983.

A22.3 The Process and the Plant

Unit 4 at Chernobyl was designed to supply steam to two turbines each with an output of 500 MWe. The reactor was therefore rated at 1000 MWe or 3200 MWt.

Unit 4 was an RBMK-1000 reactor, which is a standard design widely used in the Soviet Union. The RBMK-1000, shown in Figure A22.1, is a boiling water pressure tube, graphite moderated reactor. The reactor is cooled by boiling water, but the water does not double as the moderator, which is graphite.

The design of the reactor avoided the use of a large pressure vessel. Instead, use was made of much smaller individual pressurized fuel channels. The reactor had 1661 fuel channels. There was in each one a fuel assembly, divided into two subassemblies, each containing 18 fuel elements.

The reactor contained 192 te of uranium enriched to 2%. The subdivision of the uranium into a large number of separately cooled fuel channels greatly reduced the risk of total core meltdown.

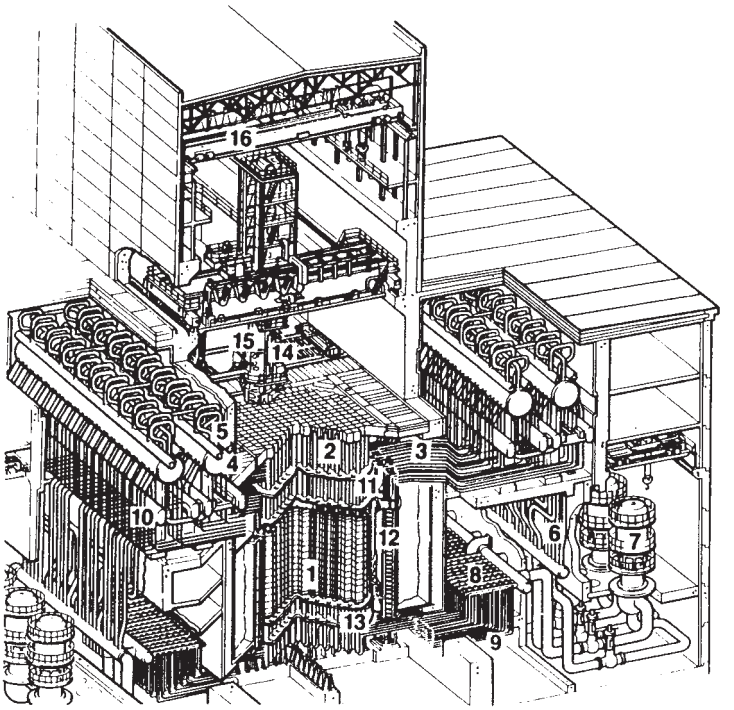
The reactor was cooled by water passing through the pressure tubes. The water was heated to boiling point and partially vaporized. The steam–water mixture with a mass steam quality of 14% passed to two separators where steam was flashed off and sent to the turbines, while water was mixed with the steam condensate and fed through downcomers to pumps which pumped it back to the reactor. There were two separate loops each with four pumps, three operating and one standby. This system constituted the multiple forced circulation circuit (MFCC).

The moderator used was graphite. The reactor contained a stack of 2488 graphite blocks with a total mass of 1700 te.

An emergency core cooling system (ECCS) was provided to remove residual heat from the core in the event of loss of coolant from the MFCC.

The reactor was provided with a control and protection system (CPS). The control system incorporated a control computer. There was a control system which controlled the power output of the reactor by moving the control rods, in and out. Automatic protective systems included a trip to bring in the ECCS and reactor shut-down trips. Reactor shut-down was effected by the insertion of control rods, and conditions which would trigger shut-down included loss of steam to the turbines and loss of level in the separators.

The reactor was housed in a containment built to withstand a pressure of 0.45 MPa. There was a 'bubble'



Key

1 Reactor
2 Fuel-channel standpipes
3 Steam/water riser pipes
4 Steam drums
5 Steam headers
6 Downcomers
7 Main circulating pumps (MCP)
8 Group distribution headers
9 Reactor inlet water pipes
10 Burst-can detection system
11 Upper biological shield
12 Side biological shield
13 Lower biological shield
14 Irradiated fuel storage pond
15 Fuelling machine
16 Bridge crane

Figure A22.1 *Simplified flow diagram of Chernobyl Unit 4 (Nuclear Regulatory Commission, 1987b)*

condenser designed to condense steam entering the containment from relief valves or from rupture of the MFCC.

An important operating feature of the reactor was its reactivity margin, or excess reactivity. Below a certain power level the reaction would be insufficient to avoid xenon poisoning. It was therefore necessary to operate with a certain excess reactivity. This reactivity could be expressed in terms of the number of CPS control rods which would need to be inserted to counter it. The operating instructions stated that a certain excess reactivity was to be maintained; the equivalent number of control rods was 30.

Another important operating characteristic was the reactor's 'positive void coefficient'. An increase in heat from the fuel elements would cause increased vaporization of water in the fuel channels and this in turn would cause increased reaction and heat output. There was therefore an inherent instability, a positive feedback, which could be controlled only by manipulation of the control rods. Control of the reactor at normal power output presented little problem, but this feature made the reactor highly sensitive at low outputs.

A22.4 Events Prior to the Release

The origin of the accident was the decision to carry out a test on the reactor. Electrical power for the water pumps and other auxiliary equipment on the reactor was supplied by the grid with diesel generators as back-up. However, in an emergency there would be a delay of about a minute before power became available from these generators. The objective of the test was to determine whether during this period the turbine could be used as it ran down to provide emergency power to the reactor. A test had already been carried out without success, so modifications had been made to the system, and the fresh test was to check whether these had had the desired effect.

A programme for the test was drawn up. It included provision to switch off the ECCS during the test, apparently to prevent its being triggered during the test.

At 1.00 on 25 April the reduction of power began. At 13.05 Turbogenerator 7 was switched off the reactor. At 14.00 the ECCS was disconnected. However, a request was received to delay shutting down since the power output was needed. It was not until 23.10 that power reduction was resumed.

At some stage the trip causing reactor shut-down on loss of steam to Turbogenerator 8 was disarmed, apparently so that if the test did not work the first time, it could be repeated. This action was not in the experimental programme.

The test programme specified that rundown of the turbine and provision of unit power requirements was to be carried out at a power output of 700–1000 MWt, or 20% of rated output. The operator switched off the local automatic control, but was unable to eliminate the resultant imbalance in the measurement function of the overall automatic controls and had difficulty in controlling the power output, which fell to 30 MWt. Only at 1.00 on 26 April was the reactor stabilized at 200 MWt, or 6% of rated output.

Meanwhile the excess reactivity available had been reduced as a result of xenon poisoning.

It was nevertheless decided to continue with the test. At 1.03 the fourth, standby pump in one of the loops of the MFCC was switched on and at 1.07 the standby pump in the other loop.

A22.5 The Release – 1

With the reactor operating at low power, the hydraulic resistance of the core was less and this combined with the use of additional pumps resulted in a high flow of water through the core. This condition was forbidden by the operating instructions, because of the danger of cavitation and vibration. The steam pressure and water level in the separators fell and other process parameters changed. In order to avoid triggering the trips which would shut-down the reactor on these parameters, the trips were disarmed.

The reactivity continued to fall and at 1.22.30 the operator saw from a printout of the reactivity evaluation program that the available excess reactivity had fallen below a level requiring immediate reactor shut-down. Despite this the test was continued.

At 1.23.04 the emergency valves on Turbogenerator 8 were closed. The reactor continued to operate at about 200 MWt, but the power soon began to rise. At 1.23.40 the unit shift foreman gave the order to press the scram button. The rods went down into the core, but within a few seconds shocks were felt and the operator saw that the rods had not gone fully in. He cut off the current to the servo drives to allow the rods to fall in under their own weight.

Within 4 s, by 1.23.44, the reactor power had risen, according to Soviet estimates, to 100 times the nominal value.

At about 1.24, according to observers outside Unit 4, there were two explosions, the second within some 3 s of the first, and debris and sparks shot into the air above the reactor.

It is thought that the fuel fragmented, causing a rapid rise in steam pressure as the water quenched the fuel elements, so that there was extensive failure of the pressure tubes. The explosive release of steam lifted the reactor top shield, exposing the core. Conditions were created for reaction between the zirconium and steam, producing hydrogen. An explosion, involving hydrogen, occurred in and ruptured the containment building, and ejecting debris and sparks were seen.

Some 30 fires broke out.

The accident was aggravated by the fact that the 200 te loading crane fell onto the core and caused further bursts of the pressure tubes.

The stricken reactor is shown in Figure A22.2.

The timetable of these and the following events is shown in Table A22.2.

A22.6 The Emergency and the Immediate Aftermath

The fire brigades from Pripyat and Chernobyl set out at 1.30. The fires in the machine hall over Turbogenerator 7 were particularly serious, because they threatened Unit 3 also. These therefore received priority. By 5.00 the fires in the machine hall roof and in the reactor roof had been extinguished.

However, the heating up of the core and its exposure to the air caused the graphite to burn. The residual activity of the radioactive fuel provided another source of heat. The core therefore became very hot and the site of raging fire.

During the next few days the fire raged and a radioactive plume rose from the reactor. The accident had

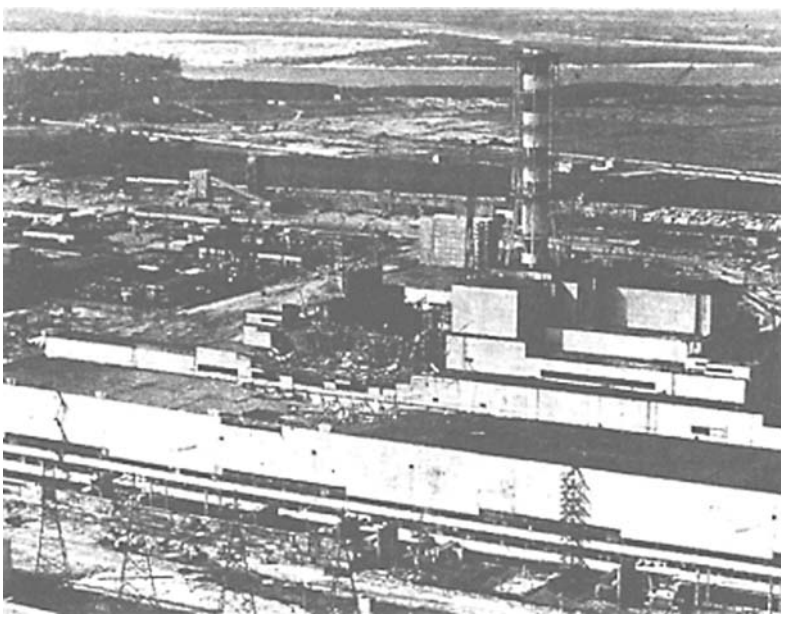


Figure A22.2 *Reactor of Chernobyl Unit 4 after the explosions (ITAR-TASS)*

Table A22.2 *Timetable of events at Chernobyl*

A Events prior to initial explosion		
25 April	1.00	Reduction of power started
	13.05	Turbogenerator 7 disconnected
	14.00	ECCS disconnected
	23.10	Power reduction resumed
26 April	00.28	Operator switches off local automatic control, but is unable to eliminate resultant imbalance in measurement function of the overall automatic controls
		Power output falls to 30 MWt
	1.00	Reactor stabilized at 200 MWt (6% rated output)
	1.03	Standby pump switched on in one loop of MFCC
	1.07	Standby pump switched on in other loop of MFCC
	before 1.19	Trips on low steam pressure and low water level disabled
	1.22.30	Printout confirming fall in excess reactivity
	1.23.04	To begin test, stop valve on steam to Turbogenerator 8 closed
		Trip on closure of both turbogenerator steam stop valves disabled
	1.23.40	Scram button pressed to drop control rods
	1.23.40	Operator hears banging noises and sees rods stopping before they reach bottom; disengages servo drives to allow rods to fall under own weight
		Rapid increase in power
	1.23.48	First explosion – extensive failure of pressure tubes, explosive release of steam, top lifted off reactor
	1.24	Second explosion – explosion within reactor space, possibly involving hydrogen, pressure increase to several MP, rupture of containment building
		Numerous fires
B Events after initial explosion		
26 April	2.54	Fire fighting units from Pripyat and Chernobyl arrive
	3.34	Most of fires in turbine room roof out
	3.54	Fire on reactor building roof out
	5.00	All fires, other than those in core, out
		Unit 3 shut-down
27 April	1.13	Units 1 and 2 shut-down
27 April		Start of smothering operation using helicopters
6 May		Discharge of radioactivity drops to several hundred Ci/h

become a major disaster. It was necessary to evacuate the population from a 30km radius round the plant and deal with the casualties and to take a whole range of measures to dampen and extinguish the fire, to cover and enclose the core, and to deal with the radioactivity in the surrounding area.

Three evacuation zones were established: a special zone, a 10km zone and 30km zone. The latter zone is shown in Figure A22.3. A total of 135,000 people were evacuated.

Accounts of the evacuation are incomplete and sometimes contradictory, but what appears to have happened is as follows. Within a few hours of the accident an emergency headquarters was set up in Pripyat. About 14.00 on 26 April there was an evacuation of some 1000 people from within a 1.6 km zone around the plant. A much larger evacuation took place about 14.00 next day, when about 1000 buses were brought in and within 2 h had evacuated some 40,000 people. However, it was not until some 9 days later that the authorities in Moscow ordered complete evacuation from a 30 km zone around the site.

First reports from Kiev spoke of no apparent concern, but as the nature of the disaster became known, parents hastened to send their children out of the city to relatives elsewhere.

A medical team was set up within 4 h of the accident and within 24 h triage of the 100 most serious cases had been effected.

A system was set up to control movements between the zones. People crossing the zone boundaries had to change clothing and vehicles were decontaminated.

In the immediate aftermath of the accident steps were taken to obtain the measurements essential to the control of the emergency. These included the measurement not only of the radioactivity in and around the plant, but also of conditions in the reactor relevant to bringing it under control. The latter was made more difficult by the fact that the regular measurement system had been disabled.

A decision had to be made whether to let the fire burn itself out or to smother it. In view of the hazard to the surrounding area, the latter course was chosen. A specialist team was assembled who began to cover the damaged reactor with compounds of boron, dolomite, sand, chalk and lead. Between 27 April and 10 May some 5000 te of material were dropped on the reactor by helicopter. By May 6 the release of radioactivity had decreased to a few hundred Ci/day and had ceased to be a major factor.

At the same time the core temperature was tackled by pumping nitrogen under pressure from the compressor

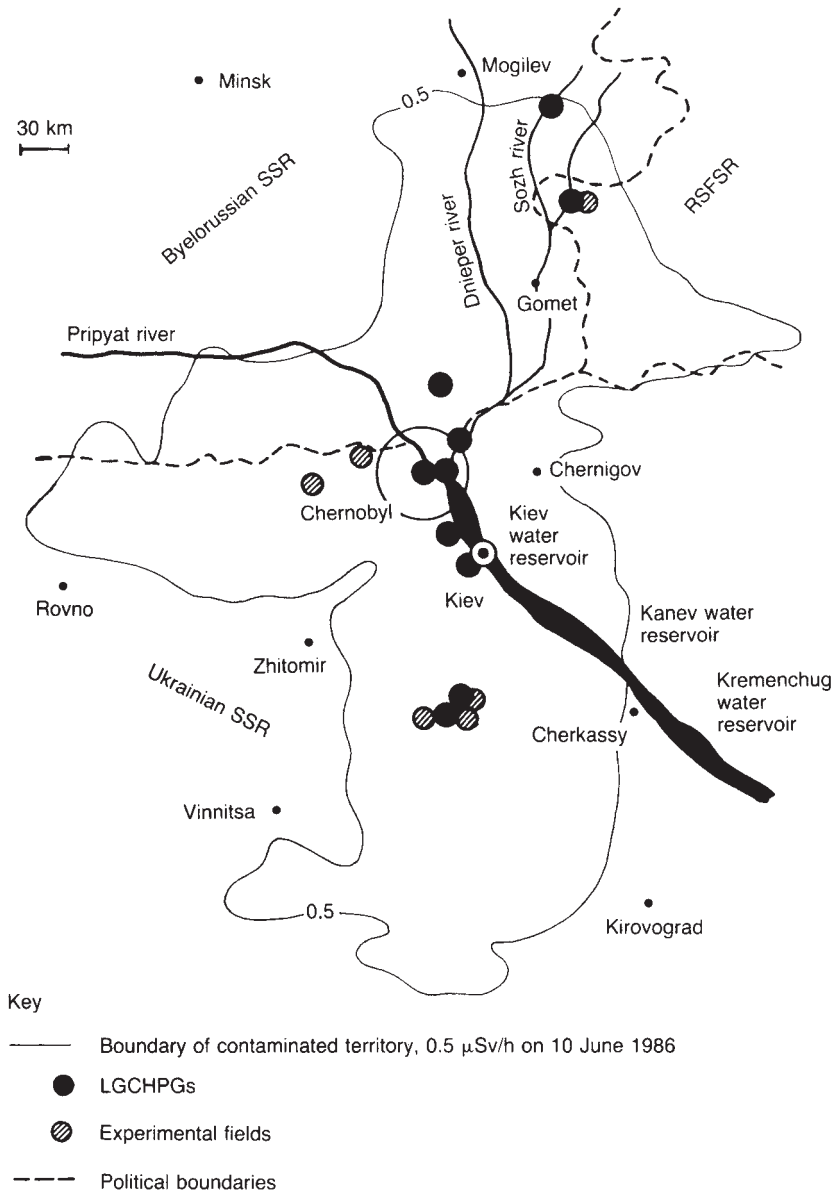


Figure A22.3 *Evacuation Zone and Contamination Zone around Chernobyl site (after Watt Committee, 1991)*

station into the space beneath the reactor vault. This reduced the oxygen concentration and the temperature. By 6 May the temperature rise had been halted and the temperature began to decline.

Meanwhile Soviet experts were concerned about the hazard of the large amount of water directly beneath the reactor. If the core were to come into contact with this water, there could be massive and explosive vaporization into steam. Engineers went down through dark passages flooded with radioactive water and succeeded in opening two large valves to allow the water to drain out.

Next an attempt was made to put a large concrete slab fitted with cooling coils beneath the core to prevent material from the core contaminating the ground and watercourses beneath it. Tunnelling in the soil at this point was difficult and it was necessary to resort to freezing the soil using liquid nitrogen, a method used in building the Leningrad Metro. The construction of this concrete bed was complete by the end of June.

Subsequently the reactor was entombed in concrete.

There was also intense activity to counter the effects of radioactivity in the surrounding area. 7000 wells were

sealed. The water supply to Kiev could no longer be taken from water near the plant and a new water supply for the city had to be constructed. A system of dikes was constructed to catch radioactive rain water from the area around the plant. A system of bore holes and barriers was created to prevent contamination of water courses.

Decontamination measures were also set in train. The site itself was divided into zones. The measures taken were to remove debris and contaminated equipment, decontaminate roofs and outer surfaces of buildings, remove a 5–10 cm layer of soil into containers, lay where necessary concrete or fresh earth on the ground, and coat certain surfaces with film-forming compounds.

Decontamination of the area outside the site was complicated by the fact that the distribution of the radionuclides changed with time according to the terrain, particularly during the first 3–4 months. Hence the full value of measures to decontaminate a particular area is generally obtained only temporarily. Buildings were hosed down and the earth around them then removed. Measures were developed to allow the contaminated land to be used for agriculture: these included changes to methods of cultivation and harvesting and the use of dust-suppression materials.

The accident was the subject of intense press interest world-wide, although hard facts were difficult to come by. Interest centred on satellite photographs of the burning core, evacuation measures taken or not taken, the assistance given by an American bone marrow transplant surgeon, potential fallout in other countries and implications for nuclear power generally.

The fire in the reactor was readily seen from above and satellite photographs appeared on the world's television screens. These were soon supplemented by Soviet pictures of the stricken reactor.

The death toll from Chernobyl cannot be known with certainty, since most deaths will be excess cancers. Two men died dealing with the accident itself. By the end of September the toll of dead in the USSR was 31 with 203 injured. The casualties are discussed further in Section A22.8.

Other European countries were also affected. Radioactive contamination was measured across Europe and many countries banned particular products for a period.

A22.7 The Investigations

A22.7.1 USSR State Committee Report

In the West the main source of information on the accident was initially the investigation described in the *USSR State Committee Report*.

Part I of the report gives a brief description of the reactor and describes the accident itself. The seven appendices of Part II describe the reactor system, the detailed design of the reactor, the measures to deal with the consequences, the quantity of radioactivity released, the dispersion of the radioactive plume and the radioactive deposition, the radio-ecological contamination caused, and the medical and biological consequences.

An important feature of the investigation was a simulation of the accident using a mathematical model. This was assisted by the fact that the control computer had a program which logged several hundred critical parameters with a minimum cycle time of 1 s.

According to the simulation a power surge occurred in the reactor which took the output to 530 MWt within 3 s. There was intense steam formation and then nucleate boiling in the fuel channels and abrupt pressure increase, causing bursting of the channels.

The primary explosion was therefore bursting of the fuel channels by high pressure steam. The formation of steam and the rapid rise in core temperature created conditions for the steam–zirconium and other reactions. These reactions gave rise to hydrogen and carbon monoxide. After the reactor space had been vented and destroyed these mixed with air and burnt causing an explosion.

The report criticises both the experimental programme and the conduct of the test. It states

> The quality of the programme was poor and the section on safety measures was drafted in a purely formal way. . . Apart from the fact that the programme made essentially no provision for additional safety measures, it called for shutting off the reactor's emergency core cooling system.
>
> Because the question of safety in these experiments had not received the necessary attention, the staff involved were not adequately prepared for the tests and were not aware of the possible dangers. Moreover, as we shall see in what follows, the staff departed from the programme and thereby created the conditions for the emergency situation.

The report highlights the positive void coefficient as a problem feature of the reactor design. It lists six violations of the operating instructions by the operators and gives the motivation for and consequences of each.

The test programme specified that the ECCS should be disconnected. In addition, the reactor shut-down trip based on turbogenerator shut-down was disarmed. During the actual test the reactor shut-down trip based on coolant parameters was disarmed. These three actions were all taken to facilitate the test. The three other violations were the reduction in the reactivity margin, the switch from local automatic power control to manual control and the switching on of the standby pumps. The first was connected with attempts to deal with the poisoning problem and it rendered the protective system ineffective. The second was an operator error and it made the reactor much more difficult to control. The third was done to make doubly sure of adequate cooling and it resulted in loss of level in the separator and the decision to disable the reactor shut-down trip based on coolant parameters.

The report also points out that at low power levels the measurement of power density in the core is less accurate.

The report gives an account of the release from the damaged reactor and of the emergency measures taken.

The report records a number of measures being taken to prevent a repetition. They include changes to the organization responsible for the reactors and to the inspection organization and intensification of research on safety aspects.

An important design modification mentioned is the use of uranium fuel enriched to 2.4% rather than 2% in order to try to avoid the positive void coefficient problem.

In presenting the report to the IAEA Legasov is reported as saying that the plant was one of the best in the country with good operators who were so convinced of its safety that they 'had lost all sense of danger'.

A22.7.2 Other reports

As described at the start of the section, there have been a number of other reports on Chernobyl. The coverage of these reports is broadly as follows:

	IAEA	*NRC*	*NEA*	*Watt Cttee*		*UKAEA*
				1	2	
Design of RBMK reactors		X	X	X		X
General account of events	X	X		X		X
Chronology of events	X	X	X			X
Radioactive release, source terms	X	X	X	X	X	
Radioactive dispersion	X	X	X		X	
Health effects	X	X		X	X	
Environmental effects, decontamination	X	X	X	X	X	
Emergency response	X	X				
Safety issues	X	X	X		X	

A22.8 The Release – 2

Estimates of the amount of radiation released are given in the *USSR State Committee Report* and several of the other reports mentioned. Table A22.3 Section A, based on figures given by Konstantinov and Gonzalez (1989), gives one such estimate of the total release, while Section B, based on the *USSR State Committee Report*, gives an estimate of the rate of release, showing the fall-off after 6 May.

According to the *USSR State Committee Report*, on 26 April the area around the site was in a low gradient pressure field with a slight wind varying in direction. At an altitude of about 1 km the wind speed was 5–10 m/s in a north-westerly direction.

The most intense plume observed was during the first 2–3 days in a northerly direction. Radiation levels in this stream at 5–10 km from the reactor and at 200m altitude were 1000 mR/h on 27 April and 500 mR/h on 28 April. According to aircraft monitoring data on 27 April the height of the stream exceeded 1200m in a north-westerly direction and the radiation level at this height was 1 mR/h. During the following days the height of the stream did not exceed 200–400 m.

Information on the radiation levels experienced at and around the site is patchy. The report states that those at the site exceeded 100 mR/h. The report also gives the following additional activities:

15 days after the accident at 30–40 km north: 35–40 mR/h

15 days after the accidents at 50–60 km west: 5 mR/h

At beginning of May in Kiev: 0.5–0.8 mR/h

Maps of the radioactive fallout in the Chernobyl region are given in the Second Watt Committee Report and by Read. Figure A22.3 from the former shows the boundary of the zone contaminated to the level of 0.5 μ Sv/h on 10 May 1986.

Accounts and maps of the radiation dispersion patterns over Europe and over the United Kingdom are given in the *UKAEA Report* and in the two *Watt Committee Reports* and by Apsimon and Davison (1986), Wheeler *et al.* (1989) and Hass *et al.* (1990).

Figure A22.4 from Gittus *et al.* (1987) shows the estimated radiation dispersion pattern across Europe on 3 May 1986.

Table A22.3 *Estimated radioactive release from Chernobyl Unit 4*

A Core inventory and estimated fraction released (after Konstantinov and Gonzalez, 1989)

Radionuclide	*Core inventory*[a] (EBq)	*Estimated fraction released*[b] (%)	*Half-life*
Kr-85	0.033	≈100	10.72 year
Xe-133	1.7	≈100	5.25 d
I-131	1.3	20	8.04 d
Te-132	0.32	15	3.26 d
Cs-137	0.29	13	30.0 year
Cs-134	0.19	10	2.06 year
Sr-89	2.0	4	50.5 d
Sr-90	0.2	4	29.12 year
Zr-95	4.4	3	64.0 d
Mo-99	4.8	2	2.75 d
Ru-103	4.1	3	39.3 d
Ru-106	2.1	3	368 d
Ba-140	2.9	6	12.7 d
Ce-141	4.4	2	32.5 d
Ce-144	3.2	3	284 d
Np-239	0.14	3	2.36 d
Pu-238	0.001	3	87.74 year
Pu-239	0.0008	3	24065 year
Pu-240	0.001	3	6537 year
Pu-241	0.17	3	14.4 year
Cm-242	0.026	3	163 d

B Estimated daily release rates (after USSR State Committee, 1986)

Date	*Time after accident* (d)	*Radioactivity released*[a] (MCi)
Apr. 26	0	12
27	1	4.0
28	2	3.4
29	3	2.6
30	4	2.0
May 1	5	2.0
2	6	4.0
3	7	5.0
4	8	7.0
5	9	8.0
6	10	0.1
9	14	≈0.01
23	28	20×10^{-6}

[a] Decay corrected to 6 May 1986. 1 Ebq = 10^{18} Bq.
[b] Stated accuracy ±50% expect for noble gases.

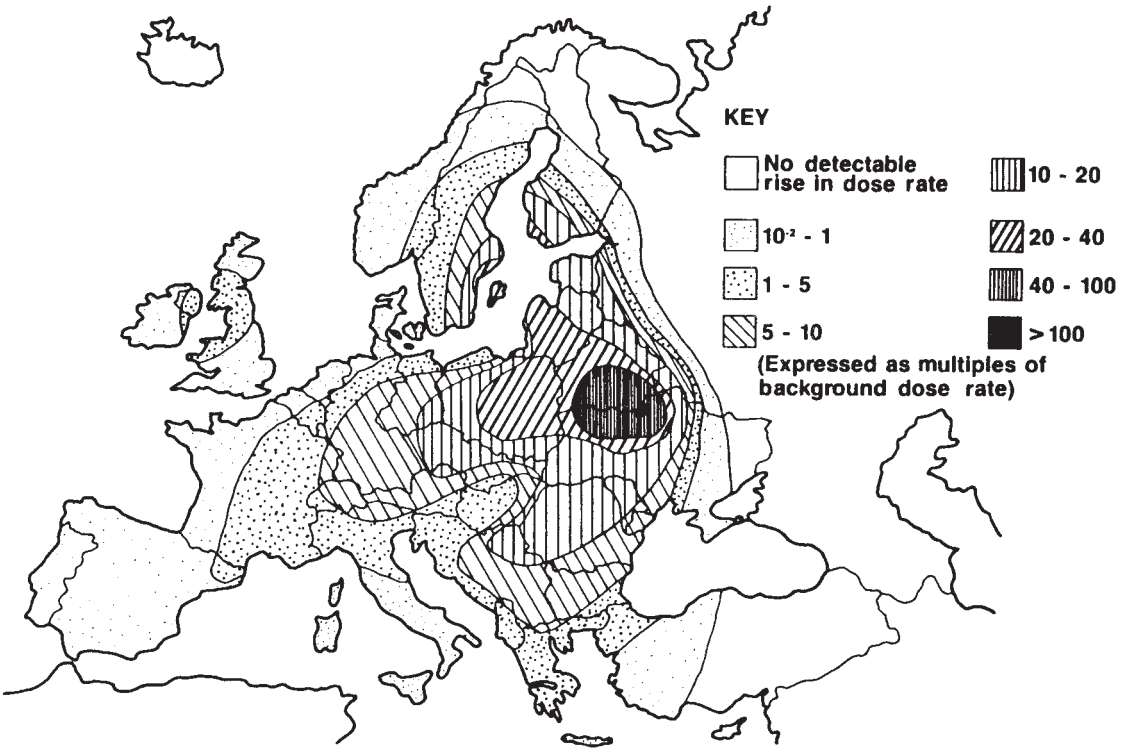


Figure A22.4 *Radiation dispersion pattern across Europe 3 May 1986 (Gittus et al., 1987)*

According to the Second *Watt Committee Report*, of the 4% of the core inventory dispersed, the distribution was approximately 0.3–0.5% on the reactor site, 1.5–2.0% within 20km and 1.0–15% beyond 20 km. The most significant isotopes outside the USSR were I-131, Cs-134 and Cs-137.

In Europe the highest dose equivalents in the year after the accident were 0.76, 0.67 and 0.59 mSv in Bulgaria, Austria and Greece, respectively, while that in the United Kingdom was 0.03 mSv.

A22.9 The Later Aftermath

Of those on site at the time, two died on site and a further 29 in hospital over the next few weeks. A further 17 are permanent invalids and 57 returned to work but with seriously affected capacity. The others on site, some 200, were affected to varying degrees. There is apparently no detailed information on the effects on the military and civilian personnel brought in to deal with the accident.

Potential health effects at relatively low doses are discussed in Appendix 20. A detailed discussion of such effects from Chernobyl is given in the Second *Watt Committee Report*. For EC countries the estimates of the NRPB in 1986 were 100 fatal thyroid cancers and 2000 fatal general cancers, or 2100 fatal cancers. For the USSR the situation is much more complex, but the report quotes an estimate by Ryin *et al.* (1990) of 1240 fatal leukaemia cases and 38,000 fatal general cancers.

Table A22.4 *Some lessons of Chernobyl*

Management of, and safety culture in, major hazard installations
Adherence to safety-related instructions
Inherent safer design of plants
Sensitivity and operability of plants
Design of plant to minimize effect of violations
Disarming of protective systems
Planning and conduct of experimental work on plants
Accidents involving human error and their assessment
Emergency planning for large accidents
Mitigating features of accidents

Measures to reduce the hazard from Unit 4 reactor have continued long after the events described, involving devoted and heroic work to limit the harm to their fellows, not only in the USSR but elsewhere.

A22.10 Some Lessons of Chernobyl

Some of the lessons of Chernobyl apply specifically to the nuclear industry and these are not considered here, but the more important ones are equally applicable to the process industries. A list of some of these is given in Table A22.4 These lessons are now considered.

A22.10.1 Management of, and safety culture in, major hazard installations

The management of the organization at the Chernobyl plant were clearly inadequate for the operation of a major hazard installation.

The defects highlighted particularly in the foregoing account are a weak safety culture and overconfidence, a potentially lethal combination.

A22.10.2 Adherence to safety-related instructions

Closely linked to this is the lesson which most commentators have highlighted as the principal one, the need to adhere to safety-related instructions. At Chernobyl a number of such instructions were violated by the operators. These violations included disconnecting the ECCS and disabling two sets of trip systems.

A22.10.3 Inherently safer design of plants

The Chernobyl reactor had a low degree of inherent safety, due particularly to the positive temperature coefficient.

The reactor did have some features, however, which might be claimed to be inherently safer. Thus by avoiding the use of a single large pressure vessel the design eliminated the hazard of catastrophic rupture of such a vessel and by subdividing the fuel into individually cooled channels it reduced the risk of total core meltdown.

On the other hand in addition to the sensitivity inherent in the positive temperature coefficient, the design also involved massive graphite blocks which could burn.

Chernobyl thus also illustrates the fact that inherently safer design does not have a single dimension, but is multidimensional.

A22.10.4 Sensitivity and operability of plants

Closely related to inherently safer design is the sensitivity and operability of plants. The nuclear reactor at Chernobyl had a regime, that of low excess reactivity, at which it was close to instability and difficult to control. This is an undesirable characteristic in any plant. This fact is recognized in the recommendation made that the uranium fuel enrichment be increased to 2.4%.

A22.10.5 Design of plant to minimize effect of violations

At Chernobyl it was necessary to avoid operating the plant with a power output less than 20% of the rated value. Where there is a feature which is so critical, it is arguable that the plant should be designed to ensure that it cannot be violated. This is another aspect of inherently safer design.

The practicality of such an approach can only be decided in the light of the particular case. As Franklin argues, it is not practical to design against all conceivable violations.

A22.10.6 Disarming of protective systems

The disarming of protective systems is a permissible practice in certain cases, but these need to be well defined and there must be proper procedures for doing so. At Chernobyl, protective systems were disarmed which should not have been.

A22.10.7 Planning and conduct of experimental work on plants

When work is to be done on a plant, whether engineering work or experimental testing, it is necessary, particularly if the work involves modification to safety-related features such as the disarming of trips, to review the potential hazards and to have specific authorized arrangements for the safe operation of the plant.

Once the test is under way, unauthorized modifications should not be made to the equipment or to the test procedure itself which have potential safety implications.

A22.10.8 Accidents involving human error and their assessment

The Chernobyl disaster was caused by a series of actions by the operators of the plant. It appears to be a case of human error which is virtually impossible to foresee and prevent. No doubt the probability of any one of the events would have been assessed as low and that of their combination is virtually incredible. But there was a common factor, namely the determination to carry out the test.

There is a need for the development of techniques, both for design and for hazard assessment of plant, for identifying potentially hazardous operator intervention sequences.

A22.10.9 Emergency planning for large accidents

The scale of the accident at Chernobyl was such that the resources required to deal with the emergency exceeded those available locally. In the event, the authorities responded by mobilizing resources on a military scale. Large numbers of military and civilian personnel were drafted in to work on the reactor itself, on evacuation and on decontamination. The evacuation on 27 April required some 1000 buses.

A22.10.10 Mitigating features of accidents

In terms of the effect of the accident on the population near the site there were several factors which mitigated the effect of the accident at Chernobyl, although the full value of these was partially lost due to hesitation in carrying out the evacuation. These mitigating features are discussed by Hawkes *et al.* (1986).

The accident occurred at night so that fewer people were exposed on site and the population outside were mostly indoors. The intense fire created the conditions for the radioactive plume to rise high and carry the release away. There was little wind so that the plume was not prevented from rising and such wind as existed was away from the large centres of population to the south. The weather was dry so that the radioactivity was not washed down on the nearby population.

Appendix 23

Rasmussen Report

Contents

A23.1 Earlier Studies A23/2
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A comprehensive hazard assessment of nuclear power plants in general is the *Reactor Safety Study: An Assessment of Accident Risks in US Commercial Nuclear Power Plants* by the Nuclear Regulatory Commission (NRC) (1975). The work was done by a team led by Professor N.C. Rasmussen and is often referred to as the *Rasmussen Report*. It is also known as the *Reactor Safety Study* (RSS) and also as *WASH 1400*. It is referred to in this appendix as the *Reactor Safety Study* but elsewhere as the *Rasmussen Report*.This study was a major exercise involving some 70 man years of work and costing $4 million. The report is a document of nine volumes some 15 cm thick.

The RSS constituted a watershed in probabilistic risk assessment. It not only brought the PRA approach to the fore as an aid in decision-making, but created a framework and brought together the various techniques needed to carry out such a study.

The work is of interest in respect of its methodology, its treatment of particular problems in risk assessment, its compilations of failure data and its presentation and evaluation of risks. Also of interest are the critiques of the report.

The methodology is based on the extensive use of fault trees and event trees and addresses the problem of uncertainty in the results obtained.

The report has been followed by further reports which have developed the methodology. In particular, a treatment of overall PRA methodology is given in the *PRA Procedures Guide* of the NRC (1982) and of human factors methodology in the *Handbook of Human Reliability Analysis with Emphasis on Nuclear Power Plant Applications. Final Report* by Swain and Guttmann (1983).

Selected references on the *Reactor Safety Study* are given in Table A23.1.

A23.1 Earlier Studies

The *RSS*, or *WASH 1400*, was not the first study of this subject. There were several earlier reports on nuclear reactor safety.

The first of these was the report *Theoretical Possibilities and Consequences of Major Accidents in Large Nuclear Power Plants* by the Atomic Energy Commission (AEC) (1957). The work was done by the Brookhaven National Laboratory and is often referred to as the Brookhaven Report and also as *WASH 740*.

WASH 740 considered as a pessimistic accident scenario, or maximum credible accident, a situation where a reactor was nearing time for refuelling and thus contained its largest inventory of fission products and suffered an accident involving loss from containment of half the core inventory in weather conditions which would carry the cloud towards a town of one million people 50 km away. It was estimated that this accident could result in 3,400 deaths, 43,000 injured and $7 billion property damage.

The report did not give an estimate of the frequency of such an event and stated in effect that the methodology to do so did not exist.

A study to update *WASH 740* was carried out by Brookhaven National Laboratory. The study was essentially complete by 1965 but was published only in 1973. It considered an even more pessimistic scenario of a large accident in a city and gave estimates of 45,000 deaths and 70,000 injuries.

Another report on reactor safety was *The Safety of Nuclear Power Reactors (Light Water Cooled) and Related Facilities* by the AEC (1973), or *WASH 1250*. This report included both accounts of policy and collections of data and contained some of the early results of WASH 1400.

Table A23.1 *Selected references on the Reactor Safety Study*

Earlier studies
AEC (1957); Ford (1977)
Reactor safety study
AEC (1975)
Reviews and critiques
AEC (1975) (Appendix XI); EPRI (1975); Hocevar (1975); Leverenz and Erdmann (1975, 1979); Boffey (1976); EPA (1976); Yellin (1976); Erdmann *et al.* (1977); Ford Foundation and Mitre Corp. (1977); UCS (1977); H.W. Lewis (1978); S. Levine (1978, 1979); ANS (1980); Hanks (1986)

A23.2 Risk Assessment Methodology

The report provides a framework for probabilistic risk assessment. The overall methodology described is based on selection of a set of release scenarios; estimation of the frequency of each scenario using fault trees and of the frequency of each associated set of outcomes using event trees; estimation of the consequences using hazard models for the physical phenomena and models of population exposure, mitigation of exposure by shelter and by escape and evacuation and injury from radioactivity and evaluation of these results using risk criteria. Table A23.2(A) indicates the subjects covered by the various volumes of the report and Table 23.2(B) some of the specific topics. Reference to the report is frequently made here, in particular with respect to (1) failure and event data; (2) lognormal distribution; (3) fault trees; (4) event trees; (5) common mode failure; (6) human error; (7) evacuation; (8) shelter; (9) FN curves and (10) risk evaluation.

The *RSS* gives risk assessments of both PWRs and BWRs, but the account given here is largely confined to the former.

A23.3 Event Data

The *RSS* contains a compilation of a large amount of failure and event data. These are based primarily on nuclear industry experience supplemented by other sources.

Most of the data refer to 2 years' experience at 17 nuclear plants which were operational in the United States in 1972. The average plant in the sample was some 4 years old.

Data for equipment are given as failure rates or probabilities of failure on demand.

It is assumed that the failures are random and that the exponential failure distribution is applicable. The possibility of failure due to ageing was considered but excluded. The report states:

> It should be recognized that the study did not include extreme ageing consideration since the applicability of its results is limited to only the next five years.

The data on failure rates and probabilities are given not as point values but as ranges. Most of these data are presented in terms of the 90% confidence range and are

Table A23.2 *Rector Safety Study: principal contents*

A Main report and appendices

Main report
Executive summary

Appendices
I Accident definition and use of event trees
II Fault trees
III Failure data
IV Bounding techniques and special techniques
V Quantitative results of accident sequences
VI Calculation of reactor accident sequences
VII Release of radioactivity in reactor accidents
VIII Physical processes in reactor meltdown accidents
IX Safety design rationale for nuclear power plants
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XI Analysis of comments

B Some specific topics

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correlated using the log–normal distribution with values quoted for the lower and upper bounds, median and error factor. This use of the lognormal distribution reflects the large amount of uncertainty in the data so that for many items it was possible to give only order of magnitude values for the failure rate or probability.

It is convenient to use as one of the parameters which describe the log–normal distribution the median. The report therefore quotes median values for much of the data.

In addition to data on failures, data for test and repair times are also given. These times are also correlated using the log–normal distribution.

It is worth emphasizing that in the report the lognormal distribution is not used to correlate times to failure. These are assumed to be exponentially distributed so that they are described by a constant failure rate. The lognormal distribution is used to describe the spread of these failure rates. On the other hand the log–normal distribution is indeed used to characterize test and repair times.

There are special studies of pipework failure and power supply failure. Reactor pressure vessel failure is also considered.

Some of the failure and event data in the *RSS* are given in Appendix 14.

A23.4 Fault Trees

The *RSS* makes extensive use of fault trees. The need to do this arises because the accident events considered can occur only if there are failures of a number of protective systems and because such failures are rare and insufficient historical data for them are available.

The volume of the report which deals with the fault trees contains some 150 figures, most of them fault tree diagrams.

The computer codes PREP and KITT were used to calculate the frequencies of the top events from those of the base events.

The PWR function unavailabilities obtained from the fault tree analyses are summarized in Table A23.3.

A23.5 Event Trees

The basic accident sequence considered is an initiating event followed by system failure and then containment failure.

The *RSS* makes extensive use of event trees for the accident sequences.

A summary of the event trees is given in Table A23.4.

A23.6 Common Mode Failure

Common mode failures are recognized in the *RSS* as a factor which may greatly increase the frequency of the hazard.

Several techniques are used to handle such common mode failures. For similar events which may in some way be coupled, such as human actions to calibrate an instrument or open a valve, lower and upper bound probabilities of failure are defined. The lower bound probability p_l is the probability calculated assuming complete independence of the events. The upper bound probability p_u is the probability calculated assuming complete coupling between the events. The actual probability p is then taken as the geometric mean, or log–normal median

$$p = (p_l p_u)^{1/2} \qquad \text{[A23.6.1]}$$

The example given is the reclosing of two valves. The probability of failing to close one valve is taken as 10^{-2}. Then, the lower bound is 10^{-4} $(10^{-2} \times 10^{-2})$ and the upper bound 10^{-2} $(10^{-2} \times 1)$, while the probability given by Equation A23.6.1 is 10^{-3} $((10^{-4} \times 10^{-2})^{1/2})$.

The method of handling coupled events in a fault tree is described below.

Other common mode failures may occur as the result of a common event such as a fire or earthquake. The treatment of such external threats is considered below.

The *RSS* concludes that common mode failures do not make a large contribution to the overall frequency of core melt failure.

A23.7 Human Error

The report gives an extensive treatment of human error and estimates for error rates for a number of types of error. It also deals with problems such as non-independence of, or coupling between, errors.

The treatment of human error in the *RSS* and the *Handbook of Human Reliability Analysis* are described in Chapters 9 and 14 and some of their error rate estimates given.

A23.8 Rare Events

An important rare event considered in the *RSS* is failure of the reactor pressure vessel. The report states

Potentially large ruptures in the vessel were considered that could prevent effective cooling of the core by the ECCS. Since certain of these ruptures appeared to be capable of causing missiles (such as the reactor vessel head) with sufficient momentum to rupture the containment, this area was explored with some care. There is some small probability that a large vessel missile could in fact impact directly on the containment and penetrate through the wall. This type of rupture could involve a core meltdown in a non-intact containment.

A study by the Advisory Committee on Reactor Safeguards (ACRS) concluded that 'the disruptive failure probability of reactor vessels designed, constructed and operated according to code is even lower than 1×10^{-6} per vessel year.' The figure used in the *RSS* is 1×10^{-7}/vessel year.

The effect of this low estimate of reactor pressure vessel failure rate is to take this event out of consideration as a cause of release. The *RSS* states

> Gross vessel rupture would have to be at least about 100 times more likely than the value estimated in order to contribute to the PWR core melt probability.

A23.9 External Threats

The *RSS* considers external threats such as fire, earthquakes and sabotage.

The prediction of earthquakes is highly uncertain and the report emphasizes this. It nevertheless states that a 'reasonable estimate (of core melt due to earthquake) is 10^{-7} per reactor year'.

The *RSS* acknowledges the threat posed by sabotage, but does not take this into account in the risk estimates made. These estimates apply to bona fide accidents and exclude those due to sabotage.

Table A23.3 *Reactor Safety Study: PWR function unavailabilities from trees (Nuclear Regulatory Commission, 1975)*

System	*Unavailability* (Q)			*Major contributors* (point estimates)			
	Q_{upper}	Q_{median}	Q_{lower}	*Hardware*	*Test and maintenance*	*Human*	*Common mode*
PWR systems							
Electric power	1.0×10^{-4}	1.0×10^{-5}	1.0×10^{-5}				
Reactor protection	1.0×10^{-4}	3.6×10^{-5}	1.3×10^{-5}	2.2×10^{-5}	1×10^{-5}		
Auxilliary feedwater							
0–8 h after small LOCA	3.0×10^{-4}	3.7×10^{-5}	7.0×10^{-6}	2.0×10^{-6}	3.2×10^{-6}		3×10^{-5}
8–24 h after small LOCA	2.6×10^{-3}	1.2×10^{-3}	5.4×10^{-4}	1.1×10^{-3}			
0–8 h without net	2.8×10^{-3}	4.5×10^{-4}	1.2×10^{-4}	2.0×10^{-6}	1.4×10^{-4}		1.1×10^{-4}[a]
Containment spray injection	7.8×10^{-3}	2.4×10^{-3}	1.0×10^{-3}	3.2×10^{-4}	1.5×10^{-4}		1.9×10^{-3}[a]
Consequence limiting control							
Hi-single train	7.2×10^{-2}	2.8×10^{-2}	1.4×10^{-2}	2.0×10^{-2}	2.1×10^{-3}	3×10^{-3}	1.0×10^{-3}[a]
Hi-both trains	4.8×10^{-3}	1.6×10^{-3}	4.8×10^{-4}	4.0×10^{-4}	8.4×10^{-5}		1.0×10^{-3}[a]
Hi-Hi single train	2.6×10^{-2}	1.2×10^{-2}	7.2×10^{-3}	4.9×10^{-3}	2.1×10^{-3}		1.0×10^{-3}[a]
Hi-Hi both trains	3.2×10^{-3}	1.1×10^{-3}	4.1×10^{-4}	6.5×10^{-5}	2.0×10^{-5}		1×10^{-3}[a]
Emergency coolant injection							
Accumulators	1.4×10^{-3}	9.5×10^{-4}	6.2×10^{-4}	4.9×10^{-4}	3.4×10^{-4}		
Low pressure injection	7.4×10^{-3}	4.7×10^{-3}	3.1×10^{-3}	3.2×10^{-4}	9.6×10^{-4}	2.5×10^{-3}	4.5×10^{-5}[a]
High pressure injection	2.7×10^{-2}	8.6×10^{-3}	4.4×10^{-3}	1.1×10^{-3}		7.0×10^{-4}	4.5×10^{-5}[a]
Safety injection control							
Single train	1.2×10^{-2}	5.8×10^{-3}	3.3×10^{-3}	3.0×10^{-3}	2.2×10^{-3}		4.5×10^{-5}[a]
Both trains	2.7×10^{-4}	9.9×10^{-5}	5.4×10^{-5}	9.0×10^{-6}	1.3×10^{-5}		4.5×10^{-5}[a]
Containment spray recirculation	9.0×10^{-4}	1.0×10^{-4}	2.5×10^{-5}	5.2×10^{-6}	4.3×10^{-5}		2.8×10^{-5}[a]
Containment heat removal	3.0×10^{-4}	8.5×10^{-5}	3.0×10^{-5}	6.4×10^{-5}			1.0×10^{-5}[a]
Low pressure recirculation	3.1×10^{-2}	1.3×10^{-2}	4.4×10^{-3}	2.7×10^{-3}	1.0×10^{-4}	1×10^{-5}	6.0×10^{-3}[a]
High pressure recirculation	2.2×10^{-2}	9.0×10^{-3}	4.3×10^{-3}	2.0×10^{-3}			6.0×10^{-3}[a]
Containment leakage							
Pressure reduced to $<\frac{1}{2}$psi[b]	7.5×10^{-4}	2.0×10^{-4}	8.4×10^{-5}	1.3×10^{-4}			
Pressure not reduced to $<\frac{1}{2}$psi	1.0×10^{-2}	2.0×10^{-3}	6.0×10^{-4}	8.8×10^{-4}			
Sodium hydroxide addition	1.1×10^{-2}	5.9×10^{-3}	3.6×10^{-3}	2.1×10^{-4}	4.8×10^{-3}		1.2×10^{-3}[a]
PWR functions							
Electrical power	1.0×10^{-4}	1.0×10^{-5}	1.0×10^{-6}				
Reactor protection	1.0×10^{-4}	3.6×10^{-5}	1.3×10^{-5}	2.7×10^{-5}	1.2×10^{-5}		
Auxilliary feedwater							
0–8 h after small LOCA	3.0×10^{-4}	3.7×10^{-5}	7.0×10^{-6}	2.0×10^{-6}	3.2×10^{-6}		3×10^{-5}[c]
8–24 h after small LOCA	2.6×10^{-3}	1.2×10^{-3}	5.3×10^{-4}	1.1×10^{-3}			
0–8 h without net	2.8×10^{-3}	4.5×10^{-4}	1.2×10^{-4}	2.0×10^{-6}	1.4×10^{-4}		1.1×10^{-4}[c]
Containment spray injection	7.8×10^{-3}	2.4×10^{-3}	1.0×10^{-3}	3.2×10^{-4}	1.5×10^{-4}		1.9×10^{-3}[c]
Emergency coolant injection							
Large LOCA	9.0×10^{-3}	5.6×10^{-3}	3.0×10^{-3}	NA	NA	NA	NA
Small LOCA (2–6 in. diam.)	3.0×10^{-2}	9.5×10^{-3}	4.0×10^{-3}	NA	NA	NA	NA
Small-small LOCA($\frac{1}{2}$–2 in. diam.)	2.7×10^{-2}	8.6×10^{-3}	4.4×10^{-3}	NA	NA	NA	NA
Containment spray recirculation	9.0×10^{-4}	1.0×10^{-4}	2.5×10^{-5}	5.2×10^{-6}	4.3×10^{-5}		2.8×10^{-5}[c]
Containment head removal	3.0×10^{-4}	8.5×10^{-5}	3.0×10^{-5}	6.4×10^{-5}			1.0×10^{-5}[c]
Emergency coolant recirculation							
Large LOCA	3.1×10^{-2}	1.3×10^{-2}	4.4×10^{-3}	2.7×10^{-3}	1.0×10^{-4}	1.0×10^{-5}	6.0×10^{-3}[c]
Small LOCA	2.2×10^{-2}	9.0×10^{-3}	4.3×10^{-3}	2.0×10^{-3}			6.0×10^{-3}[c]
Small-small LOCA		6.0×10^{-3}[d]		2.0×10^{-3}			3.0×10^{-3}[c]
Containment leakage							
Pressure reduced to $<\frac{1}{2}$psi	7.5×10^{-4}	2.0×10^{-4}	8.4×10^{-5}	1.3×10^{-4}			
Pressure not reduced to $<\frac{1}{2}$psi	1.0×10^{-2}	2.0×10^{-3}	6.0×10^{-4}	8.8×10^{-4}			
Sodium hydroxide addition	1.1×10^{-2}	5.9×10^{-3}	3.6×10^{-3}	2.1×10^{-4}	4.8×10^{-3}		1.2×10^{-3}[c]

[a] Also human error.
[b] Containment pressure must be reduced to $<\frac{1}{2}$ psi to isolate containment spray injection system.
[c] Common mode resulting from human error.
[d] Point estimate value obtained only.
NA, not applicable to combined systems.

Table A23.4 *Reactor Safety Study: PWR accident sequences from event trees (Nuclear Regulatory Commission, 1975)*

Symbol	*Meaning*
A	Intermediate to large LOCA
B	Failure of electric power to ESFs
B′	Failure to recover either on-site or off-site electric power within about 1 to 3 h following an initiating transient which is a loss of off-site a.c. power
C	Failure of the containment spray injection system
D	Failure of the emergency core cooling injection system
F	Failure of the containment spray recirculation system
G	Failure of the containment heat removal system
H	Failure of the emergency core cooling recirculation system
K	Failure of the reactor protection system
L	Failure of the secondary system steam relief valves and the auxiliary valves and the auxiliary feedwater system
M	Failure of the secondary system steam relief valves and the power conversion system
Q	Failure of the primary system safety relief valves to reclose after opening
R	Massive rupture of the reactor vessel
S_1	A small LOCA with an equivalent diameter of about 5–15 cm
S_{12}	A small LOCA with an equivalent diameter of about 1–5 cm
T	Transient event
V	Failure of low-pressure injection system check valve
α	Containment rupture due to a reactor vessel steam explosion
β	Containment failure resulting from inadequate isolation of containment openings and penetrations
γ	Containment failure due to hydrogen burning
δ	Containment failure due to overpressure
ε	Containment vessel melt-through

Sequence designation	*Event tree failure(s)*	*Containment event tree failure*
PWR sequence		
1. A	Large rupture only	None
2. A-β	Large rupture only	Containment leakage
3. AH-α	ECCS recirculation	Vessel steam explosion
4. AH-β	ECCS recirculation	Containment leakage
5. AH-ε	ECCS recirculation	Melt-through
6. AHI-α	ECCS recirculation plus sodium hydroxide	Vessel steam explosion
7. AHI-β	ECCS recirculation plus sodium hydroxide	Containment leakage
8. AHI-ε	ECCS recirculation plus sodium hydroxide	Melt-through
9. AG-δ	Containment heat removal	Overpressure
10. AHG-δ	ECCS recirculation plus containment heat removal	Overpressure
11. AHG-ε	ECCS recirculation plus containment heat removal	Melt-through
12. AHF-α	ECCS recirculation plus containment spray recirculation	Vessel steam explosion
13. AHF-β	ECCS recirculation plus containment spray recirculation	Containment leakage
14. AHF-δ	ECCS recirculation plus containment spray recirculation	Overpressure
15. AHF-ε	ECCS recirculation plus containment spray recirculation	Melt-through
16. ADI-α	ECCS injection	Vessel steam explosion
17. AD-β	ECCS injection	Containment leakage
18. AD-ε	ECCS injection	Melt-through
19. ADI-α	ECCS injection plus sodium hydroxide	Vessel steam explosion
20. ADI-ε	ECCS injection plus sodium hydroxide	Melt-through
21. ADG-ε	ECCS injection plus containment heat removal	Melt-through
22. ADGI-ε	ECCS injection plus containment heat removal plus sodium hydroxide	Melt-through
23. ADF-β	ECCS injection plus containment spray recirculation	Containment leakage
24. ADF-ε	ECCS injection plus containment spray recirculation	Melt-through
25. ACD-β	Containment spray injection plus ECCS injection	Containment leakage
26. ACD-ε	Containment spray injection plus ECCS injection	Melt-through
27. ACDGI-α	All except electric power and containment spray recirculation	Vessel steam explosion
28. ACDGI-β	All except electric power and containment spray recirculation	Containment leakage
29. ACDGI-δ	All except electric power and containment spray recirculation	Overpressure
30. ACDGI-ε	All except electric power and containment spray recirculation	Melt-through
31. AB-α	Electric power	Vessel steam explosion
32. AB-γ	Electric power	Hydrogen combustion
33. AB-ε	Electric power	Melt-through

Table A23.4 *(continued)*

34. S_2C-α	Small LOCA plus containment spray injection	Vessel steam explosion
35. S_2C-δ	Small LOCA plus containment spray injection	Overpressure
36. TMLB′-γ	Transient plus feedwater plus electric power	Hydrogen combustion
37. TMLB′-δ	Transient plus feedwater plus electric power	Overpressure
38. TMLB′-α	Transient plus feedwater plus electric power	Vessel steam explosion

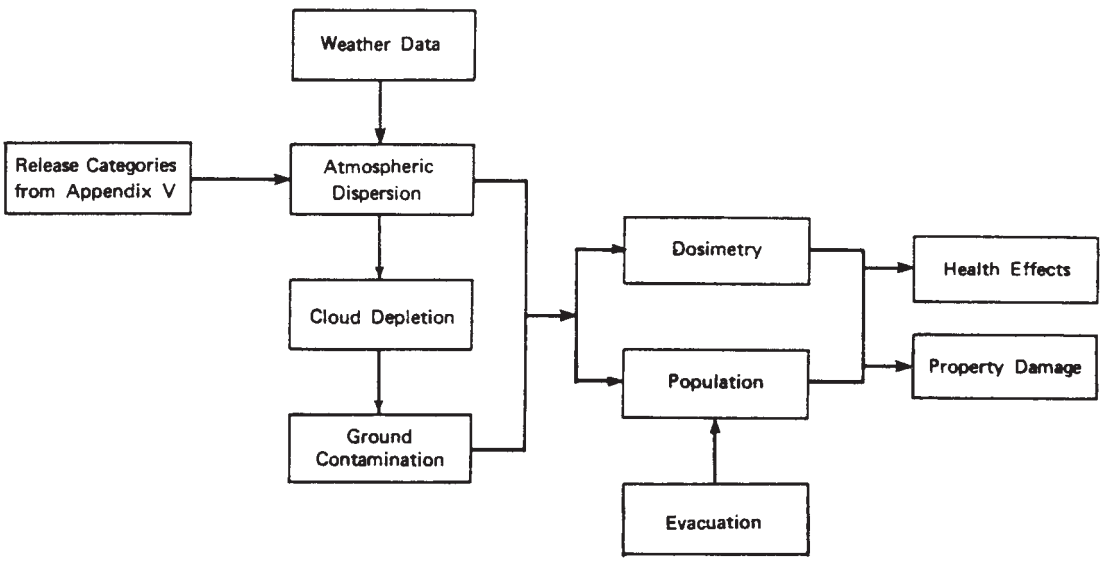

Figure A23.1 *Reactor Safety Study: Schematic outline of consequence models (Nuclear Regulatory Commission 1975)*

A23.10 Release Scenarios

The consequences of a core degradation or meltdown depend on (1) core inventory; (2) fraction released; (3) dispersion and deposition; (4) population exposed; (5) mitigating features (evacuation, shelter); and (6) injury relations.

A schematic outline of the consequence models is shown in Figure A23.1.

The initial radioactivity of the radionuclides in the reactor core is given in Table A23.5 and the reactor core inventory in Table A23.6.

The release scenarios are shown in Tables A23.7 and A23.8.

The release from the reactor is used in the report as the source term for a plume gas dispersion model. This model takes into account the deposition of solid radionuclides.

A23.11 Population Characteristics

The population at risk was characterized by a composite model based on the 68 actual sites holding the first 100 reactors. Six composite sites of different types were defined.

The population density was determined as follows. The first type of site was an Atlantic coastal site and 14 of the reactors were assigned to this composite site. The actual population around each of these reactors was determined from census data for a distance of 50 miles. For each actual site 16 sectors were defined, making 224 sectors in total. These 224 sectors were then ranked in order of population density and 16 representative sectors were determined for the composite site.

Data from a time use study by J.P. Robinson and Converse (1966) were used to determine the fraction of time spent at different locations and hence the probability that a person was inside shelter.

A23.12 Mitigation of Exposure

Factors which mitigate the exposure of the population include shelter and evacuation.

The *RSS* uses a single exponential stage evacuation model. This model is based on a study of actual evacuations by Hans and Sell (1974).

Measures to mitigate long-term exposure include interdiction of the contaminated zone and decontamination of this zone.

The effect of shelter on concentration is modelled using a single exponential stage model for ventilation.

A23.13 Injury Relations

The effects of radioactivity on people are complex and are both short-term, or prompt, and long-term.

Table A23.5 *Reactor Safety Study: initial activity of radionuclides in reactor core (Nuclear Regulatory Commission, 1975)*

No.	*Radionuclide*	*Radio inventory source* (curies $\times 10^{-8}$)	*Half-life* (days)
1	Cobalt-58	0.0078	71.0
2	Cobalt-60	0.0029	1920
3	Krypton-85	0.0056	3950
4	Krypton-85m	0.24	0.183
5	Krypton-87	0.47	0.0528
6	Krypton-88	0.68	0.117
7	Rubidium-86	0.00026	18.7
8	Strontium-89	0.94	52.1
9	Strontium-90	0.037	11,030
10	Strontium-91	1.1	0.403
11	Yttrium-90	0.039	2.67
12	Yttrium-91	1.2	59.0
13	Zirconium-95	1.5	65.2
14	Zirconium-97	1.5	0.71
15	Niobium-95	1.5	35.0
16	Molybdenum-99	1.6	2.8
17	Technetium-99m	1.4	0.25
18	Ruthenium-103	1.1	39.5
19	Ruthenium-105	0.72	0.185
20	Ruthenium-106	0.25	366
21	Rhodium-105	0.49	1.5
22	Tellurium-127	0.059	0.391
23	Tellurium-127m	0.011	109
24	Tellurium-129	0.31	0.048
25	Tellurium-129m	0.053	0.340
26	Tellurium-131m	0.13	1.25
27	Tellurium-132	1.2	3.25
28	Antimony-127	0.061	3.88
29	Antimony-129	0.33	0.179
30	Iodine-131	0.85	8.05
31	Iodine-132	1.2	0.0958
32	Iodine-133	1.7	0.875
33	Iodine-134	1.9	0.0366
34	Iodine-135	1.5	0.280
35	Xenon-133	1.7	5.28
36	Xenon-135	0.34	0.384
37	Cesium-134	0.075	750
38	Cesium-136	0.030	13.0
39	Cesium-137	0.047	11,000
40	Barium-140	1.6	12.8
41	Lanthanum-140	1.6	1.67
42	Cerium-141	1.5	32.3
43	Cerium-143	1.3	1.38
44	Cerium-144	0.85	284
45	Praseodymium-143	1.3	13.7
46	Neodymium-147	0.60	11.1
47	Neptunium-239	16.4	2.35
48	Plutonium-238	0.00057	32,500
49	Plutonium-239	0.00021	8.9×10^6
50	Plutonium-240	0.00021	2.4×10^6
51	Plutonium-241	0.034	5350
52	Americium-241	0.000017	1.5×10^5
53	Curium-242	0.0050	163
54	Curium-244	0.00023	6630

Table A23.6 *Reactor Safety Study: reactor core inventory (Nuclear Regulatory Commission, 1975)*

Location	*Total inventory* (curies)			*Fraction of core inventory*		
	Fuel	*Gap*	*Total*	*Fuel*	*Gap*	*Total*
Core[a]	8.0×10^9	1.4×10^8	8.1×10^9	9.8×10^{-1}	1.8×10^{-2}	1
Spent fuel storage pool (max.)[b]	1.3×10^9	1.3×10^7	1.3×10^9	1.6×10^{-1}	1.6×10^{-3}	1.6×10^{-1}
Spent fuel storage pool (av.)[c]	3.6×10^8	3.8×10^6	3.6×10^8	4.5×10^{-2}	4.8×10^{-4}	4.5×10^{-2}
Shipping cask[d]	2.2×10^7	3.1×10^5	2.2×10^7	2.7×10^{-3}	3.8×10^{-5}	2.7×10^{-3}
Refuelling[e]	2.2×10^7	2×10^5	2.2×10^7	2.7×10^{-3}	2.5×10^{-5}	2.7×10^{-3}
Waste gas storage tank	–	–	9.3×10^{-4}	–	–	1.2×10^{-5}
Liquid waste storage tank	–	–	9.5×10^1	–	–	1.2×10^{-8}

[a] Core inventory based on activity 1/2 h after shutdown.
[b] Inventory of 2/3 core loading; 1/3 core with 3 day decay and 1/3 core with 150 day decay.
[c] Inventory of 1/2 core loading; 1/6 core with 150 day decay and 1/3 core with 60 day decay.
[d] Inventory based on 7 PWR or 17 BWR fuel assemblies with 150 day decay.
[e] Inventory for one fuel assembly with 3 day decay.

In order to determine these effects it is first necessary to estimate the doses of radioactivity received and then to apply a dose–response relation.

The *RSS* gives a detailed treatment of all these aspects and the report contains a large number of tables and graphs showing early and late fatalities and injuries due to different modes of injury and the contribution to these of individual radionuclides.

It also deals with the contamination of land.

A23.14 Uncertainty in Results

An attempt is made in the report to put bounds on the errors of the estimates.

A number of methods are used. Failure rates and probabilities are taken not as single values but as a range of values with a lognormal distribution, as described above.

The inputs to the fault trees are therefore not single values of frequency or probability but distributions of these. The frequency or probability of the top event is then computed, also as a distribution, by sampling from the distributions of these individual events using Monte Carlo simulation.

Such simulation may also be used to take account of common mode failures by arranging coupling between the failure rates or probabilities in question.

A23.15 Presentation of Results

The risks from reactor accidents are presented in the main report principally in the form of tables of frequency–consequence results.

The results for 100 reactors are for the mix of both PWR and BRW reactors considered in the study. The risks for an individual PWR are higher than for a BWR and those for a composite single reactor based on the mix are close to those for a PWR.

Table A23.9(A) shows the societal risk of early effects from one reactor and Table A23.9(B) of those from late effects. The report gives another table showing the societal risk from 100 reactors, the frequencies simply being greater by a factor of 100. Table A23.10 shows the individual and average societal risk from 100 reactors.

The results are also given in graphical form. Figure A23.2 gives a histogram of PWR release categories. Figure A23.3 is the frequency–consequence curve, or FN curve, for early fatalities from a single reactor. The graph shows curves for a PWR, a BWR and the composite reactor.

Figure A23.4 is the frequency–consequence curve for areas in which relocation of people and decontamination would be required.

A23.16 Evaluation of Results

The *RSS* evaluates the risk from the 100 nuclear reactors by making comparisons with those from other hazards.

The main report gives numerous tables showing risks from various natural and man-made hazards such as earthquakes, hurricanes, tornadoes, meteorites, fires, dams, explosions, toxic gas releases and aircraft crashes.

One of the principle comparisons made is the FN curve for the 100 reactors and for other hazards. Figures A23.5 and Figure A23.6 show, respectively, the FN curve for early deaths for natural hazards and for man-made hazards together with the curve for 100 reactors.

The overall conclusion of the report is that the risks to the public from 100 nuclear reactors are very much less than those from other natural and man-made hazards.

The report has a slim Executive Summary which describes the report as a whole and gives a presentation and evaluation of the results. This summary does not include the societal risk estimates given in Table A23.9 and in general tends both to play down the risks and gloss over many qualifying assumptions.

A23.17 Browns Ferry Incident

The incident at Browns Ferry is widely regarded as a near miss and the *RSS* could hardly avoid reference to this incident.

On 22 March 1975 a fire started in the electrical control cables at the plant. Following a plant modification a candle was used to detect air leaks at a point where a set of electrical cables passed through a wall. The fire burned out of control for $7\frac{1}{2}$ hours and badly damaged 1600 cables of which 618 were cables related to the safety systems.

The power interruption caused disturbances on the reactors and the operators, hindered by dense smoke, had to struggle to bring them back under control. Unit 2 was shut-down and stabilized without great difficulty but Unit 1

Table A23.7 *Reactor Safety Study: PWR release scenarios ±1 (Nuclear Regulatory Commission, 1975)*

Accident category and frequency f_j	*Description of accident category*	*Duration of release* (h)	*Elevation of release* (m)	*Energy release rate* (Btu/h)	*Fraction of core inventory released*						
					Xe–Kr	*I*	*Cs = Rb*	*Te–Sb*	*Ba–Sr*	*Ru, Rh, Co, Mo, Tc*	*Y, La, Zr, Nb, Ce, Pr, Nd, Np, Pu, Am, Cm*
PWR1a and 1b 9×10^{-7} per year	Core melt-down and failure of containment spray and heat removal systems 1a – steam explosion after containment failure due to overpressure; 1b – steam explosion ruptures containment	0.5	25	20×10^6(1a) 520×10^6(1b)	0.9	0.7	0.4	0.4	0.05	0.4	3×10^{-3}
PWR2 8×10^{-6} per year	Core meltdown, failure of containment spray and heat removal systems. Containment fails through overpressure after commencement of core meltdown	0.5	0	170×10^6	0.9	0.7	0.5	0.3	0.06	0.02	4×10^{-3}
PWR3 4×10^{-6} per year	Failure of containment due to overpressure before core meltdown	1.5	0	6×10^6	0.8	0.2	0.2	0.3	0.02	0.03	3×10^{-3}

PWR4 5×10^{-7} per year	Core meltdown and failure of containment system properly to isolate; failure of containment spray system	3.0	0	1×10^{6}	0.6	0.09	0.04	0.03	5×10^{-3}	3×10^{-3}	4×10^{-4}
PWR5 7×10^{-7} per year	As PWR4, but containment spray systems operate to reduce release to atmosphere	4	0	3×10^{-5}	0.3	0.03	9×10^{-3}	5×10^{-3}	10^{-3}	6×10^{-4}	7×10^{-5}
PWR6 6×10^{-6} per year	Core melt down, failure of containment sprays. Containment maintains integrity but core melts through base	10.0	0	0	0.03	8×10^{-4}	8×10^{-4}	9×10^{-8}	9×10^{-5}	7×10^{-5}	10^{-5}
PWR7 4×10^{-5} per year	As PWR6, but containment sprays operate	10.0	0	0	6×10^{-3}	2×10^{-5}	10^{-5}	2×10^{-5}	10^{-6}	10^{-6}	2×10^{-7}
PWR8 4×10^{-5} per year	Large pipe break, containment fails properly to isolate, all other engineered safeguards work, no core meltdown	0.5	0	0	2×10^{-3}	10^{-4}	5×10^{-4}	10^{-6}	10^{-8}	0	0
PWR9 4×10^{-4} per year	As PWR8, but all engineered safeguards function as designed. Essentially PWR design basis accident	0.5	0	0	3×10^{-6}	10^{-7}	6×10^{-7}	10^{-9}	10^{-11}	0	0

Table A23.8 *Reactor Safety Study: PWR release scenarios – 2 (Nuclear Regulatory Commission, 1975)*

Fission product	*Gap release fraction*	*Melthdown release fraction*	*Vaporization release fraction*[a]	*Steam explosion fraction*[b]
Xe, Kr	0.030	0.870	0.100	(X) (Y) 0.90
I, Br	0.017	0.883	0.100	(X) (Y) 0.90
Ca, Rb	0.050	0.760	0.190	–
Te[c]	0.0001	0.150	0.850	(X) (Y) (0.60)
Sr, Ba	0.000001	0.100	0.010	–
Ru[d]	–	0.030	0.050	(X) (Y) (0.90)
La[e]	–	0.003	0.010	–

[a] Exponential loss over 2 h with half-time of 30 min. If a steam explosion occurs prior to this, only the core fraction not involved in the steam explosion can experience vaporization.
[b] X = fraction of core involved in the steam explosion. Y = fraction of inventory remaining for release by oxidation.
[c] Includes Se, Sb.
[d] Includes Mo, Pd, Rh, Tc.
[e] Includes Nd, Eu, Y, Ce, Pr, Pm, Sm, Np, Pu, Zr, Nb.

Table A23.9 *Reactor Safety Study: societal risk from one reactor (Nuclear Regulatory Commission, 1975)*

A Early effects

Chance per reactor-year	*Consequences*				
	Early fatalities	*Early illness*	*Total property damage* ($10[9])	*Decontamination area* (≈square miles)	*Relocation area* (square miles)
One in 20,000[a]	<1.0	<1.0	<0.1	<0.1	<0.1
One in 1,000,000	<1.0	300	0.9	2,000	130
One in 10,000,000	110	3,000	3	3,200	250
One in 100,000,000	900	14,000	8	–	290
One in 1,000,000,000	3300	45,000	14	–	–

B Cancer and genetic effects

Chance per reactor-year	*Consequences*		
	Latent cancer[b] *fatalities* (per year)	*Thyroid nodules*[b] (per year)	*Genetic effects*[c] (per year)
One in 20,000[d]	<1.0	<1.0	<1.0
One in 1,000,000	170	1,400	25
One in 10,000,000	460	3,500	60
One in 100,000,000	860	6,000	110
One in 1000,000,000	1,500	8,000	170
Nuclear incidence	17,000	8,000	8,000

[a] This is the predicted chance of core melt per reactor year.
[b] This rate would occur approximately in the 10–40 year period following a potential accident.
[c] This rate would apply to the first generation born after a potential accident. Subsequent generations would experience effects at a lower rate.
[d] This is the predicted chance of core melt per reactor year.

was out of control for some hours and was stabilized only after the fire was put out. Control of Unit 1 was only achieved by the use of equipment which was not part of the safety system.

The fire disabled all five emergency core cooling systems in Unit 1.

At the point when control was lost 7 out of 11 of relief valves were failed. The fire disabled the other four. The *RSS* gives an analysis of the probability that these four valves would in fact be disabled in a fire without any of the valves, from the set of seven or the set of four, being repaired over the duration of the fire. The probability estimated was 0.003.

A23.18 Critical Assumptions

The results obtained in the *RSS* depend on the validity of a number of assumptions.

Some of the more critical assumptions are

plant standards are not seriously below average;
failures are random rather than wearout;
reactor pressure vessel operating conditions are closely controlled;
site is not subject to unusually severe earthquakes;
population density around site is not unusually high;
emergency plans exist and are exercised;

Table A23.10 *Reactor Safety Study: individual and average societal risk from 100 reactors (Nuclear Regulatory Commission, 1975)*[a]

Consequence	*Societal*	*Individual*
Early fatalities[b]	3×10^{-3}	2×10^{-10}
Early illness[b]	2×10^{-1}	1×10^{-8}
Latent cancer fatalities[c]	7×10^{-2} per year	3×10^{-10} per year
Thyroidnodules[c]	7×10^{-1} per year	3×10^{-9} per year
Genetic effects[d]	1×10^{-2} per year	7×10^{-11} per year
Property damage ($)	2×10^{6}	–

[a] Based on 100 reactors at 68 current sites.
[b] The individual risk value is based on the 15 million people living in the general vicinity of the first 100 nuclear power plants.
[c] This value is the rate of occurrence per year for about a 30 year period following a potential accident. The individual rate is based on the total US population.
[d] This value is the rate of occurrence per year for the first generation born after a potential accident: subsequent generations would experience effects at a lower rate. The individual rate is based on the total US population.

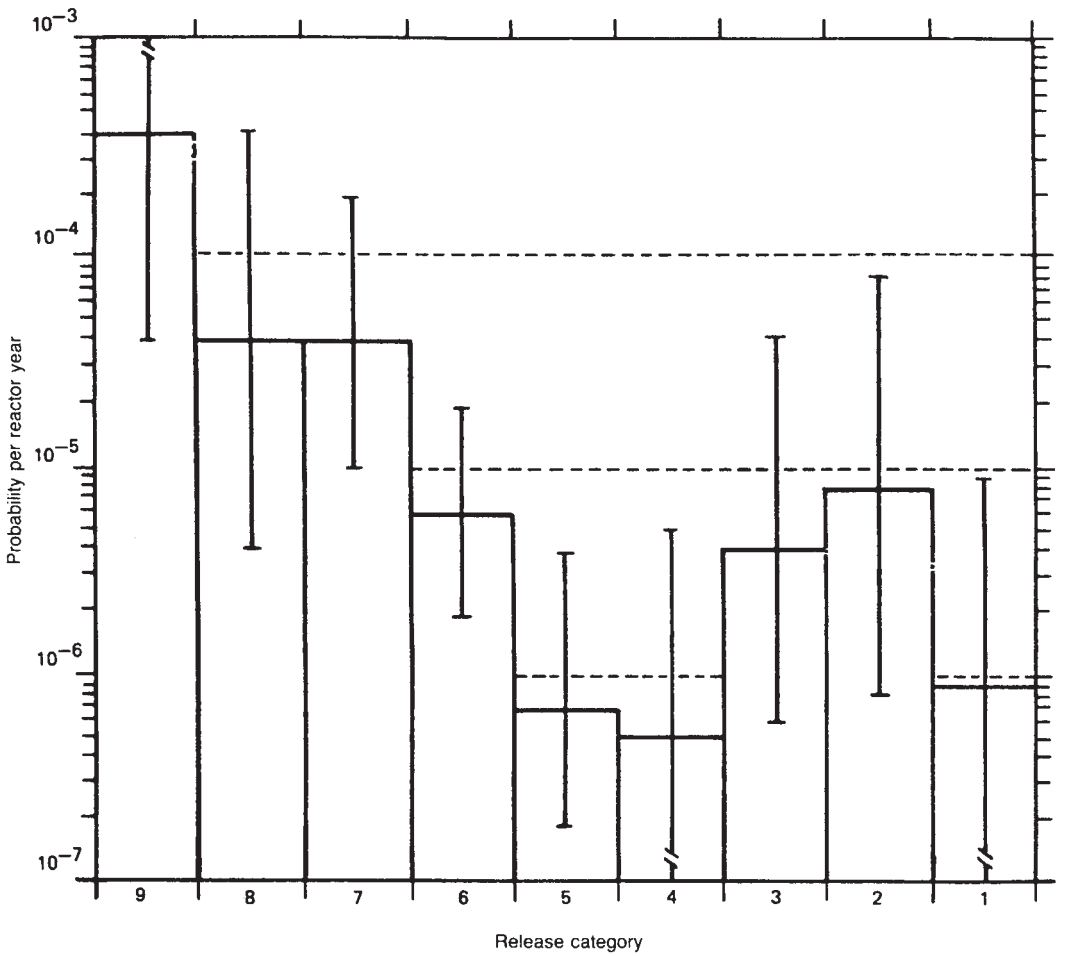

Figure A23.2 *Reactor Safety Study: histogram for frequency of PWR release categories (Nuclear Regulatory Commission, 1975)*

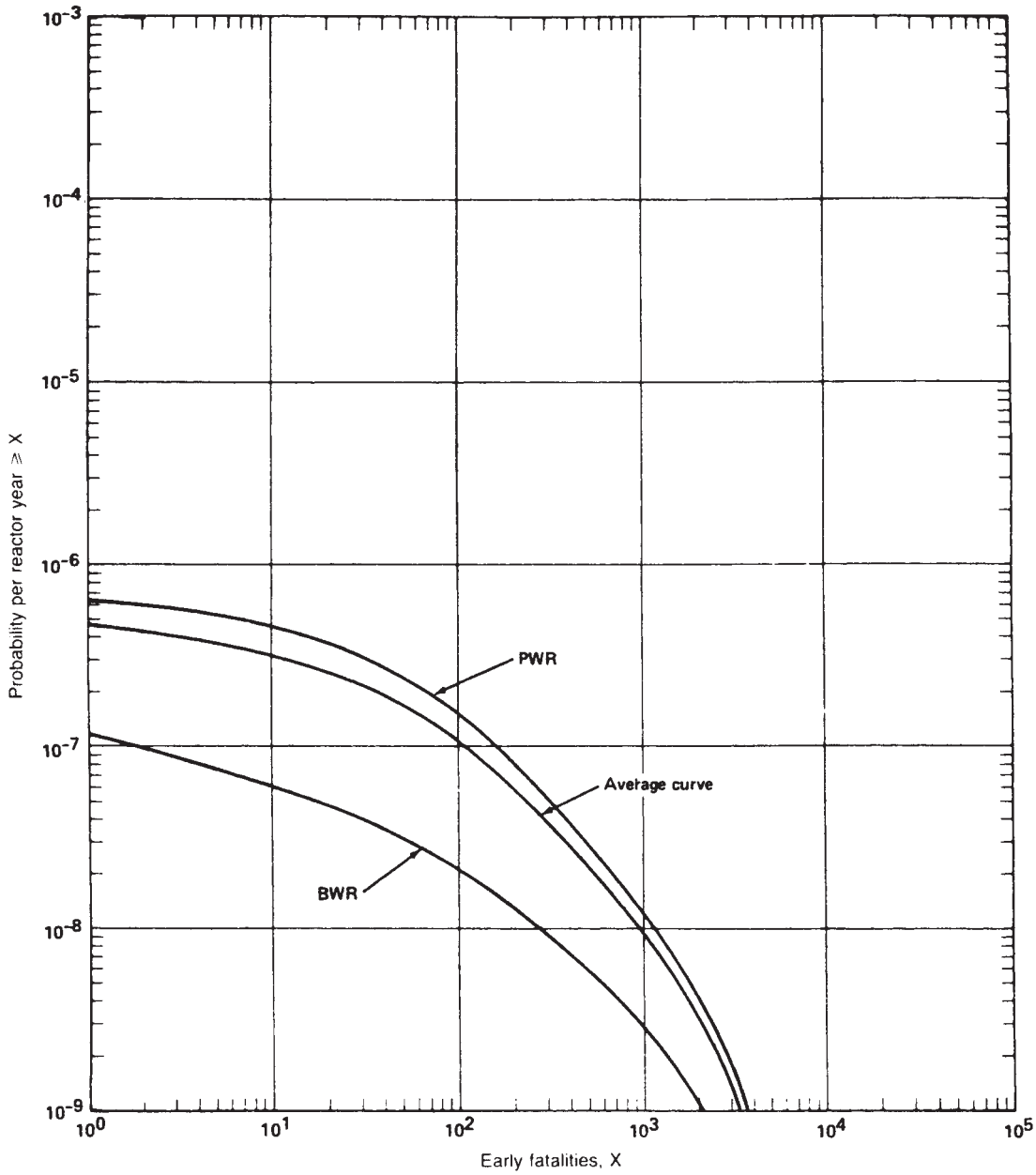

Figure A23.3 *Reactor Safety Study: FN curve for early fatalities for one reactor (Nuclear Regulatory Commission, 1975)*

medical facilities exist to handle large numbers of injured;
and also
sabotage is not considered.

A23.19 Critiques

The *RSS* has been the subject of much comment and criticism. Three principal critiques are the comments included as Appendix XI of the report itself, the *Risk Assessment Review Group Report* (H.K. Lewis, 1978) and *The Risks of Nuclear Power Reactors* by the Union of Concerned Scientists (UCS) (1977).

There are also reviews by the EPA (1976) and the American Nuclear Society (1980) and a series of reports by the Electric Power Research Institute (EPRI) (EPRI, 1975; Leverenz and Erdmann, 1975, 1979; Erdmann *et al.*, 1977).

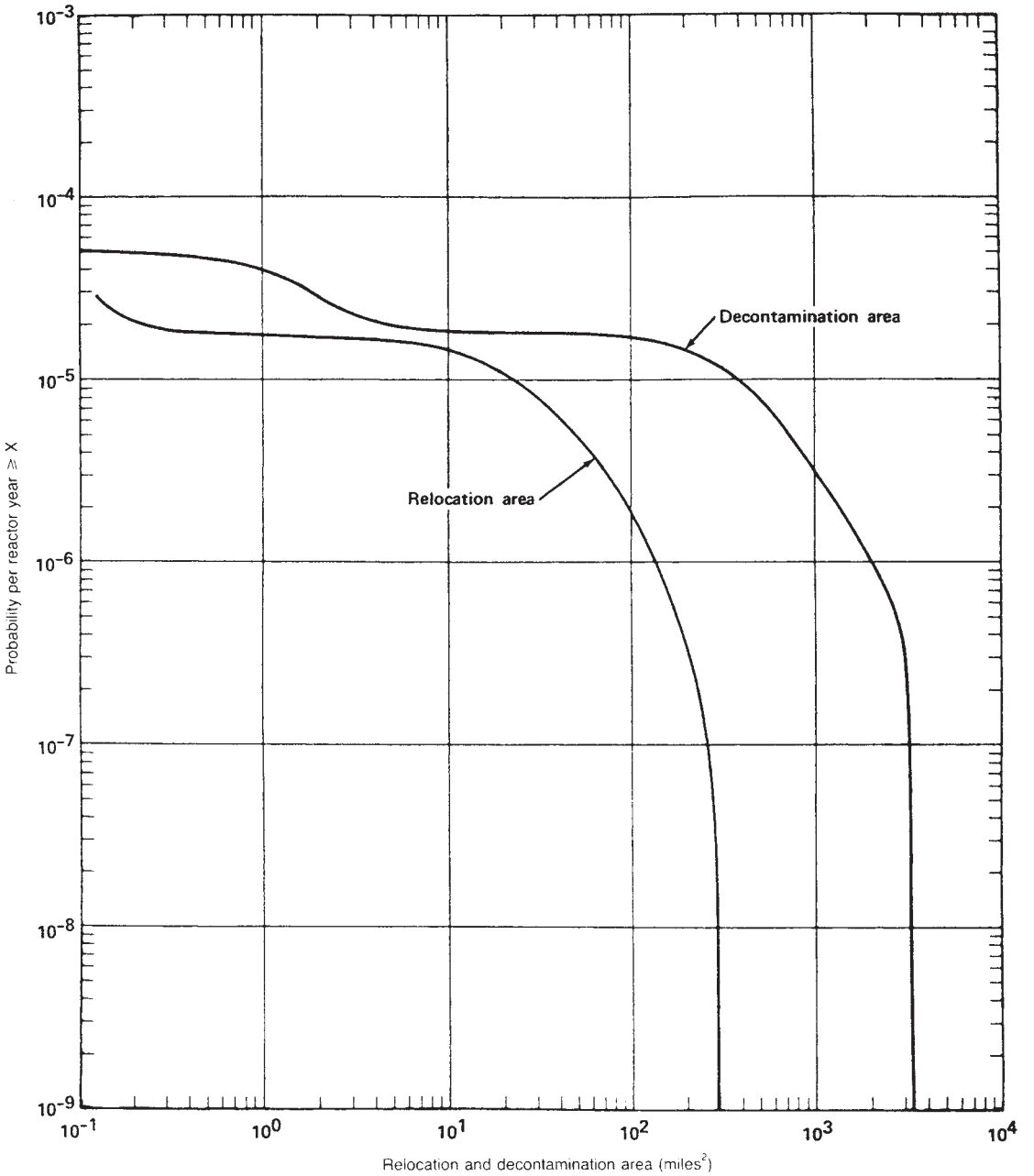

Figure A23.4 *Reactor Safety Study: frequency–consequence curve for areas requiring relocation and decontamination for one reactor (Nuclear Regulatory Commission, 1975)*

Some of the principal topics addressed in the critiques are indicated in Table A23.11.

Some of the comments made in the *Review Group Report* and the UCS review are now described.

A23.19.1 Review Group Report

The review found the *RSS* 'inscrutable'. It was difficult to follow the detailed thread of any calculation and difficult therefore to carry out a peer review.

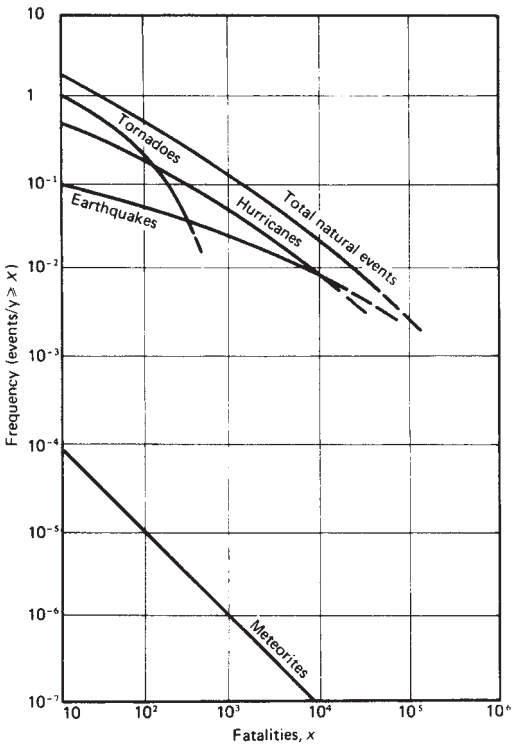

Figure A23.5 *Reactor Safety Study: FN curves for early fatalities for 100 reactors compared with natural hazards (Nuclear Regulatory Commission, 1975)*

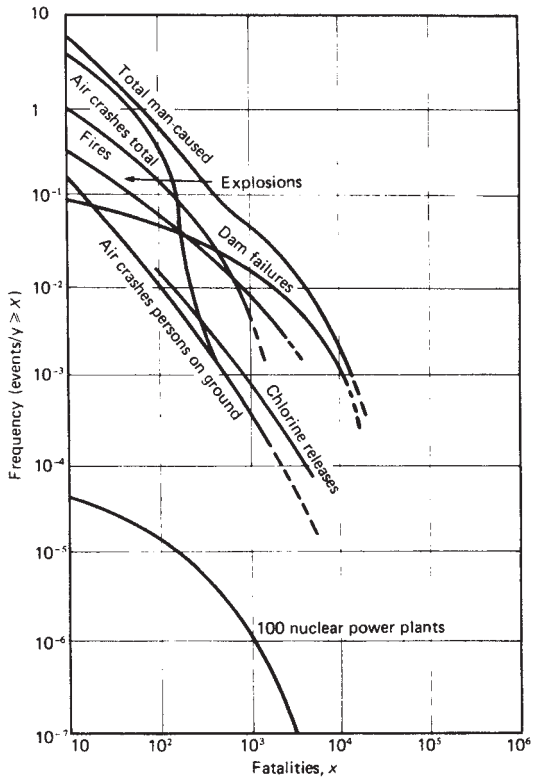

Figure A23.6 *Reactor Safety Study. FN curves for early fatalities for 100 reactors compared with man-made hazards (Nuclear Regulatory Commission, 1975). Note: car accidents caused at the time of the report about 50,000 deaths per year in the United states. These fatalities are not shown because data for large multiple-fatality accidents are not available*

The group was also critical of the Executive Summary which they felt did not give a good summary of the findings of the Main Report and was thus misleading.

The review is nevertheless sympathetic in principle to the attempt to quantify the frequency of events using fault tree and event tree methods and the consequences using hazard and injury models.

It states that it is incorrect to say that the use of fault trees and event trees is fundamentally flawed: it is just an implementation of logic.

On the other hand the practical application of the methodology involves various difficulties, including the availability of data, the statistical treatment of the data and the selection of appropriate models.

The group draws attention to the fact that the methodology is based on converting situations which are essentially continuous into discrete events and that this involves quite drastic simplification.

It is suggested that the problem of data is such that in some areas it is not appropriate to give absolute risk values but only bounding values.

The report criticizes the study for not always distinguishing clearly between different sources of values quoted: historical data, subjective judgements and models.

The review is sympathetic in principle to the use of values determined from expert judgement. Such judgements can be rather accurate as studies of betting demonstrate. It is necessary, however, to stay within the domain of experience of the expert and not require him to make estimates of events of which he has no experience.

The log–normal distribution is used to fit much of the data. The group are somewhat critical of some of the fits obtained, particularly for sparse data, but they accept the use of this distribution. With regard to the use of the median rather than the mean of this distribution, they state that this is more a matter of presentation than of substance and caused people to infer incorrectly that the study was predicting a lower failure rate than it actually did.

They are much more critical of the use made of the geometric mean, or square root bounding, and quote as an example the estimation of the probability p of failure of three adjacent BWR control rods. This probability is calculated as described above using Equation A23.6.1, where the values of the bound probabilities are the following functions of the failure probability p_x ($=10^{-4}$) of a single rod

$$p_i = p_x^3 = 10^{-12}$$

$$p_u = 0.01 p_x = 10^{-6}$$

so that

$$p = 10^{-9}$$

An alternative model is the arithmetic mean which gives

$$p = 10^{-6}$$

There is thus a large difference.

The review devotes considerable attention to the problem of common mode failures. Such failures can cause individual equipment failures, can compromise redundant systems and can activate low probability accident sequences. The principal causes of such failure listed by the group are power supply failure, human error and external threats such as fire, explosion, earthquake and sabotage. They were unconvinced that the problem had been fully dealt with in the study and suggest that the best way to handle such events is to mount a defence against them at the start and so eliminate their effects.

It is suggested in the report that the treatment of earthquakes is inadequate. Attention is drawn to the work of Hsieh and Okrent (1976) showing that design and construction errors can greatly reduce the safety factors thought to be present in a design.

Another problem discussed at some length in the review is human factors and human error. The report expresses some disappointment that there were few comments on the human factors aspects of the study. Human factors affect the study in that human error can initiate an accident, can disable protective systems and can cause escalation, while on the other hand human action can mitigate an accident situation. The report recognizes that the human factors aspects of the study represent pioneering work and were well executed, but draws attention to the lack of data. The main thrust of the group's comments, however, is to the effect that the study probably gives too little credit for the effectiveness of human action in averting an accident.

The group identified various sources of uncertainty in the work, some biased towards conservatism and some to nonconservatism. Among the former factors were pervasive regulatory influence towards the use of certain parameter values and reluctance to claim full credit for effective human adaptability during accidents. Among the latter factors were questions of completeness and common-cause failure. They were therefore unable to determine whether the accident frequencies estimated were high or low, but were convinced that the error bounds had been greatly underestimated.

The report discusses the problem of the completeness of the identification of the hazards. The probability of core melt predicted in the study is two orders of magnitude less than the upper bound value which may be estimated from the number of melt-free reactor years accumulated. The report suggests that if there are unidentified accident sequences which can lead to core melt, some precursor events in these sequences should probably be occurring, although they may remain unrecognized. They suggest it is important to subject potentially significant sequences and precursors, as they occur, to the kind of analysis given in the study.

The report suggests that the results of the study cannot be applied directly to particular reactor sites. Application to a specific site would require more detailed study of the site characteristics such as topology and meteorology.

The report gives an account of the Brown's Ferry incident.

A23.19.2 Union of Concerned Scientists report

The review of the *RSS* by the UCS is more critical.

In the view of the UCS publicly available documents on the study suggest that it was not sufficiently independent of the nuclear industry, that its results were largely predetermined, that critical reviews were suppressed and that certain sensitive issues were avoided.

The report starts with a fundamental critique of the basic methodology. It reviews experience of fault tree analysis in the aerospace industry. It quotes as an example the use of the technique to estimate the reliability of the Apollo Service Propulsion System or SPS engine. One of the authors of the UCS report, W.M. Bryan, was in charge of reliability assessment during the testing of this engine. The estimated failure probability of the engine based on fault tree analysis was 10^{-4} while that estimated after testing was 4×10^{-3} so that the theoretical analysis gave an underestimate by a factor of 40.

The authors state that fault tree analysis for Apollo also failed to assure completeness of hazard identification. Many failures in the programme resulted from events which had not been identified as 'credible' and came as complete surprises. Some 20% of ground test failures and more than 35% of in-flight failures were not identified as credible prior to their occurrence.

The report states

> Fault trees, mathematical models and event trees were developed over 20 years ago and were [later] discarded . . . by NASA and . . . by the AEC as viable tools for estimating reliability/safety quantitative values.

It lists as techniques which are used probabilistic design analysis, propagation of error techniques, reliability estimation from small samples, malfunction simulation models and others.

The methodology used in the study is to synthesize accident sequences from failure data for single items. The UCS suggest that this approach fails to utilize information which is available on multiple failure accident sequences which have actually happened.

The review draws attention to the database used in the *RSS*, which was described above. The average age of the plants used in the study was 4 years. Two difficulties which arise from this are that often data collection was not well established and that failures due to ageing would scarcely have begun to appear.

The UCS criticize the assumption of random failure and suggest that failure rates may be significantly affected by ageing.

Attention is drawn to the danger of using historical failure data. The example is cited of the Skybolt rocket motor. A minor modification was made to the welding procedure for this motor. This resulted in flaws which were not revealed by quality assurance procedures but which caused the unit to explode under pressure and led to mission failures of the first two operationally launched vehicles.

An example is given where the study may have underestimated failure probabilities. For the High Pressure Coolant System (HPCS) the study uses a failure probability of 7.8×10^{-3} per demand. The report quotes data for four

reactors in which there were 10 failures in 47 tests, a failure probability of 0.21.

Such instances also suggest that at some plants standards may be generally lower and the probability of an accident correspondingly higher, perhaps by an appreciable factor.

The report is critical of the use made in the study of the lognormal distribution to express the uncertainty in failure rate data. It suggests that it is not at all clear that this is the correct choice.

The report quotes the following comments by Yellin (1976):

The basic fault tree model therefore begins from estimates of the logarithms of the component failure probabilities, rather than from the probabilities themselves. In view of this use of the log–normal input distributions, one should also evaluate the accuracy of roughly 10–20% in their estimates of these output logarithms of failure probabilities, while it is suggested here that the evidence presented in *WASH-1400* is in fact consistent with uncertainties of order 50%. This difference of opinion is crucial, since for a typical failure probability of 10^{-6}, an accuracy of 10–20% results in an overall uncertainty factor of 10 in probability, while an accuracy of 50% results in an overall uncertainty factor of 1000.

The use of the median instead of the mean of the lognormal distribution is also criticized as incorrect. The former is some 2.5 times less than the latter. The authors believe that its use results in the study in underestimation of the risks by this factor.

The assumption of independence of events is criticized by the report, which devotes considerable space to the problem of common mode failures.

The report suggests that the *RSS* underestimates the importance of failures which occur in accident sequences as the result of previous failures and also of failures due to incorrect design.

The *RSS* found that common-cause failures do not make a significant contribution to the overall risk, but the UCS suggest that this contribution may have been underestimated. The example given is the miscalibration of four instruments in turn. The probability p of miscalibration of a single instrument is given in the study as 3×10^{-3}. For dependent failures of this kind the overall probability p of failure would be calculated using the study methodology as the geometric mean of the case for four independent failures and for tight coupling between failures. For the latter case, which gives the upper bound, the probability p_u is

$$p_u = 3 \times 10^{-3} \times 10^{-1} \times 1 \times 1 = 3 \times 10^{-4}$$

The last three terms are based on tight coupling. Then, the estimated probability p is

$$p = \left[(3 \times 10^{-3})^4 \times 3 \times 10^{-4}\right]^{1/2} \approx 2 \times 10^{-7}$$

Thus, the estimated ratio of the probability of the common-cause failure (2×10^{-7}) to the probability of the single failure (3×10^{-3}) is approximately 10^{-4}. The UCS compare this figure with their own estimate obtained by examining the common-cause failures in the *RSS* database. Out of 303 failures 33 are identified as common-cause. They take three of these failures as common-cause multiple miscalibration failures and thus obtain an estimate of 10^{-2} for the probability ratio referred to. This differs from the *RSS* estimate by a factor of 100.

The review gives the following breakdown of the 33 common-cause failures in the *RSS*

Failure	*No. of failures*
Drift of instruments, etc.	4
Miscalibration of instruments, etc.	5
Design error	6
Component failure	9
Environmental effects	6
Human error	2
Unknown	1
Total	33

The review refers to an incident on the Oak Ridge Research Reactor where the reactor had to be operated for 5 h without emergency cooling protection due to seven sequential common mode failures, each involving three parallel elements, making a total of 21 failures in all.

The review also considers what it calls common event failure which may lead to common mode failures. These events include fire, turbine missiles, earthquakes and sabotage. The UCS give an alternative analysis of the probability of core meltdown in the Brown's Ferry fire based on the relief valve failures and obtains a value of 0.03 instead of the *RSS* value of 0.003.

The review draws attention to the problem of design adequacy. The equipment may be reliable in the sense that it functions, but it may not be capable of fulfilling its task. For the Emergency Core Cooling System (ECCS) the *RSS* assigned a probability of failure on demand of less than 0.1. The UCS argue that ECCS systems have not been tested under accident conditions and may well lack the basic capability and thus have a higher failure probability.

Also, in the context of design adequacy the UCS take issue with the value used in the *RSS* for the failure frequency of the reactor pressure vessel. The *RSS* used a figure of 10^{-7} per year. The UCS argue that for non-nuclear pressure vessels the failure frequency is approximately 10^{-5} per year and that there is no justification for using a value 100 times less. They base their argument partly on the fact that the failure rates of components in nuclear plants are not greatly different from those in non-nuclear plants. They quote Professor Rasmussen

> Probably one of the most serious issues that the [nuclear power plant] intervenors can raise today, with good statistics to back their case, is that nuclear power plants have not performed with the degree of reliability we would expect from machines built with the care and attention to safety and reliability that we have so often claimed.

The UCS also refer to comments made by Sir Alan Cottrell, formerly Chief Scientific Adviser to the British Government, emphasizing the problem of dealing with deterioration of the vessel in a situation where, being radioactive, it is extremely difficult to replace. The UCS review includes an appendix by Cottrell on reactor pressure vessel integrity.

They also quote the following qualifications given in the *Marshall Report* with respect to such reactor pressure vessels:

> That it is essential to confine the operational transients to unusually narrow limits in order to avoid excessive crack growth by metal fatigue.

That emergency core cooling water should be injected at an unusually high temperature in order to minimize the risk of fracture by thermal shock.

The UCS list a number of safety issues which are addressed inadequately or not at all in the *RSS*. These include the hazards of loss of containment through electrical penetration seals, of earthquakes and of sabotage as well as the ageing problem already mentioned.

The UCS consider that the *RSS* dismisses too readily the risk from earthquakes. They give a number of quotations on the inability of seismologists to predict earthquakes. Thus, C.R. Allen (1967) states:

> Almost every large earthquake that has occurred in California has proved to be surprising in terms of what would have been expected by geologists, seismologists, and engineers at the time.

and Greensfelder (1971) states:

> Thus the San Fernando earthquake occurred in an area which has had relatively low seismicity and was not caused by movement on a major, historically active fault, such as the San Andreas or one of its branches. In fact, portions of the fault associated with this shock were not previously mapped . . .

The UCS argue that at the least the earthquake hazard introduces a much larger uncertainty than the *RSS* allows. The review includes an appendix on the earthquake hazards at the Diabolo Canyon nuclear reactor site.

On sabotage the UCS argue that it is indeed difficult to quantify but that it is a relevant factor in considering nuclear safety. They draw attention to the fact that the saboteur may be able to deliberately defeat many of the factors which normally operate to mitigate an accident.

The review makes a number of criticisms of the gas dispersion model, of the models of population exposure and of the relations for injury from radioactivity.

The UCS are doubtful about credit claimed for evacuation. Among their reasons are lack of emergency plans and failures in specific emergencies. They quote the failure to evacuate at Browns Ferry.

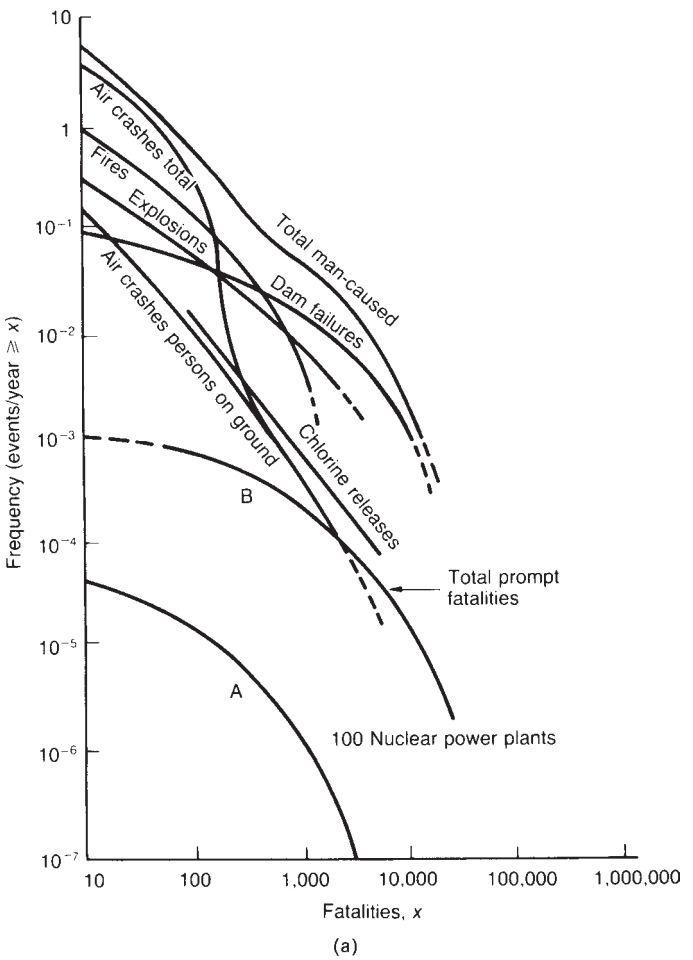

Figure A23.7 *Reactor Safety Study: Alternative FN curves for fatalities for 100 reactors proposed by the Union of Concerned Scientists (UCS, 1977): (a) early deaths and (b) total deaths. Curve A is that for early deaths given in the original study, curve B the proposed alternative*

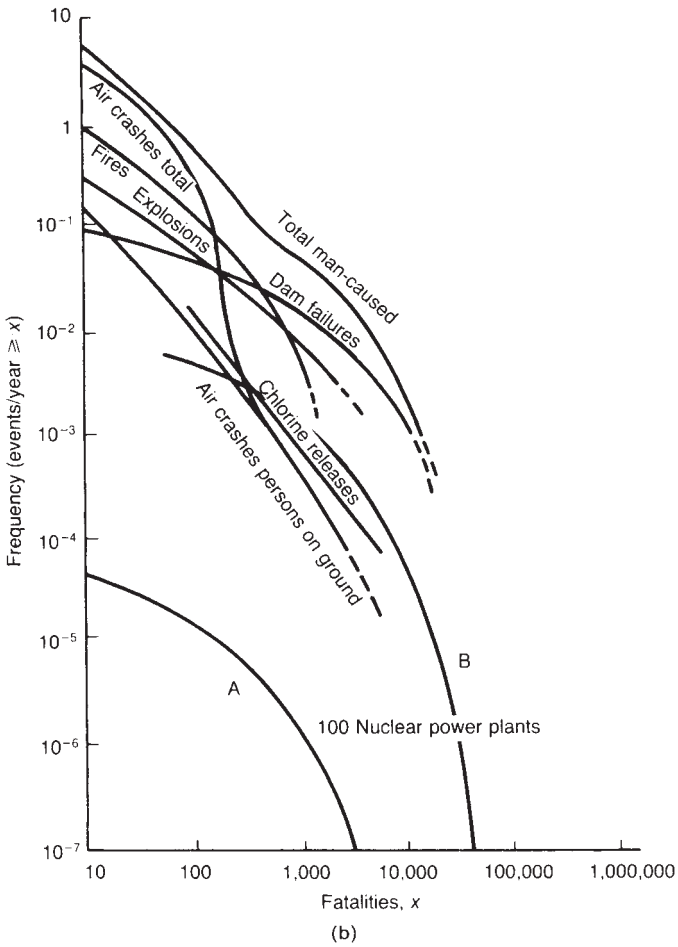

Figure A23.7 *continued*

A number of criticisms are made by the UCS of the handling of the results from the *RSS*. One criticism centres on the tendency to present the results simply as showing the risks of nuclear power to be very low and to play down the qualification and the uncertainties. Another is that the way the study was handled did not allow an effective process of peer review.

The large changes made between the draft and final reports also attract criticism. In some cases these changes exceeded the uncertainty bounds given in the draft report.

The Executive Summary is criticized as overoptimistic and misleading.

The UCS conclude that the *RSS* is not usable for policy decisions.

The review gives an alternative statement of the risks, the differences being partly of substance and partly of presentation. The UCS estimate of the frequency of a major release is 1 in 10,000 per reactor year, which is 20 times that of the *RSS*. The upper bound based on the number of incident-free reactor years was 1 in 300. The estimate of the consequences of such a release is that the early fatalities and injuries would be 10 times greater than in the *RSS*. In individual cases the consequences might be 100 or 1000 fold worse than the *RSS* predicts. The UCS estimate of the FN curve for early deaths is shown in Figure 23.7(a). The UCS also estimate that the late deaths are underestimated in the*RSS* by a factor of 2–5 and further argue that the FN curve should show the total deaths. Figure A23.7(b) shows the curve which they give for this.

A23.20 Notation

p	probability of failure
Subscripts	
l	lower bound
u	upper bound

Appendix 24

ACMH Model Licence Conditions

Contents

A24.1 Model Conditions for a Possible Licensing Scheme for Selected High Hazard Notifiable Installations A24/2

The Second Report of the Advisory Committee on Major Hazards (Harvey, 1979b) presents in an appendix a set of model controls for a major hazard installation in the form of 'Model Conditions for a Possible Licensing Scheme for Selected High Hazard Notifiable Installations', although the report leaves open the question of whether the use of licensing or regulations is the best method of implementing such controls. The appendix is prefaced by the statement:

> 'The conditions outlined in this appendix have been written to give guidance as to the range and scope of the requirements that might be required if a licensing scheme of control were adopted for major hazard installations with the highest hazard potential. . . . The Committee is not yet in a position to say if certain installations should be regulated in this way until more information is available, particularly from the proposed Hazardous Installations (Notification and Survey) Regulations. It is, however, clear that there is a gradation of hazard with size and complexity of plant, and as this is increased there should be a greater degree of control and surveillance by the organisation in control of such activities. Thus this appendix has a wider application than the possible requirements for a licensing system of control. It is recommended that any organisation operating a major hazard plant, particularly one at the highest level of hazard potential, should review and satisfy itself that it could demonstrate that the requirements given below are adequately met.'

The full text, which is reproduced by courtesy of the Health and Safety Executive (HSE) and HM Stationery Office is given below.

A24.1 Model Conditions for a Possible Licensing Scheme for Selected High Hazard Notifiable Installations

With regard to a possible licensing system it is recognized that a licence is the most stringent form of control under the Major Hazards arrangements and would be applied only to those Notifiable Installations which present the greatest hazard potential. The licence would be granted to the organization which operates the installation and would be valid only for the specified location.

The approach adopted to licensing would be that foreshadowed by the Robens Committee and embodied in the Health and Safety at Work etc. Act 1974, namely that safety is the responsibility of the organization which should demonstrate that it is taking appropriate measures to ensure effective control of the hazards.

The licensing procedure might be in two stages. At the first stage, the organization would provide the HSE with a statement of intent covering the nature of the proposed installation, the hazards and the features of the design and operation intended to control the hazards. At the second stage, the organization would provide HSE with design and operating information to show how the statement of intent is implemented.

The documentation required might be in two parts corresponding to these two stages and consist of:

Part 1
(1) The Systems Documentation;
(2) The Preliminary Design Document.

Part 2
(1) The Background Documentation;
(2) The Design Document;
(3) The Operating Document.

The Systems Documentation, which is relevant to Licence Conditions 1–9, would be concerned with the general systems which the organization has set up to ensure safety and could be used in support of more than one licence application provided that it is up-to-date.

Details of the Preliminary Design Document are given in Licence Condition 10.

The purpose of the Preliminary Design Document would be to show the general nature of the installation and of any associated hazards. The onus would be on the organization to draw attention at this stage to any special features which might have an important bearing on the granting of a licence.

The Background Document would be documentation on the implementation of Licence Conditions 1–9, in relation to the particular installation.

Details of the main Design Document and the main Operating Document are given in Licence Condition 10.

The main Design Document would be essentially a more up-to-date and detailed version of the Preliminary Design Document, including additional details, such as materials of construction for the main plant items.

The main Operating Document, which incorporates the Operating Manual, would give details of the personnel structure for the operation of the installation.

A licence would be granted for a particular installation on a given site. The licence would not itself deal with questions of siting, but the issue of a licence is an indication that an installation meets certain standards and this is relevant to siting considerations.

The licensee would be required to inform HSE of significant changes which are proposed in any of the matters within the scope of the licence.

A24.1.1 Conditions for a licence

The conditions for the issue of a licence are that the licensee shall demonstrate to the HSE that the design, construction, operation, maintenance and modification of his installation are or will be to the standard appropriate to the installation and in particular that the following features of his organization are to such a standard:

(1) The management system;
(2) The safety system;
(3) The responsible persons;
(4) The arrangement for the identification of hazards;
(5) The arrangements for the assessment of hazards;
(6) The arrangements for the design and operation of pressure systems;
(7) The arrangements for the minimization of exposure of personnel;
(8) The arrangements for the administration of emergencies;
(9) The arrangements for reporting of and learning from incidents;
(10) The design and operating documentation.

A24.1.1.1 Licence Condition: The management system

The organization should show that it has and supports a management system and staff structure which combine to ensure continuing effective control of the installation and its hazards.

The staff concerned include contractors and consultants. This aspect is considered further in Licence Condition 3.

The organization should show the management structure, making clear the distinction between executive and advisory functions, and should give a brief job description for each post.

The management system should give full support to the personnel who are responsible for the design and operation of the installation. Important elements include a suitable and well understood management structure; adequate human resources including coverage of absences, vacancies and emergency situations; recruitment, training and career planning; and effective communications.

The management system should in particular provide satisfactory arrangements in the areas which are the subject of Licence Conditions 2–9. There should be comprehensive, formal and documented set of systems and procedures.

The management should define the objectives of its system of documentation in respect of immediate a communication and of record-keeping and should specify the extent of the documentation required and the procedures for producing it.

The management system should provide for thorough initial and continuing training of personnel in their work generally and in safety in particular.

Full use should be made of appropriate standards and codes of practice. Where there are standards or codes which have statutory backing or which are commonly recognized within the United Kingdom as constituting sound practice, these should be applied as a minimum. Where there are no approved or accepted standards or codes the situation should be covered by the adoption of sound practice and the use of in-house codes.

The management system should include formal procedures for the control of modifications made to the plant or to the process, whether during design or during operation.

The management system should require the independent assessment of features which are critical to the safe operation of the installation. This independent check is essential for inspection of pressure systems and for reliability assessment of instrument trip systems. The guiding principle is that the feature is critical to safe operation of the installation. It is acceptable that the check be done by an in-house authority provided that this is genuinely independent of the interested party. Thus pressure system inspection, for example, must be done by an authority independent of the operating authority, as described by Licence Condition 6.

The management system should contain a variety of arrangements for the periodic audit both of the continuing appropriateness of systems and of the continuing effectiveness of their implementation.

Background It is considered that in the case of major hazard installations the control of the plant and its hazards requires a considerable degree of formalization of communications through written systems and procedures, standards and codes of practice. This is essentially to encourage, and where appropriate enforce, collective and personal discipline by the use of operating methods which have been carefully thought out and which contain an appropriate level of checks and counterchecks to obviate problems and reduce errors.

It is recognized that there is always the problem of over-administration through paperwork and what at times seems like 'going through the motions' without apparently contributing anything useful. However, it is considered that a careful review of incidents will, time and again, illustrate that there was a loss in discipline because appropriate procedures either did not exist or were not observed.

There should be an interlocking set of systems and procedures to ensure safety through sound engineering and management practices. There is no upper limit to the number of procedures which can be formalized, but there is nothing to be gained by deliberately trying to maximize the number. The optimum number is that which leaves no obvious gaps but avoids creating confusion by overlapping.

Many of the required procedures are implicit in the various Licence Conditions which follow. It is evident that key procedures include those for the identification of hazards, the assessment of hazards, the control of maintenance through permits-to-work, the control of modifications to process or plant, the inspection of equipment, the operation of the process (normal and emergency), the control of access, the conduct of safety audits and the reporting of incidents.

Self-auditing features should be built into the management system in the form of formal instructions for periodic checks on those parts of the system which may become degraded or unnoticed. The operation of a permit-to-work system, for example, should be subjected to regular audit by some means such as an instruction, not merely an exhortation, to the plant manager to sample a proportion of permits each week.

A24.1.1.2 Licence Condition: The safety system

The organization should show that within the management system there is a safety system which is appropriate to the level of hazard inherent in the installation.

The safety system should in particular provide for satisfactory arrangements in the areas of the safety organization, safety objectives and assessment, safety consultative committees, and safety training.

The organization should show that it has people competent to operate the safety system.

Background Most of the aspects of the safety system mentioned are already legal requirements, but it is the object of this section to review their adequacy in relation to the major hazard installation.

A distinction can be drawn between the technological and human sides of safety. On a major hazard plant the technological features are obviously particularly important. The responsibility for these aspects rests primarily with the qualified technical staff in the design and operations areas. There should be no neglect, however, of the human side. On the contrary, on a major hazard plant it is more important than ever to run a 'tight ship' as far as safety is concerned.

The authority of the safety staff should be made clear, particularly in relation to the more technical aspects of the installation. Attention should be paid to the means of ensuring that the safety officers/advisers are effective and are seen to be so.

The safety objectives set for management and the assessment of the performance in meeting these objectives should be indicated. This may not be a simple matter of accident statistics. For major hazard installations there is an additional problem of avoiding rare but catastrophic events. This makes it important to monitor both the occurrence of 'near misses' and the degree of adherence to procedures and rules.

The programme of safety training provided for employees at all levels should be outlined.

Attention is also drawn to Licence Condition 9 which is concerned with the system of reporting of and learning from incidents.

A24.1.3 Licence Condition: The Responsible Persons

The organization should nominate Responsible Persons who are in charge of the design and operation of the installation.

The term 'Responsible Person' has a specific meaning in the context and is explained below.

The organization should show the management structure down to the lowest level of executive technical management, making clear the distinction between executive and advisory functions. There should be a job description for each post; the job descriptions for the posts held by Responsible Persons are particularly important.

The level of seniority held by the Responsible Person should normally be either the lowest or second lowest level of technical executive management.

It is envisaged that persons immediately senior to the Responsible Persons will themselves normally have been or be qualified to be a Responsible Person on major hazard installations, though not necessarily on those processes of which they are now in charge.

The organization should show that a person nominated as a Responsible Person is qualified to hold the post by reasons of his academic qualifications, practical training and recent relevant experience.

On the operations side, this experience should be experience in the operation of the actual process or of a similar process. Experience limited to design of the process or of similar processes and/or to operation of dissimilar processes is not acceptable. On the design side, the experience should be in the design of similar processes.

Where the process incorporates features of considerable technical novelty as a result of which no person has first-hand experience of operation of relevant full-scale plant even greater regard must be paid to the level of competence of the individual and normally experience of pilot plant operation would be required.

Where the installation is to be designed in part or in whole by an outside contractor it is the responsibility of the organization which will operate the installation to satisfy itself and to demonstrate to HSE that the design is to an appropriate standard. The minimum requirement is that there be a nominated Responsible Person in the operating company who has the duty of liaison with the contractor. Where practical it is also desirable to have nominated Responsible Persons in charge of design in the contracting company.

For convenience, reference is made here only to design and operation. The organization should enumerate all the project activities such as fabrication, construction, inspection, commissioning and satisfy itself and HSE that there are nominated Responsible Persons responsible for these activities.

It is emphasized that the ultimate responsibility for the safety of the installation lies with the organization which operates it.

Background The concepts of 'Responsible' and 'Authorized' Persons occur in various management systems. Our usage of these words is that 'Responsible' relates to a job, for example, plant manager, and 'Authorized' to a task, for example, signing a permit-to-work.

We have considered various models for Responsible Persons. These include those in the Mines and Quarries Act, the Merchant Shipping Act, the Factories Act (radioactive substances), the Explosives Act, the Medicines Act.

We have also considered the arrangement whereby the Department of the Environment advised by the Institution of Civil Engineers recommends individuals for the design of reservoirs.

Competence to do a job must depend on the definition of the job and its relation to other jobs. We began, therefore, with a consideration of management structures and reviewed possible general models for a large and a small firm. It became apparent, however, that this was not a particularly helpful approach and it was not pursued. However, in a concrete situation we do consider the presentation of such a management structure and job descriptions desirable.

With regard to the level of seniority we started with the proposition that the Responsible Person should be at the lowest level of the executive technical management. However, this could give rise to problems in some areas. For example, it is necessary to train for succession and by definition trainees must be at a lower level. Such additional lower levels are not normal in existing practice, would be wasteful and would not offer job satisfaction. We therefore prefer to leave a degree of flexibility. But we do attach importance to ensure that the responsibility is real rather than nominal and is at the lowest practical level.

Thus we envisage that the Responsible Person on the operations side would usually be capable of 'stepping down' and carrying out the job at the next level down.

With regard to selection of Responsible Persons we consider academic qualifications, practical training and recent relevant experience essential.

We think it is desirable that the person chosen should have the sort of broad scientific and technological education which a first degree in science or engineering usually gives. We consider that such a degree should normally be a necessary qualification. Exceptionally, however, people without a degree may be considered. We also attach importance to the ability of the person to recognize problems outside his sphere of competence and to his willingness to seek the advice of other experts.

We consider that although the Flixborough disaster has emphasized the importance of the integrity of the plant, there may be other major hazards where the integrity of the process is of at least equal importance. Thus, whilst it is probable that the Responsible Person will normally be an engineer there will be cases where he will be a scientist, for example, a chemist.

We attach particular importance to the selection of Responsible Persons on the operations side.

We lay particular emphasis on recent relevant experience. There is obviously room for discussion as to the 'relevance' of experience or the 'similarity' of processes. It is up to the organization to convince HSE on these points.

We stress, however, that we would not want this emphasis on recent relevant experience in any way to inhibit technological innovation or normal career development.

We accept that technological progress requires specialization. The professional institutions already recognize this and are considering a register of persons considered competent to design and operate major hazard installations. We are maintaining contact, although, whilst welcoming their interest, we see a number of difficulties in this approach.

The requirement to nominate Responsible Persons should not be seen as detracting in any way from the necessity for a team effort by management to achieve high standards of safety in plants which have major hazards.

A24.1.1.4 Licence Condition: The arrangements for the identification of hazards

The organization should show that it uses appropriate methods of hazard identification at all stages of the project.

The terms 'hazard identification' and 'safety audit' refer to mainly qualitative techniques which review the existence of a hazard.

The application of the techniques should be matched to the stages of the project, starting with coarse scale investigations and progressing to fine scale studies to discover detailed faults.

The management system should contain a formal requirement for the use of such methods, should specify the documentation required arising from this use and should monitor this use.

The organization should show that it has people competent to implement these methods of hazard identification.

Background The first objective of hazard identification is to reveal the substances or processes which have a hazard potential. The second objective is to identify all conceivable threats to the installation or its processes which might lead to loss of containment.

As technology has progressed identifying hazards has become in some ways more difficult. In particular, there are many hazards which are not revealed by traditional visual inspection. It has become necessary, therefore, to develop additional methods of hazard identification.

An illustrative list of methods is given in Table A24.1

Since every human enterprise involves the possibility of error it follows that the soundness of the management of the potentially hazardous installation is the predominating factor and that the first essential in all cases is an audit of the management system as a whole.

It is recognized that there is a wide variety of methods of hazard identification in use in industry and that different techniques are applicable to different situations. There is no intention of imposing any particular method.

It is necessary that the use of these methods be a requirement of the management system, which also should specify the degree of recording and documentation required and should contain a mechanism for auditing the application of the techniques to ensure that they are used.

The people who have to implement these techniques must be competent to do so. HSE should be able to advise on opportunities for training in this area.

Hazard identification covers much the same ground as safety audits in the broadest sense. The Chemical Industries Association has published two guides entitled *Safety Audits: A Guide for the Chemical Industry* (1973) and *A Guide to Hazard and Operability Studies* (1977).

Table A24.1 *Some methods of hazard identification*

Project stage	*Hazard identification method*
–	Management and safety system audits
All stages	Checklists
	Feedback for workforce
Research and development	Screening and testing for
	Chemicals (toxicity, instability, explosibility)
	Reactions (explosibility)
	Impurities
	Pilot plant
Predesign	Hazard indices
	Insurance assessments
	Hazard studies (coarse scale)
Design	Process design checks
	Unit processes
	Unit operations
	Plant equipment
	Hazard and operability studies (fine scale)
	Failure modes and effects analysis
	Fault tree and event trees
	Hazard analysis
	Realibility assessments
	Operator task analysis and operating instructions
Commissioning	Checks against design, inspection, examination, testing
	Non-destructive testing, condition monitoring
	Plant safety audits
	Emergency planning
Operation	Inspection testing
	Non-destructive testing, condition monitoring
	Plant safety audits

A24.1.1.5 Licence Condition: The arrangements for the assessment of hazards

The organization should show that the hazards identified by the means described in the preceding section have been removed or that the associated risks have been reduced to a minimal level.

In this context 'minimal' means the probability that an employee or member of the public will be killed or injured or that property will be damaged is at least as low as in good modern industrial practice.

The method of demonstrating that the risks are at a minimal level should be comprehensive and logical.

The method may consist of:

(1) the use of codes of practice generally recognized in the industry;
(2) the use of special testing;
(3) the use of calculations based on appropriate data.

In many cases it will be sufficient to show for all or at least some aspects of the hazard that a generally recognized and accepted code of practice is applicable and has been followed.

Where there is any aspect of the hazard, the risk of which cannot be reduced to a minimal level by following a recognized code of practice or by special testing, then, whenever meaningful quantitative methods should be used to demonstrate that the risk has been reduced to a minimal level. These quantitative methods will normally consist of three steps:

(1) An estimate of the consequence to employees and the public.
(2) An estimate of the frequencies with which hazardous situations will occur.

(3) Comparison of (1) and (2) with the other risks to which people are normally exposed in order to show that the risk under consideration is relatively small.

The management system should contain a formal requirement that such methods of hazard assessment should be applied.

The organization should show that it has access to people competent to implement these methods.

Background Having identified hazards, as described in the previous sections, it is necessary to know that the associated risks have been reduced to a minimal level.

It is envisaged that the method of demonstrating that the risks are at a minimal level will normally be based on a fault tree approach, but that a detailed development of all parts of the tree will not generally be required.

Sometimes it is possible to remove a hazard completely, for example, by replacing a flammable or toxic raw material by a non-flammable or non-toxic one.

More often, the hazard cannot be eliminated completely, though the risk can be reduced to any desired level by the use of protective equipment. For example, the risk that a particular vessel will burst because of overpressure can be reduced by fitting a relief valve suitable for the duty, adequately sized and properly maintained. This does not eliminate the hazard completely as there is a small probability that the relief valve will fail to lift when required. Even if two relief valves are fitted, there is still a very small probability of coincident failure.

In many cases, codes of practice provide generally recognized and accepted methods of reducing a hazard to a minimum level. For example, in the case just considered, it would normally be sufficient to show that the vessel is fitted with a relief valve, adequately sized and properly maintained, as relief valves have been generally recognized for many years as an accepted way of reducing to a minimal level the probability that a vessel will burst.

Similarly, if fracture of pipework has been identified as a hazard, it would be sufficient to show that the pipework has been designed and constructed and will be operated and maintained in accordance with a recognized and relevant code of practice.

Codes of practice should not be used outside their area of applicability. Codes of practice for pipework, for example, do not cover fracture by projectiles and if it is necessary to take the latter into account, a separate study is necessary.

Moreover, codes of practice imply acceptance of some level of probability of the hazard materializing. This level will be unacceptably high in relation to some major hazards.

In some cases, it may be necessary to carry out special tests to quantify aspects of particular hazards.

Where there is no generally accepted code of practice and where the problem cannot be resolved by testing, but where it is reasonably practicable to show quantitatively that the risk has been reduced to a minimal level, this should be done. In some cases, this cannot be done because of lack of data or of a suitable model to describe the system. In these cases, judgement will have to be used.

Examples of hazards which may not be covered by recognized codes of practice and which, if they produce major effects, would have to be individually assessed, are:

(1) runaway reactions (e.g. decomposition and polymerization reactions);
(2) impact of moving objects (e.g. cranes, vehicles, missiles from explosions);
(3) failure of instrumental protective systems;
(4) failure of services (e.g. electricity, water, compressed air).

These can be described as events leading to possible loss of containment.

The hazard quantification will normally consist of three stages in which probability and consequence must both be considered; sometimes it will be necessary to consider a number of possible outcomes differing in probability and consequence. An event which has the potential to kill many people may not cause great concern if the probability of it occurring is sufficiently small. We do not prohibit football matches because there is a small chance that an aeroplane may crash on the crowd. On the other hand, we would not build a new football ground at the end of a busy runway.

(1) The first stage is the estimation of the probable consequence of the hazard. This may be based on past experience or it may be estimated from a theoretical study of the problem. The consequences may be expressed as the probability that an employee or a member of the public will be killed or injured or as the probability that extensive damage will be caused to the property of others or both.
(2) The second stage is the estimation of the probability that the hazard will occur. Again this estimate may be based on past experience, or it may be synthesized from data on the failure rates of individual components or pieces of equipment.

In estimating the probability that the hazard will occur it is necessary to assume that certain standards are followed in the operation of the equipment, for example, that relief valves are tested regularly. If these standards are not followed the conclusions of the hazard quantification are no longer valid.

(3) The third stage is comparison of (1) and (2) with the other hazards to which people are exposed in order to ensure that the risk under consideration is minimal.

This implies the use of a criterion against which risks can be judged. It is not intended that any single criterion should cover all cases.

If it is not possible to carry out a complete study as indicated (i.e. stages 1–3), it may be possible to carry out a partial study and, if so, this should be done, as it helps to identify those aspects of the problem which have most effect on the probability and consequences.

Where a new feature is used in place of one of proven reliability then it should be shown that the new feature is at least as safe as, and preferably safer than, the original. For example, if an instrumented protective system is used in place of a relief valve it should be shown to fail no more often, and preferably less often, than a relief valve.

In other cases it may be appropriate to show that the risk to an employee is no greater than that for employees in the industry as a whole or to show that the risk to a member of the public is comparable with the other risks to which the public are exposed without their consent.

It may be noted that it is difficult to find examples of instances in which members of the public have been killed as a result of accidents on major hazard installations. In most cases, if the risk to employees is minimal the risk to

the public will also be minimal; although a lower level of risk is required, the public are usually further away.

It is necessary that the use of quantitative methods, whenever meaningful, should be a requirement of the management system. This should specify the recording and documentation required.

In some cases a detailed study may be required taking many days or even weeks, but in other cases relatively simple calculations may be sufficient.

The organization should show that it has access to, and uses as necessary, people competent to assess hazards, but these people need not be in its full-time employment; they may be consultants.

Quantitative methods provide a means to assist management to choose those measures which are 'reasonably practicable' for providing a safe plant and system of work.

A24.1.1.6 Licence Condition: The arrangements for the design and operation of pressure systems

The organization should show that it has a formal and well-understood management system for controlling and monitoring the design, fabrication, commissioning, operation, inspection and testing of pipework, vessels and other equipment together forming the constituents of a pressure system which may give rise to a serious hazard.

The term 'pressure system' refers to a linked series of equipment items operating at a pressure either above atmospheric or under vacuum, together with all the interconnecting pipework. Such systems commonly form processing units, but the definition includes also storage and handling installations.

The management system of control should be in two parts, and should be effected through two recognized channels of authorization, related to Design and to Operation.

The management design authority should identify and state the design parameters within which the pressure system is to operate and the conditions for which each component part of the pressure system shall be designed. It should also define the code under which the individual components shall be designed, or where no design code exists should cause sufficient work to be undertaken to satisfy themselves, either by experiment or by the use of specialist advisers, that the design is at least as safe under all foreseeable circumstances as the standard demanded by recognized codes.

The design authority should also define the standards to be used for the pressure system during the fabrication and construction stages. Whenever possible the standards specified should be those quoted in recognized codes applicable to the particular pressure system.

Management should ensure that an appropriate inspection system is operated during fabrication and construction work to check that the standards set by the management design authority are being met. This inspection system may be in the same management organization as the design authority, or it may be appropriate to use one of the engineering insurance companies or other approved inspection agency. The inspection system should not be part of the operating authority. The design authority should also specify the written evidence required to demonstrate that the plant has been fabricated, constructed and proof-tested, in accordance with the design requirements. Copies of documentation forming this written evidence should be verified, preferably by the inspection agency before the pressure system enters service. Copies of all documentation relating to the design parameters, and to the verification by the inspection system, should be retained by the design authority and should also be available on the works on which the pressure system is operated.

The operating authority should prepare a comprehensive set of instructions based on information issued by the design authority and upon an analysis of hazards involved. These instructions should set out clearly the way in which the pressure system shall be operated in both normal and abnormal circumstances, and the way in which the pressure system is to be protected from the effect of conditions more extreme than those permitted by the design authority. These instructions, which should be readily available to all those responsible for operation, inspection and repair of the pressure system, should set the limits within which the system is to be operated. Any variation in these limits outwith the parameters set by the design authority should be referred to the design authority or other independent qualified body for approval before fresh instructions are issued. Such submission and approval should be made in writing and copies retained in the works for future reference.

The operating authority is responsible for ensuring that any repairs and modifications are designed, fabricated and tested to a standard not less than that used by the design authority for the original system. The operating authority should have a system of documentation which controls the repair and modification procedures, so that modification to the pressure system cannot be made without written authority from an authorized person.

Thus, instructions prepared by the operating authority should include formal procedures for identifying and making process modifications, for identifying and making plant modifications and for restarting the plant after discovery of a serious defect.

The operating authority should also provide and enforce the use of a code which ensures the continuing safety of the pressure system by a regular inspection of the equipment and the safety devices which are provided to protect that equipment. Such an inspection code should meet the following criteria. First, that a register is held on each works in which each item of equipment is given a unique designation and an engineering description which adequately describes the design and fabrication details and also details of operating conditions, both normal and maximum. Secondly, that the code should specify the frequency of inspection for the various classes of equipment and should also specify rules concerning the selection and training of inspectors. There should also be rules by which inspection frequencies may be increased or reduced, decisions being based upon the result of inspection records which should be held in the register. The code should specify rules which guarantee the independence of the inspecting system from the operating authority, either by appointing external inspection authorities, or by making satisfactory arrangements for the in-house inspection authority to be responsible to a senior member of the organization who has the design authority within his charge.

The organization should show that it has people competent to execute the control and monitoring functions described above in both the design authority and operating authority areas. It should also show that the inspection service is truly independent of the operating authority.

Background The control of design and operation of pressure systems is a cardinal feature for ensuring safe operation of major hazard plants.

The separation of management control into the areas of a design authority and an operating authority has been made in order to bring out clearly the separate responsibilities of these two parts of the total organization which designs, builds and operates a major hazard plant. The areas of authority interlock, and in small organizations there may be sharing of some specialist personnel. It is important, however, that the design concept and subsequent modifications to that concept should be controlled by an authority separate from the operating authority. In cases of contractor design, the organization will have to show that the contractor can carry out the duties of a design authority, particularly in the matter of documentation concerning the design parameters for the pressure system and the fabrication details, and in the provision of competent people for authorization.

The use of a regular inspection is an essential feature of the safe continued operation of a pressure system. The register of equipment and inspection reports is the linchpin around which this inspection system is built. Decisions on the frequency of inspection and the nature of satisfactory inspection procedures should be taken by the inspecting authority with advice from the design authority. An essential feature of the integrity of the system is that the inspectors and their management are not under the technical control of the operating authority. In small organizations, considerable use can be made of external inspection agencies and other specialist help. In large organizations, such facilities are likely to be provided in-house. In those cases the organization should take particular care to show the independence of the inspection agency.

It is important that safety devices such as relief valves, non-return valves and vents are included in the register of pressure systems and are subject to the same type of inspection and testing arrangements as are specified for the pressure equipment. Details of testing and frequency of examination may well be different from arrangements made for pressure equipment, but the principle of inclusion in a register, together with test and inspection notes, is essential.

A system for registering and inspecting pressure vessels and other equipment and for the keeping of verification documentation which satisfies many of these criteria is described in BS 5500: 1976 Unfired fusion welded pressure vessels, in the Pressure Vessel Inspection Code and in the draft Piping Systems Inspection Code of the Institute of Petroleum.

A24.1.1.7 Licence Condition: The arrangement for minimization of exposure of personnel

The organization should show that it has assessed the hazards to personnel involved in the installation and that where necessary it has taken steps to reduce these hazards to a minimal level. In particular, measures should be taken to limit the number of people at any one time in areas of high hazard to a minimum consistent with safe and efficient operation and to afford protection to exposed personnel, who may include operating personnel, maintenance personnel, investigation teams, construction workers and visitors.

Background This matter is fully dealt with in chapter 7 of this report.

A24.1.1.8 Licence Condition: The arrangements for the administration of emergencies

The organization should show that it has assessed the hazards involved in the installation in relation to major emergencies and has maintained emergency plans.

Emergency planning should include identification and assessment of possible major emergencies; nomination of persons responsible for administering an emergency; development of procedures for declaring, communicating and controlling the emergency and for evacuation; provision of buildings such as a control centre or refuge rooms and of equipment such as an alarm system; designation of works emergency teams and definition of duties of other workers; liaison with external services including police, fire and medical services; training and exercises for emergencies.

Background A guide *Recommended Procedures for Handling Major Emergencies* is published by the Chemical Industries Association (second edition, 1976). This covers primarily the administration of emergencies within the works.

The guide also deals briefly with the planning of action, such as evacuation, which may be required outside the works. This is particularly important for certain major hazards. It should be emphasized in this connection that for toxic gas hazards the value of the time bought by any distance separating the factory and the public may be wasted if there is no evacuation plan.

A24.1.1.9 Licence Condition: The arrangements for reporting of and learning from incidents

The organization should show that it has prepared a schedule of signals to be recorded and that the relevant instruments are housed in such a way that an accident on the plant is unlikely to prevent recovery of the records.

The organization should show that it has a system for the reporting of incidents which might endanger the installation or lead to loss of containment and that it uses the information obtained from this reporting system to learn how to reduce these hazards.

These requirements for the reporting of hazardous incidents are additional to the existing statutory requirements. They have two main objectives. One is to ensure the reporting within the company of the 'near miss' type of incidents which often precede an accident. The other is to obtain data at national level on incidents related to serious hazards. HSE may request that certain types of incident be included.

Background There already exist certain statutory requirements for the reporting of incidents. These include:

(1) The Petroleum (Consolidation) Act 1928;
(2) The Factories Act 1961;
(3) The Dangerous Occurrences (Notification) Regulations 1947;

as well as those specific to explosives factories, mines and quarries, and nuclear installations.

These requirements are mainly concerned with accidents causing plant downtime, lost-time accidents and fatalities.

It is well-known, however, that for every serious accident there are numerous incidents, including 'near misses'. Since they are more numerous, these incidents offer greater scope for learning and improvement.

It is therefore proposed that the organization should have its own reporting system covering the type of incident significant in relation to its particular hazards.

We have deliberately not specified the incidents which should be reported but we have in mind incidents relating to such matters as:

(1) incidents involving serious operator error;
(2) incidents involving trip system malfunction or disarming;
(3) malfunctions of valves, for example, pressure relief, non-return;
(4) leaks of flammable materials;
(5) leaks of toxic materials;
(6) leaks and fires at pumps;
(7) fires and explosions in furnaces;
(8) storage tank collapse.

The important point is that the reporting system should be tailored to the needs of the organization.

There may also be certain types of incident on which HSE wish to collect information nationally. In this case it may request their inclusion in the reporting scheme. Again we have not specified these incidents but an obvious one is the unconfined vapour cloud explosion.

These reporting requirements should be seen in relation to the fact that we have not recommended that all major hazard installations have a 'black box' recording instrument system. We consider that the arrangements proposed here are a more efficient way of learning both at company and national level.

The reporting system is intended primarily to assist the organization to learn from incidents and it should show that it has formal arrangements to do this.

A24.1.1.10 Licence Condition: the design and operating documentation

The organization should provide full documentation on the design and operation of the installation. The documentation required is as follows:

Part 1 Documentation
(For Part 1(a) The System Documentation see Introductory Section of this appendix.)

Part 2(b) Preliminary Design Document This should contain:

(1) A brief description of the process and should include the nature of any chemical reaction involved and the various operations to which the material in process is subjected. In addition, any other exothermic reactions which may arise if operating conditions fall outside the design values, should be specified.
(2) A comprehensive description of the nature of the hazards in the materials handled (toxic, flammable, explosive materials), of the objectives to be achieved in order to limit these hazards and of the methods in plant design and operation necessary to achieve these objectives.
(3) A statement of any less hazardous process which could have been used and the reasons for selecting the particular process in question. This might include outstanding economic advantages, factors relating to the availability of raw materials, the avoidance of particularly difficult engineering operations or the necessity of making a product of a particular purity.
(4) A process flow sheet, indicating quantities, the temperatures and pressures of materials at each stage and the vessel inventories, and the flow-rates in each of the principal flowlines. The reasons why such pressures and temperatures must be used should be given. Mass and heat balance diagrams should be given where appropriate.
(5) A list of the main plant items, specifying the capacity, design pressure, temperature limits for safe operation (upper and lower), and any special features of construction, together with the actual operating conditions. Details of services should be given.
(6) Details of the principal standards and codes to be used in the design.
(7) A statement of the inventory of all hazardous materials in process and of the steps taken to keep this at the lowest level consistent with safe and efficient operation.
(8) A statement of the method whereby the process will be controlled. Abnormal features, with particular reference to hazards, should be highlighted and references made to any special features, including trip systems.
(9) A list of all hazardous materials in bulk storage which may be endangered by a process incident and the steps to be taken to minimize the risk of their involvement.
(10) A statement of all materials and services needed to maintain safe operation of the plant and of the steps taken to ensure their continuous availability.
(11) A statement of any noxious effluents and their methods of treatment.
(12) A site layout showing the proposed plant and control room, and their position relative to other installations and buildings in the works, to loading bays at tanker terminals, to plants in neighbouring works and to the public area.
(13) A statement of the location and construction of the control room.
(14) The routing for all vehicles needing access to the plant, whether for the supply of materials and removal of products, or for maintenance or emergency purposes.
(15) An account of the procedures for maintaining effective liaison between the company and any outside organizations involved in the design or construction of the plant.
(16) Details of actual experience of the company, or of availability of experience from external sources, in operation of pilot and production scale plants, for the same or a similar process.
(17) Manning levels on the plant.
(18) Proposals for dealing with emergency situations.

Part 2 Documentation
(For Part 2(a) The Background Documentation see Introductory Section of this appendix.)

Part 2(b) The Design Document This should contain:

(1) An updated and detailed statement of all materials submitted in the Preliminary Design Document, including the process flowsheet, quantities and flowrates of all materials in process and storage areas, heat and material balances, instrument diagrams and plant layout diagrams.

(2) Details of all principal plant items, as in item 5 of Part 1(b), giving codes used, materials of construction and any special features.
(3) Installation drawings and pipe layouts.
(4) Documentation on hazard assessments and reliability studies.

Part 2(c) The Operating Document This should contain:

(1) A statement of the technical staff structure, including names of the Responsible Persons, together with details of standby arrangements for absence such as sickness or holidays, and of call-in arrangements.
(2) A statement of the numbers of operating personnel and of their training with particular reference to emergency procedures.
(3) The Operating Manual. This should include details of the start-up, normal shut-down and emergency shut-down procedures.

Appendix 25

HSE Guidelines on Developments near Major Hazards

Contents

A25.1 The Siting of Developments in the Vicinities of Major Hazards: HSE's Draft Guidelines to Planning Authorities A25/2

The Third Report of the Advisory Committee on Major Hazards (Harvey, 1984) contains an appendix on 'The Siting of Developments in the Vicinities of Major Hazards: HSE's Draft Guidelines to Planning Authorities. The full text, which is reproduced by courtesy of the HM Stationery Office, is given below.

A25.1 The Siting of Developments in the Vicinities of Major Hazards: HSE's Draft Guidelines to Planning Authorities (by the Health and Safety Executive – Major Hazards Assessment Unit)

A25.1.1 Introduction

The control of risks from major hazards may be achieved in various ways, for example:

(1) limit the amount of hazardous material present;
(2) reduce the likelihood of an accidental release of material;
(3) plan for emergencies;
(4) reduce the number of people exposed to risk.

Some of these measures may be taken within the installation, particularly at the project planning stage.

In many cases the situation in the installations is already fixed and the scope for improvement under the HSW Act is fully utilized. Even so, there may remain some residual risk. It is unlikely that the residual risk could justify the removal of existing populations by the termination of viable land uses. However, it is possible to inhibit an increase in the population at risk by control of new developments under planning legislation.

It is the purpose of HSE's advice to facilitate planning control where appropriate. Planning authorities are expected to include the factor of risk in their consideration of a planning decision. Thus, the types of development near major hazards should be deliberately chosen to minimize the population at risk.

HSE takes as a starting point the assumption that the major hazard installation complies with the requirements of HSW Act. It is then necessary to assess the level of residual risk to a proposed development in the vicinity, and to judge whether this might be a significant factor in the planning decision. HSE's assessment takes account of the consequences and likelihoods of various accident scenarios, and the implications of variations in vulnerability between different types of development. In some cases, the assumption of compliance with HSW Act implies a precise standard.

In other cases the standards are not precisely defined, or it may be possible to comply in a variety of ways. The individual characteristics of installations are taken into account where possible, but there are limits to the amount of detail which can be considered. It may be necessary to assume average performance in the absence of obvious individual variations, or for cases which are being assessed on paper.

This note deals only with the provision of advice on proposals for new developments in the vicinity of existing major hazard. The assessment techniques are used in a similar way when considering the siting of new major hazards in relation to existing buildings, but the judgement of the significance of the risks may be different. For example, the siting of a new major hazard may be constrained by the need to integrate it with existing plant. The application of a simple 'reciprocal rule' for the siting of new major hazards would neglect the differences in availability of sites for the two situations. There is also the possibility of seeking special safety standards on a new plant to facilitate its siting.

A25.1.2 Assessment: likelihood and consequences of an accident

The first part of the assessment is objective in the sense that it does not include social or political judgements, but it does include estimates of various factors where data is more or less unavailable. Thus it includes technical judgement by professional risk assessors. There is inevitably some uncertainty introduced by this judgement process and by lack of precision in basic data. This does not prevent the derivation of reasonable conclusions but it does imply that some caution is necessary. The technical judgements may tend to lead to an over-estimate of the risk level. If a planning decision is finely balanced, a more detailed review of assumptions may be worthwhile.

Assessments of risk from different materials differ in detail but they have many features in common. The basic sequence of events for LPG and chlorine are:

(1) LPG:
plant failure;
release;
vaporization;
mixture with air;
ignition;
explosion and/or fire;
blast and/or heat propagation;
impact (either directly on people, or on buildings which collapse or burn).
(2) Chlorine:
plant failure;
release;
vaporization;
mixture with air;
travel downwind;
dilution;
inhalation;
injury.

The risks from such sequences can be evaluated in two main ways, namely historical and analytical. In the historical approach, information from past incidents is used to predict the risks. *The Second Report of the Advisory Committee* contains information on some past incidents, and it derives a 'Mortality Index' to indicate the average number of fatalities per tonne of material released. This approach may be useful to devise a hazard rating for a material, but it is noticeable that the average index conceals a wide variation between cases and it is thus of questionable value for predicting individual situations. Other problems with the historical approach are the small number of cases and the incompleteness of information on cases, so it may therefore provide a rather poor statistical basis. This approach might be difficult to adapt for prediction in situations different from those already included by the accidents.

The alternative, analytical approach attempts to synthesize the risk on the basis of sequences outlined above. This approach is complex and requires assumptions to be made in the absence of data. Also, it may be difficult to select appropriate scenarios to include. It is, of course, possible to combine the approaches, and in practice this is

what is done. The historical approach is used to provide information on the likelihoods of releases, while the analytical approach is used to predict consequences. To illustrate the approach, the example of bulk pressurized LPG is used. Installations of this type comprise the majority of the major hazards in Britain, and the risks from them are relatively straightforward to assess. The assessment may begin by listing the various possible releases, either by quantity (short release, e.g. tank burst) or by rate (long release, e.g. uncontrolled pipe-split). There is a continuous range of possible release, but this can usually be simplified by identifying obvious sub-divisions. For the LPG case we might have:

Event	*Probability*	*Consequences*
Minor flange or gland weeping	Quite likely	Not felt off-site
Pipework break	Rather unlikely, especially for major cases	Localized, but could extend off-site from major cases
Tank burst: BLEVE	Very unlikely	May be harmful at considerable distances off-site
Tank burst: UVCE (delayed ignition)	Extremely unlikely	May be harmful at considerable distances off-site
Tank burst: drifting gas clouds	Extremely unlikely	May be harmful at considerable distances off-site

It is now necessary to determine more precisely what are the probabilities and consequences of these events. Obviously there could be wide variations between individual plants and between events in each sub-division. For example, the effects from pipe-break might depend on: size of hole; duration before shut-off; whether liquid gaseous or two-phase; wind-speed; delay before ignition; dispersion to below flammable limits; type of combustion, and specific site features. To simplify the problem, assumptions are made to give an indication of the realistic outcome from the most severe event within a sub-division.

The consequences in terms of likelihood of injury are derived by first calculating the impact intensity of the heat or blast at a particular distance, then relating this to the vulnerability of the population at that distance. The possibility is noted that different types of building, having different populations, might give different degrees of protection from any given intensity.

The result of this process is a list of events and risks. A decision can then be made on which events are trivial in that no injury could result. For remaining events, the consequences are considered in conjunction with the likelihood, to determine the combined risk of release and injury. This completes the objective assessment.

It should be noted that this approach does not automatically rule out from consideration any type of source event, however unlikely. Even the largest, most unlikely events are included, so there is not necessarily any cut-off corresponding to a 'maximum credible accident'. However, attention is paid to the combined risks, which may be very small from an unlikely event, so that the largest events are not necessarily significant determinants of the overall risk. In practice, assessments may be based on one or two events which may thus appear to correspond to 'maximum credible accidents;' this implies that lesser events may be more damaging but they are so unlikely as to present negligible extra risk. For the LPG example, separation distance guidelines for the siting of the first category of development near existing installations tend to be based on the provision of substantial protection from BLEVE and UVCE; this automatically gives a very high degree of protection from pipe-break and lesser events.

A25.1.3 Assessment: types of development

It was indicated earlier that different types of building may have associated with them populations whose vulnerabilities differ. This may be of great importance in a siting judgement. HSE feels that it would be inappropriate to advise against all forms of new development near major hazards nor need new major hazards to be sited away from all existing buildings. Types of developments may be distinguished by various factors which relate to the risks, for example

(1) whether residential, workplace, recreational, shopping, etc.;
(2) length of time any individual may be present;
(3) number of people who may be present and duration of occupancy;
(4) ease of evacuation;
(5) inherent vulnerability of people, for example, elderly, disabled, children;
(6) physical factors, for example building height, materials of construction, etc.

On the basis of these factors, HSE identifies three main categories of development. The first consists of developments where users would be present for most of the time, or where large numbers could be present at any one time, or where people are particularly vulnerable. Examples include housing, shopping centres or very large retail outlets, multi-storey office blocks, etc. The second category consists of less sensitive developments and includes industrial developments with low employment density, warehouses, etc. HSE also identifies a third category containing special cases such as hospitals, schools and other particularly vulnerable developments, to which particular attention should be paid in siting judgements.

It is normally advised that planning control is only necessary in respect of the first and third categories of developments near major hazard installations. There are various mitigating factors associated with the second

category, such that it would be difficult to argue that the risks to users justify inhibition of this type of land use. These factors could include ease of evacuation, low occupancy-time, fitness of population (e.g. adult workforce), small number of people, building protection or building not hazardous to occupants, etc.

A25.1.4 Summary of MHAU's advice

For LPG and similar flammable liquid gases, HSE recommends separation distance limits such that the consequences of minor releases at the limit would not be injurious, while the consequences of major releases (BLEVE, UVCE) would be unlikely to seriously injure more than a small fraction of the exposed population. In principle, unignited vapour clouds could travel to the limit, or even beyond it in unfavourable weather conditions, and people enveloped in a cloud would probably be seriously injured, but the risk to an individual from such a scenario is very low.

For chlorine, HSE recommends separation distance limits such that the consequences of major pipework failures would be unlikely to seriously injure more than a small fraction of the population downwind, in typical prevailing weather conditions. In unfavourable weather, or with larger releases from tank failure, people at greater distances could be injured, but the risk to an individual from such a scenario is very low.

A25.1.5 Presentation of advice

In presenting its advice, HSE attempts to give planning authorities clear guidance on the weight to be attached to the factor of safety. HSE tends to use one of three graded responses as follows:

Situation 1 (negligible risk): No significant reasons for refusing planning permission.

Situation 2 (marginal risk): The risks are very small and are not in themselves sufficient grounds for refusing planning permission, but they could be a factor against the development to add to any other adverse factors. This would apply near the outer limit of separation distance, or with small developments.

Situation 3 (substantial risk): While the probability of a serious incident is low, the consequences at the proposed development site could be serious. The safety issue should be a major factor and the planning authority is advised not to grant planning permission. If there were other factors which weighed strongly in favour of the application, HSE would seek to explain the technical assessment and level of risk in more detail before the planning authority's decision was made. (In exceptional cases of situation 3, where the planning authority was minded to grant permission contrary to the HSE's advice, HSE might consider whether to request a planning inquiry where the issues could be examined in detail in a public forum.)

It often happens that an initial unfavourable response from HSE leads to discussions of the scope for modifications to reduce the risk. Significant reduction may enable HSE to advise favourably. In other cases, HSE may give a conditional response, with advice on the use of planning conditions to ensure that the risk is reduced.

Appendix 26

Public Planning Inquiries

Contents

A26.1 Mossmorran A26/2
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In a limited number of cases, a planning proposal involving a major hazard goes to a public inquiry. The inquiry will then normally hear technical evidence, which is likely to centre around the hazard assessments carried out by the parties. Experience shows that there are a number of problems associated with expert testimony at public inquiries.

A study of large public inquiries is given in *The Big Public Inquiry* by Sieghart (1979).

Accounts have been given of the public inquiries at Mossmorran by McGill (1981, 1982, 1983), Pheasant Wood by Petts (1985b) and at Canvey by Petts (1985a). A comparative review of the problems of expert evidence at public inquiries and proposals for their mitigation has been given by Petts, Withers and Lees (1986).

Public accident inquiries are discussed in Chapter 27.

A26.1 Mossmorran

It is usual in Scotland for planning applications for major oil-related developments to be called in for review by the Secretary of State. In the case of the application of Shell Expro to build a gas plant and of Esso Chem to build an ethylene cracker at Mossmorran together with associated facilities at Braefoot Bay, the minister decided on a public inquiry, which was held in 1977. The local planning authority (LPA) retained the consultants Cremer and Warner to produce an assessment of the hazards. The Health and Safety Executive (HSE) also gave its own assessment. These were the two main sources of technical evidence and neither opposed the development. Opposition came from local interest groups at Aberdour, Braefoot Bay and Dalgety Bay, who produced their own assessment. There was a delay of some 18 months after the inquiry closed until 1979 before the minister gave his approval. The delay was apparently caused in part at least by the issue of ignition of 'radio sparks', which was raised after the inquiry had ended.

The Mossmorran inquiry, which has been studied by McGill (1981, 1982, 1983), illustrated the difficulties of public inquiries on hazardous installations, particularly with regard to expert testimony. The amount of information on the plant limited the contribution of the HSE and severely restricted that of the objectors. The latter considered that the statutory authorities had not made available a sufficiently full hazard assessment and they were not satisfied that the objections made to the assessments presented received sufficient weight or that either the LPA or the HSE were sufficiently independent of government and industry. The LPA were clearly in favour of the proposals before they commissioned the consultant's report.

A planning application is concerned with the development of land. The extent to which a planning inquiry should cover marine activities is perhaps a grey area. The hazards from marine activities at Braefoot Bay were briefly considered in the consultant's report and the inspector did take some evidence on shipping movements in the estuary, but marine hazards were not thoroughly revealed. The objectors were not unnaturally more concerned with the level of risk than with its source and considered that insufficient attention was given to the marine hazards, which might exceed those from land-based activities.

The inquiry exemplified the problem of assessing the risk from a plant for which the completed design is not yet available. The first stage of planning permission is outline planning permission. At this point, the design of the plant is generally available as a feasibility study only. It is outline planning permission, however, which is the important stage and it is difficult thereafter to revoke permission. In this case since the detailed design of the plant had not been done when planning permission was applied for, the assessments which could be made were that much less detailed and the uncertainties in the risks assessed that much greater. The objectors evidently thought that an adequate estimate of the risks could not be made without a hazop study, although this cannot be done until a detailed design is available.

The inquiry did demonstrate, however, the effectiveness of a planning condition. Condition 24 of the planning permission eventually given required the companies to carry out hazop studies and major studies were carried out.

The consultant's report reviewed the various hazard scenarios and graded their likelihood in qualitative terms such as 'low', 'very low' and 'extremely low', but did not give a full assessment of individual and societal risks. The HSE evidence was qualitative. The lack of any full quantitative assessment was criticized by the interest groups, who emphasized that the Canvey study, a quantitative assessment and public report, was regarded by the HSE as a major step forward in hazard control, yet such an exercise was not done for Mossmorran. These groups were also critical of various apparent inconsistencies in the HSE approach. It was alleged that the HSE estimate of the maximum credible spill at Braefoot Bay was not consistent with that given for Canvey and that the HSE was recommending a cordon sanitaire at the gas plant but not at the marine terminal, where many of the hazards were. Some of the HSE's assessments of physical phenomena were challenged and the opposition was able to call expert witnesses of some academic standing. The safety distances acceptable to the HSE were said to be less than those required in certain other countries. The opposition groups produced some risk estimates which indicated that the likelihood of a multiple fatality accident at Aberdour/Dalgety Bay marine terminal was 10^{-4}/year as opposed to the estimate of 10^{-6}/year given by the consultants.

The consultant's report, despite the absence of a quantitative assessment, gave advice on risk criteria. This raised the question whether it is the expert's job not only to do the risk estimates but also to evaluate them. On the other hand there did appear to be some opposition groups would not have been too unhappy with an annual risk of 'one in a million' (10^{-6}/year).

After the inquiry had ended, the question was raised of the possible hazard of ignition of a release of flammables by 'radio spark' transmissions from the nearby naval transmitter at Crimond. The HSE undertook extensive work on this 'radio spark' hazard.

The inquiry also illustrates another very basic problem, that if the company makes no modifications to its proposals as a result of objections posed, it appears to ride roughshod over the opposition, while if it does, it appears to be incompetent.

The inquiry and its aftermath give an impression of imbalance in the treatment of the hazards. In particular, the question of hazards associated with radio sparks received a disproportionate amount of attention relative to the hazards at the marine terminal. Despite this concession to the opposition groups, they were clearly dissatisfied with the inquiry.

A26.2 Pheasant Wood

The Pheasant Wood inquiry, which has been studied by Petts (1985b), on proposed housing development near to ICI chlorine and phosgene storages arose when the HSE asked the Secretary of State to call in the proposal for review after the LPA had indicated its intention to grant planning permission. The HSE gave its hazard assessment. The developer retained Cremer and Warner to present an alternative assessment, while ICI, although not directly involved, chose to offer its own assessment. All these parties presented technical evidence. The HSE's assessment included estimates of both frequencies and consequences of events, but did not combine these together to give individual and societal risks. They were criticized by the inquiry assessor and by ICI for this limitation. On the other hand, the other parties, although they did estimate these risks, did not always give the full basis of their estimates. Another point at issue between the HSE and the ICI evidence was some of the data used for the frequency of release. Whereas the HSE had to rely on generic data, the company was able to use data from its own installations which, depending on the viewpoint, were less pessimistic or more optimistic. The appropriateness of the gas dispersion models used was also an issue between the parties. The inspector found against HSE's case and in favour of granting planning permission. A feature of the Pheasant Wood inquiry which distinguishes it from those at Mossmorran and at Canvey was the low level of public interest.

A26.3 Canvey

The Canvey complex of oil refineries, chemical works, etc., has been the subject of several inquiries and hazard assessments, which have been described by Petts (1985a). The period 1965–73 saw a spate of planning applications and three public inquiries for oil refinery development. The economic pressures were clearly strong. The inquiry inspector's recommendations were twice overruled by the minister in favour of development. At the same time, the level of local concern over the hazards and environmental impact of the Canvey complex was rising and led to the opening, in 1975, of an inquiry into the possibility of revoking the planning permission granted to United Refineries Ltd (URL) in 1971. The technical assessor's report discussed the hazards in qualitative terms. No quantitative hazard assessments were presented.

One of the assessor's recommendations was a study of the possible hazardous interaction between the various installations at Canvey. Acting on this, the minister asked the HSE to look into the matter and the HSE commissioned a study from SRD, the First *Canvey Report*.

With the publication of this report, the minister was in a position to reopen the inquiry on the revocation of planning permission for URL. The inquiry was held in 1980 and considered both the bearing of the *Canvey Report* on the URL project and also the validity of the report itself, the parties being essentially the HSE and the objectors. The only full hazard assessment presented was that of the HSE in the form of the report. The report had not been commissioned specifically for the inquiry, but nevertheless there was for the first time available to an inquiry in Britain a full assessment of individual and societal risks.

One of the main hazards considered was a marine spill of LNG or LPG at the British Gas methane terminal. Disagreements arose over the estimates both of the frequency and the magnitude of this hazard. While the Port of London Authority (PLA) considered that the report overestimated the frequency of ship collision, the objectors presented graphic qualitative evidence of the problems of tanker handling. Estimates of the distance travelled by the flammable gas cloud before it fell to its lower flammability limit varied widely from 1 km to 28 miles.

Doubt was cast on some of the HSE's proposals for mitigating the hazards. The practicality and effectiveness of the water spray barrier against an ammonia cloud was challenged. PLA witnesses stated that the 8 knot speed limit proposed in the Scheduled Area was not practical.

The estimated risks were also matter for debate. The risk values were relatively high. For example, the calculated fatality risk attributed to the URL extension was comparable with the national fatality risk at work. The inspector considered the risks in some areas unacceptable.

Although the *Canvey Report* received praise and its overall approach was not challenged, it had certain deficiencies which detracted from it. The text was very disjointed, there were discrepancies between text and tables and there were some inaccuracies.

The inspector recommended that the URL planning permission should not be revoked, but only if the risk from the British Gas methane terminal were reduced by installing a ring of igniters at the periphery or by closure.

In 1981, the Second *Canvey Report* appeared. In this reassessment, which used revised failure data, more refined hazard models and more accurate population profiles and which took into account changes made on the installations, the assessed risks were less, some by an order of magnitude.

In 1982, another public inquiry was held, this time on the possible discontinuance of the British Gas methane terminal. British Gas produced a full hazard assessment, while the two *convey Reports* formed the basis of the HSE's evidence. The British Gas assessment used by intent broadly realistic estimates, the HSE conservative ones. The risks estimated by British Gas were lower, in some cases by two orders of magnitude. Realism rather than conservatism was not the only reason for this. The British Gas estimates of failure rates were lower and its gas dispersion estimates gave lower travel distances. The inspector stated that he found HSE's evidence much easier to understand and that he preferred their conservative approach, and he put some value on the independence of the HSE.

A number of expert witnesses were called by the objectors, notably the Castle Point District Council and the Castle Point Refineries Resistance Group. In many cases, their evidence failed to stand up to cross-examination due to weak hypotheses on accident scenarios, oversimplified assumptions, incorrect hazard models, misunderstanding of the work of others, especially the Second *Canvey Report*, and numerical errors. The technical assessor played an active role in this inquiry both in advising the inspector and in producing the report.

The inspector recommended against closing the British Gas terminal or requiring igniters.

A26.4 Sizewell

The inquiry on the proposal to construct a PWR at Sizewell B began in January 1983 and ended in February 1985. This is by any standards a 'big' public inquiry and the hazards of

a nuclear reactor are one of the topics on which much expert testimony has been heard. In the present context, the inquiry is of interest for its influence on the development of the form of such inquiries; for its influence on the formulation of risk criteria; and for the evidence given on some of the technical safety issues, particularly on rare events.

An important feature of the inquiry was the use of counsel to the inquiry. The inquiry also saw the increased use of informal 'side' meetings between experts at which issues can be clarified and misunderstandings removed.

Another feature of the inquiry is that a preconstruction safety report was available before the inquiry from the CEGB, although many design aspects remained unresolved.

With regard to risk, the Inspector suggested that where risks of the kind considered are accepted they are better described as 'tolerable' rather than 'acceptable' and encouraged the HSE to develop risk criteria. Such criteria have subsequently been published by the HSE (1988b, 1989d).

Among the many issues on hazards which the inquiry illustrates is that of the very rare event. A crucial accident scenario for a PWR is failure of the reactor pressure vessel (RPV). Such a failure is generally agreed to be a very rare event, but it may have very serious consequences. Estimation of the frequency of an event which has a high hazard potential but is very infrequent, perhaps scarcely credible, is one of the most intractable problems in hazard assessment. The inquiry is instructive not only because there were differences between experts in the methodology of estimation of the RPV failure frequency but also because there was scope for differences of perception of what was eventually established.

Evidence on the estimation of the RPV failure frequency was given for the CEGB by Dr B. Edmundson, for the Greater London Council by Technica Ltd and for the Suffolk Local Authorities by Professor Kussmaul from Germany. Another expert, Professor T.A. Kletz, gave evidence at the invitation of the inspector. On the basis of historical pressure vessel failure data Technica estimated the RPV failure rate at 1×10^{-6}/year. This figure was derived from the crude figure of 3.2×10^{-6}/year obtained from the historical data, and was intended to give credit for improved technology embodied in the RPV, but to be nevertheless a realistic rather than a conservative estimate, as the witnesses were at pains to point out. The CEGB derived their estimate of RPV failure rate using engineering principles, such as fracture mechanics, to determine the frequency of the failure modes which they considered credible, and obtained for catastrophic vessel rupture with generation of missiles an estimate of 2.4×10^{-9}/year. Professor Kussmaul preferred the CEGB's approach to that of Technica but advocated an alternative method of pressure vessel construction so as to minimize the risk of weld failure. This construction was not accepted by the CEGB and after further discussion between the parties Professor Kussmaul accepted the CEGB's approach subject to certain procedures which he specified and to which they agreed. As a result, the Suffolk Local Authorities withdrew their objections on grounds of safety, since they accepted Professor Kussmaul's advice that the risks were 'so low as to be incredible'.

There were nearly two orders of magnitude between the CEGB and Technica estimates of the RPV failure rate. The Technica estimate was in fact based on a single historical pressure vessel failure, which the CEGB regarded as so unusual as to be inconceivable on their vessel. However, even if no failure has occurred historically, it is still possible to make a statistical estimate by using the number of failure-free years and assuming that a failure is just about to occur. It therefore makes little difference to the number obtained whether the number of failures is one or zero. More important was the difference between the parties on whether the estimate should be based on historical statistics or engineering principles. Technica argued that even if the single historical failure was a bizarre one, such events cannot be completely discounted, that this stood in for the whole set of bizarre events which might occur, and that the method based on the historical data was the appropriate one to use.

In his cross-examination, counsel for the CEGB sought to identify assumptions in the Technica estimate. For Technica Dr. R.A. Cox stated clearly that the figure of 1×10^{6}/year was a 'best estimate', intended as realistic rather than conservative. However, counsel drew attention to the fact that in its written evidence Technica had at one point referred to this figure as an 'upper bound'. Dr P.J. Kayes for Technica then explained that what was meant by this was that the figure was an 'upper bound on the type of studies that would claim RPV failure to be incredible'. Counsel then asked: 'Is it intended to provide an upper bound to the likelihood of RPV failure?' and the witness replied: Yes, it is, as a best estimate'. Thus Technica were liable to believe that their figure was accepted as a realistic estimate, the CEGB that it had been conceded to be conservative.

In cross-examination, Professor Kletz commented that the two methods should not be seen as necessarily in conflict. A difference between the two by orders of magnitude was understandable. He did say, however, that while a large improvement in the reliability of the CEGB vessel over historic vessels could be expected, he had some personal scepticism whether any man-made artefact could provide such a low figure as the CEGB was claiming. In the case of the RPV the failure frequency was so low that he felt there was some justification for making allowance as Technica proposed for bizarre events and referred to possible failure due to previously unknown metallurgical phenomena. When cross-examined by one of the assessors, he agreed that his scepticism regarding very low numbers applied to a very low figure for a single event rather than one obtained as the product of the figures for a chain of events.

Thus, while the differences of opinion over points raised by Professor Kussmaul were largely settled by discussion outside the formal proceedings and the main findings reported back to the inquiry, the differences arising from the Technica evidence were not resolved at the side meetings and the parties were liable to interpret the evidence given in the inquiry cross-examination as supporting their particular positions.

A26.5 Expert Evidence

The foregoing account of some of the principal inquiries which have been held on hazardous installations indicates that there are a number of problem areas. These problems have been reviewed and proposals made for mitigating them by Petts, Withers and Lees (1986).

A26.5.1 Problems of adversarial forum

A view commonly expressed by technical experts is that the adversarial situation of a public inquiry is not an

appropriate means of examining technical issues. Many experts find the adversarial process unfamiliar and intimidating and regard it as an inappropriate means of arriving at the truth on technical matters. The adversarial process tends to lead to adoption of rigid, defensive positions.

For interest groups opposed to a development, the adversarial forum of an inquiry has the advantage that they can examine the developer's case, but can be intimidating to them also and it presents considerable difficulties for groups with few resources.

A26.5.2 Problems with hazard assessments

Many of the problems of expert testimony at public inquiries on process installations centre round hazard assessment. Most of these difficulties can be grouped under one or other of the following heads:

(1) obscurity;
(2) incompleteness;
(3) inconsistency.

Obscurity

There may be inherent difficulties in the subject matter or in its presentation.

Thus at the Sizewell inquiry the debate on engineering features of the pressure vessel was difficult to follow without engineering drawings. At the Canvey inquiry, the inspector himself had difficulties with the hazard assessment by British Gas and felt that the mode of presentation was more appropriate to a learned society than an inquiry.

Fundamentally difficult matters are typified by the arguments at Sizewell over the frequency of rare events and over probabilistic risk analyses.

Incompleteness

Information may be incomplete for many reasons. The engineering design may not be complete by the time of the inquiry, there may be deliberate selectivity in the hazards examined and there may be simple failure to identify all the hazards.

Thus at the Mossmorran and Sizewell inquiries much plant-specific information was unavailable because the projects were still in the feasibility stage. Estimates were therefore conceptual and based on generic data. This is likely to be a common situation.

Selectivity is exemplified by Mossmorran, where the objectors expressed concern about hazards at the port which seemed to have received less attention than the gas plant itself. Again at Mossmorran, there were objections to the exclusion of aircraft crashes. Later the possible hazard of ignition from radio sparks was raised and led to a separate investigation.

Inconsistencies

Some inconsistencies appear at an inquiry simply because of the lack of an agreed structure and methodology for the hazard assessment. There are also differences in the particular models used and in the basic approach to probability estimation.

Examples of differing structure and methodologies appeared at Pheasant Wood, where the assessment by the HSE did not provide any estimates of individual or societal risk, while those of the consultants and of ICI did. The HSE case was based on generic data, while the ICI case was based on plant-specific data.

At Canvey there were wide differences in the results obtained from different gas dispersion models. There have also been wide differences in the relations describing injury and damage. This is illustrated by the *Rijnmond Report,* which, although not a document presented to an inquiry, represents the type of hazard assessment which might be submitted. The report revealed ten-fold differences in estimates of the lethal concentrations of chlorine.

Such differences and uncertainties usually result in judgements being made about the likely margin of error. These judgements may occur at a number of points in the chain of calculations which make up the assessment. They may be optimistic or pessimistic.

In general, industry is anxious that the risks should not be exaggerated and presses for realistic assessments wherever possible. It may seek to avoid the use of numerical estimates of risk altogether where the confidence bounds are very wide. The HSE, on the other hand, is bound in the public interest to take a fairly cautious view and may be expected to incline towards the use of values which are to some degree conservative. In the risks assessed for the methane terminal at Canvey, the HSE and British Gas sometimes differed by a factor of a hundred, partly due to the difference between realism and conservatism.

Examples of the use of differences in approach to probability estimation were demonstrated at Sizewell, where the objectors based their estimate of pressure vessel failure rate on historical data and the CEGB its estimate on engineering considerations, the latter thereby obtaining for the event in question a frequency lower by some two orders of magnitude.

It should be recognized that public opposition to an industrial development may in some cases be so strong as to influence the character of the presentation and examination of the hazard assessments. At Pheasant Wood there was little public interest, whereas at Mossmorran this interest was strong and organized.

A26.5.3 Availability of information

An essential requirement of the parties to an inquiry is the availability of information. This information needs to be of the appropriate kind and to be provided at the right time. This requirement would in large part be met if the company makes available at the outset of the inquiry a form of open conceptual safety case.

The LPA may wish to commission an independent report from a consultant, as well as seeking advice from the HSE.

The use of open safety cases presented in a uniform style would greatly assist the LPAs to become familiar with the problems posed by hazardous installations and to instruct consultants.

The HSE may also provide for the inquiry inspector an independent hazard assessment by which he can evaluate the evidence of the other parties.

Twenty-eight days before the inquiry the LPA is required to produce a written statement. It is only the LPA which has this obligation.

A26.5.4 Parties to inquiry

The LPA will always be a party to a planning inquiry. There is no general requirement that staff from other government bodies (such as the HSE) should appear in person. In practice they often do.

The parties will often be represented by legal counsel at the inquiry. An innovation at Sizewell was the appointment

of counsel to the inquiry itself. This appears to have been of great assistance to the inspector and to have helped other parties to clarify issues. In an adversarial process, the investigatory role of such counsel appears of great value, particularly for technically complex projects.

The part played by the HSE at an inquiry needs to be seen in the context of its wider and ongoing role in the control of hazards. In order to safeguard this role, it is desirable that as far as possible the HSE should appear as an adviser rather than a protagonist and the situation where the HSE is the instigator of an inquiry is to be avoided as far as possible.

It is appropriate that at the outset of an inquiry the HSE be invited to state its role, the legislation under which it operates and the limits of its powers, that it define the set of principles by which it judges the nature of the risk and the relevant safety criteria required by the HSWA as enforced by the HSE. It may also indicate its expectations of the ability of the developer to meet these standards, while leaving it to the inquiry to balance these expectations with those of others, and with other relevant factors.

Many experts are called by objectors. The problems experienced at past inquiries have often centred around disagreements between these experts and others. It is desirable that these experts play their full part in the formal and informal meetings described below. In this way, issues can be clarified and difficulties which have arisen in the past avoided. Another class of witness is those called by the inspector, but these appear to present fewer problems.

A26.5.5 Arrangements at inquiry

A large inquiry usually has a formal preliminary meeting presided over by the inspector at which a detailed set of objectives, procedures and timetable are developed from the terms of reference. Such a meeting, which largely determines the subsequent course of the inquiry, is essential for large, technically complex projects.

The normal procedure in a public inquiry is to hear evidence by party rather than by issue, with the project's proposer having the final right of reply. This results in safety evidence being interspersed with other evidence on other topics, and not taken in its logical order. An exception tends to be made in big inquiries such as Sizewell, where hearing may be by issue. In general, hearing by issue suits the large organizations, who have little difficulty in making experts available on each issue as it arises. It may, however, create problems for smaller bodies with limited resources.

As described above, there has been some criticism of the adversarial approach inherent in public inquiries. In eyes of the public, however, it remains a safeguard, albeit imperfect, against concealment and is an important factor in legitimizing the inquiry process.

The problem of dealing with expert evidence in an adversarial forum may be mitigated by the use of non-adversarial side meetings between experts. Some of these may be formal meetings with minutes kept which are part of the inquiry record.

Appendix 27

Standards and Codes

Contents

A27.1 Globalization of Standards A27/2
A27.2 Where to Find Information on Standards A27/2

Standards and codes of practice are one of the principal means by which experience of problems and their respective solutions is transmitted and fundamental to recognized and generally accepted good industrial practice. The production of a code is normally undertaken by a group of experienced practitioners under the aegis of an appropriate organization. The code represents the consensus of this group on what constitutes good practice. There is usually some degree of consultation with the parties who will use the code.

There are a vast number of codes produced by a variety of bodies and the status of a code depends on the body which promulgates it. Inevitably a code becomes out-of-date as technology changes, so that a process of continuous revision is necessary. A 5-year update is most commonly-suggested.

The philosophy commonly adopted in writing a new code is to define limited objectives and to get the code finished, recognizing that further revision will be necessary in due course, rather than to seek to produce a definitive work. Standards and codes of practice normally use a specialized and defined terminology.

Mandatory requirements, that is, those that it is essential to satisfy, are expressed by the use of the word 'shall'. The word 'must' is used when an absolute imperative arises, for example when safety considerations apply.

Non-mandatory requirements, that is, those that are recommended or desirable are usually expressed by the use of the auxiliary 'should'. Should implies a recommendation based upon the judgement of experienced people but recognizes that some discretion is appropriate in special circumstances.

A27.1 Globalization of Standards

The ever increasing world of international trade has created a need for internationally accepted standards. When the large majority of products or services in a particular business or industry sector conform to International Standards, a state of industry-wide standardization can be said to exist. This is achieved through consensus agreements between national delegations representing all the economic stakeholders concerned – suppliers, users, government regulators and other interest groups, such as consumers. They agree on specifications and criteria to be applied consistently in the classification of materials, in the manufacture and supply of products, in testing and analysis, in terminology and in the provision of services. Hence, International Standards provide a reference framework, or a common technological language, between suppliers and their customers, thereby facilitating trade and the transfer of technology.

International Organization for Standardization (ISO) together with the International Electrotechnical Commission (IEC) and International Telecommunication Union (ITU) has built a strategic partnership with the World Trade Organization (WTO) with the common goal of promoting a free and fair global trading system. The political agreements reached within the framework of the WTO require underpinning by technical agreements. ISO, IEC and ITU, as the three principal organizations in international standardization, have the complementary scopes, the framework, the expertise and the experience to provide this technical support for the growth of the global market.

ISO is the world's largest developer of standards. ISO is a network of the national standards institutes of 148 countries, on the basis of one member per country, with a Central Secretariat in Geneva, Switzerland, that coordinates the system. ISO is a non-governmental organization, its members are not delegations of national governments. ISO occupies a position between the public and private sectors. This is because many of its member institutes are part of the governmental structure of their countries, while other members have their roots uniquely in the private sector, such as industry associations and technical societies.

Therefore, ISO is able to act as a bridging organization in which a consensus can be reached on solutions that meet both the requirements of business and the broader needs of society, such as the needs of stakeholder groups like consumers and users. The vast majority of ISO standards are highly specific to a particular product, material or process. However, the ISO 9000 and ISO 14000 standards have earned a worldwide reputation are known as 'generic management system standards'. 'Generic' means that the same standards can be applied to any organization, large or small, product or service, and whether it is a business enterprise, a public administration or a government department. 'Management system' refers to what the organization does to manage its processes, or activities. 'Generic' also signifies that no matter what the organization is or does, if it wants to establish a quality management system or an environmental management system, then such a system has a number of essential features that are spelled out in the relevant standards of the ISO 9000 or ISO 14000 standards. The US OSHA process safety management regulation is another example of the performance-based philosophy defined in the generic management system standards.

A27.1.1 Conformity assessment

Conformity assessment means checking that products, materials, services, systems or people measure up to the specifications of a relevant standard. Many products require testing for conformance with specifications or compliance with safety, or other regulations before they can be put in the stream of commerce. Even simpler products may require supporting technical documentation that includes test data. ISO has developed many of the standards against which products are assessed for conformity, as well as the standardized test methods that allow the meaningful comparison of test results so necessary for international trade.

ISO itself does not carry out conformity assessment. ISO develops ISO/IEC guides and standards to be used by organizations that carry out conformity assessment activities. The voluntary criteria contained in these guides and standards represent an international consensus on what constitutes best practice. Their use contributes to the consistency and coherence of conformity assessment worldwide.

A27.2 Where to Find Information on Standards

There are several hundred thousand standards and technical regulations in the world containing special requirements for a particular country or region. Finding information about these, or about related conformity assessment activities, can be a heavy task. ISONET, the SO Information Network, can ease the problem. This is a worldwide network of national standards information centres, which have cooperatively developed a system to

provide rapid access to information about standards, technical regulations and testing and conformity assessment activities in operation around the world. The World Trade Organization's Agreement on Technical Barriers to Trade (WTO/TBT) typically establishes a national enquiry point to answer questions on regulations and standards in each country, the ISONET and WTO enquiry points are the same. WSSN is a network of publicly accessible Web servers of standards organizations around the world. It contains links to international, regional and national standardization bodies, and also to other international and regional organizations that develop standards in their specialized subject area; available at http://www.wssn.net/WSSN/index.html.

Leading national standards institutions, which co-operate with ISO are:

- British Standards Institution (BSI);
- American National Standards Institute (ANSI);
- Deutsches Institut fur Normung (DIN);
- Verein Deutscher Ingenieure (VDI);
- Association Francaise de Normalisation (AFNOR);
- Comite de Normalisation Europeen (CEN);
- Comite de Normalisation Europeen Electrotechnique (CENELEC).

Some technical associations that generate standards and codes of practice relevant to safety and loss prevention are listed below.

- American National Standards Institute (New York);
- American Industrial Hygiene Association (Fairfax, VA);
- American Petroleum Institute (Washington, DC);
- American Society of Civil Engineers (New York);
- American Society of Heating, Refrigerating and Air-Conditioning Engineers (Atlanta, GA);
- American Society of Mechanical Engineers (New York);
- American Society for Quality Control (Milwaukee, MI);
- American Society for Testing and Materials (Philadelphia, PA);
- American Welding Society (Miami, FL);
- British Chemical Industry Safety Council;
- British Compressed Gases Association (London);
- Chemical Industry Safety and Health Council (London);
- Det Norske Veritas (Stavanger, Norway);
- Imperial Chemical Industries Pic;
- Institute of Electrical and Electronic Engineers (New York);
- Institute of Petroleum (London);
- Instrument Society of America (Research Triangle Park, NC);
- International Chamber of Shipping (London);
- International Maritime Organization (London);
- Liquefied Petroleum Gas Industry Technical Association (London);
- National Fire Protection Association (Quincy, MA);
- Oil Companies International Marine Forum (London);
- Society of International Gas Tanker and Terminal Operators (London);
- Tubular Exchangers Manufacturers Association;
- Underwriters Laboratories (Northbrook, IL);
- Verein Deutscher Ingenieure.

A27.2.1 Among the first safety codes

Modern fire safety codes and standards, and in particular those developed by the National Fire Protection Association (NFPA), trace their origins to the nineteenth-century development of automatic sprinklers. From the beginning, sprinklers performed properly as extinguishing devices; however, they were originally installed in so many different ways that their reliability was uncertain.

From the beginning, the mission of the NFPA is to reduce the burden of fire and related hazards on the quality of life. The NFPA mission today is accomplished by advocating scientifically based consensus codes and standards, research and education for fire and related safety issues. NFPA's National Fire Codes are developed by technical committees staffed by over 6000 volunteers, and are adopted and enforced throughout the world. NFPA functions as a non-profit membership organization with more than 68,000 members worldwide.

Development of NFPA standards follow the original principles still followed today by NFPA Technical Committees:

'To bring together the experience of different sections and different bodies of underwriters, to come to a mutual understanding, and, if possible, an agreement on general principles governing fire protection, to harmonize and adjust our differences so that we may go before the public with uniform rules and conditions which may appeal to their judgment is the object of this Association.'

Despite the term 'National' in NFPA, the name sometimes seems to imply the lack of international involvement.

Appendix 28

Institutional Publications

A General

American Conference of Government Industrial Hygienists
(Cincinnati, OH)

	Item
Documentation for the Biological Exposure Indices (BEIs)	1
Documentation for the Physical Agents Threshold limit Values	2
Documentation of Threshold limit Values and Biological Exposure Indices, 6th ed.	3
A Guide to OSHA Regulations on Storing and Handling Flammable and Combustible Liquids by M.M. Carmel	4
Recognition of Health Hazards in Industry by W.A. Burgess, 1981	5
Design of Industrial Ventilation Systems, 5th ed., by J.L. Alden and J. M. Kane, 1982	6
Noise Control: A Guide for Workers and Employers by R.L. Stepkin and R.E. Mosely, 1984	7
Biological Monitoring of Exposure to Chemicals: Organic Compounds edited by H.K Dillon and M.H. Ho, 1987	8
Case Studies in Industrial Hygiene ed. by J.L. Perkins and V.E. Rose, 1987	9
Guidelines for Selection of Chemical Protective Clothing, 3rd ed., by AD. Schweppe, P.P. Costas, J.O. Jackson and D.J. Weitzman, 1987	10
Health Hazard Control in the Chemical Process Industry by S. Lipton and J. Lynch, 1987	11
Industrial Radiation Hazards Deskbook by N.P. Cheremisinoff, P.N. Cheremisinoff and M.F. Teresinski, 1987	12
Inhaled Dust and Disease by P.F. Holt, 1987	13
Investigating Accidents with STEP by K. Hendrick and L. Benner, 1987	14
Underground Storage Systems: Leak Detection and Monitoring by T.G. Schwendeman and H.K Wilcox, 1987	15
Chemical Exposure and Disease by J.D. Sherman, 1988	16
Corporate Management of Health and Safety Hazards by R.E. Kasperson, J.X. Kasperson, C. Hohenemser and R.W. Kates, 1988	17
Dust Control Handbook by V. Mody and R. Jakhete, 1988	18
Emergency Care for Hazardous Materials Exposure by A.C. Bronstein and P.L. Currance, 1988	19
Guidelines for Laboratory Design, 2nd ed., by L. DiBerardinis *et al.*, 1988	20
Heating, Ventilation and Air-Conditioning Analysis and Design, 3rd ed., by F.C. McQuiston and G.D. Parker, 1988	21
Industrial Hygiene Engineering by J.T. Talty, 1988	22
Industrial Hygiene Management by J.T. Garrett, L.J. Cralley and L.V. Cralley, 1988	23
Methods of Air Sampling and Analysis ed. by J.P. Lodge, 1988	24
Methods for Biological Monitoring ed. by T.J. Knelp and J.V. Crable, 1988	25
Toxicology: A Primer on Toxicology Principles and Application by MA Kamrin, 1988	26
Air Sampling Instruments, 7th ed., 1989	27
Benzene: Occupational and Environmental Hazards edited by M.A. Mehlman, 1989	28
Chemical Hazards in the Workplace by R.M. Scott, 1989	29
Chemical Protective Clothing Performance Index Book by K. Forsberg and L.H. Keith, 1989	30
Design and Protocol for Monitoring Air Quality edited by N.L. Nagada and J.P. Harper, 1989	31
First Aid Manual for Chemical Accidents, 2nd ed., by M.J. Lefevre, 1989	32
A Guide to Monitoring Airborne Asbestos in Buildings by D.L. Keyes and J. Chesson, 1989	33
Hazardous Waste Minimization Handbook by T. Higgins, 1989	34
Industrial Emergency Preparedness by R.B. Kelley, 1989	35
In-Plant Practices for Job-Related Health Hazards Control, vols 1–2, ed. by L.V. Cralley and L.J. Cralley, 1989	36
The Risk Assessment of Environmental Hazards ed. by D.J. Paustenbach, 1989	37
Ventilation for Control of the Work Environment by W.A. Burgess, M.J. Ellenbecker and R.T. Treitman, 1989	38
Asbestos: Medical and Legal Aspects by B.L. Castleman, 1990	39
Destruction of Hazardous Chemicals in the Laboratory by G. Lunn and E.B. Sansone, 1990	40
A Guide for Control of Laser Hazards, 1990	41
Hazardous Waste Chemistry, Toxicology and Treatment by S.E. Manahan, 1990	42
Laboratory Health and Safety Handbook by R.S. Stricoff and D.B. Walters, 1990	43
The Laboratory Quality Assurance System by T.A. Radcliff, 1990	44
Managing Safety and Health Programs by R. Boylston, 1990	45
Neurotoxicity Handbook by R.M. Singer, 1990	46
Occupational and Environmental Health Management by H.R. Kavianan and C.A. Wentz, 1990	47
Radiation Protection: A Guide for Scientists and Physicians, 3rd ed., by J. Shapiro, 1990	48
Rapid Guide to Hazardous Chemicals in the Workplace, 2nd ed., by R.J. Lewis, 1990	49
SARA Title III by F.L. Fire, N.K Grant and D.H. Hoover, 1990	50
Air Monitoring for Toxic Exposures by S.A. Ness, 1991	51
Biological Monitoring of Exposure to Chemicals: Metals ed. by H.K. Dillon and M.H. Ho, 1991	52
Carcinogenically Active Chemicals: A Reference Guide by R.J. Lewis, 1991	53
Casarett and Doull's Toxicology, 4th ed., edited by M.O. Amdur, J. Doull and C.D. Klaassen, 1991	54
Chemical Hazards of the Workplace, 3rd ed., by G.J. Hathaway, N.H. Proctor, J.P. Hughes and M.L. Fischman, 1991	55
Exposure Assessment for Epidemiology and Hazard Control ed. by S.M. Rappaport and T.J. Smith, 1991	56
A Guide to OSHA Regulations on Inorganic Lead by M.M. Carmal, 1991	57

Guide for Testing Ventilation Systems, 1991 58
Handbook of Toxic and Hazardous Chemicals and Carcinogens, 3rd ed., by M. Sittig, 1991 59
Hazardous Chemicals Desk Reference, 2nd ed., by R.J. Lewis, 1991 60
Hazardous Laboratory Chemicals Disposal Guide by M.A. Armour, 1991 61
Improving Safety in the Chemical Laboratory, 2nd ed., by J.A. Young, 1991 62
Indoor Air Quality Workbook by J.D. Burton, 1991 63
Industrial First Aid: Reference and Training Manual, 1991 64
Industrial Health by J.E. Peterson, 1991 65
Industrial Ventilation: Engineering Principles by R.J. Heinsohn, 1991 66
Industrial Ventilation: A Manual of Recommended Practice, 21st ed., 1991 67
Industrial Ventilation Workbook by J.D. Burton, 1991 68
Laboratory Ventilation Workbook by J.D. Burton, 1991 69
Noise and Health ed. by T.H. Fay, 1991 70
Occupational Health Fundamentals edited by D.J. Hansen, 1991 71
The OSHA 500 by R.D. Morran and M.M. Moran, 1991 72
Patty's Industrial Hygiene and Toxicology ed. by G.D. Clayton and F.E. Clayton, 1991 73
Quantitative Industrial Hygiene: A Formula Workbook by J. Caravanos, 1991 74
Air Pollution Engineering Manual by A.J. Buonicore and W.T. Davis, 1992 75
Applied Ergonomics Handbook by M. Burke, 1992 76
Basic Statistics for Laboratories by W.D. Kelly, T.A. Ratcliff and C. Nenadic, 1992 77
Guide to Occupational Exposure Values – 1992, 1992 78
Introduction to Occupational Epidemiology by S. Hernberg, 1992 79
Threshold limit Values and Biological Exposure Indices, 1992–1993, 1992 80
The Guidebook to Successful Safety Programming by R.J. Colvin, 1992 81
Hawley's Condensed Chemical Dictionary, 12th ed., ed. by R.J. Lewis, 1992 82
Hazardous Waste Management Compliance Handbook, 1992 83
The Hazardous Waste Q&A by T.P. Wagner, 1992 84
Industrial Hygiene Workbook by J.D. Burton, 1992 85
An Introduction to Trenchless Technology by S.R. Kramer, W.J. McDonald and J.C. Thomson, 1992 86
A Practical Guide to Chemical Spill Response by J.W. Hosty, 1992 87
Respiratory Protection Program and Record Keeping, 1992 Kit by J.A. Pritchard 88
Sax's Dangerous Properties of Industrial Materials, 8th ed., by R.J. Lewis, 1992 89

American Gas Association
(Arlington, VA)

Year		Item
1967	Gas Engineers Handbook	1
1975	Purging Principles and Practice	2
1977–	Gas Measurement Manual	3
1977	Handbook of Noise Control at Gas Pipeline Facilities by R.H. Pish and C.R. Sparks	4
1979	LNG Plant Design and Construction Guide	5
1981	LNG Information Book 1981	6
1982	Basic Principles of Accident Prevention	7
1982	LNG Training Guide	8
1983	Odorization Manual	9
1984	LNG Preventive Maintenance Guide	10
1986	Introduction to LNG for Personnel Safety	11
1989	AGA Plastic Pipe Manual for Gas Service	12
1989	Engine, Turbines and Compressors Directory	13
1990	OSHA Inspection Guide	14
1990	Federal Pipeline Safety Inspectors Manual by Dept of Transportation	15
1991	Engine Analyzer Signature Directory	16
1992	Classification of Gas Utility Areas for Electrical Installations	17
1974	Evaluation of LNG vapor control methods by AD Little Inc.	18
1974	Evaluation of the influence of absorbed and absorbed-hydrogen on the mechanical properties and fracture behavior of materials to be used in a hydrogen gas transmission system by A.R. Elsea *et al.*	19
1974	An experimental study on the mitigation of flammable vapor dispersion and fire hazards immediately following LNG spills by University Engineers, Proj. IS-100-1	20
1974	Comparison of dispersion from LNG spills over land and water with LNG vapor dispersion in weather inversions by BatteUe Columbus Labs, Proj. SI-3-7	21
1974	LNG safety program. Phase II byBatteUe Columbus Labs, Proj. IS-3-1	22
1974	LNG safety study. Interim report on Phase II work, Proj IS-3-1	23
1975	Tankers and tanker terminals: a bibliography for the natural gas industry 1960–1974	24
1976	Ductile fracture arrest in gas pipeline by W.A. Maxey, Proj. NG-18	25
1977	Flameless vapor explosions by MIT Res. Center	26
1978	Simplified methods for estimating vapor concentration and dispersion distances for continuous LNG spills into dikes with flat or sloping floors by AD Little Inc.	27
1978	A theoretical model for crack propagation and arrest in pressurized pipelines by P.A. McGuire *et al.*	28
1979	A study of cathodic protection of buried steel pipeline by G.J. Hennon, Proj. PR-138-83	29
1980	Before you dig, check	30
1980	Field validation of atmospheric dispersion models for natural gas compressor stations by Engineering Science	31

1980 Workbook predicting short-term atmospheric dispersion of reciprocating engine exhaust emissions from natural gas compressor stations 32
1981 Development of an improved LNG plant failure rate data base by D.W. Johnson and J.R. Welker 33
1981 The effects of dents on failure characteristics of line pipe by R.J. Fiber *et al.* 34
1981 Pipeline response to buried explosive detonations, vols 1–2 by E.D. Esparza, R.S. Westine and A.B. Wenzel 35
1981 A study of the causes of failure of defects that have survived a prior hydrostatic test by J.F. Kiefner *et al.* 36
1981 Underground storage of gaseous fuels: a bibliography 1926–1980 37
1983 Brittle fracture arrest in gas pipelines by Maxey 38
1983 Determination of compressor station relief valve criteria by Sparks, Proj. PR-15-148 39
1984 Effect of hydrostatic retesting on stress corrosion cracking by Barlo, Eiber, Berry and Fessler 40
1984 The effect of random seas on pipeline stability, vol. 1, Wave/soil simulations and simplified design methods by L.E. Borgman and R. Hudspeth 41
1984 The effect of random seas on pipeline stability, vol. 2, Finite element modeling of pipeline response by L.E. Borgman and R. Hudspeth 42
1984 Critical evaluation of multiphase pipeline calculation methods by Gregory and Fogarasi 43
1985 Crank shaft stress reduction through improved alignment practices by Smalley and Palazzolo 44
1986 NOT needs for pipeline integrity assurance by Kiefner, Hyatt and Eiber 45
1986 Study of new joining processes for pipelines by G.R. Saltera and J. Weston 46
1986 Underground tanks in the natural gas industry 47
1987 Criteria to stop active pit growth by Thompson, Beavers and Han 48
1987 Investigation of sulfide-stress cracking at pipe seam welds by H.J. Clalone and D.N. Williams 49
1988 Crack growth behavior and modeling by T.K. Christman and F.W. Brust 50
1988 Effect of water chemistry on internal corrosion rates in offshore natural gas pipelines by D.W. Shannon *et al.* 51
1988 Emergency shutdown systems (compressors) 52
1988 Field weldability of high strength pipeline steels by D.N. Noble and R.J. Pargeter 53
1988 Heat affected zone toughness in heavy-wall pipe by A.G. Glover and D.B. Varo 54
1988 Operating safety in the natural gas industry 55
1988 Prediction of SCC susceptibility based on mechanical properties of line pipe by T.K. Christman 56
1988 Proof testing on pre-hot-tap branch connections by M. Rosenfeld and W.A. Maxey 57
1988 Relief valves in compressor stations 58
1988 A review of gas industry pipeline coating practices by S. Nunez *et al.* 59
1988 Safety factors in the assessment of realistic defects in pipeline welds by A.P. Hodgson and R.H. Leggatt 60
1989 Criteria for hot tap welding – further studies by Threadgill and Cola 61
1989 Evaluation of the capabilities of advanced AE monitoring of buried natural gas transmission pipe and AE evaluation of a known colony of SCC by F.B. Stulen 62
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1989 Remote field eddy current crack and defect detection by W. Lord 64
1989 Review of procedures for welding onto pressurized pipelines by P. Threadgill and M. Cola 65
1989 State-of-the-art methods for multiphase flow pipelines by C.J. Crowley *et al.* 66
1990 Cathodic protection anodes 67
1990 Effect of loading on the growth of deep stress corrosion cracks by J.A. Beavers *et al.* 68
1990 Methods for prioritizing pipeline maintenance and rehabilitation by J.F. Kiefner, P.H. Vieth *et al.* 69
1990 Remote field eddy detection of stress corrosion cracking, Phase I by J.B. Nestleroth 70
1991 Development of an ultrasonic stress corrosion cracking detection vehicle by C.W. Pope *et al.* 71
1991 Development and validation of a ductile flaw growth analysis for gas transmission line pipe B.N. Leis *et al.* 72
1991 Evaluation of nondestructive inspection methods for welds made onto in-service pipelines, I and II by W.A. Bruce and B.W. Kenzie 73
1991 A guide to controlling natural gas in emergencies 74
1991 Guidelines for analyses of fire protection and emergency response based on 49 CFR Part 193 75
1991 Optimizing techniques for CTOD testing of girth welds in line pipe by McGaughy and Gordon 76
1991 Technology of submersible remotely operated vehicles by F.R. Busby 77
1992 Criteria for dent acceptability of offshore pipelines by J.R. Fowler 78
1992 Development of a ductile pipe fracture model by G. Buzichelli, M.H. Kanninen *et al.* 79

1992	Development of optimized nondestructive testing inspection methods for weld made onto in-service pipelines, III by W.A. Bruce and B.W. Kenzie	80
1992	Development of simplified weld cooling rate models for in-service pipelines by M.J. Cola *et al.*	81
1992	Diverless pipeline repair clamp, Phase I by J.E. Miller and B. Knott	82
1992	Diverless pipeline repair clamp, Phase II by J.R. Fowler *et al.*	83
1992	Fracture behaviour of girth welds containing natural gas defects: comparison with existing workmanship standards by R. Denys	84
1992	Fracture behaviour of girth welds containing natural gas defects: effect of weld metal yield strength by R. Denys	85
1992	Historical manufactured gas plant sites: use of risk assessment in the development of remedial target concentrations	86
1992	Remote field eddy detection of stress corrosion cracking, Phase II by J.B. Nestleroth	87
1992	Spatial density of stress corrosion cracks in line pipe steel by R.N. Parkins *et al.*	88
1992	A study of processes for welding pipelines by J. Weston	89
1992	Subsea pig recovery concepts by H.O. Mohr	90
1993	Diver-assisted pipeline repair manual by H.O. Mohr	91
1993	Effect of weldment property variations on the behavior of line pipe by R.J. Dexter *et al.*	92
1993	Repair weld residual stress by T.C. McGaughy	93

Pipeline Incident Reports

1977	Analysis of the Office of Pipeline Safety Annual Report data for natural gas distribution companies 1970 through 1975 by J.F. Hefner and R.B. Smith	94
1981	Analysis of the Office of Pipeline Safety Operations 1970–78 Reportable Incident Data for the NG distribution companies by D.N. Gideon	95
1981	Analysis of the Office of Pipeline Safety Annual Report data for natural gas distribution companies by D.N. Gideon and R.B. Smith	96
1984	An analysis of reportable incidents for natural gas transmission and gathering lines 1970 through 1981 by Kramer, Gideon and Smith	97
*c.*1986	An analysis of reportable incidents for natural gas transmission and gathering lines: 1970–84 by Jongs, Kramer and Gideon and Smith	98
1992	An analysis of reportable incidents for natural gas transmission and gathering lines June 1984 through 1990 by R.J. Fiber and D.J. Jones	99
1992	DOT distribution, transmission and gathering incident report data since 1984 and Annual Report data for 1990	100

Annual series

Survey of Underground Gas Storage Facilities in the US and Canada	101

American Industrial Hygiene ssociation
(Fairfax, VA)

Year	*AIHA Press Publications*	*Item*
1970–	Ergonomics Guides (Annual Series)	1
1975	Basic Industrial Hygiene: A Training Manual	2
1977–	Non-ionizing Radiation Guides (series of three titles)	3
1980–	Workplace Environmental Exposure Level Guides (WEELs) (AIHA Workplace Environmental Exposure Levels Committee – Annual Series)	4
1983	Work Practices Guide for Manual Lifting by NIOSH	5
1984	Arc Welding and Your Health	6
1984	Engineering Field Reference Manual	7
1985	Biohazards Reference Manual	8
1985	Manual of Recommended Practice for Portable Direct-Reading Carbon Monoxide Indicators (AIHA Gas and Vapor Detection Systems Committee) ed. by Patrick R. Frazee	9
1986	Noise and Hearing Conservation Manual ed. by E.H. Berger, W.D. Ward, J.C. Morrill and L.H. Royster	10
1987	Occupational Exposure Limits – World-wide by W. Cook	11
1988–	Emergency Response Planning Guidelines (Annual Series)	12
1988	Hygienic Guides (series of four sets)	13
1988	Quality Assurance Manual for Industrial Hygiene Chemistry	14
1989/ 1993	Manual Material Handling: Understanding and Preventing Back Trauma (AIHA Ergonomics Committee) ed. by K.H.E. Kroemer, J.D. McGlothlin, and T.G. Bobick	15
1989	Odor Thresholds for Chemicals with Established Occupational Health Standards (TRC Environmental Consultants under contract to AIHA)	16
1990	Chemical Protective Clothing, vols 1–2, ed. by J.S. Johnson and K.J. Anderson	17
1990	Computers in Health and Safety ed. by G. Rawls	18
1990	LOGAN Workplace Evaluation System by Dupont	19
1990	Safety Auditing: A Management Tool by D.W. Kase and K.J. Wiese	20
1990	The Practitioner's Approach to Indoor Air Quality Investigations: Proceedings of the Indoor Air Quality International Symposium (AIHA Indoor Environmental Quality Committee) ed. by D.M. Weekes and R.B. Gammage	21

1991 A Strategy for Occupational Exposure Assessment by N.C. Hawkins, S.K. Norwood and J.C. Rock 22
1991 Industrial Ventilation Workbook, 2nd ed., by D.J. Burton 23
1991 Laboratory Ventilation Workbook by D.J. Burton 24
1991 Respiratory Protection: A Manual and Guideline, 2nd ed., ed. by C.E. Colton, L.R. Birkner and L.M. Brosseau 25
1992 Occupational Exposure, Toxic Properties, and Work Practice Guidelines for Fiber Glass by J.R. Bender, J.L. Konzen and G.E. Devitt 26
1993 Direct-Reading Colorimetric Indicator Tubes Manual, 2nd ed., ed. by J. Perper and B. Dawson 27
1993 Dynamic Measures of Low Back Performance, an Ergonomics Guide by W.S. Marras, J.D. McGlothlin, D.R. McIntyre, M. Nordin and K.H.E. Kroemer 28
1993 IAQ and HVAC Workbook by D.J. Burton 29
1993 Manual of Recommended Practice for Combustible Gas Indicators and Portable Direct-Reading Health Survey Meters, 2nd ed. 30
1993 Manual of Recommended Practice for Combustible Gas Indicators and Portable Direct-Reading Hydrocarbon Detectors, 2nd ed., ed. by C.F. Chelton 31
1993 Responding to Community Outrage: Strategies for Effective Risk Communication by P.M. Sandman 32
1993/1996 Sampling for Environmental Lead (AIHA Ad Hoc Committee on Sampling for Environmental Lead) 33
1993 The Industrial Hygienisfs Guide to Indoor Air Quality Investigations 34
1993 The Industrial Hygienist's Guide to Indoor Air Quality Investigations (AIHA Indoor Environmental Quality Committee) ed. by P.J. Rafferty 35
1994 An Ergonomics Guide to VDT Workstations by C. Grant and M. Brophy 36
1994 Cumulative Trauma Disorders of the Hand and Wrist, An Ergonomics Guide by T.J. Armstrong and E.A. Lackey 37
1994 Industrial Hygiene Auditing: A Manual for Practice by A.J. Leibowitz 38
1994 Radio-Frequency and Microwave Radiation, 2nd ed. 39
1994 The American Industrial Hygiene Association: Its History and Personalities, 1939–1990 ed. by G.D. Clayton and F.E. Clayton 40
1995 Biosafety Reference Manual, 2nd ed. (AIHA Biosafety Committee) 41
1995 Exploring the Dangerous Trades: The Autobiography of Alice Hamilton 42
1995 Extremely Low Frequency (ELF) Electric and Magnetic Fields 43
1995 Hazard Communication: An AIHA Protocol Guide 44
1995 Inorganic Lead Guidance Document by L.C. Hearn, Jr. 45
1995 Laboratory Chemical Hygiene: An AIHA Potocol Guide 46
1995 Particle Sampling Using Cascade Impactors: Some Practical Application Issues (AIHA Aerosol Technology Committee) ed. by J.Y. Young 47
1996 An Ergonomics Guide to Hand Tools (AIHA Ergonomics Committee) by R.G. Radwin and J.T. Haney 48
1996 An International Review of Procedures for Establishing Occupational Exposure Limits (Chemical Manufacturers Association and AIHA) 49
1996 Field Guide for the Determination of Biological Contaminants in Environmental Samples (AIHA Biosafety Committee) ed. by H. K. Dillon, P.A. Heinsohn, and J.D. Miller 50
1996 Field Guidelines for Temporary Ventilation of confined Spaces With an Emphasis on Hotwork by M. Harris, L. Booher, and S. Carter 51
1996 Management of People and Programs in Industrial Hygiene by F.M. Toca and D. Woodhull 52
1996 New Frontiers in Occupational Health and Safety: A Management Systems Approach and the ISO Model ed. by C.F. Redinger and S.P. Levine 53
1996 Occupational Health and Safety Management System: An AIHA Guidance Document (AIHA OHSMS Task Force) 54
1996 Particle Size-Selective Aerosol Sampling in the Workplace: Some Practical Application Issues (AIHA Aerosol Technology Committee) 55
1997 Laboratory Quality Assurance Manual, 2nd ed. (AIHA Sampling and Laboratory Analysis Committee) 56
1997 The Occupational Environment – Its Evaluation and Control ed. by S.R. DiNardi 57
1998 A Strategy for Assessing and Managing Occupational Exposures, 2nd ed. by J.R. Mulhausen and J. Damiano 58
1998 Communicating Risk in a Changing World ed. by T.L. Tinker, M.T. Pavlova, A.R. Gotsch and E.B. Arkin 59
1998 General Concepts for Nonionizing Radiation Protection (AIHA Nonionizing Radiation Committee) 60
1998 Hand-Arm Vibration: A Comprehensive Guide for Occupational Health Professionals, 2nd ed. by P.L. Pelmear and D.E. Wasserman 61
1998 ISO 14000: A Guide to the New Environmental Management Standards 62

1998 Physical Strength Assessment in Ergonomics ed. by S. Gallagher, J.S. Moore, and T.J. Stobbe 63
1998 The Quiet Sickness: A Photographic Chronicle of Hazardous Work in America by E. Dotter 64
1999 Engineering Reference Manual, 2nd ed., (AIHA Engineering Committee) ed. by F.N. Bolton and D.L. Johnson 65
1999 Safety Now! Controlling Chemical Exposures at Hazardous Waste Sites with Real-Time Measurements by C.S.E. Marlowe 66
2000 Current IAQ Practices Worldwide: Proceedings from the 4th IAQ Symposium 67
2000 Glossary of Occupational Hygiene Terms by S.R. DiNardi and W.E. Luttrell 68
2000 Guidelines of Hot Work in Confined Spaces: Recommended Practices for Industrial Hygienists and Safety Professionals by M.H. Finkel 69
2000 Investigations: A Handbook for Prevention Professionals by H.C. Woodcock and J. Seibert 70
2000 Laser Radiation by R.T. Hitchcock and R.J. Rockwell, Jr. 71
2000 Mathematical Models for Estimating Occupational Exposure to Chemicals (AIHA Exposure Assessment Committee) ed. by C.B. Keil 72
2000 Rapid Guide to Hazardous Chemicals in the Workplace, 4th ed. by R.P. Pohanish 73
2000 Risk Assessment Principles for the Industrial Hygienist by M. Jaycock, J. Lynch, and D.I. Nelson 74
2000 The Noise Manual, 5th ed. by E.H. Berger, L.H. Royster, J.D. Royster, D.P. Driscoll and M. Layne 75
2000 User's Guide to 'A Strategy for Assessing and Managing Occupational Exposures, 2nd ed.' (AIHA Exposure Assessment Committee) ed. by T.W. Armstrong and B.D. Silverstein 76
2001 Chemical–Biological Terrorism: Awareness and Response to the Threat 77
2001 Confined Space Entry: An AIHA Protocol Guide, 2nd ed. 78
2001 Hazardous Harvests: Exploring Occupational and Environmental Health and Safety Hazards of U.S. Farmworkers 79
2001 Industrial Hygiene Performance Metrics (AIHA Management Committee) 80
2001 Occupational Asthma: Can This Disease Be Controlled? 81
2001 Report of Microbial Growth Task Force 82
2001 Respiratory Protection: A Manual and Guideline, 3rd ed. (AIHA Respiratory Protection Committee) 83
2001 Synthetic Fibers in the Workplace: Where Less is Healthier 84
2001 Ultraviolet Radiation, 2nd ed. 85
2002 Chemical Safety Handbook: For the Semiconductor/Electronics Industry, 3rd ed. by D.G. Baldwin, M.E. Williams, and P.L. Murphy 86
2002 Ergonomics: From Concept to Practice-Making Ergonomics Work Proceedings from the AIHce 2001 Ergonomics Symposium 87
2002 Ergonomics: Regulations and Standards in the United States, Canada, and Europe 88
2002 Industrial Hygiene Reference & Study Guide by A. Fleeger, D. Lillquist 89
2002 The AIHA 2002 Emergency Response Planning Guidelines and Workplace Environmental Exposure Level Guides Handbook 90
2002 The Noise-Vibration Problem-Solution Workbook by L.H. Royster and J.D. Royster 91
2002 Welding Health and Safety: A Field Guide for OEHS Professionals by M.K. Harris 92
2003 Burton Field Guide for Industrial Hygiene by D.J. Burton 93
2003 Environmental Health and Safety for Hazardous Waste Sites by R.C. Barth, P.D. George and R.H. Hill 94
2003 Essential Resources for Industrial Hygiene: A Compendium of Current Practice Standards and Guidelines (AIHA Practice Standards and Guidelines Committee) ed. by M.K. Harris 95

American Institute of Chemical Engineers
(New york)

Year		Item
Ammonia Plant Safety and related series		
Survey of Operating Practices in Thirty-One Ammonium Nitrate Plants		1
1960	The Manufacture of Nitric Acid by Oxidation of Ammonia	2
1960–69	Safety in Air and Ammonia Plants, vols 2–11	13–12
1961–62	Operating Practices in Air and Ammonia Plants, vols 1–2	13–14
1964	Survey of Low Pressure Storage of Liquid Anhydrous Ammonia	15
1966	Safety in Ammonium Nitrate Plants	16
1970–94	Ammonia Plant Safety and Related Facilities, vols 12–34	17–38
Dow Chemical Exposure Index		
1994	Dow Chemical Exposure Index	39
Dow Fire and Explosion Index		
1973	Dew's Safety and Loss Prevention Guide, 3rd ed.	40
1976	Dow Fire and Explosion Index Hazard classfication Guide, 4th ed.	41
1981	Dow Fire and Explosion Index Hazard Classification Guide, 5th ed.	42

1987 Dew's Fire and Explosion Index Hazard Classification Guide, 6th ed. 43
1994 Dew's Fire and Explosion Index Hazard Classification Guide, 7th ed. 44

Loss prevention series
1967–81 loss Prevention vols 1–14 45–58
1991–93 Loss Prevention, vols 15–17 59–61

Safety in Polythene Plants
1973 Safety in High Pressure Polyethylene Plants, vol. 1 62
1974 Safety in Polyethylene Plants, vol. 2 63
1978 Safety in Polyethylene Plants, vol. 3 64

Safety and Loss Prevention Conferences
1987 International Symposium on Preventing Major Chemical Accidents 65
1987 International Conference on Vapor-Cloud Modeling 66
1989 International Symposium on Runaway Reactions 67

Other Safety Aspects
1972 AIChE Pilot Plant Safety Manual 68
1976 Fundamentals of Fire and Explosion 69
1989 Hazardous Chemicals – Spills and Waterborne Transportation 70

Chemical Process Technology
1967 High Pressure Technology 71
1968 Advances in Cryogenic Heat Transfer 72
1970 Methanol Technology and Economics 73
1972 Vacuum Technology at Low Temperatures 74
1974 Understanding and Conceiving Chemical Processes 75
1981 Tutorial Lectures in Electrochemical Engineering and Technology edited by R. Alkire and T. Beck 76
1982 Cryogenic Processes and Equipment ed. by T.H.K. Frederking *et al.* 77
1982 Uncertainty Analysis for Engineers 78
1983 Manual for Predicting Chemical Process Design Data edited by R.P. Danner and T.E. Daubert 79
1983 Tutorial Lectures in Electrochemical Engineering and Technology by R. Alkire and Der-Tau Chin 80
1985 Computer Modeling of Chemical Processes by J.D. Seader 81
1985 Plant Design and Cost Estimating 82
1986 Cryogenic Properties, Processes and Applications 1986 ed. by A.J. Kidnay and M.J. Hiza 83
1986 Measurements of Temperature in High Temperature Furnaces and Processes edited by D.P. Drewitt and L.F. Albright 84
1986 Storage Vessels and Other Equipment 85
1987 Process Operations 86

Computer-Aided Design
1981 Foundations of Computer-Aided Process Design edited R.S.H. Mah and W.D. Seider 87
1982 Selected Topics on Computer-Aided Design and Analysis edited by R.S.H. Mah and G.V. Reklaitis 88
1983 Data Base Implementation and Application edited by G.V. Reklaitis and J.J. Siirola 89

Data series
1984 Awareness of Information Sources edited by T.B. Selover and M. Klein 90
1985 Data Compilation Tables of Properties of Pure Compounds edited by T.E. Daubert and R.P. Danner 91
1986 Chemical Engineering Data Sources edited by D.A. Janowski and T.B. Selover 92

Engineering Construction Contracts series
1970–74 Engineering Construction Contracts, vols 1–6 93–98

National Conferences on Control of Hazardous Materials Spills
1974 Control of Hazardous Material Spills 99
1988 Control of Hazardous Material Spills 100

Nuclear Engineering series
1954–67 Nuclear Engineering, vols 1–18 101–118
1972 The Calculated Loss-of-Coolant Accident by L.J. Ybarrando, C.W. Solbrig and H.S. Isbin 119

Pollution, Effluent and Waste Disposal series
1967–75 Industrial Process Design for Pollution Control: 1967, vol. 1; 1970, vol. 2; 1971, vol. 3; 1972, vol. 4; 1974, vol. 5; 1974, vol. 6; 1975, vol. 7 120–126
1967–71 Industrial Process Design for Water Pollution Control: 1967, vol. 1; 1970, vol. 2; 1971, vol. 3 127–129
1968 Water – 1968 130
1969 Water – 1969 131
1971 Important Chemical Reactions in Air Pollution Control 132
1972 Air Pollution and Its Control 133
1972 Chemical Engineering Applications of Solid Waste Treatment 134
1972 Water – 1971 135
1974 Recent Advances in Air Pollution Control 136

1974 Water – 1974, Pt 1 Industrial Wastewater Treatment 137
1975 Ecosystems Technology: Theory and Practice 138
1975 Pollution Control and Clean Energy 139
1975 Sulfur Dioxide Processing 140
1975 Water – 1975 141
1976 Air Pollution Control and Clean Energy 142
1977 Water – 1977 143
1980 Hazardous Chemicals – Spills and Waterborne Transportation 144
1979 Control of Emissions from Stationary Combustion Sources: Pollutant Detection and Behavior in the Atmosphere 145
1980 Implications of the Clean Air Amendments of 1977 and of Energy Considerations for Air Pollution Control 146
1980 Lectures in Atmospheric Chemistry 147
1981 Water – 1980 edited by G.F. Bennett 148
1981 Research Trends in Air Pollution Control: Scrubbing, Hot Gas Clean-Up, Sampling and Analysis edited by R. Mahalingam and A.J. Engel 149

Equipment Testing Procedures

E-4 Continuous Rotary Direct Heat Driers (not in current list)
E-5 Centrifugal Pumps (Newtonian Liquids)
E-7 1965 Mixing Equipment (Impeller Type)
E-10 1962 Plate Distillation Columns
E-14 1968 Rotary Positive Displacement Pumps (Newtonian Liquids)
E-15 Heat Exchangers (not in current list)
E-16 1977 Fired Heaters
E-18 *c.*1977 Dry Solids, Paste and Dough Mixing Equipment, 2nd ed.
E-19 1978 Evaporators, 2nd ed.
E-20 1980 Particle Size Classifiers
E-21 1980 Centrifuges: A Guide to Performance Evaluation
E-22 1984 Centrifugal Pumps (Newtonian Liquids), 2nd ed.
E-23 1985 Continuous Direct-Heat Rotary Dryers: A Guide to Performance Evaluation, 2nd ed.
E-24 *c.*1986 Tray Distillation Columns, 2nd ed.
E-25 *c.*1986 Mixing Equipment (Impeller Type), 2nd ed.
E-26 1988 Spray Driers
E-27 1989 Fired Heaters

Center for Chemical Process Safety (CCPS)

1985 Guidelines for Hazard Evaluation Procedures 1
1987 Guidelines for Use of Vapor Cloud Dispersion Models by S.R. Hanna and P.J. Drivas 2
1988 Guidelines for Safe Storage and Handling of High Toxic Hazard Materials by A.D. Little Inc. and R. Levine 3
1988 Guidelines for Vapor Release Mitigation by R.W. Prugh and R.W. Johnson 4
1989 Guidelines for Chemical Process Quantitative Risk Analysis 5
1989 Guidelines for Process Equipment Reliability Data 6
1989 Guidelines for Technical Management of Process Safety 7
1989 Workbook of Test Cases for Vapor Cloud Source Dispersion Models by S.R. Hanna and D. Strimaitis 8
1992 Guidelines for Hazard Evaluation Procedures, rev. ed. 9
1992 Guidelines for Investigating Chemical Process Incidents 10
1992 Plant Guidelines for Technical Management of Chemical Process Safety 11
1993 Guidelines for Auditing Process Safety Management Systems 12
1993 Guidelines for Engineering Design for Process Safety 13
1993 Guidelines for the Safe Automation of Chemical Processes 14
1994 Guidelines for Evaluating the Characteristics of Vapor Cloud Explosions, Flash Fires and BLEVEs 15
1994 Guidelines for Implementing Process Safety Management Systems 16
1994 Guidelines for Preventing Human Error in Process Safety 17

Design Institute for Emergency Relief Systems (DIERS)

1987 Safety Valve Stability and Capacity Test Results: Pressure Relief Valve Performance Study. Final Report 150
1992 Emergency Relief Design Using DIERS Technology 151
1992 Emergency Relief Systems for Runaway Chemical Reactions and Storage Vessels: A Summary of Multiphase Flow Methods 152
1992 Bench-Scale Apparatus Design and Test Results 153
1992 Small/Large Scale Experimental Data and Analysis 154
1992 SAFIRE Computer Program and Documentation 155

Design Institute for Physical Property Data (DIPPD)

1987 Manual for Predicting Chemical Process Design Data ed. by R.P. Danner and T.E. Daubert 156
This Manual is supplemented by a series of Documentation Manuals, detailing the basis for selection of the contents of chapters in the Manual
1985 Experimental Results from the Design Institute for Physical Property Data,1: Phase Equilibria ed. by M.S. Benson and D. Zudkevich 157
1987 Experimental Results from the Design Institute for Physical Property Data,1: Phase Equilibria and Pure Component Properties ed. by C. Black 158

1989	Experimental Results from the Design Institute for Physical Property Data,1: Phase Equilibria and Pure Component Properties – R II ed. by T.T. Shih and D.K. Jones	159

American Oil Company (AMOCO)
(Chicago, IL)

Refinery	*Process Safety Booklets*	*Item*
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3	Safe Furnace Firing	3
4	Safe Ups and Downs	4
5	Hazard of Electricity	5
6	Hazard of Steam	6
7	Safe Handling of light Ends	7
8	Engineering for Safe Operation	8
9	Safe Operation of Air, Ammonia and Ammonium Nitrate Plants	9
10	Safe Operation of Refinery Steam Generators and Water Treating Facilities	10

American Petroleum Institute
(New York)

EA 7301	Guidelines on noise
EA 7102	The chronic toxicity of lead by D.C. Jessup *et al.*
EA 7402	A mortality study of petroleum refinery workers by Tabershaw–Cooper Associates
69–7	A review of the toxicology of lead by T.J. Haley
75–25	Review of inhalation toxicology of sulphuric acid and sulphates by M.C. Battigelli and J.F. Gamble
Bull. 2516	Evaporation loss from low pressure tanks, 1962
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Association of British Chemical Manufacturers
(London)

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British Chemical Industry Safety Council
(London)

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6 A Guide to Analysis of Plant Training Needs, 1971
7 A Guide to Operator Job Analysis, 1971
8 A Guide to Fault Analysis, 1971
9 A Guide to the Preparation of a Training Programme, 1971
10 Safety Training, 1971
13 A Basic Course for Adult Entrants with Chemical Process Operations and an Example Training Unit – Distillation, 1972
16 Health and Safety at Work – Everybody's Concern, 1975
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		Item
	British Chemicals and Their Manufacturers	1
	Transport Emergency Card (TREMCARD), Manuals, Vols 1–2	2
1970	The Rising Cost of Fire	3
1973	Chemical Industries Association and Chamber of Shipping of the UK: Code of Practice for the Safe Carriage of Dangerous Goods in Freight Containers	4
1973	Road Transport of Hazardous Chemicals: Manual of Safety Requirements	5
1973	CHEMSAFE: Manual of the Chemical Industry Scheme for Assistance in Freight Emergencies	6
1974	Chemical Industries Association and Confederation of British Industry: Company Safety and Health Practices – CBI Guide for Employers	7
1975	Code of Practice for the Large Scale Storage of Fully Refrigerated Ammonia in the United Kingdom	8
1975	Code of Practice for the Safe Handling and Transport of Anhydrous Ammonia by Road in the United Kingdom	9
1975	Determination of Vinyl Chloride	10

1978 Guide to Storage and Use of Highly Flammable Liquids
1978 Precautions against Fire and Explosion: Vinyl Chloride
1980 Code of Practice for the Storage of Anhydrous Ammonia under Pressure in the United Kingdom
1980 Guidelines for Bulk Handling of Chlorine at Consumer Installations
PA1 Anhydrous Ammonia – Code of Practice for Transport by Rail, 1975
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PA3 Benzene – Health Precaution Guidelines, 1980
PA8 Chlorine – Safety Advice for Bulk Installations (HS/G 28)
PA9 CIMAH Safety Case – Ammonia, 1988
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RC11 COSHH – Guidance on Health Surveillance, 1989
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RC13 Employment and Reproductive Health, 1984
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RC17 Guidelines on Waste Management – 3, Management of Wastes at Production Sites, 1989
RC18 Hazard and Operability Studies, 1977
RC19 Liability Insurance. Models Forms and Guidance, 2nd ed., 1989
RC20 Recommended Procedures for Handling Major Emergencies, 1976
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RC21 An Approach to the Categorisation of Process Plant Hazard and Control Building Design, 1979
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(London)

Year		Item
1975–	Quarterly Safety Summary	5
1976	Recommended Procedures for Handling Major Emergencies, 2nd ed.	6
1977	Hazard and Operability Studies	7

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005	Non-Refrigerated Liquid Chlorine Storage 6th ed., 1998
006	Piping Systems for Dry Chlorine 14th ed., 1998
008	Chlorine packaging manual, 5th ed., 1985
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063	First Aid and Medical Management of Chlorine Exposures, 6th ed., 1998
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065	Personal Protective Equipment for Chlor-Alkali Chemicals, 4th ed., 2001
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089	Chlorine Scrubbing Systems, 2nd ed., 1998
090	Molecular chlorine: Health and Environmental Effects, 2nd ed., 1998
098	Recommended Practices for Handling Hydrochloric Acid in Tank Cars, 2nd ed., 2001
099	Hydrogen Chloride, Anhydrous – Use, Handling, & Transportation of Cylinders or Tube Trailers, 2nd ed., 2001
121	Explosive Properties of Gaseous Mixtures Containing Hydrogen and Chlorine, 2nd ed., 1992
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161	Guidance Document: Risk Management for Hydrogen Chloride, 1998
162	Generic Risk Management Plan for Chlorine Packaging Plants & Sodium Hypochlorite Production Facilities, 1996
163	Hydrochloric Acid Storage and Piping Systems, 2001

164	Reactivity and Compatibility of Chlorine and Sodium Hydroxide with Various Materials, 2001
167	Learning From Experience, 2002

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BIBCL	Chlorine: an annotated bibliography, 1971
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CPP	Chlorine production processes ed. by J.S. Robinson, 1981
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IB/A	Instruction Booklet: Chlorine Institute Emergency Kit 'A' for 100-lb. & 150-lb. Chlorine Cylinders, 9th ed., 1996
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G-1.2	Acetylene Metering and Pipeline Transmission, 2000
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G-2	Anhydrous Ammonia, 1995
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G-3	Sulfur Dioxide, 1995
G-4	Oxygen, 1996
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G-4.3	Commodity Specification for Oxygen, 2000
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G-4.8	Safe Use of Aluminum-Structured Packing for Oxygen Distillation, 2000
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G-6.7	Safe Handling of Liquid Carbon Dioxide Containers That Have Lost Pressure, 1996
G-6.9	Dry Ice, 1998
G-7	Compressed Air for Human Respiration, 1990
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G-12	Hydrogen Sulfide, 1996
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P-8	Safe Practices Guide for Air Separation Plants,1989
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P-9	The Inert Gases: Argon, Nitrogen, and Helium, 2001
P-11	Metric Practice Guide for the Compressed Gas Industry, 1998
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P-13	Safe Handling of Liquid Carbon Monoxide, 2nd ed., 1989
P-14	Accident Prevention in Oxygen-Rich and Oxygen-Deficient Atmospheres, 1983
P-16	Recommended Procedures for Nitrogen Purging of Tank Cars, 1992
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CONCAWE

(The Hague, The Netherlands)

General Interest Reports (Yellow covers)

2/70	Corrosion: protection and inspection
3/70	Prevention of water pollution from refineries
9/70	Pollution of permeable strata by oil components
9/71	Migration of oil in soil
4/72	Surveying air pollution around oil refineries
5/73	Current methods of routine testing and leak detection in operating oil pipelines
4/74	Inland oil spill clean-up manual
2/75	Incineration of refinery wastes
3/75	Sampling of refinery liquid effluents
8/75	The identification and measurement of refinery odours
2/76	Determination of sound power levels of industrial equipment, particularly oil industry plant
6/76	Effluents and emissions from European refineries
2/77	Published regulatory guidelines of environmental concern to the oil industry in Western Europe
3/77	Test method for the measurement of noise emitted by furnaces for use in the petroleum and petrochemical industries
8/77	Measurement of vibrations complementary to sound measurement
9/77	Spillages from oil industry cross-country pipelines in Western Europe. Statistical summary of reported incidents
3/79	Protection of groundwater from oil pollution
5/79	The environmental impact of refinery effluents
9/80	Disposal techniques for spilt oil
4/81	The propagation of noise from petroleum and petrochemical complexes to neighbouring communities
7/81	Revised inland oil spill clean-up manual
9/81	A field guide to coastal oil spill control and clean-up techniques
8/82	Ecological monitoring of aqueous effluents from petroleum refineries
10/82	Methodologies for hazard analysis and risk assessment in the petroleum refining and storage industry
7/83	Guidelines for recording industrial hygiene data
10/83	A field guide to inland oil spill clean-up techniques
4/85	Investigations into the relationships between the chemical composition of mineral oils and their ability to cause skin cancer in mice
5/85	Strategies for the assessment of the biological impacts of large coastal oil spills – European coasts
7/85	Workplace noise and hearing conservation
2/86	Volatile organic compound emissions: an inventory for Western Europe
3/86	The health experience of workers in the petroleum manufacturing and distribution industry
2/87	Review of European oil industry benzene exposure data
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7/87	Health aspects of toluene and xylene exposures associated with motor gasoline

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2/88	A field guide to the application of dispersants to oil spills
5/88	Emergency planning guidance notes – Content of emergency plans/Planning for mutual aid
6/88	Emergency planning guidance notes – Refinery emergency planning
2/89	Emergency planning guidance notes – Training, exercises and rehearsal of emergency plans/Communications during emergencies
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5/90	A field guide on reduction and disposal of waste from oil refineries and marketing installations
4/92	Performance of oil industry cross-country pipelines in Western Europe – statistical summary of reported spillages 1991
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7/98	The SEVESO II directive and the oil industry
8/98	Trends in oil discharged with aqueous effluents from oil refineries in Europe – 1997 survey
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4/01	Performance of cross-country oil pipelines in Western Europe statistical summary of reported spillages – 2000
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7/02	Assessment of personal inhalation exposure to bitumen fume guidance for monitoring benzene-soluble inhalable particulate matter
8/02	Method for monitoring exposure to gasoline vapour in air – revision 2002
9/02	A survey of European gasoline exposures for the period 1999–2001
2/03	Catalogue of CONCAWE reports

Special Interest Reports (White covers)

84/52	Recommended practice for investigating and dealing with
84/54	Petroleum hydrocarbons: their absorption through and effect on skin
84/55	The study of noise from steel pipes
84/64	Experimental verification of the ISVR pipe noise model
86/69	Health aspects of worker exposures to oil mists
87/52	Cost-effectiveness of hydrocarbon emission controls in refineries from crude oil receipt to product dispatch
87/57	Review of strategies for the evaluation of employee exposures to substances hazardous to health
87/59	The prediction of noise radiating from pipe systems – an engineering procedure for plant design
88/56	Quantified risk assessment
89/53	Health risks from working in petroleum refining and from gasoline – a critique and recommendations in response to IARC monograph volume 45
89/55	Review of EC health and safety directives
90/53	An assessment of occupational exposure to noise in Western European oil refineries
91/53	The role of epidemiology in the health assessment of petroleum industry employees
91/55	The European Community legislative process
92/55	The EC Safety Data Sheet Directive
93/52	Industrial hygiene seminar
95/60	Determination of air quality standards bands for ozone
95/62	Air quality standard for particulate matter
96/54	Development of a health surveillance programme for workers in the downstream petroleum industry
96/63	Scientific basis for an air quality standard on benzene
97/51	Scientific basis for an air quality standard for carbon monoxide complaints about noise
00/52	Management of occupational health risks during refinery turnarounds
01/52	A noise exposure threshold value for hearing conservation
01/56	An assessment of occupational exposure to noise in the European oil industry (1989–1999)
02/57	Catalogue of special interest reports

Department of Employment (HM Factory Inspectorate)
(London: HM Stationery Office)

Methods for the Detection of Toxic Substances in Air Booklets

Superseded by HSE MSDS series *Methods for the Determination of Hazardous Substances*

Other publications		Item
1971	Manhole Access in Enclosed Plant	1
1972	The Factories Act 1961. A Short Guide	2
1973	Lead: Code of Practice for Health Precautions	3
1974	Precautions in the Use of Asbestos in the Construction Industry	4
1974	Safety of Scaffolding	5

Department of the Environment
(London: HM Stationery Office)

Circulars

1/72	Development Involving the Use or Storage in Bulk of Hazardous Materials, 1972
22/80	Development Control – Policy and Practice, 1980
9/84	Planning Controls over Hazardous Development, 1984
22/84	Memorandum on Structure and Local Plans, 1984
15/88	Environmental Assessment, 1988

Pollution Papers

1	The Monitoring of the Environment in the United Kingdom, 1974
2	Lead in the Environment and its Significance to Man, 1974
4	Controlling Pollution, 1973
8	Accidental Oil Pollution of the Sea, 1976
9	Pollution Control in Great Britain: How it Works, 1976
10	Environmental Mercury and Man, 1976

Other publications	*Item*
Code of Practice for Reducing the Exposure of Employed Persons to Noise, 1972	1
Towards Cleaner Air, 1973	2
Information about Industrial Emissions to the Atmosphere, 1973	3
Clean Air Today, 1974	4
Code of Practice for the Carriage of Radioactive Materials by Road, 1975	5
Railway accident. Report on the accident that occurred on February 18, 1975, at Moorgate Station on the Northern line, London Transport Railways, 1976	6

Department of Trade and Industry (DTI)
(London)

05/1998	UK chemicals regulatory atlas: an overview of how to guide your chemical through to regulatory compliance.
07/2000	BioGuide: regulations, information and support for biotechnology in the UK (2nd edition).
03/2003	Biotechnology regulatory atlas: an overview of modern biotechnology regulation and how to achieve compliance.

Det Norske Veritas
(Stavanger, Norway)

Research Division Technical Reports

79-0483	Experimental investigations of partly confined gas explosions by D.M. Solberg, J.A. Pappas and E. Skramstad, 1979
83-1317	BLOW-DOWN – a computer program for dynamic analysis of hydrocarbon processes by J. Nylund, 1983

Electrical Equipment Certification Service (closed 09/2002)
(Sheffield)

EECG2	Electrical Equipment Certification Guide, 1992
SEA 3009	Special Protection
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Electrical Power Research Institute
(Palo Alto, CA)

EPRI NP-613	On-line power plant alarm and disturbance analysis system. Interim report by B. Frogner and C.H. Meijer, 1978
EPRI NP-1379	On-line power plant alarm and disturbance analysis system. Final report by C.H. Meijer, 1980
EPRI NP-1684	Summary and evaluation of scoping and feasibility studies for disturbance analysis and surveillance systems (DASS) by A.B. Long *et al.* 1980

Engineering Equipment Users Association
(London) (predecessor to Engineering Equipment and Materials Users Association, q.v.)

Handbooks

7	Factory Stairways, Ladders and Handrails, rev. ed., 1973
8	Steam Trapping and Condensate Handling, rev. ed., 1962
9	Agitator Selection and Design, rev. ed., 1962
10	Ball and Roller Bearings (Rolling Bearings), rev. ed., 1965
11	Vacuum Producing Equipment, 1961
12	Thermal Insulation of Pipes and Vessels, 1963
15	Pneumatic Handling of Powdered Materials (including Fluidization), 1963
18	Supporting Mild Steel and Cast Iron Pipe, 1963
19	Separation of Dust from Gases, 1968
23	Pipe Joining Methods, 1968
25	Measurement and Control of Noise, 1968

26 Electrically Driven Glandless Pumps, 1968
27 Dynamic Sealing of Rotating and Reciprocating Shafts, 1971
29 Electrical Variable Speed Drives, 1968
32 The Selection of Automatic Control Valves, 1969
34 Installation of Instrumentation and Process Control Systems, 1973

Documents
4 The Use of Power Driven Portable Tools (with particular reference to their use where there may be fire or explosion risk), 1958
9 Minimum Safety Requirements for Instruments Using Electricity, 1959
12 Recommendations to Facilitate Rescue from Confined Spaces, 1962
15 Fixing of Machines in Corrosive Conditions, 1960
17 The Built-in Thermal Protection of Induction Motors to BS 2960, 1964
23 EEUA Piping Data Sheets, 1965–69
30 Materials Handling Systems and Equipment, 1965
33 Guide to Safe Design and Use of Industrial Electronic Equipment, 1969
37 The Effect on Instrument Performance of Variations in 50 Hz Mains Power Supply
45 Performance Requirements for Electrical Alarm Annunciator Systems, 1972
46 Performance Requirements for Electrical Initiating Devices for Electrical Alarm Annunciators, 1975
47 Electrical Apparatus for Use in Explosive Dust Hazards, 1973

Engineering Equipment and Materials Users Association (London)

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101 Lifting Points – A Design Guide, 1984
104 Noise: a guide to information required from equipment vendors, 1985
105 Factory Stairways, Ladders and Handrails, 2002
107 Recommendations for the Protection of Diesel Engines for Use in Zone 2 Hazardous Areas, 1992
132 Three-phase cage induction motors, rev. 1988
133 Underground armoured cable protected against solvent penetration and corrosive attack, rev., 1988
138 Design and installation of on-line analyser systems, rev., 1988
141 Guide to the use of noise procedure specification, 1980
143 Recommendations for tube end welding: tubular heat transfer equipment. Pt 1 – ferrous materials, 1977
144 90/10 copper nickel pipe for offshore applications: seamless and welded, 1987
145 90/10 copper nickel pipe for offshore applications: flanges – composite and solid, 1987
146 90/10 copper nickel pipe for offshore applications: fittings, 1987
147 Recommendations for the Design and Construction of Refrigerated Liquefied Gas Storage Tanks, 1986
148 Reliability Specification – Model clauses for inclusion in purchasing specifications for equipment items and packages, 1986
148 Code of Practice for the Identification and Checking of Materials of Construction Pressure Systems in Process Plants, 1997
149 Code of practice for the identification and checking of materials of construction in pressurised systems in process plants, 1986
153 EEMUA supplement to ASME/ANSI B31.3 – 1987 edition, including B31.3a – 1988, B31.3b – 1988 and B31.3c – 1989 for chemical plant and petroleum refinery piping, 1989
154 Guidance to Owners on Demolition of Vertical Cylindrical Steel Storage Tanks and Storage Spheres (2nd edition), 2002
155 Standard Test Method for Comparative Performance of Flammable Gas Detectors Against Poisoning, 1988
158 Construction specification for fixed offshore structures in the North Sea, 1989
159 Users' Guide to the Maintenance and Inspection of Above-ground Vertical Cylindrical Steel Storage Tanks, 1994 (2nd edition 1997 incorporating Amendment No. 1 and minor textual corrections)
161 A guide to the selection and assessment of silencers, 1988
166 Specification for line pipe for offshore, 1991
167 EEMUA specification for quality levels for carbon steel valve casing
168 A guide to the pressure testing of in-service pressurised equipment
178 A Design Guide for the Electrical Safety of Instruments, Instrument/Control Panels and Control Systems, 1994
180 Guide for Designers and Users on Frangible Roof Joints for Fixed Roof Storage Tanks, 1996
183 Guide for the Prevention of Bottom Leakage from Vertical, Cylindrical, Steel Storage Tanks, 1999
186 A Practitioner's Handbook – Electrical Installation and Maintenance in Potentially Explosive Atmospheres, 1997
189 A Guide to Fieldbus Application for the Process Industry, 1997
190 Guide for the Design, Construction and Use of Mounded Horizontal Cylindrical Vessels for Pressurised Storage of LPG at Ambient Temperatures, 2000
191 Alarm Systems – A Guide to Design, Management and Procurement, 1999
193 EEMUA Recommendations for the Training, Development & Competency Assessment of Inspection Personnel, 1999
194 Compendium of EEMUA Information Sheets on Topics Related to Pressure Containing Equipment, 1999
199 On-Line Leak Sealing of Piping – Guide to Safety Considerations
201 Process Plant Control Desks Utilising Human-Computer Interfaces – A Guide to Design, Operational and Human Interface Issues, 2002

Environmental Protection Agency
(New York)

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EPA Training Manuals	1
Standard Operating Safety Guides, 1988	2

See also Reference List

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16215	Evaluation of protection from explosion overpressure in AEC gloveboxes by C. Yao, J. de Ris and S.N. Bajolai, 1969	1
	Explosion venting of low strength equipment and structure by C. Yao, 1973	2

Fire Protection Association
(London)

Compendium of Fire Safety Data (CFSD)

Vol. 1

Organization of fire safety

OR 01	Fire Safety Structure in the United Kingdom, 1990
OR 1	Fire Protection Law, 1989
OR 2	The Fire Service, 1988
OR 3	The Health and Safety Commission and the Health and Safety Executive, 1989
OR 4	Government Departments, 1978
OR 5	Fire Research of fire risks
OR 6	Fire Test Facilities, 1991
OR 7	Security Organizations, 1989

Management of fire risks

MR 2	Fire Safety and Security Planning in Industry and Commerce, 1989
MR4	Fire Safety Patrols, 1989
MR5	Security against Fire-Raisers
MR6	Fire Precautions during Stoppages of Work, 1989
MR7	Procedure in Event of Fire, 1990
MR8	Fire Damage Control: Emergency Planning, 1987
MR9	First Day Induction Training, 1989
MR10	Fire Safety Training,
MR11	Occupational Fire Brigades and Fire Teams: Organization, Role and Functions
MR12	Fire Safety Education and Training of People at Work, 1987
MR14	Occupational Fire Brigades: Reports and Report Writing, 1989

Vol. 2

Industrial and process fire safety

FS 6011	Flammable Liquids and Gases: Explosion Hazards, 1989
FS 6012	Flammable Liquids and Gases: Explosion Control, 1989
FS 6013	Flammable Liquids and Gases: Ventilation, 1979
FS 6014	Flammable Liquids and Gases: Electrical Equipment, 1990
FS 6015	Explosible Dusts, Flammable Liquids and Gases: Explosion Suppression, 1974
FS 6016	Hydraulic Oil Systems Fire Safety, 1976
FS 6017	Piped Services, 1982
FS 6018	Corrosive Smoke: Planning to Minimize the Acid Damage Hazard, 1989
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FS 6027	Bund Walls for Flammable Liquid Storage Tanks, 1990
FS 6028	Safety Containers for Flammable Liquids, 1987
FS 6029	Reduced Sparking Tools (Non-Sparking Tools), 1989
FS 6033	Crushing and Grinding
FS 6034	Reciprocating Compressors
FS 6041	Flammable Liquids and Gases: Application of the HAZCHEM Code to These and Other Substances, 1989
FS 6042	Oil-Fired Installations, 1989

(also Fire safety in various processes)

Occupancy fire safety
(Fire safety in other industries, occupancies and activities)

Vol. 3

Housekeeping and general fire precautions

GP 1	Guide to Fire Prevention with Outside Contractors (withdrawn)
GP 2	Cutting and Welding, 1990
GP 3	Hot Work Permits, 1989
GP 4	Blowlamps
GP 5	Safe Practice in Production Areas, 1988
GP 6	Safe Practice in Storage Areas, 1988
GP 7	Outdoor Storage, 1986
GP 8	Fire Dangers of Smoking, 1989
GP 9	Waste Incinerators, 1987
GP 10	Oil Soaked Floors, 1983
GP 11	Fire Doors and Shutters: Use Care and Maintenance, 1990

Nature and behaviour of fire

NB 1	The Physics and Chemistry of Fire, 1989
NB 2	Ignition, Growth and Development of Fire, 1988
NB 3	The Physiological Effects of Fire, 1989
NB 4	The Combustion Process, 1985
NB 5	Autoignition Temperature (AIT), 1984
NB 6	Ignition of Flammable Gases and Vapours by Sparks from Electrical Equipment, 1984

Vol. 4

Information sheets on hazardous materials

H1	Acetone, 1986
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H174	Dimethyl carbonate, 1992

Vol. 5

Fire protection equipment and systems

PE 1 Automatic fire detection and alarm systems, 1989
PE 2 Fire points, 1988
PE 3 Fire blankets, 1988
PE 4 Portable fire extinguishers, 1990
PE 5 First-aid fire fighting: training, 1989
PE 6 The choice of fixed fire extinguishing systems, 1990
PE 7 Hose reels, 1988
PE 8 Hydrant systems, 1989
PE 9 Automatic sprinklers: an introduction, 1989
PE 10 Automatic sprinklers: components of a system (withdrawn)
PE 11 Automatic sprinklers: design and installation, 1989
PE 12 Automatic sprinklers: care and maintenance, 1989
PE 13 Automatic sprinklers: safety during sprinkler shutdown, 1985
PE 17 Automatic fire ventilation systems, 1989

Security precautions

SEC 1 Security equipment and systems, 1990
SEC 2 Site layout, 1990
SEC 3 Fences, gates and barriers, 1990
SEC 4 External security lighting, 1985
SEC 5 External closed circuit television systems, 1990
SEC 6 Doors, 1985
SEC 7 Windows and rooflights, 1985
SEC 8 Access control, 1991
SEC 9 Locks (withdrawn)
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Arson

AR 1 Management guide to fire
AR 2 Prevention and control of arson in warehouse and storage buildings, 1992
AR 4 Incendiary devices: information and guidance, 1990
AR 5 Investigation of vehicle fires

Vol. 6

Building and fire

Design guides

FPDG1 Fire prevention design guide: fire and the law, 1989
FPDG2 Fire prevention design guide: site requirements – space separation (withdrawn)
FPDG3 Fire prevention design guide: control of fire and smoke within a building, 1990
FPDG4 Fire prevention design guide: planning means of escape
FPDG5 Fire prevention design guide: fire fighting facilities for the fire brigade (withdrawn)
FPDG6 Fire prevention design guide: equipment for detection and warning of fire and fighting fire, 1991
FPDG7 Fire prevention design guide: fire hazard assessment, 1990
FPDG8 Fire prevention design guide: fire insurance (withdrawn)
FPDG9 Fire prevention design guide: building services, 1990
FPDG10 Fire prevention design guide: cavities and voids in building construction
FPDG11 Fire prevention design guide: suspended ceilings (withdrawn)
FPDG12 Fire prevention design guide: construction of roofs
FPDG13 Fire prevention design guide: flame retardant treatment for wood and its derivatives, 1990
FPDG14 Fire prevention design guide: fire doors and shutters
FPDG15 Fire prevention design guide: upgrading factory buildings to control fire spread
FPDG16 Air conditioning and ventilating systems, 1989

Building products

Fire properties of building products, including
B 15 Fire resistant glazing – wired glass, 1984
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Fire Safety Sheets

S3 Waste incinerators
S4 1973 Oil-soaked floors
S5 1974 Safety containers for flammable liquids
S6 1974 Fire points
S7 1974 Protection of records, plans and documents
S8 1974 Heat treatment baths
S9 Safe practice in storage areas
S10 1975 Safer practice in production areas
S11 1975 Non-sparking tools

Other publications		*Item*
1964	Storage and handling of liquefied petroleum gas	1
1964	Planning fire safety in industry	2
1965	Checklist: fire safety in industry	3
1965	What is fire?	4
1968	Guide to fire prevention in the chemical industry	5
1968	Planning guide to fire safety with electricity	6
1969	Fire prevention manual for the iron and steel industry	7
1969	Planning guide to procedures in case of fire	8
1970	Fire protection for high bay warehouses	9
1970	Planning guide to fire safety when you have outside contractors in	10
1970	Planning guide to safety during sprinkler shutdown	11
1970	Planning guide to the safe handling of flammable gases	12
1970	Study report on fire risks and fire protection in automated high bay warehouses	13
1971	Background notes on fire and its control	14
1971	The fire hazards and safe disposal of waste	15
1972	Fire precautions during stoppages of work at factories	16
1972	Guide to safety in storage	17

1972 Management strategy for fire 18
1972 Planning guide to security against fire raisers 19
1973 Guide to how factory buildings can be adapted to control fire spread 20
1973 Guide to safety with piped services 21
1974 Fire and related properties of industrial chemicals 22
1974 Guide and check list to first day induction training 23
1974 Guide to fire doors and shutters 24
1974 Guide to safety with electrical equipment 25
1974 Planning program for the prevention and control of fire 26
1975 Anatomy of a disaster 27

Fire Research Station
(London: HM Stationery Office)

Fire Notes
F1 Fire Resistance of Floors and Ceilings by G.I. Bird, 1961
F3 Roofs and Fire
F4 Tests on Roof Construction Subjected to External Fire
F5 Fire Venting in Single-Storey Buildings by G.J. Langdon-Thomas and P.L Hinkley, *c.*1965
F6 Fire Resistance of Brick and Block Walls by H.L. Malhotra
F8 Fire and the External Wall by G.J. Langdon-Thomas and M. Law, 1966

Fire Research Technical Papers
5 Heat Radiation from Fires and Building Separation by M. Law, 1963
10 Design of Roof Venting Systems for Single-Storey Buildings by P.M. Thomas and P.L. Hinkley, *c.*1964
15 The Temperature Attained by Steel in Building Fires by E.G. Butcher, T.B. Chitty and L.A. Ashton, 1966
21 Explosibility Tests for Industrial Dusts, 2nd ed., by M.M. Raftery, 1975

Fire Research Notes
298 The venting of explosions in duct systems. Part II, The venting of explosions in pentane–air mixture in a duct 6 ft long × 6 in. diameter by D.J. Rasbash and Z.W. Rogowksi, 1956
516 On the size and orientation of buoyant diffusion flames and the effect of wind by P.M. Thomas, R.W. Pickard and H.G.H. Wraight, 1963
600 Fire spread in wood cribs. Pt III, The effect of wind by P.M. Thomas
609 Fire protection of liquid fuel storage by P.M. Thomas and M. Law, 1965
658 The protection of equipment with flame arresters: 2, Effect of contents, and use of improved arresters by K.N. Palmer and Z.W. Rogowski, 1967
759 The relief of gas and vapour explosions in domestic structures by D.J. Rasbash, 1969
760 Use of mechanical ventilation to reduce explosion hazards in high flats by K.N. Palmer, 1969
810 The behaviour of automatic fire detection systems by J.F. Fry and C. Eveleigh, 1970
820 Gas explosions in dwellings, 1969: material damage and injuries by E.D. Chambers
830 Dust explosion venting – a reassessment of the data by K.N. Palmer
847 Gas explosions in multiple compartments by D.J.Rasbash, K.N. Palmer, Z.W. Rogowksi and S.A. Ames, 1971
899 Considerations of the fire size to operate and the water distribution from automatic sprinklers by M.J. O'Doghtery and P. Nash, 1971
909 Some notes on the mathematical analysis of safety by R. Baldin, 1972
910 Extreme value theory and fire losses by G. Ramachandran, 1972
913 The thermal decomposition behaviour of some commercially available flexible polyurethane foams by W.D. Woolley, A.I. Wadley and P. Field, 1972
914 Experiments with sprinklers in high-racked storages. 2, Extinction with face-mounted sprinklers by P. Nash, N.W. Bridge and R.A. Young, 1972
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920 Fires in oil refineries and outdoor chemical plant in 1969 by S.E. Chandler, 1972
921 The projection of flames from burning buildings by P.M. Thomas and M. Law, 1972
925 Compatibility of fluorochemical and protein fire-fighting foams by T.B. Chitty, D.J. Griffiths and J.G. Corrie, 1972
929 An application of the theory of extreme values for estimating the delay in the discovery of a fire by G. Ramachandran, 1972
931 Performance of metal foam as a flame arrester when fitted to gas explosion relief vents by Z.W. Rogowski and S.A. Ames, 1972
932 Failure rates of automatic fire detection and alarm systems by E.D. Chambers, 1972
937 The safety of hot self-heating materials in cool surroundings – a method of analysis by P.M. Thomas, 1972
938 The performance of some portable gas detectors with aviation fuel vapours at elevated temperatures. Pt 1 – Tests with n-hexane, 'AVTAG' and 'CIVGAS' vapours by P.J. Fardell, 1972
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959 Preliminary experiments on the use of water additives for friction reduction in fire hoses by P.F. Thorne and K. Jordan, 1973
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980 Storage properties of four foam liquids (Final report) by S.P. Benson, D.J. Griffiths, D.M. Tucker and J.G. Corrie, 1973
981 The risk of dying by fire by M.A. North, 1973
982 The economics of accident prevention – explosions by S.K.D. Coward, 1973
984 Gas explosions in buildings. Pt 1, Experimental explosion chamber by P.S. Tonkin and C.F.J. Berlemont, 1974
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992 Dust explosion hazards in pneumatic transport by K.N. Palmer, 1973
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1011 Some statistics of fire in road vehicles by N.A. North, 1974
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1019 Pressures produced by gas explosion in a vented compartment by R.N. Butlin and P.S. Tonkin, 1974
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1037 Performance of a two element crimped ribbon flame arrester by Z.W. Rogowski and A. Pitt
1044 The evaluation of an improved method of gas-freeing an aviation fuel storage tank by P.J. Fardell and B.W. Houghton, 1975
1048 The inhalation toxicity of polyvinyl chloride pyrolysis products by P.C. Bowes, J.A.C. Edginton and R.D. Lynch
1054 Estimation of maximum explosion pressure from damage to surrounding buildings. Explosion at Mersey House, Bootle, 28 August 1975 by R.N. Butlin, 1976
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1078 The construction of flammability diagrams from flash-point measurements by P.F. Thorne and A.A. Briggs, 1978

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Gas Council
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GC23 Explosion reliefs for industrial drying ovens by P.A. Cubbage and W.A. Simmonds, 1955
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GE Employers Reinsurance Corporation
(Overland Park, KS)

GE GAP Guidelines

GAP.1.0.1	A Management Program for The Protection of Property, Production and Profits
GAP.1.0.1.A	Suggested Written Statement of Corporate Management Policy Regarding Loss Prevention and Control
GAP.1.0.2	Management of Change
GAP.1.0.2.1	Replacement in Kind
GAP.1.0.2.2	Processing Requests for Change
GAP.1.0.2.3	Request for Change Forms
GAP.1.0.2.4	Auditing Management of Change
GAP.1.0.2.5	Measuring Management of Change Performance
GAP.1.0.2.6	Management of Change at Small Facilities
GAP.1.0.3	The Year 2000 (Y2k) Problem
GAP.1.0.3.A	Examples of Date Fields
GAP.1.0.3.B	Example of Hardware/Software/System Inventory Information
GAP.1.0.3.C	What Specific Fixes Exist?
GAP.1.0.4	Outside Contractors
GAP.1.1.0	Impairments to Fire Protection Systems
GAP.1.1.0.A	Elements of Rsvp (Restore Valves Promptly) Program
GAP.1.2.0	Smoking Regulations
GAP.1.3.0	Maintenance
GAP.1.3.0.A	Maintenance Inspections
GAP.1.3.0.B	Maintenance Information Systems
GAP.1.3.0.C	Seasonal Maintenance
GAP.1.3.0.1	Maintenance Program Elements
GAP.1.3.0.2	Maintenance Program Evaluation
GAP.1.3.1	Infrared Inspection
GAP.1.3.2	Life Extension
GAP.1.4.0	Employee Training
GAP.1.5.0	New Construction
GAP.1.5.0.A	Loss Control During Construction
GAP.1.5.0.B	Design, Installation and Testing of Pressure Equipment and Machinery
GAP.1.5.2	Mechanical Equipment Design and Installation
GAP.1.6.0	Insurance Company Recommendations
GAP.1.7.0	Pre-Emergency Planning
GAP.1.7.0.A	Emergency Assessment and Resources
GAP.1.7.0.B	National Emergency Radio Frequencies
GAP.1.7.0.1	Emergency Action Plans
GAP.1.7.0.1.A	Emergency Action Plan Forms
GAP.1.7.0.2	Emergency Response Teams and Incident Management Systems
GAP.1.7.0.2.A	Emergency Response Team Forms
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BPM 1	Best practicable means: an introduction, 1984
BPM 3	Petroleum works (PVC polymer plants), 1979
BPM 4	Hydrofluoric acid works (HE manufacture),1980
BPM 5	Hydrochloric acid works, 1981
BPM 10	Amines works, 1981
BPM 11	Chemical incineration works, 1981
BPM 16	Lead works, 1986

Construction Sheets

15	Confined spaces, 1991

Contract Research Reports

CRR 1/1987	Noise exposure and hearing: a new look at experimental data
CRR 5/1988	Hazard evaluation by thermal analysis
CRR 15/1989	Evaluation of the human contribution to pipework and in-line equipment failure frequencies
CRR 17/1988	Workbook on the dispersion of dense gases
CRR 20/1990	Statutory employee involvement in health and safety at the workplace: a report of the implementation and effectiveness of the Safety Representatives and Safety Committees Regulations 1977
CRR 26/1991	Guidance on HAZOP procedures for computer-controlled plants
CRR 28/1991	Investigations of machinery noise reduction at source
CRR 31/1992	Shiftwork, health and safety: an overview of the scientific literature
CRR 33/1992	Organization, management and human factors in quantified risk assessment. Report 1
CRR 34/1992	Organization, management and human factors in quantified risk assessment. Report 2
CRR 37/1992	Evaluation of the safety of composite transportable gas containers
CRR 38/1992	The development of a model to incorporate management and organisational influences in quantified risk assessment
CRR 39/1992	Review of equations of state of fluids valid to high density
CRR 51/1993	Improving safety on construction sites by changing personnel behaviour
CRR 54/1993	Attitudes towards noise as an occupational hazard, vols 1–2
CRR 57/1993	Occupational health provision at work
CRR 58/1993	A review of the state of knowledge and of current practice in selection techniques for process operators
CRR 60/1993	Safety management of process faults: human factors in control design
CRR 61/1993	Stress research and stress management: putting theory to work
CRR 62/1994	Development and testing of a procedure to evaluate dustiness of powders and dusts in industrial use

Dangerous Substances	*Item*
Major hazard aspects of the transport of dangerous substances, 1991	1

Emission Test Methods (not in current list)

ETM 1	An introduction: sampling and analysis of emissions to the air from scheduled works, 1981
ETM 2	The sampling of gaseous emissions: sampling and analysis of emissions to the air from scheduled works, 1981

Guidance Notes

Chemical safety

CS 1	Industrial use of flammable gas detectors, 1987
CS 2	The storage of highly flammable liquids, 1977 (not in current list)
CS 3	Storage and use of sodium chlorate, 1985
CS 4	The keeping of LPG in cylinders and similar containers, 1986
CS 5	Storage of LPG at fixed installations, 1981 (not in current list)
CS 6	The storage and use of LPG on construction sites, 1981
CS 9	Bulk storage and use of liquid carbon dioxide: hazards and procedures, 1985
CS 15	Cleaning and gas freeing of tanks containing flammable residues, 1985
CS 16	Chlorine vaporisers, 1985
CS 17	Packed dangerous substances, 1986 (not in current list)
CS 18	Storage and handling of ammonium nitrate, 1986
CS 21	The storage and handling of organic peroxides, 1991

Environmental hygiene

EH 1	Cadmium – health and safety precautions, 1986
EH 2	Chromium – health and safety precautions, rev., 1991
EH 3	Prevention of industrial lead poisoning (not in current list)
EH 4	Aniline – health and safety precautions, 1979
EH 5	Trichloroethylene – health and safety precautions, 1985 (not in current list)
EH 6	Chromic acid concentrations in air, rev., 1990
EH 8	Arsenic – health and safety precautions, rev., 1990
EH 10	Asbestos – exposure limits and measurement of airborne dust concentrations, rev., 1990
EH 11	Arsine – health and safety precautions, rev., 1990
EH 12	Stibine – health and safety precautions, 1977 (not in current list)
EH 13	Beryllium – health and safety precautions, 1977 (not in current list)
EH 14	Level of training for technicians making noise surveys, 1977 (not in current list)
EH 16	Isocyanates – toxic hazards and precautions, 1984
EH 17	Mercury – health and safety precautions, 1977
EH 18	Toxic substances: a precautionary policy, 1977 (not in current list)
EH 19	Antimony – health and safety precautions, 1978
EH 20	Phosphine – health and safety precautions, 1979

EH 21 Carbon dust – health and safety precautions, 1979 (not in current list)
EH 22 Ventilation of the workplace, 1988
EH 26 Occupational skin diseases: health and safety precautions, 1981 (not in current list)
EH 27 Acrylonitrile: personal protective equipment, 1981
EH 28 Control of lead: air sampling techniques and strategies, 1986
EH 34 Benzidine based dyes – health and safety precautions, 1982
EH 35 Probable asbestos dust concentrations at construction processes, rev., 1989
EH 36 Work with asbestos cement, rev., 1990
EH 37 Work with asbestos insulating board, rev., 1989
EH 38 Ozone: health hazards and precautionary measures, 1983
EH 40 Occupational exposure limits 1994, 1994
EH 41 Respiratory protective equipment for use against asbestos, 1985 (not in current list)
EH 42 Monitoring strategies for toxic substances, rev., 1989
EH 43 Carbon monoxide, 1984
EH 44 Dust in the workplace: general principles of protection, rev., 1991
EH 46 Man-made mineral fibres, rev., 1990
EH 47 Provision use and maintenance of hygiene facilities for work with asbestos insulation and coatings, rev., 1990
EH 50 Training operatives and supervisors for work with asbestos insulation, coatings and insulating boards, 1988
EH 51 Enclosures provided for work asbestos insulation, coatings and insulating board, 1989
EH 52 Removal techniques and associated waste handling for asbestos insulation, coatings and insulating board, 1989
EH 53 Respiratory protective equipment for use against airborne radioactivity, 1990
EH 54 Assessment of exposure to fume from welding and allied processes, 1990
EH 55 The control of exposure to fume from welding, brazing and similar processes, 1990
EH 56 Biological monitoring for chemical exposure in the workplace, 1992
EH 57 The problems of asbestos removal at high temperatures, 1993
EH 58 The carcinogenicity of mineral oils, 1990
EH 59 Crystalline silica, 1992
EH 60 Nickel and its inorganic compounds: health and safety precautions, 1991
EH 62 Metalworking fluids – health precautions, 1992
EH 63 Vinyl chloride: toxic hazards and precautions, 1992
EH 64 Occupational exposure limits: criteria document summaries. Synopses of the data used in setting occupational exposure limits, 1993
EH 65/ *Criteria document series, including*
EH 65/4 1,2-dichloroethane: criteria document for an occupational exposure limit, 1993
EH 65/6 Epichlorohydrin: criteria document for an occupational exposure limit, 1993
EH 66 Grain dust, 1993

General
GS 4 Safety in pressure testing, rev., 1992
GS 5 Entry into confined spaces, 1977 (not in current list)
GS 6 Avoidance of danger from overhead electrical lines, rev., 1991
GS 8 Articles and substances for use at work – guidance for designers, manufacturers, importers, suppliers, erectors and installers, 1977 (not in current list)
GS 9 Road transport in factories and similar workplaces, 1992
GS 15 General access scaffolds, 1982
GS 16 Gaseous fire extinguishing systems: precautions for toxic and asphyxiating hazards, 1984
GS 21 Assessment of the radio frequency ignition hazard to process plants where flammable atmospheres may occur, 1983 (not in current list)
GS 24 Electricity on construction sites, 1983 (not in current list)
GS 26 Access to road tankers, 1983 (not in current list)
GS 27 Protection against electric shock, 1984
GS 28 Safe erection of structures, 1984–
GS 29 Health and safety in demolition work, 1984–
GS 31 Safe use of ladders, step ladders and trestles, 1984
GS 33 Avoiding danger from buried electricity cables, 1985 (not in current list)
GS 37 Flexible leads, plugs, sockets, etc., 1985 (not in current list)
GS 38 Electrical test equipment for use by electricians, 1986
GS 39 Training of crane drivers and slingers, 1986
GS 40 Loading and unloading of bulk flammable liquids and gases at harbours and inland waterways, 1986
GS 42 Tower scaffolds, 1987
GS 47 Safety of electricaldistribution systems on factory premises, 1991
GS 49 Pre-stressed concrete, 1991

Medical
MS 4 Organic dust surveys, 1977
MS 5 Lung function, 1977 (not in current list)
MS 7 Colour vision, rev., 1987
MS 8 Isocyanates: medical surveillance, 1983 (not in current list)
MS 12 Mercury: medical surveillance, 1978
MS 13 Asbestos,rev., 1988
MS 15 Welding, 1978
MS 18 Health surveillance by routine procedures (not in current list)
MS 24 Health surveillance of occupational skin disease, 1991
MS 25 Medical aspects of occupational asthma, 1991

Plant and machinery
PM 1 Guarding of portable pipe-threading machines,1984
PM 3 Erection and dismantling of tower cranes, 1976 (not in current list)

PM 5 Automatically controlled steam and hot water boilers, rev., 1989
PM 9 Access to tower cranes, 1979 (not in current list)
PM 13 Zinc embrittlement of austenitic stainless steel, 1977
PM 14 Safety in the use of cartridge operated tools, 1978 (not in current list)
PM 15 Safety in the use of timber pallets, 1993
PM 16 Eyebolts, 1978
PM 19 Use of lasers for display purposes, 1980
PM 21 Safety in use of woodworking machines, 1981
PM 22 Training advice on the use of abrasive wheels, 1983
PM 23 Photo-electric safety systems, 1981
PM 24 Safety at rack and pinion hoists, 1981
PM 27 Construction hoists, 1981 (not in current list)
PM 28 Working platforms on forklift trucks, 1981
PM 29 Electrical hazards from steam/water pressure cleaners, rev., 1988
PM 30 Suspended access equipment, 1983
PM 32 Safe use of portable electrical apparatus, 1990
PM 38 Selection and use of electric handlamps, 1992
PM 41 Application of photo-electric safety systems to machinery, 1984
PM 53 Emergency private generation: electrical safety, 1985
PM 54 Lifting gear standards, 1985
PM 56 Noise from pneumatic systems, 1985
PM 58 Diesel engined lift trucks in hazardous areas, 1986
PM 60 Steam boiler blowdown systems, 1987
PM 64 Electrical safety in arc welding, 1986
PM 65 Worker protection at crocodile (alligator) shears, 1986
PM 73 Safety at autoclaves, 1990
PM 75 Glass reinforced plastic vessels and tanks: advice to users, 1991

Guidance Booklets

HS(G) 3 Highly flammable materials on construction sites, 1978
HS(G) 5 Hot work: welding and cutting on plant containing flammable materials, 1979
HS(G) 6 Safety in working with lift trucks, 1979
HS(G) 7 Container terminals: safe working practice, 1980
HS(G) 11 Flame arresters and explosion reliefs, 1980
HS(G) 12 Offshore construction: health, safety and welfare, 1980
HS(G) 13 Electrical testing: safety in electrical testing, 1980 (not in current list)
HS(G) 15 Storage of liquefied petroleum gas at factories, 1981 (not in current list)
HS(G) 16 Evaporating and other ovens, 1981
HS(G) 17 Safety in the use of abrasive wheels, 1984
HS(G) 19 Safety in working with power operated work platforms, 1982
HS(G) 20 Guidelines for occupational health services, 1982
HS(G) 22 Electrical apparatus for use in potentially explosive atmospheres, 1984
HS(G) 25 Control of Industrial Major Accident Hazards Regulations 1984 (CIMAH): further guidance on emergency plans, 1985
HS(G) 26 Transport of dangerous substances in tank containers, 1986
HS(G) 27 Substances for use to work: provision of information, 1985
HS(G) 28 Safety advice for bulk chlorine installations, 1986
HS(G) 30 Storage of anhydrous ammonia under pressure in the United Kingdom: spherical and cylindrical vessels
HS(G) 34 Storage of LPG at fixed installations,1987
HS(G) 37 Introduction to local exhaust ventilation, 1987
HS(G) 38 Lighting at work, 1987
HS(G) 39 Compressed air safety, 1990
HS(G) 40 Chlorine from drums and cylinders, 1987
HS(G) 43 Industrial robot safety, 1988
HS(G) 48 Human factors in industrial safety, 1989
HS(G) 51 The storage of flammable liquids in containers, 1990
HS(G) 52 The storage of flammable liquids in fixed tanks (exceeding 10,000 m^3 total capacity), 1991
HS(G) 53 Respiratory protective equipment: a practical guide for users, 1990
HS(G) 54 The maintenance, examination and testing of local exhaust ventilation, 1990
HS(G) 56 Noise at work. Noise assessment, information and control, 1990
HS(G) 61 Surveillance of people exposed to health risk at work, 1990
HS(G) 64 Assessment of fire hazards from solid materials and the precautions required for their safe storage and use, 1991
HS(G) 65 Successful health and safety management, 1991
HS(G) 71 Storage of packed dangerous substances, 1992
HS(G) 78 Container packing, 1992
HS(G) 96 The costs of accidents at work, 1993

Regulations Booklets

HS(R) 1 Packaging and Labelling of Dangerous Substances – Regulations and Guidance Notes, 1978
HS(R) 3 Guide to tanker marking regulations, 1979
HS(R) 6 Guide to the HSW Act, 1983
HS(R) 7 Guide to the Safety Signs Regulations 1980, 1981
HS(R) 8 Guide to the Diving Operations at Work Regulations 1981, 1981
HS(R) 11 First-aid at work, 1981
HS(R) 13 Guide to the Dangerous Substances (Conveyance by Road in Road Tankers) Regulations 1981, 1981
HS(R) 14 Guide to the Notification of New Substances Regulations 1982, 1982
HS(R) 15 Administrative guidance on the implementation of the European Community 'Explosive Atmospheres' Directive (76/117/EEC and 79/196/EEC), 1983
HS(R) 16 Guide to the Notification of Installations Handling Hazardous Substances Regulations 1982, 1983

HS(R) 17 Guide to the Classification and Labelling of Explosives Regulations 1983, 1983
HS(R) 18 Administrative guidance on the application of the European Community 'Low Voltage' Directive (73/23/EEC) to electrical equipment for use at work in the United Kingdom, 1984
HS(R) 19 Guide to the Asbestos (Licensing) Regulations 1983, 1984
HS(R) 21 Guide to the Control of Industrial Major Accident Hazards Regulations 1984, 1985
HS(R) 22 Guide to the Classification, Packaging and Labelling of Dangerous Substances Regulations 1984, 1985
HS(R) 23 Guide to the Reporting of Injuries, Diseases and Dangerous Occurrences Regulations 1985, 1986
HS(R) 24 Guide to the Road Transport (Carriage of Dangerous Substances in Packages, etc.) Regulations 1986, 1987
HS(R) 25 Memorandum of guidance on the Electricity at Work Regulations 1989, 1989
HS(R) 27 A Guide to Dangerous Substances in Harbour Regulations 1987, 1988
HS(R) 29 Notification and marking of sites. The Dangerous Substances (Notification and Marking of Sites) Regulations, 1990
HS(R) 30 A Guide to the Pressure Systems and Transportable Gas Containers Regulations 1989, 1990

Hazard Analysis Reports
HA 1 Canvey: A Second Report – A Summary of a Review of Potential Hazards from Operations in the Canvey Island/Thurrock Area Three Years after Publication of the Canvey Report, 1981
HA 2 Canvey: A Second Report – A Review of Potential Hazards from Operations in the Canvey Island/Thurrock Area Three Years after Publication of the Canvey Report, 1981
HA 3 Sizewell B: A Review by HM Nuclear Installations Inspectorate of the Preconstruction Safety Report, 1982
HA 4 PWR: A Report by the Health and Safety Executive to the Secretary of State for Energy on a Review of the Generic Safety Issues of Pressurised Water Reactors, 1979
HA 5 Nuclear Safety: Safety Assessment Principles for Nuclear Power Reactors, 1979

Health and Safety at Work Booklets (not in current list)
1 Lifting and Carrying
3 Safety Devices for Hand and Foot Operated Presses, 1971
4 Safety in the Use of Abrasive Wheels
6A Safety in Construction Work: General Site Safety Practice
6B Safety in Construction Work: Roofing
6C Safety in Construction Work: Excavations
6D Safety in Construction Work: Scaffolding
6E Safety in Construction Work: Demolition
6F Safety in Construction Work: System Building
10 Fire Fighting in Factories, 1970
13 Ionizing Radiations: Precautions for Industrial Users, 1970
14 Safety in the Use of Mechanical Power Presses
18 Industrial Dermatitis: Precautionary Measures
20 Drilling Machines: Guarding of Spindles and Attachments
22 Dust Explosions in Factories, 1970
24 Electrical Limit Switches and Their Applications, 1970
25 Noise and the Worker, 1971
27 Precautions in the Use of Nitrate Salt Baths, 1971
28 Plant and Machinery Maintenance, 1970
29 Carbon Monoxide Poisoning: Causes and Prevention
30 Storage of Liquefied Petroleum Gas at Factories, 1973
31 Safety in Electrical Testing
32 Repair of Drums and Small Tanks
33 Safety in the Use of Guillotines and Shears
34 Guide to the Use of Flame Arresters and Explosion Reliefs, 1965
35 Basic Rules for Safety and Health at Work, 1975
36 First Aid in Factories
37 Liquid Chlorine
38 Electric Arc Welding, 1970
40 Means of Escape in Case of Fire in Offices, Shops and Railway Premises
41 Safety in the Use of Woodworking Machines, 1970
42 Guarding of Cutters of Horizontal Milling Machines
44 Asbestos: Health Precautions in Industry, 1970
46 Evaporating and Other Ovens, rev., 1974
47 Safety in the Stacking of Materials, 1971

HSE Leaflets
HSE 1 After Flixborough?, 1976
HSE 2 Flixborough, the lessons to be learned, 1976
HSE 5 Introduction to the Employment Medical Advisory Service, 1985; rev., 1992
HSE 8 Fires and explosion due to the misuse of oxygen, 1984
HSE 9 Area office information services, 1986
HSE 11 Reporting of an injury or a dangerous occurrence, rev., 1986
HSE 16 Law on health and safety at work: essential facts for small business and the self-employed, 1986
HSE 17 Reporting a case of disease: a brief guide to the Reporting of Injuries, Diseases and Dangerous Occurrences Regulations 1985, 1986
HSE 21 Report that accident, 1988
HSE 22 The specialists, 1988; rev., 1992
HSEL 1 HSELINE: the new computerised source of health and safety at work references, 1983; rev., 1990

Industrial Advisory Committee Leaflets
IAC/L1 Guidance on the implementation of safety policies, 1982

IND(G) Leaflets
IND(G) 1 (L) Obligations on importers of machinery, plant and substances in Great Britain, 1982
IND(G) 17 (L) Asbestos and you, 1984

IND(G) 22 (L)	Danger! transport at work, 1985
IND(G) 30 (L)	Buried cables – beware!, 1985
IND(G) 35 (L)	Hot work on tanks and drums, 1985
IND(G) 39 (L)	Permits to work and you, 1986
IND(G) 64 (L)	Hazard and risk explained, 1989
IND(G) 65 (L)	Introducing COSHH, 1989
IND(G) 67 (L)	Introducing assessment, 1989 (The last three constitute the COSHH leaflet 'package')
IND(G) 78 (L)	Transport of LPG cylinders by road, 1990
IND(G) 96 (L)	Are you involved in the transport of dangerous substances by road?, 1990
IND(G) 98 (L)	Permit-to-work systems, 1992
IND(G) 115 (L)	New explosives controls, 1991
IND(G) 117 (L)	Policy statement on publication of reports of accidents, 1991
IND(G) 118 (L)	Policy statement on standards, 1991
IND(G) 119 (L)	Safer representatives and safety committees on offshore installations, 1991

L Series
See Table 3.5
This series is gradually superseding the HS(R) and COP series

Major Hazards	*Item*
Advisory Committee on Major Hazards. First Report, 1976	1
Assessment of the hazard from radio frequency ignition at the Shell and Esso sites at Braefoot Bay and Mossmorran, Fife, 1978	2
Report of the Steering Committee on radio ignition hazards at St Fergus, Scotland, 1979	3
Safety evaluation of the proposed St Fergus to Mossmorran natural gas liquids and St Fergus to Boddam gas pipelines, 1978	4
A reappraisal of the HSE safety evaluation of the proposed St Fergus to Mossmorran NGL pipeline, 1980	5
Advisory Committee on Major Hazards. Second Report, 1979	6
Advisory Committee on Major Hazards. Third Report, 1984	7
Names and addresses of sites sent to the Health and Safety Executive under Regulation 7 of the Control of Industrial Major Accident Hazards Regulations 1984 (CIMAH) or deemed to have been sent under Regulation 7(3) by means of a notification already made in accordance with Regulations 3(1) of the Notification of Installations Handling Hazardous Substances Regulations 1982 (NIHHS), 1986	8
Quantified risk assessment: its input to decision-making, 1989	9
Risk criteria for land use planning in the vicinity of major hazards, 1989	10

Medical Advice (not in current list)

MA 3	Control of lead at work: medical surveillance information and advice from the Health and Safety Executive's Medical Division
MA 4	Asbestos (Licensing) Regulations 1983: medical surveillance

Medical Series Leaflets (not in current list)

MS(A) 1	Lead and you, 1986
MS(A) 7	Cadmium and you, 1986
MS(A) 12	Hydrogen fluoride and you, 1990
MS(A) 13	Benzene and you, 1992
MS(A) 15	Silica dust and you, 1992
MS(A) 16	Chromium and you, 1991
MS(B) 1	Ulceration of the skin and inside the nose caused by chrome, 1974
MS(B) 5	Skin cancer caused by oil, 1983
MS(B) 6	Dermatitis and work (occupational dermatitis), 1983

Methods for the Determination of Hazardous Substances

MDHS 70	General methods for sampling airborne gases and vapours, 1990
MDHS 71	Analytical quality in workplace air monitoring, 1991
MDHS 72	Volatile organic compounds in air, 1992

Nuclear Installations	*Item*
Accident at Three Mile Island, 1979	1
Nuclear safety, 1979	2
PWR, 1979	3
Windscale. The management of safety, 1981	4
Emergency plans for civil nuclear installations, 1982	5
Work of HM Nuclear Installations Inspectorate, 1982	6
HM Nuclear Installations Inspectorate: a bibliography of published work 1962–1982, 1983	7
Safety assessment principles for nuclear chemical plant, 1983	8
Safety audit of BNFLs Sellafield, vols 1–2, 1986	9
Comments received on the tolerability of risk from nuclear power stations, 1988	10
The tolerability of risks from nuclear power stations, 1988 (not in current list)	11
An examination of the CEGB's R6 procedure for the assessment of the integrity of structures containing defects, 1989	12
ACSNI Study Group on Human Factors. First report on training and related matters, 1990	13
ACSNI Study Group on Human Factors. Second report: Human Reliability Assessment – a critical overview, 1991	14
A review of American nuclear emergency planning, 1991	15
Safety assessment principles for nuclear plants, 1992	16
The tolerability of risks from nuclear power stations, 1992	17
ACSNI Study Group on Human Factors. Third report: Organizing for safety, 1993	18

Sizewell B	*Item*
Sizewell B, 1982	19
Appraisal of the current situation on large LOCA calculations in the context of Sizewell B, 1984	20

Sizewell B public inquiry

NII/P/1	Sizewell B public inquiry: proof of evidence on the work and responsibilities of HM Nuclear Installations Inspectorate, 1983 (plus additional material denoted ADD1, ADD2, etc.)

NII/P/2 Sizewell B public inquiry: proof of evidence on HM Nuclear Installations Inspectorate's view of the Central Electricity Generating Board's safety case, 1983
(plus additional material denoted ADD1, ADD2, etc.)

NII/S/2 Sizewell B inquiry: the Inspectorate's approach to the assessment of code validation submissions, 1983

NII/S/4 Sizewell B inquiry: schedule of NII reservations and issues all of which require to be resolved to the Inspectorate's satisfaction prior to licensing, 1983

NII/S/5 Sizewell B power station public inquiry: safety case computer codes – categorisation and validation assessment, 1983

NII/S/83 Sizewell B power station inquiry: relationship between the NII's assessment principles and levels of risk, 1984

NII 01 Sizewell B: a review by HM Nuclear Installation Inspectorate
SUPP 1 Degraded core analysis, 1982
SUPP 2 Safety analysis, 1982
SUPP 3 External hazards – aircraft crash, 1983
SUPP 6 Reactor protection system, 1983
SUPP 7 External hazards – earthquake, 1983
SUPP 8 External hazards – fire, 1983
SUPP 9 Code validation for LOCA, 1983
SUPP 10 Reactor pressure vessel, 1983
SUPP 11 Pressure circuit components, 1983
SUPP 12 ALARP strategy for dose reduction, 1983
SUPP 13 Human factors, 1983
SUPP 14 Quality assurance, 1983

HA 3 Sizewell B: a review by HM Nuclear Installations Inspectorate of the preconstruction safety report, 1982

Occasional Papers

OP 1 Problem drinker at work, 1981

OP 2 Microprocessors in industry: safety implications of the use of programmable electronic systems in factories, 1981

OP 3 Managing safety, 1981

OP 5 Electrostatic ignition: hazards of insulating materials, 1982

OP 9 Monitoring safety

OP 10 Safety of electrical distribution systems in factories, 1985

OP 11 Measuring the effectiveness of HSE's field activities, 1985

Offshore Technology Reports

OTH 91 337 Pipeline and riser loss of containment study, 1990 (PARLOC 90)

OTH 92 389 Human factors, shift work and alertness in the offshore industry, 1993

OTI 92 585 Generic foundation data to be used in the assessment of blast and fire scenarios and typical structural details for primary, secondary and supporting structures and components, 1992

OTI 92 586 Representative range of blast and fire scenarios, 1992

OTI 92 587 The prediction of single and two-phase release rates, 1992

OTI 92 588 Legislation, codes of practice and certification requirements, 1992

OTI 92 589 Experimental facilities suitable for use in studies of fire and explosion hazards in offshore structures, 1992

OTI 92 590 The use of alternative materials in the design and construction of blast and fire resistant structures, 1992

OTI 92 591 Gas/vapour build up on offshore structures, 1992

OTI 92 592 Confined vented explosions, 1992

OTI 92 593 Explosions in highly congested volumes, 1992

OTI 92 594 The prediction of the pressure loading on structures resulting from an explosion, 1992

OTI 92 595 Possible ways of mitigating explosions on offshore structures, 1992

OTI 92 596 Oil and gas fires: characteristics and impact, 1992

OTI 92 597 Behaviour of oil and gas fires in the presence of confinement and obstacles, 1992

OTI 92 598 Current fire research: experimental, theoretical and productive modelling resources, 1993

OTI 92 599 The effects of simplifications of the explosion pressure – time history, 1988

OTI 92 601 Computerised analysis tools for assessing the response of structures subjected to blast loading, 1992

OTI 92 602 The effects of high strain rate on material properties, 1992

OTI 92 603 Analysis of projectiles, 1992

OTI 92 604 Experimental data relating to the performance of steel components at elevated temperatures, 1992

OTI 92 605 Methodologies and available tools for the design/analysis of steel components at elevated temperatures, 1992

OTI 92 606 Passive fire protection: performance requirements and test methods, 1992

OTI 92 607 Availability and properties of passive and active fire protection systems, 1992

OTI 92 608 Existing fire design criteria for secondary, support and system steelwork, 1992

OTI 92 610 Thermal response of vessels and pipework exposed to fire, 1992

Oil Industry	*Item*
A guide to the principles and operation of permit-to-work procedures as applied to the petroleum industry, 1986	1

Guidelines for occupational health services in the oil industry, 1987	2
Guidance on health and safety monitoring in the petroleum industry, 1992	3
Guidance on multiskilling in the petroleum industry, 1992	4
Guidance on permit-to-work systems in the petroleum industry, 1991	5
Offshore installations guidance notes: consolidated edition, 4th ed., 1990–	6

Promotional Leaflets

PML 6 New regulations on packaging and labels for dangerous substances: Classification, Packaging and Labelling of Dangerous Substances Regulations 1984, 1985
PML 7 Deadly maintenance: a study of fatal accidents at work, 1985
PML 10 Monitoring safety, 1986

Research Papers

RP 1 Examination of entrained air-flow rate data for large-scale water spray installations by J. McQuaid, 1978
RP 7 Decay of spherical detonations and shocks by H. Phillips, 1980
RP 8 Dispersion of heavier-than-air gases in the atmosphere: review of research, and progress report on HSE activities by J. McQuaid, 1978
RP 11 Comparative risks of electricity production systems: a critical survey of the literature by A.V. Cohen and D.K. Pritchard, 1980
RP 18 Reproducibility of asbestos counts by T.L. Ogden, 1982
RP 24 Dispersion of heavier-than-air gases in the atmosphere: a review of the organization and management of the HSE field trials 1982/84 by D.G. Wilde, 1984
RP 32 First aid retention of knowledge survey by M.C. Cullen, 1992

Research Reviews	*Item*
Shift work and health by J.M. Harrington, 1978	1
Manual handing and lifting by J.D.G. Troup and F.C. Edwards, 1985	2
Alternatives to asbestos products: a review, 1986	3

Safety Health and Welfare Leaflets

SHW 29 Phenol poisoning (cautionary notice), 1984
SHW 367 Dermatitis (cautionary notice), 1975
SHW 385 Cyanide poisoning (cautionary notice), 1983
SHW 395 Gassing and chemical burns (cautionarynotice), 1984
SHW 397 Effects of mineral oil on the skin (cautionary notice), 1982
SHW 830 Dust explosions in factories, 1975
SHW 849 Nitrate salt baths (cautionary notice), 1975
SHW 932 Dangers from carbon monoxide (cautionary notice), 1981
SHW 2125 Danger and explosion in oil storage tanks fitted with immersed heaters (cautionary notice), 1981

Sector Guidance

See Asbestos, Dangerous Substances, Major Hazards, Nuclear Installations, Oil Industry

Specialist Inspectors Reports

SIR 5 Avoiding water hammer in steam systems by S. Mortimer and D.C. Edwards, 1988
SIR 8 The National Exposure Data Base – a computer record system for occupational hygiene data by P.L. Beaumont, D.K. Burns and T.E. Taylor
SIR 9 The fire and explosion hazards of hydraulic accumulators by D.B. Pratt
SIR 16 Low volume, high velocity extraction systems by B. Fletcher
SIR 19 Fire and explosion hazards associated with the storage and handling of hydrogen peroxide by R. Merrifield
SIR 21 Assessment of the toxicity of major hazard substances by R.M. Turner and S. Fairhurst

Technical Data Notes (not in current list)

1 Dust control – the low volume, high velocity system, 2nd rev., 1976
2/73 Threshold limit values for 1975, 1976
3 Occupational cancer of the renal tract, rev., 1973
4 Stibine – health and safety precautions, 1976
5 Antimony – health and safety precautions, 1975
6 Arsine – health and safety precautions, 1975
7 Phosphine – health and safety precautions, 1975
8 Chromium – health and safety precautions, 1973
9 Arsenic – health and safety precautions
10 Aniline – health and safety precautions
11 Cadmium – health and safety precautions, rev., 1975
12 Notes for the guidance of designers on the reduction of machinery noise, 1975
13 Standards for asbestos dust concentration for use with Asbestos Regulations 1969, rev., 1974
14 Health – dust in industry
15 Methyl bromide – health and safety precautions
16 Prevention of industrial lead poisoning
17 Trichloroethylene, rev., 1973
18 The safe cleaning repair and demolition of large tanks for storing flammable liquids, rev., 1975
19 Ventilation of buildings: fresh air requirements, rev., 1975
20 Anthrax
21 Mercury, rev., 1975
24 Asbestos Regulations 1969: respiratory protective equipment, 2nd rev., 1975
25 Safe operation of automatically controlled steam and hot water boilers, 1975
26 Erection and dismantling of tower cranes, 1973
27 Access to tower cranes, 1974
29 Fire risk in the storage and industrial use of cellular plastics, rev., 1975

32 Guarding of portable pipe threading machines
33 Power press mechanisms: overrun and fall-back devices
35 Control of asbestos dust, 1975
36 Safety in the use of cartridge operated fixing tools
38 Tripping device for radial and heavy vertical drilling machines
40 Standards for chromic acid concentration in air for use with the chromium plating regulations
41 Isocyanates – toxic hazard and precautions, 1975
42 Probable asbestos dust concentration at construction processes
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1 Leading oil companies in the United Kingdom
2 Some trade associations relevant to the petroleum industry
3 A glossary of terms used in the oil industry
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SG-5	Plastic Foams – Storage, Handling and Fabrication
SG-6	Forklift Operations
SG-7	Guide for Storage and Handling of Shock and Impact Sensitive Materials
SG-8	Electrical Switch Lockout Procedure
SG-9	Disposal of Hazardous Waste
SG-10	Entering Tanks and Other Enclosed Spaces
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4	Arc physics
5	Ignition of flammable gases by arc discharges

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7 Testing of types e and N electrical equipment and testing of flameproof electrical equipment

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3 Deterioration of wire ropes
4 Metallurgical examination of faulty equipment
5 Fatigue properties of chains
6 Mechanical test facilities

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1 Fires in rigid polyurethane foam
3 Small-scale flammability tests
6 Behaviour of high-expansion foam in storage tanks

Frictional ignition
2 Frictional ignition tests with boot studs
3 Firedamp ignition hazards from light alloys
4 Firedamp ignition by hot surfaces produced by impact and friction
5 The ignition hazard from glass

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1 Use of a metallized membrane electrode in the monitoring of oxygen, carbon monoxide and other gases
2 Catalytic oxygen-deficiency detector
3 Infra-red hydrocarbon detector
4 Fluorescence-quenching oxygen monitor
5 A non-ambiguous catalytic detector for methane
6 Gas detection with semiconductor metal oxides
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SRD R134	1978	TIRION 4: a computer program for use in nuclear safety studies by L.S. Fryer and G.D. Kaiser
SRD R135	1979	A method for the estimation of the probability of damage due to earthquakes by M.A.H.G. Alderson
SRD R143	1979	Regeneration diagrams by G.W. Parry
SRD R146	1979	A study of common-mode failures by G.T. Edwards and I.A. Watson, 1979
SRD R149	1979	World-wide data on the incidence of multiple fatality accidents by L.S. Fryer and R.F. Griffiths
SRD R150	1979	Examples of the successful application of a simple model for the atmospheric dispersion of dense, cold vapours to the accidental release of anhydrous ammonia from pressurised containers by G.D. Kaiser
SRD R152	1979	DENZ – a computer program for the calculation of the dispersion of dense toxic or explosive gases in the atmosphere by L.S. Fryer and G.D. Kaiser
SRD R154	1979	The accidental release of anhydrous ammonia to the atmosphere – a systematic study of factors influencing cloud density and dispersion by R.F. Griffiths and G.D. Kaiser
SRD R155	*c.*1979	Validation of BK WAVE: a computer program for the calculation of one-dimensional shock wave propagation from explosions by F. Briscoe
SRD R173	1983	GASEX2: a two dimensional hydrodynamic code for use in gas cloud explosion calculations by D. Martin
SRD R177	1980	The metal/water explosion phenomenon – a review of present understanding by G.J. Vaughan
SRD R190	1980	The characterisation and evaluation of uncertainty in probabilistic risk analysis by G.W. Parry and P.W. Winter
SRD R196	1981	Defences against common-mode failures in redundant systems. A guide for management, designers and operators by A.J. Bourne, G.T. Edwards, D.M. Hunns, D.R. Poulter and I.A. Watson
SRD R198	1981	UK aircraft crash statistics – 1981 revision by D.W. Phillips
SRD R203	1981	A survey of defects in pressure vessels in the UK for the period 1962–1978 and its relevance to nuclear primary circuits by T.A. Smith and R.G. Warwick
SRD R210	1981	A users manual to SPILL by A.J. Prince, 1981
SRD R217	1982	Matching the results of a theoretical model with failure rates obtained from a population of non-nuclear pressure vessels by L.P. Harrop
SRD R221	1982	A survey of turbulence models with particular reference to dense gas dispersion by C.L. Farmer
SRD R229	1983	Development of CRUNCH: a dispersion model for continuous releases of a denser-than-air vapour into the atmosphere by S.F. Jagger
SRD R238	1982	The transition from pressure-energy to gravity-driven slumping during the catastrophic release of a denser-than-air gas by S.F. Jagger
SRD R240	1983	The thermal response of tanks engulfed in fire by D.L.M. Hunt, P. Ramskill, C.G. Shepherd and R. Young, 1983
SRD R241	1983	A guide to the use of a computer program to model the thermal response of a tank engulfed in fire by P.K. Ramskill, 1983
SRD R243	1983	The physics of heavy gas cloud dispersal by D.M. Webber

SRD R245	1983	Noncoherent structure theory: a review and its role in fault tree analysis by B.D. Johnston and R.H. Matthews
SRD R246	1982	Seismic design criteria and their applicability to major hazard plant within the United Kingdom by M.A.H.G. Alderson
SRD R251	1983	GASEX1 – a general one-dimensional code for gas cloud explosions by J. MacKenzie and D. Martin, 1983
SRD R252	1983	Validation calculations for the code GASEX2 by D. Martin
SRD R254	1984	A suggested method for the treatment of human error in the assessment of major hazards by R.F. White
SRD R262	1983	A computational survey of the factors influencing the pressure fields produced by unconfined vapour cloud by J. MacKenzie
SRD R263	1983	The fire hazards and counter measures for the protection of pressurized liquid petroleum gas storage on industrial sites by KW. Blything
SRD R273	1983	A method of risk assessment for a multi-plant site by R.F. White
SRD R275	1983	The physiological and pathological effects of thermal radiation by I. Hymes
SRD R276	1984	A literature review of fire modelling techniques and related subjects by I.C. Simpson and N.A. Taylor
SRD R277	1985	Application of the computer code DENZ by S.F. Jagger
SRD R292	1984	Fire/explosion probabilities on liquid gas ships by K.W. Blything and J.N. Edmondson
SRD R295	1984	Preliminary studies for the analysis of blast loaded cantilever tests by J. Jowett
SRD R297	1984	Thermal radiation hazard ranges from large hydrocarbon pool fires by M. Considine
SRD R299	1984	FIRENET – a program for performing probabilistic risk assessment of fires in buildings by S.F. Hall and W.M. Scattergood
SRD R300	*c.* 1984	MULTIPLET – a program for calculating large event trees by S.F. Hall
SRD R301	1984	An introduction to fuzzy set theory with a view to the quantification and propagation of vagueness in probabilistic risk and reliability assessment by S.D. Unwin
SRD R302	1985	A study of axisymmetric under-expanded gas jets by P.K. Ramskffl
SRD R303	1984	A study of axi-symmetric two-phase flashing jets by P.R. Appleton
SRD R304	1984	Atmospheric transmissivity – the effects of atmospheric attenuation on thermal radiation by I.C. Simpson
SRD R307	*c.*1984	A modelling study of elevated plumes at a coastal location during onshore flow by P.J. Cooper and W. Nixon
SRD R310	1984	The assessment of individual and societal risks by M. Considine
SRD R314	1986	Analysis of 100 te propane storage vessel by T.A. Smith
SRD R315	1984	A simple parametric model for the dispersion of dense flammable gases by G.C. Grint
SRD R318	1985	Thorney Island heavy gas dispersion trials – determination of path and area of cloud from photographs by A.J. Prince, D.M. Webber and P.W.M. Brighton
SRD R319	*c.*1985	Using concentration data to track clouds in the Thorney Island experiments by P.W.M. Brighton
SRD R324	1985	Details and results of spill experiments of cryogenic liquids on to land and water by A.J. Prince
SRD R325	*c.*1985	Factors influencing pool fires on porous ground by D.M. Webber
SRD R326	1984	In-service reliability data for underground cross-country oil pipelines by K.W. Blything
SRD R327	1985	A model of aerosol deposition in the lung for use in inhalation dose experiments by W. Nixon
SRD R338	1987	The assessment of site-specific aircraft crash hazards by T.M. Roberts
SRD R340	1985	Incident probabilities in liquid gas ships by K.W. Blything and R.C.E. Lewis
SRD R341	*c.*1985	The estimation of missile velocities following the failure of a vessel containing high temperature pressurised water by D.LM. Hunt and AJ. Wood
SRD R342	1985	Cargo protection afforded by hull structure of LPG carriers during grounding at low or drifting speeds by A.N. Kinkead
SRD R347	1985	Guide to reducing human error in process operation (short version) by Human Factors in Reliability Group

SRD R352	1986	Discharge rate calculation methods for use in plant safety assessment by P.K. Ramskill
SRD R353	1987	A review of stainless steel component failures by T.A. Smith
SRD R354	1987	A description of ENGULF, a computer code to model thermal response of a tank engulfed in fire by P.K. Ramskill and D.L.M. Hunt
SRD R355	1985	Comparison between data from Thorney Island heavy gas trials and predictions of simple dispersion models by C.J. Wheatley, A.J. Prince and P.W.M. Brighton
SRD R357	1986	A theory of heterogeneous equilibrium between vapour and liquid phases of binary systems and formulae for the partial pressure of HF + H_2O vapour by C.J. Wheatley
SRD R371	1986	Similarity solutions for the spreading of liquid pools by D.M. Webber and P.W.M. Brighton
SRD R372	1986	A description of the two dimensional combustion code FLARE by D. Martin
SRD R373	1986	Some calculations using the two dimensional combustion code FLARE by D. Martin
SRD R375	1987	Evaporation from a plane liquid surface into a turbulent boundary layer by P.W.M. Brighton
SRD R376	1986	Development of a model to predict the blast response of cantilevers by J. Jowett and J.P. Byrne
SRD R377	1986	Further development of a cantilever blast response model by J. Jowett, J.P. Byrne and T. Roberts
SRD R378	1986	The effects of missile impact on thin metal structures by J. Jowett
SRD R379	1986	A review of hazard identification techniques and their application to major accident hazards by S.T. Parry
SRD R382	1986	AEROSIM-S user manual by S.A. Ramsdale
SRD R383	1985	Common cause failure reliability benchmark exercise by B.D. Johnston and J. Crackett
SRD R390	1987	An integral model for spreading vaporising pools derived from shallow-layer equations by D.M. Webber and P.W.M. Brighton
SRD R393	1987	A theoretical study of NH_3 concentrations in moist air arising from accidental releases of liquefied NH_3 using the computer code TRAUMA by C.J. Wheatley
SRD R394	1987	A users guide to TRAUMA, a computer code for assessing the consequences of accidental two-phase releases of NH_3 into moist air by C.J. Wheatley
SRD R396	1988	Thermodynamics of mixing and final state of a mixture formed by the dilution of anhydrous hydrogen fluoride with moist air by P.N. Clough and C.J. Wheatley
SRD R401	1987	AEROSIM-N user manual by S.A. Ramsdale
SRD R404	1988	A model for the evaporation and boiling of liquid pools by D.M. Webber
SRD R407	1986	Experiments on some effects of obstacles on dense gas dispersion by R.E. Britter
SRD R410	1987	Discharge of liquid ammonia into moist atmospheres – a survey of experimental data and model for estimating initial conditions of dispersion by C.J. Wheatley
SRD R411	1986	Common cause failure reliability benchmark exercise. Phase II by J. Crackett
SRD R412	1987	Feasibility study of the assessment of risks involved in the conveyance of explosives by road by H. Chapman and P.L. Holden
SRD R413	1987	A users guide to ENGULF, a computer code to model the thermal response of a tank engulfed in fire by P.K. Ramskill
SRD R414	1987	The development of ENGULF to model a multi-component Liquid in a fire engulfed tank by P.K. Ramskill
SRD R418	1987	SRD Dependent Failures Procedures Guide by P. Humphreys and B.D. Johnston
SRD R421	1987	Heat conduction under a spreading pool by D.M. Webber
SRD R423	1987	Dry deposition to an urban complex by B.Y. Underwood
SRD R428	1988	FPAs Guide on Fire Precautions by G. Burke and M. Finucane
SRD R431	1988	Reliability of fire protection and detection systems by M. Finucane and D. Pinkney

SRD R435	1987	Criteria for the rapid assessment of aircraft crash onto major hazard installations by D.W. Phillips
SRD R437	1987	An integral dynamic turbulence model for heavy gas cloud dispersal close to the source by D.M. Webber and C.J. Wheatley
SRD R438	1987	Comparison and test of models for atmospheric dispersion of continuous releases of chlorine by C.J. Wheatley, B. Crabol, R.J. Carpenter, S.F. Jagger, C. Nussey, R.P. Cleaver, R.D. Fitzpatrick and A.J. Prince
SRD R 439	1987	Guidelines for the design and assessment of concrete structures subject to impact by P. Barr
SRD R441	1988	Pipework failures – a review of the historical incidents by K.W. Blything and S.T. Parry
SRD R442	1998	Dry deposition to vegetated surfaces parametric dependencies by B.Y. Underwood
SRD R 443	1987	Likelihood as a measure of uncertainty in system reliability and probabilistic safety assessment by A.R. Garlick
SRD R444	1990	Similarity solutions for two dimensional steady gravity currents by P.W.M. Brighton
SRD R455	1987	The application of quality assurance within the UKAEA by F. Allen and T.H. Nixon
SRD R467	1989	Pressures produced by instantaneous chlorine releases inside buildings by P.W.M. Brighton
SRD R468	1989	Continuous chlorine releases inside buildings: concentrations by P.W.M. Brighton
SRD R474	1988	Transport accident frequency data, their sources and their application in risk assessment by P.R. Appleton
SRD R477	1988	Assessment of missile hazards: review of incident experience relevant to major hazard plant by P.L. Holden
SRD R480	1989	ENGULF II: a computer code to model the thermal response of a tank partially or totally engulfed in fire by P.K. Ramskffl
SRD R481	1989	A user's guide to ENGULF II: a computer code to model the thermal response of a tank partially or totally engulfed in fire by P.K. Ramskill and C. Marriott
SRD R483	1989	On the interpretation of puff-trajectory modelling by B.Y. Underwood
SRD R488	1988	An initial prediction of the BLEVE frequency of a 100 te butane storage vessel by K.W. Blything and A.B. Reeves
SRD R492	1988	The predicted BLEVE frequency of a selected 2000 m^3 butane – sphere on a refinery site by M. Selway
SRD R494	1989	Generalisation of the two-phase jet model TRAUMA to substances other than ammonia by D.N. Webber and P.W.M. Brighton
SRD R495	1989	TRAUMA issue 3.5, a users update by S.C. Rutherford and D.M. Webber
SRD R500	1990	The design of bunds by D.S. Barnes
SRD R504	1989	Risk assessment of majorhazards. A brief overview of methods and information sources by P.L. Holden
SRD R507	1990	A model for pool spreading and vaporisation and its implementation in the computer code GASP by D.M. Webber
SRD R509	1990	The long term contribution to severe accident source terms and their mitigation by J.R. Mullins and P.N. Clough
SRD R510	1990	Human error in risk assessment by J. Brazendale
SRD R521	1989	A users guide to G*A*S*P* on microcomputers by D.M. Webber and S.J. Jones
SRD R530	1991	Bund overtopping – the consequences following catastrophic failure of large volume liquid storage vessels by A. Wilkinson
SRD R536	1990	Investigation into the ignition and melting characteristics of apparel fabrics subjected to a radiative heat flux by W. Boydell
SRD R552	1993	A differential phase equilibrium model for clouds, plumes and jets by D.M. Webber and T. Wren
SRD R553	1992	Description of ambient atmospheric conditions for the computer code DRIFT by A.J. Byrne, S.J. Jones, S.C. Rutherford, C.A. Tickle and D.M. Webber
SRD R563	1992	Review of experimental data for validation of the code DRIFT by P.L. Edwards

SRD R578	1992	The probability of fires in warehouses and storages by I. Hymes and J.F. Flynn
SRD R579	1992	Probabilistic risk assessment of radio frequency ignition by P.J. Harrold
SRD R582	1992	The effects of natural and man-made obstacles on heavy gas dispersion. Pt II, Dense gas dispersion over complex terrain by S.J. Jones, D. Martin, D.M. Webber and T. Wren
SRD R583	1992	The effects of natural and man-made obstacles on heavy gas dispersion – report summary by P.W.M. Brighton, S.J. Jones, D. Martin, D.M. Webber and T. Wren
SRD R584	1992	Mathematical modelling of two phase release phenomena in hazard analysis by D.M. Webber, G.A. Tickle, T. Wren and J. Kukkonen
SRD R585	1992	Mathematical modelling of two phase release phenomena in hazard analysis – report summary by D.M. Webber, G.A. Tickle, T. Wren and J. Kukkonen
SRD R 586	1992	A model of a dispersing dense gas cloud and the computer implementation DRIFT I. Instantaneous releases by D.M. Webber, S.J. Jones, G.A. Tickel and T. Wren
SRD R 587	1992	A model of a dispersing dense gas cloud and the computer implementation DRIFT II. Steady continuous releases by D.M. Webber, S.J. Jones, G.A. Tickel and T. Wren
SRD R552	1993	A differential phase equilibrium model for clouds, plumes and jets by D.M. Webber and T. Wren
SRDA R1	1991	Developing best operating procedures by Bardsley and Jenkins
SRDA R3	1991	The guide to reducing human error in process operation by P. Ball

Welding Institute
(Cambridge)

Weldability of Steel by K.G. Richards, 1967 1
Weld Preparations for Fusion Welding of Steelby K.G. Richards, 1966 2
Fatigue of Welded Structures,1969 3
Heat Treatment of Welded Structures, 2nd ed., by F.M. Burdekin, 1969 4
Welding Dissimilar Metals, 1969 5
CO_2 Welding, 3rd ed., by A.A. Smith, 1970 6
Pipe Welding, 1970 7
Welding Cast Austenitic Steels, 1970 8
Welding Creep Resistant Steels, 1970 9
Welding Procedures for Low Alloy Steels by N. Bailey, 1970 10
Advances in Welding Processes 1971 11
Brittle Fracture of Welded Structures by K.G. Richards,1971 12
Electron-Beam Welding – Principles and Practice, ed. by A.H. Meleka, 1971 (London: McGraw-Hill) 13
Fatigue of Welded Structures, 1971 14
Procedures and Recommendations for the Ultrasonic Testing of Butt Welds, 2nd ed., 1971 15
Weldability of Structures and Pressure Vessels, 1971 16
Improving Welded Product Design, 1972 17
Lamellar Tearing in Welded Steel Fabrication, 1972 18
NDT Aspects of the Significance of Weld Defects, 1972 19
Pressure Vessel Standards – the Impact of Change, 1972 20
Welding and Fabrication of Non-Ferrous Metals, 1972 21
Fatigue Performance of Welded High Strength Steels, 1973 22
Handbook of Radiographic Apparatus and Techniques, 1973 23
Surface Coatings for Savings in Engineering, 1973 24
Welding Steel without Hydrogen Cracking, 1973 25
Advances in Welding Processes, 1974 26
Quality Control and Non-Destructive Testing in Welding, 1974 27
Welding Low Temperature Containment Plant, 1974 28
Standard Data for Arc Welding, 1975 29
The Toughness of Weld Heat Affected Zones, 1975 30
Weld Decay in Austenitic Stainless Steel by T.G. Gooch and D.C. Willingham, 1975 31
Welding Processes – Engineering Design Guide by P.T. Houldcroft, 1975 (Oxford: Oxford Univ. Press) 32
Recommendations for Friction Welding of Butt Joints in Metals for High Duty Applications,1975 33
Control of Distortion in Welded Fabrication, 2nd ed., 1976 34
The Present Position Concerning the Biological Effects of Exposure to Fume in Welders by M.L Newhouse and R. Murray, 1981 35
Welding Fume – Sources, Characteristics and Control by N. Jenkins, J. Moreton, P.J. Oakley and S.M. Stevens, vols 1–2, 1981– 36
Guidelines for Fracture-Safe and Fatigue-Reliable Design of Steel Structure by W.S. Pellini, 1983 37
The Facts about Fume, 2nd ed., ed. by N. Jenkins, 1986 38
Introduction to the Non-Destructive Testing of Welded Joints by R. Halmshaw, 1988 39
A Guide to Designing Welds by J. Hicks, 1989 40
Weld Failures ed. by J. Harrison, 1989 41
Fatigue Strength of Welded Structures, 2nd ed., by S.J. Maddox, 1991 42
Health and Safety in Welding and Allied Processes, 4th ed., ed. by N.C. Balchin, 1991 43
Process Pipe and Tube Welding ed. by W. Lucas, 1991 44
Welding Structural and Corrosion Resistant Materials by J.F. Lancaster, 1992 45

World Health Organisation
(Geneva)

Environmental Health Criteria

EHC1	Mercury
EHC2	polychlorinated Biphenyls and Terphenyls
EHC3	Lead
EHC4	Oxides of Nitrogen
EHC5	Nitrates, Nitrites and N-Nitroso Compounds
EHC6	Principles and Methods for Evaluating the Toxicity of Chemicals, Pt 1
EHC7	Photochemical Oxidants
EHC8	Sulphur Oxides and Suspended Particulate Matter
EHC9	DDTand its Derivatives
EHC10	Carbon Disulphide
EHC12	Noise
EHC13	Carbon Monoxide
EHC14	Ultraviolet Radiation
EHC19	Hydrogen Suffide, 1983
EHC20	Selected Petroleum Products
EHC21	Chlorine and Hydrogen Chloride
EHC28	Acrylonitrile
EHC53	Asbestos
ECH54	Ammonia

Note:
Some of the series in this appendix which are shown with a closed range of dates are continuing series, e.g. the AIChE series on Ammonia Plant Safety

B Nuclear Regulatory Commission

Periodic Reports

NUREG-0020	Licensed operators reactor status summary
NUREG-0040	Licensee contractor and vendor inspection status report
NUREG-0090	Report to Congress on abnormal occurrences
NUREG-0304	Regulatory and technical reports (abstract index journal)
NUREG-0525	Safeguards summary event list
NUREG-0540	Title list of documents made publicly available
NUREG-0750	Indexes to nuclear regulatory commission issuances
NUREG-0933	A prioritization of generic safety issues
NUREG-0936	NRC regulatory agenda
NUREG-0940	Enforcement actions: significant actions resolved
NUREG-1125	A compilation of reports of the Advisory Committee on Reactor Safeguards
NUREG-1145	US Nuclear Regulatory Commission annual report
NUREG-1214	Historical data summary of the systematic assessment of licensee performance
NUREG-1415	Office of the Inspector General. Semi-annual Report

Acoustic Emission Monitoring

NUREG/CR-3825:1985	Acoustic emission/flaw relationship for in-service monitoring of nuclear pressure vessels
NUREG/CR-4300:1985–	Acoustic emission/flaw relationship for in-service monitoring of nuclear pressure vessels. Also 1986, 1987
NUREG/CR-5645:1991	Acoustic emission/flaw relationships for in-service monitoring of LWRs

Aerosols

NUREG/CR-1367: 1981	AEROSOL user's manual
NUREG/CR-2139: 1981	Aerosols generated by free fall of powders and solutions in static air
NUREG/CR-2299: 1982	Aerosol release and transport program
NUREG/CR-3422:1984	Aerosol release and transport program
NUREG/CR-3830:1985	Aerosol release and transport program
NUREG/CR-4342:1985	Uncertainty and sensitivity analysis of a model for multicomponent aerosol dynamics
NUREG/CR-4501:1986	Modeling of vapor generation in flashing flow
NUREG/CR-4658:1986	Aerosols generated by spills of viscous solutions and slurries
NUREG/CR-4779:1987	New data for aerosols generated by releases of pressurized powders and solutions in static air
NUREG/CR-4997:1988	Methods for describing air-borne fractions of free fall spills of powders and liquids
NUREG/CR-5162:1988	CHARM: a model for aerosol behaviour in time varying thermal–hydraulic conditions

Aging

NUREG/CR-3156:1983	A survey of state-of-the-art in aging of electronics with application to nuclear power plant instrumentation
NUREG/CR-3808:1984	Aging–seismic correlation study on class IE equipment
NUREG-1144:1985	Nuclear plant aging research (NPAR) program plan
NUREG/CR-3819:1985	Survey of aged power plant facilities
NUREG/CR-4144:1985	Importance ranking based on aging considerations of components included in probabilistic risk assessments
NUREG/CR-4156:1985	Operating experience and aging–seismic assessment of electric motors
NUREG/CR-4234:1985	Aging and service wear of electric motor-operated valves used in engineered safety-feature systems of nuclear power plants
NUREG/CR-4279:1986	Aging and service wear of hydraulic and mechanical snubbers used in safety-related piping and components of nuclear power plants

NUREG/CR-4548:1986 Correlation of electrical reactor cable failure with materials degradation

NUREG/CR-4597:1986 Aging and service wear of auxiliary feedwater pumps for PWR nuclear power plants

NUREG-1144:1987 Nuclear plant aging research (NPAR) program plan

NUREG/CR-4590:1987 Aging of nuclear station diesel generators

NUREG/CR-4715:1987 An aging assessment of relays and circuit breakers and system, interactions

NUREG/CR-4731:1987 Residual life assessment of major light water reactor components

NUREG/CR-4769:1987 Risk evaluations of aging phenomena

NUREG/CR-4928:1987 Degradation of nuclear plant temperature sensors

NUREG/CR-4747:1988 An aging failure survey of light water reactor safety systems and components

NUREG/CR-4992:1988 Aging and service wear of multistage switches used in safety systems of nuclear power plants

NUREG/CR-5057:1989 Aging mitigation and improved programs for nuclear service diesel generators

NUREG/CR-5314:1990 Life assessment procedures for major LWR components

NUREG/CR-5419:1990 Aging assessment of instrument air systems in nuclear power plants

NUREG/CP-4302: 1991 Aging and service wear of check valves used in engineered safety feature systems of nuclear power plants

Alcohol, Drug Abuse

NUREG-0903: 1982 Survey of industry and government programs to combat drug and alcohol abuse

NUREG/CR-3196:1983 Drug and alcohol abuse: the bases for employee assistance programs in the nuclear utility industry

NUREG/CR-5784:1991 Fitness for duty in the nuclear power industry

Auxiliary Feedwater System

NUREG/CR-5404:1990 Auxiliary feedwater system aging

Bolts

NUREG-1339:1990 Resolution of generic safety issue 29: bolting degradation or failure in nuclear power plants

Chernobyl

NUREG-1250:1987 Report on the accident at the Chernobyl nuclear power station

NUREG-1251:1987 Implications of the accident at Chernobyl for safety regulation of commercial nuclear power plants in the United States (draft)

NUREG-1251:1989 Implications of the accident at Chernobyl for safety regulation of commercial nuclear power plants in the United Sates

Combustion

NUREG/CR-2658:1983 Characteristics of combustion products: a review of the literature

NUREG/CR-4855:1987 Development and application of a computer model for large-scale flame acceleration experiments

NUREG/CR-5275:1989 Flame facility: the effect of obstacles and transverse venting on flame acceleration and transition for hydrogen-air mixtures

Common Cause Failure

NUREG/CR-2099:1982 Common cause fault rates for diesel generators: estimates based on Licensee Event Reports at US commercial nuclear power plants

NUREG/CR-2098:1983 Common cause fault rates for pumps: estimates based on Licensee Event Reports at US commercial nuclear power plants

NUREG/CR-2770:1983 Common cause fault rates for valves

NUREG/CR-2771:1983 Common cause fault rates for instrumentation and control assemblies

NUREG/CR-3289:1983 Common cause fault rates for instrumentation and control assemblies

NUREG/CR-3437:1983 Data analysis using binomial failure rate common cause model

NUREG/CR-4314:1985 Brief survey and comparison of common cause failure analysis

NUREG/CR-4780:1988 Procedures for treating common cause failures in safety and reliability studies

NUREG/CR-5044:1988 Estimation techniques for common cause failure events

NUREG/CR-4780:1989 Procedures for treating common cause failures in safety and reliability studies

NUREG/CR-5460:1990 A cause-defense approach to the understanding and analysis of common cause failures

Computer Reliability

NUREG/CR-2118:1981 Reactor safety system design using hardened computers

NUREG/CR-2288:1982 Computer surety

NUREG/CR-3360:1984 Computer program CDCID, an automated quality control program using CDC update

Computer Software Reliability

NUREG/CR-2186:1982 Quantitative software reliability analysis of computer codes relevant to nuclear safety

NUREG/CR-4369:1986 Quality assurance (QA) plan for computer software supporting the US Nuclear Regulatory Commission's high-level waste program

NUREG/CR-4640:1987 Handbook of software quality assurance techniques applicable to the nuclear industry

Containment

NUREG/CP-0033:1982 Proceedings of the workshop on Containment Integrity

NUREG/CR-3855:1985 Characterization of nuclear reactor containment penetration

NUREG/CR-4119:1985 Integrity of containment penetrations under severe accident conditions

NUREG/CR-4149:1985 Ultimate pressure capacity of reinforced and prestressed concrete containment

NUREG/CR-4220:1985 Reliability analysis of containment isolation systems

NUREG/CR-5096:1988 Evaluation of seals for mechanical penetrations of containment buildings

NUREG/CR-5394:1989 Evaluation of the leakage behavior of inflatable seals subject to severe accident conditions

NUREG/CR-5602:1990 Simplified containment event tree analysis for the Sequoyah ice condenser containment

Control System, Including Displays, Alarms, Computers, Computer Aids

NUREG/CR-2776:1982 Alarms within advanced display systems: alternatives and performance measures

NUREG/CR-2988:1982 An approach to modeling supervisory control of a nuclear power plant

NUREG/CR-3461:1984 Response tree evaluations – implications for the use of artificial intelligence in process control rooms

NUREG/CR-3621:1984 Safety system status monitoring

NUREG/CR-3631:1984 Response trees and expert systems for nuclear reactor operators

NUREG/CR-3655:1984 A method for analytical evaluation of computer-based decision aids

NUREG/CR-4017:1984 Interim criteria for the use of programmable digital devices in safety and control systems

NUREG/CR-3987:1985 Computerized annunciator systems

NUREG/CR-4227:1985 Human engineering guidelines for the evaluation and assessment of video display units

NUREG/CR-4272:1985 Response tree evaluation: experimental assessment of an expert system for nuclear reactor operators

NUREG/CR-3958:1986 Effects of control system failures on transients, accidents and core-melt frequencies at Combustion Engineering pressurized water reactor

NUREG/CR-4463:1986 Human factors in annunciator/alarm systems: annunciator experiment plan I

NUREG/CR-4577:1987 Automated long-term surveillance of a commercial nuclear power plant

NUREG/CR-4797:1987 Progress reviews of six safety parameter display systems

NUREG/CR-5011:1987 Application of the adaptive-predictive controllers to plant safety surveillance utilizing online plant analyzer

NUREG-1217:1988 Evaluation of safety implications of control systems in LWR nuclear power plants (draft)

NUREG-1217:1989 Evaluation of safety implications of control systems in LWR nuclear power plants (draft)

NUREG-1342:1989 A status report regarding industry implementation of safety parameter display

NUREG-1361:1989 Lessons learned in process control at the Halden reactor project

Control Room Design

NUREG-0700:1981 Guidelines for control room design reviews

NUREG-0801:1981 Evaluation criteria for detailed control room design review

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NUREG-1420:1990 Special committee review of the Nuclear Regulatory Commission's severe accident risk report (NUREG-1150)

NUREG-1150:1990 Severe accident risks: an assessment for five US nuclear power plants

NUREG/CR-4840:1990 Procedures for the external event core damage frequency analyses for NUREG-1150

NUREG-1150:1991 Severe accident risks: an assessment for five US nuclear power plants

Sizewell B

NUREG-0999:1983 Sizewell B — analysis of British application of US PWR technology

Siting

NUREG/CR-1684: 1981 A comparison of site evaluation methods

SLIM-MAUD

NUREG/CR-3518:1984 SLIM-MAUD: an approach to assessing human error probabilities using structured expert judgment

NUREG/CR-4016:1987 Application of SLIM-MAUD: a test of an interactive computer-based method for organizing expert assessment of human performance and reliability

Source Terms

NUREG-0856:1985 Reassessment of the technical bases for estimating source terms (draft)

NUREG-0956:1985 Reassessment of the technical bases for estimating source terms (draft)

NUREG-0956:1986 Reassessment of the technical bases for estimating source terms

NUREG/CR-4587:1986 Source term code package: a user's guide (MOD1)

NUREG/CR-4656:1986 Verification tests calculations for the source term code package

NUREG/CR-4688:1986 Quantification and uncertainty analysis of source terms for severe accidents in light water reactors (QUASAR)

NUREG-1265:1987 Uncertainty papers on severe accident source terms

NUREG/CR-4722:1987 Source term estimation using MENU-TACT

NUREG/CR-4883:1987 Review of research on uncertainties in estimates of source terms from severe accidents in nuclear power plants

NUREG-1228:1988 Source term estimation during incident response to severe nuclear power plant accidents

NUREG/CR-5531:1991 MELCOR 1.8: a computer code for nuclear reactor severe accident source term and risk assessment analyses

Steam Generators

NUREG/CR-4079:1985 Analytic studies pertaining to steam generator tube rupture accidents

NUREG/CR-4276:1985 Vibration and wear in steam generating tubes following chemical clearning

NUREG/CR-4276:1986 Vibration and wear in steam generating tubes following chemical clearning

Steam Supply

NUREG-0852:1987 Safety evaluation report related to the final design of the standard nuclear steam supply reference system CESSAR

NUREG-1413 Safety evaluation report related to the preliminary design of the standard steam supply reference system RESAR

Structures

NUREG/CR-2347:1982 Margins to failure – category I structures program: background and experimental program plan

NUREG/CR-2638:1982 Snow loads for the design of nuclear power plant structures

NUREG/CR-3628:1984 Probability based safety checking of nuclear plant structures

System Interactions

NUREG/CR-3922:1985 Survey and evaluation of system interaction events and sources

NUREG/CR-4261:1986 Assessment of system interaction experience in nuclear power plants

Thermal Hydraulic Analysis

NUREG/CR-1157:1981 Thermal/hydraulic analysis research program: quarterly report

NUREG/CR-1998:1981 RELAP4/MOD7: a best estimate computer program to calculate thermal and hydraulic phenomena in a nuclear reactor or related system

NUREG/CR-1826:1982 RELAP5/MOD1 code manual

NUREG/CR-3046:1983 COBRA/TRAC – a thermal hydraulics code for transient analysis of nuclear reactor vessels and primary coolant

NUREG/CR-3257:1983 RELAP5 assessment: LOFT turbine trip L6–7/L9–2

NUREG/CR-2896:1984 COMMIX 1A a three-dimensional transient single-phase computer program for thermal hydraulic analysis of single and multicomponent systems

NUREG/CR-3329:1984 Thermal/hydraulic analysis research program

NUREG/CR-3504:1984 Turbulence modeling in the COMMIX computer code

NUREG/CR-3772:1985 RELAP5 assessment: semiscale small break tests S-UT-1, S-UT-2, S-UT-6, S-UT-7 and S-UT-8

NUREG/CR-3802:1985 RELAP5 assessment: quantitative key parameters and run time statistics

NUREG/CR-3820:1985 Thermal/hydraulic analysis research program (TRAC-PF1/MOD1)

NUREG/CR-3936:1985 RELAP5 assessment: conclusions and user guidelines

NUREG/CR-4278:1985 TRAC-PF1/MOD1 development assessment

NUREG/CR-4292:1985 A comparative analysis of constitutive relations in TRAC-PFL and RELAP5/MOD1

NUREG/CR-3262:1986 COBRA-NC: a thermal hydraulic code for transient analysis of nuclear reactor components

NUREG/CR-4371:1986 COMMIX-2: a three-dimensional transient computer program for thermal – hydraulic analysis of two-phase flows

NUREG/CR-4830:1987 MELCOR validation and verification 1986 papers

NUREG/CR-4312:1988 RELAP5/MOD2 code manual

NUREG/CR-5194:1988 RELAP5/MOD2 models and correlations

NUREG/CR-5273:1989 SCDAP/RELAP5/MOD2 code manual

Three Mile Island

NUREG-0680:1981 TMI-1 restart

NUREG-0752:1981 Control room design report for TMI-1

NUREG-0698:1984 NRC plan for cleanup operations at Three Mile Island Unit 2

NUREG/CR-4978:1987 The cooldown aspects of the TMI-2 accident

NUREG-1355:1989 The status of recommendations of the President's Commission on the Accident at Three Mile Island. A ten-year review

NUREG/CR-5457:1989 A review of the Three Mile Island-1 probabilistic risk assessment

Toxic Gas

NUREG/CR-1741:1981 Models for the estimation of incapacitation times following exposure to toxic gases or vapors

NUREG/CR-3685:1984 Toxic gas accident analysis code user's manual

NUREG/CR-5656:1991 EXTRAN: a computer code for estimating concentrations oftoxic substances at control room air intakes

NUREG/CR-5669:1991 Evaluation of exposure limits to toxic gases for nuclear reactor control room operators

Transport

NUREG/CR-3499:1983 Severe rail and truck accidents:toward a definition of bounding environments for transportation packages

NUREG/CR-5717:1991 Packaging supplier inspection guide

Two-Phase Flow

NUREG/CR-2671:1982	The Marviken full scale critical flow tests
NUREG/CR-3372:1983	An analysis of wave dispersion, sonic velocity and critical flow in two-phase mixtures
NUREG/CR-4761:1986	Small break critical discharge – roles of vapor and liquid entrainment in stratified two-phase region upstream of the break

Utilities

NUREG/CR-2796:1982	Compressed air and backup nitrogen systems in nuclear power plants
NUREG/CR-2797:1982	Evaluation of events involving service water systems in nuclear power plants
NUREG/CR-3351:1985	Safety implications associated with in-plant pressurized gas storage
NUREG/CR-5472:1990	A risk-based review of instrument air systems at nuclear power plants distribution

Value-Impact Analysis

NUREG/CR-4941:1987	The application of value-impact analysis to USI A-45
NUREG/CR-5579:1990	Value/impact assessment of jet impingement loads and pipe-to-pipe impact damage

Valves

NUREG/CR-1363:1982	Data summaries of Licensee Event Reports of valves at US commercial nuclear power plants
NUREG/CR-3154:1983	The in-plant reliability data base for nuclear power components: interim data report – the valve component
NUREG/CR-3914:1985	Pump and valve qualification review guide
NUREG/CR-4141:1985	Containment purge and vent valve test program. Final report
NUREG/CR-4648:1986	A study of typical nuclear containment purge valves in an accident environment
NUREG/CR-4692:1987	Operating experience review of failures of power operated relief valves and block valves in nuclear power plants
NUREG/CR-4999:1988	Estimation of risk reduction from improved PORV reliability in PWRs
NUREG/CR-5159:1988	Prediction of check valve performance and degradation in nuclear power plant systems
NUREG-1316:1989	Technical findings and regulatory analysis related to generic issue 70. Evaluation of power operated relief valve and block valve reliability in PWR nuclear power plants
NUREG-1352:1990	Action plans for motor-operated valves and check valves
NUREG-1372:1990	Regulatory analysis for the resolution of generic issue C-8 'Main steam isolation valve leakage and LCS failure'
NUREG/CR-5583:1990	Prediction of check valve performance and degradation in nuclear power plant systems – wear and impact

Water Hammer

NUREG-0918:1982	Prevention and mitigation of steam generator water hammer events in PWR plants
NUREG/CR-2059:1982	Compilation of data concerning known and suspected water hammer events in nuclear powerplants
NUREG/CR-2781:1982	Evaluation of water hammer events in light water reactors
NUREG-0927:1983	Evaluation of water hammer experience in nuclear power plants
NUREG-0927:1984	Evaluation of water hammer occurrence in nuclear power plants
NUREG-0993:1984	Regulatory analysis for USI A-1: 'water hammer'
NUREG/CR-3939:1984	Water hammer, flow induced vibration and safety/relief valve loads
NUREG/CR-5220:1988	Diagnosis of condensation-induced water hammer

Particular Nuclear Power Stations

A Technical specifications for (name) station
B Safety evaluation report related to the operation of (name) station

	A – Technical specification	B – Safety evaluation
Beaver Valley	1259, 1279	1057
Braidwood	1223, 1261, 1276	1002
Byron	1097, 1113	0876
Calaway		0830
Catawba	1072, 1099, 1106, 1182, 1191	0954
Clinton	1202, 1235	0853
Comanche Peak		0797
Diablo Canyon	0817, 1132, 1151	0675
Enrico Fermi	1089, 1141	0798
Grand Gulf		0831
Hope Creek	1186, 1202	1048
LaSalle	1013	0519
Limerick	1088, 1149	0974, 0991
Millstone	1161, 1176	1031
Nine Mile Point	1193, 1253	1047

Onofre		0712
Palisades	1424	
Palo Verde	1111, 1133, 1173	0857
	1181, 1248, 1287	
Perry	1162, 1204	0887
River Bend	1142, 1172	0989
Salem		0517
San Onofre	1443	
Seabrook	1207, 1331	0896
Shearon Harris	1208, 1240	1038
Shoreham	1012, 1126	0420
South Texas Project	1255, 1334	0781
Susquehanna	1042	0776
Vogtle	1237, 1247, 1343	1137
Waterford	1117	0787
Watts Bar		0847
Wolf Creek	1104, 1136	0881

Appendix 29

Information Sources

Contents

A29.1 Selected Organizations Relevant to Safety and Loss Prevention 29/2

A29.1 Selected Organizations Relevant to Safety and Loss Prevention

United Kingdom

Associated Octel Company Limited,
http://www.octel-corp.com/home/home.htm
P.O. Box 17, Oil Sites Road, Ellesmere Port,
Cheshire, CH65 4HF
Phone: +44 (0) 151 355 3611, Fax: +44 (0) 151 356 2349

Association of British Chemical Manufacturers – succeeded by Chemical Industries Association

Association of British Insurers,
http://www.abi.org.uk/
51 Gresham Street, London EC2V 7HQ
Phone: +44 (0) 20 7600 3333, Fax: +44 (0) 20 7696 8999

British Approvals Service for Electrical Equipment in Flammable Atmospheres (BASEEFA) – succeeded by Electrical Equipment Certification Service

British Chemical Engineering Contractors Association (BCECA),
http://www.bceca.org.uk/
1 Regent Street, London SW1Y 4NR
Phone: +44 (0) 20 7839 6514

British Chemical Industries Safety Council – succeeded by Chemical Industries Association

British Cryogenic Council (BCC) – succeeded by British Cryoengineering Society (BCS)

British Cryoengineering Society (BCS),
http://www.bcryo.org.uk/
P.O. Box 41, Leatherhead, KT22 9YY
Phone: +44 (0) 1372 376544, Fax: +44 (0) 1372 376544

British Compressed Gas Association (BCGA),
http://www.bcga.co.uk/
6 St Mary's St, Wallingford, OX10 0EL
Phone: +44 (0) 1491 825533, Fax: +44 (0) 1491 826689

British Computer Society (BCS),
http://www1.bcs.org.uk/
1 Sanford Street, Swindon, Wiltshire, SN1 1HJ
Phone: +44 (0) 1793 417417, Fax: +44 (0) 1793 480270

British Engine Insurance Company,
39 Windsor Place, Cardiff South Glamorgan, CF10 3BW
Phone: +44 (0) 29 20237199

British Fire Services Association,
http://www.bfsa.org.uk/
86 London Road, Leicester LE2 OQR
Phone: +44 (0) 116 2542879, Fax: +44 (0) 116 2542879

British Geological Survey,
Murchison House, West Mains Road, Edinburgh EH9 3LA
Phone: +44 (0) 131 667 1000, Fax: +44 (0) 131 668 2683

British Hydromechanics Research Association – succeeded by BHR Group Limited

BHR GROUP Limited
http://www.bhrgroup.co.uk/
The Fluid Engineering Centre, Cranfield,
Bedfordshire MK43 OAJ
Phone: +44 (0) 1234 750422, Fax: +44 (0) 1234 750074

British Insurance Association – succeeded by Association of British Insurers

British Nuclear Society (BNES),
http://www.bnes.com/
1-7 Great George Street, London, SW1P 3AA
Phone: +44 (0) 20 7665 2241, Fax: +44 (0) 20 7799 1325

British Occupational Hygiene Society (BoHS),
http://www.bohs.org/
Suite 2, Georgian House, Great Northern Road,
Derby, DE1 1LT
Phone: +44 (0) 1332 298101, Fax: +44 (0) 1332 298099

British Pump Manufacturers Association (BPMA),
http://www.bpma.org.uk/
The McLaren Building, 35 Dale End, Birmingham, B4 7LM
Phone: +44 (0) 121 200 1299, Fax: +44 (0) 121 200 1306

British Rail – privatized and succeeded by the Rail Industry Training Council (RITC Ltd)

British Red Cross Society,
http://www.redcross.org.uk/
9 Grosvenor Crescent, London SW1X 7EJ
Phone: +44 (0) 20 7235 5454, Fax: +44 (0) 20 7245 6315

British Safety Council,
http://ww2.britishsafetycouncil.org/
70 Chancellors Road, London W6 9RS
Phone: +44 (0) 20 8741 1231, Fax: +44 (0) 20 8741 4555

British Standards Institution (BSI),
http://www.bsi-global.com/
389 Chiswick High Road, London, W4 4AL
Phone: +44 (0) 20 8996 9000, Fax: +44 (0) 20 8996 7001

British Waterways,
http://www.britishwaterways.co.uk/
Willow Grange, Church Road, Watford, WD17 4QA
Phone: +44 (0) 1923 201 120

Building Research Establishment Ltd (BRE),
http://www.bre.co.uk/
Garston, Watford WD25 9XX
Phone: +44 (0) 1923 664 000

Chamber of Shipping of the UK,
http://www.british-shipping.org/
Carthusian Court, 12 Carthusian Street,
London EC1M 6EZ
Phone: +44 (0) 20 7417 2800, Fax: +44 (0) 20 7726 2080

Chemical and Allied Product Industry Training Board – now disbanded

Chemical Industries Association (CIA),
http://www.cia.org.uk/
Kings Buildings, Smith Square, London SW1P 3JJ
Phone: +44 (0) 20 7834 3399, Fax: 020 7834 4469

Chemical Industry Safety and Health Council – succeeded by Chemical Industries Association

The Chemical Society – see the Royal Society for Chemistry

Chief and Assistant Fire Officers Association (CACFOA),
http://www.fire-uk.org/
9-11 Pebble Close, Tamworth, Staffordshire, B77 4RD
Phone: +44 (0) 1827 302300, Fax: +44 (0) 1827 302399

Confederation of British Industry (CBI),
http://www.cbi.org.uk/
103 New Oxford Street, London WC1A 1DU
Phone: +44 (0) 20 7379 7400, Fax: +44 (0) 20 7240 8287

Council for Oil and Gas Extraction, Chemicals Manufacturing and Petroleum Industries (COGENT)
http://www.cogent-ssc.com/
Monticello House, 45 Russell Square, London WC1B 4JP
Phone: +44 (0) 20 637 9533, Fax: +44 (0) 20 7291 6129

Electrical Equipment Certification Service (EECS) – part of HSE but disbanded in 2002

Engineering Council, (UK),
http://www.engc.org.uk/
10 Maltravers Street, London WC2R 3ER
Phone: +44 (0) 20 7240 7891, Fax: +44 (0) 20 7379 5586

Engineering Equipment Users Association – succeeded by Engineering Equipment and Materials Users Association

Engineering Equipment and Materials Users Association,
http://www.eemua.co.uk/
3rd Floor, 30 Long Lane, London EC1A 9HL
Phone: +44 (0) 20 7796 1293, Fax: +44 (0) 20 7796 1294

The Fellowship of Engineering – now The Royal Academy of Engineering

Fire Officers Committee – see Association of British Insurers

Fire Protection Association (FPA),
http://www.thefpa.co.uk/
Bastille Court, 2 Paris Garden, London SE1 8ND
Phone: +44 (0) 20 7902 5300, Fax: +44 (0) 20 7902 5301

Fire Industry Confederation (FIC)
http://www.the-fic.org.uk/
Neville House, 55 Eden Street, Kingston upon Thames, Surrey, KT1 1BW
Phone: +44 (0) 20 8549 8839, Fax: +44 (0) 20 8547 1564

Fire Research Station (FRS),
http://www.bre.co.uk/frs/
FRS, the Fire Division of BRE, Garston, Watford WD25 9XX
Phone: +44 (0) 1923 664700, Fax: +44 (0) 1923 664910

Fire Service College,
http://www.fireservicecollege.ac.uk/
Friends of the Earth Ltd.,
http://www.foe.co.uk/
26-28 Underwood Street, London N1 7JQ
Phone: +44 (0) 20 7490 1555, Fax: +44 (0) 20 7490 0881

Health and Safety Commission/Executive (HSC/E),
http://www.hse.gov.uk/
2 Rose Court, 2 Southwark Bridge, London SE1 9HS
Phone: +44 (0) 20 7556 2100, Fax: +44 (0) 20 7556 2109

Health and Safety Executive,
Research and Laboratory Division,
http://www.hse.gov.uk/research/
Broad Lane, Sheffield, S3 7HQ
Phone: +44 (0) 114 289 2000, Fax: +44 (0) 114 289 2500

High Pressure Technology Association,
http://www.liv.ac.uk/~js1/hpta.html
c/o Department of Chemistry, University of Liverpool, Liverpool L69 7ZD
Phone: +44 (0) 151 794 3530, Fax: +44 (0) 151 794 3588

HM Stationery Office (HMSO),
http://www.hmso.gov.uk/
The Stationery Office Ltd, P.O. Box 29, Norwich, NR3 1GN
Phone: +44 (0) 870 600 5522, Fax: +44 (0) 870 600 5533

Home Office,
http://www.homeoffice.gov.uk/
Room 856, 50 Queen Anne's Gate, London SW1 9AT
Phone: +44 (0) 870 000 1585, Fax: +44 (0) 20 7273 2065

Imperial Chemical Industries plc,
20 Manchester Square, London, W1U 3AN
Phone: +44 (0) 20 7009 5000, Fax: 44 (0) 20 7009 5001

Imperial Chemicals Insurance,
1 Adam Street, London WC2

Industrial Fire Protection Association of Great Britain,
140 Aldersgate Street, London EC1A 4HX
Phone: +44 (0) 20 7606 3757

Industrial Safety (Protective Equipment) Manufacturers Association,
69 Cannon Street, London EC4N 5AB

The Industrial Society – now disbanded

Institute of Cancer Research,
http://www.icr.ac.uk/
123 Old Brompton Road, London SW7 3RP
Phone: +44 (0) 20 7352 8133, Fax: +44 (0) 20 7370 5261

Institute of Geological Sciences – see British Geological Survey

Institute of Materials (IOM),
http://www.iom3.org/
1 Carlton House Terrace, London SW1Y 5DB
Phone: +44 (0) 20 7451 7300, Fax: +44 (0) 20 7839 1702

Institute of Measurement and Control,
http://www.instmc.org.uk/
87 Gower Street, London WC1E 6AA
Phone: +44 (0) 20 7387 4949, Fax: +44 (0) 20 7388 8431

Institute of Metals – see Institute of Materials

Institute of Oceanographic Sciences (IOSDL),
http://wofiles.nwo.ac.uk/
Deacon Laboratory, Brook Road, Wormley, Godalming, Surrey GU8 5UB
Phone: +44 (0) 428 684141, Fax: +44 (0) 428 683066

Institute of Offshore Engineering (IOE),
http://www.civ.hw.ac.uk/
Heriot–Watt University, Research Park, Riccarton, Currie, Edinburgh EH14 4AP
Phone: +44 (0) 131 451 3151, Fax: +44 (0) 131 449 6254

Institute of Petroleum,
http://www.petroleum.co.uk/
61 New Cavendish Street, London, W1G 7AR
Phone: +44 (0) 20 7467 7100, Fax: +44 (0) 20 7255 1472

Institute of Physics (IOP),
http://www.iop.org/
76 Portland Place, London W1B 1NT
Phone: +44 (0) 20 7470 4800, Fax: +44 (0) 20 7470 4848

Institution of Chemical Engineers (IChemE),
http://www.icheme.org/
Davis Building, 165–189 Railway Terrace,
Rugby CV21 3HQ
Phone: +44 (0) 1788 578214, Fax: +44 (0) 1788 560833

Institution of Civil Engineers (ICE),
http://www.ice.org.uk/
One Great George Street, Westminster, London SW1P 3AA
Phone: +44 (0) 20 7222 7722

Institution of Electrical Engineers (IEE),
http://www.iee.org/
Savoy Place, London WC2R OBL
Phone: +44 (0) 20 7240 1871, Fax: +44 (0) 20 7240 7735

Institution of Fire Engineers (IFE),
http://www.ife.org.uk/
148 Upper New Walk, Leicester LEI 7QB
Phone: +44 (0) 116 255 3654, Fax: +44 (0) 116 247 1231

Institution of Gas Engineers,
http://www.igaseng.com/
17 Grosvenor Crescent, London SW1X 7ES 12 York Gate
London NW1 4QG
Phone: +44 (0) 20 7487 0650, Fax: +44 (0) 20 7224 4762

Institution of Industrial Safety Officers – see Institution of Occupational Safety and Health

Institution of Marine Engineers (IMarEST),
http://www.imarest.org/

Institution of Mechanical Engineers (IMechE),
http://www.imeche.org.uk/
1 Birdcage Walk, Westminster, London, SW1H 9JJ
Phone: +44 (0) 20 7222 7899, Fax: +44 (0) 20 7222 4557

Institution of Nuclear Engineers (INE),
http://www.inuce.org.uk/
Allan House, 1 Penerley Road, London SE6 2LQ
Phone: +44 (0) 208 698 1500, Fax: +44 (0) 208 695 6409

Institution of Occupational Safety and Health (IOSH),
http://www.iosh.co.uk/
The Grange, Highfield Drive, Wigston,
Leicestershire LE18 1NN
Phone: +44 (0) 116 257 3100, Fax: +44 (0) 116 257 3101

Institution of Plant Engineers – succeeded by The Society of Operation Engineers (SOE)

Insurance Technical Bureau – now disbanded

Joint Fire Research Organisation – see Fire Research Station

Liquefied Petroleum Gas Industry Technical Association,
17 Grosvenor Crescent, London SW1X 7EF

Loss Prevention Council – purchased by BRE and now is the Fire Division (FRS) of the Building Research Establishment Ltd (BRE)

Medical Research Council (MRC),
http://www.mrc.ac.uk/
20 Park Crescent, London W1 B 1AL
Phone: +44 (0) 20 7636 5422, Fax: +44 (0) 20 7436 6179

Meteorological Office (MET),
http://www.met-office.gov.uk/
London Road, Bracknell, Berkshire RG12 2SZ
Phone: +44 (0) 845 300 0300, Fax: +44 (0) 845 300 1300

Ministry of Defence, Defence Science and Technology Laboratory (DSTL),
http://www.dstl.gov.uk/
Porton Down, Salisbury, Wiltshire SP4 0JQ
Phone: +44 (0) 1980 613121, Fax: +44 (0) 1980 613085

Ministry of Defence, Directorate of Safety Environment and Fire Policy (DSEF),
http://www.mod.uk/dsef/
Old War Office, Whitehall, London SW1A 2EU
Phone: +44 (0) 870 607 4455

Down Ministry of Defence,
Tidal Branch, Hydrographic Department (UKHO)
http://www.hydro.gov.uk/
Admiralty Way, Taunton, Somerset TA1 2DN
Phone: +44 (0) 1823 337900, Fax: +44 (0) 1823 284077

National Engineering Laboratory (NEL),
http://www.nel.uk/
East Kilbride, Glasgow, G75 0QU
Phone: +44 (0) 1355 220222, Fax: +44 (0) 1355 272999

National Society for Clean Air (NSCA),
http://www.nsca.org.uk/
44 Grand Parade Brighton, UK BN2 9QA
Phone: +44 (0) 1273 878770, Fax: +44 (0) 1273 606626

National Radiological Protection Board (NRPB),
http://www.nrpb.org/
Chilton, Didcot, Oxon, OX11 0RQ
Phone: +44 (0) 1235 831600, Fax: +44 (0) 1235 833891

National Vulcan Engineering Insurance Group,
3 St Mary, Parsonage, Manchester M60 9AP
Phone: +44 61 834 8124

Oil and Chemical Plant Manufacturers Association,
Suites 41–48, 87 Regent Street, London W1R 7HF

Petroleum Industry Training Board – succeeded by Petroleum Industry National Training Organisations (PINTO), and then by the Council for Oil and Gas Extraction, Chemicals Manufacturing and Petroleoum Industries (COGENT)

Rail Industry Training Council (RITC)
http://www.ritc.org.uk/
B118 Macmillan House, Paddington Station,
London W2 1FT
Phone: +44 (0) 870 2202773, Fax: +44 (0) 870 2202774

The Royal Academy of Engineering,
http:/www.raeng.org.uk/
29 Great Peter Street, Westminster, London SW1P 3LW
Phone: +44 (0) 20 7222 2688, Fax: +44 (0) 20 7233 0054

The Royal Institute of Chemistry – incorporated in The Royal Society of Chemistry

The Royal Meteorological Society,
http://www.royal-met-soc.org.uk/
104 Oxford Road, Berkshire RG1 7LL
Phone: +44 (0) 118 9568500, Fax: +44 (0) 118 9568571

The Royal Society,
http://www.royalsoc.ac.uk/
6-9 Carlton House Terrace, London SW1Y 5AG
Phone: +44 (0) 20 7839 5561, Fax: +44 (0) 20 7930 2170

The Royal Society of Chemistry (RSC),
http://www.rsc.org/
Burlington House, Piccadilly, London W1J 0BA
Phone: +44 (0) 20 7437 8656, Fax: +44 (0) 20 7437 8883

The Royal Society for the Prevention of Accidents (RoSPA),
http://www.rospa.com/CMS/
Edgbaston Park, 353 Bristol Road, Edgbaston,
Birmingham B5 7ST
Phone: +44 (0) 121 248 2000, Fax: +44 (0) 121 248 2001

Safety in Mines Research Establishment

Sheffield Safety and Reliability Directorate – see
UK Atomic Energy Authority

Safety and Reliability Society,
http://www.sars.u-net.com
Clayton House, 59 Piccadilly, Manchester M1 2AQ
Phone: +44 (0) 161 228 7824, Fax: +44 (0) 161 236 6977

Society of Chemical Industry (SCI),
http://www.soci.org/SCI/
14-15 Belgrave Square, London SW1X 8BS
Phone: +44 (0) 20 7598 1500, Fax: +44 (0) 20 7598 1545

Society of Gas Tanker and Terminal Operators (SIGTTO),
http://www.sigtto.org/
Liaison Office, 17 St. Helen's Palace, London, EC3A 6DG
Phone: +44 (0) 20 7628 1134, Fax: +44 (0) 20 7628 3163

Society of Occupational Medicine (SOM),
http://www.som.org.uk/
Royal College of Physicians, 6 St. Andrew's Place,
Regent's Park, London NW1 4LB
Phone: +44 (0) 20 7486 2641, Fax: +44 (0) 20 7486 0028

The Society of Operation Engineers (SOE),
http://www.soe.org.uk/soe.org/
22 Greencoat place, London, SW1P 1PR,
Phone: +44 (0) 20 7630 1111, Fax: +44 (0) 20 7630 6677

Trades Union Congress (TUC),
http://www.tuc.org.uk/
23-28 Great Russell Street, London WC1B 3LS

Transport and Road Research Laboratory (TRL),
http://www.trl.co.uk/
Old Wokingham Road, Crowthorne
Berkshire, RG45 6AU
Phone: +44 (0) 1344 770007, Fax: +44 (0) 1344 770880

TUC Centenary Institute of Occupational Health,
London School of Hygiene and Tropical Medicine,
http://www.tuc.org.uk/h_and_s/
http://www.lshtm.ac.uk/
Keppel Street, London WC1E 7HT
Phone: +44 (0) 20 7636 8636, Fax: +44 (0) 20 7436 5389

UK Atomic Energy Authority (UKAEA),
http://www.ukaea.org.uk/
Harwell International Business Centre, Didcot,
Oxon, OX11 0RA
Phone: +44 (0) 1235 820220

UK Atomic Energy Authority, Safety and Reliability
Directorate
Wigshaw Lane, Culcheth, Warrington, Lancashire

The Welding Institute (TWI),
http://www.twi.co.uk/
Granta Park, Great Abington, Cambridge CB1 6AL, UK
Phone: +44 (0) 1223 891162, Fax: +44 (0) 1223 892588

United States

Air Pollution Control Association,
Pittsburgh, PA 15230

American Association for Artificial Intelligence (AAAI)
http://www.aaai.org/
445 Burgess Drive, Menlo Park, CA 94025-3442
Phone: +1 (650) 328 3123, Fax: +1 (650) 321 4457

American Chemistry Council (ACC),
http://www.americanchemistry.com/
1300 Wilson Blvd. Arlington, VA 22209
Phone: +1 (703) 741 5000, Fax: +1 (703) 741 6000

American Chemical Society (ACS),
http://www.chemistry.org/
1155 16th Street, NW, Washington, DC 20036
1300 Wilson Blvd. Arlington, VA 22209
Phone: +1 (703) 741 5000, Fax: +1 (703) 741 6000

American Chemical Society (ACS),
http://ww.chemistry.org/
Phone: +1 (800) 227 5558 (US only), +1 (202) 872 4600
(outside the US), Fax: +1 (202) 872 4615

American Gas Association (AGA),
http://www.aga.org/
400 N. Capitol Street, N.W. Washington, DC 20001
Phone: +1 (202) 824 7000, Fax: +1 (202) 824 7115

American Industrial Hygiene Association (AIHA),
http://www.aiha.org/
2700 Prosperity Avenue, Suite 250, Fairfax, VA 22031
Phone: +1 (703) 849 8888, Fax: +1 (703) 207 3561

American Institute for Aeronautics and
Astronautics (AIAA),
http://www.aiaa.org/
1801 Alexander Bell Drive, Suite 500
Reston, VA 20191-4344
Phone: +1 (703) 264 7500, Fax: +1 (703) 264 7551

American Institute of Chemical Engineers (AIChE),
http://www.aiche.org/
3 Park Avenue, New York, NY 10016-5991
General Inquiries: +1 (212) 591 7338,
Fax: +1 (212) 591 8897

American Insurance Association (AIA),
http://www.aiadc.org/
Washington, D.C. Headquarters
1130 Connecticut Ave, NW
Ste. 1000, Washington, DC 20036
Phone: +1 (202) 828 7100, Fax: +1 (202) 293 1219

American Meteorological Society (AMS),
http://www.ametsoc.org/AMS/
Headquarters, 45 Beacon Street, Boston, MA 02108-3693
Phone: +1 (617) 227 2425, Fax: +1 (617) 742 8718

American National Standards Institute (ANSI),
http://www.ansi.org/
New York City Office (Operations), 25 West 43rd Street, 4th Floor, New York, NY 10036
Phone: +1 (212) 642 4900, Fax: +1 (212) 398 0023

American Nuclear Society (ANS),
http://www.ans.org/
555 N Kensington Avenue, Lagrange Park, IL 60525
Phone: +1 (708) 352 6611, Fax: +1 (708) 352 0499

American Petroleum Institute (API),
http:// www.api.org /
1220 L Street, NW, Washington, DC 20005-4070
Phone: +1 (202) 682 8000

American Society of Civil Engineers (ASCE),
http://www.asce.org/
1801 Alexander Bell Drive, Reston, Virginia 20191-4400
Phone: +1 (703) 295 6300, Fax: +1 (703) 295 6222

American Society of Heating, Refrigerating and Ventilating Engineers – succeeded by American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE),
http://www.ashrae.org/
1791 Tullie Circle NE, Atlanta, GA 30329
Phone: +1 (404) 636 8400, Fax: +1 (404) 321 5478

American Society of Mechanical Engineers (ASME)
http://www.asme.org/
Headquarters, Three Park Avenue, New York, NY 10016-5990
Phone: +1 (212) 591 7722, Fax: +1 (212) 591 7674

American Society for Quality (ASQ),
http://www.asq.org/
600 North Plankinton Avenue, Milwaukee, WI 53203
Phone: +1 (414) 272 8575, Fax: +1 (414) 272 1734

American Society of Safety Engineers (ASSE),
http://www.asse.org/
Customer Service: 1800 E Oakton St., Des Plaines, IL 60018
Phone: +1 (847) 699 2929, Fax: +1 (847) 768 3434

American Society for Testing and Materials (ASTM),
http://www.astm.org/
100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959
Phone: +1 (610) 832 9585, Fax: +1 (610) 832 9555

American Standards Association – now American National Standards Institute (ANSI)

American Trucking Association (ATA),
http://www.truckline.com/
2200 Mill Road, Alexandria, VA 22314-4677
Phone: +1 (703) 838 1700

American Welding Society (AWS),
http://www.aws.org/
550 Lejeune Road, Miami, FL 33126
Phone: +1 (800) 443 9353

Argonne National Laboratory,
http://www.anl.gov/
Main site: 9700 South Cass Avenue, Argonne, IL 60439
Phone: +1 (630) 252 2000
Idaho site: Argonne-West, P.O. Box 2528, Idaho Falls, ID 83403-2528.
Phone: +1 (208) 533 7341

Association of American Railroads (AAR),
http://www.aar.org/
50 F Street NW, Washington, DC 20001-1564
Phone: +1 (202) 639 2200, Fax: +1 (202) 639 2439

Atomic Energy Commission – now Nuclear Regulatory Commission

Ballistics Research Laboratories,
http://www.apg.army.mil/default.htm
Aberdeen Proving Ground, MD 21005
Phone: +1 (410) 306 1403

Battelle Columbus Laboratory,
http://www.battelle.org/default.stm
505 King Avenue, Columbus, OH 43201
Phone: +1 (614) 424 6424, Fax: (614) 424 5263

Battelle Northwest Laboratory,
http://www.pnl.gov/
092 Battelle Boulevard, Richland, WA 99352
Phone: +1 (509) 375 2121

Brookhaven National Laboratory,
http://www.bnl.gov/world/
P.O. Box 5000, Upton, NY 11973-5000
Phone: +1 (631) 344 8000

Bureau of Mines (USMB) – closed in 1996 see Minerals Information Team, USGS Geologic Division

Center for Chemical Process Safety (CCPS),
http://www.aiche.org/ccps/
American Institute of Chemical Engineers, 3 Park Ave, New York, N.Y., 10016-5991
Phone: +1 (212) 591 7319, Fax: +1 (212) 591 8895

Chemical Manufacturers Association (CMA),
www.cmahq.com/
Wilson Boulevard, Arlington, Virginia 22209
Phone: +1 (703) 741 5922, Fax: +1 (703) 741 6922

Chemical Transport Emergency Center (CHEMTREC),
http://www.chemtrec.org/
1300 Wilson Blvd, Arlington, VA. 22209
Phone: +1 (703) 741 5523, Fax: +1 (703) 741 6037

Chemical Safety and Hazard Investigation Board (CSB),
http://www.chemsafety.gov/
2175 K. Street N.W.-Suite 400, Washington, D.C. 20037-1809
Phone: +1 (202) 261 7600, Fax: +1 (202) 261 7650

Chlorine Institute,
http://www.cl2.com/
1300 Wilson Blvd., Rosslyn, VA 22209
Phone: +1 (703) 741 5760, Fax: +1 (703) 741 6068

Clearinghouse for Occupational Safety and Health Information, Public Health Service,
4676 Columbia Parkway, Cincinnati, OH 45226

Combustion Institute,
http://www.combustioninstitute.org/
5001 Baum Road, Suite 635, Pittsburgh,
PA 15213-1851 USA
Phone: +1 (412) 687 1366
Fax: +1 (412) 687 0340

Compressed Gas Association (CGA),
http://www.cganet.com/
4221 Walney Road, 5th Floor, Chantilly VA 20151-2923
Phone: +1 (703) 788 2700, Fax: +1 (703) 961 1831

Department of Transportation Research and
Special Programs Administration,
Office of Hazardous Materials (OHM)
http://hazmat.dot.gov/
DHM-1400 7th Street SW, Washington, DC 20590
Washington, DC 20590-0001
Phone: +1 (202) 366 0656, Fax: +1 (202) 366 5713

Department of Transportation, US Coast Guard
http://www.uscg.mil/hq/g-m/gmhome.htm
2100 Second Street SW, Washington, DC 20593-0001
Phone: +1 (202) 267 2200, Fax: +1 (202) 267 4839

Dow Chemical Company,
Bldg 566, Midland, MI 48640

Earthquake Engineering Research Institute (EERI),
http://www.eeri.org/
499 14th Street Suite 320, Oakland, CA 94612-1934
Phone: +1 (510) 451 0905, Fax: +1 (510) 451 5411

Electric Power Research Institute (EPRI),
http://www.epri.com/
3412 Hillview Avenue, Palo Alto, CA 94304
Phone: +1 (800) 313 3774

Environmental Protection Agency (EPA),
Office of Research and Development (ORD),
http://www.epa.gov/ord/
EPA Headquarters: Ariel Rios Building,
1200 Pennsylvania Avenue, N.W.
Mail Code 3213A, Washington, DC 20460
Phone: +1 (202) 260 2090

Ethylene Oxide Industry Council (EOIC),
2501 M Street NW, Washington, DC 20037

Factory Insurance Association – see Industrial
Risk Insurers

Factory Mutual Research Corporation (FMRC),
www.fmglobal.com
1151 Boston-Providence Turnpike, Norwood, MA 02062
Phone: +1 (781) 762 4300

Factory Mutual System,
http://www.fmglobal.com/
1301 Atwood Avenue, P.O. Box 7500 Johnston, R.I. 02919
Phone: +1 (401) 275 3000, Fax: +1 (401) 275 3029

Federal Emergency Management Agency (FEMA),
http://www.fema.gov/
500 C Street, SW Washington, DC 20472
Phone: +1 (202) 566 1600

Federal Energy Regulatory Commission (FERC),
http://www.ferc.gov/
888 First Street, N.E., Washington, DC 20426
Phone: +1 (866) 208 3372

Federal Power Commission – see Federal
Energy Regulatory Commission

Gas Technology Institute (GTI), (formed through the
merger of Institute of Gas Technology and Gas
Research Institute)
http://www.gri.org/
1700 S. Mount Prospect Road, Des Plaines, IL 60018
Phone: +1 (847) 768 0500, Fax: +1 (847) 768 0501

Hartford Steam Boiler Inspection and Insurance Company,
http://www.hsb.com/
One State Street, P.O. Box 5024, Hartford CT 06102-5024
Phone: +1 (860) 722 1866, Fax: +1 (860) 722 5106

Human Factors Society – succeeded by Human Factors
and Ergonomics Society

Human Factors and Ergonomics Society (HFES),
http://hfes.org/
Box 1369, Santa Monica, CA 90406
Phone: +1 (310) 394 1811, Fax: +1 (310) 394 2410

Idaho National Laboratory,
http://www.inel.gov/
2525 Fremont Avenue, P.O. Box 1625, Idaho Falls, ID 83415
Phone: +1 (800) 708 2680

Industrial Risk Insurers (IRI),
http://www.industrialrisk.com/
85 Woodland Street, Hartford, CT 06102-5010
Phone: +1 (860) 520 7300, Fax: +1 (860) 520 7397

Institute of Electrical and Electronic Engineers (IEEE),
http://www.ieee.org/portal/
IEEE Corporate Office, 3 Park Avenue, 17th Floor,
New York, New York, 10016-5997
Phone: +1 (212) 419 7900, Fax: +1 (212) 752 4929

Institute of Electrical and Electronic Engineers,
Reliability Society (IEEE RS),
See Institute of Electrical and Electronic Engineers (IEEE)
information

Institute of Gas Technology,
See Gas Technology Institute (GTI)

The Instrumentation, Systems, and
Automation Society (ISA),
http://www.isa.org/
67 Alexander Drive, P.O. Box 12277
Research Triangle Park, NC 27709
Phone: +1 (919) 549 8411, Fax: +1 (919) 549 8288

Lawrence Livermore National Laboratories,
http://www.llnl.gov/
7000 East Ave., Livermore, CA 94550-9234
P.O. Box 808, Livermore, CA 94551-0808
Phone: +1 (925) 422 1100, Fax: +1 (925) 422 1370

Los Alamos National Laboratory,
http://www.lanl.gov/
P.O. Box 1663, Los Alamos, NM 87545
Phone: +1 (505) 664 5265, Fax: +1 (505) 667 9819

Lovelace Biomedical and Environmental Research
Institute,
http://www.lrri.org/
2425 Ridgecrest Dr. SE, Albuquerque, NM 87108-5127
Phone: +1 (505) 348 9400, Fax: +1 (505) 348 8541

Manufacturers Standardization Society of the Valve and Fittings Industry (MSS),
http://www.mss-hq.com/
127 Park Street NE, Vienna, VA, 22180-4602
Phone: +1 (703) 281 6613, Fax: +1 (703) 281 6671

Manufacturing Chemists Association – now Chemical Manufacturers Association

Minerals Information Team, USGS Geologic Division
http://minerals.usgs.gov/minerals/
http://minerals.usgs.gov/minerals/pubs/mit/
U.S. Geological Survey, 988 National Center, Reston, VA 20192
Phone: +1 (703) 648 6140, Fax: +1 (703) 648 4995

National Academy of Science – National Academy of Engineering – National Research Council,
2101 Constitution Avenue NW, Washington, DC 20418

National Academies
http://nationalacademies.org/
2101 Constitution Avenue NW, Washington, DC 20418
Phone: +1 (202) 334 2000

National Academy of Engineering (NAE),
http://www.nae.edu/
(See National Academies)

National Academy of Science,
http://www4.nationalacademies.org/nas/nashome.nsf
(See National Academies)

National Aeronautics and Space Administration (NASA),
http://www.hq.nasa.gov/
Headquarters, Washington, DC 20546-0001
Phone: +1 (202) 358 0000

National Board of Fire Underwriters – defunct

National Bureau of Standards,
Chemical Thermodynamics Data Center
http://www.cstl.nist.gov/
Chemical Science and Technology Laboratory, NIST, 100 Bureau Drive, Stop 8300, Gaithersburg, MD 20899-8300
Phone: +1 (301) 975-NIST (6478)

National Center for Atmospheric Research (NCAR),
http://www.ncar.ucar.edu/
Box 3000, 1850 Table Mesa Drive, Boulder, CO 80305
Phone: +1 (303) 497 1000

National Fire Protection Association (NFPA),
http://www.nfpa.org/
1 Batterymarch Park, P.O. Box 9101, Quincy, MA 02269-9101
Phone: +1 (617) 770 3000, Fax: +1 (617) 770 0700

National Institute of Standards and Technology (NIST)
http://www.nist.gov/
Building and Fire Research Laboratory, Gaithersburg, MD 20899
Phone: +1 (301) 975 6850, Fax: +1 (301) 975 4032

National Institute for Occupational Safety and Health (NIOSH),
http://www.cdc.gov/niosh/
4676 Columbia Parkway, Cincinnati, OH 45226
Phone: +1 (800) 356 4674, Fax: +1 (513) 533 8573

National LP Gas Association (LPGA) – now National Propane Gas Association (NPGA)

National Propane Gas Association (NPGA),
http://www.npga.org/
1150 17th Street, NW, Suite 310, Washington, DC 20036
Phone: +1 (202) 466 7200

National Research Council (NRC),
http://nationalacademies.org/nrc/
(See National Academies)

National Response Center (NRC)
http://www.nrc.uscg.mil/
c/o United States Coast Guard (G-OPF)-Room 2611, 2100 2nd Street, Southwest Washington, DC 20593-0001
Phone: +1 (202) 267 2675, Fax: +1 (202) 267 2165
TDD: +1 (202) 267 4477 (TDD means Telecommunications Device for the Deaf)

National Safety Council (NSC),
http://www.nsc.org/
1121 Spring Lake Drive, Itasca, IL 60143-3201
Phone: +1 (630) 285 1121, Fax: +1 (630) 285 1315

National Technical Information Service (NTIS),
http://www.ntis.gov/
U.S. Department of Commerce Technology Administration, 5285 Port Royal Road, Springfield, VA 22161
Phone: +1 (703) 605 6000
TDD: (703) 487 4639

National Transportation Safety Board (NTSB),
http://www.ntsb.gov/
490 L'Enfant Plaza, SW, Washington, DC 20594
Phone: +1 (202) 314 6000

Naval Surface Weapons Center (NSWC) – now disbanded

Nuclear Regulatory Commission,
http://www.nrc.gov/
Office of Public Affairs (OPA), Washington, DC 20555
Phone: +1 (800) 368 5642

Oak Ridge National Laboratory,
http://www.ornl.gov/
One Bethel Valley Road or P.O. Box 2008, Oak Ridge, TN 37831
Phone: +1 (865) 241 7600, Fax: +1 (865) 241 7603

Occupational Safety and Health Administration (OSHA),
http://www.osha.gov/
200 Constitution Avenue NW, Washington, DC 20210
Phone: +1 (800) 321 6742

Oil Insurance Association – merged in Industrial Risk Insurers (IRI)

Reliability Division American Society for Quality (ASQ) – see information for American Society for Quality (ASQ)

Sandia National Laboratory,
http://www.sandia.gov/
Sandia National Laboratories, New Mexico, P.O. Box 5800, Albuquerque, NM 87185-(mail stop)
Corporate Ombudsman Office: Mail Stop 0620
Phone: (505) 844 9763

System Safety Society (SSS),
http://www.system-safety.org/
P.O. Box 70, Unionville, VA 22567-0070
Phone: +1 (540) 854 8630

Society of Reliability Engineers (SRE)
http://www.sre.org/

Synthetic Organic Chemical Manufacturers Association (SOCMA),
http://www.socma.com/
1850 M Street NW, Suite 700, Washington, DC 20036
Phone: +1 (202) 721 4100, Fax: +1 (202) 296 8120

Southwestern Research Institute (SwRI),
http://www.swri.edu/default.htm
6220 Culebra Road, P.O. Drawer 28510, San Antonio, TX 78228-0510
Phone: +1 (210) 684 5111

Underwriters Laboratories Inc. (UL),
http://www.ul.com/
333 Pfingsten Road, Northbrook, IL 60062-2096
Phone: +1 (708) 272 8800, Fax: +1 (708) 272 8129

Union of Concerned Scientists (UCS),
http://www.ucsusa.org/
2 Brattle Square, Cambridge, MA 02238-9105
Phone: +1 (617) 547 5552, Fax: +1 (617) 864 9405

USA Standards Institute — now American National Standards Institute (NIST)

US Department of Transportation (DOT),
http://www.dot.gov/
400 7th Street, S.W., Washington, D.C. 20590
Phone: +1 (202) 366 4000

US Government Printing Office,
http://www.access.gpo.gov/
Office of Congressional and Public Affairs, Room C804, Stop: LP
U.S. Government Printing Office
Washington, DC 20402
Phone: +1 (202) 512 1991, Fax: +1 (202) 512 12

Europe

European Chemical Industry Council (CEFIC)
http://www.cefic.be/
Avenue E. van Nieuwenhuyse, 4, B-1160, Brussels, Belgium
Phone: +32 (2) 676 72 11, Fax: +32 (2) 676 73 00

European Commission,
http://europa.eu.int/comm/
B-1049, Brussels, Belgium
Phone: +32 (2) 299 11 11

European Commission, Joint Research Centre,
http://www.jrc.cec.eu.int/
Via E. Fermi 1, I-21020 Ispra (VA), Italy
Phone: +39 (0332) 789111, Fax: +39 (0332) 789001

European Process Safety Centre,
c/o Institution of Chemical Engineers, q.v.
http://www.epsc.org/
165-189 Railway Terrace, Rugby, CV21 3HQ, UK
Phone: +44 (0) 1788 534409, Fax: +44 (0) 1788 551542

Other Countries

Canada

Canadian Centre for Occupational Health and Safety (CCOHS)
http://www.ccohs.ca/
250 Main Street East, Hamilton, Ontario, L8N 1H6
Phone: 1 (905) 570 8094, Fax: 1 (905) 572 2206

Finland

Ministry of Social Affairs and Health (STM, sosiaali- ja terveysministeriö),
http://www.vn.fi/stm/english/
Postal address: P.O. Box 33, FIN-00023 Government
Visiting address: Meritullinkatu 8, 00170 Helsinki
Phone: +358 (9) 160 01, Fax: +358 (9) 160 74126

VTT, Technical Research Centre of Finland,
http://www.vtt.fi/
Espoo: P.O. Box 1700, FIN-02044 VTT
Street address: Kemistintie 3, Espoo
Phone: +358 (9) 4561, Fax +358 (9) 456 7020

France

Societe de Chimie Industrielle,
http://www.scifrance.org/
28, Rue Saint Dominique, F-75007 Paris
Phone: +33 (0) 1 53 59 02 10, Fax: +33 (0) 1 45 55 40 33

Germany

Berufsgenossenschaft der Chemischen Industrie
Bundesanstalt fur Materialprufung, Berlin
Bundesanstalt für Materialforschung (BAM)
Federal Institute for Materials Research and Testing
http://www.bam.de/english/
Unter den Eichen 87, 12205 Berlin
Phone: +49 (30) 8104 0, Fax: +49 (30) 8112029

German Berufsgenossenschaften (GB)
(institutions for statutory accident insurance and prevention for trade and industry)
http://www.hvbg.de/

Berufsgenossenschaftliches Institut für Arbeitsschutz (BIA)
http://www.bgchemie.de/
Alte Heerstraße 111, 53754 Sankt Augustin, Bundesrepublik Deutschland
Phone: +49 (22) 41 2 31 02, Fax: +49 (22) 41 2 31 22 34

DECHEMA, Gesellschaft für Chemische Technik und Biotechnologie e.V.
http://www.dechema.de/homepage/welcome-e.html
Theodor-Heuss-Allee 25, D-60486 Frankfurt am Main
Phone: +49 (069) 7564 0, Fax: +49 (069) 7564 201

Deutsches Institut fur Normung (DIN),
http://www2.din.de/
Berlin: 10772 Berlin
Phone: +49 (030) 2601 0, Fax: +49 (030) 2601 1260
Cologne Office: Kamekestraße 8, 50672 Köln
Phone: +49 (02 21) 57 13 0

Technische Uberwachungsverein,
Postfach 21 04 20, Westendstrasse 199, W-8000 Munchen

Verein Deutscher Ingenieure (VDI),
The Association of Engineers
http://www.vdi.de/vdi/english/
Graf-Recke-Str. 84 40239 Düsseldorf
Postfach 10 11 39 40002 Düsseldorf
Phone: +49 (0) 211 62 14 0

Hong Kong

Labour Department, Occupational Safety and Health
http://www.info.gov.hk/labour/eng/osh/index.htm
Service Headquarters, 15/F, Harbour Building,
38 Pier Road, Central
Phone: 2852 4041

Japan

National Research Institute of Fire and Disaster, (NRIFD),
http://www.fri.go.jp/indexe.html
14-1, Nakahara 3 Chome, Mitaka, Tokyo 181-8633
Phone: +81 422 44 8331, Fax: +81 422 42 7719

National Institute of Industrial Safety,
http://www.anken.go.jp/english/top.html
1-4-6, Umezono, Kiyose, Tokyo 204-0024
Phone: +81 424 91 4512, Fax: +81 424 91 7846

Latin America

Pan American Center for Sanitary Engineering and
Environmental Sciences (CEPIS),
http://www.cepis.ops-oms.org/indexeng.html
Los Pinos 259, Urb. Camacho, La Molina, Lima 12
P.O. BOX 4337, Lima 100, Peru
Phone: +51 (1) 437 1077, Fax: +51 (1) 437 8289

The Netherlands

Committee for Prevention of Disasters – see Ministry of
Social Affairs

Ministry of Social Affairs,
P.O. Box 90804, 2509LV, The Hague Stichting CONCAWE,
22 President Kennedylaan, The Hague

TNO Prins Maurits Laboratory (TNO-PML)
http://www.pml.tno.nl/
Lange Kleiweg 137, P.O. Box 45, 2280 AA Rijswijk
Phone: +31 (15) 284 2842, Fax: +31 (15) 284 3991

TNO Environment, Energy and Process Innovation
(TNO-MEP)
http://www.mep.tno.nl/
Laan van Westenenk 501, P.O. Box 342, 7300 AH Apeldoorn
Phone: +31 (55) 549 35 44

Norway

Christian Michelsen Research AS,
http://www.cmr.no/
Postal address: P.O. Box 6031 Postterminalen,
N-5892 Bergen, Norway
Visiting address: Fantoftvegen 38, Fantoft
Phone: +47 (55) 57 40 40, Fax: +47 (55) 57 40 41

DNV Technology Services
http://www.dnv.com/technologyservices/
Corporate Headquarters, Oslo: Veritasveien 1, 1322 Høvik
Phone: +47 (67) 57 99 00, Fax: +47 (67) 57 99 11

Norwegian Fire Research Laboratory (NBL),
http://www.nbl.sintef.no/
Postal address: N-7465 Trondheim,
Visiting address: Tiller Bru, Trondheim
Phone: +47 (73) 59 10 78, Fax: +47 (73) 59 10 44

Norwegian Society of Chartered Engineers,
http://www.nif.no/
P.O. Box 2312, Solli, N-0201 Oslo,
Phone: +47 (22) 94 75 29, Fax: +47 (22) 94 75 59

Oreda,
http://www.sintef.no/static/TL/projects/oreda/
c/o DNV Technology Services,
c/o SINTEF Industrial Management,
SINTEF Industrial Management
http://www.sintef.no/units/indman/index.html
S.P. Andersensv. 5, 7465 Trondheim
Phone: +47 (73) 59 03 00, Fax: +47 (73) 59 03 30

Switzerland

Schweizerische Chemische Gesellschaft,
http://www.swiss-chem-soc.ch/
c/o SANW, Bärenplatz 2, 3011 Bern
Phone: +41 (0) 31 310 40 90, Fax: +41 (0) 31 312 16 78

International

Intergovernmental Maritime Consultative Organisation –
see International Maritime Organization

International Association of Fire Chiefs (IAFC),
http://www.iafc.org/
4025 Fair Ridge Dr., Suite 300, Fairfax,
VA 22033-2868, USA
Phone: +1 (703) 273 0911, Fax: +1 (703) 273 9363

International Association of Firefighters (IAFF),
http://www.iaff.org/
1750 New York Ave. NW, Washington, DC 20006-5395, USA
Phone: +1 (202) 737 8484, Fax: +1 (202) 737 8418

International Atomic Energy Agency,
http://www.iaea.or.at/
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International Council of Chemical Associations (ICCA),
http://www.icca-chem.org/
International Chamber of Shipping,
http://www.marisec.org/
12 Carthusian Street, London EC1M 6EZ, UK
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International Commission on Radiological Protection,
http://www.icrp.org/
SE-171 16 Stockholm Sweden
Fax: +46 (8) 729 729 8

International Federation of Chemical and General
Workers Unions (ICF) – see International Federation
of Chemical, Energy, Mine, and General Workers'
Unions (ICEM)

International Federation of Chemical, Energy, Mine,
and General Workers' Unions (ICEM)
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Avenue Emile de Béco, 109, B-1050 Brussels, Belgium.
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International Gas Union (IGU)
http://www.igu.org/
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International Institute for Applied Systems Analysis (IIASA),
http://www.iiasa.ac.at/
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International Institute for Refrigeration (IIR),
Institut International du Froid
http://www.iifiir.org/
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International Institute of Ammonia Refrigeration (IIAR)
http://www.iiar.org/
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VA 22201, USA
Phone: +1 730 312 4200, Fax: +1 703 312 0065

International Maritime Organization,
http://www.imo.org/home.asp
4 Albert Embankment, London, SE1 7SR, United Kingdom
Phone: +44 (0) 20 7735 7611, Fax: +44 (0) 20 7587 3210

International Labour Organisation (ILO),
http://www.ilo.org/public/english/index.htm
4, route des Morillons
CH-1211 Geneva 22, Switzerland
Phone: +41 (22) 799 6111, Fax: +41 (22) 798 8685

International Occupational Safety and Health Information Centre, International Labour Office (ILO-CIS),
http://www.ilo.org/public/english/protection/safework/cis/index.htm
CH-1211 Geneva 22, Switzerland
Phone: +41 (22) 799 6740, Fax: +41 (22) 799 8516

International Labour Office, International Standards Organization (ISO),
http://www.iso.ch/iso/en/ISOOnline.frontpage
1 rue de Varembe, Case postale 56, CH-1211 Geneva 20,
Switzerland
Phone: +41 (22) 749 01 11, Telefax: +41 (22) 733 34 30

Oil Companies International Maritime Forum (OCIMF),
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27 Queen Anne's Gate, London, SW1H 9BU,
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Organization for Economic Co-operation and Development (OECD),
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United Nations Environment Programme (UNEP),
http://www.unep.org/default.asp
United Nations Avenue, Gigiri, P.O. Box 30552,
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World LP Gas Association (WLPGA),
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United Nations Environment Programme/Division of Technology, Industry and Economics (UNEP/DTIE)
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Appendix 30

Units and Unit Conversions

Contents

A30.1 Absolute and Gauge Pressures A30/2
A30.2 Other Units and Conversions A30/2

SI units are used in this book unless otherwise stated, these are described in BS 5555:1981 *SI Units and Recommendations for the Use of their Multiples and of Certain Other Units*.

Table A30.1 gives selected references on units.

A30.1 Absolute and Gauge Pressures

It is common practice to attach to units of pressure an 'a' or a 'g', denoting 'absolute' or 'gauge', respectively (e.g. bara, psig). This is not part of the SI system, where instead the designation 'absolute' or 'gauge' or some other defining term is applied to the pressure described. In this book both practices are used.

A30.2 Other Units and Conversions

Some other units which are used in the book are

Table A30.1 *Selected references on units*

Chappelear (1981); Horvath (1986); Mullin (1986)

A30.2.1 Volumetric flux

$1\ \mathrm{l/m^2\,s} = 10^{-3}\ \mathrm{m^3/m^2\,s}$
$1\ \mathrm{l/m^2\,min} = 1.667 \times 10^{-5}\ \mathrm{m^3/m^2\,s}$
$1\ \mathrm{UK\ gal/ft^2\,min} = 8.149 \times 10^{-4}\ \mathrm{m^3/m^2\,s}$
$1\ \mathrm{US\ gal/ft^2\,min} = 6.791 \times 10^{-4}\ \mathrm{m^3/m^2\,s}$

A30.2.2 Other quantities

SI unit conversion

Conversions of other units to and from SI units are given in tables compiled by Mullin (1967) and Lees (1968). The conversion table given by the latter is reproduced in Table A30.2.

$1\ \mathrm{bbl\ (barrel)} = 42\ \mathrm{US\ gal}$
$1\ \mathrm{lusec} = 10^{-3}\ \mathrm{torr\,l/s}$
$1\ \mathrm{micron} = 10^{-6}\ \mathrm{m}$
$1\ \mathrm{mil} = 10^{-3}\ \mathrm{in.} = 2.540 \times 10^{-5}\ \mathrm{m}$
$1\ \mathrm{torr} = 1\ \mathrm{mmHg} = 1.333 \times 10^{2}\ \mathrm{N/m^2}$

Table A30.2 *SI unit conversion tables (Lees, 1968)*

Acceleration	$1\ \mathrm{cm/s^2}$	$1.0000 \times 10^{-2}\ \mathrm{m/s^2}$
	$1\ \mathrm{m/h^2}$	$7.7160 \times 10^{-8}\ \mathrm{m/s^2}$
	$1\ \mathrm{ft/s^2}$	$3.0480 \times 10^{-1}\ \mathrm{m/s^2}$
	$1\ \mathrm{ft/h^2}$	$2.3519 \times 10^{-8}\ \mathrm{m/s^2}$
	$1\ \mathrm{g}$	$9.8067\ \mathrm{m/s^2}$
Area	$1\ \mathrm{cm^2}$	$1.0000 \times 10^{-4}\ \mathrm{m^2}$
	$1\ \mathrm{ft^2}$	$9.2903 \times 10^{-2}\ \mathrm{m^2}$
	$1\ \mathrm{in.^2}$	$6.4516 \times 10^{-4}\ \mathrm{m^2}$
	$1\ \mathrm{yd^2}$	$8.3613 \times 10^{-1}\ \mathrm{m^2}$
	1 acre	$4.0469 \times 10^{3}\ \mathrm{m^2}$
	$1\ \mathrm{mile^2}$	$2.5900 \times 10^{6}\ \mathrm{m^2}$
	1 ha	$1.0000 \times 10^{4}\ \mathrm{m^2}$
Calorific value (volumetric)	$1\ \mathrm{cal/cm^3}$	$4.1868 \times 10^{6}\ \mathrm{J/m^3}$
	$1\ \mathrm{kcal/m^3}$	$4.1868 \times 10^{3}\ \mathrm{J/m^3}$
	$1\ \mathrm{Btu/ft^3}$	$3.7260 \times 10^{4}\ \mathrm{J/m^3}$
	$1\ \mathrm{Chu/ft^3}$	$6.7067 \times 10^{4}\ \mathrm{J/m^3}$
	$1\ \mathrm{therm/ft^3}$	$3.7260 \times 10^{9}\ \mathrm{J/m^3}$
	$1\ \mathrm{kcal/ft^3}$	$1.4786 \times 10^{5}\ \mathrm{J/m^3}$
Coefficient of expansion (volumetric)	$1\ \mathrm{g/cm^3\,°C}$	$1.0000 \times 10^{3}\ \mathrm{kg/m^3\,°C}$
	$1\ \mathrm{lb/ft^3\,°F}$	$2.8833 \times 10\ \mathrm{kg/m^3\,°C}$
	$1\ \mathrm{lb/ft^3\,°C}$	$1.6018 \times 10\ \mathrm{kg/m^3\,°C}$
Density	$1\ \mathrm{g/cm^3}$	$1.0000 \times 10^{3}\ \mathrm{kg/m^3}$
	$1\ \mathrm{lb/ft^3}$	$1.6018 \times 10\ \mathrm{kg/m^3}$
	1 lb/UK gal	$9.9776 \times 10\ \mathrm{kg/m^3}$
	1 lb/US gal	$1.1983 \times 10^{2}\ \mathrm{kg/m^3}$
	$1\ \mathrm{kg/ft^3}$	$3.5315 \times 10\ \mathrm{kg/m^3}$
	1 ton/vd^3	$1.3289 \times 10^{3}\ \mathrm{kg/m^3}$
	1 slug/ft^3	$5.1538 \times 10^{2}\ \mathrm{kg/m^3}$
	1 pdl/in.^{3}	$8.6032 \times 10^{2}\ \mathrm{kg/m^3}$
	$1\ \mathrm{dyn/cm^3}$	$1.0197\ \mathrm{kg/m^3}$
Diffusion coefficient – *see* Viscosity, kinematic		
Energy	1 cal	4.1868 J
	1 kcal	4.1868×10^{3} J
	1 Btu	1.0551×10^{3} J
	1 erg	1.0000×10^{-7} J
	1 hp h (metric)	2.6477×10^{6} J
	1 kW h	3.6000×10^{6} J
	1 ft pdl	4.2139×10^{-2} J

	1 ft lbf	1.3558 J
	1 Chu	1.8991×10^3 J
	1 hp h (British)	2.6845×10^6 J
	1 therm	1.0551×10^8 J
	1 thermic	4.1858×10^6 J
	1 ft kgf	2.9891 J
	1 kgf m	9.8066 J
	1 dyn cm	1.0000×10^{-7} J
Force	1 dyn	1.0000×10^{-5} N
	1 kgf	9.8067 N
	1 pdl	1.3826×10^{-1} N
	1 lbf	4.4482 N
	1 tonf (UK)	9.9640×10^3 N
	1 tonf (US)	8.8964×10^3 N
	1 tonnef	9.8067×10^3 N
Heat – *see* Energy		
Heat of combustion, formation, etc. – *see* Specific enthalpy		
Heat capacity – *see* Specific heat		
Heat flow – *see* Power		
Heat flux	1 cal/s cm^2	4.1868×10^4 W/m^2
	1 kcal/h m^2	1.1630 W/m^2
	1 Btu/h ft^2	3.1546 W/m^2
	1 Chu/h ft^2	5.6784 W/m^2
	1 kcal/h ft^2	1.2518×10 W/m^2
	1 ft lb/min ft^2	2.4323×10^{-1} W/m^2
	1 hp/ft^2	7.9168×10^3 W/m^2
	1 W/$in.^2$	1.5500×10^3 W/m^2
Heat release rate (mass)	1 cal/s g	4.1868×10^3 W/kg
	1 kcal/h kg	1.1630 W/kg
	1 Btu/h lb	6.4611×10^{-1} W/kg
Heat release rate (volumetric)	1 cal/s cm^3	4.1868×10^6 W/m^3
	1 kcal/h m^3	1.1630 W/m^3
	1 Btu/h ft^3	1.0350×10 W/m^3
	1 Chu/h ft^3	1.8629×10 W/m^3
	1 kcal/h ft^3	4.1071×10 W/m^3
Heat transfer coefficient	1 cal/s cm^2 °C	4.1868×10^4 W/m^2 °C
	1 kcal/h m^2 °C	1.1630 W/m^2 °C
	1 Btu/h ft^2 °F	5.6783 W/m^2 °C
	1 Chu/h ft^2 °C	
	1 kcal/h ft^2 °C	1.2518×10 W/m^2 °C
Henry's law constant	1 atm/(g/cm^3)	1.0133×10^2 (N/m^2)/(kg/m^3)
	1 atm/(kg/m^3)	1.0133×10^5 (N/m^2)/(kg/m^3)
	1 atm/(Ib/ft^3)	6.3258×10^3 (N/m^2)/(kg/m^3)
	1 atm/(kg/ft^3)	2.8693×10^3 (N/m^2)/(kg/m^3)
Latent heat – *see* Specific enthalpy		
Length	1 cm	1.0000×10^{-2} m
	1 ft	3.0480×10^{-1} m
	1 Ångstrom	1.0000×10^{-10} m
	1 micron	1.0000×10^{-6} m
	1 in.	2.5400×10^{-2} m
	1 yd	9.1440×10^{-1} m
	1 mile	1.6093×10^3 m
Mass	1 g	1.0000×10^{-3} kg
	1 lb	4.5359237×10^{-1} kg
	1 t (tonne)	1.0000×10^3 kg
	1 grain	6.4799×10^{-5} kg
	1 oz	2.8350×10^{-2} kg
	1 cwt	5.0802×10 kg
	1 ton (long)	1.0160×10^3 kg
	1 ton (short)	9.0719×10^2 kg
	1 dram	1.7718×10^{-3} kg

Mass per unit area	1 g/cm^2	1.0000×10 kg/m^2
	1 dyn/cm^2	1.0197×10^{-2} kg/m^2
	1 lb/ft^2	4.8824 kg/m^2
	1 oz/ft^2	3.0515×10^{-1} kg/m^2
	1 lb/in.^{2}	7.0307×10^{2} kg/m^2
	1 lb/yd^2	5.4249×10^{-1} kg/m^2
	1 long	3.9230×10^{-4} kg/m^2
	1 kg/ft^2	1.0764×10 kg/m^2
Mass flow	1 g/s	1.0000×10^{-3} kg/s
	1 kg/h	2.7778×10^{-4} kg/s
	1 lb/s	4.5359×10^{-1} kg/s
	1 t/h	2.7778×10^{-1} kg/s
	1 lb/h	1.2600×10^{-4} kg/s
	1 ton/h	2.8224×10^{-1} kg/s
Mass flux, mass velocity	1 g/s cm^2	1.0000×10 kg/s m^2
	1 kg/h m^2	2.7778×10^{-4} kg/s m^2
	1 lb/s ft^2	4.8824 kg/s m^2
	1 lb/h ft^2	1.3562×10^{-1} kg/s m^2
	1 kg/h ft^2	2.9900×10^{-3} kg/s m^2
Mass release rate (volumetric)	1 g/s cm^3	1.0000×10 kg/s m^3
	1 kg/h m^3	2.7778×10^{-1} kg/s m^3
	1 lb/s ft^3	1.6018×10 kg/s m^3
	1 lb/h ft^3	4.4496×10^{-3} kg/s m^3
	1 kg/h ft^3	9.8096×10^{-1} kg/s m^3
Mass transfer coefficient, concentration driving force – *see* Velocity		
Mass transfer coefficient, dimensionless driving force – *see* Mass flux		
Mass transfer coefficient, pressure driving force	1 g/s cm^2 atm	9.8687×10^{-5} kg/s m^2 (N/m^2)
	1 kg/h m atm	2.7413×10^{-9} kg/s m^2 (N/m^2)
	1 lb/h ft^2 atm	1.3384×10^{-8} kg/s m^2 (N/m^2)
	1 kg/h ft^2 atm	2.9507×10^{-8} kg/s m^2 (N/m^2)
Momentum, angular	1 g cm^2/s	1.0000×10^{-7} kg m^2/s
	1 lb ft^2/s	4.2140×10^{-2} kg m^2/s
	1 lb ft^2/h	1.1706×10^{-5} kg m^2/s
Momentum, linear	1 g cm/s	1.0000×10^{-5} kg m/s
	1 lb ft/s	1.3826×10^{-1} kg m/s
	1 lb ft/h	3.8404×10^{-5} kg m/s
Moment of inertia	1 g cm^2	1.0000×10^{-7} kg m^2
	1 lb ft^2	4.2140×10^{-2} kg m^2
	1 oz in.^{2}	1.8290×10^{-5} kg m^2
	1 lb yd^2	3.7926×10^{-1} kg m^2
Power	1 cal/s	4.1868 W
	1 kcal/h	1.1630 W
	1 Btu/s	1.0551×10^{3} W
	1 erg/s	1.0000×10^{-7} W
	1 tonne cal/h	1.1630×10^{3} W
	1 hp (metric)	7.3550×10^{2} W
	1 ft pdl/s	4.2140×10^{-2} W
	1 ft lbf/s	1.3558 W
	1 Btu/h	2.9307×10^{-1} W
	1 Chu/h	5.2754×10^{-1} W
	1 hp (British)	7.4570×10^{2} W
	1 ton refrigeration	3.5169×10^{3} W
	1 J/h	2.7778×10^{-4} W
	1 cm^3 atm/h	2.8146×10^{-5} W
Pressure	1 dyn/cm^2	1.0000×10^{-1} N/m^2
	1 kgf/m^2	9.8067 N/m^2
	1 pdl/ft^2	1.4882 N/m^2

	1 atm (standard)	1.0133×10^5 N/m^2
	1 at (1 kgf/cm^2)	9.8067×10^4 N/m^2
	1 bar	1.0000×10^5 N/m^2
	1 lbf/ft^2	4.7880×10 N/m^2
	1 psi (lbf/in.^{2})	6.8948×10^3 N/m^2
	1 tonf/in.^{2}	1.5444×10^7 N/m^2
	1 in. water	2.4909×10^2 N/m^2
	1 ft water	2.9891×10^3 N/m^2
	1 mmHg	1.3332×10^2 N/m^2
	1 inHg	3.3864×10^3 N/m^2
	1 torr	1.3332×10^2 N/m^2
	1 ksi	6.8948×10^6 N/m^2
	1 oz/ft^2	2.9926 N/m^2
Reaction rate – *see* Mass release rate		
Shear stress – *see* Pressure		
Specific enthalpy	1 cal/g	4.1868×10^3 J/kg
	1 Btu/lb	2.3260×10^3 J/kg
	1 Chu/lb	4.1868×10^3 J/kg
	1 kWh/lb	7.9366×10^6 J/kg
	1 ft lbf/lb	2.9891 J/kg
Specific heat	1 cal/g °C	4.1868×10^3 J/kg °C
	1 Btu/lb °F	4.1868×10^3 J/kg °C
	1 ft lbf/lb °F	5.3803 J/kg °C
	1 m kgf/kg °C	9.8067 J/kg °C
Specific volume	1 cm^3/g	1.0000×10^{-3} m^3/kg
	1 ft^3/lb	6.2428×10^{-2} m^3/kg
	1 ft^3/kg	2.8317×10^{-2} m^3/kg
Surface per unit mass	1 cm^2/g	1.0000×10^{-1} m^2/kg
	1 ft^2/lb	2.0482×10^{-1} m^2/kg
	1 m^2/g	1.0000×10^3 m^2/kg
	1 ft^2/kg	9.2903×10^{-2} m^2/kg
	1 yd^2/oz	2.9494×10 m^2/kg
	1 ft^2/oz	3.2771 m^2/kg
	1 mm^2/mg	1.0000 m^2/kg
Surface per unit volume	1 cm^2/cm^3	1.0000×10^2 m^2/m^3
	1 ft^2/ft^3	3.2808 m^2/m^3
	1 ft^2/gal	2.0436×10 m^2/m^3
	1 yd^2/gal	1.8392×10^2 m^2/m^3
Surface tension	1 dyn/cm	1.0000×10^{-3} N/m
	1 erg/cm	1.0000×10^{-3} N/m
	1 mg/in.	3.8609×10^{-4} N/m
	1 kgf/m	9.8070 N/m
	1 pdl/in.	5.4431 N/m
Temperature difference	1 deg F (deg R)	5/9 deg C (deg K)
Thermal conductivity	1 cal/s cm^2	4.1868×10^2 W/m^2 (°C/m)
	1 kcal/h m^2	1.1630 W/m^2 (°C/m)
	1 Btu/h ft^2	1.7307 W/m^2 (°C/m)
	1 Btu/h ft^2	1.4423×10^{-1} W/m^2 (°C/m)
	1 kcal/h ft^2	3.8156 W/m^2 (°C/m)
Time	1 h	3.6000×10^3 s
	1 min	6.0000×10 s
	1 d (day)	8.6400×10^4 s
	1 yr	3.1558×10^7 s
Torque – *see* Energy		
Velocity	1 cm/s	1.0000×10^{-2} m/s
	1 m/h	2.7778×10^{-4} m/s
	1 ft/s	3.0480×10^{-1} m/s
	1 ft/h	8.4667×10^{-5} m/s
	1 mile/h	4.4704×10^{-1} m/s
	1 kn	5.1444×10^{-1} m/s

Viscosity, absolute (or dynamic)	1 g/cm s (1 poise)	1.0000×10^{-1} kg/m s
	1 kg/m h	2.7778×10^{-4} kg/m s
	1 lb/ft s	1.4882 kg/m s
	1 lb/ft h	4.1338×10^{-4} kg/m s
	1 kg/ft h	9.1134×10^{-4} kg/m s
	1 lbf s/in.	6.8948×10^{3} kg/m s
	1 slug/ft s	4.7880×10 kg/m s
Viscosity, kinematic	1 cm^2/s (1 stokes)	1.0000×10^{-4} m^2/s
	1 m^2/h	2.7778×10^{-4} m^2/s
	1 ft^2/s	9.2903×10^{-2} m^2/s
	1 ft^2/h	2.5806×10^{-5} m^2/s
Volume	1 cm^3	1.0000×10^{-6} m^3
	1 ft^3	2.8317×10^{-2} m^3
	1 l (litre)	1.0000×10^{-3} m^3
	1 $in.^3$	1.6387×10^{-5} m^3
	1 yd^3	7.6456×10^{-1} m^3
	1 UK gal	4.5461×10^{-3} m^3
	1 US gal	3.7854×10^{-3} m^3
	1 UK barrel	1.6366×10^{-1} m^3
	1 US barrel	1.1924×10^{-1} m^3
	1 pt	4.7318×10^{-4} m^3
Volumetric flow	1 cm^3/s	1.0000×10^{-6} m^3/s
	1 m^3/h	2.7778×10^{-4} m^3/s
	1 ft^3/s	2.8317×10^{-2} m^3/s
	1 cm^3/min	1.6667×10^{-8} m^3/s
	1 l/min	1.6667×10^{-5} m^3/s
	1 ft^3/min	4.7195×10^{-4} m^3/s
	1 ft^3/h	7.8658×10^{-6} m^3/s
	1 yd^3/min	1.2743×10^{-2} m^3/s
	1 UK gal/min	7.5768×10^{-5} m^3/s
	1 US gal/min	6.3090×10^{-5} m^3/s
	1 UK gal/h	1.2628×10^{-6} m^3/s
	1 US gal/h	1.0515×10^{-6} m^3/s
Wetting rate (mass) – *see* Velocity, absolute		
Wetting rate (volumetric)	1 l/h in.	1.0936×10^{-5} m^3/s m
	– *see also* Viscosity, kinematic	
Work – *see* Energy		

Appendix 31

Process Safety Management (PSM) Regulation in the United States

Contents

A31.1 The Process Safety Management Programme A31/2
A31.2 Summary Comparison of OSHA Elememts with CCPS Elements A31/5

The history of safety regulations in the United States can be traced back to the year before the beginning of the twentieth century. The River and Harbor Act, the first known federal legislation in the United States relevant to safety was promulgated in 1899. This Act prohibited the creation of any obstruction not authorized by the US Congress, to the navigable capacity of any waters of the United States except on plans authorized by the Secretary of the Army. The Act was promulgated expressly to protect the nation's waterways from excessive dumping. Subsequent to the River and Harbor Act, the US Congress has passed numerous laws, which impose environmental or safety regulations on businesses. Since then, the total number of legislations has steadily increased. In addition to the federal government, local entities such as the state, county, and cities have also promulgated regulations and ordnances, which impose safety requirements on process facilities.

In 1936, the United States federal government enacted the Walsh–Healy Act to establish federal safety and health standards for activities relating to federal contracts. The Walsh–Healy Act led to early research into the identification and control of occupational diseases. The ideas behind this Act are the basis of many of today's occupational health and safety regulations.

In 1970, Congress promulgated the Occupational Safety and Health Act (OSHA). As a result of this landmark legislation, OSHA and the National Institute for Occupational Safety and Health (NIOSH) were established within the Department of Labor and the Department of Health and Human Services respectively. OSHA's mission is to, 'Assure so far as possible every working man and woman in the nation safe and healthful working conditions'. The OSHAct allows OSHA to set and enforce standards that require employers to maintain safe and healthful workplaces. NIOSH, on the other hand, does not have any regulatory or enforcement authority, but is charged with the responsibility of training of professionals and with the research and recommendation of new regulations to the Secretary of Labor.

In 1990, EPA analysed chemical incidents in the early to mid-1980s and compared them to the Bhopal incident. The analysis concluded that 17 incidents released sufficient volumes of chemicals that could have been more severe than Bhopal if the weather conditions and plant location were different. Thus, the Clean Air Act Amendments of 1990 contained specific mandates requiring OSHA and EPA to establish regulations to protect workplace employees and the public and the environment, respectively. OSHA fulfilled its mandate in 1992 by promulgating the process safety management regulation.

Although NIOSH and OSHA were created by the same Act of Congress, they are two distinct agencies with separate responsibilities. OSHA is in the Department of Labor and is responsible for creating and enforcing workplace safety and health regulations. NIOSH is in the Department of Health and Human Services and is a research agency. NIOSH identifies the causes of work-related diseases and injuries and the potential hazards of new work technologies and practices. With this information, NIOSH determines new and effective ways to protect workers from chemicals, machinery, and hazardous working conditions. Creating new ways to prevent workplace hazards is the job of NIOSH.

A31.1 The Process Safety Management Programme

The fourteen elements of the OSHA Process Safety Management (PSM) regulation (*29 CFR 1910.119*) were published in the federal register on 24 February 1992. The objective of the regulation is to prevent or minimize the consequences of catastrophic releases of toxic, reactive, flammable, or explosive chemicals. The regulation requires a comprehensive management programme: a holistic approach that integrates technologies, procedures, and management practices.

The process safety management regulation applies to processes that involve certain specified chemicals at or above threshold quantities, processes that involve flammable liquids or gases on-site in one location, in quantities of 10,000 lb or more (subject to few exceptions), and processes which involve the manufacture of explosives and pyrotechnics. Hydrocarbon fuels, which may be excluded if used solely as a fuel, are included if the fuel is part of a process covered by this regulation. In addition, the regulation does not apply to retail facilities, oil or gas well drilling or servicing operations, or normally unoccupied remote facilities.

The management system required by OSHA's process safety management regulation envisions a holistic program with checks and balances aimed at creating multiple barriers of protection. The performance-based approach does not prescribe specific methods and approaches, thus giving facilities the flexibility for customizing the methods to best meet their needs and organizational structures. The process hazard analysis (PHA) is the heart of the programme and impacts or interfaces with all of the other elements. However, it must also be pointed out that all elements of the programme must be implemented in their entirety to get the maximum benefit and accomplish the ultimate objective, that is, reduce the frequency and severity of chemical plant accidents. Each element of the process safety programme is discussed in more detail here.

A31.1.1 Employee participation

This element of the regulation requires developing a written plan of action regarding employee participation; consulting with employees and their representatives on the conduct and development of other elements of process safety management required under the regulation; and providing to employees and their representatives access to process hazard analyses and to all other information required to be developed under this regulation.

A31.1.2 Process safety information

This element of the PSM regulation requires employers to develop and maintain important information about the different processes involved. This information is intended to provide a foundation for identifying and understanding potential hazards involved in the process.

The process safety information covers three different areas, that is, chemicals, technology and equipment. A complete listing of the process safety information that must be compiled in these three areas is shown in Table A31.1. This information is intended to provide a foundation for identifying and understanding potential hazards involved in the process.

The information in Table A31.1 is essential for developing and implementing an effective process safety management programme. The fundamental concept is that complete, accurate, and up-to-date process knowledge is essential for safe and profitable operations. The information contained in the first column of Table A31.1 should be available from the Material Safety Data Sheets (MSDS) for the hazardous chemicals, which are used as primary or

Table A31.1 *Process safety information*

Chemicals	*Technology*	*Equipment*
Toxicity	Block flow diagram or process flow diagram	Design codes employed
Permissible exposure limit	Process chemistry	Materials of construction
Physical data	Maximum intended inventory	Piping and instrumentation diagrams
Reactivity data	Safe limits for process parameters	Electrical classification
Thermal and chemical stability data	Consequence of deviations	Ventilation system design
Effects of mixing		Material and energy balances
		Safety systems
		Relief system design and design basis

intermediate feedstocks or are produced as products at the plant.

The information contained in the second column of Table A31.1 pertains to the technology of the process itself. The block flow diagram can be replaced by a process flow diagram. The process chemistry information must contain the basic chemical reactions involved and a brief description of the chemistry involved. The maximum intended inventory refers to the maximum amount of any regulated chemical that may be expected to be present in the whole facility at any time. The safe limits for process parameters refer to the upper and lower bounds for the process parameters outside of which the process would be hazardous. For example, in the case of a distillation process, the upper and lower limits of the process parameters outside which the operation of the process could cause significant damage to the tower or other attached equipment would have to be stated. In this example, the process parameters for which upper and lower bounds are to be specified are temperature, pressure, composition, and flow rate. The consequence of deviation from these stated bounds must also be compiled.

Safe upper and lower limits for process parameters and equipment are also necessary for calibrating instrumentation. It is important to understand the distinction between process parameter limits and equipment limits. Safe upper and lower limits for process parameters can be defined as follows:

(1) For non-reactive processes, process parameter safe limits are defined based on equipment design ratings, relief device setpoints, and upstream and downstream conditions of the process and/or equipment.
(2) For reactive processes, process parameter safe limits are defined based on the process chemistry information or any restricted physical conditions for the reaction as well as the criteria used for non-reactive processes.

In contrast, equipment limits are specified by the manufacturer based on materials of construction and design basis. Processes must be operated and maintained within both the process parameter and equipment limits.

The final type of information that must be compiled pertains to the equipment used in the process. The intent is to assure that all equipment used in the process meets appropriate standards and codes such as those published by the American Society of Mechanical Engineers (ASME), the American Petroleum Institute (API), the American Institute of Chemical Engineers (AIChE), the American National Standards Institute (ANSI), the American Society of Testing and Materials (ASTM), and the National Fire Protection Association (NFPA). Accepted industry practices can be used to decide which standards apply. In cases where standards do not exist, generally acceptable engineering practices can be used. The materials of construction for each equipment item and the design codes employed can be compiled as separate lists or may be listed in the Piping and Instrumentation Diagram (P&ID). The P&IDs must represent the facility exactly as it exists with flanges, valves, and all other connections shown. The different electrical classifications must also be compiled for different parts of the facility. A simple plot plan showing the different areas of electrical classification would be considered to be in compliance with the regulation. Information must also be compiled on any ventilation system. This information would indicate the areas in the facility that are ventilated and the nature of ventilation. A listing of all safety systems must also be compiled that are available to the workers. This listing should include any and all equipment that is available for protection of the workers from any hazard or emergency. Information should also be available on the location of these safety systems and the procedures to use these systems.

As is apparent from the foregoing discussion, compilation of the process safety information database represents a major challenge. This is complicated even more because the process safety information must also be kept up-to-date and accurate and made accessible to employees. Many plants have therefore implemented or are in the process of implementing electronic data management systems to manage, access, and use these data. The completion and accuracy of process safety information is crucial to the implementation of other PSM elements including PHAs and mechanical integrity.

The PSM regulation requires that process equipment should comply with generally accepted engineering practices. It is therefore not only important to compile all equipment information but also to ensure that it complies with consensus standards. OSHA is recognizing that there are consensus standards for design and fabrication, installation, maintenance procedures, and inspection and testing. Therefore, equipment constructed in accordance with codes, standards, or practices no longer in use should be evaluated to ensure that they are compatible with existing standards. For example, a multi-layered vessel built years ago should be evaluated to ensure that it complies with today's engineering standards.

A31.1.3 Process hazards analysis

This element of the PSM regulation requires facilities to perform a PHA. The PHA must address the hazards of the

process, previous hazardous incidents, engineering and administrative controls, the consequences of the failure of engineering and administrative controls, human factors, and an evaluation of effects of failure of controls on employees. This element requires that the PHA be performed by one or more of the following methods or any other equivalent method:

(1) what-if;
(2) checklist;
(3) what-if/checklist;
(4) hazard and operability (HAZOP) studies;
(5) failure modes and effects analysis (FMEA);
(6) fault tree analysis.

The regulation suggests a performance-oriented requirement with respect to the PHA so that the facility has the flexibility to choose the type of analysis that will best address a particular process. PHAs may not be performed unless complete Process Safety Information is available for the process.

PHAs and the results of PHAs can and will impact the development, implementation, and practice of other elements of the PSM regulation. A PHA would help facilities identify hazards and ways to address them. PHAs also identify situations where process incidents due to control failure (e.g. pressure gauges, overfill alarms) could be prevented by redundant or backup control or by frequent maintenance and inspection practices.

Many other elements of the PSM program should flow from, or at least be revised based on, the results of the PHA. Existing standard operating procedures, training and maintenance programs, and pre-startup safety reviews may need to be revised to reflect changes in either practices or equipment that derive from the PHA. The PHA may help define critical equipment that require preventive maintenance, inspection, and testing programs. It may also help a facility focus its emergency response programs on the most likely and most serious release scenarios.

The PSM regulation also requires that the PHAs be updated and revalidated, based on their completion date. First, the PSM regulation requires that the PHAs shall be updated and revalidated. Thus, the whole PHA should not only be examined to verify that the PHA is consistent with the current process but it also should be analyzed to examine if the original analysis is valid. Second, the PSM regulation requires that the updating and revalidating be done by a team similar in qualifications to the team that conducted the original PHA. The intent of a PHA revalidation is to ensure that the PHA team evaluates the previous PHA, examines the extent of any changes that might have occurred since the PHA was implemented (or last reviewed) and decide what work is needed to make the PHA current.

A31.1.4 Operating procedures

The operating procedures must be in writing and provide clear instructions for safely operating processes; must include steps for each operating phase, operating limits, safety and health considerations and safety systems. Procedures must be readily accessible to employees, must be reviewed as often as necessary to assure they are up- to-date and must cover special circumstances such as lockout/tagout and confined space entry. The employer must certify annually that the operating procedures are current and accurate. The synergism and commonality of operating procedures to maintenance procedures is in safe work practices. These safe work practices include lockout/tagout, confined space entry, opening of process equipment or piping (i.e. hot tapping), and control of entrance into the battery limits. Even though the operations department is involved with all of these practices, maintenance also plays a very vital role in ensuring that these procedures are followed during all maintenance tasks. Many incidents have resulted from inadequate safe work practices or a failure to follow procedures when they exist.

A31.1.5 Training

The regulation requires that facilities certify that employees responsible for operating the facility have successfully completed (including means to verify understanding) the required training. The training must cover specific safety and health hazards, emergency operations and safe work practices. Initial training must occur before assignment. Refresher training must be provided at least every 3 years.

Even though this element of the PSM regulation pertains to operations staff only, it is important to remember that operations and maintenance training should be coordinated.

A31.1.6 Contractors

The PSM regulation identifies responsibilities of the employer regarding contractors involved in maintenance, repair, turnaround, major renovation or specialty work, on or near covered processes. The host employer is required to: consider safety records in selecting contractors; inform contractors of potential process hazards; explain the facility's emergency action plan; develop safe work practices for contractors in process areas; periodically evaluate contractor safety performance; and maintain an injury/illness log for contractors working in process areas. In addition, the contract employer is required to train their employees in safe work practices and document that training, assure that employees know about potential process hazards and the host employer's emergency action plan, assure that employees follow safety rules of facility and advise host employer of hazards contract work itself poses or hazards identified by contract employees.

A31.1.7 Pre-startup safety review

This element of the PSM regulation requires a pre-startup safety review of all new and modified facilities to confirm integrity of equipment; to assure that appropriate safety, operating, maintenance and emergency procedures are in place; and to verify that a PHA has been performed. Modified facilities for this purpose are defined as those for which the modification required a change in the process safety information.

Usually, changes occur during maintenance and therefore, maintenance personnel should be well versed in pre-startup safety review procedures. Maintenance should ensure that all necessary procedures have been completed prior to start-up.

A31.1.8 Mechanical integrity

This element of the PSM regulation mandates written procedures, training for process maintenance employees and inspection and testing for process equipment including pressure vessels and storage tanks; piping systems; relief and vent systems and devices; emergency shutdown systems; pumps; and controls such as monitoring devices, sensors, alarms and interlocks. The PSM regulation calls for correction of equipment deficiencies and assurance that

new equipment and maintenance materials and spare parts are suitable for the process and properly installed.

A31.1.9 Hot work permit

This element of the PSM regulation mandates a permit system for hot work operations conducted on or near a covered process. The purpose of this element of the regulation is to assure that the employer is aware of the hot work being performed, and that appropriate safety precautions have been taken prior to beginning the work. Since welding shops authorized by the employer are locations specifically designated and suited for hot work operations, the regulation does not require a permit for hot work in these locations. Additionally, hot work permits are not required in cases where the employer or an individual to whom the employer has assigned the authority to grant hot work permits is present while the hot work is performed.

A31.1.10 Management of change

This element of the regulation specifies a written programme to manage changes in chemicals, technology, equipment and procedures which addresses the technical basis for the change, impact of the change on safety and health, modification to operating procedures, time period necessary for the change, and authorization requirements for the change. The regulation requires employers to notify and train affected employees and update process safety information and operating procedures as necessary.

A31.1.11 Incident investigation

This element of the regulation requires employers to investigate as soon as possible (but no later than 48 h) incidents, which did result or could have resulted in catastrophic releases of covered chemicals. The regulation calls for an investigation team, including at least one person knowledgeable in the process (a contractor employee, if appropriate), to develop a written report of the incident. Employers must address and document their response to report findings and recommendations and review findings with affected employees and contractor employees. Reports must be retained for 5 years.

A31.1.12 Emergency planning and response

This element requires employers to develop and implement an emergency action plan according to the requirements of *29 CFR 1910.38(a)* and *29 CFR 1910.120(a), (p), and (q).*

A31.1.13 Compliance audits

This element of the regulation requires employers to certify that they have evaluated compliance with process safety requirements every 3 years and specifies retention of the audit report findings and the employer's response. Employer must retain the two most recent audits.

A31.1.14 Trade secrets

Similar to the trade secret provisions of the hazard communication regulation, the PSM regulation also requires information to be available to employees from the process hazard analyses and other documents required by the regulation. The regulation permits employers to enter into confidentiality agreements to prevent disclosure of trade secrets.

A31.2 Summary Comparison of OSHA Elements with CCPS Elements

It is important to point out that the programmes required by OSHA's PSM elements as given in 29 CFR 1910.119 are similar to the requirements of other programme requirements. The comparison matrix in Table A31.2 demonstrates the relevance of OSHA PSM elements to other programmes.

Table A31.2 *Comparison matrix showing the relevance of OSHA PSM elements to other programs*

Program element	*OSHA PSM*[1] *element*	*CAAA Sec. 304*[2] *Par. C Item(s)*	*AIChE CCPS*[3] *Guidelines*	*ACC PSC*[4] *Practice(s)*
Employee Participation	c	[5]	1	[5]
Process Safety Information	d	1	2,10	7,8
Process Hazards Analysis	e	2,3,4	4,6,7	9
Operating Procedures	f	6	6,7,8	7,18
Training	g	7	8	14,17,19,20
Pre-startup Safety Review	i	12	3,4,8	13
Mechanical Integrity	j	10,11	3,6,10	2,12,14,18
Management of Change	l	14	5	10,11
Incident Investigation	m	13	9	4,5
Audits	o	5	11	3
Safe Work Practices	[5], k	[5]	8	18
Emergency Planning/Control/Response	n	9	8	5,6,11,16
Contractors	h	8	–	12,22
Employee Fitness for Duty	–	–	–	21
Multiple Safeguards	[5]	[5]		15
Number of Chemicals	140	100 min.	–	–

[1] OSHA PSM: Occupational Safety and Health Administration Process Safety Management.
[2] CAAA: Clean Air Act Amendments.
[3] AIChE CCPS: American Institute of Chemical Engineers Center for Chemical Process Safety.
[4] ACC PSC: American Chemistry Council Process Safety Code.
[5] Either stated or inherent in other elements.

Appendix 32

Risk Management Program Regulation in the United States

Contents

A32.1 The Risk Management Program A32/2

Environmental issues affecting the public health and the environment also received wide spread attention. As a result, the Environmental Protection Agency (EPA) was established in 1970 to protect the nation's public health and environment. The EPA is responsible, 'to find ways to cleanup and prevent pollution, ensure compliance and enforcement of environmental laws, assisting states in environmental protection efforts, and scientific research and education to advance the nation's understanding of environmental issues'. In 1970, the EPA promulgated the Clean Air Act, followed by amendments to the Act in 1977 and 1990.

The Toxic Substances Control Act (TSCA), passed in 1976 gave EPA the ability to track and study the 75,000 industrial chemicals produced or imported to the United States. The TSCA is a federally enforced law and is not delegated to the state. Under this Act, the EPA has the authority to ban the manufacture or distribution in commerce, limit the use, require labelling, or place other restrictions on chemicals that pose unreasonable risk. Asbestos, chlorofluorocarbons, and ploychlorinated biphenyls are some of the chemicals regulated by EPA under TSCA.

> In 1977, the International Safe Container Act established uniform structural requirements for international cargo containers designed to be transported interchangeably by sea and land carriers. In 1983, the Surface Transportation Assistance Act established protection from reprisal by employers for truckers and certain other employees in the trucking industry involved in activity related to interstate commercial motor vehicle safety and health.

In 1990, EPA analysed chemical incidents in the early to mid-1980s and compared them to the Bhopal incident. The analysis concluded that 17 incidents released sufficient volumes of chemicals that could have been more severe than Bhopal if the weather conditions and plant location were different. Thus, the Clean Air Act Amendments of 1990 contained specific mandates requiring OSHA and EPA to establish regulations to protect workplace employees and the public and the environment respectively. OSHA fulfilled its mandate in 1992 by promulgating the process safety management regulation. EPA on the other hand promulgated the Risk Management Program regulation in 1996. The Clean Air Act Amendments of 1990 also established the Chemical Safety and Hazard Investigation Board.

A32.1 The Risk Management Program

In 1996, EPA promulgated the regulation for *Risk Management Programs for Chemical Accident Release Prevention* (40 CFR 68). This federal regulation was mandated by section 112(r) of the Clean Air Act Amendments of 1990. The regulation requires regulated facilities to develop and implement appropriate Risk Management Program to minimize the frequency and severity of chemical plant accidents. In keeping with regulatory trends, EPA required a performance-based approach towards compliance with the Risk Management Program regulation. The eligibility criteria and requirements for the three different program levels are given in Table A32.1.

The EPA regulation also requires regulated facilities to develop a Risk Management Plan (RMP). The RMP includes a description of the hazard assessment, prevention programme, and the emergency response programme. Facilities submit the RMP to the EPA and subsequently is made available to governmental agencies, the state emergency response commission, the local emergency planning committees, and communicated to the public.

The Risk Management Program regulation defines the worst-case release as the release of the largest quantity of a regulated substance from a vessel or process line failure, including administrative controls and passive mitigation that limit the total quantity involved or release rate. For gases, the worst-case release scenario assumes the quantity is released in 10 min. For liquids, the scenario assumes an instantaneous spill and that the release rate to the air is the volatilization rate from a pool 1 cm deep unless passive mitigation systems contain the substance in a smaller area. For flammables, the scenario assumes an instantaneous release and a vapour cloud explosion using a 10% yield factor. For alternative scenarios (note: EPA used the term *alternative scenario* as compared to the term *more-likely scenario* used earlier in the proposed regulation), facilities may take credit for both passive and active mitigation systems.

Appendix A of the final regulation lists endpoints for toxic substances to be used in worst-case and alternative scenario assessment. The toxic endpoints are based on ERPG-2 (Emergency Response Planning Guidelines – Level 2) or level of concern data compiled by EPA. The flammable endpoints represent vapour cloud explosion distances based on overpressure of 1 psi or radiant heat distances based on exposure to 5 kW/m^2 for 40 seconds.

Similar to OSHA's PSM regulation, coverage under the the EPA risk management program regulation is determined by a list of chemicals with associated threshold quantities. However, in contrast to the OSHA PSM regulation, the EPA Risk Management Program regulation prescribes a tiered programme based on the risk and incident history of the facility. In order to determine coverage and compliance requirements, a facility may follow the steps described below in chronological order:

(1) Check the EPA Risk Management Program list of chemicals to determine if any of the chemicals are present on site above the listed threshold quantity at any time. The threshold quantity determination is not cumulative, but the maximum that could be present on site at any given time. Other considerations that may enter into the threshold quantity determination are proximity, interconnectivity, concentration, etc. EPA also provides rules for mixtures and effect of dilution. If threshold quantity is not exceeded, then the facility is not subject to the EPA risk management program, and steps 2–4 need not be completed.
(2) If any of the listed chemicals are present at or above the listed threshold quantity, the facility must perform a worst-case scenario analysis. If the impact zone from worst-case scenario does not contain any public receptors, the facility has had no incidents in the last 5 years, and the facility's emergency response plan is coordinated with local emergency response officials; then the facility belongs in Program 1.
(3) If the facility can not claim coverage under Program 1 and the facility is classified in any of the industrial classification codes listed in Table A32.1 or the facility is covered by the OSHA PSM regulation, then the facility belongs in Program 3 and must comply with Program 3 requirements.
(4) If the facility does not belong in Program 1 or Program 3, then by default the facility is required to comply with Program 2 requirements.

Table A32.1 *Eligibility criteria and compliance requirements for different program levels – EPA's Risk Management Program regulation*

Program 1	*Program 2*	*Program 3*
Program Eligibility Criteria		
No offsite accident history No public receptors in worst-case circle Emergency response coordinated with local responders	Process not eligible for program 1 or 3	Process is subject to OSHA PSM (29 CFR 1910.119) Process is SIC code 2611, 2812, 2819, 2821, 2865, 2869, 2873, 2879, or 2911
Program Requirements		
Hazard assessment Worst-case analysis 5-year accident history Certify no additional steps needed	*Hazard assessment* Worst-case analysis Alternative releases 5-year accident history	*Hazard assessment* Worst-case analysis Alternative releases 5-year accident history
	Management program Document management system	*Management program* Document management system
	Prevention Program Safety information Hazard review Operating procedures Training Maintenance Incident investigation Compliance audit	*Prevention Program* Process safety information Process hazard analysis Operating procedures Training Mechanical integrity Incident investigation Compliance audit Management of change Pre-startup safety review Contractors Employee participation Hot work permits
	Emergency response program Develop plan and program	*Emergency response program* Develop plan and program

As stated earlier, EPA used a tiered approach based on risk and the facility's incident history. It is a recognition of the fact that one size does not fit all and the risk management program is based on a three-pronged approach. First, the hazard assessment provides information about potential off-site consequences and the incident history of the facility. The prevention programme and the emergency response programme are then developed based on the hazard assessments. It should be noted that the prevention programme requirements under Program 3 mirror the OSHA PSM programme requirements.

Appendix 33

Incident Databases

Contents

A33.1 Incident Databases A33/2
A33.2 Injury Fatality Databases (Not tied to Specific Incidents) A33/3
A33.3 Incident Investigation Reports A33/3

Accident prevention and mitigation of consequences is the focus of a number of industry programmes, regulatory initiatives. As part of these programmes and regulations, accident history data is often collected. There are two basic types of information. One is a database consisting of standardized fields of data usually for a large number of incidents. The second are more detailed reports of individual incidents.

Analysis of these accident history databases can provide insight into accident prevention needs. While the analysis and conclusions obtained from the accident database is often limited by the shortcomings of the databases themselves, the fact remains that accident history databases are very useful and can be a powerful tool in focusing risk reduction efforts. The conclusions can be used to systematically identify the greatest risks to allow prioritization of efforts to improve process safety. At the plant level this might entail identifying certain processes, types of equipment, chemicals, operations and other factors most commonly associated with incidents. Databases that cover a very large number of facilities are likely to reveal trends and patterns that no one company or facility could determine from their own experience.

Statistical knowledge of the likelihood of the release of certain types of chemicals could help emergency responders, state emergency response commissions, and local emergency planning committees determine the most likely and most serious chemical releases in their areas and plan appropriate chemical accident responses.

Incident databases may also help identify technologies and practices to prevent chemical accidents, or the need to develop them. For example, the data could indicate that inspection and preventive maintenance of equipment and instruments should become more thorough or more frequent.

The Mary Kay O'Connor Process Safety Center (MKOPSC) provides an assessment of the usefulness of US Federal databases in *Feasibility of Using Federal Incident Databases to Measure and Improve Chemical Safety.* This study identifies a number of trends and patterns of chemical incidents. It also makes a number of recommendations for improving these databases. The report defines an incident as, "An incident is the sudden unintended release of or exposure to a hazardous substance, which results in or might reasonably have resulted in, deaths, injuries, significant property or environmental damage, evacuation or sheltering in place." This definition will be used as a reference to describe the type of incidents reported in the following section.

A33.1 Incident Databases

A33.1.1 National Response Center (NRC) Incident Reporting Information System (IRIS)

The NRC is the primary initial notification system for the US federal government. It is operated 24 h a day, 7 days a week. It receives the notification of a release and forwards that information to numerous federal, state and local agencies. Approximately 25,000 incidents are reported each year. However, the majority of these incidents involve very small or unknown quantities. While reporting to the NRC is required by a number of statutes, it also receives numerous 'complaints' from the public. Many of the incidents are spills of fuel from motor vehicles, small spills of low hazard materials such as lubricating oil and oil sheens on water with unknown sources, quantities and effects. Only about 30% of the reported cases constitute an incident as defined in the MKOPSC report.

Because this system contains initial reports the information is preliminary and many times inaccurate or incomplete. There is also duplicate reporting of incidents. The completeness and accuracy of chemical names depends on the knowledge level of the person reporting the incident. It has been found that those reports from chemical manufacturing facilities are more accurate and do provide useful information. For a limited number of incidents, NRC also presents a limited number of detailed incident summaries.

A33.1.2 EPA Risk Management Plan (RMP) – 5-year accident history

The US EPA as part of its Risk Management Program requires certain facilities to report their 5-year accident history. This requirement applies to releases of a listed substance that is stored above a threshold quantity and results in fatalities, injuries, or significant environmental or property damage. The initial 5 years covered the period from mid-1993 to 1998.

Only 1900 releases are reported from about 14,500 facilities for the 5-year period. The combination of the three main reporting criteria appears to exclude a large number of incidents. The reports do address such items as the causes and consequences of the release and steps taken to prevent or mitigate future incidents. Since the reporting is from a defined universe of facilities it allows statistical treatment of the frequency of releases not available from systems that report releases from an undefined universe of facilities.

A33.1.3 Agency for Toxic Substances Disease Registry (ATSDR) – Hazardous Substances Emergency Events Surveillance (HSEES)

The ATSDR administers a programme with approximately 15 states to collect information regarding chemical releases and their health effects on workers, emergency responders and the public. This database now contains over 50,000 events and adds more than 5000 per year. This is probably the largest high quality dataset in existence. Releases from both fixed facilities and transportation systems are included. The reporting excludes releases of petroleum products unless they contain other hazardous materials. This system focuses on the health effects that are gatheredfrom numerous sources such as public records, hospitals, media and interviews. The database is expected to be available to the general public by the time this handbook is published. The agency issues annual reports summarizing the results. These reports generally exclude some details such as the quantity released that would be helpful in the analysis of incidents. However, such information will be available when the database is released.

A33.1.4 EPA Accidental Release Information Program (ARIP)

This discontinued program contains nearly 5,000 incidents collected primarily in a 3-year period in the late 1980s. Prior to the establishment of other programmes in the 1990s this was one of the best sources of data. While there was no strict criteria for reporting to this database it is one of the larger collections of incidents with details concerning, causes, consequences, operating mode, and corrective actions. Facilities reported in response to a request from the

EPA. Requests were sent to facilities that reported frequent or significant incidents. While no trends can be gathered from this system it does provide detailed information not available in other systems. The database generally excludes releases of simple hydrocarbons.

A33.1.5 Accident Investigation System (AIS) – Occupational Safety and Health Administration, US Department of Labor

This system contains reports from all OSHA-regulated facilities with accidents resulting in a fatality or three or more injuries. The most useful feature of the system is that it includes a brief description of how the incident occurred. Most systems lack this feature making it very difficult to determine what actually occurred during an incident. Also, there are no arbitrary limits on the type of chemical involved or its quantity, only on the consequences. This database contains many accidents unrelated to chemicals but does include a text search.

A33.1.6 US Department of Transportation (DOT) – Hazardous Material Incident Reporting System (HMIRS)

This reporting system includes all modes of transportation except pipelines. Reporting is required from all interstate transport companies and results in a total of about 17,000 reports per year. Like the NRC, many of these cases are of little significance and do not meet the definition of an incident in the MKOPSC report.

A33.1.7 US DOT Integrated Pipeline Information System (IPIS)

Pipelines are covered in three categories, one for natural gas distribution, one for natural gas transmission and one for all other hazardous substances.

A33.1.8 Center for Chemical Process Safety (CCPS)

CCPS maintains a private database. Only members that contribute incidents to the database are allowed to view the data.

A33.1.9 Major Accident Hazards Bureau (MAHB), Major Accident Reporting System (MARS)

This system is maintained by the European Union's MAHB. It is a hybrid between a database and a report-based system. While the data is structured it contains extensive text descriptions of the incidents. The data is sanitized to remove identifying references. There are currently about 400 cases available to the public.

A33.2 Injury and Fatality Databases (Not Tied to Specific Incidents)

The following are sources of statistical information regarding injuries and fatalities due to chemicals. They do not reveal the details of specific incidents but do provide statistical information about injuries due to chemicals in the United States.

A33.2.1 Occupational Illness and Injury Statistics (OIIS) – Occupational Safety and Health Administration, US Department of Labor

These statistics are based on an annual sampling of about 250,000 companies in the United States. This data has been collected and reported on a consistent basis since 1992. There is good detail for chemicals and industries involved in injuries. There are additional details concerning the type of injury and the body parts involved.

A33.2.2 Census of Fatal Occupational Injuries (CFOI) – Occupational Safety and Health Administration, US Department of Labor

Beginning in 1992, OSHA implemented a rigorous system of counting all fatal occupational injuries. This is based on cross checking at least two sources of information. This system also contains the chemical and industry involved. The OSHA web site features both a querying system as well as formatted tables of data.

A33.2.3 Mortality Database, Centers for Disease Control, United States

This system is based on an analysis of all death certificates in the United States. It therefore includes all commercial, transportation and residential settings. The system also includes intentional acts such as assaults, suicides and substance abuse, which are not normally considered to be chemical incidents.

US death certificates are coded to indicate the cause of death. There is also a set of codes that describe the source of injury if applicable. A variety of codes describe hazardous substances.

A33.2.4 US Coast Guard (USCG)

The USCG maintains a database of oil spills and another for chemical spills to navigable waters. The incidents are typically those observed by the Coast Guard. The vast majority involve small or unknown quantities. The data show clear progress in reducing the quantity of oil spilled over the last 30 years.

A33.2.5 National Electronic Injury Surveillance System – Consumer Product Safety Commission, USA

This system is based on data from the emergency rooms of approximately 100 US hospitals. These hospitals are chosen to reflect US demographics. Specific events are not reported to maintain patient confidentiality. Statistical information for chemical related injuries are reported.

A33.3 Incident Investigation Reports

A33.3.1 United States

United States Chemical Hazard and Safety Board (CSB)

The CSB is the primary investigatory body for fixed facility chemical accidents. They perform detailed examinations of major accidents. They also perform studies of various classes of accidents such as reactive chemicals.

United States Department of Energy

The DOE has an on-line database of Red Alerts, Yellow Alerts, Lessons and Good Work Practices. These mainly involve the contractors that operate various DOE facilities.

United States Environmental Protection Agency (EPA)

The EPA performed several investigations before the advent of the CSB.

United States Fire Administration (USFA)

The USFA investigates major fires of all types. About a dozen of these reports cover chemical incidents.

National Institute for Occupational Safety and Health (NIOSH)

The National Institute for Occupational Safety and Health (NIOSH) Fatality Assessment and Control Evaluation

(FACE) programme is a research programme designed to identify and study fatal occupational injuries. The goal of the FACE programme is to prevent occupational fatalities across the nation by identifying and investigating work situations at high risk for injury and then formulating and disseminating prevention strategies to those who can intervene in the workplace.

The FACE programme currently has two components:

(1) NIOSH in-house FACE began in 1982. Participating states voluntarily notify NIOSH of traumatic occupational fatalities resulting from specific causes of death that have included *confined spaces*, electrocutions, machine-related, falls from elevation, and logging. The confined space incidents are the ones of interest in terms of process safety. In-house FACE is currently not targeting confined space incidents.
(2) NIOSH State-based FACE began in 1989. Currently, 15 State health or labour departments have cooperative agreements with NIOSH for conducting surveillance, targeting investigations, and recommending prevention activities at the State level using the FACE model.

There are approximately 75 NIOSH reports and 70 state reports.

NIOSH has also published a series of 'Fire Fighter Fatality Investigation Reports'. Several of these are chemical related incidents.

Occupational Safety and Health Administration (OSHA)
OSHA, sometimes in collaboration with the EPA, investigated several incidents before the creation of the CSB.

National Transportation Safety Board (NTSB)
The NTSB has responsibility for investigating transportation related hazardous materials spills on highways, airlines, railroads and pipelines. NTSB classifies incidents as Hazardous Materials Accidents for all modes of transportation except pipelines. Pipeline Accident reports are listed separately. Maritime incidents are excluded, they are handled by the USCG.

The Pipeline Accident reports include about 17 incidents since 1994 which are on-line and 69 reports prior to that time which are available on paper. The Hazardous Materials Accident reports include 18 since 1998 that are on-line and 55 available on paper.

Minerals Management Service (MMS)
The MMS investigates incidents related to offshore drilling activities. In-depth reports are called 'Accident Investigation Panel Reports'. Approximately 25 of these are related to pipeline leaks, fires, explosions or blowouts.

Department of Labour – Mine Safety and Health Administration (MSHA)
The MSHA reports include approximately 20 incidents involving fatalities that meet the criteria of chemical incident. The incidents of interest are generally classified as 'Ignition or Explosion of Gas or Dust' or 'Exploding Vessels Under Pressure'.

National Fire Protection Association (NFPA)
The NFPA has produced 141 detailed fire investigations. These reports are available on-line. They are free of charge to NFPA members. Paper copies are available for purchase. Approximately 15 of the reports are chemical related incidents.

A33.3.2 Australia

Australian Transport Safety Bureau (ATSB)
The ATSB have produced 16 reports of interest. These are primarily related to engine room fires on ships.

Department of Mineral and Petroleum Resources (Western Australia)
The DMPR has produced 10 reports of interest concerning a variety of topics.

Victorian Work Cover Authority
Various reports and guidance are found in 'Alerts & Guidance Notes'.

A33.3.3 Canada

Alberta Energy and Utilities Board
The AEUB has produced several incident reports as well as studies related to the hazards of sour natural gas.

Workplace Health and Safety, Alberta
They have produced about 16 reports concerning various fires, explosions and exposures. The reports under the heading 'Fatality Reports' cover the period from 1997 to 2002.

Canadian Center for Occupational Health and Safety (CCOHS)
The CCOHS has produced approximately 60 reports mostly covering fires and explosions. Fatality Reports contains information about the circumstances surrounding occupationally related fatalities. Information is extracted from reports on inquests and inquiries into occupationally related fatalities across Canada. These reports may be from Coroners, Medical Examiners, Government Ministries, or any other body responsible for inquiry into occupational fatalities.

Database highlights are:

(1) unique safety database identifies unsafe equipment, practices, work conditions;
(2) inquest reports offer practical recommendations to prevent recurrences of fatalities.

Transport Safety Board of Canada (TSB)
The TSB is quite similar to the NTSB in the United States. Their interest is in identifying causes and recommending solutions. They do not have regulatory authority. Approximately 45 rail incidents, 14 pipeline incidents and 7 marine incidents involve hazardous materials are available. The reports are under the headings Pipeline, Marine and Rail on theirwebsite.

A33.3.4 Finland

Finland Accident Investigation Board (English summary)
The FAIB has produced 16 reports covering Rail, Maritime and Fixed facilities. Their website contains English summaries that are about one page. The actual reports in Finnish are much more detailed.

A33.3.5 United Kingdom

Health and Safety Executive
MHIDAS (Major Hazard Incident Data Service) is a database of incidents involving hazardous materials that had an off-site impact, or had the potential to have an off-site impact. Such impacts include human casualties or damage to plant, property or the natural environment.

MHIDAS is maintained by, AEA Technology plc on behalf of the UK Health and Safety Executive, and features:

(1) searchable codified and textual information on more than 11,000 incidents, involving the transportation, storage and processing of hazardous materials;
(2) worldwide coverage, with a focus on incidents occurring in the United Kingdom and United States;
(3) comprehensive coverage of incidents that have occurred during the last twenty years, plus significant earlier incidents;
(4) new data made available on a quarterly basis.

Each MHIDAS incident is coded in a standard format to include details such as:

(1) the hazardous material involved in the incident;
(2) the number of fatalities, injuries and evacuations attributable to the incident;
(3) a brief description of the circumstances of the incident.

Information from MHIDAS can be accessed:

(1) through a personalized service, provided on a fee basis through AEA Technology, or
(2) on a subscription basis, via CD-ROM or Internet, or
(3) via an on-line information Retrieval Service, for which charges are made.

Marine Accident Investigation Branch (MAIB)

The MAIB has produced seven relevant detailed reports and nine articles in their monthly "Safety Digest". The fundamental purpose of investigating an accident under these regulations is to determine its circumstances and the causes with the aim of improving the safety of life at sea and the avoidance of accidents in the future. It is not the purpose to apportion liability, nor, except so far as is necessary to achieve the fundamental purpose, to apportion blame.

Appendix 34 Web Links

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A34.1 General Information

Safety Information and the Internet, http://hazard.com/course/

The site provides general information on how to use the internet as a tool to obtain required information.

A34.2 Technical Information

Government Research Center, NTIS search engine, http://grc.ntis.gov/

The National Technical Information Service (NTIS) database offers unparalleled bibliographic coverage of research sponsored by the United States and selected foreign governments.

Risk World – First Internet Chemical Process Safety Business Portal, http://www.riskworld.com

This site has a comprehensive source of risk related information on all aspects of life – chemicals, bioterrorism, business, safety, etc.

Risk Analysis Methodologies, http://home1.pacific.net.sg/~thk/risk.html

The site is maintained by T.H. Keong and provides an overview of risk assessment methods.

Root Cause Analysis, http://www.rootcauselive.com/

A website devoted to root cause analysis practitioners.

A34.2.1 Energetic materials/reactive chemicals

Chemweb – Brethericks Databases, http://chemweb.com/databases/brethericks

Bretherick's database is a comprehensive source of information on energetic or reactive materials.

Explosion Hazards Database – National Institute of Materials and Chemical Research (NIMC), http://www.aist.go.jp/RIODB/db005/index.html

This database includes explosion hazard test data for energetic materials obtained at laboratories of the NIMC in Japan.

UK Chemical Reaction Hazard Forum, http://www.crhf.org.uk/

UK Chemical Reaction Hazards Forum is a group of process safety professionals from the UK chemical industry for mutual exchange of information, expertise and ideas

A34.2.2 Toxicology

Environmental Defense Fund – Chemical Scoreboard, http://www.scorecard.org/

Scorecard is a source for free and easily accessible local environmental information. One can learn about environmental issues in your community by typing in zip code. Scorecard carries health and environmental related information for the chemicals in its database.

National Toxicology Program, http://ntp-server.niehs.nih.gov/

National Toxicology Program (NTP) coordinates toxicological testing programmes within the Department of Health and Human Services, strengthens the science base in toxicology; develops and validates improved testing methods; and provides information about potentially toxic chemicals to health regulatory and research agencies, the scientific and medical communities, and the public.

NIOSH – Registry of Toxic Effects of Chemical Substances (RTECS), http://www.cdc.gov/niosh/rtecs.html

RTECS, maintained by National Institute for Occupational, Health, and Safety (NIOSH) is a compendium of data extracted from the open scientific literature. Six types of toxicity data are included for a chemical: (1) primary irritation; (2) mutagenic effects; (3) reproductive effects; (4) tumorigenic effects; (5) acute toxicity; and (6) other multiple dose toxicity.

A34.3 University Academic Programmes

Fire Protection Engineering Program, University of Maryland, College Park, http://www.enfp.umd.edu/

The programme offers fully accredited undergraduate program and one of two graduate degree programs in the Unitied states.

Hazard Lab Group, Michigan Tech University, http://www.chem.mtu.edu/org/hazards/hazards.html

The research of the group members focuses on generating data for flammable and reactive compounds.

Mary Kay O'Connor Process Safety Center (MKOPSC), Texas A&M University, http://process-safety.tamu.edu

The research of the center focuses on process safety in the chemical industry.

Safety, Environment and Loss Prevention, Chemical Engineering Department, Loughborough University, http://www.lboro.ac.uk/departments/cg/research.html

The research of the group focuses on sustainable process development.

Thermal Hazards Laboratory, Queens University, http://me.queensu.ca/people/birk/research/thermalHazards/

The focus of the research at the Thermal Hazards Laboratory is the safety of the storage and transportation of pressure liquified gases. The laboratory uses large scale experiments and thermodynamic modelling to study the response of a vessel in an accident situation and the possible hazards arising from vessel failure.

A34.4 Government Organizations

Health and Safety Executive (HSE), http://www.hse.gov.uk/

The UK Health and Safety Commission (HSC) and the Health and Safety Executive (HSE) are responsible for the regulation of almost all the risks to health and safety arising from work activity in Britain.

Environmental Protection Agency (EPA), http://www.epa.gov

EPA provides leadership in the nation's environmental science, research, education and assessment efforts. The Agency also works with industries and all levels of government in a wide variety of voluntary pollution prevention programmes and energy conservation efforts.

Occupational, Safety and Heath Administration, http://www.osha.gov

OSHA's mission is to prevent work-related injuries, illnesses, and deaths.

US Chemical Safety Board (CSB), http://www.chemsafety.gov/

The mission of the US Chemical Safety and Hazard Investigation Board is to promote the prevention of major chemical accidents at fixed facilities.

A34.5 Societies, Councils, Institutes

American Industrial Hygiene Association (AIHA), http://www.aiha.org/

AIHA promotes, protects, and enhances industrial hygienists and other occupational health, safety and

environmental professionals in their efforts to improve the health and well being of workers, the community, and the environment.

Center for Chemical Process Safety (CCPS), http://www.aiche.org/ccps/

CCPS brings together manufacturers, insurers, government, academia, and expert consultants to lead the way in improving manufacturing process safety.

Institute of Chemical Engineers (IChemE), http://www.icheme.org

IChemE is a leading international body, providing services for and representing the interests of those involved in chemical, biochemical and process engineering worldwide.

A34.6 Security and Vulnerability Assessment

American Chemistry Council (ACC) Site Security Guidelines, http://www.responsiblecaretoolkit.com/

ACC offers Guidelines for the U.S. Chemical Industry, developed by a group of company security professionals and designed specifically for the chemical industry, can help member companies build upon their existing security programmes.

CCPS Security and Vulnerability Analysis (SVA), http://www.aiche.org/ccps/sva/

CCPS recommends a method for industry to analyse their chemical security risks.

Sandia National Laboratory's, http://www.nlectc.org/ccfp/

Center for Civil Force Protection (CCFP) at Sandia National Laboratories (SNL) provides physical security counter terrorism assistance to state and local agencies.

References

Notes
(1) References are given in the text by surname only, except where there would be ambiguity, in which case the initials are given also.
(2) References for which no date has been established are denoted (n.d.) and head their group alphabetically. Where the approximate date is known, this is indicated, e.g. SMITH, J. (*c.* 1988).
(3) Anonymous entries are grouped at the start of the references and are in date order.
(4) In ranking a name alphabetically, elements such as de or von are disregarded, e.g. von Bismark is listed under B rather than V.
(5) Chinese names are given in the form used by the particular author, i.e. either in full or by surname with initials.
(6) The following abbreviated titles are used:

Abbreviated title	*Full title*
Ammonia Plant Safety, **1**–	*Safety in Air and Ammonia Operations Prog.s*, 1960, Vol. 2– (*Ammonia Plant Safety and Related Facilities*), 1970, Vol. 12– (both New York: Am. Inst. Chem. Engrs)
Carriage of Dangerous Goods, **1**	*Carriage of Dangerous Goods 1*
Chemical Process Hazards **1**–	*Chemical Process Hazards with Special Reference to Plant Design*, 1960, **I**-; then Hazards IX, 1986, IX- (both London, then Rugby: Inst. Chem. Engrs)
Combustion, **1**–	*Symp. on Combustion*, 1928, **1**; 1937, **2** (both Pittsburgh, PA: Combustion Inst.); 1949, **3**; 1953, **4** (both Baltimore, MD: Williams & Wilkins); 1955, **5**; 1957, **6** (both New Tork: Reinhold); 1959, **7** (London: Butterworths); 1960, **8** (Baltimore, MD: Williams & Wilkins); 1963, **9** (New York: Academic Press); 1964, **10**; 1967, **11**; 1968, **12**; 1970, **13**; 1972, **14**; 1975, **15**; 1977, **16**; 1979, **17**; 1981, **18**; 1982, **19**; 1985, **20**, 1988, **21**; 1989, **22**; 1990, **23**; 1991, **24** (all Pittsburgh, PA: Combustion Inst.)
Control of Hazardous Material Spills, **1**–	*Nat. Conf. on Hazardous Material Spills*, 1971, Houston, TX; 1974, Fransisco, CA; 1976, New Orleans, LA; 1978, 4, Miami Beach, FL; *Nat. Conf on Hazardous Material Spills*, 1980, Louisville, KY; 1986; 1988, Chicago, IL
Electrical Safety, **1**–	*Electrical Safety in Hazardous Environments*, 1971, **1**; 1975, **2**; 1982, **3**; 1984, **4** (London: Inst. Elec. Engrs)
Gastech, 6	*Gastech*, 1978, **6**; 1979, **7**; 1982, **8**; 1983, **9**; 1985, **10**; 1986, **11**, 1987, **12**; 1989, **13**; 1991, **14**; 1993, **15** (dates are those of proceedings not of conference itself)
Hazard Identification and Risk Analysis	*Int. Conf. on Hazard Identification and Risk Analysis, Human Factors and Human Reliability in Process Safety* (Rugby: Inst. Chem. Engrs), 1992
Hazards from Pressure	*Hazards from Pressure: Exothermic Reactions, Unstable Substances, Pressure Relief and Accidental Discharge* (Rugby: Inst. Chem. Engrs), 1987
Health, Safety and Loss Prevention	*Health, Safety and Loss Prevention in the Oil, Chemical and Process Industries* (Oxford: Butterworth-Heinemann), 1993
LNG Conf. 1–	*Int. LNG Conf.*, 1968, **1**, Chicago, IL; 1970, **2**, Paris; 1972, **3**, Washington, DC; 1974, **4**, Algiers; 1977, **5**, Dusseldorf (Chicago, Ill: Inst. Gas Technol. and other organizations)
LPB	*Loss Prevention Bulletin* (Institution of Chemical Engineers)
Loss Prevention and Safety Promotion 1–	*Loss Prevention and Safety Promotion in the Process Industries*, 1974, **1** (ed. by C.H. Buschmann) (Amsterdam: Elsevier); 1977, **2** (Frankfurt: DECHEMA); 1980, **3** (Basel: Swiss Soc. Chem. Ind.); 1983, **4** (Rugby: Inst. *Chem. Engrs); 1986*, **5** (Paris. Soc. Chim. Ind.); 1989, **6** (Oslo: Norwegian Soc. Engrs); 1992, **7** (Taormina, Sicily: Italian Federation of Chemical Industry)
Major Loss Prevention	*Major Loss Prevention in the Process Industries* (London: Inst. Chem. Engrs), 1971
Major Hazards Onshore and Offshore	*Major Hazards Onshore and Offshore* (Rugby: Inst. Chem. Engrs), 1992
Modelling and Mitigating the Consequences of Accidental Releases	*Int. Conf. and Workshop on Modelling and Mitigating the Consequences of Accidental Releases of Hazardous Materials* (New York: Am. Inst. Chem. Engrs), 1991
Preventing Major Chemical Accidents	*Int. Symp. on Preventing Major Chemical Accidents* (ed. J.L. Woodward) (New York: Am. Inst. Chem. Engrs), 1987
Preventing Major Chemical and Related Process Accidents	*Preventing Major Chemical and Related Process Accidents* (Rugby: Inst. Chem. Engrs), 1988
Prevention of Occupational Risks, **1**–	*Int. Symp .on Prevention of Occupational Risks*, 1970, **1**, Frankfurt-am-Main; 1973, **2**, Frankfurt-am-Main; 1976, **3** Frankfurt-am-Main; 1977, **5**, Bucharest (Heidelberg: Berufsgenossenschaft der Chem. Ind.)

Process Industry Hazards	*Process Industry Hazard – Accidental Release, Assessment, Containment and Control* (London: Inst. Chem. Engrs), 1976
Process Safety Management	*Process Safety Management* (New York: Am. Inst. Chem. Engrs), 1993
Protection of Exothermic Reactors	*The Protection of Exothermic Reactors and Pressurised Storage Vessels* (Rugby: Inst. Chem. Engrs), 1984
Runaway Reactions	*Int. Symp. on Runaway Reactions* (New York: Am. Inst. Chem. Engrs), 1989
Safety in Polyethylene Plants	*Safety in High Pressure Polyethylene Plants*, 1973, **1**; 1974, **2**; 1978, **3** (New York: Am. Inst. Chem. Engrs)
Safety and Loss Prevention in the Chemical and Oil Processing Industries	*Safety and Loss Prevention in the Chemical and Oil Processing Industries* (Rugby: Inst. Chem. Engrs), 1990
Static Electrification	*Inst. of Physics, Confs on Static Electrification*, 1954, **1** (Br. J. Appl. Phys., 1954, **4**, Suppl. 2); 1967, **2**; 1971, **3**; 1974, **4**; 1979, **5**; 1983, **6**; 1987, **7**; 1991, **8**
Vapour Cloud Modelling	*Int. Conf. on Vapour Cloud Modelling* (New York: Am. Inst. Chem. Engrs), 1987

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Acronyms

AAE	Additional Accommodation East (Piper Alpha)
AAM	accident anatomy method
AAR	Association of American Railroads
AAW	Additional Accommodation West (Piper Alpha)
ABC	general purpose dry chemical
ABCM	Association of British Chemical Manufacturers
ABI	Association of British Insurers
ABL	atmospheric boundary layer
ABMA	American Boiler Manufacturers Association
ABPI	Association of the British Pharmaceutical Industry
ACA	Advisory Committee on Asbestos
ACDS	Advisory Committee on Dangerous Substances
ACE	Army Corps of Engineers
ACGIH	American Conference of Government Industrial Hygienists
ACH	Acetone cyanohydrinbased route
ACMH	Advisory Committee on Major Hazards
ACOP	Approved Code of Practice
ACR	Average circle radius
ACRS	Advisory Committee on Reactor Safety
ACSNI	Advisory Committee on the Safety of Nuclear Installations
ACTS	Advisory Committee on Toxic Substances
ADI	acceptable daily intake
ADN	European Agreement for the International Transport of Dangerous Goods
ADNR	European Agreement for the International Transport of Dangerous Goods (River Rhine)
ADR	European Agreement concerning the International Carriage of Dangerous Goods by Road
ADT	adiabatic storage test
AE	acoustic emission
AEA	action error analysis
AEC	Atomic Energy Commission
AEL	accessible emission level
AFFF	aqueous film forming foam
AFNOR	Association Francaise de Normalisation
AFPA	Australian Fire Protection Association
AGA	American Gas Association
AGR	advanced gas-cooled reactor
AHM	acutely hazardous material
AHP	analytic hierarchy process
AI	artificial intelligence
AIA	American Insurance Association
AIB	Accident Investigation Branch
AIChE	American Institute of Chemical Engineers
AID	Aeronautical Inspection Directorate
AIHA	American Industrial Hygiene Association
AIR	American Institute for Research
AISI	American Iron and Steel Institute
AIT	autoignition temperature
AL	action level
AIARP	as low as reasonably practicable
Amoco	American Oil Company
AN	acrylonitrile
AN	ammonium nitrate
ANA	ammonium nitrate–ammonia
ANAP	action-not-as-planned
ANC	adaptive noise cancellation
ANL	Argonne National Laboratory
ANN	artificial neural network
ANSI	American National Standards Institute
AOD	argon–oxygen decarburization
APC	air pollution control
APCA	Air Pollution Control Association
APAU	Accident Prevention Advisory Unit
API	American Petroleum Institute
APJ	absolute probability judgement
APS	automatic protective system
AQ	air quality
AQD	Aeronautical Quality Assurance Directorate
AQL	acceptable quality level
AQP	average lot quality protection
AR	alcohol resistant
ARC	accelerating rate calorimetry
ASCE	American Society of Civil Engineers
ASHRAE	American Society of Healing Refrigerating and Air-conditioning Engineers
ASM	Algebraic stress model
ASME	American Society of Mechanical Engineers
ASQC	American Society of Quality Control
ASTM	American Society for Testing and Materials
ATMS	assumption-based truth maintenance system
ATN	augmented transition network
ALIT	Association of University Teachers
AWS	American Welding Society
BA	breathing apparatus
BACT	best available control technology
BAM	Bundesanstalt für Materialprüfung
BASEEFA	British Approvals Service for Electrical Equipment in Flammable Atmospheres
BASF	Badische Anilin und Soda Fabrik
BATNEC	best available technology not entailing excessive cost
BCC	British Cryogenic Council
BCF	bromochlorodifluoromethane
BCGA	British Compressed Gases Association
BCISC	British Chemical Industry Safety Council
BCME	bis(chloromethyl)ether
BCS	Beilby, Cottrell and Swinden (model)
BD	bursting disc
BFR	binomial failure rate
BG	British Gas
BGC	British Gas Corporation
BG/C&W	British Gas/Cremer and Werner (model)
BHEP	basic human error probability
BI	business interruption
BIA	Berufsgenossenschaftlicshes Institut für Arbeitssicherheit
BITC	Bureau International Technique du Chlore
BLEVE	boiling liquid expanding vapour explosion
BLV	biological limit value
BM	Bureau of Mines
BMCS	Bureau of Motor Carrier Safety
BNF	Backus–Naur form
BNFL	British Nuclear Fuels Ltd
BNL	Brookhaven National Laboratory
BNP	back-propagation network
BOCA	Building Official and Code Administration
BOD	biological oxygen demand
BOHS	British Occupational Hygiene Society

BOP	blowout preventer
BOR	boil-off rate
BP	bulk property
BPCS	basic process control system
BPEO	best practical environmental option
BPF	British Plastics Federation
BPM	best practicable means
BR	British Rail
BRE	Building Research Establishment
BRL	Ballistics Research Laboratory
BSC	bench scale calorimeter
BSC	British Safety Council
BSC	British Steel Corporation
BSI	British Standards Institute
BTC	British Transport Commission
BTM	bromotrifluoromethane
BUA	built-up area
BWR	boiling water reactor
CA	Certifying Authority
CAA	Civil Aviation Authority
CAA	Clean Air Act
CAAA	Clean Air Act Amendments
CAD	computer-aided design
CADA	critical action and decision approach
CADE	computer aided design and engineering
CADET	critical action and decision evaluation technique
CAER	Community Awareness and Emergency Response
CAF	compressed asbestos fibre
CAPE	computer aided process engineering
CAPITB	Chemical and Allied Products Industry Training Board
CAWR	Control of Asbestos at Work Regulations 1987
CBI	Central Bureau of Investigation (India)
CBI	Confederation of British Industry
CBL	convective boundary layer
CCA	copper–chrome–arsenate
CCD	cause–consequence diagram
CCF	common cause failure
CCPS	Center for Chemical Process Safety
CCS	centralized control system
CCT	cause–consequence tree
CCW	Chester–Chisnall–Whitham
CD	conceptual dependency
CDE	Chemical Defence Establishment
CDFM	conservative deterministic failure margin
CE	critical examination
CEC	Commission of the European Communities
CEFIC	European Federation of Chemical Engineering
CEGB	Central Electricity Generating Board
CEI	Chemical Exposure Index (Dow)
CELD	cause–effect logic diagram
CEN	Comité de Normalisation Européen
CENELEC	Comité de Normalisation Européen Électrotechnique
CEP	Chemical Engineering Progress
CEP	Chemical Exposure Index (DOW)
CEQ	Commission on Environmental Quality
CERCLA	Comprehensive Environmental Response, Compensation and liability Act (Superfund)
CF	certainty factor
CF	credit factor (Dow)
CFC	Chlorofluorocarbons
CFC	chlorofluorohydrocarbon
CFD	computational fluid dynamics
CGA	Compressed Gas Association
CHA	concept hazard analysis
chazop	computer HAZOP
CHEMSAFE	Chemical Industry Scheme for Assistance in Freight Emergencies
CHEMTREC	Chemical Transportation Emergency Centre
CHEP	conditional human error probability
CHETAH	chemical thermodynamics and energy hazard
CHIP	Chemicals (Hazard Information and Packaging) Regulations 1993
CHL	classification of hazardous locations
CHP	cumene hydroperoxide
CI	Chlorine Institute
CIA	Chemical Industries Association
CIB	Consell Intenrationale de Batiment
CIBS	Chartered Institute of Building Services
CIBSE	Chartered Institute of Building Services Engineers
CIIT	Chemical Industry Institute of Toxicology
CIM	computer integrated manufacturing
CIM	Uniform Rules concerning the Contract for International Carriage of Goods by Rail
CIMAH	Control of Industrial Major Accident Hazards Regulations 1984
CIP	cleaning in place
CISHC	Chemical Industry Safety and Health Council
CJ	Chapman–Jouguet
CLAW	Control of Lead at Work Regulations 1980
CLER	Classification and Labelling of Explosives Regulations 1983
CM	chemical manufacturing
CM	condition monitoring
CMA	Chemical Manufacturers Association
CME	chloromethyl ether
CMF	common mode failure
CMI	Christian Michelsen Institute
COD	chemical oxygen demand
COD	crack opening displacement
COER	Control of Explosives Regulations 1991
CONCAWE	oil companies organization
CONDAM	Construction (Design and Management) Regulations
COP	Code of Practice
COP	coefficient of performance
COPA	Control of Pollution Act
COPEP	Chlorine Out-Plant Emergency Plan
COSHH	Control of Substances Hazardous to Health Regulations 1988
COTIF	Convention concerning International Carriage by Rail
COV	collision with other vehicle
CP	cathodic protection
CP	conceptual dependency
CPA	Canadian Petroleum Association
CPD	Committee for the Prevention of Disasters
CPL	Classification, Packaging and Labelling (Regulations) 1984

CPLR	Classification Packaging and Labelling of Dangerous Substances Regulations 1984
CPR	critical pressure ratio
CPS	control and protection system
CPS	critical path scheduling
CPSC	Consumer Product Safety Commission
CRHC	Chemical Reactor Hazard Centre
CRMR	complete and rigorous model-based reconciliation
CSE	concept safety evaluation
CSF	cancer slope factor
CSO	Central Statistical Office
CSR	concept safety review
CSTR	continuous stirred tank reactor
CTM	causal tree method
CTOD	crack tip opening displacement
CTU	cargo transport unit
CV	control valve
CVCP	Committee of Vice Chancellors and Principals
CVN	Charpy V-notch (test)
CW	continuous wave
CWA	dosed world assumption
CWR	Chemical Works Regulations 1922
CWRT	Center for Waste Reduction Technology
DAP	detergent alkylate plant
DAS	disturbance analysis system
DBMS	database management system
DCF	discounted cash flow
DCL	distributed control logic
DCS	digital control systems
DCS	Distributed Control Systems
DDB	dependency-directed backtracking
DDC	direct digital control
DDP	defect detection probability
DDT	deflagration to detonation transition
DEA	diethanolamine
DF	Damage Factor (Dow)
DF	dependent failure
DFA	2,4-difluoroaniline
DFNB	2,4-difluoronitrobenzene
DG	diesel generator
DGL	Directorate General of Labour
DHSV	down-hole safety valve
DIERS	Design Institute for Emergency Relief Systems
DIMP	Design Institute for Multiphase Processing
DIN	Deutsches Institut für Normung
DMAC	*N*,*N*-dimethylacetamide
DMV	diaphragm motor valve (Bhopal)
DO	damage only (accident)
DO	dissolved oxygen
DoE	Department of the Environment
DoEm	Department of Employment
DoEn	Department of Energy
DoI	Department of Industry
DoT	Department of Trade
DOT	Department of Transportation (USA)
DPLU	Disaster Prevention and Limitation Unit
DPT	decomposition pressure test
DPT	dynamically positioned tanker
DR	discounted premium rate
DRI	Distribution Ranking Index (Dow)
DRM	deterministic reference model
DSC	differential scanning calorimetry
DSHA	Dangerous Substances in Harbour Areas (Regulations) 1987
DSIR	Department of Scientific and Industrial Research
DSM	Dutch State Mines
DTA	differential thermal analysis
DTG	differential thermogravimetry
DTI	Department of Trade and Industry
DTIC	Defense Technical Information Center
DTL	dangerous toxic load
DTp	Department of Transport (UK)
DTT	de-energize-to-trip
E/E/PES	Electrical/Electronic/Programmable Electronic Systems
EC	error cause (Whalley)
EC	European Community
ECCS	emergency core cooling system
ECCS	European Convention for Constructional Steelwork
ECETOC	European Chemical Industry Ecology and Toxicology Centre
ECOIN	European Core Inventory of Existing Substances
ED	enumeration district
EDC	ethylene dichloride
EDF	Electricité de France
EDF	equivalent discrete failure
EDP	Emergency depressurization
EECS	Electrical Equipment Certification Service
EEGL	emergency exposure guidance level
EEI	Edison Electric Institute
EEI	emergency exposure index
EEL	emergency exposure limit
EEMUA	Engineering Equipment and Materials Users Association
EEPG	Emergency Exposure Planning Guidelines
EER	evacuation, escape and rescue
EEUA	Engineering Equipment Users Association
EF	error factor
EF	Escalation Factor (Dow)
EFS	emergency feedwater system
EFV	excess flow valve
EHS	effective stack height
EHS	extraordinarily hazardous substance
EIA	environmental impact assessment
EIDAS	Explosion Incidents Data Service
EINECS	European Inventory of Commercial Chemical Substances
EIS	environmental impact statement
EIV	emergency isolation valve
EJMA	Expansion Joint Manufacturers Association
ELD	engineering line diagram
ELSA	European laboratory for Structural Assessment
EM	error mechanism (Whalley)
EMAS	Employment Medical Advisory Service
EML	estimated maximum loss
EMS	Emergency Medical Services
EMS	environmental management system
EnvIDAs	Environmental Incidents Data Service
EO	equation oriented
EO	ethylene oxide
EOQ	economical order quantity
EP	environmental protection
EPA	Environmental Protection Act

EPA	Environmental Protection Agency
EPC	error producing condition
EPCRA	Emergence Planning & Community Right to Know Act 1986
EPRI	Electrical Power Research Institute
EPSC	European Process Safety Centre
EQO	environmental quality objective
EQS	environmental quality standard
ER	equivalent radiator
ER	Exposure Radius (Dow)
ERA	Electrical Research Association
ERC	Emergency Response Commission
ERCO	Energy Resources Company
ERDS	European Reliability Data System
ERG	emergency response guidelines
ERM	equilibrium rate model
ERPG	Emergency Response Planning Guidelines
ERQ	East Replacement Quarters (Piper Alpha)
ERS	emergency relief system
ERT	Environmental Research and Technology Inc.
ERV	expiratory reserve volume
ES	environmental statement
ES	explosion severity
ESA	European Space Agency
ESD	emergency shut-down
ESD,ESS	Emergency Shutdown System
ESH	electrical surface heating
ESP	equivalent standard plant
ESTC	Explosives Storage and Transport Committee
ESV	emergency shut-down valve
ESV	emergency shut-off valve
ET	error type (Whalley)
ETA	expected time of arrival
ETT	energize-to-trip
FA	fragility analysis
FAD	failure analysis diagram
FAD	failure assessment diagram
FAE	fuel–air explosion
FAFR	failure accident frequency rate
FAR	fatal accident rate
FB	fractional bias
FBL	fracture-before-leak
FCAW	fluxed core arc welding
FCT	flux-corrected transport
FDA	Food and Dreg Administration
FDG	flue gas desulphuriration
FDM	finite difference method
FDT	fractional dead time
FECA	Federal Emission Control Act 1974
FEMA	Federal Emergency Management Agency
FERC	Federal Energy Regulatory Commission
FET	Flammability, explosiveness and toxicity
FFFP	film forming fluoroprotein (foam)
FFP	flame front projection
F&EI	Fire and Explosion Index
F&G	fire and gas
FHA	Federal Highways Authority
FIA	Factory Insurance Association
FIBC	flexible intermediate bulk container
FICA	Federal Emission Control Act (Germany)
FL	frequency–loss
FM	Factory Mutual
FMA	Fertilizer Manufacturers Association
FMD	fragment mass distribution
FMEA	failure mode and effect analysis
FMEC	Factory Mutual Engineering Corporation
FMECA	failure modes, effects and criticality analysis
FMRC	Factory Mutual Research Corporation
FN	frequency–number (curve)
FOD	Field Operations Division
FoF	figure of friction
FoI	figure of insensitiveness
FOPL	first order predicate logic
FP	fluoroprotein
FPA	Fire Precautions Act 1971
FPA	Fire Protection Association
FPC	Federal Power Commission
FPS	floating production system
FPSO	floating production, storage and offloading (system)
FR	filling ratio
FRC	fast rescue craft
FRG	Federal Republic of Germany
FRP	fibre reinforced plastic
FRS	Fire Research Station
FRV	functional residual volume
FSA	formal safety assessment
FSM	fault–symptom matrix
FTA	fault tree analysis
FTE	fracture transition elastic (point)
FTP	fracture transition plastic (point)
FTS	fault tree synthesis
FWPCA	Federal Water Pollution Control Act 1972
GAO	General Accounting Office
GCM	Gas Conservation Module (Piper Alpha)
GD	Germeles–Drake
GDA	goal-directed activity
GdF	Gaz de France
GDO	general development order
GDR	German Democratic Republic
GFM	goodness-of-fit measure
GFRP	glass fibre reinforced plastic
GIS	general incident scenario
GMAW	gas-metal arc welding
GNP	Gross National Product
GOFA	goal-oriented failure analysis
GoI	Government of India
GOM	Gulf of Mexico
GP	general purging (nitrogen)
GPH	General Process Hazard (Dow)
GRP	glass reinforced plastic
GRS	Gesselschaft für Reaktorsicherheit
GRT	Gross registered tonnage
GS(I&U)R	Gas Safety (Installations and Use) Regulations 1984
GSR	Gas Safety Regulations 1972
GT	Gaz Transport
GTAW	gas-tungsten arc welding
GTST	goal tree–success tree
GVW	gross vehicle weight
HAC	hazardous area classification
HALO	hazard assessment of landfill
HANES	Health and Nutrition Examination Survey
HAZ	heat affected zone
HAZAN	hazard analysis
HAZMAT	hazardous material

HAZOP	hazard and operability (study)
HCFC	hydrochlorfluorocarbon
HCLPF	high confidence of low probability of failure
HCR	human cognitive reliability
HD	hazard distance
HD	Hazard Division
HDPE	high density polyethylene
HDR	high discharge rate
HEART	human error assessment and reduction technique
HED	Human Error Database
HEH	homogeneous equilibrium model
HEP	human error probability
HER	human error rate
HF	hydrogen fluoride
HFC	hydrofluorocarbon
HF/E	human factors/engineering
HFLR	Highly Flammable Liquids and Liquefied Petroleum Gases Regulations 1972
HFO	heavy fuel oil
HFRG	Human Factors in Reliability Group
HGDT	heavy gas dispersion trial
HGT	heavy goods train
HGV	heavy goods vehicle
HI	hazard index
HIO	Hazardous Incident Ordinance (Germany)
HIPS	high integrity protective system
HIS	Health Interview Survey
HISS	high integrity shutdown system
HIT	hazardous installations and transport
HITI	high integrity trip initiator
HITS	high integrity trip system
HIVE	high integrity voting equipment
HM	hazardous material
HMA	Human reliability assessment
HMAP	Hydrogen Fluoride Mitigation and Assessment Program
HMCIF	HM Chief Inspector of Factories
HMFI	HM Factory Inspectorate
HMIP	HM Inspectorate of Pollution
HMIR	Hazardous Materials Incident Reporting
HMV	hydraulic master valve
HND	Higher National Diploma
HORATIO	Human Response Analyzer and Timer for Infrequent Occurrences
HP	high pressure
HPI	high pressure injection
HPIM	high purity inert medium
HPIP	human performance investigation process
HQ	hazard quotient
HRA	human reliability analysis
HRC	hydrocarbon release (database)
HRS	hazard ranking scheme
HSB	Hartford Steam Boiler
HSC	Health and Safety Commission
HSE	Health and Safety Executive
HSF	hardware, software and fire fighting
HSWA	Health and Safety at Work etc. Act 1974
HTA	hierarchical task analysis
HTF	heat transfer fluid
HTF	high temperature fluid
HTGR	high temperature gas-cooled reactor
HTHM	high toxic hazard materials
HV	high velocity
IAEA	International Atomic Energy Agency
IAPH	International Association of Ports and Harbours
IARC	International Agency for Research on Cancer
IATA	International Air Transport Association
IBC	intermediate bulk container
IC	inspiratory capacity
ICAO	International Civil Aviation Organization
ICBO	International Conference of Building Officials
ICD	inherently cleaner design
ICE	Institution of Civil Engineers
ICFTU	International Confederation of Free Trade Unions
IChemE	Institution of Chemical Engineers
ICHMAP	International Co-operative Hydrogen fluoride Mitigation and Assessment Program
ICI	Imperial Chemical Industries
ICRP	International Committee on Radiological Protection
ICS	International Chamber of Shipping
ID	identification number
IDA	influence diagram analysis
IDLH	Immediately Dangerous to life and Health (limit)
IE	index of explosibility
IEC	International Electrotechnical Commission
IEE	Institution of Electrical Engineers
IET	insulated exotherm test
IFAL	instantaneous fractional annual loss
IFE	Institution of Fire Engineers
IGE	Institution of Gas Engineers
IHVE	Institution of Heating and Ventilation Engineers
IISO	Institution of Industrial Safety Officers
IL	integrity level
ILCI	International Loss Control Institute
ILO	International Labour Office
IMechE	Institution of Mechanical Engineers
IMAS	influence modelling and assessment system
IMCO	Intergovernmental Maritime Consultative Organization
IMDG	International Maritime Dangerous Goods (Code)
IMO	International Maritime Organization
INRS	Institute National de Recherche sur la Securité
IOI	International Oil Insurers
IP	industrial platform
IP	Institute of Petroleum
IPC	integrated pollution control
IPIECA	International Petroleum Industry Environment Conservation Association
IPL	independent layer of protection
IPSG	International Process Safety Group
IR	infrared
IRI	Industrial Risk Insurers
IRIS	incident reporting and investigation system
IRLG	Interagency Regulatory Liaison Group
IRV	inspiratory reserve volume
IS	ignition severity
ISA	Instrument Society of America
ISA	Instrumentation, Systems and Automation Society

ISGHO	International Study Group on Hydrocarbon Oxidation
ISGRA	International Study Group on Risk Assessment
ISI	Inherent Safety Index
ISLO	Installations Subject to Licensing Ordinance (Germany)
ISO	International Standards Organisation
ISR	incoming solar radiation
ISRS	International Safety Rating System
IST	isothermal storage test
ITB	Industry Training Board
ITB	Insurance Technical Bureau
ITC	Interagency Testing Committee
ITOPF	International Tanker Owners Pollution Federation
ITSA	Independent Tank Storage Association
IUR	International Union of Railways
JFRO	Joint Fire Research Organization
JHEP	joint human error probability
JIT	'just-in-time'
JRC	Joint Research Centre
JSA	Job safety analysis
JT	Joule–Thomson
JTMS	justification-based truth maintenance system
KAF	knowledge acquisition facility
KASP	Kjeller Ammonia Stress Corrosion Project
KWU	Kraftwerk Union
LA	Local authority
LAAPC	local authority air pollution control
LBB	leak-before-break
LBF	leak-before-fracture
LCn	lethal concentration (n% level)
LCC	life cycle costing
LCTn	lethal toxic concentration (n% level)
LCV	level control valve
LDn	lethal dose (n% level)
LDC	London Dumping Convention
LDG	List of Dangerous Goods and Conditions of Acceptance
LDPE	low density polyethylene
LEFM	linear elastic fracture mechanics
LEL	lower explosive limit
LEPC	Local Emergency Preparedness Committee
LER	licensee event report
LEV	local exhaust ventilation
LF	landfill
LFG	liquefied flammable gas
LFL	lower flammability limit
LGC	liquefied gas carrier
LGF	Liquefied Gaseous Fuels (Spill Effects Program)
LGFSTF	Liquefied Gaseous Fuels Spill Test Facility
LGV	light goods vehicle
LITTS	large inventory top tier site
LLNL	Lawrence Livermore National Laboratory
LN	logical necessity
LNG	liquefied natural gas
LNH3	liquefied ammonia
LOCA	loss of coolant accident
LOPA	Layer of protection analysis
LOV	locally operated valve
LOX	liquid oxygen
LPA	local planning authority
LPB	*Loss Prevention Bulletin*
LPG	liquefied petroleum gas
LPGA	liquefied Petroleum Gas Association
LPGITA	Liquefied Petroleum Gas Industry Technical Association
LPI	low pressure injection
LPR	linear polarization resistance
LQW	Living Quarters West (Piper Alpha)
LR	Lloyds Register
LRA	least replaceable assembly
LS	limit switch
LS	logical sufficiency
LTA	lost time accident
LTI	lost time injury
LTMS	logic-based truth maintenance system
LTPD	lot tolerance per cent defective
LTSR	long-term safety review
LVHV	low volume, high velocity
LWR	light water reactor
MAC	maximum allowable concentration
MACT	maximum achievable control technology
MAPP	major accident prevention plan
MAPP	methyl acetylene/propadiene/propylene
MAPCO	Mid-America Pipeline Company
MAPPS	maintenance personnel performance simulator
MARPOL	International Conference on Revision of the International Regulations for Preventing Collisions at Sea
MAUD	multi-attribute utility decomposition
MAWP	maximum allowable working pressure
MB	measure of belief
MC	motor cycle
MCA	Manufacturing Chemists Association
MCC	methylcarbamoyl chloride
MCL	maximum credible loss
MCSOII	multiple-cause, systems-oriented incident investigation
MCSP	Model Code of Safe Practice (IP)
MD	measure of disbelief
MDA	modellers data archive
MDF	multiple degree-of-freedom
MDI	4,4-Diphenylmethane diisocyanate
ME	multienergy (model)
MEA	monoethanolamine
MEHQ	methyl ether of hydroquinone
MEL	maximum exposure limit
MEPC	Marine Environment Protection Committee
MES	multilinear events sequencing
MESG	maximum experimental safe gap
MF	management factor
MF	material factor
MFCC	multiple forced circulation circuit
MGL	multiple Greek letter
MHAP	Major Hazards Assessment Panel
MHAU	Major Hazards Assessment Unit
MHIDAS	Major Hazard Incidents Data Service
MIBE	methyl-t-butyl ether
MIBK	methylisobutyl ketone
MIC	methyl isocyanate
MIC	minimum igniting current
MIE	minimum ignition energy
MIG	metal inert gas
MILNP	mixed integer non-linear programming
MILP	mixed integer linear programming

MITI	Ministry of International Trade and Industry
MLS	marine LNG system
MM	methyl methacrylate
MM	modified Mercalli
M&M	Marsh and McLennan
M&M	monitoring and maintenance
MMA	Methyl Methacrylate
MO	Marshall–Olkin
MOC	Management of change
MOC	method of characteristics
MoD	Ministry of Defence
MOL	main oil line
MOR	modification of risk
MORT	Management Oversight and Risk Tree
MOV	motor operated valve
MPA	mean presented area
MPD	minimum premarketing data
MPDO	maximum probable days outage
MPE	maximum permissible exposure
MPI	magnetic particle inspection
MPPD	Maximum Probable Property Damage
MPS	multiple point source
MPST	maximum permissible surface temperature
MRC	Medical Research Council
MRS	MIC refining still (Bhopal)
MRS	Midlands Research Station
MSA	Marine Safety Agency
MSC	Maritime Safety Committee
MSDS	material safety data sheet
MSS	MIC storage system (Bhopal)
MTTF	mean time to failure
MTBF	mean time between failures
MTTFF	mean time to first failure
MV	medium velocity
MV	munitions vehicle
MW	molecular weight
MWA	Mineral Workings Act 1971
N/A	not applicable
NAAQS	National Ambient Air Quality Standards
NACE	National Association of Corrosion Engineers
NADOR	Notification of Accidents and Dangerous Occurrences Regulations 1980
NAMAS	National Measurement Accreditation Scheme
NAS	National Academy of Sciences
NASA	National Aeronautical and Space Administration
NBFU	National Board of Fire Underwriters
NBS	National Bureau of Standards
NCB	National Coal Board
NCEC	National Chemical Emergency Centre
NCSR	National Centre for Systems Reliability
NCTR	National Center for Toxicological Research
NDE	Non-destructive evidence
NDE	non-destructive examination
NDRC	National Defense Research Committee
NDT	non-ductility transition
NDT	null ductility transition
NEA	Nuclear Energy Agency
NEIC	National Earthquake Information Center
NEL	National Engineering Laboratory
NEPA	National Environmental Policy Act
NESHAP	National Exposure Standards for Hazardous Air Pollutants
NFPA	National Fire Protection Association
NG	nitroglycerine
NGL	natural gas liquids
NIG	National Interest Group
NIHHS	Notification of Installations Handling Hazardous Substances Regulations 1982
NII	Nuclear Installations Inspectorate
NIOSH	National Institute of Occupational Safety and Health
NIST	National Institute of Standards and Technology
NML	Normal Maximum Loss
NMRS	near miss reporting system
NMS	Dangerous Substances (Notification and Marking of Sites) Regulations 1990
NMSE	normalized mean square error
NMMS	near miss management system
NMTMS	Non-monotonic truth maintenance system
NNS	Norwegian North Sea
NOAEL	no observable adverse effect level
NPD	Norwegian Petroleum Directorate
NPDES	National Pollutant Discharge Elimination System
NPL	National Physical Laboratory
NPP	nuclear power plant
NPS	Naval Postgraduate School
NPSH	net positive suction head
NPV	Net Present Value
NRA	National Rivers Authority
NRC	National Research Council
NRC	Nuclear Regulatory Commission
NRPB	National Radiological Protection Board
NRTS	National Reactor Test Station
NRV	non-return valve
NSAC	Nuclear Safety Analysis Center
NSC	National Safety Council
NSCA	National Society for Clean Air
NSPS	New Source Performance Standards
NSR	New Source Reviews
NSW	New South Wales
NTIS	National Technical Information Service
NTP	National Toxicology Program
NTS	Nevada Test Site
NTSB	National Transportation Safety Board
NWC	Naval Weapons Center
OAET	operator action event tree
OARU	Occupational Accident Research Unit
OAT	operator action tree
OB	oxygen balance
OBE	operating basis earthquake
OBO	ore/bulk/oil
OC	operating characteristic
OCIMF	Oil Companies International Marine Forum
OCM	on-condition maintenance
OD	oxygen demand
ODCB	*o*-dichlorobenzene
OECD	Organization for Economic Cooperation and Development
OEL	Occupational Exposure Limit
OES	Occupational Exposure Standard
OFG	over-the-top foam generation
OIA	Oil Industry Association
OIAC	Oil Industry Advisory Committee
OHSAS	Occupational Health and Safety Management systems
OII	Oil Industry Insurance

OILPOL	International Convention on the Prevention of Pollution of the Sea by Oil
OIM	offshore installation manager
ONAN	*o*-nitroaniline
ONCB	*o*-nitrochlorobenzene
OOA	observable operational attribute
OOP	object oriented programming
OOS	object oriented system
OPCS	Office of Population Census and Surveys
OPS	operating procedure synthesis
OPSO	Office of Pipeline Safety Operations
OREDA	Offshore Reliability Data (bank)
ORNL	Oak Ridge National Laboratory
ORR	overall risk rating
OSD	Offhore Safety Division
OSHA	Occupational Safety and Health Act 1970
OSHA	Occupational Safety and Health Administration
OS&RP	Office, Shops and Railway Premises (Act) 1963
OSTP	Office of Science and Technology Policy
OSW	Office of Solid Waste
OT	overturning
OTA	Office of Technology Assessment
OTS	Office of Toxic Substances
OV	Original Value (Dow)
P/A	peak-to-average
Paris MOU	Paris Memorandum
PASS	process and storage ship
PAW	Petroleum Administration for War
PAW	plasma arc welding
PB	pushbutton
PBB	polybrominated biphenyl
PBL	planetary boundary layer
PC	paired comparison
PCA	preliminary consequence analysis
P(C)A	Petroleum (Consolidation) Act
PCB	polychlorinated biphenyl
PCM	parametric correlation method
PCV	pressure control valve
PD	Property Damage
PDF	probability density function
PDS	potentiodynamic scan
PE	programmable electronic (hardware)
PEG	polyethylene glycol
PEEL	Public Emergency Exposure Limit
PEL	permissible exposure limit
PERT	project evaluation and review technique
PES	Programmable electronic system
PETN	pentaerythritol tetranitrate
PF	potential failure
PFC	perfluorocarbon
PFD	Probability of failure on demand
PFD	process flow diagram
PG	Pasquill–Gifford
PGA	peak ground acceleration
PGR	Road Traffic (Carriage of Dangerous Substances in Packages) Regulations
PH	precipitation hardening
PHA	preliminary hazard analysis
PHA	process hazard analysis
PHEA	predictive human error analysis
PHSA	Planning (Hazardous Substances) Act 1990
PI	personal injury (accident)
PI	pressure indicator
P&I(D)	piping and instrument (diagram)
PIF	performance influencing factor
PIIS	Prototype index of inherent safety
PIS	Protective instrumented Systems
PISC	Plate Inspection Steering Committee
PITB	Petroleum Industry Training Board
PIUS	process-inherent ultimate safety
PL	propositional logic
PLA	Port of London Authority
PLC	programmable logic control
P/M	peak-to-mean
PM	preventive maintenance
PML	Probable Maximum Loss
PMMA	polymethylmethacrylate
PMN	premanufacture notice
PMN	premarketing notification
PNEUROP	European Committee of Manufacturers of Compressors, Vacuum Pumps and Pneumatic Tools
POIC	planning, organization implementation and control
PORV	power-operated relief valve
PP	polypropylene
PPA	potential problem analysis
PPE	peak pressure enhancement
PPE	personal protective equipment
PRA	probabilistic risk assessment
PRP	potentially responsible person
PRV	pressure relief valve
PS	point source
PS	polystyrene
PSA	process safety management
PSA	pressure swing adsorption
PSA	probabilistic safety assessment
PSAT	Pre-start-up acceptance test
PSD	prevention of significant deterioration
PSDI	Project Software and Development Inc.
PSF	performance shaping factor
PSII	process safety incident investigation
PSM	process safety management
PSV	pressure safety valve
PT	passenger train
PTB	Physikalische Technische Bundesanstalt
PTFE	polytetrafluoroethene
PTSD	post-traumatic stress disorder
PTW	permit-to-work
PUF	polyurethane foam
PUHF	Process Unit Hazards Factor (Dow)
PV	pressure/vacuum
PVC	polyvinyl chloride
PVH	process vent header (Bhopal)
PVQAB	Pressure Vessel Quality Assurance Board
PVTC	Pressure Vessel Technical Committee
PVM	population vulnerability model
PWG	Provinciale Waterstaat Groeningen
PWHT	post-weld heat treatment
PWR	pressurized water reactor
QA	quality assurance
QHRDCS	quantitative human reliability data collection system
QUASA	quality assessment assurance of safety analysis
QC	quality control
QC	quality circle
QF	quality factor

QPT	qualitative process theory
QRA	quantitative risk assessment
RAG	risk appraisal group
RARDE	Royal Armament Research and Development Establishment
RAT	risk assessment tool
RBE	relative biological efficiency
RBV	remotely-operated block valve
RC	resistance–capacitance
RCAS	root cause analysis system
RCEP	Royal Commission on Environmental Pollution
RCM	reliability-centred maintenance
RCRA	Resource Conservation and Recovery Act 1976
RCS	reactor cooling system
RF	radio frequency
RF	Rossi–Forelli
RfD	reference dose
RH	relative humidity
R–H	Rankin–Hugoniot
RHI	Reaction Hazard Index
RIA	Robot Institute of America
RIC	Royal Institute of Chemistry
RID	International Regulations Concerning the Carriage of Dangerous Goods by Rail
RIDDOR	Reporting of Injuries, Diseases and Dangerous Occurrences Regulations 1985
RII	relative incapacitation index
RLA	remanent life assessment
RME	reasonable maximum exposure
RMEE	relative mass extinguishing efficiency
RMP	risk management planning
RMPP	Risk Management and Prevention Program (California)
RoRo	roll-on/roll-off
RoSPA	Royal Society for the Prevention of Accidents
ROV	remotely-operated valve
RPE	respiratory protective equipment
RPI	Retail Price Index
RPT	rapid phase transition
RPV	reactor pressure vessel
RRL	Road Research Laboratory
RSPA	Research and Special Programs Administration
RSS	Reactor *Safety Study* (*Rasmussen Report*)
RSSG	Royal Society Study Group
RSST	Reactor Systems Screening Tool
RT	response type (Whalley)
RTJ	ring-type joint
RTR	Road Traffic (Carriage of Dangerous Substances in Road Tankers and Tank Containers) Regulations 1992
RV	Replacement Value (Dow)
RV	residual volume
RVVH	relief valve vent header (Bhopal)
SA	sneak analysis
SADT	self-accelerating decomposition temperature
SAI	Science Applications Inc.
SARA	Superfund Amendment and Reauthorization Act 1986
SARAH	systematic approach to the reliability assessment of humans
SAS	small area statistics
SAT	Site acceptance test
SAW	submerged arc welding
SBC	Standard Building Code
SCA	small-scale cook-off bomb
SCA	sneak circuit analysis
SCAT	systematic cause analysis technique
SCBA	self-contained breathing apparatus
SCC	stress corrosion cracking
SCCM	subjective cause–consequence model
SCI	Society of Chemical Industry
SCM	short-cut classical method
SCRA(M)	Short-cut risk assessment (method)
SCS	safety critical system
SCT	stress concentration theory
SDF	single degree of freedom
SEAOC	Structural Engineers Association of California
SEDEX	type of calorimeter
SEDF	standard equivalent discrete failure
SEER	Surveillance, Epidemiology and End Results Program
SEM	scanning electron microscopy
SEM	slip equilibrium model
SF	solid flame
SFG	signal flow graph
SGHWR	steam generating heavy water reactor
SGT	subgoal template
SHE	safety, health and environment
SHERB	Sandia Human Error Rate Bank
SHERPA	systematic human error reduction and prediction approach
SHH	substance hazardous to health
SI	safety interlock
SI	Statutory Instrument
SIC	Standard Industrial Classification
SIGTTO	Society of International Gas Tanker and Terminal Operators
SIKAREX	type of calorimeter
SIL	Safety integrity level
SIPRI	Stockholm International Peace Research Institute
SIRA	Scientific Instrument Research Association
SIS	Safety Instrumented System
SIS	safety interlock system
SIT	spontaneous ignition temperature
SITTS	small inventory top tier site
SKHCR	standardized skilled and hospitalized casualty rate
SKR	skills–rules–knowledge (model)
SL	Sandia National Laboratory
SL	support list
SLI(M)	success likelihood index (method)
SLOT	Specified Level of Toxicity
SLP	safety and loss prevention
SLT	superheat limit temperature
SM	sequential modulator
SMAW	shielded metal arc welding
SMR	Seismic margin earthquake
SMRB	Safety in Mines Research Board
SMRE	Safety in Mines Research Establishment
SMS	safety management system
SNG	synthetic natural gas
SOAP	spectrometric oil analysis programme
SOLAS	Safety of life at Sea
SOP	Standard Operating Procedure

SOT	Society of Toxicology
SPEAR	system for predictive error analysis and reduction
SPEGL	Short-term Public Emergency Guidance Level
SPH	Special Process Hazard (Dow)
SPI	Society of the Plastics Industry
SPM	shock pulse meter
SPS	Safety protection systems
SPS	submerged production station
SRD	Safety and Reliability Directorate
SRI	Stanford Research Institute
SRS	Systems Reliability Service
SRV	safety relief valve
SSD	Safety Shutdown System
SSE	safe shut-down earthquake
SSEB	South of Scotland Electricity Board
SSI	soil–structure interaction
SSIV	subsea isolation valve
SSMRP	Seismic Safety Margins Research Program
STAR	stability array (method)
STATAS	structured audit technique for the assessment of safety management systems
STCW	International Convention on Training, Certification and Watchkeeping for Seafarers
STEL	short-term exposure limit
STEP	sequentially timed events plotting procedure
STEP	sequentially timed events plot
STPL	short-term public exposure limit
SVA	single vehicle accident
SVO	collision of vehicle with stationary object
SWACER	shock-wave amplified coherent energy release
SWAN	stress wave analyser
TAFF	theoretical adiabatic flash fraction
TBC	p-t-butyl catechol
TBN	total base number
TCB	1,2,4,5-trichlorobenzene
TCDD	2,3,7,8-tetrachlorodibenzo-*p*-dioxin
TCP	2,4,5-trichlorophenol
TCPA	Town and Country Planning Act
TCPA	Toxic Catastrophe Prevention Act
TCSP	tank centre space potential
TDI	toluene diisocyanate
TEMA	Tubular Exchanger Manufacturers Association
TESEO	Tecnica Empirica Stima Errori Operatori
TFI	The Fertilizer Institute
TGZ	Technigaz
THERP	Technique for Human Error Rate Prediction
TIG	tungsten inert gas
TLC	total lung capacity
TLV	threshold limit value
TMI	Three Mile Island
TMR	triple modular redundant
TMS	truth maintenance system
TNO	Toegepast-Natuurwetenschappelijk Onderzoek
TNT	trinitrotoluene
TOA	technical options analysis
TOPS	Total Operations Processing System
TPA	third party activity
TPQ	threshold planning quantity
TQM	total quality management
TRA	total risk analysis
TRC	Thornton Research Centre
TRC	time–reliability correlation
TRI	toxic release inventory
TRRL	Transport and Road Research Laboratory
TS	turbulence scheme
TSCA	Toxic Substances Control Act
TSDF	treatment storage and disposal facility
TSR	temporary safe refuge
TT	task type (Whalley)
TUV	Technische berwachungs-Verein
TV	Tidal volume
TVA	Tennessee Valley Authority
TWA	time-weighted average
UAS	user-approved safety
UBC	Uniform Building Code
UCB	uncertainty bound
UCC	Union Carbide Corporation
UCIL	Union Carbide India Ltd
UCO	Use Classes Order
UCS	Union of Concerned Scientists
UEL	upper explosive limit
UFL	upper flammability limit
UF	uniform flux
UKAEA	UK Atomic Energy Authority
UKCIC	UK Chemical Information Centre
UKCP	UK Chlorine Producers
UKOOA	UK Oil Operators Association
UL	Underwriters Laboratories
UMC	underwater manifold centre
UN	United Nations
UNEP	UN Environment Programme
UNS	Unified Numbering System
UPS	Uninterrupted power supplies
UPS	uninterruptible power supply
UR(L)	United Refineries (Ltd)
USCG	US Coast Guard
USPHS	US Public Health Service
UST	underground storage tank
UV	ultraviolet
UVCE	unconfined vapour cloud explosion
VAE	Value of Area Exposed (Dow)
VC	vinyl chloride
VC	vital capacity
VCE	vapour cloud explosion
VCF	vapour cloud fire
VCM	vinyl chloride monomer
VDI	Verein Deutscher Ingenieure
VDU	visual display unit
VEEB	Vapour escape into, and explosion in, a building
VGS	vent gas scrubber (Bhopal)
VIM	vacuum induction melting
VKI	Von Karman Institute
VLCC	very large crude carrier
VM	Vulnerability model
VOC	volatile organic compound
VOD	vacuum–oxygen decarburization
VOD	velocity of detonation
VOF	velocity of fragment
VPM	value of production per month
VS	volumetric source
VSP	Vent Sizing Package
V&V	Verification and validation

WA	water authority
WAO	wet air oxidation
WATCH	Working Group on the Assessment of Toxic Chemicals
WE	Western Europe
WHO	World Health Organization
WI	Welding Institute
WOAD	World Offshore Accident Database
WSA	work safety analysis
WSL	Warren Spring Laboratory
WSSN	Worldwide Standard Seismographic Network
ZND	Zeldovitch–von Neumann–Döring

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